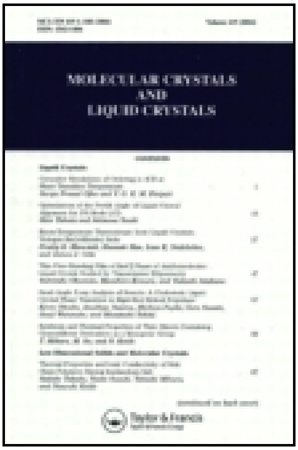


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Combination of Electron-deficient and Electron-rich Discotic Liquid Crystals in Novel Unsymmetrical Columnar Twins

Sandeep Kumar [a], Jaishri Naidu [a] & S. K. Varshney [a]

[a] Centre for Liquid Crystal Research, Bangallore, India

Version of record first published: 18 Oct 2010

To cite this article: Sandeep Kumar, Jaishri Naidu & S. K. Varshney (2004): Combination of Electron-deficient and Electron-rich Discotic Liquid Crystals in Novel Unsymmetrical Columnar Twins, Molecular Crystals and Liquid Crystals, 411:1, 355-362

To link to this article: http://dx.doi.org/10.1080/15421400490435387

Mol. Cryst. Liq. Cryst., Vol. 411, pp. 355/[1397]–362/[1404], 2004
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490435387

COMBINATION OF ELECTRON-DEFICIENT AND ELECTRON-RICH DISCOTIC LIQUID CRYSTALS IN NOVEL UNSYMMETRICAL COLUMNAR TWINS

Sandeep Kumar, Jaishri J. Naidu, and S. K. Varshney*
Centre for Liquid Crystal Research, P.O.Box 1329, Jalahalli,
Bangallore - 560 013, India

The synthesis, characterization and mesomorphic properties of a new type of discotic liquid crystalline dimer bearing an electron-rich triphenylene discotic connected to an electron-deficient anthraquinone discotic via an alkyl chain spacer are reported. This donor-sigma-acceptor type molecule displays a columnar mesophase over a wide temperature range.

Keywords: anthraquinone; columnar phase; discotic liquid crystals; triphenylene

INTRODUCTION

The design and synthesis of novel discotic liquid crystals (DLCs) is an area of increasing current interest. DLCs are a unique state of matter possessing self-organization of disc-shaped molecules [1]. These supramolecular assemblies are of fundamental importance not only as models for the study of the energy and charge migration in organized systems but also as functional materials for device applications such as, one-dimensional conductors, photoconductors, light emitting diodes, photovoltaic solar cells, gas sensors, etc [2–8].

As in traditional inorganic semiconductors, organic DLCs can function either as P-type or n-type. The most widely synthesized and studied discotic liquid crystals are electron-rich π-conjugated materials and are better hole carrier (p-type semiconductors) [9]. Recently a few examples of electron-deficient (n-type) DLCs such as bis(dithiolene)nickel complex,

We are very grateful to Professor S. Chandrasekhar for many helpful discussions. Partial financial support from Ministry of Information Technology, Government of India to Dr. S. Kumar to attend the conference and a SRF to J. J. Naidu by CSIR, New Delhi is gratefully acknowledged.

*Corresponding author. Current address: Raman Research Institute, C. V. Raman Avenue, Bangalore-560 080; E-mail: skumar@rri.res.in perylene, tricycloquinazoline, hexaazotriphenylene, anthraquinone, etc., are reported in the literature [9,10].

