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11-Aminoundecanoic Acid, Cyclodextrins (α, β) and Cucurbit[n]urils ($n = 6, 7$) as Building Blocks for Supramolecular Assemblies: A Thermodynamic Study

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Abstract

The formation of 1:1 complexes of α-, β-cyclodextrin, cucurbit[6]uril, and cucurbit[7]uril with 11-aminoundecanoic acid have been studied using calorimetric titrations. The influence of solvent composition (aqueous formic acid) upon the complex stability and the values of the reaction enthalpies and entropies has been studied in the case of α-cyclodextrin (α-CD). With increasing concentration of formic acid the values of the reaction enthalpy decrease and of the reaction entropy increase. All ligands examined form 1:1 complexes with 11-aminoundecanoic acid under the experimental conditions. However, it is also possible to study the formation of 2:1 complexes (ligand:aminocarboxylic acid ratio). Even the formation of mixed 1:1:1 complexes with two different ligands (ligand(1):ligand(2):aminocarboxylic acid ratio) can be measured.

Introduction

The study of multiple interactions between two or more complex molecules is of fundamental interest by giving new insights into molecular recognition and self-assembly processes. The ability of macrocycles such as cryptands, carcerands, crown ethers, cyclodextrins, cyclophanes, calixarenes, and cucurbit[n]urils to form stable complexes with a wide range of guest molecules makes them interesting as building blocks in the design of supramolecular assemblies [1–6]. The architectural complexity of supramolecular entities is controlled by hydrogen bonding, donor–acceptor interactions, and metal coordination interactions, which hold the components together [7, 8]. Thus, the control of non-covalent connections involved in bringing molecules together in aggregates with well-defined supramolecular entity is one of the most important issues in supramolecular assemblies. Up to date, most of the work has focused on assemblies based on hydrogen bonds in non-hydrogen bonding organic solvent aiming to minimize the solvent competition [9–12].

The cyclodextrins are known as remarkable natural cyclic hosts with hydrophobic cavity forming inclusion complexes with a large variety of guest molecules, thus leading to interesting supramolecular assemblies [13–15]. By comparing with crown ethers, cryptands, calix[n]arenes, and cyclophanes, which are hosts focused on molecular recognition of low molecular weight compounds, the cyclodextrins are able to recognize larger guests like clusters and polymers [16–18]. Due to self-assembly processes between cyclodextrins and suitable host molecules, the formation of large molecular assemblies is feasible [12]. Recently, the cyclodextrins have been used as cyclic components for the construction of nanoscale structures through self-assembly because of their well-defined ring structure [19]. Systematic investigations of inclusion complexes between α-cyclodextrin (α-CD) with aliphatic guest molecules were carried out and interesting papers were reported on this topics [20–23]. In this respect, linear long-chain aliphatic compounds bearing amino or carboxylic functional groups were used to build cyclodextrins pseudorotaxanes [15]. From NMR measurements of the interactions between some linear aliphatic α, ω-amino acids, and α-CD in aqueous solutions, it was established that there were formed simultaneously [2]- and [3]-pseudorotaxanes with α-CD [23]. Kawaguchi and Harada [24] suggested that protonation of the amino groups can be used as a stopper and, as a result, may convert the pseudorotaxanes into rotaxanes. Wenz *et al*. [25] showed that α, ω-aminocarboxylic acids form microcrystalline inclusion compounds with α-CD. These complexes were used to synthesize polyamides completely covered by cyclodextrin rings. These polyamides are highly soluble in water.

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Similarly to cyclodextrins, the cucurbit[n]urils as synthetic receptors have hydrophobic inner cavities, which allow them to form many interesting complexes [26–30]. Nevertheless, the presence of six polar carbonyl groups at each portal makes the difference to cyclodextrins. Among other applications including the binding of different guests, cucurbit[6]uril was used as a building block in supramolecular architectures. Thus, a large variety of supramolecular compounds like rotaxane dendrimers, polyrotaxanes, and rotaxane-based molecular switches using cucurbit[6]uril as a molecular bead were synthesized [31–34].

