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Introduction

In recent decades, organic solar cells have been developed extensively. Among these devices, dye-sensitized solar cells (DSSCs) have attracted increasing attention because of their low cost, easy synthesis and relatively high efficiency. The sensitizers are a very important part of DSSCs which harvest sunlight and inject electrons into the semiconductor. At present, DSSCs based on Ru^{II}-polypyridyl complexes¹ have achieved power conversion efficiencies of almost 11% at standard global air mass (AM) 1.5.² However, the large-scale application of Ru-complexes in DSSCs has been limited due to the shortage of Ru-resources and high cost of purification. In comparison with the metal complexes, metal-free organic dyes, such as cyanine,³ merocyanine,⁴ coumarin,⁵ indoline,⁶ hemicyanine,⁷ phenothiazine,⁸ porphyrin,⁹ phenoxazine¹⁰ and diketopyrrolopyrrole et al. dyes¹¹ have higher molar extinction coefficients and can be prepared and purified at lower costs. These advantages indicate that metal-free organic dyes are suitable substitutes for large-scale application in DSSCs. Great development has been made during these years. The highest overall photo-voltage conversion efficiency has been above

Structure-property relationship of different electron donors: new organic sensitizers based on bithiazole moiety for high efficiency dye-sensitized solar cells

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Three metal-free bithiazole organic dyes (**BTT-I–III**) based on D–A- π -A building blocks were designed and synthesized for dye-sensitized solar cells (DSSCs) to study the influence of different electron donors on photovoltaic properties, in which the electron donors of **BTT-I–III** were carbazole, triphenylamine and indoline moieties, respectively. The UV/Vis absorption spectra of **BTT-III** containing indoline as electron-donor displayed red-shifted absorption compared to the other two dyes with an onset close to 700 nm. The incident photon-to-current conversion efficiency (IPCE) spectra of **BTT-III** showed a wide region and kept a value higher than 10–15% during 580–650 nm. Electrochemical measurement data indicated that the HOMO and LUMO energy levels could be tuned through introducing different electron-donors in the dye molecule. It was found that the overall conversion efficiency of indoline donor based dye **BTT-III** showed the highest efficiency of 7.86% under AM 1.5 irradiation (100 mW cm⁻²). The electron lifetime calculated from electrochemical impedance spectroscopy (EIS) measurement demonstrated the reduced charge recombination and the higher open-circuit voltage.

10%, which indicates that metal-free organic dyes are a favored type of higher sensitizer for DSSCs.¹²

Most efficient metal-free organic sensitizers are constructed with donor- π bridge-acceptor (D- π -A) systems. The introduction of different π -conjugated units in dye molecules between the donor and acceptor can expand the absorption spectrum and red-shift to longer wavelengths. However, the stability of these dyes is reduced by extending the π conjugated bonding bridges. To overcome this defect, some electron-withdrawing moieties such as quinoline,¹³ isoxazole,¹⁴ thiazole moieties¹⁵ and pyrimidine ring¹⁶ were reported to be introduced into the molecular to form the D–A- π -A configuration. It was found that these systems showed more red-shifted absorption and higher stability than their analogues. The bithiazole unit is a wellknown electron deficient unit and has been widely applied in thin film transistors, photovoltaic cells, and light-emitting diodes. In our previous studies, we have identified that small molecule DSSCs based on bithiazole sensitizers with the construction of D-A-π-A configuration could achieve high performance and long stability.17 The two long alkyl chains attached on the thiazole moiety suppressed charge recombination and dye aggregation successfully, resulting in high opencircuit voltage.

As reported, the donor group can not only affect the absorption spectrum but also adjust the HOMO and LUMO energy levels. Different electron donors can lead to diverse positions of the HOMO and LUMO energy levels resulting in

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Fig. 1 The molecular structures of the dyes BTT-I-III

different driving forces for electron injection and tune shortcircuit photocurrent density (J_{sc}) . The indoline units, which have been reported in organic sensitizers, showed more powerful donor abilities,¹⁸ red-shifted absorption spectrum and less positive HOMO levels compared to traditional triphenylamine donors. To enrich the research field of bithiazole dyes for DSSCs and gain more information on the structure-property relationships, we have synthesized two new bithiazole-based sensitizers (BTT-I and BTT-III) in which the carbazole and indoline units are acting as electron donors, thiophene as a π spacer and cyanoacrylic acid as the acceptor moiety. We have also synthesized the corresponding bithiazole dye BTT-II (Fig. 1) for the purpose of comparison. All dyes were fabricated for efficient DSSCs. Finally, the three sensitizers were applied to the sensitization of nanocrystalline TiO₂-based solar cells. It was found that DSSCs based on BTT-III with an indoline electron-donor exhibited the best overall conversion efficiency of 7.86% under AM 1.5 irradiation (100 mW cm $^{-2}$). The effect of different electron-donors on the photophysical and electrochemical properties of the dyes and the solar cell performance were demonstrated in detail.

