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### Pentadecyl Phenol- and Cardanol-Functionalized Fluorescent, Room-Temperature Liquid-Crystalline Perylene Bisimides: Effect of Pendant Chain Unsaturation on Self-Assembly

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Abstract: A new perylene bisimide (PBI) building block based on pentadecyl phenol (PDP) or cardanol was developed, which upon esterification with 3,4,5-tridodecyloxy gallate resulted in highly emissive, room-temperature liquid-crystalline (LC) molecules. The self assembly in solution was studied in detail by NMR spectroscopy, UV/Vis absorption, and fluorescence spectroscopy. In solution both PDPand cardanol-based PBI exhibited similar behavior. They were molecularly dissolved in chloroform (CHCl<sub>3</sub>) but formed rotationally displaced H-type aggregates that emitted at 640 nm in methylcyclohexane (MCH). Surface morphology in dropcast films were characterized using microscopic techniques such as SEM, TEM, and atomic force microscopy (AFM). The liquidcrystalline properties were studied using differential scanning calorimetry (DSC), polarized light microscopy (PLM), and variable-temperature Xray (small-angle X-ray scattering (SAXS) and wide-angle X-ray diffrac-

**Keywords:** aggregation • liquid crystals • mesophases • pi interactions • self-assembly tion (WXRD)) studies. Variable-temperature X-ray studies in the LC phase indicated strong  $\pi$ - $\pi$  stacking interaction present in the PDP-based PBI derivative, whereas the stacking was absent in the LC phase of the cardanol-based PBI. The latter formed selforganized structures of extremely short length due to the presence of *cis* double bonds in the C15 alkyl side chain, whereas the saturated alkyl side chain in PDP could pack efficiently, thereby resulting in nanofibers that were several micrometers in length.

### Introduction

Liquid-crystalline materials that can act as charge-transport channels are highly attractive as potential materials for application in organic electronic devices such as field-effect transistors (FET),<sup>[1]</sup> electroluminescent displays,<sup>[2]</sup> photovoltaic cells.<sup>[3]</sup> Recently various examples of discotic molecules such as triphenylenes,<sup>[4,5]</sup> hexabenzocoronenes,<sup>[6]</sup> and phthalocyanines<sup>[7–9]</sup> have been reported to form  $\pi$  stacks that exhibited increased charge-carrier mobilities due to the higher molecular order imparted by the  $\pi$ -stacking arrangement. All of the above-mentioned molecules possessed electronrich aromatic cores that gave rise to columnar  $\pi$  stacks with p-type semiconducting properties. In this context,  $\pi$ -stacked liquid-crystalline n-type perylene bisimides (PBIs) are important because there are not many choices for n-type organic molecules.<sup>[10-13]</sup> The  $\pi$  stacking in perylene molecules is expected to result in an increase in the exciton diffusion length and stabilize the charge-separated states, thereby slowing down the charge recombination. The introduction of

agonal mesophases-in perylene bisimides. However, retaining the liquid-crystalline order at room temperature is an important property as far as long-term sustainability is concerned. Since the first report on liquid-crystalline perylene bisimides by Cormier et al. in 1997 based on linear and branched poly(oxyethylene) derivatives,<sup>[14,15]</sup> several reports have appeared that made use of several building motifs such as long linear alkyl chains,<sup>[16]</sup> swallowtail,<sup>[17]</sup> and dodecyloxy benzoyl substituents<sup>[18-23]</sup> to induce liquid crystallinity in perylene bisimides. Bay substitution was another approach that extended the range of absorption of perylene bisimides and at the same time improved their solubility and also decreased the clearing temperature.<sup>[20]</sup> However, it resulted in a twisting of the aromatic core, which hindered self-assembly. Recently, reports are available in which proper and well-designed bay substitution resulted in new two dimensional organization in the solid state with improved chargecarrier mobilities.<sup>[24-27]</sup> Cardanol and its saturated analogue pentadecyl phenol (PDP) are bio-based amphiphilic molecules that can function as molecular building blocks that have all the features necessary for self-assembly.<sup>[28-32]</sup> They have a phenolic group, which enables further functionalization, and a long C15 alkyl chain, which is not easily available by synthetic routes.<sup>[33-38]</sup> This C15 alkyl side chain can self-organize by interdigitation, whereas the aromatic unit can do so by  $\pi-\pi$  stacking interactions. Cardanol has an un-

3,4,5-trialkoxyphenyl substitution into the periphery has been shown to induce mesogenicity—usually columnar hex-

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saturation in this C15 side chain that differentiates it from PDP in terms of self-assembly.<sup>[30]</sup> There are several reports that describe the self-assembled nanostructures formed in systems based on cardanol or PDP; however, there are no reports on the combination of the properties of both cardanol or PDP with that of the well-studied perylene bisimides. This prompted us to design a novel building block based on these two important ingredients along with the 3,4,5-tri(dodecyloxy)phenyl substitution to impart mesogenicity with the expectation that the interesting mix and match of properties that this combination generated would definitely make this molecular design a sought-after one for future research.

In this article, we introduce a novel building block that combines perylene with PDP or cardanol and possesses a terminal phenolic functionality. These nonluminescent building blocks were converted to highly fluorescent derivatives by means of coupling with a 3,4,5-tri(dodecyloxy)phenyl group through ester linkages. The resulting molecules exhibited room-temperature liquid crystallinity (LC) and also retained their emission in the LC phase. Alkoxy phenyl substitution is usually known to result in an almost complete quenching of fluorescence in solution, probably due to photoinduced electron transfer from the electron-rich alkoxyphenyl groups to the perylene core.<sup>[20]</sup> In fact, very few examples are reported for perylene bisimides in which their dye aggregates have been shown to have intense emission.<sup>[24,39,40]</sup> Thus, without additional noncovalent interaction aids like hydrogen bonding or metal ion interaction, and making use of only  $\pi$ - $\pi$  stacking, we have been able to ach-

ieve self-organized dye aggregates that were liquid crystalline and exhibited intense emission in solution as well as in the solid state. Room-temperature liquid crystallinity is an important property that helps to retain the self-organization over long periods of time after thermal processing. Most of the reported PBIs are either monotropic or display an LC range at higher temperature.<sup>[16]</sup> In addition, they also have multiple transitions (crystalline or LC) within a narrow range of temperature. As the charge-carrier mobility is different in different LC phases, a material with single discotic LC phase over a wide temperature range is desirable for practical device application.

### **Results and Discussion**

The novel building blocks that combine pervlene tetracarboxylic dianhydride (PTCDA), pentadecyl phenol (PDP), or cardanol were synthesized as described in Scheme 1. In short, PTCDA was first coupled with 2.2 equivalents of 4amino-3-pentadecyl phenol or its unsaturated analogue based on cardanol to obtain the novel phenol-terminated building blocks 1 and 2. Cardanol, which was obtained from cashew-nut-shell liquid (CNSL), is a phenol that has a mixture of unsaturations (mono-, di-, and tri-) in the pendent C15 alkyl chain. Due to the difficulty in separating the mixture of mono-, di-, and tri-unsaturated cardanol, all three derivatives were present in the amine derivative (as confirmed by LC-MS data given in Figure S1 of the Supporting Information). The MALDI-TOF mass spectra of 2 (Figure S2 in the Supporting Information) also showed multiple peaks that correspond to various possible combinations of unsaturation in the side chain. The two diols differed in appearance with 1 being red in the solid state, whereas 2 was maroon. The diols were coupled with 3,4,5-tri(dodecyloxy)benzoyl chloride to obtain the final molecules 3 and 4. The molecules were subjected to purification procedure as described in detail in the Experimental Section. The purity of the final products was confirmed by elemental analysis and unimodal distribution curves in the size-exclusion chromatography (SEC; Figure S4 in the Supporting Information). The cardanol-based pervlene bisimide ester 4 differed in mass by 4 units compared to the PDP-based perylene bisimide ester 3, in their SEC chromatograph. The single peak



Scheme 1. Synthesis of perylene bisimides 3 and 4.

