New Donor Materials Based on Thiazole and Triphenylamine for Photovoltaic Devices

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New photovoltaic donor materials, 4,4’-(2,2’-bithiazole-5,5’-diyl)bis(N,N-diphenylbenzenamine) (BDT) and 4-(2,2’-bithiazol-5-yl)-N,N-diphenylbenzenamine (BT), were synthesized. A solution processable triphenylamine-containing bithiazole (BDT and BT) was blended with a [6,6]-phenyl C$_{61}$ butyric acid methyl ester (PCBM) acceptor to study the performance of small-molecule-based bulk heterojunction (BHJ) photovoltaic devices. Optimum device performance was achieved after annealing, for device with a BDT/PCBM ratio of 1:4. The open-circuit voltage, short-circuit current, and power conversion efficiency of the device with the aforementioned BDT/PCBM ratio were 0.51 V, 4.10 mA cm$^{-2}$, and 0.68%, respectively, under simulated AM 1.5 solar irradiation (100 mW cm$^{-2}$).

Key Words : Thiazole, Organic photovoltaic cells, Bulk-heterojunction, Triphenylamine

Introduction

Because of the current energy problem, it has become necessary to develop new renewable energy sources. Organic photovoltaics (OPVs) are considered to be one of the most promising candidates for such new energy sources because of the following advantages: ease of synthesis, low cost, and ease of device fabrication.$^{1,2}$ To date, the most successful materials for OPVs are thiophene-based polymers blended with small molecules such as fullerene and [6,6]-phenyl C$_{61}$ butyric acid methyl ester (PCBM).$^3$ Synthesis, purification, and energy level control are easier in the case of small molecules than in the case of polymers. Consequently, many research groups have focused on small-molecule OPVs in which thiophene derivatives are used as donor materials; this is because of the excellent charge-transport ability and high thermal stability of thiophene derivatives.$^4$ Furthermore, the feasibility of using triphenylamine (TPA) moiety in OPVs has been widely investigated because of its hole-transport and electron-donating ability, thermal and electrochemical stability, and isotropic optical and charge transport properties.$^{5-7}$

Recently, Shirota, Roncali, and co-workers have developed TPA derivatives with propeller-shaped and three-dimensional (3-D) star-shaped molecules; the three phenyl groups in these derivatives are not in the same plane.$^{5,6}$ In addition, Li and co-workers synthesized star-shaped organic molecules linked with electron-rich TPA units and electron-poor benzothiadiazole units.$^5$ They designed very high performance organic solar cells (OSC) by using these solution-processable organic molecules.$^{9d}$ Various electron-poor moieties such as benzothiadiazole,$^9$ thienopyrazine,$^{10}$ and thiazole$^{11}$ units have been used in organic photovoltaics.

In our previous study,$^{12}$ we synthesized solution-processable and thermally stable donor materials comprising a bithiophene unit and a TPA unit linked by conjugated bonds for bulk heterojunction photovoltaics. The device with the best performance showed a power conversion efficiency (PCE) of 0.34% under simulated AM 1.5 solar irradiation at 100 mW cm$^{-2}$. The low PCE was due to the poor morphology of the blended solid film of the donor material and PCBM. Herein, we report the design of new donor materials, 4,4’-(2,2’-bithiazole-5,5’-diyl)bis(N,N-diphenylbenzenamine) (BDT) and 4-(2,2’-bithiazol-5-yl)-N,N-diphenylbenzenamine (BT), consisting of a TPA unit and thiazole unit linked by conjugated bonds. We successfully used these donor materials for the fabrication of BHJ OPV devices (Fig. 1). The PCEs of the OPV devices fabricated using BDT and BT were better than those of the devices fabricated using thiophene derivatives$^{12}$ because of the better morphology of the solid film obtained by blending BDT and PCBM. Optimum device performance was achieved for a BDT/PCBM ratio of 1:4, after annealing; the open-circuit voltage ($V_{oc}$), short-circuit current ($J_{sc}$), and PCE of the device with the aforementioned BDT/PCBM ratio were 0.51 V, 4.10 mA cm$^{-2}$, and 0.68%, respectively, under simulated AM 1.5 solar irradiation (100 mW cm$^{-2}$).
Experimental

