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Synthesis and Electrochemical and Photophysical Studies of Tetrathiafulvalene-Annulated Phthalocyanines

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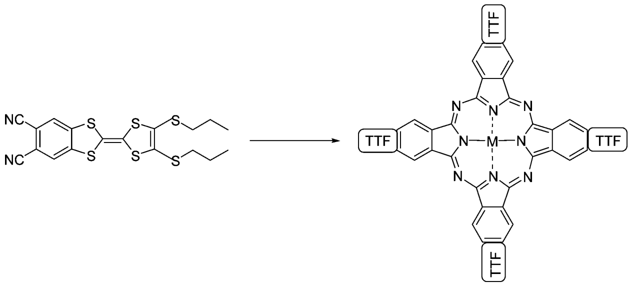

The synthesis of tetrakis(tetrathiafulvalene)-annulated metal-free and metallophthalocyanines **5**−**8** via the tetramerization of the phthalonitrile derivative **4** is reported. All of them have been fully characterized by electronic absorption spectroscopy, thin-layer cyclic voltammetry, mass spectrometry, and elemental analysis. Their solution electrochemical data show two reversible four-electron oxidation waves, indicating that these fused systems are strong π-electron donors, which give rise to tetra- or octaradical cation species. For the metal-free phthalocyanine **5**, additionally a reversible one-electron wave was found in the negative direction arising from the reduction of the macrocycle. Moreover, the tetrathiafulvalene unit acts as an efficient reductive electron-transfer quencher for the phthalocyanine emission, but upon its oxidation, an intense luminescence is switched on.

Introduction

Ensembles of covalently linked tetrathiafulvalenes (TTFs) and phthalocyanines (Pcs) or porphyrins are mainly investigated for their multielectron redox activities and photophysical properties. On one hand, the redox-active TTF unit and its derivatives are π-electron donors and the oxidation of their ring systems to the cation radical and dication species occurs sequentially and reversibly within a very accessible potential window.[1] On the other hand, it is well-known that porphyrins and in particular metalloporphyrins[2] have long been of great importance as model compounds to mimic biological functions and as materials for constructing electrocatalytic, electronic, and optical devices, but also Pcs[3] show a rich and diverse chemistry as well as specific electronic, optical, structural, and coordination properties. Obviously, there is keen interest in exploring new structural modifications to the porphyrin and Pc systems and in the present context it means to couple them with the favorable redox properties of the TTF units.

It has been shown that metal-free Pc (H_2Pc) derivatives bearing one, two, four, or eight peripheral TTF units, respectively, all linked by spacer groups exhibited the

