



Enhanced fluorescence in both solution and solid state for perylene liquid crystals with six peripheral alkyl substituents on 1,6,7,12-bay positions and imides positions



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ABSTRACT

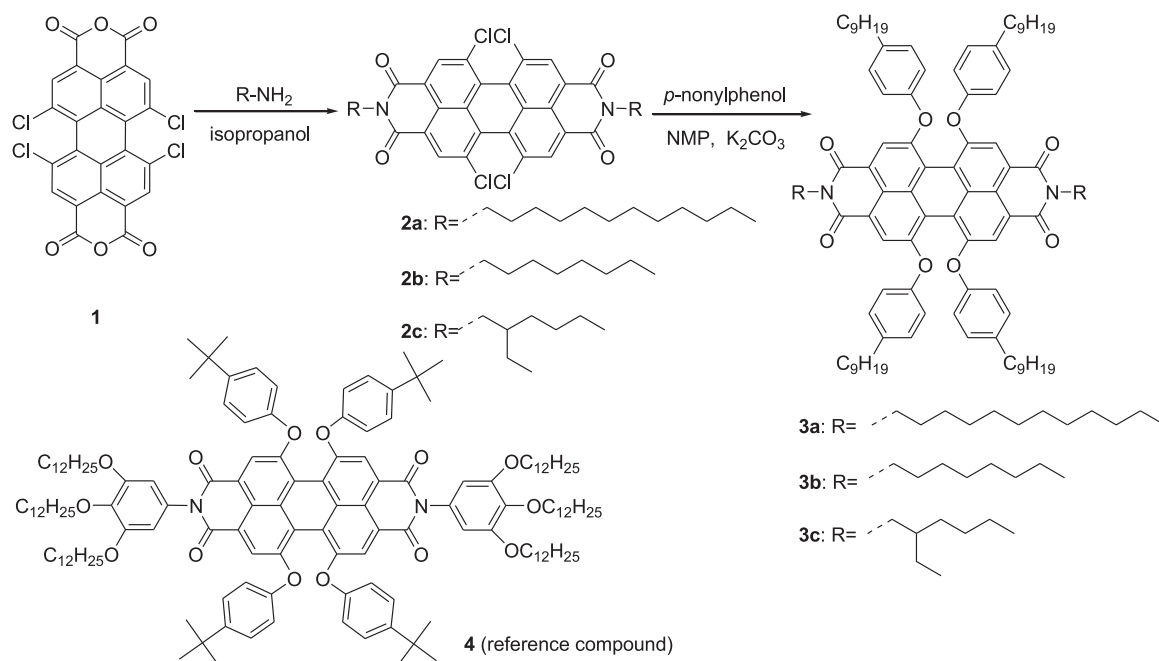
The first perylene liquid crystals bearing six peripheral alkyl substituents on both 1,6,7,12-bay positions and imides positions were designed and synthesized in yields of 72–77%. The studies on their mesomorphic behaviors suggested that they possessed good ordered hexagonal columnar mesophase with low phase transition temperatures and wide ranges of mesophase temperature in comparison with their precursors with chloric groups and the similar perylene liquid crystal with 4-*tert*-butylphenolic groups on bay positions. Their photophysical properties revealed that they also had higher fluorescence intensities and fluorescence quantum yields than that of their precursors with chloric groups and the similar perylene liquid crystal with 4-*tert*-butylphenolic groups on bay positions. The good fluorescence in both solution and solid film were observed for the first time for perylene liquid crystals. This research indicated that the introduction of long *p*-nonylphenol units on bay position is an effect strategy to obtain perylene liquid crystal with good liquid crystalline behavior and excellent fluorescent property.

