

Supplementary information

High-efficiency dye-sensitized solar cell with a novel co-adsorbent

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Synthesis of 5-(2,4-dibutoxyphenyl), thiophene-2-carbaldehyde (1a).

5-formyl-2-bromo thiophene (0.100 g, 0.523 mmol), 2,4-dibutoxy phenyl boronicacid (0.152 g, 0.575 mmol), 2 M aqNa₂CO₃ (3 ml), Pd(PPh₃)₄ (0.060 g, 10mol %) and dimethoxyethane (3 ml) were mixed and degassed. The whole system was refluxed for 20 hours under an inert atmosphere of argon. Then the reaction mixture obtained was filtered through celite, extracted with dichloromethane, dried over Na₂SO₄ and was finally purified by column chromatography on silica gel eluting with ethyl acetate-petroleum ether (1:24). Fine cream colored solid was obtained.

Yield: 0.120 g (69 %).

¹H NMR (300 MHz, CDCl₃) δ9.84 (s, 1H), 7.63 (d, *J* = 3.9 Hz, 1H), 7.58 (d, *J* = 9.2 Hz, 1H), 7.43 (d, *J* = 3.7 Hz, 1H), 6.48-6.46 (m, 1H), 4.09 (t, *J* = 6.5 Hz, 1H), 3.98 (t, *J* = 6.4 Hz, 2H), 1.98 (m, 2H), 1.79 (m, 2H), 1.62-1.45 (m, 4H), 1.04-0.97 (m, 6H).

Synthesis of Y1

5-(2,4-dibutoxyphenyl) thiophene-2-carbaldehyde (0.300 g, 0.903 mmol), cyanoacetic acid (0.076 g,

0.903 mmol) and ammonium acetate (5 mol %) were added into an acetic acid (5 ml) solution and then refluxed for 7 hours. The obtained precipitate was washed thoroughly with water (to remove excess acetic acid and cyanoacetic acid), followed by ethyl acetate: hexane (9:1), dried under vacuum to afford a bright orange colored solid, CS-1 (0.300 g, 83 %), mp.

^1H NMR (300 MHz, d_6 -DMSO) δ 8.42 (s, 1H), 7.91 (d, J = 4.2 Hz, 1H), 7.88 (d, J = 8.7 Hz, 1H), 7.74 (d, J = 4.2 Hz), 6.72 (d, J = 1.8 Hz), 6.66 (dd, J = 8.7 and 1.8 Hz), 4.17 (m, 2H), 4.05 (m, 2H), 1.88 (m, 2H), 1.72 (m, 2H), 1.53 (m, 2H), 1.46 (m, 2H), 0.97 – 0.93 (m, 6H), MS (FAB) m/z 428.2.

Synthesis of 5-(2,4-diFluorophenyl), thiophene-2-carbaldehyde (1b).

5-formyl-2-bromo thiophene (0.100 g, 0.523 mmol), 2,4-difluoro phenyl boronic acid (0.090 g, 0.575 mmol), 2 M aqNa₂CO₃ (3 ml), Pd(PPh₃)₄ (0.060 g, 10mol %) and dimethoxyethane (3 ml) were mixed and degassed. The whole system was refluxed for 5 hours under an inert atmosphere of argon. Then the reaction mixture obtained was filtered through celite, extracted with dichloromethane, dried over Na₂SO₄ and was finally purified by column chromatography on silica gel eluting with ethyl acetate-petroleum ether. Yellow crystal was obtained. Yield: 0.090 g (76 %).

