Angewandte
Chemie

DOI: 10.1002/ange.201400674

Organic Solar Cells

Twisted but Conjugated: Building Blocks for Low Bandgap Polymers**

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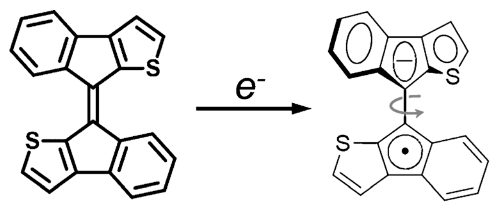
Abstract: *Here we report a novel twisted monomer based on a distorted C=C double bond for low bandgap conjugated copolymers. This new building block provides several unique characteristics when compared to classical planar systems such as high solubility, electron accepting ability, and isomeric tunability. The resulting copolymers exhibit broad absorption spanning both visible and near-infrared regions leading to promising solar cell performance.*

In the last decade, significant attention has been focused on organic solar cells (OSCs) for cost effective manufacturing of photovoltaics on large area and flexible substrates.[1,2] Traditionally, a bulk-heterojunction (BHJ) architecture is employed, with a p-type conjugated polymer in conjunction with a fullerene-based small molecule as the n-type material.[3–9] Over the last decades, various building blocks have been developed for preparation of conjugated polymers with the most recent activity being directed towards the preparation of low bandgap ($E_g < 1.5$ eV) systems.[10–20] In these systems, the conjugated polymers are derived from flat, planar aromatic monomers with large solubilizing groups attached to enhance processibility. In breaking with this restricted view of building block design for conjugated polymers, the development of novel monomers that are non-planar and have interesting electronic properties are highly desirable. Examples of crowded alkenes were initially reported by Feringa[24] as molecular switches and a similar concept also offers the opportunity to prepare new structures with improved properties and performance in polymer-based solar cells and organic electronics.[21–26]

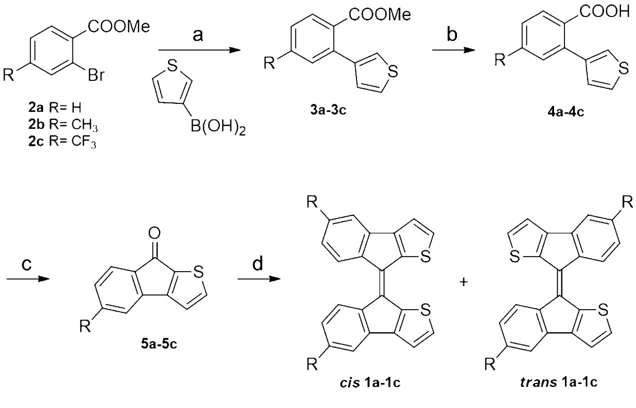
To address this challenge we report a novel, twisted monomer family based on a distorted C=C double bond. The inspiration for this work is a report describing electron-accepting materials based on 9,9′-bifluorenylidene (99′BF).[27] From these studies, 99′BF-based materials were found to readily accept electrons due to the relief of steric strain and the fulfillment of the 14-π-electron rule, making them candidates to replace PCBM (phenyl-C_{61}-butyric acid methyl ester) as the acceptor in organic solar cells. With P3HT (poly(3-hexylthiophen-2,5-diyl)) as the donor material, solar cells with 1.7% power conversion efficiency (PCE) and an open circuit voltage (V_{oc}) of 1.20 V were obtained.[28] The potential of 99′BF as a small molecule, n-type material strongly suggested that the concept of non-planar building blocks could be applied to the development of a broad monomer platform for conjugated polymers. Here we report the synthesis, properties, and polymerization of a new class of building blocks based on 8,8′-biindeno[2,1-*b*]thiophenylidene (BTP, **1a**, in Figure 1), for application as low bandgap polymers in BHJ solar cells.



1a

Figure 1. Chemical structure of (*E*)-8,8′-biindeno[2,1-b]thiophenylidene (*trans*-BTP, **1a**) and the formation of its radical anion after the addition of one electron.

