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Semi-random vs Well-Defined Alternating Donor−Acceptor Copolymers

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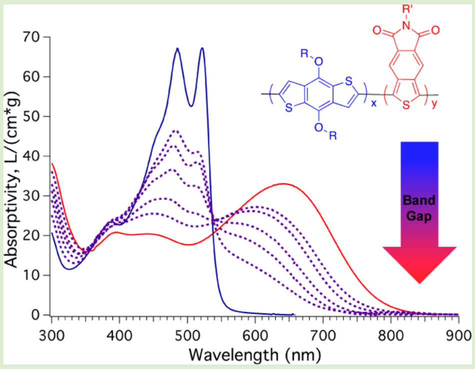
Supporting Information



ABSTRACT: The influence of backbone composition on the physical properties of donor−acceptor (D−A) copolymers composed of varying amounts of benzodithiophene (BDT) donor with the thienoisoindoledione (TID) acceptor is investigated. First, the synthesis of bis- and tris-BDT monomers is reported; these monomers are subsequently used in Stille copolymerizations to create well-defined alternating polymer structures with repeating (D−A), (D−D−A), and (D−D−D−A) units. For comparison, five semi-random D−A copolymers with a D:A ratio of 1.5, 2, 3, 4, and 7 were synthesized by reacting trimethyltin-functionalized BDT with various ratios of iodinated BDT and brominated TID. While the HOMO levels of all the resultant polymers are very similar, a systematic red shift in the absorbance spectra onset of the D−A copolymer films from 687 to 883 nm is observed with increasing acceptor content, suggesting the LUMO can be fine-tuned over a range of 0.4 eV. When the solid-state absorbance spectra of well-defined alternating copolymers are compared to those of semi-random copolymers with analogous D:A ratios, the spectra of the alternating copolymers are significantly more red-shifted. Organic photovoltaic device efficiencies show that the semi-random materials all outperform the well-defined alternating copolymers, and an optimal D:A ratio of 2 produces the highest efficiency. Additional considerations concerning fine-tuning the lifetimes of the photoconductance transients of copolymer:fullerene films measured by time-resolved microwave conductivity are discussed. Overall, the results of this work indicate that the semi-random approach is a powerful synthetic strategy for fine-tuning the optoelectronic and photophysical properties of D−A materials for a number of systematic studies, especially given the ease with which the D:A ratios in the semi-random copolymers can be tuned.

Conjugated polymers are an important class of materials for a number of organic electronic applications, including light-emitting diodes,[1] field effect transistors,[2] and organic photovoltaic (OPV) cells.[3−5] Band gap engineering has played a critical role in the development of new organic semiconductors for application in these fields, particularly for OPV, as polymer band gaps dictate photon absorption[6] and polymer energy levels influence open-circuit voltage[6,7] and charge separation in devices.[8,9] To this end, significant advances have been realized with the advent of the alternating donor−acceptor conjugated copolymer, wherein the electronic and optoelectronic properties of a material can be readily manipulated by tuning the individual electron donating (D) and accepting (A) components. However, the design parameters for new active layer OPV materials are quite complex,[10,11] and in addition to consideration of a polymer's absolute energy levels and band gap, the successful implementation of a new OPV polymer donor also requires consideration of nonenergetic parameters such as the size and density of solubilizing groups that influence polymer $\pi-\pi$ stacking,[12] polymer−fullerene intercalation,[13] nanoscale phase-separated morphologies,[14] etc.

