

Supporting information

Structural design of ruthenium sensitizer compatible with cobalt electrolyte for dye-sensitized solar cell

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Preparation and characterization of Ligand 18.

1. 2 g (11.23 mmol) NBS was dissolved in 40 mL dried DMF, then 1.95 g (14.04 mmol) 3-butyl thiophene was added. After reacting for 4 hours, the reaction was quenched with 1.0 M HCl_(aq). The product was extracted with CH₂Cl₂. The organic layer was collected and washed with saturated NaHCO_{3(aq)}, de-ionized water and saturated NaCl_(aq), respectively to remove the impurity. After washing, the organic layer was dried over anhydrous MgSO₄ and the solvent was removed by rotary evaporation to obtain the product. The crude product was further purified by chromatography with hexane as an eluent to afford 2.98 g (80.9% yield) BrnBT. ¹H NMR (300 MHz, δ/ppm in CDCl₃, *J* Hz): 7.22 (1H, d, *J* = 5.4 Hz); 6.78 (H, d, *J* = 5.7 Hz); 2.53 (2H, t, *J* = 7.5 Hz); 1.50 (2H, m); 1.25 (2H, m); 0.86 (3H, t, *J* = 7.5 Hz).
2. 0.8 g (33.33 mmol) Mg powder was added in 40 mL dried Ether, then slowly added 5.48 g (40 mmol) 1-Bromobutane, ultrasonic for 50 min at 0 °C. To the mixture, 5.08 g (23.33 mmol) 3-Bromothiophene and 0.05 g (0.09 mmol)

NiCl₂(dppp) was added for reacting 50 min. The reaction was quenched with 1.0 M HCl_(aq) and the product was extracted with ether. The organic layer was collected and the solvent was removed by rotary evaporation. The crude product was further purified by chromatography using hexane as an eluent to afford 3.58 g (78.9% yield) light yellow liquid DnBT. ¹H NMR (300 MHz, δ/ppm in CDCl₃, *J* Hz): 7.00 (1H, d, *J* = 5.1 Hz); 6.77 (1H, d, *J* = 5.1 Hz); 2.68 (2H, t, *J* = 7.5 Hz); 2.50 (2H, t, *J* = 7.5 Hz); 1.57 (4H, m); 1.35 (4H, m); 0.93 (6H, m).

- 2.33 g (11.88 mmol) DnBT was dissolved in 50 mL dried THF and cooled to -78 °C. 4.6 mL (11.5 mmol) *n*-BuLi (2.5 M in hexane) was injected slowly into the cold DnBT/THF solution and stirred for 2 hr then 2.6 g (13.0 mmol) Me₃SnCl (in 2 mL THF) was added. The temperature of the reaction mixture was raised to room temperature and stirred for 10 hr. The reaction was quenched with H₂O and the product was extracted with CH₂Cl₂. The solvent was removed under vacuum and a dark green gel TMeSn- DnBT was obtained.
- Without further purification, 3.04 g (8.46 mmol) TMeSn-DnBT and 1.65 g (10.12 mmol) 2-bromothiophene were dissolved in 40 mL dried DMF. After removing the moisture inside, 0.48 g (0.4 mmol) Pd(PPh₃)₄ (dissolved in 1 mL THF) was added and then reacts at 130 °C for 72 hr. The reaction was quenched with NH₄Cl_(aq) and the product was extracted with CH₃Cl. After purifying by chromatography using hexane as an eluent to afford 2.08 g (74% yield) green yellow liquid DnBBT. ¹H NMR (300 MHz, δ/ppm in CDCl₃, *J* Hz): 7.14 (1H, dd, *J* = 5.4 Hz, 0.9 Hz); 7.07 (1H, dd, *J* = 3.3 Hz, 0.9 Hz); 6.97 (1H, m), 6.89 (1H, s); 2.70 (2H, t, *J* = 7.5 Hz); 2.47 (2H, t, *J* = 7.5 Hz); 1.62 (4H, m); 1.47 (4H, m); 0.97 (6H, m).
- 5.1 g (18.32 mmol) DnBBT was dissolved in 80 mL dried THF and cooled down to -78 °C. 7.3 mL (18.25 mmol) *n*-BuLi (2.5 M in hexane) was injected into DnBBT/THF solution slowly. After stirring for 2 hr, 3.64 g (18.29 mmol) Me₃SnCl (in 2 mL THF) was added and the temperature was raised to room temperature and stirred for 10 hr. The reaction was quenched with H₂O and the product was extracted with CH₂Cl₂. After removing the solvent, a dark red gel TMeSn-DnBBT was obtained.
- Without further purification, 7.89 g (19.47 mmol) TMeSn-DnBBT and 2.77 g (8.85 mmol) 4,4'-Dibromo-2,2'-bipyridine were dissolved in 120 mL dried DMF.

