# **CHEMISTRY** A European Journal



### Accepted Article Title: Columnar Self-assembly of Electron deficient Dendronized bayannulated Perylene Bisimides Authors: Ravindra Kumar Gupta, D. S. Shankar Rao, S. Krishna Prasad, and Achalkumar Ammathnadu Sudhakar 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

To be cited as: Chem. Eur. J. 10.1002/chem.201705290

content of this Accepted Article.

Link to VoR: http://dx.doi.org/10.1002/chem.201705290

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### Columnar Self-assembly of Electron deficient Dendronized *bay*-annulated Perylene Bisimides

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Abstract: Three new heteroatom bay-annulated perylene bisimides (PBIs) have been synthesized by microwave-assisted synthesis in excellent yield. N-annulated and Sannulated perylene bisimides exhibited columnar hexagonal phase, while Seannulated pervlene bisimide exhibited low temperature columnar oblique phase in addition to the high temperature columnar hexagonal phase. The cup shaped bayannulated PBIs pack into columns with enhanced intermolecular interactions. In comparison to PBI, these molecules exhibited lower meting and clearing temperature, with good solubility. A small red shift in the absorption was seen in the case of Nannulated PBI, while S- and Se-annulated PBIs exhibited blue-shifted absorption spectra. Bay-annulation increased the HOMO and LUMO levels of the N-annulated pervlene bisimide, while a slight increase in the LUMO level and a decrease in the HOMO levels were observed in the case of S- and Se-annulated pervlene bisimides, in comparison to the simple perylene bisimide. The band gaps of PBI and PBI-N were almost same, while an increase in the band gaps were observed in the case of S- and Se-annulated PBIs. The tendency to freeze in the ordered glassy columnar phase for PBI-N and PBI-S will help to overcome the charge traps due to crystallization, which are detrimental to one-dimensional charge carrier mobility. These solution processable electron deficient columnar semiconductors with good thermal stability may form an easily accessible promising class of n-type materials.

### I. Introduction

Perylene bisimides are receiving increasing attention from the scientific community working in the field of organic electronics and self-assembly. They have been tested for variety of applications like organic solar cells,<sup>1</sup> field effect transistors,<sup>2</sup> light emitting diodes<sup>3</sup> and light harvesting antennae.<sup>4</sup> Although there are several *p*-type organic semiconductors reported, the number of *n*-type semiconductors are less. The progress in organic electronics always faced with a bottleneck, *i.e.* the dearth of suitable *n*-type organic semiconductors with high mobility and stability. Perylene bisimides due to their electron withdrawing imide substituents serve as electron deficient *n*-type semiconductors. PBIs, when prepared by reacting perylene tetracarboxylic acid dianhydride (PTCDA) with alkyl/aryl amines with peripheral substitution have shown the tendency to stabilize various functional supramolecular self-assemblies like J-aggregates, light harvesting assemblies, vesicles, liquid crystals and chiral discriminators.<sup>5</sup> Further modification in their physical and self-assembling properties, were realized by *bay*-substitution. But it has to be noted that bay

substitution affects the planarity of the molecule and hence the self-assembly behavior of the PBI derivatives. Recently we have realized bay-annulated perylene tetraesters (PTEs), which were planar and exhibited columnar self-assembly over a wide thermal range.<sup>6</sup> This is interesting due to the fact that, by hetero atom *bay*-annulation, one can modify the physical properties of these molecules without sacrificing the planarity and self-assembly. Dendronized PBIs prepared by connecting the various benzyl amines with peripheral substitution with flexible alkyl chains have shown to selfassemble into columnar (Col) phases.<sup>7,9</sup> Here the central PBI unit is a very rigid aromatic unit exhibiting strong  $\pi$ - $\pi$  interactions, while the peripheral trialkoxy benzyl group provides a flexible unit. Organization of these *n*-type semiconductors to form one-dimensional (1D) columnar structures, have advantages in comparison to the polymeric or single crystalline organic semiconductors.<sup>9</sup> This is because such selfassembling molecular motifs have better solubility, ease of purification, reproducibility and ease of handling in comparison to polymers and single crystals.<sup>8</sup> Col phases formed by the stacking of disc-shaped molecules provide the anisotropic charge carrier mobility along the columns, thus can be compared to molecular wires. PBIs could be a possible alternative to fullerenes, which are popular as electron accepting materials in organic solar cells. However, to become an efficient alternative to fullerene based acceptors, these molecules have to be synthetically modified and their properties have to be studied. There have been reports on the introduction of various hetero-atoms like oxygen, nitrogen, sulphur and selenium in the bay region of pervlene derivatives by annulation. This has led to transformed aromatic systems with fascinating properties. Incorporation of sulfur and selenium in organic semiconductors is widely explored due to the intermolecular S…S and Se…Se interactions, which also help to stabilize the molecular self-assembly and hence improve 1D conductivity.<sup>6b-d,10</sup> Motivated by our success in stabilizing luminescent Col selfassembly in hetero atom bay-annulated PTEs over a wide thermal range,<sup>6</sup> we envisaged the synthesis of their bisimide counterparts.

