Supporting Information: Ligand Recruitment and Spin Transitions in the Solid-State Photochemistry of Fe$^{(III)}$TPPCl

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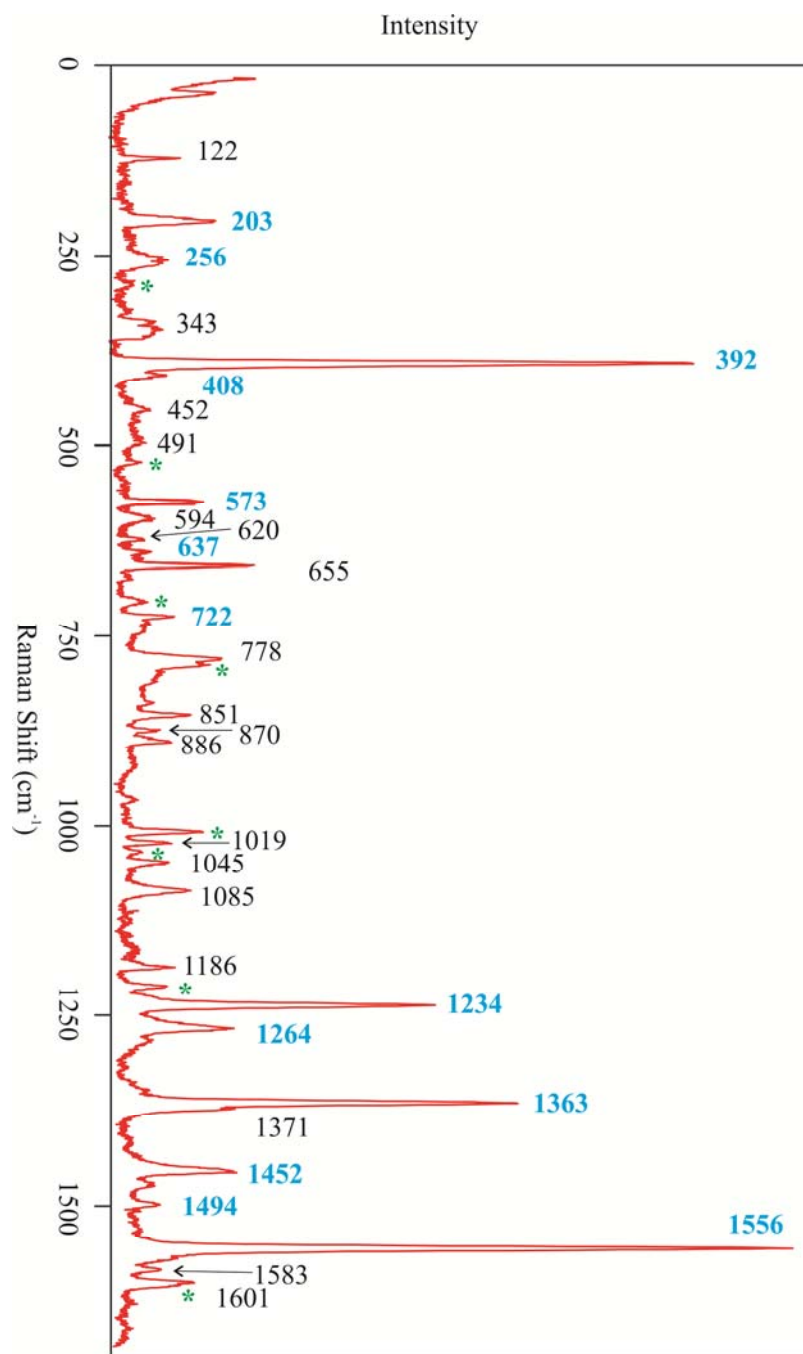
Figure S1. Low power spectrum from Figure 1 with vibrational bands labeled. The green asterisks indicate solvent bands observed in solvent only scans. The bands labeled in blue are observed with 454.5 nm excitation (Paulat, F.; Praneeth, V. K. K.; Nather, C.; Lehnert, N. *Inorg. Chem.* **2006**, *45*, 2835-2856). The bands labeled in black are additional vibrations of FeTPPCl observed with 406 nm excitation. The accuracy of the frequencies listed is ±2 cm^{-1} or better for most bands.
