Supporting Information for "Modification of Coordination Networks Through a Photoinduced Charge Transfer Process"

Timothy L. Easun, Junhua Jia, Thomas J. Reade, Xue-Zhong Sun, E. Stephen Davies, Alexander J. Blake, Michael W. George and Neil R. Champness**

Experimental

Crystallography

Single crystal X-ray diffraction data were collected at 150 K using Bruker SMART CCD area detector diffractometers equipped with Oxford Cryosystems open flow cryostats.[S1] Synchrotron radiation (λ = 0.6942 Å) was used for **ReCu** on Station 9.8 of the Daresbury Synchrotron Radiation Source. Pertinent details of crystal data and data collection are given below. Absorption corrections based on symmetry equivalent reflections were applied to the data using SADABS (Bruker AXS, Madison, WI, USA, 2004). All structures were solved by direct methods using SHELXS97[S2] and refined by full-matrix least squares on F^2 using SHELXL97.[S2] All non-hydrogen atoms were located using subsequent Fourier difference methods. In all cases, carbon bound and co-ordinated solvent hydrogen atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms. The hydrogen atoms of the co-ordinated H_2O molecule in **ReCu** could not be located, but they are included in the formula and all values derived from it. For **ReCu**, anomalous molecular geometry and unrealistic atomic displacement parameters affecting Cl1 and the C3C-O3C carbonyl group *trans* to it indicated possible disorder between these ligands. Distance restraints of 2.49(1)Å for Re1-Cl1 and Re1-Cl1', 1.92(1)Å for Re1-C3C and Re1-C3C', 1.15(1)Å for C3C-O3C and C3C'-O3C', 3.07(1)Å for Re1…O3C and Re1…O3C' were applied during refinement, where the primed atoms are the equivalent atoms in the minor disorder component. A single free variable was used to define the major and minor occupancies, which refined satisfactorily to 0.857(6) and 0.143(6), respectively, using a model where only the atoms of the major component (Cl1, C3C, O3C) were refined isotropically. The success of the disorder modelling was confirmed by the absence of anomalous features in the structure. Crystal data for **ReCu**: $C_{18}H_{15}ClCuN_3O_9Re\cdot C_3H_7NO$, M = 775.62, monoclinic, Cc, a = 10.0183(7) b = 27.574(2), c = 9.4686(6) Å, β = 95.291(1)º, U = 2604.5(3) Å^3, Z = 4, T = 150(2) K, 7561 unique reflections (R_{int} = 0.033). Refinement of 356 parameters converged at final R_1 = 0.0292, wR_2 = 0.0620, GOF = 0.91.

Instrumentation

The equipment used for ps-TRIR measurements has been described in detail previously.[S3] IR spectra were probed with IR pulses generated by difference-frequency generation (ca. 200 cm^{-1} wide). Pumping was achieved using 1 kHz 355 nm pulses (1 ns) and the time delay between the pump and probe pulses was achieved using a electronic delay.

The instrumentation used to record the low-temperature KBr disc spectra has previously been described elsewhere.[S4] Briefly, each KBr disc was cut to fit a copper cell with CaF_2 windows, the cell sealed, purged with N_2 gas, evacuated, attached to a cold finger inside a vacuum shroud and cooled to 200 K for photolysis. Photolysis was achieved using a Philips HPK medium pressure 125 W mercury arc lamp and infrared spectra were recorded on a Thermo Nicolet Avatar 360 spectrometer (with 2 cm^{-1} resolution). Infrared mapping was performed using a Thermo Nicolet Continuμm XL Infrared Microscope with 15X magnification.

Raman spectra were recorded on a confocal Horiba-Jobin-Yvon LabRAM Raman Microscope using a 785 nm diode laser and a 600 lines/mm grating. The detector was a Synapse CCD detector. The spectra shown below were recorded using ca. 0.1 mW laser power, each the average of 15 acquisitions of 10 seconds each. UV/visible absorption spectra were recorded on a Perkin-Elmer Lambda 35 spectrometer equipped with an integrating sphere.

X-band EPR spectra for samples as powders were recorded at ambient temperature on a Bruker EMX spectrometer fitted with a frequency counter. A sample of **ReCu**, continuously rotated in an EPR tube, was photolysed for 9 hours with a Philips HPK medium pressure 125 W mercury arc lamp and EPR spectra recorded prior to and after photolysis.

