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New perylene-based non-conventional discotic liquid crystals†

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The synthesis, optical properties and thermal behaviour of three novel non-conventional 3,4,9,10-tetrasubstituted perylene-based discotic oligomers are reported for the first time consisting of a perylene core attached to which are four 4-cyanobiphenyl, triphenylene and cholesteryl units *via* flexible alkyl spacers. All the oligomers self-assemble into a mesophase and exhibit excellent fluorescence emission properties making them suitable for various opto-electronic applications.

Introduction

Non-conventional liquid crystals (LCs) are those materials whose structure and properties deviate from ordinary or conventional LCs. One can get these materials of interesting properties by combining more than one contrasting or different functionalities within a molecule. Several structural contrasts within a molecule such as thermotropic–lyotropic, hydrophilic–lipophilic, disc–rod, nonpolar–polar, oligosiloxane–hydrocarbon, electron donor–electron acceptor, rigid–flexible, hydrocarbon–fluorocarbon, *etc.* are possible and can be synthesized that may display unique properties through self-organization. Non-conventional mesogens bridge the gap between entirely different chemical or physical properties. Their purification and characterization are simple, and due to the restricted motion of their components they provide and stabilize a variety of fluid phases with fascinating functions. Apart from their prospective applications, they are crucial for the theoretical understanding of the mesomorphic phenomenon. The detailed study of novel non-conventional materials may result in knowledge about novel liquid crystalline phases and deeper insights into the driving forces of their self-organization. It is well known that anisotropic molecular shape and space filling play vital role in self-assembly of mesogens. However, nano-scale segregation of irreconcilable molecular parts *i.e.* micro segregation has also been realized to play an important role in mesogenic self-assembly, resulting into new mesophase morphologies.[1–5]

Recently, a large range of different non-conventional LC architectures have been prepared and explored in terms of LC properties using different discotic cores like triphenylene based trimers,[6–8] dendrimers,[9] oligomers,[10] anthraquinone based trimers,[11] oligomers[12–14] *etc*. Among them, perylene has received significant level of scientific attraction because of its excellent electronic absorption and fluorescence emission properties. Perylene derivatives are capable materials for various opto-electronic applications such as organic solar cells,[15,16] light emitting diodes (LEDs),[17,18] field effect transistors[19,20] *etc*. Among the several structural variety of non-conventional mesogens reported, LC oligomers have drawn particular attention over the last few years. Additionally, an oligomeric approach provides a wide flexibility in molecular design towards multifunctional LCs. However, compared to calamitic oligomers, a few numbers of perylene oligomers are reported. For example, Kong *et al.* reported a columnar mesophase in a triphenylene-perylene-triphenylene-based trimer.[7] Aggregation behaviour (solution and neat phase) for perylene-triphenylene-based star shaped oligomer has been investigated by Bagui *et al.*[8,9] Some important examples of rod-like non-conventional LCs include cyanobiphenyl-based symmetric and non-symmetric dimers & trimers,[21] tetramers containing one triphenylene and three cyanobiphenyl,[22,23] imidazolium-based non-symmetric ionic dimer having one cyanobiphenyl and one triphenylene,[24] heptamer containing one anthraquinone surrounded by six and eight cyanobiphenyl moieties,[13,14] *etc*. Similarly, cholesterol-based non-conventional LCs have been widely investigated. Cholesteric, nematic and smectic phases have been reported for cholesterol-cyanobiphenyl-based dimers.[25] Donaldson *et al.* reported enantiotropic nematic, enantiotropic chiral nematic, and monotropic chiral nematic phases in a cyanobiphenyl-based symmetrical dimer, cyanobiphenyl-cholesterol-based non-symmetrical dimer and cholesterol-based symmetrical dimer respectively.[26] Smectic, TGB and chiral nematic

