

Relationship between *cis-trans* isomerism and optical and electrical properties based on benzidiimidazole-thiophene copolymer



Yun Zhao*, Xiaofeng Shen, Sile He, Xiangen Han, Zhonghai Ni*

School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221116, China

ARTICLE INFO

Keywords:

Benzidiimidazole
Configurational isomers
Thiophene
Tunable absorption
Photovoltaic material

ABSTRACT

The absorption gap and charge mobility of photovoltaic (PV) materials are usually important parameters to be optimized for enhancement of power conversion efficiency (PCE) of organic PV cells. Herein, a series of novel *cis/trans*-isomers of benzidiimidazole-thiophene copolymers (PBDIT) with different alkyl chain were conveniently synthesized. The relationship between the configurational isomerism and the optical and electrical properties of conjugated polymer was firstly investigated. Compared with their *cis*-isomers, only the *trans*-PBDITs can form quinoid structures, causing the narrower band gap and corresponding red-shifted and broader optical absorption. Theoretical calculation also illustrated that *trans*-PBDITs can form much smaller dihedral angles between imidazole and thiophene rings than their *cis*-counterparts, which facilitated the better coplanar structure and conjugated system, inducing the absorption red-shifted and higher charge mobility. The illumination of relationship between the configurational isomerism and the optical and electrical properties paves a way to design benzidiimidazole-thiophene copolymers with tunable absorption bands through regulation of side chains, which renders them promising candidates for various applications in organic PV devices.

1. Introduction

As a potential alternative to silicon-based photovoltaic (PV) cells, organic PV cells offer the combined attraction of low cost, light weight, mechanical flexibility, and amenability to manufacture by high-throughput and large-area roll-to-roll coating processes [1–5]. To date, the high power conversion efficiency (PCE) of organic PV cells over 14% has been achieved through the combined development of high-performance materials, better morphology control, and new device architectures [6–10]. The energy gap of conjugated polymers is usually an important parameter to be optimized for efficient harvesting of the solar energy. However, one of the biggest challenges for polymer PV cells is that absorption does not match the solar spectrum. Recently, successful strategies to enhance the absorption of sunlight are to lower the optical band gap of the conjugated polymers, which include “donor–acceptor” type alternating copolymer, increasing quinoid character of the polymer backbone, etc. [11–13]. Besides, the carrier mobility of conjugated polymers which regulates the charge collection efficiency, still remains to be a great challenge for improving the PCE of organic PV cells.

Benzimidazole and its derivatives are widely used in luminescent materials due to their good rigid plane structure, rich π -electrons and the π - π stacking effect of aromatic ring [14–18]. Meanwhile, because of

their molecular structures containing electron-deficient heterocyclic group (imidazole ring), benzimidazole units can be used as electron deficient “acceptor” type building blocks [19–24], and when they are alternated with electron-rich units, e.g., thiophene, low bandgap polymers can be constructed [25–28].

In this paper, we designed and synthesized three series of *cis/trans*-isomers of benzidiimidazole-thiophene copolymers (PBDIT) with different length of *n*-alkyl chains. From one side, the core of benzidiimidazole expanded the conjugation of polymer. From the other side, by adjusting the location of two *n*-alkyl chains attached to the benzidiimidazole unit, two *cis*- and *trans*-PBDIT isomers can be constructed, from which we can investigate the relationship between the configurational isomerism and the optical and electrical properties of conjugated polymer, which was never studied before.

2. Experimental

2.1. Materials and methods

4,6-Dinitrobenzene-1,3-diamine (99%), 5-bromothiophene-2-carbaldehyde (98%), 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) thiophene (98%), were purchased from Darui Finechem Co., Ltd. (Shanghai, China). The others were purchased from Sinopharm

* Corresponding authors.

E-mail addresses: zhaoyun@cumt.edu.cn, 2009yuzhao@163.com (Y. Zhao), nizhonghai@cumt.edu.cn (Z. Ni).

Chemical Reagent Co., Ltd. (Shanghai, China) and were of analytical grade.

$^1\text{H-NMR}$ spectra were collected on an AV-600 spectrometer (Bruker Co. Ltd., Germany) at 600 and 151 MHz in CDCl_3 solutions with TMS as an internal standard. Mass spectra were obtained with MALDI-TOF/TOF matrix assisted laser desorption ionization mass spectrometry (Bruker Co. Ltd., Germany). The weight-average molecular weight was estimated by P230 Gel Permeation Chromatography (GPC) (Elite, Dalian, China, column: SEC-150, XIYU Tech, Shanghai, China) with standard polystyrene as a reference. The thermo gravimetric analysis (TGA) and differential scanning calorimetry measurements (DSC) were operated on Netzsch STA 449C, under nitrogen atmosphere with a heating rate of $10^\circ\text{C}/\text{min}$. Absorption measurements were performed on a UV-3600 spectrophotometer (Shimadzu Co. Ltd., Japan). Fluorescence profiles were carried out using a Hitachi F-4600 spectrofluorimeter (Hitachi Co. Ltd., Japan). Cyclic voltammetry (CV) were performed with a CHI660A electrochemical workstation (Shanghai CH Instruments Co., China) controlled by a microcomputer with CHI660 software. The current density-voltage (J-V) characteristics of the hole-only devices were measured using a computer-controlled Keithley 2400 source meter under dark. Theoretical calculation were conducted using density functional theory (DFT) calculations (B3LYP/6-31G (d, p) basis set) with the Gaussian 09 W software package.

