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"Semi-Random" Multichromophoric rr-P3HT Analogues for Solar Photon Harvesting

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S Supporting Information

The vision of organic photovoltaics is that of a low-cost solar energy conversion platform that provides lightweight, flexible solar cells that are easily incorporated into the existing infrastructure.[1] Organic solar cells have thus been a subject of growing research interest over the past decade, and published champion level efficiencies have rapidly improved from 2.5% in 2001[2] to nearly 8% in 2010.[3] However, it is generally agreed that further increases in efficiency (>10%) will be required before these organic solar cells can become competitive with their inorganic counterparts.

The efficiency of organic solar cells is defined as $\eta = (J_{sc}V_{oc}FF)/P_{in}$, where P_{in} is the input power in the form of solar radiation and the output parameters are J_{sc} as the short-circuit current density, V_{oc} as the open-circuit voltage, and FF as the fill factor. It is clear that in order to maximize the efficiency of organic solar cells these three output parameters need to be optimized. A design principle that has been frequently used to increase the V_{oc} is based on the empirical correlation that its magnitude is directly related to the magnitude of the energetic difference between the HOMO of the donor and the LUMO of the acceptor and that by lowering the HOMO of the donor the V_{oc} can be increased.[4] Fill factors, on the other hand, can be mainly attributed to improved active layer morphologies (balanced charge transport) and extensive device optimizations[5] and are approaching (or exceeding) 70%.[3,6−8] Finally, J_{sc} is related to the product of absorption intensity and breadth of spectral absorption of the active component, where the broader the wavelength range of light that can be absorbed, the greater the number of photons that can be harvested and potentially lead to charge carriers and a higher J_{sc}.[9] Despite the correlation between light absorption and the J_{sc}, most polymers used in currently high performing solar cells have limited absorption breadths and relatively large band gaps.[3,6,10,11] This leads to a heavy reliance on fullerenes (especially $PC_{70}BM$) to absorb photons in the short wavelength range as well as considerable absorption losses in longer wavelength regions.[12] Although fullerenes absorb in the short wavelength region and are thus complementary to many polymers, evidence exists that 60% of excitons formed in the $PC_{61}BM$ phase decay before being harvested and do not contribute to J_{sc}.[13]

In order to achieve longer wavelength absorption, the donor—acceptor approach is frequently applied, in which a perfectly alternating pattern of electron-rich and electron-poor monomer units is used in the backbone to obtain polymers with low band gaps.[14] Fewer papers take an alternate approach to low-band-gap polymers by using a random sequence of electron-rich and electron-poor monomers instead of the mentioned perfectly alternating structure.[15−18] Most commonly in this random approach, two donor monomers are copolymerized with one acceptor monomer and the donor monomers can alternate with the acceptor as well as with each other.[15−17] To the best of our knowledge, only one example is known where two different acceptors are polymerized with one donor monomer to give a random polymer structure.[18] Many of these random copolymers show a considerably broadened absorption and/or two distinct absorption peaks in the short and long wavelength regions, illustrating the large potential of random polymer structures to increase J_{sc} in the future.

Here we introduce a new family of *semi-random* alkylthiophene-based copolymers, which broadly absorb sunlight due to the randomized incorporation of small amounts of acceptors in the polymer backbone. The so-called semi-random structure is defined by a random polymerization that is based on a restricted linkage pattern of the monomers due to regiospecific placement of the reactive functional groups. As a consequence, the polymers are designed to retain a higher degree of structural order than purely random analogues. Scheme 1a illustrates the concept of semi-random polymers by showing a possible segment of one of the synthesized semi-random polymer chains (the synthetic scheme is illustrated in Scheme 1b). It can be seen that no repeat unit can easily be defined because many different monomer sequences are possible, and as consequence multiple chromophores can be envisioned depending on the actual effective conjugation length of the polymer backbone. Scheme 1a schematically shows two possible chromophores as an example, with chromophore I consisting of pure regioregular poly(3-hexylthiophene) (P3HT) and thus absorbing at shorter wavelengths and chromophore II containing acceptor monomer benzothiadiazole (BTD) which lowers the band gap, allowing absorption of low-energy photons. Semi-random copolymers are thus expected to have a broader absorption than perfectly alternating copolymers (which contain a single chromophore) because they contain multiple distinct chromophores, which can absorb in different regions of the solar spectrum. Semi-random copolymers are chosen over random copolymers because they allow better control over the polymer structure and still offer the advantage