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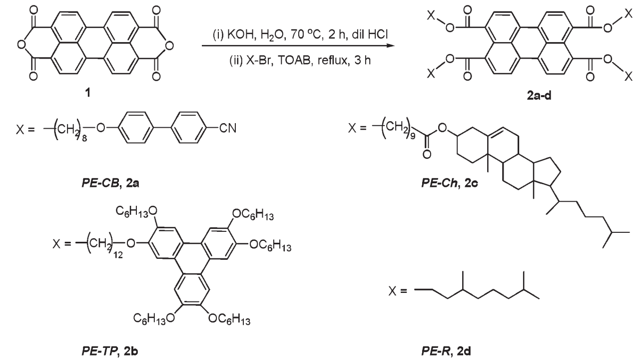

Scheme 1 Synthesis of perylene-based non-conventional LCs.

phases were observed in the case of cholesterol-cyanobiphenyl-based non-symmetric dimer by Zhang *et al.*[27]

In this context we are interested in the design and synthesis of novel functional discotic oligomeric materials and their mesophase behavior. Our molecular design is such that it contains discotic perylene moiety at the center and the perylene has been connected from four sides to four calamitic 4-cyanobiphenyl moieties (*PE-CB*), cholesterol units (*PE-Ch*) and discotic triphenylene core (*PE-TP*) *via* flexible methylene spacers in three different oligomeric molecules (Scheme 1). For comparison, central perylene core (*PE-R*) has also been linked to four branched aliphatic chains. The study reported in this paper represents a simple but useful advance in the design of a molecular system that enables fundamental insights into unconventional structure-mesophase morphology relationship. This study was motivated by two goals. First, by changing the connection of structurally different units *i.e.* cyanobiphenyl (*CB*) and cholesterol (*Ch*) around the periphery of a perylene core (*PE*), we sought to provide insight into structure–mesophase behaviour in the system. Additionally, we sought to explore the possibility of hole and electron transport properties by attaching electron rich *TP* and electron deficient *PE* moieties. These molecular double-cables, owing to their incommensurate core sizes, may stack one on top of the other in the columns to give columnar versions of double cable polymers, which could ultimately provide side-by-side percolation pathways for electrons and holes in solar cells.

In recent years, liquid crystal display research is attributed to the integration of efficient and compact LEDs as the backlighting. It has been long back since the first LED based on silicon carbide was discovered by O. V. Losev.[28] Since then a large number of LEDs like red LEDs,[29] blue and ultraviolet LEDs[30] as well as white LEDs[31] have become available for backlighting in LC display. Very recently, the progress in group III-nitride LEDs were driven in innovations to address the internal quantum efficiency and efficiency droop[32–36] and light extraction issues[37,38] which resulted in energy-efficient backlighting for LCD applications. These perylene compounds can also serve as promising LED backlit materials in LCD technology. Not only this, perylenes could be of potential interest in showing biaxial nematic (N_b) phases. Classical approaches to biaxial nematic thermotropic LC materials were based on the design of molecules. Probably, mixing board-like molecules *i.e.* perylenes with different size or aspect ratios could reduce the formation of positionally ordered phases and might lead to the N_b phase.[39–45]