An attractive feature of the bis(thiophene) analog, BTP, when compared to the 99′BF system is the ability to use well established chemistry for the introduction of functional groups to the thiophene rings. As shown in Scheme 1, synthesis of BTP derivatives proved to be a facile process from readily available starting materials. Initial Suzuki–Miyaura coupling of methyl 2-bromobenzoate, **2a**, and 3-thiopheneboronic acid is followed by ester hydrolysis and Friedel–Crafts ring closure to afford the ketone **5a** as a bright yellow solid. Treatment of the aryl ketone with Lawesson's



Scheme 1. Synthesis of BTP and its derivatives (**1a–1c**). a) Na_2CO_3, $[Pd(PPh_3)_2Cl_2]$, THF/H_2O; b) NaOH, H_2O/EtOH; c) oxalyl chloride, CH_2Cl_2 and then $AlCl_3$; d) Lawesson's reagent, toluene.

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[**] We thank the National Science Foundation (MRSEC program, DMR 1121053) and the Mitsubishi Chemical Company (Mitsubishi Chemical Center for Advanced Materials) for financial support and Dr. Guang Wu for performing single-crystal X-ray diffraction measurements.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201400674.

reagent yields the parent BTP derivative, **1a** (R = H), in excellent yield as a mixture of *cis*- and *trans*-isomers. A significant advantage of this synthetic strategy is the modularity which allows a wide range of substituted 2-bromobenzoates and thiophene derivatives to be used. To illustrate this feature, the methyl and trifluoromethyl derivatives, **1b** and **1c** respectively, were also prepared in high yields (Scheme 1).

An intriguing facet of the dimerization reaction with Lawesson's reagent is the generation of two regioisomers, one with thiophenes on opposite sides (*trans*-BTP) and the other with thiophenes on the same side (*cis*-BTP). Experimentally, the ratio of *trans* to *cis* isomer was found to be ca. 2 to 1; presumably the more abundant *trans* isomer is the thermodynamic product since steric repulsion between the proximal C-H's of the two benzene rings is avoided. Derivatives **1b** and **1c** were also shown to be a mixture of *cis*- and *trans*-isomers, albeit with slight different ratios, 1.6:1 for **1b** and 2.6:1 for **1c**. The purified isomers could be isolated by recrystallization (*trans*) or flash chromatography (*cis*) with the isomers showing distinct sets of ^{1}H and ^{13}C NMR signals, indicating different electronic environment resulting from the dissimilarity in chemical structures (Figure 2).

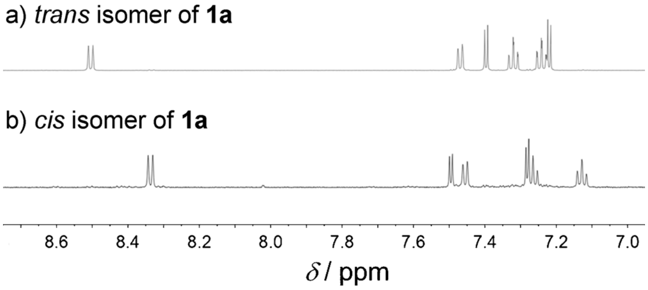


Figure 2. ^{1}H NMR spectra of BTP, **1a**, showing two distinct isomers, a) purified *trans* isomer and b) purified *cis* isomer.

Final confirmation of isomer structure was obtained by single-crystal X-ray diffraction studies of the *trans*-BTP derivative (Figure 3). From single-crystal X-ray diffraction analysis, the *trans* isomer has a twisted structure, presumably resulting from the congestion between proximal aromatic rings with the splay angle between the thiophene and benzene rings being ca. 20° (Figure 3a). Within a monoclinic lattice, these nonplanar molecules stack themselves in a fully eclipsed fashion with an intermolecular distance of about 3.5 Å and a short sulfur–sulfur distance of about 3.4 Å (Figure 3b). Significantly, this twisted, nonplanar structure leads to BTP derivatives having good to excellent solubility in common solvents, such as acetonitrile, ethyl acetate, tetrahydrofuran and dichloromethane.

