RSC Advances

PAPER

Cite this: RSC Adv., 2014, 4, 24377

Received 3rd March 2014 Accepted 12th May 2014 DOI: 10.1039/c4ra01858c

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Introduction

DSSCs have drawn increasing attention since Grätzel and O'Regan reported them in 1991.1 Research on novel highly efficient dyes has never been suspended. Compared to metal complexes, metal-free organic dyes have many advantages such as lower cost, environmental friendliness, higher molar extinction coefficient and easier molecular design. The donor- π -conjugated bridge-acceptor (D- π -A) structure is a classical molecular configuration, which has helped in the designing of many highly efficient organic dyes. However, the absorption spectra of D- π -A-structured organic dyes are narrow, which is not beneficial for higher short-circuit current density. In order to broaden the absorption band, one strategy is to decrease the energy band (ΔE_{α}) of the dyes by employing a stronger electron donor or electron acceptor. Recently, a new kind of molecular configuration named the donor-acceptor- π bridge-acceptor (D-A- π -A) structure has been reported.² For D-A- π -A-structured organic dyes, electron-withdrawing units, such as benzothiadiazole,3 benzotriazole,4 and quinoxaline,5 are generally embedded in the molecule of sensitizers located

Phenothiazine derivatives-based D $-\pi$ -A and D-A- π -A organic dyes for dye-sensitized solar cells⁺

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 $D-\pi-A$ and $D-A-\pi-A$ -structured organic dyes represent different developmental directions of photosensitizers in dye-sensitized solar cells (DSSCs). In this work, two phenothiazine derivatives-based $D-\pi-A$ and $D-A-\pi-A$ -structured organic dyes have been synthesized and applied in DSSCs. The physical and electrochemical properties of both dyes have been investigated systematically. The results show that the $D-A-\pi-A$ -structured dye exhibits a broader spectrum response but lower molar coefficient of extinction when compared to the $D-\pi-A$ -structured dye. Regarding photovoltaic performance, the $D-\pi-A$ -structured dye yields a higher efficiency (η) of 7.5% with a higher short-circuit current density (J_{sc}) of 16.36 mA cm⁻² and open-circuit voltage (V_{oc}) of 706 mV than that of the $D-A-\pi-A$ -structured dye. Incident photon-to-electron conversion efficiency (IPCE) studies and impedance analysis also support these results. These results demonstrate that the phenothiazine derivatives-based $D-\pi-A$ -structured organic dyes can compete with, and even exceed, $D-A-\pi-A$ -structured organic dyes under the same test conditions.

between the electron donor and the π -bridge, which could effectively decrease $\Delta E_{\rm g}$. Zhu and co-workers reported a highly efficient D–A– π –A-structured organic dye in 2012, which produced an efficiency of 9.0%.⁶ D– π –A- and D–A– π –A-structured dyes represent two different developmental directions in DSSCs. However, as we know, there are few reports on the systematic study of both D– π –A- and D–A– π –A-structured dyes with similar structures until now. By investigating the difference in the physical and electrochemical properties and photovoltaic performance of both dye structures, the advantages and disadvantages of both dye structures will pave the way for further molecular design.

Triphenylamine and its derivatives7-12 have been successfully used as electron donors in the construction of sensitizers. However, the rotation of the triphenylamine ring decreases the electron-donating ability of the electron donor. Indoline13,14 and tetrahydroquinoline¹⁵ are stronger electron donors with more planar spatial structures when compared to triphenylamine. In addition, phenothiazine¹⁶⁻¹⁸ is also a strong electron donor, which has been successfully employed as electron donor and π conjugated bridge in D- π -A-structured dyes. However, as we know, there are no reports of introducing phenothiazine as electron donor into a D-A- π -A structure until now. Thiophene and its derivatives¹⁹⁻²¹ always serve as a π -conjugated bridge in organic dyes. Recently, Wang et al. have reported a series of D-A- π -A-structured organic dyes with thiophene and its derivatives as π -conjugated bridge.²² The results indicate that the introduction of a long alkyl chain in a π -conjugated bridge is not beneficial for the improvement of the efficiency of dyes. In order to diminish this effect, thiophene is considered to be a



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[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ra01858c





Here, we report two phenothiazine organic dyes based on the D- π -A structure and D-A- π -A structure, coded **JH305** and **JH307**, respectively. As shown in Fig. 1, for both the dyes, a phenothiazine derivative serves as an electron donor. Traditional cyanoacrylic acid is employed as an electron acceptor to maintain the similar conjugation level, the only difference in both the dyes is that the thiophene ring adjacent to the electron donor in dye **JH305** is replaced by benzothiadiazole in dye **JH307**. The physical and electrochemical properties and the photovoltaic performance of both dyes are investigated systematically.

