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A new strategy towards the synthesis of a room-temperature discotic nematic liquid crystal by employing triphenylene and pentaalkynylbenzene units

Monika Gupta,<sup>a</sup> Santosh Prasad Gupta,<sup>a</sup> M. V. Rasna,<sup>b</sup> Debashis Adhikari,<sup>a</sup> Surajit Dhara<sup>b</sup> and Santanu Kumar Pal<sup>\*a</sup>

A new approach is reported for the design of a room-temperature discotic nematic ( $N_D$ ) liquid crystal (LC) dimer consisting of a triphenylene and a pentaalkynylbenzene unit linked *via* flexible alkyl spacers. The formation of  $N_D$  phase is realized most likely through folding of the dimeric molecule that prevent stacking between the triphenylene units, as suggested by modelling the mesophase derived from X-ray scattering results and high-level DFT calculations.

Disc shaped molecules showing nematic phase (N<sub>D</sub>) are rare but of utmost importance in many display device applications. They have garnered particular interest owing to their commercialization as optical compensation films to enhance the viewing angle of commonly used LC display based on polymerized nematic discogens.1 Unfortunately, most of the discotic nematogens reported so far exhibit  $N_D$  behaviour at high temperature and over a narrow temperature range.<sup>2</sup> In contrary, implementation of nematic discogens in devices necessitates N<sub>D</sub> phase at room temperature. A thorough literature survey reveals that hexa- and pentaalkynylbenzene derivatives have been the most investigated system among various discotic nematogens.<sup>2</sup> N<sub>D</sub> mesophase has also been observed for star-shaped 1,3,5-trisalkynylbenzene and triphenylene units linked through a short rigid  $\pi$ -conjugated diacetylene spacer as well as thiophene units.<sup>3-5</sup> Hydrogen bonding between phenol and pyridine moieties as well as between phloroglucinol and alkoxystillbazole moieties has also led to fabrication of N<sub>D</sub> phase.<sup>6</sup> However, till date, only a few approaches have been reported for the formation of room-temperature  $N_D$ phase. For instance, Kumar et al. reported first example of roomtemperature N<sub>D</sub> mesogen by using pentaalkynyl benzene derivative with branched alkyl spacers.<sup>7</sup> The room-temperature  $N_D$  phase has also been observed for the discotic triphenylene core possessing poly(ethylene oxide) side chains.<sup>8</sup> Lee & co-workers developed a

strategy to achieve room-temperature nematic discogens by perturbing lateral sidearm of pentaalkynylbenzene with a substitution ortho to the ethynyl group on peripheral phenyl ring.<sup>9</sup> They also established further that room-temperature N<sub>D</sub> phase can be obtained by introducing an attraction-enhancing unit in the lateral side arm of hexa(phenylethynyl)benzene.<sup>10</sup>

In this communication, we report a new design for the realization of room-temperature discotic N<sub>D</sub> dyad consisting of a triphenylene & pentaalkynylbenzene unit linked via flexible alkyl spacers. The earlier examples of symmetric dimers based on pentaalkynylbenzene show N<sub>D</sub> phase at higher temperature.<sup>11</sup> We believe that incompatibility of the two discs in the folded mesogen leads to improper packing resulting into the formation of a roomtemperature N<sub>D</sub> phase which persists over a wide range. Earlier we demonstrated that linking a pentaalkynylbenzene unit with a triphenylene core through flexible alkyl spacer containing a short rigid ester group in centre leads to columnar mesophase at ambient temperature.<sup>12</sup> In contrast, further increasing the flexibility of spacer, i.e., by introducing only alkyl chains leads to the desired mesophase.

The target compounds (7a-d) were synthesized by the route as depicted in scheme 1. The synthesis of intermediate compounds 2, 3, 5 and 6 has been discussed elsewhere.<sup>13</sup> Compounds 7a-d were prepared by reacting the pentayne 3 and monohydroxy triphenylene 6 in presence of cesium carbonate and potassium iodide using butanone as solvent under reflux condition (see ESI). All compounds were characterised by <sup>1</sup>H & <sup>13</sup>C NMR, IR, UV-Vis and mass (MALDI) spectrometry (ESI, Fig. S1-S9). The thermal behaviour of synthesized compounds was investigated by differential scanning calorimetry (DSC) and the mesophase behaviour was analysed by polarized optical microscopy (POM) and X-ray scattering studies.

