

Liquid Crystals

Room-Temperature Oligomeric Discotic Nematic Liquid Crystals over a Wide Temperature Range: Structure–Property Relationships

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Abstract: The design and synthesis of three room-temperature discotic nematic (N_D) liquid crystals (LCs) is presented. The LC consists of an azobenzene core attached to which are four pentaalkynylbenzene (PA) units through flexible alkyl spacers. The presence of a short azo linking group provides more disorder in the system, thereby reducing the

packing efficiency among the PA units and resulting into the formation of a room-temperature N_D phase over a wide temperature range. Dielectric constant and birefringence studies were performed to gain further insights into the physical properties of the mesophase.

Introduction

Discotic liquid crystals (LCs) formed by disc-shaped molecules generally self-organize into an ordered supramolecular architecture, giving rise to the formation of columnar mesophases owing to strong π – π interactions between the poly-aromatic cores.^[1] In contrast, discoids showing the nematic (N_D) phase where the discs have only long-range orientational order are rare, but are of particular importance in many display devices. In fact, they have obtained specific interest since their commercialization as compensation foils to enlarge the viewing angle of LC displays based on negative birefringent films formed by polymerized nematic discogens.^[2] Unfortunately, among the limited number of discotic nematogens reported so far, most are often accompanied by high clearing temperatures and a narrow temperature range of the N_D phase.^[3] However, the N_D phase at room-temperature and over a wide temperature range is vital for their usability in devices.

A literature survey reveals that hexa- and pentaalkynylbenzene (PA) derivatives have been the most investigated systems among various discotic nematic LCs.^[3] In those cases, the stacking of discs in columns is inhibited by the rotational freedom provided by the alkynyl linkers. Subsequently, few other derivatives based on triphenylene (TP), truxene, thiotruxene, naph-

thalene, etc. have also been reported to show the N_D phase.^[4] Star-shaped 1,3,5-trisalkynylbenzene and discotic twins containing two TP units linked through diacetylene spacers or thiophene units were also found to display the N_D mesophase.^[5] Recently, hydrogen bonding has also been employed for the preparation of N_D LCs. For example, Lee et al. have reported discotic nematogens through hydrogen bonding between phenol and pyridine moieties as well as between phloroglucinol and alkoxystillbazole moieties.^[6] However, in all of the above cases, the N_D phase appears at higher temperatures, which limits their widespread use in applications.

On the other hand, to date, only a very few approaches have been reported to obtain room-temperature N_D mesophases. The first example of a room-temperature N_D mesogen was reported by Kumar and co-workers, by using a PA derivative with branched alkyl spacers.^[7] Later on, the discotic TP core possessing poly(ethylene oxide) side chains was also found to possess a room-temperature N_D phase.^[8] Lee and co-workers developed a new strategy to obtain a N_D phase by replacing one side-arm of the discotic multi-alkynylbenzene with a trisalkoxy side-arm.^[9] Further, they showed a room-temperature N_D phase over a wide temperature range by introducing an attraction-enhancing protrusion onto the multi-alkynylbenzene system.^[10] Recently, we have reported a new approach for the design of a room-temperature N_D LC dimer consisting of a TP and a PA unit linked through flexible alkyl spacers. The formation of the room-temperature N_D phase is likely due to folding of the dimer, which prevents π – π stacking among the composite disc units.^[11] In this communication, we have developed another new strategy to obtain a room-temperature N_D phase over a wide temperature range by connecting four PA units to an azobenzene core through flexible alkyl spacers. We hypothesized that the presence of a short rigid azo group in these oligomers can lead to a system in which PA units will be

