Binding Enhancements of Nicotinic Acid to Water-Soluble Zinc Porphyrins Based on Triple Attractions of Coordination, Coulomb, and CH–π Interactions

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The binding of amines to artificial zinc-porphyrin receptors 1—4 was examined in basic aqueous solutions. For nicotinic acid and 3,5-dicarboxypyridine, substantial binding enhancements were observed compared to other amines with no π system or carboxyl group. This observation suggested that interligand attractions of Coulomb and CH–π interactions in addition to N-atom coordination can act effectively as recognition factors. The differences in the Coulomb interaction between carboxylate and sulfonate anions were also discussed.

Key words water-soluble zinc porphyrin; nicotinic acid; molecular recognition; coordination; Coulomb interaction; CH–π interaction

The examination of the binding of small biomolecules with artificial receptors in aqueous media is one of the traditional approaches to obtain fundamental information on molecular recognition in biological and pharmaceutical conditions. Binding enhancements and selectivity for guests by receptors result from additively and/or cooperatively combined weak non-covalent interactions. Synthetic metalloporphyrins have been widely used as receptors for biomolecules and their analogs; however, not many studies in aqueous solutions[1—12] have been reported because of the lipophilic nature of porphyrins. In a previous work,[8] we reported amino acid chiral recognition by a water-soluble zinc porphyrin, where three interactions act as the recognition factors. Two of the interactions are attractive, but the remaining interaction has not yet been identified as attractive or repulsive. Here, we examined the binding behavior of zinc porphyrins **1**—**4** with amine guests in basic aqueous solutions, where the porphyrin substituents near the central zinc ion can differently interact with the bound guests. The binding data suggested the existence of three types of simultaneous attractive interactions between the zinc porphyrins (**2**, **4**) and the anions of nicotinic acid and 3,5-dicarboxypyridine.

Results and Discussion

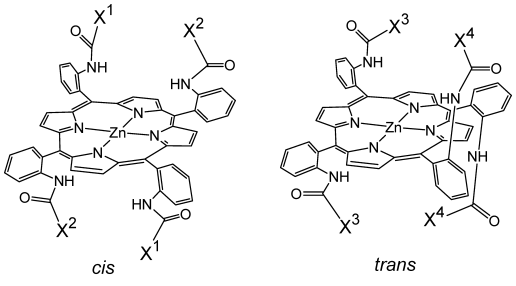
In the absence of amine, zinc porphyrins exist as five coordinated species with a bound H_2O molecule in aqueous solution.[13] The N atom of amines is not protonated under the basic experimental conditions (pH 10.4), thereby the N atom of the amines can coordinate to the zinc ion and substitute the bound H_2O of the porphyrins. The binding equilibrium between zinc porphyrin ZnP and amine L is expressed as follows:

$$ZnP \cdot H_2O + L \rightleftharpoons ZnP \cdot L + H_2O$$

where the binding constant is given as

$$K = \frac{[ZnP \cdot L]}{[ZnP \cdot H_2O][L]}$$

Figure 1 shows visible spectra of **4** upon titration of nico. The spectral changes correspond to the N coordination of the



1: $X^1 = X^2 = CH_2N(CH_3)_3 \cdot Cl$
2: $X^1 = C(CH_3)_3$, $X^2 = CH_2N(CH_3)_3 \cdot Cl$
3: $X^3 = X^4 = CH_2N(CH_3)_3 \cdot Cl$
4: $X^3 = C(CH_3)_3$, $X^4 = CH_2N(CH_3)_3 \cdot Cl$

