

Synthesis and mesomorphic properties of tetra- and octa-substituted phthalocyanines†

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Thia-bridged tetra- and octa-poly(oxyethylene)-substituted metal free- and Ni(II) phthalocyanines have been synthesized from the corresponding phthalonitrile derivatives in the presence of the anhydrous metal salt (NiCl₂) or a strong organic base. The new compounds have been characterized by elemental analyses, UV/vis, IR, NMR and mass spectra. The mesogenic properties of these new materials were studied by differential scanning calorimetry, optical microscopy and X-ray investigations. Although octa-substituted phthalocyanine derivatives are liquid, all tetra-substituted compounds show a discotic mesophase over an extremely large temperature interval including room temperature. The relationship between the structure of the mesogenic units and the mesogenic behaviour is discussed and the influence of the different heteroatoms present in the side chains on the mesomorphic properties has been determined.

Introduction

Phthalocyanines (Pcs) constitute a long-established class of commercially important dyes and pigments. The central cavity of the molecule presents a complexing site for over 70 species of metal atoms. Pcs and their symmetrically substituted derivatives have received extensive attention over the last decades due to their distinct properties and applications (*e.g.*, electrical conductivity,¹ ionoelectronics,^{1b} electrochromism,² mesophase formation³ and aggregation into monolayers of the Langmuir–Blodgett type⁴), which make them unique substrates for new materials.⁵ Pcs have usually constituted a group of crystalline or polycrystalline compounds, whose insolubility in organic solvents is very characteristic.^{6–8} A limiting factor for solution studies on pcs is the solubility of the parent compound. Peripheral substitution with bulky substituents or the use of donor solvents capable of binding to the axial position of the central metal ion have been two practical ways to overcome this hindrance. In our previous works on macrocycle-substituted pcs we have achieved the synthesis of very soluble examples in a wide range of organic solvents.⁹ In addition to novel functionalities such as alkali^{9a} or transition metal^{9c,9d} ion binding, ion channel formation,¹⁰ enhanced conductivity,¹¹ *etc.*, the solubility of pc products has reached the 10^{−3} mol dm^{−3} level.^{9a} Also, in the past few years the introduction of long-chain lipophilic substituents on the periphery of the pc ring has drastically improved their solubility in nonpolar solvents and in some cases has provided these compounds with thermotropic behaviour.^{12,13}

Pc is well-known as a disc-like molecule and it forms a one-dimensional columnar structure in condensed phases. The first mesomorphic phthalocyanines were reported in the early 1980s^{14a} and since then numerous liquid crystalline pc

derivatives have been synthesized with the aim of producing more easily controllable macroscopic structures.^{14b} These derivatives have been predominantly alkyl,¹⁵ alkoxy,¹⁶ alkoxy methyl¹⁴ or oligo(ethyleneoxy)¹⁷ octa-substituted mesogens with side chains substituted at the 2 and 3 positions on the benzene ring or octa-alkyl¹⁸ or alkoxy methyl¹⁹ compounds substituted at the 1 and 4 positions, but mesomorphic tetra-substituted compounds have been rarely synthesized.²⁰ In addition, a number of unsymmetrically substituted pcs have been shown to form thermotropic liquid crystals.²¹ The attachment of polar side chains such as oligo(ethylene oxide) moieties and crown ether rings to large aromatic macrocycles is also of interest in the construction of supramolecular wires and ion conducting channels.²² Several pcs of these types have been designed in order to investigate complexation²³ behaviour and their potential for electronic and ionoelectronic applications.²⁴

Adam *et al.* reported that a discotic liquid crystal of triphenylene substituted by alkylthio groups exhibits considerably higher charge carrier mobility in the discotic mesophase, compared with conventional organic semiconductors.^{25a} It can be inferred from this example that sulfur atoms may significantly influence the conductivity of the mesophase. Wöhrle and colleagues reported the first example of columnar mesomorphism in octakis(octylthio)-substituted phthalocyanine zinc and copper complexes.^{25b} Ohta *et al.* reported the synthesis of a series of octakis(alkylthio)phthalocyanines [abbreviated as (C_{*n*}S)₈PcH₂, *n* = 8, 10, 12, 16] and their copper complexes [abbreviated as (C_{*n*}S)₈PcCu, *n* = 8, 10, 12, 16] and thoroughly investigated their mesomorphism; they discussed the influence of sulfur atoms and chain length on the mesomorphism and the unique aggregated dimer structures in the columnar mesophase.²⁶

Although pcs with N- and O-donor substituents have been frequently encountered, those with thioether moieties are rather few.^{25b,27} The latter group essentially contains products obtained by the cyclotetramerization of thioether-substituted phthalonitriles, which themselves have been derived from nucleophilic displacement reactions of dinitriles; a literature

† Electronic supplementary information (ESI) available: optical texture of **6a**, **8a** and **8b** observed at 25 °C (Fig. S1, S2 and S3, respectively). ¹H-NMR and ¹³C-NMR spectral data for starting materials and phthalocyanines in CDCl₃ (Table S1 and S2, respectively). See <http://www.rsc.org/suppdata/nj/b3/b314995a/>

survey²⁸ also shows that most of the recent work on thioether-substituted phthalocyanines has been patented with applications as IR absorbers.

Phthalocyanine-based discotic liquid crystals can be expected to find application as conducting devices, because they have self-assembling supramolecular structures.²⁶ Also the mesomorphic phthalocyanine derivatives show well-ordered films thermally. The mass sensitivity results obtained by utilizing quartz crystal microbalance (QCM) showed that the ordered phthalocyanine films were more sensitive than the disordered ones for the detection of different organic solvent vapours.²⁹

In this paper, we describe the synthesis of new sterically hindered thia-bridged tetra- and octa-poly(oxyethylene)-substituted pcs. The influence of the presence of the thia bridges in the poly(oxyethylene) side chains on the mesomorphic properties has been determined. While tetra-substituted phthalocyanine derivatives demonstrate thermotropic phase behaviour in an extremely large temperature interval including room temperature, octa-substituted phthalocyanine derivatives do not show liquid crystalline properties at room temperature, because they are liquid at this temperature.