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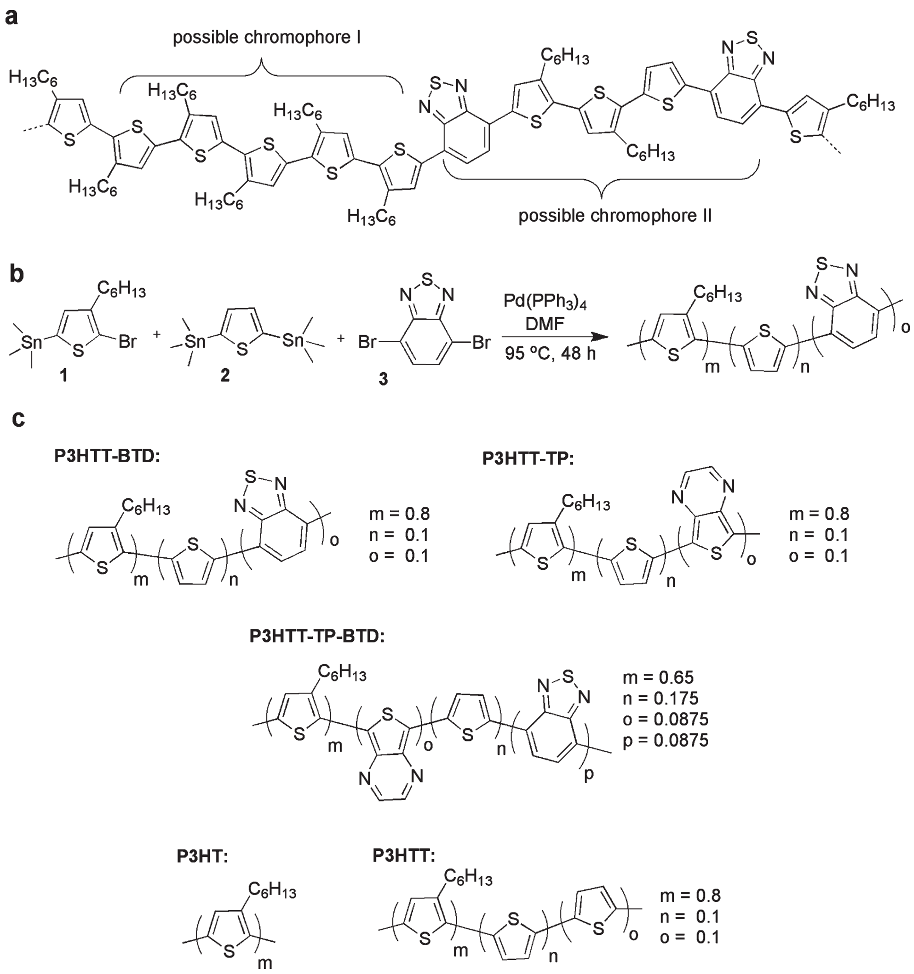
Scheme 1. Concept of Multichromophoric Semi-Random Copolymers (a) and a Representative Synthetic Scheme (b) along with the Structures of the Described Polymers (c)



of multiple chromophores. Additionally, semi-random copolymers are designed to favor short-range crystallinity (whereas random copolymers tend to be amorphous solids[16,18]) over long-range crystallinity which is known to be advantageous in the case of regioregular P3HT, where a reduction in regioregularity prevents large-scale phase separation between the polymer and fullerene but still allows high hole mobility.[19,20]