### II. Results and discussion

### II.1 Synthesis and molecular structural characterization

The synthetic route is depicted in Scheme 1. Experimental details and characterization data are provided in Electronic Supporting Information (ESI). Perylene-3,4,9,10-tetracarboxylic dianhydride was subjected to hydrolysis and the tetracarboxylate salt obtained was acidified to obtain the corresponding tetraacid. This on refluxing in the presence of Aliquat 336 and *n*-bromobutane yielded the corresponding tetraester (1) in good yield. The tetraester obtained was nitrated under mild condition to obtain the *bay*-substituted mono nitro derivative 2 in good yield. The nitro compound 2 on triethyl phosphite mediated Cadogan reaction yielded the *N*-annulated perylene tetraester (3).<sup>6</sup> The heating of nitro compound in presence of sulphur or selenium powder in anhydrous NMP yielded the corresponding S and Se annulated PTEs (Compound 6 and 8).<sup>6</sup> The *N*-annulated perylene tetraester (3) was *N*-ethylated in presence of sodium hydride as a base to give compound 4. The *bay*-

annulated tetraesters **4**, **6** and **8** on heating in the presence of *p*-toluene sulphonic acid (PTSA) monohydrate, yielded the respective anhydrides (**5**, **7** and **9**). These *bay*-annulated perylene dianhydrides were treated with tris-dodecyloxy benzyl amine under microwave conditions, to yield the corresponding bisimides **PBI-N**, **PBI-S** and **PBI-Se** in excellent yields. The application of microwave assisted synthesis in presence of zinc acetate and imidazole improved the yields ranging from 80-90%, in comparison to the conventional method.<sup>7a</sup> The synthesis of the key intermediate tris-dodecyloxy benzyl amine (**14**) is provided in scheme 2 (SI). Ethyl gallate was *O*-alkylated with *n*-dodecyl bromide under Williamson's ether conditions to obtain compound **10**. This was reduced to corresponding benzyl alcohol (**11**) on treating with lithium aluminum hydride (LAH) under anhydrous conditions. On treatment with thionyl chloride, corresponding benzyl chloride (**12**) was prepared. Reaction of

CtoHos C12H25 C12H25C COOC₄H<sub>9</sub> C<sub>4</sub>H<sub>9</sub>OOC OC12H25 C<sub>4</sub>H<sub>9</sub>OOC OC12H25 (vi) (v) OC12H25 COOC<sub>4</sub>H<sub>9</sub> C₄H₀OOĊ C₄H₀OOĊ COOC'H" (ii) (viii) C₄H<sub>9</sub>OOÇ C₄H₀OOC COOC₄H<sub>9</sub> COOC₄H₀ OC12H25 OC12H25 PBI-Se C<sub>12</sub>H<sub>25</sub>O (iiii) OC12H25 C12H25C OC12H25 OC12H25 OC12H25 PBI-N C₄H<sub>9</sub>OOĊ COOC₄H<sub>q</sub> C₄H9OOC COOC₄H<sub>g</sub> 2 (vi) (vii) (iv) C<sub>4</sub>H<sub>9</sub>OOC COOC₄H<sub>9</sub> C₄H₀OO COOC₄H<sub>q</sub> (v) (vi) (v) C12H2 C<sub>12</sub>H<sub>25</sub>C с₄н₀оос COOC'H o C₄H<sub>9</sub>OOC COOC₄H<sub>4</sub> ÓC₁₂H2 7 6 5 PBI-S

Scheme 1. Synthesis of *bay*-annulated perylene bisimides





**Figure 1.** Overlay of the expanded region of the <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>, 600 MHz) of PBI and bay-annulated PBIs.

compound 12 with phthalimide yielded it's *N*-benzylated derivative 13, which on hydrolysis yielded the corresponding benzyl amine 14, as reported earlier.<sup>7c</sup> We have prepared simple perylene bisimide from the amine 14 by reacting it with perylene bisanhydride in order to compare with the thermal and photophysical behavior of the corresponding hetero atom *bay*-annulated PBIs. All the intermediates and final compounds were characterized with <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, MALDI-TOF/ESI-HRMS techniques. The overlay of the <sup>1</sup>H NMR spectra shows the proton adjacent to the hetero atom is more deshielded, in comparison to other protons on perylene ring (Fig.1). Among the *bay*-annulated PBIs, the proton H<sub>c</sub> in **PBI-S** is more deshielded. This is in contradiction to *bay*-annulated perylene tetraesters, where the proton H<sub>c</sub> of selenium annulated perylene tetraester resonated down field.<sup>6c</sup>

### II. 2. Thermal behavior

The thermal stability of these compounds was investigated with the help of thermo gravimetric analysis (TGA). *S*-annulated compound **PBI-S** exhibited higher thermal stability in contrast to parent PBI, *N*- and *Se*-annulated PBIs (Fig.S35). Thermotropic mesomorphic behavior of the PBIs was investigated as follows. The samples sandwiched between a glass slide and a coverslip were tested for the shearability and birefringence on heating in a programmable hot stage associated with a polarizing optical microscope (POM). The phase transitions and associated enthalpies were obtained by differential scanning calorimetry (DSC) thermograms, while the mesophases are assigned with the help of X-ray diffraction (XRD) studies. In comparison to perylene bisimide without annulation the *bay*-annulated PBIs exhibited lower clearing temperatures (Fig.2). The phase transition temperatures and associated enthalpy changes are presented in Table 1.

