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The synthesis and electrochemical properties of a new tetra-(crown-ether-thiafulvalene)-annulated phthalocyanine derivative

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ABSTRACT

A novel, metal-free, crown-ether-tetrathiafulvalene annulated phthalocyanine was synthesized by tetramerization of the corresponding phthalonitrile derivative; both compounds were characterized by elemental analysis, IR, UV–vis, DPV or CV and MS spectra. The crystal structure of the precursor was determined by X-ray crystallography. The charge transfer absorption bands of the two compounds lay ~400 nm after addition of 7,7,8,8-tetracyanoquinodimethane. Electrochemical studies revealed that both compounds displayed good complexation selectivity for Na^+ ion with large positive redox shifts, indicating that they may be a new redox-active sensor.

1. Introduction

Phthalocyanine (Pc), a remarkably robust and versatile compound first developed as industrial pigment, has been applied in a wide range of photovoltaic devices [1], catalysts [2], gas sensors [3–5], electrochromic displays [6], and photodynamic therapy agents [7,8]. These properties may be modulated by central metals and huge variety of substitutions attached to the Pc cores [9,10]. By controlling such parameters, diverse functionalities can be obtained. For example, Pcs containing macrocycles such as crown ethers show potential applications as ion conducting channel or heavy metal extraction agents [11,12]. Due to the well-known ability to form stable cation radical salts, redox-active substituents such as tetrathiafulvalene (TTF) and its derivatives have been introduced to the peripheral or non-peripheral sites of Pc cores [13,14]. Cook et al. prepared a phthalocyanine system functionalized with one or two TTF units, which is the only example of TTF-appended Pc showing a liquid crystalline behavior so far [15]. Furthermore, the redox properties of the TTF core in combination with the complexing ability of crown ether may lead to modulation of the trapping properties depending on the oxidation of TTF [16]. However, up to now, very few examples for the direct annulation of the TTF unit to a Pc core have been reported [17–19]. We therefore have incorporated crown-ether-TTF units into Pc core to give a new crown-ether-TTF annulated phthalocyanine **4**. Interestingly, the system has shown to be good for new electrochemical sensor to Na^+.

2. Experimental

2.1. Apparatus

Elemental analyses for C, H, and N were performed on a Perkin–Elmer 240C analyzer. ESI-MS spectra were recorded on a Varian MAT 311A instrument. The IR spectra were taken on a Vector22 Bruker Spectrophotometer (400–4000 cm^{-1}) with KBr pellets. Mass spectra were determined with Autoflex II™ instrument for MALDI-TOF-MS. Absorption spectra were measured on a UV-3100 spectrophotometer. NMR spectra were measured on a Bruker AM 500 spectrometer. Cyclic voltammetry and differential pulse voltammetry were performed on a CHI660b electrochemical analytical instrument, with platinum as the working and counter electrodes, $Ag/AgNO_3$ as the reference electrode, and 0.1 M $n\text{-}Bu_4NClO_4$ as the supporting electrolyte. The compound 5,6-dicyanobenzene-1,3-dithiole-2-one (**1**) and the corresponding 1,3-dithiole-2-thione derivative **2** were synthesized according to literature procedures [17,20]. All solvents and chemicals were purchased from commercial sources and used as received.