The design of this novel class of polymers is based on P3HT in order to capitalize on the attractive properties of this well-known conjugated polymer. P3HT shows a good miscibility with fullerenes, forms bicontinuous networks with PCBM after thermal annealing, and is semicrystalline, which leads to high hole mobilities.[7] Additionally, composites with PCBM show very good long-term stability, which is important for commercial success of organic solar cells.[21,22] The major weakness of P3HT, the narrow spectral absorption breadth from 350 to 650 nm (limiting J_{sc} to a theoretical maximum of ~14.3 mA/cm^2),[9] is solved in our approach by copolymerizing with a small amount of acceptor monomers. Multiple acceptors can be easily used in semi-random conjugated polymers to adjust the band gap and position of the HOMO and LUMO energies while still retaining a polymer backbone that is P3HT-like.

Several papers are worth mentioning here as they are related to polymer structures synthesized in this work (Scheme 1c). The polymers of Li et al.[17] show similarity to the structures in Scheme 1c as they contain similar monomer units as well as randomized structures but differ from the polymers present here in several critical aspects. Most importantly, use of 2,5-dibromo-3-hexylthiophene as a monomer in the work of Li et al. does not allow for the formation of hexylthiophene—hexylthiophene bonds and also prevents any control over regioregularity in the polymers. In contrast, the use of the 2-bromo-5-trimethylstannyl-3-hexylthiophene monomer (**1**) in our case ensures the formation of head-to-tail 3-hexylthiophene sequences in the polymer. In addition, the content of hexylthiophene in the polymers published by Li et al. is considerably lower than in the present case (25—30% vs 65—80%, respectively). As a consequence, the semi-random copolymers we report here are unique and are regioregular P3HT analogues, which represent a simple perturbation of the regioregular P3HT structure but maintain critical elements of the polymeric structure. In comparison, several other examples are known of polymers containing extended oligothiophene segments, which are copolymerized with an acceptor monomer to give perfectly alternating polymer structures. These polymers tend to be crystalline and generally show broadened absorption spectra but have the disadvantage of complicated and lengthy monomer synthesis contrasting with our approach of using a simple synthetic procedure to obtain P3HT-like semi-random donor—acceptor copolymers.[23−25]

Table 1. Molecular Weights (PDIs), Electrochemical HOMO Values, Optical Band Gaps, and SCLC Mobilities of Synthesized Polymers

	M_n, g/mol (PDI)[a]	HOMO[b] (eV)	E_g (optical)[c] (eV)	SCLC hole mobility ($cm^2 V^{-1} s^{-1}$)
P3HT	17 178 (2.74)	5.17	1.91	2.30×10^{-4} [d]
P3HTT	47 853 (1.75)	5.29	1.96	8.21×10^{-5} [e]
P3HTT-BTD	15 308 (2.45)	5.41	1.62	2.06×10^{-4} [f]
P3HTT-TP	16 683 (2.35)	5.23	1.36	2.50×10^{-4} [e]
P3HTT-TP-BTD	16 320 (2.05)	5.11	1.27	2.35×10^{-4} [g]

[a] Determined by GPC with polystyrene as standard and *o*-DCB as eluent. [b] Cyclic voltammetry (vs Fc/Fc$^+$) in acetonitrile containing 0.1 M TBAPF$_6$. [c] Optical band gaps from onset of absorption in UV−vis spectra in films. [d] Spin-cast from CB, postannealed (after Al deposition) at 150 °C for 60 min under N$_2$. [e] Spin-cast from DCB, preannealed (before Al deposition) at 100 °C for 10 min under vacuum. [f] As cast from DCB. [g] Spin-cast from CB, preannealed (before Al deposition) at 100 °C for 30 min under vacuum.

