Details of the photophysical measurements:

The Austrian group thanks Prof. Dr. Wytze E. van der Veer for the help with some of these measurements at the University of California at Irvine.

Absorption spectra.

Absorption spectra were recorded for samples **1** – **5** using a Perkin and Elmer Lambda 900 spectrophotometer. A cell with optical path length 1 cm was used and the concentration of adjusted solutions was 5.0 x 10^{-5} M. For higher accuracy these measurements were corrected for the losses (mostly by reflection) of a cell only containing acetonitrile and no sample. The absorption data for **1** – **5** are given in the description of their syntheses. The absorption spectra for **1** – **5** are shown in Figures 1 – 4.

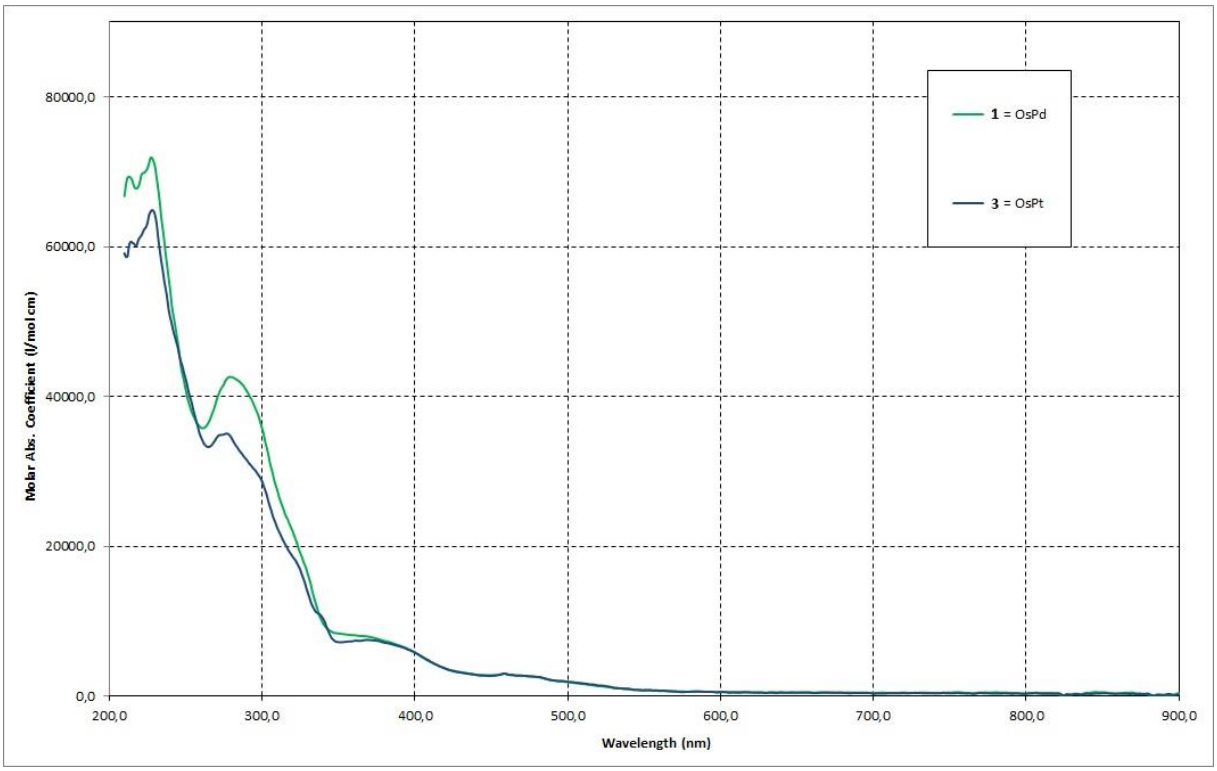

Figure 1: UV-vis absorption spectra of 5.0 x 10^{-5} M solutions in CH_3CN at ambient temperature: **1** = $[Os(bpy)_2(dppcb)Pd(bpy)](PF_6)_4$; **3** = $[Os(bpy)_2(dppcb)Pt(bpy)](PF_6)_4$.

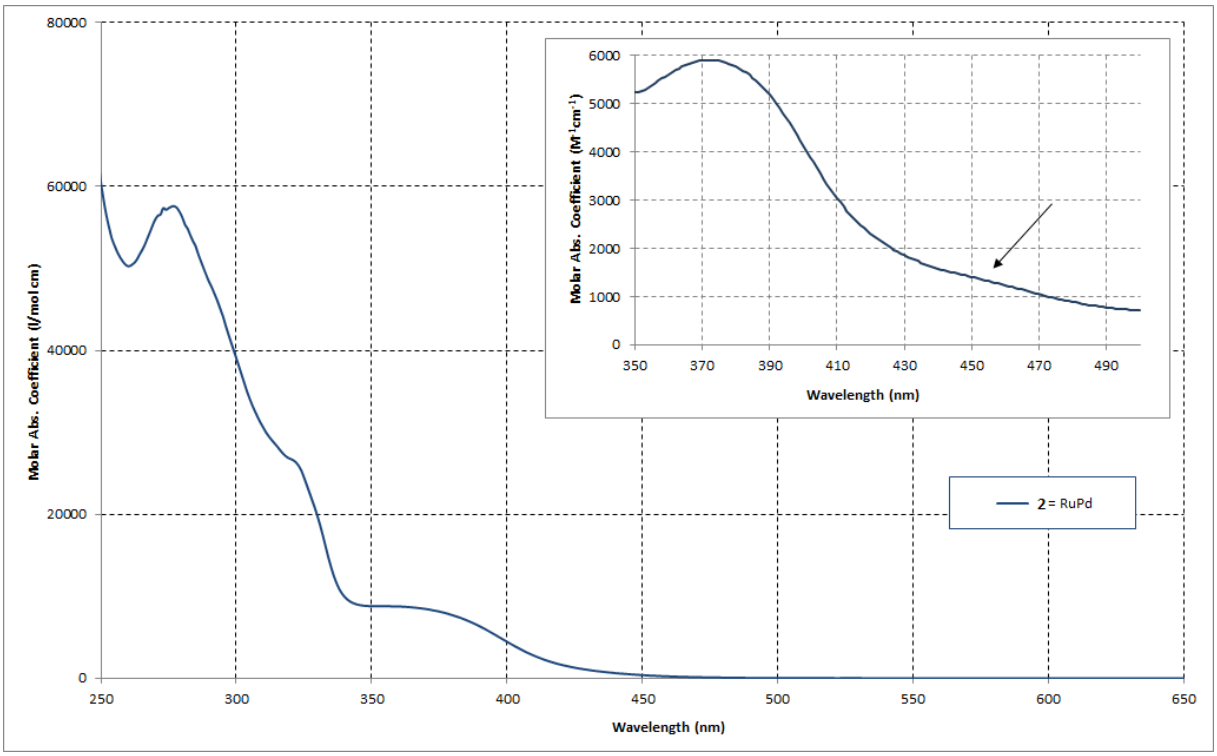

Figure 2: UV-vis absorption spectra of a 5.0 x 10^{-5} M solution in CH_3CN at ambient temperature: **2** = $[Ru(bpy)_2(dppcb)Pd(bpy)](PF_6)_4$.

