

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Novel monofunctionalized electron-deficient anthraquinone-based discotic liquid crystals

Sandeep Kumar^a; Jaishri J. Naidu^a; Sanjay K. Varshney^a

^a Centre for Liquid Crystal Research, P.O. Box 1329, Jalahalli, Bangalore--560013, India,

Online publication date: 11 November 2010

To cite this Article Kumar, Sandeep , Naidu, Jaishri J. and Varshney, Sanjay K.(2003) 'Novel monofunctionalized electron-deficient anthraquinone-based discotic liquid crystals', *Liquid Crystals*, 30: 3, 319 – 323

To link to this Article: DOI: 10.1080/0267829031000068675

URL: <http://dx.doi.org/10.1080/0267829031000068675>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Novel monofunctionalized electron-deficient anthraquinone-based discotic liquid crystals

SANDEEP KUMAR*, JAISHRI J. NAIDU and SANJAY K. VARSHNEY
Centre for Liquid Crystal Research, P.O. Box 1329, Jalahalli, Bangalore—560013,
India

(Received 14 August 2002; accepted 30 October 2002)

A series of electron-deficient 1-hydroxy-2,3,5,6,7-pentaalkoxyanthra-9,10-quinones has been synthesized. All nine members of the series were found to be liquid crystalline, forming columnar mesophases over a broad temperature range. Such supramolecular building blocks can be used for the preparation of novel discotic dimers, oligomers, polymers and metallomesogens.

1. Introduction

Recent reports that columnar phases of several derivatives of, for example, triphenylene, phthalocyanine, and coronene, exhibit very high charge carrier mobility, have created wide scientific and technological interest in discotic liquid crystals [1] as potential candidates for electro-optical applications [2]. Charge and energy migration in a number of discotic liquid crystals have been studied extensively [3–6]. Schmidt-Mende *et al.* recently used hexabenzocoronene-based discotic liquid crystals as the hole-transporting layer and a perylene dye as the electron-transporting layer to construct an efficient organic photovoltaic solar cell [7]. The device exhibits external quantum efficiencies up to 34% and power efficiencies of up to ~2%. These efficiencies are comparable to the best efficiencies reported for organic photovoltaic devices [8]. A number of discotic liquid crystals were found to be suitable as the emissive layer in organic light-emitting diodes [9]. An all-columnar bilayer LED has recently been reported by Seguy *et al.* [9a]. Conductivity along the columns in columnar mesophases has been reported to be several orders of magnitude greater than in the perpendicular direction [3]. Charge carrier mobility up to $0.38 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ has been reported in different columnar mesophases of several discotic liquid crystals [4, 5].

The majority of discotic liquid crystals are electron-rich π -conjugated materials and are better hole carriers (p-type semiconductors). Examples of electron-deficient (n-type semiconductors) are scarce and only a few derivatives of, for example, a bis(dithiolen)nickel complex [10], perylene [11, 12], tricycloquinazoline [13, 14],

and hexaazotriphenylene [15] have been reported in the literature. Moreover, while a number of methods are now available for the synthesis of functionalized electron-rich discotics, particularly triphenylene based DLCs [16], routes for the preparation of functionalized electron-deficient discotics are rare. Functionalized derivatives are the precursor molecules for the preparation of liquid crystalline dimers, oligomers, polymers and networks which are excellent materials for engineering applications, given, for example, their processability, thermal stability, and excellent mechanical properties. Therefore, new electron-acceptor monofunctionalized discotic liquid crystals are of great interest. In this paper, we report the synthesis and mesomorphic behaviour of a number of monofunctionalized anthraquinone-based discotic liquid crystals.

