

Binding Ability of Carbazolyphenyl Dendrimers with Zinc (II) Tetraphenylporphyrin Core towards Cryptands

Galina Mamardashvili, Nugzar Mamardashvili, Win Dehaen

Abstract—The processes of complexation of the Zn-tetraarylporphyrins with eight 4-(4-(3,6-bis(t-butyl)carbazol-9-yl-phenyl)-1,2,3-triazole (ZnP1) and eight 4-(4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenoxy)methyl)-2,4,6-trimethylphenyl (ZnP2) with the 1,10-diaza-4,7,13,18-tetraoxabicyclo[8.5.5]eicosane (L1), 1,10-diaza-4,7,13,16,21,24-hexaoxabicyclo[8.8.8]hexacosane (L2) and 1,10-diaza-5,6,14,15-dibenzo-4,7,13,16,21,24-hexaoxabicyclo[8.8.8]hexacosane (L3) were investigated by the method of spectrophotometric titration and ^1H NMR-spectroscopy. We determined the structures of the host-guest complexes, and their stability constants in toluene were calculated. It was found out that the ZnP1 interacts with the guest molecules L1, L2 with the formation of stable "nest" type complexes and does not form similar complexes with the L3 (presumably due to the fact that the L3 does not match the size of the porphyrin ZnP(1) cavity). On the other hand, the porphyrin ZnP2 binds all of the ligands L1-L3, however complexes thus formed are less stable than complexes ZnP1-L1, ZnP1-L2. In the report, we will also discuss the influence of the alkali cations additives on the stability of the complexes between the porphyrin ZnP1, ZnP2 hosts and guest molecules of the ligands L1-L3.

Keywords—Porphyrin, cryptand, cation, complex guest-host.

I. INTRODUCTION

THE present work is a continuation of our research devoted to the binding ability of the carbazolyphenyl-porphyrin dendrimers [1]–[4]. As it was shown in the previous reports [1], [2], the dendrimers with eight carbazolyphenyl dendrons and a Zn-tetraphenylporphyrin core are able to form stable axial complexes with substrates of different nature in which the axial ligand is coordinated to both the central zinc cation of the tetrapyrrolic core and is encapsulated inside the cavity formed by the dendrons. In another work [4], to obtain new supramolecular assemblies containing non-covalently linked molecular fragments of different nature, we prepared a supramolecular complex formed from a carbazolyphenyl-porphyrin first generation dendrimer and [2,2,2] cryptand, and investigated the influence of alkali metal cations on its formation and properties. In this work, the interactions between the dendrimers of the first generation (ZnD1-2) and

cryptands (L1-L3) and the processes of their destruction upon interaction with the alkali metal cations (Li^+ , K^+ , Na^+) were investigated.

II. EXPERIMENTAL

The octacarbazolyphenyl substituted Zn-tetraphenylporphyrin **ZnD1** was obtained according to the literature [2], **ZnD2** was obtained according to the literature [3] (Fig. 1). **ZnTPP** (Zn-tetraphenylporphyrin) from PorphChem. Cryptands (1,10-diaza-4,7,13,18-tetraoxabicyclo[8.5.5]eicosane (L1), 1,10-diaza-4,7,13,16,21,24-hexaoxabicyclo[8.8.8]hexacosane (L2) and 1,10-diaza-5,6,14,15-dibenzo-4,7,13,16,21,24-hexaoxabicyclo[8.8.8]hexacosane (L3)), LiBr, NaBr, and KBr from Sigma-Aldrich were used without further purification. The complexation processes of the porphyrins with cryptands were studied by the spectrophotometric method using Carry 300 spectrophotometer. ^1H NMR spectra were recorded on a Bruker VC-500 (500.17 MHz) instrument in CDCl_3 using TMS as the internal standard.