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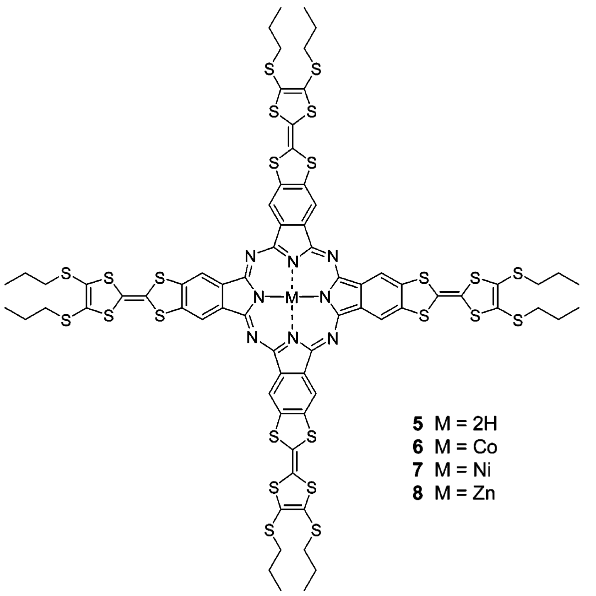
expected two-stage oxidation of the TTF units, and for the latter two cases, oxidation and reduction of the Pc core were also observed.[4] In addition, it has been demonstrated that the fluorescence from metal-free Pcs is efficiently quenched by the addition of TTF as a consequence of intermolecular electron transfer between H_2Pc* and TTF.[4c] Furthermore, a range of silicon Pc-TTF hybrids have been reported and also in these cases, the quenching of the Pc emission by electron transfer from the axially linked TTF groups has been demonstrated.[5] A zinc Pc represents a case of a metallophthalocyanine (MPc) bearing four TTF units at the periphery, again with all of them linked through spacer groups. However, its electrochemical property could not be measured due to its insufficient solubility.[6a] In the following, the synthesis of the corresponding zinc and magnesium phthalocyanines with an improved solubility was demonstrated.[6b] Very recently, tetrakis(tetrathiafulvalene-crown-ether) substituted metal-free Pc and copper Pc have been investigated for their self-assembling ability, indicating the formation of helical tapes which are nanometers wide and micrometers long. Such self-assembled materials show potentially novel electronic and structural properties.[7] Moreover, specifically for the context of molecular donor−acceptor systems that are expected to show efficient electron transfer, a study of a TTF−porphyrin dyad and a TTF−porphyrin−fullerene triad as artificial photosynthetic models has to be mentioned.[8] Finally, when it comes to the direct annulation of the TTF unit to a macrocyclic core, up to now there appeared only two reports about such fused systems in the literature. In the case of a tetrakis-TTF−porphyrin molecule,[9] the synthesis resulted, however, in a mixture of the neutral porphyrin and its corresponding radical cation porphyrin, but in a following report,[10] a pure mono-TTF-annulated porphyrin has been described: it produces an almost nonfluorescent species that can be transformed into a fluorescent one by oxidation of the TTF unit, hence, it behaves as a fluorescence switch.

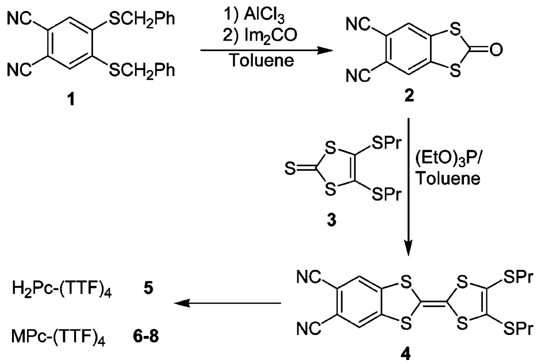
In this paper, we report the first examples of tetrakis-TTF-annulated Pc molecules (Chart 1), specifically their preparation as well as their electrochemical and photophysical characterization.

CHART 1. TTF-Annulated Phthalocyanines



5 M = 2H
6 M = Co
7 M = Ni
8 M = Zn

SCHEME 1. Synthetic Pathway for the Tetrakis-TTF-Annulated Phthalocyanine Series



Results and Discussion

Preparation of the Tetrakis-TTF-Annulated Phthalocyanines 5−8. The synthetic pathway is outlined in Scheme 1. The precursor 1,2-bis(*S*-benzylthio)-4,5-dicyanobenzene **1** was treated with $AlCl_3$ in toluene at room temperature under a nitrogen atmosphere before 1,1′-carbonyldiimidazole was added to the mixture. Purification by means of column chromatography afforded the pure compound 5,6-dicyanobenzene-1,3-dithiole-2-one **2**. The cross-coupling reaction of **2** with **3** in a mixture of triethyl phosphite and toluene at 120 °C under nitrogen gave the red 5,6-dicyano-2-(4,5-bis(propylthio)-1,3-dithio-2-ylidene)benzo[*d*]-1,3-dithioles **4** in a good yield. Compound **4** is soluble in $CHCl_3$, CH_2Cl_2, and THF, slightly soluble in CH_3CN, acetone, and DMSO, and insoluble in alcohols. The IR spectrum of **4** shows the typical C≡N stretching vibration at 2234 cm^{-1}, which disappears upon tetramerization to the phthalocyanines **5**−**8**.

