Solar energy, which can be converted into electricity using photovoltaic devices, is the largest renewable energy source. Solar cells based on inorganic semiconductors can harvest solar energy efficiently but with a high cost.1 Polymeric solar cells (PSCs) based on the bulk heterojunction (BHJ) architecture are thus pursued worldwide due to their distinctive potential for fabrication on flexible substrates with large areas, lightweight, and solution processability at a low cost.2 By blending electron-donating semiconducting polymers and electron-withdrawing fullerene derivatives together, a bicontinuous interpenetrating network with a large donor—acceptor interfacial area will endow the active layer with large photovoltaic effect.3 In the past decade, extensive research effort by many groups around the world has revealed promising features of PSCs.3 Solar energy conversion efficiency larger than 8% has been achieved based on semiconducting polymers developed in this lab.5

To explore strategies for further improving solar cell performance and probing structure/property relationships, the effect of dimensionality of conjugated systems on solar cell properties was investigated. The tetrathienoanthracene moiety with two-dimensional (2D) extended π-conjugated structure was chosen as a building block for new polymers,6 which favors stronger cofacial π−π stacking. A series of new polymers (PTAT-x) were synthesized with thieno[3,4-b]thiophene as comonomer. The results demonstrate that tetrathienoanthracene is a promising building block for the development of semiconducting polymers with high photovoltaic efficiency. Several interesting observations provide insights for further design of photovoltaic polymers.

The structures of the polymers studied here are shown in Scheme 1. The extended π-conjugated system in tetrathienoanthracene will enhance π−π stacking between the polymer chains; it may also have a side effect of reduced solubility, which will be detrimental to polymer processing. Several monomers with different side chains were thus synthesized in order to obtain processable polymers. At the same time, another PTB family polymer, PTB-8, with similar bulk side chains as those on PTAT-3, with two 2-butyloctyloxy on the benzodithiophene moiety, was also synthesized for the purpose of comparison with PTAT polymers.

The synthesis of tetrathienoanthracene monomer is described in the Supporting Information (SI). The bis-trimethyl-stannanyl monomers were polymerized with 2'-ethylhexyl-6-dibromo-3-fluorothieno[3,4-b]thiophene-2-carboxylate by the Stille polycondensation reaction to yield the designed PTAT polymers. It was found that polymer PTAT-1 with 2-ethylhexyl side chains in the tetrathienoanthracene moiety showed poor solubility and were barely processable in organic solvents; this polymer was not investigated further. However, three other new polymers (PTAT-2−4) with more bulky side chains are soluble in common organic solvents and exhibit number-average molecular weights (Mn) of 24.1, 18.1, and 18.2 kDa with polydispersity indices (PDI) of 1.6, 2.6 and 2.5, respectively. Since the side chains are bulky and long, PTB-8 possesses a high Mn of 83.3 kDa with a PDI of 2.05 due to the improved solubility in the polymerization medium.

UV/vis spectra (Figure 1a) of PTAT-2−4 show absorption peaks at 684, 664, and 665 nm with the absorption onset at 747, 737, and 752 nm, which correspond to optical band gaps around
Solar cells prepared from the other PTAT-x polymers were further studied, and representative characteristics are summarized in Table 1. The PTAT-3 system showed the highest PCE among these polymers. For the 2-ethyldecoyl-substituted polymer, PTAT-4, the solubility was found to be poorer than that of PTAT-3, leading to a lower \( J_{sc} \) (9.6 mA cm\(^{-2}\)), FF (50%), and a PCE value of only 2.98%. Another tetrathienoanthracene-based polymer, PTAT-2, with the most bulky side chain, showed excellent solubility even in CB and DCB. The devices from CB solution exhibited relatively high \( V_{oc} \) of 0.77 V, but low \( J_{sc} \) of 1.0 mA cm\(^{-2}\), resulting in a PCE of 0.37%. The low PCE can be attributed to the steric effect of highly bulky 2-decyltetradecyl side chains that will impede the cofacial \( \pi-\pi \) stacking in the polymer film. All of these results indicate that the 2-butyloctyl group is the best side chain of those studied for tetrathienoanthracene-based polymers to achieve the optimized solubility and compatibility with fullerene derivatives.

In order to explore the unique features of PTAT-x polymers with extended \( \pi \)-system, devices were fabricated using PTB-8 with similar bulky side chains. Figure 1b showed the \( J \)–\( V \) curves of the solar cells based on PTAT-3 and PTAT-4. When CF/DIO was used as cosolvent, corresponding devices of PTB-8/PC61BM showed a PCE of 2.17% with a \( V_{oc} \) of 0.79 V, \( J_{sc} \) of 5.1 mA cm\(^{-2}\), and FF of 54%. PTB-8 exhibits better solar cell performance than PTAT-x.
properties with a PCE of 2.79% \((V_{oc} = 0.83\, V, J_{sc} = 5.7\, mA/cm^2,\) and FF = 59%) when using CB/DIO as cosolvent, which was still only half of what we achieved with PTAT-3.