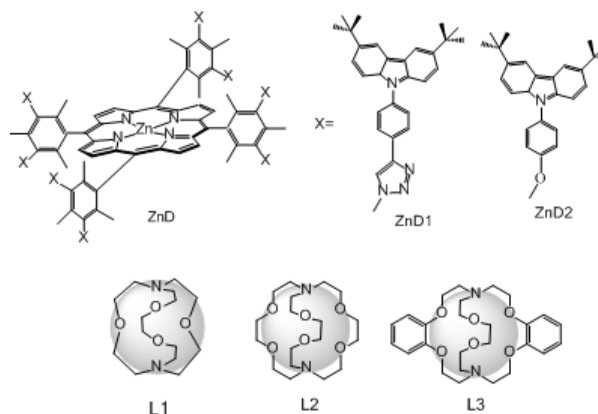


Fig. 1 Structures of the investigated compounds: the porphyrin dendrimers (ZnD) and the cryptands (L)

ZnD1 (Zn(II)-5,10,15,20-tetrakis [3,5-bis((4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenyl)-1,2,3-triazole)-2,4,6-trimethylphenyl]porphyrin), ^1H NMR (500 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS): δ = 8.70 (s_{br} , 8 H, H-pyrrole), 8.13 (s , 16 H, H-carbazole), 8.01 (d , $^3J_{\text{H,H}}$ = 7.04 Hz, 16 H, Ar-H), 7.72 (s , 8 H, H-triazole), 7.56 (d , $^3J_{\text{H,H}}$ = 8.24 Hz, 16 H, Ar-H), 7.38 (d , $^3J_{\text{H,H}}$ = 7.04 Hz, 16 H, Ar-H), 7.31 (d , $^3J_{\text{H,H}}$ = 8.6 Hz, 16 H, Ar-H), 5.69 (s_{br} , 16 H, CH_2), 2.50 (s_{br} , 12 H, 4CH_3), 1.90 (s_{br} , 24 H,

Galina Mamardashvili is with the G.A.Krestov Institute of Solution Chemistry of the Russian Academy of Sciences, Ivanovo, Russia (phone: +7(4932)336246, fax: +7(4932)336990, e-mail: gmm@isc-ras.ru).

Nugzar Mamardashvili is with the G.A.Krestov Institute of Solution Chemistry of the Russian Academy of Sciences, Ivanovo, Russia (e-mail: ngm@isc-ras.ru).

Wim Dehaen is with the Molecular Design and Synthesis, KU Leuven, Belgium (e-mail: dehaen@chem.kuleuven.be).

8CH₃), 1.42 ppm (s, 144 H, *tert*-butyl) ppm. ¹³CNMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 131.34, 127.14, 126.92, 123.76, 119.46, 116.29, 109.16 (CH-Ar), 149.85, 147.05, 143.15, 141.79, 141.20, 138.98, 138.50, 138.08, 129.17, 129.05, 123.48, 118.96 (C-Ar), 49.36 (CH₂), 34.72 (C, *tert*-butyl), 31.99 (CH₃, *tert*-butyl), 19.75 (CH₃), 16.40 (CH₃) ppm. MALDI-TOF: m/z calcd. for C₂₈₈H₂₉₂N₃₆Zn: 4318.324 [M⁺]; found 4320.7 [M + 2H⁺]. Polydispersity index (PDI) = 1.037

ZnD2 (Zn(II)-5,10,15,20-tetrakis[3,5-bis ((4-(3,6-di-*tert*-butyl-9H-carbazol-9-yl) phenoxy) methyl)-2,4,6-trimethyl-phenyl]porphyrin), ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS): δ = 8.82 (s_{br}, 8H, Hpyrrole), 8.10 (s, 16H, H-carbazole), 7.48 (s_{br}, 16H, H-Ar), 7.39 (d, 3JH,H j 7.74 Hz, 16H, H-Ar), 7.32 (s_{br}, 16H, H-Ar), 7.25 (s, 16H, HAr), 5.46 (s_{br}, 16H, CH₂), 2.93 (s, 12H, CH₃), 2.05 (s_{br}, 24H, CH₃), 1.41 ppm (s, 144H, *tert*-butyl). ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 158.15, 144.97, 142.55, 140.91, 140.16, 139.72, 131.27, 130.96, 128.35, 123.47, 123.07, 116.16, 115.77, 109.08 (C, CH-Ar), 65.86 (CH₂), 34.68 (C, *tert*-butyl), 32.00 (CH₃, *tert*-butyl), 19.32 (CH₃), 16.33 ppm (CH₃). MALDI-TOF: m/z calcd for C₂₇₂H₂₈₆N₁₂O₈Zn: 3851.26 [M⁺]; found 3851.58 [M⁺].

