HETEROCYCLES, Vol. 83, No. 8, 2011, pp. 1859 - 1866. © The Japan Institute of Heterocyclic Chemistry
Received, 14th April, 2011, Accepted, 13th May, 2011, Published online, 25th May, 2011
DOI: 10.3987/COM-11-12235

THE NORPHTHALOCYANINES BEARING TWO TTF UNITS: SYNTHESIS, PHOTOPHYSICAL AND ELECTROCHEMICAL PROPERTIES

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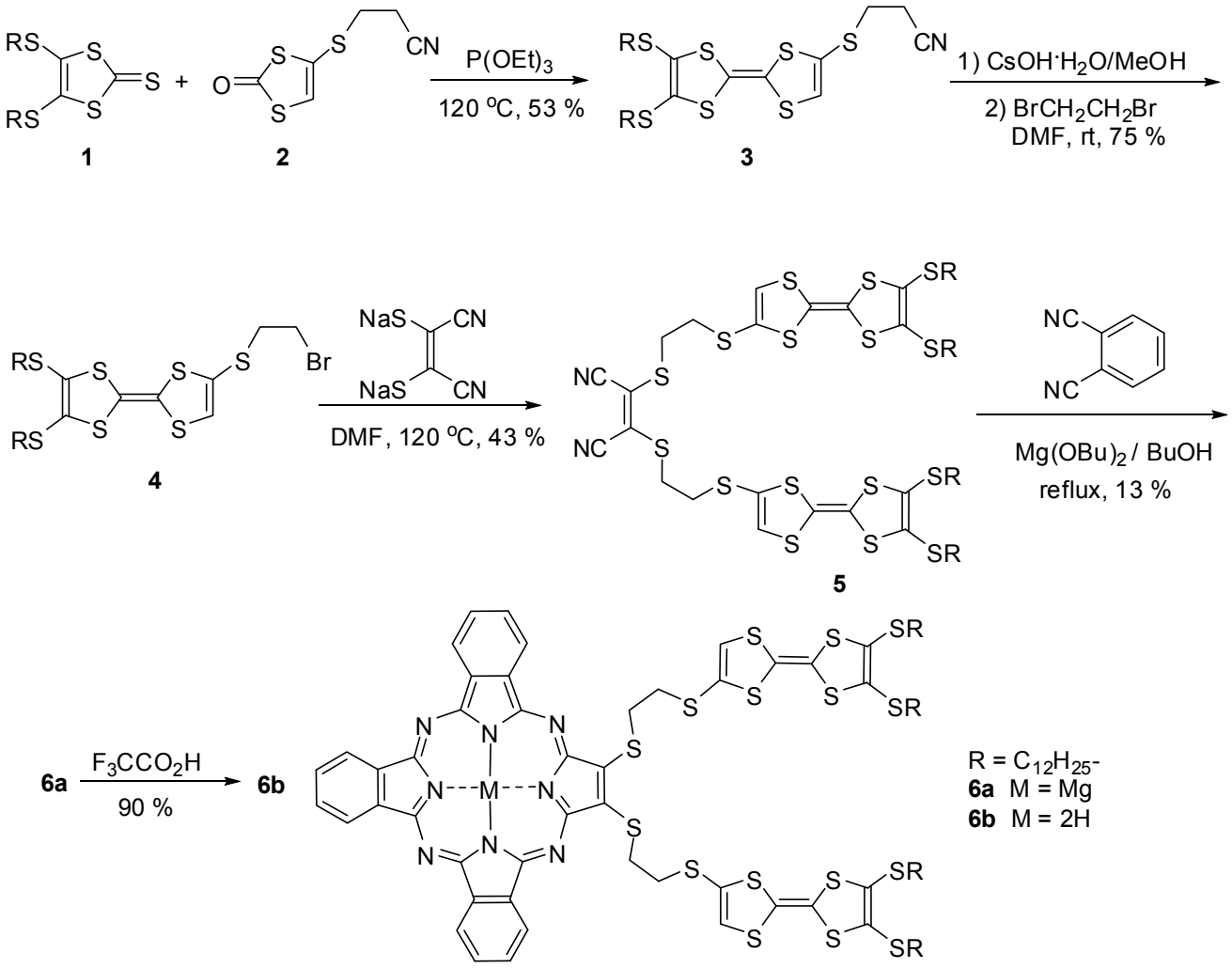
Abstract – A magnesium norphthalocyanine (**6a**) was prepared by the mixed condensation of phthalonitrile in excess with the dithiomaleonitrile bearing two TTF units (**5**), using Mg(I1) as a template. Subsequent demetalation of **6a** with acetic acid gave **6b** in good yield. The structures of target compounds were determined by EA, NMR and TOF MS and their electrochemical and optical properties were also studied by cyclic voltammetry and UV-vis spectroscopy.

