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ORIGINAL PAPER

Iodine-free organic dye sensitized solar cells with in situ polymerized hole transporting material from alkoxy-substituted TriEDOT

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Abstract An alkoxy-substituted ethylenedioxythiophene (EDOT) trimer is designed and synthesized which has shown a low oxidation potential of 0.50 V versus saturated calomel electrode (SCE). In situ polymerization of the trimer in a thin layer electrolytic cell using organic dye adsorbed on TiO_2 as the working electrode yielded alkoxy-substituted poly(ethylenedioxythiophene) (PEDOT). With D149 as the dye sensitizer and the in situ polymerized polymer as hole-transporting material (HTM), dye sensitized solar cells (DSSCs) were fabricated to show a typical power conversion efficiency of 3.97% under AM 1.5 G (100 mW cm^{-2}) illumination. The results show good promise of in situ polymerized conjugated polymers as HTM for iodine/iodide redox-free DSSC applications.

Keywords Electrochemical polymerization · Hole-transporting material · Tri-EDOT · PEDOT · Organic dye · Dye-sensitized solar cell

Introduction

Dye-sensitized solar cells (DSSCs) have attracted great interest in both academic research and industry due to their high energy conversion efficiency and low cost fabrication [1–3]. A typical DSSC comprises of a dye-sensitized semiconductor photoanode, an electrolyte-containing redox couple and a counter electrode (CE) [4, 5]. The long-term application of these DSSCs is limited by electrolyte permeability of the encapsulation and the corrosive action of the iodine–iodide redox couple in devices [4–10]. Although great success has been made to find less volatile electrolytes such as ionic liquids [6, 7], most devices still contain the

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iodine/iodide couple. Complete replacement of both liquid electrolyte system and the redox couple with in situ polymerized conjugated polymers as the HTM is one of the most promising strategies to simultaneously solve both problems [8, 9].

For in situ polymerized HTM-based DSSCs, polymerization is initiated by photo-created holes at the HOMO level of dyes adsorbed on TiO_2 surface. This requires that the electrochemical polymerization of the pre-penetrated monomers must be carried out at potentials that are lower than the oxidation limit for the dye to suppress dye oxidative degradation. So far only bis-ethylenedioxythiophene (bi-EDOT) has been used as a monomer for in situ polymerization of HTM. Since bi-EDOT has an oxidation potential of 0.80 V versus saturated calomel electrode (SCE), it is only applicable to certain dyes with oxidation potentials that are higher or close to 0.80 V, such as D149 (0.84 V vs. SCE) and Z907 (0.77 V vs. SCE) [1]. Recent studies have shown that some very promising organic dyes, such as C218 and C217 could lead to device efficiencies of up to 8.95 and 9.8% in traditional DSSCs [10, 11]. However, application of these dyes in in situ polymerized HTM-based DSSCs is greatly hampered as the oxidation potentials for C217 and D-11 are 0.29 and 0.68 V versus SCE, respectively, which are obviously lower than that for bi-EDOT. To further improve the efficiency of polymer HTM-based DSSCs and broaden its application to a variety of organic/inorganic dyes, it is highly desirable to develop new HTM monomers with a lower oxidation potential than that for most available dyes.

Recent studies have shown that tri-ethylenedioxythiophene (tri-EDOT) has an onset potential of ~0.49 V versus Ag/AgCl [12]. This oxidation potential is significantly lower than that for most available dyes and as a consequence, it should be more generally applicable to in situ polymerized HTM-based DSSCs. However, the unsubstituted TriEDOT has shown limited solubility in organic solvents, which makes it less suitable for electrochemical polymerization [12–14]. In this communication, we report the synthesis of an alkoxy-substituted EDOT trimer and its in situ polymerization in electrolytic cells during device fabrication. In addition, an indoline D149 dye-sensitized solar cell is further assembled with the in situ polymerized HTM to yield devices with an average light to electrical efficiency of 3.97% under full sun illumination (AM1.5, 100 mW/cm^2).