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in the SEC coupled with the mass spectra (MALDI-TOF) reaffirmed the high purity of the molecules under study. The PBI derivatives were structurally characterized by proton NMR spectra (Figures S5 and S6 in the Supporting Information).

**Temperature- and concentration-dependent** <sup>1</sup>H NMR spectroscopy studies: The proton NMR spectra of the perylene bisimides 3 and 4 recorded in  $CDCl_3$  exhibited a simple pattern of sharp signals with a doublet of doublet for the eight perylene protons (labeled a and b in Figure 1), which indi-



Figure 1. Temperature-dependent <sup>1</sup>H NMR (400 MHz) spectra of **3** ( $1.2 \times 10^{-2}$ M) in [D<sub>14</sub>]MCH at 0 to 85 °C and in CDCl<sub>3</sub> at 25 °C. (The signals labeled a and b are the four inner and four outer perylene ring protons, and the asterix indicates solvent).

cated that they were present in the molecularly dissolved form in chloroform. The <sup>1</sup>H NMR spectrum in nonpolar solvent methylcyclohexane (MCH, deuterated) was different from that in CDCl<sub>3</sub>. At 20°C, the spectrum was broad and peaks overlapped with each other due to the presence of different aggregated species. Figure 1 compares the expanded aromatic proton region ( $\delta = 10-6$  ppm) of PDP derivative 3 recorded in CDCl<sub>3</sub> at 25 °C and in [D<sub>14</sub>]MCH at different temperatures from 0 to 85°C. At temperatures below 60°C, the spectra remained complex and broad, thus indicating that the aggregates were stable. Upon increasing the temperature beyond 60°C, the complex pattern simplified and sharpened. The dotted line traces the four inner-ring and four outer-ring protons of the perylene bisimide aromatic core as it shifted from downfield to upfield due to shielding by the  $\pi$  systems of close neighbors in the aggregates.<sup>[21]</sup> Dilution is also known to result in breakup of aggregates in solution. Figure S8A in the Supporting Information shows a comparison of the <sup>1</sup>H NMR spectra of **3** recorded at 25 °C at two different concentrations,  $-1.2 \times 10^{-2}$  and  $1.2 \times 10^{-3}$  M. However, the sample remained fully aggregated at the low concentration as confirmed by the broad peak positions. UV/Vis absorption studies (discussed in detail later on) of samples of much lower concentration  $(5 \times 10^{-5} \text{ M})$  also

showed that the aggregates remained stable even upon heating up to 70 °C. Similar studies (variable temperature and concentration) were carried out for **4** (Figures S7 and S8 in the Supporting Information). The temperature- and concentration-dependent proton NMR spectroscopic studies clearly showed the existence of  $\pi$ - $\pi$  stacked aggregates in nonpolar solvent like methylcyclohexane.

**Photophysical studies**: Building blocks **1** and **2** were nonfluorescent, whereas after ester functionalization the fluorescence was regained. The solubility of **1** and **2** in common organic solvents like CHCl<sub>3</sub> was very poor; however, they were soluble in THF and other polar solvents. The absorption in THF indicated typical features of perylene bisimide with peaks at 521, 486, and 455 nm (Figure S9 in the Supporting Information), but the quantum yield in THF was very low ( $\Phi = 0.07$ ).

The ester derivatives **3** and **4**, on the other hand, were completely soluble in common organic solvents like chloroform, dichloromethane, methylcyclohexane, and so on. In chloroform, they exhibited the characteristic features of perylene bisimide absorption with four peaks in the range of 400 to 530 nm, which corresponded to the 0–0, 0–1, 0–2, and 0–3 electronic transitions, respectively, whereas aggregation was observed in MCH. In MCH the absorption was broad and peak maximum was blueshifted. Compound **4** also showed a similar behavior. Table 1 shows a comparison of the values of  $\lambda_{max}$  in these two solvents for both molecules **3** and **4**. Variable-concentration  $(1 \times 10^{-6} \text{ to } 5 \times 10^{-5} \text{ m})$  and variable-temperature studies were carried out for both **3** and **4** in MCH.

Table 1. Photophysical properties in  $CHCl_3$  and MCH (in brackets) at approximately 0.1 OD.

Sample	$\lambda_{\max}$ (abs) [nm]	$\lambda_{\max}$ (emission) [nm]	$\phi_{ ext{FL}}{}^{[a]}$	$ au_{ m avg}^{[b]}$ [ns]	$\chi^{2[b]}$
3	527	537	0.91	3.1 <sup>[c]</sup>	1.12 <sup>[c]</sup>
	(514)	(521)	(0.50)	$(3.2)^{[d]}$	$(1.01)^{[d]}$
				$(23.4)^{[e]}$	$(1.22)^{[e]}$
4	527	537	0.83	3.2 <sup>[c]</sup>	$1.04^{[c]}$
	(514)	(521)	(0.51)	$(3.4)^{[d]}$	(0.99) <sup>[d]</sup>
				$(20.2)^{[e]}$	$(1.09)^{[e]}$

[a] Excitation wavelength is 488 nm in CHCl<sub>3</sub> and MCH. Quantum yields were calculated using 0.1 OD rhodamine 6G solution at 488 nm in ethanol. [b] LED 458 nm; 0.1 OD at 458 nm. [c] Solvent: CHCl<sub>3</sub> and observed at 537 nm. [d] Solvent: MCH and observed at 520 nm. [e] Solvent: MCH and observed at 640 nm.

Figure 2a shows the absorption spectra for **3** as a function of concentration, which shows that the spectra became broader and less structured with increase in concentration, thus reflecting the electronic coupling between the chromophores. Furthermore, a new broad bathochromically shifted band appeared at 538 nm. Figure 2b shows the transition from the aggregated state to the molecularly dissolved state as a function of temperature for a solution of  $1 \times 10^{-6}$  M concentration. At the highest temperature of 70 °C, the absorp-



Figure 2. a) Variable-concentration and b) variable-temperature absorption spectra of **3** in MCH.

tion spectra resembled that of molecularly dissolved species as observed in chloroform. These spectral features were indicative of formation of face-to-face stacked rotationally displaced H-type aggregates. Isosbectic points were observed at 469, 490, and 529 nm during this transition from the molecularly dissolved to the aggregated species. Similar variable-temperature measurements were carried out for different concentrations that ranged from  $1 \times 10^{-6}$  to  $5 \times 10^{-5}$  M (Figure S10 in the Supporting Information; Figure S11 shows the plot for 4). At the highest concentration of  $5 \times$  $10^{-5}$  M, the aggregates remained stable until the highest temperature of 70°C, thus indicating the thermal stability of the aggregates. The aggregates in solution are dynamic and polydisperse in nature and can usually be described by the isodesmic equilibria that assumes a single equilibrium constant for every monomer addition to the growing aggregate.<sup>[41]</sup> The isodesmic model could be fitted to both variable-concentration as well as variable-temperature data. However, compared to variable-concentration measurements, variable-temperature studies spanned a wider set of data points, thereby resulting in a more accurate determination of parameters.<sup>[42]</sup> The propensity for aggregation can be quantified by calculating the degree of aggregation ( $\alpha$ ) using Equation (1):

$$\alpha(T) = \varepsilon(T) - \varepsilon(\mathbf{M}) / \varepsilon(\mathbf{A}) - \varepsilon(\mathbf{M})$$
(1)

in which  $\varepsilon(T)$  is the extinction coefficient at temperature *T*, and  $\varepsilon(M)$  and  $\varepsilon(A)$  are those for the molecularly dissolved species and fully aggregated species, respectively. The

degree of aggregation as a function of temperature could be fit very well to an isodesmic sigmoidal curve (Figure S12 in the Supporting Information). Table 2 shows a comparison of  $\alpha_{0.5}(T)$  (the temperature at which  $\alpha = 0.5$ ) obtained for these

Table 2. Degree of aggregation and stack length of **3** in MCH at various concentrations. The data in brackets are those for **4**.