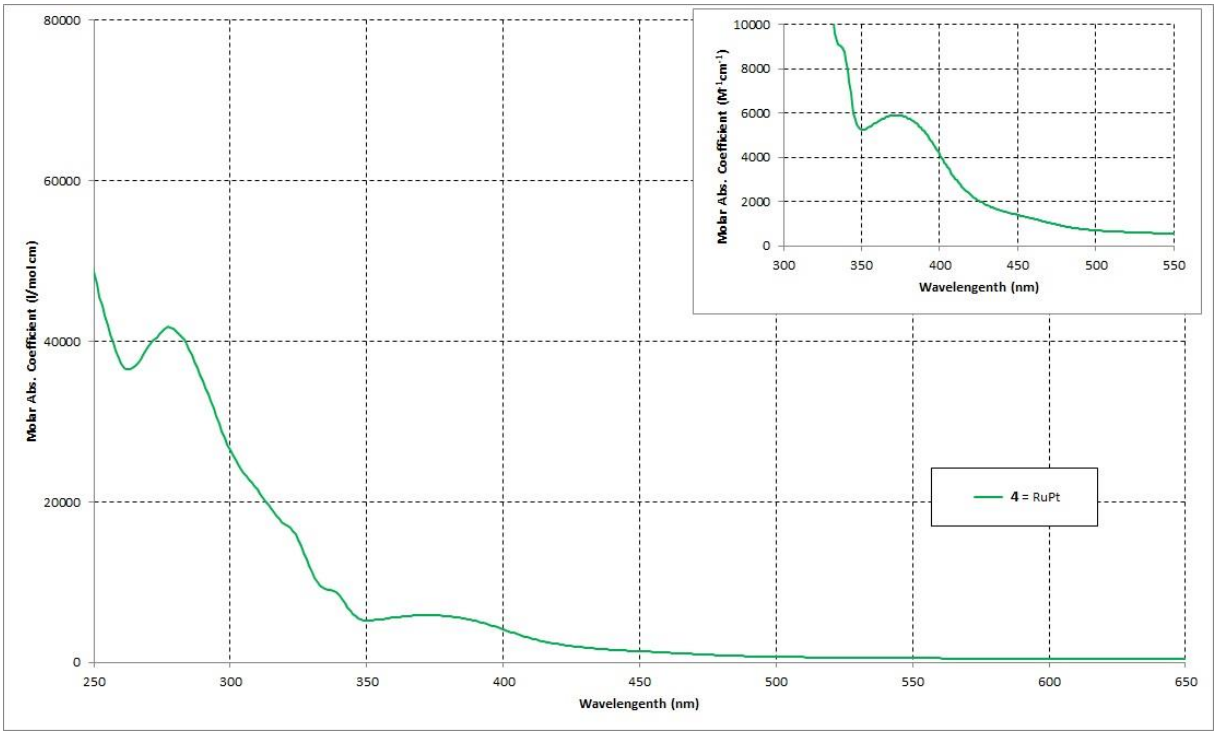

Figure 3: UV-vis absorption spectra of a 5.0 x 10^{-5} M solution in CH_3CN at ambient temperature: **4** = $[Ru(bpy)_2(dppcb)Pt(bpy)](PF_6)_4$.

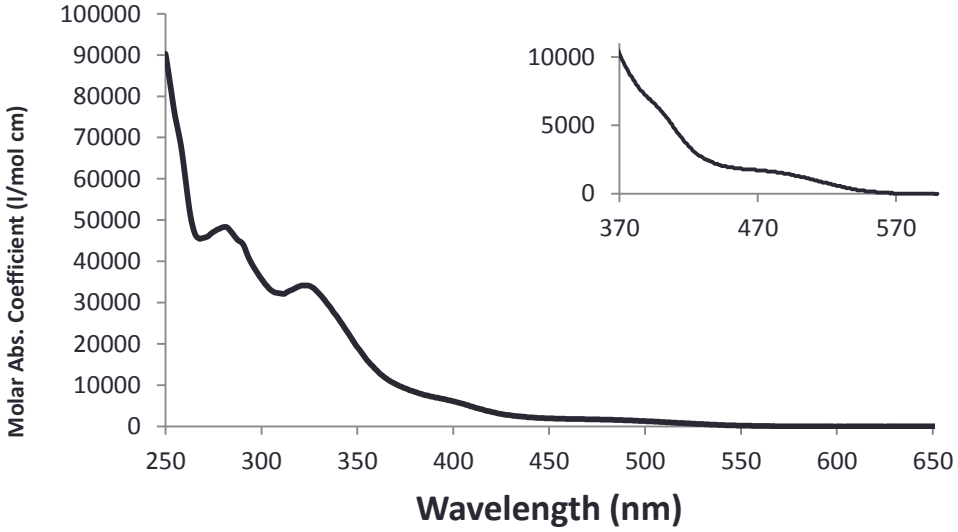

Figure 4: UV-vis absorption spectra of a 5.0 x 10^{-5} M solution in CH_3CN at ambient temperature: **5** = $[Os(bpy)_2(dppcb)Pd(dppm)](PF_6)_4$.

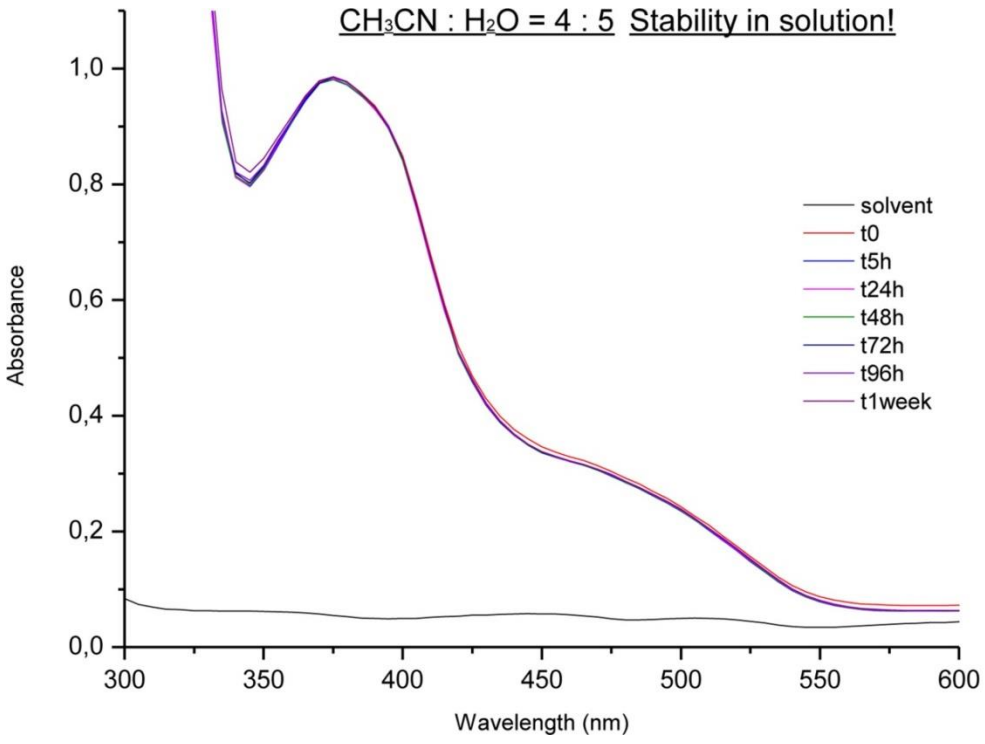

Figure 5: Stability test using UV-vis absorption spectra of a 4:5 (v/v) CH_3CN:H_2O solution containing 0.18 mg $[Os(bpy)_2(dppcb)Pd(bpy)](PF_6)_4$ (**1**) and 16 mg ascorbic acid per milliliter. This solution has been stirred for the time indicated in Figure 5 at ambient temperature in the dark.

