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Novel columnar mesogen with octupolar optical nonlinearities: synthesis, mesogenic behavior and multiphoton-fluorescence-free hyperpolarizabilities of subphthalocyanines with long aliphatic chains†

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Novel subphthalocyanines with long thioalkyl chains exhibit hexagonal columnar mesophases at room temperature; their inherent first hyperpolarizability values (β) measured by hyper-Rayleigh scattering (HRS) with fluorescence suppression are $(189 \pm 30) \times 10^{-30}$ esu at 1300 nm.

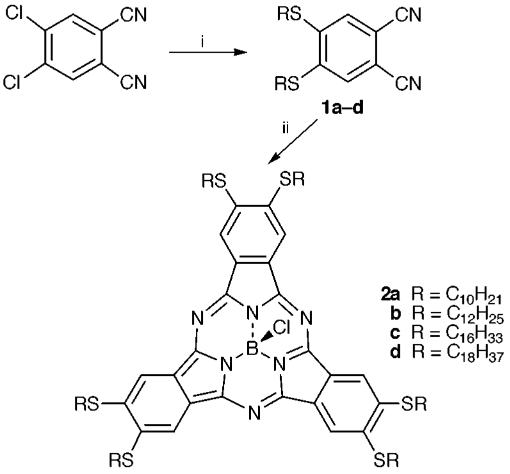
The unique supramolecular architectures of the columnar mesophases[1] have many potential applications in molecular devices.[2] Among columnar liquid crystals, bowl-shaped liquid crystals[3] have attracted considerable attention as potential ferroelectric and/or second-order nonlinear optical (NLO) materials because of their polar organization in the liquid crystalline phases.

Subphthalocyanines (SubPcs) are cone-shaped macrocycles composed of three isoindoline units with a boron inside.[4] They have been used as intermediates for the synthesis of unsymmetrical phthalocyanine (Pc) derivatives.[5] Furthermore, their unique 14 electron π-conjugated system with C_3 symmetry allows them to exhibit large molecular hyperpolarizabilities, mainly due to octupolar contributions.[6]

In our efforts to discover new columnar liquid crystals,[7] we became interested in SubPcs as potential columnar mesogens with NLO properties. Although liquid crystalline Pcs have been studied extensively,[8] there is no report on SubPc derivatives exhibiting liquid crystalline phases. Herein we report syntheses and mesogenic behavior of SubPcs containing long thioalkyl chains. Since molecular hyperpolarizabilities of SubPcs have been overestimated due to their strong fluorescence,[6a] here we also report their hyperpolarizabilities measured by hyper-Rayleigh scattering (HRS) using flurorescence suppression techniques.[9]

Subphthalocyanines containing thioalkyl groups **2a–d** were synthesized in two steps as shown in Scheme 1. Reaction of 1,2-dichloro-4,5-dicyanobenzene with alkanethiols ($C_nH_{2n+1}SH$; $n = 10$, 12, 16 and 18) yields 4,5-bis(alkylthio)phthalonitrile, cyclotrimerization of which in the presence of BCl_3 produces the desired products.‡

SubPcs **2a–d** show enantiotropic liquid crystalline behavior as revealed by differential scanning calorimetry (DSC), polarizing optical microscopy, and X-ray diffraction. The phase behavior of these compounds is summarized in Table 1. Compounds **2a** ($n = 10$) and **2b** ($n = 12$) exhibit mesomorphic behavior at room temperature. Upon heating, the transition from mesophase to isotropic liquid occurs at 90.9 and 86.1 °C for **2a** and **2b**, respectively. For these compounds, melting or crystallization peaks are not observed in the DSC scan, even down to −40 °C. As usual, the melting temperature increases while the clearing point decreases with increasing side chain length. For example, **2c** ($n = 16$) shows a phase transition from crystalline to mesophase near room temperature and transforms into an isotropic liquid at 75 °C. Furthermore, **2d** ($n = 18$) is a solid at room temperature and melts at 43 °C to form a mesophase which turns into an isotropic liquid phase at 70 °C. These compounds have good thermal stability as they decompose above 250 °C.



Scheme 1 *Reagents and conditions*: i, RSH, K_2CO_3, DMSO; ii, BCl_3, 1-chloronaphthalene.

Table 1 Optical and thermal properties of the compounds **2a–d**[a]

	T/°C (Δ*H*/J g^{-1})	
Compound	Heating	Cooling
2a ($n = 10$)	D_{hd} 90.9 (0.29) I	I 79.6 (0.28) D_{hd}
2b ($n = 12$)	D_{hd} 86.1 (0.68) I	I 70.5 (1.31) D_{hd}
2c ($n = 16$)	K 27.2 (13.42) D_{hd} 75.3 (0.35) I	I 67.6 (0.61) D_{hd} 20.9 (10.36) K
2d ($n = 18$)	K 43.4 (21.80) D_{hd} 70[b] I	I 63[b] D_{hd} 36.6 (0.53) K 33.6 (9.56) K′

[a] Transition temperatures and enthalpies of transition were determined by DSC (scan rate 10 °C min^{-1}). K, K′ = crystalline phase; D_{hd} = hexagonal columnar phase; I = isotropic phase. [b] Transition observed only by microscopy.

