

Supporting Information

Neutral, Panchromatic Ru(II) Sensitizers Bearing H₃tctpy and Pyridine Pyrazolate Chelate with Superior DSSC Performance

**Bo-So Chen, Kellen Chen, Yi-Huan Hong, Wei-Hsin Liu, Tsung-Hui Li, Chin-Hung
Lai, Pi-Tai Chou,* Yun Chi,* and Gene-Hsiang Lee**

B.-S. Chen, W.-H. Liu, T.-H. Li, C.-H. Lai, Prof. P.-T. Chou, Dr. G.-H. Lee

Department of Chemistry,

National Taiwan University, Taipei 106 (Taiwan)

Fax: (+886)2-2369-5208; E-mail: chop@ntu.edu.tw

K. Chen, Y.-H. Hong, Prof. Y. Chi

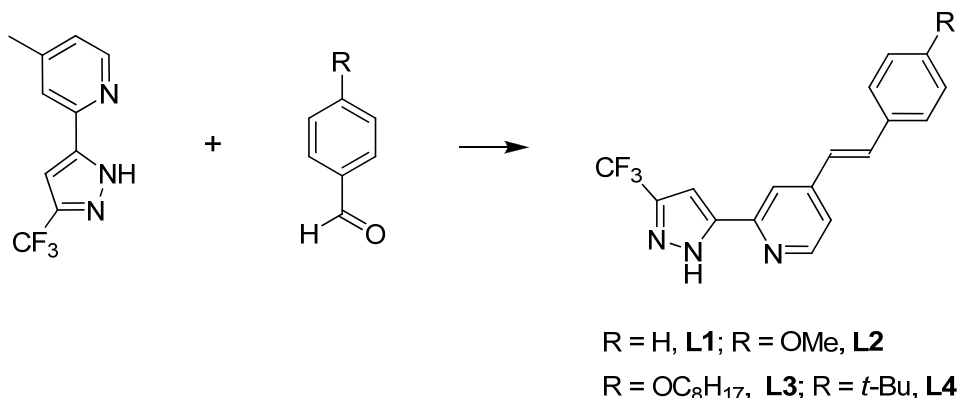
Department of Chemistry,

National Tsing Hua University, Hsinchu 300 (Taiwan)

Fax: (+886)3572-0864; E-mail: ychi@mx.nthu.edu.tw

Experimental

General procedures: Commercially available reagents were used without further purification unless otherwise stated. 4-Methyl-2-(3-(trifluoromethyl)-1H-pyrazol-5-yl)pyridine was prepared according to the literature procedures,^[1] while 4,4',4''-triethoxycarbonyl-2,2':6',2''-terpyridine was synthesized via oxidation of 4,4',4''-triethyl-2,2':6',2''-terpyridine, followed by esterification in presence of H₂SO₄.^[2] [RuCl₂(*p*-cymene)]₂ was prepared by heating RuCl₃·hydrate with phellandrene in methanol.^[3] After then, **Ru1** ~ **Ru4** were prepared by reacting [RuCl₂(*p*-cymene)]₂ with the respective functionalized 2-pyridyl pyrazoles in anhydrous methanol (60 °C, 4hr). The panchromatic Ru(II) terpyridine sensitizers **PRT1** to **PRT4** were synthesized employing 4,4',4''-triethoxycarbonyl-2,2':6',2''-terpyridine and **Ru1** ~ **Ru4**, followed by treatment with KSCN and then hydrolysis in 1.0 M NaOH solution. The solid product was then taken into a minimum amount of methanol and purified on Sephadex LH-20 column using methanol as the eluent.



Synthesis of (E)-4-styryl-2-(3-(trifluoromethyl)-1H-pyrazol-5-yl)pyridine (L1). Ligand **L1** was synthesized employing a modified literature procedure,^[4] in which solid *tert*-BuOK (1.19 g, 10.56 mmol) was added to a solution of 4-methyl-2-(3-(trifluoromethyl)-1H-pyrazol-5-yl)pyridine (0.30 g, 1.32 mmol) and benzaldehyde (0.4 mL, 3.96 mmol) in anhydrous DMF (100 mL). The resulting mixture was stirred 6 h at 100 °C under nitrogen. The solvent was then evaporated, and product was dissolved in water titrated by 2 M HCl until pH 3 ~4. The insoluble solid was filtered on a sintered crucible and recrystallized from hot ethylacetate (EA), filtered,

and washed with methanol to obtain the desired product **L1** as a beige solid (0.22 g, 51%). Other chelates **L2** ~ **L4** were prepared using identical procedures.