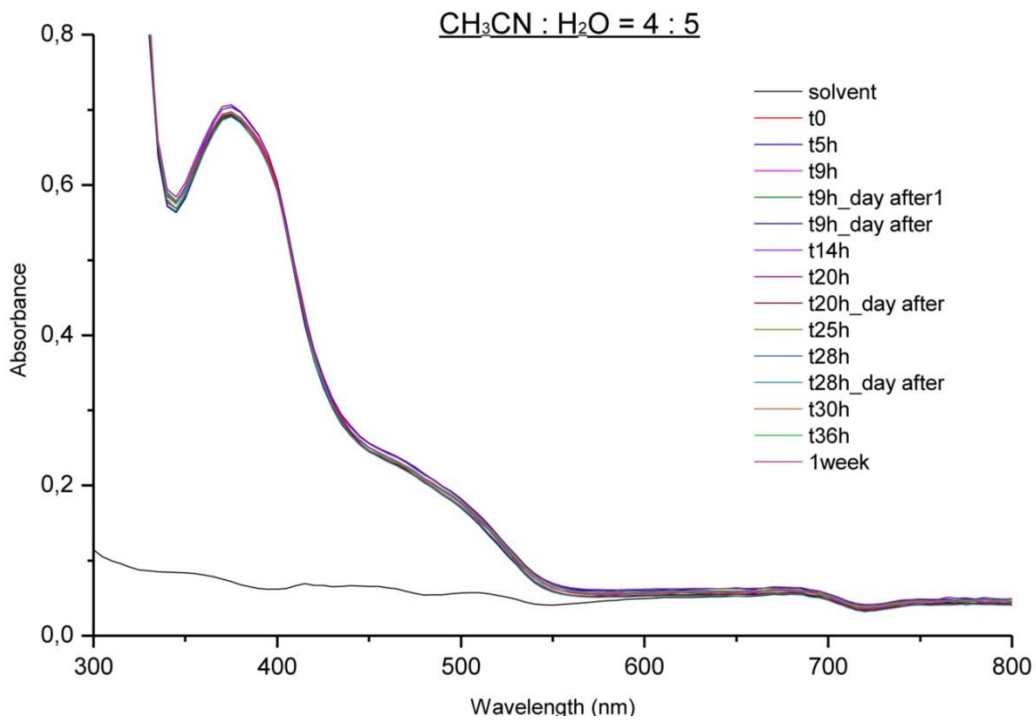

Figure 6: Stability test using UV-vis absorption spectra of a 4:5 (v/v) CH_3CN:H_2O solution containing 0.18 mg $[Os(bpy)_2(dppcb)Pd(bpy)](PF_6)_4$ (**1**) and 16 mg ascorbic acid per milliliter. This solution has been stirred for the time indicated in Figure 6 at ambient temperature under irradiation using LED light with an emission centred at 470 nm.

Luminescence spectra.

Luminescence spectra of compounds **1**–**5** at ambient temperature and 77 K were measured with a Hitachi F4500 luminescence spectrometer and a Horiba Jobin Yvon Fluorolog-3 spectrofluorometer. Contour plots are also shown in order to confirm that different emissions from ^{3}MLCT states can be present. The concentrations for these measurements are given in the Figure legends of the following Figures, respectively. The solvents are CH_3CN for room temperature and cryogenic glasses for 77K measurements, as also indicated in the Figure legends.

The spectra were recorded with the following parameters: Vpmt: 700 V, excitation range: 300 – 600 nm, excitation bandwidth: 5 nm, emission range: 400 – 700 nm, emission bandwidth: 5 nm, scan speed: 240 nm/ min. Since at 77 K **1**–**5** are extremely intense emitters, the pmt voltage in the spectrometer was reduced to 700 V. The integration time was adjusted automatically by the software to match the scan speed. These spectra are not compensated for the instrument response function. Over this range the instrument response is not expected to show strong variation.

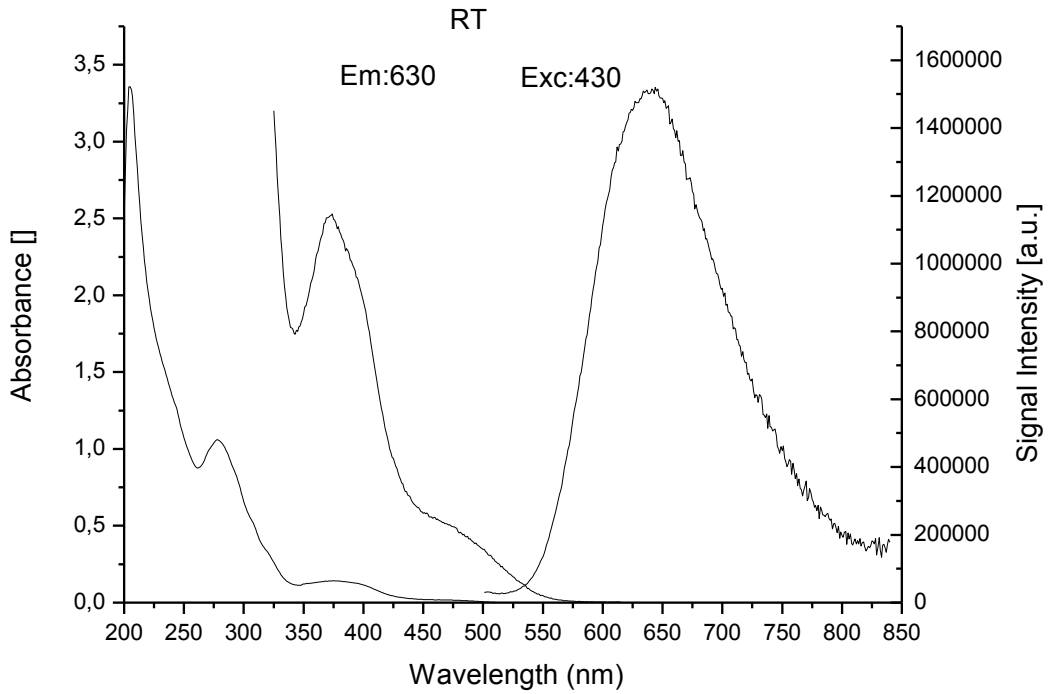

Figure 7: Excitation/Emission spectra of a CH_3CN solution containing 0.38 mg $[Os(bpy)_2(dppcb)Pd(bpy)](PF_6)_4$ (**1**) per 10 milliliters at ambient temperature. The excitation spectrum has been recorded at an emission of 630 nm. The emission spectrum has been recorded at an excitation of 430 nm. The excitation and emission maxima occur at 375 and 638 nm, respectively. For comparison also the absorption spectrum (left) is shown.

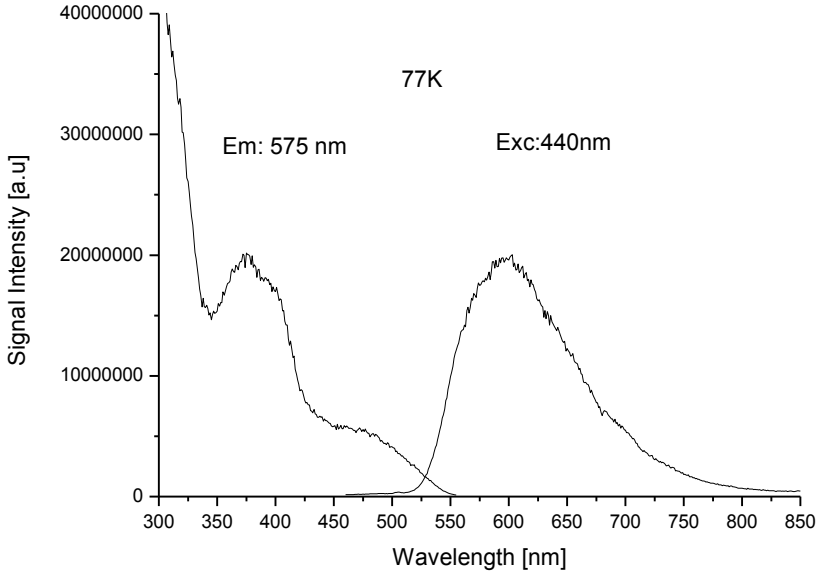

Figure 8: Excitation/Emission spectra of a 4:1:2 (v/v) EtOH–MeOH–CH_3CN cryogenic glass containing 0.38 mg $[Os(bpy)_2(dppcb)Pd(bpy)](PF_6)_4$ (**1**) per 10 milliliters at 77 K. The excitation spectrum has been recorded at an emission of 575 nm. The emission spectrum has been recorded at an excitation of 440 nm. The excitation and emission maxima occur at 372 and 604 nm, respectively.

