

Influence of the pyridine ligands nature and corresponding Ruthenium (II) dye molecular structure on the performance of dye sensitized solar cells

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Electronic Supplementary Information

Experimental.

1. a) General Procedures and Materials
b) Synthesis of the sensitizers
c) TiO₂ electrode preparation and solar cell fabrication
2. Energetic diagrams of the interface
3. Figure S1. Raman spectra for complexes **6** and **7** and the corresponding dye sensitized titania films.

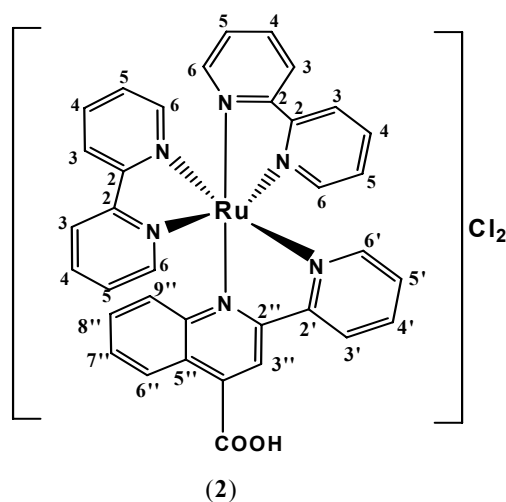
1a) General Procedures and Materials

The C, H, N analyses were carried out on a Perkin Elmer 2400 CHN elemental analyzer. Infrared spectra were measured with a Nicolet 550 Magna-IR™ spectrometer in KBr pellets in the region of 4000–400 cm⁻¹. Micro-Raman spectra were measured in backscattering configuration using a Renishaw inVia spectrometer with an Ar⁺ ion laser ($\lambda=514.5$ nm) and a high power near infrared (NIR) diode laser ($\lambda=785$ nm) as excitation sources. In all cases, very low laser power density (0.2-0.4 mW/ μm^2) was applied to avoid dye degradation. The luminescence background has been subtracted from all spectra by polynomial fitting and/or cubic spline interpolation routines. Absorption spectra in solution (1×10^{-5} M in EtOH) were recorded with a Perkin–Elmer Lambda 19 UV/Vis spectrometer. Diffuse reflectance UV/Vis spectra of the dye sensitized TiO₂ films normalized to that of a blank titania film, were obtained on a Hitachi 3010 spectrophotometer equipped with an integrating sphere. ¹H NMR spectra were measured with a Bruker Avance 500 MHz spectrometer in (CD₃)₂SO, CD₃OD, CD₃CN and D₂O. *J* values are given in Hz. Electrospray

ionization mass spectra (ESI-MS) were performed using an AQA Navigator, Finnigan Mass Spectrometer.

I-V measurements were performed by illuminating the cell through the active photoelectrode under solar simulated light from a 300W- Xe lamp operating in conjunction with an AM 1.5 filter to give a flux of 1000 W/m² at the surface of the test cell. A more detailed fabrication procedure for the nanocrystalline titania electrodes, the cell assembly and the photoelectrochemical characterization has been described elsewhere [S1]. The composite TiO₂ films were sensitized at ambient temperature at room temperature in the dark for 24 h by immersing them into a 0.3 mM solution of the dyes in ethanol. The redox electrolyte was an ionic liquid electrolyte (PMII) purchased from Dyesol Ltd, while the *cis*-[Ru(dcbpyH)₂(NCS)₂](NBu₄)₂ dye (N719) was used as a reference to compare the new sensitizers and evaluate their sensitizing ability.

1b) Synthesis of the sensitizers



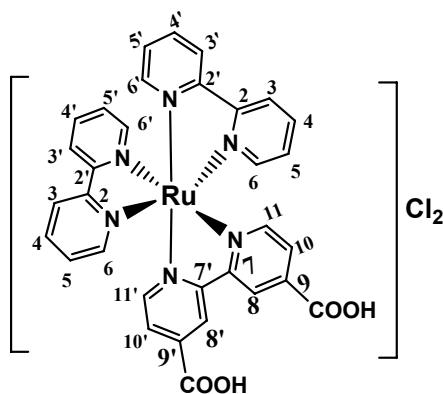
Synthesis of *cis*-[Ru(bpy)₂(L¹)]Cl₂ (2): In a 100 mL two-necked round-bottomed flask, 152.2 mg (0.292 mmol) of complex **1** were dissolved in about 40 mL of an EtOH : H₂O (1:1, v/v) mixture. Subsequently 80.0 mg (0.320 mmol) of the ligand L¹ were added as a solid in small portions and the resulting suspension was heated to a gentle reflux for 6.5 h¹ giving a dark violet solution. In the course of reaction the colour of the solution changed to dark red and at the end, the solution obtained a dark orange colour. The reaction mixture was cooled at ambient temperature and subsequently was passed through a G4 sintered glass crucible, leaving away the excess of unreacted ligand. The filtrate was reduced to a few millilitres and