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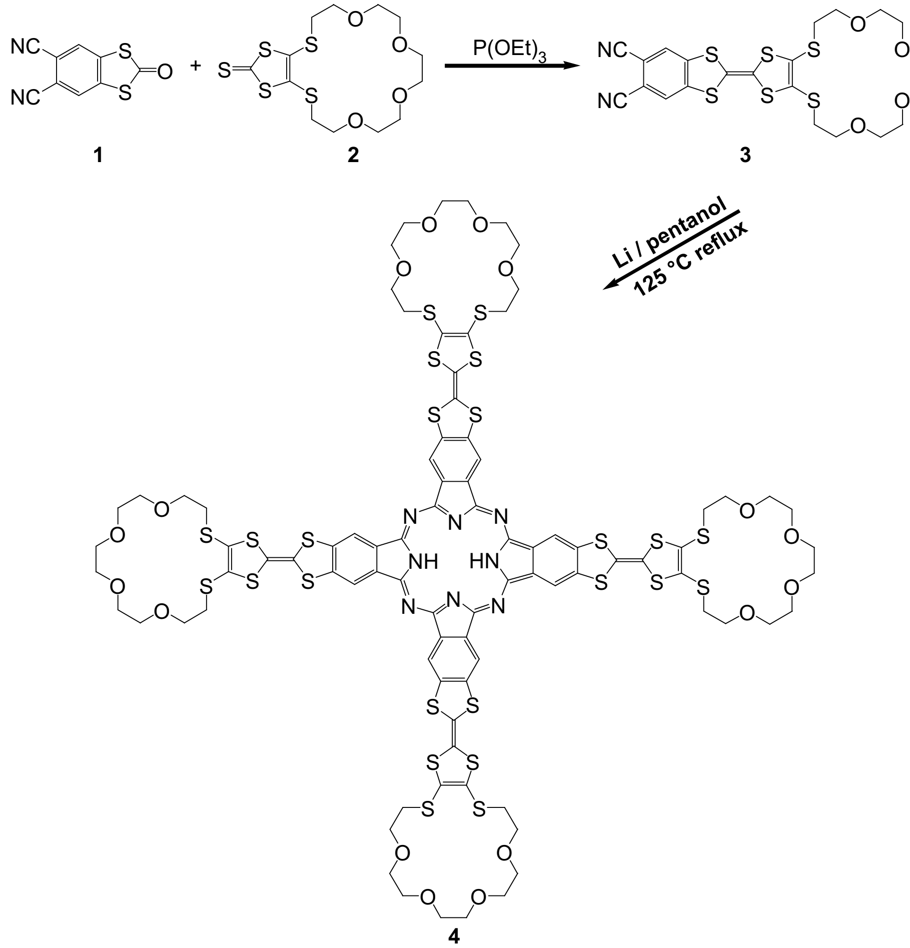

Scheme 1. Synthesis of the tetra(crown-ether-TTF)-annulated phthalocyanine **4**.

2.2. Synthesis of compounds *3* and Pc *4*

5,6-Dicyano-2-(4,5-dithia-(3′,6′,9′12′-tetraoxatetradecyl)-1,3-dithio-2-ylidene)-benzo-1,3-dithiole (**3**): under nitrogen, a solution of compound **1** (131 mg, 0.6 mmol) and compound **2** (240 mg, 0.6 mmol) in 5 mL of triethyl phosphate was heated to 100 °C for 1 h. After removal of the solvent under reduced pressure, chromatography on silica of the residue with CH_2Cl_2/hexane (3/1) as eluent afforded pure compound **3** as red crystals. Yield: 116 mg (33.9%). Anal. Calc. for $C_{22}H_{22}N_2S_6O_4$: C, 46.34; H, 3.89; N, 4.91. Found: C, 46.18; H, 3.90; N, 4.90%. IR (KBr disc): ν/cm^{-1} 3445, 3074, 2954, 2920, 2850, 2228 ($\nu_{C\equiv N}$), 1563, 1459, 1255, 1225. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.54 (s, 2H), 3.73 (m, 16H), 3.05 (t, 4H). MALDI-TOF-MS: *m*/*z* 570.060[M]$^+$, 593.066[M + Na$^+$] (Fig. S1).

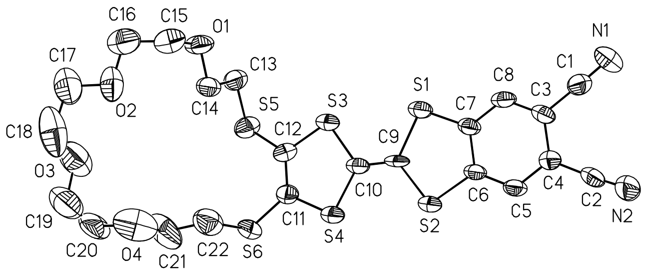

Fig. 1. Molecular structure of compound **3** (50% probability ellipsoid. Hydrogen atoms are omitted for clarity). Selected bond lengths [Å]: C6–C7 1,429(9); C6–S2 1.760(6); C7–S1 1.721(7); C9–S1 1.772(6); C9–S2 1.763(7); C9–C10 1.336(9); C10–S3 1.765(7); C10–S4 1.758(7); C11–S4 1.746(7); C11–S6 1.754(7); C12–S3 1.772(7); C12–S5 1.757(7). Selected bond angle [°]: S4–C10–S3 114.0(4); S2–C9–S1 115.0(4); C6–C5–C4 121.7(6); C5–C4–C3 118.7(6); C4–C3–C8 119.3(6); C3–C8–C7 123.1(6); C8–C7–C6 117.6(6); C7–C6–C5 119.4(6).