Chart 1. Water-Soluble Zinc Porphyrins

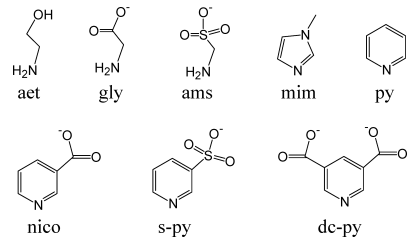


Chart 2. Amine Guests

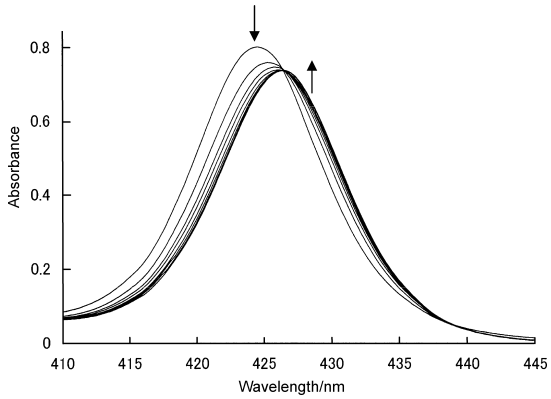


Fig. 1. Visible Absorption Spectra of **4** upon Titration of nico

At 25.0 °C in aqueous solution buffered with $NaHCO_3$–Na_2CO_3 (pH 10.4, I = 0.02). [**4**] = 3.49×10^{-6} mol/l; [nico] = 0, 1.44×10^{-3}, 2.88×10^{-3}, 4.30×10^{-3}, 5.71×10^{-3}, 7.11×10^{-3}, 8.50×10^{-3}, 9.89×10^{-3} mol/l.

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Table 1. Binding Constants (l/mol) of Amines with Zinc Porphyrins[a)]

Compd.	Amine					
	aet	gly	mim	py	nico	dc-py
1	9.9	110	59	9.4	130	1000
	(2/0)[b)]	(2/1)	(2/0)	(2/0)	(2/1)	(2/2)
2	12	57	190	42	230	1200
	(1/0)	(1/1)	(1/0)	(1/0)	(1/1)	(1/2)
3	10	150	66	15	180	1600
	(2/0)	(2/1)	(2/0)	(2/0)	(2/1)	(2/2)
4	10	66	240	64	350	2000
	(1/0)	(1/1)	(1/0)	(1/0)	(1/1)	(1/2)

a) At 25 °C, pH 10.4 (I=0.02). Errors for K are within 16%. *b*) Ratios for cation/anion are in parentheses.

amine, since the addition of acetate ion to the zinc porphyrins does not cause any spectral change. The binding constants of the amines to the zinc porphyrins were determined from the spectra and are listed in Table 1. The binding behavior reflects the interligand interactions between the bound amines and the $-C(CH_3)_3$ or $-N(CH_3)_3^+$ of the porphyrins and solvation-desolvation phenomena of the solutes, in addition to the coordination of the N atom to the central zinc ion. The K values of aet are substantially small due to the weak ligand-exchange ability of the N atom from the bound H_2O. It has also been reported that the K values for the amine binding to anionic water-soluble zinc porphyrins are small.[13)] Since the –OH and $-CH_2-$ groups of aet cannot interact strongly with the porphyrin substituents, similar K values are obtained for different porphyrins with aet, suggesting that the zinc acidity is similar in each case.

For the binding of carboxylate amines to the porphyrins, Coulomb interactions between the $-COO^-$ group of the former and the $-N(CH_3)_3^+$ group of the latter in addition to the coordination were expected. In fact, the binding constants increased with the number of possible Coulomb interactions; the K values with gly are larger as compared to those with aet, and this is more obvious for **1** and **3** (the cation/anion ratio is 2/1 in the gly adducts) than for **2** and **4** (the cation/anion ratio is 1/1). Since the pK_a values of gly (9.57)[14)] and aet (9.52)[14)] are similar, comparisons of their binding data for **2** or **4** may provide the binding enhancement factor by Coulomb interactions with a cation/anion ratio of 1/1, that can be estimated to be *ca.* 5—7 times in K and 3.9—4.6 kJ/mol in $-\Delta G°$ (25 °C). The effects of the Coulomb interaction were reasonably supported by examining the dependence of K on the ionic strength I, where the slope of the plot of log K *versus* $\sqrt{I}$ can be related to the magnitude of the Coulomb interaction.[15,16)] The slope values in Fig. 2 are well correlated to the magnitude of the possible Coulomb interactions that enhance the binding.