With so many design variables affecting device performance, systematic studies have the best chance of fueling reliable progress in this field. However, even with the most methodical of studies, it can still be difficult to disentangle all the different contributions to device performance and establish hard and fast design rules for new polymers. Indeed, subtle structural changes to a D−A copolymer intended to simply modify optoelectronic properties can have profound unintended effects on morphologies, $\pi-\pi$ stacking, and polymer−fullerene intercalation that can be difficult to quantify.[15]

Recently, a new class of materials known as semi-random D−A copolymers was introduced, where variable amounts of acceptor units were randomly incorporated into a poly(3-hexylthiophene) (P3HT) backbone.[16] Monomer sequences were partially controlled by employing appropriate linking units on the donor and acceptor comonomers to prevent formation of acceptor−acceptor linkages. This strategy provided several advantages over perfectly alternating D−A copolymers. First,

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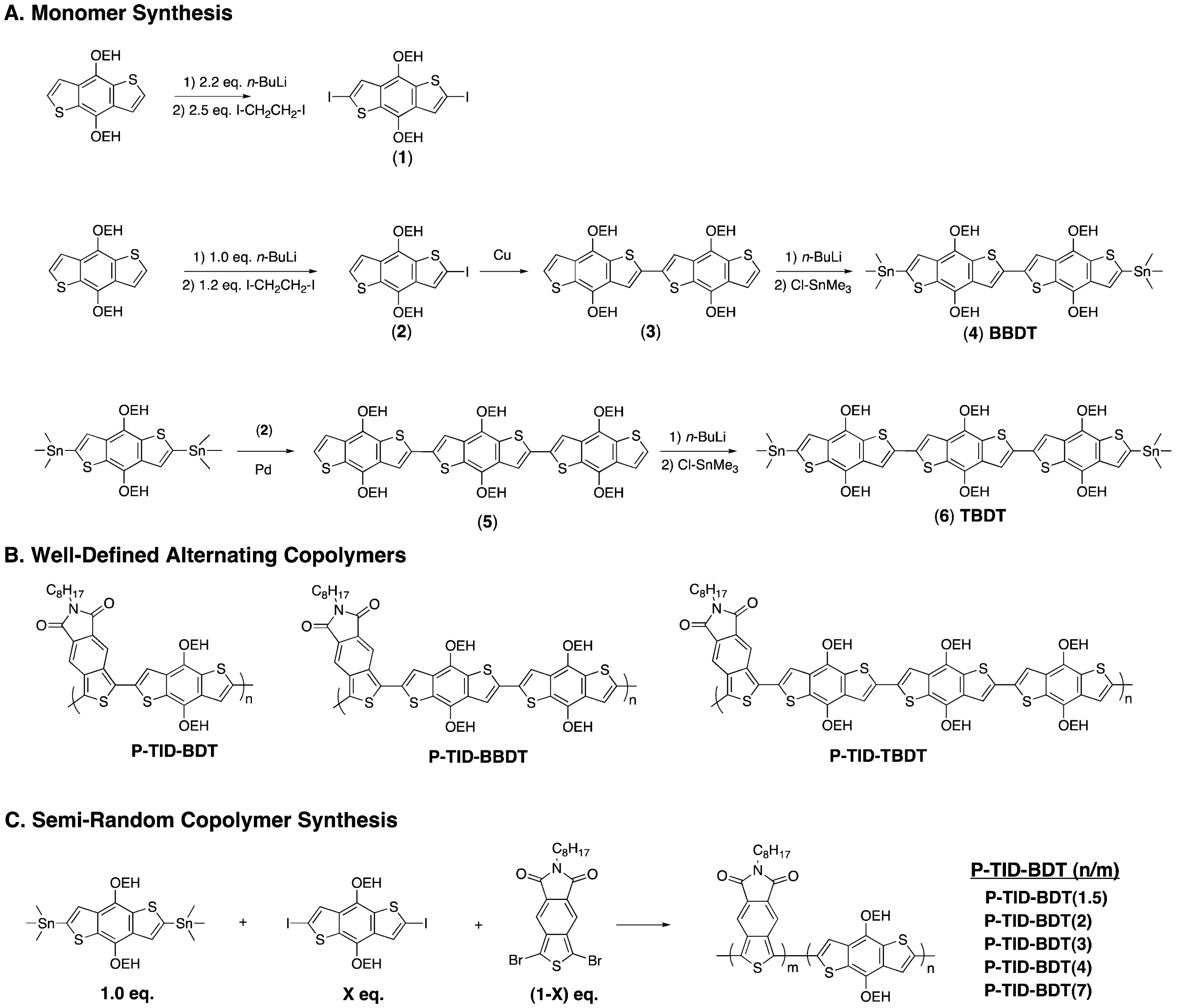
Scheme 1. (A) Synthesis of Benzodithiophene (BDT) Monomer Derivatives, (B) Semi-random Polymers Synthesized from Various Ratios of BDT Derivatives and Thienoisoindolodione (TID), and (C) Well-Defined Polymer Structures Synthesized from TID and Either Mono-, Bis-, or Tris-BDT



