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Synthesis and Optical Properties of *n*-Type Polymers Containing Perylene Moieties

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Three n-*type polymers,* **Ppe01, Ppe02***,* and **Ppe03***, containing both perylene moieties and fluorine atoms were synthesized. The synthesiszed polymeric perylene derivatives with good compatibility for solution processes were chosen as new acceptor candidates for substitution of* C_{60} *derivatives in poly(3-hexylthiophene)-based organic photovoltaic application, by considering the results based on good thermal stability, high electron affinity ranging from 3.81 to 3.96 eV, absorption property in visible region, and effective photoluminescence quenching in the blend films with P3HT. The potential of the synthesized perylene polymers was investigated by measuring the current-voltage property of the polymeric P3HT:* **Ppe01** *OPV device.*

Keywords Electron acceptor; organic photovoltaic; P3HT; perylene; PL quenching

Introduction

The development of organic photovoltaic devices (OPVs) has attracted considerable attention in recent years due to the demand for making flexible large area devices with low cost, easy process, and lightweight [1,2]. A well studied system is bulk heterojunction (BHJ)-type OPVs, where the conjugated polymer is often used as the electron donor and the fullerene (C_{60}) derivative is used as the electron acceptor. One of the BHJ OPVs consisting of poly(3-hexylthiophene):[6,6]-phenyl-C_{61}-butyric acid methyl ester (P3HT:PC_{61}BM) as a donor:acceptor pair showed the power conversion efficiency (PCE) of 4 ~ 5% [3,4]. However, it is especially attractive for

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further improving the PCE to replace the C_{60} derivatives with materials that allow light absorption in visible. Conjugated polymers, such as PCNEPV and MEH-CN-PPV, which include -CN and -F group to provide high electron affinity, have been used as electron acceptors [5,6]. Various inorganic electron acceptors, such as CdSe, ZnO, etc. have been also studied to improve the PCE of OPVs [7–9]. Unfortunately, the electron acceptors mentioned above have found to be inadequate for commercial use in OPVs. Therefore, it is still of great importance in developing new electron acceptors which can tune the electron affinity and electron mobility to improve both open circuit voltage (V_{oc}) and short circuit current (J_{sc}), thus resulting in higher PCE [10–12].

Perylene derivatives with low molecular weight have been studied as electron acceptors in bilayered OPVs fabricated by vapor deposition [13–15], since it has been known that they have high carrier mobility and easy control of the electron affinity through chemical modification with functional groups. In addition, various perylene derivatives are relatively easy to synthesize, and can be applied as electronic materials in various fields.

In this paper, polymeric perylene derivatives were chosen as new acceptor candidates for substitution of C_{60} derivatives, with good compatibility for solution processes. We synthesized three new perylene-based polymers as electron acceptors, and their optical properties and electronic band structures for application to all polymeric OPVs were investigated. We also demonstrate their potential usefulness with the current-voltage property of BHJ OPV fabricated with the blend film of P3HT and the synthesized perylene polymer.

Experimental

Materials

Thin layer chromatography (TLC) analyses were carried out on a pre-coated 0.2 mm HPTLC silica gel 60 plate (Merck, Darmstadt). Flash column chromatography was performed with silica gel (Merck silica gel 60, 70–230 mesh). Commerical grade solvents were used as received, and isoquinoline was distilled with calcium hydride under reduced pressure. 4,4′-Biphenyldiboronic acid, 4-*n*-butoxyphenol, 4,4′-diaminooctafluorobiphenyl and 2,2′-bis(trifluoromethyl)benzidine were purchased from TCI Chemical Co. All other reagents were purchased from Aldrich Chemical Co. and used without purification. The substrate glass with patterned indium-tin oxide (ITO, 20Ω/□) for OPV device was purchased from SUNIC Co. (Korea). 98% Regioregular P3HT[poly(3-hexyl thiophene)] was purchased from Rieke Metals. The weight-averaged molecular weight of P3HT was 6.4×10^4 g/mol. Poly-3,4-ethyleneoxythiophene:poly-4-sytrensulfonate (PEDOT:PSS, Baytron P VP Al 4083) used as buffer layer was received from P. H. Stark GmbH.

