CHEMISTRY A European Journal



Accepted Article Title: Room temperature columnar nematic and soft crystalline columnar assemblies of a new series of perylene-centered disc tetramers Authors: Santanu Kumar Pal, Indu Bala, Santosh Prasad Gupta, and Joydip De This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article. To be cited as: Chem. Eur. J. 10.1002/chem.201702181 Link to VoR: http://dx.doi.org/10.1002/chem.201702181

Supported by ACES



WILEY-VCH

Room temperature columnar nematic and soft crystalline columnar assemblies of a new series of perylene-centered disc tetramers

Indu Bala,^[a] Santosh Prasad Gupta,^[a] Joydip De,^[a] and Santanu Kumar Pal^[a]

Abstract: Three new oligomeric perylene (PE) tetraester derivatives are reported consisting of a PE-based core attached to which are four pentaalkynylbenzene units via flexible alkyl spacers. These derivatives were investigated for their mesomorphic properties, thermal, photophysical and electrochemical behaviour. Small and wide angle X-ray scattering (SAXS/WAXS) studies were performed to deduce the exact nature of the phases. In order to resolve indexing, overlapping reflections and facilitate their GISAXS/GIWAXS experiments were carried out on oriented thin films on ITO coated glass substrate. The corresponding electron density maps were derived from the intensities observed in the diffraction pattern. Whereas, compounds with shorter alkyl spacers (n = 6 and 8) were found to self-organize into soft crystalline columnar assemblies, the higher one (n = 10) exhibits a liquid crystal (LC) columnar nematic mesophase. This is in contrast to previous reports that describe highly symmetric 2D hexagonal and rectangular columnar structures of PE-based mesogens. The morphology of self-assembly was found to transform from soft crystal columnar to nematic columnar phase through simple variation in the number of alkyl spacers. All the compounds were found to exhibit excellent fluorescence emission properties with a very good quantum yield and large band gap. Beside high solubility and good quantum yield these compounds can serve as standards to measure quantum yields of unknown samples. These compounds also display green luminescence which may find applications for various optoelectronic devices.

Introduction

Columnar (Col) assemblies in which molecules are selforganized into an ordered supramolecular architecture and having unique physical properties are useful to the realization of many optoelectronic applications.^[1a] This is because in the Col phase, molecules are stacked one top of another due to strong π - π interactions between the poly aromatic core with significant overlap of *p*-orbitals, which help in one-dimensional charge carrier migration.^[1a] Discoid mesogens formed by disc-shaped molecules *viz.* hexa-substituted benzenes, triphenylenes, truxenes, perylenes, dibenzopyrenes, anthraquinones *etc.* are reported for the generation of such columnar phases.^[1] Among them, perylene and its derivatives have gained particular

[a] Ms. I. Bala, Dr. S. P. Gupta, Mr. J. De, and Dr. S. K. Pal* Department of Chemical Sciences Indian Institute of Science Education and Research (IISER) Mohali Sector-81, Knowledge City, Manauli-140306, India E-mail: <u>skpal@iisermohali.ac.in</u>, santanupal.20@gmail.com

Supporting information for this article is given via a link at the end of the document.

attention due to their unique features such as high thermal and chemical stability, easy functionalization, large band gap, nearunity fluorescence quantum yields in the molecular state, *n*-type semiconductor properties and so on.^[2] Due to these properties, they are ideal candidates for fabricating organic devices such as organic solar cells,^[3] organic field effect transistors (OFETs),^[4] fluorescent sensors,^[5] organic light-emitting diodes (OLEDs)^[6] etc. For example, fluorescent perylene LCs have been found to be useful as luminescent electron transport material in OLEDs.^[6] Perylene imides (mono- and di-) have been used in bulkheterojunction solar cells as well as orbital and color tuning.^[7] Recently, we have reported electroluminescent behaviour of bay annulated perylene tetraesters as emissive layers in OLEDs.^[8] In general, the optical and electronic properties of these derivatives are due to local π - π interactions of the perylene chromophore that lead to molecular aggregation and these aggregations further provide means for efficient electron conduction within the aggregates.^[9,10] Besides, perylene derivatives (bisimides and tetraesters) are found to show crystalline as well as LC phases considering their flexibility of the core as an important parameter for the supramolecular self-assembly.

Certainly, room temperature columnar mesophase with a wide temperature range is suitable for practical applications in electronic devices. Given that perylene has several positions available for structural modification with a variety of substituents in the core, their mesomorphic, optical and electronic properties can be tuned and tested easily for such type of applications.^[11] Therefore, properly substituted room temperature LC perylene derivatives with good self-assembly properties are highly desired for practical point of view.

Literature survey reveals a wide range of PE LCs based on pervlene bisimides.^[12-18] But, there are a very few reports for pervlene tetraesters exhibiting LC behaviour.^[19,20] Unfortunately, most of the reported PE-tetraester compounds show 1) LC mesophase at higher temperature^[19] [only a few of them show room temperature (RT) LC behaviour^[20]] and 2) self-assemble into either a columnar hexagonal or a columnar rectangular mesophase.^[19,20] In contrary, implementation of discogens in devices necessitates Col phase at room temperature along with the formation of highly ordered phase over a wide temperature range.^[21] To attain such kind of mesophases at RT and improve their usability in devices certain structural modifications and further understanding of packing in the mesophases are required. In this paper, we report a new class of luminescent materials based on oligomeric PE tetraesters and show that attaching four pentaalkynylbenzene units to the PE core via flexible spacers helps to improve the thermal behaviour leading to RT soft crystal columnar and nematic columnar assemblies of these hybrids. In addition, we have demonstrated how the simple variation of alkyl chain leads to different self-assembly behaviour (via X-ray scattering and electron density mapping) which serve to further understand the packing in the mesophase.

10.1002/chem.201702181

WILEY-VCH

It should be noted that because of electron withdrawing ester groups, PE tetraesters are less electron deficient than perylene bisimides suggesting that former materials could be effectively used as hole-transporting emissive layers in OLEDs.^[19c,22,23] As mentioned earlier, there are only a few reports of perylene tetraesters LCs exhibiting room temperature mesophase which limits their widespread use in applications. With this idea keeping in mind we sought to explore new strategies to functionalize the PE tetraesters that bring down the mesophase behaviour down to room temperature over a wide range. In literature, the major practice to lower down the temperature is to introduce branched chains. The use of the branched chains often reduces melting and isotropic temperatures because of increased disorder and stereoheterogenity but, do not affect the type of mesophase in many cases. Alternatively, the attachment of multiynes to a discotic core leads to room temperature discotic phases.^[24] For example, we have reported that linking a pentaalkynylbenzene unit with a triphenylene core through flexible alkyl spacer containing a short rigid ester group in centre leads to columnar mesophase at ambient temperature.^[25a] Room-temperature columnar structures over a long range have been reported using multialkynylbenzene-bridged triphenylenebased dyad systems.^[25b] In this paper, an oligomeric approach has been employed by connecting four pentaalkynylbenzene units to the PE core for the realization of room temperature mesophase and their packing behaviour.