Experimental

General

All solvents were purified as described in Perrin and Armarego.³⁰ 1,2-Dichloro-4,5-dicyanobenzene^{27b} (**4**), 4-nitrophthalonitrile³¹ (**5**) and 1,3-di[2-(2-ethoxyethoxy)ethoxy]-2-propanol³² (**1**) were prepared according to the reported procedures. All other reagents and solvents were reagent grade quality and were obtained from commercial suppliers.

Elemental analyses were obtained with a Carlo Erba 1106 instrument. Infrared spectra in sodium chloride cells for oily compounds or KBr pellets were recorded on a Bio-Rad FTS 175C FT-IR spectrophotometer. Optical spectra in the UV-visible region were recorded with a Shimadzu 2001 UV Pc spectrophotometer using 1 cm path length cuvettes at room temperature. Mass spectra were recorded on a VG Zab-Spec spectrometer using the fast atomic bombardment (FAB) technique (35 kV) or electron impact technique. ¹H and ¹³C NMR spectra were recorded in CDCl₃ solutions on a Bruker 500 MHz spectrometer using TMS as an internal reference. Transition temperatures were determined at scan rates of 10 °C min⁻¹ using a Perkin Elmer DSC 6 differential scanning calorimeter. The phase transition behaviour of these compounds was observed with a Leitz Wetzlar Orthoplan-pol polarizing microscope equipped with a Linkam TMS 93 hot stage and a Linkam LNP temperature controller. X-Ray measurements were performed with Cu-K α radiation using a Rigaku Kristalloflex diffractometer (Dmax 2200) at room temperature.

Synthesis of tosyl, thiol and phthalonitrile derivatives

2-[2-(2-Ethoxyethoxy)ethoxy]-1-[2-(2-ethoxyethoxy)ethoxymethyl] ethyl 4-methyl-1-benzene sulfonate (2). A solution of 1,3-di[2-(2-ethoxyethoxy)ethoxy]-2-propanol (**1**; 19.10 g, 58.88 mmol) in dry pyridine (65 ml) was cooled to 0 °C and a solution of *p*-toluenesulfonyl chloride (12.35 g, 64.80 mmol) in dry pyridine (25 ml) was added with stirring under argon at a rate so that the temperature of the reaction mixture never exceeded 5 °C. After stirring for 48 h at room temperature, the reaction mixture was poured over crushed ice and the resulting aqueous solution was extracted with dichloromethane (100 ml \times 3). The organic layer was washed at 0 °C with 6 N HCl solution, with H₂O, dried with Na₂SO₄ and evaporated to give a viscous oil that was chromatographed on Al₂O₃ (dichloromethane-methanol 100:1). This compound is a colourless viscous oil. Yield: 22 g (81%). Anal. found

C 55.13, H 7.89%; C₂₂H₃₈O₉S (478.60) requires C 55.21, H 8.00%. IR (KBr cell): $\nu_{\max}/\text{cm}^{-1}$ 2980–2880 (CH₂), 1600, 1450, 1350 (SO₂), 1190–1180 (SO₂), 1120–1100 (C–O–C), 940, 820, 780, 680, 550; MS (EI): *m/z* (%) 479 (5) [M]⁺, 328.1 (10), 346 (20) [M – (OCH₂CH₂)₂OC₂H₅]⁺, 306.2 (30) [M – OTos]⁺, 214 (55) [M – 2(OCH₂CH₂)₂OC₂H₅]⁺, 177 (100), 117 (60).

1,3-Di[2-(2-(2-ethoxyethoxy)ethoxy)]-2-propanethiol (3). Compound **2** (8.05 g, 16.8 mmol) was dissolved in anhydrous ethanol (60 ml) and thiourea (1.60 g, 21 mmol) was added. The mixture was refluxed for 48 h under stirring, after which time the solvent was removed by distillation until the total volume was 30 ml. To the resulting solution, a solution of sodium hydroxide (1.35 g, 33.75 mmol) in 30 ml H₂O (degassed with argon) was added under argon atmosphere. This mixture was refluxed and stirred for an additional 6 h, under argon. The two-phase system that resulted was cooled and separated; the upper aqueous phase was acidified with dilute HCl and extracted with diethyl ether (50 ml \times 3). The ether layer was combined with the oily organic layer from the reaction mixture and this solution was dried over Na₂SO₄. The dried ether solution was filtered and evaporated, giving a thick liquid that was purified by column chromatography on Al₂O₃ using dichloromethane-methanol (100:1) as eluent. Yield: 2.50 g (44%). Anal. found C 52.88, H 9.03%; C₁₅H₃₂O₆S (340.48) requires C 52.92, H 9.47%. IR (KBr cell): $\nu_{\max}/\text{cm}^{-1}$ 2990–2850 (CH₂), 2580 (SH), 1450, 1380, 1350, 1320, 1300, 1240, 1120–1100 (C–O–C), 940, 880, 840, 750. MS (EI): *m/z* (%) 340.1 (5) [M]⁺, 328.1 (10), 298 (5), 278.9 (10), 206.9 (80) [M – (OCH₂CH₂)₂OC₂H₅]⁺, 172.9 (70), 147 (73), 135 (90), 115.9 (100), 99 (78), 91 (75), 74 (63) [M – 2(OCH₂CH₂)₂OC₂H₅]⁺, 61 (65).