In the present contribution we report our ongoing study on step-by-step formation of complexes consisting of one host molecule and different guest molecules [35]. Both groups of ligands under investigation possess a rigid and non-polar cavity. Taking into account the preferences of cucurbiturils to form complexes with ionic species and of cyclodextrins to complex hydrophobic groups it should be possible to use 11-aminoundecanoic acid to simultaneously form complexes with both types of ligands.

Experimental

The 11-Aminoundecanoic acid (purity ≥ 99%, Merck) is used without further purification. α- and β-CD (both Wacker) are of the highest purity available. The ligands cucurbit[6]uril [33] and cucurbit[7]uril [36] are synthesized and purified as described in detail in the literature (Chart 1). Since the solubility at 298.15 K of cucurbit[6]uril (Cuc[6]) is low in aqueous solution (1.8×10^{-5} M [37], 2×10^{-5} M [28]) but increases in aqueous formic acid (55% v/v; 6×10^{-2} M [33]) all calorimetric titrations are performed in aqueous formic acid. As solvent bidistilled water or aqueous formic acid (50% v/v) is used.

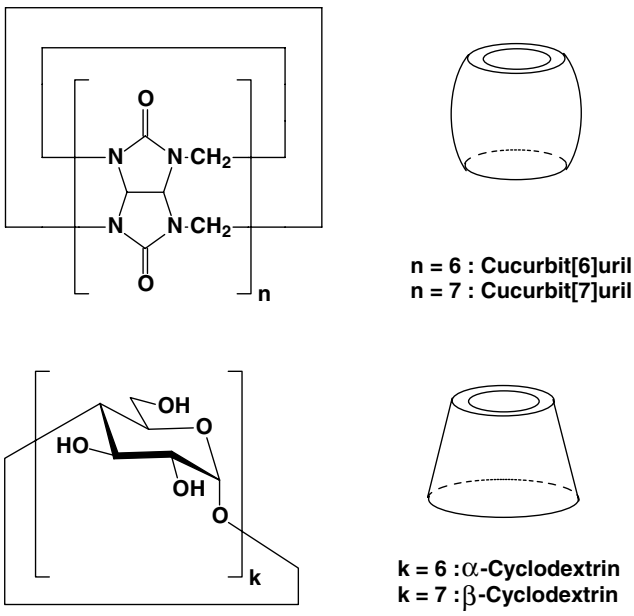

Chart 1. The structures of ligands used in experiments.

Potentiometric titrations were performed using a GLpKa analyser (Sirius Analytical Instruments, Forest Row). The pH value of a solution containing 11-aminoundecanoic acid (5×10^{-4}–2×10^{-3} M) and a tenfold excess of the corresponding ligand was adjusted to pH = 2 using HCl (0.5 M). This solution (20 ml) was titrated with a standard solution of KOH (0.5 M) until a pH = 12 is achieved. The protonation constants and the stability constants were calculated directly from the experimental data using the software package Refinement Pro (Version V1.114, Sirius Analytical Instruments, Forest Row). During the titrations the ionic strength was kept constant with KCl at 0.15 M.

The calorimetric titrations are performed using a Tronac Model 450 calorimeter (TRONAC Inc.). During the calorimetric titration a solution of one ligand (0.06–0.08 M) is added continuously to a solution containing the aminocarboxylic acid ($4–5 \times 10^{-3}$ M) or to the mixture of the aminocarboxylic acid ($4–5 \times 10^{-3}$ M) and these or another macrocyclic ligand (4×10^{-3}–10^{-2} M). Under these experimental conditions the concentration of the ligand titrated into the solution is much smaller compared to the concentration of the aminocarboxylic acid or to the mixture with another ligand. The heat Q produced during the titrations is related to the reaction enthalpy ΔH after correction for all non-chemical heat effects by the following equation:

