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Synthesis and characterization of porphyrins bearing four redox-active phenylenediamine pendant groups as a dimensionally oriented π-conjugated system

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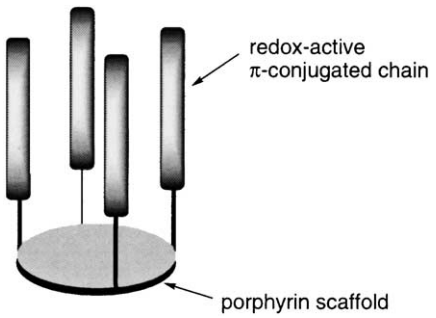
Abstract—Porphyrins bearing phenylenediamine pendant groups were synthesized to afford dimensionally oriented π-conjugated systems. The structural and electronic characteristics depend on the αααα and αβαβ atropisomers. In the fluorescence emission spectra, the emission from the porphyrin moiety was almost completely quenched. Zinc complexation of the αααα isomer with zinc(II) acetate led to the corresponding zinc complex.

1. Introduction

Architecturally ordered orientation of π-conjugated molecular chains is expected to construct novel π-electronic systems, but only few reports have appeared on the alignment of π-conjugated polymer or telomer chains.[1] Dimensional orientation of π-conjugated molecular chains in one molecule is envisioned to provide such a system. In this context, the utilization of a porphyrin scaffold is considered to be a convenient approach to orient the π-conjugated molecular chains.

A number of porphyrin–chromophore hybrid systems have been synthesized since porphyrins are photochemically and redox active. Electronic communication and/or photoinduced electron and energy transfer between the porphyrin and chromophore are achieved in these systems.[2] Chromophores are introduced along or onto the porphyrin plane to construct two-dimensionally[3] or face-to-face[4] arrayed electronic systems, respectively. The latter interaction has been reported in strapped porphyrins[4a–e] and other linked porphyrins.[4f–j] π-Conjugated oligomer chains such as oligothiophene[5] and oligophenylene[6] have been also introduced to the porphyrin ring to form two-dimensional π-electronic systems, in which π-conjugated oligomers are incorporated along the porphyrin plane. *meso*-Tetraarylporphyrin, in which four aromatic rings at the *meso*-position are perpendicular to the porphyrin plane, can be used for perpendicular alignment of π-conjugated chains on the porphyrin plane. Furthermore, atropisomerism of *meso*-tetraarylporphyrins has an advantage of aligning π-conjugated pendant groups under the controlled orientation. Such an alignment is considered to permit electronic communication among the π-conjugated pendant groups or between the pendant group and porphyrin ring although the expanded π-conjugation is disrupted. In this context, porphyrins bearing redox-active phenylenediamine pendant groups were designed in a previous study.[7] We herein describe the full scope of these porphyrins and the zinc complexes.



2. Results and discussion

2.1. Synthesis

The porphyrin scaffold **1** for the above-mentioned π-conjugated compounds was prepared by condensation of pyrrole and 2-(ethoxycarbonylmethoxy)naphthalenecarbaldehyde according to Lindsey's method.[8] Porphyrin **1** was obtained as a mixture of the four atropisomers. These αβαβ, ααββ, αααβ and αααα atropisomers were separated by silica-gel column chromatography and assigned by

Keywords: π-conjugated pendant group; redox-active system; porphyrin; zinc porphyrin.

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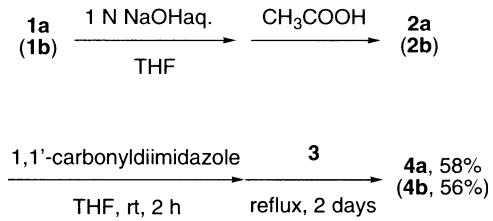


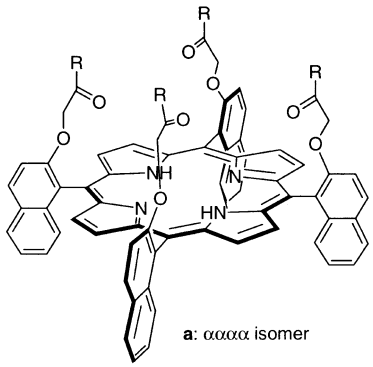
Scheme 1.

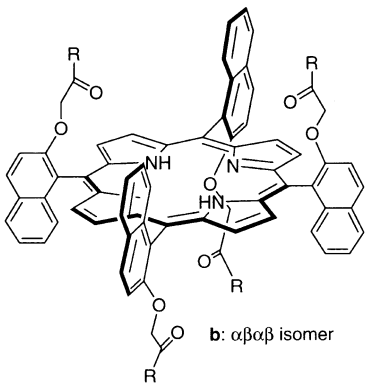
comparison with the polarity and spectral data of the related compounds.[9,10] Hydrolysis of the isolated αααα (**1a**) and αβαβ (**1b**) isomers led to the corresponding acids **2a** and **2b**, respectively.[9] The porphyrins **4a** and **4b** were synthesized by amidation of **2a** and **2b** with **3**, via the acylimidazolides, in 58 and 56% yields, respectively (Scheme 1). Four phenylenediamine pendant groups were introduced into the porphyrin scaffold without atropisomerization under the conditions employed here. No atropisomerized derivative was detected in the reaction mixture.[10] The porphyrins **4a** and **4b** are soluble in DMSO, DMF, and THF, but are insoluble in a less polar solvent such as $CHCl_3$, CH_2Cl_2, and toluene. The porphyrins **5** bearing the anilinoanilino pendant groups were prepared similarly. In the synthesis of **5a**, use of EDCI·HCl (N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride) and HOBt (1-hydroxybenzotriazole) as condensation agents improved the yield (68%). In contrast to **4**, **5a** and **5b** are soluble in $CHCl_3$, CH_2Cl_2, or $ClCH_2CH_2Cl$.

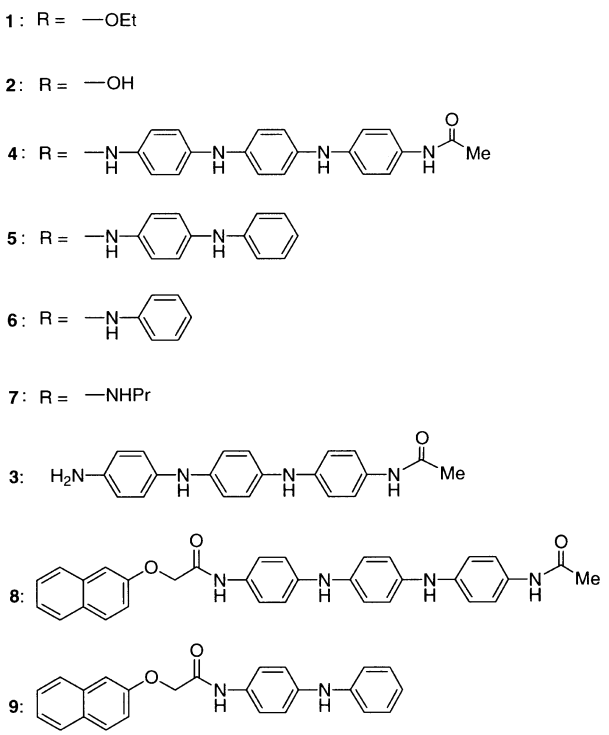
2.2. Spectroscopy

The structure of these porphyrins was elucidated by ^1H NMR, FT-IR, and MS (MALDI-TOF or FAB) spectrometry. In the ^1H NMR spectrum of **4a** in DMSO-d_6, the protons of the phenylenediamine pendant groups, especially the phenylene protons close to the porphyrin ring, were observed in a higher field as compared with **8**, a single-pendant unit of **4** (Table 1). The shift is likely to be explained by a ring-current effect of the porphyrin π-ring system. Furthermore, the phenylene protons of the strands of **4b** shifted to a higher field than **4a**, indicating that the protons of **4b** are more susceptible to the effect. Moreover, the signals of the phenylene protons, H_a and H_b, of **4a** were broadened, suggesting that the movement of the pendant groups is conformationally restricted. To ascertain the spectral change more precisely in a less polar solvent under the conditions independent of perturbation by hydrogen bonding with the solvent, the porphyrins **5a** and **5b** soluble in a less polar solvent were studied. The porphyrins **5a** and **5b** showed similar ^1H NMR spectral behavior in $CDCl_3$ as observed in **4**, namely, the pendant groups of **5b** are more influenced by the ring-current effect of the porphyrin ring than those of **5a**. Taking the similar spectral inclination between **4** in DMSO-d_6 and **5** in $CDCl_3$ into account, the pendant groups of **4a** and **4b** are likely to be magnetically present in a conformation similar to **5a** and **5b**, respectively. These results are in contrast to the finding that the difference in the effect between the propyl-substituted porphyrins **7a** and **7b** was much smaller.