Experimental

Synthesis of alkoxy-substituted TriEDOT

*Synthesis of 2-2,5,8,11-tetraoxadodecyl-2,3-dihydrothieno[3,4-b][1,4]dioxine (**4**) [15]*

(2,3-Dihydrothieno[3,4-b] [1,4]dioxin-2-yl)methanol (**3**) (0.45 g, 2.91 mmol) was dissolved in 15 mL of anhydrous DMF, and sodium hydride (1.26 g, 31.6 mmol) was added and stirred for 30 min before 1-bromo-2-(2-(2-methoxyethoxy) ethoxy)ethane (**2**) (1.44 g, 6.32 mmol) was further added into the solution. The mixture was stirred for another 12 h at 90 °C. After the mixture was cooled down to room temperature, 100 mL of water was added. The resulting mixture was extracted with chloroform (50 mL × 3) and the combined organic extracts were washed with water (50 mL × 3) and brine (50 mL × 1). The organic mixture was dried over anhydrous magnesium sulfate. After filtration, the solvent was removed by rotary evaporation and the crude product was purified by column chromatography using n-hexane/ethyl acetate = 2:1 as eluent to give **4** (0.68 g, 82%) as a colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 6.31–6.30 (m, 2H), 4.31–4.23 (m, 2H), 4.07–4.02 (m, 1H), 3.78–3.74 (m, 12H), 3.68–3.65 (m, 2H), 3.36 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 141.60, 141.52, 99.61, 99.53, 72.63, 71.93, 71.19, 70.64, 70.60, 70.55, 70.52, 69.63, 66.12, 58.99.

*Synthesis of 5,7-dibromo-2-((2-(2-(2-methoxyethoxy)ethoxy)ethoxy) methyl)-2,3-dihydrothieno[3,4-b][1,4]dioxine (**5**)*

Compound **4** (0.60 g, 1.88 mmol) and NBS (0.77 g, 4.33 mmol) were dissolved in 15 mL of DMF. The mixture was stirred for 12 h at 90 °C under nitrogen protection. After the reaction was cooled down to room temperature, 100 mL of chloroform was added. The organic layer was subsequently washed with water (100 mL × 5) and brine. After drying over anhydrous magnesium sulfate, the solvent was removed by rotary evaporation to give **5** (0.62 g, 70% yield) as a colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 4.33–4.30 (m, 2H), 4.12–4.08 (m, 1H), 3.80–3.77 (m, 1H), 3.70–3.66 (m, 3H), 3.62–3.60 (m, 8H), 3.52–3.50 (m, 2H), 3.34 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 139.45, 139.39, 85.10, 85.08, 72.95, 71.72, 71.10, 70.44, 70.40, 70.31, 68.82, 66.24, 58.80. EI: 475.9.

*Synthesis of 5,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2-((2-(2-(2-methoxyethoxy)ethoxy)ethoxy)methyl)-2,3-dihydrothieno[3,4-b][1,4]dioxine (**7**)*

Compound **5** (200 mg, 0.42 mmol), 2-(tributylstannyl)-3,4-(ethylenedioxy)thiophene (**6**) [16] (600 mg), $Pd(PPh_3)_2Cl_2$ (15.2 mg), and 2,6-ditertbutyl phenol (4.0 mg) were mixed together in a 25-mL round-bottom flask before 5 mL of THF was added. The mixture was stirred for 24 h at 75 °C under nitrogen protection. After the reaction was cooled down to room temperature, the mixture was poured into water and extracted with chloroform (25 mL × 3). The combined organic layer was washed with brine and dried over anhydrous magnesium sulfate. After filtration, the solvent was removed by rotary evaporation and the crude product was purified by column chromatography using *n*-hexane/ethyl acetate (v/v = 2:1) as eluent to afford **7** (120 mg, 48% yield) as sticky liquid. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 6.26 (s, 1H), 6.25 (s, 1H), 4.34–4.20 (m, 10H), 3.75–3.53 (m, 14H), 3.36 (s, 3H). MALDI-TOF: 598.604.