Materials and Instrument. 4-(Diphenylamino)phenylboronic acid, tetrakis(triphenyl-phospine)palladium(0) (Pd(PPh$_3$)$_4$), PCBM, and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) were purchased from Aldrich and LMC. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) was purchased from Baytron. 5,5’-Dibromo-2,2’-bithiazole 1 and 5-bromo-2,2’-bithiazole 2 were synthesized according to previously reported procedures. A mixture of carbonate (168 mg, 1.21 mmol) in THF (15 mL) and tetrakis(triphenyl-phospine)palladium(0) (35 mg, 0.03 mmol), and potassium carbonate (340 mg, 2.45 mmol) in ethyl acetate-hexane as the column chromatography using ethyl acetate-hexane as the eluent and recrystallized from dichloromethane and hexane to afford an orange-red solid product (yield: 240 mg, 96%). 1H NMR (300 MHz, CDCl$_3$) δ 7.97 (s, 1H), 7.92 (d, 3 Hz, 1H), 7.47 (m, 18 Hz, 3H), 7.32 (m, 15 Hz, 3H), 7.12 (m, 10 Hz, 9H). 13C NMR (125 MHz, CDCl$_3$) δ 162.1, 159.3, 148.8, 147.3, 144.1, 141.8, 138.6, 129.7, 127.8, 125.2, 124.2, 123.9, 123.1, 120.8. Mass: calcd. for C$_{32}$H$_7$N$_2$S$_2$ [M$^+$] 411.0864, HR-Mass: 411.0870.

Results and Discussion

The organic phase was washed with water and dried over Na$_2$SO$_4$. The solvent was evaporated to give an orange-reddish product; the crude product was purified by silica gel column chromatography using ethyl acetate-hexane as the eluent and recrystallized from dichloromethane and hexane to afford an orange-red solid product (yield: 240 mg, 96%). The UV-Vis spectra in CHCl$_3$ solution showed two absorption bands with maxima at 300 and 437 nm for BDT and BT and PCBM at different weight ratios (1:3 to 1:5) onto the BCP layer. We measured the device performance before and after annealing at 80 °C for 20 min in a nitrogen glove box. Current-voltage ($J$-$V$) measurements for the devices were performed using a Keithley 237 instrument. The device performances were characterized under uniform illumination (AM 1.5 G illumination intensity of 100 mW cm$^{-2}$) using a solar simulator. The light intensity at each wavelength was calibrated using a standard Si solar cell as a reference.

DFT and TD-DFT calculations were performed using the B3LYP functional with the 6-31G basis set for all atoms. The absorption and emission spectra of DFT and BT in CH$_2$Cl$_2$, quartz solid film, and films composed of a BT/PCBM blend were shown in Figure 2 and S1†. Table 1 lists the main photophysical and electrochemical properties of BDT and BT. The absorption peak at 300 nm was due to the triphenylamine unit, and the peaks at 437
and 399 nm were due to the bithiazole unit. The absorption spectra in quartz solid film showed maxima at 306 and 442 nm for BDT and at 307 and 412 nm for BT. The emission spectra in CH₂Cl₂ solution showed maxima at 544 nm and 530 nm for BDT and BT, respectively. In the quartz solid film, the emission spectra showed a maximum at 552 nm for BDT and at 545 nm for BT. The emission spectra of BDT and BT in the quartz solid film were red-shifted with respect to those in CH₂Cl₂ solution by approximately 8 and 15 nm, respectively, because of self-aggregation and intermolecular interactions. The UV-vis absorption and PL emission of BDT were red-shifted with respect to those of BT owing to the longer conjugation length of BDT. The emission spectra of the BDT/PCBM and BT/PCBM blend films were drastically quenched by PCBM (Fig. 2(b)). This phenomenon indicates energy transfer from the excited states of BDT and BT to PCBM and intermolecular photoinduced charge transfer (PICT).

