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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-with-drawing 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 bisimidazole displayed the transient, electronic and optical properties of symmetric bisimide and symmetric 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.

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PIGMENTS

1. Introduction

Pervlene 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

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stability as well as electron transfer through π - π stacking [8]; many perylene derivatives have been described [5,9–13].

A key issue for pervlenes 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 pervlene constituent imparted longer wavelength absorption, it worsened solubility. However, it is considered that modification of such structures via pervlene 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).

¹H NMR spectra were recorded in CDCl₃ 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 (Bu₄NBF₄) in anhydrous acetonitrile and tetrabutylammonium hexafluorophosphate (Bu₄NBF₆) in dichloromethane. A platinum wire was used as the counter electrode and an Ag/AgNO₃ 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 K₂CO₃ (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 MgSO₄ and filtered. The solvent was removed by rotary evaporation and the mixture was purified (95%) by column chromatography on silica gel.

¹H NMR (CDCl₃, 300 MHz): $\delta_{ppm} = 0.88-0.92$ (t, 12H, CH₃), 1.36– 1.47 (m, 16H, CH₂), 1.53–1.71 (m, 2H), 3.86 (d, 4H, CH₂), 3.90 (s, 3H, OCH₃), 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. LiAlH₄ (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 MgSO₄, 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 N₂. 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 MgSO₄ 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%).

¹H NMR (CDCl₃, 300 MHz): $\delta_{ppm} = 0.88-0.92$ (t, 12H, CH₃), 1.36– 1.47 (m, 16H, CH₂), 1.53–1.71 (m, 2H), 3.80–3.82 (d, 4H, OCH₂), 4.27 (s, 2H, OCH₂), 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%). ¹H NMR (DMSO-d₆, 300 MHz): $\delta_{ppm} = 0.79$ (t, 6H, CH₃), 0.94–1.78 (m, 48H), 1.99 (m, 1H, CH), 4.3 (d, 2H, OCH₂), 4.6 (br, 2H, NH₂), 5.2 (br, 2H, NH₂), 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 N₂ 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% K₂CO₃ solution (150 mL) and heated to reflux for 30 min. The mixture was cooled and filtered. The filtered cake was rinsed with warm 10% K₂CO₃ 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).

¹H NMR (**4**, CDCl₃, 300 MHz): $\delta_{ppm} = 0.83$ (t, 12H, CH₃), 1.25 (m, 56H, CH₂), 1.86 (m, 4H, CH₂), 2.24 (m, 4H), 5.18 (m, 2H), 8.67 (m, 8H). ¹H NMR (**5** CDCl₂, 300 MHz): $\delta_{m} = 0.73$ (t, 6H, CH₂), 111–181

¹H NMR (**5**, CDCl₃, 300 MHz): $\delta_{ppm} = 0.73$ (t, 6H, CH₃), 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 N₂ at 180 °C for 12 h. The cooled mixture was diluted with ethanol (20 mL), yielding a suspend mixture. The suspension was filtered and washed with 5%-aqueous HCl (100 mL). The resulted mixture was filtered and dried (10 h/2 torr/80 °C) to afford PIZ2 (**6b**, 1.14 g, 75%). The product was further purified by silica gel-chromatography with chloroform as an eluent.

¹H NMR (**6b**, 1/1-isomer mixture, CDCl₃, 300 MHz): $\delta_{ppm} = 0.85$ (m; 6H, CH₃), 1.19–1.21 (m; 28H), 1.98–2.00 (m; 2H), 2.21–2.33 (m; 2H), 3.78 (s, 1.5H, OCH₃), 3.79 (s, 1.5H, OCH₃), 5.20 (m, 1H, NCH), 6.65 (d, J = 9 Hz, 0.5H), 6.74 (d, J = 9 Hz, 0.5H), 6.94 (s, 0.5H), 7.37 (d, J = 9 Hz, 0.5H), 7.43 (s, 0.5H), 7.81 (d, J = 9 Hz, 0.5H), 8.41–8.62 (m, 8H); UV-Vis_{max} = 564 nm (CDCl₃), 504 nm (film); IR (KBr, cm⁻¹): 1697, 1654, 1592. MALDI-TOF MS: Calcd. for C₅₀H₅₃N₃O₄: 759.98, Found: m/z = 759.20 [M⁺].

