

Notes

Color Tuning of Perylene Based Lyotropic Chromonic Liquid Crystal

Jaishri J. Naidu, Yun Ju Bae, Kwang-Un Jeong, Seunghan Shin,[†] and Myong-Hoon Lee^{*}

Department of Polymer/Nano Science and Technology, Chonbuk National University, Chonju, Chonbuk 561-756, Korea

^{*}E-mail: mhlee2@chonbuk.ac.kr

[†]Korea Institute of Industrial Technology (KITECH), Chonan, Chungnam 330-825, Korea

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Perylene bisimides (PBIs) are widely used as dyes and pigments since they show outstanding chemical, thermal and photochemical stability. Compared to other dyes and pigments, PBIs have advantages such as better solubility, synthetic simplicity, and less trouble in purification. Beside the conventional uses, PBIs are key chromophores for high-tech applications such as reprographic processes,¹ fluorescent solar collectors,² photovoltaic cells,³ optical switches,⁴ and lasers.⁵ In this context, PBIs are generally referred to as functional dyes. Especially, PBIs having ionic periphery have attracted much attention because they can form lyotropic chromonic liquid crystal (LCLC) in aqueous solution. The anisotropic orientation of molecules with π - π stacking of aromatic core can exploit their intrinsic properties most efficiently in the potential applications such as coatable polarizers,⁶ oriented optical films,⁷ and biosensors.⁸ In recent years, emphasis has been given on tailoring the functional groups of PBI so that the desired optical and/or electronic properties can be achieved. In that sense and many advantages of PBI taken into account, color tuning of PBI dye is one of the key issues especially in optical and photonic applications because most of PBIs are only red or orange colored.

Color tuning of PBI dye can be achieved by substitution at the bay area (1,7-position of the perylene core). Stalke *et al.* reported a series of compounds with different substituents at bay region of perylene core.⁹ Würthner *et al.* also reported a series of thermotropic liquid crystals based on PBI dyes with different substituents at the bay area (1,6,7,12 positions of the perylene core).¹⁰ According to their reports, PBI derivatives with electron-donating substituents at the bay area exhibit a large bathochromic shift of the absorption maxima (λ_{ax}) compared to the unsubstituted PBI, reflecting pronounced electronic interactions between the perylene core and the electron-donating groups in bay area. In contrast, PBI derivatives

with electron-withdrawing substituents such as Cl, Br, or pentafluorophenoxy groups at the bay positions showed hypsochromic shift of λ_{max} with respect to that of the unsubstituted PBI.

However, structural modification of PBI having ionic peripheries for the generation of LCLC is synthetically complicated because the resulting PBI molecules often have limited solubility in common organic solvents due to their ionic nature. In addition, substitution at the bay area can cause a twisting of aromatic core possibly hindering π - π stacking which is crucial for the formation of lyotropic columnar liquid crystal. Therefore, it is challenging to design and synthesize a lyotropic liquid crystalline PBI molecule having green or blue color. In this work, we report the first synthesis of green lyotropic liquid crystalline compound based on PBI core having pyrrolidine substituent at the bay area.

Bromination of perylene dianhydride was performed according to the BASF patent.¹¹ The bromination under this condition afforded a mixture of 1,7- and 1,6-dibrominated compounds with trace amount of 1,6,7-tribrominated analogues (Figure 1). The resulting mixture was insoluble in organic solvents, and therefore, could not be purified by any means. The crude mixture was used for the subsequent imidization (Figure 2) with *N,N*-diethylethylene diamine in a mixed solvent of H₂O/*n*-PrOH (2:1 v/v) at 80 °C. After the reaction, the product became soluble in organic solvents such as CH₂Cl₂ and chloroform, which enabled the separation of regioisomers by column chromatography. From the first chromatography, 1,6,7-tribrominated perylene bisimide was separated (in less than 1% yield) from the mixture of 1,7- and 1,6-dibrominated compounds. 400MHz ¹H-NMR analysis of the residual mixture revealed a 80:20 ratio of the 1,7- and 1,6-