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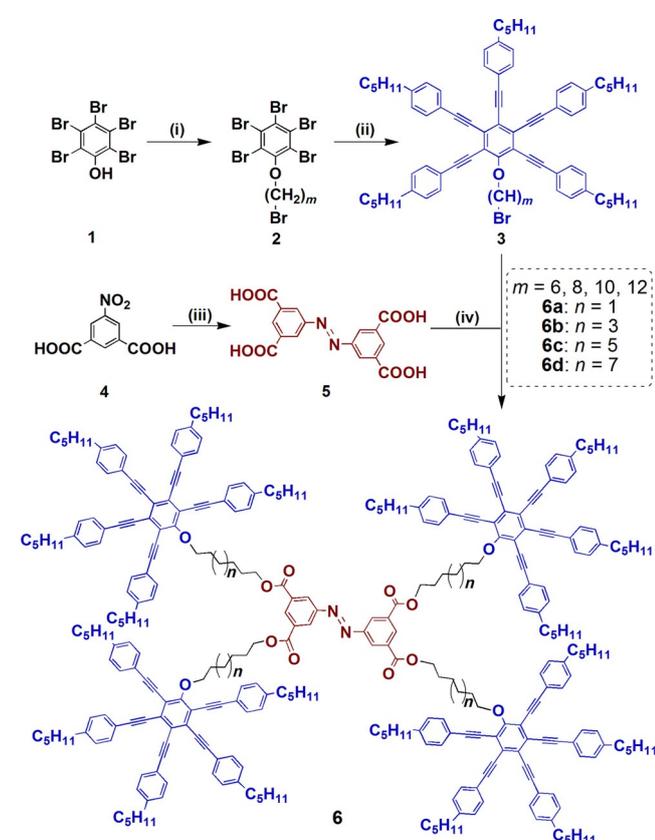
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randomly oriented with respect to each other. Consequently, these oligomeric units could be disordered enough to prevent efficient packing of the molecules and thus, may lead to the realization of a room-temperature N_D phase.

Results and Discussion

Target compounds **6a–d** were synthesized by the route outlined in Scheme 1. The synthesis of compounds **2**, **3**, and **5** has been discussed previously.^[12] Compounds **6** were prepared by reacting the pentayne **3** and azobenzene tetracarboxylic acid **5** in presence of potassium hydroxide and tetrabutylammonium bromide under reflux conditions (see the Experimental Section). All the compounds were characterized by ^1H NMR, ^{13}C NMR, IR, UV/vis, and elemental analysis (Supporting Information, Figures S1–S10).



Scheme 1. Synthesis of the target compounds **6**. Reagents and conditions: (i) K_2CO_3 , KI, $\text{Br}-(\text{CH}_2)_n-\text{Br}$, butanone, 80°C , 18 h, 88%; (ii) $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, 4-pentylphenylacetylene, PPh_3 , CuI, Et_3N , 100°C , 15 h, 85%; (iii) NaOH, dextrose, 80°C , HCl, 70%; (iv) KOH, H_2O , tetraoctylammonium bromide (TOAB), reflux, 5 h, 50%.

The thermal behavior of the compounds **6a–d** (precise transition temperatures in $^\circ\text{C}$ and respective enthalpy changes in kJ mol^{-1}) was examined by differential scanning calorimetry (DSC, Table 1) whereas the mesophase behavior was investigated by polarizing optical microscopy (POM) and X-ray scattering studies. Among the synthesized compounds, **6a–c** displayed bright birefringent textures at room temperature (with sheara-

Table 1. Thermal behavior of the synthesized compounds 6 . ^[a,b]		
Compd.	Heating scan	Cooling scan
6a	N_D 45.44 (0.42) I	I 42.08 (0.32) N_D
6b	N_D 57.50 (0.52) I	I 51.16 (0.37) N_D
6c	N_D 60.44 (1.02) I	I 55.68 (0.78) N_D
6d	–	I 51.6 G

[a] Phase transition temperatures (peak) in $^\circ\text{C}$ and transition enthalpies in kJ mol^{-1} (in parentheses). [b] Phase assignments: N_D = discotic nematic, G = glassy, I = isotropic.

bility) and were transformed to isotropic liquids at various temperatures on heating (see below). On cooling from the isotropic phase, a nice schlieren texture (typical of a nematic phase) was obtained for all of these oligomers (Figure 1a, Figure S11 in the Supporting Information). Interestingly, compound **6d** was in the isotropic state at room-temperature as it displayed a dark appearance in POM observations (Figure S11 in the Supporting Information). However, on cooling below room temperature, a peak was observed at -51.6°C (Figure S12a in the Supporting Information), which is probably due to formation of a glassy state.

