Synthesis of perylene dianhydride-incorporated main chain polyimides and sequential structural transformation through a dipolar cycloaddition

Mieon Choi, Jung Yun Do *

Department of Chemistry Education, Pusan National University, Pusan 609-735, Republic of Korea

ABSTRACT

Perylene dianhydride (PDA)-incorporated polyimides were prepared. The perylene unit in the polyimide was thermally converted to the corresponding N-heterocyclic polyarene unit through a Diels–Alder reaction. The monomer, 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane (6FAP), was modified via O-alkylation to improve the solubility of the polymer. 2-Ethylhexyl-attached **6FAP** yielded a soluble copolyimide that contained ca. 70 mol% **PDA** using pyromellitic dianhydride. The perylene unit of the copolyimide transformed to a polyarene unit through the dipolar cycloaddition of 4-aryl-1,2,4-triazole-3,5-dione (TAD) and maleic anhydride. The perylene transformation of the polyimide occurred with 50% conversion with maleic anhydride and quantitatively with **TAD**. The **PDA**-copolymer exhibited a spectral blue-shift and red-shift by maleic anhydride and **TAD**, respectively.

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1. Introduction

Perylene is a promising polycyclic semi-conductor because of its electronic properties, such as high electron mobility and large molar absorption coefficients in the UV–Vis range, and high quantum efficiency [1–3]. This compound has frequently been used in chemical reactions as a useful dianhydride derivative and transformed to diimide analogues to relieve the solvent resistivity caused by the strong pi-stacking planar structure [4]. Several perylene derivatives have been reported through a range of structural modifications for optical and electronic applications including organic solar cells [5], organic thin-film transistors (OTFT) [6], organic light-emitting diodes (OLED) [7], sensors [8] and tracers in the biochemical field [9]. Sterically hindered and electronic polarizing groups attached to the bay position of perylene diimides perturb the intrinsic electronic energy levels of the perylene groups and modulate the energy band gap [10]. Wang and Mullen suggested an extension of the aromatic pi-length through an intriguing successive carbon-bond formation from perylenes [11–13]. The absorption band of planar perylene derivatives shifted to a longer wavelength depending on the conjugation length. Langhals et al. reported a triazolinedione adduct of perylene imides that

showed absorption in the near-infrared region through N-heterocyclization [14,15].

The strong pi-aggregation of perylene-based materials, which causes solubility problems is generally weakened by bulky substituents or by polymeric attachment, allowing thin film applications. Various perylene-incorporated polymers have been developed for solar cells with the expectation of spontaneous self-assembly of perylene groups in a polymer film [16–18]. The perylene group was introduced in a diblock copolymer or a side-chain polymer through transition metal-catalyzed aryl–aryl coupling or an olefinic metathesis reaction [5,19–22]. The polymerization of perylene dianhydride and a diamine monomer afforded a perylene-backbone polyimide. The polymerization suffered from the low reactivity of perylene dianhydride and was limited to the formation of a copolyimide because of its low solubility [23,24]. The perylene-containing polyimide developed in the previous study was soluble when the perylene content was low [25]. However, a high concentration of perylene is required to use perylene-containing polymers in electronic and optical applications because adjacent perylene groups are capable of transporting electrons or light. A perylene monomer has generally been modified based on consideration of the final polymer [25–27]. A chemical reaction that uses the polymer provides a simple route to control optical and physical properties but is limited due to the reactivity and solubility of the polymer. In this study, the thermal reaction of a

perylene-polyimide is used to generate a new polyimide with a high dye content that exhibits near-infrared absorption.