Porphyrinic macrocycles, such as porphyrins (Prs), phthalocyanines (Pcs) and porphyrazines (Pzs), are the subject of great interest in areas such as catalysis, photodynamic therapy, and in the fabrication of molecular electronic or magnetic devices.[1] Up to now, a great variety of symmetrical porphyrinic macrocycles have been extensively studied.[2] However, there have been only a limited number of reports on unsymmetrical porphyrinic macrocycles,[3] mainly because they are much more difficult to synthesize and purify. In recent years, there has been a growing interest in the properties of the unsymmetrically Pcs because they display second- and third-order nonlinear optical properties in solution, high thermal stability, mesogenic behavior, Langmuir–Blodgett film formation and semiconducting properties.[4] Recently, we reported a series of symmetrical and unsymmetrical Pzs bearing tetrathiafulvalene (TTF) units, including the Pzs annulated directly with four TTF units and linked TTF units with either crown ether or ethylenedithio spacers.[5] These Pzs bearing multi-TTF units show good electron-donating properties and give rise to two-, octa- or hexadeca- radical cationic species of TTF moieties.

In the present work, we describe the synthesis, photophysical and electrochemical properties of two new norphthalocyanine derivatives **6a–b,** which are composed of two TTF units as electron donor and a norphthalocyanine ring as acceptor moieties covalently linked with two ethylenedithio spacers.



Scheme 1

Cross-coupling reaction of **1** and **2** in the triethyl phosphite at 120 °C under Ar gave the red mono-cyanoethyl protected tetrathiafulvalene derivatives **3** in a reasonable yield. Compound **3** was deprotected by treatment with cesium hydroxide in a mixture of DMF and MeOH and the obtained thiolate ion was reacted with excess 1,2-dibromoethane to yield compound **4** which was subsequently converted into key intermediate dithiomaleonitrile **5** bearing two tetrathiafulvalene units linked with two ethylenedithio spacers by reaction with disodium maleonitrile 2,3-dithiolate in DMF. The IR spectrum of **5** shows the typical C≡N stretching vibration at 2212 cm^{-1}, which disappears upon tetramerization to the norphthalocyanine **6a**. A mixed condensation of 1 equiv. of dithiomaleonitrile **5** (A) and 30 equiv. of phthalonitrile (B) under classic Linstead macrocyclization conditions (magnesium *n*-Butoxide/*n*-Butanol) produced two porphyrinic products, the desired norphthalocyanine **6a** (AB_3) and the phthalocyanine (B_4) (Scheme 1). Fortunately, the large polarity differrences among products allow us to separate easily the desired norphthalocyanine **6a**. Demetallation of **6a** with acetic acid gave a free base norphthalocyanine **6b** in 86% yield as a deep blue powder. Compound **6a-b** were soluble in the usual organic solvents except

for alcoholic solvents. The MALDI-TOF mass spectra of **6a-b** featured peaks at *m/z* 1876.18 $[M + H]^+$ and 1854.47 $[M+H]^+$, respectively, corresponding to M^+ (1875.52) of **6a** and M^+ (1853.55) of **6b**, respectively. The ^1H NMR spectra of **6a-b** recorded in $CDCl_3$ at 25 °C showed a bit broadened signals except for the terminal methyl groups, which could be explained by considering aggregation in concentrated solutions.[5] In the ^1H NMR spectrum of **6b**, the typical shielding of the inner core NH protons was observed as broad signals at δ = -3.39, which could be exchanged with D_2O. Elemental analyses of these compounds were in accord with the proposed molecular formulae.

