Dyes and Pigments 95 (2012) 244–251

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

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

New efficient dyes containing *tert*-butyl in donor for dye-sensitized solar cells

Jie Shi [a], Zhaofei Chai [a], Cheng Zhong [a], Wenjun Wu [b], Jianli Hua [b], Yongqiang Dong [c], Jingui Qin [a], Qianqian Li [a,**], Zhen Li [a,*]

[a] *Department of Chemistry, Hubei Key Lab on Organic and Polymeric Opto-Electronic Materials, Wuhan University, Wuhan 430072, China*
[b] *Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science & Technology, Shanghai 200237, China*
[c] *Department of Chemistry, Beijing Normal University, Beijing 100875, China*

ARTICLE INFO

Article history:
Received 15 January 2012
Received in revised form
23 March 2012
Accepted 26 March 2012
Available online 20 April 2012

Keywords:
Tert-butyl
Triphenylamine
Anti-aggregation
Dye-sensitized solar cells
Sensitizers
Power conversion effciency

ABSTRACT

A series of D–π–A organic sensitizers that contains two 4-*tert*-butylbenzene moieties in the donor part of triphenylamine group are designed and characterized. All these dyes comprise the same donor and acceptor units while the different aromatic units are introduced as linkers between the donor and acceptor units. It is found that the tuning of the HOMO and LUMO energy level can be conveniently achieved by alternating the conjugate bridge. The DSSCs based on **LI-17** show the best light to electricity conversion efficiency of 5.35% ($J_{sc} = 12.65$ mA cm^{-2}, $V_{oc} = 675$ mV, $ff = 0.63$) under standard global AM 1.5 solar light conditions (100 mW cm^{-2}), indicating that the introduction of *tert*-butyl groups may be able to play an anti-aggregation effect.

1. Introduction

With the consumption of fossil energy and the increasing intensity of global warming, solar energy will play an important role in the future world for its feature of renewable and clean [1]. In 1991, dye-sensitized solar cells (DSSCs) was first fabricated with the Ru-complexes dye, and now some Ru sensitizers could achieve the power conversion efficiencies in excess of 11% subsequently [2–11]. However, due to its rarity of this precious metal, large amounts of researches have been carried out on metal-free organic dyes for its advantages of low cost, easy synthesis, and high molar coefficient. In order to improve photovoltaic efficiencies of DSSCs, many metal-free dyes have been synthesized and shown impressive η values in the range of 5–10.3% [12–32]. Four critical processes determine the photovoltaic performance of the DSSCs: electron injection from the dye to the conduction band of TiO_2; recombination of the injected electrons on TiO_2 with the oxidized dye; dark current generated due to the reduction of I_3^- by the injected electrons; and the regeneration of the dye by the electrolyte which is dependent on the HOMO level of the dye and the redox potential of the electrolyte [33–36]. From the viewpoint of chemists, it is necessary to remodel the molecular design of dyes. And an effective method to improve photovoltaic performance of DSSCs is to inhibit intermolecular π–π aggregation. The phenomenon of π-stacked aggregation on the TiO_2 electrodes always shortens the lifetime of excited electrons which results in decreased photocurrent or leads to molecules residing in the system that are not functionally attached to the surface of TiO_2 and thus act as filters, directly decreasing the electron injection greatly [37,38]. To weaken or avoid the aggregation from a strong intermolecular π–π interaction, some co-adsorbents such as deoxycholic acid (DCA) or chenodeoxycholic acid (CDCA) have often been utilized with the aim to enhance its performance in devices [39,40]. In addition, possible aggregation could be avoided through appropriate structural modification such as introducing alkyl to aniline and thiophene units [41–46]. Aromatic rings have also been introduced to pyrrole *via* N–H bond in order to restrain the aggregation of the dyes and achieve good performance in our previous research [47–49]. Thiophene derivatives have been widely used as conjugated bridge for sensitizers because of their high polarizability, tunable spectroscopic and electrochemical properties. A lot of studies are concerning dyes containing thiophene or furan as conjugated bridge, which reached high photovoltaic efficiencies. However, it is relatively difficult to introduce anti-

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* Corresponding author. Tel.: +86 27 62254108; fax: +86 27 68756757.
** Corresponding author. Tel.: +86 27 62306885; fax: +86 27 68756757.
E-mail addresses: qianqian-alinda@163.com (Q. Li), lizhen@whu.edu.cn (Z. Li).

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doi:10.1016/j.dyepig.2012.03.027

aggregation group to thiophene and furan units [50–53]. Therefore, we try to synthesize the molecules which contain anti-aggregation groups in donor, and set thiophene derivatives and furan as conjugated bridge.

Tert-butyl was widely used in many opto-electronic materials such as organic light-emitting diodes (OLED), for its superior performance in preventing π–π stacking. Some dyes possess coplanar structure also introduced *tert*-butyl to inhibit aggregation [54–56]. Interestingly, a few research groups reported some D–π–A dyes bearing *tert*-butyl moiety and its functions in molecule design was to improve the solubility [57]. Herein, two 4-*tert*-butylbenzene moieties were chosen as additional groups of triphenylamine. First, the solubility of the dye will be significantly improved; secondly, the introduction of the benzene ring could expand the molecular conjugated system thus enhancing their ability of light harvesting, and thirdly, there are two *tert*-butyl in the donor side just like two umbrellas, which keep a certain distance between molecules, reflecting their function to prevent aggregation. Thiophene, 2,2′-bithiophene, 3,4-ethylenedioxythiophene (EDOT) and furan group were selected to serve as conjugation bridge for their excellent performance in electronic transmission (Scheme 1).