Experimental

Photovoltaic performance measurements

Photovoltaic measurements employed an AM 1.5 solar simulator equipped with a 300 W xenon lamp (Model No. 91160, Oriel). The power of the simulated light was calibrated to 100 mW cm⁻² by using a Newport Oriel PV reference cell system (Model 91150 V). *J–V* curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter.

The voltage step and delay time of the photocurrent were 10 mV and 40 ms, respectively. Action spectra of the incident monochromatic photon-to-electron conversion efficiency (IPCE) for the solar cells were obtained with a Newport-74125 system (Newport Instruments). The intensity of mono-chromatic light was measured with a Si detector (Newport-71640).

Materials

Dichloromethane (DCM) was dried over calcium hydroxide and then distilled under normal pressure. Conductive glass substrates (F: SnO₂, transmission > 90% in the visible, sheet resistance 15 Ω square⁻¹) were obtained from the Geao Science and Educational Co. Ltd. of China. 1,2-dimethyl-3-npropylimidazolium iodide (DMPII) were purchased from Aldrich. 4-*tert*-butylpyridine (TBP) and lithium iodide were from Fluka and iodine (99.999%) was from Alfa Aesar. Starting materials 5-(5'-bromo-4,4'-dihexyl-2,2'-bithiazol-5-yl)thiophene-2-carbaldehyde (Compound 1) was pre-pared according to the literature method.¹⁷ All other solvents and chemicals used in this work were of reagent grade and used without further purification unless other-wise noted.

Device fabrication

The nanocrystal TiO₂ films were fabricated according to the published procedure.¹⁷ These nanocrystal titania films were treated with 40 mM TiCl₄ aqueous solution at room temperature overnight, following by sintering at 450 °C for 30 min. After cooling to 80 °C, these films absorbed the coabsorption chenodeoxycholic acid (CDCA) for 2 h or 4 h in 10 mM CDCA in ethanol. After rinsing with ethanol and drying, these films were dipped into a 3 \times 10⁻⁴ M solution of dyes (BTT-I-III) in dichloromethane for 16 h at room temperature. After this, the electrodes were rinsed with CH₂Cl₂ and ethanol and then dried. The size of the electrodes was 0.25 cm². The Pt-counter electrodes were prepared following the literature.¹⁷ For assembly of DSSCs as a sandwich type, the TiO₂ photo electrodes and Pt-counter electrodes were sealed with a hotmelt gasket of 45 µm thickness. The electrolyte of liquid-state DSSCs was 0.1 M LiI, 0.05 M I₂, 0.6 M DMPII, and 0.5 M TBP in acetonitrile.

Synthesis

5-(4,4'-dihexyl-5'-(9-octyl-9H-carbazol-3-yl)-2,2'-bithiazol-5yl)thiophene-2-carbaldehyde (2). Compound 1 (190 mg, 0.36 mmol), Pd (PPh₃)₄ (42 mg, 0.036 mmol), and K₂CO₃ (5 mL, 2 M aqueous solution) in 8 mL of THF were heated to 45 °C under an argon atmosphere for 30 min. A solution of 9-octyl-9H-carbazol-3-ylboronic acid (234 mg, 0.72 mmol) in cyclohexane (5 mL) was added slowly, and the mixture was refluxed for further 12 h. After cooling to room temperature, the mixture was extracted with CH₂Cl₂. The combined organic layers were washed with water and brine and dried with anhydrous Na₂SO₄. The solvent was evaporated, and the residue was purified by column chromatography on silica gel (PE/CH₂Cl₂ = 2/1-1/1, v/v) to give an orange solid (250 mg, yield: 95%). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 9.91 (s, 1H), 8.18 (s, 1H), 8.11 (d, J = 7.6 Hz, 1H), 7.73 (d, J = 4.0 Hz, 1H), 7.55 (d, J = 8.4 Hz, 1H)1H), 7.51 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 8.1 Hz, 2H), 7.27 (m,

2H), 4.32 (t, J = 7.2 Hz, 2H), 3.01 (t, J = 7.8 Hz, 2H), 2.90 (t, J = 7.6 Hz, 2H), 1.94–1.88 (m, 2H), 1.86–1.79 (m, 4H), 1.44–1.25 (m, 22H), 0.91–0.84 (m, 9H).