Having developed a facile synthetic approach to twisted, bis(thiophene) derivatives, **1a–c**, the electronic and physical properties of this novel family of building blocks was examined. The ability to accept two electrons, presumably favored by release of steric strain from proximal aromatic rings and development of a 14-π electron system was studied by cyclic voltammetry (CV) measurement which shows two clear reversible reduction waves (Figure S1 in the Supporting Information). The first reduction wave could be attributed to the formation of the radical anion with the second corresponding to formation of the dianion.[29] Using ferrocene as the internal standard, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for **1a** were calculated to be −5.55 eV and −3.45 eV (cf. PC$_{61}$BM −3.8 eV) with a bandgap E_g^{CV} = 2.10 eV. Further investigation using CV reveals lower bandgaps for the substituted BTP derivatives; **1b** has a bandgap of 2.06 eV while introduction of trifluoromethyl groups further decreases the bandgap of **1c** to 1.95 eV (Figure 4a). A similar trend is observed in the UV/Vis absorption spectra of **1a–1c** with all derivatives showing a broad absorption extending to

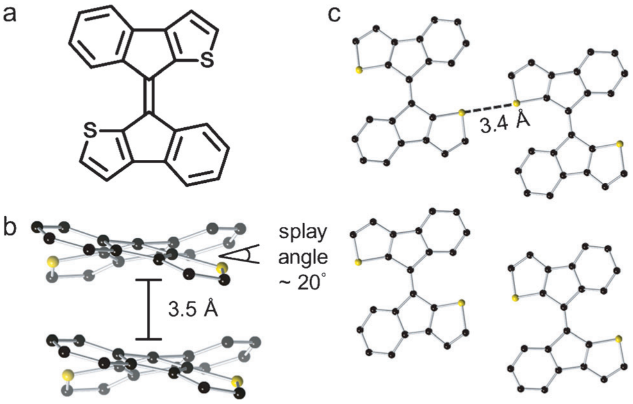


Figure 3. a) Chemical structure of **1a**: b) side view of *trans*-BTP molecules, **1a**, in the crystal structure with a splay angle about 20° between proximal benzene and thiophene rings. The intermolecular distance is about 3.5 Å. b) BTP molecules arrange in monoclinic fashion with a close intermolecular sulfur–sulfur distance about 3.4 Å.

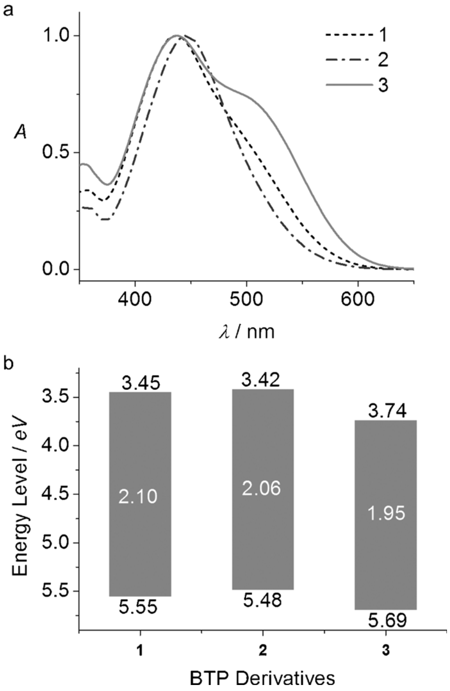
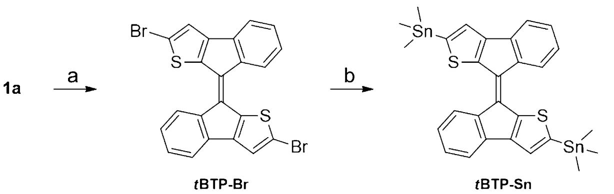


Figure 4. a) UV/Vis absorption spectra of **1a–1c**. b) HOMO, LUMO and bandgap of **1a–1c**.