The electronic environment of these porphyrins was investigated by absorption spectra as shown in Table 2. It







should be noted that the Soret band was slightly red-shifted with the lower molar coefficient in both cases of **4a** and **4b** in THF, as compared with **7a** and **7b** (Fig. 1). Furthermore, the Soret and Q bands of **4b** were broadened in comparison with those of **4a**, again being in contrast to the lack of typical spectral difference between the atropisomers **7**. The Soret and Q bands of **5** in $ClCH_2CH_2Cl$ were also red-shifted with the lower absorbance as observed in **4**.

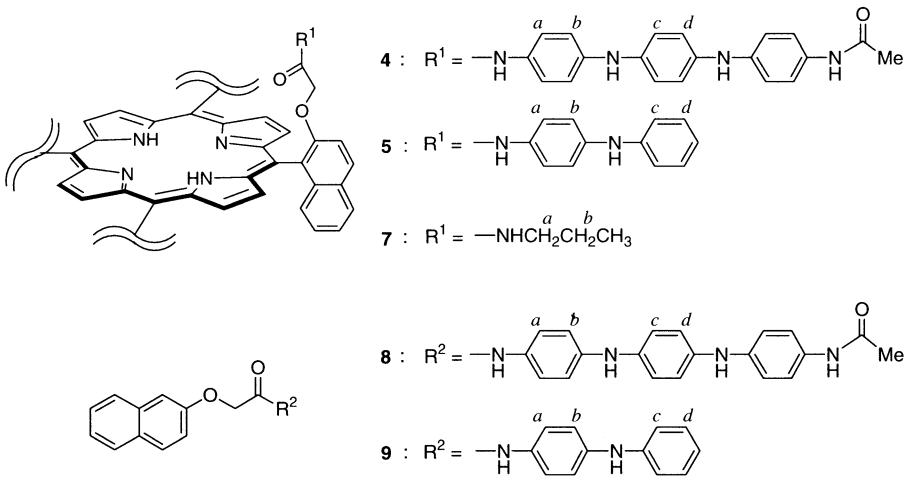


Table 1. Chemical shifts of **4**, **5** and **7**–**9** (400 MHz)

Compound	Solvent (mM)	H_a	H_b	H_c	H_d
4a	DMSO-d_6 (1.0)	6.15–6.35 (br)		6.77 (d)	6.82–6.92[a]
4b	DMSO-d_6 (1.0)	4.04–4.24[a]	4.99 (d)	6.36 (d)	6.68 (d)
5a	$CDCl_3$ (0.75)	5.29 (br)	5.61 (br)	6.63 (d)	7.14 (dd)
5b	$CDCl_3$ (0.75)	3.69 (d)	4.67 (d)	6.42 (d)	6.97 (dd)
7a	$CDCl_3$ (0.75)	2.33–2.28	0.25 (qt)		
7b	$CDCl_3$ (0.75)	2.18–2.13	−0.09 (qt)		
8	DMSO-d_6 (4.0)	7.46 (d)	6.93 (d)	6.90–7.00 (m)	
9	$CDCl_3$ (3.0)	7.49 (d)	7.09 (d)	7.05 (d)	7.23–7.30[a]

Chemical shifts in ppm from residual solvents as an internal standard.
[a] Chemical shift was not determined because of overlap with the signals of other protons.

Table 2. Absorption maxima λ_{max} and molar extinction coefficient log ε of **4**–**7**

Compound	Solvent	λ_{max} (nm) (log ε)					
		D[a]	Porphyrin				
		$\pi-\pi^*$	Soret	$Q_y(1,0)$	$Q_y(0,0)$	$Q_x(1,0)$	$Q_x(0,0)$
4a	THF	325 (5.15)	428 (5.33)	517 (4.32)	–[b]	590 (3.84)	644 (3.45)
4b	THF	325 (5.16)	430 (5.23)	517 (4.26)	–[b]	588 (3.81)	643 (3.46)
5a	$ClCH_2CH_2Cl$	297 (5.00)	429 (5.33)	518 (4.26)	–[b]	589 (3.76)	644 (3.37)
5b	$ClCH_2CH_2Cl$	297 (4.98)	429 (5.16)	518 (4.17)	–[b]	588 (3.71)	642 (3.20)
6a	$ClCH_2CH_2Cl$		428 (5.44)	517 (4.35)	548 (3.66)	589 (3.86)	644 (3.46)
6b	$ClCH_2CH_2Cl$		429 (5.38)	517 (4.34)	548 (3.64)	587 (3.85)	642 (3.37)
7a	$ClCH_2CH_2Cl$		426 (5.47)	517 (4.34)	549 (3.66)	591 (3.82)	648 (3.23)
7b	$ClCH_2CH_2Cl$		426 (5.47)	516 (4.34)	548 (3.66)	591 (3.83)	647 (3.30)
7a	THF		426 (5.45)	516 (4.34)	548 (3.74)	592 (3.86)	647 (3.44)
7b	THF		426 (5.44)	516 (4.32)	549 (3.73)	593 (3.84)	648 (3.45)

Measured in 5.0×10^{-6} M solution.
[a] D: phenylenediamine pendant group.
[b] The λ_{max} was not detected due to the broadening.

The spectral difference between the αααα and αβαβ isomers observed in ^{1}H NMR and absorption spectra is probably accounted for as follows. The pendant groups of the αβαβ isomer might be in equilibrium with the conformers, in which one or more strands lean toward the porphyrin ring. The equilibrium of the conformers might be related to the distortion and fluctuation of the porphyrin ring as indicated by the broadened Soret and Q bands.[11] On the other hand, such a conformation is less accessible in the αααα isomer probably due to the steric crowdedness, being accompanied by the restricted motion of the phenylene moieties of the pendant groups. It is consistent with the broad signals in ^{1}H NMR spectra.

Molecular dynamics calculation also supports the above-mentioned conformation of **5a** and **5b**. In one of the most stable conformations of the αβαβ isomer **5b**, the pendant groups lean toward the porphyrin ring, which is more distorted from planarity than that of the αααα isomer **5a**.

The reference porphyrin **12** bearing one anilinoanilino pendant group was prepared from **10** as illustrated

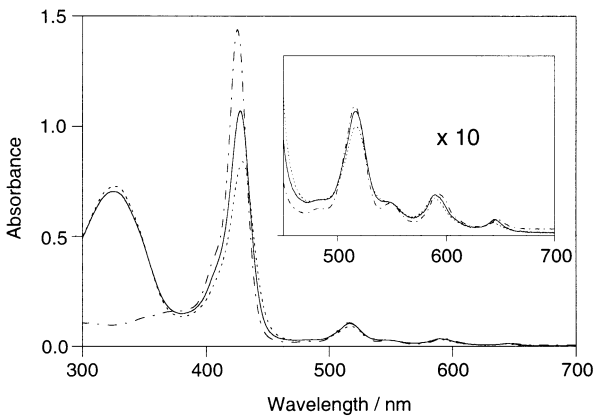
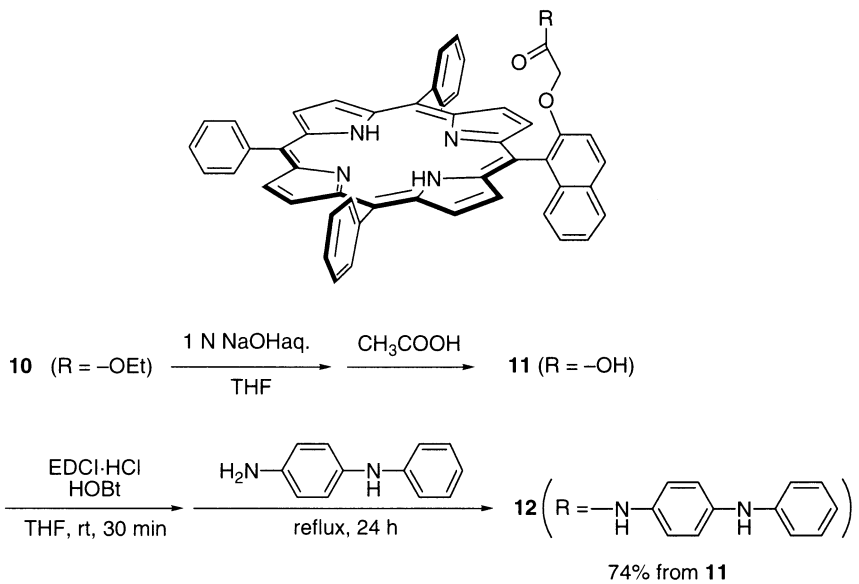


Figure 1. Absorption spectra in THF (5.0×10^{-6} M) of porphyrins **4a** (—), **4b** (– – –), and **7a** (–·–·–).

