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A Direct Comparison of the Aggregation Behavior of Phthalocyanines and 2,3-Naphthalocyanines

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Abstract—Two pairs of analogous zinc(II) phthalocyanines and 2,3-naphthalocyanines with eight butylthio or 3,6-dioxa-1-decylthio substituents have been synthesized and shown to exhibit a substantial aggregation tendency in organic solvents. The visible spectra of the octakis(3,6-dioxa-1-decylthio) naphthalocyanine **7** have been recorded in THF with different concentrations and the data have been analyzed using a nonlinear least-squares fitting procedure giving ϵ_m (777 nm), ϵ_d (777 nm), and K_d at 1.95×10^6 M^{-1} cm^{-1}, 1.29×10^5 M^{-1} cm^{-1}, and 2.72×10^5 M^{-1}, respectively. Simulated visible spectra for the pure monomeric and dimeric **7** have also been obtained. By variable-concentration and variable-temperature visible spectroscopic studies, the heats of aggregation of all these macrocycles in toluene have also been determined (-17.1 to -105.0 kJ mol^{-1}). These values depend largely on the additional interactions due to the substituents.

Introduction

Phthalocyanines are one of the major types of tetrapyrrole derivative showing a wide range of applications in materials science, medicine, and catalysis.[1] Owing to the extended π system, it is well-known that these macrocyclic compounds exhibit a high aggregation tendency forming dimeric and oligomeric species in solutions.[2] It has been shown that this molecular association greatly influences the intrinsic nature of the macrocycles including their spectroscopic,[2,3] photophysical,[4] electrochemical,[5] and conducting properties,[6] and eventually their performance as superior molecular materials. The strong intermolecular interactions also hinder the purification and characterization processes. Phthalocyanines that are not substituted appropriately have a poor mobility in silica gel and alumina columns and purification can only be performed by the less efficient Soxhlet extraction procedure and re-precipitation.

A substantial number of investigations have been focused on the aggregation behavior of substituted phthalocyanines in various solvent systems in which the aggregation number and some thermodynamic parameters have been determined.[2,7] Being larger π systems, 2,3-naphthalocyanines are expected to have an even higher aggregation tendency. Studies in this area, however, have been extremely rare.[8] As synthetic routes to differently substituted 2,3-naphthalocyanines have been recently developed,[9] these open up an entry to allow a more detailed examination of the characteristics of these larger macrocyclic π system and a comparison with those of their phthalocyanine analogues.

This paper reports the preparation of two pairs of phthalocyanines and 2,3-naphthalocyanines containing alkylthio or dioxaalkylthio side chains. The aggregation behavior of these compounds, as probed by variable-concentration and temperature UV–Vis spectroscopy, is discussed and compared.

Results and Discussion

The naphthalocyanines **6** and **7** were prepared by the method reported by us[9c,d] and Kitahara et al.,[10] which involves the aromatic nucleophilic substitution of dibromonaphthalene **1** with the corresponding thiolate ions, followed by a typical base-promoted cyclization (Scheme 1). The first step of these reactions is promoted by copper(I) oxide, which increases the yield of the dinitriles **4** and **5** from ca. 30 to 70%. Two types of substituents, namely butylthio (SC_4H_9) and 3,6-dioxa-1-decylthio [$S(CH_2CH_2O)_2C_4H_9$] groups, which have very different chain length and polarity were selected. To compare directly the aggregation behavior of naphthalocyanines and phthalocyanines, the phthalocyanine analogues with identical substituents were also prepared by similar methodology. Thus treatment of dichlorobenzene **8** with thiols **2** and **3**, in the presence of sodium hydride and copper(I) oxide, afforded the dinitriles **9** and **10**, respectively, which underwent cyclization to give the respective phthalocyanines **11** and **12** (Scheme 2). The former

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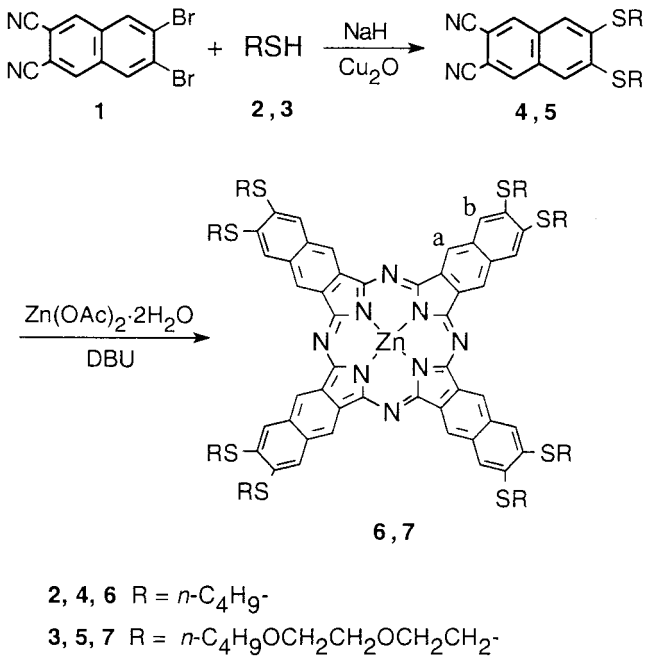


