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Design and Synthesis of Discotic Nematic Liquid Crystals

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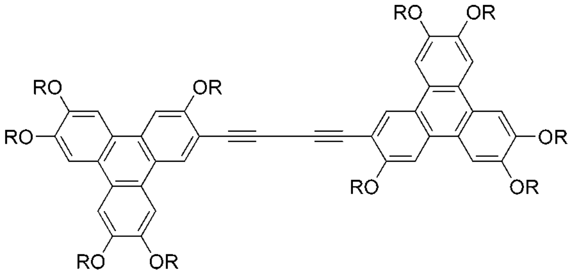
ABSTRACT



A new principle for the design of discotic nematic liquid crystals is presented. The first examples of compounds which contain two triphenylene discotic mesogens connected via a rigid π-conjugated diacetylene spacer are reported. These discotic twins form a discotic nematic mesophase over a wide temperature range.

Liquid crystals formed by disc-shaped molecules[1] are attracting much attention due to their remarkable electrooptical properties. For the last few years considerable effort has been underway to design, synthesize, and characterize various discotic liquid crystals.[2] Mesophases formed by disc-shaped molecules are primarily of two types: nematic and columnar. A few discotic molecules are also reported to form a discotic lamellar mesophase, but the structural arrangement in this phase is not yet completely elucidated.[3,4]

Discotic liquid crystals have very high charge carrier mobility in columnar mesophases, which offers potential applications as organic charge transport materials in a variety of devices such as one-dimensional conductors, photoconductors, field effect transistors, photovoltaic solar cells, etc.[5−8] Further, nematic discotic liquid crystals have recently been reported to be useful for wide viewing angle LCDs.[9,10]

Liquid crystal displays consist of two glass plates that sandwich a thin liquid crystal layer. The twisted nematic and supertwisted nematic display devices have dominated commercial displays since their invention. The liquid crystal layer in these devices is exclusively the calamitic liquid crystals (composed of rod-shaped molecules). The major disadvantage with these types of devices is the narrow and nonuniform

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viewing cone. The growing emphasis toward higher quality wide viewing angle LCDs has fostered numerous development efforts such as the multidomain technique,[11] the introduction of an optical compensator to reduce the amount of light leakage in the dark state,[12] the application of an electric field parallel to the plane of the substrates,[13] the so-called "amorphous" twisted nematic liquid crystals,[14] etc. The negative birefringence film formed by polymerized nematic discotic LCs can also be used as compensation foils to enlarge the viewing angle of twisted nematic LCDs.[15] The viewing angle of LCDs for gray scale and color has significantly improved over the last few years due to these recent developments. However, some additional complex processes must be used. We have recently disclosed a novel approach to overcome this problem by utilizing discotic nematic liquid crystals instead of calamitic nematic liquid crystals.[9,10]

Compared to the large number of calamitic molecules with a nematic phase, the number of disc-shaped molecules with a discotic nematic phase (N_D) is low. Only a few derivatives of triphenylene,[16,17] truxene,[18] thiotruxene,[19] naphthalene,[20] alkynylbenzenes,[17,21] etc., are known to show a stable N_D phase. In the discotic nematic phase, there is an orientationally ordered arrangement of discs with no long-range translational order (Figure 1a). However, unlike the usual calamitic nematic phase, N_D is optically negative. On the other hand, in the columnar phase, the discs are stacked one on top of another to form columns (Figure 1b). A majority of discotic liquid crystals form columnar mesophases probably due to intense $\pi-\pi$ interactions of polyaromatic cores. While it is often easy to design discotic LCs forming columnar phases with basic structural features, flat or nearly flat aromatic cores surrounded by plural flexible side chains, it is rather difficult to design molecules which may form the N_D phase. This could be a reason why only a comparatively small number of nematic discotic liquid crystals are known so far.

