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Selective recognition of sodium cyanide and potassium cyanide by diaza-crown ether-capped Zn-porphyrin receptors in polar solvents

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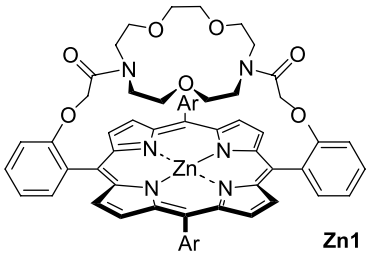
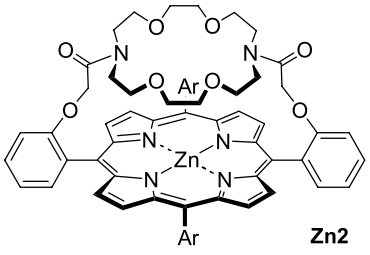
Abstract—Two new ditopic porphyrin receptors **Zn1**, incorporating a diaza-15-crown-5 unit, and **Zn2**, incorporating a diaza-18-crown-6 unit, have been prepared and characterized. UV–vis study in polar methanol has revealed that **Zn1** is able to selectively recognize sodium cyanide over potassium cyanide (the ratio of their binding constant is ca. 56), whereas **Zn2** exhibits a higher binding affinity for potassium cyanide over sodium cyanide (the ratio of their binding constant is ca. 12). In contrast, both receptors display substantially weaker binding affinity for sodium thiocyanate and potassium thiocyanate presumably due to a monotopic binding fashion.

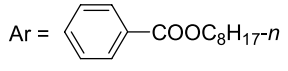
1. Introduction

Considerable attention has been focused upon the design of synthetic receptors for the detection of biologically and environmentally important small species.[1,2] A large number of receptors have been reported, which can bind simple inorganic cations or anions. However, the development of receptors for selective recognition of ion pairs in competitive solvents would be of more importance, because the physical, chemical, and biological properties of any ionic molecule are always controlled by both its cation and anion.[3]

Sodium cyanide and potassium cyanide are among the most concerned inorganic salts in the environment because of their high toxicity and wide applications in industries. Development of selective and sensitive receptors for both salts in polar solvent should be of special value, because efficient detection of these salts are potentially useful for monitoring their metabolism in nature,[4] the analysis of drinking water,[5] and environment protection.[6] Recently, several synthetic receptors for complexing cyanide anion in dichloromethane or aqueous media have been reported.[7] A Zn-porphyrin-crown ether conjugate for ion pair recognition of sodium cyanide in nonpolar organic solvent has also been developed.[8] Herein, we describe the selective complexation of NaCN and KCN in polar solvents by two novel aza-crown ether-capped porphyrins **Zn1** and **Zn2**. To the best of our knowledge, this represents the first example of synthetic receptors that are able to discriminate between NaCN and KCN in polar solvents.







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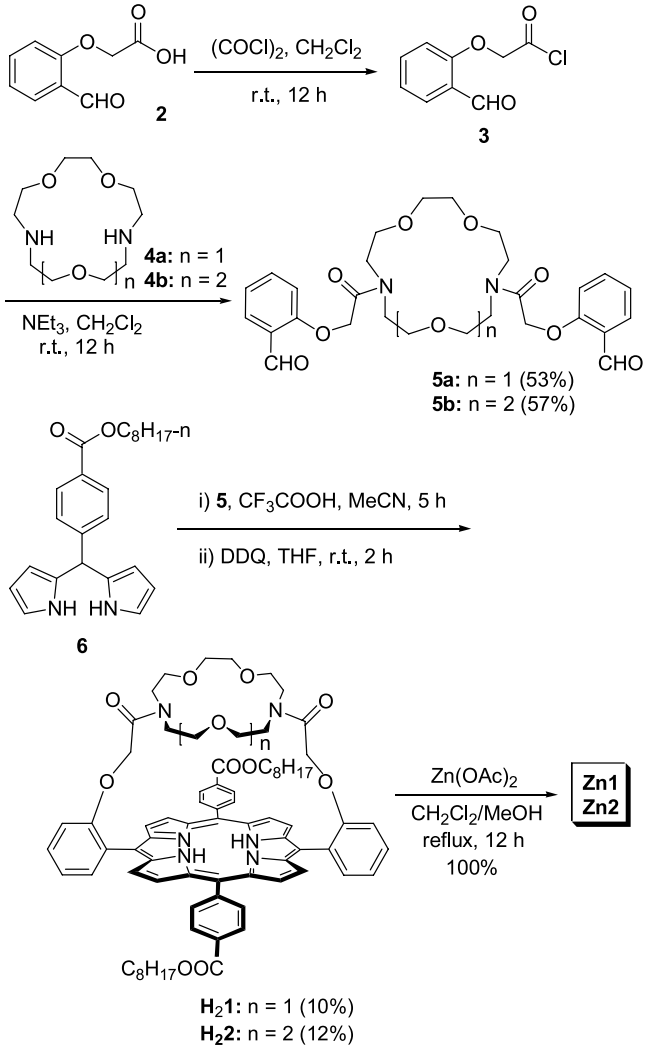
2. Results and discussion