It is well known that connecting two discotic molecules together via a spacer (discotic dimers) stabilizes the columnar mesophase significantly and often leads to the formation of glassy materials. They can be considered as a prepolymer and are well suited for model studies due to their ease of purification and characterization. Discotic twins based on benzene core was first reported by Lillya [11]. Recently, several other dimers based on various discotic cores are appeared in the literature [12]. Hexasubstituted triphenylenes are among the most widely synthesized and studied discotic liquid crystals and many examples of both symmetrical and unsymmetrical twins based on triphenylenes are known [12,13]. Such electron-rich DLCs when doped with electron acceptor like trinitrofluorenone (TNF), formation of charge-transfer (C-T) complex has been found. C-T interaction has a profound effect on the induction and stabilization mesophases [14]. An interesting example is the creation of a columnar nematic and columnar hexagonal phase by mixing non-liquid crystalline multiynes with TNF [14,15]. Computer simulation studies by Bates and Luckhurst indicate that the quadrupolar interaction may be responsible to form such chemically induced liquid crystalline phases [16]. Recently, several examples of dimers were reported in which an electron acceptor like TNF or anthraquinone was co-valently connected to the electron-rich donar [17]. In all the reported examples the electron-deficient moiety has been limited to the non-liquid crystalline molecules. To the best of our knowledge, a donar-acceptor dimer in which both the components are discotic liquid crystalline has so far not been prepared. In this paper, we present the synthesis and characterization of the first example of a discotic twin in which an electron-rich triphenylene based DLC is connected to an electron-deficient anthraquinone DLC via an alkyl chain spacer.

EXPERIMENTAL

The monohydroxytriphenylene **1** and monohydroxyanthraquinone **3** were prepared as reported [18,19]. A mixture of **1** (250 mg, 0.33 mmol), K_2CO_3 (278 mg, 2.0 mmol) and 1,12-dibromododecane (879 mg, 2.68 mmol) in dry methylethylketone (15 ml) was heated at 100°C for 15 h under anhydrous reaction condition. Usual work-up followed by column chromatographic purification afforded the compound 2 in 60% yield.

^{1}H NMR (200 MHz, $CDCL_3$): δ 7.84(s, 6H), 4.23 (t, 12H), 3.40 (t, 2H), 2.0–1.2(m, 60H), 0.93 (t, 15H).

The dimer **4** was prepared by heating a mixture of 2 (82 mg, 0.083 mmol), K_2CO_3 (20 mg, 0.14 mmol) and monohydroxyanthraquinone

3 (50 mg, 0.07 mmol) in dry DMF at 100°C for 24 h. Usual work-up followed by the purification of the crude product by column chromatography over silica gel furnished the dimer **4** in 48% yield.

Mass (FAB): m/z 1334

^{1}H NMR (200 MHz, $CDCL_3$): δ 7.84(s, 6H), 7.59 (s, 2H), 4.15 (m, 20H), 1.9–1.2 (m, 104H), 0.92 (m, 30H).

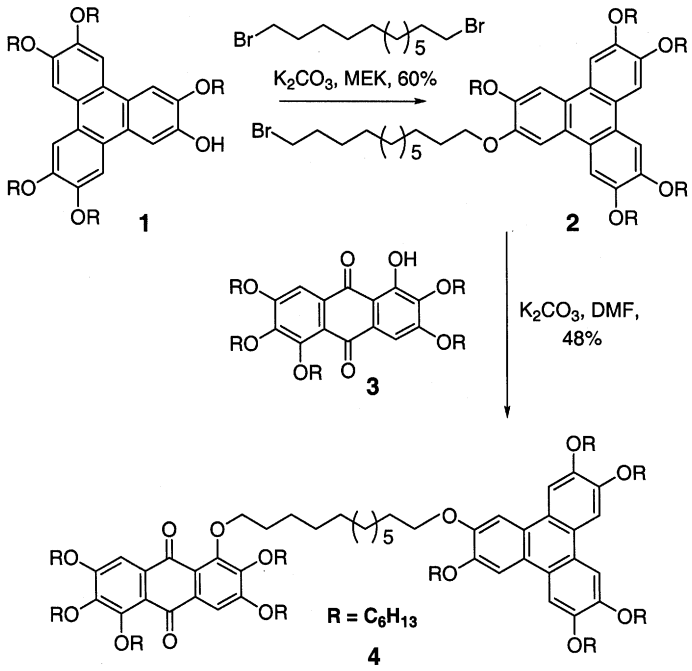
^{13}C NMR (100 MHz, $CDCL_3$): δ 181.2, 157.5, 153.9, 149.0, 146.9, 132.6, 123.6, 120.4, 107.3, 107.0, 74.7, 74.1, 69.7, 31.7, 31.5, 30.3, 29.7, 29.6, 29.0, 26.2, 26.0, 25.8, 25.7, 22.6, 14.0