Spectral data: ^1H NMR (CDCl_3 , 400 MHz) δ : 11.54 (br, 1H, NH), 8.56 (d, $J_{\text{HH}} = 5.6$ Hz, 1H), 7.68 (s, 1H), 7.56 (d, $J_{\text{HH}} = 7.6$ Hz, 2H), 7.42 ~ 7.34 (m, 5H), 7.05 (d, $J_{\text{HH}} = 16$ Hz, 1H), 7.00 (s, 1H).

(E)-4-(4-methoxystyryl)-2-(3-(trifluoromethyl)-1H-pyrazol-5-yl) pyridine (L2). Yield 52 %.

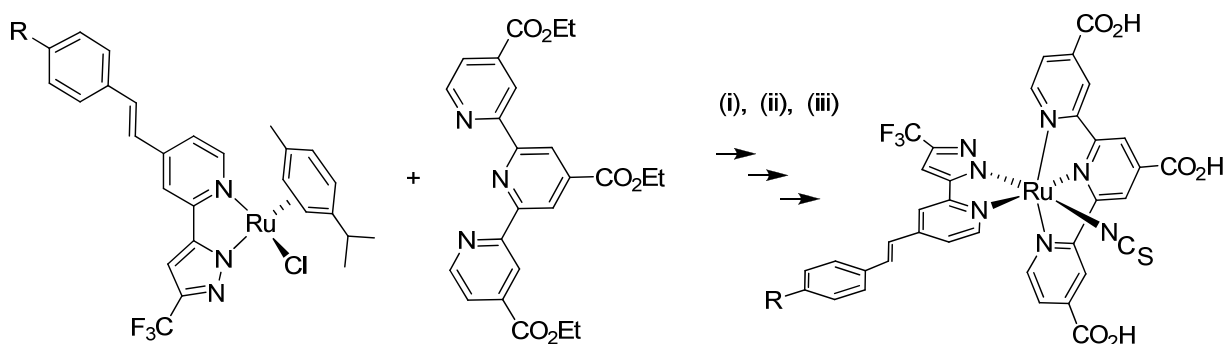
Spectral data: ^1H NMR (CDCl_3 , 400 MHz) δ : 8.53 (d, $J_{\text{HH}} = 5.2$ Hz, 1H), 7.65 (s, 1H), 7.50 (d, $J_{\text{HH}} = 8.8$ Hz, 2H), 7.34 ~ 7.29 (m, 2H), 6.99 (s, 1H), 6.45 ~ 6.89 (m, 3H), 3.84 (s, 3H).

(E)-4-(4-(octyloxy)styryl)-2-(3-(trifluoromethyl)-1H-pyrazol-5-yl)pyridine (L3). Yield 55 %.

Spectral data: ^1H NMR (CDCl_3 , 400 MHz) δ : 11.56 (br, 1H, NH), 8.51 (d, $J = 5.2$ Hz, 1H), 7.64 (s, 1H), 7.48 (d, $J = 8.8$ Hz, 2H), 7.34 ~ 7.29 (m, 2H), 6.99 (s, 1H), 6.92 ~ 6.87 (m, 3H), 3.98 (t, $J = 6.4$ Hz, 2H), 1.80 ~ 1.75 (m, 2H), 1.47 ~ 1.43 (m, 2H), 1.33 ~ 1.28 (m, 8H), 0.87 (t, $J = 6.4$ Hz, 3H).

(E)-4-(4-tert-butylstyryl)-2-(3-(trifluoromethyl)-1H-pyrazol-5-yl)pyridine (L4). Yield 64 %.