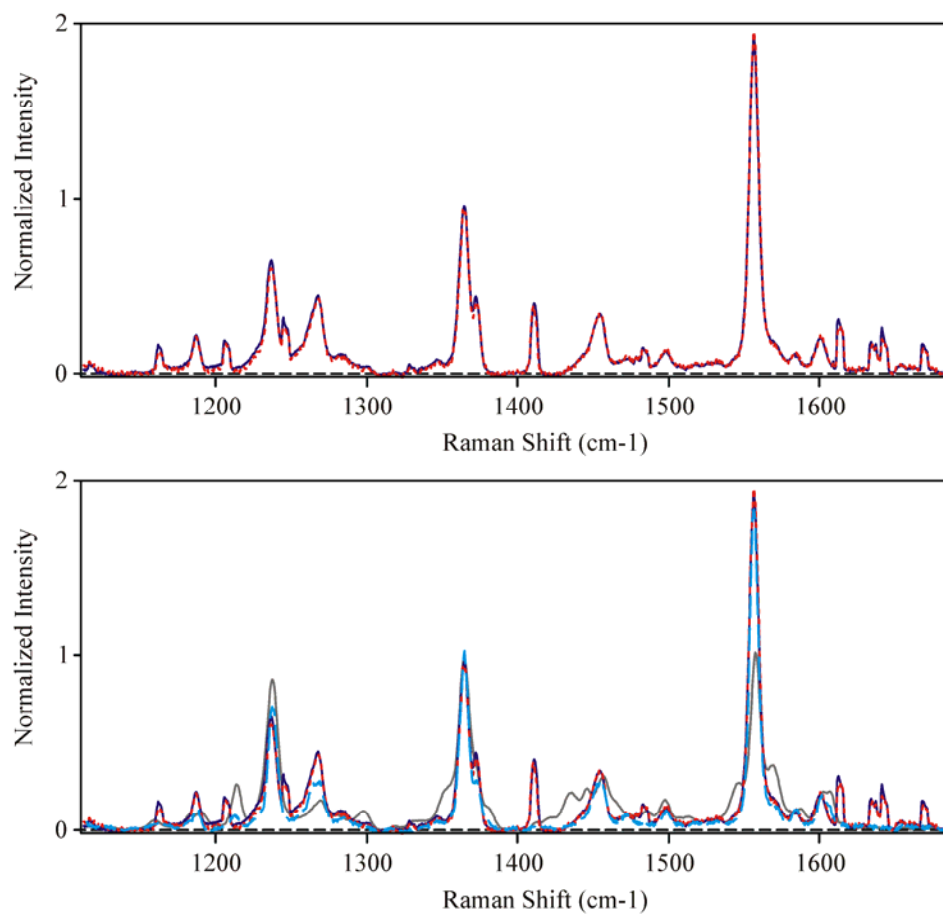
Figure S2. Influence of laser power on the spectrum of $Fe^{(III)}TPPCl$ in CH_2Cl_2 at 77K. (Top) Spectrum with 2 mW excitation – Red; Spectrum with 7-8 mW excitation – Blue. (Bottom) Same two spectra compared with those obtained in 1:1 CH_2Cl_2:Toluene at 1 mW – light blue and 7-8 mW – grey. The low power spectrum in the 1:1 solvent mixture resembles the spectrum in CH_2Cl_2. The 7-8 mW spectrum in the 1:1 solvent mixture exhibits a number of new bands. All spectra were obtained with a parallel polarization geometry,
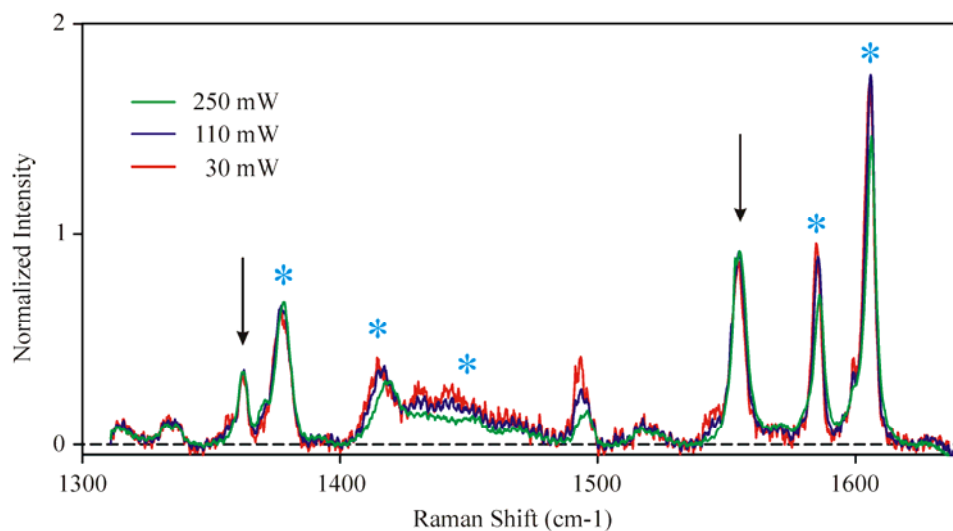