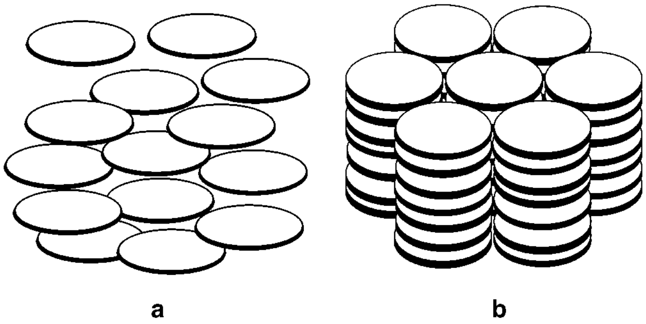

Figure 1. Schematic representation of the (a) discotic nematic and (b) columnar phase.

We anticipated that linking two discotic molecules via a short rigid spacer may experience some steric hindrance due to overlapping or interdigitating aliphatic side chains and a weak distortion of the planarity of the core. This may reduce the strong $\pi-\pi$ interactions. The rigid molecules may stay in more or less a parallel position having orientational order but losing their long-range translational order and, therefore, are likely to form a discotic nematic phase (Figure 2). It should be noted that discotic twins linked via a long flexible alkyl chain spacer are well-known to form a columnar phase.[22] This is because the molecules have sufficient flexibility to stack in adjacent columns. To date, no effort has been made to link two discotics with a short rigid spacer. Novel rigid covalently attached conjugated dimeric ferroelectric smectic liquid crystalline systems with negative birefringence have recently been reported by Walba and coworkers.[23]

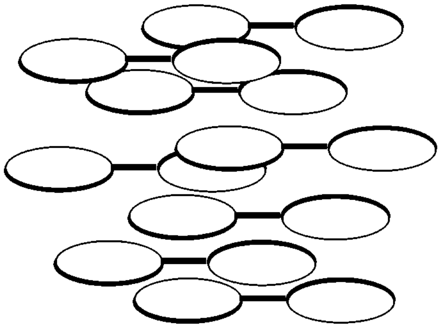

Figure 2. Schematic representation of the nematic phase formed by rigid discotic twins.

To pursue our idea, we connected two well-known alkoxytriphenylene molecules via a π-conjugated diacetylene bridge (Scheme 1). The monoacetylenes **2** were prepared starting from hexaalkoxytriphenylene (HAT) in five steps.

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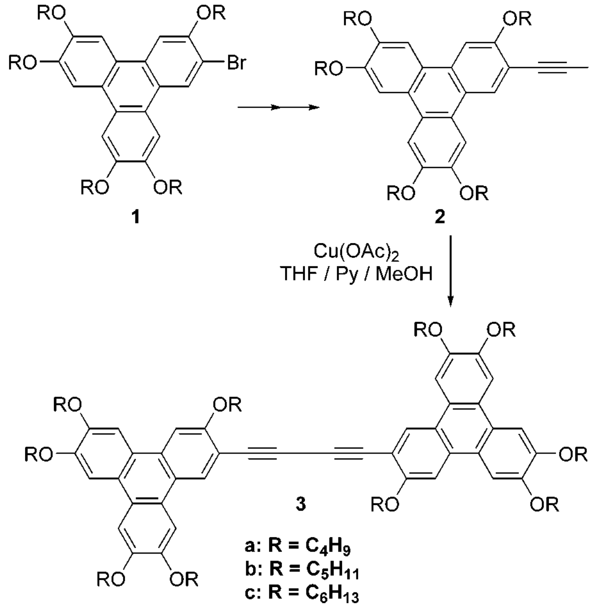
Scheme 1. Synthesis of Dimers **3a−c**