¹ The progress of the reaction was monitored by UV/Vis spectroscopy: A small aliquot (1-2 drops) of the reaction mixture was sampled and diluted in 4mL of EtOH : H₂O (1:1) mixture. The UV-Vis absorption spectrum showed maxima at 450 and 478 nm after heating at 115-120° C for 6.5 h.

upon addition of acetone (30 mL) an orange solid was precipitated. The orange solid was washed with acetone (10 mL) and Et₂O (2 × 5 mL) and was then dried overnight in an oven at 100 °C. Yield: 193 mg (90%). **IR** (KBr) $\nu_{\max}/\text{cm}^{-1}$ 3036 (w, $\nu(\text{C-H, aromatic})$), 2623 (w), 2569 (w), 2527 (w), 1978 (w), 1735 (vs, $\nu(\text{C=O})$), 1624 (w, $\nu_{\text{as}}(\text{CO}_2^-)$), 1601 (s, $\nu(\text{C=C})$), 1542 (m), 1483 (w), 1463 (s), 1443 (s), 1421 (m), 1380 (s, $\nu_s(\text{CO}_2^-)$), 1328 (s), 1310 (m), 1269 (w), 1211 (m), 1160 (m), 1120 (m), 1066 (m), 1027 (w), 1007 (w), 964 (w), 895 (w), 863 (w), 788 (w), 765 (vs), 730 (m), 648 (w), 584 (w), 546 (w), 517 (w). **Raman** (r.t) $\nu_{\max}/\text{cm}^{-1}$ 1601.9 (m, $\nu(\text{C=C})$), 1543.4 (s, $\nu(\text{C=C})$), 1480.0 (vs, $\nu(\text{C=N})$), 1460.3 (m, $\nu(\text{C=N})$), 1353.3 (s, $\nu(\text{C=N})$), 1272.9 (w, $\nu(\text{C=C})$), 1168.1 (w), 1122.4 (w), 1036.5 (w). δ_{H} (500 MHz, (CD₃)₂SO, 298 K) 7.30 (1H, t, $^3J_{\text{H,H}} = 7.44$, H₈), 7.48 (5H, m, H₆+3H₅+H₉), 7.63 (4H, m, H₅+H₅+H₆+H₇), 7.71 (1H, d, $^3J_{\text{H,H}} = 5.36$, H₆), 8.03 (2H, m, H₄+H₆), 8.21 (5H, m, H₆+3H₄+H₄), 8.57 (1H, d, $^3J_{\text{H,H}} = 8.46$ Hz, H₆), 8.62 (1H, d, $^3J_{\text{H,H}} = 8.15$, H₃), 8.69 (1H, d, $^3J_{\text{H,H}} = 8.03$, H₃), 8.97 (2H, m, H₃+H₃), 9.17 (1H, d, $^3J_{\text{H,H}} = 8.22$, H₃). δ_{C} ((CD₃)₂SO, 125.8 MHz, 298 K) 119.7 (C₃), 124.2 (C₃), 124.5 (C₃), 125.0 (C₃, 2C), 125.3 (C₅), 125.4 (C₃), 127.0 (C₆), 127.2 (C₇), 127.8 (C₅), 127.9 (C₅), 128.1 (C₅), 128.2 (C₅), 129.8 (C₈), 131.2 (C₉), 138.1-138.6 (overlapped, 4 × C₄, C₄, C₄), 150.2 (C₁₀), 150.6 (C₆), 150.9 (C₆), 151.4 (C₆), 151.6 (C₆), 153.6 (C₆), 156.5-156.7 (overlapped, 4 × C₂), 157.9 (C₂ or C₂), 159.0 (C₂ or C₂), 166.6 (CO). **UV/Vis** λ_{\max} (EtOH)/nm 289 ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ 64930), 452 (12720). **ESI-MS** (CH₃CN, +Q1MS mode): m/z 663.2 (M²⁺, 3%), 495.4 (24), 332.3 ([M/2]²⁺, 8) 248.7 ([L₁ + H]⁺, 7), 157.4 ([bpy + H]⁺, 100).

