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A novel strapped porphyrin receptor for molecular recognition

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Abstract—A novel strapped porphyrin receptor **Zn1**, in which two electron-rich bis(*p*-phenylene)-34-crown ether-10 units are incorporated, has been designed and synthesized from the newly developed intermediate **7** for investigating new chemistry of molecular recognition. ^{1}H NMR and UV–Vis studies revealed that **Zn1** displays relatively weak binding abilities to neutral electron deficient naphthalene-1,8,4,5-tetracarboxydiimide (NDI) derivatives **13** (no simple complexing stoichiometry was observed), **19** (K_a=48(±5) M^{-1}) and **30** (K_a=46(±5) M^{-1}) in chloroform-d, strong binding ability to pyridine derivative **25**, (K_a=1.5(±0.12)×10^3 M^{-1}) in chloroform, moderately strong binding ability to tetracationic compound **35**·4PF$_6$ (K_a=475(±50) M^{-1}) in acetone-d$_6$, and very strong binding affinity to compound **22** (K_a=6.5(±0.7)×10^5 M^{-1}), which consists of one pyridine and two NDI units, in chloroform. Remarkable cooperative effect of the intermolecular metal–ligand coordination and donor–acceptor interactions in complex **Zn1**·**22** was observed by comparing the complexing behaviors between **Zn1** and the appropriately designed guests. Complex **Zn1**·**22** possesses an unique three-dimensional tri-site binding feature. For comparison, the complexing affinity of **1** toward compounds **13**, **19**, and **30** in chloroform-d and **35**·4PF$_6$ in acetone-d$_6$ has also been investigated and the binding patterns in different complexes were explored. The results demonstrate that strapped porphyrin derivatives are ideal precursors for constructing new generation of three-dimensional multi-site artificial receptors for molecular recognition and host–guest chemistry.

1. Introduction

An ongoing enterprise in supramolecular chemistry is the design, synthesis, and study of abiotic receptors with convergent recognition and/or self-assembling functionalities.[1] Due to their fascinating photophysical, coordination, and geometrical properties, porphyrins are ideal building blocks for constructing linear and planar artificial molecular switches,[2] molecular wires,[3] and photosynthetic systems.[4] In the past two decades, a variety of porphyrin-based artificial receptors have also been reported, which could strongly bind ions,[5] organic molecules,[6] and biological species.[7] Most reported porphyrin receptors have been constructed from artificial *meso* tetraphenyl- or diphenyl porphyrin derivatives because of their synthetic facility and versatile modifiability. In principle, incorporating multiple functional moieties into the *meta*- or *ortho*-positions of the *meso* phenyl rings could generate three-dimensional binding pockets for new molecular recognition chemistry. However, examples of this kind are very limited,[8,9] due to atropisomerization of the *meso* functionalized phenyl groups as a result of their rotation around the linking carbon–carbon axis.[10] We believed that efficient control of such kind of rotation should greatly promote design of new generation of porphyrin receptors for further investigation of multi-site molecular recognition.

There are two general approaches, which can be used to prevent atropisomerization of 5,15-diphenyl porphyrins. The first one involves introduction of a bulky group to the *ortho*-positions of the phenyl groups or the pyrrolyl β-positions adjacent to the phenyl moieties. However, separation of the corresponding *trans*- and *cis*-atropisomers are usually time-consuming[11] and the differentiation of the atropisomers based on NMR spectra is difficult and sometimes even misleading.[12] The second one is to directly connect the two opposite phenyls with an additional chain of suitable length, which usually leads to exclusive formation of the conformationally restricted porphyrins.[13] Surprisingly, although, with this approach, a range of hemoprotein models have been developed with the strapped porphyrin unit as a spacer and/or a binding site,[14] to our knowledge, there have been no reports of strapped porphyrin derivatives being used as artificial receptors for investigating molecular recognition or host–guest chemistry. We considered that appropriately designed strapped metal porphyrins with additional binding moieties might become novel generation of multi-site receptors since all the additional binding units are definitely positioned to the strap-free side and any intermolecular porphyrin metal–ligand interaction can occur also only from this side. In this paper, we describe the design and synthesis of the first strapped porphyrin receptor **Zn1** of this kind, which incorporates two electron-rich macrocyclic ether moieties, and a systematic evaluation

Keywords: porphyrin; crown ether; molecular recognition; coordination; donor–acceptor interaction.

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of its binding properties toward several kinds of organic guests.

2. Results and discussion

Different from calix[4]arenes and cyclodextrins which have pre-organized conformations for design of efficient three-dimensional artificial receptors, porphyrins possess a π-conjugated planar structure which is unfavorable for selective three-dimensional molecular recognition. Although a number of strapped porphyrins have been reported,[13] there have been no reports in the literature for further modifications of strapped porphyrins with additional functional groups. Successful development of efficient method to prepare functionalized strapped porphyrin precursors would greatly promote the design and synthesis of new generation of porphyrin receptors. We therefore had proposed a general strategy to develop this kind of porphyrin receptors by incorporating two well-studied electron rich bis(*p*-phenylene)-34-crown-10 units to the porphyrin skeleton,[15] as outlined in Figure 1. We synthesized compound **1** and its zinc complex **Zn1** as our first class of three-dimensional tri-site porphyrin receptor. ^{1}H NMR and UV–Vis studies have demonstrated that **Zn1** is a versatile receptor which can bind a range of neutral and ionic guests.

Compound **1** was prepared from the reaction of two key intermediates diol **7** and acyl chloride **12**. The synthetic route to **7** is outlined in Scheme 1. Thus, acid **2** was firstly octylated with octyl bromide in DMF with potassium carbonate as the base to give compound **3** in 84% yield. The introduction of the octyl group in **3** was used to improve the solubility of the resulting porphyrin in common organic solvents. Compound **3** reacted with pyrrole in refluxed toluene in the presence of a catalytic amount of *p*-toluenesulfonic acid, to afford ester **4** in 65% yield. Another intermediate **6** was prepared in 72% yield from the reaction of phenol **5** and 1,10-dibromodecane in DMF with potassium carbonate as the base. Then, the key porphyrin precursor **7** was synthesized in 7% isolated yield from the condensation reaction of **6** with **4**, with trifluoroacetic acid as the catalyst, followed by oxidation with DDQ. The decamethylene chain was chosen since previous investigations showed that it is long enough for the porphyrin framework to maintain its planarity.[16]

The synthesis of another intermediate **12** and the target molecules **1** and **Zn1** are shown in Scheme 2. Ditosylate **8** was first treated with compound **9** in refluxing acetonitrile in