The design of the new receptors are based on the ditopic feature of the well-established crown ether-capped porphyrins.[9] The crown ether moiety is typical binding units for alkaline metal ions, whereas the Zn-porphyrin moiety is well-known to coordinate nitrogen ligand. The synthesis of **Zn1** and **Zn2** is provided in Scheme 1. In brief, compounds **5a** and **5b** were first prepared from acyl chloride **3** and diaza-crown ether **4a** or **4b**, respectively, and then coupled with dipyrrole **6** with trifluoroacetic acid as catalyst, followed by oxidation by 2,3-dichloro-5,6-dicyano-1,4-quinone (DDQ), to afford $\mathbf{H_2 1}$ and $\mathbf{H_2 2}$. Treatment of $\mathbf{H_2 1}$ and $\mathbf{H_2 2}$ with zinc acetate in dichloromethane and methanol produced **Zn1** and **Zn2** in quantitative yield. Compounds **Zn1** and **Zn2** had been characterized by the ^{1}H NMR, ^{13}C NMR, mass spectroscopy, and elemental analysis.



Scheme 1.

The proximate location of the diaza-crown ether moiety to the porpyirin unit of both molecules is confirmed by the ^{1}H NMR spectrum in $CDCl_3$, which revealed substantial upfield shifts (up to 4.5 ppm) for the crown ether methylene signals. Molecular modeling revealed a distance of ca. 3.2 and 3.6 Å between the porphyrin moiety and the diazo-crown ether unit for **Zn1** and **Zn2**, respectively. The Soret bands of both compounds (at 403 and 424 nm) in chloroform (2.5 μM) were not split, indicating that the crown ether does not present significant perturbation.[10] The Soret bands maintained a constant shape and gave unchanged ε value (4.09×10^5 M^{-1} cm^{-1}) over the concentration range of 0.5–100 μM, ruling out any important intermolecular aggregation in this range.

When NaCN was added to the CD_3OD solution of **Zn1** (1.0 mM), the signals of the pyrrole protons shifted upfield pronouncedly (ca. −0.12 ppm with 10 equiv of NaCN) as a result of coordination between the cyanide ion and the central zinc of **Zn1**, whereas the crown ether ethylene proton signals shifted downfield (0.11 ppm) owing to the binding of cation Na^+ to the oxygen atoms of the aza-crown ether. These results indicate that NaCN is complexed by **Zn1** in a ditopic fashion (Fig. 1).[11,12] The addition of NaCN to the solution of **Zn1** (3.0 μM) in methanol also caused the solution color to change from purple to pale green (Fig. 2). In contrast, addition of potassium or sodium fluoride did not cause similar significant shifting. UV–vis study revealed a remarkable red shift (ca. 17 and 14 nm for the major Soret band and the Q band of the Zn-porphyrin. Moreover, the UV–vis absorption spectra recorded as a function of the NaCN) concentration displayed two clear isosbestic points at 434 and 565 nm, which also confirms a two-component equilibrium (Fig. 3).[11,12] By fitting the UV–vis titration data to a function containing K_{assoc} as a variable parameter,[13,14] the association constant K_{assoc} of complex **Zn1**·NaCN was determined to be approximately 7.4×10^5 M^{-1} (Table 1).

