Electronic Supplementary Material (ESI) for Dalton Transactions.

--Supporting Information--

Photoinduced Jahn-Teller switch in Mn(III) terpyridine complexes

Kyle Barlow,[1] Julien Eng,[2] Iona Ivalo,[1] Marco Coletta,[1] Euan K. Brechin,[1] Thomas J. Penfold,[2] and J. Olof Johansson*

[1]*EaStCHEM School of Chemistry, University of Edinburgh, David Brewster Road, EH9 3FJ, Edinburgh, UK*

[2]*Chemistry, School of Natural and Environmental Sciences, Newcastle University,*

Newcastle upon Tyne, UK.

**Email: olof.johansson@ed.ac.uk*

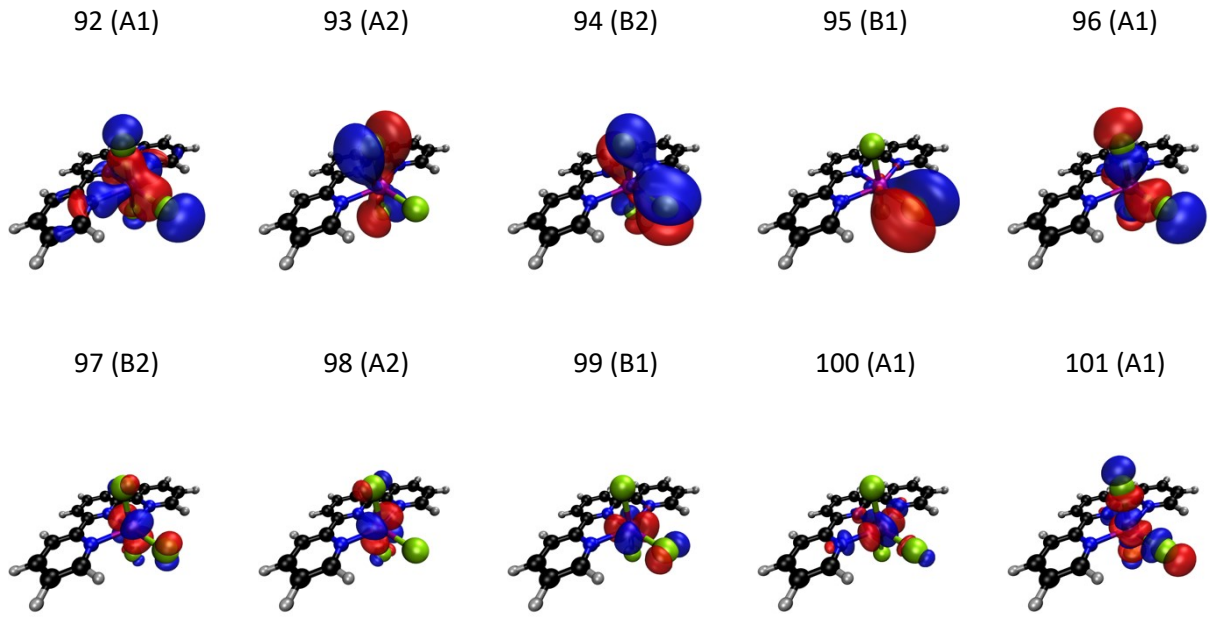

Figure S1: Molecular orbitals of [Mn(terpy)Cl_3] that compose the active space of the CASSCF/NEVPT2 calculations. The index and symmetry label are given for all orbitals. The top five orbitals are the bonding metal-ligand orbitals and the bottom five are their anti-bonding counterparts. The name of the d orbital involved is shown between square brackets.

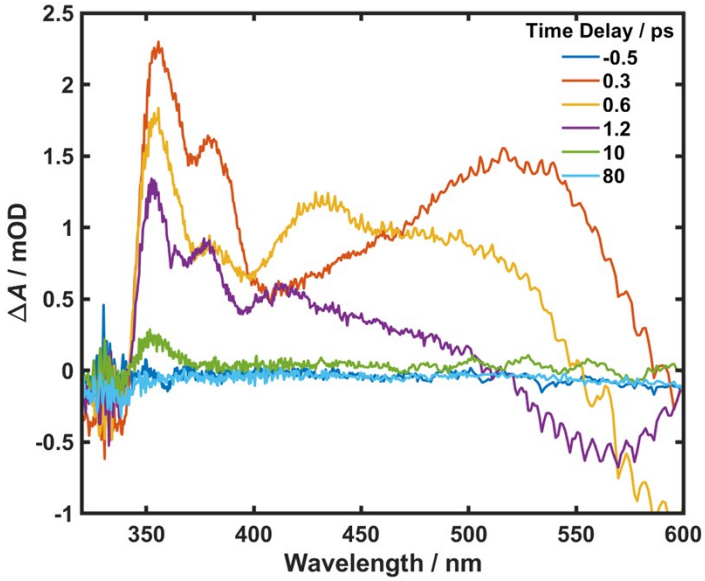

Figure S2: Difference spectra at various time delays of [Mn(terpy)Cl_3] after exciting at 940 nm.

