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1. Introduction

Discotic liquid crystals (DLCs) are unique self-assembled supramolecular nanoarchitectures, which typically consist of a π -conjugated disc-like polycyclic aromatic core substituted with three or more flexible insulating mantles of aliphatic chains.^{1–3} The anisotropic disc-shape molecules self-organize one on the top of another to form columnar self-assemblies due to various supramolecular weak interactions such as van der Waals forces, hydrogen bonding, π - π interaction, dipolar or quadrupolar interaction, charge transfer interactions, *etc.* DLCs mainly exhibit stable columnar and nematic mesophases. The columnar phases are acquired by one-dimensional stacking arrangement of the disc-like molecules with a long-range orientational and positional order. They attract tremendous scientific-technological interest owing to their incredible one-dimensional charge and energy migration properties along the columnar axis.⁴⁻¹³ The least ordered discotic

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Novel phenazine fused triphenylene discotic liquid crystals: synthesis, characterisation, thermal, optical and nonlinear optical properties[†]

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A straightforward synthesis of novel phenazine fused triphenylene discotic liquid crystals (DLCs) is realized. The condensation of 3,4-diaminobenzoic acid with a triphenylene-1,2-diquinone intermediate gives an acid derivative which upon esterification with aliphatic alcohols produces the corresponding monomeric ester derivatives of the phenazine fused triphenylene discotic liquid crystals. The intermediate acid derivative exhibits a rectangular columnar phase along with a high isotropic phase transition temperature. However, the monomeric ester derivatives show a hexagonal columnar mesophase over a broad temperature range and stable when decreased to room temperature upon cooling from the isotropic phase. The mesomorphic properties of the acid and monomeric ester derivatives of the phenazine fused optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction studies (XRD). The molecular structures of the intermediate and final compounds were characterised by spectral and elemental analysis. The photophysical properties of all the monomeric ester compounds were investigated in an anhydrous chloroform solvent and absorption bands around 291–472 nm and the corresponding emission bands at 658–661 nm were observed, respectively. The π -extended conjugation in these materials gives rise to high nonlinear optical properties. These materials have immense potential for use in electro-optical applications.

nematic phase (N_D) with self-organization of disc-like molecules having only a long-range orientational order is less commonly observed but it finds intriguing applications like optical compensative films used to enlarge the viewing angle of liquid crystal display (LCD) devices.^{14–18} Indeed, the functional capabilities of DLC smart materials have enormous advantages presumably because of their easy fabrication, high intrinsic charge-carrier mobility, spontaneous alignment between electrodes, self-healing and self-assembled ability, which have massive potential for use in device applications.^{13–26} The columnar self-assembly of DLCs has find applications in active components in organic semiconductor devices such as organic light emitting diodes (OLED),^{27–29} organic field effect transistors (OFETs),^{30–33} solar cells and sensors,^{34–37} etc.

Triphenylene (TP) based DLCs are the most rigorously explored scaffold in the family of DLCs exhibiting the discotic nematic phase along with other highly ordered columnar mesophases.^{1,2,38–45} Because of strong interdisc interactions such as π - π interactions associated with rigid, flat aromatic structures, DLCs often exhibit stable columnar mesophases. Presently, more than 1000 DLCs derived from the TP core are known. Accordingly, they have been described as 'the workhorses' in the field of discotics. They are alluring materials owing to their one-dimensional energy and electron transport



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properties.⁴⁶⁻⁵⁰ Significant synthetic efforts have been made to extend the TP discotic core through π -conjugation.^{51–53} However, the most convenient synthetic route involves the condensation of triphenylene-1,2-diquinone with o-phenylenediamine to generate heteroaromatic triphenylene DLCs. We have previously reported the extension of a TP core by the condensation of triphenylene-1,2-diquinone with o-phenylenediamine to produce phenanthro[a] phenazine and phenanthro[b] phenazine DLCs.^{54,55} We have also reported an imidazole fused with a TP core for the extension of heteroaromatic π -conjugation. The heteroaromatic imidazole fused TP DLCs exhibit a stable columnar phase and interesting photophysical properties.⁵⁶ Recently we have also reported that, alkanethiols and alkoxy chains containing phenazine-fused triphenylene DLCs exhibit p-type (hole) mobility of the order of 10^{-4} cm² V⁻¹ s⁻¹ in their hexagonal columnar phase.⁵⁷ Cammidge et al. reported on TP twin units that were fused via a pyrazine heteroaromatic ring, which exhibit a stable hexagonal columnar phase over a broad range of temperature.⁵⁸

In this article, we have designed and synthesised phenazine fused triphenylene based DLCs bearing a monomeric ester chain. The intermediate acid derivative exhibits a rectangular columnar phase (Col_r), while all the monomeric ester derivatives display an enantiotropic hexagonal columnar phase (Col_h) over a broad range of temperature. We anticipated that the incorporation of a monomeric ester substituted phenazine core would alter the thermal and electronic properties and, therefore may be interesting materials for device applications. Here, we present the synthesis, mesomorphic characterization, photophysical properties and nonlinear optical studies of new DLCs. The molecular structures of all the compounds were examined by using spectral and elemental analysis. The liquid crystalline properties of all DLCs were investigated by polarized optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD) studies.