Synthesis of *cis*-[Ru(bpy)₂(L¹)](PF₆)₂ (3): In a 100 mL beaker, 43.3 mg (0.059 mmol) of complex (2) were dissolved in about 2 mL of H₂O under stirring, giving a dark red solution. 28.8 mg (0.177 mmol) of solid NH₄PF₆ was added and a brown solid was immediately precipitated. The mixture was stirred for about 3 hours at room temperature and then was filtered in the air. The brown solid was washed with cold water (0 °C) and Et₂O (2 × 10 mL) and subsequently was redissolved in the minimum amount of CH₃CN (5 mL). 20 mL of Et₂O were added affording a sticky solid that was stored in the refrigerator for 2 hours (at 5 °C). The solvent was decanted off and 50 mL of Et₂O was added. Upon stirring for some minutes a fine brown powder was obtained which was dried at 55 °C for 2 hours and was stored in vacuum desiccator over P₂O₅ overnight. Yield: 28 mg (50%). Found: C, 44.47; H, 2.87; N, 8.90. Calc. for C₃₅H₂₆F₁₂N₆P₂Ru : C, 44.08; H, 2.75; N, 8.81. **IR** (KBr) $\nu_{\max}/\text{cm}^{-1}$ 3083 (w, $\nu(\text{C-H aromatic})$), 1974 (m), 1714 (m, $\nu(\text{C=O asym})$), 1603 (s), 1467 (s), 1542 (m), 1467 (m), 1447 (s), 1422 (m), 1395 (w), 1313 (w), 1242 (m), 1222 (m), 1161 (w), 1124 (w), 1067 (w), 1030 (w), 967 (w), 840 (vs, $\nu(\text{P-F})$), 762 (s), 730 (m), 648 (w), 557 (s, $\nu(\text{P-F})$). **Raman** (r.t) $\nu_{\max}/\text{cm}^{-1}$ 1603.4 (m, $\nu(\text{C=C})$), 1544.9 (s, $\nu(\text{C=C})$), 1481.5 (vs, $\nu(\text{C=N})$), 1460.3 (m, $\nu(\text{C=N})$),

1354.8 (s, $\nu(\text{C}=\text{N})$), 1272.9 (w, $\nu(\text{C}=\text{C})$), 1169.7 (w), 1124.0 (w), 1036.5 (w). δ_{H} (500 MHz, $(\text{CD}_3)_2\text{SO}$, 298 K) 7.27 (1H, t, $^3J_{\text{H,H}} = 7.59$, H_8), 7.47 (5H, m, $\text{H}_6+3\text{H}_5+\text{H}_{9'}$), 7.56 (1H, t, $^3J_{\text{H,H}} = 6.51$, $\text{H}_{5'}$), 7.62 (3H, m, $\text{H}_5+\text{H}_6+\text{H}_{7'}$), 7.70 (1H, d, $^3J_{\text{H,H}} = 5.35$, H_6), 8.02 (2H, m, H_4+H_6), 8.21 (5H, m, $\text{H}_6+3\text{H}_4+\text{H}_4'$), 8.58 (2H, m, $\text{H}_3+\text{H}_{6'}$), 8.67 (1H, d, $^3J_{\text{H,H}} = 8.38$, H_3), 8.93 (3H, m, $2 \times \text{H}_3+\text{H}_{3'}$), 9.14 (1H, d, $^3J_{\text{H,H}} = 7.76$, $\text{H}_{3'}$). δ_{C} ($(\text{CD}_3)_2\text{SO}$, 125.8 MHz, 298 K) : δ (ppm) = 118.7 ($\text{C}_{3'}$), 124.0 (C_3), 124.3 (C_3), 124.8 (C_3 , 2C), 124.8 ($\text{C}_{3'}$), 125.1 ($\text{C}_{5'}$), 125.5 ($\text{C}_{6'}$), 126.8 ($\text{C}_{7'}$), 127.51 (C_5), 127.7 (C_5), 127.7 (C_5), 127.8 (C_5), 129.0 ($\text{C}_{8'}$), 130.9 ($\text{C}_{9'}$), 137.9-138.3 (overlapped, $4 \times \text{C}_4$, $\text{C}_{4'}$, $\text{C}_{4'}$), 149.95 ($\text{C}_{10'}$), 150.4 (C_6), 150.8 (C_6), 151.3 (C_6), 151.4 (C_6), 153.4 ($\text{C}_{6'}$), 156.4-156.7 (overlapped, $4 \times \text{C}_2$), 158.0 ($\text{C}_{2'}$ or C_2), 158.7 ($\text{C}_{2'}$ or C_2), 166.6 (CO). **UV/Vis** λ_{max} (EtOH)/nm 289 ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ 58670), 454 (13370). **ESI-MS** (CH_3CN , +Q1MS mode): m/z (%) = 332.0 ($[\text{M}/2]^{2+}$, 100).



