SYNTHESIS AND DONOR-π-ACCEPTOR PROPERTIES OF POLYFLUORENE DERIVATIVES CONTAINING A PHENAZASILINE MOIETY AND AN ELECTRON ACCEPTOR

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Abstract – Two polyfluorene derivatives containing a phenazasiline moiety and an electron acceptor were synthesized by the Suzuki coupling reaction. Molecular weight analysis showed that the two polymers had approximately 14 and 9 fluorene units as well as functional groups. Since these polymers had donor-π-acceptor systems, their absorption edges were red-shifted compared to that of polyfluorene. Cyclic voltammetry experiments indicated that the polymers showed amphoteric redox behavior. Bulk heterojunction solar cells were fabricated using films made of the polymers and a fullerene derivative, and their photovoltaic properties were investigated.

Currently, extensive research is being carried out on conjugated polymers, with special focus on the development of electronic devices such as bulk heterojunction (BHJ) solar cells.[1] Conjugated polymers with donor-π-acceptor systems have attracted considerable attention as candidate materials for BHJ solar cells.[2] Their HOMO and LUMO energy levels can be controlled by appropriate choice of the donor and acceptor groups, and thus, semiconducting polymers with the desired band structures can be obtained. On the other hand, polyfluorenes containing alkyl chains are useful as organic-soluble polymer backbones, and several polyfluorene derivatives with donor-π-acceptor systems have been synthesized and investigated for use in BHJ solar cells.[3] Furthermore, some phenazasiline polymers exhibiting p-type semiconducting behavior have been reported.[4] Therefore, in this study, we synthesized polyfluorene derivatives containing a phenazasiline moiety and an electron acceptor such as 2,1,3-benzothiadiazole or anthraquinone via Suzuki coupling (Scheme 1). Herein, we report the synthesis and spectroscopic and electrochemical properties of polyfluorene derivatives (**1**) and (**2**), as well as the use of these polymers in

the fabrication of BHJ solar cells.
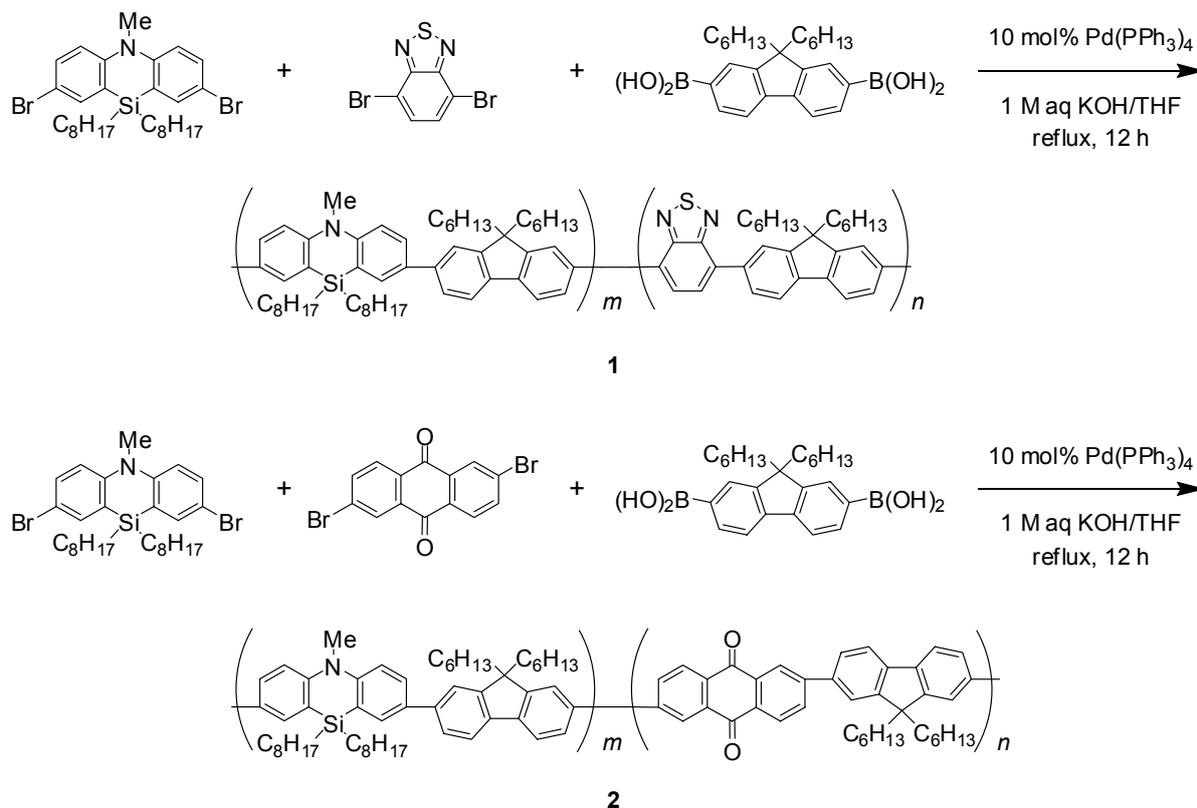
Scheme 1. Synthesis of polyfluorene derivatives (**1**) and (**2**); reaction conditions: phenazasiline[4b] (0.51 mmol), electron acceptor (0.68 mmol), 9,9-dihexylfluorene-2,7-diboronic acid (1.35 mmol); yield: **1** (0.30 g), **2** (0.75 g)