Red crystals suitable for an X-ray diffraction study of the key precursor **4** have been obtained by cooling a saturated DMSO solution of **4**. The ORTEP plot (Figure 1) emphasizes not only the planar geometry of the functionalized TTF unit, which finally tetramerizes to the flat Pc core, but also the solubilizing effect of the flexible end groups.

Finally, cyclization of **4** in 1-pentanol in the presence of lithium pentoxide at 125 °C under argon resulted in the formation of the metal-free phthalocyanine H_2Pc-$(TTF)_4$ **5**. The compound is soluble in $CHCl_3$, CH_2Cl_2, and

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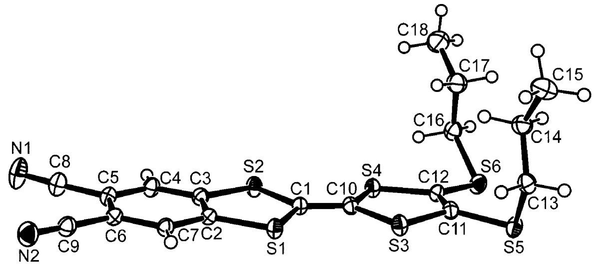

FIGURE 1. Crystal structure of compound **4**.

TABLE 1. Cyclic Voltammetry Data for 4−8[a]

compd	$E^1_{1/2}$/V	$E^2_{1/2}$/V	$E^3_{1/2}$/V
4		0.31	0.65
5	−0.98	0.11	0.62
6		0.14	0.60
7		0.14	0.60
8		0.14	0.59

[a] vs Fc$^+$/Fc.

pyridine and slightly soluble in THF and DMSO. The good solubility is due to substitution at the tetrathiafulvalene unit with thiopropyl groups. In the MALDI mass spectrum of **5**, a peak was observed at *m/z* 1809.89, which corresponds to the monoisotopic mass. An additional peak was found at *m/z* 1723.79, which was assigned to a fragment of **5** with two missing propyl groups. The metallophthalocyanines CoPc-(TTF)$_4$ **6**, NiPc-(TTF)$_4$ **7**, and ZnPc-(TTF)$_4$ **8** have been prepared by refluxing **4** in the presence of an appropriate anhydrous metal salt in DMAE under argon. Compounds **6**−**8** are soluble in $CHCl_3$, CH_2Cl_2, THF, and pyridine, but not in alcohols. The MALDI mass spectra of **6**−**8** display the monoisotopic molecular peaks at *m/z* 1866.77, 1865.79, and 1871.73. In the case of CoPc-(TTF)$_4$ **6** and NiPc-(TTF)$_4$ **7**, a peak is found at a higher *m/z* value corresponding to the phthalocyanines containing one water molecule. The mass spectra of all metallophthalocyanines show additional fragment peaks which indicate the loss of propyl groups.

