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Molecular engineering of dithiafulvene organic sensitizers with pyridine acceptor for high efficiency dye-sensitized solar cells

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ABSTRACT Donor- π -acceptor (D- π -A) organic compounds have drawn keen interests as photosensitizers in dye sensitized solar cells (DSSCs). Recent studies showed that pyridine ring as an electron-withdrawing anchoring group could lead to efficient electron injection. To improve the performance of pyridine containing sensitizers based DSSCs, the electron donor, π -bridge and the whole structure should be well engineered at molecular level. In this work, we prepared two monomer type dithiafulvene based sensitizers both with a pyridine acceptor but differing in the phenyl-thienyl (DTFPy3) and thienyl-phenyl π -bridges (DTFPy4), and two corresponding dimeric congeners D-DTFPy3 and D-DTFPy4, and tested them in DSSCs. It was found that the arrangement of the electron-rich thienyl group adjacent to the electron donor moiety in the π -bridge red-shifted in the absorption, and the dimeric sensitizers exhibited significantly enhanced absorption. Among them, D-DTFPy4 garnered the highest light harvesting efficiency, yielding an overall power conversion efficiency up to 5.26%.

Keywords: dye sensitized solar cells, dithiafulvene, pyridine acceptor, dimeric sensitizer

INTRODUCTION

Since the pioneering work on dye sensitized solar cells (DSSCs) by Grätzel and O'Regan in 1991 [1], many studies have focused on both material development and cell fabrication for improving the cell performance [2–18]. Over the past decades, donor- π -acceptor (D- π -A) type organic compounds as photosensitizers have drawn keen interests due to their advantages of high molar extinction coefficients, flexible structure design, low material cost

and simple preparation process [19–28]. In a typical D- π -A organic sensitizer, cyanoacrylic acid is frequently used both as an electron acceptor and as an anchoring group for attachment to a mesoporous TiO₂ surface. The carboxyl group enables a good electron communication between the sensitizer and TiO₂ by forming a strong bidentate bridging linkage with Brønsted acid sites on the TiO₂ surface [29–34]. Considering that the formation of coordinate bonds between the lone pair of electrons on the nitrogen atom of the pyridine ring and the Lewis acid sites of the TiO₂ surface would enable efficient electron injection arising, various organic sensitizers using pyridine as an electron-withdrawing anchoring group have been prepared and studied in DSSCs [31,35–41].

One of the drawbacks of organic sensitizers with a pyridine anchoring group is their relatively narrow absorption spectrum and low absorption intensity. The optimal organic sensitizer for solar cell applications should possess a broad absorption spectrum in order to produce large photocurrent response [10]. In order to address this issue, organic sensitizers comprising electron donor, π -bridge and molecular structure should be well engineered at molecular level to meet the efficiency. For example, adjusting the π -bridge components in an organic sensitizer molecule can increase the intramolecular charge transfer (ICT) effect, and lead to red-shift of the absorption [42]. In addition, organic sensitizers bearing a monomer D- π -A type structure often afford limited electron extraction. If the light-harvesting units are increased in single sensitizer molecule, the absorption bands may be broadened and the intensity

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can be increased. Actually, among organic sensitizers using cyanoacrylic acid as acceptor, double D- π -A branched sensitizers with two light-harvesting units have shown improved light response, increased photocurrent compared to its monobranched analogues [43,44].

In our previous work, monobranched D- π -A dithiafulvene (DTF) derivatives have shown great potential for high efficient DSSCs, owing to their well-known electron-donating ability, easy synthesis, compact dye adsorption and effective charge separation [45]. However, the strategies to improve the performance of DTF-based organic sensitizers using pyridine as electron-withdrawing anchoring group are still limited. In this work, in order to investigate how to improve the light-harvesting ability of the organic sensitizers, we prepared two monobranched DTF-based sensitizers both with a pyridine anchoring group but differing in the phenyl-thienyl (DTFPy3) and thienyl-phenyl π -bridges (DTFPy4), and, two corresponding dimeric congeners of these two monomers **D-DTFPy3** and **D-DTFPy4**, as shown in Scheme1. By adjusting the electron rich thienyl group adjacent to the DTF donor moiety in the π -bridge, **DTFPy4** exhibits absorption red-shifting compared to **DTFPy3** with an electron poor phenyl group adjacent to the DTF moiety. Furthermore, after increasing the light-harvesting units, both **D-DTFPy3** and **D-DTFPy4** show significantly enhanced absorption intensity. Finally, **D-DTFPy4** sensitized solar cells exhibit the highest power conversion efficiency (η) of 5.26%, with a short-circuit photocurrent density (J_{sc}) of 11.7 mA cm⁻², an open-circuit photovoltage (V_{oc}) of 630 mV, and a fill factor (FF) of 0.71, under standard global AM 1.5 solar light condition.

EXPERIMENTAL SECTION

Materials

All solvents and reagents, unless otherwise stated, were of high-purity and used as received. 4-Formylphenylboronic acid, 2-bromothiophene, 4-bromobenzaldehyde, pyridine-4-boronic acid, 5-bromo-2-thiophenecarboxaldehyde, 4-bromophenylboronic acid, triethyl phosphite and Pd(PPh₃)₄ were purchased from Energy Chemical.

General

NMR spectra (¹H and ¹³C) were recorded at room temperature on Bruker AV 600 MHz spectrometer. Data are listed in parts per million (ppm) on the delta scale (δ) and coupling constants were reported in Hz. The splitting patterns are designated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet) and br (broad). Mass spectra

measured on Microflex MALDI-TOF MS. UV-vis spectra of dye in solution and loading on TiO₂ films were measured with a HITIACH U-3900 spectrometer at room temperature. Photoluminescent (PL) spectra were recorded in a Horiba Fluoromax 4 spectrometer. Cyclic voltammetry (CV) was carried out on a CHI600E Electrochemical Analyzer at a scan rate of 0.1 V s⁻¹. The oxidation potential of the sensitizer was measured in dimethylformamide (DMF) with TBAPF₆ (0.1 mol L⁻¹) as electrolyte and glassy carbon as working electrode, Ag/Ag⁺ as reference electrode, Pt as counter electrode. The potential of the reference electrode was calibrated with Fc/Fc⁺ as an internal reference and converted to normal hydrogen electrode (NHE) by addition of 630 mV. Theoretical calculations using density functional theory (DFT) were performed using the Gaussian03 package at the B3LYP/6-31G* level.