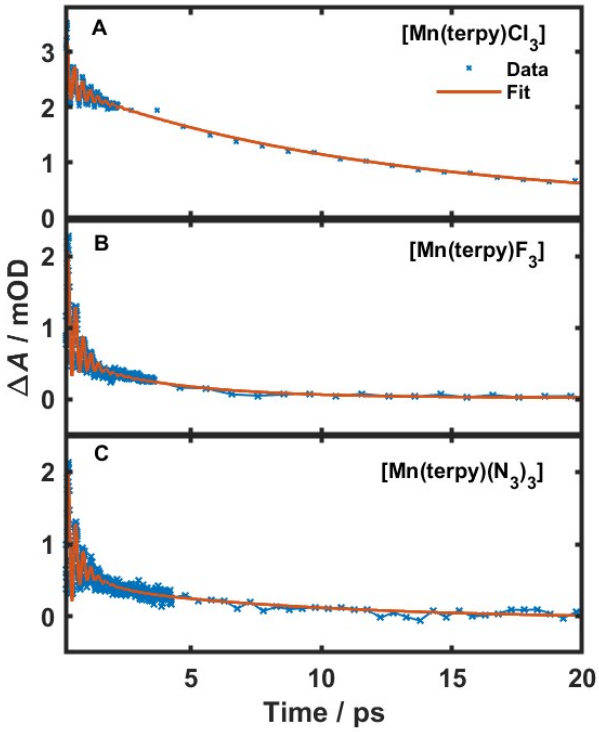

Figure S3: Kinetic trace data and fit up to 20 ps at the peak of the excited state absorption. A: kinetic trace at 350 nm in TA spectrum of [Mn(terpy)Cl-$_3$] after exciting at 400 nm, B: kinetic trace at 340 nm in TA spectrum of [Mn(terpy)F_3] after exciting at 750 nm. C: kinetic trace at 343 nm in TA spectrum of [Mn(terpy)$(N_3)_3$] after exciting at 400 nm. The data have been fitted with the sum of 2 exponential

decays and a single-frequency oscillatory component with dephasing time τ_d as shown in Equation 1 of main text.

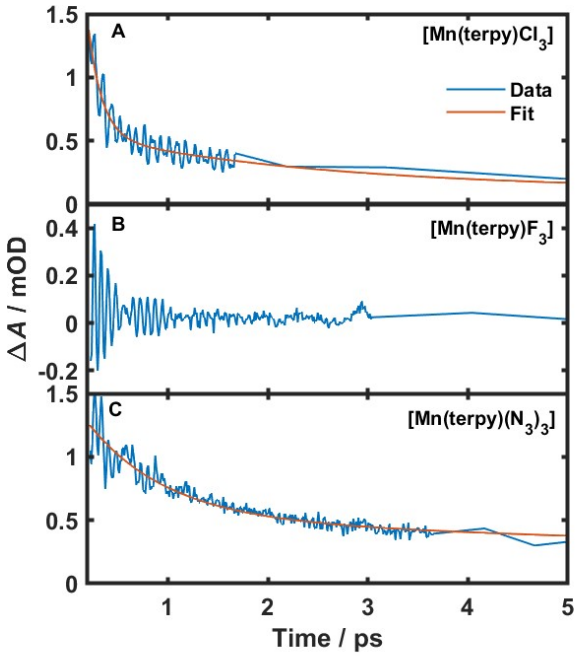

Figure S4: Kinetic trace data and fit up to 5 ps at 460 nm. A: kinetic trace in TA spectrum of [Mn(terpy)Cl_3] after exciting at 400 nm, B: kinetic trace in TA spectrum of [Mn(terpy)F_3] after exciting at 750 nm. C: kinetic trace in TA spectrum of [Mn(terpy)$(N_3)_3$] after exciting at 400 nm. The data have been fitted with the sum of 2 exponential decays apart from [Mn(terpy)F_3] which showed no decay kinetics at this wavelength.