the low acceptor content of the semi-random copolymers of P3HT allowed many important properties of the P3HT homopolymer to be preserved, including semicrystallinity and high hole mobility. Second, some of the highest published values of short-circuit current densities among polymer solar cells have been reported for semi-random D−A copolymers.[17] This has been attributed to the polymer absorption profile. While the absorption spectrum for a perfectly alternating D−A copolymer often merely red-shifts relative to the pure homopolymer, absorption of the semi-random material truly broadens across the visible and near-infrared regions. This broad absorption effectively increases photon harvesting from the solar spectrum, resulting from the randomized sequence distribution of the D−A components that generate numerous possible chromophores defined by effective conjugation length.

To date, the literature reports for these semi-random D−A materials consist predominantly of thiophene donor units copolymerized with various acceptor or donor units,[16−20] which was done specifically to retain some of the aforementioned beneficial properties of P3HT in OPV devices. Here, we expand upon this original concept by copolymerizing the benzodithiophene (BDT) donor with the thienoisoindolodione (TID) acceptor in a semi-random fashion to generate five new semi-random D−A copolymers. Materials with a D/A ratio of 1.5, 2, 3, 4, and 7 were synthesized by reacting trimethyltin-functionalized BDT with the appropriate ratios of iodinated BDT and brominated TID. Furthermore, we report the synthesis of bis- and tris-BDT monomers and their subsequent use in Stille copolymerizations with TID to create well-defined alternating polymer structures with repeating (D−A), (D−D−A), and (D−D−D−A) units for comparison with the semi-random structures (Scheme 1). BDT was chosen as the donor monomer as it has been used in several literature systems, achieving impressive device efficiencies above 8%.[21,22] We expect that the development of bis- and tris-BDT could thus find application with a number of existing acceptor comonomers. TID was investigated here because our recent work with a TID−BDT copolymer suggested that the very low-lying LUMO of this donor polymer might be hindering efficient charge separation with the fullerene acceptor in OPV devices, contributing to its relatively low efficiency around 2%.[15] A series of semi-random copolymers of TID and BDT could yield

Table 1. Elemental Analysis, Number-Average Molecular Weight (M_n), Dispersity (M_w/M_n), and Optical Properties of Polymers

polymer[a]	nitrogen % calculated	nitrogen % found	M_n (kDa)	M_w/M_n	$\lambda_{0.1\max}$ (nm)[b] solution[c]	$\lambda_{0.1\max}$ (nm) film	E_g^{opt} (eV)[d]
P-TID–BDT	1.84	1.85	33	3.4	798	883	1.40
P-TID–BDT(1.5)	1.43	1.40	21	2.9	757	828	1.50
P-TID–BDT(2)	1.16	1.12	20	4.3	741	803	1.54
P-TID–BDT(3)	0.85	0.83	19	3.5	708	758	1.64
P-TID–BDT(4)	0.67	0.66	17	4.2	687	731	1.70
P-TID–BDT(7)	0.41	0.40	17	3.9	665	687	1.80
P-BDT	0	0	11	3.1	546	562	2.21
P-TID–BBDT	1.16	1.15	42	4.8	730	829	1.50
P-TID–TBDT	0.85	0.64	12	3.0	688	775	1.60

[a] Number in parentheses = ratio of BDT/TID units in semi-random polymers. [b] $\lambda_{0.1\max}$ = wavelength at which absorption is 0.1 its maximum value. [c] Measured in chloroform solution. [d] Calculated from film $\lambda_{0.1\max}$.

materials with very systematic and fine-tuned energy levels that would allow us to probe optimal polymer:fullerene energy level offsets; meanwhile, differences in nonenergetic parameters across this series of polymers, such as polymer–fullerene intercalation, might be minimized.