ZnD1-L2, ¹H NMR (500MHz, CDCl₃, 25 °C, TMS): δ = 8.70 (s_{br}, 8H, H-pyrrole), 8.14 (s, 16H, H-carbazole), 8.01 (d, 16H, Ar-H), 7.73 (s, 8H, H-triazole), 7.56 (d, 16H, Ar-H), 7.38 (d,

16H, Ar-H), 7.31 (d, 16H, Ar-H), 5.69 (s_{br}, 16H, CH₂), 3.68 (s_{br}, 12H, O-CH₂-CH₂-O), 3.60 (t, 6H, O-CH₂-CH₂-N), 2.65 (t, 6H, O-CH₂-CH₂-N), 2.50 (s_{br}, 12H, 4 - CH₃), 1.90 (s_{br}, 24H, 8 - CH₃), 1.42 (s, 144H, *tert*-butyl), 0.76 (t, 6H, O-CH₂-CH₂-N), 3.05 (t, O-CH₂-CH₂-N).

UV-Vis spectra of the porphyrins and their evolution upon addition of the ligand were measured on a Carry 300 spectrophotometer. The UV-visible absorption spectral studies reveal red shifted Soret and visible bands upon addition of the ligand to a solution of the investigated receptor porphyrins, thus confirming that the N-containing entity of the ligands binds to the Zn-cation of the coordination center of the tetrapyrrolic macrocycle.

The stability constant of the metalloporphyrin complexes with the ligand in ratio of 1:1 (K_{assoc.}) was calculated in accordance with the literature [5] based on spectrophotometric data at two wavelengths (decreasing and increasing) using the following relationships:

$$K = \frac{[A-B]}{[A] \cdot [B]} = \frac{1}{[B]} \left(\frac{\Delta A_{i,\lambda_1}}{\Delta A_{o,\lambda_1}} \cdot \frac{\Delta A_{o,\lambda_2}}{\Delta A_{i,\lambda_2}} \right), M^{-1}$$

where, λ₁ is the decreasing wavelength, λ₂ is the increasing wavelength, [A] is the Zn-porphyrin concentration, [B] is the ligand concentration, ΔA_o is the maximal change of the optical density at the given wavelength, ΔA_i is the change of the optical density of the solution at a given wavelength at a given concentration.

III. RESULTS AND DISCUSSIONS

A characteristic feature of the flat Zn-porphyrin macrocycles is the axial binding of the additional ligands by the central coordinatively-unsaturated Zinc cation of the macrocycle (Fig. 2). Stability of the resulting axial complexes depends on the nature of the porphyrin macrocycle, the polarity of the solvent, the basicity of the small organic ligand. With the conformational mobile cryptands the Zn-porphyrins form relatively weak complexes in comparison with the conformationally rigid DABCO [2], [4].

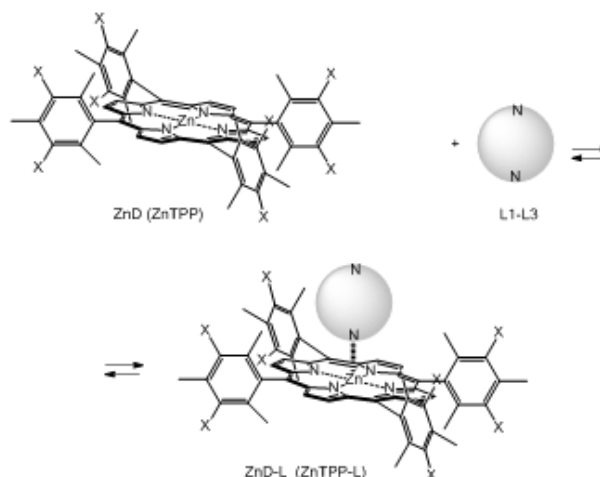


Fig. 2 Scheme of the ZnD (ZnTPP) interaction with the L1-L3

Studied porphyrin dendrimers have binding cavities on both sides of the macrocycle. In the case where the geometry of these cavities is in good geometric and electronic match to the size of the ligand, occurs the formation of the stable "guest-host" complexes (ZnD-L) substantially capsular type (Fig. 3). The obtained results show that such matching occurs at binding ZnD1 cryptands L1 and L2 (log K = 5, 96, and 5.87, respectively) (Fig. 4, Table I). But, the bulkier cryptand L3, presumably exceed the dimensions of the cavity, and the process of the complex ZnD1-L3 formation is not observed.

