Electronic Supplementary Material (ESI) for RSC Advances

Influence of Different Methylene Units on the Performance of Rhodanine Organic Dyes for Dye-sensitized Solar Cells

Jianghua Zhao,[a] Xichuan Yang,*[a] Ming Cheng,[a] Weihan Wang,[a] and Licheng Sun *[a,b]

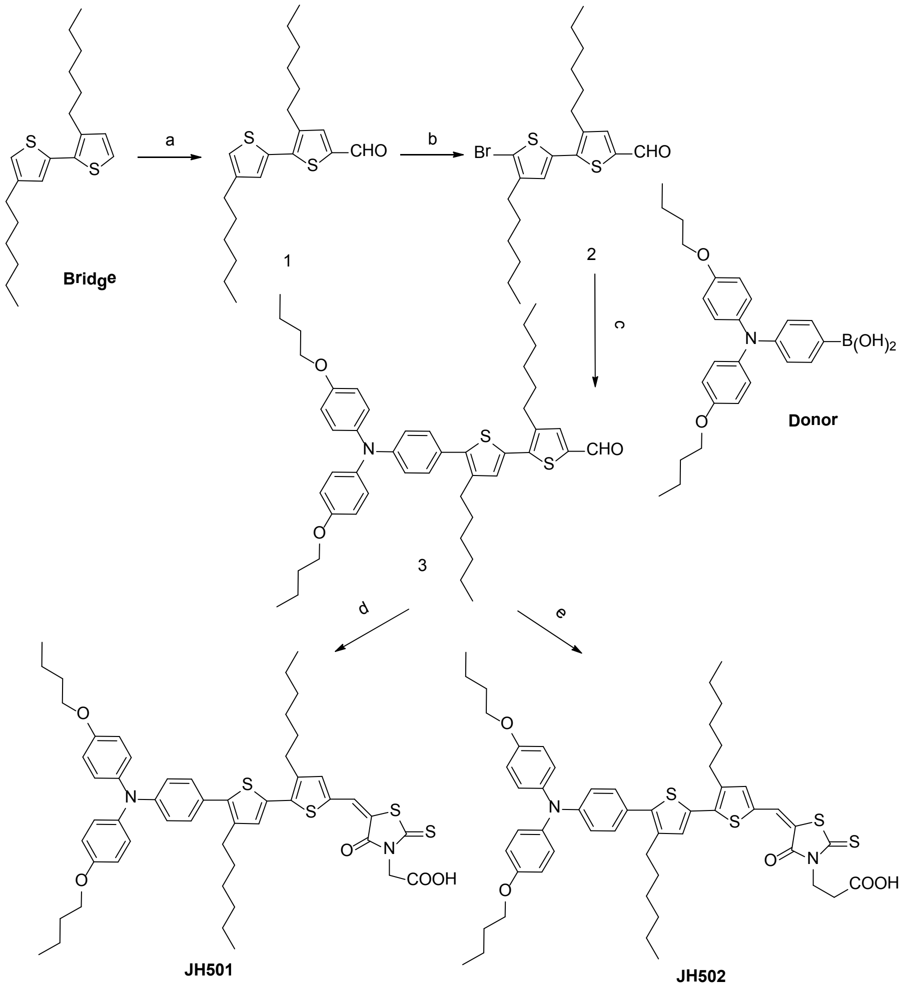
Experimental section

Synthetic routes

Schemes 1 show the synthetic routes of **JH501** and **JH502**. The solvents used in these reactions were distilled freshly according to standard procedures. The commercial reagents were directly used without further purification. Donor and bridge was synthesized by previous report by our group. [1] The structures of the compounds were identified by ^{1}H NMR and MS.

General synthetic procedures

Scheme 1: The synthetic routes of dye JH501 and dye JH502



(a) *n*-BuLi, THF, – 78 °C, DMF, 2 h; (b) NBS, THF, 0 °C; (c) K_2CO_3, Pd(pph$_3$)$_4$, THF/H_2O, reflux, 12 h; (d) rhodanine-3-acetic acid, pyperidine, CH_3CN, rt, 2 h. (e) rhodanine-3-propionic acid.

3,4'-dihexyl-[2,2'-bithiophene]-5-carbaldehyde (1) 3,4'-dihexyl-2,2'-bithiophene (3 g, 9 mmol) was desolved in dry THF solution under N_2. *n*-BuLi (4.5 ml, 11.25 mmol) was dropwised at –78 ^{o}C, then the mixture was stirred for 1 h. DMF (1.31 g, 18 mmol) was added and the result mixture was kept for 2 h at room temperature. When the reaction was finished, water was added, and the mixture was extracted by EtOAc. After removing the solvent by rotary evaporation, the crude product was purified by CH_2Cl_2 / petroleum ether (2 : 1) to give compound **1** (2.7 g, 82%**)** as yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.58 (s, 1H), 7.46 (s, 1H), 7.25 (d, J = 9.8 Hz, 1H), 2.67 – 2.55 (m, 4H), 1.73 – 1.55 (m, 4H), 1.35 – 1.29 (m, 12H), 0.93 – 0.85 (m, 9H). $[M]^+$ calcd. For $C_{21}H_{30}OS_2$, 362.1738; found,362.1741.