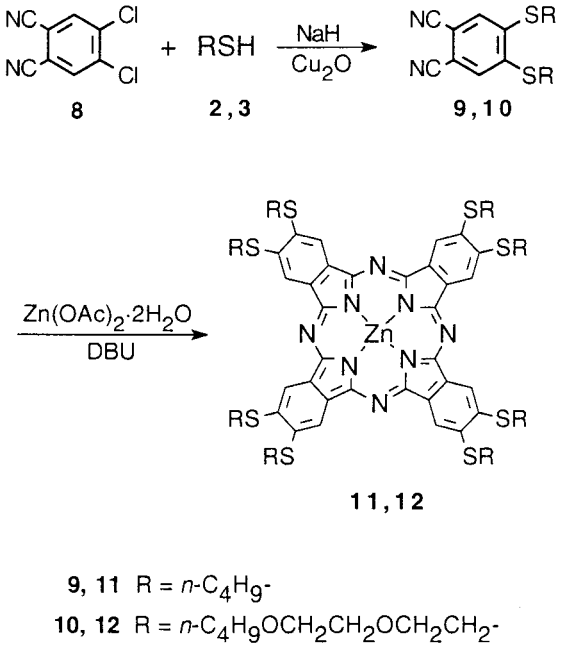
2, 4, 6 R = *n*-C_4H_9-

3, 5, 7 R = *n*-$C_4H_9OCH_2CH_2OCH_2CH_2$-

Scheme 1.

macrocycle was synthesized previously by metallation of the metal-free analogue which was prepared from 1,2-dibutylthiobenzene using a different synthetic route.[11]

Due to the eight peripheral substituents, all macrocycles possessed good solubility in common organic solvents and could be purified by column chromatography using THF as a co-eluent, which breaks up the molecular aggregation and increases the mobility of these compounds on silica gel columns.[9d] All new compounds were characterized using various spectroscopic methods and elemental analyses.[12]



9, 11 R = *n*-C_4H_9-

10, 12 R = *n*-$C_4H_9OCH_2CH_2OCH_2CH_2$-

Scheme 2.

^{1}H NMR spectra of the naphthalocyanines **6** and **7** were recorded in $CDCl_3$ and showed only broad signals for the substituents while the aromatic protons' signals were not observed. However, in the presence of pyridine-d_5, the latter emerged as two relatively broad bands at δ 8.87–9.00 and 7.85–8.04, which could be assigned to the H_a and H_b protons, respectively, and the aliphatic protons' signals were better resolved. This observation suggests that the π–π interactions of these macrocycles are significant in chloroform and can be partially disrupted by pyridine as described previously.[9d,13] The phthalocyanine analogues **11** and **12** have similar spectral properties. The downfield aromatic proton signal was clearly seen at δ 9.28 [for **11** (7.8 mM)] or δ 9.61 [for **12** (1.5 mM)] in pyridine-d_5. As the latter signal was much broader than the former, even though it was recorded at a lower concentration, compound **12** seems to be more strongly aggregated than the thiobutyl counterpart **11**.

The UV–Vis spectra of all these macrocycles in THF displayed a typical B band (354–366 nm) and Q band (775–778 nm for **6** and **7**, 701–709 nm for **11** and **12**), along with up to two vibronic bands near the latter. Due to the extended conjugation, the Q band of the naphthalocyanines **6** and **7** was red-shifted by ca. 70 nm compared with that of the phthalocyanine analogues. As the effects of aggregation on the spectral properties of phthalocyanines have been well-documented,[2–4] special emphasis was placed on the naphthalocyanine system. Fig. 1 shows the changes in the visible spectrum of **7** in THF with concentration. It can be seen that the molar absorptivity of the Q band increases from 9.8×10^5 to 2.2×10^6 M^{-1} cm^{-1} as the concentration decreases from 4.20×10^{-6} to 7.31×10^{-8} M which can be attributed to the effect of aggregation. In contrast with the phthalocyanine system in which the Q band due to the aggregated (mainly dimeric) species is normally blue-shifted by ca. 30 nm compared with that of the monomeric

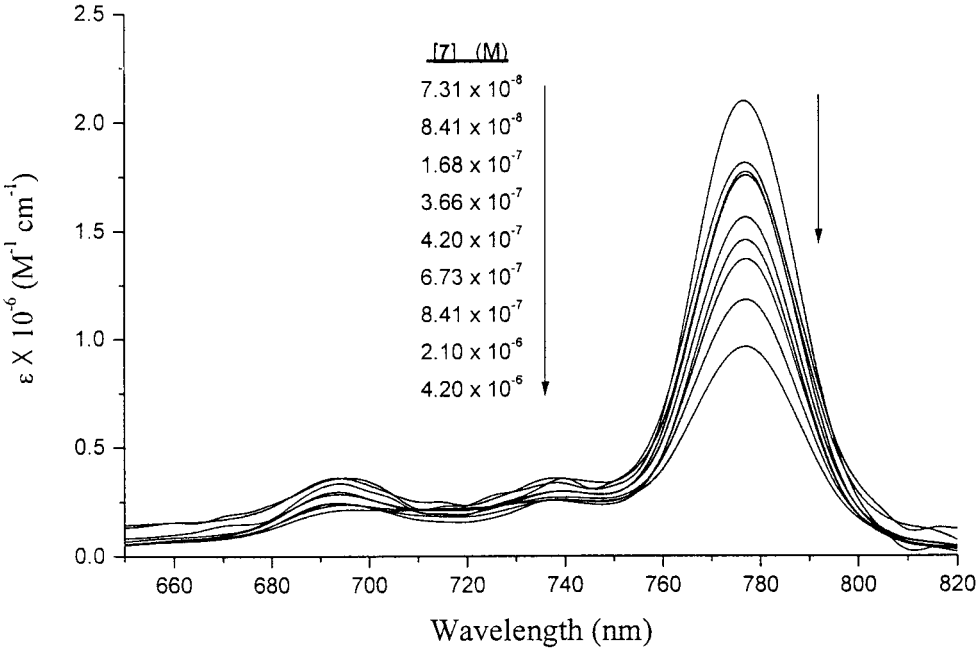


Figure 1. Concentration dependence of visible spectrum of **7** in THF.