Table 1
Crystal data, data collection and structure refinement for **3**

Empirical formula	$C_{22}H_{22}N_2O_4S_6$
Formula weight	570.78
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\overline{1}$
a (Å)	5.185(3)
b (Å)	14.816(8)
c (Å)	18.029(8)
α (°)	111.918(18)
β (°)	90.171(9)
γ (°)	94.791(9)
Volume (Å^3)	1279.5(12)
Z	2
D_{calc} (g/cm^3)	1.481
μ (mm^{-1})	0.567
F (000)	592
θ range for data collection (°)	2.25–25.00
No. reflections collected	6372
No. independent reflections	4427
R (int)	0.1509
Data/restraints/parameters	4427/0/307
Goodness-of-fit on F^2	0.797
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0808$, $wR_2 = 0.2043$
Largest difference peak and hole (e Å^{-3})	0.740/−0.472

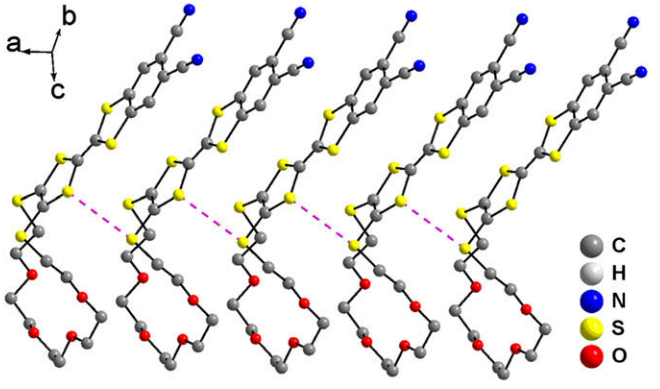

Fig. 2. View of the crystal packing arrangement of **3** (the dotted line representing S···S non-bonded contacts less than 3.7 Å).

2,3,9,10,16,17,23,24-Tetrakis[4′,5′-dithia-(3′,6′,9′12′-tetraoxatetradecyl)tetrathiafulvalene]phthalocyanine (**4**): lithium metal (80 mg, 10 mmol) was dissolved in 30 mL of 1-pentanol at 80 °C and then compound **3** (57 mg, 0.1 mmol) was added. The reaction mixture was heated up to 125 °C and refluxed for 5 h. The dark blue solution was allowed to cool down to room temperature. A mixture of ethanol (20 mL) and glacial acetic acid (20 mL) was added. The resulting suspension was standing for 12 h. A dark blue solid was obtained by decantation and centrifugation. The crude product was purified by washing with a combination of ethanol and ether. Then it was purified with CH_2Cl_2 by column chromatography on silica gel. Yield: 20 mg (35.1%). Anal. Calc. for $C_{88}H_{90}N_8S_{24}O_{16}$: C, 46.30; H, 3.97; N, 4.91. Found: C, 46.23; H, 3.96; N, 4.92%. IR (KBr disc): ν/cm^{-1} 3423, 2970, 2923, 2853, 1401, 1070, 1022. MALDI-TOF-MS: m/z 2283.799[M]$^+$ (Fig. S2).

2.3. Crystallography

The data were collected on a Bruker Smart Apex CCD diffractometer equipped with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation using a ω–2θ scan mode at 293 K. The highly redundant datasets were reduced using SAINT and corrected for Lorentz and polarization effects. Absorption corrections were applied using SADABS supplied by Bruker. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 using SHELXTL-97. All non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, refined anisotropically. Crystallographic data for the structure of **3** have been deposited with the Cambridge Crystallographic Data Centre as supplemental publication CCDC 665476.

