

Supporting information of

Tris-bipyridine based dinuclear Ruthenium(II)-Osmium(III) complexes dyads grafted on TiO₂ nanoparticles for artificial photosynthesis Z-scheme mimicking

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Experimental section

Materials. Thin-layer chromatography (TLC) was performed on aluminium sheets precoated with Merck 5735 Kieselgel 60F254. Column chromatography was carried out either with Merck 5735 Kieselgel 60F (0.040-0.063 mm mesh). Chemicals were purchased from Sigma-Aldrich or Alfa Aesar and used as received. Chenodeoxycholic acid, titanium dioxide screen printing pastes were purchased from Solaronix SA (Switzerland) and Dyesol SA (Australia). Conductive glass substrates (F-doped SnO₂) were purchased from Pilkington (TEC8, sheet resistance 8 Ω/square).

Instrumentation and Methods. ¹H and ¹³C NMR spectra were recorded on an *AVANCE 400 BRUKER* or *AVANCE III 500 BRUKER*. Chemical shifts for ¹H NMR spectra are referenced relative to residual protium in the deuterated solvent (**CDCl₃** δ = 7.26 ppm for ¹H and δ = 77.16 ppm for ¹³C; **MeOD-d₄** δ = 3.31 ppm for ¹H and δ = 49.00 ppm for ¹³C; **CD₃CN** δ = 1.94 ppm for ¹H, δ = 1.32 and δ = 118.26 ppm for ¹³C). Spectra were recorded at room temperature, chemical shifts are written in ppm and coupling constants in Hz. High-resolution mass (HR-MS) spectra were obtained either by electrospray ionization coupled with high resolution ion trap orbitrap (LTQ-Orbitrap, ThermoFisher Scientific,) or by MALDI-TOF-TOF (Autoflex III, Bruker), both working in ion-positive mode and with 2,5-ihydroxybenzoic acid (DHB) or dithranol as matrix. Electrochemical measurements were performed with a potentiostat-galvanostat *AutoLab PGSTAT 302N* controlled by resident GPES software (General Purpose Electrochemical System 4.9) using a conventional single-compartment three-electrode cell. The working electrode was a glassy carbon, a platinum electrode or a FTO coated glass plate, with a layer of mesoporous TiO₂ (18NR-T), dyed with the studied sensitizer. The auxiliary was a Pt plate of 1 cm² and the reference electrode was the saturated potassium chloride calomel electrode (SCE). The supporting electrolyte was 0.1 N *n*-Bu₄NPF₆ (TBAP) in adapted dry solvent and solutions were purged with argon before the measurements. All potentials are quoted relative to SCE. In all the experiments the scan rate was 100 mV/s. UV-Visible absorption spectra were recorded on a *UV-2401PC Shimadzu* spectrophotometer. Fluorescence spectra were recorded on a *SPEX Fluoromax* fluorimeter.

TiO₂ electrode preparation. Conductive glass substrates were successively cleaned by sonication in soapy water, then ethanol for 10 min before being fired at 450 °C for 30 min. Once cooled down to room temperature, FTO plates were rinsed with ethanol and dried in ambient air. TiO₂ films were then prepared in three steps. A first treatment is applied by immersion for 30 min in an aqueous TiCl₄ solution at 80 °C. Layers of TiO₂ were then screen printed with transparent colloidal paste 18NR-T (from Dyesol), with drying steps at 150 °C for 20 min between each layer. A final light scattering overlayer was eventually screen printed (18NR AO, Dyesol) over the transparent layer. The obtained substrates were then sintered at 450 °C, following a progressive heating ramp (135 °C for 15 min, 325 °C for 5 min, 375 °C for 5 min, 450 °C for 30 min). A second TiCl₄ treatment was applied while cells are still hot, followed by a final firing at 450°C for 30 min. The prepared TiO₂ electrodes were soaked while still

hot (80 °C) in a solution (0.16 mM) of each compound during one night. A solution of ethanol was used for all ruthenium and osmium compounds.

Synthesis of Complex Ru(Hbpy)₂(bisbpy) (4). A stirred solution of Ru(bpy)₂Cl₂ (107 mg, 0.206 mmol) and ligand bisbpy (3) (81.1 mg, 0.206 mmol) in a mixture of EtOH and water (34 ml, 4/1) freed from oxygen by argon bubbling while sonicating (15 min) under argon atmosphere was refluxed for 4 hours. The solvent was removed and the residual orange material purified by flash chromatography (silica gel, acetonitrile/water/KNO₃ sat., 40/4/1). Fractions containing the desired product were concentrated and the resulting salt was dissolved in as little H₂O as possible and then added dropwise to a saturated solution of NH₄PF₆ (2 mL). The orange precipitate was filtered off and dried overnight to yield the title compound (104 mg, 46%).