Concentration [µм]	$T_{\rm m}^{[{\rm a}]} ({\rm at} \; \alpha_{0.5})$	$\alpha^{[b]}$	$DP_{N}^{[b]}$
1	32 (28)	0.81 (0.78)	2.31 (2.15)
5	44 (42)	0.97 (0.96)	5.77 (4.78)
10	53 (47)	0.99 (0.98)	8.86 (6.89)
50	57 (53)	0.99 (0.99)	38.48 (10.62)

[a]  $T_m$ =melting temperature of aggregates that have an aggregation value of 0.5. [b] Values determined at 20 °C.

different concentrations. It could be seen that this temperature increased from 32 °C at low concentration  $(1 \times 10^{-6} \text{ M})$  to 57 °C at high concentration  $(5 \times 10^{-5} \text{ M})$ , thus indicating better stability of the aggregates. Similar plots were also observed for **4** (Figure S13). The  $a_{0.5}(T)$  values were slightly lower for **4** (Table 2) than for the saturated counterpart, thus suggesting lower thermal stability for the aggregates. From the degree of aggregation, the average stack length  $(DP_N)$  of the aggregates was calculated by using Equation (2):

$$DP_N(T) = 1/\sqrt{1-\alpha(T)}$$
<sup>(2)</sup>

As expected, the size of the aggregates decreased with an increase in temperature. Table 2 compares the average stack length  $(DP_N)$  at room temperature as a function of increase in concentration. The stack length increased linearly with concentration and at the highest concentration studied that is,  $5 \times 10^{-5}$  M (50 µM), at which the sample remained aggregated even at the highest temperature of 70°C, the stack length was as high as 38 for the PDP derivative (3). This is typical of isodesmic assembly by which the stack length of the aggregated species increased slowly and only at high concentrations associated with high association constants, larger-sized architectures were formed. For 4, the transition temperatures as well as the stack length were lower, with the stack length at the highest concentration of  $5 \times 10^{-5}$  M being less than half the value relative to its saturated counterpart.

The emission characteristics of the perylene bisimide molecules were studied in CHCl<sub>3</sub> by excitation at 458 nm. Both the molecules gave the typical emission with peak maxima at 537, 576, and 626 nm. The quantum yields were calculated using rhodamine 6G as the standard; the values are given in Table 1. The quantum yield values were 0.91 and 0.83 for **3** and **4**, respectively, in CHCl<sub>3</sub>, thereby indicating that upon formation of the ester linkage, the hitherto nonluminescent building blocks **1** and **2** converted to highly luminescent PBI derivatives. In MCH, a new redshifted peak was observed at 643 nm, and the onset was also redshifted. These are all signatures of face-to-face  $\pi$ -stacking H aggregation, which confirms the observation from the UV/Vis absorption spectra.

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Figure 3. a) Concentration-dependent fluorescence spectra of **3** in MCH (excited at 458 nm) without normalization and b) after normalization at 524 nm. c) Temperature-dependent fluorescence spectra of **3** in MCH at  $5 \times 10^{-5}$  M concentration without normalization and d) after normalization at 524 nm. e) Temperature-dependent fluorescence spectra of **3** in MCH at  $1 \times 10^{-6}$  M without normalization and f) after normalization at 524 nm.

Figure 3a shows the evolution of the new peak at 643 nm as a function of increasing concentration in MCH. Figure 3c-f shows the increase in intensity of the emission at 643 nm as a function of temperature for solutions of increasing concentrations. For the highest concentration of  $5 \times 10^{-5}$  M, even at 70°C, which was the highest temperature of measurement, emission from the aggregates was pronounced with a noticeable difference in the peak intensity ratios that is suggestive of H aggregates. The intensity of the aggregate emission at 640 nm at the lowest temperature of 10°C was 20 times higher for  $5 \times 10^{-5}$  M solution relative to that for the lowest concentration of  $1 \times 10^{-6}$  M, thus indicating that the aggregates were highly emitting species. Similar spectral features were observed for **4** (Figure S14 in the Supporting Information).

Thin-film samples were prepared by dropcasting the solutions from MCH. The emission from film did not have the monomer peak at 520 nm, only aggregate emission at 640 nm. Thin films of melt-cooled samples were also prepared on glass substrates by heating the samples to isotropic melt and then slowly cooling to room temperature. Polarized light microscopy (PLM) studies confirmed that these melt-cooled samples retained the LC textures upon cooling to room temperature. Figure 4 shows the intense emission for the melt-cooled sample, which had an emission only at 640 nm without any monomer emission. The inset in Figure 4 shows the normalized UV/Vis absorption spectra of the LC films for the two ester derivatives. All these results indicated the highly emissive nature of both the derivatives **3** and **4** in dropcast film as well as solid melt-cooled state, which are highly desirable for practical application in devices.

Fluorescence lifetimes were studied for nitrogen-bubbled 0.1 OD solutions (OD = optical density) in chloroform as well as in MCH for the two ester derivatives, **3** and **4**. The decay was monitored both at the monomer band of 520 nm as well the aggregate band at as 640 nm. Table 1 gives the fit parameters, for which the data brackets represents the in decay obtained in MCH (Figures S15 and S16 in the Supporting Information). When the data was fitted to single-exponential function, high  $\chi^2$ values were obtained for the fit. A greatly improved fit with

 $\chi^2$  values around 1 was obtained using a double-exponential function. The resulting short and long lifetimes were approximately 1.7 and 3.4 ns, respectively, for the monomer decay in both chloroform and MCH for both samples **3** and **4**. The average lifetime decay (taking into account their percentage contribution) was 3.1 ns in chloroform and around 3.2 and



Figure 4. Fluorescence spectra of **3** and **4** in the melt-cooled state. Inset: Corresponding normalized UV/Vis absorption spectra.

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3.4 ns, respectively, in MCH for samples **3** and **4**, which was similar to literature reports.<sup>[21]</sup> As discussed by Winnik et al. for a perylene-labeled polymer, a double-exponential fit does not imply that there were two distinct species with different lifetimes.<sup>[43]</sup> A single emitting species could exhibit nonexponential decay, which is represented by sums of two or more exponentials due to solvent relaxation processes.<sup>[44]</sup> The aggregate band at 640 nm was observed only in MCH and it exhibited a much slower decay with a value of  $\tau_{agg(av)}$ =23 and 20 ns, respectively, for samples **3** and **4**.<sup>[21]</sup> Thus, the aggregate fluorescence lifetime was six times higher than the monomer fluorescence lifetime, and also among the two systems, the PDP-based perylene derivative had longer aggregate fluorescence lifetime, thereby indicating a more stable species.