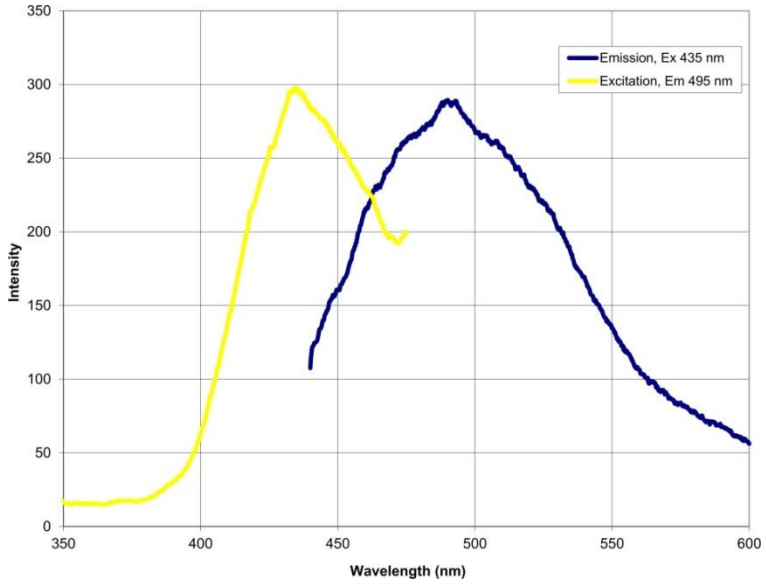

Figure 9: Excitation/Emission spectra of a CH_3CN solution containing 0.11 mg $[Ru(bpy)_2(dppcb)Pd(bpy)](SbF_6)_4$ (**2**) per 10 milliliters at ambient temperature. The excitation spectrum has been recorded at an emission of 495 nm. The emission spectrum has been recorded at an excitation of 435 nm. The excitation and emission maxima occur at 435 and 494 nm, respectively.

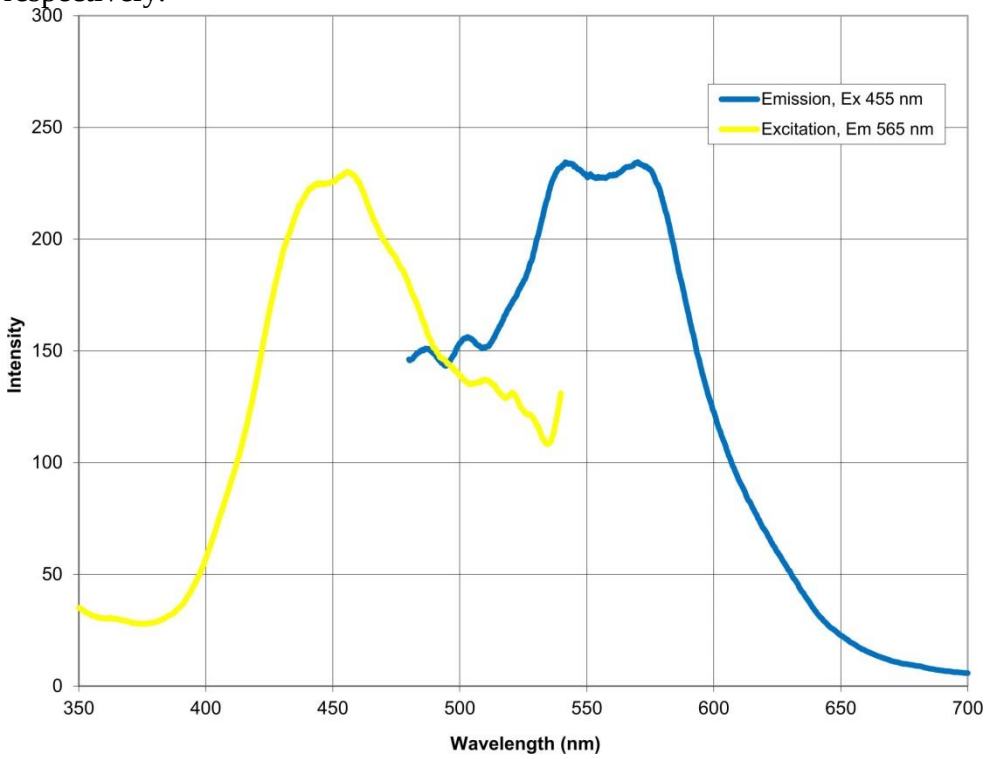

Figure 10: Excitation/Emission spectra of a 4:1:2 (v/v) EtOH–MeOH–CH_3CN cryogenic glass containing 0.11 mg $[Ru(bpy)_2(dppcb)Pd(bpy)](SbF_6)_4$ (**2**) per 10 milliliters at 77 K. The excitation spectrum has been recorded at an emission of 565 nm. The emission spectrum has been recorded at an excitation of 455 nm. The excitation and emission maxima occur at 440 and 543 nm, respectively.

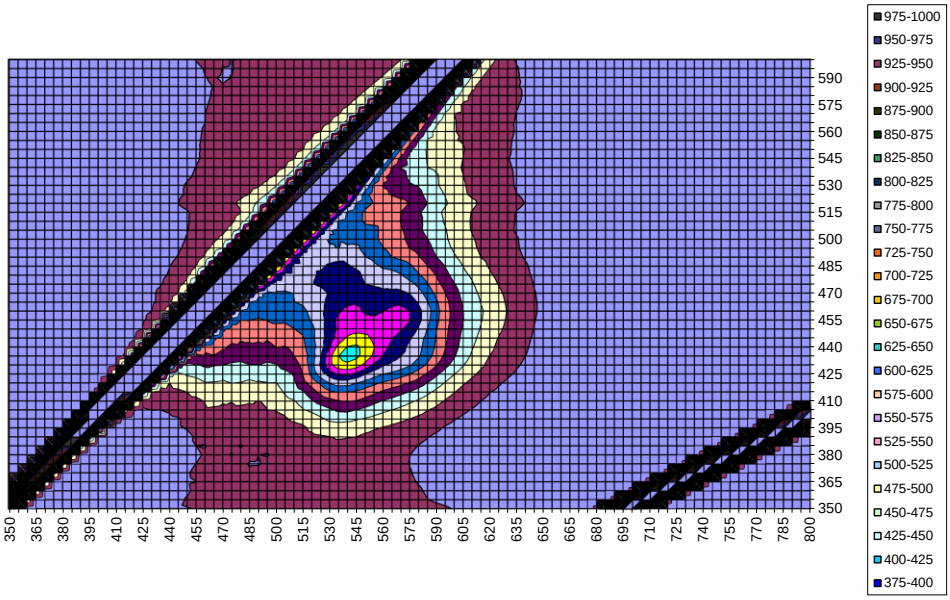

Figure 11: Contour plot of the combined excitation and luminescence spectra of a 4:1:2 (v/v) EtOH–MeOH–CH_3CN cryogenic glass containing 0.11 mg $[Ru(bpy)_2(dppcb)Pd(bpy)](SbF_6)_4$ (**2**) per 10 milliliters at 77 K. This plot shows a strong single emission, where the oval features are due to Raleigh scattering.

