Synthesis and Complexation Properties of an Oligooxaethylene-Spacered Porphyrin Dimer – Toward the Construction of a New Switchable Porphyrin Array

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A new linear switchable diporphyrin array has been synthesized in good yield by a Williamson coupling of 5-(4′-hydroxyphenyl)-10,15,20-triphenylporphyrin with tetraethylene glycol ditosylate. ^{1}H-NMR binding studies reveal that the title receptor binds to Na^+ and K^+ salts to give a supramolecular complex with stability constants (K) of 30 and 160 M^{-1}, respectively ($CD_3CN/CDCl_3$, 1:1). The formation of the host-guest complexes promotes a change of the geometry of the system toward a topology in which the two tetrapyrrolic macrocycles tend to face together. UV/Vis and fluorescence spectroscopy give indications of the actual geometry of the assembly. The system reported represents an important step toward the construction of a supramolecular model of relevant biological systems.

Introduction

The synthesis and the study of porphyrin dimers is an attractive and challenging field of research yet to be fully exploited. These molecules constitute interesting models of biological systems of vital importance, like the ones involved in the photosynthetic machinery.[1] The photosynthetic reaction center of *Rhodopseudomonas viridis* and *Rhodobacter spheroides*, for example, features two bacteriochlorophyll moieties held at a precise distance and spatial orientation by a protein matrix.[2] Moreover, cofacial metallo-diporphyrins[3] are regarded as promising mimics of redox-active metalloproteins such as haemoglobin, myoglobin, and cytochrome c oxidases. We have recently reported on the synthesis and photophysical properties of unsymmetrical porphyrin dimers,[4] pointing out some interesting features in terms of a directional, efficient energy transfer between the covalently linked macrocycles.[4c]

Most of the synthetic strategies adopted so far for the construction of the target architectures rely on either covalent or supramolecular assemblies of the chosen porphyrin subunits. The first approach,[5] though it provides a good control over the geometric and electronic properties of the molecule, usually suffers the drawback of requiring time-consuming and low-yield ending syntheses. The second approach, based on noncovalent interactions such as electrostatic interactions,[6a–6c] hydrogen bonding,[6d–6h] and metal coordination,[6i–6r] deals with elements achievable by less demanding protocols but rests on assemblies which too often show low stability in protic or coordinating media.[7] The design of a *switchable linear porphyrin array* would represent a simple and elegant way for circumventing these problems.[8] We report here on the synthesis of a new porphyrin dimer **1a** and its zinc derivative **1b** by a facile synthetic route which entails the functionalization of the basic molecular frame of an oligooxaethylenic chain with two tetrapyrrolic macrocycles. We also present evidences of a conformational change of the system induced by a host-guest interaction with alkali metal ions (Figure 1).

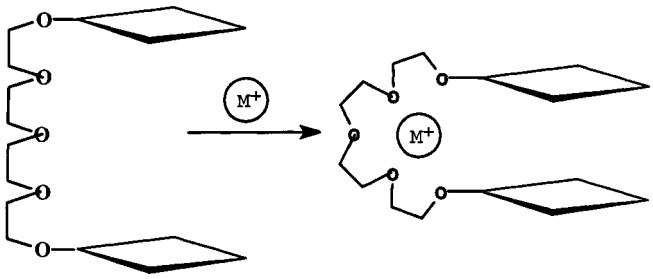

Figure 1. Cation-induced conformational change of diporphyrin receptors

Results and Discussion

Synthesis of the Target Molecules

The porphyrin dimer **1a** and its metal derivative **1b** have been prepared according to the procedure outlined in Scheme 1. Condensation of pyrrole and 4-methoxybenzaldehyde in the presence of a ten-fold excess of benzaldehyde in refluxing propionic acid[9] gave a mixture of *meso*-tetraphenylporphyrin (H_2TPP) and 5-(*p*-methoxyphenyl)-10,15,20-triphenylporphyrin (**2**). After chromatographic