Experimental section

Analytical measurements

The absorption spectra were recorded on HP8453 (USA). Electrochemical redox potentials were obtained by cyclic voltammetry (CV) on an electrochemistry workstation (BAS100B, USA). A traditional three-electrode system was used. The working electrode, auxiliary electrode and reference electrode are a glassy carbon disk electrode, Pt wire and Ag/Ag⁺ electrode, respectively. The photocurrent–voltage (*J*–*V*) properties were measured under AM 1.5G illumination (16S-002, Solar Light Co. Ltd., USA). The incident light intensity was 100 mW cm⁻², which was calibrated with a standard Si solar cell. The working areas of the cells were masked to be 0.1256 cm². The *J*–*V* data were collected by an electrochemical workstation (LK9805, Lanlike Co. Ltd., China). The measurement of the IPCE was obtained by a Hypermono-light (SM-25, Jasco Co. Ltd., Japan).

Synthesis of JH305 and JH307

Scheme 1 shows the synthetic routes of **JH305** and **JH307**. The organic solvents used in these reactions were freshly distilled according to standard procedures. The commercial reagents were directly used without further purification. Compound **1** and (2,4-dibutoxyphenyl)boronic acid were synthesized according to a previously reported method by our group.^{23,24} Almost all the structures were identified by ¹H NMR and MS except for pinacolato boronate, which was identified by MS.

10-Butyl-3-(2,4-dibutoxyphenyl)-10*H***-phenothiazine** (2). Compound **1** (4 g, 12 mmol), (2,4-dibutoxyphenyl)boronic acid



Scheme 1 Synthetic routes of JH305 and JH307. (a) K_2CO_3 , Pd(PPh₃)₄, THF–H₂O, reflux, 12 h; (b) NBS, THF, 0 °C, 2 h; (c) *n*-BuLi, THF, -78 °C, pinacolato boronate, 2 h; (d) Br₂, HBr (40%), 90 °C, 12 h; (e) POCl₃, DMF, CHCl₃, 60 °C; (f) cyanoacetic acid, pyperidine, THF, reflux, 2 h.

(3.83 g, 14.4 mmol), K_2CO_3 (2.48 g, 18 mmol), and $Pd(PPh_3)_4$ (60 mg) were dissolved in THF-H₂O (5 : 1, v/v) under N₂. The mixture was refluxed for 12 h. When the reaction was cooled to room temperature, water (40 ml) was added and the mixture was extracted by CH₂Cl₂. The crude product was purified by petroleum-CH₂Cl₂ (8 : 1) to give compound 2 (2.33 g, 42%) as a colourless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.43 (s, 1H), 7.28 (d, *J* = 4.1 Hz, 1H), 7.09 (dt, *J* = 13.3, 5.5 Hz, 3H), 6.82 (d, *J* = 8.5 Hz, 3H), 6.50 (s, 1H), 4.01 (t, *J* = 6.4 Hz, 3H), 3.88 (t, *J* = 15.3, 8.9 Hz, 3H), 1.84–1.73 (m, 4H), 1.42 (tt, *J* = 13.5, 6.9 Hz, 6H), 0.91 (dd, *J* = 17.3, 10.1 Hz, 9H). [M]⁺ calcd for C₃₀H₃₇NO₂S, 475.2545; found, 475.2544.

