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Molecular engineering and synthesis of symmetric metal-free organic sensitizers with A- π -D- π -A architecture for DSSC applications: the effect of bridge unit

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Abstract

Herein, we report the design and synthesis of six symmetric metal-free organic sensitizers (**llyu1a**, **llyu1b**, **llyu1c**, **llyu2a**, **llyu2b**, and **llyu2c**) based on fluorene or dimethyl fluorene donors core carrying double acceptors. All these dyes were characterized using UV–Vis, ESI-MS, and ¹HNMR. To study the influence of π -bridges on total solar-to-electric conversion efficiency ($\%\eta$) for DSSCs, three different π -bridges thiophene, furane, or benzene were introduced into the sensitizers. Their device performances were studied and showed a distinctive difference in efficiency with a maximum of PCE of 2.35% (*Jsc* = 5.63 mA cm – 2, *V_{OC}* = 0.60 V and *FF* = 70.00%) for dye **llyu1a**. Density functional theory (DFT) and time-dependent density functional theory calculations were used to probe the relationship between chemical structure, photophysical, and photoelectrochemical properties. DFT studies showed that the dihedral angle between thiophene and donor is 26.6°, indicating that the dyes bearing thiophene π -bridge possess more efficient photoexcitation compared to dyes bearing benzene π -bridge (36.6° for both **llyu2c** and **llyu1c**) and less aggregation than dyes bearing furane π -bridge (0° for **llyu1b** and **llyu2b**). This new finding of influence of π -bridges on total solar-to-electric conversion efficiency would open the door for the molecular engineering of better light harvesting and more efficient metal-free organic sensitizers for DSSCs.

Keywords DSSCs \cdot Symmetric organic dyes \cdot Fluorene \cdot Double π -acceptors

Introduction

Dye-sensitized solar cells (DSSCs), a promising approach of solar energy utilization, have gained widespread interest owing to their environmental-friendliness, high efficiency and low production cost, as reported by Grätzel and O'Regan in 1991 [1]. All components of DSSCs including electrode, semiconductor, electrolyte, and sensitizers reveal significant impacts on the photovoltaic performance [2–8]. Ruthenium complexes as sensitizers showed good stability for DSSCs and relatively high power conversion efficiency compared to conventional silicon-based solar cells [9]. However, in

Luping Lyu mailofllp@126.com view of the low extinction coefficient of ruthenium photosensitizers, high manufacturing costs, numerous purification steps and rarity of the ruthenium metal, metal-free organic dyes have attracted strong interest due to their advantages over metal-based sensitizers, such as higher molar extinction coefficient, the presence of no expensive rare metal, suitability for back-irradiated solar cells, and modulation of band gap [10, 11]. Most successful design of metal-free organic dyes adopts D- π -A architectures due to their strong spectral response, some of which even displayed higher conversion efficiency compared to benchmark dye N719 [12, 13]. Through molecular modification approaches, recent studies have further improved conversion efficiency of DSSCs based on metal-free organic dyes [14, 15]. For example, in 2015, Hung and Brogdon proposed the concept of an A- π -D- π -A motif for designing a novel double donor/acceptor and extending π -bridge. In these studies, strong anchoring groups such as multiple carboxylic acids and multiple cyanoacetic acids have been employed to achieve long-term stability and higher conversion efficiency of DSSCs [16, 17]. Co-sensitization is another effective design strategy, which

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includes an extension of the π -electron delocalization and improvement in absorption spectrum [18, 19]. On the other hand, competitive adsorption of co-sensitizers on the surface of TiO₂ may decrease the photovoltaic performance [20]. Recently, organic dyes containing double-pinched D-π-A segments have been reported to suppress dark current and hence enhance the photovoltaic performance [21, 22]. In contrast, dyes with two symmetric D- π -A chains not only exhibit broader absorption spectrum range but also provide more electron extraction paths [23-25]. Furthermore, the incorporation of multiple anchoring groups enables organic dyes to bind significantly stronger than single anchoring group to avoid dye displacement during repeated exposure [16]. The anchoring groups widely employed are cyanoacetic acid and rhodanine-3-acetic acid due to their strong electron-withdrawing nature and strong binding force on the surface of mesoporous TiO₂ through carboxylic acid anchoring groups [26]. Some dyes with double thiophene π -bridge and cyanoacetic acid acceptor have exhibited better suppression of dark current and higher conversion efficiency of 8.32% exceeding the N719-based cell [17]. Recently, phenothiazine donor, diphenylamine donor, indole donor, etc., have been largely incorporated into $D-(\pi-A)_2$ dyes and showed satisfactory photovoltaic performance [24, 27, 28]. However, $D(\pi-A)_2$ dyes with fluorene donor were rarely reported although dyes based on fluorene donor exhibit high conversion efficiency [29]. With above consideration in mind, we have designed and synthesized six metal-free organic dyes with fluorene donor, double thiophene, furane, or benzene π -bridge (Scheme 1). Double cyanoacetic acid acceptors were utilized to anchor the dyes with TiO₂ and helped the photoinduced electrons inject into the photoanode. New fluorine-based dyes have been synthesized by following synthetic strategies such as Suzuki cross-coupling and Knoevenagel condensation reactions. They were characterized by NMR and mass spectra. Their physical properties



Scheme 1 Synthesis of dyes with A-π-D-π-A architecture

and photovoltaic performance were investigated using UV–Vis absorption and fluorescent emission spectroscopy. Furthermore, electronic distribution in its FMO energy levels was evaluated by cyclic voltammetry (CV) method and theoretical calculations were performed using Gaussian 09 package [30, 31].

Experimental

Materials and methods

The solvents and chemicals used in the current study were procured from commercial vendors and used as received. All solvents and reagents in reaction were purified and dried by standard methods prior to use. Nuclear magnetic resonance (¹H and ¹³C) spectra were measured in DMSO d_6 on a Bruker AM 500 spectrometer. The chemical shift (δ) was expressed in ppm with tetramethylsilane (TMS) as an internal standard, and coupling constant (*J*) is expressed in Hz. Further, fluorescence spectra were obtained using an F-7000 fluorescence spectrophotometer in a solution of 5×10^{-5} mol L⁻¹. UV–Vis absorption spectra were measured by using SHIMADZU UV-2550 spectrophotometer.

Fabrication of DSSCs

The fluorine-doped tin oxide (FTO) glass was rinsed with a detergent solution in an ultrasonic bath for 15 min and then followed by acetone for 15 min. For the preparation of photoelectrodes, titanium nano-oxide colloids (particle size ~ 13 nm) were deposited by screen-printing to obtain a double-layer TiO₂ photoelectrodes in thickness with a 12-µm-thick TiO₂ film. The TiO₂ electrodes were firstly sintered at 325 °C for 5 min, and then followed by 375 °C for 5 min, 450° C for 15 min, and 500° C for 15 min. TiO₂ electrodes were immersed into the dye solutions of a mixture of MeOH and CHCl₃ (V_{MeOH} : V_{CHCI3} =1:10) and then kept at 25 °C for 24 h to adsorb complete dye onto the TiO₂ surface.

The counter electrodes were prepared by screen-printing a 50-nm Pt-paste on the washed FTO glasses. Sandwich cells were fabricated using TiO₂-coated working electrodes and platinum-coated counter electrodes and were sealed through heating of the polymer frame. The redox electrolyte consisted of the CH₃CN solution of 0.3 M 1, 2-dimethyl-3-propylimidazolium iodide (DMPII), 0.03 M I₂, 0.07 M LiI, 0.1 M guanidine thiocyanate, and 0.4 M 4-*tert*-butylpyridine (TBP). The active area of DSSCs was 0.36 cm².

Photovoltaic characterization

The photovoltaic measurements of the DSSCs were taken using a Keithley digital source meter (Keithley 2420, USA) at an AM 1.5 G illumination (100 mW/cm⁻²; Sol3A, Newport, USA). Monochromatic incident photon-to-current conversion efficiency (IPCE) measurements of solar cell were made on a Hypermonolight (SM-25, Jasco, Japan). Electrochemical impedance spectroscopy (EIS) images were recorded using a computer-controlled potentiostat (ZeniumZahner, Germany) over a frequency range from 100 kHz to 1 MHz at 298 K. The AC amplitude was set to 10 mV, while the bias of all EIS measurements was set at the V_{OC} of the corresponding dyes. The DFT calculations were conducted with the Gaussian 09 package [30, 31].

Synthesis

Synthesis of 3, 6-dibromo-9H-fluorene (1)

A mixture of 3,6-dibromo-9H-fluoren-9-one (5.10 g, 15.00 mmol), diazene monohydrate (5.25 mL, 105 mmol), and diethylene glycol (200 ml) was heated at 80 °C for 1 h, and then heated at 100 °C for 4 h. A solution of KOH (5.89 g, 105 mmol) in water (15 mL) was added dropwise to the mixture at 120 °C; after 4 h, the mixture was poured into 500 ml water under vigorous stirring and the formed yellow solid was filtered and dried to obtain yellow powder, yield 87%, ¹HNMR (500 MHz CDCl₃) δ : 7.85 (*s*, 2H), 7.43–7.37 (*m*, 4H), 3.79 (*s*, 2H).

Synthesis of 3, 6-dibromo-9, 9-dimethyl-9H-fluorene (2)

A mixture of **1** (8.90 g, 27.5 mmol), sodium hydride (5.258 g, 22 mmol), and dried THF (100 ml) was cooled to 0 °C, and then CH₃I (13.73 g, 220 mmol) was added dropwise to the mixture and kept stirring overnight. Water was added into the mixture to quench reaction. The mixture was extracted with ethyl acetate for several times. The organic layers were dried over anhydrous Mg₂SO₄ and evaporated to remove the solvent. The crude product was purified by column chromatography using silica gel and petroleum ether: ethyl acetate (5:1) as mobile phase to yield pale yellow powder 7.99 g (22.9 mmol, 83%). ¹HNMR (500 MHz CDCl₃) δ :7.80 (*d*, *J*=1.8 Hz, 1H), 7.45 (*dd*, *J*=8.0, 1.8 Hz, 1H), 7.29 (*d*, *J*=8.0 Hz, 1H), 1.45 (*s*, 3H).

Synthesis of 5, 5'-(9H-fluorene-3, 6-diyl) bis(thiophene-2-carbaldehyde) (**3a**)

To a solution of 1 (780.00 mg, 2.50 mmol), tetrakis(triphenylphosphine)palladium (115.53 mg 0.1 mmol), and 5-formylthiophen-2-boronic acid (1590.00, 10 mmol) in tetrahydrofuran (20 mL), an aqueous 2 M potassium carbonate solution (5 mL) was added at room temperature under nitrogen. After the mixture was refluxed at 75 °C for 20 h, the reaction mixture was concentrated

to give crude product under reduced pressure. The crude product was purified by silica gel chromatography eluting (petroleum ether: ethyl acetate = 20:1), yield 15.4%, melting point 202–205 °C. ¹HNMR (500 MHz, DMSO) δ : 10.11 (*s*, 1H), 8.52 (*s*, 1H), 8.34 (*s*, 1H), 7.95 (*d*, *J*=3.9 Hz, 1H), 7.87 (*d*, *J*=3.9 Hz, 1H), 7.75 (*d*, *J*=1.5 Hz, 1H), 4.07 (*s*, 1H).

Synthesis of 5, 5[′]-(9H-fluorene-3, 6-diyl) bis(furan-2-carbaldehyde) (**3b**)

Compound **3b** (320.0 mg, 27.6%) was synthesized in a similar way to compound **3a** by using compound **1**, melting point 212–214 °C. ¹HNMR (500 MHz, CDCl₃) δ : 9.66 (*s*, 1H), 8.43 (*d*, *J*=1.5 Hz, 1H), 7.80 (*dd*, *J*=7.9, 1.6 Hz, 1H), 7.44 (*d*, *J*=7.9 Hz, 1H), 7.34 (*d*, *J*=3.7 Hz, 1H), 6.93 (*d*, *J*=3.7 Hz, 1H), 4.10 (*s*, 1H).

Synthesis of 5, 5⁷-(9H-fluorene-3,6-diyl) bis(benzene-2-carbaldehyde) (**3c**)

Compound **3c** (250.0 mg, 26.7%) was synthesized in a similar way to compound **3a** by using compound **1**, melting point 234–236 °C. ¹HNMR (500 MHz, CDCl₃) δ 10.11 (*s*, 1H), 8.13 (*d*, *J*=1.4 Hz, 1H), 8.02 (*d*, *J*=8.3 Hz, 2H), 7.89 (*d*, *J*=8.2 Hz, 2H), 7.71 (*d*, *J*=7.8 Hz, 1H), 7.65 (*dd*, *J*=7.8, 1.7 Hz, 1H), 4.05 (*s*, 1H).

Synthesis of (2Z, 2[']Z)-3,3[']-((9H-fluorene-3,6-diyl) bis(thiophene-5,2-diyl))bis(2-cyanoacrylic acid) (**llyu1a**)

A solution of **3a** (150 mg, 0.39 mmol), cyanoacetic acid (270 mg, 2.52 mmol), and piperidine (90.0 g, 1.1 mmol) in 1,2-dichloroethane (10 mL) was refluxed under nitrogen atmosphere for 9 h. The resulted red precipitate was filtered and recrystallized with ethanol to give red powder **llyu1a** (170.0 mg, 83.8%), melting points 343–346 °C. ¹HNMR (500 MHz, DMSO) δ :8.50 (*s*, 1H), 8.31 (*s*, 1H), 7.92 (*d*, *J*=3.9 Hz, 1H), 7.83 (*d*, *J*=3.9 Hz, 1H), 7.73 (*d*, *J*=1.5 Hz, 1H), 7.71 (*s*, 1H), 4.05 (*s*, 1H); HRMS (ESI) m/z 519.0405(M-H)⁻, calcd for C₂₉H₁₅N₂O₄S₂ 519.0479.

Synthesis of (2Z, 2[']Z)-3,3[']-((9H-fluorene-3,6-diyl) bis(furan-5,2-diyl))bis(2-cyanoacrylic acid) (**llyu1b**)

Compound **llyu1b** (250.0 mg, 82.8%) was synthesized in a similar way to compound **llyu1a** by using compound **3b**, melting points > 350 °C. ¹HNMR (500 MHz, DMSO) δ :8.42 (*d*, *J* = 1.1 Hz, 1H), 7.95 (*s*, 1H), 7.92 (*dd*, *J* = 7.9, 1.4 Hz, 1H), 7.75 (*d*, *J* = 7.9 Hz, 1H), 7.45 (*d*, *J* = 3.7 Hz, 1H), 7.30 (*d*, *J* = 3.6 Hz, 1H), 4.51 (*s*, 3H); HRMS (ESI) m/z (M-H)⁻ 487.0970, calcd for C₂₉H₁₅N₂O₆ 487.0936.

Synthesis of (2Z, 2[']Z)-3,3[']-((9H-fluorene-3,6-diyl) bis(4,1-phenylene))bis(2-cyanoacrylic acid) (**llyu1c**)

Compound **llyu1c** (180.0 mg, 77.6%) was synthesized in a similar way to compound **llyu1a** by using compound **3c**, melting points > 350 °C. ¹HNMR (500 MHz, DMSO) δ :8.42 (*d*, *J*=1.1 Hz, 1H), 7.95 (*s*, 1H), 7.92 (*dd*, *J*=7.9, 1.4 Hz, 1H), 7.75 (*d*, *J*=7.9 Hz, 1H), 7.45 (*d*, *J*=3.7 Hz, 1H), 7.30 (*d*, *J*=3.6 Hz, 1H), 4.51 (*s*, 3H), HRMS (ESI) m/z (M-H)⁻ 487.0970, calcd for C₂₉H₁₅N₂O₆ 487.0936.

Synthesis of 5, 5'-(9,9-dimethyl-9H-fluorene-3,6-diyl) bis(thiophene-2-carbaldehyde) (**4a**)

To a solution of **2** (650.0 mg, 2.0 mmol), tetrakis(triphenylphosphine)palladium (230.0 mg 0.20 mmol), and 5-formylthiophen-2-boronic acid (1.26 g, 8 mmol) in tetrahydrofuran (20 mL), an aqueous 2 M potassium carbonate solution (16 mL) was added at room temperature under nitrogen. After the mixture was refluxed at 75 °C for 20 h, the reaction mixture was concentrated to give crude product under reduced pressure. The crude product was purified by silica gel chromatography eluting (petroleum ether: ethyl acetate = 20:1) to give red powder **4a**(200.0 mg 15.4%), melting point 286–288 °C. ¹HNMR (500 MHz, DMSO) δ : 9.88 (*s*, 1H), 8.41 (*d*, *J*=1.5 Hz, 1H), 7.95 (*dd*, *J*=7.9, 1.6 Hz, 1H), 7.67 (*d*, *J*=7.9 Hz, 1H), 7.50 (*d*, *J*=3.7 Hz, 1H), 7.02 (*d*, *J*=3.7 Hz, 1H), 1.60 (*s*, 3H).

Synthesis of 5, 5[']-(9, 9-dimethyl-9H-fluorene-3, 6-diyl) bis(furane-2-carbaldehyde) (**4b**)

Compound **4b** (350.0 mg, 32.0%) was synthesized in a similar way to compound **3a** by using compound **2**, melting point, 263-265 °C. ¹H NMR (500 MHz, CDCl₃) δ :9.72 (*s*, 1H), 8.31 (*d*, *J*=1.5 Hz, 1H), 7.85 (*dd*, *J*=7.9, 1.6 Hz, 1H), 7.54 (*d*, *J*=7.9 Hz, 1H), 7.40 (*d*, *J*=3.7 Hz, 1H), 6.98 (*d*, *J*=3.7 Hz, 1H), 1.56 (*s*, 3H).

Synthesis of 4, 4'-(9,9-dimethyl-9H-fluorene-3,6-diyl) dibenzaldehyde (**4c**)

Compound **4c** (360.0 mg, 31.3%) was synthesized in a similar way to compound **3a** by using compound **2**, melting point 227–230 °C. ¹H NMR (500 MHz, CDCl₃) δ : 10.10 (*s*, 1H), 8.07 (*d*, *J*=1.3 Hz, 1H), 8.01 (*d*, *J*=8.4 Hz, 2H), 7.87 (*d*, *J*=8.2 Hz, 2H), 7.65 (*dd*, *J*=7.8, 1.7 Hz, 1H), 7.59 (*d*, *J*=7.8 Hz, 1H), 1.60 (*s*, 3H).

Synthesis of (2Z,2[']Z)-3,3[']-((9,9-dimethyl-9H-fluorene-3,6-d iyl)bis(thiophene-5,2-diyl))bis(2-cyanoacrylic acid) (**Ilyu2a**)

A solution of **4a** (120 mg, 0.29 mmol), cyanoacetic acid (100 mg, 1.16 mmol), and piperidine (30.0 g, 0.29 mmol) in 1,2-dichloroethane (10 mL) was refluxed under nitrogen atmosphere for 10 h. The obtained red precipitate was filtered and recrystallized with THF to give red powder **llyu2a** (130.0 mg, 83.8%), melting points > 350 °C. ¹HNMR (500 MHz, DMSO) δ : 9.19 (*s*, 1H), 8.41 (*d*, *J*=1.5 Hz, 1H), 8.14 (*s*, 1H), 7.80 (*d*, *J*=4.0 Hz, 1H), 7.76 (*d*, *J*=3.9 Hz, 1H), 7.72 (*dd*, *J*=7.9, 1.7 Hz, 1H), 7.68 (*d*, *J*=7.9 Hz, 1H), 1.50 (*s*, 3H); HRMS (ESI) m/z (M-H)⁻ 547.0803, calcd for C₃₁H₁₉N₂O₄S₂ 547.0792.

Synthesis of (2Z,2[']Z)-3,3[']-((9,9-dimethyl-9H-fluorene-3,6-d iyl)bis(furane-5,2-diyl))bis(2-cyanoacrylic acid) (**Ilyu2b**)

Compound **llyu2b** (60.0 mg, 89.4%) was synthesized in a similar way to compound **llyu2a** by using compound **4b**, melting points > 350 °C. ¹HNMR (500 MHz, DMSO) δ 9.05 (*s*, 1H), 8.42 (*d*, *J* = 1.1 Hz, 1H), 7.95 (*s*, 1H), 7.92 (*d*d, *J* = 7.9, 1.4 Hz, 1H), 7.75 (*d*, *J* = 7.9 Hz, 1H), 7.45 (*d*, *J* = 3.7 Hz, 1H), 7.30 (*d*, *J* = 3.6 Hz, 1H), 1.51 (*s*, 3H), HRMS (ESI) m/z (M-H)⁻ 515.1267, calcd for C₃₁H₁₉N₂O₆ 515.1249.

Synthesis of (2Z,2⁷Z)-3,3⁷-((9,9-dimethyl-9H-fluorene-3,6-d iyl)bis(4,1-phenylene))bis(2-cyanoacrylic acid) (**llyu2c**)

Compound **llyu2c** (200.0 mg, 84.8%) was synthesized in a similar way to compound **llyu2a** by using compound **4c**, melting points 343–346 °C. ¹H NMR (500 MHz, DMSO) δ : 8.98 (*s*, 1H), 8.47 (*s*, 1H), 8.13 (*s*, 1H), 8.09 (*d*, *J*=8.4 Hz, 2H), 7.98 (*d*, *J*=8.4 Hz, 2H), 7.77 (*dd*, *J*=7.9, 1.4 Hz, 1H), 7.70 (*d*, *J*=7.9 Hz, 1H), 1.53 (*s*, 3H). HRMS (ESI) m/z (M-H)⁻ 535.1692, calcd for C₃₅H₂₃N₂O₄ 535.1663.

Results and discussion

Synthesis

The synthetic routes of two series of metal-free organic dyes **llyu1a-1c** and **llyu2a-2c** are depicted in Scheme 1. 3,6-Dibromo-9H-fluoren-9-one was reduced at C atom of carbonyl group with diazene monohydrate to obtain 3,6-dibromo-9H-fluorene(1), and then compound 1 was methylated with CH₃I to form 3,6-dibromo-9,9-dimethyl-9H-fluorene(2). After that various π -bridges were introduced into donor via Suzuki coupling reaction to give key double π -bridges precursor aldehyde **3a–3c** and **4a–4c**, respectively. At the last step, the target compounds **llyu1a-1c** and

llyu2a-2c were obtained through Knoevenagel condensation between dialdehyde compounds and cyanoacetic acid in good yield.

Optical characterization

The UV–Vis spectra of synthesized dyes in CHCl₃–CH₃OH solution $(3 \times 10^{-4} \text{ M})$ and on TiO₂ film, emission spectra are depicted in Fig. 1a–c, respectively. The corresponding results are summarized in Table 1. From the absorption spectra in solution, both of the series of dyes possess one absorption band between 360 and 420 nm, which is ascribed to π - π^* electron transition of conjugated molecules. Interestingly, dyes **llyu1b** showed an obvious redshifted absorption compared with other dyes, which may be attributed to better coplanar of furan group. Furthermore, the molar extinction coefficient of dyes **llyu2a** was found to be 3.61 M⁻¹ cm⁻¹, higher than those of other dyes as shown in Table 1.

The UV–Vis absorption spectra of dyes loaded on TiO_2 film are displayed in Fig. 1b. The absorption of dyes on TiO_2 film exhibited redshifted and broader absorption spectra compared to those of dyes in solutions, which indicates electronic coupling of dyes and molecular aggregation on the surface of TiO_2 [32, 33]. On the other hand, more **llyu1b** and **llyu2b** were found to be adsorbed on TiO_2 surface compared to other dyes, which indicates relatively better photovoltaic performance for these two dyes.

Computational analysis

Model structures of the dyes have been optimized using density functional theory (DFT) at the B3LYP hybrid density functional method in the Gaussian 09 program. Calculations were implemented at polarized 6-31G (d) basis set for geometry optimization in the case of isolated dye molecules in dimethylformamide. The optimized structures of these dyes are shown in Fig. 2. As shown in the front view, all dyes display a butterfly-shaped structure. The dihedral angles between thiophene or furan π -bridge and donors (0° for llyu1b and llyu2b; 26.6° for llyu1a and llyu2a) are smaller than dihedral angles between benzene π -bridge and donor (36.6° for **llyu2c** and **llyu1c**), indicating that the dyes based on thiophene or furan π -bridge are relatively more coplanar and have higher efficient photoexcitation compared to dyes based on benzene π -bridge, which increases the electron injection efficiency from dyes based on benzene π -bridge into the TiO₂ and final photovoltaic performance, in good agreement with the higher efficiency of the dyes based on thiophene or furan π -bridge. Figure 3 and Table 2 display that the energy gaps of these dyes range from 2.69 to 3.15 eV, while dyes based on benzene π -bridge owned the largest energy gaps with 3.08 eV and 3.15 eV, which results in their bathochromic shift of λ_{max} . In the meantime, the



Fig.1 UV–Vis absorption spectra of dyes with A- π -D- π -A architecture: **a** dyes in CHCl₃–CH₃OH solution (V_{CHCl3}:V_{CH3OH}=10:1); **b** dyes on TiO₂ film; **c** emission spectra of dyes in CHCl₃–CH₃OH solutions

incorporation of dimethyl accounts for widening their energy gap and leads to a hypochromatic shift of λ_{max} , respectively. As shown in Fig. 4, the HOMO of these dyes is nearly delocalized on the whole molecule, while LUMO is composed

of two acceptor moieties. Under the light illumination, electrons are excited and will transfer from HOMO to LUMO and finally inject into CB edge of TiO_2 effectively.

Photovoltaic performance

The photovoltaic performances of DSSCs fabricated using the aforementioned dyes under standard AM 1.5G, 100 mW cm⁻² light intensity were measured in the presence of an iodine electrolyte. Figure 5a, b reveals the action spectra of the incident photon-to-current conversion efficiency (IPCE) for DSSCs and their characteristic J-Vcurves, respectively. Their detailed photovoltaic parameters along with a similar reported sensitizer are summarized in Table 3. Similar to the absorption spectra on TiO_2 , among these dyes, thiophene-based and furane-based dyes show obviously superior IPCE spectra to benzene-based dyes and exhibit broader IPCE-responsive region. Llyu1c reaches the maximum IPCE value 53% at 390 nm; however, it does not keep a broad absorption plateau at the visible region, which is attributed to its severe dye aggregation on the TiO_2 film because of its almost coplanar molecular structure. In contract, owing to its anti-aggregation effect of non-coplanar molecular structure and better conjugation system of the whole molecule, llvu1a reaches its maximum IPCE value 43.8% at 400 nm and keeps a plateau from 360 nm to 440 nm with more than 40% IPCE values, leading to better light capture and conversion efficiency. On the other hand, **llyu1b** shows lower J_{SC} which may be related to its high noncoplanar molecular structure. Generally, better IPCE action spectra correspond to higher J_{SC} . J_{SC} for six dyes ranks by the order of llyu1a > llyu1b > llyu2b > llyu2a > llyu1c > ll yu2c. On the other hand, among thiophene-based dyes, the increased J_{SC} may thank for the higher amount of **llyu1a** adsorbed on the TiO₂ surface compared to llyu2a as shown in Table 1. Therefore, it was found that thiophene-based dye llyu1a exhibits photovoltaic performance of 2.35% with its superior J_{SC} of 5.63 mA cm⁻² and V_{OC} of 0.60 V.

Electrochemical properties

Electrochemical impedance spectroscopy (EIS) is used to evaluate charge recombination, electron lifetime, and chemical capacitance of DSSCs based on the aforementioned dyes. Figure 6 shows the corresponding Nyquist and Bode spectra. Generally, smaller radius of the intermediate-frequency semicircle in the Nyquist plot leads to the lower electron transport resistance. On the other hand, the higher the charge recombination resistance in the Nyquist plot, the better the V_{OC} for DSSCs [35, 36]. In the Nyquist spectrum shown in Fig. 6, there is the order of **llyu2b > llyu1c > llyu2a > llyu2c > llyu1b > llyu1a**, which is in good agreement with the V_{OC} of DSSCs. Moreover,

Table 1 Optical properties of dyes with A-π-D-π-A architecture

Compd.	$\lambda_{\rm max}^{\rm a}/({\rm nm})$	$\epsilon/(\mathrm{mol}^{-1} \mathrm{cm}^{-1})$	$\lambda_{\rm max}^{\rm b}/({\rm nm})$	$\lambda_{\rm max}^{\rm c}/({\rm nm})$	LA ^d /(mmol cm ⁻²)
llyu1a	385	21,400	390	536	3.7*10 ⁻⁷
llyu1b	417	13,900	399	543	5.3×10^{-7}
llyu1c	343	22,167	390	494	$2.8*10^{-7}$
llyu2a	355	36,100	394	531	$2.2*10^{-7}$
llyu2b	376	25,667	397	558	5.3×10^{-7}
llyu2c	330	21,567	368	547	$4.5*10^{-7}$

^aMaximum absorption wavelength λ_{max} and molar extinction coefficient at λ_{max} of dyes measured in CHCl₃–CH₃OH solution

^bMaximum absorption wavelength λ_{max} of dyes on sensitized TiO₂ electrodes

^cMaximum emission wavelength measured in CHCl₃-CH₃OH solution

^dAmount of sensitizers loaded on the TiO₂ film



Fig. 2 Optimized geometries (side view) of llyu1a-llyu2c at the B3LYP/6-31G(d) level



Fig.3 Energy level of the frontier molecular orbitals of dyes at B3LYP/6-31G(d)

Table 2 Energy level data of dyes at the B3LYP/6-31G(d)

	НОМО	E ₀₋₀	LUMO
llyu1a	-5.40	3.02	-2.38
llyu1b	-5.50	2.69	-2.81
llyu1c	-5.45	3.08	-2.37
llyu2a	-5.40	3.05	-2.35
llyu2b	-5.41	3.01	-2.40
llyu2c	- 5.44	3.15	-2.29

as shown in Fig. 6, the Bode plots can be used to evaluate eTiO₂ (injected electrons in the conduction band of TiO₂) by using the relation ($\tau_{\rm eff} = 1/2\pi f$), where $\tau_{\rm eff}$ is the life-time of electrons in TiO₂ and *f* is the midpoint frequency from Bode plot. Normally, the longer electron lifetime for a sensitizer will lead to improved V_{OC} . As shown in the



Fig. 4 Frontier molecular orbital (HOMO and LUMO) of llyu1a - llyu2c



Fig. 5 Incident photon-to-current conversion efficiency (IPCE) curve (a) and current density-potential (I–V) curve (b) of dyes

Bode spectra, the lifetime in CB edge of TiO_2 of DSSCs was found to be the order of llyu2b > llyu1c > llyu2a > lly u2c > llyu1b > llyu1a. In the present study, it is observed that llyu2b has the highest $eTiO_2$ and llyu1a has the lowest $eTiO_2$, meaning that they have the highest and lowest V_{OC} ,

Table 3 Parameters for DSSCs based on dyes with A- π -D- π -A architecture

Compd.	$J_{\rm sc}({\rm mA~cm^{-2}})$	$V_{OC}(\mathbf{V})$	FF	η (%)
llyu1a	5.63	0.60	0.70	2.35
llyu1b	4.47	0.60	0.73	1.95
llyu1c	1.61	0.63	0.77	0.78
llyu2a	3.79	0.63	0.70	1.68
llyu2b	3.93	0.65	0.77	1.96
llyu2c	0.88	0.63	0.79	0.43
SQ33 [34]	13.64	0.48	0.57	3.75

respectively, which is also in accordance with the V_{OC} of the devices shown in Table 3.

Conclusions

We have successfully synthesized six symmetric A- π -D- π -A dyes based on fluorene or dimethyl fluorene donor with three different π -bridges using Suzuki coupling reaction and Knoevenagel condensation. The absorption of dyes on TiO₂ film exhibited redshifted and broader absorption spectra compared to those of dyes in solutions, which indicated electronic coupling of dyes and molecular aggregation on the surface of TiO_2 . All the dyes meet the thermodynamic requirements for electron injection into the conduction band edge of TiO₂ and dye regeneration of the electrolyte species. Furthermore, from the electrochemical impedance spectroscopy (EIS), llyu2b has the highest eTiO₂ and **llyu1a** has the lowest eTiO₂, meaning that they have the highest and lowest V_{OC} , respectively, which is also in accordance with the V_{OC} of the devices. However, the device fabricated with llyu1a bearing thiophene π -bridge and fluorene donor showed higher PCE of 2.35%. Its J_{SC} , V_{OC} , and IPCE values were found to be 5.63 mA/cm², 0.60 V, and 70%, respectively. The higher J_{SC} value indicates that dyes bearing thiophene π -bridge and fluorene donor exhibit better conjugation system and



Fig. 6 Electrochemical impedance spectra for DSSCs based on dyes with A- π -D- π -A architecture. **a** Nyquist plot; **b** Bode plot

better absorption amount than the dyes containing furan or benzene π -bridge. Moreover, DFT studies show that the dihedral angle between thiophene and donor is 26.6° for **llyu1a** and **llyu2a**, indicating that the dyes bearing thiophene π -bridge possess more efficient photoexcitation compared to dyes bearing benzene π -bridge (36.6° for **llyu1c** and **llyu2c**) and less aggregation than dyes bearing furane π -bridge (0° for **llyu1b** and **llyu2b**), which is in agreement with its higher photovoltaic performance and the final higher efficiency of the dyes. Hence, the geometry of the π -bridge with respect to the donor plays a key role in the efficiency of dye as a sensitizer for DSSCs.

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