



Conjugated copolymers of triazoloquinoxaline-*alt*-fluorene with imine chain bridge for photovoltaic solar cells



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ABSTRACT

A series of copolymers based on triazoloquinoxaline and fluorene derivatives have been synthesized by Suzuki polycondensation, which have aryl imine chain bridge in fluorene unit. N-(aryl)-9H-fluoren-9-imine was first synthesized and used to construct conjugated polymers, which were applied in organic photovoltaics. The thermal, electrochemical, and photovoltaic properties were characterized. These good solution-processable copolymers showed broad absorption from 350 nm to 800 nm region with the optical bandgap of ~ 1.55 eV. Preliminary bulk heterojunction solar cells of P3:PC₆₁BM (1:2 w/w) exhibited maximum power conversion efficiency of 1.56% with J_{sc} of 4.50 mA cm⁻², V_{oc} of 0.79 V, and FF of 0.44.

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1. Introduction

Bulk heterojunction (BHJ) [1] polymer solar cells (PSCs) have drawn considerable interests in the field of renewable energy generation technologies, mainly due to their potential in mass-production of low cost, light-weight and large-scale flexible devices [2]. Significant progress has been achieved in pursuing high-performance BHJ devices, with a champion record of power conversion efficiency (PCE) over 11.8% [3]. Great efforts have been made in novel materials development (e.g. narrow bandgap polymers [4,5] and fullerene derivatives [6]), device engineering (e.g. tandem [7], inverted [8] and ternary [9] structure design, as well as annealing, solvent processing [10] and interfacial modifications [11]). However, the PCEs obtained from small-area devices are still far away from the commercialization.

For the development of donor-acceptor (D-A) structural narrow bandgap polymer, the matching of D and A unit is a great concern in structure design. Previous we have synthesized series of conjugated polymers based on fluorene and triazoloquinoxaline [12] for PSCs [13,14]. To further fine-adjust donor unit electron affinity, two-dimensional (2D) fluorene called N-(aryl)-9H-fluoren-9-imine was developed. By conjugated imine chain bridge on fluorene 9 position, an extended π -conjugation system was constructed to form a highly rigid coplanar backbone. The structures provided

strong intermolecular π -overlapping and electron-donating/accepting properties to enhance charge separation, transport, and energy-level tunability. Polymer based on imine chain bridge donor unit showed unprecedented precision tuned HOMO/LUMO energy levels reported by other group [15]. However, copolymers based on different substituent aryl fluoren-9-imine have never been reported. Further correlation studies on the different structure of imine chain bridge alternating polymers with same acceptor unit and their physiochemical properties might offer some helpful insight in designing novel narrow bandgap polymers.

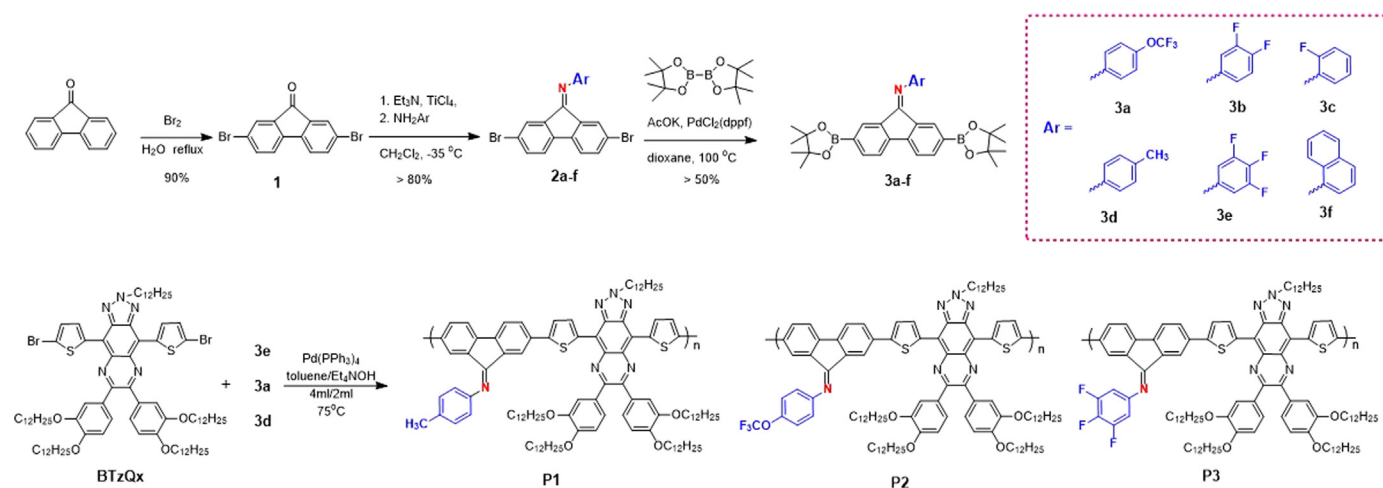
In this work, novel electron donor units and narrow bandgap copolymers based on aryl fluoren-9-imine and triazoloquinoxaline unit were designed and prepared for the first time. The correlation studies of aryl fluoren-9-imine unit structure with the optical, electronic properties and photovoltaic performance of the resulted polymers (see Scheme 1) were presented. The best device delivered a maximum PCE of 1.56%, with an open circuit voltage (V_{oc}) of 0.79 V, a short circuit current (J_{sc}) of 3.31 mA/cm² and a fill factor (FF) of 44%.

