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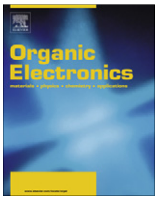

A neutral state yellow to navy polymer electrochrome with pyrene scaffold

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ABSTRACT

A new pyrene based soluble polymer, namely poly(3,3-didecyl-6-(1-(3,3-didecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)pyren-6-yl)-3,4-dihydro-2H-thieno[3,4-b][1,4] dioxepine), **P5**, which is synthesized by both chemical and electrochemical methods, is highlighted. The polymer shows both electrochromic and fluorescent properties (the emission of yellow (545 nm) and yellowish green light (524 nm) in solid state and in THF solution, respectively). It is noteworthy that **P5** has a specific optical band gap (2.2 eV) to reflect the yellow color in the neutral state. Furthermore, the optical and electrochemical features of the polymer were investigated.

1. Introduction

The design and synthesis of novel organic materials, specifically the conjugated polymers, are of considerable interest since they hold great promise for advanced technological applications in the fields of light emitting diodes (LEDs) [1,2], photovoltaics [3,4], and transistors [5,6]. In particular, they have been envisioned as one of the most useful electrochromes for high performance innovative devices [7,8], displays [9], smart windows [10,11], mirrors [12,13] and camouflage materials [14,15]. Organic polymer electrochromes (PECs) [16,17] can show high optical contrast ratio, high redox stability, long cycle life, multicolors with the same material, low response time and low operation voltage when compared to inorganic variants. For polymeric RGB applications in an industrial platform, it is important to process organic PECs onto large area surfaces: Compatibility, tunable intrinsic properties and also processablity of these materials offered by the structural design pave the way of this. Therefore, significant effort has been devoted to design and synthesize of novel solution-processable PECs [16,17], which exhibnit many distinct and saturated colors of the spectrum including blue [18–20], green [20–25] and black [26–28] in the neutral state. In this context, we recently reported a series of solution processable D-A type PECs with tunable colors and performance [20]. Furthermore, it was shown that the neutral state colors of the PECs can easily be controlled through rational design of the backbone structures which mainly control the optical properties and allow spectral engineering [20,25,27,29]. However, it should be noted that the palette of colors that are available with PECs, should be extended, if the full color displays are desired where the PEC is an active colorant. At this stage, it is desired to design and synthesize of new PECs with yellow color on which scant studies have been done [30] one leg of the CMY (Cyan-Magenta-Yellow) color space [16].

On the other hand, pyrene and its derivatives are valuable fluorescent probes due to their unique fluorescence properties, which can be used in a variety of applications including sensors [31–35], LEDs [36,37] and transistors [38]. Also, having both electrochromism and fluorescent properties in a single molecule gets some advantages such

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as multifunctionality and miniaturization [39]. In contrast to these numerous applications of pyrene derivatives, regioregular polymeric systems with pyrene scaffold in the main chain are uncommon [40], albeit a few random copolymers of pyrene with pyrrole [41], 3,4-ethylenedioxythiophene [42] and bithiophene [43] have been reported.

In this paper, we wish to report the synthesis and properties of a novel processable regioregular PEC which is based on pyrene (**Py**) and didecylpropylenedioxythiophene (**P**). In this unique combination, **P** units provide solubility and low oxidation potential as well as electrochromic features whereas **Py** scaffold contributes with its fluorescence to this dual electrochromic and luminescent system. It is noteworthy that this novel processable PEC has a specific optical band gap (2.2 eV) to reflect or transmit the yellow color in the neutral state, which can be switched to a navy state upon doping. Furthermore, the optical and electrochemical features of this PEC were investigated.

