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MOLECULAR DESIGN, SYNTHESIS AND CHARACTERIZATION OF CONJUGATED POLYMERS FOR APPLICATION IN ORGANIC OPTOELECTRONIC DEVICES

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ABSTRACT

Solar cells are considered as one of the most promising renewable energy technologies as they harvest the energy of the sun to generate electricity. Organic photovoltaics based on conjugated polymers are envisioned to generate electricity at very low cost compared with the classical silicon-based photovoltaics. Up till now, several donor-acceptor alternating polymers were designed, synthesized and utilized for polymer solar cells (PSCs). Power conversion efficiencies exceeding 10% have been registered from such devices. However, further optimization of the conjugated polymer structure is required to attain efficiencies high enough to make this technology economically attractive and thus, the main focus of this work was to design and synthesize new conjugated polymers and to characterize their photovoltaic performances in solar cell devices.

In order to achieve high performance with organic bulk heterojunction (BHJ) cells, it is very crucial to develop donor photoactive materials which have suitable molecular energy levels. Donor conjugated polymers with low-lying highest occupied molecular orbital (HOMO) levels provide high open circuit voltage (V_{oc}) and thus high efficiencies. In this regard, we designed and synthesized the high bandgap (> 1.9 eV) conjugated polymer **PBDTTS-FTAZ** with deep HOMO energy level from fluorinated benzotriazole acceptor unit and a benzodithiophene-based donor unit incorporating octylthiol side chains. We observed from the electrochemical studies that **PBDTTS-FTAZ** had a deeper HOMO energy level compared to the polymer with octyl side chain (**PBDTT-FTAZ**). **PBDTTS-FTAZ** and **PBDTT-FTAZ** were used in the fabrication of BHJ polymer solar cells. The device based on **PBDTTS-FTAZ**:$PC_{71}BM$ showed an enhanced V_{oc} of 0.83 V, J_{sc} of 14.0 mA cm^{-2}, and FF of 0.71, resulting in a much improved PCE of 8.3%,

which is among the highest efficiencies recorded for conventional BHJ solar cells based on high bandgap polymers and the highest efficiency reported to date for benzotriazole-based polymers.

All-polymer solar cells (all-PSC) with conventional and inverted device architectures were also fabricated using **PBDTTS-FTAZ** and **PBDTT-FTAZ** as donors and low bandgap naphthalene diimide (NDI)-based polymers as acceptors. The two donor polymers presented complementary absorption spectra to the acceptors **PNDI-T10** and **N2200**, which led to better coverage of the solar irradiation. The acceptors exhibited high LUMO levels as compared to PCBM. Hence, the lower-lying HOMO of **PBDTTS-FTAZ** and the higher-lying LUMO levels of the acceptor polymers would enable higher V_{oc} in the resulting all-PSCs. The inverted all-PSCs using a **PBDTTS-FTAZ**:**PNDI-T10** blend active layer attained a high PCE of 6.9% with a V_{oc} of 0.89 V, a J_{sc} of 12.3 mA cm^{-2} and FF of 0.63. This PCE was stable without obvious efficiency decay over 60 days. However, inverted all-PSCs based on **PBDTT-FTAZ**:**PNDI-T10** showed a moderate PCE of 5.0%.

All-PSCs were also fabricated form **PBDTTS-FTAZ** and a new acceptor polymer **PIID-PyDPP** synthesized from pyridine-flanked diketopyrrolopyrrole (PyDPP) and isoindigo (IID) units. The **PBDTTS-FTAZ**:**PIID-PyDPP** all-PSC exhibited a more complementary absorption spectrum resulting in an encouraging PCE of 4.2% with a very high V_{oc} of 1.07 V due to its low energy loss of 0.62 eV. A stability study of this all-PSC revealed that there was no obvious reduction in PCE and more than 90% of the initial PCE was retained after two weeks.

Inspired by the results of fluorinated benzotriazole-containing high bandgap polymers, ladder-type high bandgap polymers (**PIDTT-FTAZ-*p***, **PIDTT-FTAZ-*m*** and **PIDT-FTAZ-*m***) were synthesized using indacenodithieno[3,2-*b*]thiophene (IDTT) and indacenodithiophene (IDT) as donors and fluorinated benzotriazole as acceptor and used as electron-donating materials in BHJ PSCs. A high V_{oc} of 0.95 V was obtained from the *meta*-substituted IDT polymer **PIDT-FTAZ-*m***-based PSC. The best PCE recorded was 6.4% for the device made from *para*-substituted IDTT-based polymer **PIDTT-FTAZ-*p*** and PC$_{71}$BM.