3-Bromo-10-butyl-7-(2,4-dibutoxyphenyl)-10H-phenothiazine (3). Compound 2 (2.2 g, 4.63 mmol) was dissolved in THF solution at 0 °C. NBS (824 mg, 4.63 mmol) was added slowly for 2 h. Water (30 ml) was added when the reaction was finished, and the mixture was extracted by CH_2Cl_2 . The organic layer was collected and concentrated by rotary evaporation. The crude product was purified by petroleum– CH_2Cl_2 (8 : 1) to give compound 3 (2.28 g, 89%) as a colourless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.42 (s, 1H), 7.26 (dd, J = 6.3, 3.0 Hz, 2H), 7.24 (d, J = 2.8 Hz, 1H), 7.20 (d, J = 2.3 Hz, 1H), 6.84 (d, J = 8.7 Hz, 1H), 6.69 (d, J = 8.2 Hz, 1H), 6.51 (d, J = 8.1 Hz, 1H), 4.01 (t, J = 24.8, 6.4 Hz, 3H), 3.91 (t, J = 15.7, 9.1 Hz, 3H), 1.90–1.73 (m, 6H), 1.44 (m, J = 14.6, 7.3, 4.4 Hz, 6H), 0.97–0.91 (m, 9H). [M]⁺ calcd for $C_{30}H_{36}NO_2SBr$, 553.1650; found, 553.2.

10-Butyl-3-(2,4-dibutoxyphenyl)-7-(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)-10*H*-phenothiazine (4). Compound 3 (2.1 g, 3.8 mmol) was dissolved in dry THF under N₂. After the addition of *n*-BuLi (1.9 ml, 4.6 mmol) at -78 °C, the resulting mixture was stirred for 2 h at -78 °C. After isopropyl pinacolato boronate (0.85 ml, 4.2 mmol) was added, the mixture was heated to room temperature and maintained for 12 h. The mixture was then poured into water and extracted by CH₂Cl₂. The crude product was purified by petroleum-CH₂Cl₂ (4 : 1) to give compound 4 (1.32 g, 58%). [M]⁺ calcd for C₃₆H₄₈BNO₄S, 601.3405; found, 601.3397.

[2,2'-Bithiophene]-5-carbaldehyde (5). 5-Bromothiophene-2carbaldehyde (1.5 g, 7.9 mmol), thiophen-2-ylboronic acid (1.23 g, 9.48 mmol), K₂CO₃ (1.64 g, 11.85 mmol), and Pd(PPh₃)₄ (30 mg) were dissolved in THF-H₂O (5 : 1, v/v) under N₂. The mixture was refluxed for 12 h. When the reaction was finished, water (30 ml) was added and the mixture was extracted by CH₂Cl₂. The crude product was purified by petroleum–CH₂Cl₂ (1 : 2) to give compound 5 (1 g, 67%) as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 9.85 (s, 1H), 7.66 (d, *J* = 3.9 Hz, 1H), 7.39– 7.30 (m, 2H), 7.24 (d, *J* = 3.9 Hz, 1H), 7.06 (dd, *J* = 4.9, 3.8 Hz, 1H). [M]⁺ calcd for C₉H₆OS₂, 193.9860; found, 193.9865.

5'-Bromo-[2,2'-bithiophene]-5-carbaldehyde (6). Compound 5 (950 mg, 4.92 mmol) was dissolved in THF solution at 0 °C. NBS (875 mg, 4.92 mmol) was added slowly several times. When the reaction finished, water (30 ml) was added and the mixture was extracted by CH₂Cl₂. The organic layer was then collected and concentrated by rotary evaporation. The crude product was purified by petroleum–CH₂Cl₂ (1 : 2, v/v) to give compound **6** (986 mg, 74%) as yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 9.85 (d, *J* = 16.9 Hz, 1H), 7.66 (d, *J* = 4.0 Hz, 1H), 7.18 (d, *J* = 3.9 Hz, 1H), 7.11 (d, *J* = 3.9 Hz, 1H), 7.04 (d, *J* = 3.9 Hz, 1H). [M]⁺ calcd for C₉H₅BrOS₂, 271.8965; found, 271.8974.