Spectral data: ^1H NMR (CDCl_3 , 400 MHz) δ : 8.59 (d, $J_{\text{HH}} = 7.2$ Hz, 1H), 7.70 (s, 1H), 7.51 (d, $J_{\text{HH}} = 8.4$ Hz, 2H), 7.44 (d, $J_{\text{HH}} = 8.4$ Hz, 2H), 7.39~7.35 (m, 2H), 7.03 (s, 1H), 7.02 (d, $J_{\text{HH}} = 16.0$ Hz, 1H), 1.35 (s, 9H).



R = H, **Ru1**; R = OMe, **Ru2**

R = OC_8H_{17} , **Ru3**; R = Bu^t , **Ru4**

R = H, **PRT1**; R = OMe, **PRT2**

R = OC_8H_{17} , **PRT3**; R = Bu^t , **PRT4**

Rxn conditions: (i) DGME, 160°C, 8 hr; (ii) KSCN, DMF, 160°C, 6 hr; (iii) NaOH, 24 hr.

Preparation of PRT1. In a typical experiment, **Ru1** (100 mg, 0.16 mmol) and 4,4',4''-triethoxycarbonyl- 2,2':6',2''-terpyridine (70 mg, 0.16 mmol) were dissolved in a diethylene glycol monoethyl ether solution (DGME, 20 mL). The mixture was heated at 160°C for 8 h under constant stirring. Solvent was then reduced and product was purified by flash column chromatography using CH₂Cl₂/methanol (95: 5) as the eluent. The resulting product and excess KSCN (155 mg, 1.60 mmol) were then dissolved in DMF solution (15 mL) and refluxed for additional 8 h at 160°C. Next, the solvent was removed under vacuum, and the residue was dissolved into a mixture of 5 mL of acetone and 5 mL of 1.0 M NaOH solution and heated at reflux for 24 h. Finally, the solution was concentrated to one-half of its original volume and neutralized with 2M HCl solution to pH = 3 to afford a brown precipitate. This brown product was then taken into a minimum amount of methanol and purified on Sephadex LH-20 column using methanol as the eluent. The main band was collected and solvent was evaporated to dryness. After then, the brown precipitate was washed with deionized water, acetone and diethyl ether in sequence, giving **PRT1** as powdery material (32 mg, 24 %).

Selected spectral data: MS (FAB, ¹⁰²Ru): m/z 840 (M+2⁺). ¹H NMR (d₆-DMSO, 400MHz) δ: 9.24 (d, 1H, *J* = 5.6 Hz), 9.21 (s, 2H), 9.06 (s, 2H), 8.44 (s, 1H), 8.01 (d, 2H, *J* = 5.6 Hz), 7.95 (d, 1H, *J* = 5.6 Hz), 7.89 ~ 7.84 (m, 3H), 7.74 (d, 2H, *J* = 8.0 Hz), 7.52 ~ 7.38 (m, 4H), 7.08 (s, 1H). MS (FAB, Ru¹⁰²): m/z 840 (M+2⁺). Anal. Calcd for C₃₆H₂₂F₃N₇O₆RuS · 4H₂O: C, 47.47; N, 10.76; H, 3.32. Found: C, 47.15; N, 10.39; H, 3.39.

Preparation of PRT2. Dark brown powder of **PRT2** (35 mg, 27 %) was prepared employing **Ru2** (100 mg, 0.15 mmol) with synthetic procedures identical to those for preparing **PRT1**.