4-Chloro-5{2-[2-(2-ethoxyethoxy)ethoxy]-1-[2-(2-ethoxyethoxy)ethoxymethyl]ethylsulfanyl}phthalonitrile (6). 1,2-Dichloro-4,5-dicyanobenzene (**4**; 0.99 g, 5 mmol) was dissolved in anhydrous dimethyl sulfoxide (9 ml) under argon and 1,3-di[2-(2-ethoxyethoxy)ethoxy]-2-propanethiol (**3**; 3.40 g, 10 mmol) was added. After stirring for 15 min at 50 °C, dry and finely powdered potassium carbonate (2.50 g, 18 mmol) was added portion wise over 0.5 h with efficient stirring. The reaction mixture was stirred under argon at 50 °C for 48 h. After cooling, the reddish-brown mixture was filtered off and solvent was evaporated under reduced pressure. The product was purified by column chromatography on Al₂O₃ using dichloromethane-methanol (50:1) as the eluent. The product is oily at room temperature. Yield: 1.50 g (60%). Anal. found C 54.94, H 6.75, N 5.34%; C₂₃H₃₃ClN₂O₆S (501.04) requires C 55.14, H 6.64, N 5.59%. IR (KBr cell): $\nu_{\max}/\text{cm}^{-1}$ 3040 (ArCH), 2990–2850 (CH₂), 2220 (C \equiv N), 1570 (ArC=C), 1460, 1350, 1220, 1120–1100 (C–O–C), 920, 750. MS (FAB, *m*-NBA): *m/z* (%) 501.1 (20) [M]⁺, 400.1 (10), 367.0 (13) [M – (OCH₂CH₂)₂OC₂H₅]⁺, 235.1 (35) [M – 2(OCH₂CH₂)₂OC₂H₅]⁺, 173.1 (95).

4,5-Di{2-[2-(2-ethoxyethoxy)ethoxy]-1-[2-((2-ethoxyethoxy)ethoxymethyl]ethylsulfanyl}phthalonitrile (7). Compound **7** was prepared by the same procedure as described for **6** by starting with **4** (0.74 g, 3.76 mmol), a large excess of **3** (4.45 g, 13.07 mmol) and potassium carbonate (1.96 g, 14.20 mmol). The resulting light-brown oily product was purified by column chromatography on Al₂O₃ using dichloromethane-methanol (50:1) as the eluent. Yield: 1.90 g (63%). This compound is a light yellow viscous oil. Anal. found C 56.55, H 7.95, N 3.36%; C₃₈H₆₄N₂O₁₂S₂ (805.06) requires C 56.69, H 8.01, N 3.48%. IR (KBr cell): $\nu_{\max}/\text{cm}^{-1}$ 3040 (ArCH), 2980–2940 (CH₂), 2220 (C \equiv N), 1560 (ArC=C), 1450, 1350, 1240, 1200, 1120–1100 (C–O–C), 920, 880, 840. MS

(EI): m/z (%) 805.3 (10) $[M]^+$, 670.2 (100) $[M - (OCH_2CH_2)_2 - OC_2H_5]^+$, 598.1 (10), 554.1 (11), 537.1 (4) $[M - 2(OCH_2CH_2)_2 - OC_2H_5]^+$, 360.2 (10), 272.4 (5) $[M - 4(OCH_2CH_2)_2OC_2H_5]^+$, 256 (5), 230 (25), 189.1 (34), 173.1 (46), 117.1 (100).

4-{2-[2-(2-Ethoxyethoxy)ethoxy]-1-[2-(2-ethoxyethoxy)ethoxy)methyl]ethylsulfanyl}phthalonitrile (8). **8** was prepared according to the same procedure as described for **6** by starting from with 4-nitrophthalonitrile (**5**; 0.866 g, 5 mmol), **3** (3.4 g, 10 mmol) and potassium carbonate (1.10 g, 7.97 mmol). The light-brown waxy product was purified by column chromatography on Al_2O_3 using dichloromethane–methanol (50:1) as the eluent. Yield: 1.40 g (60%). The product is a light yellow viscous oil at room temperature. Anal. found C 59.11, H 7.22, N 5.95%; $C_{23}H_{34}N_2O_6S_2$ (466.60) requires C 59.21, H 7.35, N 6.00%. IR (KBr cell): ν_{max}/cm^{-1} 3040 (ArCH), 2980–2940 (CH_2), 2220 ($C\equiv N$), 1580 ($ArC=C$), 1540, 1470, 1350, 1300, 1240, 1120–1100 ($C-O-C$), 940, 870, 840. MS (EI): m/z (%) 466.3 (10) $[M]^+$, 379.2 (35), 332.1 (20) $[M - (OCH_2CH_2)_2 - OC_2H_5]^+$, 306.2 (12), 233.1 (10), 218.1 (20), 205.1 (40), 200.1 (30) $[M - 2(OCH_2CH_2)_2OC_2H_5]^+$, 189.1 (35), 173.1 (40), 161.1 (38), 117.1 (100).

Synthesis of phthalocyanines

NiPc (6a). **6** (0.64 g, 1.27 mmol), 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU; 0.19 g, 1.27 mmol), anhydrous $NiCl_2$ (0.21 g, 1.62 mmol) and dried 1-pentanol (4 ml) were refluxed with stirring under argon atmosphere for 72 h. The 1-pentanol was removed under reduced pressure and the crude green product was purified by column chromatography (Al_2O_3 , CH_2Cl_2 –methanol 30:1). The dark green waxy compound was soluble in CH_2Cl_2 , $CHCl_3$, diethyl ether, methanol, ethanol, acetone, ethyl acetate. Yield: 0.140 g (21%). Anal. found C 53.85, H 6.25, N 5.25%; $C_{92}Cl_4H_{132}N_8NiO_{24}S_4$ (2062.86) requires C 53.57, H 6.45, N 5.43%. IR (KBr cell): ν_{max}/cm^{-1} 3040 (ArCH), 2980–2850 (CH_2), 1600 ($ArC=C$), 1450, 1410, 1380, 1340, 1280, 1240, 1120–1080 ($C-O-C$), 960, 880, 780, 750, 700. MS (FAB): m/z (%) 2062.3 (75) $[M + 1]^+$, 1754.6 (20) $[M - CH[CH_2(OCH_2CH_2)_2OC_2H_5]]^+$, 1447.4 (15) $[M - 2\{CH[CH_2(OCH_2CH_2)_2OC_2H_5]\}_2]^+$, 1142.9 (17) $[M - 3\{CH[CH_2(OCH_2CH_2)_2OC_2H_5]\}_3]^+$, 834.8 (78) $[M - 4\{CH[CH_2(OCH_2CH_2)_2OC_2H_5]\}_4]^+$.