species, the Q band of **7** remains essentially unshifted as observed previously in other naphthalocyanines.[8,9c]

These spectral data were analyzed using a nonlinear least-squares fitting method, which assumes that no higher aggregates than dimers are formed.[14] According to some previous studies,[2a,7a,14,15] this assumption is normally valid, in particular in such dilute solutions. In this case, the observed absorbance, A, of a solution in a 1-cm cell can be written as:

$$A = \epsilon_m[m] + 2\epsilon_d[d] \quad (1)$$

where ϵ_m and ϵ_d are molar absorptivities ($M^{-1}\,cm^{-1}$) of monomer and dimer, respectively, at a given wavelength, with ϵ_d expressed in terms of the monomer, and [m] and [d] being concentrations (M) of monomer and dimer, respectively. The dimerization constant (K_d) and the total concentration [C_t] can be expressed as:

$$K_d = [d]/[m]^2 \quad (2)$$

$$[C_t] = [m] + 2[d] \quad (3)$$

Eqs. (1)–(3) can be combined and rearranged to give:

$$A = \epsilon_d[C_t] + (\epsilon_m - \epsilon_d)[-1 + \sqrt{(1 + 8K_d[C_t])}]/4K_d \quad (4)$$

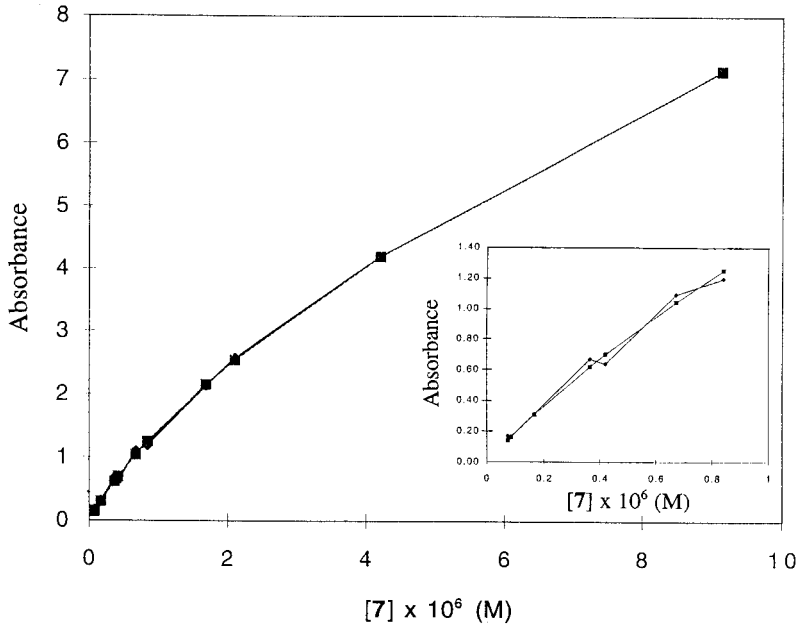


Figure 2. Plots of experimental (◆) and calculated (■) absorbances vs. the concentration of **7** in THF. The inset shows an expansion of the lower-concentration region.

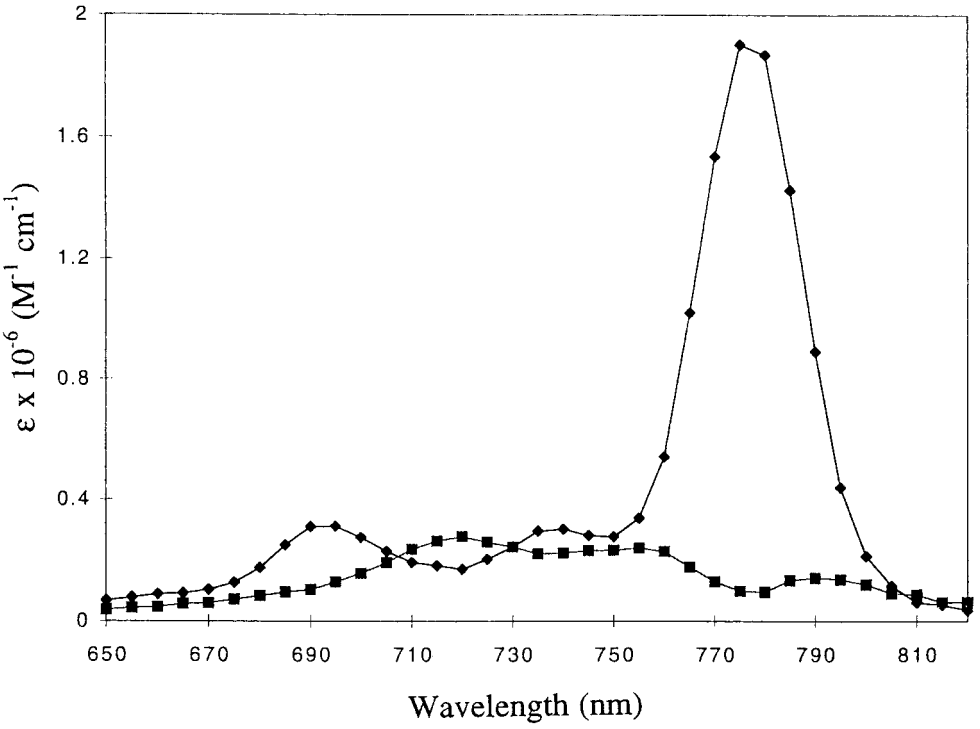


Figure 3. Simulated visible spectra for pure monomeric (◆) and dimeric (■) **7** in THF.

