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Synthesis of novel dyes having EDOT-containing oligothiophenes as π-linker for panchromatic dye-sensitized solar cells

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ABSTRACT

Novel donor–π–acceptor (D–π–A) dyes composed of oligothiophenes having 3,4-ethylenedioxythiophene (EDOT) as a π-linker have been synthesized. The introduction of EDOT unit in oligothiophenes and the elongation of π-conjugation length of oligothiophenes led to a red-shift of absorption bands of the D–π–A dyes. It was found that a D–π–A dye having EDOT-containing quaterthiophene exhibited the excellent light-harvesting ability up to 800 nm.

1. Introduction

Since the first report in 1991 by O'Regan and Grätzel [1], dye-sensitized solar cells (DSSCs) have attracted a considerable attention due to their high conversion efficiency of incident light to electricity and low production cost [2]. In order to improve the power conversion efficiency, many researches have been focused on the development of novel dyes [3]. Since donor–π–acceptor (D–π–A) dyes consisting of an electron donor (D) and an electron acceptor (A) linked through a π-conjugated bridge (π-linker) possess high molar absorption coefficients and their electronic properties can be easily tuned by molecular modifications, many types of D–π–A dyes have been enthusiastically synthesized [4]. The role of π-linker is not only to facilitate an intramolecular charge transport from D unit to A unit, but also to enhance a light-harvesting ability. In view of this, a variety of π-conjugated moieties such as vinylene, phenylene, and thienylene have been developed as π-linkers. Among them, oligothiophene is a strong candidate of π-linker in D–π–A dyes for DSSCs with high performances, because of the versatility of synthetic design, the high coplanarity responsible for the elongation of π-conjugation length, and the tunability of light-harvesting properties by controlling the chain length of oligothiophenes and/or by introducing substituents. For example, Tan et al. synthesized D–π–A dyes composed of triphenylamine as a D unit, cyanoacrylic acid as an A unit, and oligothiophenes with different chain lengths (thiophene monomer, trimer and hexamer) as π-linker and succeeded in the adjustment of optical, electrochemical, and photovoltaic properties by optimizing their chemical structures of oligothiophenes [5]. We also have synthesized a new family of oligothiophene derivatives partially containing 3,4-ethylenedioxythiophene (EDOT) unit and found that the introduction of EDOT unit into oligothiophenes induced a remarkable red-shift of absorption bands, together with an enhanced coplanarity and improved charge transport properties [6].

In the present paper, we describe the synthesis and characterization of two novel D–π–A dyes having EDOT-containing oligothiophenes (Fig. 1) and their application to photosensitizers in DSSCs. Although D–π–A dyes having EDOT or EDOT-containing bithiophenes were already reported [7], there are no reports on photosensitizing dyes having oligothiophenes with longer π-conjugated chains such as trimer or tetramer. It is expected that the introduction of EDOT unit in the oligothiophenes with longer π-conjugation length will enhance the light-harvesting ability in the visible region.

2. Experimental

2.1. Materials

n-Hexane, toluene, tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), acetic acid (AcOH), chloroform ($CHCl_3$), dichloromethane, and acetonitrile were purified by standard methods and used immediately after purification. Tetrabutylammonium perchlorate (TBAP) and *N*-bromosuccinimide (NBS) were purified by recrystallization from ethanol and benzene, respectively, and dried

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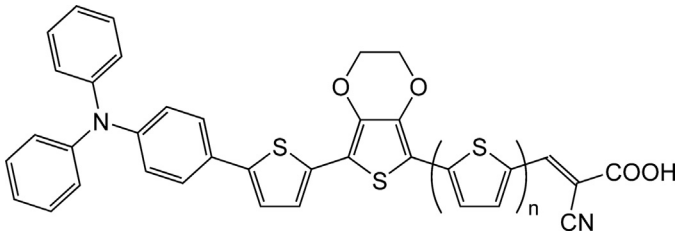


Fig. 1. Chemical structures of **PE3T** ($n = 1$) and **PE4T** ($n = 2$).

under vacuum. EDOT, 2-thiopheneboronic acid, 4-(*N*,*N*-diphenylamino) phenylboronic acid, 5-formyl-2-thiopheneboronic acid, and cyanoacetic acid were purchased from Tokyo Chemical Industry and used without further purification. Tetrakis(triphenylphosphine) palladium(0) ($Pd(PPh_3)_4$) purchased from Kanto Chemical was used as the catalyst of the Suzuki reaction.

