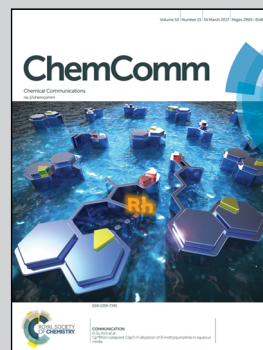


Showcasing research from the group of Dr Santanu Kumar Pal
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A new strategy towards the synthesis of a room-temperature
discotic nematic liquid crystal employing triphenylene and
pentaalkynylbenzene units

Two new discotic dyads showing N_D phase at room temperature
were prepared. Modelling the mesophase as derived from X-ray
scattering results, high-level DFT calculations as well as dielectric
and birefringence studies suggested that the formation of N_D
phase was realized most likely through folding of the dimeric
molecules through π - π interactions.

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

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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 the N_D phase is realized most likely through folding of the dimeric molecule that prevent stacking between the triphenylene units, as suggested by modelling in the mesophase derived from X-ray scattering results and high-level DFT calculations.

Disc shaped molecules showing a nematic phase (N_D) are rare but are 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 displays 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.² In contrast, implementation of nematic discogens in devices necessitates the N_D phase at room temperature. A thorough literature survey reveals that hexa- and pentaalkynylbenzene derivatives have been the most investigated systems among various discotic nematogens.² The N_D mesophase has also been observed for star-shaped 1,3,5-trisalkynylbenzene and triphenylene units linked through a short rigid π -conjugated diacetylene spacer as well as thiophene units.^{3–5} Hydrogen bonding between phenol and pyridine moieties as well as between phloroglucinol and alkoxy stilbazole moieties has also led to fabrication of the N_D phase.⁶ However, to date, only a few approaches have been reported for the formation of the room-temperature N_D phase. For instance, Kumar *et al.* reported the first example of a room-temperature N_D mesogen by using a pentaalkynyl benzene derivative with branched alkyl spacers.⁷ The room-temperature N_D phase has also been observed for the discotic triphenylene core possessing poly(ethylene

oxide) side chains.⁸ Lee & co-workers developed a strategy to achieve room-temperature nematic discogens by perturbing the lateral side-arm of pentaalkynylbenzene with a substitution ortho to the ethynyl group on the peripheral phenyl ring.⁹ They also established further that the room-temperature N_D phase can be obtained by introducing an attraction-enhancing unit in the lateral side arm of hexa(phenylethynyl)benzene.¹⁰

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

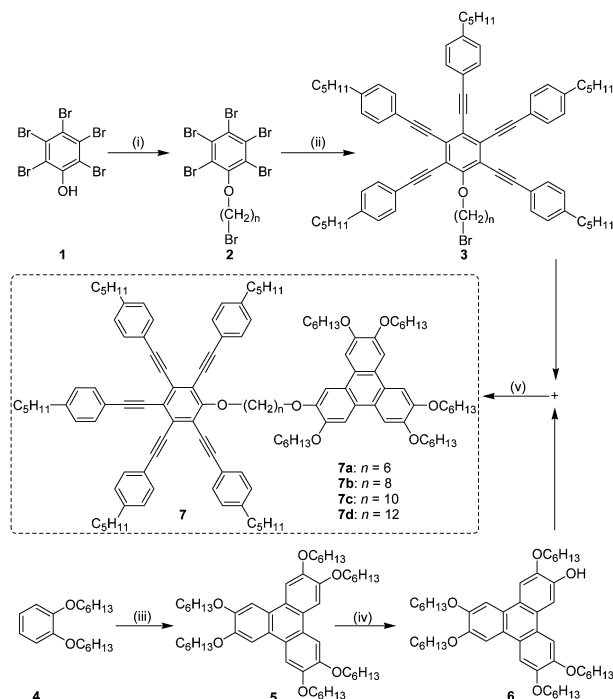
The target compounds (**7a–d**) were synthesized by the route depicted in Scheme 1. The synthesis of intermediate compounds **2**, **3**, **5** and **6** has been discussed elsewhere.¹³ Compounds **7a–d** were prepared by reacting the pentayne **3** with monohydroxy triphenylene **6** in the presence of cesium carbonate and potassium iodide using butanone as a solvent under reflux conditions (see the ESI†). All compounds were characterised by ¹H & ¹³C NMR, IR, UV-Vis and mass (MALDI) spectrometry (ESI,† Fig. S1–S9). The thermal behaviour of the 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

