Soluble Asymmetric Perylene Derivatives for Organic Solar Cells

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Summary: Organic acceptor material has been developed based on soluble perylene derivative for an organic solar cell. Asymmetric perylene derivatives with an imide and an imidazole group produce absorption spectra close to poly(3-hexylthiophene) (P3HT) as a donor material. The frontier energy levels of the perylene derivatives can adjust to reasonable charge transmission within a blended polymer layer through the introduction of substituents such as alkoxy, nitro and alkoxycarbonyl group. The nitro group unlike the others leads to the exceeding decrement of the frontier energy levels, which would be unfavorable for efficient charge transfer. Cyclic voltammetry analysis is performed to determine the energy levels of the perylene derivatives.

Keywords: asymmetric perylene derivative; band gap; organic solar cell; perylene imidazole; perylene imide

Introduction

Organic materials for the solar cell based on conducting polymers are attractive because most of them can be easily processed from solution via spin-coating, enabling the manufacture of large area, flexible and light-weight devices.[1]

We have studied organic based solar cells with polymer blends made of P3HT and perylene derivative as an electron donor and acceptor, respectively, for efficient charge generation. The mechanisms governing the operation of organic solar cell have been adequately described at quantum chemical energy levels.[2] The excitons generated by absorbing the incident light need to migrate toward donor-acceptor interface for the charge separation to be converted into electric charges. The donor-acceptor blend serves a wide contact area and is considered as a reasonable material structure for the organic solar cell.[2] But inhomogeneous blend by poor solvent solubility or incompatibility of the donor and acceptor often increases the surface roughness of a thin film, which hinders the interfacial charge conduction and makes the device useless. In the research, we aimed at developing new acceptor derivatives compatible with a polymer. Many researches have demonstrated useful polymer blends using conducting polymers such as polyacetylene, poly(*p*-phenylene vinylene), polyfluorene, polythiophene and their derivatives with a low band gap.[3–6] The polymers were mixed with small organic molecules for the efficient photo charge generation. Phthalocyanine, fullerene and its derivatives have been widely utilized.[7,8] The perylene derivatives deposited on the polymer layer improved a device performance through the generation of a highly conducting direction along the π-π stacking axis,[9,10] The perylenes were structurally derived for the better polymer blend enabling the solution process.[11,12] The frontier energy levels of donor and acceptor are widely accepted to describe exciton dissociation for the operation of

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organic solar cells.[13] The successive charge transfers require balanced energy levels of the lowest unoccupied molecular orbitals (LUMO) and the highest occupied molecular orbitals (HOMO) of donor and acceptor. Asymmetric perylene derivatives will be developed under the consideration of these orbital energy levels.

Experimental Part

Synthesis of Asymmetric Perylene Imidazole Derivatives (PIZs)

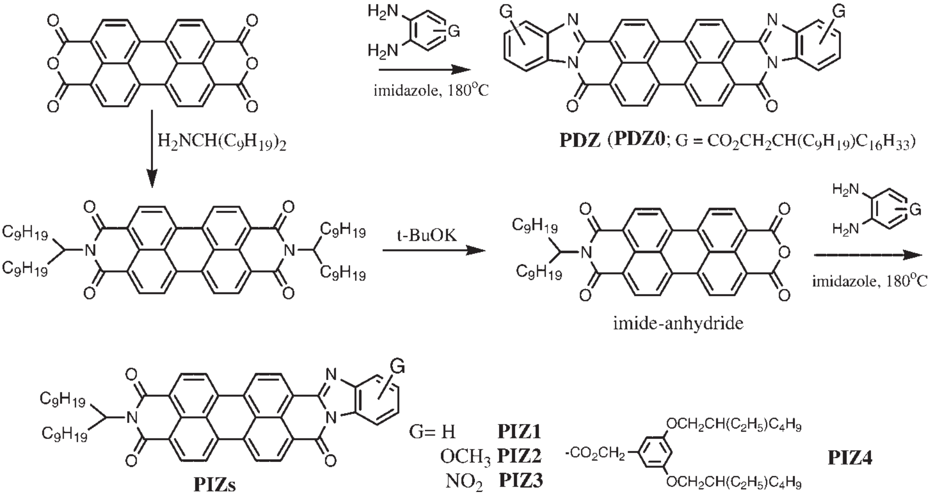
PIZs were synthesized through the condensation reaction of 1,2-diaminophenyls and an intermediate (imide-anhydride) derived from 3,4,9,10-perylene carboxylic dianhydride.