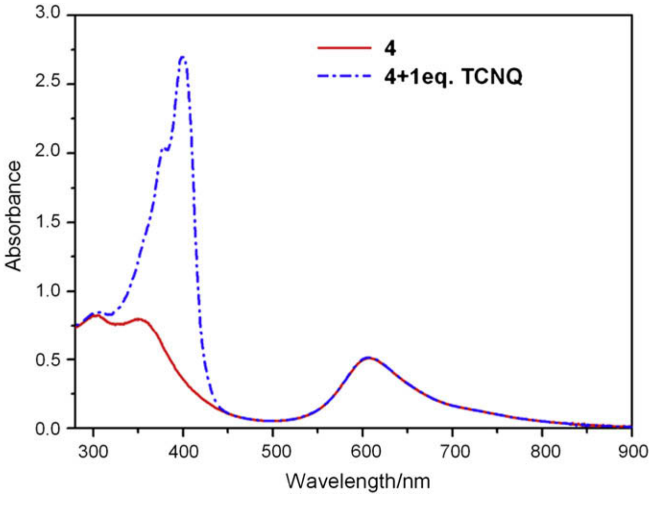

Fig. 3. UV–vis spectrum of compound **4** before (red, solid) and after (blue, dash dot) TCNQ was added; performed in CH_2Cl_2 (10^{-5} M).

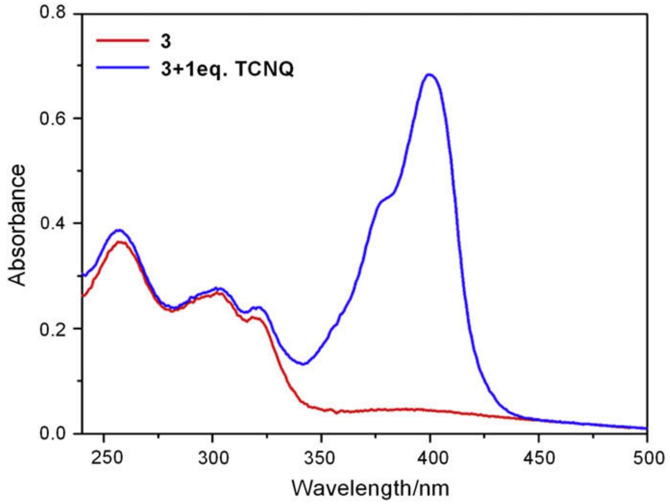

Fig. 4. UV–vis spectrum of compound **3** before (red) and after (blue) TCNQ was added; performed in CH_2Cl_2 (10^{-5} M).

3. Results and discussion

3.1. Synthesis and characterization

The phthalonitrile precursor **3** was obtained from the cross-coupling reaction. Then the tetramerization of **3** in the presence of lithium pentoxide at 125 °C under nitrogen afforded Pc **4** (Scheme 1) which is soluble in $CHCl_3$, CH_2Cl_2 and DMF. ^{1}H NMR spectrum of **3** is entirely consistent with its crystal structure. Tetramerization of **3** into Pc **4** was confirmed by the disappearance of the sharp C≡N stretching vibration in the IR spectra at 2228 cm^{-1} of the precursor. For **4**, the resonances at 3423 and 1070 cm^{-1} are assigned to the N–H stretching and bending vibrations. In addition, the presence of the characteristic molecular ion peak at $m/z = 2283.799$[M]$^+$ in the mass spectrum also supports the proposed structure for this compound. However, for the octa-substituted TTF-annulated Pc **4**, ^{1}H NMR spectra in $CDCl_3$ are not available due to the high aggregation of the Pcs, which is frequently encountered at the concentrations used for NMR measurements [2,19].

3.2. Crystal structure analysis

Crystals suitable for X-ray diffraction study of the key precursor **3** have been obtained by recrystallization from dichloromethane. The ORTEP of the molecule with the atomic numbering scheme is shown in Fig. 1. Parameters for data collection and refinement of **3** are summarized in Table 1. This compound crystallizes in a triclinic crystal system, space group $P\overline{1}$. The bond lengths and angles are all in normal range. As some other TTF/monocrown compounds, the

Table 2
CV data for compounds **3** and **4** (Ag/Ag$^+$ as reference electrode)

Compounds	$E_1^{1/2}$ (V)	$E_2^{1/2}$ (V)	$\Delta E_1^{1/2}$ (mV)
3	0.387	0.603	52
4	0.264	0.592	80