4,7-Dibromobenzo[*c*][**1,2,5**]**thiadiazole** (7). Compound benzo[*c*][**1,2,5**]thiadiazole (10 g, 73.6 mmol) was dissolved in 250 ml HBr (40%) solution at room temperature. Br₂ (11 ml, 220 mmol) was added slowly, and then the mixture was heated to 90 °C for 12 h. When the reaction finished, Na₂S₂O₃ was added to deal with the excess Br₂. CH₂Cl₂ was then added to the mixture and the organic phase was concentrated by rotary evaporation. The crude product was purified by petroleum–CH₂Cl₂ (4 : 1, v/v) to give compound 7 (10.28 g, 48%) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 9.82 (d, *J* = 1.9 Hz, 1H), 7.57 (d, *J* = 3.8 Hz, 1H), 6.97–6.88 (m, 1H), 2.61–2.51 (m, 4H), 1.74–1.51 (m, 4H), 1.34–1.28 (m, 12H), 0.93–0.85 (m, 9H). [M]⁺ calcd for C₆H₂N₂SBr₂, 291.8305; found, 291.8314.

4-Bromo-7-(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (8). Compound 7 (4 g, 13.8 mmol), thiophen-2-ylboronic acid (2.49 g, 20.6 mmol), K_2CO_3 (2.85 g, 20.6 mmol), and Pd(PPh_3)_4 (70 mg) were dissolved in THF-H₂O (5 : 1, v/v) under N₂. The mixture was refluxed for 12 h. When the reaction finished, water (30 ml) was added and the mixture was extracted by CH₂Cl₂. The crude product was purified by petroleum-CH₂Cl₂ (2 : 1, v/v) to give compound **8** (2.11 g, 52%) as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 9.99 (s, 1H), 8.18 (d, 1H), 7.92 (d, 1H), 7.86–7.84 (m, 2H). [M]⁺ calcd for C₁₀H₅N₂S₂Br, 295.9078; found, 295.9081.

5-(7-Bromobenzo[c][1,2,5]thiadiazol-4-yl)thiophene-2-carbaldehyde (9). Compound 8 (2 g, 6.78 mmol) and DMF (0.99 g, 1.36 mmol) were dissolved in CHCl₃ (40 ml) solution, and then POCl₃ (0.93 ml, 10.17 mmol) was added at room temperature. The mixture was then heated to 60 °C for 12 h. When the reaction finished, 1 M NaOH solution was added slowly to deal with excess POCl₃. Then, water was added to the mixture and the organic phase was concentrated by rotary evaporation. The crude product was purified by CH₂Cl₂ to give compound **9** (262 mg, 12%) as an orange solid. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (dt, J = 3.7, 1.7 Hz, 1H), 7.82–7.74 (m, 1H), 7.67–7.61 (m, 1H), 7.48–7.41 (m, 1H), 7.17 (ddd, J = 6.2, 5.1, 3.7 Hz, 1H). [M]⁺ calcd for C₁₁H₅BrN₂OS₂, 323.9027; found, 323.9027.

5'-(10-Butyl-7-(2,4-dibutoxyphenyl)-10H-phenothiazin-3-yl) [**2,2'-bithiophene]-5-carbaldehyde (10).** Compound **6** (150 mg, 0.55 mmol), compound **4** (400 mg, 0.67 mmol), K₂CO₃ (114 mg, 0.86 mmol), and Pd(PPh₃)₄ (10 mg) were dissolved in THF–H₂O (5 : 1, v/v) under N₂ and the mixture was refluxed for 12 h. When the reaction finished, water (20 ml) was added and the mixture was extracted by CH₂Cl₂. The crude product was purified by petroleum–CH₂Cl₂ (1 : 3, v/v) to give compound **10** (286 mg, 64%) as an orange solid. ¹H NMR (400 MHz, CDCl₃) δ 9.81 (s, 1H), 7.64–7.57 (d, 1H), 7.37–7.28 (m, 3H), 7.27–7.22 (m, 2H), 7.21–7.14 (m, 2H), 7.11 (d, *J* = 6.6 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 2H), 6.54–6.47 (s, 2H), 4.09–3.71 (m, 6H), 1.83–1.72 (m, 4H), 1.54–1.40 (m, 6H), 1.02–0.88 (m, 9H). [M]⁺ calcd for C₃₉H₄₁NO₃S₃, 667.2249; found, 667.2263.