2.3. Electrochemistry

The electrochemical behavior of these porphyrins was studied by cyclic or differential pulse voltammetry (Table 3). In the cyclic voltammograms of **4**, the redox processes attributable to the phenylenediamine and porphyrin moieties were observed as illustrated in Scheme 3. Although the oxidation potentials of the phenylenediamine moieties of **4a** and **4b** were not largely different, they are more cathodic than that of **8**. A similar trend was observed in the case of **5a** bearing the anilinoanilino pendant groups, and **9** (Fig. 2). It should be noted that the porphyrin **12** exhibited the ca. 100 mV anodic oxidation potential of the anilinoanilino moiety. This shift might be based on the characteristics of the present π-conjugated system, which suggests a possibility of an electronic interaction between the pendant groups on the porphyrin scaffold.[13]



Scheme 2.

in Scheme 2. In the ^{1}H NMR spectrum of **12** in CD_2Cl_2, the signals of the phenylene protons, H_a and H_b, of the pendant group were observed in a higher field (δ=4.19 and 4.92, respectively) as observed in the αβαβ isomer **5b**.[12] These results support the above-mentioned conformation of **5b**, in which the pendant groups and porphyrin ring are present in close proximity.

Table 3. Redox potentials of the porphyrins and reference compounds

Compound (mM)	E (Por/Por$^{\cdot-}$)	E (D/D$^{\cdot+}$)[a]	E (D$^{\cdot+}$/D^{2+})
4a (0.25)[b]	−1.66	−0.12	+0.24
4b (0.25)[b]	−1.64	−0.10	+0.25
5a (0.25)[c]	−1.65	+0.28	
5b (0.25)[c]	−1.63	+0.28	
7a (0.25)[b]	−1.63		
7b (0.25)[b]	−1.60		
8 (1.0)[b]		−0.02	+0.33
9 (1.0)[c]		+0.36	
12 (1.0)[c]	−1.73	+0.38	

Potentials, V vs Fc/Fc$^+$; solv. THF containing 0.1 M Bu_4NClO_4.
[a] D: phenylenediamine moiety.
[b] Measured by cyclic voltammetry (scan rate=100 mV s^{-1}).
[c] Measured by differential pulse voltammetry (scan rate=20 mV s^{-1}).

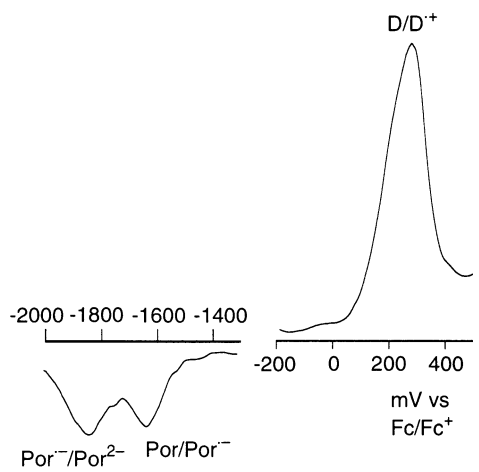
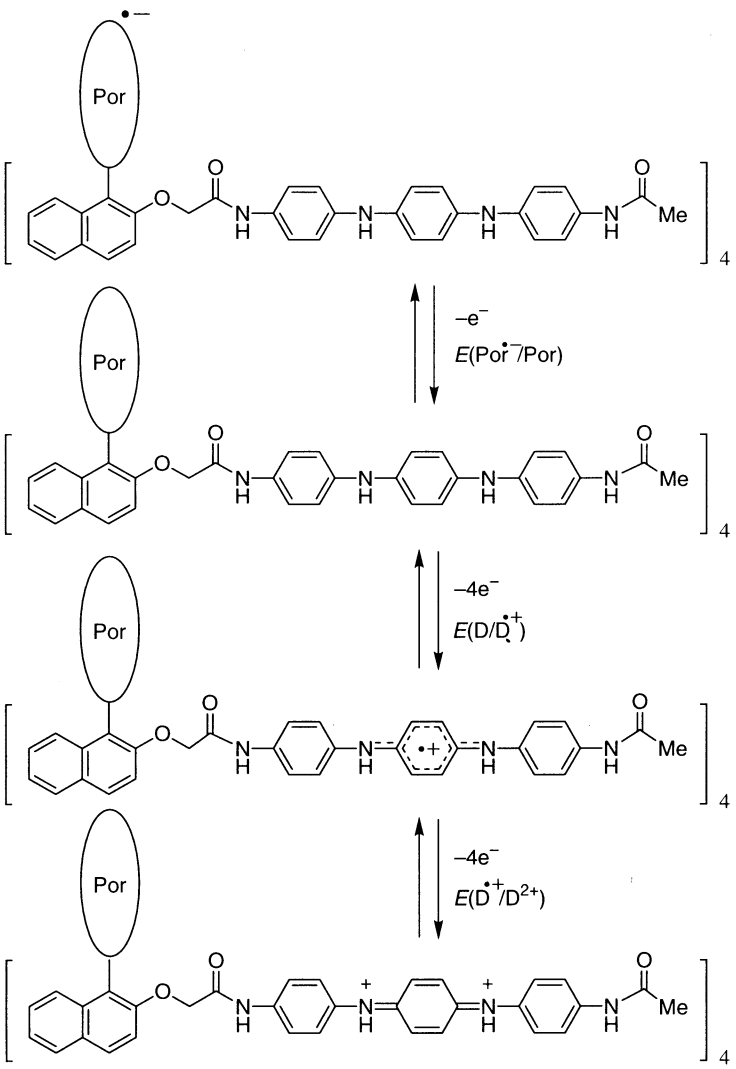


Figure 2. Differential pulse voltammogram of **5a**. [**5a**]=2.5×10^{-4} M, Solv. THF containing 0.1 M Bu_4NClO_4; scan rate: 20 mV s^{-1}; pulse width: 50 ms.



Scheme 3.

2.4. Fluorescence emission spectroscopy

The fluorescence emission spectroscopy with excitation of the *Q*(1,0) band was studied. Noteworthy is that the emission from the porphyrin moiety observed in **7** was almost completely quenched (<1%) in the case of both atropisomers **4a** and **4b**. Contrary to **4**, a similar quenching did not occur with **6** bearing the anilino pendant groups. Quenching of the emission of **4** appears to depend on the phenylenediamine function of the pendant group. This process is consistent with the difference in the redox potentials of each unit. In the case of **4a**, the photoinduced intramolecular electron transfer from the phenylenediamine moiety D to the excited singlet state of the porphyrin $^{1}Por^{*}$ is thermodynamically feasible.[14] The quenching behavior of **4b** is explained similarly.