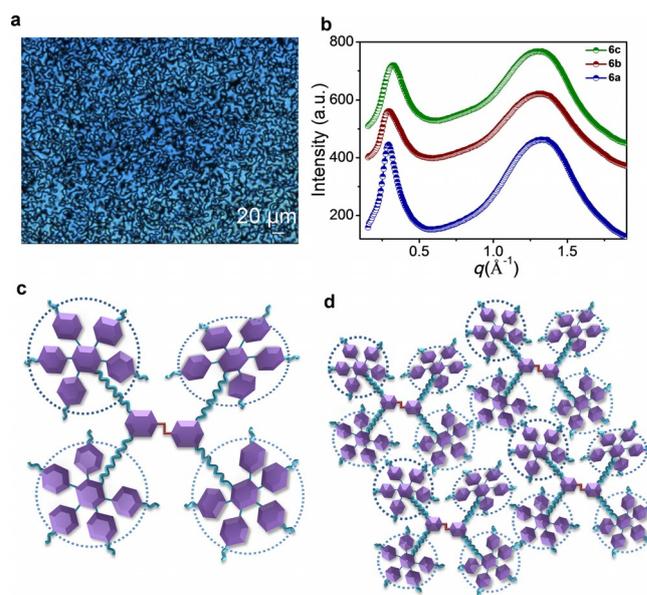


Figure 1. (a) Optical photomicrograph of compound **6a** at 30°C (on cooling, crossed polarizers). (b) X-ray diffraction patterns of compound **6a**, **6b**, and **6c** in their mesophase. (c) Schematic of the structure of compound **6**, modeled as four pentakis(phenylethynyl)benzene discs connected with flexible chains to azobenzene core. (d) Local arrangement of the model unit in the nematic phase.

The DSC thermogram of compound **6a** exhibited a peak at 45.44°C ($\Delta H = 0.42 \text{ kJ mol}^{-1}$) corresponding to a mesophase to isotropic transition (Figure S12b in the Supporting Information). On cooling, it displayed a transition from isotropic to mesophase at 42.08°C ($\Delta H = 0.32 \text{ kJ mol}^{-1}$). Similarly, the isotropization temperatures for compounds **6b** and **6c** were

found to be 57.50 °C ($\Delta H=0.52 \text{ kJ mol}^{-1}$) and 60.44 °C ($\Delta H=1.02 \text{ kJ mol}^{-1}$), respectively. Upon further cooling, a mesophase appeared at 51.16 °C for **6b** ($\Delta H=0.37 \text{ kJ mol}^{-1}$) and 55.68 °C ($\Delta H=0.78 \text{ kJ mol}^{-1}$) for **6c**. No sign of crystallization was observed until -50°C for all the compounds.

