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A new processable electrochromic polymer based on an electron deficient fluorene derivative with a high coloration efficiency

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ABSTRACT

A new fluorenone based soluble polymer, namely poly(2,7-bis-(3,3-dihexyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)-fluoren-9-one) (PPFP), containing propylenedioxythiophene (ProDOT) as a donor and fluorenone (FO) as an acceptor group is highlighted. Electrochemical polymerization of 2,7-bis-(3,3-dihexyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)-fluoren-9-one (PFP) was achieved in dichloromethane/acetonitrile mixture with 0.1 M tetrabutylammonium hexafluorophosphate via potential cycling. The polymer shows an electrochromic behavior, a color change from orange to dark blue during oxidation with a high coloration efficiency (422 cm^2/C at 684 nm) and orange to yellow during reduction with high optical and electrochemical stability as compared to its close analogues, in addition it is found to be both p and n dopable. Furthermore, this soluble polymer exhibits fluorescent properties (the emission of orange light (578 nm) in THF solution).

1. Introduction

The design and synthesis of new π-conjugated polymers, are of still considerable interest due to their great promise for advanced technological applications including solar cells [1,2] and organic light-emitting diodes [3–5]. Among a great number of conjugated polymers with different emissive colors, polyfluorenes (PFs) are of great importance as a blue light emitting emissive layer not only due to its high thermal and chemical stability but also its high photoluminescence efficiency and good photostability [6–8]. However, PFs suffer from a number of drawbacks such as aggregation and excimer formation in the solid state, high energy barrier for hole injection and poor solubility in common solvents which limits their applications [9–12]. Besides these, it is also known that, labile H atoms in the 9-position may cause irreversible changes in the emission spectra [13]. In order to overcome these problems and to enhance the properties of PFs there have been a growing interest on the preparation of new fluorene based copolymers and/or functionalized homopolymers.

For example, it is well known that, substitution of the C-9 position of fluorene by alkyl chains enhances the solubility of PFs without changing optical and electrical properties of the polymer [14]. On the other hand, an electron withdrawing substituent at C-9 lowers the conduction band of the polymer and enhances the electron injection [15,16].

An example of such a fluorene derivative bearing an electron withdrawing group at C-9 position is fluorenone (FO), which was polymerized by chemical and electrochemical ways [17–21]. Besides functionalization, copolymerization of fluorene with various aryl partners allows easy tuning of electronic properties which is especially important for those PFs whose electronic properties are not easily tuned by chemical modifications [22]. For example, it is reported that the presence of anthracane along the polymer chain inhibits the excimer formation, in the copolymers prepared from hexylfluorene and anthracane [23]. Charas and his coworkers synthesized alternating copolymers combining fluorene and thiophene-based moieties and reported the possibility of tuning of emission color by modifying thiophene based moiety [24,25]. On the other hand, the band gap of PFs is also an important property not only for the color tuning purposes but also for the solar cell applications. It is known that a regular alternation of donor and acceptor groups reduces the band gap via broadening of the valence and conduction bands [26–28] therefore, various donor–acceptor type copolymers based on fluorene were prepared [29–36]. Wu and his co-workers reported that acceptor group strength is also important in color tuning [37]. Since fluorenone, bearing a strong electron withdrawing group, provides sites for facile and stable n-doping copolymers of fluorenone with benzene, furan and thiophene were synthesized. It is reported that the copolymers exhibit relatively lower band gap (1.9 eV) [38,39]. More recently, we reported synthesis and electrochemical polymerization of a monomer utilizing FO as acceptor and 3,4-ethylenedioxythiophene (EDOT) as the donor group. It is found that the polymer synthesized is both p and n dopable and also exhibits electrochromic behavior with high

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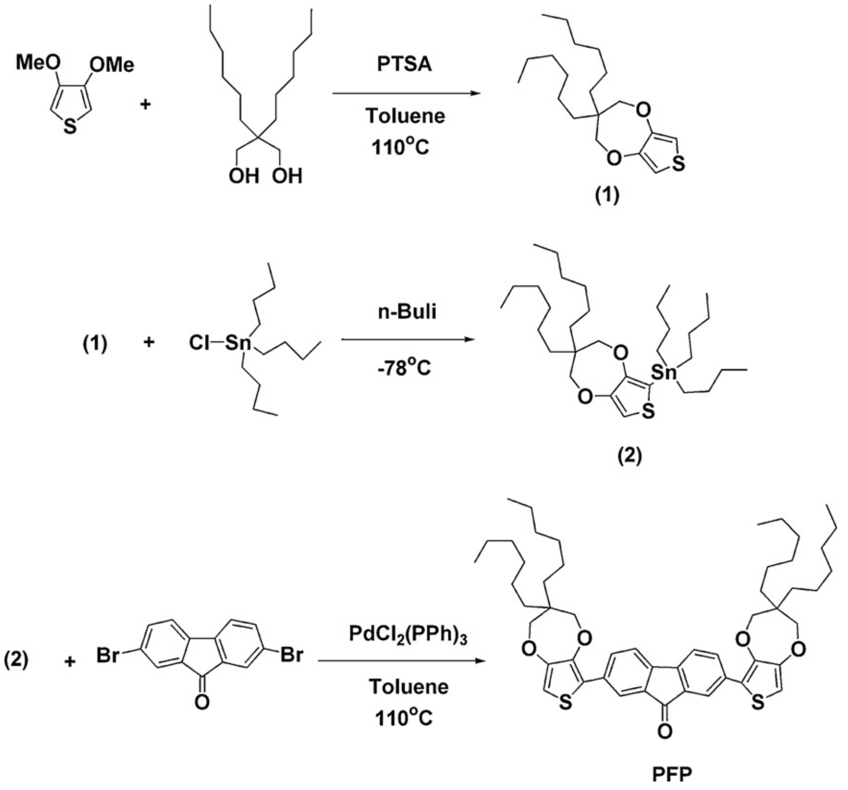

