



## Synthesis and photovoltaic performance of asymmetric di-anchoring organic dyes



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### ABSTRACT

Two novel metal-free organic dyes bearing two asymmetric double donor–acceptor segments were synthesized. Their physical, optical, electrochemical properties and photovoltaic performances were investigated. Compared with the mono-anchoring dye containing single donor–acceptor chain, these new dyes exhibited a broader and much stronger absorption in the light wavelength ranging from 400 to 600 nm, showed higher IPCE values and short-circuit current density, which led to more efficient photovoltaic performance. The dye with triphenylamine and phenothiazine as two electron donors and two cyanoacrylic acids as two electron acceptors exhibited an impressive power conversion efficiency of 5.92% under simulated AM 1.5 G illumination condition with an open-circuit photovoltage of 796 mV, a short-circuit photocurrent density of 11.24 mA/cm<sup>2</sup>, which is 22% higher than that of the mono-anchoring dye based counterpart. The results indicate that the asymmetric di-anchoring organic dyes are promising sensitizers for high efficient dye-sensitized solar cells.

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### 1. Introduction

In recent years, energy issues have become so important that many scientific investigations have been focused on the development of new sustainable energy resources. Solar energy is one of the most useful alternative sustainable energy sources as its abundance is “virtually unlimited” and free. Since the breakthrough in 1991 by O'Regan and Grätzel [1], dye-sensitized solar cells (DSSCs) have shown the great potential due to high solar energy to electricity conversion efficiency and low-cost of production [2–5]. Recently, nanostructured TiO<sub>2</sub> photoelectrodes have exhibited significant enhancements in power conversion efficiency of DSSCs [6]. Towards the realization of higher photovoltaic performance and durability in DSSCs, the development of the sensitizers is of

great significance [3–5]. The record power conversion efficiency (PCE) over 13.0% has been achieved by a Zn–porphyrin complex-based DSSC recently [7,8]. In addition to transition metal complexes, metal-free sensitizers have received numerous interests for their flexibility in tuning molecular architecture, easy purification, cost-effectiveness, high molar extinction coefficients and compliance with environmental issues [3–5]. Very recently, an impressively high cell efficiency of 12.5% has also been achieved by a novel metal-free alkoxy-silyl carbazole dye [9].

Organic sensitizers featuring rod-like donor– $\pi$ –acceptor (D– $\pi$ –A) architecture have been extensively studied [3–5,9–17]. Compared with Ru(II) sensitizers in which 1–4 anchoring groups are present for an efficient electron transfer [18–22], one of the drawbacks of such kind of the organic dyes is that the presence of only one anchoring group might lead to inferior performance. In addition, these organic dyes frequently present a single, narrow absorption band in the visible region [23]. To enhance the photovoltaic performance of DSSCs, considerable efforts have been devoted to optimize the structure of the organic dyes, such as increasing the amount of anchoring groups and/or extending  $\pi$ -

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conjugation to increase the molar extinction coefficient of the absorption band, which can improve the light harvesting ability of the dyes [3,4,24–29]. The dye containing double/multiple anchor groups exhibited a unique advantage of stronger bonding with the TiO<sub>2</sub> surface [28,29]. The binding strength of dye on the TiO<sub>2</sub> surface is one of the major factors which affect the PCE and stability of DSSC. Strong binding of the dyes on TiO<sub>2</sub> not only improves adsorption but also leads to red shift in absorption, efficient charge injection [30] and photocurrent generation [31]. Up till now the synthesis of di-anchoring dyes (2A dyes) with high solar power-to-electricity conversion efficiency is of particular interest to synthetic chemists [23,28,29,31–36]. Mostly, the 2A dyes containing single donor and two anchors (D(–π–A)<sub>2</sub>) [28,32,34,35] frequently have higher photocurrent than their congeners with only single anchor due to their longer wavelength absorption and higher absorption capability. However, compared with the single anchor dye, most of the D(–π–A)<sub>2</sub> dyes often show a lower open-circuit photovoltage (*V*<sub>oc</sub>) as these molecules may cause more serious charge recombination [31] and protons releasing, in which protons releasing lowers the Fermi level of TiO<sub>2</sub> [36]. Therefore, it is still of great necessity to further chemical structure optimization of the double anchoring dyes to achieve more efficient DSSCs. However, most of the related works focus on the symmetric architecture, while reports on the asymmetric 2A dyes are still quite rare [23].