H₂Pc (6b). A mixture of **6** (1.2 g, 2.4 mmol) and DBU (0.186 g, 1.27 mmol) in dried 1-pentanol (8 ml) was refluxed under argon atmosphere for 72 h. Evaporation of the solvent under reduced pressure left a green product mixture. The crude product was passed through an Al_2O_3 column using CH_2Cl_2 –methanol (20:1) as eluent. This product was further purified by preparative thin layer chromatography (TLC) using a 30:1 CH_2Cl_2 –MeOH solvent system. This compound has a similar solubility as **6a**. Yield: 0.120 g (10%). Anal. found C 55.18, H 6.81, N 5.36%; $C_{92}Cl_4H_{134}N_8O_{24}S_4$ (2006.18) requires C 55.08, H 6.73, N 5.59%. IR (KBr cell): ν_{max}/cm^{-1} 3300 (NH), 3040 (ArCH), 2980–2850 (CH_2), 1600 ($ArC=C$), 1450, 1420, 1380, 1350, 1280, 1240, 1120–1080 ($C-O-C$), 1020, 930, 880, 800, 750, 680. MS (FAB): m/z (%) 2006.2 (55) $[M + 1]^+$, 1698.3 (17) $[M - CH[CH_2(OCH_2CH_2)_2OC_2H_5]]^+$, 1391 (6) $[M - 2\{CH[CH_2(OCH_2CH_2)_2OC_2H_5]\}_2]^+$, 1085 (8) $[M - 3\{CH[CH_2(OCH_2CH_2)_2OC_2H_5]\}_3]^+$, 778.9 (35) $[M - 4\{CH[CH_2(OCH_2CH_2)_2OC_2H_5]\}_4]^+$, 329.2(70).

NiPc (7a). A mixture of **7** (0.80 g, 1 mmol), anhydrous $NiCl_2$ (0.13 g, 1 mmol) and anhydrous quinoline (3 ml) was heated and stirred at 180–185 °C for 48 h under argon atmosphere. After cooling to room temperature, the reaction mixture was treated with *n*-hexane and a waxy precipitate was separated.

The crude product was purified by column chromatography over Al_2O_3 with a mixture of dichloromethane–methanol (30:1). Yield: 0.110 g (13%). Anal. found C 55.72, H 7.88, N 3.12%; $C_{152}H_{256}N_8NiO_{48}S_8$ (3278.93) requires C 55.68, H 7.87, N 3.42%. IR (KBr cell): ν_{max}/cm^{-1} 3040 (ArCH), 2980–2850 (CH_2), 1600 ($ArC=C$), 1520, 1450, 1410, 1380, 1340, 1280, 1240, 1120–1080 ($C-O-C$), 960, 880, 780, 750, 710. MS (FAB): m/z (%) 3278 (98) $[M + 1]^+$, 2971 (28) $[M - CH[CH_2(OCH_2CH_2)_2OC_2H_5]]^+$, 2664 (20) $[M - 2\{CH[CH_2(OCH_2CH_2)_2OC_2H_5]\}_2]^+$, 2358 (15) $[M - 3\{CH[CH_2(OCH_2CH_2)_2OC_2H_5]\}_3]^+$, 825 (19) $[M - 4\{CH[CH_2(OCH_2CH_2)_2OC_2H_5]\}_4]^+$.

H₂Pc (7b). A solution of **7** (0.85 g, 1.06 mmol) in dry 2-(dimethylamino)ethanol (1.8 ml) was refluxed under argon atmosphere for 72 h and then the solvent was removed under reduced pressure. The crude product was dissolved in dichloromethane and filtered. This mixture was passed through an Al_2O_3 column using a mixture of 30:1 CH_2Cl_2 –MeOH as eluent. This product was further purified by preparative TLC (silica gel) using a 20:1 CH_2Cl_2 –MeOH solvent system. Yield: 0.100 g (12%). Anal. found C 56.16, H 8.07, N 3.12%; $C_{152}H_{258}N_8O_{48}S_8$ (3222.26) requires C 56.66, H 8.07, N 3.48%. IR (KBr cell): ν_{max}/cm^{-1} 3300 (NH), 3040 (ArCH), 2980–2850 (CH_2), 1600 ($ArC=C$), 1450, 1420, 1380, 1330, 1280, 1240, 1120–1080 ($C-O-C$), 950, 880, 750, 680. MS (FAB): m/z (%) 3222 (100) $[M + 1]^+$, 2884 (25) $[M - SCH[CH_2(OCH_2CH_2)_2OC_2H_5]]^+$, 2384 (15), 1714 (26), 1610 (90), 1381 (10) $[M - 6\{CH[CH_2(OCH_2CH_2)_2OC_2H_5]\}_6]^+$, 1074 (12) $[M - 7\{CH[CH_2(OCH_2CH_2)_2OC_2H_5]\}_7]^+$, 799 (20) $[M - 8\{CH[CH_2(OCH_2CH_2)_2OC_2H_5]\}_8]^+$.

