Available online at www.sciencedirect.com

SCIENCE DIRECT®

Tetrahedron 62 (2006) 3543–3549

Tetrahedron

Synthesis of tetrathiafulvalene-annulated phthalocyanines

Chantal A. Donders,[a] Shi-Xia Liu,[a,*] Claudia Loosli,[a] Lionel Sanguinet,[c]
Antonia Neels[b] and Silvio Decurtins[a]

[a]*Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, 3012 Bern, Switzerland*
[b]*Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux, 51, 2007 Neuchâtel, Switzerland*
[c]*Laboratoire de Chimie, Ingénierie Moléculaire et Matériaux d'Angers (CIMMA), UMR 6200 du CNRS, 2 Bd Lavoisier, 49045 Angers, Cedex, France*

Received 22 November 2005; revised 16 January 2006; accepted 30 January 2006

Abstract—The synthesis of three new TTF-annulated phthalocyanine (Pc) derivatives **5a–c** are described. All of them have been characterized by elemental analysis, IR and UV–vis spectroscopy. In all cases, the incorporation of long and flexible aliphatic side-chains into the rigid TTF-annulated Pc core did not promote the formation of a discotic mesophase.

1. Introduction

Being a versatile class of functional dyes and pigments, phthalocyanines (Pcs) have been studied extensively over the last few decades.[1–2] Since they exhibit high thermal and chemical stability, well-defined optical absorption, semiconducting and photoconducting properties, and self-organizing abilities to form columnar mesophases, Langmuir–Blodgett (LB) multilayers, or aggregates in solution,[3–5] Pcs have been employed as subunits for the construction of functional materials. In particular, a great and growing interest in liquid crystalline Pc systems aroused because a columnar arrangement of Pc cores gives rise to a low dimensional conduction pathway and therefore can be considered as molecular wires, which can transport charge or excitons.[6–10] As a consequence, the mesophase structures of a number of Pcs with variations in the number, length, type and position of flexible side-chains, including linear alkyl, alkoxymethyl and alkoxy chains, have been investigated.[1,11] It has been demonstrated that in contrast to crystalline phases, liquid-crystalline phases are more suitable for applications in electronic devices due to their improved processing characteristics and self-healing of structural defects.[12]

Tetrathiafulvalene (TTF) and its derivatives can sequentially and reversibly be oxidized to the stable cation radicals and dications and therefore, they act as π-electron donor molecules.[13] Moreover, liquid crystalline TTF derivatives have been reported, in which nematic, smectic A and columnar phases were observed.[14]

Within this context, several Pcs linked with appended TTF moieties by various spacers have been reported in the last 10 years.[15–20] Interestingly, it has been found that covalent linkage of TTF units to a Pc system can lead to fluorescence quenching due to intramolecular charge transfer between TTF units and Pc*.[15] Noteworthy, so far only one example of a TTF-appended Pc shows a liquid crystalline behavior.[19] Based on an efficient synthetic approach to TTF-annulated Pc derivatives developed in our group,[21] much effort will be devoted to characterize new systems with peripheral substitutions.

In the present work, we describe the synthesis and properties of three new TTF-annulated Pc derivatives **5a–c**, substituted with four or eight long and flexible aliphatic chains at the periphery (Scheme 1). Such systems are of prime interest because the suitably functionalized derivatives could show a discotic liquid crystalline phase due to the increase in the aromatic core size and overall planarity of the molecules.

2. Result and discussion

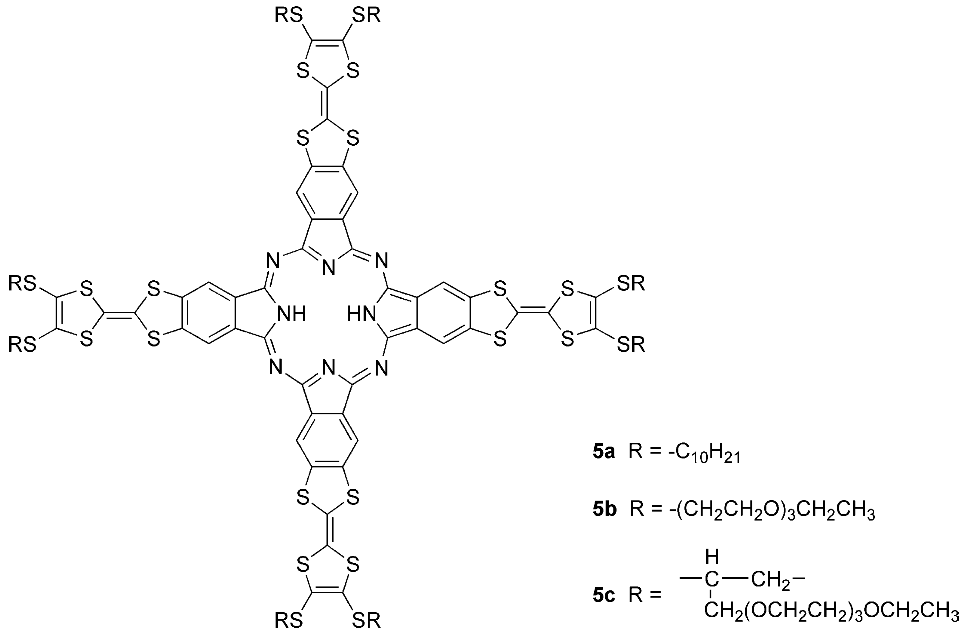
The synthesis of **5a–c** required the preparation of the key phthalonitrile precursors **4a–c** (Scheme 2). The latter were obtained from the cross-coupling reaction of **3** with the corresponding 1,3-dithiole-2-thione derivatives **2**, bearing