All compounds exhibited light blue fluorescence in solution. The representative absorption spectrum obtained for **7b** showed the maxima centred at 264, 280, 338 and 416 nm with two shoulder peaks at 237 & 380 nm (ESI, Fig. S10). Emission spectra of all compounds were recorded by exciting their solutions at their absorption maxima. The spectra showed blue light emission with the maxima centred at 452 nm for all fluorophores. The

<sup>&</sup>lt;sup>a.</sup>Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Mohali, Sector-81, Knowledge City, Manauli-140306, India. Email: skpal@iisermohali.ac.in

<sup>&</sup>lt;sup>b.</sup> School of Physics, University of Hyderabad, Hyderabad-500046, India

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representative emission spectrum for compound **7b** is also shown in Fig. S10, ESI.

Compounds **7a** and **7d** were found to be non-liquid crystalline. Compound **7b** was solid at room temperature and displayed a melting transition (centred at 39.93 °C) to the mesophase with a heat of transition ( $\Delta H$ ) of 1.57 kJ mol<sup>-1</sup>. On further heating, mesophase was cleared at 57.48 °C ( $\Delta H$  = 0.48 kJ mol<sup>-1</sup>). On the other hand, cooling scan showed the appearance of a well-defined schlieren texture (ESI, Fig. S11) at 55 °C that remained stable down to room temperature (even upto -19.4 °C). Compound **7c** was liquid crystalline at room temperature and exhibited isotropization at 50 °C ( $\Delta H$  = 0.30 kJ mol<sup>-1</sup>). On further cooling, mesophase emerged at 46.83 °C ( $\Delta H$  = 0.29 kJ mol<sup>-1</sup>) which was stable upto -22.36 °C. The DSC traces obtained from heating and cooling runs with **7c** are shown in Fig. 1a. Gratifyingly, the photomicrograph of compound **7c** at 40 °C (Fig. 1b) obtained during cooling from the isotropic liquid clearly displays a signature of N<sub>D</sub> phase.

To investigate the detailed structure of the N<sub>D</sub> phase, X-ray diffraction experiments were performed. Diffractograms of mesophases of both **7b** and **7c** (Fig. 2 & Fig. S12) displayed a sharp small angle peak corresponding to the presence of local columnar-like orientational alterations within the nematic phase, and a broad peak at wide angle which is ascribed to liquid like order of alkyl chains. This pattern conclusively affirms the presence of a N<sub>D</sub> phase.<sup>14</sup> In addition, one broad peak in the mid-angle range was also observed which was further confirmed by full q range fitting of diffraction pattern with Lorentzian profiles.

The calculated d- spacing of 19.81 Å for the signal in the small angle for **7b** (Fig. 2a) represents the average inter-disc distance

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Scheme 1 Synthesis of the target compounds 7. Reagents and Conditions: (i) Dibromoalkane, K<sub>2</sub>CO<sub>3</sub>, KI, butanone, 80 °C, 18 h, 89%; (ii) Pd(Ph<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, 4-pentylphenylacetylene, PPh<sub>3</sub>, Cul, Et<sub>3</sub>N,100 °C, 15h, 82%; (iii)FeCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, RT, 1 h, 70%; (iv) Cat-B-Br, CH<sub>2</sub>Cl<sub>2</sub>, RT, 48 h, 40%; (v) Cs<sub>2</sub>CO<sub>3</sub>, KI, butanone, 80 °C, 18 h, 85%.



**Fig. 1** (a) DSC trace of compound **7c** on heating and cooling (scan rate 5  $^{\circ}$ C min<sup>-1</sup>). (b) Polarizing optical photomicrograph of compounds **7c** at 40  $^{\circ}$ C (on cooling, crossed polarizers).

(side by side separation) along the disc plane and approximates the diameter of the composite disc unit, ~19 Å. The spacing from the wide angle peak is calculated to be 4.68 Å which mainly originates from the liquid-like correlation of the molten chains. The reflection in the mid-angle region corresponds to a distance of 8.78 Å which is attributable to the weak correlation of dyad along the normal to the disc plane (face to face correlation) and corresponds to the effective thickness of the folded dimer. This thickness, ~8 Å is a result of folding of the dyad which was further supported by DFT calculations (*vide infra*). The diffraction pattern for the nematic phases of compound **7c** is very similar to **7b** and provides very similar conclusions (Fig. 2b).