Electrochemical Studies. The electrochemical characterization of compounds **4**−**8** was carried out by using cyclic and thin layer cyclic voltammetry (Table 1). Figure 2a shows the deconvoluted voltammogram of the tetrathiafulvalene derivative **4** with two oxidation waves. Each oxidation wave was assigned to a one-electron process. The TTF unit is oxidized to the radical cation TTF$^{\cdot+}$ at a potential of 0.31 V vs Fc$^+$/Fc. The second oxidation potential corresponding to the formation of the dication TTF^{2+} is located at 0.65 V. In comparison to the tetrathiafulvalene molecule, both oxidation steps are shifted by 0.34 and 0.38 V, respectively, to higher oxidation potentials due to the electron-withdrawing effect of the cyano groups. The thin layer cyclic voltammograms of the phthalocyanines **5**−**8** reveal that the TTF moieties are oxidized in two reversible steps involving two four-electron processes (Figure 2b for **5** as an example). Noteworthy, the oxidation potentials to the radical cations show a negative shift of some 0.2 V compared to that of the precursor compound **4**. The splitting of the first oxidation potential is characteristic for a molecular system in which the donor moieties interact through conjugation and/or through space.[11] In the present system it is caused by the annulation of the four TTF units to the phthalocyanine core, which results in a high degree of aggregation and also a stabilization of the monoradical cation. After oxidation of one TTF unit has taken place, the degree of aggregation decreases, which leads to a stabilization of the HOMO level. Therefore, further oxidation of the remaining three TTF units is now shifted to a more positive potential. As a result of the Coulombic repulsion among the positively charged species, the four TTF units now behave like isolated molecules and an additional four electrons are removed at the same potential. In the case of the metal-free phthalocyanine **5**, a reversible one-electron wave was also found at −0.98 V vs Fc$^+$/Fc, which can be assigned to a reduction of the phthalocyanine ring system.

Photophysical Studies. The electronic absorption spectrum for ZnPc-(TTF)$_4$ **8** dissolved in THF ($c = 2 \times 10^{-6}$ M) in its neutral and tetraradical cationic states is shown in Figure 3a. In its neutral form, ZnPc-(TTF)$_4$ **8** shows very similar absorption bands in THF and pyridine with the main difference being that in THF the broader component of the Q-band at higher energy is more intense than the sharper band centered at 700 nm, whereas in pyridine it is the opposite. The sharper band being due to a monomeric species,[12] this indicates a higher degree of aggregation in THF than in pyridine.

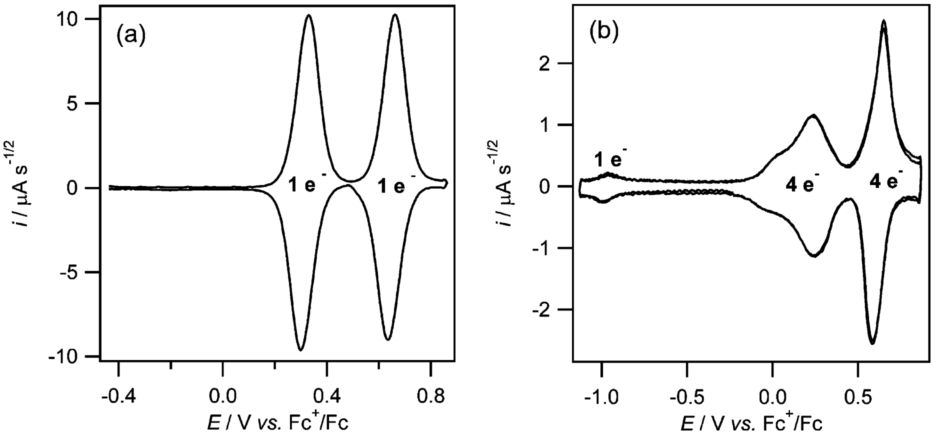

FIGURE 2. Thin layer cyclic voltammogram of **4** (a) and of H$_2$Pc-(TTF)$_4$ **5** (b), in 0.1 M tetrabutylammonium hexafluorophosphate in CH_2Cl_2/CH_3CN (9.5/0.5, v/v) at 0.1 V s^{-1}, Pt electrode.