5'-bromo-3,4'-dihexyl-[2,2'-bithiophene]-5-carbaldehyde (2) Compound **1** (2.5 g, 5.68 mmol) was dissolved in THF at 0 °C, NBS (1.01 g, 5.68 mmol) was added slowly and the result mixture was stirred for 3 h. When the reaction was finished, water was added and the mixture was extracted by CH_2Cl_2, organic layer was collected and concentrated by rotary evaporation. Crude product was purified by CH_2Cl_2 / petroleum ether (2 : 1) to give compound **2** (1.9 g, 78%**)** as yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.58 (s, 1H), 7.11 (t, J = 3.4 Hz, 1H), 7.04 – 6.99 (m, 1H), 2.67 – 2.56 (m, 4H), 1.73 – 1.59 (m, 4H), 1.34 – 1.28 (m, 12H), 0.91 – 0.87 (m, 9H). $[M]^+$ calcd. For $C_{21}H_{29}OS_2$, 440.0843; found, 440.0851.

5'-(4-(bis(4-butoxyphenyl)amino)phenyl)-3,4'-dihexyl-[2,2'-bithiophene]-5-carbaldehyde (3) Compound **2** (1.5 g, 3.41mmol), (4-(bis(4-butoxyphenyl)amino)phenyl)boronic acid (1.8 g, 4.1 mmol), K_2CO_3 (0.71g , 5.1 mmol), $Pd(PPh_3)_4$ (35 mg) were dissolved in THF/H_2O (5 : 1, v/v) under N_2. The mixture was refluxed for 12 h. then the reaction was cooled to the room temperature, water was added and extracted by CH_2Cl_2. The combined organic phase was dried over anhydrous $MgSO_4$ and the solvent was removed by rotary evaporation. The crude product was purified by CH_2Cl_2 / petroleum ether (1: 1) to give compound **3** (1.7 g, 67%**)** as orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.58 (d, *J* = 3.7 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.27 – 7.18 (m, 3H), 7.14 (d, *J* = 11.7 Hz, 1H), 7.10 (d, *J* = 8.5 Hz, 2H), 7.04 (d, 2H), 6.95 (t, *J* = 8.2 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 3H), 3.98 – 3.89 (m, 4H), 2.64 (dd, *J* = 15.4, 7.7 Hz, 4H), 1.87 – 1.61 (m, 4H), 1.56 – 1.43 (m, 8H), 1.28 (m, *J* = 23.1, 12.8 Hz, 12H), 1.02 – 0.81 (m, *J* = 21.8 Hz, 12H). $[M]^+$ calcd. For $C_{47}H_{59}NO_3S_2$, 749.3936; found,749.1826.

(E)-2-(5-((5'-(4-(bis(4-butoxyphenyl)amino)phenyl)-3,4'-dihexyl-[2,2'-bithiophen]-5-yl)methylene)-4-oxo-2-thioxothiazolidin-3-yl)acetic acid (JH501) Compound **3** (300 mg, 0.32mmol), rhodanine-3 acetic acid (91 mg, 0.48 mmol) was dissolved in CH_3CN solution in room temperature for 2 h. when the reaction was finished, water was added and the mixture was extracted by CH_2Cl_2, organic layer was collected and concentrated by rotary evaporation. Crude product was purified by CH_2Cl_2 /CH_3OH (7 : 1) to give **JH501** (0.18 mg, 62%**)** as red solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.23 (d, *J* = 2.6 Hz, 2H), 7.14 (s, 1H), 7.10 (s, 2H), 7.08 (d, *J* = 3.3 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.87 – 6.84 (m, 2H), 6.83 (s, 2H), 4.47 – 4.40 (m, 2H), 3.95 (t, *J* = 6.5 Hz, 4H), 2.82 (dd, *J* = 15.3, 7.5 Hz, 4H), 2.69 – 2.61 (m, 2H), 1.82 – 1.72 (m, 4H), 1.50 (dd, *J* = 15.0, 7.5 Hz, 8H), 1.31 (m, *J* = 8.1, 3.0 Hz, 12H), 0.98- 0.88 (m, *J* = 6.7 Hz, 12H). $[M]^+$ calcd. For $C_{52}H_{62}N_2O_5S_4$, 922.3542; found, $[M-1]^+$,921.4.