¹H NMR (400 MHz, CD₃CN): δ_H = 8.79 (4H, d, ³J = 8.4 Hz), 8.71 (4H, m), 8.50 (2H, d, ³J = 7.2 Hz), 8.18 (4H, t, ³J = 8.0 Hz), 8.02 (4H, m), 7.83 (2H, q, ³J = 5.6 Hz), 7.55 (6H, m), 7.44 (1H, d, ³J = 5.7 Hz), 7.39 (1H, d, ³J = 5.7 Hz), 2.91 (4H, m), 2.60 (3H, s), 2.55 (3H, s), 1.86 (4H, m).

¹³C NMR (100 MHz, CD₃CN): δ_C = 158.3, 158.2, 157.8, 157.7, 155.4, 152.7, 152.6, 152.0, 151.7, 151.4, 148.2, 147.6, 138.8, 129.5, 128.7, 127.6, 126.9, 126.1, 125.4, 125.3, 123.9, 123.2, 35.8, 35.5, 30.6, 21.6, 21.1.

MALDI-TOF: m/z calculated for 953.2212 [M]⁺, Found 953.2205 [M]⁺, Δ = 0.7 ppm.

Synthesis of dyad RuH-Os(dcebpy) (6). A stirred solution of Ru(Hbpy)₂(bisbpy) (100 mg, 0.091 mmol) and Os(dcebpy)₂Cl₂ (66.2 mg, 0.076 mmol) in a mixture of EtOH and water (22 ml, 1/1) was freed from oxygen by argon bubbling while sonicating (15 min) under argon atmosphere and then refluxed for 3 days. The solvent was removed and the residual brown material purified by flash chromatography (silica gel, acetonitrile/water/KNO₃ sat./NH₄OH, 40/4/1/0 to 40/4/1/4). The first brown fractions containing the desired product were concentrated and the resulting salt was dissolved in as little H₂O as possible and then added dropwise to a saturated solution of NH₄PF₆ (2 mL). The brown precipitate was filtered off and dried overnight to yield the title compound (30 mg, 18%). The second brown fractions containing the desired product with partially hydrolysed ester were concentrated and the resulting salt was dissolved in as little H₂O as possible and then added dropwise to a saturated solution of NH₄PF₆ (2 mL). The brown precipitate was filtered off and dried overnight to yield the partially hydrolysed compound (12 mg, 7%).

¹H NMR (400 MHz, CD₃CN): δ_H = 9.04 (4H, m), 8.48 (4H, d, ³J = 6.4 Hz), 8.37 (4H, t, ³J = 8.4 Hz), 8.04 (4H, td, ³J = 7.2 Hz and ⁴J = 0.8 Hz), 7.84 (2H, t, ³J = 4.4 Hz), 7.78 (2H, m), 7.73 (6H, m), 7.65 (2H, dd, ³J = 4.8 Hz and ⁴J = 1.2 Hz), 7.55 (1H, d, ³J = 4.8 Hz), 7.53 (1H, d, ³J = 4.8 Hz), 7.39 (6H, m), 7.22 (4H, m), 4.46 (8H, m), 2.91 (2H, t, ³J = 6.9 Hz), 2.84 (2H, t, ³J = 6.9 Hz), 2.61 (3H, s), 2.52 (3H, s), 1.79 (4H, m), 1.41 (12H, m).

¹³C NMR (100 MHz, CD₃CN): δ_C = 164.2, 164.1, 160.9, 160.5, 160.1, 158.6, 158.4, 158.1, 158.0, 157.7, 157.5, 156.3, 155.3, 153.3, 153.2, 152.8, 152.7, 152.6, 152.5, 152.4, 152.0, 151.8, 151.5, 151.3, 151.2, 140.2, 139.4, 139.3, 138.6, 130.0, 129.3, 129.2, 128.5, 128.4, 126.5, 126.0, 125.7, 125.3, 125.2, 125.1, 125.0, 124.9, 63.7, 35.4, 35.3, 30.7, 30.6, 21.3, 21.2, 14.5, 14.4.

ESI-LTQ-Orbitrap: m/z calculated for 945.1842 [M]²⁺, Found 945.1851 [M]²⁺, Δ = 0.9 ppm.

Synthesis of dyad RuH-Os. A stirred solution of dyad RuH-Os(dcebpy) (42 mg, 0.019 mmol) in HCl (4N) was refluxed for 16 hours under argon atmosphere. The solvent was concentrated to 2 mL and then added dropwise to a saturated solution of NH₄PF₆ (2 mL). The brown precipitate was filtered off and dried overnight to yield the title compound (30 mg, 75%).