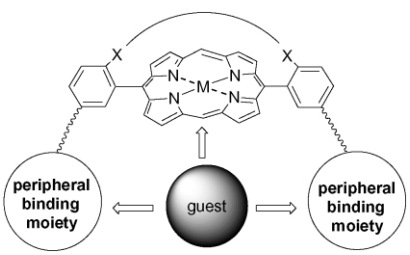
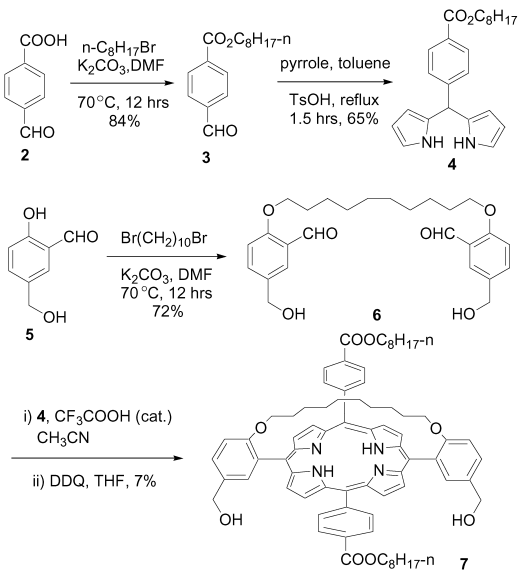
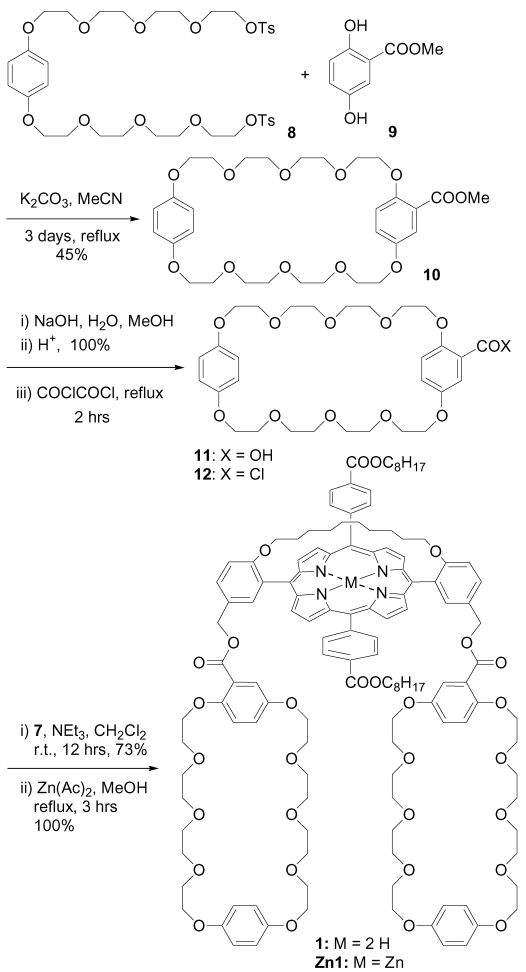


Figure 1. Design scheme of strapped porphyrin receptor for multi-site recognitions.



Scheme 1.

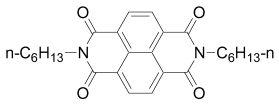
the presence of potassium carbonate to afford macrocyclic compound **10** in 45% yield. Compound **10** was hydrolyzed quantitatively with sodium hydroxide and the resulting carboxylic acid was converted to **12** with oxalyl chloride. Treatment of **12** with diol **7** in dichloromethane with triethylamine as a base led to the formation of **1** in 73%



Scheme 2.

yield. Porphyrin **1** could be conveniently converted to its Zn(II) complex **Zn1** with zinc acetate.

Receptors **1** and **Zn1** possess three electron rich moieties, i.e. two macrocyclic ether units[15f] and one porphyrin unit.[17] Therefore, their ability to complex the typical electron deficient naphthalene-1,8,4,5-tetracarboxydiimide (NDI) derivative **13**[18] was first examined by ^{1}H NMR. As expectedly, small but noticeable upfield shifts were observed for the NDI-H signal (−0.07 and −0.09 ppm) of **13** when the same ratio of **1** or **Zn1** and **13** were dissolved in chloroform-d (0.02 M) at room temperature. However, data for the ^{1}H NMR titration of **13** in chloroform-d, with its NDI-H signal as the probe, with changing amounts of **1** or **Zn1** did not fit a 1:1 or 2:1 binding model well, implying that complicated complexation modes departing from simple stoichiometry prevailed.



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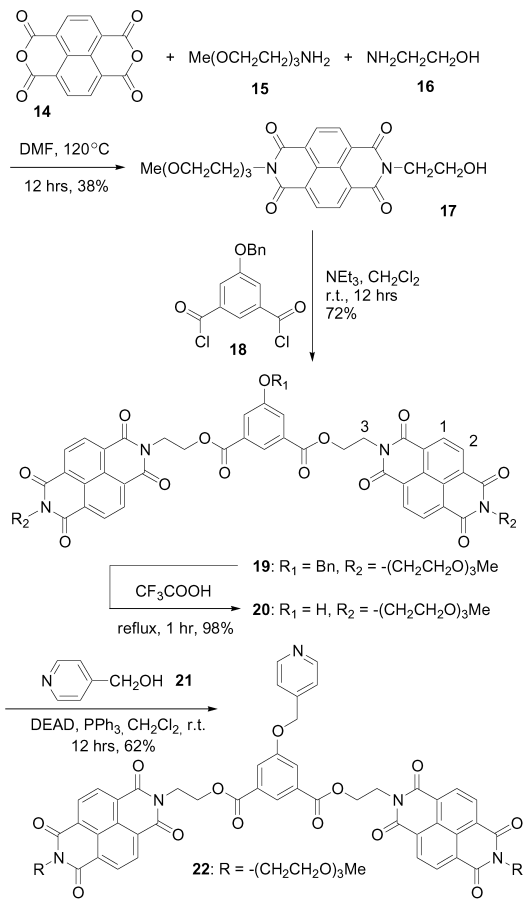
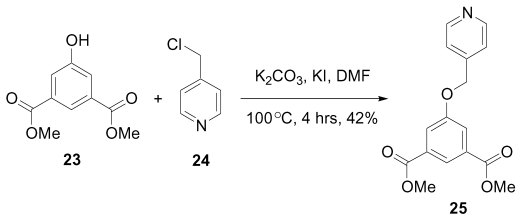
Then, the complexing behaviors of **Zn1** toward guests **19**, **22** and **25** were investigated, with an aim of exploring the cooperative effect of the intermolecular donor–acceptor interaction and the zinc–pyridine coordination. The synthesis of compound **19** and **22** are outlined in Scheme 3. Thus, compound **17** was first prepared in 38% yield from the unsymmetrical imidation of **14** with **15**, and **16** in DMF and subsequently treated with diacyl chloride **18** in dichloromethane in the presence of triethyl amine to afford compound **19** in 72% yield. Compound **19** was then deprotected in refluxing trifluoroacetic acid to give phenol **20** in quantitative yield. Guest **22** was obtained in 62% yield from the Mitsunobu reaction of compounds **20** and **21**. Initially, we had prepared a compound similar to **19** but with R_2=*n*-C_8H_{17}, which was found to be unusable because of its insufficient solubility in common solvents such as chloroform, acetone, and methanol. The hydrogenolysis of **19** by hydrogen gas with Pd–C as catalyst had also been attempted but unexpectedly, **20** could not be obtained from the reaction. Treatment of phenol **23** with **24** in DMF in the presence of potassium carbonate afforded compound **25** in 42% yield (Scheme 4).