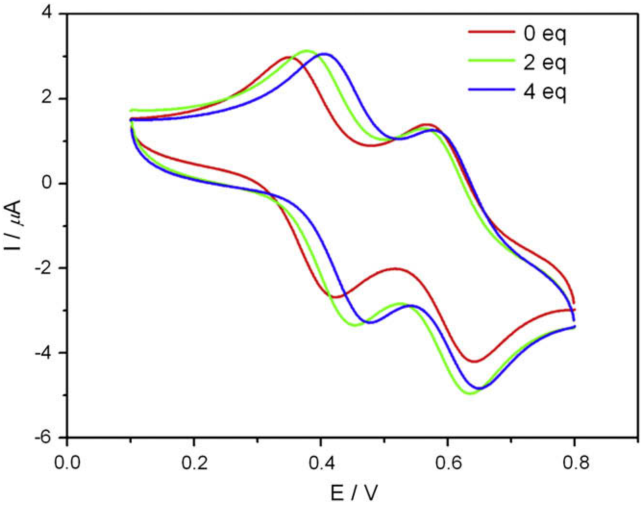

Fig. 5. CV of compound **3** recorded in a mixture of CH_2Cl_2/MeCN (3/2, v/v) at 5×10^{-4} M with *n*-Bu_4NClO_4 (0.1 M) as the supporting electrolyte in the presence of increasing amounts of Na^+.

macrocycle adopts a crown conformation, which is favored for the metal coordination. The S_2O_4 crown ether group is bent toward one side of the TTF unit. In the TTF unit, the conjugated π system of this molecule is extended to all of the eight sulfur atoms. The TTF-fused phthalonitrile moiety is virtually planar with an rms deviation of 0.06 Å from the least-squares plane. Fig. 2 highlights the mutual arrangement of the molecules in the crystal structure. A noticeable feature is the parallel head-to-head alignment with intermolecular S···S contacts of 3.662 Å, which are less than the sum of the van der Waals radii (3.70 Å).

3.3. UV–vis spectra and electrochemical properties

The UV–vis spectrum of **4** in CH_2Cl_2 was shown in Fig. 3. In the ultraviolet region, B-band (or Soret band) of Pc (at 320–370 nm) and absorption band of TTF moieties (at 240–400 nm) are overlapped and lead to the superimposed bands [15,21–24]. In contrast to the split Q-band originating from non-aggregated metal-free Pc at 618 and 687 nm in DMF (Fig. S3), a single (blue-shifted and broadened) absorption peak at 601 nm in CH_2Cl_2 is observed for **4**. This gives the direct spectroscopic evidence of Pc core aggregation in CH_2Cl_2 [25,26]. After addition of 1 equiv of 7,7,8,8-tetracyanoquinodimethane; TCNQ (note: incompatible with strong acids, strong bases, strong reducing agents, strong oxidizing agents) to the respective CH_2Cl_2 solution of **3** (Fig. 4) and **4**, the charge transfer (from electron donor TTF to electron acceptor TCNQ) absorption bands both occur around 400 nm.

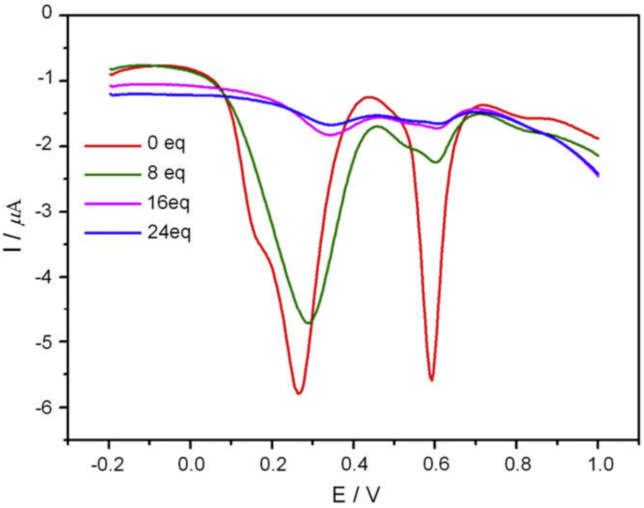

Fig. 6. DPV of compound **4** recorded in a mixture of CH_2Cl_2/MeCN (3/2, v/v) at 5×10^{-4} M with *n*-Bu_4NClO_4 (0.1 M) as the supporting electrolyte in the presence of increasing amounts of Na^+.

The electrochemical properties for compounds **3** and **4** are investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The data are listed in Table 2. Compound **3** undergoes two reversible one-electron oxidation processes corresponding to the successive reversible oxidation of neutral TTF (TTF^0) to the radical-cation (TTF^+) and then to the dication (TTF^{2+}). Interestingly, in the presence of 4 equiv of sodium perchlorate, a maximum of a ca. 52 mV shift of $E_1^{1/2}$ ($\Delta E_1^{1/2}$) to a more positive potential was observed for **3** (Fig. 5). This phenomenon is attributed to the electrostatic inductive effect of the crown ether bound metal which causes the withdrawal of the electron density from the TTF moiety. The second redox potential remains essentially unchanged (±5 mV) after the addition of sodium perchlorate because of the increased repulsive electrostatic interactions between the cation and the doubly charged oxidized TTF^{2+} unit [27].