2. Results and discussion

2.1. Synthesis and characterisation

The synthesis of an unsymmetrical monomeric ester containing phenazine fused triphenylene derivatives is shown in Scheme 1. The key intermediate monohydroxytriphenylene 4 was synthesised from catechol.59 Oxidation of 2-hydroxy-3,6,7,10,11-pentakis(alkyloxy)triphenylene 4 with ceric ammonium nitrate gives a triphenylene-1,2-diquinone derivative, that is, 3,6,7,10,11-pentakis(alkyloxy)triphenylene-1,2-dione 5.⁶⁰ Further it was condensed with commercially available 3,4-diaminobenzoic acid in the presence of a glacial acetic acid and toluene (7:3) solvent medium under reflux conditions to afford the corresponding intermediate inseparable acid derivatives 2,3,6,7,10-pentaalkoxyphenanthro[9,10-a]-14-carboxylic acid 6(i) and its regioisomer, 2,3,6,7,10-pentaalkoxyphenanthro[9,10-a]-13-carboxylic acid 6(ii). This mixture is designated as 6. The esterification of 6 with aliphatic alcohols produces an inseparable mixture of final mesogenic ester derivatives 7(i) and 7(ii), designated as 7. The chromatographic purification of the intermediate and the final



Scheme 1 (i) alkyl halide, anhy. K₂CO₃, DMF, reflux, 24 h; (ii) anhy. FeCl₃, DCM, 15 min, r.t.; (iii) B-bromocatecholborane, DCM, 24 h, r.t.; (iv) ceric ammonium nitrate, acetonitrile, r.t., 30 min; (v) 3,4-diaminobenzoic acid, acetic acid : toluene (7 : 3), 100 °C, 8 h; (vi) alkyl alcohol, EDCI-HCl, HOBt, DMAP, DCM, 24 h, r.t.

mesogens using silica gel and recrystallization with an appropriate solvent ensure high purity. The intermediate acid derivative **6** is sparingly soluble in organic solvents like chloroform and dichloromethane. However, the final compounds (7**a**–7**e**) were freely soluble in all chlorinated solvents.

2.2. Thermal properties

The thermotropic liquid crystalline textures of all the compounds (6, 7a–7e) were investigated by POM under cross polarisers (ESI,† Fig. S1). The phase transition temperature (peak in °C) along with the enthalpy of phase transition values (ΔH in kJ mol⁻¹) were examined with the help of DSC measurements upon both heating and subsequent cooling at a scan rate of 10 °C min⁻¹, under a nitrogen atmosphere and the thermal values are summarised in Table 1.

The intermediate acid derivative 6 exhibits an enantiotropic Col_r phase over a broad range of temperature along with two types of endothermic phase transitions from the Cr phase to Col_r at lower temperature and Col_r to the isotropic phase at higher temperature. The peak temperature at 95.3 °C along with the corresponding enthalpy of phase transition ($\Delta H = 45.30 \text{ kJ mol}^{-1}$) is attributed to the crystalline phase to Col_r phase transition while the peak temperature at 237.4 °C ($\Delta H = 25.40 \text{ kJ mol}^{-1}$) is referred to the Col_r phase to isotropic liquid transition (ESI,† Fig. S2). Upon slow cooling under a POM, the appearance of a microscopic texture at 232.7 °C revealed the existence of the Col_r phase, which crystallizes at 84 °C. The Col_r phase structure was confirmed by XRD investigations as discussed later.

Similarly, all the ester derivatives (7a–7e) exhibit two types of endothermic phase transitions from Cr to Col_h at lower temperature and Col_h to isotropic phase at higher temperature. The Col_h phase is retained up to room temperature, upon cooling from the isotropic liquid phase. Compound 7a exhibited a crystal–crystal transition at 46.4 °C ($\Delta H = 10.40 \text{ kJ mol}^{-1}$) and melted to the Col_h phase at 68 °C with an enthalpy change ($\Delta H = 40.52 \text{ kJ mol}^{-1}$) and transformed to isotropic liquid at 200.1 °C ($\Delta H = 4.31 \text{ kJ mol}^{-1}$) (ESI,† Fig. S3). Upon cooling under a POM, the appearance of rectilinear defect textures was observed, which are characteristics of the hexagonal columnar mesophase as shown in Fig. 1a, viewed at 100× magnification. On the other hand, compounds 7b and 7c show the Cr and Col_h phases at 71.1 °C ($\Delta H = 47.88 \text{ kJ mol}^{-1}$) and 63.4 °C ($\Delta H = 46.17 \text{ kJ mol}^{-1}$), respectively, and a phase transition from the Col_h phase to the



