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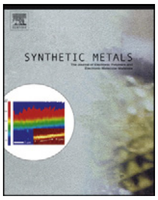

Electrosynthesis and characterization of a novel electrochromic copolymer based on 1,4-bis(3-hexylthiophen-2-yl)benzene and perylene dye

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ABSTRACT

An electrochromic copolymer based on 1,4-bis(3-hexylthiophen-2-yl)benzene (BHThBe) and perylene was electrochemically synthesized in dichloromethane (DCM) containing tetrabutylammonium perchlorate (TBAP) via the direct oxidation of BHThBe/perylene mixtures. The morphology and structure of as-prepared P(BHThBe–perylene) copolymer were characterized by SEM and FT-IR, respectively. The band gap energy (E_g) of P(BHThBe–perylene) in the neutral state was calculated to be 2.03 eV based on the onset of the second π–π^* transition. The copolymer exhibited four different colors (brick red, grey brown, grey green, and black blue) during a wide potential ranging from 0.40 to 1.20 V. Tunable electrochromism as well as smooth morphology made this copolymer a great candidate for many applications.

1. Introduction

Electrochromic (EC) materials have fascinated many scientists due to their potential applications in energy-saving "smart" windows [1], displays [2,3] and electrochromic paper [4]. Many types of chemical species, such as inorganic metal oxide [5,6], organic small molecules [7] and conjugated polymers [8,9] exhibit electrochromism, but only those with favorable electrochromic performance parameters (fast response time, long-term stability and high contrast) are potentially useful in commercial applications. Among a series of EC materials, conjugated polymers have drawn more and more attentions due to their tunable energy gap (E_g), higher switching rate and low cost. Conjugated polymers can be synthesized by either chemical or electrochemical polymerization. Although chemical routes are easy to get products on a large scale, insoluble polymers are difficult to be processed during the film coating in the process of device fabrication. Compared with the chemical routes, electrochemical polymerization can obtain conjugated polymer film on conductive substrates directly. This not only enlarges the scope of candidate polymers [10,11], but also simplifies the procedure of the film coating [12].

Recently, the enhancement of optical contrast and color modulation of conjugated polymers by using dye-containing synthesis solutions has been reported [13–15]. Other characteristics such as response time, electrochromic stability, and mechanical properties could also be improved [13,16], which lead to good electrochromic devices. Among various dyes, perylene is a naturally occurring symmetric polycyclic aromatic hydrocarbon which contains both anthracenes and phenanthrenes. And its high fluorescent quantum yields, photostability, thermal stability and chemical inertness make perylene an excellent organic semiconductor material [17]. Perylene derivatives have been attracting considerable attention as laser dyes, optical amplification, highly efficient fluorescent probe and photovoltaic active layer. However, little attention was paid to the potential applications as electrochromic materials. A key issue for perylene is its very low solubility, which seriously effects film formation in the context of application. Therefore, the use of vacuum evaporation is usually necessary for thin film fabrication.

In this study, a novel copolymer based on perylene and 1,4-bis(3- hexylthiophen-2-yl)benzene (BHThBe) was successfully synthesized via the electrochemical oxidation polymerization of perylene/BHThBe mixtures. The influence of the perylene dye on the electrochromic properties was investigated. The obtained copolymers were characterized by cyclic voltammetry (CV), FT-IR and UV–vis spectra. The basic structure of the copolymer and the reaction were illustrated in Scheme 1.

2. Experimental

2.1. Materials

2-Bromo-3-hexylthiophene (Huicheng chemical, 98%), 1,4-dibromobenzene (Acros, 99%), 1,1′-bis(diphenylphosphino) ferrocene palladium dichloride (Pd(dppf) Cl_2) (J&K Chemical, 99%),

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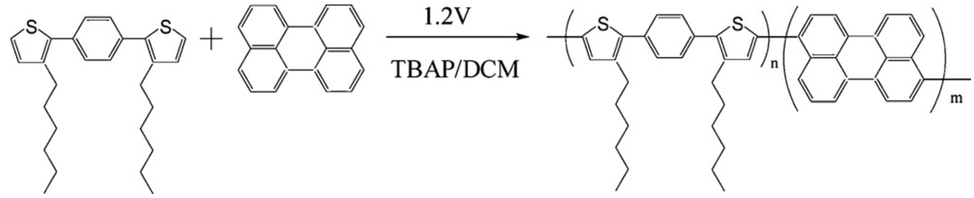
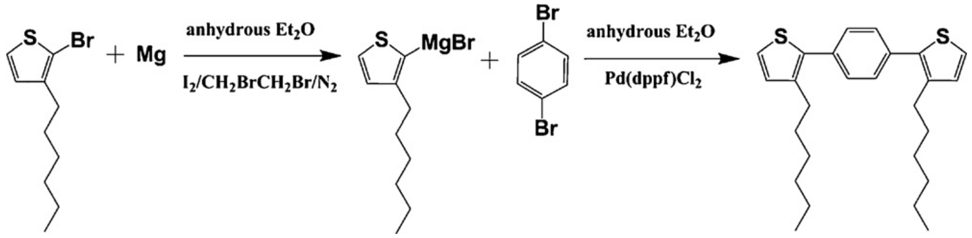


Scheme 1. Electrochemical copolymerization reaction of BHThBe and perylene.