Scheme 3.



23 **24** **25**

Scheme 4.

Quantitative ^{1}H NMR binding studies of **Zn1** with **19** were first performed by diluting a 1:1 solution of **Zn1** and **19** in chloroform-d. Small but significant downfield shifts in the ^{1}H NMR signals were observed for H-1, H-2, and H-3 of compound **19** with the decrease in the concentration and the plot of the $\Delta\delta$ data of H-1 (H-2) vs [**19**] (=[**Zn1**]) is shown in Figure 2.[19] A fit of the chemical shift data to a 1:1 binding isotherm gave a K_a of 48(±5) M^{-1}.[20] By using the same method, the binding constant for the complex of **1** with **19** was also determined to be 45(±6) M^{-1} (based on the data of the NDI protons, Fig. 2).

Potentially, the *iso*-phthalic acid diester moiety in **19** might also form π–π stacking with the bis(*p*-phenylene)-34-crown-10 unit or porphyrin unit of **1** or **Zn1** within the weak complexes **1/19** and **Zn1/19**. Such stacking might also contribute to the binding stability of these two complexes. To evaluate if it is the case, compound **30**, in which the two

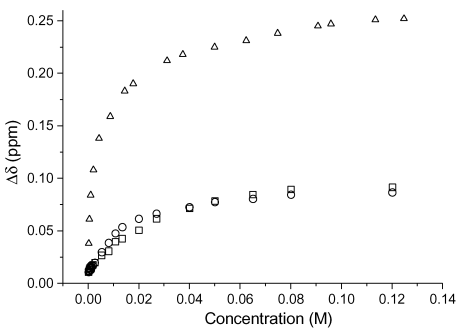
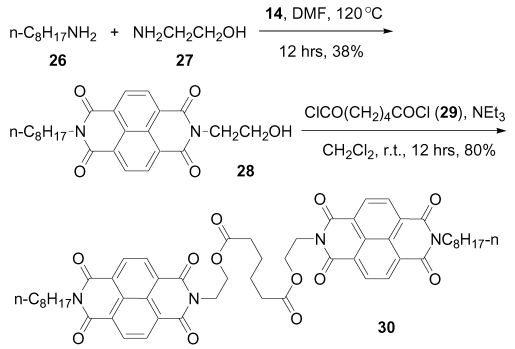


Figure 2. Plot of $\Delta\delta$ of the H-1 signal of **19** vs [**1**] (=[**19**]) (□) or [**Zn1**] (=[**19**]) (○) in the 1:1 solution of **19** and **1** or **Zn1** in chloroform-d, and plot of $\Delta\delta$ of the H-1 signal of **35**·4PF_6 vs [**Zn1**] (=[**35**·4PF_6] (△) in the 1:1 solution of **35**·4PF_6 and **Zn1** in acetone-d_6 in the ^{1}H NMR dilution study.



Scheme 5.

NDI moieties are connected with an aliphatic chain of comparative length, was synthesized as outlined in Scheme 5. A ^{1}H NMR dilution study of the 1:1 mixtures of **Zn1** and **30** in chloroform-d gave a binding constant of 46(±5) M^{-1} for the complex **Zn1/30**, by fitting a 1:1 binding model. Within experimental error for the ^{1}H NMR measurements, this value is comparable to those of the complexes **1/19** and **Zn1/19**, suggesting that no pronounced π−π stacking exists between the *iso*-phthalic acid diester moiety in **19** and the porphyrin unit of **1** or **Zn1** within the complexes.

Theoretically, both the bis(*p*-phenylene)-34-crown-10 moiety and the porphyrin moiety in **1** or **Zn1** could complex the NDI unit of **19** when mixing them together. In order to evaluate the relative contribution of these two possible binding patterns, the binding studies of compounds **7** and **10** toward **13** in chloroform-d were also carried out by ^{1}H NMR titration of 15 mM solutions of **13** with **7** (0.25–150 mM) or **10** (0.50–130 mM), which afforded a K_a of ca. 10 M^{-1} for **7**·**13** and 20 M^{-1} for **10**·**13**, respectively. These results suggest that the electron deficient NDI units might interact with both the porphyrin and bis(*p*-phenylene)-34-crown-10 units, forming an equilibrium of two different binding patterns in **1**·**19** and **Zn1**·**19**,[21] which is similar to that of **Zn1**·**35**·4PF_6 shown in Figure 5 (vide infra). Decreasing the temperature of the 1:1 solution of **1** and **19** (0.03 M) in chloroform-d to −50°C did not induce splitting of the NDI-H signal of **19** in their ^{1}H NMR spectra, indicating that the exchanging process between the different binding patterns is rapid on the ^{1}H NMR time scale even at low temperature.**3**. By comparing this result with those of the above two-site binding complexes **1**·**19**, **Zn1**·**19**, and **Zn1**·**30**, it can be said that no cooperative effect exists within the two-site binding complexes.

Addition of 1 equiv. of **Zn1** to the solution of **22** (0.05 M) in chloroform-d caused the ^{1}H NMR chemical shifts of many signals of both compounds to change substantially, suggesting the formation of a tri-site binding pattern as depicted in Figure 3. The changes of the important chemical shifts of both compounds in the complex are also listed in Figure 3. The signals of the pyridine α- and β-protons of **22** moved upfield 6.60 and 2.52 ppm, respectively, indicating that they were completely engulfed in the shielding region of the ring current of the porphyrin π-systems.[8c,22] These shifts are also diagnostic of the formation of **Zn1**·**22** through a coordination interaction and two donor–acceptor interactions between the two compounds. The 1:1 binding

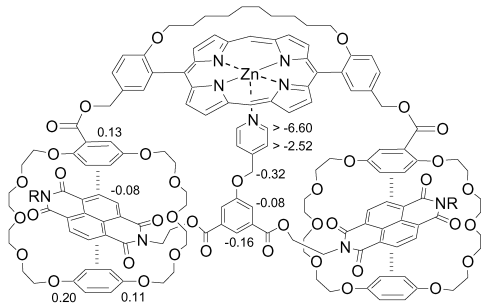


Figure 3. Tri-site binding module of complex **Zn1**·22 and the important ^{1}H NMR shift changes compared with those of the pure compounds **Zn1** and **22** in chloroform-d.

stoichiometry of the complex was deduced from the Job's plot of the DNI proton signals vs the mole fraction of **22**, in which the maximum signal change was observed at 0.5 mol fraction.[23] However, quantitative binding study could not be performed by ^{1}H NMR method as a result of reduced resolution of the spectra of the diluted solutions. Theoretically, the two unsymmetrical bis(*p*-phenylene)-34-crown-10 units of **Zn1** might generate two intermolecular donor–acceptor binding patterns (*cis*–*cis* or *cis*–*trans*), depending on the relative location of the ester linker in the complex. The ^{1}H NMR spectrum even at lower temperature of −50°C did not display further splitting for the NDI proton signals, implying quick exchange process always exists between the two patterns on the ^{1}H NMR time scale. NOE experiment in chloroform-d was also performed for complex **Zn1**·**22**, which unfortunately did not reveal intermolecular interactions.