Synthesis of Perylene Monomers

The synthetic scheme of the perylene monomers, compound **5** and **6**, is illustrated in Figure 1.

N,N′-Bis-n-propyl-3,4,9,10-perylenetetra-carboxdiimide (1). Propylamine (11.53 mL, 15 eq) was added to a suspension of 3,4,9,10-perylenetetracarboxdiimide (5.0 g,

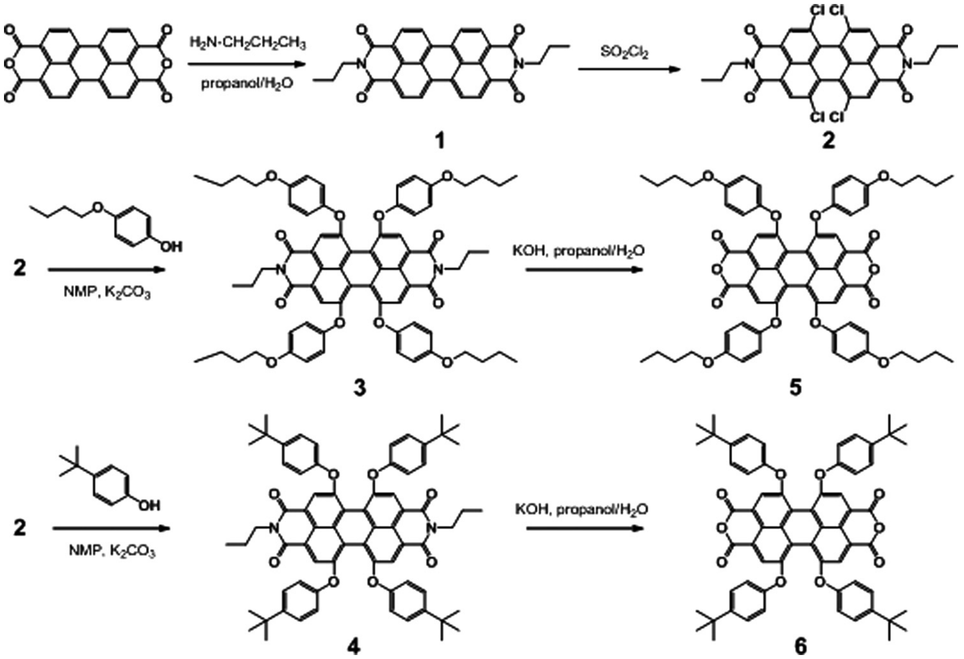

Figure 1. Synthetic route to perylene monomers, **5** and **6**.

12.74 mmol) in 300 mL of water/propanol (1:1). The mixture was stirred under argon at 65°C for 12 hr. After cooling to room temperature, the mixture was poured into 150 mL of a 2 M HCl aqueous solution under stirring. The red solid was washed with water and dried at 90°C, yielding 6.05 g of compound **1** as a red powder with a yield of 92%. This product was used without further purification for the synthesis of **2**.

N,N′-Bis-n-propyl-1,6,7,12-tetrachloroperylene-3,4,9,10- Tetracarboxdiimide (2). Compound **1** (5.0 g, 10.54 mmol), nitrobenzene (30 mL), iodine (800 mg, 3 eq), and iodobenzene (0.36 mL, 3 eq) were added to the round flask under nitrogen flow. And then, sulfuryl chloride (SO_2Cl_2, 5.28 mL, 6 eq) was added dropwise for 2 hr at 80°C while stirring. The reaction mixture was stirred under nitrogen at 80°C for 12 hr. Methanol (200 mL) was added, and then stirred for an additional 6 hr. The precipitate was filtered to obtain 5.16 g of **2** as an orange powder, with a yield of 80% [13]. Purification was performed via flash recrystallization from dichlorobenzene. R_f 0.32 (CH_2Cl_2); FAB-MS calcd for $C_{30}H_{18}Cl_4N_2O_4$: 610.00, found: m/z 611.11 $(M+H)^+$.