---

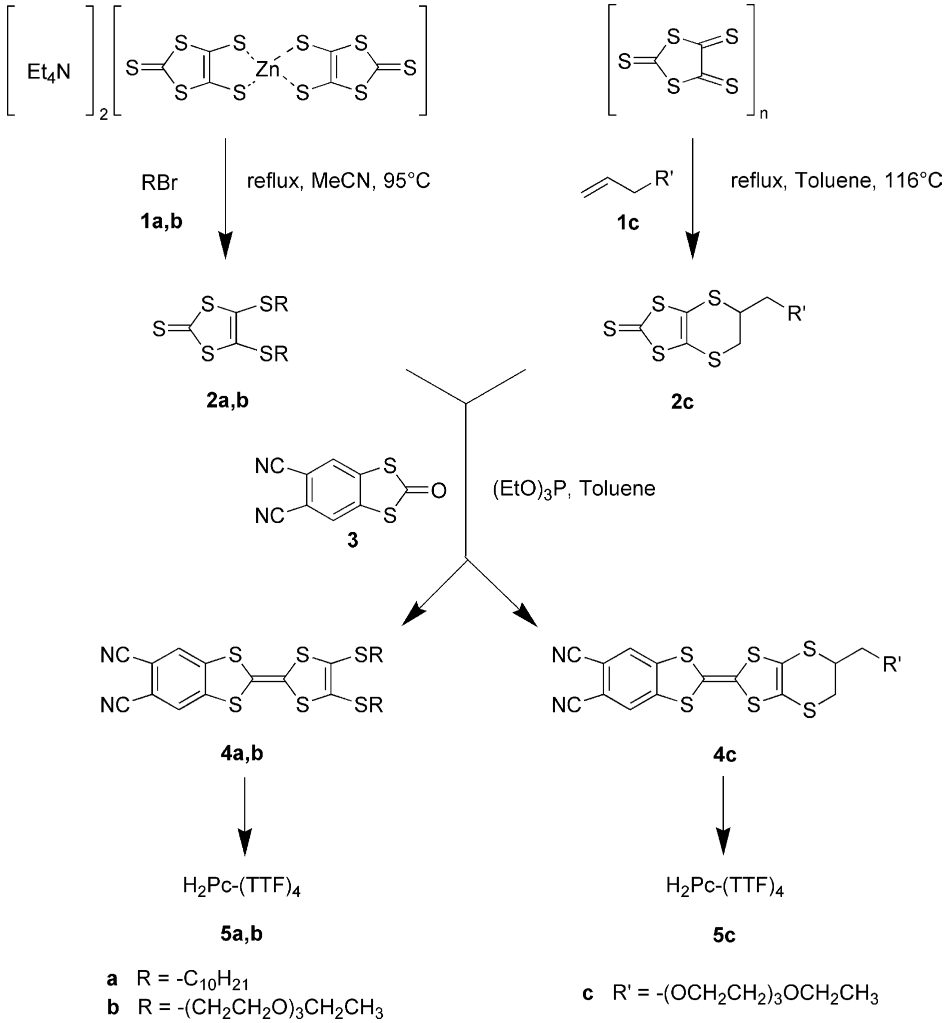
Keywords: Synthesis; Tetrathiafulvalene-annulated phthalocyanines; Phthalonitrile derivatives; Liquid crystal.

* Corresponding author. Tel.: +41 31 6314296; fax: +41 31 6313995; e-mail: liu@iac.unibe.ch

0040–4020/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2006.01.098



Scheme 1. Molecular structure of the TTF-annulated Pc derivatives.



Scheme 2. Synthesis of the tetrakis-TTF-annulated Pc derivatives.

the different flexible aliphatic chains. The thione intermediates **2a–c** were prepared by using two different strategies. The well-established substitution reaction of bis(tetraethylammonium)bis(1,3-dithiole-2-thione-4,5-dithiolate)zincate with the suitable bromide gave compounds **2a** and **2b** in high yields, while the Diels–Alder reaction of oligo(1,3-dithiole-2,4,5-trithione) with **1c** in toluene at 116 °C afforded compound **2c** in a good yield. The phosphite-mediated cross-coupling reaction of **3** with **2a–c** produced phthalonitrile intermediates **4a–c** in reasonable yields, and their tetramerization in the presence of lithium pentoxide at 120 °C under nitrogen resulted in the formation of the corresponding metal-free Pc derivatives **5a–c**.

All new precursors have been purified by column chromatography and fully characterized by elemental analysis, NMR, IR and MS as listed in the Section 4. Compound **4a** is soluble in THF and slightly soluble in $CHCl_3$, CH_2Cl_2 and ether, **4b** soluble in $CHCl_3$, CH_2Cl_2, THF, CH_3CN, acetone, DMSO, EtOAc and ether, and **4c** soluble in $CHCl_3$, CH_2Cl_2, THF, DMSO, EtOAc and slightly soluble in CH_3CN.