Results and discussion

Synthesis

Target molecules **2a–2d** were prepared applying a method already described in literature with some modification in the synthetic method.[46,47] Although tetraesters of perylene has been synthesized by various other methods also.[48,49] These methods involve (a) treatment of perylene-3,4,9,10-tetracarboxylic dianhydride with a mixture of alkyl halide/alkyl tosylate and alkyl alcohol by refluxing in presence of potassium carbonate for 2–7 days,[47,48] (b) refluxing a mixture of perylene-3,4,9,10-tetracarboxylic dianhydride, alcohol, alkyl halide and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in acetonitrile for overnight,[50] (c) transesterification of tetramethyl ester of perylene-3,4,9,10-tetracarboxylic acid with suitable alcohol by boiling in presence of sodium alcoholate for 80 h,[51] (d) another track goes *via* hydrolysis of perylene-3,4,9,10-tetracarboxylic acid dianhydride by refluxing it in aqueous potassium hydroxide followed by acidification to pH 8–9 with aqueous dilute H_2SO_4 or HCl to provide perylene-3,4,9,10-tetracarboxylic acid.[47] This was followed by *in situ* addition of alkyl bromide and tetraoctylammonium bromide (TOAB) as phase transfer catalyst and refluxing the mixture vigorously for 1–2 h.[47] In our current case, we need to attach mesogenic groups *i.e.* cyanobiphenyl, cholesterol or triphenylene to the central perylene core. In order to apply method (a) or method (b), we need to have both ω-hydroxy and ω-bromo terminated precursors of cyanobiphenyl, cholesterol or triphenylene, which will increase the number of steps in the synthetic method. Again, overall reaction time in these two methods varies between overnight to one week. The complicated and time-consuming approach of conventional transesterification, method (c), can be replaced by the simpler method (d). Another benefit of method (d) is that we need to have only the ω-bromo terminated precursor in order to achieve the final tetraester. The total time consumed in this pathway was not more than 5 h. All the compounds were characterized by ^1H NMR, ^{13}C NMR, IR and elemental analysis (See electronic supplementary information (ESI†), Fig. S1–S12).

Thermal behaviour

The thermal behaviour of all target materials (TM) was investigated by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The transition temperature and associated enthalpy data obtained from the heating and cooling cycles of DSC (see ESI† for details, Fig. S13–S16) or POM are collected in Table 1. The peak temperatures are given in degree Celsius and the numbers in parentheses indicate the transition enthalpy (ΔH) in kJ mol^{-1}.

Compounds **2a**, **2b** and **2d** were found to be LC glassy materials in their neat form at room temperature. However, the cholesterol derivative **2c** was crystalline material at room temperature in its virgin condition. Compound **2a** (*PE-CB*) exhibited an enantiotropic nematic phase. It showed an undefined mobile texture at room temperature, which cleared at around 113 °C upon heating. On cooling from isotropic liquid, under a microscope a typical

Table 1 Phase transition temperatures (peak, °C) and associated enthalpy changes (kJ mol^{-1}, in parentheses) of novel perylene-based oligomers[a]

TM	Heating scan	Cooling scan
2a	N 105.3 (5.54) I	I 89.6 (2.87) N
2b	Col$_h$ 103.9 (78.83) I	[b]I 101 Col$_h$
2c	Cr 114.3 (22.43) Cr 146.2 (35.27) Cr 169.5 (259.9) I	I 135 (31.8) N*
2d	Col$_h$ 150.2 (6.23) I	I 147 (0.4) Col$_h$

[a] Phase assignments: Cr = crystal, N = nematic, N* = chiral nematic, I = isotropic. [b] From POM.

schlieren texture of the nematic phase is displayed, as shown in Fig. 1a. In DSC, it showed one endothermic transition at 105.3 °C (mesophase to isotropic transition) in the first heating cycle and one exothermic transition at 89.6 °C on first cooling. However, the LC phase was stable up to room temperature on cooling. Compound **2b**, *PE-TP* derivative, exhibited characteristic mosaic like texture corresponding to columnar phase at 101 °C on cooling from isotropic phase (Fig. 1b). In DSC, it showed one endothermic transitions at 103.9 °C in the first heating cycle that corresponds to mesophase to isotropic transition temperature. The cholesterol derivative, **2c**, *PE-Ch* was found to be non-LC at room temperature. However, it exhibited a monotropic nematic (N*) phase on cooling. On first heating in DSC it showed a melting temperature at around 169.5 °C. Before melting it displayed two low energy crystal-to-crystal transitions at about 114.3 °C and 146.2 °C which could be due to some conformational reorganization of molecules by passing into different crystalline configurations. These transitions in thermal analysis (DSC) arise from the different stability of two crystalline polymorphs; evidence accompanying by polarizing optical microscopic (POM) textures and powder X-ray diffraction studies as observed in past studies.[52,53] We also observed minor structural changes at Cr–Cr transition temperatures of the compounds reported here under POM and the samples remained solid even after these transitions. On cooling, it (**2c**) showed a transition in DSC centered at 135 °C, which was stable down to room temperature. The chiral nematic phase was assigned on the basis of the observation of fan texture when viewed through a polarized light microscope: representative texture is shown as Fig. 1c. The fan texture gave the characteristic Grandjean texture upon shearing. The DSC thermogram of neat *PE-R* (**2d**) exhibited one peak at around 150.2 °C on first heating which corresponds to mesophase-to-isotropic phase transition. On cooling, the isotropic-to-mesophase transition peak appeared at 147 °C (Fig. 1d). It is noteworthy that the mesophase range of *PE-TP* is much higher compared to that for hexaalkoxytriphenylene reported earlier.[54]