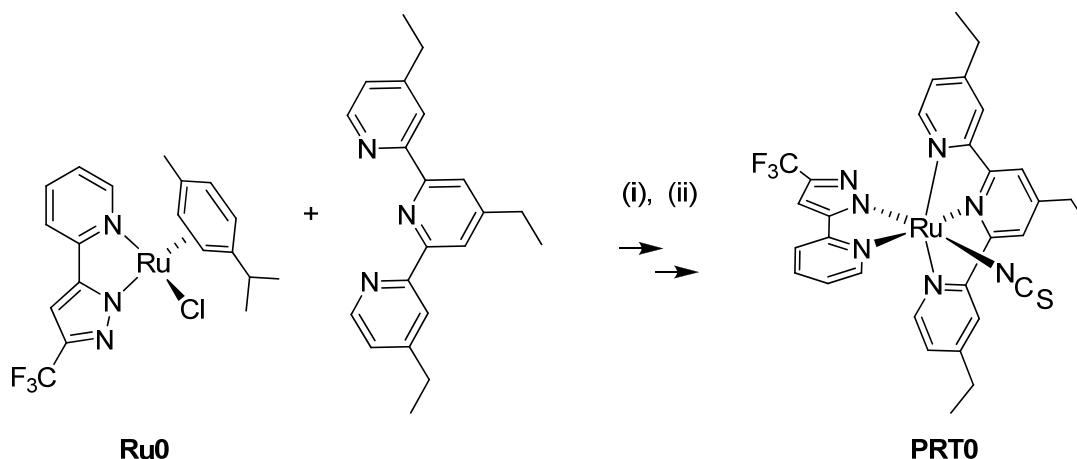
Selected spectral data: MS (FAB, ¹⁰²Ru): m/z 869 (M+1⁺). ¹H NMR (d₆-DMSO, 400MHz) δ: 9.21 (d, 1H, *J* = 5.6 Hz), 9.18 (s, 2H), 9.04 (s, 2H), 8.36 (s, 1H), 8.01 (d, 2H, *J* = 5.6 Hz), 7.86 ~ 7.84 (m, 3H), 7.77(d, 1H, *J* = 16 Hz), 7.64 (d, 2H, *J* = 8.0 Hz), 7.29 (d, 1H, *J* = 16 Hz), 7.05 ~ 7.02 (m, 3H), 3.82 (s, 3H). Anal. Calcd for C₃₇H₂₄F₃N₇O₇RuS · .5H₂O: C, 46.35; N, 10.23; H, 3.57. Found: C, 46.61; N, 10.22; H, 3.41.

Preparation of PRT3. Dark brown powder of **PRT3** (37 mg, 30 %) was prepared employing **Ru3** (100 mg, 0.13 mmol) with synthetic procedures identical to those for preparing **PRT1**.

Selected spectral data: MS (FAB, ^{102}Ru): m/z 968 ($M+1^+$). ^1H NMR (d_6 -DMSO, 400MHz) δ : 9.22 (s, 2H), 9.17 (d, 1H, $J = 5.6$ Hz), 9.08 (s, 2H), 8.40 (s, 1H), 7.99 (d, 2H, $J = 5.6$ Hz), 7.90 (d, 1H, $J = 5.6$ Hz), 7.84 ~ 7.78 (m, 3H), 7.64 (d, 2H, $J = 8.0$ Hz), 7.30 (d, 1H, $J = 16$ Hz), 7.10 (s, 1H), 7.00 (d, 2H, $J = 8.4$ Hz), 4.00 (t, 2H, $J = 6.4$ Hz), 1.70 (m, 2H), 1.40 ~ 1.20 (m, 10H), 0.84 (t, 3H, $J = 6.4$ Hz). Anal. Calcd for $\text{C}_{44}\text{H}_{38}\text{F}_3\text{N}_7\text{O}_7\text{RuS} \cdot 5\text{H}_2\text{O}$: C, 50.00; N, 9.28; H, 4.58. Found: C, 49.92; N, 9.30; H, 4.44.

Preparation of PRT4. Dark brown powder of **PRT4** (40 mg, 30 %) was prepared employing **Ru4** (100 mg, 0.14 mmol) with synthetic procedures identical to those for preparing **PRT1**.

Selected spectral data: MS (FAB, ^{102}Ru): m/z 895 ($M+1^+$). ^1H NMR(d_6 -DMSO, 400MHz) δ : 9.23 (d, 1H, $J = 5.6$ Hz), 9.18 (s, 2H), 9.04 (s, 2H), 8.40 (s, 1H), 7.98 (d, 2H, $J = 5.6$ Hz), 7.90 (d, 1H, $J = 5.6$ Hz), 7.96 ~ 7.82 (m, 4H), 7.67 (d, 2H, $J = 8.0$ Hz), 7.51 (d, 2H, $J = 8.0$ Hz), 7.44 (d, 1H, $J = 16$ Hz), 7.10 (s, 1H), 1.33 (s, 9H). Anal. Calcd for $\text{C}_{40}\text{H}_{30}\text{F}_3\text{N}_7\text{O}_6\text{RuS} \cdot \text{CH}_3\text{OH} \cdot 3\text{H}_2\text{O}$: C, 50.20; N, 10.00; H, 4.11. Found: C, 50.35; N, 10.30; H, 4.28.