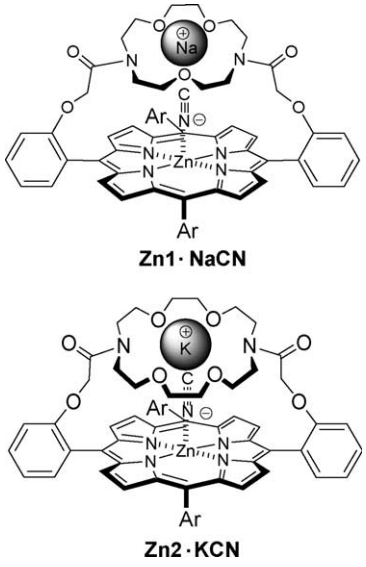


Figure 1. Proposed ditopic binding modes (another two aryl groups are not shown for clarity).

Adding KCN (10 equiv) to the solution of **Zn1** (1.0 mM) in CD_3OD caused the ^{1}H NMR signals of the pyrrole and diazo-crown ether protons to shift upfield (ca. 0.11 ppm) and downfield (0.06 ppm), respectively. Red shift was also observed for the Soret and Q bands (up to 15 and 13 nm) of the Zn-porphyrin moiety when adding KCN to the solution of **Zn1** in methanol. These results also indicate that a 1:1

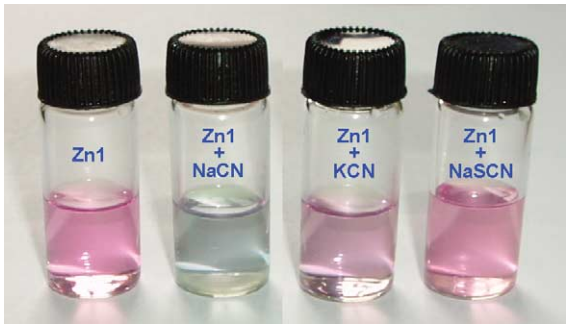


Figure 2. Color changes of the methanol solution of **Zn1** (3.0×10^{-6} M) after addition of inorganic salts (0.5 mM) at 25 °C.

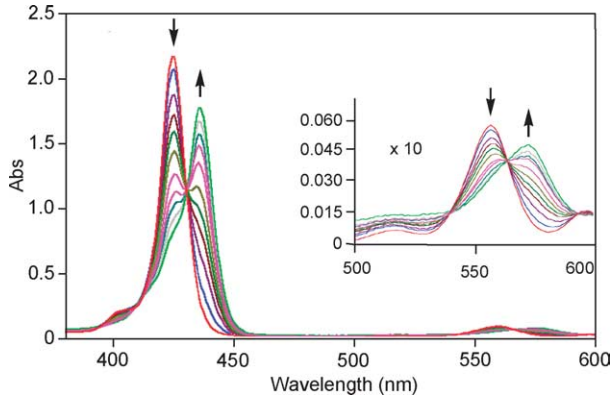


Figure 3. Absorption spectral changes of **Zn1** (5.5×10^{-6} M) in MeOH upon addition of NaCN (1.0×10^{-6}–1.0×10^{-3} M).

complex, that is, **Zn1**·KCN, was formed between the two compounds. From the UV–vis titration experiments, we determined the K_{assoc} of **Zn1**·KCN to be ca. 1.3×10^{4} M^{-1}. This value is significantly lower than that observed for NaCN, revealing a binding selectivity of **Zn1** for NaCN over KCN.

The binding behaviors of **Zn2** with both salts were then investigated. Addition of KCN to the solution of **Zn2** in CD_3OD led to significant upfield shifting of one of the crown ether signals (Fig. 4). The signals of the aromatic protons of **Zn2** also notably shifted upfield (albeit to a smaller extent) as a result of complexation. Similar changes were also observed for the system of **Zn2** and NaCN. The association constants of complexe between **Zn2** and NaCN and KCN in methanol were obtained also with the UV–vis

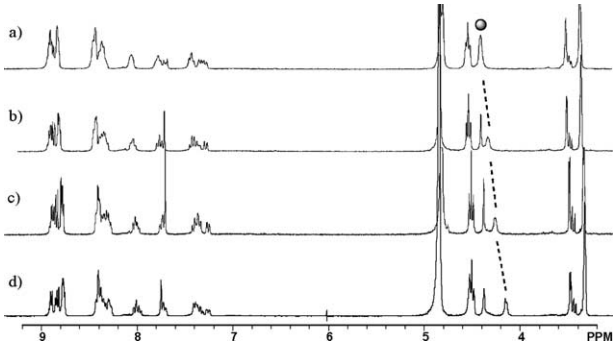


Figure 4. Partial ^{1}H NMR (500 MHz, [**Zn2**] = 1.0 mM) spectra of (a) **Zn2**, (b) **Zn2** + KCN (0.2 equiv), (c) **Zn2** + KCN (0.5 equiv), and (d) **Zn2** + KCN (5.0 equiv) in methanol-*d* at 23 °C.