Fabrication of D149-dye-sensitized TiO_2 photoelectrode

Firstly, TiO_2 dense film was prepared by spraying 0.2 M $Ti(OPr)_2(Acac)_2$ on cleaned FTO/glass (TEC15, LOF) at 450 °C. The diluted TiO_2 paste (Solaronix T/SP) was doctor-bladed on the surface of the dense film. The film was sintered at

125 °C for 20 min, 325 °C for 15 min, 375 °C for 15 min and 450 °C for 20 min, respectively. The film was then treated with 40 mM $TiCl_4$ aqueous solution at 70 °C for 30 min and sintered again at 450 °C for 30 min. After cooling to 80 °C, the film was immersed into a solution containing 0.3 mM D149 and 0.3 mM deoxycholic acid in a mixture of acetonitrile and *tert*-butyl alcohol (v/v = 1/1). The films were kept for 2 h at room temperature, which were followed by rinsing with acetone and dried under nitrogen gas flow.

In situ polymerization of tri-EDOT

For in situ polymerization, dye-sensitized TiO_2 photoelectrode and pyrolyzed Pt/FTO electrode were clipped together to assemble the thin layer electrolytic cell. Parafilm was used as the spacer and sealant. 0.04 M tri-EDOT and 0.1 M lithium perchlorate in acetonitrile solution was used for polymerization. Filtered (500–1100 nm) xenon lamp light of 25 mW/cm^2 was used to illuminate the thin layer cell from the Pt/FTO side. The polymerization lasted for 1500 s with the current density maintained at 10 μA/cm^2.

Cell assembly

The dye-sensitized TiO_2 photoelectrode with in situ polymerized polymer layer was then treated with 25 mM lithium bistrifluoromethanesulfonimide in propylene carbonate solution for 1 day. The photoelectrode was subsequently dried under strong N_2 gas flow and clipped with the CE to form DSSCs. The CE was gold-coated FTO/glass, which was obtained through sputtering Au at 20 mA for 300 s. The active area of the cells was 0.15 cm^2.

Characterization

All chemicals and organic solvents were purchased from Sigma-Aldrich chemical company unless otherwise noted.

NMR spectra were collected on a Bruker DPX 500 spectrometer with *d*-chloroform as the solvent. Maldi-TOF mass was tested using a Bruker Autoflex II with THF as the solvent and 2,5-dihydroxybenzoic acid (DHB) as the matrix. EI-mass was tested on Micromass 7034E mass spectrometer. The cyclic voltammetry was conducted in dry DMF (refluxed with CaH_2) with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the electrolyte at a scan rate of 100 mV/s. A glassy carbon was used as the working electrode, and a Pt wire was used as the CE with $Ag/AgNO_3$ as the reference electrode. The potential was calibrated with ferrocene.

UV–Vis transmittance spectrum of D149-sensitized TiO_2 layer was collected with a Shimadzu UV-1700 spectrophotometer. The cyclic voltammetry measurements were performed on Autolab (PGSTAT30) electrochemical workstation. The photocurrent–photovoltage measurements were recorded by the electrochemical workstation (PGSTAT30, Autolab). A solar simulator (XES-151S, San-EI Electric) was used as the light source for measuring the solar cells with an XUL0385 filter. The intensity of incident light was calibrated using a reference cell (OptoPolymer, ISE CalLab) before each experiment. Incident photon to collected electron efficiency (IPCE) was measured using a 300 W xenon light source (MAX-310, Asahi Spectra) and a monochromator (TMS300, Bentham). The Au was sputtered using auto fine coater JFC-1600, JEOL. All measurements and cell assembly were performed in air.