10-Butyl-3-(2,4-dibutoxyphenyl)-7-(7-(thiophen-2-yl)benzo[c]-[1,2,5]thiadiazol-4-yl)-10H-phenothiazine (11). Compound 10 (150 mg, 0.46 mmol), compound 4 (331 mg, 0.67 mmol), K₂CO₃ (95 mg, 0.69 mmol), and $Pd(PPh_3)_4$ (10 mg) were dissolved in THF-H₂O (5 : 1, v/v) under N₂ and the mixture was refluxed for 12 h. When the reaction finished, water (20 ml) was added and the mixture was extracted by CH₂Cl₂. The crude product was purified by petroleum– CH_2Cl_2 (1 : 2) to give compound 11 (259) mg, 56%) as an orange-red solid. ¹H NMR (400 MHz, CDCl₃) δ 9.98 (d, *J* = 1.7 Hz, 1H), 8.22 (dd, *J* = 6.8, 4.0 Hz, 1H), 8.10–7.99 (m, 1H), 7.91–7.81 (m, 2H), 7.77 (dd, J = 9.0, 4.3 Hz, 1H), 7.71 (dt, J = 14.4, 4.4 Hz, 1H), 7.55 (s, 1H), 7.35 (d, J = 2.0 Hz, 1H),7.08–6.98 (m, 1H), 6.89 (dd, J = 11.4, 6.6 Hz, 2H), 6.68 (d, J = 7.4 Hz, 1H), 6.54-6.43 (m, 1H), 4.02-3.93 (m, 6H), 1.58-1.49 (m, 6H), 1.33-1.24 (m, 6H), 1.05-0.94 (m, 9H). [M]⁺ calcd for C₄₁H₄₁N₃O₃S₃, 719.2310; found, 719.2318.

(E)-3-(5'-(10-Butyl-7-(2,4-dibutoxyphenyl)-10H-phenothiazin-3-yl)-[2,2'-bithiophen]-5-yl)-2-cyanoacrylic acid (JH305). Compound 10 (200 mg, 0.3 mmol) and cyanoacetic acid (31 mg, 0.36 mmol) were dissolved in THF solution and refluxed for 12 h. Water was added to the mixture, and the mixture was extracted by CH₂Cl₂. The solvent was dried by evaporation and the crude product was purified by column purification with $CH_2Cl_2-CH_3OH$ (1:8, v/v) to give red solid JH305 (158 mg, 72%).¹H NMR (400 MHz, DMSO) δ 8.23-8.18 (m, 1H), 7.98-7.86 (m, 1H), 7.61-7.53 (m, 2H), 7.32 (d, J = 14.2 Hz, 2H), 7.20 (d, J =8.3 Hz, 2H), 7.06 (d, J = 12.2 Hz, 1H), 6.78 (d, J = 8.7 Hz, 2H), 6.66 (s, 2H), 4.11-3.83 (m, 6H), 1.81-1.68 (m, 4H), 1.46 (m, 7.4 Hz, 6H), 1.00–0.83 (m, 9H). $[M]^+$ calcd for $C_{42}H_{42}N_2O_4S_3$, 734.2307; found, 734.2319.

(*E*)-3-(5-(7-(10-Butyl-7-(2,4-dibutoxyphenyl)-10*H*-phenothiazin-3-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)thiophen-2-yl)-2-cyanoacrylic acid (JH307). Compound 11 (200 mg, 0.29 mmol) and cyanoacetic acid (30 mg, 0.35 mmol) were dissolved in THF solution and refluxed for 12 h. Water was added to the mixture, and the mixture was extracted by CH₂Cl₂. The solvent was dried by evaporation and the crude product was purified by column purification with silica gel CH₂Cl₂–CH₃OH (1 : 30) to give red solid **JH307** (175 mg, 77%).¹H NMR (400 MHz, DMSO) δ 8.14 (s, 1H), 7.71 (d, J = 5.8 Hz, 1H), 7.55–7.44 (m, 4H), 7.42 (s, 1H), 7.32–7.27 (m, 2H), 7.20 (d, J = 8.3 Hz, 1H), 7.04 (dd, J = 8.0, 5.5Hz, 2H), 6.63–6.52 (s, 1H), 3.98 (dd, J = 14.9, 6.5 Hz, 3H), 3.90 (d, J = 7.1 Hz, 2H), 1.75–1.65 (m, 4H), 1.43 (td, J = 14.5, 7.3 Hz, 6H), 0.93 (m, 9H). [M]⁺ calcd for C₄₄H₄₂N₄O₄S₃, 786.2368; found, 786.2359.