Supplementary Figures

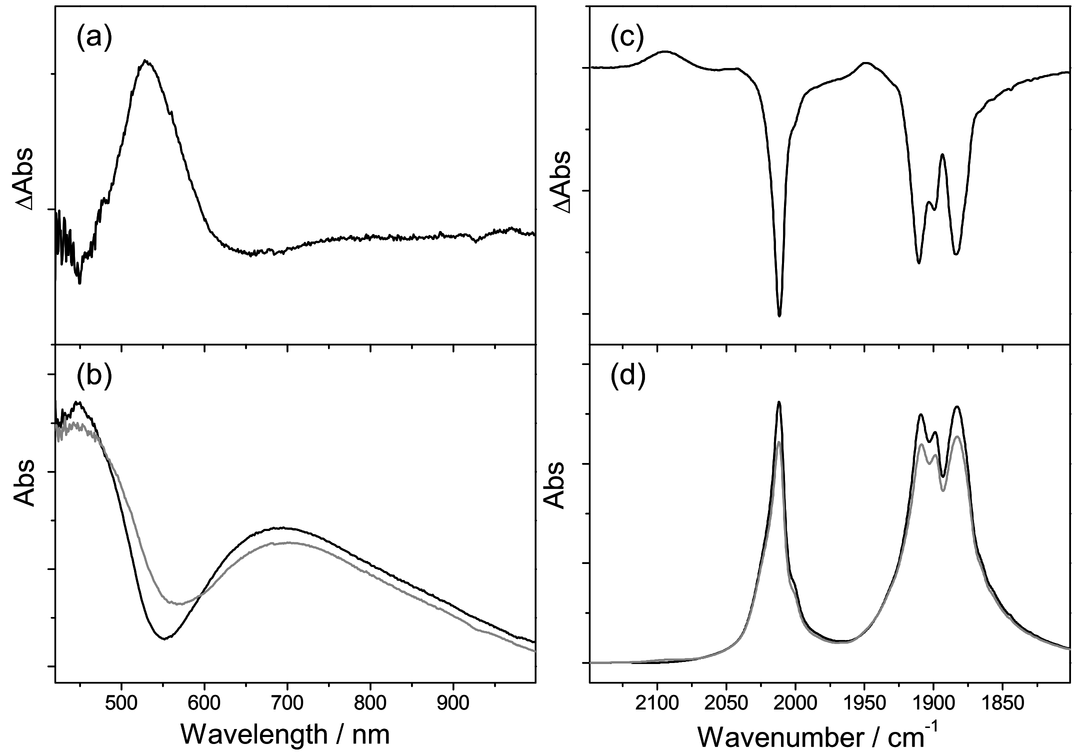

Figure S1. (a) Difference UV/vis diffuse reflectance absorption spectrum of **ReCu** in a KBr disc at 100 K after 22 hours photolysis; (b) UV/vis absorption spectra of the disc at 100 K before (black) and after photolysis (grey); (c) difference FTIR spectrum of the same disc after photolysis, and (d) FTIR spectra of the disc before (black) and after (grey) photolysis.

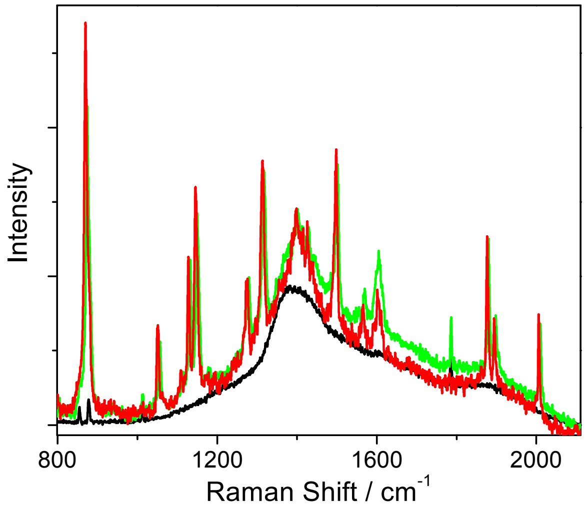

Figure S2. Raman spectra of a single crystal of **ReCu** before (*red*) and after (*green*) 325 nm laser irradiation recorded on the horizontal line of photolysis. The *black* spectrum is the off-sample background Raman spectrum.

References

[S1] J. Cosier, A.M. Glazer, *J. Appl. Crystallogr.* **1986**, *19*, 105.

[S2] G.M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112-122.

[S3] A. H. Alamiry, N. M. Boyle, C. C. Brookes, M. W. George, C. Long, P. Portius, M. T. Pryce, K. L. Ronayne, X. -Z. Sun, M. Towrie, K. Q. Vuong, *Organometallics*, **2009**, *28*, 1461-1468

[S4] A. I. Cooper , M. Poliakoff, *Chem. Phys. Lett.*, **1993**, *212*, 611-616