

# Fluorescein-Bridged Perylene Bisimide Dimer for Use as Liquid Crystal: Studies on Mesomorphic and Fluorescence Properties

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## Research Article

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# Abstract

A novel fluorescein-bridged perylene bisimide (PBI) dimer for liquid crystal (LC) with geometrically symmetric structure was developed. The mesomorphic results indicated that the energetically stable and unstable conformers of fluorescein fragments could lead to the transformation of mesophases from a hexagonal columnar mesophase to an uncertain phase at 136.9 °C in heating, whilst a stable hexagonal columnar mesophase maintained between 175.6 °C and 58.6 °C in cooling. The selectively excited fluorescence characters in THF solution demonstrated that the fluorescence resonance energy transfer (FRET) effect between fluorescein fragments and PBI units could provide a means to effectively impose strong fluorescence of the dimeric PBIs modified with suitable chromophore at the N-imide position, which alternatively serves as a platform for the further study of multi-functional PBI-based LCs.

## Introduction

Boasting the natural virtues of fascinating photophysical properties (e.g., longer excitation wavelength, high fluorescence quantum yield, long fluorescence lifetime, and the stability to light and thermal-exposure), perylene bisimide (PBI) is a recurring and overwhelming motif in various fields of solar photovoltaics[1-4], organic electronic devices[5,6], photoelectrocatalysis[7], photoisomerization[8], near-infrared photothermal conversion[9], phosphorescence[10], moisture detection[11], bioimaging[12,13], theranostics[14,15], and biosensing/bioassay[16]. Additionally, the self-assembled  $\pi$ - $\pi$  interaction of perylene core plays a decisive role in its functional characteristic and renders it possible to develop various supramolecular species involving host-guest recognition[17,18], gelator[19-21], LCs[22], and so on. On account of 1D charge transport pathways in supramolecular columnar mesophase, discotic PBI-based LCs can be used to fabricate thin semiconducting devices over large areas[23-25]. In fact, bringing the discotic PBI-based LCs more closely to practical applications requires excellent mesomorphic and emission properties. Up to now, although a plenty of discotic PBI-based LCs were achieved using various mesomorphic groups such as triphenylene[26-30], cholesterol[31,32], siloxane[33], dendritic peptides[34], cyclotetrasiloxane[35], oligosiloxane[36], polyhedral oligosilsesquioxane (POSS)[37], and gallic acid derivatives[38-42], most of their fluorescence emission were regulated and managed by substituted groups through the intramolecular charge-transfer (ICT) and/or  $\pi$ -extended conjugation system. While hardly affecting the alteration of emission peak, the substituents at the N-imide positions can weaken the fluorescence because of the photoinduced electron transfer (PET)[22], which limit the practical application of the fluorescent PBI-based LCs in photoelectronic and electroluminescent devices. Thus, to realize the modulation of excited fluorescence of PBIs, modification at the N-imide positions is crucial for development of novel functional LCs.

In order to construct discotic PBI-based LCs, it had been reported that the integration of the perylene core into six peripheral alkyl chains could effectively control over molecular alignment for fabricating a stable hexagonal columnar mesophase[43,44]. On the other hand, a large number of researches have focused the attention on the study and development of some polyploid PBIs for new materials[2,4,45-51]. Unfortunately, a previously reported exploration on the dimeric PBI-based LCs focused on

functionalization with two PBI units through different length of poly methylene spacer at the N-imide position, which has a distinctive feature of little changed emission in free solution state according to Kasha's rule[50]. However, how to trigger changes in emission properties of dimeric PBI-based LCs with suitable substitution at the N-imide position still remains difficult.

In this work, in terms of the enhanced fluorescence originating from FRET effect of bis-chromophoric groups[42,44], a novel fluorescein-bridged PBI dimer for LC was firstly synthesized as shown in Scheme 1. The target PBI 3 exhibited different LC behaviors due to the presence of fluorescein unit, while the emission spectrum of PBIs in THF solution could be improved by transferring the energy from fluorescein fragment to PBI core. This study was an innovative approach to demonstrate the methodology on building two different chromophores functionalized LCs.

