

A columnar mesophase from a disc-shaped molecule derived from triphenylamine: synthesis, mesomorphic behaviour and optical properties[☆]

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Abstract—The design and synthesis of a disc-like liquid crystalline compound using triphenylamine as a core has been achieved. The mesogenic properties were characterized by polarizing microscopy and differential scanning calorimetry and XRD studies. The compound existed as a hexagonal columnar mesophase. The fluorescence properties revealed the presence of intermolecular excimer formation.

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Recently discotic liquid crystals have attracted considerable interest among chemists as well as physicists due to their unique structural features and unusual material characteristics.¹ The type of mesophase of thermotropic liquid crystals largely depends on the molecular shapes. The shape of the molecule plays a very important role in the self-organization of the molecules within the liquid crystalline phase² and leads to different liquid crystalline phases with long range orientational order and segregation of distinct incompatible molecular units to promote layered or columnar phases. The disc-like molecules self-organize to give columnar mesophases. Columnar liquid crystals usually comprise flat aromatic cores with flexible end alkyl chains, which give rise to hexagonal 2D periodic organization. These flat cores are capable of stacking spontaneously into individual molecular columns behaving electronically as one-dimensional molecular ‘wires’.³ These interesting structures show a number of potential applications in organic charge-transport materials in a variety of devices such as one-dimensional conductors, photo-conductors, field effect transistors and photovoltaic solar cells.⁴

Molecules derived from triphenylamine (TPA)-based compounds have been widely investigated as active materials for hole-transport and electroluminescence.⁵ The amorphous character of these materials offers possibilities to develop active materials for solar cells⁶ with isotropic optical and charge-transport properties. The use of TPA-based materials for photovoltaic conversion has been scarcely considered.⁷ They also play an important role in photorefractive (PR) materials, which have attracted much interest in recent years because of the potential applications in holographic optical data storage and real time imaging processes. Hence, we became interested in designing and synthesizing a new class of disc-like molecule with a tetrahedral or pyramidal central core which can promote electron injection and also exhibit liquid crystalline behaviour.

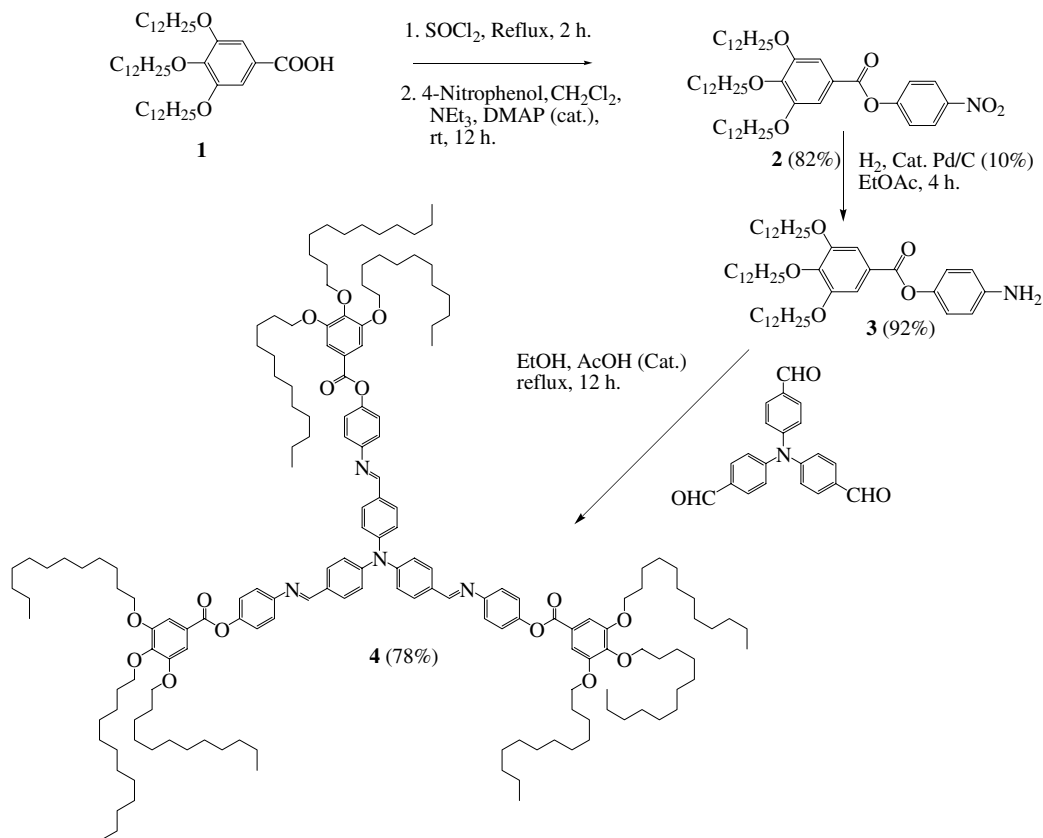
To the best of our knowledge there is only one very recent report⁸ of triphenylamine-containing discotic liquid crystals. In this Letter, we report a novel disc-like compound possessing triphenylamine at the core.