2. Experimental

2.1. General information

Chemicals and solvents (AR quality) were used without purification. Column chromatographic separations were performed on silica gel (230–400 mesh) and neutral aluminium oxide. Thin layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (Merck, Kieselgel 60, F254). HPLC analysis was performed using a Merck-Hitachi LaChrom 2000 chromatograph equipped with a UV detector and a Merck LiChrospher Si60 (5 μm) column. Mass spectra were recorded on a Jeol J600H spectrometer in FAB⁺ mode using a *m*-nitrobenzyl alcohol (NBA) matrix. NMR spectra were recorded on a 200 MHz Bruker spectrometer. All chemical shifts are reported in δ units downfield from Me_4Si , and *J* values are given in Hz. Transition temperatures were measured using a Mettler FP82HT hot stage and central processor in conjunction

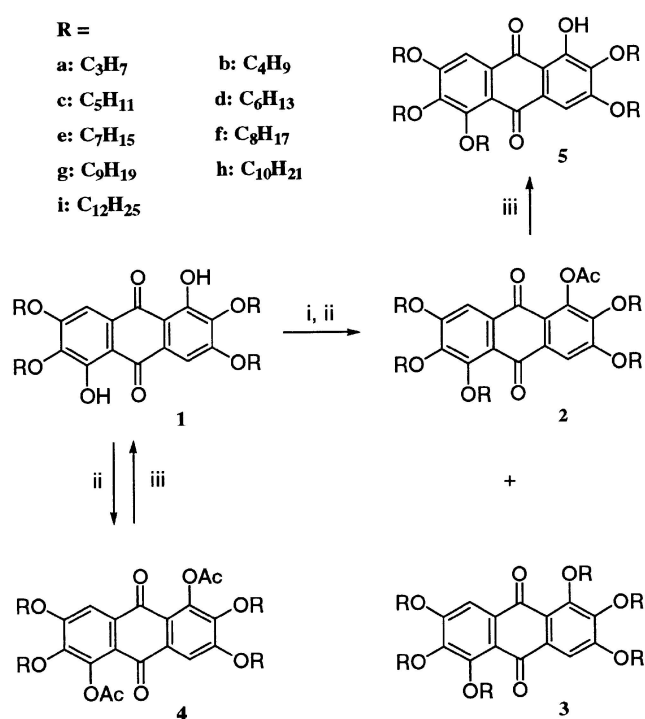
* Author for correspondence;
e-mail: sandkumar@hotmail.com

with a Leitz DMRXP polarizing microscope as well as by differential scanning calorimetry (DSC7 Perkin-Elmer). The synthesis of different monofunctionalized anthraquinones is outlined in the scheme. The 1,5-dihydroxy-2,3,6,7-tetraalkoxyanthra-9,10-quinones **1** were prepared following a literature method [17].

2.2. Synthesis and characterization

2.2.1. Preparation of compounds **2** and **3** from compound **1**

To a solution of compound **1** (1 mmol) in dry DMF, was added CsCO₃ (1.2 mmol) and alkyl bromide (1.2 mmol). The reaction mixture was heated at 100°C for 20 h under a nitrogen atmosphere. The mixture was cooled to room temperature, water added and the mixture extracted with chloroform. The combined extracts were washed with water and dried over anhydrous sodium sulphate. The solvent was removed under vacuum. The dried crude product was acetylated by heating at reflux in acetic anhydride and pyridine for 18 h under N₂. The cooled reaction mixture was poured into ice, acidified with 5% HCl and extracted with diethyl ether. The combined extracts were washed with water and brine and dried over anhydrous sodium sulphate. The dried crude organic phase was purified by column chromatography over silica gel. Chromatographic separation gave



Scheme. Synthesis of monofunctionalized anthraquinone-based derivatives. Reagents and conditions: i) CsCO₃, DMF, RBr, 100°C, 20h. ii) Ac₂O, pyridine, reflux. iii) Aq. NaOH, EtOH, reflux.

mainly two products: hexaalkoxyanthraquinone **3** in about 60% yield and pentaalkoxymonoacetoxyanthraquinone **2** in about 30% yield. Spectral and thermal properties of all the hexaalkoxyanthraquinones **3a-i** were in accordance with literature data.