The optical spectra of all norphthalocyanine exhibit two main bands, a Soret or B band ($\pi\rightarrow\pi^*$, corresponds to a deep $\pi \rightarrow$ LUMO transition) between 339-359 nm and another around 650 nm, denoted the Q band ($\pi\rightarrow\pi^*$) (Figure 1a). In general, the 4-fold symmetric porphyrinic macrocycles have similar optical spectra, with single transitions for both the Q and B bands. In contrast, the optical spectra of unsymmetrical norphthalocyanines **6a-b**, with three fused benzo rings and two TTF units substituted dithiolene moiety, clearly show a splitting of the Q band. Their optical spectra look quite like those of the norphthalocyanines substituted with 2,3-dialkylthio groups in the literatures.[3,6] These differences can be rationalized through Gouterman's highly simplified four orbital model for the optical spectra of porphyrinic macrocycles.[7] For both of **6a** and **6b**, the Q band strictly followed the Lambert-Beer law (up to 10 μM), indicating that these compounds are essentially free from aggregation in CH_2Cl_2, THF and DMF. The spectrum of **6a** is given as an example (Figure 1b).

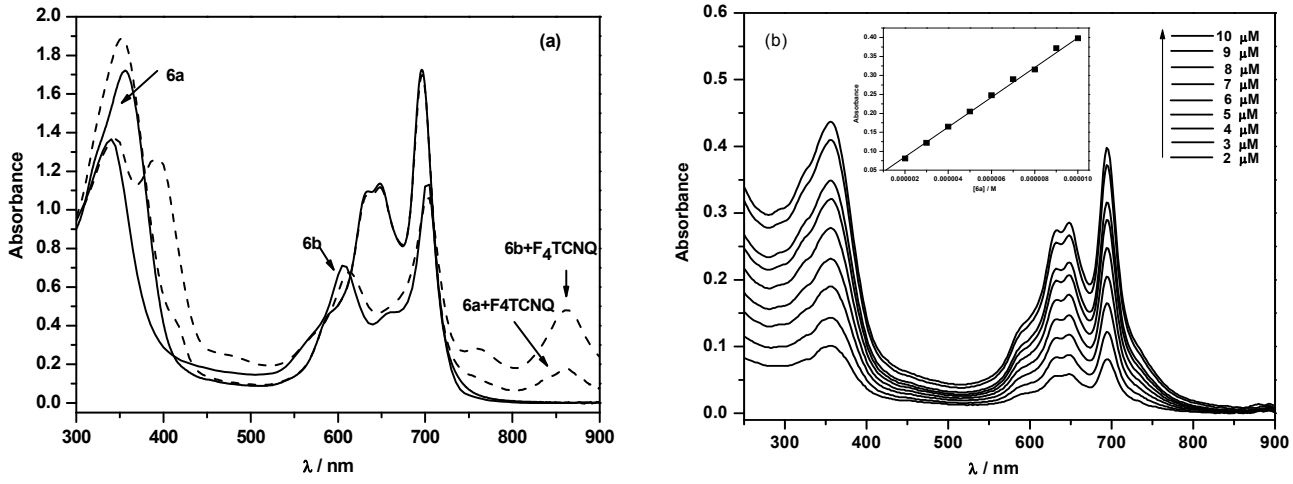


Figure 1. (a) Electronic absorption spectra of **6a** and **6b** in CH_2Cl_2 (10^{-5} M) before and after addition of 1 equiv. F_4TCNQ; (b) Electronic absorption spectra of **6a** at different concentrations in CH_2Cl_2 (10^{-5} M). The insert plots the Q-band absorbance at 697 nm versus the concentration of **6a**.