After removing the moisture in the solution, 0.5 g (0.42 mmol) Pd(PPh₃)₄ dissolved in 2 mL THF was added. The mixture was stirred at 130 °C for 72 hr. The reaction was quenched with saturated NH₄Cl_(aq) and the product was extracted with CH₃Cl. The solvent was removed with vacuum and the crude product was purified with Soxhlet and then washed down with ethylacetate. Removing ethylacetate under vacuum to obtain 3.65 g yellow solid **Ligand-B18**, yield 58%. ¹H NMR (300 MHz, δ/ppm in CDCl₃, *J* Hz): 8.66 (2H, d, *J* = 5.1 Hz); 8.62 (2H, s); 7.55 (2H, d, *J* = 3.9 Hz); 7.47 (2H, dd, *J* = 5.1 Hz, 1.8 Hz); 7.11 (2H, d, *J* = 3.6 Hz); 7.00 (2H, s); 2.74 (4H, t, *J* = 7.5 Hz); 2.51 (4H, t, *J* = 7.5 Hz); 1.59 (8H, m); 1.41 (8H, m); 0.94 (12H, m).

Preparation of CYC-B11H.

(a) Preparation of Ligand 11

Ligand 11 was prepared according to the literature reported.^{S1}

(b) Preparation of CYC-B11H

CYC-B11H was prepared with the same procedures as that for CYC-B11 reported in literature.^{S1} 0.202 g (0.330 mmol) [RuCl₂(p-cymene)]₂, 0.473 g (0.660 mmol) Ligand-11, 0.161 g (0.660 mmol) dcbpy (4,4'-dicarboxylic acid-2,2'-bipyridine) and excess NH₄NCS were used in the reaction. The crude product was dissolved in a mixture of methanol and tetra-butyl ammonium hydroxide (TBAOH) aqueous solution (40 wt% in H₂O) and then purified on a Sephadex LH-20 column, using methanol as an eluent. The main band was collected and the pH value of the collected solution was lowered by adding dilute HNO_{3(aq)} until most solid was precipitated (pH < 3.0, the pH value in solution was used to control the final product to be an ammonia or proton form). The collected precipitate was washed with water and dried under vacuum. After purification, a purple solid 0.40 g (0.28 mmol, 42.7% yield) was obtained. ¹H-NMR spectrum of CYC-B11H is similar to that for CYC-B11 except no signal corresponding to butyl group was observed. MS calcd: *m/z* 1178 HRFAB-MS found: 1178.1551,