We have designed polymers with a number of structural features in mind. First, monomers for semi-random Stille polymerization shown in Scheme 1b are carefully chosen to inherently avoid sterically unfavorable linkages. Reaction of the monomer 2-bromo-5-trimethyltinhexylthiophene (**1**) with itself gives head-to-tail P3HT, which is desirable for efficient solar cells and is illustrated in chromophore **I** in Scheme 1a. Scheme 1b also shows that acceptor monomers such as 4,7-dibromo-2,l,3-benzothiadiazole (**3**) can only react with donor monomers (**1** or 2,5-bis(trimethyltin)thiophene (**2**)) but not with themselves, which avoids large (insoluble) segments of acceptor in polymers. These restrictions in monomer connectivities help to overcome some of the limitations random copolymers have, namely, an amorphous morphology and likely low hole mobilities as a consequence.[16,18] Second, as can be seen in Scheme 1c, between 65% and 80% of 2-bromo-5-trimethyltinhexylthiophene (**1**) is used in the polymer chains in order to retain the favorable properties of P3HT. Third, the amount of acceptor is kept small (between 10% and 17.5%), but the strength of acceptors is varied from the weaker acceptor benzothiadiazole (BTD) to the strong acceptor thienopyrazine (TP) and finally a combination of the two acceptors in order to tune the energy levels.

Scheme 1b shows an example for the established semi-random Stille polymerization (using DMF as the solvent and Pd(PPh$_3$)$_4$ as the catalyst) which was used to synthesize polymers P3HTT-BTD, P3HTT-TP, and P3HTT-TP-BTD which are shown in Scheme 1c. The polymerization method is highly reproducible and independent of the order of mixing of reactants. Careful purification using a standard Soxhlet extraction followed by a filtration through Celite was used to obtain high-quality polymers. P3HT and P3HTT were made as reference polymers using the exact same polymerization conditions. The acronyms stand for poly(3-hexylthiophene)−thiophene (P3HTT) to take into account the additional nonalkylated thiophene ring in the backbone with the second part of the acronym indicating the respective acceptor(s) (TP = thienopyrazine and BTD = benzothiadiazole). For the synthesis of P3HTT-BTD, P3HTT-TP, and P3HTT-TP-BTD monomers **1** and **2** were copolymerized with the selected ratios of dibromobenzothiadiazole and/or dibromothienopyrazine (see Supporting Information). Molecular weights were determined by dissolving polymers in *o*-dichlorobenzene using GPC against polystyrene standards. The results are summarized in Table 1 and show that the molecular weights (M_n) are all in the same range (15 000−17 000 g/mol) with the exception of P3HTT. Integration via ^{1}H NMR indicates that composition of the polymers matches the monomer feed ratios (see Supporting Information).

