Supplementary information

Effect of electron-donor ancillary ligands on the heteroleptic ruthenium complexes: synthesis, characterization, and application to high performance dye-sensitized solar cells

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Synthesis of 4,4'-bis(4-methylthiophenyl)-2,2'-bipyridine (Ligand 1): 4,4'-dibromo-2,2'-bipyridine (157 mg, 0.5 mmol), (4-methylthiophenyl) boronic acid (184.8 mg, 1.1 mmol), K_2CO_3 (1.03 g, 7.5 mmol) and $Pd(PPh_3)_4$ (45 mg, 0.04 mmol) were dissolved in DMF/H_2O (9:1, v/v, 50 mL). The mixture was refluxed under Ar for 24 h. The organic layers, extracted with $CHCl_3$ for three times, were washed with brine, dried with anhydrous Na_2SO_4. After the solvent was evaporated, the crude product was purified by column chromatography (CH_2Cl_2/CH_3OH, 25:1, v/v) obtained the target

compound Ligand-1 as a litter yellow powder. (84 mg, yield 42%). ^{1}H NMR (400 MHz, $CDCl_3$): δ /ppm: 9.37 (s, 2H), 8.89 (d, 2H), 8.02 (s, 4H), 7.96 (s, 2H), 7.47 (dd, 4H), 2.59 (s, 6H).

Synthesis of 4,4'-bis(4-methoxyphenyl)-2,2'-bipyridine (Ligand 2): A mixture of compound 4,4'-dibromo-2,2'-bipyridine (157 mg, 0.5 mmol), (4-methoxyphenyl) boronic acid (167.2 mg, 1.1 mmol) and $Pd(PPh_3)_4$ (45 mg, 0.04 mmol) were dissolved in 1,4-dioxane (40 mL) under magnetic stirring for half hours. Then, K_2CO_3 (1.03 g, 7.5 mmol) in 5mL deionized water was added and the mixture was refluxed under Ar for 24 h. The organic layer, after cooled to room temperature, was extracted with CH_2Cl_2 for three times. The combined organic layers were washed with brine, dried with anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure. The purification of remaining crude product by column chromatography (CH_2Cl_2/CH_3OH, 50:1, v/v) obtained Ligand-2 as a white powder. (105 mg, yield 57 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ /ppm: 8.76 (m, 4H), 7.83-7.82 (m, 4H), 7.60 (s, 2H), 7.09-7.06 (dd, 4H), 3.92 (s, 6H).

***Synthesis of 4,4'-bis(3,4-Methylenedioxyphenyl)-2,2'-bipyridine (Ligand 3)*:** 4,4'-dibromo-2,2'-bipyridine (157 mg, 0.5 mmol), (3, 4-Methylenedioxyphenyl) boronic acid (182.5 mg, 1.1 mmol), K_2CO_3 (1.03 g, 7.5 mmol) and $Pd(PPh_3)_4$ (45 mg, 0.04 mmol) were dissolved in toluene/EtOH/H_2O (2:1:1, v/v/v, 40 mL). The mixture was refluxed under Ar for 24 h. The organic layers, extracted with $CHCl_3$ for three times, were washed with brine, dried with anhydrous Na_2SO_4. The solvent was removed on a rotary evaporator under vacuum and the crude product was purified by column

chromatography (CH_2Cl_2/CH_3OH, 200:1, v/v) obtained the target compound Ligand-3 as a yellow powder. (93 mg, yield 47 %).^{1}H NMR (400 MHz, $CDCl_3$): δ /ppm: 9.18 (s, 2H), 8.89 (s, 2H), 8.00 (s, 2H), 7.82 (d, 2H), 7.63 (d, 2H), 7.10 (d, 2H), 6.15 (s, 4H).