6a (82% yield) MALDI-TOF MS: Calcd. for $C_{49}H_{51}N_3O_3$: 729.39, Found: $m/z = 729.27 \text{ [M}^+\text{]}$

6c (70% yield). MALDI-TOF MS: Calcd. for $C_{49}H_{50}N_4O_5$: 774.38, Found: $m/z = 774.34 \text{ [M^+]}$

6d (69% yield). MALDI-TOF MS: Calcd. for $C_{73}H_{89}N_3O_7$:1119.67, Found: m/z = 1119.65 [M⁺].

2.2.4. Synthesis of symmetric imidazole derivative of perylene (7)

Perylene-3,4,9,10-tetracarboxyldianhydride (0.57 g, 1.45 mmol), and 2-decyloctadecyl 3,4-diaminobenzoate (1.74 g, 3.19 mmol) in imidazole (4 g) were heated under N₂ at 180 °C for 12 h. The reaction mixture was cooled to room temperature, dispersed into ethanol (100 mL), and mixed with 2 M HCl (300 mL) overnight. The resulting solid was filtered and washed with distilled water. The solid was dried in a vacuum at 100 °C to give 1.23 g (60%).

¹H NMR (CDCl₃, 300 MHz): $\delta_{ppm} = 0.83$ (t, 12H), 1.04–1.72 (m, 84H), 2.07 (m, 2H,-CH), 6.88–7.02 (m, 6H), 7.09 (s, 2H), 7.18–7.24 (d, 2H), 7.29–7.32 (m, 4H); IR (KBr, cm⁻¹): 1709, 1694, 1594, 1282, 1240. MALDI-TOF MASS: Calcd. For C₉₄H₁₂₈N₄O₆: 1408.98, Found: *m*/*z* = 1408.97 [M⁺].



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С

Fig. 1. Preparation of 3,4-diaminophenyl esters (a) and asymmetric (b) and symmetric perylene derivatives (c).

3. Results and discussion

Substituents in the bay area of perylene bisimides (1,6,7,12positions) have been demonstrated to enhance solvent solubility, mainly due to a twisted phenyl system with a torsion angle depending on the substituent size [9]. Electron enrichment on the π -system of the pervlene induced a red shift of the absorption wavelength but loss of the flatness for fused rings may have affected the electron mobility in solid film applications. The bay substituent occasionally showed thermal instability by decomposing below 150 °C [10]. The high-energy band gap (2.50 eV) of perylene [18] was reduced by 2.13 eV with perylene bisimide derivation as a *n*-type semiconductor. The high LUMO level of 3.69 eV of the diimide was adequate to increase the driven voltage in a solar cell using polythiophene [6]. The band gap was further reduced by an imidazole derivative with 1.7 eV [10]. Two phenyl imidazole groups extended the conjugation length of perylene structure but the decrement of the LUMO level to 4.4 eV resulted in the disadvantage of reducing the driven voltage. Because the voltage is determined from the energy difference of LUMO level of an *n*-type material and HOMO level of a *p*-type material, it is desired that the LUMO level of the perylene derivatives is just below that of polythiophene. Furthermore, the imidazole derivation of pervlene degraded the solubility so that the thin film processing was achieved through thermal evaporation. Thus, an asymmetric derivation of perylene was considered with both imide and imidazole functionalities. The phenyl attached, asymmetric, imide-imidazole derivative was previously reported for photovoltaic applications [10]. It was soluble due to the alkyl-C19 attached on N-imide and evidently revealed a red-shifted absorption compared to a perylene bisimide. We tried to change the electronic polarity of the asymmetric derivative for further red-shifted absorption. A convenient way of introducing a substituent on the imidazole ring was employed. The synthesis began with bisimide (4) and partially hydrolyzed anhydride-imide (5) was condensed with 1,2-phenylenediamine to afford the asymmetric imide-imidazole (6a), as reported previously [10]. The continuous synthesis is outlined in Fig. 1.

