SUPRAMOLECULAR NANOSTRUCTURES

BASED ON CALIXARENES

by

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ABSTRACT

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This dissertation describes a systematic approach towards the design, synthesis, characterization, and application of calixarene-based supramolecular nanostructures. Chapter 1 briefly overviews the field of supramolecular chemistry and highlights its horizons. Chapter 2 introduces a modular strategy towards synthesis of nanoscale receptor macromolecules—calix–peptide conjugates. This strategy combines the unique host–guest capabilities of calixarene chemistry with synthetically flexible peptide synthesis. A series of calixarene amino acids was prepared and further utilized to synthesize calixarene dipeptides. Through this approach, calixarene amino acids are now available to be incorporated into peptide networks and nanostructured biologically relevant materials. Chapter 3 demonstrates supramolecular applications of calixarene-

peptide conjugates. These calixarene amino acids serve as building blocks for the construction of a novel type of calixarene peptide dendrimers. Calixarene amino acids, peptides, and peptide dendrimers containing tetra-ester functions at their lower rims can extract sodium cations from aqueous solutions. Calixarene-peptide conjugates, possessing urea moieties at the upper rim, were demonstrated to reversibly form self-assembling capsules and supramolecular polymers in apolar solvents. Chapter 4 shows how CO_2 gas can be used to construct novel types of supramolecular polymers. These polymers employ both hydrogen bonding and dynamic, thermally reversible carbamate bonds. Addition of a competitive solvent, such as DMSO, breaks hydrogen bonding in the assembled structures but does not influence the carbamate linkers. On the other hand, thermal release of CO_2 was easily accomplished but the hydrogen bonded capsules remained intact. Chapter 5 demonstrates functions of supramolecular, calix-peptide based polymers. A switchable, supramolecular polymer is introduced, which is held together through hydrogen bonding and reversibly precipitates-redissolves upon changing the pH. Precipitating, it entraps and stores guest molecules within the self-assembling capsules, incorporated within the polymeric chain. CO_2 was used to build switchable, supramolecular polymeric materials, which has fluorescent properties. Formation of a cross-linked, porous supramolecular polymer leads to instant entrapment of organic guest species. These can be stored and then released upon changing solvent polarity, temperature, pH, and concentration.

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CHAPTER 1

INTRODUCTION

Supramolecular chemistry has developed in the past decades as a scientific field between chemistry, physics, and biology. The concept and term of supramolecular chemistry was introduced by Lehn et al. in 1978.[1] This area of chemistry was defined as "chemistry beyond the molecule", based on organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces.[2]

As molecular chemistry deals with molecules, supramolecular chemistry deals with supramolecular species, which are usually called "molecular receptor" and "substrate" (Figure 1.1). Binding of a substrate by a receptor yields supramolecules, and the binding process reflects molecular recognition. The substrates can be essentially anything, including cations, anions, neutral organic molecules, and even gases, while receptor molecules must have complimentary molecular size, shape and architecture with the substrates, establishing non-covalent binding interactions.[3] Macrocyclic compounds possess numerous branches, bridges and connections which in most cases contain intramolecular cavities for a variety of substrates, and thus have become favorites as receptors. Among these macrocyclic compounds, crown ethers, cyclodexdrins, and calixarenes are most intensively investigated.[4]

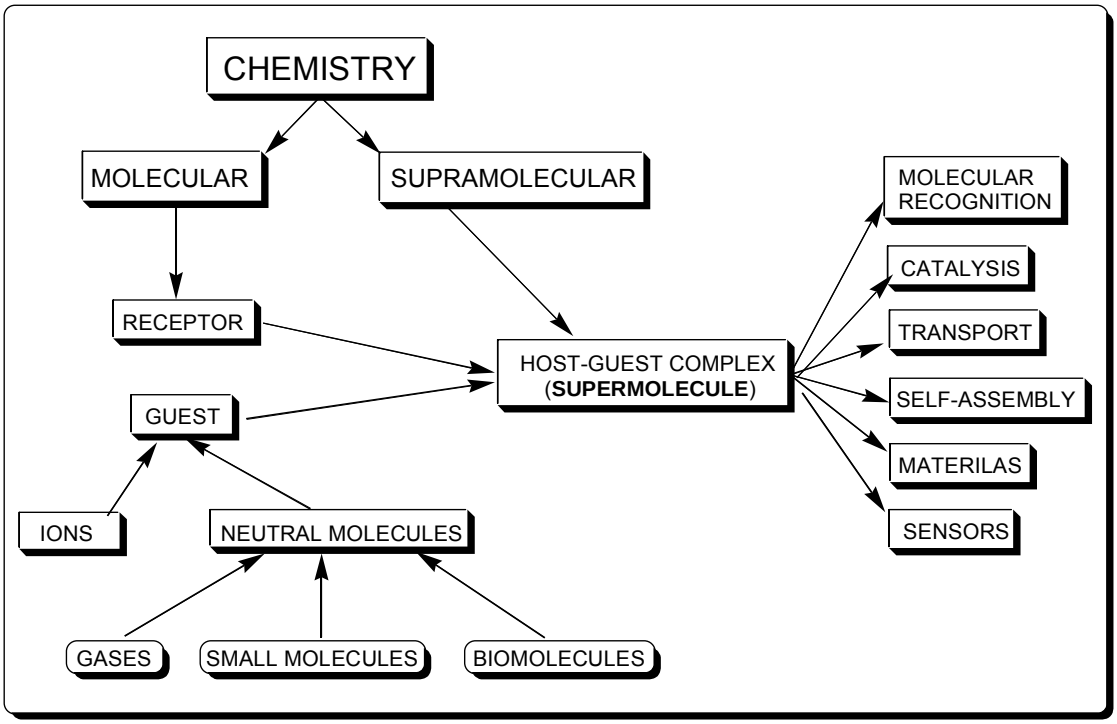


Figure 1.1 From molecular to supramolecular chemistry.

Crown ethers are macrocyclic compounds. They were discovered in the middle of 1960s by Charles Pedersen and based on repeating -OCH_2CH_2- units, derived from ethylene glycol.[5] Varying the number of these units results in different size of the crown ether (Figure 1.2A). These compounds showed strong affinities to metal cations, such as Li^+, Na^+, K^+. The applications of crown ethers led to phase-transfer catalysis, biological ion transfer, membrane transport, extractions, etc.[6]

Cryptands are another important class of macrocyclic compounds which contain three-dimensional, spherical cavities (Figure 1.2B). This work started in 1967 by Lehn[7] shortly after discovery of crown ethers. Cryptands entirely surround the bound ions and form stronger complexes than the flat shaped macrocycles, thus displaying *spherical*

recognition of appropriate cations and anions. Numerous effects from these strong complexes have been studied in detail, such as: stabilization of alkalides and electrides, dissociation of ion pairs, anion activation, isotope separation, toxic metal binding, etc.[8]

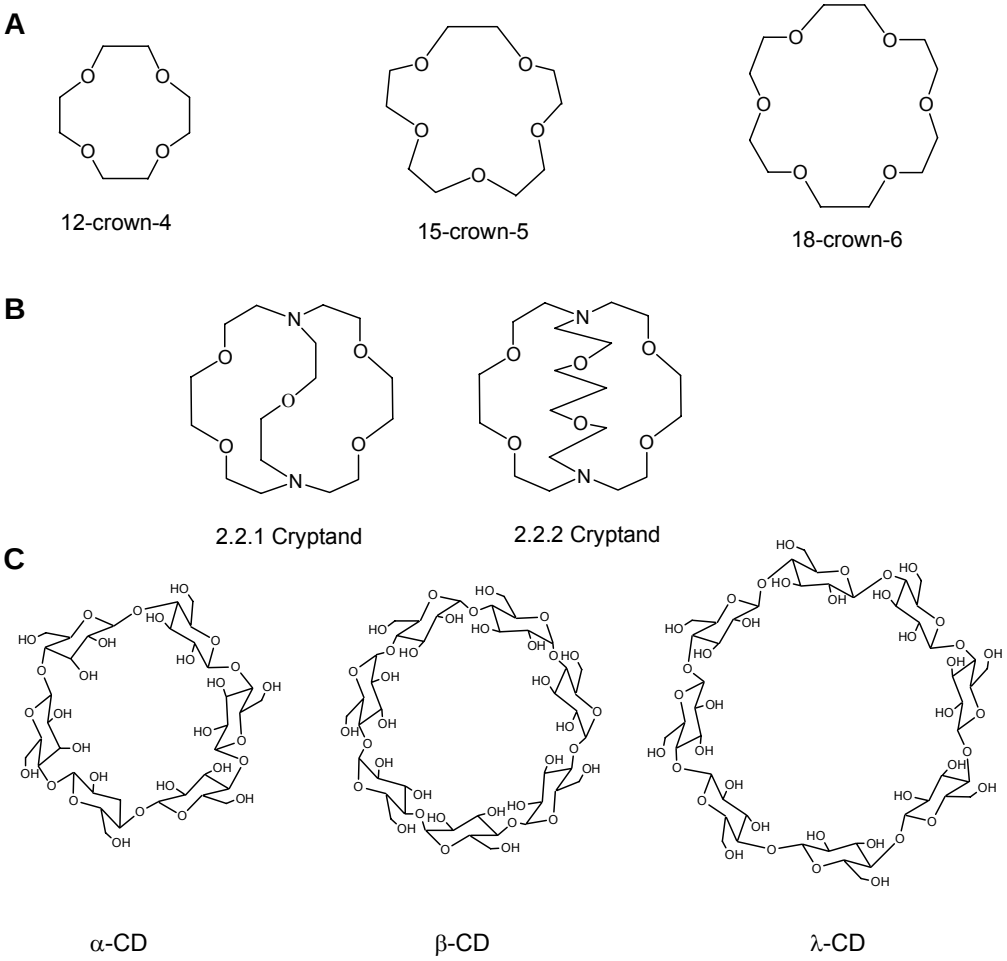


Figure 1.2 Structures of crown ethers A, cryptands B, and cyclodextrins C.

Cyclodextrins, comprised of 6, 7 and 8 glucose units (α, β, and γ cyclodextrin, respectively), are bucket-shaped oligosaccharides produced from starch (Figure 1.2C). Due to their molecular structure and shape, they possess a unique ability to act as molecular containers by entrapping guest molecules in their internal cavities. The resulting inclusion complexes are one of most popular classes of host-guest

supramolecules in academic research and they also offer a number of potential advantages in pharmaceutical formulations.[9]

Calixarenes were introduced in 1978 by C. D. Gutsche[10] as cup-like shapes, capable of complexing guest molecules. Since then, calixarenes have spanned the total field of molecular recognition. Earlier work focused on functionalizing calixarenes on both its upper and lower rims to afford variety of cavities of different shapes and sizes. These calixarenes were most studied for their capability as a receptor for metal cations. More recently, calixarenes have been utilized to construct cavitands, (hemi)carcerands and self-assembling capsules, in which larger neutral organic molecules, cations, anions, were bound.[11]

Besides binding of one molecule by another, supramolecular chemistry studies the self-assembly of multiple molecules into supramolecular structures. Self-assembly is the autonomous organization of components into patterns or structures.[12] Although self-assembling processes are common throughout nature and technology, it has mainly been studied in biology and physics.[13,14] Supramolecular chemistry provides ways and means for chemical science to explore this area and apply its power of design and control.[3] Through the self–assembly process, receptors, transport agents, enzyme models, and extended arrays can be constructed. These artificial assemblies are being utilized to mimic biological systems and applied in emerging scientific fields, especially nanotechnology. Self-assembly has become a rapidly growing field for two reasons. First, it is a crucial concept to understand many biologically important structures. Second, it provides a solution to the problem of synthesizing larger structures.

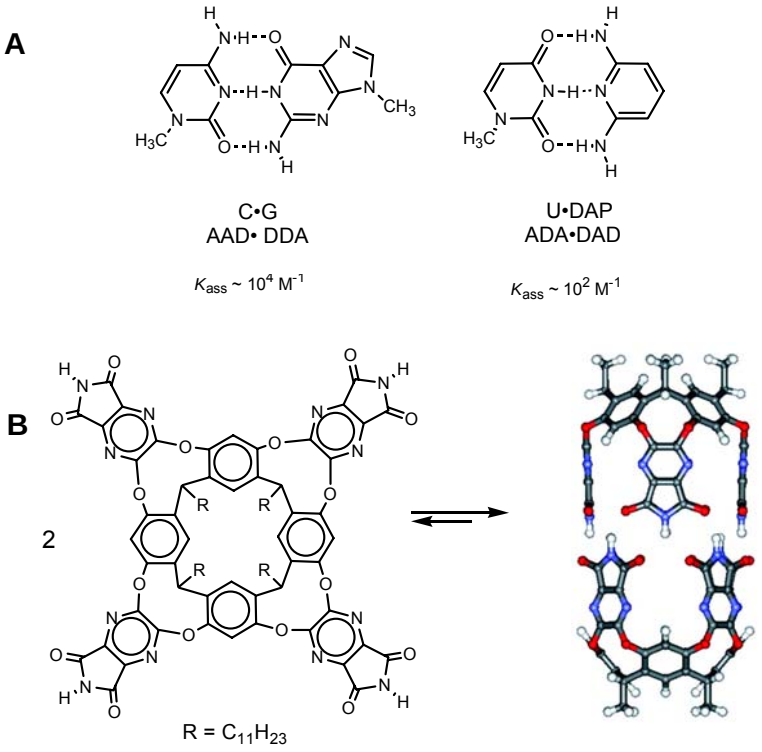


Figure 1.3 Hydrogen-bonded dimers A and capsules B.

Hydrogen bonding is most frequently utilized in self-assembling systems, because it is directional, specific, and biologically relevant. Numerous self-assembly models on organic supramolecular structures have been reported in the literature, which can be categorized as dimers, multimers, capsules, polymers and nano-scale architectures, etc .[15]

Stable H-bond directed assemblies in most cases require multiple hydrogen bonds, while a variety of small organic functionalities, such as phenols, amines, and amides can dimerize through single H-bond. For stable assemblies, the number of hydrogen bonds is certainly not the only important parameter. “Cooperativity” is

usually considered a key factor in increasing the stability of assemblies. The Jorgensen model was used as a basic rule to qualitively predict the association constant between the individual units. These differences in stability can be largely attributed to attractive and repulsive secondary interactions. Stabilization arises from electrostatic attraction between positively and negatively polarized atoms in adjacent H-bonds, whereas destabilization is likewise the result of electrostatic repulsion between two positively or negatively polarized atoms (Figure 1.3 A).[16] According to this model, AA•DD (A refers to Acceptor, D refers to Donor) in 2-H-bond modules and AAA•DDD in 3-H-bond modules were predicted to have highest association constant values. These predictions have been proven by experimental data.[17] In 4-H-bond modules, AADD•DDAA arrays have shown the high stability with the association constant > 10^6 M^{-1}.[18] Apart from the expected increase in stability, the even number of H-bond donors and acceptors in 4-H-bond modules allows self-complementarity to be introduced in these motifs. Self-complementarity provides an attractive property for applications in polymeric materials or molecular capsules.

Numerous dimeric, cyclic, polymeric, even capsule-like structures with variety of size and shape were designed and synthesized through noncovalent forces (For example, capsules[19] on Figure 1.3 have ~ 460 $Å^3$ internal volume and are capable of entrapping up to three $CHCl_3$ molecules). The next question concerns the application of these supramolecules.

The development, characterization, and exploitation of novel materials based on the assembly of molecular components is an exceptionally active and rapidly expanding

field in materials science. Electronic, magnetic, optical, structural, mechanical, and chemical characteristics have been considered.[3] The formation of supramolecular entities from photoactive components may be expected to give rise to novel properties. Assembling individual components into supramolecular systems may initialize a number of processes: excitation energy migration, photo-induced charge separation by electron and proton transfer, perturbation of optical transitions and polarizabilities, modification of redox potentials, selective photochemical reactions, etc.[4] For example, efficient energy transfer devices has been designed and synthesized based on a rigid linear array of porphyrin units.[20] Self-assembled heterocyclic ribbons were shown to allow the directed long-range transfer of protons, thus functioning as proton-conducting channel.[21]

Molecular self-assembly may offer an alternative paradigm for preparing functional nanostructures. Nanotechnology aims to construct materials and operative system in the nano-dimension. Several potential applications can be envisioned: targeted drug delivery systems, tissue engineering scaffolds, photonic crystals, and micro/nano fluidic and computational devices.

Using peptides as building blocks in self-assembly has several advantages: 1) 20 naturally occurring amino acids are available; the properties of materials are dictated by the individual amino acid; 2) peptide bonds are stable; 3) peptides can be designed to adopt well-known secondary structures such as α-helix and β-sheet.

Natural and synthetic peptides have been utilized as a starting point for the construction of functional materials, for example, self-assembling peptide nanotubes

(SAPN). Introduced by Ghadiri in 1993, SAPN are a new class of supramolecular structures based on the hydrogen bonding stacking of cyclic peptides with an even number of alternating D/L amino acids (Figure 1.4).[22] This stacking forms an open channel of between 5 and 13 Å depending on the number of amino acids making up the peptide ring. Because the subunit employed for self-assembly is a cyclic peptide, the properties of the supramolecular tube can be adjusted by the selection of amino acids in the subunit ring.

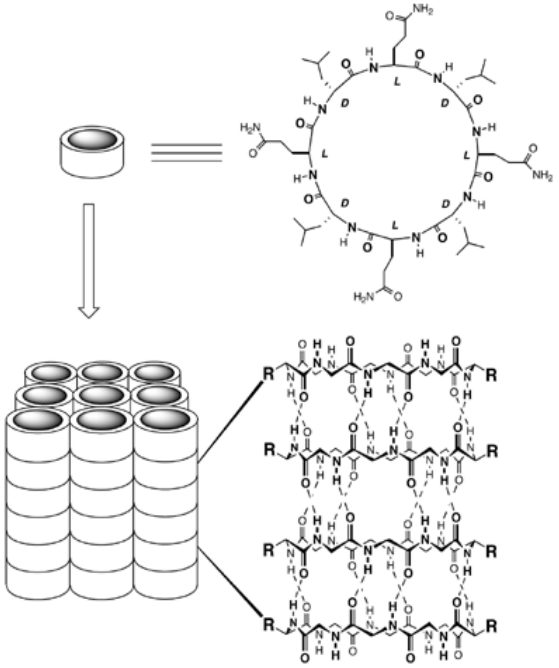


Figure 1.4 Self-assembling peptide nanotubes achieved by Ghadiri.[22]

Peptide nanotubes have a wide range of functional attributes that are useful in biological and materials science. For example, these nanotubes can function as artificial ion channels in lipid bilayer membranes by self-assembling across the membrane.[23] The ion-transport rates are comparable to those of naturally occurring ion channels. The

unique and highly oriented surface characteristics of solid-state tubular assemblies can also be exploited in the fabrication of nanoclusters of transition-metal oxides for potential applications in catalysis and photonics.[24]

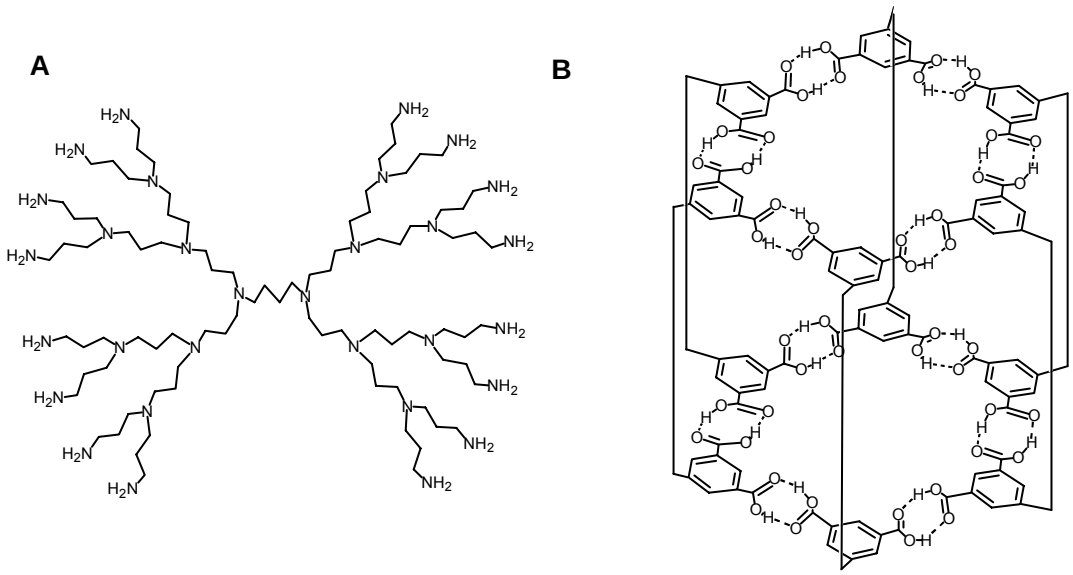


Figure 1.5 Dendrimer A and self-assembling dendrimer B.

Another important class of supramolecular materials is dendrimers.[25] Dendrimers, bearing highly branched architectures and unique properties, have been extensively investigated and become one of most exciting areas of modern nanotechnology (see for example, Figure 1.5A).[26] Synthetically, dendrimers are constructed in an iterative fashion. This leads to a stepwise synthetic growth which distinguishes dendrimers from normal polymers. Such a complex, branched and globular dendrimer molecule can also be constructed by small and synthetically accessible building blocks which simply self-assemble *via* non-covalent forces. For example, Zimmerman and coworkers[27] designed and synthesized tetraacids, in which

two isophthalic acid units were held in a synorientation by a rigid spacer. By normal pairing of carboxylic acids into hydrogen bonded dimers, these molecules can self-assemble into double-layer, cyclic hexamer (Figure 1.5B). Fréchet-type polyether dendrons, up to the fourth generation, were attached to the spacer unit of tetraacids. NMR and size-exclusion chromatography (SEC) studies indicated that self-assembling dendrimers formed in apolar solvent. More importantly, by varying the size of attached polyether dendrons, it is possible to exert a degree of control over the orientation of the assembly.

It is of great interest to prepare "smart" materials whose morphologies and associative functions can change in response to their environment. While peptides tend to assemble slowly into thermodynamically stable structures, such as β-sheets, which limit the capability of the peptides to responsed to external environmental stimuli, Schneider et al.[28] developed an ingenious way to prepare responsive materials from peptides. This group demonstrated that chemical responsiveness can be specifically engineered into the material by linking intramolecular folding to changes in solution pH, and mechanical responsiveness, by linking hydrogelation to self-assembly.

Self-assembling monolayers (SAMs) with controllable properties have also led to functional materials. SAMs are formed when surfactant molecules spontaneously adsorb in a monomolecular layer on surfaces. Two of the most widely studied systems of SAMs are gold-alkyl thiolate monolayers and alkylsilane monolayers. The first gold-alkyl thiolate monolayer was produced by Allara and Nuzzo[29] at Bell laboratories in 1983 and later the group of Whitesides[30] made valuable contributions to this field.

By using thiol molecules with different tail groups, the resulting chemical surface functionality can be varied within wide limits (see for example, Figure 1.6). Numerous applications of this technique in, for example, corrosion inhibition,[31] nano-fabrication of electronic devices[32] have been reported in the last decade. These studies demonstrated the fusion of structure and application and showed how to bridge molecular structure and macroscopic and materials structure in organic surface science.

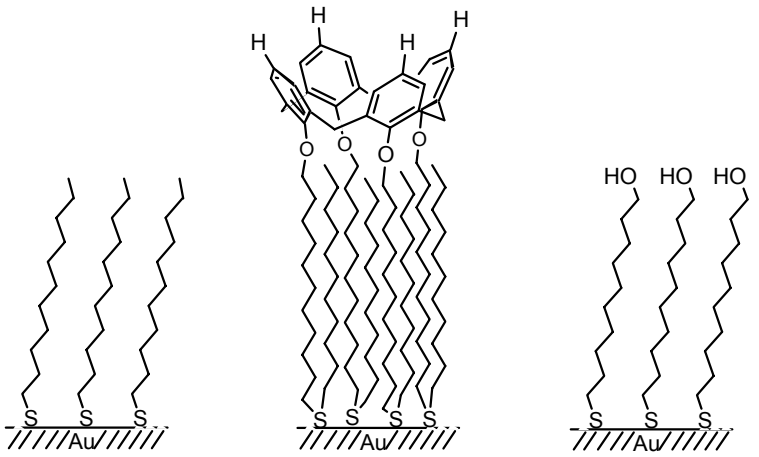


Figure 1.6 Self-assembling monolayers.[29,33]

Beyond the molecule, supramolecular chemistry aims at developing highly complex chemical systems from components interacting by noncovalent intermolecular forces. It has been growing into a major field over a quarter of last century and fueled numerous developments at the interface with physics and biology. Through appropriate manipulations of intermolecular noncovalent interactions, storage of information at the molecular level has become feasible and retrieval, transfer, and processing of the information can then be accomplished. This venture involves design and investigation

of well pre-organized receptors, capable of binding to substrate with high efficiency and selectivity. Supramolecular chemistry opens new perspectives in materials science toward an area of supramolecular materials, ‘‘smart’’ materials whose features depend on molecular information. It allows the design of materials and the control of their build-up from suitable units by self-organization. Supramolecular chemistry is gaining a lot of attention in the field of nanoscience. Indeed, the spontaneous but controlled generation of well-defined, functional supramolecular nanostructures through self-organization offers a very powerful alternative to nanofabrication and nanomanipulation, bypassing the implementation of tedious procedures and providing a chemical approach to nanoscience and technology.[34]

CHAPTER 2

CALIXARENE-PEPTIDE CONJUGATES

The name "calixarenes" was coined by C. D. Gutsche in 1978.[10] Since then, calixarenes have been extremely popular platforms and building blocks in molecular recognition, and they have had a great impact in the history of supramolecular chemistry.[11] Calix[n]arenes (n refers to the number of aromatic rings in a molecule) are macrocyclic compounds, derived from the base-catalyzed condensation of *p*-alkyl phenol and formaldehyde. Convenient procedures have been elaborated that make the cyclic tetra-, hexa-, and octamer-selectively available from *t*-butylphenol in large quantities and yield. Calix[4]arenes are cyclic tetramers; they adopt four extreme conformations called cone, partial cone, 1,2-alternate, and 1,3-alternate which differ in the orientation of the phenol rings (Figure 2.1). These conformational isomers afford unique cavities with different sizes and different shapes. Furthermore, the three-dimensional conformations, commercial availability and rigid structures make calixarenes most convenient for synthetic elaboration. Calixarenes are sometime called "third generation" of macrocyclic molecules, which follow crown ethers and cyclodextrins.[35]

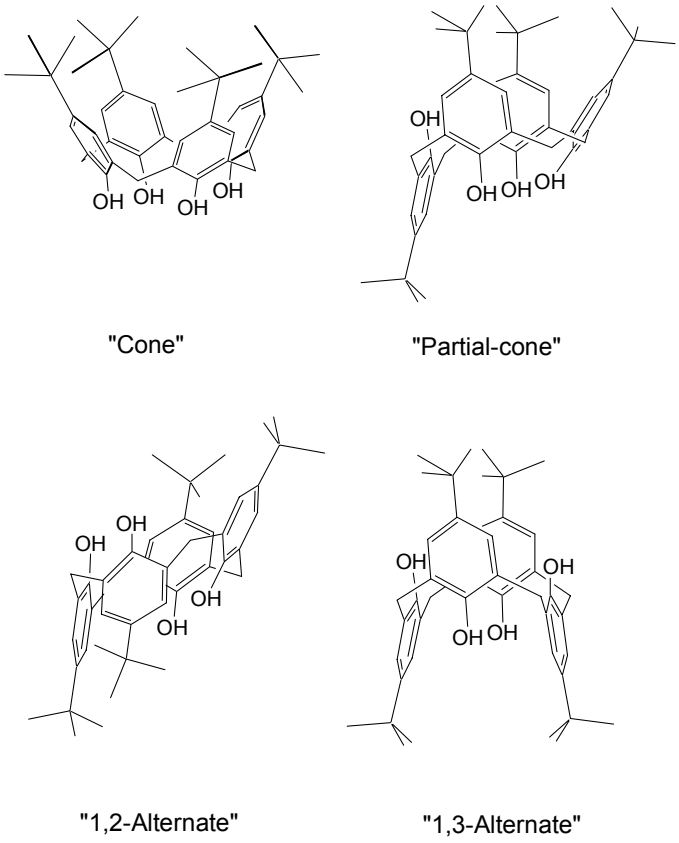


Figure 2.1 Four stable conformations of calix[4]arenes.

Calixarene-based receptors are among the most effective and selective for cations; they are widely used to transport and extraction of various inorganic ions such as Na^+, K^+, and Cs^+,[36,37,38] lanthanides and actinides,[39] as well as organic cationic species.[40] Calixarene-based anion receptors show record binding thermodynamics and selectivities for phosphate, sulfate and chloride.[41,42] Many calixarenes crystallize with solvent molecules inside, such as benzene, toluene and xylene. Thus calixarenes can function as molecular baskets for neutral molecules. Along this line, calixarenes have been employed for the construction of cavitands,[43,44] (hemi)carcerands[45] and self-

assembling capsules.[46] Many classic cavity-shaped molecules in the literature are constructed by covalent linking and/or self-assembling calixarene moieties.

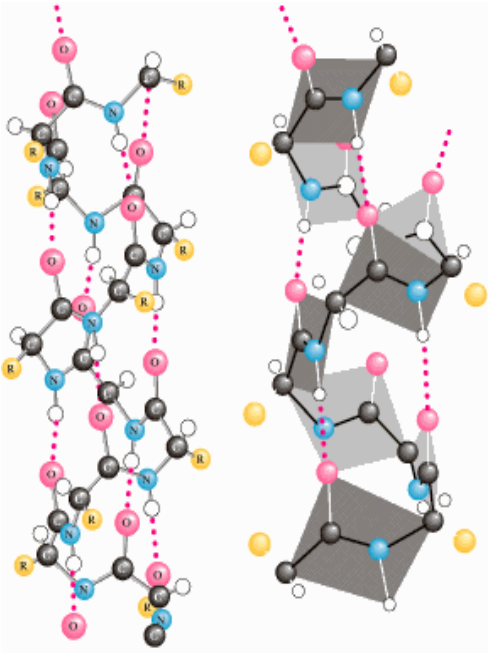


Figure 2.2 α-Helix in peptides.[47]

Nature employs amino acids as building blocks, *modules* to assemble – quickly and effectively - a huge variety of proteins and enzymes. Indeed, in the course of evolution, nature has developed enzymes and proteins of nanometer size that perform catalysis and molecular recognition in an exquisite fashion. Polypeptides were thus selected as the construction materials of these sophisticated molecular systems not only because of their bifunctional and chiral nature, but also the stability of peptide bond. Moreover, polypeptide chains fold into predictable conformations in solution such as the α-helix (Figure 2.2) or the β-sheet. In recent years, extensive studies have been

devoted to the development of peptide nanostrucutures, which can be used in the preparation of "smart" new materials.[48]

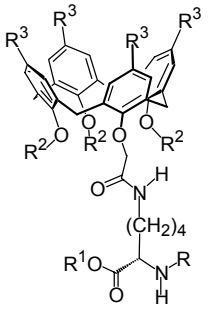
In the studies described in this chapter, we take advantage of this established peptide chemistry and introduce a general modular strategy towards multifunctional receptor macromolecules – calix-amino acids and calix-peptides (Figure 2.3).[49,50] This approach combines the highly functional, receptor-oriented calixarene chemistry with the synthetically diverse peptide synthesis. The design and synthesis of modules – calixarene amino acids are presented. Further, modular assembly of nanostructures – calixarene-peptides is demonstrated. In general, the "receptor – amino acid" based modular approach described herein may be useful for the construction of wide variety of multifunctional nanostructures.

2.1 Design

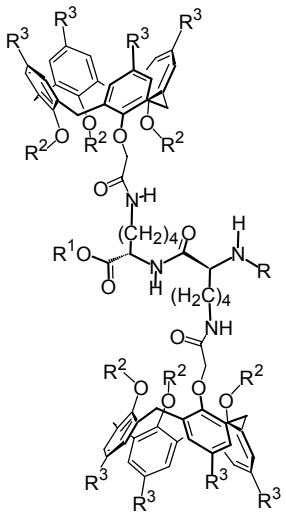
The proposed strategy is demonstrated for representative preparation of calix[4]arene amino acids **1** and calix[4]arene dipeptides **2** (Figure 2.3).

In the synthesis of calix[4]arene amino acids, we took advantage of trifunctional lysine, which possesses a carboxylic group and two NH_2 groups of distinguishable reactivity.[51] The ε-NH_2 group was attached to the calixarene fragment, while the α-NH_2 group was used in the coupling reactions with the other lysine C(O)OH group to form a peptide bond. This is an important feature of the proposed modular approach: both ends of amino acids are readily available for further peptide growth. Notably, while a number of calix[4]arene-amino acid conjugates are known,[52] they are attached either via *N*- or

(O)O-terminus and therefore cannot be involved in the repetitive, multivalent peptide chain elongation.



1a R=C(O)$(CH_2)_6CH_3$, R^1=Bn,
R^2=$CH_2C(O)OEt$, R^3= *t*-Bu
1b R=Cbz, R^1=Me,
R^2=$CH_2C(O)OEt$, R^3= *t*-Bu
1c R= Cbz, R^1=p-t-Bu-C_6H_4
R^2=$CH_2C(O)OEt$, R^3= *t*-Bu
1d R=BOC, R^1=Me,
R^2=$CH_2C(O)OEt$, R^3= *t*-Bu
1e R=C(O)$(CH_2)_6CH_3$, R^1=H,
R^2=$CH_2C(O)OEt$, R^3= *t*-Bu
1f R=BOC, R^1=Me,
R^2=$CH_2C(O)OEt$, R^3= *t*-Bu
1g R=BOC, R^1=Me,
R^2=n-Pr, R^3=$NHC(O)NH(CH_2)_5CH_3$



2a R=C(O)$(CH_2)_6CH_3$, R^1=Me,
R^2=$CH_2C(O)OEt$, R^3= *t*-Bu
2b R=BOC, R^1=Me,
R^2=$CH_2C(O)OEt$, R^3= *t*-Bu
2c R=BOC, R^1=Me,
R^2=n-Pr, R^3=$NHC(O)NH(CH_2)_5CH_3$

Figure 2.3 Calixarene lysines **1a-g** and dipeptides **2a-c**.

Two types of the calixarene components were chosen to create a variety of peptide-based calixarene nanostructures. One type of calixarenes is functionlized with esters at the low rim, while the other has urea functions at the upper rim.

The choice of the calixarene tetraester was justified by its strong affinity towards Na^+ cation (Figure 2.4). It has been known for years that calix[4]arenes, functionalized with either ester or amide groups (or both) at the lower rim, demonstrate a unique Na^+ selectivity, with the K_{ass} >> 10^6 M^{-1} in apolar solvent.[36] Moreover, the

calixarene lower rim is relatively easy to functionalize. In our studies, the calixarene Na^+ receptors were readily converted into the corresponding acids for coupling with lysine derivatives.

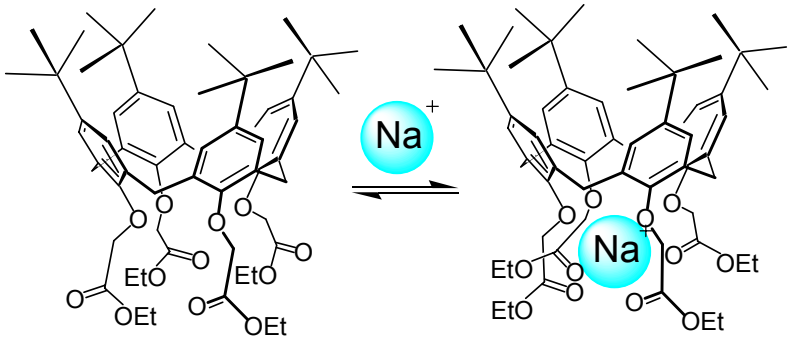


Figure 2.4 Sodium complexation within the lower rim of calix[4]arene tetraester.[36]

On the other hand, calix[4]arene tetraureas were chosen as they strongly tend to dimerize in apolar solvent to create capsules (Figure 2.5). These capsules are, probably, the most studied and publicized class of capsules to date. Discovered ten years ago by

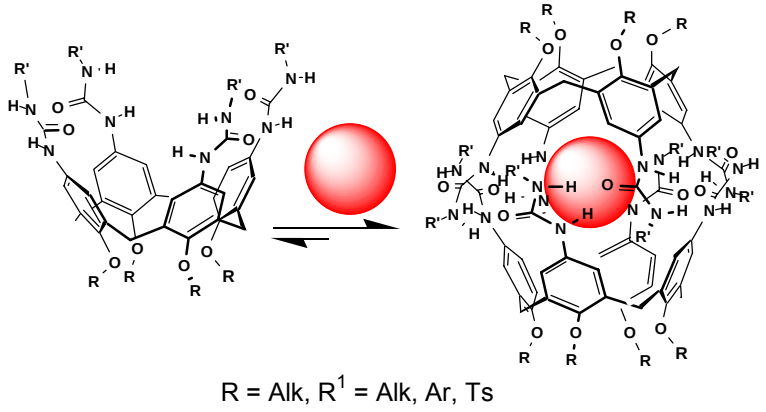


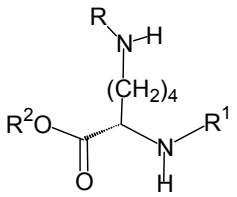
Figure 2.5 Hydrogen-bonded calix[4]arene tetraurea capsules.[53,54]

Rebek[53] and Böhmer,[54] these capsules are held together by a seam of sixteen intermolecular C=O•••H-N hydrogen bonds at the upper rims. This results in a rigid

cavity of ~200 $Å^3$, which reversibly encapsulates one solvent molecule or a benzene-sized guest. Furthermore, the urea functions do not interfere with introducing amino acids to their lower rims.

The choice of covalent attachment to the side chain of lysine is not only limited by calixarenes. Other macrocyclic compounds, such as porphyrin, cyclodextrins, crown ethers, can be also chosen to incorporate into peptide networks for various binding purposes.

2.2 Calixarene Amino Acids



3 R = BOC, R_1 = R_2 = H
4 R = BOC, R_1 = $C(O)(CH_2)_6CH_3$, R_2 = H
5 R = BOC, R_1 = $C(O)(CH_2)_6CH_3$, R_2 = Bn
6 R = H•$CF_3C(O)OH$, R_1 = $C(O)(CH_2)_6CH_3$, R_2 = Bn
7 R = BOC, R_1 = Cbz, R_2 = H
8 R = BOC, R_1 = Cbz, R_2 = Me
9 R = BOC, R_1 = Cbz, R_2 = p-t-Bu-C_6H_4
10 R = H•$CF_3C(O)OH$, R_1 = Cbz, R_2 = Me
11 R = H•$CF_3C(O)OH$, R_1 = Cbz, R_2 = p-t-Bu-C_6H_4
12 R = Cbz, R_1 = BOC, R_2 = H
13 R = Cbz, R_1 = BOC, R_2 = Me
14 R = H, R_1 = BOC, R_2 = Me
15 R = Cbz, R_1 = H•$CF_3C(O)OH$, R_2 = Me
16 R = BOC, R_1 = BOC, R_2 = H
17 R = BOC, R_1 = BOC, R_2 = Me
18 R = BOC, R_1 = BOC, R_2 = Bn
19 R = H•$CF_3C(O)OH$, R^1 = H•$CF_3C(O)OH$, R_2 = Me
20 R = H•$CF_3C(O)OH$, R^1 = H•$CF_3C(O)OH$, R_2 = Bn
21 R = Cbz, R_1 = R_2 = H
22 R = Cbz, R1 = $C(O)(CH_2)_6CH_3$, R_2 = H
23 R = BOC, R_1 = H, R_2 = Me

Figure 2.6 Lysine derivatives as building blocks for calixarene amino acids.

First, we prepared a series of chemoselective protected lysine derivatives (Figure 2.6). Thus, commercially available *N*-ε-BOC-*l*-lysine **3** was coupled with *n*-octanoyl chloride in the two-phase system EtOAc-H_2O, 1:1 in the presence of K_2CO_3 to afford *N*-α-acylated derivative **4** in 77% yield. The long aliphatic chain was used for

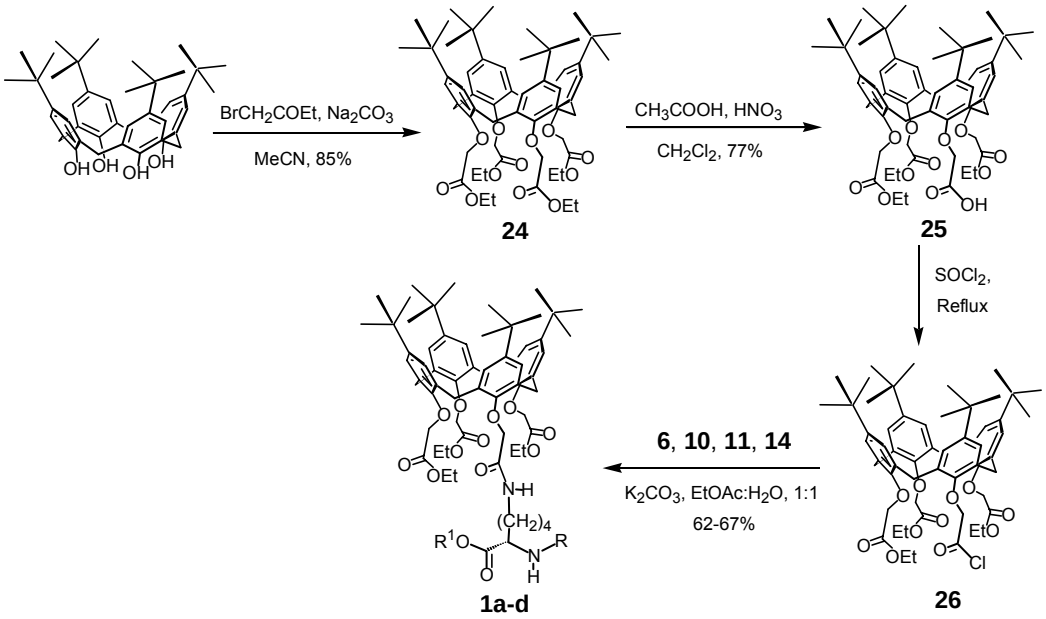
solubility reasons. As followed from the absence of optical activity (see Experimental Part) and subsequent ^{1}H NMR analysis, compound **4** was obtained as a racemate. Apparently, base-catalyzed racemization[55] occurred as a result of rather basic conditions for acylation of enantiomerically pure **3**. The carboxylic group in **4** was then protected through benzylation. Namely, acid **4** was treated with benzyl alcohol and 1,3-dicyclohexylcarbodiimide (DCC) in CH_2Cl_2, containing catalytic quantities of 4-dimethylaminopyridine (DMAP) under nitrogen with the formation of benzyl ester **5** in 61% yield. Subsequently, the BOC protecting group in **5** was cleaved with TFA-THF, 1:4 mixture, to afford the TFA salt of amine **6** in quantitative yield.

In another series of experiments, *N*-ε-BOC-*l*-lysine **3** was protected by a Cbz group (Cbz-Cl, Na_2CO_3) with the formation of *N*-α-Cbz-*N*-ε-BOC-*l*-lysine **7** in 65%.[56] Derivative **7** is optically active and, as will follow from the NMR analysis, enantiomerically pure. The carboxylic group in **7** was methylated (Cs_2CO_3, CH_3I, DMF) to form the corresponding ester **8** in 58% yield.[57] Reaction between **7**, 4-*t*-butylphenol, DCC and catalytic amount of DMAP in CH_2Cl_2 afforded phenyl ester **9** in 62% yield. After the BOC deprotection with TFA, amine salts **10** and **11** were isolated in a quantitative yield.

For *N*-α-BOC-*N*-ε-Cbz-*l*-lysine **12**, the carboxylic group was similarly methylated (Cs_2CO_3, CH_3I, DMF) to form the corresponding ester **13** in 65% yield.[58] The Cbz moiety was then cleaved with 10% Pd/C in CH_3OH to yield pure lysine **14** in quantitative yield.[59] After the α-BOC protecting group in **13** was cleaved with TFA in THF, lysine derivative **15** was isolated as a TFA salt in quantitative yield.

The carboxyl group in *N*-α-BOC-*N*-ε-BOC-*l*-lysine **16**[60] was methylated (CH_3I, Cs_2CO_3, DMF, 65%) and also benzylated (benzyl bromide, Cs_2CO_3, DMF, 68%) to afford *O*-benzyl esters **17** and **18**, respectively. Both the α- and ε-BOC groups in these were quantitatively cleaved with TFA in THF, yielding lysines **19** and **20** as TFA salts.

Finally, *N*-ε-Cbz-*l*-lysine **21**[61] was acylated with *n*-octanoyl chloride (K_2CO_3, EtOAc-H_2O, 1:1) to yield lysine acid **22** in 71% yield. The α-Cbz group in **8** was cleaved with 10% Pd/C in CH_3OH to yield **23** in quantitative yield.[62]



Scheme 2.1 Synthetic approach towards calix[4]arene amino acids.

In the coupling experiments between calixarenes and lysines, calix[4]arene acid chloride **26** was employed, which was prepared from the corresponding triester monoacid calix[4]arene **25** and $SOCl_2$ (Scheme 2.1).[63] An equimolar amount of **26** in EtOAc was added to a solution of ε-deprotected lysines **6, 10, 11**, or **14** in EtOAc-H_2O,

1:1 and excess K_2CO_3. The reaction was complete in ~3 h and afforded calixarene lysines **1a-d** in 62-67% yield after column chromatography (Scheme 2.1).

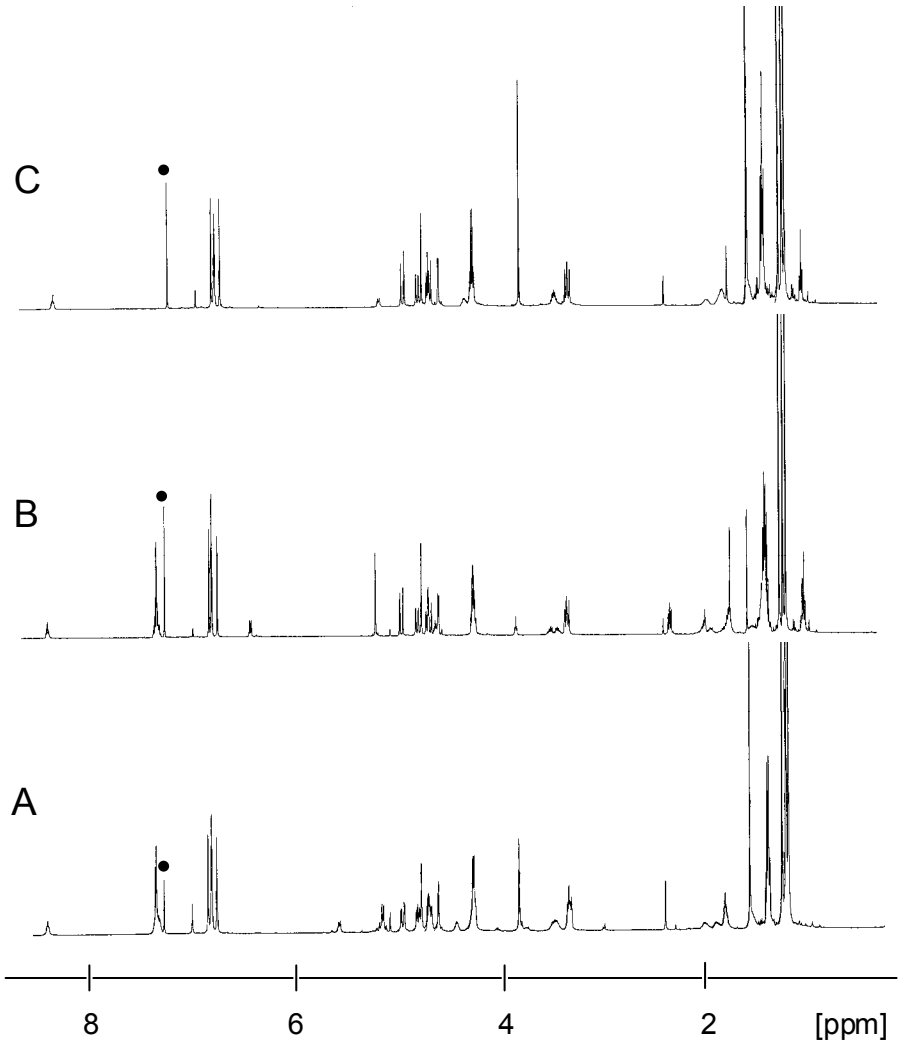


Figure 2.7 ^{1}H NMR spectra (500 MHz, $CDCl_3$, 295 ± 1 K) of calixarene lysines: A) **1b**. B) **1a**. C) **1d**. The residual $CHCl_3$ signals are marked "•".

The structure of compounds **1a-d** was confirmed by high-resolution ^{1}H NMR spectroscopy and MALDI mass spectrometry. Typical ^{1}H NMR spectra are consistent with the mono-substituted calix[4]arene pattern, and contain in particular three calixarene aromatic (apparent) singlets in 1:2:1 ratio and three calixarene *t*-Bu singlets

in 1:2:1 ratio ($CDCl_3$, 295 K) (Figure 2.7). The ε-NH-C(O) amide proton is seen far down field as a triplet at ~8.4 ppm and apparently involved in the C=O•••H-N hydrogen bonding with the calixarene lower rim carbonyl oxygens in apolar $CDCl_3$.[64]

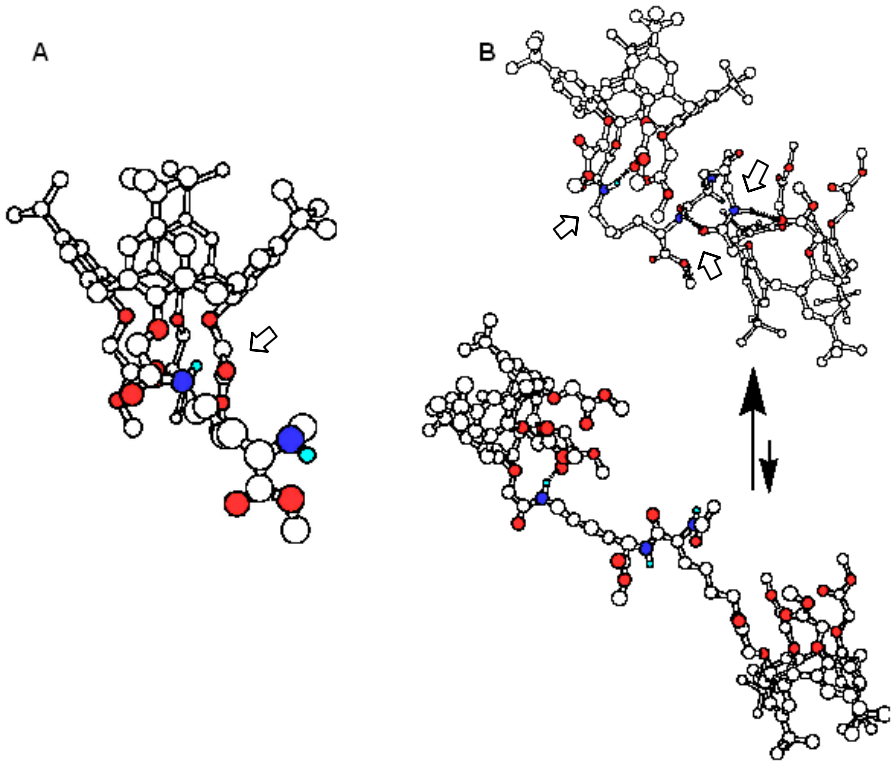


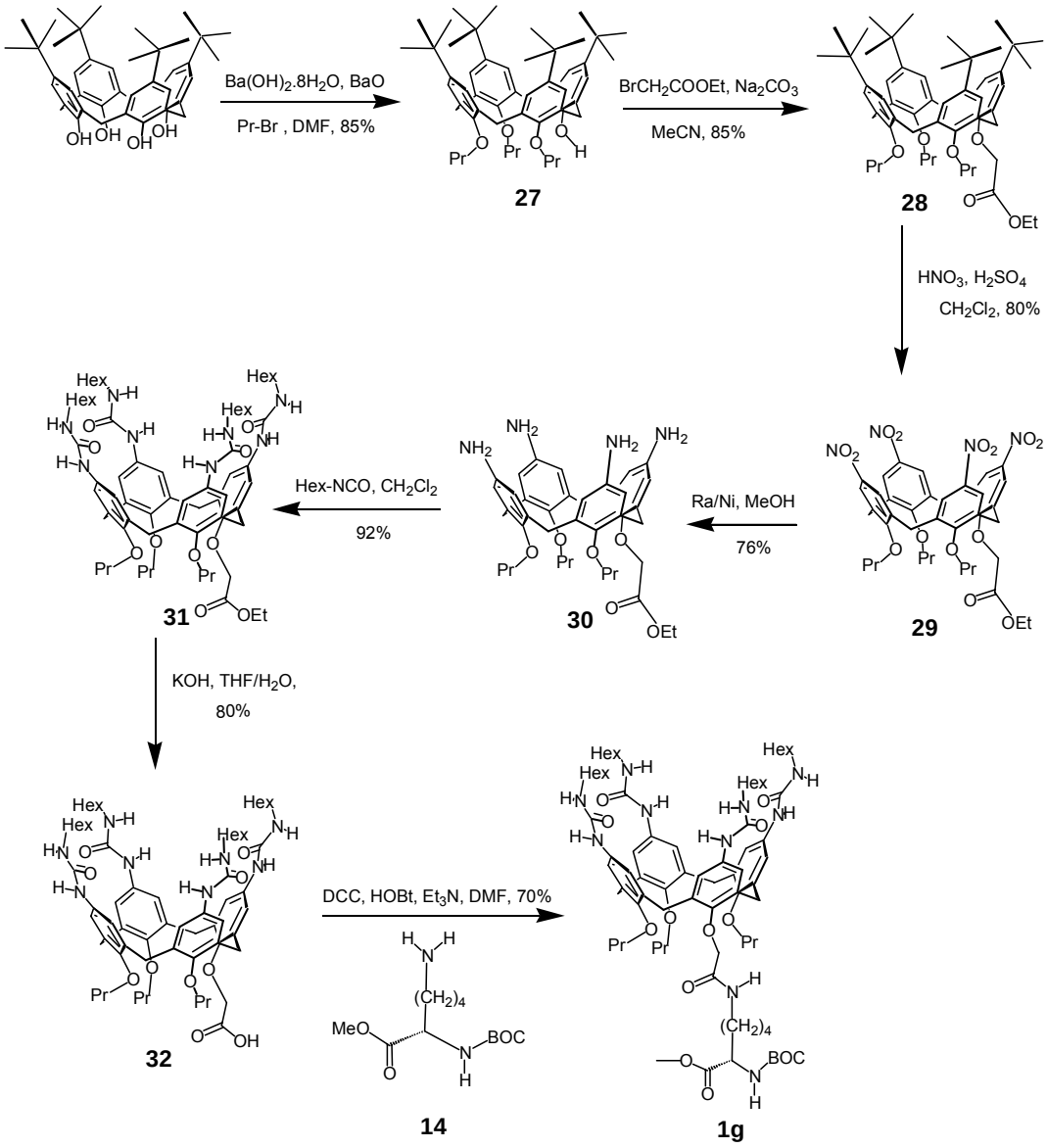
Figure 2.8 MacroModel 7.1 (Amber* ForceField) representation of calix[4]arene lysine **1** (A) and calixarene dipeptide **2** (B). Possible C=O•••H-N hydrogen bonding is marked by arrows. For dipeptide **2**, both folded and unfolded structures are shown. The CH hydrogens and long alkyl chains are omitted for viewing clarity.

The α-NH-C(O) proton is observed as a doublet and seen at ~5.5 ppm for carbamate derivatives **1b-d**, and at 6.4 ppm for amide derivative **1a**. As follows from molecular modeling (Figure 2.8), the calix[4]arene fragment is positioned ~5-7 Å away from the amino acid fragment and should not sterically interfere with the peptide bond

formation. It can also easily fit within the peptide/dendritic superstructures without disrupting hydrogen bonding and intramolecular folding processes.

Standard manipulation with protecting groups afforded calixarene amino acids with free either NH_2 or C(O)OH ends. For example, removal of the *O*-benzyl group in calix lysine **1a** was accomplished by catalytic hydrogenolysis with 10% Pd/C in CH_3OH and afforded free acid **1e**. Cleavage of the BOC protection group in derivative **1d** was carried out with TFA in THF to give lysine **1f** containing an amino group.

In the synthesis of calixarene tetraurea amino acids, parent calixarene was first alkylated with *n*-propyl bromide in presence of $Ba(OH)_2 \bullet 8H_2O$ and BaO to generate tripropyl calixarene **27** in 85% yield (Scheme 2.2). Compound **27** was obtained by alkylation with ethyl bromoacetate to afford the ethyl ester **28** in 85% yield. Calixarene monoester **28** was successfully transformed into tetranitro derivative **29** with fuming HNO_3 and was then converted into tetraamine **30** (Ra/Ni, H_2, MeOH) and then tetraurea **31** (*n*-hexyl isocyanate, CH_2Cl_2). Basic hydrolysis of **31** with aqueous LiOH afforded the monoacid **32** (80% yield). Finally, lysine derivative **14** was coupled with the monoacid (EDCI, HOBt and Et_3N) to generate the calixarene tetraurea amino acid **1g** in 75% yield. Compound **1g** bearing a carboxyl group on this lower rim is readily incorporated into the peptide networks by the formation of amide bonds.



Scheme 2.2 Synthesis of calixarene tetraurea amino acid **1g**.

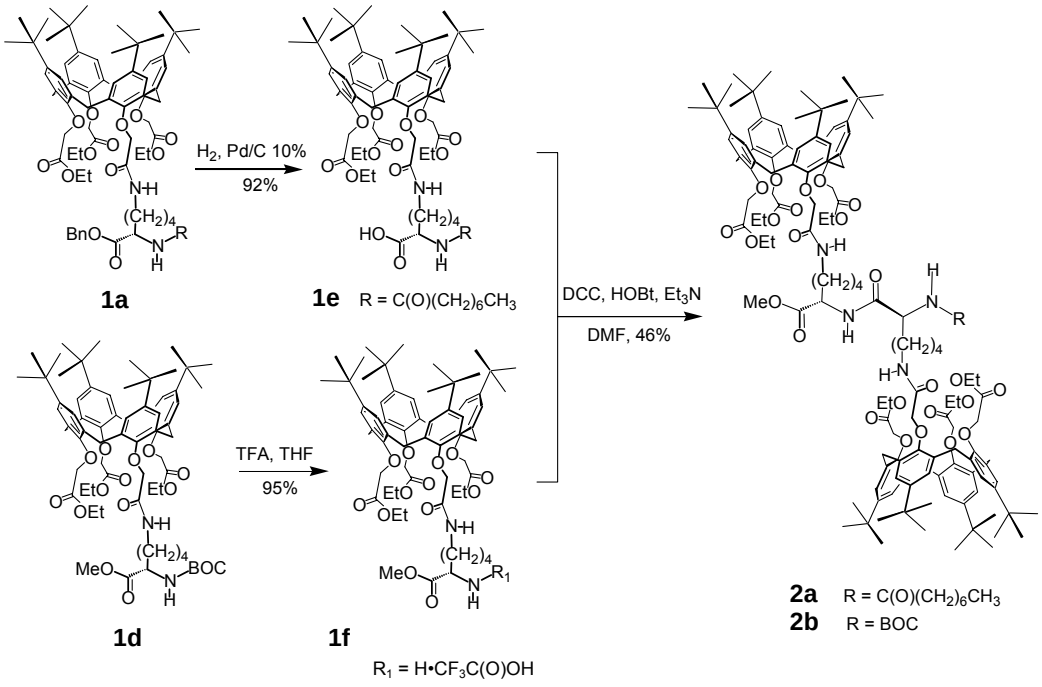
2.3 Calixarene Peptides

Synthetic peptides have already been functionalized with binding and catalytic sites.[65] For example, metalloporphyrin-containing *de novo* designed proteins effectively mimic natural photosynthetic centers.[66] Peptide-based fluorescent metal ion sensors

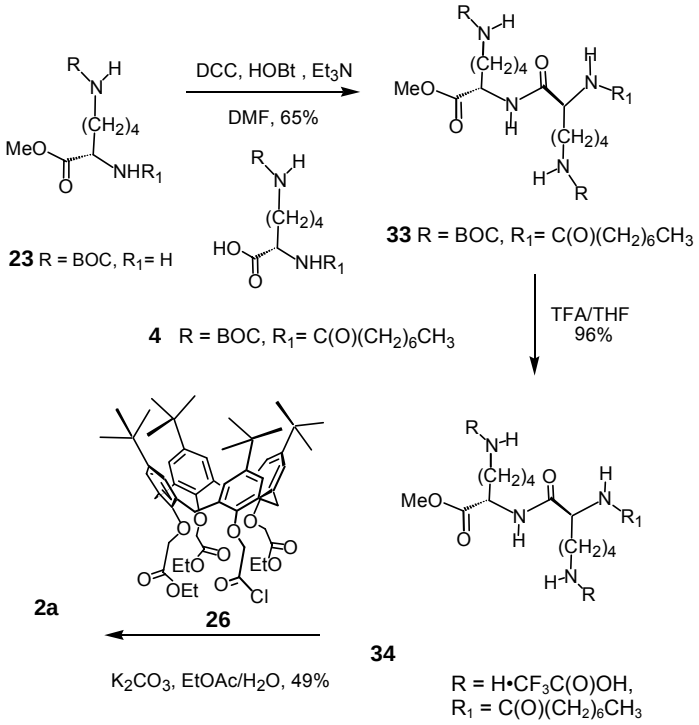
comprising a metal recognition domain and a signal transduction moiety that is triggered upon metal ion binding have been assembled.[67] A number of selective sensors have been constructed which are based on naturally occurring zinc fingers, serum albumin proteins and siderophores.[68] Another important area of application is based on the DNA binding ability of proteins and their assemblies.[69]

In principle, any modified amino acids can be incorporated within the polymeric peptide sequence. Preparative organic chemistry of amino acids and peptide bond formation is well developed.[70] Secondary and even higher order structures of peptides largely depend on the solvent, temperature, etc. and can be studied by standard spectroscopic techniques and also somewhat predicted by molecular modeling. As follows from our own molecular modeling, the calix[4]arene platform is ≤10 Å in its dimensions, so it can easily fit into the peptide network.

In the synthesis of calixarene peptides, standard peptide coupling methods were employed (Scheme 2.3). Lysines **1f** and **1e**, possessing free amino and carboxylic groups respectively, were mixed with equimolar amounts of DCC and HOBT in DMF and stirred at room temperature for 36 h. Standard workup and chromatography afforded calix dipepide **2a** in 46% yield.

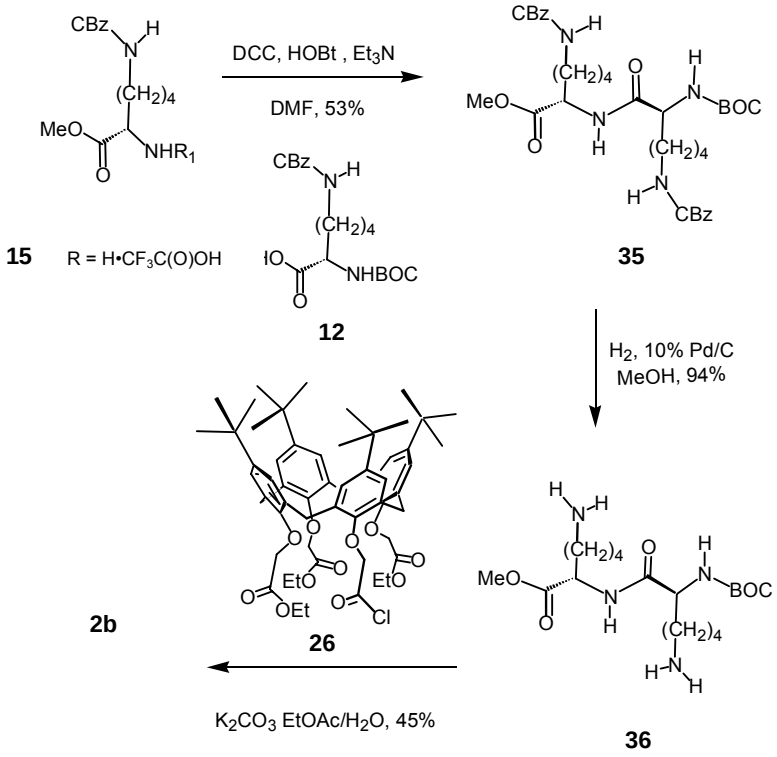


Scheme 2.3 Synthetic approach towards calix[4]arene dipeptide **2** (Approach 1).



Scheme 2.4 Synthetic approach towards calix[4]arene dipeptide **2a** (Approach 2).

In an alternative procedure (Scheme 2.4), 2.4 equivalents of calixarene acid chloride **26** were coupled with the ε-NH_2 groups of *preformed* bis-lysine derivative **34** (K_2CO_3, EtOAc-H_2O, 1:1) with the formation of **2a** in 49% yield after column chromatography. Bis-lysine **34** was prepared from bis-BOC derivative **33**, which itself was synthesized from from amino acids **23** and **4** (DCC, HOBT, DMF, 64%). *Both* protocols gave comparable quantities of calix dipeptide **2a**.



Scheme 2.5 Synthetic approach towards calix[4]arene dipeptide **2b** (Approach 2).

Similarly, bis-lysine **35**[71] was prepared from amino acids **12** and **15** (DCC, HOBT, DMF, 53%) (Scheme 2.5). This was then deprotected with Pd/C in CH_3OH resulting in **36** in 94% yield. Bis-lysine **36** reacted with 2.4 equivalents of monoacid

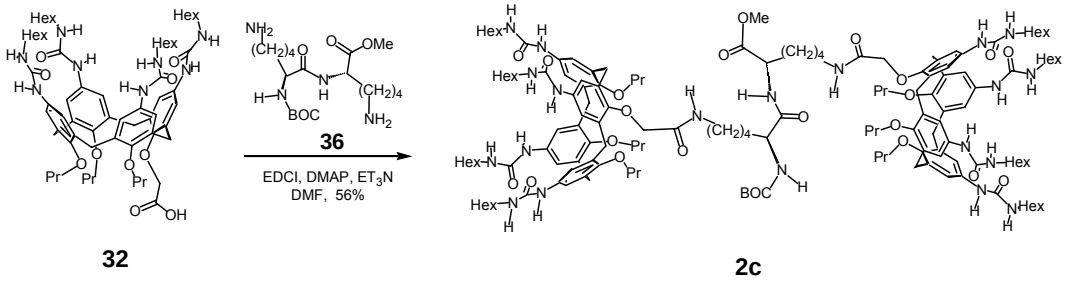
chloride **26** in presence of K_2CO_3 (EtOAc-H_2O, 1:1) with the formation of calixarene dipeptide **2b** in 45% yield after column chromatography.

The structure of calixarene dipeptides **2a,b** was confirmed by FTIR, ^{1}H and COSY NMR spectroscopy, and MALDI mass spectrometry. Although the compounds were reasonably soluble in $CDCl_3$, the corresponding ^{1}H NMR spectra appeared to be rather broad, most probably due to noncovalent aggregation. Molecular modeling (MM2 and Amber Force Field) suggests that not only the ε-NH-C(O) amide protons participate in the C=O•••H-N hydrogen bonding with the calixarene lower rim carbonyl oxygens, but also the α-NH-C(O) proton is now involved in the intramolecular folding process (Figure 2.8, Page 23). The FTIR spectra of **2a,b** in KBr contain mostly associated NH stretching at ~3300 cm^{-1}.

In contrast, DMSO-d_6 competes with hydrogen bonding and thus produces sharper peaks. Typically, the ^{1}H NMR spectra are consistent with the mono-substituted calix[4]arene pattern. Dipeptide **2a** and also **33** and **34** exhibit two ~1:1 sets of signals for all groups of protons, indicating that pairs of diastereomeric products are formed in these cases. We attribute this to the base-catalyzed racemization of the amino acid precursor **4**, which was subsequently used in the preparation of racemic calixarene lysine **1e**, and also resulted in pairs of diastereomers for dipeptides **33** and **34**. This is not the case for dipeptides **2b**, **35**, and **36**, which were obtained enantiomerically pure (optical rotation, ^{1}H NMR analysis in different solvents).

Two equivalents of calixarene tetraurea **32** bearing a carboxyl group on its lower rim were introduced to the side chains of dilysine molecule **36** by standard

peptide coupling (EDCI, HOBt, Et_3N). The resulting calixarene peptide **2c** was isolated by flash column chromatography in 56% yield (Scheme 2.6). Compound **2c** was fully characterized by FTIR, ^{1}H, ^{13}C and COSY NMR spectroscopy, MALDI mass spectrometry.



Scheme 2.6 Synthesis of calix[4]arene tetraurea dipeptide.

In summary, we have developed a modular strategy towards synthesis of nanoscale receptor macromolecules—calix–peptides. These compounds combine the unique host–guest capabilities of calixarene chemistry with the general utility of peptide synthesis. A series of calixarene amino acids were prepared, which were further utilized to synthesize calixarene dipeptides. Through this approach, calixarene amino acids are now available to be incorporated into peptide networks and nanostructured biological materials. This opens novel perspectives for the modular design of multifunctional receptors and sensors, multiply attached cavities and capsules, macromolecular devices and smart polymeric materials.

CHAPTER 3

SUPRAMOLECULAR APPLICATIONS OF CALIXARENE-PEPTIDE CONJUGATES

The design and construction of macromolecular entities, composed of many identical components functioning as receptors, are among the new challenges of chemistry.[72] Multifunctionality of receptor molecules reflects a current trend of chemical sciences going towards "smart" materials, informationally rich molecular devices, and nanofabrication.[73] Through multiple, multivalent interactions macromolecular receptors display an increased affinity towards substrates, including biologically relevant ones. Such an increase is due to either purely statistical reasons or positive cooperative effects. It is important therefore to assemble molecules into supramolecular structures, the properties of which surpass those of the molecular collection. This requires understanding the structure and dynamics of intra- and intermolecular interactions so that the properties of such molecular collections can be predicted and controlled.

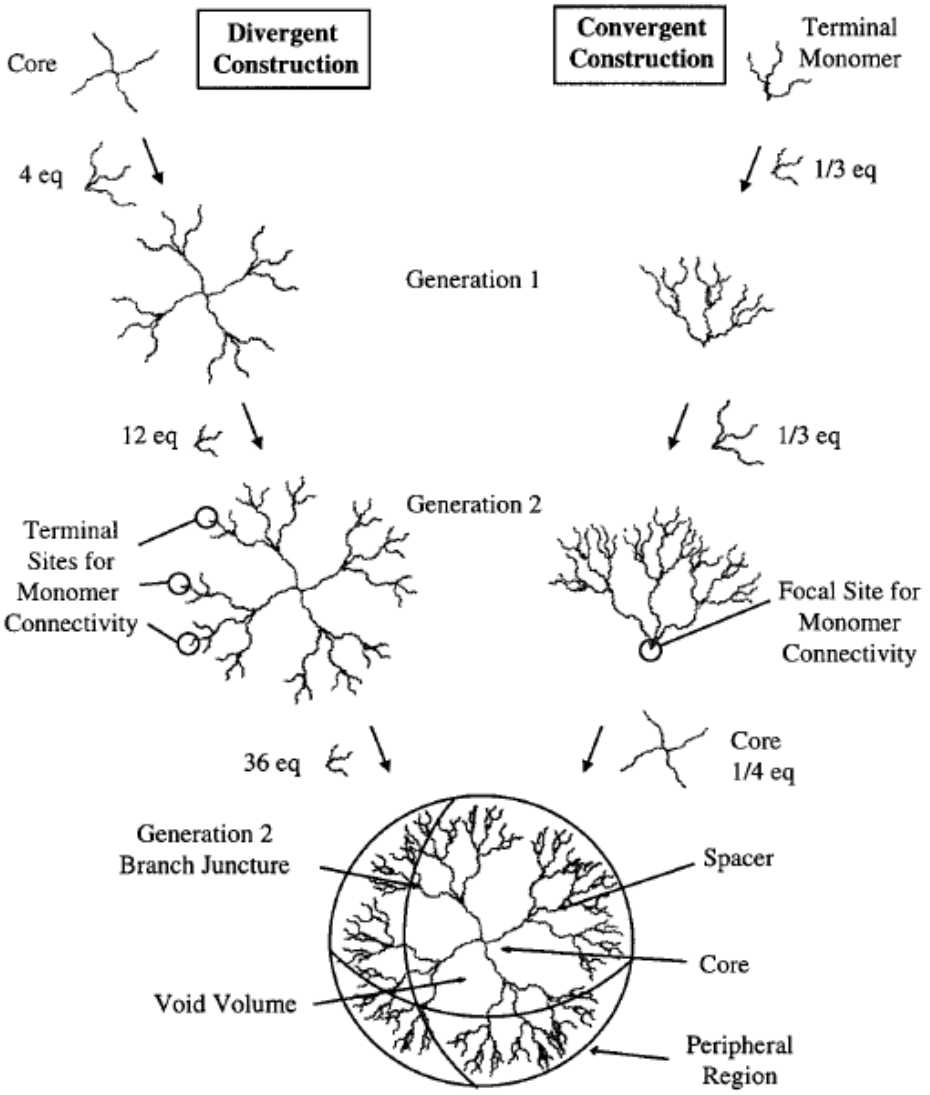
In the work described in Chapter 2, we took advantage of peptide chemistry and introduced a novel, *modular strategy* towards receptor macromolecules. This strategy combined synthetically diverse peptide synthesis with highly functional calixarene chemistry. Our approach resulted in novel macromolecular entities-calixarene amino acids and calixarene peptides. Here, we demonstrate supramolecular properties of

calixarene- peptide conjugates described in Chapter 2.[49,50] Specifically, these peptide-based calixarenes were further utilized to construct nanostructures – calixarene-peptide dendrimers, peptide-based self-assembling calixarene capsules and supramolecular polymers. Moreover, calixarene amino acids, peptides, and peptide dendrimers containing tetra-ester functions at their lower rims were used for the complexation of Na^+ cations.

3.1 Calixarene Peptide Dendrimers

Over recent years, dendrimers have revolutionarily entered supramolecular and materials chemistry.[74] The layered, nanoscale architecture, globular shape, controlled nanomolar dimensions and easy modification have made dendrimers possess unique supramolecular properties. Multivalent surfaces of dendrimers offer a unique opportunity for the substrate binding, providing strength and, often, cooperativity, with minimalized energy loses for reorganization and diffusion.

Synthetically, dendrimers are constructed in an iterative fashion. This leads to a stepwise synthetic growth which distinguishes dendrimers from normal polymers. In the literature, two different synthetic approaches have been utilized to construct high-generation dendrimers: the convergent approach[75] and divergent approach[76] (Scheme 3.1). In the divergent synthesis, the dendrimer is built in a stepwise manner from the central core out to the periphery. In contrast to the divergent synthesis, the convergent synthesis builds dendrimers from the periphery toward the central core.



Scheme 3.1 Representative 'divergent' and 'convergent'protocols for dendrimer construction with common terminology.[77] (Adapted from *Chem. Rev.* **1999**)

It is always challenging and time consuming to synthesize high-generation dendrimers. However, there have been many classic and complex dendrimers reported in the literature for different purposes (Figure 3.1). While synthesis of dendritic systems is a crucial issue for their development, more attention is being devoted to study the

three dimensional structures of dendrimers and their use in biological and materials applications.

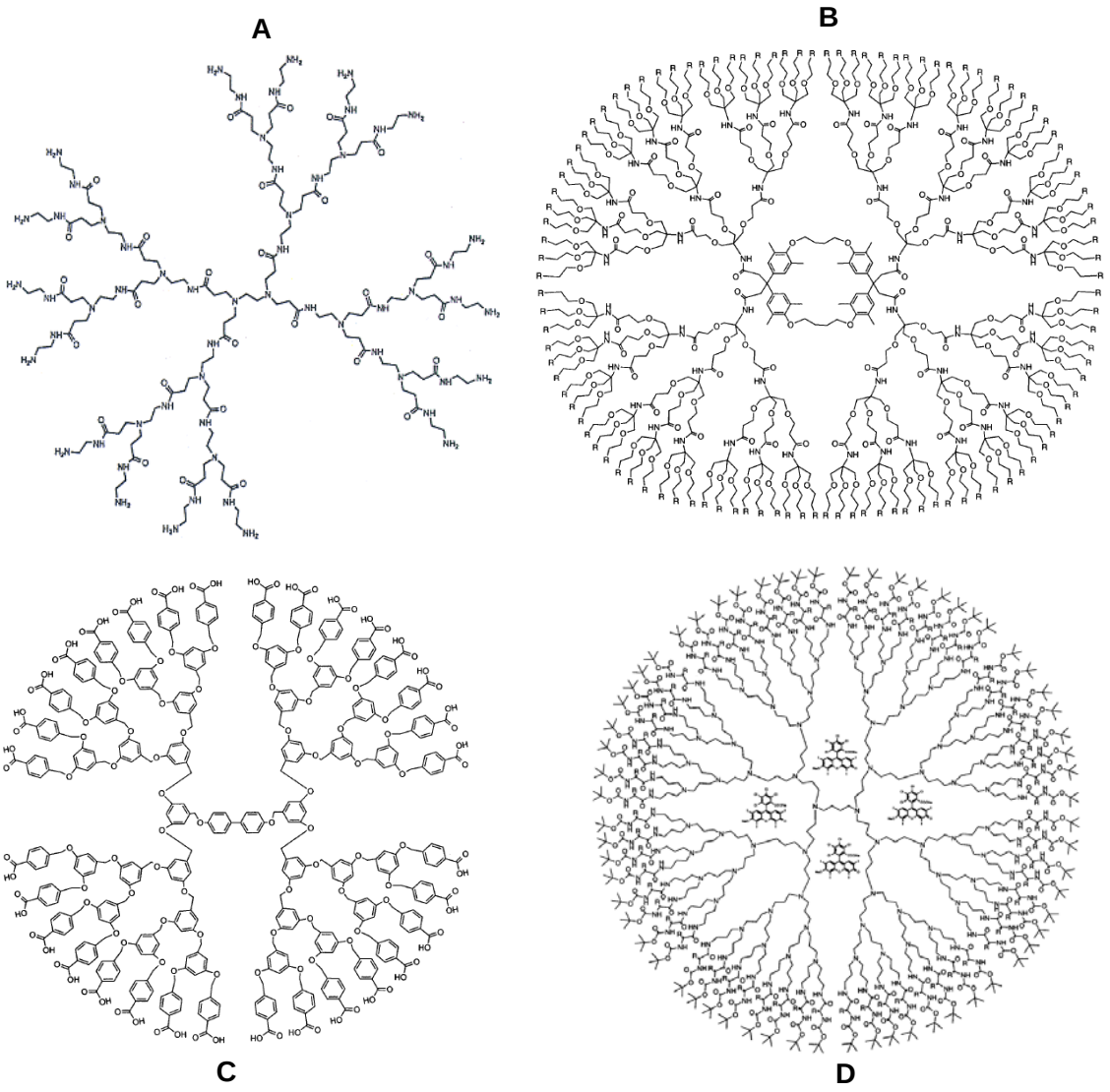
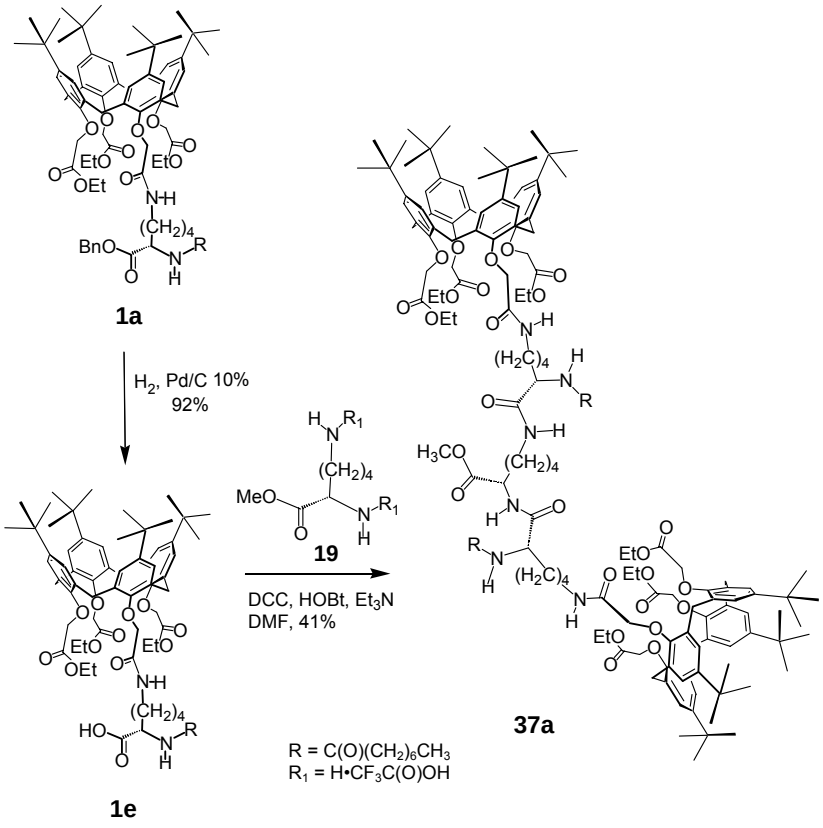


Figure 3.1 A) Tomalia's poly(aminoamine) (PAMAM) dendrimer.[78] B) Dendrophanes reported by Diederich and co-workers.[79] C) A water-soluable polyaryl ether dendrimer reported by Frechet.[80] D) Meijer's dendritic box with Bengal Rose molecules inside.[81]

Surprisingly, to date, only limited progress has been reported in the literature on the preparation of calixarene dendrimers. For example, our search with SciFinder Scholar performed in 2002 produced ~6000 references on dendrimers and ~5000 references on calixarenes, but less than 10 papers on calixarene-based dendrimers. A calix[4]arene platform was used as a *core* to which photochromic dyes and carbohydrate dendrons were attached.[82] This was relatively easy to achieve through standard, symmetrical tetrafunctionalization of calixarene. However, prior to our work in this area, only two published examples,[83] involving calixarenes as *branches* and/or *surface elements*, were reported. The repetitive branching strategy for the preparation of higher dendritic generations had not been demonstrated. In a single report, Böhmer and co-workers postulated the *divergent* approach towards dendrimers, based on the multiple amide bond formation between appropriately functionalized calix[4]arene amines and calix[4]arene acid chlorides.[84] Experimentally, this had not been accomplished. In this chapter, we propose a *convergent*[85] approach towards calixarene-containing dendrimers, which employs peptide chemistry. In such dendrimers, calixarene fragments are situated on the surface, thus providing the multivalency, and peptide groups serve as branching units. Our structures appeared to be among the earliest calixarene dendrimers in the literature. After this work, Appelhans designed and synthesized a novel dentritic core based on thiacalixarene derivatives,[86] and Vicens reported calix[4]-dendrimers with a 'tren' unit as a core.[87]

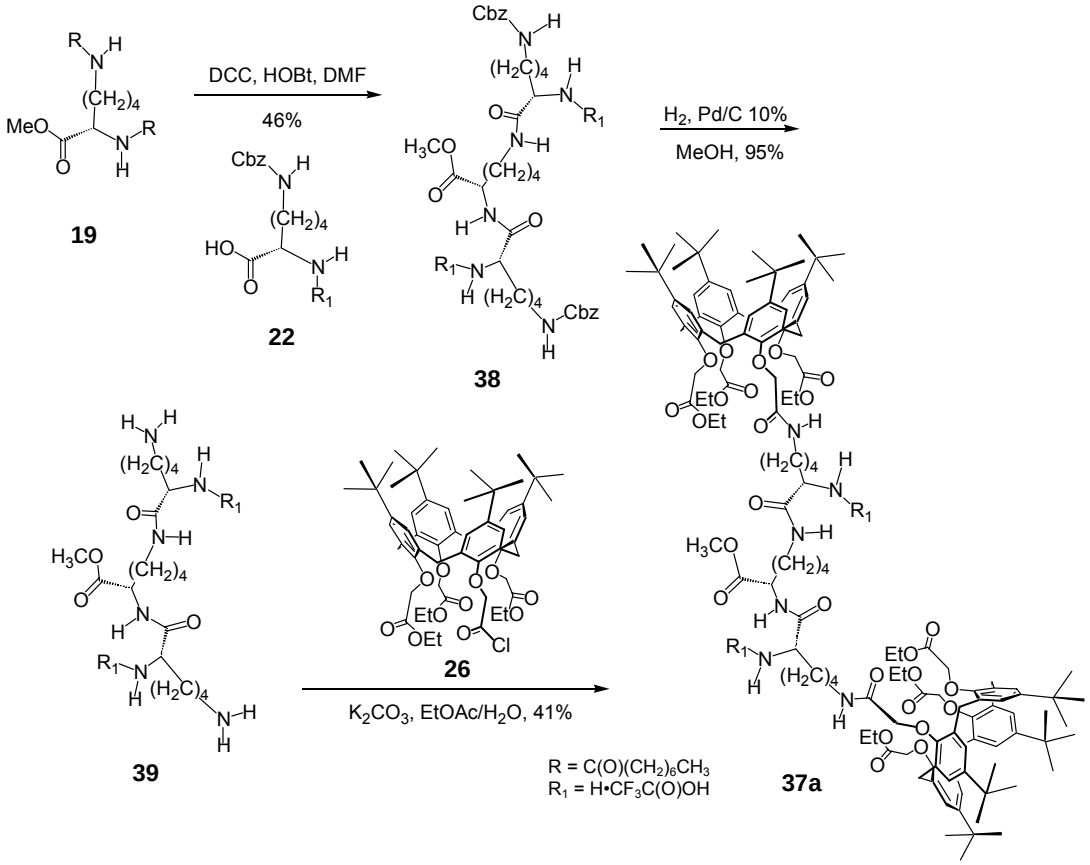
In principle, peptide dendrimers are broadly defined as any dendrimer containing peptide fragments.[88] They are well suited for various biochemical and

biotechnological applications, including diagnostic reagents, protein mimetics, anticancer and antiviral agents, caccines, and drug delivery systems.[89] Synthetically, amino acids are appealing building blocks because of well-developed peptide-coupling techniques. Polyamino acids consisting of branches of a trifunctional acid, especially lysine, represent the largest and most popular group of branching units being used today.[88] The diamino nature of lysine creates a unique situation where each additional level of lysines effectively doubles the number of sites to which monomers are attached.



Scheme 3.2 Synthesis of the first generation of calixarene dendrimer **37a** (Approach 1).

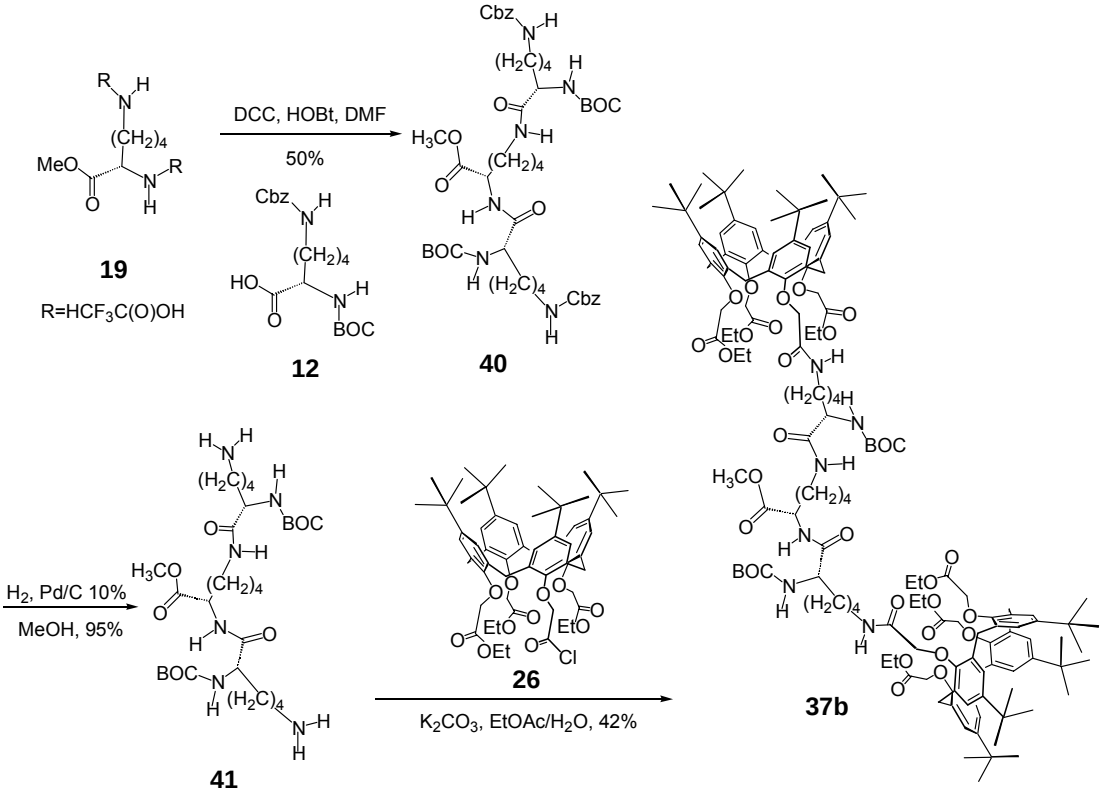
In the synthesis of calixarene dendrimers, two equivalents of calix amino acid **1e** were submitted to the coupling reaction with lysine methyl ester **19** in the presence of equimolar amounts of DCC and HOBT in DMF producing, after purification, 41% of dendritic bis-calixarene **37a** (Scheme 3.2).



Scheme 3.3 Synthesis of first generation of calixarene dendrimer **37a** (Approach 2).

In the alternative procedure (Scheme 3.3), triester monoacid chloride **26** was coupled with the preformed, first-generation lysine dendrimer **39** in presence of K_2CO_3 (EtOAc-H_2O, 1:1). This yields 47% of **37a** after column chromatography on silica gel. Bis-lysine **39** was prepared by the Pd/C catalyzed hydrogenation of bis-Cbz derivative

38 in CH_3OH, which in its turn was obtained from amino acids **22** and *O*-methyl ester of *l*-lysine **19**. Accordingly, *both* procedures successfully yielded the same dendrimer. Since racemic lysine **4** was employed (see Chapter 2, Figure 2.6), dendrimer **37a** in our experiments was obtained as a mixture of diastereomers, which is highly difficult to separate. Similarly, calixarene acid chloride **26** was coupled with the preformed, first-generation lysine dendrimer **41** (K_2CO_3, EtOAc-H_2O) to afford optically pure dendrimer **37b** in 42% after column chromatography. Precursor dendrimer **41** was prepared by the Pd/C catalyzed hydrogenation of bis-Cbz derivative **40**, which was obtained from amino acids **12** and **19** (Scheme 3.4).



Scheme 3.4 Synthesis of first generation of calixarene dendrimer **37b** (Approach 2).

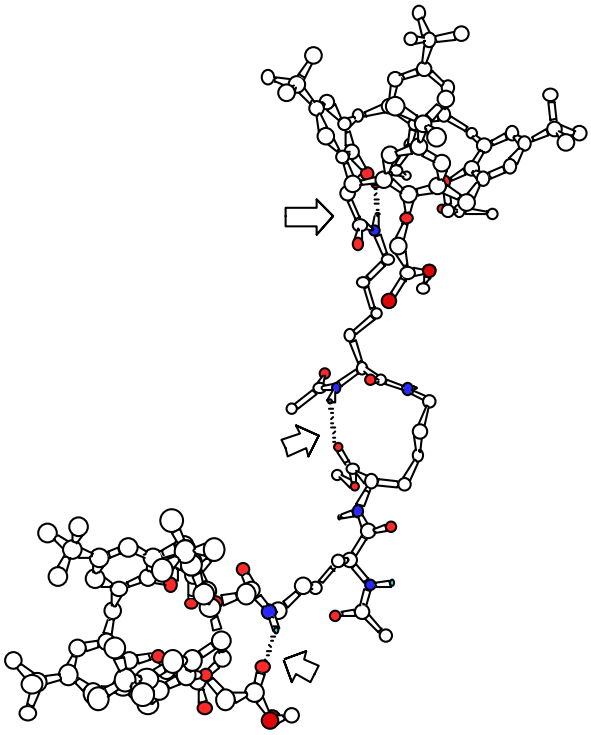


Figure 3.2 MacroModel 7.1 (Amber* ForceField) representation of calix[4]arene dendrimer **37**. Possible C=O•••H-N hydrogen bonding is marked by arrows.

The structure of compounds **37a,b** was confirmed by high-resolution ^{1}H and COSY NMR spectroscopy and MALDI mass spectrometry. With their nanoscale dimensions and masses of >2500 Daltons, the structural assignments of **37a,b** were heavily depended on the similarity of spectral features of simpler precursors such as tripeptides **38-41** and also calix lysines **1a-f**. Although soluble in $CDCl_3$, **37a,b** exhibit broad peaks in the ^{1}H NMR spectra, probably due to noncovalent aggregation. As expected, DMSO-d_6 competes with hydrogen bonding and thus produces sharper peaks. Similar to dipeptides **2a,b**, molecular modeling suggests that not only the ε-NH-C(O) amide protons are involved in the C=O•••H-N hydrogen bonding with the calixarene

lower rim carbonyl oxygens, but also the α-NH-C(O) proton participates in the intramolecular folding process (Figure 3.2). In the folded conformation, the calix[4]arene fragments are positioned ~15 Å away from each other. Such a long distance is important for building next generations of calix dendrimers.