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† Electronic supplementary information (ESI) available: Detailed synthetic procedure, characterization details, 2D diffraction patterns and photoluminescence spectra. See DOI: 10.1039/c6cc09509g



Scheme 1 Synthesis of the target compounds **7**. Reagents and conditions: (i) dibromoalkane, K_2CO_3 , KI, butanone, 80 °C, 18 h, 89%; (ii) $Pd(Ph_3)_2Cl_2$, 4-pentylphenylacetylene, PPh_3 , CuI, Et_3N , 100 °C, 15 h, 82%; (iii) $FeCl_3$, CH_2Cl_2 , H_2SO_4 , RT, 1 h, 70%; (iv) Cat-B-Br, CH_2Cl_2 , RT, 48 h, 40%; and (v) Cs_2CO_3 , KI, butanone, 80 °C, 18 h, 85%.

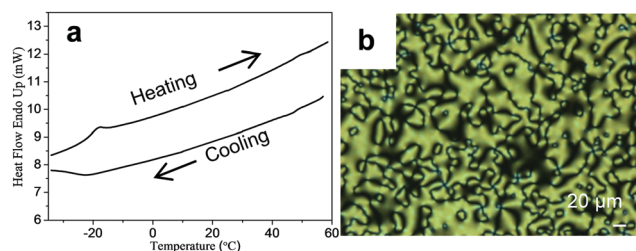


Fig. 1 (a) DSC traces of compound **7c** upon heating and cooling (scan rate 5 °C min⁻¹). (b) Polarizing optical photomicrograph of compound **7c** at 40 °C (upon cooling, crossed polarizers).

the maxima centred at 452 nm for all fluorophores. The 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 (ΔH) of 1.57 kJ mol⁻¹. Upon further heating, the mesophase was cleared at 57.48 °C (ΔH = 0.48 kJ mol⁻¹). On the other hand, the 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 up to -19.4 °C). Compound **7c** was liquid crystalline at room temperature and exhibited isotropization at 50 °C (ΔH = 0.30 kJ mol⁻¹). Upon further cooling, the mesophase emerged at 46.83 °C (ΔH = 0.29 kJ mol⁻¹), which was stable up to -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 the N_D phase.

To investigate the detailed structure of the N_D phase, X-ray diffraction experiments were performed. Diffractograms of mesophases of both **7b** and **7c** (Fig. 2 and Fig. S12, ESI†) 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 the liquid like order of the alkyl chains. This pattern conclusively affirms the presence of a N_D phase.¹⁴ In addition, one broad peak in the mid-angle range was also observed, which was further confirmed by full q range fitting of diffraction patterns with Lorentzian profiles.

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

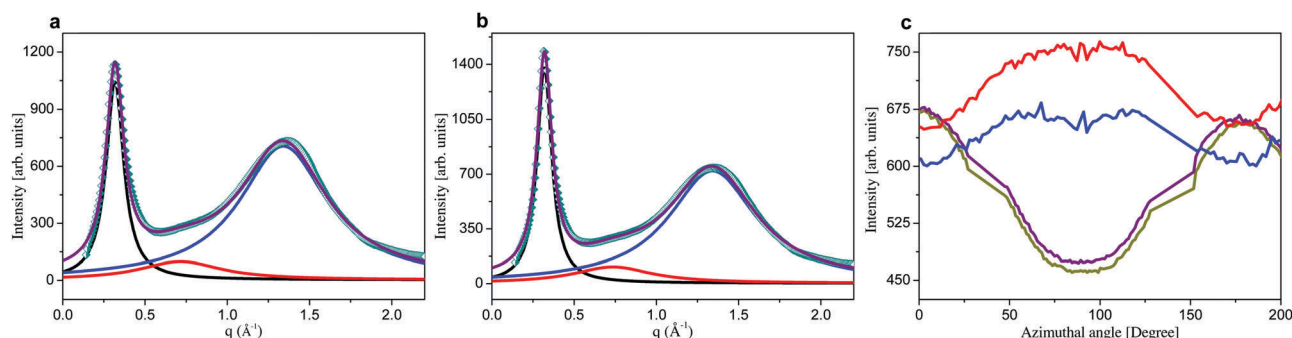


Fig. 2 X-ray diffraction patterns of compounds (a) **7b** and (b) **7c** (half filled diamonds in dark cyan colour) along with the Lorentzian fittings. Black, red and blue curves are the Lorentzian profiles corresponding to small, mid and wide angle peaks, respectively. The purple curve is the sum of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