2a-i. ¹H NMR (200 MHz, CDCl₃): all the monoacetates gave similar spectra differing in only the number of alkyl chain CH₂ protons; δ 7.71 (s, 1H), 7.55 (s, 1H), 4.1 (m, 10H), 2.48 (s, 3H), 2.0–1.3 (m, alkyl chain CH₂), 0.98 (m, 15H). ¹³C NMR (50.3 MHz, CDCl₃): all the compounds **2a-i** gave similar spectra differing in only the number of alkyl chain C signals; δ 180.9, 180.6, 169.2, 157.6, 157.4, 154.2, 147.4, 145.4, 132.1, 131.9, 120.5, 118.8, 108.8, 107.1, 74.8, 74.2, 74.1, 69.4, 69.2, 31.9–14.1 (alkyl chain carbons). IR: the same spectrum was obtained for all the compounds **2a-i**; ν_{max}/cm⁻¹ 2958, 2926, 2872, 2857, 1762, 1668, 1573, 1467, 1328, 1201, 1129. UV-Vis: all samples were measured in dichloromethane and a similar spectrum was observed for all the compounds; λ_{max}/nm 287, 322. MS (FAB): *m/z*; **2a** 557.1 (100%); **2b** 627.0 (100%); **2c** 697.3 (100%); **2d** 768.1 (20%); **2e** 837.8 (20%); **2f** 907.6 (25%); **2g** 977.4 (50%); **2h** 1047.3 (25%); **2i** 1187.7 (15%).

2.2.2. Tetraalkoxy-diacetoxyanthraquinones, **4a-i**

Acetylation of 1,5-dihydroxy-2,3,6,7-tetraalkoxyanthra-9,10-quinones **1a-i** under classical acetylation reaction conditions (pyridine, acetic anhydride, reflux) gave the diacetates **4a-i** in about 70% yield. ¹H NMR (200 MHz, CDCl₃): all the diacetates gave similar spectra differing only in the number of alkyl chain CH₂ protons; δ 7.65 (s, 2H), 4.14 (t, 4H), 4.05 (t, 4H), 2.48 (s, 6H), 2.0–1.3 (m, alkyl chain CH₂), 1.06–0.88 (m, 12H). ¹³C NMR (50.3 MHz, CDCl₃): all the compounds **4a-i** gave similar spectra differing only in the number of alkyl chain C signals; δ 180.2, 169.1, 157.4, 154.2, 145.8, 144.0, 131.4, 118.9, 108.8, 74.1, 69.5, 30.0–14.0 (alkyl chain carbons). IR: the same spectrum was obtained for all the compounds; ν_{max}/cm⁻¹ 2962, 2940, 2872, 2857, 1771, 1666, 1579, 1320, 1196, 1115. UV-Vis: all samples were measured in dichloromethane and a similar spectrum was observed for all the compounds; λ_{max}/nm 286, 320. MS (FAB): *m/z*; **4a** 557.4; **4b** 613.2; **4c** 669.3; **4d** 725.7; **4e** 781.2; **4f** 837.4; **4g** 893.0; **4h** 949.9; **4i** 1061.5.

2.2.3. 1-Hydroxy-2,3,5,6,7-pentahexyloxy-9,10-anthraquinones, **5a-i**

Pure monoacetates **2a-i** were hydrolysed by heating at reflux for about 1 h in ethanol containing 5% aqueous NaOH. All the compounds were purified by repeated column chromatography. Pale yellow solid or semisolid materials were obtained upon the addition of ethyl alcohol and dried under vacuum. HPLC analysis of all the materials was 98–99%. ¹H NMR (200 MHz, CDCl₃):