Synthesis of RC-15 (Ru[(dcbpy)(Ligand-1)(NCS)$_2$]): Dichloro(p-cymene) ruthenium(II) dimmer (153 mg, 0.25 mmol) and Ligand-1 (184 mg, 0.50 mmol) were dissolved in DMF. The mixture was stirred at 90 °C for 4 h under Ar in the dark. Subsequently, 4,4'-dicarboxylic acid-2,2'-bipyridine (122.2 mg, 0.50 mmol) was added into the flask and the reaction mixture was heated up to 140 °C for 6 h. Next, an excess of potassium thiocyanate (1.13 g, 15 mmol) was added to the resulting dark solution and it was continued for 6 h at 140 °C. Then the reaction mixture was cooled to room temperature overnight. After the solvent was evaporated under vacuum, H_2O was added to get the precipitate. The solid was collected on a sintered glass crucible by suction filtration, washed intensively with diethyl ether, and dried under vacuum. The crude product was dissolved in basic methanol (with NaOH) and purified on a Sephadex LH-20 column with MeOH as eluent. The collected main band was collected and slowly dropped with an acidic methanol solution to pH 5.9. Yield (3×): 43%. The precipitate was collected on a sintered glass crucible by suction filtration and dried in air. ^{1}H NMR(400 MHz, DMSO-D6): δ /ppm: 9.27 (m, 2H), 9.12 (m, 2H), 8.39-8.35 (d, 2H), 8.22 (d, 2H), 7.93 (m, 4H), 7.20 (d, 2H), 7.56 (m, 4H), 7.43 (d, 2H), 2.62 (s, 6H). MALDI-TOF-MS (m/z): calcd for $(M-Na)^-$ $C_{38}H_{28}N_6O_4RuS_4$: 862.1098, found: 862.1112.

Synthesis of RC-16 (Ru[(dcbpy)(Ligand-2)(NCS)$_2$]): Dichloro(p-cymene)

ruthenium(II) dimmer (153 mg, 0.25 mmol) and Ligand-2 (200 mg, 0.50 mmol) were dissolved in DMF. The mixture was stirred at 90 °C for 4 h under Ar in the dark. Subsequently, 4,4'-dicarboxylic acid-2,2'-bipyridine (122.2 mg, 0.50 mmol) was added into the flask and the reaction mixture was heated up to 140 °C for 6 h. Next, an excess of potassium thiocyanate (1.13 g, 15 mmol) was added to the resulting dark solution and it was continued for 6 h at 140 °C. Then the reaction mixture was cooled to room temperature overnight. After the solvent was evaporated under vacuum, H_2O was added to get the precipitate. The solid was collected on a sintered glass crucible by suction filtration, washed intensively with diethyl ether, and dried under vacuum. The column purification was done with the same procedures described above for **RC-15**. After collecting the main band, the precipitate was concentrated on a sintered glass crucible by suction filtration and dried in air. Yield with Sephadex LH-20 column purification (3×): 47%. ^{1}H NMR(400 MHz, DMSO-D6): δ/ppm: 9.52 (m, 2H), 9.32-9.02 (m, 4H), 8.49-8.37 (m, 2H), 8.24 (m, 2H), 8.20-7.95 (m, 4H), 7.69-7.40 (m, 2H), 7.25-7.12 (dd, 4H), 3.90 (s, 3H), 3.84 (s, 3H). MALDI-TOF-MS (m/z): calcd for $(M\text{-}NCS)^+$ $C_{38}H_{28}N_6O_6RuS_2$: 772.3704, found: 772.3709.

Synthesis of RC-22 (Ru[(dcbpy)(Ligand-3)(NCS)$_2$])*:* Dichloro(p-cymene) ruthenium(II) dimmer (153 mg, 0.25 mmol) and Ligand-3 (240 mg, 0.50 mmol) were dissolved in DMF. The mixture was stirred at 90 °C for 4 h under Ar in the dark. Subsequently, 4,4'-dicarboxylic acid-2,2'-bipyridine (122.2 mg, 0.50 mmol) was added into the flask and the reaction mixture was heated up to 140 °C for 6 h. Then, an excess of potassium thiocyanate (1.13 g, 15 mmol) was added to the resulting dark solution

and it was continued for 6 h at 140 °C. Then the reaction mixture was cooled to room temperature overnight. After the solvent was evaporated under vacuum, H_2O was added to get the precipitate. The solid was collected on a sintered glass crucible by suction filtration, washed intensively with diethyl ether, and dried under vacuum. The column purification was done with the same procedures described above for **RC-15**. After collecting the main band, the precipitate was concentrated on a sintered glass crucible by suction filtration and dried in air. Yield with Sephadex LH-20 column purification (3×): 41%. ^{1}H NMR(400 MHz, DMSO-D6):δ/ppm: 9.49-8.99 (m, 6H), 8.34 (m, 2H), 7.91 (m, 2H), 7.80-7.62 (m, 4H), 7.50-7.47 (m, 2H), 7.25-7.12 (dd, 2H), 6.22-6.13 (d, 4H). MALDI-TOF-MS (m/z): calcd for (M-Na)- $C_{38}H_{28}N_6O_6RuS_2$: 858.2941, found: 858.2999