The quantitative study of the nematic phases of these compounds was detailed by small angle X-ray scattering (SAXS)/wide angle X-ray scattering (WAXS) investigations (Figure 1b, Figures S13 and S14 in the Supporting Information). Diffraction patterns of compounds **6a–6c** (recorded at 25 °C) are very similar to the monomeric PA derivatives.^[3] However, in comparison to most of the PA derivatives, the N_D mesophase is observed even at room temperature for compounds **6a–6c**. The diffraction pattern corresponding to mesophase of **6a** showed one relatively strong reflection in the small angle region and one broad peak in the wide angle regime. The calculated d -spacing of 21.40 Å for the signal in the small angle region corresponds to intra and intermolecular correlation of the PA units and approximates the diameter of the single PA disc ($\approx 19 \text{ Å}$). The spacing of the wide angle peak is calculated to be 4.74 Å, which mainly originates from the liquid-like correlation of the molten chains. The diffraction pattern corresponding to the nematic phases of compounds **6b** and **6c** are identical to **6a** and were analyzed in a similar way (Figure 1b). The d -spacing corresponding to first peak is found to deviate in a decreasing manner from **6a** to **6c** (Table 2). According to POM observations, compound **6d** exists as an isotropic liquid.

Table 2. X-ray reflections and corresponding correlation lengths obtained after fitting the peak profiles with Lorentzian profiles in the nematic phase of compounds **6a–c** and in the isotropic phase of compound **6d**.

Compd.	Properties	Small-angle peak	Wide-angle peak
6a	d -spacing [Å]	21.40 ± 0.20	4.74 ± 0.30
	correlation length (ξ) [Å]	32.66 ± 2.52	8.64 ± 1.75
	ξ/d	1.53 ± 0.13	1.82 ± 0.48
6b	d -spacing [Å]	20.86 ± 0.25	4.79 ± 0.35
	correlation length (ξ) [Å]	27.04 ± 2.52	8.41 ± 1.75
	ξ/d	1.30 ± 0.14	1.76 ± 0.49
6c	d -spacing [Å]	19.24 ± 0.30	4.80 ± 0.35
	correlation length (ξ) [Å]	24.17 ± 2.52	8.35 ± 1.75
	ξ/d	1.26 ± 0.15	1.74 ± 0.49
6d	d -spacing [Å]	19.04 ± 0.30	4.81 ± 0.35
	correlation length (ξ) [Å]	21.76 ± 2.86	8.23 ± 1.75
	ξ/d	1.14 ± 0.17	1.71 ± 0.49

To get further insights into this atypical behavior of **6d**, we have recorded its diffraction pattern in the isotropic state. The diffraction pattern showed two peaks; one in the small angle and another in the wide angle regime, similar to other compounds exhibiting mesophases (Figure S14 in the Supporting Information). However, the calculated d -spacing for the small angle peak is found to be 19.04 Å, which is about 2 Å less than in compound **6a** and is almost comparable to compound **6c**. The spacing of the wide angle peak is calculated to be 4.80 Å, which is nearly the same as observed in other compounds.

The correlation length, that is, the degree of order within the mesophase, was calculated by using $\xi = [k2\pi]/[(\Delta q)]$;

equivalent to Scherrer's equation. Here, k is the shape factor, a typical value of which is 0.89, λ is the wavelength of the incident X-ray, q is the scattering vector ($q=4\pi\sin\theta/\lambda$), θ is the maximum of the reflection, and Δq is the broadening in q at half of the maximum intensity. The Δq is obtained by Lorentzian fitting of the peaks obtained in the diffraction pattern (Figures S15–S16 in the Supporting Information). For compound **6a**, the correlation lengths for the reflections at 21.40 Å and 4.74 Å are calculated to be 32.66 Å and 8.64 Å, respectively. For effective comparison, the correlation length was divided by the d -spacing values, which results in a measure for the spatial order in terms of the molecular length scale. The respective correlation lengths for compounds **6** were found to decrease with increasing chain length of the alkyl spacer. The decrease in correlation length is significant for the reflection corresponding to the small angle region (Table 2). Variation of correlation length (ξ ; corresponding to reflection at small angles) with respect to number of methylene groups of alkyl spacers (m) for compounds **6a–d** is shown in the Figure 2,