Compound **PBI-N** on heating showed a transition around 102 °C, with an increase in the birefringence along with the fluidity, which corresponds to a crystal to mesophase transition, before reaching the clearing temperature of 156 °C (Fig.3a). On

cooling the isotropic liquid at rate of 5 °C/min), showed the formation of highly birefringent mosaic pattern starting at 152 °C. At around 69 °C, a transition with an



**Figure 2.** Molecular structures of PBI and bay-annulated PBIs and the bargraph representing their thermal behavior (based on first cooling scan)



**Figure 3.** DSC thermograms obtained for **PBI-N** (a); **PBI-S** (b) and **PBI-Se** (c) in the first cooling and second heating scans.

**Table 1.** Phase transition temperatures <sup>a</sup> (<sup>o</sup>C) and corresponding enthalpies (kJ/mol) of DLCs

Phase sequence					
Entry	Second Heating	First Cooling			
PBI-N	Col <sub>h2</sub> 77.8 (0.7) Col <sub>h1</sub> 156.1 (1.4) I	I 152 (1.7) Col <sub>h1</sub> 69.4 (1.5) Col <sub>h2</sub> <sup>c</sup>			
PBI-S	Col <sub>h</sub> 200.6 (2.3)	I 196.4 (2.9) Col <sub>h</sub> <sup>c</sup>			
PBI-Se	Cr 78.6 (2.3) Col <sub>ob</sub> 125.1 (9.4) Col <sub>h</sub> 202.5 (2.2) I	I 198.6 (2.7) Col <sub>h</sub> 70 Col <sub>ob</sub> <sup>b, d</sup>			
<sup>a</sup> Peak temperatures in the DSC thermograms obtained during the second heating and first cooling					
cycles at 5 °C/min; <sup>b</sup> The transition observed only under microscope. <sup>c</sup> the mesophase freezing in the					
glassy state; <sup>d</sup> Crystallization was not detected on cooling; Cr = Crystal phase; Col <sub>h</sub> = Columnar					
hexagonal phase; Col <sub>ob</sub> = Columnar oblique phase; I = Isotropic phase.					

enthalpy change of 1.5 kJ was observed, but no change was observed in the optical texture, which remained unchanged till room temperature, without any signs of crystallization (Fig.3a). In the second heating a transition at 78 °C ( $\Delta H = 0.7 \text{ kJ/mol}$ ) with a slight increase in the brightness and fluidity was noted. This phase existed till 156 °C, after which the phase transformed into an isotropic liquid. These changes were corresponding to high and low temperature phases, which were difficult to

distinguish, except a decrease in the birefringence in the low temperature phase (Fig.4a and b). Thus we decided to investigate these mesophases by XRD studies at different temperature intervals. XRD studies of the sample carried out at 145 °C after



**Figure 4.** POM images obtained for **PBI-N** (a) and (b); the XRD profiles depicting the intensity against the 2 $\theta$  obtained for the Col<sub>h1</sub> phase at 145 °C (c) and Col<sub>h2</sub> phase 28 °C (d).

cooling from its isotropic melt showed a intense sharp peak at low angle with a Bragg spacing d = 27.97 Å in the low angle region. Further several reflections with dspacing of 16.12, 13.94 and 10.52 Å were observed in the middle-angle region ( $5^{\circ}$  <  $2\theta < 10^{\circ}$ ). These reflections could be indexed into Miller indices of 100, 110, 200 and 210 with the ratio of  $1:1/\sqrt{3}:1/\sqrt{4}:1/\sqrt{7}$  and therefore these values fit very well with the lattice of the Col<sub>h</sub> phase (Fig.4c). In the wide-angle region two diffused peaks were observed at a *d*-spacing of 4.64 and 3.54 Å. The first of these peaks can be attributed to the packing of floppy alkyl chains and the second one is arising from the packing of aromatic cores within the column. It is interesting to note that within the Col phase these molecules are packing with an intimate overlap of aromatic cores, which is beneficial for 1D charge migration. The calculated lattice parameter 'a' was found to be 32.3 Å, which is approximately 35% lesser than the molecular diameter obtained from the molecular model in its all trans conformation (Fig.5, Table 2). This decrease may be due to the folding of the peripheral flexible chains, which decrease the effective diameter of the molecule in the Col phase or due to the interdigitation of the flexible chains of **PBI-N** of one column with that of the neighbouring column. From