7,14 BDT and BT were used as the electron donor materials, and PCBM was used as the electron acceptor material in the BDT/PCBM and BT/PCBM blended films. This PICT process also occurs in the case of a conducting conjugated polymer and PCBM blend.14

The cyclic voltammograms of BDT and BT revealed a reversible oxidation process (Fig. 3). The oxidation potential energies of BDT and BT were measured to be E_{1/2,ox} = 0.69 and 0.70 V vs. Ag/Ag⁺, respectively. The HOMO energy levels of BDT (~5.01 eV) and BT (~5.02 eV) were calculated from E_{1/2,ox} after correction for the vacuum energy level (4.50 eV) (Table 1). The LUMO energy levels of BDT (~2.51 eV) and BT (~2.31 eV) were calculated from the cross-sectional wavelength between the absorption and emission spectra (Table 1). The electrochemical bandgap of BDT was slightly narrower than that of BT because of the difference in the conjugation lengths of BDT and BT; this difference in the conjugation length was in turn due to the difference in the number of TPA units in these two donors.

### Table 1. Photophysical and electrochemical properties of BDT and BT

<table>
<thead>
<tr>
<th></th>
<th>Absorption (λ_{max}) (\text{nm}) a</th>
<th>Emission (λ_{max}) a</th>
<th>HOMO (eV) b</th>
<th>LUMO (eV) b</th>
<th>ΔE (eV) b</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDT</td>
<td>300 (60140), 437 (67855) (solution)</td>
<td>544 (solution)</td>
<td>-5.01</td>
<td>-2.51</td>
<td>2.50</td>
</tr>
<tr>
<td></td>
<td>306, 442 (film)</td>
<td>552 (film)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BT</td>
<td>300 (21085), 399 (27505) (solution)</td>
<td>530 (solution)</td>
<td>-5.02</td>
<td>-2.31</td>
<td>2.71</td>
</tr>
<tr>
<td></td>
<td>307, 412 (film)</td>
<td>545 (film)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

aAbsorption and emission spectra were measured in 0.02 mM CH₂Cl₂ solution and quartz solid film. bHOMO energy levels were determined in CH₂Cl₂ solution (0.1 M TBAPF₆) vs. AgNO₃. HOMO = E_{1/2,ox} + 4.50 eV. cLUMO energy levels were calculated from the cross-sectional wavelength between absorption and emission spectra. dΔE = HOMO-LUMO.
To examine the photovoltaic performances, bulk heterojunction solar cell devices were fabricated with a sandwich structure: ITO/PEDOT:PSS (30 nm)/BDT or BT:PCBM (45 nm)/BCP (10 nm)/Al (100 nm). The $J$-$V$ performances of the devices are shown in Figure 4 and S2†, and summarized in Table 2. In order to optimize the device properties, different BDT or BT and PCBM ratios were employed. In a case where BDT/PCBM or BT/PCBM = 1:3, the power conversion efficiencies of the devices were 0.15% and 0.018%, respectively. As the PCBM concentration increased, in the case of BDT/PCBM or BT/PCBM = 1:4, the power conversion efficiencies of the devices increased by ca. 4 times and 10 times, to 0.53% and 0.17%, respectively. Similarly, in the case of BDT/PCBM or BT/PCBM = 1:5, the power conversion efficiencies of the devices were 0.56% and 0.44%, respectively. As a result, for both BDT and BT, by increasing the PCBM concentration from 1:3 to 1:5, the power conversion efficiencies of the devices were improved due to efficient PICT to PCBM. Since the extinction coefficient of BDT is larger than BT, the power conversion efficiency of the BDT/PCBM blended devices was better than that of the BT/PCBM blended devices.

Figure 4 shows the $J$-$V$ curves of bulk heterojunction devices before and after annealing. In the case of BDT/PCBM or BT/PCBM = 1:3 after annealing, the power conversion efficiencies of the devices increased by ca. four times and two times to 0.54% and 0.031%, respectively. After the annealing of BDT/PCBM or BT/PCBM = 1:4, the power conversion efficiencies of the devices were slightly increased to 0.68% and 0.42%, respectively. Similarly, in the case of BT/PCBM = 1:5, the power conversion efficiency of the device was 0.49%. Consequently, in all cases of BDT/PCBM or BT/PCBM, the open-circuit voltage, short-circuit current, and fill factor of the devices increased after annealing, with two exceptions (BDT/PCBM = 1:4 and 1:5). The overall device data based on BDT or BT are summarized in Table 2.