$$Q = \Delta n \cdot \Delta H \tag{1}$$

with Δn indicating the number of moles of the complex formed. The mathematical treatment of the experimental data has been described in detail in the literature [38–40]. From the experimental data obtained during the formation of the 1:1:1 complexes, no evidence for a replacement reaction of the ligand already forming a 1:1 complex with 11-aminoundecanoic acid is obtained. The accuracy of the calorimeter used is controlled using as standard the reaction between β-cyclodextrin (β-CD) and cyclohexanol (log $K = 2.92 \pm 0.03$ and $\Delta H = -11.8 \pm 0.6$ kJ mol^{-1}) in aqueous solution. These values agree well with the results reported in the literature (log $K = 2.78 \pm 0.02$ and $\Delta H = -9.9 \pm 0.2$ kJ mol^{-1}) [14].

Results and discussion

The cucurbit[6]uril (Cuc[6]) and cucurbit[7]uril (Cuc[7]) have cavities with approximate diameters of 5.8 and 7.3 Å, respectively, which are accessible from the exterior through two carbonyl-fringed portals of 3.9 and 5.4 Å diameter, respectively [26–29, 31]. The internal diameter of α-CD is about 4.9 Å and of β-CD it is about 6.2 Å. Regarding the cavity size, Cuc[6] and Cuc[7] are analogous to α-, and β-CD, respectively [27, 30].

The solvent composition is expected to influence to reaction between the CDs and 11-aminoundecanoic acid. For calorimetric titrations the solubility of Cuc[6] is high enough only in aqueous formic acid (50% v/v).

Table 1. Stability constants log K (K in l mol^{-1}) and thermodynamic values ΔH and $T\Delta S$ (kJ mol^{-1}) for the complex formation of α-, and β-CD with 11-aminoundecanoic acid in pure water and in aqueous solutions with different amounts of formic acid (% v/v) at 298.15 K

	α-CD			β-CD		
Formic acid	log K	$-\Delta H$	$T\Delta S$	log K	$-\Delta H$	$T\Delta S$
0	–[a]	28.5 ± 0.2[a]		3.10 ± 0.02	13.3 ± 0.6	4.3 ± 0.7
	4.00 ± 0.03[b]	25.7 ± 0.6[b]	−3.0 ± 0.8[b]			
	3.16[c]	30.0[c]	−12.1			
	3.35[d]	26.6[d]	−7.6[d]			
	3.98 (1:1)[e]	22.6 (1:1)[e]	0.0[e]			
	3.36 (2:1)[e]	4.0 (2:1)[e]	15.1[e]			
	2.71 (2:1)[f]					
	3.68 (1:1)[g]					
	2.71 (2:1)[g]					
2.5	3.32 ± 0.02	21.1 ± 0.6	−2.2 ± 0.7	3.34 ± 0.03	10.7 ± 0.3	8.3 ± 0.5
5	2.93 ± 0.03	14.9 ± 0.6	1.8 ± 0.7	3.25 ± 0.04	8.9 ± 0.5	9.6 ± 0.7
10	2.64 ± 0.01	9.7 ± 0.7	5.3 ± 0.8	3.42 ± 0.02	6.5 ± 0.3	12.9 ± 0.5
25	2.69 ± 0.02	3.9 ± 0.2	11.4 ± 0.3	3.27 ± 0.02	3.4 ± 0.1	15.2 ± 0.2
50	2.63 ± 0.03	1.1 ± 0.2	13.8 ± 0.4	2.98 ± 0.03	3.0 ± 0.1	13.9 ± 0.3

[a]Thermogram not suitable for the calculation of the stability constant.
[b]From Ref. [41] (cal. titration using the sodium salt of 11-aminoundecanoic acid).
[c]From Ref. [30] (pH ≈ 6.5, 25 °C, cal. titration).
[d]From Ref. [21] (pH = 6.7, 25 °C, cal. titration).
[e]From Ref. [25] (pH = 4.7 (sodium acetate buffer), 25 °C, microcal. titration).
[f]From Ref. [42] (pH ≈ 6.5, 25 °C, cal. titration).
[g]From Ref. [43] (25 °C; microcal. titration).

