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Polyhedron 26 (2007) 4551-4556



Synthesis and characterization of liquid crystalline unsymmetrically substituted phthalocyanines

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> Received 1 March 2007; accepted 9 June 2007 Available online 30 June 2007

Abstract

The synthesis of unsymmetrically substituted phthalocyanines bearing two *p*-tolyl-sulfonyl (tosyl)amido and six alkylthio moieties was achieved by cyclotetramerisation of two different phthalonitrile derivatives, namely 1,2-di(alkylthio)-4,5-dicyanobenzene and 4,5-dicyano-N,N'-ditosyl-o-phenylenediamine in the presence of an anhydrous metal salt and strong base. The new compounds were characterized by elemental analyses, UV/Vis, IR, NMR and mass spectra. The mesogenic properties of these new materials were studied by differential scanning calorimetry (DSC) and polarizing optical microscopy. The mesogenic properties of these compounds were compared to that of their symmetric analogous, octaalkythia substituted phthalocyanine derivatives. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Phthalocyanine; Asymmetric phthalocyanine; Liquid crystal; Metallomesogen

1. Introduction

Phthalocyanines (Pcs) have attracted great research attention because of their fascinating electronic and optical properties for many applications such as chemical sensors, liquid crystals, catalysis and non-linear optics [1,2]. These properties also strongly depend on the peripheral and axial substitution pattern [1–3]. Upto now, a variety of symmetrical pcs have been reported [1–3], whilst there have been only a limited number of reports on unsymmetrical pcs because of synthesis and purification difficulties. Recent researches have indicated that asymmetric pcs possess interesting properties in various areas such as liquid crystals [4–6], Langmuir Blodget (LB) film formation [7–9], photodynamic therapy of cancer [10,11] and second-order non-linear optics [12–14].

Different methods are known for the preparation of asymmetric pcs: statistical condensation of two differently

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substituted phthalonitriles or the corresponding 1,3-diiminoisoindolines [14,15]; reaction of a polymer-bonded phthalonitrile or 1,3-diiminoisoindoline with excess of another differently substituted one [16,17]; ring expansion of a so-called sub-phthalocyanine with a substituted 1,3diiminoisoindoline [12,18–21] or phthalonitrile [11,22]. Each method has different advantages and disadvantages. In general, the statistical condensation strategy is the most widely preferred.

Pcs are known to form columnar liquid crystals. The liquid crystalline properties of pcs depend on the number, position and character of substituents, and the nature of the central metal atom. It has been found that numerous pc derivatives which are peripherally or non-pheripherally octa- and tetra-substituted with alkyl- [23], alkoxy-[24], alkoxymethyl- [25], oligo(ethyleneoxy) [5,26], alkylthia [27,28], oligo (ethyleneoxy)thia [29] or even? crowned? [30–32] groups exhibit thermotropic or lyotropic mesomorphism. Similar behaviour is demonstrated by asymmetrically substituted pc derivatives. Contrary to symmetric pcs, there are fewer studies on the liquid crystalline properties of asymmetric pcs [4–6].

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Our previous studies have focused on the synthesis of new pcs exhibiting liquid crystal and gas sensor properties [27–29,33–39]. The films of the pcs showing mesomorphic properties at room temperature have been proven to be used as photoconductors and gas sensors in molecular electronic devices. The ordered pc films obtained from liquid crystalline pc compounds are more sensitive than disordered pc films [28,39]. Recently, we have reported the synthesis of peripherally symmetrical substituted octa p-tolyl-sulfonyl (tosyl) amido pcs and their NMR and UV spectra investigations in different solvents and pH [40]. We have found that the hydrogen bonding capacity and deprotonation of the tosylamido groups causes interesting spectroscopic properties. Their potential application as chemical gas sensor is being investigated. However, only tosylamido substitution of the pc ring was not enough to exhibit mesogenic properties. Therefore, we designed electron-with-drawing tosylamido and donor alkylthia substituted novel unsymmetrical pcs which are liquid crystals owing to the alkyl chains. The synthesis, characterization and investigation of mesogenic properties are reported here. Also, the influence of the presence of the tosylamido unit on the phthalocyanine core on the mesomorphic properties was determined.