It has been noted that the order of the melting point values for the compounds **4** of similar side-chain length is as follows: alkyl > oxyethylene. Quite probably, the difference is related to the greater rigidity of the alkyl chains.

Suitable crystals of compound **4a** for a X-ray diffraction study could be obtained by recrystallization from acetonitrile. This compound crystallizes in a triclinic space group (*P*-1) and an ORTEP[22] plot of the molecule with the atomic numbering scheme is shown in Figure 1. As expected, the TTF-fused phthalonitrile moiety is essentially planar with a rms deviation of 0.05 Å from the least-squares plane through all atoms comprising the unit. This moiety is nearly perpendicular to the mean plane consisting of the aliphatic side-chains with a dihedral angle of 83°.

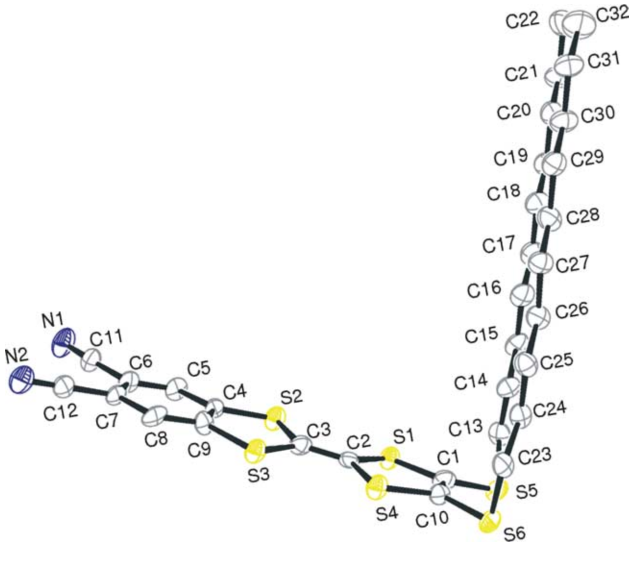


Figure 1. Molecular structure of compound **4a** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: C1–S5 1.730; C1–S1 1.765; C2–C3 1.328; C2–S1 1.740; C2–S4 1.764; C3–S3 1.756; C3–S2 1.773; C4–C9 1.400; C4–S2 1.739; C9–S3 1.736; C10–S6 1.756; C10–S4 1.761. Selected bond angles [°]: S3–C3–S2 114.24; S1–C2–S4 114.16; C9–C8–C7 119.40; C8–C7–C6 119.76; C5–C6–C7 120.10; C6–C5–C4 120.78; C5–C4–C9 119.29; C8–C9–C4 120.60.

In the crystal lattice of **4a**, along the *a*-axis, the molecules are arranged in layers exhibiting C8-H···N1 type of hydrogen bonds [C···N 3.222 Å]. Along the *b* direction, molecules related by a center of symmetry are mutually shifted and form dimers via a C–H···N hydrogen bond, C14-H14B···N2 [C···N 3.593 Å], with an interplanar separation of 3.46 Å (in the dimer) and 3.39 Å (between adjacent dimers), respectively (Fig. 2). Obviously, the resulting peculiar stacks are dominated by H-bonds and van der Waals forces between the side-chains.

The Pc derivative **5a** is soluble in $CHCl_3$, CH_2Cl_2, THF and ethers, and **5b** is soluble in $CHCl_3$, CH_2Cl_2, THF, acetone, DMSO, EtOAc, ethers and slightly soluble in CH_3CN. In contrast, **5c** is very insoluble in most common organic solvents. In the mass spectrum of **5a**, the monoisotopic mass was observed at *m*/*z* 2594. An additional peak was found at *m*/*z* 2312, corresponding to the fragment of **5a** with two missing side-chains. The mass spectrum of **5b** displays the monoisotopic molecular peak at *m*/*z* 2754. The TGA measurements reveal that the compounds contain solvent molecules in agreement with the elemental analysis results.

For the octasubstituted TTF-annulated Pcs **5a** and **5b**, ^1H NMR spectra are not available due to the high aggregation of the Pcs, a fact which is frequently encountered at the concentrations used for NMR measurements.[23] Their UV–vis spectra in CH_2Cl_2 exhibit characteristic, rather broad Q-band absorptions of $\pi \rightarrow \pi^*$ transitions at 616 and 627 nm, respectively. For the tetra-substituted compound **5c**, solution properties are impossible to be investigated owing to its extreme insolubility.

In order to address the electrochemical properties, **5a** was studied by cyclic voltammetry. A variety of experiments under different conditions have been carried out and the discrepancies of cyclic voltammograms are observed due to strong aggregation phenomena in solutions, which was reported in the literature.[24] The best cyclic voltammogram obtained is shown in Figure 3. Two reversible oxidation processes were observed at 0.16 and 0.57 V (vs Fc^+/Fc), which correspond to the formation of the radical tetracation and octacation species of the TTF moieties and are comparable to those of its analogue with propyl groups at the periphery.[21] However, a redox wave in the negative direction, presumably arising from the reduction of the Pc macrocycle, is hardly to be assigned. Unfortunately, more detailed information can not be provided by differential-pulse voltammetry (DPV), thin-layer cyclic voltammetry, and spectroelectrochemical measurements because of a high degree of aggregation.