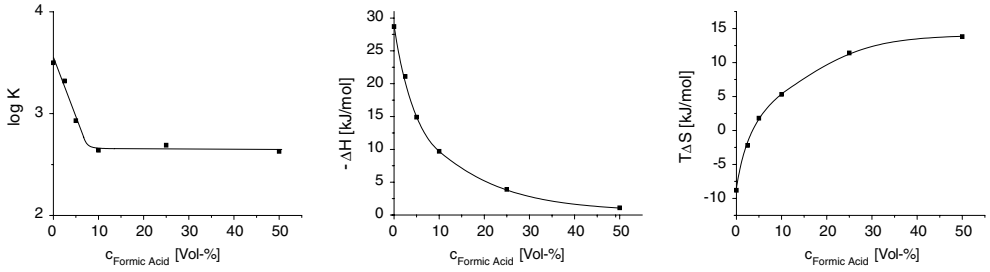

Figure 1. Dependence of the stability constant (log K), reaction enthalpy ΔH and reaction entropy $T\Delta S$ on the concentration of formic acid for the reaction of α-CD with 11-aminoundecanoic acid.

To get some information about the influence of the solvent composition, the reaction between α-CD, β-CD and 11-aminoundecanoic acid is studied in different mixtures of water with formic acid. These results are summarized in Table 1.

In pure water and similar conditions concerning the pH, temperature and method, our results on the complex formation (Table 1) are in accordance with previously published results [21, 25, 30, 42], but in Wenz's experiments [25] where the pH = 4.7 was set by sodium acetate buffer. With the increase of acid formic concentration, the values of the stability constants and reaction enthalpies decrease and the reaction entropies increase (Figure 1). The values of the reaction enthalpies decrease nearly to zero. At higher acid concentration, the entropic contributions are mainly responsible for complex formation. It is well known from crystal structures that α-CD forms a hydrate with six water molecules [44]. Four water molecules are located outside and two inside the cavity. The water molecules inside the cavity of α-CD are energetically not comparable with water molecules in the bulk phase. Thus Saenger *et al.* [45] called them "high energy water". Therefore the release of water molecules from the cavity should result in favorable enthalpic and entropic contributions. This explanation is valid only for the reaction in pure aqueous solution. Also the solvation of the polar amino acid results in further contributions to the overall values of the reaction enthalpy and entropy. At high concentration of the formic acid, the solvent molecules released from the cavity hydrate the formic acid molecules. The interactions between the formic acid molecules and water molecules in the bulk phase influence the measured values of the reaction enthalpy and entropy too. As a result only small values of the reaction enthalpy are observed. However, these water molecules increase the disorder of the solvent. A more detailed discussion about the different distributions to the overall measured

Table 2. Stability constants log K (K in l mol^{-1}) and thermodynamic values ΔH (kJ mol^{-1}) and $T\Delta S$ (kJ mol^{-1}) for the complex formation of 11–aminoundecanoic acid with different macrocyclic ligands in aqueous solution at 298.15 K

Ligand	log K	$-\Delta H$	$T\Delta S$
α-CD	2.56 ± 0.04[a]		
	2.63 ± 0.03[b]	1.1 ± 0.2[b]	13.8 ± 0.4[b]
β-CD	2.81 ± 0.03[a]		
	3.08 ± 0.02[b]	3.1 ± 0.2[b]	14.4 ± 0.3[b]
Cuc[6]	2.65 ± 0.04[a]		
	2.68 ± 0.04[b]	2.3 ± 0.1[b]	12.9 ± 0.2[b]
Cuc[7]	2.47 ± 0.12[a]		
	2.69 ± 0.01[b]	6.1 ± 0.9[b]	9.2 ± 0.4[b]

[a]From pH-metric titrations in aqueous solution.
[b]From calorimetric titrations in aqueous formic acid (50% v/v).

values of the reaction enthalpy and entropy is not possible due to the absence of information about the solvation of amino acids in these solvents. The results for β-CD show the same tendency.