Table 1 X-ray reflections and the corresponding correlation lengths obtained after fitting the full q range profile with Lorentzian profiles in the nematic phases of compounds **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

pattern for the nematic phase 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, λ is the wavelength of the incident X-rays, $\Delta 2\theta$ is the broadening in 2θ at half of the maximum intensity (FWHM) in radians, θ is the maximum of the reflection, q is the scattering vector ($q = 4\pi \sin \theta/\lambda$) and the Δq is broadening in q at half of the maximum intensity. The Δq is obtained by Lorentzian fitting of the diffraction pattern. For compound **7b**, the correlation lengths for the reflections at 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 the 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 wide angles are in opposite phases, which reflects that the growth of the side by side correlation of the composite disc and chain-chain correlation are in the orthogonal plane. The intensity variation is also broad in nature, which further supports that the structure is locally planar.

To investigate the folding behavior of the two discs in **7b**, we carried out a high-level DFT analysis. The computational analysis on a slightly truncated model (see the ESI† for coordinates) reveals that the folded form of the molecule is electronically stable by 22.6 kcal mol^{−1} (B3LYP-D3/6-311G**) over its unfolded, linear congener.¹⁵ Considering the entropic penalty associated with the folding event, the free energy difference (ΔG) was calculated to be 14.7 kcal mol^{−1} in favor of the folded state. As can be observed from Fig. 3A, one of the phenyl groups of the phenyl acetylenes is nicely engaged in π - π interaction with the triphenylene unit, keeping the interacting C...C distances within 3.5–3.7 Å. To ensure further that the stabilization for the folded state is not much biased by the choice of the level of theory, we recalculated the electronic energy difference at M06-D3/6-311G**. The difference came out to be 29.4 kcal mol^{−1} in favor of the 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 under neat conditions. Most notably, this folded behavior of **7b** is also consistent with our X-ray analysis.

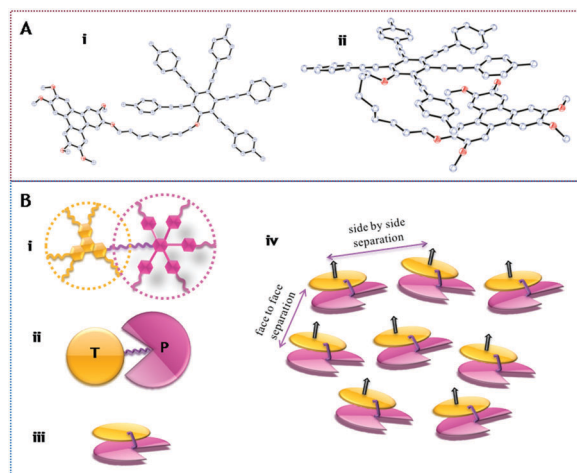


Fig. 3 Panel A: Computationally optimized structures of (i) linear and (ii) folded dimers. The folded form is electronically stable by 22.6 kcal mol^{−1} (B3LYP-D3/6-311G**) over the unfolded form. Panel B: Schematic of (i) the structure of compounds **7**. (ii) Modeled as two discs connected with a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

To investigate the physical properties of the room temperature N_D LCs, the 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 the samples was measured as a function of voltage at a fixed frequency of 1 kHz (Fig. 4a). The dielectric constant increases beyond the Fréedericksz threshold voltage and tends to saturate at higher voltages. In particular, for samples **7b** and **7c** the threshold voltages are 9.5 V and 11.8 V, respectively. The director is homeotropic below the Fréedericksz threshold voltage and becomes planar at a 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 (≈ -0.01). Although the value of the dielectric constant is comparable to other room-temperature N_D LCs, the anisotropy is much smaller than most of the other N_D compounds known in the literature.¹⁷

To measure the change in the birefringence ($\Delta n = n_e - n_o$) of the samples, its voltage dependence was tested in the N_D phase at a fixed temperature, which is shown in Fig. 4b. Above the Fréedericksz threshold voltage, Δn increases gradually and saturates at ≈ 20 V. The saturation of Δn indicates the planar state of the director as discussed earlier. Furthermore, a voltage of 23 V was applied to measure the temperature dependent birefringence.