Finally, the Pc derivatives **5a–c** as well as the precursors **4a–c** were investigated by DSC measurements. In all cases, the attachment of long and flexible aliphatic side-chains to the TTF moieties and also to the TTF-annulated Pc cores did not promote the formation of a discotic liquid crystalline phase. Noteworthy, **4b** exhibits two peaks at 86 and 119 °C, but no mesophase could be observed by the polarized optical microscope.

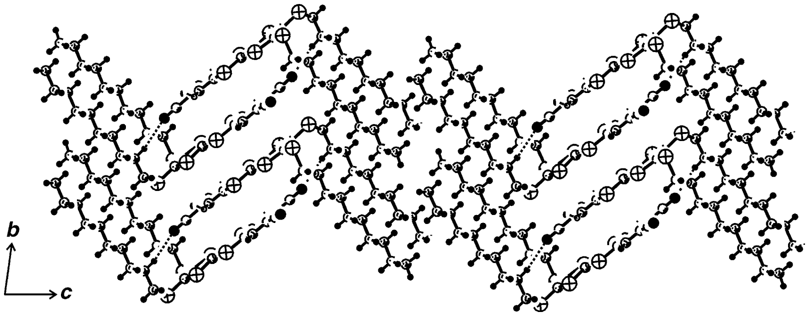


Figure 2. *bc* Projection of the crystal structure of **4a**, showing the formation of hydrogen bonded (dashed lines) dimers.

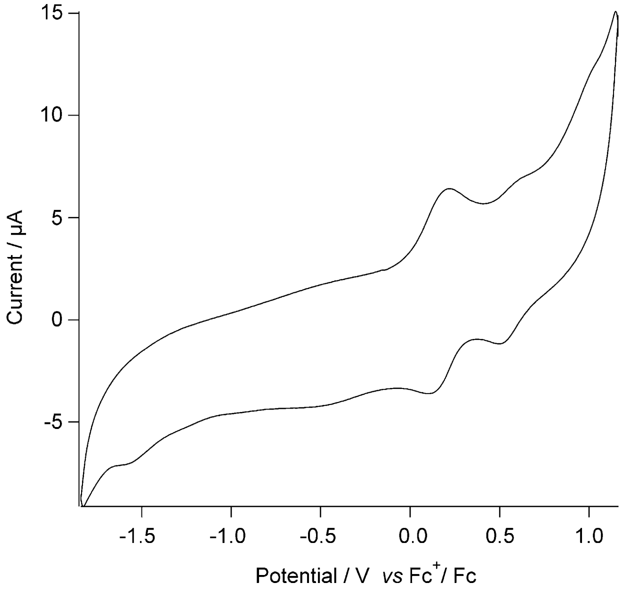


Figure 3. Cyclic voltammogram for **5a**.

3. Conclusion

We achieved the syntheses of new tetra- and octa-substituted TTF-annulated Pc derivatives with long and flexible alkyl or oxyethylene chains at the periphery. However, in all cases, no mesophases were observed. Probably, branching of the side-chain could introduce disorder and hence a decrease in the transition temperature. Therefore, studies are underway to prepare TTF-annulated Pc derivatives appropriately functionalized with branched hydrocarbon substituents to further investigate their liquid crystalline behavior.

4. Experimental

4.1. Equipment

^{1}H NMR spectra were obtained on a Bruker AC 300 and AC 400 spectrometer operating at 300.18 MHz: chemical shifts reported in parts per million relative to TMS. The following abbreviations were used s, singlet; d, doublet; t, triplet; m, multiplet. ^{13}C NMR spectra were performed on a Bruker AC 500 spectrometer operating at 100.61 MHz. UV–vis absorption spectra were recorded on a Perkin–Elmer Lambda 10 spectrometer. Elemental analyses were performed on a Carlo Erba EA 1110 CHN apparatus. Infrared spectra were recorded on a Perkin–Elmer Spectrum One FT-IR spectrometer using KBr pellets or with a JACSO FT/IR-460Plus spectrometer in the case of oily substances. EI spectra were recorded using an Auto SpecQ spectrometer. MALDI-MS was carried out with a FTMS 4.7 TBioAPEX II TOF apparatus. Cyclic voltammetric measurements were conducted on a Metrohm VA-Stand 663 electrochemical analyser. All oxidation potentials were determined under N_2 in CH_2Cl_2 versus Ag/AgCl at room temperature. Measurements have been done at a scan rate of 100 mV s^{-1} using 0.1 M Bu_4NPF_6 as electrolyte and Pt as working electrode. Solid state measurements for thermogravimetry were performed with a Mettler TG 50 system and differential scanning calorimetry with a Mettler DSC 25 apparatus.

