Synthesis, spectroscopy and electrochemistry of phthalocyanine derivatives functionalised with four and eight peripheral tetrathiafulvalene units

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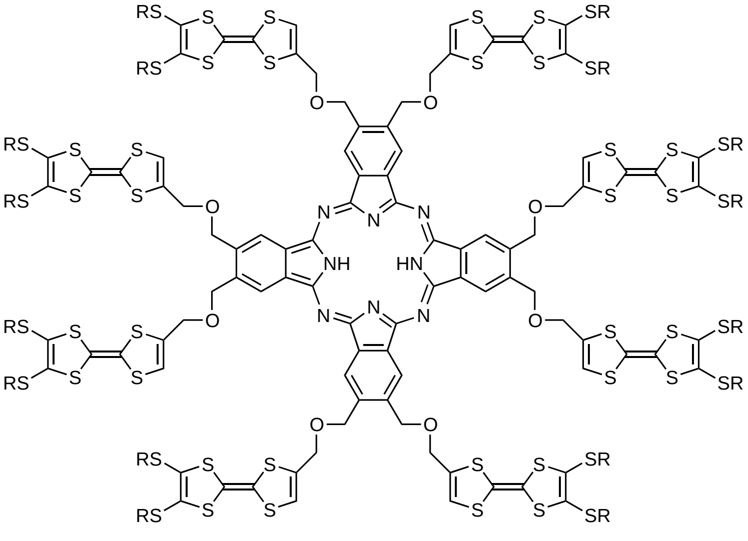
Metal-free phthalocyanine derivatives 2 and 14 bearing eight and four peripheral tetrathiafulvalene (TTF) units, respectively, have been synthesised, and their solution electrochemistry and optical spectroscopy have been studied. The compounds display redox properties arising from the TTF and from the phthalocyanine groups. ^{1}H NMR and UV–VIS spectroscopic studies in solution show that aggregation is strongly solvent dependent. Quenching of the fluorescence of the phthalocyanine core by the TTF units was observed. The X-ray crystal structure of 4,5-bis(hexylthio)-4′,5′-bis(hydroxymethyl)-TTF 11, which was synthesised during the course of this work, has been determined. The hydroxy groups of 11 engage in intermolecular (and interstack) hydrogen bonds. Computer modelling studies on phthalocyanine derivatives 2 and 14 are reported.

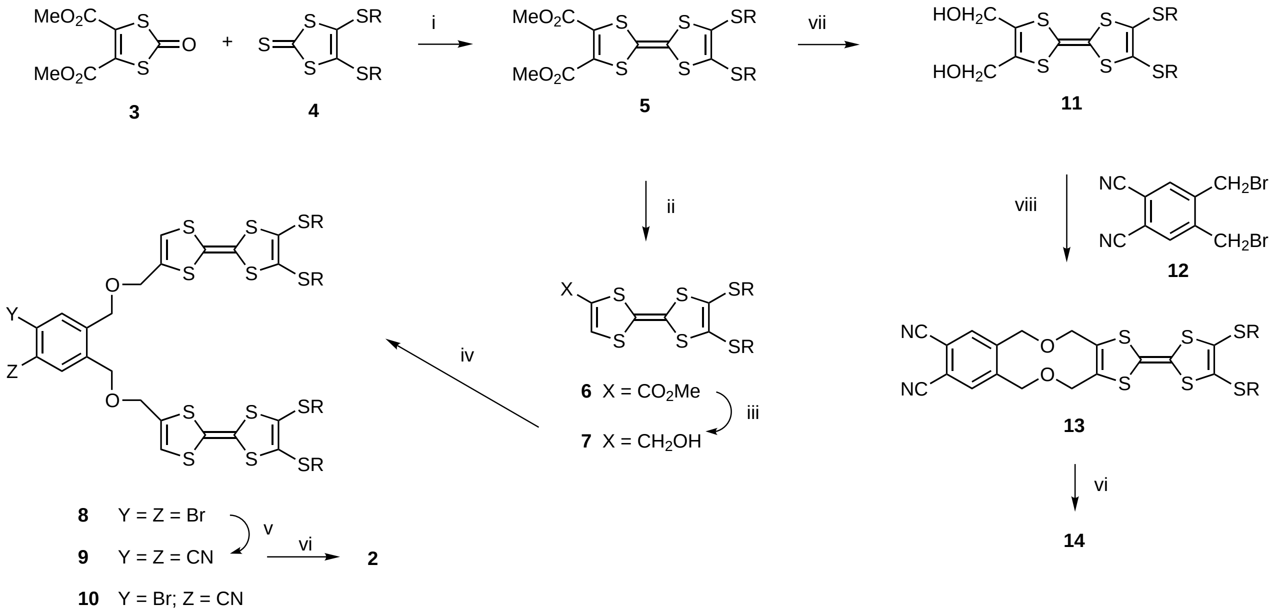
Introduction

For many years phthalocyanine derivatives have attracted considerable attention as a consequence of their diverse electronic, optical, structural and coordination properties, which offer applications in the fields of non-linear optics, liquid crystals, Langmuir–Blodgett films, electrochromic devices, molecular metals, gas sensors, photosensitisers and diagnostic and therapeutic agents in pharmacology.[1] There is keen current interest in exploring new structural modifications to the phthalocyanine system, including the study of binuclear derivatives,[2] heterocyclic analogues[3] in which the benzene rings are replaced by nitrogen-containing[3a–d] or sulfur-containing[3e,f] heterocycles, and derivatives with specially-designed ‘active’ peripheral substituents, *viz.* thiolate groups which coordinate transition metals,[4] a fullerene moiety which undergoes electrochemical reduction,[5] flexible unsymmetrical substituents which result in glasses,[6] mesogenic metal-chelated crown ethers which form nanometre-sized molecular cables,[7] glycol side-chains to hinder aggregation and thereby increase the luminescence quantum yield[8] and liquid crystalline ferrocenyl- and tetrathiafulvalenyl-phthalocyanine derivatives.[9]