This investigation was motivated by two goals. First, by attaching four pentaalkynylbenzene (PT) units around periphery of perylene (PE) core, we sought to provide insight into structural details of mesophase in the system. Second, we sought to explore additional insight about the packing of the hybrids in the mesophase through simple variation in the number of alkyl spacers (n = 6, 8, 10) connecting the PE and multiyne units. Our findings perceived that compounds with shorter alkyl spacers (n = 6 and 8) connecting to PE and PT units arrange exclusively in soft, condis crystals, which are defined as conformationally disordered mesophases.^[26] Compound with longer alkyl spacer (n = 10) exhibits room temperature columnar nematic phase. Till today, no reports are there for such columnar assemblies based on PE tetraesters. In addition, they exhibit high quantum yield and exhibit green emission that might be useful for OLEDs applications. Moreover, the band gap values of the compounds were found to be larger in comparison to other PE-tetraesters reported so far.[19, 20]

Results and Discussion

Synthesis and Characterisation

The synthetic strategy to obtain target compounds **5** is illustrated in Scheme 1. The synthesis of intermediate compounds **2** and **3** has been reported earlier.^[24b,25a, b] Compounds **5** were prepared by reacting the pentalkynylbenzene (PT) **3** with perylene-3,4,9,10-tetracarboxylic dianhydride **4** as follows. The step involves the hydrolysis of **4** (1 equiv.) by refluxing it in aqueous potassium hydroxide followed by acidification to pH 8-9 with dilute HCl to provide perylene-3,4,9,10-tetracarboxylic acid. This was followed by *in situ* addition of **3** (8 equiv.) and tetraoctylammonium bromide (TOAB) (0.8 equiv.) as phase transfer catalyst and refluxing it for overnight. The structures of all the new intermediates and target molecules were characterized by ¹H NMR, ¹³C NMR, FT-IR, UV-vis spectroscopy and elemental analysis (see ESI, Fig. S1-S7, S13).



Scheme 1. Synthesis of the target compounds **5**. Reagents and conditions: (i) K_2CO_3 , KI, $Br(CH_2)_nBr$, acetone, reflux, 12 hrs, 80 % (ii) $Pd(PPh_3)_2CI_2$, 4-pentylphenylacetylene, Cul, Et_3N , 100 °C, 80 % (iii) hydrolysis of **4** with KOH, H₂O, 70 °C, 2h, dilute HCl followed by **3**, TOAB, reflux, overnight, 78 %.

Thermal behaviour

The thermal behaviour of the perylene derivatives were investigated by polarised optical microscopy (POM, Fig. 1 and Fig. S8, Table 1) and differential scanning calorimetry (DSC). Compound **5a** with shortest alkyl spacer (n = 6) was highly viscous (Fig. S10a, see ESI) and is still shearable showing their soft behaviour. The shearability of the textures in one direction has been shown at room temperature (Fig. S9a & b, see ESI). They displayed an unspecific texture with the growth of smaller domains ^[1c,25b,c] (Fig. 1a). The phase remained stable over a wide temperature range and was cleared at 106 °C with an enthalpy change (Δ H) of 6.2 kJ/mol. On cooling, texture appeared at 103 °C (bright birefringent textures observed under POM) which remained stable down to room temperature.

Compound **5b** (n = 8) also exhibited similar soft crystal behaviour as that of compound **5a**. Under POM, an unidentified texture was appeared (Fig. 1b) which cleared at about 85 °C and are shearable at room temperature (Fig S9c & d, see ESI). The viscosity of the phase was measured at room temperature (Fig. S10b, see ESI). On cooling, the phase appeared at 78 °C that remained stable down to room temperature (up to -50 °C). Interestingly, with increasing the spacer length further (n = 10), destabilized the order in the mesophase of the hybrid.



Figure 1. Polarizing optical micrograph of compounds (a) 5a and (b) 5b at 67 °C and 25 °C, respectively, showing unspecific growth of textures. (c) Blurred schlieren texture of compound 5c at 49.6 °C under POM. All these

textures were observed on cooling from the isotropic phase (scan rate 5 $^{\circ}\text{C/min},$ crossed polarizers, magnification X 500).

For instance, compound **5c** (n = 10) showed the appearance of columnar textures ^[25c] at room temperature (Fig. 1c). In DSC, it showed mesophase to isotropic transition at 66 °C with a heat of transition of 0.4 kJ mol⁻¹. On cooling, the mesophase appeared at 65 °C (ΔH = 0.4 kJ/mol). The DSC traces obtained on heating and cooling of compound **5c** was shown in Fig. S11 (see ESI).

The exact nature of the columnar phases formed by these compounds could be deduced only from detailed XRD studies. We performed detailed XRD analysis to judge the exact nature of the mesophases and their corresponding electron density maps were derived from the intensities of the peaks observed in the diffraction patterns (see below for details).

Table 1. Thermal properties of the target compounds.						
Compound		Phase transitions, T [°C] (ΔH [kJ mol ⁻¹])				
5a	Heating Cooling	Cr_{colob} (soft crystal) 106 (6.2) $Iso^{[a]}$ Iso 103 Cr_{colob} $^{[b]}$				
5b	Heating	Cr _{colob} 85 Iso ^[b]				
	Cooling	Iso 78 Cr _{colob} ^[b]				
5c	Heating Cooling	N _{col} 66 (0.4) Iso ^[a] Iso 65 (0.4)N _{col} ^[a]				

[a] Transition temperature obtained from DSC. [b] obtained from POM. Abbreviations: Cr_{colob} = soft crystal columnar oblique, N_{col} = Columnar nematic, Iso = isotropic liquid.

X-ray diffraction study

The detailed study of the mesophases of the compounds 5a-5c has been performed by small angle and wide angle X-ray scattering (SAXS/WAXS) & Grazing- incidence X-ray scattering (GISAXS/GIWAXS) experiments. The SAXS profile of compound 5a in the isotropic phase (at 110 °C) shows two broad peaks in small angle region and one broad peak in wide angle regime (Fig. 2b). As the compound consists of pervlene (PE) unit connected with four pentaalkynylbenzene (PT) units via flexible spacers, so, the first and second peak in the small angle with observed d-spacing of 32.74 Å and 21.16 Å correspond to side to side PE-PE correlations and side to side PT-PT correlations, respectively (Table S1, see ESI). However, side to side PE-PE correlations d-spacing is smaller than expected (~ 40 Å), which indicates inter-digitations of the PT discs up-to some extent in the isotropic phase. Further, the wide angle peak of d-spacing of 4.87 Å corresponds to the fluid chainchain correlations.

WILEY-VCH



Figure 2. Powder X-ray diffraction pattern for compound **5a** with indexing for small angle and wide angle (inset) peaks (a) at 67 °C and (b) in the isotropic phase at 110 °C; h_a - fluid chain-chain correlations, h_{ac} - partially crystallize chain-chain correlations and h_c – perylene (PE) core-core (face to face) correlations. PE-PE corresponds to side to side PE correlations and PT-PT corresponds to side to side pentaalkynylbenzene (PT) correlations in the mesophase.

However, in the temperature range from 20 °C to 106 °C the diffraction patterns are found to be unchanged. The un-oriented SAXS pattern showed many sharp Bragg peaks (at 67 °C) (Fig. 2a), and also the sample is shearable suggesting the possible existence of a soft crystal phase (Fig. S9a, b, see ESI).