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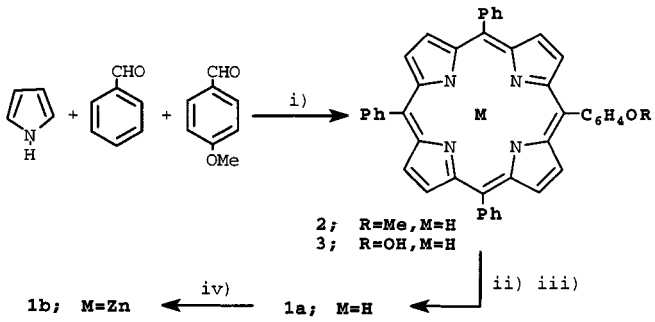
separation, porphyrin **2** was subjected to demethylation with BBr_3[10] to give the relative phenolic derivative **3**, which is in turn coupled with tetraethylene glycol ditosylate under Williamson conditions[11] to give the title porphyrin **1a** in good yield. The zinc derivative **1b** was obtained in quantitative yield by stirring a chloroform solution of **1a** with an excess of a saturated methanolic solution of zinc diacetate at reflux temperature.[9]



Scheme 1. Synthesis of diporphyrin **1a**, **1b**, and **2**; i) propionic acid, reflux, 3 h; ii) BBr_3, CH_2Cl_2, 0°C then room temp. overnight; iii) tetraethylene glycol ditosylate, anhydrous K_2CO_3, DMF, 80°C, 12 h; iv) MeOH/$Zn(OAc)_2$, $CHCl_3$, reflux, 3 h

The UV/Vis spectra of **1a** show features similar to the ones observed for the reference porphyrin **2** ruling out the occurrence of any detectable ground-state interaction between the appended tetrapyrrolic macrocycles.

NMR Studies

^{1}H-NMR spectroscopy was found to be a convenient tool for the study of the supramolecular cation-receptor interaction. At room temperature, rapid exchange between complexed and uncomplexed species is observed on the NMR time-scale at 300 MHz. The ^{1}H-NMR spectra of the bis(porphyrin) receptors feature a complex multiplet at δ = 8.4−8.8 (β-H pyrrole protons) and three set of signals for the phenyl rings. The AX spin system relative to the aromatic protons of the ring linked to the spacer (C_6H_4O) is clearly visible as a double doublet in the aromatic region (see Experimental Section). The resonances of the protons of the oxyethylenic spacer lie in the range δ = 3.4−4.2. The N−H protons resonate, as expected, at $\delta \approx -3$. The addition of Na^+ or K^+ salts (SCN^- in $CDCl_3/CD_3CN$, 1:1 mixture) to a $5 \cdot 10^{-4}$ M solution of the porphyrin dimer **1a** causes a gradual shift of some of the signals of the aromatic part as well as the signals of the linker. The chemical shifts, however, did not reach a limiting value even at relatively high concentration of the added guest, indicating the formation of a weak complexes with low *K* values. The expected downfield shift (up to 50 Hz) of the ethylenic proton signals of the spacer is consistent with that observed in the case of crown ethers and related open-chain compounds.[12] More remarkable is the change observed for the β-H pyrrolic set of signals which undergo a pronounced change into a set of a triplet and two doublets. The phenomenon is accompanied by a concomitant upfield shift (up to 150 Hz) of the signals. This is a clear indication of the occurrence of a change of topology due to the incipient cofacialization of the tetrapyrrolic units caused by the wrapping of the molecule around the cation. The induced conformational change of the receptor reflects itself in the mutual shielding of the proton of the porphyrin planes by effect of the ring current of the π-electron systems.[13] The protons of the phenyl rings at the *meso* positions experience a similar upfield splitting effect. The AB spin system of the C_6H_4O moiety is instead downfield shifted. This result can be also explained in terms of the above anisotropic ring-current effect of the porphyrin rings assuming that the protons are located at the deshielding region. However, an effect of the depletion of the electronic charge caused by the electrostatic interaction of the cation with the oxygen atoms could not be excluded a priori. The signals of the inner N−H protons, though to a lower extent, are also upfield shifted. The invariance of the chemical shift of some of the signals, upon addition of salts, can be an indication of the geometry of the porphyrin planes within the frame of the supramolecular complex (vide infra). The association constant for the complexation of the receptors with the metal ions can be evaluated by non linear least-squares regression of the chemical shift values of the chosen signals as a function of the metal cation concentration. In all cases, a clear 1:1 binding isotherm is obtained (Figure 2). K^+ binds to receptors **1a** somewhat more strongly than Na^+ giving $K_{(K+)}$ = 160 and $K_{(Na+)}$ = 50 M^{-1}.