In Table 2 the results for the formation of 1:1-complexes between Cuc[6], Cuc[7], α-CD, and β-CD and 11-aminoundecanoic acid obtained from calorimetric and potentiometric titrations are presented. The stability constants calculated from potentiometric titrations in aqueous solution and by calorimetric titrations in aqueous formic acid (50% v/v) are nearly identical taking into account the differences in the solvent composition. The values of the reaction enthalpies are rather small for all ligands. The reaction is mainly favored by entropic contributions. From the similarity of the values of the reaction entropy, one can conclude that the number of solvent molecules released during the complex formation are quantitatively similar for all guest molecules. In the case of the CDs, it is known that in their cavities water molecules are present, which are released upon guest inclusion [44, 46]. Also, cucurbit[6]uril shows strong interactions with water molecules [47].

To study the threading of more than one host molecule on 11-aminoundecanoic acid (A), one adds a solution of a ligand (L_1) to a solution containing 11-aminoundecanoic acid and this or another ligand (L_1 or L_2). Both possible reactions are shown in Equations (2) and (3):

$$L_1 + AL_1 \leftrightarrow A(L_1)_2 \quad (2)$$

or

$$L_1 + AL_2 \leftrightarrow AL_1L_2 \quad (3)$$

If no complexation reaction takes place, no heat effect is detected during the titration. According to the molecular dimensions of 11-aminoundecanoic acid a maximum of two ligand molecules can be threaded [25]. Increasing the concentration of the ligand in the solution with 11-aminoundecanoic acid leads already to the formation of a 2:1 complex (L:A). Under these conditions, the addition of a solution containing the identical ligand results in no reaction and that's why no heat effect is observable.

However, if the ligand (L_2) in the preformed 2:1 complexes and in the added ligand solution (L_1) are different, a replacement reaction is possible if the ligand L_1 forms a stronger complex than L_2:

$$L_1 + A(L_2)_2 \leftrightarrow AL_1L_2 + L_2 \quad (4)$$

The results for the reactions according to Equations (2)–(4) are summarized in Table 3. From the results obtained for the titrations of solutions of α-CD into solutions of 11-aminoundecanoic acid already containing

Table 3. Stability constants log K (K in l mol^{-1}) and thermodynamic values ΔH (kJ mol^{-1}) and $T\Delta S$ (kJ mol^{-1}) for the complex formation of a macrocyclic ligand with preformed complexes of 11-aminoundecanoic acid (molar ratio of 11-aminoundecanioc acid to macrocyclic ligand in brackets) in aqueous formic acid (50% v/v) at 298.15 K

No.	Titration with	11-Aminoundecanoic acid complex with	log K	$-\Delta H$	$T\Delta S$
1	α-CD	α-CD (1:1)	2.55 ± 0.05	1.0 ± 0.1	13.5 ± 0.4
2	α-CD	α-CD (1:5)	2.57 ± 0.01	0.8 ± 0.2	13.8 ± 0.3
3	α-CD	α-CD (1:10)	2.57 ± 0.02	0.5 ± 0.3	14.1 ± 0.5
4	α-CD	α-CD (1:20)	–[a]	< 0.3	
5	α-CD	β-CD (1:1)	2.46 ± 0.04	0.9 ± 0.1	13.1 ± 0.3
6	α-CD	β-CD (1:5)	2.43 ± 0.03	1.4 ± 0.3	12.4 ± 0.5
7	α-CD	β-CD (1:10)	2.12 ± 0.06	2.8 ± 0.2	9.3 ± 0.9
8	α-CD	β-CD (1:20)	2.27 ± 0.07	2.7 ± 0.3	10.2 ± 0.7
9	α-CD	Cuc[6] (1:1)	2.68 ± 0.05	1.3 ± 0.2	13.9 ± 0.5
10	α-CD	Cuc[6] (1:5)	2.67 ± 0.01	1.9 ± 0.4	13.3 ± 0.4
11	α-CD	Cuc[7] (1:1)	2.53 ± 0.03	2.4 ± 0.1	12.0 ± 0.3
12	β-CD	Cuc[6] (1:1)	2.70 ± 0.06	0.9 ± 0.1	14.4 ± 0.5
13	β-CD	Cuc[7] (1:1)	3.26 ± 0.07	6.7 ± 0.4	11.8 ± 0.8
14	Cuc[6]	α-CD (1:1)	2.68 ± 0.04	2.3 ± 0.1	12.9 ± 0.1
15	Cuc[6]	β-CD (1:1)	2.76 ± 0.08	2.1 ± 0.4	13.6 ± 0.1
16	Cuc[7]	α-CD (1:1)	2.57 ± 0.03	2.6 ± 0.1	12.0 ± 0.3
17	Cuc[7]	β-CD (1:1)	2.75 ± 0.01	4.4 ± 0.3	11.2 ± 0.4

