



The effect of the different donor units on fluorescent conjugated polymers containing 2,1,3-benzooxadiazole as the acceptor unit



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ABSTRACT

A series of monomers were synthesized via Stille coupling to obtain low-band gap conjugated polymers namely poly(5,6-bis(octyloxy)-4,7-di(thieno[3,2-b]thiophen-2-yl)benzo[c][1,2,5]oxadiazole (PTTBO)), poly(5,6-bis(octyloxy)-4,7-di(selenophen-2-yl)benzo[c][1,2,5]oxadiazole (PSBO)) and poly(5,6-bis(octyloxy)-4,7-di(furan-2-yl)benzo[c][1,2,5]oxadiazole (PFBO)) which comprise electron-rich thieno[3,2-b]thiophene (TT), selenophene and furan, as the donor units in conjugation with electron-deficient 2,1,3-benzooxadiazole (BO) moiety as the acceptor unit. All three polymers were synthesized electrochemically and well characterized. These polymers exhibited broad spectral absorptions, low-lying highest occupied molecular orbital (−5.71, −5.88, −5.76 eV), and as well as low band gap ranging from 1.45 eV to 1.56 eV. Introducing different donor moieties on the polymer backbone provides to alter the optoelectronic properties.

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1. Introduction

Conjugated polymers have an extended sequence of alternating single and double bonds that provide π orbital delocalization throughout the structure resulting in enhanced conductivity [1]. Conducting polymers provide interesting properties like solution processability, easy band gap alternation via structural modification, low cost and flexibility [2] for many applications such as solar cells (OPVs) [3], organic light emitting diodes (OLEDs) [4], organic field effect transistors (OFETs) [5], biosensors [6] and electrochromics (ECs) [7]. Change in planarity, bond length alternation, resonance effects along the polymer backbone, interchain effects and donor–acceptor approach can be classified as the numerous strategies to control the band gap and modulate electronic properties of polymers. Up to date, the donor–acceptor (D–A) approach is verified to be the most efficient strategy in the synthesis of conducting polymers to obtain low band gap polymers for desired applications. During the past few years, 2,1,3-benzothiadiazole (BT) [8], 1,2,3-benzotriazole (BTz) [9], thieno[3,4-b]pyrazine [10], and diketopyrrolopyrrole (DPP) [11] and benzoquinoxalines [12] are typically used A-type aromatic heterocycles to achieve low

band gap D–A type polymers. 2,1,3-Benzooxadiazole (BO) moiety has gained much attention as a strong electron acceptor unit due to two electron withdrawing imine groups in the backbone. Strong electron affinity of oxygen atom makes benzooxadiazole more effective acceptor than its counterparts such as benzotriazole and benzothiadiazole. Li et al. reported syntheses of three polymers containing benzooxadiazole, benzotriazole and benzothiadiazole as the acceptor moieties and it is revealed that internal charge transfer decreases for a relatively weaker electron-withdrawing nature of benzotriazole and benzothiadiazole units compared to benzooxadiazole. As well as experimental evidence, Gratzel and coworkers showed that theoretical simulations prove the electron-withdrawing capability increases in the sequence benzotriazole, benzothiadiazole, benzooxadiazole.

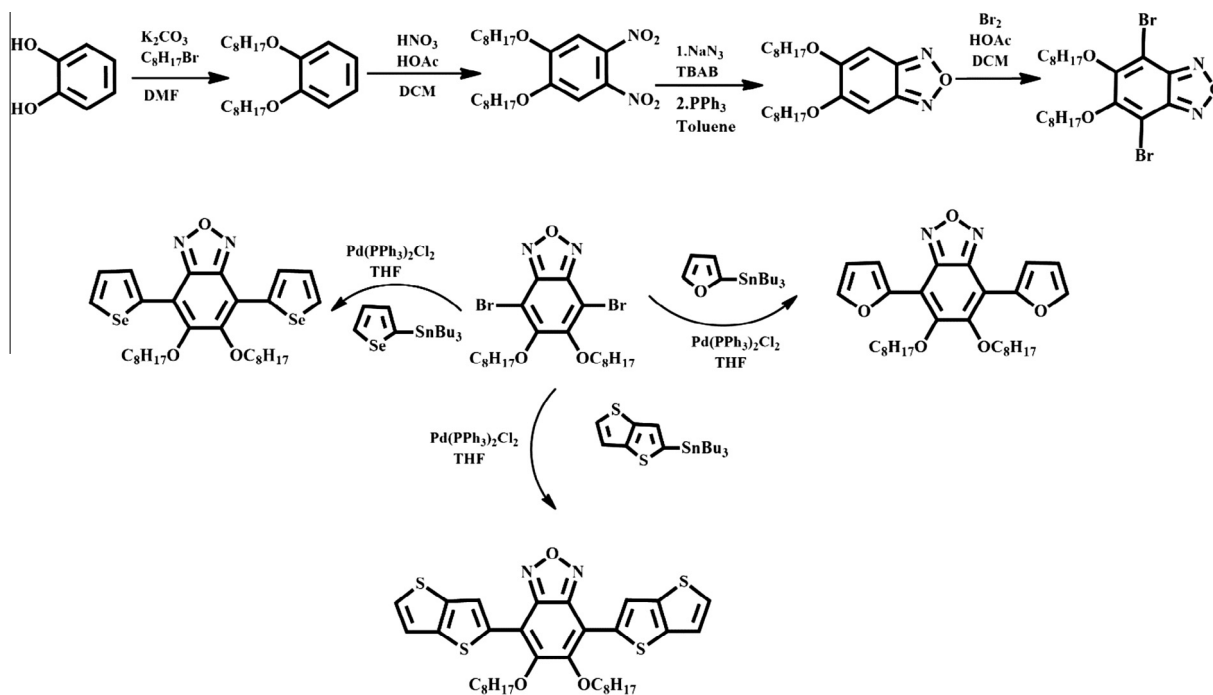
Low band gap polymers comprising benzooxadiazole unit can be obtained due to its good electron accepting property, coplanar structure and ability to adopt a quinoid structure. Therefore, benzooxadiazole is one of the most efficient hetero-aromatic moieties used in the synthesis of D–A type polymers. In addition, alkyl chain substitution on 5th and 6th positions of benzooxadiazole results in polymers with better solubility [13]. In the literature, thiophene is mostly used as an electron donor in the conjugated polymers however its selenium counterpart lately draws attention as a novel class of donor unit in the conjugated materials. Selenium atom in the polymer backbone provides promising optoelectronic