The emission of **5a** or **5b** was quenched as observed in **4** (ca. 1%). On the contrary, **12** showed emission with ca. 50% intensity as compared with that of **7** (Fig. 3). The quenching in **5** and **12** is also based on the photoinduced intramolecular electron transfer from the phenylenediamine moiety to the excited singlet state of the porphyrin. The difference

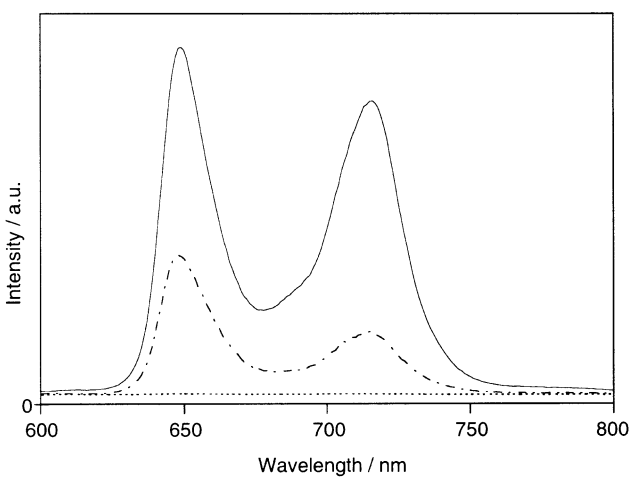
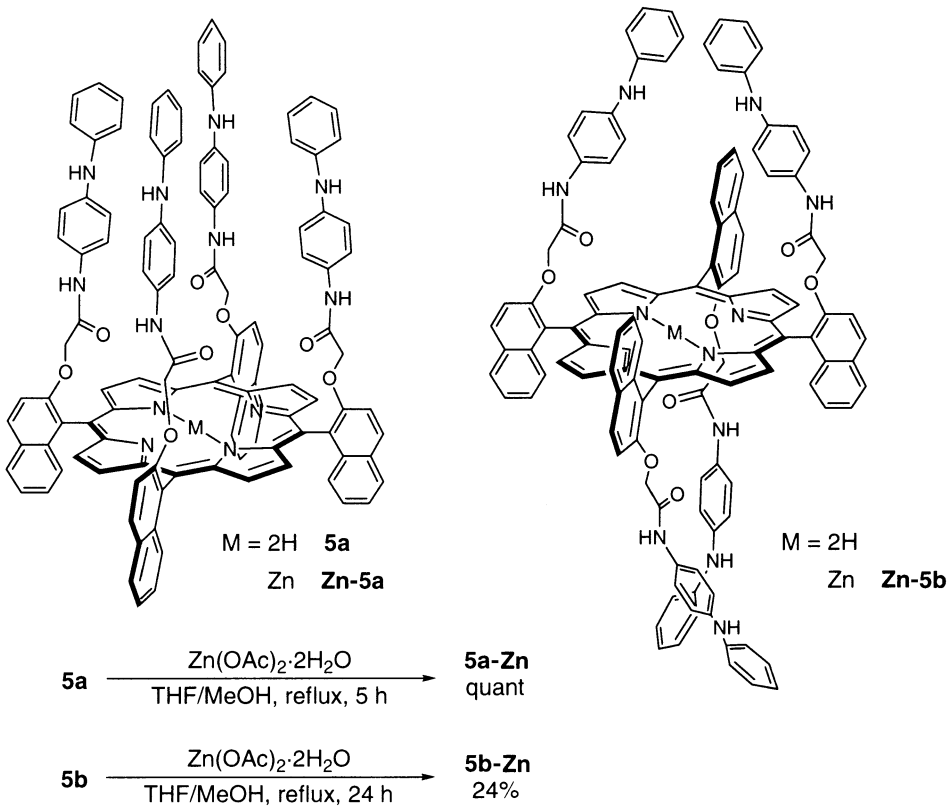


Figure 3. Fluorescence emission spectra in THF (5.0×10^{-6} M) of porphyrins **5a**,**b** (– – –), **7a** (—), and **12** (–·–·–) with excitation at Q_y(1,0) band.



Scheme 4.

observed between **5** and **12** might be reflected by the π-conjugated system of **5**, in which the pendant group undergoes the more facile oxidation.

2.5. Zinc complexation

The formation of the zinc complex of **5a** was performed by treatment with zinc(II) acetate dihydrate to give Zn-**5a** quantitatively (Scheme 4). In the zinc complexation, a zinc(II) species is likely to be introduced selectively from the side opposite to the phenylenediamine strand side because the corresponding αβαβ atropisomer **5b** was metallated with less efficiency in less than 24% yield.

In the ^{1}H NMR spectra of Zn-**5a**, the phenylene protons of the pendant moiety were not largely shifted in comparison with the corresponding free base **5a**. The broad signals of the phenylene protons close to the porphyrin moiety of Zn-**5a** were observed as described in **5a**, suggesting a similar structural circumstance of the pendant groups.

The oxidation potential of the phenylenediamine pendant groups of Zn-**5a** (+0.29 V vs Fc/Fc^{+}), which was not changed by complexation, was more cathodic than that of Zn-**12** (+0.38 V). Furthermore, the fluorescence emission of the porphyrin moiety of Zn-**5a** was quenched with more ease than that of Zn-**12** as observed in the free base **5** and **12**. The four-pendant group effect was again observed with the zinc complexes.

An αααα complex, in which four pendant groups are located on one side of the porphyrin plane, is considered to accommodate a coordination ligand on the other side.[15]

3. Conclusion

The porphyrins and the corresponding zinc complexes bearing dimensionally oriented π-conjugated pendant groups were synthesized and characterized. The structural and electronic characteristics depend on the atropisomers bearing the αααα and αβαβ pendant groups. The relatively fast photoinduced intramolecular electron transfer from the phenylenediamine moiety to the excited singlet state of the porphyrin moiety was demonstrated in both atropisomers. These π-conjugated systems are of potential use in a variety of photoreflactive electron transfer systems such as photocatalysis.

4. Experimental

4.1. General

All reagents and solvents were purchased from commercial sources and were further purified by the standard methods, if necessary. Thin-layer chromatography was carried on a Merck Kiesegel 60F_{254}. Melting points were determined on a Yanagimoto Micromelting Point Apparatus and were uncorrected. Infrared spectra were recorded on a Horiba FT-720. ^{1}H NMR or ^{13}C NMR spectra were recorded on a Varian INOVA 600 spectrometer (600 MHz) or a JEOL JNM-GSX-400 spectrometer (400 MHz) with a residual solvent as an internal standard. Mass spectra were recorded on a PerSeptive Biosystems Voyager RP (MALDI-TOF, a dithranol matrix) or a JEOL JMS-DX-303 (FAB, *m*-nitrobenzyl alcohol matrix) mass spectrometer. Absorption spectra were taken on a HITACHI

U-3000 spectrophotometer at 5.0×10^{-6} M concentration in $ClCH_2CH_2Cl$ or THF at 30°C. Fluorescence spectra were taken on a Shimadzu RF-5300PC spectrofluorophotometer at 5.0×10^{-6} M concentration in deaerated THF at room temperature. The cyclic and differential pulse voltammetry measurements were performed on a BAS CV-50W voltammetry analyzer with a three-electrode system consisting of a highly polished glassy carbon working electrode (BAS), a platinum auxiliary electrode (BAS), and an $Ag/AgNO_3$ (0.01 M) reference electrode (BAS) in deaerated THF containing 0.1 M Bu_4NClO_4 as a supporting electrolyte at room temperature. Potentials are given vs. Fc/Fc^+. The molecular dynamics calculation was performed using Discover 3 program of the Insight II molecular-modeling package from Molecular Simulations Inc.