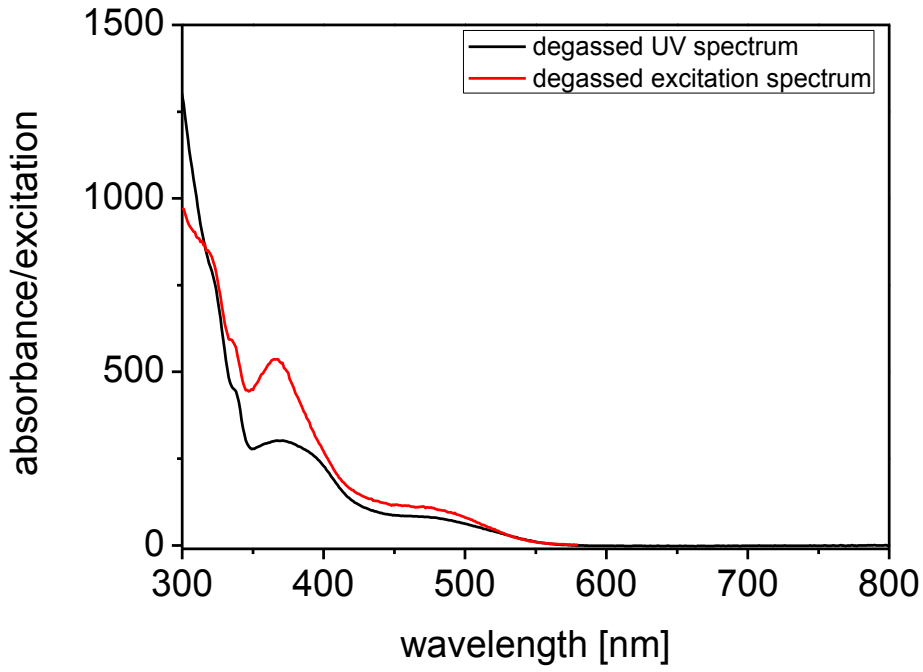

Figure 12: Comparison of the excitation (red) and absorption (black) spectra of a CH_3CN solution containing 0.22 mg $[Os(bpy)_2(dppcb)Pt(bpy)](PF_6)_4$ (**3**) per 10 milliliters at ambient temperature. The excitation spectrum has been recorded monitoring the emission at 620 nm. The excitation maximum occurs at 367 nm.

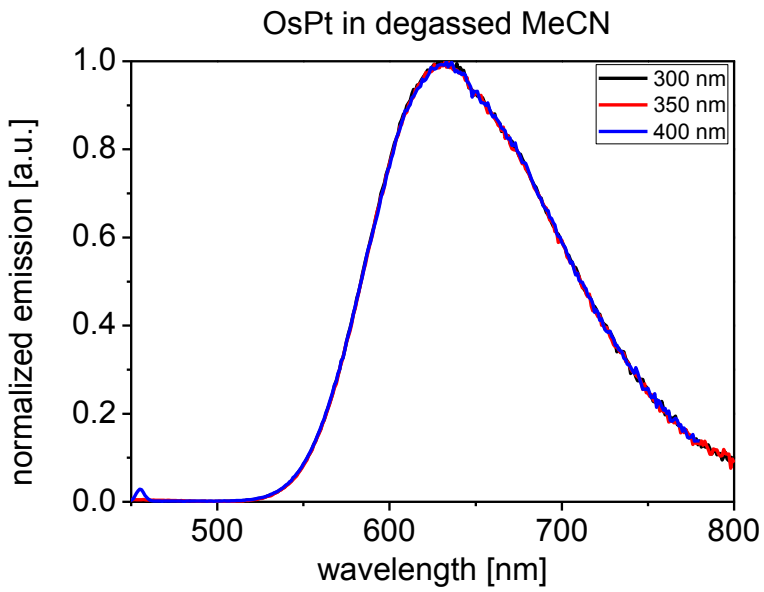

Figure 13: Emission spectra of a CH_3CN solution containing 0.22 mg $[Os(bpy)_2(dppcb)Pt(bpy)](PF_6)_4$ (**3**) per 10 milliliters at ambient temperature. This emission is independent of the excitation wavelength between 300 and 400 nm. The emission maximum occurs at 633 nm.

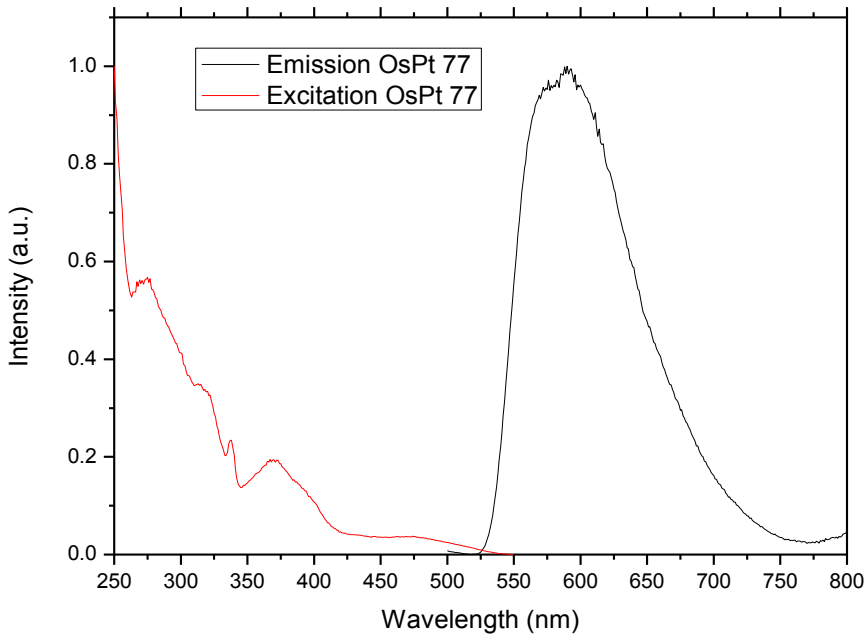

Figure 14: Excitation/Emission spectra of a 4:1:2 (v/v) EtOH–MeOH–CH_3CN cryogenic glass containing 0.22 mg $[Os(bpy)_2(dppcb)Pt(bpy)](PF_6)_4$ (**3**) per 10 milliliters at 77 K. The excitation spectrum has been recorded at an emission of 586 nm. The emission spectrum has been recorded at an excitation of 370 nm. The excitation and emission maxima occur at 370 and 586 nm, respectively.

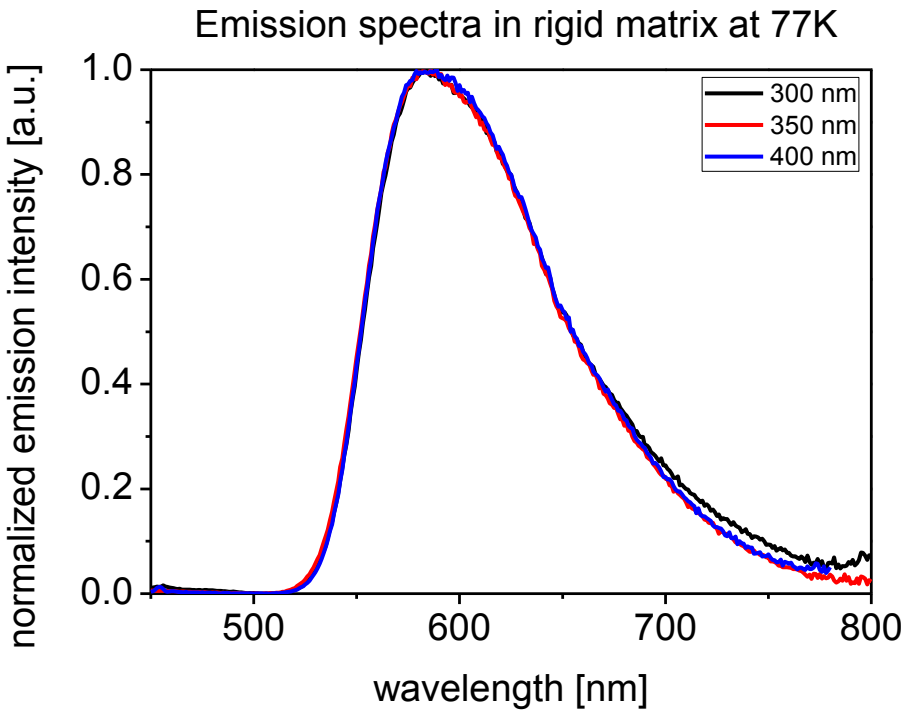

Figure 15: Emission spectra of a 4:1:2 (v/v) EtOH–MeOH–CH_3CN cryogenic glass containing 0.22 mg $[Os(bpy)_2(dppcb)Pt(bpy)](PF_6)_4$ (**3**) per 10 milliliters at 77 K. This emission is nearly independent of the excitation wavelength between 300 and 400 nm.