Fig. 1 Polarised optical microscopy textures recorded in the hexagonal columnar phase, upon cooling from isotropic liquid. (a) Compound **7a** at 176 °C, viewed at 100× magnification, scale bar = 100 μ m and (b) compound **7d** at 122 °C, and viewed at 200× magnification, scale bar = 50 μ m, respectively.

isotropic phase at 207.2 °C (ΔH = 8.12 kJ mol⁻¹) and 155.2 °C $(\Delta H = 1.12 \text{ kJ mol}^{-1})$, respectively (ESI,† Fig. S4). Upon cooling under a POM from the isotropic phase, compounds 7b and 7c showed the appearance of a Col_h texture at 205.7 $^\circ\mathrm{C}$ and 154.1 °C, respectively. Similarly, branched chain compounds 7d and 7e exhibit an enantiotropic phase transition from the Cr phase to the Col_h phase at a lower temperature of 69.7 °C $(\Delta H = 67.66 \text{ kJ mol}^{-1})$ and 43 °C ($\Delta H = 54.61 \text{ kJ mol}^{-1}$), respectively, and a phase transition from the Col_b phase to the isotropic phase at 191.7 °C ($\Delta H = 0.58$ kJ mol⁻¹) and 173.1 °C ($\Delta H = 8.31$ kJ mol⁻¹), respectively (ESI,† Fig. S5 and S6). Under a POM, compound 7d exhibits a fan shaped texture with large domains, upon slow cooling from the isotropic liquid phase as shown in Fig. 1b, viewed at 200× magnification. On the other hand, compound 7e displayed the mesophase at 171.4 °C, upon cooling from isotropic liquid. Eventually, it can be noticed that the acid derivative shows a much higher isotropic temperature in comparison to the ester derivatives, which could be due to the formation of H-bonding.61 As a representative, the DSC thermograms of compound 7b are shown in Fig. 2.

2.3. X-ray diffraction studies

The mesophase structures of the acid and other ester derivatives (6 and 7a-7e) were investigated with the help of X-ray diffraction studies using unoriented liquid crystal samples filled in Lindemann capillaries. The XRD data were recorded in the columnar mesophase at both heating and cooling temperatures and the values are summarised in Table 2 and ESI† Fig. S7, respectively. The XRD diffractogram obtained for acid compound 6 at 120 °C upon cooling is shown in Fig. 3a

Table 1 Phase transition temperatures of all the mesogens 6 & 7a-7e (both heating and cooling cycles). Cr = crystalline phase; Col_r = rectangular columnar phase; Col_h = hexagonal columnar phase; I = isotropic phase

	Phase transition peak temperature (°C); (ΔH , [kJ mol ⁻¹])			
Compound	Second heating scan	Second cooling scan		
6 7a 7b 7c 7d 7e	$ \begin{array}{c} {\rm Cr}\;95.3\;[45.30]\;{\rm Col_r}\;237.4\;[25.40]\;{\rm I}\\ {\rm Cr_1}\;46.4\;[10.40]\;{\rm Cr_2}\;68.0\;[40.52]\;{\rm Col_h}\;200.1\;[4.31]\;{\rm I}\\ {\rm Cr}\;71.1\;[47.88]\;{\rm Col_h}\;207.2\;[8.12]\;{\rm I}\\ {\rm Cr}\;63.4\;[46.17]\;{\rm Col_h}\;155.2\;[1.12]\;{\rm I}\\ {\rm Cr}\;69.7\;[67.66]\;{\rm Col_h}\;191.7\;[0.58]\;{\rm I}\\ {\rm Cr}\;43.0\;[54.61]\;{\rm Col_h}\;173.1\;[8.31]\;{\rm I}\\ \end{array} $	I 232.7 [-23.80] Col _r 84 [-30.53] Cr I 197.1 [-4.41] Col _h 16.9 [-53.31] Cr I 205.7 [-7.41] Col _h 22.6 [-47.45] Cr I 154.1 [-2.52] Col _h 31.6 [-62.89] Cr I 180.4 [-0.63] Col _h 21.8 [-57.55] Cr I 171.4 [-7.96] Col _h 21 [-57.51] Cr		



