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# OLIGOMERIC DITHIENOPYRROLE-THIENOPYRROLEDIONE (DTP-TPD) DONOR-ACCEPTOR COPOLYMER FOR ORGANIC PHOTOVOLTAICS

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ABSTRACT

A new donor-acceptor copolymer system based upon a dithienopyrrole (DTP) donor moiety and a thienopyrrolodione (TPD) accepting moiety has been designed and synthesized for organic photovoltaic (OPV) applications. The TPD accepting moiety has recently gained significant attention in the OPV community and is being incorporated into a number of different polymer systems. In contrast, the DTP donor moiety has received only limited attention, likely due in part to synthetic difficulties relating to the monomer. In our hands, the bis(trimethyltin)-DTP monomer was indelibly contaminated with ~5% of the mono-destannylated DTP, which limited the Stille polymerization with the dibromo-TPD monomer (>99% pure) to produce material with M_n ~ 4130 g/mol (PDI = 1.10), corresponding to around eight repeat units. Despite this limitation, UV-visible absorption spectroscopy demonstrates strong absorption for this material with a band gap of ~1.6 eV. Cyclic voltammetry indicates a highest occupied molecular orbital (HOMO) energy level of -5.3 eV, which is much lower than calculations predicted. Initial bulk heterojunction OPV devices fabricated with the fullerene acceptor phenyl C_{61} butyric acid methyl ester (PCBM) exhibit V_{oc} ~ 700 mV, which supports the deep HOMO value obtained from CV. These results suggest the promise of this copolymer system.

MOLECULAR DESIGN

We have designed a new copolymer system based upon a dithienopyrrole (DTP) donor moiety and a thienopyrroledione (TPD) accepting moiety for organic photovoltaic (OPV) applications (see Fig. 1). The TPD moiety is a relatively new component in donor-acceptor polymers for solar cell applications, but it has attracted enormous attention due to its powerful electron-withdrawing capabilities, which produce a strong donor-acceptor effect when incorporated into polymers with electron-rich moieties.[1-3] In contrast, the DTP moiety has received relatively little attention for OPV applications, due in part to its extremely electron-rich nature. The excessive electron density results in relatively shallow HOMO energy levels when incorporated into donor-acceptor copolymers.[4-6] This in turn limits the open-circuit voltage (V_{oc}) of bulk heterojunction (BHJ) OPV devices made from these polymers and fullerene acceptors. According to our preliminary density function theory (DFT) calculations, however, the TPD acceptor moiety has sufficient electron-withdrawing power to produce reasonably deep HOMO levels in copolymers with DTP.
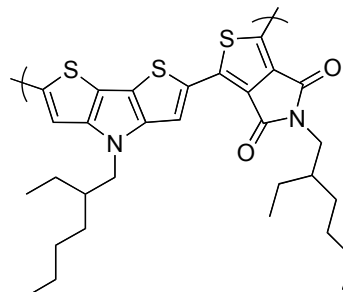
Chemical Formula: $C_{30}H_{36}N_2O_2S_3$ ••
Molecular Weight: 552.81

Figure 1 Structure of TPD-DTP copolymer.

CALCULATIONS

We used the Gaussian 09 electronic structure program[7] to perform geometry optimized DFT calculations at the B3LYP/6-31G(d) level to predict the energetic properties of the DTP-TPD copolymer system. Surprisingly, the lowest energy conformation has the thiophene moieties in an all-cis configuration (see Fig. 2). We have computed the relevant molecular properties for the n=1 and n=2 monomer cases using the 6-31G(d) basis set (see Table 1). Furthermore, we have also explored the effect of using larger basis sets on the computed molecular properties for n=1 (see Table 1).
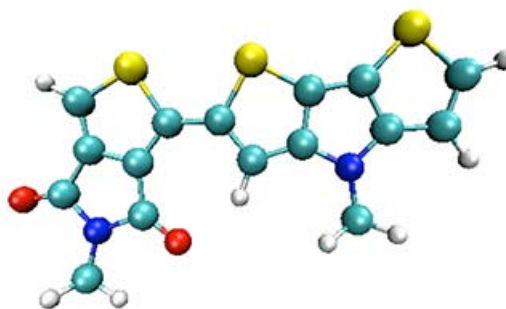
Figure 2 Optimized DFT geometry of TPD-DTP for n=1.

