Electronic Supplementary Material (ESI) for RSC Advances.

Organic D-π-A sensitizer with pyridinium as acceptor group for dye-sensitized solar cells

Jie Tian,[a] Xichuan Yang,*[a] Jianghua Zhao,[a] Lei Wang,[a] Weihan Wang, [a]Jiajia Li[a] and Licheng Sun[a,b]

a State Key Laboratory of Fine Chemicals, DUT–KTH Joint Education and Research Centre on Molecular Devices, Dalian University of Technology (DUT), 2 Linggong Rd., 116024 Dalian, China. E-mail: yangxc@dlut.edu.cn; Fax: +86 411 84986250; Tel: +86 411 84986247

b School of Chemical Science and Engineering, Centre of Molecular Devices, Department of Chemistry, KTH Royal Institute of Technology, Teknikringen 30, 10044 Stockholm, Sweden. E-mail: lichengs@kth.se; Fax: +46-8-791-2333

Experimental Section

Fabrication of DSSCs

The DSSCs sensitized by **TJ101**, **TJ102** and **TJ101R** were fabricated according to a previous literature procedure.[1, 2] A layer of 2 μm TiO_2(18 NRT, Dyesol) was coated on the FTO conducting glass(TEC15, 15 Ω/square, Pilkington, USA) by screen printing and then dried for 5 min at 130 °C. This procedure was repeated 5 times (10 μm). Next the FTO conducting glass was coated with a layer (4 μm) of TiO_2 paste (DHS-SLP1, Heptachroma, China) as the scattering layer and dried for another 5 min at 130 °C. The double-layer TiO_2 electrodes (area: 6 mm × 6 mm) were heated under an air flow at 500 °C for 60 min and then cooled to room temperature. The sintered film was further treated with a 40 mM $TiCl_4$ aqueous solution at 70 °C for 30 min, then washed with water, and heated at 500 °C for 60 min, then continue cooled to room temperature. We can get the TiO_2 photoanode.

The TiO_2 photoanode was immersed into a 0.2 mM dye bath (CH_2Cl_2) with saturated chenodeoxycholic acid (CDCA) and kept for 18 h in the dark at room temperature. The electrode was then rinsed and dried with dry CH_2Cl_2. 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 (25 μm, Dupont). The redox electrolyte containing 0.04 M I_2, 0.06 M LiI, 0.4 M 4- tert-butylpyridine (4-TBP), and 0.6 M 3-propyl-1, 2-dimethylimida-zolium iodide (DMPII) in CH_3CN was introduced through a hole drilled in the back of the counter electrode. Finally, the hole was also sealed with the Surlyn film.

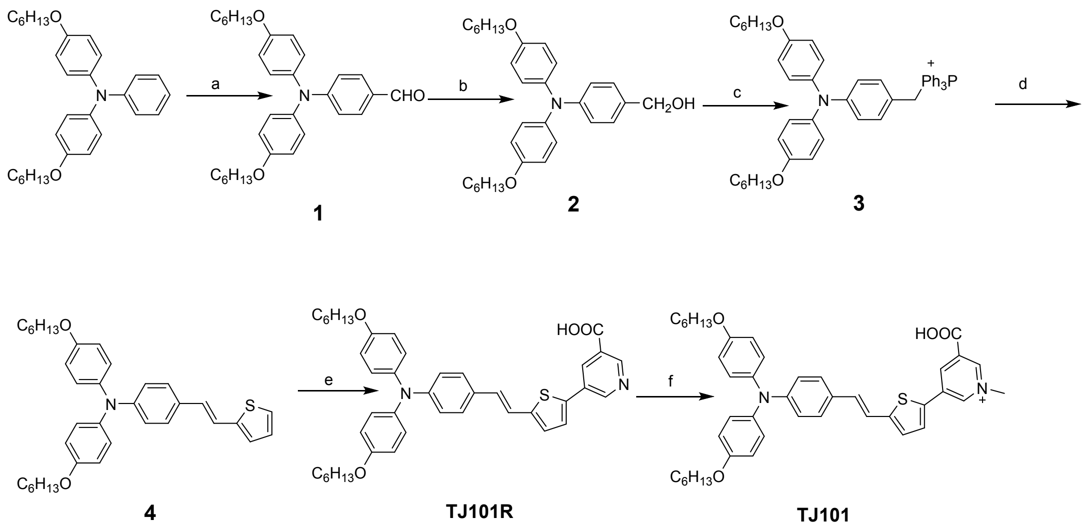
Analytical Measurements

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, *Pt*-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