Figure 4 shows the influence of added **22** on the absorption spectral change of **Zn1** in chloroform at room temperature. The λ_{max} for the Soret band (428 nm) of the porphyrin unit in **Zn1** shifts a little to longer wavelength (430 nm) and the absorbance reduced remarkably with the addition of **22**. A tight isosbestic point (404 nm) was also displayed. These results also support the view that the pyridine unit in **22** is coordinated to Zn(II) in **Zn1**. A binding constant of 6.5(±0.7)×10^5 M^{-1} was obtained from a plot of ΔA_{430} vs [**22**] (inserted in Fig. 4) for the 1:1 complex **Zn1**·**22**. Under the similar measurement conditions, the binding constant of complex **Zn1**·**25** in chloroform was determined to be 1.5(±0.12)×10^3 M^{-1}.

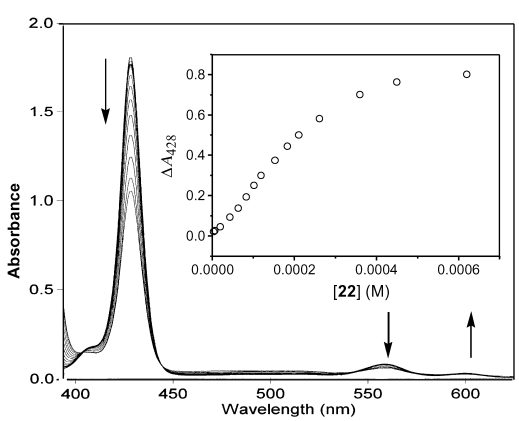
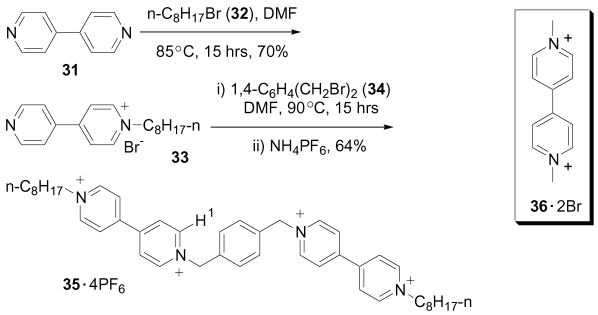


Figure 4. Absorption spectral change in **Zn1** (4.1×10^{-6} M) vs [**22**] in chloroform at 25°C. Insert: ΔA_{428} vs [**22**] plot.



Scheme 6.

Comparison of the stabilities of **Zn1**·**30** (46 M^{-1}, $\Delta G=-2.3$ kcal/mol) and **Zn1**·**25** (1.8×10^3 M^{-1}, $\Delta G=-4.4$ kcal/mol) with that of **Zn1**·**22** (6.5×10^5 M^{-1}, −7.9 kcal/mol) indicates that the increase in the stability of complex **Zn1**·**22** is not just a result of the additive effect from the peripheral donor–acceptor interactions between the bis(*p*-phenylene)-34-crown-10 units of **Zn1** and the NDI units of **22**. Instead, these data show that the binding between the two compounds is a substantially cooperative, entropically favorable process.[24]

Viologens are typical electron deficient compounds, which have been widely applied in molecular recognitions and self-assembly.[25] Therefore a viologen derivative **35**·$4PF_6$ was also designed as guest for receptor **Zn1**. The synthesis of compound **35**·$4PF_6$ from dipyridine **31** is outlined in Scheme 6. It was found that adding 1 equiv. of **Zn1** to the solution of **35**·$4PF_6$ in acetone-d_6 led to remarkable upfield movements of the chemical shifts of the pyridine proton signals ($\Delta\delta$ 0.27, 0.29 ppm for α-H's, and 0.39, 0.37 ppm for β-H's, respectively), indicating significant interaction between the two compounds. The phenylene proton signal did not exhibit obvious chemical shift change, implying that there is no substantial intermolecular interaction imposed on this unit or significant shielding effect from **Zn1**. It was also found that the signals of the pyrrole protons of the porphyrin protons shifted downfield substantially (0.22 and 0.15 ppm). A Job's plot analysis of the ^{1}H NMR spectra revealed a 1:1 binding stoichiometry. Considering that the linker between the two viologen units of **35**·$4PF_6$ is quite rigid, it is reasonable to exclude the binding pattern where one **35**·$4PF_6$ adopts an U-type conformation to bind only one bis(*p*-phenylene)-34-crown-10 moiety. Therefore, the above results suggest that two discrete donor–acceptor interaction patterns might exist for complex **Zn1**·**35**·$4PF_6$, as shown in Figure 5. A ^{1}H NMR dilution study of the 1:1 mixtures of **Zn1** and **35**·$4PF_6$ (from 0.13 M to 1.0 mM) in acetone-d_6 was then performed and the corresponding results are presented in Figure 2, which afforded a K_a of 475(±50) M^{-1} for **Zn1**·**35**·$4PF_6$. By using the same method, a binding constant of 430(±45) M^{-1} for **1**·**35**·$4PF_6$ was determined. Reducing the temperature of the solution of **Zn1**·**35**·$4PF_6$ to −40°C caused the ^{1}H NMR signals to shift pronouncedly, however, no further splitting was observed for the aromatic proton signals of **35**·$4PF_6$, indicating that a fast exchange also exists between the two binding patterns shown in Figure 5 on the ^{1}H NMR time scale. In order to check if there exists a cooperative effect of the two binding sites within these two complexes, the stability of the 1:1 complexes of **7**·**36**·2Br and **10**·**36**·2Br in acetone-d_6 were

