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Random copolymers of 1,2,3-benzotriazole and alkoxy-modified naptho[2,3-*b*:3,4-*b*′]dithiophene: Syntheses, characterization and optoelectronic properties

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ABSTRACT

Naphthodithiophene is a thiophene fused naphthalene with a rigid and planar structure with extended π-conjugation system and due its electron rich nature it has been recently employed in donor-acceptor type conducting polymers. In this study, alkoxy functionalized naphthodithiophene bearing two new random copolymers namely poly4-(5″-(5,6-bis(dodecyloxy)naphtho[2,1-*b*:3,4-*b*′]dithiophen-2-yl)-[2,2′:5′,2″-terthiophen]-5-yl)-2-dodecyl-7-(thiophen-2-yl)-2H-benzo[*d*] [1,2,3]triazole (P1) and poly4-(5″″-(5,6-bis(dodecyloxy)naphtho[2,1-*b*:3,4-*b*′]dithiophen-2-yl)-[2,2′:5′,2″:5″,2″′:5″′,2″″-quinquethiophen]-5-yl)-2-dodecyl-7-(thiophen-2-yl)-2H-benzo[*d*] [1,2,3]triazole (P2) were synthesized via Stille coupling reaction in order to monitor the effect of thiophene and bithiophene bridge units on electrochemical and optical properties of the corresponding polymers. As the acceptor moiety in the polymer backbone electron deficient benzotriazole moiety was used. Thiophene and bithiophene units were used as π-linkers to enhance electron delocalization through polymer chain. Via alkoxy modification, synthesized polymers were highly soluble in common solvents like THF, chloroform, chlorobenzene. Altering π bridge from thiophene bridge to bithiophene, kinetic properties of the polymers were improved. Electrochemical studies revealed that while P1 has only *p*-dopable nature, P2 has ambipolar character. Change of π-bridge from thiophene to bithiophene has affected the optoelectronic properties of the polymers in a favorable manner for different application areas. The polymers exhibited low lying highest occupied molecular orbital (−5.40 eV for P1 and −5.30 eV for P2) and moderate band gaps which are 2.05 eV and 2.02 eV for P1 and P2, respectively.

1. Introduction

Remarkable effort has been exerted in recent years for the development of novel semiconducting materials for several applications such as organic solar cells [1], electrochromic devices [2] and biosensors [3]. Design and synthesis are the key features of conjugated polymers to attain required optoelectronic properties. Extensively employed donor-acceptor approach allows modulation of optical band gap, absorption band and HOMO and LUMO energy levels of the polymers with the effective combination of electron rich donor and electron deficient acceptor units in the polymer backbone [4]. Another strategy for the enhancement in the optoelectronic properties is to synthesize random D-A type conjugated copolymers. Random copolymerization concept with three monomers has recently been chosen as an effective way to tune the band gap and energy levels of the conjugated polymers. One of the main reasons for the synthesis of semiconducting polymers with several components is broadening of their absorption spectra resulting in low band gap polymers. Moreover, this strategy provides to alter the molecular packing via components favoring π–π stacking. HOMO and LUMO energy levels of the polymers can be tuned by introducing components having different electron affinities. For regular alternating copolymers HOMO and LUMO are likely to be extended over all different units, resulting in sharp absorption bands, whereas in random copolymers the several sections with different chemical compositions can lead to broadening of spectra and possible formation of trap sites. However, formation of trap sites depends on the electronic nature of the monomers and hence does not necessarily lower the photovoltaic performances [5]. McCulloch and coworkers demonstrated solar cells with power

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conversion efficiencies as high as 5.14% with random terpolymers, compared to 2.68% for an alternating copolymer analogue. Also, they illustrated that solubility and processability of the polymers can be improved by random donor–acceptor terpolymers. Through variation of the third component in the copolymers, the frontier energy levels were successfully tuned and this approach clearly illustrated several benefits in relation to OPV device performance [6]. Random copolymers generally reveal broad absorption of the solar spectrum, and solar cell efficiencies of up to 8.11% with $PC_{71}BM$ have been reported [7]. Janssen et al. stated that random copolymerization is an effective strategy to develop state-of-the-art semiconducting polymers. They also demonstrated that random copolymers have good solubility and processability due to reduced crystallinity and π–π stacking [8]. Among various donor building blocks developed to date, thiophene fused heteroaromatic compounds such as benzodithiophenes (BDT), naphthodithiophenes (NDT) and anthradithiophenes (ADT) have drawn considerable interest recently [9]. In 2011, NDT was firstly reported as a novel donor material by Marks and coworkers. This study opened a new door for the syntheses and development of NDT derivatives [10]. Lee et al. first reported zNDT as a donor material in the small molecule system [11]. As an emerging donor building block, naphthodithiophene is drawing more attention in the field of organic semiconductors. With the rigid and coplanar molecule structure, NDT exhibits more application space relying on its own advantage for facilitating the charge carrier transport. Although, NDT-based polymer semiconductors have several attractive properties, they possess limited solubility in common organic solvents which hinders their widespread applications in organic electronics and optoelectronics. To achieve the solubility and thin film uniformity for solution processed OPVs and OFETs, two alkoxy groups were introduced to NDT units to further improve the photovoltaic performance of the zNDT-based small molecules [12,13]. Despite the extensive use of benzodithiophene, naphthodithiophene has been explored as a promising donor moiety for the synthesis of conjugated polymers due to its prominent properties. When incorporated into polymer backbone naphthodithiophene can provide extended π-conjugation due to its rigid, symmetrical and planar structure which are anticipated to promote charge carrier property of the copolymers. With the development of new synthetic methods and innovations in device processing conditions, different structural isomers and improvements in the power conversion efficiency in the NDT-based organic solar cells were reported. Wong et al. copolymerized alkoxy functionalized NDT core with benzothiadiazole moiety which revealed a PCE of 5.27%. Here alkoxy functionalization provides a solution to the possible solubility problem of the resulting copolymer [14].