titration method. The results are provided in Table 1. It can be found that the values of both **Zn2**·NaCN and **Zn2**·KCN are larger than that of the related complexes **Zn1**·NaCN and **Zn1**·KCN. However, different from receptor **Zn1**, which exhibited a binding selectivity for NaCN, receptor **Zn2** showed a remarkably higher binding affinity to KCN. It has been reported that the binding ability of diaza-15-crown-5 to both Na^+ and K^+ is lower than that of diaza-18-crown-6 in methanol.[15] If we assume that the diacylated diazo-15-crown-5 and diaza-18-crown-6 units in the present receptors possess a similar binding affinity, the above results imply that the steric effect, produced in **Zn1** by the reduced ring size of the diazacrown ether and consequently the shorter distance between the porphyrin and diazacrown ether units compared to **Zn2**, might play a crucial role for the selective recognition of **Zn1** to the smaller NaCN. The distance between the porphyrin and diazo-crown ether in **Zn1** is more suitable for the smaller NaCN, while the larger KCN suffers a greater steric hindrance. As expected, the complexing affinity of both **Zn1** and **Zn2** for both NaCN and KCN was remarkably decreased when water or DMSO of higher polarity was added to the solvent (Table 1). However, the complexing selectivity of **Zn1** for NaCN and **Zn2** for KCN did not change.

The binding ability of **Zn1** and **Zn2** to NaSCN and KSCN in methanol was also investigated. As shown in Table 1, all the 1:1 complexes between the receptors and the salts displayed comparable binding stability, which suggests a simple monotopic binding fashion between **Zn1** and **Zn2** and these larger salts. That is, the SCN^- anion bound the porphyrin zinc from the diaza-crown ether-free side, while the cation played a negligible role for the stability of the complexes.

Table 1. Association constants (M^{-1}) and the associated free energy change (kcal/mol) for the complexes between **Zn1** and **Zn2** and inorganic salts obtained from UV–vis titration experiments in methanol at 25 °C[a]

Salt	**Zn1**	ΔG	Salt	**Zn2**	ΔG
NaCN	7.4×10^5	8.0	NaCN	8.0×10^5	8.1
NaCN[b]	1.9×10^5	7.2	NaCN[b]	2.0×10^5	7.3
NaCN[c]	8.5×10^4	6.7	KCN	9.5×10^6	9.5
KCN	1.3×10^4	5.6	KCN[b]	1.8×10^6	8.5
KCN[b]	2.5×10^3	4.6	NaSCN	1.4×10^3	4.3
KCN[c]	1.9×10^3	4.5	KSCN	1.6×10^3	4.4
NaSCN	1.1×10^3	4.1			
KSCN	9.3×10^2	4.0			

[a] Values are the average of two separate measurements and with error of ±15%.
[b] Obtained in MeOH–water (v/v 19:1).
[c] Obtained in MeOH–DMSO (v/v 9:1).

3. Conclusion

We have reported the synthesis and characterization of two new aza-crown ether-capped porphyrins **Zn1** and **Zn2**. The new artificial receptors are able to selectively recognize sodium cyanide and potassium cyanide in a ditopic binding fashion in polar methanol solvent. The binding selectivity of receptor **Zn1** for sodium cyanide is ca. 56 times as high as that for potassium cyanide, whereas the selectivity of receptor **Zn2** for potassium cyanide is ca. 12 times as high as that for sodium cyanide. In contrast, both receptors display remarkably reduced binding affinity for sodium thiocyanate and potassium thiocyanate, presumably due to a monotopic binding fashion. Current efforts will be focused on the modification of the Zn-porphyrin receptors to explore the selective recognition of cyanides in aqueous media.

4. Experimental

4.1. General methods

Melting points are uncorrected. All reactions were performed under an atmosphere of dry nitrogen. The ^{1}H NMR spectra were recorded on 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 7.27 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. Compounds **4a**[16] and **4b**[17] were prepared according to reported methods.

