

Supplementary Information

Near-infrared room temperature emission from a novel class of Ru(II) heteroleptic complexes with quinonoid organometallic linker

Aurélie Damas,^a Maria Pia Gullo,^b Marie Noelle Rager,^d Anny Jutand,^c Andrea Barbieri,^b
and Hani Amouri*^a

Electrochemical behavior of the heterodinuclear ruthenium complexes (2-4).

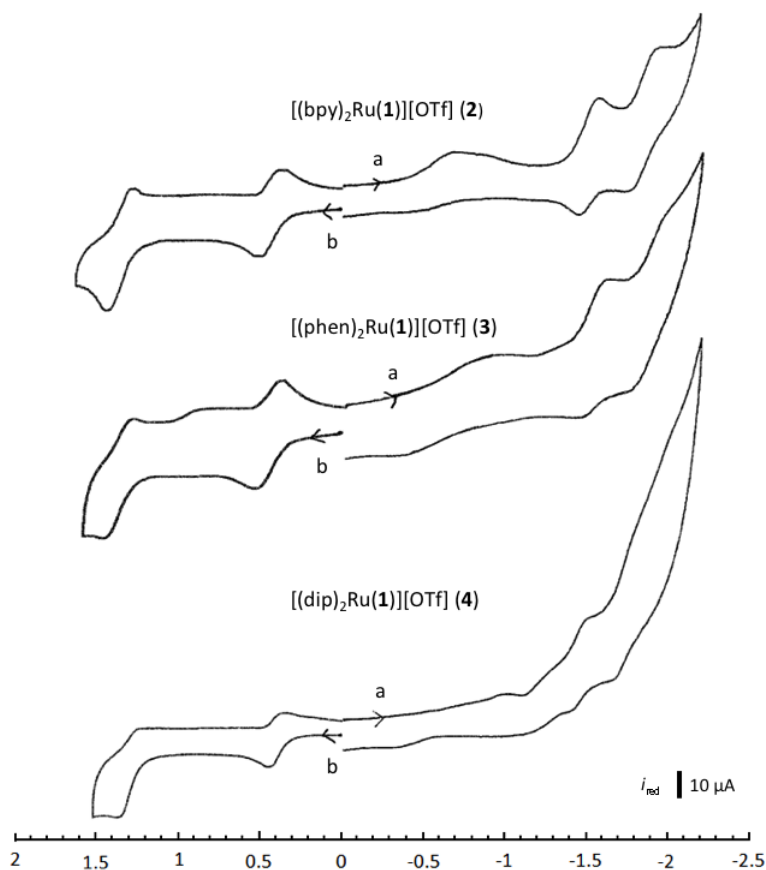


Figure S1. Cyclic voltammetry of complexes **2-4** (2 mM) in CH_2Cl_2 containing nBu_4NBF_4 (0.3 M) at gold working electrode ($d = 0.125$ mm) at scan rate of $50 V \cdot s^{-1}$ for **2** and **3** and at scan rate of $20 V \cdot s^{-1}$ for **4**. a) Reduction first. b) Oxidation first. Potentials are referred *versus* SCE (oxidation peak potential of ferrocene = $+0.507$ V vs SCE).

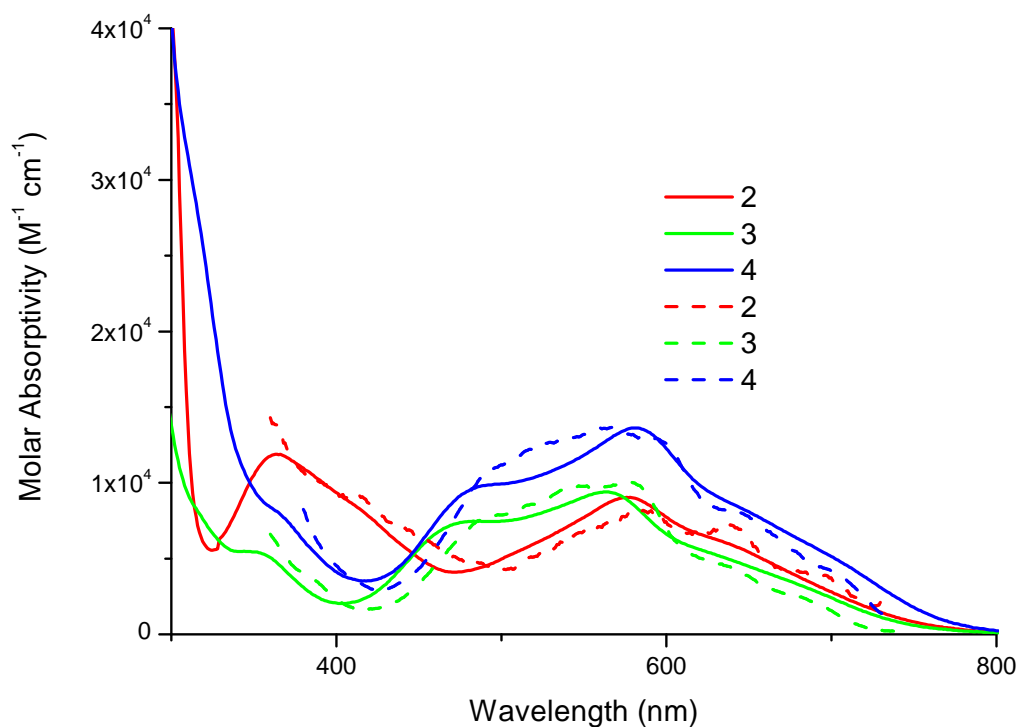


Figure SI2. Comparison between absorption (full lines) and excitation (dotted lines) spectra of complexes **2-4** in CH_2Cl_2 solution. Excitation spectra are normalised to match the MLCT absorption band.