Figure S3. Power dependence observed with 514.53 nm excitation. Parallel Raman scattering for $Fe^{(III)}TPPCl$ in 1:1 CH_2Cl_2 at 77 K. The arrows designate the dominant solute Raman bands. The asterisks designate solvent bands. High power seems to soften the sample as seen in the CH_2Cl_2 band around 1415 cm-1, but no side bands appear around 1556 cm-1.
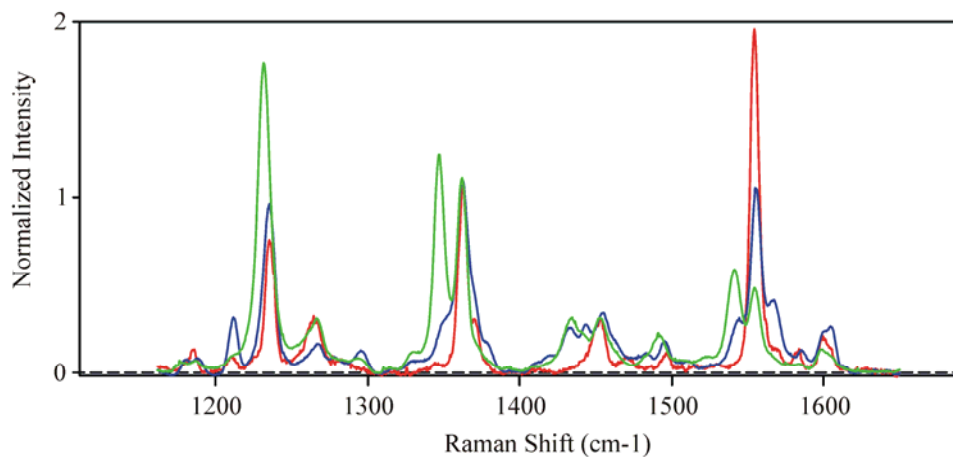

Figure S4. Comparison of photochemically reduced FeTPPCl in the presence of a small amount of residual acetone (green) with the spectrum observed at high power in 1:1 CH_2Cl_2:Toluene in the absence of acetone (blue). The low power spectrum is shown for comparison (red).