2. Experimental methods

2.1. Materials

The 4,5-dicyano-N,N'-ditosyl-o-phenylenediamine (1) [40] and 1,2-di(alkylthio)-4,5-dicyanobenzene derivatives (**2a**-**2c**) [41,42] were synthesized according to published procedures. All other reagents and solvents were reagent-grade quality, obtained from commercial suppliers and dried before use as described by Perrin and Armarego [43].

3. Measurements

Elemental analyses were obtained from Thermo Finnigan Flash 1112. Infrared spectra in KBr pellets were recorded on a Bio-Rad FTS 175C FT IR spectrophotometer. Optical spectra in the UV-Vis region were recorded with a Shimadzu 2001 UV PC spectrophotometer using a 1 cm pathlength cuvette at room temperature The mass spectra were recorded on a LCQ-ion trap (Thermofinnigan, San Jose, CA, USA), equipped with an Electrospray (ES) source. ¹H and ¹³C NMR spectra were recorded in CDCl₃ solutions on a Varian 500 MHz spectrometer. Thermogravimetric analyses were carried out on Mettler Toledo Star^e Thermal Analysis System at a rate of 10 °C min⁻¹in a nitrogen flow (50 ml min⁻¹). The phase transition behaviour of these compounds was observed by means of a polarizing microscope (Leitz Wetzler Orthoplan-pol.) equipped with a hot stage (Linkam TMS 93) and temperature-controller (Linkam LNP). Transition temperatures were determined with a scan rate of 10 °C min⁻¹ using a Mettler Toledo Star^e Thermal Analysis System/DSC

822^e. The differential scanning calorimeter system was calibrated with indium from 3 to 4 mg samples under nitrogen atmosphere.

3.1. Synthesis of asymmetric phthalocyanines

3.1.1. 2,3,9,10,16,17-Hexakis(hexylthio)-23,24bis(tosilamido)phthalocyaninato nickel(II) (3a)

A mixture of 1,2-di(hexylthio)-4,5-dicyanobenzene (2a) 4,5-dicyano-N,N'-ditosyl-o-phenylenediamine (2 mmol), (1) (1 mmol), anhydrous NiCl₂ (1.5 mmol), 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU, 3 mmol) and 4 ml dried n-hexanol were heated to reflux for 18 h under an argon atmosphere. After cooling to room temperature the mixture was treated with ethanol (10 ml), filtered off and washed several times with ethanol. The dark green product was purified by preparative thin layer chromatography (TLC) using a 5:2 CH_2Cl_2/n -hexane solvent system. Yield: 8%. Elemental Anal. Calc. for C₈₂H₁₀₂N₁₀NiO₄S₈ (1605): C, 61.29; H, 6.40; N, 8.72. Found: C, 61.10; H, 6.35; N, 8.70%. IR (KBr) v_{max} (cm⁻¹): 3258 (NH), 2956–2856 (CH₂, CH₃), 1599 (Car=N), 1350, 1163 (SO₂), 560 (CS). MS (ES–MS), m/z (%): 1606 (100) $[M+H]^+$, 1607 (50) $[M+2H]^+$. ¹H NMR (CDCl₃) δ : 0.94–1.18 (m, 18H, CH₃), 1.43-2.00 (m, 36H, CH₂), 2.21 (t, 6H, Ar-CH₃), 3.05-3.58 (m, 24H, CH₂), 7.9-8.42 (m, 18H, NH, CH_{ar}). ¹³C NMR (CDCl₃, Decoupled) δ : 13.09 (CH₃), 13.16 (CH₃), 20.59 (CH₂), 21.59 (C_{ar}CH₃), 27.72–28.16 (CH₂), 30.50-33.07 (CH₂), 118.5 (CarH), 124.10 (CarH), 127.08 (CarH), 128.8 (Car), 129.85 (CarH), 132.05 (Car), 132.72 (Car), 134.7 (Car), 138.71 (Car), 139.11 (Car), 141.00 (Car), 143.01 (CN), 143.50 (CN).