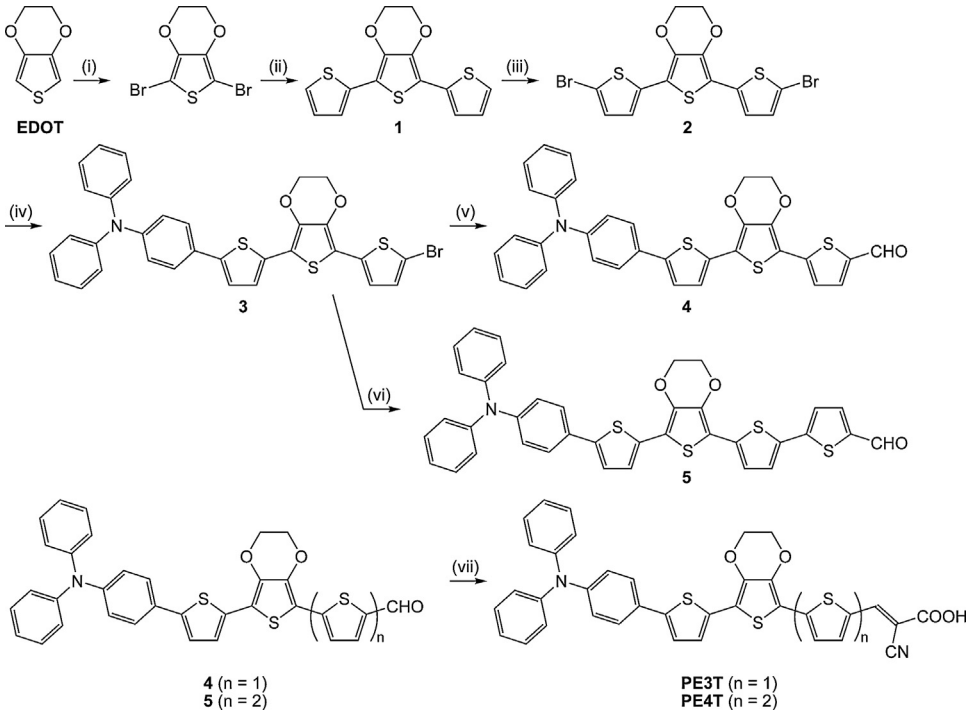
2.2. Synthesis

Synthetic routes of **PE3T** and **PE4T** are shown in Scheme 1 and the detailed synthetic processes are described below. 2,5-Dibromo-3,4-ethylenedioxythiophene and 3′,4′-ethylenedioxy-2,2′:5′,2″-terthiophene (**1**) were synthesized according to our previous report [6a].

2.2.1. 5,5″-Dibromo-3′,4′-ethylenedioxy-2,2′:5′,2″-terthiophene (2). To a $CHCl_3$/AcOH (50 mL/50 mL) solution of **1** (0.84 g, 2.75 mmol), NBS (0.97 g, 5.46 mmol) was slowly added in the dark at −10 °C. The reaction mixture was stirred in the dark at −10 °C for 2 h. The reaction mixture was poured into water and extracted two times with $CHCl_3$ (100 mL each). The combined organic extracts were washed with Na_2CO_3 aq. and water and dried over Na_2SO_4. The solvent was removed by a rotary evaporator. Compound **2** (0.59 g, 1.27 mmol) was obtained as a yellow needle crystal after the purification by recrystallization from *n*-hexane. Yield: 90%. ^{1}H NMR (500 MHz, $(CD_3)_2CO$, δ, ppm): 4.49 (s, 4H, OCH_2CH_2O), 7.04 (d, $J = 4.00$ Hz, 2H, thienylene-**H**), 7.12 (d, $J = 4.00$ Hz, 2H, thienylene-**H**). HRMS (EI) *m*/*z* calcd for $C_{14}H_8Br_2O_2S_3$ 461.8053 (M^+), found 461.8053 (M^+).