Room-temperature wide-angle X-ray diffraction (WXRD) studies: The only structural difference between the two building blocks 1 and 2 was the presence of double bonds in the C15 side chain in 2. Both 1 and 2 were high melting compounds (>400 °C), and due to their high melting temperatures, it could not be confirmed by DSC or PLM studies whether they formed LC phases. The difference in the solid-state packing in these two building blocks was studied using WXRD. Room-temperature WXRD studies clearly indicated the difference in the packing of the two molecules as a consequence of the unsaturation in the side chain (Figure S17 in the Supporting Information).

The PDP derivative 1 was more crystalline with sharp peaks at  $2\theta = 4.70$  (18.77 Å), 9.50 (9.29 Å), 11.06 (7.99 Å), and 12.43° (7.12 Å). It also had a broad peak around  $2\theta$  $\approx 20^{\circ}$  (4.25 Å), which corresponded to the loosely packed alkyl chains, and a peak around  $2\theta = 24.7^{\circ}$  (3.59 Å) that indicated the presence of  $\pi$ - $\pi$  stacking. Compound 2 also had similar peaks, but the intensity of the peaks was lower and the peaks were diffused. The main difference between 1 and 2 was observed in the alkyl chain region. Sharp shoulders could be observed in the  $2\theta \approx 20^{\circ}$  region in the case of 1 in contrast to the broad featureless hump present in this region for 2. Additionally, the peak at  $2\theta = 24.7^{\circ}$  (3.59 Å) that corresponded to  $\pi$ - $\pi$  stacking was absent in 2. The *cis* double bonds in the latter made the alkyl chain packing difficult and reduced close contact between the aromatic core. Molecular modeling using density functional theory clearly demonstrated this difference in alkyl chain packing. Figure 5 shows the energy-minimized structures of the two molecules obtained using DFT.<sup>[45-50]</sup> In both molecules, the perylene core was perfectly flat with the phenyl ring perpendicular to the perylene plane.

**Thermal and liquid-crystal characteristics**: The thermal stability of the perylene bisimides were studied using thermogravimetric analysis (TGA) under a nitrogen atmosphere. They were found to be thermally stable until 380 °C. The thermotropic liquid-crystalline tendency of the series was studied using DSC analysis coupled with PLM and temperature-dependent small-angle X-ray scattering (SAXS) and



Figure 5. Energy-minimized structure (using density functional theory) of compounds **1** and **2** viewed orthogonally to the polyaromatic plane.

wide-angle X-ray diffraction studies. The DSC analysis gives information about the phase transitions and the enthalpies associated with these transitions; PLM helps identify the liquid-crystalline mesophases based on the texture observed; and X-ray diffraction gives detailed information about the molecular organization within the various phases at different temperatures.

Figure 6 shows the second heating and first cooling cycles of **3** and **4** at a scanning rate of  $10 \,^{\circ}\text{Cmin}^{-1}$ . In DSC, compound **3** showed three reversible transitions in the heating cycle at 20 (60.52 kJ mol<sup>-1</sup>), 167 (5.84 kJ mol<sup>-1</sup>), and 215  $^{\circ}\text{C}$  (16.72 kJ mol<sup>-1</sup>), whereas the corresponding transitions during cooling were observed at 202 (15.31 kJ mol<sup>-1</sup>), 163 (12.65 kJ mol<sup>-1</sup>), and 13  $^{\circ}\text{C}$  (52.55 kJ mol<sup>-1</sup>) (Table 3). The



Figure 6. DSC thermograms of **3** and **4** showing second heating and first cooling cycle at  $10^{\circ}$ Cmin<sup>-1</sup> with respective transition temperatures.

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first transition in the cooling corresponded to disordered columnar hexagonal ( $Col_{hd}$ ) mesophase as confirmed by the snow-crystal-like dendritic texture observed under PLM. Figure 7a and b show the large dendritic textures characteristic of a  $Col_h$  mesophase obtained after annealing the sample at 200 °C.<sup>[21]</sup>

Table 3. Phase-transition temperatures and enthalpies of mesophases.

Sample	Phase transitions <sup>[a]</sup> [ $T$ in °C ( $\Delta H$ in kJ mol <sup>-1</sup> )]
3	Cr 20 (60.52)→Col <sub>hp</sub> 167 (5.84)→Col <sub>hd</sub> 215 (16.72)→I
	$I 202 (15.31) \rightarrow Col_{hd} 163 (12.65) \rightarrow Col_{hp} 13 (52.55) \rightarrow Cr$
4	Cr 29 (42.78) $\rightarrow$ Col <sub>hd</sub> 195 °C (6.16) $\rightarrow$ I
	I 169 (3.49)→Col <sub>hd</sub> 17 (40.66)→Cr

[a] Phase-transition temperature [°C] observed during the first cooling and second heating cycle in DSC thermogram.

X-ray diffraction studies were also in accordance with a columnar hexagonal ordering of mesogens.<sup>[17-19]</sup> Although DSC showed a transition at 163 °C and shearability was also lost beyond this temperature, the dendritic textures did not show any visible changes under PLM until room temperature (25 °C). But the X-ray data clearly showed changes that occur around 160 °C as will be discussed in detail below. DSC showed further transition around 13 °C; however, the polarized light microscopic studies as well as the X-ray scattering studies could not be performed below room temperature. The LC nature was reversible with repeated heating

and cooling scans during DSC and X-ray analysis as well as when observed under PLM.

Variable-temperature small-angle X-ray scattering studies were undertaken both during heating and cooling cycles. Figure 8A shows the SAXS data as a plot of intensity versus  $2\theta$  (1.0–3.0°) at 25 (curve a) and 230°C (curve b) during heating, and at 200, 160, 100, and 25 °C (curves c, d, e, and f) during cooling for 3. Only a single peak that corresponded to  $d_{100}$  reflection was observed in the  $2\theta$  region between 1.0 and 3.0° that was studied.<sup>[51]</sup> The  $d_{100}$  value increased from 38.96 Å at 200 °C (2 $\theta$ =2.26°) to 43.69 Å at 25 °C (2 $\theta$ = 1.98°). The calculated  $a_{\text{hex}}$  lattice parameter  $(a_{\text{hex}} =$  $^{2}\sqrt{\binom{4}{3}d_{100}^{2}}$  increased from 44.99 Å at 200 °C to 50.45 Å at 25°C. The fully extended length of the molecule from one end to the other end was calculated to be around 57 Å using ChemDraw. The  $a_{hex}$  value at 25 °C was closer to this molecular length than that at higher temperature. Figure 8B shows the stack plot of the wide-angle X-ray diffraction studies taken during the cooling scan from the isotropic temperature at 230 °C and cooling to 25 °C for 3.