## Experimental

### Materials and Equipments

Acetonitrile (MeCN 98%, Alfa Aesar) was dried over  $P_2O_5$  under a nitrogen atmosphere and distilled before use. The anhydrous potassium carbonate ( $K_2CO_3$ ) was prepared in a muffle furnace at 400 °C for 12 h. All other commercially purchased chemicals were used without further purification. Column chromatographic separation was performed on silica gel (200–300 mesh). Thin-layer chromatography (TLC) was performed on glass plates precoated with silica gel. All proton nuclear magnetic resonance ( $^1H$  and  $^{13}C$  NMR) spectra were conducted with a Bruker-ARX 400 spectrometer in  $CDCl_3$  solvent, and calibrated using tetramethylsilane (TMS,  $\delta = 0$  ppm) as internal standard. Chemical shifts were quoted in parts per million (ppm), and coupling constants were made out as  $J$ -values in Hz. MALDI-MS spectrum was determined on a Bruker MALDI-Mass spectrometer. Fourier transform infrared (FT-IR) spectra were measured on Perkin Elmer Spectrum 100 FT-IR spectrometer with solid KBr pellets. DSC measurements were determined in a hermetic aluminium pan using a thermal analyzer (Q100) at a scanning rate of 5 °C  $min^{-1}$  from -30 °C to 270 °C under a nitrogen atmosphere. The mesomorphic texture of the sample was captured with a polarization optical microscope (Leica DMRX), operated with a temperature-controlled heating setup (Linkam THMSE 600). The mesomorphic structure of the sample was carried out by XRD measurement using an X-ray diffractometer (XRD7, SEIFERT-FPM), equipped with Cu K $\alpha$  radiation ( $\lambda = 1.54056$  Å) at 40 kV and 30 mA. UV-visible absorption spectrophotometer (Shimadzu, UV-2550) and fluorescence spectrophotometer (Shimadzu, RF-5301PC) were employed to investigate the photophysical properties of the sample. Experimentally, the emission spectra of the samples were recorded in THF (10  $\mu$ M solutions) using 1 cm quartz cuvette, when slit widths were  $\Delta\lambda_{ex} = 3$  nm and  $\Delta\lambda_{em} = 5$  nm, respectively. The fluorescence absolute quantum yields ( $\Phi_F$ ) were measured on an Edinburgh Instruments FLS920 fluorescence spectrometer with a calibrated integrating sphere.

### *Synthesis of fluorescein-bridged perylene bisimide dimer 3*

Under a nitrogen atmosphere, PBI intermediate (compound **2**) (1.29 g, 0.8 mmol), and fluorescein (0.14 g, 0.4 mmol) were placed into a suspension of anhydrous K<sub>2</sub>CO<sub>3</sub> (0.14 g, 1 mmol) in 35 mL of anhydrous MeCN. The mixture was refluxed in 18 h under magnetically stirring condition. Reaction was monitored by TLC. As completion of the reaction, the mixture was cooled to room temperature, the excess solvent was then evaporated under reduced pressure. After admixing with 30 mL of HCl solution (1 M), the resulting mixture was extracted with 40 mL of DCM. The organic phase was washed with brine (3 × 30 mL), dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated with a rotary evaporator to afford a red residue. The residue was further purified by a silica gel column (DCM/petroleum ether (2:1, v/v)) to give compound **3** as a red solid in yield of 70%. FT-IR (KBr),  $\nu/\text{cm}^{-1}$ : 1698, 1660 (C=O); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ ppm: 8.20 (bs, 8H, Per-H), 7.54 (d,  $J = 8.0$  Hz, 2H, Flu-H), 7.36 (s, 2H, Flu-H), 7.19 (bs, 16H, Ar-H), 7.15-7.12 (m, 4H, Flu-H), 7.00 (s, 2H, Flu-H), 6.84 (bs, 16H, Ar-H), 4.92 (s, 2H, OCH<sub>2</sub>CO), 4.31 (m, 2H, FluOCH<sub>2</sub>CO), 4.09 (t,  $J = 8.0$  Hz, 8H, NCH<sub>2</sub>), 3.61 (t,  $J = 8.0$  Hz, 4H, OCH<sub>2</sub>), 1.68-0.86 (m, 214H, CH<sub>2</sub> and CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ ppm: 167.12, 165.53, 163.93, 161.59, 160.66, 159.43, 157.44, 155.97, 152.58, 149.61, 147.13, 144.51, 141.33, 137.86, 135.25, 132.73, 128.74, 127.50, 125.93, 122.00, 119.00, 114.00, 110.26, 105.43, 102.44, 100.73, 97.99, 68.20, 65.05, 62.22, 42.61, 31.69, 29.34, 26.19, 24.19, 21.01, 18.76, 14.84; anal. Calcd for C<sub>228</sub>H<sub>280</sub>N<sub>4</sub>O<sub>25</sub>: C, 78.77; H, 8.12; N, 1.61. Found: C, 79.01; H, 8.10; N, 1.68. MALDI-MS (C<sub>228</sub>H<sub>280</sub>N<sub>4</sub>O<sub>25</sub>) [M]<sup>+</sup>: calcd: m/z = 3476.08. found: m/z = 3476.24.