In order to resolve overlapping reflections and facilitate their indexing, GISAXS experiments were carried out on oriented thin films on an ITO-coated glass substrate. For this purpose, a thin film was melt-cast on an ITO-coated glass substrate and annealed for 1 day at 70 °C. The same diffraction peaks were observed both in the GISAXS of thin film and in the SAXS pattern of the un-oriented sample (Fig. 3a and 2a, respectively).



Figure 3. (a) GISAXS and (b) GIWAXS pattern of thin film of compound 5a on an ITO coated glass substrate recorded at 67 °C obtained after annealing the sample for one day at 70 °C. (c) Partially aligned 2D SAXS diffraction pattern of compound 5a at 67 °C obtained by shining the X-ray into the sample near to the wall of the glass capillary.

If, the reciprocal lattice vectors, a^* and b^* is assigned along the equator and meridian, respectively, it could lead to the assembly of the compound having two different kind of structurally different domains. But, this is unlikely as soft crystal generally self-organize in a more compact way to exhibit a single phase. Next, we performed X-ray diffraction experiment with sample filled in

the glass capillary and shine the X-ray which exposes the sample near to the wall of glass capillary (at 67 °C). In-result, we found a partially aligned pattern which could be indexed on an oblique lattice as shown in the figure 3c. Therefore, for the thin-film pattern a^* and b^* are more likely along the meridian and c^* along the equator (Fig. 3a) and hence indexing of the unoriented pattern is done accordingly. Therefore, Bragg's reflections for the compound **5a** at 67 °C were indexed on 2D oblique lattice and space group is determined to be P2/m (Fig. 2a, 3a,c). The cell parameter, c, is determined from the reflection, h_c , due to perylene (PE) core to core (face by face) correlations in the wide angle region (Fig. 2a inset). The observed and calculated d-spacing values are listed in Table 2.

Table 2. The indices observed and calculated d-spacings and planes of the diffraction peaks of the oblique lattice of compound **5a** observed at 67 °C. The space group is P2/m and lattice parameters are: a = 42.67 Å, b = 38.99 Å, $\alpha = 84.15$ degree and c = 3.70 Å.

Miller indices <i>hk</i>	d _{obs} (Å) ^[a]	d _{ca/} (Å) ^[b]	Relative Intensity <i>I(hk)</i>	Multiplicity	Phase Φ(hk)
10	42.45	42.45	87.95	2	0
01	38.79	38.79	100.00	2	0
11	30.21	30.21	62.65	2	0
-11	27.32	27.28	48.19	2	0
20	21.30	21.22	54.22	2	π
02	19.39	19.39	42.17	2	Π
12	18.21	18.36	38.55	2	0
-12	17.03	17.00	30.12	2	0
22	15.07	15.10	32.53	2	0
-22	13.69	13.64	18.07	2	0
13	12.80	12.73	6.02	2	0
32	12.01	12.03	3.61	2	
23	11.49	11.59	2.41	2	
ha	4.99				
h _{ac}	4.39				
hc	3.70				

[a] d_{obs} :experimental *d*-spacing. [b] d_{cal} : calculated *d*-spacing by using the relation: $\frac{1}{d^2} = \frac{1}{\sin^2 a} \left[\frac{h^2}{a^2} + \frac{k^2}{b^2} - \frac{2 h k \cos a}{a b} \right]$; *h*, *k* are the indices of the reflections corresponding to the oblique lattice; a, b & c are the unit cell parameters, α is the angle between \vec{a} and \vec{b} where $|\vec{a}| = a$ and $|\vec{b}| = b$. h_{a} , h_{ac} and h_c spacings appear due to fluid chain-chain, partially crystallize chain-chain and perylene (PE) core-core (face to face) correlations, respectively.

The calculated cell parameters are *a* = 42.67 Å, *b* = 38.99 Å, *c* = 3.70 Å, and α = 84.15 degree. In-addition to h_c, there are h_a and h_{ac} reflections in the wide angle region of spacing 4.99 Å and 4.39 Å, respectively. These reflections are attributing to the fluid chain-chain and partially crystallize chain-chain correlations. In GISAXS/GIWAXS, the strong Bragg peaks has a maximum intensity on the meridian confirming the presence for planar alignment (Fig. 3a, b). Further, no wide-angle peaks were perceived, indicating inadequate diffraction contrast from long-range ordered columnar π - π stacking of the molecules in any orientation (Fig. 3b).^[25e] Based on indexing and because the compound was highly viscous, shearable and exhibits sharp reflections confirming the occurrence of soft crystal columnar oblique (Cr_{colob}) phase.

In order to understand the details of the arrangment of the columns on the 2D oblique lattice, their corresponding 2D electron density map is constructed from the diffraction pattern. The procedure is described in the ESI. Red colour represents the highest electron density and dark blue the lowest. Here, PE core stack on top of each other and form columns and these columns arranged on two dimensional oblique lattices (Fig. 4a).

WILEY-VCH



Figure 4 Reconstructed electron density map of compound (a) **5a** and (b) **5b** showing the arrangement of the column on the 2D oblique lattice. Red represents the highest electron density and deep blue is the lowest. Parallelogram on the map shows the respective 2 D unit cell.

The powder X-ray diffraction pattern of compound **5b** at 25 °C shows reflections in the small and wide angle region and remained same up to the isotropic phase. These peaks could be indexed on an oblique lattice and the calculated lattice parameters are found to be a = 48.90 Å, b = 34.13 Å, α = 126.3 degree and c = 3.60 Å (Fig 5a; Table 3). In order to facilitate their indexing GISAXS/GIWAXS experiments were carried out on oriented thin films on an ITO-coated glass substrate. However, in GISAXS pattern only the most intense two peaks

(20 and 11) were observed with same d-spacing as that of powder diffraction pattern, while other less intense peaks were not appeared possibly because of their insufficient diffraction contrast or inappropriate alignment (Fig. 5b). Further in GIWAXS studies (Fig 5c) no peaks were observed in the wide angle region. Therefore, nature of the lattice could not be deduced from the aligned pattern. Hence the structure of the assembly has been determined according to the indexing of unoriented pattern (mentioned above).

Based on indexing of the unoriented pattern and because the compound **5b** exhibits many reflections in the wide angle along with the peak observed at 3.6 Å (which is due to disc to disc separation in a column) and less shearable confirmed the occurrence of soft crystal columnar oblique (Cr_{colob}) phase. The corresponding 2D electron density map of compound **5b** based on powder diffraction pattern has been shown in Fig. 4b. The X-ray diffraction pattern in the isotropic phase (85 °C) is similar as seen in compound **5a** and can be explained similarly. However, spacing due to PE-PE correlations is higher than **5a** which is expected due to higher spacer length (Fig 5d, Table S2, see ESI).