2. Materials and methods

All the starting materials were utilized by purchasing commercially without further purification. The synthetic route of monomers and copolymers were shown in Scheme 1, and the detailed synthetic procedures were presented in the Supporting

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Scheme 1. Synthetic route for monomers and copolymers.

Table 1
Molecular weights, thermal property, bandgap and energy levels of the polymers.

polymers	M_w^a	M_n^a	PDI ^a	T_d^b (°C)	λ_{max} (nm) ^c	λ_{max} (nm) ^d	λ_{onset} (nm) ^d	E_g^{opt} (eV)	HOMO (eV)	LUMO (eV)
P1	32,790	12,100	2.71	387	657	700	0.80	1.50	−5.20	−3.70
P2	22,816	9200	2.48	400	629	660	0.79	1.56	−5.19	−3.63
P3	23,852	8900	2.68	393	606	629	0.98	1.55	−5.38	−3.83

^a M_w , M_n , and PDI of the polymers were determined by GPC using polystyrene standards in THF.

^b The 5% weight-loss temperatures under N₂ and heat from 50 to 800 °C at a rate of 20 °C/min.

^c Solution. ^d Film.

material. Suzuki cross-coupling reaction was employed for the synthesis of **P1–P3**. These copolymers showed excellent solubility in organic solvents, including THF, CHCl₃ and *o*-dichlorobenzene. The gel permeation chromatography (GPC) results indicated that three copolymers have the number-average molecular weight (M_n) of 8–12 kDa with a PDI of 2.4~2.7 (Table 1). **P2** and **P3** showed a low M_n , probably due to the strong electron affinity substituent of benzene unit resulted to polymerize inefficiency [15].

3. Results and discussion

3.1. Thermal properties, absorption properties and electrochemical properties

All copolymers exhibited good thermal stability with decomposition temperature (T_d) (5% weight loss) at 387, 400 and 392 °C for **P1**, **P2** and **P3**, respectively (Fig. 1a). Fig. 1(b and c) showed the UV–vis absorption spectra of monomers and polymers in CHCl₃ solution or film. The monomers displayed an absorption band in the range of 300–500 nm. Monomer **3a** displayed most broad absorption band, which had suspended naphthalene. There was a contradictory conclusion that electron accepting group (such as –OCF₃ and –F) had absorption band blue-shifted than electron donating group (naphthalene and –CH₃). The results illustrated that differ substituents could tune aryl fluoren-9-imine backbone absorption band where donating group's conjugated effect was stronger than accepting group's induced effect through C=N bonding. These polymers films exhibited a broad absorption band in the range of 300–800 nm, which was 20–40 nm red-shifted in comparison to their absorption spectra in solution. The red-shifted absorption of polymers film indicated that strong intermolecular interaction and aggregation exist in the solid-state of these polymers. They all exhibited two evident absorption bands, the shorter wavelength absorption band was attributed to the π - π^* transition

of the conjugated main chain and the longer wavelength was owed to the internal charge transfer interaction between the aryl fluoren-9-imine donating unit and BTzQx accepting unit. It was revealed that substituted aryl fluoren-9-imine stronger broaden spectrum absorption than alkyl fluoren-9-ylidene [13,16]. The optical bandgaps (E_g^{opt}) of copolymers were determined from the UV–vis absorption onsets in the solid state according to the empirical equation: $E_g^{opt} = 1240/\lambda_{onset}$ eV. The E_g^{opt} of **P1**, **P2** and **P3** were determined to be 1.56, 1.50 and 1.55 eV, respectively. the E_g^{opt} data of polymers could conclude that E_g^{opt} of polymers was mainly dependent upon their electron-withdrawing ability of polymer backbone, but a little effect of substituted aryl fluoren-9-imine. The results also indicated that the incorporating of the different electron affinity unit into the backbone of polymer should be an effective method to finely control the optical band-gap and absorption band. The highest occupied molecular orbital (HOMO) energy levels of the conjugated polymers were determined by electrochemical cyclic voltammetry (CV) (seen Fig. s34). The HOMO level of the polymers were calculated from the onset oxidation potentials (E_{ox}), while the LUMO levels were calculated using HOMO and optical E_g^{opt} according to the following equations [17]: HOMO = $-e(E_{ox} + 4.4)$ (eV); LUMO = HOMO + E_g^{opt} (eV). The onset potential for oxidation (E_{ox}) were observed to be 0.79, 0.80, and 0.98 eV for **P1**, **P2** and **P3**, respectively. Accordingly, the corresponding HOMO energy level of **P1**, **P2** and **P3** were calculated to be −5.19, −5.20 and −5.38 eV, respectively. The deep HOMO levels of these polymers should be beneficial to their chemical stability and be desirable for higher V_{oc} of the PSCs [18]. The LUMO level of **P1**, **P2** and **P3** were thus calculated to be −3.70, −3.63, −3.83 eV, respectively. The HOMO–LUMO energy diagrams of the polymers and PC₆₁BM were shown in Fig. 2a.

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