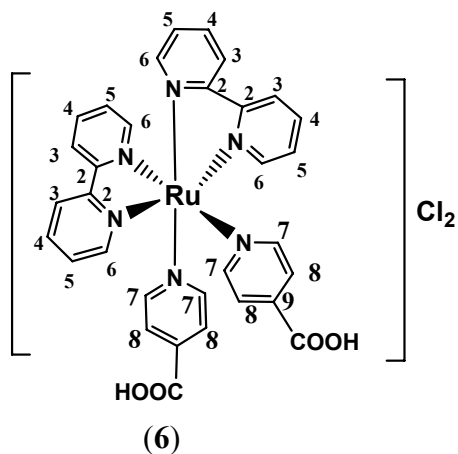
(4)

Synthesis of *cis*-[Ru(bpy)₂(L²)]Cl₂ (4): In a 100 mL two-necked round-bottomed flask, 145.6 mg (0.320 mmol) of the ligand L² were suspended in H₂O (16.5 mL). An aqueous solution of NaOH, 1M (3.5 mL) was added to the suspension to dissolve the solid, followed by the addition of hydrochloric acid 3M dropwise until a faint cloudiness to appear. 281.5 mg (0.541 mmol) of complex **1** was added to the solution and the purple mixture was heating to a gentle reflux for 3 hours. After 1 hour of heating, the colour of the solution changed from dark violet to red. The solution filtered while hot and the volume of the filtrate was reduced to about 5 mL. 30 mL of Me₂CO was added giving a dark orange precipitate which was filtered, washed with Et₂O (2 × 5 mL) and dried in an oven at 100 °C for 2h. The solid was dissolved in the minimum amount of water, followed by the addition of hydrochloric acid 2M

dropwise until pH = 2.30. The volume of the filtrate was reduced to approximately 1-2 mL and precipitated by the addition of Me₂CO (30 mL). The solid was dried at 75 °C for 2 hours and was stored overnight in a dessicator over P₂O₅. The orange solid was dissolved to the minimum amount of (CH₃)₂SO, filtered from an insoluble white solid and precipitated by the addition of acetone in excess. Yield: 312 mg (80%). **IR** (KBr) $\nu_{\max}/\text{cm}^{-1}$ 3073 (w, br, $\nu(\text{C-H arom})$), 1728 (vs, $\nu(\text{C=O})$), 1635 (w, $\nu_{\text{as}}(\text{CO}_2^-)$), 1602 (m), 1552 (w), 1462 (m), 1443 (s), 1421 (w), 1397 (w), 1312 (vs), 1260 (s), 1235 (s), 1221 (s), 1132 (w), 1115 (w), 1100 (w), 1024 (m), 900 (w), 876 (w), 768 (vs, $\nu(\text{P-F})$), 748 (vs), 732 (vs), 720 (w), 682, (m), 672 (m), 660 (w), 647 (w), 565 (s,br), 527 (w, br). **Raman** (r.t) $\nu_{\max}/\text{cm}^{-1}$ 1731.5 (w, $\nu(\text{C=O})$), 1613.7 (s, $\nu(\text{C=C})$), 1552.9 (m, $\nu(\text{C=C})$), 1472.1 (m, $\nu(\text{C=N})$), 1442.2 (m, $\nu(\text{C=N})$), 1321.9 (m, $\nu(\text{C=N})$), 1262.9 (s, $\nu(\text{C=C})$), 1041.2 (s), 1027.84 (vs), 1036.5 (w). δ_{H} (500 MHz, (CD₃)₂SO, 298 K) 7.50-7.56 (2H, tt, $^3J = 6.6$, 2H₅+2H_{5'}), 7.71-7.75 (4H, dd, $^3J = 5.4$, 2H₆+2H_{6'}), 7.88 (2H, d, $^3J = 5.7$, H₁₀+H_{10'}), 7.95 (2H, d, $^3J = 5.7$, H₁₁+H_{11'}), 8.19 (4H, m, 2H₄, 2H_{4'}), 8.89 (4H, m, 2H₃+2H_{3'}), 9.23 (2H, s, H₈+H_{8'}). δ_{H} (500 MHz, D₂O, 298 K) 7.39 (4H, m, 2H₅+2H_{5'}), 7.74 (2H, d, $^3J = 5.8$, H₁₀+H_{10'}), 7.79-7.83 (4H, dd, $^3J = 5.6$, $^3J = 5.4$ Hz, 2H₆+2H_{6'}), 7.98 (2H, d, $^3J = 5.8$, H₁₁+H_{11'}), 8.07 (4H, m, 2H₄+2H_{4'}), 8.56 (4H, d, $^3J = 8.2$, 2H₃+2H_{3'}), 8.97 (2H, s, H₈,H_{8'}). δ_{C} (125.8 MHz, (CD₃)₂SO, 298 K) 123.2 (C₈, C_{8'}), 123.9 (2 × C₃, 2 × C_{3'}), 124.5 (C₁₀, C_{10'}), 125.2-125.3 (2 × C₅, 2 × C_{5'}), 139.6 (2 × C₄, 2 × C_{4'}, 4C), 151.5 (C₉, C_{9'}, 2C), 151.0 (2 × C₆, 2 × C_{6'}), 151.8 (C₁₁, C_{11'}), 156.2 (2 × C₂, 2 × C_{2'}), 157.2 (C₇, C_{7'}), 164.8 (2CO). **UV/Vis** λ_{\max} (EtOH)/nm 289 ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ 58670), 454 (13370). **ESI-MS** (CH₃OH/H₂O, +Q1MS mode): m/z (%) = 328.9 ([M/2]²⁺, 100).