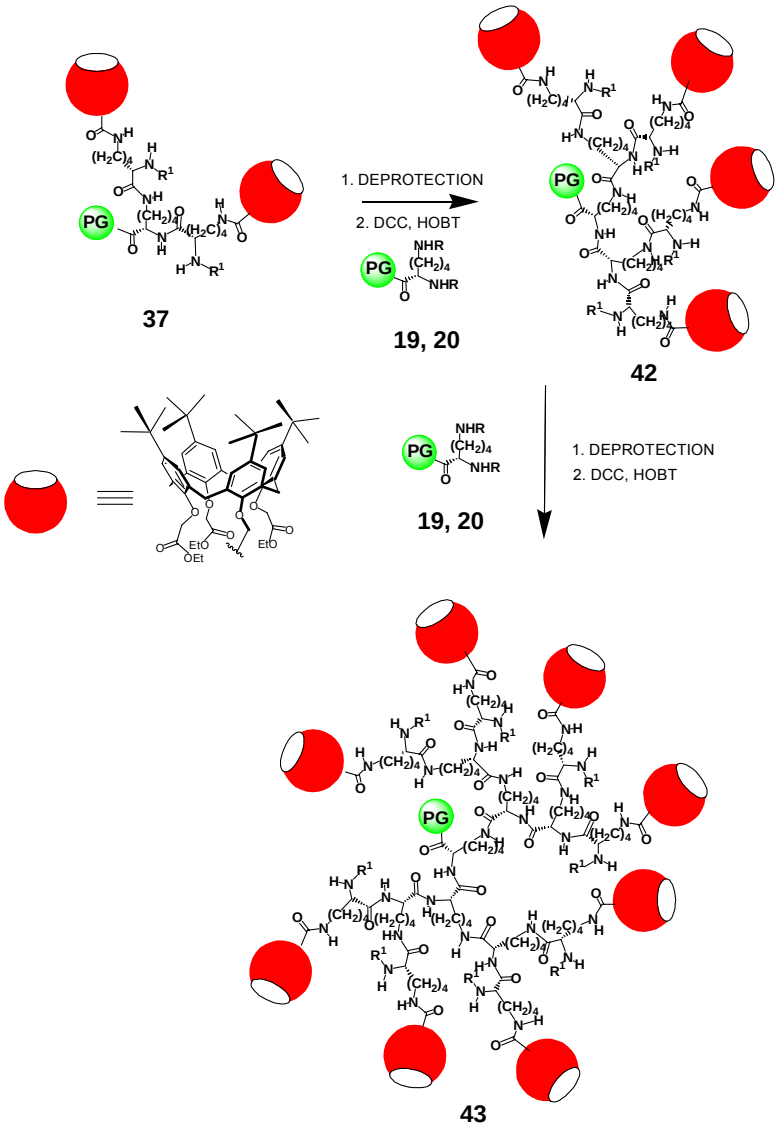
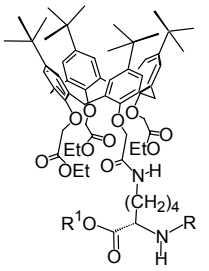


Figure 3.3 Towards higher generations of calixarene peptide dendrimers.

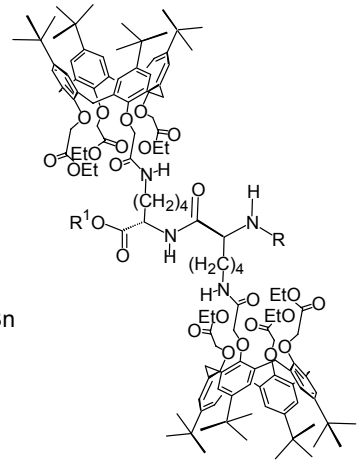
Dendritic structures **37a,b** may be regarded as a first generation of more expanded peptide dendrimers with calixarene surfaces. Indeed, in the convergent strategy, the C(O)OMe group of the core may be deprotected, activated and used in the coupling step with lysine esters **19** or **20**. This will result in the second generation of calix peptide dendrimers **42**. Subsequently, the core ester group may be further deprotected again, activated and coupled with **19** or **20** to afford the third generation of dendrimer **43**. These steps can be repeated (Figure 3.3).

3.2 Na^+ Complexation Experiments

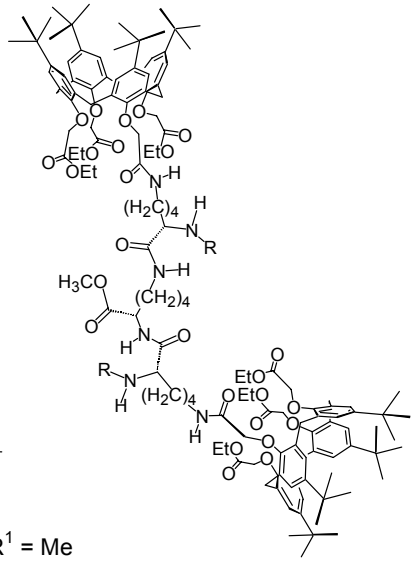
Calix[4]arene functionalized with C(O)OAlk ester and/or $C(O)NHAlk/C(O)NAlk_2$ amide groups at the lower rim demonstrate a unique affinity and selectivity towards Na^+ cation not only in single solvents, but also in extraction experiments from water to organic solvent and in the transport experiments through bulk liquid and supported liquid membranes.[90] Solid-state and NMR-derived structures showed perfect Na^+ coordination within the lower rim pocket, consisting of eight basic, ether and carbonyl oxygen atoms. Such complexes are kinetically stable on the NMR time scale (e.g., $K_{ass} >> 10^6$ M^{-1}), and the exchange between free calixarenes and complexes is slow.[36]



1a R = $C(O)(CH_2)_6CH_3$, R^1 = Bn
1b R = Cbz, R^1 = Me
1c R = Cbz, R^1 = *p-t*-Bu-C_6H_4
1d R = BOC, R^1 = Me



2a R = $C(O)(CH_2)_6CH_3$, R^1 = Me
2b R = BOC, R^1 = Me



37a R = $C(O)(CH_2)_6CH_3$
37b R = BOC

Figure 3.4 Calixarene lysines **1a-d**, dipeptides **2a-b**, and calixarene dendrimers **37a-b**.

We found that calix amino acids **1a-d**, calix peptides **2a,b** and dendrimer **37a,b** strongly complex Na^+ cations within their binding pockets. In the preliminary experiments, extraction was studied from aqueous solution of $NaClO_4$ to CH_2Cl_2. $NaClO_4$ was chosen because of its lipophilicity and low dehydration energy.[11]

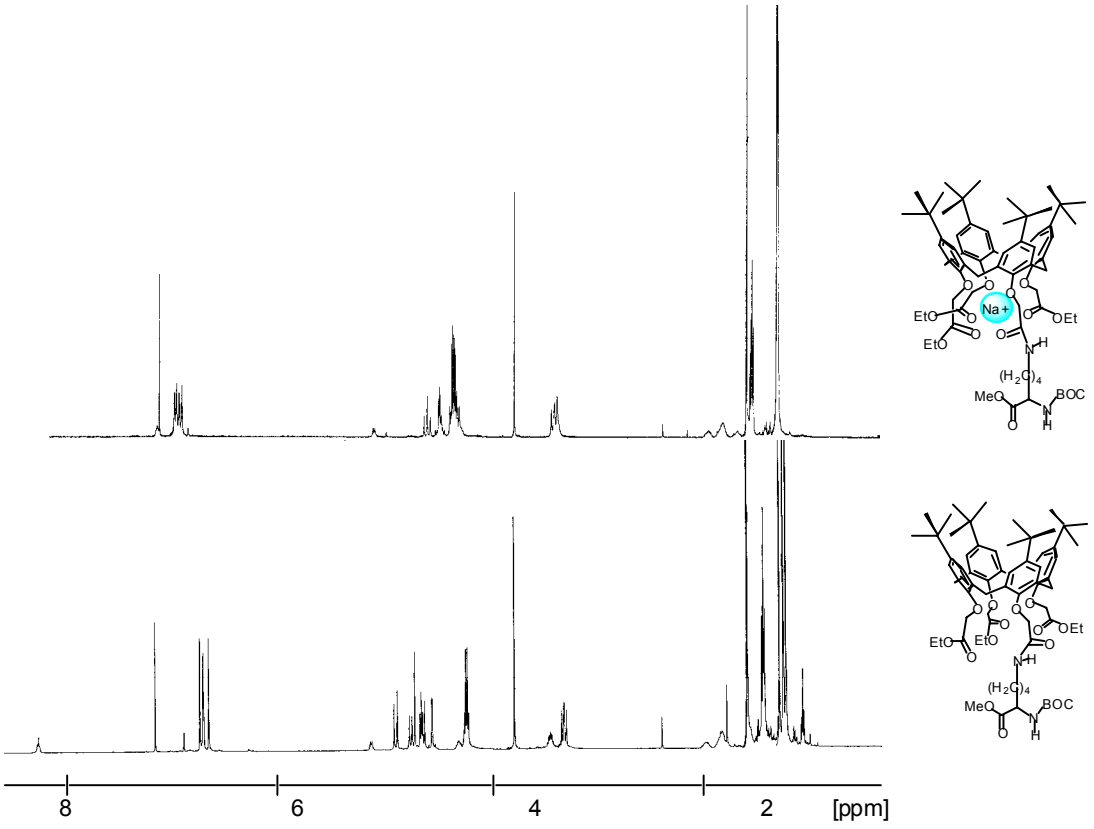


Figure 3.5 ^1H NMR spectra (500 MHz, $CDCl_3$, 295 ± 1 K) of calixarene lysines: a) **1d**. b) **1d**•$Na^+ClO_4^-$.

Specifically, **1a-d**, **2a,b**, and **37a,b** were dissolved in CH_2Cl_2 and stirred overnight with equal volumes of saturated aqueous solution of $NaClO_4$. Organic layers were then separated, evaporated under reduced pressure, dried in vacuum and analyzed by high-resolution ^1H NMR spectroscopy in $CDCl_3$. The corresponding Na^+ complexes formed quantitatively. The NMR spectra changed dramatically and exhibited new sets

of signals for all protons. Especially notable are ~0.3 ppm down field shift of the calixarene aromatic protons, and ~0.2 ppm down field shift of the OCH_2 ethyl ester protons (Figure 3.5). This is attributed to the electron-withdrawing nature of Na^+ cation. The methylene CH_2 protons next to the carbonyl at the lower rim are shifted up field, which has been observed for simpler calixarene-Na^+ complexes and is caused by complexation-induced fixation of the carbonyls. Also of interest, the ~1 ppm up field shift of the lower rim C(O)NH proton. Apparently, Na^+ cation disrupts the intramolecular C=O•••H-N hydrogen bonding at the lower rim upon complexation (Figure 3.6). No residual uncomplexed receptors were detected (Figure 3.5).

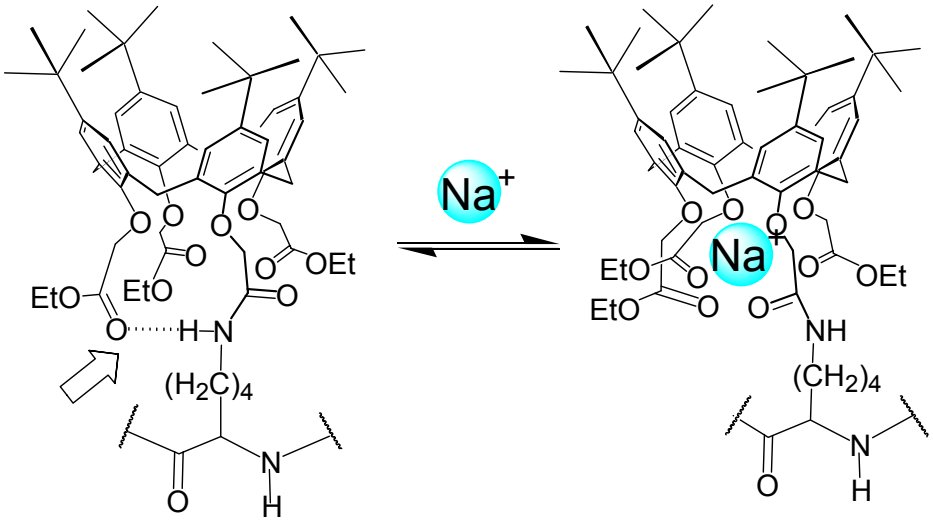


Figure 3.6 Complexation of Na^+ cation at the lower rims of multiple calix[4]arene fragments in amino acids **1a-d,** and peptides **2a, 2b** and **37**. Addition of Na^+ disrupts intramolecular C=O•••H-N hydrogen bonding. The ester C=O groups turn around to coordinate the cation.

The efficiency of compounds **1a-d**, **2a,b**, and **37a,b** as Na^+ receptors was also evident in the MALDI mass spectra: exclusively $[M+Na]^+$ parent ions were observed. This behavior is in contrast to most MALDI mass spectra of peptides which yield predominantly $[M+H]^+$ parent ions. At the same time, decomplexation of Na^+ cation was readily achieved by an excessive washing with water.

While cooperativity in Na^+ binding is not expected for **2a,b**, and **37a,b**, the presence of (a) multiple binding sites on the periphery/surface of such nanoscale receptors and (b) unique, intramolecular hydrogen bonding within their peptide scaffolds may offer strong and specific affinity towards guests. In contrast to simple collections of small receptor-molecules, which might require prior assembly/ reorganization for transport and delivery, nanostructures **2a,b,** and **37a,b** and especially their larger relatives can use intramolecular forces to arrange their multiple and interconnected components in ways that minimize free energy. Such intramolecular processes may lead to the shape changes, specific internal microenvironments, and cooperative organization of ion binding surfaces.

3.3 Self-assembly of Calix[4]arene Peptides

Self-assembly is the spontaneous, noncovalent association of two or more molecules under equilibrium conditions into stable, well-defined aggregates. In nature, self-assembly is a ubiquitous strategy responsible for the formation of cell membranes, double-stranded nucleic acids and viruses. In chemistry, self-assembly offers a rapid way to construct receptors and materials. The rather weak intermolecular forces-hydrogen bonding, metal co-ordination, charge transfer interactions and van der Waals-make self-assembly occur, bringing molecules together into two or three dimensional well-defined supramolecular architectures.

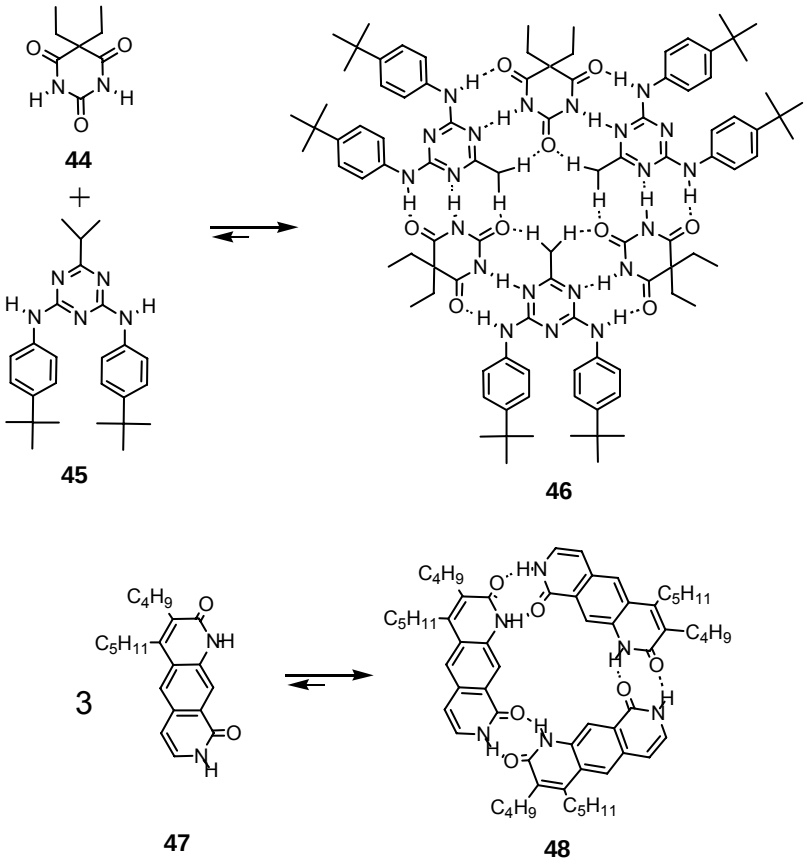


Figure 3.7 Examples of two-dimensional assemblies based on hydrogen bonding.

Hydrogen bonding is a favorite intermolecular force among those noncovalent interactions by virtue of its directionality, specificity, and biological relevance. Using hydrogen bonding to create artificial assemblies has attracted considerable interest in the last decade. Earlier studies focused on assembling individual subunits into a cyclic or linear array. For example, Whitesides discovered rosette-like molecular assemblies (for example **46**) using triple hydrogen bonding interactions between cyanuric acid **44** (CA) and melamine **45** (M). Six molecules (3 CA and 3 M) were held together by 18 hydrogen bonds to form a hexagonal network resembling a rosette (Figure 3.7).[91] The well defined hexamers can be obtained not only in the crystalline state, but also in apolar solvents. Covalent attachments of the rosette components to a molecular skeleton led to well defined structures differing by the number of particles, thus exhibiting different stability due to entropic factors. The Zimmerman group demonstrated three flat, heterocyclic pyridoquinoline molecules formed an extremely robust cyclic trimer **48** via hydrogen bonding (Figure 3.7).[92] These studies have led to the design of hydrogen bonded two-dimensional self-assemblies.

Later, Rebek[93] showed that two or more units can form self-assembling capsules with the enclosed cavities and used tennis balls, softballs, jelly donuts, and other items to illustrate the shapes of these molecular structures. These self-assembling capsules emphasize their three-dimensional features by the ability to encapsulate smaller guests. In the "tennis ball",[94] two identical C-shaped glycouril molecules **49**, or monomers, join each other in solution at right angles by means of eight hydrogen bonds and form a hollow dimer **50**. This assembly is able to encapsulate smaller molecules such as noble

gases, CH_4 and CH_2Cl_2 (Figure 3.8). Inspired by this work, Rebek,[19] Fujita,[95] Reinhoudt,[96] Dalcanale,[97] Atwood[98], and many others have designed and synthesized larger and more complex self-assembly capsules, in which one, two, even more guest molecules were co-encapsulated and even reactions were performed and accelerated.

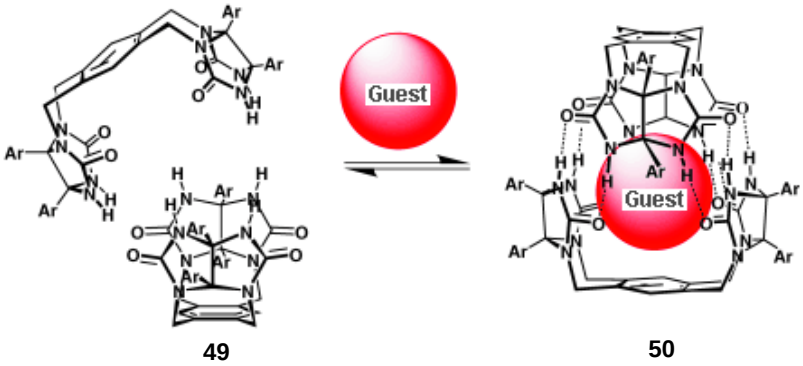


Figure 3.8 A self-assembling capsule: "Rebek's tennis ball".[94]

Self-assembling supramolecular polymers have been also introduced.[3,99] These are polymers based on monomeric units held together with *directional* and *reversible* secondary interactions.[99] Supramolecular polymers represent a novel, unique class of materials: they combine attractive features of conventional polymers with properties, resulting from the bonding reversibility. Structural and dynamic parameters, that determine polymer properties - degree of polymerization, lifetime of the chain, and its conformation - are a function of the noncovalent bonds' strength and can be reversibly adjusted.

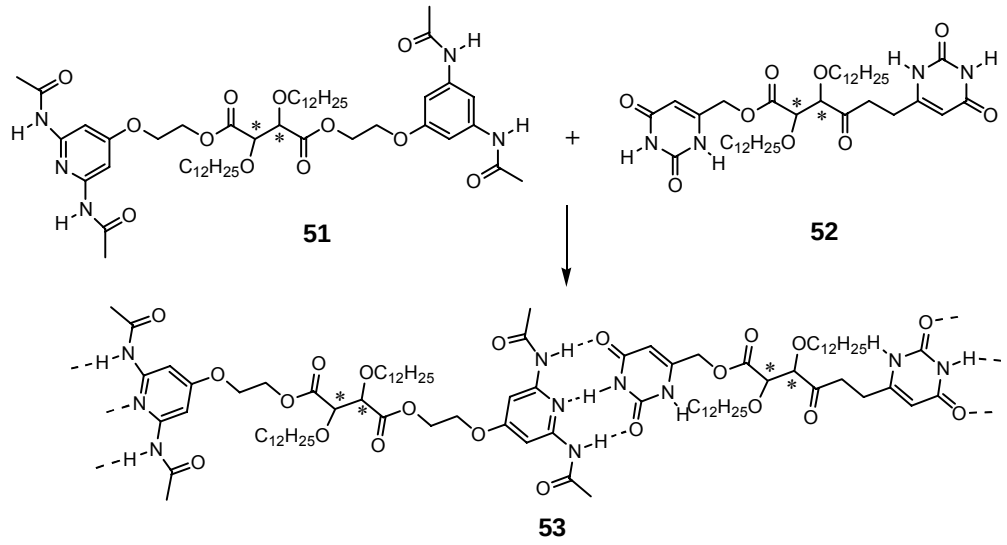


Figure 3.9 Liquid crystalline supramolecular polymers based on triple hydrogen bonds.[100]

Lehn et al. pioneered the field.[100] He showed that triple cooperative hydrogen bonding between difunctional diaminopyridines and difunctional uracil derivatives form a supramolecular main-chain polymer **53** (Figure 3.9). The 1:1 mixture of **51** and **52** exhibits liquid crystalline over a broad temperature range, whereas, in contrast, the pure compounds are solid which melt in isotropic liquid without displaying a liquid crystalline phase.

Later, Mejier discovered the strong dimerization of derivatives of 2-ureido-4-pyrimidone (dimerization constant $K_D > 10^6$ M^{-1} in $CHCl_3$), by means of a self-complementary DDAA (donor- donor-acceptor-acceptor) array of 4 hydrogen bonds. [101] These findings led to the synthesis of self-complementary bidentate, compounds, possessing two ureidopyrimidinone units, which form a stable, long and reversible

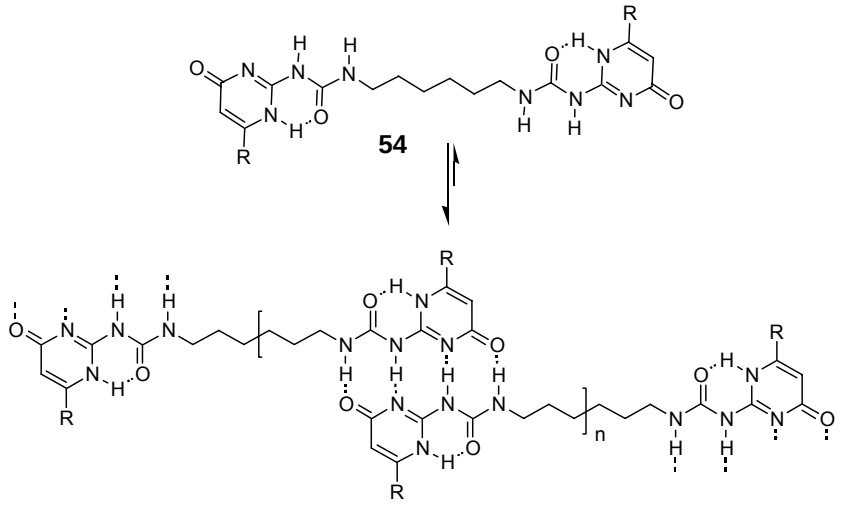


Figure 3.10 Polymeric assembly of a bifunctional ureidopirimidinone derivative.[101]

linear polymer **55** in the solution. The thermal and environmental control over lifetime and bond strength makes many properties, such as viscosity, chain length, and composition, tunable in a way not accessible to traditional polymers. This polymer was the first supramolecular polymer with the high-agree of polymerization in solution (DP = 7×10^2 at 40 mM in $CHCl_3$).[101]

The group of Rebek developed supramolecular polymers **56** using hydrogen-bonded calixarene tetraurea capsules (Figure 3.11).[102] Two calixarene urea moieties were covalently attached to a rigid linker. In apolar solvents, hydrogen bonding between urea functionalized calixarenes results in a polymeric chain. More interestingly, multiple solvent molecules/benzene size guests were encapsulated in the calixarene capsules upon polymerization.

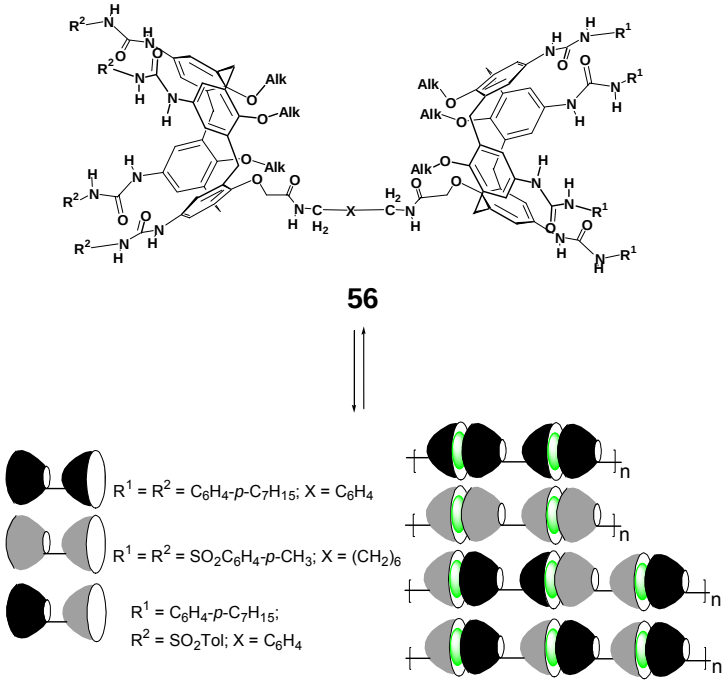


Figure 3.11 Supramolecular polymers featuring self-assembling calixarene tetraurea capsules.[102]

In our work, dimeric calix[4]arene tetraurea capsules (see Figure 2.5, Page 18) were utilized to construct calixarene amino acid capsules and calixarene peptide supramolecular polymers (Figure 3.12). Specifically, the calixarene moieties in calixarene amino acid **1g** were functionlized with hexyl ureas and as expected, strongly dimerized in apolar solvent, such as ($CHCl_3$, benzene, xylene) with the formation of capsules **1g•1g**. Typically, due to the lack of symmetry in **1g•1g**, a multiple set of NH urea signals was recorded in C_6D_6, $CDCl_3$, and $CDCl_2CDCl_2$. These are characteristically shifted down field, showing the key features of the capsule formation (Figure 3.13).[53,54]

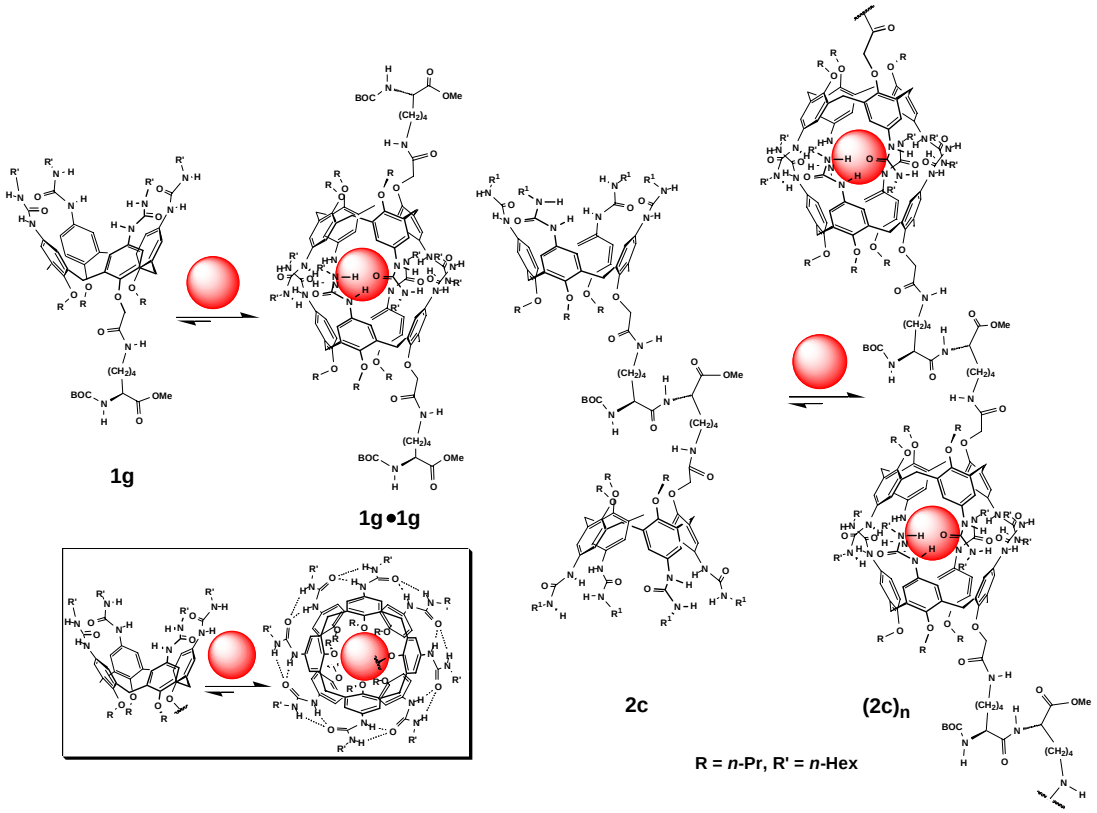


Figure 3.12 Formation of self-assembly calixarene capsule and supramolecular polymer.

As expected, calix-dipeptide **2c** self-assembles in apolar solution with the formation of supramolecular polymer **(2c)**$_n$ (Figure 3.12)**.** Due to the lack of symmetry, a multiple set of NH protons was recorded in the ^{1}H NMR spectra of **2c** in $CDCl_3$, $(CDCl_2)_2$, and benzene-d_6. These were shifted down field (≥2 ppm), which is a characteristic feature of capsule formation (for example, Figure 3.14). Both a proximal and distal regioisomers of the calixarene dimer can form, with respect to the orientation

of the acetamide $OCH_2C(O)NH$-substituents at the lower rims of each calixarene **2c**. Moreover, the circular array of hydrogen bonds can be arranged either clockwise or

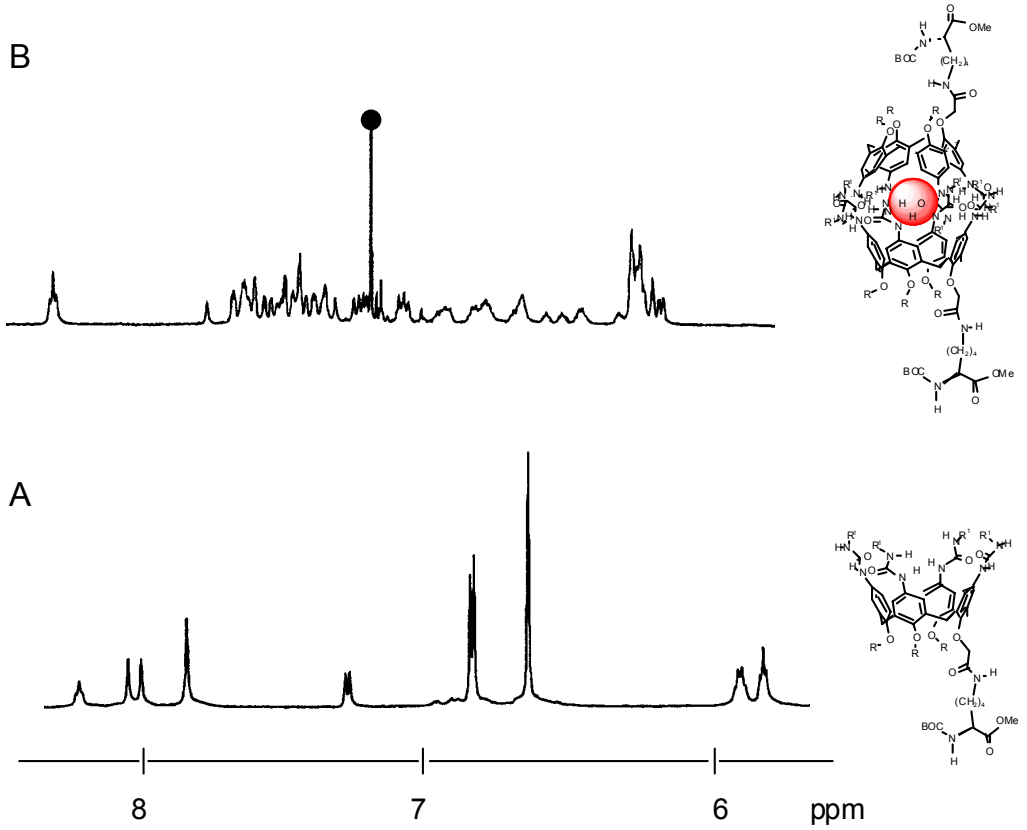


Figure 3.13 Downfield portions of ^{1}H NMR spectra (500 MHz, 295 ± 1 K) of: (A) calixarene **1g** in DMSO-d_6. (B) capsule **1g•1g** in $CDCl_3$.

counterclockwise. With the dimerization constant $K_D > 10^6$ M^{-1} for each calixarene capsule,[103] the average degree of polymerization of at least 100 can be estimated for structure **2c** at the NMR concentration range. Due to the steric restrains in the design, no intramolecular cyclization of two calixarene tetraureas in **2c** occurs.

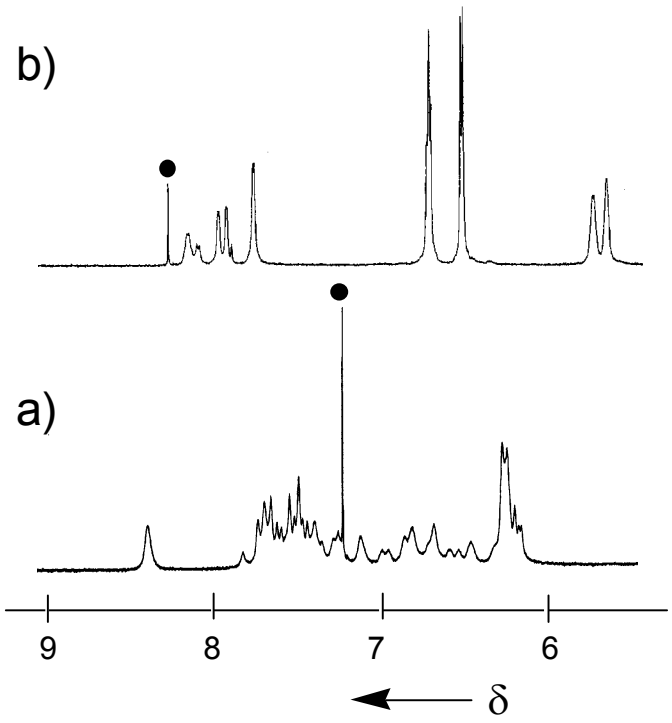


Figure 3.14 Downfield portions of ^{1}H NMR spectra (500 MHz, 295 ± 1 K) of: a) polymeric capsules **(2c)**$_n$ in $CDCl_3$. b) biscalixarene **2c** in DMSO-d_6. The spectrum was obtained upon dissociation of **(2c)**$_n$ in DMSO-d_6. The residual solvent signals are marked as before.

Significantly increased viscosities were observed for $CHCl_3$ solutions of biscalixarenes **2c** compared to the precursor **32**. While relative viscosity of **32** is similar to the solvent and does not apparently change with the concentration, dramatic changes (≥5-fold, concentration range from 5 to 40 mM) were detected for the biscalixarene. Specific viscosities (η_{sp}) of derivatives **32** and **2c** were measured as a function of concentration, and the double-logarithmic plots are represented on Figure 3.15a. As expected, for calixarene **32** the viscosities are low and the plot has a slope of 1.1 ± 0.1. Such linear relationship between specific viscosity and concentration indicates that only small aggregates (e.g. capsules) are formed, which are of constant size and apparently do not

interact with each other. In contrast, the double-logarithmic relationship between specific viscosities and concentration for biscalixarene **2c** exhibits a slope of ~2. The constant high slope of the plot suggests that, over the concentration range studied, the viscosity of **2c** follows Cates's model for reversibly breakable polymers above the overlap concentration.[104]

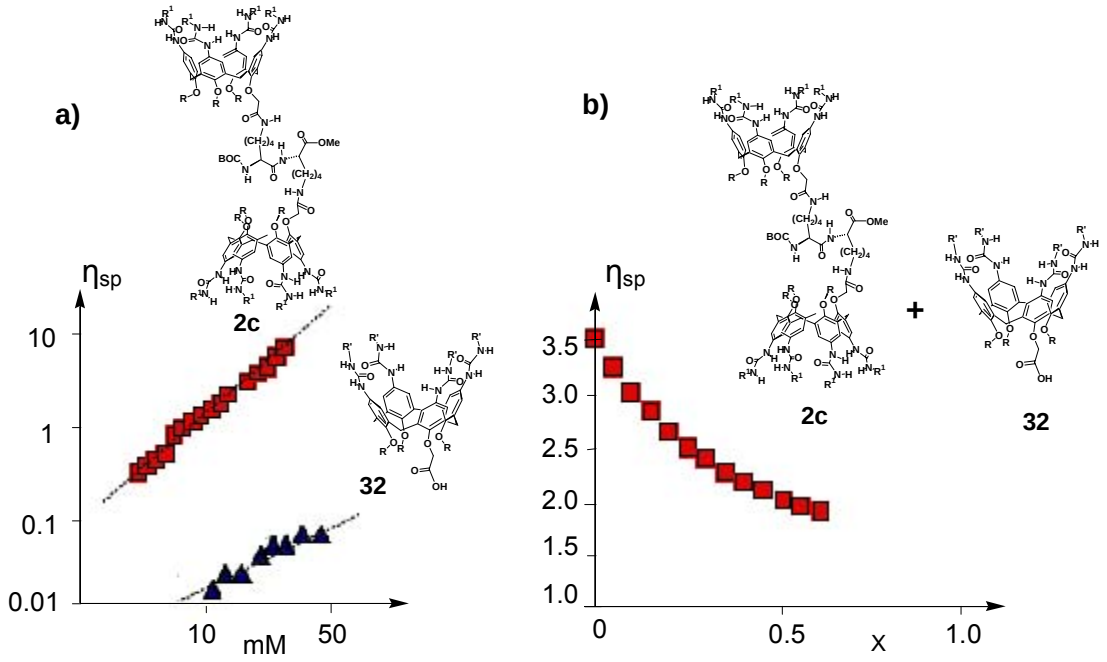


Figure 3.15 Viscosity measurements with calixarenes **32** and **2c** in $CHCl_3$ (295 ± 1 K): a) specific viscosities vs concentration (6 – 35 mM range), a double-logarithmic plot; b) effect of the addition of **32** (mole fraction x) on the specific viscosity of **2c** at 20 mM.

Addition of small quantities of calixarene **32** to the $CHCl_3$ solution of biscalixarene **2c** resulted in a dramatic decrease in viscosity (Figure 3.15b). Acting as a chain stopper, compound **32** may competitively participate in hydrogen bonding with the calixarene fragments in **2c** and its polymeric chains. Based on these viscosity measurements and using approach developed by Meijer and co-workers,[101] the degree

of polymerization (DP) value for biscalixarene **2c** of ~2.8 x 10^2 was estimated at 20 mM, which corresponds to the average molar mass of ~7.6 x 10^5 g/mol. When 1% and 2% (mol) of stopper **32** were used, the DP numbers dropped to 1.2 x 10^2 and 7.5 x 10^1, respectively. These observations once again confirm reversibility of the described polymerization processes, which occurs through multiple capsule formation. The molecular modeling of the calixarene polymer $(\mathbf{2c})_n$ is depicted in Figure 3.16.

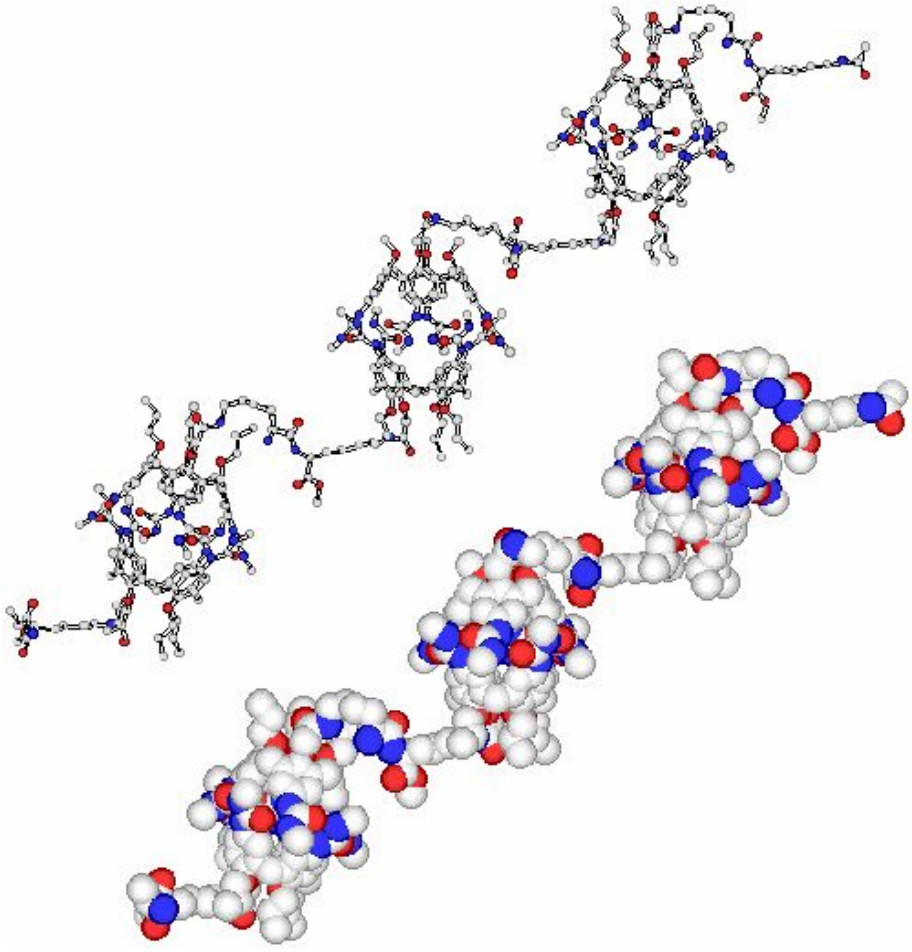


Figure 3.16 MacroModel 7.1 (MM2) representations of supramolecular polymer $(\mathbf{2c})_n$: a fragment of the chain. The CH hydrogens and long alkyl chains are omitted for viewing clarity.

In summary, we have demonstrated that calixarene amino acids can serve as building blocks to construct a novel type of calixarene peptide dendrimers. The first generation of calixarene dendrimers was synthesized and fully characterized. Calixarene amino acids, peptides, and peptide dendrimers containing tetra-ester functions at their lower rims can extract sodium cations from aqueous solutions. Calixarene-peptide conjugates, possessing urea moieties at the upper rim, were demonstrated to reversibly form self-assembling capsules and supramolecular polymers in apolar solvents. In principle, self-assembling capsules can encapsulate guests and dipeptides can be readily modified through either their C and/ or N terminus. This brings new perspectives to the construction of functional supramolecular materials.

CHAPTER 4

CARBON DIOXIDE AND SUPRAMOLECULAR POLYMERS

Carbon dioxide (further CO_2) is one of the major greenhouse gases.[105] It circulates in the environment through a variety of processes known as the *carbon cycle* (Figure 4.1). Large-scale industrial processes, volcanoes and living systems release huge quantities of CO_2 into the atmosphere. On the other hand, plants and also oceans, lakes, and rivers collect it. Although the concentration of CO_2 in the earth atmosphere is low (~0.04% by volume), CO_2 is a very important component, because it absorbs infrared radiation and enhances the greenhouse effect. CO_2 in the atmosphere is accumulating much faster than the Earth's natural processes can absorb it. The CO_2 levels in the atmosphere have risen by more than 30% over the last 250 years and these concentrations may well double or even triple in the next century. Such extensive CO_2 circulation in atmosphere, industry and agriculture requires not only its systematic monitoring under a variety of conditions, but more importantly, necessitates the development of improved methods of the CO_2 chemical utilization.

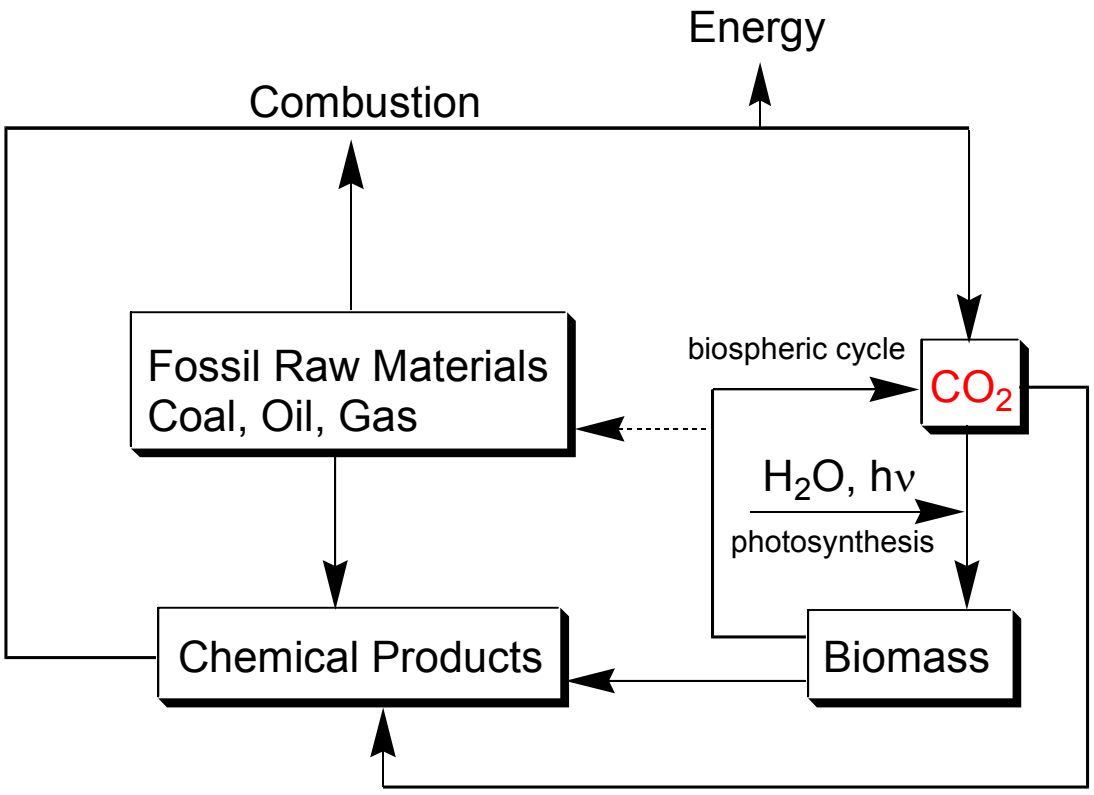


Figure 4.1 Circulation of carbon dioxide: *Carbon Cycle*.

The reactions between CO_2 and amines readily occur at ordinary temperatures and pressures to yield carbamates, presumably by way of the corresponding carbamic acids. Notably, carbamates are thermally unstable and release CO_2 upon heating (Figure 4.2).[106]

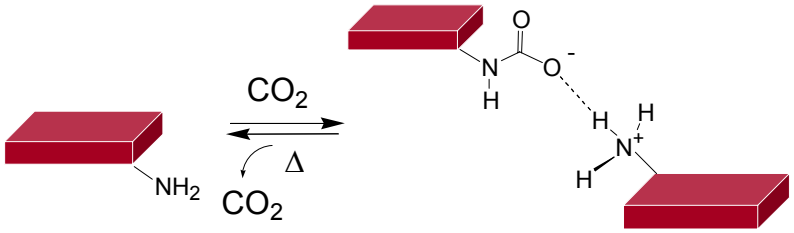


Figure 4.2 Reversible covalent chemistry between CO_2 and amines: self-assembly of molecular blocks.

Accordingly, polymer-bound amines have been employed in industry as reusable CO_2 scrubbers, removing CO_2 from industrial exhaust streams.[107] It has been demonstrated that amine containing ionic liquids also trap CO_2 (Figure 4.3).[108] Imprinted polymers have been introduced, in which a template can be attached and then removed through a carbamate linker.[109]

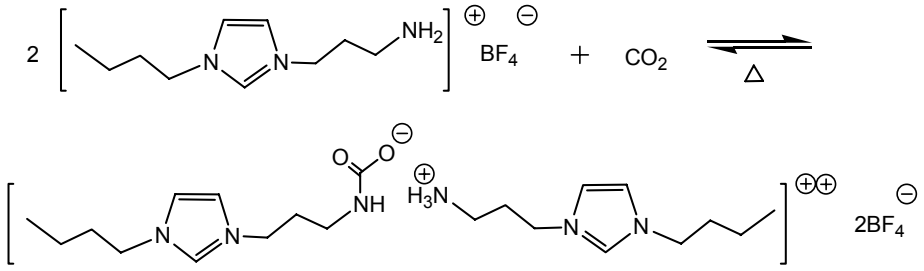


Figure 4.3 Structure of a CO_2-trapping ionic liquid. [108]

Finally, reactions between CO_2 and immobilized amines have been employed by our laboratory for gas sensing (Figure 4.4).[110] Specifically, 1-aminomethylpyrene readily reacts with CO_2 in polar aprotic solvent to form the corresponding carbamic acid, which exhibits at least 10 times more fluorescence emission than the amine. Here,

the disruption of proton induced electron transfer quenching by resonance between the lone pair on nitrogen and carbonyl oxygen is responsible for the increased fluorescence.

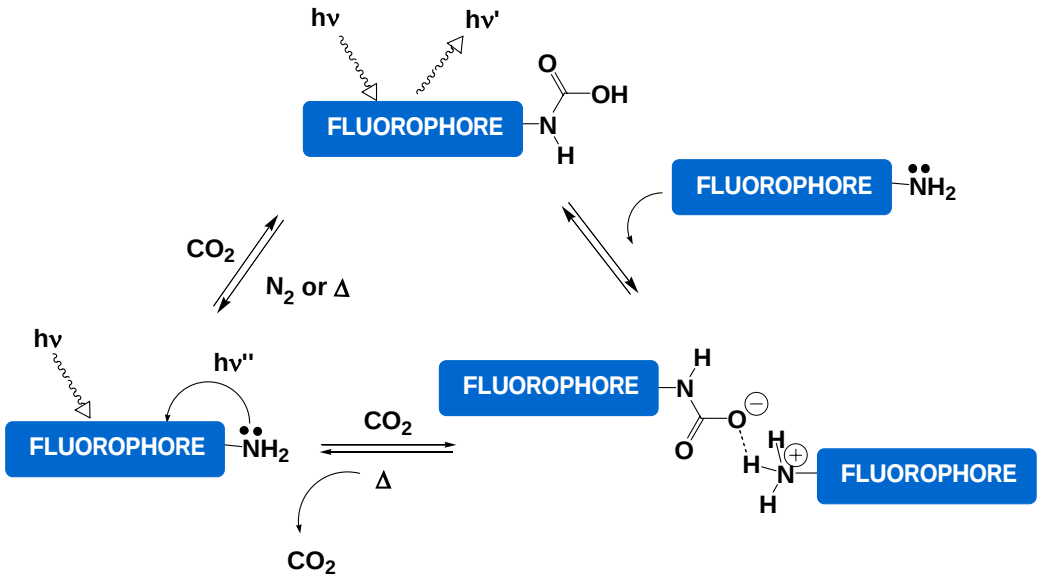


Figure 4.4 Model for fluorimetric sensing of CO_2.[110]

Dynamic covalent chemistry (DCC) is now quickly emerging as a promising alternative to noncovalent self-assembly.[111] It offers an elegant opportunity of incorporating covalent bonds into self-assembly. One of the most important advantages here is the robustness of covalently organized structures, which on the other hand can be reversibly broken, at will. We proposed, that carbamate bonds could be employed for wider variety of DCC experiments.[110]

Non-covalent self-assembly has been very well explored in the past two decades and has led to well defined nano-scale structures, such as capsules, supramolecular polymers, etc. Covalent, still reversible, assembly is in an early stage. This carbamate

chemistry, simply introduced from CO_2 and alkyl amines, could offer us a good opportunity to quickly assemble a variety of robust nanostructures and "smart" materials. Furthermore, the reversible nature of carbamate bonds may lead to possibilities of switching structures and properties.

Simultaneously with us, Weiss and co-workers demonstrated that chemically reversible organogels could be prepared with CO_2 and aliphatic amines as latent gelators.[112] The organogelation process was simple and reliable. Rapid uptake of CO_2 by aliphatic amines produced the ammonium carbamate-based gel, while thermal release of CO_2 transformed gel into the amine solutions. The gel-solution cycles can be repeated for at least 10 times without losing efficiency. Gels are viscoelastic liquid like or viscoelistic solid like materials. Due to their thermo-reversibility and great diversity of structures on the microscopic and mesoscopic scales, gels are attracting much attention in the field of supramolecular chemistry.[113]

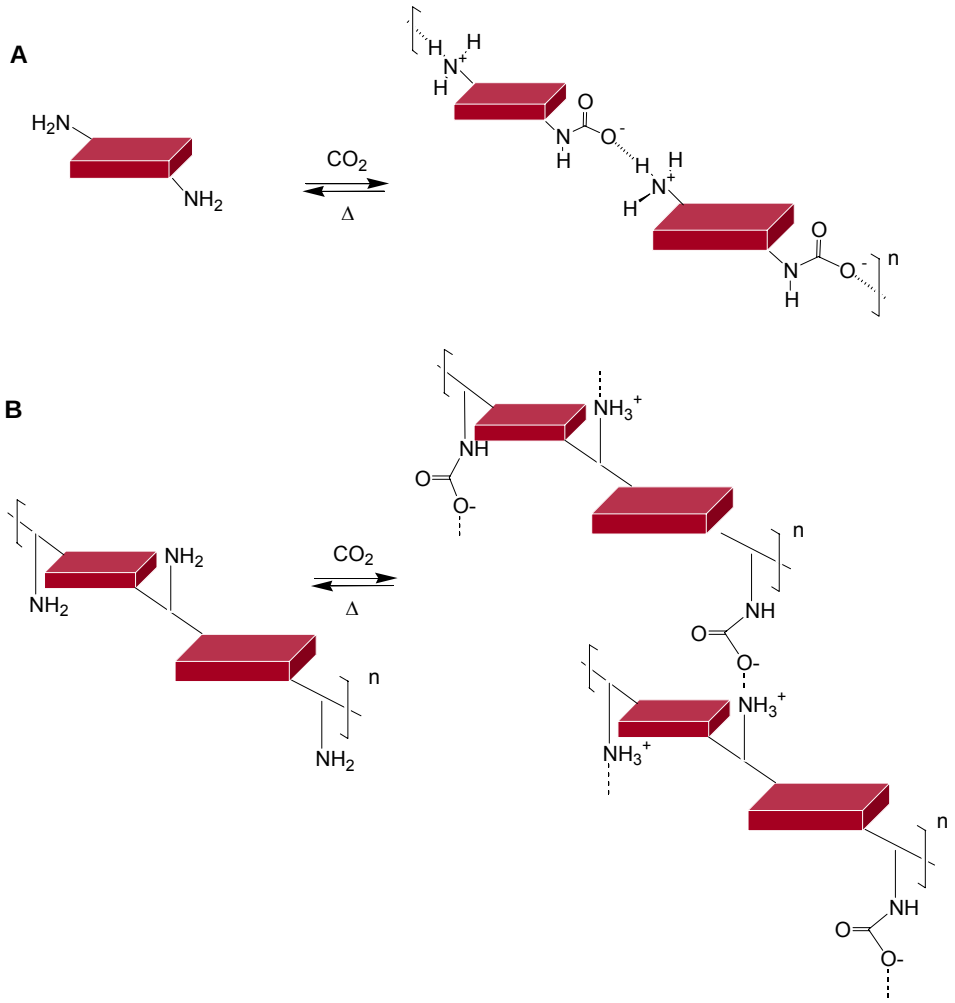


Figure 4.5 Reversible covalent chemistry between CO_2 and amines. Self-assembly of molecular blocks leads to linear (case A) and cross-linked polymers (case B).

Reactions between CO_2 and di- or even polyamines are very interesting, since they can lead to reversibly formed polymeric chains or even cross-linked 3D networks (Figure 4.5A and 4.5B). In one case, such structures have been proposed for polycarbamate $[---H_3N^+(CH_2)_{12}NHC(O)O^-{---}H_3N^+(CH_2)_{12}NHC(O)O^-{---}]_n$, which forms thermally reversible organogels.[112]

With this in mind, we employed CO_2 as a cross-linking agent to build supramolecular polymeric materials.[114,115,116] Supramolecular polymers represent a novel class of macromolecules, in which monomeric units are held together by reversible forces. Supramolecular polymers thus combine features of conventional polymers with properties, resulting from the bonding reversibility. Structural parameters of supramolecular polymeric materials, in particular their two- and three-dimensional architectures, can be switched "on-off" through the main chain assembly dissociation processes. On the other hand, their strength and degree of polymerization rely on how tight the monomeric units are aggregated. In this chapter, we introduce a strategy to build supramolecular polymers, which utilize hydrogen bonding and take advantages of dynamic, reversible chemistry between CO_2 and amines. These polymers are also functional. They possess multiple self-assembling capsules that may encapsulate guests. We demonstrate that subtle, two parameter control over hydrogen bonding and CO_2-amine chemistry leads to switchable materials, which reversibly trap, store and then release guest-molecules. And finally using CO_2, we convert linear supramolecular polymeric chains into supramolecular, three-dimensional polymeric networks. These are also switchable and can be transformed back to the linear chains without breaking them. Indeed, while supramolecular cross-linked polymers are known,[117] they break upon dissociation of noncovalent aggregates, which compose them. Our materials are different, as they only release CO_2, keeping hydrogen bonding intact.

4.1 Design and Synthesis

The chemistry between CO_2 and amines is essentially an acid-base equilibrium, and the formation of carbamate salts is thermally reversible. CO_2 can typically be released by simple heating at ~80 °C.

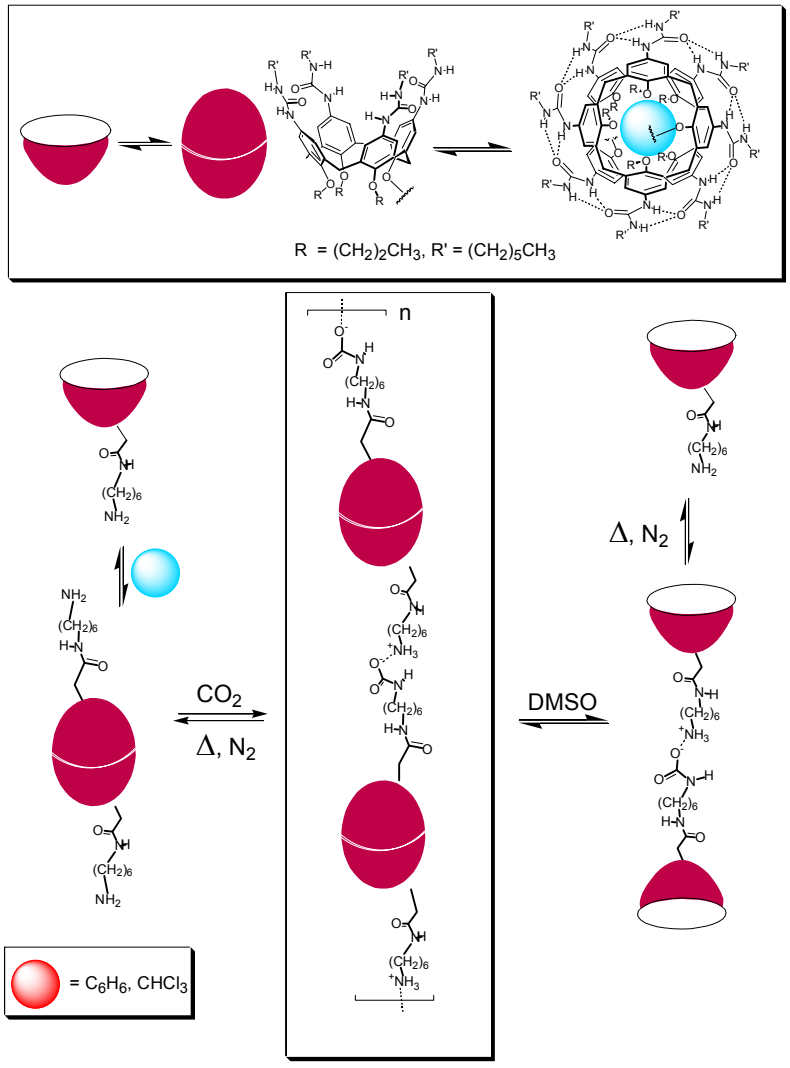


Figure 4.6 CO_2 can link calixarene capsules into a linear supramolecular polymer.

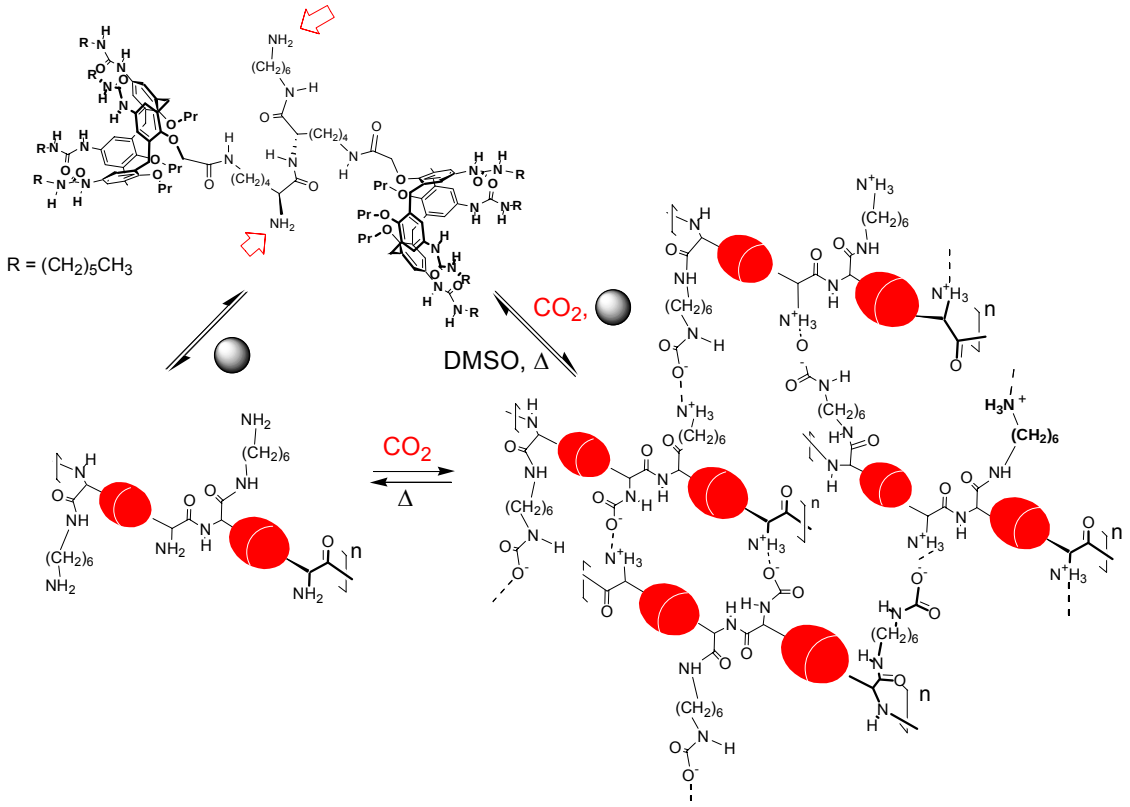
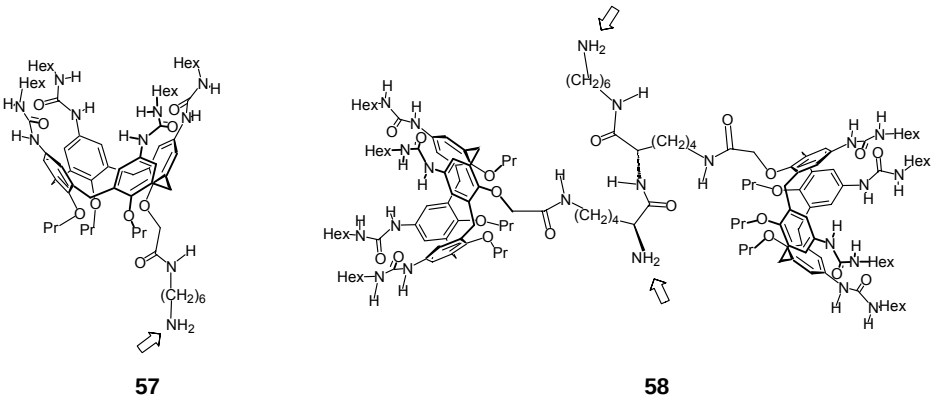


Figure 4.7 CO_2 cross-links polymeric calixarene chains into a three-dimensional supramolecular network.

Our approach is sketched on Figure 4.6 and Figure 4.7 and introduces two generations of CO_2-based self-assembling nanostructures. Monomeric units were designed, which *a)* strongly aggregate/dimerize in apolar solution, *b)* possess "CO_2-philic" primary amino groups on the periphery, and *c)* form capsules upon self-assembly. For cross-linking, two such monomeric units were covalently attached with the appropriate orientation for linear, noncovalent polymerization (Figure 4.7). The CO_2-philic amino groups were then introduced perpendicular to the main chain. In apolar solvent, once CO_2 is involved, multiple carbamate salt bridges should form,

resulting in either linear supramolecular aggregates (Figure 4.6) or three-dimensional supramolecular networks (Figure 4.7). Addition of competitive solvent breaks self-assembly but not the carbamate linkers. On the other hand, thermal release of CO_2 can be easily accomplished, but it does not influence the noncovalent aggregates, and the capsules do not dissociate.

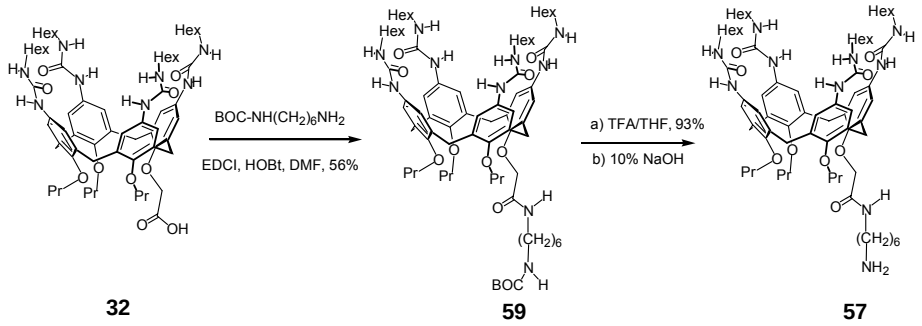


57 **58**

Figure 4.8 Calixarene building blocks for supramolecular polymers. The amino groups are marked.

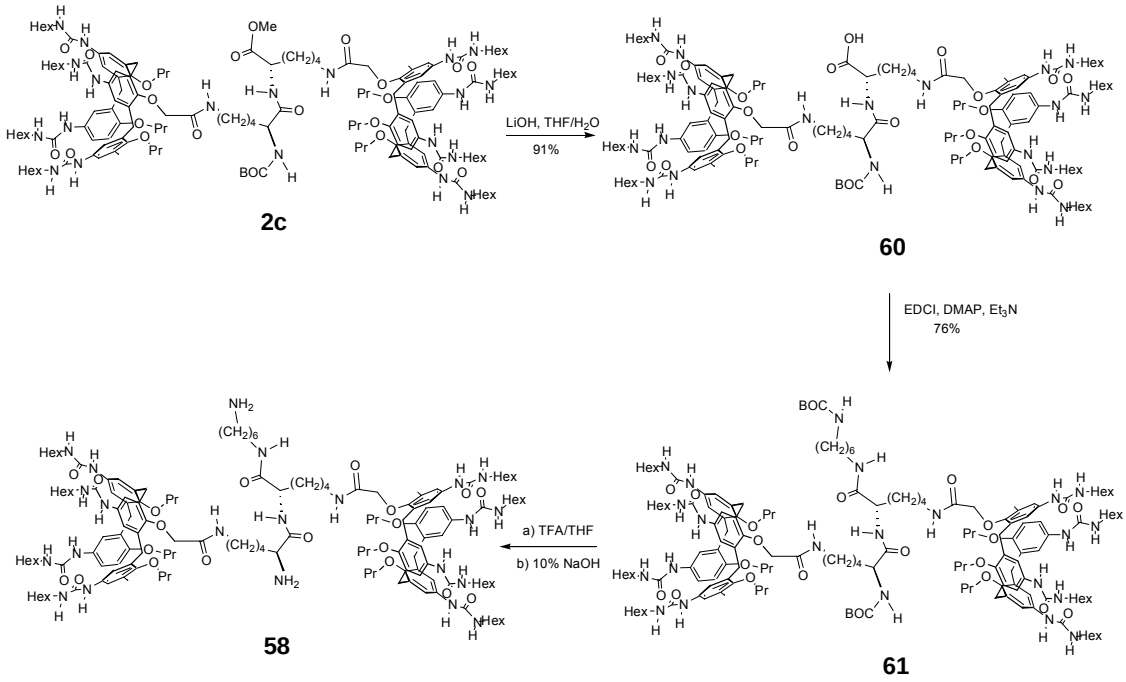
In the design of monomeric units, we took advantage of calixarenes as both self-assembling and cavity forming modules (see Chapter 3, Pages 51-56). For this study, calix[4]arene tetraureas **57** and **58** were synthesized, which possesses amino groups on the periphery (Figure 4.8). Specifically, calixarene **57** is functionalized with hexylamine fragment at the lower rim. In biscalix[4]arene **58** two calixarene tetraurea moieties are linked with a dipeptide, di-L-lysine. Calixarenes were attached to the ε-NH_2 ends, so the dilysine module orients them away from each other, in roughly opposite directions. According to extensive molecular modeling, this also prevents the intramolecular

assembly. Hexamethyleneamine chain was then attached to the carboxylic side of the dipeptide.



Scheme 4.1 Synthesis of calixarene tetraurea amine **57**.

The key building block for the syntheses of **57** and **58** is calix[4]arene tetraurea acid **32** (Scheme 3.1). It was prepared from known calixarene precursors in five steps starting with the parent tetrakis-*t*-butyl calix[4]arene (see Chapter 2, Page 25). Calixarene amine **57** was synthesized (as a TFA-salt) from acid **32** and 1-*N*-BOC protected 1,6-diaminohexane (DCC, HOBT, Et_3N, DMF, 72%), followed by deprotection with TFA (THF, 93%). Biscalix[4]arene diamine **58** was prepared (as a TFA-salt) from bis-*N*-BOC protected dipeptide **61** (THF, TFA, >95%). Compound **61** was obtained from calix dipeptide methyl ester **2c** by basic hydrolysis (LiOH, H_2O-THF, 91%) of the ester, followed by reaction with 1-*N*-BOC protected 1,6-diaminohexane (EDCI, HOBT, DMF, 76%). Dipeptide **2c** was obtained by a conventional peptide coupling procedure from 2 equiv of acid **32** and 1 equiv of di-*l*-lysine **36** (see Chapter 2, Page 29). The amino groups in **57** and **58** were subsequently liberated from TFA by washing with aq NaOH solution.



Scheme 4.2 Synthesis of biscalixarene diamine **58**.

4.2 Self-Assembly

As expected, calixarene tetraurea **57** dimerizes in apolar solution (^{1}H NMR, ESI-MS) with the formation of capsule **62** (Figure 4.9 and 4.10). Due to the lack of symmetry in **62**, a multiple set of NH urea signals was recorded in C_6D_6, $CDCl_3$, and $CDCl_2CDCl_2$ between δ = 6 and 8.5 (for example, Figure 4.10A). These are characteristically shifted down field ($\delta \geq 2$), compared to model, non-dimerized ureas, showing the key features of the capsule formation.[53,54] Statistically, both a proximal and a distal regioisomers of **62** form, with respect to the orientation of the acetamid

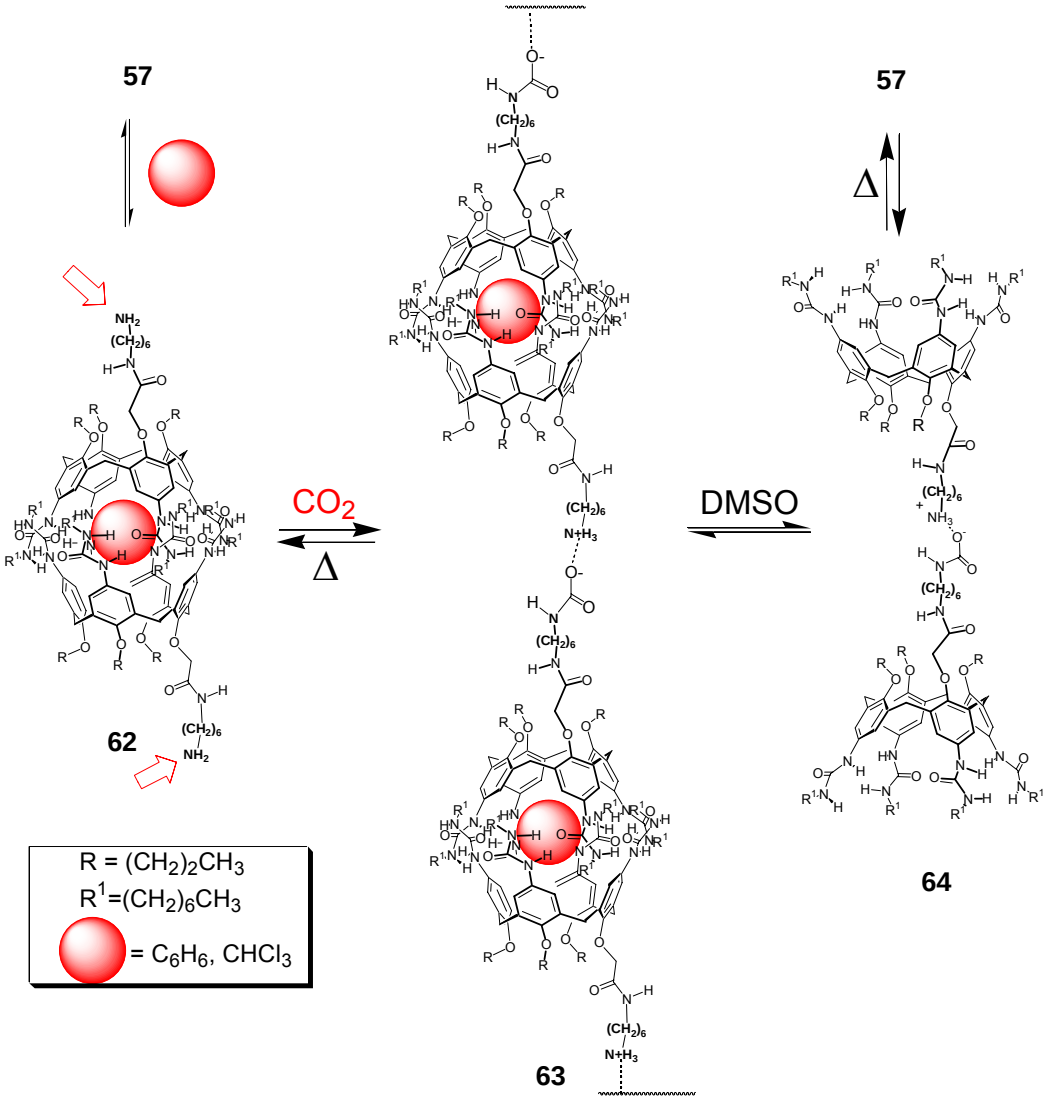


Figure 4.9 Formation and dissociation of linear supramolecular polymer **63**.

$OCH_2C(O)NH$-substituents at the lower rims of each calixarene **57**. Moreover, the circular array of hydrogen bonds can be arranged either clockwise or counterclockwise.[53] Capsule **62** dissociates to monomeric tetraurea **57** in DMSO-d_6. This results in a much simpler ^{1}H NMR picture, reflecting the presence of a vertical symmetry plane in **57** (Figure 4.10B). For example, three ArNHC(O) urea singlets in a

ratio 1:1:2 at δ = 8.05, 8.00, and 7.85 and three aromatic CH singlets in a ratio 2:2:4 at δ = 6.81, 6.79, and 6.61 are clearly seen in the down field region of the spectrum.

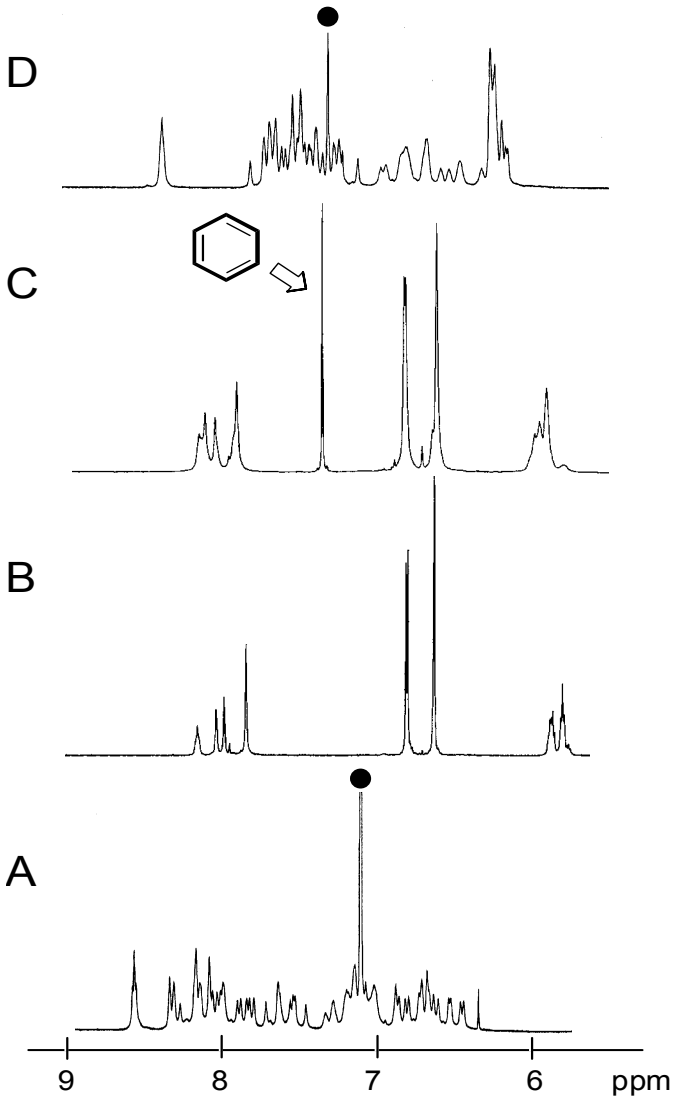


Figure 4.10 Downfield regions of ^{1}H NMR spectra (500 MHz, 295 ± 1 K) of: A) capsule **62** in C_6D_6. B) calixarene amine **57** in DMSO-d_6. C) salt **64**, prepared upon dissociation of polymer **63** in DMSO-d_6. For this experiment, polymer **63** was obtained upon bubbling CO_2 to a benzene solution of **57** and thus entraps benzene. The benzene signal is shown by an arrow. D) polymer **63**, obtained from CO_2 and **57** in $CHCl_3$-hexanes, 1:2 solution and redissolved in $CDCl_3$. The residual solvent signals are marked as "•".

Having two calixarene modules for assembly, compound **58** forms linear supramolecular polymers **65** in apolar solution (Figure 4.11). The viscosity experiments indicated the degree of polymerization (DP) value for its precursor **2c** was ~2.8 x 10^2 at 20 mM in chloroform solution, which corresponds to the average molar mass of ~7.6 x 10^5 g/mol (see Chapter 3, Pages 54-56).

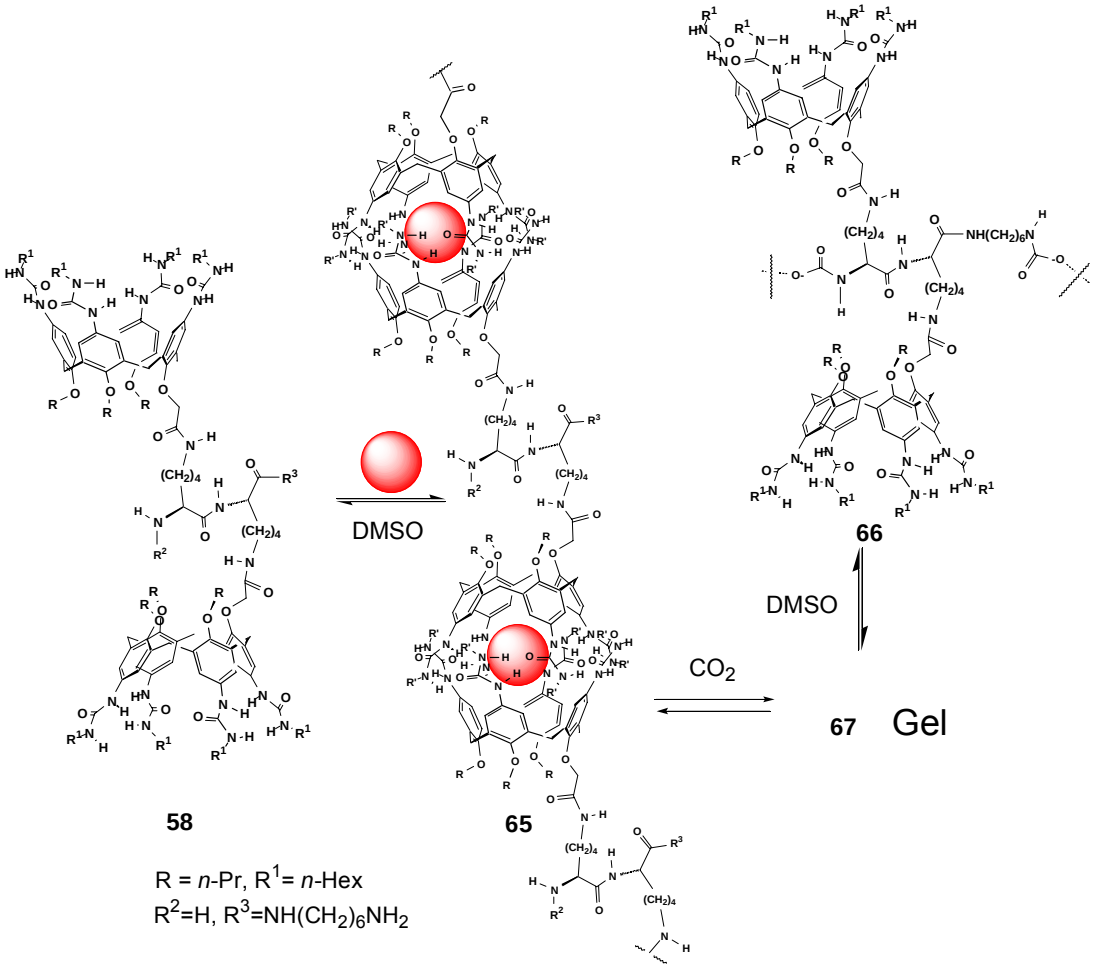


Figure 4.11 Formation and dissociation of linear supramolecular polymers **65** and cross-linked supramolecular material **67**.

4.3 Reactions with CO_2 - First Generation

Bubbling CO_2 through solution of **57** in benzene causes a rapid precipitation of carbamate-linked supramolecular material **63**. This belongs to the first generation. The chains in **63** are held together by the calixarene hydrogen bonds and carbamate $CH_2N^+H_3$•••$O^-C(O)NHCH_2$ salt bridges (Figure 4.9). Initially, one molecule of an amine reacts with CO_2 to form the corresponding carbamic acid. It is highly unstable and rapidly transfers the acidic proton to the second amine molecule, thus producing a relatively robust carbamate salt.[106] Formation of the carbamate bridges was confirmed by ^1H and ^{13}C NMR spectroscopy. In the ^1H NMR spectrum of **57** in DMSO-d_6, the terminal -CH_2NH$_2$ protons were seen as a triplet at $\delta = 2.53$ ($J = 6.0$ Hz). In the salt **64**, which is formed upon dissociation of polymer **63** in DMSO-d_6, these split in two 1:1 sets -CH_2N$^+$H$_3$•••O$^-$C(O)NHCH_2-: a triplet at $\delta = 2.58$ ($J = 6.4$ Hz) and an apparent multiplet at $\delta \sim 2.9$, respectively. These were assigned through NMR experiments with model alkyl amines, COSY and from the literature.[112] A broad carbamate NH signal was detected at $\delta \sim 6$ (^1H NMR, COSY). A resonance at $\delta \sim 160$ in the ^{13}C NMR spectrum of **64** unambiguously identified the carbamic (-HN-*C*(O)O-) carbon atom. Notably, when amine **57** was treated with large excess of CO_2 in DMSO-d_6, the corresponding free carbamic acid formed, which was studied by ^1H, ^{13}C NMR and COSY spectroscopy. For example, the HN-*C*OOH resonance was clearly seen at $\delta =$ 158 in the ^{13}C NMR spectrum. Free carbamic acids are still rare and elusive.[106] Supramolecular material **63** is a colorless solid, soluble in chlorinated solvents and insoluble in aromatic solvents. It was also obtained by the CO_2-induced precipitation

from solutions of **57** in $CHCl_3$-hexanes, 1:2. A multiple set of downfield NH urea signals of **63**, recorded in $CDCl_3$, clearly indicates the hydrogen bonding assembly of polymeric chains (Figure 4.10). At the same time, viscosities of capsules **62** and material **63**, obtained after the reaction with CO_2**,** appeared to be similar ($CHCl_3$ and $CHCl_3$–benzene). These viscosities were low, apparently concentration independent (5 - 25 mM range) and comparable with relative viscosities of precursor **32**. Obviously, **63** is *not* significantly aggregated under these conditions. The dimerization constant for each calixarene capsule in **62** is high,[103] and the carbamate ammonium electrostatic interactions are also very strong in apolar solvents.[118] These features do not allow the high concentrations of free end groups in structures **63**. On the other hand, the electrostatic interaction is not directional and may offer significant flexibility to the resulting structures. We propose that for **63**, oligomeric rings rather than long polymeric chains are formed upon reaction of **62** with CO_2. The double-logarithmic plots of specific viscosities η_{sp} vs concentration obtained for monomer **57** and also polymer **63** in $CHCl_3$ are low and show slopes of ~1. Apparently, the specific viscosities of solutions of **57** increase very regularly with concentration. According to the Cates' model,[104] aggregates of constant size are formed, which do not interact with each other. Due to the low viscosity, these rings may not be large.

Another effect that attributes to the low viscosity might be the equilibrium between carbamate and free amine.[119] At low concentrations, free amine dominates in the solution. In contrast, carbamate becomes major component in high concentration. This idea was further supported by our research in the later stage.

The problem does not exist for already *preformed*, linear supramolecular polymer **58**, for which CO_2 serves as a cross-linking agent.

4.4 Reactions with CO_2 - Second Generation

Bubbling the CO_2 gas through a solution of **58** in $CHCl_3$ or benzene yields material **65**, which is clearly a gel (Figure 4.11). The main chains in **65** are held together by hydrogen bonding assembly of capsules, and multiple carbamate $-N^+H_3 \bullet\bullet\bullet O^-C(O)NH-$ bridges cross-link these chains. This is clearly a three-dimensional network, since the side amine groups are oriented in all three directions. Moreover, structure **58** possesses two types of amino groups, and several possibilities for the carbamate formation exist (see for example, Figure 4.7). Model experiments with CO_2 and simpler aliphatic amines and ε-*N*-CBz-protected lysine showed that these reactions readily occur. Formation of the carbamate bridges was further confirmed by ^{13}C NMR spectroscopy. To be sure, we used $^{13}CO_2$ gas and prepared the carbamate ^{13}C-labeled gel **67**. In the ^{13}C NMR spectrum of diamine **58**, prior the reaction, in DMSO-d_6, four C=O carbonyl signals were clearly detected – three for the amide fragments at δ = 175.4, 171.7 and 169.4, and one, intense signal for the upper rim ureas at δ = 155.8 (Figure 4.12a). In the spectrum of the ^{13}C-labeled salt **66**, which is formed upon dissociation of the ^{13}C-labeled polymer **67** in DMSO-d_6, in addition to these signals, two new singlets of high intensity appeared at δ = 163.5 and 162.8 (Figure 4.12b). We attribute these to the carbamate α-HN-$^{13}C(O)O-$ and $(CH_2)_6HN-^{13}C(O)O-$ groups. Notably, these two signals disappeared after heating solution **66** for 1 h at ~100 ºC and bubbling N_2 through it.

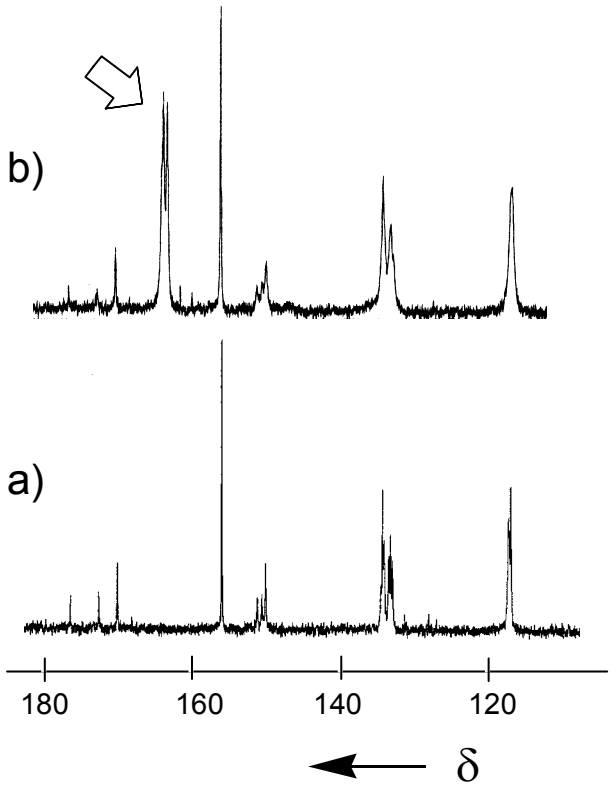


Figure 4.12 Portions of ^{13}C NMR spectra (500 MHz, DMSO-d_6, 295 ± 1 K) of: a) biscalixarene **58**. b) carbamate salt **66** obtained upon dissociation of ^{13}C-labeled gel **67**. The gel was prepared from **58** and $^{13}CO_2$ in $CHCl_3$. The carbamate ^{13}C-enriched signals are marked. For the corresponding ^1H NMR spectra, see Figure 4.13.

The ^1H NMR spectra of material **67** is difficult to obtain, which is obviously due to the cross-linked structure and numerous possibilities to form carbamic bridges. At the same time, the same trend as for simpler oligomer **63** can be clearly observed (compare Figure 4.13 with Figure 4.10). Rather similar to capsule **62**, multiple sets of NH urea signals were seen in the corresponding ^1H NMR spectra of precursor **58** in $CDCl_3$; viscous polymer **65** formed (Figure 4.13a). These NH signals were characteristically shifted down field. As expected, **65** fully dissociate to monomeric **58**

in polar DMSO-d_6 (Figure 4.13b). Similar to **57**, this results in a simpler ^{1}H NMR spectrum, reflecting the apparent vertical symmetry plane in the molecule. Being insoluble in apolar solvents, material **67** readily dissociates in DMSO to form a mixture of carbamate salts **66**. The corresponding ^{1}H NMR spectrum resembles those for carbamate salt **64** (Figure 4.10c and 4.13c).

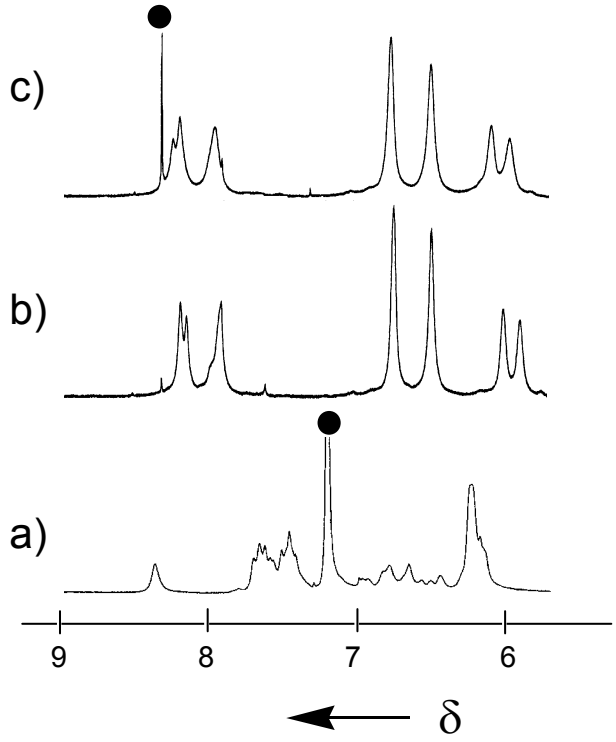


Figure 4.13. Downfield portions of ^{1}H NMR spectra (500 MHz, 295 ± 1 K) of: a) calixarene **58** in $CDCl_3$ (e.g., polymeric chain **65**). b) calixarene **58** in DMSO-d_6. c) salt **66**, prepared upon dissociation of polymeric gel **67** in DMSO-d_6. For this experiment, polymer **67** was obtained upon bubbling CO_2 to $CHCl_3$ solution of **58** (e.g., **65**). The $CHCl_3$ signal is marked as "•".

4.5 Properties

Self-assembling materials **63** and **67** exhibit unique properties. They assemble and dissipate in a two-fashion way - upon changing either the solvent polarity or temperature. The calixarene capsules completely dissociate in DMSO, so only carbamate salts **64** and **66**, respectively, can be detected (Figure 4.10c and Figure 4.13c). Salts **64** and **66**, most probably, undergo further solvolysis, generating loose ion pairs. The carbamate C-N bonds are not broken under these conditions. At the same time, they can be dismantled upon heating for 1 h at ~100 °C, thus releasing CO_2. In the case for **64**, in apolar solution monomeric capsules **62** form, and in DMSO free amine **57** is regenerated. For **66**, in apolar solution linear, hydrogen bonded polymer **65** forms, and in DMSO biscalixarene **58** is completely regenerated. In both cases, carbamate polymers **63** and **67** can be reconstructed simply by reintroducing CO_2.

Another interesting feature of materials **63** and **67** is their multiple capsules. These are already preformed in apolar solutions, but then convert into solids/gels upon exposure to CO_2. Upon this, CO_2-initiated polymerization, they trap guest molecules and transport them to the solid state. This results in *guest storing materials*.

In a preliminary test, a sample obtained from benzene and carefully dried (0.1 mm Hg, rt, 24 h), polymer **63** did not release benzene when the capsules were intact. In suspension of **63** in a solvent *p*-xylene-d_6, no trace of benzene was detected (^{1}H NMR, 500 MHz), but when polymer **63** was dissolved in DMSO-d_6, polymeric capsules dissociated and released visible quantities of benzene – approximately one bezene molecule per capsule (Figure 4.10c). We fully expect similar behavior from gel **67**.