The methodology for the synthesis of the disc-type material **4** is depicted in Scheme 1. The final compound was easily obtained by Schiff’s base formation between the aniline **3** and triphenylaminetri-aldehyde in ethanol in the presence of a catalytic amount of AcOH. The tri-aldehyde was prepared by Vilsmeier–Haack formylation⁹ in good yield. Aniline **3** was prepared from methyl gallate. Alkylation of the three hydroxyl groups

Keywords: Discotic liquid crystal; Hexagonal columnar mesophase; Triphenylamine derivative; Intermolecular excimer.

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Scheme 1.

using dodecyl bromide was performed in acetone–potassium carbonate under reflux for 72 h. The ester group was then hydrolyzed and the resulting 3,4,5-tridodecyloxybenzoic acid was esterified with *p*-nitrophenol in the presence of triethylamine and DMAP (cat.). The nitro group was reduced by $\text{H}_2/\text{Pd-C}$ in ethyl acetate to give the desired aniline **3**. Compound **4** was purified by repeated precipitation from benzene with ethanol and was characterized¹⁰ by ^1H NMR, IR and MALDI-TOF mass spectra. In the MALDI-TOF mass spectrum, the peak at 2572.91 clearly indicated the formation of the desired compound. Also in its ^1H NMR spectrum, a three-proton singlet at δ 8.07 indicated the formation of the symmetrical Schiff's base compound **4**. In the IR spectrum, a peak at 1623 cm^{-1} supported formation of the Schiff's base.

Compound **4** exists as a soft wax-type solid at room temperature. The sample did not crystallize even after several weeks at room temperature. It transforms into an isotropic phase at $83.1\text{ }^\circ\text{C}$ during the heating cycle. However, on cooling the sample, sandwiched between a glass slide and a cover slip, it exhibits a fan-shaped texture, Figure 1b. This indicates that the orientational director of the pyramidal-like molecular discs, that is the column axis is not exactly perpendicular to the substrate surface. Further, in compounds with long alkyl chains, the molecules preferably orient homeotropically which is not occurring here. In addition, when a polyimide-coated thin cell with a cell gap of $d = 5 \pm 0.2\text{ }\mu\text{m}$ was

filled with **4**, a typical spherulitic texture was exhibited, Figure 1a, characterizing the phase as a columnar phase. The liquid crystal isotropic phase transition temperatures are $83.1\text{ }^\circ\text{C}$ [$\Delta H = 2.01\text{ kJ/mol}$; $\Delta S = 5.64\text{ J/mol/K}$; scan rate = $10\text{ }^\circ\text{C/min}$] and $77.3\text{ }^\circ\text{C}$ [$\Delta H = 2.13\text{ kJ/mol}$; $\Delta S = 6.10\text{ J/mol/K}$] in the heating and cooling cycles, respectively. The hysteresis in the transition temperature is due to the fast heating rate, when heating was carried out at $2\text{ }^\circ\text{C/min}$ the hysteresis drastically reduced to less than $1\text{ }^\circ\text{C}$. Compound **4** is highly stable and the differential scanning calorimetry spectrum exhibited excellent reproducibility in the mesophase-isotropic transition and associated thermodynamic parameters even after repeated heating and cooling cycles.



Figure 1a. Optical textures of compound **4** at $68.6\text{ }^\circ\text{C}$, in a polyimide-coated thin-cell with a cell gap of $d = 5 \pm 0.2\text{ }\mu\text{m}$ with homogeneous planar boundary conditions.

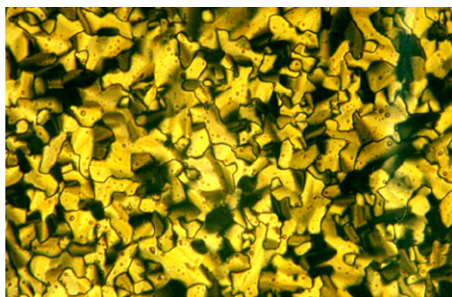


Figure 1b. Optical textures of compound **4** on a glass plate covered with a cover slip at 70.2 °C (cooling).

