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ARTICLE TYPE

Cation assisted complexation of octacarbazolyphenyl substituted Zn(II)-tetraphenylporphyrin with [2,2,2]cryptand

Galina M. Mamardashvili^a, Olga V. Maltseva^a, Nugzar Zh. Mamardashvili^{*,a}, Nguyen Tran Nguyen^b, Wim Dehaen^{*,b}

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A supramolecular complex formed from a carbazolyphenyl-porphyrin first generation dendrimer and [2,2,2]cryptand was prepared. The influence of alkali metal cations on its formation and some properties were investigated by spectrophotometric and ¹H NMR titration methods. It was established that the complexation occurring between potassium cation and [2,2,2]cryptand affects the complexation between the octacarbazolyphenyl substituted Zn(II)-tetraphenylporphyrin and the cryptand. This on-off behavior can be used in the development of cation assisted molecular switches and polyfunctional materials for chemical sensors and actuators.

Introduction

The host-guest chemistry of polyfunctional macrocyclic devices is a very interesting and recently vigorously developing area of supramolecular chemistry [1-9]. Application of the principles of molecular recognition opens up interesting approaches to create functional materials with desired receptor, sensing and transport properties [10-12]. On the other hand, devices can be obtained by the combination of different classes of organic compounds (cryptands, crown[n]ethers, calix[n]arenes, calix[n]pyrroles, porphyrins, and others) into one macrocycle or supramolecular assembly. Different reports have appeared [13-19] describing compounds formed as the result of the covalent linking of calix[4]arenes, calix[4]pyrroles and porphyrins, which, on the one hand, retain their individual properties and, on the other hand, gain new properties compared to the starting fragments. In this work, 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.

Result and discussion

The present work is a continuation of our research devoted to the binding ability of the carbazolyphenyl-porphyrin dendrimers. As it was shown in previous reports [20, 21] 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.

Previously, we have studied the binding ability of the carbazolyphenyl-porphyrin dendrimers of the first and second

generations towards small organic molecules, such as imidazoles, triazoles and pyridine. In this work, studies have been performed on the complexation of octacarbazolyphenyl substituted Zn(II)-tetraphenylporphyrin with [2,2,2]cryptand, including the influence of alkali metal cations on the complexation.

It is well known that nitrogen-containing cryptands have high selectivity towards cations [22-26]. 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 1** shows the [2,2,2] cryptand binding constants (lg K) with different alkali metals cations in methanol at 25 °C [25].

Table 1. The binding constants of ligand L with Li⁺, Na⁺ and K⁺ cations in methanol at 25 °C [25]

Metal cation/ Ionic radius, Å	Li ⁺ , 1.36	Na ⁺ , 1.90	K ⁺ , 2.66
<i>Binding constant</i>	1.80	7.21	9.75

It should be noted that upon complexation of cryptand [2,2,2] with metal cation certain conformational rearrangements of the host molecules take place (**Fig.1**).

Figure 1. Conformational rearrangement of the [2,2,2]cryptand upon complexation with K⁺ [26].

Other than acting as good hosts for cations, cryptands, in turn, can perform the role of guest molecules, forming stable complexes with host molecules with enhanced molecular cavities, such as carbazolyphenyl-porphyrin dendrimers. The anchoring

point of this binding is the axial coordination of one of the nitrogen atoms of the guest molecule to the coordinatively unsaturated metal cation of a metalloporphyrin macrocycle. The axial binding occurs at the result of a donor-acceptor interaction, and the complex stability, depending on the basicity of the ligand, can vary widely. Thus, for example, in toluene and benzene the stability of Zn-TPP axial complexes along the series: aniline < pyrrole < triazole < pyridine < imidazole < piperidine < triethylenediamine increases nearly for 5 orders of magnitude [27-29].

By the combination of spectrophotometric titration and ^1H NMR spectroscopy methods, we have studied the axial coordination of the cryptand **L** by **ZnD** and the influence of alkali metal cations (Li^+ , Na^+ and K^+) on the complexation in toluene and a toluene-methanol mixture (9:1). The influence of the K^+ cation on the complexation was quantitatively determined. Complexation of **L** with **Zn-TPP** was investigated as a model system.