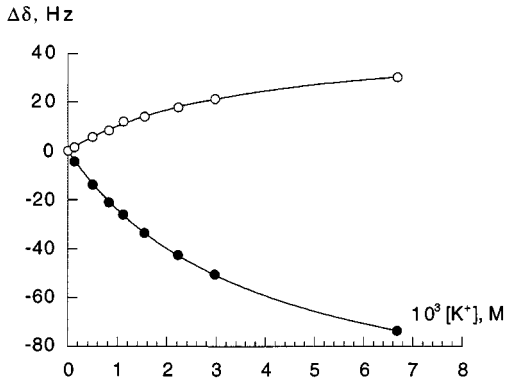


Figure 2. ^{1}H-NMR (300 MHz, $CD_3CN/CDCl_3$ 1:1 solvent mixture) titration curves of different sets of signals for the binding of KSCN to **1a** (●: β-H pyrrolic; ○: C_6H_4OR aromatic protons); solid lines represent the theoretical curves for a 1:1 complex formation

This degree of selectivity between cations with different ionic radii is in line with the values reported for related open-chain podands bearing different aromatic ends,[14] and can be accounted for by the intrinsic flexibility of the ligand which can easily adapt itself to the required conformational change. The binding constant values for the complexation of Na^+ and K^+ cations to the zinc derivative receptor **1b** are similar to the values obtained for the free-base **1a**. This finding rules out the possibility that ion-pairing with the central zinc ions plays a significant role for the observed conformational change.

Negligible variations were observed in the case of the reference porphyrin **2**, indicating that the complexation of the cation only takes place at the oligooxyethylenic site. Moreover, neither the UV/Vis nor the ^{1}H-NMR spectral pattern of the porphyrins **1a** and **1b** show any appreciable variation upon addition of an excess of Bu_4NClO_4 salt, excluding the occurrence of self-aggregation phenomena, like π-π stacking,[15] that could be induced by the increased ionic strength of the medium.[16] The formation of dimers or higher aggregates is a common phenomenon, which is, however, usually seen in the case of charged derivatives in aqueous solvents,[17] and is evidenced by both the broadening and the batochromic shift of the Soret band.

The complexation studies were also extended to ^{23}Na-NMR spectroscopy.[18] When a solution of receptor **1a** in $CDCl_3/CD_3CN$ (1:1) is added to a solution of Na^+ in the same solvent mixture at room temperature, the relaxation time (T_1) of the Na^+ nucleus gradually decreases from 23 ms (free cation) to 10 ms for a [**1a**]/[Na^+] ratio of 0.2. This is ascribed to the formation of the more rigid molecular complex [Na@**1a**] as a consequence of the wrapping of the oxyethylenic segment around the metal cation.[19] The same behaviour is observed in the case of receptor **1b**. UV/Vis spectra of the porphyrin derivatives in the presence of an excess of Na^+ or K^+ salts, however, show negligible variations. This observation sheds some light on the actual geometry of the supramolecular complexes. In the case of cofacial diporphyrin derivatives with an interplanar distance ranging from 4.5 to 6.5 Å, a hypsochromic shift of the Soret band is usually observed[5][20] as a consequence of the electronic interaction of the π-electron systems of the two macrocycles. In our case the two tetrapyrrolic planes are not closely faced but more probably are somewhat displaced apart in a more "open" configuration.

Fluorescence Quenching Experiments

Preliminary fluorescence studies on porphyrin **1a** were carried out in acetonitrile solution by using several quenchers, i.e. NaI, KI, KSCN. The idea was to analyze how the binding of Na^+ or K^+ ions to the sample, causing a structural rearrangement of the entire molecule, affects the photophysical properties of the two porphyrin moieties.