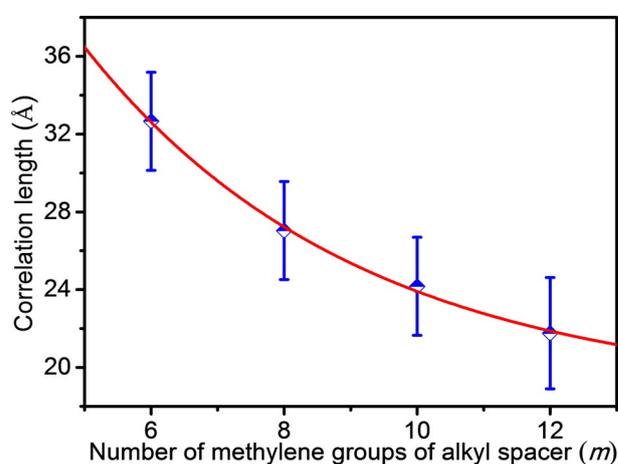


Figure 2. Variation of correlation lengths corresponding to reflections at small angles for compounds **6a–d** with respect to the varying number of methylene groups of the alkyl spacer (m). The half-filled blue diamonds show the correlation length (ξ) data with error bars. The red line shows the fit to the data, which follows an exponential decay ($\xi = a + \xi_0 \exp(-m/m_c)$). The characteristic number of methylene groups of the alkyl spacer (m_c) is 4.11 ± 0.89 , which describes that the correlation length decreases moderately with m .

which follows an exponential decay ($\xi = a + \xi_0 \exp(-m/m_c)$). The characteristic number of methylene groups of the alkyl spacer (m_c) is 4.11 ± 0.89 , which describes that the correlation length decreases moderately with m . The decrease in correlation length can be explained as follows. As compounds **6** are discotic mesogenic quadric based on pentakis(phenylethynyl)-benzene linked through flexible alkyl spacers, they could be modeled as four PA discs linked with flexible chains to an azobenzene core (Figure 1c). In the case of PA, the phenyl rings are generally not in-plane because of the rotational freedom provided by the ethynyl linkers, which prevents columnar stacking. In addition, orientational freedom of the PA group in-

creases on increasing the spacer length, which is reflected in the decreasing value of the corresponding correlation lengths. However, the decrease in correlation length for compound **6d** is large enough to avoid mesophase formation at room temperature and, thus, it is found to exhibit an isotropic phase.

The physical properties (e.g., elastic constants, birefringence, dielectric anisotropy) of the nematic mesogens strongly affects the electro-optical characteristics of LC displays and thus are the main factors to be considered. Therefore, to further explore the behavior of the N_D phase of compounds **6a–c**, we measured some physical properties such as birefringence and dielectric constant as a function of voltage and temperature. The details of the cell preparation are given in the Supporting Information. We have used a phase modulation technique to measure the birefringence and an impedance analyzer for measuring the dielectric constant simultaneously.^[13–15] Compounds **6a–6c** could not be aligned homogeneously and thus it was impossible to conduct direct measurements of birefringence. However, the samples showed good homeotropic alignment on AL-1254 polyimide coated cells. Hence, we first measured the birefringence at a fixed temperature as a function of voltage. To study the temperature dependence of the birefringence, we applied higher voltage than the Fréedericksz threshold voltage to get voltage-induced homogeneous alignment. The dielectric constant of the samples was also measured as a function of voltage at a fixed frequency (2 kHz) by using an impedance analyzer.^[16]

The insets of Figure 3a–c show the variation of voltage-dependent birefringence. The birefringence is zero at zero voltage as expected owing to the homeotropic state. It increases beyond a particular voltage and finally leads to saturation. The Fréedericksz threshold voltage (V_{th}) at a relative voltage is slightly higher in compound **6c** than **6a** and **6b**. For example, V_{th} for compounds **6a** and **6b** is about 2.5 V whereas it is about 5 V for **6c**. For measuring the temperature-dependent birefringence, a voltage of 20 V was applied for all the samples. At a relative temperature, the birefringence of compound **6a** is slightly lower than **6b** and **6c**. For example, at $T-T_{NI} = -12^\circ\text{C}$, Δn for **6a** is 0.055 whereas in case of **6b** and **6c**, it is about 0.08. This is expected because the polarizability anisotropy

and hence the birefringence increases with increasing length of the flexible alkyl spacer.