As shown in Fig. 4c, the birefringence increases gradually with voltage along the isotropic to N_D transition instead of a discontinuous jump, often seen for first order phase transitions. This is due to the large isotropic- N_D coexisting region (≈ 4 to 5 °C), which was observed indeed under POM. The maximum birefringence values obtained at room temperature for compounds **7b** and **7c** are ≈ 0.082 and ≈ 0.071 , respectively. The very small dielectric anisotropy and

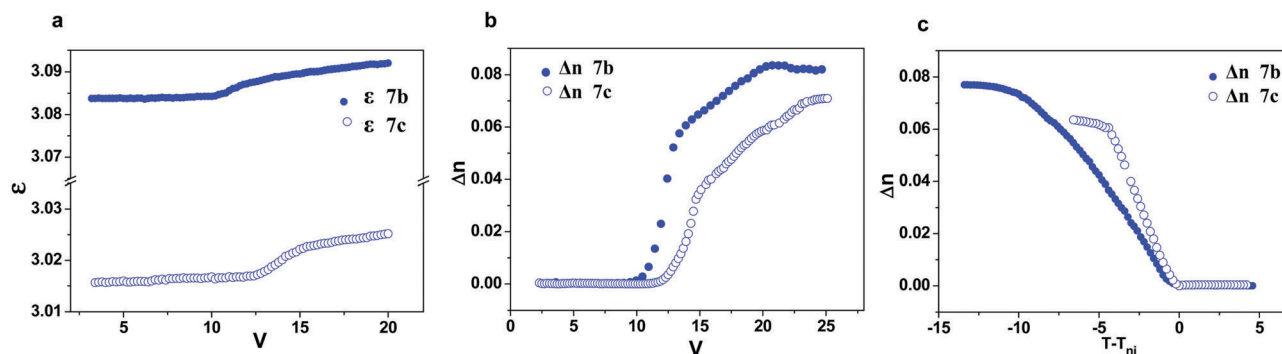


Fig. 4 (a) The voltage dependent dielectric constant for **7b** and **7c**. (b) Voltage dependent birefringence of compounds **7b** (37 °C) and **7c** (43 °C) and (c) the temperature dependent birefringence of compounds **7b** and **7c**.

the optical birefringence indicate that the orientational order in such systems is relatively lower than many other discotic compounds at room temperature.^{6,7,17} 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.

Earlier reports disclosed that the mesophase behaviour of a discotic dimer generally relies on the position of the 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.¹⁸ In general, discotic dimers having shorter spacers tend to fold and arrange themselves in an intra-1,3 or intra-1,4 fashion to give a columnar arrangement. In our studies, we indicate a possibility of folding of the molecule due to π - π interactions between the triphenylene unit and the phenyl rings of pentaalkynylbenzene. However, due to the poor tendency of the pentaalkynylbenzene units to pack into columns, a N_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 the effective thickness of the folded dimer; (ii) DFT calculations that disclose that the folded state is significantly more stable than the unfolded state; and (iii) smaller values of dielectric anisotropy and optical birefringence. On the basis of these results, we propose a schematic of the N_D phase shown in Fig. 3, where the mesogenic dyad (**7b** or **7c**) is modelled as two discs linked *via* flexible chains, in which one of the discs is truncated. These discs of the dyad can fold to form a composite disc, which can further assemble into a N_D phase. The slight non-planarity of these composite discs avoids the formation of a columnar phase as it prevents the π - π stacking among these units. Also, the incompatibility of the two discs present in the composite disc leads to improper packing resulting in a mesophase at room temperature.