Synthetic procedures for all monomers and their precursors illustrated in Scheme 1A are described in the Supporting Information, as are full synthetic procedures for the polymerizations. Brominated thienoisoindolodione was synthesized according to a literature procedure,[15] as was bisiodination of the BDT precursor.[9] Monoiodination proceeded surprisingly clean and was isolated in >90% yield after work-up. An Ullmann coupling was employed to synthesize the bisbenzodithiophene (**3**) (BBDT) using a procedure similar to that for generating bistheinopyrrolodione.[23] Tris-BDT was obtained with a Stille coupling of 2 equiv of the monoiodinated BDT with stannylated BDT to give **5**. This product was quite pure, according to ^{1}H NMR (Supporting Information). However, ^{1}H NMR revealed that compound (**6**) was always contaminated with a significant fraction of monostanylated product, attributed to the very poor solubility of trisbenzodithiophene (TBDT) at the low temperatures required for reaction with *n*-BuLi. However, even with as much as 50% contamination of compound **6** with the monofunctionalized TBDT, which would typically terminate a step-growth polymerization at very low molecular weights, decent molecular weights could still be obtained in Stille polymerizations (>12 kDa) as the TBDT is already effectively a trimer.

Standard Stille coupling techniques were employed to synthesize well-defined alternating copolymers of mono-, bis-, and tris-BDT with TID. By employing mixtures of halogenated and stannylated BDT together with TID, semi-random copolymers with a systematic range of monomer ratios were also attained using Stille coupling. High molecular weights could be attained (Table 1) as long as equivalent amounts of halogenated and stannylated functional groups were present in solution. Characterization of the monomer ratios was first attempted with ^{1}H NMR, but regardless of the concentrations or temperatures (up to 120 °C in 1,1,2,2-tetrachloroethane-d_2, see Supporting Information), the broad resonances were not quantifiable. Elemental analysis was thus used to confirm the composition of the polymeric materials (Table 1). The amounts of nitrogen calculated and found in these matierals (originating from the TID monomer) were found to be in excellent agreement with each other. The one outlier was the copolymer with TBDT. The nitrogen content found in this material suggested the ratio of BDT to TID was closer to 4:1, which is consistent with a low molecular weight polymer "end-capped" by two monofunctional TBDT units. A trend in polymer molecular weights was also observed to steadily decrease from 33 K down to 11 K and could be correlated with the amount of iodo-BDT used in the reaction. This was attributed to the instability of iodo-BDT (**1**) at elevated temperatures. All copolymerizations were conducted at 80 °C; when polymerization temperature was increased to 110 °C, molecular weights were 10–50% lower.

The absorption spectra of the polymers were measured both in RT chloroform (Figure 1) and as thin films (Supporting Information). The optical properties are recorded in Table 1. A number of trends and observations concerning both the semi-random and the well-defined alternating copolymers are worth noting. First, the use of mono-, bis-, and tris-BDT alternating