5-(4,4'-dihexyl-5'-(4-p-tolyl-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-yl)-2,2'-bithiazol-5-yl)thiophene-2-carbaldehyde (4). The synthesis method resembles that of compound 2 using 4-p-tolyl-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-ylboronic acid reaction with compound 1, and the compound was purified by column chromatography on silica gel (PE/CH₂Cl₂ = 1/1, v/v) to give a red solid (150 mg, yield: 91%) ¹H NMR(CDCl₃, 400 MHz), δ (ppm): 9.91 (s, 1H), 7.73 (d, *J* = 4.0 Hz, 1H), 7.26 (d, *J* = 4.0 Hz, 1H), 7.22–7.16 (m, 5H), 7.12 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 4.84 (t, *J* = 6.6 Hz, 1H), 3.85 (t, *J* = 7.2 Hz, 1H), 3.74 (t, *J* = 6.2 Hz, 1H), 2.99 (t, *J* = 7.8 Hz, 2H), 2.83 (t, *J* = 8.0 Hz, 2H), 2.34 (s, 3H), 2.12–2.03 (m, 1H), 1.95–1.87 (m, 2H), 1.83–1.76 (m, 4H), 1.63–1.59 (m, 1H), 1.45–1.29 (m, 13H), 0.91–0.86 (m, 6H).

2-cyano-3-(5-(4,4'-dihexyl-5'-(9-octyl-9H-carbazol-3-yl)-2,2'-bithiazol-5-yl)thiophen-2-yl)acrylic acid (BTT-I). Compound 2 (100 mg, 0.138 mmol), 2-cyanoacetic acid (83 mg, 0.98 mmol) and ammonium acetate (200 mg) in acetic acid (8 mL) at reflux for 6 h. After cooling the solution, the mixture was poured into water to quench the reaction. The precipitate was filtered and washed with water. The residue was purified by column chromatography on silica gel (CH₂Cl₂ to $CH_2Cl_2/EtOH = 20/1$, v/v) to yield 83 mg of dark red solid (yield 75.4%). ¹H NMR (THF- d_8 , 400 MHz), δ (ppm): 8.32 (s, 1H), 8.21 (d, J = 7.6 Hz, 1H), 7.80 (s, 1H), 7.69–7.63 (m, 2H), 7.56–7.48 (m, 4H), 7.23 (t, J = 7.2 Hz, 1H), 4.41 (t, J = 6.0 Hz, 2H), 2.96 (t, J = 7.4 Hz, 2H), 2.85 (t, J = 7.0 Hz, 2H), 1.76-1.71 (m, 6H), 1.30-1.17(m, 22H), 0.86-0.78(m, 9H).¹³C NMR(THFd₈, 100 MHz), 165.2, 162.2, 161.7, 158.9, 146.5, 145.8, 143.4, 142.2, 142.1, 133.2, 131.7, 131.5, 128.8, 128.0, 127.2, 126.6, 126.4, 125.8, 125.7, 124.6, 114.6, 114.5, 84.2, 83.8, 83.5, 59.4, 48.2, 37.3, 37.2, 36.3, 35.2, 35.0, 34.9, 34.8, 34.7, 34.6, 34.5, 32.7, 28.1, 19.0. HRMS (m/z): $[M + H]^+$ Calcd for C₄₆H₅₅N₄O₂S₃ 791.3487, Found: 791.3508.