3.1.2. 2,3,9,10,16,17-Hexakis(dodecylthio)-23,24bis(tosilamido) phthalocyaninato nickel(II) (**3b**)

A mixture of 1,2-di(dodecylthio)-4,5-dicyanobenzene (2b) (2 mmol), 4,5-dicyano-N,N'-ditosyl-o-phenylenediamine (1) (1 mmol), anhydrous NiCl₂ (1.5 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 3 mmol) and 4 ml dried *n*-hexanol were heated to reflux for 18 h under an argon atmosphere. After cooling to room temperature the mixture was treated with ethanol (10 ml), filtered off and washed several times with ethanol. The dark green product was purified by preparative thin layer chromatography (TLC) using a 5:1 CH_2Cl_2/n -hexane solvent system. Yield: 7%. Elemental Anal. Calc. for C₁₁₈H₁₇₄N₁₀Ni O₄S₈ (2110): C, 67.11; H, 8.30; N, 6.63. Found: C, 67.00; H, 8.31; N, 6.70%. IR (KBr) v_{max} (cm⁻¹): 3263 (NH), 2957–2856 (CH₂, CH₃), 1598 (Car=N), 1348, 1164 (SO₂), 559 (CS). MS (ES-MS), *m*/*z* (%): 2111 (100) [M+H]⁺. ¹H NMR $(CDCl_3)$ δ : 0.98–1.27 (m, 18H, CH₃), 1.47-2.13 (m, 84H, CH₂), 2.32 (t, 6H, Ar–CH₃), 3.10-3.65 (m, 48H, CH₂), 7.8–8.62 (m, 18H, NH, CH_{ar}). ¹³C NMR (CDCl₃, Decoupled) \delta: 13.08 (CH₃), 13.24 (CH₃), 20.59 (CH₂), 21.52 (CarCH₃), 27.80–28.32 (CH₂), 30.56–33.12 (CH₂), 118.67 (CarH), 124.32 (CarH), 127.12 (CarH), 127.54 (CarH), 128.8 (Car), 129.96 (CarH), 132.15 (Car), 132.87 (Car),

134.75 (C_{ar}), 138.79 (C_{ar}), 139.31 (C_{ar}), 141.10 (C_{ar}), 143.01 (CN), 143.65 (CN).

3.1.3. 2,3,9,10,16,17-Hexakis(hexadecylthio)-23,24bis(tosilamido)phthalocyaninato nickel(II) (3c)