Table 2 compares binding constants for carboxylates and sulfonates. The pK_a value of 9.57 for gly is considerably higher than that of 5.75[17)] for ams, indicating an appreciably weaker donor ability of the N atom of ams than that of gly. However, the binding constants for ams are only slightly small as compared to those for gly. Since the binding data cannot be correlated to the difference in pK_a, this may be explained in terms of the increased Coulomb interaction with the sulfonate anion than with the carboxylate anion that eclipses the poor donor ability of ams. A similar result can

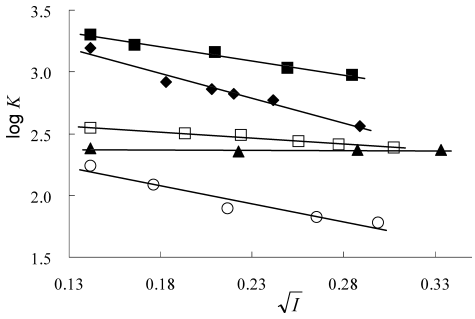

Fig. 2. Correlation of log K with $\sqrt{I}$

■; **4**+dc-py (1/2, −2.26), ◆; **3**+dc-py (2/2, −4.04), □; **4**+nico (1/1, −0.97), ▲; **4**+mim (1/0, −0.06), ○; **3**+nico (2/1 −2.92), respectively. The cation/anion ratio and the slope value are in parentheses.

Table 2. Binding Constants (l/mol) of Sulfonates[a)]

Compd.	K(ams)	K(ams)/K(gly)	K(s-py)	K(s-py)/K(nico)
1	76	0.69	120	0.94
2	nd[b)]		190	0.82
3	120	0.80	160	0.92
4	nd		300	0.86

a) At 25 °C, pH 10.4 (I=0.02). *b*) Could not be determined due to their small spectral changes.

Table 3. ^{1}H-NMR Shifts[a)] upon Addition of dc-py

Compd.	$\delta C(CH_3)_3$		$\Delta\delta$	$\delta N(CH_3)_3$		$\Delta\delta$
		+dc-py			+dc-py	
1				2.326	2.336	0.010
2	−0.079	−0.271	−0.192	2.005	2.091	0.086
3				2.281	2.243	−0.038
4	−0.064	−0.241	−0.177	1.931	1.934	0.004

a) At 27 °C in D_2O, 4×10^{-3} mol/l Na_2CO_3; [porphyrin]=5×10^{-4} mol/l, [dc-py]=5×10^{-3} mol/l.

Table 4. Binding Constants[a)] (l/mol) in H_2O[b)]/CH_3OH (1/1)

Compd.	Amine			
	aet	mim	nico	dc-py
3	nd[c)]	15	nd[c)]	900
4	5.0	80	156	670

a) At 25°C. *b*) pH 10.4 (I=0.02). *c*) Could not be determined due to their small spectral changes.

be observed for the binding of nico and s-py, where the binding constants for these amines are fairly close.

Another apparent feature shown in Table 1 is that the binding constants for mim and pyridines, which have π systems, are large with **2** and **4** containing $-C(CH_3)_3$ groups. The fact that the $-C(CH_3)_3$ signals of **2** and **4** in ^{1}H-NMR substantially shift upfield upon dc-py binding indicates that the $-CH_3$ groups exist above the π system of the bound amines (Table 3).[18)] When the binding was examined in CH_3OH/H_2O (1 : 1), similar binding enhancements have been retained (Table 4).[19)] These results suggest that the binding enhancements of the amines with π system for **2** and **4** could be attributed to the CH–π[20,21)] or van der Waals interactions but