Compounds	Phase	$d_{\rm obs}(\rm \AA)$	$d_{\rm cal}({\rm \AA})$	Miller	Lattice parameters (Å),
$(D/\text{\AA})$	$(T/^{\circ}C)$			indices	Lattice area S ( $Å^2$ ),
				(hkl)	Molecular volume V ( $Å^3$ )
	145	27.97	27.97	100	a = 32.30
	(Col <sub>h1</sub> )	16.12	16.15	110	c = 3.54
		13.94	13.99	200	S = 903.6
		10.52	10.57	210	V = 3203
		$4.64(h_a)$			Z = 1.1
		$3.54(h_c)$		001	
	100	27.89	27.89	100	<i>a</i> = 32.21
	$(Col_{h1})$	16.08	16.10	110	c = 3.51
RG-381	,	13.91	13.95	200	S = 898.2
PBI-N		10.50	10.54	210	V = 3157.1
(40,45)		$4.57(h_a)$			Z = 1.1
(49.43)		$3.51(h_c)$		001	
	40	32.11	32.11	100	a = 37.08
	$(Col_{h2})$	9.08	(diffuse)		c = 3.53
	( 112)	$4.47(h_a)$	(		S = 1190.8
		$3.53(h_c)$			V = 4205.6
		(-0)			Z = 1.5
	194	28.15	28.15	100	a = 32.51
	(Col <sub>b</sub> )	16.21	16.25	110	c = 3.51
	(0001)	14.03	14.08	200	S = 915.2
		10.60	10.64	210	V = 3208.4
		$4.71(h_a)$			Z = 1.1
		$3.51(h_c)$		001	2
	120	27.69	27.69	100	<i>a</i> = 31.97
	(Col <sub>h</sub> )	15.94	15.99	110	c = 3.46
		13.81	13.84	200	S = 885.3
		10.42	10.47	210	V = 3064.1
PC 378		9.18	9.23	300	Z = 1.1
PRI-S		$4.62(h_a)$			
1015		$3.46(h_c)$		001	
(48.37)	80	27.47	27.47	100	<i>a</i> = 31.72
	(Col <sub>h</sub> )	15.81	15.86	110	c = 3.44
		13.69	13.74	200	S = 871.5
		10.33	10.38	210	V = 3000.6
		$4.54(h_a)$			Z = 1.1
		$3.44(h_c)$		001	
	40	27.93	27.93	100	<i>a</i> = 32.25
	(Col <sub>h</sub> )	16.13	16.13	110	<i>c</i> = 3.43
		13.86	13.97	200	S = 900.9
		9.58	(diffuse)	300	V = 3092.5
		$4.48(h_a)$			Z = 1.1
-		$3.43(h_c)$		001	
<sup>a</sup> The diameter (D) of the disk (estimated from Chem 3D Pro 8.0 molecular model					
software from Cambridge Soft). $d_{obs}$ : spacing observed; $d_{cal}$ : spacing calculated					
(deduced from the lattice parameters; $a$ for Col <sub>b</sub> phase; $c$ is height of the unit cell).					
The spacings marked $h_a$ and $h_c$ correspond to diffuse reflections in the wide-angle					
region arising from correlations between the alkyl chains and core regions					
respectively. Z indicates the number of molecules per columnar slice of thickness					
h estimated from the lattice area S and the volume V					
$n_c$ estimated from the lattice area 5 and the volume $v$ .					

## **Table 2**. Results of (hkl) indexation of XRD profiles of **PBI-N** and **PBI-S** at a given temperature (T) of mesophases<sup>a</sup>

the lattice parameter 'a', we could calculate the number of molecules (Z) present in the unit hexagonal cell with the height ( $h_c$ ) of 3.54 Å and found to be one. This means that each stratum of the column is formed by single molecule, which is packed with

an intermolecular distance of 3.54 Å. The XRD pattern obtained at lower temperature (at 100 °C) in high temperature phase regime was almost same with a lowering of '*a*' and the core-core distance ( $h_c$ ) (see the table and Fig.S36a).



**Figure 5.** Schematic showing the energy minimized structure of **PBI-N** and its self-assembly into columnar hexagonal ( $Col_{h1}$ ) phase (XRD data at 145 °C is considered for the illustration).

We were curious to know the nature of the low temperature phase, thus the XRD studies were carried out at 40 °C. The XRD pattern obtained at 40 °C, exhibited a single sharp peak at low angle, along with two diffused peak at wide angle, which confirms the phase to be a Col<sub>h</sub>. A diffused peak with a *d*-spacing of 9.1 Å was observed and the ratio of this with the first *d*-spacing was found to be  $1:1/\sqrt{3}$ , which usually corresponds to the Miller indices 220 in a hexagonal lattice (Fig.4c). Though it is not explicit to assign the Col<sub>h</sub> phase from the observation of single sharp peak at low angle, the absence of other peaks has been ascribed to a minimum in the form factor.<sup>11</sup>The optical texture remained unaffected even at ambient temperature, and the sample was not shearable, suggesting the freezing of Col<sub>h</sub> phase in the glassy state. For the sake of identification, we have denoted the high temperature Col<sub>h</sub> phase as Col<sub>h1</sub> and the low temperature Col<sub>h</sub> phase as Col<sub>h2</sub>. Such transitions between Col<sub>h</sub> phases are rarely observed.<sup>12</sup>The self-assembly of **PBI-N** in Col<sub>h1</sub> phase is illustrated in Fig.5.