all the compounds gave similar spectra differing only in the number of alkyl chain CH₂ protons; δ 12.66 (s, 1H), 7.64 (s, 1H), 7.38 (s, 1H), 4.08 (m, 10H), 1.87–1.26 (m, alkyl chain CH₂), 1.07–0.88 (m, 15H). ¹³C NMR (50.3 MHz, CDCl₃): all the compounds **5a–i** gave similar spectra differing only in the number of alkyl chain C signals; δ 186.9, 180.5, 158.4, 157.4, 156.5, 154.8, 148.1, 140.0, 130.7, 121.1, 111.4, 106.8, 104.8, 74.4, 73.9, 73.3, 69.1, 68.9, 32.4–13.9 (alkyl chain carbons). IR: the same spectrum was obtained for all the compounds **5a–i**: $\nu_{\max}/\text{cm}^{-1}$ 3430, 2958, 2930, 2872, 2857, 1664, 1632, 1574, 1505, 1470, 1427, 1352, 1323, 1282, 1135. UV-Vis all samples were measured in dichloromethane and a similar spectrum was observed for all the compounds; λ_{\max}/nm 286, 333, 408. MS (FAB): m/z ; **5a** 515.1 (100%); **5b** 584.8 (100%); **5c** 655.2 (100%); **5d** 725.5 (100%); **5e** 794.9 (50%); **5f** 865.6 (100%); **5g** 935.7 (100%); **5h** 1005.2 (100%); **5i** 1144.6 (25%).

3. Results and discussion

3.1. Synthesis

1,2,3,5,6,7-Hexahydroxyanthraquinone (rufigallol) derivatives comprise one of the earliest systems reported to form columnar mesophases. Billard and co-workers reported the first discotic liquid crystalline hexaesters of rufigallol in 1980 and since then more than 50 different discotic liquid crystalline derivatives of this molecule have been prepared [17]. Acid-catalysed self-condensation of gallic acid yields crude ruffigallol, which can be esterified to obtain liquid crystalline hexaesters [17*a*]. Similarly, hexaethers can be prepared by the etherification of the hexaphenol or its hexaacetate [17*d*]. The two hydroxyl groups at the 1- and 5-positions in rufigallol are hydrogen-bonded and, therefore, are less reactive. This unequal reactivity leads to the preparation of several unsymmetrical rufigallol derivatives [17*f–i*]. Furthermore, as these two functional groups are readily available, main chain polymers of the tetraalkoxyrufigallol can be easily prepared [18]. Anthraquinone-based discotic liquid crystals have been studied recently as materials which exhibit one-dimensional electrical conductivity [19].

A survey of the literature reveals that although a number of anthraquinone derivatives are known, monofunctionalized rufigallol derivatives having identical peripheral chains are not readily accessible. Efforts have been made to prepare monofunctionalized anthraquinone derivatives using one polar peripheral chain [17*h*]. However, to investigate structure–property relationships, the simplicity of a molecule having identical peripheral chains is generally preferred and, therefore, a new strategy has been developed for the preparation of monofunctionalized anthraquinone-based derivatives having identical peripheral chains.

The synthesis of 1-hydroxy-2,3,5,6,7-pentaalkoxyanthra-9,10-quinones was achieved by the partial alkylation of tetraalkoxyrufigallol as shown in the scheme. Rufigallol [20] and its tetraethers were prepared following a reported procedure [17] and purified through their diacetates. Further alkylation of the tetraether to prepare pentaalkoxy (monofunctionalized) derivatives under different reaction conditions results in the formation of a mixture of unreacted (tetraalkylated), pentaalkylated and hexalkylated products. All efforts to isolate pure monohydroxy-pentaalkoxyanthraquinone were futile. Given that the tetraalkoxydiacetoxanthraquinone, pentaalkoxymonoacetoxanthraquinone, and hexaalkoxyanthraquinone may have significantly different R_f values on a chromatographic column, the crude product was acetylated using excess of acetic anhydride and pyridine. All three products could now be separated readily by column chromatography. Pure pentaalkoxymonoacetoxanthraquinones **2a–i** were hydrolysed to afford the desired monofunctionalized anthraquinone derivatives **5a–i**. Partial alkylation of **1** using cesium carbonate in DMF was found to give the best yield of desired monofunctionalized rufigallol derivatives. All the monofunctionalized anthraquinones were purified by repeated column chromatography and isolated as solids or semi-solids upon the addition of ethanol to the ethereal solution of pure material. The products were obtained by filtration washed with ethanol and dried under vacuum. Compounds **5a** and **5b** are yellow powders, **5c** is a sticky yellow solid while **5d–i** are waxy yellow–orange solids.

