Polymer 107 (2016) 191–199

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Molecular design for tuning electronic structure of π-conjugated polymers containing fused dithienobenzimidazole units

Koji Takagi [a, *], Tomoharu Kuroda [a], Masanori Sakaida [a], Hyuma Masu [b]

[a] *Life Science and Applied Chemistry, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso, Showa, Nagoya, 466-8555, Japan*
[b] *Center for Analytical Instrumentation, Chiba University, 1-33 Yayoi, Inage, Chiba, 263-8522, Japan*

ARTICLE INFO

Article history:
Received 29 August 2016
Received in revised form
4 November 2016
Accepted 8 November 2016
Available online 9 November 2016

Keywords:
π-Conjugated polymer
Oxidation
Protonation

ABSTRACT

Three dithienobenzimidazole derivative monomers (**M1**, **M2**, and **M3**) were prepared, where **M3** was obtained by the oxidation of **M1** and identified by the X-ray crystallographic analysis. π-Conjugated homopolymers (**P1-0**, **P2-0**, and **P3-0**) and copolymers (**P1-2**, **P3-1**, and **P3-2**) were synthesized by the palladium-catalyzed coupling polymerizations of **M1**, **M2**, and **M3**. The absorption spectra of the reference compounds (fused **R1** and non-fused **R2**), in conjunction with the optimized ground state structure, certified the importance of the fused dithienobenzimidazole skeleton to increase the effective conjugation length of the polymers. On the basis of the absorption and emission spectra of the π-conjugated polymers in $CHCl_3$, the influence of the thiophene-*S*,*S*-dioxide as well as the comonomer structure were investigated to find out that **P3-0** and **P3-2** exhibited peak maxima at the relatively longer wavelength region due to the donor-acceptor interaction. In addition, the protonation of the imidazole imine group further tuned the optical properties of the π-conjugated polymers by promoting the charge transfer interaction along the polymer main chain, which was supported by the theoretical calculations in detail.

1. Introduction

Optoelectronic devices fabricated from organic materials have many advantages over inorganic silicon-based devices owing to the light-weight and flexible characteristics, low-cost and mild manufacturing processes, and the finely tunable energy level of frontier molecular orbitals (FMOs). π-Conjugated polymers are promising candidates with the potential application to large area displays, wearable sensors, and stretchable memories. For example, bulk heterojunction solar cells comprised of π-conjugated polymer donor and fullerene derivative acceptor materials have attracted increasing attention in recent years [1–6]. However, at the present stage, organic and polymer semiconductors do not have enough performances to supersede silicon semiconductors because of the low power conversion efficiency and the short device lifetime. These parameters should be improved for the demand of commercialization. Much efforts have been devoted to the development of π-conjugated polymers with the good solution processability, the high charge carrier mobility, the broad light absorption profile, the large absorption coefficient, the appropriate energy levels, and the favorable blend morphology. The incorporation of electron-rich and electron-deficient units, for many cases in an alternating fashion, into the polymer main chain is a reliable method to optimize the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels by virtue of the intramolecular charge transfer interaction [7–10]. These donor-acceptor architectures have been keenly studied, giving rise to many high performance devices in the recent decades.

On the other hand, the introduction of π-extended systems into the polymer backbone determines not only the electronic structure but also the intermolecular π-π stacking structure to affect the semiconducting properties of materials. The strong π-π stacking interaction leads to the good crystallinity and the high electronic conductivity in some occasions, but it reduces the polymer solubility, making the solution processability difficult in other occasions. Thus the careful choice of π-extended systems including the attachment of solubilizing groups is much important to obtain semiconducting polymers with the better performance [11]. Recently, in addition to fused ring systems consisting of the electron-rich aromatic rings (thienothiophene [12], benzodithiophene [13], naphthodithiophene [11,14], and benzotrithiophene [15,16]), those carrying both donor and acceptor constituents in one

---

* Corresponding author. Tel.: +81 052 735 5264.
E-mail address: takagi.koji@nitech.ac.jp (K. Takagi).

http://dx.doi.org/10.1016/j.polymer.2016.11.013
0032-3861/© 2016 Elsevier Ltd. All rights reserved.

fused ring system have been investigated. For example, thiophene-fused conjugated skeletons having the electron-accepting imide group were installed in some π-conjugated polymers [17–20]. These π-conjugated polymers showed a potential utility as the field effect transistor and photovoltaic cell materials. Low band gap oligomers and polymers consisting of thiophene-fused boron dipyrromethane (BODIPY) repeat units were also synthesized [21,22]. The large overlap between HOMO and LUMO is realized to effectively lower the band gap energy, and the strong electron-accepting ability of BODIPY decreases the HOMO energy level to improve the air stability of the materials.