in which A and $[C_t]$ are measurable quantities and the three variables ϵ_m, ϵ_d and K_d can be determined by a nonlinear least-squares fitting procedure using a series of absorbances at a given wavelength measured at different concentrations. By recording the visible spectra of **7** in THF at concentrations ranging from 7.31×10^{-8} to 4.20×10^{-6} M and using the observed absorbance at the Q band (777 nm), the best-fitted values of ϵ_m (777 nm), ϵ_d (777 nm), and K_d were determined to be 1.95×10^6 M^{-1} cm^{-1}, 1.29×10^5 M^{-1} cm^{-1}, and 2.72×10^5 M^{-1}, respectively. As shown in Fig. 2, the calculated values of absorbance are very close to the observed values and the aggregation causes a deviation from the Beer–Lambert law. The former two ϵ values are higher than the corresponding values for phthalocyanines by ca. one order of magnitude,[2b,14] while the dimerization constant falls into the region (10^4–10^6 M^{-1}) which is typical for other phthalocyanines and naphthalocyanines in various solvent systems.[2b,8,14,15]

By repeating this procedure at different wavelengths (from 650 to 820 nm) with a fixed value of K_d (2.72×10^5 M^{-1}), a series of (ϵ_m, ϵ_d) values were obtained which could be used

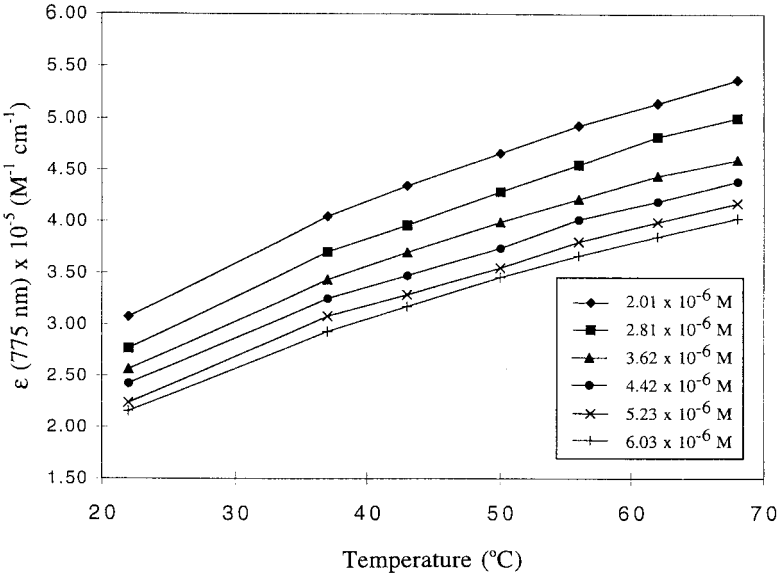


Figure 4. Variation of molar absorptivity at 775 nm for **7** in toluene with concentration and temperature.

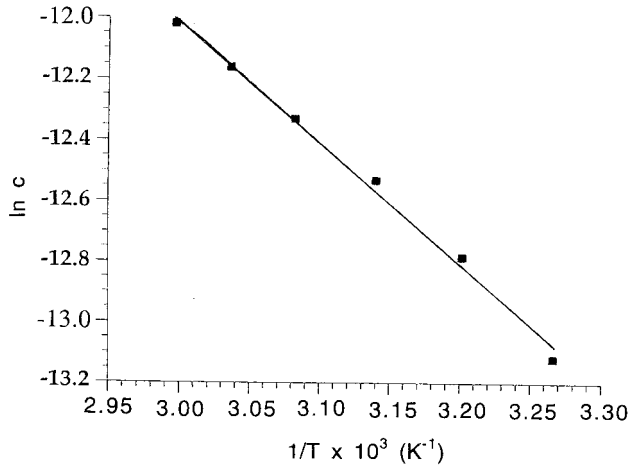


Figure 5. Plot of ln c vs. $1/T\times10^3$ for **7** in toluene.

to simulate the visible spectra of pure monomeric **7** and dimeric **7** in THF (Fig. 3). It can be seen that the monomeric spectrum shows a typical and very intense Q band and two well-resolved vibronic bands, while the dimeric spectrum exhibits three relatively weak bands at 720, 755 and 790 nm. This spectrum resembles the simulated dimeric spectra of the tetrahalophthalocyanine analogues,[14b] which also display three absorption bands from ca. 620–700 nm but with lower absorptivities. As the differences in absorptivities between the monomeric and dimeric species are much larger in the naphthalocyanine system than in the phthalocyanine counterpart, this may explain why the Q band of naphthalocyanines remains essentially unshifted even in the presence of a significant amount of dimeric species.