Results and discussion

Synthesis of tri-EDOT

The synthetic entry to tri-EDOT is shown in Fig. 1. 1-Bromo-2-(2-(2-methoxyethoxy) ethoxy) ethane (**2**) was obtained in 56% yield by dropping PBr_3 into 2-(2-(2-methoxyethoxy)ethoxy)ethanol (**1**) in an ice bath. Reaction between (2,3-dihydrothieno[3,4-b]1,4]dioxin-2-yl)methanol (**3**) and **2** in basic condition led to alkoxyl substituted EDOT **4** in 82% yield. Treatment of **4** with NBS in DMF in the absence of light gave **5** in 70% yield. The 2,3-dihydrothieno[3,4-b]-1,4-dioxintin reagent (**6**) was obtained by treatment of EDOT with butyllithium in THF at −78 °C, followed by the addition of tributyltin chloride. In the last step, coupling between **5** and **6** under the

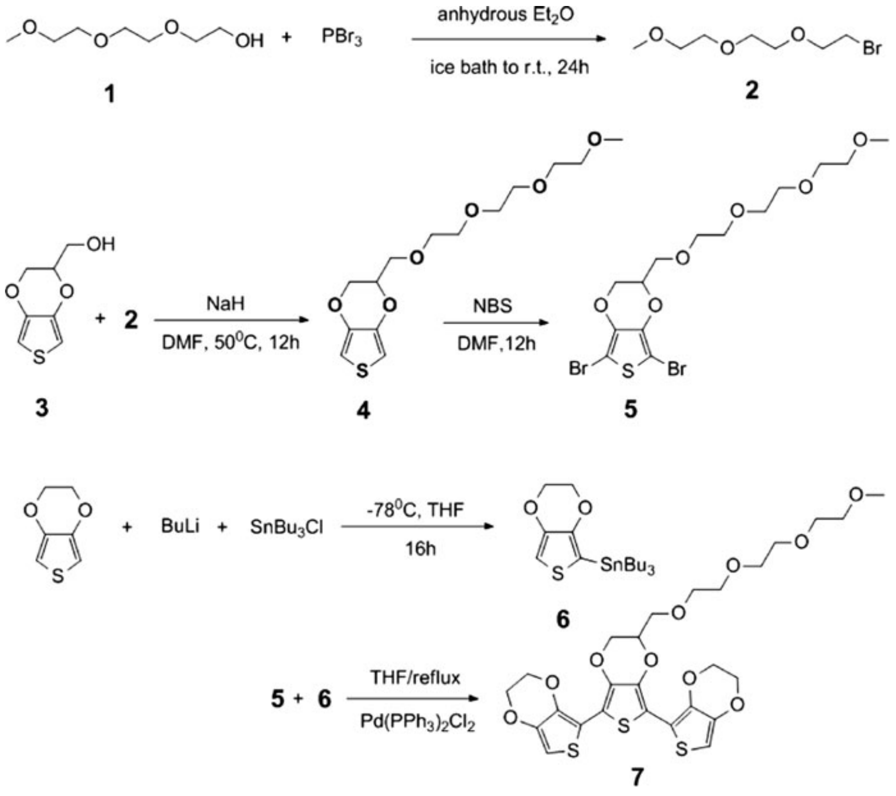

Fig. 1 Synthetic route of tri-EDOT

Stille reaction condition in THF using $Pd(PPh_3)_2Cl_2$ as the catalyst afforded the target molecule **7** in 48% yield. The right chemical structures of **7** and the intermediates were verified by ^{1}H NMR, ^{13}C NMR, and MS spectra.

Electrical property of alkoxy-substituted tri-EDOT

The electrochemical properties of alkoxy-substituted tri-EDOT together with bi-EDOT and EDOT were studied using cyclic voltammetry in acetonitrile with 0.1 M $TBAPF_6$ as electrolyte. Figure 2 shows the curves of first electrochemical scan for each monomer. The onset oxidation potentials were measured to be 1.39, 0.78, and 0.50 V (vs. SCE) for EDOT, bi-EDOT and alkoxy-substituted tri-EDOT, respectively. The potential of Ag/Ag^+ reference electrode is 0.37 V (vs. SCE), which is calibrated using Fc/Fc^+ redox as an internal standard. Further scans led to polymerization for all monomers to yield blue color materials with a similar onset oxidation potential for PEDOT and alkoxy-substituted PEDOT. It is obvious that the oxidation potential of tri-EDOT is significantly lower than that of the most widely used organic dyes, which has great potentials to be used as the new monomer for in situ polymerization in DSSCs.