The correlation length, the degree of order within the mesophases, was calculated using the formula  $\xi = [k2\pi]/[(\Delta q)]$ which is equivalent to Scherrer's equation,  $\xi = [k \lambda]/[(\Delta 2\theta) \cos \theta]$ . In the above formula, k is the shape factor whose typical value is 0.89,  $\lambda$  is the wavelength of the incident X-ray,  $\Delta 2\theta$  is the broadening in 20 at half of the maximum intensity (FWHM) in radian unit,  $\theta$  is the maximum of the reflection, q is the scattering vector (q=  $4\pi Sin\theta/\lambda$ ) and the  $\Delta q$  is broadening in q at half of the maximum intensity. The  $\Delta q$  is obtained by Lorentzian fitting of the diffraction pattern. For compound **7b**, the correlation lengths for the reflections 19.81, 8.78 and 4.68 Å are calculated to be 43.05, 9.48 and 8.66 Å respectively (Table 1). For compound 7c the respective correlation lengths have been increased and this is more prominent for the reflection in the small angle region (Table 1). For direct comparison, the correlation length was divided by d-spacing, which results in a measure for the spatial order in terms of dimensions of the molecular length scale. Fig. 2c displays the azimuthal plot for small and wide angle peaks of compounds 7b and 7c. Azimuthal intensity variations in small and and wide angles are in opposite phase which reflects that the growth of the side by side correlation of the composite disc and chain-chain correlation are in orthogonal plane. Since the intensity variation is broad in nature which further resonates that the structure is locally planar.

To investigate the folding behavior of two discs in **7b**, we carried out a high-level DFT analysis. The computational analysis on a slightly truncated model (see ESI for coordinates) reveals that the folded form of the molecule is electronically stable by 22.6 kcal mol<sup>-1</sup> (B3LYP-D3/6-311G\*\*) over its unfolded, linear congener.<sup>15</sup> Considering the entropic penalty associated with the folding event, free energy difference ( $\Delta G$ ) was calculated to be 14.7 kcal mol<sup>-1</sup> in favor of the folded state. As can be observed from Fig. 3, one of the phenyl group of the phenyl acetylenes is nicely engaged in  $\pi$ - $\pi$  interaction with the triphenylene unit, keeping the interacting C...C distances within 3.5-3.7 Å. To ensure further that the stabilization for folded state is not much biased by the choice of the level of

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**Fig. 2** X-ray diffraction patterns of compound (a) **7b** and (b) **7c** (half filled diamond in dark cyan colour) along with the Lorentzian fittings). Black, red and blue colour is the Lorentzian profiles corresponding to small, mid and wide angle peak, respectively. Purple colour is the sum of all these Lorentzian profiles and fits to the full q range profile of the data. (c) Azimuthal plot for small and wide angle peak of the compound **7b** (blue & dark yellow) and **7c** (red & purple) respectively.

theory, we recalculated the electronic energy difference in M06-D3/6-311G\*\*.<sup>16</sup> The difference came out to be 29.4 kcal mol<sup>-1</sup> in favor of folded State, unambiguously confirming that the optimized folded state is significantly stable over the linear geometries and such a large difference further indicates that the molecule may remain preferentially folded even in neat condition. Most notably, this folded behavior of **7b** is also consistent with our X-ray analysis.

To investigate the physical properties of the room temperature N<sub>D</sub> LCs, dielectric constant and birefringence were measured as a function of voltage and temperature (details of the cell preparation for these measurements are given in the ESI). The dielectric constant of samples was measured as a function of voltage at a fixed frequency of 1 KHz (Fig. 4a). The dielectric constant increases beyond the Freedericksz' threshold voltage and tend to saturate at higher voltages. In particular, for sample 7b and 7c the threshold voltages are 9.5 V and 11.8 V, respectively. The director is homeotropic below the Freedericksz threshold voltage and becomes planar at much higher voltage. This voltage-scan enables us to measure the effective dielectric anisotropy at a particular temperature. The dielectric anisotropy of the samples was found to be negative and very small ( $\approx$  -0.01). Although the value of the dielectric constant is comparable to other room-temperature N<sub>D</sub> LCs, the anisotropy is much smaller than most of the other  $N_{\ensuremath{\text{D}}}$  compounds known in the literature.17

To measure the change in birefringence ( $\Delta n = n_e \cdot n_o$ ) of samples, its voltage dependence was tested in the N<sub>D</sub> phase at a fixed temperature which is shown in Figure 4b. Above the Freedericksz threshold voltage,  $\Delta n$  increases gradually and saturates at  $\approx 20$  V. The saturation of  $\Delta n$  indicates the planar state of the director as discussed earlier. Furthermore, a voltage of 23 V was applied to measure the temperature dependent birefringence.