**Figure 6.** POM images obtained for **PBI-S** (a) and (b); the XRD profiles depicting the intensity against the 2 $\theta$  obtained for the Col<sub>h</sub> phases at 194 °C (c) and at 40 °C (d).

**PBI-S** and **PBI-Se** exhibited enantiotropic Col<sub>h</sub> phase, but with higher melting and clearing temperatures than PBI-N, which may be due to the enhanced S<sup>...</sup>S and Se<sup>...</sup>Se interactions (intra or intercolumnar).<sup>6a,c,10</sup> In addition, we should note that these compounds do not have an ethyl substitution near to the core as in the case of PBI-N, which might reduce the core-core interactions. The thermal range of Col phase of both these molecules was found to be almost same. Compound PBI-S, on heating, melted at  $\approx 123$  °C, with a large enthalphy change ( $\Delta H = 34.2$  kJ/mol) corresponding to Cr-mesophase transition as noted in DSC scans in concurrence with the POM observations. This mesophase cleared at  $\approx 201$  °C. On cooling the isotropic liquid, pseudofocal conic fan-like texture appeared which persisted till room temperature (Fig.6a,b). DSC cooling scan did not show any signs of crystallization even up to 0 °C (Fig.3b), however the material was not shearable, which confirmed the freezing of the mesophase in glassy state. XRD studies at different temperature intervals, like 194 °C, 120 °C, 80 °C and 40 °C were performed. All the XRD profiles exhibited a similar pattern corresponding to Col<sub>h</sub> phase. For example, the XRD pattern at 194 °C (Fig.6c), exhibited a strong reflection with a *d*-spacing of 28.2 Å at low angle region along with low intensity reflections at the middle angle region with d-spacings of 16.21 Å, 14.03 Å, 10.6 Å. The reciprocal spacing ratio was found to be  $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$ . These *d*-spacings can be indexed into Miller indices of 100, 110, 200 and 210 of a hexagonal lattice (Table 2). At wide angle, diffused spacings corresponding to 4.71 Å and 3.51 Å were observed, which are corresponding to the alkyl chain packing and core-core stacking respectively. This confirms the Col<sub>h</sub> phase, and further the XRD

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profiles obtained at low temperature (Fig.S36b,c and Fig.6d) also corresponds to the same confirming the monomesomorphic behavior of **PBI-S**.

Compounds	Phase (Tr/9C)	$d_{\rm obs}({\rm \AA})$	$d_{\rm cal}({\rm \AA})$	Miller	lattice parameters (Å),
(D/A)	(1/°C)			( <i>hkl</i> )	molecular volume V ( $Å^3$ )
	195	28.24	28.24	100	a = 32.60
	(Col <sub>b</sub> )	16.25	16.30	110	c = 3.51
	(0001)	14.07	14.12	200	S = 920.6
		10.62	10.67	210	V = 3233.9
		$4.69(h_a)$		-	Z = 1.1
		$3.51(h_c)$		001	
	140	27.86	27.47	100	<i>a</i> = 31.72
RG-379	(Col <sub>h</sub> )	16.03	15.86	110	c = 3.48
PBI-Se		13.88	13.74	200	S = 871.5
		10.48	10.38	210	V = 3035.6
(49,4(9))		$4.59(h_a)$			Z = 1
(48.468)		$3.48(h_c)$		001	
	80	27.43	27.86	100	<i>a</i> = 32.17
	(Col <sub>h</sub> )	15.81	16.09	110	<i>c</i> = 3.45
		13.69	13.93	200	<i>S</i> = 896.5
		10.34	10.53	210	V = 3099.7
		$4.43(h_a)$			Z = 1.1
		$3.45(h_c)$		001	
	RT/24	45.98	45.98	01	<i>a</i> = 28.04
		27.24	27.24	11	<i>b</i> = 48.96
	(Col <sub>ob</sub> )	26.33	26.33	10	c = 3.44
		22.96	22.99	02	$\gamma = 69.9^{\circ}$
		15.21	15.33	03	S = 1289.2
		13.58	13.62	22	V = 4434.8
		11.31	11.50	04	Z = 1.5
		9.08	9.08	33	
		8.26	8.15	16	
		6.47	6.52	45	
		4.31	diffuse		
		4.26	4.26	-54	
		3.99	4.01	-55	
		3.84	3.88	-63	
2-1 11		3.44	3.52	-65	
"The diameter	(D) of the	e disk (esti	mated fron	n Chem 3D I	ro 8.0 molecular model
software from Cambridge Soft). <i>d</i> <sub>obs</sub> : spacing observed; <i>d</i> <sub>cal</sub> : spacing calculated					
(deduced from the lattice parameters; a for $Col_h$ phase; a and b for $Col_{ob}$ phase; c					
is height of the unit cell). The spacings marked $h_a$ and $h_c$ correspond to diffuse					
reflections in the wide-angle region arising from correlations between the alkyl					
chains and core regions, respectively. Z indicates the number of molecules per					
columnar slice of thickness $h_c$ estimated from the lattice area S and the volume V.					