## Results And Discussion

### Synthesis and characterization

Fluorescein, as a highly preferable fluorescent chromophore, has been widely applied for biological assays as well as biolabeling due to its exceptional fluorescence properties[52-59], whereas little attention was paid to disk-like LCs of fluorescein. In our previous studies, designing and controlling the effect of a rigid chromophore building block into the columnar mesophase architectures could ensure the mesomorphic nature to optimize photophysical properties, which provided an approach for the design of multifunctional LC materials[60, 61]. With a view to the stiff planar quinoid scaffold of fluorescein as well as the extraordinary mesogenic properties of PBI **1**, the dimeric PBI-based LC **3** was constructed by inserting a fluorescein unite between two PBIs **1** at the N-imide position. The straightforward one-step synthetic route for the dimeric PBI-based LC **3** is illustrated in Scheme 1. With the key intermediate PBI **1** in hand,[44] PBI **3** was easily prepared by nucleophilic substitution of PBI **1** with fluorescein. In the presence of K<sub>2</sub>CO<sub>3</sub>, the red solid of final compound **3** was obtained by refluxing compound **1** and **2** in MeCN with a yield of 70%. To check the solubility of compound **3**, it was dissolved in different organic solvents including chloroform, dichloromethane (DCM), Toluene, THF and DMF. Compound **3** exhibited relatively good solubility in chloroform, dichloromethane and THF.

The chemical structure of target compound **3** was fully characterized by various characterization techniques (NMR, MALDI-MS, FT-IR and elemental analysis), and the results fitted well to the expected structure. <sup>1</sup>H NMR spectrum and the details of other characterization spectra were listed in the Supporting

Information. In Figure S1, one can see the clear splits for aromatic protons of fluorescein units but broad signals for aromatic protons of nonylphenoxy and perylene skeleton. After examining the proton signals of same skeleton of compound **3**, its precursor **1** and reference compounds **4** and **5**, we noticed all of them showed the broad signals for the H<sub>a</sub>, H<sub>b</sub> and H<sub>c</sub> [43, 44]. The phenomena suggested that this kind of broad signals for the H<sub>a</sub>, H<sub>b</sub> and H<sub>c</sub> could be ascribed to internal structural features for these compounds. By analysing this structural feature, it could be observed that the aromatic ring away from perylene skeleton (such as fluorescein unit in compound **3**) can rotate freely around the single bond due to the small steric resistance, resulting in the clear splits for protons. However, due to the big steric resistance and the long alkyl chains on nonylphenoxy units, the rotation of nonylphenoxy units on perylene skeleton was limited and slow, resulting in compound **3** adopted various conformations which possessed different intersection angles between nonylphenoxy units and perylene skeleton. The signals of H<sub>a</sub>, H<sub>b</sub> and H<sub>c</sub> in Figure S1 were the overlapped and mixed signals of H<sub>a</sub>, H<sub>b</sub> and H<sub>c</sub> in different conformation and changing spatial orientation of compound **3**. Thus, the broad signals for H<sub>a</sub>, H<sub>b</sub> and H<sub>c</sub> were observed. On the other hand, the specific protons of OCH<sub>2</sub>CO, FluOCH<sub>2</sub>CO and OCH<sub>2</sub> function groups established self-governed chemical shifts at 4.92 (g), 4.31 (f), and 3.61 (e) ppm, respectively. The relative integrals of all peaks agree with the number for protons. Therefore, the well-defined target compound **3** was successfully obtained with good purity.