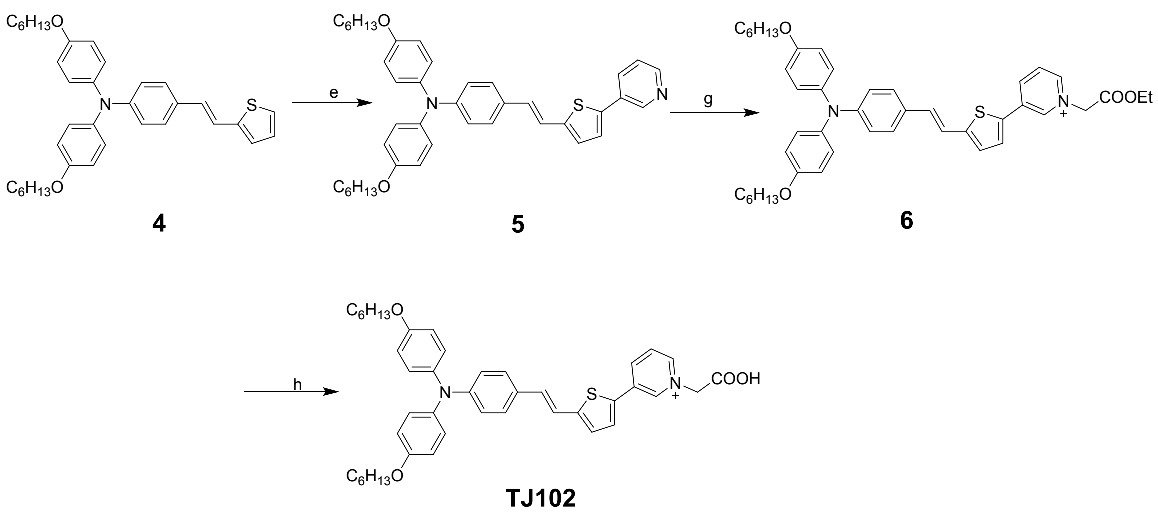
2273, USA) under dark condition, with forward bias – 0.7 V. The alternate current (AC) amplitude was set at 10 mV.

Synthesis

The structures of the dyes **TJ101**, **TJ102** and **TJ101R** are shown in Figure 1. These dyes were synthesized by a stepwise synthetic protocol, shown in Scheme 1, Scheme 2. The synthesis of dyes **TJ101**, **TJ102** and **TJ101R** is shown in supporting information. ^{1}HNMR spectra were recorded on a VARIAN INOVA 400 MHz spectrometer (USA) with the chemical shifts by using TMS as standard. HR-MS data were obtained with GCT CA156 (UK), HP1100 LC/MSD (USA) and LC/Q-TOF MS (UK).



Scheme 1 synthetic routes for dyes **TJ101** and **TJ101R**: Reagents and conditions: a) $CHCl_3$, $POCl_3$/DMF, 6 h; b) CH_3CH_2OH, $NaBH_4$, 1 h; c) $CHCl_3$, Ph_3P HBr, reflux, 2 h; d) thiophene-2-carbaldhyde, DMF, K_2CO_3, 18-crown-6-ether, Rt, 2 h; e) THF, n-BuLi, isopropenylboronic acid pinacol ester,-78 °C / THF, 5-bromonicotinic acid, K_2CO_3, $Pd(PPh_3)_4$, reflux, 12 h; f) CH_3CN, CH_3I, reflux, 12 h.



Scheme 2 synthetic routes for dye **TJ102** Reagents and conditions: g) CH_3CN, $BrCH_2COOEt$, reflux, 12 h; h) CH_3CH_2OH, $LiOH+H_2O$.