4.1.1. Compound 3. To a stirred solution of salicylaldehyde (6.00 g, 49.2 mmol) and chloroacetic acid (4.65 g, 49.2 mmol) in water (10 mL) was slowly added sodium hydroxide (3.60 g, 90.0 mmol) within 3 h at room temperature. The solution was stirred at 70 °C for 1.5 h and then acidified with dilute hydrochloric acid (2 N) to pH=7. The resulting solid was filtered and purified by recrystallization from water to give (2-formyl-phenoxy)-acetyl acid **2** as a white solid (6.00 g, 68%). Mp 129–130 °C [129–131 °C].[18] ^{1}H NMR (DMSO-d_6): δ 4.91 (s, 2H), 7.10 (m, 2H), 7.64 (m, 2H), 10.47 (s, 1H), 13.08 (br, 1H). ME (EI): *m*/*z* 180 $[M]^+$. To a solution of the above acid (3.60 g, 20.0 mmol) in dichloromethane (20 mL) was added oxalyl chloride (2 mL, 25.0 mmol) and drops of DMF. The mixture was stirred at room temperature for 12 h and then evaporated in vacuo to give **3** as a crude product, which was used directly for the next step without further purification.

4.1.2. Compound 5a. To a stirred solution of compound **4a** (2.18 g, 10.0 mmol) and triethylamine (1.0 mL) in dichloromethane (40 mL) was added a solution of the above **3** in dichloromethane (10 mL). The mixture was stirred at room temperature for 12 h and then washed with dilute hydrochloric acid, water, brine, and dried over magnesium sulfate. After the solvent was removed in vacuo, the crude product was purified by column chromatography (CH_2Cl_2/MeOH, 20:1) to give **5a** as a white solid (2.87 g, 53%). ^{1}H NMR ($CDCl_3$): δ 3.53–3.81 (m, 20H), 4.84 (s, 4H), 6.97 (d, J=7.5 Hz, 2H), 7.04 (t, J=6.5 Hz, 2H), 7.52 (t, J=6.5 Hz, 2H), 7.83 (d, J=7.5 Hz, 2H), 10.53 (s, 2H). IR (KBr): ν 2870, 1712, 1660, 1600 cm^{-1}. MS (ESI): *m*/*z* 543 $[M+H]^+$. Anal. Calcd for $C_{28}H_{34}N_2O_9\cdot 0.5H_2O$: C, 60.97; H, 6.40, N, 5.08. Found: C, 60.92; H, 6.36, N, 4.78.

4.1.3. Compound 5b. This intermediate was synthesized from the reaction of compounds **3** and **4b** in 57% yield by using the same procedure described for preparing compound **5a**. ^{1}H NMR ($CDCl_3$): δ 3.67–3.96 (m, 24H), 4.69 (s, 4H), 6.96 (d, J=7.5 Hz, 2H), 7.18 (t, J=6.5 Hz, 2H), 7.59 (t, J=6.5 Hz, 2H), 7.81 (d, J=7.5 Hz, 2H), 10.53 (s, 2H). MS (ESI): *m*/*z* 587 $[M+H]^+$, 610 $[M+Na]^+$. Anal. Calcd for $C_{30}H_{38}N_2O_{10}$: C, 61.42; H, 6.53; N, 4.78. Found: C, 61.08; H, 6.41; N, 4.59.

4.1.4. Compound 6. The solution of *n*-octyl 4-formylbenzoate[19] (8.70 g, 33.2 mmol) and pyrrole (23 mL, 66.4 mmol) in toluene (250 mL) was degassed by a stream of nitrogen for 30 min. Hot saturated *p*-toluenesulfonic acid solution in toluene (1.0 mL) was added in one portion. The solution was heated under reflux for 1.5 h and cooled to room temperature. The solution was washed with aqueous potassium carbonate solution (2 N), water, brine, and dried over sodium sulfate. Evaporation of the solvent under reduced pressure gave a brown oil, which was purified by column chromatography (chloroform) and recrystallization (chloroform/hexane) to give compound **6** (8.13 g, 65%) 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.