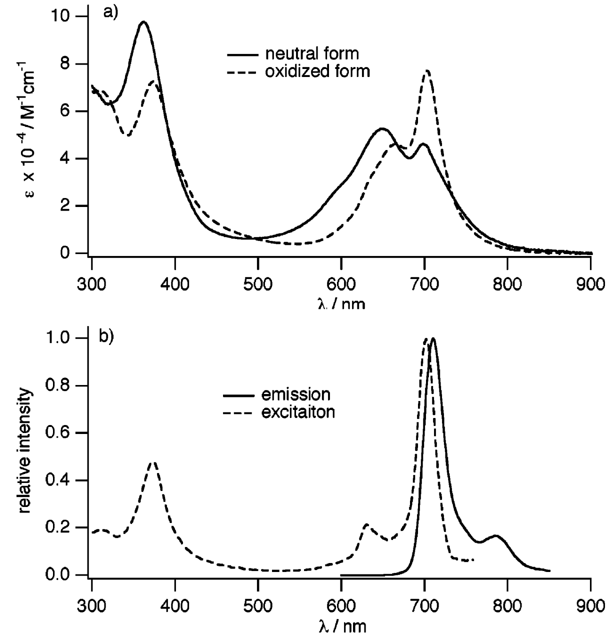

FIGURE 3. (a) Absorption spectra of ZnPc-(TTF)$_4$ **8** in THF ($c = 2 \times 10^{-6}$ M): (—) neutral form, (- - -) oxidized form. (b) Emission spectrum (—) and excitation spectrum (- - -) of the oxidized form of **8** in THF.

Importantly, in its neutral form a freshly prepared solution of **8** dissolved in THF does not show any luminescence above the detection threshold of the experimental setup. This is due to the presence of the electron-donating TTF units fused to the phthalocyanine chromophore. As has also been observed for monoannulated porphyrin, the TTF is an efficient reductive electron-transfer quencher.[10]

Upon addition of a 5-fold excess of $FeCl_3$ as mild oxidizing agent, the absorption spectrum changes quite dramatically. The sharper peak of the Q-band at 700 nm gains substantially in intensity at the expense of the broader component. This indicates that upon oxidation the now positively charged species have less tendency to aggregate. In contrast to the neutral compound, the oxidized species exhibits a very strong luminescence. The corresponding luminescence spectrum ($\lambda_{ex} = 380$ nm), included in Figure 3b, consists of two well-resolved bands at 710 (14 080 cm^{-1}) and 786 nm (12 720 cm^{-1}) with a separation of 1360 cm^{-1} between them. Except for a red shift of some 25 nm, the luminescence spectrum is identical with that of phthalocyanine monomers without TTF functionalities,[12] and it can therefore be attributed to the fluorescence from the Q-band with a characteristically small Stokes' shift of only ~200 cm^{-1}. At first sight, the luminescence spectrum does not show the typical mirror image of the absorption, hence, the broader component of the Q-band exhibits fluorescence quenching. However, the excitation spectrum ($\lambda_{det} = 780$ nm), also included in Figure 3b, is indeed the mirror image of the fluorescence. The fact that it differs from the absorption spectrum in the range of the broader component of the Q-band could also be taken as an indication that even with the quite substantial excess of the oxidizing agent $FeCl_3$, oxidation of the four TTF units is still not quite complete, and that in order for the fluorescence to be switched on, all four TTF units have to be oxidized simultaneously.

Concluding Remarks. During this study we developed an efficient synthetic route to the important precursor 5,6-dicyanobenzene-1,3-dithiole-2-one **2**, which can readily react with corresponding thiones in the presence of a phosphorus(III) compound to afford phthalonitrile derivatives in good yields. Furthermore, we demonstrated that redox-active TTF units can be annulated to a Pc core and it could be shown that these fused systems are good π-electron donors. Interestingly, the closed shell derivatives exhibit an intense redox-state dependent emission. With the key building block **2** at hand, this new set of large π-systems might be extended in a straightforward manner, specifically at the periphery of the TTF units. More TTF-annulated Pcs with further functionalities are under investigation.

Experimental Section

Synthesis. All reagents were of commercial quality and used as supplied unless otherwise stated; solvents were dried where necessary using standard procedures. All reactions were carried out under an inert atmosphere. 1,2-Bis(*S*-benzylthio)-4,5-dicyanobenzene **1**[13] and 4,5-bis(propylthio)-1,3-dithiole-2-thione **3**[14] were prepared according to literature procedures (see the Supporting Information).