[a]Heat effect too small for the calculation of the stability constant.

different amounts of α-CD, one clearly see the decrease of the values of the reaction enthalpy with increasing ratio of α-CD to the amino acid (Table 3, titrations 1–4). The amount of the preformed 2:1 complex increases and, as a result, the number of moles of the 2:1 complex formed during the titration with α-CD decreases together with the measured heat of the reaction. The stability constant for the formation of the 2:1 complex with α-CD is in good accordance with the values reported in literature (see Table 1). Due to the differences in the solvent composition these results are not strictly comparable. Since the cavity dimensions of all ligands used are similar and the formation of 2:1 complexes of α-CD with 11-aminoundecanoic acid has been proven from NMR measurements [48] the formation of other 2:1 complexes is very probable too.

Unfortunately, no data are available so far for the formation of 2:1 complexes of β-CD with 11-aminoundecanoic acid. In the case that only the 1:1 complex is present in solution, the stability constant and the reaction enthalpy for the reaction of this preformed complex with α-CD is identical with the values obtained for the formation of the 2:1 complex solely with α-CD. Increasing the concentration of β-CD in the presence of the amino acid results in an increase of the measured heat and the calculated value of the reaction enthalpy, respectively (Table 3, titrations 5–8). At high concentrations of β-CD the addition of α-CD to the now completely preformed 2:1 complex with β-CD leads to the displacement of one molecule of β-CD through α-CD and the formation of a 1:1:1 complex (see Reaction (4)). This reaction is obviously favored by enthalpic contributions.

Cucurbit[n]urils include non-polar parts of molecules in their cavities like CDs. However, due to the presence of six carbonyl groups located at each portal, they are able to interact via ion-dipole interactions with charged groups of the guest molecules too. Thus, one portal of these ligands is located at the nitrogen atom of the amino acid. It is known from the literature that without amino group, only weak complexes with cucurbit[6]uril are formed [42]. Consequently, only 1:1 complexes of 11-aminoundecanoic acid and cucurbit[n]urils, $n = 6, 7$ are formed. It follows that the molar ratio of cucurbit[n]urils to the amino acid does not influence the formation of 1:1:1 with α- and β-CD (Table 3, titrations 9–13). Hence the addition of cucurbit[n]urils, $n = 6, 7$ to solutions containing 1:1 complexes of 11-aminoundecanoic acid and α- and β-CD leads to the formation of 1:1:1 complexes (Table 3, titrations 14–17).

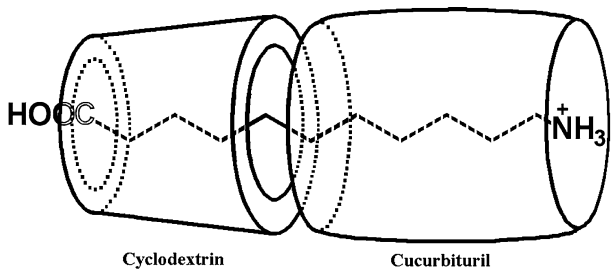

Figure 2. Schematic presentation of a 1:1:1 complex of 11-aminoundecanoic acid with one molecule of CD and cucurbituril.