DPV of Pc **4** shown in Fig. 6 displays two reversible oxidation waves with no discernable oxidation of the phthalocyanine core. It reveals that the TTF moieties are oxidized in two steps involving two four-electron processes but there is no obvious interaction between TTFs and Pc core. The annulation of the four TTF units to the Pc core results in a high degree of aggregation and a stabilization of the monoradical cation, which caused the slight splitting of the first oxidation potential [18,28]. The degree of aggregation decreases with the oxidation of one TTF unit and further oxidation of the rest TTF units shifts to a more positive potential, all of which behave like isolated molecules. The additional four electrons are removed at the uniform potential. Similar to **3**, in the presence of 24 equiv of sodium perchlorate, free-metal Pc **4** also exhibits a maximum of positive shift of $E_1^{1/2}$ (ca. 80 mV). Whereas the $E_2^{1/2}$ value is not altered yet in the presence of Na^+. It is noteworthy that no shift of $E_1^{1/2}$ has been observed upon addition of a wide variety of other alkali metal, such as Li^+, K^+, Cs^+, suggesting the good complexation selectivity of **3** and **4** for Na^+ [29].

4. Conclusions

A new crown-ether-TTF annulated phthalocyanine has been prepared and characterized. In the presence of 24 equiv of sodium perchlorate, a maximum of a ca. 80 mV shift of $E_1^{1/2}$ ($\Delta E_1^{1/2}$) to a more positive potential was observed for **4**, indicating that it may be a good candidate for redox-active Na^+ cation sensor.

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Appendix. Supplementary information

Supplementary information associated with this article can be found in the online version at doi:10.1016/j.dyepig.2008.09.001.

References

[1] Nazeeruddin MK, Humphry-Baker R, Grätzel M, Murrer BA. Efficient near IR sensitization of nanocrystalline TiO_2 films by ruthenium phthalocyanines. Chemical Communications 1998:719–20.

[2] Kaliya OL, Lukyanets EA, Vorozhtsov GN. Catalysis and photocatalysis by phthalocyanines for technology, ecology and medicine. Journal of Porphyrins and Phthalocyanines 1999;3:592–610.

[3] Hacıvelioğlu F, Durmuş M, Yeşilot S, Gürek AG, Kılıç A, Ahsen V. The synthesis, spectroscopic and thermal properties of phenoxycyclotriphosphazenyl-substituted phthalocyanines. Dyes and Pigments 2008;79:14–23.

[4] Ding X, Shen S, Zhou Q, Xu H. The synthesis of asymmetrically substituted amphiphilic phthalocyanines and their gas-sensing properties. Dyes and Pigments 1999;40:187–91.

[5] Odabaş Z, Altındal A, Salih B, Bulut M, Bekaroğlu Ö. Synthesis, characterization and electrical properties of novel mono- and cofacial bisphthalocyanines bridged with four [1a,8b-dihydronaphtho[*b*]naphthofuro[3,2-*d*]furan-7,10-diyl] units. Tetrahedron Letters 2007;48:6326–9.

[6] Somani PR, Radhakrishnan S. Electrochromic materials and devices: present and future. Materials Chemistry and Physics 2002;77:117–33.

[7] Clarke MJ. Ruthenium metallopharmaceuticals. Coordination Chemistry Reviews 2002;232:69–93.

[8] Hu YY, Lai GQ, Shen YJ, Li YF. Synthesis, optical spectroscopy and electrochemistry of TTF-derived metallophthalocyanine complexes. Dyes and Pigments 2005;66:49–53.

[9] Liu W, Lee C-H, Li H-W, Lam C-K, Wang JZ, Mak TCW, et al. Formation and crystal structure of an unexpected inclusion complex of a metal-free phthalocyanine and oxalic acid. Chemical Communications 2002:628–9.

[10] Rusanova J, Pilkington M, Decurtins S. A novel fully conjugated phenanthroline-appended phthalocyanine: synthesis and characterisation. Chemical Communications 2002:2236–7.

[11] Arslanoğlu Y, Koca A, Hamuryudan E. Synthesis of novel unsymmetrical phthalocyanines substituted with crown ether and nitro groups. Polyhedron 2007;26:891–6.

