

Molecular Design Strategies of Photovoltaic Materials for Polymer Solar Cells

Polymer solar cells (PSCs) are composed of a blend active layer of a *p*-type conjugated polymer (*p*-CP) as donor and an *n*-type organic semiconductor (*n*-OS) as acceptor, sandwiched between a transparent electrode and a metal electrode. The photovoltaic materials and devices of the PSCs have attracted great attention in recent years, due to their advantages of low-cost solution-processing, light weight, thin active layer, and capability to be fabricated into flexible and semitransparent devices.

The solution-processed PSC, with bulk-heterojunction blend active layer of a *p*-CP MEH-PPV as donor and a soluble C₆₀ derivative PCBM as acceptor, was first reported in 1995, with a power conversion efficiency (PCE) of less than 1%. Then, the fullerene derivatives, including PCBM and PC₇₁BM, dominated the acceptors used in the PSCs for 20 years owing to their advantages of high electron mobility and high electron affinity. PCE of the PSCs is proportional to its open circuit voltage (V_{oc}), short circuit current density (J_{sc}) and fill factor (FF), where V_{oc} is proportional to the energy difference between the lowest unoccupied molecular orbital energy level (E_{LUMO}) of the acceptor and the highest occupied molecular orbital energy level (E_{HOMO}) of the donor, J_{sc} depends on the absorption wavelength range and absorption intensity of the active layer, and FF is related to the charge carrier mobility and series resistance of the device. Therefore, the donor and acceptor photovoltaic materials should possess complementary absorption in the visible-near infrared region, the donor materials should have higher hole mobility and the acceptor materials should have higher electron mobility. In addition, the E_{LUMO} and E_{HOMO} energy level matching (the E_{LUMO} and E_{HOMO} of donor should be higher than those of the acceptor) of the donor and acceptor materials are crucial for higher exciton dissociation efficiency to get high J_{sc} . Because the organic semiconductors absorb photons to produce excitons (electron-hole pair) with binding energy of ca. 0.3 eV, and the excitons diffuse to the donor/acceptor interface where the excitons dissociate into electrons in the acceptor phase and holes in the donor phase if the energy level difference is higher than the exciton binding energy. However, due to the wide energy bandgap (with absorption spectrum in the wavelength range shorter than 500 nm) and difficulty to tune the E_{LUMO} of the fullerene derivative acceptors, the low bandgap and broad absorption *p*-CP donors with higher hole mobility and lower E_{HOMO} should be designed and synthesized for realizing higher PCE of the PSCs. D-A copolymerization of electron-donating (D) unit and electron-accepting (A) unit is a powerful strategy to tune the absorption and electronic

energy levels of the *p*-CP donors, by selecting different D- and A-units. Attaching conjugated side chain is an effective approach for broadening absorption and increasing hole mobility of the polymer donors. Among the various D-units, the benzodithiophene (BDT) with thiophene conjugated side chains is a star D-unit in constructing high performance D-A copolymer donors. The side chain engineering with alkylthio and electron-withdrawing substituents (such as carboxylate and fluorine substitution) is widely used to down-shift E_{HOMO} of the donor materials. After the efforts of molecular design, the narrow bandgap conjugated polymer donors with absorption edge at ca. 800 nm and lower E_{HOMO} lead the fullerene acceptor-based PSCs to a higher PCE of ca. 10% before 2015.