2. Experimental details

All chemicals were purchased from Aldrich Chemical and used as received unless otherwise noted. 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) dissolved in dichloromethane (DCM) and acetonitrile (ACN) was used as electrolyte solution. A platinum disk (0.02 cm^2) and a platinum wire were used as working and counter electrodes, respectively, as well as a Ag/ AgCl reference electrode (calibrated externally using 10 mM solution of ferrocene/ferrocenium couple which is an internal standard calibrated to be 0.44 V in ACN solution vs. Ag/AgCl). Repetitive cycling or constant potential electrolysis was used to obtain the polymer films. Electro-optical properties were investigated by using an indium tin oxide (ITO, Delta Tech. 8–12 Ω, 0.7 × 5 cm) electrode as well as a platinum wire as counter electrode and an Ag wire as a pseudo-reference electrode. For the spectroelectrochemical measurements, **P5** polymer film was coated on ITO electrode via cyclic voltammetry (between 0 and 1.15 V, 10 cycles) from a solution of **5** (5×10^{-3} M) in 0.1 M TBAH/ACN. In order to break in the polymer film, it was switched between 0.0 and 1.25 V in a monomer-free electrolytic solution during five cycles. Electroanalytical measurements were performed using a Gamry PCI4/300 potentiostat–galvanostat. The electro-optical spectra were monitored on a Hewlett–Packard8453A diode array spectrometer. FTIR spectra were recorded on Nicolet 510 FTIR with an attenuated total reflectance (ATR). High resolution mass spectrometry analysis of **5** was done via Water, Synapt HRMS instrument. GPC analysis of polymer was carried out with Polymer Laboratories PL-GPC 220 instrument. TGA analysis was done via Perkin Elmer Pyris 1 TGA under nitrogen atmosphere with 10 °C/minute heating rate. Bromination of pyrene (**1**) [44] and the synthesis of **4** [20] were carried out according to previously reported procedures.

2.1. Synthesis of 5

To an argon-degassed solution of **2** (150 mg, 0.417 mmol) and **4** (635 mg, 0.875 mmol) in dry toluene (30 mL) was added $Pd(PPh_3)_2Cl_2$ (62 mg, 0.0875 mmol) and the mixture was heated under reflux during 5 days. After being cooled to room temperature, the solvent was removed under reduced pressure. The crude mixture was chromatographed on silica gel by eluting with hexane: methylene chloride (10:1, v/v) to give **5**. 56% yield, yellow viscous liquid.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.18–7.93 (m, 8H, Ar H), 6.55 (s, 2H, Ar H), 3.92 (s, 4H), 3.80 (s, 4H), 1.46–1.09 (m, 72H), 0.88–0.76 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 149.64, 146.35, 131.00, 129.89, 129.14, 129.11, 127.20, 126.26, 124.89, 124.56, 120.36, 103.98, 77.02, 49.56, 38.08, 31.92, 30.50, 29.65, 29.63, 29.56, 29.34, 22.96, 22.69, 14.11.

FTIR (ATR, cm^{-1}): 2926, 2950, 1609, 1509, 1487, 1467, 1405, 1375, 1270, 1176, 1042, 942, 849, 808, 732, 683.

2.2. Chemical polymerization of 5

Compound **5** (145 mg, 0.135 mmol) was dissolved in chloroform (50 mL). A solution of anhydrous $FeCl_3$ (110 mg, 0.675 mmol, 5 equiv) in nitromethane was added dropwise over a period of 45 min to the stirred monomer at room temperature (the bright yellow monomer solution turned progressively dark blue with addition of oxidizing agent). The mixture was stirred 48 h at room temperature. It was then precipitated into methanol (300 mL). The precipitate was filtered, redissolved in chloroform (300 mL), and stirred for 6 h with hydrazine monohydrate (6 mL) (the color of the solution was turned from dark blue to yellow after addition of the hydrazine monohydrate). After evaporation, the concentrate (dark blue) was precipitated into methanol (300 mL), the precipitate was filtered through a Soxhlet thimble and purified via Soxhlet extraction for 48 h with methanol. The polymer was extracted with chloroform and concentrated by evaporation. Then, the polymer was precipitated in methanol (300 mL) and collected as a black solid (52% yield).

3. Results and discussion

The synthesis of the target compound **5** (**PPyP**) started with the bromination of pyrene (**1**), as outlined in Scheme 1. This reaction yielded a mixture of 1,6- (**2**) and 1,4-dibromopyrene (**3**), from which 1,6-regioisomer (**2**) was isolated by repeated recrystallization from toluene [44,45]. Stille coupling reaction of 2 with tributyl(3,3-didecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-8-yl)stannane (**4**) [20] in the next step provided **5** in a yield of 56% (Scheme 2). Compound **5** was initially characterized by spectral (^{1}H, ^{13}C NMR, FTIR, see supporting information Fig. S1–S3) data, which was in well aggreement with the structure.

UV–vis absorption and emission spectra of **5** were depicted in Fig. 1. It was found that **5** emits blue light (431 nm) in THF solution as it is the case for many pyrene derivatives. It should be noted that organic compounds with emissions in the solid state are quite rare, since even bright organic fluorophores pack very tightly in the crystalline state or amorphous solid phase (as thin films), leading to very significant quenching [46–48]. As π–π stacking is