1. Introduction

In the past decades, perylene bisimides (PBIs) and their derivatives, as an important part of organic charge-transport materials, have been paid much attention due to their potential applications in the fields of molecular electronic and optical devices, such as light-emitting diodes [1,2], photochromic materials [3,4], LCD color filters [5,6], and photovoltaic cells [7–10]. In order to tune the self-organization behavior to improve the electrical and optical responses as well as easy film processing, PBI liquid crystalline derivatives attracted much research interest because of their long-range ordered π -aggregates in columnar superstructures and good charge carrier mobility [11–14]. As a result, various PBI liquid crystals, including the nematic, smectic and ordered columnar PBI liquid crystals, had been synthesized and their photophysical and mesomorphic properties were also investigated up to now [15–18]. By introducing alkyl esters, polyoxyethylene chain, dendritic peptides, siloxane, organosilica, alkoxy or alkyl groups, fluoro-pentenyl groups, cholesterol units, and triphenylene groups onto perylene imide groups, series of perylene discotic liquid crystals were obtained conveniently [19–34]. However, these studies suggested that, although the mesomorphic properties of PBI liquid crystals were adjusted greatly

by changing the substituents onto imide positions, their photophysical properties were difficult to be improved because of their same perylene skeletons. On the other hand, literatures had revealed that the photophysical properties of PBI derivatives could be tuned by the substituents on bay positions of perylene skeleton [1–10,35,36]. The different bay position produced various electronic effects, which usually resulted in ICT effect in different solvents. Thus, few PBI liquid crystals with bay substituents were also investigated to obtain excellent luminescent properties [37–41]. But the substituents on bay-positions, which resulted in a twisting of the coplanar perylene core based on the strong hindrance, might be not favorable for the π - π columnar stacking action of perylene core. These researches suggested a complicated balance between the photophysical property and the mesomorphic property. Most recently, two examples of PBI liquid crystals with cholesterol or multiple alkyl-phenoxy on bay positions exhibited good columnar mesophase [42,43]. These results implied that the adjustment of the structures of bay substituents might realize the purpose of tuning both good luminescent and mesomorphic properties. Inspiring by these two researches, in this paper, we designed and synthesized the first examples of PBI derivatives with six alkyl substituents on both two imides positions and four phenoxy of bay positions. The experimental results

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Scheme 1. The synthetic routes of perylene bisimides **3a**, **3b** and **3c** with six peripheral alkyl tails on both imides and bay positions (compound **4** was used for comparison of properties [25]).

showed that, by comparing with the similar perylene derivative without bay substituent, the PBI derivatives with six peripheral alkyl tails on both imides and bay positions not only showed good liquid crystalline properties, but also enhanced the luminescent property greatly. The perylene liquid crystals with good fluorescence emission both in solution and solid film were observed for the first time. The structures and synthetic routes of novel perylene liquid crystals with six peripheral alkyl tails on both imides and bay positions were shown in **Scheme 1**.

2. Experimental

All chemical reagents were purchased from Aladdin Co., Ltd. and were purified according to standard anhydrous methods before use. TLC analysis was carried out on pre-coated glass plates. The 100–200 mesh of silica gel was used for column chromatography. ^1H NMR and ^{13}C NMR spectra were obtained in CDCl_3 on a Bruker-ARX 400 instrument at 30°C with tetramethylsilane (TMS) as internal standard. ESI-MS spectra were recorded from Bruker mass spectrometer. The thermal analysis was performed by differential scanning calorimeter (DSC) (Thermal Analysis Q100) with a scanning rate of $10^\circ\text{C}/\text{min}$ under N_2 atmosphere. The phase transitions were examined by polarized optical microscopy (Leica DMRX) with a hot stage (Linkam THMSE 600). X-ray diffraction (XRD) experiments were done on SEIFERT-FPM (XRD7), using $\text{Cu K}\alpha$ 1.5406 \AA as the radiation source with 40 kV, 30 mA power. UV-Vis spectra were investigated on Varian spectrometer. Fluorescence spectra were carried out on a Hitachi F-4500 spectrometer with a conventional quartz cell ($10 \times 10 \times 45 \text{ nm}$) at 25°C . The excitation and emission slits were 10 nm wide. The fluorescence absolute values (Φ_f) were measured on an Edinburgh Instruments FLS920 Fluorescence Spectrometer with a 6-in. integrating sphere.