3.2. Thermal behaviour

The thermal behaviour of all the compounds was investigated by polarizing microscopy and differential scanning calorimetry. Phase transition temperatures and enthalpy measurements were carried out on 4–5 mg samples using a Perkin-Elmer DSC7 with heating and cooling rates of 10°C min⁻¹. Melted materials were used to fill the sample cells and, therefore, data from a first heating cycle could not be obtained. Data from the second heating and cooling cycles are collected in the table.

All the monofunctionalized anthraquinone-based derivatives **5a–i** were found to be liquid crystalline with very broad mesophase temperature ranges. In all cases, columnar mesophases appear upon cooling from the isotropic phase and remain stable down to room temperature (~30°C). The observed optical textures are very similar to the characteristic textures for the Col_h phase shown by several well-characterized discotic liquid crystals. Figure 3 shows two representative examples of photomicrographs obtained for compounds **5d** and **5h** on cooling from the isotropic liquid.

Table. Phase transition temperatures (peak temperature/ $^{\circ}\text{C}$) and associated enthalpy changes (kJ mol^{-1} in parentheses) of monofunctionalized anthraquinone-based derivatives **5a–i** observed on second heating and cooling scans. Cr = solid or semisolid, Col = columnar liquid crystalline phase, I = isotropic.

Compound	Heating scan	Cooling scan
5a	Cr 68.4 (7.2) Col 106.6 (5.4) I	I 103.9 (5.4) Col
5b	Cr 57.7 (5.9) Col 127.6 (6.4) I	I 124.9 (6.4) Col
5c	Cr 32.4 (1.4) Col 125.3 (5.8) I	I 123.5 (5.8) Col
5d	Col 113 (4.2) I	I 111.1 (4.1) Col
5e	Col 104.8 (5.4) I	I 103.1 (5.2) Col
5f	Col 90.4 (4.0) I	I 88.1 (3.8) Col
5g	Col 86.4 (3.9) I	I 84.6 (3.7) Col
5h	Col 80.6 (3.7) I	I 77.8 (3.5) Col
5i	Col 67.5 (2.9) I	I 65.5 (2.9) Col

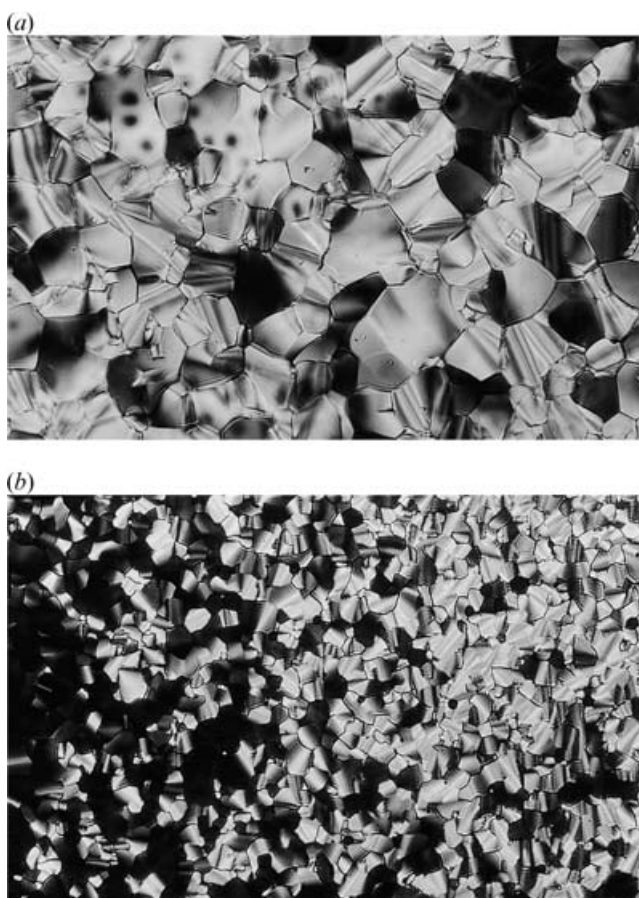


Figure 1. (a) Optical texture of **5d** obtained on cooling from the isotropic liquid at 30°C (crossed polarizers, magnification $\times 200$). (b) The texture of **5h** obtained on cooling from the isotropic liquid at 30°C (crossed polarizers, magnification $\times 100$).