The X-ray diffractogram of compound **4** in the liquid crystalline phase recorded at 79 °C is shown in Figure 2. The diffractogram displayed the diffraction pattern of a two-dimensional hexagonal lattice with one intense peak and two weaker peaks. Another diffuse peak was observed at $\theta = 9.72$ for the liquid-like order of the aliphatic alkoxy chains. The calculated intermolecular distance from the XRD data is 46.378 Å. These data were also quite consistent with the relatively small transition enthalpy of the columnar to isotropic phase as obtained by DSC analysis. The disc-like molecular structure must lead to preferable formation of columnar phases rather than the layered structure or interdigitated nematic molecular arrangements. The diffractogram complements the thermal microscopy results and confirms the nature of the hexagonal columnar phase.

The optical properties of compound **4** in solution were studied in various solvents of different concentrations to obtain information regarding absorption and emission maxima, and the Stokes shift of fluorescence. Two peaks at 393 nm ($\epsilon \sim 85,000 \text{ L mol}^{-1} \text{ cm}^{-1}$) and 278 nm ($\epsilon \sim 60,000 \text{ L mol}^{-1} \text{ cm}^{-1}$) were observed in the absorption spectrum. The peak at 393 nm (3.15 eV) with large molar coefficient is due to the π - π^* transition of the highly π -conjugated system with the triphenylamine unit at the core. Further, we investigated the fluorescence spectrum to observe the excited state characteristics of the designed liquid crystalline material. Interestingly, in the less polar solvent (benzene), emissions at 325 and

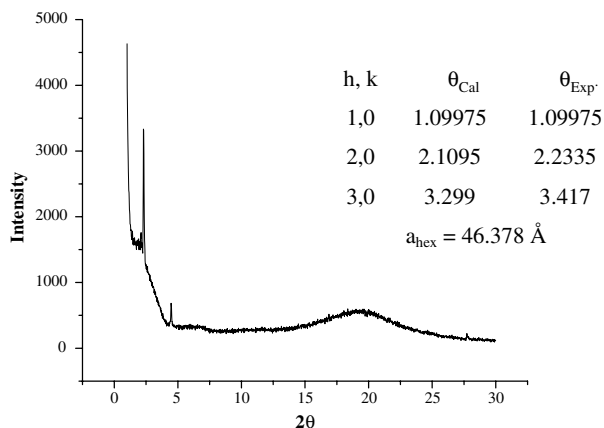


Figure 2. X-ray diffraction patterns of compound **4** ($n = 12$) at 79 °C.

436 nm (concn $4.66 \times 10^{-6} \text{ M}$) were observed on excitation at 278 nm. The emission peak at 436 nm (2.84 eV) with a Stokes shift of the order of 43 nm (0.31 eV) was attributed to the formation of an intermolecular excimer. The plot of the fluorescence spectra at different concentrations shows that the relative intensity of the peak at 336 nm gradually diminishes with dilution indicating the formation of an intermolecular excimer (Fig. 3). These results are in line with the formation of molecular *J*-aggregates¹¹ in which the excitonic energy is delocalized as a result of intermolecular coupling within the head-to-tail arrangement of the molecules in solution. We also noticed a broad peak at 442 nm upon excitation at 393 nm. The absorption spectra of the same in different solvents but at the same concentration showed no characteristic change indicating no significant ground state interaction between the peripheral trialkoxybenzene and the triphenylamine core unit. The designed discotic mesogen was also found to exhibit a solvent effect in the excited state. On gradually moving from less polar to a more polar solvent, the emission peak at 325 nm shifted to 348 nm with significant quenching in fluorescence intensity. In addition, high polar solvents facilitate excimer formation suggesting a highly ordered arrangement of the π -stacking groups of the compound in solution.

The potential application of these materials can be visualized from their ability to inject holes and electrons from the measured electrochemical properties viz., ionization potential and electron affinity, respectively. In the cyclic voltammetry (CV) experiment, Figure 4, both oxidation and reduction processes, irreversible oxidation ($E^{\text{ox}} = 0.47 \text{ V vs SCE}$) and reduction ($E^{\text{red}} = -0.23 \text{ V vs SCE}$) peaks were observed. Hence, the stability of the radical cation and anion was poor in this solution. The imine linkage in dichloromethane can be susceptible to acid and hence the poor chemical stability of the radical ions in solution is justified.