(Table 2). Compound **6** showed two strong reflections in the small angle region with a high intensity and several additional weak reflections in the wide angle regions of low intensity (Fig. 3a). In the XRD pattern, the *d*-spacings of the first peak and the third peak, and the second peak and the fourth peak are in the ratio of 1:1/2 owing to the lamellar arrangement of the discotic structure in two different directions. The two intense peaks located in the small angle region are most commonly detected for the rectangular columnar phase. These reflections were characterised as (200), (110), (400), (020), (220) and (600) of a two-dimensional rectangular lattice with lattice spacings a = 69.36 Å and b = 29.47 Å, respectively. In the wide angle region, a broad halo reflection around 4.76 Å and a

Table 2 XRD data of compounds 6 and 7a-7

shoulder peak at 3.63 Å were observed, which correspond to the average distance between the alkyl chains (h_a) and the core-core separation of the columnar stacks. Similarly, an XRD pattern was obtained for the ester derivatives (7a-7e) in the hexagonal columnar phase (Fig. 3b) (Table 2). All the ester derivatives show an ascending order of the diffraction angle along with d-spacings of the first reflection to the second reflection in a ratio of $1:1/\sqrt{3}:1/2:1/\sqrt{7}$, respectively. These diffraction values correspond to the two-dimensional hexagonal columnar phase. The broad halo peak at the wide angle region corresponds to the average distance between the alkyl chains, and the shoulder peak shows the average distance between core-core separation. The intercolumnar distance (a) can be calculated by adopting the relation $a = d_{10}/(\cos 30^\circ)$, where the d_{10} spacing corresponds to the highest intensity peak in the small angle region (Table 2). As a representative, the XRD diffractogram obtained for compound 7e in the hexagonal columnar phase at 70 °C upon cooling is shown in Fig. 3b. The highest intensity peak in the small angle region shows d-spacing, $d_1 = 25.68$ Å and other three d-spacings corresponding to a lower intensity was observed at $d_2 = 14.81$ Å, $d_3 = 12.85$ Å and $d_4 = 9.70$ Å, respectively. All the values agree with the hexagonal columnar lattice parameters. The broad halo peak in the wide angle region at approximately 4.52 Å corresponds to the average distance between the alkyl chains. The prominent peak at 3.50 Å was assigned to the π - π stacking of the aromatic discotic cores.

3. Photophysical properties

The photophysical properties of the monomeric ester derivatives (7a-7e) were investigated by UV-Vis and photoluminescence spectroscopy (PL) in a very dilute solution as shown in

Compound	Temperature (°C)	2θ (degrees)	<i>d</i> -spacings/Å observed (calculated)	Miller indeces	Phase (lattice constant)	Alkyl-chain length (Å)	Core–core separation (Å)	Intercolumnar distance (a) (Å)
6	120	2.63	33.65	200	$\text{Col}_{r} a = 69.36, b = 29.47$	4.76	3.63	31.32
		3.25	27.14	110				
		5.11	17.24 (17.34)	400				
		6.01	14.68 (14.73)	020				
		6.56	13.45 (13.56)	220				
		7.69	11.48 (11.56)	600				
7a	130	3.59	24.54 (24.53)	100	$Col_h a = 28.33$	4.64	3.55	28.33
		6.24	14.13 (14.16)	110				
		7.21	12.23 (12.26)	200				
7 b	110	3.51	25.10 (25.09)	100	$Col_{h} a = 28.98$	4.58	3.52	28.98
		6.11	14.44 (14.48)	110				
		7.06	12.50 (12.54)	200				
		9.34	9.45 (9.48)	210				
7 c	110	3.332	26.48 (26.47)	100	$Col_h a = 30.57$	4.84	3.58	30.57
		5.77	15.28 (15.27)	110				
		6.66	13.24 (13.23)	200				
		8.71	10.14(10.00)	210				
7 d	85	3.51	25.41 (25.40)	100	$Col_h a = 29.34$	4.53	3.50	24.64
		6.11	14.50 (14.66)	110				
		7.06	12.57 (12.70)	200				
7e	70	3.43	25.68 (25.67)	100	$Col_{h} a = 29.65$	4.52	3.50	29.65
		5.95	14.81(14.82)	110				
		6.87	12.85 (12.83)	200				
		9.10	9.70 (9.70)	210				

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Fig. 3 XRD diffractograms of (a) acid derivative **6**, recorded at 120 °C upon cooling in the Col_r phase, (b) ester derivative **7e** recorded at 70 °C upon cooling in the Col_n phase.