N,N′-Bis-n-propyl-1,6,7,12-tetrakis(4-n-Butyloxyphenoxy)perylene-3,4,9,10-tetra-Carboxdiimide (3). Compound **2** (5.0 g, 8.17 mmol), 4-*n*-butyloxyphenol (8.15 g, 6 eq), potassium carbonate (6.78 g, 6 eq), and *N*-methylpyrrolidinone (200 mL) were added to a round bottom flask charged with N_2, and the reaction mixture was stirred at 160°C for 6 hr. After cooling to room temperature, 2 M HCl solution (200 mL) was added dropwise with stirring to obtain a dark-red precipitate. The precipitate was filtered, washed with water and methanol, and then vacuum-dried.

The crude product was purified by flash column chromatography (SiO_2, CH_2Cl_2) to obtain 7.30 g of **3** as an orange powder with a yield of 79%. R_f 0.40 (EtOAc-hexane 1:9); FAB-MS calcd for $C_{70}H_{70}N_2O_{12}$: 1130.49, found: m/z 1129.08 $(M\text{-}H)^+$.

N,N′-Bis-n-propyl-1,6,7,12-tetrakis(4-tert-Butylphenoxy)perylene-3,4,9,10-tetra-Carboxdiimide (4). The synthetic route and work-up were similar to those of **3** except that *p*-tert-butylphenol (7.42 g, 49.02 mmol) instead of 4-*n*-butyloxyphenol was used. Compound **4** was obtained as a red powder with a yield of 86%. R_f 0.35 (EtOAc-hexane 1:9); FAB-MS calcd for $C_{70}H_{70}N_2O_8$: 1066.51, found: m/z 1066.18 $(M-H)^+$.

1,6,7,12-Tetrakis(4-n-butyloxyphenoxy)perylene-3,4,9,10-tetracarboxylic dianhydride (5). To a suspension of diimide **3** (5.0 g, 4.52 mmol) in 1 L of 2-propanol were added to 100 mL of water and 150 g of KOH. The vigorously stirred reaction mixture was refluxed under N_2 for 24 hr. During the reaction, the color changed from red to green. After cooling to room temperature, the reaction mixture was poured under stirring into 2.0 L of a 2 M HCl aqueous solution. A precipitate was washed with water, and then dried under vacuum. Recrystallization from CH_2Cl_2/MeOH afforded 3.71 g of **5** as a dark-red powder with a yield of 80%. R_f 0.25 (EtOAc-hexane 1:9); ^1H NMR ($CDCl_3$, 400 MHz) δ (*ppm*) 8.22 (s, 4H), 7.15 (d, $J = 8.5$ Hz, 8H), 7.05 (d, $J = 8.5$ Hz, 8H), 4.39 (t, $J = 7.5$ Hz, 8H), 1.78 (m, 8H), 1.55 (m, 8H), 0.99 (t, $J = 7.1$ Hz, 12H); FAB-MS calcd for $C_{64}H_{56}O_{14}$: 1048.37, found: m/z 1048.58 $(M)^+$.

1,6,7,12-Tetrakis(4-tert-butylphenoxy)perylene-3,4,9,10-tetracarboxylic dianhydride (6). The synthetic route and work-up were similar to those of **5**. The compound **6** was obtained as a red powder with a yield of 86%. R_f 0.20 (EtOAc-hexane 1:9); ^1H NMR ($CDCl_3$, 400 MHz) δ (*ppm*) 8.33 (s, 4H), 7.29 (d, $J = 8.2$ Hz, 8H), 6.99 (d, $J = 8.2$ Hz, 8H), 1.34 (s, 36H); FAB-MS calcd for $C_{64}H_{56}O_{10}$: 984.39, found: m/z 985.11 $(M+H)^+$.