Synthesis

Compound **HDT** (4,5-bis(hexylthio)-1,3-dithiole-2-thione) was synthesized as reported in our previous work [45].

Compound **1** 2-(4-formylphenyl)thiophene. 4-Formylphenylboronic acid (1.62 g, 10.8 mmol) was treated with 2-bromothiophene (1.47 g, 9 mmol) in the presence of Pd(PPh₃)₄ (326 mg, 282 μ mol), 1 mol L⁻¹ aqueous solution of K₂CO₃ (18 mL) and 1,2-dimethoxyethane (70 mL). The mixture was refluxed for 6 h under nitrogen atmosphere. After cooling down to room temperature, and addition of dichloromethane, the mixture was washed with water and dried on magnesium sulfate. The solvent was removed by rotary evaporation and the residue was purified by silicon gel column chromatography with petroleum ether:ethyl acetate (6:1, v:v) as eluent to afford **1** as a yellow solid (1.02 g, yield 60%). ¹H NMR (600 MHz, CDCl₃, ppm): δ = 10.01 (s, 1H), 7.89 (d, 2H, J = 8.4 Hz), 7.77 (d, 2H, J = 8.4 Hz), 7.47 (d, 1H, J = 7.2 Hz), 7.40 (d, 1H, J = 7.2 Hz), 7.14 (m, 1H). MALDI-TOF: m/z [M]⁺ calcd. C₁₁H₈OS, 188.2456; found: 188.2453.

Compound **2** 4-(5-bromothiophen-2-yl)benzaldehyde. To a stirred solution of **1** (2.0 g, 10.6 mmol) in 20 mL of tetrahydrofuran (THF) in a 100 mL flask was slowly added *N*-bromosuccinimide (2.27 g, 12.8 mmol) and acetic acid (20 mL). After the addition, the mixture was stirred at room temperature for 4 h until TLC showed no starting material left. The mixture was washed with water, dried with anhydrous magnesium sulfate, and filtered. The product was obtained after evaporation of the solvent and dried in vacuum to afford **2** as white solid (2.52 g, yield: 88%). ¹H NMR (600 MHz, CDCl₃, ppm): δ = 10.00 (s,

1H), 7.88 (d, 2H, $J = 8.2$ Hz), 7.67 (d, 2H, $J = 8.2$ Hz), 7.21 (d, 1H, $J = 3.9$ Hz), 7.09 (d, 1H, $J = 3.9$ Hz). MALDI-TOF: m/z [M]⁺ calcd. C₁₁H₇BrOS, 265.9401; found: 265.9399.

Compound 3 4-(5-(pyridin-4-yl)thiophen-2-yl)benzaldehyde. Pyridine-4-boronic acid (1.11 g, 9 mmol) was treated with **2** (0.9 g, 3.4 mmol) in the presence of Pd(PPh₃)₄ (145 mg, 125 μmol), 1 mol L⁻¹ aqueous solution of K₂CO₃ (15 mL) and 1,2-dimethoxyethane (75 mL). The mixture was refluxed for 6 h under nitrogen atmosphere. After cooling down to room temperature, and addition of dichloromethane, the mixture was washed with water and dried on magnesium sulfate. The solvent was removed by rotary evaporation and the residue was purified by silicon gel column chromatography with petroleum ether:ethyl acetate (6:1, $v:v$) as eluent to afford **3** as a yellow solid (538 mg, yield 60%). ¹H NMR (600 MHz, CDCl₃, ppm): δ = 10.03 (s, 1H), 8.64 (d, 2H, $J = 6.1$ Hz), 7.93 (d, 2H, $J = 8.4$ Hz), 7.80 (d, 2H, $J = 8.3$ Hz), 7.54 (d, 1H, $J = 3.9$ Hz), 7.51 (d, 2H, $J = 6.8$ Hz), 7.49 (d, 1H, $J = 3.9$ Hz). MALDI-TOF: m/z [M]⁺ calcd. C₁₆H₁₁NOS, 265.0561; found: 265.0559.

Compound 4 5-(4-bromophenyl)thiophene-2-carbaldehyde. 4-Bromophenylboronic acid (1.93 g, 9.6 mmol) was treated with 5-bromo-2-thiophenecarboxaldehyde (1.53 g, 8 mmol) in the presence of Pd(PPh₃)₄ (290 mg, 250 μmol), 1 mol L⁻¹ aqueous solution of K₂CO₃ (20 mL) and 1,2-dimethoxyethane (90 mL). The mixture was refluxed for 6 h under nitrogen atmosphere. After cooling down to room temperature, and addition of dichloromethane, the mixture was washed with water and dried on magnesium sulfate. The solvent was removed by rotary evaporation and the residue was purified by silicon gel column chromatography with petroleum ether:ethyl acetate (6:1, $v:v$) as eluent to afford **4** as yellow solid (576 mg, yield 27%). ¹H NMR (600 MHz, CDCl₃, ppm): δ = 9.90 (s, 1H), 7.74 (d, 1H, $J = 3.9$ Hz), 7.57 (d, 2H, $J = 8.7$ Hz), 7.54 (d, 2H, $J = 8.8$ Hz), 7.40 (d, 1H, $J = 3.9$ Hz). MALDI-TOF: m/z [M]⁺ calcd. C₁₁H₇BrOS, 265.9401; found: 265.9398.