¹H NMR (500 MHz, CD₃OD): δ_H = 9.09 (4H, m), 8.65 (4H, d, ³J = 7.9 Hz), 8.49 (4H, m), 8.10 (4H, m), 7.87 (4H, m), 7.77 (8H, m), 7.60 (1H, d, ³J = 5.9 Hz), 7.57 (1H, d, ³J = 5.8 Hz), 7.45 (6H, m), 7.30 (4H, t, ³J = 6.0 Hz), 2.96 (2H, m), 2.88 (2H, m), 2.65 (3H, s), 2.56 (3H, s), 1.79 (4H, m).

¹³C NMR (125 MHz, CD₃OD): δ_C = 167.3, 167.2, 167.1, 161.0, 160.9, 160.6, 158.9, 158.7, 158.5, 158.4, 158.3, 158.2, 157.9, 157.7, 156.4, 155.8, 152.9, 152.7, 152.6, 152.4, 152.3, 152.2, 152.1, 151.8, 151.4, 151.0, 150.7, 141.8, 141.5, 139.0, 130.4, 129.7, 129.5, 128.9, 128.8, 128.6, 126.7, 126.2, 125.9, 125.4, 125.3, 125.1, 125.0, 35.7, 35.0, 30.6, 30.5, 21.3, 21.2.

ESI-LTQ-Orbitrap: m/z calculated for 889.12091 [M-2PF₆]²⁺, Found 889.12158 [M-2PF₆]²⁺, Δ= 0.75 ppm.

Synthesis of Complex Ru(CF₃bpy)₂(bpy). A stirred solution of Ru(CF₃bpy)₂Cl₂ (30 mg, 0.040 mmol) and 4,4'-dimethyl-2,2'-dipyridyl (8.0 mg, 0.044 mmol) in a mixture of EtOH and water (7.5 ml, 1/2) freed from oxygen by argon bubbling while sonicating (15 min) under argon atmosphere was refluxed for 8 hours. The solvent was removed and the residual orange material was dissolved in as little H₂O as possible and then added dropwise to a saturated solution of NH₄PF₆ (2 mL). The red precipitate was filtered off and dried overnight to yield the title compound (42 mg, 91%).

¹H NMR (400 MHz, CD₃CN): δ_H = 8.92 (4H, d, ³J = 4.3 Hz), 8.39 (2H, brs), 7.98 (4H, m), 7.71 (2H, dd, ³J = 5.9 Hz and ³J = 1.2 Hz), 7.67 (2H, dd, ³J = 5.9 Hz and ³J = 1.2 Hz), 7.49 (2H, d, ³J = 5.8 Hz), 7.27 (2H, d, ³J = 5.8 Hz), 2.56 (6H, s).

¹³C NMR (100 MHz, CD₃CN): δ_C = 158.7, 157.0, 155.0, 154.4, 152.8, 152.2, 139.7 (4C, q, ³J = 32.3 Hz), 129.7, 126.4, 125.0, 124.8, 122.6, 122.1, 21.4.

MALDI-TOF: m/z calculated for 870.0909 [M]⁺, Found 870.0918 [M]⁺, Δ= 1.0 ppm.

Synthesis of Complex Ru(CF₃bpy)₂(bisbpy) (5). A stirred solution of Ru(CF₃bpy)₂Cl₂ (110 mg, 0.145 mmol) and ligand bisbpy (3) (57.4 mg, 0.145 mmol) in a mixture of EtOH and water (24 ml, 4/1) freed from oxygen by argon bubbling while sonicating (15 min) under argon atmosphere was refluxed for 8 hours. The solvent was removed and the residual orange material purified by flash chromatography (silica gel, acetonitrile/water/KNO₃ sat., 40/4/1). Fractions containing the desired product were concentrated and the resulting salt was dissolved in as little H₂O as possible and then added dropwise to a saturated solution of NH₄PF₆ (2 mL). The orange precipitate was filtered off and dried overnight to yield the title compound (37 mg, 34%).

¹H NMR (400 MHz, CD₃CN): δ_H = 8.92 (4H, brs), 8.65 (1H, d, ³J = 5.3 Hz), 8.62 (1H, d, ³J = 5.6 Hz), 8.40 (2H, d, ³J = 10.6 Hz), 8.32 (2H, d, ³J = 15.3 Hz), 7.99 (4H, m), 7.71-7.63 (6H, m), 7.52 (1H, d, ³J = 5.7 Hz), 7.49 (1H, d, ³J = 5.7 Hz), 7.28 (2H, t, ³J = 4.3 Hz), 2.94 (2H, t, ³J = 7.8 Hz), 2.89 (2H, t, ³J = 7.9 Hz), 2.62 (3H, s), 2.55 (3H, s), 1.83 (4H, m).