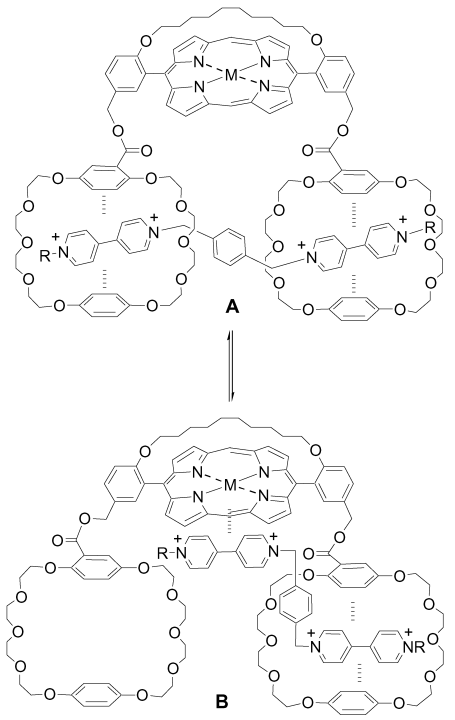


Figure 5. Two possible binding patterns for complexes **Zn1**·**35**·$4PF_6$ and **1**·**35**·$4PF_6$.

also investigated by ^{1}H NMR titration method, which afforded a binding constant of ca. 75 M^{-1} for **7**·**36**·2Br and 150 M^{-1} for **10**·**36**·2Br, respectively.[26] Therefore, it can be said that no cooperative effect exists in the two-site binding complexes **1**·**35**·$4PF_6$ and **Zn1**·**35**·$4PF_6$.

3. Conclusion

In conclusion, we have developed a new efficient approach to strapped porphyrin diol **7** and the synthesis of a new generation of three dimensional porphyrin receptors **Zn1** and **1** with three binding sites by incorporating two electron-rich cyclophane to the strapped porphyrin diol. The new porphyrin receptors display strong binding ability toward a structurally matched guest consisting of one pyridine unit and two naphthalene-1,8,4,5-tetracarboxydiimide units, as a result of cooperative effect of intermolecular metal–ligand coordination and donor–acceptor interactions. The work represents the first step to develop novel strapped multi-site porphyrin receptors. Further work will focus on modification of compound **7** with other functional groups to generate new, highly selective porphyrin receptors and on development of new rigid strapped porphyrin blocks for self-assembly of new supramolecular systems.

4. Experimental

4.1. General

Melting points are uncorrected. All reactions were performed under an atmosphere of dry nitrogen. The ^{1}H NMR spectra were recorded on 600, 400, or 300 MHz spectrometers in the indicated solvents. Chemical shifts are

expressed in parts per million (δ) using residual solvent protons as internal standards. Chloroform (δ 7.26 ppm) was used as an internal standard for chloroform-d. Elemental analysis was carried out at the SIOC Analytical Center. Unless otherwise indicated, all starting materials were obtained from commercial suppliers and were used without further purification. All solvents were dried before use following standard procedures. Compound **13** was prepared according to a reported procedure.[14c]

4.1.1. Compound 3.[27] To a stirred solution of compounds **2** (15.0 g, 0.10 mol) and *n*-octyl bromide (19.2 g, 0.10 mol) in DMF (300 mL) was added potassium carbonate (27.6 g, 0.20 mol) at room temperature. The mixture was then stirred at 70°C for 12 h. The solvent was removed under reduced pressure and the residue was triturated with dichloromethane (500 mL). The organic phase was washed with water (100 mL×3), brine (100 mL), and dried over sodium sulfate. After the solvent was removed with an evaporator under reduced pressure, the resulting residue was subjected to column chromatography (CH_2Cl_2/EtAc 10:1), to give 22.0 g of compound **3** (84%) as an oily solid. ^{1}H NMR ($CDCl_3$): δ 0.86 (t, J=6.6 Hz, 3H), 1.28–1.46 (m, 10H), 1.73–1.84 (m, 2H), 4.35 (t, J=6.7 Hz, 2H), 7.95 (d, J=8.2 Hz, 2H), 8.19 (d, J=8.2 Hz, 2H), 10.10 (s, 1H). MS (EI): m/z 262 $[M]^+$.

4.1.2. Compound 4. A solution of compound **3** (8.70 g, 33.2 mmol) and pyrrole (23 mL, 0.33 mol) in toluene (250 mL) was degassed by a stream of nitrogen for 30 min. To the degassed solution was added hot (ca. 100°C) toluene (1 mL) previously saturated with *p*-toluenesulfonic acid. The solution was heated under reflux for 1.5 h and cooled to room temperature. The solution was washed with aqueous K_2CO_3 (2N, 40 mL), water (40 mL×2), and dried over sodium sulfate. Evaporation of solvent gave a brown oil, which was subjected to flash chromatography ($CHCl_3$) and further purified by recrystallization (chloroform/hexane), to give 8.11 g of pure product **4** in 65% yield as a white solid. Mp 84–85°C. ^{1}H NMR ($CDCl_3$): δ 0.89 (t, J=6.7 Hz, 3H), 1.27–1.44 (m, 10H), 1.71–1.78 (m, 2H), 4.30 (t, J=6.6 Hz, 2H), 5.53 (s, 1H), 5.90 (s, 2H), 6.15–6.18 (m, 2H), 6.70–6.73 (m, 2H), 7.24–7.30 (m, 2H), 7.97 (s, 2H), 8.00 (s, 2H). MS (EI): m/z 378 $[M]^+$. Anal. calcd for $C_{24}H_{30}N_2O_2$: C 76.16, H 7.99, N 7.40. Found: C 76.25, H 7.99, N 7.29.

4.1.3. Compound 6. To a stirred mixture of compound **5**[28] (16.1 g, 0.11 mol) and K_2CO_3 (22.8 g, 0.17 mol) in DMF (150 mL) was added 1,10-dibromodecane (15.0 g, 50.0 mmol). The mixture was stirred at 70°C for 12 h and then the solid was filtered off. The solvent was removed under reduced pressure and the resulting residue was triturated with ethyl acetate (500 mL). The organic solution was washed with aqueous potassium hydroxide solution (0.5N, 100 mL×3), water (100 mL×2), brine (100 mL), and dried over sodium sulfate. After the solvent was removed, the residue was recrystallized from dichloromethane/*n*-hexane (1:2) to give compound **6** as a white solid (16.0 g, 72%). Mp 79–80°C. ^{1}H NMR ($CDCl_3$): δ 1.36–1.51 (m, 12H), 1.80–1.91 (m, 4H), 2.18 (s, 2H), 4.10 (t, J=6.5 Hz, 4H), 4.66 (s, 4H), 7.00 (d, J=8.7 Hz, 2H), 7.59 (d, d, J=8.7, 2.1 Hz, 2H), 7.80 (d, J=2.1 Hz, 2H), 10.50 (s, 2H). MS (EI): m/z 424 $[M-OH]^+$. Anal. calcd for $C_{26}H_{34}O_6 \cdot 0.5H_2O$: C 69.16, H 7.81. Found: C 69.10, H 7.73.