Preparation of the DSSCs

The DSSCs sensitized by JH305 and JH307 were fabricated by modifying those previously reported.25 A layer of 2 µm TiO2 (13 nm paste, Heptachroma, China) was coated onto the F-doped tin oxide conducting glass (TEC15, 15 Ω per square, Pilkington, USA) by screen printing, and then dried for 5 min at 120 °C. This procedure was repeated 5 times (10 µm) and a final coating of 4 µm of TiO₂ paste (DHS-SLP1, Heptachroma, China) as the scattering layer was applied. The double-layer TiO₂ electrodes (area: 6×6 mm) were sintered under an air flow at 500 °C for 60 min, and then cooled to room temperature. The sintered film was further treated with 40 mM TiCl₄ aqueous solution at 70 °C for 30 min, washed with water, and then sintered at 500 °C for 60 min. After the film was cooled to room temperature, it was immersed into a 2×10^{-4} M dye bath for 12 h. The electrode was then rinsed with ethanol and dried. Hermetically sealed cells were fabricated by assembling the dye-loaded film as the working electrode and Pt-coated conducting glass as the counter electrode separated by a Surlyn 1702 film (60 µm, Dupont).

Results and Discussion

The UV-visible absorption spectra of JH305 and JH307 are shown in Fig. 2, and the corresponding data are listed in Table 1. As displayed in Fig. 2(a), D- π -A-structured organic dye JH305 and D-A- π -A-structured organic dye JH307 show two main absorption bands. In the higher energy region, the absorption band for JH305 at 362 nm and JH307 at 410 nm is assigned to the $\pi \rightarrow \pi^*$ transition. The distinct absorption band at 457 nm for JH305 and 498 nm for JH307 relates to the $S_0 \rightarrow S_1$ transition. It can be noted that JH307 exhibits a red shift of 41 nm compared with that of JH305. This phenomenon is probably due to the introduction of benzothiadiazole, which exhibits a strong electron-withdrawing ability. Furthermore, it can be found that JH305 presents a higher molar extinction coefficient $(33\ 542\ M^{-1}\ cm^{-1})$ compared with **JH307** (16 256 M⁻¹ cm⁻¹), indicating that D- π -A-structured organic dye JH305 shows a stronger ability to capture photons than that of D-A- π -Astructured organic dye JH307.

Fig. 2(b) shows the normalized absorption spectra of both dyes on TiO_2 film. When anchored on TiO_2 film, a blue shift of 19 nm and 33 nm has been observed for dye **JH305** and dye **JH307**, respectively. This kind of blue shift results from H-type aggregation.²⁶ This is mainly caused by the formation of the



Fig. 2 Absorption spectra of JH305 and JH307 in CH_2Cl_2 solution (a) and on TiO₂ film (b).

carboxylate-titania nanocrystal structure, which decreases the intensity of the electron withdrawing ability of an electron acceptor. It can be noted that D–A– π –A-structured organic dye **JH307** shows a widened spectrum response when compared to D– π –A-structured organic dye **JH305**.

The electrochemical properties of **JH305** and **JH307** on TiO₂ film have been studied by cyclic voltammetry, and the corresponding data are given in Table 1. The highest occupied molecular orbitals (HOMO) of **JH305** and **JH307** are more positive than the I^-/I_3^- shuttle,²⁷ indicating that the oxidized dyes can regenerate effectively. Meanwhile, the lowest unoccupied molecular orbitals (LUMO) of both the structured dyes are more negative than the conduction band (E_{cb}) of TiO₂,²⁸ which ensures electron injection thermodynamically. Because of the introduction of benzothiadiazole, D–A– π –A-structured organic dye **JH307** exhibits positive LUMO levels in comparison with D– π –A-structured organic dye **JH305**. It can be noted that the introduction of benzothiadiazole has a negligible effect on the HOMO levels of the dye.