In conclusion, we have synthesised two new discotic dyads showing the N_D phase at room temperature possibly arising from the folding of two discs through π - π 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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Notes and references

- (a) M. Lu and K. H. Yang, *Jpn. J. Appl. Phys.*, 2000, **36**, L412–L415; (b) H. Mori, Y. Itoh, Y. Nishuira, T. Nakamura and Y. Shinagawa, *Jpn. J. Appl. Phys.*, 1997, **36**, 143–147.
- H. K. Bisoyi and S. Kumar, *Chem. Soc. Rev.*, 2010, **39**, 264–285.
- B. G. Kim, S. Kim and S. Y. Park, *Tetrahedron Lett.*, 2001, **42**, 2697–2699.
- (a) S. Kumar and S. K. Varshney, *Org. Lett.*, 2002, **4**, 157–159; (b) S. Kumar and S. K. Varshney, *Liq. Cryst.*, 2001, **28**, 161–163.
- (a) L. Zhang, D. L. Hughes and A. N. Cammidge, *J. Org. Chem.*, 2012, **77**, 4288–4297; (b) L. Zhang, H. Gopee, D. L. Hughes and A. N. Cammidge, *Chem. Commun.*, 2010, **46**, 4255–4257.
- (a) J. H. Lee, I. Jang, S. H. Hwang, S. J. Lee, S. H. Yoo and J. Y. Jho, *Liq. Cryst.*, 2012, **39**, 973–981; (b) J. H. Lee, M.-J. Han, S. H. Hwang, I. Jang, S. J. Lee, S. H. Yoo, J. Y. Jho and S.-Y. Park, *Tetrahedron Lett.*, 2005, **46**, 7143–7146.
- (a) S. Kumar and S. K. Varshney, *Angew. Chem., Int. Ed.*, 2000, **112**, 3270–3272; (b) S. Kumar, S. K. Varshney and D. Chauhan, *Mol. Cryst. Liq. Cryst.*, 2003, **396**, 241–250; (c) S. K. Varshney, V. Prasad and H. Takezoe, *Liq. Cryst.*, 2011, **38**, 53–60.
- S. Kohmoto, E. Mori and K. Kishikawa, *J. Am. Chem. Soc.*, 2007, **129**, 13364–13365.
- S. C. Chien, H. H. Chen, H. C. Chen, Y. L. Yang, H. F. Hsu, T. L. Shih and J. J. Lee, *Adv. Funct. Mater.*, 2007, **17**, 1896–1902.
- H.-H. Chen, H.-A. Lin, S.-C. Chien, T.-H. Wang, H.-F. Hsu, T.-L. Shih and C. Wu, *J. Mater. Chem.*, 2012, **22**, 12718–12722.
- K. Praefcke, B. Kohne, D. Singer, D. Demus, G. Pelzl and S. Diele, *Liq. Cryst.*, 1990, **7**, 589–594.
- M. Gupta, I. Bala and S. K. Pal, *Tetrahedron Lett.*, 2014, **55**, 5836–5840.
- (a) M. Gupta and S. K. Pal, *Liq. Cryst.*, 2015, **42**, 1250–1256; (b) M. Gupta and S. K. Pal, *Langmuir*, 2016, **32**, 1120–1126.
- C. T. Imrie, Z. Lu, S. J. Picken and Z. Yildirim, *Chem. Commun.*, 2007, 1245–1247.
- (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652; (b) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
- Y. Zhao and D. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215–241.
- D. VenkataSai, G. Mirri, P. Kouwer, R. Sahoo, I. Musevic and S. Dhara, *Soft Matter*, 2016, **12**, 2960–2964.
- (a) K. J. A. Bozek and V. E. Williams, *Soft Matter*, 2014, **10**, 5749–5754; (b) N. Boden, R. J. Bushby, A. N. Cammidge, A. El-Mansoury, P. S. Martin and Z. Lu, *J. Mater. Chem.*, 1999, **9**, 1391–1402; (c) M. C. Tzeng, S. C. Liao, T. H. Chang, S. C. Yang, M. W. Weng, H. C. Yang, M. Y. Chiang, Z. Kai, J. Wu and C. W. Ong, *J. Mater. Chem.*, 2011, **21**, 1704–1712.