The first pattern in the isotropic phase (230 °C) showed only one broad diffuse peak around  $2\theta = 15-20^{\circ}$  (4–5 Å) that corresponded to loosely packed liquidlike alkyl chains.<sup>[17]</sup> The second pattern for the sample annealed at 200 °C showed only a single sharp peak at  $2\theta = 4.62^{\circ}$ (19.13 Å). No long-range intracolumnar order was observed at this temperature. The two peaks at  $2\theta = 2.26$  (SAXS) and 4.62° (WXRD) in the LC phase at 200 °C could be indexed



Figure 7. a),b) Polarization optical microscopic images of the snow-crystal-like dendritic texture obtained for **3** at 200 °C and c),d) for **4** showing spherulitic textures with maltase crosses at 185 °C.

to the 100, 200 Bragg reflection with the typical ratio of  $1:1/\sqrt{4}$  for a hexagonal system, and the structural information is comparable to reported literature.<sup>[18]</sup> The DSC thermogram showed a transition around 160°C, and the WXRD pattern at 160 °C showed multiple sharp diffractions both in the small-angle and wide-angle region. The appearance of the sharp peaks in the diffuse halo region of 15-20° indicated the crystallization of the alkyl chains. Also noticeable was the appearance of the sharp peak at  $2\theta = 21.5^{\circ}$  (4.1 Å), which corresponded to perylene  $\pi$ - $\pi$ stacking interaction. For the powder pattern at 160°C, the characteristic ratios of 1:1/  $\sqrt{4:1}/\sqrt{7:1}/\sqrt{12}$  of the (100), (200), (210), (220) reflections of the hexagonal lattice found reasonable agreement with the observed peaks (Table S1 in the Supporting Information).<sup>[18]</sup> The absence of any

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Figure 8. Variable-temperature a) SAXS and b) WXRD traces of **3** at various temperature intervals.

other peaks in the wide-angle region in the LC phase at 200 °C indicated the existence of a disordered columnar packing at higher temperatures. Upon cooling, the phase shifted from the 2D disordered hexagonal system at 200 °C to a highly ordered 3D monoclinic system at 25 °C. Correspondingly, the  $\pi$ - $\pi$  stacking also became stronger (decreased from 4.1 Å ( $2\theta$ =21.5°) at 160 °C to 3.77 Å ( $2\theta$ =23.5°) at 25 °C). SAXS had shown an expansion of the  $a_{hex}$  parameter upon cooling from 160 to 25 °C, which indicated an extended conformation of the alkyl chains at 25 °C. All these facts along with the observation that the shearability was lost below 160 °C suggested a plastic columnar hexagonal phase (Col<sub>hp</sub>) at lower temperatures. Figure 9 shows schematically the molecular ordering in the LC phase at various temperatures.

Compound **4** showed only two reversible transitions in the heating cycle (DSC) at 29 ( $42.78 \text{ kJ mol}^{-1}$ ) and 195 °C ( $6.16 \text{ kJ mol}^{-1}$ ), whereas during cooling transitions were observed at 169 ( $3.49 \text{ kJ mol}^{-1}$ ) and 17 °C ( $40.66 \text{ kJ mol}^{-1}$ ; Figure 6). The clearing temperature at 195 °C was approximately 20 °C lower than the saturated analogue, which was attributed to loosely packed nature of **4**. Upon cooling from the isotropic phase, spherulitic textures with maltese crosses, typical for columnar hexagonal organization (Figure 7c and d), were observed around 185 °C.



Figure 9. Schematic diagram showing the molecular ordering of **3** in the liquid crystalline phase.

Variable-temperature SAXS and WXRD studies were carried out for 4 at various temperature intervals during heating and cooling (Figure S18 in the Supporting Information). The SAXS showed a single peak around  $2\theta = 2.09 - 2.26^{\circ}$  similar to the observation for the PDP derivative. At room temperature (25 °C), a single peak was observed at  $2\theta = 2.09^{\circ}$ that corresponded to a  $d_{100}$  value of 42.19 Å. The  $a_{hex}$  lattice parameter was calculated to be  $(a_{\text{hex}} = \sqrt[2]{(\frac{4}{3}d_{100}^2)})$  of 48.72 Å. In the mesophase at 100 °C, the  $2\theta$  increased to 2.18°, which corresponded to a d spacing of 40.36 Å. This peak totally vanished in the isotropic phase at 230 °C, and during cooling, the single peak reappeared at 165 °C at  $2\theta$  of 2.26° that corresponded to a *d* spacing of 38.84 Å. This also corresponded with the first transition observed in DSC upon cooling at 169°C. Thereafter upon cooling further to 25°C, although no visible transition was observed in the DSC, the SAXS revealed an increase in d spacing to 40.36 Å at 100 °C and finally to 42.19 Å at 25 °C. The d spacing in the mesophase during heating and cooling were identical. It is interesting to note that the  $d_{100}$  value at the start of the LC phase—200 °C for 3 and 165°C for 4-were exactly identical and corresponded to a value of 38.84 Å. This corresponded to the disordered hexagonal phase in both systems. Upon cooling, the  $d_{100}$  value increased for both the molecules; however, unlike the PDP system in which the pentadecyl chain could stabilize in the fully extended form, the cis double bond in the cardanol chain restricted a fully extended packing. Hence the unit-cell dimension for **4** was smaller  $(a_{\text{hex}} = 48.71 \text{ \AA})$ than that of **3** ( $a_{\text{hex}} = 50.45$  Å).

In sharp contrast to the PDP derivative **3**, the cardanol derivative **4** did not show many sharp peaks in the WXRD. Also noticeable was the absence of the peak around  $2\theta = 22-26^{\circ}$  that corresponded to the  $\pi$ - $\pi$ -stacking interaction. The lower propensity of the pendant cardanol chain to pack effectively resulted in this lower  $\pi$ - $\pi$ -stacking interaction in **4**. The sample that crystallized as solution at 25 °C showed sharp peaks at  $2\theta = 4.9$  and 5.8° and two broad peaks around  $2\theta = 10-15$  and 15-25°. The broad peak between 15-

25°, which is usually attributed to alkyl chain packing, showed sharp spikes. The second pattern was for the LC phase at 100°C during heating and it showed a sharp peak around  $2\theta = 4.77^{\circ}$ . In the isotropic state at 230 °C, this peak disappeared and only the two broad peaks at around  $2\theta =$ 10-15 and 15-25° remained. The WXRD pattern at 190°C also showed that the sample was still in the isotropic phase. But at 180 °C, a small peak appeared around  $2\theta = 4.49^{\circ}$ . Although DSC and SAXS did not show any noticeable change, observation under the PLM had showed that spherulitic pattern started to appear around this temperature. Compared with the WXRD pattern at 100 °C during heating, the intensity of the peak at  $2\theta = 4.77^{\circ}$  remained very low, even when cooling to 25 °C. Thus, although both pervlene derivatives 3

and 4 exhibited columnar LC phases, there were also sharp contrasts in their packing that were highlighted by the absence of  $\pi$ - $\pi$ -stacking interaction in the latter. The cis double bond in the C15 side chain of 4 made a difference in the LC packing as well as the LC pattern observed since it reduced the overall ordering of the alkyl chain.

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Another comparison between the two molecules was the total enthalpy changes observed during the heating and cooling cycles in DSC. The enthalpy change in the heating cycle for **3** was  $83.08 \text{ kJ mol}^{-1}$ , whereas for **4** it was 48.94 kJ mol<sup>-1</sup>, thus indicating more ordered phases for the former. This could be also supported by the enthalpy of isotropization, which was higher for **3** (16.72 kJ mol<sup>-1</sup>), since the energy required to break the initially formed ordered structures was more for 3, whereas in the case of 4, less-ordered structures could be easily broken with a small enthalpy change of 6.16 kJ mol<sup>-1</sup>. Importantly, both the samples remained frozen in the LC phase up to room temperature, and textures were stable for several weeks, which is a very useful property as far as device fabrication in the LC phase is concerned.<sup>[52-53]</sup>

Solid-state morphology: Evidence for aggregate formation in both the perylene bisimides 3 and 4 were obtained from microscopy techniques such as SEM, TEM, and contactmode AFM. SEM was recorded on silicon wafers for dropcast samples from MCH at a concentration of  $1 \times 10^{-4}$  M.

Figure 10a-c show the images obtained for 3, which revealed featherlike patterns. These were observed uniformly over the entire sample and were several micrometers long with diameters in the nanometer range. The TEM images of **3** gave more insight into the featherlike morphology.