2.2.2. 5-[4-(N,N-Diphenylamino)phenyl]-5″-bromo-3′,4′-ethylenedioxy-2,2′:5′,2″-terthiophene (3). Under an argon atmosphere, a mixture of **2** (1.15 g, 2.48 mmol), 4-(*N*,*N*-diphenylamino)phenylboronic acid (0.70 g, 2.48 mmol), and $Pd(PPh_3)_4$ (0.27 g, 0.24 mmol) was dissolved in THF (10 mL). To this solution, Na_2CO_3 (0.53 g, 5.00 mmol) in water (5 mL) was added. The resulting solution was stirred at 80 °C for 24 h. The mixture was extracted with dichloromethane. The organic extract was dried over Na_2SO_4. After removal of the solvent, the residue was purified by a column chromatography (silica gel, *n*-hexane/dichloromethane (3/1)). Compound **3** (0.56 g, 0.88 mmol) was obtained as a yellow powder. Yield: 36%. ^{1}H NMR (500 MHz, $(CD_3)_2CO$, δ, ppm): 4.50 (s, 4H, OCH_2CH_2O), 7.05 (d, $J = 3.85$ Hz, 1H, thienylene-***H***), 7.05 (d, $J = 8.74$ Hz, 2H, phenylene-**H**), 7.08–7.12 (m, 6H, phenyl-**H**), 7.12 (d, $J = 3.85$ Hz, 1H, thienylene-**H**), 7.26 (d, $J = 3.85$ Hz, 1H, thienylene-**H**), 7.31–7.36 (m, 4H, phenyl-**H**), 7.35 (d, $J = 3.85$ Hz, 1H, thienylene-**H**), 7.59 (d, $J = 8.74$ Hz, 2H, phenylene-**H**). HRMS (EI) *m*/*z* calcd for $C_{32}H_{22}BrNO_2S_3$ 626.9996 (M^+), found 626.9988 (M^+).

2.2.3. 5-[4-(N,N-Diphenylamino)phenyl]-5″-formyl-3′,4′-ethylenedioxy-2,2′:5′,2″-terthiophene (4). Under an argon atmosphere, a mixture of **3** (0.24 g, 0.38 mmol) and magnesium (0.12 g, 4.77 mmol) was dissolved in THF (5 mL). After exothermic reaction was completed, DMF (2 mL) was added and stirred at room temperature for 2 h. The mixture was extracted with dichloromethane. The organic extract was dried over Na_2SO_4. After removal of the solvent, the residue was purified by a column chromatography (silica gel, dichloromethane). Compound **4** (67 mg, 0.11 mmol) was obtained as a red powder. Yield: 31%. ^{1}H NMR (500 MHz, $(CD_3)_2CO$, δ, ppm): 4.53–4.60 (m, 4H, OCH_2CH_2O), 7.05 (d, $J = 8.80$ Hz, 2H, phenylene-**H**), 7.09–7.13 (m, 6H, phenyl-**H**),



Scheme 1. Synthetic route of **PE3T** and **PE4T**: (i) NBS, THF/AcOH (1/1), r.t., 2 h; (ii) 2-thiopheneboronic acid, $Pd(PPh_3)_4$, Na_2CO_3, THF, reflux, 16 h; (iii) NBS, $CHCl_3$/AcOH (1/1), −10 °C, 2 h; (iv) 4-(*N*,*N*-diphenylamino) phenylboronic acid, $Pd(PPh_3)_4$, Na_2CO_3, THF, reflux, 24 h; (v) Mg, DMF, r.t., 2 h; (vi) 5-formyl-2-thiopheneboronic acid, $Pd(PPh_3)_4$, Na_2CO_3, THF, reflux, 24 h; (vii) cyanoacetic acid, ammonium acetate, reflux, 16 h.