**Table 3.** Results of (hkl) indexation of XRD profiles of **PBI-Se** at a given temperature (T) of mesophases<sup>a</sup>

Selenium annulated PBI (**PBI-Se**) on heating melted at  $\approx 130$  °C, with a large enthalphy change ( $\Delta H = 32.8$  kJ/mol) corresponding to Cr-mesophase transition. This was in accordance with the POM observation that showed increased fluidity and birefringence.



**Figure 7.** POM images obtained for **PBI-Se** (a) and (b); the XRD profiles depicting the intensity against the 2 $\theta$  obtained for the Col<sub>h</sub> phase at 195 °C (c) and for the Col<sub>ob</sub> phase at 24 °C (d).



**Figure 8.** Schematic showing the energy minimized structure of **PBI-Se** and its self-assembly into  $\text{Col}_h$  phase (XRD data at 80 °C is considered for the illustration) and  $\text{Col}_{ob}$  phase (XRD data at 24 °C is considered for the illustration).

The clearing point was almost same with that of the **PBI-S**, but the melting point was higher than that of **PBI-S**. As per the DSC scan in cooling cycle a transition

corresponding to isotropic to mesophase was observed (Fig.3c). It was very hard to detect any change in the pseudo focal conic texture except the blurring of the dark homeotropic background (Fig.7a,b), which was seen around 70 °C. Thus we have carried out XRD at different temperature intervals. The XRD patterns obtained at 195 °C, 140 °C and 80 °C were almost same corresponding to Col<sub>b</sub> phase (Fig.7c and Fig.S36d,e, Table 3), while the one obtained at room temperature (Fig.7d) showed several peaks at low and middle angle region. These d-spacings could be indexed to a Col phase with a parallelogram lattice of an oblique symmetry (Col<sub>ob</sub>), with the lattice parameters a = 28.04 and b = 48.96 Å with a tilt angle  $\gamma = 69.9^{\circ}$ . The core-core stacking distance 'c' was found to be 3.44 Å. Thus the number of discs present in a unit cell (Z) turns to be 1.5. Thus, **PBI-Se** exhibited a bimesomorphic behavior, with high temperature Col<sub>b</sub> phase and low temperature Col<sub>ob</sub> phase. This phase appears to be 3D-ordered, although the XRD peaks can be assigned to Col<sub>ob</sub> phase. The presence of a non-negligible diffuse maximum at wide angles does suggest enough disorder in the medium, which could be of either plastic or glassy in nature. Conclusive evidence was not found, as no peak required all non-zero hkl values. The observation of Colob phase corresponds to the enhanced intermolecular interactions in PBI-Se in comparison to the other two PBIs, which is also reflected in its higher melting point in comparison to **PBI-S**. However, the second heating showed a cold crystallization at  $\approx$ 79 °C (2.3 kJ/mol), which was not noticed during the first cooling cycle in DSC (Fig.3c). It also should be noted that the XRD at room temperature was taken in the first cooling cycle. Thus somewhere below this temperature crystallization occurs, which was not seen in the case of PBI-N and PBI-S.

During these X-ray studies we had some interesting findings, which is due to the minute structural differences arising from the bay annulation. The XRD patterns obtained for **PBI-N** at low temperature *i.e.* Col<sub>h2</sub> phase shows that this phase is less ordered in comparison to the high temperature  $Col_{h1}$  phase. This is in contradiction to what is expected on lowering the temperature. Usually the phase becomes more ordered, due to the reduced mobility of the molecules along with a lowered corecore distance. But the observed difference, where the peaks at low angle become broad and diffuse was found to be reproducible and genuine. Similar effect was noticed in the case of **PBI-S**, but it was not that drastic. The main structural aspect that should be borne in mind is that in the case of PBI-N where the effect is drastic has an ethyl group substitution at the *bay*-nitrogen position. This can, in principle be considered like an extended arm of the hydrocarbon having substantial degree of freedom to move about the plane of the perylene core. At high temperatures, *i.e.* in the  $Col_{h1}$  phase, when the terminal chains have a substantial folded character (molten chains), the effect due to the ethylene part is less dominant. Thus the interfaces between the lattice planes are reasonably flat, a feature that is evident from the stronger signal for the peak associated with the core-core correlation. Concomitantly the core-core distance is also lower. At much lower temperature, in the  $Col_{h2}$  phase, a large increase in the diameter (a) of the columns is seen (increasing by ~ 5 Å from the value in the  $Col_{h1}$  phase) signifies that the terminal chains are more spread out. Intuitively, this should have led to a flatter lattice plane and consequently better-packed molecular cores. However, the experiments show the opposite as seen by reduced number of sharp peaks at low angles, and a far weaker core-core peak. This must be due to the increasing influence of the wagging by the ethyl group in the core region. The reduced overall entropy of the system must be making the ethyl group to occupying regions above or below the plane of the core, and less biased towards being in that plane; this should increase the corecore distance as is clear from the X-ray studies. This diminishes the interaction between the neighbouring discs, a feature evident from the weakened core-core peak, making the lattice plane interfaces rough and in turn reducing the number of low-angle peaks. The presence of the sulphur atom in the **PBI-S** case also has some of these features, but the effect is much smaller, as sulphur is less bulky compared to the ethyl group. It is possible that the rarely observed transition between two hexagonal columnar phases  $(Col_{h1}-Col_{h2})$  is caused by the presence of the ethyl group in the core-region. In the selenium case (PBI-Se) probably the disturbance leads towards the tilting of the columnar lattice (Col<sub>ob</sub> phase), although only after a three-dimensional ordering (as seen by a number of sharp peaks) sets in.