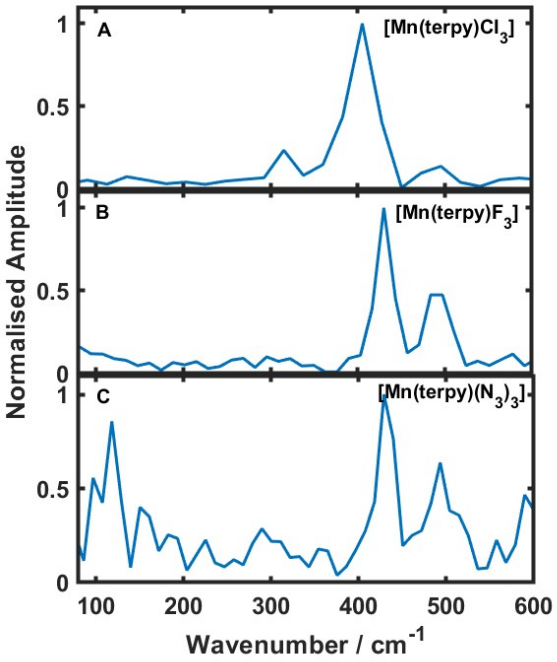

Figure S5: Fast Fourier transform of the residuals of the kinetic fit of the 460 nm traces. A: FFT of [Mn(terpy)Cl-$_3$] after exciting at 400 nm. B: FFT of [Mn(terpy)F_3] after exciting at 750 nm. C: FFT of [Mn(terpy)$(N_3)_3$] after exciting at 400 nm.

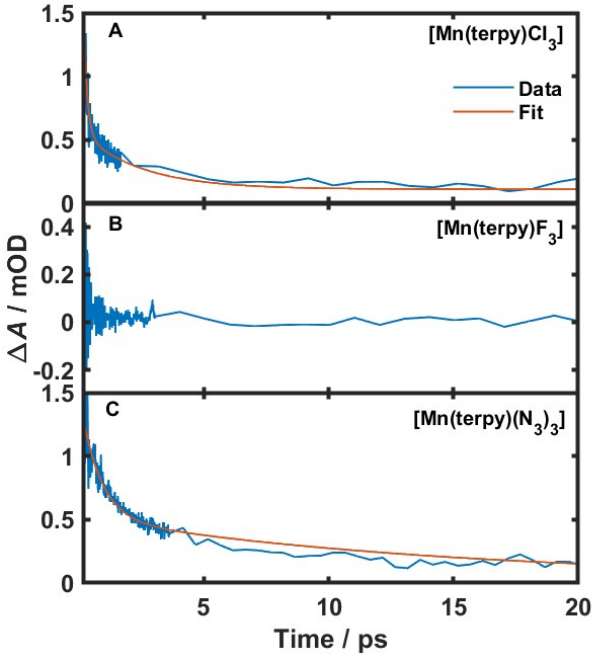

Figure S6: Kinetic trace data and fit up to 20 ps at 460 nm. A: kinetic trace in TA spectrum of [Mn(terpy)Cl-$_3$] after exciting at 400 nm, B: kinetic trace in TA spectrum of [Mn(terpy)F_3] after exciting at 750 nm. C: kinetic trace in TA spectrum of [Mn(terpy)$(N_3)_3$] after exciting at 400 nm. The data have been fitted with the sum of 2 exponential decays apart from [Mn(terpy)F_3] which showed no decay kinetics at this wavelength.

To isolate the oscillations arising from the sample from the solvent and cuvette, transient absorption was carried out using neat solvent and cuvette only. The kinetic traces are shown in Figures S7-8 along with the fast Fourier transform. These results confirm that the oscillations with frequency above 400 cm^{-1} observed are from the neat solvent or cuvette.