However, in addition to be encapsulated, guest/solvent molecules are entrapped within the gel three-dimensional network[120] (see for example, Figure 4.13c).

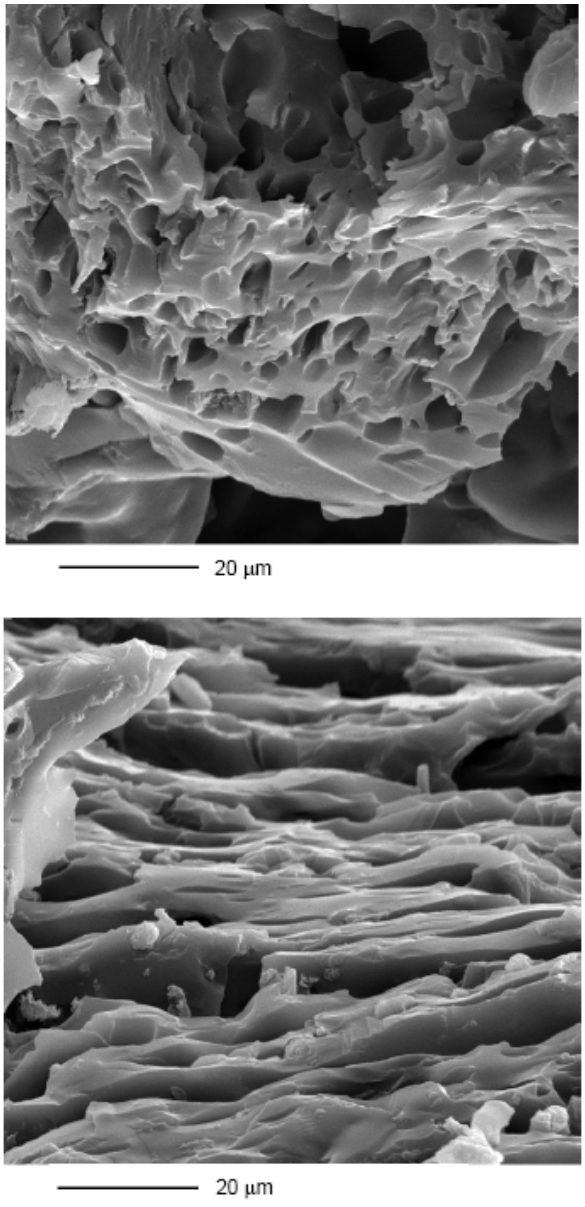


Figure 4.14. SEM pictures of xerogel **67** obtained upon bubbling CO_2 to $CHCl_3$ solution of **58** (bar 20 µm).

To obtain visual insight into the aggregation mode and morphology in **67**, dry samples were prepared for SEM analysis. While its precursor **65** is soluble in $CHCl_3$, gel **67** precipitates from $CHCl_3$ and exhibits a three-dimensional network in SEM analysis (Figure 4.14). These pictures clearly showed numerous micro-scale pores inside the materials, which can be used for solvent and/or guest encapsulations. These encapsulation properties can lead to functional materials.

In summary, CO_2 gas was used to construct novel types of supramolecular polymers. Self-assembling nanostructures **63** and **67** were prepared, which employ both hydrogen bonding and dynamic, thermally reversible carbamate bonds. Addition of competitive solvent breaks hydrogen bonding in assembling structures **63** and **67**, but does not influence the carbamate linkers. Carbamate salts **64** and **66**, respectively were obtained. On the other hand, thermal release of CO_2 from **63** and **67** was easily accomplished (1 h, 100 °C) with retaining the hydrogen bonding capsules. Thus, three-dimensional polymeric networks **67** were transformed back to linear polymeric chains **65** without their break up. Encapsulation and storage of solvent molecules by **63** and **67** were demonstrated. This opens a way to switchable materials, which reversibly trap, store and then release guest-molecules. The further applications of these materials will be discussed in the upcoming chapter.

CHAPTER 5

FUNCTIONS OF SUPRAMOLECULAR POLYMERS

In Chapter 3, we introduced a new type of peptide-based supramolecular polymer, which possesses multiple calixarene tetraurea capsules (Figure 5.1). The possibility of functionalization on the polymer chains distinguishes this polymer from the existing ones. For example, peptide backbones in the polymer can be modified to incorporate a binding site, functionalities, etc. Moreover, calixarene capsules may store smaller guest molecules. These features make the formation of our polymer not only reversible, but also functional.

In Chapter 4, we discovered that CO_2 can be incorporated into supramolecular polymers (Figure 5.2).[114,115] Thermally reversible carbamate chemistry together with hydrogen bonding was utilized to construct a two-way switchable, three-dimensional supramolecular polymer. The resulting polymer is novel: addition of competitive solvent breaks hydrogen bonding in polymers, but does not influence the carbamate linkers. On the other hand, thermal release of CO_2 from polymers is easily accomplished with retaining the hydrogen bonding capsules. The three-dimensional polymer, freshly prepared from $CHCl_3$, is a gel. The gelation process simply introduced by CO_2 may offer a new way to capture molecules from solutions and then release them with thermal, concentration or solvent control.

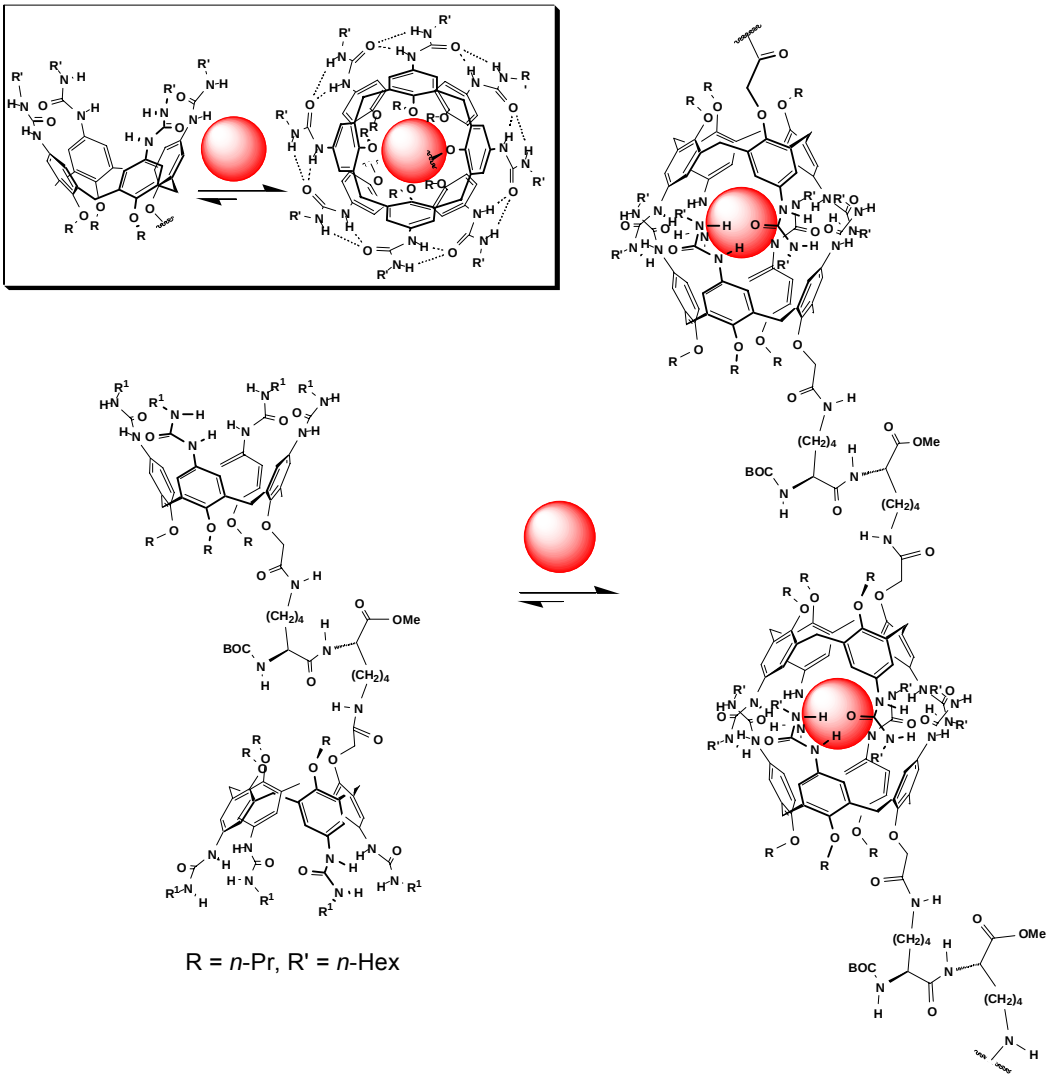


Figure 5.1 A peptide-based calixarene supramolecular polymer.

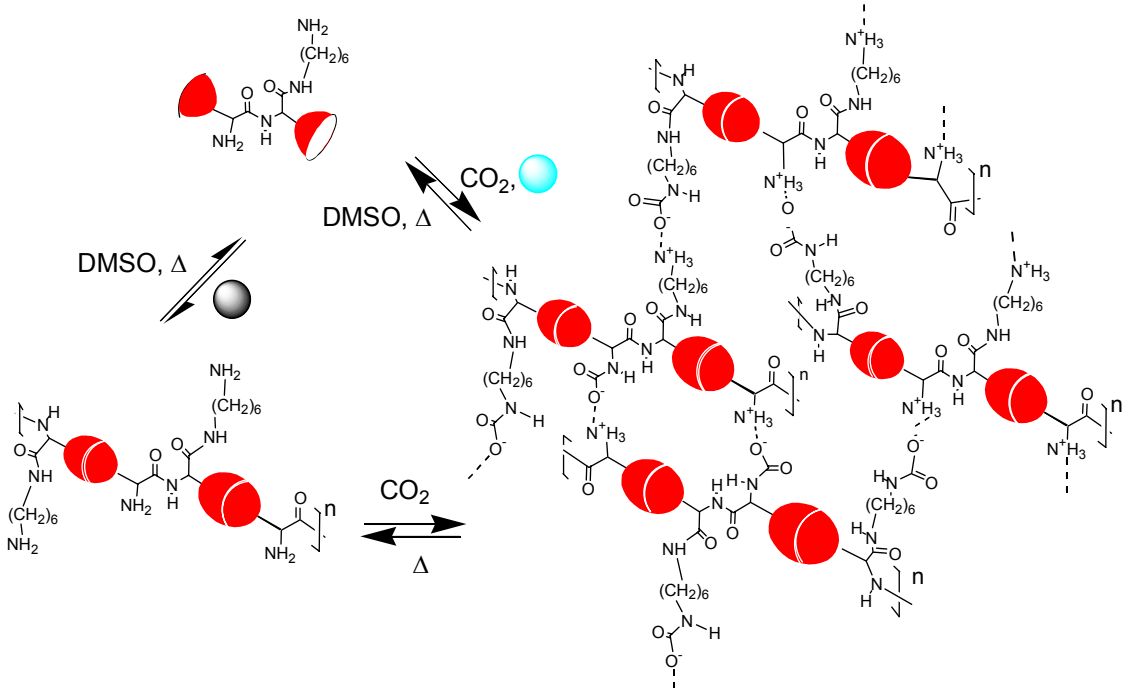


Figure 5.2 Supramolecular polymers incorporating CO_2.

After these novel types of supramolecular polymers were discovered, our attention was directed to their applications. We now discuss 1) functionalization of supramolecular polymer chains and 2) controlling capture and release of guest molecules using supramolecular polymers.

5.1 A pH Switch in Supramolecular Polymer

Here, we disclose how to switch properties of supramolecular polymers *without* breaking their unique polymeric structure. We introduce pH-switchable supramolecular polymers which take advantage of the side-chain acid-sensitive functionalities (Figure 5.3). These polymers also possess multiple self-assembling capsules and precipitate together with encapsulated guests upon lowering the solution pH.[50]

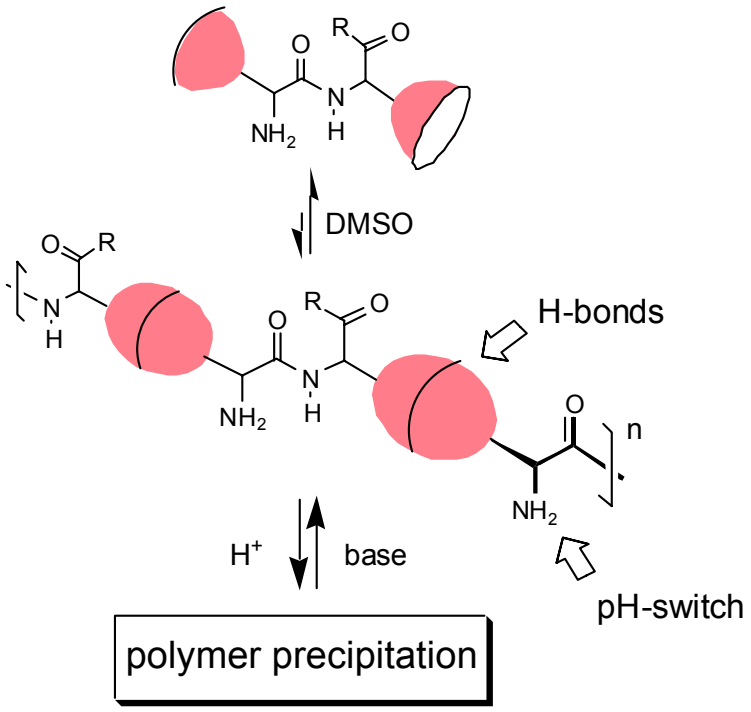
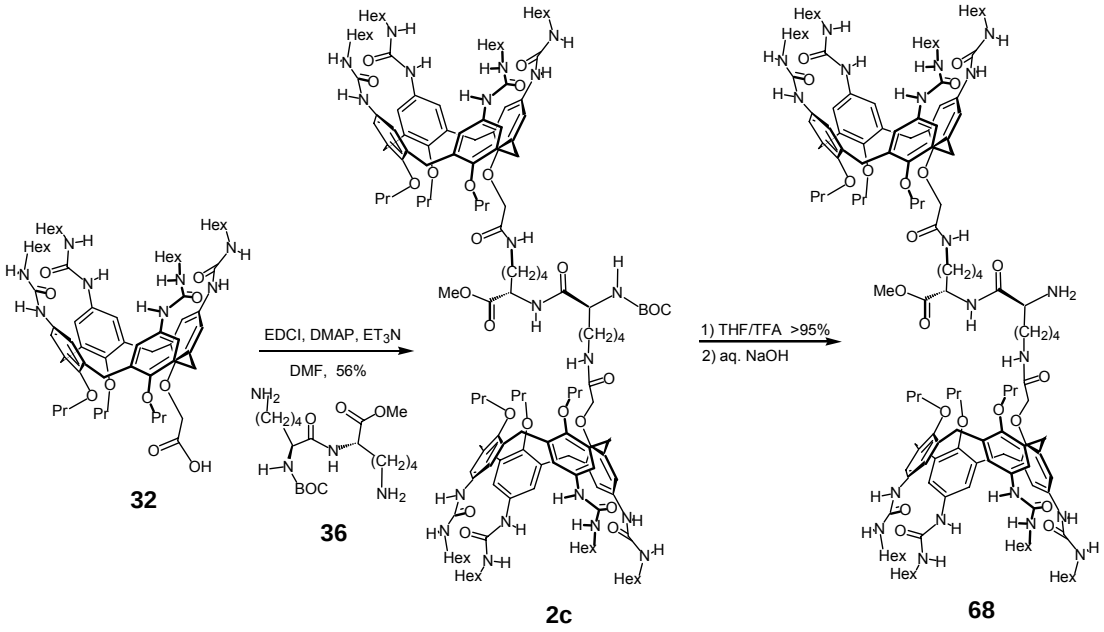


Figure 5.3 pH switchable supramolecular polymers.

In this study, we still took advantage of calixarenes as both self-assembling and cavity forming modules.[53,54] Calix[4]arene peptide **2c** was chosen for further functionalization. According to standard peptide chemistry, either C- or N- terminus of dipeptide chain is available for modification. For the pH switchable property, biscalix[4]arene **68** was prepared, in which two calix[4]arene tetraurea moieties are stitched together with a dipeptide chain (Scheme 5.1). Combining capsules with amino acids, we employed trifunctional lysine, which possesses a carboxylic group and two amino groups of distinguishable reactivity. Calixarenes were attached to the ε-NH_2 ends. The dilysine module orients them away from each other, in roughly opposite

directions, and also prevents the intramolecular assembly. It also possesses a pH-sensitive α-NH_2 group.



Scheme 5.1 Synthesis of amino functionalized biscalixarene **68**.

Biscalix[4]arene **68** was prepared (as a TFA-salt) by a conventional peptide coupling procedure from 2 equiv of calix[4]arene tetraurea **32** and 1 equiv of di-*l*-lysine **36** (EDCI, HOBT, DMF, 56%) followed by the α-*N*-BOC deprotection (TFA, THF, >95%). The α-NH_2 group was then liberated with aq NaOH (Scheme 5.1). As expected, **68** self-assembles in apolar solution ($CDCl_3$, $(CDCl_2)_2$, benzene-d_6) with the formation of supramolecular polymer **69** (Figure 5.3, Figure 5.4, and viscosity measurements for its precursor see: Chapter 3, Pages 54-56). Due to the lack of symmetry, a multiple set of NH urea signals were observed in the ^{1}H NMR spectra of **69** in $CHCl_3$, $(CDCl_2)_2$ and

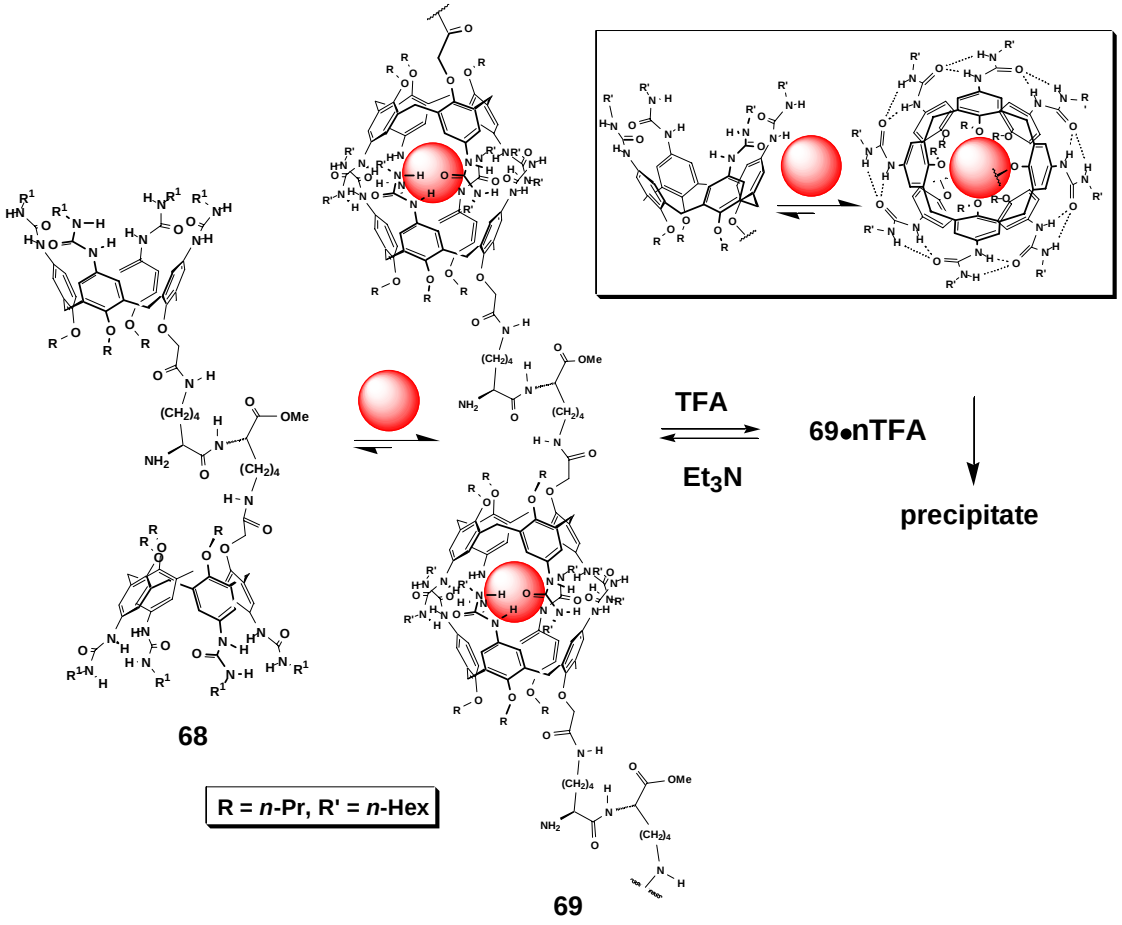


Figure 5.4 Switchable transformations with polymeric capsules **69**.

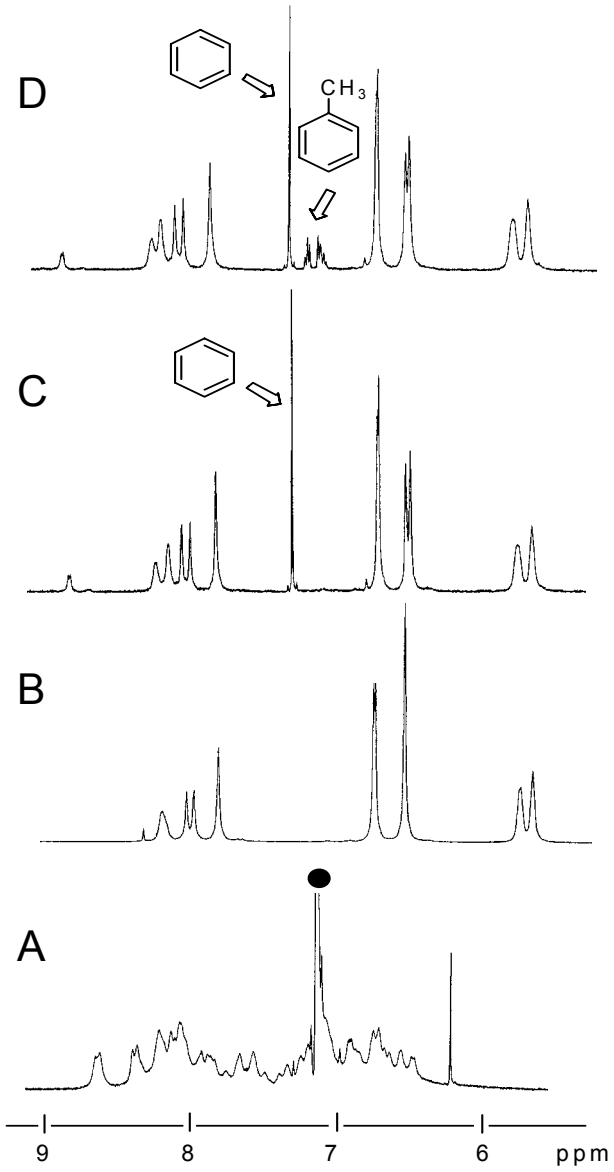


Figure 5.5 Selected downfield portions of the ^{1}H NMR spectra (500 MHz, 295±1 K) of: A) polymer **69** in benzene-d_6; B) biscalixarene **68** in DMSO-d_6; C) polymer (**69**•TFA•Benzene)$_n$ obtained from **69** in benzene upon addition of TFA, in DMSO-d_6; D) polymer (**68**•TFA•Benzene•Toluene)$_n$ obtained from **69** in benzene-toluene, 2:1 upon addition of TFA, in DMSO-d_6. The residual benzene peak is marked (•). Arrows mark the entrapped benzene and toluene signals.

benzene-d_6. These were shifted downfield (~2 ppm), which is a characteristic feature of capsule formation (for example, Figure 5.5A). Both proximal and distal regioisomers of **69** can form, with respect to the orientation of the acetamide-$OCH_2C(O)NH$-substituents at the lower rims of each calixarene **68**. Capsules **69** dissociate to monomeric dipeptide **68** in DMSO-d_6 (for example, Figure 5.5B). This results in a simpler ^{1}H NMR picture, reflecting the presence of a vertical symmetry plane in **68**.

Addition of 5-7 equiv of trifluoroacetic acid (TFA) to the benzene solution of **69** (e.g., (**69**•Benzene)$_n$) results in instant precipitation of material **69**•nTFA (Figure 5.4). Obviously, the-NH_2 groups in **69** become protonated, and the insoluble TFA-salt formed. Being a proton donor, TFA can strongly compete for hydrogen bond acceptors and cause the capsule dissociation. We determined, that at ≤20 equiv TFA per capsule, ≤30% dissociation occurs (Figure 5.6). Accordingly, a pH-switch can be provided at low concentrations of acids without breaking the self-assembling polymeric chain.

Polymer **69**•nTFA is a colorless solid, which readily dissolves in chlorinated solvents, DMSO, DMF, and insoluble in aromatic solvents. A multiple set of the down field NH urea signals of **69**•nTFA, recorded in $CDCl_3$ and $(CDCl_2)_2$, clearly indicates the hydrogen bonding assembly of polymeric chains. Likewise **69**, capsules **69**•nTFA dissociate to monomers **68**•TFA in DMSO-d_6. Indeed, once the cyclic hydrogen bonds

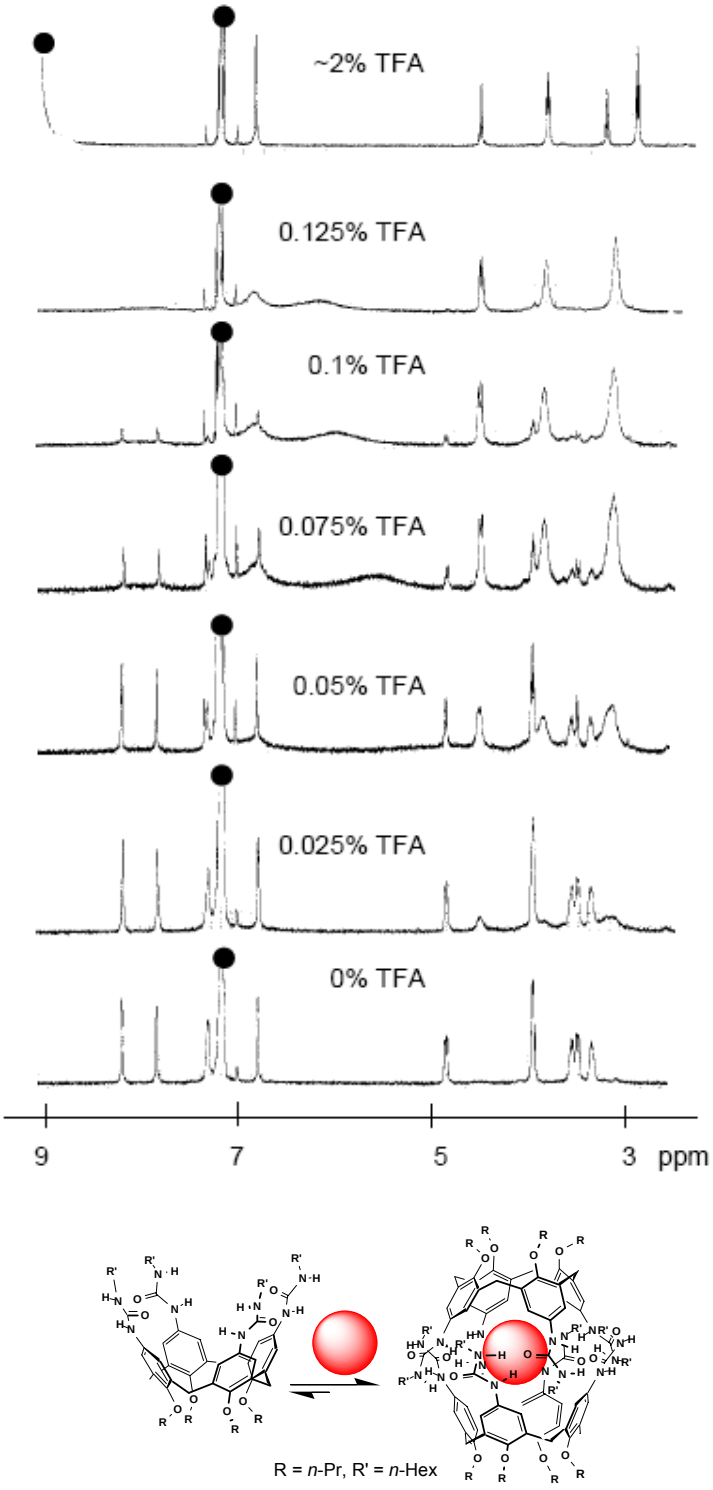


Figure 5.6 TFA titration of model calixarene capsule.

are broken, the apparent plane of symmetry in the calixarene fragment is restored. On the other hand, addition of Et_3N to the suspension of **69**•nTFA in benzene quickly regenerates **69**, which dissolves without dissociation of the capsules.

Polymer **69** exhibits unique properties. Similar to other hydrogen bonding supramolecular polymers, it assembles and dissipates upon varying the solvent polarity. At the same time, it changes aggregation properties upon pH changes with the polymeric chains remaining intact.

The most interesting feature of material **69** is, probably, in its capsules. These are already preformed in apolar solution, but precipitates as the salt **69**•nTFA only upon protonation. While precipitating, they capture and store guest/solvent molecules. Thus, polymer **69** entraps benzene already in solution, upon the capsules' formation, and then precipitates with it as **69**•nTFA. The benzene is protected inside the capsules. In a preliminary test, obtained from benzene and carefully dried (0.1 mm Hg, rt, 24 h) material **69**•nTFA did not release the guest when the capsules were intact. In a suspension of this polymer in noncompetitive *p*-xylene-d_{10}, no traces of benzene were detected, but when DMSO-d_6 was applied, the capsules dissociated and released visible quantities of benzene – approximately one benzene per capsule (Figure 5.5C). Both benzene and toluene were analogously entrapped upon precipitation from the mixture of these solvents (Figure 5.5D). The guest escape may be arranged even without the dissociation. Indeed, when redissolved in $CDCl_3$ or $(CDCl_2)_2$, polymer **69**•nTFA releases benzene simply because the solvent now competes for the cavities.

In summary, a pH-switch has been demonstrated, resulting in precipitation-dissolution of polymeric self-assembling capsules and trapping guest molecules inside. In principle, redox-, temperature-, light- and other switching processes can also be involved.[121] The most immediate applications, however, are in encapsulation. Our findings thus open an opportunity to construct materials which reversibly trap and store molecules.

5.2 Fluorescent, Cross-linked Carbamate Supramolecular Polymers

In chapter 4, we introduced a strategy to build *two-parameter* switchable supramolecular polymers/networks, which utilize hydrogen bonding *and* dynamic chemistry between CO_2 and primary amines (e.g. carbamate chemistry). We employed CO_2 as a cross-linking agent. Linear, hydrogen bonding polymeric chains were reversibly converted into robust three-dimensional networks by simply introducing and thermally releasing CO_2. Here, we address *functionalization* of such supramolecular polymers and networks and demonstrate the preparation of switchable supramolecular materials with fluorescent properties (Figure 5.7).[122]

Monomeric units **73** were designed, which *a)* strongly aggregate in apolar solution with the formation of polymeric, hydrogen bonding capsules **74**, *b)* possess a CO_2-philic primary amino group on the periphery, and *c)* functionalized with a fluorophore (Scheme 5.2). The CO_2-philic amino groups were introduced roughly perpendicular to the main self-assembling chain **74**. In apolar solvent, once CO_2 is added, multiple carbamate bridges form and result in three-dimensional supramolecular networks with multiple fluorophores. Addition of competitive solvent breaks self-

assembly but not the carbamate linkers. Thermal release of CO_2 can be easily accomplished, but it does not influence the noncovalent aggregates, and the capsules do not dissociate.

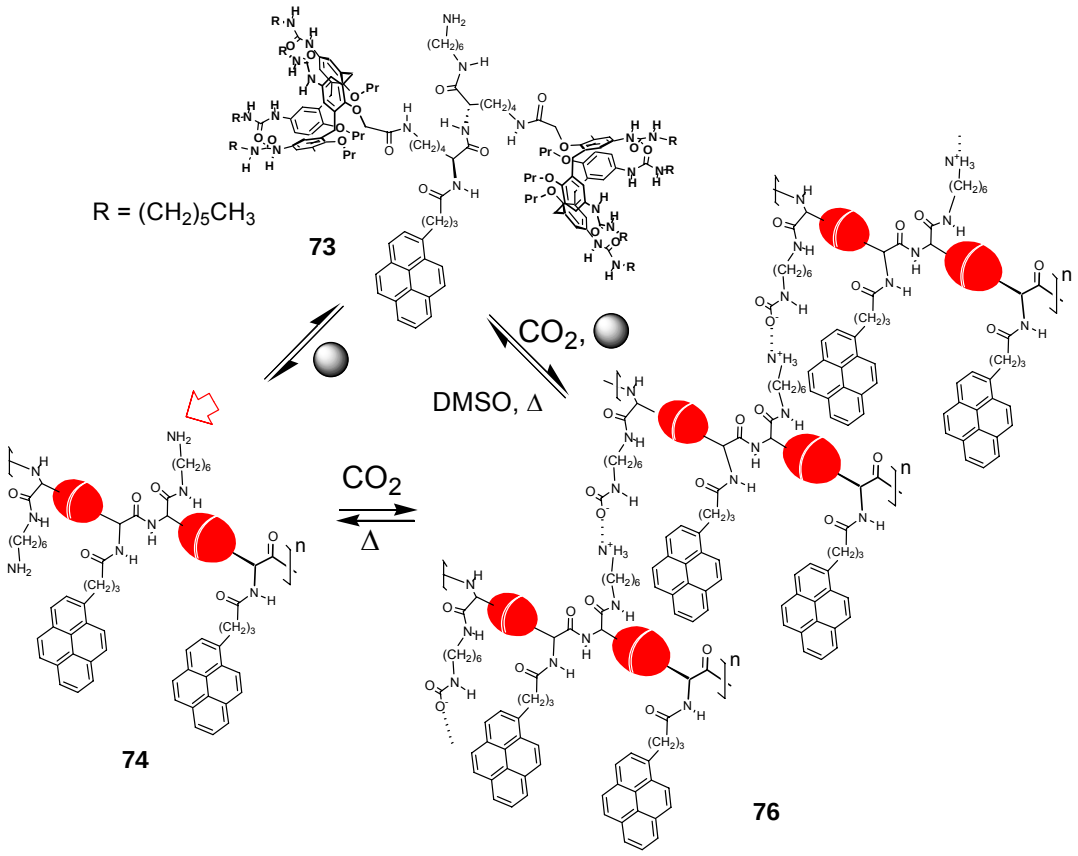
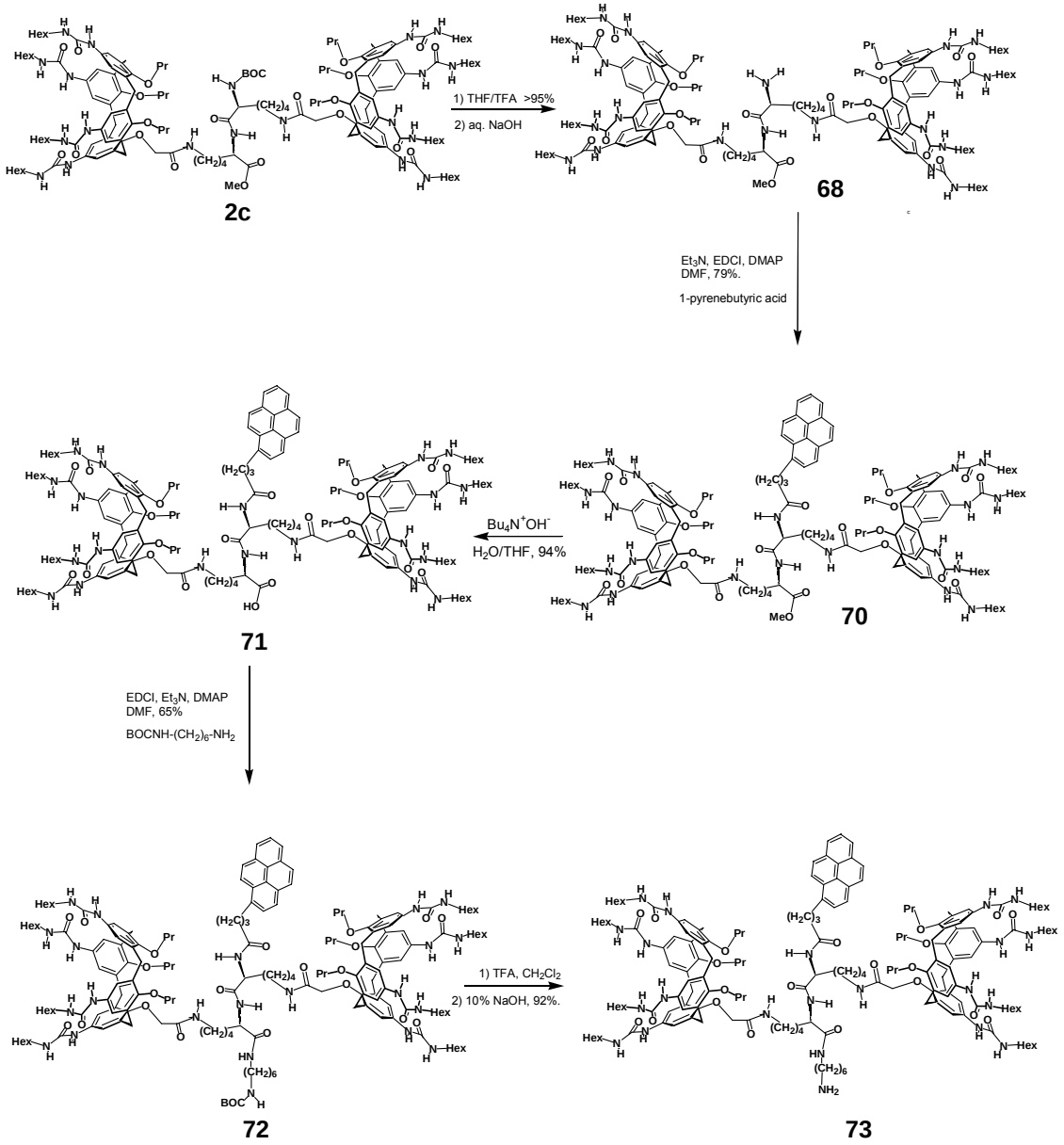


Figure 5.7 Fluorescent, carbamate cross-linked supramolecular network.

Our synthetic strategy is based on modular combination of calixarene building blocks with amino acids and short peptides. This allows for a great flexibility in the construction of multifunctional nanostructures.



Scheme 5.2 Synthetic approach towards pyrene functionalized biscalixarene **73**.

In short, biscalixarene dipeptide **2c** was quantitative deprotected with TFA in THF in quantitative yield and subsequently washed with aq NaOH. 1-Pyrenebutyric acid was introduced through the EDCI coupling (Et_3N, DMAP, DMF) with the formation of derivative **70** in 79% yield. In the next step, the methyl ester was hydrolyzed with $Bu_4N^+OH^-$ (H_2O/THF, 94%), and BOCNH-$(CH_2)_6$-NH_2 was then attached (EDCI, Et_3N, DMAP, DMF), resulting in biscalixarene **72** in 65% yield. The terminal BOC-protecting group was then cleaved (TFA, CH_2Cl_2) in quantitative yield, and the amino group was liberated with aq NaOH for the subsequent reaction with CO_2.

We previously established a strong tendency for biscalixarene dipeptides, such as **2c** and its structural relatives, to polymerize through hydrogen bonding (see Chapter 3, Pages 54-56). Similar behavior is fully expected for the structurally related biscalixarene **73**, which is only modified on the periphery.

Aggregation of **73** and its immediate precursor **72** was studied in detail by ^1H NMR spectroscopy. Biscalixarenes **73** and **72** exhibit quite simple and resolved spectra in DMSO-d_6 and more complex and broad spectra in $CDCl_3$. Such difference implies supramolecular polymerization in apolar media. The chemical shifts for the upper rim urea NH signals in **73** and **72** are in the same region as for model **1g** in both solvents (Figure 5.8).

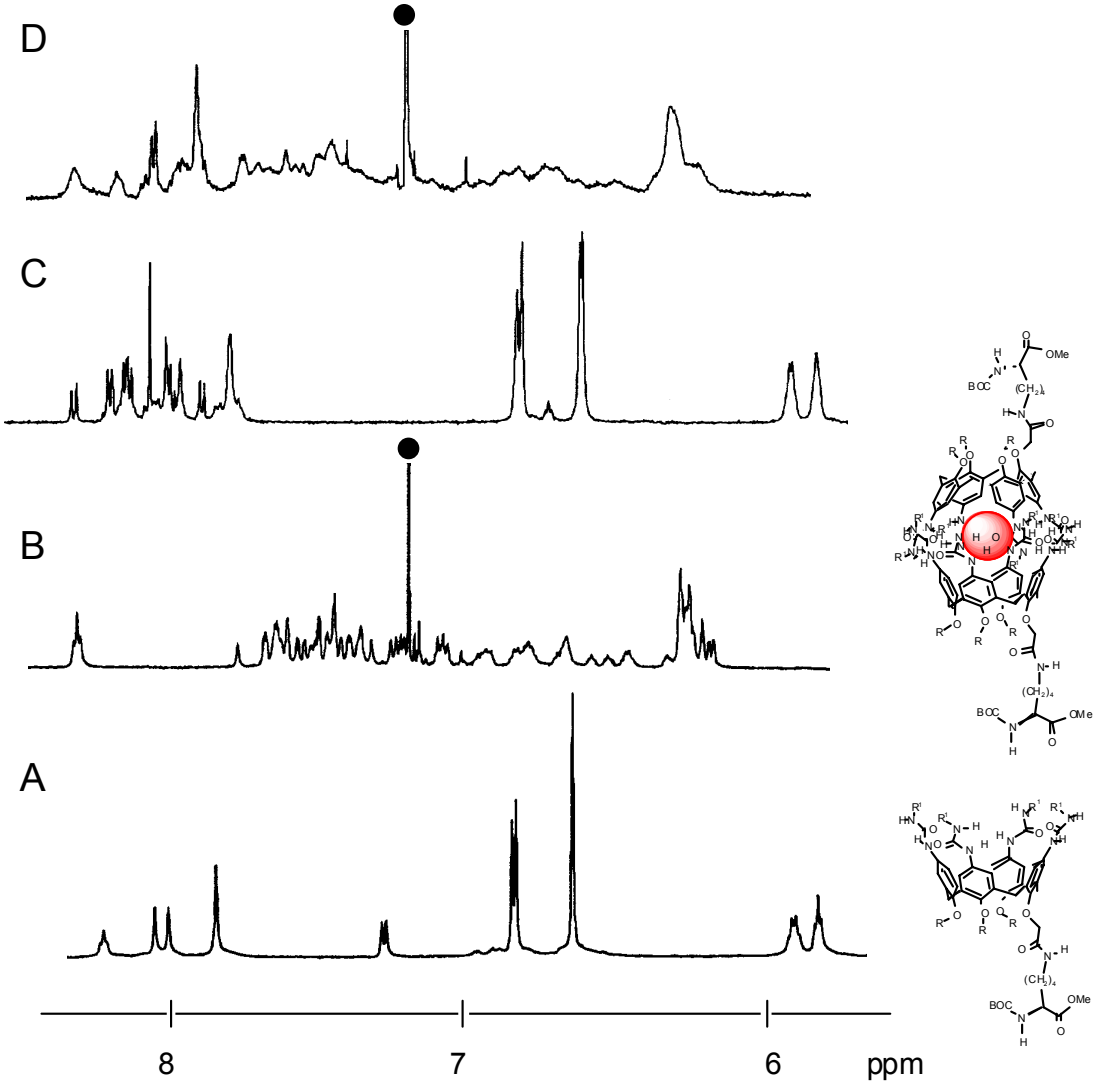


Figure 5.8 Downfield portions of ^{1}H NMR spectra (500 MHz, 295 ±1 K) of: (A) calixarene **1g** in DMSO-d_6; (B) capsule**1g•1g** in $CDCl_3$, only one regioisomer is depicted; (C) biscalixarene **72** in DMSO-d_6; (D) polymeric **72**$_n$ in $CDCl_3$. Spectra of **73** and **74** are similar to those of **72** and **72**$_n$, respectively. The residual solvent signals are marked with a "•".

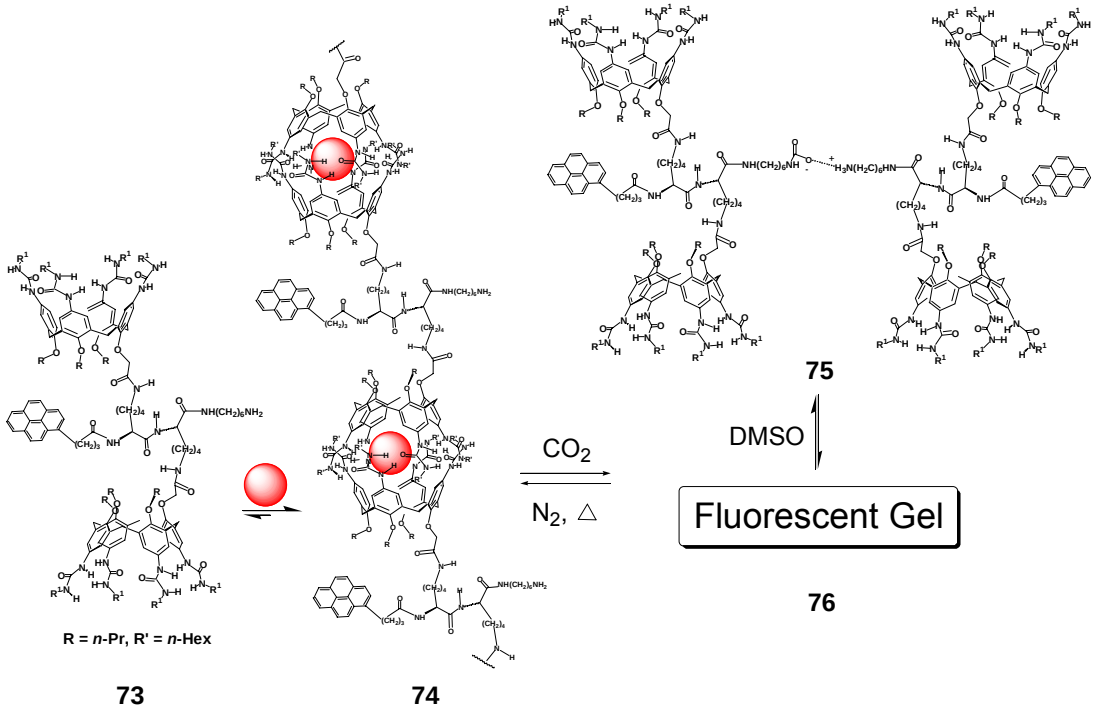


Figure 5.9 Reaction between biscalixarene **73** and CO_2. Formation of carbamate cross-linked supramolecular polymer **76** and its dissociation to carbamate **75**.

Bubbling CO_2 gas through solutions of **73** (e.g., **74**) in benzene or benzene-$CHCl_3$ yields material **76**, which is an insoluble gel (Figure 5.7 and 5.9). The main chains in **76** are held together by hydrogen bonding assembly of capsules, and multiple carbamate $-NH^+{}_3 \bullet\bullet\bullet O^-C(O)NH-$ bridges cross-link these chains. The result is a three-dimensional network, since the side amine groups are oriented in all three dimensions.

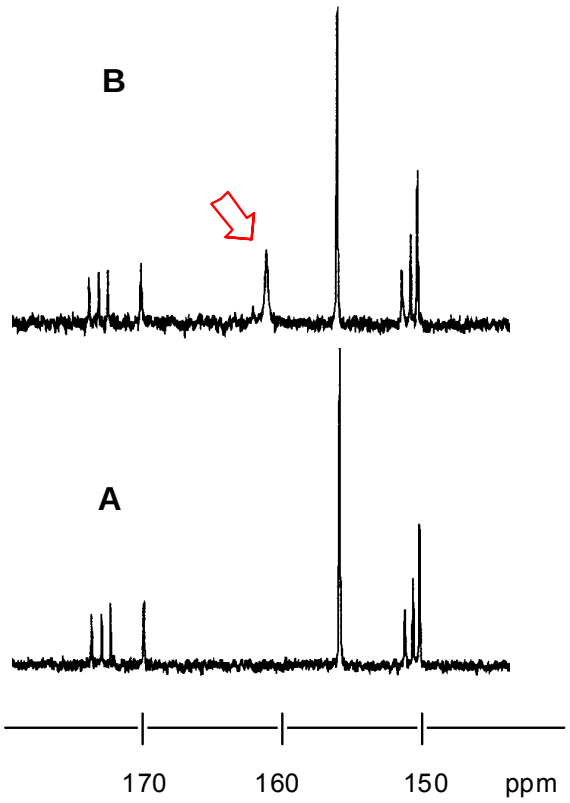


Figure 5.10 Downfield portions of ^{13}C NMR spectra (500 MHz, DMSO-d_6, 295 ±1 K) of (A) biscalixarene **73**; (B) carbamate salt **75** obtained upon dissociation of ^{13}C-labeled gel **76**. The gel was prepared from **73** and $^{13}CO_2$ in benzene. The carbamate ^{13}C-enriched signal is marked.

Formation of the carbamate bridges was confirmed by ^{13}C NMR spectroscopy. Using $^{13}CO_2$ gas, we prepared the carbamate ^{13}C-labeled gel **76**. In the ^{13}C NMR spectrum of biscalixarene **73**, prior to the reaction with the gas, in DMSO-d_6 five C=O carbonyl signals were clearly detected — four for the amide fragments at 172.9, 172.0 171.6, and 169.3 ppm, and one, intense signal for the upper rim ureas at 155.8 ppm (Figure 5.10A). In the spectrum of the ^{13}C-labeled salt **75**, which is formed upon dissociation of the ^{13}C -labeled polymer **76** in DMSO-d_6, in addition to these signals, a

new singlet of higher intensity appeared at 160.7 ppm (Figure 5.10B). This is attributed to the carbamate HN-^{13}C(O)O $^{-}$ group. The signal disappeared after heating solution **75** for 1 h at ~100 °C and bubbling N_2 through it.

Gel **76** can assemble and disassemble in two ways - either upon changing the solvent polarity or temperature. The calixarene capsules completely dissociate in DMSO with the formation of carbamate salt **75**. It, most probably, undergoes further solvolysis, generating loose ion pairs. The carbamate C-N bonds are not broken under these conditions. At the same time, they can be destroyed upon heating for 1 h at ~100°C, thus releasing CO_2. In the case of apolar solutions, linear hydrogen bonded polymer **74** forms, and in DMSO biscalixarene **73** is completely regenerated. Gel **76** can be reconstructed simply by reintroducing CO_2 (Figure 5.9).

Further insight into the aggregation mode and morphology in material **76** was obtained with scanning electron microscopy (SEM). For this, freeze-dried samples, xerogels **76** were obtained from **73** and CO_2 in benzene and benzene-nitrobenzene, 95:5. The three-dimensional network in the xerogels is obvious (Figure 5.11). Of particular interest are well-defined pores of ~1-3 μm diameter, which can be used for guest/solvent entrapment.

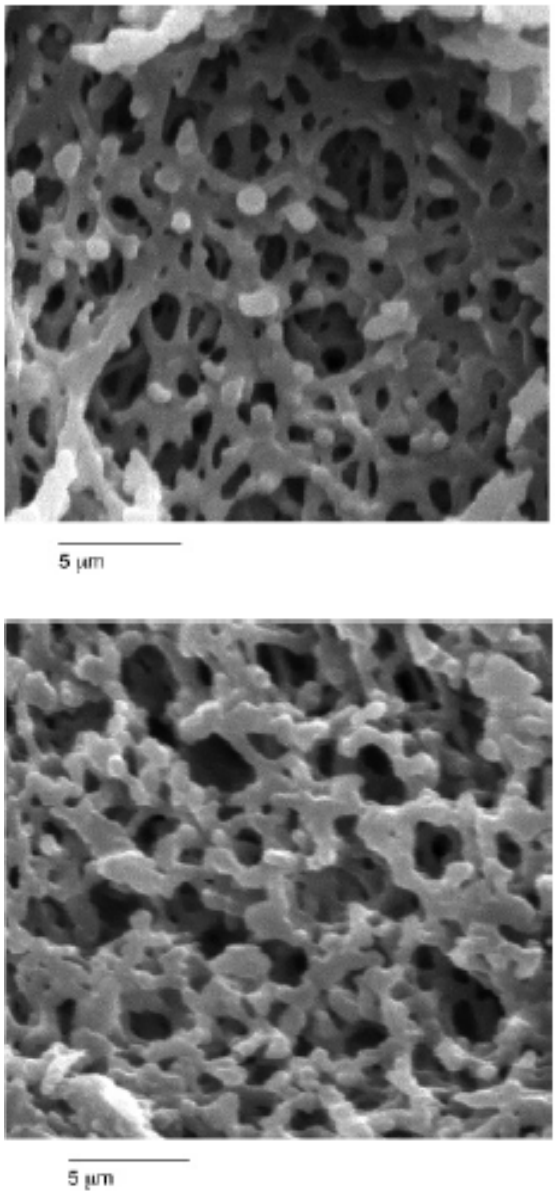


Figure 5.11 SEM pictures of xerogels **76** obtained upon bubbling CO_2 to benzene (left) and benzene-nitrobenzene 95:5 (right) solutions of **73** (bar 5 μm).

Figure 5.12 Xerogels **76** obtained upon bubbling CO_2 to benzene (left) and benzene-nitrobenzene, 95:5 (right) solutions of **73**.

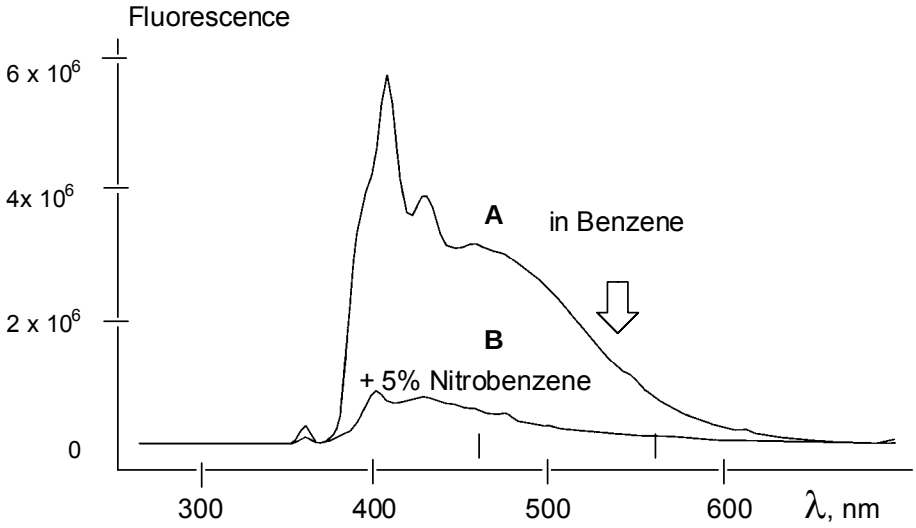


Figure 5.13 Fluorescence measurements with gels **76** obtained upon bubbling CO_2 to benzene (A) and benzene-nitrobenzene, 95:5 (B) solutions of **73** (λ_{ex} = 347 nm).

Material **76** possesses multiple fluorophore units, brought together through hydrogen bonding and carbamate bridges, and thus may act as a vehicle for energy migration.[123] The aggregation degree and therefore the fluorophore local concentrations can be controlled and switched on-off, as described earlier. In the preliminary photophysical experiments, we noticed a striking contrast in fluorescent behavior of xerogels **76**, obtained from benzene and benzene-nitrobenzene, 95:5 solutions (Figure 5.12 and 5.13). The former is strongly fluorescent (λ_{ex} = 347 nm), but the latter is not. Nitrobenzene is known to quench fluorescence of pyrene.[124] Incorporated within the gel's pores, molecules of nitrobenzene appear in close proximity to the multiple pyrene donors, and the energy transfer effectively occurs. This observation could be useful in the design of switchable light harvesting materials.

In summary, CO_2 can now be used to build switchable, supramolecular polymeric materials and gels. These can be further functionalized. Exploring on-off photophysics and mechanical properties of such gels is of great interest. Incorporating other functionalities within the dynamic three-dimensional networks, such as capsules, ionophores, catalytic sites, polymerizable groups for covalent cross-linking, etc is also possible. Using above approaches and given highly diverse peptide synthesis, the capabilities to build multifunctional self-assembling materials beyond the present limits of supramolecular chemistry.

5.3 Controlling Capture and Release of Guests from Cross-linked Supramolecular Polymers

Our cross-linked, three-dimensional supramolecular networks **67**, that simultaneously utilize two different forces: hydrogen bonding and reversible chemistry between CO_2 and amines, can be used to capture, store, and release guests (Figure 5.14).[125] A number of cross-linked supramolecular polymers are known; however, they have not been used for guest entrapment and release.[126,127] Our results thus offer opportunities for the design of switchable, three-dimensional supramolecular polymers for molecular storage.

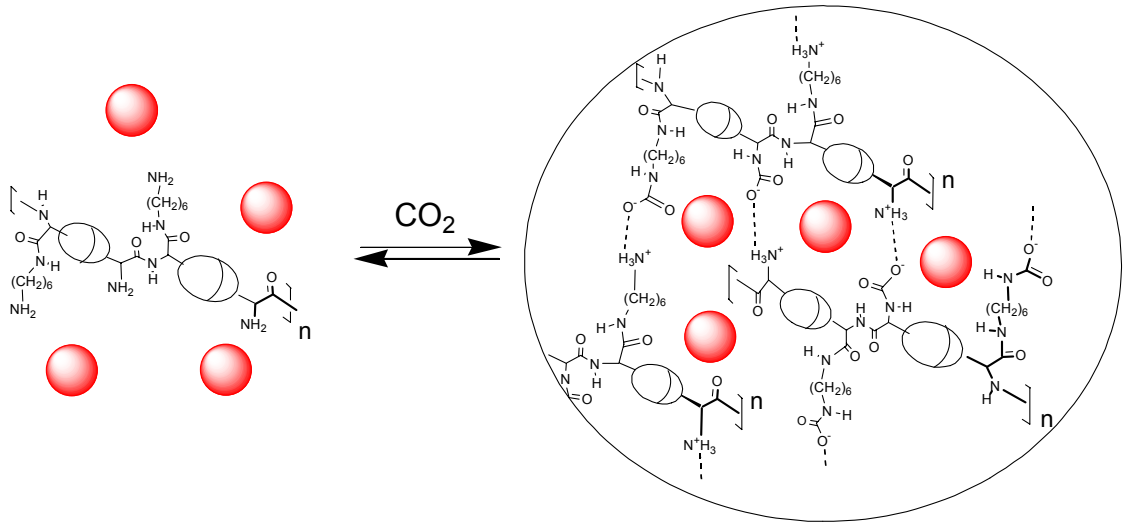


Figure 5.14 Two-parameter guest release in cross-linked supramolecular polymers, a general cartoon.

The synthesis and characterization of the supramolecular polymers **67** are described in Chapter 4. Briefly, two calix[4]arene tetraureas are attached to a dipeptide, dilysine chain. Calix[4]arene tetraureas are popular self-assembling modules that form well-defined hydrogen bonded dimers in apolar solution. Such design leads to very long

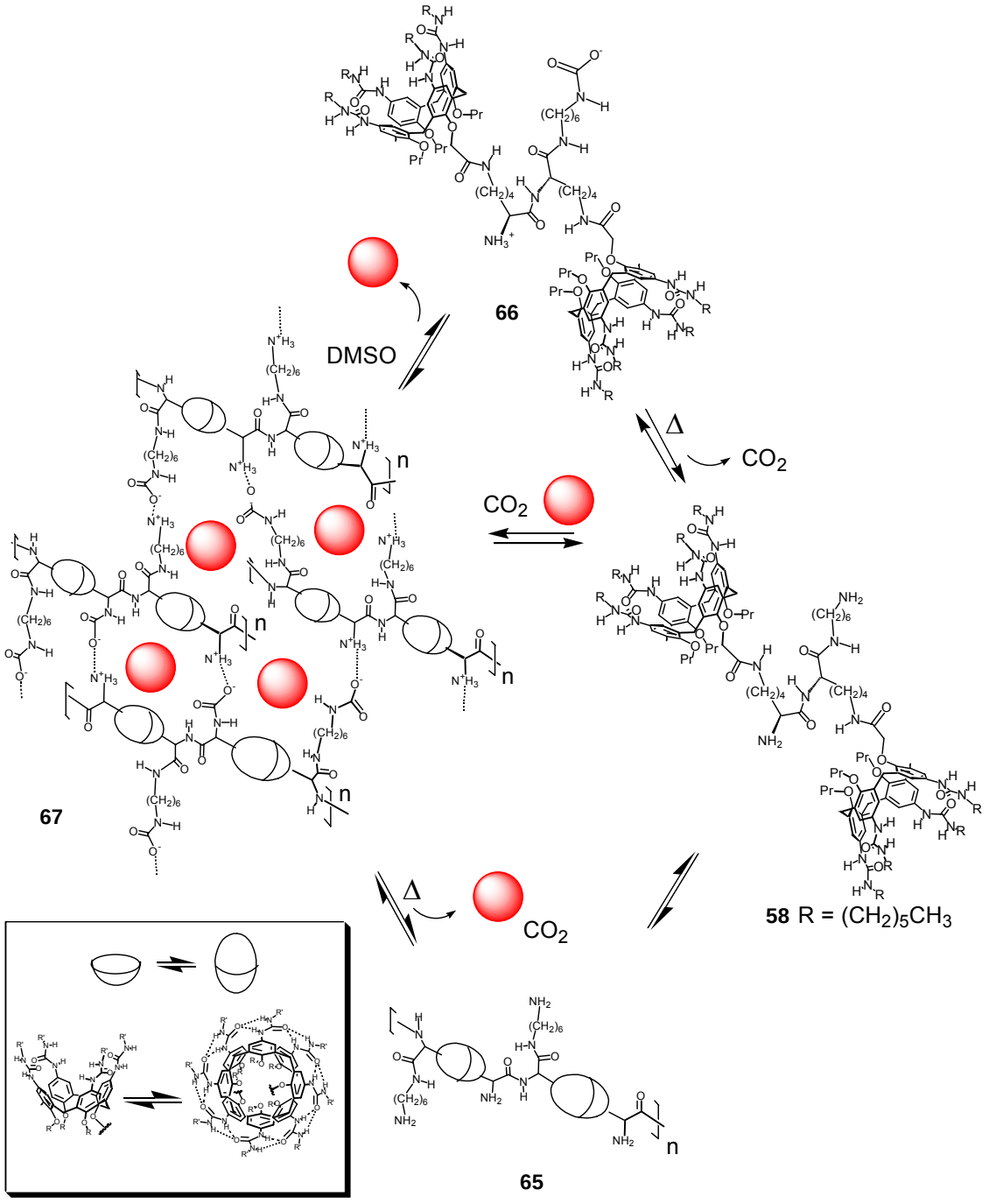


Figure 5.15 Biscalix[4]arene **58** forms supramolecular polymer chains **65** in apolar solution, which can be cross-linked with CO_2 into supramolecular polymer gels **67**. Solvents and other organic guests can be trapped, stored and released from **67** upon changing solvent polarity, temperature, pH and/or concentration.

supramolecular polymer chains **65** with a degree of polymerization of ~300 at NMR concentrations in $CHCl_3$ (see Chapter 3, Pages 54-56). Chains **65** possess "CO_2-philic" primary amino groups on the periphery. In an apolar solvent, once CO_2 is added, multiple carbamate salt bridges form and thus cross-link **65** into three-dimensional supramolecular polymer networks **67** (Figure 5.15). These are gels.

Scanning electron micrographs of freeze-dried samples or xerogels **67** revealed a highly developed three-dimensional network with defined pores and channels of ~5 μm (see Chapter 4, Page 79). On a molecular level, multiple voids are generated between the supramolecular polymer calixarene chains and the lysine-carbamate bridges that have dimensions of 15-20 Å. We have now discovered that when CO_2 cross-links supramolecular polymer chains **65** in the presence of organic guests of 1-1.5 nm size, gels **67** instantly entrap them. For this project, we used supramolecular gel **67** to trap commercial dyes such as Coumarin 314 **77** and porphyrin **78** and employed conventional UV-vis spectrophotometry to monitor their release. At the same time, the same rules can apply for other guests of comparable dimensions. Coumarin **77** or porphyrin **78** was added to a solution of up to 4-fold excess of biscalixarene **58** in a small volume of $CHCl_3$ (~57 g/L, 20 mmol/L). CO_2 was bubbled through the solution for 1-2 min. Colored gels **67** were formed and then briefly washed with $CHCl_3$ until solvent discoloration was observed. The ^{1}H NMR analysis revealed that ~7 ± 1% of **77** and **78** was entrapped; no selectivity was detected. The guests can be stored in dried gels indefinitely and released upon gel disassembly.

The release experiments were performed at least in triplicate (Figures 5.16 and 5.17). $CHCl_3$ was added to a round-bottom flask containing guest-stuffed gels **67** (0.5-1.3 g/L), and the mixtures were mechanically shaken for an extended time. The gel slowly dissolved, releasing the dyes.

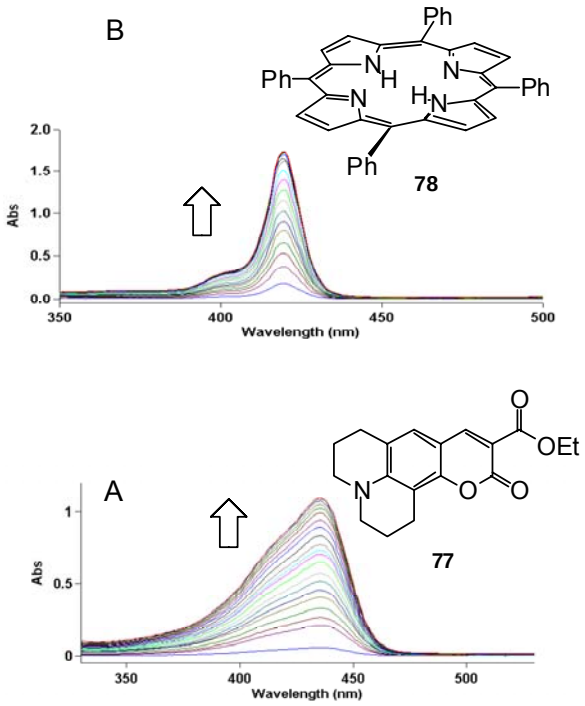


Figure 5.16 UV-vis spectra of coumarin **77** (A) and porphyrin **78** (B) in $CHCl_3$.

Samples were taken every 1-3 min, and increased absorptions of coumarin **77** at λ_{max} = 434 nm and porphyrin **78** at λ_{max} = 420 (Soret-band) and 552 nm (Q-band) were monitored (Figure 5.16). Under these conditions at 25 °C, coumarin **77** was completely released within 40 min, and porphyrin **78** was released after 20 min. From these experiments, the release rates of 0.12 and 0.24 mmol/min, respectively, were

determined (Figure 5.17A). These are much slower than simple dissolution of **77** and **78** under the same conditions, which occurs within seconds (> 40 mmol/min).

The release appears to be concentration dependent, and using smaller volumes of $CHCl_3$ significantly slows it down. For example, when 40 times less $CHCl_3$ (20 mg/mL compared to 0.5 mg/L) was used, the ~5-fold rate decrease (0.05 mmol/min) for porphyrin **78** was observed (Figure 5.17B).

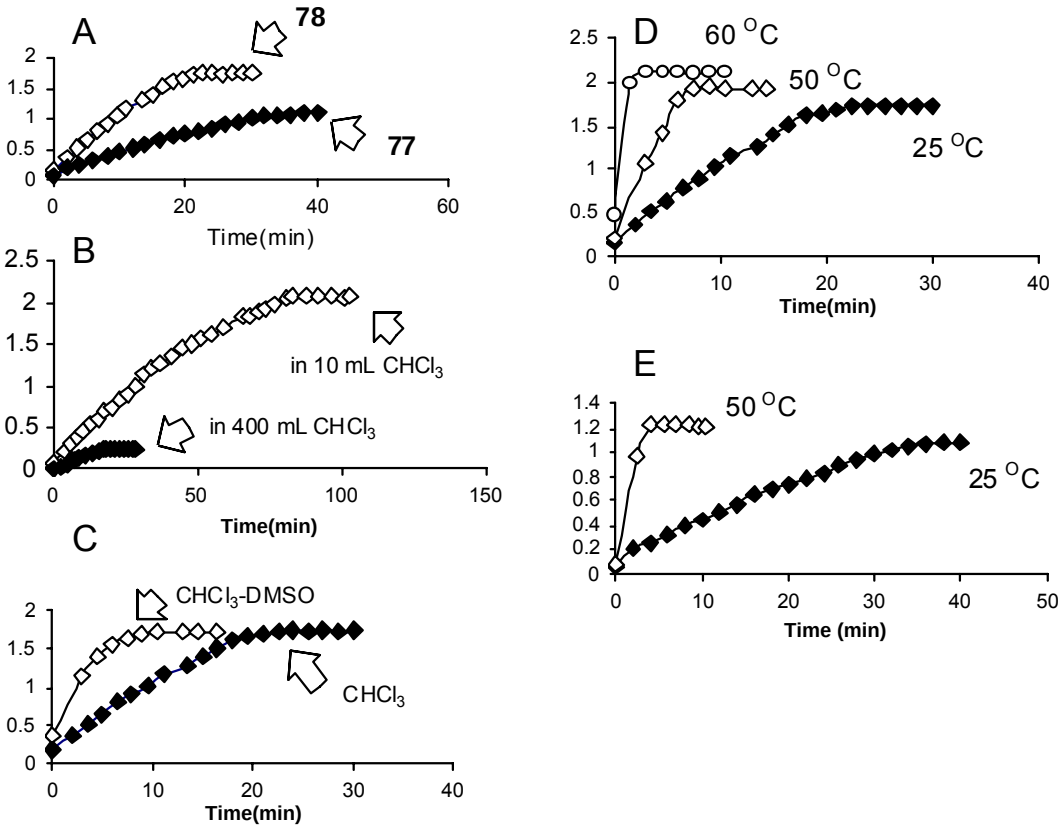


Figure 5.17 (A) Release curves of **77** and **78** at 25 °C at 0.5-1.3 mg/mL of **67** in $CHCl_3$. (B) Release of porphyrin **78** in $CHCl_3$ at 0.5 mg/mL (black squares) and 20 mg/mL (white squares) at 25 °C. (C) Release of porphyrin **78** in $CHCl_3$ (black squares) and $CHCl_3$-DMSO 1:1 (white squares) at 25 °C at 0.5 mg/mL of **67**. (D) Release of porphyrin **78** at 25, 50, and 60 °C at 0.5 mg/mL of **67**. (E) Release of coumarin **77** at 25 and 50 °C at 1.3 mg/mL of **67**.

In addition to simple diffusion, the dissociation of carbamate salt bridges and release of CO_2 are responsible for such concentration effects. Release of CO_2 was confirmed by ^{13}C NMR spectroscopy. In the ^{13}C NMR spectrum of monomer **58** in DMSO-d_6, four C=O carbonyl signals were observed, three for the amide fragments at 175.4, 171.7, and 169.4 ppm and an intense signal for the upper rim ureas at 155.8 ppm (Figure 5.18). Using $^{13}CO_2$ gas, we prepared the carbamate ^{13}C-labeled gel **67**. In the spectrum of the ^{13}C-labeled salt, formed upon dissolution of this gel in DMSO-d_6, in addition to the amide signals, new peaks of higher intensity appeared at ~162 ppm. These are attributed to the carbamate HN-$^{13}C(O)O$- group. The signal disappeared after diluting the mixture of **67** with larger quantities of $CHCl_3$ (from 3 to 300 mL for 0.2 g of **67**; ~20 to ~0.2 mmol/L). That carbamate bridges can dissociate back to free amine and CO_2 in diluted apolar solution is novel. Initially, it was assumed that traces of HCl in $CHCl_3$ might be primarily responsible for carbamate dissociation in diluted solutions. However, in model experiments, using thorough prewashes with aq Na_2CO_3 and then water $CHCl_3$, the same results were obtained. Addition of HCl and TFA to the NMR samples caused slower dissociation rates than high dilution (^{13}C NMR). Finally, similar concentration effects were observed for model alkylammonium carbamates in THF, MeCN, EtOAc, CH_2Cl_2, and benzene (see Appendix 47 for NMR evidence).

Faster guest release can be achieved upon increasing the solvent polarity. Addition of a competitive solvent such as DMSO breaks hydrogen bonding calixarene capsules and destroys gels **67** within minutes. At the 1:1 $CHCl_3$-DMSO ratio, the

process reflects dissolution of the gel, and the release rates are now ~ 4 times higher for both guests (for example, Figure 5.17C).

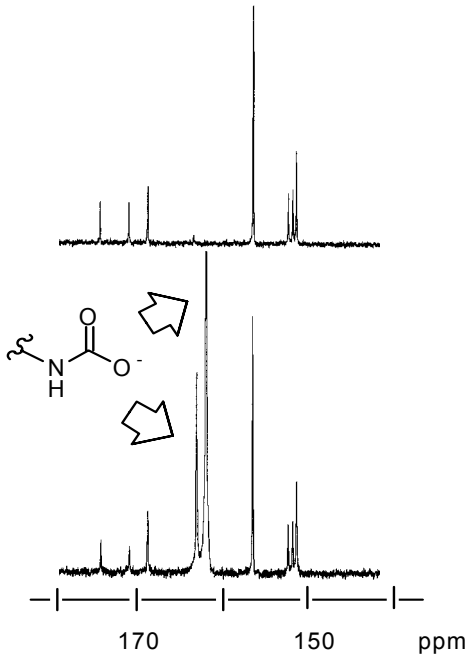


Figure 5.18 Portions of the ^{13}C NMR spectra (500 MHz, DMSO-d_6) of carbamate **66** (bottom) and calixarene **58** (top), obtained upon 100-fold dilution of **67** in $CHCl_3$.

Alternatively, guest departure from **67** can be accomplished through the thermal release of CO_2 (Figures 5.17D and 5.17E). The process takes place in an apolar solvent, and the calixarene capsules do not dissociate. At the same time, the carbamic salt bridges break easily. At 50 °C, coumarin **77** and porphyrin **78** were completely released within 4 and 5 min, respectively. Accordingly, release rates of 1.2 and 1.0 mmol/min, respectively, were obtained. At 60 °C, the release appeared to be even faster. For example, porphyrin **78** was released within 2 min at a rate of 2.4 mmol/min. Simple diffusion at elevated temperatures may also be responsible; however, release of CO_2

under these conditions was confirmed by ^{13}C NMR spectroscopy. Such rather fast dissociation of otherwise stable carbamate salt bridges was somewhat unexpected but promising. Indeed, this delicate property can now be used in dynamic covalent chemistry for the design of reversibly formed nanostructures and combinatorial libraries. Moreover, we found that traces of acids (HCl, TFA) also catalyze dissociation of carbamate bridges in **67**.[128]

In summary, we have demonstrated that carbamate-based cross-linked supramolecular polymers can serve for entrapment and switchable release of organic guests. Conventional organogels have been effectively used to trap small organic molecules; however, supramolecular polymers, with their highly directional, relatively strong, and yet reversible forces, may bring further improvements. Of particular interest are (a) the CO_2-initiated guest capture and (b) a multiparameter switch, allowing control over the release through solvent polarity, temperature, pH, concentration, etc.[129] Our results thus offer opportunities for the design of switchable, three-dimensional supramolecular polymers for molecular storage. Moreover, the use of CO_2 opens gates to environmentally responsive materials and devices.

CHAPTER 6

EXPERIMENTAL SECTION

6.1 General Information

Melting points were determined on a Mel-Temp apparatus (Laboratory Devices, Inc.) and are uncorrected. ^{1}H, ^{13}C NMR and COSY spectra were recorded at 295 ± 1 °C on JEOL Eclipse 500 MHz spectrometer. Chemical shifts were measured relative to residual non-deuterated solvent resonances. FTIR spectra were recorded on a Bruker Vector 22 FTIR spectrometer. ESI-MS spectra were obtained on a Finnigan LCQ Ion Trap apparatus. MALDI-TOF mass spectra were recorded on a delayed extraction MALDI-TOF mass spectrophotometer Voyager DE (Applied Biosystems). HRMS MALDI spectra were obtained on an Ion Spec Ultima FTMS. Elemental analysis was performed on a Perkin-Elmer 2400 CHN analyzer. Scanning Electron Microscopy (SEM) images were obtained on JEOL 35C microscope.

All experiments with moisture- and/or air-sensitive compounds were conducted under a dried nitrogen atmosphere. For column chromatography, Silica Gel 60 Å (Sorbent Technologies, Inc.; 200–425 mesh) was used. Parent tetrahydroxycalix[4]arene[130] was prepared according to the published procedures. Molecular modeling was performed using commercial MacroModel 7.1.

6.2 Synthesis

Calixarene lysine 1a.

A solution of calix[4]arene triester monoacid chloride **26** (0.49 g, 0.50 mmol) in EtOAc (10 mL) was added under vigorous stirring to a solution of TFA salt **6** (0.20 g, 0.42 mmol) and K_2CO_3 (0.58 g, 4.20 mmol) in EtOAc (10 mL) and H_2O (20 mL). The reaction mixture was stirred at rt for 3 h. The organic layer was separated and evaporated under reduced pressure. The residue was chromatographed on silica gel with THF–hexanes, 3:2 as eluents to afford **1a** (0.36 g, 65%) as a colorless solid: mp 69–70 °C; ^{1}H NMR ($CDCl_3$): δ 8.42 (t, J = 6.4 Hz, 1H), 7.34 (m, 5H), 6.82 (s, 2H), 6.79 (s, 4H), 6.73 (s, 2H), 6.39 (d, J = 7.3 Hz, 1H), 5.15 (s, 2H), 4.89 (d, J = 13.0 Hz, 2H), 4.74 (d, J = 13.0 Hz, 2H), 4.69 (s, 2H), 4.65 (m, 4H), 4.55 (m, 1H), 4.52 (m, 2H), 4.16 (m, 6H), 3.39 (m, 1H), 3.26 (m, 1H), 3.25 (d, J = 13.0 Hz, 2H), 3.21 (d, J = 13.0 Hz, 2H), 2.20 (t, J = 7.3 Hz, 2H), 1.85–1.50 (m, 6H), 1.25 (m, 19H), 1.11 (s, 9H), 1.07 (s, 18H), 1.03 (s, 9H), 0.85 (t, J = 7.5 Hz, 3H); IR (KBr): ν 3377, 2954, 2868, 1754, 1651, 1547, 1480, 1193, 1070 cm^{-1}; MALDI-TOF MS, m/z 1331.9 ([M+Na$^+$], calcd for $C_{79}H_{108}N_2O_{14}Na$ 1332.7). Anal. calcd for $C_{79}H_{108}N_2O_{14}$: C, 72.45; H, 8.31; N, 2.14. Found: C, 72.15, H, 8.67, N, 2.40.

Calixarene lysine 1b.

A solution of monoacid chloride (0.58 g, 0.59 mmol) in 10 ml of EtOAc was added under vigorously stirring to a solution of of lysine TFA salt **10** (0.20 g, 0.49 mmol) and

K_2CO_3 (0.68 g, 4.90 mmol) of EtOAc (10 mL) and H_2O (20 mL). The reaction mixture was stirred at rt for 3 hrs. The organic layer was separated and evaporated under reduced pressure. The residue was chromatographed on silica gel with THF–hexanes, 3:2 as eluents to afford **1b** (0.41 g, 67%) as a colorless solid: mp 71–72 °C; ^{1}H NMR ($CDCl_3$): δ 8.41 (t, J = 6.0 Hz, 1H), 7.33 (m, 5H), 6.82 (s, 2H), 6.78 (s, 4H), 6.73 (s, 2H), 5.52 (d, J = 8.3 Hz, 1H), 5.11 (d, J = 12.4 Hz, 1H), 5.06 (d, J = 12.4 Hz, 1H), 4.90 (d, J = 12.5 Hz, 2H), 4.73 (d, J = 12.8 Hz, 2H), 4.70 (s, 2H), 4.63 (m, 4H), 4.50 (br s, 2H), 4.35 (m, 1H), 4.18 (m, 6H), 3.73 (s, 3H), 3.35 (m, 2H), 3.22 (m, 4H), 2.0–1.5 (m, 6H), 1.24 (m, 9H), 1.11 (s, 9H), 1.07 (s, 18H), 1.04 (s, 9H); MALDI-TOF MS, *m*/*z* 1265.2 ([M+Na$^+$], calcd for $C_{73}H_{96}N_2O_{15}Na$ 1264.6). Anal. calcd for $C_{73}H_{96}N_2O_{15}$: C, 70.62; H, 7.79; N, 2.26. Found: C, 70.81, H, 7.69, N, 2.53.

Calixarene lysine 1c.

A solution of monoacid chloride (0.45 g, 0.46 mmol) in 10 ml of EtOAc was added under vigorously stirring to a solution of of lysine TFA salt **11** (0.20 g, 0.38 mmol) and K_2CO_3 (0.53 g, 3.80 mmol) in EtOAc (10 mL) and H_2O (20 mL). The reaction mixture was stirred at rt for 3 hrs. The organic layer was separated and evaporated under reduced pressure. The residue was chromatographed on silica gel with THF–hexanes, 3:2 as eluents to afford **1c** (0.33 g, 64%) as a colorless solid: mp 70–72 °C; ^{1}H NMR ($CDCl_3$): δ 8.43 (t, J = 6.0 Hz, 1H), 7.34 (m, 7H), 7.01 (d, J = 8.7 Hz, 2H), 6.82 (s, 2H), 6.77 (s, 4H), 6.73 (s, 2H), 5.62 (d, J = 8.3 Hz, 1H), 5.13 (d, J = 12.3 Hz, 1H), 5.09 (d, J = 12.3 Hz, 1H), 4.88 (d, J = 12.4 Hz, 2H), 4.75 (d, J = 12.9 Hz, 2H), 4.70 (s, 2H), 4.62

(m, 4H), 4.55 (m, 1H), 4.52 (d, J = 2.8 Hz, 2H), 4.17 (m, 6H), 3.44 (m, 1H), 3.39 (m, 1H), 3.24 (d, J = 13.2 Hz, 2H), 3.22 (d, J = 13.2 Hz, 2H), 2.1–1.5 (m, 6H), 1.30 (s, 9H), 1.24 (m, 9H), 1.11 (s, 9H), 1.07 (s, 18H), 1.04 (s, 9H); MALDI-TOF MS, m/z 1382.9 ([M+Na^+], calcd for $C_{82}H_{106}N_2O_{15}Na$ 1382.7). Anal. calcd for $C_{82}H_{106}N_2O_{15}$: C, 72.43; H, 7.86; N, 2.06. Found: C, 72.12, H, 7.74, N, 1.94.

Calixarene lysine 1d.

A solution of calix[4]arene triester monoacid chloride **26** (0.91 g, 0.92 mmol) in EtOAc (10 mL) was added under vigorous stirring to a solution of TFA salt **14** (0.20 g, 0.77 mmol) and K_2CO_3 (1.06 g, 7.70 mmol) in EtOAc (10 mL) and H_2O (20 mL). The reaction mixture was stirred at rt for 3 h. The organic layer was separated and evaporated under reduced pressure. The residue was chromatographed on silica gel with THF–hexanes, 1:1 as eluents to afford **1d** (0.58 g, 62%) as a colorless solid: mp 74–75 °C; $[\alpha]_D^{23}$ = −2.8 (c = 0.02, EtOH); ^{1}H NMR ($CDCl_3$): δ 8.37 (t, J = 6.0 Hz, 1H), 6.82 (s, 2H), 6.78 (s, 4H), 6.73 (s, 2H), 5.13 (d, J = 8.3 Hz, 1H), 4.89 (d, J = 12.5 Hz, 2H), 4.74 (d, J = 12.8 Hz, 2H), 4.70 (s, 2H), 4.63 (m, 4H), 4.53 (s, 2H), 4.28 (m, 1H), 4.19 (m, 6H), 3.72 (s, 3H), 3.37 (m, 2H), 3.24 (d, J = 12.8 Hz, 2H), 3.21 (d, J = 12.8 Hz, 2H), 1.88 (m, 1H), 1.65 (m, 3H), 1.42 (s, 9H), 1.28 (m, 9H), 1.11 (s, 9H), 1.07 (s, 18H), 1.01 (s, 9H); FTIR (KBr): ν 3382, 2961, 2869, 1755, 1720, 1673, 1480, 1363, 1194, 1128, 1069 cm^{-1}; MALDI-TOF MS, m/z 1229.9 ([M+Na^+], calcd for $C_{70}H_{98}N_2O_{15}Na$ 1230.5). Anal. calcd for $C_{70}H_{98}N_2O_{15}$: C, 69.63; H, 8.18; N, 2.32. Found: C, 69.60, H, 8.28, N, 2.48.

Calixarene lysine 1e.

A solution of benzyl ester **1a** (0.20 g, 0.15 mmol) in CH_3OH (10 mL) was mixed with 10% Pd/C (20 mg) and stirred under a hydrogen atmosphere for 4 h. The reaction mixture was filtered through Celite and concentrated in vacuo to give pure **1e** (0.18 g, 98%) as a colorless solid: ^{1}H NMR ($CDCl_3$) δ 8.62 (t, J = 6.4 Hz, 1H), 6.99 (d, J = 5.0 Hz, 1H), 6.82 (s, 2H), 6.78 (s, 4H), 6.72 (s, 2H), 5.0–4.8 (m, 2H), 4.80–4.62 (m, 8H), 4.62–4.40 (m, 2H), 4.18 (m, 6H), 3.50 (dt, J = 6.9, 6.4 Hz, 1H), 3.34 (m, 2H), 3.24 (d, J = 13.2 Hz, 2H), 3.22 (d, J = 13.2 Hz, 2H), 2.26 (t, J = 6.4 Hz, 2H), 2.00–1.15 (m, 25H), 1.11 (s, 9H), 1.07 (s, 18H), 1.04 (s, 9H), 0.85 (t, J = 6.9 Hz, 3H).

Calixarene lysine 1f.

A solution of **1b** (0.20 g, 0.16 mmol) in CH_3OH (10 mL) was treated with 10% Pd/C (20 mg) and stirred under a hydrogen atmosphere for 4 h. The mixture was filtered through Celite and concentrated in vacuo. The residue was dried under high vacuum to give 0.17 g (96%) of amine **1f** as a colorless solid. ^{1}H NMR ($CDCl_3$): δ 8.47 (t, J = 6.0 Hz, 1H), 6.77 (m, 8H), 4.95–4.80 (m, 2H), 4.80–4.65 (m, 4H), 4.65–4.52 (m, 4H), 4.52–4.45 (m, 2H), 4.15 (m, 6H), 3.72 (s, 3H), 3.60 (m, 1H), 3.35 (m, 2H), 3.26 (d, J = 12.8 Hz, 2H), 3.21 (d, J = 12.8 Hz, 2H), 2.0–1.5 (m, 6H), 1.24 (m, 9H), 1.12 (s, 9H), 1.07 (s, 9H), 1.04 (s, 9H), 1.02 (s, 9H).

***N*-α-BOC-*N*-ε-(calix[4]arenetetraurea)-*l*-lysine, Methyl Ester 1g.**

To an ice-cooled solution of *N*-α-BOC-*l*-lysine methyl ester **14** (0.26 g, 1.00 mmol) in DMF (30 mL) were added calixarene tetraurea acid **32** (1.19 g, 1.00 mmol), DCC (0.41 g, 2.00 mmol), and HOBt (0.27 g, 2.00 mmol). The mixture was allowed to stir for 30 min at 0 °C and for 24 h at rt, filtered, concentrated, diluted with $CHCl_3$, and washed successively with 1 N $NaHSO_4$ (4 × 100 mL), water (3 × 100 mL), 1 N $NaHCO_3$ (4 × 100 mL), and again water (3 × 100 mL). The organic layer was then dried over anhydrous Na_2SO_4 and evaporated. The residue was chromatographed on silica gel eluting with $CHCl_3$-CH_3OH, 95:5 to afford calix[4]arene amino acid **1g** (1.00 g, 70%). ^{1}H NMR (DMSO-d_6) δ 8.21 (t, *J* = 5.7 Hz, 1H), 8.03 (s, 1H), 7.99 (s, 1H), 7.83 (s, 2H), 7.24 (d, *J* = 7.6 Hz, 1H), 6.82 (s, 2H), 6.81 (s, 2H), 6.61 (s, 4H), 5.9 (m, 2H), 5.77 (t, *J* = 5.0 Hz, 2H), 4.37 (d, *J* = 8.0 Hz, 2H), 4.32 (d, *J* = 12.8 Hz, 2H), 4.26 (d, *J* = 12.8 Hz, 2H), 4.0 (m, 1H), 3.76 (t, *J* = 7.3 Hz, 4H), 3.71 (t, *J* = 7.3 Hz, 2H), 3.61(s, 3H), 3.2 (m, 2H), 3.0 (m, 12H), 1.80 (m, 6H), 1.65 (m, 2H), 1.50 (m, 2H), 1.37 (s, 9H), 1.23 (m, 34H), 0.87 (t, J = 7.3 Hz, 21H); FTIR (KBr): ν 3332, 2930, 2859, 1654, 1559, 1474, 1219 cm^{-1}; MALDI-FTMS *m*/*z* 1419.9255 [$(M + H)^+$, calcd for $C_{79}H_{123}N_{10}O_{13}$ 1419.9265]. Anal. Calcd for $C_{79}H_{122}N_{10}O_{13}$: C, 66.83; H, 8.66; N, 9.86. Found: C, 66.44, H, 8.76, N, 9.67.

Calixarene dipeptide 2a.

Procedure 1. To a stirred and ice-cooled solution of calix amino acid derivative **1e** (0.15 g, 0.14 mmol) in DMF (15 mL) was added successively **1f** (0.17 g, 0.14 mmol), HOBT (0.04 g, 0.28 mmol), and DCC (0.06 g, 0.28 mmol). The mixture was stirred for 30 min at 0 °C and then for 36 h at rt. The mixture was filtered, concentrated, diluted with EtOAc (200 mL), and washed successively with 1N $NaHSO_4$ (4 × 50 mL), water (3 × 50 mL), 1N $NaHCO_3$ (4 × 50 mL), and again water (3 × 50 mL). The organic layer was then dried over anhydrous Na_2SO_4 and evaporated. The residue was chromatographed on silica gel eluting with THF–hexanes, 7:3 to afford calix–peptide **2a** (two diastereomers, 1:1, 0.15 g, 46%) as a colorless solid: mp 97–98 °C; FTIR (KBr): *v* 3378, 2959, 2868, 1752, 1671, 1540, 1474, 1369, 1297, 1191, 1124, 1066 cm^{-1}; ^1H NMR (DMSO-d_6, one diastereomer is shown): δ 8.30 (d, J = 7.8 Hz, 1H), 8.10 (m, 2H), 7.89 (d, J = 8.0 Hz, 1H), 6.84 (m, 16H), 4.85–4.75 (m, 4H), 4.70–4.50 (m, 16H), 4.36 (m, 4H), 4.22 (m, 1H), 4.13 (m, 12H), 3.62 (s, 3H), 3.40–3.15 (m, 12H), 2.11 (m, 2H), 2.0–1.1 (m, 40H), 1.05 (m, 72H), 0.85 (t, J = 7.7 Hz, 3H); ^1H NMR (DMSO-d_6, the other diastereomer): δ 8.26 (d, J = 7.8 Hz, 1H), 8.10 (m, 2H), 7.87 (d, J = 8.0 Hz, 1H), 6.84 (m, 16H), 4.85–4.75 (m, 4H), 4.70–4.50 (m, 16H), 4.36 (m, 4H), 4.22 (m, 1H), 4.13 (m, 12H), 3.61 (s, 3H), 3.40–3.15 (m, 12H), 2.11 (m, 2H), 2.0–1.1 (m, 40H), 1.05 (m, 72H), 0.85 (t, J = 7.7 Hz, 3H); MALDI-TOF MS, *m*/*z* 2332.6 ([M+Na^+], calcd for $C_{137}H_{190}N_4O_{26}Na$ 2332.0).

Procedure 2. A solution of acid chloride **26** (0.37 g, 0.38 mmol) in EtOAc (10 mL) was added to a vigorously stirred solution of dipeptide **34** (0.10 g, 0.16 mmol) and K_2CO_3 (0.53 g, 3.80 mmol) in EtOAc (10 mL) and H_2O (20 mL). The reaction mixture was stirred at rt for 6 h, and the organic layer was separated and evaporated. The residue was chromatographed on silica gel eluting with THF–hexanes, 7:3 to afford **2a** (0.18 g, 49%).

Calixarene dipeptide 2b.

A solution of acid chloride **26** (0.61 g, 0.62 mmol) in EtOAc (10 mL) was added under vigorous stirring to a solution of dipeptide **36** (0.10 g, 0.26 mmol) and K_2CO_3 (0.86 g, 6.2 mmol) in EtOAc (10 mL) and H_2O (20 mL). The reaction mixture was stirred for 6 h at rt. The organic layer was separated and evaporated. The residue was chromatographed on silica gel eluting with THF–hexanes, 7:3 to afford calix dipeptide **2b** (0.27 g, 45%) as a colorless solid: mp 109–110 °C; $[\alpha]_D^{23} = -5.1$ (c = 0.02, EtOH); ^{1}H NMR (DMSO-d_6): δ 8.16 (d, J = 7.3 Hz, 1H), 8.11 (m, 2H), 6.96 (d, J = 6.9 Hz, 1H), 6.85 (m, 16H), 4.78 (m, 4H), 4.7–4.5 (m, 16H), 4.37 (m, 4H), 4.25 (m, 1H), 4.2–4.0 (m, 12H), 3.96 (m, 1H), 3.60 (s, 3H), 3.22 (m, 12H), 1.38 (s, 9H), 2.0–1.1 (m, 30H), 1.1–0.9 (m, 72H); FTIR (KBr): ν 3333, 2959, 2864, 2358, 1752, 1673, 1540, 1475, 1368, 1300, 1190, 1125, 1056 cm^{-1}; MALDI-TOF MS, m/z 2306.8 ([M+Na$^+$], calcd for $C_{134}H_{185}N_4O_{27}Na$ 2305.9). Anal. calcd for $C_{135}H_{184}N_4O_{27}$: C, 70.50; H, 8.12; N, 2.45. Found: C, 70.63, H, 8.19, N, 2.61.