4.1.4. Compound 7. A stirred solution of compounds **4** (3.98 g, 10.5 mmol) and **6** (2.33 g, 5.30 mmol) in acetonitrile (700 mL) was degassed with nitrogen for 30 min at room temperature. Then, trifluoroacetic acid (0.20 mL) was added in one portion. The solution was shielded from light and stirred at room temperature for 5 h, after which a solution of 2,3-dichloro-4,5-dicyanoquinone (DDQ) (2.63 g, 10.5 mmol) in THF (100 mL) was added and the mixture was stirred at room temperature for another 2 h. The solvent was evaporated and the residue purified by column chromatography (CH_2Cl_2/MeOH, 40:1). Compound **7** was obtained as a purple solid (0.43 g, 7%). Mp 102–102.5°C. ^{1}H NMR ($CDCl_3$): δ −2.70 (s, 2H), −1.30 (br, s, 4H), −1.03 (m, 4H), −0.03 (m, 4H), 0.63 (br, 4H), 0.878 (m, 6H), 1.16–1.44 (m, 18H), 1.56 (m, 4H), 1.88 (m, 4H), 3.67 (t, J=5.1 Hz, 4H), 4.47 (t, J=6.6 Hz, 4H), 4.94 (s, 4H), 7.20–7.73 (m, 4H), 7.76 (d-d, J=8.1, 2.1 Hz, 2H), 8.15 (d, J=8.1 Hz, 2H), 8.28 (d, J=2.0 Hz, 2H), 8.37–8.48 (m, 4H), 8.75 (d, J=5.2 Hz, 4H), 8.82 (d, J=5.2 Hz, 4H). MS (ESI): m/z 1159 $[M+H]^+$. Anal. calcd for $C_{74}H_{84}N_4O_8$: C 76.79, H 7.31, N 4.84. Found: C 76.72, H 7.26, N 4.71.

4.1.5. Compound 10. To a stirred solution of ditosylate **8**[29] (3.50 g, 4.50 mmol) and ester **9** (0.76 g, 4.50 mmol) in acetonitrile (120 mL) was added potassium carbonate (6.20 g, 0.45 mol) and the mixture was stirred under reflux for 3 days. After the mixture was cooled to room temperature, the solid was filtered off and the solvent was evaporated. The residue was triturated with acetate (200 mL) and the solution was washed with water (40 mL×2), brine (40 mL), and dried over sodium sulfate. After the solvent was removed under reduced pressure, the crude material was subjected to column chromatography (EtOAc/MeOH 60:1). Compound **10** (1.22 g) was obtained in 45% yield as a pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 3.65–3.74 (14H, m), 3.78–3.86 (10 H, m), 3.94–4.05 (8H, m), 6.73 (4H, s), 6.79 (1H, J=6.0 Hz, d), 6.81–6.94 (1H, m), 7.28 (1H, J=6.0 Hz, d). MS (EI): m/z 594 $[M]^+$. Anal. calcd for $C_{30}H_{42}O_{12}$: C, 60.59; H, 7.12. Found: C, 60.51; H, 7.12.

4.1.6. Compound 11. A solution of sodium hydroxide (40.0 mg, 1.00 mmol) in water (15 mL) was added to a solution of compound **10** (0.51 g, 0.86 mmol) in methanol (25 mL) and the resulting solution was stirred under reflux for 2 h. Upon cooling to room temperature, the reaction mixture was concentrated to a volume of 15 mL which was then adjusted to pH 4 by slow addition of 1N hydrochloric acid. The aqueous solution was extracted with $CHCl_3$ (50 mL×3) and the combined organic phase was washed with water (30 mL×2), brine (30 mL), and dried over sodium sulfate. After the solvent was removed in vacuo, the residue was purified by flash chromatography (dichloromethane/methanol 10:1), to afford compound **11** (0.50 g) in 100% yield as a pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 3.60–3.79 (14H, m), 3.84–4.03 (18H, m), 6.78 (4H, s), 6.80 (1H, J=6.5 Hz, d), 6.84–6.97 (1H, m), 7.28–7.29 (1H, J=6.6 Hz, d). MS (EI): m/z 580 $[M]^+$. Anal. calcd for $C_{29}H_{40}O_{12}$: C, 59.99; H, 6.94. Found: 60.31; H, 7.10.

4.1.7. Compounds 1 and Zn1. A solution of acid **11** (0.15 g, 0.26 mmol) in oxalyl chloride (5 mL) was stirred under reflux for 2 h and the unreacted oxalyl chloride was removed in vacuo. The resulting residue, acyl chloride **12**, was then dissolved in dichloromethane (10 mL) and used directly for the next step without further purification. To a stirred solution of compound **7** (99.0 mg, 0.086 mmol) and Et_3N (0.3 mL) in dichloromethane (10 mL) at 0°C was added the above dichloromethane solution of **12** within 5 min. The solution was stirred overnight at room temperature and then washed with hydrochloride (1N) solution (5 mL), sodium carbonate solution (1N, 5 mL), water (5 mL×2), brine (5 mL), and dried over sodium sulfate. The solution was concentrated and the resulting residue was purified by column chromatography (CH_2Cl_2/MeOH 30:1), to give compound **1** (143 mg) in 73% yield as a purple solid. Mp 62–63°C. ^{1}H NMR ($CDCl_3$) δ −2.68 (s, 2H), −1.24 (br, 4H), −0.83 (br, 4H), −0.56 (br, 4H), 0.65–0.70 (m, 4H), 0.91 (t, *J*=6.5 Hz, 6H), 1.15–1.60 (m, 20H), 1.92 (p, *J*=7.5 Hz, 4H), 3.291 (s, br, 8H), 3.36–3.39 (m, 4H), 3.461–3.490 (m, 4H), 3.60–3.73 (m, 36H), 3.81–3.88 (m, 8H), 3.93–3.99 (m, 8H), 4.50 (t, *J*=6.8 Hz, 4H), 5.60 (s, 4H), 6.67 (s, 8H), 6.78 (d, *J*=8.9 Hz, 2H), 6.89 (d, d, *J*=8.9, 3.3 Hz, 2H), 7.26 (d, *J*=8.6 Hz, 2H), 7.42 (d, *J*=3.3 Hz, 2H), 7.84 (d, d, *J*=8.6, 2.1 Hz, 2H), 8.17 (d, *J*=7.4 Hz, 2H), 8.39–8.42 (m, 6H), 8.47 (d, *J*=7.4 Hz, 2H), 8.76 (d, *J*=4.7 Hz, 4H), 8.85 (d, *J*=4.7 Hz, 4H). MS (ESI): *m/z* 2283 $[M+H]^+$. Anal. calcd for $C_{132}H_{160}N_4O_{30}$: C 69.45, H 7.06, N 2.45. Found: C 69.52, H 7.32, N 2.17. Porphyrin **1** was dissolved in CH_2Cl_2/CH_3OH (3:1) and zinc acetate (10.0 equiv.) was added. The reaction mixture was stirred under reflux for 3 h. The solvent was removed in vacuo, and the crude product was subjected to flash chromatography (dichloromethane/methanol 20:1), to afford **Zn1** in 100% yield. Mp 63–64°C. ^{1}H NMR ($CDCl_3$) δ: −1.54 (br, 4H), −1.02 (t, *J*=7.73 Hz, 4H), −0.77 (br, 4H), 0.62 (br, 4H), 0.91 (t, *J*=6.8 Hz, 6H), 1.05–1.62 (m, 20H), 1.91 (q, *J*=7.2 Hz, 4H), 2.87–3.85 (m, 68H), 4.49 (t, *J*=6.6 Hz, 4H), 5.67 (s, 4H), 6.17 (d, *J*=8.7 Hz, 4H), 6.35 (d, *J*=8.7 Hz, 4H), 6.51 (d, *J*=9.0 Hz, 2H), 6.77 (d, d, *J*=3.3, 9.0 Hz, 2H), 7.26–7.35 (m, 4H), 7.76 (d, d, *J*=8.4, 2.1 Hz, 2H), 7.97 (d, *J*=8.6 Hz, 2H), 8.30 (d, *J*=8.7 Hz, 4H), 8.39 (d, *J*=8.7 Hz, 4H), 8.76 (d, *J*=4.7 Hz, 4H), 8.85 (d, *J*=4.7 Hz, 4H). MS (ESI): *m/z* 2347 $[M+H]^+$.