At the 6-31G(d) level, the computed HOMOs for n=1 and n=2 monomers show a strong upward trend in the HOMO energy on increasing oligomer size. For the n=2 case, the HOMO energy of ~-4.9 eV is already rather shallow for an OPV copolymer system, and further changes in the HOMO level on increasing oligomer size might be expected to result in a relatively poor V_{oc} in BHJ OPV devices. Due to the considerable role lone pair orbitals might be expected to play in the energetics of the DTP-TPD copolymer system, we also explored the use of larger

basis sets [6-31+G(d) and 6-311+G(d)] that more adequately account for the orbitals involved in such lone pair states. These larger basis sets result in significantly deeper HOMO and unoccupied molecular orbital (LUMO) energy levels for the n=1 monomer, with minimal change to the calculated energy gap. This effect is likely to extend as well to larger oligomer systems (n ≥ 2), suggesting the DTP-TPD copolymer may have deep enough HOMO energy level to ensure adequate V_{oc} in BHJ OPV devices.

Table 1 DFT Calculated Molecular Properties of TPD-DTP Copolymer System.

Structure/Basis	HOMO (eV)	LUMO (eV)	Energy Gap (eV)	Optical LUMO (eV)
n=1 / 6-31G(d)	-5.23	-2.05	2.95	-2.28
n=2 / 6-31G(d)	-4.92	-2.34	2.18	-2.74
Larger Basis				
n=1 / 6-31+G(d)	-5.50	-2.40	2.87	-2.63
n=1 / 6-311+G(d)	-5.53	-2.45	2.89	-2.64

SYNTHESIS

We synthesized dibromo(2-ethylhexyl)TPD according to the literature procedure.[2] We synthesized (2-ethylhexyl)DTP following a modified literature procedure[6] and prepared the bis(trimethyltin) derivative according to the published method.[6] The excessive electron density/ shallow HOMO of the DTP moiety results in a relatively unstable monomer; generally DTP has been converted into the bis(trimethyltin) derivative and used directly without further purification. However, the resulting polymers are often very low molecular weight[4] due to the presence of some mono-tin DTP as a result of oxidative degradation of the electron-rich monomer. In our case the crude monomer was ~95% pure, and using it directly in a Stille polymerization with the TPD monomer (≥99% pure) resulted in a polymer with a number-averaged molecular weight (M_n) of 4130 g/mol and a polydispersity index (PDI) of 1.10, corresponding to ~ eight repeat units (see Fig. 3).

We subsequently developed a purification method for the monomer that involves dissolving it in hot hexanes, cooling to -78°C in a dry ice/acetone bath, and then filtering to remove the less-soluble mono-tin DTP. This procedure resulted in monomer ≥98% pure, which was used in a Stille polymerization with the TPD monomer. The resulting polymer had a significantly higher molecular weight (see Fig. 3) but also exhibited poor solubility, leading to excessive aggregation in the analytical GPC instrument (in CHCl₃) and preventing calculation of an accurate M_n and PDI. This suggests larger alkyl chains on the donor and/or the acceptor might be desirable to increase the solubility of the polymer.
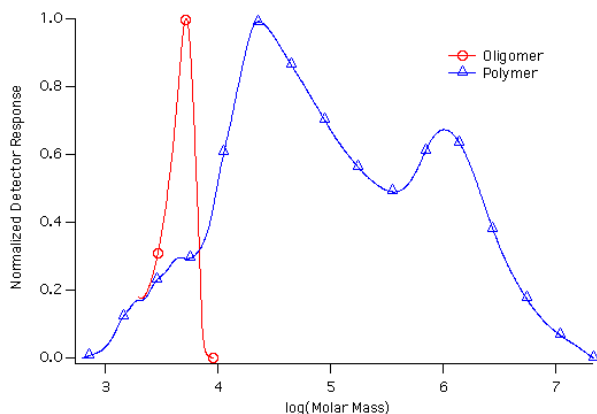

Figure 3 GPC chromatograms of oliogmeric and polymeric DTP-TPD materials.

MOLECULAR CHARACTERIZATION

While the oligomer is quite soluble in chloroform, as well as chlorobenzene and *o*-dichlorobenzene, the polymeric material is comparatively poorly soluble in those solvents. In dilute chloroform solutions, DTP-TPD absorbs broadly (see Fig. 4), with a λ_{max} of 600 nm for the oligomer and 610 nm for the polymer. In thin films (as cast from chloroform) the λ_{max} is 610 nm for the oligomer and 630 nm for the polymer. In both cases the oligomeric material exhibits a distinct shoulder that is not evident in the polymeric material. This suggests the polymeric material may exhibit an improved polymer π-π stacking morphology that is only present to a small degree in the oligomeric material.