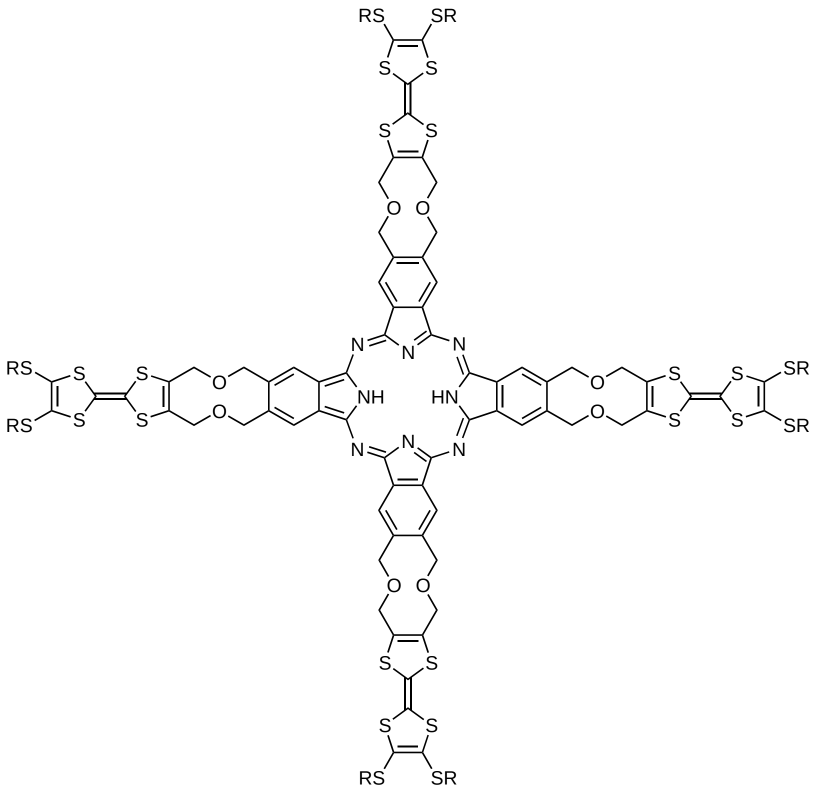
In a recent communication we reported the synthesis of compound **1** bearing eight tetrathiafulvalene (TTF) substituents which provided the first example of the covalent attachment of phthalocyanine (Pc) and TTF units.[10] Subsequently Cook and co-workers described a phthalocyanine system functionalised with one TTF unit which displayed liquid crystalline behaviour.[9b] We chose TTF as a substituent for our studies because of its well-known ability to form stable cation radicals,[11] and we were interested in exploring the electrochemical and optical properties of the different redox units in Pc–(TTF)$_x$ (x = 4 and 8) assemblies. The extreme insolubility of compound **1** in almost all organic solvents severely hindered purification and characterisation studies, but nonetheless ^{1}H NMR spectra were obtained in [^{2}H$_6$]dimethyl sulfoxide ([^{2}H$_6$]DMSO) and optical spectroscopic data and cyclic voltammograms were obtained in dimethylformamide (DMF). In an extension of this work, we now report the synthesis and characterisation of an analogous Pc–(TTF)$_8$ system **2**, which by virtue of the sixteen



1 SR = H
2 SR = S-C$_6$H$_{13}$



Scheme 1 R = C_6H_{13}, *Reagents and conditions:* i, triethyl phosphite, 120 °C; ii, lithium bromide, HMPA, 80 °C; iii, DIBALH, THF, −78 to 20 °C; iv, NaH, THF, 40 °C, then 1,2-dibromo-4,5-bis(bromomethyl)benzene, 20 °C; v, copper cyanide, DMF, 140 °C; vi, lithium pentoxide, pentanol, 125 °C; vii, DIBALH, THF, −10 to 20 °C; viii, NaH, THF, reflux, then compound **12**, 20 °C



14 R = C_6H_{13}

peripheral hexylthio substituents is soluble in organic solvents, and the first example of a Pc–(TTF)$_4$ derivative, *viz*. compound **14**, which also contains solubilising substituents.

Results and discussion

Synthesis

The synthesis of our target molecules **2** and **14** is shown in Scheme 1. The key intermediate for both compounds is TTF derivative **5** which was obtained in 63% yield by the standard phosphite-induced cross-coupling[12] of the 1,3-dithiole-2-one and -2-thione fragments **3** and **4**. One of the ester substituents of compound **5** was removed by treatment with lithium bromide in hexamethylphosphoric triamide (HMPA) at 80 °C,[13] to afford monoester derivative **6** (88% yield) which was reduced with diisobutylaluminium hydride (DIBALH) to yield the alcohol derivative **7** (86% yield). Compound **7** was deprotonated by treatment with sodium hydride in dry tetrahydrofuran (THF) and the derived alkoxide anion (2 equiv.) reacted with 2,3-dibromo-4,5-bis(bromomethyl)benzene to yield the bis-(TTF) system **8** (64% yield). The conversion of dibromo derivative **8** into dicyano analogue **9** was the most problematical step in the synthesis of **2**: reaction with copper cyanide in DMF at 140 °C produced dicyano derivative **9** in an optimised yield of

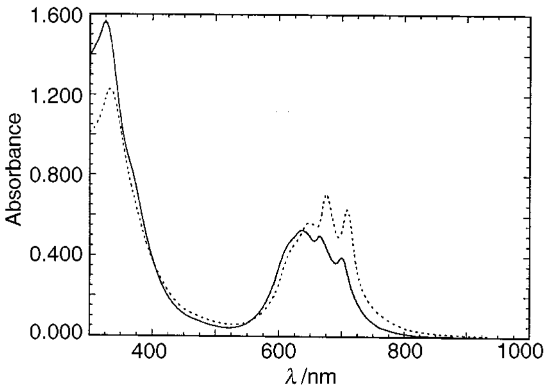


Fig. 1 UV–VIS spectra of compound **2** (solid line, 1.1746 × 10^{-5} M) and compound **14** (dashed line, 1.4376 × 10^{-5} M) in toluene–pyridine solution (99 : 1 v/v)

28% after chromatographic separation from the bromo-cyano analogue **10** (22%) which was always present in the product mixture. After much experimentation, we had previously found[10] that lithium pentoxide in pentanol[14] at 140 °C were the optimum reagents and conditions for the tetramerisation of the dinitrile precursor to form phthalocyanine derivative **1**: we, therefore, adopted similar conditions for the tetramerisation of **9**, and obtained phthalocyanine derivative **2** in 56% yield at 125 °C.

For the synthesis of compound **14** bearing four TTF units, we first reduced diester **5** with diisobutylaluminium hydride to yield dialcohol **11** (75% yield), the X-ray crystal structure of which is reported below. Compound **11** was then deprotonated by treatment with sodium hydride (2 equiv.) and the dianion was reacted with 4,5-bis(bromomethyl)phthalonitrile **12** (prepared by bromination of dimethylphthalonitrile using *N*-bromosuccinimide) to yield compound **13** (12% yield). Although the yield of this step is low (predictably for the synthesis of a 10-membered ring) the use of the phthalonitrile derivative had the advantage of circumventing the cyanation step (*cf.* the inefficient conversion of **8** into **9**, discussed above). Compound **13** was tetramerised to afford phthalocyanine system **14** in 48% yield, by direct analogy with the preparation of **2**.

Compounds **2** and **14** were both isolated as dark green solids which, in marked contrast to analogue **1**,[10] were soluble in a range of organic solvents (*e.g.* chloroform, carbon disulfide, dichloromethane and toluene) but insoluble in alcohols, acetonitrile and dimethylformamide. Spectroscopic data, elemental analysis and MALDI TOF mass spectra were entirely consistent with the proposed structures. The ^{1}H NMR spectra of **2** and **14** at room temperature in $CDCl_3$ gave broad peaks with no fine structure; ^{13}C NMR spectra were obtained at 50 °C in $CDCl_3$ and the peaks for compound **2** were much sharper than those for compound **14**, suggesting that the latter compound is more aggregated in $CDCl_3$ solution at the relatively high concentration of the NMR sample. A very recent quantitative study emphasises the important effects of concentration and temperature on the aggregation and hence the ^{1}H NMR chemical shifts of octaalkynylphthalocyanines.[15] No EPR signals were observed for samples of **2** or **14**, suggesting that the broad NMR spectra were not due to radical impurities.

