

## Rational Synthetic Strategy for Nanocarbon-based Polymer Solar Cells

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Organic materials have attracted much attention due to their potential applications in organic electronics. In this regard, charge-transporting properties of organic thin films have found to be important in organic transistors, whereas excellent charge separation (CS) and charge-transporting properties of organic thin films are essential for organic photovoltaics (OPVs). In this talk I will present some of our recent studies relating to solar energy applications.<sup>1-4</sup>

Polymer solar cells (PSCs) have drawn much attention for applications in renewable energy because of their potential for low cost, lightweight, and large-area processability. On the basis of bulk heterojunction (BHJ) concept using blends of p-type semiconducting polymers and n-type semiconducting fullerenes, device performances have been improved rapidly. Low-bandgap conjugated polymers have been developed intensively in recent years with the aim of better matching between the absorption and solar spectra, reaching a power conversion efficiency ( $\eta$ ) more than 7%. On the other hand, [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester ([60]PCBM) and its corresponding C<sub>70</sub> derivative ([70]PCBM) are exclusively employed as an acceptor in the highly efficient PSCs.

Thermal conversion strategy was utilized in the synthesis of a novel low bandgap polymer containing isothianaphthene (ITN) dimer structure and benzodithiophene (BDT) unit in the backbone (PBIBDT).<sup>2,3</sup> First, a highly soluble precursor polymer with an alternating main chain structure of bicyclo[2.2.2]octadiene-fused thiophene dimer and BDT (PPBIBDT) was synthesized by palladium(0)-catalyzed Stille coupling reaction. Then, heating of the yellow PPBIBDT film spin-coated on a glass plate yielded dark blue film of PBIBDT that was insoluble in any organic solvents. Thermogravimetric analysis of PPBIBDT showed 14% weight loss with an onset at 230 °C, corroborating the occurrence of the thermally induced retro-Diels-Alder reaction. The PBIBDT film showed red-shifted, broad absorption in visible and near infrared region with a maximum at 706 nm compared to the precursor polymer PPBIBDT with an absorption peak at 445 nm. The introduction of ITN dimer unit in the backbone lowered the bandgap owing to the stabilized quinoid resonance structure. The field-effect hole mobility of PBIBDT was determined to be  $1.1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  with an on-off ratio of  $2.5 \times 10^2$ , while PPBIBDT-based device revealed no p- and n-type responses. Organic photovoltaic devices were fabricated based on the planar BHJ structure of PBIBDT and [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) and showed a power conversion efficiency of 0.07% under standard AM1.5 sunlight (100

mW cm<sup>-2</sup>). These results obtained here will provide fundamental information on the design of thermally-induced low-bandgap polymers for device applications.

Drawback of PCBM is a relatively low energy level of the lowest unoccupied molecular orbital (LUMO), which limits the open circuit potential ( $V_{OC}$ ) that is known to be proportional to the difference between the LUMO of the acceptor and the highest occupied molecular orbital (HOMO) of the donor. To surmount the problem, fullerene derivatives with higher LUMO levels have been prepared for PSCs. Among these fullerene derivatives, fullerene bisadducts have found to increase  $V_{OC}$  by 0.1-0.2 V compared with the corresponding monoadducts because of lowering the electron-accepting property by the partial loss of  $\pi$ -conjugation. Despite of successful application of fullerene bisadducts to PSCs, their regioisomer mixtures have been used directly without separating each isomer. Considering that molecular packing and arrangement of fullerene derivatives in the active layer of conjugated polymers with them have a large impact on charge separation and electron-transporting properties, pure bisadduct isomer with the two substituents at specific positions on C<sub>60</sub> would yield more desirable network comprised of the bisadduct in the active layer, leading to better device performance. Regioisomerically pure 56- $\pi$ -electron methanofullerene was selectively prepared for PSCs, whereas each fullerene bisadduct has yet to be separated from the corresponding regioisomeric mixture for PSCs owing to the difficulty of separating and obtaining sufficient amount of each isomer for device fabrication.

To examine the effects of fullerene bisadduct regioisomers on solar cell performance, separated fullerene bisadduct regioisomers were applied to PSCs.<sup>4</sup> The two substituent positions on C<sub>60</sub> were found to have a large impact on the device performance. Such structure-performance relationship will provide valuable, basic information on the rational design of fullerene bisadducts as an acceptor for highly efficient PSCs.

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