### ***Mesomorphic studies***

To evaluate the mesomorphic properties, the basically recognized results of the thermal phase transition temperatures and enthalpies of the target PBI **3** with differential scanning calorimetry (DSC) were presented in Figure 1, quoting the first cooling and second heating runs to erase the thermal history. The relevant data were summarized in Table 1. Subsequently, the mesomorphic birefringence textures from the crossed polarizing optical microscope (POM) of specimen were observed in the heating-cooling cycles as displayed in Figure 2. During second heating process, the mesomorphic properties of PBI **3** exhibited three endothermic peaks for three transitions, which were subjected to the crystal-LC (61.3 °C), LC-LC (136.9 °C), LC-isotropic (182.2 °C) transitions. This was further supported by the observation of LC textures. Upon heating from the melting temperature at a rate of 2.0 °C min<sup>-1</sup>, intriguing pseudo-focal conical fan-shaped textures with a large area of homeotropic alignment domains for the column stacks were observed in the temperature range from 61 °C to 137 °C. Figure 2(a) was captured at 95 °C and consistent with the images of the monomeric PBI-based LCs with multistrand peripheral alkyl chains [40]. From Figure 1 and Table 1, a comparative study of the involved PBIs revealed that the mesomorphic phase of PBI **3** occurred at 61.3 °C well above its analogues PBI **4** (46.8 °C) and PBI **5** (56.2 °C) in the course of heating. Such thermotropic behavior was attributed to the rigid structure of fluorescein group needing more energy cost to melt. Moreover, In comparison with PBIs **4** and **5**, PBI **3** had a higher clearing temperature at 182.2 °C and a wider mesomorphic temperature range of ~120 °C. Notably, there was an endothermic peak for LC-LC (136.9 °C) transition in heating trace, suggesting the mesophase changed from one phase to another formation. As shown in Figure 2(b), a temperature rise induced dramatic changes, giving the randomly oriented textures from 137 °C to 182 °C. Figure 2b was pictured at 158 °C in

heating. This observation leads to the conclusion that a separation of the metastable mesophase occurred at 136.9 °C ( $\Delta H = 4.7 \text{ kJ mol}^{-1}$ ) because the fluoresceine fragment were dispersed within the mobile aliphatic chains rather than in the perylene stacks. In addition, another transformation peak of LC-isotropic was observed at 182.2 °C, the POM image of PBI **3** changed into a dark field as the temperature exceeding the clear point (182 °C) in the heating process.

<b>Table 1</b> Transition temperatures (°C) and enthalpies $\Delta H$ (kJ mol <sup>-1</sup> ) of target compound <b>3</b> , reference compounds <b>4</b> and <b>5</b> .	
PBIs.	Phase transitions <sup>[a]</sup> [°C (kJ mol <sup>-1</sup> )]
<b>3</b>	Cr 61.3 (9.2) → Col <sub>h</sub> 136.9 (4.7) → Col 182.2 (11.5) → Iso Iso 175.6 (9.6) → Col <sub>h</sub> 58.6 (10.3) → Cr
<b>4</b> <sup>[b]</sup>	Cr 46.8 (12.6) → Col <sub>h</sub> 155.7 (21.4) → Iso Iso 144.7 (20.5) → Col <sub>h</sub> 42.0 (8.3) → Cr
<b>5</b> <sup>[c]</sup>	Cr 56.2 (16.84) → Col <sub>h</sub> 106.5 (10.36) → Iso Iso 157.3 (11.18) → Col <sub>h</sub> 49.6 (17.35) → Cr
[a] Cr = crystalline, Col <sub>h</sub> = hexagonal columnar mesophase, Col = columnar mesophase, Iso = isotropic.	
[b] The data are cited from ref. [43].	
[c] The data are cited from ref. [44].	