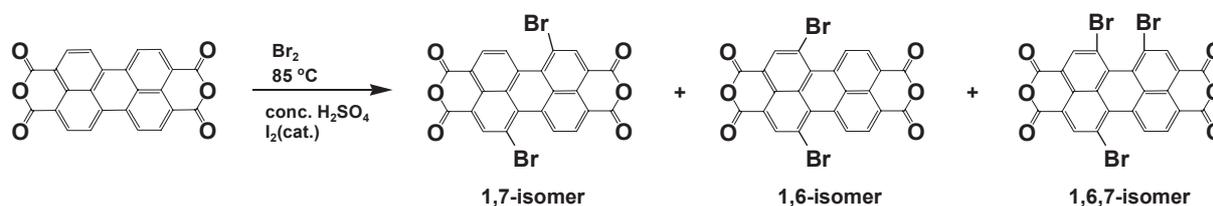


Figure 1. Bromination products of perylene dianhydride

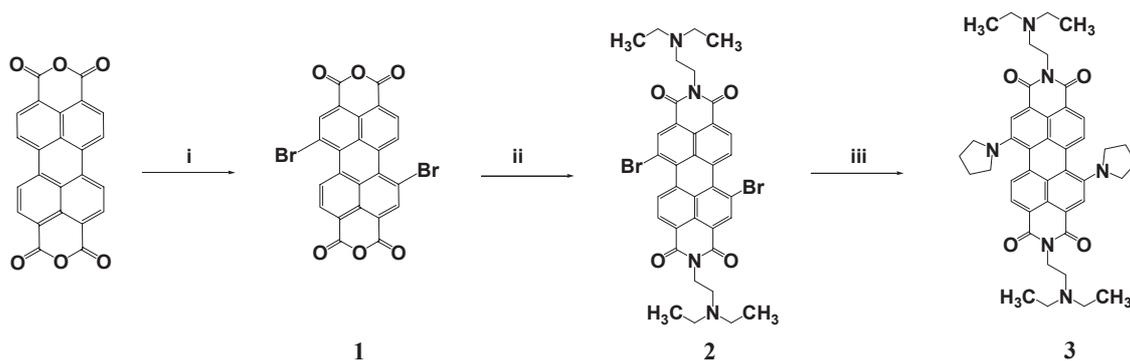


Figure 2. Synthesis of pyrrolidine-substituted perylene bisimide. i) Br_2 , conc. H_2SO_4 , I_2 (cat.), 85°C , 12h; ii) N,N -diethylethylenediamine, 85°C , 12 h; iii) pyrrolidone, 55°C , 24h, Ar atmosphere

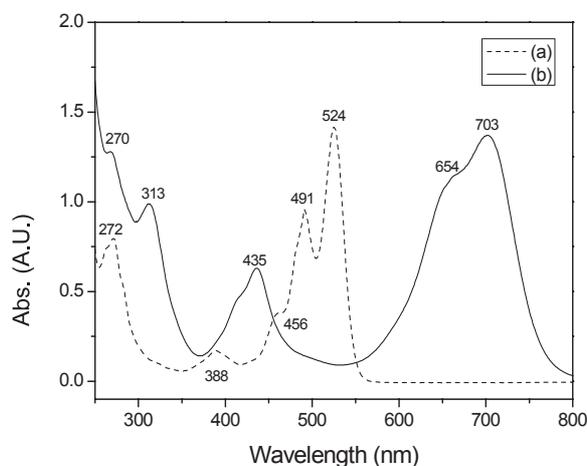


Figure 3. UV/vis absorption spectra of perylene bisimides in methanol solution: (a) bromo-substituted perylene bisimide; (b) pyrrolidine-substituted perylene bisimide

regioisomers. 1,7-Dibrominated compound (**2**) was separated from this mixture as a major component (in 61% yield) after the second column chromatography. The nucleophilic substitution of 1,7-dibromoperylene bisimide with pyrrolidine according to Wasielewski's method¹² afforded the corresponding 1,7-dipyrrolidinylperylene bisimide (**3**) as a green solid in 60% yield after column chromatography. Good solubility in organic solvents, and water as well as high thermal stability was observed for N,N -diethyl ethylenediamine 1,7-dipyrrolidinylperylene-3,4:9,10-tetracarboxylic acid bisimide (**3**).