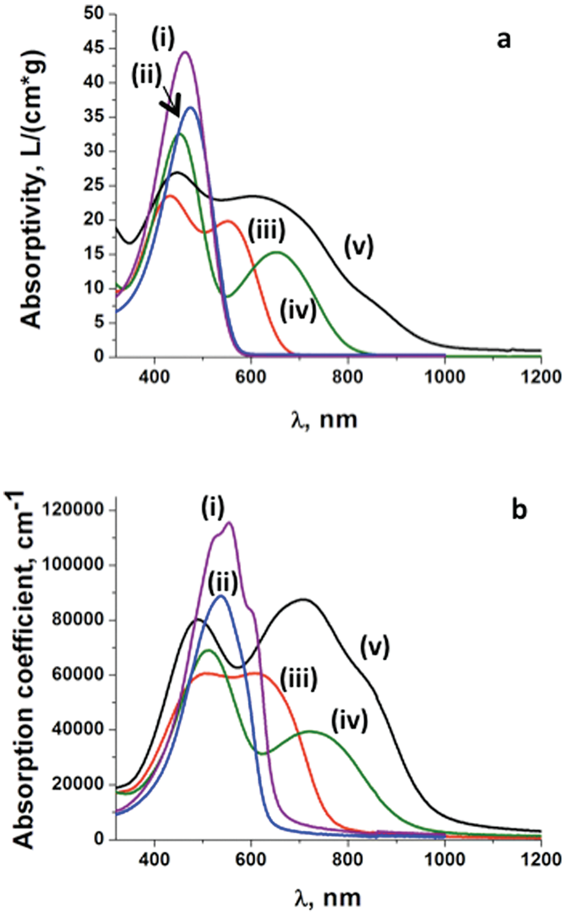


Figure 1. UV−vis absorption of all five polymers in (a) solution (*o*-dichlorobenzene or *o*-DCB) and (b) thin film (spin-coated from *o*-DCB and annealed for 30 min at 60 °C under N$_2$) where (i) is P3HT, (ii) is P3HTT, (iii) is P3HTT-BTD, (iv) is P3HTT-TP, and (v) is P3HTT-TP-BTD.

UV−vis absorption spectra were recorded for all five polymers in solution (*o*-DCB) and in annealed thin films. The results are summarized in Figure 1. As can be seen from the UV−vis absorption spectra, all three donor−acceptor semi-random copolymers have considerably broadened absorption spectra compared to P3HT and P3HTT. Red shifts of the absorption peaks when comparing solution spectra to thin film spectra are between 50 and 100 nm, which indicates ordering and planarization of the polymer chains in the solid state. The largest shift (103 nm) is observed for the long wavelength absorption peak of P3HTT-TP-BTD. In the solid state the area underneath the absorption curve of P3HTT-TP-BTD is nearly twice as large as for P3HT, which means that twice as many photons are absorbed in films of the same thickness and J_{sc} can potentially be much higher.[9] Because the absorption of P3HTT-TP-BTD blankets the whole visible region with a high absorption coefficient, it is a "black" polymer. The optical band gaps defined by the onset of absorption in the thin film spectra are summarized in Table 1 and are

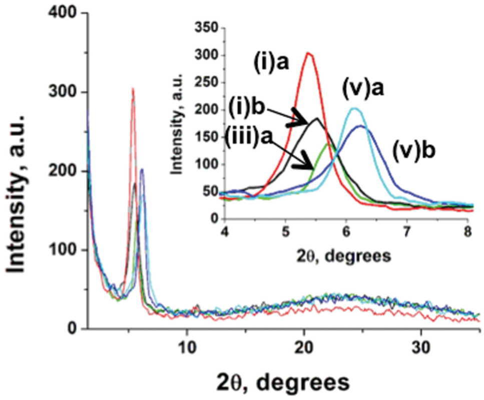


Figure 2. Grazing-incidence X-ray diffraction of thin films spin-coated from chlorobenzene (CB) before and after annealing at 150 °C for 30 min under N_2. The inset shows the region around $2\theta = 5°-7°$ in greater detail. Polymers shown are P3HT ((i)a, (i)b), P3HTT-BTD ((iii)a), and P3HTT-TP-BTD ((v)a and (v)b), where "b" stands for before annealing and "a" for after annealing.

considerably lower for the donor/acceptor copolymers than for P3HT.

In order to validate our concept that the semi-random approach allows the retention of attractive properties of P3HT, such as semicrystallinity, while broadening the absorption, the copolymers were analyzed by grazing-incidence X-ray diffraction (GIXRD). As can be seen in Figure 2, P3HT and P3HTT-TP-BTD exhibit peaks in the 2θ range of 5°−7°, without thermal treatment, which are referenced as (100) in relation to P3HT.[7] These peaks become even more pronounced after thermal annealing, which is evidence for increased crystallinity. P3HTT-BTD, on the other hand, only develops semicrystalline features after annealing at 150 °C. As has already been mentioned, this is different from random copolymers and a considerable advantage of the semi-random concept.[16,18] The interchain packing distance (100) for P3HTT-BTD is calculated as 15.6 Å and for P3HTT-TP-BTD as 14.4 Å (for comparison, we measured an interchain packing distance of 16.4 Å for P3HT).[7] Interestingly, P3HTT displayed a possible melting transition in DSC measurements (see Supporting Information) but showed no evidence of crystallinity in X-ray studies. P3HTT-TP, on the other hand, seems to be completely amorphous as neither X-ray nor DSC studies show any signs of crystallinity, which could however be due to nonoptimized processing conditions.