Rxn conditions: (i) DGME, 160°C, 8 hr; (ii) KSCN, DMF, 160°C, 6 hr.

Preparation of PRT0. Dark brown powder of **PRT0** (55 mg, 40 %) was prepared employing **Ru0** (100 mg, 0.20 mmol) and 4,4',4''-triethyl-2,2':6',2''-terpyridine (60 mg, 0.19 mmol) in DGME, followed by treatment with KSCN (200 mg, 2.08 mmol) in DMF at 160°C for 8 hr.

After removal of solvent, the residue was separated using silica gel column chromatography eluting with pure CH₂Cl₂. Single crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether vapor into a DMSO solution of **PRT0** at room temperature.

Selected spectral data: MS (FAB, ¹⁰²Ru): m/z 689 (M⁺). ¹H NMR(CDCl₃, 400MHz) δ: 9.54 (d, 1H, *J* = 5.6 Hz), 7.90 (s, 2H), 7.86 ~ 7.76 (m, 5H), 7.50 (d, 2H, *J* = 5.6 Hz), 7.42 (t, 1H, *J* = 8.0 Hz), 6.91 (d, 1H, *J* = 4.4 Hz), 6.76 (s, 1H), 2.88 (q, 2H, *J* = 7.6 Hz), 2.69 (q, 4H, *J* = 7.6 Hz), 1.43 (t, 3H, *J* = 7.6 Hz), 1.24 (t, 6H, *J* = 7.6 Hz).

Selected crystal data: C₃₅H₄₀F₃N₇O₂RuS₃, *M* = 844.99, triclinic, space group *P* $\bar{1}$, *a* = 11.5042(9), *b* = 11.5173(9), *c* = 14.7032(11) Å, α = 97.757(2), β = 103.199(2), γ = 90.266(2)°, *V* = 1878.0(3) Å³, *Z* = 2, ρ_{calcd} = 1.494 mgm⁻³, *F*(000) = 868, crystal size = 0.27 × 0.08 × 0.04 mm³, $\lambda(\text{Mo-K}\alpha)$ = 0.7107 Å, *T* = 150(2) K, μ = 0.641 mm⁻¹, 6639 independent reflections collected (*R*_{int} = 0.0781), GOF = 1.048, final *R*₁[*I* > 2σ(*I*)] = 0.0708 and *wR*₂(all data) = 0.1716, residual electron density = 0.938 and -1.008 e/Å³.

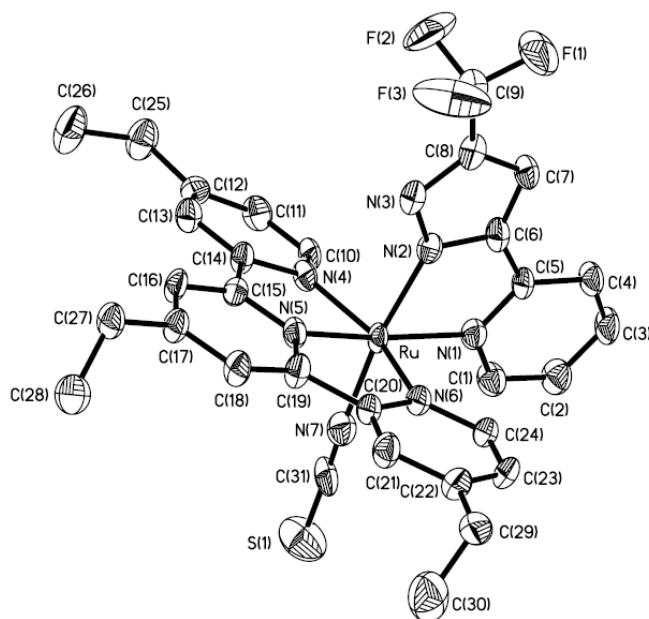


Figure S1. ORTEP diagram of **PRT0** with thermal ellipsoids shown at 50% probability level; selected bond lengths (Å): Ru-N(1) = 2.116(5), Ru-N(2) = 2.025(5), Ru-N(4) = 2.066(5), Ru-N(5) = 1.953(5), Ru-N(6) = 2.057(5), Ru-N(7) = 2.043(6).