The optical properties of bromo-substituted and pyrrolidine-substituted PBIs (**2**, **3**) were investigated by UV/vis spectroscopy as shown in Figure 3. Both dyes in methanol solution exhibited multiple S_0 - S_1 absorption bands with λ_{max} at 524 and 703 nm, respectively. The λ_{max} of bromo-substituted PBI was shifted only slightly from that of the unsubstituted PBI ($\lambda_{\text{max}} = 527$ nm in CH_2Cl_2).¹³ In contrast, the λ_{max} of compound **3** showed a bathochromic shift by 76 nm with showing green color, which is mainly due to the electron-donating pyrrolidine groups directly attached to perylene core at the bay area. Additionally, band shape of the compound **3** was broader than those of compound **2** or unsubstituted PBI, which is probably attributed to the loss of planarity of perylene core due to the steric hindrance at the bay area.¹⁰ Hydrochloride

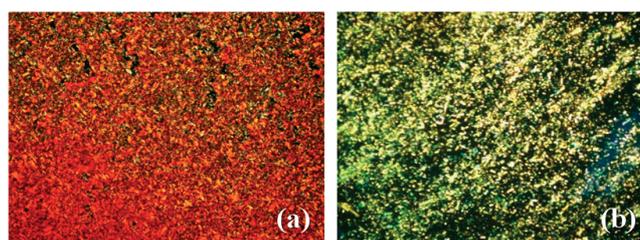


Figure 4. Optical microscopic pictures of perylene bisimides (1.0 wt% aqueous solution) at room temperature: (a) bromo-substituted perylene bisimide; (b) pyrrolidine-substituted perylene bisimide

salts of compound **2** and **3** were dissolved in distilled water (1 wt%), and their optical textures were examined by polarized optical microscope (POM). As depicted in Figure 4, both of solution samples exhibited typical texture of columnar phase and well-flowing behaviour confirming that the synthesized compounds are lyotropic liquid crystals. Further characterization of liquid crystalline behavior and structural analyses including X-ray diffraction and phase diagram studies are now in progress, which will be published in due course.

In summary, we reported the first example of the green lyotropic chromonic liquid crystalline compound based on perylene bisimide. The color tuning of perylene bisimide was achieved by introducing electron-donating substituents at the bay area. The syntheses proceeded in good yields via a short and convenient synthetic route. This dye exhibits good thermal stability, solubility in water and organic solvents as well. The structure was characterized by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, mass, and UV/Vis spectroscopies. Aqueous solution of hydrochloride salt exhibited lyotropic chromonic liquid crystalline columnar phase at room temperature examined by polarized optical microscopy.

Experimental Section

***N,N*-Diethylethylenediamine 1,7-bromoperylene-3,4:9,10-tetracarboxylic acid bisimide (**2**).** A mixture of perylene-3,4:9,10-tetracarboxylic acid anhydride (15.65 g, 80.0 mmol) and conc. sulfuric acid (236 g) was stirred for 12 h at room temperature, and subsequently, 0.385 g of I_2 (3.0 mmol) was added. The reaction mixture was heated to 85°C , and bromine (14.1 g, 176 mmol) was added dropwise over a time period of 8 h. After bromine addition, the reaction mixture was heated