The visible spectra of these macrocycles were found to be not only concentration dependent but also temperature dependent. Fig. 4 shows the variation of the molar absorptivity at 775 nm (the apparent Q band maximum) for **7** in toluene with concentration and temperature. It can be seen that a higher temperature, similar to the effect of lower concentration, can also reduce the extent of aggregation leading to a higher absorptivity. At a fixed value of ϵ_{obs} which can be achieved by changing the concentration and temperature of the solutions, the weight fraction of the monomer is constant and the following relationship holds:[7b,16]

$$\Delta H_a = \mathrm{R}\,\Delta \ln c/\Delta(1/T) \quad (5)$$

where ΔH_a is the heat of association, R is the gas constant, c and T are the concentration and temperature, respectively. Based on the data in Fig. 4, there are six pairs of (c, T) values at an arbitrary value of ϵ_{obs} which can be used to generate a plot of ln c vs. $1/T$. As shown in Fig. 5, a best-fitted straight line is obtained from which the ΔH_a value for **7** in toluene can be estimated to be -38.4 kJ mol^{-1}. Since the spectral features were more susceptible to concentration than to temperature, a rather narrow concentration range had to be maintained; otherwise, the spectral changes could not be restored within attainable temperatures. The other three macrocycles **6**, **11** and **12** behaved similarly and by using a similar treatment, the heats of association for these compounds were also determined to be -26.4, -17.1, and -105.0 kJ mol^{-1}, respectively. It is clear that the substituents greatly affect the aggregation tendency of these π systems. With nonpolar butylthio substituents, the naphthalocyanine system appears to be slightly more aggregated and releases more thermal energy as the molecules associate. This is expected due to the larger π system of naphthalocyanines. The value is comparable with those of tetrasulfonated phthalocyanines in water.[17] But with longer and more polar 3,6-dioxa-1-decylthio groups, a reversed order is observed showing that the dipole–dipole interactions associated with the side chains play a crucial role. It seems that the macrocycle **12**, under the influence of the substituents, has a better molecular contact than the naphthalocyanine analogue **7**. The results are in accord with the NMR data as described above. It is worth noting that the ΔH_a value of **12** is comparable with that of the metal-free phthalocyanine prepared by Nolte et al.,[7b] which contains four fused benzo 18-crown-6 moieties (-125 kJ mol^{-1}). As **12** does not contain peripheral benzene rings, the extraordinary high ΔH_a value of the Nolte's phthalocyanine may not be due to the additional $\pi-\pi$ interactions arising from the peripheral benzene rings as suggested by the authors, but rather may arise from the interactions due to the oligo(oxyethylene) units.

In summary, we have prepared two pairs of phthalocyanine and naphthalocyanine analogues for a direct comparison of their aggregation behavior. Both classes of tetrapyrrole derivatives show a substantial aggregation tendency in solution and the degree of association depends largely on the additional interactions due to the substituents.

Experimental

General

Reactions were performed under an atmosphere of nitrogen. THF was distilled from sodium benzophenone ketyl. Butan-1-ol and hexan-1-ol were distilled from sodium prior to use. *N*,*N*-Dimethylformamide (DMF) was pre-dried over barium oxide and distilled under reduced pressure. Chromatographic purifications were performed on silica gel columns (Merck, Kieselgel 60, 70–230 mesh) with the indicated eluents. The hexane used in chromatography was distilled from anhydrous $CaCl_2$. All other reagents and solvents were of reagent grade and used as received. 2,3-Dibromo-6,7-dicyanonaphthalene (**1**)[18] and 1,2-dichloro-4,5-dicyanobenzene (**8**)[19] were prepared according to literature procedures.

Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer (^{1}H, 300; ^{13}C, 75.4 MHz) or a Bruker ARX 500 spectrometer (^{1}H, 500 MHz) with $SiMe_4$ as an internal reference. IR spectra were measured on a Nicolet Magna 550 FT-IR spectrometer as KBr pellets. UV–Vis spectra were taken on a Hitachi U-3300 spectrophotometer equipped with a temperature controller. Electron impact (EI) and liquid secondary-ion (LSI) mass spectra were recorded on a Hewlett–Packard 5989B mass spectrometer and Bruker APEX 47e Fourier transform ion cyclotron resonance (FTICR) mass spectrometer, respectively. The latter employed 3-nitrobenzyl

alcohol as the matrix. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

General procedure for the preparation of dinitriles

1-Butanethiol (**2**) or 3,6-dioxa-1-decanethiol (**3**) (2.1 equiv.) was added slowly to an ice-cooled suspension of NaH (60% dispersion in mineral oil, 2.5 equiv.) in DMF. The mixture was stirred for a few minutes until the evolution of hydrogen gas was complete. 2,3-Dibromo-6,7-dicyanonaphthalene (**1**) or 1,2-dichloro-4,5-dicyanobenzene (**8**) (1.0 equiv.) and copper(I) oxide (2.0 equiv.) were then added and the mixture was refluxed for 3 h. The cooled mixture was poured into ice then extracted with diethyl ether. The combined organic portions were washed with ammonia solution (35%) and water, then dried over anhydrous $CaCl_2$. The volatiles were removed by rotary evaporation and the residue was purified by column chromatography.

2,3-Dibutylthio-6,7-dicyanonaphthalene (4). According to the general procedure, compound **1** (0.68 g, 2.0 mmol) was treated with 1-butanethiol (**2**) (0.45 mL, 4.2 mmol) in DMF (50 mL) to give **4**, which was purified by chromatography with $CHCl_3$ as eluent. A yellow solid was obtained. Yield: 0.46 g (65%), mp 148–150°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.16 (s, 2H, ArH), 7.58 (s, 2H, ArH), 3.09 (t, J=7.5 Hz, 4H, SCH_2), 1.79 (quintet, J=7.5 Hz, 4H, CH_2), 1.55 (sextet, J=7.5 Hz, 4H, CH_2), 0.99 (t, J=7.5 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.4 MHz): δ 142.7, 134.1, 130.8, 123.0, 116.1, 109.3, 32.6, 30.1, 22.2, 13.6. MS (EI): m/z 354 (M^+). Anal. Calcd for $C_{20}H_{22}N_2S_2$: C, 67.76; H, 6.25; N, 7.90. Found: C, 67.70; H, 6.24; N, 7.76.

