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Synthesis and Characterization of 5-Octylthieno[3,4-*c*]pyrrole-4,6-dione Derivatives As New Monomers for Conjugated Copolymers

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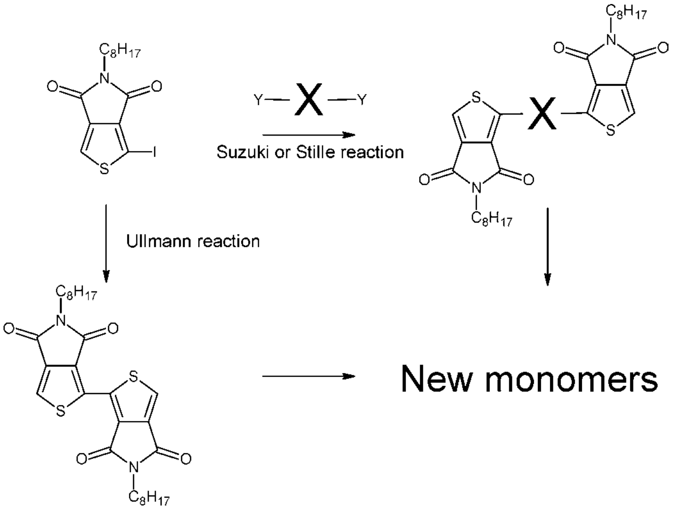
ABSTRACT



An efficient route for the synthesis of 1-iodo-5-octyl-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione as a key intermediate to build new electron-deficient monomers and related conjugated polymers is reported. Along these lines, two new low bandgap copolymers were synthesized from Stille or Suzuki coupling. These polymers were characterized and their properties compared to those of analogous conjugated polymers.

The synthesis of new low bandgap semiconducting polymers has become a very intense research field.[1] Recently, poly(thieno[3,4-*c*]pyrrole-4,6-dione), p(TPD), derivatives have attracted a lot of attention since they can lead to high-power conversion efficiencies when used as active components in bulk heterojunction (BHJ) solar cells.[2−6] Furthermore, the synthesis of the TPD unit is simple and its relatively low cost increases its potential for commercial applications. To expand its versatility and utility, we wanted to develop an

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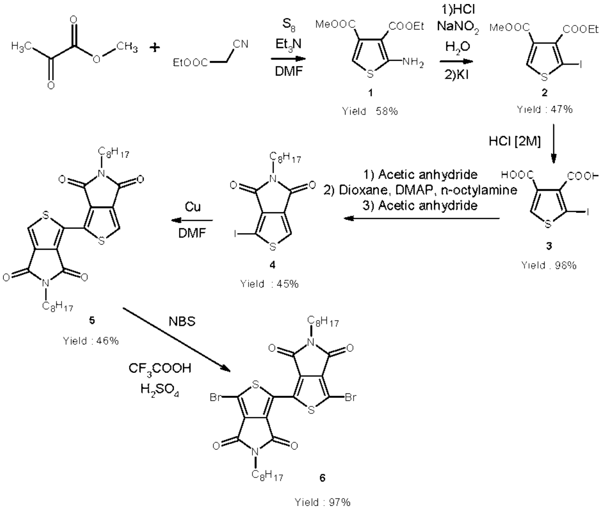
efficient methodology to synthesize new TPD derivatives. We believe that these new monomeric units should lead to fully conjugated polymers with lower LUMO, HOMO, and bandgap together with a better processability and stability.

TPD-based conjugated polymers were first reported by Tour et al. in 1997.[7] A few years later, Pomerantz et al. reported a study on a dimer of TPD.[8] Their synthetic procedures were based on the bromination of the TPD unit with 1 equiv of NBS. We tried to repeat these procedures but with limited success (see Scheme S6 in the Supporting Information). This is probably due to a reaction called halogen dance[9] that makes the conditions hard to control to obtain the desired product with a good yield. To keep the advantage of an easy synthesis of TPD derivatives, we decided to develop a new synthetic route based on a Gewald-type reaction.[10] This reaction allows compound **2** to form with an amine at the 2-position and two ester functions at the 3- and 4-positions. Those functions were strategically placed to reach our target **4** (see Scheme 1). Then, we substituted the amine of **2** by an iodide with a Sandmeyer-type reaction. To obtain **3**, we performed an hydrolysis, in acidic conditions, of the two ester functions. We finally closed the pyrroledione ring with the same conditions previouly used by Koeckelberghs et al.[11]