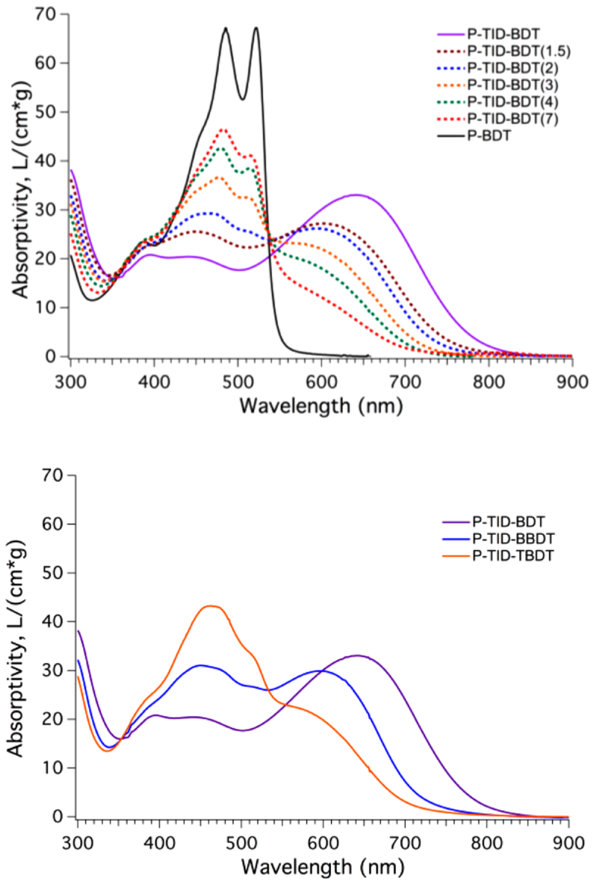


Figure 1. Absorptivity of semi-random (top) and well-defined (bottom) alternating copolymers in RT chloroform solutions.

Table 2. Device Characteristics of Photovoltaic Solar Cells from Polymers with $PC_{61}BM$

polymer	polymer:fullerene blend ratio	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE (%)
P-TID−BDT[a]	1:1	0.76	4.6	0.46	1.6
P-TID−BBDT[a]	1:1	0.70	4.7	0.28	0.9
P-TID−TBDT[b]	1:1	0.78	3.5	0.42	1.2
P-BDT[b]	1:2	0.79	3.1	0.45	1.1
P-TID−BDT(2)[a]	1:1	0.78	6.8	0.52	2.7
P-TID−BDT(3)[b]	1:1	0.84	6.2	0.38	1.9
P-TID−BDT(4)[b]	1:2	0.86	6.0	0.37	1.9

[a] Spun from chlorobenzene with 4% v/v diiodooctane. [b] Spun from chlorobenzene.

copolymers provides a systematic route for band gap tuning: gaps of 1.40, 1.50, and 1.60 eV were observed in the solid state for these three respective copolymers. However, extending this strategy to include longer analogues (e.g., tetra- or penta-BDT) for additional tuning does not seem practical given the tedious synthesis and the difficulty already encountered purifying tris-BDT. By contrast, an infinite number of D/A ratios are accessible with the semi-random approach with no additional monomer synthesis required. Five permutations were investigated here to highlight the power of the technique, resulting in an incremental and systematic tuning of the optical band gap over 0.4 eV (Table 1).

Concerning the difference in the solid-state and solution spectra (Figure S11, Supporting Information), there is a dramatic red shift in $\lambda_{0.1\max}$ (wavelength at which absorption is 0.1 its maximum value) for all of the alternating copolymers in the solid state compared to their solution spectra. Red shifts of 85, 99, and 87 nm are observed for the mono-, bis-, and tris-BDT copolymers, respectively, which can likely be attributed to the increased polymer packing in the solid state that allows for greater electron delocalization through π−π interactions.[24] It is difficult to make direct comparisons of the $\lambda_{0.1\max}$ values between the semi-random copolymers and well-defined alternating copolymers because a shoulder is observed in the well-defined alternating samples that is not observed for the semi-random copolymers (see Figure S11, Supporting Information). The very presence of this shoulder in the well-defined alternating copolymer thin films does suggest, however, that these samples may pack more efficiently than their semi-random analogues.

