



Synthesis of phenothiazine-based di-anchoring dyes containing fluorene linker and their photovoltaic performance



Xue-Xin Dai ^a, Hao-Lin Feng ^b, Zu-Sheng Huang ^a, Meng-Jiao Wang ^a, Lingyun Wang ^a, Dai-Bin Kuang ^{b,*}, Herbert Meier ^c, Derong Cao ^{a,*}

^a School of Chemistry and Chemical Engineering, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510641, China

^b MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, KLGEI of Environment and Energy Chemistry, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, China

^c Institute of Organic Chemistry, University of Mainz, Mainz 55099, Germany

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ABSTRACT

A new di-anchoring organic dye based on phenothiazine featuring A-D- π -D-A (acceptor-donor- π -linker-donor-acceptor) configuration with fluorene as the π linker was designed and successfully synthesized. Compared to the corresponding mono-anchoring D-A congener, this new dye exhibited a broader and stronger absorption in the light wavelength ranging from 400 nm to 600 nm and thus showed a more efficient photovoltaic performance for dye-sensitized solar cells (DSSCs). The overall power conversion efficiency (η) of this new dye in a sensitized solar cell amounted to 5.70%, which is 17% higher than that of the equivalent based counterpart (4.87%). On the other hand, the introduction of two thiophene units at position-2 and -7 of the fluorene unit gave another new dye with extended conjugation. This extended conjugation dye showed a higher molar extinction coefficient (ϵ), but exhibited π -stacked aggregation on the TiO₂ surface, resulting in low efficiency of electron injection. The results indicate that the di-anchoring dye with fluorene as π linker is a promising candidate for efficient DSSCs.

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1. Introduction

Solar energy is regarded as one of the most perfect energy sources that have the largest potential to cater for the growing energy need without an appreciable greenhouse effect. Among the available technologies, dye-sensitized solar cells (DSSCs), the third generation photovoltaic technology, represent one of the most promising photovoltaic devices due to the low material cost, high solar-to-electric power conversion efficiencies (η), and ease of fabrication [1,2]. A typical DSSC includes three main ingredients: a nano-TiO₂ photo-electrode [3–6], a redox electrolyte, and a dye sensitizer. Among these three key components, metal-complex and metal-free organic sensitizers play a vital role in absorbing solar photons and generating photocurrent. To date, ruthenium complex sensitizers and zinc porphyrin dyes have

reached η values exceeding 11% and 12%, respectively [7–10]. Compared to those transition-metal complex sensitizers, the organic dyes have the advantages of an easy purification procedure, convenient variation of molecular structures and cost-effectiveness. In general, the conventional organic dyes consist of donor, π -conjugated bridge, and acceptor groups (i.e., a D- π -A molecular structure). However, these compounds frequently present a single, narrow absorption band in the visible region [11]. Moreover, such kind of a rod-like structure usually causes dye aggregation, which was considered to be one of the major factors accounting for the charge recombination and thus lowering the photovoltaic performance [12].

Recently, organic sensitizers with two anchor groups (2A dyes) has attracted increasing attention. As 2A dyes gave several advantages including stronger bonding, red shift in absorption [13,14], favorable electron injection, leading to a higher generated photocurrent [15]. Several di-anchoring organic dyes have been synthesized and applied for DSSCs with better η than single D- π -A dyes [13–21]. The 2A dyes with A- π -D- π -D- π -A structure exhibit large molar extinction coefficients for the charge transfer transition due to the presence of two identical D- π -A chromophores [16]. A high

* Corresponding author. Tel./fax: +86 20 87110245.

** Corresponding author. Tel.: +86 20 84113015.

E-mail addresses: kuangdb@mail.sysu.edu.cn (D.-B. Kuang), drcao@scut.edu.cn (D. Cao).

molar extinction coefficient in the visible light wavelength region means a good light harvesting ability, thus it will contribute to an enhanced short-circuit current [22,23]. The other important advantage is that they would allow the use of thinner nano-structure oxide semiconductor films with a comparable light-harvesting efficiency as the thicker one, a key factor in the practical solid state DSSCs [24].