Nevertheless, the mesomorphic properties of PBI **3** exhibited two exothermic peaks for two transitions in DSC cooling cycle, which were subjected to the isotropic-LC (175.6 °C), LC-crystal (58.6 °C) transitions. When the sample was cooled from the isotropic liquid state at a rate of 2.0 °C min<sup>-1</sup>, the single mesophase was maintained in the whole DSC cooling curve and stable up to the crystallization of PBI **3** (58.6 °C), and there was no significant phase transition below the crystallized peak. PBI **3** cooled from the isotropic melt until a fully developed LC texture was observed under POM at approximately 175 °C. The mass-produced pseudo-focal conical fan-shaped textures as well as optically isotropic homeotropic domains for PBI **3** were observed between 175 °C and 58 °C in cooling process, which well agreed with the observed result in DSC. Figure 2c was captured at 142 °C in the cooling-down stage, and it represented the POM texture within a temperature range from 175 °C to 58 °C in cooling, similar to the one observed at 95 °C in the heating (Figure 2a). PBI **3** exhibited the two double reversible humps of

crystalline-mesophase and mesophase-isotropic transitions appearing at around melting point and clearing point in DSC curves, respectively. The reversible transition temperatures in the cooling-down stage were below the relative temperatures in heating, known as the hysteresis, referring to the formation of LC germs at lower temperature on cooling. As a consequence, the detailed analysis of mesomorphic properties with a combination of DSC and POM confirmed that fluorescein-bridged perylene dimer **3** hold a stable columnar mesophase between 175.6 °C and 58.6 °C in cooling, while it had two kinds of mesophases with a mesomorphic temperature range of ~120 °C in heating. Insufficiently, more information on the stacked structure of PBI **3** in mesophase could not be obtained via DSC and POM means.

With the comprehensive understanding on the mesomorphic properties via DSC and POM means, we further lucubrated the theoretical packing parameters of LC **3** by variable-temperature XRD measurements at a rate of 2 °C /min under the first cooling and second heating runs. The XRD traces were carried out in Figure 3. The relevant data were summarized in Table 2. In Figure 3(a), the sample heated at 68 °C shows two diffraction peaks at  $2\theta = 3.84^\circ$  and  $2\theta = 25.87^\circ$  owing to the self-assembly by halves. In heating, both of Figure 3(b) and (c) exhibit that there is a sharp scattering peak (75 °C,  $2\theta = 3.84^\circ$ ; 95 °C,  $2\theta = 3.84^\circ$ ) along with two weak peaks (75 °C,  $2\theta = 6.70^\circ$  and  $7.44^\circ$ ; 95 °C,  $2\theta = 6.69^\circ$  and  $7.45^\circ$ ) in the small-angle region, respectively. The calculated  $d$ -spacings of 22.99 Å, 13.18 Å, and 11.87 Å at 75 °C and 22.99 Å, 13.20 Å, and 11.86 Å at 95 °C, confirmed the interplanar  $d$ -spacing ratio of 1:1/ $\sqrt{3}$ :1/ $\sqrt{4}$  for the  $[d_{100}]$ ,  $[d_{110}]$  and  $[d_{200}]$  planes in a columnar hexagonal mesophase. In the wide-angle region, a broad diffuse halo at  $2\theta = 15\text{-}30^\circ$  arising from the molten alkyl chains and a subtle reflection peak at approximately  $2\theta = 25.80^\circ$  (3.44 Å) corresponding to the  $\pi$ - $\pi$  stacking distance of the closest PBI cores for  $[d_{001}]$  plane were clearly observed at both 75 °C and 95 °C in heating. Based on these reflections, the observed textures (Figure 2(a)) and DSC data, it proves strongly the existence of the columnar hexagonal mesophase with a temperature range from 61 °C to 137 °C on heating.

<b>Table 2</b> Summary of the structural information and lattice parameters in mesophases for LC <b>3</b> (derived from variable-temperature XRD diffraction experiments)					
$T$ [°C].	Cycle state	Phase <sup>[a]</sup>	$d_{100}$ [Å]	$a$ <sup>[b]</sup> [Å]	$c$ <sup>[c]</sup> [Å]
68	heating	Col <sub>h</sub>	22.99	26.55	3.44
75	heating	Col <sub>h</sub>	22.99	26.55	3.43
95	heating	Col <sub>h</sub>	22.99	26.55	3.45
158	heating	U	/	/	/
142	cooling	Col <sub>h</sub>	22.87	26.41	3.44

[a] Col<sub>h</sub> = hexagonal columnar mesophase, U = uncertain mesophase;  
[b]  $a = \sqrt{(4/3 \times d_{100}^2)}$ ;  
[c] Intracolumnar layer spacing  $c$  [Å].

However, only one reflection at  $2\theta = 2.10^\circ$  (42.04 Å) in the low-angle region was monitored in heating, and it even remained unchanged in the temperature range from 137 °C to 182 °C. Figure 3(d) was recorded at 158 °C in heating. By comparison to the diffraction profiles of samples at 75 °C and 95 °C in heating (Figures 3(b) and (c)), no more scattering information was acquired in Figure 3(d). Thus, the mesophase model for LC **3** was ill-defined with raising the temperature from 137 °C to 182 °C upon second heating, which was consistent with the results of DSC and POM measurements from 137 °C to 182 °C upon second heating. This observation also indicated that the fluorescein fragment dispersed within the mobile aliphatic chains rather than in the perylene stacks. On the other hand, when the sample was annealed from the isotropic liquid state at a rate of 2.0 °C min<sup>-1</sup>, only one XRD pattern was measured during 175 °C to 58 °C in cooling process and the XRD trace (Figure 3(e)) at 142 °C served as representative. The dominating  $d$ -spacing ratio of the  $[d_{100}]$  ( $2\theta = 3.86^\circ$ , 22.87 Å),  $[d_{110}]$  ( $2\theta = 6.68^\circ$ , 13.22 Å) and  $[d_{200}]$  ( $2\theta = 7.44^\circ$ , 11.87 Å) planes were also 1:1/ $\sqrt{3}$ :1/ $\sqrt{4}$ , similar to the scattering peaks in figures 3(b) and (c). This observation indicated that a columnar hexagonal mesophase could be processed over a broad temperature range from 175 °C and 58 °C on cooling. Moreover, the 2D correlation of a columnar hexagonal mesophase is again present in cooling process. This could be explained that the molecular motion of PBI **3** was reduced and the fluorescein fragment dispersed within the mobile aliphatic chains rather than in the perylene stacks. In addition, the average lattice parameter ( $a = 26.48$  Å) of LC **3** nears the space length ( $\sim 29.54$  Å) between PBI core and fluorescein fragment (furnished with Chem 3D Pro 17 software from Cambridge Soft). Taking together with the results of DSC, POM and XRD experiments, the integration of PBI-fluorescein-PBI **3** made a hexagonal columnar model from 61 to 137 °C in heating as well as a broad temperature range of 117 °C in cooling, whilst the mesophase model could not be ascertained between 137 °C and 182 °C in heating. Due to the orderless dispersion of fluorescein might influence on the ordered columnar hexagonal mesophase of perylene skeleton and resulted in the

imperfect XRD diffraction model for mesophase of compound **3**, the signals of XRD diffraction became broad than that of normal perylene liquid crystals (as shown in Figure 3).

### Photophysical properties

The photophysical properties of PBI **3** were investigated by the UV-vis absorption and fluorescence spectra. The solvent effect for absorption and fluorescence spectra of PBI **3** was demonstrated in Figure S5 and S6, respectively (see the ESI†). The mirror-image symmetry could be observed between the emission and absorption spectra in various organic solvents (10  $\mu\text{M}$  solutions). On account of the excellent fluorescence of PBI **3** in THF solvent, THF was chosen for exploring efficiently the emission behaviour of PBI **3**. To compare the photophysical properties of PBI **1**, PBI **3**, and fluorescein raw material, their absorption and emission spectra, measured within 5 min of dispersing them in THF solvent (10  $\mu\text{M}$ ), were presented in Figure 4 and 5, respectively. The relevant data was summarized in Table 3. In Figure 4, the absorption spectrum of fluorescein raw material exhibits two distinctive peaks at 456 and 485 nm in the range of 400- 500 nm due to its lactone and quinoid structures. When compared to the spectrum of PBI **1** with three symbolic bands of 0-2, 0-1, and 0-0 transitions positioned at 446, 534, and 575 nm, the absorption spectrum of PBI **3** exhibits the similar signature of perylene core and the unchanged absorption maxima. Whereas the absorption band of PBI **3** at around 446 nm exhibited a considerably improved profile, the absorbance intensity ratios of peak at 575 nm to that at 446 nm in the absorption spectra of PBI **1** was higher than that of PBI **3**. The ratio values were 2.33 and 1.45 for PBI **1** and PBI **3**, respectively. These results indicated that the absorption of PBI **3** overlaps the absorption of fluorescein fragment in the range of 400-500 nm, and that no electronic coupling existed between PBI chromophores and fluorescein fragment in the ground state.