In the case of the films, the shoulder results in an identical cut-off wavelength of 760 nm for the two materials, corresponding to a band gap of 1.61 eV. This strong, broad absorption is ideal for PV applications due to favorable overlap with the AM1.5 solar spectrum.
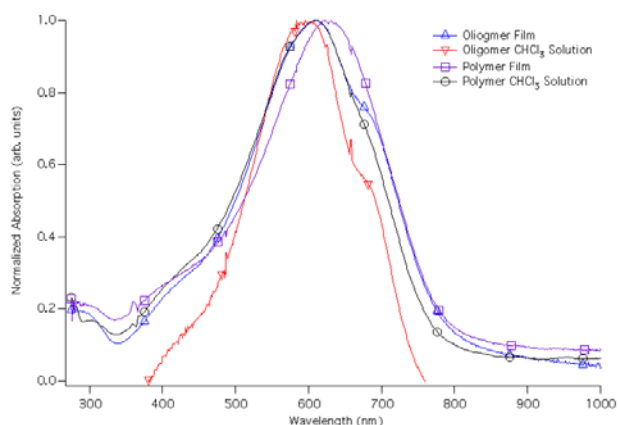

Figure 4 Absorption of oliogmeric and polymeric DTP-TPD materials in thin films and chloroform solutions.

We have performed cyclic voltammetry (CV) on thin films of oligomeric TPD-DTP in an electrolyte solution of 0.1 M

tetrabutylammonium hexafluorophosphate in acetonitrile to explore the energy levels for this copolymer system (see Fig. 5). Using platinum working and counter electrodes and a Ag/AgCl reference electrode at a scan rate of 50 mV/s, we obtained an oxidation potential ($E_{1/2}^{(ox)}$) of 0.918 V for the TPD-DTP oligomer. Although the peak is somewhat poorly reversible ($I_{pc}/I_{pa} \sim 4.8$), it is sufficient for calculation of a reasonable $E_{1/2}$. Under these conditions, ferrocene (HOMO = -4.8 eV)[8] exhibited an $E_{1/2}^{(ox)}$ of 0.39 V. This corresponds to a HOMO of -5.33 eV for DTP-TPD.

The deep HOMO level measured substantiates the larger basis set DFT calculations and suggests the TPD acceptor moiety is highly effective at withdrawing electron density from the electron-rich DTP donor moiety. The oligomer also exhibited an irreversible reduction around -0.65 V, corresponding to a lowest unoccupied molecular orbital (LUMO) energy level of ~-3.76 eV. It is interesting to note that the electrochemical band gap of ~1.57 eV is extremely close to the optical band gap of 1.61 eV (film), which is unusual for polymer systems.
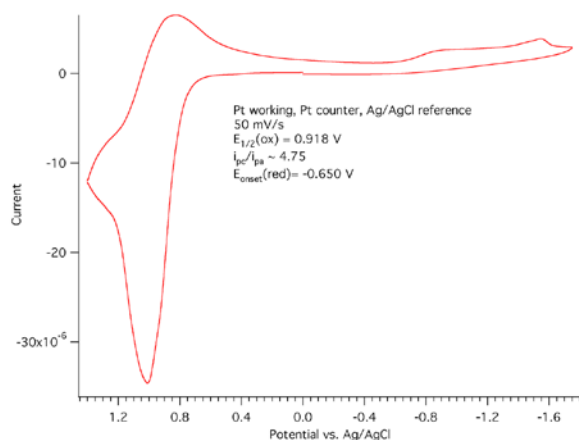

Figure 5 Cyclic voltammetry of TPD-DTP oligomer.
DEVICE RESULTS

Initial BHJ OPV devices with the TPD-DTP oligomer and the fullerene acceptor phenyl C_{61} butyric acid methyl ester (PCBM) were fabricated in order to further evaluate the potential of this copolymer system. The devices were prepared using a conventional OPV device structure consisting of: ITO/PEDOT:PSS/BHJ/Ca/Al. The active layer was a 1:2 DTP-TPD:PCBM ratio, deposited via spin casting from chlorobenzene at room temperature. A representative current density-voltage trace is presented in Figure 6.

