# High Efficient Donor-Acceptor Ruthenium Complex for Dye-sensitized Solar Cell Applications

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# Electronic Supplementary Information

## Experimental Procedures.

Electrochemical data were obtained by cyclic-voltammetry using a three-electrode cell and an Auto lab System (PGSTAT 30, GPES 4.8 software). The working electrode was a 0.03 $cm^2$ glassy carbon disk, the auxiliary electrode was a platinum plate, and a platinum wire was used as quasi-reference electrode. The sensitizers were dissolved in dimethylformamide (DMF) containing 0.1 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte. After the measurement, ferrocene was added as the internal reference for calibration.

The FTO glass substrates were immersed in 40 mM $TiCl_4$ *aq.* at 70 °C for 30 min and washed with water and ethanol. The 13 μm thick mesoporous nano-$TiO_2$ films composed of 20 nm anatase $TiO_2$ particles were coated on the FTO glass plates by repetitive screen printing. After drying the nanocrystalline $TiO_2$ layer at 125 ˚C, a 5 μm thick second layer of 400 nm sized light scattering anatase particles (CCIC, HPW-400) was deposited by screen printing onto the transparent layer. The $TiO_2$ electrodes were gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min and 500 °C for 15 min. The $TiO_2$ electrodes were treated again by $TiCl_4$ and sintered at 500 °C for 30 min. The dye-adsorbed $TiO_2$ electrode and thermally platinized counter electrode were assembled into a sealed sandwich type cell with a gap of a hot-melt ionomer film (Surlyn 1702, 25 μm thickness, Du-Pont).

The measurement of incident photon-to-current conversion efficiency (IPCE) was plotted as a function of excitation wavelength by using the incident light from a 300 W xenon lamp (ILC Technology, USA), which was focused through a Gemini-180 double monochromator (Jobin Yvon

Ltd.). In order to reduce scattered light from the edge of the glass electrodes of the dyed $TiO_2$ layer, a light shading mask was used onto the DSCs, so active area of DSCs was fixed to 0.2 $cm^2$. The irradiation source was a 450 W xenon light source (Osram XBO 450, USA), whose power of an AM 1.5 solar simulator was calibrated by using a reference Si photodiode equipped with an IR cut-off filter (KG-3, Schott) in order to reduce the mismatch in the region of 350-750 nm between the simulated light and AM 1.5 to less than 2%. The measurement delay time of photo I-V characteristics of DSCs was fixed to 40 ms.

$^1$H spectra was recorded on a Bruker 400 MHz spectrometer. The absorption was recorded on a Hewlett-Packard 8453 UV-visible spectrometer.

**Synthesis of IJ-1.** A mixture of [$\{RuCl_2(p\text{-cymene})\}_2$] (0.038 g, 0.066 mmol) and **L1** (0.1 g, 0.133 mmol) was vacuum-dried and added DMF (30 mL). The reaction mixture was heated at 80 ℃ under nitrogen for 4 h and then, 2,2′-bipyridyl-4,4′-dicarboxylic acid (0.033 g, 0.133 mmol)was added to the solution. The reaction mixture was refluxed at 140 ℃ for another 4 h under dark condition to avoid light induced cis to trans isomerisation. Then an excess of $NH_4NCS$ (1.60 mmol) was added to the reaction mixture and heated at 120 ℃ for overnight. The solvent was removed using a rotary-evaporator under vacuum. Water was added to the resulting semisolid to remove excess $NH_4NCS$. The water-insoluble product was collected on a sintered glass crucible by suction filtration and washed with distilled water, followed by diethyl ether and dried. The crude complex was dissolved methanol (4 mL). Complex was isolated by Sephadex LH-20 (2×30 cm) column and eluted with methanol. $^1$H NMR (400 MHz, DMSO): $\delta$ 9.23 (d, 1H), 9.13 (d, 1H), 8.90 (s, 1H), 8.82 (d, 1H), 8.75 (s, 1H), $\delta$ 8.65 (s, 1H), 8.14 (d, 1H), 8.02 (d, 1H), 7.86 (d, 1H), 7.62～7.58 (m, 4H), 7.53～7.47 (m, 3H), 7.35～7.28 (m, 3H), 7.19～7.13 (m, 8H), 7.05～6.92 (m, 11H), 6.85 (d, 1H), 2.30 (s, 6H), 2.27 (s, 6H).

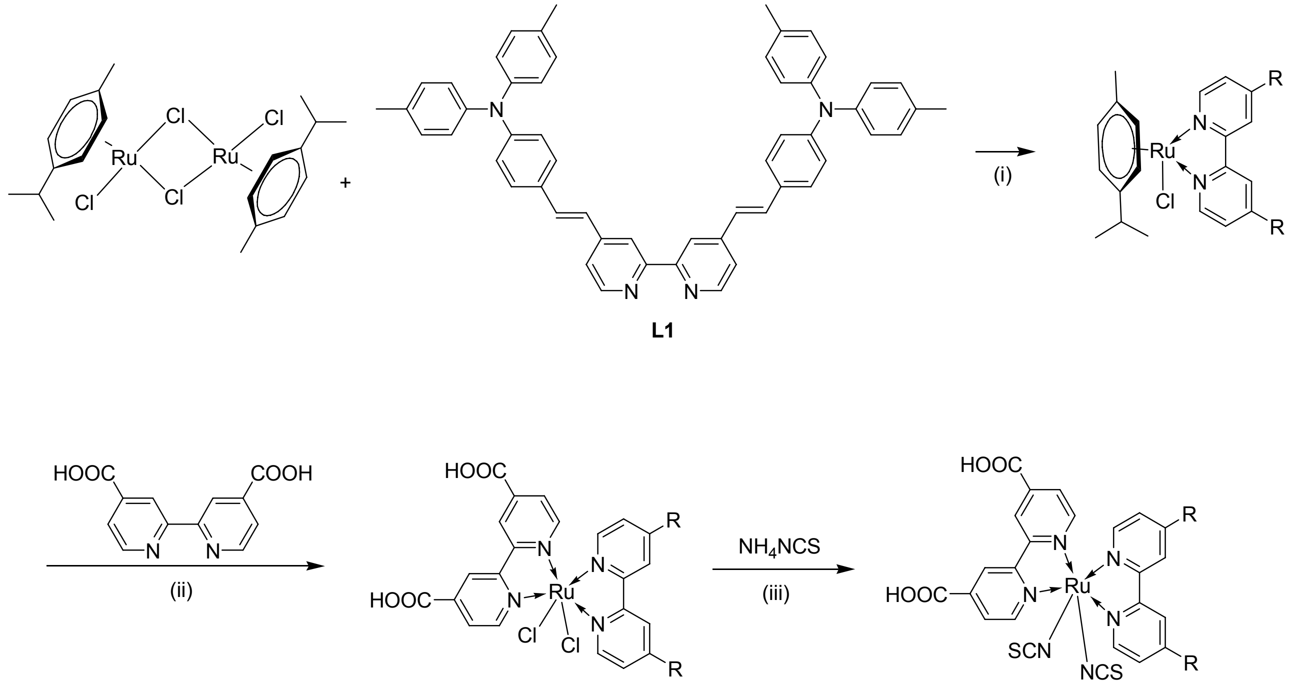

Figure S1. The synthetic strategy of IJ-1. R = 4-(N,N-Di-p-tolylamino)phneylethene, (i) DMF, 80 ℃, 4hr (ii) 140 ℃, 4hr (iii) 120 ℃, overnight