UV-vis: λ_{max} (nm): 249, 258, 267, 277, 312, 318, 343

RESULTS AND DISCUSSION

Moleculer architecture of the type D-σ-A, with an electron donar D and an electron acceptor A, separated by a sigma bond is of interest since a long time. In 1974, Aviram and Ratner proposed that a single organic molecular structure of the D-σ-A, form could perform as a rectifier of electric current [20]. The mechanism has recently been verified experimently [21]. In the field of discotic liquid crystals, several triphenylene and alkynylbenzene derivatives were prepared in which a non-liquid crystalline electron-deficient molecule such as TNF or anthraquinone was attached to the donar molecule co-valently [17]. Intermolecular C-T interaction has been noticed in such systems. With the idea that combining a electron-rich DLC and a electron deficient DLC may create novel supramolecular structures, we designed a donar acceptor twin **4** bearing a discotic liquid crystalline triphenylene donar unit tethered to a discotic liquid crystalline anthraquinone acceptor unit.

The retro synthetic analysis reveals that connecting the monofunctionalized donar and acceptor parts with a difunctional spacer can easily assemble the desired dimer **4**. The monofunctionalized donar and acceptor molecules are prerequisites to prepare the dimers. While a number of sound synthetic strategies have been established to prepare electron rich monofunctionalized triphenylene derivative [18], monofunctionalized electron-deficient DLCs are not easily accessible. We prepared the monohydroxy-pentakis(hexyloxy)triphenylene as reported earlier [18]. The synthesis of monohydroxy-pentakis(hexyloxy)anthraquinone was achieved by the partial alkylation of 1,5-dihydroxy-2,3,6,7-tetrahexyloxyanthra-9,10-quinone [19]. It was purified as its acetate and the free phenol was regenerated by the hydrolysis of pure acetate. The dimer **4** was prepared in two steps (Scheme). Alkylation of monohydroxy-pentahexyloxytriphenylene 1 with excess of 1,12-dibromododecane furnished the triphenylene-dodecylbromide 2 carrying one terminal bromine substituent. The desired



SCHEME Synthesis of discotic D-σ-A dimer.

dimer **4** was prepared by reacting **2** with monohydroxyanthraquinone under classical alkylation reaction conditions. It was fully characterized from its ^{1}H NMR, ^{13}C NMR, UV-vis and Mass spectral analysis.

The thermal behaviour of the dimer **4** was investigated by polarizing optical microscopy using a Mettler FP82HT hot stage and central processor in conjunction with Leitz DMRXP polarizing microscope and by differential scanning calorimetry (DSC7 Perkin-Elmer). On first heating, **4** gives one weak broad peak, probably a glass transition, in the DSC at about 40°C and the mesophase to isotropic phase transition at 96.9°C (ΔH 8.5 Jg^{-1}). Upon cooling, the isotropic to columnar phase transition appears at 94.3°C(ΔH 7.6 Jg^{-1}). The DSC does not show any crystallization or glass transition peak down to room temperature. On subsequent heating, the DSC shows only mesophase to isotropic transition and the weak transition at 40°C was not discernible. DSC traces obtained on the heating and cooling runs are shown in Figure 1.

Microscopy with polarized light suggested that the dimer **4** form columnar mesophase. A classical texture of columnar mesophase appeared upon cooling from the isotropic liquid and remains stable down to room