Biscalixarene 2c.

Calixarene tetraurea acid **32** (1.00 g, 0.84 mmol), EDCI (0.32 g, 1.68 mmol), and HOBt (0.23 g, 1.68 mmol) were added to a stirred and ice-cooled solution of dipeptide **36** (0.16 g, 0.42 mmol) in DMF (30 mL). The mixture was stirred for 30 min at 0 °C and for 24 h at RT, filtered, concentrated, diluted with $CHCl_3$, and washed with water (3 × 100 mL). The organic layer was then dried over anhydrous Na_2SO_4 and evaporated. The residue was separated chromatographically on silica gel eluting with $CHCl_3/CH_3OH$ (9.5:0.5) to afford calix dipeptide **2c** (0.64 g, 56%). mp >180 °C (decomp); ^{1}H NMR (DMSO-d_6): δ 8.19 (m, 2H), 8.12 (d, J = 7.8 Hz, 1H), 8.02 (s, 1H), 8.01 (s, 1H), 7.97 (s, 1H), 7.96 (s, 1H), 7.81 (s, 2H), 7.80 (s, 2H), 6.79 (s, 2H), 6.78 (s, 4H), 6.77 (s, 2H), 6.59 (s, 4H), 6.58 (s, 4H), 5.84 (m, 4H), 5.76 (m, 4H), 4.33 (br s, 4H), 4.30 (d, J = 12.4 Hz, 4H), 4.23 (d, J = 12.4 Hz, 4H), 3.91 (m, 1H), 3.72 (t, J = 6.9 Hz, 8H), 3.68 (t, J = 6.9 Hz, 4H), 3.58 (s, 3H), 3.20 (m, 4H), 3.08-2.90 (m, 24H), 1.77 (m, 12H), 1.53 (m, 4H), 1.34 (s, 9H), 1.18 (m, 72H), 0.86 (m, 42H); ^{13}C NMR (DMSO-d_6): δ 173.0, 172.9, 169.3, 155.74, 155.7, 151.25, 151.2, 150.7, 150.3, 135.3, 135.16, 135.1, 135.0, 134.5, 134.46, 134.2, 134.1, 134.0, 118.8, 118.72, 118.5, 118.4, 78.5, 77.3, 76.5, 74.8, 54.5, 52.3, 32.3, 31.6, 31.4, 31.2, 30.4, 30.1, 29.9, 28.7, 26.7, 23.6, 23.4, 23.0, 22.9, 22.7, 14.5, 10.6; FTIR (KBr): ν 3333, 2931, 2858, 1653, 1559, 1213, 1042, 965 cm^{-1}; MALDI-FTMS: m/z: calcd for $C_{152}H_{232}N_{20}O_{23}Na$: 2728.7491; found: 2728.7671 $[M+Na]^+$.

***N*-α-(*n*-Octanoyl)-*N*-ε-BOC-(±)-lysine 4.**

A solution of *N*-ε-BOC-*l*-lysine **3** (0.50 g, 2.00 mmol) in mixture of H_2O (20 mL) and EtOAc (20 mL) was treated with *n*-octanoyl chloride (3.30 g, 20.30 mmol) and then stirred at rt for 3 h. The reaction mixture was diluted with aq HCl (5% vol, 50 mL) and CH_2Cl_2 (80 mL). The formed layers were separated. The aqueous layer was extracted by CH_2Cl_2 (3×30 mL), and the combined organic layer was then dried over anhydrous Na_2SO_4 and evaporated. The residue was solidified with hexane, yielding pure **4** (0.57 g, 77%) as a colorless solid: mp 115–116 °C; $[\alpha]_D^{23} = 0.0$ (c = 0.02, EtOH); ^{1}H NMR (DMSO-d_6): δ 7.99 (d, J = 7.8 Hz, 1H), 6.77 (t, J = 7.1 Hz, 1H), 4.12 (dt, J = 8.5, 7.8 Hz, 1H), 2.87 (dt, J = 7.6, 7.1 Hz, 2H), 2.09 (dt, J = 7.3, 2.5 Hz, 2H), 1.65 (m, 1H), 1.54 (m, 1H), 1.47 (m, 2H), 1.36 (s, 9H), 1.23 (m, 12H), 0.85 (t, J = 6.6 Hz, 3H); ^{13}C NMR (DMSO-d_6): δ 174.5, 172.9, 156.1, 77.9, 52.2, 35.6, 31.8, 31.3, 29.6, 29.1, 29.0, 28.8, 25.8, 23.4, 22.6, 14.5; MS-EI m/z 371.9 (M^+, calcd for $C_{19}H_{36}N_2O_5$ 372.5).

***N*-α-(*n*-Octanoyl)-*N*-ε-BOC-(±)-lysine, *O*-benzyl ester 5.**

A solution of free acid **4** (0.37 g, 1.00 mmol) in THF (20 mL) was mixed with DCC (0.21 g. 1.00 mmol), catalytic amount of DMAP, and benzyl alcohol (0.13 g, 1.20 mmol). The solution was stirred at rt overnight, filtered, and concentrated in vacuo. Column chromatography on silica gel with EtOAc–CH_2Cl_2, 3:7 as an eluent afforded **5** (0.28 g, 61%) as a colorless oil: ^{1}H NMR ($CDCl_3$): δ 7.36 (m, 5H), 6.03 (d, J = 7.8 Hz, 1H), 5.16 (d, J = 12.4 Hz, 1H), 5.12 (d, J = 12.4 Hz, 1H), 4.64 (dt, J = 7.8, 5.0 Hz, 1H),

4.51 (br s, 1H), 3.04 (dt, J = 7.3, 6.0 Hz, 2H), 2.21 (t, J = 7.3 Hz, 2H), 1.81 (m, 1H), 1.65 (m, 1H), 1.60 (m, 2H), 1.43 (s, 9H), 1.25 (m, 12H), 0.87 (t, J = 6.9 Hz, 3H); MS-EI m/z 461.8 (M^+, calcd for $C_{26}H_{42}N_2O_5$ 462.6).

_N_-α-(_n_-Octanoyl)-(±)-lysine, _O_-benzyl ester, TFA salt 6.

A solution of **5** (0.46 g, 1.00 mmol) in THF (20 mL) was stirred with TFA (5 mL) at rt for 2 h. The reaction mixture was concentrated in vacuo to afford salt **6** (0.45 g, 94%), which was used without further purification. ^{1}H NMR ($CDCl_3$): δ 7.33 (m, 5H), 6.71 (d, J = 7.8 Hz, 1H), 5.16 (d, J = 12.4, 1H), 5.12 (d, J = 12.4 Hz, 1H), 4.55 (dt, J = 8.3, 5.0 Hz, 1H), 2.93 (m, 2H), 2.23 (t, J = 7.3 Hz, 2H), 2.0–1.0 (m, 16H), 0.87 (t, J = 6.9 Hz, 3H).

_N_-α-Cbz-_N_-ε-BOC-_l_-lysine, _O_-(4-_tert_-butyl)phenyl ester 9.

A solution of **7** (0.50 g, 1.30 mmol, $[\alpha]_D^{23} = -3.6$ (c = 0.03, EtOH) in dry CH_2Cl_2 (20 mL) was stirred with DCC (0.27 g, 1.3 mmol), catalytic amount of DMAP, and 4-_t_-butylphenol (0.24 g, 1.60 mmol) at rt overnight. The reaction mixture was then filtered and concentrated in vacuo. Column chromatography with EtOAc–CH_2Cl_2, 2:8 as an eluent afforded phenyl ester **9** (0.41 g, 62%) as an oil: ^{1}H NMR ($CDCl_3$): δ 7.35 (m, 7H), 7.0 (d, J = 8.7 Hz, 2H), 5.54 (d, J = 7.3 Hz, 1H), 5.13 (s, 2H), 4.58 (m, 2H), 3.12 (m, 2H), 1.42 (s, 9H), 1.25 (s, 9H), 1.82 (m, 1H), 1.75(m, 1H), 1.40 (m, 4H).

***N*-α-Cbz-*l*-lysine, *O*-methyl ester, TFA salt 10.**

A solution of **8** (0.39 g, 1.00 mmol) in THF (20 mL) was treated with TFA (5 mL) at rt for 2 h. The reaction mixture was concentrated in vacuo to afford pure salt **10** (0.38 g, 92%). ^{1}H NMR ($CDCl_3$): δ 7.30 (m, 5H), 5.74 (d, J = 7.3 Hz, 1H), 5.06, 5.03 (2×d, J = 11.9 Hz, 2H), 4.26 (m, 1H), 3.69 (s, 3H), 2.89 (m, 2H), 1.75 (m, 1H), 1.62 (m, 3H), 1.36 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 173.0, 162.0 (q, J_{C-F} = 37.9 Hz), 156.4, 136.2, 128.6, 128.3, 128.0, 127.8, 116.9 (q, J_{C-F} = 308.1 Hz), 67.1, 53.7, 52.6, 39.5, 31.7, 26.8, 22.1.

***N*-α-Cbz-*l*-lysine, *O*-(4-*tert*-butyl)phenyl ester, TFA salt 11.**

Prepared analogously to compound **10** in a 95% yield. ^{1}H NMR ($CDCl_3$): δ 7.35 (m, 7H), 6.96 (d, J = 8.3 Hz, 2H), 5.71 (d, J = 7.3 Hz, 1H), 5.12 (d, J = 12.4 Hz, 1H), 5.07 (d, J = 12.4 Hz, 1H), 4.50 (dt, J = 8.3, 4.1 Hz, 1H), 2.92 (m, 2H), 1.95 (m, 1H), 1.78 (m, 1H), 1.70 (m, 2H), 1.50 (m, 2H), 1.27 (s, 9H).

***N*-ε-Cbz-*l*-lysine, *O*-methyl ester, TFA salt 15.**[131]

A solution of **13** (0.20 g, 0.51 mmol) in THF (15 mL) was treated with TFA (4 mL) and then stirred at rt for 2 h. The reaction mixture was concentrated in vacuo to afford salt **15** (0.15 g, 95%). ^{1}H NMR ($CDCl_3$) δ 7.30 (m, 5H), 5.16 (br s, 1H), 5.05 (s, 2H), 3.98 (m, 1H), 3.76 (s, 3H), 3.13 (m, 2H), 1.92 (m, 2H), 1.40 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 170.2, 162.0 (q, J_{C-F} = 36.0 Hz), 157.1, 136.6, 128.6, 128.2, 128.0, 127.9, 127.8, 116.4 (q, J_{C-F} = 291.7 Hz), 62.7, 53.2, 53.1, 40.4, 29.8, 29.1, 21.8.

***N*,*N*-α,ε -Bis-BOC-*l*-lysine, *O*-methyl ester 17.**[132]

To a solution of *l*-lysine (2.00 g, 13.70 mmol) in water–dioxane, 1:1 (40 mL) were added BOC_2O (7.50 g, 34.30 mmol) and 1N NaOH (14 mL). The reaction mixture was stirred for 6 h at rt, then concentrated till 15 mL. The pH was adjusted to 2.4 by adding aqueous $NaHSO_4$, and the product was extracted with EtOAc (2 × 40 mL). The solvent was evaporated to give **16** (3.37 g, 71%) as an oil: ^{1}H NMR (DMSO-d_6): δ 6.98 (br s, 1H), 6.74 (br s, 1H), 3.83 (m, 1H), 2.86 (m, 2H), 1.35 (s, 18H), 1.7–1.1 (m, 6H). Diprotected derivative **16** (1.0 g, 2.9 mmol) was dissolved in THF (30 mL) and H_2O (6 mL), and the solution was neutralized till pH 7 with 20% aqueous Cs_2CO_3 and evaporated to dryness. The cesium salt was then stirred CH_3I (0.49 g, 3.5 mmol) in DMF (20 mL) for 2 h. Upon removal of the solvent by evaporation and treatment with H_2O (80 mL), the product was extracted with EtOAc (3 × 50 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford methyl ester **17** (0.68 g, 65%) as an oil: ^{1}H NMR ($CDCl_3$) δ 5.10 (br s, 1H), 4.59 (br s, 1H), 4.26 (m, 1H), 3.72 (s, 3H), 3.08 (m, 2H), 1.42 (s, 18H), 2.0–1.2 (m, 6H).

***N*,*N*-α,ε -Bis-BOC-*l*-lysine, *O*-benzyl ester 18.**[133]

Free acid **16** (1.00 g, 2.90 mmol) was dissolved in CH_3OH (30 mL) and H_2O (6 mL), and the solution was neutralized till pH 7 with 20% aqueous Cs_2CO_3 and evaporated to dryness. The resulting cesium salt was then stirred with benzyl bromide (0.60 g, 3.5 mmol) in DMF (20 mL) for 2 h. The solution was evaporated, and the product was

partitioned between H_2O (60 mL) and EtOAc (120 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford ester **18** (0.86 g, 68%): ^{1}H NMR ($CDCl_3$) δ 7.32 (m, 5H), 5.16, 5.10 (2×d, J = 11.9 Hz, 2H), 5.10 (br s, 1H), 4.57 (br s, 1H), 4.28 (dt, J = 7.8, 5.0 Hz, 1H), 3.04 (dt, J = 6.9, 6.4 Hz, 2H), 1.43 (s, 18H), 2.0–1.0 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 172.8, 156.2, 155.6, 135.5, 128.6, 128.5, 128.3, 79.8, 79.1, 67.2, 53.3, 40.1, 32.1, 29.6, 28.5, 28.4, 22.5.

_l_-Lysine, _O_-methyl ester, bis-TFA salt 19.

A solution of **17** (0.50 g, 1.40 mmol) in THF (20 mL) was treated with TFA (5 mL) and stirred at rt for 2 h. The reaction mixture was concentrated to afford pure **19** (0.51 g, 95%). ^{1}H NMR (DMSO-d_6): δ 4.03 (br s, 1H), 3.75 (s, 3H), 2.75 (m, 2H), 1.77 (m, 3H), 1.6–1.3 (m, 3H); ^{13}C NMR (DMSO-d_6): δ 170.6, 159.3 (q, $J_{C–F}$ = 31.7 Hz), 117.6 (q, $J_{C–F}$ = 298.5 Hz), 53.2, 52.3, 38.9, 30.0, 26.9, 21.8. Benzyl ester **20** was prepared analogously in 82% yield: ^{1}H NMR (DMSO-d_6): δ 7.37 (m, 5H), 5.20 (s, 2H), 4.06 (m, 1H), 2.70 (dt, J = 8.3, 6.4 Hz, 2H), 1.78 (m, 2H), 1.50 (m, 2H), 1.37 (m, 1H), 1.26 (m, 1H); ^{13}C NMR (DMSO-d_6): δ 169.9, 159.3 (q, $J_{C–F}$ = 32.2 Hz), 135.7, 129.0, 128.8, 128.8, 117.6 (q, $J_{C–F}$ = 298.0 Hz), 67.6, 52.2, 38.9, 30.1, 26.9, 21.7.

_N_-α-(_n_-Octanoyl)-_N_-ε-Cbz-(±)-lysine 22.

A solution of _N_-ε-Cbz-_l_-lysine **21** (0.50 g, 1.78 mmol) in water (20 mL) and EtOAc (20 mL) was treated with _n_-octanoyl chloride (2.46 g, 17.80 mmol) and stirred at rt for 3 h, after which 5% HCl (50 mL) and CH_2Cl_2 (80 mL) were added. After separation, the

aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL) times, and the combined organic layers were dried over anhydrous Na_2SO_4 and evaporated. The residue was solidified in hexane to yield **22** (0.51 g, 71%) as a colorless solid: mp 119–120 °C; $[\alpha]_D^{23} = 0.0$ (c = 0.02, EtOH); ^{1}H NMR (DMSO-d_6) δ 12.44 (s, 1H), 7.99 (d, J = 7.8 Hz, 1H), 7.34 (m, 5H), 7.20 (t, J = 5.3 Hz, 1H), 4.99 (s, 2H), 4.12 (m, 1H), 2.96 (m, 2H), 2.08 (m, 2H), 1.65 (m, 1H), 1.51 (m, 1H), 1.46 (m, 2H), 1.35 (m, 2H), 1.21 (m, 10H), 0.84 (t, J = 6.6 Hz, 3H); ^{13}C NMR (DMSO-d_6) δ 174.5, 172.9, 156.6, 137.8, 128.9, 128.3, 128.2, 65.7, 52.2, 35.6, 31.8, 31.2, 29.6, 29.1, 29.0, 25.8, 23.4, 22.6, 14.5.

Calix[4]arene tetraurea monoester 31.

n-Hexyl isocyanate (1.78 mL, 12.25 mmol) was added to a solution of the tetraaminocalix[4]arene **30**[134] (2.00 g, 2.45 mmol) in dry CH_2Cl_2 (80 mL), and the reaction mixture was stirred at RT for 4 h. The solvent was removed in vacuo, and the residue was triturated with hexane to yield the tetraurea ester as a tan powder (2.72 g, 2.25 mmol, 92 %). ^{1}H NMR (DMSO-d_6) : δ 8.06 (s, 1H), 8.05 (s, 1H), 7.81 (s, 2H), 6.87 (s, 2H), 6.84 (s, 2H), 6.53 (m, 4H), 5.88 (m, 2H), 5.69 (t, J = 5.0 Hz, 2H), 4.71 (s, 2H), 4.50 (d, J = 13.3 Hz, 2H), 4.29 (d, J = 12.37 Hz, 2H), 4.12 (q, J = 7.3 Hz, 2H), 3.75 (t, J = 7.8 Hz, 2H), 3.68 (t, J = 7.8 Hz, 2H), 3.62 (t, J = 7.8 Hz, 2H), 3.15-2.90 (m, 12H), 1.92 (m, 2H), 1.82 (m, 4H), 1.25 (m, 32H), 0.89 (m, 24H)

Calix[4]arene tetraurea acid 32.

A mixture of the tetraurea ester **31** (1.50 g, 1.20 mmol) and KOH (0.67 g, 12.0 mmol) in THF/H_2O, (5:1, 60 mL) was placed under reflux overnight, after which H_2O (60 mL) was added, and the pH was adjusted to 2 with aqueous HCl (1 M). The product was extracted with $CHCl_3$ (3 × 60 mL), the organic layer was dried over Na_2SO_4, evaporated, and recrystallized from MeOH to give tetraurea acid **32** as a yellow powder (1.13 g, 80 %): mp >300 °C; ^{1}H NMR (DMSO-d_6): δ 8.07 (s, 1H), 8.03 (s, 1H), 7.83 (s, 2H), 6.87 (s, 4H), 6.59 (s, 4H), 5.88 (m, 2H), 5.72 (t, J = 5.0 Hz, 2H), 4.56 (s, 2H), 4.43 (d, J = 12.6 Hz, 2H), 4.27 (d, J = 12.6 Hz, 2H), 3.76 (t, J = 7.8 Hz, 2H), 3.69 (t, J = 7.8 Hz, 2H), 3.67 (t, J = 7.8 Hz, 2H), 3.01 (m, 8H), 2.95 (m, 4H), 1.84 (m, 6H), 1.34 (m, 32H), 0.9 (m, 21H); ^{13}C NMR (DMSO-d_6): δ 171.5, 155.8, 151.1, 150.4, 150.2, 135.6, 135.3, 135.1, 134.8, 134.3, 134.1, 118.7, 77.5, 77.2, 71.2, 31.7, 30.4, 30.3, 26.7, 23.1, 23.0, 22.7, 14.4, 10.8, 10.5; FTIR (KBr): ν 3376, 3333, 2961, 2931, 2858, 1761, 1654, 1558, 1478, 1213 cm^{-1}; MALDI-FTMS: m/z: calcd for $C_{67}H_{101}N_8O_{10}$: 1177.7635; found: 1177.7632 $[M+H]^+$.

Dipeptide 34, two diastereomers.

To a stirred and ice cooled solution of amine **23** (0.10 g, 0.38 mmol) in DMF (15 mL) was added carboxylic acid **4** (0.14 g, 0.38 mmol), HOBT (0.10 mg, 0.76 mmol), and DCC (0.16 g, 0.76 mmol). The reaction mixture was stirred for 30 min at 0°C and for 36 h at rt. The mixture was filtered, concentrated, diluted with EtOAc (200 mL) and washed successively with 1N $NaHSO_4$ (4 × 50 mL), water (3 × 50 mL), 1N $NaHCO_3$ (4

× 50 mL), and again water (3 × 50 mL). The organic layer was then dried over anhydrous Na_2SO_4 and evaporated. The residue was chromatographed on silica gel eluting with THF–hexanes, 1:1 to afford dipeptide **33** (two diastereomers, 1:1, 0.15 g, 64%) as an oil: ^{1}H NMR (DMSO-d_6, one diastereomer): δ 8.23 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 6.73 (m, 2H), 4.29 (m, 1H), 4.18 (dt, J = 8.5, 5.5 Hz, 1H), 3.61 (s, 3H), 2.87 (m, 4H), 2.10 (m, 2H), 1.60 (m, 2H), 1.46 (m, 4H), 1.36 (s, 18H), 1.34 (m, 4H), 1.24 (m, 12H), 0.85 (t, J = 6.6 Hz, 3H); ^{1}H NMR (DMSO-d_6, the other diastereomer): δ 8.20 (d, J = 7.8 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 6.73 (m, 2H), 4.29 (m, 1H), 4.18 (dt, J = 8.5, 5.5 Hz, 1H), 3.60 (s, 3H), 2.87 (m, 4H), 2.10 (m, 2H), 1.60 (m, 2H), 1.46 (m, 4H), 1.36 (s, 18H), 1.34 (m, 4H), 1.24 (m, 12H), 0.85 (t, J = 6.6 Hz, 3H).

A solution of **33** (0.50 g, 0.81 mmol) in THF (20 mL) was treated with TFA (5 mL) and stirred at rt for 2 h. The reaction mixture was concentrated to afford pure **34** (two diastereomers, 1:1, 0.50 g, 96%). ^{1}H NMR (DMSO-d_6, one diastereomer): δ 8.30 (d, J = 7.6 Hz, 1H), 7.95 (d, J=7.8 Hz, 1H), 4.22 (m, 1H), 3.62 (s, 3H), 2.75 (m, 4H), 2.10 (m, 2H), 1.60 (m, 2H), 1.48 (m, 4H), 1.34 (m, 4H), 1.25 (m, 12H), 0.85 (t, J = 6.6 Hz, 3H); ^{1}H NMR (DMSO-d_6, the other diastereomer): δ 8.28 (d, J = 7.6 Hz, 1H), 7.93 (d, J=7.8 Hz, 1H), 4.22 (m, 1H), 3.61 (s, 3H), 2.75 (m, 4H), 2.10 (m, 2H), 1.60 (m, 2H), 1.48 (m, 4H), 1.34 (m, 4H), 1.25 (m, 12H), 0.85 (t, J = 6.6 Hz, 3H).

Dipeptide 36.

To a stirred and ice-cooled solution of *N*-ε-Cbz-L-lysine TFA salt **15** (1.00 g, 2.45 mmol) in DMF (30 mL), Et_3N (0.34 mL, 2.45 mmol) was added. Then, after 15 min, acid *N*-α-Boc-*N*-ε-Cbz-L-lysine **12** (0.93 g, 2.45 mmol), HOBt (0.66 g, 4.90 mmol), and DCC (1.01 g, 4.90 mmol) were successively added. The mixture was stirred for 30 min at 0 °C and for 24 h at RT, then filtered, concentrated under reduced pressure, diluted with EtOAc (200 mL), and washed successively with 1 N $NaHSO_4$ (4 × 50 mL), water (3 × 50 mL), 1 N $NaHCO_3$ (4 × 50 mL), and again with water (3 × 50 mL). The organic layer was then dried over anhydrous Na_2SO_4 and evaporated. The residue was separated chromatographically on silica gel eluting with THF/hexanes (2:3) to afford the desired Cbz-protected dipeptide **35** (1.14 g, 71 %). ^{1}H NMR (DMSO-d_6): δ 8.10 (d, J = 7.3 Hz, 1H), 7.34 (m, 10H), 7.22 (t, J = 5.5 Hz, 2H), 6.78 (d, J = 8.0 Hz, 1H), 4.99 (s, 4H), 4.20 (m, 1H), 3.90 (m, 1H), 3.59 (s, 3H), 2.96 (m, 4H), 1.67 (m, 1H), 1.58 (m, 2H), 1.48 (m, 1H), 1.32 (s, 9H), 1.28 (m, 8H); ^{13}C NMR ($CDCl_3$): δ 172.8, 172.7, 156.8, 156.0, 136.7, 136.6, 128.6, 128.57, 128.3, 128.2, 128.2, 80.1, 66.8, 66.7, 54.1, 52.4, 52.1, 40.5, 32.2, 31.6, 29.4, 29.2, 28.4, 22.6, 22.3; FTIR (KBr): ν 3359, 3036, 2948, 1699, 1544, 1259 cm^{-1}.

A solution of the Cbz-protected dipeptide **35** (0.20 g, 0.30 mmol) in CH_3OH (10 mL) was treated with 10 % Pd/C (20 mg) and stirred under an H_2 atmosphere for 6 h. The mixture was filtered through Celite and concentrated under reduced pressure to give product **36** as an oil (0.11 g, 94 %). ^{1}H NMR (DMSO-d_6): δ 8.28 (d, J = 7.3 Hz, 1H),

6.86 (d, J = 8.5 Hz, 1H), 4.22 (m, 1H), 3.93 (m, 1H), 3.62 (s, 3H), 2.72 (t, J = 7.1 Hz, 4H), 1.36 (s, 9H), 2.0-1.0 (m, 12H); MALDI-TOF MS: m/z: calcd for $C_{18}H_{36}N_4O_5$: 388.5; found: 388.8 $[M]^+$.

Dendrimer 37a.

Procedure 1. To a stirred and ice cooled solution of salt **19** (0.08 g, 0.21 mmol) DMF (8 mL) was added Et_3N (0.06 mL, 0.42 mmol) and then after 15 min, calix amino acid **1e** (0.51 g, 0.42 mmol), HOBT (0.11 g, 0.84 mmol), and DCC (0.17 g, 0.84 mmol). The mixture was allowed to stir for 30 min at 0 °C and for 48 h at rt, then filtered, concentrated in vacuo, diluted with EtOAc (200 mL), and washed successively with 1N $NaHSO_4$ (4 × 50 mL), water (3 × 50 mL), 1N $NaHCO_3$ (4 × 50 mL), and again water (3 × 50 mL). The organic layer was then dried over anhydrous Na_2SO_4 and evaporated. The residue was chromatographed on silica gel eluting with $CHCl_3$–CH_3OH, 9:1 to afford **37a** (two diastereomers, 3:2, 0.22 g, 41%). ^{1}H NMR (DMSO-d_6, major diastereomer): δ 8.23 (br s, 1H), 8.10 (br s, 2H), 7.87 (m, 3H), 6.81 (m, 16H), 4.80 (m, 4H), 4.60 (m, 16H), 4.34 (s, 4H), 4.30 (m, 1H), 4.10 (m, 13H), 3.95 (m, 1H), 3.58 (s, 3H), 3.25–3.05 (m, 12H), 3.02 (m, 2H), 2.08 (m, 4H), 2.0–1.1 (m, 66H), 1.0 (m, 72H), 0.83 (t, J = 7.2 Hz, 3H); ^{1}H NMR (DMSO-d_6, minor diastereomer): δ 8.23 (br s, 1H), 8.10 (br s, 2H), 7.87 (m, 3H), 6.81 (m, 16H), 4.80 (m, 4H), 4.60 (m, 16H), 4.34 (s, 4H), 4.30 (m, 1H), 4.1 (m, 13H), 3.95 (m, 1H), 3.59 (s, 3H), 3.10 (m, 12H), 3.02 (m, 2H), 2.08 (m, 4H), 2.0–1.1 (m, 66H), 1.0 (m, 72H), 0.83 (t, J = 7.2 Hz, 3H); MALDI-TOF MS, m/z 2588.7 ([M+Na^+], calcd for $C_{151}H_{216}N_6O_{28}Na$ 2586.3).

Procedure 2. A solution of acid chloride **26** (0.30 g, 0.30 mmol) in EtOAc (20 mL) was added to a vigorously stirring solution of tripeptide **39** (0.10 g, 0.15 mmol) and K_2CO_3 (0.41 g, 3.00 mmol) in EtOAc (10 mL) and H_2O (20 mL). The reaction mixture was stirred for 6 h at rt, the organic layer was separated and evaporated. The residue was chromatographed on silica gel eluting with $CHCl_3$–CH_3OH, 9:1 to afford **37a** (0.18 g, 47%).

Dendrimer 37b.

A solution of monoacid chloride **26** (0.38 g, 0.38 mmol) in EtOAc (10 mL) was added to a vigorously stirred solution of **41** (0.10 g, 0.16 mmol) and K_2CO_3 (0.22 g, 1.60 mmol) in EtOAc (5 mL) and H_2O (15 mL). The reaction mixture was stirred for 6 h at rt. The organic layer was separated and evaporated under reduced pressure. The residue was chromatographed on silica gel with $CHCl_3$–MeOH, 9:1 as eluents to afford **37b** (0.17 g, 42%); $[\alpha]_D^{23} = -4.5$ (c = 0.02, EtOH); ^{1}H NMR (DMSO-d_6): δ 8.11 (m, 3H), 7.78 (t, J = 6.0 Hz, 1H), 6.8 (m, 16H), 6.72 (m, 2H), 4.85–4.72 (m, 4H), 4.72–4.45 (m, 16H), 4.35 (m, 4H), 4.22 (m, 1H), 4.10 (m, 12H), 3.93 (m, 1H), 3.83 (m, 1H), 3.65 (s, 3H), 3.2 (m, 12H), 3.0 (m, 2H), 1.8–1.4 (m, 18H), 1.36 (s, 18H), 1.7–1.25 (m, 18H), 1.06 (s, 18H), 1.03 (s, 27H), 1.02 (s, 27H); FTIR (KBr): ν 3370, 2962, 2867, 1758, 1724, 1663, 1547, 1480, 1190, 1128, 1069 cm^{-1}; MALDI-TOF MS, m/z 2532 ([M+Na$^+$], calcd for $C_{145}H_{204}N_6O_{30}$ 2532).

Tripeptide 39, a mixture of diastereomers.

To a stirred and ice-cooled solution of **19** (0.19 g, 0.50 mmol) in DMF (15 mL) was added Et_3N (0.14 mL, 1.00 mmol) and then acid **22** (0.42 g, 1.00 mmol), HOBT (0.28 g, 2.00 mmol), and DCC (0.43 g, 2.00 mmol). The reaction mixture was allowed to stir for 30 min at 0 °C and for 36 h at rt, filtered, concentrated, diluted with EtOAc (200 mL), and washed successively with 1N $NaHSO_4$ (4 × 50 mL), water (3 × 50 mL), 1N $NaHCO_3$ (4 × 50 mL), and again water (3 × 50 mL). The organic layer was then dried over anhydrous Na_2SO_4 and evaporated. The residue was chromatographed on silica gel eluting with $CHCl_3$–CH_3OH, 9:1 to afford bis-Cbz-protected trilysine **38** (two diastereomers, 3:2, 0.21 g, 45%) as an oil: ^{1}H NMR (DMSO-d_6, major diastereomer): δ 8.20 (br s, 1H), 7.84 (m, 3H), 7.33 (m, 10H), 7.20 (t, J = 5.5 Hz, 2H), 4.98 (s, 4H), 4.25 (m, 1H), 4.15 (m, 2H), 3.58 (s, 3H), 2.94 (m, 6H), 2.10 (m, 4H), 1.8–1.1 (m, 38H), 0.84 (t, J = 6.4 Hz, 3H); ^{1}H NMR (DMSO-d_6, minor diastereomer): δ 8.23 (br s, 1H), 7.86 (m, 3H), 7.33 (m, 10H), 7.20 (t, J = 5.5 Hz, 2H), 4.98 (s, 4H), 4.25 (m, 1H), 4.15 (m, 2H), 3.60 (s, 3H), 2.94 (m, 6H), 2.10 (m, 4H), 1.8–1.1 (m, 38H), 0.84 (t, J = 6.4 Hz, 3H).

A solution of tripeptide **38** (0.15 g, 0.16 mmol) in CH_3OH (10 mL) was treated with 10% Pd/C (15 mg) and stirred under a hydrogen atmosphere for 6 h. The mixture was filtered through Celite and concentrated. The residue was dried under high vacuum to give **39** (two diastereomers, 3:2, 0.10 g, 93%) as an oil: ^{1}H NMR (DMSO-d_6, major diastereomer) δ 8.20 (br s, 1H), 7.84 (m, 3H), 4.25 (m, 1H), 4.14 (m, 2H), 3.56 (s, 3H),

3.42 (m, 4H), 3.02 (m, 2H), 2.06 (m, 4H), 1.8–1.0 (m, 38H), 0.81 (t, J = 6.9 Hz, 6H). ^{1}H NMR (DMSO-d_6, minor diastereomer) δ 8.27 (br s, 1H), 7.84 (m, 3H), 4.25 (m, 1H), 4.14 (m, 2H), 3.56 (s, 3H), 3.42 (m, 4H), 3.02 (m, 2H), 2.06 (m, 4H), 1.8–1.0 (m, 38H), 0.81 (t, J = 6.9 Hz, 6H).

Tripeptide 41.

To a stirred and ice cooled solution of **19** (0.17 g, 0.43 mmol) in DMF (20 mL) was added Et_3N (0.12 mL, 0.86 mmol) and then after 15 min, lysine **12** (0.33 g, 0.86 mmol), HOBT (0.24 g, 1.72 mmol) and DCC (0.35 g, 1.72 mmol). The mixture was allowed to stir for 30 min at 0 °C and for 36 h at rt, then filtered, concentrated in vacuo, diluted with EtOAc (200 mL), and washed successively with 1N $NaHSO_4$ (4 × 50 mL), water (3 × 50 mL), 1N $NaHCO_3$ (4 × 50 mL), and again water (3 × 50 mL).The organic layer was then dried over anhydrous Na_2SO_4 and evaporated. The residue was chromatographed on silica gel eluting with $CHCl_3$–CH_3OH, 9:1 to afford **40** (0.19 g, 50%): $[\alpha]_D^{23} = -12.4$ (c = 0.02, EtOH); ^{1}H NMR (DMSO-d_6): δ 8.13 (br s, 1H), 7.75 (br s, 1H), 7.34 (m, 10H), 7.21 (t, J = 6.0 Hz, 2H), 6.78 (d, J = 6.4 Hz, 1H), 6.73 (d, J = 7.8 Hz, 1H), 5.01 (s, 4H), 4.20 (m, 1H), 3.91 (m, 1H), 3.79 (m, 1H), 3.59 (s, 3H), 3.15 (m, 4H), 3.04 (m, 2H), 2.0–1.0 (m, 18H), 1.36 (s, 18H); MALDI-TOF MS, m/z 908 ([M+Na^+], calcd for $C_{45}H_{68}N_6O_{12}$ 908).

A solution of **40** (0.15 g, 0.17 mmol) in CH_3OH (10 mL) was treated with 10% Pd/C (15 mg) and stirred under a hydrogen atmosphere for 4 h. The mixture was filtered through Celite and concentrated. The residue was dried under high vacuum to give

tripeptide **41** (0.10 g, 95%): ^{1}H NMR (DMSO-d_6): δ 8.16 (br s, 1H), 7.80 (br s, 1H), 6.81 (d, J = 8.3 Hz, 1H), 6.75 (d, J = 7.1 Hz , 1H), 4.21 (m, 1H), 3.91 (m, 1H), 3.80 (m, 1H), 3.60 (s, 1H), 3.06 (m, 4H), 2.96 (m, 2H), 1.35 (s, 18H), 2.0–1.0 (m, 18H).

Calixarene 57.

N-Boc-1,6-diaminohexane (0.38 mL, 1.68 mmol), DCC (0.35 g, 1.68 mmol), HOBt (0.23 g, 1.68 mmol), and Et_3N (0.23 mL, 1.68 mmol) were added to a stirred and ice-cooled solution of **3** (1.00 g, 0.84 mmol) in DMF (30 mL). The mixture was stirred for 30 min at 0 °C and for 24 h at RT, then filtered, concentrated in vacuo, diluted with $CHCl_3$, and washed successively with 1 N $NaHSO_4$ (4 × 100 mL), water (3 × 100 mL), 1 N $NaHCO_3$ (4 × 100 mL), and again with water (3 × 100 mL). The organic layer was then dried over anhydrous Na_2SO_4 and evaporated. The residue was separated chromatographically on silica gel eluting with $CHCl_3$/CH_3OH (95:5) to afford **59** as a colorless solid (0.84 g, 72 %). mp >185 °C (decomp); ^{1}H NMR (DMSO-d_6): δ 8.17 (t, J = 5.7 Hz, 1H), 8.02 (br s, 1H), 7.98 (br s, 1H), 7.83 (br s, 2H), 6.81 (s, 2H), 6.79 (s, 2H), 6.76 (t, J = 5.5 Hz, 1H), 6.62 (br s, 4H), 5.82 (m, 2H), 5.77 (t, J = 5.3 Hz, 2H), 4.35 (s, 2H), 4.33 (d, J = 12.6 Hz, 2H), 4.27 (d, J = 12.6 Hz, 2H), 3.76 (t, J = 7.3 Hz, 4H), 3.72 (t, J = 7.3 Hz, 2H), 3.24 (m, 2H), 3.00 (m, 12H), 2.91 (m, 2H), 1.80 (m, 6H), 1.53 (m, 2H), 1.36 (s, 9H), 1.24 (m, 38H), 0.87 (m, 21H); ^{13}C NMR (DMSO-d_6): δ 169.2, 156.1, 155.74, 155.7, 151.2, 150.7, 150.3, 135.4, 135.1, 135.0, 134.5, 134.2, 134.1, 118.7, 118.4, 77.8, 77.3, 76.5, 74.8, 31.6, 30.4, 28.83, 28.8, 26.7, 23.0, 22.9, 22.7, 14.5, 10.63, 10.6; FTIR (KBr): ν 3329, 2928, 2852, 1628, 1559, 1476, 1213 cm^{-1}.

A solution of the N-Boc-protected **59** (0.50 g, 0.36 mmol) in THF (15 mL) was treated with TFA (5 mL) and stirred at RT for 2 h. The reaction mixture was concentrated in vacuo to afford the pure TFA salt of **57** (0.47 g, 93 %). ^{1}H NMR (DMSO-d_6): δ 8.18 (t, J = 5.5 Hz, 1H), 8.05 (s, 1H), 7.99 (s, 1H), 7.84 (s, 2H), 6.80 (s, 2H), 6.63 (s, 2H), 6.60 (s, 2H), 5.88 (m, 2H), 5.78 (t, J = 5.5 Hz, 2H), 4.37 (s, 2H), 4.32 (d, J = 12.8 Hz, 2H), 4.26 (d, J = 12.8 Hz, 2H), 3.75 (t, J = 7.2 Hz, 4H), 3.71 (t, J = 7.2 Hz, 2H), 3.26 (m, 2H), 3.0 (m, 12H), 2.78 (m, 2H), 1.80 (m, 6H), 1.53 (m, 4H), 1.41 (m, 12H), 1.25 (m, 24H), 0.86 (m, 21H); ^{13}C NMR (DMSO-d_6): δ 169.4, 155.8, 151.3, 150.7, 150.4, 135.3, 135.1, 135.0, 135.0, 134.5, 134.2, 134.0, 118.8, 118.54, 118.5, 77.3, 76.6, 74.8, 31.6, 30.4, 27.6, 26.6, 26.2, 22.9, 22.7, 14.5, 10.7, 10.6; FTIR (KBr): ν 3339, 2932, 2859, 1659, 1599, 1562, 1468, 1213 cm^{-1}; ESI-MS: m/z: calcd for $C_{75}H_{115}F_3N_{10}O_{11}$: 1389; found: 1389.

The TFA salt (0.50 g, 0.36 mmol) in $CHCl_3$ (100 mL) was washed with aqueous 10 % NaOH (2 × 50 mL), then evaporated and dried in high vacuo to afford amine **57**. ^{1}H NMR (DMSO-d_6): δ 8.18 (t, J = 5 Hz, 1H), 8.05 (br s, 1H), 8.00 (br s, 1H), 7.85 (br s, 2H), 6.80 (2 × m, 4H), 6.61 (s, 4H), 5.88 (m, 2H), 5.80 (t, J = 5.5 Hz, 2H), 4.36 (s, 2H), 4.32 (d, J = 12.8 Hz, 2H), 4.26 (d, J = 12.8 Hz, 2H), 3.76 (t, J = 7.8 Hz, 4H), 3.69 (t, J = 7.8 Hz, 2H), 3.22 (m, 2H), 2.99 (m, 12H), 2.53 (t, J = 6.0 Hz, 2H), 1.80 (m, 6H), 1.53 (m, 2H), 1.30 (m, 38H), 0.90 (m, 21H); ^{13}C NMR (DMSO-d_6): δ 169.3, 155.8, 155.7, 151.2, 150.7, 150.4, 135.4, 135.1, 135.0, 134.5, 134.2, 134.1, 118.8, 118.7, 118.5, 118.47, 77.3, 76.5, 74.8, 31.6, 30.4, 26.7, 22.9, 22.7, 14.5, 10.6; FTIR (KBr): ν 3344,

2930, 2858, 1654, 1559, 1475, 1213 cm^{-1}; ESI MS: *m/z*: calcd for $C_{73}H_{114}N_{10}O_9$: 1275; found: 1276 $[M+H]^+$, 2552 $[2M+2\ H]^+$.

Biscalixarene 58.

A solution of **61** (0.20 g, 0.07 mmol) in THF (20 mL) was treated with TFA (20 mL) and then stirred at RT for 4 h. The reaction mixture was concentrated in vacuo to afford the pure TFA-salt of **58**. The salt was then dissolved in $CHCl_3$ (60 mL) and washed with 10 % NaOH (2 × 30 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to give free amine **58** (0.18 g, 96 %). ^1H NMR (DMSO-d_6): δ 8.22 (br s, 4H), 8.17 (br s, 2H), 8.01 (br s, 1H), 7.94 (br s, 5H), 6.82 (s, 2H), 6.81 (s, 4H), 6.80 (s, 2H), 6.56 (s, 4H), 6.55 (s, 4H), 6.07 (br s, 4H), 5.97 (br s, 4H), 4.35 (s, 4H), 4.33-4.19 (m, 8H), 4.14 (m, 1H), 3.80-3.60 (m, 12H), 3.22 (m, 4H), 3.10-2.90 (m, 26H), 1.75 (m, 14H), 1.53 (m, 6H), 1.36 (m, 28H), 1.24 (m, 48H), 0.85 (m, 42H); ^{13}C NMR (DMSO-d_6): δ 175.4, 171.7, 169.4, 155.9, 155.8, 151.3, 150.7, 150.3, 135.4, 135.2, 135.0, 134.4, 134.2, 133.9, 133.89, 118.9, 118.8, 118.6, 77.3, 76.5, 74.8, 55.3, 52.6, 31.6, 30.4, 29.6, 28.7, 26.9, 26.7, 23.3, 23.1, 22.7, 22.6, 14.5, 10.6; FTIR (KBr): ν 3340, 2928, 2863, 1657, 1557, 1470, 1213 cm^{-1}; MALDI-TOF: *m*/*z*: calcd for $C_{152}H_{236}N_{20}O_{2O}Na$: 2712.8; found: 2712.0 $[M+Na]^+$; ESI-MS: *m*/*z*: calcd for $C_{152}H_{237}N_{20}O_{20}$: 2691; found: 2692 $[M+H]^+$.

Biscalixarene 61.

A mixture of **2c** (2.00 g, 0.74 mmol), THF (25 mL), and aqueous LiOH (1 N, 10 mL) was stirred overnight at RT, after which H_2O (30 mL) was added, and the pH was adjusted to 6 with aqueous 1 M HCl. The product was extracted with $CHCl_3$ (3 × 60 mL). The organic layer was dried over Na_2SO_4 and evaporated to give the tetraurea acid **60** (1.81 g, 91 %). mp >300 °C; ^{1}H NMR (DMSO-d_6): δ 8.22 (br s, 2H), 8.09 (br s, 2H), 7.99 (br s, 2H), 7.93 (d, J = 7.8 Hz, 1H), 7.83 (br s, 4H), 6.83 (s, 2H), 6.82 (s, 4H), 6.81 (s, 2H), 6.62 (s, 4H), 6.61 (s, 4H), 5.85 (m, 4H), 5.78 (m, 4H), 4.35 (br s, 4H), 4.33 (d, J = 13.3 Hz, 4H), 4.22 (d, J = 13.3 Hz, 4H), 4.19 (m, 1H), 3.94 (m, 1H), 3.75 (t, J = 6.9 Hz, 8H), 3.69 (t, J = 6.9 Hz, 4H), 3.22 (m, 4H), 3.10-2.90 (m, 24H), 1.34 (s, 9H), 1.77 (m, 12H), 1.53 (m, 4H), 1.36 (s, 9H), 1.18 (m, 72H), 0.86 (m, 42H); ^{13}C NMR (DMSO-d_6): δ 174.1, 172.7, 169.3, 155.8, 151.3, 151.2, 150.7, 150.3, 135.4, 135.2, 134.9, 134.4, 134.2, 134.0, 118.8, 118.5, 78.5, 77.3, 76.5, 74.8, 67.6, 54.7, 52.2, 31.7, 31.5, 31.2, 30.4, 30.1, 30.0, 28.7, 26.7, 25.7, 23.7, 23.4, 23.0, 22.9, 22.6, 14.4, 10.6; FTIR (KBr): ν 3349, 2930, 1664, 1560, 1472, 1367, 1216 cm^{-1}.

N-Boc-1,6-diaminohexane (0.17 mL, 0.74 mmol), EDCI (0.14 g, 0.74 mmol), HOBt (0.10 g, 0.74 mmol), and Et_3N (0.10 mL, 0.74 mmol) were added to a stirred and ice-cooled solution of the above-mentioned acid **60** (1.00 g, 0.37 mmol) in DMF (20 mL). The mixture was stirred for 30 min at 0 °C and for 24 h at RT, filtered, concentrated, diluted with $CHCl_3$, and washed successively with 1 N $NaHSO_4$ (3 × 80 mL), water (2 × 80 mL), 1 N $NaHCO_3$ (3 × 80 mL), and again with water (3 × 80 mL). The organic

layer was then dried over anhydrous Na_2SO_4 and evaporated. The residue was separated chromatographically on silica gel eluting with $CHCl_3/CH_3OH$ (94:6) to afford **61** (0.81 g, 76 %). mp >185 °C (decomp); ^{1}H NMR (DMSO-d_6): δ 8.20 (br s, 2H), 8.04 (br s, 2H), 8.00 (br s, 2H), 7.87 (br s, 1H), 7.82 (s, 4H), 7.73 (d, J = 7.8 Hz, 1H), 6.98 (d, J = 7.3 Hz, 1H), 6.82 (s, 2H), 6.81 (s, 4H), 6.80 (s, 2H), 6.73 (t, J = 7.1 Hz, 1H), 6.61 (s, 4H), 6.60 (s, 4H), 5.87 (m, 4H), 5.78 (m, 4H), 4.35 (s, 4H), 4.32 (d, J = 12.8 Hz, 4H), 4.26 (d, J = 12.8 Hz, 4H), 3.87 (m, 1H), 3.74 (t, J = 6.9 Hz, 8H), 3.70 (t, J = 6.9 Hz, 4H), 3.21 (m, 4H), 3.00 (m, 24H), 2.86 (m, 4H), 1.78 (m, 12H), 1.77 (m, 2H), 1.53 (m, 6H), 1.36 (s, 9H), 1.34 (s, 9H), 1.26 (m, 76H), 0.86 (m, 42H); ^{13}C NMR (DMSO-d_6): δ 172.4, 171.6, 169.3, 169.29, 156.1, 156.0, 155.8, 151.3, 151.2, 150.7, 150.3, 135.4, 135.2, 135.0, 134.4, 134.2, 134.0, 118.7, 118.5, 118.45, 78.6, 77.7, 77.3, 76.5, 74.8, 55.2, 52.9, 39.2, 39.0, 31.6, 31.5, 30.4, 30.0, 29.5, 28.8, 28.7, 26.7, 26.5, 23.8, 23.3, 23.0, 22.9, 22.7, 14.4, 10.6, 10.57; FTIR (KBr): ν 3325, 2929, 2864, 1659, 1556, 1471, 1214 cm^{-1}.

Supramolecular oligomer 63 and salt 64.

Calixarene **57** (0.50 g, 0.39 mmol) in benzene (6 mL) was placed in a test tube (13 × 100 mm) and dry CO_2 was then bubbled through the solution for 5 min at 35 °C. Oligomer **63** quantitively precipitated, was filtered off, and dried under vacuum at RT. The experiment was performed at least five times giving reproducible results. Upon dissolution in DMSO, material **63** dissociated to give carbamate salt **64**. mp >140 °C (decomp); ^{1}H NMR (DMSO-d_6): δ 8.18 (2 × br s, 4H), 8.11 (br s, 2H), 7.96 (br s, 4H),

6.89 (2 × m, 8H), 6.66 (s, 8H), 6.00 (br s, 2H), 5.95 (br s, 2H), 5.91 (br s, 4H), 5.80 (br s, 1H), 4.42 (s, 4H), 4.37 (d, J = 12.4 Hz, 4H), 4.29 (d, J = 12.4 Hz, 4H), 3.77 (m, 12H), 3.26 (m, 4H), 3.04 (m, 26H), 2.58 (t, J = 6.4 Hz, 2H), 1.80 (m, 12H), 1.54 (m, 4H), 1.34 (m, 76H), 0.86 (m, 42H); ^{13}C NMR (DMSO-d_6): δ 169.3, 159.8, 155.8, 151.3, 150.8, 150.3, 135.5, 135.2, 135.1, 134.5, 134.2, 134.0, 134.0, 118.8, 118.6, 77.3, 76.5, 74.8, 31.7, 31.5, 30.4, 27.1, 26.7, 23.0, 22.9, 22.7, 14.4, 10.6, 10.59.

Supramolecular polymer 67 and carbamate salts 66.

Diamine **58** (0.20 g, 0.07 mmol) in $CHCl_3$ (5 mL) was placed in a test tube (13 × 100 mm) and dry CO_2 ($^{13}CO_2$) was then bubbled through the solution for 3 min at RT. Material **67** formed as a gel, which was then dried under high vacuum at RT. The experiment was performed at least five times giving reproducible results. Upon dissolution in DMSO, material **67** dissociated to form carbamate salts of type **66**. ^{1}H NMR (DMSO-d_6): δ 8.27 (br s), 8.22 (br s), 8.12-7.90 (br s), 6.90-6.70 (br s), 6.70-6.50 (br s), 6.14 (br s), 6.02 (br s), 4.36 (br s), 4.25 (m), 3.90-3.60 (m), 3.50-3.30 (m), 3.22 (m), 3.15-2.85 (m), 1.85-1.70 (m), 1.59-1.53 (m), 1.33 (m), 1.23 (m), 0.95-0.85 (m); ^{13}C NMR (DMSO-d_6): δ 175.5, 171.8, 169.4, 163.3, 162.9, 155.9, 151.4, 150.8, 150.3, 135.4, 135.2, 134.9, 134.4, 134.1, 133.8, 118.9, 118.6, 77.4, 76.3, 74.5, 31.6, 30.4, 26.7, 23.4, 23.1, 22.9, 22.7, 14.5, 10.6.

Biscalixarene Dipeptide 68.

A solution of the BOC-protected dipeptide **2c** (0.50 g, 0.18 mmol) in THF (15 mL) was treated with TFA (10 mL) and then stirred at rt for 4 h. The reaction mixture was concentrated in vacuo to afford pure TFA-salt of **68**: ^{1}H NMR (DMSO-d_6) δ 8.78 (d, J = 7.3 Hz, 1 H), 8.24 (br s, 2H), 8.06 (s, 2H), 8.01 (s, 2H), 7.84 (s, 4H), 6.80 (s, 4H), 6.79 (s, 4H), 6.62 (s, 4H), 6.59 (s, 4H), 5.9 (m, 4H), 5.8 (m, 4H), 4.40 (s, 4H), 4.33 (d, J = 12.3 Hz, 4H), 4.24 (d, J = 12.3 Hz, 4H), 4.2 (m, 1H), 3.8 (m, 1H), 3.75 (t, J = 7.0 Hz, 8 H), 3.69 (t, J = 7.0 Hz, 4H), 3.62 (s, 3H), 3.2 (m, 4H), 3.0 (m, 24H), 1.78 (m, 12H), 1.54 (m, 4H), 1.28(m, 72H), 0.9 (m, 42H); FTIR (KBr): ν 3347, 3082, 2932, 2860, 1670, 1599, 1474, 1205; ESI-MS m/z 2719 (M^+, calcd for $C_{149}H_{224}N_{20}O_{23}F_3$ 2719). The TFA-salt of **68** was then dissolved in $CHCl_3$ (60 mL) and washed with 10% NaOH (2 × 30 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to give free amine **68** as a colorless solid (0.44 g, 92%): ^{1}H NMR (DMSO-d_6) δ 8.19 (br s, 3 H), 8.04 (s, 2H), 7.99 (s, 2H), 7.83 (s, 4H), 6.82 (s, 4H), 6.81 (s, 4H), 6.62 (s, 8H), 5.86 (m, 4H), 5.78 (t, J = 5.0 Hz, 4H), 4.38 (s, 4H), 4.34 (d, J = 12.3 Hz, 4H), 4.25 (d, J = 12.3 Hz, 4H), 3.76 (t, J = 7.0 Hz, 8H), 3.71 (t, J = 7.0 Hz, 4H), 3.62 (s, 3H), 3.22 (m, 4 H), 3.0 (m, 24H), 1.78 (m, 12H), 1.54 (m, 4H), 1.28(m, 72H), 0.9 (m, 42H); ^{13}C NMR (DMSO-d_6) δ 175.9, 173.1, 169.3, 155.7, 151.2, 150.7, 150.3, 135.3, 135.1, 134.9, 134.4, 134.1, 133.9, 118.7, 118.5, 79.6, 77.2, 76.5, 74.7, 54.9, 52.2, 52.0, 35.5, 31.6, 31.4, 30.3, 29.8, 26.6, 23.4, 22.8, 22.6, 14.4, 10.5; ESI-MS m/z 2608 ($[M + H]^+$, calcd for $C_{147}H_{224}N_{20}O_{21}$ 2607).

Biscalixarene 70.

To a stirred and ice-cooled solution of the TFA-salt of **68** (0.50 g, 0.18 mmol) in DMF (15 mL) was added Et_3N (0.05 mL, 0.36 mmol), and then after 15 min, successively 1-pyrenebutyric acid (0.10 g, 0.36 mmol), EDCI (0.14 g, 0.72 mmol), and DMAP (cat.). The mixture was allowed to stir for 30 min at 0 °C and for 24 h at room temperature and then filtered, concentrated under reduced pressure, diluted with $CHCl_3$ (100 mL), and washed with water (3 × 100 mL). The organic layer was then dried over anhydrous Na_2SO_4 and evaporated. The residue was chromatographed on silica gel eluting with $CHCl_3$-CH_3OH, 95:5 to afford pyrene functionalized calixarene **70** (0.41 g, 79%): mp > 180 °C (decomp); ^{1}H NMR (DMSO-d_6) δ 8.4-7.9 (m, 17H), 7.8 (m, 4H), 6.8 (m, 8H), 6.6 (m, 8H), 5.9 (m, 4H), 5.8 (m, 4H). 4.4 (m, 2H), 4.36 (s, 4H), 4.32 (d, J = 12.8 Hz, 4 H), 4.20 (d, J = 12.8 Hz, 4H), 3.70 (m, 12H), 3.59 (s, 3H), 3.30 (t, J = 7.3 Hz, 2H), 3.21 (m, 4H), 3.0 (m, 24H), 2.31 (t, J = 6.9 Hz, 2H), 2.0 (m, 2H), 1.74 (m, 12H), 1.55 (m, 4H), 1.35 (m, 20H), 1.24 (m, 52H), 0.9 (m, 42H); FTIR (KBr): ν 3337, 2957, 2930, 2858, 1654, 1601, 1558, 1473, 1213 cm^{-1}.

Biscalixarene 72.

To a stirred and ice-cooled solution of dipeptide **70** (0.30 g, 0.10 mmol) in THF/H_2O, 15:1 (10 mL) was added a 40% aqueous solution of n-Bu_4NOH (0.20 mL, 0.30 mmol). The mixture was allowed to stir for 1.5 h at 0 °C, after which H_2O (20 mL) was added, and the pH was adjusted to 2 with aq 1 M HCl. The product was extracted with $CHCl_3$ (2 × 30 mL), and the organic layer was dried over anhydrous Na_2SO_4 and then

evaporated. The resulting free acid **71** (0.27 g, 94%) was used without further purification: ^{1}H NMR (DMSO-d_6) δ 8.40-7.88 (m, 17H), 7.83 (br s, 4H), 6.82 (m, 8H), 6.61 (br s, 8H), 5.9 (m, 4H), 5.8 (m, 4H), 4.4 (m, 2H), 4.34 (s, 4H), 4.31 (d, *J* = 12.8 Hz, 4H), 4.20 (d, *J* = 12.8 Hz, 4H), 3.7 (m, 12H), 3.30 (t, *J* = 7.3 Hz, 2H), 3.2 (m, 4H), 3.1-2.9 (m, 24H), 2.97 (t, *J* = 6.9 Hz, 2H), 2.0 (m, 2H), 1.73 (m, 12H), 1.54 (m, 4H), 1.35 (m, 20H), 1.23 (m, 52H), 0.9 (m, 42H); FTIR ν 3337, 2958, 2930, 2858, 1654, 1601, 1558, 1473, 1415, 1214 cm^{-1}. To a stirred and ice-cooled solution of the obtained acid **71** (0.30 g, 0.10 mmol) in DMF (15 mL) were added *N*-BOC-1,6-diaminohexane (0.05 mL, 0.20 mmol), EDCI (0.08 g, 0.40 mmol), DMAP (catalyst), and Et_3N (0.03 mL, 0.20 mmol). The mixture was allowed to stir for 30 min at 0 °C and for 24 h at rt, filtered, concentrated, diluted with $CHCl_3$, and washed with water (3 × 100 mL). The organic layer was then dried over anhydrous Na_2SO_4 and evaporated. The residue was chromatographed on silica gel eluting with $CHCl_3$-CH_3OH, 96:4 to afford biscalixarene **72** (0.20 g, 65%): mp 160 °C (decomp); ^{1}H NMR (DMSO-d_6) δ 8.40-7.75 (m, 22H), 6.82 (m, 8H), 6.71 (t, *J* = 6.0 Hz, 1H), 6.6 (m, 8H), 5.9 (m, 4H), 5.8 (m, 4H), 4.35 (br s, 4H), 4.28 (d, *J* = 12.8 Hz, 4H), 4.20 (d, *J* = 12.8 Hz, 4H), 3.7 (m, 12H), 3.30 (t, *J* = 7.3 Hz, 2H), 3.2 (m, 4H), 3.1-2.9 (m, 26H), 2.85 (dt, *J* = 6.9 Hz, *J* = 6.4 Hz, 2H), 2.31 (t, *J* = 7.3 Hz, 2H), 2.0 (m, 2H), 1.72 (m, 12H), 1.55 (m, 4H), 1.35 (m, 80H), 1.33 (s, 9H), 0.90 (m, 42H); FTIR (KBr): ν 3335, 2930, 2859, 1653, 1558, 1473, 1245, 1214 cm^{-1}; MALDI-TOF *m*/*z* 3083 ([M + Na]$^+$, calcd for $C_{177}H_{258}N_{22}O_{23}Na$ 3083). Anal. Calcd for $C_{177}H_{258}N_{22}O_{23}$: C, 69.43; H, 8.49; N, 10.06. Found: C, 69.08; H, 8.45; N, 9.85.

Biscalixarene 73.

A solution of the BOC-protected calixarene **72** (0.20 g, 0.07 mmol) in CH_2Cl_2 (10 mL) was treated with TFA (10 mL) and then stirred at rt for 4 h. The reaction mixture was concentrated in vacuo to afford the pure TFA-salt. This was then dissolved in $CHCl_3$ (60 mL) and washed with 10% NaOH (2 × 30 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to give free amine **73** (0.19 g, 92%): ^{1}H NMR (DMSO-d_6) δ 8.3-7.7 (m, 22H), 6.8 (m, 8H), 6.6 (m, 8H), 5.9 (m, 4H), 5.8 (m, 4H), 4.34 (br s, 4H), 4.28 (d, J = 12.8 Hz, 4H), 4.22 (d, J = 12.8 Hz, 4H), 4.2 (m, 1H), 4.1 (m, 1 H), 3.7 (m, 12H), 3.30 (t, J = 7.3 Hz, 2H), 3.2 (m, 4H), 3.0 (m, 26H), 2.55 (t, J = 6.9 Hz, 2H), 2.31 (t, J = 7.8 Hz, 2H), 2.0 (m, 2H), 1.72 (m, 12H), 1.55 (m, 4H), 1.25 (m, 80H), 0.9 (m, 42H); FTIR (KBr): ν 3337, 2958, 2930, 2859, 1654, 1601, 1559, 1416, 1245, 1214 cm^{-1}; ESI-TOF m/z 2960.9355 ($[M + H]^+$, calcd for $C_{172}H_{251}N_{22}O_{21}$ 2960.9243). Anal. Calcd for $C_{172}H_{250}N_{22}O_{21}\cdot 2CHCl_3$: C, 65.27; H, 7.96; N, 9.62. Found: C, 64.93; H, 7.81; N, 9.32.

Reaction of Biscalixarene 73 with CO_2.

Freshly prepared biscalixarene **73** (120 mg) was dissolved in benzene (5 mL), and dry CO_2 (or $^{13}CO_2$) was then bubbled through the solution for 2 min at ~35 °C. Material **76** was dried in high vacuum at rt for 6 h. Upon dissolution in DMSO, **76** dissociated to carbamate salt **75**: ^{1}H NMR (DMSO-d_6) δ 8.35 (br), 8.22 (m), 8.17 (m), 8.08 (m), 8.03 (m), 7.95-7.75 (m), 6.82 (m), 6.60 (m), 5.90 (m), 5.81 (m), 4.35 (m), 4.29 (m), 4.21 (m), 3.80-3.60 (m), 3.35 (m), 3.20 (m), 3.10-2.80 (m), 2.49 (m), 2.32 (m), 2.01 (m), 1.72

(m), 1.54 (m), 1.34 (m), 1.23 (m), 0.84 (m); ^{13}C NMR (DMSO-d_6) δ 172.9, 172.0, 171.6, 169.3, 160.7, 155.8, 151.3, 151.26, 150.7, 150.3, 137.1, 135.2, 135.1, 135.0, 134.4, 134.2, 134.0, 131.5, 131.0, 129.9, 128.9, 128.7, 128.0, 127.97, 127.7, 127.0, 126.6, 125.4, 125.3, 124.8, 124.75, 124.1, 118.8, 118.6, 118.5, 77.3, 76.5, 74.8, 53.6, 53.2, 41.9, 39.2, 39.0, 35.5, 32.9, 31.6, 30.4, 30.1, 29.5, 28.2, 26.7, 26.6, 23.7, 23.5, 23.0, 22.96, 22.9, 22.7, 14.5, 10.6.

Liquid–Liquid Extraction Experiments.

Compounds**1a-d**, **2a,b**, and **37a,b** were dissolved in CH_2Cl_2 (~ 5×10^{-3} M, 10 mL) and vigorously stirred overnight with saturated aqueous solution of $NaClO_4$ (10 mL) at rt. Organic layers were then separated, evaporated under reduced pressure, dried in vacuo and analyzed by high-resolution ^{1}H NMR spectroscopy in $CDCl_3$.

Scanning Electron Microscope (SEM).

Samples of **67** and **76** were prepared by a conventional procedure, previously described by Shinkai and co-workers.[135] The gel was placed in a flask and frozen in liquid nitrogen. The frozen specimen was dried in vacuo for 24 h and then coated with palladium-gold at the UTA Center for Electron Microscopy.

Viscosity.

Viscosity measurements for calixarenes **2c**, **32**, **57**, and **63** in $CHCl_3$ and $CHCl_3$/benzene were performed in a standard glass viscometer using conventional

protocols.[136] All experiments were performed at least twice showing good reproducibility. The DP values for biscalixarene **2c** in the presence of chain stopper **32** were estimated using an earlier-derived equation[101] (see below), assuming that the dimerization constant K_D for a calixarene tetraurea capsule[103] was 10^6 M^{-1}:

$$DP = \frac{2([\mathbf{2c}] + [\mathbf{32}])}{[\mathbf{32}] - \frac{1}{4K_D}\left[1 - \sqrt{1 + 8K_D([\mathbf{32}] + 2[\mathbf{2c}])}\right]}$$

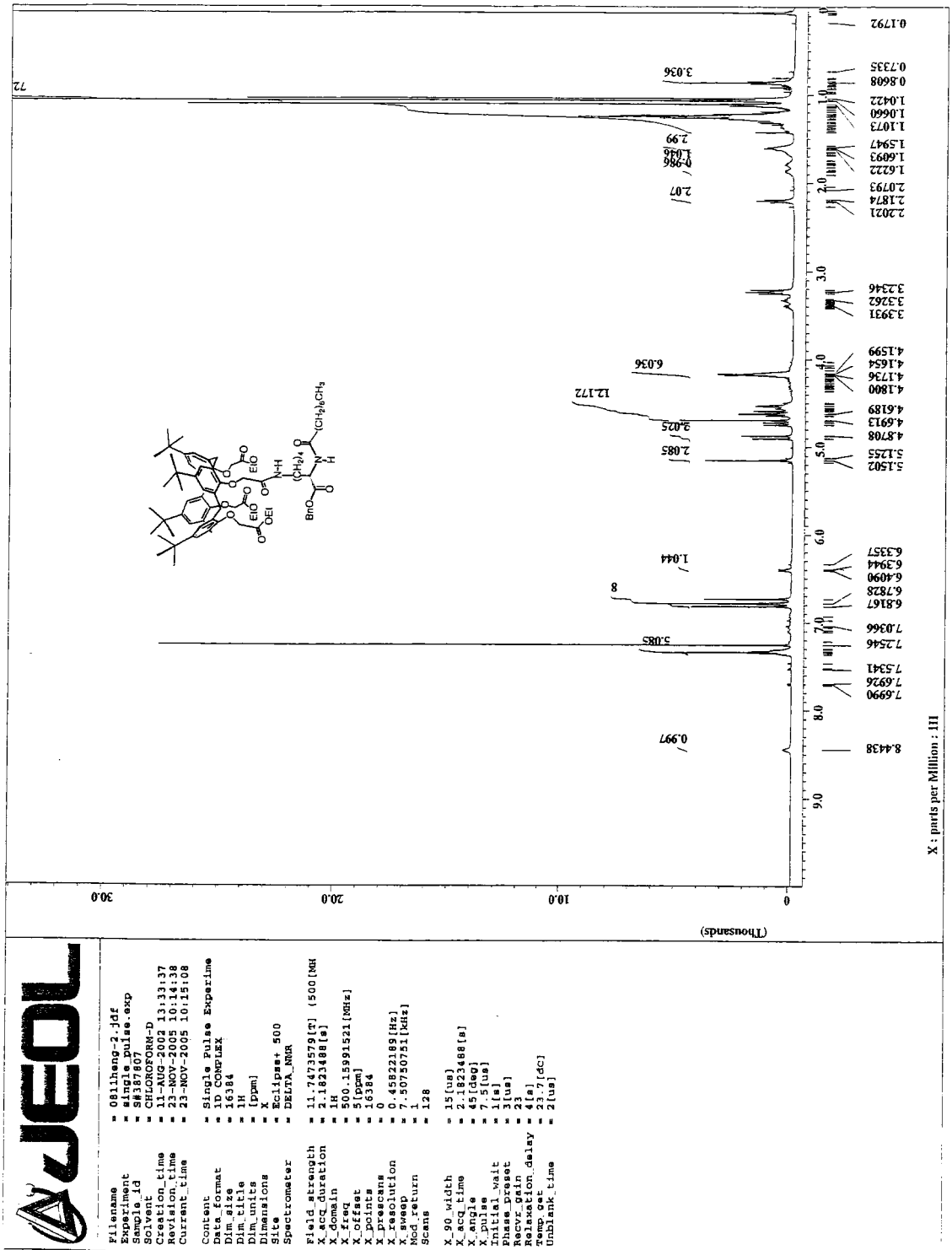
Entrapment and Release Experiments

Calixarene dipeptide **58**•2 × TFA salt (0.20 g, 0.07 mmol) was suspended in $CHCl_3$ (100 mL), successively washed with 10% aq NaOH (100 mL) and H_2O (100 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo to 3.5 mL. This solution was then transferred to a test tube and Coumarin 314 **77** (0.01 g, 0.04 mmol) or porphyne **78** (0.01 g, 0.02 mmol) was added. Bubbling CO_2 into the $CHCl_3$ solution for 1-2 min resulted in gel **67**. This was transferred into a round-bottom flask and washed with $CHCl_3$ (200 mL). Finally, $CHCl_3$ (150 mL for **77** or 400 mL for **78**) was added into the flask. The mixtures were mechanically shaken for an extended time. Samples were taken every 1-3 minutes. The dye release was monitored by UV-vis spectrophotometry. The absorptions of coumarin **77** at λmax = 434 nm and porphyne **78** at λmax = 420 (Soret-band) and 552 nm (Q-band) were monitored. Guest release experiments were performed at least in triplicate.

APPENDIX 1

^{1}H NMR and MASS SPECTRA OF

Calixarene lysine (1a)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Unblank_time = 2[us]
(Thousands)
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7.6926
7.5341
7.2546
7.0366
6.8167
6.7828
6.4090
6.3944
6.3357
5.1502
5.1255
4.8708
4.6913
4.6189
4.1800
4.1736
4.1654
4.1599
3.3931
3.3262
3.2346
2.2021
2.1874
2.0793
1.6222
1.6093
1.5947
1.1073
1.0660
1.0422
0.8608
0.7335
0.1792
0.997
1.044
2.085
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2.07
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2.99
3.036
5.085
8

Profile MS Report

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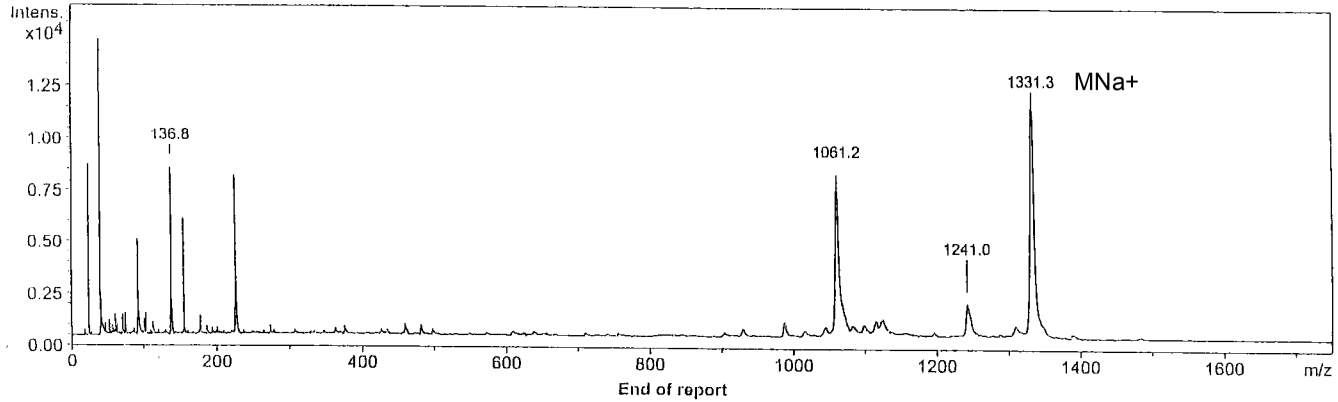
Instrument: TOF
Description: MW1308.78

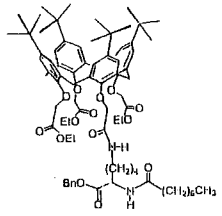
Printed: Sun Oct 13 11:31:18 2002

Operator :

Profile Spectrum, No.: 1, Time: 0 s



End of report

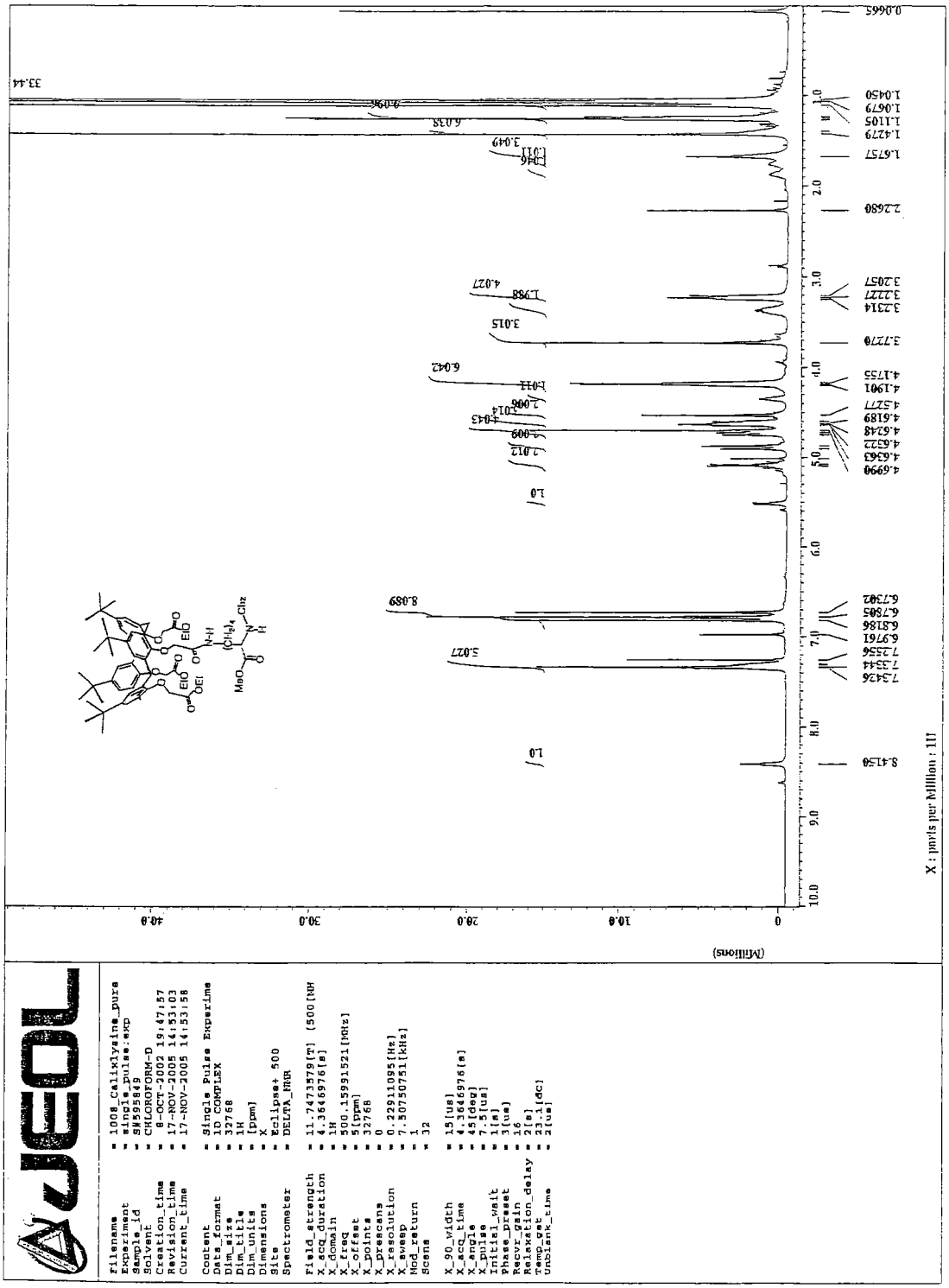


$C_{79}H_{108}N_2O_{14}$
Exact Mass: 1308.78
Mol. Wt.: 1309.71
C, 72.45; H, 8.31; N, 2.14; O, 17.10

APPENDIX 2

^{1}H NMR and MASS SPECTRA OF

Calixarene lysine (1b)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Relaxation_delay = 2[s]
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Unblank_time = 2[us]
(Millions)
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6.9761
6.8186
6.7805
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4.6363
4.6322
4.6248
4.6189
4.5277
4.1901
4.1755
3.7770
3.2314
3.2327
3.2057
2.2680
1.6757
1.4279
1.1105
1.0679
1.0450
0.0665
8.089
6.042
6.038
5.027
4.027
3.049
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2.988
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2.009
2.006
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1.0
33.44
9.096

Profile MS Report

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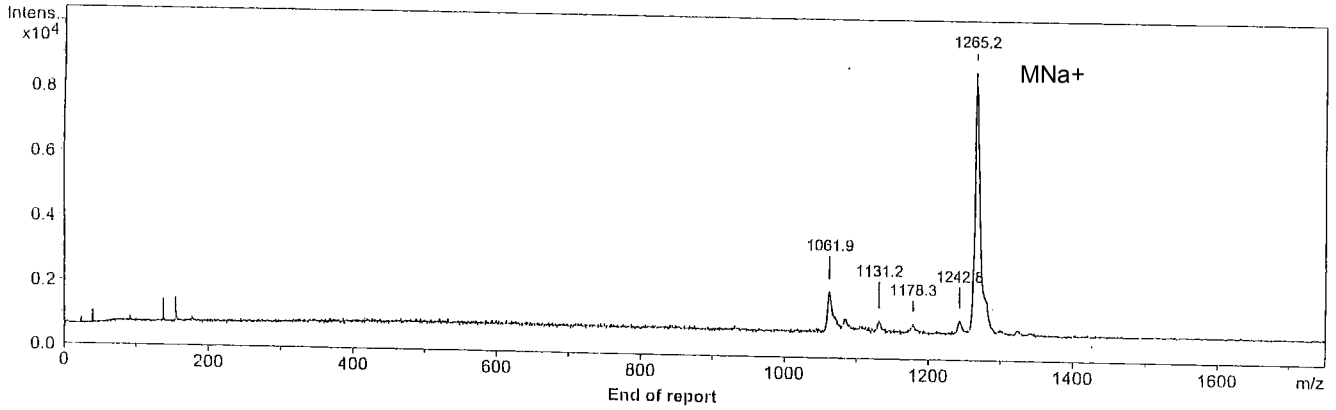
Instrument: TOF
Description: MW1240.68

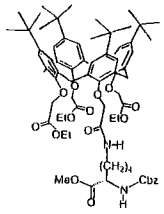
Printed: Sun Oct 13 11:37:42 2002

Operator :

Profile Spectrum, No.: 1, Time: 0 s



End of report

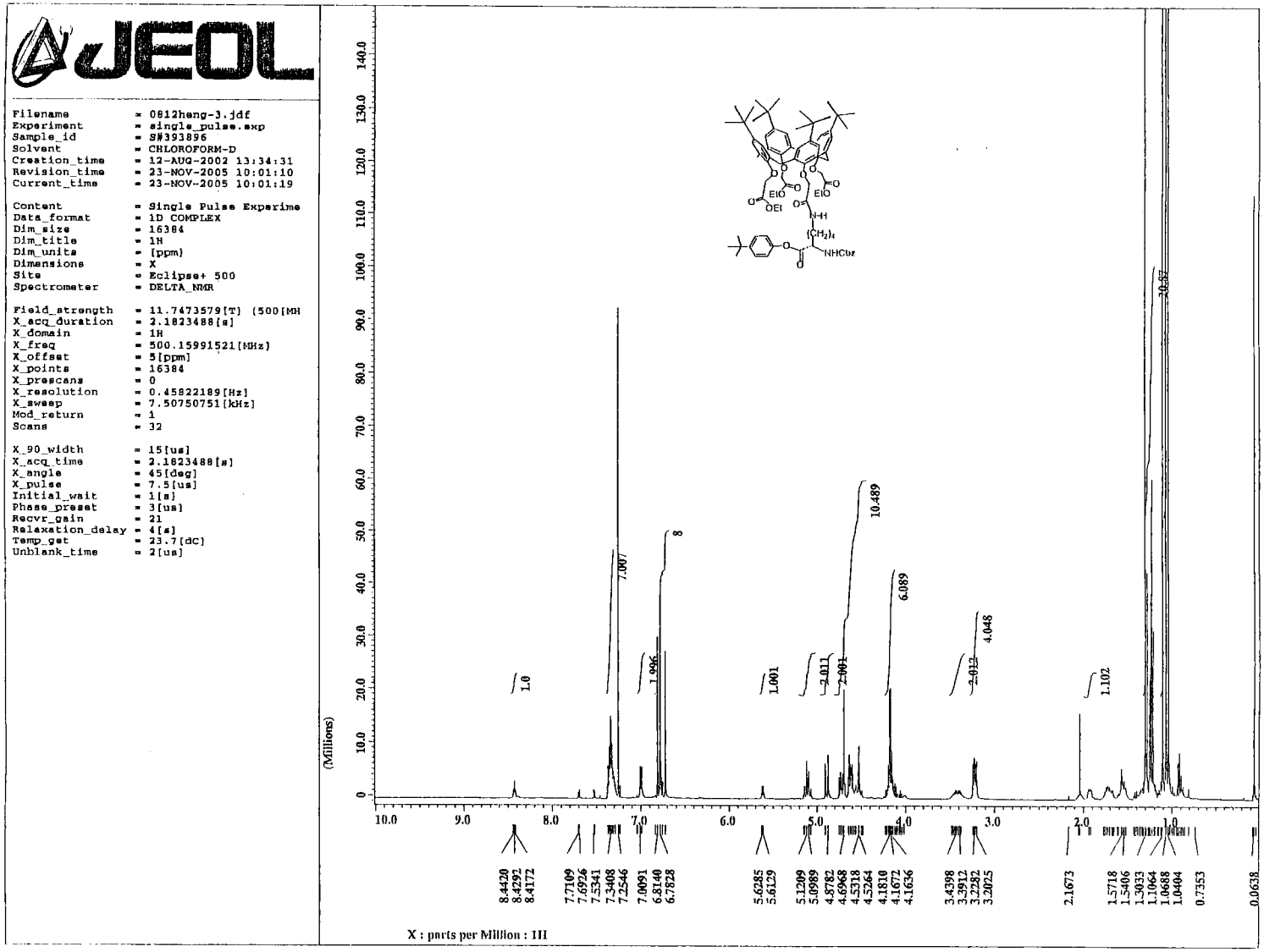


$C_{73}H_{96}N_2O_{15}$
Exact Mass: 1240.68
Mol. Wt.: 1241.55
C, 70.62; H, 7.79; N, 2.26; O, 19.33

APPENDIX 3

^{1}H NMR and MASS SPECTRA OF

Calixarene lysine (1c)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Phase_preset = 3[us]
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(Millions)
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1.001
3.011
2.001
2.012
1.102
7.007
8
10.489
6.089
4.048
NHCbz
8.4420
8.4292
8.4172
7.7109
7.6926
7.5341
7.3408
7.2546
7.0091
6.8140
6.7828
5.6285
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3.3912
3.2282
3.2025
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Profile MS Report

Analysis Info:

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Instrument: TOF
Description: MW1383

Printed: Mon Oct 14 00:11:47 2002

Operator :

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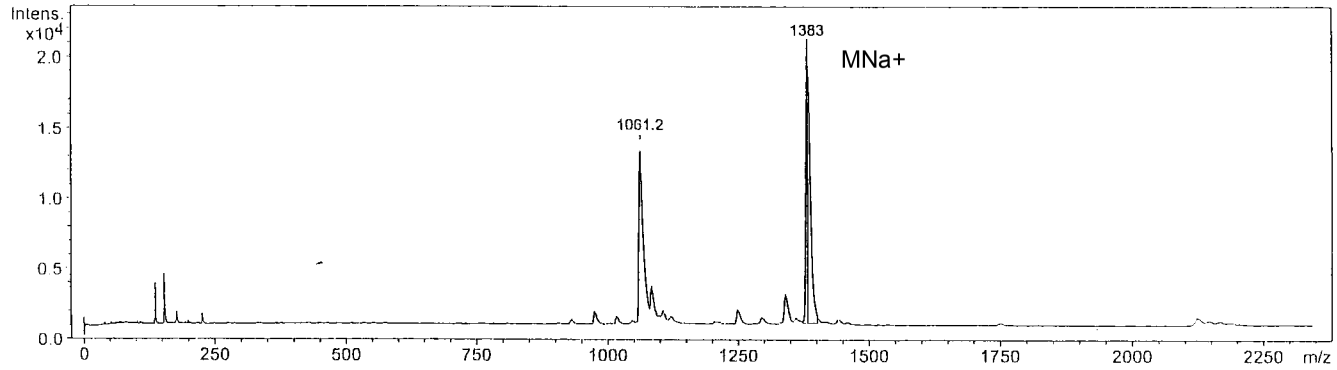

MS Peak List (Time-of-Flight Spectrum):

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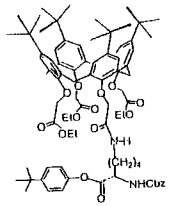
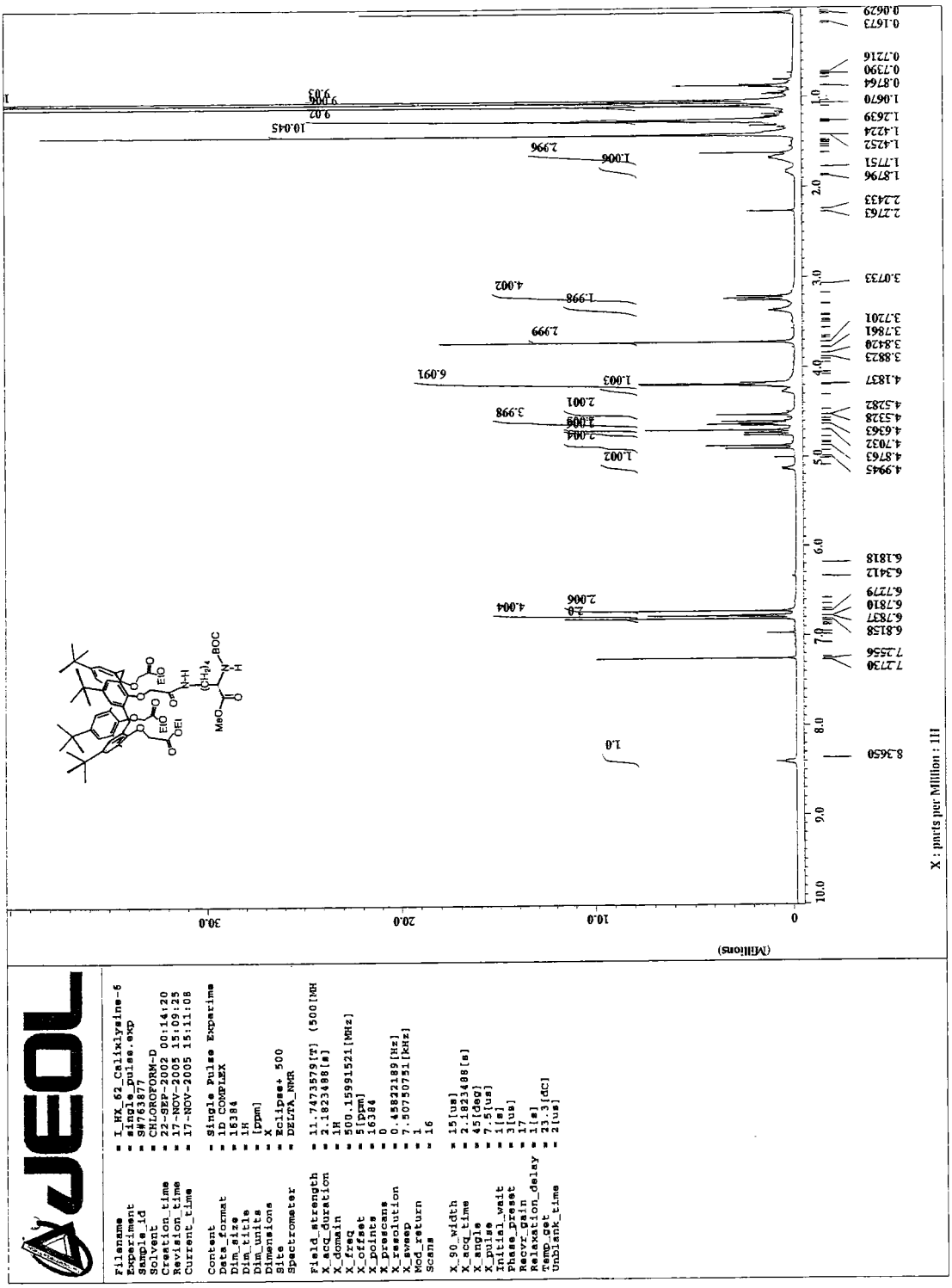
End of report



$C_{82}H_{106}N_2O_{15}$
Exact Mass: 1358.76
Mol. Wt.: 1359.72
C, 72.43; H, 7.86; N, 2.06; O, 17.65

APPENDIX 4

^{1}H NMR and MASS SPECTRA OF
Calixarene lysine (1d)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Mod_return = 1
Scans = 16
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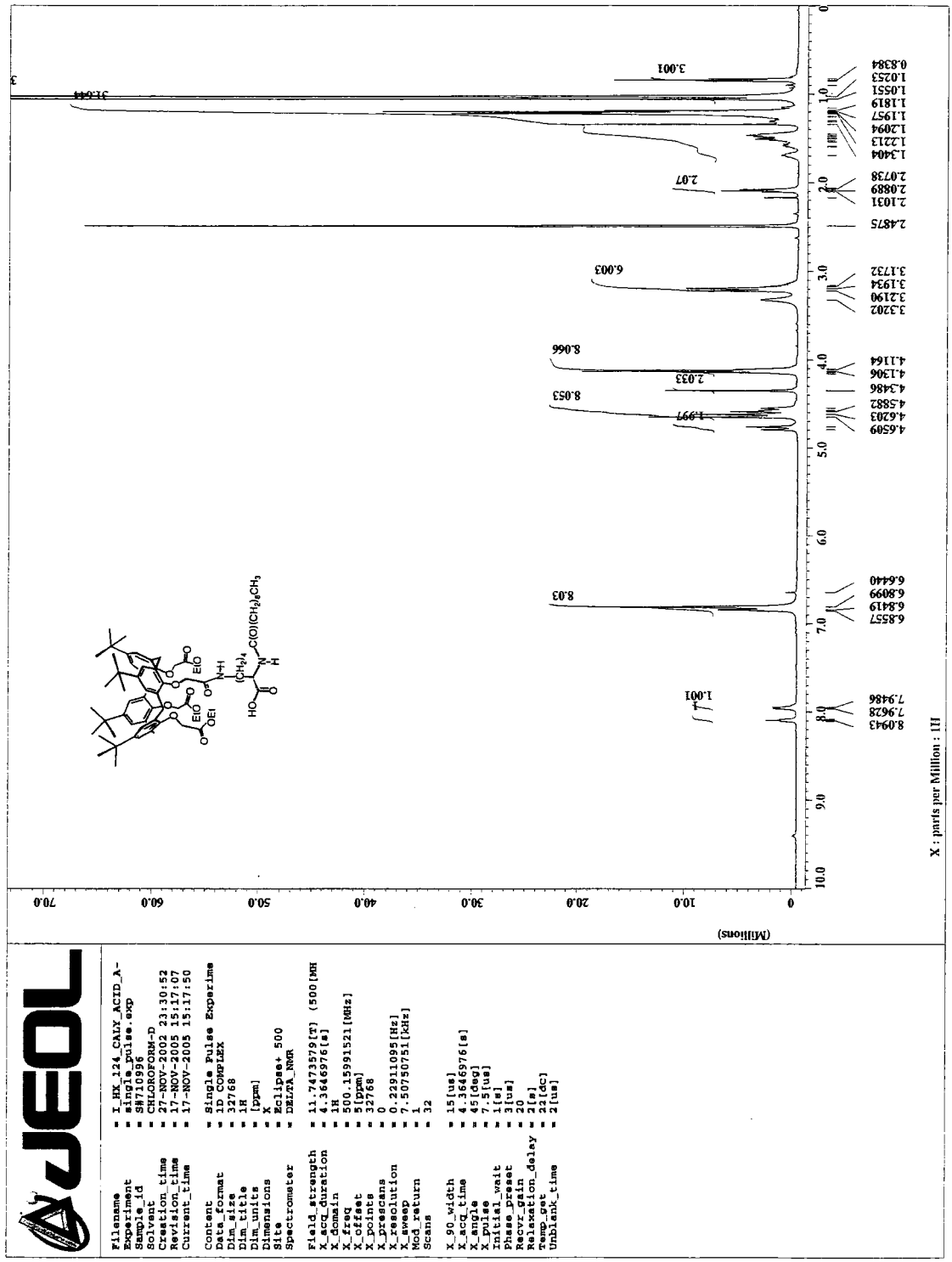
(Millions)
X : parts per Million : 111

APPENDIX 5

^{1}H NMR SPECTRUM OF

Calixarene lysine (1e)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Mod_return = 1
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Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 20
Relaxation_delay = 2[s]
Temp_get = 23[dC]
Unblank_time = 2[us]
(Millions)
X : parts per Million : 1H
31.644
3.001
2.07
6.003
8.066
2.033
8.053
1.997
8.03
1.001
2.4875
1.3404
1.2213
1.2094
1.1957
1.1819
1.0551
1.0253
0.8384
2.1031
2.0889
2.0738
3.3202
3.2190
3.1934
3.1732
4.6509
4.6203
4.5882
4.3486
4.1306
4.1164
8.0943
7.9628
7.9486
6.8557
6.8419
6.8099
6.6440

APPENDIX 6

^{1}H NMR SPECTRUM OF
Calixarene lysine (1f)

JEOL
Filename = I_HK_77_Calix1ysine_Z
Experiment = single_pulse.exp
Sample_id = S#586952
Solvent = CHLOROFORM-D
Creation_time = 8-OCT-2002 19:29:44
Revision_time = 17-NOV-2005 19:41:20
Current_time = 17-NOV-2005 19:42:06
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.74713579[T] (500[MH
X_acq_duration = 2.18234888[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.18234888[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 20
Relaxation_delay = 1[s]
Temp_set = 23.1[dC]
Unblank_time = 2[us]
(Millions)
X : parts per Million : 1H
25
8
10.029
6.035
2.006
1.525
7.042
7.473
12.343
1.093
8.4731
7.2556
6.8424
6.7663
6.7508
4.8717
4.7252
4.6262
4.6125
4.5941
4.2084
4.1837
3.7467
3.7201
3.5800
3.3602
3.3264
3.2108
2.3807
2.0399
1.6808
1.6670
1.2694
1.2658
1.1265
1.0697
1.0578
1.0486
1.0386
0.0629