X-ray diffraction studies

In order to reveal the mesophase structure and hence the supramolecular organization of these compounds, X-ray diffraction experiments were carried out using unoriented samples. X-ray diffraction patterns for all perylene-based compounds were recorded in the liquid crystalline phase while cooling from the isotropic phase. The X-ray diffraction pattern of the mesophase exhibited by cholesterol and cyanobiphenyl-based derivatives is supportive of a nematic arrangement, while triphenylene and aliphatic substituted compounds were found to demonstrate hexagonal columnar arrangement of molecules within the liquid crystalline phase.

In the N phase of compounds **2a** and **2c** two diffuse reflections were observed in the wide and the small angle region. These indicate the absence of any positional order in the mesophase and thereby exclude the existence of smectic and columnar phase structure of these oligomers, consistent with their microscopy textures.

The broad small angle reflection for **2a** showed a *d*-spacing of 16.57 Å (2θ = 5.33) in the mesophase (at 80 °C, Fig. 2a). This corresponds to the average length and diameter of the rod (∼24.4 Å) and discs (∼7.6 Å), respectively, indicating a molecularly mixed N phase (See ESI†, Fig. S18). Obviously, much smaller reflection at small angle than that of the total length of the hybrid confirms the compatibility (homogeneously mixed) of both components (disc and rod) in the mesophase and no nanophase segregation occurs between them. Similar diffraction pattern was

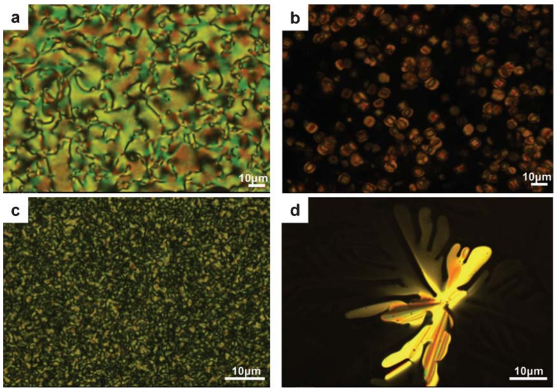

Fig. 1 Optical photomicrograph of compounds (a) **2a** (b) **2b** (c) **2c** and (d) **2d** at 80 °C, 100 °C, 125 °C and 140 °C, respectively (on cooling, crossed polarizers, scale bar 10 μm).

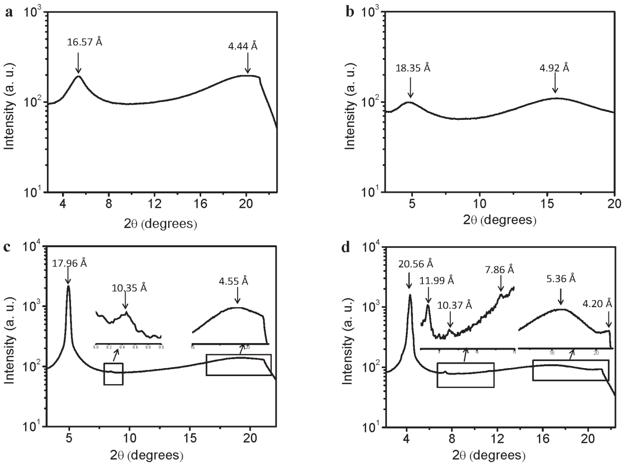

Fig. 2 The intensity profile of the X-ray pattern exhibited by *PE-CB* (a), *PE-Ch* (b), *PE-TP* (c), and *PE-R* (d) at 80 °C, 130 °C, 90 °C and 140 °C, respectively. See ESI† (Fig. S17) for X-ray diffractions pattern obtained at those temperatures.