Furthermore, the TID content in the semi-random copolymers appears to be qualitatively correlated with the degree of vibronic structure observed in the absorbance spectra. As can be seen both in solution (Figure 1) and in solid-state films (Figure S11, Supporting Information), pronounced vibronic structure is observed in the range of 450−550 nm for the homopolymer *P*-BDT, whereas peaks in the spectrum of *P*-TID−BDT are all quite broad. Indeed, conformational modeling has suggested that the backbone of *P*-TID−BDT is quite twisted.[15] A smaller distribution of torsional conformers and conjugation lengths is thus likely present in the *P*-BDT homopolymer. As the BDT/TID ratio increases from 1.5 to 2, 3, 4, and then 7, the vibronic structure in the region of 450−550 nm becomes progressively more pronounced, suggesting that the random incoporation of increasing amounts of TID may lead to a broader distribution of conformers and conjugation lengths. Additionally, the solid-state spectra of *P*-TID−BDT(3), *P*-TID−BDT(4), and *P*-TID−BDT(7) (Figure S11, Supporting Information) display more pronounced features than their respective solution spectra. This may suggest that as the polymer chains become more extended and planar in the films they have a more narrow distribution of conformers and conjugation lengths.

Characterization of the electronic energy levels by cyclic voltammetry were complicated by the fact that the voltammograms were generally irreversible; the highest occupied molecular orbital (HOMO) values were thus calculated by onset potentials and determined to essentially all be the same (−5.4 eV) across the entire range of nine polymers investigated in this work (see Supporting Information for experimental details). We further attempted to verify this similarity of energy levels with both ultraviolet photoelectron spectroscopy (UPS) and indirectly with open-circuit voltages (V_{OC}) in solar cell devices. Generally speaking, while the poor conductivity of the more BDT-rich films (*P*-TID−BDT(4), *P*-TID−BDT(7), and *P*-BDT) prevented accurate measurments with UPS, the ionization energies of the other six polymers were all within ±0.1 eV of each other. A similar range of values was seen for device V_{OC}, with no real trends to speak of when taking all of the data into account. However, given the similar HOMO values determined by CV, the similar ionization energies determined by UPS, and the similar V_{OC} device data, the fact that the optical gap can clearly be tuned in these materials over a wide range of values (from 1.4 to 2.2 eV) suggests that the LUMOs across this series of polymers can be dramatically tuned. This has direct implications on tuning the LUMO−LUMO offset in polymer:fullerene solar cell devices.

As mentioned above, TID was specifically investigated here because our recent work with a TID−BDT copolymer suggested that the very low-lying LUMO of this donor polymer might be hindering efficient charge separation with a fullerene acceptor in OPV devices. We hoped that a systematic series of materials with fine-tuned energy levels would potentially allow us to probe optimal energy level offsets. Several polymer:fullerene blend ratios were investigated, and the optimal results with regard to efficiency are presented here. While we did not exhaustively investigate all of the copolymers from this study in devices, the device data in Table 2 for the semi-random polymers indicate an optimal BDT:TID ratio of 2:1. An efficiency of 2.7% was observed for a device with this material, compared to 1.9% for the other semi-random copolymers and 1.6% for *P*-TID−BDT. Also of note is the fact that the semi-random copolymers all outperformed the alternating copolymers, which is interesting given that the optical data suggest the perfectly alternating copolymers may π-stack more efficiently that their respective semi-random analogues.

Contactless photoconductivity has previously been used by our group[15,25,26] and others[27,28] to study the photophysics of free carrier generation and decay in bulk heterojunctions of polymer donor materials with $PC_{61}BM$. The general methodology for time-resolved microwave conductivity (TRMC) and experimental details are presented in the Supporting