APPENDIX 7

^{1}H NMR, ^{13}C NMR and MASS SPECTRUM OF

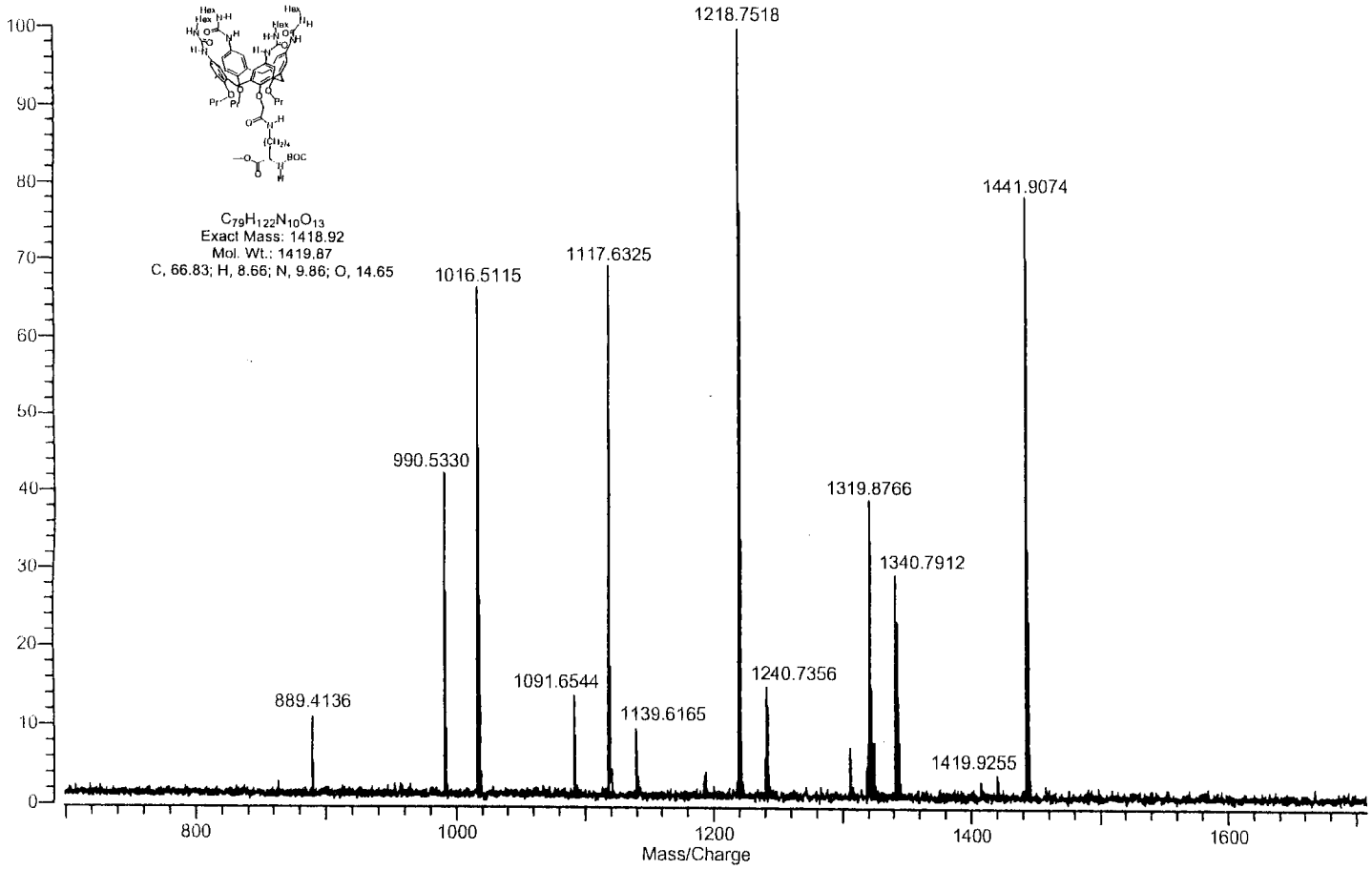
N-α-BOC-*N*-ε-(calix[4]arenetetraurea)-*l*-lysine, Methyl Ester (1g)

JEOL
Filename = T_HX_387_tetra_urea_1
Experiment = single_pulse.exp
Sample_id = SH357782
Solvent = CHLOROFORM-D
Creation_time = 6-JUN-2003 15:43:07
Revision_time = 17-NOV-2005 15:40:49
Current_time = 17-NOV-2005 15:41:10
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 4.3646976[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.2291095[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 32
X_90_width = 15[us]
X_acq_time = 4.3646976[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 15
Relaxation_delay = 2[s]
Temp_get = 22.3[dC]
Unblank_time = 2[us]
(Millions)
X : parts per Million : 1H

IonSpec HiResMALDI
File: WP20030509_0041_MALDI.trans Sample Tracking No. SRGS
2524

Mode: Positive
Scans: 5

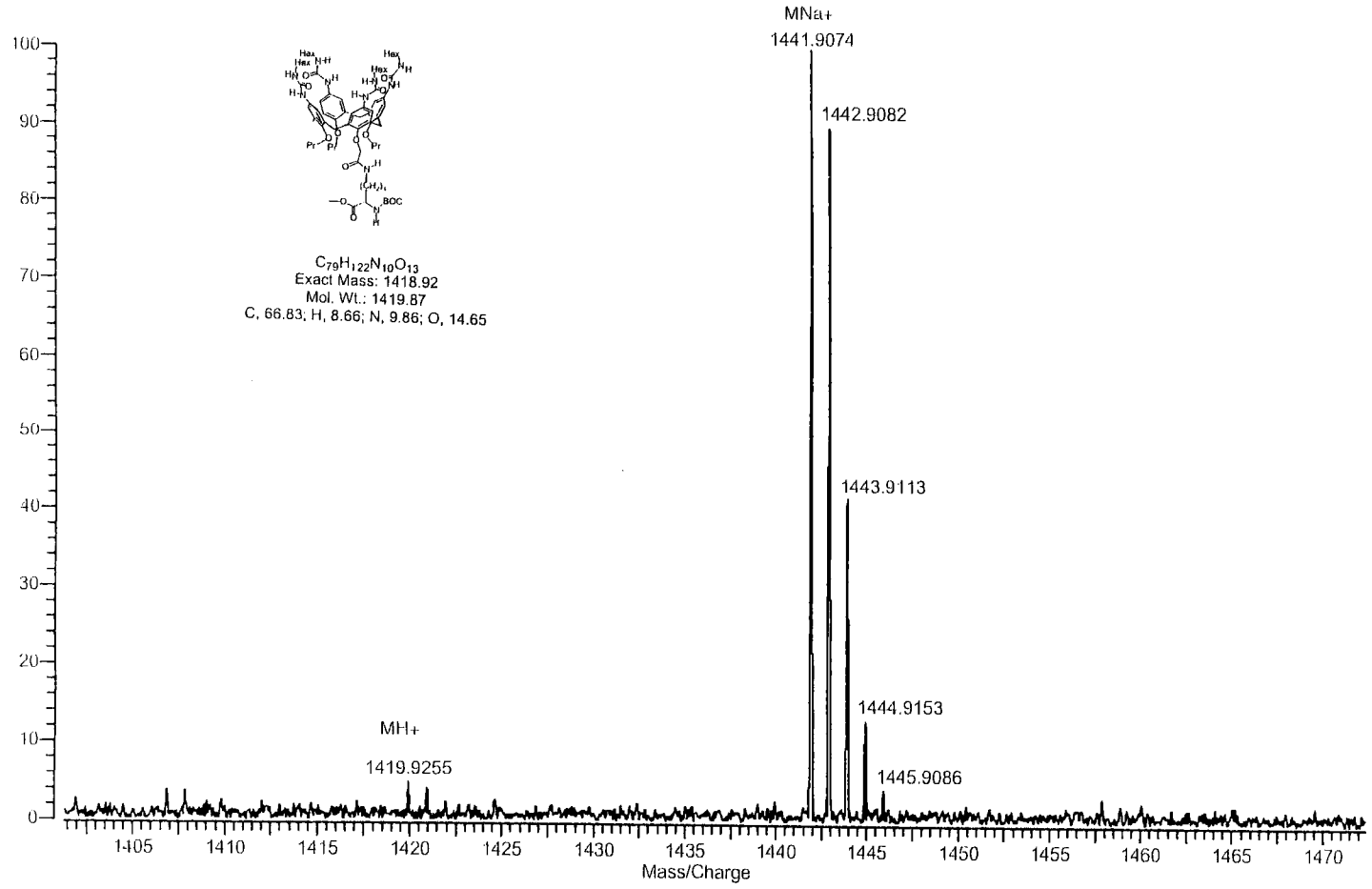
Date: 09-MAY-2003
Time: 14:22:13
Scale: 234.9925



IonSpec HiResMALDI
File: WP20030509_0041_MALDI.trans Sample Tracking No. SRGS
2524

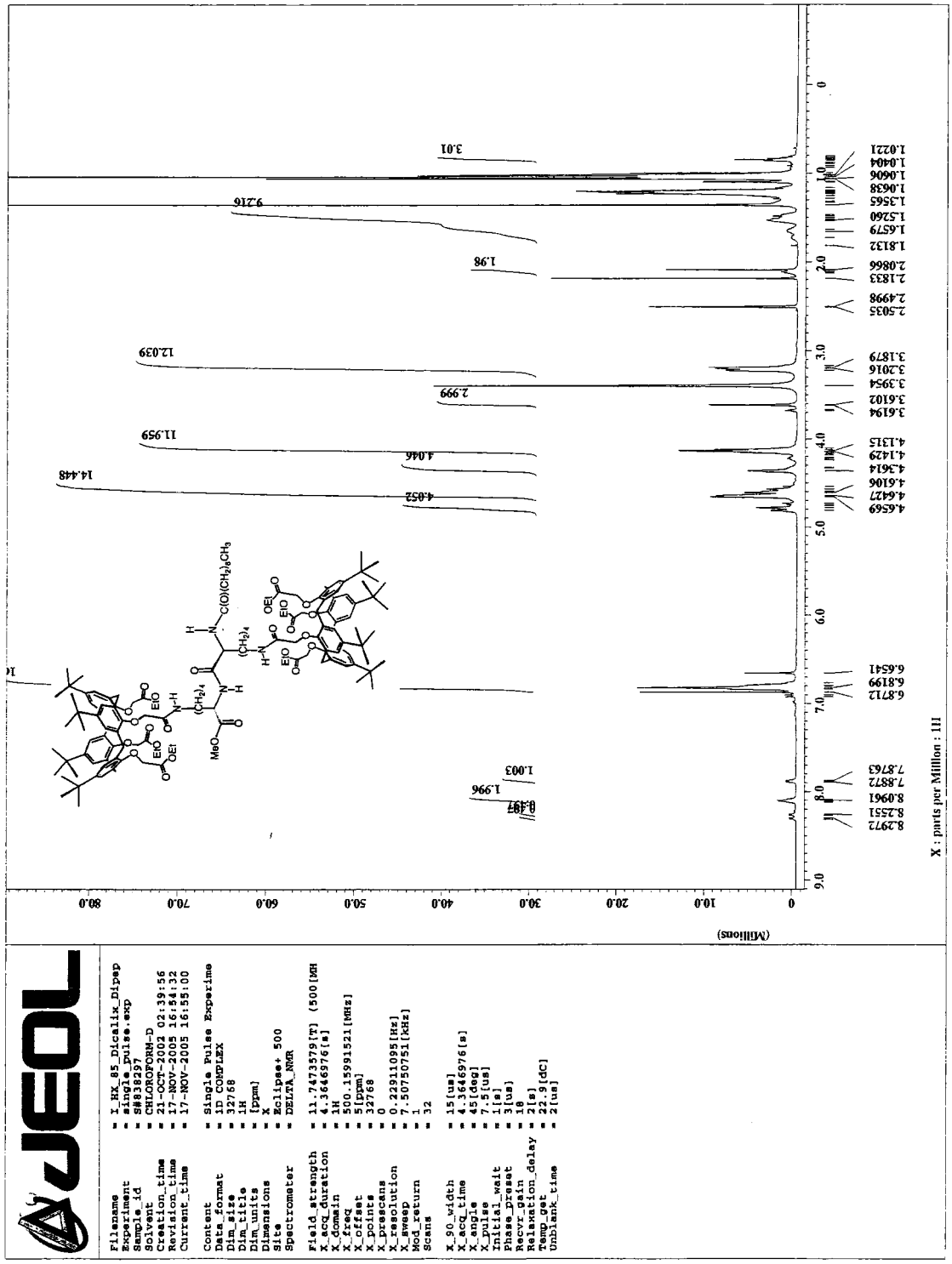
Mode: Positive
Scans: 5

Date: 09-MAY-2003
Time: 14:22:13
Scale: 298.8748



APPENDIX 8

^{1}H NMR and MASS SPECTRA OF
Calixarene dipeptide (2a)


JEOL
Filename = I_HX_85_Dicalix_Dipep
Experiment = single_pulse.exp
Sample_id = S#838297
Solvent = CHLOROFORM-D
Creation_time = 21-OCT-2002 02:39:56
Revision_time = 17-NOV-2005 16:54:32
Current_time = 17-NOV-2005 16:55:00
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 4.3646976[s]
X_domain = 1H
X_freq = 500.159931521[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.229110095[Hz]
X_sweep = 7.507507751[kHz]
Mod_return = 1
Scans = 32
X_90_width = 15[us]
X_acq_time = 4.3646976[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 18
Relaxation_delay = 2[s]
Temp_get = 22.9[dC]
Unblank_time = 2[us]
(Millions)
X : parts per Million : 111
14.448
12.039
11.959
9.216
4.052
4.046
3.01
2.999
1.98
1.003
1.996
8.2972
8.2551
8.0961
7.8872
7.8763
6.8712
6.8199
6.6541
4.6569
4.6427
4.6106
4.5614
4.1429
4.1315
3.6194
3.6102
3.3954
3.2016
3.1879
2.5035
2.4998
2.1833
2.0866
1.8132
1.6579
1.5260
1.3565
1.0638
1.0606
1.0404
1.0221

Profile MS Report

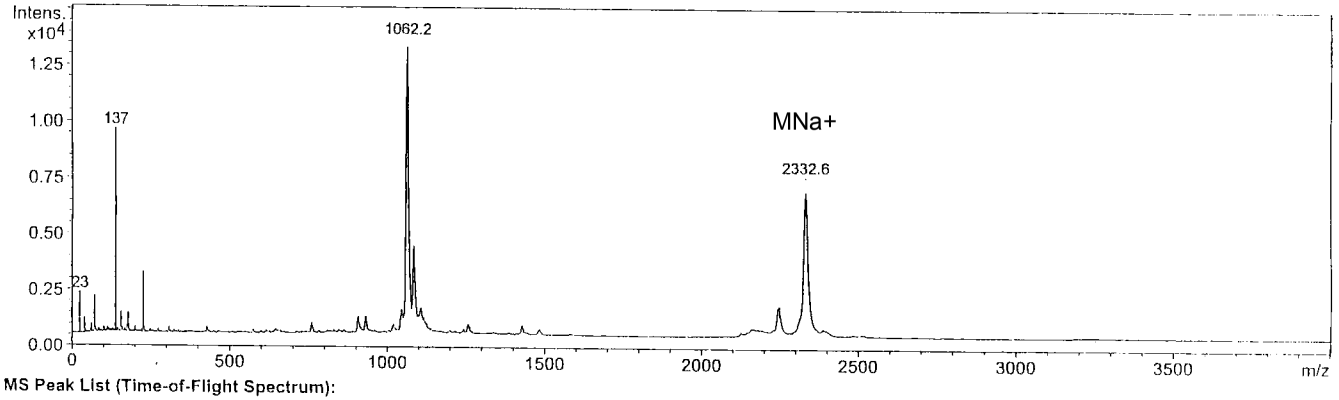
Analysis Info:

File: C:\JIANG\SAMPLES\RUDKEV-1\HENG\CALIXD-1\OCTANO-1\1LIN
Date acquired: Mon Nov 04 00:16:01 2002
Instrument: TOF
Description: MW2310

Printed: Sun Nov 03 23:43:36 2002

Operator :

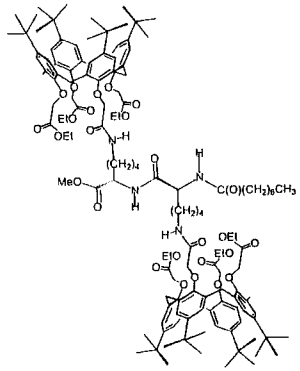
Profile Spectrum, No.: 1, Time: 0 s



MS Peak List (Time-of-Flight Spectrum):

Mass	Intensity	Width	Mass	Intensity	Width	Mass	Intensity	Width
23.1595	2394	0.31	137.2920	9705	0.76			

End of report

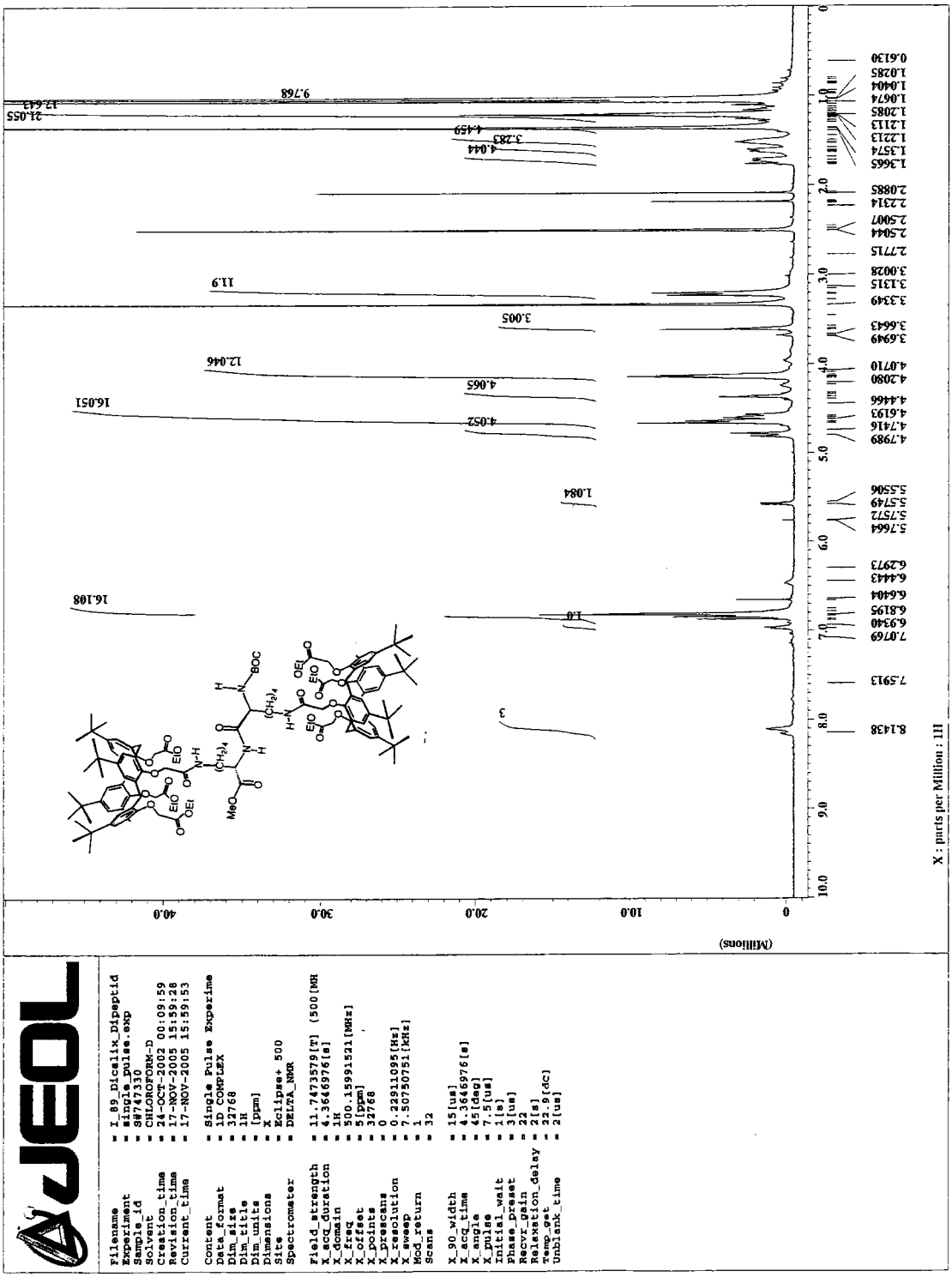


$C_{137}H_{190}N_4O_{26}$
Exact Mass: 2307.37
Mol. Wt.: 2308.99
C, 71.26; H, 8.29; N, 2.43; O, 18.02

APPENDIX 9

^{1}H NMR and MASS SPECTRA OF

Calixarene dipeptide (2b)


JEOL
Filename = I_89_Dicalix_Dipeptid
Experiment = single_pulse.exp
Sample_id = 9#7473330
Solvent = CHLOROFORM-D
Creation_time = 24-OCT-2002 00:09:59
Revision_time = 17-NOV-2005 15:59:28
Current_time = 17-NOV-2005 15:59:53
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 4.36469761[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.22911095[Hz]
X_sweep = 7.50750751[kHz]
X_width = 1
Mod_return = 32
Scans
X_90_width = 15[us]
X_acq_time = 4.36469761[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 22
Relaxation_delay = 2[s]
Temp_get = 22.9[dc]
Unblank_time = 2[us]
(Millions)
X : parts per Million : 1H
16.108
16.051
12.046
11.9
9.768
3.005
1.084
1.0
3
8.1438
7.5913
7.0769
6.9340
6.8195
6.6404
6.4443
6.2973
5.7664
5.7572
5.5749
5.5506
4.7989
4.7416
4.6193
4.4466
4.2080
4.0710
3.6949
3.6643
3.3349
3.1315
3.0028
2.7715
2.5044
2.5007
2.2314
2.0885
1.3665
1.3574
1.2213
1.2113
1.2085
1.0674
1.0404
1.0285
0.6130

Profile MS Report

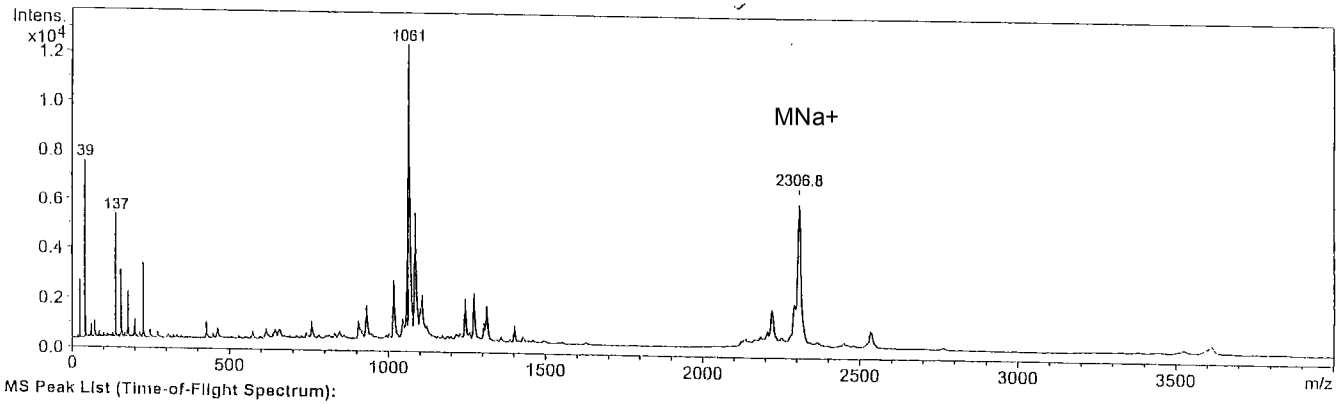
Analysis Info:

File: C:\JIANG\SAMPLES\RUDKEV-1\HENG\CALIXD-1\DIPEPT-2\1LIN
Date acquired: Sun Nov 03 23:56:18 2002
Instrument: TOF

Printed: Sun Nov 03 23:40:59 2002

Operator :

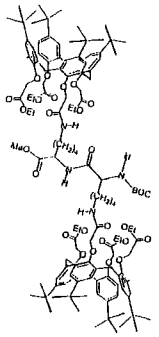
Profile Spectrum, No.: 1, Time: 0 s



MS Peak List (Time-of-Flight Spectrum):

Mass	Intensity	Width	Mass	Intensity	Width	Mass	Intensity	Width
38.9792	7590	0.32	137.0189	5415	0.60	1061.1555	12452	4.63

End of report

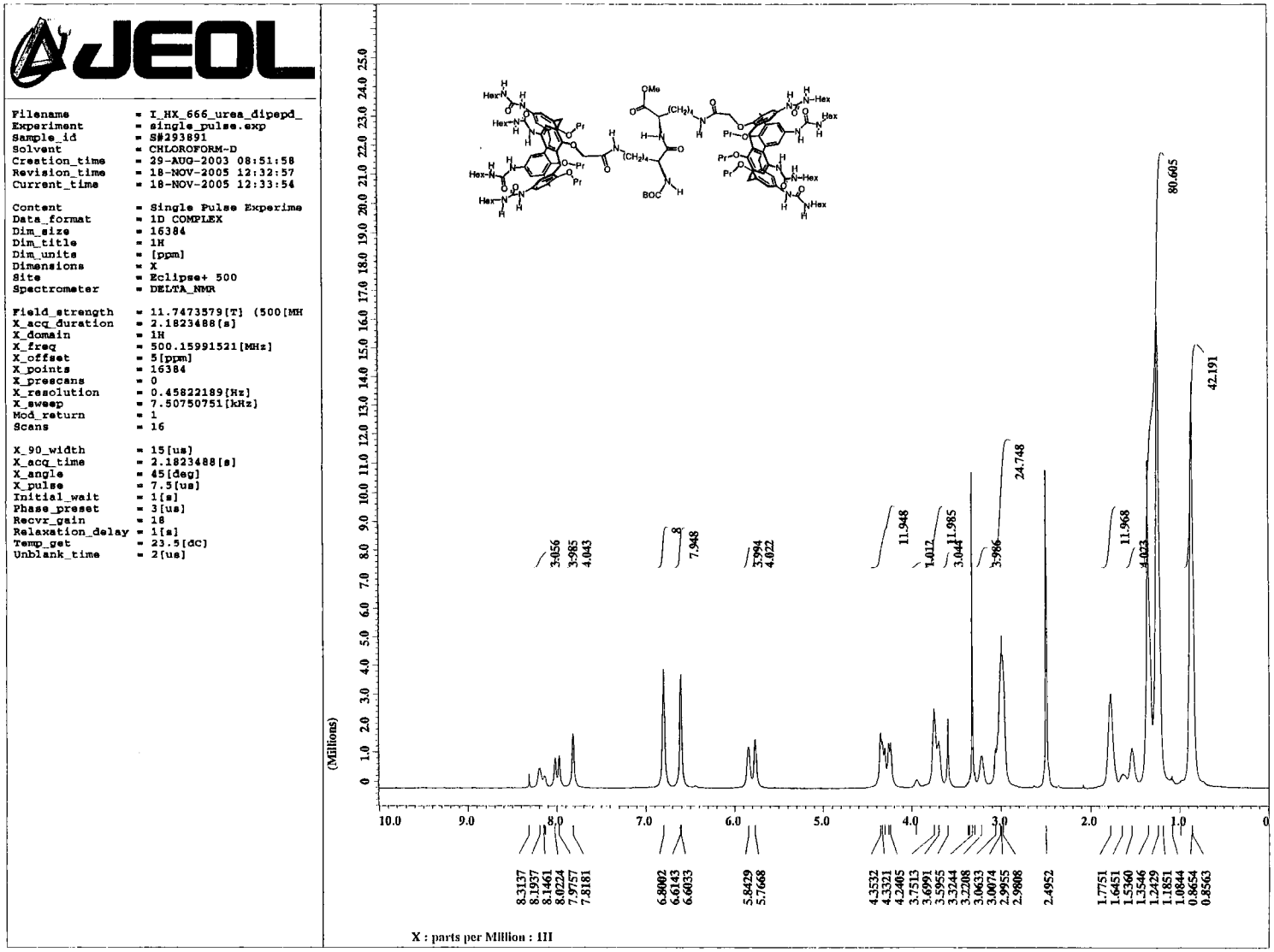


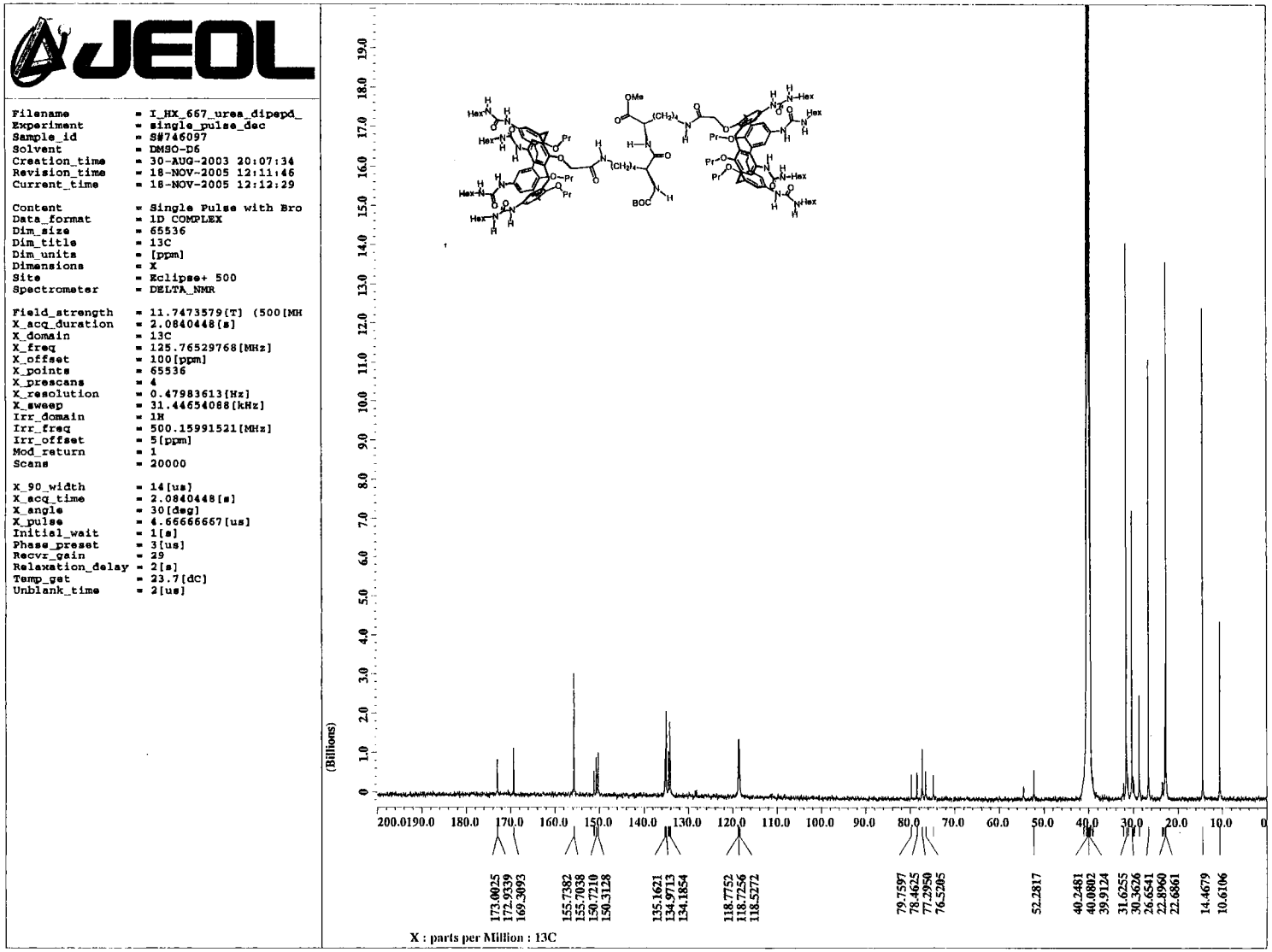
$C_{134}H_{186}N_4O_{27}$
Exact Mass: 2282.32
Mol. Wt.: 2283.91
C, 70.47; H, 8.16; N, 2.45; O, 18.91

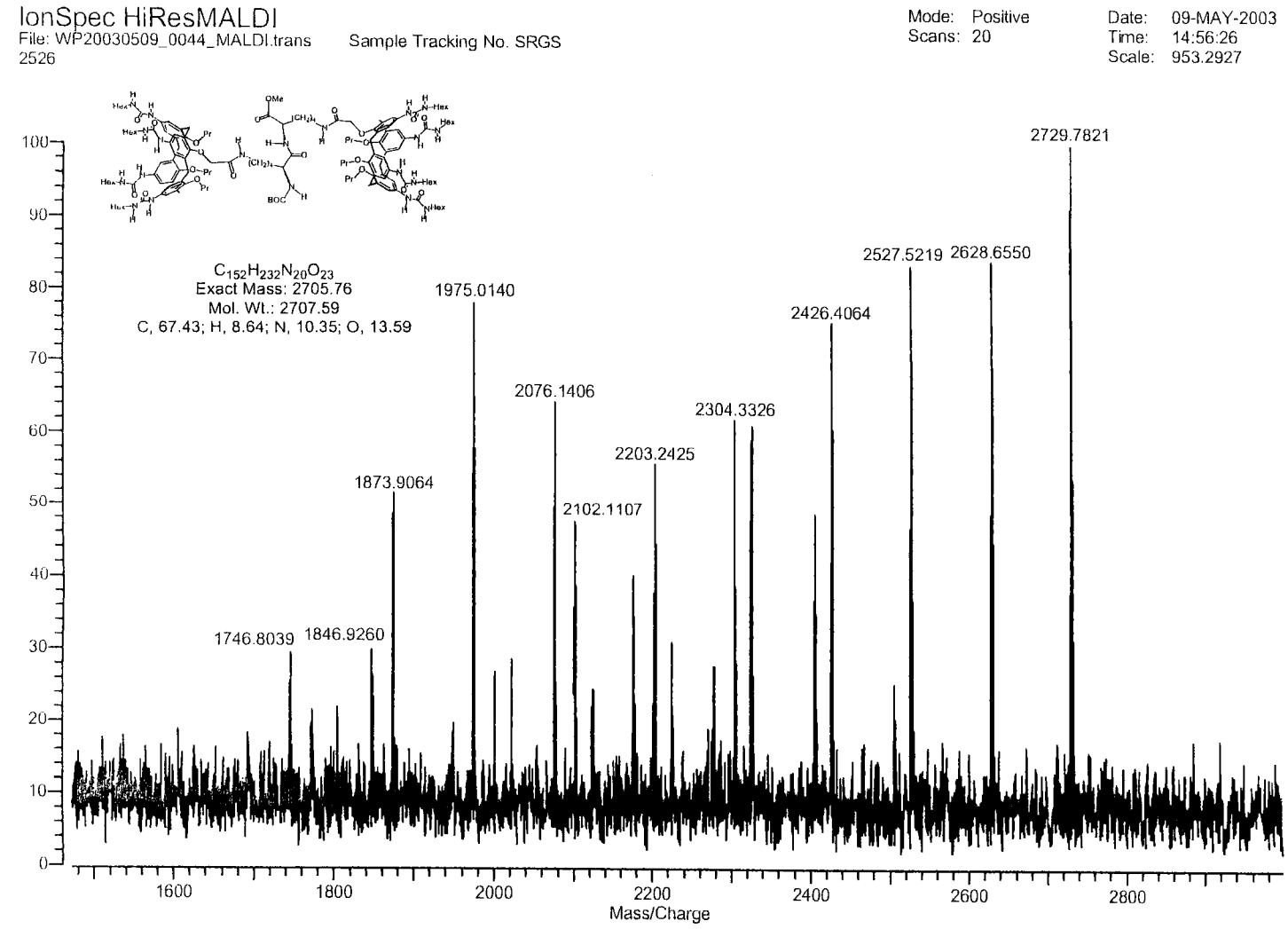
APPENDIX 10

^{1}H NMR, ^{13}C NMR and MASS SPECTRA OF

Biscalixarene (2c)


JEOL
Filename = I_HX_666_urea_dipepd_
Experiment = single_pulse.exp
Sample_id = S#293891
Solvent = CHLOROFORM-D
Creation_time = 29-AUG-2003 08:51:58
Revision_time = 18-NOV-2005 12:32:57
Current_time = 18-NOV-2005 12:33:54
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 18
Relaxation_delay = 1[s]
Temp_get = 23.5[dC]
Unblank_time = 2[us]
(Millions)
3.056
3.985
4.043
8
7.948
3.994
4.022
11.948
1.012
11.985
3.044
3.986
24.748
11.968
4.023
80.605
42.191
8.3137
8.1937
8.1461
8.0224
7.9757
7.8181
6.8002
6.6143
6.6033
5.8429
5.7668
4.3532
4.3321
4.2405
3.7513
3.6991
3.5955
3.3244
3.2208
3.0633
3.0074
2.9955
2.9808
2.4952
1.7751
1.6451
1.5360
1.3546
1.2429
1.1851
1.0844
0.8654
0.8563
X : parts per Million : 1H

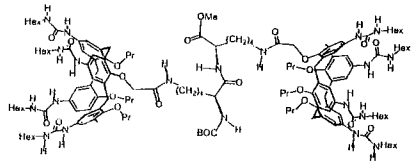

JEOL
Filename = I_HX_667_urea_dipepd_
Experiment = single_pulse_dec
Sample_id = S#746097
Solvent = DMSO-D6
Creation_time = 30-AUG-2003 20:07:34
Revision_time = 18-NOV-2005 12:11:46
Current_time = 18-NOV-2005 12:12:29
Content = Single Pulse with Bro
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Mod_return = 1
Scans = 20000
X_90_width = 14[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.66666667[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 29
Relaxation_delay = 2[s]
Temp_get = 23.7[dC]
Unblank_time = 2[us]
(Billions)
173.0025
172.9339
169.3093
155.7382
155.7038
150.7210
150.3128
135.1621
134.9713
134.1854
118.7752
118.7256
118.5272
79.7597
78.4625
77.2950
76.5205
52.2817
40.2481
40.0882
39.9124
31.6255
30.3626
26.6541
22.8960
22.6861
14.4679
10.6106
X : parts per Million : 13C


IonSpec HiResMALDI
File: WP20030509_0044_MALDI.trans Sample Tracking No. SRGS
2526
Mode: Positive
Scans: 20
Date: 09-MAY-2003
Time: 14:56:26
Scale: 953.2927
C152H232N20O23
Exact Mass: 2705.76
Mol. Wt.: 2707.59
C, 67.43; H, 8.64; N, 10.35; O, 13.59
1746.8039
1846.9260
1873.9064
1975.0140
2076.1406
2102.1107
2203.2425
2304.3326
2426.4064
2527.5219
2628.6550
2729.7821
Mass/Charge

IonSpec HiResMALDI
File: WP20030509_0044_MALDI.trans Sample Tracking No. SRGS
2526

Mode: Positive
Scans: 20

Date: 09-MAY-2003
Time: 14:56:26
Scale: 953.2927

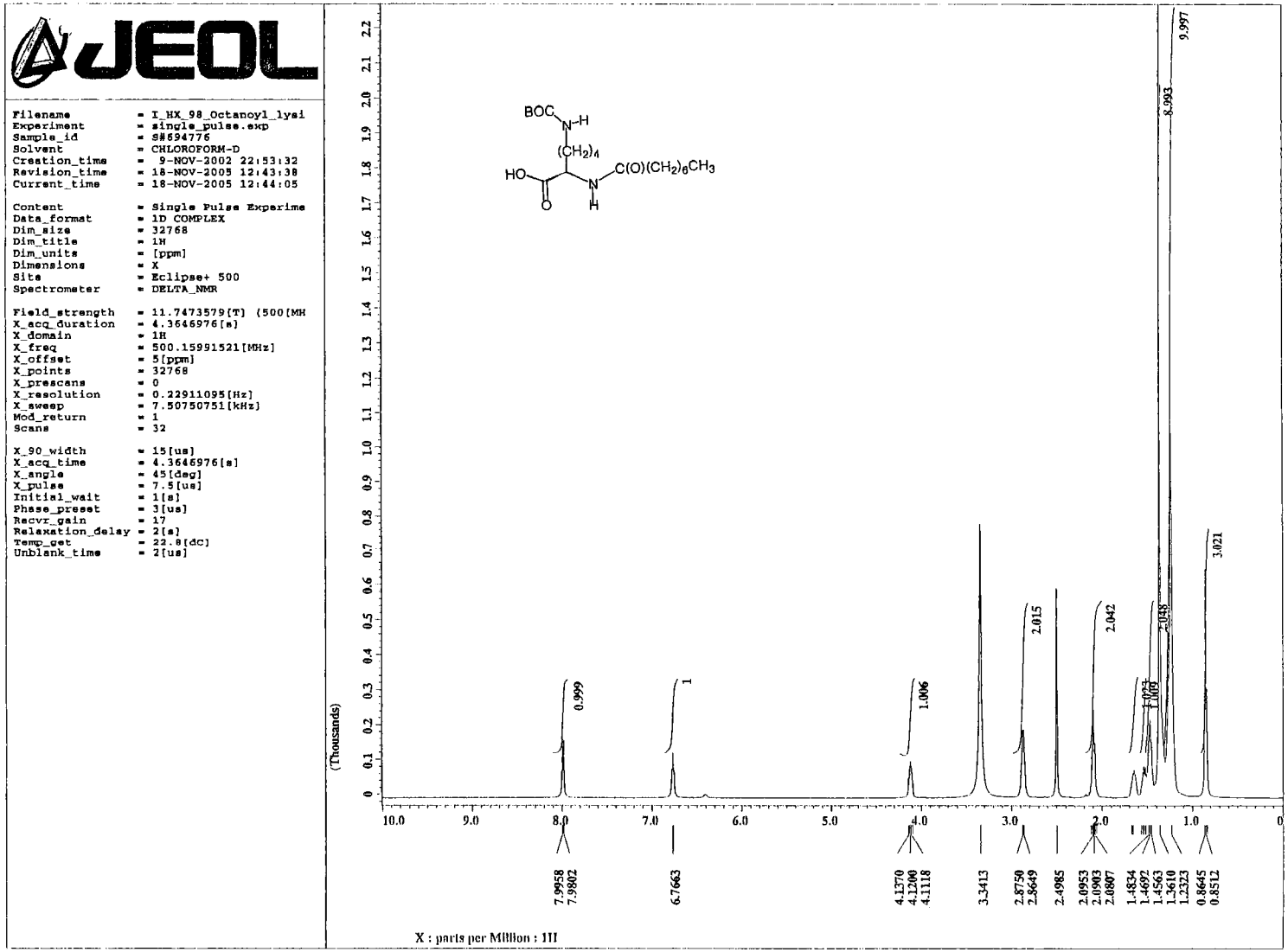


$C_{152}H_{232}N_{20}O_{23}$
Exact Mass: 2705.76
Mol. Wt.: 2707.59
C, 67.43; H, 8.64; N, 10.35; O, 13.59

APPENDIX 11

^{1}H NMR SPECTRUM OF

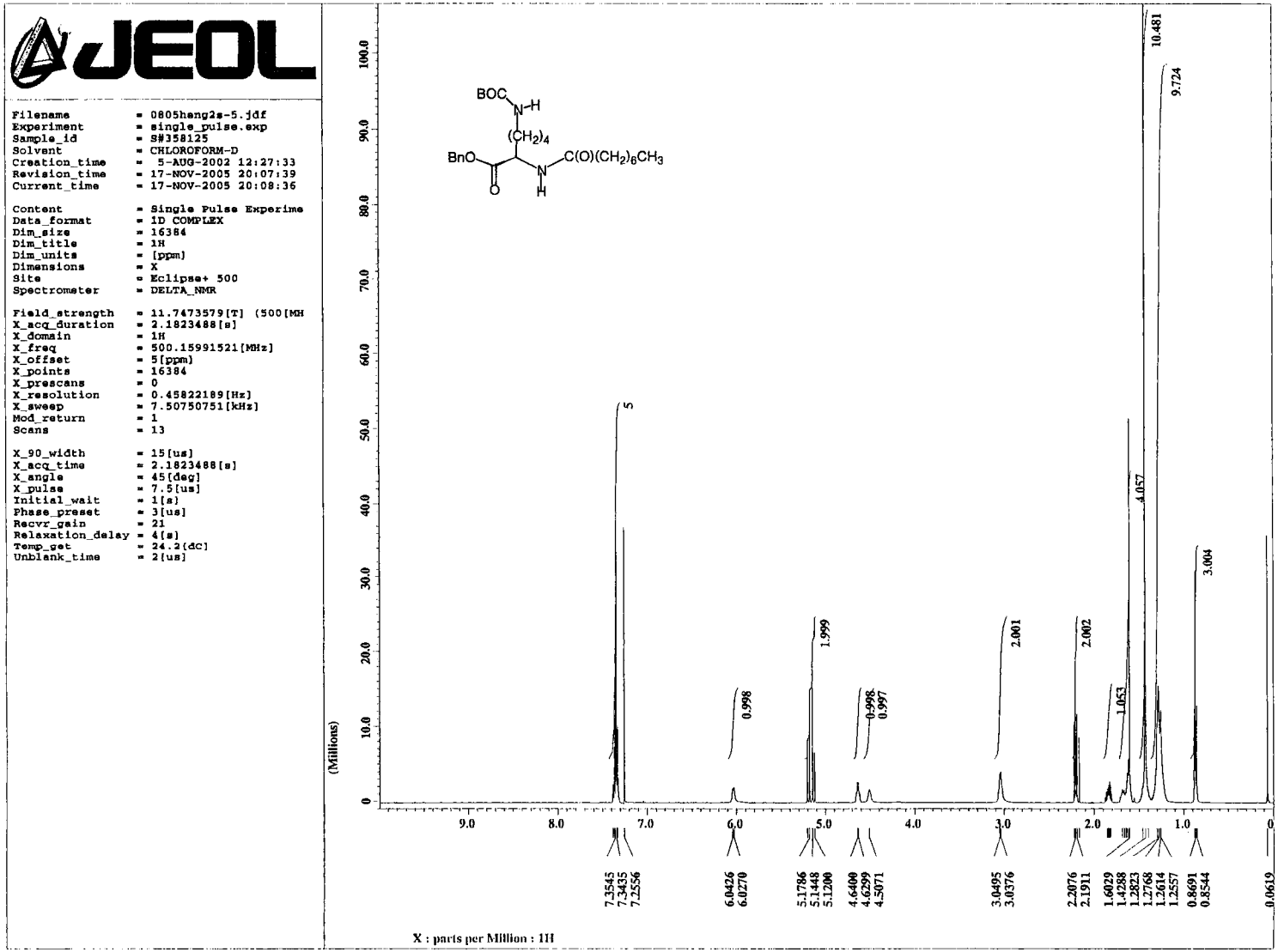
N-α-(*n*-Octanoyl)-*N*-ε-BOC-(±)-lysine (4)


JEOL
Filename = I_HX_98_Octanoyl_lysi
Experiment = single_pulse.exp
Sample_id = S#894776
Solvent = CHLOROFORM-D
Creation_time = 9-NOV-2002 22:53:32
Revision_time = 18-NOV-2005 12:43:38
Current_time = 18-NOV-2005 12:44:05
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 4.3646976[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.22911095[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 32
X_90_width = 15[us]
X_acq_time = 4.3646976[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 17
Relaxation_delay = 2[s]
Temp_get = 22.8[dC]
Unblank_time = 2[us]
BOC
N
H
(CH2)4
HO
C(O)(CH2)6CH3
O
N
H
(Thousands)
0.999
1
1.006
2.015
2.042
8.993
9.997
3.021
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.9958
7.9802
6.7663
4.1370
4.1200
4.1118
3.3413
2.8750
2.8649
2.4985
2.0953
2.0903
2.0807
1.4834
1.4692
1.4563
1.3610
1.2323
0.8645
0.8512
X : parts per Million : 111

APPENDIX 12

^{1}H NMR SPECTRUM OF

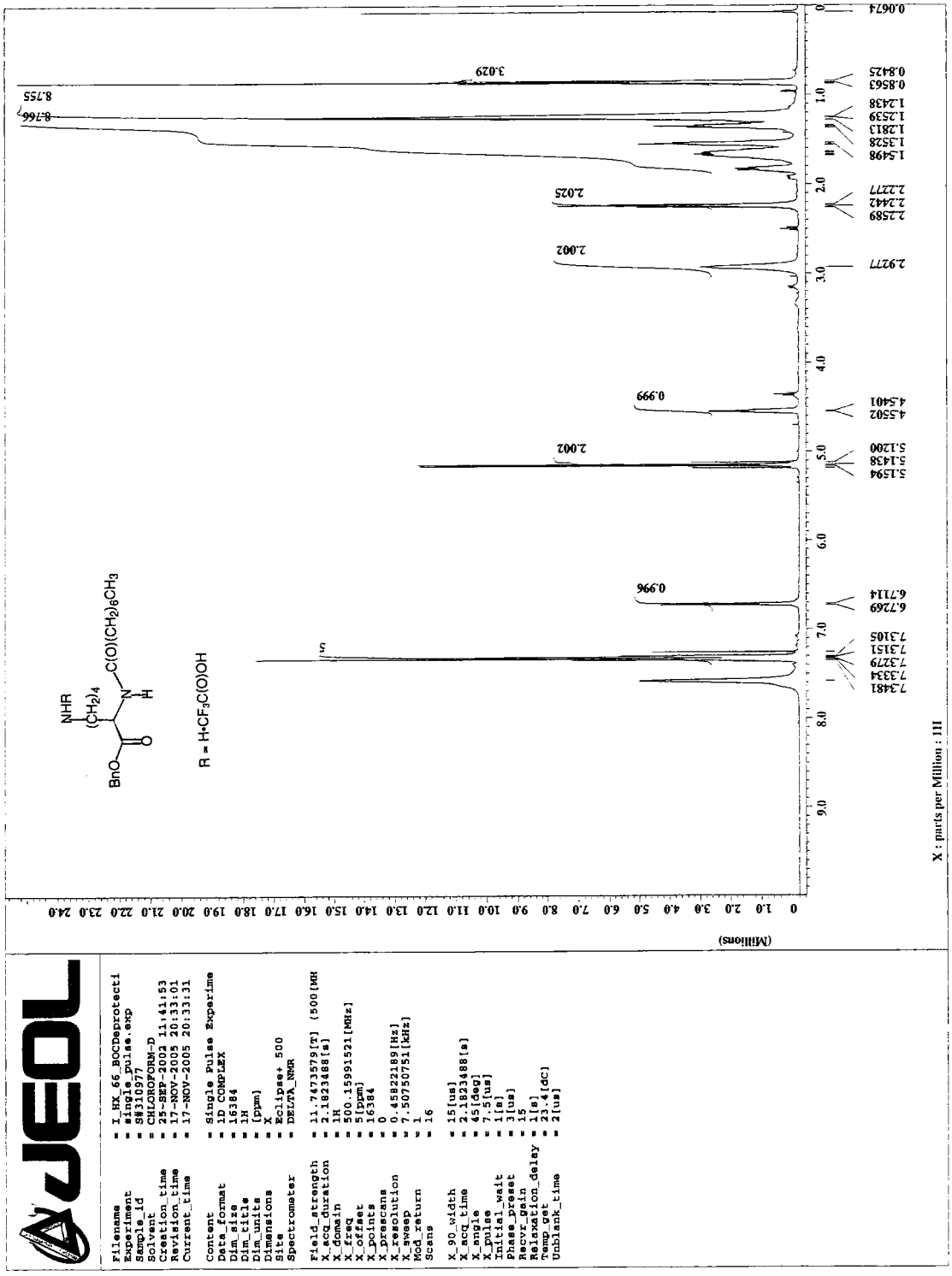
N-α-(*n*-Octanoyl)-*N*-ε-BOC-(±)-lysine, *O*-benzyl ester (5)


JEOL
Filename = 0805hang2s-5.jdf
Experiment = single_pulse.exp
Sample_id = S#358125
Solvent = CHLOROFORM-D
Creation_time = 5-AUG-2002 12:27:33
Revision_time = 17-NOV-2005 20:07:39
Current_time = 17-NOV-2005 20:08:36
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 13
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 21
Relaxation_delay = 4[s]
Temp_get = 24.2[dC]
Unblank_time = 2[us]
BOC
N-H
(CH2)4
BnO
C(O)(CH2)6CH3
O
H
(Millions)
5
0.998
1.999
0.998
0.997
2.001
2.002
1.053
4.057
10.481
9.724
3.004
7.3545
7.3435
7.2556
6.0426
6.0270
5.1786
5.1448
5.1200
4.6400
4.6299
4.5071
3.0495
3.0376
2.2076
2.1911
1.6029
1.4288
1.2823
1.2768
1.2614
1.2557
0.8691
0.8544
0.0619
X : parts per Million : 1H

APPENDIX 13

^{1}H NMR SPECTRUM OF

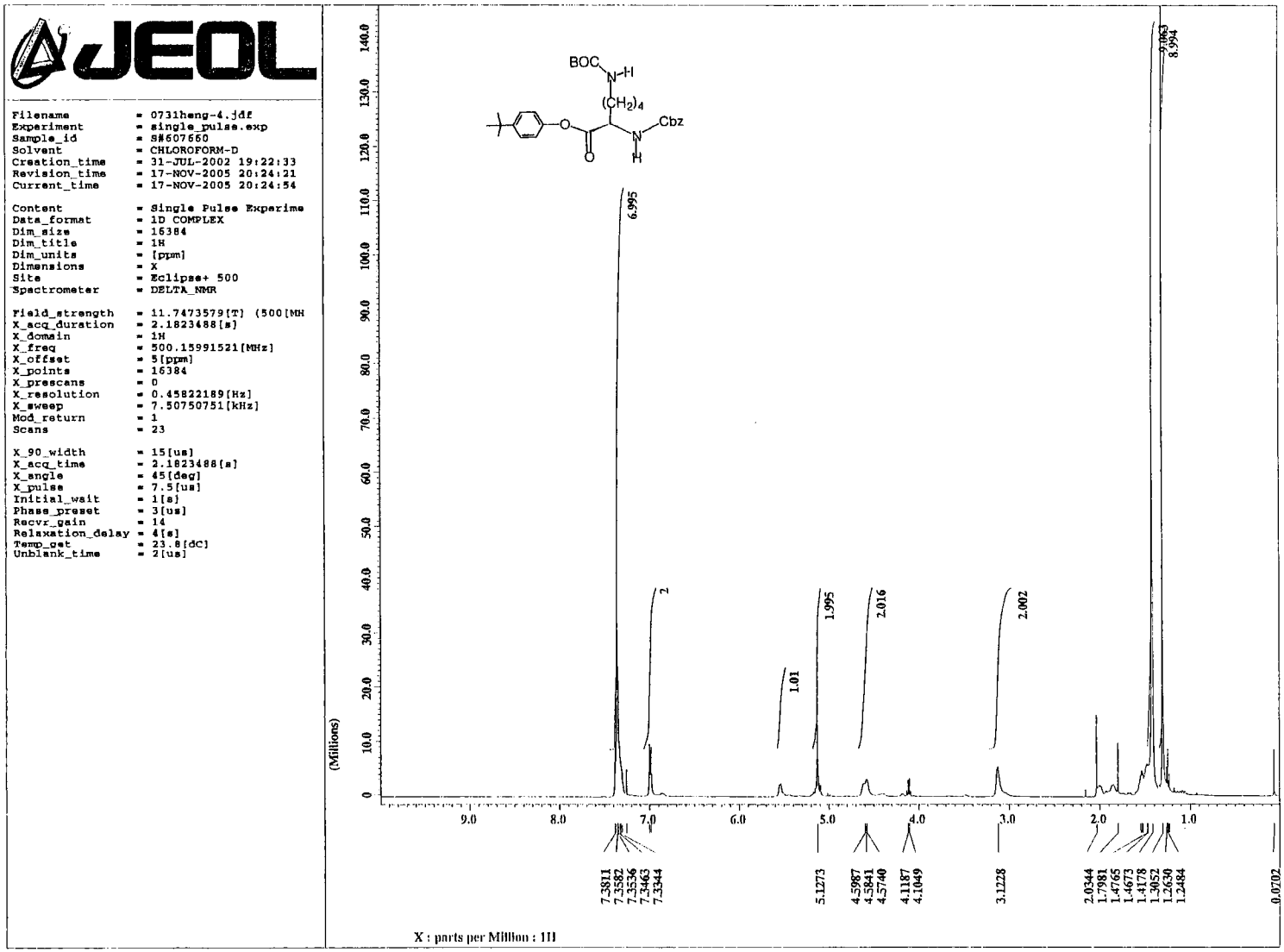
N-α-(*n*-Octanoyl)-(±)-lysine, *O*-benzyl ester, TFA salt (6)


JEOL
Filename = I_HX_66_BOCDeprotect1
Experiment = single_pulse.exp
Sample_id = SH310977
Solvent = CHLOROFORM-D
Creation_time = 25-NOV-2005 11:41:53
Revision_time = 17-NOV-2005 20:33:01
Current_time = 17-NOV-2005 20:33:31
Content = Single Pulse Experime
Data format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.18234888[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.18234888[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 15
Relaxation_delay = 1[s]
Temperature = 23.4[dC]
Unblank_time = 2[us]
NHR
(CH2)4
BnO
C(O)(CH2)8CH3
R = H+CF3C(O)OH
(Millionths)
X : parts per Million : 1H
8.755
8.166
7.481
7.334
7.279
7.151
7.105
6.771
6.711
5.159
5.143
5.120
4.550
4.540
2.927
2.258
2.244
2.227
1.549
1.352
1.281
1.253
1.243
0.856
0.842
0.067
3.029
2.025
2.002
0.999
0.996
5

APPENDIX 14

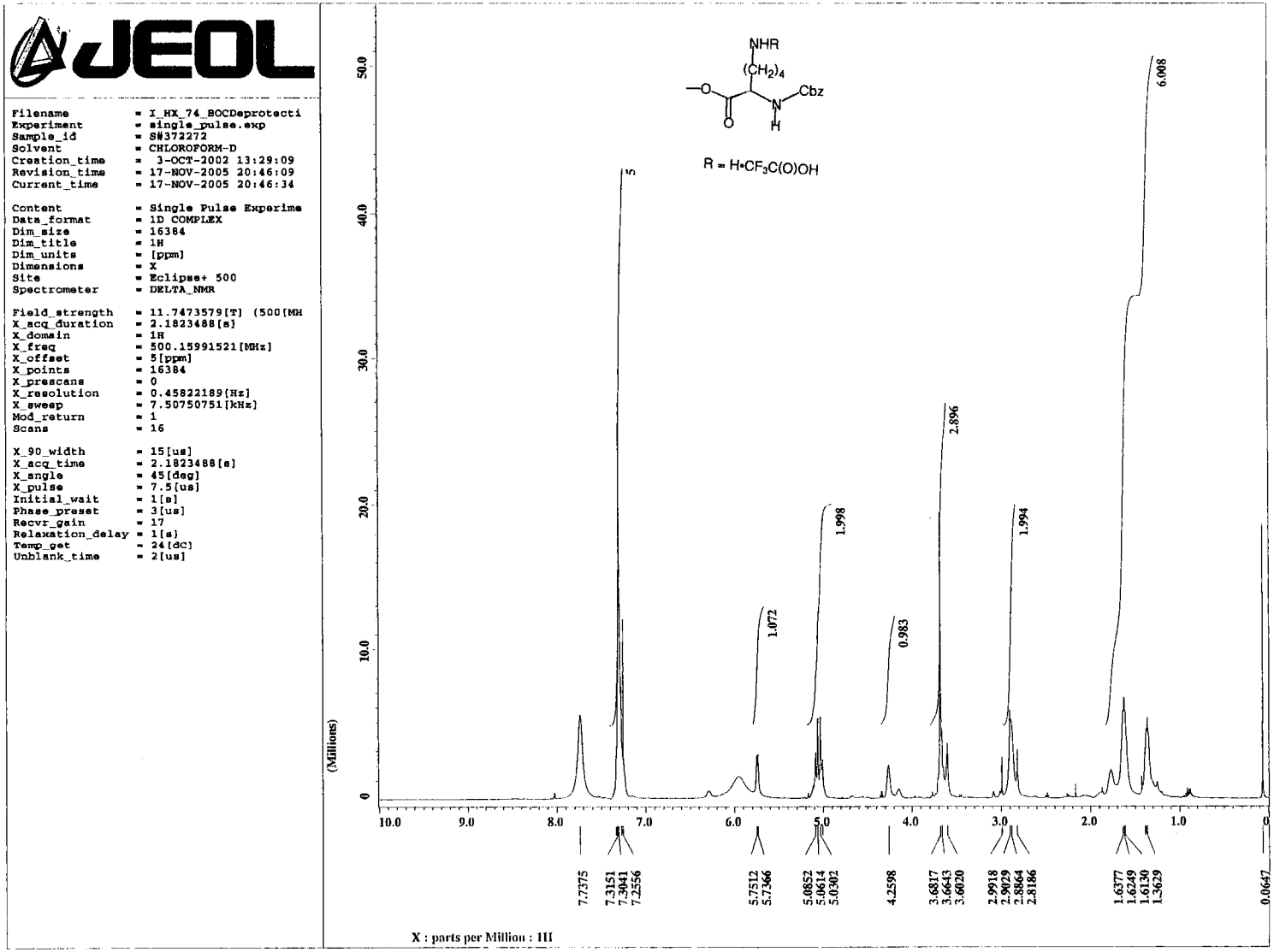
^{1}H NMR SPECTRUM OF

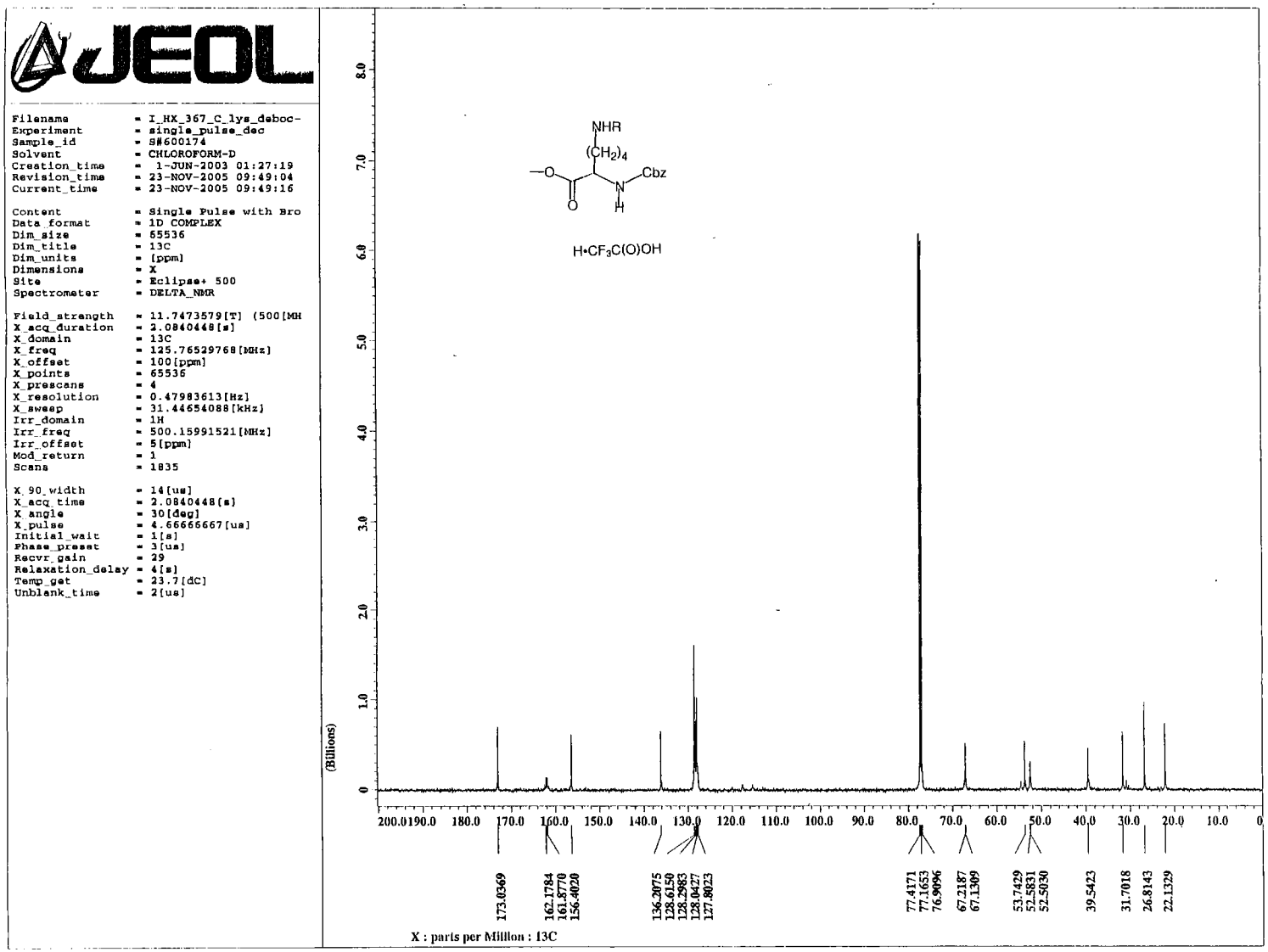
N-α-Cbz-*N*-ε-BOC-*l*-lysine, *O*-(4-*tert*-butyl)phenyl ester (9)


JEOL
Filename = 0731heng-4.jdf
Experiment = single_pulse.exp
Sample_id = S#607660
Solvent = CHLOROFORM-D
Creation_time = 31-JUL-2002 19:22:33
Revision_time = 17-NOV-2005 20:24:21
Current_time = 17-NOV-2005 20:24:54
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 23
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 14
Relaxation_delay = 4[s]
Temp_get = 23.8[dC]
Unblank_time = 2[us]
BOC
N-H
(CH2)4
Cbz
N
H
O
O
9.003
8.994
6.995
2
1.01
1.995
2.016
2.002
(Millions)
7.3811
7.3582
7.3536
7.3463
7.3344
5.1273
4.5987
4.5841
4.5740
4.1187
4.1049
3.1228
2.0344
1.7981
1.4765
1.4673
1.4178
1.3652
1.2630
1.2484
0.0702
X : parts per Million : 1H

APPENDIX 15

^{1}H NMR and ^{13}C NMR SPECTRA OF
N-α-Cbz-*l*-lysine, *O*-methyl ester, TFA salt (10)

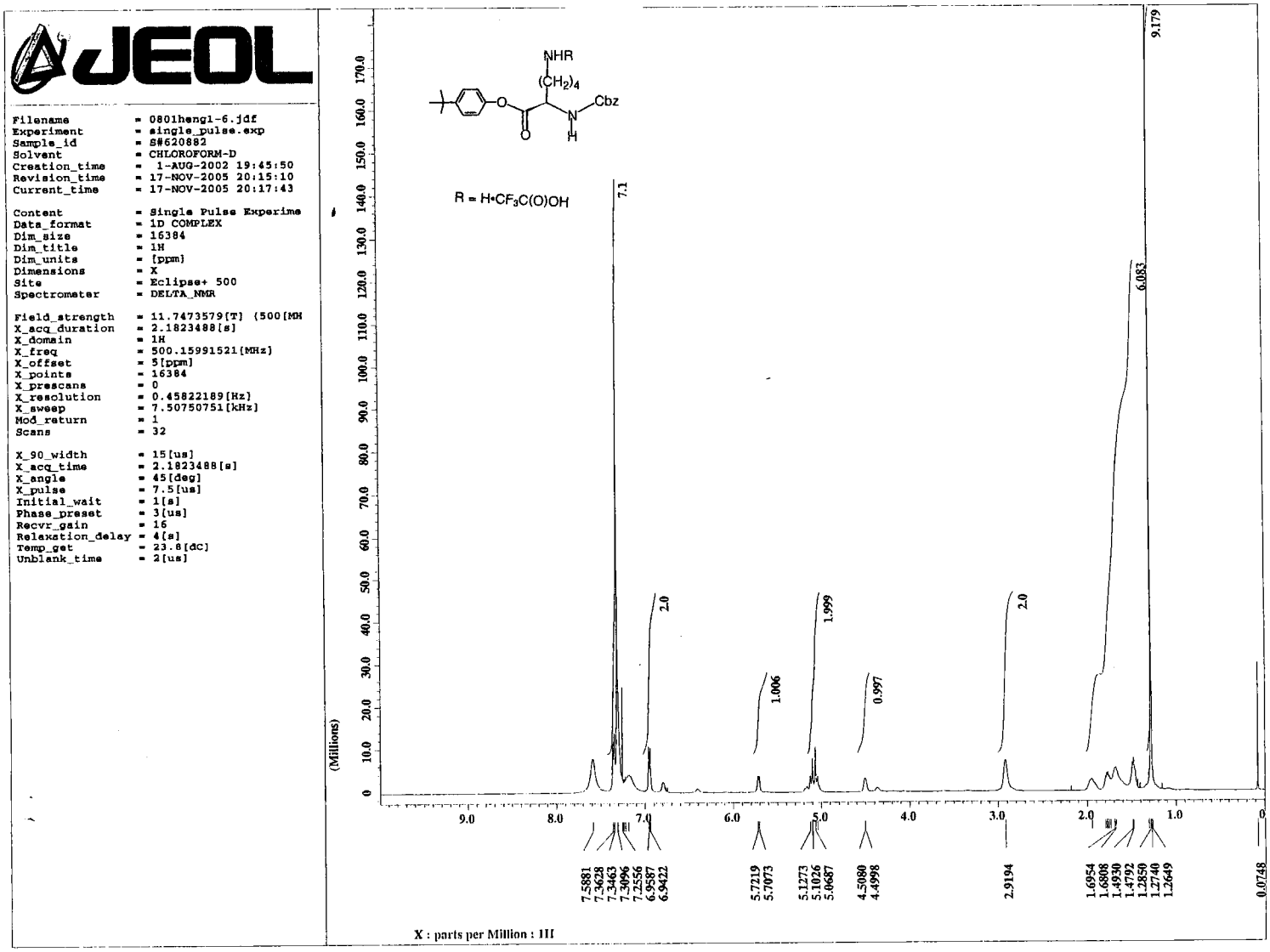

JEOL
Filename = I_HX_74_BOCDeprotecti
Experiment = single_pulse.exp
Sample_id = S#372272
Solvent = CHLOROFORM-D
Creation_time = 3-OCT-2002 13:29:09
Revision_time = 17-NOV-2005 20:46:09
Current_time = 17-NOV-2005 20:46:34
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 17
Relaxation_delay = 1[s]
Temp_get = 24[dC]
Unblank_time = 2[us]
NHR
(CH2)4
Cbz
R = H•CF3C(O)OH
(Millions)
50.0
40.0
30.0
20.0
10.0
0
1.072
1.998
0.983
2.896
1.994
6.008
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.7375
7.3151
7.3041
7.2556
5.7512
5.7366
5.0852
5.0614
5.0362
4.2598
3.6817
3.6643
3.6020
2.9918
2.9029
2.8864
2.8186
1.6377
1.6249
1.6130
1.3629
0.0647
X : parts per Million : 1H


JEOL
Filename = I_HX_367_C_lys_deboc-
Experiment = single_pulse_dec
Sample_id = S#600174
Solvent = CHLOROFORM-D
Creation_time = 1-JUN-2003 01:27:19
Revision_time = 23-NOV-2005 09:49:04
Current_time = 23-NOV-2005 09:49:16
Content = Single Pulse with Bro
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Mod_return = 1
Scans = 1835
X_90_width = 14[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.66666667[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 29
Relaxation_delay = 4[s]
Temp_get = 23.7[dC]
Unblank_time = 2[us]
NHR
(CH2)4
Cbz
H•CF3C(O)OH
(Billions)
X : parts per Million : 13C
173.0369
162.1784
161.8770
156.4020
136.2075
128.6150
128.2983
128.0427
127.8023
77.4171
77.1653
76.9096
67.2187
67.1309
53.7429
52.5831
52.5030
39.5423
31.7018
26.8143
22.1329

APPENDIX 16

^{1}H NMR SPECTRUM OF

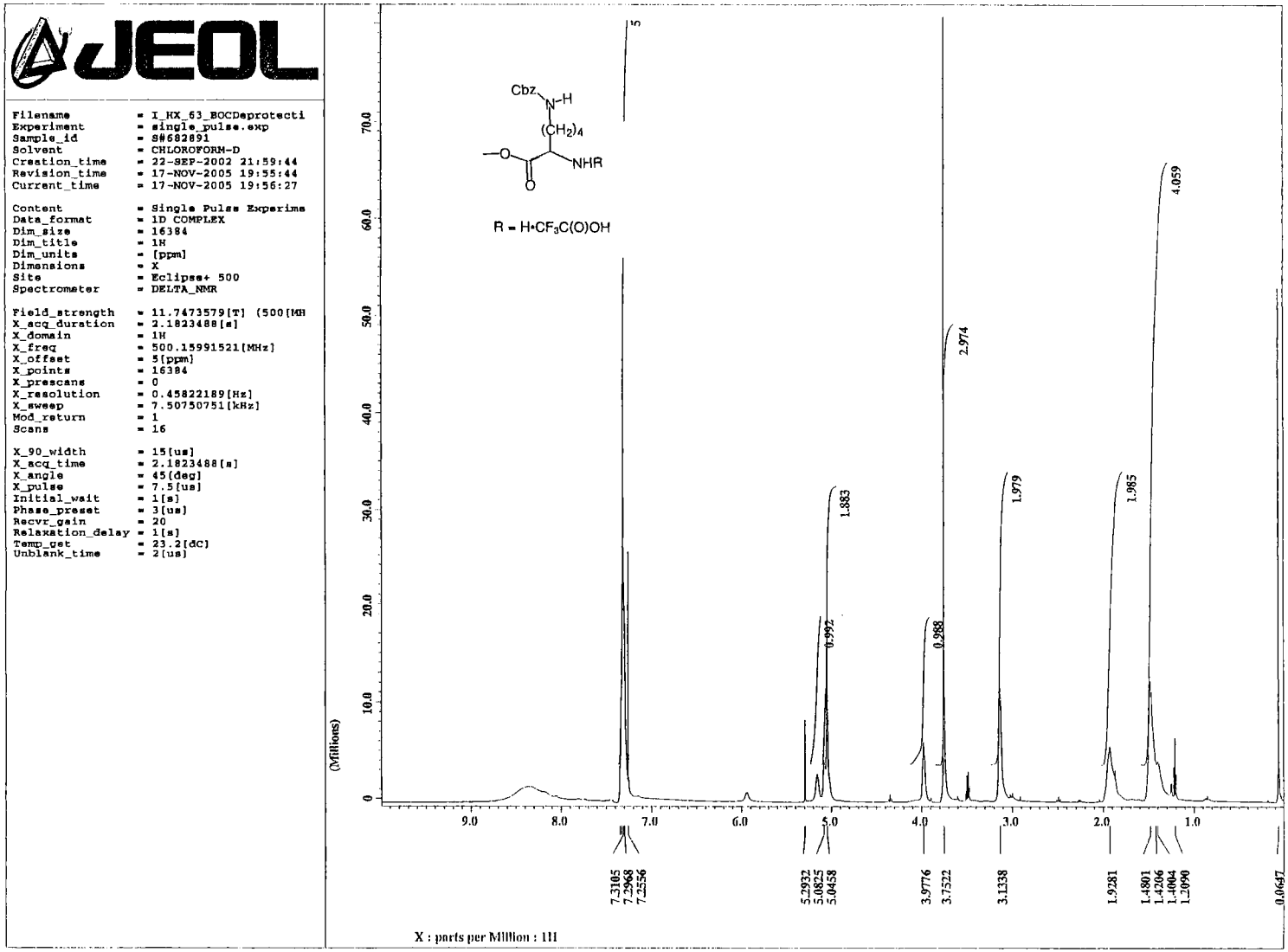
N-α-Cbz-*l*-lysine, *O*-(4-*tert*-butyl)phenyl ester, TFA salt (11)

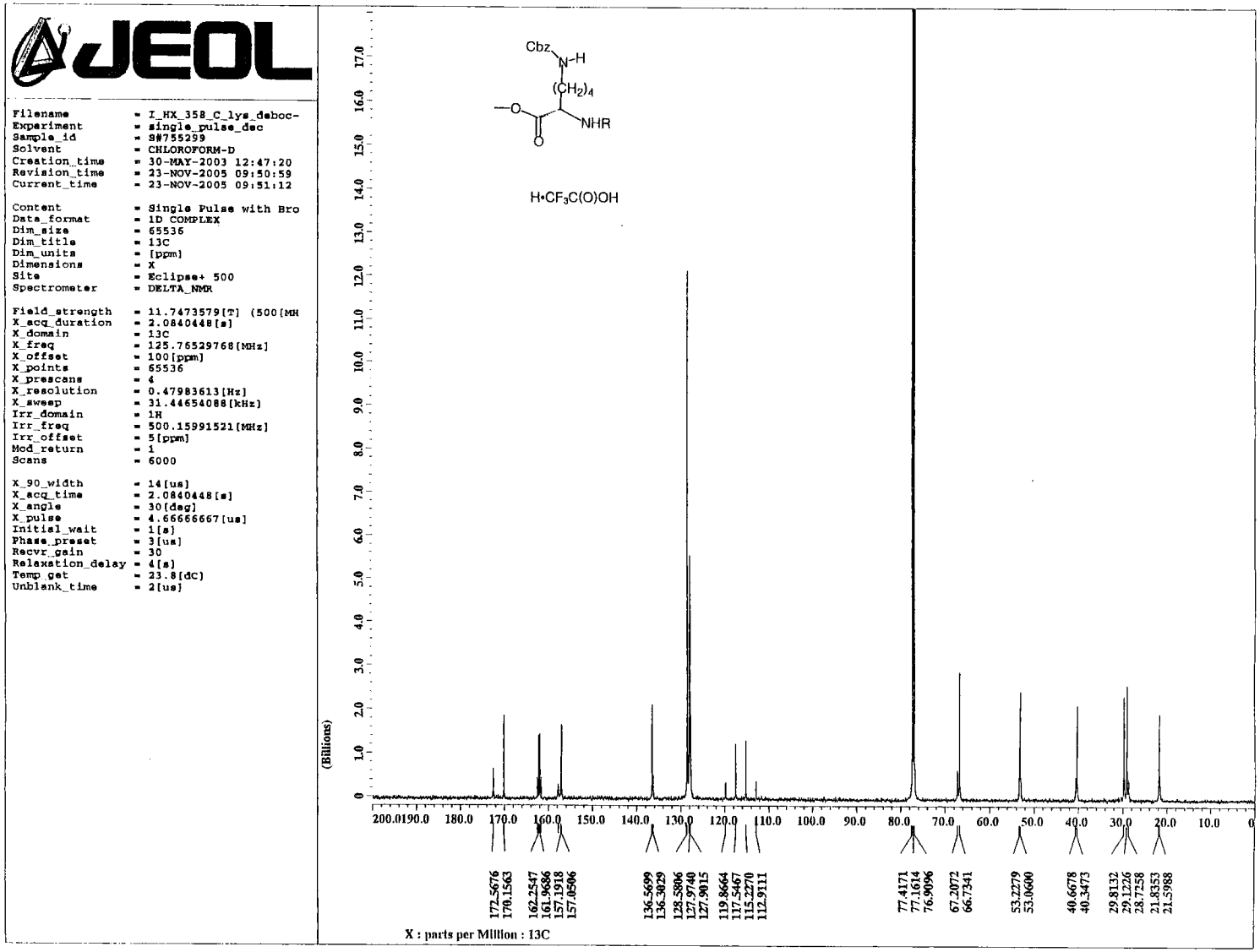

JEOL
Filename = 0801hengl-6.jdf
Experiment = single_pulse.exp
Sample_id = S#620882
Solvent = CHLOROFORM-D
Creation_time = 1-AUG-2002 19:45:50
Revision_time = 17-NOV-2005 20:15:10
Current_time = 17-NOV-2005 20:17:43
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 32
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 16
Relaxation_delay = 4[s]
Temp_get = 23.8[dC]
Unblank_time = 2[us]
NHR
(CH2)4
Cbz
O
N
H
R = H•CF3C(O)OH
(Millions)
X : parts per Million : 1H

APPENDIX 17

^{1}H NMR and ^{13}C NMR SPECTRA OF

N-ε-Cbz-*l*-lysine, *O*-methyl ester, TFA salt (15)

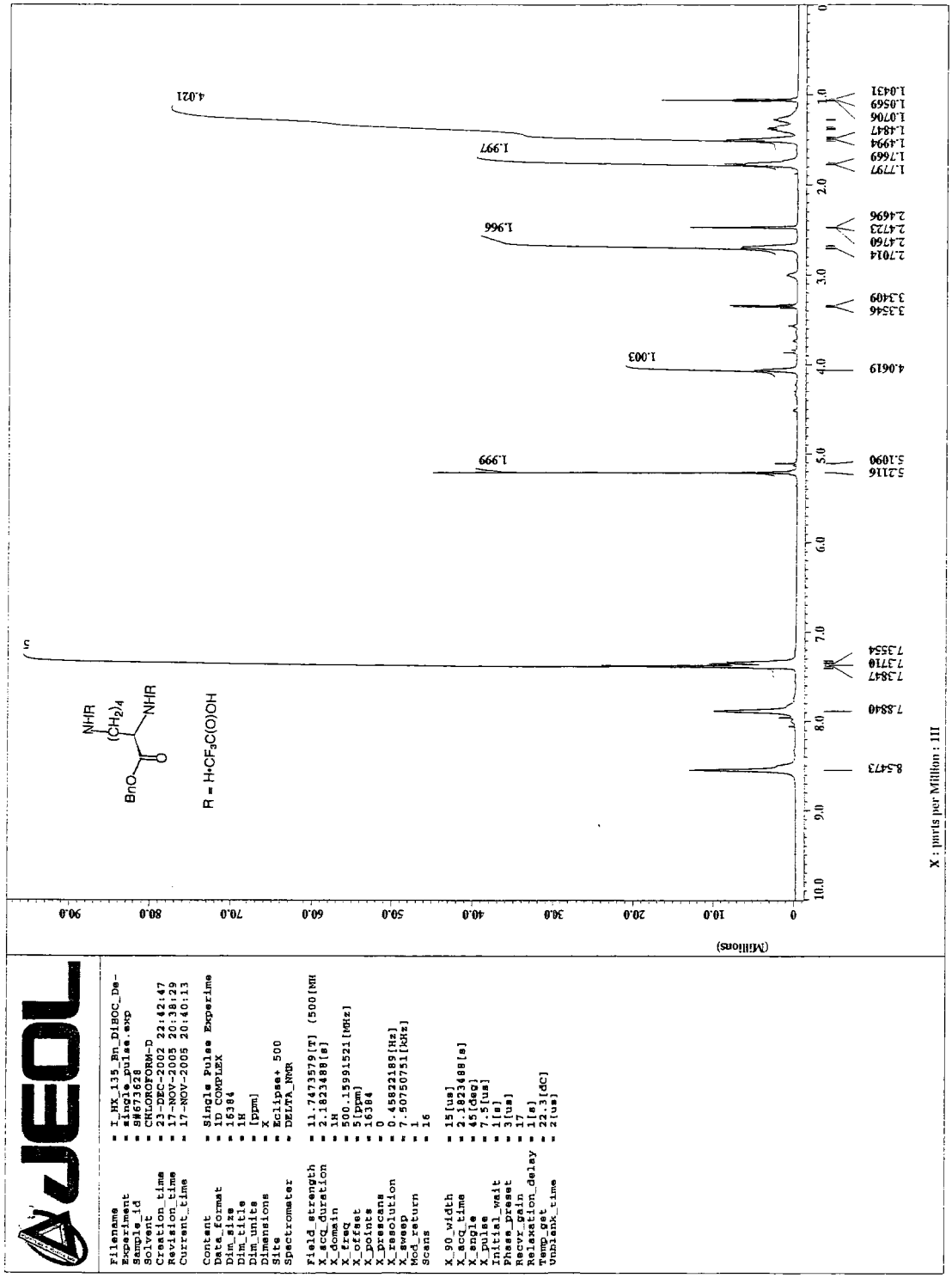

JEOL
Filename = I_HX_63_BOCDeprotecti
Experiment = single_pulse.exp
Sample_id = S#682891
Solvent = CHLOROFORM-D
Creation_time = 22-SEP-2002 21:59:44
Revision_time = 17-NOV-2005 19:55:44
Current_time = 17-NOV-2005 19:56:27
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 20
Relaxation_delay = 1[s]
Temp_set = 23.2[dC]
Unblank_time = 2[us]
Cbz
N-H
(CH2)4
O
NHR
O
R = H•CF3C(O)OH
(Millions)
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
4.059
2.974
1.883
1.979
1.985
0.992
0.988
7.3105
7.2968
7.2556
5.2932
5.0825
5.0458
3.9776
3.7522
3.1338
1.9281
1.4801
1.4206
1.4004
1.2090
0.0647
X : parts per Million : 111


JEOL
Filename = I_HX_358_C_lys_deboc-
Experiment = single_pulse_dec
Sample_id = S#755299
Solvent = CHLOROFORM-D
Creation_time = 30-MAY-2003 12:47:20
Revision_time = 23-NOV-2005 09:50:59
Current_time = 23-NOV-2005 09:51:12
Content = Single Pulse with Bro
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Mod_return = 1
Scans = 6000
X_90_width = 14[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.66666667[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 4[s]
Temp_get = 23.8[dC]
Unblank_time = 2[us]
Cbz
N-H
(CH2)4
O
NHR
O
H•CF3C(O)OH
(Billions)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
172.5676
170.1563
162.2547
161.9686
157.1918
157.0506
136.5699
136.3029
128.5806
127.9740
127.9015
119.8664
117.5467
115.2270
112.9111
77.4171
77.1614
76.9096
67.2072
66.7341
53.2279
53.0600
40.6678
40.3473
29.8132
29.1226
28.7258
21.8353
21.5988
X : parts per Million : 13C

APPENDIX 18

^{1}H NMR SPECTRUM OF

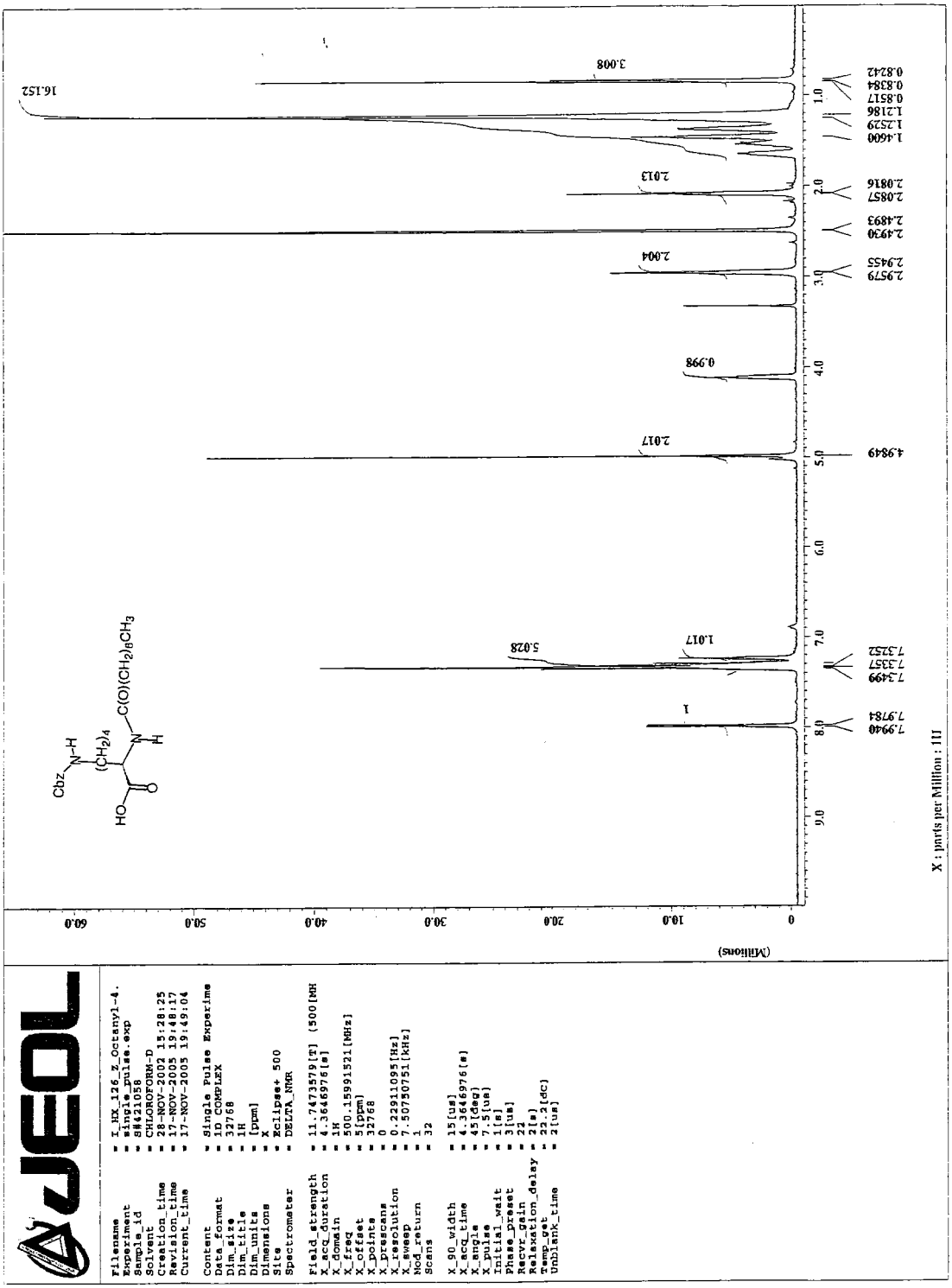
N-ε-Cbz-*l*-lysine, *O*-benzyl ester, TFA salt (20)


JEOL
Filename = T_HX_135_Bn_DiBOC_De-
Experiment = single_pulse.exp
Sample_id = #673628
Solvent = CHLOROFORM-D
Creation_time = 23-DEC-2002 22:42:47
Revision_time = 17-NOV-2005 20:38:29
Current_time = 17-NOV-2005 20:40:13
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 17
Relaxation_delay = 1[s]
Temp_get = 22.3[dC]
Unblank_time = 2[us]
NHR
(CH2)4
NHR
BnO
O
R = H•CF3C(O)OH
5
4.021
1.997
1.966
1.003
1.999
8.5473
7.8840
7.3847
7.3710
7.3554
5.1116
5.1090
4.0619
3.3546
3.3409
2.7014
2.4760
2.4723
2.4696
1.7797
1.7669
1.4994
1.4847
1.0706
1.0569
1.0431
(Millions)
X : parts per Million : 1H

APPENDIX 19

^{1}H NMR SPECTRUM OF

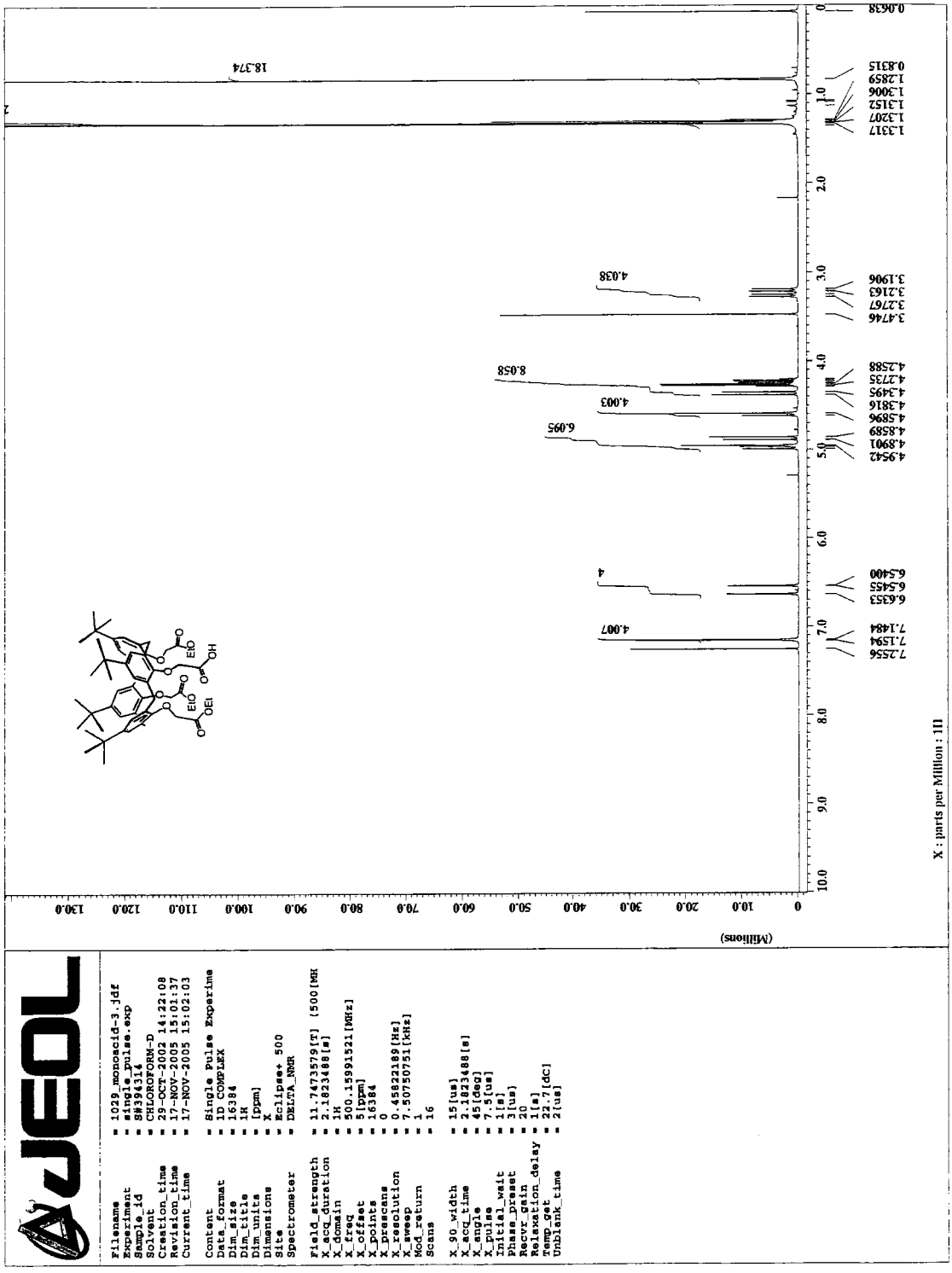
N-α-(*n*-Octanoyl)-*N*-ε-Cbz-(±)-lysine (22)