Fig. 4 and the data are presented in Table 3. Both absorption and emission spectra were recorded by dissolving the liquid crystalline compounds in an anhydrous chloroform solvent and recorded at room temperature. The absorption spectra of all the monomeric ester derivatives were similar, irrespective of the number of alkyl chains with maximum absorption bands located below 580 nm as shown in Fig. 4a. The maximum absorption bands at 290, 312, 338, 352 nm, along with shoulder peaks at 240-275 nm observed at shorter wavelengths are attributed to the π - π * transition, while the intense peak at 472 nm corresponds to the n- π^* transition at a longer wavelength. The maximum absorption at the longer wavelengths may be due to the extended π -conjugation of the heteroaromatic structure, which causes an increase in the intensity of absorption. The intensity of light absorption eventually relies on the number of molecules that absorb light at a given wavelength, which presumably causes a bathochromic shift. Similarly, the emission spectra of all the

Table 3 Photophysical properties of the monomeric ester derivatives (7a-7e)

Compound	Absorption λ_{abs}/nm	Molar absorption coefficient (ε/L mol ⁻¹ cm ⁻¹)	Emission $\lambda_{\rm em}/{\rm nm}$
7a	292, 312, 339, 352, 472	$\begin{array}{l} 4.0714 \times 10^{6} \\ 4.8422 \times 10^{6} \\ 3.1202 \times 10^{6} \\ 4.5197 \times 10^{6} \\ 3.9871 \times 10^{6} \end{array}$	661
7b	292, 312, 338, 352, 472		658
7c	293, 312, 338, 352, 472		659
7d	292, 311, 337, 352, 472		659
7e	291, 311, 338, 352, 472		660
7c	293, 312, 338, 352, 472	$3.1202 \times 10^{6} \ 4.5197 \times 10^{6} \ 3.9871 \times 10^{6}$	659
7d	292, 311, 337, 352, 472		659
7e	291, 311, 338, 352, 472		660

compounds (7a–7e) were obtained by dissolving the compounds in an anhydrous chloroform solvent and exciting the solution of all the compounds at $\lambda_{ex} = 474$ nm as shown in Fig. 4b. The emission spectra of all the compounds show strong emission bands around 658–661 nm. No significant changes were observed with increasing number of alkyl chain lengths.



Fig. 4 (a) UV-Visible absorption and (b) photoluminescence emission spectra of all the final compounds (7a-7e).

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Fig. 5 (a) Open aperture Z-scan curves for 7a-7e compounds at an energy of 3 μ J. Solid curves are numerical fits to the experimental data obtained using eqn (4). (b) Normalized transmission as a function of input laser fluence, calculated from the open aperture Z-scan measurements.

4. Nonlinear optical transmission studies

Nonlinear optical transmission measurements were performed by dissolving the monomeric ester compounds (7**a-7e**) in an anhydrous chloroform solvent taken in a 1 mm cuvette using the open aperture Z-scan technique at an excitation wavelength of 532 nm. The samples were excited using 5 ns laser pulses generated from a frequency doubled Nd:YAG laser (Continuum Minilite I).

In our open aperture Z-scan experiment, the laser beam was focused using a plano-convex lens (f = 10 cm). The transmission was recorded at different positions with respect to the beam focus (z = 0). The samples experience a different fluence at each position, with the maximum fluence at the focus and the linear transmission of the samples was fixed at 65% for a wavelength of 532 nm. The Z scans measured for all the samples at a laser pulse energy of 3 µJ are given in Fig. 5. From the Z scan curve it is clear that the samples exhibit strong optical limiting properties as the transmission decreases at higher laser fluence.

For a spatially Gaussian laser beam, the fluence (Fin(z)) at any position *z* can be obtained from the relation:

$$F_{\rm in}(z) = 4(\ln 2)^{\frac{1}{2}} E_{\rm in} / \pi^{\frac{3}{2}} \omega(z)^2$$
 (1)

with the beam radius $\omega(z)$ given by

$$\omega(z) = \omega_0 \left(1 + \left(\frac{z}{z_0}\right)^2 \right)^{\frac{1}{2}}$$
(2)

where ω_0 is the focal spot radius, and z_0 is the Rayleigh length given by $z_0 = \pi \omega_0^2 / \lambda$. We found that the nonlinear transmission has contributions from both excited state absorption (ESA)⁶²

and saturable absorption (SA).⁶³ The net nonlinear absorption coefficient is given by,

$$\alpha(I) = \frac{\alpha_0}{\left(1 + \frac{I}{I_s}\right)} + \beta I \tag{3}$$

where I_s is the saturation intensity (W m⁻²) and β is the excited state absorption coefficient (W m⁻²). I_s and β can be obtained by numerically fitting the light propagation equation to the measured transmission data:

$$\frac{\mathrm{d}I}{\mathrm{d}x} = -\left[\frac{\alpha_0}{\left(1 + \frac{I}{I_{\mathrm{s}}}\right)} + \beta I\right]I\tag{4}$$

where x is the propagation distance through the sample. The obtained values are tabulated in Table 4.