Synthesis of Perylene Polymers. The synthetic scheme of the perylene polymers studied in this study is illustrated in Figure 2.

Synthesis of Ppe01. 1.0 g (0.95 mmol) of **5** and 464 mg (4 eq) of benzoic acid were added to 5 mL of *m*-cresol under N_2 atmosphere. The mixture was stirred at room temperature for 10 min. 2,2′-Bis(trifluoromethyl)benzidine (310 mg, 1 eq) was dissolved in 2 mL of *m*-cresol, and added to the above reaction mixture. The temperature was raised to 190°C. After stirring for 12 hr, 253 mg (2 eq) of isoquinoline dissolved in 2 mL of *m*-cresol were added, and the reaction time was extended to 48 hr. After cooling to room temperature, 5 mL of CH_2Cl_2 was added, and the resulting solution was poured dropwise into 500 mL of MeOH. The resulting precipitate was centrifuged, and redissolved in 5 mL of CH_2Cl_2, and then reprecipitated from MeOH. This procedure was repeated three times, and the final product was dried in vacuum at 90°C. The polymerized compound ***Ppe01*** was obtained in a yield of 88% as a red powder. ^1H NMR ($CDCl_3$, 400 MHz) δ (*ppm*) 8.38 (bs, 4H), 7.55–7.47 (m, 22H), 4.49 (bs, 8H), 1.82 (bs, 8H), 1.58 (bs, 8H), 1.02 (bs, 12H); GPC (THF) M_w 12,340 M_n 8,200; Anal. calcd for $(C_{78}H_{62}F_6N_2O_{12})_n$: C, 70.26; H, 4.69; N, 2.10. found C, 71.22; H, 4.11; N, 2.61; UV-vis (CH_2Cl_2): $\lambda_{max} = 460$, 558, 602 nm.

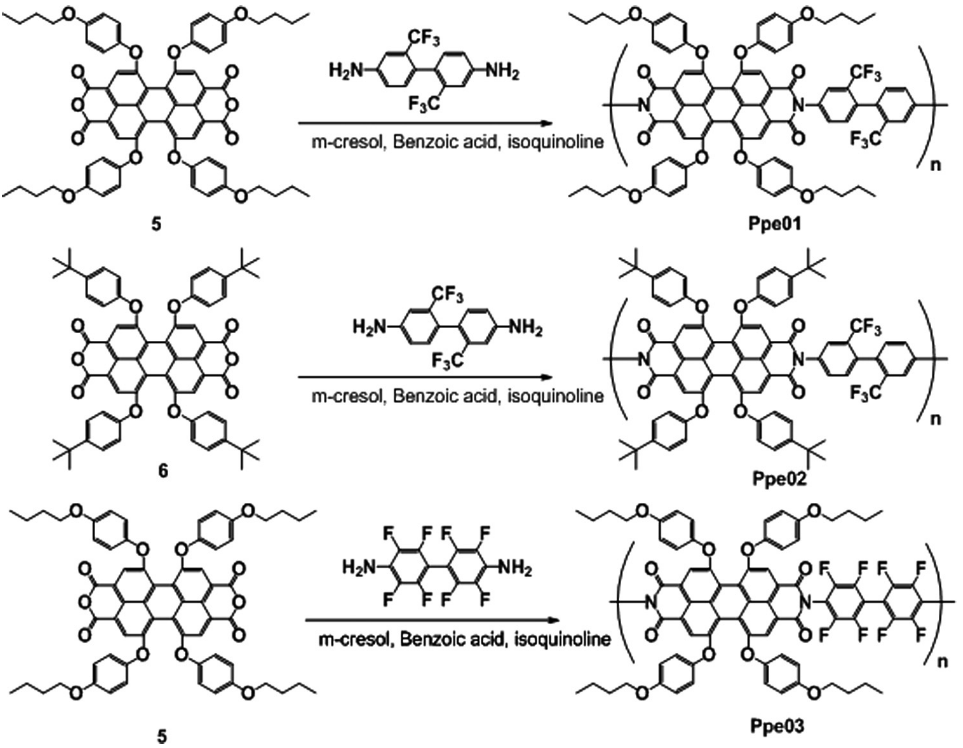

Figure 2. Synthetic routes to perylene polymers.