A mixture of 1,2-di(hexadecylthio)-4,5-dicyanobenzene (2c) (2 mmol), 4.5-dicyano-N, N'-ditosyl-o-phenylenediamine (1) (1 mmol), anhydrous NiCl₂ (1.5 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 3 mmol) and 4 ml dried *n*-hexanol were heated to reflux for 18 h under an argon atmosphere. After cooling to room temperature the mixture was treated with ethanol (10 ml), filtered off and washed several times with ethanol. The dark green product was purified by preparative thin layer chromatography (TLC) using a 5:1 CH_2Cl_2/n -hexane solvent system. Yield: 6%. Elemental Anal. Calc. for C₁₄₂H₂₂₂N₁₀NiO₄S₈ (2445): C, 69.65; H, 9.16; N, 5.72. Found: C, 69.60; H, 9.20; N, 5.70%. IR (KBr) v_{max} (cm⁻¹): 3258 (NH), 2955–2851 (CH₂, CH₃), 1599 (C_{ar}=N), 1350, 1163 (SO₂), 560 (CS). MS (ES-MS), *m*/*z* (%): 2446 (40) [M+H]⁺. ¹H NMR (CDCl₃) δ : 0.97–1.29 (m, 18H, CH₃), 1.37–2.17 (m, 108H, CH₂), 2.36 (t, 6H, Ar–CH₃), 3.12–3.69 (m, 52H, CH₂), 7.81-8.60 (m, 18H, NH, CH_{ar}). ¹³C NMR (CDCl₃, Decoupled) \delta: 13.06 (CH₃), 13.21 (CH₃), 20.52 (CH₂), 21.50 (CarCH₃), 27.72-28.36 (CH₂), 30.44-33.24 (CH₂), 118.77 (C_{ar}H), 124.44 (C_{ar}H), 127.24 (C_{ar}H), 127.56 (C_{ar}H), 128.82 (Car), 129.76 (CarH), 132.21 (Car), 132.67 (Car), 134.70 (Car), 138.70 (Car), 139.21 (Car), 141.105 (Car), 143.01 (CN), 143.55 (CN).

4. Result and discussions

4.1. Synthesis and characterization

The synthetic route of the pcs is shown in Scheme 1. 1,2-Di(alkylthio)-4,5-dicyanobenzenes (2a-2c) and 4,5-dicyano-N,N'-ditosyl-o-phenylenediamin (1) were synthesized according to the published procedures [40–42]. For the preparation of the pcs, we tried two different methods: ring expansion of corresponding sub-pc and statistical condensation of the phthalonitriles. For the first method, the diiminoisondoline derivative of 1 is required. Probably due to hydrolysis of the tosyl groups, it could not be obtained according to the literature [45-47]. Therefore, we adopted the second method (the statistical condensation method) for the preparation of the asymmetric pcs (3a-3c). Mixed condensation of 1,2-di(alkylthio)-4,5-dicyanobenzene (2a-**2c)** and 4,5-dicyano-N, N'-ditosyl-o-phenylenediamin (1) in the presence of anhydrous nickel (II) chloride. DBU as a strong nitrogen base and *n*-hexanol as the solvent afforded the asymmetric pcs (3a-3c). Generally, this method predicts that the reaction of two different phthalonitriles of the same reactivity in a 3:1 ratio will afford a mixture of products in the following percentages: A₄ 33%, A₃B 44%, other cross-condensation products 23% [44]. In our case, the 1,2-di(alkylthio)-4,5-dicyanobenzene derivatives (2a-2c) are much more reactive than 4.5-dicvano-N.N'ditosyl-o-phenylenediamine (1), therefore the symmetric octaalkylthio phthalocyanine (A₄) derivatives were found to be more preferable than the asymmetric 3a-3c pcs (A_3B) . To increase the yield of the asymmetric pcs (3a -3c) we tried several experiments with different molar ratios, and a 2:1 ratio of two dinitrile derivatives 2a-2c and 1 was found to be the most appropriate. The asymmetric pcs (3a -3c) were separated by preparative thin layer chromatography from the corresponding symmetric octaalkylthio substituted Ni(II) pc derivatives [NiPc(SR)₈] and the other products.

Elemental analysis results and the spectral data (¹H NMR, ¹³C NMR, FT IR, UV–Vis and MS) for the newly synthesized pcs (**3a–3c**) were consistent with the assigned formulations. The results are given in the experimental section.

The IR spectral results of the pcs (3a-3c) are different from the precursors 1 and 2a-2c, so the sharp peak for the C=N vibrations around 2220-2240 cm⁻¹, associated



Scheme 1. Synthesis of phthalocyanines 3a-3c (i) metal salt, DBU, n-hexanol, reflux.

with the nitrile groups, disappeared after conversion into the pcs. The NH groups gave absorption bands at around 3260 cm^{-1} and the characteristic vibration of SO₂ groups appeared at around 1340 and 1160 cm⁻¹ in the spectra of all the pcs, and confirmed the presence of the tosylamido groups. In addition, a group of intense absorption bands was also seen in the range 2856–2957 cm⁻¹ in the IR spectra of **3a–3c**. These can be attributed to the C-H stretching vibrations of the substituted alkyl chains.