4.1.1. *meso*-Tetrakis[2-(ethoxycarbonylmethoxy)-naphthyl]porphyrin (1). 2-(Ethoxycarbonylmethoxy)-naphthalenecarbaldehyde (2.58 g, 10.0 mmol) and Ph_4PCl (11.6 mg, 0.0310 mmol) were added to 100 mL of CH_2Cl_2 in a 200 mL round bottom flask under argon. Pyrrole (671 mg, 10.0 mmol) and then 1.0 mL of a stock solution of $BF_3{\cdot}OEt_2$ in CH_2Cl_2 (1.0 M, 1.0 mmol) were added. After stirring at room temperature for 30 min, DDQ (1.71 g, 7.50 mmol) was added. The dark brown mixture was stirred for 60 min, and then treated with 1 mL of triethylamine. The mixture was concentrated and the residue was washed with 150 mL of methanol. The crude product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give the porphyrin **1** as a mixture of the four atropisomers (αβαβ, ααββ, αααβ, and αααα, in the order of elution) in 30% yield. The four atropisomers were separated by further column chromatography on silica gel using solvents with gradient from CH_2Cl_2 to CH_2Cl_2–ethyl acetate (20:1 v/v). Furthermore, the αααα isomer (**1a**) and the αβαβ isomer (**1b**) were purified by recrystallization from CH_2Cl_2-methanol. **1a**: mp 290–291°C; R_f=0.10 (SiO_2, CH_2Cl_2); IR (KBr) 3318, 3058, 2979, 2927, 1756, 1735, 1508, 1288, 1200 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.51 (bs, 8H), 8.25 (d, 4H, J=9.1 Hz), 8.01 (d, 4H, J=8.2 Hz), 7.58 (d, 4H, J=9.1 Hz), 7.33 (dd, 4H, J=8.2, 6.8 Hz,), 7.00 (dd, 4H, J=8.6, 6.8 Hz), 6.90 (d, 4H, J=8.6 Hz) 4.37 (s, 8H), 3.96 (q, 8H, J=7.1 Hz), 0.97 (t, 12H, J=7.1 Hz), −2.14 (bs, 2H); ^{13}C NMR[16] ($CDCl_3$, 150 MHz) 169.1, 156.0, 137.9, 130.4, 129.0, 127.6, 127.4, 126.6, 125.8, 123.9, 114.6, 112.7, 66.8, 60.9, 13.9 ppm; MS (MALDI-TOF) m/z 1222.4 (M^+); UV–vis ($ClCH_2CH_2Cl$) λ_{abs} (log ε) 425 (5.55), 516 (4.37), 547 (3.69), 590 (3.88), 644 (3.27) nm; Anal. calcd for $C_{76}H_{62}N_4O_{12}{\cdot}0.5H_2O$: C, 74.07; H, 5.15, N, 4.55. Found: C, 74.02; H, 5.07; N, 4.42. **1b**: mp 285–287°C; R_f=0.63 (SiO_2, CH_2Cl_2); IR (KBr) 3321, 3060, 2960, 2931, 1757, 1740, 1506, 1286, 1201 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.52 (bs, 8H), 8.25 (d, 4H, J=9.2 Hz), 8.03 (d, 4H, J=8.2 Hz), 7.57 (d, 4H, J=9.2 Hz), 7.34 (dd, 4H, J=8.2, 6.9 Hz), 6.98 (dd, 4H, J=8.6, 6.9 Hz), 6.88 (d, 4H, J=8.6 Hz), 4.38 (s, 8H), 3.93 (q, 8H, J=7.1 Hz), 0.93 (t, 12H, J=7.1 Hz), −2.12 (bs, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) 169.0, 155.8, 138.0, 130.4, 128.9, 127.7, 127.4, 126.4, 125.6, 123.8, 114.3, 112.6, 66.5, 60.9, 13.9 ppm; MS (MALDI-TOF) m/z 1222.6 (M^+); Anal. calcd for $C_{76}H_{62}N_4O_{12}$: C, 74.62; H, 5.11; N, 4.58. Found: C, 74.42; H, 5.10; N, 4.47.

4.1.2. *meso*-Tetrakis[2-(carboxymethoxy)naphthyl]porphyrin (2). Porphyrin **2** was prepared by hydrolysis of **1** as reported in a literature.[9] In a 100 mL round bottom flask, 3.0 mL of aqueous NaOH (1 M, 3.0 mmol) was added to the THF solution of **1a** (73 mg, 0.060 mmol), and the mixture was stirred overnight at room temperature. The solvent was evaporated to dryness. The residue was dissolved in water, and then 10% (v/v) acetic acid in water was added to the solution until the solution was neutralized and the solid deposited. The solid was filtrated and dried under vacuum to give **2a** in 92% yield. Formation of **2a** was confirmed by disappearance of signals for four ethyl groups in the ^1H NMR spectrum. The porphyrin **2b** was synthesized by the same procedure for **2a**. These products were used for further synthesis without purification.

4.1.3. *N*-(4-Acetylaminophenyl)-*N*′-(4-aminophenyl)-1,4-phenylenediamine (3). *Procedure 1*: A 200 mL round bottom flask with a dropping funnel was charged with *N*,*N*′-bis(4′-aminophenyl)-1,4-phenylenediamine[17] (1.45 g, 5.00 mmol) in THF (20 mL) under argon and the solution was cooled to 0°C. Triethylamine (1 mL) was added, and then 40 mL of a THF solution of acetic anhydride (510 mg, 5.00 mmol) was added dropwise. After stirring at 0°C for 1 h, the reaction mixture was dropped to 500 mL of water to reprecipate the solid mixture of *N*,*N*′-bis(4′-aminophenyl)-1,4-phenylenediamine, *N*-(4-acetylaminophenyl)-*N*′-(4-aminophenyl)-1,4-phenylenediamine, and *N*,*N*′-bis(4′-acetylaminophenyl)-1,4-phenylenediamine. The column chromatography on silica gel eluting with ethyl acetate, followed by further reprecipitation from hexane (200 mL), gave **3** in 48% yield (total yield from *p*-phenylenediamine was 12%). *Procedure 2*: **3** was also prepared by oxidative coupling of *p*-phenylenediamine (0.97 g, 9.0 mmol) with *N*-acetyl-*N*′-phenyl-1,4-phenylenediamine (1.70 g, 7.5 mmol) using the same procedure for the preparation of *N*,*N*′-bis(4′-aminophenyl)-1,4-phenylenediamine. In this reaction, *N*-acetyl-*N*′-phenyl-1,4-phenylenediamine was added as a 10 mL of the DMF solution. Total yield (60%) of **3** from *p*-phenylenediamine was higher as compared with that obtained in the procedure 1. **3**: mp 201–203°C; R_f=0.28 (SiO_2, ethyl acetate); IR (KBr) 3363, 3302, 3039, 1650, 1605, 1550, 1504, 1288, 1226, 872, 825 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6) δ 9.62 (bs, 1H), 7.51 (bs, 1H), 7.33 (d, 2H, J=8.9 Hz), 7.20 (bs, 1H), 6.88 (d, 2H, J=8.5 Hz), 6.81 (d, 2H, J=8.9 Hz), 6.79–6.75 (m, 4H), 6.51 (d, 2H, J=8.5 Hz), 4.64 (bs, 2H), 1.98 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) 167.6, 143.0, 141.5, 140.5, 134.5, 133.4, 130.7, 120.9, 120.8, 120.4, 116.0, 115.0, 23.94 ppm; MS (FAB) m/z 332 (M^+); Anal. calcd for $C_{20}H_{20}N_4O$: C, 72.27; H, 6.06; N, 16.86. Found: C, 71.88; H, 6.21; N, 16.41.

4.1.4. *meso*-Tetrakis-[2-[[[4-[4-(4-acetylaminoanilino)-anilino]phenyl]carbamoyl]methoxy]naphthyl]porphyrin (4). In a 100 mL round bottom flask with a reflux condenser, a mixture of **2a** (50.0 mg, 0.0450 mmol) and 1,1′-carbonyldiimidazole (43.8 mg, 0.270 mmol) in THF (20 mL) was stirred at room temperature for 1.5 h. Then, a THF solution (20 mL) of **3** (120 mg, 0.360 mmol) was added to the reaction mixture, which was stirred at refluxing temperature for 2 days. After the reaction completed, the reaction mixture was evaporated in vacuo. **4a** was isolated in 58% yield by column chromatography of the residue on silica gel