We have observed that the excited state absorption and saturable absorption properties of the molecules give rise to high nonlinear optical properties. The delocalization of π electrons results from extended π -conjugation in the triphenylene fused phenazine ester derivatives, which increases the nonlinear optical properties in these DLCs.

Table 4 ESA coefficient (β) and saturation intensity (I_{sat}) calculated for the samples (**7a–7e**) from the data given in Fig. 5a and b

Compounds	Laser pulse energy (µJ)	Sample linear transmission (%)	Beta (β) $(\times 10^{-10} \text{ mW}^{-1})$	$I_{\rm sat}$ (×10 ¹¹ W m ⁻²)
7a	3	65	10.8	8.5
7b	3	65	10.2	6.0
7c	3	65	9.5	8.0
7d	3	65	9.4	8.5
7e	3	65	9.2	6.0

5. Experimental section

5.1. General procedure for the synthesis of the intermediate and final compounds

The intermediate compound 3,6,7,10,11-pentakis(dodecyloxy)triphenylene-1,2-diones 5 were synthesised as reported previously and confirmed by spectral and elemental analysis.⁶⁰ The intermediate 3,4-diamino benzoic acid was obtained from a commercial source. Compound **6** is not characterised by ¹³C NMR due to insufficient solubility in the CDCl₃ solvent.

5.1.1. Synthesis of 2,3,6,7,10-pentakis(dodecyloxy)phenanthro[9,10-a]phenazine-13-carboxylic acid (6). A mixture of compound 5 (0.5 g, 1 equiv.) and 3,4-diaminobenzoic acid (1.1 equiv.) was dissolved in a mixture of glacial acetic acid: toluene solvent (7:3). The resultant reaction mixture was refluxed at 100 °C for 8 h. After completion of the reaction, the reaction mixture was cooled to room temperature and subsequently quenched with ice cold water, and extracted with dichloromethane (3 \times 100 mL). The combined extracts were dried over Na₂SO₄ and the solvent was evaporated under vacuum. The crude compound was purified by column chromatography using silica gel (n-hexane/dichloromethane 6:4). Recrystallisation of the pure product with ethanol affords a red colour solid, 6, yield: 80%. IR (film) ν_{max} : 2953.12, 2908.75, 2852.81, 1691.63, 1612.54, 1454.38, 1377.22, 1261.49, 1166.97, 1101.39 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 10.57 (s, 1H), 8.84 (s, 1H), 8.26-8.17 (m, 2H), 7.75-7.58 (m, 4H), 4.42-4.34 (m, 4 H), 4.17-4.01 (m, 6H), 2.14-2.08 (m, 4H), 1.94-1.87 (m, 8H), 1.66-1.21 (m, 91H), 0.81 pm (m, 15H); elemental analysis: C₈₅H₁₃₄N₂O₇, calculated: C, 78.77; H, 10.42; N, 2.16. % found: C, 78.02; H, 10.59; N, 2.32. ¹H NMR spectra are shown in the ESI,† Fig. S8.

5.1.2. Synthesis of the monomeric ester discotic mesogens (7a–7e). All the mesogenic derivatives were prepared by the esterification reaction between the intermediate acid compounds 6 and various aliphatic alcohols. The general method is depicted as follows.

In a two neck-flask containing compound 6 (0.2 g, 0.154 mmol), alkyl alcohol (1.2 eq.) and a catalytic amount of 4-dimethylaminopyridine (DMAP) (0.01 g, 0.07 mmol) were added in a dry dichloromethane (DCM) solvent (50 mL) under argon at room temperature. After stirring for 10 min, *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC-HCl) (0.047 g, 0.30 mmol) and *N*-hydroxybenzotriazole (HOBt) (0.04 g, 0.26 mmol) were added. The resulting mixture was stirred at room temperature for 24 h. After completion of the reaction, water was added and extracted with DCM (3 × 50 mL). The combined extracts were dried over Na₂SO₄ and concentrated under vacuum. The residue was purified by column chromatography using silica gel (*n*-hexane/dichloromethane 9:1). Recrystallisation of the pure product with ethanol affords a red colour solid, **7a–7e**. Yield: 80–90%.