NiPc (8a). A mixture of **8** (0.326, 0.7 mmol), DBU (0.16 ml, 1.1 mmol) and anhydrous $NiCl_2$ (0.185 g, 1.14 mmol) in pentanol (5 ml) was refluxed under argon atmosphere for 72 h. The 1-pentanol was removed under reduced pressure and the crude product was first purified by column chromatography over Al_2O_3 with a mixture of CH_2Cl_2 –MeOH (30:1). This product was then purified with preparative TLC (silica gel) using a 20:1 CH_2Cl_2 –MeOH solvent system. Yield: 0.070 g (21%). Anal. found C 56.94, H 7.23, N 5.46%; $C_{92}H_{136}N_8NiO_{24}S_4$ (1925.08) requires C 57.40, H 7.12, N 5.82%. IR (KBr cell): ν_{max}/cm^{-1} 3040 (ArCH), 2980–2850 (CH_2), 1600 ($ArC=C$), 1530, 1450, 1400, 1380, 1350, 1310, 1260, 1240, 1120–1080 ($C-O-C$), 930, 880, 810, 780, 750. MS (FAB): m/z (%) 1925 (100) $[M + 1]^+$, 1618 (55) $[M - CH[CH_2(OCH_2CH_2)_2OC_2H_5]]^+$, 1310 (17) $[M - 2\{CH[CH_2(OCH_2CH_2)_2OC_2H_5]\}_2]^+$, 1003 (13) $[M - 3\{CH[CH_2(OCH_2CH_2)_2OC_2H_5]\}_3]^+$, 695 (45) $[M - 4\{CH[CH_2(OCH_2CH_2)_2OC_2H_5]\}_4]^+$.

H₂Pc (8b). A solution of **8** (0.54 g, 1.16 mmol) in dry 2-(dimethylamino)ethanol (2 ml) was refluxed under argon atmosphere for 48 h and then the solvent was removed under reduced pressure. The crude product was dissolved in dichloromethane and filtered. The mixture was passed through an Al_2O_3 column using a CH_2Cl_2 –MeOH (30:1) solvent system. This product was further purified with preparative TLC (silica gel) using a 20:1 CH_2Cl_2 –MeOH solvent system. Yield: 0.155 g (29%). Anal. found C 59.21, H 7.26, N 6.04%; $C_{92}H_{138}N_8O_{24}S_4$ (1868.40) requires C 59.14, H 7.45, N 6.00%. IR (KBr cell): ν_{max}/cm^{-1} 3300 (NH), 3040 (ArCH), 2980–2850 (CH_2), 1600 ($ArC=C$), 1450, 1420, 1400, 1350, 1320, 1280, 1260, 1120–1080 ($C-O-C$), 1020, 930, 880, 800, 750. MS (FAB): m/z (%) 1868 (42) $[M + 1]^+$, 1561 (13) $[M - CH[CH_2(OCH_2CH_2)_2OC_2H_5]]^+$, 1254 (10) $[M - 2\{CH[CH_2(OCH_2CH_2)_2OC_2H_5]\}_2]^+$, 948 (13) $[M - 3\{CH[CH_2(OCH_2CH_2)_2OC_2H_5]\}_3]^+$, 641 (35) $[M - 4\{CH[CH_2(OCH_2CH_2)_2OC_2H_5]\}_4]^+$.