2. Experimental

2.1. Materials and characterizations

All reagents were purchased from the Sigma–Aldrich Chemical Co., and the reagent-grade solvents were dried when necessary and purified by vacuum distillation. Benzophenone-3,3′,4,4′-tetra-carboxylic dianhydride (BTDA), pyromellitic dianhydride (PMDA) and 4,4′-oxydiphthalic anhydride (ODPA) were purified using a conventional sublimation process. 2,2-Bis(3-amino-4-hydroxy-phenyl)hexafluoropropane (6FAP) and perylene-3,4,9,10-tetra-carboxylic dianhydride (PDA) were used as received. Column chromatography for the purification of products was performed using silica gel (Merck, 250–430 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ as an internal reference on a Varian Mercury 300 MHz and 75 MHz, respectively. FT-IR data were recorded on a Varian FTS 800 using KBr pellets. High-resolution mass spectrometry (HRMS) was performed on a JEOL JMS-700 mass spectrometer under fast atom bombardment (FAB) conditions. The UV–Vis spectra were measured using a Shimadzu UV-1601 UV–Vis spectrometer. The molecular weights of the polymers were estimated using q Tosoh gel permeation chromatography system. Thermal analyses were conducted on a Mettler Toledo TGA/SDTA 851e analyzer.

2.2. Synthesis of **PDI** and **CPTAD**

Perylene diimide (PDI) and 4-(4-chlorophenyl)-1,2,4-triazole-3,5-dione (CPTAD) were prepared according to the methods reported in the literature [25], as described in supplementary data.

2.3. Preparation of **PDI-T**

CPTAD (15.0 mmol, 3.14 g) and *p*-chloranil (7.50 mmol, 1.84 g) were added to a solution of perylene diimide **PDI** (1.50 mmol, 1.38 g) in dried benzene (15 mL). The mixture was heated at 75 °C under N_2 atmosphere for 7 days. The resulting mixture was concentrated, re-dissolved in n-hexane, and filtered through a sintered glass. The filtrate was evaporated to dryness and roughly purified by column chromatography using chloroform and acetone/chloroform (1/10, v/v) as eluents. An isolated dark blue product was precipitated into methanol to afford **PDI-T** (1.70 g, 85%). IR (KBr): 3106, 2955, 2854, 1776, 1731, 1703, 1661, 1603, 1572, 1495, 1369, 1300, 1232, 1174, 829, 806, 774, 731 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 8.87 (m, 4H), 7.65 (d, 4H), 7.49 (d, 4H), 4.94 (m, 2H), 2.11 (m, 4H), 1.83 (m, 4H), 1.25 (m, 56H), 0.83 (t, 12H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 161.8, 157.4, 143.0, 135.5, 133.3, 129.9, 128.3, 127.9, 125.6, 124.0, 123.4, 116.3, 55.9, 32.2, 29.9, 29.8, 29.6, 27.3, 22.9, 14.4. UV–Vis (CHCl$_3$): λ_{max} (ε, L mol^{-1} cm^{-1}) = 703 (1.5 × 10^4), 773 nm (1.9 × 10^4). HRMS (FAB+): *m/z* = 1337.6331 [MH$^+$] (Calcd: 1337.6337). Anal. Calcd for C$_{78}$H$_{90}$Cl$_2$N$_8$O$_8$: C, 69.99; H, 6.78; Cl, 5.30; N, 8.37; O, 9.56. Found: C, 70.47; H, 6.72; Cl, 5.21; N, 8.24; O, 9.36.

2.4. Preparation of **PDI-A**

PDI (0.5 g, 0.72 mmol) and *p*-chloranil (0.35 g, 1.44 mmol) were dissolved in maleic anhydride (1.5 g) with the addition of a few mL of acetone. The mixture was heated at 202 °C for 12 h. The reaction mixture was cooled, dispersed in acetone (2 mL) and then precipitated into methanol. The resulting dark yellow solid was collected by filtration, washed with methanol and dried under vacuum at 60 °C to afford an orange solid (0.37 g, 65%). IR (KBr): 2929, 2856, 1852, 1770, 1703, 1661, 1409, 1362, 1317, 1162, 909 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 10.25 (s, 2H), 9.45 (d, 2H), 9.22 (br. S, 2H), 5.28 (m, 2H), 1.88–2.01 (m, 4H), 1.10–1.42 (m, 32H), 0.80 (t, 12H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 164.2, 162.3, 133.6, 129.1, 129.0, 128.1, 127.4, 127.3, 125.7, 125.0, 124.0, 123.4, 123.3, 56.8, 55.1, 34.2, 32.0, 31.9, 29.9, 26.9, 22.8, 14.8, 13.7. UV–Vis (CHCl$_3$): λ_{max} (ε, L mol^{-1} cm^{-1}) = 438 (3.7 × 10^4), 468 nm (5.3 × 10^4). HRMS (FAB+): *m/z* = 1016.6180 [MH$^+$] (Calcd: 1016.6279). Anal. Calcd for C$_{66}$H$_{84}$N$_2$O$_7$: C, 77.92; H, 8.32; N, 2.75; O, 11.01. Found: C, 77.75; H, 8.37; N, 2.64; O, 11.24.