In all the experiments the emission spectrum of the porphyrin chromophore was strictly preserved (λ_{em} = 648 nm, FWHM = 21 nm), showing no additional radiative contributions from Charge Transfer (CT) or excimer-like species. This finding supports the idea that the ion-binding process forces the molecule to attain a conformation that does not involve strong intramolecular π-π interactions between the two porphyrin moieties as also suggested by UV/Vis experiments. Accordingly, fluorescence intensity measurements at different KSCN concentrations show that the porphyrin quantum yield is little affected by the ion binding, again a clear evidence of the weak intramolecular interaction between the porphyrin chromophores. The binding of Na^+ and K^+ ions to **1a** is clearly shown by the Stern−Volmer plots relative to fluorescence quenching experiments of the porphyrin emission by NaI and KI. In these experiments, the iodine quencher is constrained in proximity of the sample by the ion binding, affecting the quantum yield of the porphyrin moieties. Interesting differences between the binding of Na^+ and K^+ ions are shown by the quenching experiment results reported in Figure 3. The Stern−Volmer plot relative to the NaI quencher is linearly dependent on the NaI concentration, exhibiting only a dynamic quenching of the porphyrin chromophore emission. KI quenching experiments exhibit an upward curvature of the Stern−Volmer plot, indicating a complex quenching mechanism arising form both static and dynamic (collisional) processes.[21] Static contributions to the overall quenching are usually ascribed to a ground-state complex formation, particularly evident in this case due to higher affinity of the K^+ ion to **1a**.

Interestingly the Stern−Volmer plot of the KI quenching experiments on **2** (Figure 3), shows only a dynamic contribution to the overall quenching process enhanced by proximity effects.

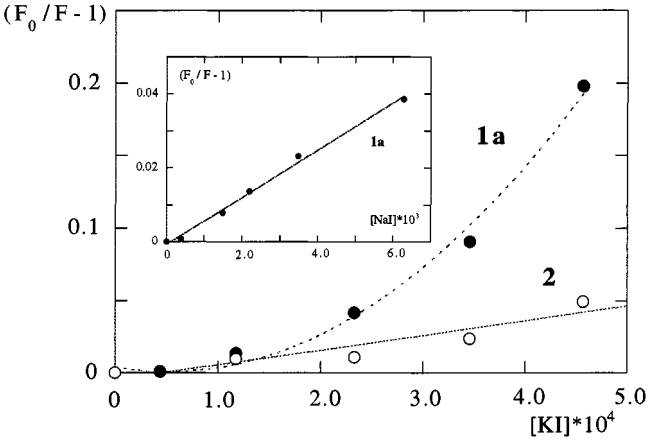


Figure 3. Stern−Volmer plot for the quenching of porphyrin **1a** and **2** with KI and for the quenching of **1a** with NaI (inset)

Gas-Phase Complexation Studies by FAB Mass Spectrometry

Fast atom bombardment mass spectrometry has been widely applied in the field of host−guest complexation chemistry.[22] The mass spectra of bis(porphyrin) **1a** in the presence of KSCN provide clear evidence for the formation of the complex. Peaks at 1416 and 1455 correspond to the **1a** and [K@**1a**] cation, respectively. The same result is observed in the case of the addition of an excess of NaSCN to a slurry of **1a** in NBA matrix. The fact that $[M + K]^+$ corresponds to the most intense peak of the spectrum (100% intensity), whereas in the analogous experiment the intensity of $[M + Na]^+$ presents a value of about 40%, gives an indication of the different stability of the molecular complexes in the gas phase which nicely parallels the trend observed in solution.[23]

Conclusions

The chemistry of porphyrin dimers have attracted increasing attention since these molecules represent good models of key enzymatic systems. The approach we followed for the construction of the required architectures entails the functionalization of an oligo(oxaethylenic) chain with two porphyrin platforms. The promising features of the podand-like structure obtained resides on the possibility of the change of topology toward a cofacial arrangement induced by the supramolecular host-guest interaction of the oxyethylenic segment with an alkali metal ion. Studies directed toward the elaboration of some of the structural features of the receptors aimed at the achievement of an optimal geometry as well as higher binding constants and increased selectivity toward different metal cations are in progress. A step along this direction could be, for example, the introduction of the so-called "Donor End Groups".[14] This would result in a favourable enthalpic contribution to the association as a consequence of the increased number of binding sites. The systems presented in this work may have also important applications in the field of supramolecular switches,[8a,24] and ion recognition.