The temperature- and voltage-dependent variation of dielectric constants of compounds **6b** and **6c** are shown in Figure 4 (owing to the very high ionic conductivity of **6a** and difficulty in alignment of the sample, its measurement was not carried out). The insets show that beyond the Fréedericksz threshold

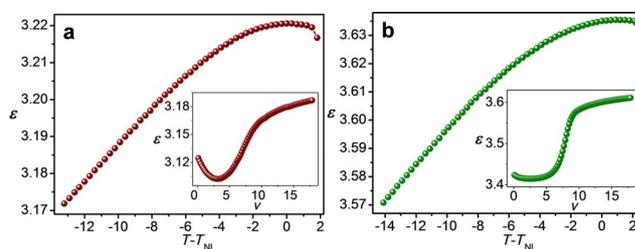


Figure 4. Temperature-dependent dielectric (ϵ) of compound (a) **6b** at a fixed voltage of 15 V and frequency of 2 kHz, inset: voltage-dependent dielectric (ϵ) at a fixed temperature, $T-T_{NI} = -5^\circ\text{C}$; and (b) **6c** at a fixed voltage of 15 V and frequency of 2 kHz, inset: voltage-dependent dielectric (ϵ) at a fixed temperature, $T-T_{NI} = -6^\circ\text{C}$.

at zero voltage, the dielectric constant increases and tends to saturate. The approximate dielectric anisotropy ($\Delta\epsilon$), that is, the difference between the dielectric constant measured at zero voltage and at 20 V is much smaller in **6b** than **6c**. For example, for **6b**, $\Delta\epsilon \approx 0.07$ whereas for **6c**, $\Delta\epsilon \approx 0.2$. The temperature-dependent dielectric constant was studied at 20 V simultaneously. Although absolute values of the dielectric constants of compounds **6b** and **6c** are slightly different, their temperature-dependent behavior is similar.

Further, the bend elastic constant (K_{33}) of the samples can also be estimated from the Fréedericksz threshold voltage, $V_{th} = \pi \sqrt{K_{33}/\epsilon_0 \Delta\epsilon}$ of the voltage dependent dielectric data. For example, the Fréedericksz threshold voltages for **6b** and **6c** are 3.7 V and 4.9 V, respectively. The corresponding bend elastic constants at those temperatures are calculated to be 0.1 pN and 0.42 pN, respectively. There are a few reports that describe the detailed physical properties of room-temperature discotic