¹³C NMR (100 MHz, CD₃CN): δ_C = 160.3, 158.6, 157.6, 157.1, 157.0, 156.5, 154.9, 154.4, 152.8, 152.3, 152.1, 147.9, 147.8, 147.1, 146.1, 139.6 (2C, q, ³J = 35.0 Hz), 139.5 (2C, q, ³J = 35.0 Hz), 129.6, 128.9, 128.7, 128.0, 127.4, 126.3, 125.5, 124.9, 124.7, 124.6, 123.9, 122.5, 122.0, 35.9, 35.4, 30.2, 22.0, 21.3.

ESI-LTQ-Orbitrap: m/z calculated for 1225.17076 [M-PF₆]⁺, Found 1225.17163 [M-PF₆]⁺, Δ= 0.71 ppm.

Synthesis of dyad RuCF₃-Os(dcebpy) (7). A stirred solution of Ru(CF₃bpy)₂(bisbpy) (57 mg, 0.042 mmol) and Os(bpyCO₂Et)₂Cl₂ (38 mg, 0.044 mmol) in a mixture of EtOH and water (13 ml, 1/1) freed from oxygen by argon bubbling while sonicating (15 min) under argon atmosphere was refluxed for 3 days. The solvent was removed and the residual brown material purified by flash chromatography (silica gel, acetonitrile/water/KNO₃ sat./NH₄OH, 40/4/1/0 to 40/4/1/4). The first brown fractions containing the desired product were concentrated and the resulting salt was dissolved in as little H₂O as possible and then added dropwise to a saturated solution of NH₄PF₆ (2 mL). The brown precipitate was filtered off and dried overnight to yield the title compound (34 mg, 33%). The second brown fractions containing the desired product with partially hydrolysed ester were concentrated and the resulting salt was dissolved in as little H₂O as possible and then added dropwise to a saturated solution of NH₄PF₆ (2 mL). The brown precipitate was filtered off and dried overnight to yield the partially hydrolysed compound (15mg, 15%).

¹H NMR (400 MHz, CD₃CN): δ_H = 9.03 (4H, d, ³J = 9.8 Hz), 8.92 (4H, brs), 8.40 (4H, m), 7.98 (4H, m), 7.85 (2H, m), 7.79 (2H, m), 7.76-7.63 (8H, m), 7.52 (1H, d, ³J = 5.6 Hz), 7.49 (1H, d, ³J = 5.3 Hz), 7.36 (1H, d, ³J = 5.9 Hz), 7.34 (1H, d, ³J = 5.9 Hz), 7.27 (2H, d, ³J = 5.6 Hz), 7.21 (2H, brs), 4.45 (8H, m), 2.88 (4H, m), 2.61 (3H, s), 2.54 (3H, s), 1.80 (4H, brs), 1.40 (12H, m).

¹³C NMR (100 MHz, CD₃CN): δ_C = 164.1, 160.8, 160.4, 158.6, 158.5, 157.1, 157.0, 156.6, 156.3, 155.0, 154.4, 153.3, 152.8, 152.6, 152.5, 152.3, 152.1, 151.3, 151.1, 139.5 (2C, q, ³J = 35.9 Hz), 139.4 (2C, q, ³J = 35.3 Hz), 139.3, 139.2, 129.9, 129.6, 129.1, 128.8, 128.4, 126.5, 126.3, 125.7, 125.5, 124.9, 124.7, 122.5, 122.0, 63.6, 35.4, 35.3, 30.6, 30.5, 21.3, 21.2, 14.4.

ESI-LTQ-Orbitrap: m/z calculated for 672.45105 [M-3PF₆]³⁺, Found 672.45166 [M-3PF₆]³⁺, Δ= 0.9 ppm.

Synthesis of dyad RuCF₃-Os. A stirred solution of **dyad RuCF₃-Os(dcebpy)** (49 mg, 0.020 mmol) in HCl (4N) was refluxed for 16 hours under argon atmosphere. The solvent was concentrated to 2 mL and then added dropwise to a saturated solution of NH₄PF₆ (2 mL). The brown precipitate was filtered off and dried overnight to yield the title compound (23 mg, 49%).