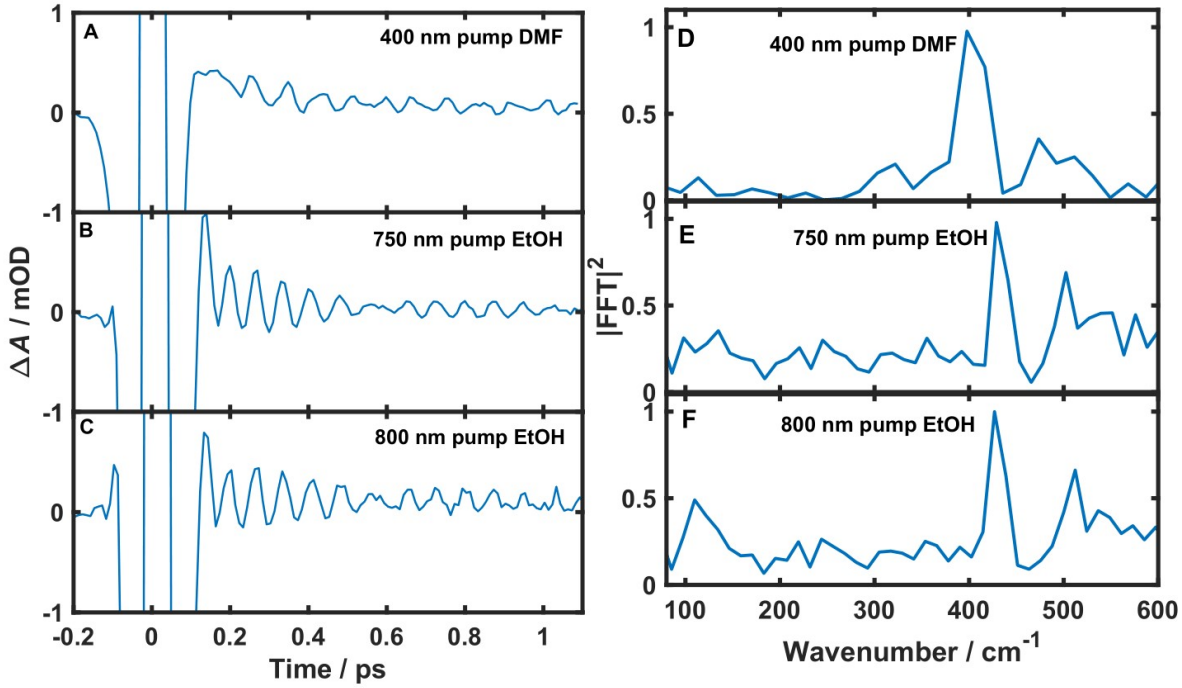

Figure S7: Kinetic traces in neat solvents for kinetic traces in at 460 nm and fast Fourier transform of the traces between 0.2 and 2 ps. A: kinetic trace at 460 nm after pumping neat DMF at 400 nm. B: kinetic trace at 460 nm after pumping neat ethanol at 750 nm. C: kinetic trace at 460 nm after pumping neat ethanol at 800 nm. D: FFT of A. E: FFT of B. F: FFT of C.

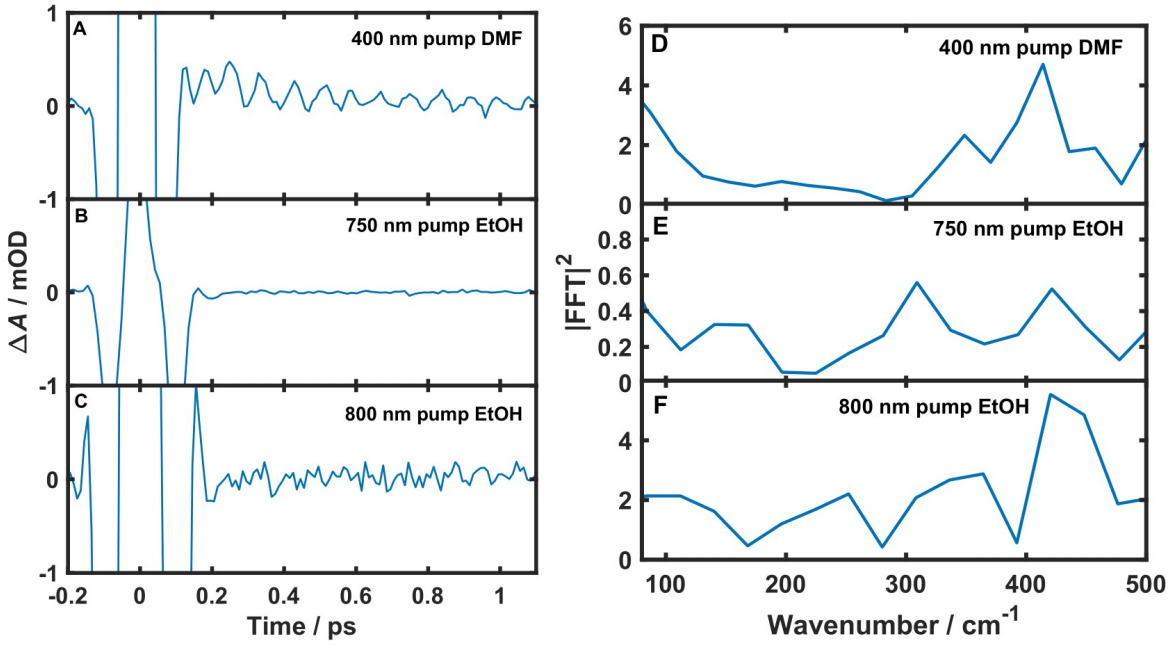

Figure S8: Kinetic traces in neat solvents for kinetic traces in the UV and fast Fourier transform of the traces between 0.2 and 2 ps. A: kinetic trace at 350 nm after pumping neat DMF at 400 nm. B: kinetic trace at 340 nm after pumping neat ethanol at 750 nm. C: kinetic trace at 343 nm after pumping neat ethanol at 800 nm. D: FFT of A. E: FFT of B. F: FFT of C.