4-(bis(4-(hexyloxy)phenyl)amino)benzaldehyde (1). To dry DMF (3.9 mL, 67.2 mmol) in an ice water bath, phosphorus oxychloride (6.3 mL, 67.2 mmol) was added slowly below 5 ^{o}C. Then the temperature was raised to 30 ^{o}C, the compound 4-(hexyloxy)-N-(4-(hexyloxy)phenyl)-N-phenylaniline (7.5 g, 16.8 mmol) was added rapidly and the bath was heated to 50 °C. After 4 h, the reaction was quenched with ice water, to which was then added sodium hydroxide for neutralizing to pH = 10-11 and the organic layer was extracted with CH_2Cl_2, the solvent was removed with a rotary evaporator. Then the residue was purified by column chromatography on silica gel using CH_2Cl_2: petroleum ether (1:1, v/v) as eluent to give out the product as pale yellow liquid (6.3 g，80 %). ^{1}HNMR (400 MHz, Acetone) δ = 9.75 (d, *J* = 4.1, 1H), 7.70 – 7.55 (m, 2H), 7.34 – 7.07 (m, 4H), 7.03 – 6.88 (m, 4H), 6.82 – 6.58 (m, 2H), 4.03 – 3.93 (m, 4H), 1.85 – 1.69 (m, 4H), 1.58 – 1.18 (m, 12H), 0.99 – 0.84 (m, 6H). GC/TOF HRMS-EI (m/z): found, 474.3007, calcd. for $C_{31}H_{39}NO_3$, 474.2996.

(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)methanol (2). A flask containing compound **1** (6.3 g, 13.3 mmol) and $NaBH_4$ (1 g, 26.6 mmol) equipped with a magnetic stirrer in CH_2Cl_2 and EtOH (3:1, v/v) solution, the temperature was at room temperature. After 1 h, the reaction was quenched with water and the organic layer was extracted with CH_2Cl_2 and evaporated to dryness. The product was purified by column chromatography on silica gel using CH_2Cl_2 (5.9 g, 95%). ^{1}HNMR (400 MHz, Acetone) δ = 7.20 – 7.15 (m, 1H), 7.02 – 6.94 (m, 2H), 6.89 – 6.81 (m, 3H), 4.53 (d, *J* = 5.8, 1H), 4.04 – 3.91 (m, 2H), 1.81 – 1.69 (m, 2H), 1.52 – 1.42 (m, 2H), 1.39 – 1.30 (m, 4H), 0.91 (dq, *J* = 7.2, 2.4, 3H). GC/TOF HRMS-EI (m/z): found, 475.3082; calcd. for $C_{31}H_{41}NO_3$, 475.3086.

Compound **2** (5.9 g, 12.5 mmol) and Ph_3PHBr (4.5 g, 13.1 mmol) was dissolved in $CHCl_3$ (40mL) and refuxed for 2 h. After removing the solvent, the residue was solidified with ether to get the compound **3**.

(E)-4-(hexyloxy)-N-(4-(hexyloxy)phenyl)-N-(4-(2-(thiophen-2-yl)vinyl)phenyl)aniline (4). To a solution of thiophene-2-carbaldehyde (1.3 g, 11.9 mmol), 18-crown-6-ether (100 mg) and anhydrous K_2CO_3(3.4 g, 25 mmol) in DMF, another solution of compound **3** (12.4 mmol) in DMF was added slowly with a magnetic stirrer at room temperature. After 3h, the reaction was quenched with water and the organic layer was extracted with CH3COOEt and evaporated to dryness. The product was purified by column chromatography on silica gel using CH_2Cl_2: petroleum ether (1:5, v/v) as eluent to give out the product as pale green liquid (3.87 g, 56%). ^{1}H NMR (400 MHz, Acetone) δ = 7.36 – 7.30 (m, 2H), 7.26 (d, *J*=5.1, 1H), 7.22 – 7.16 (m, 1H), 7.07 (d, *J* = 3.2, 1H), 7.05 – 6.95 (m, 5H), 6.92 – 6.77 (m, 7H), 3.94 (t, *J* = 6.5, 4H), 1.75 (dq, *J* = 12.9, 6.5, 4H), 1.50 – 1.29 (m, 12H), 0.96 – 0.84 (m, 6H). GC/TOF HRMS-EI (m/z): found, 553.1971; calcd. for $C_{36}H_{43}NO_2S$, 553.3015.