A methoxy group to enrich the electrons and a nitro group to induce an electron deficiency on the imidazole were employed for **6b** and **6c**, respectively. A hyperbranched alkyl was adapted to attain a level of solvent solubility comparable to that of the bisimide **(4)**. 3,5-Ethylhexyloxybenzyl alcohol **(1)** was esterified with 3,5-diaminobenzoic acid under the Mitsunobu coupling condition [19] to provide **6d**. A symmetric imidazole derivative with **3b** was synthesized under refluxing imidazole solvent but it exhibited



Fig. 3. Emission spectra of perylene derivatives in chloroform irradiated at a wavelength of the parentheses.

insufficient solubility during solution analysis. Thus, an exceedingly long alkyl chain was designed. A primary alcohol from the aldol condensation of decanal and ethyl stearate was coupled with 3,4-daminobenzoic acid to afford 3,4-diaminobenzoate 3a. Thermal condensation of 3,4,9,10-perylenetetracarboxylic dianhydride and two equimolar amount of 3a generated a symmetric perylene imidazole 7, exhibiting a moderate solubility of ca. 30 mg/mL in chloroform. A potential isomerism during the preparation of perylene derivatives in Fig. 1 was expected and was observed on the ¹H NMR spectrum. The equal formation of two isomers of 6b was defined with an integral ratio (1/1) of two singlet peaks (3.78 and 3.79 ppm) assigned to an unlikely placed methoxy group on the imidazole phenyl. Six isomers are potentially possible for 7 due to the ester positions as well as *cis* and *trans*-bisimidazole. However, the chromatographic isolation of each isomer was unsuccessful due to their similar polarities and the ¹H NMR spectrum of isomeric mixture 7 showed a complicated pattern. Infrared absorption bands of imide carbonyls around 1694 cm⁻¹ and mass analysis substantially proved the formation of 7.

The prepared soluble perylene derivatives were optically analyzed and the absorption spectra were presented in Fig. 2. The maximum peak of the symmetric imidazole (**PDZ**) appeared at the longest wavelength among the derivatives as expected. The asymmetric imide-imidazole derivatives (**PIZ**s) were apparently placed between a symmetric imide (PDI) and an imidazole



Fig. 2. UV-vis absorption spectra of perylene derivatives in chloroform.



Fig. 4. Comparison of UV-vis absorption spectra of a thin film and chloroform solution.

Perylene derivatives	UV-vis absorption, CHCl ₃		Emission		Energy level, eV		Eg ^f ,eV
	λ _{max} , nm	$\epsilon^* 10^3$, molar absorptivity	λ_{peak} , nm CHCl ₃ ^a	$\Phi_{\rm PL}(\%)^{\rm c}$	HOMO ^d	LUMO ^e	
PDI	525 (489) ^b	58.0 (36.5) ^b	553, 574	77	5.82	3.69	2.13
PIZ1	574 (534)	31.5 (28.4)	597, 638	28	5.72	3.72	2.00
PIZ2	565	24.0	652	2	5.60	3.65	1.95
PIZ3	528 (550)	23.5 (22.0)	572, 621	25	5.54	3.77	1.77
PIZ4	524 (562)	30.0 (17.4)	584, 628	36	5.65	3.75	1.90
PDZ	602 (560)	27.0 (24.3)	658	40	5.80	3.86	1.94

 Table 1

 Summarized optical and electrical properties of the prepared perylene derivatives.

All UV–vis and emission spectra were measured with 1.0*10⁻⁵ mol/L-chloroform solution.