2. Experimental

2.1. Materials

Tetrahydrofuran (THF) was dried over and distilled from K–Na alloy under an atmosphere of dry nitrogen. *N*,*N*-Dimethylformamide (DMF) was dried over and distilled from CaH_2 under an atmosphere of dry nitrogen. 1,2-Dichloromethane was dried over and distilled from phosphorus pentoxide. Phosphorus oxychloride was freshly distilled before use. All reagents were purchased from Alfa Aesar and used as received. Compound 2- and 4-(diphenylamino)benzaldehyde was prepared following the procedure reported in the literature [58].

2.2. Instrumentation

^{1}H and ^{13}C NMR spectroscopy study was conducted with a Varian Mercury 300 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. UV–visible spectra were obtained using a Shimadzu UV-2550 spectrometer. Differential pulse voltammetric (DPV) was carried out on a CHI 660 voltammetric analyzer at room temperature in nitrogen-purged anhydrous acetonitrile with tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte at a scanning rate of 100 mV/s. A platinum disk and an Ag/AgCl electrode were used as the working electrode and quasi-reference electrode, respectively. The ferrocene/ferrocenium redox couple was used for potential calibration. Elemental analyses were performed by a Carlo Erba 1106 microelemental analyzer. HR-ESI-TOF mass spectra were recorded on a Waters Micromass LCT Premier XE.

2.2.1. Synthesis of 4-(bis-(4-bromo-phenyl)-amino)-benzaldehyde

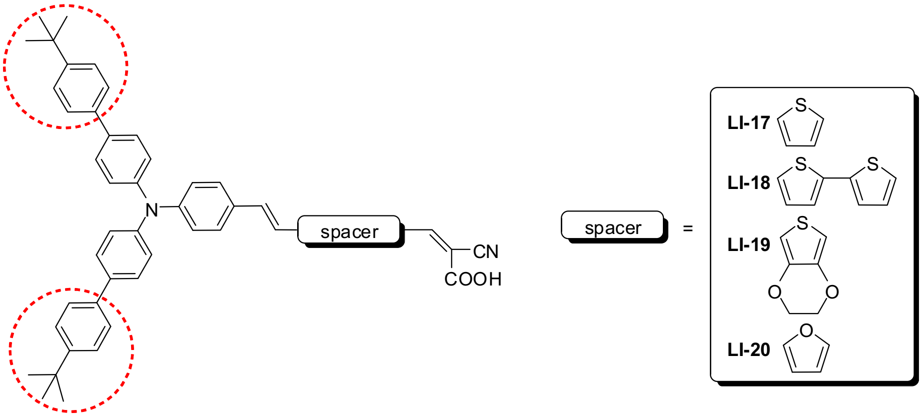
To a solution of 4-(diphenylamino) benzaldehyde (30 mmol, 8.0 g) in dichloromethane (150 mL) was added bromine (60.0 mmol, 9.6 g) dropwise within 1.5 h at 0 °C. The resultant mixture was stirred at room temperature for 6 h and then aqueous KOH was added. The mixture was extracted with dichloromethane. The organic layer was collected, washed with water, dried over anhydrous sodium sulfate. Filtered and the solvent was removed by rotator evaporation. The residue was purified by column chromatography over silica gel to give the product (9.20 g, 71%) as green yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 9.84 (s, 1H, –CHO), 7.71 (d, $J = 8.7$ Hz, 2H, ArH), 7.48 (d, $J = 8.7$ Hz, 4H, ArH), 7.06–7.01 (m, 6H, ArH).

2.2.2. Synthesis of **1**

A mixture of 4-(bis-(4-bromo-phenyl)-amino)-benzaldehyde (11.6 mmol, 5.0 g), 4-*tert*-butylphenylboronic acid (25.5 mmol, 4.5 g), sodium carbonate (10.0 or 20.0 equiv), THF (monomer concentration about 0.025 M)/water (2:1 in volume), and tetrakis(triphenylphosphine)palladium $Pd(PPh_3)_4$ (3–5 mol%) was carefully degassed and charged with nitrogen. The reaction was stirred for 32 h at 80 °C. After cooled to room temperature, the organic layer was separated, dried over sodium sulfate, and evaporated to dryness. The crude product was purified by column chromatography over silica gel to give the product (4.84 g, 78%) as a yellow solid. Yield: 75%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 9.76 (s, 1H, –CHO), 7.64 (d, $J = 8.1$ Hz, 1H, ArH), 7.55–7.41 (m, 8H, ArH), 7.26–7.16 (m, 5H, ArH), 7.06 (d, $J = 4.8$ Hz, 2H, ArH), 6.98 (d, $J = 8.1$ Hz, 2H, ArH), 6.91–6.83 (m, 2H, ArH), 1.36 (s, 18H, $-CH_3$).

2.2.3. General synthesis of **3a–d**

To a solution of the (4-(bis(4′-tert-butylbiphenyl-4-yl)amino) phenyl)methanol (5.4 g, 10 mmol) in 25 mL triethylphosphite was added iodine (2.53 g, 10 mmol) at 0 °C slowly. The resulting mixture was stirred for 5 min at 0 °C, then warmed to room temperature and stirred for 2.5 h. After evaporation of triethylphosphite, column chromatography and removal of trace triethyl phosphate under vacuum at 50 °C afforded compound **2** as light green solid (5.33 g, 85%). Compound **2** (3 mmol) was suspended in 20 mL of anhydrous



Scheme 1. The structures of **LI-17**, **LI-18**, **LI-19** and **LI-20**.