for an additional 10 h at 85 °C, and cooled to room temperature. The excess bromine was removed by a gentle stream of N₂ gas, and 32.5 ml of distilled water was added carefully. The resulting precipitate was separated by filtration through a G4 funnel, washed with 86% sulfuric acid (150 ml) and large amount of distilled water, and dried in a vacuum to give a crude mixture of 1,7- and 1,6-dibromo- and 1,7,6-tribromo-PBIs. The solid was dried under vacuum to obtain isomeric mixture of compound **1** in 89.4% yield. A suspension of above mixture (0.95 g, 1.72 mmol), *N,N*-diethylethylene diamine (0.502 g, 5.07 mmol), and acetic acid (0.50 g, 8.33 mmol) in 20 ml of 2:1 mixture of H₂O/*n*-PrOH (v/v) was stirred at 85 °C under Ar atmosphere for 8 h. After the mixture was cooled to room temperature, the precipitate was separated by filtration, washed with 100 ml of methanol and dried in a vacuum. The crude product was purified by silica gel column chromatography with CH₂Cl₂ as eluent to give a red powder (750 mg, 61%) which was a regioisomeric mixture of 1,7- and 1,6-dibromo PBIs with 80:20 ratio as revealed by 400MHz ¹H-NMR analyses. Second column chromatography gave a pure 1,7-dibromo compound **2** which was confirmed by ¹H- and ¹³C-NMR spectra and mass spectroscopy. ¹H-NMR (400 MHz in CDCl₃): δ (ppm) 9.4 (d, 2H, *J*=8.1 Hz), 8.9 (s, 2H), 8.6 (d, 2H, *J*=8.1 Hz), 4.3 (t, 6H), 2.8 (t, 6H), 2.6 (q, 16H), 1.1 (t, 12H); ¹³C-NMR (400MHz, in CDCl₃): δ (ppm) 159.4, 136.2, 133.0, 132.0, 130.9, 130.7, 129.2, 128.5, 128.1, 124.0, 123.8, 50.2, 49.2, 47.7, 13.3; MS (EI, 70 eV) *m/z*: 746.09; UV/vis (in methanol): λ_{max}: 388, 456, 491, 524 (nm).

***N,N*-Diethylethylenediamine 1,7-dipyrrolidinylperylene-3,4,9,10-tetracarboxylic acid bisimide (3)**. A mixture of 1,7-dibromo PBI (**2**) (95.0 mg, 0.133 mol) and pyrrolidine (4.30 g, 59.7 mmol) was stirred for 24 h at 55 °C (external, oil bath) under Ar atmosphere. Subsequently, the reaction mixture was poured into 15 ml of 12% HCl with stirring. The solution mixture was extracted with methylene chloride (3×20 ml), dried over MgSO₄, and concentrated by rotary evaporation. The resulting solid was purified by column chromatography on silica gel with CH₂Cl₂/hexane (40:1, v/v) as eluent to yield 62 mg (50%) of a green solid. ¹H-NMR (400 MHz in CDCl₃): δ (ppm) 8.38-8.34 (d, 2H, *J* = 8.1 Hz), 8.32 (s, 2H), 7.5-7.4 (d, 2H, *J* = 8.1 Hz), 4.52 (t, 3H), 3.67 (t, 3H), 3.2 (t, 3H), 3.0 (t, 4H), 1.9 (m, 5H), 1.41 (t, 3H); ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) 159.4, 152.9, 134.3, 133.0, 131.5, 130.9, 128.3, 127.7, 122.2, 119.9, 118.0, 52.2, 49.2, 47.7, 25.5, 13.3; MS (EI, 70 eV) *m/z*: [M⁺] 726.39; UV/vis (in methanol): λ_{max}: 416, 435, 654, 703 (nm).

Hydrochloride salt of compound **3** was prepared by completely dissolving compound **3** in conc. HCl, with subsequent evaporation of remaining HCl by rotary evaporator under reduced pressure. The resulting solid was dried in vacuum oven at room temperature for 24 h.

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