4.2. Crystallography

An orange plate-like crystal of compound **4a** was mounted on a Stoe Mark II-Imaging Plate Diffractometer System[25] equipped with a graphite-monochromator. Data collection was performed at −100 °C using Mo Kα radiation (λ= 0.71073 Å). 128 Exposures (10 min per exposure) were obtained at an image plate distance of 135 mm, 128 frames with ϕ=0° and $0<\omega<180°$ with the crystal oscillating through 1.4° in ω. The resolution was D_{min}–D_{max} 23.99–0.82 Å. The structure was solved by direct methods using the program SHELXS-97[26] and refined by full matrix least squares on F^2 with SHELXL-97.[27] The hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically. No absorption correction was applied. Crystal data has been deposited at the Cambridge Crystallographic Data Centre, reference CCDC 290264. Copy of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

4.3. Materials

All reagents and solvents were of commercial quality and distilled or dried when necessary using standard procedures. All reactions were carried out under inert atmosphere unless otherwise stated. Bis(tetraethylammonium)bis(1,3-dithiole-2-thione-4,5-dithiolate)-zincate,[28] oligo(1,3-dithiole-2,4,5-trithione),[28] 5,6-dicyanobenzene-1,3-dithiole-2-one **3**[21] and 1-bromo-3,6,9-trioxaundecane **1b**[29] were prepared according to literature procedures.

4.3.1. 4,7,10,13-Tetraoxapentadecene (1c). A mixture of triethylenglycolmonoethylether (2.96 ml, 16.9 mmol), NaOH aqueous solution (6 N, 14.6 ml) and tetrabutylammoniumhydrogensulfat (0.57, 1.68 mmol) was stirred for 30 min at 30 °C under nitrogen. Allylchloride (4.15 ml, 51 mmol) was then added dropwise and stirred for an additional 1 h. The resulting solution was heated up to 45 °C and stirred overnight. The product was extracted with ethyl acetate and washed with water. The combined organic phases were dried over Na_2SO_4 and concentrated. The crude product was purified by column chromatography (SiO_2) with a gradient of 100–0% hexane in EtOAc. Yield: 3.19 g (88%), colorless oil. MS (EI): *m/z* 218 (M^+, 13%). ^{1}H NMR ($CDCl_3$) δ: 5.75–5.63 (m, 1H), 5.02–4.92 (m, 2H), 3.82–3.79 (m, 2H), 3.49–3.27 (m, 14H), 1.01 (t, $J=7.05$ Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 134.73, 116.94, 72.15, 70.60, 70.57, 70.54, 69.76, 69.37, 66.54, 15.07. IR (thin film, cm^{-1}): 2862, 1454, 1348, 1293, 1247, 1105, 995, 921, 847.

4.3.2. 4,5-Bis(decylthio)-1,3-dithiole-2-thione (2a). Bis(tetraethylammonium)bis(1,3-dithiole-2-thione-4,5-dithiolate)zincate (2.5 g, 3.48 mmol) was dissolved in 45 ml acetonitrile and degassed under N_2 for 20 min. Then, 1-bromodecane (3.5 ml, 14.84 mmol) was carefully added to the dark red solution. This mixture was refluxed for at least 4 h at 95 °C. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO_2) eluting initially with hexane and then with dichloromethane, to afford **2a** as a yellow solid. Yield: 2.83 g (85%), mp 41 °C. Anal. Calcd for $C_{23}H_{42}S_5$: C 57.68, H 8.84; found C 57.98, H 9.00. MS (EI): *m/z* 478 (M^+, 59%). ^{1}H NMR ($CDCl_3$) δ: 2.88 (t, $J=7.34$ Hz, 4H), 1.69–1.63 (m, 4H), 1.42–1.25 (m, 28H), 0.89 (t, $J=6.69$ Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 211.48, 136.34, 36.75, 31.85, 29.64, 29.50, 29.45, 29.26, 29.05, 28.48, 22.65, 14.08. IR (KBr, cm^{-1}): 2919, 2849, 1471, 1059, 1029, 889, 719.

4.3.3. 4,5-Bis(3,6,9-trioxaundecylthio)-1,3-dithiole-2-thione (2b). Bis(tetraethylammonium)bis(1,3-dithiole-2-thione-4,5-dithiolate)zincate (0.6 g 0.84 mmol) was dissolved in 10 ml acetonitrile and degassed for 15 min. Then, 1-bromo-3,6,9-trioxaundecane (0.86 g, 3.6 mmol) was carefully added to the dark red solution. This mixture was refluxed for at least 4 h at 95 °C. After cooling to room temperature, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, initially with pure hexane and then with ethyl acetate as eluting solvent), to afford **2b** as a yellow oil. Yield: 0.727 g (83%). Anal. Calcd for $C_{19}H_{34}O_6S_5$: C 43.99, H 6.61; found C 44.60, H 6.87. MS (EI): *m/z* 518 (M^+, 19%). ^{1}H NMR ($CDCl_3$) δ: 3.65 (t, $J=6.39$ Hz, 4H), 3.59–3.48 (m, 20H), 3.08 (t, $J=6.40$ Hz, 4H), 1.22 (t, $J=6.96$ Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 211.41, 136.95, 71.17, 71.05, 70.97, 70.26, 70.22, 67.04, 36.54, 15.57. IR (thin film, cm^{-1}): 2970, 2862, 1459, 1348, 1285, 1244, 1102, 1060, 941, 887, 847.

