Dyes and Pigments 121 (2015) 118–127

Contents lists available at ScienceDirect

Dyes and Pigments

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

Effect of structural modification on the performances of phenothiazine-dye sensitized solar cells

Xuxu Liu [a], Jun Long [a], Guo Wang [a], Yong Pei [a], Bin Zhao [a, b], Songting Tan [a, b, *]

[a] College of Chemistry, and Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, Xiangtan University, Xiangtan 411105, PR China

[b] Key Laboratory of Advanced Functional Polymeric Materials of College of Hunan Province, Key Laboratory of Polymeric Materials & Application Technology of Hunan Province, Xiangtan University, Xiangtan 411105, PR China

ARTICLE INFO

Article history:
Received 8 January 2015
Received in revised form
31 March 2015
Accepted 11 May 2015
Available online 19 May 2015

Keywords:
Dye-sensitized solar cells
Phenothiazine
Benzothiadiazole
Photovoltaic performances
Triphenylamine
Synthesis

ABSTRACT

Three novel dyes **DX1**, **DX2** and **DX3** containing phenothiazine are designed and synthesized for dye-sensitized solar cells (DSSCs). Photophysical, electrochemical and photovoltaic properties of the three dyes have been systematically investigated. The results show that the **DX1**-based DSSC with 0.5 mM chenodeoxycholic acid (CDCA) obtains the power conversion efficiency (PCE) of 5.69%. When an additional electron-deficient benzothiadiazole (BT) unit is introduced into the molecular structures of the dyes **DX2** and **DX3**, the absorption spectra are broadened. But the short-circuit photocurrent density (J_{sc}) of the devices are decreased due to the blocked electron transfer, so the DSSC device based on **DX2** only obtains the PCE of 3.43%. Furthermore, a triphenylamine (TPA) unit with high electron-donating ability is joined onto the nitrogen atom of phenothiazine donor in **DX3**, which enhances the electron injection efficiency and reduces the dye aggregation. Thus, the J_{sc} is improved, resulting in a higher PCE of 4.41% in the DX3-based dye than the **DX2**-based one.

1. Introduction

As a promising alternative to conventional inorganic photovoltaic devices, dye-sensitized solar cells (DSSCs) have drawn much attention since their introduction in 1991 [1], due to their potentially low-cost fabrication, possibility of transparency and color selectivity, which can be integrated into building and automobile applications [2–5]. As is well-known, the sensitizer is always a crucial element in DSSCs, exerting a significant influence on the power conversion efficiency (PCE) as well as the device stability. To date, DSSCs incorporating ruthenium based dyes and zinc–porphyrin based co-dyes have reached high efficiency over 11% [6,7], and 12% [8,9], respectively. Thereinto, a new dye based on zinc–porphyrin, SM315, which was reported by Grätzel et al., showed a record-high PCE of 13.0% [10]. However, metal-free organic dyes, commonly constructed with donor-π bridge-acceptor (D–π–A) configuration, have become increasingly attractive for the merits of high molar extinction coefficients, low cost, environment-friendly property and high flexibility of molecular design [6,11]. Thus, some dyes such as triphenylamine- (TPA-), carbazole-, phenothiazine-, and indoline-based ones have achieved relatively high PCEs by using iodide/triiodide-based electrolytes [12–21]. However, most of the D–π–A dyes tend to form intermolecular aggregation on the TiO_2 surface, which affects the light absorption and loss in the photogenerated electrons. Therefore, further studies are needed to develop new dyes to maximize the electron accumulation in the TiO_2 conduction band, reduce the charge recombination and absorb light intensely in the red to near-infrared (NIR) region, which accounts for about 50% of solar energy [22,23].

Phenothiazine-based dyes have been intensively explored in recent years. In phenothiazine system, two phenyl groups are arranged with a small torsion angle related to the nitrogen and sulfur atoms, ensuring that the π-delocalization can be extended over the entire chromophore [15,24–28]. Meanwhile, attaching a bulky or branched alkyl chain to the nitrogen atom of phenothiazine unit leads to the non-planar butterfly conformation of phenothiazine, which can sufficiently inhibit molecular aggregation and further enhance the charge separation on the TiO_2 interface [29,30]. Furthermore, a new type of dyes with an additional electron-deficient unit introduced between the donor and π-bridge have

* Corresponding author. College of Chemistry, and Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, Xiangtan University, Xiangtan 411105, PR China.
E-mail address: tanst2008@163.com (S. Tan).

http://dx.doi.org/10.1016/j.dyepig.2015.05.012
0143-7208/

been designed and characterized as a D–A–π–A architecture [31]. In the novel D–A–π–A configuration dyes, the additional acceptor chromophore, which extends the range of π-electron delocalization, can facilitate intramolecular charge transfer and adjust the band gap for harvesting more near-infrared (NIR) light [32]. Among all the additional electron-deficient units, benzothiadiazole (BT) has been one of the most widely utilized in DSSCs [33–37]. Here, we designed and synthesized three novel dyes (**DX1**, **DX2** and **DX3**, Scheme 1), which contained phenothiazine donors and cyanoacrylic acid acceptors bridged by a 3-hexylthiophene unit as a π-spacer. Additionally, a BT unit was applied as an additional acceptor into the dyes **DX2** and **DX3** to realize a broadened absorption spectrum. Notably, the 3D nonplanar TPA [38,39] was introduced to the 10-position nitrogen atom of phenothiazine donor in **DX3** to obtain a double-donor structure, which resulted in enhanced electron-donating ability and reduced dye aggregation. Photophysical, electrochemical and photovoltaic properties of the three dyes were systematically investigated.