### Density functional theory studies

We have used density functional theory (DFT) calculations to visualize the energyminimized structures of the PBIs and the energy levels of the frontier molecular orbitals (HOMO-LUMO) of all the compounds (See the SI). The energy minimized structures for **PBI**, **PBI-N**, **PBI-S** and **PBI-Se** showed in Fig.9a. Images of frontier molecular orbitals (FMOs) and the differences in their energies provide knowledge about the length of conjugation and band gap level, which helps in comparing the perylene bisimide with its *bay*-annulated derivatives. In the energy minimized structures, we can notice the planar perylene and two out of plane benzyl rings. Side view presented in Fig.9b distinguishes the *bay*-annulated PBIs from the parent PBI. In the case of parent PBI, the benzyl wings are positioned at two different planes, while in the case of bay-annulated PBIs, two benzyl wings are on the same side of the central perylene ring, leading to a cup shape. Such an orientation helps the molecules to pack into more ordered columns as shown in Fig.5 and Fig. 8.<sup>7a</sup>

The contours of the HOMO and LUMO of PBIs are shown in Fig. 9c and d.The HOMO-LUMO energy levels of PBIs are distributed on the entire aromatic ring. PBIs are considered as closed chromophoric (electronically decoupled) systems due to the presence of nodes of the HOMO and LUMO orbitals on imide nitrogen atoms. Thus the substitution at imide nitrogen does not alter the optical properties significantly.<sup>13</sup> Bay-annulation increased the HOMO and LUMO levels in comparison to the simple perylene bisimide. In the case of annulated derivatives, HOMO and LUMO levels were found to be spreading over heteroatom. The theoretical band gaps for **PBI, PBI-N, PBI-S** and **PBI-Se** were found to be 2.27 eV, 2.3 eV, 2.14 eV and 2.32 eV respectively.



**Figure 9.** Optimized geometry of compounds **PBI**, **PBI-N**, **PBI-S** and **PBI-Se** (a); side view of the same (b); HOMO (c) and LUMO (d) frontier molecular orbitals of compounds **PBI**, **PBI-N**, **PBI-S** and **PBI-Se** at the B3LYP/6-31G(dp) level.  $E_H$  and  $E_L$  denote energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively.

### Photophysical and electrochemical studies

Photophysical properties of these compounds were explored by obtaining their absorption and emission spectra in micromolar chloroform solutions (Table 4 and Fig.10). The absorption spectra of these PBIs were well-structured and showed the characteristic four vibronic bands, with the longest absorption wavelength was centered in the range of 503-532 nm. Compound **PBI-N** was slightly red-shifted in comparison to **PBI**, while **PBI-S** and **PBI-Se** exhibited slightly blue shifted absorption spectra. All the PBIs exhibited high molar extinction coefficients at their absorption maxima ( $\varepsilon$ : 14,700 to 20,300 Lmol<sup>-1</sup>cm<sup>-1</sup>). The optical band gap calculated from the absorption onset showed that the optical band gap of **PBI** and **PBI-N** were almost matching while that of the **PBI-S** and **PBI-Se** shown an increase. Emission spectra of these compounds showed two main bands, with the high intensity band was in the range of 517-545 nm. The Stoke's shift was found to be less in the range of 448-596 cm<sup>-1</sup>.