The synthesis of our polyfluorene derivatives is illustrated in Scheme 1. Polymers (**1**) and (**2**) were obtained as yellow and orange solids, respectively. These polymers are soluble in chloroform and THF. By gel permeation chromatography (GPC) analysis of their chloroform solutions, the number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the products were estimated: **1**, M_n = 7900, M_w = 24900; **2**, M_n = 5500, M_w = 16000. This result suggested that **1** and **2** had approximately 14 and 9 fluorene units, respectively, as well as functional groups. The phenazasiline-to-electron-acceptor ratio (m/n) in **1** and **2** was estimated to be 5/9 and 3/6, respectively, by elemental analysis.[5] Thermogravimetry (TG) studies showed that the polymers were stable up to 300 °C; a 5% weight loss was observed at 348 °C and 336 °C in the case of **1** and **2**, respectively. The UV–vis absorption spectra of the polymers in dichloromethane are shown in Figure 1. The absorption maxima of **1** were observed at λ_{max} = 442, 371, and 340 nm; the longest absorption maximum (442 nm) was similar to that of poly(3-hexylthiophene-2,5-diyl) (P3HT) (λ_{max} = 449 nm). Polymer (**2**) showed absorption bands with λ_{max} = 430 (sh), 380, and 358 nm. The absorption edges of **1** and **2** were red-shifted compared to that of poly(9,9-di-*n*-octylfluorenyl-2,7-diyl) (PFO), indicating the formation of donor-π-acceptor systems in the

former case.
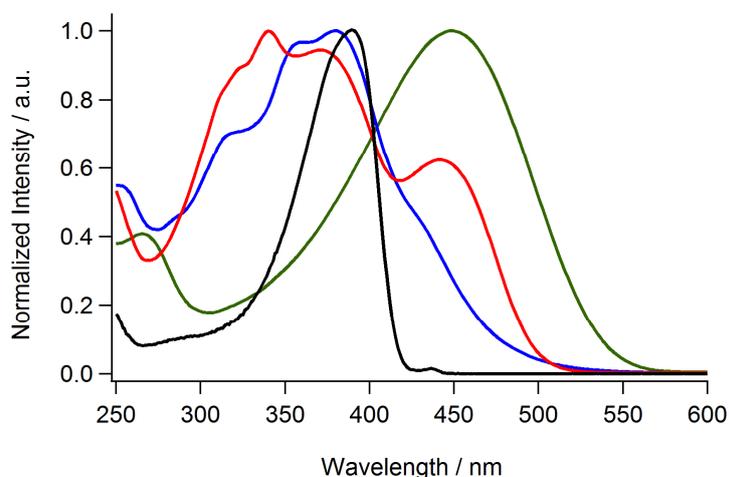
Figure 1. UV–vis absorption spectra of polymers in dichloromethane; ▬: **1**, ▬: **2**, ▬: PFO, ▬: P3HT