^a Irradiated at 525, 534, 490, 528, 524, 602 nm for PDI, PIZ1, PIZ2, PIZ3, PIZ4, PDZ respectively.

⁹ Second highest peak.

^c The PL quantum yields in chloroform solution were determined against 9,10-diphenylanthracene in ethanol as a standard ($\Phi_{PL} = 91\%$) [21].

^d Calculated using an optical band gap and LUMO level.

^e The energy levels were determined with CV analysis in the 0.1 M Bu₄NBF₄/CHCl₃ (Supplementary Data).

^f Optical band gap was determined from the edge of absorption tail in chloroform solution.

derivative (**PDZ**) in the comparison of the maximum wavelengths. The introduction of polar substituents on the asymmetric derivatives caused spectral shifts. The electronic contribution was observed with a distinct emission band as shown in Fig. 3. When the derivatives were excited with their maximum absorption wavelengths, electron-withdrawing group derivatives (**PIZ3** and **PIZ4**) presented shorter emissive wavelengths than **PIZ1** while the methoxy derivative (**PIZ2**) presented longer wavelengths. **PIZ3** exhibited a peculiar broad absorption tailed up to 745 nm. Many perylene derivatives have been demonstrated to aggregate in solid films where head-to-tail interaction and face-to-face packing induced bathochromic and hypsochromic shifts, respectively [9].

Fig. 4 compares the absorption spectra of a solution and a solid film of selected derivatives. The hypsochromic shift of the PIZ2 film was conspicuous while the electron-withdrawn derivative (PIZ3) exhibited a bathochromic shift. Electronic supplementation tends to induce a favorable intermolecular π -interaction of the perylenes. The spans of these spectra were increased in the solid film, suggesting the action of various interactions including face-to-face and long alkyl-tails aggregation. Self-assembled perylene structures in the solid film were promising for electronic applications accompanying charge conduction such as OTFT, organic light emitting diodes, and solar cells [20]. The adjustment of the energy levels of constituent organics is required for charge injection or collection across metallic electrodes or heterojunction surface. The frontier orbital energies were determined from a cyclic voltammetric analysis of perylene derivative solutions and the results are summarized in Table 1. The LUMO levels of the imidazole derivatives were comparatively stabilized over bisimide (PDI). The attachment of a nitro group on an asymmetric imidazole decreased the LUMO level by 0.05 eV. The methoxy-donating group of PIZ2 increased the LUMO level over the unsubstituted derivative (PIZ1). The addition of substituents is a convenient strategy to adjust the energy levels of perylene imidazole derivatives.

4. Conclusion

Symmetric and asymmetric perylene derivatives were synthesized to enhance their solubility and regulate the energy bands by modifying the imidazole rings. The solvent solubility of the previous imidazole derivative was enhanced with extremely a long alkyl chain or a hyperbranched alkyl. Soluble asymmetric imideimidazole derivatives were investigated optically and electronically. The electronic derivation on the imidazole ring of these derivatives resulted in the regular alteration of the frontier energy levels and light absorption pattern. The asymmetric imideimidazoles exhibited a transient absorption feature of symmetric bisimide and symmetric bisimidazole spectra. The electron-withdrawing and -donating groups decreased and increased the LUMO levels of the asymmetric perylene derivatives, respectively. These asymmetric derivations contributed to the widening absorption span of the solid films along with the elaborate adjustment of the perylene energy levels. The absorptive spectral shifts occurred with the solid films of the asymmetric perylene derivatives where methoxy and nitro groups induced opposite shifts.

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Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.dyepig.2009.10.001.