¹H NMR (500 MHz, CD₃OD): δ_H = 9.31 (4H, s), 9.09 (4H, brs), 8.64 (4H, brs), 8.18 (4H, m), 7.90-7.70 (12H, m), 7.66 (1H, brs), 7.61 (1H, brs), 7.48 (1H, brs), 7.37 (1H, brs), 7.30 (2H, brs), 2.94 (4H, m), 2.67 (3H, s), 2.60 (3H, s), 1.83 (4H, brs).

¹³C NMR (125 MHz, CD₃OD): δ_C = 161.1, 160.7, 159.6, 159.5, 159.4, 159.3, 157.6, 157.5, 157.0, 156.0, 155.0, 154.8, 154.5, 154.4, 153.4, 152.5, 152.4, 151.9, 151.1, 150.9, 140.6 (2C, q, ³J = 34.4 Hz), 140.4 (2C, q, ³J = 35.5 Hz), 130.3, 130.2, 129.6, 129.5, 128.9, 127.0, 126.9, 126.8, 126.2, 126.1, 125.4, 124.7, 123.0, 122.5, 120.4, 36.0, 35.8, 31.0, 30.7, 21.3, 21.1.

ESI-LTQ-Orbitrap / MALDI-TOF: Found but not with enough signal to measure.

Transient absorption and photoemission experiments

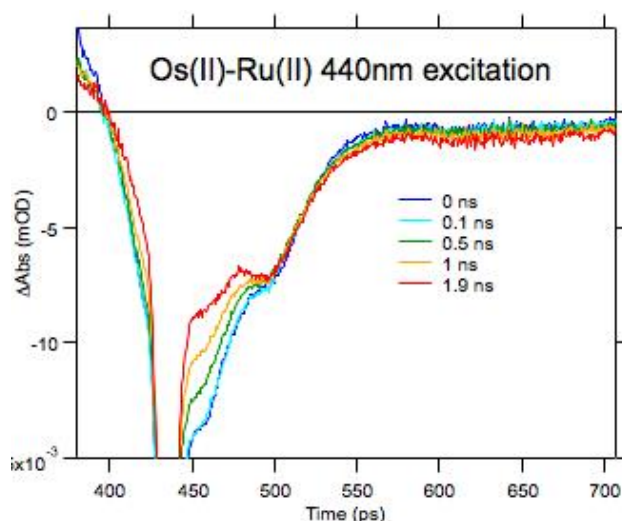


Figure S1. Transient absorption data in acetonitrile/water (0.9/0.1) for **RuH-Os** in the Ru^{II}-Os^{II} state, after excitation with 150 fs pulses at 435 nm. The excitation pulse excites both Ru^{II} and Os^{II} units, leading to absorption bleach over the entire visible region. The excitation power is low enough that simultaneous excitation of both units in the same molecule can be neglected. IN the molecules where Ru^{II} is excited, energy transfer to Os^{II} occurs with a lifetime of ca. 1 ns, leading to partial bleach recovery around 450 nm and a further bleach of the Os^{II} ground state absorption at 550 -700 nm.

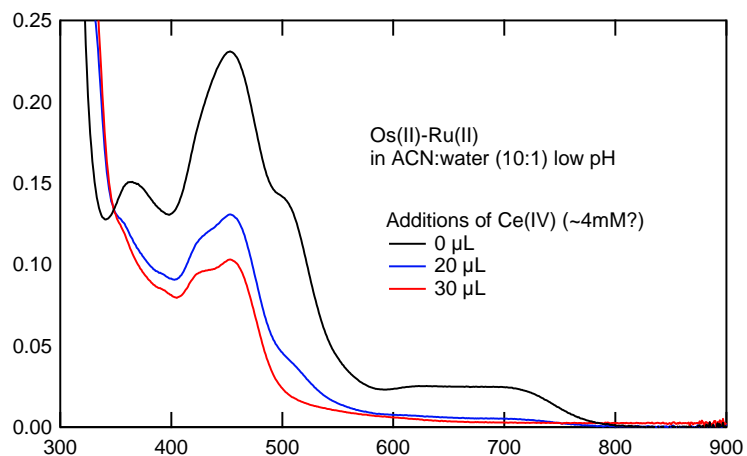


Figure S2. Absorption spectra for RuH-Os in acetonitrile/water (0.9/0.1), before (black line) and after (blue line) addition of *ca.* 1 equivalent of cerium(IV) ammonium nitrate.