4.1.8. Compound 17. A mixture of dianhydride **14** (5.36 g, 20.0 mmol), amine **15** (3.26 g, 20.0 mmol), and ethanolamine **16** (1.20 mL. 20.0 mmol) in DMF (150 mL) was stirred overnight at 120°C. The mixture was cooled to room temperature and the solid filtered off. The filtrate was concentrated in vacuo and the resulting residue was triturated with 300 mL of dichloromethane. The organic phase was washed with water (2×50 mL), brine (50 mL), and dried over Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (CH_2Cl_2/MeOH 30:1), to give 3.49 g of compound **17** as a pale yellow solid in 38% yield. Mp 144–144.5°C. ^{1}H NMR ($CDCl_3$): δ 2.16 (br, 1H), 3.32 (s, 3H), 3.47 (t, *J*=4.8 Hz, 2H), 3.57–3.64 (m, 4H), 3.72 (t, *J*=4.8 Hz, 4H), 3.86 (t, *J*=5.7 Hz, 2H), 4.01 (br, 2H), 4.45–4.50 (m, 4H), 8.76 (s, 4H). MS (EI): *m/z* 456 $[M]^+$. Anal. calcd for $C_{23}H_{24}N_2O_8$: C 60.52, H 5.29, N 5.93. Found: C 60.41, H 5.31, N 5.98.

4.1.9. Compound 19. To a stirred solution of compound **17** (1.30 g, 2.60 mmol) and triethylamine (0.30 mL, 2.90 mmol) in dichloromethane (100 mL) was added a solution of compound **18**[30] (0.33 g, 1.13 mmol) in dichloromethane (10 mL) at room temperature. The mixture was then stirred overnight and washed with water (30 mL×3), brine (30 mL), and dried over sodium sulfate. After the solvent was evaporated, the residue was purified by column chromatography (CH_2Cl_2/EtOAc/MeOH 25:5:1), to give compound **19** as a pale orange solid (0.94 g, 72%). Mp 196–197°C. ^{1}H NMR ($CDCl_3$) δ: 3.31 (s, 6H), 3.46 (t, *J*=4.65 Hz, 4H), 3.56–3.63 (m, 8H), 3.71 (t, 4.5 Hz, 4H), 3.84 (t, *J*=5.8 Hz, 4H), 4.45 (t, *J*=5.8 Hz, 4H), 4.65 (br, 8H), 5.06 (s, 2H), 7.41 (br, 5H), 7.73 (s, 2H), 8.12 (s, 1H), 8.71 (d, *J*=7.8 Hz, 4H), 8.75 (d, *J*=7.8 Hz, 4H). MS (ESI): *m/z* 1149 $[M+H]^+$. Anal. calcd for $C_{61}H_{56}N_4O_{19}$: C 63.76, H 4.91, N 4.88. Found: C 63.55, H 4.77, N 4.81.

4.1.10. Compound 22. A solution of compound **19** (0.35 g, 0.30 mmol) in trifluoroacetic acid (10 mL) was refluxed for 1 h. After which time TLC indicated that **19** had been consumed completely. The solvent was removed under reduced pressure to give crude product **20** which was used directly for the next step without further purification. To a stirred solution of the above compound **20**, triphenylphosphine (0.21 g, 0.81 mmol), and 4-pyridylcarbinol **21** (0.11 g, 1.00 mmol) in dichloromethane (60 mL) at room temperature was added dropwise a solution of DEAD (0.36 g, 40% in toluene) in dichloromethane (10 mL). The mixture was stirred at room temperature for 12 h. The solution was washed with 0.5N potassium carbonate solution (10 mL×2), water (10 mL×2), brine (10 mL), dried over sodium sulfate. The solvent was then evaporated and the resulting residue was purified by column chromatography (dichloromethane/methanol 20:1), to afford compound **22** as a pale orange solid (189 mg, 62%). Mp 196–197°C. ^{1}H NMR ($CDCl_3$) δ: 3.31 (s, 6H), 3.45–3.48 (m, 4H), 3.56–3.63 (m, 8H), 3.69–3.72 (m, 4H), 3.84 (t, *J*=5.8 Hz, 4H), 4.45 (t, *J*=5.8 Hz, 4H), 4.65 (s, 8H), 5.13 (s, 2H), 7.36 (d, *J*=5.1 Hz, 2H), 7.74 (s, 1H), 8.13 (s, 1H), 8.64 (br, 2H), 8.74 (s, 8H). MS (ESI): *m/z* 1150 $[M+H]^+$. Anal. calcd for $C_{60}H_{55}N_5O_{19}$·MeOH: C 61.99, H 5.03, N 5.92. Found: C 62.07, H 5.15, N 5.68.