4.1.5. Compound $H_2$1. Compounds **5a** (5.42 g, 10.0 mmol) and **6** (7.56 g, 20.0 mmol) were dissolved in acetonitrile (1000 mL). The solution was degassed for 30 min and the trifluoroacetic acid (0.2 mL) was added in one portion. The solution was shielded from light and stirred at room temperature for 5 h. Then, a solution of DDQ (5.26 g) in THF (100 mL) was added and the mixture was stirred at room temperature for another 2 h. The solvent was evaporated in vacuo and the residue was triturated with chloroform (300 mL). The solution was washed with diluted sodium carbonate solution, water, brine, and dried over sodium sulfate. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (dichloromethane/methanol, 40:1) to afford compound **$H_2$1** (1.26 g, 10%). Mp >235 °C. ^{1}H NMR ($CDCl_3$): δ −2.71 (s, 2H), 0.96 (t, J=6.5 Hz, 6H), 1.24 (br, 8H), 1.36–1.62 (m, 20H), 1.92 (p, J=6.8 Hz, 4H), 2.13 (br, 4H), 2.87 (br, 8H), 4.50 (t, J=7.0 Hz, 4H), 4.67 (s, 4H), 7.20–7.25 (m, 2H), 7.44–7.49 (m, 2H), 7.73–7.79 (m, 2H), 8.04–8.08 (m, 2H), 8.30–8.34 (m, 4H), 8.42–8.48 (m, 4H), 8.81–8.86 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 14.3, 22.9, 26.4, 29.1, 29.5 (d), 32.0, 46.5 (d), 49.6, 63.2, 65.7, 66.9, 67.2, 67.4, 68.0 (d), 69.1, 70.2, 70.9 (d), 111.9, 113.0, 116.1 (d), 119.2, 121.3 (d), 121.8, 128.3 (d), 130.2, 130.7 (d), 131.2, 131.6 (d), 132.9, 134.7 (d), 135.1 (d), 134.0, 146.6 (d), 157.2, 158.3, 166.2, 167.0 (d), 167.2. IR (KBr): ν 2924,

1718, 1653, 1272, 1112 cm^{-1}. MS (MALDI): *m/z*: 1257 $[M+H]^+$, 1279 $[M+Na]^+$. HRMS: Calcd for $C_{76}H_{85}N_6O_{11}$: 1257.6276. Found: 1257.6268 $[M+H]^+$. Anal. Calcd for $C_{76}H_{84}N_6O_{11}\cdot H_2O$: C, 72.06; H, 6.78; N, 6.64. Found: C, 72.06; H, 6.47; N, 6.52.

4.1.6. Porphyrin $H_2$2. This compound was prepared (12%) as purple solid from the reaction of **5b** and **6** by a method analogous to $\mathbf{H_2}$**1**. Mp >230 °C. ^{1}H NMR ($CDCl_3$): δ −2.71 (s, 2H), 0.96 (t, J=7.0 Hz, 6H), 1.24 (br, 8H), 1.36–1.62 (m, 20H), 1.92 (p, J=7.0 Hz, 4H), 2.13 (br, 8H), 2.87 (s, 8H), 4.50 (t, J=7.1 Hz, 4H), 4.67 (s, 4H), 7.22–7.25 (m, 2H), 7.46–7.49 (m, 2H), 7.76–7.80 (m, 2H), 8.04–8.06 (m, 2H), 8.30–8.33 (m, 4H), 8.44–8.47 (m, 4H), 8.81–8.85 (m, 8H). IR (KBr): ν 2925, 1718, 1653, 1271, 1115 cm^{-1}. MS (MALDI): *m/z*: 1300 $[M]^+$. Anal. Calcd for $C_{78}H_{88}N_6O_{12}$: C, 71.98; H, 6.81; N, 6.46. Found: 71.69; H, 6.70; N, 6.31.