Compound 5 5-(4-(pyridin-4-yl)phenyl)thiophene-2-carbaldehyde. Pyridine-4-boronic acid (369 mg, 3.0 mmol) was treated with **4** (548 mg, 2.5 mmol) in the presence of Pd(PPh₃)₄ (92 mg, 79 μmol), 1 mol L⁻¹ aqueous solution of K₂CO₃ (4 mL) and 1,2-dimethoxyethane (30 mL). The mixture was refluxed for 6 h under nitrogen atmosphere. After cooling down to room temperature, and addition of dichloromethane, the mixture was washed with water and dried on magnesium sulfate. The solvent was removed by rotary evaporation and the residue was purified by silicon gel column chromatography with petroleum ether:ethyl acetate (6:1, $v:v$) as eluent to afford **5** as a yellow solid (330

mg, yield 49%). ¹H NMR (600 MHz, CDCl₃, ppm): δ = 9.93 (s, 1H); 8.70 (d, 2H, $J = 6.1$ Hz); 7.81 (d, 2H, $J = 8.6$ Hz); 7.79 (d, 1H, $J = 3.9$ Hz); 7.73 (d, 2H, $J = 8.6$ Hz); 7.54 (d, 2H, $J = 6.1$ Hz); 7.49 (d, 1H, $J = 3.9$ Hz). MALDI-TOF: m/z [M]⁺ calcd. C₁₆H₁₁NOS, 265.0561; found: 265.0558.

Compound DTFPy3 4-(5-(4-((4,5-bis(hexylthio)-1,3-dithiol-2-ylidene)methyl)phenyl)thiophen-2-yl)pyridine. **HDT** (878.4 mg, 2.4 mmol) and **3** (400 mg, 1.51 mmol) were dissolved in 20 mL of boiling toluene under nitrogen atmosphere, then P(OEt)₃ (7 mL) was added. The resulting mixture was refluxed for 3 h. After cooling and addition of dichloromethane, the mixture was washed with brine and dried on magnesium sulfate. The solvent was removed by rotary evaporation and the residue was purified by silicon gel column chromatography with petroleum ether:ethyl acetate (4:1, $v:v$) as eluent to afford **DTFPy3** as an orange solid (626 mg, yield 71%). ¹H NMR (600 MHz, CDCl₃, ppm): δ = 8.60 (d, 2H, $J = 6.0$ Hz); 7.63 (d, 2H, $J = 8.4$ Hz); 7.49 (d, 1H, $J = 3.8$ Hz); 7.48 (d, 2H, $J = 6.8$ Hz); 7.33 (d, 1H, $J = 3.8$ Hz); 7.25 (d, 2H, $J = 8.4$ Hz); 6.48 (s, 1H); 2.84 (t, 4H, $J = 7.4$ Hz); 1.66 (m, 4H); 1.43 (m, 4H); 1.32 (m, 8H); 0.90 (t, 6H). ¹³C NMR (151 MHz, CDCl₃, ppm): δ = 153.33; 148.91; 144.14; 139.13; 136.49; 133.72; 130.76; 129.34; 128.76; 127.75; 126.93; 122.35; 116.37; 106.77; 39.06; 34.24; 32.65; 31.15; 25.44; 16.91. MALDI-TOF: m/z [M]⁺ calcd. C₃₁H₃₇NS₅, 583.9572; found: 583.9569.

Compound DTFPy4 4-(4-(5-((4,5-bis(hexylthio)-1,3-dithiol-2-ylidene)methyl)thiophen-2-yl)phenyl)pyridine. A procedure similar to that for synthesizing compound **DTFPy3** was followed but using compound **5** (400 mg, 1.5 mmol) instead of compound **3**. After removing the solvent, the residue underwent recrystallization from acetone and gave **DTFPy4** as an orange solid (495 mg, yield 56%). ¹H NMR (600 MHz, CDCl₃, ppm): δ = 8.67 (d, 2H, $J = 6.0$ Hz); 7.72 (d, 2H, $J = 8.4$ Hz); 7.66 (d, 2H, $J = 8.4$ Hz); 7.53 (d, 2H, $J = 6.1$ Hz); 7.34 (d, 1H, $J = 3.8$ Hz); 6.86 (d, 1H, $J = 4.4$ Hz); 6.68 (s, 1H); 2.86 (t, 4H, $J = 7.2$ Hz); 1.67 (m, 4H); 1.43 (m, 4H); 1.31 (m, 8H); 0.90 (t, 6H). ¹³C-NMR (151 MHz, CDCl₃, ppm): δ = 149.32; 146.49; 140.37; 139.70; 135.49; 134.12; 130.75; 127.59; 126.41; 124.87; 124.01; 123.04; 120.17; 106.77; 35.30; 30.33; 28.72; 27.23; 21.54; 13.03. MALDI-TOF: m/z [M]⁺ calcd. C₃₁H₃₇NS₅; 583.9572. Found: 583.9570.

Compound D-DTFPy3 4-(5-(4-(1,2-bis(4,5-bis(hexylthio)-1,3-dithiol-2-ylidene)-2-(4-(5-(pyridin-4-yl)thiophen-2-yl)phenyl)ethyl)phenyl)thiophen-2-yl)pyridine. **DTFPy3** (500 mg, 0.86 mmol) and iodine (654 mg, 2.57 mmol) were added in dichloromethane (20 mL), and the mixture was stirred at room temperature for 5 h. A

saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ was added, and the resulting mixture was stirred at room temperature for another 1 h. The organic layer was separated, washed with H_2O , dried over MgSO_4 . The solvents were removed by rotary evaporation and the residue was purified by silicon gel column chromatography with petroleum ether:ethyl acetate (4:1, *v:v*) as eluent to afford **D-DTFPy3** as a brown semisolid (320 mg, yield 64%). ^1H NMR (600 MHz, CDCl_3 , ppm): δ = 8.59 (d, 4H, J = 6.0 Hz); 7.61 (d, 4H, J = 8.4 Hz); 7.48 (d, 2H, J = 3.8 Hz); 7.46 (m, 8H); 7.31 (d, 2H, J = 3.8 Hz); 2.85 (t, 4H, J = 7.2 Hz); 2.77 (t, 4H, J = 7.2 Hz); 1.66 (m, 6H); 1.59 (m, 6H); 1.43 (m, 4H); 1.32 (m, 8H); 1.26 (m, 8H); 0.90 (t, 6H); 0.86 (t, 6H). ^{13}C -NMR (151 MHz, CDCl_3 , ppm): δ = 149.56; 146.24; 141.87; 139.51; 137.98; 136.87; 131.65; 129.04; 127.28; 127.03; 126.85; 126.05; 125.97; 124.24; 119.60; 36.18; 35.98; 31.32; 31.18; 29.65; 29.59; 28.21; 22.52; 22.38; 14.03; 13.97. MALDI-TOF: m/z $[\text{M}]^+$ calcd. $\text{C}_{62}\text{H}_{72}\text{N}_2\text{S}_{10}$, 1164.2903; found: 1164.2901.