Results and discussion

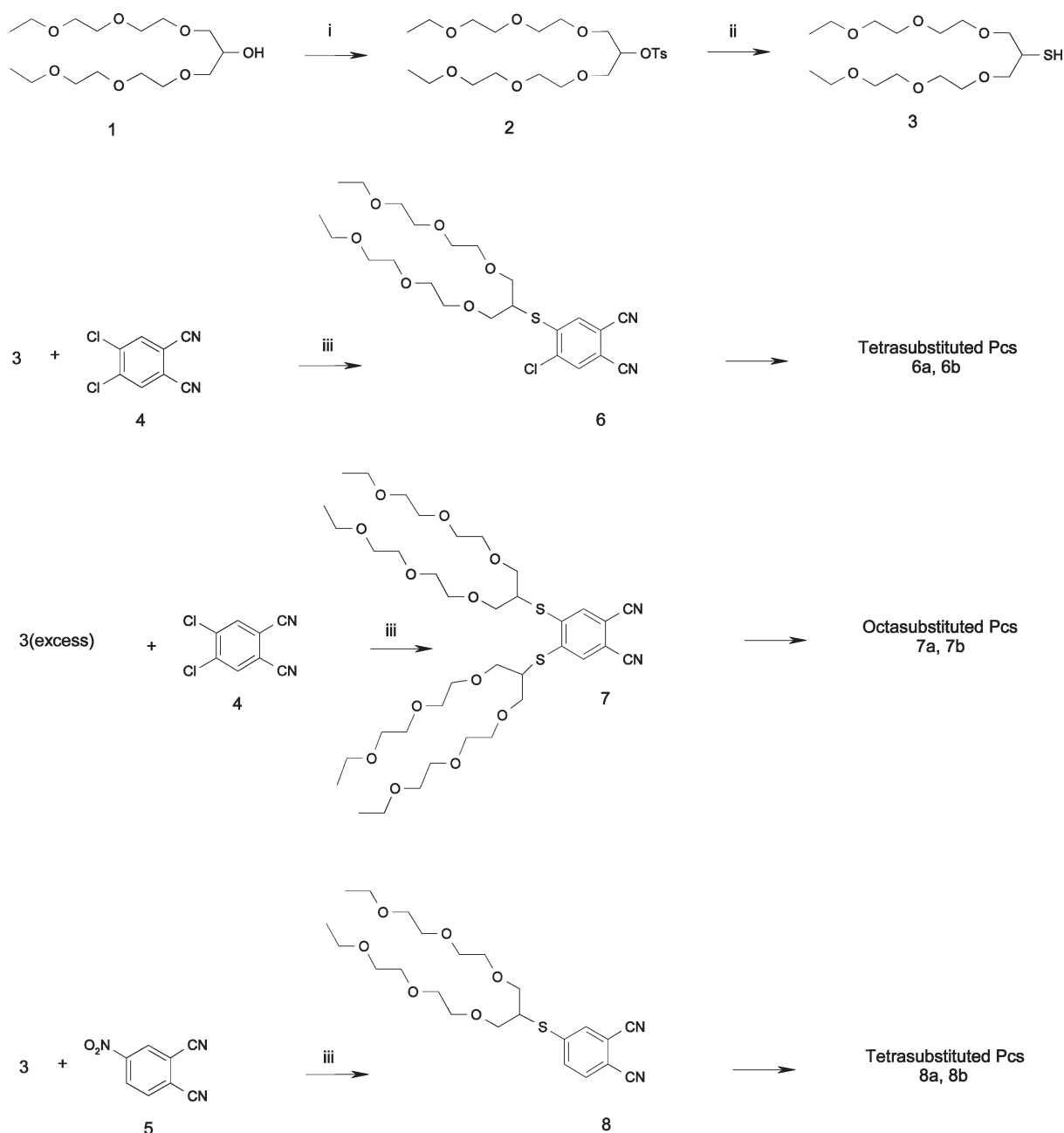
Synthesis

Phthalocyanines (**6a,b**, **7a,b**, **8a,b**) were prepared by the route shown in Scheme 1. This route is based on the thiol compound **3** and 1,2-dichloro-4,5-dicyanobenzene (**4**). Commercially available 4,5-dichlorophthalic acid was converted into **4** as described previously.^{27b} Attempts to prepare the thiol compound **3** from 1,3-di[2-(2-ethoxyethoxy)ethoxy]-2-propanol (**1**) according to the usual methods were unsuccessful. Instead, this conversion was achieved through the tosyl derivative **2** in two steps according to the reported procedure.^{34a,35} Tosylation of the hydroxy group was carried out in dry pyridine at room temperature with *p*-toluenesulfonyl chloride. Conversion of the tosyl compound **2** into the thiol derivative **3** was accomplished by boiling dry ethanol in the presence of thiourea for 48 h. In these reactions, the long reaction times were necessary for good yields.

4-Nitro-1,2-dicyanobenzene (**5**) was also used recently to prepare 4-monosubstituted phthalonitrile derivatives, through

base-catalyzed nucleophilic aromatic displacement.^{27,33,34} The same route was applied to prepare the monosubstituted dinitrile derivative **8** from **3** and **5**. Similarly, under the same conditions **4** resulted in the expected compounds **6** and **7** by using an excess amount and a large excess of **3**, respectively. The reactions were carried out in dimethyl sulfoxide (DMSO) at 50 °C with potassium carbonate, which was used as the base.

The preparation of pc derivatives from the aromatic nitriles required different reaction conditions.⁶ For various substituted dinitriles, the reaction in the presence of strong non-nucleophilic bases such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), either in 1-pentanol or in bulk with yields of phthalocyanines up to 90%, is the most efficient in comparison to other methods.^{27a,36} In addition, these reactions are easy to perform, work under relatively mild conditions and yield pure pcs. Therefore, the tetra-substituted metal-free pc derivatives **6b** and **8b** were obtained directly from the reaction of dicyano compounds **6** and **8** in 1-pentanol at reflux temperature in the presence of DBU (Fig. 1). Also, cyclotetramerization of dinitrile derivatives



Scheme 1 (i) *p*-MeC₆H₄SO₂Cl, pyridine, room temperature; (ii) a: thiourea, EtOH, reflux, 48 h; b: NaOH/H₂O, 3 h reflux in Ar atmosphere; (iii) DMSO, K₂CO₃, 50 °C, 48 h.

6 and **8** in the presence of anhydrous NiCl_2 and DBU in 1-pentanol gave the octa-substituted nickel(II) pcs **6a** and **8a**, respectively. The reaction of disubstituted dinitrile derivative **7** in 2-(dimethylamino)ethanol yields the octa-substituted metal-free pc **7b**. In the case of octa-substituted Nipc **7a**, cyclomerization was carried out in quinoline in the presence of anhydrous NiCl_2 salt. We expect that **6a,b**, and **8a,b** were prepared as a statistical mixture of four regioisomers owing to the various possible positions of the oligo(ethyleneoxy) side-chains relative to one another. From their molecular symmetry of D_{4h} , C_{4h} , C_{2v} and C_s each isomer would be prepared with a relative distribution of 1:1:2:4, respectively.³⁷ No attempt was made to separate the isomers of **6a**, **6b**, **8a** and **8b**.

The thia-bridged tetra- and octa-poly(oxyethylene)-substituted pcs (**6a,b**, **7a,b**, **8a,b**) were purified in each case by column chromatography (Al_2O_3) and preparative thin-layer chromatography (TLC) using a mixed solvent system of dichloromethane–methanol as eluent. The intense green waxy products are very soluble in polar and apolar solvents such as chloroform, benzene, diethyl ether, carbon tetrachloride, *N,N*-dimethylformamide, ethanol and acetone. They could thus be thoroughly investigated by ^1H and ^{13}C NMR. In addition to elemental analysis results, mass spectra (see Experimental) of the new organic intermediate compounds and pcs obtained by the EI and FAB techniques show relatively intense molecular ion peaks. Another common point in all pcs derivative mass spectra is the clear appearance of the fragmentation ion peaks corresponding to the stepwise loss of poly(oxyethylene) $\{\text{CH}[\text{CH}_2(\text{OCH}_2\text{CH}_2)_2\text{OC}_2\text{H}_5]_2\}$ side chains. NMR investigation of all compounds have provide the characteristic chemical shifts for the structures as expected (Tables S1 and S2, Electronic supplementary information).

