Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Ruthenium complexes sensitizers with phenyl-based bipyridine anchoring ligands for efficiently dye-sensitized solar cells

Yin Huang [ab], Wang-Chao Chen *[da], Xian-Xi Zhang [c], Rahim Ghadari [e], Xia-Qin Fang [a], Ting Yu [ab], Fan-Tai Kong *[a]

[a] *Key Laboratory of Photovoltaic and Energy Conservation Materials, Institute of Applied Technology, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei, 230088, P. R. China. *E-mail address: kongfantai@163.com (F. T. Kong)*

[b] *University of Science and Technology of China, Hefei, 230026, P. R. China*

[c] *Shandong Provincial Key Laboratory/Collaborative Innovation Center of Chemical Energy Storage & Novel Cell Technology, Liaocheng University*

[d] *School of Chemistry and Chemical Engineering, Anhui Province Key Laboratory of Advanced Catalytic Materials and Reaction Engineering, Hefei University of Technology, Hefei 230009, China. *E-mail address: rudyecwc@163.com (W. C. Chen)*

[e] *Computational Chemistry Laboratory, Department of Organic and Biochemistry, Faculty of Chemistry, University of Tabriz, 5166616471 Tabriz, Iran*

1. Materials and equipments

In this work, the 4,4'-dibromo-2,2'-bipyridine, 3-methoxycarbonylphenylboronic acid and 3-fluoro-5-methoxycarbonylphenylboronic acid we used were purchased from TCI and Alfa. In addition, what needs illustration is that all solvents and chemicals were puriss grade and without further purification.

The information about the instrument and its model involved in this work are as follows. The structure of ligands and dye sensitizers were identified by Bruker Advance 400 spectrometer (^{1}H NMR and ^{13}C NMR spectra) and LTQ Orbitrap XL Mass Spectrometer (Mass spectra). The elemental analysis of ruthenium sensitizers was tested by elemental analyzer (Elementar vario EL cube, Germany). The UV-Vis spectra of the dyes and the sensitized TiO_2 films were measured by the spectrophotometer U-3900H (Hitachi, Japan). The cyclic voltammetry (CV) were performed through a CHI-660d electrochemical analyzer which is a typical three-electrode electrochemical cell including a Pt disk working electrode, a NHE reference electrode and a platinum wire counter electrode. The thickness of TiO_2 thin film electrode was measured by a profilometer (XP-2, AMBIOS Technology Inc., USA).

The performance of the devices were characterized. The photocurrent density-voltage (*J*-*V*) characteristics of the solar cells were obtained by 3A grade solar simulator (Newport, USA, 94043A) under AM 1.5G (100mW cm^{-2}) illumination. The incident monochromatic photon-to-current conversion efficiency (IPCE) spectra were measured on QE/IPCE measurement kit (Newport, USA). Electrochemical impedance spectroscopy (EIS) was measured by an Autolab PGSTAT 302N analyzer (Metrohm, Switzerland) in the frequency region from 50 mHz to 1000 kHz. Transient absorption spectra (TAS) were carried out using a laser flash spectrophotometer (LP920, Edinburgh Instruments Ltd. Scotland) in conjunction with a nanosecond tunable laser (OPOLette 355II. Opotek, Inc., CA). The probe light from a pulsed xenon arc lamp was passed through various optical elements and a monochromator before being detected by a fast photomultiplier tube and recorded with a digital signal analyzer (TDS 3012C, Tektronix, USA).