Experimental Section

Instrumentation: ^{1}H- and ^{23}Na-NMR spectra were recorded with a Bruker AC 300 P (300 MHz) spectrometer. Chemical shifts are given in ppm relative to tetramethylsilane (TMS) and are referenced against residual solvent signals. − Routine UV/Vis spectra were performed with a Varian Cary 1/E spectrophotometer. A Perkin −Elmer λ 18 instrument was used for more delicate UV/Vis measurements. − Fluorescence quenching experiments were performed with a SPEX Fluoromax spectrofluorimeter operating in Single Photon Counting mode. − Mass spectra (FAB) were recorded with a VG-Quattro spectrometer by using *m*-nitrobenzyl alcohol (NBA, Aldrich) as a matrix. − Silica gel 60 (70−230 mesh, Merck) was used for column chromatography. − Reagents (Aldrich, Fluka or Carlo Erba) were of the highest grade available and were used without further purification. Tetraethylene glycol ditosylate was synthesized according to published procedures.[26] Solvents were dried, degassed, and distilled before use, by using standard procedures.[27] A small amount of activated 4-Å molecular sieves was added to NMR solvents in order to remove traces of water.

5-(4′-Methoxyphenyl)-10,15,20-triphenylporphyrin (2): To a solution of 35 g (0.33 mol) of benzaldehyde, 4.5 g of 4-methoxybenzaldehyde (0.033 mol) in 2 L of propionic acid at reflux temperature, a solution of 28 g of freshly distilled pyrrole (0.42 mol) in 100 mL of propionic acid was added dropwise over the period of 30 min. The reaction mixture was stirred at reflux temperature for additional 3 h, then cooled to room temperature. The solvent was evaporated under reduced pressure to give a black tarry residue which was dissolved in chloroform (250 mL) and a saturated $NaHCO_3$ aqueous solution was added. The mixture was vigorously stirred until evolution of gas ceased and the organic phase separated, washed with a 10% Na_2CO_3 aqueous solution (3 × 200 mL) and then with brine until neutrality. The solution was dried with anhydrous Na_2SO_4. In order to remove polymeric by-products silica gel (200 g) was added to the solution and the resulting mixture stirred for 30 min. The silica gel was filtered off and the solid residue repeatedly washed with $CHCl_3$ until a UV/Vis check run showed the disappearance of the typical absorption band (λ = 419−420 nm, Soret) of the title porphyrins in the eluent. The filtrate and the washings were collected, reduced to a small volume by rotary evaporation, and the residue applied to a silica gel column. The elution with $CHCl_3$ gave H_2TPP as a first moving band. The subsequent elution with a 1% methanol/chloroform mixture gave 4.5 g of the porphyrin **2** (0.07 mol, 21% yield) which was used without further purification. − ^{1}H NMR ($CDCl_3$), δ = 8.8−8.9 (m, 8 H, β-H pyrrolic), 8.20−8.24 (dd, J_1 = 7.1 Hz, J_2 = 2.3 Hz, 6 H, aromatics), 8.13 (d, J = 9.2 Hz, 2 H, 3′-, 5′-H, C_6H_4OMe), 7.76 (m, 9 H, aromatics), 7.28 (d, J = 9.2 Hz, 2 H, 2′-, 6′-H, C_6H_4OMe), 4.09 (s, 3 H, OMe), −2.8 (br. s, 2 H, NH). − UV/Vis ($CHCl_3$): λ_{max} = 420 (Soret), 516, 550, 592, 650 nm. − FAB MS (NBA); *m/z* (%): 646 (100) $[M]^+$, 614 (15) $[M - OMe]^+$.