2-Cyano-3-(5-(5'-(4-(diphenylamino)phenyl)-4,4'-dihexyl-2,2'-bithiazol-5-yl)thiophen-2-yl)acrylic acid (BTT-II). The synthesis method resembles that of **BTT-I** using compound **3** reaction with 2-cyanoacetic acid, and the compound was purified by column chromatography on silica gel (CH₂Cl₂/EtOH = 20/1, v/v) to yield red solid (133 mg, yield 82.6%). ¹H NMR (THF- d_8 , 400 MHz), δ : 8.54 (s, 1H), 8.04 (d, J = 4.0 Hz, 1H), 7.62 (d, J = 3.2 Hz, 1H), 7.43 (d, J = 8.0 Hz, 2H), 7.36 (t, J = 8.0 Hz, 4H), 7.15–7.10 (m, 6H), 7.01 (d, J = 8.0 Hz, 2H), 2.98 (t, J = 7.4 Hz, 2H), 2.80 (t, J = 7.4 Hz, 2H), 1.78–1.65 (m, 4H), 1.30–1.23 (m, 12H), 0.85 (t, J = 6.8 Hz, 6H). ¹³C NMR (THF- d_8 , 100 MHz), 165.1, 162.0, 159.0, 158.7, 156.0, 150.6, 149.7, 147.5, 144.2, 140.6, 138.8, 137.6, 132.2, 131.6, 130.2, 128.6, 127.3, 126.9, 125.9, 124.6, 118.1, 117.9, 34.2, 34.0, 33.0, 32.0, 31.9, 31.8, 31.4, 30.4, 29.4, 27.9, 27.8, 24.9, 23.8, 15.8. HRMS (m/z): [M + H]⁺ Calcd for C₄₄H₄₅N₄O₂S₃, 757.2705; Found, 757.2714.

2-Cyano-3-(5-(4,4'-dihexyl-5'-(4-p-tolyl-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-yl)-2,2'-bithiazol-5-yl)thiophen-2yl)acrylic acid (BTT-III). The synthesis method resembles that of BTT-I using compound 4 reaction with 2-cyanoacetic acid, and the compound was purified by column chromatography on silica gel (CH₂Cl₂/EtOH = 20/1, v/v) to give a dark red solid (110 mg, yield: 85%) ¹H NMR (THF- d_8 , 400 MHz), δ : 8.34 (s, 1H), 7.65 (d, J = 4.0 Hz, 1H), 7.32 (s, 1H), 7.25 (d, J = 8.4 Hz, 1H), 7.16–7.06 (m, 3H), 7.04 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.0 Hz, 1H), 4.78 (t, J = 6.6 Hz, 1H), 4.15 (t, J = 7.0 Hz, 1H), 3.82 (t, J = 8.8 Hz, 1H), 3.01-2.92 (m, 6H), 2.21 (s, 3H), 2.04–1.97 (m, 1H), 1.77–1.71 (m, 4H), 1.56–1.53 (m, 1H), 1.37–1.24 (m, 13H), 0.86 (t, J = 6.8 Hz, 6H). ¹³C NMR (THF-*d*₈, 100 MHz), 159.7, 156.0, 155.7, 152.7, 148.3, 140.0, 137.8, 137.7, 136.6, 135.6, 131.5, 129.9, 129.6, 128.5, 127.6, 127.5, 126.0, 125.4, 120.8, 120.3, 116.1, 107.0, 69.1, 67.7, 53.9, 45.2, 35.1, 33.4, 31.7, 30.8, 29.6, 29.5, 29.1, 29.0, 27.0, 22.6, 22.5, 22.0, 19.9, 13.5. HRMS (m/z): $[M + H]^+$ Calcd for C₄₄H₄₉N₄O₂S₃ 761.3018, Found: 761.3014.

Results and discussion

Synthesis

The synthetic route to the bithiazole-based dyes (BTT-I-III) containing carbazole, triphenylamine and indoline as elec-



Scheme 1 The synthesis of the dyes BTT-I-III



Fig. 2 The absorption spectra of BTT-I–III in dichloromethane.

tron-donor is depicted in Scheme 1. The hexyl chain on the bithiazole moiety can improve the solubility and photo-voltage performance through forming a tightly packed insulating monolayer blocking I_3^- or cations approaching the TiO₂. The electron donors were connected to the intermediate molecule 1 through Suzuki coupling reaction, using 5-(5'-bromo-4,4'-dihexyl-2,2'-bithiazol-5-yl)thiophene-2-carbaldehyde with 9-octyl-9H-carbazol-3-ylboronic acid, 4-(di-phenylamino)phenylboronic acid and 4-p-tolyl-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-ylboronic acid to afford compounds 2-4, respectively. In the next step, the target products (BTT-I-III) were synthesized via the Knoevenagel condensation reaction of aldehydes 2-4 with cyanoacetic acid in the presence of acetic acid and ammonium acetate. All the intermediates and compounds were characterized by ¹H and ¹³CNMR spectroscopy and HRMS.