The X-ray diffraction pattern of compound 5c in the isotropic phase is very similar as observed for compounds 5a and 5b and can be explained in a similar manner (Fig. 6a,c; Table 4). However, at temperature below 65 °C, the PE-PE correlation is becoming narrower and PT-PT correlation peak is more or less same as in the isotropic phase. The X-ray diffraction pattern of compound 5c at 25 °C is shown in Fig. 6b, d. In addition to PE-PE and PT-PT correlation peak, two other peaks (hac and hc) appear in the wide angle region (Fig. 6b, Table 4). Moreover, these two peaks are not seen in the isotropic phase. Further, the sharp h_c peak appears due to strong PE core to core correlations which reveal its columnar nature. Including the narrow PE-PE peak in the small angle region along with the above, confirmed the occurrence of columnar nematic (N_{col}) phase (schematic is shown in Fig. 6e). The d-spacing corresponding to h_c is found to be 4.09 Å. Because the reported face to face distance between two π -conjugated molecules is about 3.51 Å, perylene cores are packed with a tilting angle of 30.88 degree with respect to the axis of the perylene columns.^[27]

а

WILEY-VCH

d Manusc

eptec



GIWAXS pattern of thin film of compound 5b on an ITO-coated glass substrate recorded at 25 °C. (d) X-ray pattern for 5b in the isotropic phase at 85 °C; h_afluid chain-chain correlations, $h_{ac}\text{-}$ crystallize chain-chain correlations $% h_{ac}\text{-}$ and $h_{c}\text{-}$ perylene (PE) core-core (face to face) correlations, PE-PE corresponds to side to side PE correlations and PT-PT corresponds to side to side PT correlations

Figure 5. Powder X-ray diffraction pattern for compound 5b with indexing for

Table 3. The indices observed and calculated <i>d</i> -spacings and planes of
the diffraction peaks of the oblique lattice observed at 25 °C of compound
5b . The plane group is $P2/m$ and lattice parameters are: $a = 48.90$ Å, $b =$
34.13 Å, $c = 3.60$ Å and $\alpha = 126.3$ degree.

			and the second			
i	Miller ndices <i>hk</i>	d _{obs} (Å) ^[a]	d _{ca/} (Å) ^[b]	Relative Intensity <i>I(hk)</i>	Multiplicity	Phase Φ(hk)
	20	19.84	19.70	38.82	2	0
	11	18.10	18.08	100.00	2	0
ĺ.	-32	14.70	14.86	15.02	2	0
	21	12.71	12.82	16.10	2	0
	-33	11.43	11.28	18.57	2	0
	-43	10.30	10.49	14.49	2	0
	40	9.58	9.85	14.86	2	π
	-44	8.3	8.46	17.14	2	π
	32	7.40	7.53	19.13	2	0
	42	6.22	6.41			
/	70	5.60	5.63			
	34	4.96	5.00			
	06	4.59	4.58			
	81	4.45	4.42			
	h _{ac}	4.19				
	h _c	3.60				
	84	3.19	3.20			

[a] d_{obs} :experimental d-spacing. [b] d_{cal} : calculated d-spacing by using the relation: $\frac{1}{d^2} = \frac{1}{\sin^2 \alpha} \left[\frac{h^2}{a^2} + \frac{k^2}{b^2} - \frac{2hk \cos \alpha}{\alpha b} \right]; h, k \text{ are the indices of the}$ reflections corresponding to the oblique lattice; a, b & c are the unit cell parameters, α is the angle between \vec{a} and \vec{b} where $|\vec{a}| = a$ and $|\vec{b}| = b$. h_a , h_{ac} and h_c spacings appear due to fluid chain-chain, partially crystallize chain-chain and perylene (PE) core-core (face to face) correlations, respectively.



WILEY-VCH

FULL PAPER



Figure 6. Smaller angle (left inset), small angle and wide angle (right inset) X-ray diffraction pattern for compound **5c** showing (a) isotropic phase and (b) N_{Col} phase at 70 °C and 25 °C, respectively. h_a - fluid chain-chain correlations, h_{ac} - crystallize chain-chain correlations and h_c – perylene (PE) core-core (face to face) corresponds to side to side to side PE correlations and PT-PT corresponds to side to side PT correlations in the mesophase. Corresponding 2D small angle and wide angle (in inset) X-ray diffraction patterns at (c) 70 °C, (d) 25 °C, respectively. (e) Schematic: (i) compound **5c** and (ii) arrangement of the compound **5c** in the N_{col} phase.

Transition from soft crystal columnar oblique (Cr_{colob}) phase to columnar nematic (N_{col}) phase which happens with increasing the spacer length is due to symmetry breaking. Cr_{colob} phase exhibits long range positional order (PO), bond orientational order (BO) and orientational order (OO); whereas columnar nematic phase show only quasi long range orientational order (OO). Moreover, this transition could be explained in terms of the *flexibility induced orientational freedom* (FIOF) to PT group. As spacer chain length increases, flexibility increases in same way which permits more orientational freedom to PT discs and leads to Cr_{colob} to N_{col} transition.



[a] Temperature. [b] Columnar nematic. [c] Isotropic. [d] PE-PE corresponds to side to side PE correlations and PT-PT corresponds to side to side PT correlations in the mesophase. [e] h_a - fluid chain-chain correlations, h_{ac} - partially crystallize chain-chain correlations and h_c – perylene (PE) core-core (face to face) correlations.

Photophysical and electrochemical studies

All the perylene derivatives exhibit good luminescence properties as evident from their absorption and emission studies in solution as well as in the solid state. In solution state, they showed similar absorption and emission spectra indicating that varying spacer length between PE and pentaalkynylbenzene moieties does not affect their spectral behaviour in solution.

The absorption spectra recorded in μ M THF solution of compound **5a** showed peaks at 240, 261, 337, 416, 441 & 471 nm with a shoulder peak at 380 nm (Fig. 7a, Table 5) due to perylene^[19d] and pentaalkynylbenzene moiety.^[25a,b] Other homologues of the series displayed (**5b** and **5c**) peaks more or less at same wavelength (Table 5, Fig. S13, see ESI). All the compounds emit green light even under daylight conditions (Fig. 7a inset).

Emission spectra exhibits two strong peaks at 487 & 517 nm (which were obtained by exciting the solutions of these compounds at their absorption maxima) characteristic of mainly PE core^[19d] (Fig. 7a, Table 5) with a Stokes' shift of 150 nm. The solid state absorption and emission spectra were obtained for compound **5a** and **5b**. The absorption bands became broader and red-shifted as clearly observed in the spectrum (Fig. S13d, see ESI). The fluorescence bands in the solid state are significantly red-shifted and merged as compared to those in solution state (in μ M THF solution) which mainly correlate the arrangement of the π -conjugated molecules in solid state (Fig. 7b).

WILEY-VCH



Figure 7. (a) Absorption and emission spectra of compounds 5a and 5b in micromolar THF solutions. Inset shows green fluorescence for 5b in micromolar THF solution under daylight condition. (b) Emission spectra for the spin-coated thin films of compounds 5a and 5b. Inset shows green fluorescence of 5b in the solid state.

Table 5. Optical data of the compounds 5 ^[a]						
Compoun d	Absorption (nm)	Emission (nm)	Stokes shift ^[b]			
5a	240,261,337,380,416,441,471	487,517,558	150			
5b	238,265,337,380,417,441,471	487,518,558	150			
5c	239,262,337,380,416,441,471	487,517,558	150			

[a] in micromolar solutions in THF. [b] Corresponding to excitation wavelength 337 nm for all compounds.