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† Experimental and spectral data for **2a–d** are available from the RSC web site, see http://www.rsc.org/suppdata/cc/1999/1661/

In polarizing optical microscopy, **2a–d** in mesophases exhibit pseudo-focal conic textures, which are characteristic of columnar mesophases. Except for **2d**, these textures are maintained at room temperature, demonstrating the stability of the liquid crystalline phases at room temperature. To obtain information on the structures of **2a–d** in the mesophases, X-ray diffraction studies were carried out using synchrotron radiation. The X-ray pattern (Fig. 1) of the mesophase of **2c** at room temperature shows an intense peak and two weak peaks in the small-angle region with reciprocal Bragg spacings in a ratio $1:\sqrt{3}:2$. These peaks were assigned to the (100), (110) and (200) reflections of a hexagonal arrangement with a lattice constant $a = 33.02$ Å. In the wide-angle region a broad halo at 4.43 Å is observed, which is related to the liquid-like correlations between the molten aliphatic chains. Similar X-ray diffraction patterns are observed for other compounds in their mesophases. It is not clear how the cone-shaped molecules are arranged in the mesophase. However, as previously suggested in bowl-shaped mesogens, the cones may be stacked in a head-to-tail fashion to form a polar column which in turn forms a hexagonal array with random polarity.

We measured the molecular first hyperpolarizabilities (β) of **2a–c** using HRS techniques.[10] Regardless of the alkyl chain length these compounds have a strong absorption band at ~602 nm and an intense emission at ~612 nm. Since they are highly fluorescent, high-frequency demodulation of multiphoton fluorescence was used to retrieve their fluorescence-free first hyperpolarizability values. A detailed description of the experimental set-up is given elsewhere.[9a] The measurements were performed in $CHCl_3$ solution. Disperse Red 1 was used as the external reference with $\beta = 54 \times 10^{-30}$ esu at 1300 nm.[9c] The inherent fluorescence-free first hyperpolarizability values for **2a–c** are the same within the experimental uncertainties: $(189 \pm 30) \times 10^{-30}$ esu at 1300 nm. Using a three-level model,[11] the dispersion-free β value (β_0) was calculated to be $(21 \pm 3) \times 10^{-30}$ esu. These results are in good agreement with the recently reported β value of 40×10^{-30} esu at 1460 nm and β_0 value of 10×10^{-30} esu for a similar SubPc compound.[6b]

In summary, we have synthesized liquid crystalline SubPcs exhibiting hexagonal columnar mesophases at room temperature. Since they are highly fluorescent, their inherent first hyperpolarizability values were measured by HRS using fluorescence suppression techniques. In the mesophases, the cone-shaped molecules appear to be stacked in a head-to-tail fashion to form a polar column which in turn forms a hexagonal array with random polarity. Despite the nonlinearity/transparency trade-off that appears better for dipolar that for octupolar chromophores,[12] the incorporation of dipolar chromophores into stable macroscopic ensembles has been hampered by strong antiparallel dipolar interactions, leading to centrosymmetric arrangements with zero bulk susceptibility. The polar organization of these SubPcs in the liquid crystalline phase will results in a thermodynamically stable non-zero second order susceptibility. The next challenging goal is to align all the columns with the same polarity to achieve large ferroelectricity and second order bulk susceptibility. We are currently working along this line.

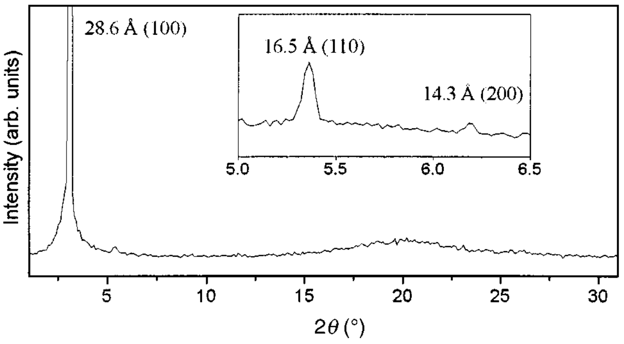

Fig. 1 X-Ray diffraction pattern of **2c** taken at room temperature.

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Notes and references

‡ All the compounds have been fully characterized by ^1H NMR, UV-VIS, IR and mass spectrometry and gave satisfactory elemental analyses. *Selected data* for **2a**: Compound **1a** (2.13 g, 4.50 mmol) was dissolved in 1-chloronaphthalene (4 ml) under Ar. After cooling of the solution in an ice bath a solution of BCl_3 (1.5 ml, 1.5 mmol, 1 M solution in *n*-heptane) was added. The mixture was stirred at 0 °C for 10 min and then heated to 100 °C for 4 h. After cooling to room temperature, the mixture was diluted with acetone. The crude product was isolated by filtration and purified by column chromatography on silica gel using CH_2Cl_2 as eluent (0.30 g, 14%); $\delta_H(CDCl_3$, 300 MHz) 0.88 (t, 18H), 1.59 (m, 84H), 1.89 (m, 12H), 3.31 (m, 12H), 8.51 (s, 6H); $\delta_C(CDCl_3$, 75 MHz) 14.52, 23.09, 28.86, 29.56, 29.72, 29.74, 29.96, 30.01, 32.31, 34.08, 119.91, 128.69, 141.23, 149.53; ν_{max}(KBr)/cm^{-1} 2955, 2924, 2853, 2360, 2342, 1597, 1462, 1419, 1368, 1080, 979; $\lambda_{max}(CHCl_3)$/nm (log ε) 602 (5.00), 558 (4.50), 415 (4.53), 389 (4.52), 306 (4.85); Fluorescence (excitation was at 360 nm, $CHCl_3$): λ_{max}/nm 613, 504; *m*/*z* (FAB-MS) 1463 [M+H]$^+$ (Calc. for $C_{84}H_{132}BClN_6S_6$: C, 68.88; H, 9.08; N, 5.74. Found: C, 68.48; H, 9.18; N, 5.48%). Compounds **2b–d** were synthesized by the same method as **2a**.

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