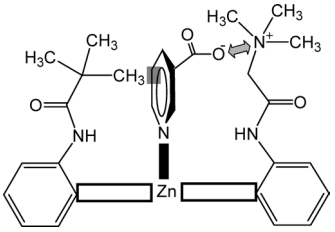

Fig. 3. Schematic Representation for the Binding Enhancement of nico to **2** and **4** Based on Coordination (▬), Coulomb (⟺), and CH–π (▬) Interactions

not to the hydrophobic interactions. The comparison of the binding data of py between **1** and **2** or **3** and **4** showed the binding enhancement factor between the py π system and $-C(CH_3)_3$ to be *ca.* 4 times in K and 3.5—3.6 kJ/mol in $-\Delta G°$ (25 °C). A similar binding enhancement has been reported in nonpolar organic solvents,[22] but it was hardly observed in aqueous solutions due to the strong solvent–solute interactions.[13] Another attraction between the bound amines with π systems and $-N(CH_3)_3^+$ may be possible in aqueous solutions in the form of cation–π interactions that play biologically important roles.[23,24] For **1** and **3**, however, the comparison of the binding data of aet and py suggested that such the interactions can be negligible here. Further, the fact that no upfield shift of the $-N(CH_3)_3^+$ signal upon dc-py binding is observed supports this suggestion.

With regard to atropisomerism, *cis*-types **1** and **3** show somewhat small K values except for aet than *trans*-types **2** and **4**. Although binding enhancements for *trans*-types with nico and dc-py are more apparent than *cis*-types, the differences between **1** and **3** or **2** and **4** are not sufficiently large to affect the selectivity for amines. Together with the NMR data, the relative configuration of the porphyrin substituents in the two atropisomers might provide similar interactions with the guest amines.

In conclusion, receptors **2** and **4** apparently induce attractions for the nitrogen atom as a donor, anionic group, and π system of a guest molecule based on coordination, Coulomb interaction, and CH–π interaction, respectively (Fig. 3). The binding enhancements for nico and dc-py are additive for the double interactions; for example, a comparison of the binding data of **3**-py and **4**-nico systems yields the stability factor of 23 times in K and 7.6 kJ/mol in $-\Delta G°$, which well agree with the two additive contributions noted above. The combined weak attractions effectively recognize these small guest molecules. These porphyrins also showed a possibility to act as a receptor for nicotine derivatives in aqueous solution.

Experimental

General All chemicals were purchased commercially and were used as received without further purification unless otherwise noted. Aminoethanole (aet), 1-methylimidazole (mim), and pyridine (py) were purified by distillation. Water for visible spectral measurements was purified by use of a SIBATA PP-101 water purification apparatus. Silica gel for column chromatography was Wakogel C-200 (Wako).

Visible absorption spectra were recorded on a Hitachi U-3000 spectrophotometer. Proton NMR spectra were obtained from a JEOL JNM-ECP-500 (500 MHz) or a JEOL JNM-GSX-400 (400 MHz) spectrometer with tetramethylsilane or sodium 3-trimethylsilyl-propanesulfonate as the internal standard. FAB-MS spectra were measured on a JEOL JMS-SX-102A mass spectrometer using magic bullet as matrix.

Binding Experiments Visible absorption spectra were recorded on a Hitachi U-3000 spectrophotometer. The binding of amines to the porphyrins were examined by spectrophotometric titration of amines in aqueous solution buffered with $NaHCO_3$–Na_2CO_3 (pH 10.4, I=0.02). The ionic strength I was changed with NaCl. The binding constants were determined based on the published method.[25,26]

Synthesis Compound **2** was obtained according to the literature.[25] Compounds **1**, **3**, and **4** were prepared by methods similar to that for **2**.

5α,10α,15β,20β-Tetrakis(2-aminophenyl)porphyrinatozinc(II) (5) To a solution of 5α,10α,15β,20β-tetrakis(2-aminophenyl)porphyrin (0.200 g, 0.296 mmol) and 2,6-lutidine (0.30 ml, 1.3 mmol) in tetrahydrofuran (100 ml) was added zinc chloride (0.300 g, 2.20 mmol). After stirring the solution for 4 h at room temperature, the volume was reduced to a quarter on an evaporator. Chloroform (200 ml) was added to the solution and the mixture was washed twice with water (200 ml). The organic layer was dried over anhydrous Na_2SO_4 then was evaporated to dryness. The solid was purified on a silica-gel column (2.5×20 cm, chloroform); yield 0.168 g (76.7%). ^{1}H-NMR (500 MHz, DMF-d_7) δ 4.59 (s, 8H, NH_2), 7.06 (t, 4H, ph), 7.22 (d, 4H, ph), 7.55 (t, 4H, ph), 7.80 (d, 4H, ph), 8.86 (s, 8H, pyrrole); Vis ($CHCl_3$) λ_{max} 426, 517 (sh), 555, 595 nm. MS m/z 737 ($(M+H)^+$) (Calcd for $C_{44}H_{32}N_8Zn$: 736).