4.3.4. 4,5-(2,5,8,11-Tetraoxatridecylethylenedithio)-1,3-dithiole-2-thione (2c). 4,7,10,13-Tetraoxapentadecene (2.5 g 11.4 mmol) was dissolved in 25 ml toluene and stirred for 20 min at 30 °C. Then, 4.4 g of oligo(1,3-dithiole-2,4,5-trithione) was added. The orange suspension was stirred for another 20 min at 30 °C, and then heated up to 116 °C and refluxed for at least 4 h. A dark brown solution was formed, cooled down to room temperature, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, EtOAc/hexane 2:1). Yield: 2.54 g (54%), a yellow oil. Anal. Calcd for $C_{14}H_{22}O_4S_5$: C 40.55, H 5.35; found C 40.66, H 5.34. MS (EI): *m/z* 414 (M^+, 17%). ^{1}H NMR ($CDCl_3$) δ: 3.91–3.81 (m, 2H), 3.67–3.48 (m, 15H), 3.41–2.28 (m, 2H), 1.22 (t, $J=7.06$ Hz, 3H). ^{13}C NMR ($CDCl_3$) δ: 207.79, 123.38, 122.11, 71.89, 70.95, 70.63, 70.57, 70.42, 69.75, 66.56, 42.43, 31.29, 15.10. IR (thin film, cm^{-1}): 2861, 1736, 1486, 1348, 1295, 1237, 1105, 1055, 924, 887, 867, 847, 787.

4.3.5. 5,6-Dicyano-2-(4,5-bis(decylthio)-1,3-dithio-2-ylidene)-benzo[*d*]-1,3-dithiole (4a). Compounds **3** (50 mg, 0.23 mmol) and **2a** (218 mg, 0.46 mmol) were dissolved in a mixture of triethyl phosphite (0.41 ml) and toluene (2.5 ml). This solution was heated to 120 °C and refluxed for 4 h. After cooling to room temperature, a red precipitate was formed and filtered off. The crude product was purified by column chromatography on silica gel eluting with a gradient of 100–0% hexane in CH_2Cl_2 to afford compound **4a** as an orange solid. Yield: 60.2 mg (40%), mp 178 °C. Anal. Calcd for $C_{32}H_{44}N_2S_6$: C 59.21, H 6.83, N 4.32; found C 59.25, H 6.90, N 4.06. MS (EI): *m/z* 648 (M^+, 44%). ^{1}H NMR ($CDCl_3$) δ: 7.51 (s, 2H), 2.84 (t, $J=7.25$ Hz, 4H), 1.67–1.57 (m, 4H), 1.41–1.25 (m, 28H), 0.89 (t, $J=6.69$ Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 145.05, 128.41, 125.35, 118.01, 115.14, 113.38, 104.49, 36.85, 32.3, 30.12, 29.95, 29.90, 29.71, 29.50, 28.88, 23.08, 14.51. IR (KBr, cm^{-1}): 2923, 2849, 2235, 1567, 1465, 1128, 873, 773, 726.

4.3.6. 5,6-Dicyano-2-(4,5-bis(3,6,9-trioxaundecylthio)-1,3-dithio-2-ylidene)-benzo[*d*]-1,3-dithiole (4b). Compounds **3** (230 mg, 1.05 mmol) and **2b** (1.1 g, 2.12 mmol) were dissolved in a mixture of triethyl phosphite (1.88 ml) and toluene (7.5 ml). The resulting solution was refluxed at 120 °C for 4 h. After cooling to room temperature, hexane was added to the brownish solution. A red solid was formed immediately, filtered off and washed with hexane. The crude product was purified by column chromatography on silica gel, initially with hexane and then with EtOAc as eluent. Compound **4b** was obtained as a red solid. Yield: 185.2 mg (26%), mp 119 °C. Anal. Calcd for $C_{28}H_{36}N_2O_6S_6$: C 48.81, H 5.27, N 4.07; found C 48.98, H 5.27, N 3.82. MS (EI): *m/z* 688 (M^+, 79%). ^{1}H NMR ($CDCl_3$) δ: 7.53 (s, 2H), 3.64–3.48 (m, 24H), 3.04 (t, $J=6.68$ Hz, 4H), 1.22 (t, $J=6.9$ Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 144.88, 128.52, 125.42, 117.27, 115.12, 113.43, 105.54, 71.17, 70.97, 70.38, 70.22, 67.07, 36.01, 15.57. IR (KBr, cm^{-1}): 2864, 2232, 1565, 1456, 1354, 1246, 1115, 1037, 875, 859, 774, 725.

4.3.7. 5,6-Dicyano-2-(4,5-(2,5,8,11-tetraoxatridecylethylenedithio)-1,3-dithio-2-ylidene)-benzo[*d*]-1,3-dithiole (4c). Compound **2c** (0.514 g 1.23 mmol) was dissolved in a mixture of toluene (5.5 ml) and triethyl phosphite (1.14 ml) and stirred for 5 min at 30 °C. 5,6-Dicyanobenzene-1,3-dithiole-2-one was added. The mixture was heated up to 115 °C and refluxed for 3 h. After cooling down to room temperature, a red solid was formed upon the addition of hexane. After filtration, the red solid was washed thoroughly with hexane and purified by column chromatography on silica gel, initially with hexane and then with EtOAc. Yield: 223 mg (55%), mp 117 °C. Anal. Calcd for $C_{23}H_{24}N_2O_4S_6$: C 47.24, H 4.14, N 4.79; found C 47.40, H 4.12, N 4.51. MS (EI): *m/z* 584 (M^+, 39%). ^{1}H NMR ($CDCl_3$) δ: 7.53 (s, 2H), 3.89–3.76 (m, 2H) 3.68–3.48 (m, 15H), 3.33–3.19 (m, 2H), 1.22 (t, $J=7.07$ Hz, 3H). IR (KBr, cm^{-1}): 2905, 2873, 2229, 1565, 1458, 1348, 1244, 1128, 1102, 964, 885, 773.