(E)-5-(5-(4-(bis(4-(hexyloxy)phenyl)amino)styryl)thiophen-2-yl)nicotinic acid (TJ101R). A flask containing compound **4** (2 g, 3.6 mmol) in dry THF under N_2 atmosphere, n-BuLi (2.5 M, 4.52 mmol) was added slowly with a magnetic stirrer at -78 ^{o}C, after that keep the temperature for 1h, then a solution of pinacol ester (0.81 mL, 3.9 mmol) was added rapidly for 4h. After removing the solvent, our group get the intermediate compound.

Under nitrogen conditions, the all intermediate and 5-bromonicotinic acid (0.72 g, 3.6 mmol), potassium carbonate (0.99 g, 7.2 mmol), (beta-4)-platinum (174 mg, 0.15 mmol) were placed in a flask and dissolved in 60 mL of THF: H_2O (5:1; v/v), after the mixture was bubbled with the nitrogen with 15 minutes, the mixtures was stirred at reflux temperature for 12 h. Then 40 mL of water was added and the organic layer was extracted with CH_2Cl_2 and evaporated to dryness. The product was purified by column chromatography on silica gel using CH_2Cl_2: CH_3OH (10:1, v/v) as eluent to give the yellow solid product (1.21 g, 51%). ^{1}HNMR (400 MHz, DMSO) δ = 9.08 (s, 1H), 8.93 (d, *J* = 1.7, 1H), 8.36 (s, 1H), 7.70 (d, *J* = 3.6, 1H), 7.40 (d, *J* = 8.8, 2H), 7.22 (dd, *J* = 17.1, 10.0, 2H), 7.02 (s, 4H), 6.92 (s, 5H), 6.72 (d, *J* = 8.7, 2H), 3.94 (t, *J* = 6.4, 4H), 1.71 (dd, *J* = 14.3, 7.6, 4H), 1.34 (dd, *J* = 22.6, 19.3, 12H), 0.88 (s, 6H). GC/TOF HRMS-EI (m/z): found, 674.3159, calcd. for $C_{42}H_{46}N_2O_4S$, 674.3178.

(E)-3-(5-(4-(bis(4-(hexyloxy)phenyl)amino)styryl)thiophen-2-yl)-5-carboxy-1-methylpyridin-1-ium (TJ101). A flask containing dye **TJ101R** (0.8 g, 1.2 mmol) dissolved in CH_3CN and CH_3I (1.7 g, 12.0 mmol) was added rapidly with a magnetic stirrer at a reflux temperature for 12 h. Then the solution was evaporated to dryness and purified by column chromatography on silica gel using CH_2Cl_2:CH_3OH (3:1, v/v) as eluent to give the red solid product (0.37 g, 45%). ^{1}HNMR (400 MHz, DMSO) δ = 9.25 (s, 1H), 9.04 (s, 1H), 8.77 (s, 1H), 7.82 (d, *J* = 3.8, 1H), 7.41 (d, *J* = 8.7, 2H), 7.30 – 7.24 (m, 2H), 7.02 (t, *J* = 10.5, 5H), 6.92 (d, *J* = 9.0, 4H), 6.73 (d, *J* = 8.5, 2H), 4.36 (s, 3H), 3.94 (t, *J* = 6.5, 4H), 1.74 – 1.66 (m, 4H), 1.34 (dd, *J* = 23.0, 19.8, 12H), 0.88 (s, 6H). GC/TOF HRMS-EI (m/z): found, 689.3528; calcd. for $C_{43}H_{42}N_2O_4S$, 689.3408.

(E)-4-(hexyloxy)-N-(4-(hexyloxy)phenyl)-N-(4-(2-(5-(pyridin-3-yl)thiophen-2-yl)vinyl)phenyl)aniline (5). A procedure similar to that for compound **TJ101R**. ^{1}HNMR (400 MHz, Acetone) δ = 8.90 (s, 1H), 8.49 (s, 1H), 8.05 – 7.96 (m, 1H), 7.49 (d, *J* = 3.8, 1H), 7.45 – 7.36 (m, 3H), 7.24 (d, *J* = 16.0, 1H), 7.15 (d, *J* = 3.8, 1H), 7.10 – 7.03 (m, 4H), 6.98 (d, *J* = 16.1, 1H), 6.95 – 6.89 (m, 4H), 6.83 (d, *J* = 8.7, 2H), 3.99 (dd, *J* = 8.2, 4.7, 4H), 1.83 – 1.71 (m, 4H), 1.35 (ddd, *J* = 22.3, 13.2, 10.2, 12H), 0.91 (ddd, *J* = 7.2, 4.9, 2.5, 6H). GC/TOF HRMS-EI (m/z): found, 630.3310; calcd. for $C_{41}H_{46}N_2O_2S$, 630.3280.