The columnar phase–isotropic transition temperature, decreases, as expected, on increasing the number of carbon atoms in the peripheral chains (see the table). The melting temperatures of all the monofunctionalized derivatives **5a–i** are slightly lower than for the hexaalkoxyanthraquinone derivatives. The mesophase ranges of all the monohydroxy derivatives are much higher than those of the corresponding hexaalkoxyanthraquinones [17*d*]. The low melting temperatures may be due to the unsymmetrical nature of these materials. The decrease in the melting transition and increase in the mesophase range due to unsymmetric substitution is well known in discotic liquid crystals [21]. All the tetraalkoxydiacetates **4a–i** and pentaalkoxymonoacetates **2a–i** were found to be non-liquid crystalline. This may be because of unfilled space around the core and the steric hindrance of the acetate group(s).

5. Conclusion

The synthesis of several mesogenic electron-deficient monofunctionalized anthraquinone-based derivatives has been described. All the compounds form very broad temperature range columnar mesophases which are stable below ambient temperature and, therefore, are good candidates for electron migration studies in self-organized systems. They can also be utilized as precursor molecules to prepare metallomesogens [22] and liquid crystalline donor–sigma–acceptor type dimers [23].

We are grateful to Professor S. Chandrasekhar for many helpful discussions.

References

- [1] CHANDRASEKHAR, S., SADASHIVA, B. K., and SURESH, K. A., 1977, *Pramana*, **9**, 471.
- [2] (a) BODEN, N., and MOVAGHAR, B., 1998, *Hand Book of Liquid Crystals*, Vol. 2B, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill (Wiley-VCH), Chap. IX; (b) CHANDRASEKHAR, S., 1998, *Hand Book of Liquid Crystals*, Vol. 2B, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill (Wiley-VCH), Chap. VIII.
- [3] (a) BODEN, N., BUSHBY, R. J., and CLEMENTS, J., 1993, *J. chem. Phys.*, **98**, 5920; (b) BODEN, N., BUSHBY, R. J., CAMMIDGE, A. N., CLEMENTS, J., and LUO, R., 1995, *Mol. Cryst. liq. Cryst.*, **261**, 251; (c) BODEN, N., BORNER, R. C., BUSHBY, R. J., and CLEMENTS, J., 1994, *J. Am. chem. Soc.*, **116**, 10 807; (d) BALAGURUSAMY, V. S. K., PRASAD, S. K., CHANDRASEKHAR, S., KUMAR, S., MANICKAM, M., and YELAMAGGAD, C. V., 1999, *Pramana J Phys*, **53**, 3.
- [4] (a) ADAM, D., SCHUHMACHER, P., SIMMERER, J., HÄUSSLING, L., SIEMENSMEYER, K., ETZBACH, K. H., RINGSDOF, H., and HAARER, D., 1994, *Nature*, **371**, 141; (b) ADAM, D., SCHUHMACHER, P., SIMMERER, J., HÄUSSLING, L., PAULUS, W., SIEMENSMEYER, K., ETZBACH, K. H., RINGSDOF, H., and HAARER, D., 1995, *Adv. Mater.*, **7**, 276; (c) SIMMERER, J., GLUSEN, B.,