4.3.8. 2,3,9,10,16,17,23,24-Tetrakis[4′,5′-bis(decylthio)-tetrathiafulvalene]phthalocyanine (5a). Lithium metal (33.4 mg, 4.81 mmol) was dissolved in 1-pentanol (2.6 ml) at 60–80 °C. To this lithium pentoxide solution was added compound **4a** (30 mg, 0.046 mmol). The mixture was heated up to 120 °C and refluxed for 5 h. The color of the solution turned within 15 min from red to an intensive green. The green solution was allowed to cool down to room temperature. A mixture of ethanol (10 ml) and glacial acetic acid (10 ml) was added. The resulting suspension was kept overnight. A dark green solid was obtained by decantation and centrifugation. The crude product was purified by washing with a combination of water, ethanol and acetone. The solid was dried at 45 °C and also in vacuo. Yield: 20.8 mg (66%). It decomposes at 300 °C. Anal. Calcd for $C_{128}H_{178}N_8S_{24}\cdot 5H_2O$: C 57.18, H 7.04, N 4.17; found C 56.73, H 6.62, N 3.68. MS (MALDI, dithranol as matrix): *m/z* 2594 (M^+). UV–vis λ_{max} (dichloromethane, $\varepsilon \times 10^{-3}$ M^{-1} cm^{-1}): 615.7 (51.9), 356.79 (76.3), 305.79 (71.2). IR (KBr, cm^{-1}): 2923, 2853, 1458, 1429, 1407, 1376, 1324, 1071, 1022, 870, 776, 742, 720.

4.3.9. 2,3,9,10,16,17,23,24-Tetrakis[4′,5′-bis(3,6,9-trioxaundecylthio)tetrathiafulvalene]phthalocyanine (5b). Lithium metal (39.44 g, 5.68 mol) was dissolved in 1-pentanol (3.2 ml) at 60–80 °C. To this lithium pentoxide solution was added compound **4b** (40 mg, 0.058 mmol). The mixture was heated to 120 °C and stirred for 5 h. After cooling to room temperature, a mixture of ethanol (10 ml) and glacial acetic acid (10 ml) was added to the green solution. The solution was allowed to stand overnight and neutralized with aqueous NaOH solution. After extraction with CH_2Cl_2 (50 ml), the combined organic phases were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was washed with a mixture of hexane and ethyl acetate (15/1). The green sticky compound was dried at 45 °C and also in vacuo. Yield: 42.07 mg (26%). It decomposes at 285 °C. Anal. Calcd for $C_{112}H_{146}N_8O_{24}S_{24}\cdot 5H_2O$: C 47.23, H 5.52, N 3.93; found C 46.82, H 4.98, N 3.53. MS (MALDI, dithranol as matrix): *m/z* 2754 (M^+). UV–vis λ_{max} (dichloromethane, $\varepsilon \times 10^{-3}$ M^{-1} cm^{-1}): 627.0 (56.1), 358.64 (79.2), 308.70 (68.3). IR (KBr, cm^{-1}): 3438, 2863, 1565, 1409, 1377, 1349, 1112, 1072, 1023, 776, 740, 680.

4.3.10. 2,3,9,10,16,17,23,24-Tetrakis[4′,5′-(2,5,8,11-tetraoxatridecylethylenedithio)tetrathiafulvalene]phthalocyanine (5c). Lithium metal (23.3 mg, 3.35 mmol) was dissolved in 1-pentanol (1.90 ml) at 60–80 °C. To this lithium pentoxide solution was added compound **4c** (20 mg, 0.034 mmol). The mixture was heated up to 120 °C and stirred for 5 h. The color of the resulting solution changed from red over brownish to green. Then, the solution was allowed to cool down to room temperature and a mixture of hexane (10 ml) and glacial acetic acid (10 ml) was added. The mixture was kept overnight. A dark green solid was obtained by centrifugation. The crude product was purified by washing with a combination of hexane and ethylacetate. The solid was dried at 45 °C and also in vacuo. Yield: 9 mg (45%). It decomposes at 150 °C. Anal. Calcd for $C_{92}H_{98}N_8O_{16}S_{24}\cdot C_6H_{14}$: C 48.48, H 4.65, N 4.62; found C 47.98, H 4.36, N 4.36. IR (KBr, cm^{-1}): 2861, 1728, 1452, 1406, 1372, 1106, 1071, 1021, 934, 875, 771, 678.

Acknowledgements

This work was supported by the Swiss National Science Foundation (grant no. 200020-107589 and COST Action D31) as well as by the ESF programme—SONS (NANOSYN). We thank Prof. Robert Deschenaux, University of Neuchâtel, for the assistance in polarized optical microscopy and differential scanning calorimetry (DSC) measurements.