We have previously reported the synthesis of π-conjugated polymers based on a fused dithienobenzimidazole unit in the main chain, and found that the substitution pattern of the fused ring system as well as the chemical structure of the comonomer affect the optoelectronic characteristics of the π-conjugated polymers [23]. Imidazole has been utilized as the building unit of the π-conjugated molecules and polymers [24,25], and the transformation to imidazolium cation imparts new properties to the molecules owing to its ionic character and strong electron-accepting nature [26–29]. In this paper, we describe the chemical modification of the dithienobenzimidazole-containing π-conjugated polymers for further tuning of the electronic structure (Fig. 1). As a result, the control of FMO energy levels was possible by the choice of the comonomer, the oxidation of the thiophene ring, and the protonation of the imidazole moiety.

2. Experimental

2.1. Materials

[1,3-Bis(diphenylphosphino)propane]dichloronickel(II) [Ni(dppp)Cl_2] was purchased from Tokyo Chemical Industry. Tetrakis(triphenylphosphine)palladium(0) [Pd(PPh_3)$_4$], 9,9-dihexylfluorene-2,7-diboronic acid, and *i*-PrMgCl solution (2.0 M in tetrahydrofuran (THF)) were purchased from Aldrich. *n*-Butyllithium solution (*n*-BuLi, 1.6 M in hexane) was purchased from Kanto Chemical. Benzo[1,2-*b*:6,5-*b*′]dithiophene-4,5-dione [30], 1,2-di(thiophen-3-yl)ethane-1,2-dione [30], benzo[2,1-*b*:5,6-*b*′]dithiophene-4,5-dione [31], and 3,3′-dihexyl-5,5′-bis(tributylstannyl)-2,2′-bithiophene [32] were prepared as reported previously. All reactions were performed under dry nitrogen atmosphere unless otherwise noted.

2.2. Instrumentations

Microwave reactions were performed on a Biotage Initiator 8 in the normal absorption level. ^{1}H and ^{13}C nuclear magnetic resonance (^{1}H-NMR and ^{13}C-NMR) spectra were recorded on a Bruker AvanceIII HD 400 FT-NMR spectrometer in $CDCl_3$. Melting points (Mp) were determined on a Yanagimoto micro melting point apparatus MP-500D and were uncorrected. High resolution electrospray ionization mass spectra (HR ESI-MS) were performed on a Waters Synapt G2 HDMS in the positive mode. Elemental analyses (EA) were performed on a Elementar vario EL cube. Gel permeation chromatography (GPC) analyses were carried out on a Shodex 104 system using tandem LF-404 columns (THF as an eluent, flow rate = 1.0 mL/min, 40 °C) equipped with an ultraviolet–visible (UV–vis) detector (Shimadzu SPP-20A). Number-averaged molecular weight (M_n) and molecular weight distribution (M_w/M_n) were determined on the basis of a calibration curve made from standard polystyrene samples and ethylbenzene. UV–vis and fluorescence spectra were recorded on a Shimadzu UV-1650 spectrophotometer and a Shimadzu RF-5300 spectrofluorometer, respectively, using a 1 cm quartz cell. Fluorescence quantum yields (QYs) in solution were determined relative to quinine sulfate in 0.1 M H_2SO_4 with QY of 0.55. Cyclic voltammetry (CV) measurements were performed on with a potentiostat (Hokuto HZ-5000, Hokuto Denko). The working electrode (Peek-coated platinum disk) was separated from the counter electrode (platinum wire) and the Ag/Ag + reference electrode using a glass filter (G4). Polymer films were drop-cast on to a platinum electrode from their $CHCl_3$ solutions. All measurements were performed at room temperature (25 ± 1 °C) and nitrogen gas was used to degas the solutions before use and flowed over the solutions during experiments.

2.3. Monomer syntheses

2.3.1. 5,8-Dibromo-2-(p-octyloxyphenyl)-1-pentyldithieno[3′,2′:3,4:2″,3″:5,6]benzimidazole (M1)

Step 1: To a EtOH solution (10 mL) of benzo[1,2-*b*:6,5-*b*′]dithiophene-4,5-dione (97 mg, 0.44 mmol) were added 4-octyloxybenzaldehyde (0.15 g, 0.62 mmol) and ammonium acetate (0.17 g, 2.2 mmol), and the reaction mixture was heated to reflux overnight. After solvents were removed, CH_2Cl_2 was added and washed with water. The organic phase was dried over $MgSO_4$, and the crude product was purified by SiO_2 column chromatography (gradually changing the solvent composition from CH_2Cl_2 to ethyl acetate, Rf = 0.80) to give 2-(*p*-octyloxyphenyl)dithieno[3′,2′:3,4:2″,3″:5,6]benzimidazole as a colorless solid (0.17 g, 90% yield). Mp 236–238 °C; ^{1}H NMR ($CDCl_3$) δ ppm 0.84–0.93 (m, 3H), 1.21–1.43 (m, 10H), 1.77–1.83 (m, 2H), 3.99 (brs, 2H), 6.94–7.01 (m, 2H), 7.50 (d, $J = 4.89$ Hz, 2H), 7.84 (brs, 2H), 8.04 (d, $J = 7.09$ Hz, 2H).

