Supporting Information

Simple Organic Molecules Bearing 3,4-Ethylenedioxythiophene Linker for Efficient Dye-Sensitized Solar Cells

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^b Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan. E-mail: <u>ychi@mx.nthu.edu.tw</u> *General procedures*: All reactions were performed under argon atmosphere and solvents were distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored using pre-coated TLC plates (0.20 mm with fluorescent indicator UV₂₅₄). Mass spectra were obtained on a JEOL SX-102A instrument operating in electron impact (EI) or fast atom bombardment (FAB) mode. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury-400 or an INOVA-500 instrument. Elemental analysis was carried out with a Heraeus CHN-O Rapid Elementary Analyzer.

1. 7-Bromo-2,3-dihydrothieno[3,4-b][1,4]dioxine-5-carbaldehyde (1)



A THF (30 mL) solution of 3,4-ethylenedioxythiophene (EDOT, 1 g, 7.04 mmol) was cooled to -78 °C. *n*-Butyl lithium (4.8 mL, 1.6 M, 7.74 mmol) was added dropwise over a period of 10 mins to the above mixture with the temperature maintained at -78 °C. After then, anhydrous DMF (1 mL, 8.4 mmol) was added and the mixture was allowed to attain RT slowly and stirred overnight. The reaction was quenched by pouring this mixture into a chilled 0.5 N HCl solution (30 mL), giving a colorless precipitate which was subsequently collected by filtration, followed by washing with deionized water. Moreover, this precipitate was dried under vacuum and dissolved into a mixture of DMF (20 mL) and N-bromosuccinimide (NBS, 1.02 g, 8.02 mmol). After stirring at RT for two hours, the mixture was poured over crushed ice (100 g) to obtain the desired colorless precipitate; yield: 1.57 g, 90%.

Spectral data of 1: MS (EI): m/z 249 (M⁺). ¹H NMR (400 MHz, CDCl₃, 298 K): δ 9.80 (s, 1H), 4.34 (s, 4H). ¹³C NMR (100 MHz, CDCl₃, 298K): δ 178.6, 147.6, 140.1, 118.2, 101.5, 65.1, 64.7.

2. 7-(4-(Diphenylamino)phenyl)-2,3-dihydrothieno[3,4-b][1,4]dioxine-5carbaldehyde (2)



4-(Diphenylamino)phenylboronic acid (300 mg, 1.03 mmol) was treated with carbaldehyde (1) (259 mg, 1.03 mmol) in the presence of Pd(PPh₃)₄ (59.4 mg, 0.05 mmol), 2N aqueous solution of K₂CO₃ (1 mL) and THF (30 mL). After the completion of the reaction, the solvent was removed under vacuum and the residue dissolved into minimal amount of CH₂Cl₂. It was then filtered and purified by column chromatography on silica gel using a 4:1 mixture of hexane and CH₂Cl₂ as eluent; yield: 276 mg, 0.67 mmol, 65%. **Spectral data of 2**: MS (EI): m/z 413 (M⁺). ¹H NMR (400 MHz, CDCl₃, 298 K): δ 9.88 (s, 1H), 7.62 (2H, d, *J* = 8.1 Hz), 7.28 (4H, t, *J* = 8.1 Hz), 7.10 (4H, d, *J* = 8.1 Hz), 7.06 ~ 7.01 (4H, m), 4.39 (2H, t, *J* = 5.2 Hz), 4.35 (2H, t, *J* = 5.2 Hz). ¹³C NMR (125 MHz, CDCl₃, 298K): δ 179.3, 149.0, 148.2, 146.9, 136.8, 129.3, 127.7, 125.0, 124.8, 123.6, 122.1, 114.6, 65.0, 64.4. Anal. Calcd. for C₂₅H₁₉NO₃S: C, 72.62; H, 4.63; N, 3.39. Found: C, 72.36; H, 4.53; N, 3.65.