In order to explain the difference in the PCEs of the devices, atomic force microscopy (AFM) was employed to examine the film morphologies of the blended films.15,16 The AFM images of the devices are shown in Figure 5 and S3†. The surface of the blended film with a BDT/PCBM ratio of 1:3 had a surface with a root-mean-square (rms) roughness of 0.13 nm; the film with a BDT/PCBM ratio of 1:4 had an rms roughness of 0.19 nm. Similarly, the rms roughnesses of
the BT:PCBM = 1:4 blended film (0.20 nm) and BT:PCBM = 1:5 blended film (0.28 nm) were slightly higher than those of the BT-containing blended films due to the more efficient self-aggregation of the BT molecules. A molecule containing one TPA unit (BT) has a flatter surface than a molecule containing two TPA units (BDT). Interestingly, the rms roughnesses of the annealed devices were 0.075 nm, 0.087 nm, and 0.21 nm in the cases of BT/PCBM = 1:3, BDT/PCBM = 1:4, BT/PCBM = 1:4, and BT/PCBM = 1:5, respectively. The effect of the increased PCBM ratio on the rms roughnesses of the BDT and BT films blended with PCBM is not presently clear. The smooth film morphology helps increase the PCE because of the suppressed phase separation of the donor and acceptor and helps improve the contact with the active layer and Al electrode.15 Assuming that the donor-donor or acceptor-acceptor interactions are intrinsically stronger than the donor-acceptor interactions, severe phase separation results. For all the annealed devices, the AFM images reveal a very small degree of phase separation (Fig. 5 and S3†), indicating that the donor-acceptor interactions were more favorable than the donor-donor or acceptor-acceptor interactions. The surface roughness of the film slightly decreased in the case of the annealed devices. Thus, we could state that thermal annealing helped in preventing phase separation.

Table 2. Device performance of bulk heterojunction solar cell based on BDT or BT and PCBM with different ratios (1:3 to 1:5) and annealing under simulated AM 1.5 solar irradiation at 100 mW cm⁻²

<table>
<thead>
<tr>
<th>Active layer</th>
<th>( V_{OC} (V) )</th>
<th>( J_{SC} ) (mA cm⁻²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDT</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Donor:PCBM</td>
<td>As cast (^c)</td>
<td>Annealed (^b)</td>
<td>As cast (^c)</td>
<td>Annealed (^b)</td>
</tr>
<tr>
<td>1:3</td>
<td>0.19</td>
<td>0.49</td>
<td>2.79</td>
<td>3.70</td>
</tr>
<tr>
<td>1:4</td>
<td>0.39</td>
<td>0.51</td>
<td>4.44</td>
<td>4.10</td>
</tr>
<tr>
<td>1:5</td>
<td>0.47</td>
<td>0.54</td>
<td>4.05</td>
<td>3.18</td>
</tr>
<tr>
<td>BT</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Donor:PCBM</td>
<td>As cast (^c)</td>
<td>Annealed (^b)</td>
<td>As cast (^c)</td>
<td>Annealed (^b)</td>
</tr>
<tr>
<td>1:3</td>
<td>0.04</td>
<td>0.07</td>
<td>1.64</td>
<td>1.68</td>
</tr>
<tr>
<td>1:4</td>
<td>0.26</td>
<td>0.44</td>
<td>2.35</td>
<td>3.20</td>
</tr>
<tr>
<td>1:5</td>
<td>0.46</td>
<td>0.49</td>
<td>3.21</td>
<td>3.28</td>
</tr>
</tbody>
</table>

\(^{c}\)Devices without annealing. \(^{b}\)Devices annealed at 80 °C for 20 min.

Conclusion

We developed new solution-processable donor materials, BDT and BT, which consist of thiazole and triphenylamine units linked by conjugated bonds. BHJ devices were fabricated by spin coating a blended solution of BDT or BT and PCBM at different weight ratios (1:3, 1:4, 1:5, w/w). We confirmed that the film morphology and PCE were better in the case of annealed devices than in the case of non-annealed devices. Optimum device performance was observed for the annealed device with a BDT/PCBM ratio of 1:4; the maximum open-circuit voltage, short-circuit current, and PCE of this device were 0.51 V, 4.10 mA cm⁻², and 0.68%, respectively, under simulated AM 1.5 solar irradiation (100 mW cm⁻²). Our results show that thiazole derivatives are promising donor materials for BHJ solar cells.

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References