observed for certain mesogenic compounds having both rod and disc like moieties. The small angle halos shift to 18.35 Å ($2\theta = 4.82$) at 150 °C (Fig. 2b) in the N* phase of **2c** (on cooling) which corresponds to the average length of the cholesterol moiety (~29.72 Å) and the discs (~7.6 Å) as expected. In all these two cases (**2a** and **2c**), we observed a very diffuse peak at around 4.44 Å ($2\theta = 19.79$) and 4.92 Å ($2\theta = 15.75$), respectively, indicating liquid like order. The X-ray patterns of *PE-TP* consisted of a diffuse scattering halo in the wide-angle region, centered around 4.55 Å ($2\theta = 19.23$), corresponding to the liquid-like order of the molten aliphatic chains. In the small-angle region, two reflections (Fig. 2c) were detected, with the reciprocal spacings in the ratios of $1 : 1/\sqrt{3}$, which were indexed as (10), (11), respectively. These reflections are in good agreement with a hexagonal lattice. The intercolumnar distances, a, calculated using the relation, $a = d_{10}/(\cos 30°)$, where d_{10} is the spacing corresponding to the strong peak in the small angle region ($d_{10} = 17.96$ Å at $2\theta = 4.93$), was found to be 20.7 Å. This value is lower as compared to the diffraction data reported in case of hexahexyloxytriphenylene (H6TP) and 3,4,9,10-tetra-(n-decyloxy-carbonyl)-perylene reported earlier.[47] It can be assumed that columns are dominated by triphenylene disks rather than perylene disks and these columns are arranged in hexagonal pattern to construct the mesophase. This shrinkage of the intercolumnar distance in the oligomers is expected upon covalently linking the two molecules. X-ray diffraction pattern of compound *PE-R* and its one-dimensional intensity *vs.* two theta (2θ) graph derived from the pattern are shown in the Fig. 2d. As can be seen from the Fig. 2d, in the small angle region, four peaks, one very strong and three weak reflections are seen whose d-spacings are in the ratio $1 : 1/\sqrt{3} : 1/\sqrt{4} : 1/\sqrt{7}$, consistent with a two-dimensional hexagonal lattice. In the wide-angle region, a diffuse reflection appears at 5.36 Å ($2\theta = 16.79$). This corresponds to the liquid-like order of the aliphatic chains. The relatively narrow peak at high angle region at 4.20 Å ($2\theta = 21.25$) corresponds to the core-core separation (intracolumnar distance) of the columns. Interestingly, we did not observe any distinct peak that corresponds to the core-core separation of the compound *PE-TP*. We hypothesized that the absence of the higher angle peak in case of *PE-TP* could be due to non-existence of the periodicity along the columns similar to those observed by other groups.[55] The intercolumnar distances, a, calculated by using the relation $a = d_{10}/(\cos 30°)$, where d_{10} is the spacing corresponding to the strongest peak in the small angle region ($d_{10} = 20.56$ Å at $2\theta = 4.29$), was found to be 23.75 Å. All the features fit into the well-known model for the Col$_h$ phase, in which the disc-like core of the molecules stack one on top of the other to form columns surrounded by alkyl chains and these columns in turn arrange themselves in a two-dimensional hexagonal lattice.

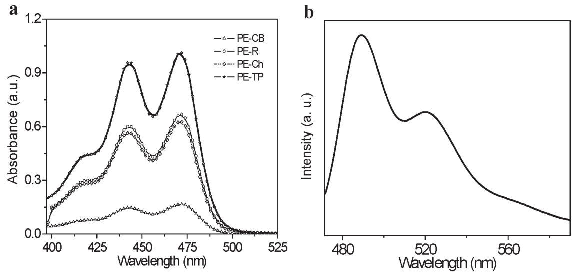

Fig. 3 (a) UV/vis absorption spectra of *PE-CB*, *PE-R*, *PE-Ch* and *PE-TP* in CHCl$_3$. (b) Representative fluorescence spectra of *PE-CB* in CHCl$_3$.