Herein, we focused on designing and synthesizing efficient phenothiazine (PTZ) di-anchoring dyes. PTZ is a well-known donor with electron-rich sulfur and nitrogen atoms. Its unique non-planar “butterfly” structure can impede the molecular aggregation and the exciplex formation [25,26], which is favorable for achieving high photovoltage. Therefore, phenothiazine-based dyes are promising organic sensitizers for DSSCs because of their excellent photo-response in the visible region and high V_{oc} [19,26–31]. The purpose of incorporating fluorene as linker is attributable to following factors: 1) fluorene-based organic materials can be active ingredients in electronic devices such as organic light-emitting diodes (OLEDs) [32–34] and DSSCs [17,20,35–39] due to their unique charge transporting property and pronounced thermal stability [40,41]; 2) the hydrophobic alkyl chains on the fluorene moiety can not only improve the solubility, but also reduce dye aggregation and effectively suppress the charge recombination for a higher value of J_{sc} , which has been proved by many previous works [42–44].

With the aforementioned benefits, we were therefore interested in exploring a novel 2A organic dye (**DP-1**) by incorporating fluorene as the π -linker and PTZ as the donor. To study the impact of the π -linker on the photovoltaic properties, two thiophene units were introduced at position-2 and -7 in the fluorene skeleton of **DP-1**, affording a new 2A dye **DP-2** with a conjugation extension of the π linker. In addition, the single D-A dye **SP** was synthesized for comparison (Fig. 1). The photophysical, electrochemical and photovoltaic properties of the three dyes were systematically investigated.

2. Experimental

The solvents (tetrahydrofuran (THF), 1,4-dioxane, toluene) were distilled over sodium/benzophenone before use. Other reagents

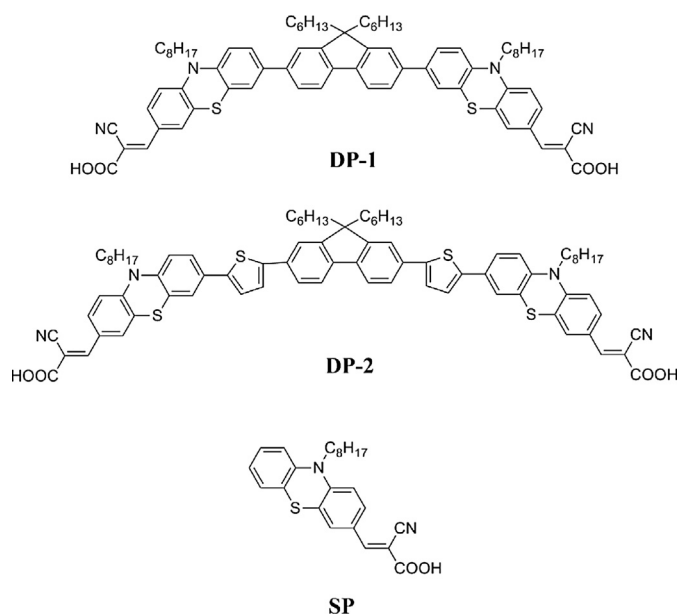


Fig. 1. The structures of dyes **DP-1**, **DP-2** and **SP**.

were purchased from commercial sources and used without further purification. All the reactions were carried out under an inert atmosphere (nitrogen or argon). Reactions were monitored by using TLC and purified by silica gel column chromatographic (300–400 mesh) and preparative TLC.

2.1. Synthesis

7-Bromo-10-octyl-10*H*-phenothiazine-3-carbaldehyde (**1**), 10-octyl-10*H*-phenothiazine-3-carbaldehyde (**4**) was synthesized according to the methods reported in the literature [45,46].