UV–VIS and fluorescence spectroscopy

UV–VIS spectra of solutions of compounds **2** and **14** in a mixture of toluene and pyridine (99 : 1 v/v) at 20 °C are shown in Fig. 1. The split Q-band, which is characteristic of a metal-free phthalocyanine, is observed at λ_{max} 665 and 700 nm (for compound **2**) and at λ_{max} 674 and 709 nm (for compound **14**). The presence of an additional broader hypsochromically-shifted band in the optical spectra at λ_{max} 636 nm (for **2**) and 648 nm (for **14**) is indicative of aggregated species.[6,7a,8] This band was detected even in extremely dilute solutions of both compounds **2** and **14**; however its relative intensity decreased while that of the low energy Q-band increased with increasing dilution. If we assume that the relative intensities of the highest energy and lowest energy bands are a qualitative indication of the extent of aggregation of **2** and **14** in solution, then at the same concentration in chloroform, compound **14** was found to be the more highly aggregated, which is in agreement with the NMR results discussed above. In the 300–500 nm region the spectra show superimposed bands of TTF and phthalocyanine species. In dichloromethane solution, the intensity of the lowest wavelength Q-band of compound **2** decreased and was bathochromically shifted to 642 nm (the other bands shifted only very slightly to 667 and 701 nm), whereas no change was observed for compound **14**. These data suggest that compound **2** is less aggregated in dichloromethane than in toluene–pyridine.

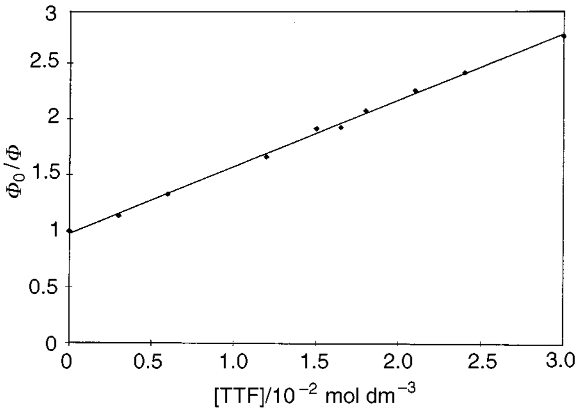


Fig. 2 Stern–Volmer plot for quenching of the fluorescence from Bu_4PcH_2 by TTF; τ_f 5.6 ns; λ_{ex} 630 nm

The luminescence emission from compounds **2** and **14** was found to be of very low intensity and fell in the same spectral region as that of unsubstituted metal-free phthalocyanines. Fluorescence quantum yields were $<10^{-4}$ and 1.7 ± 0.3 × 10^{-3}, for **2** and **14**, respectively. These values are very much lower than that obtained for a metal-free Pc lacking the TTF moieties, *cf.* Bu_4PcH_2, $\Phi = 0.50$.[16] However, we have demonstrated that the fluorescence from Bu_4PcH_2 is efficiently quenched by the addition of TTF to the solution. Thus, in toluene the rate constant for the quenching of Bu_4PcH_2 by TTF was found to be diffusion controlled, $k_Q = 1.1 \pm 0.1 \times 10^{10}$ dm^3 mol^{-1} s^{-1} (Fig. 2). This quenching is likely to be due to an intermolecular electron transfer reaction between the excited singlet state of the Pc and TTF. Calculations based upon the known redox potentials of TTF (see below) and Pc derivatives[17] indicate that the excited singlet state of the Pc is capable of oxidising TTF. In the tethered compounds **2** and **14**, we propose that rapid intramolecular electron transfer occurs between the Pc core and a peripheral TTF.

Cyclic voltammetric studies

The solution redox properties of phthalocyanine derivatives **2** and **14** were studied by cyclic voltammetry (CV), and these data are presented in Table 1, along with those of the new TTF systems reported herein. In dry benzonitrile, compounds **5**–**13** exhibited two reversible redox waves typical of TTF derivatives.[18] It is well known that both ester[18a,b] and thioalkyl substituents[18c,d] raise the oxidation potential of TTF, and accordingly, compounds **5** and **6** are the poorest donors in the present series of compounds. The redox waves for bis(TTF) derivatives **8**, **9** and **10** are assumed to be two-electron couples with no interaction between the two TTF systems. It has been shown in previous CV studies on bis(TTF) derivatives linked by a variety of spacer groups[19] that there is usually no observable inter-

Table 1 Cyclic voltammetry data[a]

Compound	$E^1_{\frac{1}{2}}$/V	$E^2_{\frac{1}{2}}$/V	$E^3_{\frac{1}{2}}$/V	E^4_p/V
TTF	0.34	0.73		
2	−0.51	0.50	0.87	1.18
5	0.74	1.08		
6	0.66	1.04		
7	0.52	0.89		
8	0.54	0.92		
9	0.56	0.92		
10	0.55	0.92		
11	0.48	0.86		
13	0.61	0.96		
14[b]	−0.50	0.54	0.92	1.15

[a] Electrodes: working: Pt, 1.6 mm diameter; counter: Pt; reference: Ag/AgCl. Supporting electrolyte: 0.1 M tetrabutylammonium hexafluorophosphate in benzonitrile. Scan rate: 100 mV s^{-1}. [b] In dichloromethane.

action between the TTF ring systems unless they are linked *via* a single-atom spacer[20] or are directly attached, *i.e.* bi(tetrathiafulvalenyl).[21] The CV data for phthalocyanine systems **2** and **14** are more interesting. In dichloromethane solution, compound **2** exhibits two TTF redox waves at $E_1^{\frac{1}{2}}$ +0.49 V and $E_2^{\frac{1}{2}}$ +0.91 V, with no discernable oxidation (and only a very shallow reduction) of the phthalocyanine core [Fig. 3(*a*)]. However, in benzonitrile solution, a third oxidation peak is seen for compound **2** at +1.18 V (the corresponding reduction is not seen on the reverse sweep) and on the cathodic sweep a reduction peak is observed at $E^{\frac{1}{2}}$ −0.51 V [Fig. 3(*b*)]. Based on literature precedents,[17] we assign these additional redox waves to a single-electron oxidation and reduction, respectively, of the phthalocyanine core unit. The differential pulse voltammogram (DPV) of **2** [Fig. 3(*c*)] shows the Pc reduction wave clearly, although the Pc oxidation wave is more apparent in the CV scan. The electrochemistry of **14** was also found to be solvent dependent. In benzonitrile, the redox waves of the Pc unit were weak, and the oxidation wave was partly hidden under the second TTF wave. However, in dichloromethane, in contrast to **2**, both the reduction and the oxidation of the Pc group were clearly observed. The CV and DPV for **14** in dichloromethane are shown in Figs. 4(*a*) and 4(*b*), respectively.