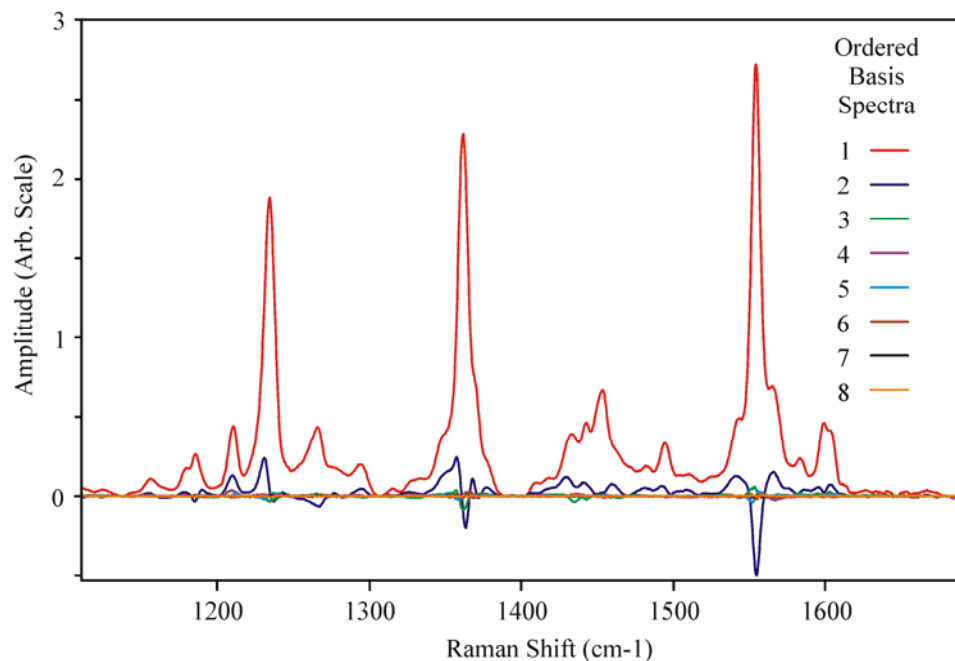
Figure S5. Basis vectors obtained from the singular value decomposition analysis. The basis vectors plotted are **U·S** and represent the scaled contribution of each spectral feature to the total data set. The first and second spectra contain the dominant contributions. The third spectrum (green) is dominated by small features at the Raman shifts of the strong peaks. While this is not random noise, it reflects noise in the absolute intensities of these peaks.
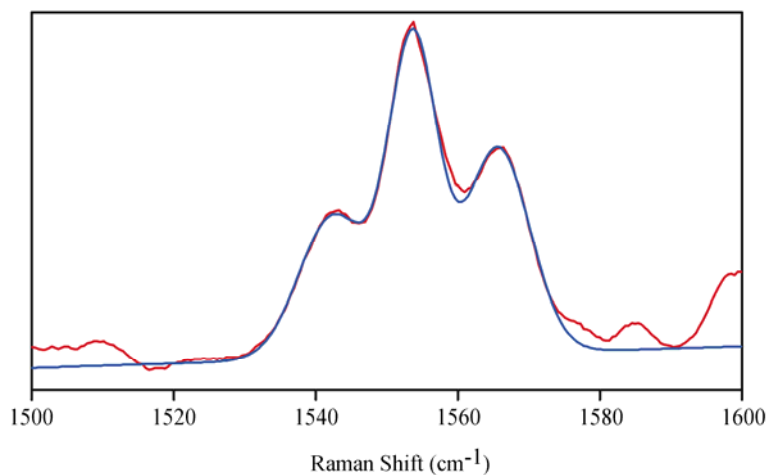

Figure S6. Gaussian fit to the best estimate photoproduct spectrum. This provides the relative intensity estimates given in the text. The relative intensity of the central peak is very sensitive to the value of α in Equation 3. The ratio of the high frequency peak to the low frequency peak is not very sensitive to the value of α.