Compound **D-DTFPy4** 4-(4-(5-(1,2-bis(4,5-bis(hexylthio)-1,3-dithiol-2-ylidene)-2-(5-(4-(pyridin-4-yl)phenyl)thiophen-2-yl)phenyl)pyridine. A procedure similar to that for synthesizing compound **D-DTFPy3** was followed but using compound **DTFPy4** (700 mg, 1.20 mmol) instead of compound **DTFPy3**. After removing the solvents, the residue was purified by silicon gel column chromatography with petroleum ether:ethyl acetate (4:1, *v:v*) as eluent to afford **D-DTFPy4** as a dark-red solid (480 mg, yield 68%). ^1H NMR (600 MHz, CDCl_3 , ppm): δ = 8.66 (d, 4H, J = 6.0 Hz); 7.71 (d, 4H, J = 8.4 Hz); 7.64 (d, 4H, J = 8.4 Hz); 7.52 (d, 4H, J = 6.0 Hz); 7.33 (d, 2H, J = 4.2 Hz); 6.96 (d, 2H, J = 4.2 Hz); 2.93 (t, 4H, J = 7.2 Hz); 2.80 (t, 4H, J = 7.2 Hz); 1.72 (m, 4H); 1.60 (m, 12H); 1.48 (m, 4H); 1.34 (m, 12H); 0.92 (t, 6H); 0.84 (t, 6H). ^{13}C -NMR (151 MHz, CDCl_3 , ppm): δ = 150.17; 147.61; 141.52; 140.27; 136.62; 136.42; 135.18; 130.63; 127.37; 126.32; 125.98; 125.05; 124.35; 121.19; 118.14; 36.44; 36.07; 31.38; 31.29; 29.71; 29.59; 28.27; 28.16; 22.57; 22.49; 14.08; 14.01. MALDI-TOF: m/z $[\text{M}]^+$ calcd. $\text{C}_{62}\text{H}_{72}\text{N}_2\text{S}_{10}$, 1164.2903; found: 1164.2900.

DSSCs fabrication and photovoltaic measurements

The preparation of DSSCs photoanode and electrolyte followed the previous literature [45]. In cell assembly, the sensitizers were loaded onto the TiO_2 (~14 μm thick) film by immersion into its THF solutions (0.2 mmol L^{-1} dye) without any co-absorbants for 30 h at room temperature. Before drying under vacuum, the films were rinsed with acetonitrile to remove the unabsorbed sensitizers multiple times

until the solution became clear. Then, the films were assembled into a solar cell together with a Pt-sputtered FTO counter electrode and acetonitrile/valeronitrile (85:15, volume ratio) electrolyte containing 0.6 mol L^{-1} 1,2-dimethyl-3-propylimidazoliumiodide, 0.03 mol L^{-1} I_2 , 0.1 mol L^{-1} guanidinium thiocyanate, and 0.5 mol L^{-1} 4-tertbutylpyridine. The active area of the photoanode film for the DSSC performance test was typically 0.25 cm^2 .

The photocurrent density-voltage (J - V) characteristics curves were measured by the Newport PVIV-3A system. The light source (Oriel solar simulator, 450 W Xe lamp, AM 1.5 global filter) was calibrated to 1 sun (100 mW cm^{-2}). Incident photon to current efficiency (IPCE) was measured at varying wavelengths (350–750 nm) with an interval of 5 nm. Nyquist spectroscopy was measured on the electrochemical workstation (Zahner, Zennium) with a frequency response analyzer under an intensity modulated (5–70 W m^{-2}) light emitting diode (525 nm) driven by a Zahner (PP211) source supply. The frequency range was set from 100 KHz to 0.1 Hz.

RESULTS AND DISCUSSION

Synthesis

The synthetic routes of monomeric **DTFPy3** and **DTFPy4**, and, dimeric **D-DTFPy3** and **D-DTFPy4** are depicted in Scheme 1. Bromide aromatic aldehydes **2** and **4** reacted with pyridine-4-boronic acid via Suzuki coupling to give the key intermediate aldehydes **3** and **5**, respectively. Compounds **3** and **5** were then subjected to a phosphite-induced Horner-Wittig condensation with thione **HDT** to produce monomeric **DTFPy3** and **DTFPy4**. With the monomers in hand, iodine-induced oxidative dimerization reactions were undertaken in dichloromethane at room temperature. The crude products of the dimerization reactions **D-DTFPy3** and **D-DTFPy4** were obtained after a brief reductive aqueous workup with $\text{Na}_2\text{S}_2\text{O}_3$. Column chromatographic purification then afforded dimeric **D-DTFPy3** and **D-DTFPy4** as brown semisolid and dark-red solid, respectively. The molecular structures of these compounds were characterized on the basis of ^1H NMR, ^{13}C NMR and mass spectra.

Optical and electrochemical properties

The UV-Vis absorption spectra of these sensitizers in dilute THF are shown in Fig. 1a and the corresponding spectroscopic parameters extracted are summarized in Table 1. All of the sensitizers exhibit strong absorption bands in the range of 400–450 nm and weak bands around 300–350 nm.

Scheme 1 Synthetic routes of DTFPy3, DTFPy4, D-DTFPy3 and D-DTFPy4.

Figure 1 (a) UV-vis spectra of DTFPy3, DTFPy4, D-DTFPy3 and D-DTFPy4 in dilute THF solution ($1 \times 10^{-5} \text{ mol L}^{-1}$), and (b) normalized UV-vis spectra of DTFPy3, DTFPy4, D-DTFPy3 and D-DTFPy4 on TiO_2 films.