2.2. Synthesis of monomers

2.2.1. 2,6-Bis(5-bromothiophen-2-yl)-1,5-dihydrobenzo[1,2-d:4,5-d']diimidazole (1)

The synthetic pathway was shown in Fig. 1. Firstly, 5-bromothiophene-2-carbaldehyde (4.2 g, 22.0 mmol) in DMF (15 mL) was added dropwise into a solution of 4,6-dinitrobenzene-1,3-diamine (1.98 g, 10.0 mmol) in DMF (40 mL). Then, the mixture was kept at 120°C and stirred for 4 h. After that, the reaction mixture was cooled down to room temperature, added dropwise with $\text{Na}_2\text{S}_2\text{O}_4$ (2.7 g) in water (20 mL) and stirred at 120°C for 12 h. The resulting mixture was cooled to room temperature, filtered, washed by water, and dried in vacuum. The obtained dark yellow solid (3.5 g, 72%) was used directly for the next step, since it was hard to purify for its bad solubility.

2.2.2. Monomers *cis/trans*-benzidiimidazole-thiophene (BDITs)

Firstly, 1-bromobutane (2.079 g, 15.4 mmol) was added to a solution of **1** (3.4 g, 7 mmol) and NaH (0.56 g, 14 mmol) in DMF (50 mL). Then, the mixture was kept at 120°C and stirred for 12 h. After that, the reaction mixture was cooled down to room temperature, added CHCl_3 (50 mL) and poured into water (200 mL). Then, the solution after filtration was extracted with CHCl_3 ($3 \times 40\text{ mL}$). After drying over MgSO_4 , the solvent was removed. The resulting crude black product purified with column chromatography using hexane/ethyl acetate as eluent. The obtained monomers *cis*-M1 and *trans*-M1 are a pair of isomers with n-butyl group as the side chains, which were separated and purified by column chromatography followed by recrystallization. Both

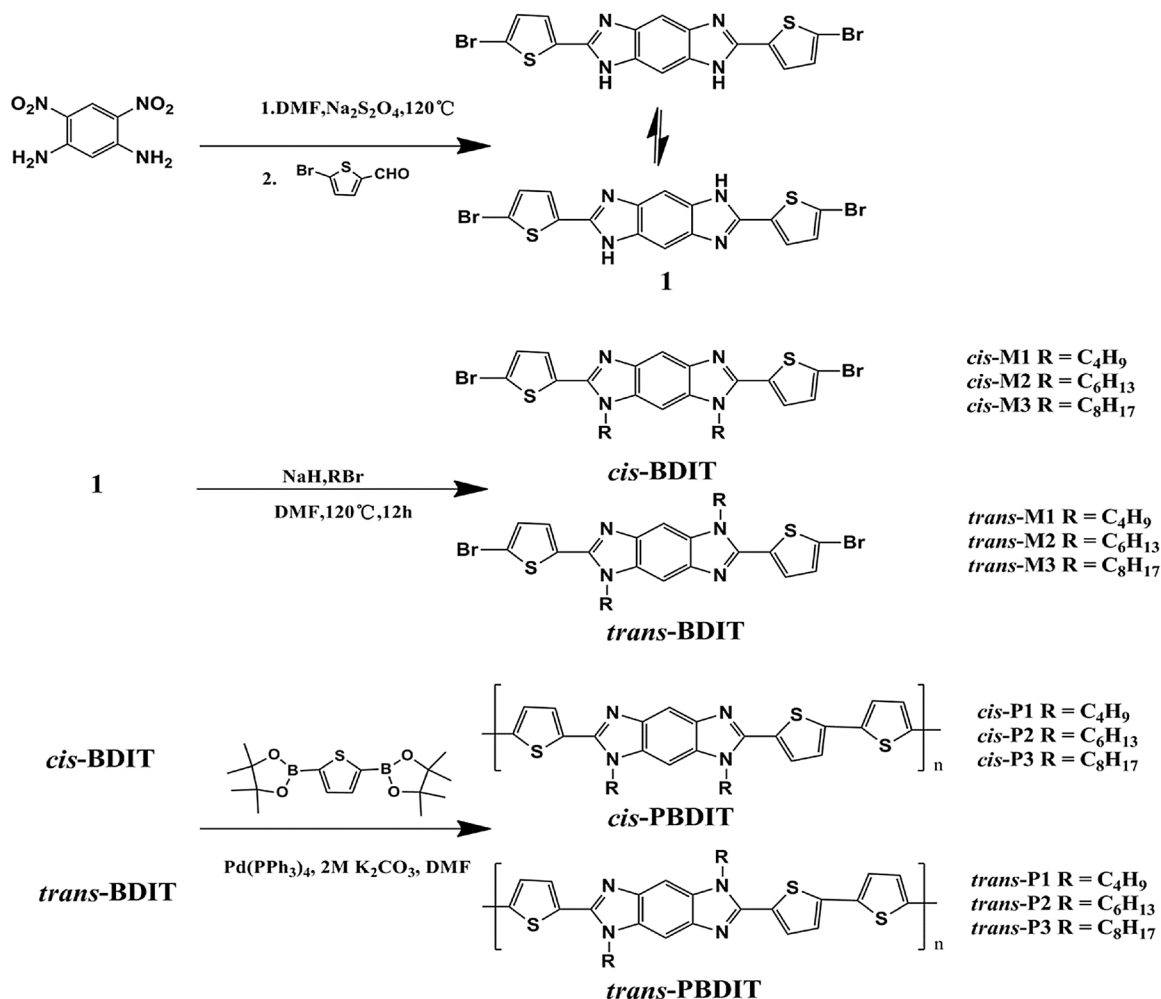


Fig. 1. Synthetic pathway of monomers and polymers.

Download English Version:

<https://daneshyari.com/en/article/9953504>

Download Persian Version:

<https://daneshyari.com/article/9953504>

[Daneshyari.com](https://daneshyari.com)