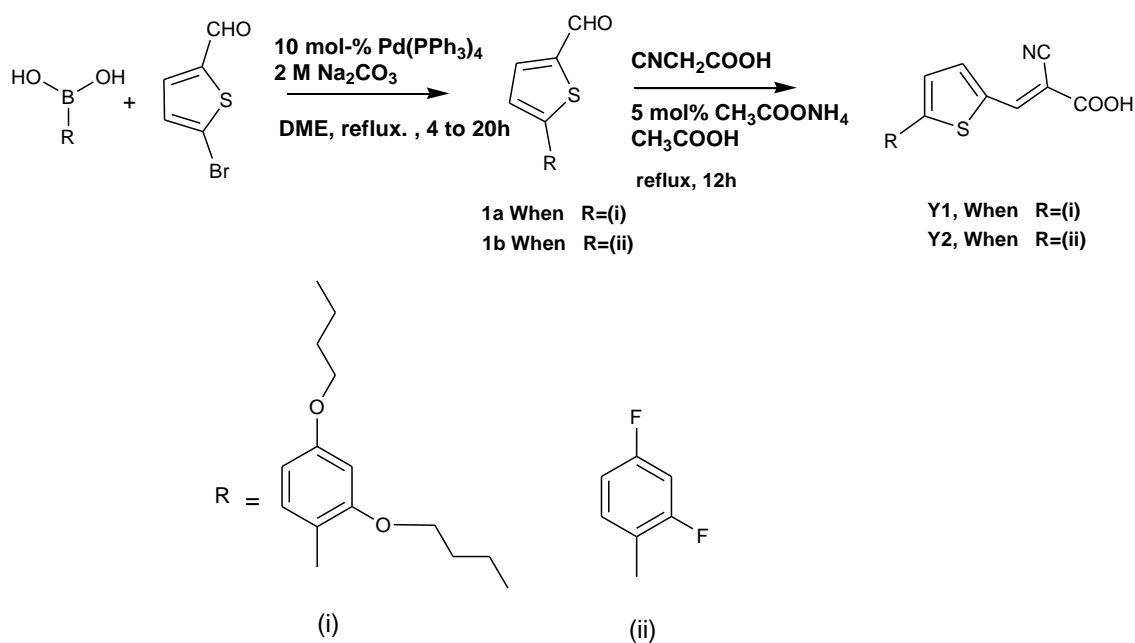
^1H NMR (300 MHz, CDCl₃) δ 9.90 (s, 1H), 7.73 (d, J = 3.9 Hz, 1H), 7.69-7.61 (m, 1H), 7.48 (dd, J = 1.3, 3.9 Hz, 1H), 7.02-6.92 (m, 2H), MS (FAB) m/z 428.2.

Synthesis of Y2

5-(2,4-difluorophenyl) thiophene-2-carbaldehyde (0.050 g, 0.223 mmol) cyanoacetic acid (0.018 g,

0.223 mmol), ammonium acetate (5 mol %) were added into an acetic acid (2 ml) solution and then refluxed for 2 hours. The obtained precipitate was washed thoroughly with water (to remove excess acetic acid and cyanoacetic acid), hexane and finally with a 10 % (ethylacetate + hexane) mixture to afford a yellow solid, CS-2 (0.060 g, 93 %).

^1H NMR (300 MHz, d_6 -DMSO) δ 8.20 (s, 1H), 7.94 (m, 1H), 7.82 (d, $J = 3.9$ Hz), 7.68 (d, $J = 3.9$ Hz), 7.46 (m, 1H), 7.24 (m, 1H).



