



Tetraindole-based saddle-shaped organic dyes for efficient dye-sensitized solar cells



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ABSTRACT

Two new metal-free organic dyes which consist of a saddle-shaped tetraindole donor, a cyanoacrylic acid acceptor/anchoring group and a thiophene or bithiophene π -bridge have been successfully designed and synthesized for dye-sensitized solar cells. The two dyes showed good photoelectric properties, and the saddle-shaped structure of the tetraindole unit was found to be favorable for preventing intermolecular aggregation and enhancing the photovoltage. The two tetraindole-based dyes exhibited good photovoltaic performances in solar cells. An efficiency up to 6.46% with a high open-circuit photovoltage of 762 mV was achieved for the dye **JY15** with a 2,2'-bithiophene moiety as the π -bridge using an iodine electrolyte under standard conditions.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have received considerable attention as promising alternatives to traditional silicon-based photovoltaic devices due to their potential low cost, easy manufacturing processes and high photovoltaic performance [1]. A typical DSSC includes four main components: nanocrystalline semiconductor electrode, redox electrolyte, counter electrode and dye sensitizer [2]. As a critical component in DSSCs, the sensitizer plays a vital role in the light-harvesting, charge transfer and the performance of the solar cells [3]. In comparison with well-known metal complex sensitizers, more attention has recently been paid to metal-free organic sensitizers because of their low cost, easy synthesis, high molar extinction coefficient, as well as low toxicity [4].

Donor- π -acceptor (D- π -A) type dyes have proven to be a powerful design for metal-free organic dyes owing to their highly efficient intramolecular charge transfer (ICT) and some of them have achieved high power conversion efficiency (PCE) [5]. However, the rod-like configuration of most D- π -A dyes may facilitate

undesirable dye aggregation and charge recombination [6]. The intermolecular π - π stacking of dye molecules can cause self-quenching of excited states and hence inefficient electron injection [7]. Consequently, much effort has been devoted to controlling the intermolecular π - π stacking of organic dyes, such as using coabsorbents, introducing long alkyl chains into the dye skeleton, employing starburst bulky multidonors and designing double D- π -A branched dyes with "X" or "H" shape [8].

Indole derivatives are important heteroaromatic compounds in structurally diverse natural products. Because of their good electron-donating characteristic, strong ICT, and high synthetic flexibility, indole derivatives have also been extensively investigated in hole transporting materials [9], organic-light-emitting diodes (OLEDs) [10], two-photon absorption (TPA) materials [11], organic photovoltaic cells (OPVs) [12], as well as DSSCs [13]. Tetraindole has a unique natural saddle-shaped structure and might benefit the suppression of intermolecular aggregation [14]. In the meantime, the cyclooctatetraene scaffold with four electron-rich indole subunits should result in excellent electron-donating potential for intense ICT. But up to now, the photoelectric properties of tetraindole have been very rarely studied. Herein, we report the design, synthesis and characterization of two new D- π -A type dyes (**JY14** and **JY15**) based on tetraindole for the first time. These organic dyes consist of a tetraindole moiety acting as the electron donor and a cyanoacrylic acid unit acting as the electron acceptor/

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anchoring group. Thiophene and 2,2'-bithiophene have been selected to act as the π -conjugated linkers, respectively. The molecular structures of **JY14** and **JY15** are shown in Fig. 1.

2. Experimental

2.1. Materials and instruments

All chemicals obtained from commercial sources were used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker 400 MHz spectrometer using TMS as the internal standard. UV–vis spectra were obtained on a Varian Cary 300 Conc UV–visible spectrophotometer. HR-MS data was obtained on a Varian 7.0T FTMS. IR measurements were carried out by a Bruker Tensor 27 System with KBr disks. Cyclic voltammetry experiments and electrochemical impedance spectroscopy (EIS) were recorded using a Zennium electrochemical workstation (Zahner, Germany). Cyclic voltammetry experiments were carried out using a conventional three-electrode system [15].

2.2. Fabrication and characterization of DSSCs

The photoanodes and counter electrodes were prepared according to our previous work [16]. A 20 nm TiO_2 film (thickness, $\sim 10\ \mu\text{m}$) was prepared by doctor-blade method using a commercial 20 nm TiO_2 sol (Heptachroma Corporation) onto the FTO glass (Nippon Sheet Glass, sheet resistance of $15\ \Omega/\text{sq}$). A 200 nm scattering layer (thickness, $\sim 4\ \mu\text{m}$) (Heptachroma Corporation) was prepared over the transparent layer, and then heated to $500\ ^\circ\text{C}$ and sintered for 60 min. The prepared TiO_2 photoanodes were treated by 40 mM TiCl_4 aqueous solution at $70\ ^\circ\text{C}$ for 60 min and sintered again at $500\ ^\circ\text{C}$ for 60 min. The counter electrode was prepared by thermal deposition a Pt layer on FTO glass at $450\ ^\circ\text{C}$ for 30 min. The adsorption of the tetraindole-based dyes on photoanode was carried out in 0.3 mM dye bath in tetrahydrofuran with or without co-adsorption of 10 mM CDCA (chenodeoxycholic acid) for 12 h. The adsorption of **N719** dyes on photoanode was also carried out in 0.3 mM dye ethanol solution for 12 h. The amounts of dye loading were measured according to the desorption amount of dye molecules on immersion of sensitized TiO_2 photoanode in a basic solution (0.1 M NaOH in THF/ H_2O = 1:1) and calibrated absorption