Table 2 Absorption and fluorescence data's of novel perylene-based oligomers[a]

TM	Absorption peaks (nm)	Fluorescence peaks (nm)
2a	442, 472, 416	488, 519
2b	442, 472, 416	489, 521
2c	442, 472, 416	488, 520
2d	442, 472, 418	489, 519

[a] measured in CHCl$_3$ solvent.

Absorption and fluorescence spectra

These compounds showed yellow-green fluorescence in solution even under daylight condition. No noticeable difference was witnessed for the spectral properties in solution among these perylene-based compounds indicating that the attachment of various moieties around perylene core does not affect their spectral behaviour in solution. Fig. 3 displays the typical absorption and fluorescence spectra of perylene-based hybrids (*PE-TP*, *PE-CB*, *PE-R* and *PE-Ch*) in 15 μM CHCl$_3$ solution. In all cases, the absorption bands show three peaks (including a shoulder peak at low wavelength) whereas fluorescence spectrum exhibits two peaks, characteristic of perylene core.

The absorption and fluorescence peaks have been documented in Table 2. The absorption spectrum of *PE-TP* has two peaks at 442 and 472 nm and one shoulder at 416 nm, while the fluorescence peaks appear at 488 and 520 nm. The spectra of other perylene-based compounds were similar (See ESI†, Fig. S19).

In order to understand the changes in the nanoenvironment of the perylene-based hybrid fluorophores and their ordered molecular system, fluorescence lifetime and steady state anisotropy measurements were performed in dilute solution (Table 3, 15 μM in CHCl$_3$). Interestingly, except *PE-TP*, the measured life time in all other hybrids is close to 4 ns whereas, measured life time value reported for perylene is 5.2 ns in ethanol solution.[56] The observed decrease in the fluorescence life time could be due to higher non-radiative rate involved in the processes due to a change of size and shape of the hybrid molecules and thus molecular interactions. Surprisingly, among all these perylene hybrids reported in this paper, we noted a high value of fluorescence anisotropy and shortest fluorescence lifetime in case of *PE-TP*. We hypothesized that bulky triphenylene units attached

Table 3 Fluorescence life time (measured life time) and steady state anisotropy data's of novel perylene-based oligomers

TM	Γ_{av} (ns)	Steady state anisotropy
2a	4.01	0.057
2b	2.17	0.149
2c	4.18	0.061
2d	4.04	0.031

to perylene core resulted in restricted molecular motion of the hybrid and thus increased fluorescence anisotropy. The lower anisotropy observed for *PE-R* ($r = 0.031$) could be due to higher rotational diffusion (because of less rigid molecular environment) that may occur during the lifetime of the excited state and displaces the emission dipole of the fluorophore.

Conclusions

In conclusion, a novel series of disc-rod oligomers have been synthesized for the first time consisting of a perylene core attached to which are four 4-cyanobiphenyl, triphenylene and cholesteryl units *via* flexible alkyl spacers. Whereas, attachment of *CB* and *Ch* units to the *PE* core leads to the formation of N and N* phase, respectively, *TP* and simple alkyl chain resulted a regular hexagonal mesophase. We have demonstrated that the combination of rod and disc-like moieties in the *PE-CB* and *PE-Ch* series has sufficiently perturbed the molecular shape to yield calamitic mesophases. Although biaxiality is likely to be seen at small length scales, as a result of large aspect ratios between two components, there is no direct evidence for the formation of biaxial N phase in our study. In addition, we have shown that all the hybrid materials exhibit excellent fluorescence emission properties making them suitable for various opto-electronic applications. Such materials combine an exceptionally high degree of self-organization at the nanometer scale with the advantages that LCs provide.

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