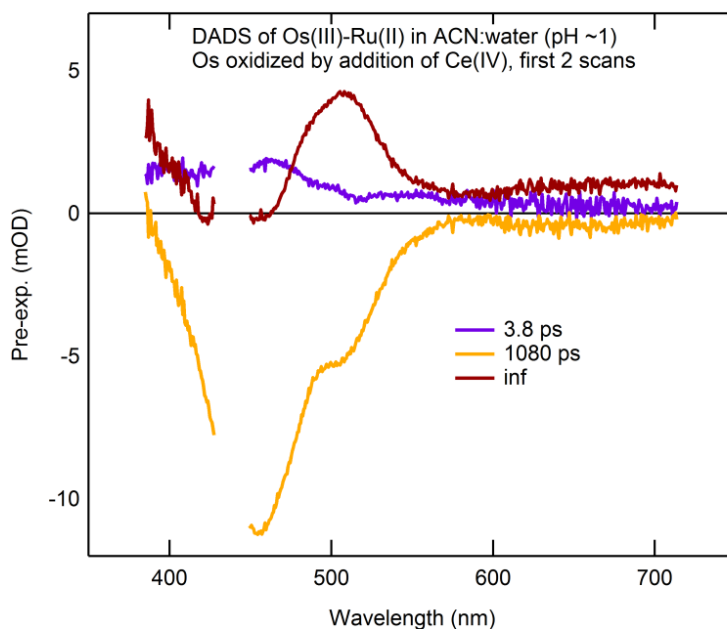


Figure S3. Decay-associated spectra from a global fit to the data in acetonitrile/water (0.9/0.1) for **RuH-Os** in the Ru^{II}-Os^{II} state. A sum of two exponentials and an offset ($\tau = \infty$) was used.

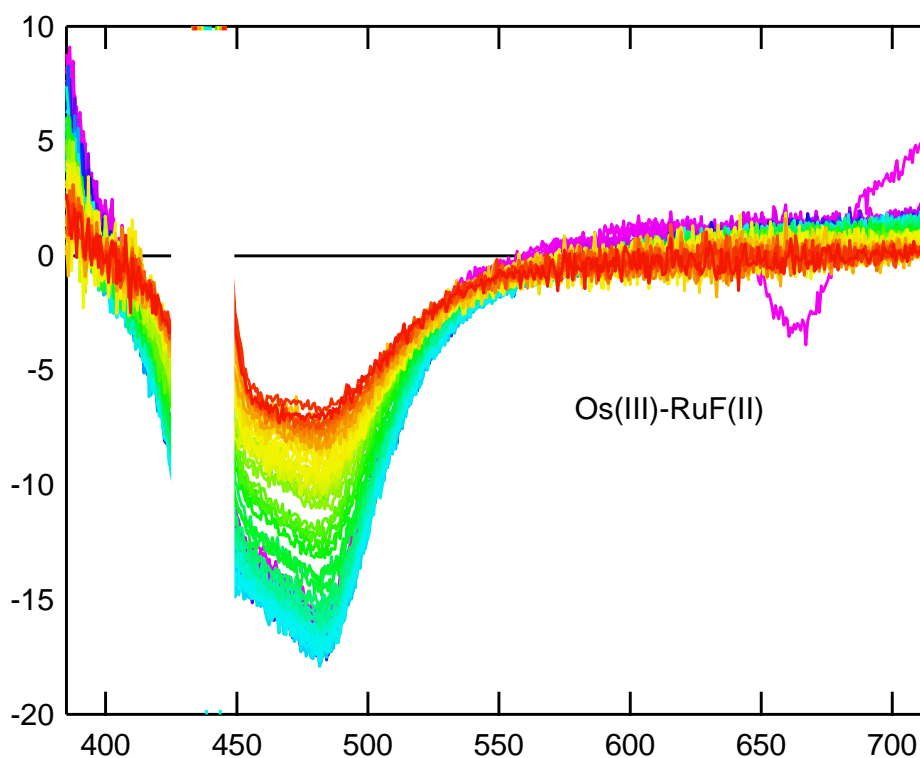


Figure S4. Transient absorption spectra of **RuCF₃-Os** in acetonitrile/water (0.9/0.1) after 150 fs excitation at 435 nm. Before excitation, **RuCF₃-Os** was oxidized to the Ru^{II}-Os^{III} state by one equivalent of cerium(IV) ammonium nitrate. Note that there is no formation of Os^{II} at 510 nm as the Ru^{II} bleach recovers ($\tau \sim 1.0$ ns). The remaining bleach around 450 nm is attributed to unquenched *Ru^{II} due to photodegradation.