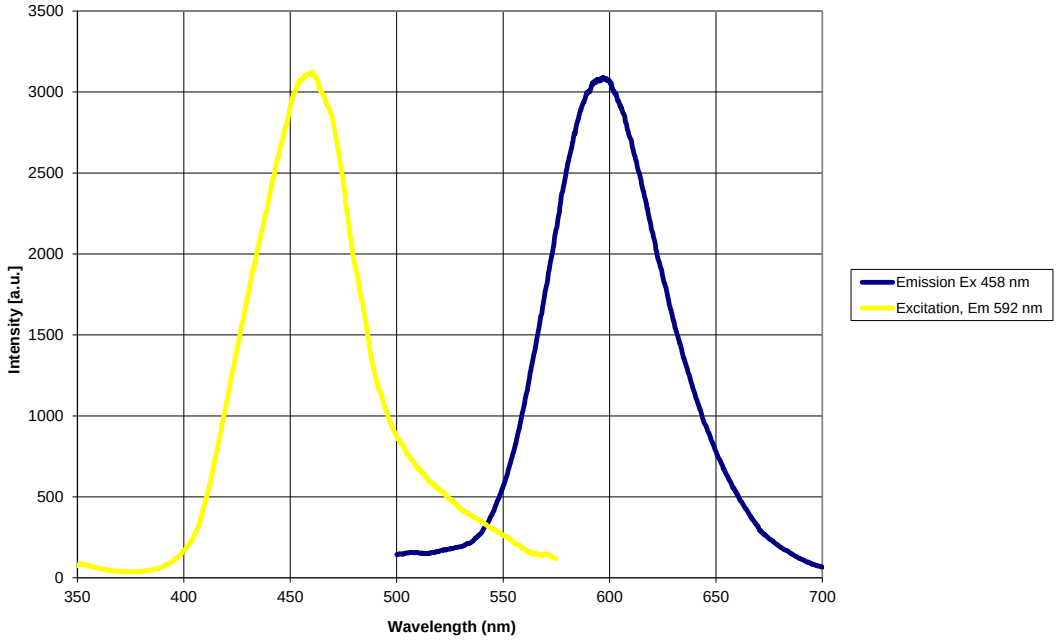

Figure 16: Excitation/Emission spectra of a CH_3CN solution containing 0.16 mg $[Ru(bpy)_2(dppcb)Pt(bpy)](SbF_6)_4$ (**4**) per 10 milliliters at ambient temperature. The excitation spectrum has been recorded at an emission of 592 nm. The emission spectrum has been recorded at an excitation of 458 nm. The excitation and emission maxima occur at 460 and 596 nm, respectively.

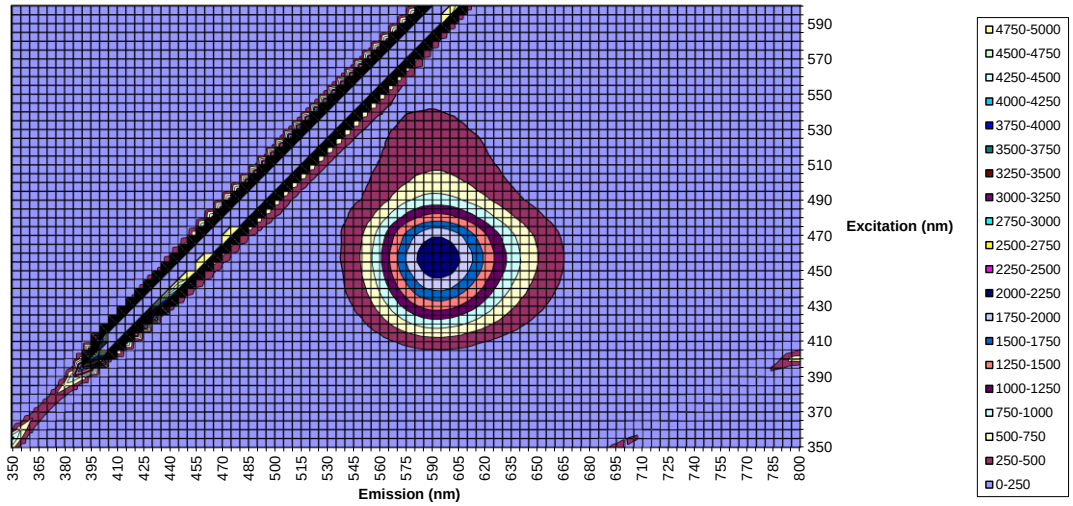

Figure 17: Contour plot of the combined excitation and luminescence spectra of a CH_3CN solution containing 0.16 mg $[Ru(bpy)_2(dppcb)Pt(bpy)](SbF_6)_4$ (**4**) per 10 milliliters at ambient temperature. This plot shows a strong single emission, where the oval features are due to Raleigh scattering.

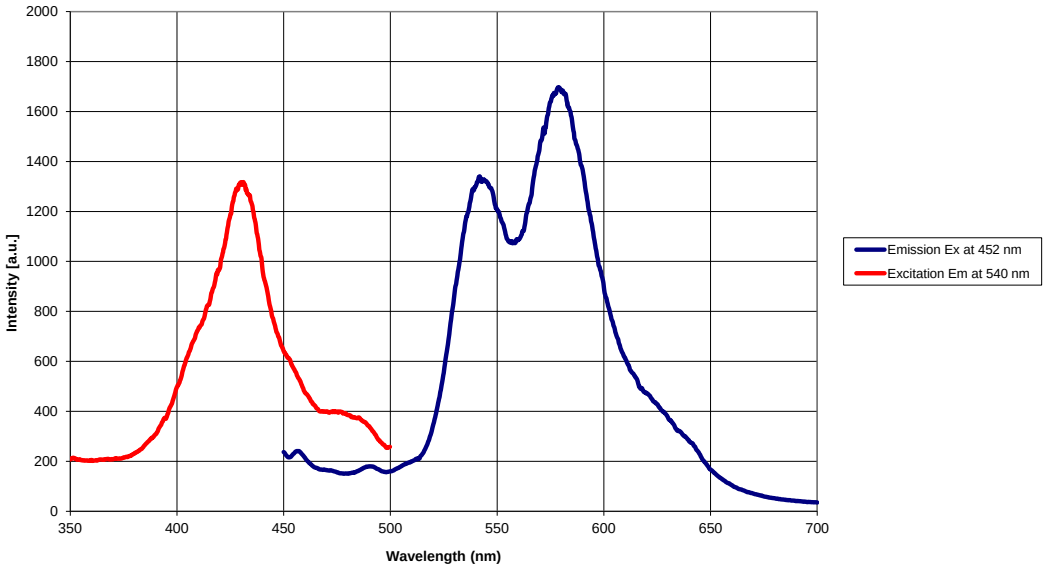

Figure 18: Excitation/Emission spectra of a 4:1:2 (v/v) EtOH–MeOH–CH_3CN cryogenic glass containing 0.16 mg $[Ru(bpy)_2(dppcb)Pt(bpy)](SbF_6)_4$ (**4**) per 10 milliliters at 77 K. The excitation spectrum has been recorded at an emission of 540 nm. The emission spectrum has been recorded at an excitation of 452 nm. The excitation and emission maxima occur at 434 and 581 nm, respectively.