2. Synthesis of the anchoring ligands and ruthenium sensitizers.

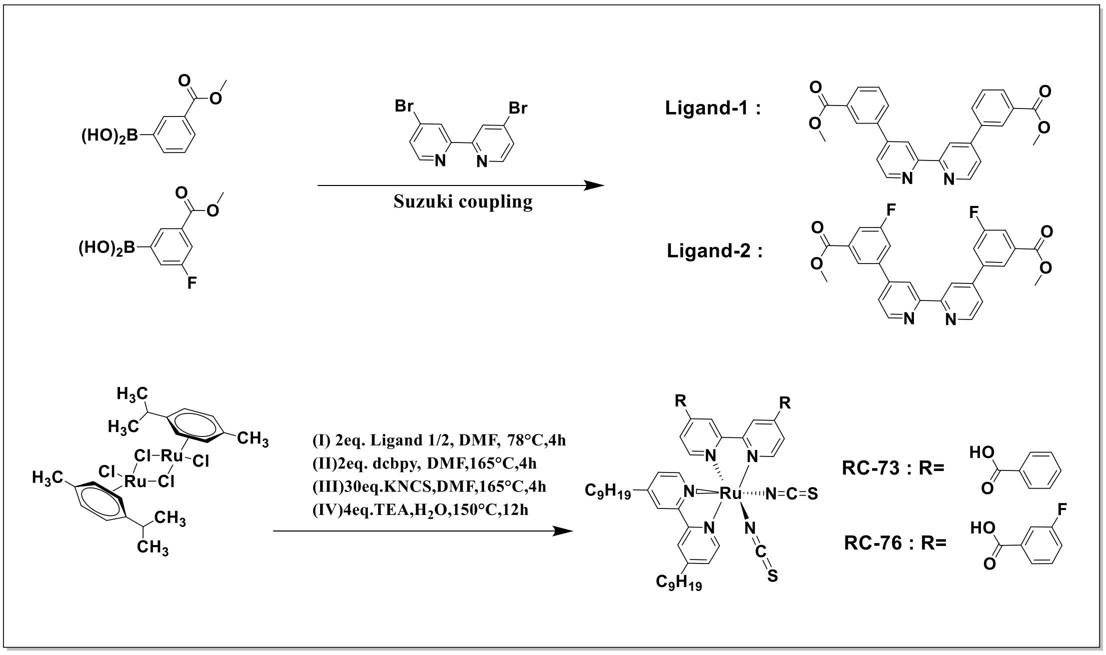

Fig. S1. Synthetic routes for phenyl-based bipyridine anchoring ligands and RC dye sensitizers.

Synthesis of Ligand-1.

The 4,4′-dibromo-2,2′-bipyridine (0.314 g, 1.0 mmol), 3-methoxycarbonylphenylboronic acid (0.485 g, 2.5 mmol) and K_3PO_4 (2.97 g, 14 mmol) were dissolved in DMF/H_2O (9:1, v/v, 50mL). The mixture was refluxed at 110 °C under Ar for 24 h after the Pd $(PPh_3)_4$ (0.060 g, 0.05 mmol) was added as a catalyst.

After the reaction ended, target products and impurities were obtained because of incomplete reaction. To eliminate the interference of inorganic matters and obtain the target product, the organic layers were extracted by CH_2Cl_2 for three times, washed with brine and dried with anhydrous $MgSO_4$. Then evaporated the solvent, crude products were further purified by column chromatography (CH_2Cl_2/CH_3OH, 100:1, v/v). The target compound was obtained as a white powder (164.6 mg, yield 42%). ^1H NMR (400 MHz, $CDCl_3$) δ 9.25 (s, 2H), 8.94 (s, 2H), 8.54 (s, 2H), 8.24 (s, 4H), 7.94 (s, 2H), 7.73 (s, 2H), 1.48 (s, 6H). MALDI-TOF-MS (m/z): calcd for [M] $C_{26}H_{20}O_4N_2$: 424.4617, found: 424.4586.

Synthesis of RC-73.

The reaction process consists of three steps. In anhydrous DMF (50 mL), dichloro(p-cymene)ruthenium(II) dimmer (153 mg, 0.25 mmol) and **Ligand-1** (217 mg, 0.50 mmol) were dissolved and stirred at 85 °C for 4 h under Ar in the dark. And then, 4, 4'-dicarboxylic acid-2, 2'-bipyridine (122.2mg, 0.50 mmol) was added at 165 °C for 4 h. Next, the potassium thiocyanate (730 mg, 7.5 mmol) was added to the reaction system and continued at 165 °C for 4 h. Finally, trimethylamine (101 mg, 1 mmol) and H_2O (2 mL) were added into the reaction system to hydrolyze the corresponding esters to obtain carboxylic acid derivatives.