Scheme 1. Synthetic Route for 1-Iodo-5-octyl-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione and 1,1′-Dibromo-5,5′-dioctyl-[3,3′]bi[thieno[3,4-*c*]pyrrolyl]-4,6,4′,6′-tetraone



This approach has resulted in an efficient method to obtain the key intermediate **4**, which can then lead to the desired TPD dimers with an Ullmann reaction. To understand the solid-state behavior of TPD dimers, we elucidated the X-ray crystallographic structure of compound **5.**

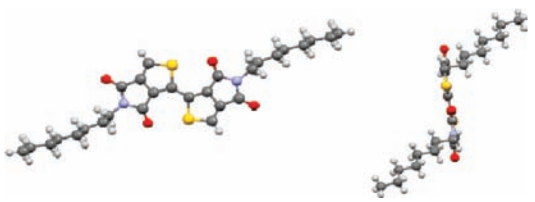
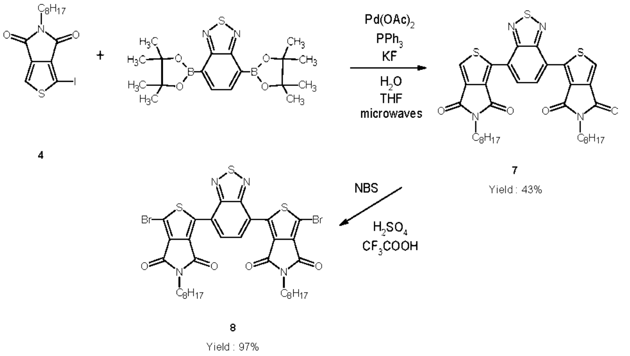


Figure 1. X-ray structure of compound **5**.

As seen in Figure 1, the dimer adopts an anti-coplanar conformation probably related to the formation of strong noncovalent interactions between the oxygen atoms and the sulfur atoms.[12] One can assume that such favorable interactions will exist into related polymeric structures, probably leading to better intermolecular interactions. Such electron-deficient units should also lead to lower LUMO energy levels and bandgaps together with a better processability due to the presence of solubilizing side chains.

Scheme 2. Synthesis of 1,1′-(2,1,3-Benzothiadiazole-4,7-diyl)bis(3-bromo-5-octyl-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione)



We envisioned that compound **4** can also be used to elaborate a large number of new conjugated monomers. For instance, we synthesized 4,4-di(3,3-dibromo-5-octylthieno[3,4-*c*]pyrrole-4,6-dione)benzodiathiadiazole (compound **8**) by performing a Suzuki cross-coupling reaction under microwave conditions on compound **4** followed by a bromination reaction (Scheme 2).

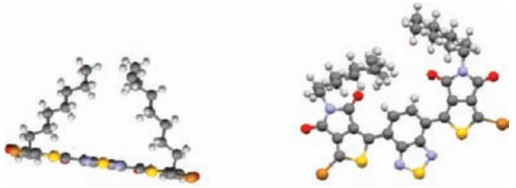


Figure 2. X-ray structure of compound **8**.

To understand the solid-state behavior of compound **8**, we solved its X-ray crystallographic structure. As seen in Figure

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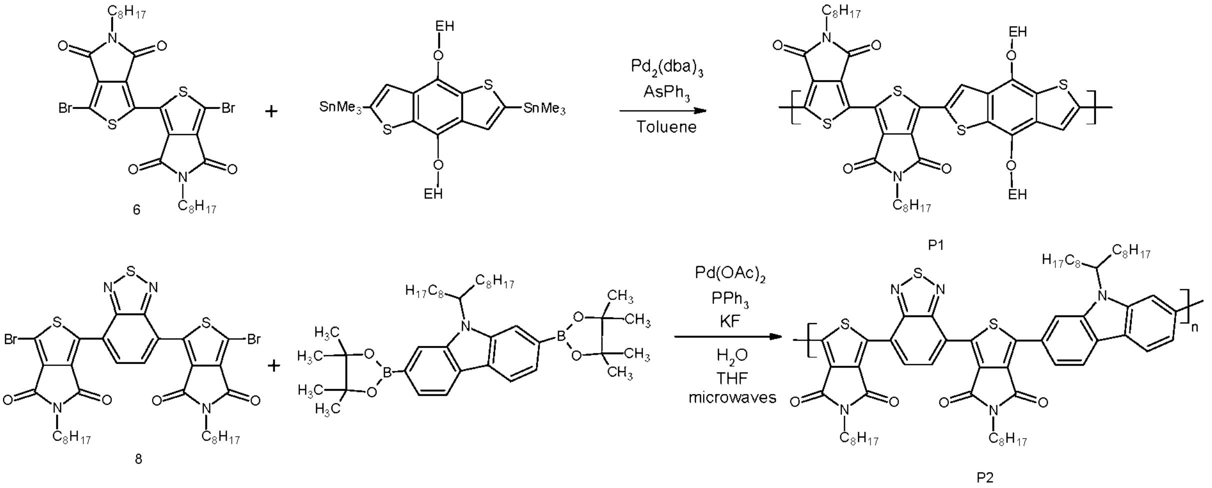
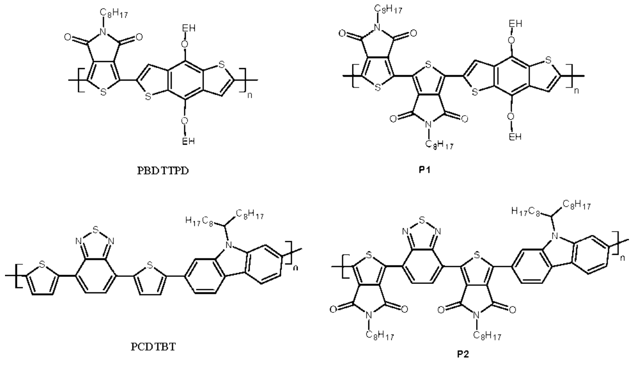
Scheme 3. Synthesis of **P1** and **P2**