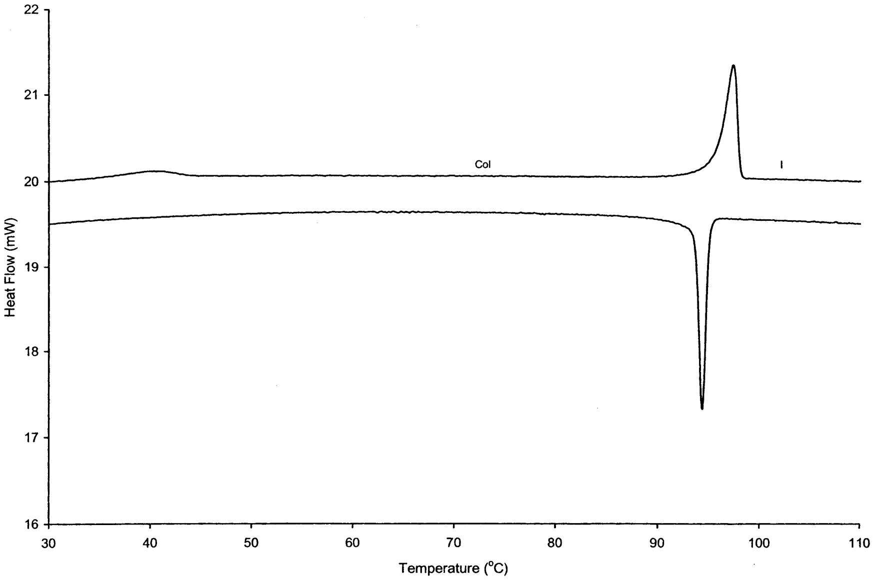


FIGURE 1 DSC traces for compound **4** on heating and cooling (scan rate 5°C min^{-1}).

temperature. The texture is very similar to the known texture for the hexagonal columnar mesophase shown by several well-characterized discotic liquid crystals. The mesophase is miscible with the $\mathrm{Col_h}$ phase of hexaalkoxy-triphenylene and anthraquinone derivatives. Photomicroscopic pictures of compound **4** obtained on cooling from the isotropic liquid at 94°C and at 25°C are shown in Figure 2.

The formation of liquid crystalline structure in a donar-acceptor molecule can arise from simple π-π interaction of the aromatic cores or from charge-transfer or complimentary polytropic interaction (CPI) between donar and acceptor units. Formation of C-T complexes by electron-rich discotic materials such as triphenyleneethers, alkynylbenzenes upon doping with non-liquid crystalline acceptor molecule like TNF is well-documented [17]. Columnar aggregates of alternating donors and acceptors in the C-T complexes may cause the stabilization as well as the induction of the liquid crystalline phases. Recently, Boden group reported that the stabilization of mesophase in binary systems could be due to CPI interaction [22]. The 1:1 mixture of several triphenylene and azatriphenylenes give columnar mesophases having much higher clearing temperature [22].

In order to understand how the molecules of **4** are stacked within the superstructure, we looked at the UV-Vis and thermal behaviour of the

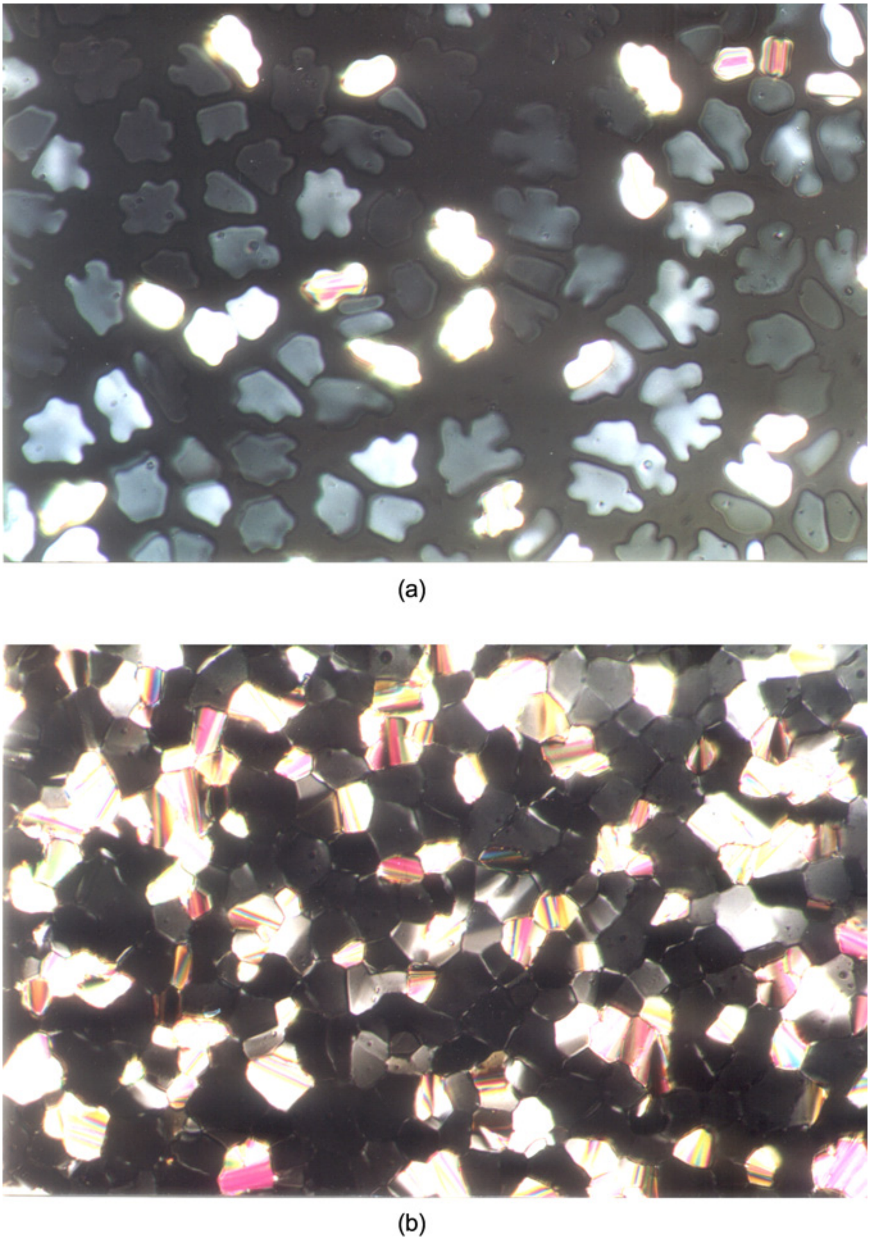


FIGURE 2 (a) Optical texture of **4** obtained on cooling from the isotropic liquid at 94°C (b) Optical texture of **4** obtained on cooling from the isotropic liquid at 25°C (crossed polarizer, magnification X200). (See COLOR PLATE X)

dimer **4**, monomers *i.e.* hexahexyloxytriphenylene and hexahexyloxyanthraquinone and their 1:1 mixture. The UV spectrum of the dimer **4** or of the (1:1) mixture of donor and acceptor component does not show any additional absorption band as compared to the separate donor and acceptor. It is essentially a sum of the donor and acceptor units. The colour of the dimer **4** as well that of the (1:1) mixture is almost matching with the colour of the acceptor. Therefore, it is unlikely that the dimer **4** forms intermolecular or intramolecular C-T complex. The thermal behaviour of the dimer **4** (X 40°C Col 96.9°C I) is also comparable to the donor (Cr 68°C Col 99.5°C I) and acceptor (Cr 53°C Col 105°C I). As here is no significant change in the isotropic temperature, it is difficult to say that CPI plays any dominant role. It could be possible that the discotic liquid crystalline donor and acceptor subunits are segregated in different columns due to simply π-π interaction. However, further studies are needed to confirm the detailed structure.

CONCLUSIONS

We have synthesized the first example of a liquid crystalline dimer composed of a discotic liquid crystalline donor and a discotic liquid crystalline acceptor connected via an alkyl chain spacer. The D-σ-A dimer shows a columnar mesophase over a wide temperature range.

REFERENCES

[1] Chandrasekhar, S., Sadashiva, B. K., & Suresh, K. A. (1977). *Pramana.*, *9*, 471.

[2] Boden, N. & Movaghar, B. (1998). In: *Hand Book of Liquid Crystals*, Demus, D., Goodby, J., Gray, G.W., Spiess, H.-W., & Vill, V. (Eds.), Wiley-VCH, Vol. 2B, Chapter 1X.

[3] Chandrasekhar, S. (1998). In: *Hand Book of Liquid Crystals*, Demus, D., Goodby, J., Gray, G. W., Spiess, H.-W., & Vill, V. (Eds.), Wiley-VCH, Vol. 2B, Chapter VIII.

[4] Schmidt-Mende, L., Fechtenkotter, A., Mullen, K., Moons, E., Friend, R. H., & Mackenzie, J. D. (2001). *Science*, *293*, 1119.

[5] Seguy, I., Destruel, P., & Bock, H. (2000). *Synth. Met.*, *15*, 111–112.