<b>Table 3</b> Photophysical properties of PBI <b>3</b> , PBI <b>1</b> , and fluorescein <b>2</b> in solution (10 $\mu\text{M}$ )							
Compd.	$\lambda_{\text{abs}}$ (nm)	$\lambda_{\text{em}}$ (nm)	Stokes shift nm ( $\text{cm}^{-1}$ )	$\tau_{\text{f}}$ <sup>[a]</sup> (ns)	$\tau_{\text{f}}$ <sup>[b]</sup> (ns)	$\phi_{\text{f}}$ <sup>[a]</sup>	$\phi_{\text{f}}$ <sup>[b]</sup>
<b>1</b>	575	616	41 (1158)	2.89	2.90	0.35	0.80
<b>2</b>	456/485	540	55 (2100)	/	/	/	/
<b>3</b>	572	616	44 (1249)	3.27	3.03	0.86	0.74
[a] Excited at 450 nm in THF solution; [b] Excited at 550 nm in THF solution.							

As shown in Figure 5, the emission spectrum of fluorescein raw material displayed a band at 540 nm ( $\lambda_{\text{ex}} = 450$  nm). PBI **1** had an emission peak concentrated at 616 nm ( $\lambda_{\text{ex}} = 550$  nm). The fluorescence spectrum of target PBI **3** also exhibited a peak at 616 nm ( $\lambda_{\text{ex}} = 550$  nm) due to the substitution at N-imide positions of the PBI core. When selectively excited at  $\lambda_{\text{ex}} = 450$  nm for efficient excitations of the PBI chromophores and fluorescein fragment, the emission spectrum of PBI **3** just showed an enhanced band located at 616 nm, where the intensity was 1.5-fold higher than that of the substantial excitation of

PBI **3** at  $\lambda_{\text{ex}} = 550$  nm, indicating the intramolecular FRET between the PBI chromophores and fluorescein fragment as excited at 450 nm.

Moreover, the fluorescence quantum yield ( $\phi_f$ ) of PBI **3** is 0.86 and 0.74 (in Table 3) when selectively excited at 450 nm and 550 nm in pure THF solution, respectively. It should be noted that, when excited at 550 nm in pure THF solution, the fluorescence quantum yield ( $\phi_f$ ) of PBI **3** is 0.74, matching rather closely with those of PBI **1** (0.80). However, when excited at 450 nm in pure THF solution, the fluorescence quantum yield ( $\phi_f$ ) of PBI **3** exhibits remarkable value of 0.86 relative to PBI **1** (0.35), which is further supported by the intramolecular FRET between the PBI chromophores and fluorescein segment as excited at 450 nm. Similarly, the principle of FRET also greatly affects the fluorescence lifetime  $\tau_f$  (ns) of PBI **3**. The  $\tau_f$  value of PBI **3** (3.27) is greater than PBI **1** (2.89) as excited at 450 nm. The above discussion demonstrated that the PBI **3** showed different fluorescence specificities due to the intramolecular FRET between the PBI chromophores and fluorescein fragment when the fluorescein fragment was excited at 450 nm. On the other hand, probably because PBI **3** was reciprocally intertwined with a complicated aggregation, the very weakened fluorescence intensity of PBI **3** was detected in solid state. The proposed FRET mechanism for PBI **3** was described in Figure 6.

## Conclusion

A novel well-defined perylene liquid crystal with two mesogenic PBIs unit and one fluorescein unit linked by soft spacers at the N-imide position, was successfully obtained and well characterized by NMR, FT-IR, elemental analyses, and MALDI-MS. The mesophase model of target LC was determined to form a hexagonal columnar mesophase and an uncertain phase in heating. The hexagonal columnar mesophase existed stably from 175.6 °C to 58.6 °C on cooling. The fluorescence intensity of PBI **3** excited at 450 nm was 1.5-fold higher than that of the substantial excitation of PBI **3** at 550 nm, giving possible strategy to enhance fluorescence via FRET effect for PBI-based LC.

## Declarations

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**Data Availability** All the data and materials from this manuscript will be made available on request.

**Compliance with Ethical Standards**

**Competing Interests** No potential conflict of interest was reported by the authors.

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