The liquid crystal behaviour can be explained as follows. The additional driving force for the self-organization in these molecules is micro-segregation of two types of

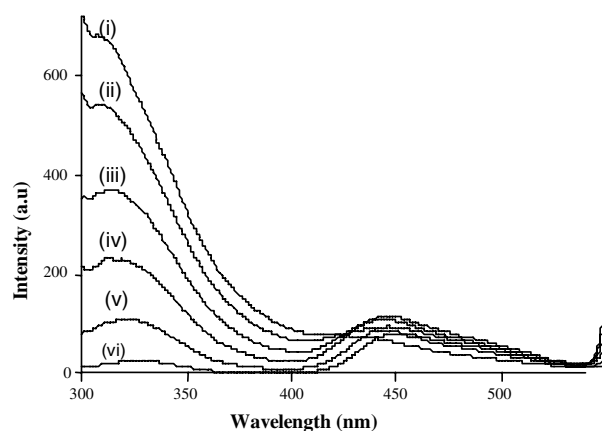


Figure 3. Concentration dependent fluorescence spectra: solvent: benzene, excitation—278 nm, concentrations: (i) $1.55 \times 10^{-6} \text{ M}$; (ii) $3.11 \times 10^{-6} \text{ M}$; (iii) $6.22 \times 10^{-6} \text{ M}$; (iv) $9.33 \times 10^{-6} \text{ M}$; (v) $1.55 \times 10^{-5} \text{ M}$; (vi) $3.11 \times 10^{-5} \text{ M}$.

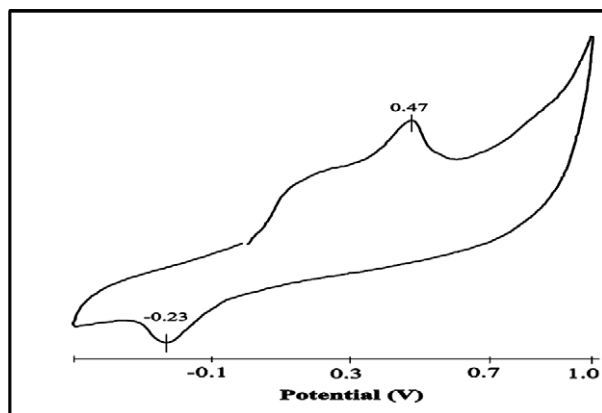


Figure 4. Cyclic voltammetry in a $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ mixture (3:1 v/v) containing NBU_4ClO_4 as a supporting electrolyte with a platinum electrode (scan rate: 50 mV/s).

regions, viz., the promesogenic polar ester of 4-(3',4',5'-trioxy-benzoyloxy-*N*-phenyl benzylidene) and the non-polar hydrophobic terminal alkyl chain. The polar 4-benzoyloxy-*N*-(phenylbenzylidene) (consisting of the carboxy and imine groups, the aromatic rings and the ether oxygen) molecules accumulate to form a distinct polar-region in the centre of the molecules. In the self-assembly, the polar and non-polar regions can segregate into separate micro-domains to promote the arrangement of individual molecules into columns with a polar column assembled in the centre. Each molecule is surrounded by nine hydrophobic dodecyl alkyl groups which are large enough to efficiently assemble to surround the polar-regions and thus allow separation of the polar and non-polar regions.

In conclusion, we have succeeded in the design, synthesis and mesophase characterisation of a new class of disc-like mesogen derived from triphenylamine containing a permanent dipole. To our knowledge this is only the second example⁸ of a discotic liquid crystalline material containing triphenylamine. We are currently investigating the liquid crystalline behaviour of this new class of organic mesogen and a full account of this will be communicated later.

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- Compound 4**: IR (KBr): 1185, 1623($\nu_{\text{C=N}}$), 1732($\nu_{\text{C=O}}$), 2923(ν_{CH}) cm^{-1} ; ^1H NMR (C_6D_6 , 400 MHz): δ 8.07 (s, 3H) 7.83 (s, 6H) 7.77 (d, $J=8.3$ Hz, 6H) 7.24 (d, $J=8.5$ Hz, 6H) 7.18 (d, $J=8.5$ Hz, 6H) 7.03(d, $J=8.3$ Hz, 6H) 4.27 (t, $J=6.2$ Hz, 6H) 3.75 (t, $J=5.9$ Hz, 12H) 1.9–0.9 (m, 207H). ^{13}C NMR (C_6D_6 , 100 MHz): 165.33, 159.04, 153.82, 150.40, 149.88, 149.56, 143.91, 132.55, 130.58, 128.66, 124.67, 124.60, 123.04, 122.33, 109.13, 73.61, 69.18, 32.36, 31.03, 30.28, 30.25, 30.20, 30.16, 30.12, 29.86, 29.76, 26.67, 26.49, 23.14, 14.39. MALDI-TOF/mass spectra: 2572.91.
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