3. 2-Cyano-3-(7-(4-(diphenylamino)phenyl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-5yl) acrylic acid (LJ1)



The carbaldehyde (2) (100 mg, 0.24 mmol), with cyanoacetic acid (24.6 mg, 0.29 mmol), ammonium acetate (5 mg, 0.06 mmol) and glacial acetic acid (20 mL) were mixed together and the solution heated to reflux for 4 h. After cooling to RT, the mixture was poured into a chilled aqueous solution to yield a dark red precipitate. It was filtered and thoroughly washed with deionized water (3×30 mL), and a 1:1 mixture of hexane and diethylether (3×20 mL). The obtained red precipitate was then purified by crystallization from a mixture of THF and hexane; yield: 72 mg, 0.15 mmol, 62%.

Spectral data of LJ1: MS (FAB): m/z 480 (M⁺). ¹H NMR (400 MHz, d₆-DMSO, 298 K): δ 8.19 (1H, s), 7.67 (2H, d, *J* = 8.1 Hz), 7.35 (4H, t, *J* = 8.1 Hz), 7.13 ~ 7.07 (6H, m), 6.98 (2H, d, *J* = 8.1 Hz), 4.49 (2H, s), 4.40 (2H, s). ¹³C NMR (125 MHz, d₆-DMSO, 298 K): δ 164.5, 150.0, 148.4, 146.7, 140.4, 137.9, 130.2, 128.3, 127.7, 125.4, 124.5, 124.4, 122.0, 117.5, 108.3, 93.5, 66.1, 65.0. Anal. Calcd. for C₂₈H₂₀N₂O₄S: C, 69.98; H, 4.20; N, 5.83. Found: C, 70.11; H, 4.10; N, 5.98.

4. 2-(5-((7-(4-(Diphenylamino)phenyl)2,3-dihydrothieno[3,4,b][1,4]dioxin-5-yl)met hylene)-4-oxo-2-thioxothiazolidin-3-yl)acetic acid (LJ3)



The compound **2** (100 mg, 0.24 mmol), rhodamine 3-acetic acid (55.1 mg, 0.29 mmol), ammonium acetate (5 mg, 0.06 mmol) and glacial acetic acid (20 mL) were mixed together and the solution heated to reflux for 4 h. After cooling to RT, the mixture was poured into chilled aqueous solution to yield a black precipitate. It was filtered and thoroughly washed with deionized water (3×30 mL), and a 1:1 mixture of hexane and diethylether (3×20 mL). This compound was further purified by crystallization from a mixture of THF and hexane; yield: 79 mg, 0.13 mmol, 56%.

Spectral data of LJ3: MS (FAB): m/z 586 (M⁺). ¹H NMR (400 MHz, d₆-DMSO, 298 K): δ 7.76 (1H, s) 7.67 (2H, d, J = 8.1 Hz), 7.33 (4H, t, J = 8.1 Hz), 7.13 ~ 7.07 (6H, m), 6.96 (2H, d, J = 8.1 Hz), 4.66 (2H, s), 4.48 (2H, s), 4.40 (2H, s). ¹³C NMR (125 MHz, d₆-DMSO, 298K): δ 191.4, 167.2, 165.8, 147.6, 146.8, 146.4, 138.1, 129.7, 127.4, 126.7, 124.8, 124.4, 123.9, 121.7, 121.3, 114.5, 109.3, 65.4, 64.6, 45.2. Anal. Calcd. for C₃₀H₂₂N₂O₅S₃: C, 61.41; H, 3.78; N, 4.77. Found: C, 61.58; H, 3.84; N, 4.91.

5. Preparation of LJ2



This compound was prepared using method established for LJ3.