Information. In short, the TRMC figure of merit ($\phi\Sigma\mu$) measured during the experiment is a product of the quantum efficiency of free carrier generation per photon absorbed (ϕ) and the sum of the mobilities of electrons and holes ($\Sigma\mu$). Clear correlations are emerging between the magnitude of the photoconductivity measured by TRMC and the performance of complete OPV devices.[15,28,29] We illustrate in the Supporting Information for bulk heterojunction blends of 50% and 80% PCBM loading by weight how the magnitudes of $\phi\Sigma\mu$ are all quite similar to each other and on the order of 10^{-2} cm^2/(V s). This is approximately the same value measured previously for *P*-BDT−TID and about an order of magnitude lower than higher performing systems (~5% PCE) in the literature.[15] These data are also fully consistent with the device efficiencies reported in Table 2 being lower than 3%. We also illustrate in Figure 2 the transient decays for 50% blends at an absorbed photon flux of ~10^{12} photons/cm^2/pulse. This figure demonstrates that the photoconductance transient lifetimes of these materials can be dramatically tuned with the D:A comonomer ratio. For *P*-BDT, free carriers are quite long-lived, comparable with some highly efficient systems.[15] A very systematic decrease in the transient decays is observed with an increase in the TID content. In addition, and of particular interest to this paper, Figure 2 shows that the photoconductance decays of these blends for the ordered and random copolymers of the same D to A ratio are the same: the decay for *P*-TID−BBDT is very close to the one for *P*-TID−BDT(2), and the decay for *P*-TID−TBDT is very similar to that for *P*-TID−BDT(3). We propose that the "tunability" of the transient lifetimes demonstrated here will ultimately be an advantage for studying decay and recombination mechanisms; further analysis and discussion of these phenomena will be presented elsewhere.

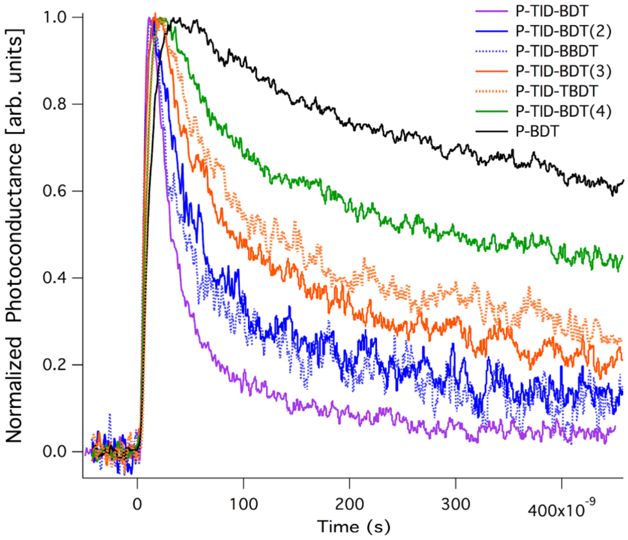


Figure 2. Time-resolved microwave conductivity transients of thin films of 50% blends of polymer:$PC_{61}BM$ deposited on quartz. The absorbed photon flux was ~10^{12} photons/cm^2/pulse. *P*-BDT−TID was excited near its λ_{max} at 660 nm, *P*-BDT near its λ_{max} at 525 nm, and the remaining polymers at 610 nm.

Overall, the synthesis of a series of semi-random copolymers with tunable band gaps was considerably more time- and cost-effective than the synthesis of an analogous series of alternating copolymers. While optical data suggested the alternating structures may pack more efficiently, this did not improve their performance in OPV devices over the semi-random copolymers. Ultimately, a much broader subset of data will be necessary to draw any definite conclusions about optimal polymer:fullerene LUMO−LUMO offsets in devices with these materials. However, these preliminary results confirm that the semi-random approach to copolymerization is a powerful technique for fine-tuning optoelectronic and photophysical properties, and it provides a route to systematic studies that are crucial to fueling reliable progress in this field. Our work to expand the range of monomers employed in this technique to study the generality of these results, as well as study the photophysics of free carrier generation and decay in these materials, is ongoing.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Synthetic details for monomers and polymers, NMR data for polymers, solid-state absorbance spectra, UPS data, and TRMC data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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