DSSC Experimental Section

The Pt counter electrode was prepared by spin-coating a 50mM H_2PtCl_6 in isopropyl alcohol on FTO glass, followed by sintering at 385 °C for 15–30 min. Transparent TiO_2 paste was prepared using published procedures.^[5] The transparent TiO_2 thin film with thickness of 18 μm was first deposited on a transparent conducting oxide (F-doped SnO_2 , FTO). This film was dried at 150 °C for 15 min and then a 4 μm thick layer of 400 nm TiO_2 particles (Ti-Nanoxide 300 paste from Solaronix) was deposited again by a doctor-blade method to form a square with dimension of $0.4 \times 0.4 \text{ cm}^2$. Afterwards, the double-layered films were sintered at 500 °C for 30 min. After sintering, the TiO_2 films were treated with 40mM of TiCl_4 solution, rinsed with water and ethanol, and sintered at 500 °C for 30 min. After cooling to 80 °C, the TiO_2 electrode was immersed into a solution containing 0.3mM of **PRT** dyes, 10 mM of deoxycholic acid (DCA) in mixed DMF and *tert*-butanol solution (volume ratio: 1:1) overnight. After being rinsed with EtOH, the dye-coated TiO_2 electrode was incorporated into a sandwich cell structure with a Pt-coated FTO as counter electrode, and a film (Surlyn 1702, 25 μm) as a spacer between the electrodes. The electrolyte solution was then injected into the cell through a drilled hole in the back of the counter electrode. Lastly, the hole was sealed using a hot-melt ionomer film and a cover glass. Light-to-electricity conversion efficiency values were measured using a modified light source, 450 W Xe lamp (Oriel, 6266), an Oriel 81088 Air Mass 1.5 Global Filter and a digital source meter purchased from Keithley Instruments Inc. The incident light intensity was calibrated using a standard solar cell composed of a crystalline silicon solar cell and an IR cutoff filter (Schott, KG-5), giving the photoresponse range of amorphous silicon solar cell.

Stability Test: The photoanodes of the device employed in this study were composed of a 7 μm transparent TiO_2 thin film and 4 μm thick layer of 400 nm TiO_2 particles. A 405 nm cut-off long pass filter was placed on the cell surface during illumination. The cell was irradiated under a Suntest CPS plus lamp (ATLAS GmbH, 100Mw cm^{-2}) during visible-light soaking at 60 °C. Electrolyte was switched to nonvolatile blend that consists of a mixture of DMII/EMII/EMITCB/ I_2 /NBB/GNCS in molar ratio of 12/12/16/1.67/3.33/0.67.^[6] Dimethylimidazolium iodide (DMII) were prepared according to the reported procedure.^[7] 1-ethyl-3methyl imidazolium iodide (EMII) was purchased from TCI. Iodine and

1-ethyl-3-methylimidazolium tetracyanoborate (EMITCB) were purchased from Merck. 3-Methoxy-propionitril and Guanidinium thiocyanate (GNCS) were purchased from Fluka. N-butylbenzimidazole (NBB) was synthesized according to the literature method.^[8]

Computational Methodology: Time-dependent PBE0 calculations are based on the geometry optimized structures at PBE0 level. The basis set for the geometry optimization and the excitation energy calculation are both a double- ζ quality basis set consisting of Hay and Wadt's quasi-relativistic effective core potentials (LANL2DZ) for Ir(III) atom; a 6-31G* basis set was employed for the H, C, N, O, F and S atoms. Typically, the lowest triplet and singlet roots of the nonhermitian eigenvalue equations were obtained to determine the vertical excitation energies. Oscillator strengths were deduced from the dipole transition matrix elements (for singlet states only). All the calculations were performed with the Gaussian 03 package.

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