Spectral data of LJ2: MS (FAB): m/z 528 (M⁺). ¹H NMR (400 MHz, d₆-DMSO, 298 K): δ 8.13 (1H, s), 7.80 (1H, d, J = 4.2 Hz) 7.69 (2H, d, J = 8.1 Hz), 7.63 (1H, d, J = 4.2 Hz) 7.35 (4H, t, J = 8.1 Hz), 7.14 ~ 7.08 (6H, m), 6.95 (2H, d, J = 8.1 Hz), 4.71 (2H, s). ¹³C NMR (125 MHz, d₆-DMSO, 298K): δ 191.8, 167.2, 165.9, 152.5, 148.3, 146.4, 138.4, 135.2, 129.7, 127.1, 127.0, 125.6, 124.9, 124.7, 124.0, 121.8, 117.7, 45.1. Anal. Calcd. for C₂₈H₂₀N₂O₃S₃: C, 63.31; H, 3.81; N, 5.30. Found: C, 63.49; H, 3.67; N, 5.57.

6. Preparation of 6.



This compound was prepared using method established for 2.

Spectral data of 6: MS (FAB): m/z 591 (M⁺). ¹H NMR (400 MHz, CDCl₃, 298 K): δ 9.96 (1H, s), 7.68 (2H, dd, J = 6.9, 1.8 Hz), 7.26 (4H, t, J = 8.1 Hz), 7.11 (4H, d, J = 8.1 Hz) 7.05 (2H, t, J = 7.2 Hz), 7.02 (2H, d, J = 7.2 Hz), 4.49 (2H, m), 4.13 (2H, m), 3.78 (2H, m), 3.69 (2H, m), 3.64 (2H, m), 3.56 (2H, m), 3.52 (2H, m), 3.45 (2H, m), 3.35 (3H, s), 3.25 (3H, s). ¹³C NMR (125 MHz, CDCl₃, 298K): δ 181.1, 156.8, 148.6, 147.0, 143.8, 137.6, 129.4, 128.0, 125.2, 124.9, 123.7, 121.9, 121.6, 77.2, 73.1, 72.1, 71.9, 70.6, 70.5, 70.0, 69.9, 59.0, 58.9. Anal. Calcd. for C₃₃H₃₇NO₇S: C, 66.98; H, 6.30; N, 2.37. Found: C, 66.85; H, 6.13; N, 2.21.



This compound was prepared using method established for LJ1.

Spectral data of LJ4: MS (FAB): m/z 658 (M⁺). ¹H NMR (400 MHz, CDCl₃, 298 K): δ 8.53 (1H, s), 7.72 (2H, d, *J* = 8.8 Hz), 7.27 (4H, t, *J* = 7.6 Hz), 7.12 (4H, d, *J* = 8.2 Hz), 7.07 (2H, t, *J* = 7.4 Hz), 7.00 (2H, d, *J* = 8.8 Hz), 4.48 (2H, m), 4.11 (2H, m), 3.75 (2H, m), 3.68 (2H, m), 3.65 (2H, m), 3.56 ~ 3.54 (4H, m), 3.45 (2H, m), 3.35 (3H, s), 3.25 (3H, s). ¹³C NMR (125 MHz, CDCl₃, 298K): δ 168.0, 157.5, 149.1, 146.8, 144.1, 143.9, 139.1, 129.4, 128.3, 125.3, 124.3, 124.0, 121.5, 116.4, 92.9 76.6, 73.0, 72.1, 71.8, 70.5, 70.4, 69.9, 69.8, 59.0, 58.9. Anal. Calcd. for C₃₆H₃₈N₂O₈S: C, 65.64; H, 5.81; N, 4.25. Found: C, 65.32; H, 5.57; N, 4.12.