Previously, our group designed several organic sensitizers featuring two different non-conjugated D–π–A chains [37]. It is found that the DSSCs based on these dyes have better cell performance (*i.e.* better short-circuit current (*J*<sub>sc</sub>) and *V*<sub>oc</sub>) than those with only single D–π–A chain. Recently we synthesized two symmetric di-anchoring dyes **DP-1** and **DP-2** which contained two identical light-harvesting units in one molecule, and found that they had higher molar extinction coefficients and exhibited a red-shift of the absorption spectra in comparison with the corresponding mono-anchoring D–A congener [38]. In order to extend π-conjugation to enhance the molar extinction coefficient and broaden the absorption band in the visible range by conjugating link between two different D–A branches, here we designed and synthesized two novel asymmetric 2A dyes (**DP-3** and **DP-4**), where phenothiazine (PTZ) and triphenylamine (TPA) were used as the electron donor units, while cyanoacrylic acid as the acceptor (Fig. 1). For comparison, a single acceptor dye **SP** was synthesized. These dyes were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR and HRMS spectra. Their photophysical, electrochemical properties and photovoltaic performance were systematically investigated.

## 2. Experimental

### 2.1. Materials and reagents

The solvents (tetrahydrofuran (THF), 1,4-dioxane, toluene and dimethylformamide (DMF)) were dried by standard procedures. Other reagents 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 chromatographic separations were performed with silica gel (200–300 or 300–400 mesh).

### 2.2. Synthesis

(*E*)-2-Cyano-3-(10-octyl-10*H*-phenothiazin-3-yl)-acrylic acid (**SP**) was synthesized according to the literature [38]. 10-Octyl-10*H*-phenothiazine-3-carbaldehyde (**1**) and 7-bromo-10-octyl-10*H*-phenothiazine-3-carbaldehyde (**2**) were synthesized according to the reported methods [39,40].

#### 2.2.1. 7-[4-(Diphenylamino)phenyl]-10-octyl-10*H*-phenothiazine-3-carbaldehyde (**3**)

A mixture of **2** (210 mg, 0.50 mmol), [4-(diphenylamino)phenyl]boronic acid (174 mg, 0.60 mmol), tetrakis (triphenylphosphine) palladium(0) (37 mg, 0.032 mmol), and potassium carbonate (2 mL of 0.5 M aqueous solution, 1.0 mmol) in 1,4-dioxane (10 mL) was stirred and heated to reflux under argon for 20 h. The reaction mixture was poured into water (150 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (DCM). The combined extract was washed with brine and dried over anhydrous sodium sulfate. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (petroleum ether:ethyl acetate (PE:EA) = 25:1 as eluent) to give **3** as a yellow solid in 83% (242 mg) yield, mp 48–50 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm) δ 9.78 (s, 1H), 7.61–7.64 (m, 1H), 7.57–7.58 (m, 1H), 7.37–7.39 (m, 2H), 7.32–7.34 (m, 1H), 7.24–7.29 (m, 5H), 7.09–7.12 (m, 6H), 7.00–7.04 (m, 2H), 6.90 (d, *J* = 3.2 Hz, 1H), 6.87 (d, *J* = 3.2 Hz, 1H), 3.88 (t, *J* = 7.2 Hz, 2H), 1.79–1.86 (m, 2H), 1.41–1.48 (m, 2H), 1.26–1.30 (m, 8H), 0.86 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm) δ 190.0, 150.5, 147.6, 147.2, 142.1, 136.2, 133.4, 131.0, 130.2, 129.3, 128.4, 127.2, 125.6, 125.4, 124.6, 124.5, 124.1, 123.9, 123.0, 116.1, 114.7, 48.1, 31.7, 29.2, 29.2, 26.8, 26.8, 22.6, 14.1. HRMS (ESI): calcd for C<sub>39</sub>H<sub>39</sub>N<sub>2</sub>O<sub>5</sub> [M + H]<sup>+</sup>: 583.2778, found: 583.2783.