In order to know the reorientational dynamics of molecules in solution, fluorescence lifetime and steady state anisotropy measurements (Table 6) were performed in dilute solutions (10 μ M in THF). Interestingly, the fluorescence lifetime in all the hybrid oligomers is close to 4 ns whereas, the measured lifetime for perylene is 5.2 ns in ethanol solution.^[19c,28] The observed decrease in lifetime with increasing spacer chain length could be due to higher non-radiative rate involved in the processes

(competing for the relaxation of the excited state) because of the change in shape and size of the hybrid oligomers and thus the molecular interactions as reported earlier (Table 6).^[28] The fluorescence decay spectra were recorded for all the three compounds (Fig. S14, see ESI). We also measured steady state anisotropy of the compounds **5a-5c** and found that the value increases with increasing number of alkyl spacer connecting between PE and pentaalkynylbenzene units. In general, anisotropy values affects by molecular motion which mainly depends on local environment factors such as viscosity, molecular confinement and the size of the hybrid molecule. In the present case, the increased value of fluorescence anisotropy with increasing the molecular size (from **5a** to **5c**) implies that mobility decreases and hence anisotropy values increases (Table 6).

Table 6. Optical data of the compounds 5^[a]

	Ţ1(α1) (ns)	Ţ ₂ (α ₂) (ns)	T _{av} (ns) ^[b]	$\phi_{FL}{}^{[c]}$	Steady State Anisotropy
5a	2.91 (0.66)	5.40 (0.34)	3.74	0.89	2.23 x 10 ⁻³
5b	2.82 (0.52)	4.72 (0.48)	3.73	0.84	3.17 x 10 ⁻³
5c	2.79 (0.53)	4.66 (0.47)	3.67	0.81	3.30 x 10 ⁻³

[a] in micromolar solutions in THF. [b] Average fluorescence lifetime. [c] Relative to quinine sulphate in 0.1 (M) H_2SO_4 (ϕ_{FL} = 0.54).

Apart from these, quantum yields calculations were carried out using quinine sulphate in 0.1 M H_2SO_4 solution (Fig. S12, Table 6 & Table S3, see ESI) as a standard as it absorbs at around the same wavelength (347 nm) as that of our title compounds (337 nm). Quantum yield is affected by how quickly energy leaves the system through alternative processes (non-radiative processes & intersystem crossing). In all the compounds, the quantum yield value is close to 0.9, which means that alternative processes occur at significantly lower rates compared to fluorescence.

Cyclic Voltammetry

In order to find out the electronic energy level that determines the energy and electron transfer processes, cyclic voltammetry (CV) was carried out. CV studies were performed in millimolar (mM) solutions of compounds **5a-5c** in oxygen free dichloromethane solvent, as shown in Fig. 8a and Fig. S15 (see ESI).

10.1002/chem.201702181

WILEY-VCH



Figure 8. (a) Cyclic voltammogram of compound 5a in HPLC DCM solution of TBAH (0.1M) at scanning rate of 100 mV/s. (b) The HOMO and LUMO energy levels obtained for compound 5a, 5b and 5c.

A single compartment cell containing Ag/AgNO₃ (0.1 M) reference electrode, a platinum rod as a counter electrode, and a glassy carbon as a working electrode was used for the CV measurements. As a supporting electrolyte 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBAH) was used during the experiment. For the calculation of absolute values of HOMO and LUMO levels, the redox data was calibrated with respect to ferrocene-ferrocenium couple (Fc/Fc⁺), assuming the energy-level of Fc/Fc⁺ pair is 4.8 eV below the vacuum level.^[29] The cyclic voltammograms were recorded with a scanning rate of 0.1 Vs⁻¹. All the perylene derivatives displayed reversible oxidation and reduction processes. It should be noted that perylene derivatives exhibit good electron affinity and hence, they are easy to be reduced and rather difficult to be oxidized.

Table 7. Electrochemical data of the compounds 5 ^[a]							
	λ _{max} (nm)	ΔE_{UV} [b],[c]	E _{1red} ^{[b}]	E _{1oxd} ^[d]	E _{HOMO} ^[b] ,[e]	E _{LUMO} ^{[b],} [f]	ΔE _{g,CV} ^[b] ,[c], [g]
5a	337	3.68	-1.65	0.97	-5.63	3.74	3.13
5b	337	3.68	-1.65	1.02	-5.93	3.73	3.48
5c	337	3.68	-1.65	0.94	-5.58	3.67	3.07

[a] Experimental conditions: Ag/AgNO₃ as reference electrode, glassy carbon working electrode, platinum wire counter electrode, TBAH (0.1M) as a supporting electrolyte. [b] Electron volts (eV). [c] Band gap calculated from the absorption maxima (ΔE_{UV} = 1240/ λ_{max}). [d] in volts (V). [e] Calculated by using formula E_{HOMO} = -(4.8- $E_{1/2,Fo/Fo}$ ⁺ + $E_{oxd,onset}$) eV. [f] Calculated by using formula E_{LUMO} = -(4.8- $E_{1/2,Fo/Fo}$ ⁺ + $E_{red,onset}$) eV. [g] calculated by formula $\Delta E_{g,CV}$ = E_{LUMO} -E_{HOMO}.

The optical band gap (ΔE_{UV}) was obtained from the absorption maxima of the absorption spectra of the compounds **5a-5c** by using the formula E=1240/ λ .^[30] The electronic properties of all the compounds were found to be almost similar. In general, the redox processes are ground-state properties associated with the absorption spectra which resulted similar electrochemical behaviour irrespective of spacer length (Fig. S15, see ESI).

The LUMO energy levels were obtained by the formula E_{LUMO} = - (4.8- $E_{1/2, Fc,Fc}$ ⁺+ $E_{red, onset}$) eV, while the HOMO energy levels by E_{HOMO} = - (4.8- $E_{1/2, Fc,Fc}$ ⁺+ E_{ox} , onset) eV (Fig. 8b & Table 7). All the values of LUMO and HOMO energy levels (E_{LUMO} & E_{HOMO}) and electrochemical band gap ($\Delta E_{g,CV}$ = E_{LUMO} - E_{HOMO}) are summarised in Table 7. Both the UV-Vis spectra and CV results have showed that different spacer length (n = 6, 8, 10 for **5a**, **5b** and **5c**, respectively) had little influence on the electrochemical properties.

Conductivity measurements in the soft crystal columnar phase

The electrical characterization of columnar assemblies is important for finding their application as charge or ion conductors. The ac impedance spectroscopy is an important technique for measuring conductivity by applying fixed alternate voltage with varying frequency that ranges from megahertz to millihertz. The impedance measurements performed in their LC state were interpreted in terms of equivalent circuits consisting of electrical components as capacitors, resistors and inductors.



Figure 9. Impedance Z_{im} vs Z_r of compound **5a** in their Cr_{colob} phase and their corresponding circuit. Expt. represents plot obtained from measurement, Fitted represents plot obtained after fitting through software (details in instrumentation part, see ESI).