Absorption properties in solution and on TiO₂ film

The UV/Vis absorption spectra in dichloromethane of the dyes **BTT-I-III** are shown in Fig. 2 and the corresponding data are summarized in Table 1. In the UV/Vis spectra, these three dyes exhibit two major bands, appearing at 250–320 nm and 420–550 nm, respectively. The absorption band at 250–320 nm is ascribed to a localized aromatic π – π * transition typical of carbazole, triphenylamine and indoline units, and the prominent bands at 420–550 nm can be attributed to the intramolecular charge transfer (ICT) between the donor and the acceptor. For the charge-transfer band, the absorption

maxima in CH₂Cl₂ are at 456, 457, and 464 nm for BTT-I-III, respectively. Compared to BTT-I and BTT-II, the dye BTT-III exhibits absorption red-shifted for 8 and 7 nm, respectively. Especially, the threshold wavelength of BTT-III is red-shifted above 50 nm. This result reveals that the indoline donor is beneficial to extend the light absorption spectrum in comparison to carbazole and triphenylamine donors. The dye BTT-I containing a weaker carbazole moiety as donor exists slightly blue-shifted absorption compared with BTT-II. The molar extinction coefficients (ε_{max}) of **BTT-I–III** in dichloromethane are 32 500, 34 400, and 28 100 M⁻¹ cm⁻¹, respectively. In comparison with conventional ruthenium complexes (for example, $1.39 \times 10 \text{ M}^{-1} \text{ cm}^{-1}$ for N719),¹⁹ the molar extinction coefficients of the dyes (BTT-I-III) are obviously larger than that of N719, indicating that these dyes have good light-harvesting ability. The greater maximum absorption coefficients of the organic dyes allows for a correspondingly thinner nano-crystalline film so as to avoid the decrease in the film's mechanical strength. This also benefits the electrolyte diffusion in the film and reduces the recombination possibility of the light-induced charges during transportation.20

In order to explain the experimental spectra and gain insights into the structural properties of the chromophores, density functional theory (DFT) calculations were performed on a B3LYP/6-31G* with Gaussian 03. From Fig. 4, in the ground state the electrons are distributed at the donor for the dyes of BTT-II and BTT-III, obviously; but for BTT-I, the electrons are distributed around the whole molecule in the ground state, which is attributed to the weaker electron donor, and not beneficial for the performance of DSSCs. Upon light illumination, the electrons were exited to the LUMO orbitals, which is delocalized across the accepter part (cyanide acid) for all three dyes. On the other hand, the calculation absorption maximums of these dyes BTT-I-III are 459.9, 467.6 and 481.5 nm, which is similar to the experimental absorption maximums. The weaker electron donor of carbazole presents a blue-shifted absorption peak for BTT-I, and the stronger electron donor of indoline decides the red-shifted absorption for BTT-III.

The absorption spectra of **BTT-I–III** on thin transparent TiO_2 films (4 µm thickness) after 4 h adsorption in DCM solution are shown in Fig. 3. The maximum absorption peaks for **BTT-I–III** on the TiO_2 film are located at 441, 433, and 436 nm, respectively. The absorption peaks are blue-shifted by 15, 24, and 28 nm, respectively, from the solution spectra. The blue

Table 1 The optical and electrochemical properties of dyes BTT-I-III and calculation absorption maximums

Dye	λ^{a}_{\max}/nm ($\varepsilon \times 10^{4} \text{ M}^{-1} \text{ cm}^{-1}$)	λ^{b}_{\max}/nm Load ^c (×10 ⁻⁸ mol cm ⁻²)	E_{0-0}^{e}/eV	$E_{\mathrm{D}\ \mathrm{D}^{-1+}}^{d}/\mathrm{V}$	$E_{\mathrm{D}^*/\mathrm{D}^+}^{f}/\mathrm{V}$	λ^{g}_{\max}/nm
BTT-I	308(1.79), 456(3.25)	441(9.84)	2.25	1.14	-1.11	459.5
BTT-II	300(2.39), 457(3.44)	433(8.43)	2.42	1.06	-1.36	467.6
BTT-III	464(2.81)	436(11.6)	2.08	0.68	-1.40	481.5

^{*a*} Absorption maximum in CH₂Cl₂. ^{*b*} Absorption maximum on TiO₂ film. ^{*c*} The dye loads are calculated from absorbance data of the sensitized TiO₂ electrodes.^{24 d} $E_{\rm D D^{-1+}}$ is measured by using an SCE as reference electrode and ferrocene/ferrocenium (Fc/Fc⁺) redox couple as an external standard in dichloridemethane. ^{*e*} E_{0-0} is estimated from the absorption thresholds in dichloromethane. ^{*f*} E_{D^*/D^+} is estimated by subtracting $E_{0.0}$ to $E_{\rm D D^{-1+}}$ if The calculation absorption maximums.