The last three steps of this reaction were monitored by the absorption spectra. By confirming that the values of the MLCT peak compared with the ILCT peak is not increasing the chemical reaction was almost over. The solid crude product was obtained when solvent of the mixture was evaporated after cooled to room temperature. The deionized water was used to remove water soluble impurities and then the precipitate was collected by suction filtration. Further, the precipitate was purified by diethyl ether. The crude product after initial purification was dissolved in methanol (MeOH) and tetrabutylammonium hydroxide (TBAOH) (MeOH/TBAOH, 80:1, v/v). Purified on a Sephadex LH-20 column with MeOH as eluent. The main band was collected and slowly dropped with an acidic methanol solution. After the target product was collected, the pH of the solution was adjusted to 5 by NaOH solution. The precipitate was collected on a sintered glass crucible by suction filtration and dried in air. Yield (3×): 68.8%. ^{1}H NMR (400 MHz, DMSO) δ 11.36 (s, 1H), 9.21 (d, 1H), 9.16 (s, 1H), 9.07-8.98 (m, 2H), 8.60-8.31 (m, 2H), 8.30-8.11 (m, 2H), 8.01 (s, 1H), 7.89 (d, 1H), 7.67 (d, 2H), 7.53 (t, 2H), 7.47 (s, 2H), 7.31 (d, 2H), 6.97 (d, 2H), 3.24 (s, 4H), 1.68 (s, 14H), 1.34-1.12 (d, 12H), 0.85 (m, 4H). ^{13}C NMR (101 MHz, DMSO-D6) δ 167.03, 166.87, 159.31, 157.93, 157.86, 156.71, 152.65, 152.03, 151.56, 150.95, 146.33, 145.60, 136.73, 136.35, 133.31, 132.06, 131.95, 131.84, 131.79, 130.57, 130.44, 129.67, 129.57, 127.97, 127.01, 126.32, 123.80, 123.51, 121.38, 121.27, 57.64, 34.70, 34.33, 29.03, 28.99, 28.83, 28.71, 28.60, 28.50, 23.15, 22.12, 22.04, 19.29, 14.06, 13.96, 13.55. MALDI-TOF-MS (m/z): calcd for $[M+H]^{+}\cdot 2H_2O$ $C_{52}H_{55}N_6O_4RuS_2Na\cdot 2H_2O$: 1052.26, found: 1052.12.

Synthesis of Ligand-2.

The 4,4′-dibromo-2,2′-bipyridine (0.314 g, 1.0 mmol), 3-fluoro-5-methoxycarbonylphenylboronic acid (0.494 g, 2.4 mmol) and K_3PO_4 (2.97 g, 14 mmol) were dissolved in DMF/H_2O (9:1, v/v, 50mL). The Pd $(PPh_3)_4$ (0.060 g, 0.05 mmol) was added as a catalyst. The mixture was refluxed at 120 °C under Ar for 24 h.

After the reaction ended, target products and impurities were obtained because of incomplete reaction. To eliminate the interference of inorganic matters and obtain the target product, the organic layers were extracted by CH_2Cl_2 for three times, washed with brine and dried with anhydrous $MgSO_4$. Then evaporated the solvent, crude products were further purified by column chromatography (CH_2Cl_2/CH_3OH, 100:1, v/v). The target compound was obtained as a white powder (350.5 mg, yield 76.1%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, 4H), 8.33 (s, 2H), 8.00-7.67 (m, 6H), 4.02 (s, 6H). MALDI-TOF-MS (m/z): calcd for [M] $C_{26}H_{18}F_2O_4N_2$: 460.12, found: 460.05

Synthesis of RC-76.

The reaction process consists of three steps. In anhydrous DMF (50 mL), dichloro(p-cymene)ruthenium(II) dimmer (153 mg, 0.25 mmol) and **Ligand-2** (230 mg, 0.50 mmol) were dissolved and stirred at 85 °C for 4 h under Ar in the dark. And then, 4,4'-dicarboxylic acid-2,2'-bipyridine (122.2mg, 0.50 mmol) was added at 165 °C for 4 h. Next, the potassium thiocyanate (730 mg, 7.5 mmol) was added to the reaction system and continued at 165 °C for 4 h. Finally, trimethylamine (101 mg, 1 mmol) and H_2O (2 mL) were added into the reaction system to hydrolyze the corresponding esters to obtain carboxylic acid derivatives.