5α,10α,15β,20β-Tetrakis(2-(*N*,*N*-dimethylaminomethylcarbonylamino)phenyl)porphyrinatozinc(II) (6) To a suspended solution of $(CH_3)_2NCH_2COOH\cdot HCl$ (0.600 g, 4.30 mmol) in CH_2Cl_2 (30 ml) was added dropwise $(COCl)_2$ (2.00 ml, 15.5 mmol). The mixture was stirred for 2 h at room temperature and was evaporated to dryness then dissolving the solid in CH_2Cl_2 (30 ml). To an ice-cold solution of **5** (0.150 g, 0.203 mmol) and triethylamine (8 ml) in CH_2Cl_2 (100 ml) was added the above acid-chloride solution. After stirring for 3 h at room temperature, the solution was washed twice with water (100 ml). The solution was dried over anhydrous Na_2SO_4 then was evaporated to dryness. The solid was purified on a silica-gel column (2.5×20 cm, chloroform); yield 0.108 g (49.3%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.21 (s, 24H, $N(CH_3)_2$), 2.19 (s (br), 8H, CH_2), 7.53 (s, 4H, ph), 7.82 (s, 4H, ph), 7.97 (s, 4H, ph), 8.69 (m, 8H, ph, NHCO), 8.86 (s, 8H, pyrrole); Vis ($CHCl_3$) λ_{max} 427, 517 (sh), 557, 595 nm. MS m/z 1077 ($(M+H)^+$) (Calcd for $C_{60}H_{60}N_{12}O_4Zn$: 1076).

5α,10α,15β,20β-Tetrakis(2-(trimethylammoniomethylcarbonylamino)phenyl)porphyrinatozinc(II) Chloride (1) A solution of **6** (0.090 g, 0.083 mmol) in *N*,*N*-dimethylformamide (10 ml) and CH_3I (0.500 ml, 6.44 mmol) was stirred for 3 h at room temperature. The addition of ether to the solution afforded a solid of the corresponding iodide of **1**. The iodide was converted to chloride, **1**, by ion-exchange column chromatography (CH_3OH, 3×30 cm (Amberlyst A-21)); yield 0.057 g (53%). ^{1}H-NMR (400 MHz, DMSO-d_6) δ 2.27 (s, 36H, $N(CH_3)_3$), 7.70 (t, 4H, ph), 7.87 (t, 4H, ph), 7.97 (d, 4H, ph), 8.10 (d, 4H, ph), 8.54 (s, 4H, pyrrole), 8.59 (s, 4H, pyrrole), 8.95 (s, 4H, NHCO); Vis (H_2O/$NaHCO_3$-Na_2CO_3, pH 10.4) λ_{max} (log ε) 425 (5.51), 520 (sh) (3.46), 558 (4.24), 597 (3.69) nm; *Anal.* Calcd for $C_{64}H_{72}N_{12}O_4ZnCl_4\cdot 8H_2O$: C, 53.96; H, 6.23; N, 11.80. Found: C, 54.01; H, 5.90; N, 11.78. MS m/z 1243 (M^+) (Calcd for $C_{64}H_{72}N_{12}O_4ZnCl_3$: 1243).

