SYNTHESIS OF WIDE BANDGAP CONJUGATED π-COPOLYMERS INCORPORATING 9H-CARBAZOL-3-YL DITHIENO[3,2-F:2',3'-H]QUINOXALINE UNITS

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Abstract

A new wide bandgap material, P1, was synthesized and compared by the optical and electrochemical properties with the well-known copolymer PM6. Upon employing the narrow bandgap non-fullerene acceptor Y6, the organic solar cells based on P1 and PM6 under identical processing conditions exhibited overall power conversion efficiencies of 13.48 and 14.81%, respectively. Utilizing P1 as the secondary donor led to the optimized ternary organic solar cell with a power conversion efficiency of 17.11%, exceeding that of the binary counterparts.

**Key words:** synthesis, copolymer, organic solar cell, photovoltaic application.
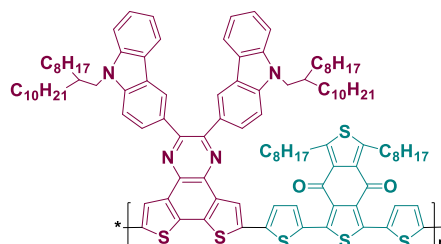
Introduction

Currently, the majority of π-conjugated polymers utilized in polymer solar cells (PSCs) are predominantly produced by the polycondensation method using the Stille cross-coupling [1]. However, this approach presents various challenges, such as the preliminary multi-step synthesis of aryl tin reactants and the production of harmful by-products. To overcome these challenges, the idea of utilizing a novel polycondensation process through direct arylation has emerged as an attractive and environmentally friendly alternative to the traditional coupling reactions. This approach eliminates the need for stannyl derivatives and the requirement for organometallic reagents, leading to a reduction in the synthesis steps and costs. Given the significant interest in conjugated polymers containing quinoxaline (Qx) units [2–4], there is a push for further enhancements towards simpler, quicker, and more cost-effective synthetic approaches. However, the development of Qx-conjugated polymers *via* direct polycondensation remains exceedingly scarce and poorly understood [5]. To address the challenges mentioned above, this study undertook the synthesis of a novel π-conjugated Qx-containing polymer P1 through a direct heteroaryl polycondensation reaction.

Results and discussion

In this study, we developed and synthesized a monomer, M1, and utilized it to obtain a new π-conjugated polymer, P1, through the direct heteroarylation procedure (Scheme 1).

The resulting copolymer P1 is soluble in common organic solvents, such as chloroform (CF) and chlorobenzene, with a number average molecular weight (M_n) of 20.1 kDa and a polydispersity index (PDI) of 2.40 (Table S1 in the Electronic supplementary information (ESI)). The high value of M_n and the low PDI of P1 support enhanced charge transport characteristics. The thermal gravimetric analysis (TGA) revealed a decomposition temperature (T_d) of 358 °C for P1, indicating its suitability for use in fabricating organic photoelectronic devices. The absorption spectra of P1 in CF and thin film as well as those of PM6 [6] and Y6 [7] thin films are depicted in Fig. 1. The absorption spectrum of P1 in thin film exhibits a significant red shift compared to the spectrum in solution, with the primary absorption peak located at 427 nm. This observation suggests the presence of a more ordered structure and π–π stacking interactions in the solid state, contributing to enhanced charge mobility of the polymer in this state. Finally, the optical band gap (E_g^{opt}) of wide-band P1 is determined to be 2.06 eV.
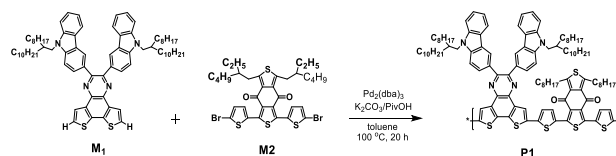
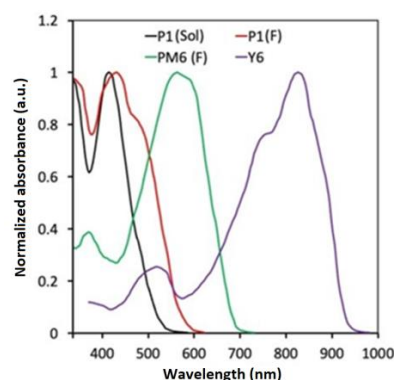

Scheme 1. Synthetic route to copolymer P1.