Filename = T_HX_126_Z_Octanyl-4.
Experiment = single_pulse.exp
Sample_id = sH421058
Solvent = CHLOROFORM-D
Creation_time = 28-NOV-2002 15:28:25
Revision_time = 17-NOV-2005 19:48:17
Current_time = 17-NOV-2005 19:49:04
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 1.3646976[s]
X_domain = 1H
X_freq = 500.15991321[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.229110095[Hz]
X_sweep = 7.50730751[kHz]
Nod_return = 1
Scans = 32
X_90_width = 15[us]
X_acq_time = 4.3646976[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 22
Relaxation_delay = 2[s]
Temp_get = 22.2[dc]
UnblankX_time = 2[us]
Cbz
HO
C(O)(CH2)8CH3
16.152
3.008
2.013
2.004
0.998
2.017
4.9849
1.017
5.028
1
7.9940
7.9784
7.3499
7.3357
7.3252
2.9579
2.9455
2.4930
2.4893
2.0857
2.0816
1.4600
1.2529
1.2186
0.8517
0.8384
0.8242
(Millions)
X : parts per Million : 1H

APPENDIX 20

^{1}H NMR SPECTRUM OF

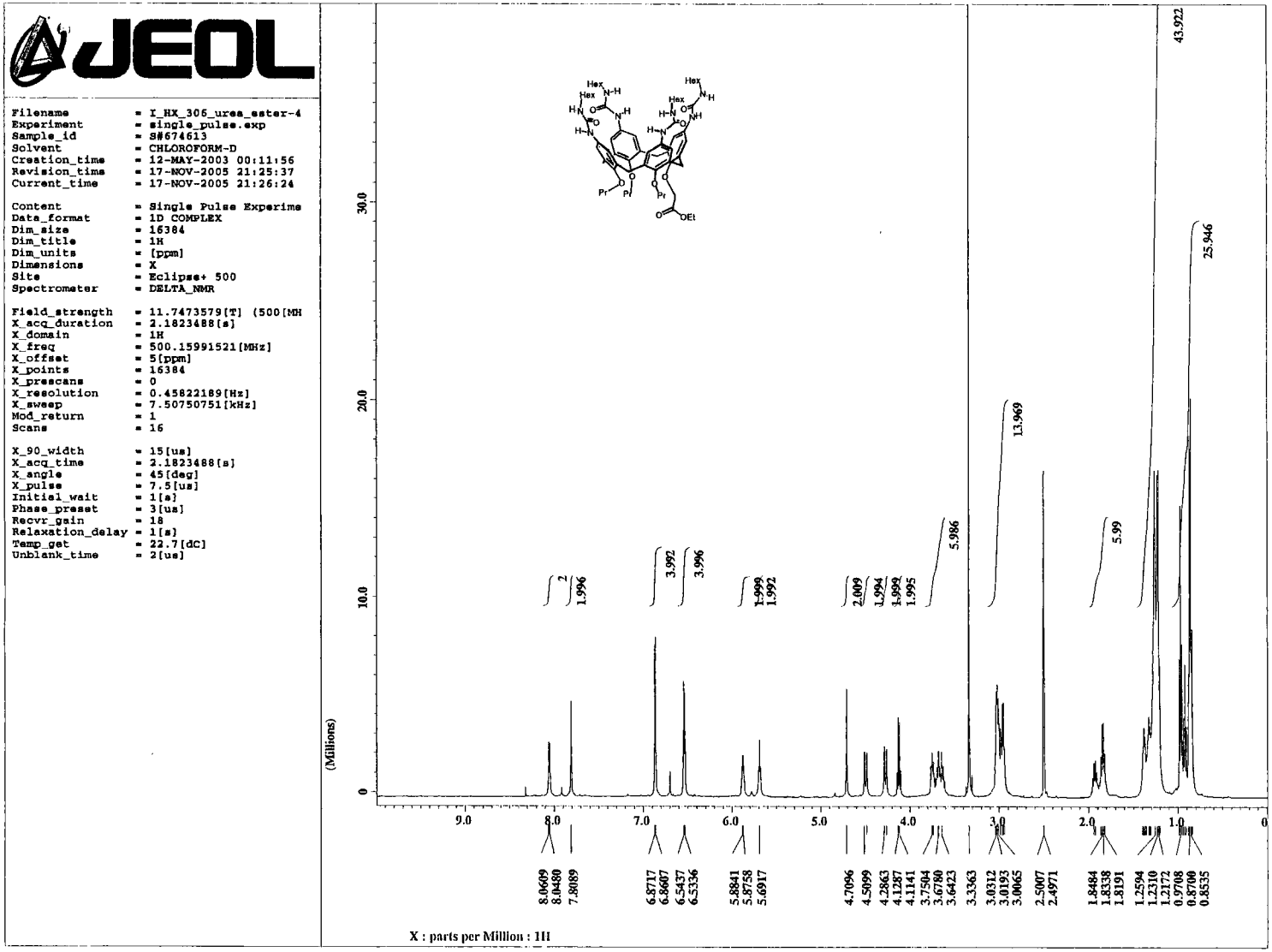
Calixarene monoacid (25)


JEOL
Filename = 1029_monoacid-3.jdf
Experiment = single_pulse.exp
Sample_id = SW394314
Solvent = CHLOROFORM-D
Creation_time = 29-OCT-2002 14:22:08
Revision_time = 17-NOV-2005 15:01:37
Current_time = 17-NOV-2005 15:02:03
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.18234688[s]
X_domain = 1H
X_freq = 500.159921521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.458221189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.18234688[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 20
Relaxation_delay = 1[s]
Temp_get = 22.7[dC]
Unblank_time = 2[us]
OEt
OEt
OEt
OH
18.374
8.058
6.095
4.038
4.003
4.007
4
(Millions)
X : parts per Million : 1H

APPENDIX 21

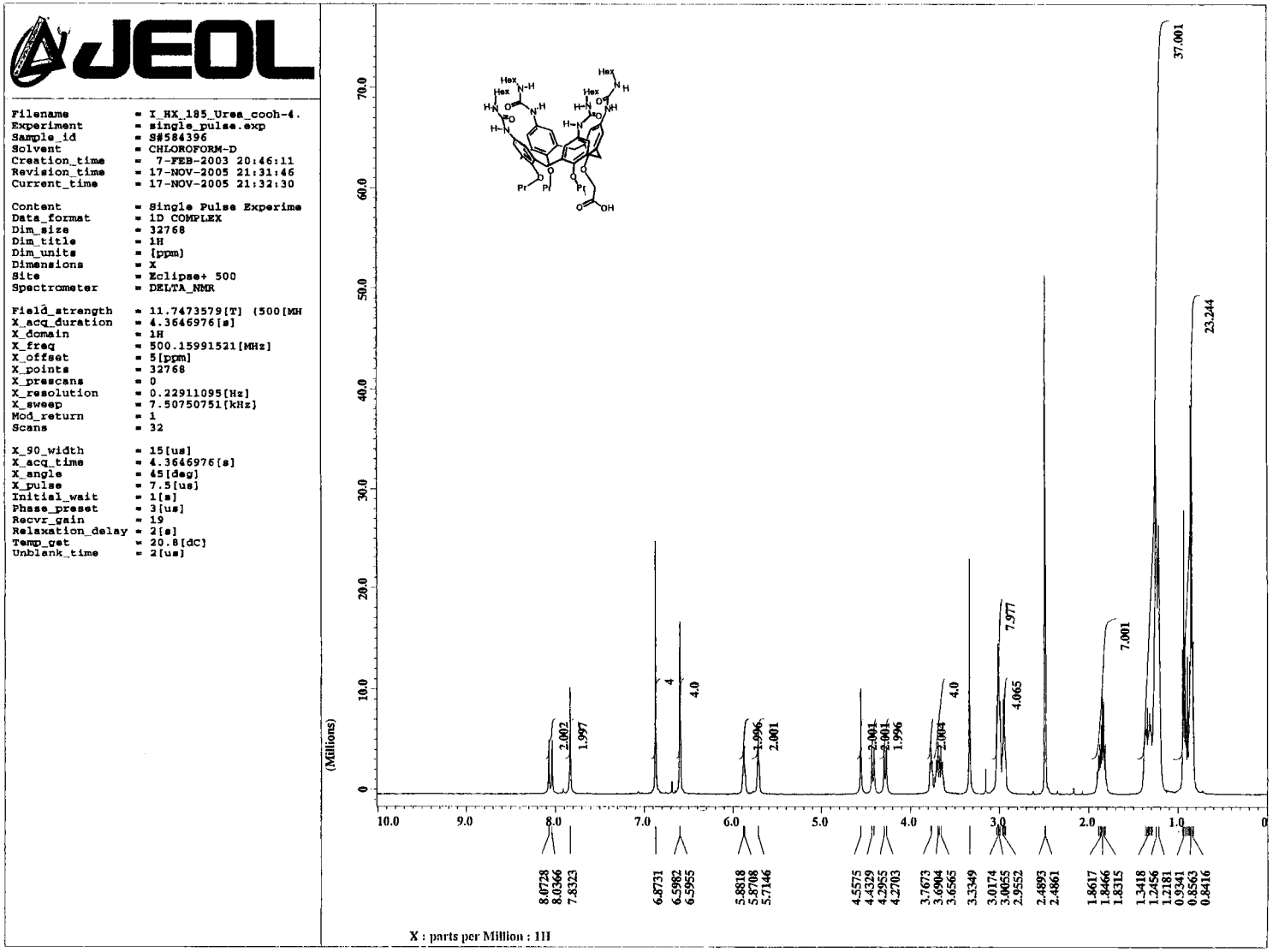
^{1}H NMR SPECTRUM OF

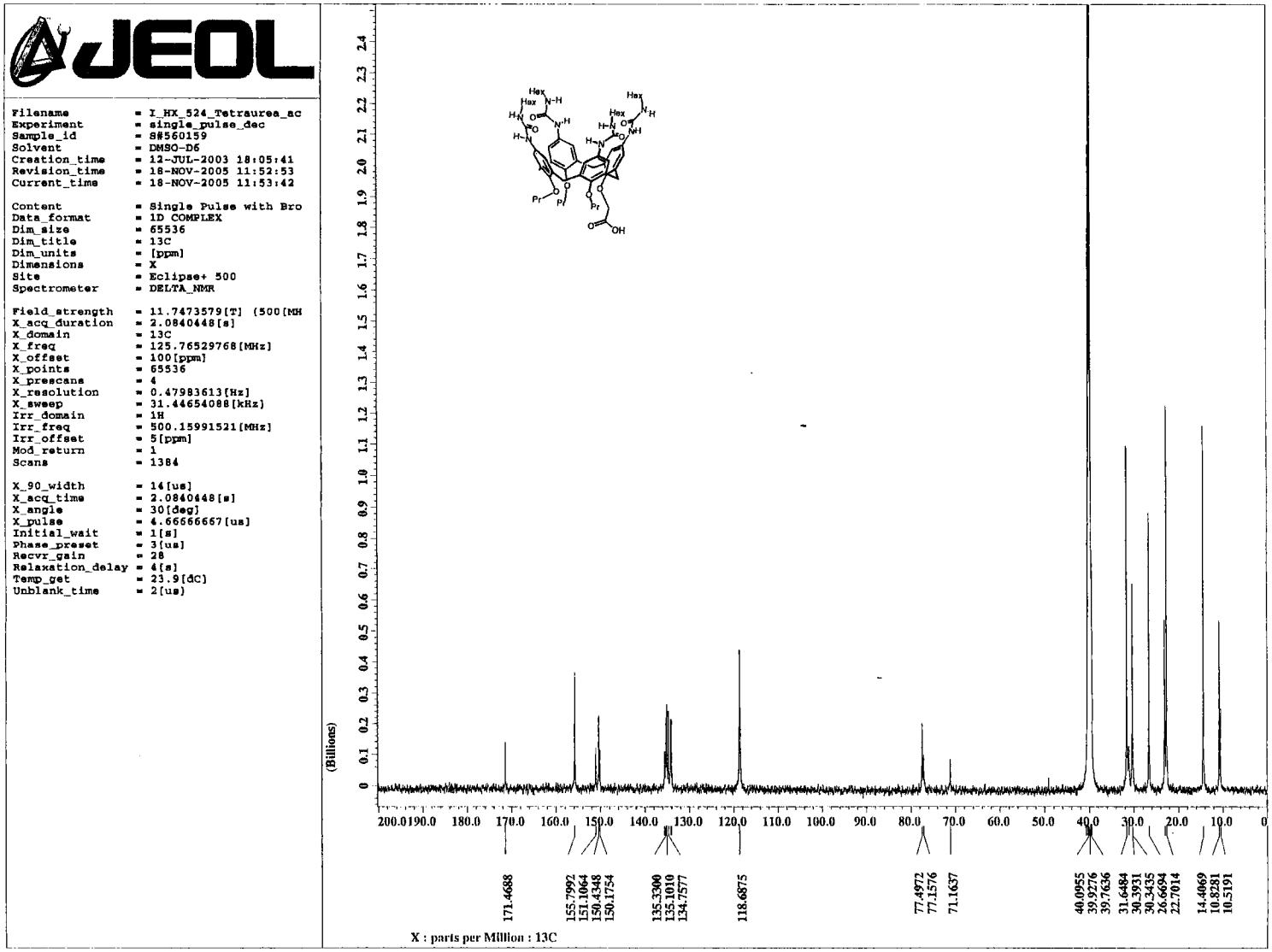
Calixarene tetraurea monoester (31)


JEOL
Filename = I_HX_306_urea_ester-4
Experiment = single_pulse.exp
Sample_id = S#674613
Solvent = CHLOROFORM-D
Creation_time = 12-MAY-2003 00:11:56
Revision_time = 17-NOV-2005 21:25:37
Current_time = 17-NOV-2005 21:26:24
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 18
Relaxation_delay = 1[s]
Temp_get = 22.7[dC]
Unblank_time = 2[us]
(Millions)
X : parts per Million : 1H

APPENDIX 22

^{1}H NMR, ^{13}C NMR and MASS SPECTRA OF
Calixarene tetraurea acid (32)

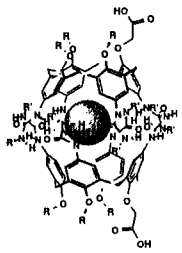

JEOL
Filename = I_HX_185_Urea_cooh-4.
Experiment = single_pulse.exp
Sample_id = S#584396
Solvent = CHLOROFORM-D
Creation_time = 7-FEB-2003 20:46:11
Revision_time = 17-NOV-2005 21:31:46
Current_time = 17-NOV-2005 21:32:30
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 4.3646976[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.22911095[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 32
X_90_width = 15[us]
X_acq_time = 4.3646976[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 19
Relaxation_delay = 2[s]
Temp_get = 20.8[dC]
Unblank_time = 2[us]
(Millions)
X : parts per Million : 1H


JEOL
Filename = I_HX_524_Tetraurea_ac
Experiment = single_pulse_dec
Sample_id = S#560159
Solvent = DMSO-D6
Creation_time = 12-JUL-2003 18:05:41
Revision_time = 18-NOV-2005 11:52:53
Current_time = 18-NOV-2005 11:53:42
Content = Single Pulse with Bro
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Mod_return = 1
Scans = 1384
X_90_width = 14[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.66666667[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 28
Relaxation_delay = 4[s]
Temp_get = 23.9[dC]
Unblank_time = 2[us]
(Billions)
171.4688
155.7992
151.1064
150.4348
150.1754
135.3300
135.1010
134.7577
118.6875
77.4972
77.1576
71.1637
40.0955
39.9276
39.7636
31.6484
30.3931
30.3435
26.6694
22.7014
14.4069
10.8281
10.5191
X : parts per Million : 13C

JEOL
Filename = I_HX_420_urea_acid_wh
Experiment = single_pulse.exp
Sample_id = S#510893
Solvent = CHLOROFORM-D
Creation_time = 15-JUN-2003 20:01:28
Revision_time = 16-JUN-2003 13:04:42
Current_time = 17-NOV-2005 21:38:48
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.159991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.458222189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 3[s]
Phase_preset = 1[us]
Relaxation_delay = 15[s]
Temp_get = 22.6[dC]
Unblank_time = 2[us]
R = n-Pr, R' = n-Hexyl
(Millions)
X : parts per Million : 1H
8.1781
7.7888
7.5130
7.4553
7.4498
6.8378
6.5996
6.3348
6.2112
6.2047
5.0156
4.5062
4.4595
4.4357
4.0967
3.9565
3.8841
3.5616
3.5506
3.4783
3.0907
3.0669
2.1663
1.6991
1.6835
1.6698
1.4243
1.1842
0.8709
0.8691
0.7307
0.0629
-0.0022

JEOL

Filename	= I_HX_428_urea_acid_gr
Experiment	= single_pulse.exp
Sample_id	= S#460122
Solvent	= CHLOROFORM-D
Creation_time	= 16-JUN-2003 18:37:25
Revision_time	= 17-NOV-2005 21:40:41
Current_time	= 17-NOV-2005 21:42:30
Content	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 16384
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.1823488[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 0
X_resolution	= 0.45822189[Hz]
X_sweep	= 7.50750751[kHz]
Mod_return	= 1
Scans	= 16
X_90_width	= 15[us]
X_acq_time	= 2.1823488[s]
X_angle	= 45[deg]
X_pulse	= 7.5[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 15
Relaxation_delay	= 1[s]
Temp_get	= 22.8[dC]
Unblank_time	= 2[us]



R = *n*-Pr, R' = *n*-Hexyl

APPENDIX 23

^{1}H NMR SPECTRUM OF

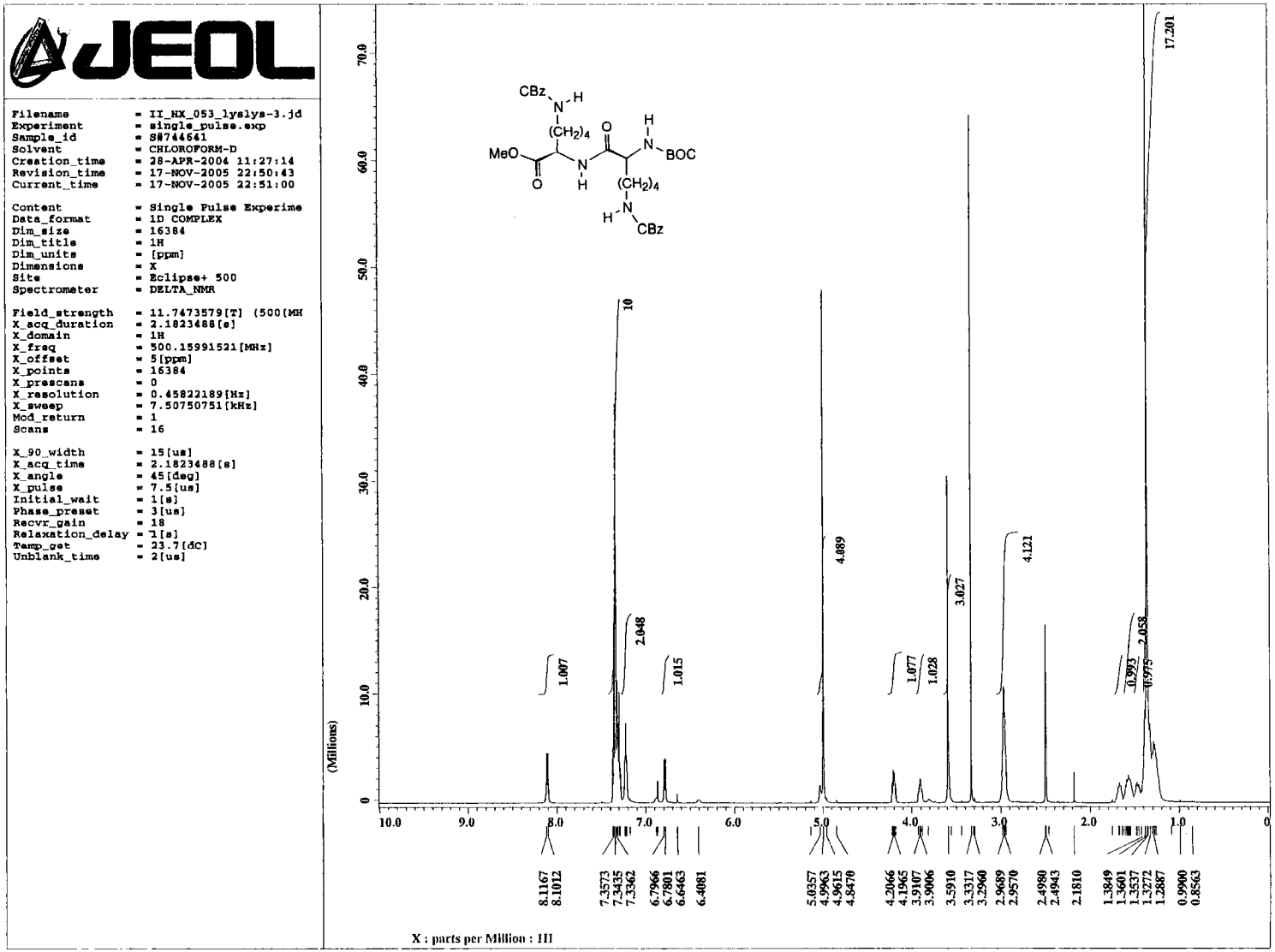
Lysine dipeptide (33)

JEOL
Filename = T_HX_81_Dipeptide_DMS
Experiment = single_pulse.exp
Sample_id = S#470969
Solvent = CHLOROFORM-D
Creation_time = 17-OCT-2002 16:25:40
Revision_time = 17-NOV-2005 22:37:29
Current_time = 17-NOV-2005 22:37:40
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 4.3646976[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.22911095[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 32
X_90_width = 15[us]
X_acq_time = 4.3646976[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 14
Relaxation_delay = 2[s]
Temp_get = 22.9[dC]
Unblank_time = 2[us]
(Millions)
X : parts per Million : 1H
16.069
11.946
4.002
3.005
3.043
2.028
2.028
3.099
2.078
1.042
1.082
2
1.006
0.969
8.2074
8.1928
7.8424
7.8350
6.7421
6.7361
6.7302
5.7480
5.5836
5.5676
4.1883
4.1773
4.1727
4.1617
3.6097
3.6010
3.3702
3.3372
2.8677
2.8562
2.5012
2.4975
2.1091
2.0953
2.0816
1.4627
1.3601
1.3294
1.2607
1.2452
1.2273
0.8480
0.8338

APPENDIX 24

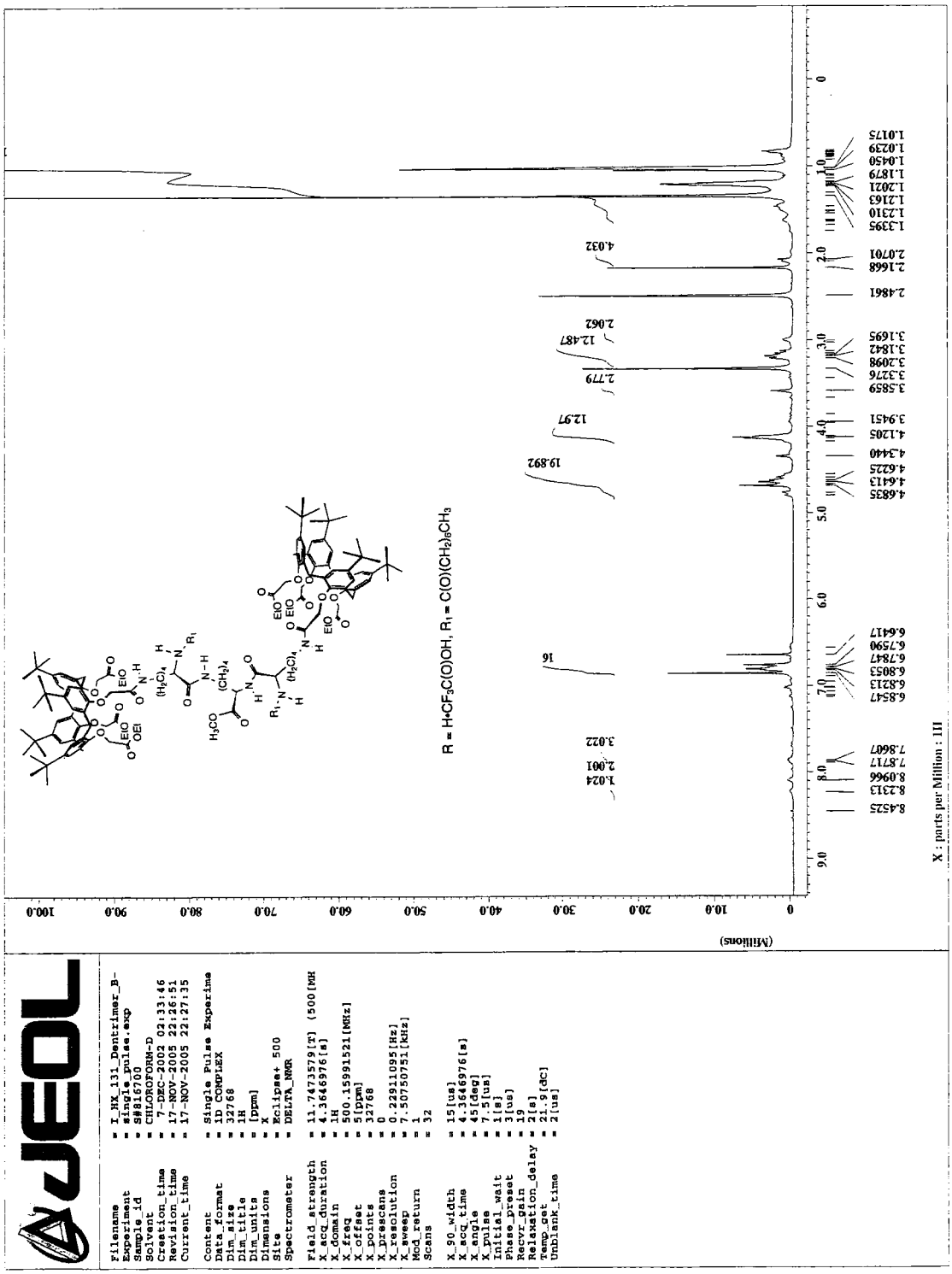
^{1}H NMR SPECTRUM OF

Lysine dipeptide (35)


JEOL
Filename = II_HX_053_lyslys-3.jd
Experiment = single_pulse.exp
Sample_id = S#744641
Solvent = CHLOROFORM-D
Creation_time = 28-APR-2004 11:27:14
Revision_time = 17-NOV-2005 22:50:43
Current_time = 17-NOV-2005 22:51:00
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 18
Relaxation_delay = 1[s]
Temp_get = 23.7[dC]
Unblank_time = 2[us]
CBz
N
H
(CH2)4
O
H
N
BOC
MeO
N
H
(CH2)4
H
N
CBz
O
(Millions)
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
17.201
10
4.889
4.121
3.027
2.048
2.058
1.067
1.015
1.077
1.028
0.993
0.975
8.1167
8.1012
7.3573
7.3435
7.3362
6.7966
6.7801
6.6463
6.4081
5.0357
4.9963
4.9615
4.8470
4.2066
4.1965
3.9107
3.9006
3.5910
3.3317
3.2960
2.9689
2.9570
2.4980
2.4943
2.1810
1.3849
1.3601
1.3537
1.3272
1.2587
0.9990
0.8563
X : parts per Million : 1H

APPENDIX 25

^{1}H NMR and MASS SPECTRA OF
Calixarene dendrimer (37a)

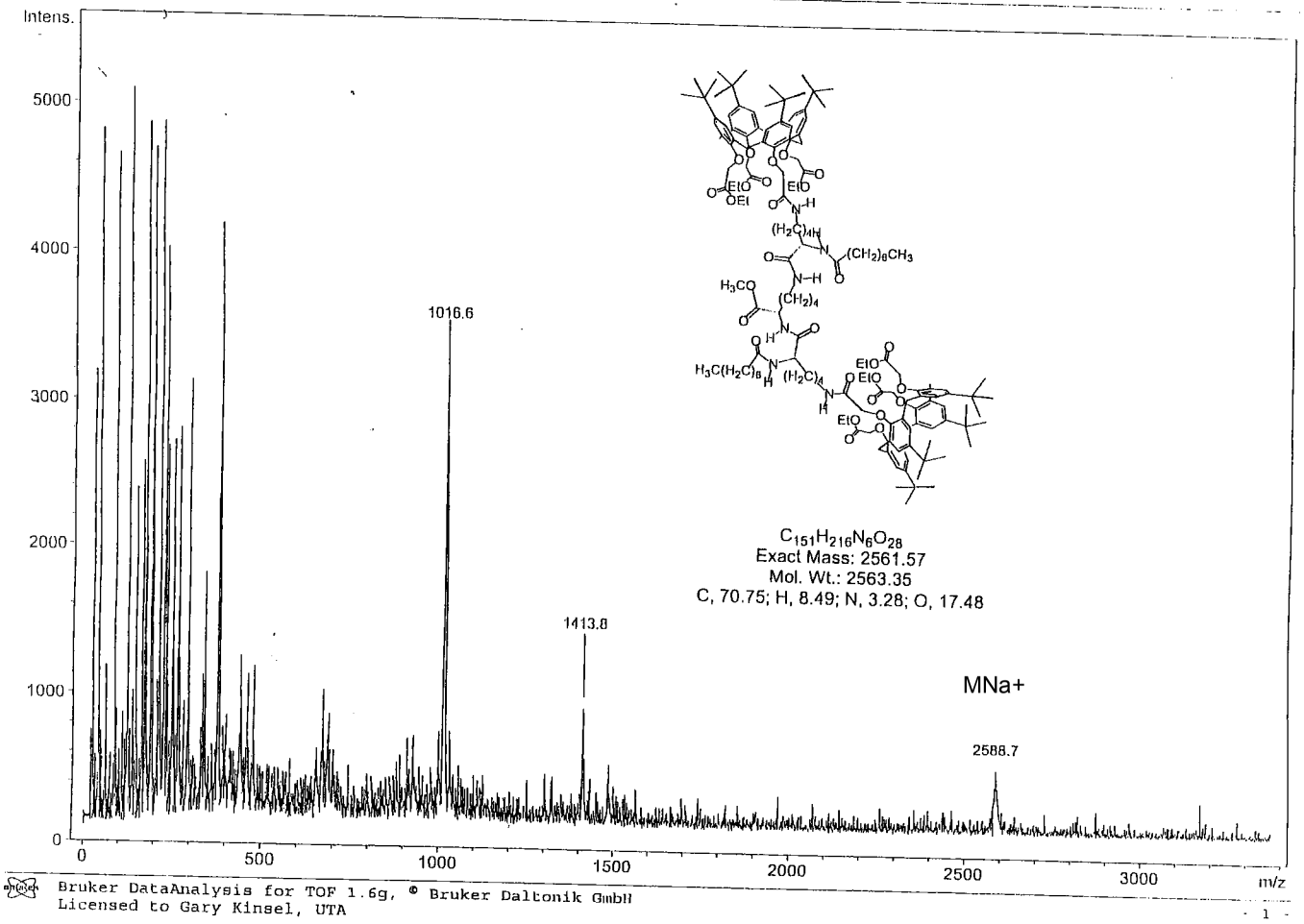

JEOL
Filename = I_HX_131_Dentrimer_B-
Experiment = single_pulse.exp
Sample_id = SH816700
Solvent = CHLOROFORM-D
Creation_time = 7-DEC-2002 02:33:46
Revision_time = 17-NOV-2005 22:26:51
Current_time = 17-NOV-2005 22:27:35
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.74735791[T] (500[MH
X_acq_duration = 4.36469761[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.22911095[Hz]
X_sweep = 7.50750751[kHz]
Wod_return = 1
Scans = 32
X_90_width = 15[us]
X_acq_time = 4.36469761[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 19
Relaxation_delay = 2[s]
Temp_get = 21.9[dC]
UnBlank_time = 2[us]
R = H•CF3C(O)OH, R1 = C(O)(CH2)6CH3
16
19.892
12.97
12.487
4.032
3.022
2.779
2.062
2.024
2.001
X : parts per Million : 1H
(Millions)

Display Report

Analysis Info:

File: C:\DOCUME~1\ALLUSE~1\DOCUME~1\HENG\DENTRR~1\1LIN
Date acquired: Mon Dec 09 21:36:13 2002
Instrument: TOF
Operator :

Printed: Mon Dec 09 22:00:41 2002

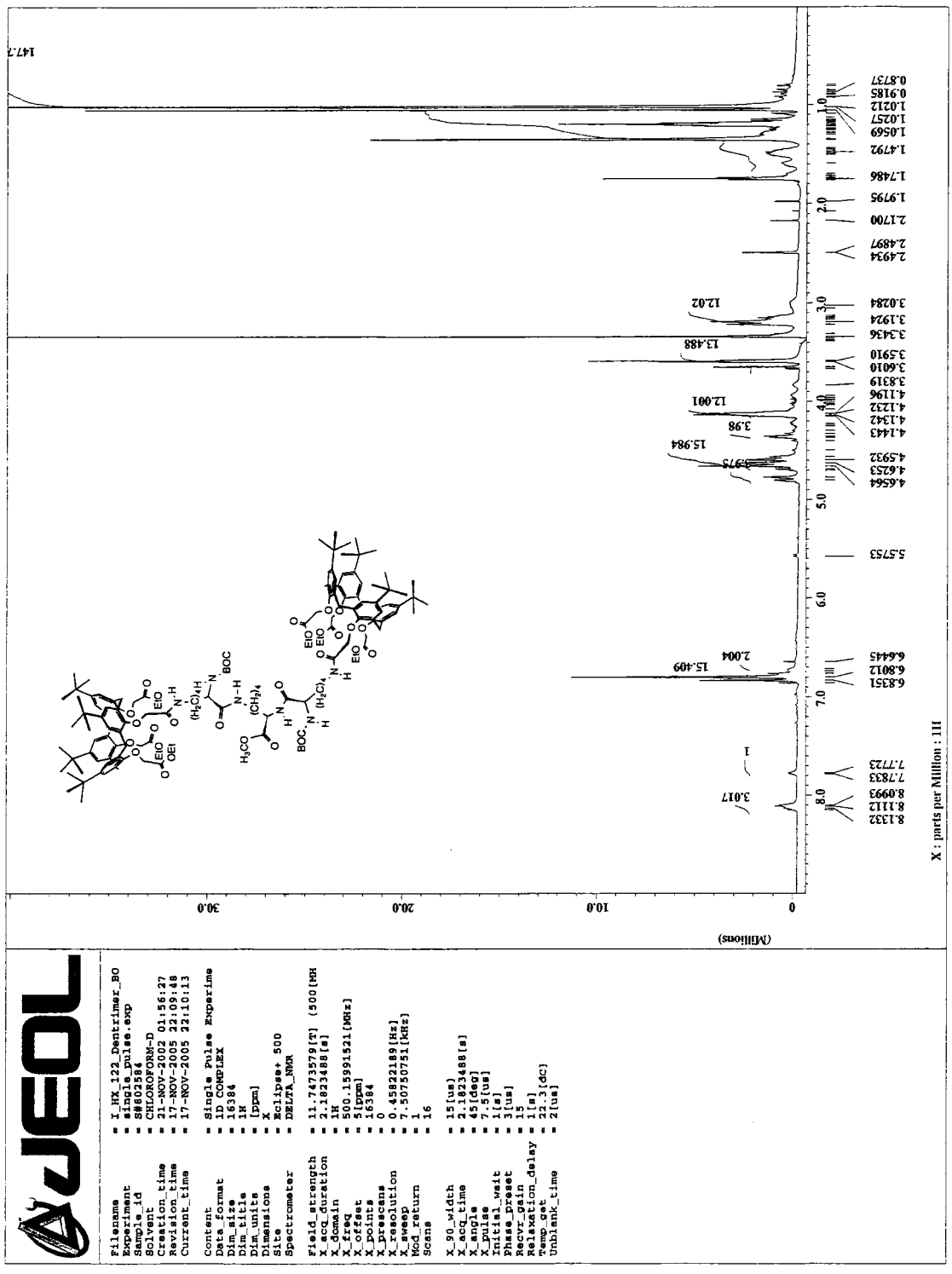


$C_{151}H_{216}N_6O_{28}$
Exact Mass: 2561.57
Mol. Wt.: 2563.35
C, 70.75; H, 8.49; N, 3.28; O, 17.48

APPENDIX 26

^{1}H NMR and MASS SPECTRA OF

Calixarene dendrimer (37b)


JEOL
Filename = I_HK_122_Dentrimer_BO
Experiment = single_pulse.exp
Sample_id = S#8021584
Solvent = CHLOROFORM-D
Creation_time = 21-NOV-2002 01:56:27
Revision_time = 17-NOV-2005 22:09:48
Current_time = 17-NOV-2005 22:10:13
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.458221891[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 15
Relaxation_delay = 1[s]
Temp_get = 22.3[dC]
Unblank_time = 2[us]
(Millions)
X : parts per Million : 1H
8.1332
8.1112
8.0993
7.7833
7.7723
6.8351
6.8012
6.6445
5.5753
4.6564
4.6253
4.5932
4.1443
4.1342
4.1232
4.1196
3.8319
3.6010
3.5910
3.3436
3.1924
3.0284
2.4934
2.4897
2.1700
1.9795
1.7486
1.4792
1.0569
1.0257
1.0212
0.9185
0.8737
3.017
2.004
15.409
3.98
15.984
12.001
13.488
12.02
147.7

Display Report

Analysis Info:
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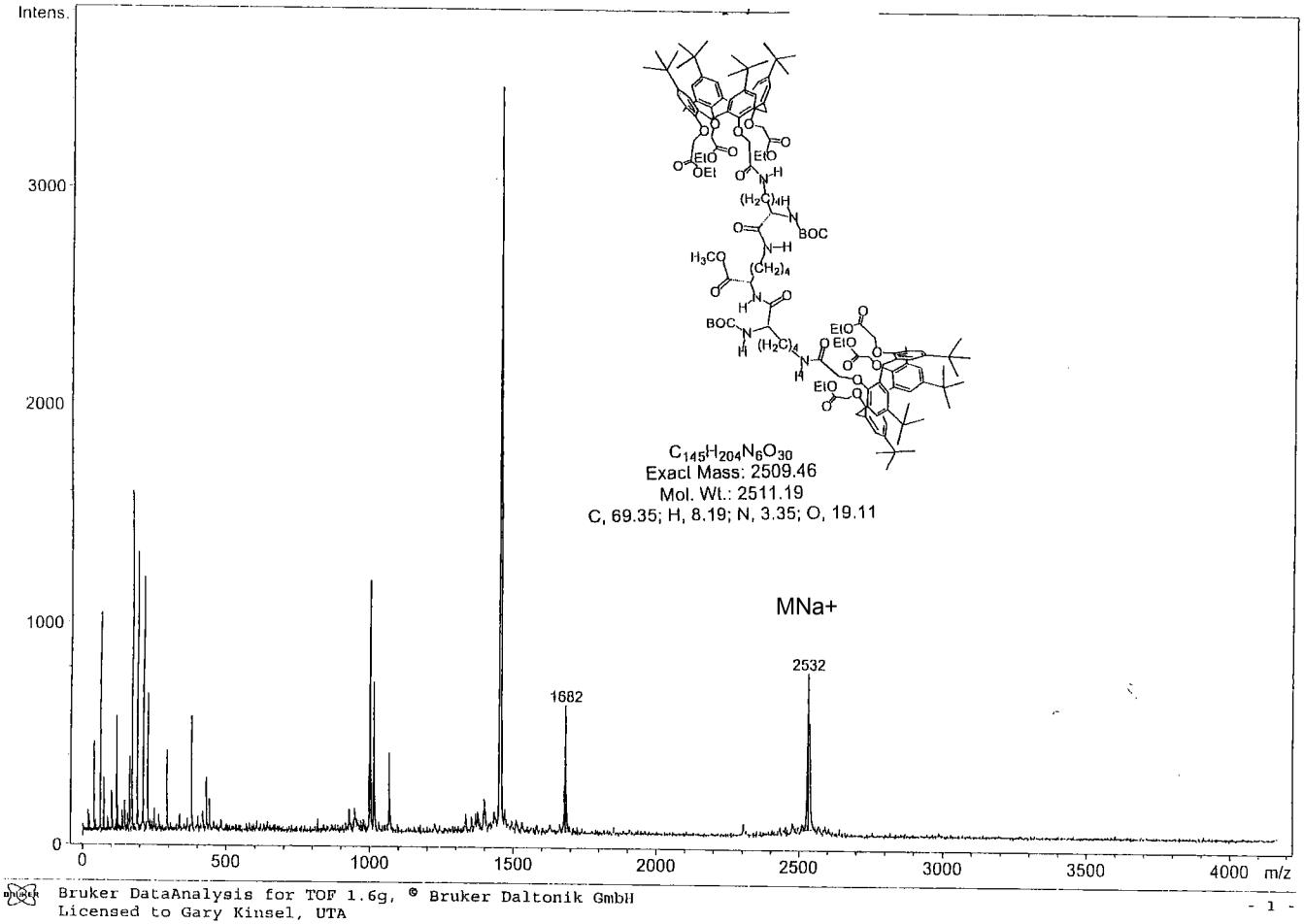
Date acquired: Wed Dec 18 15:32:01 2002
Instrument: TOF

Printed: Thu Dec 19 09:57:04 2002

Operator :



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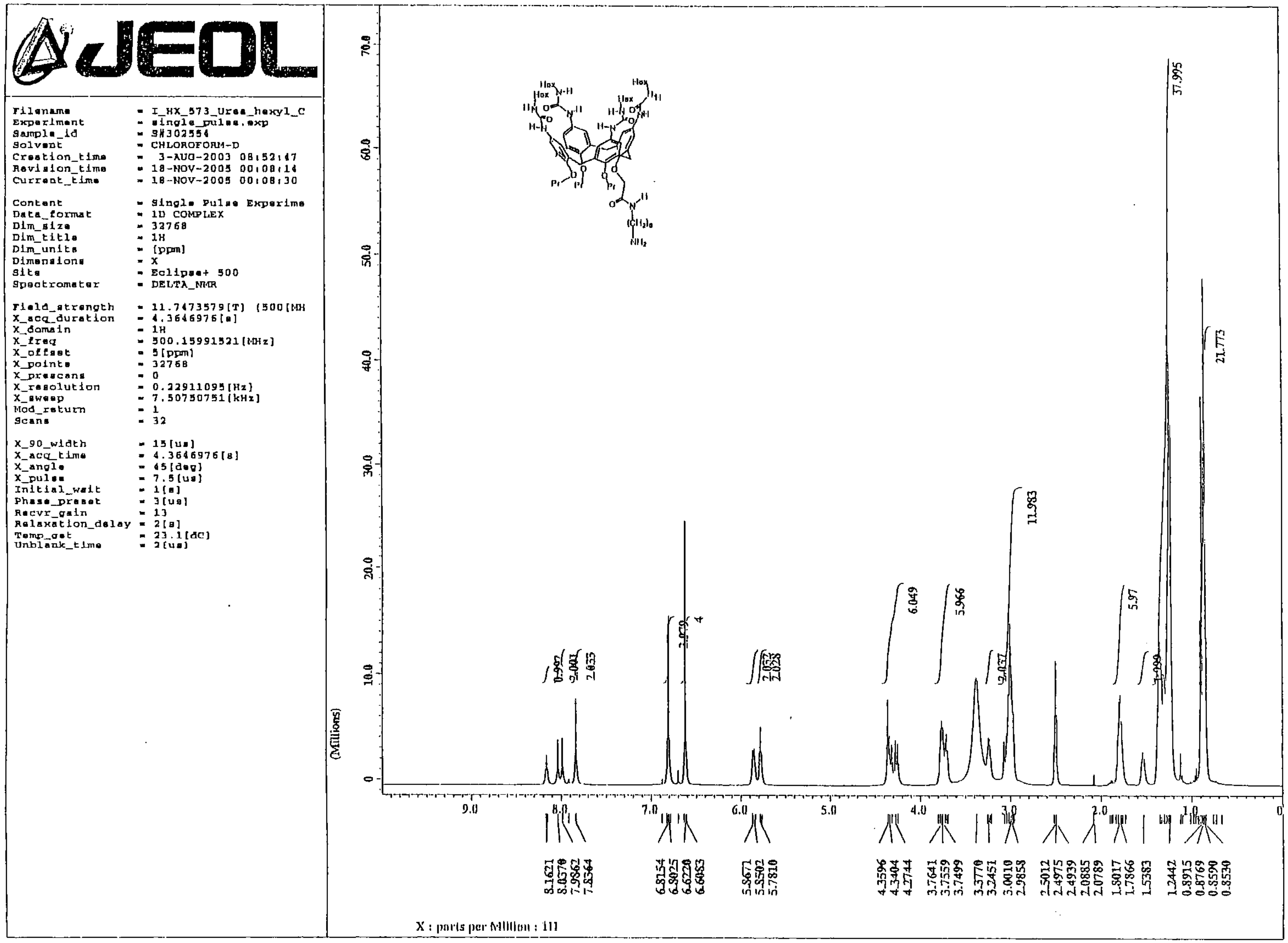
- 1 -

APPENDIX 27

^{1}H NMR, ^{13}C NMR and MASS SPECTRA OF

Calixarene hexylamine (57)


JEOL
Filename = I_HX_573_Urea_hexyl_C
Experiment = single_pulse.exp
Sample_id = SH302554
Solvent = CHLOROFORM-D
Creation_time = 3-AUG-2003 08:52:47
Revision_time = 18-NOV-2005 00:08:14
Current_time = 18-NOV-2005 00:08:30
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Data_format = 1D COMPLEX
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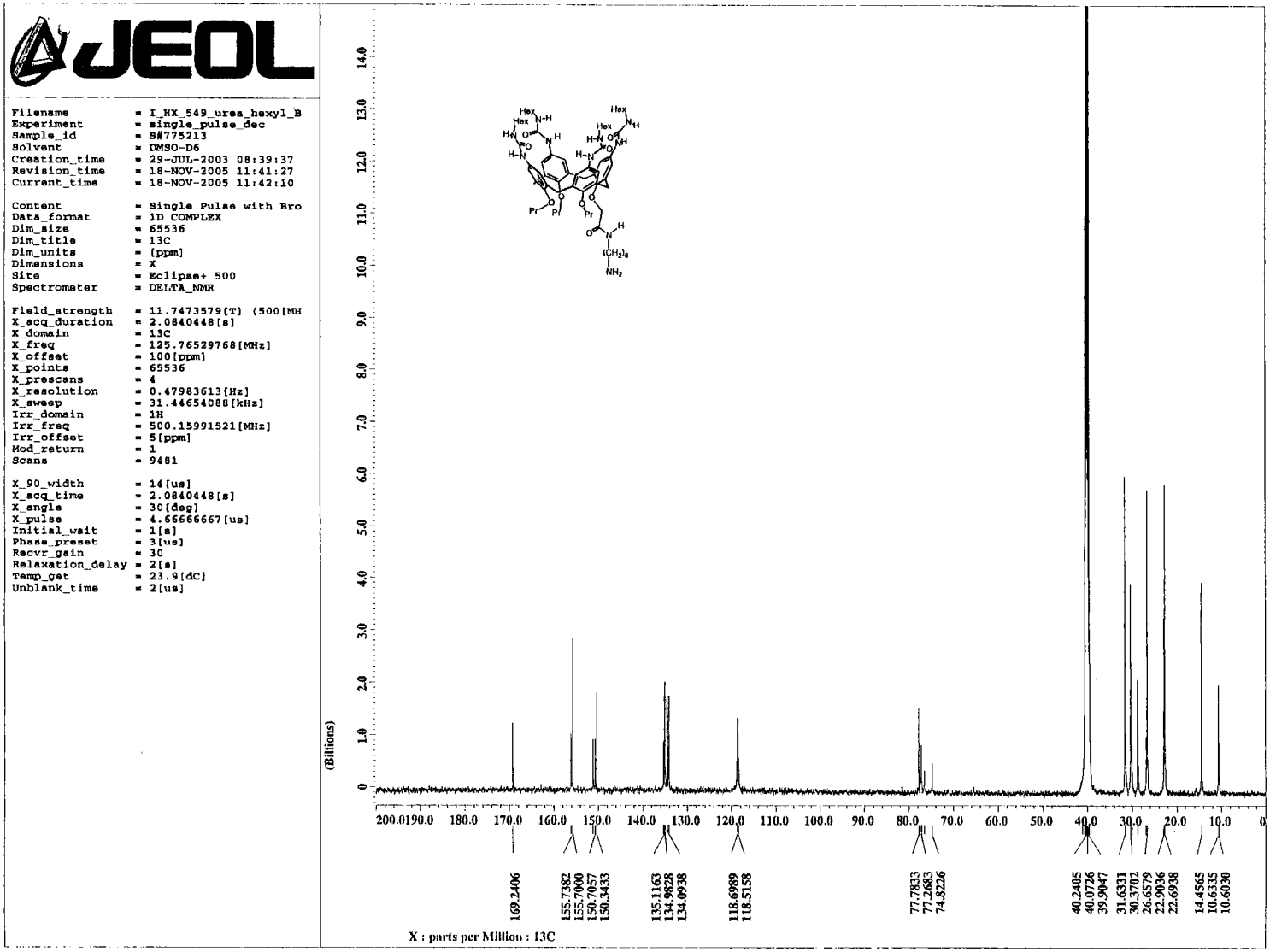
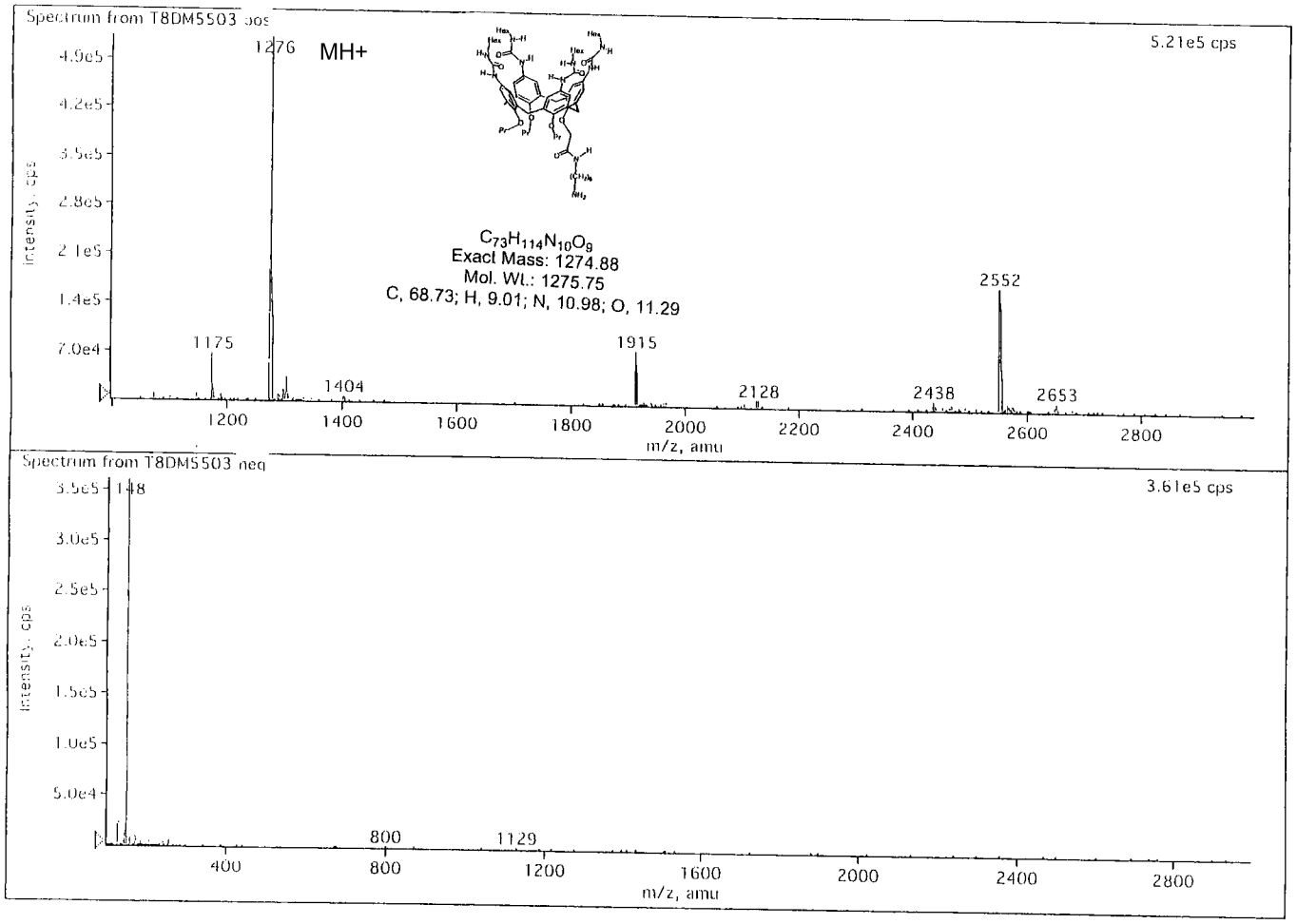
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 4.3646976[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.22911095[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 32
X_90_width = 15[us]
X_acq_time = 4.3646976[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 13
Relaxation_delay = 2[s]
Temp_get = 23.1[dC]
Unblank_time = 2[us]
(Millions)
X : parts per Million : 1H
37.995
21.773
11.983
6.049
5.966
5.97
2.037
1.099
2.079
4
2.057
2.028
0.997
2.001
2.035
8.1621
8.0370
7.9862
7.8364
6.8154
6.8025
6.6220
6.6083
5.8671
5.8502
5.7810
4.3596
4.3404
4.2744
3.7641
3.7559
3.7499
3.3770
3.2451
3.0010
2.9858
2.5012
2.4975
2.4939
2.0885
2.0789
1.8017
1.7866
1.5383
1.2442
0.8915
0.8769
0.8590
0.8530


JEOL
Filename = I_HX_549_urea_hexyl_B
Experiment = single_pulse_dec
Sample_id = S#775213
Solvent = DMSO-D6
Creation_time = 29-JUL-2003 08:39:37
Revision_time = 18-NOV-2005 11:41:27
Current_time = 18-NOV-2005 11:42:10
Content = Single Pulse with Bro
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Mod_return = 1
Scans = 9481
X_90_width = 14[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.66666667[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 2[s]
Temp_get = 23.9[dC]
Unblank_time = 2[us]
(Billions)
169.2406
155.7382
155.7000
150.7057
150.3433
135.1163
134.9828
134.0938
118.6989
118.5158
77.7833
77.2683
74.8226
40.2405
40.0726
39.9047
31.6331
30.3702
26.6579
22.9036
22.6938
14.4565
10.6335
10.6030
X : parts per Million : 13C


Spectrum from T8DM5503 pos
5.21e5 cps
1276
MH+
4.9e5
4.2e5
3.5e5
2.8e5
2.1e5
1.4e5
7.0e4
Intensity, cps
1175
1404
1915
2128
2438
2552
2653
1200
1400
1600
1800
2000
2200
2400
2600
2800
m/z, amu
C73H114N10O9
Exact Mass: 1274.88
Mol. Wt.: 1275.75
C, 68.73; H, 9.01; N, 10.98; O, 11.29
Spectrum from T8DM5503 neg
3.61e5 cps
3.5e5
3.0e5
2.5e5
2.0e5
1.5e5
1.0e5
5.0e4
Intensity, cps
148
800
1129
400
800
1200
1600
2000
2400
2800
m/z, amu

MALDI-TOF REFLECTRON

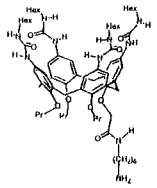
Original Filename: e:\data\routine\2003\august\080503\5503.ms

This File # 5 = E:\DATA\ROUTINE\2003\AUGUST\080503\5503.MS

Comment

Method: RDE2000K
Mode: Reflector
Accelerating Voltage: 20000
Grid Voltage: 72.000 %
Guide Wire Voltage: 0.030 %
Delay: 75 ON
Sample: 13

Laser : 2240
Scans Averaged: 43
Pressure: 1.94e-07
Low Mass Gate: 500.0
Timed Ion Selector: 379.0 OFF
Negative Ions: OFF
Collected: 8/6/03 0:43 AM

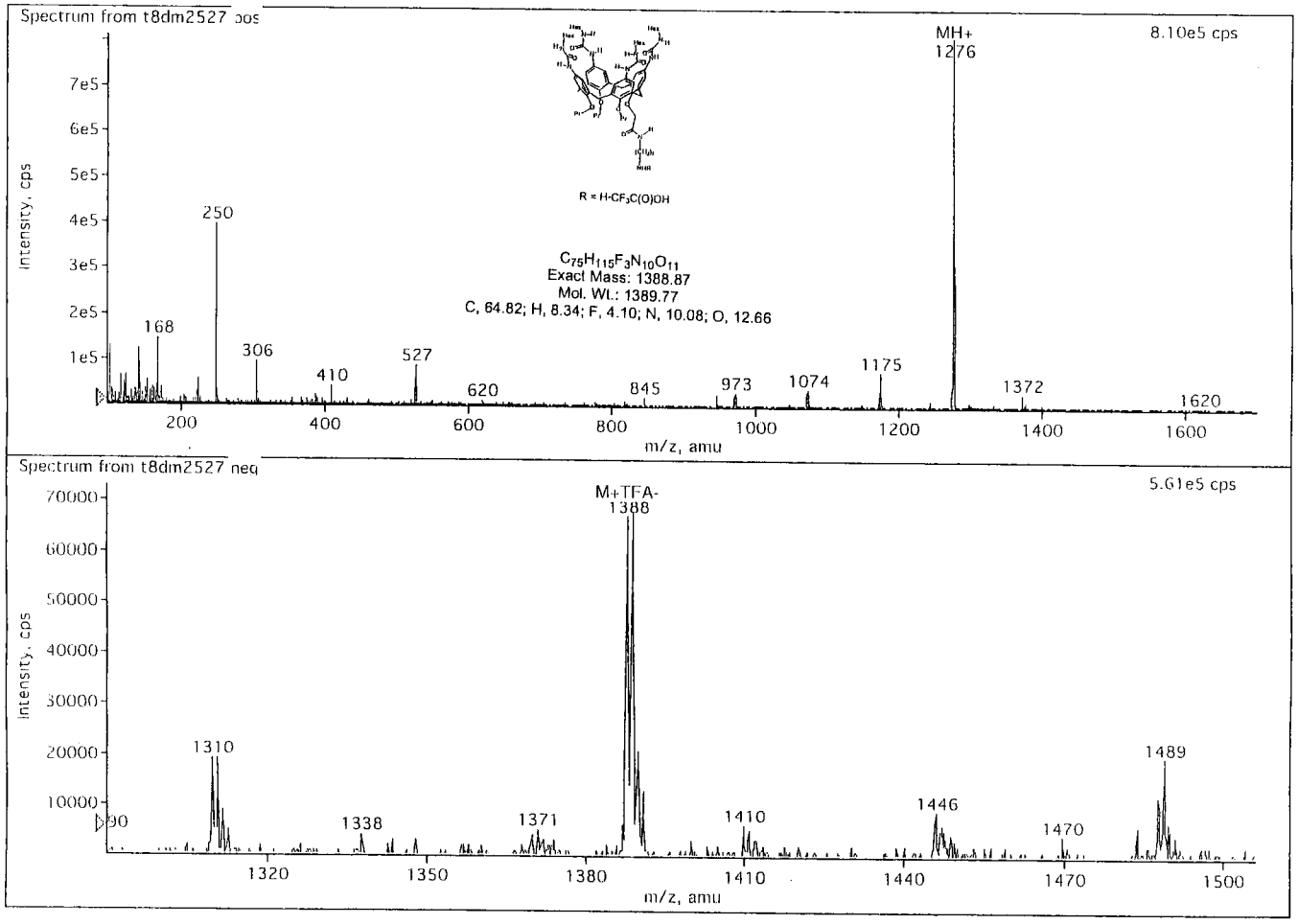


$C_{73}H_{114}N_{10}O_9$
Exact Mass: 1274.88
Mol. Wt.: 1275.75
C, 68.73; H, 9.01; N, 10.98; O, 11.29

APPENDIX 28

^{1}H NMR and MASS SPECTRA OF
TFA salt of (57)

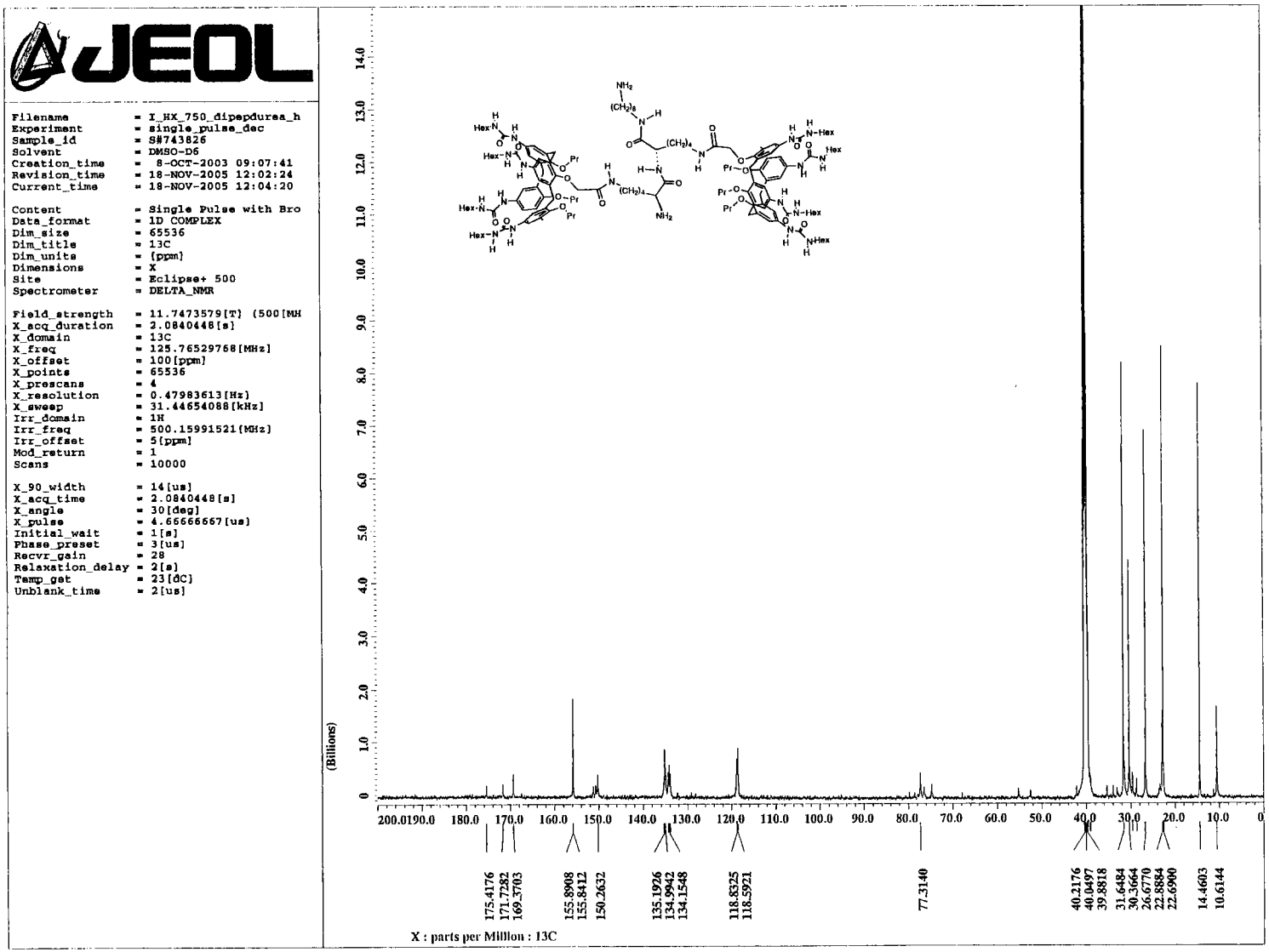
JEOL
Filename = I_HX_588_urea_hexyl_f
Experiment = single_pulse.exp
Sample_id = 9H40282
Solvent = CHLOROFORM-D
Creation_time = 6-AUG-2003 12:41:02
Revision_time = 17-NOV-2005 23:52:36
Current_time = 17-NOV-2005 23:53:39
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.74735791[T] (500[MH
X_acq_duration = 2.18234881[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.18234881[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 20
Relaxation_delay = 1[s]
Temp_get = 23.5[dc]
Unblank_time = 2[us]
R = H+CF3C(O)OH
X : parts per Million : 1H
(Millions)
24.141
21.081
12.26
6.024
4.094
3.987
2.0
8.1754
8.0153
7.9903
7.8401
7.6458
6.8039
6.7950
6.6344
6.5987
5.8777
5.8520
5.7824
4.3697
4.3422
4.2707
3.7650
3.7504
3.7082
3.0330
3.0092
2.9973
2.9836
2.9707
2.4980
2.4952
1.8063
1.7916
1.5360
1.2474
1.2383
0.8975
0.8627
0.8572


Spectrum from t8dm2527 pos
8.10e5 cps
MH+
1276
R = H-CF3C(O)OH
C75H115F3N10O11
Exact Mass: 1388.87
Mol. Wt.: 1389.77
C, 64.82; H, 8.34; F, 4.10; N, 10.08; O, 12.66
Intensity, cps
m/z, amu
Spectrum from t8dm2527 neg
5.61e5 cps
M+TFA-
1388
1310
1338
1371
1410
1446
1470
1489

APPENDIX 29

^{1}H NMR, ^{13}C NMR and MASS SPECTRA OF Biscalixarene (58)

JEOL
Filename = I_HX_788_ureadipapd_h
Experiment = single_pulse.exp
Sample_id = SH291628
Solvent = CHLOROFORM-D
Creation_time = 28-OCT-2003 18:36:27
Revision_time = 18-NOV-2005 08:59:14
Current_time = 18-NOV-2005 09:00:16
Content = Single Pulse Expazine
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.74735791[T] (500[MH
X_acq_duration = 2.182348[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.182348[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 15
Relaxation_delay = 1[s]
Temp_get = 22.3[dC]
Unblank_time = 2[us]
(Millions)
X : parts per Million : 1H
42.361
48.396
28.0
6.076
14.003
25.687
4.002
11.906
12.018
1.063
4.065
4.074
8.046
8
12.087
8.3403
8.2148
8.1735
7.9436
7.6532
6.8048
6.5538
6.0774
5.9684
4.3541
4.2506
4.2277
4.1416
3.7385
3.5406
3.3537
3.2804
3.2172
3.1585
2.9955
2.9744
2.4952
2.0775
1.7587
1.3592
1.3473
1.3345
1.2392
0.9753
0.8471


JEOL
Filename = I_HX_750_dipepdurea_h
Experiment = single_pulse_dec
Sample_id = S#743826
Solvent = DMSO-D6
Creation_time = 8-OCT-2003 09:07:41
Revision_time = 18-NOV-2005 12:02:24
Current_time = 18-NOV-2005 12:04:20
Content = Single Pulse with Bro
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Mod_return = 1
Scans = 10000
X_90_width = 14[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.66666667[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 28
Relaxation_delay = 2[s]
Temp_get = 23[dC]
Unblank_time = 2[us]
(Billions)
175.4176
171.7282
169.3703
155.8908
155.8412
150.2632
135.1926
134.9942
134.1548
118.8325
118.5921
77.3140
40.2176
40.0497
39.8818
31.6484
30.3664
26.6770
22.8884
22.6900
14.4603
10.6144
X : parts per Million : 13C

MALDI-TOF REFLECTRON

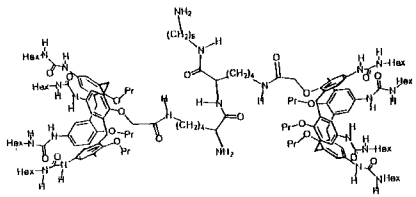
Original Filename: e:\data\routine\2003\oct\102103\8180dp2.ms

This File # 4 : E:\DATA\ROUTINE\2003\OCT\102103\SMOOTH.MS

Comment:

Method: PEPTIDE
Mode: Linear
Accelerating Voltage: 20000
Grid Voltage: 96.300 %
Guide Wire Voltage: 0.030 %
Delay: 100 ON
Sample: 43
Savitsky-Golay Order = 2 Points = 19

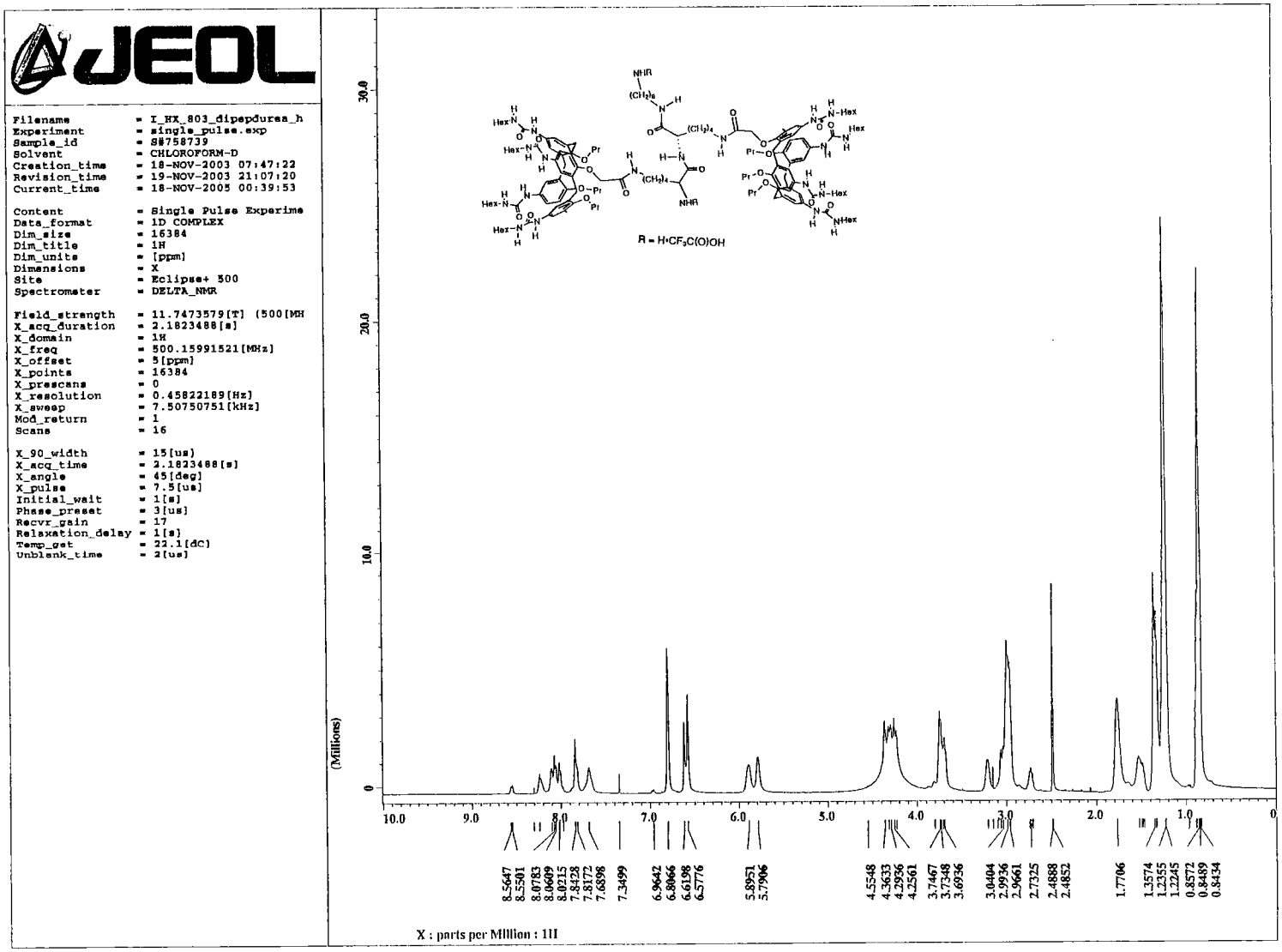
Laser : 2150
Scans Averaged: 38
Pressure: 3.53e-07
Low Mass Gate: 800.0
Timed Ion Selector: 24.6 OFF
Negative Ions: OFF
Collected: 10/22/03 3:24 AM



$C_{152}H_{236}N_{22}O_{20}$
Exact Mass: 2689.81
Mol. Wt.: 2691.64
C, 67.83; H, 8.84; N, 11.45; O, 11.89

APPENDIX 30

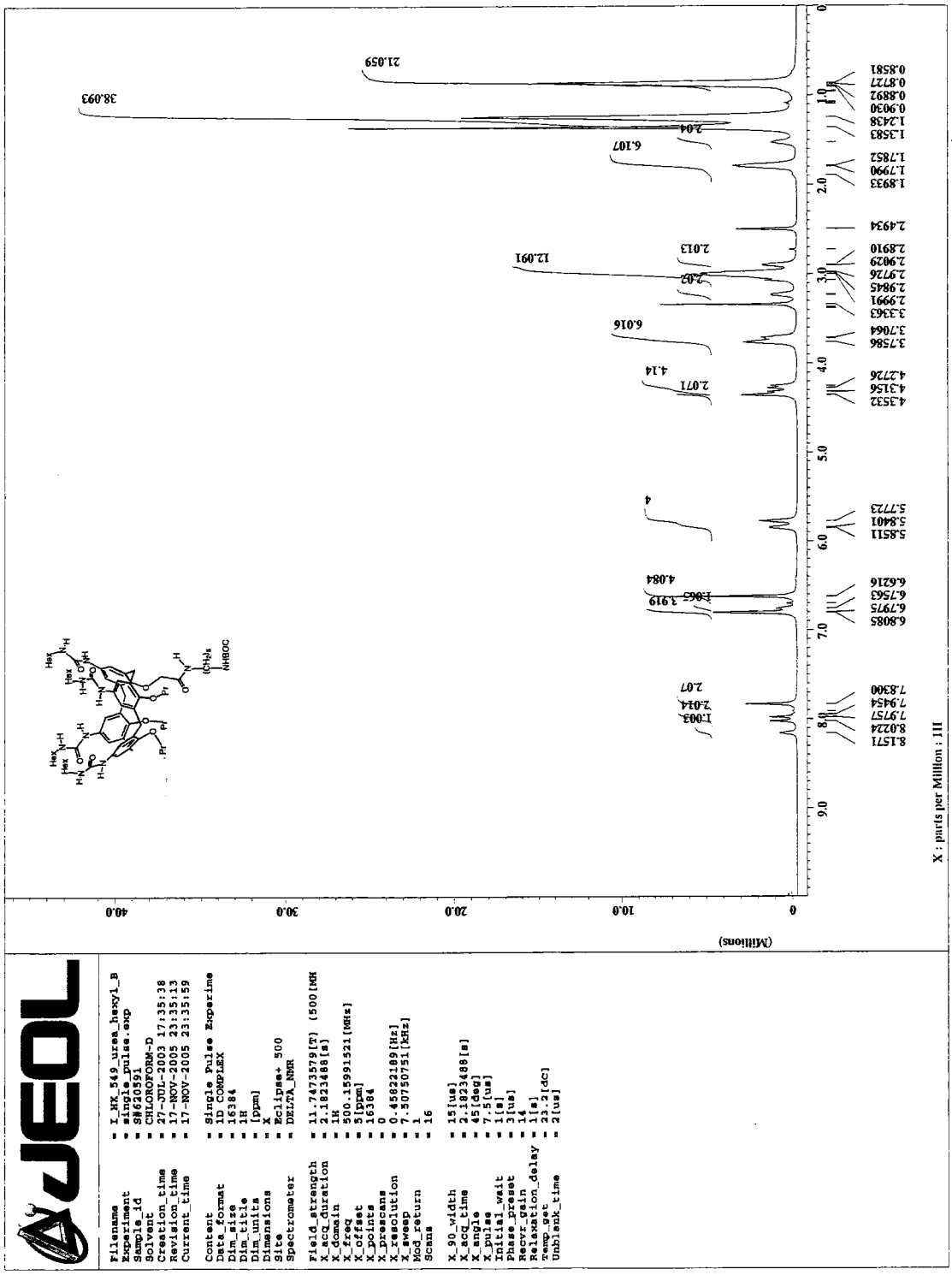
^{1}H NMR SPECTRUM OF
TFA salt of Biscalixarene (58)


JEOL
Filename = I_HX_803_dipepdurea_h
Experiment = single_pulse.exp
Sample_id = S#758739
Solvent = CHLOROFORM-D
Creation_time = 18-NOV-2003 07:47:22
Revision_time = 19-NOV-2003 21:07:20
Current_time = 18-NOV-2005 00:39:53
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 17
Relaxation_delay = 1[s]
Temp_get = 22.1[dC]
Unblank_time = 2[us]
R = H•CF3C(O)OH
(Millions)
30.0
20.0
10.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.5647
8.5501
8.0783
8.0609
8.0215
7.8428
7.8172
7.6898
7.3499
6.9642
6.8066
6.6198
6.5776
5.8951
5.7906
4.5548
4.3633
4.2936
4.2561
3.7467
3.7348
3.6936
3.0404
2.9936
2.9661
2.7325
2.4888
2.4852
1.7706
1.3574
1.2355
1.2245
0.8572
0.8489
0.8434
X : parts per Million : 1H

APPENDIX 31

^{1}H NMR SPECTRUM OF

Calixarene (59)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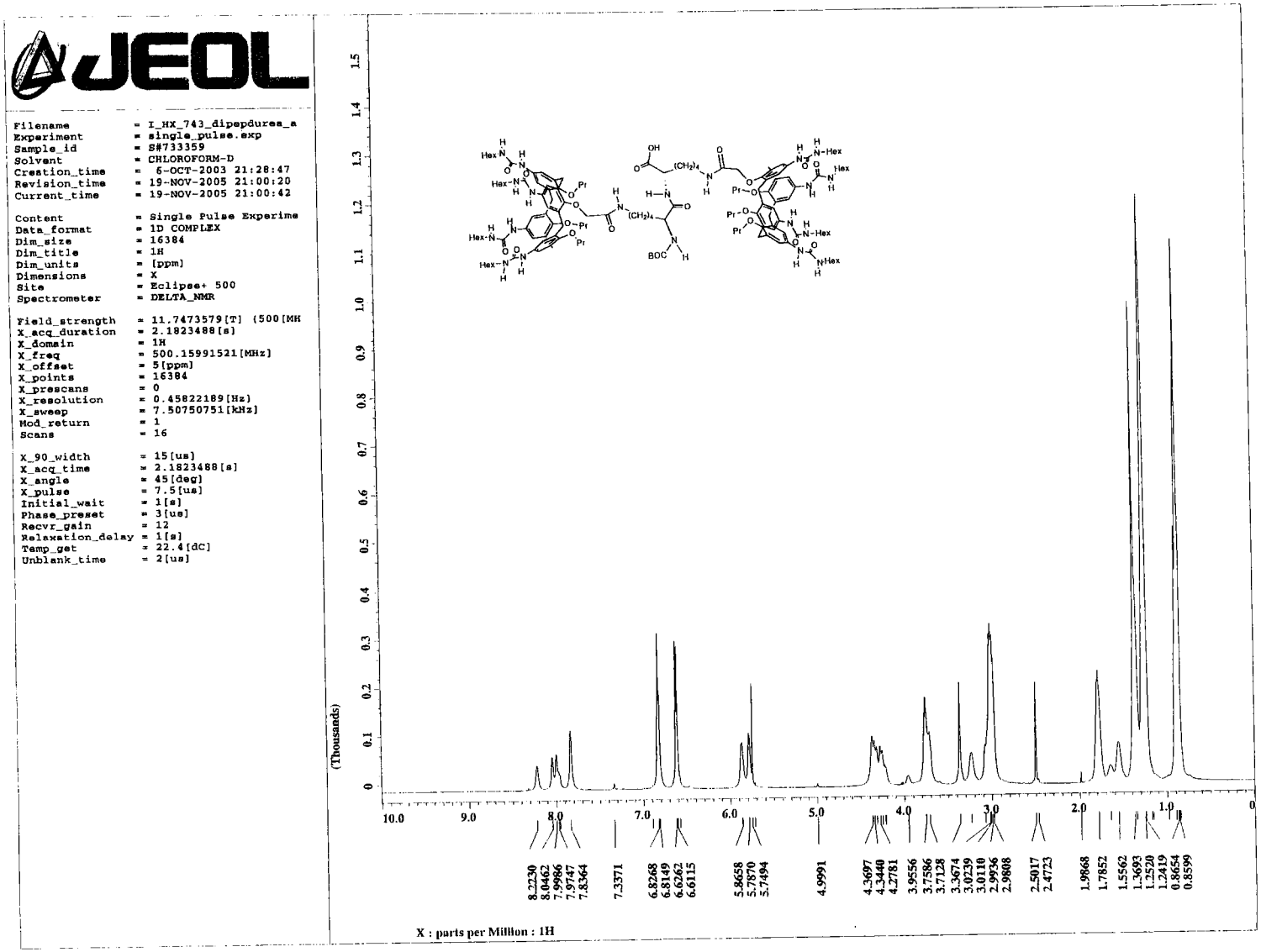
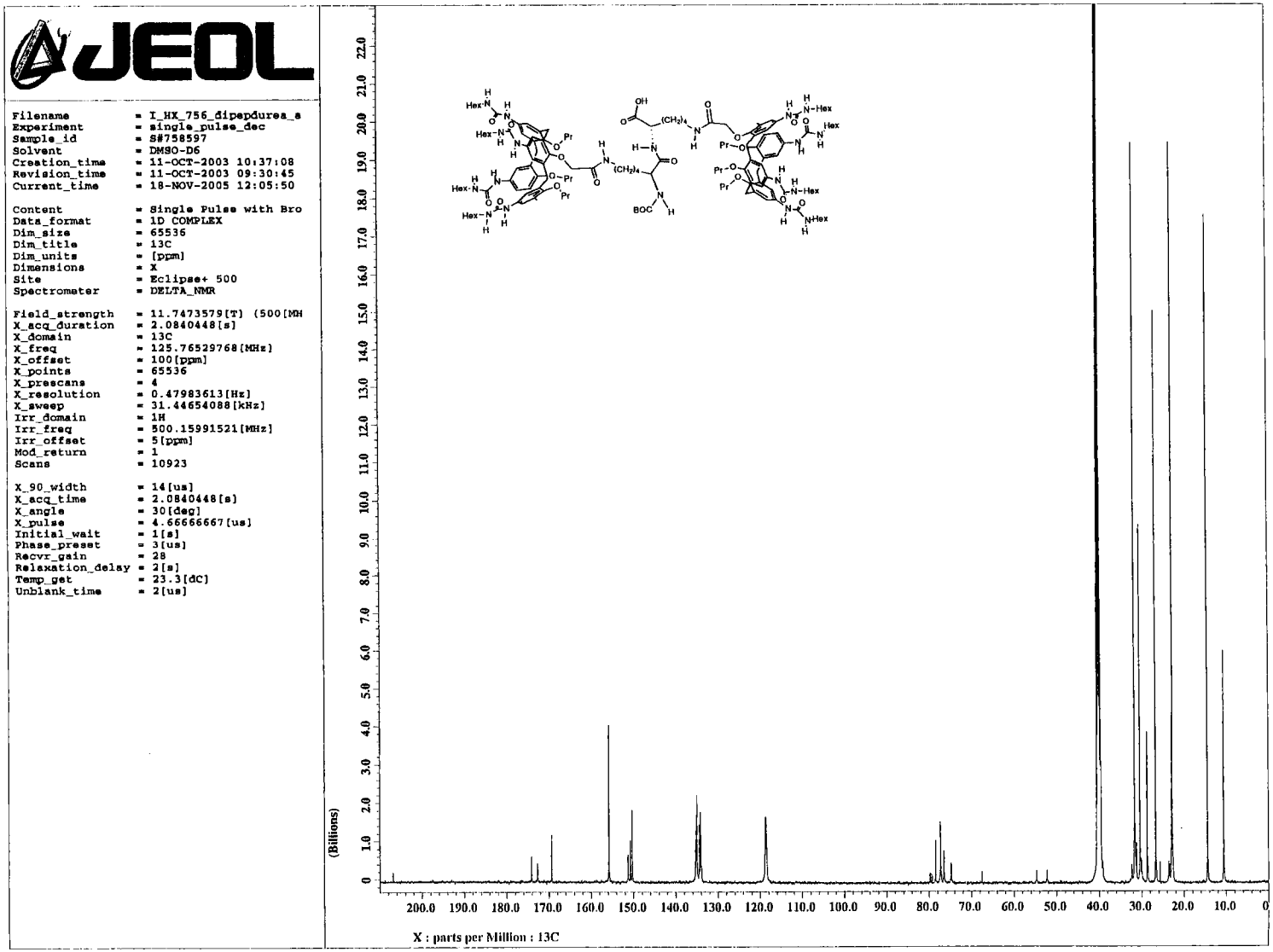
Filename = I_HK_549_urea_hexyl_B
Experiment = single_pulse.exp
Sample_id = S#620591
Solvent = CHLOROFORM-D
Creation_time = 27-JUL-2003 17:35:38
Revision_time = 17-NOV-2005 23:35:13
Current_time = 17-NOV-2005 23:35:59
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[KHz]
Mod_return = 16
Scans
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 14
Relaxation_delay = 1[s]
Temp_get = 23.2[dC]
Unblank_time = 2[us]
(Millions)
X : parts per Million : 1H
38.093
21.059
12.091
6.107
6.016
4.084
4.14
3.919
2.071
2.07
2.04
2.02
2.013
2.014
1.003
Hex
NHBOC

APPENDIX 32

^{1}H NMR and ^{13}C NMR SPECTRA OF
Biscalixarene (60)


JEOL
Filename = I_HX_743_dipepdurea_a
Experiment = single_pulse.exp
Sample_id = S#733359
Solvent = CHLOROFORM-D
Creation_time = 6-OCT-2003 21:28:47
Revision_time = 19-NOV-2005 21:00:20
Current_time = 19-NOV-2005 21:00:42
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 12
Relaxation_delay = 1[s]
Temp_get = 22.4[dC]
Unblank_time = 2[us]
(Thousands)
X : parts per Million : 1H
8.2230
8.0462
7.9986
7.9747
7.8364
7.3571
6.8268
6.8149
6.6262
6.6115
5.8658
5.7870
5.7494
4.9991
4.3697
4.3440
4.2781
3.9556
3.7586
3.7128
3.3674
3.0239
3.0110
2.9936
2.9808
2.5017
2.4723
1.9868
1.7852
1.5562
1.3693
1.2520
1.2419
0.8654
0.8599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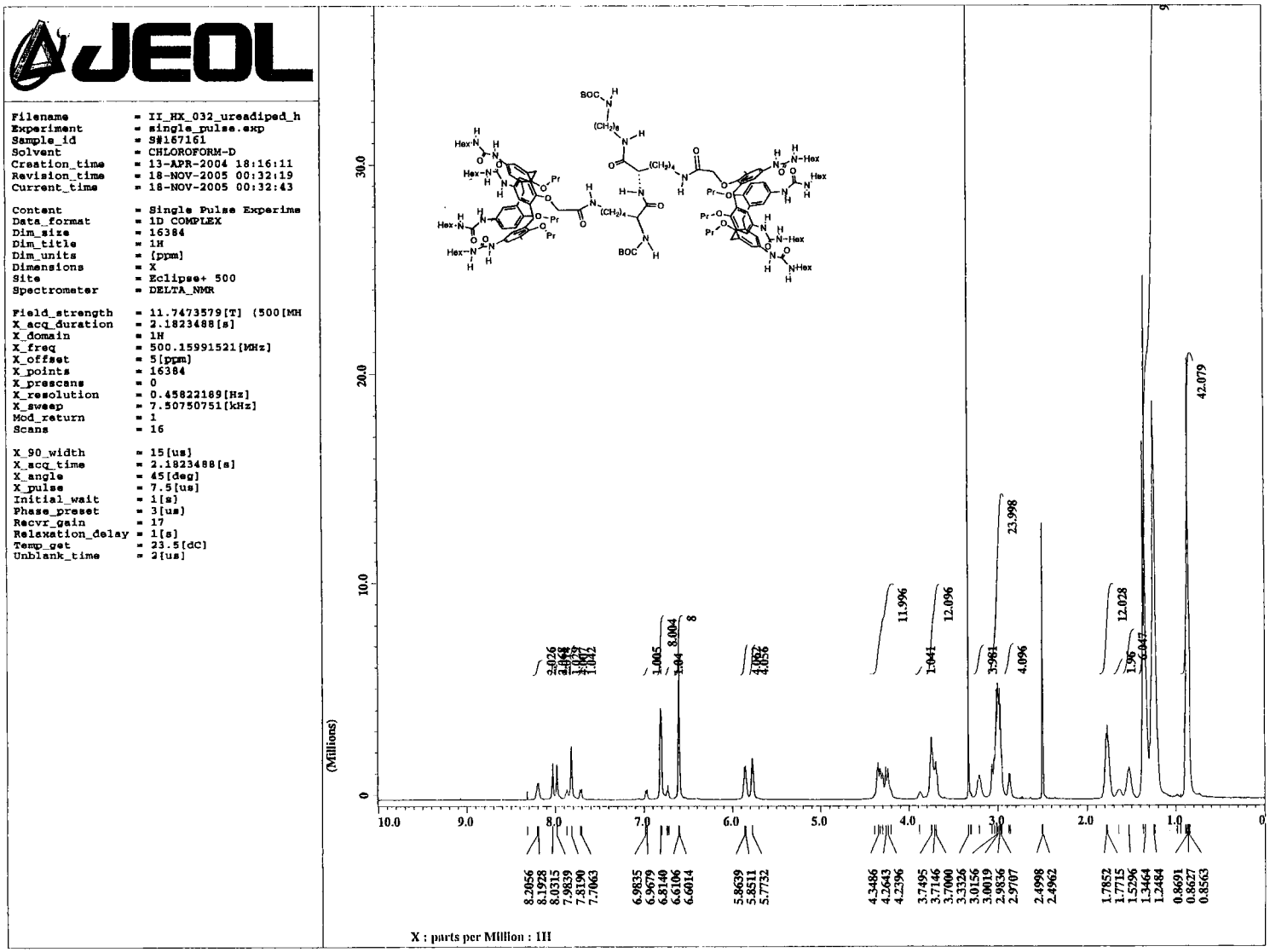
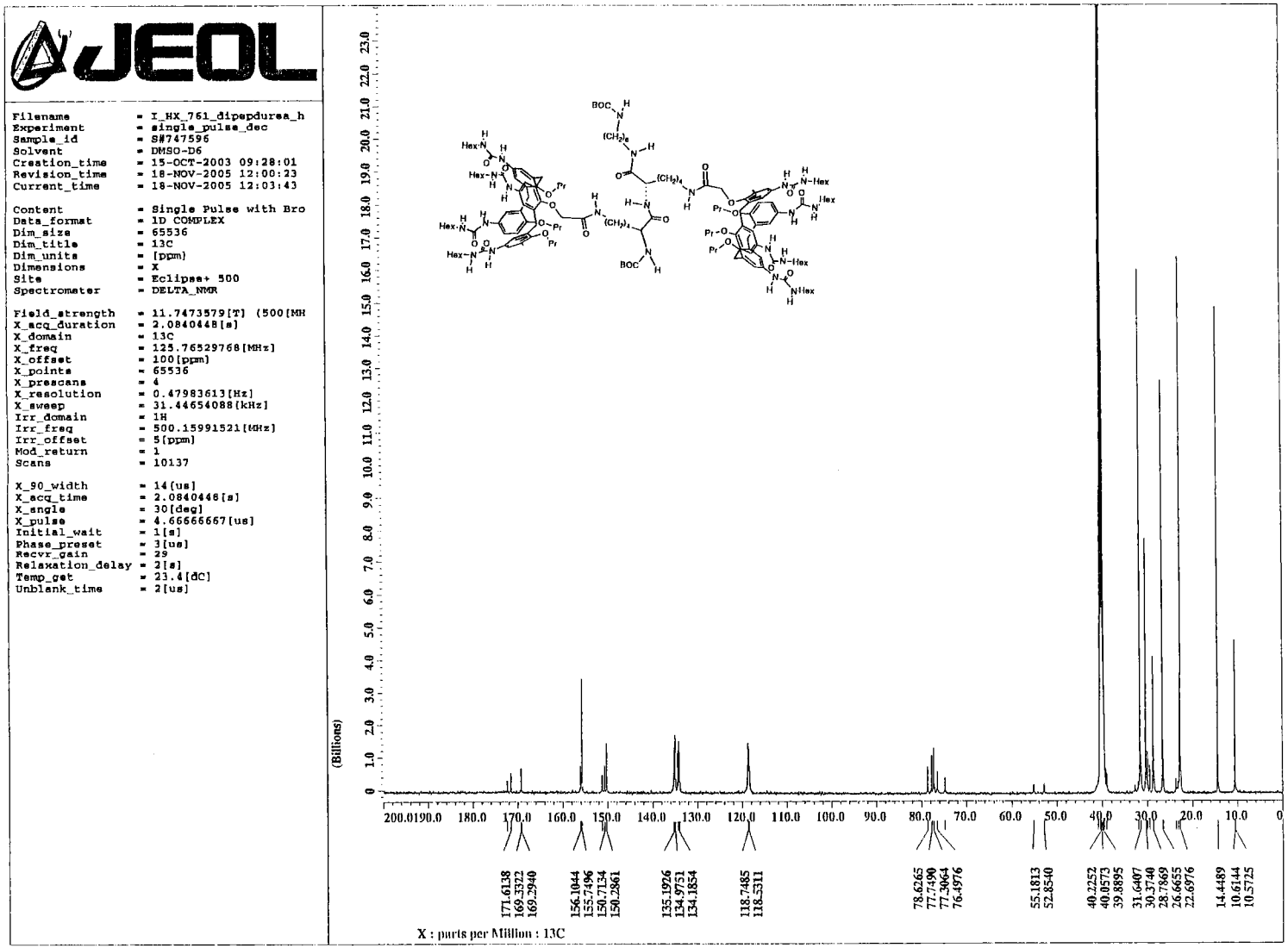
Filename = I_HX_756_dipepdurea_s
Experiment = single_pulse_dec
Sample_id = S#758597
Solvent = DMSO-D6
Creation_time = 11-OCT-2003 10:37:08
Revision_time = 11-OCT-2003 09:30:45
Current_time = 18-NOV-2005 12:05:50
Content = Single Pulse with Bro
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Mod_return = 1
Scans = 10923
X_90_width = 14[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.66666667[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 28
Relaxation_delay = 2[s]
Temp_get = 23.3[dC]
Unblank_time = 2[us]
(Billions)
X : parts per Million : 13C