Based on the current passed for the CV peaks of compounds **2** and **14**, we suggest that all the TTF units are oxidised, although it is noteworthy that for compound **2** the second TTF wave was less intense than the first wave, possibly due to adsorption phenomena, instability of the fully oxidised TTF units and/or the relatively slow motion (on the CV timescale) of the TTF units around the Pc centre. At lower scan rates the current for the second TTF wave increased slightly, but even at 10 mV s^{-1} this wave was less intense than the second TTF wave. The solvent dependency of the electrochemistry of both **2** and **13** suggests that the conformation and/or extent of aggregation vary considerably with the solvent, as implied by the UV–VIS spectra discussed above. We have recently obtained qualitatively similar data for a pyrazinoporphyrazine system with appended TTF groups.[22]

Molecular modelling studies

Molecular modelling studies of compounds **2** and **14** have been performed. The energy-minimised structure for compound **2**, shown in Fig. 5, possesses four TTF units on each side of the mean macrocycle plane. If the molecules of **2** adopt a similar conformation in solution[23] to the computer-optimised structure, the phthalocyanine core will be partly shielded by the TTF units and their attached alkyl chains; this could be an important factor in modulating the electrochemical properties of the core of the molecule, such as in the case of **2** in dichloromethane. In addition, the aggregation of molecules, which is similarly solvent dependent, is another significant factor influencing the electrochemistry of large molecules. The energy-minimized structure for derivative **14** (Fig. 6) gives a very different conformation for the molecule, again with some shielding of the phthalocyanine core, arising from folding of the ten-membered rings about their O···O vectors.

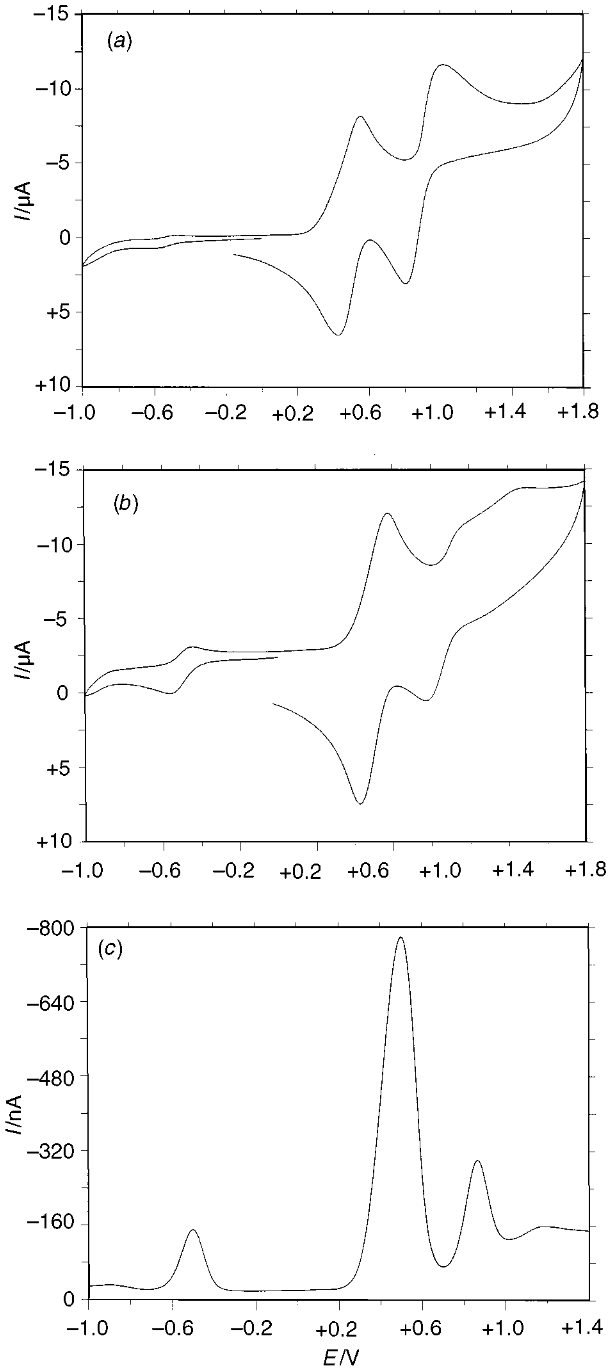


Fig. 3 (*a*) Cyclic voltammogram of compound **2** in dichloromethane; (*b*) cyclic voltammogram of compound **2** in benzonitrile (for conditions see Table 1); (*c*) differential pulse voltammogram of compound **2** in benzonitrile: sample width, 8 ms; pulse amplitude, 50 mV; pulse width 10 ms; pulse period, 200 ms; electrodes as in Table 1

X-Ray crystal structure of compound 11

The molecular structure of **11** is shown in Fig. 7. The crystal packing, illustrated in Fig. 8, is relatively loose (22 Å^3 per non-H atom *vs.* ‘normal’ 18 Å^3). All atoms of the *n*-hexyl chains except the C(7) and C(13) (which are directly bonded to sulfur) are disordered, C(8) to C(12) over two positions (A and B) and C(14) to C(18) over three positions (A, B and C). Both positions of the former chain lie in the same area but in different orientations. The same is true about the A and B positions of

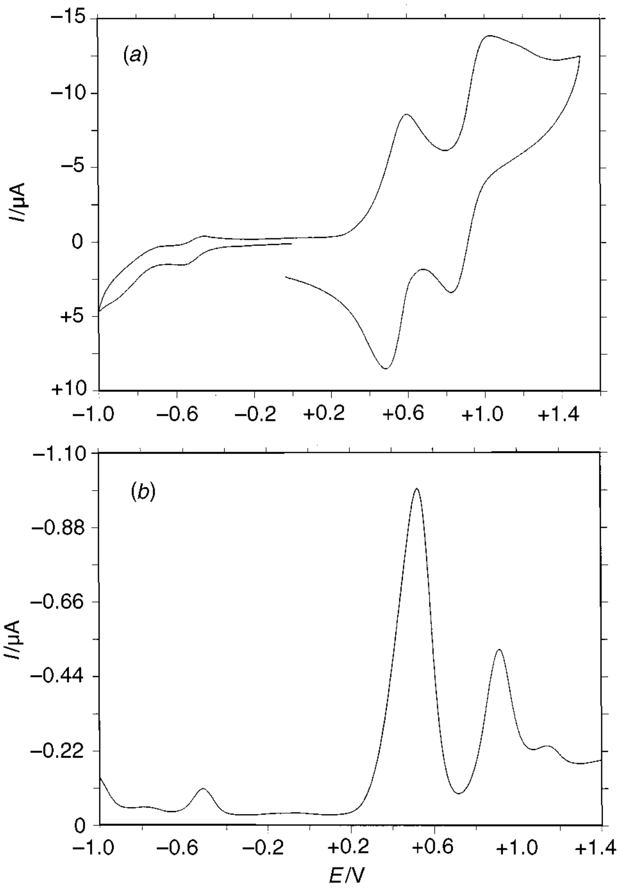


Fig. 4 (*a*) Cyclic voltammogram of compound **14** in dichloromethane (for conditions see Table 1); (*b*) differential pulse voltammogram of compound **14** in dichloromethane: same conditions as Fig. 3(*c*)