Synthesis of *cis*-[Ru(bpy)₂(L²)](PF₆)₂ (5): In a 50 mL beaker, 130 mg (0.178 mmol) of complex **4** were dissolved in about 10 mL of H₂O under stirring, giving a dark red solution. 58.9 mg (0.361 mmol) of solid NH₄PF₆ was added and a brown solid was precipitated immediately. The mixture was stirred at room temperature for about 30 minutes was filtered and the resulting brown-solid was washed with cold water (0 °C) and Et₂O (2 × 10 mL). Finally, the solid was dried at 100 °C for 2 hours and was stored overnight in a dessicator over P₂O₅. Yield: 95 mg (56%). Found: C, 40.63; H, 3.03; N, 8.80. Calc for C₃₂H₂₄F₁₂N₆O₄P₂Ru: C, 40.56; H, 2.55; N, 8.87. **IR** (KBr) $\nu_{\max}/\text{cm}^{-1}$ 3085 (vw, br, $\nu(\text{C-H aromatic})$), 1980 (vw), 1709 (m, $\nu(\text{C=O})$), 1605 (m),

1570 (w), 1549 (w), 1466 (m), 1446 (s), 1425 (w), 1402 (w), 1366 (m), 1314 (m), 1265 (s), 1230 (s), 1174 (w), 1163 (w), 1124 (w), 1070 (w), 1022 (m), 961 (w), 868 (vs, $\nu(\text{P-F})$), 756 (vs), 729 (s), 679 (w), 661 (w), 646 (w), 556 (s, $\nu(\text{P-F})$). **Raman** (r.t) $\nu_{\text{max}}/\text{cm}^{-1}$ 1717.3 (w, $\nu(\text{C=O})$), 1610.3 (vs, $\nu(\text{C=C})$), 1551.2 (m, $\nu(\text{C=C})$), 1493.1 (m, $\nu(\text{C=N})$), 1473.0 (m, $\nu(\text{C=N})$), 1320.1 (m, $\nu(\text{C=N})$), 1271.5 (w, $\nu(\text{C=C}$ intern ring)), 1267.5 (w, $\nu(\text{C=C}$ intern ring)), 1044.0 (w), 1030.7 (vs). δ_{H} (500 MHz, $(\text{CD}_3)_2\text{SO}$, 298 K) 7.50-7.55 (2H, m, 2H_5 , $2\text{H}_5'$), 7.71-7.75 (4H, dd, $2\text{H}+2\text{H}_6'$), 7.85 (2H, d, $^3J = 4.8$, $\text{H}_{10}+\text{H}_{10}'$), 7.88 (2H, d, $\text{H}_{11}+\text{H}_{11}'$), 8.19 (4H, m, $2\text{H}_4+2\text{H}_4'$), 8.84 (4H, m, $2\text{H}_3+2\text{H}_3'$), 9.21 (2H, s, $\text{H}_8+\text{H}_8'$). δ_{H} (500 MHz, D_2O , 298 K) 7.39 (4H, m, 2H_5 , $2\text{H}_5'$), 7.73 (2H, d, $^3J = 5.0$, $\text{H}_{10}+\text{H}_{10}'$), 7.79-7.83 (4H, dd, $^3J = 5.3$, $^3J = 5.1$, $2\text{H}_6+2\text{H}_6'$), 7.98 (2H, d, $^3J = 5.7$, $\text{H}_{11}+\text{H}_{11}'$), 8.07 (4H, m, $2\text{H}_4+2\text{H}_4'$), 8.55 (4H, d, $^3J = 6.64$, $2\text{H}_3+2\text{H}_3'$), 8.97 (2H, s, $\text{H}_8+\text{H}_8'$). δ_{H} (500 MHz, CD_3OD , 298 K) 7.50 (4H, m, $2\text{H}_5+2\text{H}_5'$), 7.82 (4H, d, $^3J = 5.3$, $2\text{H}_6+2\text{H}_6'$), 7.91 (d, $^3J = 5.3$, H_{10}' , H_{10} , 2H), 7.95 (2H, d, $^3J = 5.8$, $\text{H}_{11}+\text{H}_{11}'$), 8.15 (4H, m, $2\text{H}_4+2\text{H}_4'$), 8.71 (4H, m, $2\text{H}_3+2\text{H}_3'$), 9.12 (2H, s, $\text{H}_8+\text{H}_8'$). δ_{C} (125.8 MHz, $(\text{CD}_3)_2\text{SO}$, 298 K) 123.7 (C_8 , C_8' , 2C), 124.5 (2C_3 , $2\text{C}_3'$, 4C), 126.8 (C_{10} , C_{10}' , 2C), 127.9 (2C_5 , $2\text{C}_5'$, 4C), 138.1 (2C_4 , $2\text{C}_4'$, 4C), 151.5 (C_9 , C_9' , 2C), 151.0 (2C_6 , $2\text{C}_6'$, 4C), 151.8 (C_{11} , C_{11}' , 2C), 156.3 (2C_2 , $2\text{C}_2'$, 4C), 157.0 (C_7 , C_7' , 2C), 164.9 (2C_{CO}). **UV/Vis** λ_{max} (EtOH)/nm 289 ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ 75390), 454 (17270). **ESI-MS** ($\text{CH}_3\text{OH}/\text{H}_2\text{O}$, +Q1MS mode): m/z (%) = 329.0 ($[\text{M}/2]^2+$, 100).



Synthesis of *cis*-[Ru(bpy)₂(L')₂]Cl₂ (6): In a 100 mL two-necked round-bottomed flask, 202.3 mg (0.389 mmol) of complex **1** were dissolved in about 50 mL of an EtOH : H₂O (1:1, v/v) mixture. Subsequently 96.6 mg (0.785 mmol) of the ligand L' were added as a solid in small portions and the resulting suspension was heated to reflux for 5 hours in the dark under argon, giving a dark orange solution. After 2 hours of heating, the colour of the solution changed from dark violet to dark orange.