[6] Adam, D., Schuhmacher, P., Simmerer, J., Häussling, H., Siemensmeyer, K., Etzbach, K. H., Ringsdorf, H., & Haarer, D. (1994). *Nature*, *371*, 141.

[7] Markovitsi, D., Marguet, S., Bondkowski, J., & Kumar, S. (2001). *J. Phys. Chem. B*, *105*, 1299.

[8] van de Craats, A. M. & Warman, J. M. (2001). *Adv. Mater.*, *13*, 130.

[9] Cammidge, A. N. & Bushby, R. J. (1998). In: *Hand Book of Liquid Crystals*, Demus, D., Goodby, J., Gray, G. W., Spiess, H.-W., & Vill, V. (Eds.), Wiley-VCH, Vol. 2B, Chapter VII.

[10] Ohta, K., Hasebe, H., Ema, H., Moriya, M., Fujimoto, T., & Yamamoto, I. (1991). *Mol. Cryst. Liq. Cryst.*, *208*, 21. Wurthner, F., Thalacker, C., Diele, S., & Tschierske, C. (2001). *Chem. Eur. J.*, *7*, 2245. Pieterse, K., van Hal, P. A., Kleppinger, R., Vekemans, J. A. J. M., Janssen, R. A. J., & Meijer, E. W. (2001). *Chem. Mater.*, *13*, 2675. Kumar, S., Shankar Rao, D. S., & Krishna Prasad, S. (1999). *J. Mater Chem.*, *9*, 2751.

[11] Lillya, C. P. & Murthy, Y. L. N. (1985). *Mol. Cryst. Liq. Cryst.*, *2*, 121.

[12] Kumar, S., Manickam, M., & Schonherr, H. (1999). *Liq. Cryst.*, *26*, 1567 and their references their in.

[13] Boden, N., Bushby, R. J., Cammidge, A. N., El-Mansoury, A., Martin, P. S., & Lu, Z. (1999). *J. Mater. Chem.*, *9*, 1391 and references their in.

[14] Praefcke, K. & Singer, D. (1998). In: *Hand Book of Liquid Crystals*, Demus, D., Goodby, J., Gray, G. W., Spiess H.-W. & Vill, V. (Eds.), Wiley-VCH, Vol. 2B, Chapter XVI.

[15] Praefcke, K., Singer, D., Kohne, B., Ebert, M., Liebmann, A., & Wendorf, J. H. (1991). *Liq. Cryst.*, *10*, 147.

[16] Bates, M. A. & Luckhurst, G. R. (1998). *Liq. Cryst.*, *24*, 229.

[17] Moller, M., Tsukruk, V., Wendorff, J. H., Bengs, H. & Ringsdorf, H. (1992). *Liq. Cryst.*, *12*, 17. Mahlstedt, S., Janietz, D., Stracke, A., & Wendorff, J. H. (2000). *Chem. Commun.*, 15. Schultz, A., laschat, S., Abbott, A. P., Langner, M., & Reeve, T. B. (2000). *J. Chem. Soc. Perkin, 1*, 3356. Cooke, G., Kaushal, N., Boden, N., Bushby, R. J., Lu, Z., & Lozman, O. (2000). *Tet. Lett.*, *41*, 7955.

[18] Kumar, S. & Manickam, M. (1998). *Synthesis*, 1119.

[19] Kumar, S. & Naidu, J. J. (2002). *Mol. Crys. Liq. Cryst.*, *378*, 123.

[20] Aviram, A & Ratner, M. A. (1974). *Chem. Phys. Lett.*, *29*, 277.

[21] Metzger, R. M., Chen, B., Hopfner, U., Lakshmikantham, M. V., Vuillaume, D., Kawai, T., Wu, X., Tachibana, H., Hughes, T. V., Sakurai, H., Baldwin, J. W., Hosch, C., Cava, M. P, Brehmer, L., & Ashwell, G. J. (1997). *J. Am. Chem. Soc.*, *119*, 10455.

[22] Boden, N., Bushby, R. J., Cooke, G., Lozman, O. R., & Lu, Z. (2001). *J. Am. Chem. Soc.*, *123*, 7915.