#### 2.2.2. 7-[4-[4-Formylphenyl(phenyl)amino]phenyl]-10-octyl-10*H*-phenothiazine-3-carbaldehyde (**4**)

To a solution of **3** (228 mg, 0.39 mmol) and dry dimethylformamide (DMF) (1.0 mL) in 1,2-dichloroethane (20 mL) was slowly added phosphorus oxychloride (0.1 mL) at 0 °C in an ice-water bath. Then the bath was heated to 50 °C and maintained for 6 h. Dilute aqueous solution of sodium hydroxide was added, and the mixture was extracted three times with DCM (3 × 20 mL). The combined organic phases were washed with brine and dried over anhydrous sodium sulfate. The solvent was removed via rotary evaporation, and the crude product was purified by column chromatography (PE:EA = 7:1 as eluent) to give the product as a yellow solid in 83% (150 mg) yield, mp 64–66 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm) δ 9.82 (s, 1H), 9.80 (s, 1H), 7.69–7.71 (m, 2H), 7.63–7.66 (m, 1H), 7.59 (m, 1H), 7.47–7.49 (m, 2H), 7.32–7.38 (m, 4H), 7.19–7.21 (m, 5H), 7.06–7.08 (m, 2H), 6.90–6.94 (m, 2H), 3.91 (t, *J* = 7.0 Hz, 2H), 1.81–1.88 (m, 2H), 1.43–1.48 (m, 2H), 1.26–1.33 (m, 8H), 0.87 (t, *J* = 6.0 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm) δ 190.4, 189.9, 153.2, 150.4, 146.1, 145.4, 142.6, 136.1, 135.7, 131.3, 131.1, 130.2, 129.8, 129.4, 128.4, 127.6, 126.4, 126.2, 125.9, 125.6, 125.3, 124.6, 124.3, 119.8, 116.1, 114.8, 48.1, 31.7, 29.2, 29.1, 26.8, 26.7, 23.0, 14.1. HRMS (ESI): calcd for C<sub>40</sub>H<sub>39</sub>N<sub>2</sub>O<sub>2</sub>S [M + H]<sup>+</sup>: 611.2727, found: 611.2741.

#### 2.2.3. (*E*)-3-(4-((4-(7-((*E*)-2-Cyano-2-cyano-2-vinyl)-10-octyl-10*H*-phenothiazin-3-yl) phenyl)(phenyl)amino)phenyl)-2-cyanoacrylic acid (**DP-3**)

A mixture of **1** (122 mg, 0.20 mmol), *tert*-butyl cyanoacetate (186 mg, 1.3 mmol), ammonium acetate (101 mg, 1.3 mmol), and acetic acid (2 mL) in toluene (25 mL) was placed in a flask. Air was removed and the solution was heated under reflux under argon atmosphere for 4 h. After cooling, the reaction was quenched by addition of water and the mixture was extracted with DCM. The organic layer was dried over anhydrous sodium sulfate and evaporated under vacuum. The crude product was obtained by silica gel chromatography (PE:EA = 7:1 as eluent) as a red solid and used in the further reaction. This red solid was stirred with trifluoroacetic acid (10 mL) for 2 h, then 140 mL of pure water was added and the resulting solid was collected by filtration. The pure product was obtained by repeatedly water washing and centrifugation as a dark red powder in 61% (91 mg) yield, mp 189–191 °C. <sup>1</sup>H NMR (THF-*d*<sub>6</sub>, 400 MHz, ppm) δ 8.11 (s, 1H), 8.08 (s, 1H), 7.92–7.98 (m, 3H), 7.77

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