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The synthesis of symmetric and asymmetric perylene derivatives and their optical properties

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ABSTRACT

Symmetric bisimidazole and asymmetric imide-imidazole derivatives having a perylene structure were synthesized. Long, hyperbranched alkyl groups, attached to the benzimidazole moeity, enhanced the solubility of the imidazole derivatives. Soluble asymmetric imide-imidazoles were prepared using 1,2-diaminophenyls which contained methoxy, nitro and ester groups. The effects of both electron-withdrawing and donating groups were examined optically and electronically using both absorption and emission spectroscopy. Photoluminescence spectroscopy revealed that the various perylene derivatives displayed varying quantum yield; frontier orbital energy levels were determined using cyclic voltammetric analysis. The asymmetric imide-imidazole displayed the transient, electronic and optical properties of symmetric bisimide and symmetric bisimidazole perylene derivatives. Nitro derivation reduced the LUMO energy level of the asymmetric perylene by 0.05 eV while methoxy derivation increased it by 0.07 eV, in comparison with that of the unsubstituted, asymmetric perylene. Either bathochromic or hypsochromic spectral shifts of the asymmetric imidazoles were observed in solid film, depending on electronic substituent.

1. Introduction

Perylene derivatives with a planar structure have attracted interest in the context of liquid crystal materials and light emitting diodes [1,2]. The excellent charge transporting character of such aligned perylenes is favorable for organic thin films transistor (OTFT) applications [3] as the electron transfer process is both rapid and effective [4]. Recent organic photovoltaic research has adopted perylene derivatives as the *n*-type semiconductor for the fullerene derivative, [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) [5]; many organic solar cells have been fabricated using PCBM, despite its demerits of high synthesis cost, low solvent solubility and low charge carrier mobility [6]. In terms the cascade of energy transfer from an exited chromophore in a heterojunction solar cell, the LUMO energy level of fullerenes has to be located between that of the chromophore and the anode work function [7]. Fullerene derivation is difficult and, synthetically, is limited to the maintenance of π-conjugation. Perylenes are similar to fullerenes in character and display reversible redox properties and good thermal and optical stability as well as electron transfer through π–π stacking [8]; many perylene derivatives have been described [5,9–13].

A key issue for perylenes is their solvent solubility, this being of significance in the context of film formation [9]; their nonpolar, planar and rigid structure imparts very low solubility and necessitates the use of vacuum evaporation for thin film fabrication [8]. The introduction of a long chain alkyl substituent in perylene derivatives enhances their solubility and many studies have involved the use of perylene carboxylic dianhydride. Perylene bisimides are soluble derivatives that contain long alkyl chains [14] which have also been further derivatised to modify specific optical properties such as electronic energy levels and absorption wavelength [10,15,16]. In this context, amino and alkoxy groups extend absorption to longer wavelengths or lower the band gap [9]. Such bulky substituent distort the phenyl groups of the planar perylene structure and induce aggregation, which diminishes the conduction channel of the electrons [9]. An imidazole derivative as a perylene imide analogue was employed as an *n*-type semiconductor [10,17] in which, whilst the novel, planar ring formation beyond the four phenyls of the perylene constituent imparted longer wavelength absorption, it worsened solubility. However, it is considered that modification of such structures via perylene carboxylic dianhydride should be possible employing an appropriate synthetic pathway.

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This paper concerns the selective synthesis of an asymmetric imide-imidazole derivative that exhibits the transient electronic property of both symmetric imidazole and symmetric imide perelyne derivatives. All derivatives were analyzed in solution phaseso as to suppress strong intermolecular interactions that inevitably occur in solid films. The electronic energy levels of the asymmetric perylene derivative that has undergone electronic modification via imidazole rings are discussed.

2. Experimental

2.1. Materials and instrumentations

All reagents such as perylene-3,4,9,10-tetracarboxyldianhydride, 4-nitro-*o*-phenylenediamine, methoxy-1,2-phenylenediamine dihydrochloride, diaminobenzoic acid, and steric acid ethyl ester were purchased from Aldrich Chemical Co.. These were used without further purification unless otherwise noted. Solvents were dried and purified by fractional distillation over sodium and handled in a moisture-free atmosphere. Column chromatography was performed using silica gel (Merck, 250–430 mesh).