The oligomeric devices yielded an average V_{oc} of 699 ± 9 mV, which supports the deep HOMO value measured by CV and predicted by the large basis set DFT calculations. It may be possible to enhance this voltage further in fully optimized devices. The average short-circuit current density (J_{sc}) for these devices was 3.52 ± 0.32 mA/cm^2, which is quite low given the low band gap for TPD-DTP. This is suggestive of a relatively poor BHJ blend

morphology in these initial devices preventing complete harvesting of photogenerated excitons. This might be expected from the low M_n oligomeric nature of this material and is consistent with the UV-vis absorption data. The devices also exhibit a relatively low average fill factor of 40.9 ± 1.2%, which is likely due in part to poor morphology, but also in part due to an inherently lower hole mobility in the oligomer as compared to a high M_n polymer. The average power conversion efficiency (PCE) of the oligomeric devices was 0.985 ± 0.066%.
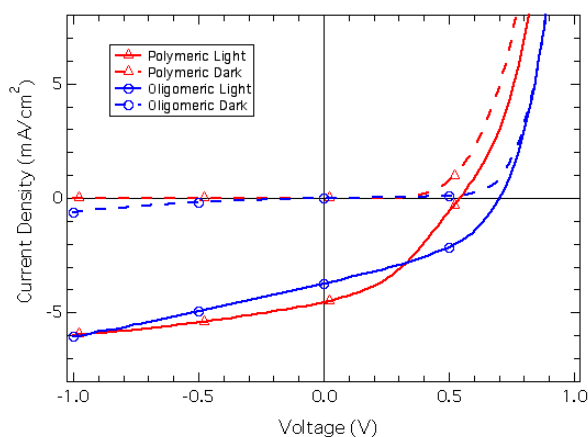

Figure 6 Representative DTP-TPD BHJ OPV device results.

Our subsequent attempts to make devices using the higher molecular weight polymeric DTP-TPD material were hampered by the limited solubility of this material. We retained the same 1:2 DTP-TPD:PCBM weight ratio as in the oligomeric devices. Films cast from chlorobenzene at various temperatures indicated the best performance was obtained when films were cast from solutions at 120˚C. A representative current density-voltage trace is presented in Figure 6.

The polymeric devices yielded an average V_{oc} of just 542 ± 3 mV, which is substantially lower than that of the oligomeric devices. We hypothesize that this result is due solely to the poor film quality obtained due to limited solubility of the polymeric DTP-TPD material. Although it is possible that the increased chain length might result in a shallower HOMO and thus lower V_{oc}, as there was minimal change in the band gap between the oligomeric and polymeric materials, we feel this is unlikely. The average J_{sc} for the polymeric devices, 4.37 ± 0.13 mA/cm^2, was slightly higher than for the oligomeric devices, which may be indicative of an improved BHJ blend morphology, or perhaps simply increased absorption coefficient for the longer chains. The fill factor for the polymeric devices, 38.3 ± 0.51%, was even lower than for the oligomeric devices, however, suggesting a poorer blend morphology. The average PCE of the polymeric devices was 0.874 ± 0.032%. The poor solubility of the polymeric material apparently hampers the DTP-TPD device performance

0.032%. The poor solubility of the polymeric material apparently hampers the DTP-TPD device performance even more than the short chain length does in the oligomeric material.

CONCLUSIONS

In conclusion, we have designed and synthesized a new donor-acceptor copolymer system based on DTP-TPD and investigated its properties for application in OPV devices. The relatively electron-rich DTP moiety results in a poorly stable bis(trimethyltin) monomer that, when used directly, leads to a strictly oligomeric product. A purification method was developed that allowed preparation of a higher-molecular-weight polymer, which exhibited limited solubility. Both the oligomer and the polymer exhibit strong and broad absorption both in solution and thin films, with a band gap of 1.61 eV. Electrochemistry experiments measured a HOMO of -5.33 eV for the oligomeric material, which supports the hypothesis that the strongly electron-withdrawing TPD acceptor moiety is sufficient to remove excess electron density from the DTP donor. This is further supported by initial BHJ device results that demonstrate V_{oc} of around 700 mV for the oligomeric material. Although the J_{sc} and FF for this material are low, this is likely due to poor morphology and hole transport due to the oligomeric nature of the material. In contrast, the high-molecular-weight material exhibits poor device performance due to its limited solubility. This suggests the need for larger alkyl groups on the donor and/or acceptor to improve the solubility of the polymeric material, which may allow for optimized device performance.

ACKNOWLEDGMENTS

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