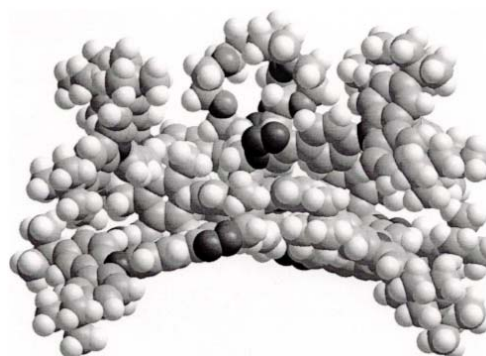


Fig. 3 The structure of the complex ZnD1-L2 obtained by computer simulation [5]

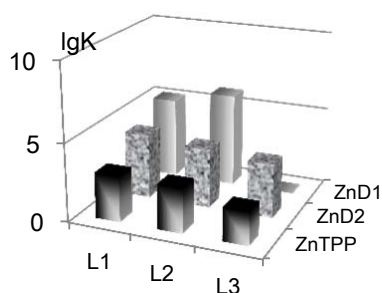


Fig. 4 Stability constants of ZnTPP and octasubstituted dendrimers ZnD1, ZnD2, with L1-L3 in toluene, 25 °C

TABLE I
BINDING CONSTANTS (K , M^{-1}) OF THE LIGAND L BY THE ZNTPP AND ZND IN
TOLUENE-METHANOL MIXTURE (9:1) AT 20 °C

| | L1 | L2 | L3 |
|-------|--------|--------|------|
| ZnTPP | 740 | 580 | 120 |
| ZnD1 | 135000 | 740000 | - |
| ZnD2 | 12400 | 5400 | 2600 |

Error in the constants determination is of 5-7%

The complexation between ZnD and L is characterized by red shifts of the Soret band (Fig. 5) and up-field shifts of the ligands H-protons of the corresponding NMR spectra (see the experimental part).

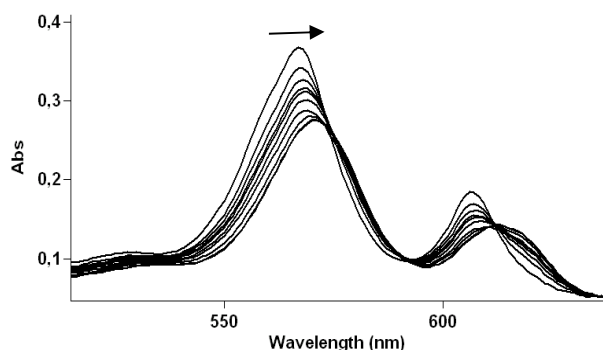


Fig. 5 The changes in the UV-Vis spectra of the system ZnD1-L2 in toluene-methanol mixture at 20 °C, $C_{ZnD} = 0 \div 1.0 \times 10^{-5}$ M

TABLE II
BINDING CONSTANTS (LOG K) OF THE LIGAND L WITH Li^+ , Na^+ AND K^+
CATIONS IN-METHANOL AT 25 °C [6]

| Metal cation (Ionic radius, Å) | Li^+ , 1.36 | Na^+ , 1.90 | K^+ , 2.66 |
|-----------------------------------|------------------|------------------|-----------------|
| L1 | 8.92 | - | - |
| L2 | - | 7.21 | 9.75 |

Among the investigated cryptands, the ZnD2 forms the most stable complexes with the smallest cryptand (L1). On the other hand, it is well known that nitrogen-containing cryptands have high selectivity towards cations [6], [7]. The high selectivity of cryptands is due to the three-dimensional nature of their cavities, which allows them to recognize cations. While they form stable complexes with cations of one type, cryptands with macrobicyclic cavities may not be able to adapt to binding of other cations. They cannot be compressed

enough to bind cations of too small size, or expand, adapting to a cation radius greater than that required for optimal size conformity. Table II shows the binding constants (lg K) of L1-L3 with different alkali metals cations in methanol at 25 °C.