600 nm with optical bandgaps estimated from the onset of absorption matching well with those determined from CV measurement (Figure 4b). Significantly, it was found that the purified *trans-* and *cis-* isomers, for each BTP derivative show essentially the same absorption and electrochemical profile which demonstrates the utility of BTP as a building block platform for the preparation of low bandgap conjugated polymers.

Synthetically, a key advantage of incorporating thiophene units into the BTP structure is the facile functionalization of the 2-position of the thiophene rings. In analogy with standard thiophene chemistry, dibromination and subsequent stannylation of **1a** proved to be essentially quantitative reactions which allow monomers suitable for metal-catalyzed polymerization to be easily prepared (Scheme 2). It is worth noting that when the pure *cis*-isomer, or the mixture of isomers (*trans*:*cis* ≈ 2:1), was subjected to bromination using *N*-bromosuccinimide (NBS), significant isomerization was observed with the brominated product being obtained with a *trans*:*cis* ratio of ca. 7:1 with pure *cis-* or *trans*-derivatives being isolated by recrystallization (Figure S3). This observation is consistent with radical-catalyzed isomerization of the strained double bond during bromination of the thiophene rings.[30]

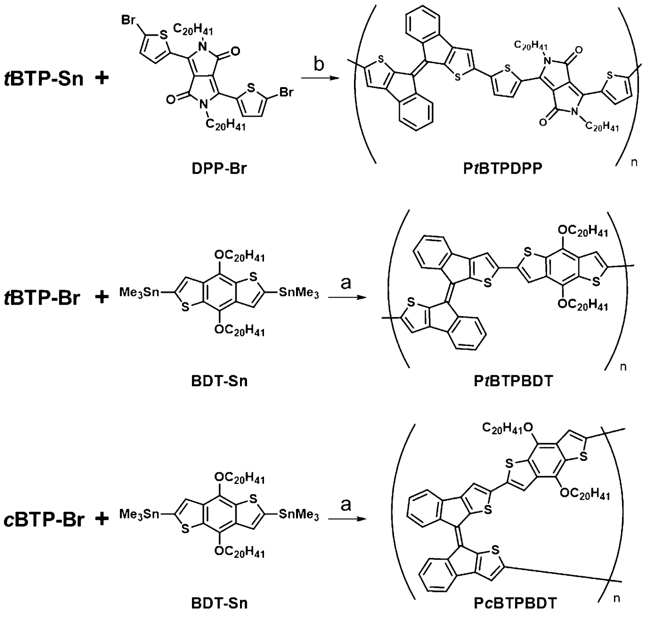


Scheme 2. Synthesis of brominated *trans*-BTP (*t*BTP-Br) and stannylated *trans*-BTP (*t*BTP-Sn). a) NBS, DCM; b) *n*BuLi, hexane and then $SnMe_3Cl$, THF.

Low bandgap conjugated polymers were then prepared from both the *trans-* and *cis*-BTP derivatives by copolymerization with the appropriately functionalized diketopyrrolopyrrole (DPP) and benzodithiophene (BDT) monomers by Stille coupling (Scheme 3). While polymer growth was slower and reached substantially lower molecular weights for the *cis*-isomer when compared to the *trans*-isomer, high molecular weight materials were prepared in all cases (Table 1). From a structural viewpoint, the reduced reactivity of the *cis*-isomer is understandable given the “kinked” nature of the resulting repeat unit. Optical properties for the BTP-based copolymers were then investigated by UV/Vis spectroscopy in both solution and as spin-coated films (Figure 5 and Table 1).

Table 1: GPC and photophysical properties of both BTP-based copolymers.