Synthesis of Ppe02. ***Ppe02*** was obtained from compound **6** (1 g, 1.02 mmol), as a red powder, with a yield of 68%. The synthetic route and work-up were similar to those of ***Ppe01***. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (*ppm*) 8.47 (s, 4H), 7.78 (d, $J = 8.0$ Hz, 8H), 7.43 (m, 14H), 1.37 (s, 36H); GPC (THF) M_w 7,500 M_n 5,772; Anal. calcd for $(C_{78}H_{62}F_6N_2O_8)_n$: C, 73.81; H, 4.92; N, 2.21. found C, 73.02; H, 5.51; N, 2.21; UV-vis (CH_2Cl_2): $\lambda_{max} = 460$, 547, 590 nm.

Synthesis of Ppe03. The synthetic route and work-up were similar to those of ***Ppe01***, except that 4,4′-diaminooctafluorobiphenyl (312 mg, 0.95 mmol) instead of 2,2′-bis(trifluoromethyl)benzidine was used. ***Ppe03*** was obtained as a red powder with a yield of 71%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (*ppm*) 8.52 (bs, 4H), 7.39 (m, 16H), 4.59 (bs, 8H), 1.80 (bs, 8H), 1.65 (bs, 8H), 1.00 (bs, 12H); GPC (THF) M_w 9,940 M_n 7,993; Anal. calcd for $(C_{76}H_{56}F_8N_2O_{12})_n$: C, 68.06; H, 4.21; N, 2.09. found C, 68.82; H, 4.71; N, 2.01; UV-vis (CH_2Cl_2): $\lambda_{max} = 464$, 550, 593 nm.

Device Fabrication. ITO glasses were cleaned by ultrasonic treatment in acetone, detergent, de-ionized water and iso-propyl alcohol sequentially, and dried in a vacuum oven. Afterward, the O_2 plasma treatment was conducted for 3 min. to remove organic residue on ITO. PEDOT:PSS was spin-coated onto ITO at 3000 rpm, and dried at 140°C for 15 min. to give a thickness of 30 nm. The chlorobenzene solution containing P3HT and ***Ppe01*** (1:2 by weight) were spin-coated onto the PEDOT:PSS layer at 700 rpm and dried at 50°C for 40 min. to give a thickness of 120 nm. Finally, 1 nm of LiF layer and 120 nm of Al film were vapor-deposited under a pressure of 1.33×10^{-4} Pa to yield an OPV device with the configuration of ITO/PEDOT:PSS/P3HT:***Ppe01***/LiF/Al. The device was sealed with glass cap to protect from the air. The active area of the device, defined by shadow mask, is $3 \times 3\,\text{mm}^2$. The devices were annealed directly on the top of a hotplate.

Measurements

The ^{1}H NMR spectra of the synthesized materials in $CDCl_3$ were recorded using a 400 MHz Bruker AM-400 spectrometer. Elemental analyses were performed on a Carlo Erba 1106 analyzer. Thermal properties were obtained from a TG/DTA SDT Q600 analyzer (TA Instrument). Mass spectral data were obtained from the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer. UV-visible absorption spectra were obtained using a Varian Easy 50 Conc spectrophotometer. The photoluminescence spectra excited by a 150-W Xe lamp were monitored with a Jasco FP-6500 spectrofluorometer. The ionization potential (I_p) was measured using a photoelectron spectroscope (Riken Keiki, AC-2). The weight (M_w) and number (M_n) average molecular weight of the polymers were evaluated using gel permeation chromatography (Waters, alliance 2000, THF, polystyrene universal calibration) at room temperature. Photocurrent-voltage measurement was performed with a Keithley model 2400 Source Meter and a Newport 91192 solar simulator system (equipped with 1 KW xenon arc lamp, Oriel). Light intensity was adjusted to simulated AM 1.5 radiation at $100\,\text{mW/cm}^2$ with a Radiant Power Energy Meter (model 70260, Oriel). All measurements were carried out under ambient conditions at room temperature.