2,3-Dicyano-6,7-bis(3,6-dioxa-1-decylthio)naphthalene (5). By using compound **1** (0.34 g, 1.0 mmol) and 3,6-dioxa-1-decanethiol (**3**) (0.37 g, 2.1 mmol) as the starting materials and following the general procedure, compound **5** was obtained as a yellow solid after being purified by chromatography with hexane/ethyl acetate (3:2) as eluent. Yield: 0.38 g (72%), mp 45–47°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.18 (s, 2H, ArH), 7.77 (s, 2H, ArH), 3.82 (t, J=7.5 Hz, 4H, OCH_2), 3.65–3.68 (m, 4H, OCH_2), 3.57–3.60 (m, 4H, OCH_2), 3.46 (t, J=7.5 Hz, 4H, OCH_2), 3.31 (t, J=7.5 Hz, 4H, SCH_2), 1.56 (quintet, J=7.5 Hz, 4H, CH_2), 1.35 (sextet, J=7.5 Hz, 4H, CH_2), 0.91 (t, J=7.5 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.4 MHz): δ 142.1, 134.2, 131.1, 124.4, 115.9, 109.5, 71.3, 70.7, 70.0, 69.2, 32.7, 31.6, 19.2, 13.9. MS (EI): m/z 530 (M^+). Anal. Calcd for $C_{28}H_{38}N_2O_4S_2$: C, 63.37; H, 7.22; N, 5.28; S, 12.08. Found: C, 63.64; H, 7.24; N, 5.49; S, 12.38.

1,2-Dibutylthio-4,5-dicyanobenzene (9). By using the general procedure, compound **8** (0.79 g, 4.0 mmol) was treated with 1-butanethiol (**2**) (0.9 mL, 8.4 mmol) in DMF (50 mL) to give **9**. The crude product was purified by chromatography with $CHCl_3$ as eluent to yield a white solid. Yield: 1.13 g (93%), mp 109–111°C (lit.[11] mp 110–112°C). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.4 MHz): δ 144.2, 128.1, 115.7, 111.0, 32.4, 30.0, 22.0, 13.6. MS (EI): m/z 304 (M^+).

1,2-Dicyano-4,5-bis(3,6-dioxa-1-decylthio)benzene (10). By using compound **8** (0.39 g, 2.0 mmol) and 3,6-dioxa-1-decanethiol (**3**) (0.75 g, 4.2 mmol) as the starting materials and following the general procedure, compound **10** was obtained as a white solid after being purified by chromatography with hexane/ethyl acetate (9:1) as eluent. Yield: 0.87 g (90%), mp 40–41°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.63 (s, 2H, ArH), 3.80 (t, J=7.5 Hz, 4H, OCH_2), 3.63–3.66 (m, 4H, OCH_2), 3.56–3.59 (m, 4H, OCH_2), 3.46 (t, J=7.5 Hz, 4H, OCH_2), 3.24 (t, J=7.5 Hz, 4H, SCH_2), 1.57 (quintet, J=7.5 Hz, 4H, CH_2), 1.35 (sextet, J=7.5 Hz, 4H, CH_2), 0.92 (t, J=7.5 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.4 MHz): δ 144.0, 129.4, 115.5, 111.5, 71.3, 70.8, 70.0, 69.3, 32.7, 31.7, 19.2, 13.9. MS (EI): m/z 480 (M^+). Anal. Calcd for $C_{24}H_{36}N_2O_4S_2$: C, 59.97; H, 7.55; N, 5.83. Found: C, 59.45; H, 7.88; N, 5.35.

General procedure for the cyclization of dinitriles

A mixture of dinitrile (2.6 equiv.) and $Zn(OAc)_2{\cdot}2H_2O$ (1.0 equiv.) in butan-1-ol or hexan-1-ol was heated to 90°C, then 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (ca. 0.5 mL) was added and the mixture was stirred at 140°C for 3 h. The mixture was cooled then added dropwise to a mixture of methanol/water (1:1). The precipitate formed was filtered and washed with water, acetone and methanol successively. The crude product was then purified by chromatography giving a green solid.

(3,4,12,13,21,22,30,31-Octabutylthio-2,3-naphthalocyaninato)zinc(II) (6). According to the general procedure, dinitrile **4** (354 mg, 1.0 mmol) was treated with $Zn(OAc)_2{\cdot}2H_2O$ (82 mg, 0.37 mmol) in butan-1-ol (5 mL) to give **6**, which was purified by chromatography with toluene/THF (7:3) as eluent. Yield: 236 mg (64%). ^{1}H NMR [$CDCl_3$/pyridine-d_5 (7:3), 300 MHz]: δ 8.87 (br. s, 8H, ArH), 7.85 (br. s, 8H, ArH), 3.04–3.16 (m, 16H, SCH_2), 1.70–1.90 (m, 16H, CH_2), 1.45–1.65 (m, 16H, CH_2), 0.96 (t, J=7.5 Hz, 24H, CH_3). UV–Vis (THF, λ_{max} nm): 355, 693, 745, 778. MS (LSI): an isotopic cluster peaking at m/z 1482.33 (Calcd for M^+ 1482.42).

