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445. Adsorption and aggregation properties of hyperbranched poly(2-hydroxypropyl methacrylate) type nonionic surfactants without molecular weight distribution control.

446. Intrinsically immiscible interactions and self-assembly of amphiphilic after- building copolymers in aqueous solutions: coordination with cysteamine.

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451. Adsorption and aggregation properties of hydrocarbon-fluorocarbon hybrid-type gemini surfactants with cationic or quaternary amonium moieties.

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**Introduction**

- Previous research of DPP-based polymer

![Diagram](image)

**Characterization of pristine polymer in this study**

![Diagram](image)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( M_w ) (kDa)</th>
<th>POI</th>
<th>( E_f \text{opt} ) (eV)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTDP2T</td>
<td>135</td>
<td>1.66</td>
<td>1.32</td>
<td>-5.20</td>
<td>-3.88</td>
</tr>
<tr>
<td>PR1</td>
<td>149</td>
<td>1.68</td>
<td>1.35</td>
<td>-5.24</td>
<td>-3.89</td>
</tr>
<tr>
<td>PR2</td>
<td>162</td>
<td>1.61</td>
<td>1.37</td>
<td>-5.30</td>
<td>-3.93</td>
</tr>
<tr>
<td>PR3</td>
<td>153</td>
<td>1.66</td>
<td>1.40</td>
<td>-5.32</td>
<td>-3.92</td>
</tr>
<tr>
<td>PPyyDP2T</td>
<td>112</td>
<td>1.85</td>
<td>1.60</td>
<td>-5.63</td>
<td>-4.03</td>
</tr>
</tbody>
</table>

*Calculated from LUMO = HOMO + \( E_f \text{opt} \)

- The HOMO energy level and bandgap of the polymers become deeper and wider as the PyDP content in random copolymer is increased.

**Objectives**

- To synthesize a series of conjugated random copolymers consisting of pyridine- and thiophene-capped diketopyrrolopyrrole as co-electron accepting unit
- To enhance both \( J_{SC} \) and \( V_{OC} \) of random copolymers by varying the feed ratio of PyDP to TDPP for copolymerization

**Results**

- **Characterization of pristine polymer in this study**

![Diagram](image)

**Electrical properties of photovoltaic cells**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( G_{sc} ) (mA/cm²)</th>
<th>( M_{h,sc} ) (cm/V s)</th>
<th>( J_{sc} ) (mA/cm²)</th>
<th>( V_{oc} ) (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTDP2T</td>
<td>7.08 ( \times 10^4 )</td>
<td>7.76 ( \times 10^{-4} )</td>
<td>15.05</td>
<td>0.65</td>
<td>0.70</td>
<td>6.70</td>
</tr>
<tr>
<td>PR1</td>
<td>7.86 ( \times 10^4 )</td>
<td>1.91 ( \times 10^{-3} )</td>
<td>15.91</td>
<td>0.67</td>
<td>0.71</td>
<td>7.59</td>
</tr>
<tr>
<td>PR2</td>
<td>8.17 ( \times 10^4 )</td>
<td>2.72 ( \times 10^{-3} )</td>
<td>16.44</td>
<td>0.69</td>
<td>0.71</td>
<td>8.11</td>
</tr>
<tr>
<td>PR3</td>
<td>7.60 ( \times 10^4 )</td>
<td>3.29 ( \times 10^{-3} )</td>
<td>13.51</td>
<td>0.72</td>
<td>0.64</td>
<td>6.29</td>
</tr>
<tr>
<td>PPyyDP2T</td>
<td>5.97 ( \times 10^4 )</td>
<td>4.10 ( \times 10^{-4} )</td>
<td>8.38</td>
<td>0.83</td>
<td>0.59</td>
<td>4.14</td>
</tr>
</tbody>
</table>

*PR2 shows the highest PCE of 8.11% with higher \( V_{oc} \) and \( J_{sc} \) as compared with PTDP2T which is due to deep HOMO energy level, higher light absorption and hole mobility.

**Electrical properties of photovoltaic cells**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>PTDP2T</th>
<th>PR1</th>
<th>PR2</th>
<th>PR3</th>
<th>PPyyDP2T</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine polymer ( q_1 ) (Å(^{-1}))</td>
<td>1.662</td>
<td>1.688</td>
<td>1.707</td>
<td>1.720</td>
<td>1.726</td>
</tr>
<tr>
<td>( d )-spacing (Å)</td>
<td>3.780</td>
<td>3.722</td>
<td>3.680</td>
<td>3.653</td>
<td>3.640</td>
</tr>
<tr>
<td>BHJ ( q_1 ) (Å(^{-1}))</td>
<td>1.663</td>
<td>1.702</td>
<td>1.719</td>
<td>1.730</td>
<td>1.778</td>
</tr>
<tr>
<td>( d )-spacing (Å)</td>
<td>3.778</td>
<td>3.691</td>
<td>3.655</td>
<td>3.631</td>
<td>3.513</td>
</tr>
</tbody>
</table>

*The intensity of (010) peak in \( q_1 \) direction increases and the \( n \)-\( n \) stacking distance decreases, as the pyridine content in polymer backbone is increased.

**TEM images**

- As the pyridine content in polymer backbone is increased, the fibril width of the polymer becomes larger, which interrupts efficient charge separation from excitons to free charge carriers.

**Conclusions**

- The solar cell device based on the random copolymer with the feed ratio of 3:1 (TDPP:PyDP) shows higher PCE (8.11%) than that of reference homopolymer (6.70%), which is attributed to enhancement of \( J_{SC} \) and \( V_{OC} \).
Conjugated random copolymers consisting of pyridine- and thiophene-capped diketopyrrolopyrrole as co-electron accepting unit for efficient polymer solar cells

Jong Won Lee, Won Ho Jo*

Department of Materials Science and Engineering, Seoul National University

One of the most successful approaches to achieve high power conversion efficiency (PCE) of polymer solar cells (PSCs) is to develop new alternating push–pull type copolymers, which consist of electron-rich (D) and electron–poor (A) unit in polymer backbone. Although intensive research efforts have been devoted to developing new D and A moieties, a few D–A alternating copolymers have shown high PCE. Random copolymers composed of one D unit and two different A units can be used as a promising donor material for high performance PSCs, if the absorptions of two electron accepting units are complementary to each other and therefore the resulting copolymer shows broad absorption. Both thiophene-capped (T) and pyridine-capped (Py) diketopyrrolopyrrole (DPP) have been used as electron accepting units for D–A type conjugated polymers for PSCs and OFETs: A low bandgap polymer (pTDPP2T) composed of TDPP and bithiophene (2T) shows high short circuit current due to its low bandgap, while the polymer composed of PyDPP and 2T exhibits high open circuit voltage ($V_{OC}$) due to its low-lying HOMO energy level. In this work, a new series of conjugated random copolymer was synthesized by copolymerization of 2T (an electron donating unit) with TDPP and PyDPP (co-electron accepting units). The $V_{OC}$ of random copolymer can systematically be controlled by varying the feed ratio of PyDPP to TDPP for polymerization. The $V_{OC}$ was increased with increasing the PyDPP content in the random copolymer, since electron withdrawing power of pyridine is stronger than that of thiophene and thus lower the HOMO energy level: The HOMO energy level becomes deeper as the PyDPP content in the random copolymer is increased. Consequently, the solar cell device based on the random copolymer with the feed ratio of 1:1 shows higher PCE of 7.1% with higher $V_{OC}$ of 0.70 V as compared with those (6.6%, 0.62 V) of the reference homopolymer (pTDPP2T).