**Table 1** X-ray reflections and corresponding correlation lengthsobtained after fitting the full q range profile with Lorentzianprofiles in the nematic phases of compound **7b** & **7c**.

Sample Name	Properties	Small angle peak	Mid angle peak	Wide angle peak
7b	d spacing d(Å)	19.81±0.01	8.78±0.02	4.68±0.01
	Correlation Length (ξ) (Å)	43.05±0.03	9.48±0.12	8.66±0.02
	ξ/d	2.17	1.08	1.85
7c	d spacing d(Å)	19.67±0.01	8.54±0.02	4.68±0.01
	Correlation Length (ξ) (Å)	51.21±0.03	9.62±0.12	8.69±0.02
	ξ/d	2.60	1.13	1.86

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As shown in Fig. 4c, the birefringence increases gradually with voltage along the isotropic to N<sub>D</sub> transition instead of a discontinuous jump, often seen for first order phase transitions. This is due to the large isotropic-N<sub>D</sub> coexisting region ( $\approx$  4 to 5 °C), which was observed indeed under POM. The maximum birefringence obtained at room temperature for the compounds **7b** and **7c** are  $\approx$  0.082 and  $\approx$  0.071, respectively. The very small dielectric anisotropy and the optical birefringence indicate that the orientational order in such systems is relatively lower than many other discotic compounds at room temperature.<sup>6,7,17</sup> Most possibly, this stems from the folding of the two disc units and the presence of a flexible linking chain. Such linking is responsible for poor stacking of the two disc-like units that prevent short-range columnar order in the nematic phase. Notably, the present study did not show any evidence of phase biaxiality in these systems, which may originate from improper stacking of the two neighbouring disc-like units.



**Fig. 3** Panel A: Computionally optimized structures of (i) linear and (ii) folded dimer. The folded form is electronically stable by 22.6 kcal mol<sup>-1</sup> (B3LYP-D3/6-311G<sup>\*\*</sup>) over unfolded form. Panel B: Schematic of (i) the structure of compounds **7**. (ii) Modeled as two discs connected with a flexible chain (T- triphenylene, P- pentaalkynylbenzene) in which disc P is truncated. (iii) A composite disc results after folding of these two discs. (iv) A possible schematic representation of N<sub>D</sub> phase of the composite discs. Alkyl chains are omitted for better clarity. Arrow in black color show the direction of the composite disc normal.





Fig. 4 (a) The voltage dependent dielectric constant for 7b and 7c. (b) Voltage dependent birefringence of compounds 7b (37 °C) and 7c (43 °C) and (c) the temperature dependent birefringence of compounds 7b and 7c.

Earlier reports disclosed that the mesophase behaviour of a discotic dimer generally relies on the position of equilibrium existing between the folded and unfolded conformers which in turn depends on the subtle interactions between the two discs, linking as well as the peripheral alkyl chains.<sup>18</sup> In general, discotic dimers having shorter spacers tend to fold and arrange themselves in intra-1,3 or intra-1,4 fashion to give columnar arrangement. In our studies, we indicate a possibility of folding of the molecule due to  $\pi$ - $\pi$  interactions between the triphenylene unit and phenyl rings of pentaalkynylbenzene. However, due to poor tendency of pentaalkynylbenzene units to pack into columns, a  $N_{\mbox{\scriptsize D}}$  mesophase is observed. In addition, we propose the possibility of folding in compound 7 from three different experimental results; i) the spacing of the mid angle peak in X-ray diffraction corresponding to effective thickness of the folded dimer ii) DFT calculations disclose that the folded state is significantly more stable than the unfolded state iii) smaller values of dielectric anisotropy and optical birefringence. On the basis of these results we propose a schematic of  $N_{\text{\tiny D}}$ phase shown in Fig. 3, where, mesogenic dyad (7b or 7c) is modelled as two discs linked via flexible chains, in which one of the disc is truncated. These discs of the dyad can fold to form a composite disc which further assembled into a  $N_{\ensuremath{\text{D}}}$  phase. The slight non-planarity of these composite discs avoids the formation of columnar phase as it prevents the  $\pi$ - $\pi$  stacking among these units. Also, the incompatibility of the two discs present in the composite disc leads to improper packing resulting into mesophase at room temperature.

In conclusion, we have synthesised two new discotic dyads showing  $N_D$  phase at room temperature possibly arising due to folding of two discs through  $\pi$ - $\pi$  interactions. XRD analysis, DFT calculations as well as the lower values of the birefringence and dielectric anisotropy are consistent with the prescribed model of the compounds.

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