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properties [14a] ranging from high conductivity [14b] to high hole mobility [14c]. Selenium has less electronegativity and more polarizability than sulfur atom therefore tuning the band gap, optical and electronic properties can easily be achieved by introducing

selenophene unit into polymer backbone [15]. Electrophilic substitution into selenophene is easier than its sulfur counterpart. On the other hand, oligofuran [16] synthesis revealed that furan-based conjugated polymers can be classified as a promising hole



Scheme 1. Synthetic route for monomers.

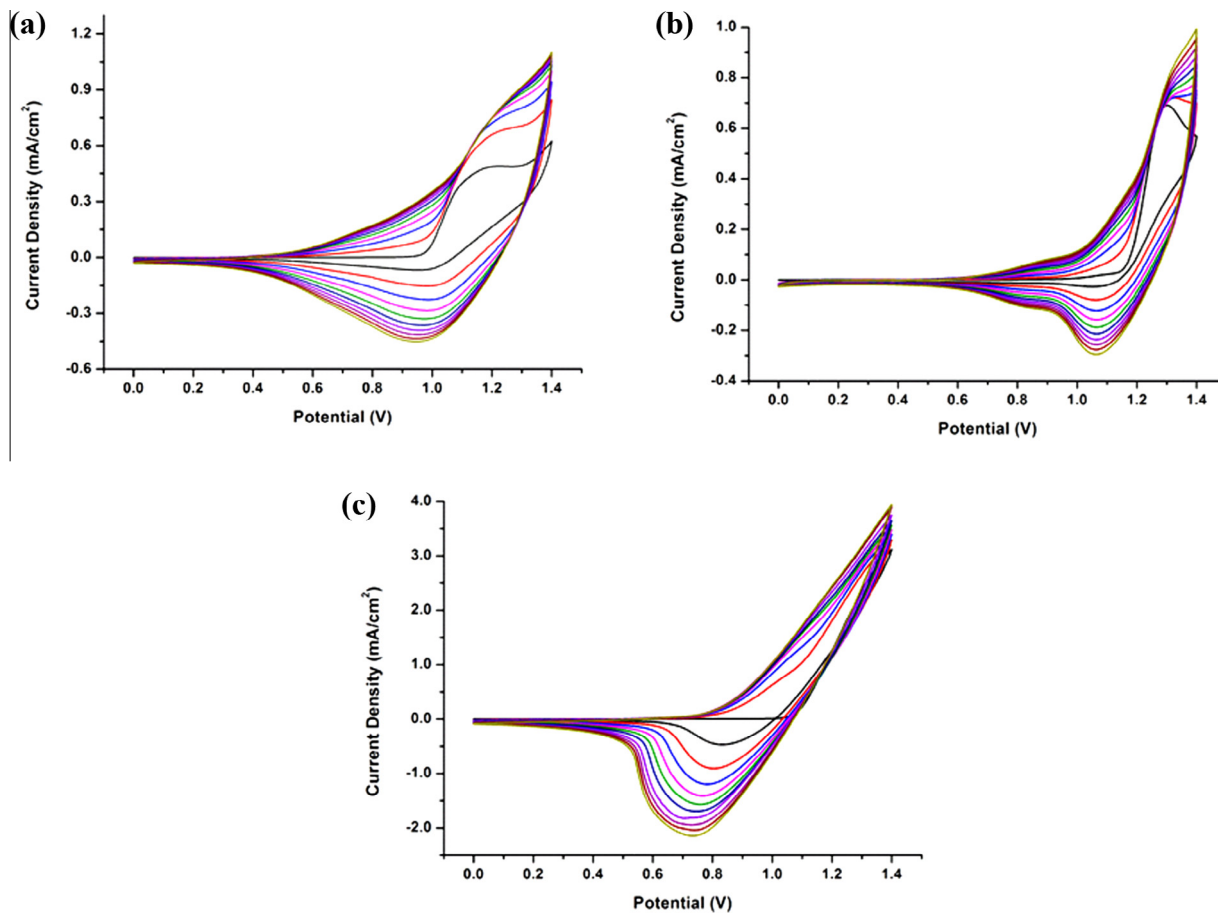


Fig. 1. Electrochemical deposition of (a) PTTBO, (b) PSBO and (c) PFBO on ITO in 0.1 M NaClO₄-LiClO₄/DCM/ACN electrolyte/solvent couple at a scan rate of 100 mV s⁻¹.

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