2, **8** shows a coplanar conformation for the three conjugated moieties. It is highly possible that this conformation also would be present in a polymer material containing this unit. Both compounds **6** and **8** were then utilized to make two new low bandgap copolymers. We decided to prepare polymers **P1** and **P2** since their respective analogues, PBDTTPD[2−5] and PCDTBT,[13,14] have shown remarkable properties when used in BHJ solar cells. As discussed above, it is assumed that new **P1** and **P2** should exhibit better stability (lower HOMO), lower LUMO energy levels, and bandgaps. These properties could lead to good polymeric donors as well as allowing the design of new polymeric acceptors. As shown in Scheme 3, **P1** was synthesized by Stille coupling whereas **P2** was obtained through a Suzuki reaction.

P1 and **P2** were then characterized and their properties were compared with those previously reported for PBDTTPD and PCDTBT (Scheme 4). **P1** and **P2** are thermally stable up to 456 and 330 °C, respectively. We observed a glass transition at 178 °C for **P1** and at 206 °C for **P2**. No crystallization and melting peaks were observed for **P1** and **P2**.

Scheme 4. The New Conjugated Polymers **P1** and **P2** and Their Respective Analogues



We measured a M_n of 29 000 g/mol and M_w of 70 000 g/mol for **P1** and a M_n of 6 200 g/mol and M_w of 16 000 g/mol for **P2**. The optical and electrochemical properties of **P1** and **P2** (Table 1) were determined in parallel with their analogues. In the case of **P2**, we observed a lower bandgap than that reported for PCDTBT by about 0.1 eV. Adding the BTPD instead of the TPD in **P1** has a significant influence on the LUMO and a slight one on the HOMO energy level. Although **P2** and PCDTBT have comparable bandgaps, the HOMO and LUMO orbitals of the former are considerably lower (0.47 eV for the HOMO and 0.54 eV for the LUMO). This kind of substitution can be really useful for a fine-tuning of the electronic properties of various conjugated polymers.

Table 1. Electronic Properties of **P1**, **P2**, and Their Analogues Obtained by Cyclic Voltemperometry and UV−Vis (see Figures S1−S4, Supporting Information)

			bandgap (eV)	
polymers	HOMO (eV)	LUMO (eV)	electrochemical	optical
P1	−5.57	−3.94	1.63	1.67
PBDTTPD	−5.64	−3.83	1.81	1.81
P2	−5.98	−4.13	1.85	1.85
PCDTBT	−5.51	−3.59	1.92	1.89

In conclusion, a new efficient synthetic route was elaborated for the preparation of the 1-iodo-5-octyl-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione. From this building block, we were able to expand the TPD-based copolymer family. Two new polymers were compared to their analogues and show significant modulation of the energy levels. In our future

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work, we will test these materials in BHJ solar cells as donors and acceptors. We will also synthesize a full series of derivatives to continue to expand the TPD-based copolymer family.

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Supporting Information Available: Experimental procedures, electrochemical measurement, spectroscopic data, NMR spectra, and X-ray crystallographic details. This material is available free of charge via the Internet at http://pubs.acs.org.

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