A selective cleavage of one of the six alkoxy chains of HAT yielded monohydroxypentaalkoxytriphenylene.[24] The key precursor monobromopentaalkoxytriphenylene **1** can be prepared in two different ways: (1) from monohydroxypentaalkoxytriphenylene via the reduction of the phenolic group by activation with a tetrazole unit followed by catalytic hydrogenation[24] or (2) via the biphenyl route using the oxidative coupling of a tetraalkoxybiphenyl with alkoxybromobenzene.[24,25] Palladium−copper catalyzed alkynylation of monobromopentaalkoxytriphenylene with 2-methyl-3-butyn-2-ol followed by hydrolysis yields acetylene **2** in high yields. These monoacetylenes **2** were dimerized using standard reaction conditions.[26] Final compounds **3a−c** were purified by repeated column chromatography and characterized using ^{1}H NMR, ^{13}C NMR, mass, IR, and elemental analysis.[27]The thermal behavior of all compounds was investigated by polarizing optical microscopy and differential scanning calorimetry (Perkin-Elmer DSC7) with heating and cooling rates of 5° min^{-1}. Data from heating and cooling cycles are collected in Table 1. The peak temperatures are given in °C and the numbers in parentheses indicate the transition enthalpy (ΔH).

Table 1. Phase Transition Temperatures (°C) and Enthalpies (kJ mol^{-1}, in Parentheses) of Dimers **3a−c**. Cr = Crystal, N_D = Nematic Discotic Liquid Crystalline Phase, I = Isotropic

3	heating scan	cooling scan
3a	Cr 188.6 (18.7) N_D 243.5 (1.1) I	I 238.8 (0.8) N_D 172.8 (16.0) Cr
3b	Cr 161.0 (19.1) N_D 215.9 (0.6) I	I 214.4 (0.7) N_D152.8 (19.2) Cr
3c	Cr 135.3 (22.6) N_D 172.8 (0.9) I	I 170.7 (0.8) N_D126.5 (21.8) Cr

As may be seen from the data, all three dimers **3a−c** were found to be mesogenic. They display a typical schlieren texture (Figure 3) and a high fluidity characteristic of the N_D phase. It should be noted that the monomers show only an ordered columnar mesophase.

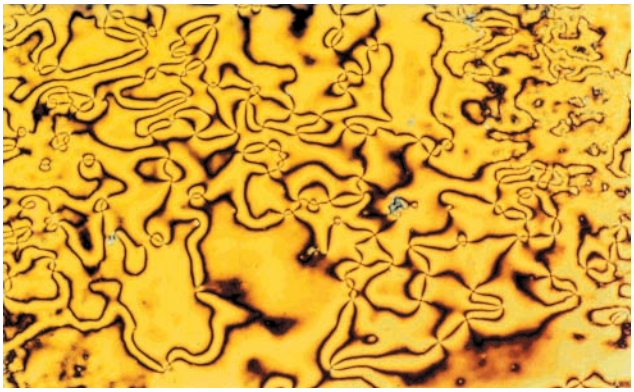


Figure 3. Optical textures of **3a**. Photomicroscopic pictures of the mesophase were obtained with a polarizing microscope (Leitz DMRXP equipped with a Mettler FP82HT hot stage) on cooling from the isotropic liquid at 190 °C (crossed polarizer, magnification X 200).

We have shown that a desired mesophase can be created by careful synthetic design. This, in conjunction with our recently reported methodology[10] for the control of the thermal behavior of the N_D phase, may lead to the design and synthesis of a variety of novel nematic discotic liquid crystals.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) Selected data for **3a**: MS (FAB); *m/z* 1223.8; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (s, 2H), 7.89 (s, 2H), 7.87 (s, 2H), 7.81 (s, 4H), 7.79 (s, 2H), 4.32 (t, 4H), 4.25 (m, 16H), 2.0 (m, 20H), 1.7−1.5 (m, 20H), 1.0 (m, 30H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.5, 150.6, 149.6, 149.0, 148.7, 131.0, 130.0, 125.6, 123.3, 123.0, 122.8, 122.7, 111.3, 108.1, 107.5, 106.8, 106.2, 104.7, 79.8, 78.3, 69.6, 69.5, 69.2, 69.0, 31.4, 29.7, 19.7, 14.0. IR (KBr, cm^{-1}): 2958, 2872, 2360, 2140, 1609, 1518, 1432, 1386, 1262, 1174, 1044. Compounds **3b** and **3c** show similar spectra, in agreement with their structure. All compounds give satisfactory elemental analysis (see Supporting Information for details).