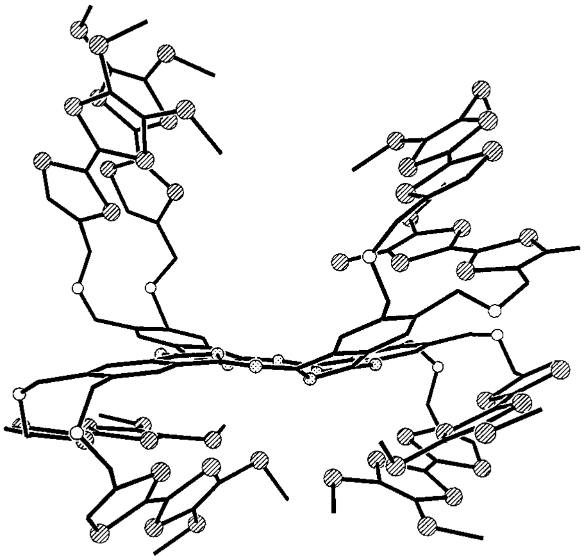


Fig. 5 Energy-minimised structure of compound **2** (side chains omitted for clarity) viewed side-on to the Pc ring

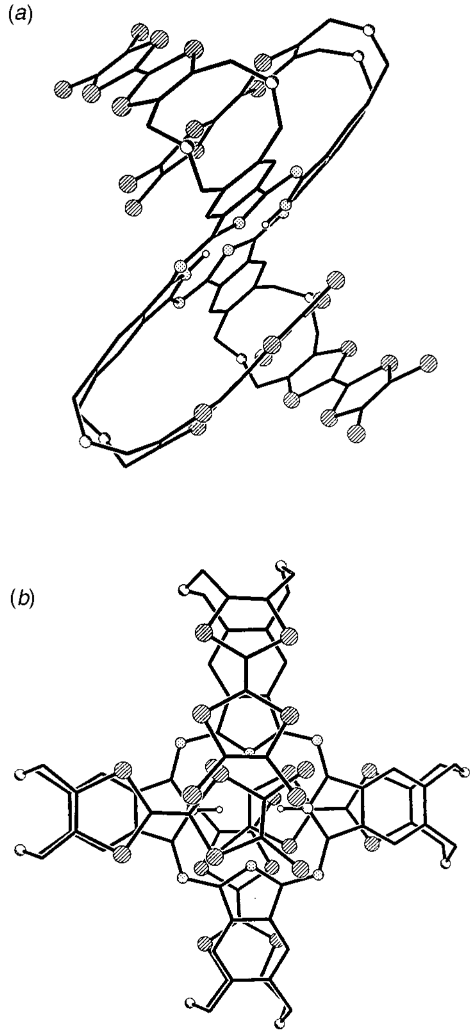


Fig. 6 Energy-minimised structure of compound **14** (side chains omitted for clarity): (*a*) view showing folding of the molecule around the Pc core; (*b*) view onto the plane of the Pc ring

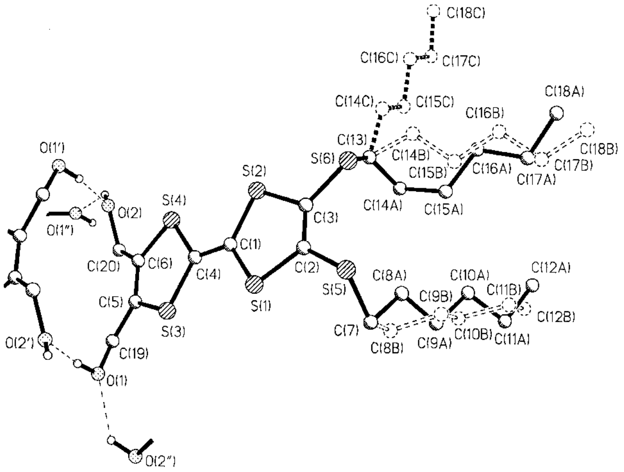


Fig. 7 Perspective view of molecule **11**, showing the disorder of hexyl groups and intermolecular hydrogen bonding. Primed atoms are related *via* inversion centre, double-primed *via* 2_1 axis. H atoms (except hydroxy ones) are omitted. Selected bond distances (Å): C(1)–C(4) 1.34(1), S(1)–C(1) 1.759(8), S(2)–C(1) 1.754(9), S(1)–C(2) 1.749(11), S(2)–C(3) 1.788(9), S(3)–C(4) 1.747(9), S(4)–C(4) 1.788(8), S(3)–C(5) 1.767(9), S(4)–C(6) 1.755(9), C(2)–C(3) 1.32(1), C(5)–C(6) 1.35(1), O(1)···O(2′) 2.705(8), O(2)···O(1″) 2.707(8).

the latter chain, while its C position overlaps (in its terminal part) with the A and B positions of the same chain of a neighbouring molecule [see Fig. 8(*b*)]. This disorder is probably responsible for the rather poor quality of the crystals. No evidence of a superlattice has been found.

The TTF moiety of **11** is folded along the S(1)···S(2) and S(3)···S(4) vectors by 9 and 10°, respectively, in a boat fashion. These moieties form a peculiar stack parallel to the crystallographic *z* direction [Fig. 8(*a*)] in which the long axes of adjacent molecules are mutually perpendicular (89.7°) and their central C_2S_4 planes parallel within 2° with uniform interplanar separations of *ca.* 3.64 Å. Both hydroxy groups are simultaneously donors and acceptors of intermolecular (and interstack) hydrogen bonds (Fig. 7).[24] O(1)H···O(2′) bonds link molecules into

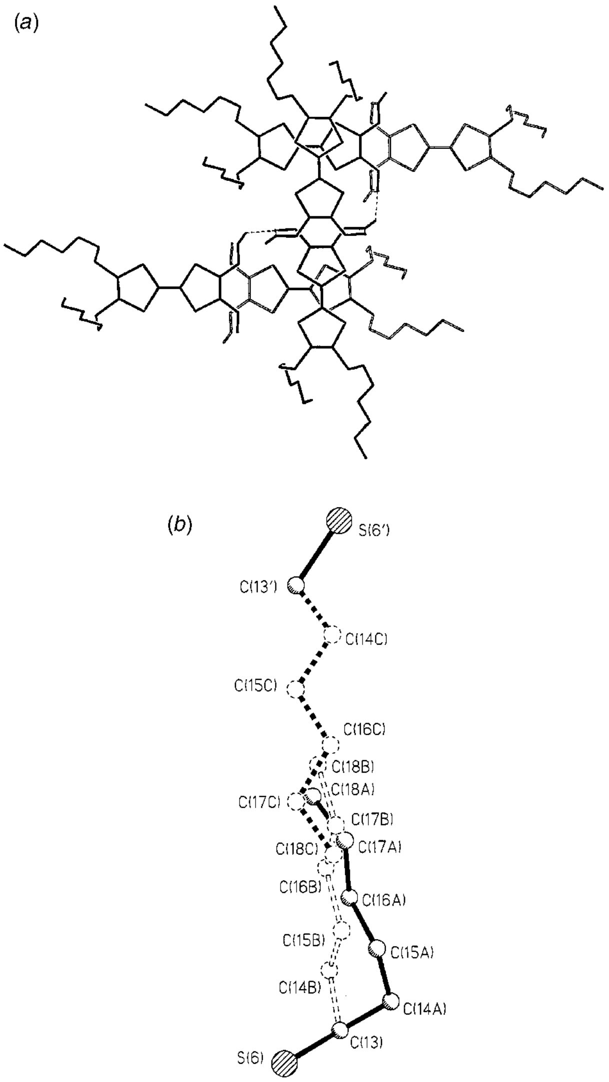


Fig. 8 Crystal packing of **11**: (*a*) hydrogen-bonded chains of molecules; parallel projections down *z* axis, all but one position of the disordered groups and all H atoms are omitted; (*b*) overlap of different positions of the same hexyl chain between molecules related *via* 2_1 axis