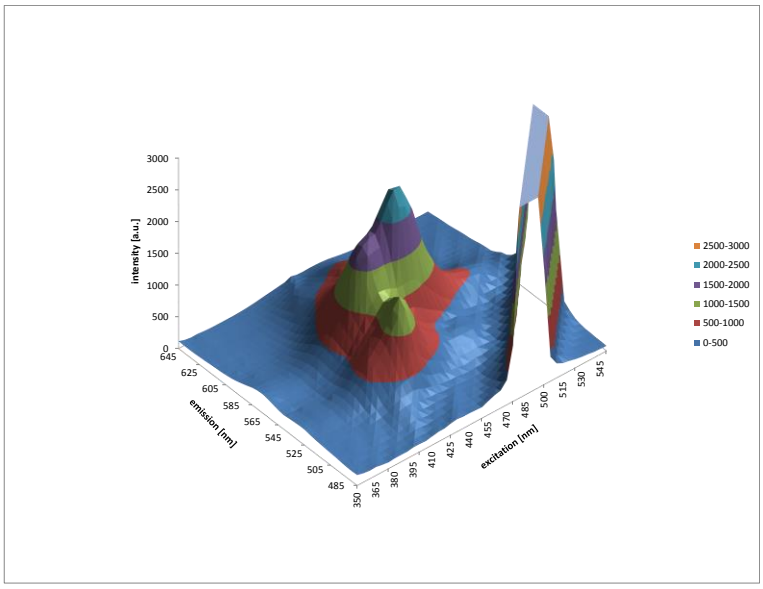

Figure 19: Contour plot of the combined excitation and luminescence spectra of a 4:1:2 (v/v) EtOH–MeOH–CH_3CN cryogenic glass containing 0.16 mg $[Ru(bpy)_2(dppcb)Pt(bpy)](SbF_6)_4$ (**4**) per 10 milliliters at 77 K. This plot shows a strong and a weak emission, where the feature on the right side of the picture is due to Raleigh scattering.

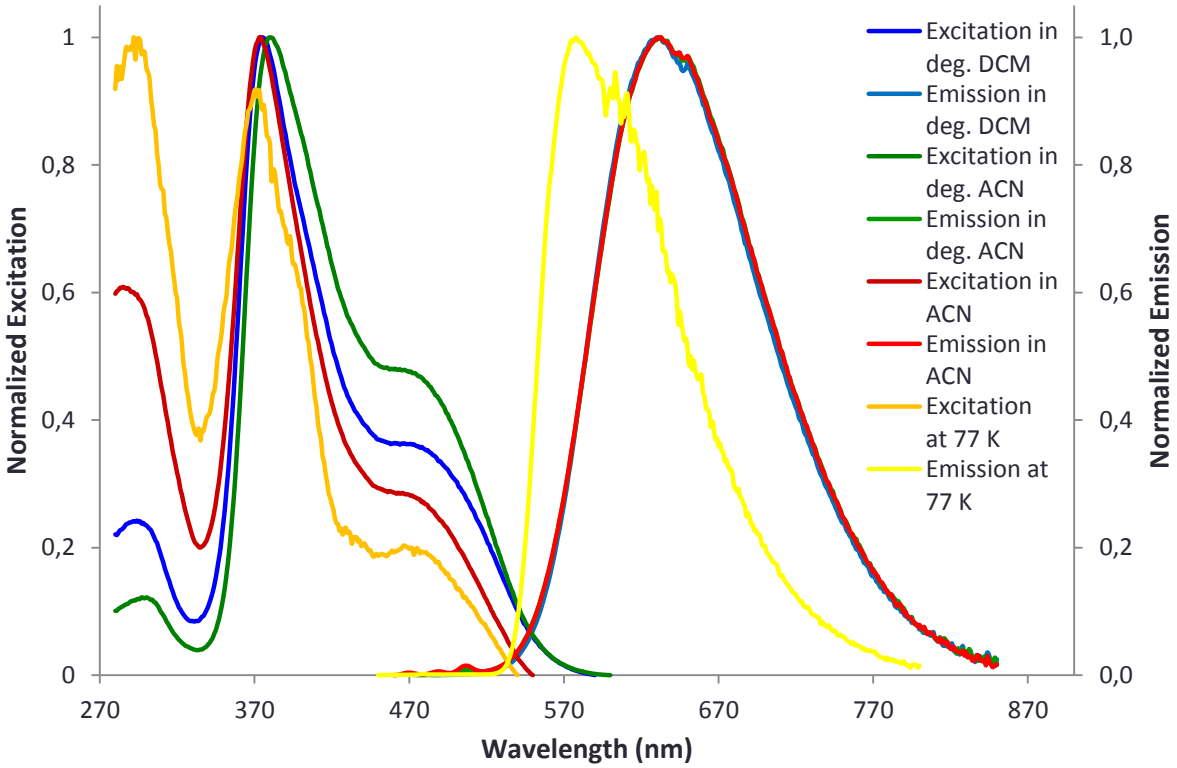

Figure 20: Excitation/Emission spectra of a CH_3CN solution containing 0.15 mg $[Os(bpy)_2(dppcb)Pd(dppm)](PF_6)_4$ (**5**) per 10 milliliters at ambient temperature and in a 4:1:2 (v/v) EtOH–MeOH–CH_3CN cryogenic glass at 77 K. The excitation spectra have been recorded at emissions of 632 nm (298 K) and 578 nm (77 K). The emission spectra have been recorded at excitations of 378 nm (298 K) and 375 nm (77 K). The excitation and emission maxima occur at the same wavelengths, respectively.

Excited state lifetimes.

The luminescence lifetimes for complexes **1** – **5** at 298 K in acetonitrile solutions are given in Table 1 of the communication. Figures 19 and 20 show plots of ln τ vs. 1000/T (K^{-1}) for **2** and **4**. Lifetimes were measured with a nanosecond laser/OPO system (Continuum Surelite). The luminescence radiation is collected and directed into a monochromator (Spex 270M) and detected with a photo multiplier (Hamamatsu R928). The electric signal from the pmt was digitized and averaged over 250 shots with a digital sampling oscilloscope (LeCroy 9350A). For each measurement a background signal was also recorded and subtracted from the signal.

The samples were measured in a cell with optical path length 1 cm. The concentrations and solvents for the measurements at 298 K were the same as given above. For variable temperature lifetime measurements between 77 and 293 K the samples for the measurements at 77 K were used as given above. In the case of **2** all lifetimes can be fitted by single exponential decay functions for an excitation at 450 nm and an emission at 542 nm in the whole temperature range 77–161 K (Figure 19). The same is true in the case of **4** for an excitation at 455 nm and an emission at 580 nm in the whole temperature range 77–293 K (Figure 20). The strong temperature dependence of the luminescence lifetimes in Figures 19 and 20 clearly indicate that these emissions stem from ^{3}MLCT states (see ref. 5). For all photophysical measurements carefully purified crystals were used and dissolved in the corresponding degassed spectrograde quality solvents.