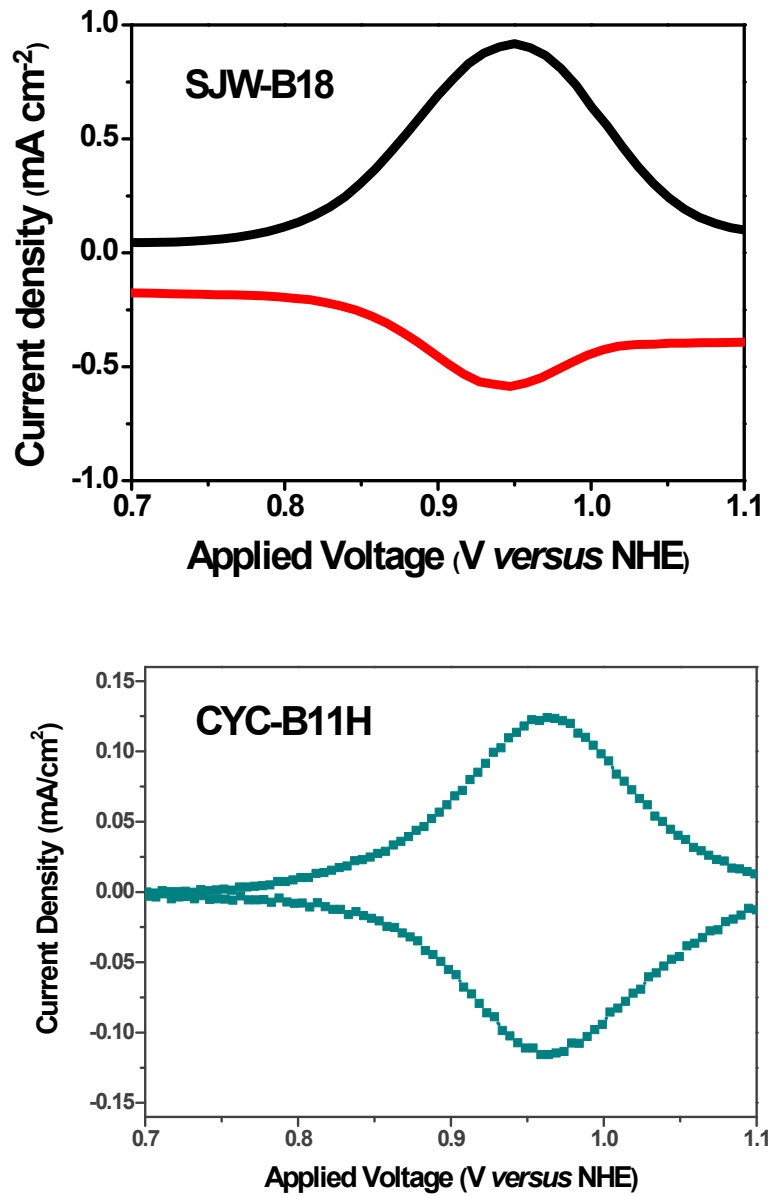


Figure S1: The square-wave voltammograms of **SJW-B18** and **CYC-B11H** (in DMF).