using solvents with gradient from ethyl acetate to ethyl acetate–methanol (19:1 v/v) and reprecipitation from THF–ether. **4b** was synthesized from **2b** by the same procedure for **4a**. Isolation by column chromatography of the residue on silica gel using solvents with gradient from ethyl acetate to ethyl acetate–methanol (9:1 v/v) and recrystallization from THF–methanol gave **4b** in 56% yield. **4a**: mp 276–278°C; R_f=0.58 (SiO_2, ethyl acetate–methanol=5:1 v/v); IR (KBr) 3379, 3325, 3062, 1674, 1612, 1512, 1304, 1273, 1111, 818, 748 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 9.66 (bs, 4H), 8.55 (bs, 8H), 8.34 (d, 4H, J=9.2 Hz), 8.11 (d, 4H, J=8.4 Hz), 8.04 (bs, 4H), 7.68 (d, 4H, J=9.2 Hz), 7.65 (bs, 4H), 7.44 (bs, 4H), 7.40–7.33 (m, 12H), 7.12 (dd, 4H, J=8.8, 6.8 Hz), 6.92–6.82 (m, 20H), 6.77 (d, 8H, J=8.8 Hz), 6.35–6.15 (br, 16H), 4.26 (bs, 8H), 2.09 (bs, 12H), −2.06 (bs, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) 167.3, 164.7, 155.5, 140.3, 140.2, 136.9, 136.6, 136.0, 130.9, 130.6, 128.5, 128.1, 127.7, 126.9, 126.2, 123.4, 122.8, 120.4, 119.8, 118.9, 118.5, 115.7, 114.5, 113.9, 113.0, 66.4, 23.7 ppm; MS (MALDI-TOF) m/z 2370.8 $(M+H)^+$; Anal. calcd for $C_{148}H_{118}N_{20}O_{12}\cdot 3H_2O$: C, 73.37; H, 5.16; N, 11.56. Found: C, 73.14; H, 5.06; N, 11.44. **4b**: mp 257–260°C; R_f=0.45 (SiO_2, ethyl acetate–methanol=5:1 v/v); IR (KBr) 3377, 3319, 3028, 1672, 1612, 1504, 1304, 1267, 1093, 822, 748 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 9.70 (bs, 4H), 8.46 (bs, 8H), 8.19 (d, 4H, J=9.2 Hz), 8.07 (d, 4H, J=8.4 Hz), 7.53–7.46 (m, 8H), 7.42–7.30 (m, 12H), 7.09 (bs, 4H), 6.98 (d, 4H, J=8.5 Hz), 6.86–6.74 (m, 12H), 6.68 (d, 8H, J=8.3 Hz), 6.36 (d, 8H, J=8.3 Hz), 5.21 (bs, 4H), 4.99 (d, 8H, J=8.3 Hz), 4.24–4.04 (m, 16H), 2.03 (bs, 12H), −1.66 (bs, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) 167.5, 163.5, 155.1, 140.2, 140.0, 136.5, 136.2, 135.2, 130.9, 128.2, 127.7, 126.8, 126.6, 123.6, 122.7, 120.6, 118.9, 118.1, 117.7, 115.7, 114.2, 113.4, 112.5, 66.4, 23.8 ppm; MS (MALDI-TOF) m/z 2368.9 (M^+); Anal. calcd for $C_{148}H_{118}N_{20}O_{12}\cdot 3H_2O$: C, 73.37; H, 5.16; N, 11.56. Found: C, 73.40; H, 4.98; N, 11.40.

4.1.5. *meso*-Tetrakis[2-[(4-anilinophenyl)carbamoyl]-methoxy]naphthylporphyrin (5). The porphyrins **5a** and **5b** were prepared as mentioned in the preparation of **4**. **5a** was isolated in 42% yield by column chromatography on silica gel using solvents with gradient from CH_2Cl_2 to CH_2Cl_2–ethyl acetate (8:2 v/v) and recrystallization from THF–methanol. **5b** was isolated in 82% yield by column chromatography on silica gel using solvents with gradient from CH_2Cl_2 to CH_2Cl_2–ethyl acetate (7:3 v/v) and recrystallization from THF–methanol.

For another procedure, **5a** was also synthesized by condensation using EDCl·HCl as the condensation agent. EDCI·HCl (22.3 mg, 0.117 mmol) and HOBt (59.4 mg, 0.117 mmol) were added to a THF solution (10 mL) of **2** (21.6 mg, 0.0194 mmol) at room temperature and the mixture solution was stirred for 30 min. Then, a THF solution (15 mL) of *N*-phenyl-1,4-phenylenediamine (21.5 mg, 0.117 mmol) was added to the reaction mixture, which was stirred for 24 h and then evaporated. Purification of the crude product by the above-mentioned procedure gave **5a** in 68% yield. **5a**: mp 135–140°C; R_f=0.13 (SiO_2, CH_2Cl_2–ethyl acetate=1: 1 v/v); IR (KBr) 3381, 3356, 3325, 3053, 2922, 2852, 1684, 1595, 1512, 1496, 1325, 1271, 1109, 1076, 800, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.62 (bs, 8H), 8.27 (d, 4H, J=9.2 Hz), 8.12 (d, 4H, J=8.3 Hz), 7.50–7.43 (m, 8H), 7.33 (d, 4H, J=9.2 Hz), 7.31–7.24 (m, 4H), 7.14 (dd, 8H, J=8.0, 7.3 Hz), 6.82 (t, 4H, J=7.3 Hz), 6.63 (d, 8H, J=8.0 Hz), 5.78 (bs, 4H), 5.61 (br, 8H), 5.29 (br, 8H), 5.20 (bs, 4H), 3.62 (bs, 8H), −1.80 (bs, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) 164.6, 155.2, 142.8, 138.4, 137.0, 131.4, 129.2, 129.0, 127.9, 127.4, 127.4, 124.3, 124.0, 120.3, 119.6, 116.6, 113.8, 112.5, 66.8 ppm; MS (MALDI-TOF) m/z 1777.1 $(M+H)^+$; Anal. calcd for $C_{116}H_{86}N_{12}O_8\cdot H_2O$: C, 77.66; H, 4.94; N, 9.37. Found: C, 77.53; H, 4.96; N, 9.53. **5b**: mp 167°C (decomp.); R_f=0.34 (SiO_2, CH_2Cl_2–ethyl acetate=1:1 v/v); IR (KBr) 3384, 3356, 3315, 3053, 2918, 2845, 1680, 1595, 1512, 1497, 1325, 1269, 1093, 806, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.54 (bs, 8H), 8.29 (d, 4H, J=9.1 Hz), 8.07 (d, 4H, J=8.3 Hz), 7.37 (dd, 4H J=8.3, 6.8 Hz), 7.31–7.25 (m, 8H), 6.97 (dd, 8H, J=8.6, 7.3 Hz), 6.89 (dd, 4H, J=8.6, 6.8 Hz), 6.67 (t, 4H, J=7.3 Hz), 6.42 (d, 8H, J=8.6 Hz), 4.94 (bs, 4H), 4.68–4.66 (m, 12H), 4.05 (bs, 8H), 3.69 (d, 8H, J=8.6 Hz), −1.58 (bs, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) 163.5, 154.8, 142.5, 137.6, 136.7, 131.3, 129.0, 128.9, 128.7, 127.8, 127.6, 127.4, 124.4, 123.6, 120.0, 117.6, 116.2, 115.5, 114.7, 114.1, 112.9, 66.9 ppm; MS (MALDI-TOF) m/z 1777.4 $(M+H)^+$; Anal. calcd for $C_{116}H_{86}N_{12}O_8\cdot H_2O$: C, 77.66; H, 4.94; N, 9.37. Found: C, 77.76; H, 4.89; N, 9.34.

4.1.6. *meso*-Tetrakis[2-(phenylcarbamoyl)methoxy]-naphthylporphyrin (6). Porphyrins **6** were similarly prepared as mentioned in the preparation of **4**. **6a** was isolated in 48% yield by column chromatography on silica gel using solvents with gradient from CH_2Cl_2 to CH_2Cl_2–ethyl acetate (10:3 v/v) and recrystallization from THF–ether. **6b** was isolated in 82% yield by column chromatography on silica gel using solvents with gradient from CH_2Cl_2 to CH_2Cl_2–ethyl acetate (7:3 v/v) and recrystallization from THF–methanol or THF–ether. **6a**: mp 296–298°C; R_f=0.48 (SiO_2, CH_2Cl_2–ethyl acetate=1:1 v/v); IR (KBr) 3384, 3320, 3059, 2922, 1691, 1601, 1531, 1508, 1442, 1333, 1271, 1240 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$), δ 8.65 (bs, 8H), 8.36 (d, 4H, J=9.1 Hz), 8.13 (d, 4H, J=8.1 Hz), 7.50–7.46 (m, 12H), 7.30–7.27 (m, 4H), 6.34 (t, 4H, J=7.6 Hz), 5.91 (dd, 8H, J=8.0, 7.6 Hz), 5.80 (bs, 4H), 5.36 (d, 8H, J=8.0 Hz), 3.74 (bs, 8H), −1.72 (bs, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) 164.8, 155.1, 138.1, 135.4, 131.6, 129.0, 127.9, 127.5, 127.4, 127.3, 124.4, 124.1, 123.2, 118.2, 113.7, 112.3, 66.9 ppm; MS (MALDI-TOF) m/z 1412.9 $(M+H)^+$; Anal. calcd for $C_{92}H_{66}N_8O_8\cdot H_2O$: C, 77.30; H, 4.79; N, 7.84. Found: C, 77.25; H, 4.67; N, 7.81. **6b**: mp >300°C; R_f=0.59 (SiO_2, CH_2Cl_2–ethyl acetate=1:1 v/v); IR (KBr) 3384, 3319, 3057, 2917, 2854, 1697, 1601, 1533, 1508, 1444, 1335, 1269, 1240 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.62 (bs, 8H), 8.35 (d, 4H, J=9.0 Hz), 8.08 (d, 4H, J=8.3 Hz), 7.51 (d, 4H, J=9.0 Hz), 7.39 (dd, 4H, J=8.3, 7.0 Hz), 7.07 (d, 4H, J=8.4 Hz), 6.81 (dd, 4H, J=8.4, 7.0 Hz), 6.02 (t, 4H, J=7.5 Hz), 5.13 (dd, 8H, J=8.1, 7.5 Hz), 4.96 (bs, 4H), 4.37 (bs, 8H), 4.07 (d, 8H, J=8.1 Hz), −1.44 (bs, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) 163.9, 154.9, 136.8, 134.8, 131.5, 128.9, 127.7, 127.5, 127.5, 126.5, 124.4, 123.4, 122.7, 116.8, 113.9, 112.8, 67.2 ppm; MS (MALDI-TOF) m/z 1412.7 $(M+H)^+$; Anal. calcd for $C_{92}H_{66}N_8O_8\cdot H_2O$: C, 77.30; H, 4.79; N, 7.84. Found: C, 77.50; H, 4.64; N, 7.81.