7. Fabrication of DSSC and Photovoltaic Measurements

TiO₂ anatase nanoparticles of 20 nm were prepared using published procedures.[1] TiO₂ particles were dispersed in α -terpineol with ethyl cellulose as a binder. The TiO₂ thin films of 12 µm were prepared by a doctor-blade method on a transparent conducting oxide (F-doped SnO₂, FTO). These films were dried at 150 °C for 15 min and then a 4 µm thick layer of 200 nm TiO₂ particles (ST-41, particles were obtained from Ishihara Sangyo, Japan) was deposited again by a doctor-blade method with a dimension of 0.5 × 0.5 cm². Afterwards, the double-layered films were sintered at 500 °C for 30 min. After sintering, the TiO₂ films were treated with 50mM TiCl₄ solution, rinsed with water and ethanol, and sintered at 500 °C for 30 min. After cooling to 80 °C, the TiO₂ electrode was coated with dyes by dipping the film in a solutions of 3×10^{-4} M dye and 1 mM deoxycholic acid (DCA) in acetonitrile and tert-butanol (volume ratio: 1:1) overnight. After being rinsed with EtOH, the dye-coated TiO₂ electrode was incorporated into a thin-layer sandwich-type cell with a Pt-coated FTO as counter electrode, a spacer film (Surlyn 1702, 25 µm), and an organic electrolyte was then injected into the space. Lastly, the cell sealed with Torr Seal cement (Varian, MA) to measure the solar cell performance. The Pt counterelectrode was prepared by spin-coating a 0.05M H₂PtCl₆ in isopropyl alcohol solution on FTO glass followed by sintering at 385 °C for 15-30 min. The electrolyte contained 0.6 Μ 1-butyl-3-methylimidazolium iodide (BMII), 0.1 M LiI, 0.05 M I₂, 0.5 M 4-tert-butylpyridine (TBP) in acetonitrile solvent. Light-to-electricity conversion efficiency values were measured using a standard AM1.5 solar simulator-Oriel 66 924 Arc lamp source with a 6266 450 W Xe lamp, an Oriel 81088 Air Mass 1.5 Global Filter and a digital source meter purchased from Keithley Instruments Inc. The incident light intensity was calibrated by using a standard solar cell composed of a crystalline silicon solar cell and an IR cutoff filter (Schott, KG-5), giving the photoresponse range of amorphous silicon solar cell.

We estimated the short circuit current density of cell LJ1 by integrating the IPCE value of the device versus the sun AM1.5G spectrum from 400 to 650 nm (see the Figure S2), the calculated short circuit current density is 11.2mA/cm², which is smaller than the measured value (15.5 mA/cm²) from AM1.5 simulated light source. We think that two reasons may contribute to the differences. First, the intensity of the monochromated light longer than 600 nm of our system is low, which can lead to more prominent dark current and lower IPCE. The other factor is that the integration is performed only from 400 to 650 nm. The contribution from wavelength shorter than 400 nm is ignored, so that the calculated current may be underestimated. Similarly, lower current density calculated from IPCE is deduced

for other devices (LJ2-LJ4). Moreover, similar trends, i.e. lower current density calculated from IPCE in comparison to that obtained from solar simulated measurement, have been reported in our recent paper [2] and other literatures.[3,4]

Figure S3 shows the Bode phase plot of device LJ1 and device LJ3 at open circuit voltage (OCV) (-0.6V), 1 sun. The Bode phase plot indicates that the characteristic frequency of device LJ1 (~ 127 Hz) is lower than that of device LJ3 (~721 Hz) (ref. C4). The results provide supplementary support in that the electron lifetime is shorter in device LJ3. This can be ascribed to certain degrees of the disruption of the π^* electron conjugation between rhodanine and the carboxylic acid (due to the addition of a methylene group in between) in LJ3, resulting in a decrease of the electron injection efficiency in a dynamic manner.

8. Theoretical Approach:

All calculations are done by Gaussian 03 program.[5] The geometries of TPA dyes are optimized by B3LYP/6-31G*, following by the vibrational frequency analysis to confirm the number of imaginary frequency is zero for a minimum.[6] After obtaining the converged geometries, the time-dependent B3LYP functional is combined with the same basis set and used to calculate the vertical excitation energies of these dyes.[7]



Fig. S1. Emission spectra of L1, LJ1, LJ2, LJ3 and LJ4 in *tert*-butanol/acetonitrile (1/1) solution.



Fig. S2. The standard AM1.5G irradiance spectrum and the IPCE spectra for DSSCs based on LJ1



Fig. S3. Bode phase plot of device **LJ1** (-•-•-) and device **LJ3** (-•-•-) at OCV (-0.6V), 1 sun.

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