2.1. Synthesis of perylene bisimides **2a**, **2b** and **2c**

Under N_2 atmosphere, 1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic acid (0.106 g, 2 mmol) and corresponding 1-aminoalkane (2.2 mmol) were mixed into the 35 mL of isopropanol. A drop of glacial acetic acid was added as catalyst. The mixture was stirred and refluxed for 12 h. The progress of the reaction was continuously monitored by

thin-layer chromatography (TLC). As the starting materials were disappeared, the reaction mixture was cooled to room temperature and then dispersed into 50 mL of ice-water. The obtained precipitate was filtered, washed thoroughly with distilled water to afford crude product. The crude product was further purified by chromatography column (silica gel 100–200 mesh, CH_2Cl_2 as the eluant). The perylene bisimides **2a**, **2b** and **2c** were collected as golden yellow solid in yields of 85%, 87% and 82%, respectively. Compound **2a**: ^1H NMR (400 MHz, CDCl_3) δ ppm: 8.66 (s, 4H, Per-H), 4.19 (t, $J = 8.0 \text{ Hz}$, 4H, NCH_2), 1.72 (m, 4H, CH_2), 1.24–1.42 (m, 36H, CH_2), 0.86 (t, $J = 8.0 \text{ Hz}$, 6H, CH_3); MALDI-TOF-MS ($\text{C}_{48}\text{H}_{54}\text{Cl}_4\text{N}_2\text{O}_4$) $[\text{M}]^+$: Calcd.: 864.2. found: 882.1 ($\text{M}^+ + \text{H}_2\text{O}$), 904.1 ($\text{M} + \text{K}^+$). Compound **2b**: ^1H NMR (400 MHz, CDCl_3) δ ppm: 8.67 (s, 4H, Per-H), 4.20 (t, $J = 8.0 \text{ Hz}$, 4H, NCH_2), 1.73 (m, 4H, CH_2), 1.28–1.42 (m, 20H, CH_2), 0.87 (t, $J = 8.0 \text{ Hz}$, 6H, CH_3); MALDI-TOF-MS ($\text{C}_{40}\text{H}_{38}\text{Cl}_4\text{N}_2\text{O}_4$) $[\text{M}]^+$: Calcd.: 752.1. found: 751.7. Compound **2c**: ^1H NMR (400 MHz, CDCl_3) δ ppm: 8.66 (s, 4H, Per-H), 4.13 (m, 4H, NCH_2), 1.93 (m, 2H, CH), 1.31–1.41 (m, 16H, CH_2), 0.89–0.96 (m, 12H, CH_3); MALDI-TOF-MS ($\text{C}_{40}\text{H}_{38}\text{Cl}_4\text{N}_2\text{O}_4$) $[\text{M}]^+$: Calcd.: 752.1. found: 751.7.

2.2. Synthesis of perylene bisimides **3a**, **3b** and **3c** with six alkyl substituents on 1,6,7,12- phenoxy of bay positions and imides positions

Corresponding compound **2** (1.0 mmol), 1.6 mL of *p*-nonylphenol (11.65 mmol) and K_2CO_3 (1.38 g, 10 mmol) was dispersed in 25 mL of anhydrous *N*-Methyl pyrrolidone (NMP). The mixture was stirred at 120°C overnight under N_2 atmosphere. As the disappearance of compound **2** under the detection of TLC, the reaction mixture was cooled and 50 mL of HCl solution (1 M) was added. The mixture was extracted with 40 mL of CH_2Cl_2 . The obtained organic layer was washed with NaOH solution (1 M) ($3 \times 50 \text{ mL}$) and dried over anhydrous MgSO_4 . After filtration, the solution was concentrated under reduced pressure. The residue was further purified by chromatography column (silica gel 100–200 mesh, CH_2Cl_2 /petroleum ether (6:1, V/V) as eluant). The compounds **3a**, **3b** and **3c** were collected as red purple solids in yields of 72%, 75% and 77%, respectively. Compound **3a**: ^1H NMR (400 MHz, CDCl_3) δ ppm: 8.20 (bs, 4H, Per-H), 7.19 (bs, 8H, Ar-H), 6.85 (bs, 8H, Ar-H), 4.11 (bs, 4H, NCH_2), 0.79–1.80 (m, 122H, CH_2 and CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ ppm: 163.40, 155.94, 152.77, 144.50, 132.68,

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