The samples were heated to their isotropic temperature and were filled through capillary action in an ITO (Indium-Tin oxide) cell separated by a 20 μ m spacer and then allowed to cool slowly until the mesophase temperature reached for measurement. This procedure is usually done to align the sample homeotropically, so that conductivity can be measured in the direction of column organization. After several attempts, the sample was not aligned properly for both the compounds (**5a** & **5b**) as observed by their POM images (not shown). Fig. 9 shows the complex Impedance graphs (Z_{im} vs Z_r) for compound **5a** showing well defined semicircle fitted by using a software (details in instrumentation part, see ESI) which results into a

circuit having constant phase element (CPE) in parallel with resistance (R) and wurburg impedance (W), where R is defined as a bulk resistance. Through proper fitting of the plot, R value was obtained. After substituting R values, the conductivity could be obtained by using formula: $\sigma = d/(R.A)$, where d represents the thickness of the cell (20 µm) and A is the area of the cell. Compound **5b** also shows the similar behaviour (Fig. S16, see ESI). The conductivity values obtained for the compound **5a** and **5b** in the soft columnar crystal phase are 5.07 X 10⁻⁷ and 1.25 X 10⁻⁷ S m⁻¹, respectively. The conductivity values can be further improved by proper alignment and the mixing of some ions and then these derivatives may find application for further device investigation.

Conclusions

In summary, the main conclusions of the study reported in this paper are threefold. First, we have synthesized a new series of novel perylene tetraester derivatives showing soft crystal columnar and nematic columnar mesophases at room temperature over a wide temperature range. Specifically, we observed that compounds 5a and 5b with shorter alkyl spacer (n = 6, 8) connecting to PE and pentalkynylbenzene units show soft crystal columnar oblique phase. Interestingly, compound (5c) with longer spacer (n = 10) is found to self-organize into a room temperature columnar nematic phase. Second, all the molecules showed a green emission in the solution and in the solid state visible to naked eye with a very good quantum yield and large band gap. The length of the peripheral alkyl spacers did not have much effect on the photo-physical properties. This new class of perylene discotics with easy synthesis, room temperature nematic columnar and soft crystal columnar behavior over a wide temperature range, near unity quantum yield, highly emissive nature and large band gap make them potential candidates for their use in solid state displays. In addition, this new class of materials may open up a new field to explore the structure property relationships for various oligomers based on PE tetraesters.

Experimental Section

General synthetic procedure for the synthesis of intermediates (2 & 3a-c) and final compounds (5a-c)

The synthesis of series of target compound **5** (Scheme 1 in the manuscript) was commenced from the Williamson alkylation of pentabromophenol with the corresponding alkyl bromide as reported in the earlier reports.^[24b,25] Then the sonoghshira of alkylated compound **2** (500 mg) was done by taking 30 ml of dry triethylamine in a round bottom flask which was degassed followed by the addition of Pd(PPh₃)₂Cl₂ (50 mg), Cul (50 mg) & PPh₃ (100 mg). The mixture was stirred for 15 minutes followed by the gradual addition of 4-pentylphenylacetylene. The reaction mixture was stirred at 100 °C for 24 h under nitrogen atmosphere & after cooling to room temperature it was poured into 30 ml of 5M HCI. The final step involves the hydrolysis of perylene-3,4,9,10-tetracarboxylic dianhydride (1 equiv.) by refluxing it in aqueous potassium hydroxide followed by activity and the sonoghad structure to the sonoghad structure t

provide perylene-3,4,9,10-tetracarboxylic acid followed by *in situ* addition of alkyl bromide (8 equiv.) and tetraoctylammonium bromide (TOAB) (0.8 equiv.) as phase transfer catalyst and refluxing it for a overnight. The final products were purified on neutral alumina by using hexane/ethylacetate as an eluent.

The synthesized compounds were characterized by ¹H NMR, ¹³C NMR, FT-IR and elemental analysis as shown below. Detailed spectra are in Supporting information (ESI):

5a: Eluent for purification (hexane/ethyl acetate 9:1). Yield: 68 %, yellow solid. R_f: 0.71 (hexane/ethyl acetate 5:2); m.p: see Table 1; ¹H NMR (400 MHz, CDCl₃, 20 °C, TMS, δ in ppm): δ-8.31 (d, 4H, *J* = 8.16 Hz), 8.05 (d, 4H, *J* = 7.84 Hz), 7.56-7.48 (m, 40H), 7.18-7.13 (m, 40H), 4.37 (t, 8H, *J* = 5.92, 6.04 Hz), 4.29 (t, 8H, *J* = 6.56, 6.44 Hz), 2.69-2.54 (m, 40H), 1.96 (m, 8H), 1.80-1.73 (m, 8H), 1.67-1.56 (m, 40H), 1.36-1.25 (m, 96H), 0.95-0.84 (m, 60H); ¹³C NMR (100 MHz, CDCl₃, 20 °C, TMS, δ in ppm): δ - 168.43, 143.96, 143.91, 131.78, 131.54, 129.51, 128.49, 120.73, 120.46, 120.08, 99.38, 87.11, 84.09, 36.00, 31.52, 31.49, 30.9, 26.5, 23.02, 22.57, 22.53, 14.17, 14.08, 14.06; FT-IR (cm⁻¹): v- 3027.15, 2958.26, 2927.31, 2856.55, 2209.10, 1906.00, 1723.24, 1591.72, 1513.60, 1465.68, 1425.91, 1378.57, 1347.58, 1264.10, 1164.05, 1085.24, 1020.16, 836.63, 805.97, 750.12, 551.40, 530.10; elemental Analysis calculated (%) for – C₃₂₇H₃₄₈O₁₂: C 87.86, H 7.85; found: C 87.85, H 8.07

5b: Eluent for purification (hexane/ethyl acetate 10:1). Yield: 72 %, yellow solid. R_i: 0.73 (hexane/ethyl acetate 5:2); m.p: see Table 1; ¹H NMR (400 MHz, CDCl₃, 20 °C, TMS, *δ* in ppm): *δ*- 8.31 (d, 4H, *J* = 8.2 Hz), 8.05 (d, 4H, *J* = 7.8 Hz), 7.56-7.48 (m, 40H), 7.18-7.13 (m, 40H), 4.37 (t, 8H, *J* = 6.16, 6.2 Hz), 4.29 (t, 8H, *J* = 6.68, 6.8 Hz), 2.69-2.54 (m, 40H), 1.96 (m, 8H), 1.80-1.73 (m, 8H), 1.67-1.56 (m, 40H), 1.36-1.25 (m, 112H), 0.95-0.84 (m, 60H); ¹³C NMR (100 MHz, CDCl₃, 20 °C, TMS, *δ* in ppm): *δ* - 168.47, 143.91, 131.77, 131.56, 128.53, 120.49, 120.09, 99.55, 84.09, 74.69, 36.00, 31.48, 30.97, 26.39, 23.02, 22.57, 14.07; FT-IR (cm⁻¹): v-3026.40, 2956.48, 2927.26, 2855.62, 2210.6, 1902.00, 1716.40, 1513.52 1466.17, 1425.53, 1348.80, 1272.96, 1162.98, 1086.30, 1019.00, 962.17 838.27, 813.20, 749.36, 724.53, 554.29, 532.10; elemental Analysis calculated (%) for – C₃₃₅H₃₆₄O₁₂: C 87.80, H 8.01; found: C 87.65, H 8.02