In situ polymerization of tri-EDOT

The in situ polymerization of 40 mM tri-EDOT in the presence of 0.1 M lithium perchlorate in acetonitrile solution was conducted in thin layer electrolytic cell, where D149-sensitized TiO_2 photoelectrode and pyrolyzed Pt/FTO electrode were clipped together to serve as the working electrode and CE, respectively. Figure 3a, b shows the surface morphology of dye-sensitized TiO_2 layer before and after in situ polymerization of tri-EDOT. A layer of PEDOT is clearly observed on the surface of dye-sensitized TiO_2 film in Fig. 3b, which indicates successful electropolymerization. The electropolymerized HTM layer has a smoother surface with a smaller pore size as compared to that for TiO_2 layer, which favors direct contact between the alkoxy-substituted PEDOT with Au CE.

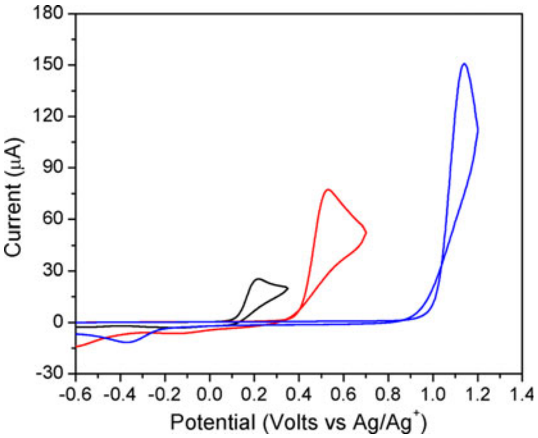

Fig. 2 The cyclic voltammetry curves for 5 mM EDOT (*blue*), 5 mM bi-EDOT (*red*) or 5 mM tri-EDOT (*black*) in 0.1 M $TBAPF_6$/acetonitrile solution on Pt disk electrode at 100 mV/s. (Color figure online)

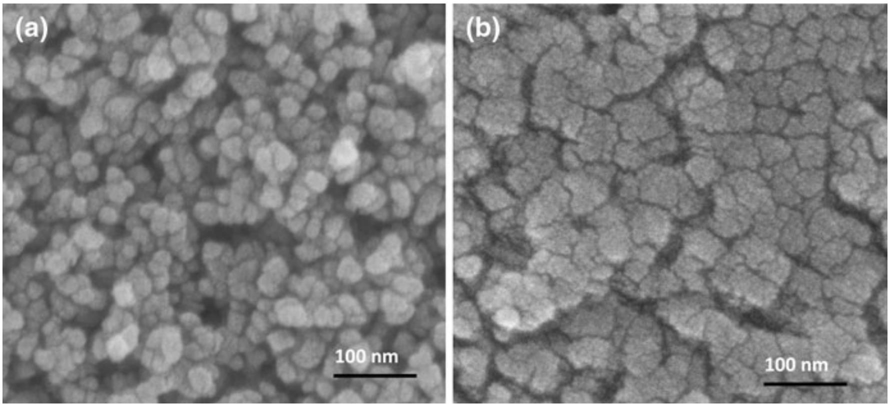

Fig. 3 SEM images of the dye-sensitized TiO_2 photoelectrode before (**a**) and after (**b**) polymerization to form an alkoxy-substituted PEDOT layer on top of TiO_2