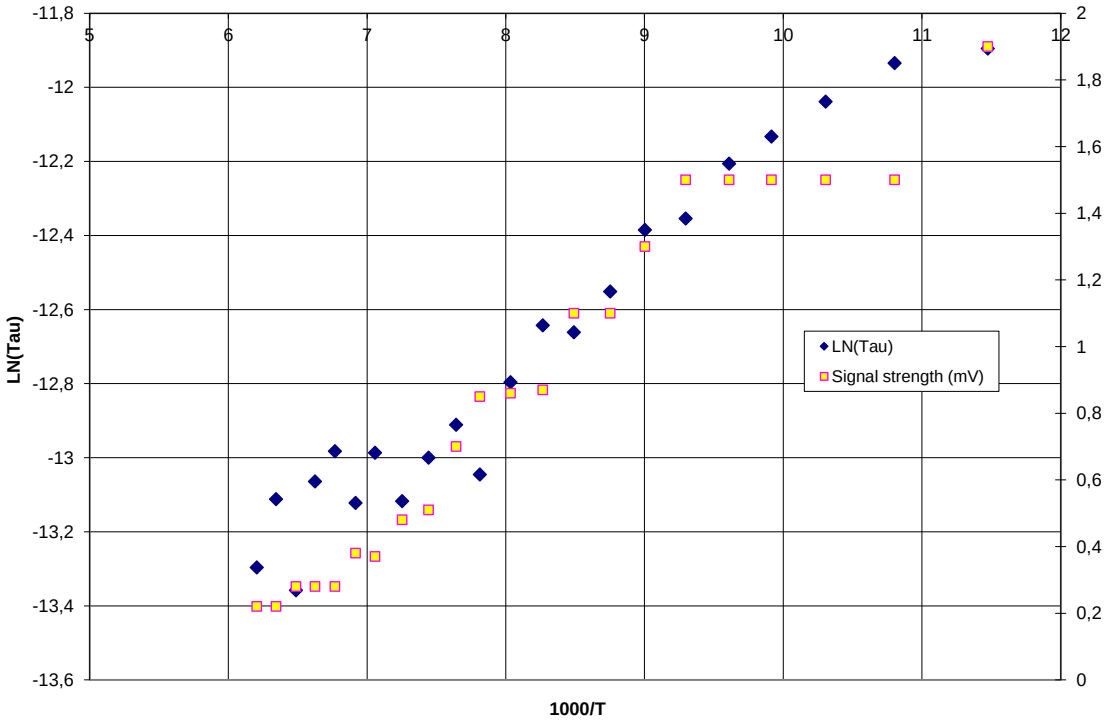

Figure 21: Plot of ln τ vs. 1000/T (K^{-1}) of a 4:1:2 (v/v) EtOH–MeOH–CH_3CN cryogenic glass containing 0.11 mg $[Ru(bpy)_2(dppcb)Pd(bpy)](SbF_6)_4$ (**2**) per 10 milliliters in the temperature range 77–161 K. The diminishing signal strength during warm-up is also shown. These lifetimes have been measured for an excitation at 450 nm and an emission at 542 nm.

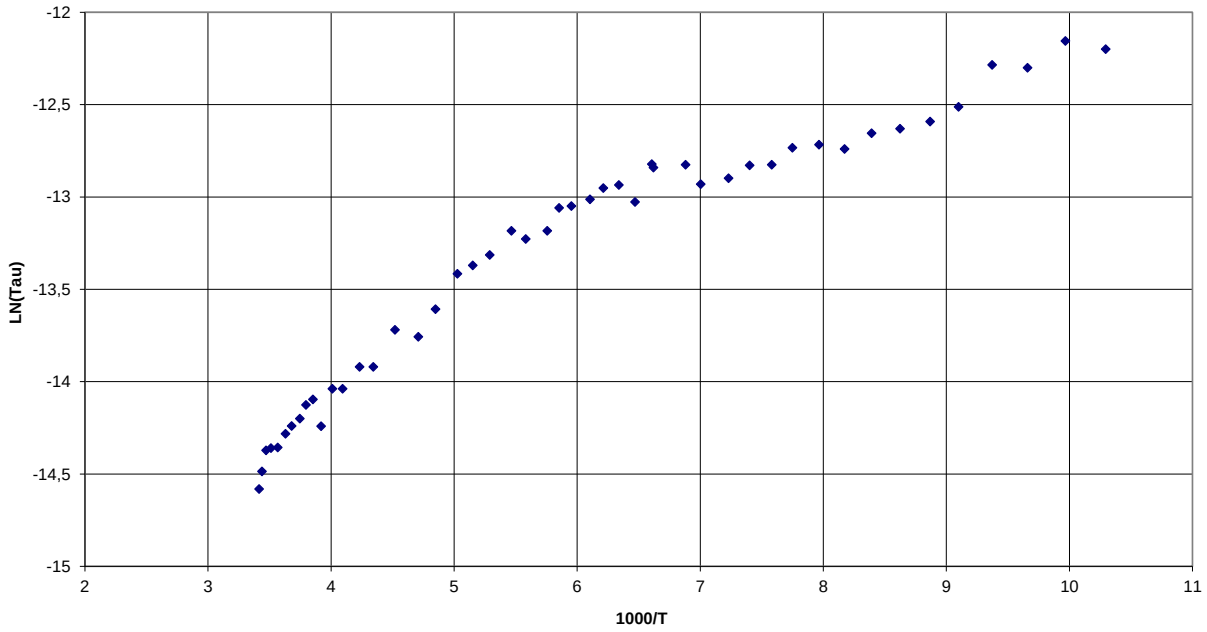

Figure 22: Plot of ln τ vs. 1000/T (K^{-1}) of a 4:1:2 (v/v) EtOH–MeOH–CH_3CN cryogenic glass containing 0.16 mg $[Ru(bpy)_2(dppcb)Pt(bpy)](SbF_6)_4$ (**4**) per 10 milliliters in the temperature range 77–293 K. These lifetimes have been measured for an excitation at 455 nm and an emission at 580 nm.

Details of the electrochemical measurements:

Electrochemical measurements of **1** – **5** were made with an EG&G PAR Model 264A voltameter. Cyclic voltammetry was carried out with a 2-mm platinum-disk working electrode, a platinum-wire counter electrode and a Ag/AgCl pseudoreference electrode. 0.05 M Me_4NClO_4 was used as the electrolyte. Potentials are quoted relative to a SCE at a scan rate of 100 mV s^{-1} and in degassed MeCN ($4 \cdot 10^{-3}$ M) of purissimum grade quality at room temperature.

Details of the H_2 detection measurements:

Since the detection of small amounts of H_2 is not straightforward, three different methods have been used in order to get reliable results:
1) For a fast analysis, if any H_2 gas is present in the catalytic systems, the H_2 gas detector ″Wöhler Gasspürer GS 1″ of the German Company ″Wöhler″ has been used.
2) In order to obtain highly sensitive and quantitative results, the sector field mass spectrometer ″H-Sense 1.5″ of the Austrian Company ″V&F Analyse und Messtechnik GmbH″ has been utilized. The Austrian group thanks Dr. Siegfried Praun and Dr. Werner Tirler for providing this device.

3) The results of the ″H-Sense 1.5″ have been confirmed using the gas chromatograph ″3000 Micro GC″ of the German Company ″Inficon″.

All parameters have been corrected for pressure effects, where for this purpose calibration gases at different pressures have been used. The samples have been measured directly in the Schlenk tubes and dissolved H_2 in the reaction mixtures has been neglected in all cases. Comparing the results shows a maximum error of about 2%.

One drawback of our systems is the production of colloidal palladium during irradiation due to the destruction of the catalysts after a certain time. It is well-known, that colloidal palladium is also able to produce hydrogen in the presence of electron donors and chromophors (see ref. 6 of the communication). To avoid contribution to hydrogen production by colloidal metal, a small amount of Hg, which acts as a so-called ″colloid poison″, is added to the reaction mixture. In the course of our investigations it turned out, that colloidal palladium was not able to produce hydrogen under our irradiation conditions. As soon as metallic palladium emerged in our reaction vessels, no further hydrogen production was detected.