The optimized ground state geometries of **JH307** and **JH305** were obtained in the gas phase using density functional theory (DFT) calculation at B3LYP/6-31G level. The results are shown in Table 2. Excited energies of both the dyes were calculated by TD-DFT at the CAMB3LYP/6-31G levels of theory with CPCM mode

Table 1	Absorption and	electrochemical	data of JH305	and JH307
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Dye	$\lambda_{\max}^{a}(nm)$	ε at $\lambda_{\rm max} \left({\rm M}^{-1} \ {\rm cm}^{-1} \right)$	λ_{\max}^{b} on film (nm)	$E_{0-0}{}^{c}\left(V\right)$	E_{HOMO}^{d} (V) (vs. NHE)	E_{LUMO} (V) (vs. NHE)
JH305	457	33500	438	2.28	0.61	-1.67
JH307	498	16200	465	2.01	0.62	-1.39

^{*a*} Absorption spectra in solution were measured in CH_2Cl_2 solution $(2 \times 10^{-5} \text{ M})$. ^{*b*} Absorption spectra on TiO₂ film were measured with dye-loaded TiO₂ film immersed in CH_2Cl_2 solution $(2 \times 10^{-5} \text{ M})$. ^{*c*} E_{0-0} was determined from the intersection of the tangent of absorption on TiO₂ film and the *X* axis by 1240/ λ . ^{*d*} The oxidation potentials of the dyes were measured on TiO₂ film with TBAPF₆ (0.1 M) as an electrolyte, ferrocene/ferrocenium (F_c/F_c⁺) as an internal reference and converted to NHE by the addition of 440 mV.

Table 2 Optimized Structures of Electron Distribution in HOMO and LUMO Levels of JH305 and JH307



Table 3 Photovoltaic performance a of DSSCs based on JH305 and JH307

Dye ^b	$J_{\rm sc} ({ m mA \ cm}^{-2})$	$V_{\rm oc}$ (mV)	FF (%)	η (%)
JH305	16.36	706	64.5	7.5
JH307	14.71	645	67.3	6.4

 a Irradiation light: AM 1.5 simulated solar light (100 mW cm⁻²) at room temperature; working area: 0.1256 cm², electrolyte: 0.6 M DMPII, 0.06 M LiI, 0.4 M TBP, 0.02 M I₂ in dry acetonitrile. b Dye bath 2 \times 10⁻⁴ M in CH₂Cl₂.

in CH₂Cl₂ solution, and the corresponding data are listed in Table SI (see ESI[†]). As shown in Table 3, for **JH305** and **JH307**, effective electron separation can be observed on HOMO and LUMO levels, respectively. Meanwhile, the electron distribution is similar for both the dyes on HOMO levels. However, an obvious difference can be observed on LUMO levels. Compared to dye **JH305**, dye **JH307** has more electron distribution on the benzothiadiazole unit rather than the cyanoacrylic group due to the strong withdrawing ability of the benzothiadiazole unit, which does not facilitate electron injection.

The current density-voltage behaviour of DSSCs based on **JH305** and **JH307** was monitored under the standard AM 1.5G illumination and the curves are given in Fig. 3. The detailed data are tabulated in Table 3. It can be noted that the D- π -A-structured organic dye **JH305**-based device yields a photon-to-electron conversion efficiency (η) of 7.5%, corresponding to a $J_{\rm sc}$



Fig. 3 J-V curves of the devices sensitized by JH305 and JH307.

of 16.36 mA cm⁻², a V_{oc} of 706 mV and an FF of 64.5%. In contrast, the D–A– π -A-structured organic dye **JH307**-based device produces a lower η of 6.4% with a lower J_{sc} of 14.71 mA cm⁻², a lower V_{oc} of 645 mV but a slightly higher FF of 67.3%. The reason for **JH307** exhibiting a lower J_{sc} in comparison with **JH305** is partially due to the poor light harvesting efficiency. Meanwhile, DFT calculation indicates that **JH307** has more electron distribution on the benzothiadiazole unit rather than the cyanoacrylic acid group in LUMO levels, which hinders effective electron injection. This can be considered as another support for the lower J_{sc} of **JH307**.