These results showed that solar cell properties strongly depend on the electronic and solid-state structures. The significant differences among the PTAT-x and PTB-8 are related not only to electronic but also to morphological differences. The purported ideal morphology is comprised of an interpenetrating nanoscale network between donor and acceptor, which enables a large interface area for exciton dissociation and continuous percolating paths for hole and electron transport to the corresponding electrodes. TEM images of PTAT-3 and PTAT-4 (Figure 2a,b) with different alkyl chains exhibited fine domains, and no large phases can be found. In contrast, the film of PTB-8 from CB/DIO shows obvious domains of aggregation as shown in Figure 2c, which suggests that benzo[1,2-b:4,5-b’]dithiophene with 2-butyloxy side chains would reduce the miscibility of PTB-8 with PC61BM and lead to the low PCE of solar cells via exciton losses.

Since TEM studies generally do not provide definitive information on the 3D phase separation in bulk samples, small angle neutron scattering (SANS) measurements were carried out on PTAT-3 and PTB-8. The SANS profiles for as-spun thin films of PTAT-3/PC61BM and PTB-8/PC61BM blend films at room temperature are shown in Figure 2d. Using the empirical unified exponential/power-law method developed by G. Beaucage,\(^7\) the averaged domain sizes in PTAT-3/PC61BM and PTB-8/PC61BM blend films could be achieved as 29 ± 5 and 168 ± 119 nm, respectively. These scattering results are echoed with the TEM data as shown above. It is known that large domains in BHJ solar cells are detrimental to exciton migration and charge separation. The relatively small domain size in the PTAT-3/PC61BM film will enhance the donor–acceptor interfacial area and enhance the solar cell properties.

Besides the miscibility with PC61BM, the dimensionality of the comonomer will also influence the molecular packing structures significantly. As shown in Figure 3a,b, grazing incidence wide-angle X-ray scattering (GIWAXS) studies revealed that the π-stacking of both PTAT-3/PC61BM and PTB-8/PC61BM films are parallel to the substrate surface, namely in a face-down orientation that is helpful to hole transport in the polymer films between two electrodes. As shown in Figure 3c,d, the in-plane linecuts of GIWAXS show a lamellar spacing of about 23.7 Å for the PTAT-3/PC61BM blend film and 20.4 Å for the PTB-8/PC61BM blend film.\(^8\) The difference of about 3.3 Å in polymer lamella distance between PTAT-3 and PTB-8 is consistent with the size difference in the comonomer because of the different connection positions of the side chains. The out-of-plane GIWAXS profiles (Figure 3c) show the π–π distance between the backbones is 3.6 Å for the PTAT-3/PC61BM film and 4.1 Å for the PTB-8/PC61BM film. Although the scattering arising from the π–π stacking of polymer backbones in the PTB-8/PC61BM blend film overlaps with one of the Bragg diffractions of PC61BM, a broadened shoulder showed up around 1.5–1.55 Å\(^{-1}\), which corresponds to the π–π distance between the backbones. This was further confirmed by GIWAXS results of the neat PTB-8 homopolymer film (SI, Figure S7). A distinctive scattering was observed in vertical \((q_z)\) of 1.50 Å\(^{-1}\), which coincides with the blend film with a π–π stacking distance of about 4.1 Å. Therefore, by using extended π-conjugated monomer in PTAT-3, the π–π stacking distance is reduced by 0.5 Å compared to the PTB-8 polymer with relatively smaller benzo[1,2-b:4,5-b’]dithiophene monomer, which is one of the major reasons why the PCE of devices based on PTAT-3 is much higher than that of PTB-8. This difference is also reflected in the hole mobility, which has been measured by the method based on the space charge limited current (SCLC) model.\(^9\) The hole mobility is found to be around 1.69 × 10\(^{-4}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) for PTAT-3 and 1.11 × 10\(^{-5}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) for PTB-8, respectively, which coincides with the GIWAXS results. Higher hole mobility will favor the charge transport in the film devices and, hence, result in better performance.

In conclusion, a series of new semiconducting polymers with extended π-conjugated unit, tetra[1,2-b:4,5-b’]thienoanthracene, were synthesized. The polymer PTAT-3 with 2-butyloxy alkyl side chains exhibited power conversion efficiency about 5.6% with PC61BM from CF/DIO cosolvent. The tetra[1,2-b:4,5-b’]thienoanthracene can reinforce π–π stacking in the solid films, which enhances the device properties through more efficient charge transport. The results indicate that with similar side chains, polymers with larger π systems exhibit better solar cell properties in the systems studied here. However, as the dimensionality of π systems in monomers increases, the poor solubility of the resulting polymers will compromise this advantage. A good solution is to balance the two conflicting effects in search of further enhancement of solar cell properties.

**ASSOCIATED CONTENT**

Supporting Information. Experimental procedures, synthesis of monomers and polymers, cyclic voltammograms, EQE data, and GIWAXS of homopolymer films. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Corresponding Author

Lupingyu@uchicago.edu
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