The last three steps of this reaction were monitored by the absorption spectra. By confirming that the values of the MLCT peak compared with the ILCT peak is not increasing the chemical reaction was almost over. The solid crude product was obtained when solvent of the mixture was evaporated after cooled to room temperature. The deionized water was used to remove water soluble impurities and then the precipitate was collected by suction filtration. Further, the precipitate was purified by diethyl ether. The crude product after initial purification was dissolved in methanol (MeOH) and tetrabutylammonium hydroxide (TBAOH) (MeOH/TBAOH, 80:1, v/v). Purified on a Sephadex LH-20 column with MeOH as eluent. The main band was collected and slowly dropped with an acidic methanol solution. After the target product was collected, the pH of the solution was adjusted to 5 by NaOH solution. The precipitate was collected on a sintered glass crucible by suction filtration and dried in air. Yield (3×):58%. ^{1}H NMR (400 MHz, DMSO) δ 9.39 (d, 1H), 9.31 (s, 1H), 9.16 (d, 2H), 8.71 (s, 1H), 8.54 (d, 2H), 8.37 (s, 2H), 8.28-8.05 (m, 2H), 7.85 (d, 2H), 7.77 (d, 2H), 7.66 (s, 2H), 7.47 (d, 1H), 7.14 (d, 1H), 3.93 (s, 4H), 1.85-1.68 (s, 16H), 1.42-1.37 (d, 14H), 0.82 (m, 4H). ^{13}C NMR (101 MHz, DMSO-D6) δ 166.07, 165.83, 164.74, 163.77, 163.59, 161.48, 161.17, 159.33, 157.77, 156.63, 152.80, 152.62, 152.19, 151.55, 151.39, 150.91, 144.84, 144.12, 139.02, 134.71, 133.86, 133.47, 127.05, 126.31, 124.39, 124.00, 123.42, 121.47, 121.40, 119.16, 118.64, 116.81, 71.92, 52.74, 52.65, 34.65, 34.28, 31.39, 31.17, 29.86, 29.61, 28.96, 28.85, 28.80, 28.71, 28.68, 28.57, 22.09, 22.00, 13.91, 13.85. MALDI-TOF-MS (m/z): calcd for $[M+H]^+ \cdot 2H_2O$ $C_{54}H_{57}F_2N_6O_4RuS_2Na \cdot 2H_2O$: 1116.29, found: 1116.13.

3. Device fabrication

The structure of the solar cells consists mainly of the negative electrode and the counter electrode. The negative electrode was made of a SnO_2 transparent conductive glass doped with fluorine (FTO glass) (12-14 Ω per square, TEC 15, USA) which printed with a double layer film of TiO_2 mesoporous particles. The TiO_2 films (0.25 cm^2) included a layer of 4 μm thick 20 nm sized TiO_2 particles film and a layer of 10 μm thick 400 nm sized light scattering anatase particles. The TiO_2 films was produced after sintered at 450 °C for 30 min in air. An acetonitrile/tert-butanol (50:50, v/v) mixed solvent containing 300 μM dye sensitizers and 20 mM chenodeoxycholic acid was prepared to soak the ready-made TiO_2 thin films for 12 h, then took the film out of the solution and rinsed with anhydrous acetonitrile. When additives were needed, the co-adsorbent DPA was added to the dye solution at a molar ratio of 1:1. Pt was deposited on FTO glass by spraying H_2PtCl_6 solution and treated at 450°C for 20min to prepare the counter electrode.

A 45 μm thermal adhesive film (Surlyn, USA) was used to separate the two electrodes and seal the two glasses by heating. Then a liquid electrolyte was injected into the gap between the two glasses through small holes on the counter electrode. The electrolyte-injecting holes on the counter electrode glass substrate was sealed with a thin glass cover by heating. The organic electrolyte solution was a mixture of 1 M 1,3-dimethylimidazolium iodide (DMII), 50 mM LiI, 30 mM I_2, 0.5 M TBP in acetonitrile and 0.1 M Guanidinium thiocyanate (GuNCS). A low volatility electrolyte was applied for long-term stability testing, containing 1 M DMII, 0.15 M I_2, 0.5 M N-butylbenzimidazole and 0.1 M GuNCS in methoxypropionitrile.