5c: Eluent for purification (hexane/ethyl acetate 12.5:1). Yield: 69 %, yellow solid. R_i: 0.76 (hexane/ethyl acetate 5:2); m.p: see Table 1; ¹H NMR (400 MHz, CDCl₃, 20 °C, TMS, *δ* in ppm): *δ*- 8.35 (d, 4H, *J* = 8.2 Hz), 8.07 (d, 4H, *J* = 7.84 Hz), 7.56-7.51 (m, 40H), 7.19-7.17 (m, 40H), 4.36 (t, 8H, *J* = 6.28, 6.28 Hz), 4.31 (t, 8H, *J* = 6.76, 6.84 Hz), 2.66-2.61 (m, 40H), 1.93 (m, 8H), 1.78 (m, 8H), 1.66-1.61 (m, 40H), 1.36-1.32 (m, 128H), 0.94-0.85 (m, 60H); ¹³C NMR (100 MHz, CDCl₃, 20 °C, TMS, *δ* in ppm): *δ*-168.48, 160.23 144.00, 143.89, 143.69, 131.78, 128.53, 128.51, 124.09, 120.53, 120.49, 120.11, 99.54, 99.37, 99.31, 87.11, 86.64, 84.11 74.76, 36.00, 31.96, 31.51, 30.97, 29.40, 22.73, 22.57, 14.07; FT-IR (cm⁻¹): v-3021.90, 2958.62, 2924.68, 2854.05, 2208.90, 1903.60, 1719.00, 1513.30, 1464.62, 1427.80, 1378.10, 1349.70, 1262.06, 1162.75, 1087.77, 1020.25, 802.19, 753.25, 721.30, 554.44, 533.14; elemental Analysis calculated (%) for – C₃₄₃H₃₈₀O₁₂: C 87.75, H 8.16; found: C 87.87 H 8.32.

Acknowledgements

This work was carried out with the financial support from IISER Mohali. Dr. S. K. Pal is grateful for INSA Medal for Young Scientist 2015 and the financial support from INSA bearing sanction No. SP/YSP/124/2015/433. We are grateful to NMR,

WILEY-VCH

Cyclic Voltammetry, Elemental Analysis facility at IISER Mohali, INST Mohali and NIPER Mohali, respectively. We thank Dr. S. Gayen for useful discussions related to conductivity measurements. I. Bala acknowledges the receipt of a graduate fellowship from CSIR-NET. We also gratefully acknowledge the SAXS/WAXS facility at IISER Mohali for recording X-ray diffraction pattern.

Keywords: Perylene • columnar liquid crystals • room temperature • pentaalkynylbenzene • Luminescent

- a) T. Wohrle, I. Wurzbach, J. Kirres, A. Kostidou, N. Kapernaum, J. Litterscheidt, J. C. Haenle, P. Staffeld, A. Baro, F. Giesselmann, S. Laschat, *Chem. Rev.* 2016, *116*, 1139–1241; b) I. Bala, S. K. Pal, *Liquid crystals* 2016, *43*, 963–971; c) J. De, S. Setia, S. K. Pal, *Chemistry Select* 2016, *1*, 1–9.
- [2] S. Chen, P. Slattum, C. Wang, L. Zang, Chem. Rev. 2015, 115, 11967-11998.
- [3] a) K. Balakrishnan, A. Datar, R. Oitker, H. Chen, J. M. Zuo, L. Zang, J. Am. Chem. Soc. 2005, 127, 10496-10497; b) C. Li, H. Wonneberger, Adv. Mater. 2012, 24, 613-636; c) X. W. Zhan, A. Facchetti, S. Barlow, T. J. Marks, M. A. Ratner, M. R. Wasielewski, S. R. Marder, Adv. Mater. 2011, 23, 268-284; d) K.-Y. Law, Chem. Rev. 1993, 93, 449-486; e) G. Griffini, L. Brambilla, M. Levi, M. D. Zoppo, S. Turri, Dyes Pigm. 2013, 111, 41-48; f) X.-L. Zhang, J.-F. Song, X.-B. Li, J. Feng, H.-B. Sun, Org. Electron. 2013, 14, 1577-1585.
- [4] a) A. Ringk, W. S. C. Roelofs, E. C. P. Smits, C. Van der Marel, I. Salzmann, A. Neuhold, G. H. Gelinck, R. Resel, D. M. de Leeuw, P. Strohriegl, *Org. Electron.* **2013**, *14*, 1297-1304; b) S. R. Puniredd, A. Kiersnowski, G. Battagliarin, W. Zajaczkowski, W. W. H. Wong, N. Kirby, K. Mullen, W. Pisula, J. *Mater. Chem. B.* **2013**, *1*, 2433-2440; c) C. D. Dimitrakopoulos, P. R. L. Malenfant, *Adv. Mater.* **2002**, *14*, 99-117.
- [5] X. Zhang, S. Rehm, Marina M. Safont-Sempere, F. Würthner, Nature Chemistry 2009, 1, 623 – 629.
- [6] a) X. Chu, M. Guan, Y. Zhang, Y. Y. Li, X. F. Liu, Y. Zeng, *RSC Adv.* 2013, *3*, 9509-9513; b) M. Mosca, R. Macaluso, E. Feltin, C. Calii, *Electron. Lett* 2012, *48*, 1417-1419; c) X.-L. Zhang, J.-F. Song, X.-B. Li, J. Feng, H.-B. Sun, *Org. Electron.* 2013, *14*, 1577-1585.
- [7] A. J. Breeze, A. Salomon, D. S. Ginley, B. A. Gregg, H. Tillmann, H. -H. Hörhold, *Appl. Phys. Lett.* **2002**, *81*, 3085-3087.
- [8] R. K. Gupta, D. Das, M. Gupta, S. K. Pal, P. K. Iyer, A. A. Sudhakar, J. Mater. Chem. C 2017, DOI: 10.1039/C6TC04166C.
- [9] a) F. Würthner, *Chem. Commun.* 2004, 1564-1579; b) D. Görl, X.
 Zhang, F. Würthner, *Angew. Chem. Int. Ed.* 2012, *51*, 6328-6348; c) Y.-S. Ma, C.-H. Wang, Y.-J. Zhao, Y. Yu, C.-X. Han, X.-J. Qiu, Z. Shi, *Supramol. Chem.* 2007, *19*, 141-149.
- [10] a) Q. Zhao, S. Zhang, Y. Liu, J. Mei, S. Chen, P. Lu, A. Qin, Y. Ma, J. Z. Sun, B. Z. Tang, *J. Mater. Chem.* **2012**, *22*, 7387-7394; b) B. A. Gregg, *J. Phys. Chem.* **1996**, *100*, 852-859; c) H, Marciniak, X.-Q. Li, F. Würthner, S. Lochbrunner, *J. Phys. Chem. A* **2011**, *115*, 648-654.
- [11] C. Li, H. Wonneberger, Adv. Mater. 2012, 24, 613-636.
- [12] a) M. Funahashi, A. Sonodab, J. Mater. Chem. 2012, 22, 25190–25197; b) R. A. Cormier, B. A. Gregg, Chem. Mater. 1998, 10, 1309-1319; c) K. P. Prajitha, S. Chithiravel, K. Krishnamoorthy, S. K. Asha, J. Mater. Chem. C 2014, 2, 9882–9891.
- a) M. A. Muth, G. Gupta, A. Wicklein, M. Carrasco-Orozco, J. Phys. Chem. C 2014, 118, 92–102; b) J. Kelber, M. F. Achard, H. Bock, Chem. Eur. J. 2011, 17, 8145 – 8155; c) M. Zhu, H. Guo, F. Yang, Z. Wanga, Dyes and Pigments 2016, 133, 387–394.
- [14] a) A. Wicklein, A. Lang, M. Muth, M. Thelakkat, J. Am. Chem. Soc.
 2009, 131, 14442–14453; b) F. Würthner, C. Thalacker, S. Diele, C. Tschierske, Chem. Eur. J. 2001, 7, 2245-2253; c) J. Kelber, H. Bock, O. Thiebaut, E. Grelet, H. Langhals, Eur. J. Org. Chem. 2011, 4, 707–712.