Experimental Section

All experimental reactions were carried out at room temperature using standard Schlenk techniques. Solvents were dried and distilled under argon atmosphere by standard procedures prior to use. All reagents obtained from commercial suppliers were used as received. The metallated *o*-quinone $[\text{Cs}][\text{Cp}^*\text{Ru}(\eta^4\text{-C}_6\text{H}_4\text{O}_2)]$ (**1-Cs**) and the binuclear complex $[(\text{bpy})_2\text{Ru}(\mathbf{1})][\text{OTf}]$ (**2**), as well as the halogenated precursors $[(\text{phen})_2\text{RuCl}_2]$ and $[(\text{dip})_2\text{RuCl}_2]$ were prepared according to literature procedures.^[2c, 4, 13] Elemental analyses were performed by microanalytical services of ICSN at Gif-sur-Yvette on a Perkin-Elmer 2400 apparatus. All NMR data were acquired on Bruker Avance 400 spectrometer in CD_2Cl_2 at 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR. NMR chemical shifts are reported in parts per million referenced to the residual solvent proton ($\delta = 5.32$ ppm) for ^1H NMR and carbon ($\delta = 53.1$ ppm) for ^{13}C NMR. IR spectra were recorded on a Bruker Tensor 27 equipped with an ATR Harricks apparatus.

Synthesis of 3. A colorless acetone solution (5 mL) of AgOTf (103 mg, 0.40 mmol) was added to a dark-purple acetone suspension (5 mL) of [(phen)₂RuCl₂] (107 mg, 0.20 mmol). Meanwhile, two equivalents of Cs₂CO₃ (130 mg, 0.40 mmol) were added at once to an acetone solution (5 mL) of [Cp*₂Ru(η⁶-C₆H₆O₂)]⁺[OTf]⁻ (100 mg, 0.20 mmol). After 2h of respectively stirring, the AgCl formed in the first Schlenk tube was filtered through celite and the filtered burgundy solution of [(phen)₂Ru]²⁺ was added to the catecholate ruthenium complex suspension [Cs][Cp*₂Ru(η⁴-C₆H₄O₂)] (1-Cs) generated *in situ*. The reaction mixture was stirred for an additional hour and the solvent was removed under vacuum. Then the residue was dissolved in CH₂Cl₂ and filtered through alumina. Evaporation of CH₂Cl₂ under vacuum provided the bimetallic complex [(phen)₂Ru(1)]⁺[OTf]⁻ (3) as black microcrystals (189 mg, 0.20 mmol). Yield: 99%. Anal. Calcd for C₄₁H₃₅F₃N₄O₅Ru₂S.H₂O (972.96 g.mol⁻¹): C, 50.61; H, 3.83; found: C, 50.14; H, 3.87. ¹H NMR (400 MHz, CD₂Cl₂): δ = 1.64 (s, 15H, CH₃-Cp*); 4.47-4.49 (m, 2H, Hγ,δ); 4.81 (dd, 1H, J = 4.3, 2.3 Hz, Hε); 5.04 (dd, 1H, J = 4.3, 2.3 Hz, Hβ); 7.23 (dd, 1H, J = 8.1, 5.4 Hz, H8'); 7.30 (dd, 1H, J = 8.1, 5.4 Hz, H8); 7.64 (dd, 1H, J = 5.4, 1.1 Hz, H9'); 7.87-7.89 (m, 1H, H9); 7.90 (dd, 1H, J = 8.1, 5.3 Hz, H3'); 7.96 (d, 1H, J = 8.8 Hz, H6'); 8.02 (dd, 1H, J = 8.2, 1.1 Hz, H7'); 8.05 (d, 1H, J = 8.8 Hz, H6); 8.07 (d, 1H, J = 8.8 Hz, H5'); 8.12 (dd, 1H, J = 8.1, 1.1 Hz, H7); 8.15-8.19 (m, 2H, H3,5); 8.42 (dd, 1H, J = 8.2, 1.2 Hz, H4'); 8.57 (dd, 1H, J = 8.2, 1.2 Hz, H4); 9.37 (dd, 1H, J = 5.3, 1.2 Hz, H2'); 9.76 (dd, 1H, J = 5.1, 1.2 Hz, H2). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ = 10.0 (CH₃-Cp*); 75.0 (Cε); 76.1 (Cδ); 76.5 (Cγ); 77.4 (Cβ); 89.3 (Cq-Cp*); 123.4 (C8'); 123.8 (C8); 124.2 (C3'); 124.8 (C3); 127.1 (C6'); 127.2 (C6,5'); 127.3 (C5); 129.8 (C4a,4a'); 130.0 (C6a); 130.2 (C6a'); 131.5 (C7'); 132.1 (C7); 133.2 (C4); 133.4 (C4'); 142.5 (Cα); 147.9 (Cζ); 148.7 (C1a'); 149.1 (C1a); 151.0 (C10a,10a'); 151.2 (C2'); 151.6 (C2); 152.5 (C9'); 153.2 (C9). IR (ATR, cm⁻¹): ν = 3380; 3054; 2906; 1628; 1567; 1504; 1463; 1445; 1425; 1407; 1383; 1353; 1256; 1221; 1195; 1139; 1093; 1071; 1052; 1027; 912; 868; 837; 768; 731; 716; 634; 603; 572; 557; 538; 515; 455; 407; 384; 346; 327; 309; 291; 275; 246; 211.