5α,10β,15α,20β-Tetrakis(2-(trimethylammoniomethylcarbonylamino)phenyl)porphyrinatozinc(II) Chloride (3) Compound **3** was obtained by a procedure similar to that for **1** by using 5α,10β,15α,20β-tetrakis(2-aminophenyl)porphyrin instead of 5α,10α,15β,20β-tetrakis(2-aminophenyl)porphyrin as the starting material. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 2.44 (s, 36H, $N(CH_3)_3$), 7.72 (t, 4H, ph), 7.85 (m, 8H, ph), 8.08 (d, 4H, ph), 8.52 (s, 8H, pyrrole), 9.13 (s, 4H, NHCO); Vis (H_2O/$NaHCO_3$–Na_2CO_3, pH 10.4) λ_{max} (log ε) 424 (5.57), 519 (sh) (3.46), 558 (4.24), 597 (3.69) nm; *Anal.* Calcd for $C_{64}H_{72}N_{12}O_4ZnCl_4\cdot 5H_2O$: C, 56.08; H, 6.03; N, 12.26. Found: C, 55.99; H, 5.91; N, 12.09. MS m/z 1243 (M^+) (Calcd for $C_{64}H_{72}N_{12}O_4ZnCl_3$: 1243).

5α,10β-Bis((2-(trimethylammoniomethylcarbonylamino)phenyl)-15α,20β-bis(2-pivalamidophenyl)porphyrinatozinc(II) Chloride (4) was obtained by a procedure similar to that for **2** by using 5α,10β,15α,20β-tetrakis(2-aminophenyl)porphyrin instead of 5α,10α,15β,20β-tetrakis(2-aminophenyl)porphyrin as the starting material. The synthesis of **4** is as follows.

5α,10β-Bis(2-(triphenylmethylamino)phenyl)-15α,20β-bis(2-aminophenyl)porphyrin (7) To an ice-cold solution of 5α,10β,15α,20β-tetrakis(2-aminophenyl)porphyrin (2.000 g, 2.96 mmol) and triethylamine (5.0 ml) in CH_2Cl_2 (800 ml) was added dropwise a solution of triphenylmethyl bromide (2.08 g, 6.44 mmol) in CH_2Cl_2 (400 ml). The reaction mixture containing some kinds of partly amino-protected porphyrins was evaporated to dryness and the solid was chromatographed on a silica-gel column (benzene, 4×30 cm). The third band of **7** was separated and evaporated to dryness, yield 0.836 g. (24.4%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ −2.69 (s, 2H, pyrrole–NH), 3.61 (s, 4H, NH_2), 5.09 (s, 6H, Cph_3), 6.65 (d, 2H, ph),

6.94 (d, 12H, Cph_3), 7.03 (d, 12H, Cph_3), 7.19 (m, 8H, ph), 7.61 (d, 2H, ph), 7.64 (t, 2H, ph), 7.89 (d, 2H, ph), 8.90 (d, 2H, ph), 8.94 (m, 8H, pyrrole); Vis ($CHCl_3$) λ_{max} 420, 519, 553, 591, 654 nm. MS *m/z* 1159 ($(M+H)^+$) (Calcd for $C_{82}H_{62}N_8$: 1158).

5α,10β-Bis(2-aminophenyl)-15α,20β-bis(2-pivalamidophenyl)porphyrin (8) Compound **7** (0.800 g, 0.690 mmol) was dissolved in CH_2Cl_2 (80 ml) containing triethylamine (1.1 ml). To the solution, pivaloyl chloride (0.35 ml, 2.8 mmol) was added then stirred for 3 h at room temperature. The reactant solution was treated with a mixture of dilute HCl (6 mol/l, 10 ml) and CH_3COOH (10 ml) for 1 h at room temperature, deprotecting the two amino groups. After neutralization with aqueous ammonia in an ice bath, the organic layer was dried over anhydrous Na_2SO_4 then evaporated to dryness. The solid of **8** was purified by silica-gel column chromatography ($CHCl_3$, 2.5×30 cm); yield 0.346 g (59.5%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ −2.62 (s, 2H, pyrrole–NH), 0.18 (s, 18H, $C(CH_3)_3$), 1.55 (s, 4H, NH_2), 7.16 (m, 4H, ph), 7.22 (s, 2H, NHCO), 7.51 (t, 2H, ph), 7.62 (t, 2H, ph), 7.80 (t, 2H, ph), 7.85 (d, 2H, ph), 7.96 (d, 2H, ph), 8.72 (d, 2H, ph), 8.81 (m, 4H, pyrrole), 8.94 (m, 4H, pyrrole); Vis ($CHCl_3$) λ_{max} 420, 516, 550, 589, 647 nm. MS *m/z* 843 ($(M+H)^+$) (Calcd for $C_{54}H_{50}N_8O_2$: 842).