Fig. 3 The absorption spectra of BTT-I–III on 4 μm TiO_2 films without CDCA and with CDCA for 2 h.

shift of the absorption spectra of **BTT-I–III** on TiO_2 film could be ascribed to the formation of H-aggregates (extended headto-tail stacking).⁸ We tested the absorption spectra of the dye sensitized TiO₂ films with co-absorbent (CDCA) for 2 h to explain the reason (Fig. 3). The maximum absorption peaks for **BTT-I–III** with CDCA are located at 446, 447, and 448 nm, respectively, in which these absorption peaks show smaller blue-shifts compared to the spectrum on TiO₂ film without CDCA, revealing the formation of dyes aggregation on TiO₂ film. Meanwhile, this result also proves that the co-adsorption of CDCA can retard the aggregation of the dyes **BTT-I–III**.



Fig. 4 The cyclic voltammetry plots of bithiazole dyes (a) BTT-I, (b) BTT-III and (c) the optimized structures and electron distribution in HOMO and LUMO levels of the BTT dyes.

Electrochemical properties

The electrochemical properties and energy diagram of the three dyes are listed in Table 1 and depicted in Fig. 4. The first oxidation potentials (E_{ox}) , corresponding to the HOMO level of these dyes, were obtained by cyclic voltammetry (CV) with 0.1 M tetrabutylammoniumhexafluorophosphate as the supporting electrolyte, Pt as the working electrode and counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The SCE reference electrode was calibrated by using a ferrocene/ferrocenium (Fc/Fc⁺). As shown in Table 1 and Fig. 4, the HOMO levels of these dyes were 1.14 V for BTT-I, 1.06 V for BTT-II and 0.68 V for BTT-III vs. NHE, respectively. They are all more positive than the iodine/iodide redox potential value (0.4 V vs. NHE), indicating that the oxidized dyes, formed after electron injection into the conduction band of TiO2, could accept electrons from the electrolyte thermodynamically. The HOMO level of BTT-III was less positive in comparison to the dyes BTT-II and BTT-I, which is ascribed to the strong electron donor ability of indoline unit. At the same time, BTT-I exhibited the most positive HOMO level, which is attributed to the weakest donor of carbazole unit. The LUMO levels of BTT-I-III were -1.11, -1.36 and -1.40 V vs. NHE, respectively. All the dyes' levels were more negative than conduction-band-edge energy level of the TiO₂ electrode (-0.5 V vs. NHE). These results indicate that the light-harvesting excited dyes can provide enough driving force for electron injection into the TiO₂ conduction band. Compared to BTT-I and BTT-II, the dye BTT-III has a much higher LUMO level, which suggests that the dye BTT-III has larger electron driving force and affords a higher photocurrent (J_{sc}) than **BTT-I** and **BTT-II**.

Photovoltaic device performance

As we know, the dyes exhibit diversified interaction between the dyes and solvents,²¹ which could cause changes of the physical and chemical properties between the dyes and semiconductor surface. Therefore, the suitable solvent for semiconductor sensitization is important to obtain good overall conversion efficiency (η), in which the effect of DCM and THF solvents on photovoltaic performance of the dyes BTT-I-III was explored. Fig. 5 shows the J-V curves for different dye baths of BTT-I-III -based DSSCs, and the corresponding photovoltaic data are collected in Table 2. The data show large differences in the performance of BTT-I-III-based DSSCs fabricated in DCM and THF dye baths. When DCM solutions of BTT-I-III were introduced to sensitize the semiconductor electrode, the DSSCs obtained the optimized η value of 5.53%, 6.19% and 6.63%, respectively; while BTT-I-III gives only 4.64%, 5.68% and 6.04% η values when the dye bath is changed to THF. The solvent effect on DSSCs performance is complicated. The possible explanation is the adsorbed amount of BTT-I-III on the TiO2 surface and the excellent surface binding modes of anchored dye in DCM. In fact, such a phenomenon has been also found in other organic dyes.²²

To reduce aggregation, the nonchromophoric adsorbents chenodeoxycholic acid (CDCA) was used as a co-absorbent for **BTT-I-III** to improve the photo-electric conversion efficiency, as it has been proven that this can improve solar cell



Fig. 5 The Current–voltage (*I–V*) characteristics of DSSCs based on BTT-I–III in solvents and co-adsorption with CDCA: (a) BTT-I, (b) BTT-II, (c) BTT-III; (d) BTT-I–III coabsorbed with 10 mM CDCA in ethanol for 2 h were listed together for comparison between these dyes.

performance significantly.²² The semiconductor films were deposited in 10 mM CDCA in ethanol for 2 h and 4 h before sensitization in **BTT-I-III** DCM solution. The *I*–*V* performances (V_{oc} , J_{sc} , ff, η) and IPCE were shown in Table 2, Fig. 5 and 6.