For substances **6a,b**, **7a,b**, **8a,b** the typical absorption spectra of phthalocyanines were observed,⁵ showing absorption bands in the Soret band region of 300–400 nm and Q band transitions at 600–700 nm (Table 1). The metal-free phthalocyanines **6b**, **7b** and **8b** give doublet Q band as a result of the D_{2h} symmetry. The nickel(II) phthalocyanines **6a**, **7a** and **8a** exhibit intense Q bands around 700 nm with a relatively sharp absorption peak and almost no shoulder on the higher energy side, which would correspond to aggregated species. For all the phthalocyanines the effect of thia-substitution was a shift of these intense Q bands to higher wavelengths when

Table 1 Electronic spectra detail of phthalocyanines in chloroform

Compound	$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)	
	Soret band region	Q band region
6a	261.5 (5.22), 312.5 (9.46), 402.5 (2.56)	619.5 (4.16), 657.5, ^a 688.5 (21.70)
6b	238.5 (3.80), 308.0 (5.28), 351.5 (7.84)	620.5 (3.28), 651.5, ^a 682.5 (13.58), 715.5 (15.94)
7a	272.0 (6.12), 322.5 (10.06), 422.0 (3.22)	630.5 (0.92), 669.5, ^a 702.0 (20.68)
7b	266.0 (3.68), 359.5 (5.64), 432.0 (2.78)	635.5 (2.68), 673.5, ^a 700.5 (11.16), 730 (12.60)
8a	260.0 (4.94), 303.0 (8.26), 392.0 (2.60)	615.0 (4.10), 650.0, ^a 682.0 (22.54)
8b	297.0 (5.66), 345.5 (7.68), 411.5 (2.96)	616.0 (3.24), 651.0, ^a 678.0 (13.84), 711.5 (16.42)

^a Shoulder.

compared with unsubstituted, alkyl- or alkoxy-substituted derivatives.

For phthalocyanines, the aggregation behaviour in solution is a good indication of interaction between the aromatic macrocycles. Aggregation is easily detected from optical absorption studies. Any increase in concentration results in aggregation of phthalocyanine molecules, which is accompanied by a blue shift of the Q band with some decrease in intensity.³ It has been concluded that aggregation is enhanced by solvent polarity and the presence of aliphatic side chains.^{9,24} This has been indeed observed with octa-substituted derivatives [Fig. 2(A)].

The optical absorption spectra of compounds **6a,b**, **7a,b**, **8a,b** are dependent on the solvent used. Aggregation is not detectable in tetrahydrofuran or chloroform. The tendency to form aggregates increases in the order: tetrahydrofuran < chloroform < dimethylformamide < carbon tetrachloride < ethanol < methanol for octa-substituted Ni(II) pc (**7a**). Interestingly, in methanol, the peak corresponding to monomer is still present in the absorption spectrum [Fig. 2(B)] whereas it disappeared for the octa-substituted metal-free pc derivative (**7b**). Similar spectra have been obtained in the case of both tetra-substituted phthalocyanine derivatives **6a,b** and **8a,b**.

Compound	R ₁	R ₂	M
6a	$\text{SCH}(\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{C}_2\text{H}_5)_2$	Cl	Ni
6b	$\text{SCH}(\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{C}_2\text{H}_5)_2$	Cl	2H
7a	$\text{SCH}(\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{C}_2\text{H}_5)_2$	$\text{SCH}(\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{C}_2\text{H}_5)_2$	Ni
7b	$\text{SCH}(\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{C}_2\text{H}_5)_2$	$\text{SCH}(\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{C}_2\text{H}_5)_2$	2H
8a	$\text{SCH}(\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{C}_2\text{H}_5)_2$	H	Ni
8b	$\text{SCH}(\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{C}_2\text{H}_5)_2$	H	2H

Fig. 1 Chemical structure of the tetra- and octa-substituted phthalocyanine derivatives.

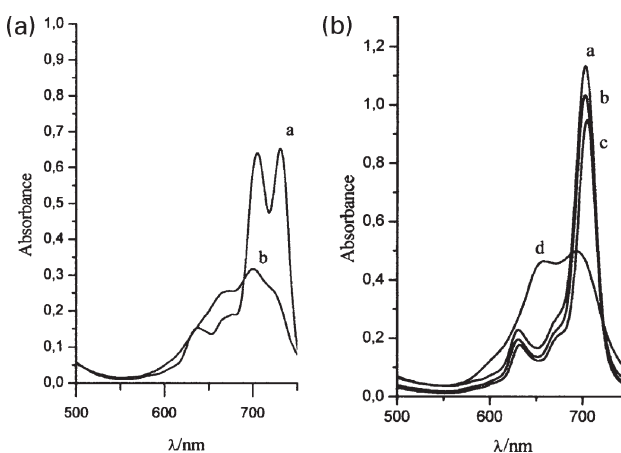


Fig. 2 (A) Visible absorption spectra of the octa-substituted metal-free pc derivative **7b** in (a) benzene, (b) MeOH. (B) Visible absorption spectra of the octa-substituted Ni(II) pc derivative **7a** in (a) tetrahydrofuran, (b) chloroform, (c) carbon tetrachloride, (d) MeOH.

Characterization of the mesophase

Table 2 lists the phase transition temperatures established by DSC and polarizing microscopic observations for the tetra-substituted pc derivatives (**6b**, **8a,b**). All mesophases were found to be very viscous at lower temperatures. As a consequence, not all DSC peaks could be confirmed optically. As can be seen from Table 3, all tetra-substituted pc derivatives show only one mesophase, Col_h. However, the octa-substituted pc derivatives (**7a,b**) exhibit no mesomorphism and are viscous oils at room temperature. The textures observed by polarizing optical microscopy for the compounds studied are very similar to those described in refs. 17 and 34. Excellent

Table 2 Phase transition temperatures and enthalpies for the tetra-substituted phthalocyanine derivatives as determined by DSC^a

Compound	R ₂	M	T _{Col h → I} /°C (ΔH/kJ mol ⁻¹)	
			Heating	Cooling
6a	Cl	Ni	222.2 (1.330)	216.6 (1.048)
6b	Cl	2H	160.0 (1.223)	156.7 (1.130)
7a	–SCH[CH ₂ O(CH ₂ CH ₂ O) ₂ C ₂ H ₅] ₂	Ni	Liquid	–
7b	–SCH[CH ₂ O(CH ₂ CH ₂ O) ₂ C ₂ H ₅] ₂	2H	Liquid	–
8a	H	Ni	230.5 (0.906)	220.0 (0.614)
8b	H	2H	198.0 (0.957)	183.3 (0.579)

^a Heating and cooling rates: 10 °C min⁻¹, heating range: 10–300 °C.