Table 2. Binding constants ($\lg K_{\text{assoc.}} \text{M}^{-1}$) of the ligand **L** by the **ZnTPP** and **ZnD** in toluene and toluene-methanol mixture (9:1) at 20°C

ZnTPP (toluene)	ZnD (toluene)	ZnTPP (toluene- methanol)	ZnD (toluene- methanol)
2.88	5.96	2.76	5.87

The error in the determination of the constants is 5-7%

From the spectrophotometric titration of **ZnTPP** with the cryptand **L** it was observed that the titration curve has one step (Fig. 2a), indicating that only one kind of complexes are formed between the porphyrinate and the ligand. The slope of the plots of the logarithmic dependence of the optical density of the reaction system ($\log[(A_0-A_i)/(A_i-A_f)]$) in function of the ligand concentration ($\log C_{\text{ligand}}$) is equal to one (Fig. 1_S1), indicating the formation of the complex with the ratio of 1: 1 (**ZnTPP-L**).

Figure 2. a) The binding isotherm of the system **ZnTPP-L** in toluene at 20°C, $C_{\text{ZnTPP}} = 1.5 \times 10^{-5} \text{ M}$; b) The changes in the UV-Vis spectra of the system **ZnTPP-L** in toluene at 20°C, $C_{\text{ZnTPP}} = 0$ to $1.0 \times 10^{-2} \text{ M}$.

The changes in the UV-Vis spectra of the system **ZnTPP-L** in toluene are depicted in Fig. 2b. In general, the stability of the **ZnTPP-L** complex in toluene (Table 2) is one or two orders of magnitude lower in comparison with the stability of similar complexes between **ZnTPP** and primary, secondary and tertiary alkyl amines [30], which may be due to the presence of the nearby oxygens in the cryptand structure.

As we have shown in an earlier report [31], in the binary solvent toluene - methanol the axial ligand binding to the Zn-porphyrin is reduced, and the process of binding is accompanied by smaller shifts of the absorption bands in the UV-Vis spectra of the reaction mixture. Thus, as might be expected, the axial ligand **L** binding to **ZnTPP** in the mixture toluene-methanol (9: 1) is somewhat lower than in pure toluene (table 2).

The presence of the bulky carbazolyphenyl substituents on the periphery of the tetrapyrrolic macrocycle of the **ZnD** leads to the formation of additional binding cavities above and below the

porphyrin core. If the size of the cavity is much larger than that of the axial ligand, the presence of the latter practically does not influence the binding process of the axial ligands. If the size of the ligand exceeds that of the cavity, the axial binding becomes difficult or even impossible. In case of good electronic and geometric correspondence between the cavity and the ligand, the ligand is coordinated not only on the central cation of the tetrapyrrolic macrocycle coordination center, but is encapsulated by the intramolecular cavity, which greatly improves the stability of the resulting axial complex, sometimes by several orders of magnitude.

As it is shown by quantum-chemical calculations, the carbazolyphenyl branches in the **ZnD** are able to form intramolecular cavities that can exhibit binding ability towards cryptand 2,2,2 (Fig. 2_S1). Depicted in the Fig. 3_S1 and Table_S1 are also structures of the ligand **L** and the complex **L-K⁺** obtained by the DFT/B3LYP/6-31G** method. All calculations were performed using the software package Gaussian 98 [32].

The study of complex formation between the **ZnD** and the ligand **L** in toluene and in the binary solvent toluene-methanol (9:1) showed that the Zn-porphyrinate forms complexes of one type (Fig. 3), the stability of which is significantly higher as compared with the stability of the **ZnTPP** complexes with the same ligand (Table 2).

Figure 3. a) The binding isotherm of the system **ZnD-L** in toluene at 20°C, $C_{\text{ZnD}} = 1.3 \times 10^{-5} \text{ M}$; b) The changes in the UV-Vis spectra of the system **ZnD-L** in toluene at 20°C, $C_{\text{ZnD}} = 0$ to $1.0 \times 10^{-5} \text{ M}$.

The presence of the internal cavity formed by four carbazolyphenyl branches probably has a favorable effect on the ligand binding. Due to a good geometric match between the host-guest molecules, the stability of the resulting complex **ZnD-L** in toluene is more than 1200 times higher than that of **ZnTPP-L** complex (Table 2).