[12] Sly J, Kasák P, Gomar-Nadal E, Rovira C, Górriz L, Thordarson P, et al. Chiral molecular tapes from novel tetra(thiafulvalene-crown-ether)-substituted phthalocyanine building blocks. Chemical Communications 2005:1255–7.

[13] Batsanov AS, Svenstrup N, Lau J, Becher J, Bryce MR, Howard JAK. Stacked supramolecular structures involving hydrogen-bonded networks in highly functionalized tetrathiafulvalene derivatives. Journal of the Chemical Society – Chemical Communications 1995:1201–2.

[14] Bryce MR. Recent progress on conducting organic charge-transfer salts. Chemical Society Reviews 1991;20:355–90.

[15] Cook MJ, Cooke G, Jafari-Fini A. A liquid crystalline tetrathiafulvalenyl-phthalocyanine. Chemical Communications 1996:1925–6.

[16] Le Derf F, Sallé M, Mazari M, Mercier N, Riou A, Belyasmine A, et al. Electrochemical control of the complexation/expulsion processes of metallic cations by crown ether TTF derivatives. Synthetic Metals 1999;102:1461.

[17] Loosli C, Jia CY, Liu S-X, Haas M, Dias M, Levillain E, et al. Synthesis and electrochemical and photophysical studies of tetrathiafulvalene-annulated phthalocyanines. Journal of Organic Chemistry 2005;70: 4988–92.

[18] Donders CA, Liu S-X, Loosli C, Sanguinet L, Neels A, Decurtins S. Synthesis of tetrathiafulvalene-annulated phthalocyanines. Tetrahedron 2006;62: 3543–9.

[19] Delahaye S, Loosli C, Liu S-X, Decurtins S, Labat G, Neels A, et al. Inter- and intramolecular interactions in some supramolecular photochemical systems. Advanced Functional Materials 2006;16:286–95.

[20] Hansen TK, Jørgensen T, Stein PC, Becher J. Crown ether derivatives of tetrathiafulvalene. Journal of Organic Chemistry 1992;57:6403–9.

[21] Bıyıklıoğlu Z, Kantekin H, Özil M. Microwave-assisted synthesis and characterization of novel metal-free and metallophthalocyanines containing four 14-membered tetraaza macrocycles. Journal of Organometallic Chemistry 2007;692:2436–40.

[22] Hu YY, Shen YJ. Synthesis of zincic phthalocyanine derivative functionalized with four peripheral tetrathiafulvalene units. Journal of Heterocyclic Chemistry 2002;39:1071–5.

[23] Bilgin A, Ertem B, Gök Y. The synthesis and characterization of a new metal-free phthalocyanine substituted with four diloop macrocyclic moieties. Tetrahedron Letters 2003;44:3829–33.

[24] Kameyama K, Satake A, Kobuke Y. Light-harvesting composites of directly connected porphyrin-phthalocyanine dyads and their coordination dimers. Tetrahedron Letters 2004;45:7617–20.

[25] Kroon JM, Koehorst RBM, Dijk MV, Sanders GM, Sudhölter EJR. Self-assembling properties of non-ionic tetraphenylporphyrins and discotic phthalocyanines carrying oligo(ethylene oxide) alkyl or alkoxy units. Journal of Material Chemistry 1997;7:615–24.

[26] Kobayashi N, Togashi M, Osa T, Ishii K, Yamauchi S, Hino H. Low symmetrical phthalocyanine analogues substituted with three crown ether voids and their cation-induced supermolecules. Journal of the American Chemical Society 1996;118:1073–85.

[27] Le Derf F, Mazari M, Mercier N, Levillain E, Richomme P, Becher J, et al. Electroregulated metal-binding with a crown ether tetrathiafulvalene derivative: toward electrochemically addressed metal cations sponges. Inorganic Chemistry 1999;38:6096–100.

[28] Khodorkovsky V, Becker JY. In: Farges J-P, editor. Organic conductors: fundamentals and applications. New York: Marcel Dekker; 1994.

[29] Ji Y, Zhang R, Li Y-J, Li Y-Z, Zuo J-L, You X-Z. Synthesis, structures, and electrochemical properties of platinum(II) complexes containing di-tert-butylbipyridine and crown ether annelated dithiolate ligands. Inorganic Chemistry 2007;46:866–73.