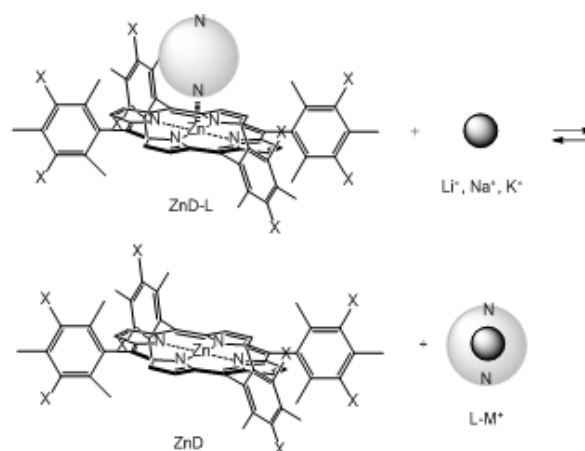


Fig. 6 Scheme of the complexes ZnD-L dissociation in the cations Li^+ , Na^+ and K^+ presence

Spectrophotometric studies of the interaction between the ZnD and L in the presence of alkali metal cations are carried out in the binary solvent toluene-methanol (9: 1). Addition of methanol is needed to ensure solubility of LiBr, NaBr, and KBr. It was established that the addition of KBr to a solution of ZnD1-L leads to the dissociation of the host-guest complex (Fig. 6). The blue shift of the Soret band in the UV-Vis spectrum of the reaction mixture indicates the loss of the interaction between the Zn cation of the porphyrinate and the nitrogen atom of the cryptand (Fig. 7). Another confirmation of this complex dissociation is the presence of a clear triplet of the CH_2-N protons at 2.58 ppm in the 1H NMR spectrum of the reaction system which, according to the literature [4], indicates the formation of the cryptate ($L2-K^+$). It can be concluded that the intra-activity complex $ZnP-[L2-K^+]$ is not formed upon complexation of ZnD with the $[L2-K^+]$ complex. It should be mentioned that we did not observe a significant influence of Li^+ and Na^+ cations on the complexation of the ZnD with the cryptand L2 (Figs. 8 and 9). However, upon addition of the LiBr to the complex ZnD1-L1, its destruction occurs. Upon interaction of the complexes ZnD2-L1, ZnD2-L2, and ZnD2-L3 with the LiBr, NaBr, and KBr solutions, the complexes destruction according with the scheme (Fig. 6) also occurs, but under the higher concentrations of the titrant (Fig. 10).

Probably, these experimental findings are due to the influence of two factors. Firstly, as supported by calculations, complexation of the [2,2,2] cryptand with potassium cation is accompanied by a change in electron density of the cryptand nitrogen atoms. Secondly, as it was mentioned above, the formation of potassium cryptate is accompanied by conformational rearrangements of the cryptand. The data obtained indicate that the combined effect of these two factors lead to the dissociation of the porphyrin-L2 complex upon

addition of potassium cations to the solution, and, in turn, hinders complexation between the Zn-porphyrinate and the potassium cryptate. Li^+ cation interacts similarly in case of the L1. That is, the complexation occurring in the cryptand binding cavity affects the complexation between the octacarbazolyphenyl substituted Zn(II)-tetraphenylporphyrin and the cryptands L1-L2. These «on-off» behavior results can be used in the development of cation assisted molecular devices and polyfunctional materials based on them.

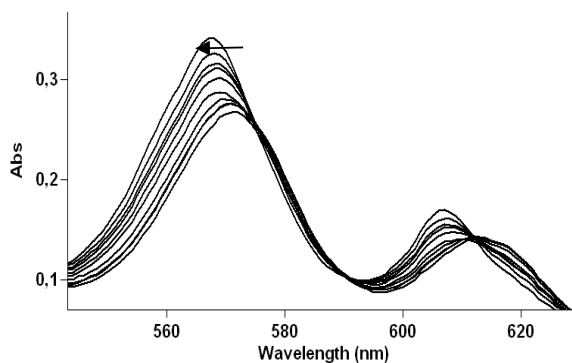


Fig. 7 The changes in the UV-Vis spectra of the system [ZnD1-L2] – K^+ in toluene-methanol at 20 °C, $C_{\text{ZnD}} = 0$ to 1.0×10^{-5} M