To evaluate the potential of target compounds to act as a electron donor, the electrochemical characterization of compounds **6a-b** were carried out by using cyclic voltammetry (CV) in a mixture of CH_2Cl_2/CH_3CN (9:1, v/v). Figure 2a shows the cyclic and differential pulse voltammograms (DPV) of **6a**

within a −2000 mV to +2000 mV potential window. Compound **6a** shows two reduction couples ($E_{1/2}$ = -1.435 V and -1.000 V) and three oxidation couples ($E_{1/2}$ = 0.475 V, 0.863 V and 1.386 V) within the potential window of the CH_2Cl_2-CH_3CN / Bu_4PF_6 electrolyte system. The five couples observed were assigned to Pz^{-3}/Pz^{-4} (I), Pz^{-2}/Pz^{-3} (II), $TTF^{+\bullet}$ /TTF (III), TTF^{+2}/ $TTF^{+\bullet}$ (IV), Pz^{-1}/Pz^{-2} (V) on the basis of results in the literature.[8] Processes I-II and V are irreversible in terms of the ratio of anodic to cathodic

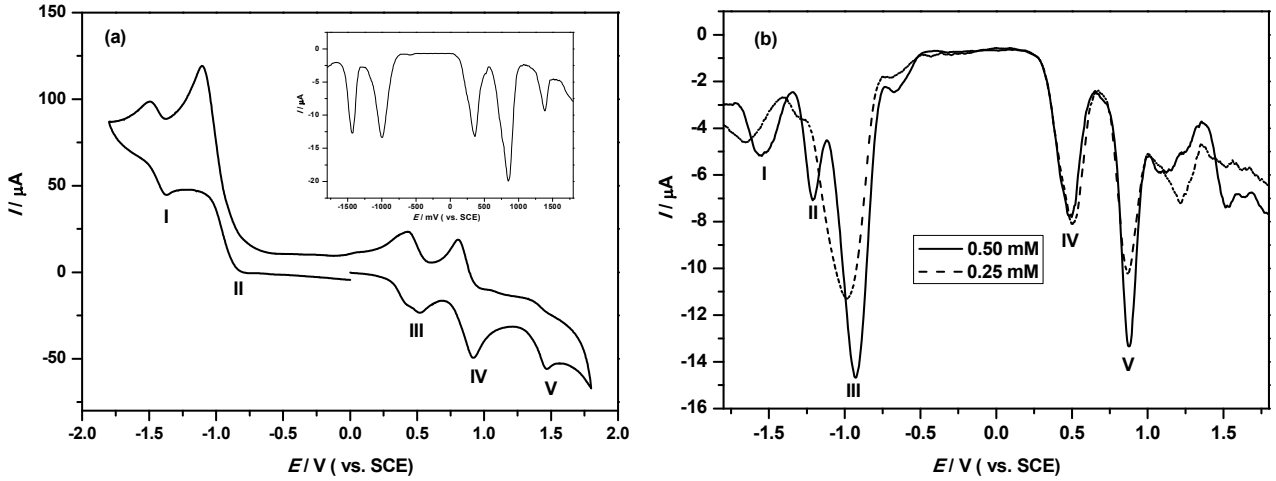


Figure 2. (a) CV of **6a** (5×10^{-4} M) in 0.1 M tetrabutylammonium hexafluorophosphate in a mixture of CH_2Cl_2/MeCN (9:1, v/v) at 0.1 V s^{-1} (inset: DPV of **6a** at same condition); (b) DPVs of **6b** recorded at different concentrations in a mixture of CH_2Cl_2/MeCN (9:1, V/V) at 0.1V s^{-1} scan rate.

peak currents. Processes III-IV, which can be assigned to the simultaneous first and second oxidations of the TTF unit, are quasi-reversible with anodic to cathodic peak separation (ΔE) of 0.083 V and 0.102 V, respectively, and the unity of the $\boldsymbol{I}_{pa}$ / $\boldsymbol{I}_{pc}$ ratios at all scan rates and linear variation of the peak currents.