Table 1 Optical and electrochemical properties of DTFPy3, DTFPy4, D-DTFPy3 and D-DTFPy4

Sensitizer	$\lambda_{\text{max}}^{\text{abs}}$ (nm)	ϵ ($\text{L mol}^{-1} \text{ cm}^{-1}$)	$\lambda_{\text{max}}^{\text{cms}}$ (nm)	E_{ox} (V vs. NHE)	$E_{0-0}^{\text{abs/cms}}$ (eV)	$E_{\text{ox}} - E_{0-0}$ (V vs. NHE)	LHE
DTFPy3	407	4.35×10^4	514	1.23	2.71	-1.48	0.888
DTFPy4	417	3.85×10^4	507	1.22	2.69	-1.47	0.929
D-DTFPy3	405	7.82×10^4	503	1.09	2.78	-1.69	0.946
D-DTFPy4	419	8.27×10^4	506	1.10	2.70	-1.60	0.962

The weak absorption bands are assigned to a more localized aromatic $\pi-\pi^*$ transition, and the strong absorption bands are attributed to the ICT effect between the donor and acceptor. The absorption maximum (λ_{max}) was observed at

407 nm (molar extinction coefficient $\epsilon = 4.35 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) for DTFPy3 and 417 nm ($\epsilon = 3.85 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) for DTFPy4. Such a bathochromic shift of DTFPy4 can be attributed to the adjusted electron-rich thienyl group adja-

cent to the donor part in the π -bridge. After increasing the light-harvesting units, as expected, the dimeric **D-DTFPy3** and **D-DTFPy4** possess broader and more intensive absorption in the ultraviolet and visible region, which could produce a higher J_{sc} in the DSSCs. The ϵ of **D-DTFPy3** ($7.82 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) and **D-DTFPy4** ($8.27 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) are much higher than those of their monomers in the range of 400–500 nm, indicating that the dimeric sensitizers have good light-harvesting ability. While the trend of extinction coefficient is plausible, the λ_{max} for **D-DTFPy3** (405 nm) and **D-DTFPy4** (419 nm) are similar to that of **DTFPy3** and **DTFPy4**, which indicates the ICT effect is not impacted by dimerization.

The profiles of the absorption spectra of TiO_2 films (4 μm) with these sensitizers loading show dramatically broaden and red-shift absorption relative to their solution spectra, as shown in Fig. 1b. These observations can be related to the formation of J-aggregates of these sensitizers on the TiO_2 surfaces. The broadened absorption band and the red-shifted absorption onset on the thin film afford increased light harvesting. Especially, **D-DTFPy4** possesses the broadest light response range among the four sensitizers, and thus is expected to yield improved performance for DSSCs.

The molecular orbital energy levels of the sensitizers were derived from CV (Fig. S1) in combination with the excitation transition energies (E_{0-0}) determined by the intersection of absorption and photoluminescence spectra (Fig. S2), and are presented in Table 1. The first oxidation potentials (E_{ox}) of the ground state of **DTFPy3**, **DTFPy4**, **D-DTFPy3** and **D-DTFPy4** are corresponding to their highest occupied molecular orbit (HOMO) levels. It was found that the HOMO levels of the dimeric sensitizers **D-DTFPy3** and **D-DTFPy4** are slightly higher than that of monomeric sensitizers **DTFPy3** and **DTFPy4**. All of the HOMO levels of these four sensitizers are more positive than the iodide/triiodide couple (0.40 V vs. NHE), indicating a thermodynamically downhill regeneration of the photo oxidized sensitizers by accepting electrons from the surrounding I^- ions. The lowest unoccupied molecular orbit (LUMO) levels of **DTFPy3**, **DTFPy4**, **D-DTFPy3** and **D-DTFPy4**, calculated as $E_{ox} - E_{0-0}$, are sufficiently negative relative to the conduction-band edge of TiO_2 (−0.5 V vs. NHE), ensuring an efficient excite electron injection driving force.

Theoretical calculations

In order to understand the photo-induced charge separation of **DTFPy3**, **DTFPy4**, **D-DTFPy3** and **D-DTFPy4**,

the time dependent density functional (TD-DFT) calculations were performed on electron-density distribution of the HOMOs and LUMOs of the four sensitizers. To facilitate the calculation, the hexyl chains were replaced by methyl groups. As shown in Fig. 2, the HOMO electron density for the sensitizers is mainly located at the electron-donor part and the adjacent aromatic rings, while the electron density of LUMO is transferred to the pyridine acceptor unit. More obvious electron density separation going from **DTFPy3** to **DTFPy4** and **D-DTFPy3** to **D-DTFPy4** is observed, which explains the red-shifted absorption of **DTFPy4** and **D-DTFPy4** with the featured π -bridge arrangement. It demonstrates that the 4-pyridyl group is predominantly adsorbed onto the TiO_2 through coordinate bond between the pyridyl group and the Lewis-acidic sites on the TiO_2 surface. Therefore upon photo-excitation, the electron density is redistributed in the LUMO moving towards the pyridine moiety anchored on TiO_2 and the π -bridge arrangement in **DTFPy4** and **D-DTFPy4** appears to be more desirable for the required charge separation in DSSCs.

Furthermore, the light harvesting efficiencies (LHEs) of the four sensitizers were calculated using the oscillator strengths obtained by the TD-DFT calculation. The sensitizers with high LHE generally ensure a better photocurrent response. From Table 1, it is found that the LHE

Figure 2 Electron-density distributions for the HOMOs and LUMOs of the **DTFPy3**, **DTFPy4**, **D-DTFPy3** and **D-DTFPy4**.

becomes greater with the increase of the light-harvesting units from DTFPy3 and DTFPy4 to D-DTFPy3 and D-DTFPy4, as reflected by the increase in LHE from 0.888 to 0.962. This finding clearly indicates that the dimeric sensitizers D-DTFPy4 afford the best LHE and highest J_{sc} .