The solution was evaporated to a few millilitres and was stored overnight in the refrigerator. The solution was passed through a G4 sintered glass crucible, leaving away the excess of unreacted ligand. The filtrate was evaporated to dryness and the solid was washed with Me₂CO and Et₂O. The solid was stored overnight in a dessicator over P₂O₅. Yield: 194 mg (70%). **IR** (KBr) $\nu_{\max}/\text{cm}^{-1}$ 1716 (s, $\nu_{\text{as}}(\text{C}=\text{O})$), 1640 (w), 1602 (s), 1467 (m), 1556 (w), 1506 (m), 1498 (w), 1464 (m), 1443 (m), 1408 (s), 1325 (w), 1310 (w), 1257 (s), 1227 (s), 1202 (w), 1158 (w), 1133 (m), 1089 (m), 1052 (w), 1027 (m), 1008 (w), 886 (m), 858(m), 837 (m), 800 (m), 764(s), 730 (m), 699 (m), 674 (w), 650 (w). **Raman** (r.t) $\nu_{\max}/\text{cm}^{-1}$ 1603.4 (s, $\nu(\text{C}=\text{C})$), 1552.1 (s, $\nu(\text{C}=\text{C})$), 1484.2 (vs, $\nu(\text{C}=\text{N})$), 1320.6 (s, $\nu(\text{C}=\text{N})$), 1267.9 (w, $\nu(\text{C}=\text{C})$), 1169.4 (m, $\nu(\text{C}-\text{H})$), 1021.8 (m, $\nu(\text{C}-\text{H})$), 667.3(m). δ_{H} (500 MHz, (CD₃)₂SO, 298 K) 7.30 (1H, t, $J = 6.6$, H₅), 7.36 (1H, t, $^3J = 6.6$, H₅), 7.55 (1H, d, $^3J = 5.6$, H₆), 7.71 (2H, m, H₃+H₅), 7.81 (4H, m, 4 × H₈), 7.90 (3H, m, H₄ +H₅+ H₆), 8.17 (2H, m, H₃ +H₄), 8.50 (1H, d, $^3J = 5.6$, H₆), 8.60 (1H, d, $^3J = 8.2$, H₃), 8.68 (1H, t, $^3J = 7.1$, 2 × H₄), 8.77 (4H, d, $^3J = 4.7$, 4×H₇), 8.80 (1H, d, $^3J = 8.3$, H₃), 9.82 (1H, d, $^3J = 5.6$, H₆). δ_{C} (125.8 MHz, (CD₃)₂SO, 298 K) 122.7 (2 × C₈), 123.1- 123.6 - 123.7 (3 × C₃), 123.9 (2 × C₈), 124.0 (C₃), 126.2-126.7- 127.2- 127.280 (4 × C₅), 135.7- 136.3- 136.4-136.8 (4 × C₄), 138.1-138.5 (2 × C₉), 150.6 (2 × C₇), 151.4-151.9-152.3-152.5 (4 × C₆), 154.1(2 × C₇), 157.3- 157.6- 157.9- 158.8 (4 × C₂), 165.3-166.1 (2 × CO). **UV/Vis** λ_{\max} (EtOH)/nm 292 ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ 30120), 354 (7420), 459 (4850).

Synthesis of *cis*-[Ru(bpy)₂(L')₂](PF₆)₂ (7): This complex was synthesized as described [ref 12 in the text]. Yield: 45 mg (53%). **IR** (KBr) $\nu_{\max}/\text{cm}^{-1}$ 1715 (m, $\nu(\text{C}=\text{O})$), 1603 (s), 1546 (m), 1466 (m), 1445 (m), 1417 (m), 1376 (m), 1326 (w), 1312 (w), 1270 (m), 1243 (w), 1227 (w), 1207 (w), 1160 (w), 