A close investigation of the mass spectra of 3a-3c confirmed the proposed structures. The mass spectra of these compounds were obtained by the electron spray (ES) technique. We observed the molecular ion peaks of the pcs at m/z: 1606 for 3a, m/z: 2111 for 3b and m/z: 2446 for 3c.

A common feature of the ¹H NMR spectra of the pcs (**3a–3c**) is the broad absorptions probably caused by the aggregation of the pc, which is frequently encountered at the concentrations used for NMR measurements. The ¹H NMR spectra of **3b** and **3c** are similar to that of **3a**. The ¹H NMR spectrum of **3a** exhibits the aromatic and NH protons at 7.90–8.42 ppm as multiplets, the aliphatic CH₂ protons between 1.43 and 3.58 ppm as multiplets, CH₃ protons at δ 0.94–1.18 and ArC–CH₃ protons at around 2.21 ppm. The ratio of aromatic to aliphatic protons appears to show that the benzo groups with two different substituents are present in a 3:1 ratio. The ¹³C NMR spectral data of **3a–3c** given in experimental section are also in accord with the expected structures.

The blue-green pcs show typical electronic spectra with two strong absorption bands: a Soret (B) band at around 300-350 nm and a Q band at around 600-700 nm. The UV-Vis. spectra of 3a-c were obtained in chloroform and the results are given in Table 1. All of these pcs gave very similar spectra; they show the Q band at 697 nm and the B band at 323 nm. Increasing the length of the alkyl chain caused a decrease of the intensity of the Q band as expected. The electronic spectrum is given for compound 3a (Fig. 1). In addition to this octatosylamido Ni(II) and octahexilthia Ni(II) phthalocyanines are given in Fig. 1 to compare the absorption bands. The electronic absorption spectrum of octatosylamido Ni(II) phthalocyanine gave two Q bands in chloroform: a monomeric Q band around 680 nm together with a blue-shifted intense band around 640 nm corresponding to aggregated species. No additional band around 640 nm corresponding to aggregated species was observed in the electronic spectra of the asymmetric species (3a-3c). Octahexylthia substituted Ni(II) phthalocyanine also a gave different electronic spectrum from its

Table 1				
Electronic spectra	of the	phthalocyanines	in	chloroform

Compound	$\lambda_{\rm max}/{\rm nm}~(\epsilon/10^4~{\rm dm^3~mol^{-1}~cm^{-1}})$			
	Soret band region	Q band region		
3a	322.5(13.32) 413.0(3.64)	697.0(16.61)		
3b	323.0(13.00) 414.0(3.22)	697.5(15.82)		
3c	323.5(13.10) 413.5(3.50)	698.0(15.11)		



Fig. 1. Visible absorption spectra of octahexzilthia Ni(II) phthalocyanine (a), unsymmetrical substituted Ni(II) pc derivative (**3a**) (b) and octatosilamido Ni(II) phthalocyanine (c) in chloroform. Concentration = 3.74×10^{-6} mol dm⁻³.

asymmetric derivative (3a), with a Q band around 702 nm and a higher extinction coefficient than 3a.