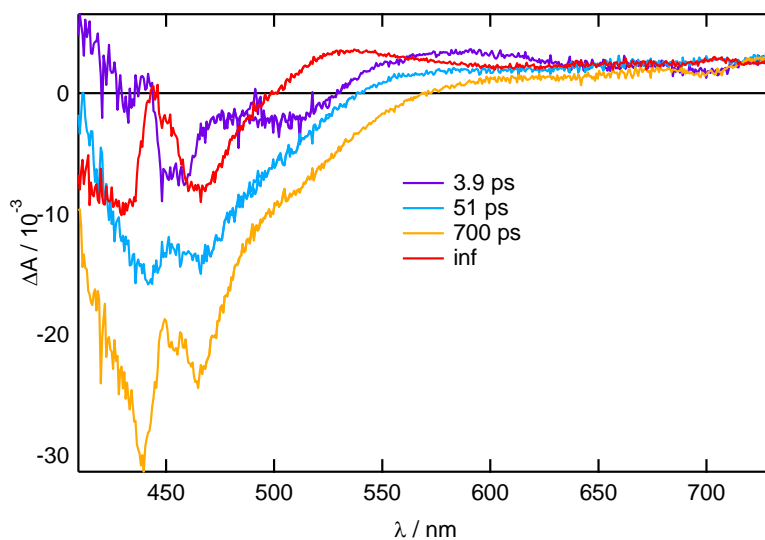


Figure S5. Decay-associated spectra from a global fit to the data on TiO₂ for **RuH-Os** in the Ru^{II}-Os^{II} state. A sum of three exponentials and an offset ($\tau = \infty$) was used.

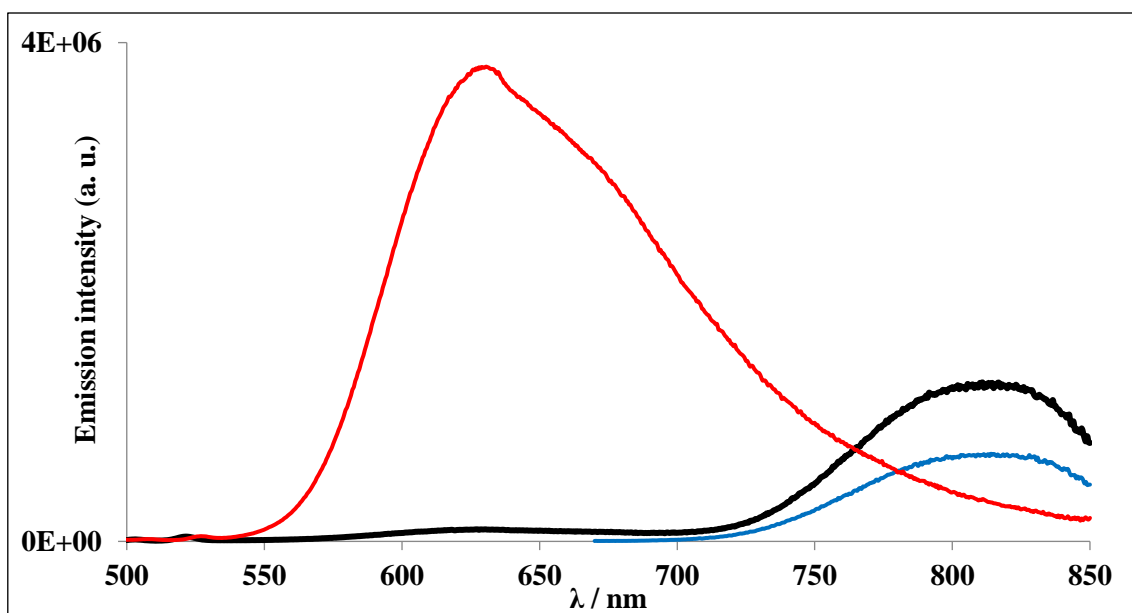


Figure S6. Room temperature emission spectra recorded in degazed acetonitrile at 298 K of the dyad **RuH-Os** (black) along with those of its constituents **Os bpy(dcbpy)₂** (blue) and **Ru(bpy)₃** (red), $\lambda_{\text{exci}} = 450$ nm for ruthenium center and 629 nm for osmium complex.