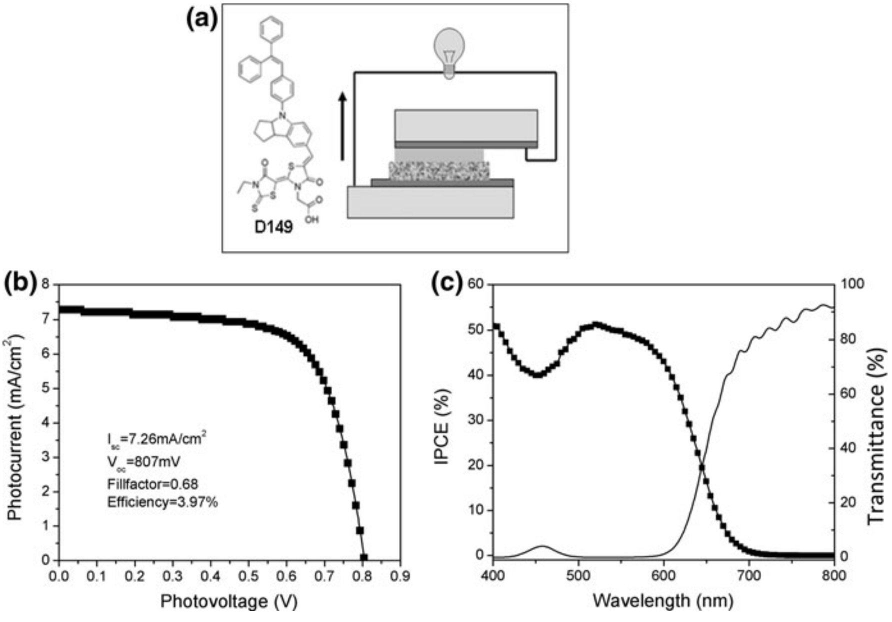

Fig. 4 **a** The chemical structure of D149 and the device configuration. The photocurrent–photovoltage curve (**b**) and the IPCE spectrum (**c**) of D149 sensitized solar cell with in situ polymerized tri-EDOT as the hole-transporting material. The transmittance spectrum of D149 sensitized TiO_2 layer is also shown in (**c**)

Performance of dye-sensitized solar cells

The chemical structure of D149 and the device configuration are shown in Fig. 4a. To fabricate the device, compact TiO_2 (c-TiO_2) is firstly deposited on the fluorine-doped SnO_2 (FTO) glass substrate as a blocking layer. Nanoparticle-TiO_2 film is then deposited on the c-TiO_2 layer as the electron-collecting electrode, which is followed by dye adsorption. The HTM is then in situ polymerized on the dye-modified TiO_2 film, and the cell is finally assembled by clipping the TiO_2 film with Au on FTO as the CE. The performance of the obtained DSSCs is shown in Fig. 4b. Under 100 mW/cm^2 AM1.5 illumination, the D149-sensitized devices have a short circuit photocurrent of 7.26 mA/cm^2, an open circuit voltage of 870 mV and a fill factor of 0.68, which yield an efficiency of 3.97%. This result is approaching the performance for small molecule HTM-based DSSCs [17]. Figure 4c shows the device incident photon-to-current efficiency (IPCE) spectrum and the transmittance spectrum of the dye-sensitized TiO_2 layer. IPCE reflects the light response of photovoltaic devices, which is directly related to the short circuit current. The IPCE curve is mainly in the 400–600 nm region with a tail extending to 700 nm. The transmittance measurement shows that the absorption of the dye-sensitized TiO_2 layer is well coincident with the IPCE spectrum. This indicates that nearly all absorbed photons could be used for electrical generation. However, the maximum value of the absorption ($\sim$100%) is significantly higher than that for the IPCE ($\sim$50%). The difference clearly indicates that $\sim$50% of photo-electrons have been degenerated due to recombination process.

Conclusions

In summary, we report the synthesis of an alkoxy-substituted EDOT trimer, and demonstrate that tri-EDOT could be in situ polymerized to serve as HTM in DSSCs. With D149 as the dye sensitizer and the in situ polymerized polymer as HTM, DSSCs were fabricated to show a power conversion efficiency of 3.97% under AM 1.5 G (100 mW cm^{-2}) illumination. It is important to note that the tri-EDOT has shown a significantly reduced oxidation potential as compared to that of bi-EDOT, which makes it possible for many new organic/inorganic dyes to serve as dye sensitizers in in situ polymerized HTM-based devices. Further improvement in dye sensitizers and in situ polymerization conditions is likely to yield devices with further improved efficiency.

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