- PAULUS, W., KETTNER, A., SCHUHMACHER, P., ADAM, D., ETZBACH, K. H., SIEMENSMEYER, K., WENDORFF, J. H., RINGDORF, H., and HAARER, D., 1996, *Adv. Mater.*, **8**, 815; (d) OCHSE, A., KETTNER, A., KOPITZKE, J., WENDORFF, J. H., and BASSLER, H., 1999, *Phys. Chem. chem. Phys.*, **1**, 1757; (e) PALENBERG, M. A., SILBEY, R. J., MALAGOLI, M., and BREDAS, J.-L., 2000, *J. chem. Phys.*, **112**, 1541.
- [5] (a) SCHOUTEN, P. G., WARMAN, J. M., DE HAAS, M. P., FOX, M. A., and PAN, H. L., 1991, *Nature*, **353**, 736; (b) VAUGHAN, G. B. M., HEINEY, P. A., MCCAULEY, JR., J. P., and SMITH, III, A. B., 1992, *Phys. Rev. B*, **46**, 2787; (c) SCHOUTEN, P. G., WARMAN, J. M., DE HAAS, M. P., VAN NOSTRUM, C. F., GELINCK, G. H., NOLTE, R. J. M., COPYN, M. J., ZWIKKER, J. W., ENGEL, M. K., HANACK, M., CHANG, Y. H., and FORD, W. T., 1994, *J. Am. chem. Soc.*, **116**, 6880; (d) VAN DE CRAATS, A. M., SIEBBELES, L. D. A., BLEYL, I., HAARER, D., BERLIN, Y. A., ZHARIKOV, A. A., and WARMAN, J. M., 1998, *J. phys. Chem. B*, **102**, 9625; (e) VAN DE CRAATS, A. M., DE HASS, M. P., and WARMAN, J. M., 1997, *Synth. Met.*, **86**, 2125; (f) BODEN, N., BORNER, R. C., BUSHBY, R. J., CLEMENTS, J., MOVAGHAR, B., DONOVAN, K. J., and KREOUZIS, T., 1995, *Phys. Rev.*, **52**, 13 274; (g) VAN DE CRAATS, A. M., and WARMAN, J. M., 2001, *Adv. Mater.*, **13**, 130.
- [6] (a) MARKOVITSI, D., GERMAIN, A., MILLIE, P., LECUYER, P., GALLOS, L. K., ARGYRAKIS, P., BENGIS, H., and RINGSDORF, H., 1995, *J. Phys. Chem.*, **99**, 1005; (b) MARGUET, S., MARKOVITSI, D., MILLIE, P., SIGAL, H., and KUMAR, S., 1998, *J. Phys. Chem. B*, **102**, 4697; (c) MARKOVITSI, D., MARGUET, S., BONDKOWSKI, J., and KUMAR, S., 2001, *J. phys. Chem. B*, **105**, 1299.
- [7] SCHMIDT-MENDE, L., FECHTENKOTTER, A., MULLEN, K., MOONS, X., FRIEND, R. H., and MACKENZIE, J. D., 2001, *Science*, **293**, 1119.
- [8] KUMAR, S., 2002, *Curr. Sci.*, **82**, 256.
- [9] (a) SEGUY, I., DESTRUEL, P., and BOCK, H., 2000, *Synth. Met.*, **111–112**, 15; (b) BACHER, A., BLEYL, I., ERDELEN, C. H., HAARER, D., PAULUS, W., and SCHMIDT, H.-W., 1997, *Adv. Mater.*, **9**, 1031; (c) STAPPE, I. H., STUMPFLIN, V., WENDORFF, J. H., SPOHN, D. B., and MOBIUS, D., 1997, *Liq. Cryst.*, **23**, 613; (d) CHRIST, T., GLUSEN, B., GREINER, A., KETTNER, A., SANDER, R., STUMPFLIN, V., TSUKRUK, V., and WENDORFF, J. H., 1997, *Adv. Mater.*, **9**, 48.
- [10] OHTA, K., HASEBE, H., EMA, H., MORIYA, M., FUJIMOTO, T., and YAMAMOTO, I., 1991, *Mol. Cryst. liq. Cryst.*, **208**, 21.
- [11] GOLTNER, C., PRESSNER, D., MULLEN, K., and SPIESS, H. W., 1993, *Angew. Chem. int. Ed.*, **32**, 1660.