4.2. Mesomorphic properties

The phase transition behaviours of the compounds 3a-**3c** were determined by differential scanning calorimetry (DSC) and polarizing microscopic observations. Phase transition temperatures and enthalpy changes of these products are presented in Table 2. The DSC-measurement of compounds 3a-3c show a significant sharp peak in the vicinity of 150 °C, which relates to the melting transition. Furthermore the DSC diagram of 3b and 3c depict a weak peak at about 227 °C and 205 °C, respectively that belongs to the clearing point. These investigations indicate that the compounds exhibit a thermotropic liquid crystalline phase between the melting and clearing point [25–28,32–34]. No such additional peak is observed for compound 3a, which excludes further phase transitions. Only the melting to the mesophase is present. The phthalocyanine derivative 3a did not give any isotropic transition until 280 °C. Therefore the heating cycles were interrupted before reaching any clearing point to avoid decomposition for 3a. The thermal stability of the phthalocyanines (3a-3c) has been investigated by thermal gravimetric analysis (TGA). The initial decomposition of the compounds 3a, 3b and 3c determined

Table 2

Phase transition temperatures and enthalpies for the compound 3a-3c as determined by DSC^a

Compound	nd Heating		Cooling		
	$C \to Col_h \to$	Ι	$I \to Col_h \to C$		
3a	165 (3.90)	not observed	not observed	120 (4.06)	
3b	161 (32.54)	227 (1.19)	218 (2.96)	91 (21.11)	
3c	144 (42.53)	205 (6.17)	198 (5.52)	23 (50.59)	

Heating and cooling rates: 10 °C, heating range: 0-280 °C.

^a Phase nomenclature: $Col_h = discotic$ hexagonal columnar phase, I = isotropic phase.



Fig. 2. Optical texture of **3b** observed at 170 °C (Magnification ×16).



Fig. 3. Optical texture of 3c observed at 170 °C (Magnification ×50).

by thermogravimetry occur above 298, 290 and 295 °C, respectively, and show negligible differences according to the length of the alkyl-chains. The main decomposition points are 325, 335 and 330 °C, respectively.

Also, the phase transition temperatures of the complexes (3a-3c) have been surveyed by polarization microscopy. The birefringence textures of the samples were obtained by slow cooling $(5 \,^{\circ}\text{C} \,^{\min})$ from the isotropic melt. The microscopic observation gave magnificent results for these complexes (3a-3c). Figs. 2 and 3 shows the photomicrograph of the mesophase of 3b and 3c, respectively at 170 $^{\circ}$ C. For this typical fan-shaped texture, often observed for Col_h, these mesophases could be thus confirmed as the Col_h phases [27–29,33,34].

According to the literature, the mesophase transition temperature of the symmetric hexylthia and dodecylylthia substituted Ni(II) Pcs were 36 and 20 °C [28]. When compared with their asymmetric derivatives (3a-3c), it could be seen that addition of tosylamido groups to the phthalocyanine core increases the liquid crystal phase transition

temperatures but decreases the clearing temperature. The isotropic liquid phase was not observed for hexylthia and dodecylthia substituted Ni(II) Pcs until 300 °C in the literature [28], though isotropic transitions were observed for the asymmetric derivatives (**3b**, **3c**) at 227 and 205 °C respectively. Furthermore, increasing the length of the alkyl chain decreases the melting and isotropic phase transition temperatures of compounds **3a**–**3c**.

5. Conclusions

Asymmetric mesogenic phthalocyanines are rather few. In the present work, the synthesis of new asymmetric Ni(II) phthalocyanines are described and characterized by standard methods (¹H and ¹³C NMR, elemental analysis, IR, UV/Vis and mass spectrometry). The asymmetric Ni(II) phthalocyanine derivatives (3a-3c) exhibit a hexagonal columnar (Col_b) structure. The influence of nature of the side chains upon the mesomorphic properties was compared for the asymmetric pcs (3a-3c) and also with their symmetric analogous without the tosylamido group [NiPc(SR)₈]. It could be seen that addition of the tosylamido group to the phthalocyanine core increases liquid crystal phase transition temperatures but decreases clearing temperatures. In addition to this, increasing the length of alkyl chain decreases the melting and isotropic phase transition temperatures of the compounds 3a-3c.

Acknowledgements

The authors thank to Colette LEBRUN for ES mass spectra and Prof. Ayşe Gül GÜREK for fruitful discussions.

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