4.1.11. Compound 25. A stirred mixture of compound **23**[31] (1.90 g, 10.0 mmol) and K_2CO_3 (4.30 g, 31.0 mmol) in DMF (50 mL) was heated to 100°C. Then, a solution of the hydrochloride salt of compound **24** (0.82 g, 5.00 mmol) in DMF (10 mL) was added dropwise. The mixture was stirred at 100°C for 4 h and then cooled to room temperature. Water (200 mL) was added and the resulting precipitate was filtered, washed with water completely, dried, and purified by column chromatography (ethyl acetate/petroleum ether 10:1), to give compound **25** as a white solid (0.63 g, 42%). Mp 101.5–102°C. ^{1}H NMR ($CDCl_3$) δ: 3.95 (s, 6H), 5.18 (s, 2H), 7.38 (d, t, *J*=5.1, 1.0 Hz, 2H), 7.83 (d, *J*=1.0 Hz, 2H), 8.33 (t, *J*=1.8 Hz, 1H), 8.65 (d, d, *J*=5.1, 1.8 Hz, 2H). MS (EI): *m/z* 301 $[M]^+$. Anal. calcd for $C_{16}H_{15}NO_5$: C, 63.78; H, 5.02; N, 4.65. Found: C, 63.49; H, 4.71; N, 4.49.

4.1.12. Compound 28. A mixture of dianhydride **14** (10.72 g, 40.0 mmol), *n*-octylamine **26** (5.15 g, 40.0 mmol), and ethanolamine **27** (2.40 mL, 40.0 mmol)

in DMF (250 mL) was stirred at 120°C for 12 h. The mixture was cooled to room temperature and the precipitate was filtered. The filtrate was concentrated in vacuo and the residue was triturated with chloroform (300 mL). The organic phase was washed with water (50 mL×3), brine (50 mL), and dried over sodium sulfate. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (CH_2Cl_2/MeOH 30:1), to afford compound **28** as a pale orange solid (3.49 g, 29%). Mp 154–156°C. ^{1}H NMR ($CDCl_3$) δ: 0.90 (t, 3H), 1.24–1.52 (m, 10H), 1.78 (t, J=5.0 Hz, 2H), 4.04 (t, J=5.0 Hz, 2H), 4.22 (t, J=5.5 Hz, 2H), 4.51 (t, J=5.5 Hz, 2H), 8.79 (s, 4H). MS (EI): m/z 422 $[M]^+$. Anal. calcd for $C_{24}H_{26}N_2O_5$: C 68.23, H 6.20, N 6.63. Found: C 67.90, H 6.35, N 6.34.

4.1.13. Compound 30. A solution of diacyl chloride **29** (87.0 mg, 0.50 mmol) in dichloromethane (10 mL) was added to a stirred solution of compound **28** (0.42 g, 1.00 mmol) and triethylamine (0.15 mL, 1.45 mmol) in dichloromethane (50 mL) at room temperature. Upon stirring overnight, the solution was washed with water (15 mL×3), brine (15 mL), and dried over sodium sulfate. After the solvent was evaporated, the residue was purified by column chromatography (CH_2Cl_2/MeOH 25:1), to give compound **30** as a pale orange solid (0.34 g, 70%). Mp 178–180°C. ^{1}H NMR ($CDCl_3$) δ: 0.89 (t, 6H), 1.18–1.54 (m, 24H), 1.62–1.80 (m, 4H), 2.21 (t, 4.5 Hz, 4H), 4.18 (t, J=4.5 Hz, 4H), 4.45–4.51 (m, 8H), 8.75 (s, 8H). MS (MALDI): m/z 955 $[M+H]^+$. Anal. calcd for $C_{54}H_{58}N_4O_{12}$: C 67.91, H 6.12, N 5.87. Found: C 68.14, H 6.50, N 5.64.

4.1.14. Compound 33. A solution of 4,4′-bipyridyl **31** (4.70 g, 30.0 mmol) and *n*-octyl bromide **32** (2.90 g, 15.0 mmol) in DMF (30 mL) was stirred at 85°C for 15 h and then cooled to room temperature. Ether (100 mL) was added to generate a whtie precipitate, which was collected by filtration, washed with ether thoroughly, and purified by column chromatography (chloroform/methanol 10:1), to give compound **33** as a white solid (3.65 g, 70%). Mp>189°C [no datum available in lit.[32]] ^{1}H NMR ($CDCl_3$): δ 0.85 (t, J=6.8 Hz, 3H), 1.21–1.37 (m, 10H), 2.08 (q, J=7.4 Hz, 2H), 5.02 (t, J=7.4 Hz, 2H), 7.74 (d, d, J=1.5, 4.8 Hz, 2H), 8.45 (d, J=7.2 Hz, 2H), 8.87 (d, J=4.8 Hz, 2H), 9.66 (d, J=7.2 Hz, 2H). MS (ESI): m/z 269 $[M-Br]^+$.

4.1.15. Compound 35. A mixture of **33** (0.44 g, 1.25 mmol) and α,α′-dibromo-*p*-xylene **34** (0.17 g, 0.63 mmol) in DMF (8 mL) was stirred at 90°C for 15 h and then cooled to room temperature. Ether (30 mL) was added and white precipitate was generated. The precipitate was filtered, washed with ether completely, and purified by column chromatography (MeOH/2M NH_4Cl/CH_3NO_2 7:2:1). The crude product was dissolved in hot water (5 mL), and saturated aqueous NH_4PF_6 solution was added dropwise until no more precipitate was formed. The precipitate was filtered, washed with THF, and dried in vacuo, to give tetracationic compound **35** as a white solid (0.47 g, 62%). Mp 185°C (decom.). ^{1}H NMR (acetone-d_6): δ 0.84 (t, 6H), 1.27–1.50 (m, 20H), 2.08 (q, J=7.7 Hz, 4H), 4.95 (t, J=7.7 Hz, 4H), 6.22 (s, 4H), 7.81 (s, 4H), 8.82–8.74 (m, 8H), 9.43 (d, J=6.6 Hz, 4H), 9.47 (d, J=7.2 Hz, 4H). MS (ESI): m/z 1077 $[M-PF_6]^+$. Anal. calcd for $C_{24}H_{58}N_4P_4F_{24}$: C 43.22, N 4.58, H 4.78. Found: C 43.40, N, 4.47, H 4.97.

4.2. Binding studies

All ^{1}H NMR binding studies were carried out at 25°C. $CDCl_3$ used in binding studies was passed though a short column of dry, activated basic alumina prior to use. Acetone-d_6 were used as provided without further purification. Volumetric flasks and syringes used in preparing solutions were washed with dried CH_2Cl_2 and dried in vacuum before use. Samples (usually 0.6 mL) were prepared from stocks solutions, transferred to the NMR tubes and diluted accordingly with syringes. For one series, usually 13–20 samples were prepared and binding constants reported are the average of two or three experiments, which were obtained by fitting chemical shift change data to 1:1 binding isotherms with standard nonlinear curve-fitting procedures.[33] The nonlinear equations were derived from mass-balance equations and the relationship between the concentrations of free and complexed sample and the weighted chemical shifts under the condition of rapid exchange.[33] UV–Vis binding study was performed in a manner similar to that reported in the literature.[33]

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