APPENDIX 33

^{1}H NMR and ^{13}C NMR SPECTRA OF
Biscalixarene (61)

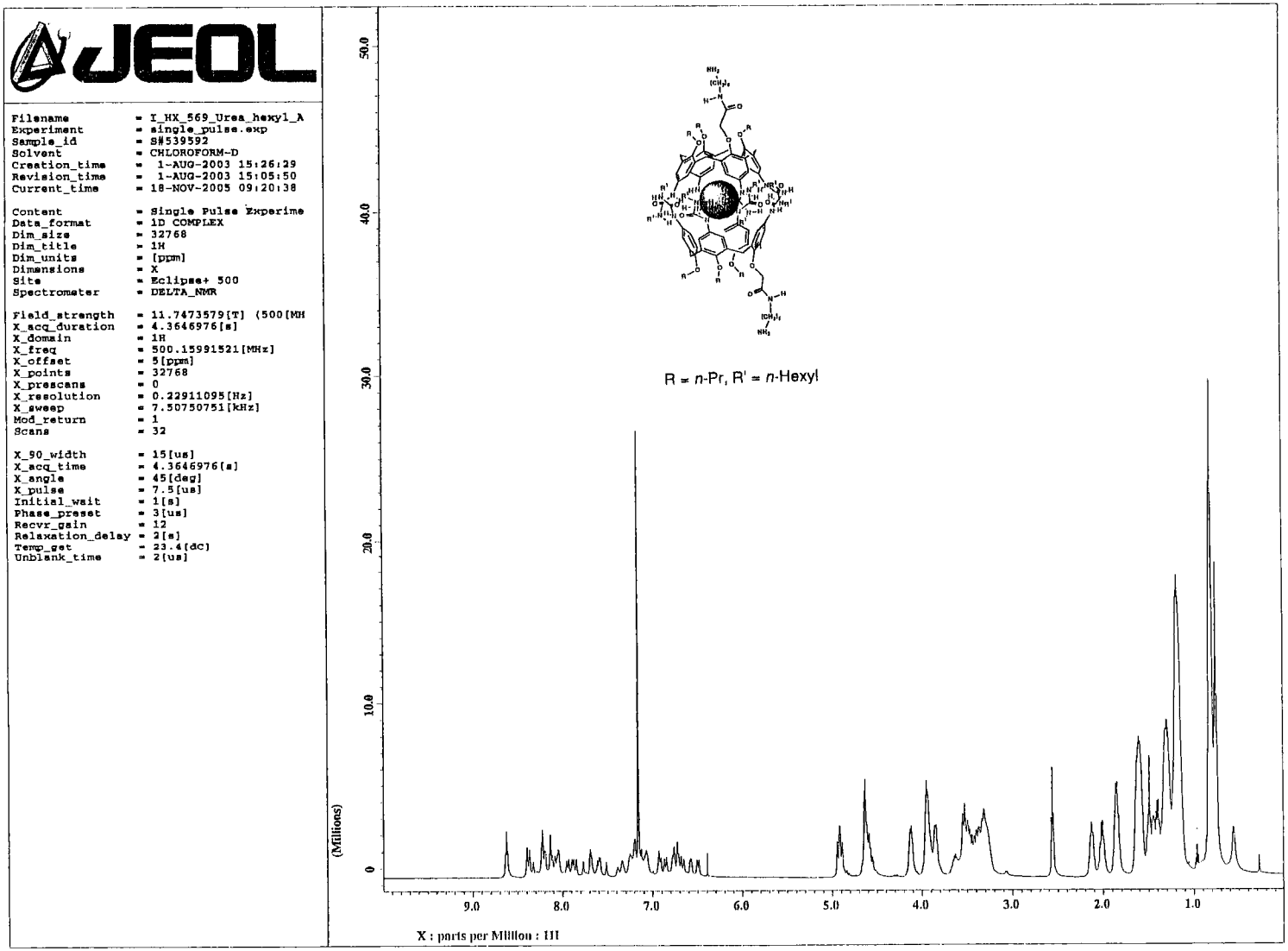

JEOL
Filename = II_HX_032_ureadiped_h
Experiment = single_pulse.exp
Sample_id = S#167161
Solvent = CHLOROFORM-D
Creation_time = 13-APR-2004 18:16:11
Revision_time = 18-NOV-2005 00:32:19
Current_time = 18-NOV-2005 00:32:43
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 17
Relaxation_delay = 1[s]
Temp_get = 23.5[dC]
Unblank_time = 2[us]
(Millions)
30.0
20.0
10.0
0
11.996
12.096
23.998
12.028
42.079
8.004
8
3.981
4.096
1.041
1.005
1.04
1.96
6.047
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
8.2056
8.1928
8.0315
7.9839
7.8190
7.7063
6.9835
6.9679
6.8140
6.6106
6.6014
5.8639
5.8511
5.7732
4.3486
4.2643
4.2396
3.7495
3.7146
3.7000
3.3326
3.0156
3.0019
2.9836
2.9707
2.4998
2.4962
1.7852
1.7715
1.5296
1.3464
1.2484
0.8691
0.8627
0.8563
X : parts per Million : 1H


JEOL
Filename = I_HX_761_dipapdurea_h
Experiment = single_pulse_dec
Sample_id = S#747596
Solvent = DMSO-D6
Creation_time = 15-OCT-2003 09:28:01
Revision_time = 18-NOV-2005 12:00:23
Current_time = 18-NOV-2005 12:03:43
Content = Single Pulse with Bro
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Mod_return = 1
Scans = 10137
X_90_width = 14[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.66666667[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 29
Relaxation_delay = 2[s]
Temp_get = 23.4[dC]
Unblank_time = 2[us]
(Billions)
171.6138
169.3322
169.2940
156.1044
155.7496
150.7134
150.2861
135.1926
134.9751
134.1854
118.7485
118.5311
78.6265
77.7490
77.3064
76.4976
55.1813
52.8540
40.2252
40.0573
39.8895
31.6407
30.3740
28.7869
26.6655
22.6976
14.4489
10.6144
10.5725
X : parts per Million : 13C

APPENDIX 34

^{1}H NMR SPECTRUM OF

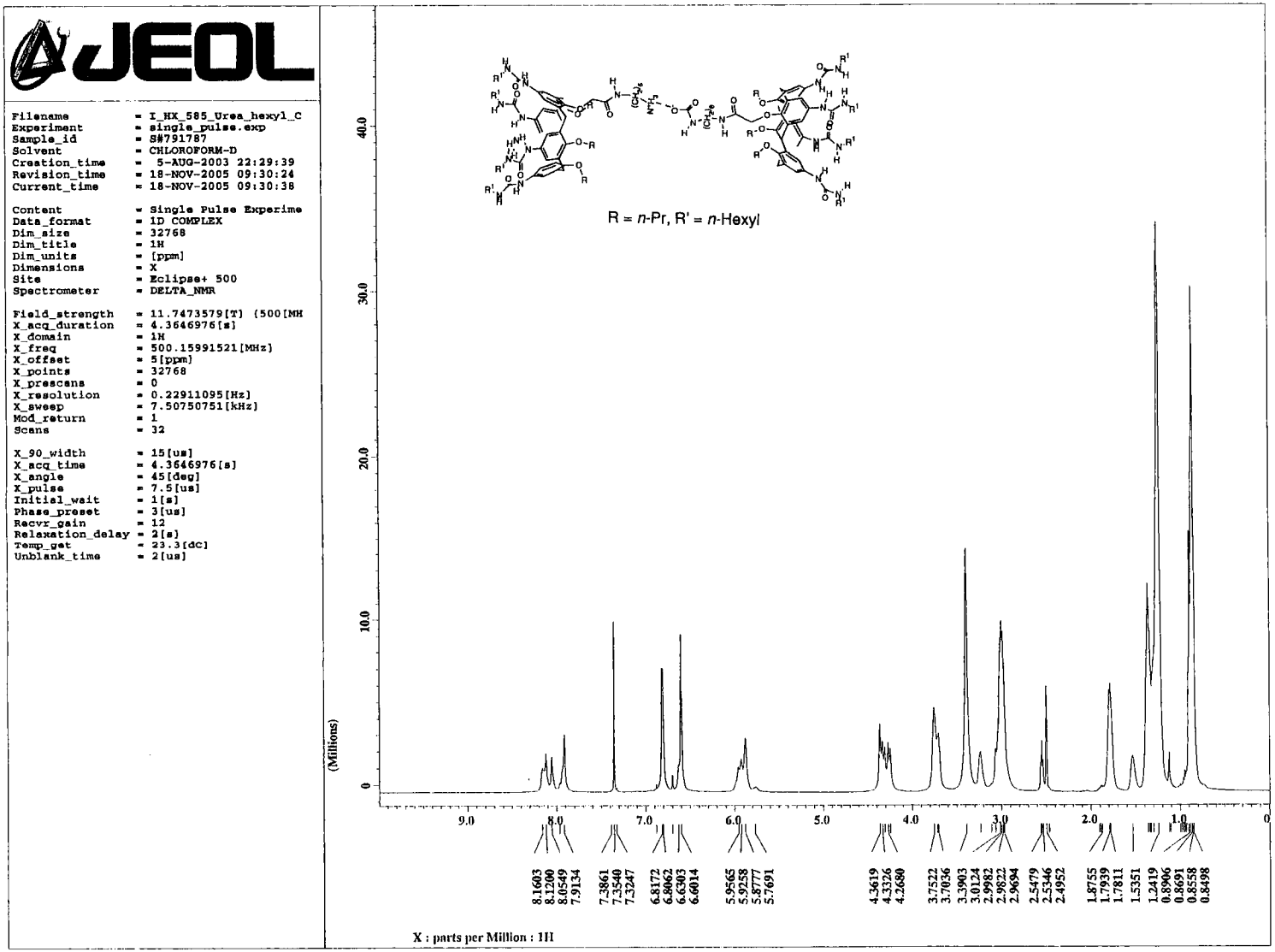
Calixarene Capsule (62)

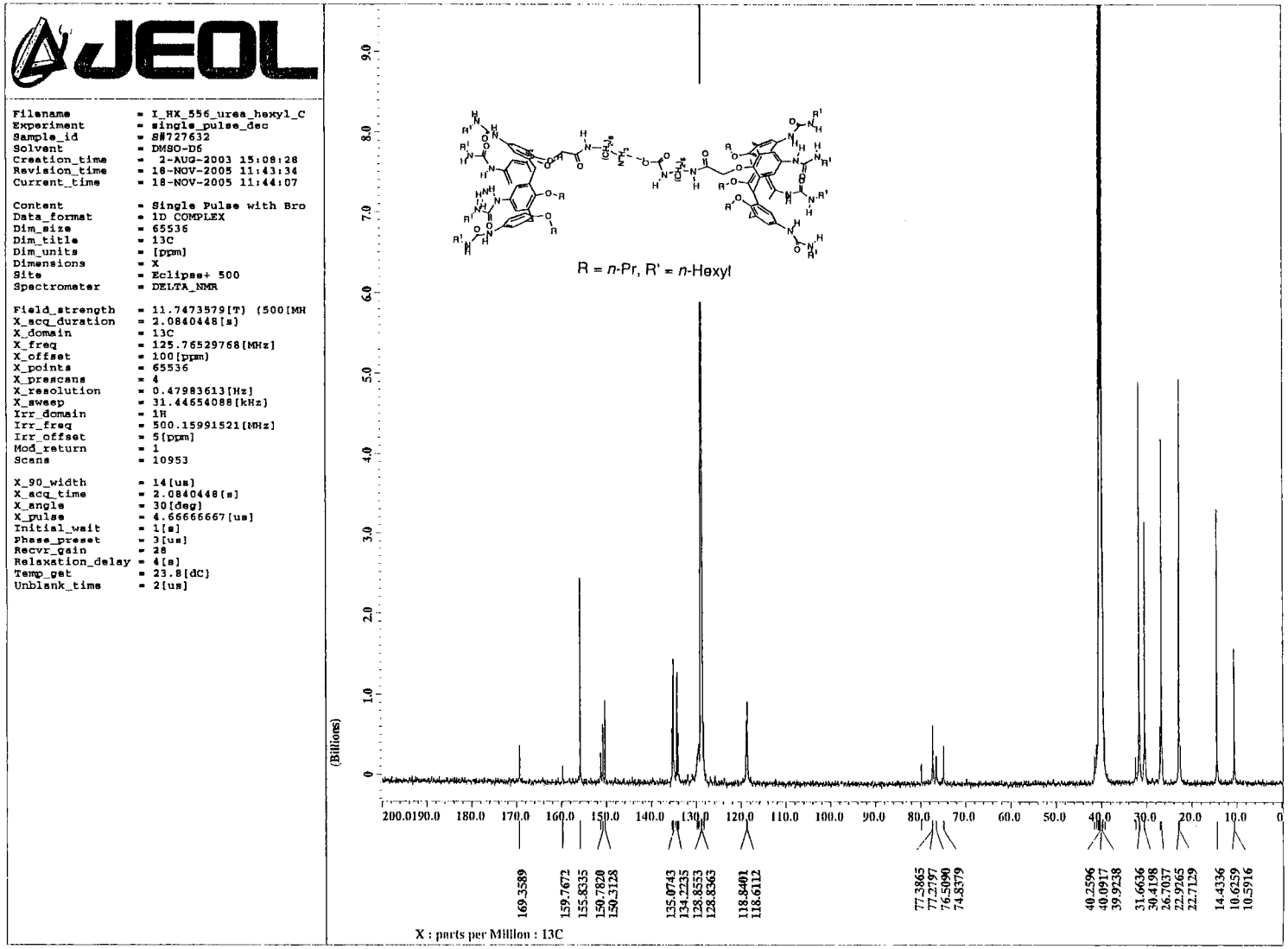

JEOL
Filename = I_HX_569_Urea_hexyl_A
Experiment = single_pulse.exp
Sample_id = S#539592
Solvent = CHLOROFORM-D
Creation_time = 1-AUG-2003 15:26:29
Revision_time = 1-AUG-2003 15:05:50
Current_time = 18-NOV-2005 09:20:38
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 4.3646976[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.22911095[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 32
X_90_width = 15[us]
X_acq_time = 4.3646976[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 12
Relaxation_delay = 2[s]
Temp_get = 23.4[dC]
Unblank_time = 2[us]
R = n-Pr, R' = n-Hexyl
(Millions)
50.0
40.0
30.0
20.0
10.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : 1H

APPENDIX 35

^{1}H NMR and ^{13}C NMR SPECTRA OF

Calixarene carbamate salt (64)

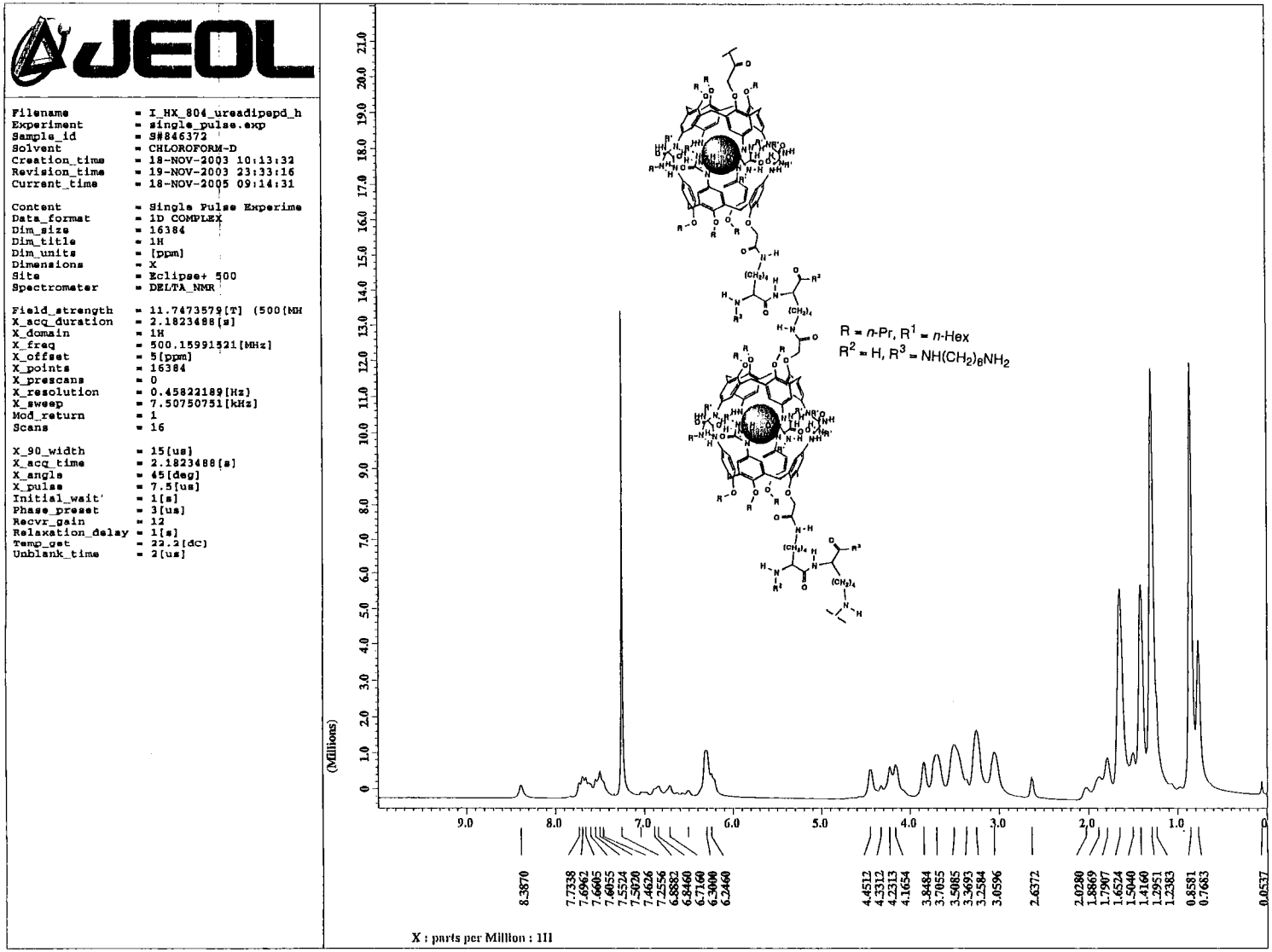

JEOL
Filename = I_HX_585_Urea_hexyl_C
Experiment = single_pulse.exp
Sample_id = S#791787
Solvent = CHLOROFORM-D
Creation_time = 5-AUG-2003 22:29:39
Revision_time = 18-NOV-2005 09:30:24
Current_time = 18-NOV-2005 09:30:38
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 4.3646976[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.22911095[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 32
X_90_width = 15[us]
X_acq_time = 4.3646976[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 12
Relaxation_delay = 2[s]
Temp_get = 23.3[dC]
Unblank_time = 2[us]
R = n-Pr, R' = n-Hexyl
(Millions)
40.0
30.0
20.0
10.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.1603
8.1200
8.0549
7.9134
7.3861
7.3540
7.3247
6.8172
6.8062
6.6303
6.6014
5.9565
5.9258
5.8777
5.7691
4.3619
4.3326
4.2680
3.7522
3.7036
3.3903
3.0124
2.9982
2.9822
2.9694
2.5479
2.5346
2.4952
1.8755
1.7939
1.7811
1.5351
1.2419
0.8906
0.8691
0.8558
0.8498
X : parts per Million : 1H


JEOL
Filename = I_HX_556_urea_hexyl_C
Experiment = single_pulse_dec
Sample_id = S#727632
Solvent = DMSO-D6
Creation_time = 2-AUG-2003 15:08:28
Revision_time = 18-NOV-2005 11:43:34
Current_time = 18-NOV-2005 11:44:07
Content = Single Pulse with Bro
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Mod_return = 1
Scans = 10953
X_90_width = 14[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.66666667[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 28
Relaxation_delay = 4[s]
Temp_get = 23.8[dC]
Unblank_time = 2[us]
R = n-Pr, R' = n-Hexyl
(Billions)
169.3589
159.7672
155.8335
150.7820
150.3128
135.0743
134.2235
128.8553
128.8363
118.8401
118.6112
77.3865
77.2797
76.5090
74.8379
40.2596
40.0917
39.9238
31.6636
30.4198
26.7037
22.9265
22.7129
14.4336
10.6259
10.5916
X : parts per Million : 13C

APPENDIX 36

^{1}H NMR SPECTRUM OF

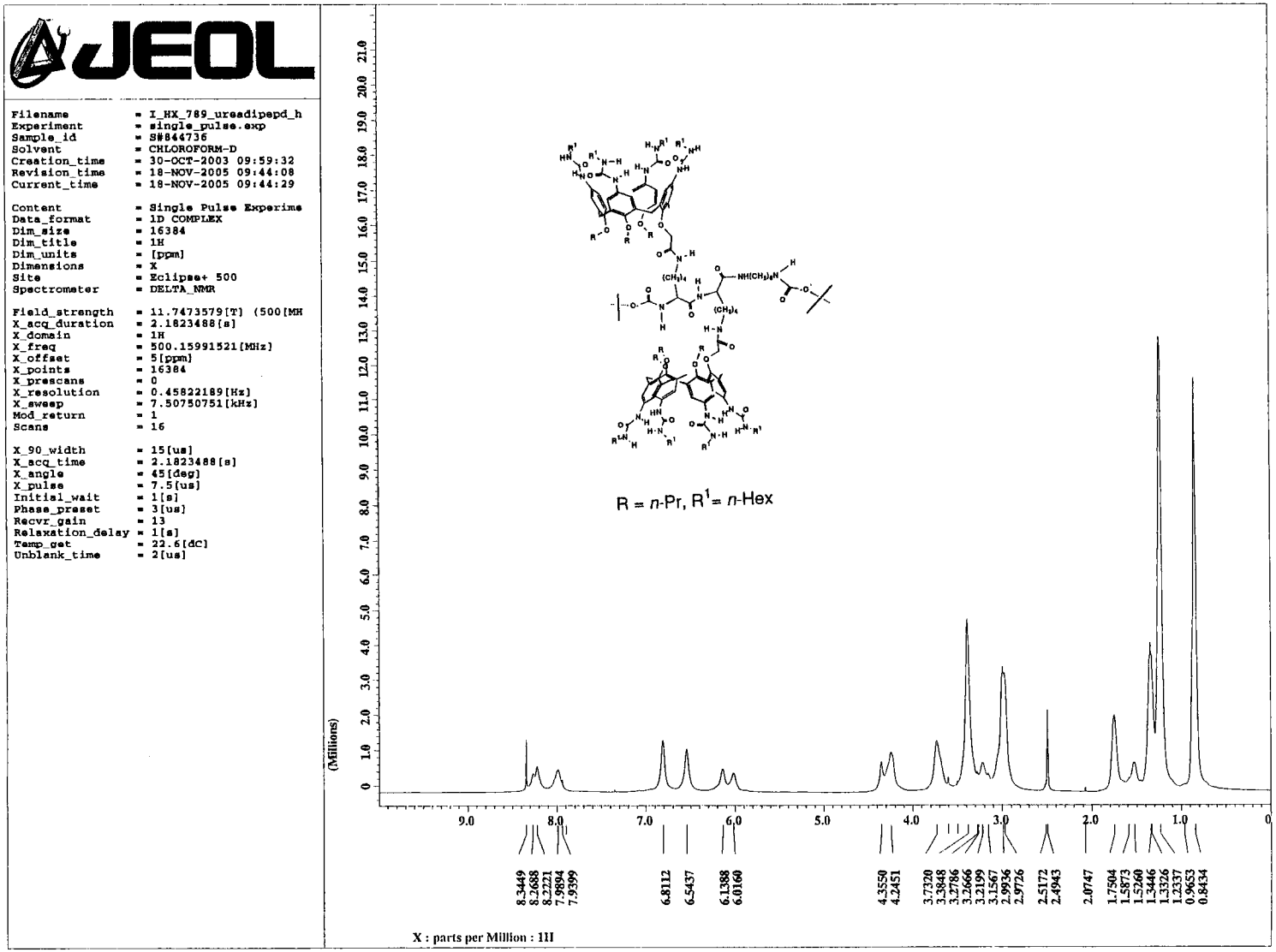
Calixarene supramolecular polymer (65)

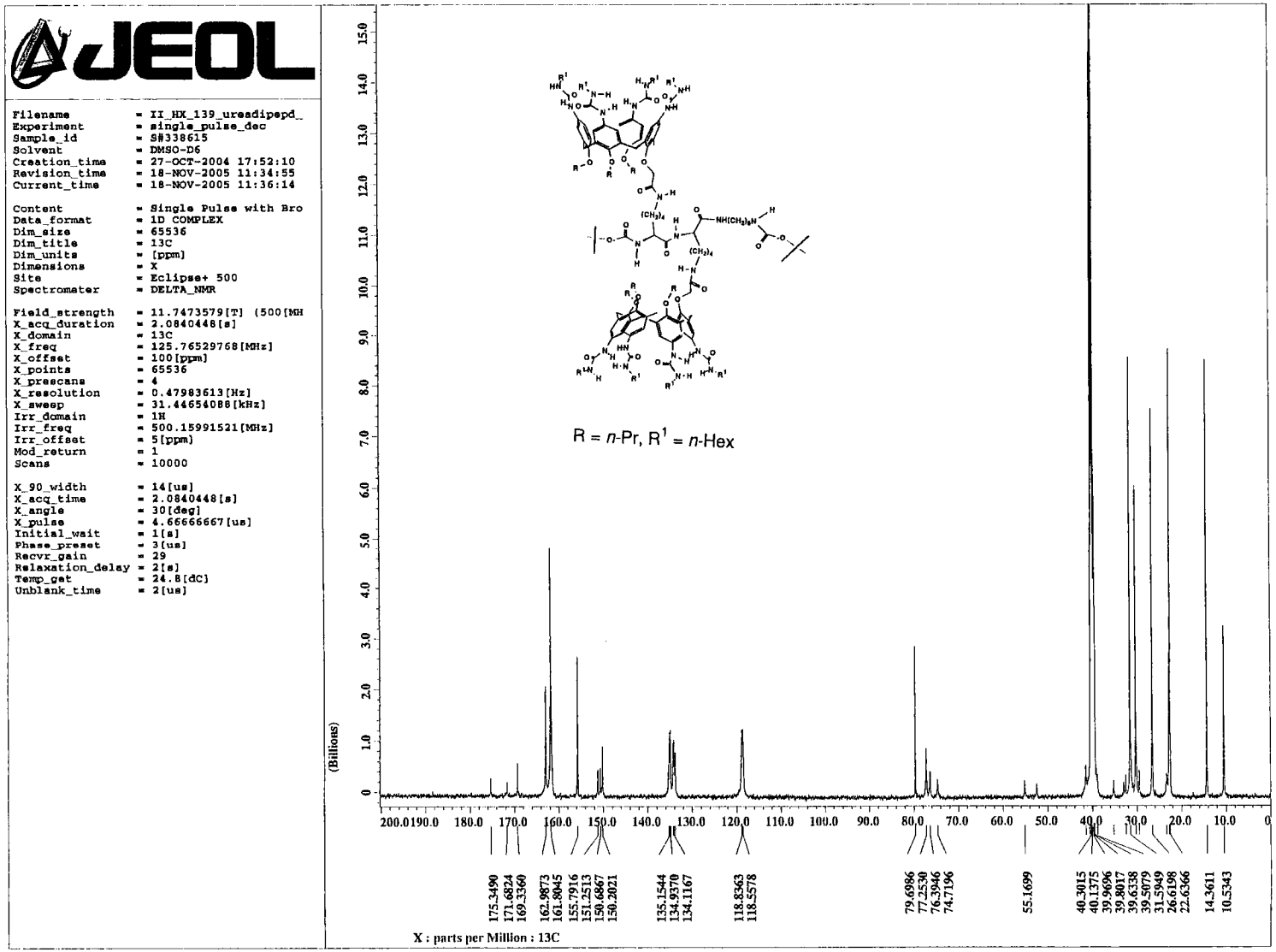

JEOL
Filename = I_HX_804_ureadipepd_h
Experiment = single_pulse.exp
Sample_id = S#846372
Solvent = CHLOROFORM-D
Creation_time = 18-NOV-2003 10:13:32
Revision_time = 19-NOV-2003 23:33:16
Current_time = 18-NOV-2005 09:14:31
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 12
Relaxation_delay = 1[s]
Temp_get = 22.2[dC]
Unblank_time = 2[us]
R = n-Pr, R1 = n-Hex
R2 = H, R3 = NH(CH2)8NH2
(Millions)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
8.3870
7.7338
7.6962
7.6605
7.6055
7.5524
7.5020
7.4626
7.2556
6.8882
6.8460
6.7160
6.5000
6.2460
4.4512
4.3312
4.2313
4.1654
3.8484
3.7055
3.5085
3.3693
3.2584
3.0596
2.6372
2.0280
1.8869
1.7997
1.6524
1.5040
1.4160
1.2951
1.2383
0.8581
0.7683
0.0537
X : parts per Million : 111

APPENDIX 37

^{1}H NMR and ^{13}C NMR SPECTRA OF

Biscalixarene carbamate salt (66)

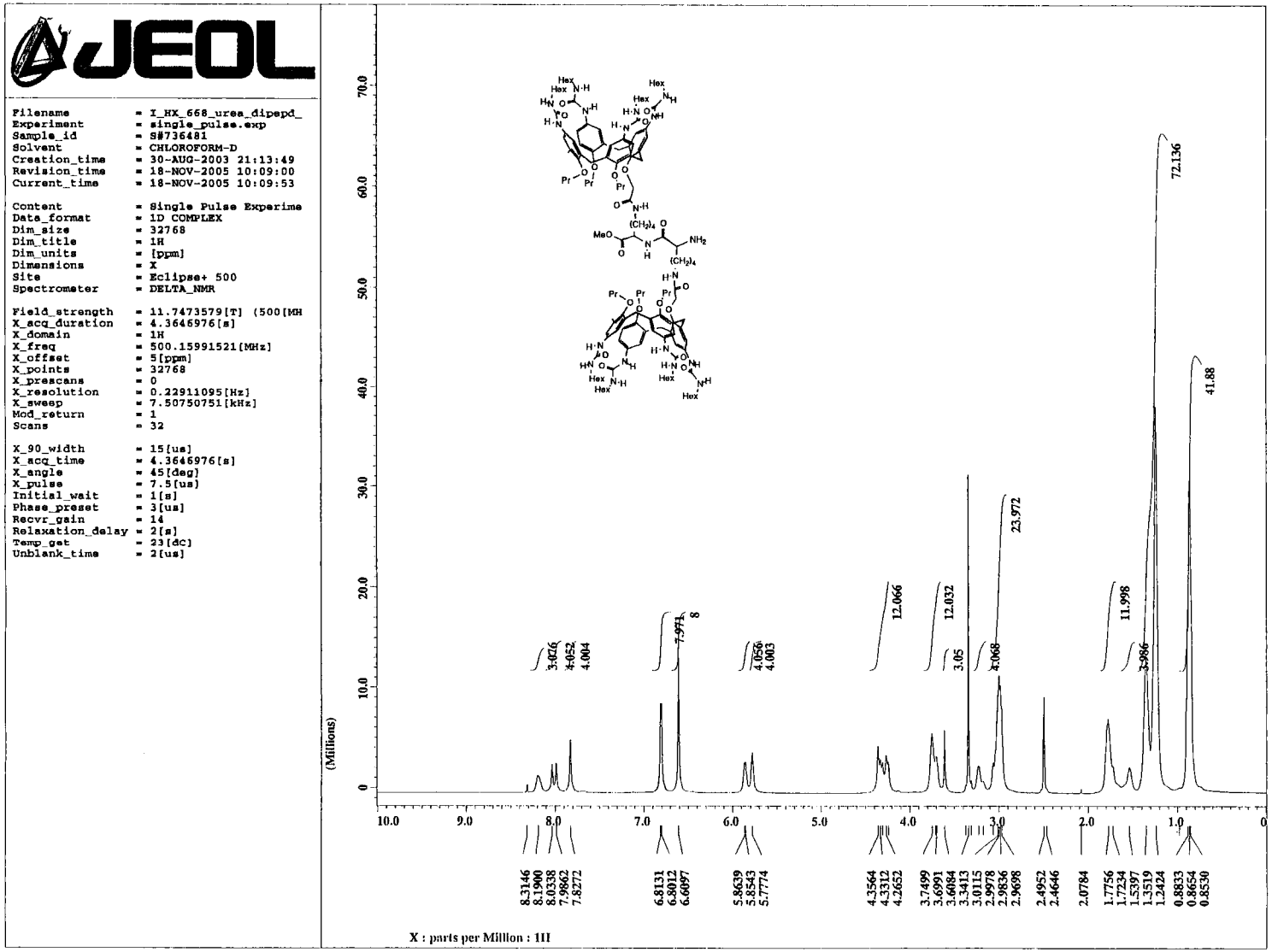

JEOL
Filename = I_HX_789_ureadipepd_h
Experiment = single_pulse.exp
Sample_id = S#844736
Solvent = CHLOROFORM-D
Creation_time = 30-OCT-2003 09:59:32
Revision_time = 18-NOV-2005 09:44:08
Current_time = 18-NOV-2005 09:44:29
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 13
Relaxation_delay = 1[s]
Temp_get = 22.6[dC]
Unblank_time = 2[us]
R = n-Pr, R1 = n-Hex
(Millions)
8.3449
8.2688
8.2221
7.9894
7.9399
6.8112
6.5437
6.1388
6.0160
4.3550
4.2451
3.7320
3.3848
3.2786
3.2666
3.2199
3.1567
2.9936
2.9726
2.5172
2.4943
2.0747
1.7504
1.5873
1.5260
1.3446
1.3326
1.2337
0.9653
0.8434
X : parts per Million : 1H

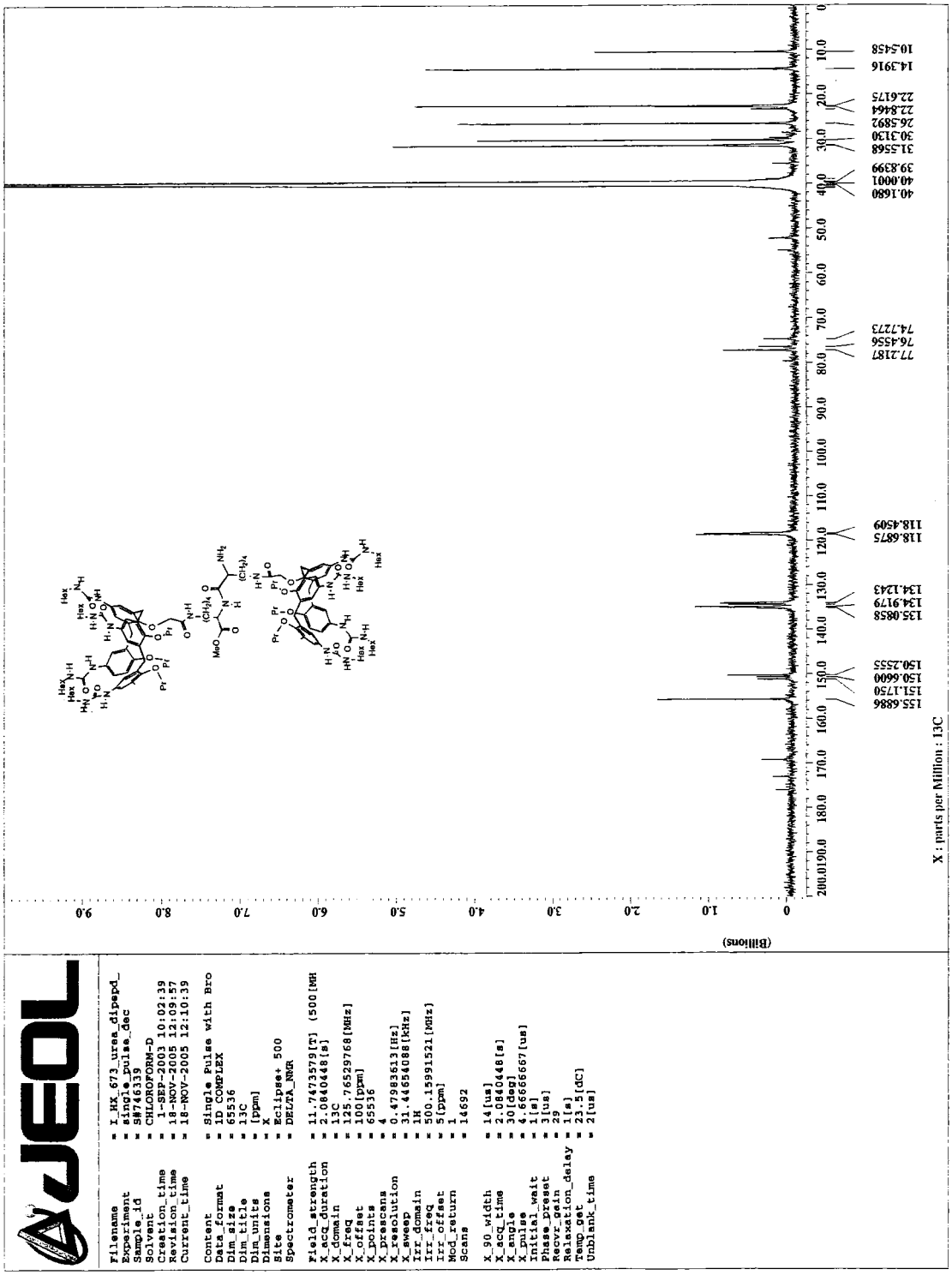

Filename = II_HX_139_ureadipepd_
Experiment = single_pulse_dec
Sample_id = S#338615
Solvent = DMSO-D6
Creation_time = 27-OCT-2004 17:52:10
Revision_time = 18-NOV-2005 11:34:55
Current_time = 18-NOV-2005 11:36:14
Content = Single Pulse with Bro
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Mod_return = 1
Scans = 10000
X_90_width = 14[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.66666667[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 29
Relaxation_delay = 2[s]
Temp_get = 24.8[dC]
Unblank_time = 2[us]
R = n-Pr, R1 = n-Hex
(Billions)
175.3490
171.6824
169.3360
162.9873
161.8045
155.7916
151.2513
150.6867
150.2021
135.1544
134.9370
134.1167
118.8363
118.5578
79.6986
77.2530
76.3946
74.7196
55.1699
40.3015
40.1375
39.9696
39.8017
39.6338
39.5079
31.5949
26.6198
22.6366
14.3611
10.5343
X : parts per Million : 13C

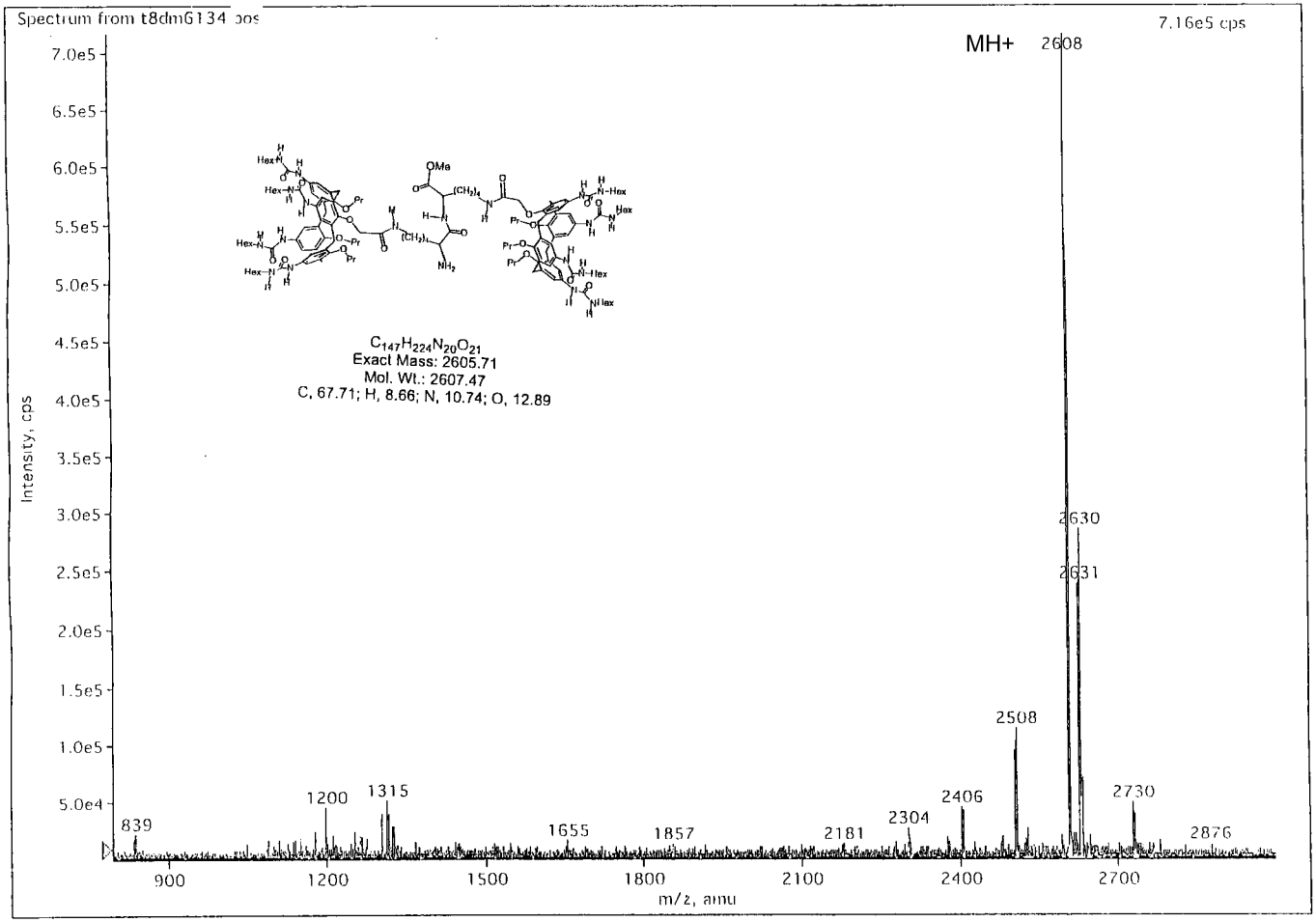
APPENDIX 38

^{1}H NMR and ^{13}C NMR SPECTRA OF

Biscalixarene (68)


JEOL
Filename = I_HX_668_urea_dipepd_
Experiment = single_pulse.exp
Sample_id = S#736481
Solvent = CHLOROFORM-D
Creation_time = 30-AUG-2003 21:13:49
Revision_time = 18-NOV-2005 10:09:00
Current_time = 18-NOV-2005 10:09:53
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 4.3646976[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.22911095[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 32
X_90_width = 15[us]
X_acq_time = 4.3646976[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 14
Relaxation_delay = 2[s]
Temp_get = 23[dC]
Unblank_time = 2[us]
(Millions)
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
3.026
4.052
4.004
7.971
8
4.056
4.003
12.066
12.032
3.05
4.068
23.972
11.998
3.986
72.136
41.88
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.3146
8.1900
8.0338
7.9862
7.8272
6.8131
6.8012
6.6897
5.8639
5.8543
5.7774
4.3564
4.3312
4.2652
3.7499
3.6991
3.6084
3.3413
3.0115
2.9978
2.9836
2.9698
2.4952
2.4646
2.0784
1.7756
1.7234
1.5397
1.3519
1.2424
0.8833
0.8654
0.8530
X : parts per Million : 1H


JEOL
Filename = I_HX_673_urea_dipepd_
Experiment = single_pulse_dec
Sample_id = S#746339
Solvent = CHLOROFORM-D
Creation_time = 1-SEP-2003 10:02:39
Revision_time = 18-NOV-2005 12:09:57
Current_time = 18-NOV-2005 12:10:39
Content = Single Pulse with Bro
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.765297681MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.159991521[MHz]
Irr_offset = 5[ppm]
Mod_return = 1
Scans = 14692
X_90_width = 14[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.66666667[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 29
Relaxation_delay = 1[s]
Temp_get = 23.5[dC]
Unblank_time = 2[us]
(Billions)
X : parts per Million : 13C
155.6886
151.1750
150.6600
150.2555
135.0858
134.9179
134.1243
118.6875
118.4509
77.2187
76.4556
74.7273
40.1680
40.0001
39.8399
31.5568
30.3130
26.5892
22.8464
22.6175
14.3916
10.5458

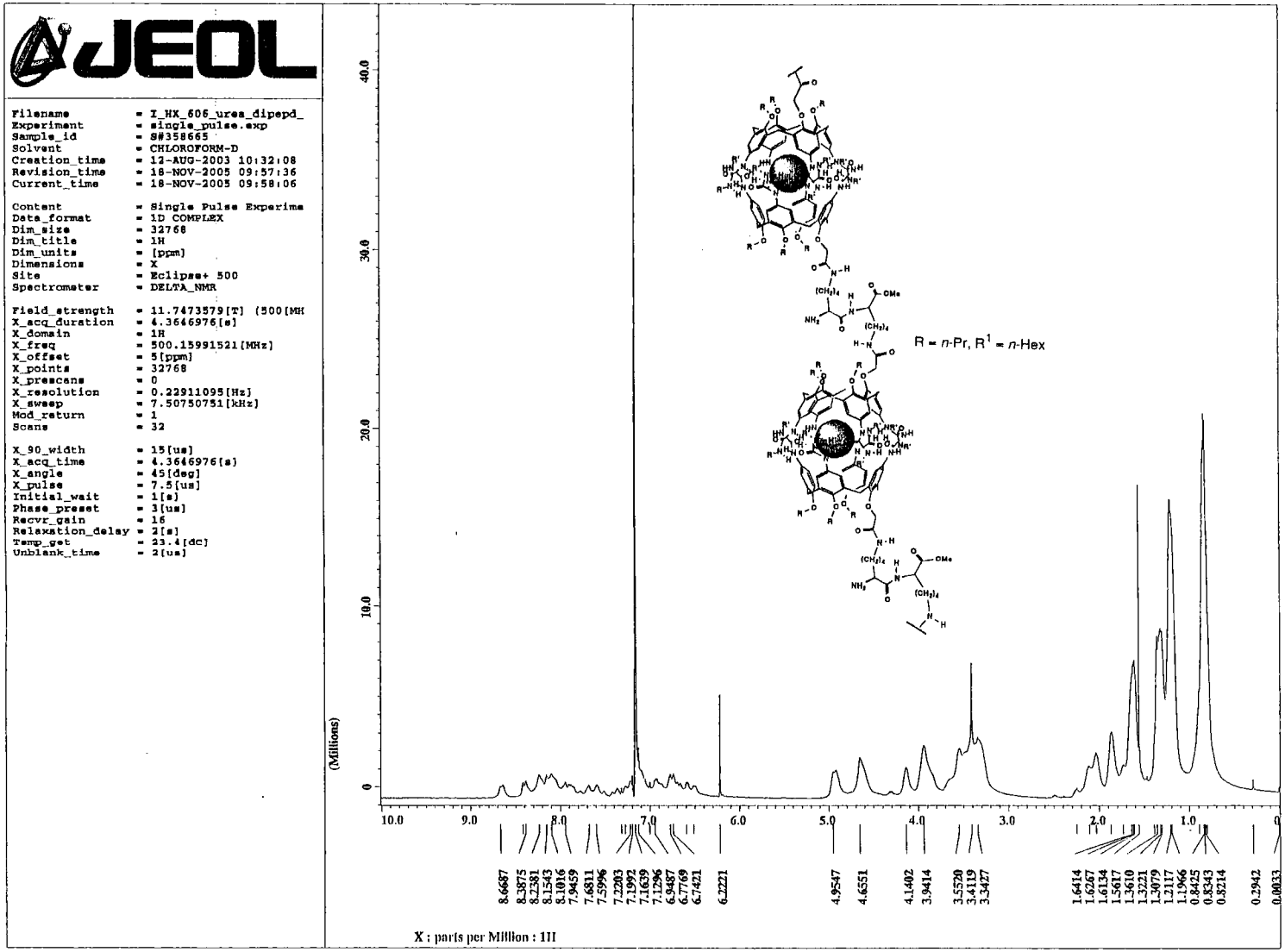


$C_{147}H_{224}N_{20}O_{21}$
Exact Mass: 2605.71
Mol. Wt.: 2607.47
C, 67.71; H, 8.66; N, 10.74; O, 12.89

APPENDIX 39

^{1}H NMR SPECTRUM OF

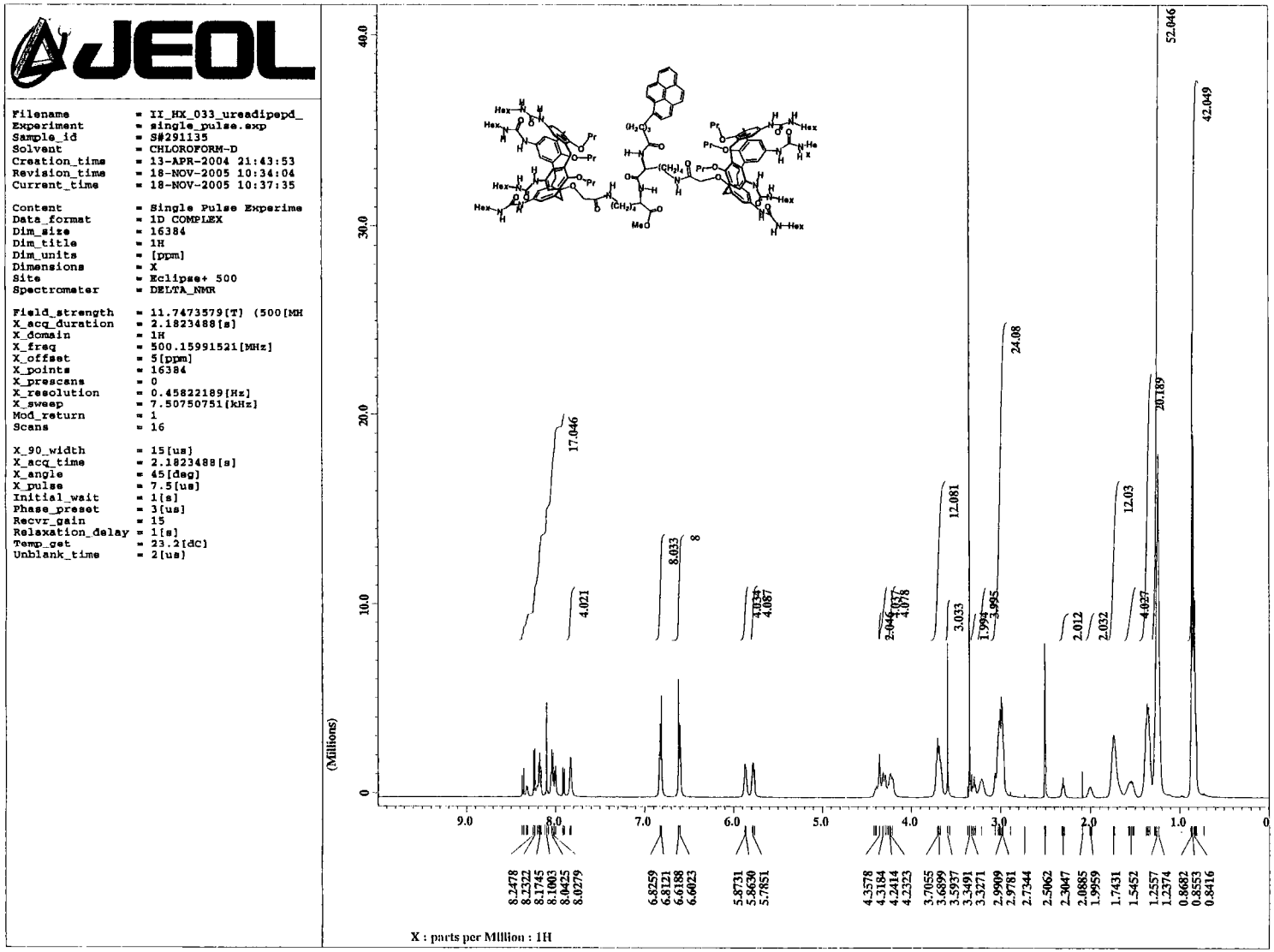
Calixarene supramolecular polymer (69)


JEOL
Filename = I_HX_606_ures_dipepd_
Experiment = single_pulse.exp
Sample_id = S#358665
Solvent = CHLOROFORM-D
Creation_time = 12-AUG-2003 10:32:08
Revision_time = 18-NOV-2005 09:57:36
Current_time = 18-NOV-2005 09:58:06
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 4.3646976[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 0
X_resolution = 0.22911095[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 32
X_90_width = 15[us]
X_acq_time = 4.3646976[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 16
Relaxation_delay = 2[s]
Temp_get = 23.4[dc]
Unblank_time = 2[us]
R = n-Pr, R1 = n-Hex
(Millions)
40.0
30.0
20.0
10.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
8.6687
8.3875
8.2381
8.1543
8.1016
7.9459
7.6811
7.5996
7.2203
7.1992
7.1639
7.1296
6.9487
6.7769
6.7421
6.2221
4.9547
4.6551
4.1402
3.9414
3.5520
3.4119
3.3427
1.6414
1.6267
1.6134
1.5617
1.3610
1.3221
1.3079
1.2117
1.1966
0.8425
0.8343
0.8214
0.2942
0.0033
X : parts per Million : 1H

APPENDIX 40

^{1}H NMR SPECTRUM OF

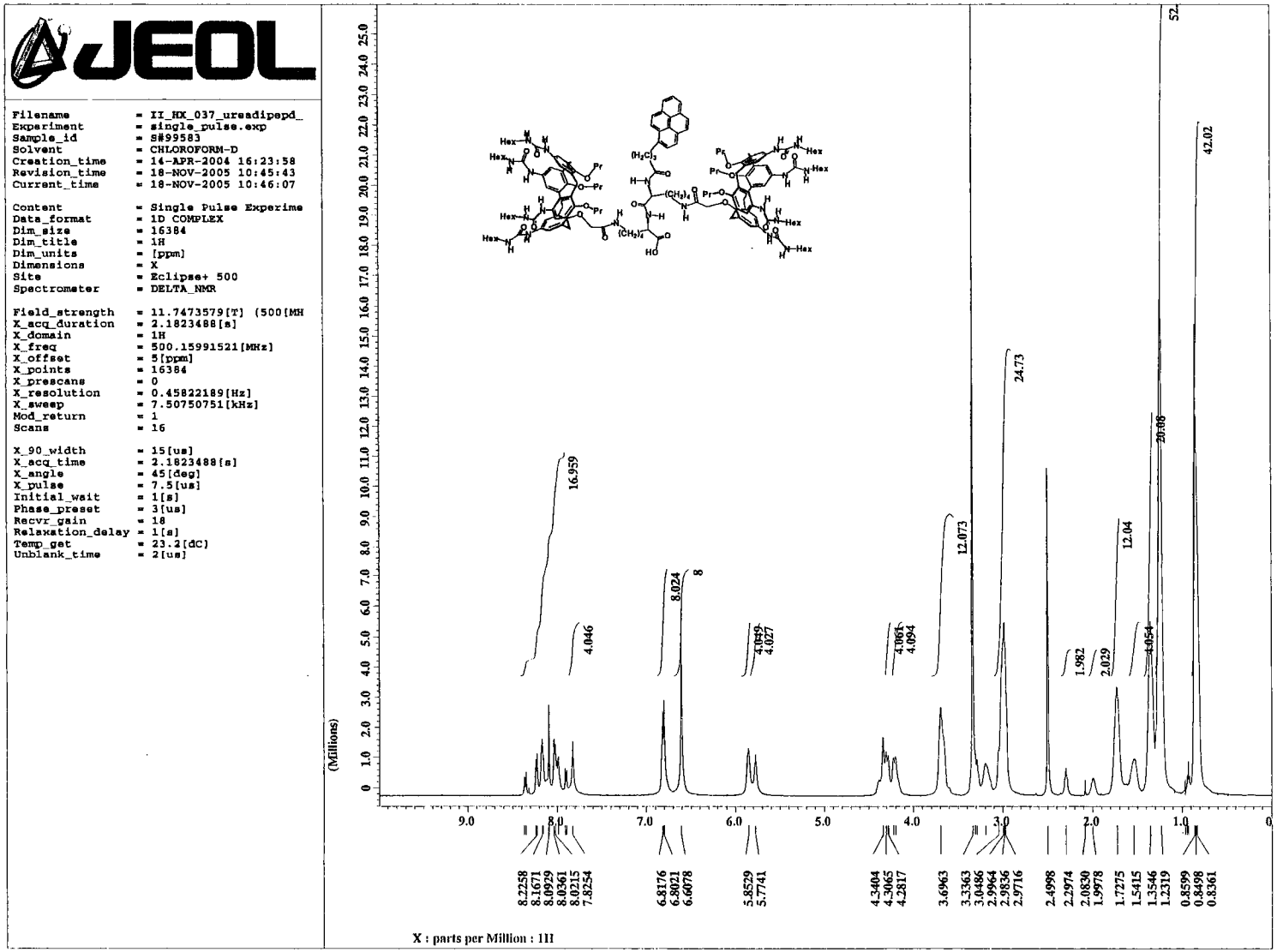
Biscalixarene (70)


JEOL
Filename = II_HX_033_ureadipepd_
Experiment = single_pulse.exp
Sample_id = S#291135
Solvent = CHLOROFORM-D
Creation_time = 13-APR-2004 21:43:53
Revision_time = 18-NOV-2005 10:34:04
Current_time = 18-NOV-2005 10:37:35
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 15
Relaxation_delay = 1[s]
Temp_get = 23.2[dC]
Unblank_time = 2[us]
(Millions)
X : parts per Million : 1H

APPENDIX 41

^{1}H NMR SPECTRUM OF

Biscalixarene (71)



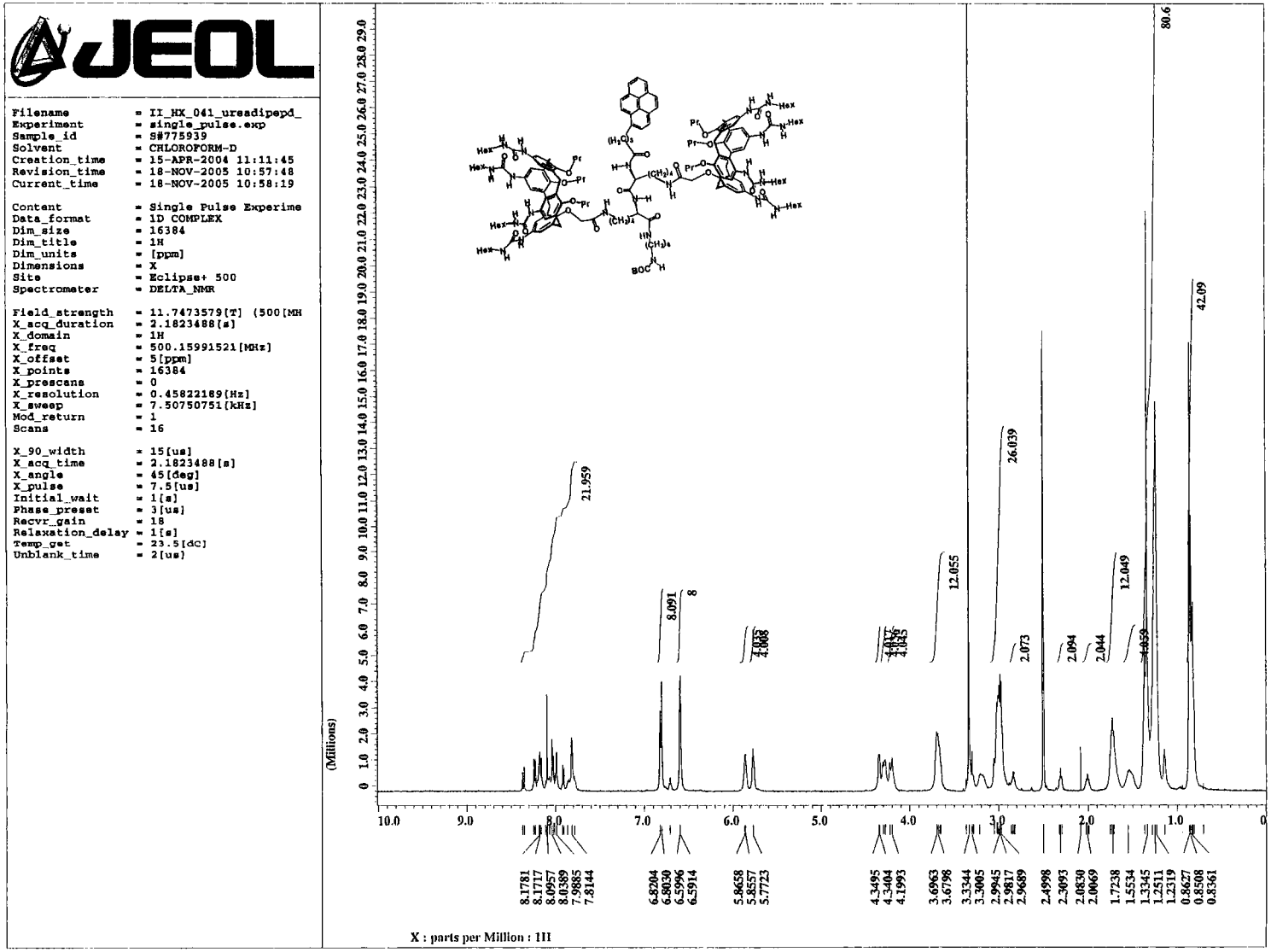
JEOL

Filename	= II_HX_037_uresadipepd_
Experiment	= single_pulse.exp
Sample_id	= S#99583
Solvent	= CHLOROFORM-D
Creation_time	= 14-APR-2004 16:23:58
Revision_time	= 18-NOV-2005 10:45:43
Current_time	= 18-NOV-2005 10:46:07
Content	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 16384
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.1823488[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 0
X_resolution	= 0.45822189[Hz]
X_sweep	= 7.50750751[kHz]
Mod_return	= 1
Scans	= 16
X_90_width	= 15[us]
X_acq_time	= 2.1823488[s]
X_angle	= 45[deg]
X_pulse	= 7.5[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 18
Relaxation_delay	= 1[s]
Temp_get	= 23.2[dC]
Unblank_time	= 2[us]

APPENDIX 42

^{1}H NMR and MASS SPECTRA OF

Biscalixarene (72)

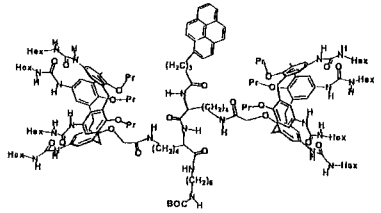

JEOL
Filename = II_HX_041_uresadipepd_
Experiment = single_pulse.exp
Sample_id = S#775939
Solvent = CHLOROFORM-D
Creation_time = 15-APR-2004 11:11:45
Revision_time = 18-NOV-2005 10:57:48
Current_time = 18-NOV-2005 10:58:19
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 18
Relaxation_delay = 1[s]
Temp_get = 23.5[dC]
Unblank_time = 2[us]
(Millions)
21.959
8.091
8
12.055
26.039
2.073
2.094
2.044
12.049
42.09
80.6
8.1781
8.1717
8.0957
8.0389
7.9885
7.8144
6.8204
6.8030
6.5996
6.5914
5.8658
5.8557
5.7723
4.3495
4.3404
4.1993
3.6963
3.6798
3.3344
3.3005
2.9945
2.9817
2.9689
2.4998
2.3093
2.0830
2.0069
1.7238
1.5534
1.3345
1.2511
1.2319
0.8627
0.8508
0.8361
X : parts per Million : 1H

MALDI TOF

Original Filename: d:\data\2004\april\041204\i606.ms
This File # 1 : D:\DATA\2004\APRIL\041204\SMOOTH.MS
Comment

Method: MYO1
Accelerating Voltage: 25000
Grid Voltage: 90.000 %
Guide Wire Voltage: 0.150 %
Delay: 100 ON
Sample: 45

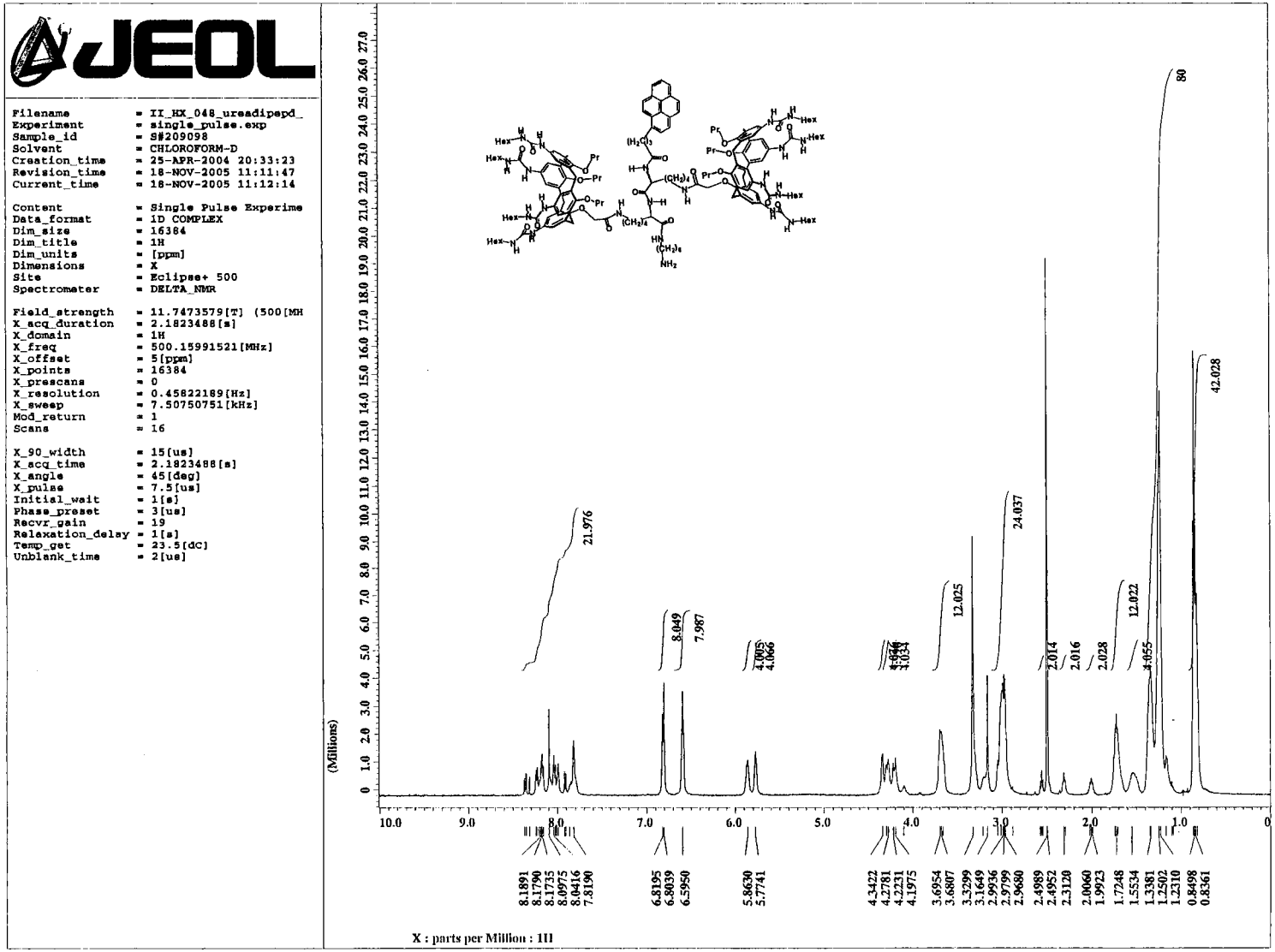
Laser : 1900
Scans Averaged: 65
Pressure: 3.58e-07
Low Mass Gate: 400.0
Negative Ions: OFF
Collected: 4/12/04 9:44 AM



$C_{177}H_{258}N_{22}O_{23}$
Exact Mass: 3059.97
Mol. Wt.: 3062.08
C, 69.43; H, 8.49; N, 10.06; O, 12.02

APPENDIX 43

^{1}H NMR, ^{13}C NMR and MASS SPECTRA OF Biscalixarene (73)


JEOL
Filename = II_HX_048_ureadipepd_
Experiment = single_pulse.exp
Sample_id = S#209098
Solvent = CHLOROFORM-D
Creation_time = 25-APR-2004 20:33:23
Revision_time = 18-NOV-2005 11:11:47
Current_time = 18-NOV-2005 11:12:14
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 19
Relaxation_delay = 1[s]
Temp_get = 23.5[dC]
Unblank_time = 2[us]
(Millions)
21.976
8.049
7.987
4.005
4.066
12.025
24.037
2.014
2.016
2.028
12.022
4.055
80
42.028
8.1891
8.1790
8.1735
8.0975
8.0416
7.8190
6.8195
6.8039
6.5950
5.8630
5.7741
4.3422
4.2781
4.2231
4.1975
3.6954
3.6807
3.3299
3.1649
2.9936
2.9799
2.9680
2.4989
2.4952
2.3120
2.0060
1.9923
1.7248
1.5534
1.3381
1.2502
1.2310
0.8498
0.8361
X : parts per Million : 111

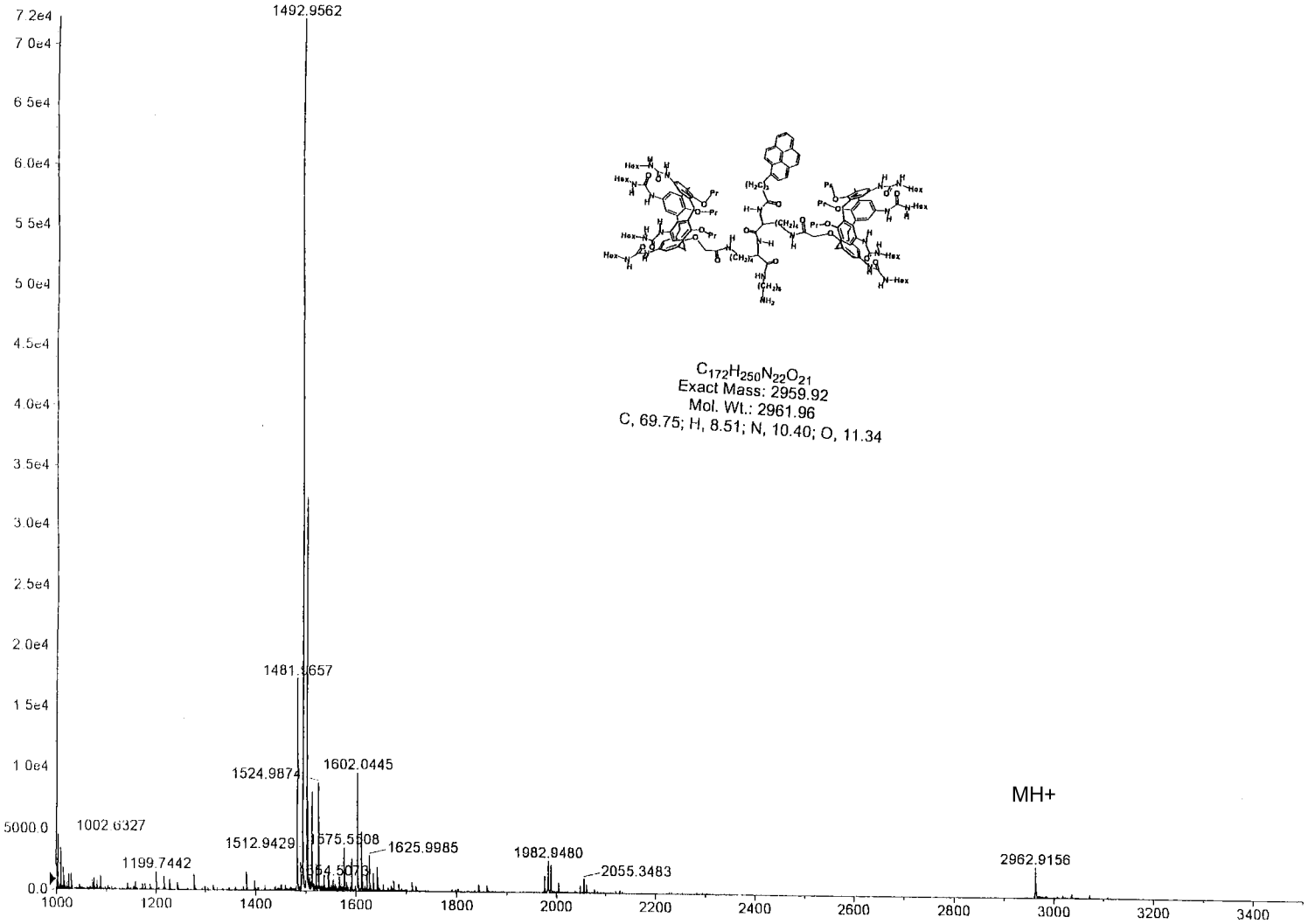
JEOL
Filename = II_HX_052_ureadipapd_
Experiment = single_pulse_dec
Sample_id = SAMPLE
Solvent = DMSO-D6
Creation_time = 27-APR-2004 11:26:33
Revision_time = 18-NOV-2005 11:38:56
Current_time = 18-NOV-2005 11:39:08
Content = Single Pulse with Bro
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.0840448[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613[Hz]
X_sweep = 31.44654088[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5[ppm]
Mod_return = 1
Scans = 10224
X_90_width = 14[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.66666667[us]
Initial_wait = 1[s]
Phase_preset = 2[us]
Recycle_delay = 2[s]
Relaxation_delay = 24.4[dC]
Unblank_time = 2[us]
(Billions)
X : parts per Million : 13C
172.9033
171.6023
169.3513
169.3055
155.7992
155.7572
150.7172
150.2784
135.1773
134.9637
134.4181
134.1930
133.9679
128.8668
118.7600
118.5387
77.2683
76.4670
74.7921
40.2329
40.0650
39.8971
31.6255
30.3664
26.7876
26.6579
22.8617
22.6823
14.4450
10.5916

larity/Scan Type: Positive

+TOF MS. 0.552 min from Sample 1 (t8dm4607) of 040904050.wiff Agilent

Printing Date: 12/04/20

Max. 1.5e5 coun



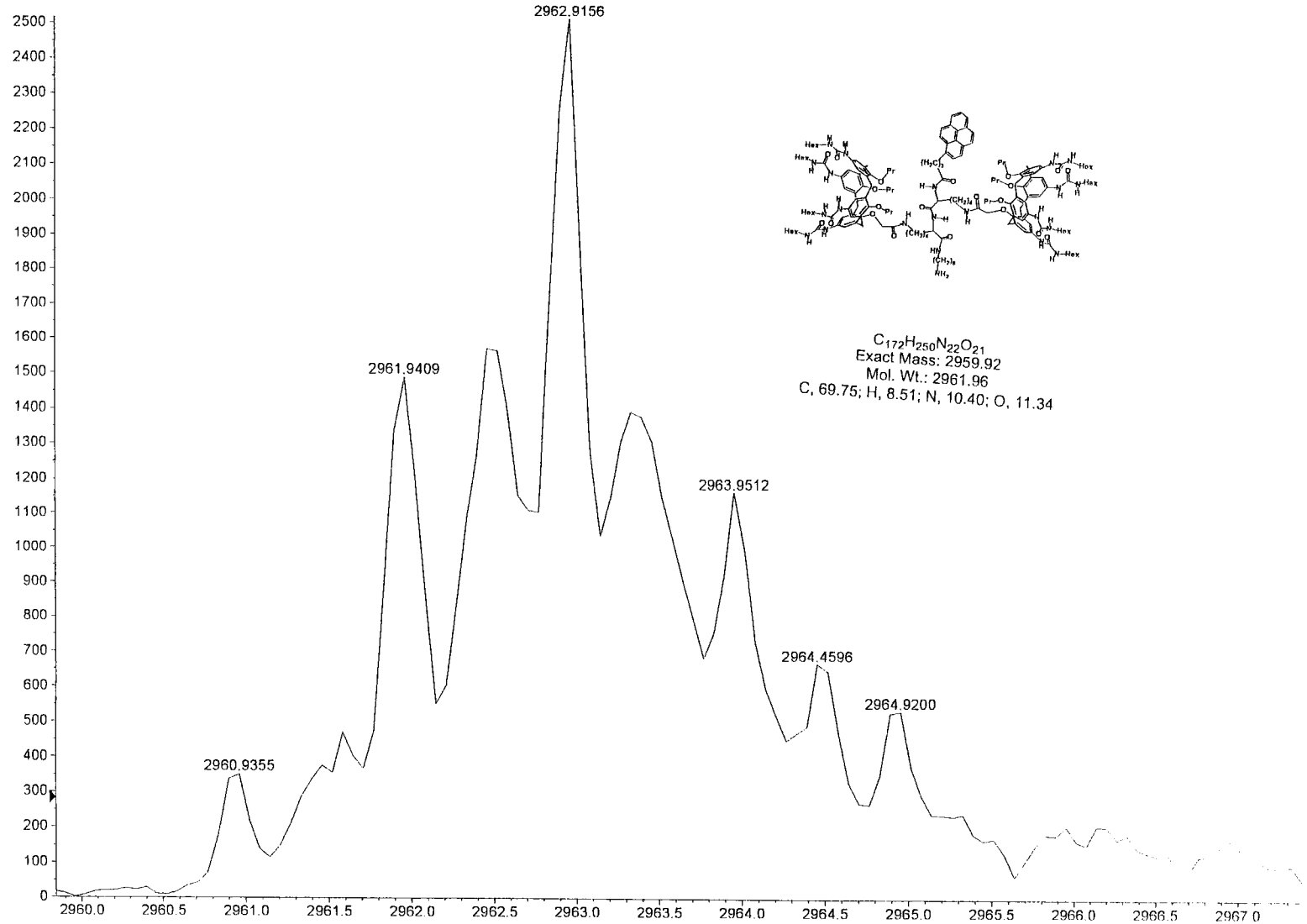
$C_{172}H_{250}N_{22}O_{21}$
Exact Mass: 2959.92
Mol. Wt.: 2961.96
C, 69.75; H, 8.51; N, 10.40; O, 11.34

larity/Scan Type: Positive

Printing Date: 12/04/20

+TOF MS: 0.552 min from Sample 1 (t8dm4607) of 040904050.wiff Agilent

Max. 1.5e5 coun



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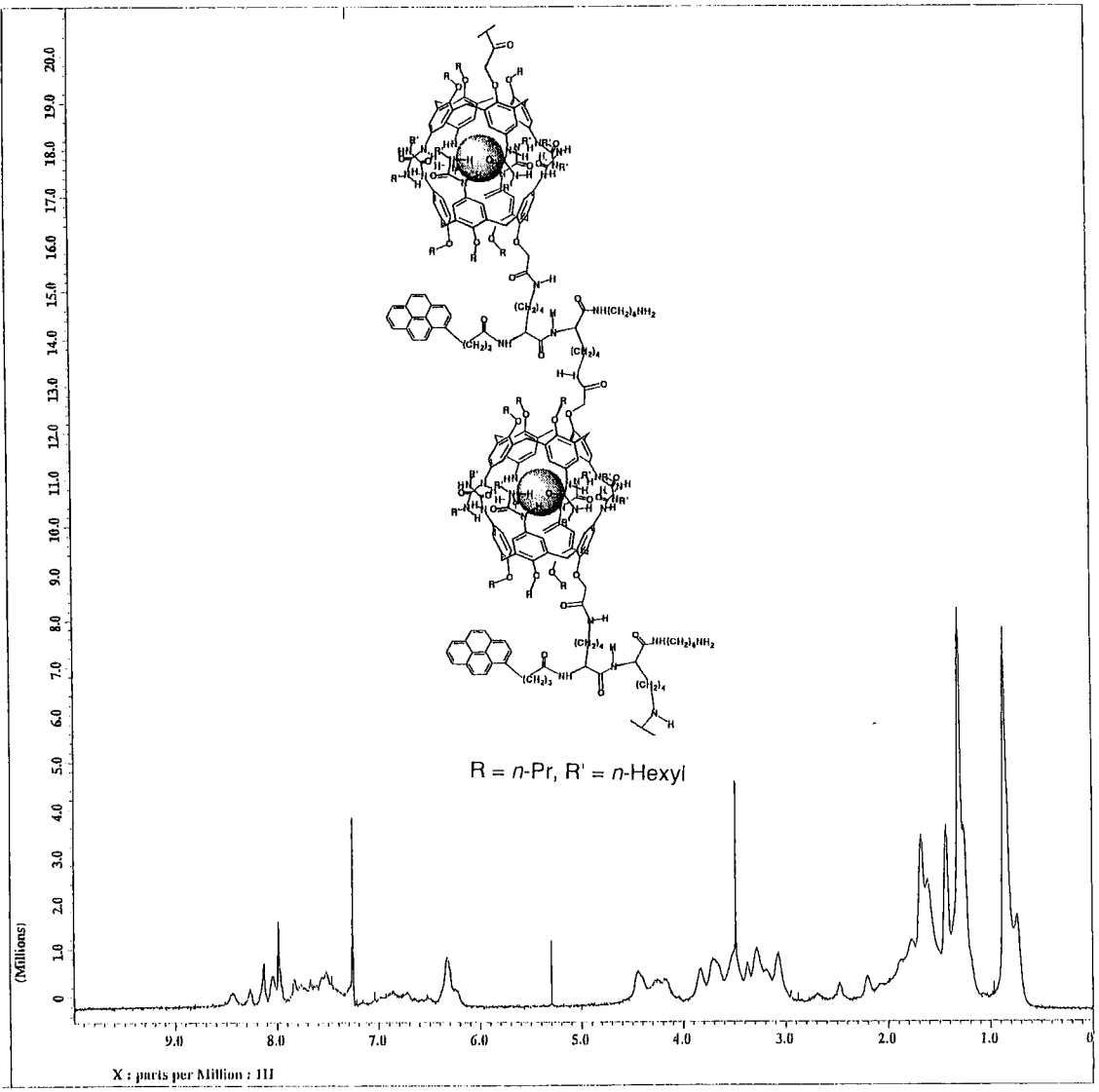
APPENDIX 44

^{1}H NMR SPECTRUM OF

Calixarene supramolecular polymer (74)

JEOL

Filename	= II_HX_049_ureadipepd_
Experiment	= single_pulse.exp
Sample_id	= S#219890
Solvent	= CHLOROFORM-D
Creation_time	= 25-APR-2004 20:50:55
Revision_time	= 1-MAY-2004 06:08:28
Current_time	= 18-NOV-2005 11:24:29
Content	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 16384
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.1823488[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 0
X_resolution	= 0.45822189[Hz]
X_sweep	= 7.50750751[kHz]
Mod_return	= 1
Scans	= 16
X_90_width	= 15[us]
X_acq_time	= 2.1823488[s]
X_angle	= 45[deg]
X_pulse	= 7.5[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 20
Relaxation_delay	= 1[s]
Temp_set	= 23.4[dC]
Unblank_time	= 2[us]



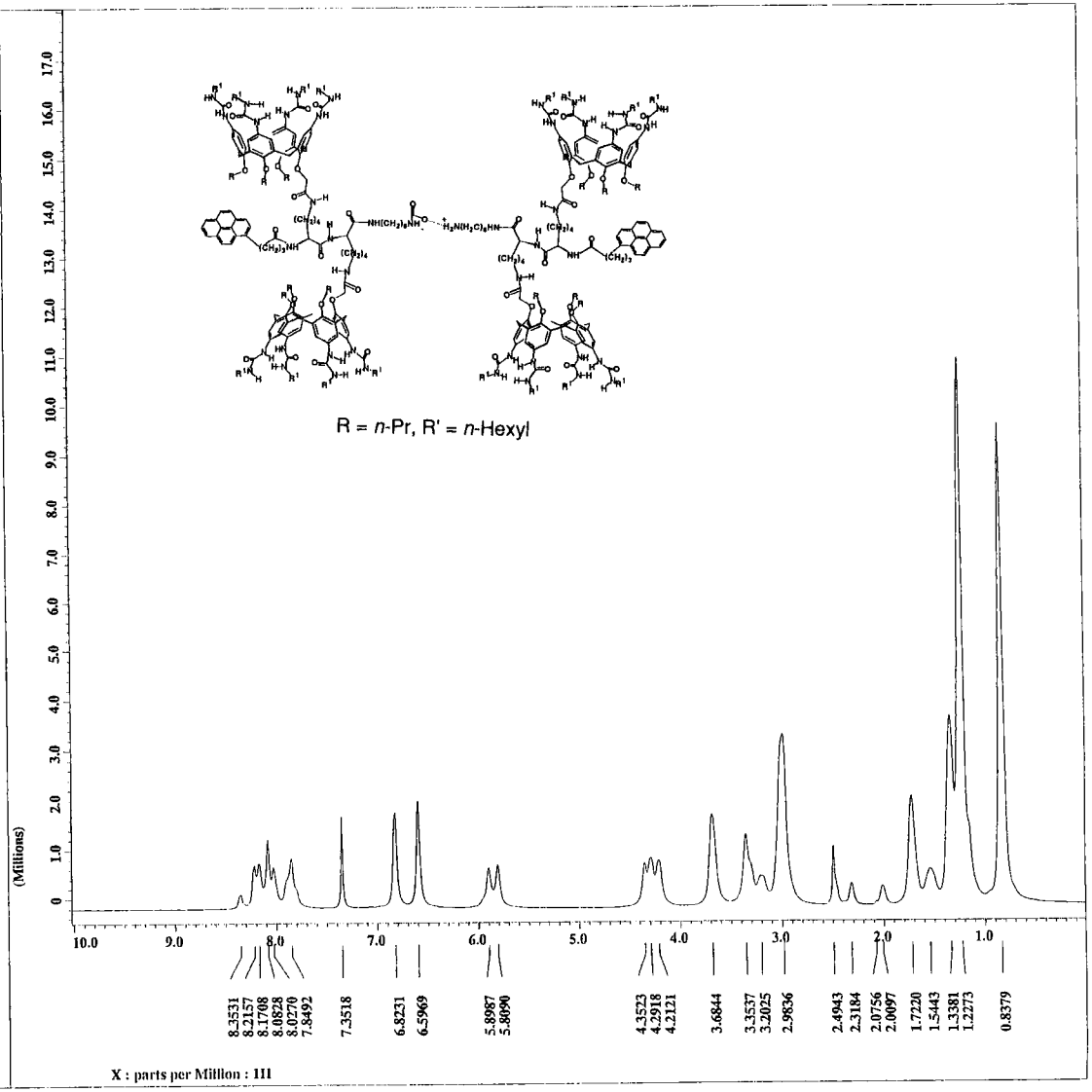
APPENDIX 45

^{1}H NMR and ^{13}C NMR SPECTRA OF

Biscalixarene (75)

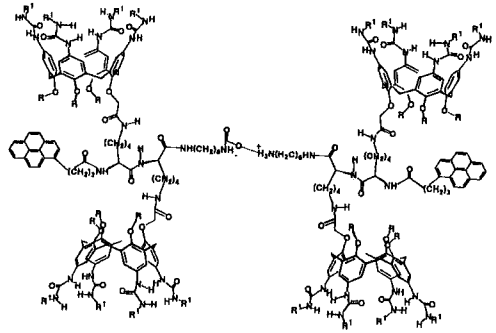
JEOL

Filename	= II_HX_046_ureadipepd_
Experiment	= single_pulse.exp
Sample_id	= S#316623
Solvent	= CHLOROFORM-D
Creation_time	= 21-APR-2004 22:29:48
Revision_time	= 18-NOV-2005 11:18:33
Current_time	= 18-NOV-2005 11:19:37
Content	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 16384
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectromster	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.1823488[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 0
X_resolution	= 0.45822189[Hz]
X_sweep	= 7.50750751[kHz]
Mod_return	= 1
Scans	= 16
X_90_width	= 15[us]
X_acq_time	= 2.1823488[s]
X_angle	= 45[deg]
X_pulse	= 7.5[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 12
Relaxation_delay	= 1[s]
Temp_get	= 23.4[dC]
Unblank_time	= 2[us]



JEOL

Filename	= II_HX_046_uresadipepd_
Experiment	= single_pulse_dec
Sample_id	= S#321157
Solvent	= DMSO-D6
Creation_time	= 22-APR-2004 10:08:36
Revision_time	= 18-NOV-2005 11:37:03
Current_time	= 18-NOV-2005 11:37:21
Content	= Single Pulse with Bro
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.0840448[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.47983613[Hz]
X_sweep	= 31.44654088[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5[ppm]
Mod_return	= 1
Scans	= 10138
X_90_width	= 14[us]
X_acq_time	= 2.0840448[s]
X_angle	= 30[deg]
X_pulse	= 4.66666667[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 28
Relaxation_delay	= 2[s]
Temp_get	= 23.9[dC]
Unblank_time	= 2[us]



R = *n*-Pr, R' = *n*-Hexyl

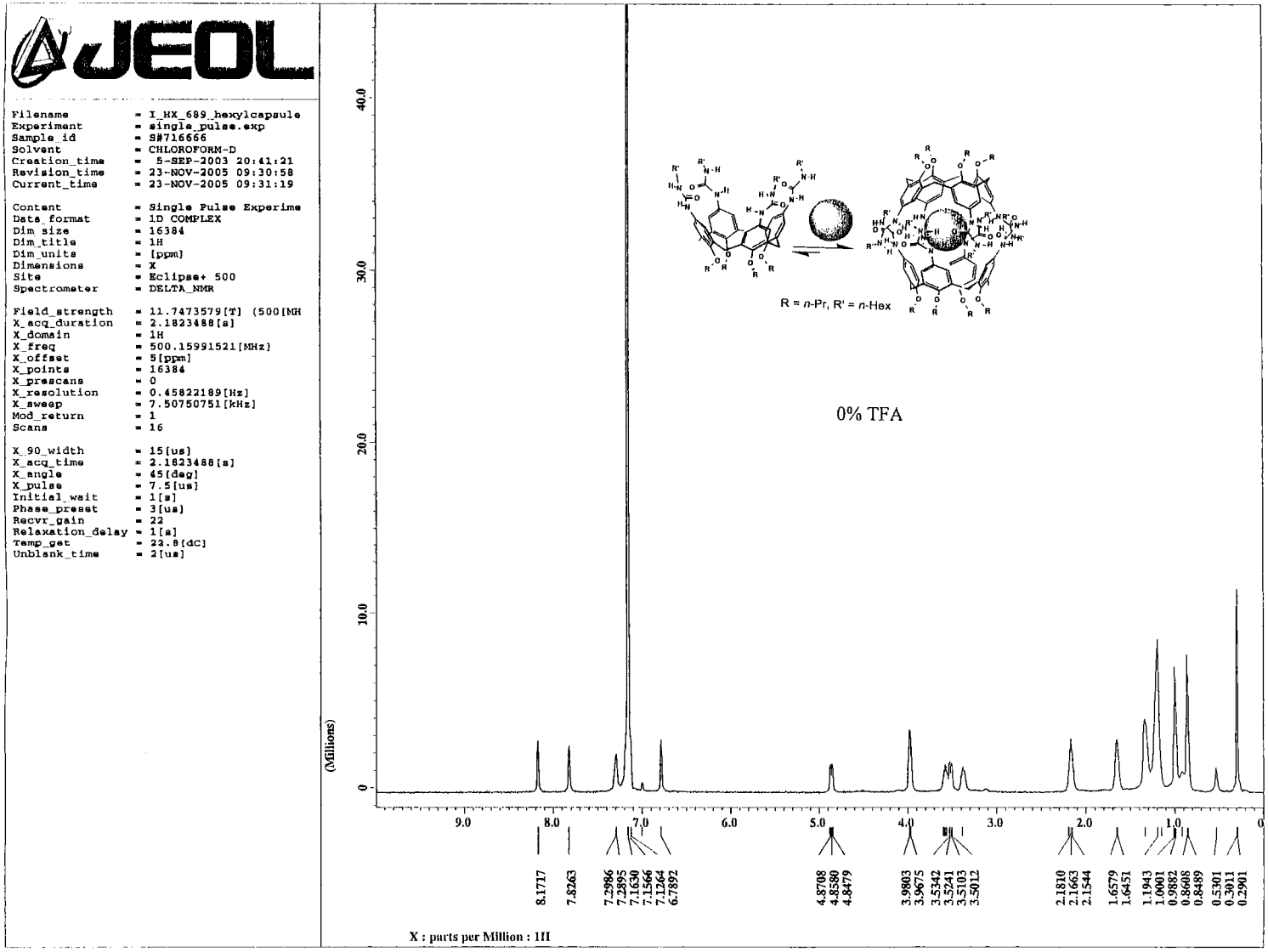
(Billions)

171.6099
169.3665
169.3207
160.6714
155.7725
150.7248
150.2670
135.1812
134.9789
134.4028
134.1892
128.8706
118.7752
118.5539
77.2645
76.4594
74.8074
40.5724
40.4084
40.2445
40.0726
39.9086
39.7407
39.5766
14.4527
10.5954