4.1.7. *meso*-Tetrakis[2-(propylcarbamoyl)methoxy]-naphthylporphyrin (7). Porphyrins **7** were prepared as mentioned in the preparation of **4**. **7a** was isolated in 81% yield by column chromatography on silica gel using solvents with gradient from chloroform–ethyl acetate (1:1 v/v) and recrystallization from THF–ether. **7b** was similarly isolated in 46% yield. **7a**: mp 287–288°C; R_f=0.025 (SiO_2, CH_2Cl_2–ethyl acetate=1:1 v/v); IR (KBr) 3410, 3319, 3060, 2962, 2931, 2873, 1684, 1590, 1541, 1508, 1338, 1270, 1219, 1107, 810, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 8.51 (bs, 8H), 8.34 (d, 4H, *J*=9.2 Hz), 8.07 (d, 4H, *J*=8.3 Hz), 7.65 (d, 4H, *J*=9.2 Hz), 7.39 (dd, 4H, *J*=8.3, 6.7 Hz), 7.07 (dd, 4H, *J*=8.6, 6.7 Hz), 6.91 (d, 4H, *J*=8.6 Hz), 5.27 (bs, 4H), 4.42 (bs, 8H), 2.33–2.28 (m, 8H), 0.25 (qt, 8H, *J*=7.3, 7.3 Hz), −0.17 (t, 12H, *J*=7.3 Hz), −2.07 (bs, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) 167.6, 155.6, 155.6, 137.5, 131.5, 129.2, 127.8, 127.4, 127.1, 125.0, 124.9, 124.4, 114.0, 113.3, 68.8, 39.8, 21.6, 10.2 ppm; MS (MALDI-TOF) *m/z* 1276.6 $(M+H)^+$; Anal. calcd for $C_{80}H_{74}N_8O_8$: C, 75.33; H, 5.85; N, 8.79. Found: C, 75.38; H, 5.88; N, 8.78. **7b**: mp 288–289°C; R_f=0.32 (SiO_2, CH_2Cl_2–ethyl acetate=1:1 v/v); IR (KBr) 3410, 3317, 3062, 2962, 2931, 2870, 1681, 1589, 1527, 1512, 1335, 1265, 1211, 1095, 810, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.52 (bs, 8H), 8.35 (d, 4H, *J*=9.2 Hz), 8.10 (d, 4H, *J*=8.3 Hz), 7.60 (d, 4H, *J*=9.2 Hz), 7.43 (dd, 4H, *J*=8.3, 6.8 Hz), 7.11 (dd, 4H, *J*=8.6, 6.8 Hz), 6.97 (d, 4H, *J*=8.6 Hz), 4.95 (br, 4H), 4.41 (bs, 8H), 2.18–2.13 (m, 8H), −0.096 (qt, 8H, *J*=7.3, 7.3 Hz), −0.52 (t, 12H, *J*=7.3 Hz), −2.05 (bs, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) 167.5, 155.2, 137.4, 131.5, 129.1, 127.9, 127.2, 127.0, 124.7, 124.4, 113.5, 113.2, 66.1, 39.6, 21.4, 9.9 ppm; MS (MALDI-TOF) *m/z* 1276.4 $(M+H)^+$; Anal. calcd for $C_{80}H_{74}N_8O_8$: C, 75.37; H, 5.87; N, 8.86. Found: C, 75.38; H, 5.88; N, 8.78.

4.1.8. 2-[[[4-[4-(4-Acetylaminoanilino)anilino]phenyl]-carbamoyl]methoxy]naphthalene (8). In a 100 mL round bottom flask, a mixture of 2-(carboxymethoxy)naphthalene[13] (61 mg, 0.30 mmol) and 1,1′-carbonyldiimidazole (73 mg, 0.45 mmol) in THF was stirred at room temperature for 1.5 h. Then, 20 mL of a THF solution of **3** (100 mg, 0.30 mmol) was added to the reaction mixture, which was stirred for 12 h. After the reaction completed, the reaction mixture was evaporated in vacuum. After addition of $CHCl_3$ (ca. 100 mL), the insoluble solid was filtrated and washed with $CHCl_3$ to give **8** without further purification in a quantitative yield. **8**: mp 232–233°C; R_f=0.20 (SiO_2, $CHCl_3$–ethyl acetate=2:1 v/v); IR (KBr) 3402, 3286, 3140, 3054, 3032, 1680, 1666, 1604, 1512, 1304, 1257, 1219, 1180, 1018, 1057, 818, 741 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 9.89 (bs, 1H), 9.66 (bs, 1H), 7.90–7.82 (m, 2H), 7.80 (d, 1H, *J*=8.3 Hz), 7.77 (bs, 1H), 7.72 (bs, 1H), 7.50–7.40 (m, 3H), 7.40–7.29 (m, 5H), 7.00–6.85 (m, 8H), 4.77 (s, 2H), 1.99 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) 167.7, 165.8, 155.9, 141.4, 140.5, 137.1, 136.5, 134.2, 131.3, 129.9, 129.6, 128.9, 127.7, 127.0, 126.7, 124.1, 121.6, 120.7, 119.5, 118.9, 118.9, 116.1, 115.6, 107.4, 67.5, 24.0 ppm; MS (FAB) *m/z* 516 (M^+); Anal. calcd for $C_{32}H_{28}N_4O_3$: C, 74.40; H, 5.46; N, 10.85. Found: C, 74.02; H, 5.45; N, 10.90.

4.1.9. 2-[(4-Anilinophenyl)carbamoyl]methoxynaphthalene (9). Compound **9** was prepared as mentioned in the preparation of **8** and it was isolated in 83% yield by column chromatography of the residue on silica gel using solvents with gradient from CH_2Cl_2 to CH_2Cl_2–ethyl acetate (9:1 v/v) and recrystallization from $CHCl_3$–hexane. **9**: mp 181–182°C; R_f=0.75 (SiO_2, CH_2Cl_2–ethyl acetate=8.5:1 v/v); IR (KBr) 3392, 3290, 3040, 2915, 1680, 1660, 1597, 1514, 1500, 1313, 1255, 1219, 1182, 1060, 1039, 841, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.23 (bs, 1H), 7.85–7.77 (m, 3H), 7.52–7.48 (m, 3H), 7.41 (ddd, 1H, *J*=8.4, 6.8, 1.5 Hz), 7.30–7.23 (m, 4H), 7.10–7.04 (m, 4H), 6.93 (dt, 1H, *J*=7.3, 1.1 Hz), 5.69 (bs, 1H), 4.76 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) 165.9, 154.8, 143.2, 140.2, 134.3, 130.3, 130.1, 129.6, 129.4, 127.7, 127.1, 126.9, 124.5, 121.8, 120.9, 118.8, 118.0, 117.4, 107.9, 67.6 ppm; MS (FAB) *m/z* 368 (M^+); Anal. calcd for $C_{24}H_{20}N_2O_2$: C, 78.24; H, 5.47; N, 7.60. Found: C, 78.16; H, 5.51; N, 7.63.