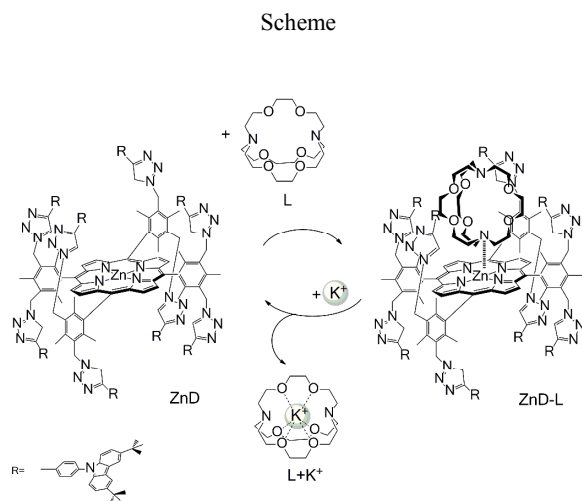
Based on the results of investigation of the **ZnD** and **ZnTPP** complexation with the **L** at 20°C, 25°C and 30°C in toluene the enthalpy and entropy contributions to the complexes **ZnD-L** and **ZnTPP-L** stability were calculated. The small contribution of the entropy component to the stability of the complex **ZnD-L** in toluene (table 3) indicates that the additional affinity of the **ZnD** to the **L** is not connected with a solvophobic interaction in the investigated reaction system.

Table 3. The thermodynamic parameters of the complexation of **ZnD** and **ZTPP** with the ligand **L** in toluene at 25°C.

Complex	$\ln K$	$\Delta H^\circ, \text{ J mol}^{-1}$	$\Delta S^\circ, \text{ J mol}^{-1} \text{ K}^{-1}$
ZnD-L	13.71	-44 000	-34
ZnTPP-L	6.62	-28 000	-39

$$\Delta G^\circ = -RT \ln K = \Delta H^\circ - T\Delta S^\circ; \Delta H^\circ = R \frac{T_2 \times T_1}{T_2 - T_1} \ln \frac{K_2}{K_1}$$

The structure of the complex **ZnD-L**, obtained by computer simulation is shown in Fig. 1_S1 of the SI.



¹H NMR-spectroscopic data also point to the formation of stable complexes **ZnD-L** at an equivalent concentration ratio of the reagents. Splitting of the ligand protons signals occurs in the spectra of the bounded cryptand (Fig. 4_SI). The signal of the hydrogens which are located closer to the porphyrin macrocycle are up field shifted.

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 **ZnD-L** leads to the dissociation of the host-guest complex (scheme). The blue shift of the Soret band in the UV-Vis spectrum of the reaction mixture (Fig. 4) indicates the loss of the interaction between the Zn cation of the porphyrinate and the nitrogen atom of the cryptand. Another confirmation of this complex dissociation is the presence of a clear triplet of the CH₂-N protons at 2.58 p.p.m. in the ¹H NMR spectrum of the reaction system, which, according to the literature [23], indicates the formation of the cryptate (**L-K⁺**). It can be concluded that the intracavity complex **ZnP-[L-K⁺]** is not formed upon complexation of **ZnD** with the [**L-K⁺**] complex. It should be mentioned that we did not observe a significant influence of Li⁺ and Na⁺ cations on the complexation of **ZnD** with the cryptand **L**.

Figure 4. The changes in the UV-Vis spectra of the system [**ZnD-L**] - **K⁺** in toluene-methanol at 20°C, C_{ZnD} = 0 to 1.0 × 10⁻⁵ M.