2.5. Preparation of **Ac-diamine**

2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane (6-FAP) (5.5 mmol, 2.0 g) and acetic anhydride (32.8 mmol, 3.1 mL) were dissolved in tetrahydrofuran (THF) (20 mL) containing pyridine (50 mmol, 4.1 mL) at 0 °C. After stirring for 4 h at 20 °C, the mixture was concentrated and mixed with methanol (40 mL) to precipitate a white solid. The filtered solid was re-dissolved in THF (12 mL) and treated with a 25% aqueous NaOH solution (1.3 g) and tetrabutylammonium hydroxide (0.2 g). The reaction mixture was stirred for 20 h at 20 °C and concentrated under reduced pressure to remove tetrahydrofuran. The resulting solution was neutralized with an aqueous NH$_4$Cl solution. A white solid was filtered and dried to afford **Ac-diamine** (1.76 g, 71%). IR (KBr): 3409, 3094 (br), 2977, 1653, 1552, 1429, 1253, 12.05, 965, 821 cm^{-1}. ^{1}H NMR (DMSO-d6, 300 MHz): δ = 10.3 (s, 2H), 9.36 (s, 2H), 7.91 (s, 2H), 6.91–6.88 (d, 4H), 2.05 (m, 6H). LCMS: *m/z* = 450.15 [M$^+$] (Calcd: 450.10).

2.6. Preparation of **diamine**

2.6.1. Preparation of **R1-diamine**

The acetyl-protected 6-FAP (Ac-diamine) (1.35 g, 3.0 mmol), n-octyl bromide (2.32 g, 12.0 mmol) and potassium carbonate (0.83 g, 6.0 mmol) were dissolved in dimethylformamide (10 mL) and stirred at 30 °C for 32 h. The reaction mixture was diluted with water and extracted with ethyl acetate. The organic layers were washed several times with water, dried over anhydrous MgSO$_4$ and filtered. The solvent was removed by rotary evaporation. The crude product was dissolved in a co-solvent of ethyl acetate (1 mL) and methanol (4 mL). Thionyl chloride (0.28 g, 2.4 mmol) was slowly added, and the mixture was stirred at 30 °C for 8 h. The reaction mixture was quenched via the addition of water (10 mL) and neutralized to pH 7 with an aqueous potassium carbonate solution. The resulting mixture was extracted with ethyl acetate, washed with water and dried over anhydrous MgSO$_4$. The concentrated organic mixture was purified by column chromatography on silica gel using a EA/Hex (1/10, v/v) co-solvent to afford **R1-diamine** (1.08 g, 61%). IR (KBr): 3489, 3392, 2955, 2931, 2862, 1613, 1517, 1240, 1160 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 6.91–6.62 (m, 6H), 4.05 (t, 4H), 3.8 (s, 4H), 1.88 (m, 4H), 1.80–1.25 (m, 20H), 0.99 (t, 6H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 147.1, 135.9, 126.1, 124.5 (q), 120.7, 117.2, 110.3, 68.4, 63.9 (m), 32.2, 29.6, 29.5, 29.5, 26.4, 22.9, 14.3. LCMS: *m/z* = 590.30 [M$^+$] (Calcd: 590.33).

2.6.2. Preparation of **R2-diamine**

The acetyl-protected 6-FAP (Ac-diamine) (1.35 g, 3.0 mmol), 2-ethylhexyl bromide (2.32 g, 12.0 mmol) and potassium carbonate (0.83 g, 6.0 mmol) were dissolved in dimethylformamide (10 mL) and stirred at 50 °C for 24 h. The reaction mixture was diluted with water and extracted with ethyl acetate. The organic layers were washed several times with water, dried over anhydrous MgSO$_4$ and filtered. The solvent was removed by rotary evaporation. The