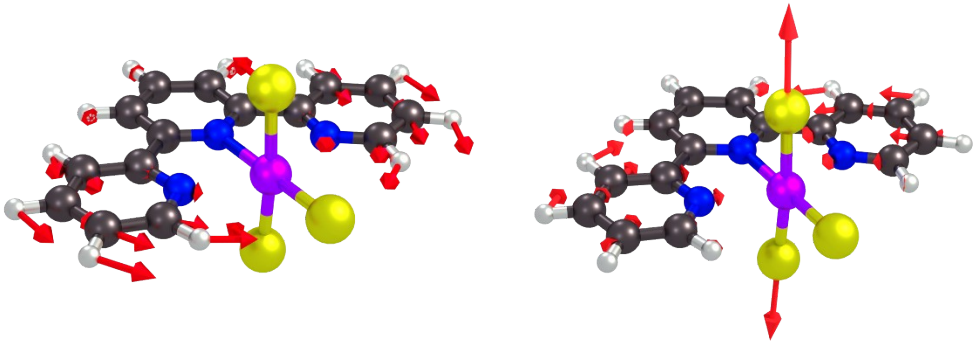

Figure S9: The normal modes that decrease the energy gap the most between Q_1 and Q_0 in [Mn(terpy)Cl_3]. Left: The pincer-like mode q_{10} (ω_{10} = 97.861 cm^{-1}) that is observed in the transient absorption spectra. Right: The symmetrical breathing mode q_{21} (ω_{21} = 273.370 cm^{-1}).

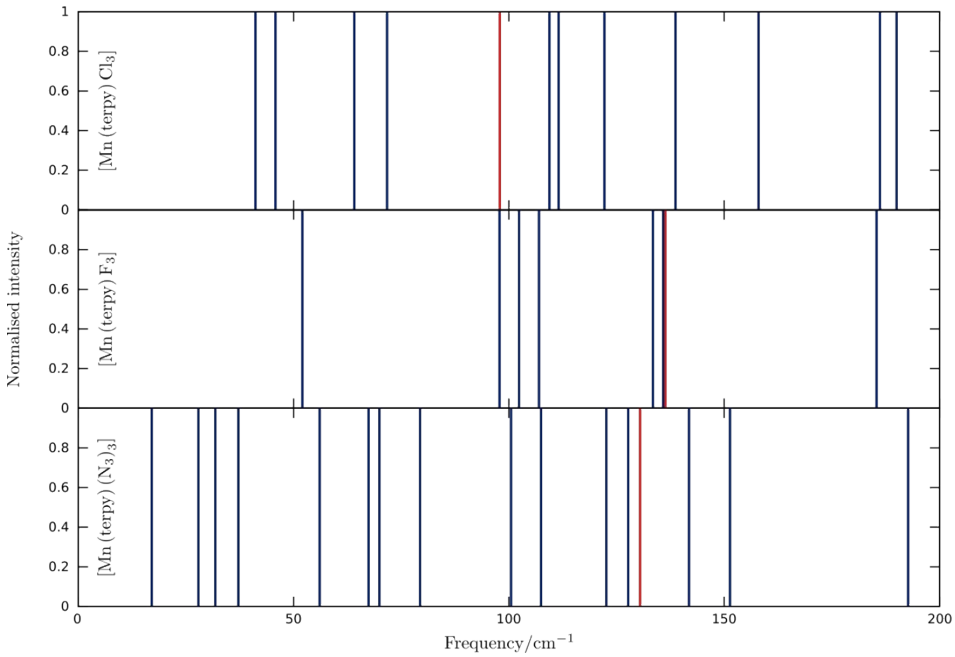

Figure S10: representation of the vibrational level for [Mn(terpy)Cl_3] (top), [Mn(terpy)F_3] (center) and [Mn(terpy)$(N_3)_3$] (bottom) below 200cm^{-1}. The “pincer-like” motion is emphasized in red. All intensities were normalised to unity for clarity.