Cyclic voltammetry (CV) measurements were performed to investigate the redox properties of the two polyfluorene derivatives. The electrochemical activities of **1** and **2** were evaluated by performing CV experiments using cast polymer films deposited on Pt disks (Figure 2).[6] The voltammograms of the films of **1** and **2** showed quasi-reversible oxidation and reduction waves: **1**, $E_p^{ox} = +0.66$ V, $E_p^{red} = -1.96$ V; **2**, $E_p^{ox} = +0.66$ V, $E_p^{red} = -1.39$ V (vs. Fc/Fc$^+$). This indicated that polymers (**1**) and (**2**) had amphoteric redox properties. The oxidation potentials of **1** and **2** were similar to each other and were more positive than the first oxidation potential of a phenazasiline homopolymer ($E_p^{ox1} = +0.26$ V, $E_p^{ox2} = +0.63$ V).[7] However, the reduction potential of **1** was more negative than that of **2**, and the reduction potentials of both the polymers were similar to those of the corresponding electron-accepting units: 4,7-dibromo-2,1,3-benzothiadiazole ($E_{1/2}^{red} = -1.65$ V) and 2,6-dibromoanthraquinone ($E_{1/2}^{red} = -1.19$ V).[7]
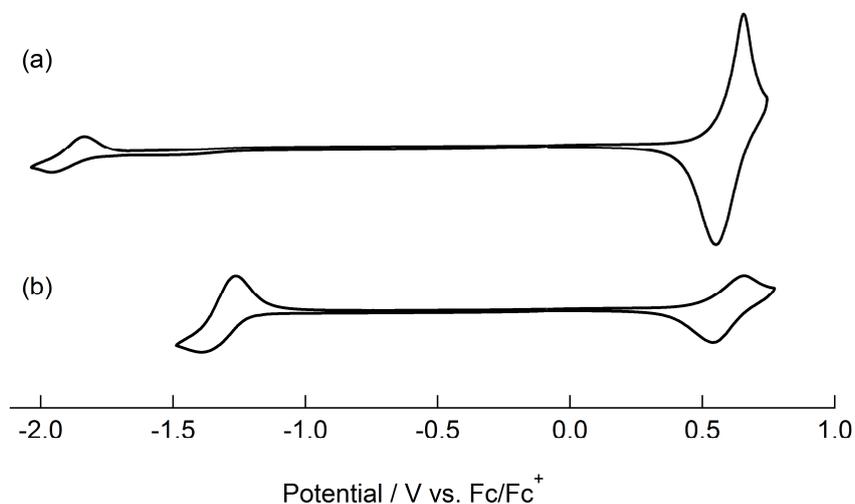
Figure 2. Cyclic voltammograms of polymer films; (a) **1** and (b) **2**

Figure 3 shows the HOMO/LUMO energy diagram of **1** and **2**. The HOMO levels were determined from the onset potentials of the oxidation waves in the voltammograms.[8] The LUMO levels were calculated from the sum of the corresponding HOMO and HOMO–LUMO energies. The HOMO–LUMO gaps were determined from the absorption edges measured for the polymer films. The energy levels of P3HT were consistent with those reported in the literature.[3a] The HOMO levels of **1** and **2** were lower than that of P3HT; this suggested an increase in the open-circuit voltage (V_{oc}) of the BHJ solar cells because the V_{oc} value could be attributed to the difference between the HOMO level of the polymer and the LUMO level of an electron acceptor such as [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM).[1f] However, the LUMO levels of **1** and **2** were higher than that of P3HT, and consequently, the HOMO–LUMO gaps in the polymers were large.
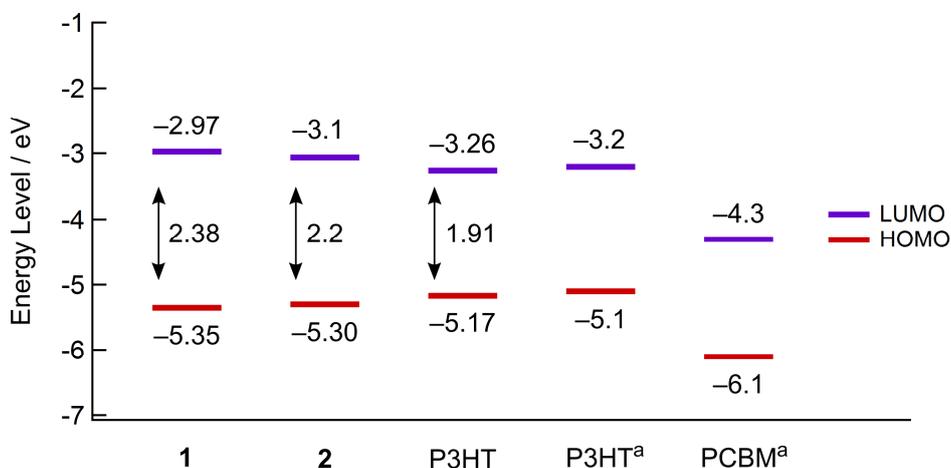
Figure 3. HOMO/LUMO energy diagram of polymers (**1**) and (**2**) with P3HT and PCBM ([a]Ref. 3a); values given in eV