References

- Qu J, Zhang J, Grimsdale AC, Müllen K, Jaiser F, Yang X, et al. Dendronized perylene diimide emitters: synthesis, luminescence, and electron and energy transfer studies. Macromolecules 2004;37:8297–306.
- [2] Liu SG, Sui G, Cormier RA, Leblanc RM, Gregg BA. Self-organizing liquid crystal perylene diimide thin films: spectroscopy, crystallinity, and molecular orientation. The Journal of Physical Chemistry B 2002;106:1307–15.
- [3] Mallik AB, Locklin J, Mannsfeld SCB, Reese C, Roberts ME, Senatore ML, et al. In: Bao Z, Locklin J, editors. Organic field-effect transistors. CRC Press; 2007. p. 159–252.
- [4] Kampen TU. Electronic structure of organic interfaces-a case study on perylene derivatives. Applied Physics A-Materials Science & Processing 2006;82:457-70.
- [5] Wanga M, Wang X. P3HT/ZnO bulk-heterojunction solar cell sensitized by a perylene derivative. Solar Energy Materials and Solar Cells 2008;92:766–71.
- [6] Kim JY, Lee K, Coates NE, Moses D, Nguyen TQ, Dante M, et al. Efficient tandem polymer solar cells fabricated by all-solution processing. Science 2007;317:222-5.
- [7] Brabec CJ, Cravino A, Meissner D, Sariciftci NS, Fromherz T, Rispens MT, et al. Origin of the open circuit voltage of plastic solar cells. Advanced Functional Materials 2001;11:374–80.
- [8] Weitz RT, Amsharov K, Zschieschang U, Villas EB, Goswami DK, Burghard M, et al. Organic n-channel transistors based on core-cyanated perylene carboxylic diimide derivatives. Journal of The American Chemical Society 2008;130:4637–45.
- [9] Würthner F. Perylene bisimide dyes as versatile building blocks for functional supramolecular architectures. Chemical Communications 2004:1564–79.
- [10] Shin WS, Jeong HH, Kim MK, Jin SH, Kim MR, Lee JK, et al. Effects of functional groups at perylene diimide derivatives on organic photovoltaic device application. Journal of Materials Chemistry 2006;16:384–90.
- [11] Dimitrakopoulos CD, Malenfant PRL. Organic thin film transistors for large area electronics. Advanced Materials 2002;14:99–117.

- [12] Fan L, Xu Y, Tian H. 1,6-Disubstituted perylene bisimides: concise synthesis and characterization as near-infrared fluorescent dyes. Tetrahedron Letters 2005;46:4443–7.
- [13] Pan J, Zhu W, Li S, Xu J, Tian H. Synthesis of carrier-transporting dendrimers with perylenebis(dicarboximide)s as a luminescent core. European Journal of Organic Chemistry 2006:986–1001.
- [14] Langhals H, Demmig S, Potrawa T. The relation between packing effects and solid state fluorescence of dyes. Journal fur Praktische Chemie 1991;333:733-48.
- [15] Zhao Y, Wasielewski MR. 3,4,9,10-Perylenebis(dicarboximide) chromophores that function as both electron donors and acceptors. Tetrahedron Letters 1999;40:7047–51.
- [16] Jones BA, Ahrens MJ, Yoon MH, Facchetti A, Marks TJ, Wasielewski MR. Angewandte Chemie International Edition 2004;43:6363–6.
- [17] Vázquez1 H, Gao W, Flores F, Kahn A. Energy level alignment at organic heterojunctions: role of the charge neutrality level. Physical Review B 2005;71:041306.
- [18] Kang SJ, Yi Y, Cho K, Jeong K, Yoo KH, Whang CN. Electronic structure of perylene on Au studied by ultraviolet photoelectron spectroscopy and density functional theory. Synthetic Metals 2005;151:120–3.
- [19] Do JY, Ju JJ. Polyester dendrimers carrying NLO chromophores: synthesis and optical characterization. Macromolecular Chemistry and Physics 2005;206: 1326–31.
- [20] Klauk H, editor. Organic electronics: materials, manufacturing and applications. Wiley-VCH; 2006.
- [21] Joshi HS, Jamshidi R, Tor Y. Conjugated 1,10-phenanthrolines as tunable fluorophores. Angewandte Chemie International Edition 1999;38:2722-5.