Figure 11a-c shows TEM images obtained for  $1 \times 10^{-5}$  M sample dropcast from MCH onto 200 mesh-sized carboncoated copper grids. Long cylindrical bundles of nanorods that were several micrometers in length with average bundle



Figure 10. SEM images of a)-c) 3 and d)-f) 4 dropcast from MCH.



Figure 11. TEM images of a)-c) 3 and d-f) 4 dropcast from MCH.

diameter in the range of 300-400 nm could be observed. The observation from TEM was in accordance with that from SEM, with the bundles not being in one straight length but sickle-shaped with bifurcation at regular intervals. Similar studies were carried also out for 4. Figure 10d-f shows the SEM images recorded for a  $1 \times 10^{-4}$  M sample dropcast from MCH. It could be observed that the features were similar except for the shorter length. The TEM images for 4 (Figure 11d-f) were in sharp contrast to that for 3. The sickle-shaped nanorod bundles were extremely short, and many of them were observed to twist around into coils or springs with an average bundle diameter of around 250 nm. This observation was very much in agreement with the observation from solution studies in MCH whereby shorter average aggregate length  $(DP_N)$  was obtained for the cardanol derivative than the PDP derivative. Figure 12a-c shows the AFM images of 3 taken in contact mode for samples dropcast from MCH onto silicon wafers at a concentration of  $1 \times 10^{-4}$  m. The AFM images also showed features identical to that observed using TEM, that is, sickle-shaped bundles of nanorods with widths in the range of 300-400 nm, lengths in micrometers, and vertical distances of 20-30 nm obtained from the height profile. The AFM images of the cardanol derivative in Figure 12d-f also clearly show the short V-shaped aggregates in conformity with the SEM images.

Based on this direct evidence, a model for the self-organization of these novel PBI derivatives could be established. These molecules showed fibrous aggregate formation driven by strong  $\pi$ - $\pi$ -stacking interactions. Often fibrous network formation observed in small molecules is driven by additional forces in the form of hydrogen bonding.<sup>[29]</sup> It is interesting to ponder the driving forces that lead to high levels of aggregate formation in the PBI derivatives reported here. The difference in the aggregate size in the two samples indicated different packing in the two systems. The X-ray data also in-

dicated a clear difference in the packing interaction of the two molecules. The sample of 3-both in the RT as well as in the LC-RT-had a sharp peak in the wide-angle region that corresponded to a  $\pi$ - $\pi$ -stacking interaction of 3.77 Å, which was clearly absent in the cardanol-based PBI derivative 4. The difference in packing in the two systems, especially in the solid state, was driven by the packing constraints of the C15 alkyl side chain of cardanol, which had the cis double bond. In both the PDP as well as the cardanol system, the  $\pi$ - $\pi$  stacking of the pervlene core was rotationally displaced by the steric hindrance of the C15 chain. Although this difference was not very strong in the solution, in the bulk samples the initially formed aggregates of 3 packed into columns with pendant C15 alkyl chains. Such packing was hindered by the twist caused by the cis double bond present in the cardanol-based PBI 4. By using ChemDraw, the total length of the molecule was calculated to be approximately 5.7 nm. Taking into consideration the  $\pi$ - $\pi$ -stacking distance of 3.77 Å along with sufficient alkyl chain interdigitation, it could be assumed that around 100 molecules were arranged laterally in each bundles and approximately 3000 molecules were stacked to form continuous rods in the PDP derivative. This sort of extensive packing was not possible in the cardanol derivative due to the presence of the kink in the C15 alkyl chain, thereby resulting in short twisted and coiled structures.

### Conclusion

Two novel perylene bisimide esters based on cardanol and pentadecyl phenol were synthesized and fully characterized. These perylene bisimide esters not only exhibited hexagonal columnar liquid-crystalline mesophases that were retained at room temperature but were also found to be highly emissive both in solution and melt-cooled solid film. A compari-

> son of structure and self-assembly in solution as well as in bulk for the pentadecyl phenol

> versus cardanol perylene bisimide derivative provided valuable insight into the packing

in these two systems. The pres-

ence of the long C15 alkyl

chain in the ortho position to

the imide linkage did not nega-

tively affect the propensity of these novel PBIs to form H-

type aggregates. Interestingly, a

kink in the alkyl chain introduced by way of the *cis* double

bond also did not result in a change in the type of aggregate formation, but there was a

drastic reduction in the aggre-

gate length. The X-ray measurements highlighted the simi-





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larities as well as differences in packing brought about by the presence of the *cis* double bond in the pendant alkyl substituent. Although both molecules exhibited columnar hexagonal mesophases, the LC window as well as the melting temperature were different due to the difference in their columnar ordering. The novel PBIs reported here remained in the LC phase at room temperature (25 °C) with low clearing temperature, which is highly desirable for practical device applications.

#### **Experimental Section**

General procedures: Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA), 3-pentadecyl phenol, zinc acetate, imidazole, methyl-3,4,5-trihydroxybenzoate, triethylamine, and 1-bromododecane were purchased from Sigma-Aldrich and used without further purification. Other reagents were purchased locally and purified using standard procedures. Cardanol was purified by double-vacuum distillation of cashew-nut-shell liquid (CNSL). All solvents were of analytical reagent grade and were used as received. DMF and THF were dried using the standard procedure.<sup>[54]</sup> <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using a Bruker AVENS 200 MHz spectrometer. Chemical shifts ( $\delta$ ) are reported in ppm at 25 °C using CDCl<sub>3</sub> or CDCl<sub>3</sub>/TFA as solvent with a small amount of tetramethylsilane (TMS) as internal standard. Variable-temperature measurements were recorded using a Bruker AVENS 400 MHz spectrometer with  $[D_{14}]$ MCH as solvent, and the spectra were calibrated against TMS. The purity of the compounds was determined by elemental analysis as well as MALDI-TOF in combination with SEC. SEC was performed using polystyrene standards for the calibration in CHCl3 as eluent. The flow rate of CHCl3 was maintained as 1 µLmin<sup>-1</sup> throughout the experiments, and the sample solutions at concentrations 3-4 mgmL<sup>-1</sup> were filtered and injected for recording the chromatograms at 30 °C. Elemental analysis was done using a Thermo Finnigan Flash EA 1112 series CHNS analyzer. Infrared spectra were recorded using a Bruker FTIR (ATR mode) spectrophotometer in the 4000-600 cm<sup>-1</sup> range. UV/Vis spectra were recorded using a Perkin-Elmer Lambda -35 UV/Vis spectrometer with a Peltier setup in the 0-100 °C range for variable temperature measurements. Steady-state fluorescence emission, variable-temperature, and time-resolved fluorescence lifetime measurements were performed using a Fluorolog HORIBA Jobin Yvon fluorescence spectrophotometer. The emission as well as excitation slit width was maintained at 1 nm throughout the experiments, and the data was obtained in  $S_{1/R_1}$  mode (to account for the variations in lamp intensity). Measurements were made at 90° positions for solutions and 22.5° in front-face films. The fluorescence quantum yields of the pervlene derivatives were determined in CHCl<sub>3</sub> using rhodamine 6G in ethanol ( $\Phi = 0.95$ ) as the standard by exciting at 488 nm. The optical density at  $\lambda_{488}$  was maintained at  $(0.1 \pm 0.05)$  to avoid reabsorption artifacts. Temperature-dependent fluorescence was recorded by using a Peltier sample compartment with a Peltier Sample Cooler F-3004 attached to a thermoelectric temperature controller (model no. LFI-3751) with an autotune PIDw supplied by Wavelength Electronics. The temperature was set manually for each reading and it was equilibrated for 10 min at each temperature before recording the spectrum. The tolerance range for each set temperature was maintained at 0.5 °C. For lifetime measurements, decay curves were obtained by the time-correlated single-photon counting (TCSPC) technique using a HORIBA Jobin Yvon Nano-LED source with wavelength 458 nm. Emission was collected at a monomeric emission of 520 nm and the aggregate emission at 640 nm. The samples were prepared by making the optical density (0.1  $\pm$ 0.05) at excitation wavelength ( $\lambda_{ex} \approx 459 \text{ nm}$ ) in CHCl<sub>3</sub> as well as in MCH. All samples were purged with gentle flow of nitrogen for 5 min. All experiments were performed under identical conditions. Fluorescence lifetime values were determined by deconvoluting the data with exponential decay using DAS6 decay analysis software. The quality of fit was judged by fitting parameters such as  $\chi^2 \approx 1$ , as well as the visual inspection of the residuals. The thermal stability of the PBIs was analyzed using a Perkin–Elmer STA 6000 thermogravimetric analyzer under a nitrogen atmosphere from 40 to 800 °C at 10 °C min<sup>-1</sup>. Differential scanning calorimetry was performed using a TA Q10 differential scanning calorimeter. Typically, 2–3 mg of samples was placed in aluminum pan, sealed properly, and scanned at 10 °C min<sup>-1</sup>. The instrument was calibrated with indium standards before measurements. The phase behaviors of the molecules were analyzed using a Leica DM2500P polarized optical microscope equipped with a Linkam TMS 94 heating and cooling stage connected to a Linkam TMS 600 temperature programmer. The transition from an isotropic to liquid-crystalline phase can be monitored by the evolution of characteristic textures. To remove the thermal history of the samples, the first heating cycles of DSC were neglected.