5α,10β-Bis(2-aminophenyl)-15α,20β-bis(2-pivalamidophenyl)porphyrinatozinc(II) (9) Zinc ion was inserted to **8** by a method similar to that of **5**, giving **9** as a purple solid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.14 (s, 18H, $C(CH_3)_3$), 1.56 (s (br), 4H, NH_2), 6.75 (s, 2H, NHCO), 7.17 (m, 4H, ph), 7.52 (m, 4H, ph), 7.77 (d, 2H, ph), 7.83 (t, 2H, ph), 7.98 (d, 2H, ph), 8.71 (d, 2H, ph), 8.86 (m, 4H, pyrrole), 8.89 (s, 4H, pyrrole); Vis ($CHCl_3$) λ_{max} 427, 517 (sh), 556, 595 nm. MS *m/z* 904 (M^+) (Calcd for $C_{54}H_{48}N_8O_2Zn$: 904).

5α,10β-Bis((2-(*N*,*N*-dimethylaminomethylcarbonylamino)phenyl)-15α,20β-bis(2-pivalamidophenyl)porphyrinatozinc(II) (10) This compound was prepared from **9** by a procedure similar to that for **6** from **5**. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.03 (s, 18H, $C(CH_3)_3$), 0.09 (s, 12H, $N(CH_3)_2$), 1.90 (s (br), 4H, CH_2), 6.99 (s, 2H, NHCO), 7.55 (m, 4H, ph), 7.79 (t, 2H, ph), 7.84 (t, 2H, ph), 8.03 (d, 2H, ph), 8.12 (m, 2H, ph), 8.48 (m, 2H, ph), 8.65 (d, 2H, ph), 8.85 (d, 2H, ph), 8.89 (s, 4H, pyrrole), 8.91 (s, 4H, pyrrole); Vis ($CHCl_3$) λ_{max} 427, 518 (sh), 557, 596 nm. MS *m/z* 1075 ($(M+H)^+$) (Calcd for $C_{62}H_{62}N_{10}O_4Zn$: 1074).

5α,10β-Bis((2-(trimethylammoniomethylcarbonylamino)phenyl)-15α,20β-bis(2-pivalamidophenyl)porphyrinatozinc(II) Chloride (4) This compound was prepared from **10** by a procedure similar to that for **1** from **6**. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 0.06 (s, 18H, $C(CH_3)_3$), 2.28 (s, 18H, $N(CH_3)_3$), 7.37 (s, 2H, NHCO), 7.60 (t, 2H, ph), 7.72 (t, 2H, ph), 7.80 (t, 2H, ph), 7.86 (m, 4H, ph), 8.07 (d, 2H, ph), 8.15 (d, 2H, ph), 8.37 (d, 2H, ph), 8.52 (s, 2H, pyrrole), 8.56 (d, 2H, pyrrole), 8.60 (d, 2H, pyrrole), 8.62 (s, 2H, pyrrole), 8.94 (s, 2H, NHCO); Vis (H_2O/$NaHCO_3$–Na_2CO_3, pH 10.4) λ_{max} (log ε) 425 (5.36), 520 (sh) (3.38), 558 (4.15), 596 (3.55) nm; *Anal.* Calcd for $C_{64}H_{68}N_{10}O_4ZnCl_2\cdot 5H_2O$: C, 60.64; H, 6.20; N, 11.05. Found: C, 60.65; H, 6.06; N, 11.00. MS *m/z* 1141 (M^+) (Calcd for $C_{64}H_{68}N_{10}O_4ZnCl$: 1141).

References and Notes

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