2. Experimental section

2.1. Materials

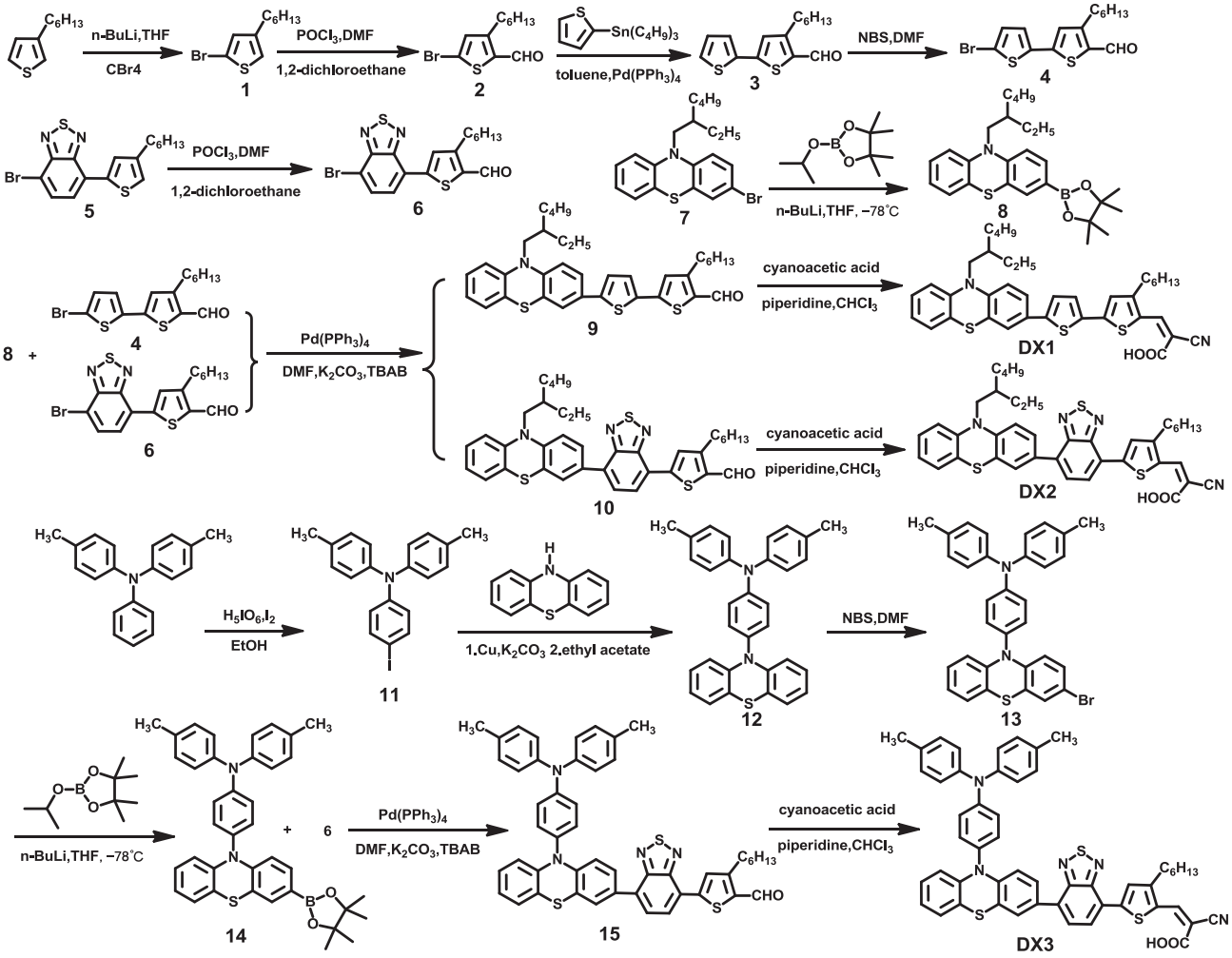
All the chemicals were purchased from Alfa Aesar and Chem Greatwall Chemical Company (Wuhan, China) and used without further purification. Toluene and tetrahydrofuran (THF) were dried and distilled over sodium and benzophenone. N,N-Dimethylformamide (DMF) was dried over and distilled from CaH_2 under an atmosphere of dry nitrogen. Phosphorus oxychloride and 1,2-dichloroethane were atmospheric distillation. All other commercially available materials were used as received unless noted otherwise. 4-Bromo-7-(4-hexylthiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (**5**) [40], and 3-bromo-10-(2-ethylhexyl)-10H-phenothiazine (**7**) [41] were prepared according to literature procedures.

2.2. Synthesis

The synthetic routes and molecular structures of the dyes are shown in Scheme 1. The detailed synthetic processes are as follows.

2.2.1. 2-Bromo-4-hexylthiophene (*1*)

A solution of 3-hexylthiophene (8.00 g, 47.53 mmol) in anhydrous THF (100 mL) was cooled down to −78 °C under argon atmosphere, and n-BuLi (2.5 M in hexane, 22.82 mL, 57.04 mmol) was added dropwise. After stirring for 3 h, carbon tetrabromide (18.92 g, 57.04 mmol) in anhydrous THF (30 mL) was added dropwise and the reaction medium was slowly warmed to the room temperature. Water was added for quenching the reaction, and the solution was extracted with CH_2Cl_2. The organic layer was washed with H_2O and dried over $MgSO_4$. Solvent was removed by rotary evaporation. The crude product was purified on silica gel column chromatography



Scheme 1. Synthetic routes and molecular structures of the three dyes **DX1**, **DX2** and **DX3**.