2.1.1. 10-Octyl-7-(thiophen-2-yl)-10*H*-phenothiazine-3-carbaldehyde (**2**)

A mixture of **1** (420 mg, 1.00 mmol), thiophen-2-ylboronic acid (154 mg, 1.20 mmol), tetrakis(triphenylphosphine)palladium(0) (148 mg, 0.128 mmol), and potassium carbonate (4 mL of 0.5 M aqueous solution, 2.0 mmol) in 1,4-dioxane (20 mL) was stirred and heated to reflux under argon for 20 h. The reaction mixture was poured into water (150 mL) and extracted with CH₂Cl₂ (DCM). The combined extract was washed with brine and dried over anhydrous Na₂SO₄. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography on silica gel (PE: EA (petroleum ether: ethyl acetate) = 25: 1 as eluent) to give the product as a yellow powder in 84% (354 mg) yield, mp 53–55 °C. ¹H NMR (CDCl₃, 400 MHz, ppm): δ 9.80 (s, 1H), 7.63–7.65 (m, 1H), 7.59 (m, 1H), 7.37–7.39 (m, 1H), 7.34 (m, 1H), 7.21–7.25 (m, 2H), 7.05–7.07 (m, 1H), 6.90 (d, J = 8.4 Hz, 1H), 6.86 (d, J = 8.4 Hz, 1H), 3.89 (t, J = 7.0 Hz, 2H), 1.79–1.86 (m, 2H), 1.41–1.48 (m, 2H), 1.26–1.38 (m, 8H), 0.87 (t, J = 6.2 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 189.9, 150.3, 143.0, 142.5, 131.1, 130.2, 130.2, 128.4, 128.0, 125.2, 124.7, 124.5, 124.4, 124.3, 122.7, 116.1, 114.8, 48.1, 31.7, 29.2, 29.1, 26.8, 26.7, 22.6, 14.1. HRMS (ESI) calcd for C₂₅H₂₈NOS₂ [M+H]⁺: 422.1607; found: 422.1611.

2.1.2. 7,7'-(9,9-Dihexyl-9*H*-fluorene-2,7-diyl)bis(10-octyl-10*H*-phenothiazine-3-carbaldehyde) (**3-a**)

A mixture of **1** (245 mg, 0.588 mmol), 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (162 mg, 0.323 mmol), tetrakis(triphenylphosphine) palladium(0) (34 mg, 0.029 mmol), and potassium carbonate (3 mL of 0.5 M aqueous solution, 1.5 mmol) in 1,4-dioxane (20 mL) was stirred and heated to reflux under argon for 20 h. The reaction mixture was poured into water (50 mL) and extracted with DCM. The combined extract was washed with brine and dried over anhydrous Na₂SO₄. The solvent was removed by rotary evaporation, and the crude product was purified by silica gel pad (PE: EA: DCM = 20: 1: 4 as eluent) to give the product as a yellow solid in 39% (103 mg) yield. ¹H NMR (CDCl₃, 400 MHz, ppm): δ 9.79 (s, 2H), 7.71–7.73 (m, 2H), 7.60–7.65 (m, 4H), 7.44–7.51 (m, 6H), 7.41 (m, 2H), 6.89–6.96 (m, 4H), 3.91 (t, J = 7.0 Hz, 4H), 2.01–2.05 (m, 4H), 1.81–1.88 (m, 4H), 1.42–1.53 (m, 4H), 1.26–1.31 (m, 16H), 1.06–1.12 (m, 12H), 0.87 (t, J = 6.2 Hz, 6H), 0.76 (t, J = 6.8 Hz, 6H), 0.70 (m, 4H). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 190.0, 151.8, 150.5, 142.4, 140.0, 138.5, 137.2, 131.1, 130.3, 128.4, 126.2, 125.9, 125.5, 124.6, 124.2, 120.8, 120.1, 116.1, 114.7, 55.3, 48.1, 40.5, 31.8, 31.5, 29.7, 29.2, 29.2, 26.9, 26.8, 23.8, 22.6, 22.6, 14.1, 14.1. HRMS (ESI) calcd for C₆₇H₈₁N₂O₂S₂ [M+H]⁺: 1009.5734; found: 1009.5748.

2.1.3. 7,7'-[5,5'-(9,9-Dihexyl-9*H*-fluorene-2,7-diyl)bis(thiophene-5,2-diyl)]bis(10-octyl-10*H*-phenothiazine-3-carbaldehyde) (**3-b**)

Compound **3-b** was synthesized by the following two steps: bromination firstly, and then Suzuki-Miyaura coupling reaction. A mixture of **2** (330 mg, 0.784 mmol) was dissolved in dry THF (15 mL) and the solution was cooled to 0 °C. N-Bromosuccinimide

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