Polymer	M_n [kDa]	M_w [kDa]	PDI	λ_{max} [nm] *Solution*	*Film*	λ_{onset} [nm] *Solution*	*Film*	E_g^{opt} [eV, *film*]
P*t*BTPDPP	27.0	49.5	1.83	881	890	982	1020	1.21
P*t*BTPBDT	70.1	133	1.89	735	742	835	845	1.46
P*c*BTPBDT	27.0	70.0	2.58	735	735	835	837	1.48



Scheme 3. Synthesis of BTP-based conjugated polymers by Stille coupling. a) $[Pd_2(dba)_3]$, P(*o*-tol)$_3$, chlorobenzene; b) $[Pd_2(dba)_3]$, P(*o*-tol)$_3$, chlorobenzene, microwave reaction.

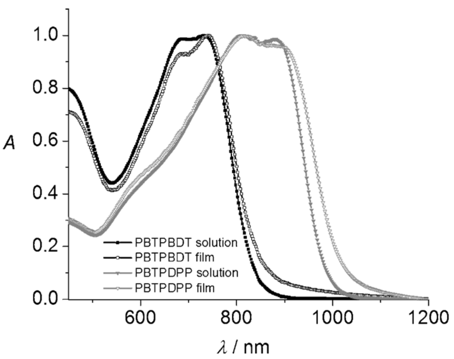


Figure 5. UV/Vis absorption of *trans*-PBTPBDT and *trans*-PBTPDPP in solutions and as-cast films.

Significantly, the introduction of the BTP unit gives rise to broad absorption covering the visible and near-IR region with the BTP-DPP copolymer (P*t*BTPDPP) displaying thin film absorption above 1100 nm. The optical bandgap estimated from the onset of absorption was determined to be 1.46 eV for P*t*BTPBDT and 1.21 eV for P*t*BTPDPP.

Photovoltaic performance was investigated with a conventional bulk-heterojunction device configuration of ITO/PEDOT:PSS/polymer:PCBM/Ca/Al and is summarized in Table 2. Although P*t*BTPDPP has a broad, strong near-infrared absorption which is required for harvesting the lower energy portion of solar spectrum, the highest power conversion efficiency with $PC_{61}BM$ was only 0.9% (Table 2). We infer that a low lying LUMO energy level for the copolymer impedes efficient charge carrier separation due to a LUMO mismatch with $PC_{61}BM$ (LUMO = −3.8 eV). In order to improve charge separation by

Table 2: Averaged solar cell device performance of *t*BTP-based copolymers.

Polymer	PCBM	DIO Ratio (v/v%)	Thickness [nm]	V_{oc} [V]	J_{sc} [mA cm^{-2}]	ff	η [%]
P*t*BTPBDT	PC$_{61}$BM	0	75	0.66	4.84	0.50	1.6
P*t*BTPBDT	PC$_{61}$BM	1.5	66	0.67	7.93	0.56	3.0
P*t*BTPBDT	PC$_{71}$BM	2.5	89	0.67	10.2	0.56	3.8
P*t*BTPDPP	PC$_{61}$BM	0	58	0.59	0.91	0.48	0.26
P*t*BTPDPP	PC$_{61}$BM	2	68	0.60	2.47	0.61	0.91

increasing the energy difference between LUMO levels, the DPP units was replaced with benzodithiophene (BDT) based monomers and copolymerization with **1a**, gave the desired P*t*BTPBDT systems. Using CV measurements to estimate the HOMO with LUMO calculated from the optical bandgap, it is determined that P*t*BTPDPP has HOMO = −5.07 eV and LUMO = −3.86 eV and P*t*BTPBDT gives HOMO = −5.09 eV and LUMO = −3.63 eV. As a result, solar cells based on the *trans*-isomer of PBTPBDT gave an initial power conversion efficiency of 1.6%; with the addition of diiodooctane (DIO) as a process additive resulting in a significant improvement in performance with $\eta = 3.0\%$, $V_{oc} = 0.67$ V, $J_{sc} = 7.9$ mA cm^{-2} and $ff = 0.56$ (Figure 6a). This improvement correlates with changes in the film morphology from large sub-micrometer domains without DIO to a fine nanoscale morphology with DIO (Figure S4). In addition, the external quantum efficiency (EQE) curve in Figure 6b shows that P*t*BTPBDT has substantial contribution in photo current generation between 500 nm to 850 nm. Further increase in performance was observed on changing the acceptor to PC$_{71}$BM with a non-optimized averaged power conversion efficiency of 3.8% which corresponds to an increase in J_{sc} from 7.9 mA cm^{-2} to 10.2 mA cm^{-2} (Figure 6a).