(E)-3-(5-(4-(bis(4-(hexyloxy)phenyl)amino)styryl)thiophen-2-yl)-1-(2-ethoxy-2-oxoethyl)pyridin-1-ium (6). To the solution of compound **5** (631 mg, 1 mmol) in CH_3CN (50mL), ethyl bromoacetate (250 mg,1.5 mmol) was added, then react at 85 ºC for 24 h, remove the solvent by rotary evaporation and the residue was purified by chromatography on silica gel using CH_2Cl_2: CH_3OH (15:1, v/v) to provide product **6** (645 mg, 91%). ^{1}HNMR (400 MHz, Acetone) δ = 10.38 (s, 1H), 9.23 (d, *J* = 6.1, 1H), 8.70 (d, *J* = 8.9, 1H), 8.14 (dd, *J* = 8.2, 6.1, 1H), 8.04 (d, *J* = 3.9, 1H), 7.32 (d, *J* = 8.8, 2H), 7.12 (dd, *J* = 10.0, 5.8, 2H), 7.02 – 6.96 (m, 4H), 6.93 – 6.85 (m, 5H), 6.77 (d, *J* = 8.7, 2H), 6.35 (s, 2H), 4.29 (q, *J* = 7.1, 2H), 3.96 (t, *J* = 6.5, 4H), 1.76 (dq, *J* = 12.8, 6.5, 4H), 1.42 – 1.23 (m, 12H), 0.96 – 0.86 (m, 6H). GC/TOF HRMS-EI (m/z): found, 717.3682; calcd. for $C_{45}H_{53}N_2O_4S$, 717.3726.

(E)-3-(5-(4-(bis(4-(hexyloxy)phenyl)amino)styryl)thiophen-2-yl)-1-(carboxymethyl)pyridin-1-ium (TJ102). To the solution of compound **6**(717 mg, 1 mmol) in 50 mL ethanol: H_2O (9:1, v/v), LiOH (838 mg, 20 mmol) was added, stirred at room temperature for 12 h. Then 1 M hydrochloric acid and adjust pH value to 2 – 3, then the solution extracted with CH_2Cl_2. Remove the CH_2Cl_2 by rotary evaporation and the residue was purified by chromatography on silica gel using CH_2Cl_2:CH_3OH (5:1, v/v) as eluent to provide red product. (268 mg, 39%).^{1}HNMR (400

MHz, DMSO) δ = 9.24 (s, 1H), 8.69 (d, *J* = 5.9, 1H), 8.64 (d, *J* = 9.0, 1H), 8.04 (dd, *J* = 8.2, 6.0, 1H), 7.81 (d, *J* = 3.9, 1H), 7.41 (d, *J* = 8.8, 2H), 7.31 – 7.23 (m, 2H), 7.04 (d, *J*=8.9, 4H), 6.92 (d, *J* = 9.0, 4H), 6.72 (d, *J* = 8.7, 2H), 4.91 (s, 2H), 3.94 (s, 4H), 1.76 – 1.61 (m, 4H), 1.31 (d, *J* = 3.9, 12H), 0.88 (s, 6H). GC/TOF HRMS-EI (m/z): found, 689.3406; calcd. for $C_{43}H_{49}N_2O_4S$, 689.3413.

1. J. Zhao, X. Yang, M. Cheng, S. Li and L. Sun, *ACS applied materials & interfaces*, 2013, **5**, 5227.
2. M. Cheng, X. Yang, C. Chen, J. Zhao, Q. Tan and L. Sun, *Physical chemistry chemical physics : PCCP*, 2013, **15**, 17452.