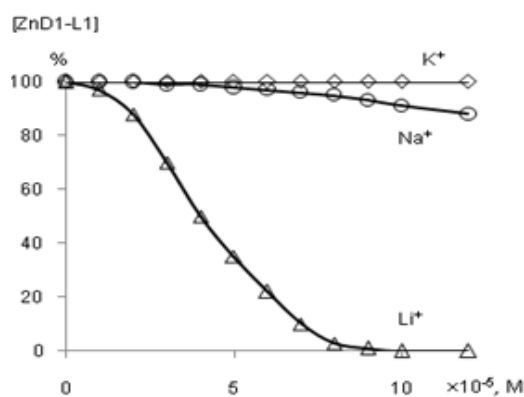


Fig. 8 The complex ZnD1-L1 destruction (%) upon interaction with LiBr, NaBr, and KBr (toluene-methanol (9:1), 25 °C)

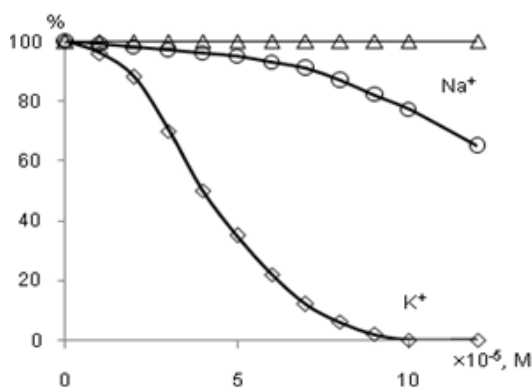


Fig. 9 The complex ZnD1-L2 destruction (%) upon interaction with LiBr, NaBr, and KBr (toluene-methanol (9:1), 25 °C)

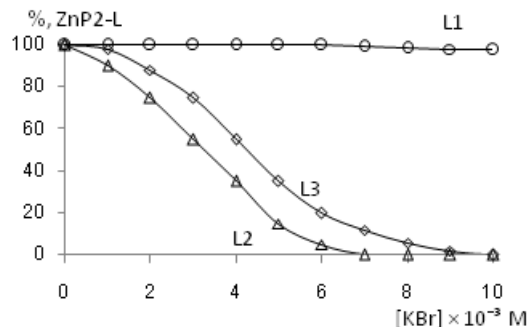


Fig. 10 The complexes ZnD1-L1, ZnD1-L2 and ZnD1-L3 destruction (%) upon interaction with KBr (toluene-methanol (9:1), 25 °C)

ACKNOWLEDGMENT

This work was supported by the Russian Scientific Foundation, grant №14-13-00232.

REFERENCES

- [1] T. Nguyen, G. Mamardashvili, M. Gruzdev, N. Mamardashvili, W. Dehaen, "Binding ability of Zn-tetraarylporphyrins with two, four and eight 4-(4-(3,6-bis(t-butyl)carbazol-9-ylphenyl)-1,2,3-triazole end groups towards N-containing substrates of different nature", *Supramolecular Chemistry*, vol. 25, no 3, pp. 180–188, 2013.
- [2] N. T. Nguyen, G. M. Mamardashvili, O.M. Kulikova, N. Zh. Mamardashvili, W. Dehaen, " Binding ability of first and second generation/carbazolyphenyl dendrimers with Zn(II) tetraphenylporphyrin core towards small heterocyclic substrates", *RSC Advances*, vol.4, pp.19703-19709, 2014.
- [3] N. T. Nguyen, J. Hofkens, I. G. Scherblykin, M. Kruk, W. Dehaen " Click Reaction Synthesis and Photophysical Studies of Dendritic Metalloporphyrins, *Eur. J. Org. Chem.*, vol. 2014, no.8 , pp.1766-1777, 2014.
- [4] G. M. Mamardashvili, O. V. Maltceva, N. Zh. Mamardashvili, N. T. Nguyen, W. Dehaen "Cation assisted complexation of octacarbazolyphenyl substituted Zn(II)-tetraphenylporphyrin with [2,2,2]cryptand", *RSC Advances*, vol. 5, pp. 44557–44562, 2015.
- [5] Meites, L. *Introduction to Chemical Equilibrium and Kinetics*; Pergamon: Oxford, 1981.
- [6] Lehn J.-M. *Supramolecular Chemistry: Concepts and perspectives*. Weinheim: VCH, 1995.
- [7] J. W. Steed, J. L. Atwood *Supramolecular Chemistry*. 2nd, Edition V. John Wiley&Sons, 2009.