- [12] WRUTHNER, F., THALACKER, C., DIELE, S., and TSCHERSKE, C., 2001, *Chem. Eur. J.*, **7**, 2245.
- [13] KUMAR, S., SHANKAR RAO, D. S., and PRASAD, S. K., 1999, *J. mater. Chem.*, **9**, 2751.
- [14] BODEN, N., BUSHBY, R. J., DONOVAN, K., LIU, Q., LU, Z., KREOUZIS, T., and WOOD, A., 2001, *Liq. Cryst.*, **28**, 1739.
- [15] PIETERSE, K., VAN HAL, P. A., KLEPPINGER, R., VEKEMANS, J. A. J. M., JANSSEN, R. A. J., and MEIJER, E. W., 2001, *Chem. Mater.*, **13**, 2675.
- [16] (a) KREUDER, W., and RINGSDORF, H., 1983, *Makromol. Chem. rapid Commun.*, **4**, 807; (b) WERTH, M., VALLERIE, S. H., and SPIESS, H. W., 1991, *Liq. Cryst.*, **10**, 759; (c) HENDERSON, P., RINGSDORF, H., and SCHUHMACHER, P., 1995, *Liq. Cryst.*, **18**, 191; (d) KUMAR, S., and MANICKAM, M., 1997, *Chem. Commun.*, 1615; (e) KUMAR, S., and MANICKAM, M., 1998, *Synthesis*, 1119.
- [17] (a) QUEGUINER, A., ZANN, A., DUBOIS, J. C., and BILLARD, J., 1980, in Proceedings of the International Conference on Liquid Crystals, Bangalore, edited by S. Chandrasekhar (London: Heyden), p. 35; (b) BILLARD, J., DUBOIS, J. C., VAUCHER, C., and LEVELUT, A. M., 1981, *Mol. Cryst. liq. Cryst.*, **66**, 115; (c) CARFUGNA, C., ROVIELLO, A., and SIRIGU, A., 1985, *Mol. Cryst. liq. Cryst.*, **122**, 151; (d) CARFUGNA, C., IANNELLI, P., ROVIELLO, A., and SIRIGU, A., 1987, *Liq. Cryst.*, **2**, 611; (e) BILLARD, J., LUZ, Z., POUPKO, R., and ZIMMERMANN, H., 1994, *Liq. Cryst.*, **16**, 333; (f) RAJA, K. S., RAMAKRISHNAN, S., and RAGHUNATHAN, V. A., 1997, *Chem. Mater.*, **9**, 1630; (g) KRISHNAN, K., and BALAGURUSAMY, V. S. K., 2000, *Liq. Cryst.*, **27**, 991; (h) PRASAD, V., KRISHNAN, K., and BALAGURUSAMY, V. S. K., 2000, *Liq. Cryst.*, **27**, 1075; (i) KRISHNAN, K., and BALAGURUSAMY, V. S. K., 2000, *Mol. Cryst. liq. Cryst.*, **350**, 1; (j) PRASAD, V., and SHANKAR RAO, D. S., 2000, *Mol. Cryst. liq. Cryst.*, **350**, 51; (k) PRASAD, V., *Liq. Cryst.*, **28**, 647.
- [18] RAJA, K. S., RAMAKRISHNAN, S., and RAGHUNATHAN, V. A., 1998, *Macromolecules*, **31**, 3807.
- [19] CHANDRASEKHAR, S., and BALAGURUSAMY, V. S. K., 2002, *Proc. r. Soc. Lond. A*, **458**, 1783.
- [20] GRIMSHAW, J., and HAWORTH, R. D., 1956, *J. Chem. Soc.*, 4225.
- [21] (a) CROSS, S. J., GOODBY, J. W., HALL, A. W., HIRD, M., KELLY, S. M., TOYNE, K. J., and WU, C., 1998, *Liq. Cryst.*, **25**, 1; (b) KUMAR, S., MANICKAM, M., VARSHNEY, S. K., SHANKAR RAO, D. S., and PRASAD, S. K., 2000, *J. mater. Chem.*, **10**, 2483.
- [22] (a) KUMAR, S., and NAIDU, J. J. *Mol. Cryst. Liq. Cryst.* (in the press); (b) KUMAR, S., and NAIDU, J. J., 2002, *Liq. Cryst.*, **29**, 1369.
- [23] KUMAR, S., NAIDU, J. J., and VARSHNEY, S. K., 2002, presented at the 19th ILCC, Edinburgh.