Results and Discussion

Synthesis and Characterization

We have designed and synthesized three perylene polymers, ***Ppe01, Ppe02***, and ***Ppe03***, with *n*-type characteristics to apply to OPVs. These perylene polymers were modified with the introduction of strong electron withdrawing F atoms in order to improve the solubility and air-stability by raising their polarities and electron affinities [16]. Compound **5** and **6** as perylene monomers were obtained from 3,4,9,10-perylenetetracarboxdiimide using condensation, chlorination, alkylation, and dehydro-condensation reactions according to previously reported procedures [13]. The polymeric compounds were synthesized by a condensation reaction as shown in Figure 2.

^{1}H NMR and elemental analysis confirmed the structure of the intermediates and target materials. For the final polymeric compounds, the proton signals of the parent perylene structure were all shifted down-field relative to those of monomeric compounds (**5** and **6**) in the ^{1}H NMR spectra. This effect was probably induced by a de-shielding effect from electron withdrawing moieties, such as octafluorobiphenyl and bis(trifluoromethyl)benzidine. The proton signals were also broader due to the polymeric state of the compounds (***Ppe01, Ppe02**, and **Ppe03***).

The synthesized compounds were also confirmed by elemental analysis, showing the analyzed data in good agreement with the calculated values and implying high purity of the synthesized compounds [17]. Thermo gravimetric analysis (TGA) showed that the decomposition temperature of ***Ppe01*** $\sim$ ***03***, where over 95% of their mass remained, under nitrogen atmosphere was in the range of 430 and 456°C, demonstrating good thermal stability of the compounds. The molecular weight of the compounds was measured by gel permeation chromatography (GPC) using polystyrene standards and THF as an eluent. The molecular weights (M_w) of ***Ppe01, 02, and 03*** were 12,340, 7,500, and 9,940 g/mol with polydispersity indices (PDI) of 1.29, 1.62, and 1.48, respectively.

Optical and Electronic Band Structures of Perylene Polymers

Figure 3 presents UV-Visible absorption and PL spectra of the polymers measured in 0.1 mM CH_2Cl_2 solution. All absorption spectra show three absorption maxima attributed to perylene moieties [18]. The absorption maxima ($\lambda_{max,UV}$) of ***Ppe01*** $\sim$ ***03*** were measured to be 602, 590, and 593 nm, and PL maxima ($\lambda_{max,PL}$) were observed at 649, 624, and 624 nm, respectively. Absorption maxima of monomers, **5** and **6**, were detected at 590 and 585 nm, and their PL maxima were showed at 626 and 622 nm, respectively. Absorption and PL maxima of the polymers were red-shifted relative to the corresponding monomers. This result showed that expanded π-conjugation along the polymer backbone yielded low electron transition energy.

The absorption maximum of ***Ppe01*** was showed in rather longer wavelength compared to those of other polymers. This may be due to the stronger electron donating effect of 4-*n*-butyloxyphenoxy group in ***Ppe01*** than that of *p*-tert-butylphenoxy moiety in ***Ppe02***. In addition, the octafluoro groups have stronger electron withdrawing character than that of bis(trifluoromethyl) groups [19].

The ionization potentials (HOMO, I_p) of ***Ppe01*** $\sim$ ***03*** measured by photoelectron spectroscopic analysis were 5.84, 5.79, and 5.77 eV, respectively. The band gap energies (E_g) of ***Ppe01*** $\sim$ ***03*** calculated from the absorption onset of a 0.1 mM solution in dichloromethane were 1.88, 1.91, and 1.96 eV, respectively. The electron affinities (LUMO, E_a) were calculated to be 3.96, 3.72, and 3.81 eV, respectively. These high electron affinities suggest that the synthesized compounds have a potential as electron acceptors to apply to OPV device. Table 1 summarizes the optical and molecular orbital energies of ***Ppe01*** $\sim$ ***03***.