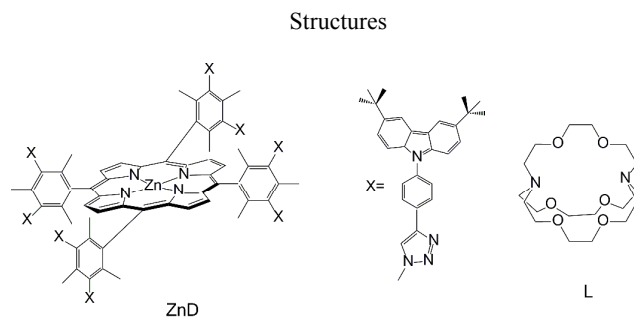
Probably, these experimental findings are due to the influence of two factors. Firstly, as supported by calculations, complexation of the [2,2,2]cryptand with potassium cation is accompanied by a change in electron density of the cryptand nitrogen atoms. Secondly, as it was mentioned above, the formation of the potassium cryptate is accompanied by conformational rearrangements of the cryptand. Secondly, according to the literature [1] in the complexes with metal cations the cryptands are preferably arranged in the *endo-endo* conformation in which the nitrogen atom lone electron pairs are directed inside of the ligand binding cavity, and thus are no longer available to bind to the Zn-cation of the tetrapyrrolic macrocycle in an axial manner. The data obtained indicate that the combined effect of these two

factors leads to the dissociation of the porphyrin-cryptand complex upon addition of potassium cations to the solution, and, in turn, hinders complexation between the Zn-porphyrinate and the potassium cryptate. That is, the complexation occurring in the cryptand binding cavity affects the complexation between the octacarbazolyphenyl substituted Zn(II)-tetraphenylporphyrin and the [2,2,2]cryptand. It should be noted that the destruction of the **ZnD-L** complex upon addition of trifluoroacetic acid (2 × 10⁻⁶ M) to the **ZnD-L** toluene-methanol solution was also estimated. In general it can be noted that, if the location of the potassium cation in the cryptand cavity can have a significant impact on the ligand size and adversely affect on the geometric match between the porphyrin receptor and the substrate parameters, the main reason for the release of the cryptand molecules from the porphyrin receptor cavity upon acid addition to the **ZnD-L** toluene-methanol solution should be the destruction of the donor-acceptor **Zn-N** bond and protonation of the cryptand N-atom. According to literature [1, 33-35], when to a solution of cryptand an acid is added, the protonation of the cryptand tertiary nitrogen atoms occurs with the formation of a bicyclic quaternary ammonium salt with *endo-endo* conformation in which the two H-atoms are situated inside of the molecule. This on-off behavior results can be used in the development of cation assisted molecular switches and polyfunctional materials based on these.

Experimental

The octacarbazolyphenyl substituted Zn-tetraphenylporphyrin **ZnD** was obtained according to the literature [36]. Zn-Tetraphenylporphyrin (**ZnTPP**) from Sigma-Aldrich was subjected to column chromatography on silica gel using toluene as the eluent. [2,2,2]Cryptand (**L**), LiBr, NaBr and KBr from Sigma-Aldrich were used without further purification. ¹H NMR spectra were recorded on a Bruker VC-500 (500.17 MHz) instrument in CDCl₃ using TMS as the internal standard.

ZnD-L, ¹H NMR (500.17 MHz, CDCl₃, 25°C, TMS): δ = 8.70 (s_{br}, 8 H, H-pyrrole), 8.13 (s, 16 H, H-carbazole), 8.01 (d, 16 H, Ar-H), 7.72 (s, 8 H, H-triazole), 7.56 (d, 16 H, Ar-H), 7.38 (d, 16 H, Ar-H), 7.31 (d, 16 H, Ar-H), 5.69 (s_{br}, 16 H, CH₂), 3.68 (s_{br}, 12 H, O-CH₂-CH₂-O), 3.60 (t, 6 H, O-CH₂-CH₂-N), 2.65 (t, 6H, O-CH₂-CH₂-N), 2.50 (s_{br}, 12 H, 4 × CH₃), 1.90 (s_{br}, 24 H, 8 × CH₃), 1.42 (s, 144 H, *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 100 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 method [37] based on spectrophotometric data at two wavelengths (decreasing and increasing) using the following relationship:

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

where, λ_1 is the decreasing wavelength, λ_2 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.

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^a *Coordination Chemistry of Macrocyclic Compounds*, G.A. Krestov Institute of Solution Chemistry of Russian Academy of Sciences, Akademicheskaya St.1, 153045 Ivanovo, Russia

^b *Molecular Design and Synthesis*, Department of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium. Fax: (+32) 16 327990; Tel: +32 16 3 27439; E-mail: wim.dehaen@chem.kuleuven.be

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