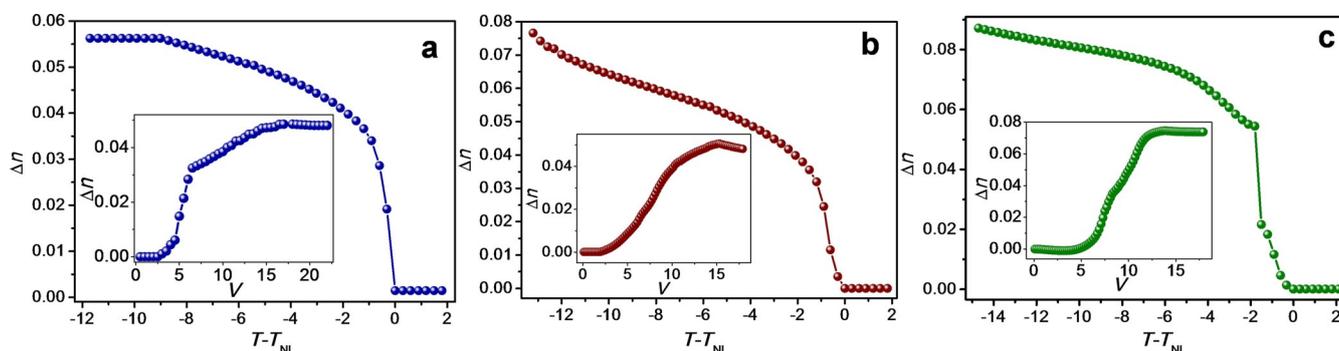


Figure 3. Temperature-dependent birefringence (Δn) of (a) **6a** at a fixed voltage of 20 V and frequency of 4 kHz, inset: voltage-dependent birefringence (Δn) at a fixed temperature, $T-T_{NI} = -4.89^\circ\text{C}$; (b) **6b** at a fixed voltage of 15 V and frequency of 2 kHz, inset: voltage-dependent birefringence (Δn) at a fixed temperature, $T-T_{NI} = -5^\circ\text{C}$; and (c) **6c** at a fixed voltage of 15 V and frequency of 2 kHz, inset: voltage-dependent birefringence (Δn) at a fixed temperature, $T-T_{NI} = -6^\circ\text{C}$.

nematic compounds.^[14] We observed that the birefringence and dielectric anisotropies of the synthesized compounds are significantly lower in comparison to those reported in the literature. The low birefringence of these compounds could be advantageous for employing them as compensating films in LC devices where the difference in the value of birefringence between the device material and the compensating film has to be lower.

Overall, we observed that a combination of four PA units linked with the azo group sufficiently perturbed the system to yield a room-temperature N_D phase. In the assembly of PA units of monomeric derivatives, efficient packing of the discs is forbidden as a result of free rotation of phenyl rings provided by the ethynyl linkers. However, in most of the cases, the packing is not disordered enough to exhibit the nematic phase at room temperature. Previously, room-temperature N_D mesophases have been obtained by perturbing the symmetry of the PA unit leading to more disordered systems.^[9–10] Here, we reveal that grouping of PA units by connecting them with a short azobenzene linking unit by flexible spacers could show a room-temperature N_D phase. In general, several other factors, such as molecular topology, micro-segregation, etc. might also be involved in the mesophase formation, however, conformational flexibility plays the main role here. This is also evident from the X-ray studies that show a decrease in correlation length with increasing number of alkyl spacers. In fact, we found that compound **6d** with the longest alkyl spacer displays isotropic behavior at room temperature. This observation can be explained on the basis that PA discs within each oligomer are randomly oriented and so the oligomer is too. Hence, the doubly disordered effect owing to random orientation of (i) individual PA units of each oligomer and thus (ii) oligomers composed of PA discs, reduces the packing efficiency enough to result in a room-temperature N_D phase. However, in compound **6d**, the disorder was high enough to avoid the emergence of a N_D phase.

Conclusion

We have synthesized three new oligomeric LCs showing N_D phases at room temperature. The N_D mesophase has been characterized by POM, DSC, and XRD studies and was further explored by voltage- and temperature-dependent dielectric and birefringence studies. These compounds are promising materials for display device applications and also point the way towards development of new anisotropic soft materials.

Experimental Section

For the synthesis of the final compounds **6**, compound **5** (1 equivalent) was dissolved in aqueous KOH (1.1 equivalent) solution. To that solution, compound **3** (6 equivalents) was added followed by the addition of tetraoctylammonium bromide in catalytic amounts. The reaction mixture was heated at reflux under vigorous stirring for 5 h and was then cooled to room temperature. The compound was extracted with chloroform. The organic layer was washed with brine and dried over anhydrous sodium sulfate. The chloroform

was removed by rotary evaporation and the resulting residue was purified by column chromatography over silica gel by using hexane and ethyl acetate as the eluent. Full characterization details and 2D diffraction patterns are provided in the Supporting Information.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: azobenzene · birefringence · dielectric · discotic nematic · pentaalkynylbenzene

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