The experimental results clearly indicate the formation of complexes between 11-aminoundecanoic acid and the macrocyclic ligands α- and β-CDs and cucurbit[n]urils, $n = 6, 7$. A schematic presentation of a 1:1:1 complex of 11-aminoundecanoic acid and a CD (α, β) and cucurbit[n]urils, $n = 6, 7$ molecule is shown in Figure 2. Since the CDs have two different portals and their orientation in the complex is not known small differences depending on of the sequence of adding the ligands are possible. Just recently a cooperative effect during the formation of a 1:1:1 complex of dihexylamine with CDs and cucurbit[6]uril has been reported [48].

Using the α-CD complex of 11-aminoundecanoic acid, Wenz *et al.* [25] synthesized polyamide rotaxanes. In our studies, all complexes formed in solution can be used to synthesize a large variety of polyamide rotaxanes with different arrangements of threaded molecules. Mixing solid complexes of 11-aminoundecanoic acid with α-, β-CD, cucurbit[6]uril and cucurbit[7]uril and all possible mixed complexes of the ligands together with the uncomplexed 11-aminoundecanoic acid render the synthesis of several different polyrotaxanes feasible. One may expect that the polymer properties depend on the different molecules threaded and the number of these molecules. The investigations are in progress and these results will be reported later.

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References

1. J.-M. Lehn: *Supramolecular Chemistry, Concepts and Perspectives*, VCH, Weinheim (1995).
2. J. Szejtli and T. Osa: *Comprehensive Supramolecular Chemistry* Vol. 3, Elsevier, Oxford (1996)Cyclodextrins.
3. L.F. Lindoy and I.M. Atkinson: *Self-Assembly in Supramolecular Systems*, The Royal Society of Chemistry, Cambridge, UK (2000).
4. D.J. Cram: *Nature* **29**, 356 (1992).
5. B. Escuder, A.E. Rowan, M.C. Feiters, and R.J.M. Nolte: *Tetrahedron* **60**, 291 (2004).
6. A. Mulder, J. Huskens, and D.N. Reinhoudt: *Org. Biomol. Chem.* **2**, 3409 (2004).
7. M. Mammen, S.-K. Choi, and G.M. Whitesides: *Angew. Chem. Int. Ed. Engl.* **37**, 2755 (1998).
8. M. Whitesides, J.P. Mathias, and C.T. Seto: *Science* **254**, 1312 (1991).
9. J.-M. Lehn: *PNAS* **99**, 4763 (2002).
10. J.-M. Lehn: *Science* **295**, 2400 (2002).
11. J. Rebek Jr.: *Angew. Chem. Int. Ed. Engl.* **29**, 245 (1990).
12. D. Philp and J.F. Stoddart: *Angew. Chem. Int. Ed. Engl.* **35**, 1154 (1996).
13. A. Harada: In J.A. Semlyen (ed.), *Large Ring Molecules*, J.Wiley & Sons Ltd., Chichester (1996), pp. 407–432.