Table 3 X-Ray diffraction data of the tetra-substituted phthalocyanine derivatives

Compound	Observed spacing/Å	Theoretical spacing/Å	Lattice constant/Å	Ratio	Miller indices
6a	24.44	24.44		1	(100)
	13.97	14.10	<i>a</i> = 27.94	√3	(110)
	12.19	12.21	Col _{hd} ^a	√4	(200)
	9.19	9.23		√7	(210)
	8.02	8.14		√9	(300)
	6.69	6.70		√12	(311)
	4.19	–			
	3.59	–			
6b	24.35	24.35		1	(100)
	13.62	14.06		√3	(110)
	11.93	12.17	<i>a</i> = 28.12	√4	(200)
	9.41	9.20	Col _{hd} ^a	√7	(210)
	8.01	8.11		√9	(300)
	7.11	7.03		√12	(311)
	4.30	–			
	3.57	–			
8a	22.76	22.76		1	(100)
	13.02	13.14	<i>a</i> = 26.28	√3	(110)
	11.40	11.38	Col _{hd} ^a	√4	(200)
	8.71	8.60		√7	(210)
	4.35	–			
	3.61	–			
8b	25.57	25.57		1	(100)
	14.18	14.76		√3	(110)
	12.85	12.80		√4	(200)
	9.71	9.66	<i>a</i> = 29.53	√7	(210)
	8.54	8.52	Col _{hd} ^a	√9	(300)
	7.49	7.38		√12	(311)
	7.06	7.03			
	4.26	–			
	3.41	–			

^a At 25 °C.

textures of samples, preferentially fan- or flower-like textures (Fig. 3, Figures S1–S3, Electronic supplementary information) of the mesophases were obtained by slow cooling from the isotropic melt.

The mesophases were identified by microscopic observation and X-ray diffraction measurements at 30 °C. The X-ray data are summarized in Table 3. Powder diffraction patterns of **6a,b**, **8a** and **8b** contain the typical reflections of a columnar mesophase of substituted pcs.¹² Tetra-substituted pcs gave five sharp peaks whose spacings are in a ratio of 1 : 1/√3 : 1/2 : 1/√7 : 1/3 : 1 in the low angle region, so that each of the mesophases could be established as a discotic hexagonal columnar (Col_h) mesophase. In the wide angle region the compounds **6a,b**, **8a** and **8b** show a diffuse halo at 4.2, 4.3, 4.35 and 4.26 Å respectively, which is compatible with the disorder of parafin tails in the side chains. An additional reflection at 3.4 Å is also observed, which may be assigned to the packing of macrocyclic subunits in the columns. **6a,b**, **8a** and **8b** show a diffuse reflection, indicating that there is no long-range translational order of the molecules along the axis of stacks, which is associated with the discotic hexagonal disordered Col_{hd} mesophase.³⁴

Conclusion

Phthalocyanines showing mesogenic properties that contain both sulfur and oxygen donors are rather rare. In the present work, the synthesis of new tetra- and octa-thia(polyoxyethylene)-substituted Ni(II) and metal-free phthalocyanines and their characterization by standard methods (¹H and ¹³C-NMR, elemental analysis, IR, UV/vis and mass spectrometry) was described. The compounds prepared are soluble in most solvents ranging from carbon tetrachloride to methanol. Tetra-substituted Ni(II) and metal-free phthalocyanine derivatives are stable over a wide temperature range and exhibit a disordered hexagonal columnar (Col_{hd}) structure. However,

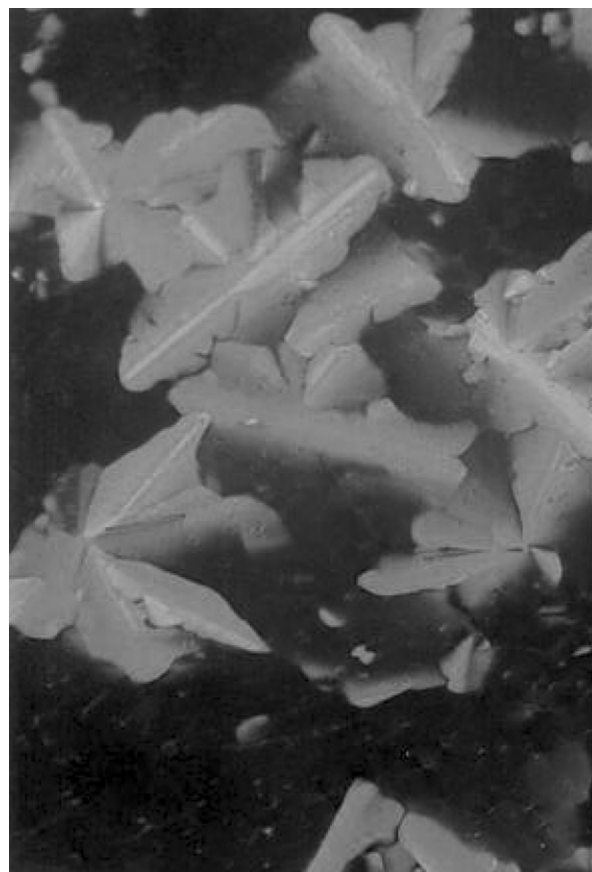


Fig. 3 Optical texture of **6b** observed at 25 °C (magnification × 16).

octa-substituted pc derivatives (**7a,b**) exhibit no mesomorphism and are viscous oils at room temperature. Comparing the mesophases of the branched thioether pc derivatives and their analogous oxoether derivatives, a Col_h mesophase could be seen over a wide temperature region for the thioether pc derivatives. Future investigations will focus on the chemical sensor properties of these mesogenic compounds.

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