X : parts per Million : 13C

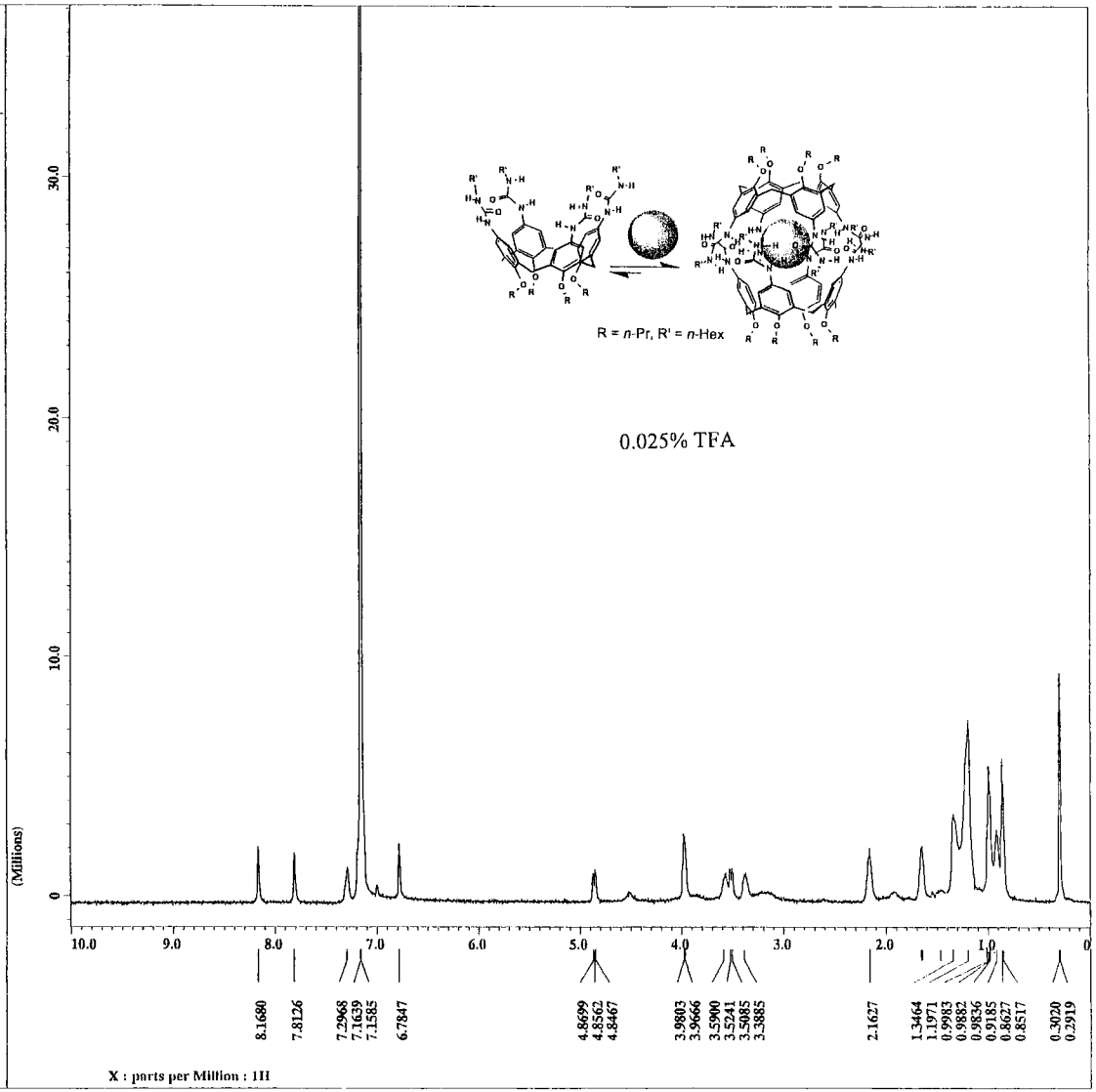
APPENDIX 46

^{1}H NMR SPECTRA OF
TFA Titration Experiments


JEOL
Filename = I_HX_689_hexylcapsule
Experiment = single_pulse.exp
Sample_id = S#716666
Solvent = CHLOROFORM-D
Creation_time = 5-SEP-2003 20:41:21
Revision_time = 23-NOV-2005 09:30:58
Current_time = 23-NOV-2005 09:31:19
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 22
Relaxation_delay = 1[s]
Temp_get = 22.8[dC]
Unblank_time = 2[us]
R = n-Pr, R' = n-Hex
0% TFA
(Millions)
40.0
30.0
20.0
10.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.1717
7.8263
7.2986
7.2895
7.1630
7.1566
7.1264
6.7892
4.8708
4.8580
4.8479
3.9803
3.9675
3.5342
3.5241
3.5103
3.5012
2.1830
2.1663
2.1544
1.6579
1.6451
1.1943
1.0001
0.9882
0.8608
0.8489
0.5301
0.3011
0.2901
X : parts per Million : 1H

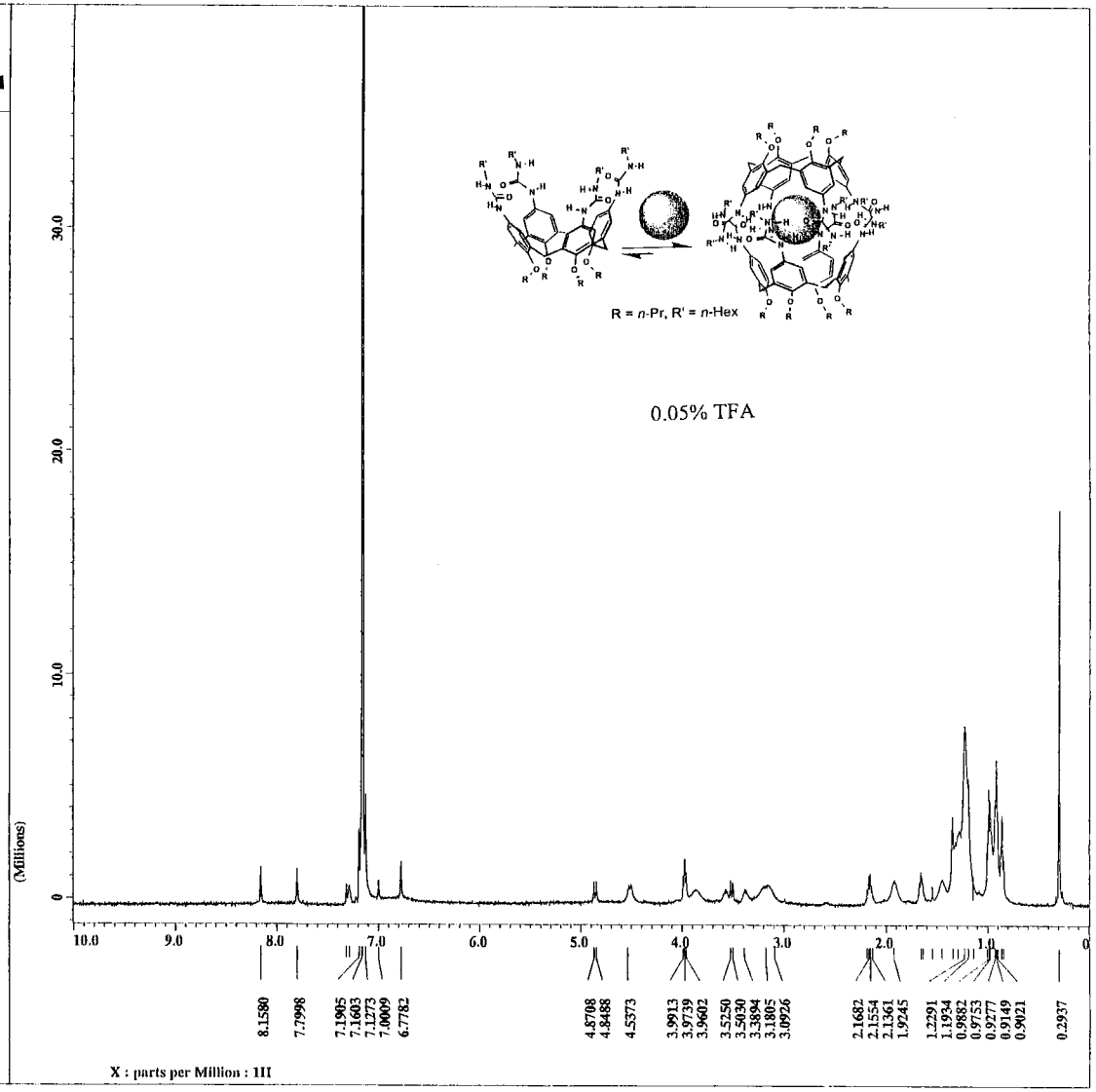
JEOL

Filename	= I_HX_691_hexylcapsule
Experiment	= single_pulse.exp
Sample_id	= S#752071
Solvent	= CHLOROFORM-D
Creation_time	= 5-SEP-2003 21:40:22
Revision_time	= 23-NOV-2005 09:35:02
Current_time	= 23-NOV-2005 09:35:14
Content	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 16384
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.1823488[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 0
X_resolution	= 0.45822189[Hz]
X_sweep	= 7.50750751[kHz]
Mod_return	= 1
Scans	= 16
X_90_width	= 15[us]
X_acq_time	= 2.1823488[s]
X_angle	= 45[deg]
X_pulse	= 7.5[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 22
Relaxation_delay	= 1[s]
Temp_get	= 22.8[dC]
Unblank_time	= 2[us]



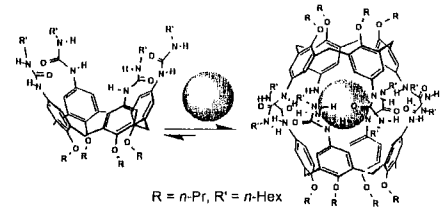
JEOL

Filename	= I_HX_692_hexylcapsule
Experiment	= single_pulse.exp
Sample_id	= S#759759
Solvent	= CHLOROFORM-D
Creation_time	= 5-SEP-2003 21:53:09
Revision_time	= 23-NOV-2005 09:33:13
Current_time	= 23-NOV-2005 09:33:32
Content	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 16384
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.1823488[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 0
X_resolution	= 0.45822189[Hz]
X_sweep	= 7.50750751[kHz]
Mod_return	= 1
Scans	= 16
X_90_width	= 15[us]
X_acq_time	= 2.1823488[s]
X_angle	= 45[deg]
X_pulse	= 7.5[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 22
Relaxation_delay	= 1[s]
Temp_get	= 22.8[dC]
Unblank_time	= 2[us]



JEOL

Filename	= I_HX_693_hexylcapsule
Experiment	= single_pulse.exp
Sample_id	= S#766016
Solvent	= CHLOROFORM-D
Creation_time	= 5-SEP-2003 22:03:42
Revision_time	= 23-NOV-2005 09:35:56
Current_time	= 23-NOV-2005 09:36:08
Content	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 16384
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.1823488[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 0
X_resolution	= 0.45822189[Hz]
X_sweep	= 7.50750751[kHz]
Mod_return	= 1
Scans	= 16
X_90_width	= 15[us]
X_acq_time	= 2.1823488[s]
X_angle	= 45[deg]
X_pulse	= 7.5[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 21
Relaxation_delay	= 1[s]
Temp_get	= 22.8[dC]
Unblank_time	= 2[us]



R = *n*-Pr, R' = *n*-Hex

0.075% TFA

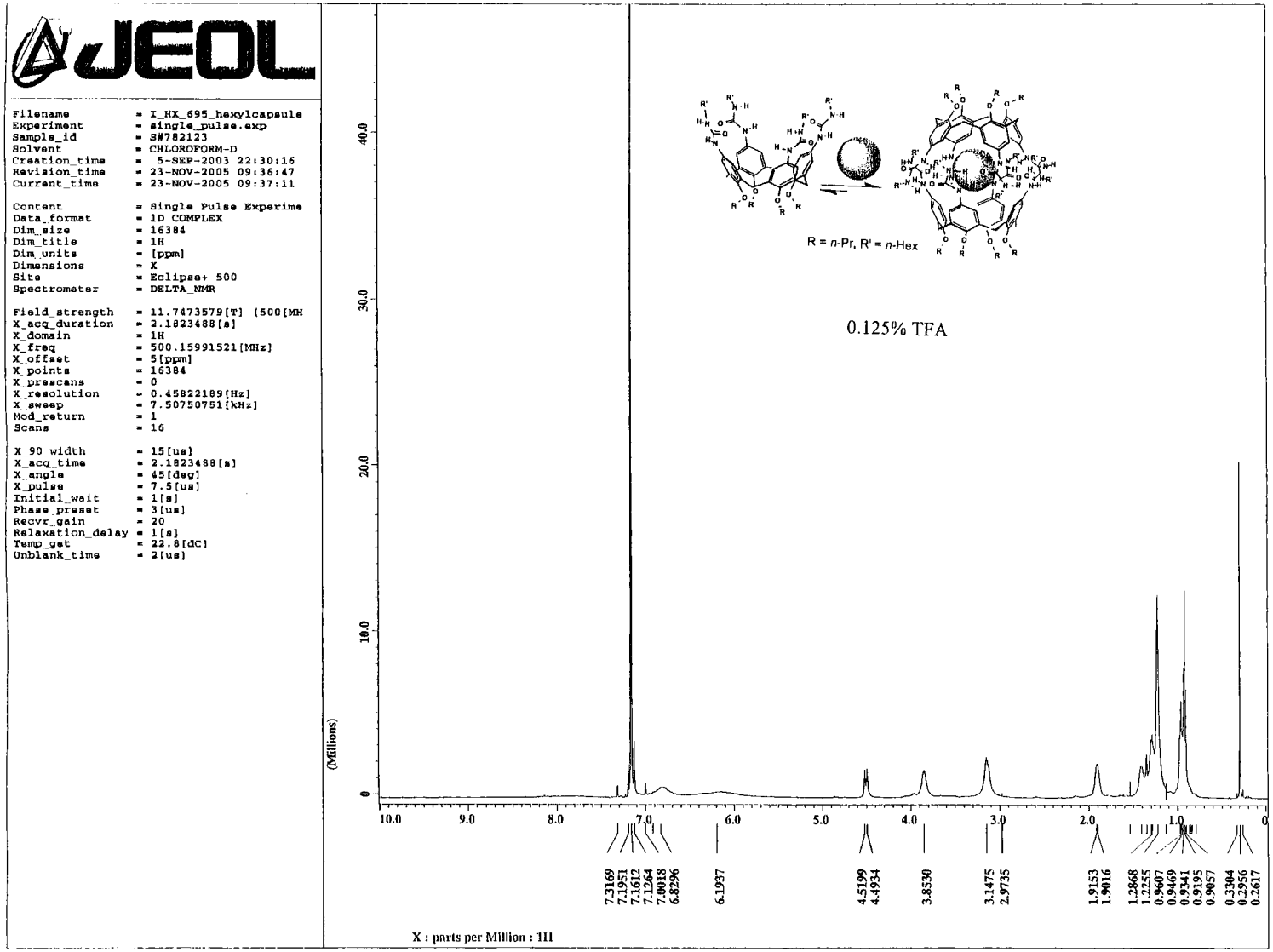
(Millions)

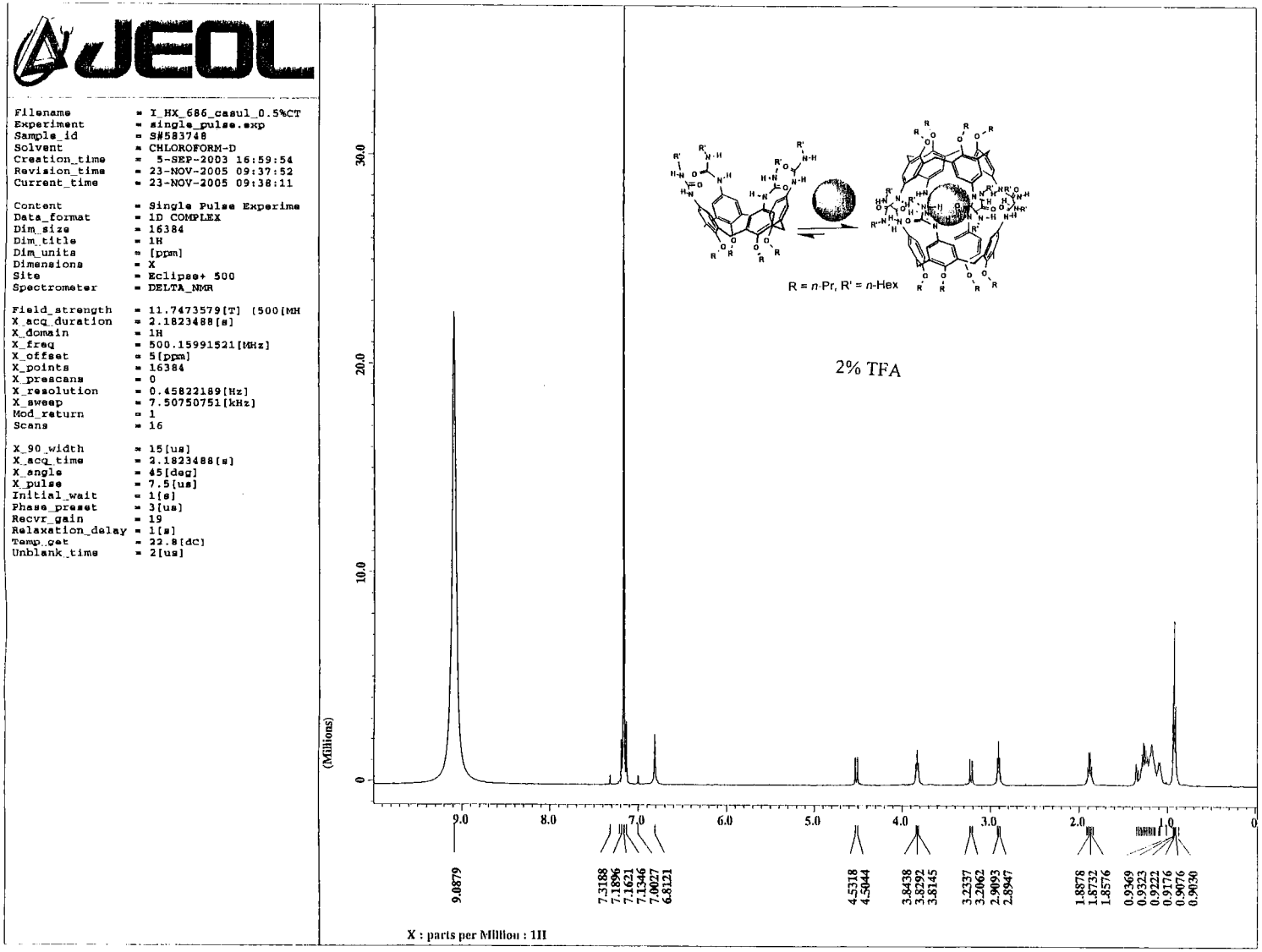
30.0
20.0
10.0
0

9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

8.1516 7.7924 7.3160 7.1914 7.1603 7.1255 7.0000 6.7755 4.8690 4.8470 4.5254 4.5007 3.9748 3.9583 3.8576 3.5259 3.5021 3.1787 3.1530 2.1663 2.1508 1.9172 1.4371 1.3491 1.2850 1.2273 0.9295 0.9167 0.9021 0.3267 0.2946 0.2617

X : parts per Million : 1H

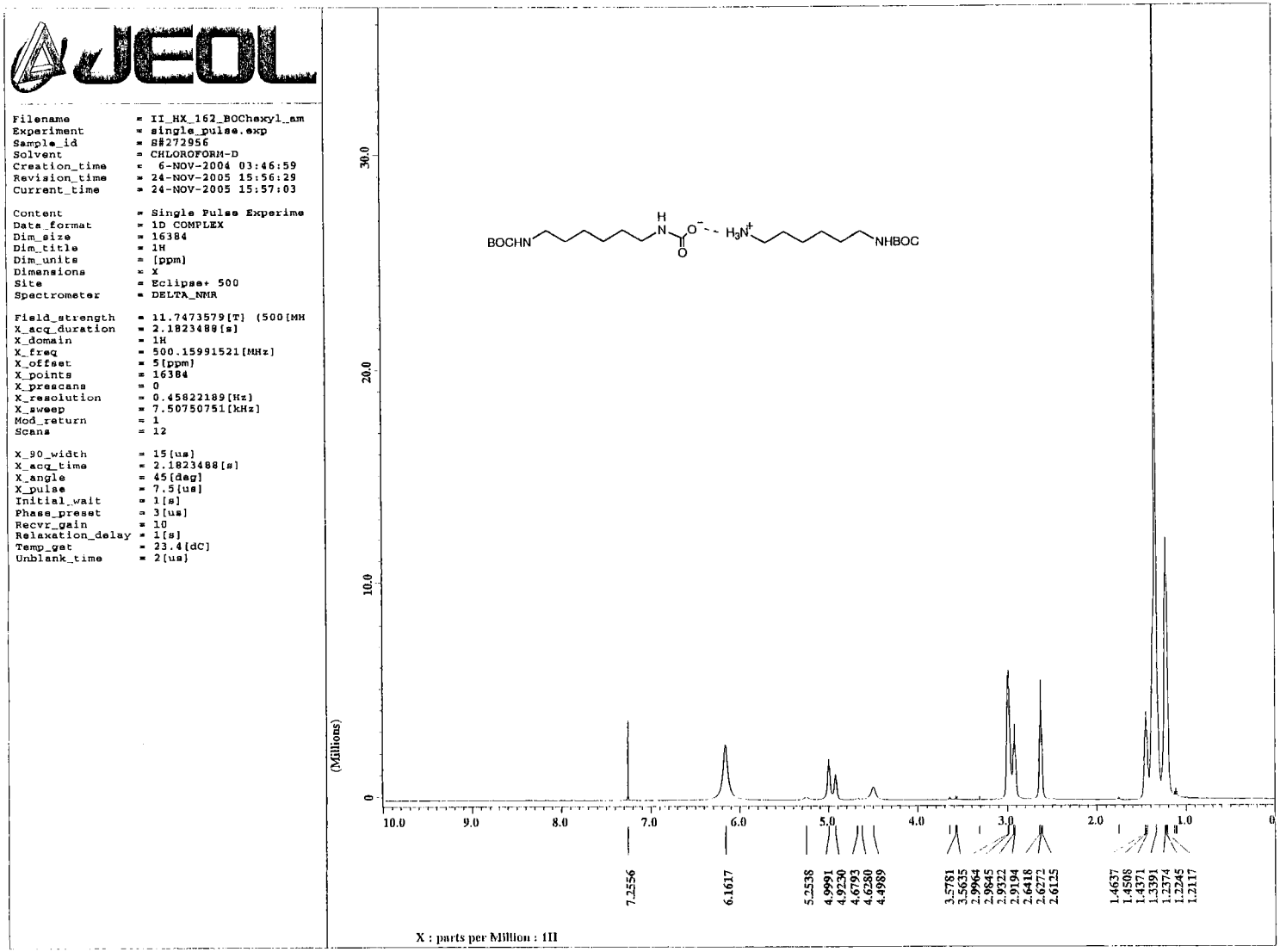

JEOL
Filename = I_HX_695_hexylcapsule
Experiment = single_pulse.exp
Sample_id = SW782123
Solvent = CHLOROFORM-D
Creation_time = 5-SEP-2003 22:30:16
Revision_time = 23-NOV-2005 09:36:47
Current_time = 23-NOV-2005 09:37:11
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 20
Relaxation_delay = 1[s]
Temp_get = 22.8[dC]
Unblank_time = 2[us]
R = n-Pr, R' = n-Hex
0.125% TFA
(Millions)
40.0
30.0
20.0
10.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.3169
7.1951
7.1612
7.1264
7.0018
6.8296
6.1937
4.5199
4.4934
3.8530
3.1475
2.9735
1.9153
1.9016
1.2868
1.2255
0.9607
0.9469
0.9341
0.9195
0.9057
0.3304
0.2956
0.2617
X : parts per Million : 111


JEOL
Filename = I_HX_686_casul_0.5%CT
Experiment = single_pulse.exp
Sample_id = S#583748
Solvent = CHLOROFORM-D
Creation_time = 5-SEP-2003 16:59:54
Revision_time = 23-NOV-2005 09:37:52
Current_time = 23-NOV-2005 09:38:11
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 19
Relaxation_delay = 1[s]
Temp_set = 22.8[dC]
Unblank_time = 2[us]
R = n-Pr, R' = n-Hex
2% TFA
(Millions)
30.0
20.0
10.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.0879
7.3188
7.1896
7.1621
7.1346
7.0027
6.8121
4.5318
4.5044
3.8438
3.8292
3.8145
3.2337
3.2062
2.9093
2.8947
1.8878
1.8732
1.8576
0.9369
0.9323
0.9222
0.9176
0.9076
0.9030
X : parts per Million : 1H

APPENDIX 47

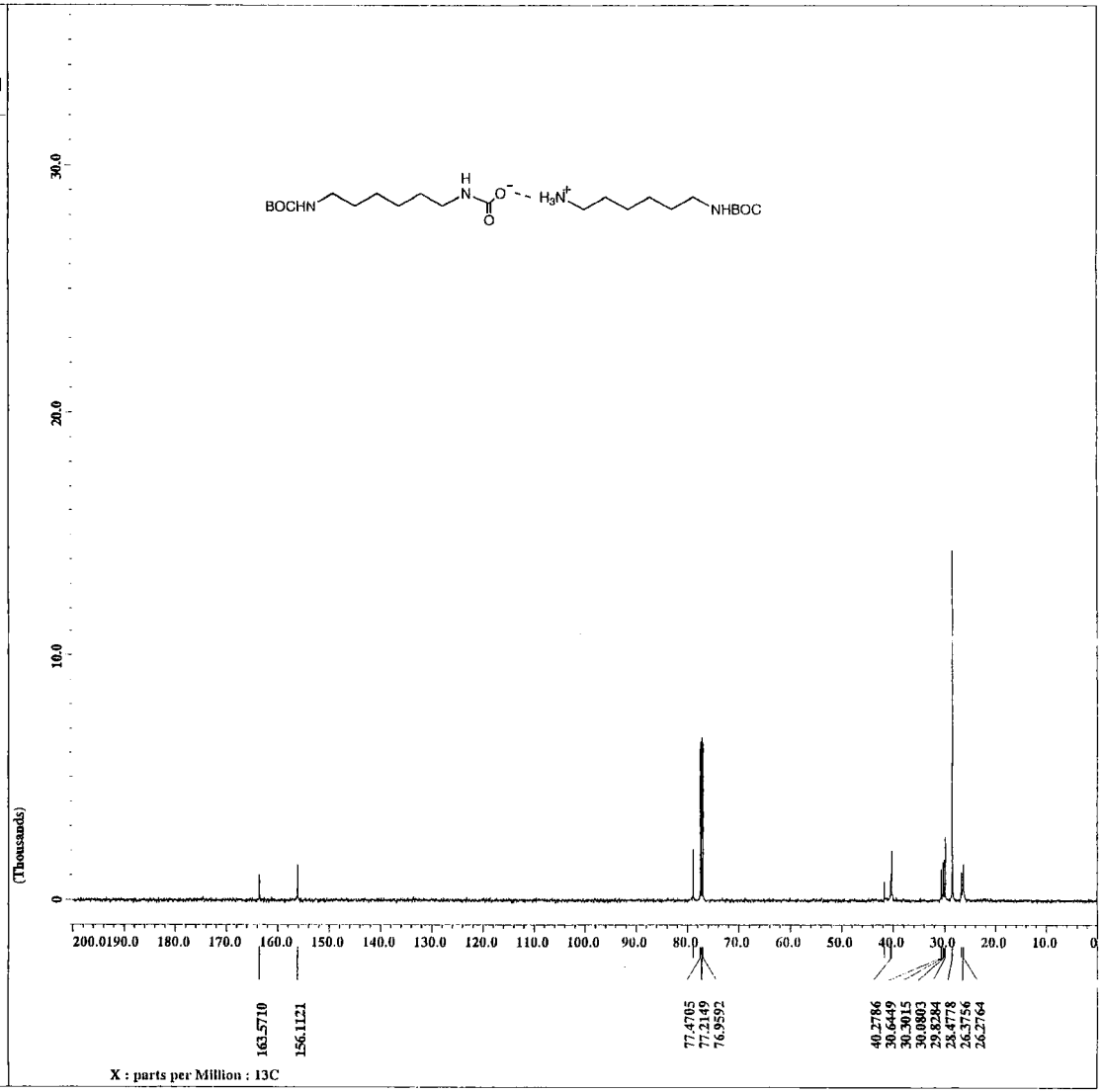
^{1}H NMR and ^{13}C NMR SPECTRA OF

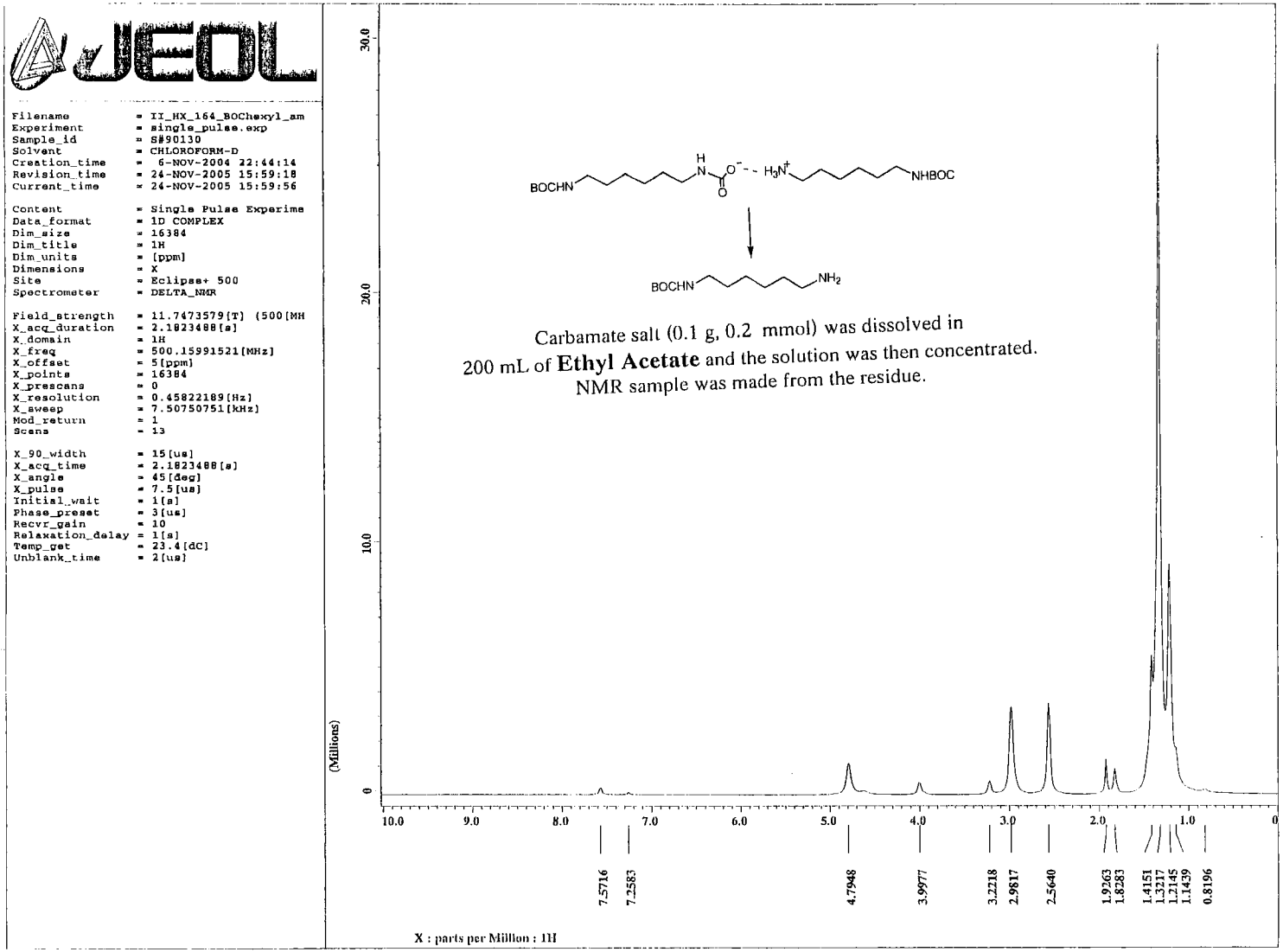
Model ammonium carbamates in MeCN, EtOAc, CH_2Cl_2, benzene, and THF


JEOL
Filename = II_HX_162_BOChexyl_am
Experiment = single_pulse.exp
Sample_id = S#272956
Solvent = CHLOROFORM-D
Creation_time = 6-NOV-2004 03:46:59
Revision_time = 24-NOV-2005 15:56:29
Current_time = 24-NOV-2005 15:57:03
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 12
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 10
Relaxation_delay = 1[s]
Temp_get = 23.4[dC]
Unblank_time = 2[us]
BOCHN
NHBOC
(Millions)
30.0
20.0
10.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.2556
6.1617
5.2538
4.9991
4.9230
4.6793
4.6280
4.4989
3.5781
3.5635
2.9964
2.9845
2.9322
2.9194
2.6418
2.6272
2.6125
1.4637
1.4508
1.4371
1.3391
1.2374
1.2245
1.2117
X : parts per Million : 1H

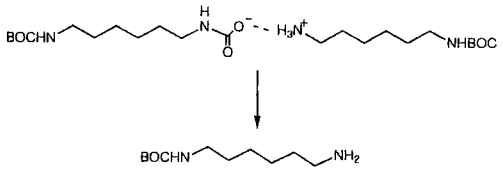
JEOL

Filename	= II_HX_162_BOChexyl_am
Experiment	= single_pulse_dec
Sample_id	= S#274002
Solvent	= CHLOROFORM-D
Creation_time	= 6-NOV-2004 03:58:18
Revision_time	= 24-NOV-2005 16:09:10
Current_time	= 24-NOV-2005 16:09:35
Content	= Single Pulse with Bro
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.0840448[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.47983613[Hz]
X_sweep	= 31.44654088[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5[ppm]
Mod_return	= 1
Scans	= 133
X_90_width	= 14[us]
X_acq_time	= 2.0840448[s]
X_angle	= 30[deg]
X_pulse	= 4.66666667[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 29
Relaxation_delay	= 2[s]
Temp_get	= 24.2[dC]
Unblank_time	= 2[us]

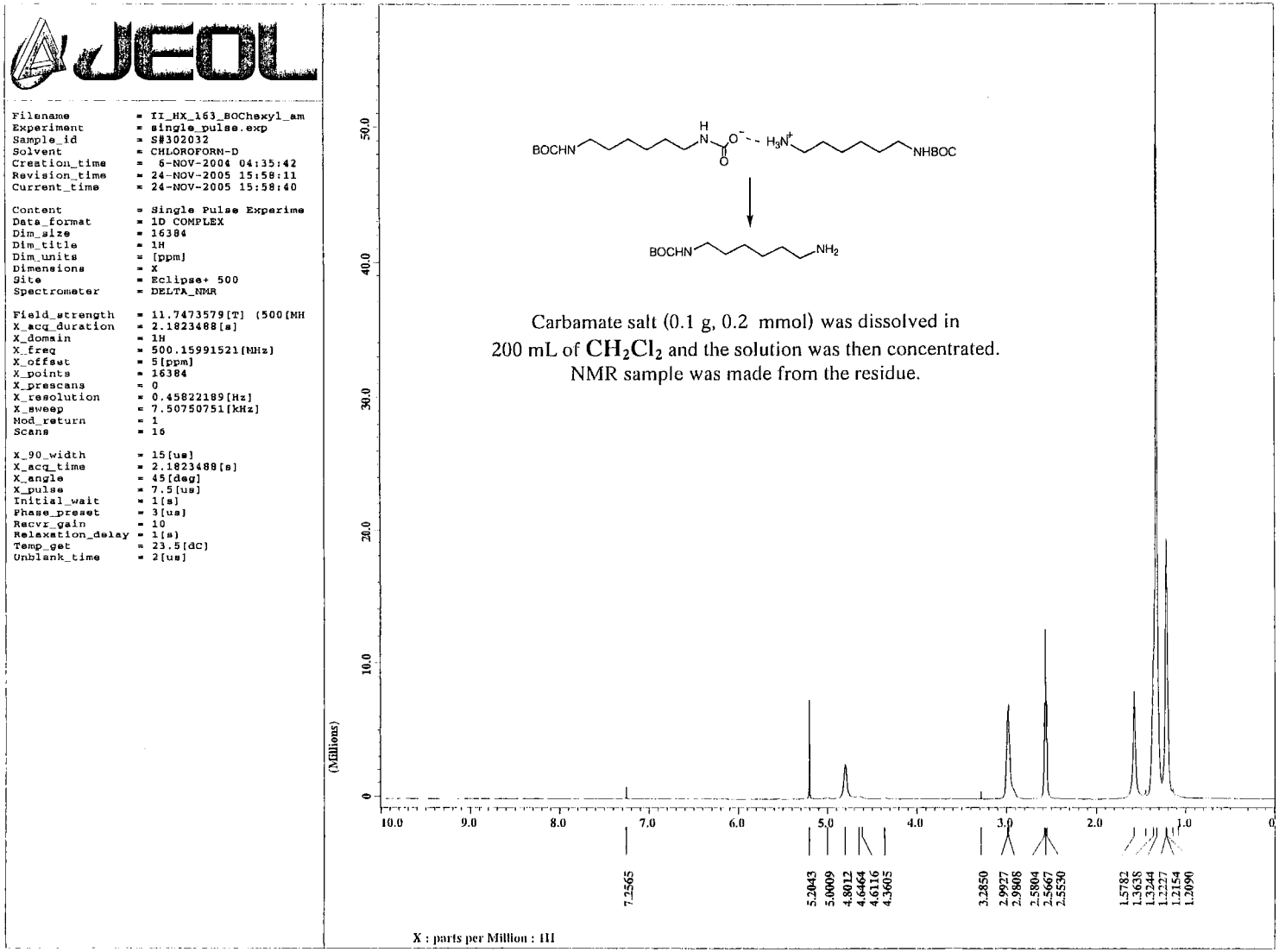



JEOL
Filename = II_HX_164_BOChexyl_am
Experiment = single_pulse.exp
Sample_id = S#90130
Solvent = CHLOROFORM-D
Creation_time = 6-NOV-2004 22:44:14
Revision_time = 24-NOV-2005 15:59:18
Current_time = 24-NOV-2005 15:59:56
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 13
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 10
Relaxation_delay = 1[s]
Temp_get = 23.4[dC]
Unblank_time = 2[us]
BOCHN
NHBOC
BOCHN
NH2
Carbamate salt (0.1 g, 0.2 mmol) was dissolved in
200 mL of Ethyl Acetate and the solution was then concentrated.
NMR sample was made from the residue.
(Millions)
30.0
20.0
10.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.5716
7.2583
4.7948
3.9977
3.2218
2.9817
2.5640
1.9263
1.8283
1.4151
1.3217
1.2145
1.1439
0.8196
X : parts per Million : 1H

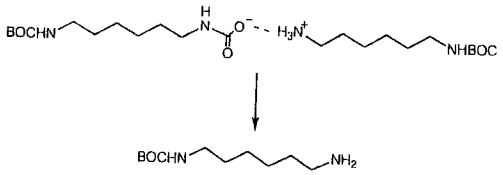
Filename	= II_HX_BOChexyl_amine_
Experiment	= single_pulse_dec
Sample_id	= S#92359
Solvent	= CHLOROFORM-D
Creation_time	= 6-NOV-2004 22:55:49
Revision_time	= 24-NOV-2005 16:13:00
Current_time	= 24-NOV-2005 16:13:31
Content	= Single Pulse with Bro
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.0840448[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.47983613[Hz]
X_sweep	= 31.44654088[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5[ppm]
Mod_return	= 1
Scans	= 127
X_90_width	= 14[us]
X_acq_time	= 2.0840448[s]
X_angle	= 30[deg]
X_pulse	= 4.66666667[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 30
Relaxation_delay	= 2[s]
Temp_get	= 24.2[dC]
Unblank_time	= 2[us]



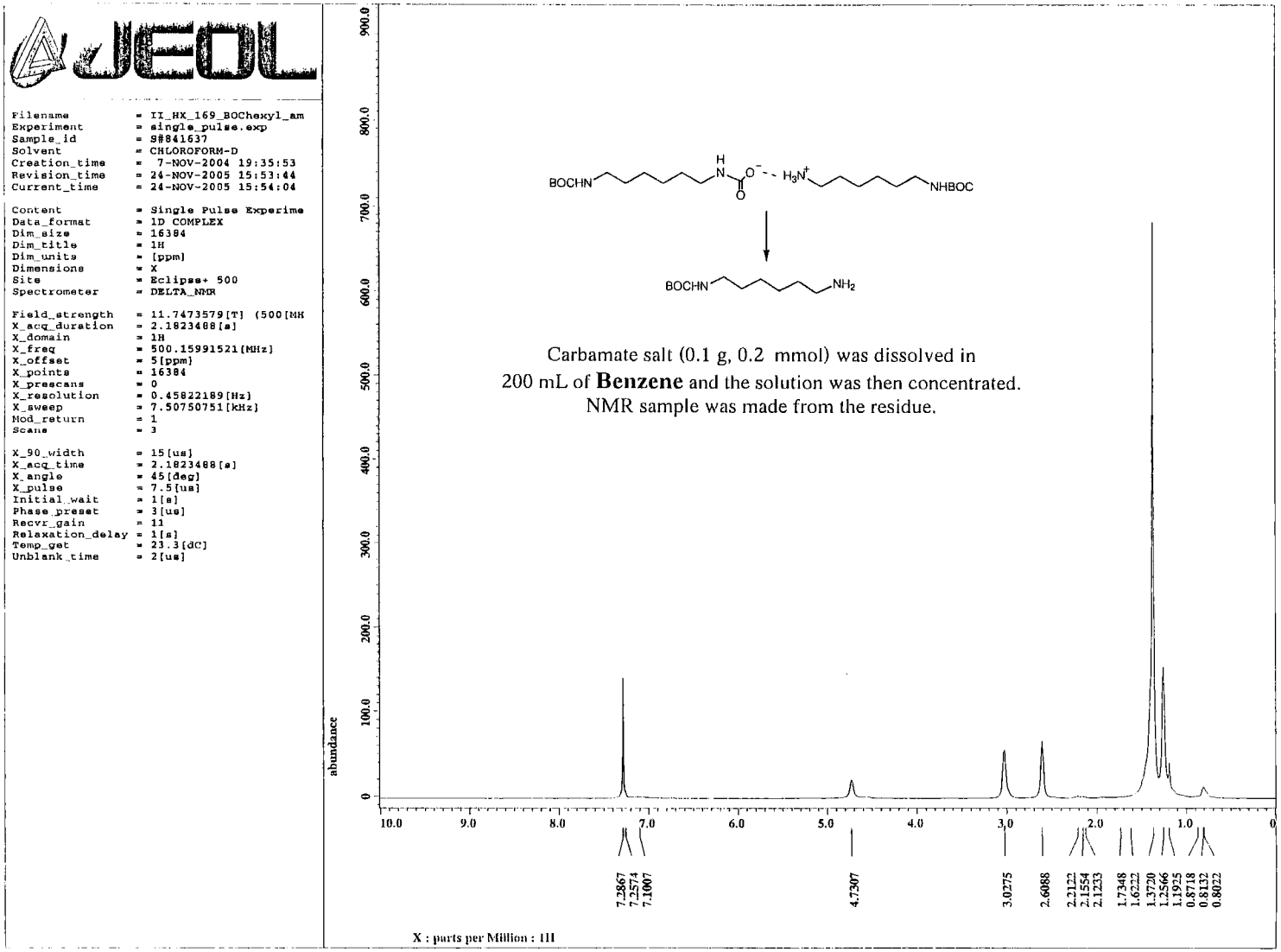
Carbamate salt (0.1 g, 0.2 mmol) was dissolved in 200 mL of **Ethyl Acetate** and the solution was then concentrated. NMR sample was made from the residue.


JEOL
Filename = II_HX_163_BOChexyl_am
Experiment = single_pulse.exp
Sample_id = S#302032
Solvent = CHLOROFORM-D
Creation_time = 6-NOV-2004 04:35:42
Revision_time = 24-NOV-2005 15:58:11
Current_time = 24-NOV-2005 15:58:40
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 10
Relaxation_delay = 1[s]
Temp_get = 23.5[dC]
Unblank_time = 2[us]
BOCHN
NHBOC
BOCHN
NH2
Carbamate salt (0.1 g, 0.2 mmol) was dissolved in
200 mL of CH2Cl2 and the solution was then concentrated.
NMR sample was made from the residue.
(Millions)
50.0
40.0
30.0
20.0
10.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.2565
5.2043
5.0909
4.8012
4.6464
4.6116
4.3605
3.2850
2.9927
2.9808
2.5804
2.5667
2.5530
1.5782
1.3638
1.3244
1.2227
1.2154
1.2090
X : parts per Million : 1H

```
Filename          = II_HX_BOChexyl_amine_
Experiment        = single_pulse_dec
Sample_id         = S#302910
Solvent           = CHLOROFORM-D
Creation_time     =  6-NOV-2004 04:43:05
Revision_time     = 24-NOV-2005 16:11:36
Current_time      = 24-NOV-2005 16:12:01

Content           = Single Pulse with Bro
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Mod_return        = 1
Scans             = 82

X_90_width        = 14[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.66666667[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 2[s]
Temp_get          = 24.2[dC]
Unblank_time      = 2[us]
```

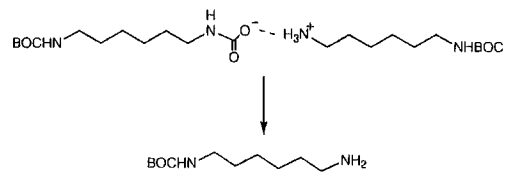


Carbamate salt (0.1 g, 0.2 mmol) was dissolved in 200 mL of CH_2Cl_2 and the solution was then concentrated. NMR sample was made from the residue.


Filename = II_HX_169_BOChexyl_am
Experiment = single_pulse.exp
Sample_id = S#841637
Solvent = CHLOROFORM-D
Creation_time = 7-NOV-2004 19:35:53
Revision_time = 24-NOV-2005 15:53:44
Current_time = 24-NOV-2005 15:54:04
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 3
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 11
Relaxation_delay = 1[s]
Temp_get = 23.3[dC]
Unblank_time = 2[us]
BOCHN
NHBOC
BOCHN
NH2
Carbamate salt (0.1 g, 0.2 mmol) was dissolved in
200 mL of Benzene and the solution was then concentrated.
NMR sample was made from the residue.
abundance
900.0
800.0
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.3867
7.2574
7.1007
4.7307
3.0275
2.6088
2.2122
2.1554
2.1233
1.7348
1.6222
1.3720
1.2566
1.1925
0.8718
0.8132
0.8022
X : parts per Million : 111

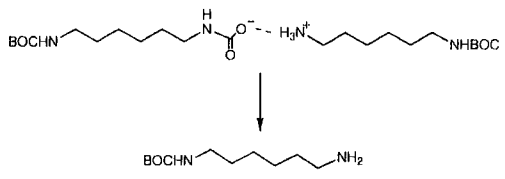
JEOL

Filename	= II_HX_169_BOChexyl_am
Experiment	= single_pulse_dec
Sample_id	= S#842794
Solvent	= CHLOROFORM-D
Creation_time	= 7-NOV-2004 19:45:12
Revision_time	= 24-NOV-2005 16:06:16
Current_time	= 24-NOV-2005 16:06:30
Content	= Single Pulse with Bro
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.0840448[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.47983613[Hz]
X_sweep	= 31.44654088[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5[ppm]
Mod_return	= 1
Scans	= 102
X_90_width	= 14[us]
X_acq_time	= 2.0840448[s]
X_angle	= 30[deg]
X_pulse	= 4.66666667[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 29
Relaxation_delay	= 2[s]
Temp_get	= 24.1[dC]
Unblank_time	= 2[us]

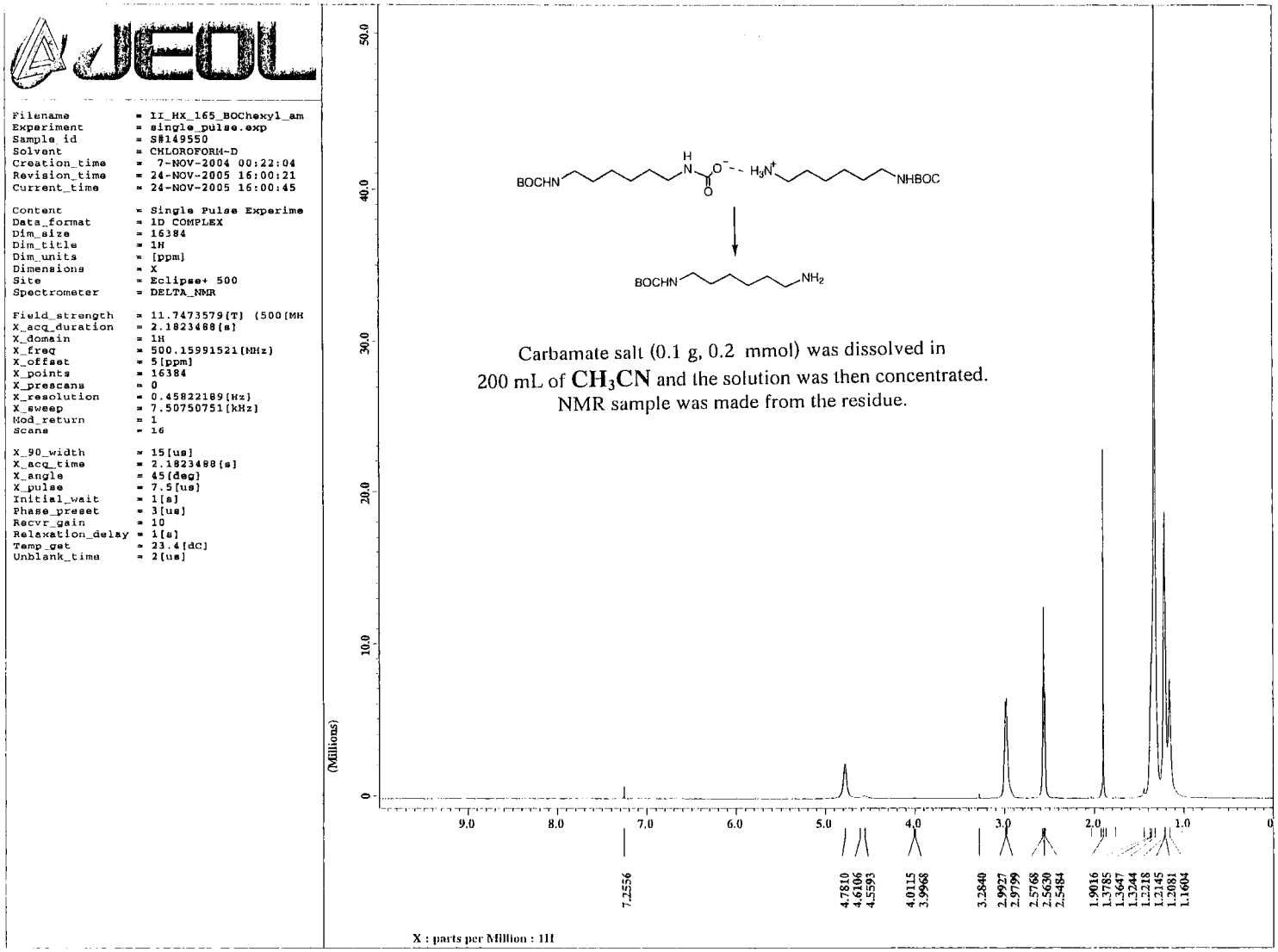


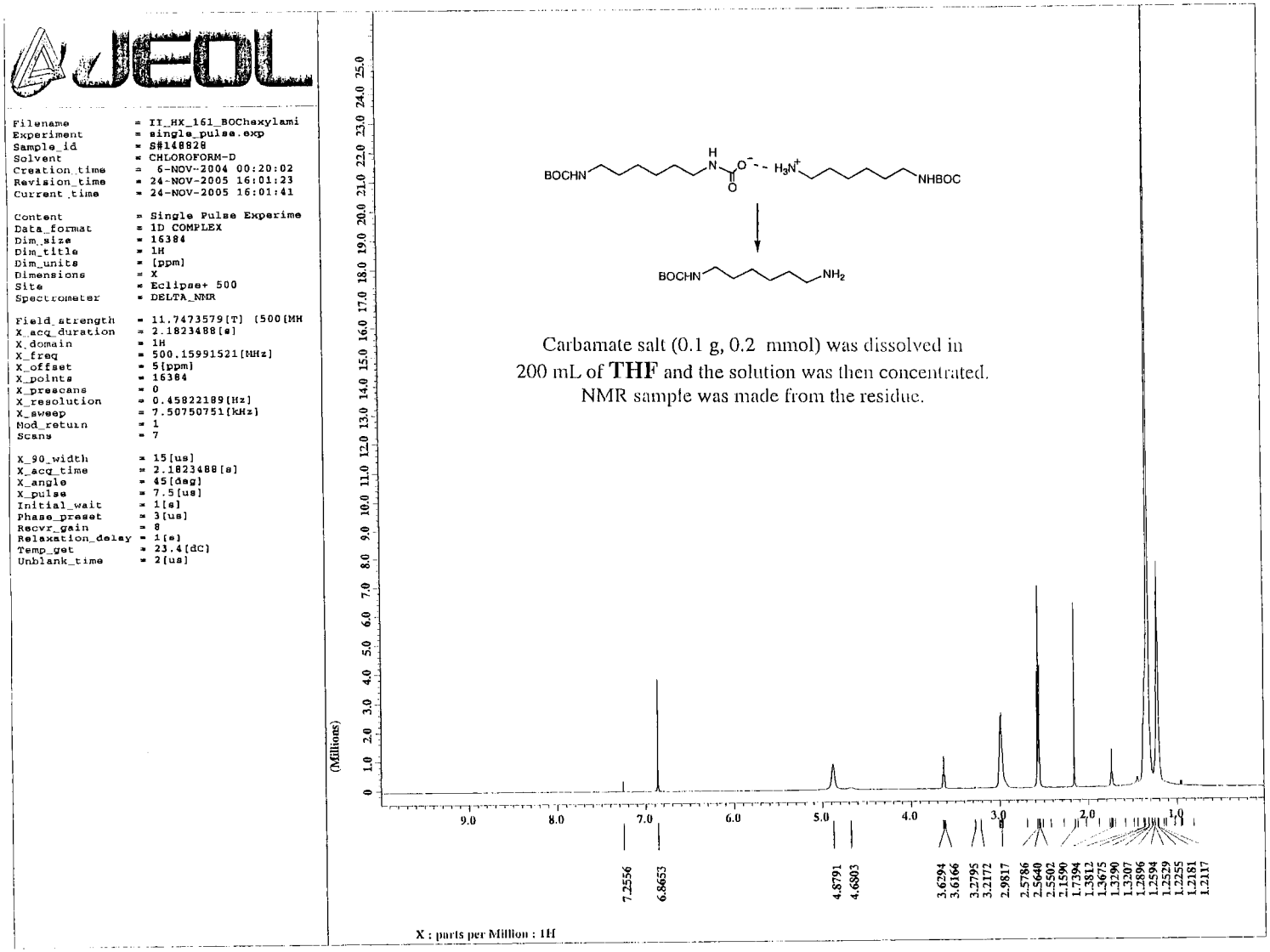
Carbamate salt (0.1 g, 0.2 mmol) was dissolved in 200 mL of **Benzene** and the solution was then concentrated. NMR sample was made from the residue.

Filename	= II_HX_165_BOChexyl_am
Experiment	= single_pulse_dec
Sample_id	= S#150486
Solvent	= CHLOROFORM-D
Creation_time	= 7-NOV-2004 00:57:26
Revision_time	= 24-NOV-2005 16:20:48
Current_time	= 24-NOV-2005 16:21:08
Content	= Single Pulse with Bro
Data_format	= 1D COMPLEX
Dim_size	= 65536
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.0840448[s]
X_domain	= 13C
X_freq	= 125.76529768[MHz]
X_offset	= 100[ppm]
X_points	= 65536
X_prescans	= 4
X_resolution	= 0.47983613[Hz]
X_sweep	= 31.44654088[kHz]
Irr_domain	= 1H
Irr_freq	= 500.15991521[MHz]
Irr_offset	= 5[ppm]
Mod_return	= 1
Scans	= 490
X_90_width	= 14[us]
X_acq_time	= 2.0840448[s]
X_angle	= 30[deg]
X_pulse	= 4.66666667[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 29
Relaxation_delay	= 2[s]
Temp_get	= 24.4[dC]
Unblank_time	= 2[us]



Carbamate salt (0.1 g, 0.2 mmol) was dissolved in 200 mL of CH_3CN and the solution was then concentrated. NMR sample was made from the residue.


JEOL
Filename = II_HX_165_BOChexyl_am
Experiment = single_pulse.exp
Sample_id = S#149550
Solvent = CHLOROFORM-D
Creation_time = 7-NOV-2004 00:22:04
Revision_time = 24-NOV-2005 16:00:21
Current_time = 24-NOV-2005 16:00:45
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 10
Relaxation_delay = 1[s]
Temp_get = 23.4[dC]
Unblank_time = 2[us]
BOCHN
NHBOC
BOCHN
NH2
Carbamate salt (0.1 g, 0.2 mmol) was dissolved in
200 mL of CH3CN and the solution was then concentrated.
NMR sample was made from the residue.
(Millions)
50.0
40.0
30.0
20.0
10.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.2556
4.7810
4.6166
4.5593
4.0115
3.9968
3.2840
2.9927
2.9799
2.5768
2.5630
2.5484
1.9016
1.3785
1.3647
1.3244
1.2218
1.2145
1.2081
1.1604
X : parts per Million : 1H


JEOL
Filename = II_HX_161_BOChexylami
Experiment = single_pulse.exp
Sample_id = S#148828
Solvent = CHLOROFORM-D
Creation_time = 6-NOV-2004 00:20:02
Revision_time = 24-NOV-2005 16:01:23
Current_time = 24-NOV-2005 16:01:41
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 7
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 8
Relaxation_delay = 1[s]
Temp_get = 23.4[dC]
Unblank_time = 2[us]
BOCHN
NHBOC
BOCHN
NH2
Carbamate salt (0.1 g, 0.2 mmol) was dissolved in
200 mL of THF and the solution was then concentrated.
NMR sample was made from the residue.
(Millions)
7.2556
6.8653
4.8791
4.6803
3.6294
3.6166
3.2795
3.2172
2.9817
2.5786
2.5640
2.5502
2.1590
1.7394
1.3812
1.3675
1.3290
1.3207
1.2896
1.2594
1.2529
1.2255
1.2181
1.2117
X : parts per Million : 1H

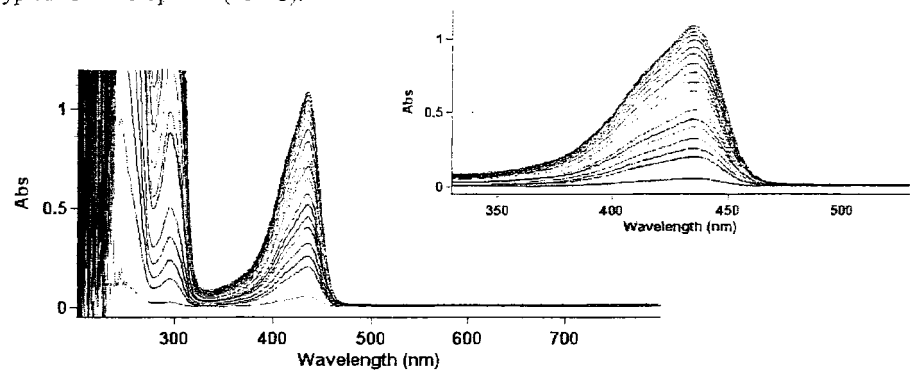
APPENDIX 48

UV SPECTRA OF

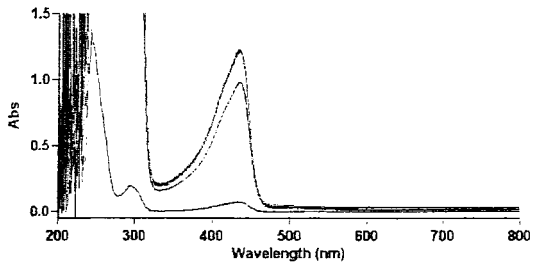
Release experiments

Coumarin 77 Release Experiments

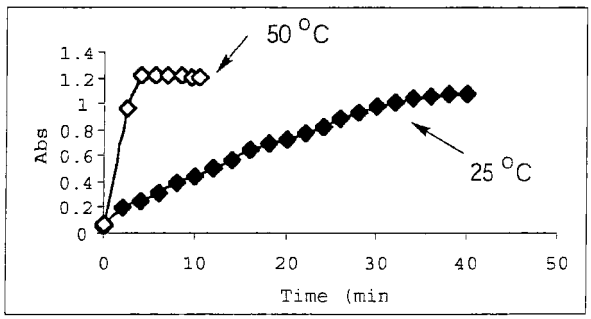
Typical UV-vis Spectra (25 ^{O}C):



UV-vis Spectra (50 ^{O}C):

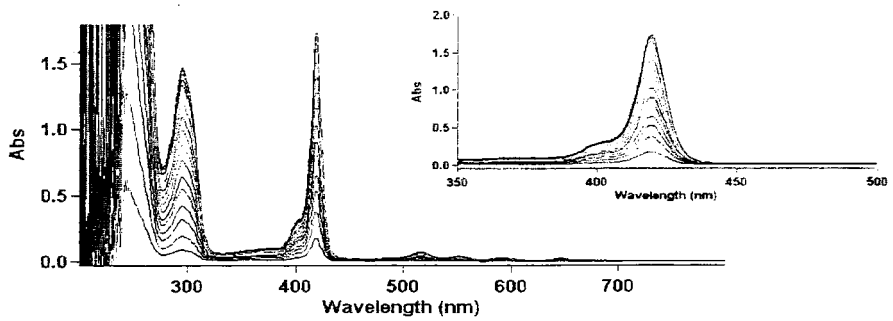


Temperature effects:

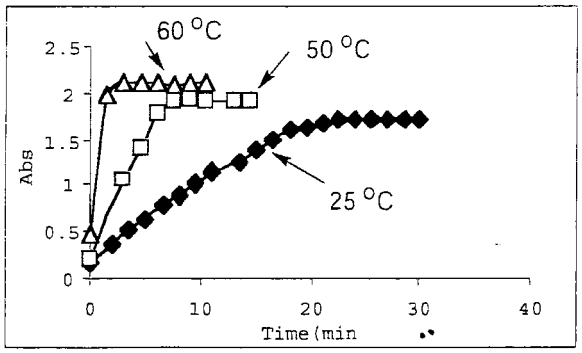


Porphyne 78 Release Experiments

Typical UV-vis Spectra (25 ^{o}C):

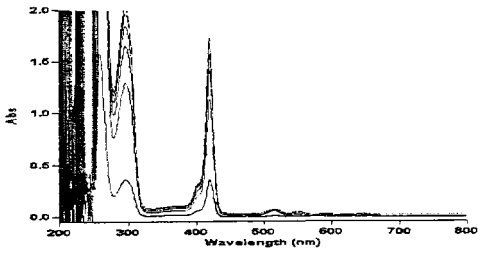


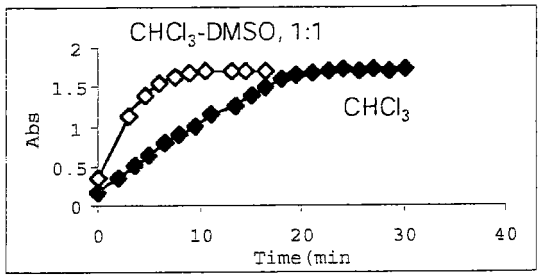
Various temperatures:



Porphyne **78** Release Experiments (continued)

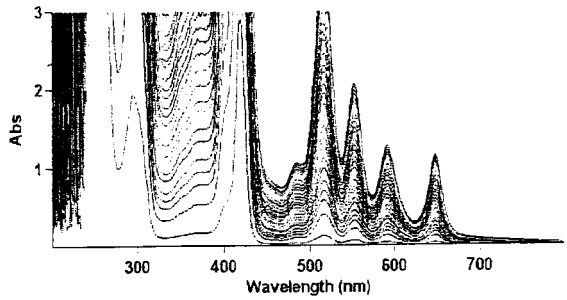
Solvent effect; UV-vis spectra in $CHCl_3$-DMSO, 1:1 (25 ^{O}C):

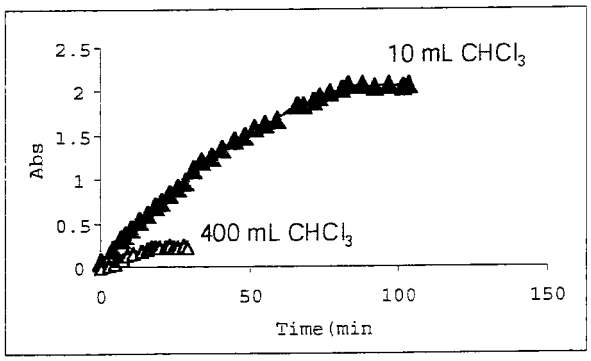




Porphyne **78** Release Experiments (continued)

Concentration effect; UV-vis spectra in $CHCl_3$ (25 ^{o}C):





REFERENCES

(1) Lehn, J.-M. *Pure Appl. Chem.* **1978**, *50*, 871-892.

(2) Lehn, J.-M. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 89-112.

(3) Lehn, J.-M. *Supramolecular Chemistry. Concepts and Perspectives, VCH, Weinhein,* **1995**.

(4) Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D.;Vögtle, F.; Lehn, J.-M. eds.**1996**, *Comprehensive Supramolecular Chemistry* (Pergamon, Oxford).

(5) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017-7036.

(6) Pedersen, C. J. *Angew. Chem. Int. Ed. Engl*. **1988**, *27*, 1021-1027.

(7) Dietrich, B.; Lehn, J.-M.; Sauvage, J.-P. *Tetrahedron Lett.* **1969**, *34*, 2885-2888.

(8) Lehn, J.-M. *Acc. Chem. Res.* **1978**, *11,* 49-57.

(9) Uekama, K; Hirayama, F.; Irie, T. *Chem. Rev.* **1998,** *98,* 2045-2076.

(10) Gutsche, C. D.; Muthukrishnan, R. *J. Org. Chem.* **1978**, *43*, 4905-4906.

(11) (a) Gutsche, C. D. *Calixarenes Revisited*; The Royal Society of Chemistry: Cambridge, **1998**. b) *Calixarenes 2001*; Eds.: Asfari, Z.; Böhmer, V.; Harrowfield, J. and Vicens, J. ; Kluwer Academic Publishers, Dordrecht, **2001**.

(12) Whitesides, G. M.; Grzybowski, B. *Science* **2002**, *295*, 2418-2421.

(13) Voet, D. and Voet, J. G. *Biochemistry*, 3rd ed., Wiley, **2004**.

(14) Cramer, F. *Chaos and Order, The Complex Structure of Living Systems, VCH, Weinheim,* **1993**, Chap.7.

(15) Prins, L. J.; Reinhoudt, D. N.; Timmerman, P. *Angew. Chem. Int. Ed.* **2001**, *40*, 2382-2426.

(16) (a) Jorgenson, W. L.; Pranata, J. *J. Am. Chem. Soc.* **1990**, *112*, 2008-2010. (b) Pranata, J.; Wierschke, S. G.; Jorgenson, W. L. *J. Am. Chem. Soc.* **1991**, *113*, 2810-2819.

(17) (a) Murray, T. J.; Zimmerman, S. C. *J. Am. Chem. Soc.* **1992**, *114*, 4010-4011. (b) Fenlon, E. E.; Murray, T. J.; Baloga, M. H.; Zimmerman, S. C. *J. Org. Chem.* **1993**, *58*, 6625-6628.

(18) (a) Beijer, F. H.; Kooijman, H.; Spek, A. L.; Sijbesma, R. P.; Meijer, E. W. *Angew. Chem. Int. Ed.* **1998**, *37*, 75-78. (b) Beijer, F. H.; Sijbesma, R. P.; Kooijman, H.; Spek, A. L.; Meijer, E. W. *J. Am. Chem. Soc.* **1998**, *120*, 6761-6769.

(19) Heinz, T.; Rudkevich, D. M.; Rebek, Jr., J. *Nature* **1998**, *394*, 764-766.

(20) Wagner, R. W.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 9759-9760.

(21) Lehn, J.-M.; Mascal, M.; DeCian, A.; Fischer, J. *J. Chem. Soc., Perkin Trans. 2,* **1992**, 461.

(22) Ghadiri, M. R., Granja, J. R. & Buehler, L. K. *Nature* **1994** *369*, 301–304.

(23) Granja, J. R.; Ghadiri, M. R. *J. Am. Chem. Soc*. **1994**, *116*, 10785-10786.

(24) Hartgerink, J. D.; Clark, T. D.; Ghadiri, M. R. *Chem Eur. J.* **1998**, *4*, 1367-1372.

(25) Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681-1712.

(26) Tomalia, D. A.; Baker, H.; Dewald, J. R.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Macromolecules* **1986**, *19*, 2466-2468.

(27) Zimmerman, S. C.; Zeng, F. W.; Reichert, D. E. C.; Kolotuchin, S. V. *Science* **1996**, *271*, 1095-1098.

(28) (a) Schneider, J. P.; Pochan, D. J.; Ozbas, B.; Rajagopal, K; Pakstis, L.; Kretsinger, J. *J. Am. Chem. Soc.* **2002**, *124*, 15030-15037. (b) Pochan, D. J.; Schneider, J. P.; Kretsinger, J.; Ozbas, B.; Rajagopal, K.; Haines, L. *J. Am. Chem. Soc.* **2003**, *125*, 11802-11803. (c) Rajagopal, K.; Schneider, J. P. *Curr. Opin. Chem. Biol.* **2004**, *14*, 480–486.

(29) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481-4483.

(30) Bain, C. D.; Troughton, E. B.; Tao, Y-T; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321-335.

(31) Scherer, J.; Vogt, M. R.; Magnussen, O. M.; Behm, R. J. *Langmuir* **1997**, *13*, 7045-7051.

(32) Schon, J. H.; Meng, H.; Bao, Z. *Nature* **2001**, *413*, 713-716.

(33) (a) Huisman, B. H.; Thoden van velzen, E. U.; Veggel, F. C. J. M. van; Engbersen, J. F. J.; Reinhoudt, D. N. *Tetrahedron Lett.* **1995**, *36*, 3273-3276. (b) Huisman, B.-H.; Rudkevich, D. M.; FarrAn, A; Verboom, W.; Veggel, F. C. J. M. van; Reinhoudt, D. N. *Eur. J. Org. Chem.* **2000**, 269-274.

(34) Lehn, J.-M. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4763–4768.

(35) Shinkai, S. *Tetrahedron* **1993**, *49*, 8933-8968.

(36) Arnaud-Neu, F.; Collins, E. M.; Deasy, M.; Ferguson, G.; Harris, S. J.; Kaitner, B.; Lough, A. J.; McKervey, M. A.; Marques, M.; Ruhl, B. L.; Schwing-Weill, M. J.; Seward, E. M. *J. Am. Chem. Soc.* **1989**, *111*, 8681-8689.

(37) Casnati, A.; Pochini, A.; Ungaro, R.; Bocchi, F.; Ugozzoli, F.; Egberink, R. J. M.; Struijk, H.; Lugtenberg, R.; de Jong, F.; Reinhoudt, D. N. *Chem. Eur. J.* **1996**, *2*, 436-445.

(38) Casnati, A.; Pochini, A.; Ungaro, R.; Ugozzoli, F.; Arnaud, F.; Fanni, S.; Schwing, M.-J.; Egberink, R. J. M.; de Jong, F.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 2767-2777.

(39) (a) Arnaud-Neu, F.; Schwing-Weill, M. J.; Dozol, J.-F. In: *Calixarene 2001*; Eds.: Asfari, Z.; Böhmer, V.; Harrowfield, J. and Vicens, J. ; Kluwer Academic Publishers, Dordrecht, **2001**, pp. 642-662. (b) Steemers, F. J.; Verboom, W.; Reinhoudt, D. N.; van der Tol, E. B.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 9408-9414. (c) Rudkevich, D. M.; Verboom, W.; van der Tol, E.; van Staveren, C. J.; Kaspersen, F. M.; Verhoeven, J. W.; Reinhoudt, D. N. *J. Chem. Soc., Perkin Trans 2* **1995**, 131-134.

(40) (a) Ikeda, A.; Shinkai, S. *Chem. Rev.* **1997**, *97*, 1713-1734. (b) Lhotak, P.; Shinkai, S. *J. Phys. Org. Chem.* **1997**, *10*, 273-285.

(41) (a) Rudkevich, D. M.; Verboom, W.; Reinhoudt, D. N. *J. Org. Chem.* **1994**, *59*, 3683-3686. (b) Morzherin, Yu.; Rudkevich, D. M.; Verboom, W.; Reinhoudt, D. N. *J. Org. Chem.* **1993**, *58*, 7602-7605. (c) Ditopic receptors: Rudkevich, D. M.; Mercer-Chalmers, J. D.; Verboom, W.; Ungaro, R.; de Jong, F.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 6124-6125.

(42) (a) Beer, P. D.; Gale, P. A. *Angew. Chem. Int. Ed.* **2001**, *40*, 486-516. (b) Rudkevich, D. M.; Scheerder, J.; Reinhoudt, D. N. In: *Molecular Design and Bioorganic Catalysis*, Eds.: Wilcox, C. S. and Hamilton, A. D.; Kluwer Academic Publischers, Dordrecht, Boston, London, **1996**, p. 137-162.

(43) (a) Starnes, S. D.; Rudkevich, D. M.; Rebek, Jr., J. *J. Am. Chem. Soc.* **2001**, *123*, 4659-4669. (b) Lücking, U.; Tucci, F. C.; Rudkevich, D. M.; Rebek, Jr., J. *J. Am. Chem. Soc.* **2000**, *122*, 8880-8889.

(44) (a) Rudkevich, D. M.; Rebek, Jr., J. *Eur. J. Org. Chem.* **1999**, 1991-2005. (b) Rudkevich, D. M. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 393-413.

(45) Cram, D. J.; Cram, J. M. *Container Molecules and their Guests*; The Royal Society of Chemistry: Cambridge, **1994**.

(46) Hof, F.; Craig, S. L.; Nuckolls, C.; Rebek, J., Jr. *Angew. Chem. Int. Ed.* **2002**, *41*, 1488-1508.

(47) Garrett, R. H.; Grisham, C. M. *Biochemistry*, 3rd ed., Saunders, **2004**.

(48) Stupp, S. I.; Le Bonheur, V.; Walker, K.; Li, L. S.; Huggins, K.; Keser, M.; Amstutz, Amstutz, A. *Science* **1997**, *276*, 384.

(49) Xu, H.; Kinsel, G. R.; Zhang, J.; Li, M.; Rudkevich, D. M. *Tetrahedron* **2003**, *59*, 5837-5848.

(50) Xu, H.; Stampp, S. P.; Rudkevich, D. M. *Org. Lett.* **2003**, *5*, 4583-4586.

(51) Hamada, T.; Nishida, A.; Matsumoto, Y.; Yonemitsu, O. *J. Am. Chem. Soc.* **1980**, *102*, 3978-3980.

(52) (a) Lazzarotto, M.; Sansone, F.; Baldini, L.; Casnati, A.; Cozzini, P.; Ungaro, R. *Eur. J. Org. Chem.* **2001**, 595-602. (b) Hioki, H.; Yamada, T.; Fujioka, C.; Kodama, M. *Tetrahedron Lett.* **1999**, *40*, 6821-6825. (c) Hioki, H.; Kubo, M.; Yoshida, H.; Bando, M.; Ohnishi, Y.; Kodama, M. *Tetrahedron Lett.* **2002**, *43*, 7949-7952. (d) Frkanec, L.; Visnjevac, A.; Kojic-Prodic, B.; Zinic, M. *Chem. Eur. J.* **2000**, *6*, 442-453. (e) Shuker, S. B.; Esterbrook, J.; Gonzalez, J. *Synlett* **2001**, 210-213.

(53) (a) Shimizu, K. D.; Rebek, J., Jr. *Proc. Natl. Acad. Sci. U.S.A.* **1995**, *92*, 12403-12407. Reviews: (b) Rebek, J., Jr. *Chem. Commun.* **2000**, 637-643.

(54) (a) Mogck, O.; Böhmer, V.; Vogt, W. *Tetrahedron* **1996**, *52*, 8489-8496. (b) Mogck, O.; Paulus, E. F.; Böhmer, V.; Thondorf, I.; Vogt, W. *Chem. Commun.* **1996**, *52*, 2533-2534 (X-ray structure).

(55) Timely review: Ebbers, E. J.; Ariaans, G. J. A.; Houbiers, J. P. M.; Bruggink, A.; Zwanenburg, B. *Tetrahedron* **1997**, *53*, 9417-9476.

(56) Rappoport, H.; Buckley, T. F. *J. Am. Chem. Soc*. **1982**, *104*, 4446-4450.

(57) Wang, S.; Gisin, B.F.; Winter, D. P.; Makofske, R.; Kulesha, I. D.; Tzougraki, C.; Meienhofer, J. *J. Org. Chem.* **1977**, *42*, 1286-1290.

(58) (a) Itoh, M.; Hagiwara, D.; Kamiya, T. *Tetrahedron Lett*. **1975**, *16*, 4393-4394. (b) Rosowsky, A.; Forsch, R. A.; Freisheim, J. H.; Galivan, J.; Wick, M. *J. Med. Chem.* **1984**, *27*, 888-893.

(59) Talaga, P.; Benezra, C.; Stampf, J.-L. *Bioorg. Chem.* **1990**, *18*, 199-206.

(60) Keller, O.; Jeller, W. E.; van Look, G.; Wersin, G. *Org. Synth*. **1985**, *63*, 160-170.

(61) Paquet, A. *Can. J. Chem*. **1976**, *54*,733-737.

(62) Manesis, N. J.; Goodman, M. *J. Org. Chem.* **1987**, *52*, 5331-5341.

(63) McKervey, M. A.; Owens, M.; Schulten, H.-R.; Vogt, W.; Bohmer, V. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 280-282.

(64) For related systems, see: Cho, Y. L.; Rudkevich, D. M.; Shivanyuk, A.; Rissanen, K.; Rebek, Jr., J. *Chem. Eur. J.* **2000**, *6*, 3788-3796.

(65) (a) Voyer, N. *Top. Curr. Chem.* **1996**, *184*, 1-37. (b) Bryson, J. W.; Betz, S. F.; Lu, H. S.; Suich, D. J.; Zhou, H. X.; O'Neil, K. T.; DeGrado, W. F. *Science* **1995**, *270*, 935-941. (c) Takahashi, Y.; Ueno, A.; Mihara, H. *Chem. Eur. J.* **1998**, *4*, 2475-2484. (d) Ueno, M.; Murakami, A.; Makino, K.; Morii, T. *J. Am. Chem. Soc.* **1993**, *115*, 12575-12576. (e) Kraatz, H.-B.; Lusztyk, J.; Enright, G. E. *Inorg. Chem.* **1997**, *36*, 2400-2405. (f) Severin, K.; Bergs, R.; Beck, W. *Angew. Chem. Int. Ed.* **1998,** *37*, 1634-1654.

(66) DeGrado, W. F.; Summa, C. M.; Pavone, V.; Nastri, F.; Lombardi, A. *Ann. Rev. Biochem.* **1999**, *68*, 779-819.

(67) Imperiali, B.; Roy, R. Sinha; Walkup, G. K.; Wang, L. In: In: *Molecular Design and Bioorganic Catalysis*, Eds.: Wilcox, C. S. and Hamilton, A. D.; Kluwer Academic Publischers, Dordrecht, Boston, London, **1996**, p. 35-52.

(68) Hitomi, Y.; Outten, C. E.; O'Halloran, T. V. *J. Am. Chem. Soc.* **2001,** *123,* 8614-8615.

(69) Davies, D. R.; Interthal, H.; Champoux, J. J.; Hol, W. G. J. *J. Med. Chem.* **2004,** *47,* 829-837.

(70) Albericio, F. *Biopolymers* **2000**, *55*, 99-100.

(71) Sisido, M.; Imanishi, Y. *Macromolecules* **1986**, *19*, 2187-2193.

(72) Smaglik, P. *Nature* **2000**, *406*, 807 – 808.

(73) (a) Mammen, M.; Chio, S.-K.; Whitesides, G. M. *Angew. Chem. Int. Ed.* **1998**, *37*, 2755-2794. (b) Zhang, S.; Marini, D. M.; Hwang, W.; Santoso, S. *Curr. Opin. Chem. Biol.* **2002**, *6*, 865-871. (c) Xia, Y.; Rogers, J. A.; Paul, K. E.; Whitesides, G. M. *Chem. Rev.* **1999**, *99*, 1823-1848. (d) Whitesides, G. M.; Mathias, J. P.; Seto, C. T. *Science* **1991**, *254*, 1312-1319. (e) Isaacs, L.; Chin, D. N.; Bowden, N.: Xia, Y.; Whitesides, G. M. *Perspectives in Supramolecular Chemistry* **1999**, *4*, 1-46.

(74) (a) Frechet, J. M. J. *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4782-4787. (b) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665-1688.

(75) Hawker, C.; Fréchet, J. M. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1010-1013.

(76) Newkome, G. R.; Yao, Z.; Baker, G. R.; Gupta, V. K. *J. Org. Chem.* **1985**, *50*, 2003-2004.

(77) Newkome, G. R.; He, E.; Moorefield, C. N. *Chem. Rev.* **1999,** *99,* 1689-1746.

(78) (a) Tomalia, D. A.; Baker, H.; Dewald, J. R.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Polym. J. (Tokyo)* **1985**, *17*, 117-132.

(79) Mattei, S.; Seiler, P.; Diederich, F.; Gramlich, V. *Helvetica Chim. Acta* **1995**, *78*,1904-1912.

(80) Hawker, C. J.; Wooley, K. L.; Fréchet, J. M. J. *J. Chem. Soc., Perkin Trans. 1* **1993**, *21*, 1287-1297.

(81) (a) Jansen, J. F. G. A.; de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Science* **1994**, *266*, 1226-1229. (b) Jansen, J. F. G. A.; de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Rec. Trav. Chim. Pays-Bas* **1995**, *114*, 225- 230. (c) Jansen, J. F. G. A.; Janssen, R. A. J.; de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Adv. Mater.* **1995**, *7*, 561-564. (d) Jansen, J. F. G. A.; Meijer, E. W.; de Brabander-van den Berg, E. M. M. *Macromol. Symp.* **1996**, *102*, 27-33.

(82) (a) Nagasaki, T.; Tamagaki, S.; Ogino, K. *Chem. Lett.* **1997**, 717-718. (b) Roy, R.; Kim, J. M. *Angew. Chem. Int. Ed.* **1999**, *38*, 369-372.

(83) (a) Szemes, F.; Drew, M. G. B.; Beer, P. D. *Chem. Commun.* **2002**, 1228-1229. (b) Lhotak, P.; Shinkai, S. *Tetrahedron* **1995**, *51*, 7681-7696.

(84) Mogck, O.; Parzuchowski, P.; Nissinen, M.; Böhmer, V.; Rokicki, G.; Rissanen, K. *Tetrahedron* **1998**, *54*, 10053-10068.

(85) Grayson, S. M.; Fréchet, J. M. J. *Chem. Rev.* **2001**, *101*, 3819-3867.

(86) Appelhans, D.; Stastny, V; Komber, H.; Voigt, D.; Voit, B. ; Lhoták, P; Stibor, I. *Tetrahedron. Lett.* **2004**, *45,* 7145-7149.

(87) Cheriaa, N.; Abidiand R.; Vicens, J. *Tetrahedron. Lett.* **2005**, *46,* 1533-1536.

(88) Cloninger, M. J. *Curr. Opin. Chem. Biol.* **2002**, *6*, 742-748.

(89) Sadler, K.; Tam, J. P. *Rev. Mol. Biotech.* **2002**, *90*, 195-229.

(90) Arnaud-Neu, F.; McKervey, M. A.; Schwing-Weill, M.-J. In: *Calixarenes 2001*; Eds.: Asfari, Z.; Böhmer, V.; Harrowfield, J. and Vicens, J. ; Kluwer Academic Publishers, Dordrecht, **2001**, p. 385-406 and literature therein.

(91) (a) Seto, C. T.; Whitesides, G. M. *J. Am. Chem. Soc.* **1990**, *112*, 6409-6411. (b) Whitesides, G. M.; Mathias, J. P.; Seto, C. T. *Science* **1991**, *254*, 1312-1319. (c) Seto, C. T.; Whitesides, G. M. *J. Am. Chem. Soc.* **1991**, *113*, 712-713. (d) Seto, C. T.; Whitesides, G. M. *J. Am. Chem. Soc.* **1993**, *115*, 1330-1340. (e) Seto, C. T.; Whitesides, G. M. *J. Am. Chem. Soc.* **1993**, *115*, 905-916. (f) Mathias, J. P.; Simanek, E. E.; Seto, C. T.; Whitesides, G. M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1766-1769. (g) Seto, C. T.; Mathias, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1993**, *115*, 1321-1329. (h) Mathias, J. P.; Simanek, E. E.; Zerowski, J. A.; Seto, C. T.; Whitesides, G. M. *J. Am. Chem. Soc.* **1994**, *116*, 4316-4325. (i) Mathias, J. P.; Simanek, E. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1994**, *116*, 4326-4340. (j) Mathias, J. P.; Seto, C. T.; Simanek, E. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1994**, *116*, 1725-1736.

(92) Zimmerman, S. C.; Duerr, B. F. *J. Org. Chem.* **1992**, *57*, 2215-2217.

(93) Conn, M. M.; Rebek, J., Jr. *Chem. Rev.* **1997,** *97*, 1647-1668.

(94) (a) Wyler, R.; de Mendoza, J.; Rebek, J. J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1699-1701. (b) Mohamadi, F.; Richards, N. G.; Guida, W. C.; Liskamp, R.; Lipton, M.; Caufield, C.; Chang, G.; Hendrickson, T.; Still, W. C. *J. Comput. Chem.* **1990**, *11*, 440-467.

(95) Takeda, N.;Umemoto, K.;Yamaguchi, K.; Fujita, M. *Nature* **1999**, *398*, 794-796.

(96) Corbellini, F.; Fiammengo, R.; Timmerman, P.; Crego-Calama, M.; Versluis, K.; Heck, A. J. R.; Luyten, I.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **2002**, *124*, 6569-6575.

(97) Fochi, F.; Jacopozzi, P.; Wegelius, E.; Rissanen, K.; Cozzini, P.; Marastoni, E.; Fisicaro, E.; Manini, P.; Fokkens, R.; Dalcanale, E. *J. Am. Chem. Soc.* **2001**, *123,* 7539-7552.

(98) MacGillivray, L. R.; Atwood, J. L. *Nature*, **1997**, *389*, 469-472.

(99) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071-4097.

(100) (a) Fouquey, C.; Lehn, J.-M.; Levelut, A.-M. *Adv. Mater.* **1990**, *2*, 254-257. (b) Lehn, J.-M. *Makromol. Chem., Macromol. Symp.* **1993**, *69*, 1-17.

(101) (a) Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J. H. K. K.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. *Science* **1997**, *278*, 1601-1604.

(102) (a) Castellano, R. K.; Rudkevich, D. M.; Rebek, J., Jr. *Proc. Natl. Acad. Sci. U.S.A.* **1997**, *94*, 7132-7137. (b) Castellano, R. K.; Nuckolls, C.; Eichhorn, S. H.; Wood, M. R.; Lovinger, A. J.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1996**, *38*, 2603-2606. (c) Castellano, R. K.; Clark, R.; Craig, S. L.; Nuckolls, C.; Rebek, J., Jr. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 12418-12421.

(103) Castellano, R. K.; Craig, S. L.; Nuckolls, C.; Rebek, J., Jr. *J. Am. Chem. Soc.* **2000**, *122*, 7876 –7882.

(104) Cates, M. E. *Macromolecules* **1987**, *20*, 2289-2296.

(105) (a) Stigliani, W. M.; Spiro, T. G.; *Chemistry and the Environment.* 2nd ed. Prentice Hall, New Jersey, **2003**, pp. 3-178. (b) Schimel, D. S.; House, J. I.; Hibbard, K. A.; Bousquet, P.; Ciais, P.; Peylin, P.; Braswell, B. H.; Apps, M. J.; Baker, D.; Bondeau, A.; Canadell, J.; Churkina, G.; Cramer, W.; Denning, A. S.; Field, C. B.; Friedlingstein, P.; Goodale, C.; Heimann, M.; Houghton, R. A.; Melillo, J. M.; Moore, B.; Murdiyarso, III, D.; Noble, I.; Pacala, S. W.; Prentice, I. C.; Raupach, M. R.; Rayner, P. J.; Scholes, R. J.; Steffen, W. L.; Wirth, C. *Nature* **2001**, *414*, 169-172. (c) Cole, C. V.; Duxbury, J.; Freney, J.; Heinemeyer, O.; Minami, K.; Mosier, A.; Paustian, K.; Rosenberg, N.; Sampson, N.; Sauerbeck, D.; Zhao, Q. *Nutrient Cycling in Agroecosystems* **1997**, *49*, 221-228.

(106) (a) Dell Amico, D. B.; Calderazzo, F.; Labella, L.; Marchetti, F.; Pampaloni, G. *Chem. Rev.* **2003**, *103*, 3857-3898. (b) McGhee, W. D.; Riley, D.; Christ, K.; Pan, Y.; Parnas, B. *J. Org. Chem*. **1995**, *60*, 2820-2830. (c) Waldman, T. E.; McGhee, W. D. *J. Chem. Soc., Chem. Comm.* **1994**, 957-958. (d) Salvatore, R. N.; Shin, S. I.; Nagle, A. S.; Jung, K. W. *J. Org. Chem.* **2001**, *66*, 1035-1037. (e) Aresta, M.; Quaranta, E. *Tetrahedron* **1992**, *48*, 1515-1530.

(107) (a) Yamaguchi, T.; Boetje, L. M.; Koval, C. A.; Noble, R. D.; Bowman, C. N. *Ind. Eng. Chem. Res.* **1995**, *34*, 4071-4077. (b) Yamaguchi, T.; Koval, C. A.; Nobel, R. D.; Bowman, C. N. *Chem. Eng. Sci.* **1996**, *51*, 4781-4789.

(108) Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, Jr., J. H. *J. Am. Chem. Soc.* **2002**, *124*, 926-927.

(109) Ki, C. D.; Oh, C.; Oh, S.-G.; Chang, J. Y. *J. Am. Chem. Soc.* **2002**, *124*, 14838-14839.

(110) Hampe, E. M.; Rudkevich, D. M. *Tetrahedron* **2003**, *59*, 9619-9625.

(111) (a) Lehn, J.-M. *Chem. Eur. J.*, **1999**, *5*, 2455-2463. (b) Rowan, S. J.; Cantrill, S. J.;Cousins, G. R. L.; Sanders, J. K. M.; Stoddart, J. F. *Angew. Chem. Int. Ed.*, **2002**, *41*, 899-952.

(112) (a) George, M.; Weiss, R. G. *J. Am. Chem. Soc.* **2001**, *123*, 10393-10394. (b) George, M.; Weiss, R. G. *Langmuir* **2002**, *18*, 7124-7135. (c) Carretti, E.; Dei, L.; Baglioni, P.; Weiss, R. G. *J. Am. Chem. Soc.* **2003**, *125*, 5121-5129. (d) George, M.; Weiss, R. G. *Langmuir* **2003**, *19*, 1017-1025. (e) George, M.; Weiss, R. G. *Langmuir* **2003**, *19*, 8168-8176.

(113) Terech, P.; Weiss, R. G. *Chem. Rev.*, **1997**, *97*, 3133–3159.

(114) Xu, H.; Hampe, E. M.; Rudkevich, D. M. *Chem. Commun.* **2003**, 2828-2829.

(115) Xu, H.; Rudkevich, D. M. *Chem. Eur. J.* **2004**, *10*, 5432-5442.

(116) Review: Rudkevich, D. M.; Xu, H. *Chem. Commun.* **2005**, 2651-2659.

(117) (a) Ten Cate, T. A.; Sijbesma, R. P. *Macromol. Rapid Commun.* **2002**, *23*, 1094-1112. (b) Schubert, U. S.; Eschbaumer, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 2892-2926. (c) Schmuck, C.; Wienand, W. *Angew. Chem., Int. Ed.* **2001**, *40*, 4363-4369.

(118) Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, J. H., Jr. *J. Am. Chem. Soc.* **2002**, *124*, 926-927.

(119) (a) Aresta, M.; Quaranta, E. *Tetrahedron* **1992**, *48*, 1515-1530. (b) Masuda, K.; Ito, Y.; Horiguchi, M.; Fujita, H. *Tetrahedron* **2004**, *61*, 213-229.

(120) Reviews on organogels: a) Abdallah, D. J.; Weiss, R. G. *Adv. Mater.* **2000**, *12*, 1237-1247; b) van Esch, J. H.; Feringa, B. L. *Angew. Chem. Int. Ed.* **2000**, *39*, 2263-2266.

(121) Tunable cyclic/linear chain in self-assembling polymers: (a) Vollmer, M. S.; Clark, T. D.; Steinem, C.; Ghadiri, M. R. *Angew. Chem., Int. Ed.* **1999**, *38*, 1598-1601 (photoswitch). (b) Folmers, B. J. B.; Sijbesma, R. P.; Meijer, E. W. *J. Am. Chem. Soc.* **2001**, *123*, 2093-2094 (temperature control).

(122) Xu, H.; Rudkevich, D. M. *J. Org. Chem*. **2004**, *69*, 8609-8617.

(123) (a) Choi, M.-S.; Yamazaki, T.; Yamazaki, I.; Aida, T. *Angew.Chem.*, *Int. Ed.* **2004**, *43*, 150-158. (b) Balzani, V.; Ceroni, P.; Maestri, M.; Vicinelli, V. *Curr. Opin. Chem. Biol.* **2003**, *7*, 657-665.

(124) Aoki, I.; Sakaki, T.; Shinkai, S. *J. Chem. Soc.*, *Chem. Commun.* **1992**, 730-732 and references therein.

(125) Xu, H.; Rudkevich, D. M. *Org. Lett.* **2005**, *7*, 3223-3226.

(126) Xu and co-workers recently described a stable metal coordination polymer that binds apolar organic molecules from aqueous solutions; see: Xing, B.; Choi, M.-F.; Xu, B. *Chem. Commun.* **2002**, 362-363. However, in contrast to our material, this gel has to be preformed *prior* to the guest entrapment.

(127) Gronwald, O.; Snip, E.; Shinkai, S. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 148-156.

(128) Ewing, S. P.; Lockshon, D.; Jencks, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 3072-3084.

(129) Reversible carbamate bridges were used to cross-link conventional polymers; see: Carretti, E.; Dei, L.; Macherelli, A.; Weiss, R. G. *Langmuir* **2004**, *20*, 8414-8418. For noncovalent forces in conventional polymers, see: Pollino, J. M.; Weck, M. *Chem. Soc. Rev.* **2005**, *34*, 193-207.

(130) Gutsche, C. D.; Iqbal, M. *Org. Synth.* **1990**, *68*, 234-237.

(131) Vatele, J. M. *Tetrahedron*, **2004**, *60*, 4251-4260 and references therein.

(132) Davies, C. E.; Heightman, T. D.; Hermitage, S. A.; Stephen, A. M.; Moloney, M. G. *Synth. Commun.* **1996**, *26*, 687–696.

(133) Pechar, M.l; Strohalm, J.; Ulbrich, K. *Collect. Czech. Chem. Commun.* **1995**, *60*, 1765-1780.

(134) Castellano, R. K.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1998**, *120*, 3657-3663.

(135) Jung, J. H.; Ono, Y.; Shinkai, S. *Chem. Eur. J.* **2000**, *6*, 4552-4557.

(136) Sime, R. J. *Physical Chemistry—Methods, Techniques and Experiments*, Saunders, Philadelphia, **1990**, pp.522-527.

BIOGRAPHICAL INFORMATION

Heng Xu, born in Jiaxiang City, Shangdong Province, P. R.China, obtained his B.S. in 1998 from Nanjing University, Nanjing, China. He came to The United States in 2001 and began his doctoral studies at the University of Texas at Arlington under the supervision of Professor Dmitry M. Rudkevich. He received his Doctor of Philosophy degree in Chemistry in 2005. His research interests are in synthetic organic and supramolecular chemistry.