4.1.7. Porphyrin Zn1. The free base porphyrin $\mathbf{H_2}$**1** (1.00 g, 0.08 mmol) was dissolved in dichloromethane/methanol (3:1, 200 mL) and zinc acetate (0.60 g, 5.00 mmol) was added with stirring. The mixture was stirred under reflux overnight. The solvent was removed in vacuo, and the product was subjected to column chromatography (dichloromethane/methanol 40:1) to afford porphyrin **Zn1** as a purple solid in quantitative yield. Mp >260 °C. ^{1}H NMR ($CDCl_3$): δ −0.85 (t, J=7.0 Hz, 4H), 0.32 (t, J=7.0 Hz, 4H), 0.98 (br, 8H), 1.36–1.90 (m, 22H), 2.89 (s, 8H), 4.23–4.67 (m, 12H), 7.20–7.25 (m, 2H), 7.40–7.43 (m, 2H), 7.71–7.72 (m, 2H), 8.00–8.09 (m, 2H), 8.31–8.33 (m, 4H), 8.46–8.49 (m, 4H), 8.80–8.85 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 26.1, 28.8, 29.3 (d), 31.8, 43.6, 46.8, 62.6, 65.5, 67.3 (d), 68.8, 69.4, 70.4, 71.0, 72.2, 115.2, 115.9, 117.4, 119.7, 119.8, 122.1, 127.7 (d), 129.6, 130.3, 131.6, 132.0 (d), 133.7, 134.3 (d), 134.6, 147.4, 149.4 (d), 150.0 (d), 157.1, 159.1, 166.0, 166.8 (d), 167.5. IR (KBr): ν 2926, 1719, 1647, 1271, 1116 cm^{-1}. MS (MALDI): *m/z* 1320 $[M+H]^+$. Anal. Calcd for $C_{76}H_{82}N_6O_{11}Zn$: C, 69.11; H, 6.26; N, 6.36. Found: C, 69.50; H, 6.43; N, 5.98.

4.1.8. Porphyrin Zn2. This compound was prepared as a purple solid from the reaction of $\mathbf{H_2}$**2** and zinc acetate by a method similar to that for **Zn1**. Mp >250 °C. ^{1}H NMR ($CDCl_3$): δ 0.72 (br, 4H), 0.96 (t, J=6.7 Hz, 8H), 1.11–1.58 (m, 18H), 1.84–1.96 (m, 8H), 2.81–2.31 (m, 8H), 4.36–4.42 (m, 4H), 4.50 (t, J=6.5 Hz, 12H), 7.17–7.27 (m, 2H), 7.37–7.48 (m, 2H), 7.71–7.80 (m, 2H), 7.97–8.10 (m, 2H), 8.29 (d, J=7.8 Hz, 4H), 8.43 (d, J=7.8 Hz, 4H), 8.75–8.91 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 26.2, 28.9, 29.3 (d), 31.8, 45.8 (d), 47.1 (d), 65.5, 65.7, 67.4, 67.7, 68.2, 68.9, 69.3, 69.7, 70.3, 112.9, 114.6, 116.3, 116.5, 119.4 (d), 120.9, 121.3, 127.7 (d), 129.6, 130.0, 131.7, 132.5, 133.0, 134.3, 134.8, 135.4 (d), 147.6, 149.4 (d), 150.2 (d), 157.6, 158.0, 166.9 (d), 167.1. IR (KBr): ν 2924, 1718, 1653, 1271, 1114 cm^{-1}. MS (MALDI): *m/z*: 1363 $[M+H]^+$. HRMS: Calcd for $C_{78}H_{86}N_6O_{12}Zn$: 1363.5673. Found: 1363.5689. Anal. Calcd for $C_{78}H_{86}N_6O_{12}Zn$: C, 68.64; H, 6.35, N, 6.16. Found: C, 68.42; H, 6.39; N, 6.11.

4.2. Binding studies

For the UV–vis absorption titration experiments, typically a methanol solution of **Zn1** or **Zn2** was prepared at a fixed concentration. Methanol solutions of inorganic salts were prepared at concentrations of 0.1 M, 2.5 mL of the mixture solution with the fixed [**Zn1**] or [**Zn2**] and the changing concentration of guests was placed in a cuvette and the UV–vis absorption spectrum were sequentially recorded. The values of the absorbance at fixed wavelengths were used. Origin6.0 software was used to fit the data to a 1:1 binding isotherm: $\Delta A=(\Delta A_{max}/[\mathbf{Zn1}\cdot\mathbf{Zn1}])\times\{0.5[G]+0.5([\mathbf{Zn1}\cdot\mathbf{Zn1}]+K_d)-0.5[[G]^2+(2[G](K_d-[\mathbf{Zn1}\cdot\mathbf{Zn1}])+(K_d+[\mathbf{Zn1}\cdot\mathbf{Zn1}])^2)^{1/2}]\}$, where [G] is the salt guest concentration, $K_d=(K_{assoc})^{-1}$. Association constants reported are the average of two experiments.[14]

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