(E)-3-(5-((5'-(4-(bis(4-butoxyphenyl)amino)phenyl)-3,4'-dihexyl-[2,2'-bithiophen]-5-yl)methylene)-4-oxo-2-thioxothiazolidin-3-yl)propanoic acid (JH502)

Compound **3** (300 mg, 0.32mmol), rhodanine-3 propionic acid (97 mg, 0.48 mmol) was dissolved in CH_3CN solution in room temperature for 2 h. when the reaction was finished, water was added and the mixture was extracted by CH_2Cl_2, organic layer was collected and concentrated by rotary evaporation. Crude product was purified by CH_2Cl_2 /CH_3OH (5 : 1) to give **JH502** (0.2 mg, 68%**)** as red solid. ^{1}H NMR (400 MHz, DMSO) δ 7.95 (s, 1H), 7.65 (s, 1H), 7.33 (m, 2H), 7.07 (d, J = 8.5 Hz, 4H), 6.93 (d, J = 8.7 Hz, 4H), 6.78 (d, J = 9.1 Hz, 2H), 4.43 (s, 2H), 3.95 (t, J = 6.1 Hz, 4H), 2.78 – 2.6 (m, 6H), 1.74 – 1.64 (m, 4H), 1.44 (dd, J = 15.0, 7.3 Hz, 8H), 1.26 (d, J = 16.4 Hz, 12H), 0.91 (dd, J = 27.7, 20.3 Hz, 12H). $[M]^+$ calcd. For $C_{53}H_{64}N_2O_5S_4$, 936.3698; found, $[M-1]^+$,935.4.

Analytical measurements

The absorption spectra were recorded on HP8453 (USA). Electrochemical redox potentials were obtained by cyclic voltammetry (CV) on electrochemistry workstation (BAS100B, USA). Traditional three-electrode system was used. Working electrode, auxiliary electrode and reference electrode is glassy carbon disk electrode, P_t-wire and Ag/Ag^+ electrode, respectively. The photocurrent–voltage (*J–V*) properties were measured under AM 1.5G illumination (16S-002, Solar Light Co. Ltd., USA). The incident light intensity was 100 mW/cm^2 calibrated with a standard Si solar cell. The working areas of the cells were masked to 0.159 cm^2. The *J–V* data were collected by an electrochemical workstation (LK9805, Lanlike Co. Ltd., China). The measurement of the IPCE was obtained by a Hypermono–light (SM–25, Jasco Co. Ltd., Japan). Electrochemical impedance spectroscopy (EIS) was measured with an impedance/gain–phase analyzer (PARSTAT 2273, USA) under dark condition, with forward bias – 0.7 V. The alternate current (AC) amplitude was set at 10 mV. Nanosecond time-resolved transient difference absorption spectroscopy: Nanosecond time-resolved transient difference absorption spectra were recorded on a LP 920 laser flash photolysis spectrometer (Edinburgh Instruments, Livingston, UK). The samples were excited with a 532 nm laser and the transient signals were recorded on a Tektronix TDS 3012B oscilloscope.

Preparation of the DSSCs

The DSSCs sensitized by **JH201–JH203** were fabricated by modifying the previous report.[1] A layer of 2 μm TiO_2 (13 nm paste, Heptachroma, China) was coated on the F-doped tin oxide conducting glass (TEC15, 15Ω/square, Pilkington, USA) by screen printing and then dried for 5 min at 120 °C. This procedure was repeated 5 times (10 μm) and finally coated by a layer (4 μm) of TiO_2 paste (DHS-SLP1, Heptachroma, China) as the scattering layer. The double-layer TiO_2 electrodes (area: 6 × 6 mm) were heated under an air flow at 500 °C for 60 min, and then cooled to room temperature. The sintered film wasfurther treated with 40 mM $TiCl_4$ aqueous solution at 70 °C for 30 min, then washed with water, and annealed at 500 °C for 60 min. After the film was cooled to room temperature, it was immersed into a 2×10^{-4} M dye bath. The electrode was then rinsed with ethanol and dried. The hermetically sealed cells were fabricated by assembling the dye-loaded film as the working electrode and *Pt*-coated conducting glass as the counter electrode separated with a hot–melt Surlyn 1702 film (60 µm, Dupont).

Reference

(1) J. Zhao, X. Yang, M. Cheng, S. Li, X. Wang and L. Sun, *J. Mater. Chem. A*, 2013**,** **1,** 2441.

(2) C. Teng, X. Yang, C. Yang, S. Li, M. Cheng, A. Hagfeldt and L. Sun, *J. Phys. Chem. C*, 2010, **114**, 9101.

Table 2S. TDDFT (CAMB3LYP) calculated data of **JH501** and **JH502**

Dyes	State	Composition [a]	*E*(eV)	*f*	exp.(eV,nm)
JH501	S1	H→L (45%) H–1→L (51%) H→L+1 (10%)	2.62 eV (473 nm)	1.5318	2.32 eV (534nm)
	S2	H–4→L (54%) H–4→L+1 (41%) H–4→L+1 (19%)	3.37 eV (368 nm)	0.0004	3.51 eV (353 nm)
JH502	S1	H→L (44%) H–1→L (51%) H→L+1 (14%)	2.63 eV (471 nm)	1.5387	2.46 eV (505 nm)

S2	H–4→L (54%) H–4→L+1 (40%) H–4→L+2 (19%)	3.34 eV (371 nm)	0.0002	3.63 eV (342 nm)

[a] H=HOMO, L= LUMO, L+2= LUMO+2, H–1=HOMO–1, H–4=HOMO–4, L+1= LUMO+1.