Synthesis and Characterization of Indigo-containing Conjugated Polymers

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Introduction: Indigo as a very stable chromophore is of high interest as building block for conjugated polymers for organic electronic applications. The strong blue absorption is based on the crossed assembly of electron-accepting and electron-donating building blocks. High chemical stability of indigo in solid-state and solution is observed and is the reason why it is used to dye the ‘blue jeans’. Due to these properties, polymers containing indigo units have been proposed for application in organic solar cells, and. We have investigated novel donor-acceptor copolymers with indigo as acceptor unit combined with donor moieties like dialkylfluorene or dialkycyclopentadienothiophene. Two polymers, Poly[(2,2′-biindoiylium-3,3′-dion-6,6′-diyl)]2,7-(9,9-diiodfluorene)] (PFI) as well as Poly[(2,2- biiodindoles)-3,3′-dion-6,6′-diyl)-2,6-(4,4-bis(2-dodecyl)cyclopenta[2,1-b.3,4-b′]dithiophene)] (PCI) were synthesized. To increase the solubility, tert-butyl dicarboxylate groups were used as substituent of the -NHфункциональность indigo. The HOMO and LUMO levels of the copolymers were estimated by atmospheric pressure photoelectron spectroscopy (AC-2).

Characterization of PFI and PFI-βoc

![Image 1: Synthesis of PFI (R=H) and PFI-βoc (R=βoc); bottom: HOMO and LUMO energy levels of PFI and PFI-βoc]

Table: Fraction of PFI

<table>
<thead>
<tr>
<th>Polymer</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
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<tbody>
<tr>
<td>PFI</td>
<td>-5.67</td>
<td>-3.47</td>
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<tr>
<td>PFI-βoc</td>
<td>-5.80</td>
<td>-3.59</td>
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![Image 2: top: absorption spectra of the DCM fraction of PFI in solution and solid-state; bottom: GPC-results of PFI]

![Image 3: top: absorption spectra of the EE fraction of PFI-βoc in solution and solid-state; bottom: GPC-results of PFI-βoc]

Characterization of PCI and PCI-βoc

![Image 4: top: Synthesis of PCI (R=H) and PCI-βoc (R=βoc); bottom: HOMO and LUMO energy levels of PCI and PCI-βoc]

Table: Fraction of PCI

<table>
<thead>
<tr>
<th>Polymer</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCI</td>
<td>-5.39</td>
<td>-3.46</td>
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<tr>
<td>PCI-βoc</td>
<td>-5.40</td>
<td>-3.30</td>
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![Image 5: top: absorption spectra of the DCM fraction of PCI in solution and solid-state; bottom: GPC-results of PCI]

![Image 6: top: absorption spectra of the EE fraction of PCI-βoc in solution and solid-state; bottom: GPC-results of PCI-βoc]

Conclusion and Outlook:

We have synthesized four different alternating donor-acceptor-type copolymers based on two scaffolds: indigo-dialkfluorene and indigo-dialkycyclopentadienothiophene. The high chemical stability of indigo and its derivatizes permitted its use under the reaction conditions of Suzuki and Stille-type cross couplings. When introducing βoc solubilizing groups at the indigo units a hypochromic shift in absorption spectra of PFI-βoc and PCI-βoc can be observed.

The application of the copolymers as donor component of organic solar cells will be tested in further experiments. Moreover a more detailed investigation of the optical properties is planned. For the optimization of overall yields and purification processes, an alternative synthesis of the 6,6′-dibromoindigo monomer will be explored.

References: