View Article Online View Journal

Photochemical & Photobiological Sciences

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: J. He, Y. Liu, J. Gao and L. Han, *Photochem. Photobiol. Sci.*, 2017, DOI: 10.1039/C6PP00410E.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/pps

Published on 25 April 2017. Downloaded by University of California - San Diego on 28/04/2017 15:28:17.

ROYAL SOCIETY OF CHEMISTRY

Journal Name

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

New D-D-π-A Triphenylamine-coumarin Sensitizers for Dye Sensitized Solar Cells

Ji He, Yang Liu, Jianrong Gao, Liang Han*

Three D-D- π -A triphenylamine-coumarin sensitizers were designed and synthesized with the triphenylamine and coumarin double donor and cyanoacrylic acid acceptor. Thiophene, bithiophene and phenylthiophene were used as π -bridge respectively and the effects of different π -bridges on the photophysical properties and the photovoltaic performance were investigated. With the incorporation of additional thiophene unit, bithiophene π -bridge contributes to better light absorption and hence superior J_{sc} compared with thiophene π -bridge. Though dye with phenylthiophene π -bridge exhibits inferior absorption spectrum to that with thiophene π -bridge, it obtains the photoelectrical conversion efficiency 4.99% and exhibits the optimal photovoltaic performance among three sensitizers ascribing to efficient photon-to-current conversion efficiency, slow charge recombination rate and good electron injection efficiency.

1. Intruduction

Dye sensitized solar cells (DSSCs) have attracted considerable interests due to its characteristics with high efficiency, low costs and easy manufacturing process, which have become one of a promising environmentally friendly photovoltaic device for converting sunlight to electricity.¹⁻³ DSSC is composed of a sandwich structure: a metal oxide layer covered with dye molecules and a counter electrode filling with an electrolyte. Under sun illumination, the metal oxide accepts the photoelectron from the LUMO of the excited dye. The electron is transferred to the counter electrode through the external circuit. The electrolyte acquires the electron from the ground state. Thus, the whole cell circuit is accomplished and solar light is transformed to electrical energy.⁴

In DSSCs, sensitizers play a critical role in determining the photovoltaic performance.⁵ Sensitizers with good light harvesting ability and appropriate energy level may lead to satisfactory photoelectric conversion efficiency. From the functional ruthenium(II)-polypyridyl complexes investigated earlier to metal-free organic sensitizing dyes, considerable improvement has been witnessed.⁶⁻⁸ More efforts have been made to design the metal-free organic sensitizing dyes possessing good photophysical properties and matched energy level with both the photoanode and the electrolyte due to their advantages of large diversity in molecular structure and simple preparation process.^{9,10}

Various electron donors such as indoline, 11,12 triarylamine, 13,14 coumarin, 15,16 which provide the electron to

the acceptor, have been exploited and are the crucial part to determine the absorption spectra of the sensitizers. Cyanoacrylic acid is the most used acceptor to inject the electron from the donor into the photoanode. π -Bridge links the donor and the acceptor and helps the intramolecular charge transfer. Therefore, the typical formula of metal-free organic sensitizers is donor- π -bridge-acceptor (D- π -A) structure.⁵ Molecular engineering on the variety of the donors and π -bridges has contributed to lots of sensitizers with good photovoltaic performance.¹⁷ In addition, double donors or acceptors are introduced into the sensitizer molecular structure.

The structure and properties of the sensitizer donor will influence both the molecular energy levels and the light harvesting ability. Compared with the sensitizers with single donor, double donor may endow the sensitizers with the expanded absorption region, improved molar extinction coefficients and enhanced thermostability.¹⁸ For example, Yu et al incorporated the carbazole donor into the coumarin sensitizers and observed more than 100% enhancement in overall conversion efficiency (5.53%) for 2D- π -A carbazole-coumarin sensitizer when compared with D- π -A coumarin sensitizer.¹⁹ In Jia's work, phenothiazine dye exhibited increased electron-donating ability and inhibited aggregation rate between dye molecules through the introduction of dithiafulvenyl unit as additional donor, which improves the power conversion efficiencies to 5.87% from 4.16%.²⁰

Triarylamine derivatives are widely used as the donor of the sensitizers for their well-known electron-rich properties and characteristic propeller structure.²¹ On the other hand, coumarin compounds, a type of donor investigated earlier, have good optical properties and are widely used in the field of photosensitive materials, OLED emitters and laser dyes.²² We try to combine triphenylamine and coumarin into the

College of Chemical Engineering, Zhejiang University of Technology, Hangzhou, 310032, China. Email: hanliang814@163.com

DOI: 10.1039/C6PP00410E Journal Name

ARTICLE

sensitizers and design double donor sensitizers with D-D- π -A structure. The typical π -bridge thiophene was used and based on this the additional thiophene was incorporated to investigate the effects of the π -bridge length. Moreover, benzene unit often favour the improvement of photovoltage compared with thiophene unit. Therefore, besides thiophene and bithiophene bridges, phenylthiophene bridge was also introduced. Hence, three D-D- π -A triphenylamine-coumarin sensitizers were synthesized and exhibited the photoelectric conversion efficiency of 4.40-4.99%.

2. Experimental

2.1. Materials and reagents

All of the reactions were carried out under N_2 atmosphere. N,N-Dimethylformamide (DMF) was dried over and distilled from CaH₂ under N₂ atmosphere. Phosphorus oxychloride was freshly distilled before use. Tetrahydrofuran (THF) was dried over sodium and then distilled before used. All other solvents and chemicals used in this work were analytical grade and used without further purification. Column chromatography purifications were performed through 100-200 mesh silica gel.

2.2. Instruments

¹H NMR and ¹³C NMR spectra were recorded on a Bruker AM-400 spectrometer in DMSO-d6 or CDCl₃. MS data were obtained using a Waters Xevo Q-Tof Mass Spectrometer. UVvis absorption spectra were measured using a SHIMADZU (model UV2550) UV-Vis spectrophotometer. Fluorescence spectra were performed with a SHIMADZU RF-5301PC spectrofluorometer.

2.3. Photovoltaic characterization

DSSCs based on the dyes were fabricated according to the process reported by Ref²³. Photovoltaic performance of the DSSCs was evaluated at AM 1.5 G illumination (100mW/cm²; Peccell-L15, Peccell, Japan) using a Keithley digital source meter (Keithley 2601, USA). Incident light intensity was 100mW/cm² calibrated with a standard Si solar cell (BS-520, Japan). The action spectra of monochromatic incident photonto-current conversion efficiency (IPCE) for solar cell were recorded by using a commercial setup (PEC-S20 IPCE Measurement System, Peccell, Japan). The electrolyte used here is composed of the CH₃CN solution of 0.3 M 1-methyl-3propylimidazolium iodide (MPII), 0.03 M I₂, 0.07 M LiI, 0.1 M guandine thiocyanate and 0.4 M 4-tert-butylpyridine (TBP). The TiO₂ active area of DSSCs was 0.16 cm^2 , and the total thickness of TiO₂ film was 18 mm with light scattering anatase particles.

Electrochemical impedance spectroscopy (EIS) experiments were conducted using a computer controlled potentiostat (ZeniumZahner, Germany). The measured frequency ranged from 100 mHz to 1 MHz while the AC amplitude was set to 10 mV. The bias of all EIS measurements was set to the V_{oc} of the corresponding dyes. Cyclic voltammetric experiments were performed at room temperature in DMF with a conventional three-electrode cell consisting of a Pt working electrode, a Pt wire counter electrode and an Ag/AgNO₃ reference electrode. Measurement was recorded through a computer controlled electrochemical analyzer (IviumStat, Holland) with Bu_4PF_6 as a supporting electrolyte at a scan rate of 50 mV/s. Ferrocene was used as the internal reference.

2.4. The detailed experimental procedures and characterization data

2.4.1. Synthesis of compound 1

The solution of 4-bromo-N,N-diphenylaniline (1.62 g, 5.0 mmol) in anhydrous THF (25 mL) was cooled to -78 °C, and then n-BuLi (4.0 mL, 6.0 mmol, 1.6 mol/L in hexane) was slowly added dropwise. After the addition, the reaction mixture was stirred for 1 h and then trimethyl borate (2.0 mL, 20.0 mmol) was added at once. The mixture was allowed to warm to room temperature and stirred for 24 h. The obtained solution was used directly in the subsequent Suzuki coupling without further treatment.

A mixture of 6-bromo-3-thienylcoumarin (1.54 g, 5 mmol), Pd(PPh₃)₄ (0.58 g, 0.5 mmol) and aqueous K₂CO₃ (10 mL, 2 mol/L) was dissolved in THF (30 mL), and then the above solution was added under N₂ atmosphere. The reactant was refluxed for 10 h. The mixture was extracted with dichloromethane and washed with water, then dried over anhydrous Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography (V_{PE}: V_{CH2CI2}=10:1) to afford compound **1** as a yellow solid (1.41 g, 60%). m.p. 226-228 °C; ¹H NMR (500 MHz, CDCl₃) δ : 8.07 (s, 1H, Ar-H), 7.85 (dd, J = 3.7, 1.1 Hz, 1H, Ar-H), 7.75-7.71 (m, 2H, Ar-H), 7.50-7.48 (m, 2H, Ar-H), 7.46 (dd, J = 5.1, 1.1 Hz, 1H, Ar-H), 7.44-7.42 (m, 1H, Ar-H), 7.33- 7.28 (m, 4H, Ar-H), 7.19-7.15 (m, 7H, Ar-H), 7.10-7.06 (m, 2H, Ar-H); HREIMS m/z 472.1365 [M+H]⁺, cacld C₃₁H₂₁NO₂S for: 471.1293.

2.4.2. Synthesis of compound 2

Phosphoryl chloride (1.3 mL) was added dropwise to DMF (2.6 mL) and then the mixture was stirred for 1 h at 0 °C. Then a solution of compound 1 (1.18 g, 2.5 mmol) in DMF (8 mL) was added and the reactant was stirred at 70 °C for 8 h. The mixture was poured into the ice water, neutralized with sodium hydroxide solution, then extracted with CH₂Cl₂ for three times. The combined organic layer was concentrated and the residue was purified by column chromatography (V_{PF}:V_{CH2CI2}=1:1) to give **2** as a yellow solid (0.87 g, 70%). m.p. 237-239 °C; ¹H NMR (500 MHz, CDCl₃) δ: 9.86 (s, 1H, CHO), 8.08 (s, 1H, Ar-H), 7.85 (dd, J = 3.7, 1.1 Hz, 1H, Ar-H), 7.77-7.72 (m, 4H, Ar-H), 7.60-7.56 (m, 2H, Ar-H), 7.49-7.43(m, 2H, Ar-H), 7.39 (tt, J = 4.6, 2.1 Hz, 2H, Ar-H), 7.30-7.26 (m, 2H, Ar-H), 7.25-7.22 (m, 3H, Ar-H), 7.16 (dd, J = 5.1, 3.8 Hz, 1H, Ar-H), 7.12 (d, J = 8.7 Hz, 2H, Ar-H); HREIMS m/z 500.1318 [M+H]⁺, cacld C₃₂H₂₁NO₃S for: 499.1242.

2.4.3. Synthesis of HJ-1

To the solution of ${\bf 2}$ (0.20 g, 0.4 mmol) in chloroform (15 mL), cyanoacetic acid (0.07 g, 0.84 mmol) and piperidine (0.20 mL)

Journal Name

were added. The solution was refluxed for 8 h. Then the solvent was removed in vacuo and the residue was purified by column chromatography (V_{HAC} : V_{MeOH} : V_{CH2CI2} =1:4:400) to afford **HJ-1** as an orange solid (0.15 g, 65%). m.p. 201-203 °C; ¹H NMR (500 MHz, DMSO) δ: 8.62 (s, 1H, CH=C), 8.16 (s, 1H, Ar-H), 8.12 (d, J = 2.2 Hz, 1H, Ar-H), 7.98-7.93 (m, 3H, Ar-H), 7.89 (dd, J = 3.7, 1.1 Hz, 1H, Ar-H), 7.78 (d, J = 8.6 Hz, 2H, Ar-H), 7.73 (dd, J = 5.1, 1.0 Hz, 1H, Ar-H), 7.55 (d, J = 8.6 Hz, 1H, Ar-H), 7.47 (t, J = 8.0 Hz, 2H, Ar-H), 7.32 (d, J = 8.6 Hz, 2H, Ar-H), 7.30-7.25 (m, 3H, Ar-H), 7.22 (dd, J = 5.1, 3.8 Hz, 1H, Ar-H), 6.98 (d, J = 9.0 Hz, 2H, Ar-H); ¹³C NMR (125 MHz, DMSO) δ: 164.10, 158.98, 153.17, 151.61, 151.53, 145.22, 145.06, 136.22, 135.98, 135.39, 135.36, 132.90 (3C), 130.19 (2C), 129.70, 128.98, 128.20 (2C), 127.53, 126.84, 126.58 (2C), 126.38 (2C), 125.99, 125.87, 123.53, 120.96, 119.73, 119.05 (2C), 116.58, 98.64; HREIMS m/z 565.1235 [M-H]⁻, cacld C₃₅H₂₂N₂O₄S for: 566.1300.

2.4.4. Synthesis of compound 3

Compound **1** (0.71 g, 1.5 mmol) and NBS (0.29 g, 1.6 mmol) were dissolved in DMF (22 mL). After stirring for 24 h, the reactant was poured into ice water (100 mL) and the yellow solid was precipitated. The precipitate was filtered and purified by column chromatography (V_{CH2Cl2} : V_{PE} = 1:3) to give 3 as a yellow solid (0.81 g, 98%). m.p.: 206-208 °C; ¹H NMR (500 MHz, CDCl₃) δ : 8.07 (s, 1H, Ar-H), 7.87-7.83 (m, 1H, Ar-H), 7.73 (tq, *J* = 4.2, 2.1 Hz, 2H, Ar-H), 7.53-7.42 (m, 4H, Ar-H), 7.40 (t, *J* = 8.5 Hz, 2H, Ar-H), 7.31 (td, *J* = 7.5, 5.6 Hz, 2H, Ar-H), 7.12 (T, 3 (m, 5H, Ar-H), 7.12-7.06 (m, 1H, Ar-H), 7.04-7.00 (m, 2H, Ar-H); HREIMS m/z 550.0476, 551.2932 [M+H]⁺, cacld C₃₁H₂₀BrNO₂S for: 549.0398.

2.4.5. Synthesis of compound 4a

A mixture of compound **3** (1.10 g, 2.0 mmol), (5-formylthiophen-2-yl)boronic acid (0.47 g, 3.0 mmol), Pd(PPh₃)₄ (0.23 g, 0.2 mmol), aqueous K₂CO₃ (2 M, 5 mL) in THF (30 mL) was refluxed for 10 h. The reactant was extracted with dichloromethane, washed with water, and then dried over anhydrous Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography (V_{CH2CI2}:V_{PE} = 1:2) to afford **4a** as a red solid (0.31 g, 27%). m.p.: 225-227 °C; ¹H NMR (500 MHz, CDCl₃) δ 9.88 (s, 1H, CHO), 8.08 (s, 1H, Ar-H), 7.85 (dt, *J* = 3.7, 1.1 Hz, 1H, Ar-H), 7.75-7.72 (m, 3H, Ar-H), 7.61-7.52 (m, 4H, Ar-H), 7.34 (dd, *J* = 3.6, 1.3 Hz, 1H, Ar-H), 7.24 (dd, *J* = 6.6, 4.6 Hz, 2H, Ar-H), 7.22-7.20 (m, 2H, Ar-H), 7.13 (m, 3H, Ar-H), 7.09-7.06 (m, 1H, Ar-H) ; HREIMS m/z 582.1187 [M+H]⁺, cacld C₃₆H₂₃NO₃S₂ for: 581.1119.

2.4.6. Synthesis of compound 4b

A mixture of compound **3** (1.10 g, 2.0 mmol), (4formylphenyl)boronic acid (0.45 g, 3.0 mmol), Pd(PPh₃)₄(0.23 g, 0.2 mmol), aqueous K₂CO₃ (2 M, 5 mL) in THF (30 mL) was refluxed for 10 h. The reactant was extracted with dichloromethane, washed with water, and then dried over anhydrous Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography (V_{CH2CI2}:V_{PE} = 1:2) to afford **4b** as an orange red solid (0.40 g, 35%). m.p.: 252-254 °C; ¹H NMR (500 MHz, CDCl₃) δ 10.06 (s, 1H, CHO), 8.08 (s, 1H, Ar-H), 7.96 (d, J = 8.0 Hz, 2H, Ar-H), 7.85 (dd, J = 3.7, 1.1 Hz, 1H, Ar-H), 7.77 (s, 1H, Ar-H), 7.76-7.74 (m, 3H, Ar-H), 7.58 (d, J = 8.5 Hz, 2H, Ar-H), 7.54 (d, J = 9.0 Hz, 2H, Ar-H), 7.47 (dd, J = 5.1, 1.1 Hz, 1H, Ar-H), 7.44 (d, J = 4.7 Hz, 1H, Ar-H), 7.35 (t, J = 8.5 Hz, 2H, Ar-H), 7.26-7.21 (m, 6H, Ar-H), 7.18-7.12 (m, 2H, Ar-H); HREIMS m/z 576.1628 [M+H]⁺, cacld C₃₈H₂₆NO₃S for: 575.1555.

2.4.7. Synthesis of HJ-2

To the solution of 4a (0.23 g, 0.4 mmol) in chloroform (15 mL), cyanoacetic acid (0.07 g, 0.84 mmol) and piperidine (0.20 mL) were added. The solution was refluxed for 8 h. Then the solvent was removed in vacuo and the residue was purified by column chromatography (V_{HAC} : V_{MeOH} : V_{CH2CI2} =1:4:400) to afford HJ-2 as a red solid (0.20 g, 80%). m.p. 237-239 °C; ¹H NMR (500 MHz, DMSO) δ 13.68 (s, 1H, COOH), 8.63 (s, 1H, CH=C), 8.47 (d, J = 2.6 Hz, 1H, Ar-H), 8.10 (t, J = 2.1 Hz, 1H, Ar-H), 8.00 (dd, J = 4.1, 2.4 Hz, 1H, Ar-H), 7.92 (dt, J = 8.5, 1.9 Hz, 1H, Ar-H), 7.89 (dd, J = 3.7, 1.1 Hz, 1H, Ar-H), 7.76-7.72 (m, 5H, Ar-H), 7.68 (dd, J = 10.1, 4.0 Hz, 1H, Ar-H), 7.56-7.53 (m, 2H, Ar-H), 7.41 (t, J = 7.9 Hz, 1H, Ar-H), 7.24-7.17 (m, 5H, Ar-H), 7.13-7.07 (m, 3H, Ar-H); ¹³C NMR (125 MHz, DMSO) δ: 163.70, 158.92, 151.40, 146.38, 146.16, 145.73, 136.19 (2C), 135.32 (2C), 133.90, 133.70 (2C), 132.60, 129.88 (2C), 129.48, 128.89, 127.97, 127.85 (2C), 127.51 (2C), 127.45(2C), 126.75, 126.52, 125.67, 125.33 (2C), 124.97, 124.66(2C), 124.09, 123.10, 122.42, 120.84, 119.65, 116.47; HREIMS m/z 647.1132 [M-H]⁻, cacld $C_{39}H_{24}N_2O_4S_2$ for: 648.1177.

2.4.8. Synthesis of HJ-3

To the solution of 4b (0.23 g, 0.4 mmol) in chloroform (15 mL), cyanoacetic acid (0.07 g, 0.84 mmol) and piperidine (0.20 mL) were added. The solution was refluxed for 8 h. Then the solvent was removed in vacuo and the residue was purified by column chromatography (V_{HAC}:V_{MeOH}:V_{CH2CI2}=1:4:400) to afford HJ-3 as a purple solid (0.22 g, 85%). m.p. 187-189°C; ¹H NMR (500 MHz, DMSO) δ 14.02 (s, 1H, COOH), 8.62 (s, 1H, CH=C), 8.36 (s, 1H, Ar-H), 8.13 (d, J = 8.6 Hz, 2H, Ar-H), 8.09 (d, J = 2.2 Hz, 1H, Ar-H), 7.94-7.87 (m, 4H, Ar-H), 7.78 (d, J = 7.0 Hz, 2H, Ar-H), 7.74-7.69 (m, 3H, Ar-H), 7.53 (d, J = 8.6 Hz, 1H, Ar-H), 7.40 (t, J = 8.0 Hz, 2H, Ar-H), 7.22 (dd, J = 5.1, 3.8 Hz, 1H, Ar-H), 7.21-7.15 (m, 5H, Ar-H), 7.13 (d, J = 8.7 Hz, 2H, Ar-H); ¹³C NMR (125 Hz, DMSO) δ: 163.42, 158.93, 153.60, 151.35, 147.57, 146.49, 146.46, 143.78, 136.19, 136.16, 135.33, 133.27, 132.13, 131.47 (2C), 129.93, 129.81 (2C), 129.46, 128.88, 128.06 (2C), 127.79 (2C), 127.45, 126.47, 126.57 (2C), 125.62, 125.08 (2C), 124.24 (2C), 124.13, 122.99 (2C), 120.82, 119.64, 116.44, 116.40, 102.71; HREIMS m/z 641.1559 [M-H]⁻, cacld C₄₁H₂₆N₂O₄S for: 642.1613.

3. Results and discussion

3.1 Synthesis

The designed new dyes are composed of a triphenylamine donor, a coumarin auxiliary donor, a conjugated bridge bearing thiophene unit and cyanoacrylic acid acceptor. Syntheses of Published on 25 April 2017. Downloaded by University of California - San Diego on 28/04/2017 15:28:17.





new dyes were accomplished following the general synthetic route depicted in **Scheme 1** and **Scheme 2**.

Triphenylamine bromide was converted to organic borate and then coupled with 6-bromo-3-thienylcoumarin to give compound **1**. The aldehyde group was introduced into the thiophene ring of compound **1** and then condensed with cyanoacetic acid in the presence of piperidine to give dye **HJ-1** (Scheme **1**). The bromide **3**, obtained through the bromination of compound **1** with NBS, went through the second Suzuki coupling reaction with formylarylboronic acids to form the intermediate aldehydes **4**. Knoevenagel condensation between the aldehydes **4** and cyanoacetic acid produces **HJ-2** or **HJ-3** (Scheme **2**).

3.2 Photophysical properties

The optical spectra of triphenylamine-coumarin dyes recorded in $CHCl_3-CH_3OH$ are displayed in **Fig. 1** and the pertinent data are listed in **Table 1**. All dyes exhibit two distinct absorption peaks. The lower energy absorption peaks at around 400-470



nm can be attributed to intramolecular charge transfer (ICT) from the triphenylamine donor to cyanoacrylic acid acceptor while the peaks appearing at higher energy region originate from π - π * electronic excitation.

Compared with HJ-1, the presence of another thiophene shifts the ICT peak bathochromically by 30 nm and λ_{max} of HJ-2 appears at 467 nm. At the same time the onset of HJ-2 shifts to 550 nm from 500 nm of HJ-1. In addition, HJ-2 exhibits the improvement of absorbance intensity and the molar extinction coefficients for $\pi \rightarrow \pi^*$ and ICT peaks of HJ-2 are both better than those of HJ-1. Therefore, the incorporation of another electron-rich thiophene distinctly benefits the improvement of the absorption spectrum, indicating superior light harvesting ability of **HJ-2** to **HJ-1**. However, the hypochromatic λ_{max} and a little narrow spectrum of HJ-3 are observed relative with HJ-1. The introduction of benzene seems not favour better absorption spectrum considering HJ-3 exhibits a lower ε for ICT peak than HJ-1 either. Noteworthily, the incorporation of another aryl ring helps the increase of absorbance intensity of $\pi \rightarrow \pi^*$ peak suggesting the improvement of blue light region.

Table 1 Optical properties of triphenylamine-coumarin dyes						
Compd	λ_{\max}^{a}	ε ^a	λ_{\max}^{b}	λ_{\max}^{c}	Adsorption capacity	
	/ (nm)	/ (M ⁻¹ cm ⁻¹)	/ (nm)	/ (nm)	/(mmol cm ⁻²)	
HJ-1	343, 432	20967, 29667	450	564	$2.11*10^{-7}$	
HJ-2	350, 467	46533, 33867	473	594	3.92*10 ⁻⁷	
HJ-3	340, 408	43700, 28933	450	562	2.92*10 ⁻⁷	

^a Maximum absorption wavelength λ_{max} and molar extinction coefficient at λ_{max} of dyes measured in CHCl₃-CH₃OH solution (V_{CH3OH} :V_{CHCI3}=1:10);

 $^{\text{b}}$ Maximum absorption wavelength λ_{max} of dyes on sensitized TiO_2 electrodes;

^c Maximum emission wavelength measured in CHCl₃-CH₃OH solution.

This journal is $\ensuremath{\mathbb{C}}$ The Royal Society of Chemistry 20xx

Accepted Manuscript

Photochemical & Photobiological Sciences

Journal Name

ARTICLE

When organic dyes are adsorbed onto TiO₂ films, the absorption spectra may show red shift or blue shift as compared to those in solution. Generally, deprotonation and H-aggregates result in the hypsochromical absorption peak while the bathochromical shift is caused by J-aggregates. The λ_{max} of three triphenylamine-coumarin dyes shows 6-50 nm bathochromical shift, which means these dyes go through Jaggregates. Moreover, the absorption spectra of HJ-1-HJ-3 on TiO₂ are broader than those in solution and the onsets were extended bathochromically by about 50 nm. Similar to in solution, the broadest absorption spectrum on TiO₂ is observed in the case of HJ-2 among three triphenylaminecoumarin dyes and it exhibits high absorbance at 390-520 nm. This superiority of light absorption for HJ-2 on TiO₂ may derive from its better absorption spectrum in solution and the highest adsorption capacity on TiO₂, which ensure better lightharvesting ability and hence improved photon-to-current conversion efficiency. Though it shows a little narrower absorption spectrum in solution than HJ-1, HJ-3 has higher loading amount on TiO₂ along with distinctly improved absorbance at blue light region, which contributes to its similar absorption spectrum on TiO₂ with HJ-1.

3.3. Theoretical calculations

To gain insight into the relationship of the geometrical structure and electronic distribution with the optical properties, DFT calculations were performed on dyes **HJ-1-HJ-3** by B3LYP hybrid density functional method in conjunction with the *d*-polarized 6-31G (d) basis set implemented in the Gaussian 03 program. The fully optimized geometrical structures of three dyes are shown in **Fig. 2**.

As can be seen, the triphenylamine donor keeps a nonplanar butterfly conformation, which is the structural characteristic of triarylamine compounds and endows these dyes with antiaggregation properties. In the case of **HJ-1**, the auxiliary coumarin donor, thiophene π -bridge and cyanoacrylic acid



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

acceptor align in the same plane. The introduction of another thiophene in **HJ-2** enlarges the conjugative system without impairing the coplanarity of the whole molecule, which leads to longer maximum absorption wavelength of **HJ-2** than **HJ-1**. On the other hand, the presence of six-member bulky benzene weakens the coplanarity of **HJ-3** and a large dihedral angle between thiophene and benzene is observed. This means the incorporation of benzene is unhelpful to the enlargement of the conjugated system and therefore the λ_{max} of **HJ-3** is shorter than that of **HJ-1**.

Energy level data of dyes **HJ-1-HJ-3** are listed in **Table 2** and the energy gap are distributed at 2.26-2.35 eV. HOMO energy levels of these dyes are located at -5.24--5.17 eV and lower than the potential of the redox couple I/I_3^- (-4.9 eV). LUMO energy levels of **HJ-1-HJ-3** are observed at -2.95--2.82 eV, which are higher than the conduction band of TiO₂ (-4.0 eV). Therefore, the excited dyes can efficiently inject the electron into the TiO₂ conduction band and simultaneously the oxidized dyes may be reduced back into the ground state through the reception of the electron from the electrolyte. The experimental energy levels were obtained through cyclic

Table 2 Energy lever of triphenylamine countain dyes						
compound	Experimental			Calculated ^d		
	E _{HOMO} ^a /eV	E ₀₋₀ ^b /eV	E _{LUMO} ^c /eV	Е _{номо} /eV	E ₀₋₀ /eV	E _{LUMO} /eV
HJ-1	-5.17	2.5	-2.67	-5.24	2.28	-2.95
HJ-2	-5.05	2.32	-2.73	-5.20	2.26	-2.94
HJ-3	-5.05	2.52	-2.54	-5.17	2.35	-2.82

[able]	2 Energy	level o	ftrinhen	vlamine-coumai	rin d	ves
abic	LITERSY	IEVELU	i triprieri	yiaiiiiiie-couiiiai	ini u	yes

^a E_{HOMO} was obtained from E_{HOMO} = -(E_{ox} + 4.4 eV) and the oxidation potential E_{ox} in DMF was derived by the first anodic peak potential in cyclic voltammogram;

^b E₀₋₀ was determined from E₀₋₀ = 1240/ λ_{int} and λ_{int} was the intersection of the normalized absorption and emission spectra in CHCl₃-CH₃OH cosolvent (v: v =10:1);

^c Deduced using the formula E_{LUMO}=E_{HOMO}-E₀₋₀;

^d B3LYP/6-31G(d) calculate values in vaccum.

Page 6 of 9

Journal Name

ARTICLE

Published on 25 April 2017. Downloaded by University of California - San Diego on 28/04/2017 15:28:17.



Fig. 3 Electronic distributions in the frontier molecular orbitals of triphenylamine-coumarin dyes

voltammetry method and basically agreed with the calculated value. As can be seen from the data obtained by the cyclic voltammetry method, **HJ-3** exhibits the highest LUMO energy level among three triphenylamine-coumarin dyes. Generally, higher E_{LUMO} means larger energy level gap between the dye excited state and the conduction band level of TiO₂, leading to more efficient electron injection [7,24]. Therefore, the presence of benzene ring in **HJ-3** is beneficial for the enhancement of the electron injection efficiency.

The electronic distribution of frontier molecular orbitals is displayed in **Fig.3**. In three dyes, the HOMO is delocalized over the triphenylamine donor moiety and partly spread over coumarin donor, while the LUMO is mainly populated on the auxiliary coumarin donor, π -bridge and the acceptor. The HOMOs and LUMOs are overlapping reasonably, which favours an efficient electron transfer from the triphenylamine donor of the dyes to the TiO₂ conduction band edge.

3.4 Electrochemical properties

Fig. 4 listed Nyquist and Bode spectra of three triphenylaminecoumarin dyes, which were obtained from the electrochemical impedance spectroscopy (EIS) measurement in the dark and under the forward bias. At the same time of the electron injection into the conduction band (CB) of TiO₂ from the LUMO of the dye, the electron also may combine with the oxidized dye or the oxidized redox electrolytes, which causes the dark current and hence the decrease of V_{oC} . EIS is an efficient tool to investigate the interfacial charge transfer process in DSSC and find the presence of the possible charge recombination. The related parameters in **Table 3** were obtained from an equivalent circuit through the software (ZSimpWin). In this equivalent circuit with a constant phase element (CPE) and resistance (R), R_{CE} and R_{S} represent the charge-transfer resistance at the counter electrode and the overall series



Fig. 4 Electrochemical impedance spectra for DSSCs based on triphenylamine-coumarin dyes(a) Nyquist plot; (b) Bode plot; (c) equivalent circuit

resistances respectively. R_{ct} denotes the charge transfer resistance at the photoanode/electrolyte interface, which corresponds to the diameter of the semicircle in the Nyquist diagram and the peak frequency in the Bode diagram. Large diameter and low frequency mean high R_{ct} , indicating low charge recombination rate.

As can be seen, **HJ-1** shows the largest semicircle in Nyquist diagram and the lowest peak frequency in Bode diagram, suggesting the largest resistance and the lowest charge recombination rate. With the extension of π -bridge, R_{ct} of three triphenylamine-coumarin dyes follows the order: **HJ-1** (28.65 Ω) > **HJ-3** (10.97 Ω) > **HJ-2** (6.31 Ω) and the incorporation of the additional aryl ring provokes the decrease of R_{ct}. **HJ-2** exhibits the lowest R_{ct} maybe due to its easiest tendency to form aggregates derived from the largest conjugation system. Moreover, **HJ-3** shows higher R_{ct} than **HJ-2** perhaps thanks for the twisted structure between the benzene ring and the thiophene ring which destroys the coplanarity and prevents the formation of the aggregates.

Table 3 Parameters obtained by fitting the impedance spectra of DSSCs based on triphenylamine-coumarin dyes using the equivalent circuit

HJ-3	4.46	10.97
HJ-2	11.34	6.31
HJ-1	8.62	28.65
Compd.	R _s (Ω)	R _{ct} (Ω)
equivalent circuit		

3.5 Photovoltaic performance

The action spectra of monochromatic incident photon-tocurrent conversion efficiency (IPCE) for solar cells based on three dyes were measured under AM 1.5 G irradiation (100 mW/cm²) and listed in Fig. 5 (a) as a function of light excitation wavelength. With the introduction of another aryl ring, HJ-2 and HJ-3 obtain higher monochromatic incident photon-tocurrent conversion efficiency than HJ-1 with single thiophene π -bridge. Consistent with its superior absorption spectrum on TiO₂, HJ-2 exhibits the highest IPCE value among three dyes and owns higher IPCE value exceeding 50% from 380 nm to 520 nm reaching the maximum IPCE value 62% at 460 nm. Compared with HJ-2, HJ-3 with phenylthiophene π -bridge has only the maximum value of 54% and exhibits inferior IPCE spectrum at 370-540 nm but with a little higher IPCE value at 540-650 nm. It is noteworthy that HJ-3 shows better IPCE though with similar absorption spectrum on TiO₂ when compared with HJ-1. A result can be ascribed to better electron injection efficiency of HJ-3 owing to its higher ELUMO. HJ-3 shows a distinctly higher monochromatic incident photon-to-current conversion efficiency at 350-600 nm than HJ-1.



Fig. 5 IPCE curves (a) and current-potential (*J-V*) curves (b) for DSSCs based on triphenylamine-coumarin dyes with 18.0 mm nanocrystalline TiO₂ electrodes

The photocurrent-voltage (*J-V*) curves of DSSCs based on triphenylamine-coumarin dyes are shown in **Fig. 5 (b)**. The corresponding parameters open-circuit photovoltage V_{OC} , short circuit photocurrent density J_{SC} , fill factor *ff* and solar energy-to-electricity conversion efficiency η are listed in **Table 4.** J_{SC} for DSSCs based on the dyes follows the trend **HJ-1 < HJ-3** \approx **HJ-2**, which is in agreement with the result of IPCE and **HJ-2** sensitized DSSC obtains the highest J_{SC} . In fact, **HJ-3** has a similar J_{SC} with **HJ-2**, which means the little better IPCE spectrum of **HJ-3** at 540-650 nm plays a role on the improvement of the photocurrent density.

Voc for the dyes sensitized DSSCs ranks by the order of HJ-2 < HJ-1 < HJ-3. As mentioned above, larger R_{ct} indicates lower charge recombination, which may prevent the dark current and benefit the improvement of V_{OC} . As a result, HJ-3 exhibits larger V_{OC} than HJ-2 ascribing to its higher R_{ct} . It is noteworthy that HJ-1 exhibits lower V_{oc} than HJ-3 though with the highest R_{ct} perhaps due to its low electron injection efficiency. HJ-1 has similar absorption spectrum with HJ-3 on TiO₂ film suggesting their similar light harvesting ability. However, better IPCE spectrum of HJ-3 is observed when compared with HJ-1, which means HJ-3 may have better electron injection efficiency since IPCE is generally determined by the light harvesting ability and electron injection efficiency.⁷ In addition, higher ELUMO of HJ-3 means larger energy level difference of the excited state relative to $TiO_2 E_{CB}$, which also endow HJ-3 with the fast electron injection speed and hence the enhancement of the electron injection efficiency. On the other hand, Voc is mainly determined by the electron injection efficiency and charge recombination rate.⁷ Therefore, the inferior electron injection efficiency of HJ-1 may counteract its lower charge recombination rate, which leads to its lower V_{oc} than that of HJ-3. Among three dyes sensitized DSSSs, a maximum η value of 4.99% has been achieved (J_{sc} = 9.17 mA/cm^2 , $V_{oc} = 0.70$ V, and ff = 0.78) for DSSC based on HJ-3, which should attribute to efficient photon-to-current conversion efficiency, slow charge recombination rate and good electron injection efficiency.

Table 4 Parameters for DSSCs based on triphenylamine-coumarin dyes

Compd	V _{oc} (V)	J _{sc} (mA·cm⁻²)	ff	η (%)
HJ-1	0.65	8.20	0.85	4.52
HJ-2	0.64	9.21	0.75	4.40
HJ-3	0.70	9.17	0.78	4.99

4. Conclusion

3-Thienylcoumarin was coupled with triphenylamine through Suzuki coupling reaction to afford triphenylamine-coumarin double donor unit bearing thiophene ring. Then with the introduction of additional thiophene or benzene ring and the incorporation of the acceptor, three D-D- π -A triphenylamine-

ARTICLE

coumarin sensitizers were synthesized with thiophene, bithiophene and phenylthiophene π -bridge respectively. Their ICT peaks occur at 400-470 nm with molar extinction coefficients about 30000 M⁻¹ cm⁻¹ and the sensitizer with bithiophene exhibits the best absorption spectrum in solution. On the other hand, though evoking the inferior absorption spectrum, the incorporation of additional benzene favours the antiaggregation of dye with phenylthiophene π -bridge and the enhancement of the electron injection efficiency. Therefore, with better J_{SC} and the highest V_{OC} , dye with phenylthiophene π -bridge shows the best photoelectric conversion efficiency among three triphenylamine-coumarin sensitizers.

Acknowledgement

The authors gratefully acknowledge for the funding of National Natural Science Foundation of China (21406202).

Notes and references

1 A. Hafeldt, G. Boschloo, L. C. Sun, L. Kloo and H. Pettersson, Dye-sensitized solar cells, Chem. Rev. 2010, **110**, 6595-6663.

2 F. Bella, C. Gerbaldi, C. Barolo and M. Grätzel, Aqueous dyesensitized solar cells, Chem. Soc. Rev. 2015, **44**, 3431-3473.

3 S. Zhang, X. Yang, Y. Numata and L. Han, Highly efficient dye-sensitized solar cells: progress and future challenges, Energy Environ. Sci. 2013, **6**, 1443-1464.

4 C. Clement Raj and R. Prasanth, A critical review of recent developments in nanomaterials for photoelectrodes in dye sensitized solar cells, J. Power Source 2016, **317**, 120-132.

5 A. Mishra, M.K.R. Fischer and P. Bäuerle, Metal-free organic dyes for dye-sensitized solar cells: form structure: property relationships to design rules, Angew. Chem. Int. Ed. 2009, **48**, 2474-2499.

6 R. K. Kanaparthi, J. Kandhadi and L. Giribabu, Metal-free organic dyes for dye-sensitized solar cells: recent advances, Tetrahedron, 2012, **68**, 8383-8393.

7 J. Z. Ning, Y. Fu and H. Tian, Improvement of dye-sensitized solar cells: what we know and what we need to know, Energy Environ. Sci. 2010, **3**, 1170-1181.

8 M. Urbani, M. Grätzel, M.K. Nazeeruddin and T. Torres, Meso-substituted porphyrins for dye-sensitized solar cells, Chem. Rev. 2014, **114**, 12330-12396.

9 S. Chaurasia and J.T. Lin, Metal-free sensitizers for dyesensitized solar cells, Chem. Rec. 2016, **16**, 1311-1336.

10 L. Zhang and J.M. Cole, Anchoring groups for dye-sensitized solar cells, ACS Appl. Mater. Interfaces 2015, **7**, 3427-3455.

11 B. Liu, B. Wang, R. Wang, L. Gao, S.H. Huo, Q. B. Liu, X. Y. Li and W. H. Zhu, Influence of conjugated π -linker in D-D- π -A indoline dyes: towards long-term stable and efficient dyesensitized solar cells with high photovoltage, J. Mater. Chem. A 2014, **2**, 804-812.

12 C. V. Kumar, D. Raptis, E. N. Koukaras, L. Sygellou and P. Lianos, Study of an indoline-phenothiazine based organic dye for Dye-Sensitized Solar Cells. Theoretical calculations and experimental data, Org. Electron. 2015, **25**, 66-73.

13 C. C. Yan, W. T. Ma, Y. M. Ren, M. Zhang and P. Wang, Efficient triarylamine perylene dye-sensitized solar cells: Influence of triple-bond insertion on charge recombination, ACS ACS Appl. Mater. Interfaces 2015, **7**, 801-809.

14 R. Yuan, Z. T. Liu, Y. Wan, Y. Liu, Y. J. Wang and W. H. Ge, New D-D-pi-A-type indol-triarylamine sensitizers for efficient dye-sensitized solar cells, Synth. Met. 2016, **215**, 21-27.

15 R. Rattanawan, V. Promarak, T. Sudyoadsuk, S. Namuangruk, N, Kungwan, S. Yuan and S. Jungsuttiwong, Theoretical design of coumarin derivatives incorporating auxiliary acceptor with D-pi-A-pi-A configuration for dye-sensitized solar cells, J. Photochem. Photobio. A. 2016, **322**, 16-26.

16 J. H. Wang, M. Li, D. Qi, W. Shen, R.X. He and S.H. Lin, Exploring photophysical properties of metal-free coumarin sensitizers: an efficient strategy to improve the performance of dye-sensitized solar cells, RSC Adv. 2014, **4**, 53927-53938.

17 B. G. Kim, K. Chung and J. Kim, Molecular design principle of all-organic dyes for dye-sensitized solar cells, Chem. Eur. J. 2013, **19**, 5220-5230.

18 Y. P. Hong, J. Y. Liao, J. L. Fu, D. B. Kuang, H. Meier, C. Y. Su and D. R. Cao, Performance of dye-sensitized solar cells based on novel sensitizers bearing asymmetric double D-pi-A chains with arylamines as donors, Dyes Pigm, 2012, **94**, 481-489.

19 B. Liu, R. Wang, W. J. Mi, X. Y. Li and H. T. Yu, Novel branched coumarin dyes for dye-sensitized solar cells: significant improvement in photovoltaic performance by simple structure modification, J. Mater. Chem. 2012, **22**, 15379-15387.

20 Z. Q. Wan, C. Y. Jia, Y. Wang, J. S. Luo and X. J. Yao, Significant improvement of phenothiazine organic dyesensitized solar cell performance using dithiafulvenyl unit as additional donor, Org. Electron. 2015, **27**, 107-113.

21 A. Mahmood, Triphenylamine based dyes for dye sensitized solar cells: A review, Sol. Energy 2016, **123**, 127-144. 22 K. D. Seo, I. Choi, Y. G. Park, S. Kang, J. Y. Lee and H. K. Kim, Novel D-A- π -A coumarin dyes containing low band-gap chromophores for dye-sensitised solar cells, Dyes Pigm., 2012, **94**, 469-474.

23 Y. Liu, J. He, L. Han and J. R. Gao, Influence of the auxiliary acceptor and p-bridge in carbazole dyes on photovoltaic properties, J. Photochem. Photobio. A, 2017, **332**, 283-292.

24 S. P. Singh, M. S. Roy, K. R. J. Thomas, S. Balaiah, K. Bhanuprakash, and G. D. Sharma, New triphenylamine-based organic dyes with different numbers of anchoring groups for dye-sensitized solar cells, J. Phys. Chem. C, 2012, **116**, 5941-5950.

Published on 25 April 2017. Downloaded by University of California - San Diego on 28/04/2017 15:28:17.

New D-D-π-A Triphenylamine-coumarin Sensitizers for Dye

Sensitized Solar Cells

Ji He, Yang Liu, Jianrong Gao, Liang Han^{*} (College of Chemical Engineering, Zhejiang University of Technology, Hangzhou, 310032)



photoelectric conversion efficiency η %: 4.40-4.99%

Three D-D- π -A triphenylamine-coumarin sensitizers were synthesized with π -bridge bearing thiophene unit and cyanoacrylic acid acceptor and showed the optimal photoelectric conversion efficienty of 4.99% ($V_{OC} = 700 \text{ mV}$, $J_{SC} = 9.17 \text{ mA/cm}^2$, and ff = 0.78) under simulated AM 1.5 irradiation (100 mW/cm²).

^{*} Corresponding author: hanliang814@163.com