Ladder-type high bandgap polymers based on bithiazole and IDTT with (**P29**) and without (**P28**) thiophene π-spacer were also developed for PSCs. Both polymers showed a similar bandgap (2.0 eV), but the polymer with thiophene π-spacer (**P29**) exhibited a higher molecular weight. Although **P28**-based PSC devices showed higher V_{oc}s due to the deeper HOMO energy level of the polymer, **P29** showed a higher PCE of 4.5% with enhanced J_{sc} of 10.4 mA cm^{-2} and FF of 0.52.

BHJ solar cells based on photoactive materials need to have broad absorption to harvest more photon flux and thus maximize the photocurrent and PCE. Random terpolymer and ternary blend systems have been used to extend the light absorption of the active layer. In this regard, we synthesized random terpolymers from the electron-rich unit thiophene and electron-deficient moieties quinoxaline and isoindigo. PSCs fabricated from these terpolymers were compared with those fabricated from the ternary blends of two alternating polymers to explore the best strategy for extending the light absorption range. The two approaches showed similar V_{oc}s but different J_{sc}s. The terpolymer strategy broadened the light absorption range and provided a high PCE of 5.8%. This is due to a high J_{sc} and high hole mobility. The device fabricated from the ternary blend exhibited a lower PCE (3.5%) compared to those fabricated from the terpolymers and alternating polymer blends due to the morphological incompatibility of the donor polymers.

A series of new D-A_1-D-A_2 random terpolymers were prepared for application in PSCs, in which fluorinated benzotriazole and thienothiophene-capped diketopyrrolopyrrole (TTDPP) were used as electron-accepting moieties and thienyl-substituted benzodithiophene as the electron-donating moiety. The study revealed that varying the ratio of FTAZ/TTDPP significantly affects absorption and energy levels of the copolymer. The terpolymer with high content of the strong electron withdrawing units showed strong and broad absorptions between 300–900 nm. The best PCE of 5.7% with J_{sc} of 15.70 mA cm^{-2} was recorded from the device fabricated from the terpolymer with the highest content of strong acceptor unit (TTDPP) and $PC_{71}BM$.

In order to study the effect of donor units on the optoelectronic properties of polymers, D-A type polymers based on triazolopyridine acceptor and BDT and IDT donors were designed and synthesized. The optical and electrochemical properties of the polymers were tuned by varying the donor units. Regioregular and regiorandom polymers based on triazolopyridine were also prepared. In contrast to the regiorandom polymer, the regioregular polymer exhibited relatively broader absorption and deeper HOMO energy level.

Two D-A alternating polymers (**PIDT-TPD, PIDT-2TPD**) based on bithienopyrrolodione (2TPD) and thieno[3,4-*c*]pyrrole-4,6-dione (TPD) as acceptor units and IDT as donor unit were designed and prepared for use in optoelectronic devices. In contrast to **PIDT-TPD**, **PIDT-2TPD** showed red-shifted absorption spectra and deeper HOMO and LUMO energy levels. High V_{oc}s around 1 V were recorded for PSCs fabricated from these polymers.

PIDT-2TPD and **PIDT-TPD** were used as host polymers to fabricate polymer light-emitting diodes (PLEDs). PLEDs based on **PIDT-2TPD** and donor-acceptor donor type NIR-emitting units showed the best performance in the NIR with external quantum efficiency up to 1.16% with turn-on voltage of 1.7 V.

PIDT-2TPD was also used as non-fullerene acceptor to fabricate all-polymer photodetectors with the donor **P3HT**. The **P3HT**:**PIDT-2TPD** blend exhibited spectral response from 300 nm up to the NIR. External quantum efficiency of 34% and high detectivity of 1.3×10^{12} Jones was recorded from **P3HT**:**PIDT-2TPD** blend BHJ all-polymer photodetectors.

D–A low bandgap polymers based on unsubstituted benzodithiophene and isoindigo units were also designed and synthesized. The polymer **P39** with more branched side chains, both on the thiophene and isoindigo units, showed high molecular weight and deep HOMO energy level. The PSC based on **P39**:$PC_{71}BM$ showed a high V_{oc} of 0.91 V.