Typical Procedure

Intermediate (imide-anhydride) was prepared by base-mediated hydrolysis of perylene diimide according to the literature.[12] The imide-anhydride (1.32 g, 2.0 mmol) and 1,2-diamino-4-nitrobezene dihydrochloride (1.12 g, 4.8 mmol) were placed at a 50 ml-round bottom flask equipped with a reflux condenser containing imidazole (15 g) as a solvent. The mixture was heated for 12 hrs at 180 °C and cooled to dilute with ethanol (20 mL), yielding a suspended mixture. The suspension was filtered and washed with 5%-aqueous HCl (100 mL). The resulted mixture was filtered and dried (10 hrs/2 torr/80 °C) to yield **PIZ2**($G = OCH_3$) (1.14 g, 75%). The product was further purified by a silicagel-chromatography with a chloroform eluant. 1H-NMR (ppm, $CDCl_3$) a 1/1-isomer mixture: 0.85 (m; 6H, CH_3), 1.19–1.21 (m; 28H), 1.98–2.00 (m; 2H), 2.21–2.33 (m; 2H), 3.78 (s, 1.5H, OCH_3), 3.79 (s, 1.5H, OCH_3), 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$_{max} = 563$, 505 nm ($CHCl_3$), 504 nm (film); IR (KBr, cm^{-1}): 1697, 1659, 1592.

Results and Discussion

Perylene diimides were variously modified for adjusting electronic energy levels and for the fabrication process of the organic solar cell. A few substituents at the perylene diimide often cause their thermal decomposition or obstructing π-π channel formation from planar perylene structure. It has been demonstrated that imidazole functionality on a perylene derivative is thermally stable and tends to shift absorption spectrum to the longer wavelength comparative to perylene diimide.[12] But, the imidazole group on perylene structure brings severe solubility problem, which degrades the film morphology of the blended polymer layer. Most symmetric imidazole derivatives **PDZ**s except **PDZ0** were completely insoluble in most of organic solvents (such as tetrahydrofuran, chloroform, chlorobenzene and N-methylpyrrolidinone) while the solubility was improved with new asymmetric imides (**PIZ**s) to some extent. Accordingly, we designed asymmetric derivatives with an imidazole and an imide at each end of a perylene structure. As described in Scheme 1, symmetric perylenes were prepared through thermal condensation with alkylamine and 1,2-diaminophenyl to yield diimide (**PDI**) and diimidazole (**PDZ**) derivative, respectively. For the asymmetric derivatives (**PIZ**s), the symmetric perylene diimide was partially hydrolyzed with potassium *tert*-butoxide and dehydrated to afford an imide-anhydride. It was finally condensed with several 1,2-diaminophenyls in more than 75% yield. All of the asymmetric derivatives were soluble in chloroform and structurally identified with nmr-analysis and confirmed with mass spectroscopy. The introduction of a hyper-branching alkyl group at the symmetric perylene diimidazole did not improve the solvent solubility. But, exceedingly long alkyl substitution led to increasing its solubility enough to analyze the optical property of the symmetric perylene diimidazole. UV-Vis absorption experiment was performed to observe spectral shifts according



Scheme 1.
Synthetic procedure of perylene diimide, diimidazole and imide-imidazoles.

to the substituents at the perylene derivative.

Asymmetric imide-imidazole derivative (**PIZ2**) showed apparent red-shifted spectrum compared to the diimide (**PDI**) as drawn in Figure 1(a). A benzimidazole group expands π-conjugation for the low electron transition energy, which is evidently understood with symmetric diimidazole derivative (**PDZ0**) viewing the longest maximum absorption wavelength ($\lambda_{max} = 601$ nm). The spectral ranges of **PDZ** and **PIZ**s closely match with that of donor polymer (P3HT) with a low band gap and broad absorption wavelengths while **PDI** do not overlap with P3HT at wavelengths longer than 550 nm. It is desirable that the spectral overlap between donor and acceptor material occurs at whole solar spectrum for the efficient performance of a solar cell. The symmetric and asymmetric perylene imidszoles are thus perceived as a better acceptor than **PDI**. Most of the substituents at imidazole group of the asymmetric perylenes (**PIZ**s) merely altered the spectrum shape without a noticeable spectral shift except ester substituent (**PZI4**). Cyclic voltammetry (CV) analysis was performed to determine the HOMO and LUMO energy levels of the perylene derivatives. The film samples of perylene derivatives were prepared on ITO-glass and observed redox data were standardized with a ferrocene-ferricenium couple. Each reduction potential of the samples was obviously observed for the LUMO but the oxidation potential for the HOMO failed to determine from CV-curve. The HOMO levels were estimated by the optical band gap determined by the absorption edge of each material spectrum. The resultant energy levels of the perylene derivatives are summarized in Figure 2 with a hypothesized relative energy diagram. From the proposed device structure, the blend layer composed of P3HT and perylene derivatives has place between two electrodes. When electrons generated by the donor absorption migrate from the LUMO of the donor to the Al-electrode through LUMO of the acceptor, cascading energy levels with a low energy barrier among materials are desirable for efficient electron transfer. All derivatives except **PIZ3** have LUMO levels between the LUMO of P3HT and the work function of Al-electrode (4.3eV). The nitro substituent strongly decreases the LUMO level of **PIZ3** which is considered as an inappropriate electron transfer material or poor acceptor for this device structure. The energy level reduction by a nitro electron-withdrawing group is relieved with