In the meantime, several thiophene comprising polymeric materials have been reported in literature since thiophene based materials result in good harvesting of sunlight due to broad absorption, suitable molecular energy levels which provide good charge separation. Since thiophene based building blocks have good stability, high contrast and fast switching times, they can be great candidates for optoelectronic applications [15]. On the other hand, Hsu and coworkers demonstrated that polymers based on bithiophene reveal more extended conjugation, lower band gap and stronger intermolecular interaction due to its fully coplanar structure [16]. It was demonstrated that bithiophene-bridged D-A copolymers have better thermal stabilities than that of the corresponding thiophene-bridged copolymers. The hole mobility of the bithiophene-bridged copolymers is improved compared to thiophene based counterparts which is beneficial as photovoltaic donor materials in PSCs [17].

In this study naphtho[2,3-*b*:3,4-*b*′]dithiophene unit bearing donor-acceptor type of random copolymers were designed and synthesized via Stille polycondensation reaction. NDT was suited as the donor moiety in the copolymer backbone. Dodecyloxy groups were embedded in NDT unit for solution processability of corresponding polymers. As an acceptor moiety, diimine bearing benzotriazole moiety was chosen due to its electron deficient nature. Combination of NDT and BTz moieties in the same polymer backbone was missing in literature hence our purpose is to gain insight on the electrochemical, spectroelectrochemical and optical properties of polymers comprising these moieties. On the other hand, thiophene and bithiophene units were also used in the synthesis of random copolymers to investigate the effect of conjugation length and hence to enhance optoelectronic properties of the polymers.

2. Experimental

2.1. Materials and methods

All chemicals were purchased from Sigma-Aldrich and used without any purification in the synthesis and characterizations of polymers. THF and toluene were freshly distilled from Na-benzophenone ketyl before use. Merck Silica Gel 60 was used in column chromatography for the purification process. Structural characterization of compounds was performed with ^{1}H and ^{13}C NMR spectra which were recorded with Bruker Spectrospin Avance DPX-400 Spectrometer. All chemical shifts were given in ppm with respect to tetramethylsilane (TMS) as the internal reference. High Resolution Mass Spectroscopy measurements were carried out with Waters Synapt MS system. Gel Permeation Chromatography (GPC) was utilized in order to determine the average molecular weights and polydispersity index of polymers with Shimadzu GPC, with polystyrene standards where chloroform was the choice of eluent. Electrochemical studies were conducted by GAMRY Reference 600 Potentiostat with a three-electrode cell system containing indium tin oxide (ITO) coated glass as the working electrode, Pt wire as the counter electrode and Ag wire as the reference electrode in 0.1 M solution of tetrabutylammonium hexafluorophosphate-acetonitrile (ACN). HOMO and LUMO energy levels of polymers were calculated taking NHE as −4.75 eV with respect to vacuum. Spectroelectrochemical characterization of the polymers were completed with Varian Cary 5000 UV–Vis-NIR Spectrophotometer.

2.2. Syntheses

4,7-Bis(5-bromothiophen-2-yl)-2-dodecyl-2H-benzo[*d*] [1,2,3]triazole was synthesized according to literature and 5,6-bis(dodecyloxy)naphtho[2,1-*b*:3,4-*b*′]dithiophene was synthesized with a modification in previously described procedures [18].

2.2.1. Synthesis of 1,2-bis(dodecyloxy)benzene (1)

Pyrocatechol (4.00 g, 36 mmol) and K_2CO_3 (14.9 g, 108 mmol) were dissolved in anhydrous DMF (30 mL) under argon atmosphere. 1-Bromododecane (20.7 g, 83.2 mmol) was then added to the reaction mixture and refluxed for 40 h under inert atmosphere. After the reaction was completed, it was cooled down to room temperature and washed with excess distilled water. The product was extracted with dichloromethane (DCM), organic layer was separated and dried with $MgSO_4$. Solvent was evaporated under vacuum and the crude product was recrystallized from methanol, filtered and washed with methanol several times to get white solid with 64% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.88 (s, 4H), 3.99 (t, $J = 6.64$ Hz, 4H), 1.80 (q, $J = 6.78$ Hz, 4H), 1.26–1.50 (m, 36H), 0.88 (t, $J = 6.55$ Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 121.0, 114.2, 69.34, 31.94, 29.71, 29.66, 29.48, 29.38, 26.06, 22.70, 14.10 (3 missing peaks are due to overlaps)

2.2.2. Synthesis of 1,2-dibromo-4,5-bis(dodecyloxy)benzene (2)

1,2-Bis(dodecyloxy)benzene (1.00 g, 2.24 mmol) was dissolved in DCM (20 mL) in a three-neck round bottom flask connected to condenser with gas outlet filled with 10% aqueous NaOH solution. Bromine (0.23 mL, 4.48 mmol) in DCM (5 mL) was then added to the reaction mixture drop wise at 0 °C. The reaction mixture was stirred overnight under dark at room temperature. Completion of reaction was monitored