Synthesis and Properties of Indigo based Donor-Acceptor Conjugated Polymers

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Introduction

Organic thin-film transistors (OTFTs): 

Transistors: work as electronic switches to control the electrical current between source/drain electrodes by applying an input voltage on "gate". Transport holes or electrons, depending on the organic semiconductor.

Polymer semiconductors normally bearing donor-acceptor (D-A) structure synthesized by transition metal catalyzed D-A units crossing-coupling reactions.

D-A Polymer:

Indigo (ID) Molecule:

A natural dye indigo used as early as 1600 BCE. A strong electron withdrawing unit, with a highly coplanar geometry. An isomer of isoidnigo (IID), which shows good performance in OTFTs. No report to make the molecule soluble for polymerization yet. What if indigo molecule could be incorporated into polymers as an acceptor unit as below?

Polymer Synthesis

Characterization of OTFTs:

Transfer and output curves of OTFT devices with P1 and P2 thin films annealed at 150 C for 20 min.

Molecule Weight:

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<th>Mn[kDa]</th>
<th>PDI</th>
<th>Mw[kDa]</th>
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<tr>
<td>P1</td>
<td>125</td>
<td>2.92</td>
<td>112</td>
</tr>
<tr>
<td>P2</td>
<td>124</td>
<td>3.91</td>
<td>111</td>
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Characterized by Gel Permeation Chromatography (GPC), by using polystyrenes as standards and chlorobenzene as an eluent at column temperature of 40 °C.

The lower than expected field effect performance of these polymers in comparison to their counterpart isoindigo polymers was considered to be due to the backbone twisting according to the simulation result, as corroborated by the thermal analysis data.

Indigo unit.

Electrochemistry and energy levels of PIDBT:

E_HOMO calculated from the oxidative onset potential: -5.69 eV for P1 and -5.73 eV for P2 (ferrocene as the standard).

Lower E_LUMO of P2 than that of iso indigo based polymers, due to the stronger electron-withdrawing effect of indigo unit.

Further increasing the annealing temperature to 200 °C resulted in the absence of field effect performance for both polymers, due to the deteriorated molecular ordering caused by thermal decomposition of the side chains.

The observed mobility values are much lower in comparison to isoindigo counterpart.

Chloroindigo (Yutsus people)

Thermal analysis was performed to determine the thermal stability of the polymers. The TGA and DSC traces showed that both polymers are stable up to 300 °C, with P1 showing slightly better thermal stability than P2. The chlorine substituents on the indigo units are responsible for these improved thermal properties.

Simulated geometry of ID and IID:

The dihedral angle between the two indol moieties (1), as well as that between two thiophen units (2), was not much influenced by thermal annealing.

Thin film AFM images:

The backbone twisting led to the poor main chain conjugation, then resulted in the relatively low mobility.

Conclusions

For the first time, the novel D-A polymers based on indigo as acceptor, were synthesized and applied as organic semiconductor in OTFTs. The line-lying HOMOLUMO levels and rather low band gap manifested the strong electron withdrawing capability of the indigo moiety.

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