Synthesis and Electrochemical and Photophysical Studies of Tetrathiafulvalene-Annulated Phthalocyanines

Claudia Loosli, Chunyang Jia, Shi-Xia Liu, Marco Haas, Marylène Dias, Eric Levillain, Antonia Neels, Gael Labat, Andreas Hauser, and Silvio Decurtins*

Departement für Chemie und Biochemie, Université Bern, Freiestrasse 3, 3012 Bern, Switzerland, Groupe Systèmes Conjugués Linéaires, Laboratoire de Chimie, Ingénierie Moléculaire et Matériaux d’Angers, UMR CNRS 6200, 2 Bd Lavoisier, 49045 Angers, France, Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, 2007 Neuchâtel, Switzerland, and Département de Chimie Physique, Université de Genève, 30 Quai Ernest-Ansermet, 1211 Genève 4, Switzerland
decurtins@iac.unibe.ch

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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 \( \pi \)-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 \( \pi \)-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 \( \text{Pc} (\text{H}_2\text{Pc}) \) derivatives bearing one, two, four, or eight peripheral TTF units, respectively, all linked by spacer groups exhibited the...
Preparation of the Tetrakis-TTF-Annulated Phthalocyanines 5–8

The synthetic pathway is out-

lined in Scheme 1. The precursor 1,2-bis(S-benzylthio)-4,5-dicyanobenzene 1 was treated with AlCl3 in toluene at room temperature under a nitrogen atmosphere before 1,1′-carbonyldimidazole 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 triethylphosphate 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 CHCl3, CH2Cl2, and THF, slightly soluble in CH3CN, acetonitrile, 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 H3Pc-(TTF)4. The compound is soluble in CHCl3, CH2Cl2, and
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)\textsubscript{4} \( \text{compd} \quad E_{1/2}/V \quad E_{2/3}^a/V \quad E_{3/4}^a/V \)

<table>
<thead>
<tr>
<th>compd</th>
<th>( E_{1/2}/V )</th>
<th>( E_{2/3}^a/V )</th>
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<td>4</td>
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<tr>
<td>5</td>
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<td>0.11</td>
<td>0.62</td>
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<td>0.14</td>
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<td>7</td>
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<td>8</td>
<td>0.14</td>
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\( ^a \) vs Fc\(^+/Fc\).

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\(^+\) 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)\textsubscript{4} 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)\textsubscript{4} 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\textsubscript{2}Pc-(TTF)\textsubscript{4} (b), in 0.1 M tetrabutylammonium hexafluorophosphate in CH\textsubscript{2}Cl\textsubscript{2}/CH\textsubscript{3}CN (9.5/0.5, v/v) at 0.1 V s\(^{-1}\), Pt electrode.

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 phthalocyanine 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 $\pi$-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 $\pi$-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(benzothiazol-2-yl)imidazole (1), 4,5-dicyanobenzene 1$^1$ and 4,5-bis(propylthio)-1,3-dithiole-2-thione 3$^1$ 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′-carbonyldimidazole (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$_2$Cl$_2$/hexane (3/1) 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, 112.4; IR (KBr) v$_{max}$ 3234 (C-H, COL), 1731 (C=O), 1660 cm$^{-1}$; EI-MS m/z (rel. intensity, %) 218 (M$,^+$, 43). Anal. Calcd for C$_{36}$H$_{26}$N$_6$: C, 79.53; H, 4.92; N, 12.56. Found: C, 79.59; H, 4.73; N, 12.56.

**5,6-Dicyanobenzene-1,3-dithiole-2-one (2).** 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$_2$Cl$_2$/hexane (3/1) as eluent afforded 66 mg (85%) of compound 4. Single crystals suitable for X-ray diffraction determination were obtained by cooling a saturated DMSO solution: mp 239 °C; $^1$H NMR (DMSO-$d_6$) δ 8.30 (s, 2H), 2.88 (t, 4H, $J = 7.14$ Hz), 1.84 (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) v$_{max}$ 3437, 3078, 2960, 2933, 2873, 2234 (C=O); $^1$H NMR (DMSO-$d_6$) δ 8.68 (s, 2H), 2.88 (t, 4H, $J = 7.14$ Hz), 1.84 (m, 4H, $J = 7.14$ 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) v$_{max}$ 3437, 3078, 2960, 2933, 2873, 2234 (C=O), 1566, 1458, 1458, 1236, 1216, 1126 cm$^{-1}$; EI-MS m/z (rel. intensity, %) 218 (M$,^+$, 43). Anal. Calcd for C$_{36}$H$_{26}$N$_6$: C, 79.53; H, 4.92; N, 12.56. Found: C, 79.59; H, 4.73; N, 12.56.

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) $\lambda_{\text{max}} (e)$ 355 (45 000), 617 (22 000) nm; IR (KBr) $\nu_{\text{max}}$ 3430, 2959, 2923, 2869, 1407, 1071, 1021 cm$^{-1}$; MS calcd for C$_{72}$H$_{66}$N$_8$S$_{24}$ 1809.87 (M$^+$), found (MALDI) 1809.89 (M$^+$), 1823.79 (M$^+$ - 86). Anal. Calcd for C$_{72}$H$_{66}$N$_8$S$_{24}$: 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) $\lambda_{\text{max}} (e)$ 333 (114 000), 473 (shoulder, 23 000), 641 (40 000), 687 (42 000) nm; IR (KBr) $\nu_{\text{max}}$ 2959, 2927, 2870, 1413, 1377, 1063 cm$^{-1}$; MS calcd for C$_{72}$H$_{64}$N$_8$S$_{24}$Co 1866.79 (M$^+$), found (MALDI): 1866.77 (M$^+$), 1884.76 (M$^+$ + H$_2$O). Anal. Calcd for C$_{72}$H$_{64}$N$_8$S$_{24}$Co: C, 46.25; H, 3.45; N, 5.99. Found: C, 46.11; H, 3.52; N, 5.95.

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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. JO0501801