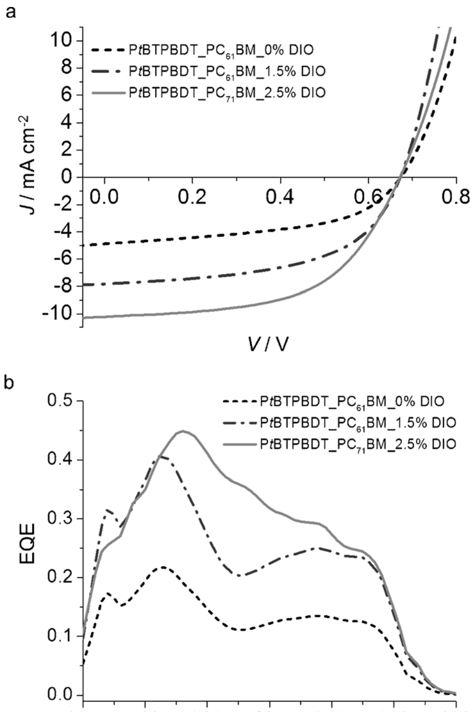


Figure 6. a) Current–voltage curves of PBTPBDT polymer solar cell devices with and without DIO additive under AM 1.5G illumination. The device structure is ITO/PEDOT:PSS/*trans*-PBTPBDT):PC$_{61}$BM (1:2 weight ratio)/Ca/Al. Polymer solution was prepared in chlorobenzene. b) EQE curve for Figure 6a, devices prepared from mixtures of chlorobenzene and 0.0–2.5% (v/v) DIO.

For these materials based on a distorted double bond, a fundamentally important control is the direct comparison with the corresponding regioisomer prepared using the *cis*-BTP isomer and BDT. In the UV/Vis spectroscopy, the peak wavelength is identical in both solution and solid state while the onset wavelength is slightly higher in film than that in solution. In solar cells, the performance was significantly reduced when compared to the *trans* derivative with the best device characteristics having $\eta = 1.2\%$, $V_{oc} = 0.61$ V, $J_{sc} = 3.6$ mA cm^{-2} and $ff = 0.54$. It is proposed that this clear difference in performance is the result of a major change in polymer conformation on going from the linear, *trans*-BTP unit to the kinked, *cis*-BTP units, significantly reducing intermolecular charge transport. This effect might also reflect on the photophysical properties based on UV/Vis absorption measurements. A difference is also observed in the thin film morphology with the overall result being a low J_{sc} and associated low efficiency (Figure S5).[31]

In conclusion, we have synthesized and characterized a new class of isomeric building blocks for low bandgap conjugated polymers based on a distorted C=C double bond. A major advantage of these *cis*- and *trans*-BTP derivatives is their ease of synthesis and modular structure which allows a wide range of BTP-based materials to be prepared for organic electronics applications. While non-planar, the twisted nature of these repeat units still allows for conjugation along the polymer backbones with broad visible and near-infrared absorbance and inherent high solubility. Direct comparison of materials prepared from the *cis*- and *trans*-isomers reveals superior performance in organic solar cell devices for the *trans*-based systems with preliminary results showing a power conversion efficiency of 3.8%. These results demonstrate the design of new monomers that deviate from the accepted view of conjugated polymer building blocks and offer the opportunity to prepare new structures with improved properties and performance for the broad field of polymer-based solar cells and organic electronic.

Received: January 21, 2014
Published online: March 6, 2014

Keywords: building blocks · electron acceptors · low bandgap · polymers · solar cells

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