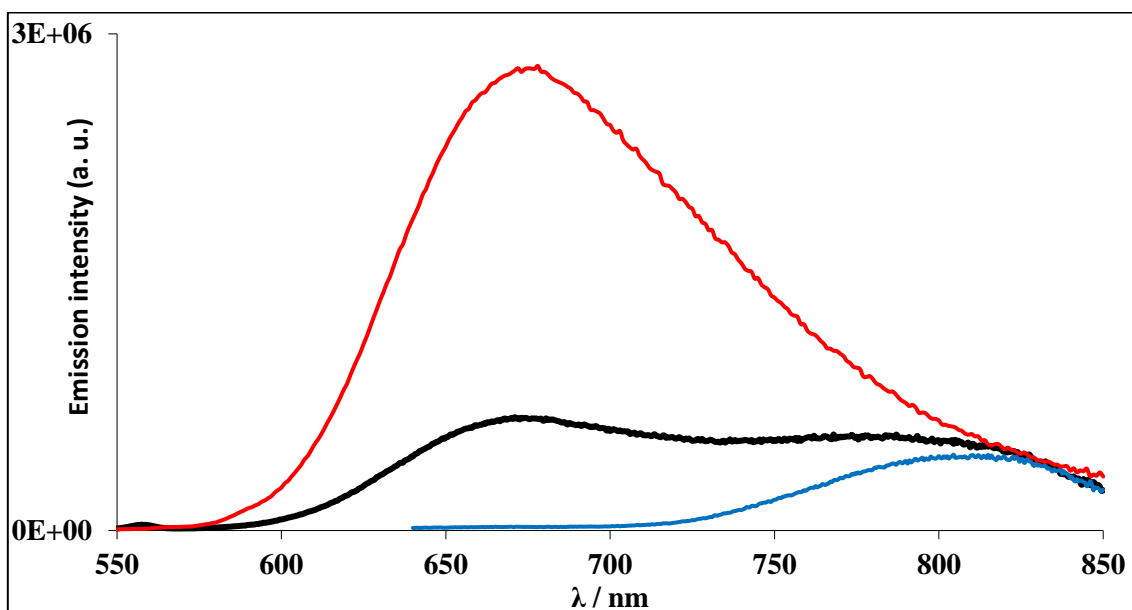


Figure S7. Room temperature emission spectra recorded in degazed acetonitrile at 298 K of the dyad **RuCF₃-Os** (black) along with those of its constituents **Os bpy(dcbpy)₂** (blue) and **Ru(CF₃bpy)₂(bpy)** (red), $\lambda_{\text{exci}} = 480$ nm for ruthenium center and 629 nm for osmium complex.

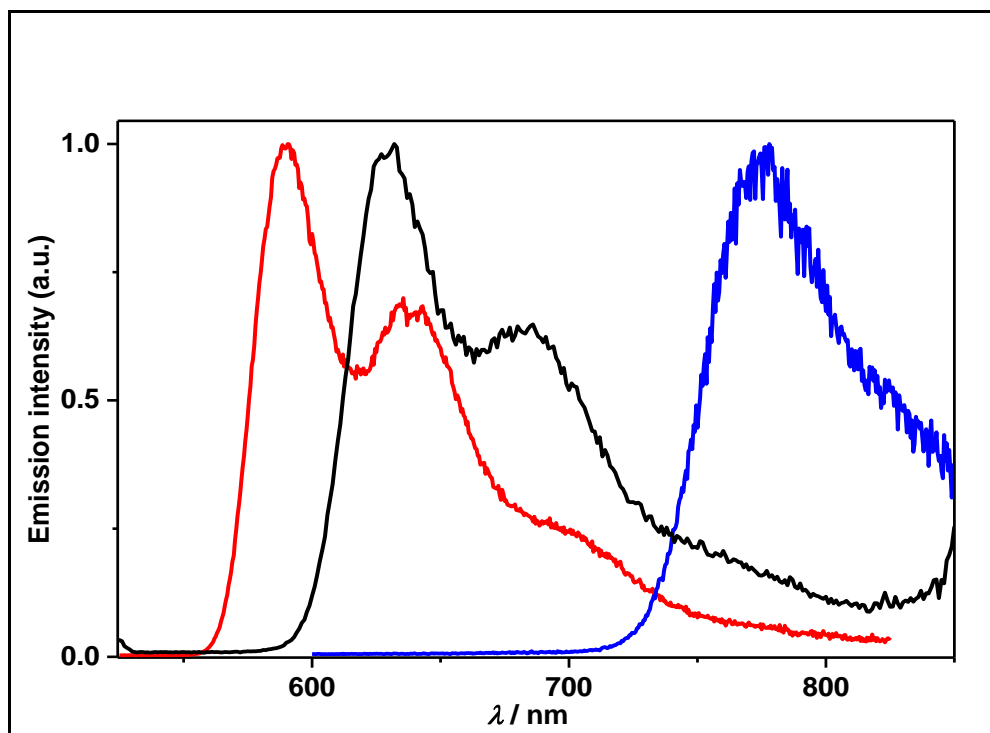


Figure S8. Emission spectra recorded at 77K in a frozen matrix (4/1 ethanol/methanol) of the reference complexes **Ru(CF₃bpy)₂(bpy)** (black) **Os bpy(dcbpy)₂** (blue) and **Rubpy₃** (red).