BHJ solar cells with the following structure were fabricated using PCBM as the electron acceptor: ITO/PEDOT:PSS/active layer/Al. The active layers were formed by spin coating an *o*-dichloro-benzene solution of the polymer and PCBM (1:1 weight ratio) on PEDOT:PSS substrates and subsequent annealing at 100 °C. Figure 4 shows the photocurrent density–voltage characteristics determined for the solar cells fabricated using **1** and **2** (denoted as cell 1 and cell 2, respectively), after irradiation with AM 1.5 solar light (100 mW cm^{-2}). Although both cells 1 and 2 generated photocurrent density upon irradiation, the current density was very low. The reason for this was as follows. The low viscosity of the polymer solutions resulted in insufficient growth of the active layers; that is, active layers had low thicknesses and hence did not absorb light efficiently. On the other hand, the photocurrent density generated from the device fabricated using P3HT (cell P3HT) was high because of the large thickness of the active layer grown from a solution of P3HT, which has high molecular weight. Thus, the power conversion efficiencies (PCEs) of cells 1 and 2 were much lower than that of cell P3HT (Table 1).
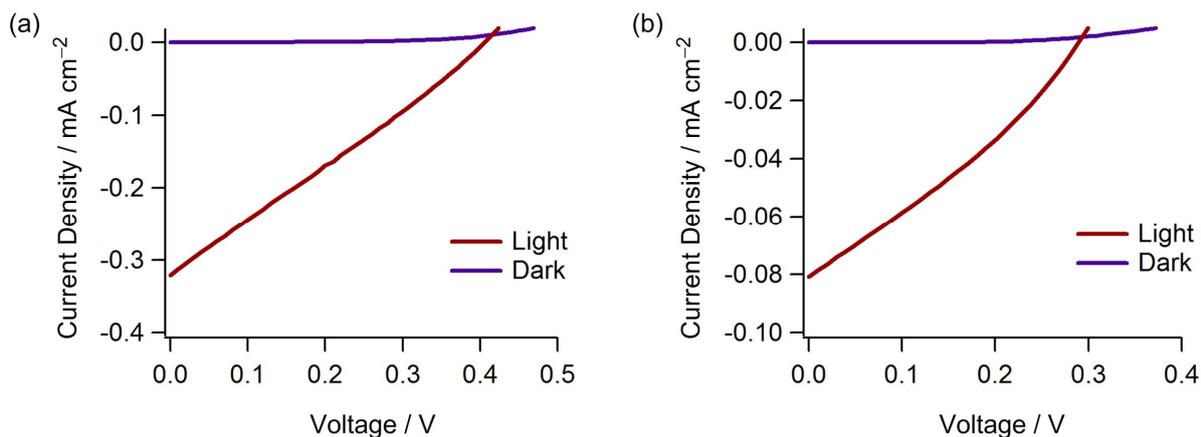
Figure 4. Photovoltaic performance of BHJ solar cells: (a) cell 1 and (b) cell 2

Table 1. Photovoltaic performance of solar cells using polymers (**1**) and (**2**)[a]

Cell	J_{sc}[b]/mA cm^{-2}	V_{oc}[c]/V	FF[d]/%	PCE[e]/%
1	0.32	0.41	27	0.04
2	0.08	0.29	30	0.01
P3HT	7.82	0.55	63	2.71

[a]Device structure: ITO-coated glass/PEDOT:PSS/polymer:PCBM (1:1)/Al. [b]Short-circuit current density. [c]Open-circuit voltage. [d]Fill factor. [e]Power conversion efficiency.

In conclusion, we synthesized two polyfluorene derivatives with a phenazasiline moiety and an electron acceptor by Suzuki coupling. According to the results of GPC analysis, these polymers had approximately 14 and 9 fluorene units as well as functional groups. The absorption edges of the polymers were red-shifted compared to that of a fluorene homopolymer (PFO), indicating the formation of donor-π-acceptor systems in the former case. CV experiments confirmed that films prepared from the two polymers showed amphoteric redox properties. Although the solar cells fabricated using the synthesized polymers and PCBM showed photovoltaic activity under light irradiation, the generated photocurrent density was very low. Further investigation of the polymer synthesis and device fabrication procedures is being carried out with the aim of improving the photovoltaic properties of the solar cells.

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5. Elemental analysis for **1** and **2**.   Polymer (**1**): Anal. Calcd for $C_{549}H_{683}N_{23}S_9Si_5$ ($m = 5$, $n = 9$): C, 82.08; H, 8.57; N, 4.01.   Found: C, 81.74; H, 8.40; N, 3.35.   Polymer (**2**): Anal. Calcd for $C_{396}H_{455}N_3O_{12}Si_3$ ($m = 3$, $n = 6$): C, 85.96; H, 8.29; N, 0.76.   Found: C, 85.76; H, 8.20; N, 0.74.

6. The CV measurements of the polymer films were performed in CH_3CN with 0.1 M n-Bu_4NPF_6 at a scanning rate of 100 mV s^{-1} using Pt and Ag/Ag$^+$ electrodes.   The values are expressed in potentials vs. Fc/Fc$^+$.

7. The CV measurements were performed in CH_2Cl_2 with 0.1 M n-Bu_4NClO_4 at a scanning rate of 100 mV s^{-1} using Pt and Ag/Ag$^+$ electrodes.   The values are expressed in potentials vs. Fc/Fc$^+$.

8. The HOMO energy levels in eV were calculated from the following equation: $E_{HOMO} = -[(E_{onset}^{ox}$ vs. SCE) $+ 4.4]$.[9]   The redox potential of Fc/Fc$^+$ is +0.39 V vs. SCE.

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