5-(4′-Hydroxyphenyl)-10,15,20-triphenylporphyrin (3): Porphyrin **2** (0.323 g, 0.5 mmol) was dissolved in 25 mL of carefully dried and degassed CH_2Cl_2. The solution was cooled to −10°C and BBr_3 (250 mL, 2.6 mmol) added dropwise. The bluish-green reaction mixture was allowed to warm to room temperature and stirred overnight under nitrogen. The mixture was then quenched with methanol (5 mL), cautiously poured into a mixture of ice and saturated aqueous solution of Na_2CO_3. Chloroform (50 mL) was added to the suspension, the organic layer separated, washed with brine until neutrality, and dried (Na_2SO_4). The solution was reduced to a small volume under reduced pressure and chromatographed (SiO_2) eluting with a 3% methanol/chloroform mixture to give 0.24 g (0.38 mmol, 75% yield) of the title compound which was used without further purification. − ^{1}H NMR ($CDCl_3$), δ = 9.0−8.7 (m, 8 H, β-H pyrrolic), 8.25−8.20 (dd, J_1 = 7.0 Hz, J_2 = 2.0 Hz, 6 H, aromatic), 8.13 (d, J = 8.7 Hz, 2 H, 3′-, 5′-H, C_6H_4OH), 7.76 (m, 9 H, aromatics), 7.28 (d, J = 8.7 Hz, 2 H, 2′-, 5′-H, C_6H_4OH), 4.1 (s, 3 H, OMe), −2.7 (br. s, 2 H, NH). − UV/Vis ($CHCl_3$): λ_{max} = 420 (Soret), 518, 551, 590, 650 nm. − FAB MS (NBA); *m/z* (%): 631 (100) [M + H], 614 (15) [M − OH].

α,ω-Bis[5,10,15-triphenylporphyrinyl-20-(4-phenyloxyl)]tetraethylene Glycol [H_4(P)TEG(P), 1a]: 50 mg of porphyrin **3** (0.08 mmol), 20 mg of tetraethylene glycol ditosylate (0.04 mmol) and 250 mg of anhydrous K_2CO_3 in 10 mL of freshly dried and distilled DMF were stirred at reflux temperature for 12 h under an inert atmosphere. The solvent was then stripped off in vacuo to give a purple residue which was dissolved in 50 mL of $CHCl_3$ and washed with brine until neutrality. The organic solution was dried (Na_2SO_4), reduced to a small volume, and chromatographed (SiO_2) eluting with a 3% methanol/chloroform mixture to give 78 mg of pure **1a** (0.055 mmol, 68% yield). − ^{1}H NMR, ($CDCl_3$) δ = 8.9−8.8 (m, 16 H, β-H pyrrolic), 8.2−8.1 (m, 10 H, aromatic), 8.09 (d, J = 8.1 Hz, 4 H, C_6H_4OR) 7.74−7.68 (m, 20 H, aromatic), 7.28 (d, J = 8.1 Hz, 4 H, C_6H_4OR), 4.4 (br. t, J = 4.8 Hz, 4 H, CH_2CH_2O), 4.1 (br. t, J = 6.0 Hz, 4 H, CH_2CH_2O), 3.9−3.8 (m, 8 H, CH_2CH_2O), −2.77 (br. s, 4 H, NH). − ^{13}C NMR ($CDCl_3$): δ = 158.6 (C-4′, C_6H_4OR), 142.1 (C-1′, phenyl), 135.6 (C-2′, C_6H_4OR), 134.7 (C-1′, C_6H_4OR) 134.6 (C-2′, phenyl), 131.2 (C-4′, phenyl), 130.0 (br., C-α), 129.0 (br., C-α), 128.5 (br., C-α), 127.7 (C-β), 126.7 (C-3′, phenyl), 120.1 (C-*meso*), 120.0 (C-*meso*), 119.9 (C-*meso*), 112.9 (C-3′, anisyloxy), 71.1 (CH_2CH_2O), 70.9 (CH_2CH_2O), 70.0 (CH_2CH_2O), 67.8 (CH_2CH_2O). − UV/Vis ($CHCl_3$): λ_{max} = 418 (Soret), 517, 552, 590, 645 nm. − FAB MS (NBA); *m/z* (%): cluster centered at 1416 (100) $[M^+]$.

Zn_2(P)TEG(P) (1b): In a 25-mL round-bottomed flask, equipped with a reflux condenser and a nitrogen inlet tube was placed 50 mg of porphyrin **1a** (0.035 mmol) in 15 mL of chloroform. The mixture was brought to reflux temperature and 1 mL of a saturated meth-