Synthesis of 4. This compound was prepared in the dark according to the procedure described for complex 3 using the following amounts: AgOTf (51.4 mg, 0.20 mmol), [(dip)₂RuCl₂] (83.7 mg, 0.10 mmol) instead of [(phen)₂RuCl₂], Cs₂CO₃ (65.2 mg, 0.20 mmol) and [Cp*₂Ru(η⁶-C₆H₆O₂)]⁺[OTf]⁻ (49.5 mg, 0.10 mmol). Evaporation of acetone immediately provided the bimetallic complex [(dip)₂Ru(1)]⁺[OTf]⁻ (4) as a black microcrystalline solid (121 mg, 86.0 μmol). Yield: 86%. Anal. Calcd for C₆₅H₅₁F₃N₄O₅Ru₂S.4(CH₃)₂CO (1491.64 g.mol⁻¹): C, 62.00; H, 5.07; found: C, 62.13; H, 5.21. ¹H NMR (400 MHz, CD₂Cl₂): δ = 1.69 (s,

15H, CH₃-Cp*); 4.50-4.55 (m, 2H, H_γ,δ); 4.88-4.90 (m, 1H, H_ε); 5.09-5.11 (m, 1H, H_β); 7.32-8.22 (m, 30H, H_{3,9,8,6,5,3',9',8',6',5',Phenyl}); 9.46 (d, 1H, *J* = 5.5 Hz, H_{2'}); 9.85 (d, 1H, *J* = 5.3 Hz, H₂). IR (ATR, cm⁻¹): $\bar{\nu}$ = 3441; 3056; 2968; 2909; 1697; 1621; 1600; 1547; 1507; 1463; 1444; 1413; 1353; 1254; 1221; 1144; 1080; 1028; 911; 884; 845; 764; 734; 700; 669; 635; 605; 572; 515; 451; 400; 349; 323; 236; 215.

General procedures for cyclic voltammetry. Cyclic voltammetry was performed in a three-electrode cell connected to a vacuum line, at room temperature. The counter electrode was a platinum wire of ca. 1 cm² apparent surface area. The reference was a saturated calomel electrode (Radiometer Analytical) separated from the solution by a bridge filled with 3 mL of CH₂Cl₂ containing *n*Bu₄NBF₄ (0.3 M). The working electrode was a stationary gold disk (0.5 mm diameter for scan rates from 0.1 to 10 V.s⁻¹ and 0.125 mm diameter for scan rates from 20 to 50 V.s⁻¹). The cyclic voltammetry of complexes **2**, **3** and **4** in 15 mL of CH₂Cl₂ (2 mM) containing *n*Bu₄NBF₄ (0.3 M) was performed at various scan rates.

Optical Spectroscopy. All solvents used for photophysical studies were spectroscopic grade (C. Erba). 1 cm path length square optical Suprasil Quartz (QS) cuvettes were used for measurements at room temperature of dilute solutions. The absorption spectra of dilute solutions were obtained by using a Perkin–Elmer Lambda 950 UV/VIS/NIR spectrophotometer. Molar absorptivity values (ϵ) were calculated by applying the Lambert-Beer law to low absorbance spectra (*A* < 1) recorded at successive dilutions. Steady-state photoluminescence spectra were measured in right-angle mode by using an Edinburgh FLS920 fluorometer, equipped with a Peltier-cooled Hamamatsu R928 (200-900 nm) and a supercooled Hamamatsu R5509-72 (600-1,800 nm) PMTs. Luminescence quantum efficiencies in solution were evaluated by comparing the wavelength integrated intensities with reference to [Ru(bpy)₃]Cl₂ ($\phi = 0.040$ in air-equilibrated water, from *Coord. Chem. Rev.* **2010**, *254*, 2449). Luminescence lifetimes were measured with an IBH 5000F TCSPC apparatus, by using pulsed NanoLED excitation sources at $\lambda_{exc} = 465$ nm. Band maxima, relative luminescence intensities and lifetimes were obtained with uncertainty of 2 nm, 20% and 10%, respectively.