Solution state						
	Absorption (nm)	$\varepsilon$ (Lmol <sup>-1</sup> cm <sup>-1</sup> )	Emission <sup>b</sup> (nm)	Stokes shift (cm <sup>-1</sup> )	$\Delta E^{\rm c}_{\rm g, opt}$ (eV)	
PBI	528, 491, 460 430	18259	544, 580	557	2.28	
PBI-N	532, 496, 468, 438	14797	545, 584	448	2.27	
PBI-S	503, 470, 442, 417	16600	517, 551	538	2.39	
PBI-Se	510, 476, 449, 421	20310	526, 560	596	2.34	
<sup>a</sup> micromolar solutions in CHCl <sub>3</sub> ; <sup>b</sup> the excitation wavelength $\lambda_{ex} = 460, 468, 442$ and 449 nm respectively for compound <b>PBI, PBI-N, PBI-S</b> and <b>PBI-Se</b> ; <sup>c</sup> calculated from the red edge of the absorption band;						

#### Table 4. Photophysical properties of PBIs in solution

Cyclic voltammetry (CV) studies are carried out to understand the electronic energy levels that decide the energy and electron transfer process and reversibility of a redox process. CV studies were carried out in anhydrous dichloromethane solutions (Table 5). PBIs are known to be electron deficient n-type semiconductors and known to have high electron affinity. Among these compounds, only **PBI** and **PBI-N** exhibited two reversible reduction peaks (Fig.11a). It was difficult to obtain the oxidation potentials of these electron deficient compounds even with a CV measurement window up to +1 V *vs* Ag/AgNO<sub>3</sub>. Thus we have calculated the HOMO levels, by subtracting the LUMO energy values from the optical band gap that was obtained from the absorption onset of the compounds in solutions. From the CV studies it is found that the bay-annulated PBIs showed increased LUMO levels in comparison to **PBI** (Fig.11b). A small increase of 0.18 eV in the HOMO level was noted in the case of **PBI-N**, while **PBI-S** and **PBI-Se** displayed a lowering of HOMO levels by 0.08 and 0.04 eV respectively (Fig.11b). The values obtained from CV studies followed the same general trend that was obtained from DFT calculations.



Figure 10. (a) Absorption and (b) emission spectra in micromolar THF solution for PBI, PBI-N, PBI-S and PBI-Se.





**Table 5.** Electrochemical properties of PBIs in solution<sup>a,b</sup>

Entry	E <sup>c</sup> <sub>1red</sub>	E <sup>d,e</sup> LUMO	E <sup>d,f</sup> <sub>HOMO</sub>	$\Delta E^{d,g}_{g, opt}$		
PBI	-0.57	-3.68	-5.96	2.28		
PBI-N	-0.74	-3.51	-5.78	2.27		
PBI-S	-0.60	-3.65	-6.04	2.39		
PBI-Se	-0.59	-3.66	-6.00	2.34		
<sup>a</sup> in Dichloromethane solutions; <sup>b</sup> Experimental conditions:						
Ag/AgNO <sub>3</sub> as reference electrode, Glassy carbon working						
electrode, Platinum wire counter electrode, TBAP (0.1 M) as						
a supporting electrolyte, room temperature; <sup>c</sup> in volts (V); <sup>d</sup> in						
$eV^{eEstimated}$ from the formula by using $E_{LUMO} = -(4.8 - 1.0)$						
$E_{1/2}$ , Fc/Fc <sup>+</sup> + $E_{red}$ , onset) eV; <sup>f</sup> Estimated from the formula						
$E_{\rm HOMO} = E_{\rm LUMO} - E_{\rm g}$ , opt) eV; <sup>g</sup> calculated from the red edge						
of the absorption band (544, 547, 519, 530 nm respectively).						
$E_{1/2}$ , Fc/Fc <sup>+</sup> = 0.55						

### Conclusions

In conclusion, we have synthesized three new electron deficient hetero atom *bay*-annulated perylene bisimides stabilizing ordered columnar phase over a wide temperature range. The N- and S-annulated perylene bisimides showed columnar hexagonal phase, while the *Se*-annulated perylene bisimide exhibited columnar oblique phase in addition to the columnar hexagonal phase. The Col phase on cooling freezes into glassy state, this is quite impressive to obtain the highly ordered structure in the devices, by thermal annealing. These molecules exhibit high molar extinction coefficients along with the absorption spectra covering the most of the visible spectrum, which will be important for solar cells with a scope to improve further by the structure modulation. The optical band gaps are low with minor differences observed in the HOMO and LUMO levels. Further structural modifications are needed to approach the fullerene's HOMO and LUMO levels, however this serves as

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a starting point. DFT calculations revealed the cup-like conformation of these molecules in the energy-minimized structure, which may support their columnar self-assembly along with the  $\pi$ - $\pi$  interactions and nanophase segregation. Considering the scarcity of n-type semiconductors in literature, these compounds could give rise to a variety of alternatives to synthesize highly ordered n-type columnar self-assemblies. The microwave-assisted synthesis further improved the synthetic access to such materials in good yields.

**Acknowledgements.** ASA sincerely thanks Science and Engineering Board (SERB), DST, Govt. of India and BRNS-DAE for funding this work through project No. SB/S1/PC-37/2012 and No.2012/34/31/BRNS/1039 respectively. We thank the Ministry of Human Resource Development for Centre of Excellence in FAST (F. No. 5-7/2014-TS-VII). We thank CIF, IIT Guwahati for analytical facilities.

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