14. M.V. Rekharsky and Y. Inoue: *Chem. Rev.* **98**, 1875 (1998).
15. S.A. Nepogodiev and J.F. Stoddart: *Chem. Rev.* **98**, 1959 (1998).
16. L. Liu and Q.-X. Guo: *J. Incl. Phenom. Macrocyclic Chem.* **42**, 1 (2002).
17. S. Shinkai: *Tetrahedron* **49**, 8933 (1993).
18. H.-J. Buschmann, E. Schollmeyer, and L. Mutihac: *Biolog. J. Armenia. Cyclodextrins* **50**, 58 (2001).
19. J.F. Stoddart: *Angew. Chem. Int. Ed. Engl.* **31**, 846 (1992).
20. A. Harada: *Coord. Chem. Rev.* **148**, 115 (1996).
21. G. Castronuovo, V. Elia, D. Fessas, A. Giordano, and F. Velleca: *Carbohydr. Res.* **272**, 31 (1995).
22. A. Rontoyianni and I. M. Mavridis: *Supramol. Chem.* **10**, 213 (1999).
23. K. Eliadou, K. Yannakopoulou, A. Rontoyianni, and I.M. Mavridis: *J. Org. Chem.* **64**, 6217 (1999).
24. Y. Kawaguchi and A. Harada: *J. Am. Chem. Soc.* **122**, 3797 (2000).
25. G. Wenz, M.B. Steinbrunm, and K. Landfester: *Tetrahedron* **53**, 15575 (1997).
26. W.A. Freeman, W.L. Mock, and N.-Y. Shih: *J. Am. Chem. Soc.* **103**, 7367 (1981).
27. J.W. Lee, S. Samal, N. Selvapalam, H.-J. Kim, and K. Kim: *Acc. Chem. Res.* **36**, 621 (2003).
28. C. Marquez, R.R. Hudgins, and W.M. Nau: *J. Am. Chem. Soc.* **126**, 5806 (2004).
29. R. Hoffmann, W. Knoche, C. Fenn, and H.-J. Buschmann: *J. Chem. Soc. Faraday Trans.* **90**, 1507 (1994).
30. H.-J. Buschmann, E. Schollmeyer, and L. Mutihac: *Thermochim. Acta* **399**, 203 (2003).
31. A. Day, A.P. Arnold, R.J. Blanch, and B. Snushall: *J. Org. Chem.* **66**, 8094 (2001).
32. J.W. Lee and K. Kim: *Top. Curr. Chem.* **228**, 111 (2003).
33. K. Jansen, H.-J. Buschmann, A. Wego, D. Döpp, C. Mayer, H.-J. Drexler, H.-J. Holdt, and E. Schollmeyer: *J. Incl. Phenom. Macrocyclic Chem.* **39**, 357 (2001).
34. J. Lagona, P. Mukhopadhyay, S. Chakrabarti, and L. Isaacs: *Angew. Chem. Int. Ed.* **44**, 4844 (2005).
35. H.-J. Buschmann, L. Mutihac, and E. Schollmeyer: *Supramol. Chem.* **17**, 447 (2005).
36. C. Marquez, F. Huang, and W.M. Nau: *IEEE Trans. Nanobiosci.* **3**, 39 (2004).
37. H.-J. Buschmann, E. Cleve, K. Jansen, A. Wego, and E. Schollmeyer: *Materials Sci. Eng. C* **14**, 35 (2001).
38. J.J. Christensen, J. Ruckman, D.J. Eatough, and R.M. Izatt: *Thermochim. Acta* **3**, 203 (1972).
39. D.J. Eatough, R.M. Izatt, and J.J. Christensen: *Thermochim. Acta* **3**, 219 (1972).
40. D.J. Eatough, R.M. Izatt, and J.J. Christensen: *Thermochim. Acta* **3**, 233 (1972).
41. H.-J. Buschmann and E. Schollmeyer: *J. Solution Chem.* **34**, 731 (2005).
42. H.-J. Buschmann, K. Jansen, and E. Schollmeyer: *Acta Chim. Slov.* **46**, 405 (1999).
43. M.B. Steinbrunn and G. Wenz: *Angew. Chem. Int. Ed.* **35**, 2139 (1996).
44. P.C. Manor and W Saenger: *Nature* **237**, 392 (1972).
45. W. Saenger, M. Noltemayer, P.C. Manor, B. Hingerty, and B. Klar: *Bioorg. Chem.* **5**, 187 (1976).
46. P.D. Ross and M.V. Rekharsky: *Biophys. J.* **71**, 2144 (1996).
47. P. Germain, J.M. Létoffé, M.P. Merlin, and H.-J. Buschmann: *Thermochim. Acta* **315**, 87 (1998).
48. M.V. Rekharsky, H. Yamamura, M. Kawai, I. Osaka, R. Arakawa, A. Sato, Y.H. Ko, N. Selvapalam, K. Kim, and Y. Inoue: *Org. Lett.* **8**, 815 (2006).