Step 2: To a THF solution (100 mL) of 2-(*p*-octyloxyphenyl)dithieno[3′,2′:3,4:2″,3″:5,6]benzimidazole (4.2 g, 9.5 mmol) was added NaH (55% oil suspension) (0.69 g, 29 mmol), and the reaction mixture was heated to reflux for 1 h. 1-Iodopentane (2.3 g, 11 mmol) was added, and the reaction mixture was heated to reflux overnight. After solvents were removed, CH_2Cl_2 was added and washed with water. The organic phase was dried over $MgSO_4$, and the crude product was purified by SiO_2 column chromatography (hexane:ethyl acetate = 1:3, Rf = 0.50) to give 2-(*p*-octyloxyphenyl)-1-pentyldithieno[3′,2′:3,4:2″,3″:5,6]benzimidazole (**R1**, reference compound) as a colorless solid (3.0 g, 61% yield). Mp 90–92 °C; ^{1}H NMR ($CDCl_3$) δ ppm 0.84–0.91 (m, 5H), 1.25–1.38 (m, 13H), 1.46–1.54 (m, 2H), 1.82–1.93 (m, 4H), 4.05 (t, $J = 6.60$ Hz, 2H), 4.50 (s, 2H), 7.06 (d, $J = 8.56$ Hz, 2H), 7.50 (d, $J = 5.38$ Hz, 1H), 7.55 (d, $J = 5.38$ Hz, 1H), 7.63–7.67 (m, 2H), 7.70 (d, $J = 5.62$ Hz, 1H), 8.04 (d, $J = 5.38$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ ppm 13.9, 14.1, 22.1, 22.7, 26.1, 28.6, 29.2, 29.4, 29.7, 30.2, 31.8, 46.0, 68.2, 114.7, 119.9, 122.1, 122.9, 123.4, 124.4, 124.6, 128.9, 130.0, 130.3, 131.1, 136.4, 151.3, 160.1; Anal Calcd for $C_{30}H_{36}N_2OS_2$: C, 71.39%; H, 7.19%; N, 5.55%; S, 12.71%, Found C, 72.52%; H, 8.12%; N, 4.81%; S, 11.28%.

Step 3: To a *N*,*N*-dimethylformamide (DMF) solution (20 mL) of 2-(*p*-octyloxyphenyl)-1-pentyldithieno[3′,2′:3,4:2″,3″:5,6]benzimidazole (0.10 g, 0.20 mmol) was added *N*-bromosuccinimide (NBS) (70 mg, 0.42 mmol), and the reaction mixture was stirred at room temperature overnight. After solvents were removed, $CHCl_3$ was added and washed with water. The organic phase was dried over $MgSO_4$, and the crude product was purified by SiO_2 column chromatography (CH_2Cl_2, Rf = 0.50) followed by recrystallization from hexane/$CHCl_3$ to give **M1** as a colorless solid (0.10 g, 77% yield). Mp 145–147 °C; ^{1}H NMR ($CDCl_3$) δ ppm 7.99 (s, 1H), 7.61 (d, $J = 8.7$ Hz, 2H), 7.60 (s, 1H), 7.05 (d, $J = 8.7$ Hz, 2H), 4.42 (t, $J = 7.6$ Hz, 2H), 4.05 (t, $J = 6.5$ Hz, 2H), 1.90–1.80 (4H), 1.56–1.20 (14H), 0.94–0.81 (6H); ^{13}C NMR ($CDCl_3$) δ ppm 160.1, 151.7, 135.5, 132.4, 129.9, 129.5, 129.3, 128.4, 128.3, 126.2, 123.3, 122.7, 122.3, 116.0, 115.4, 113.1, 113.0, 68.2, 45.8, 31.9, 29.9, 29.3, 28.6, 26.1, 22.7, 22.0, 13.1; Anal Calcd for $C_{30}H_{34}Br_2N_2OS_2$: C, 54.38%; H, 5.17%; N, 4.23%; S, 9.68%, Found: C, 54.41%; H, 5.28%; N, 4.09%; S, 9.62.