^{1}H NMR spectra were recorded in $CDCl_3$ on a Varian Mercury 300 MHz. The absorption and photoluminescence (PL) spectra were measured using a Jasco V-570 UV–Vis spectrometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. Cyclic voltammetry (CV) was carried out with a Bioanalytical Systems CV-50W voltammetric analyzer at a potential scan rate of 100–150 mV/s in a 0.1 M solution of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) in anhydrous acetonitrile and tetrabutylammonium hexafluorophosphate (Bu_4NBPF_6) in dichloromethane. A platinum wire was used as the counter electrode and an $Ag/AgNO_3$ electrode was used as the reference electrode.

2.2. Synthesis

*2.2.1. Synthesis of alkyl 3,4-diaminobenzoate (**3**)*

2.2.1.1. Synthesis of methyl 3,5-bis(2-ethylhexyloxy)benzoate. In a 205-mL round flask, methyl 3,5-dihydroxybenzoate (5.04 g, 30.0 mmol), 3-(bromomethyl)heptane (30.66 g, 156 mmol), TBAB (4.87 g, 15.0 mmol), and K_2CO_3 (16.6 g, 120 mmol) were dissolved with 120 mL absolute acetone and stirred at 80 °C for 48 h. The reaction mixture was diluted with water and extracted with ethyl acetate. The organic layers were washed several times further with water, dried over anhydrous $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the mixture was purified (95%) by column chromatography on silica gel.

^{1}H NMR ($CDCl_3$, 300 MHz): $\delta_{ppm} = 0.88–0.92$ (t, 12H, CH_3), 1.36–1.47 (m, 16H, CH_2), 1.53–1.71 (m, 2H), 3.86 (d, 4H, CH_2), 3.90 (s, 3H, OCH_3), 6.64 (s, 1H), 7.16 (s, 2H); IR (KBr, cm^{-1}): 1697, 1661, 1593, 1426, 1305, 1347, 1343.

*2.2.1.2. Synthesis of 3, 5-bis(2′-ethylhexyloxy)benzyl-3,4-diaminobenzoate (**3b**).* In a 250-mL round flask, methyl 3,5-bis(2-ethylhexyloxy)benzoate (10 g) was dissolved in 90 ml THF. $LiAlH_4$ (caution: incompatible with heat, water, alcohols, acids, transition metal salts, oxidizing agents, and a wide variety of other substances; violently reacts with oxidants; corrosive, toxic; hazardous decomposition products: 0.59 g, 15 mmol) was added slowly and the mixture was stirred at room temperature for 40 min. The reaction was quenched with water and then extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated to give 3,5-bis(2-ethylhexyloxy)benzyl alcohol (**1**) with 74% yield.

A solution of 3,5-bis(2-ethylhexyloxy)benzyl alcohol (**1**) (7.28 g, crude) in dried THF (40 ml) was added to 3,5-diaminobenzoic acid (2.97 g, 19 mmol), and triphenylphosphine (caution: incompatible with oxidizing agents and acids; 4.98 g, 19 mmol) in DMF (20 ml) under N_2. The mixture was stirred for 10 min and diethyl azodicarboxylate (DEAD) (caution: can explode if heated under confinement; shock sensitive; decomposes vigorously >100 °C; incompatible with strong acids, strong bases, strong oxidizing agents, strong reducing agents; light sensitive; 3.3 ml, 19 mmol) was added dropwise at -15 °C. The resulting mixture was stirred at room temperature for 36 h. The reaction mixture was diluted with ethyl acetate and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and the mixture was purified by column chromatography on silica gel with ethyl acetate/hexane (1/4) as an eluent to yield 7.72 g (78%).

^{1}H NMR ($CDCl_3$, 300 MHz): $\delta_{ppm} = 0.88–0.92$ (t, 12H, CH_3), 1.36–1.47 (m, 16H, CH_2), 1.53–1.71 (m, 2H), 3.80–3.82 (d, 4H, OCH_2), 4.27 (s, 2H, OCH_2), 6.40 (s, 1H), 6.55 (s, 2H), 6.70–6.73 (d, $J = 9$ Hz, 1H), 7.52 (s,1H), 7.58–7.61 (d, $J = 9$ Hz, 1H).