Hexyl 2,3,6,7,10-pentakis(dodecyloxy)phenanthro[9,10-a]phenazine-13-carboxylate (7a). IR (film) ν_{max} : 2951, 2918, 2852, 1716, 1560, 1518, 1454, 1377, 1340, 1263, 1182, 1071 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 10.70 (s, 1H), 8.95 (s, 1H), 8.41-8.35 (m, 2H), 8 (s, 1H), 7.89-7.86 (m, 3H), 4.44 (t, J = 6.5 Hz, 4H), 4.38 (t, J = 6.5 Hz, 2H), 4.25–4.19 (m, 6H), 2.12–2.11 (m, 4H), 2.09–2 (m, 6H), 1.93–1.77 (m, 2H), 1.60–1.16 (m, 96H), 0.86 (t, J = 6.5 Hz, 3H), 0.80 ppm (t, J = 6 Hz, 15H); ¹³C NMR (125 MHz, CDCl₃): $\delta = 165.96$, 151.58, 151.11, 149.62, 148.90, 148.34, 145.44, 141.70, 140.10, 138.37, 132.08, 131.78, 130.62, 130.17, 128.78, 127, 124.91, 124.68, 122.64, 118.16, 112.42, 108.17, 106.53, 106.34, 105.80, 69.96, 69.77, 69.64, 69.28, 68.90, 65.81, 31.95, 31.55, 29.77, 29.71, 29.69, 29.61, 29.57, 29.49, 29.41, 29.39, 29, 28.82, 26.33, 26.25, 25.77, 22.71, 22.61, 14.13 ppm; elemental analysis: C₉₁H₁₄₆N₂O₇, calculated: C, 79.19; H, 10.66; N, 2.03. % found: C, 79.28; H, 10.73; N, 1.99. ¹H NMR and ¹³C NMR spectra are shown in the ESI,† Fig. S9.

Decyl 2,3,6,7,10-pentakis(dodecyloxy)phenanthro[9,10-a]phenazine-13-carboxylate (7b). IR (film) ν_{max} : 2955, 2924, 2852, 1718, 1618, 1518, 1454, 1377, 1313, 1263, 1168, 1070 cm^{-1} ; ¹H NMR (500 MHz, CDCl₃): δ = 10.69 (s, 1H), 8.93 (s, 1H), 8.38-8.36 (m, 2H), 7.97 (s, 1H), 7.87–7.84 (m, 3H), 4.43 (t, J = 6.5 Hz, 4H), 4.38 (t, J = 6.5 Hz, 2H), 4.23-4.19 (m, 6H), 2.10-2.01 (m, 2H), 1.93-1.89 (m, 2H), 1.89-1.78 (m, 8H), 1.62-1.57 (m, 13H), 1.54-1.16 (m, 91), 0.81-0.79 ppm (m, 18H); ¹³C NMR (125 MHz, $CDCl_3$: $\delta = 165.94$, 151.55, 151.09, 149.62, 148.89, 148.32, 145.43, 141.67, 140.07, 138.35, 132.08, 131.75, 130.59, 130.13, 128.75, 126.99, 124.92, 124.66, 122.63, 118.14, 112.44, 108.17, 106.54, 106.32, 105.80, 69.95, 69.77, 69.62, 69.27, 68.89, 65.80, 31.95, 31.91, 29.79, 29.76, 29.74, 29.71, 29.61, 29.57, 29.51, 29.41, 29.34, 29.01, 28.87, 26.33, 26.25, 26.09, 22.70, 14.11 ppm; elemental analysis: C₉₅H₁₅₄N₂O₇, calculated: C, 79.44; H, 10.81; N, 1.95. % found: C, 79.50; H, 10.87; N, 1.21. ¹H NMR and ¹³C NMR spectra are shown in the ESI,† Fig. S10.

Hexadecyl 2,3,6,7,10-pentakis(dodecyloxy)phenanthro[9,10-a]phenazine-13-carboxylate (7c). IR (film) ν_{max} : 2956, 2918, 2852, 1718, 1616, 1518, 1454, 1377, 1338, 1263, 1182, 1078 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 10.66 (s, 1H), 8.89 (s, 1H), 8.38– 8.33 (m, 2H), 7.91 (s, 1H), 7.84–7.81 (m, 3H), 4.41–4.36 (m, 6H), 4.23-4.16 (m, 6H), 2.10-2.08 (m, 2H), 2.03-2.0 (m, 2H), 1.93-1.90 (m, 6H), 1.81-1.57 (m, 2H), 1.58 (m, 8H), 1.37-1.16 (m, 108H), 0.79 ppm (t, J = 6 Hz, 18H); ¹³C NMR (125 MHz, CDCl₃): $\delta = 165.93, 151.49, 151.04, 149.57, 148.83, 148.26, 145.39,$ 141.62, 140.01, 138.28, 132.06, 131.69, 130.55, 130.10, 128.71, 126.93, 124.90, 124.61, 122.58, 118.06, 112.38, 108.06, 106.44, 106.22, 105.70, 69.89, 69.73, 69.55, 69.23, 68.86, 65.80, 31.96, 29.81, 29.78, 29.73, 29.68, 29.64, 29.60, 29.53, 29.42, 29.38, 28.87, 26.35, 26.26, 26.10, 22.71, 14.13 ppm; elemental analysis: C101H166N2O7, calculated: C, 79.79; H, 11; N, 1.84. % found: C, 79.86; H, 11.05; N, 1.88. ¹H NMR and ¹³C NMR spectra are shown in the ESI,† Fig. S11.