5,6-Dicyanobenzene-1,3-dithiole-2-one (2). A solution of compound **1** (1 g, 2.7 mmol) and $AlCl_3$ (2.9 g, 21.5 mmol) in toluene (60 mL) was stirred under nitrogen at room temperature for 2 h, then 1,1′-carbonyldiimidazole (0.87 g, 5.4 mmol) was added to the yellow mixture and it was stirred for an additional 0.5 h. The solvent was removed under reduced pressure. Chromatography of the residue on a silica gel column with CH_2Cl_2/hexane (3/1) as eluent afforded 0.5 g (85%) of compound **2** as a white powder: mp 239 °C; ^{1}H NMR (DMSO-d_6) δ 8.68 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 188.5, 138.6, 128.7, 115.4, 112.4; IR (KBr) ν_{max} 2234 (C≡N), 1731 (C=O), 1660 cm^{-1}; EI-MS *m/z* (rel intensity, %) 218 (M$^+$, 43). Anal. Calcd for $C_9H_2N_2S_2O$: C, 49.53; H, 0.92; N, 12.84. Found: C, 49.39; H, 0.99; N, 12.56.

5,6-Dicyano-2-(4,5-bis(propylthio)-1,3-dithio-2-ylidene)-benzo[*d*]-1,3-dithiole (4). A solution of compound **2** (50 mg, 0.23 mmol) and compound **3** (156 mg, 0.34 mmol) in a mixture of triethyl phosphite (10 mL) and toluene (5 mL) was heated to 120 °C under nitrogen for 3 h. After removal of the solvent under reduced pressure, chromatography on silica of the residue with CH_2Cl_2/hexane (2/1) as eluent afforded 66 mg (68%) of compound **4** as a red powder. Single crystals suitable for X-ray diffraction determination were obtained by cooling a saturated DMSO solution: mp 233 °C; ^{1}H NMR (DMSO-d_6) δ 8.30 (s, 2H), 2.88 (t, 4H, $J = 7.14$ Hz), 1.64 (m, 4H, $J = 7.14$ Hz, $J = 7.35$ Hz), 0.98 (t, 6H, $J = 7.35$ Hz); ^{13}C NMR (DMSO-d_6) δ 143.1, 126.8, 126.2, 114.9, 113.1, 111.8, 107.1, 37.3, 22.3, 12.3; IR (KBr) ν_{max} 3437, 3078, 2960, 2933, 2873, 2234 (C≡N), 1566, 1458, 1236, 1216, 1126 cm^{-1}; EI-MS *m/z* (rel intensity, %) 452 (M$^+$, 100). Anal. Calcd for $C_{18}H_{16}N_2S_6$: C, 47.75; H, 3.56; N, 6.19. Found: C, 47.77; H, 3.54; N, 5.91.

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2,3,9,10,16,17,23,24-Tetrakis[4′,5′-bis(propylthio)tetrathiafulvalene]phthalocyanine (5). Lithium metal (0.3060 g, 46.9 mmol) was dissolved in 1-pentanol (25 mL) at 80 °C under argon. To this lithium pentoxide solution was added 0.2033 g (0.45 mmol) of compound **4** and the mixture was heated to 125 °C under argon and stirred at this temperature for 5 h. The color changed to an intense green within 15 min. The green mixture was cooled to room temperature, ethanol (80 mL) and glacial acetic acid (80 mL) were added, and the suspension was allowed to stand overnight. A dark green solid was obtained by decantation, centrifugation, and washing with large amounts of ethanol, a mixture of ethanol and water, and ether. The solid was dried at 45 °C and in vacuo yielding 0.140 g (68%): mp >250 °C dec; UV−vis (pyridine) λ_{max} (ϵ) 355 (45 000), 617 (27 000), 691 (22 000) nm; IR (KBr) ν_{max} 3430, 2959, 2923, 2869, 1407, 1071, 1021 cm^{-1}; MS calcd for $C_{72}H_{66}N_8S_{24}$ 1809.87 (M$^+$), found (MALDI) 1809.89 (M$^+$), 1823.79 (M$^+$ − 86). Anal. Calcd for $C_{72}H_{66}N_8S_{24}$: C, 47.70; H, 3.67; N, 6.18. Found: C, 48.00; H, 3.79; N, 5.81.