**WXRD**: WXRDs were recorded using a Philips analytical diffractometer with  $Cu_{K\alpha}$  emission, and the spectra were recorded in the (2 $\theta$ ) range of 3–50° and analyzed using X'pert software. Powder X-ray diffraction of all the samples was carried out using a PANalytical X'pert Pro dual goniometer diffractometer. An X'celerator solid-state detector was employed in wide-angle experiments. The radiation used was  $Cu_{K\alpha}$  (1.54 Å) with a Ni filter, and the data collection was carried out using a flat holder in Bragg–Brentano geometry. Care was taken to avoid sample displacement effects. Variable-temperature in situ XRD experiments were carried out using an Anton–Paar XRK900 reactor.

**SAXS**: SAXS measurements were made using a Bruker Nanostar ( $Cu_{K\alpha}$  radiation). The Nanostar was equipped with an 18 kW rotating anode generator and a 2D multiwire detector, with a sample-detector distance of roughly 1 m. The entire X-ray flight path including the sample chamber was evacuated to minimize air scattering. Samples were placed in capillaries and were mounted on the Bruker heating stage. The two-dimensional SAXS data was azimuthally averaged, and 1D data is presented after background subtraction.

**SEM**: SEM images were recorded using an FEI Quanta 200 3D scanning electron microscope with tungsten filament as electron source. Samples were prepared by dropcasting the sample (10  $\mu$ L, 10<sup>-4</sup>  $\mu$  concentration) from MCH onto a silicon wafer and allowed to dry for 4 to 5 days at ambient temperature followed by gold coating (3 nm) before subjection to SEM analysis.

**TEM**: An FEI Tecnai F30 electron microscope operating at 100 kV was used for HRTEM sample observation. It was equipped with a Gatan digital camera for recording micrographs. Samples were prepared from  $1 \times 10^{-5}$  M MCH solution dropcast onto a holey carbon-coated copper grid of 200 mesh size (Ted Pella) and allowed to dry at room temperature for 3 to 4 days. The size of nanorods was analyzed from TEM images using ImagePro software.

**AFM**: AFM images were taken by a Multimode scanning probe microscope equipped with a Nanoscope IV controller from Veeco Instruments, Inc. in the contact mode using an SiN probe, with a maximum scan size of 10  $\mu$ m ×10  $\mu$ m and with a vertical range of 2.5  $\mu$ m. For the AFM studies, samples were prepared by dropcasting  $1 \times 10^{-4}$  M solution in MCH onto silicon wafers and allowed to dry before being subjected to AFM analysis.

**MALDI-TOF**: Solution  $(1 \ \mu M)$  was premixed with dithranol matrix in CHCl<sub>3</sub> and mixed well before spotting on 96-well stainless steel MALDI plate by dried droplet method. It was then used for MALDI analysis. The mass spectral analysis was carried out using a Voyager-De-STR MALDI-TOF (Applied Biosystems, Framingham, MA, USA) instrument equipped with 337 nm pulsed nitrogen laser used for desorption and ionization. The mode of operation was in a reflector mode with an accelerating voltage of 25 kV. All spectra were acquired by accumulating 50 single laser shots over each sample spot with all the analysis was done in 5 to 6 replications. They were processed for advanced baseline correction and noise removal using Data Explorer software (Applied Biosystems).

**Molecular modeling**: All the calculations were carried out using density functional theory using the Turbomole suite of programs.<sup>[45]</sup> Geometry optimizations were performed using the B–P 86 functional.<sup>[46,47]</sup> The electronic configuration of the atoms was described by a triple- $\xi$  basis set augmented by a polarization function (TURBOMOLE basis set TZVP).<sup>[48]</sup> The resolution of identity (RI)<sup>[49]</sup> along with the multipole ac-

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celerated resolution of identity (marij)<sup>[50]</sup> approximations were employed for an accurate and efficient treatment of the electronic Coulomb term in the density functional calculations.

Synthesis of 4-amino-3-pentadecyl phenol: 4-Amino-3-pentadecyl phenol was synthesized form pentadecyl phenol (PDP) by following the literature procedure.<sup>[55]</sup>

Cardanol was obtained from double vacuum distillation of CNSL and was converted to the amine derivative by following the same procedure as that for PDP derivative.

Synthesis of 1: PTCDA (5 g, 0.013 mol, 1 equiv) was heated with 4amino-3-pentadecylphenol (8.9 g, 0.028 mol, 2.2 equiv) and Zn (OAc)<sub>2</sub> (0.5 g) in imidazole (40 g) at 160 °C for 4 h. The reaction mixture was then cooled to room temperature and precipitated by adding 2N HCl and washed with deionized water (1 L). The crude product was purified by dissolving in a minimum amount of THF and precipitating into methanol. The methanol washing was continued until the washings were clear and finally washed with hexane. The purified dark red solid was dried in a vacuum oven at 80°C for 12 h. Yield: 11.0 g (74%); m.p. > 400°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>+TFA):  $\delta = 8.91$  (s, 8H; perylene), 6.89–7.16 (m, 6H; ArH-PDP), 2.39 (t, 4H; Ar-CH<sub>2</sub>), 1.53 (t, 4H; Ar-CH<sub>2</sub>-CH<sub>2</sub>), 1.0-1.4 (br, 48H; aliphatic CH<sub>2</sub>), 0.84 ppm (t, 6H; terminal CH<sub>3</sub>); <sup>13</sup>C NMR:  $\delta =$ 166.27, 163.21, 162.65, 160.62, 155.86,143.08, 136.66, 134.16, 130.32, 127.00, 126.14, 124.92, 123.12, 122.59, 115.03, 111.82, 106.19, 32.17, 31.28, 29.92, 29.60, 22.85, 13.81 ppm; FTIR:  $\tilde{\nu}$  = 3359 ( $\nu$ (-OH<sub>stretch</sub>)), 2922, 2853, 1698 (v(C=O<sub>imide</sub>)), 1656, 1592, 1498, 1403, 1360, 1348, 1300, 1250, 1231, 1198, 1176, 967, 862, 813, 796, 750  $\rm cm^{-1};~MALDI-TOF~(dithranol$ matrix): m/z calcd for C<sub>66</sub>H<sub>78</sub>N<sub>2</sub>O<sub>6</sub>: 995.34; found: 996.65 [M+1], 1018.58 [M+Na].