[3,4,12,13,21,22,30,31-Octakis(3,6-dioxa-1-decylthio)-2,3-naphthalocyaninato]zinc(II) (7). By using the general procedure, dinitrile **5** (200 mg, 0.38 mmol) was treated with $Zn(OAc)_2{\cdot}2H_2O$ (30 mg, 0.14 mmol) in hexan-1-ol (10 mL) to give **7**, which was purified by chromatography with toluene/THF (1:1) as eluent. Yield: 93 mg (45%). ^{1}H NMR [$CDCl_3$/pyridine-d_5 (7:3), 300 MHz]: δ 9.00 (br. s, 8H, ArH), 8.04 (br. s, 8H, ArH), 3.90 (t, J=7.5 Hz, 16H, OCH_2), 3.67–3.69 (m, 16H, OCH_2), 3.58–3.60 (m, 16H, OCH_2), 3.34–3.45 (m, 32H, OCH_2 and SCH_2), 1.51 (quintet, J=7.5 Hz, 16H, CH_2), 1.28 (sextet, J=7.5 Hz, 16H, CH_2), 0.79 (t, J=7.5 Hz, 24H, CH_3). ^{13}C{^{1}H} NMR [$CDCl_3$/pyridine-d_5 (7:3), 75.4 MHz]: δ 152.0, 135.5, 134.7, 131.4, 128.0, 120.0, 71.0, 70.4, 69.9, 69.4, 32.9, 31.5, 19.0, 13.7. UV–Vis (THF, λ_{max} nm): 354, 702, 740, 777. MS (LSI): an isotopic cluster peaking at m/z 2186.7 (Calcd for M^+ 2186.8). Anal. Calcd for $C_{112}H_{152}N_8O_{16}S_8Zn$: C, 61.47; H, 7.00; N, 5.12; S, 11.72. Found: C, 60.88; H, 7.35; N, 4.77; S, 10.82.

(2,3,9,10,16,17,23,24-Octabutylthiophthalocyaninato)-zinc(II) (11).[11] According to the general procedure, dinitrile **9** (0.61 g, 2.0 mmol) was treated with $Zn(OAc)_2{\cdot}2H_2O$ (0.16 g, 0.73 mmol) in butan-1-ol (10 mL) to give **11**, which was purified by chromatography with toluene/THF (4:1) as eluent. Yield: 0.47 g (73%). ^1H NMR [pyridine-d_5, 300 MHz]: δ 9.28 (s, 8H, ArH), 3.60 (t, J=7.5 Hz, 16H, SCH_2), 2.06 (quintet, J=7.5 Hz, 16H, CH_2), 1.76 (sextet, J=7.5 Hz, 16H, CH_2), 1.11 (t, J=7.5 Hz, 24H, CH_3). $^{13}C\{^1H\}$ NMR [$CDCl_3$/pyridine-d_5 (7:3), 75.4 MHz]: δ 151.4, 138.3, 134.9, 119.9, 33.1, 30.6, 22.1, 13.5. MS (LSI): an isotopic cluster peaking at m/z 1282.29 (Calcd for M^+ 1282.35). Anal. Calcd for $C_{64}H_{80}N_8S_8Zn$: C, 59.90; H, 6.28; N, 8.73. Found: C, 58.92; H, 6.33; N, 8.26.

[2,3,9,10,16,17,23,24-Octakis(3,6-dioxa-1-decylthio)-phthalocyaninato]zinc(II) (12). According to the general procedure, dinitrile **10** (0.86 g, 1.79 mmol) was treated with $Zn(OAc)_2{\cdot}2H_2O$ (0.14 g, 0.64 mmol) in hexan-1-ol (25 mL) to give **12**, which was purified by chromatography with toluene/THF (1:1) as eluent. Yield: 0.18 g (20%). ^1H NMR (pyridine-d_5, 500 MHz): δ 9.61 (br. s, 8H, ArH), 4.24–4.25 (m, 16H, OCH_2), 3.89–3.93 (m, 16H, OCH_2), 3.77–3.82 (m, 32H, OCH_2), 3.53 (t, J=6.3 Hz, 16H, SCH_2), 1.61 (quintet, J=7.0 Hz, 16H, CH_2), 1.40 (sextet, J=7.4 Hz, 16H, CH_2), 0.84 (t, J=7.4 Hz, 24H, CH_3). UV–Vis (THF, λ_{max} nm): 366, 632, 701. MS (LSI): an isotopic cluster peaking at m/z 1986.7 (Calcd for M^+ 1986.8). Anal. Calcd for $C_{96}H_{144}N_8O_{16}S_8Zn$: C, 58.00; H, 7.30; N, 5.64. Found: C, 57.01; H, 7.37; N, 5.33.

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References

1. (a) *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Lever, A. B. P. Eds.; VCH: New York, 1989; Vol. 1; 1993; Vols. 2 and 3; 1996; Vol. 4. (b) McKeown, N. B. *Phthalocyanine Materials: Synthesis, Structure and Function*; Cambridge University Press: Cambridge, 1998. (c) Lukyanets, E. A. *J. Porphyrins Phthalocyanines* **1999**, *3*, 424. (d) Ali, H.; van Lier, J. E. *Chem. Rev.* **1999**, *99*, 2379.

2. (a) Nevin, W. A.; Liu, W.; Lever, A. B. P. *Can. J. Chem.* **1987**, *65*, 855 and references therein. (b) Schutte, W. J.; Sluyters-Rehbach, M.; Sluyters, J. H. *J. Phys. Chem.* **1993**, *97*, 6069. (c) Zelina, J. P.; Njue, C. K.; Rusling, J. F.; Kamau, G. N.; Masila, M.; Kibugu, J. *J. Porphyrins Phthalocyanines* **1999**, *3*, 188 and references therein.

3. (a) Abkowitz, M.; Monahan, A. R. *J. Chem. Phys.* **1973**, *58*, 2281. (b) Kobayashi, N.; Higashi, R.; Ishii, K.; Hatsusaka, K.; Ohta, K. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1263.