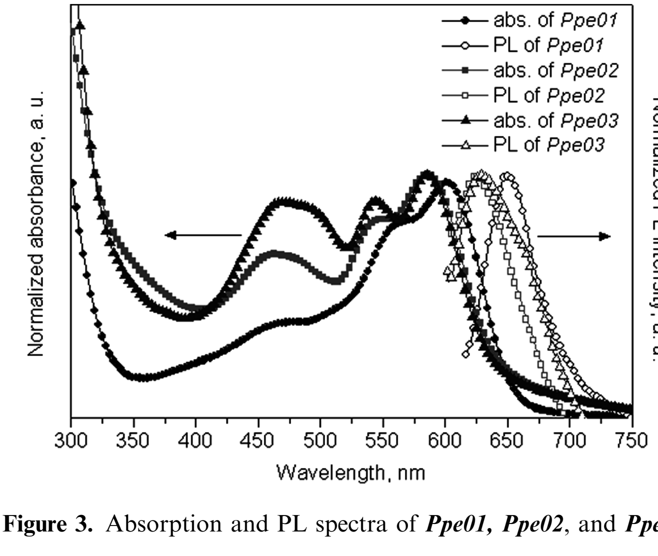

Figure 3. Absorption and PL spectra of ***Ppe01, Ppe02***, and ***Ppe03***.

Table 1. Optical and electrochemical properties of ***Ppe01, Ppe02***, and ***Ppe03***

Polymers	$\lambda_{max,UV}$[a] (nm)	$\lambda_{max,PL}$[a] (nm)	T_d[e] (°C)	M_n	M_w	PDI	E_g (eV)	I_p (eV)	E_a[f] (eV)
Ppe01	460[b], 558[c], 602[d]	649	456	8,200	12,340	1.29	1.88	5.84	3.96
Ppe02	460[b], 547[c], 590[d]	624	430	5,772	7,500	1.62	1.91	5.79	3.88
Ppe03	464[b], 550[c], 593[d]	628	456	7,993	9,940	1.48	1.96	5.77	3.81

[a] Measured in 0.1 mM CH_2Cl_2 solution.
[b] $S_0 \rightarrow S_1$ absorption peak.
[c] $S_1 \rightarrow S_0$ absorption peak.
[d] $T_1 \rightarrow T_n$ absorption peak [13].
[e] Thermal decomposition temperature.
[f] Calculated by $E_a = I_p - E_g$.

Photovoltaic Properties of Ppe01

From the measured E_a and I_p, it was thought that ***Ppe01*** would be able to act as an electron acceptor in OPV devices. Figure 4 shows PL spectra of P3HT and P3HT:Ppe01 thin films excited at 510 nm. As compared to P3HT, blend film of P3HT:***Ppe01*** (1:1 by weight) displayed sharp drop of PL intensity, and P3HT:***Ppe01*** (1:2) film also showed more effective PL quenching. It demonstrates that the PL intensity of P3HT dramatically quenched by the presence of perylene polymer. The phenomenon of PL quenching which is essential to obtain photovoltaic effects must be originated from efficient intramolecular electron transfer from the electron donor (P3HT) to the electron acceptor (***Ppe01***).

An OPV with the configuration, ITO (150 nm)/PEDOT:PSS (30 nm)/ P3HT:***Ppe01*** (1:2 by weight, 120 nm)/LiF (1 nm)/Al (150 nm), was fabricated in order to investigate photovoltaic properties of ***Ppe01***. Figure 5 shows the energy diagram of the materials used in the OPV device. It appears that the molecular energy levels of ***Ppe01*** and P3HT are relatively positioned to each other such that they are allowed to separate excitons and generate free charges at the interface of