**Synthesis of 2**: Compound **2** was synthesized by following the above procedure by using 4-amino-3-pentadec(8-ene-yl)phenol as the amine. The final maroon solid was dried in a vacuum oven at 80 °C for 12 h. Yield: 8.00 g (63%); m.p.>400 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>+TFA):  $\delta$ =8.91 (s, 8H; perylene), 6.89–7.17 (6H; ArH-cardanol), 5.23 (s, 4H; CH<sub>2</sub>-*CH*=*CH*-CH<sub>2</sub>), 2.39 (t, 4H; Ar–*CH*<sub>2</sub>), 1.9 (m, 8H; *CH*<sub>2</sub>-CH=*CH*-*CH*<sub>2</sub>), 1.53 (t, 4H; Ar-CH<sub>2</sub>-*CH*<sub>2</sub>), 1.0–1.4 (br, 32 H; aliphatic *CH*<sub>2</sub>), 0.83 ppm (t, 6H; terminal *CH*<sub>3</sub>); <sup>13</sup>C NMR:  $\delta$ =166.33, 163.54, 162.68, 161.82, 160.95, 155.81, 142.96, 136.73, 134.20, 130.42, 127.01, 126.19, 124.94, 123.07, 122.57, 117.43, 115.06, 111.79, 106.15, 31.98, 33.72, 31.23, 29.89, 29.38, 27.34, 25.09, 22.81, 13.77 ppm; FTIR:  $\tilde{\nu}$ =3333 ( $\nu$ (-OH<sub>stretch</sub>)), 3006 ( $\nu$ (=C–H<sub>stretch</sub>)), 2925, 2852, 1699 ( $\nu$ (C=O<sub>imide</sub>)), 1652, 1593, 1499, 1403, 1360, 1349, 1320, 1293, 1256, 1228, 1198, 1176, 969, 864, 812, 799, 749 cm<sup>-1</sup>; MALDI-TOF (dithranol matrix): *m/z* calcd for C<sub>66</sub>H<sub>74</sub>N<sub>2</sub>O<sub>6</sub>: 991.30; found: 992.62 [*M*+1], 1014.58 [*M*+Na].

**Synthesis of ester-functionalized perylene bisimides**: 3,4,5-Tri(dodecyloxy)benzoic acid was synthesized using literature procedure<sup>[56]</sup> and converted to the acid chloride by heating to reflux in an excess amount of thionyl chloride. The conversion was monitored by IR spectroscopy.

Compound 3: Compound 1 (0.5 g, 0.5 mmol) was dissolved in dry THF (15 mL) and the solution was cooled to 0°C. A small amount of triethyl amine was added as catalyst. 3,4,5-Tri(dodecyloxy)benzoyl chloride (0.77 g, 1.1 mmol) dissolved in dry THF (5 mL) was added dropwise over a period of 10 min while the temperature was maintained at 0 °C. The reaction mixture was left stirring under ice-cold conditions for 4 h. For workup, THF was distilled and removed. The crude product was purified by column chromatography in hexane. Yield: 0.64 g (55%); m.p. 215°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 8.7-8.9$  (dd, 8H; perylene), 7.44 (4H, s; Ar-H), 7.25-7.40 (m, 6H; ArH-PDP), 4.06 (t, 12H; Ar-O-CH<sub>2</sub>), 2.48 (t, 4H; PDP Ar-CH<sub>2</sub>), 1.0-1.9 (m, 172 H; aliphatic CH<sub>2</sub>), 0.87 ppm (m, 24 H; terminal  $CH_3$ ; <sup>13</sup>C NMR:  $\delta = 164.70$ , 163.42, 152.95, 151.46, 150.50, 146.75, 142.93, 142.13, 135.08, 132.04, 131.16, 129.96, 126.78, 123.86, 123.39, 122.00, 120.38, 108.50, 73.60, 69.24, 31.92, 31.13, 30.33, 29.37, 26.09, 22.69, 14.11; FTIR:  $\tilde{\nu} = 2962$  ( $\nu$ (-CH<sub>stretch</sub>)), 2923, 2853, 1730( $\nu$ (C=O<sub>ester</sub>)),  $1702(\nu(C\!\!=\!\!O_{imide})),\ 1663,\ 1593,\ 1503,\ 1465,\ 1429,\ 1359,\ 1337,\ 1260,\ 1199,$ 1098, 1025, 970, 805, 751 cm<sup>-1</sup>; MALDI-TOF (dithranol matrix): m/z calcd for C<sub>152</sub>H<sub>230</sub>N<sub>2</sub>O<sub>14</sub>: 2307.73; found: 2331.78 [M+Na], 2347.73 [M+K]; elemental analysis calcd (%): C 79.05, H 10.04, N 1.21; found: C 78.85, H 10.00, N 1.21.

**Compound 4**: This was synthesized following a similar procedure as for **3** but using **2**. The crude product was then purified by column chromatography in hexane. Yield: 0.325 g (28%); m.p. 195 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ =8.7–8.8 (dd, 8H; perylene), 7.45 (s, 4H; Ar–*H*), 7.25–7.40 (m, 6H; Ar*H*-cardanol), 5.20 (br, 4H; CH<sub>2</sub>-*CH*=*CH*-CH<sub>2</sub>), 4.06 (t, 12H; Ar-O-*CH*<sub>2</sub>), 2.48 (t, 4H; cardanol-Ar-*CH*<sub>2</sub>), 1.0–1.95 (m, 164H; aliphatic *CH*<sub>2</sub>), 0.87 ppm (t, 24H; terminal *CH*<sub>3</sub>); <sup>13</sup>C NMR:  $\delta$ =164.72, 163.33, 153.00, 151.51, 143.05, 141.99, 134.94, 131.90, 131.19, 129.89, 126.67, 123.92, 123.41, 122.86, 120.49, 108.60, 73.61, 69.30, 31.96, 31.17, 30.40, 29.60, 29.40, 29.22, 28.94, 27.15, 26.14, 22.72, 14.14 ppm; FTIR:  $\tilde{\nu}$ =3079 ( $\nu$ (= C–H<sub>stretch</sub>)), 2960 ( $\nu$ (-CH)<sub>stretch</sub>), 2925, 2853, 1731 ( $\nu$ (C=O<sub>ester</sub>)), 1703 ( $\nu$ (C=O<sub>mide</sub>)), 1664, 1594, 1503, 1464, 1430, 1359, 1338, 1260, 1197, 1103, 1021, 863, 804, 750 cm<sup>-1</sup>; MALDI-TOF (dithranol matrix): *m*/*z* calcd for C<sub>152</sub>H<sub>226</sub>N<sub>2</sub>O<sub>14</sub>: 2303.70; found: 2326.89 [*M*+Na]; elemental analysis calcd (%): C 79.19, H 9.88, N 1.22; found: C 78.85, H 9.64, N 1.24.

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