1125 (w), 1099 (w), 1051 (m), 1022 (m), 832 (vs, $\nu(\text{P}-\text{F})$), 760 (s), 731 (m), 705 (w), 675 (w), 648 (w), 555 (s, $\nu(\text{P}-\text{F})$). **Raman** (r.t) $\nu_{\max}/\text{cm}^{-1}$ 1604.5 (s, $\nu(\text{C}=\text{C})$), 1558.1 (s, $\nu(\text{C}=\text{C})$), 1485.8 (vs, $\nu(\text{C}=\text{N})$), 1317.48 (s, $\nu(\text{C}=\text{N})$), 1269.4 (w), 1210.1 (w), 1170.9 (s), 1037.8 (w) 1023.4 (m), 667.3 (m). **UV/Vis** λ_{\max} (EtOH)/nm 291 ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ 60840), 351 (17010), 458 (10320).

1c) TiO₂ electrode preparation and solar cell fabrication

The composition of the precursor paste is crucial for the homogeneity, adherence and morphological characteristics of the nanostructures TiO₂ porous thin films. The titania electrodes contain three different layers. The first layer was prepared from an aqueous paste based on a Degussa P25 powder dispersed in distilled water, deposited on a TEC15 ($R = 10 \Omega\text{hm}/\text{cm}^2$) transparent conducting glass (K-GLASS) using the doctor-blade technique. The second layer was a scattering layer composed on a mixture of commercial available paste (Solaronix) with Degussa P25 deposited on the first layer using the doctor-blade technique. The third layer was a titania compact layer prepared from an aqueous solution of TiCl₄. Between each deposition, the films were heated at 120 °C for 30 minutes and at 550 °C for 60 minutes. Dye adsorption was performed following their immersion in a 0.3 mM dye solution in ethanol, for 24 h at room temperature in the dark. The counter electrode was a F-doped SnO₂ transparent conductive glass on which a very thin platinum layer was sputtered to give a catalytic effect on the electron donor reduction. The redox electrolyte was an ionic based electrolyte (PMII) purchased from Dyesol Ltd. Dye-sensitized solar cells of the following structure (TEC15/TiO₂/dye/electrolyte/TEC15) were fabricated by sandwiching the liquid electrolyte between the derivatized nanocrystalline titania photoelectrode and the platinized counter electrode. The two electrodes were brought in close proximity with the help of an adhesive tape mask, in order to avoid short-circuiting between the two conductive glass surfaces.