HOMO levels of the polymers were determined by cyclic voltammetry vs ferrocene, and the values are summarized in Table 1 (see Supporting Information for CV traces). P3HTT-BTD shows a considerably lower HOMO than P3HT (5.41 vs 5.17 eV), which is expected due to the electron-withdrawing effects of BTD. Interestingly, the HOMO level of P3HTT-TP-BTD (5.11 eV) is higher than the HOMO levels of both P3HTT-TP (5.23 eV) and P3HTT-BTD (5.41 eV) and close to the value measured for P3HT (5.17 eV).

Hole mobilities were determined using space-charge limit current (SCLC) method and are (except for P3HTT) extremely close to the hole mobility of P3HT (see Table 1 for values), which further validates the concept of these semi-random polymers. High hole mobilities are important in order to match the electron mobility of fullerenes and avoid space charge buildup which limits device performance.[26]

The goal of this Communication is the introduction of the concept of semi-random P3HT-like polymers that show broadened absorption; nevertheless, preliminary solar cell results are presented here, while rigorous optimization is currently underway. The photovoltaic properties of semi-random polymers were studied in bulk-heterojunction solar cells using $PC_{61}BM$ as the acceptor in a conventional device configuration of ITO/PEDOT:PSS/polymer:$PC_{61}BM$/Al. A detailed device fabrication process is described in the Supporting Information. All three donor−acceptor polymers exhibit promising preliminary photovoltaic properties under simulated AM 1.5G conditions (100 mW/cm^2). A peak power conversion efficiency (η%) of 0.71% was observed for the P3HTT-TP:$PC_{61}BM$ solar cells (polymer:$PC_{61}BM$, w/w 1:0.8) with a V_{oc} of 0.44 V, a J_{sc} of 3.22 mA/cm^2, and a FF of 0.50. The maximum efficiency of P3HTT-BTD:$PC_{61}BM$ (w/w 1:5) solar cells reaches 0.75% with a V_{oc} of 0.79 V, a J_{sc} of 2.87 mA/cm^2, and a FF of 0.33. P3HTT-TP-BTD:$PCB_{61}BM$ (w/w 1:0.8) showed an efficiency of 0.43% with a V_{oc} of 0.39 V, a J_{sc} of 3.04 mA/cm^2, and a FF of 0.37. For reference, P3HT-PCBM solar cells were found to give a peak efficiency of 3.89% with a V_{oc} of 0.59 V, a J_{sc} of 10.22 mA/cm^2, and a FF of 0.64. Further improvements in efficiency with these donor−acceptor polymers are targeted in the future via optimization of fabrication procedures with respect to solvent choice and annealing conditions as well as through the development of new structural analogues.

In summary, we have described a family of semi-random donor−acceptor copolymers based on regioregular P3HT. In our preliminary investigations, we have found that the attractive properties of P3HT are retained, and despite the randomized polymerization, semicrystalline polymers with high charge carrier mobilities are realized. In addition, broad and intense spectral absorption is achieved with only a limited content (10−17.5%) of acceptor units in the polymer backbone using a simple polymerization method based on easily synthesized monomers. Rigorous optimization of bulk-heterojunction solar cells based on these promising polymers is underway, along with more detailed characterization of the polymer electronic structures and synthesis of tailored structural analogues.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Synthetic and solar cell fabrication procedures, NMR, CV, DSC, and mobility data. This material is available free of charge via the Internet at http://pubs.acs.org.

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