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

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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 TiO2(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 TiO2 paste (DHS-SLP1, Heptachroma, China) as the scattering layer and dried for another 5 min at 130 °C. The double-layer TiO2 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 TiCl4 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 TiO2 photoanode.

The TiO2 photoanode was immersed into a 0.2 mM dye bath (CH3Cl2) 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 CH3Cl2. 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 I2, 0.06 M LiI, 0.4 M 4- tert-butylpyridine (4-TBP), and 0.6 M 3-propyl-1, 2-dimethylimidazolium iodide (DMPII) in CH3CN 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/cm² calibrated with a standard Si solar cell. The working areas of the cells were masked to 0.159 cm². 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. ¹HNMR 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) CHCl₃, POCl₃/DMF, 6 h; b) CH₃CH₂OH, NaBH₄, 1 h; c) CHCl₃, Ph₃P HBr, reflux, 2 h; d) thiophene-2-carbaldhyde, DMF, K₂CO₃, 18-crown-6-ether, Rt, 2 h; e) THF, n-BuLi, isopropenylboronic acid pinacol ester, -78 °C / THF, 5-bromonicotinic acid, K₂CO₃, Pd(PPh₃)₄, reflux, 12 h; f) CH₃CN, CH₃I, reflux, 12 h.

Scheme 2 synthetic routes for dye TJ102 Reagents and conditions: g) CH₃CN, BrCH₂COOEt, reflux, 12 h; h) CH₃CH₂OH, LiOH+H₂O.
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 °C. Then the temperature was raised to 30 °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 CH2Cl2, the solvent was removed with a rotary evaporator. Then the residue was purified by column chromatography on silica gel using CH2Cl2: petroleum ether (1:1, v/v) as eluent to give out the product as pale yellow liquid (6.3 g, 80%). 1H NMR (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 C31H30NO3, 474.2996.

(4-bis(4-(hexyloxy)phenyl)amino)phenyl)methanol (2). A flask containing compound 1 (6.3 g, 13.3 mmol) and NaBH4 (1 g, 26.6 mmol) equipped with a magnetic stirrer in CH2Cl2 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 CH2Cl2 and evaporated to dryness. The product was purified by column chromatography on silica gel using CH2Cl2 (5.9 g, 95%). 1H NMR (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 C31H41NO3, 475.3086.

Compound 2 (5.9 g, 12.5 mmol) and Ph3PBr (4.5 g, 13.1 mmol) was dissolved in CHCl3 (40mL) and refluxed 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-(2-(thiophen-2-yl)vinyl)phenylaniline (4). To a solution of thiophene-2-carbaldehyde (1.3 g, 11.9 mmol), 18-crown-6-ether (100 mg) and anhydrous K2CO3 (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 CH2Cl2: petroleum ether (1:5, v/v) as eluent to give out the product as pale green liquid (3.87 g, 56%). 1H 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 C33H43NO2S, 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 N2 atmosphere, n-BuLi (2.5 M, 4.52 mmol) was added slowly with a magnetic stirrer at -78 °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: H₂O (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 CH₂Cl₂ and evaporated to dryness. The product was purifed by column chromatography on silica gel using CH₂Cl₂: CH₃OH (10:1, v/v) as eluent to give the yellow solid product (1.21 g, 51%). ¹H NMR (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 C₄₂H₄₆N₂O₄S, 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 CH₃CN and CH₃I (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 CH₂Cl₂:CH₃OH (3:1, v/v) as eluent to give the red solid product (0.37 g, 45%). ¹H NMR (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 C₄₃H₄₆N₂O₄S, 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. ¹H NMR (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 C₄₁H₄₆N₂O₂S, 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 CH₃CN (50mL), ethyl bromoacetate (250 mg, 1.5 mmol) was added, then react at 85 °C for 24 h, remove the solvent by rotary evaporation and the residue was purified by chromatography on silica gel using CH₂Cl₂: CH₃OH (15:1, v/v) to provide product 6 (645 mg, 91%). ¹H NMR (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 C₄₅H₄₅N₂O₄S, 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: H₂O (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 CH₂Cl₂. Remove the CH₂Cl₂ by rotary evaporation and the residue was purified by chromatography on silica gel using CH₂Cl₂:CH₃OH (5:1, v/v) as eluent to provide red product. (268 mg, 39%). ¹H NMR (400 MHz, DMSO-d₆) δ = 11.30 (s, 1H), 9.13 (d, J = 6.5, 1H), 8.71 (t, J = 7.0, 1H), 8.29 (d, J = 8.5, 2H), 7.74 (d, J = 7.8, 2H), 7.48 (d, J = 8.9, 2H), 7.12 – 7.01 (m, 4H), 7.01 – 6.85 (m, 5H), 6.76 (d, J = 8.7, 2H), 6.35 (s, 2H), 4.28 (q, J = 7.3, 2H), 3.73 (t, J = 6.5, 4H), 1.76 (dq, J = 12.8, 6.5, 4H), 1.43 – 1.23 (m, 12H), 0.96 – 0.86 (m, 6H). GC/TOF HRMS-EI (m/z): found, 721.3682; calcd. for C₄₅H₄₅N₂O₄S, 721.3726.
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_{2}O_{4}S, 689.3413.