Photovoltaic properties

The J - V characteristics of the solar cells sensitized with sensitizers DTFPy3, DTFPy4, D-DTFPy3 and D-DTFPy4 measured under standard AM 1.5G conditions (100 mW cm^{-2}) are shown in Fig. 3a. Relevant photovoltaic parameters are collected in Table 2. For monomer-type sensitizers, DTFPy4 exhibits better cell performance parameters ($\eta = 3.14\%$; $J_{sc} = 7.25 \text{ mA cm}^{-2}$, $V_{oc} = 626 \text{ mV}$, FF = 0.69) compared to DTFPy3 ($\eta = 2.74\%$; $J_{sc} = 6.96 \text{ mA cm}^{-2}$, $V_{oc} = 607 \text{ mV}$, FF = 0.65) as the adjusting of the π -bridge. Compared to their monomeric counterparts, both dimeric D-DTFPy3 and D-DTFPy4 exhibit enhanced photovoltaic performances under the similar fabricating and measuring conditions. With an enhanced J_{sc} , the DSSC based on D-DTFPy3 exhibits a higher η of 4.03%. The DSSC based on D-DTFPy4 shows the best photovoltaic performance with a J_{sc} of 11.7 mA cm^{-2} , a V_{oc} of 630 mV, and an FF of 0.71, corresponding to the η of 5.26%.

It is noted that the amount of the monomer-type sensitizers adsorbed on TiO_2 is larger than that of the dimer-type

sensitizers, but the J_{sc} for the four sensitizers decreases in the order D-DTFPy4 > D-DTFPy3 > DTFPy4 > DTFPy3. This result may be rationalized by the following reasons: (1) the dye adsorption is directly related to the structure and the molecular size of the sensitizers. Monomeric sensitizers DTFPy3 or DTFPy4 exhibit higher loading on the TiO_2 surface, because they have smaller sizes; (2) each monomeric molecule of DTFPy3 or DTFPy4 contains only one light-harvesting unit, while each dimeric molecule of D-DTFPy3 or D-DTFPy4 has doubled light-harvesting units adsorbed on TiO_2 , which determines the light-harvesting efficiency and η of the DSSC. Further study of the IPCE spectra confirmed the trend of J_{sc} . Compared to the cells based on DTFPy3 and DTFPy4 with a narrow and relatively low IPCE values, the cells based on D-DTFPy3 and D-DTFPy4 exhibit remarkably broadened and increased IPCE action spectra covering the visible region from 400 to 550 nm. The IPCE curve of D-DTFPy4 is slightly superior to that of D-DTFPy3 in magnitude with values over 80% in the region of 400–450 nm, which is much higher than that of DTFPy4 and DTFPy3 (~60%). The IPCE as a function of wavelength is directly related to the LHE, charge injection efficiency and charger collection efficiency. Considering the reducing amounts of adsorbed sensitizers from monomer-type sensitizers to dimer-type sensitizers as well as the same anchoring group for the

Figure 3 (a) J - V curves of DTFPy3, DTFPy4, D-DTFPy3 and D-DTFPy4 based DSSCs, and (b) IPCE spectra of DTFPy3, DTFPy4, D-DTFPy3 and D-DTFPy4 based DSSCs.

Table 2 Properties of DTFPy3, DTFPy4, D-DTFPy3 and D-DTFPy4 based on DSSCs

Sensitizer	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	η (%)	Dye absorbed amounts (mol cm^{-2})
DTFPy3	6.96	607	0.65	2.74	$(5.85 \pm 0.1) \times 10^{-8}$
DTFPy4	7.25	626	0.69	3.14	$(5.32 \pm 0.1) \times 10^{-8}$
D-DTFPy3	9.43	611	0.70	4.03	$(4.93 \pm 0.1) \times 10^{-8}$
D-DTFPy4	11.70	630	0.71	5.26	$(4.74 \pm 0.1) \times 10^{-8}$

four sensitizers, a higher IPCE value for **D-DTFPy4** can be ascribed to the higher light-harvesting efficiency.

Electrochemical impedance spectroscopy analysis

To further elucidate the photovoltaic results and display more dynamic information of the interfacial charge transfer process in DSSCs sensitized by **DTFPy3**, **DTFPy4**, **D-DTFPy3** and **D-DTFPy4**, electrochemical impedance spectroscopy (EIS) was also performed in dark under a forward bias of 0.6 V with a frequency range of 0.1 Hz–100 kHz. In general, R_s , R_{rec} and R_{CE} represent series resistance and charge transfer processes at the sensitizer/TiO₂/electrolyte interface and counter electrode, respectively. R_s and R_{CE} show almost the same values in all the DSSCs, due to their same electrode and electrolyte. Moreover, the R_{rec} corresponding to the larger semicircle is related to the charge recombination rate between the TiO₂ film and the electrolyte. Generally, a larger R_{rec} value indicates a slower charge recombination, thus giving a higher V_{oc} . The Nyquist plots for the DSSCs based on the sensitizers are displayed in Fig. 4. The corresponding R_{rec} values for **DTFPy3**, **DTFPy4**, **D-DTFPy3** and **D-DTFPy4** are 24.1, 25.3, 24.5 and 26.6 $\Omega \text{ cm}^{-2}$, respectively. The R_{rec} values trend in order of **DTFPy3** < **D-DTFPy3** < **DTFPy4** < **D-DTFPy4** is in good consistent with the V_{oc} results of these four sensitizers. Considering all of these four sensitizers have the same length of π -bridges, we hypothesize that the dimeric sensitizers **D-DTFPy3** and **D-DTFPy4** may adopt staggered molecular packing on TiO₂ surface, thus leading to more efficient suppression of back reaction of the injected electrons with the redox electrolyte.

Figure 4 The Nyquist plots of DSSCs based on **DTFPy3**, **DTFPy4**, **D-DTFPy3** and **D-DTFPy4**.

CONCLUSIONS

In summary, two monobranched dithiafulvene based sensitizers using pyridine as acceptor (**DTFPy3** and **DTFPy4**), and their corresponding dimeric congeners with two pinched D- π -A units (**D-DTFPy3** and **D-DTFPy4**) were synthesized and tested in DSSCs. It was demonstrated that controlling the electron distribution in the π -bridges, such as arranging an electron rich thienyl group adjacent to the donor moiety and an electron poor phenyl group next to the acceptor moiety, could lead to red-shift of the absorption. Moreover, dimerization of the sensitizers with doubled light harvesting units could significantly enhance the absorption. As a result, **D-DTFPy4**, which features the dimeric D- π -A units with thienyl-phenyl π -bridges between dithiafulvene donors and pyridine acceptors, has achieved the highest power conversion efficiency at 5.26% under standard AM 1.5 solar condition, mainly due to the relatively high light harvesting efficiency. These findings may pave a new path for developing high-performance DSSCs based on pyridine containing sensitizers.