centrosymmetric dimers, while O(2)H···O(1″) bonds generate infinite chains of molecules (related *via* the 2_1 axis) along the *x* direction [Fig. 8(*a*)]. The closest intrastack S···S contacts are as long as 3.85 Å [shortest sulfur–carbon, S(1)···C(6) of 3.51 Å] and there are no direct interstack S···S contacts whatsoever.

Conclusions

We have synthesised new phthalocyanine derivatives bearing peripheral TTF substituents which are soluble in a range of organic solvents. We have demonstrated that the fluorescence from metal-free Pcs is efficiently quenched by the addition of TTF, which would be a consequence of intermolecular electron transfer between H_2Pc* and TTF. Quenching of the fluorescence of compounds **2** and **14** is likely to be due to a rapid intramolecular electron transfer reaction between the excited singlet state of the Pc and TTF. Solution electrochemical studies establish that the redox behaviour of these macromolecules is strongly solvent dependent. We have observed the expected two-stage oxidation of the TTF units, and oxidation and reduction of the Pc core. The energy-minimised structures for compound **2** and **14** suggest that the phthalocyanine core is partly shielded by the TTF units and their attached alkyl chains; this could be an important factor in modulating the electrochemical properties of the core of the molecule.

Experimental

General

All reagents and solvents were of commercial quality (purchased from Aldrich or Fluka) and were dried where necessary using standard procedures. Light petroleum refers to the fraction with bp 40–60 °C. ^{1}H NMR spectra were obtained on a VXR 200 spectrometer operating at 200.14 MHz: chemical shifts are quoted downfield of tetramethylsilane. *J* values are in Hz. ^{13}C NMR spectra were obtained on a VXR 500 spectrometer operating at 100.581 MHz. UV–VIS spectra were recorded on a Unicam UV2 spectrometer and the data were processed by a Vision Scan V2.11 program. Mass spectra (EI and CI) were recorded using a VG7070E instrument operating at 70 eV. MALDI TOF mass spectra were obtained on a Kratos IV instrument in the reflection mode, operating with irradiation from a nitrogen laser at 337 nm. The matrix was 2,5-dihydroxybenzoic acid, and spectra were averaged over 100 pulses whilst scanning across the sample: peak half-widths were between 6 and 10 amu. Melting points were obtained on a Kofler hot-stage microscope apparatus and are uncorrected. Electrochemical data were obtained on a BAS CV-50W Voltammetric Analyser. The counter, working and reference electrodes were Pt wire, Pt disc (1.6 mm diameter from BAS) and Ag/AgCl respectively. Cyclic voltammetry was performed under argon using IR compensation. Molecular modelling studies were performed using the Discover 2.9.7/95.0/3.0.0. program in the Insight II 95.0 package and figures were processed by the XP program in the SHELXTL package.[25] Fluorescence spectra and quantum yields were recorded on a Perkin-Elmer LS-50B fluorimeter. Quantum yields were measured using the reported method,[26] relative to ZnPc in toluene–pyridine solution (99:1 v/v), $\Phi_f = 0.30$,[27] and disulfonated aluminium Pc in methanol, $\Phi_f = 0.56$.[28]

4,5-Bis(hexylthio)-4′,5′-bis(methoxycarbonyl)tetrathiafulvalene 5

4,5-Bis(hexylthio)-1,3-dithiole-2-thione **4**[29] (3.67 g, 10 mmol) and 1,3-bis(metoxycarbonyl)-1,3-dithiol-2-one **3**[14*b*] (2.34 g, 10 mmol) were mixed with triethyl phosphite (30 ml) and heated to 120 °C with stirring under argon for 50 min. Removal of the phosphite *in vacuo* gave a deep red oily residue which was chromatographed on a silica column [eluent light petroleum–dichloromethane (1:1 v/v)] to give compound **5** as a dark red oil (3.50 g, 63%) (Calc. for $C_{22}H_{32}O_4S_6$: C, 47.79; H, 5.83. Found: C, 48.13; H, 5.99%); δ_H(CDCl$_3$) 3.84 (s, 6H) 2.80 (t, *J* 7.2, 4H), 1.63 (m, 4H), 1.30 (m, 12H), 0.88 (m, 6H); δ_C(CDCl$_3$) 160.45, 132.49, 131.14, 130.54, 128.47, 53.86, 36.93, 31.80, 30.20, 28.69, 23.04, 14.53.

4,5-Bis(hexylthio)-4′-methoxycarbonyltetrathiafulvalene 6

Compound **5** (3.29 g, 5.95 mmol) and lithium bromide (1.0 g) were mixed with HMPA (40 ml) followed by the addition of 2 drops of water with stirring. The reaction mixture was warmed gradually from room temperature to 80 °C and then stirred at 80 °C for 1.5 h. The mixture was then cooled to room temperature, water (250 ml) and hydrochloric acid (2 drops) were added then the mixture was extracted with chloroform (3 × 30 ml). The organic layer was separated, dried (MgSO$_4$), concentrated *in vacuo* and then chromatographed [silica column, eluent light petroleum–dichloromethane (1:1 v/v)] yielding compound **6** as a red–orange oil (2.6 g, 88%) (Calc. for $C_{20}H_{30}O_2S_6$: C, 48.54; H, 6.11. Found: C, 48.50; H, 6.13%); δ_H(CDCl$_3$) 7.35 (s, 1H), 3.82 (s, 3H), 2.81 (dt, *J* 7.2, 4H), 1.63 (m, 4H), 1.30 (m, 12H), 0.89 (m, 6H).