spectra of each dye. The iodine electrolyte was composed of 0.3 M DMPII, 0.1 M LiI, 0.05 M I_2 and 0.5 M TBP in CH_3CN . The DSSCs were illuminated by a solar simulator (CHF-XM-500W, Trusttech Co. Ltd.) under $100\ \text{mW cm}^{-2}$ irradiation, which was calibrated by a standard silicon solar cell (91150V, Newport Corporation). The photocurrent intensity–voltage (J – V) characteristic curves of the DSSC were recorded on a workstation (Zennium, Zahner Corporation). The measurement of the incident photon-to-current conversion efficiency (IPCE) was performed by an IPCE system (QTest Station 2000 IPCE Measurement System, CROWNTech).

2.3. Synthesis

2.3.1. Synthesis of 5,10,15,20-tetraoctyl-cycloocta[1,2-b:3,4-b':5,6-b'':7,8-b''']tetraindole (2)

A mixture of tetraindole (compound **1**) (0.46 g, 1.0 mmol) and *t*-BuOK (0.67 g, 6.0 mmol) in THF (20 mL) was heated under reflux for 0.5 h. Then *n*- $\text{C}_8\text{H}_{17}\text{Br}$ (1.2 g, 6.0 mmol) was added dropwise, and the mixture was heated under reflux for 12 h before being evaporated. The mixture was extracted with dichloromethane, washed with water and brine. The organic layer was dried with Na_2SO_4 and the solvents were evaporated under vacuum. The crude product was purified by column chromatography using CH_2Cl_2 /petroleum ether (1:4) as the eluant to afford compound **2** as a pale yellow solid (yield: 63.2%). IR (KBr): 2954, 2925, 2853, 1610, 1574, 1462, 1337, 1227, 743, $694\ \text{cm}^{-1}$. ^1H NMR (400 MHz, CDCl_3) δ 7.36 (t, J = 9.0 Hz, 8H), 7.15 (t, J = 7.5 Hz, 4H), 7.06 (t, J = 7.4 Hz, 4H), 4.30–4.04 (m, 8H), 1.52–1.41 (m, 4H), 1.33–1.24 (m, 4H), 1.05–0.93 (m, 8H), 0.85–0.76 (m, 8H), 0.72 (t, J = 7.1 Hz, 12H), 0.64–0.46 (m, 12H), 0.46–0.34 (m, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 138.33, 137.21, 127.52, 121.07, 119.84, 118.79, 110.35, 107.16, 44.76, 31.89, 29.30, 29.19, 28.26, 26.07, 22.45, 14.10. HR-MS (MALDI): m/z $[\text{M}]^+$ calcd for $\text{C}_{64}\text{H}_{84}\text{N}_4$, 908.6696; found, 908.6695.

2.3.2. Synthesis of 5-(5,10,15,20-tetraoctyl-cycloocta[1,2-b:3,4-b':5,6-b'':7,8-b''']tetraindol-2-yl)thiophene-2-carbaldehyde (3a)

A solution of *N*-bromosuccinimide (NBS) (29 mg, 0.16 mmol) in DMF (2 mL) was added dropwise to a mixture of compound **2** (149 mg, 0.16 mmol) in CHCl_3 (20 mL) at $0\ ^\circ\text{C}$. The mixture was slowly warmed to room temperature and stirred for an additional 1 h before it was poured into water. Then, the organic phase was

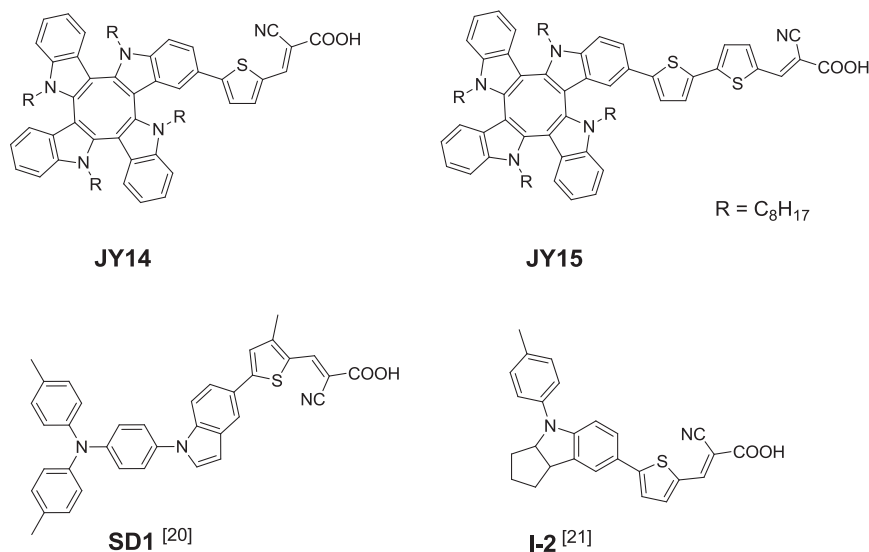


Fig. 1. Chemical structures of **JY14**, **JY15**, **SD1** and **I-2**.

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