Metal free norphthalocyanine **6b** shows an aggregation tendency in concentrated solution, so the redox processes are complex due to the splitting of original waves, which are also induced by electron transfer of aggregated and monomeric species. Two reduction and two oxidation processes are recorded with the complex **6b** at −1.566, −0.93 (−1.212) , 0.476, and 0.875 V vs. SCE, respectively, at 0.100 Vs^{-1} scan rate. The second reduction couple of the complex are split into two peaks due to aggregation of the species.[9] Dilution of the solution of the complex causes the peak current of the waves assigned to the aggregated species decrease to more than that of the monomeric species, supporting the existence of the aggregation-disaggregation equilibrium (Figure 2b).

To further address the donor properties of the newly synthesized compounds, doping studies were conducted using 7,7,8,8-tetracyanoquinodimethane (TCNQ) and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane (F_4TCNQ) in CH_2Cl_2. Compounds **6a-b** doped with 4 equiv. TCNQ in CH_2Cl_2, no CT bands were observed in the 600-1000 nm region. But when **6a-b** was doped with 1 equiv. F_4TCNQ, a new absorption band was produced around λ_{max} 866 nm in the UV-Vis spectrum (Figure 1a). This new band corresponds to the cation radical species of the TTF moieties.[10] The formation of the charge-transfer

complex between **6a** with F_4TCNQ in CH_2Cl_2 was also confirmed by the FT-IR. The FT-IR spectrum of a mixture of **6a** and F_4TCNQ (1:1) shows the nitrile stretch of the F_4TCNQ radical anion at 2196 cm^{-1} compared to the neutral state of 2218 cm^{-1}.

In summary, we first synthesized two norphthalocyanines (**6a-b**) bearing two TTF units linked by an ethylenedithio spacer. Compound **6a-b** were sufficiently stable for purification and for further experiments. Metal-free norphthalocyanine **6b** shows an aggregation tendency in concentrated solution, so a reduction couple is split into two waves due to electron transfer of aggregated and monomeric species. The ability of compounds **6a-b** to function as a donor for F_4TCNQ was established, and the formation of charge-transfer complexes were confirmed by the UV-Vis and FT-IR spectroscopy. The remetallation of metal-free norphthalocyanine **6a** and determination of mesogenic properties of norphthalocyanines are in progress.

EXPERIMENTAL

The ^1H NMR spectra were recorded with a Bruker AV-300 spectrometer, and chemical shifts were referenced relative to tetramethylsilane. The UV-vis spectra were taken on a Hitachi U-3010 spectrophotometer. MALDI-TOF-MS data were obtained by a Shimadzu AXIMA-CFR^{TM} *plus* spectrometer, using a 1,8,9-anthracenetriol (DITH) matrix. Cyclic voltammetry was carried out on a Potentiostat/Galvanostat 273A instrucment employing 0.1M Bu_4NPF_6 as the supporting electrolyte in chloroform, with sweep speed of 100 mv/s. Counter and working electrdes were made of platinum and Glass-Carbon (GCE, 4.00 mm diameter), respectively, and the reference electrode was calomel electrode (SCE). Starting materials **1** and **2** were prepared according to reference.[11]