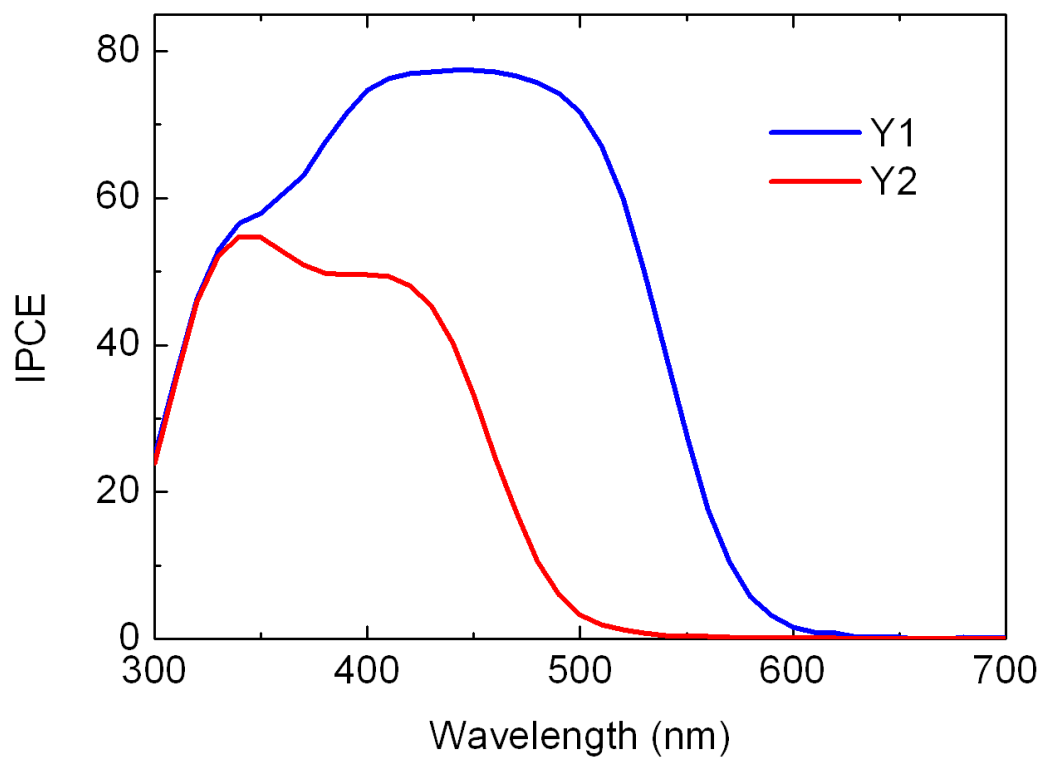


Figure S1. IPCE spectra. The IPCE curve of DSCs sensitized with **Y1** (blue line) and **Y2** (red line).

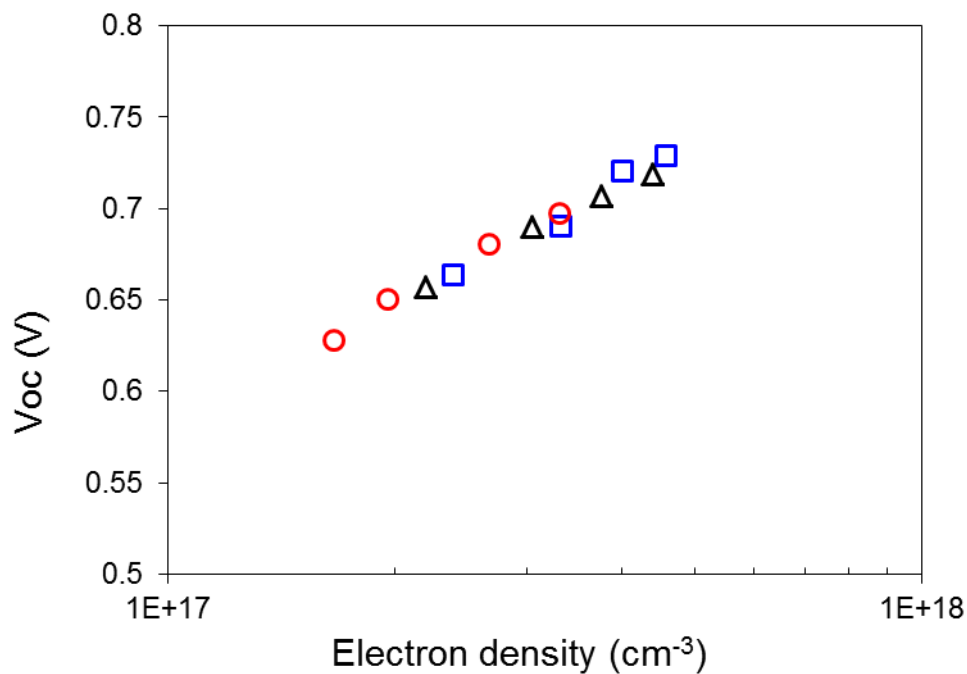


Figure S2. V_{oc} versus electron density. The V_{oc} values against electron density in DSCs sensitized by black dye with coadsorbent **Y1** (open square), without coadsorbent (open triangle) and with coadsorbent **Y2** (open circle) were derived by using a charge extraction method. Charge extraction from TiO_2 was calculated by integration of the transient current detected when the laser illumination was turned off and the DSC was simultaneously stepped from open-circuit to short-circuit.