4,5-Bis(hexylthio)-4′-(hydroxymethyl)tetrathiafulvalene 7

Compound **6** (2.6 g, 5.25 mmol) was dissolved in dry THF (50 ml) and the solution was cooled to −78 °C under argon atmosphere. DIBALH (16 ml, 16 mmol, 1.0 M solution in hexane) was added dropwise to the stirred solution. The reaction mixture was left in the cooling bath overnight allowing the temperature to rise gradually to 20 °C: an orange solution formed. Methanol was added very slowly until gas evolution subsided. Solvent (*ca.* 35 ml) was removed by evaporation *in vacuo* and 2 M hydrochloric acid (*ca.* 50 ml) was added to the gel-like orange residue. Extraction of the mixture with chloroform (3 × 30 ml) gave an orange solution which was dried ($MgSO_4$) and chromatographed on a silica column (eluent dichloromethane) affording compound **7** as orange oil (2.11 g, 86%) which crystallised by cooling overnight in a freezer, mp 37.0–38.5 °C (Calc. for $C_{19}H_{30}OS_6$: C, 48.88; H, 6.48. Found: C, 48.88; H, 6.49%); $\delta_H(CDCl_3)$ 6.24 (s, 1H), 4.40 (d, *J* 6.2, 2H), 3.75 (t, *J* 6.6, 1H), 2.81 (t, *J* 7.2, 4H), 1.61 (m, 4H), 1.30 (m, 12H), 0.89 (m, 6H).

1,2-Dibromo-4,5-bis[4′,5′-bis(hexylthio)tetrathiafulvalen-4-ylmethoxymethyl]benzene 8

Compound **7** (2.10 g, 4.50 mmol) was dissolved in dry THF (50 ml) at ambient temperature under argon and sodium hydride (210 mg, 60% dispersion in mineral oil, 5.25 mmol) was added in one portion. The mixture was warmed to 40 °C and stirred for 2 h. 1,2-Dibromo-4,5-bis(bromomethyl)benzene[30] (0.95 g, 2.25 mmol) was added and the mixture was stirred at room temperature for 3 h to afford an orange–yellow solution. The insoluble precipitate was removed by suction filtration and the filtrate was concentrated *in vacuo* to afford an oil which was chromatographed on a silica column [eluent light petroleum–dichloromethane (1:1 v/v)] to give compound **8** as an orange oil (1.72 g, 64%) (Calc. for $C_{46}H_{64}Br_2O_2S_{12}$: C, 46.29; H, 5.40. Found: C, 46.38; H, 5.41%); $\delta_H(CDCl_3)$ 7.63 (s, 2H), 6.26 (s, 2H), 4.48 (s, 4H), 4.29 (s, 4H), 2.81 (t, *J* 7.2, 8H), 1.63 (m, 8H), *ca.* 1.30 (m, 24H), 0.89 (m, 12H).

4,5-Bis[4′,5′-bis(hexylthio)tetrathiafulvalen-4-ylmethoxymethyl]benzene-1,2-dicarbonitrile 9 and 2-bromo-4,5-bis[4′,5′-bis(hexylthio)tetrathiafulvalen-4-ylmethoxymethyl]benzene-1-carbonitrile 10

Compound **8** (506 mg, 0.424 mmol) and CuCN (350 mg, 3.9 mmol) in dry DMF (5 ml) were heated to 140 °C and stirred for 12 h under argon. After cooling to room temperature, inorganic solids in the reaction mixture were removed by suction filtration and washed with acetone. A mixture of water (20 ml) and 35% aqueous ammonia solution (2 ml) was added to the filtrate and the brown oil solids which precipitated were collected by decantation and suction filtration and chromatographed [silica column, eluent light petroleum–dichloromethane 1:1 (v/v)] giving compound **10** as a brownish orange oil (103 mg, 22%) followed by compound **9** as a brown oil (128 mg, 28%). Compound **9** (Calc. for $C_{48}H_{64}N_2O_2S_{12}$: C, 53.10; H, 5.94; N, 2.58. Found: C, 52.82; H, 5.96; N, 2.19%); $\delta_H(CDCl_3)$ 7.88 (s, 2H), 6.32 (s, 2H), 4.58 (s, 4H), 4.38 (s, 4H), 2.82 (t, *J* 7.2, 8H), 1.63 (m, 8H), 1.30 (m, 24H), 0.89 (m, 12H). Compound **10** (Calc. for $C_{47}H_{64}BrNO_2S_{12}$: C, 49.53; H, 5.66; N, 1.23. Found: C, 49.59; H, 5.75; N, 1.52%); $\delta_H(CDCl_3)$ 7.88 (s, 1H), 7.66 (s, 1H), 6.294 (s, 1H), 6.288 (s, 1H), 4.57 (s, 2H), 4.49 (s, 2H), 4.35 (s, 2H), 4.32 (s, 2), 2.81 (t, *J* 7.2, 8H), 1.63 (m, 8H), 1.30 (m, 24H), 0.89 (m, 12H).

4,5-Bis(hexylthio)-4′,5′-bis(hydroxymethyl)tetrathiafulvalene 11

Compound **5** (3.20 g, 5.79 mmol) was dissolved in dry THF (120 ml) under an argon atmosphere and the solution was cooled to −10 °C. DIBALH (35 ml, 35 mmol, 1.0 M solution in hexane) was added dropwise. After stirring at this temperature for 2 h, the cooling bath was removed and stirring was continued for an additional 0.5 h. The orange reaction mixture was evaporated *in vacuo* until *ca.* 30 ml of an oily residue remained. Hydrochloric acid (1 M) was added to the residue very slowly at −70 °C until gas evolution ceased, then HCl (1 M, 50 ml) was added. The mixture was extracted with dichloromethane (3 × 50 ml) and the red organic phase was separated, dried ($MgSO_4$) and chromatographed (silica column, eluent ethyl acetate), giving compound **11** as yellow–orange crystals (2.15 g, 75%), mp 97.5–99.0 °C. Recrystallisation from ethyl acetate gave yellow plates which were suitable for the X-ray crystallographic analysis (Calc. for $C_{20}H_{32}O_2S_6$: C, 48.35; H, 6.49. Found: C, 48.39; H, 6.51%); $\delta_H(CDCl_3)$ 4.41 (d, *J* 6.0, 4H), 2.81 (t, *J* 7.2, 4H), 2.50 (br s, 2H), 1.63 (m, 4H), 1.30 (m, 12H), 0.89 (t, *J* 6.6, 6H).

4,5-Bis(bromomethyl)phthalonitrile 12

4,5-Dimethylphthalonitrile[31] (prepared by reacting 4,5-dibromo-*o*-xylene with CuCN in DMF; 1.56 g, 10 mmol), *N*-bromosuccinimide (NBS) (3.80 g, 21.3 mmol) and benzoyl peroxide (*ca.* 10 mg) were mixed in carbon tetrachloride (10 ml) and the mixture was stirred vigorously and warmed outdoors under bright sunshine for *ca.* 1.5 h (returning to the shade at intervals when the reaction became too violent) until all the NBS was converted to succinimide which was floating on the surface of the solution. The mixture was filtered by suction and the filtrate was evaporated *in vacuo* to yield a pale yellow solid residue. The precipitate in the Büchner funnel was triturated with a large amount of water and a second portion of pale yellow solid was obtained. The two portions of solid were combined and chromatographed on a silica column (eluent dichloromethane), giving a white oil (3.0 g), which crystallised in methanol to give **12** as white crystals (2.23 g, 71%), mp 110–122 °C (Calc. for $C_{10}H_{16}Br_2N_2$: C, 38.26; H, 1.93; N, 8.92. Found: C, 37.72; H, 1.77; N, 8.43%); *m/z* (%): 314 [M$^+$] (7.79 EI), 332 [M$^+$ + 18] (0.43, DCI); $\delta_H(CDCl_3)$ 7.83 (s, 2H), 4.61 (s, 4H).