References and notes

1. McKeown, N. B. *Phthalocyanine Materials: Synthesis, Structure and Function*; Cambridge University Press: Cambridge, 1998.
2. Calvete, M. J. F.; Dini, D.; Flom, S. R.; Hanack, M.; Pong, R. G. S.; Shirk, J. S. *Eur. J. Org. Chem.* **2005**, 3499–3509.
3. Cook, M. J. *Chem. Rec.* **2002**, *2*, 225–236.
4. Inabe, T.; Tajima, H. *Chem. Rev.* **2004**, *104*, 5503–5533.
5. Piechocki, C.; Simon, J.; Skoulios, A.; Guillon, D.; Weber, P. *J. Am. Chem. Soc.* **1982**, *104*, 5245–5247.
6. Tant, J.; Geerts, Y. H.; Lehmann, M.; De Cupere, V.; Zucchi, G.; Laursen, B. W.; Bjornholm, T.; Lemaur, V.; Marcq, V.; Burquel, A.; Hennebicq, E.; Gardebien, F.; Viville, P.; Beljonne, D.; Lazzaroni, R.; Cornil, J. *J. Phys. Chem. B* **2005**, *109*, 20315–20323.
7. Adam, D.; Closs, F.; Frey, T.; Funhoff, D.; Haarer, D.; Ringsdorf, H.; Schuhmacher, P.; Siemensmeyer, K. *Phys. Rev. Lett.* **1993**, *70*, 457–460.
8. Markovitsi, D.; Germain, A.; Millié, P.; Lécuyer, P. *J. Phys. Chem.* **1995**, *99*, 1005–1017.
9. Markovitsi, D.; Lécuyer, I.; Simon, J. *J. Phys. Chem.* **1991**, *95*, 3620–3626.
10. Boden, N.; Bushby, R. J.; Clements, J. *J. Chem. Phys.* **1993**, *98*, 5920–5931.
11. Gearba, R. I.; Bondar, A. I.; Goderis, B.; Bras, W.; Ivanov, D. A. *Chem. Mater.* **2005**, *17*, 2825–2832.
12. Lemaur, V.; da Silva Filho, D. A.; Coropceanu, V.; Lehmann, M.; Geerts, Y.; Piris, J.; Debije, M. G.; van de Craats, A. M.; Senthilkumar, K.; Siebbeles, L. D. A.; Warman, J. M.; Brédas, J.-L.; Cornil, J. *J. Am. Chem. Soc.* **2004**, *126*, 3271–3279.
13. Segura, J. L.; Martín, N. *Angew. Chem., Int. Ed.* **2001**, *40*, 1372–1409.
14. Allard, E.; Oswald, F.; Donnio, B.; Guillon, D.; Delgado, J. L.; Langa, F.; Deschenaux, R. *Org. Lett.* **2005**, *7*, 383–386.
15. Wang, C.; Bryce, M. R.; Batsanov, A. S.; Stanley, C. F.; Beeby, A.; Howard, J. A. K. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1671–1678.
16. Hu, Y.; Shen, Y. *J. Heterocycl. Chem.* **2002**, *39*, 1071–1075.

17. Hu, Y.; Lai, G.; Shen, Y.; Li, Y. *Chemical Monthly* **2004**, *135*, 1167–1172.
18. Hu, Y.; Lai, G.; Shen, Y.; Li, Y. *J. Porphyrins Phthalocyanines* **2004**, *8*, 1042–1046.
19. Cook, M. J.; Cooke, G.; Jafari-Fini, A. *Chem. Commun.* **1996**, 1925–1926.
20. Blower, M. A.; Bryce, M. R.; Devonport, W. *Adv. Mater.* **1996**, *8*, 63–65.
21. Loosli, C.; Jia, C.; Liu, S.-X.; Haas, M.; Dias, M.; Levillain, E.; Neels, A.; Labat, G.; Hauser, A.; Decurtins, S. *J. Org. Chem.* **2005**, *70*, 4988–4992.
22. Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.
23. Leznoff, C. C.; Lever, A. B. P. In *Phthalocyanines, Properties and Applications*, *Vols. 1–4*; VCH: New York, 1989–1996.
24. Kadish, K. M.; Smith, K. M.; Guilard, R. Phthalocyanines: Spectroscopic and Electrochemical Characterization In *The Porphyrin Handbook*, *Vol. 16*; Academic: Amsterdam, 2003.
25. Stoe and Cie, *IPDS Software*; Stoe and Cie GmbH: Darmstadt, Germany, 2005.
26. Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.
27. Sheldrick, G. M., *SHELXL-97: Program for crystal structure refinement*, University of Göttingen: Germany, 1997.
28. Svenstrup, N.; Becher, J. *Synthesis* **1995**, 215–235.
29. Perchonock, C. D.; Uzinskas, I.; McCarthy, M. E.; Erhard, K. F.; Gleason, J. G.; Wasserman, M. A.; Muccitellli, R. M.; DeVan, J. F.; Tucker, S. S.; Vickery, L. M.; Kirchner, T.; Weichman, B. M.; Mong, S.; Scott, M. O.; Chi-Rosso, G.; Wu, H. L.; Crooke, S. T.; Newton, J. F. *J. Med. Chem* **1986**, *29*, 1442–1452.