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- O'Regan B, Grätzel M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature*, 1991, 353: 737–740
- Grätzel M. Mesoscopic solar cells for electricity and hydrogen production from sunlight. *Chem Lett*, 2005, 34: 8–13
- Li B, Wang L, Kang B, *et al.* Review of recent progress in solid-state dye-sensitized solar cells. *Solar Energy Mater Solar Cells*, 2006, 90: 549–573
- Zhao Z, Liu G, Li B, *et al.* Dye-sensitized solar cells based on hierarchically structured porous TiO₂ filled with nanoparticles. *J Mater Chem A*, 2015, 3: 11320–11329
- Snaith HJ, Schmidt-Mende L. Advances in liquid-electrolyte and solid-state dye-sensitized solar cells. *Adv Mater*, 2007, 19: 3187–3200
- Zhu K, Neale NR, Miedaner A, *et al.* Enhanced charge-collection efficiencies and light scattering in dye-sensitized solar cells using oriented TiO₂ nanotubes arrays. *Nano Lett*, 2007, 7: 69–74
- Zheng X, Wei Z, Chen H, *et al.* In-situ fabrication of dual porous titanium dioxide films as anode for carbon cathode based perovskite solar cell. *J Energy Chem*, 2015, 24: 736–743
- Ning Z, Tian H. Triarylamine: a promising core unit for efficient photovoltaic materials. *Chem Commun*, 2009, 5483
- Mishra A, Fischer MKR, Bäuerle P. Metal-free organic dyes for dye-sensitized solar cells: from structure: property relationships to design rules. *Angew Chem Int Ed*, 2009, 48: 2474–2499
- Hagfeldt A, Boschloo G, Sun L, *et al.* Dye-sensitized solar cells. *Chem Rev*, 2010, 110: 6595–6663
- Yella A, Lee HW, Tsao HN, *et al.* Porphyrin-sensitized solar cells with cobalt (II/III)-based redox electrolyte exceed 12 percent efficiency. *Science*, 2011, 334: 629–634
- Qiu Y, Leung SF, Zhang Q, *et al.* Nanobowl optical concentrator for efficient light trapping and high-performance organic photovoltaics. *Sci Bull*, 2015, 60: 109–115
- Qiu Y, Chen W, Yang S. Double-layered photoanodes from