Table 2 Photovoltaic performance of DSSCs based on the dyes BTT-I-III in various solvents and co-absorption with CDCA with a liquid electrolyte^a

Dye	Solvent	CDCA Time/h	$V_{\rm oc}/{ m V}$	$J_{\rm sc}/{ m mA~cm^{-2}}$	ff	η /%
BTT-I	THF	0	0.677	9.62	0.71	4.64
	CH ₂ Cl ₂	0	0.671	11.90	0.69	5.53
	2 2	2	0.728	12.16	0.70	6.23
		4	0.627	11.67	0.69	5.04
BTT-II	THF	0	0.726	10.65	0.73	5.68
	CH_2Cl_2	0	0.693	13.04	0.69	6.19
		2	0.734	13.37	0.73	7.12
		4	0.667	13.09	0.70	6.07
BTT-III	THF	0	0.677	12.80	0.69	6.04
	CH_2Cl_2	0	0.740	14.04	0.64	6.63
		2	0.747	15.26	0.69	7.86
		4	0.686	13.80	0.70	6.62

 a The liquid electrolyte was 0.1 M LiI, 0.05 M I_2, 0.6 M DMPII, and 0.5 M TBP in acetonitrile.

Upon co-adsorption with CDCA for 2 h, the maximum plateau of the IPCE curves were lifted from around 70% to 80% for these three dyes (Fig. 5a, 5b and 5c), and the J_{sc} increased from 11.90 to 12.16 mA cm⁻², 13.04 to 13.37 mA cm⁻², and 14.04 to 15.26 mA cm⁻² for **BTT-I–III**, respectively (Fig. 6a, 6b and 6c). The remarkable enhancement of IPCE was attributed to higher injection efficiency resulting from relative independent dye molecules arraying on semiconductor surface.¹⁸ Here, the increased V_{oc} from 0.671 to 0.728 V for BTT-I, 0.693 to 0.734 V for BTT-II and 0.740 to 0.747 V for BTT-III was caused by the retarded charge recombination because of co-adsorption. The remarkable decrease of IPCE and J_{sc} could be found when the films were absorbed with CDCA for 4 h. This may be attributed to the substitution of CDCA molecular for dyes on films, resulting in the reduction of the dyes' adsorption amount. Finally, upon co-adsorption with CDCA for 2 h, three dyes yielded an increased overall conversion efficiency of 6.23%, 7.12% and 7.86%, respectively.

Among these dyes, Fig. 5d showed the current-voltage characteristics of DSSCs fabricated with **BTT-I-III** as sensitizers co-absorbed with 10 mM CDCA in ethanol for 2 h under standard global AM 1.5 solar light condition. The similar opencircuit voltages of these dyes were about 728–747 mV. The





Fig. 6 The IPCE spectra of DSSCs based on BTT-I–III in solvents and co-absorption with CDCA: (a) BTT-I, (b) BTT-II, (c) BTT-III, (d) BTT-I–III co-absorbed with 10 mM CDCA in ethanol for 2 h were listed together for comparison between these dyes.

higher V_{oc} was ascribed to decrease of electron recombination because of two long alkyl chains attached on thiazole moiety. The similar dark current of these dyes shown in Fig. 5d also proved this phenomenon. In comparison with the dyes BTT-I and BTT-II, the short-circuit current of BTT-III was higher, which was attributed to a much broader absorption spectra and the more negative LUMO levels due to a stronger electron driving-force for excited dyes' electron injection. Although the molar extinction coefficient of BTT-III was lower than those of BTT-I and BTT-II, BTT-III had the largest adsorption amount of 11.6 \times 10⁻⁸ mol cm⁻² (Table 1). The much greater adsorption of BTT-III can counteract this influence, indicating that the BTT-III can harvest sunlight more efficiently. The dyes BTT-I and BTT-II had similar absorption spectra, but the dye BTT-I had a lower short-circuit current than BTT-II. This could be explained by the decreased driving-force for electron-injection. The photocurrent improvement trend accorded very well with the IPCE measurements shown in Fig. 6d.