4. (a) Spikes, D. J. *Photochem. Photobiol.* **1986**, *43*, 691. (b) Vacus, J.; Simon, J. *Adv. Mater.* **1995**, *7*, 797. (b) Dhami, S.; Phillips, D. *J. Photochem. Photobiol. A: Chem.* **1996**, *100*, 77. (c) Howe, L.; Zhang, J. Z. *J. Phys. Chem. A* **1997**, *101*, 3207. (d) Lang, K.; Kubát, P.; Mosinger, J.; Wagnerová, D. M. *J. Photochem. Photobiol. A: Chem.* **1998**, *119*, 47. (e) Ng, A. C. H.; Li, X.-Y.; Ng, D. K. P. *Macromolecules* **1999**, *32*, 5292.

5. (a) Louati, A.; El Meray, M.; André, J. J.; Simon, J.; Kadish, K. M.; Gross, M.; Giraudeau, A. *Inorg. Chem.* **1985**, *24*, 1175. (b) Isago, H.; Leznoff, C. C.; Ryan, M. F.; Metcalfe, R. A.; Davids, R.; Lever, A. B. P. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1039.

6. (a) Law, K.-Y. *J. Phys. Chem.* **1988**, *92*, 4226. (b) Deng, H.; Mao, H.; Lu, Z.; Xu, H. *Thin Solid Films* **1998**, *315*, 244.

7. See for example: (a) Schelly, Z. A.; Harward, D. J.; Hemmes, P.; Eyring, E. M. *J. Phys. Chem.* **1970**, *74*, 3040. (b) van Nostrum, C. F.; Picken, S. J.; Schouten, A.-J.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1995**, *117*, 9957. (c) Zhou, J.; Wang, Y.; Qiu, J.; Cai, L.; Ren, D.; Di, Z. *Chem. Commun.* **1996**, 2555. (d) Amaral, C. L. C.; Politi, M. J. *Langmuir* **1997**, *13*, 4219.

8. Tai, S.; Hayashi, N. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1275.

9. (a) Polley, R.; Hanack, M. *J. Org. Chem.* **1995**, *60*, 8278. (b) Cammidge, A. N.; Chambrier, I.; Cook, M. J.; Garland, A. D.; Heeney, M. J.; Welford, K. *J. Porphyrins Phthalocyanines* **1997**, *1*, 77. (c) Yeung, Y.-O.; Liu, R. C. W.; Law, W.-F.; Lau, P.-L.; Jiang, J.; Ng, D. K. P. *Tetrahedron* **1997**, *53*, 9087. (d) Ng, D. K. P.; Yeung, Y.-O.; Chan, W. K.; Yu, S.-C. *Tetrahedron Lett.* **1997**, *38*, 6701. (e) Brewis, M.; Clarkson, G. J.; Humberstone, P.; Makhseed, S.; McKeown, N. B. *Chem. Eur. J.* **1998**, *4*, 1633.

10. (a) Kitahara, K.; Asano, T.; Hamano, K.-I.; Tokita, S.; Nishi, H. *J. Heterocycl. Chem.* **1990**, *27*, 2219. (b) Kitahara, K.; Asano, T.; Kayama, S.; Tokita, S.; Nishi, H. *Phosphorus, Sulfur Silicon* **1992**, *67*, 373.

11. Takahashi, K.; Kawashima, M.; Tomita, Y.; Itoh, M. *Inorg. Chim. Acta* **1995**, *232*, 69.

12. Satisfactory analytical data for **6** could not be obtained, but it was deemed to be pure by chromatographic and spectroscopic analyses. The experimental carbon content for **11** and **12** was slightly lower than the corresponding calculated value which could be related to the difficulty in complete combustion of these macrocycles (see Hu, M.; Brasseur, N.; Yildiz, S. Z., van Lier, J. E.; Leznoff, C. C. *J. Med. Chem.* **1998** *41*, 1789).

13. Law, W.-F.; Lui, K. M.; Ng, D. K. P. *J. Mater. Chem.* **1997**, *7*, 2063.

14. (a) Yang, Y.-C.; Ward, J. R.; Seiders, R. P. *Inorg. Chem.* **1985**, *24*, 1765. (b) Zhang, X.-F.; Xu, H.-J. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 3347.

15. (a) Schelly, Z. A.; Farina, R. D.; Eyring, E. M. *J. Phys. Chem.* **1970**, *74*, 617. (b) Monahan, A. R.; Brado, J. A.; DeLuca, A. F. *J. Phys. Chem.* **1972**, *76*, 446. (c) Monahan, A. R.; Brado, J. A.; DeLuca, A. F. *J. Phys. Chem.* **1972**, *76*, 1994. (d) Osburn, E. J.; Chau, L.-K.; Chen, S.-Y.; Collins, N.; O'Brien, D. F.; Armstrong, N. R. *Langmuir* **1996**, *12*, 4784.

16. Oelschlaeger, H. *J. Colloid Interface Sci.* **1969**, *31*, 503.

17. (a) Kratky, O.; Oelschlaeger, H. *J. Colloid Interface Sci.* **1969**, *31*, 490. (b) Farina, R. D.; Halko, D. J.; Swinehart, J. H. *J. Phys. Chem.* **1972**, *76*, 2343.

18. Kovshev, E. I.; Puchnova, V. A.; Luk'yanets, E. A. *Zh. Org. Khim.* **1971**, *7*, 369.

19. Wöhrle, D.; Eskes, M.; Shigehara, K.; Yamada, A. *Synthesis* **1993**, 194.