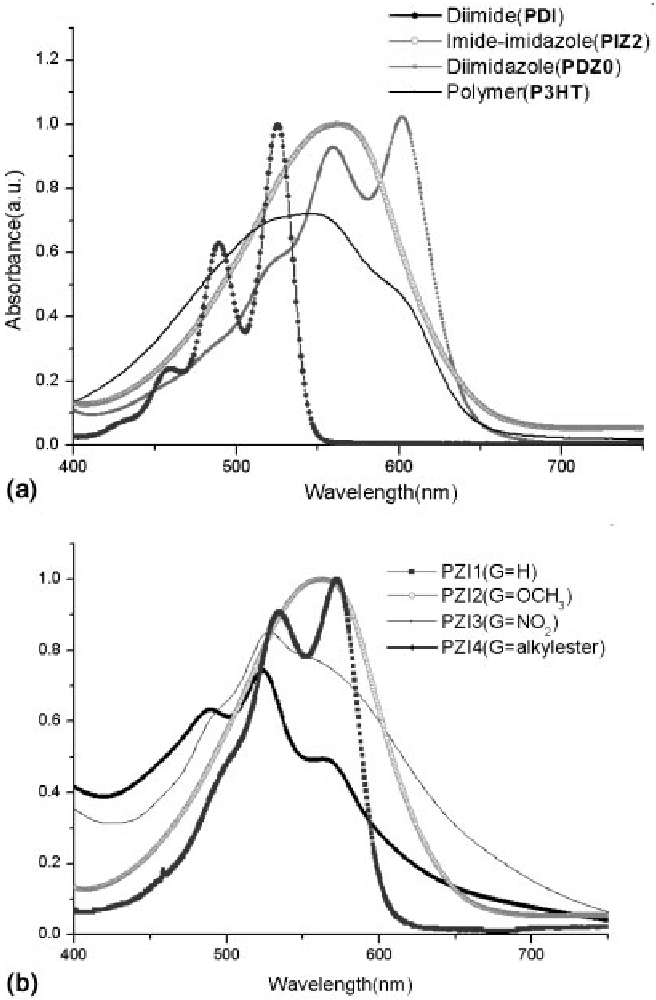


Figure 1.
UV-Vis absorption of perylene diimide, imide-imidazole and diimidazole derivatives in chloroform solution.

an ester group. Two ester groups of **PDZ0** lead to 0.07 eV reduction based on the LUMO level of unsubstituted imidazole derivative (**PIZ1**). Electron donating methoxy group slightly elevates the LUMO and HOMO levels. Similarly, efficient hole-transmission from an excited perylene to the ITO electrode through a carrier material requires lower HOMO level of the perylene derivative than the HOMO of P3HT. Low energy barriers between P3HT and perylenes such as **PIZ1**, **PIZ2** and **PDZ0** would promote the hole-transmission compared to **PDI** or **PIZ3**.

Conclusion

Several perylene imide and imidazole derivatives were developed for the acceptor material of the organic solar cell. Most of the prepared asymmetric imidazoles and symmetric perylene imidazole with a long alkyl chain exhibited solvent solubility desirable for the polymer blending or film casting. The derivatives were optically observed with broad absorption bands and red-shifted spectra enough nearly to overlap with the absorption spectrum of the donor polymer (P3HT). The

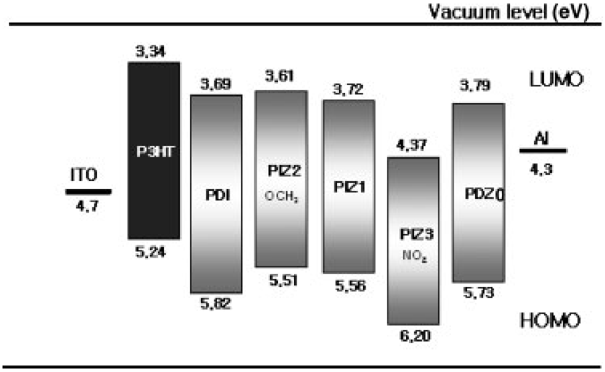


Figure 2.
Hypothesized energy diagram of simple device (ITO/P3HT:perylenes/Al).

electron-donating and electron-withdrawing substituents at the asymmetric perylene imidazole altered the HOMO and LUMO energy levels of corresponding perylene derivatives. Nitro group was inappropriate for efficient charge transfer due to unfavorable energy barrier in P3HT blending. Methoxy group and ester group led to increasing and decreasing, respectively, the HOMO and LUMO levels of the perylene derivative. The solar cell performance of the prepared materials is under study.

Acknowledgements: This research was supported by the MIC (Ministry of Information and Communication), Korea, under the ITRC (Information Technology Research Center) support program supervised by the IITA (Institute of Information Technology Assessment).

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