*2.2.1.3. 2‘-Nonyloctadecyl -3,4-diaminobenzoate (**3a**) (52%).* ^{1}H NMR (DMSO-d_6, 300 MHz): $\delta_{ppm} = 0.79$ (t, 6H, CH_3), 0.94–1.78 (m, 48H), 1.99 (m, 1H, CH), 4.3 (d, 2H, OCH_2), 4.6 (br, 2H, NH_2), 5.2 (br, 2H, NH_2), 6.46 (d, $J = 8.1$ Hz, 2H), 7.03 (d, $J = 8.1$ Hz, 2H), 7.10 (s, 1H).

*2.2.2. Synthesis of asymmetric anhydride-imide derivative of perylene, N-(1- nonyldecyl)perylene-3,4,9,10-tetracarboxyl-3, 4-anhydride-9,10-imide (**5**)*

Symmetric diimide (**4**, **PDI**) was prepared through a known synthetic process [10]. Perylene-3,4,9,10-tetracarboxyldianhydride (1.44 g, 3.7 mmol), and 10-nonyldecyl amine (2.667 g, 9.4 mmol) with imidazole (caution: incompatible with acids, strong oxidizing agents; protect from moisture; 6 g) were heated under N_2 at 180 °C for 3 h. The reaction mixture was cooled, dispersed in 100 mL ethanol, and then treated with 2 M HCl (300 mL) overnight. The resulting red solid was filtered and washed with distilled water. The solid was dried in vacuum at 100 °C to give N,N′-bis(10-nonyldecyl)perylene-3,4,9,10-tetracarboxyl bisimide (**4**)

In a 250-mL round flask, **PDI** (3.66 g, 5.24 mmol) was suspended in *t*-BuOH (97 mL) and treated with solid KOH (85%, 982 mg, 17.5 mmol). The reaction mixture was heated with vigorous stirring to reflux until the solution turned dark purple for ca. 30 min. The mixture was cooled to room temperature, treated with acetic acid (80 mL) and 2N HCl (40 mL), and stirred overnight. The dark red precipitate was filtered, washed with distilled water, and dried at 130 °C. This solid was suspended in 10% K_2CO_3 solution (150 mL) and heated to reflux for 30 min. The mixture was cooled and filtered. The filtered cake was rinsed with warm 10% K_2CO_3 until the filtrate was clear, rinsed twice with 2 N HCl (100 mL), and dried at 130 °C. The solid was then suspended in boiling water (100 mL) and triethylamine was added until the solution presented a dark purple color. The insoluble solid was filtered out and dark purple filtrate was acidified with 2N HCl overnight. The resulting dark red precipitate was filtered, rinsed with water, and dried at 130 °C. The resultant solid was further purified through the same process above with water and triethylamine to yield 1.14 g (40%) of red solid (**5**).

^{1}H NMR (**4**, $CDCl_3$, 300 MHz): $\delta_{ppm} = 0.83$ (t, 12H, CH_3), 1.25 (m, 56H, CH_2), 1.86 (m, 4H, CH_2), 2.24 (m, 4H), 5.18 (m, 2H), 8.67 (m, 8H).

^{1}H NMR (**5**, $CDCl_3$, 300 MHz): $\delta_{ppm} = 0.73$ (t, 6H, CH_3), 1.11–1.81 (m, 28H), 1.98 (m, 2H), 2.31 (m, 2H), 5.12 (br, 1H, CHN), 8.61 (br, 8H).

*2.2.3. Synthesis of asymmetric imide-imidazole derivatives of perylene (**6**)*

General procedure: In a 50-mL round flask, the anhydride-imide (**5**) (1.32 g, 2.0 mmol), methoxy-1,2-phenylenediamine dihydrochloride (1.12 g, 4.8 mmol), and imidazole (15 g) were heated under N_2 at 180 °C for 12 h. The cooled mixture was diluted with ethanol