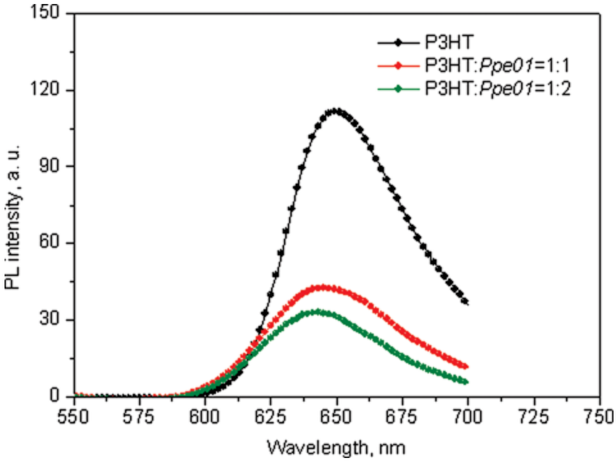

Figure 4. PL spectra of films; P3HT, P3HT/***Ppe01*** (1:1) and P3HT/***Ppe02*** (1:2).

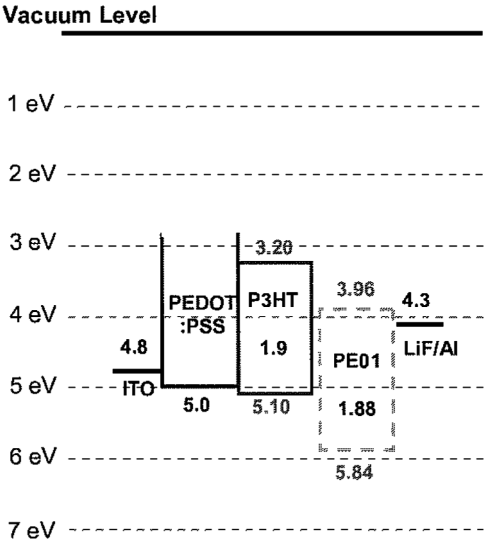

Figure 5. Energy diagram of OPV containing ***Ppe01***.

P3HT and ***Ppe01***. The device exhibited J_{sc} of 0.214 mA/cm^2, V_{oc} of 0.563 V, and fill factor (FF) of 26.45% under the illumination of 100 mW/cm^2. The PCE for this solar cell was 0.03%.

The reason for the poor photovoltaic properties, such as low J_{sc} and PCE, is possibly attributable to the incomplete formation of bicontinuous phase between the electron donor (P3HT) and electron acceptor (***Ppe01***). The bicontinuous phase which is one of the main factors to improve PCE in bulk hetero-junction type OPVs can be obtained by formation of phase separation (or nanodomain) between the electron donor and acceptor. Various methods such as post thermal annealing [20,21], solvent annealing [22], and incorporation of an additive [23] in active layer have been investigated to enhance phase separation by increasing structural order of the electron donor and acceptor.

In the viewpoint of chemical structure, the electron donor and acceptor should have crystallinity enough to easily form phase separation. Therefore, improvements in PCE in this study could be likely realized by controlling phase separation of P3HT:***Ppe01*** active layer or modifying the chemical structure to get increased crystallinity of ***Ppe01***, for example, insertion of aliphatic spacer into mainchain of ***Ppe01***. Further studies aimed at optimizing the OPV devices are in progress using thermal annealing, incorporation of an additive and chemical modification of ***Ppe01***.

Conclusions

In summary, highly soluble *n*-type perylene polymers were synthesized, and their optical and electronic properties were investigated. The synthesized polymers showed high thermal stabilities and high electron affinities. When considering their electron affinities, the synthesized perylene polymers were suitable candidates for the electron acceptor with P3HT as the electron donor in OPV devices. Although the synthesized perylene derivatives provided excellent thermal stability, high electron affinity and absorption property in visible region, the performance of all polymeric OPV device fabricated with P3HT: ***Ppe01*** blend films as the active layer was found to be limited from unfavorable phase separation, indicating that additional improvement on the performance of OPV devices could be possible with further controlling morphology of the blend films with the device processing conditions.

Acknowledgments

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