2) Energetic diagrams of the interface

Cyclic voltammetry experiments have been performed in [10-12, S2] for the determination of the oxidation potentials for the Ru³⁺/Ru²⁺ couple. The calculated HOMO energy levels for complexes **2**, **3**, **4**, **5** and **7** are reported in Table 1 (in V, vs. SCE). The lowest unoccupied molecular orbital (LUMO) level was calculated from the HOMO level and the excitation energy of the dyes adsorbed on TiO₂ which is determined from the absorption threshold of their lowest-energy MLCT bands (approximately derived from the low energy tail of the TiO₂/dye absorption spectrum, right Fig. 2B). It is clear that electron injection from the excited dyes molecules into the conduction band of the semiconductor is thermodynamically possible for dyes **2-5**. However, the excited state of dyes **4,5** matches better the lower bound of the conduction band of the semiconductor than the LUMOs of the complexes **2** and **3**,

thus minimizing energy losses during the electron transfer process. The better matching plays a crucial role making more favorable the electron injection to TiO₂ [S3].

Table S1. HOMO–LUMO energies of Ru²⁺ complexes and Absorption threshold values.

Dye	HOMO ^c (V vs. SCE)	Absorption Threshold ^d (eV)	LUMO ^e (V vs. SCE)
2^a	1.27	2.14	-0.87
3^a	1.27	2.10	-0.83
4^b	1.27	2.03	-0.76
5^b	1.44	2.14	-0.70
7^b	1.30	1.92	-0.62

^a in DMF, ^b in CH₃CN, ^celectrochemical data, ^dderived from Fig 2B, ^ecalculated

3) Figure S1

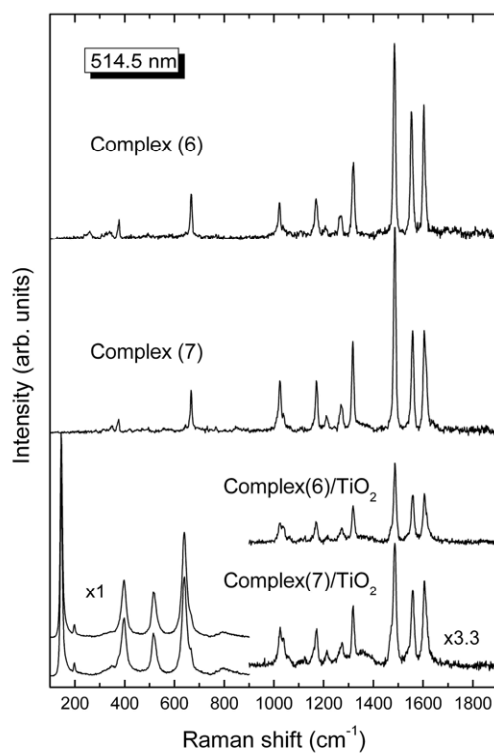


Fig. S1. Micro-Raman spectra of complexes **6** and **7** in powder form, in comparison with the corresponding dye sensitized titania films at 514.5 nm.

References

- S1. T. Stergiopoulos, I. M. Arabatzis, G. Katsaros, P. Falaras, binary polyethylene oxide/titania solid-state redox electrolyte for highly efficient nanocrystalline TiO₂ photoelectrochemical cells, *Nano Lett.*, 2002, **2**, 1259–1261.
- S2. P-H Xie, Y-J Hou, B-W Zhang, Yi Cao, F. Wu, W-J Tian, J-C Shen, Spectroscopic and electrochemical properties of ruthenium(II) polypyridyl complexes, *J. Chem. Soc., Dalton Trans.*, 1999, **23**, 4217-4221.
- S3. K. Srikanth, V.R. Marathe and M.K. Mishra. Role of electronic structure of ruthenium polypyridyl dyes in the photoconversion efficiency of dye-sensitized solar cells: Semiempirical investigation, *Int. J. Quantum Chem.* 2002, **89**, 535-549.