6,7-Bis(dodecylthio)-2-(2-cyanoethyl)thiotetrathiafulvalene (3): A suspension of compound **1** (9.48 g, 17.7 mmol) and **2** (3.0 g, 14.8 mmol) in freshly distilled $P(OEt)_3$ (60 mL) under Ar was stirred at 120 °C for 4 h and then the reaction mixture cooled to rt. The $P(OEt)_3$ was removed in vacuum and the residue was purified by column chromatography on silica gel with CH_2Cl_2/pet. ether (1:1, v/v) as an eluent to afford a yellow powder. The solid was recrystallized from MeCN-EtOH to gave **3** as orange needles 4.0 g, yield 53%, mp 73-74 °C. ^1H NMR ($CDCl_3$): δ 0.88 (m, 6H), 1.20-1.50 (m, 36H), 1.59-1.67 (m, 4H), 2.70 (t, J = 7.2 Hz, 2H), 2.83 (t, J = 7.2 Hz, 4H), 3.00 (t, J = 7.2 Hz, 2H), 6.56 (s, 1H); TOF-MS, *m/z* (%) = 689.24 (M^+, 100). Anal. Calcd for $C_{33}H_{55}NS_7$: C, 57.42; H, 8.03; N, 2.03. Found: C, 57.60; H, 8.09; N, 2.12.

2-(2-Bromoethylthio)-6,7-bis(dodecylthio)tetrathiafulvalene (4): To a solution of **3** (1.0 g, 1.45 mmol) in dry DMF (28 mL) was added a solution of $CsOH·H_2O$ (292 mg, 1.74 mmol) in anhydrous MeOH (5 mL) over a period of 45 min. The mixture was stirred for an additional 30 min and 1,2-dibromoethane

(2.72 g, 14.5 mmol) was injected to the mixture in 45 min. The solution was stirred overnight. After seperation by column chromatography on silica gel with CH_2Cl_2/pet. ether (60-90 °C) (1:3, v/v) as eluant, **4** was obtained as a reddish yellow solid. The solid was recrystallized from CH_2Cl_2-EtOH to gave an orange needles 0.81g, yield 75%, mp 41-42 °C. ^{1}H NMR ($CDCl_3$): δ 0.88 (m, 6H), 1.26 (br, 32H), 1.40 (br, 4H), 1.63 (br, 4H), 2.82 (br, 4H), 3.13 (t, *J* = 7.4 Hz, 2H), 3.50 (t, J = 7.4 Hz, 2H), 6.47 (s, 1H); TOF-MS, m/z (%) = 744.15 (M^+, 100); Anal. Calcd for $C_{32}H_{55}BrS_7$: C, 51.65; H, 7.45. Found: C, 51.41; H, 7.49.

1,2-Bis[6,7-bis(dodecylthio)tetrathiafulvalen-2-ylthioethylthio]-1,2-dicyanoethene (5): A solution of **4** (500 mg, 0.672 mmol) and disodium maleonitrile-2,3-dithiolate (63 mg, 0.336 mmol) in anhydrous degassed DMF (20 mL) were stirred at 90 °C for overnight under Ar. The solvent was removed in vacuum and the residue was purified by column chromatography on silica gel with CH_2Cl_2/pet. ether (1:1, v/v) as an eluent to afford **5** as a brown powder 231 mg, yield 43%, mp 47-48 °C. ^{1}H NMR ($CDCl_3$): δ 0.88 (t, *J* = 7.61 Hz, 12H), 1.26 (m, 64H), 1.40 (br, 8H), 1.61-1.64 (m, 8H), 2.82(t, *J* = 6.7 Hz, 4H), 3.05 (t, *J* = 7.2 Hz, 4H), 3.39 (t, *J* = 7.2 Hz, 2H), 6.52 (s, 2H); MALDI-TOF MS *m/z* (%) = 1467.88(M^+ + 1, 100).; Anal. Calcd for $C_{68}H_{110}N_2S_{16}$: C, 55.61; H, 7.55; N, 1.91. Found: C, 55.15; H, 7.50; N, 1.88.