- [15] a) M. R. Hansen, T. Schnitzler, W. Pisula, R. Graf, K. Mullen, H. Wolfgang Spiess, *Angew. Chem. Int. Ed.* **2009**, *48*, 4621 –4624; b) J. A. Quintana, J. M. Villalvilla, A. de la Peña, J. L. Segura, M. A. Diaz-Garcia, *J. Phys. Chem. C* **2014**, *118*, 26577–26583; c) N. Mizoshita, T. Tani, S. Inagaki, *Adv. Funct. Mater.* **2011**, *21*, 3291–3296.
- [16] a) T. Zhang, D. Sun, X. Ren, L. Liu, G. Wen, Z. Ren, H. Lia, S. Yan, Soft Matter 2013, 9, 10739–10745; b) B. Gao, D. Xia, L. Zhang, Q. Bai, L. Bai, T. Yangab, X. Ba, J. Mater. Chem. 2011, 21, 15975–15980; c) M. Funahashi, M. Yamaoka, K. Takenamia, A. Sonodab, J. Mater. Chem. C 2013, 1, 7872–7878.
- [17] a) M. Funahashi, A. Sonoda, *Dalton Trans.*, **2013**, *42*, 15987–15994; b)
 L. Meng, Q. Wu, F. Yang, H. Guo, *New J. Chem.* **2015**, *39*, 72–76; c) A.
 Wicklein, P. Kohn, L. Ghazaryan, T. Thurn-Albrecht, M. Thelakkat, *Chem. Commun.* **2010**, *46*, 2328–2330; d) G. A. Bhavsar, S. K. Asha, *Chem. Eur. J.* **2011**, *17*, 12646–12658.
- [18] a) X. Kong, Z. He, Y. Zhang, L. Mu, C. Liang, B. Chen, X. Jing, A. N. A. Cammidge, *Org. Lett.* **2011**, *13*, 764–767; b) A. Wicklein, M. A. Muth, M Thelakkat, *J. Mater. Chem.* **2010**, *20*, 8646–8652.
- [19] a) R. K. Gupta, S. K. Pathak, B. Pradhan, M. Gupta, S. K. Pal, A. A. Sudhakar, *Chem Phys Chem* 2016, *17*, 859 872; b) R.K. Gupta, S. K. Pathak, B. Pradhan, D. S. Shankar Rao, S. K. Prasad, A. S. Achalkumar, *Soft Matter* 2015, *11*, 3629–3636; c) S. Benning, H.-S. Kitzerow, H. Bock, M.-F. Achard, *Liquid Crystals* 2000, *27*, 901-906; d) S. K. Gupta, S. Setia, S. Sidiq, M. Gupta, S. Kumar, S. K. Pal, *RSC Adv* 2013, *3*, 12060–12065.
- [20] O. Thiebaut, H. Bock, E. Grelet, J. Am. Chem. Soc. 2010, 132, 6886–6887.
- [21] Y. Wang, C. Zhang, H. Wu, J. Pu, J. Mater. Chem. C 2014, 2, 1667– 1674.
- [22] Hassheider, S. A. Benning, H.-S. Kitzerow, M.-F. Achard, H. Bock, Angew. Chem. Int. Ed. 2001, 40, 2060–2063; Angew. Chem. 2001, 113, 2119–2122
- [23] a) I. Seguy, P. Destruel, H. Bock, *Synth. Met.* 2000, *111*, 15–18; b) I.
 Seguy, P. Jolinat, P. Destruel, R. Mamy, H. Allouchi, C. Courseille, M.
 Cotrait, H. Bock, *Chem Phys Chem* 2001, *2*, 448–452; c) I. Seguy, P.
 Jolinat, P. Destruel, J. Farenc, R. Mamy, H. Bock, J. Ip, T. P. Nguyen, *J Appl. Phys.* 2001, *89*, 5442–5448.
- [24] a) H. K. Bisoyi, S. Kumar, *Chem. Soc. Rev.* 2010, *39*, 264–285; b) M.
 Gupta, S. P. Gupta, M. V. Rasna, D. Adhikari, S. Dhara, S. K. Pal, *Chem. Commun.* 2017, DOI: 10.1039/C6CC09509G
- [25] a) M. Gupta, I. Bala, S. K. Pal, *Tetrahedron Letters* 2014, *55*, 5836-5840; b) M. Gupta, S. K. Pal, *Langmuir* 2016, *32*, 1120-1126; c) S. Setia, S. K. Pal, *Chemistry Select* 2016, *5*, 880-885; d) H. Shi, Y. Zhao, X. Zhang, Y. Zhou, Y. Xu, S. Zhou, D. Wang, C. C. Han, D. Xu, *Polymer* 2004, *45*, 6299-6307; e) M. J. Jurow, B. A. Hageman, E. DiMasi, C.-Y. Nam, C. Pabon, C. T. Black, C. M. Drain, *J. Mater. Chem. A*, 2013, *1*, 1557-1565.
- [26] a) M. Lehmann, S. Gloza, S. Roth, *Chem. Mater.* 2015, *27*, 8181–8184;
 b) M. Lehmann, P. Maier, M. Grene, M. Hegel, *Chem. Eur. J.* 2017, *23*, 1060-1068;
 c) M. Lehmann, M. Jahr, F. C. Grozema, R. D. Abellon, L. D. A. Siebbeles, M. Mu''ller, *Adv. Mater.* 2008, *20*, 4414–4418;
 d) M. Lehmann, C. K. Herbert Meier, S. Renker, A. Oehlhof, *J. Mater. Chem.*, 2006, *16*, 441–451.
- [27] a) R. Goddard, M. W. Haenel, W. C. Herndon, C. Krüger, M. Zander, J. Am. Chem. Soc. 1995, 117, 30 41; b) X. Feng, W. Pisula, T. Kudernac, D. Wu, L. Zhi, S. De Feyter, K. Müllen, J. Am. Chem. Soc. 2009, 131, 4439 4448.
- [28] L. B.-Å. Johansson, Spectrochimica Acta A 1991, 47, 857-861.
- [29] Y. Jiang, L. Lu, M. Yang, C. Zhan, Z. Xie, F. Verpoort, S. Xiao, *Polym. Chem.* 2013, 4, 5612–5620.
- [30] C.-W Chang, H.-Y Tsai, K.-Yu Chen, Materials 2014, 7, 5488-5506.

WILEY-VCH

Table of Contents

FULL PAPER

New perylene-centered disc tetraester derivatives have been designed and synthesized that show soft crystal columnar behaviour and nematic columnar mesophase at room temperature over a wide temperature range. materials These may find applications for optoelectronic and solid state devices.



I. Bala, Dr. S. P. Gupta, J. De, Dr. S. K. Pal*

1-12

Room temperature columnar nematic and soft crystalline columnar assemblies of a new series of perylene-centered disc tetramers