- variable-size anatase TiO₂ nanospindles: a candidate for high-efficiency dye-sensitized solar cells. *Angew Chim Int Ed*, 2010, 49: 3675–3679
- 14 Yan K, Qiu Y, Chen W, *et al.* A double layered photoanode made of highly crystalline TiO₂ nanooctahedra and agglutinated mesoporous TiO₂ microspheres for high efficiency dye sensitized solar cells. *Energy Environ Sci*, 2011, 4: 2168–2176
 - 15 Liu T, Hou J, Wang B, *et al.* Correlation between the in-plain substrate strain and electrocatalytic activity of strontium ruthenate thin films in dye-sensitized solar cells. *J Mater Chem A*, 2016, 4: 10794–10800
 - 16 Shen T, Tian J, Li B, *et al.* Ultrathin ALD coating on TiO₂ photoanodes with enhanced quantum dot loading and charge collection in quantum dots sensitized solar cells. *Sci China Mater*, 2016, 59: 833–841
 - 17 Huo Z, Li T, Dai S, *et al.* Quasi-solid-state dye sensitized solar cells using supramolecular gel electrolyte formed from two-component low molecular mass organogelators. *Sci China Mater*, 2015, 58: 447–454
 - 18 Cheng J, Zhang F, Li K, *et al.* A planar dithiafulvene based sensitizer forming J-aggregates on TiO₂ photoanode to enhance the performance of dye-sensitized solar cells. *Dyes Pigments*, 2017, 136: 97–103
 - 19 Koumura N, Wang ZS, Mori S, *et al.* Alkyl-functionalized organic dyes for efficient molecular photovoltaics. *J Am Chem Soc*, 2006, 128: 14256–14257
 - 20 Imahori H, Umeyama T, Ito S. Large π -aromatic molecules as potential sensitizers for highly efficient dye-sensitized solar cells. *Acc Chem Res*, 2009, 42: 1809–1818
 - 21 Ito S, Miura H, Uchida S, *et al.* High-conversion-efficiency organic dye-sensitized solar cells with a novel indoline dye. *Chem Commun*, 2008, 5194
 - 22 Zhang G, Bala H, Cheng Y, *et al.* High efficiency and stable dye-sensitized solar cells with an organic chromophore featuring a binary π -conjugated spacer. *Chem Commun*, 2009, 2198
 - 23 Feldt SM, Gibson EA, Gabrielsson E, *et al.* Design of organic dyes and cobalt polypyridine redox mediators for high-efficiency dye-sensitized solar cells. *J Am Chem Soc*, 2010, 132: 16714–16724
 - 24 Zeng W, Cao Y, Bai Y, *et al.* Efficient dye-sensitized solar cells with an organic photosensitizer featuring orderly conjugated ethylenedioxythiophene and dithienosilole blocks. *Chem Mater*, 2010, 22: 1915–1925
 - 25 Cai N, Moon SJ, Cevey-Ha L, *et al.* An organic D- π -A dye for record efficiency solid-state sensitized heterojunction solar cells. *Nano Lett*, 2011, 11: 1452–1456
 - 26 Choi H, Shin M, Song K, *et al.* The impact of an indeno[1,2-b]thiophene spacer on dye-sensitized solar cell performances of cyclic thiourea functionalized organic sensitizers. *J Mater Chem A*, 2014, 2: 12931–12939
 - 27 Liu B, Wang B, Wang R, *et al.* Influence of conjugated π -linker in D-D- π -A indoline dyes: towards long-term stable and efficient dye-sensitized solar cells with high photovoltage. *J Mater Chem A*, 2014, 2: 804–812
 - 28 Yao Z, Zhang M, Wu H, *et al.* Donor/acceptor indenoperylene dye for highly efficient organic dye-sensitized solar cells. *J Am Chem Soc*, 2015, 137: 3799–3802
 - 29 Lee W, Yuk SB, Choi J, *et al.* The effects of the number of anchoring groups and N-substitution on the performance of phenoxazine dyes in dye-sensitized solar cells. *Dyes Pigments*, 2014, 102: 13–21
 - 30 Kim WR, Park H, Choi WY. Conical islands of TiO₂ nanotube arrays in the photoelectrode of dye-sensitized solar cells. *Nanoscale Res Lett*, 2015, 10: 63
 - 31 Zhang L, Cole JM. Anchoring groups for dye-sensitized solar cells. *ACS Appl Mater Interf*, 2015, 7: 3427–3455
 - 32 Wei T, Sun X, Li X, *et al.* Systematic investigations on the roles of the electron acceptor and neighboring ethynylene moiety in porphyrins for dye-sensitized solar cells. *ACS Appl Mater Interf*, 2015, 7: 21956–21965
 - 33 Chitpakdee C, Namuangruk S, Suttisintong K, *et al.* Effects of π -linker, anchoring group and capped carbazole at meso-substituted zinc-porphyrins on conversion efficiency of DSSCs. *Dyes Pigments*, 2015, 118: 64–75
 - 34 Yang L, Yao Z, Liu J, *et al.* A systematic study on the influence of electron-acceptors in phenanthrocarbazole dye-sensitized solar cells. *ACS Appl Mater Interf*, 2016, 8: 9839–9848
 - 35 Ooyama Y, Inoue S, Nagano T, *et al.* Dye-sensitized solar cells based on donor-acceptor π -conjugated fluorescent dyes with a pyridine ring as an electron-withdrawing anchoring group. *Angew Chem Int Ed*, 2011, 50: 7429–7433
 - 36 Ooyama Y, Nagano T, Inoue S, *et al.* Dye-sensitized solar cells based on donor- π -acceptor fluorescent dyes with a pyridine ring as an electron-withdrawing-injecting anchoring group. *Chem Eur J*, 2011, 17: 14837–14843
 - 37 Daphnomili D, Landrou G, Prakash Singh S, *et al.* Photophysical, electrochemical and photovoltaic properties of dye sensitized solar cells using a series of pyridyl functionalized porphyrin dyes. *RSC Adv*, 2012, 2: 12899–12908
 - 38 Mao J, Wang D, Liu SH, *et al.* Dye-sensitized solar cells based on functionally separated D- π -A dyes with 2-cyanopyridine as an electron-accepting and anchoring group. *Asian J Organic Chem*, 2014, 3: 153–160
 - 39 Wang L, Yang X, Li S, *et al.* A new type of organic sensitizers with pyridine-N-oxide as the anchoring group for dye-sensitized solar cells. *RSC Adv*, 2013, 3: 13677
 - 40 Lu J, Xu X, Li Z, *et al.* Zinc porphyrins with a pyridine-ring-anchoring group for dye-sensitized solar cells. *Chem Asian J*, 2013, 8: 956–962
 - 41 Ooyama Y, Yamaguchi N, Imae I, *et al.* Dye-sensitized solar cells based on D- π -A fluorescent dyes with two pyridyl groups as an electron-withdrawing-injecting anchoring group. *Chem Commun*, 2013, 49: 2548–2550
 - 42 Bai Y, Zhang J, Zhou D, *et al.* Engineering organic sensitizers for iodine-free dye-sensitized solar cells: red-shifted current response concomitant with attenuated charge recombination. *J Am Chem Soc*, 2011, 133: 11442–11445
 - 43 Cao D, Peng J, Hong Y, *et al.* Enhanced performance of the dye-sensitized solar cells with phenothiazine-based dyes containing double D-A branches. *Org Lett*, 2011, 13: 1610–1613
 - 44 Hong Y, Liao JY, Cao D, *et al.* Organic dye bearing asymmetric double donor- π -acceptor chains for dye-sensitized solar cells. *J Org Chem*, 2011, 76: 8015–8021
 - 45 Guo K, Yan K, Lu X, *et al.* Dithiafulvenyl unit as a new donor for high-efficiency dye-sensitized solar cells: synthesis and demonstration of a family of metal-free organic sensitizers. *Org Lett*, 2012, 14: 2214–2217

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Author contributions Cao Y synthesized the dimeric sensitizers and performed the DSCs measurements. Cheng J synthesized the monomeric sensitizers. Zhang F assembled the solar cells. Liang X performed the CVs measurements. Li J provided the theoretical simulation. Guo K analyzed the results and wrote the paper. Yang S supervised the research and revised the manuscript. All authors reviewed the manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information The calculation of LHE, SEM images of TiO₂ film, cyclic voltammograms and the absorption and PL spectra are available in the online version of this paper.

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分子工程优化含吡啶受体的二硫富瓦烯敏化剂用于高效染料敏化太阳电池

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摘要 近年来,具有给体- π 桥-受体结构的有机化合物作为光敏剂用于染料敏化太阳电池的研究引起广泛关注. 研究发现吡啶作为电子受体和吸附基团时可实现有效的电子注入. 为了提高含吡啶受体有机敏化剂的性能,需要通过分子工程对电子给体, π 桥和分子结构在分子层面上进行优化. 本研究以二硫富瓦烯为电子给体, 吡啶为电子受体, 合成了两个 π 桥结构分别为噻吩-苯和苯-噻吩的单体型敏化剂DTFPy3和DTFPy4, 对二者及其对应的二聚体型敏化剂D-DTFPy3和D-DTFPy4的研究发现, 调整 π 桥上富电子噻吩靠近给体一端时可使敏化剂的吸收波长红移. 另外, 二聚体型敏化剂可有效提高敏化剂的吸光强度. 在这四个敏化剂中, D-DTFPy4表现出最佳的光捕获效率, 以其制备的染料敏化太阳电池, 光电转换效率可达5.26%.