The incident photon-to-electron conversion efficiency (IPCE) spectra of the IH305 and IH307-based devices are displayed in Fig. 4. The result indicates that the JH305-based device exhibits a higher IPCE spectrum response than the JH307-based device in the range of 400-600 nm. This trend can be explained by the higher molar extinction coefficient and greater electron injection dynamics for dye JH305 than that of JH307 in this spectral region. However, dye JH307-based device gives a higher IPCE response at 640 nm and it can even reach up to 900 nm, which is probably due to the broadened absorption spectrum of dye JH307 in distant wavelength regions. These results indicate that although D-A- π -A-structured organic dye JH307 shows a widened absorption and IPCE response, unfortunately, these advantages do not facilitate an improvement in the J_{sc} and V_{oc} when compared to $D-\pi$ -A-structured organic dye **IH305**.

Electrochemical impedance spectroscopy (EIS) analysis²⁹ was performed to investigate the interface charge transfer process of the DSSCs based on JH305 and JH307. EIS spectra of solar cells sensitized by both the dyes were measured with an impedance/ gain-phase analyzer (PARSTAT 2273, USA) under dark conditions with a bias of -0.7 V. The alternating current (AC) amplitude was set at 10 mV. As shown in Fig. 5, Nyquist plots in the high-frequency $(10^5 \text{ to } 10^6 \text{ Hz})$ region indicate an electron



Fig. 4 IPCE spectra of the DSSCs based on JH305 and JH307.



Fig. 5 Nyquist plots of DSSCs based on JH305 and JH307.

transfer resistance on the counter electrode/electrolyte (R_{ce}) interface, corresponding to the first small semicircle. For the similar Pt counter electrode and electrolyte, a similar R_{ce} for both JH305 and JH307-based devices can be obtained. The larger semicircle in the mid-frequency region $(10^4 \text{ to } 10^5 \text{ Hz})$ reflects the recombination resistance (R_{ct}) on the TiO₂/dye/ electrolyte surface. It can be observed that the JH305-based device exhibits a larger $R_{\rm ct}$ (91.8 Ω cm⁻²) compared with the **JH307**-based device with a $R_{\rm ct}$ of 19.6 Ω cm⁻², indicating that the JH305-based device can suppress recombination on the TiO₂/dye/electrolyte interface more effectively than the JH307based device. This phenomenon can be explained by the introduction of the benzothiadiazole unit, which aggravates recombination with electrons in TiO₂ due to strong electronwithdrawing ability. Regarding J-V parameters, the JH305-based device produces a higher Voc than that of the JH307-based device.

Conclusions

D- π -A-structured organic dye JH305 and D-A- π -A-structured organic dye JH307 were synthesized and investigated systematically. The results indicate that the phenothiazine-based D-A- π -A-structured organic dye shows a wider spectrum response but a lower molar extinction coefficient in comparison with the D- π -A-structured organic dye with a similar structure. When applied in DSSCs, the D- π -A-structured organic dye yields a higher J_{sc} , V_{oc} , and η than the D–A– π –A-structured organic dye. IPCE study indicates that the D- π -A-structured organic dye exhibits a higher IPCE response in certain regions, which provides a support for the higher J_{sc} . The recombination behaviour on a TiO2/dye/electrolyte interface explains the higher $V_{\rm oc}$ of D- π -A-structured dyes than that of D-A- π -Astructured organic dyes. In summary, this work reveals that not all D–A– π –A-structured organic dyes exhibit a better photovoltaic performance than that of D- π -A-structured dyes. We can conclude that phenothiazine is more suitable for D- π -A dyes, while indoline and triphenylamine, which have been reported with similar structures, are more suitable for D-A- π -A dyes, which will pave the way for further molecular design of highly efficient organic dyes.

Acknowledgements

We gratefully acknowledge the financial support for this work from China Natural Science Foundation (Grant 21276044, 21120102036, 91233201), the National Basic Research Program of China (Grant no. 2014CB239402).

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