4. Photophysical and electrochemical properties

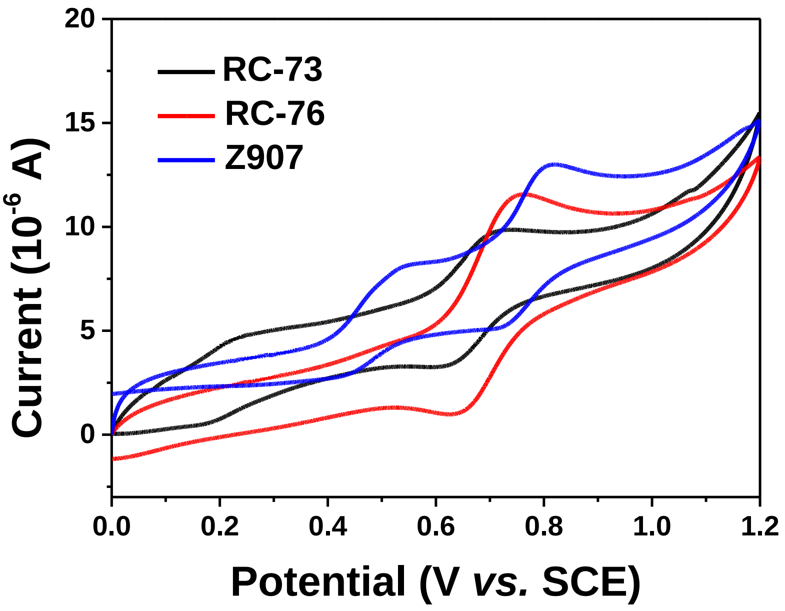

Fig. S2. Cyclic voltammetric curves of **RC-73**, **RC-76**, and Z907 with 0.1 M (n-$C_4H_9)_4NPF_6$ DMF solution.

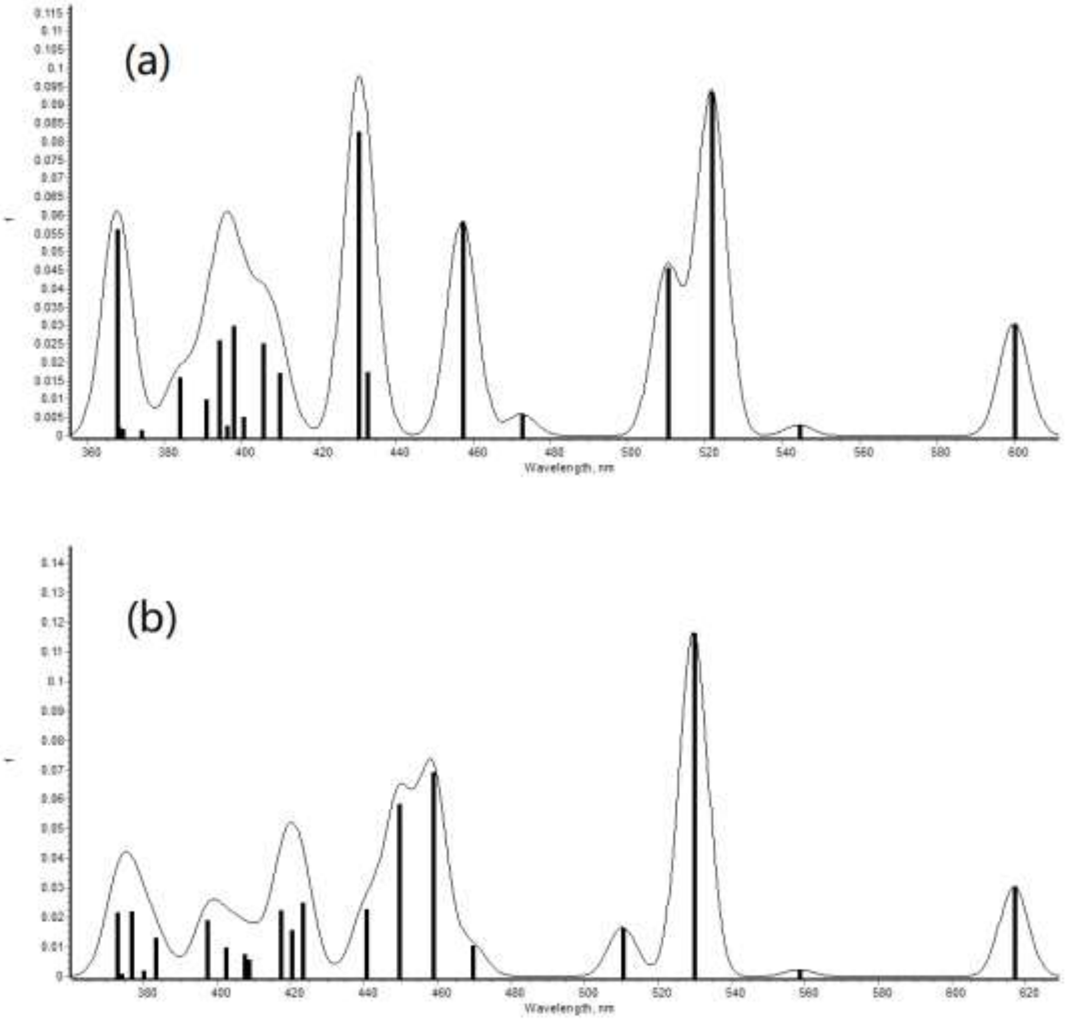

Fig. S3. Theoretical UV-Vis spectra of (a) **RC-73** and (b) **RC-76** in DMF solvent.