Scheme 2. Synthetic route of monomer BHThBe.

magnesium powder (Alfa-Aesar, 99.8%), perylene (Acros Organics, 95%), tetrabutylammonium perchlorate (TBAP, Acros Organics, 95%) and dichloromethane (DCM, Shanghai Chemical Reagent Company) were used without further purification. All other regents were commercial products used as received. 1,4-Bis(3-hexylthiophen-2-yl)benzene (BHThBe) was synthesized according to our groups' previous work [18]. Indium-tin-oxide-coated (ITO) glass (CSG Holding Co., Ltd., Sheet resistance: <10 Ω^{-1}) was washed successively with ethanol, acetonization and deionized water under ultrasonic, and then dried by N_2 flow.

2.2. Synthesis of monomer BHThBe

Synthetic route of monomer BHThBe was illustrated in Scheme 2 and described briefly as follows. 14.94 g 2-bromo-3-hexylthiophene in 15 mL diethyl ether (Et_2O) was added dropwise into stirred suspension of magnesium powder in anhydrous Et_2O. After stirred for 2 h, the obtained Grignard reagent was added into Et_2O solution of 1,4-dibromobenzene (2.12 g) and $Pd(dppf)Cl_2$ (0.1 g) in iced bath. The mixture solution was stirred at room temperature for 36 h under nitrogen atmosphere. The reaction mixture was poured into 2 M HCl, and then the aqueous layer was extracted with chloroform. The evaporation residue was further purified by elution chromatography on a silica column with n-hexane as mobile phase. Finally, the pure BHThBe was obtained as a yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.46 (s, 4H, benzene); 7.24 (d, 2H, thiophene); 6.99 (d, 2H, thiophene); 2.69 (t, 4H, 2× Th-CH_2-C_5H_{11}); 1.63 (m, 4H, 2× Th-CH_2-CH_2-C_4H_9); 1.31 (m, 12H, 2× Th-C_2H_4-C_3H_6-CH_3); 0.86 (t, 6H, 2× Th-C_5H_{10}-CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 138.8; 137.3; 133.7; 129.6; 129.3; 123.8; 31.6; 31.0; 29.2; 28.7; 22.6; 14.1. EM: m/z (relative intensity) 410.2 (M^+, 100%). HRMS: calculated for $C_{26}H_{34}S_2$ m/z 410.2136, found m/z 410.2148.

2.3. Electrochemistry

Electrochemical experiments were carried out in a typical three-electrode cell, and an ITO/glass (surface area of 1 cm^2) was used as the working electrode, a platinum sheet was used as a counter electrode and an Ag/AgCl (saturated KCl) was used as a reference electrode. The electrochemical experiments were performed using a CHI 660 C Electrochemical Analyzer under N_2 atmosphere at room temperature.

All electrochemical polymerization and CV tests were taken in DCM solution containing 0.1 M TBAP as a supporting electrolyte. Both the concentrations of perylene and BHThBe in 0.1 M TBAP/DCM for polymerization were 5 mM. The homopolymer and copolymer films were obtained potentiostatically (1.2 V). After polymerization, electrochemical dedoping of copolymer was carried out at −0.4 V for 10 min, then the copolymers were washed with DCM for 3 times to remove the supporting electrolyte and oligomers/monomers.

2.4. Characterizations

Infrared spectra were recorded using a Bruker Vertex 70 FT-IR spectrometer with KBr pellets. UV–vis spectra were performed on a Varian Cary 100 UV-vis spectrophotometer. SEM measurements were taken by using a Hitachi S-4800 scanning electron microscopy.

3. Results and discussion

3.1. Electrochemical properties

The electropolymerization process of the copolymer and homopolymer was showed by CV curves. Fig. 1 displays the successive electropolymerization CV curves of BHThBe, perylene and

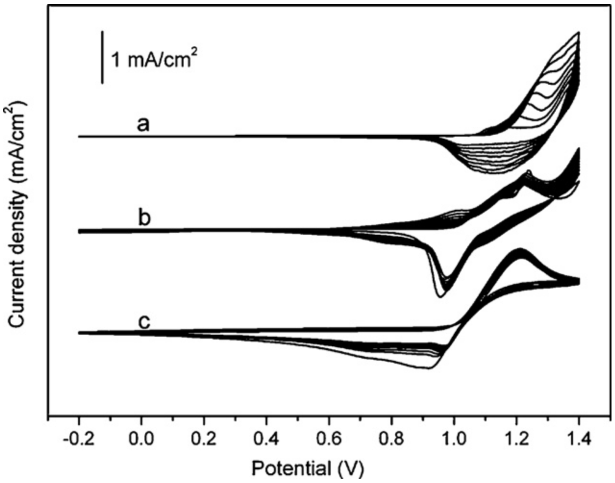


Fig. 1. Cyclic voltammogram curves of (a) 5 mM BHThBe, (b) the mixture of 5 mM BHThBe and 5 mM perylene and (c) 5 mM perylene in 0.1 M TBAP/DCM solution at a scan rate of 100 mV s^{-1}.