In 2015, the invention of narrow bandgap A-D-A structured small molecule acceptors (SMAs) (or called as non-fullerene acceptors), with a fused ring central D-unit and two strong electron-withdrawing end groups, overcome the limitation of fullerene acceptors and opened a new way in designing high performance acceptor materials. The SMAs possess the advantages of narrow bandgap, broad and strong absorption at long wavelength region with absorption edge at ca. 800 nm, suitable and tunable E_{LUMO} and E_{HOMO} energy levels, and higher electron mobility. By using the absorption-complementary wide bandgap conjugated polymer donor, PCE of the PSCs with the A-D-A type SMA as acceptor reached the level of 10%~14%. In 2019, the appearance of the A-DA'D-A SMA Y6 with further red-shifted absorption to the wavelength longer than 900 nm and enhanced absorbance at the long wavelength region, further improved the PCE of the PSCs to over 15%, and promoted the research on PSCs to a new stage. Then, PCE of the PSCs increased rapidly and reached over 19% recently by the side chain engineering of the A-DA'D-A type SMA (upper side chains and inner side chains optimization of Y6) and the development of high performance wide bandgap polymer donors. Now, efficiency of the PSCs has reached the threshold for application. While for realizing the application of the PSCs, it is urgent to address the cost and stability issues.

At present, most of the high performance wide bandgap polymer donors and narrow bandgap SMAs possess complicated molecular structures, which results in multiple synthetic steps, low yield and high cost of the photovoltaic materials. The complicated molecular structure of the A-DA'D-A type SMAs is inevitable for the high efficiency PSCs, the efforts on reducing cost should be devoted to the optimization of synthetic method of the SMAs. However, the complicated molecular structure of

the wide bandgap polymer donors is not inevitable, there is large space for reducing the cost of wide bandgap polymer donors by simplifying their molecular structure. For example, a low cost and simple structured D-A copolymer PTQ10 was synthesized in 2018 by using thiophene as D-unit and difluoro-quinoxaline as A-unit through two synthetic steps with high yield of close to 90%, and the PCE of the PTQ10-based PSCs reached 18%~19% recently by using a Y6 derivative with thienyl outer side chains as acceptor.

In considering the stability issue, the all-polymer solar cells (all-PSCs), with *p*-CP as donor and *n*-type conjugated polymer (*n*-CP) as acceptor, are promising for future application because of their excellent morphology stability, as well as the good thermal- and photo-stability. Actually, the first all-PSC was reported in the same year with the report of bulk-heterojunction PSCs in 1995. However, due to the lack of high performance polymer acceptors, the development of the all-PSCs lags behind the PSCs based on the fullerene derivative or SMA acceptors for a long time. In 2017, a strategy of polymerized small molecule acceptors (PSMAs) was proposed, which changed the situation and lead the all-PSCs developing quickly and becoming a hot research direction recently. PSMAs remain the advantages of SMAs on the narrow bandgap, broad and strong absorption in the long wavelength region, and good aggregation properties, and increase the advantages of the polymers with mechanical flexibility, good morphology and photo-stability. Benefitted from the A-DA'D-A SAMs, the high efficiency PSMAs were synthesized from the A-DA'D-A SAMs, and the PCE of the all-PSCs based on the PSMA polymer acceptor reached over 17% recently.

The PSCs are a new technology for converting sunlight to electricity, and the studies on the photovoltaic materials and devices of the PSCs are mainly developed in the 21st century. After the development of more than 20 years, PCE of the PSCs has rapidly increased from *ca.* 1% at the year of 2000 to over 19% recently, and the Chinese researchers make great contributions on the development

of the PSCs. Especially, the developments of SMAs, PSMAs and the low cost polymer donors by the Chinese researchers since 2015 have significantly promoted the research of PSCs to the new stage for possible application. For realizing practical application, the researchers on photovoltaic materials should do their efforts on the following aspects in next steps: (1) Continuing the development of high performance new donor and acceptor photovoltaic materials, mainly on the simple structured polymer donors and new synthetic method for the A-DA'D-A SMAs, for further increasing PCE and reducing cost of the PSCs. (2) Large scale (hundred gram to kg scale) synthesis of the donor and acceptor photovoltaic materials for the fabrication of large area PSCs. (3) Investigation on the mechanism influencing stability of the photovoltaic materials, and strategies of improving the stabilities. (4) Optimizing the synthetic method of high performance PSMAs to improve reproducibility of its photovoltaic performance and reduce cost of the PSMAs for the application of flexible all-PSCs. I believe the product of flexible PSCs will enter our daily life in near future.



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The views expressed in this editorial are those of the author.