3,7-Dimethyloctyl 2,3,6,7,10-pentakis(dodecyloxy)phenanthro-[9,10-a]phenazine-13-carboxylate (7d). IR (film) ν_{max} : 2951, 2924, 2852, 1716, 1618, 1518, 1454, 1377, 1313, 1263, 1182, 1078 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 10.71 (s, 1H), 8.96 (s, 1H), 8.41–8.35 (m, 2H), 8.02 (s, 1H), 7.90–7.87 (m, 3H), 4.46–4.42 (m, 6H), 4.24–4.19 (m, 6H), 2.11 (m, 2H), 2.02 (m, 2H), 1.93–1.89 (m, 6H), 1.62 (m, 6H), 1.59–1.16 (m, 96H), 0.80 ppm (m, 24H); ¹³C NMR (125 MHz, CDCl₃): δ = 164.93, 150.57, 150.10, 148.62, 147.90, 147.34, 144.43, 139.10, 130.70, 129.15, 127.74, 126, 123.89, 68.95, 68.75, 68.63, 68.27, 67.88, 63.33, 38.23, 36.22, 34.71, 30.92, 29.11, 28.74, 28.72, 28.68, 28.66, 28.57, 28.53, 28.46, 28.37, 28.35, 27.97, 26.95, 25.30, 25.21, 23.64, 21.67, 21.58, 18.67, 13.09 ppm; elemental analysis: $C_{95}H_{154}N_2O_7$, calculated: C, 79.44; H, 10.81; N, 1.95. % found: C, 79.68; H, 10.93; N, 2.06. ¹H NMR and ¹³C NMR spectra are shown in the ESI,† Fig. S12.

2-Hexyldecyl 2,3,6,7,10-pentakis(dodecyloxy)phenanthro[9,10-a]phenazine-13-carboxylate (7e). IR (film) ν_{max} : 2953, 2924, 2852, 1720, 1614, 1514, 1454, 1377, 1303, 1263, 1182, 1078 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 10.79 (s, 1H), 9.07 (s, 1H), 8.52-8.45 (m, 2H), 8.15 (s, 1H), 8.01-7.99 (m, 3H), 4.59-4.54 (m, 4H), 4.40–4.30 (m, 6H), 4.23–4.20 (m, 2H), 2.11–2.08 (m, 2H), 2.03-1.90 (m, 7H), 1.69-1.26 (m, 116H), 0.91-0.94 ppm (m, 21H); ¹³C NMR (125 MHz, CDCl₃): δ = 166.06, 151.58, 151.13, 149.64, 148.92, 148.40, 145.46, 141.72, 140.17, 138.38, 132.07, 131.88, 130.62, 130.21, 128.77, 127.03, 124.91, 124.71, 122.65, 118.21, 112.41, 108.20, 106.55, 106.37, 105.83, 69.98, 69.77, 69.66, 69.29, 68.88, 68.38, 37.55, 31.95, 31.91, 31.88, 31.45, 30.01, 29.79, 29.77, 29.71, 29.68, 29.64, 29.60, 29.56, 29.49, 29.41, 29.38, 29.34, 28.99, 26.82, 26.79, 26.40, 26.24, 22.71, 22.67, 14 ppm; elemental analysis: C101H166N2O7, calculated: C, 79.79; H, 11; N, 1.84. % found: C, 79.91; H, 11.28; N, 1.96. ¹H NMR and ¹³C NMR spectra are shown in the ESI,† Fig. S13.

6. Conclusions

The synthesis and characterisation of five novel extended π -conjugated monomeric ester containing phenazine fused triphenylene discotic liquid crystals are reported. The intermediate acid derivative **6** exhibits a rectangular columnar phase (Col_r) over a broad range of temperature, while the monomeric ester derivatives exhibit a hexagonal columnar phase, which remains stable till room temperature upon cooling from the isotropic phase. All the ester derivatives exhibit strong photoluminescence properties in an anhydrous chloroform solvent upon excitation at 474 nm. The π -extended conjugation in the triphenylene fused phenazine based DLCs enhance the nonlinear optical properties. Such ordered supramolecular structures may find applications in various semiconducting devices.

Conflicts of interest

There are no conflicts to declare.

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