Figure 1. Absorption spectra of P1 in CF and P1, PM6, Y6 in thin film.

We fabricated the bulk heterojunction (BHJ) organic solar cells (OSCs) (ITO/PEDOT:PSS/BHJ active layer/PFN-Br/Al), using P1 as the donor and Y6 as the acceptor and evaluated their photovoltaic performance in comparison to the PM6 donor under identical processing conditions. The optimized active layer was subjected to solvent vapor annealing by exposing it to tetrahydrofuran (THF) vapors for 40 s. The J–V characteristics of the optimized OSCs are presented in Table 1.

Table 1. Photovoltaic parameters of the optimized binary and ternary OSCs

Device	J_{SC}, [mA/cm^2]	V_{OC}, [V]	FF	PCE, [%]
P1:Y6	21.54 (21.29)[a]	0.957	0.654	13.48 (13.23)[b]
PM6:Y6	24.62 (24.39)[a]	0.840	0.716	14.81 (14.54)[b]
PM6:P1:Y6	25.74 (25.52)[a]	0.908	0.732	17.11 (16.87)[b]

[a] estimated from the integration of external quantum efficiency (EQE) spectra;
[b] average of eight identical devices; J_{SC} is the short circuit current; V_{OC} is the open circuit voltage; FF is the fill factor; PCE is the power conversion efficiency.

The optimized OSCs based on PM6:Y6 and P1:Y6 achieved PCEs of 13.48 and 14.81%, respectively. The value of V_{OC} of P1-based OSCs (0.957 V) surpassed that of its PM6 counterpart (0.84 V) due to a deeper highest occupied molecular orbital (HOMO) energy level of P1 relative to PM6. This variation in the values of V_{OC} for the active layer-based OSCs reflects the energy difference between the acceptor lowest unoccupied molecular orbital (LUMO) and the donor HOMO. The higher value of J_{SC} for the PM6-based OSCs, in contrast to P1, arises from the efficient dissociation of excitons at the PM6/Y6 interfaces, substantiated by the more effective photoluminescence (PL) quenching of Y6 for Y6:PM6 relative to Y6:P1. The optimized ternary OSC exhibits a PCE of approximately 17.11%, surpassing that of its binary counterparts owing to the increased J_{SC} and FF values.

Conclusions

We developed a new donor-acceptor (D-A) copolymer, P1, which demonstrates a deeper HOMO level and a larger dipole moment compared to PM6. Although the optimized P1:Y6 active layer-based OSCs exhibited a PCE of 13.38%, lower than that of the PM6 counterpart (14.81%), the P1-based OSC showcased a higher value of V_{OC}, attributed to its deeper HOMO energy level. Leveraging the higher V_{OC} for the P1-based device and the complementary absorption spectra of P1 and PM6, the ternary OSC based on the P1:PM6:Y6 (0.2:0.8:1.2) active layer achieved an overall PCE of 17.11%, surpassing that for binary counterparts. An increase in the values of J_{SC} and FF for the ternary OSC is attributed to the higher exciton generation and

their more effective dissociation into free charge carriers owing to the appropriate phase separation and morphology of the ternary active layer.

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Electronic supplementary information

Electronic supplementary information (ESI) available online: the experimental section, NMR spectra, cyclic voltammograms, molecular weights and thermal properties of P1, as well as the details of the device fabrication. For ESI, see DOI: 10.32931/io2507a.

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