{2,3-Bis[6,7-bis(dodecylthio)tetrafulvalen-2-ylthioethylthio]norphthalocyanine}magnesium(II) (6a)
Magnesium (16.3 mg, 0.68 mmol) metal was dissolved in anhydrous *n*-BuOH (45 mL) at reflux under Ar. To this magnesium butoxide solution was added the compound **5** (100 mg, 0.068 mmol) and phthalonitrile (174 mg, 1.36 mmol). The mixture was refluxed for 26 h under Ar. The solution color changed from purplish red to deep blue. The blue mixture was cooled to rt. The precipitate was collected by suction and washed with large amounts of $CHCl_3$. The blue solid was purified by chromatography on silica gel with CH_2Cl_2/pet. ether (200:1~100:1, v/v) to give **6a** as a deep blue solid 15.2 mg, yield 12.5%. Reprecipitation of **6a** from CH_2Cl_2-MeOH gave a deep blue powder, mp > 250 °C (by DTA). ^{1}H- NMR ($CDCl_3$), δ : 0.85 (t, *J* = 5.85 Hz, 12H), 1.15 (br, 64H), 1.40 (br , 8H), 2.42 (br , 8H), 2.57 (br, 8H), 3.05 (br, 4H), 3.84 (br, 4H), 6.07 (s, 2H) 7.81 (br, 2H), 7.99 (br, 8H), 8.23 (br, 2H), 8.85 (br, 8H); UV (CH_2Cl_2) λ_{max}: 697 (ε = 69100), 650 (ε = 47800), 635 (sh, ε =44700), 331 (sh, ε = 20900), 357 (ε = 70000); MALDI-TOF MS m/z (%) = 1876.18 (M^+ + 1, 100); Anal. Calcd for $C_{92}H_{122}MgN_8S_{16}$: C, 58.86; H, 6.55; N, 5.97. Found: C, 57.64; H, 7.06; N, 5.80.

2,3-Bis[6,7-bis(dodecylthio)tetrafulvalen-2-ylthioethylthio]norphthalocyanine (6b)
A solution of magnesium norphthalocyanine **6a** (20.0 mg, 0.011 mmol) in a mixture of acetic acid (0.5 mL) and CH_2Cl_2 (0.5 mL) was stirred at room temperature for 72 h, then Et_2O was added and the resulting suspension brought to pH 7 with 1M NaOH. The organic phase was washed with a saturated NH_4Cl aq. and water, dried over $MgSO_4$. The solution was concentrated in vacuo and the residue was purified by

column chromatography on silica gel (CH_2Cl_2/pet. ether, 3:1) to give a blue solid. Reprecipitation of the solid from CH_2Cl_2-MeOH gave **6b** as a deep blue powder. Yield: 17 mg (86%), mp 106 °C (to be soften). ^{1}H NMR ($CDCl_3$): δ -3.39 (br, 2H), 0.86 (t, J = 3 Hz, 12H), 1.00-1.80 (m, 78H), 2.42 (t, J = 6.6 Hz, 4H), 2.57 (t, J = 6.6 Hz, 4H), 3.26 (t, J = 6.7 Hz, 4H), 4.06 (t, J = 6.6 Hz, 4H), 6.28 (s, 2H), 7.26-7.72 (m, 8H), 8.14 (d, J = 6.7 Hz, 4H), 8.27 (d, J = 6.7 Hz, 2H); UV (CH_2Cl_2) λ_{max}: 704 (ε = 39900), 670 (ε = 9700), 610 (ε = 29000), 566 (sh, ε =15600), 338 (ε = 57200); MALDI-TOP MS m/z: 1854.47 (M^++1, 100); Anal. Calcd. for $C_{92}H_{124}N_8S_{16}$: C, 59.57; H, 6.74; N, 6.04. Found: C, 59.61 ; H, 6.70 ; N, 6.05.

ACKNOWLEDGEMENTS

The authors acknowledge financial support from the National Natural Science Foundation of China (grant No.21062022), the Specialized Research Fund for the Doctoral Program of Higher Education (Grant No. 20102201110001) and the Open Project of the State Key Laboratory of Supramolecular Structure and Materials, Jilin University.

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