anolic solution of $Zn(OAc)_2$ was added under stirring. The stirring and heating were prolonged for 3 h, the mixture was then allowed to cool to room temperature, the solvent was removed in vacuo, the cherry-red residue dissolved in 50 mL of chloroform, washed with brine (3 × 50 mL), and dried (Na_2SO_4). The solvent was reduced to a small volume and the residue chromatographed (SiO_2) on a short column eluting with a 3% methanol/chloroform mixture to give 0.052 mg of the pure title compound (0.034 mmol, 97% yield). The product can be further purified by crystallization from dichloromethane/hexane. − ^{1}H NMR ($CDCl_3$): δ = 8.95−8.86 (m, 16 H, β-H pyrrolic), 8,18−8.12 (m, 10 H, aromatic), 8.02 (d, *J* = 8.4 Hz, 4 H, C_6H_4OR), 7.75−7.66 (m, 20 H, aromatic), 7.04 (d, *J* = 8.4 Hz, 4 H, C_6H_4OR), 3.87−3.82 (m, 4 H, CH_2CH_2O), 3.53 (br. q, 4 H, CH_2CH_2O), 3.35−3.15 (m, 8 H, CH_2CH_2O). − ^{13}C NMR ($CDCl_3$) δ = 158.3 (C-4′, C_6H_4OR), 142.9 (C-1′, phenyl), 135.4 (C-2′, C_6H_4OR), 134.5 (C-1′, C_6H_4OR), 132.1 (C-2′, phenyl), 131.9 (C-2′, phenyl), 132.0 (C-α), 131.9 (C-4′, phenyl), 127.4 (C-β), 126.5 (C-3′, phenyl), 121.0 (C-*meso*), 120.9 (C-*meso*), 70.5 (CH_2CH_2O), 70.3 (CH_2CH_2O), 69.6 (CH_2CH_2O), 67.3 (CH_2CH_2O). − UV/Vis ($CHCl_3$): λ_{max} = 423 (Soret), 551, 594 nm. − FAB MS (NBA); *m/z* (%): cluster centered at 1546 (100) [M^+].

^{1}H- and ^{23}Na-NMR Titration: A $CDCl_3/CD_3CN$ (1:1 v/v) solvent mixture was used for solubility reason. The temperature was held constant within ±0.2 K at 298 K. A general procedure for ^{1}H-NMR titration is as follows. Solutions of alkali metal ions were prepared by dissolving in a 2-mL volumetric flask the required amount of salt in a solution of bis(porphyrin) receptor. The resulting solution was added portionwise with a microsyringe to 500 μL of the porphyrin solution placed in an NMR sample tube. This procedure ensures a constant concentration of the receptor throughout the NMR titration. ^{23}Na-NMR titration was performed by adding a solution of porphyrin host to a solution of Na^+, maintaining the concentration of the salt at a constant value. ^{23}Na-NMR relaxation times (T_1) have been measured by 180-τ-90 inversion recovery sequences using the Bruker Aspect 3000 Automatic Program Library.

Data Analysis: The stability constants (*K*) for 1:1 complexation were calculated from the chemical shift of the chosen signals. The values obtained for different signals were the same within the experimental error (5%). The equation used for analyzing NMR titration data was of the general form[28] $\Delta\delta_{obs} = \Delta\delta_i K[M^+]/(1 + K[M^+])$, were $\Delta\delta_{obs} = \delta_{obs} - \delta_0$, δ_{obs} is the observed NMR shift of a specific acceptor proton in the equilibrium solution, and δ_0 is the shift of the free acceptor proton. $\Delta\delta_i = \delta_i - \delta_0$, δ_i is the shift of the acceptor proton at infinite concentration of the added guest. The unknown parameters, $\Delta\delta_i$ and *K*, were obtained using the least-squares curve-fitting program Kaleidagraph© with data of 6−8 measurements. The regression values (r^2) for the computer fitting were usually better than 0.99. Experiments were duplicated and were found to be in excellent agreement within the experimental error (standard deviation σ^2 5%).

Fluorescence Experiments: Fluorescence quenching measurements were performed in a Single Photon Counting mode. The signal was acquired in a sample vs. reference acquisition mode (S/R), compensating for instabilities and intensity variations of the lamp (Xe, 300 W). All measurements were performed on freshly prepared, thermostated (*T* = 300 K) solutions with optical densities less than 0.1 (*l* = 1 cm, UV suprasil quartz cell).

Fast Atom Bombardment Mass Spectrometry (FAB MS): Cesium iodide was used as primary beam of atoms. Samples were mixed with the minimum amount of *m*-nitrobenzyl alcohol matrix and placed on the tip of a stainless steel probe. The spectra were recorded in the positive-ion mode.

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