General Procedure for the Synthesis of Tetrakis-TTF-Annulated Metallophthalocyanines. A mixture of 0.050 g (0.110 mmol) of **4** and 0.037 mmol of the appropriate anhydrous metal chloride was heated in 1 mL of DMAE to 135 °C under argon overnight. The mixture was cooled to room temperature, and MeOH was added to precipitate the product. The dark green solid was obtained by decantation, centrifugation, and washing with large amounts of MeOH, a mixture of MeOH and water, and ether. The solid was dried at 45 °C and in vacuo.

{2,3,9,10,16,17,23,24-Tetrakis[4′,5′-bis(propylthio)tetrathiafulvalene]phthalocyaninato}cobalt(II) (6). Yield 0.042 g (61%): mp >250 °C dec; UV−vis (pyridine) λ_{max} (ϵ) 333 (114 000), 473 (shoulder, 23 000), 641 (40 000), 687 (42 000) nm; IR (KBr) ν_{max} 2959, 2927, 2869, 1420, 1386, 1068 cm^{-1}; MS calcd for $C_{72}H_{64}N_8S_{24}Co$ 1866.79 (M$^+$), found (MALDI) 1866.77 (M$^+$), 1884.76 (M$^+$+ H_2O). Anal. Calcd for $C_{72}H_{64}N_8S_{24}Co$: C, 46.25; H, 3.45; N, 5.99. Found: C, 46.11; H, 3.52; N, 5.95.

{2,3,9,10,16,17,23,24-Tetrakis[4′,5′-bis(propylthio)tetrathiafulvalene]phthalocyaninato}nickel(II) (7). Yield 0.061 g (88%): mp >250 °C dec; UV−vis (pyridine) λ_{max} (ϵ) 328 (99 000), 620 (26 000) nm; IR (KBr) ν_{max} 2959, 2925, 2867, 1423, 1388, 1069 cm^{-1}; MS calcd for $C_{72}H_{64}N_8S_{24}Ni$ 1865.79 (M$^+$), found (MALDI):1865.79 (M$^+$), 1883.76 (M$^+$+ H_2O). Anal. Calcd for $C_{72}H_{64}N_8S_{24}Ni$: C, 46.25; H, 3.45; N, 5.99. Found: C, 46.05; H, 3.54; N, 5.90.

{2,3,9,10,16,17,23,24-Tetrakis[4′,5′-bis(propylthio)tetrathiafulvalene]phthalocyaninato}zinc(II) (8). Yield 0.036 g (52%): mp >250 °C dec; UV−vis (pyridine) λ_{max} (ϵ) 367 (125 000), 655 (70 000), 706 (75 000) nm; IR (KBr) ν_{max} 3432, 2959, 2927, 2870, 1413, 1377, 1063 cm^{-1}; MS calcd for $C_{72}H_{64}N_8S_{24}Zn$:1871.78 (M$^+$), found (MALDI) 1871.73 (M$^+$), 1786.69 (M$^+$ − 86). Anal. Calcd for $C_{72}H_{64}N_8S_{24}Zn$: C, 46.09; H, 3.44; N, 5.97. Found: C, 46.11; H, 3.51; N, 5.93.

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Supporting Information Available: General experimental methods, detailed experimental procedures and characterization data for compounds **1** and **3**, ^{1}H and ^{13}C NMR spectra for compounds **2** and **4**, UV−vis spectra of compounds **5**−**8**, and thin layer cyclic voltammogram of compounds **6**−**8,** as well as an X-ray crystallographic file for **4** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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