4.1.10. 5-[2-(Ethoxycarbonylmethoxy)naphthyl]-10,15,20-triphenylporphyrin (10). 2-(Ethoxycarbonylmethoxy)naphthalenecarbaldehyde (647 mg, 2.5 mmol), benzardehyde (901 mg, 7.5 mmol) and Ph_4PCl (11.6 mg, 0.0310 mmol) were added to 100 mL of CH_2Cl_2 in a 200 mL round bottom flask under argon. Pyrrole (671 mg, 10.0 mmol) and then 1.0 mL of a stock solution of $BF_3{\cdot}(OEt)_2$ in CH_2Cl_2 (1.0 M, 1.0 mmol) were added. After stirring at room temperature for 30 min, DDQ (1.71 g, 7.50 mmol) was added. The dark brown mixture was stirred for 60 min, and then treated with 1 mL of triethylamine. The crude product was purified by chromatography on silica gel using CH_2Cl_2 to afford four fractions mainly. The first fraction was 5,10,15,20-tetraphenylporphyrin (5.5% yield). The porphyrin **10** was eluted as the second fraction (22%). The third and fourth fractions were found to be two atropisomers (αα and αβ) of 5,10-bis[2-(ethoxycarbonylmethoxy)naphthyl-15,20-diphenylporphyrin (2.3 and 3.0%, respectively). **10**: mp >300°C; R_f=0.55 (SiO_2, CH_2Cl_2); IR (KBr) 3315, 3053, 2955, 2925, 1757, 1736, 1473, 1348, 1193 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6) δ 8.86 (bs, 4H), 8.75 (d, 2H, *J*=4.8 Hz), 8.66 (d, 2H, *J*=4.8 Hz), 8.41 (d, 1H, *J*=9.1 Hz), 8.31–8.20 (m, 6H), 8.14 (d, 1H, *J*=8.3 Hz), 7.89–7.75 (m, 10H), 7.36 (dd, 1H, *J*=8.3, 6.7 Hz), 7.01 (dd, 1H, *J*=8.5, 6.7 Hz), 6.68 (d, 1H, *J*=8.5 Hz), 4.62 (s, 2H), 3.96 (q, 2H, *J*=7.1 Hz), 0.97 (t, 3H, *J*=7.1 Hz), −2.56 (bs, 2H); ^{13}C NMR (acetone-d_6, 150 MHz) 168.8, 156.4, 142.4, 142.3, 138.4, 134.7, 134.6, 131.0, 129.2, 128.3, 128.2, 128.1, 127.2, 127.1, 127.0, 124.5, 124.0, 120.8, 120.3, 120.2, 114.2, 114.0, 65.7, 60.8, 22.8, 13.8 ppm; MS (MALDI-TOF) *m/z* 767 $(M+H)^+$; Anal. calcd for $C_{52}H_{38}N_4O_3$: C, 81.44; H, 4.99, N, 7.31. Found: C, 81.15; H, 5.00; N, 7.28.

4.1.11. 5-[2-(Carboxymethoxy)naphthyl]-10,15,20-triphenylporphyrin (11). Porphyrin **11** was prepared by hydrolysis of **10** according to the similar procedure to that of **2**. The porphyrin **11** was used for the synthesis of **12** without purification.

4.1.12. 5-[2-[[(4-Anilinophenyl)carbamoyl]methoxy]-naphthyl]-10,15,20-triphenylporphyrin (12). In a round-bottom flask with a reflux condenser, EDCI·HCl (23.3 mg, 122 μmol) and HOBt (16.4 mg, 122 μmol) were added to a THF solution (50 mL) of **11** (60.0 mg, 81.2 mmol) at room

temperature and the mixture solution was stirred for 30 min. Then, a THF solution (10 mL) of *N*-phenyl-1,4-phenylenediamine (20.6 mg, 122 μmol) was added to the reaction mixture, which was stirred for 24 h and then evaporated. Purification of the crude product by column chromatography on silica gel eluting with CH_2Cl_2 and further reprecipitation from CH_2Cl_2–hexane afforded **12** as a purple crystal in 74% yield. **12**: mp 150–151°C; R_f=0.20 (SiO_2, CH_2Cl_2); IR (KBr) 3382, 3317, 3054, 2921, 2852, 1687, 1596, 1512, 1496, 1347, 1322, 1269, 1104, 1072, 965, 802 cm^{-1}; ^1H NMR (600 MHz, CD_2Cl_2) δ 8.85 (br, 4H), 8.79 (d, 2H, *J*=4.3 Hz), 8.62 (d, 2H, *J*=4.3 Hz), 8.39 (dd, 1H, *J*=9.2, 0.7 Hz), 8.27 (d, 1H, *J*=7.1 Hz), 8.20 (d, 2H, *J*=7.1 Hz), 8.16 (d, 1H, *J*=8.5 Hz), 8.03 (d, 1H, *J*=7.1 Hz), 7.99 (d, 2H, *J*=7.1 Hz), 7.83–7.67 (m, 9H), 7.65 (d, 1H, *J*=9.2 Hz), 7.48 (ddd, 1H, *J*=8.5, 6.6, 1.1 Hz), 7.37 (d, 1H, *J*=8.5 Hz), 7.22 (ddd, 1H, *J*=8.5, 6.6, 1.1 Hz), 7.11 (dd, 2H, *J*=8.5, 7.3 Hz), 6.83 (dt, 1H, *J*=7.3, 1.1 Hz), 6.43 (dd, 2H, *J*=8.5, 1.1 Hz), 5.26 (bs, 1H), 4.97 (bs, 1H), 4.92 (d, 2H, *J*=8.7 Hz), 4.53 (bs, 2H), 4.16 (d, 2H, *J*=8.7 Hz), −2.54 (bs, 2H); ^{13}C NMR (150 MHz, CD_2Cl_2) 164.6, 155.9, 143.1, 142.3, 142.1, 138.4, 137.5, 135.1, 134.9, 134.8, 131.6, 129.7, 129.5, 129.3, 128.2, 128.1, 127.8, 127.5, 127.2, 127.1, 127.0, 125.7, 124.7, 121.4, 120.8, 120.6, 118.7, 117.0, 116.9, 114.6, 112.4, 68.7 ppm; MS (MALDI-TOF) *m/z* 906 $(M+H)^+$; Anal. calcd for $C_{62}H_{44}N_6O_2{\cdot}0.2CH_2Cl_2$: C, 81.02; H, 4.85; N, 9.11. Found: C, 81.28; H, 5.14; N, 8.84.

4.1.13. Zinc complexation of 5a to Zn-5a. A THF solution (5 mL) of **5a** (24 mg, 14 μmol) was added to a methanol solution of zinc(II) acetate dihydrate (13 mg, 70 μmol), which was refluxed under argon for 12 h and then evaporated. Purification of the crude product by column chromatography on alumina (acetone–methanol 95:5 v/v) gave Zn-**5a** in 90% yield. Zn-**5a**: mp 223–225°C (uncorrected); R_f=0.60 (SiO_2, ethyl acetate); IR (KBr) 3380, 3051, 1678, 1593, 1511, 1496, 1323, 1271, 1109, 799 cm^{-1}; ^1H NMR (600 MHz, CD_2Cl_2) δ 8.71 (bs, 8H), 8.28 (d, 4H, *J*=9.2 Hz), 8.12 (d, 4H, *J*=8.5 Hz), 7.45 (dd, 4H, *J*=8.5, 6.6 Hz), 7.41 (d, 4H, *J*=8.7 Hz), 7.35 (d, 4H, *J*=9.2 Hz), 7.23 (dd, 4H, *J*=8.7, 6.6 Hz), 7.13 (dd, 8H, *J*=8.2, 7.3 Hz), 6.80 (t, 4H, *J*=7.3 Hz), 6.64 (d, 8H, *J*=8.2 Hz), 5.71 (bs, 4H), 5.67–5.60 (br, 8H), 5.28 (bs, 4H), 5.24–5.12 (br, 8H), 3.60 (bs, 8H); MS (TOF) *m/z* 1838.8 $(M+2H)^+$; UV–vis (CH_2Cl_2) λ_{max} (log ε) 549 (4.34), 430 (5.45), 303 (4.95); Anal. calcd for $C_{116}H_{84}N_{12}O_8Zn{\cdot}H_2O$: C, 75.01; H, 4.67; N, 9.05. Found: C, 74.90; H, 4.78; N, 8.91.

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