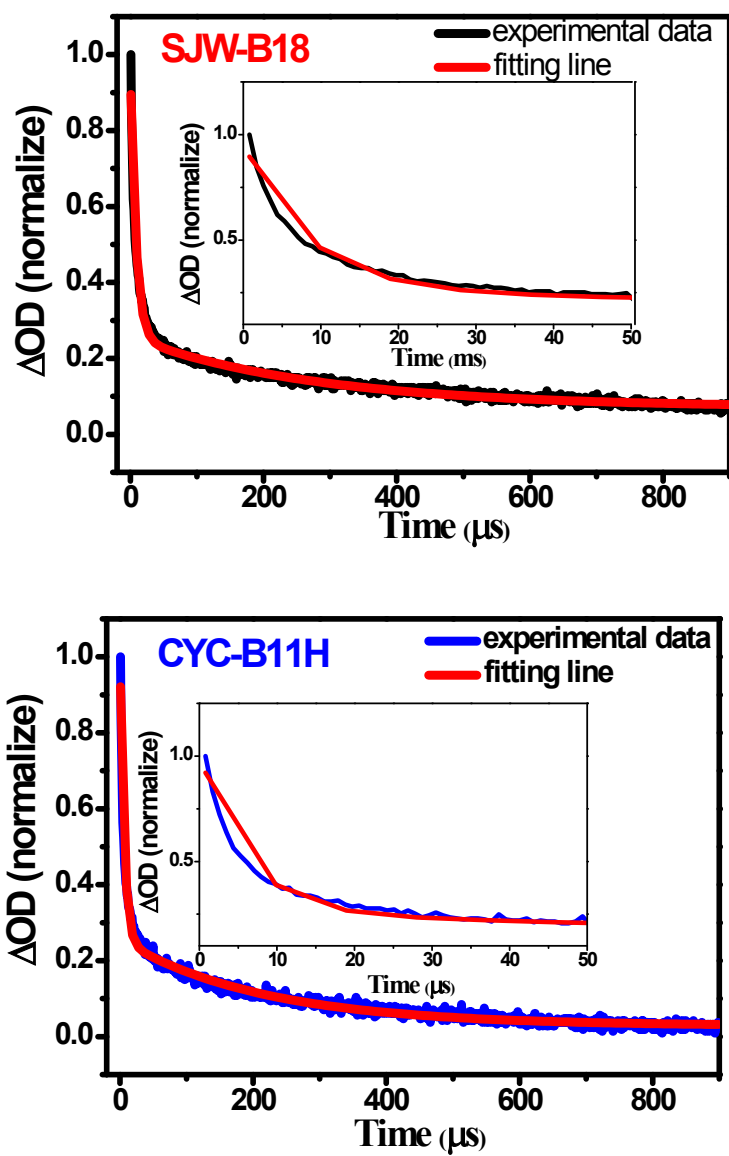


Figure S2: the transient absorption spectra of the devices sensitized with SJW-B18 and CYC-B11H using I^-/I_3^- electrolyte.

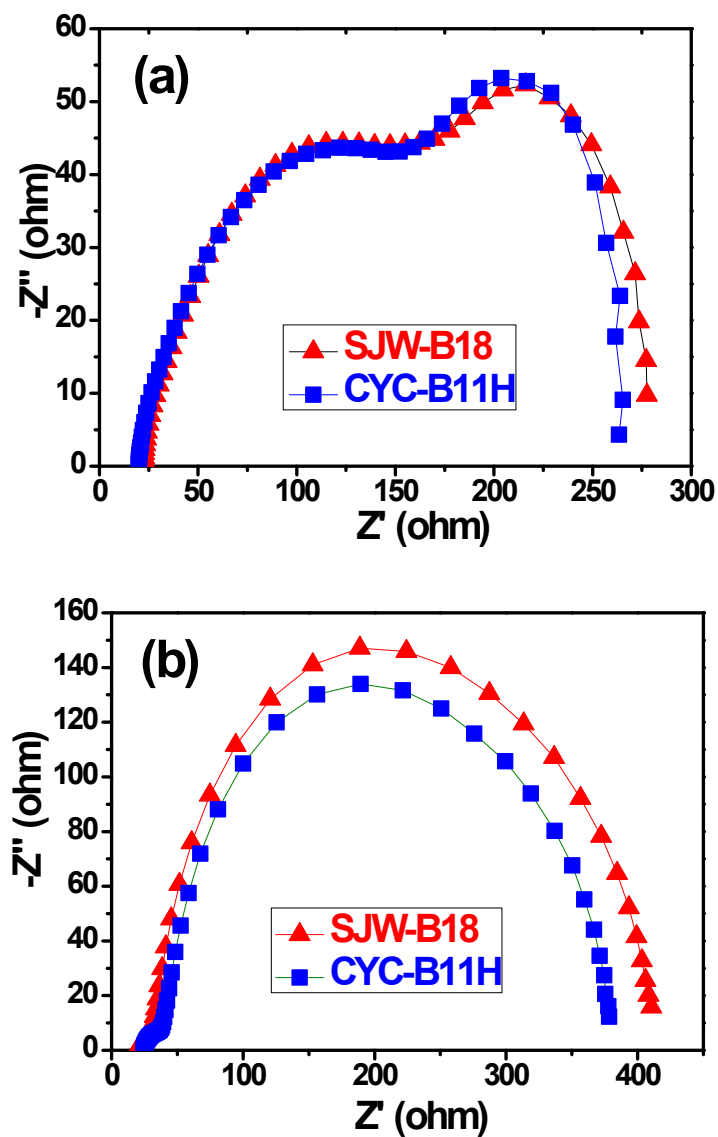


Figure S3: Electrochemical impedance plots measured at the dark for the devices sensitized with SJW-B18 and CYC-B11H: (a) thick TiO_2 anode. (b) thin TiO_2 anode.

Reference:

- [S1] C. Y. Chen, M. Wang, J. Y. Li, N. Postrakulchote, L. Alibabaei, C. H. Ngoc-le, J. D. Decoppet, J. H. Tsai, C. Grätzel, C. G. Wu, S. M. Zakeeruddin, M. Grätzel, *ACS Nano* **2009**, *3*, 3103.