Scheme 1. Synthetic route of PFP.

coloration efficiency [21]. Unfortunately, the polymer was partially soluble only in THF. It is well-known that the presence of alkyl chains attached to 3,4-propylenedioxythiophene (ProDOT) units increases the solubility and the processability of the corresponding system [40–42]. Morover, dialkyl substituted thiophenes are expected to yield regioregular and isotactic polymers. In the light of this foreground, we designed and synthesized a new fluorenone derivative bearing ProDOT side groups as donor and fluorenone as acceptor. It is expected that the presence of dialkyl substituted ProDOT units would not only enhance the solubility but also change the optoelectronic properties by changing the band gap. Furthermore, the polymer is expected to be regioregular, which is also an important factor in determining the optical properties of conjugated polymers, and most PFs suffer from the problem of low regioregularity due to branching through positions other than 2 and 7 positions of PF.

In this paper, we wish to report our results concerning the synthesis and electrochemical polymerization of a new monomer, 2,7-bis-(3,3-dihexyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)-fluoren-9-one (PFP). Electrochemical, electro-optical and electrochromic properties of the corresponding polymer poly(2,7-bis-(3,3-dihexyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)-fluoren-9-one (PPFP) were investigated using cyclic voltammetry (CV) and *in situ* spectroelectrochemical techniques. In order to elucidate the effect of donor group, the results obtained for PPFP are compared with its close analogues containing thiophene and EDOT as donor groups.

2. Experimental

2.1. General information

All chemicals were purchased from Aldrich Chemical. 0.1 M tetrabutylammonium-hexafluorophosphate ($TBAPF_6$) used as electrolyte, dissolved in dichloromethane (DCM) and acetonitrile (ACN) which was freshly distilled over CaH_2 prior to its use.

A platinum disc (0.02 cm^2) and platinum wire were used as working and counter electrodes, respectively. Ag/AgCl in 3 M NaCl (aq.) solution was also used as reference electrode.

Polymer films were obtained via repetitive cycling and their electrochemical and optical behaviors were investigated in monomer free electrolyte solutions. For spectroelectrochemical studies, platinum and silver (calibrated externally using 5 mM solution of ferrocene/ferrocenium couple) wires were used as counter and reference electrodes, respectively. An indium-tin oxide (ITO, Delta Tech. 8–12 Ω, 0.7 cm × 5 cm) coated by the polymer film was

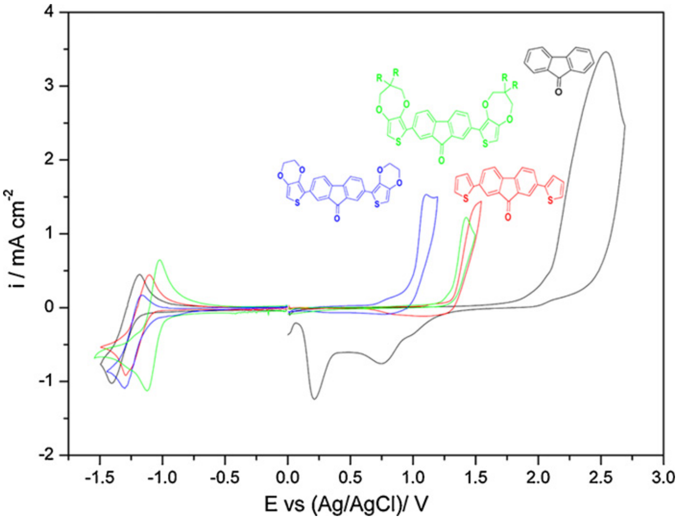

Fig. 1. First oxidation potential comparison of FO, TFT, EFE and PFP in 0.1 M $TBAPF_6$/DCM at 100 mV/s onto a Pt disc (area = 0.02 cm^2).