Fig. 6d showed the spectra of the incident photon-to-current conversion efficiency (IPCE) based on these dyes upon coadsorption with CDCA for 2 h. All the dyes exhibited a high plateau in the visible region between 350–580 nm. Although **BTT-III** had a little lower IPCE value in the region between 350–520 nm compared to **BTT-II**, **BTT-III** exhibited a broader spectrum and kept higher IPCE value during 580–650 nm. It conformed very closely to the absorption spectrum on the film with the co-absorbent. The region of the IPCE spectra of **BTT-I** resembled that of **BTT-II** due to the similar absorption spectrum on the film with the co-absorbent. However, the maximum value of **BTT-I** was reduced compared to **BTT-II**, which indicated the lowest photocurrent, as a result of the weakest electron-injection driving-force of carbazole.

Electron lifetime and EIS measurements

In addition, electrochemical impedance spectroscopy (EIS) was employed to study the electron recombination in DSSCs based on these dyes upon co-adsorption with CDCA for 2 h under -0.70 V bias applied voltages in the dark and analyzed by the software ZSimpWin. The EIS measurement was shown in Fig. 7, and the data was listed in Table 3. $R_{\rm S}$, $R_{\rm rec}$, and $R_{\rm CE}$ represent series resistance and charge-transfer resistance at the dye/TiO₂/electrolyte interface and counter electrode (CE), respectively. The value of $R_{\rm S}$ and $R_{\rm CE}$ (the first semi-circle in the Nyquist plot) were almost the same for these three dyes



Fig. 7 Impedance spectra of DSSCs based on dyes **BTT-I–III**. (a) Nyquist plots, (b) Bode phase plots, (c) the equivalent circuits. The lines of (a) and (b) show theoretical fits using the equivalent circuits (c).

because of the same electrode material and same electrolyte. The charge-transfer resistance was determined by the middle semi-circle in Nyquist plot. From the EIS measurements, the electron lifetime (τ_e) expressing the electron recombination

Table 3 Parameters obtained by fitting the impedance spectra of the DSSCs with sensitizers $^{\rm a}$

Dye	$R_{ m S}/\Omega$	$R_{\rm CE}/\Omega$	$R_{ m rec}/\Omega$	$\tau_{\rm e}/{\rm ms}$
BTT-I	18.47	$6.04 \\ 6.00 \\ 5.52$	45.92	16.5
BTT-II	17.41		50.51	17.3
BTT-III	15.63		53.73	19.1

^{*a*} All the parameters were obtained from the software ZSimpWin, using the equivalent circuits Fig. 7(c).

between the electrolyte and TiO₂ was calculated following a literature procedure.²³ The $R_{\rm rec}$ for dyes **BTT-I–III** were 45.92, 50.51 and 53.73 Ω , respectively. The larger resistance of $R_{\rm rec}$ indicated that the higher open-circuit voltage for these dyes. The calculated electron lifetimes of **BTT-I–III** were 16.5, 17.3 and 19.1 ms, respectively. Among **BTT-I–III**, **BTT-III**-based cell has longer electron lifetime, which leads to lower rate of charge recombination and thus improved $V_{\rm oc}$.

Conclusions

In summary, three metal-free bithiazole-based organic dyes containing different electron donors (carbazole, triphenylamine and indoline) in the D-A- π -A configuration were synthesized and characterized for application in DSSCs. The results demonstrated that modification of the electron donor is an effective method to control the electrochemical and absorption properties. Notably, the HOMO and LUMO energy levels can be tuned by introducing different electron donors in the dye molecule. Co-adsorption of 10 mM CDCA for 2 h can significantly enhance photovoltaic performance of these dyes. Moreover, the power conversion efficiency was shown to be sensitive to the structural modifications of electron-donor units. Among the three dyes, DSSCs based on the BTT-III with indoline donor exhibits the best overall conversion efficiency of 7.86% (J_{sc} = 15.26 mA cm⁻², V_{oc} = 747 mV, ff = 0.69) under standard AM 1.5 (100 mW cm⁻²). This research enriches the application of bithiazole-based derivatives in DSSCs and indicates that the donor of the dye molecules can efficiently impact the optoelectronic properties.

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