2-[4,5-Bis(hexylthio)-1,3-dithiol-2-ylidene]-2*H*,4*H*,6*H*,11*H*,13*H*-[1,3]dithiol[4,5-*d*][2,7]benzodioxecine-8,9-dicarbonitrile 13

To a solution of compound **11** (737 mg, 1.48 mmol) in dry THF (50 ml) under argon, sodium hydride (120 mg, 3 mmol, 60% dispersion in mineral oil) was added in one portion and the mixture was stirred and refluxed for 4 h. Compound **12** (460 mg, 1.47 mmol) was added and the mixture was stirred at room temperature for 4 h to obtain a brown solution. The precipitate which formed during the reaction was removed by suction filtration through Celite and the filtrate was concentrated and chromatographed (silica column, eluent dichloromethane), affording compound **13** as yellow plates (110 mg, 11.6%), mp 175.0–175.5 °C (Calc. for $C_{30}H_{36}N_2O_2S_6$: C, 55.52; H, 5.59; N, 4.32. Found: C, 55.29; H, 5.49; N, 4.16%); $\delta_H(CDCl_3)$ 7.89 (s, 2H), 4.76 (s, 4H), 4.17 (s, 4H), 2.85 (t, *J* 7.2, 4H), 1.65 (m, 4H), 1.30 (m, 12H), 0.89 (t, *J* 6.6, 6H).

2,3,9,10,16,17,23,24-Octakis[4′,5′-bis(hexylthio)tetrathiafulvalen-4-ylmethoxymethyl]phthalocyanine 2

To a lithium pentoxide solution [prepared from lithium (180 mg) and dry pentanol (15 ml)], compound **9** (275 mg) was added and the mixture was suddenly heated to 125 °C and vigorously stirred under argon for 5 h. The colour changed from yellow to intense green. The solvent was removed *in vacuo* and ethanol (20 ml) was added to the green residue. Acetic acid (20 ml) was added and the mixture was left overnight. A dark green solid was obtained by decantation, suction filtration and washing with a large amount of ethanol. The solid was extracted thrice with boiling ethanol then dissolved in dichloromethane (20 ml) to get an intense green solution. This solution was filtered through Celite then evaporated *in vacuo*, giving compound **2** as a dark green amorphous solid (153 mg, 56%) (Calc. for $C_{192}H_{258}N_8O_8S_{48}$: C, 53.07; H, 5.98; N, 2.58. Found: C, 53.32; H, 6.02; N, 2.51%); MALDI-MS, *m/z*, Found 4308; Calc. for $C_{192}H_{258}N_8O_8S_{48}$ 4339; $\delta_H(CDCl_3$, 50 °C) 8.53 (br, 1H), 6.65 (br s, 1H), 4.99 (br s, 2H), 4.72 (br s, 2H), 2.85 (t, *J* 6.8, 2H), 2.78 (t, *J* 6.8, 2H), 1.66 (m, 4H), 1.31 (m, 12H), 0.90 (t, *J* 6.8, 6H); $\delta_C(CDCl_3$, 50 °C) 148.03, 137.82, 134.55, 127.96, 122.54, 117.25, 113.62, 107.66, 70.76, 68.40, 36.41, 31.38, 31.29, 29.77, 29.68, 28.29, 28.17, 22.54, 22.43, 13.98, 13.90; λ_{max}/nm (toluene) (ε) 324.5 (133 580), 636.0 (45 037), 664.5 (42 654), 700.0 (33 459).

2,14,26,38-Tetrakis[4,5-bis(hexylthio)-1,3-dithiol-2-ylidene]-4*H*,6*H*,10*H*,12*H*,16*H*,18*H*,22*H*,24*H*,28*H*,30*H*,34*H*,36*H*,40*H*,42*H*,46*H*,48*H*-tetrakis([1,3]dithiolo[4,5-*c*]dioxecino)[7,8-*b*;7′,8′-*k*;7″,8″-*t*;7‴,8‴-*c*′]phthalocyanine 14

Following the procedure for the preparation of **2**, compound **14** was synthesised from compound **9** (31 mg) and lithium pentoxide [from lithium (55 mg) and dry pentanol (5 ml)] and isolated as a dark green amorphous solid (yield 15 mg, 48%) (Calc. for $C_{120}H_{146}N_8O_8S_{24}$: C, 55.48; H, 5.67; N, 4.31. Found: C, 55.39; H, 5.77; N, 4.48%); MALDI-MS, *m*/*z*, Found 2588; Calc. for $C_{120}H_{146}N_8O_8S_{24}$ 2594; δ_H($CDCl_3$) *ca.* 8.2 (v br), *ca.* 4.6 (br), *ca.* 4.1 (br), 2.82 (br), 1.33 and 0.93 (overlapping br peaks); λ_{max}/nm (toluene) (ε) 333.0 (85 493), 648.5 (39 303), 674.5 (49 320), 709.0 (43 894) nm.

X-Ray crystallography

The X-ray diffraction experiment on **11** was carried out at *T* 150 K on a Siemens 3-circle diffractometer with a CCD area detector, using graphite-monochromated Mo-Kα radiation, $\bar{\lambda} = 0.710\,73$ Å. *Crystal data*: $C_{20}H_{32}O_2S_6$, $M = 496.8$; monoclinic, space group $P2_1/c$ (No. 14), $a = 25.359(2)$, $b = 12.554(1)$, $c = 7.867(1)$ Å, $\beta = 97.26(1)°$, $V = 2484.4(4)$ Å^3 (from 442 setting reflections with $10 < \theta < 23°$), $Z = 4$, $D_c = 1.33$ g cm^{-3}, $F(000) = 1056$, $\mu = 5.7$ cm^{-1}, crystal size 0.5 × 0.25 × 0.06 mm. 12 298 data with $2\theta \leqslant 48°$ were collected in ω scan mode (0.3° steps); of these 3874 data were unique and 2120 ‘observed’ with $I \geqslant 2\sigma(I)$. Semi-empirical absorption correction on Laue equivalents was performed, min/max transmission 0.69/0.98, $R_{int} = 0.16$ before and 0.14 after correction. The structure was solved by direct methods and refined by full-matrix least squares against F^2 of 3091 non-negative data, sing SHELXTL software.[25] Ordered non-H atoms were refined anisotropically, disordered C atoms isotropically [C(8) to C(12) with 50% occupancies, C(14) to C(18) with 33%] with C−C bonds restrained to 1.53(1) Å. Hydroxy H atoms refined, other H atoms ‘riding’ (265 variables, 25 restraints), converging at $wR(F^2$, all data$) = 0.292$, goodness-of-fit 1.17, $R(F$, obs. data$) = 0.099$; residual electron density features $\Delta\rho_{max} = 0.39$, $\Delta\rho_{min} = -0.51$ e Å^{-3}. Atomic coordinates and displacement parameters, bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre.†

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† For details of the CCDC deposition scheme, see ‘Instructions for Authors’, *J. Chem. Soc., Perkin Trans. 2*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/84.

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