Photochemical activation of an azido manganese-monosubstituted Keggin polyoxometalate: on the road to a Mn(V)-nitrido derivative.

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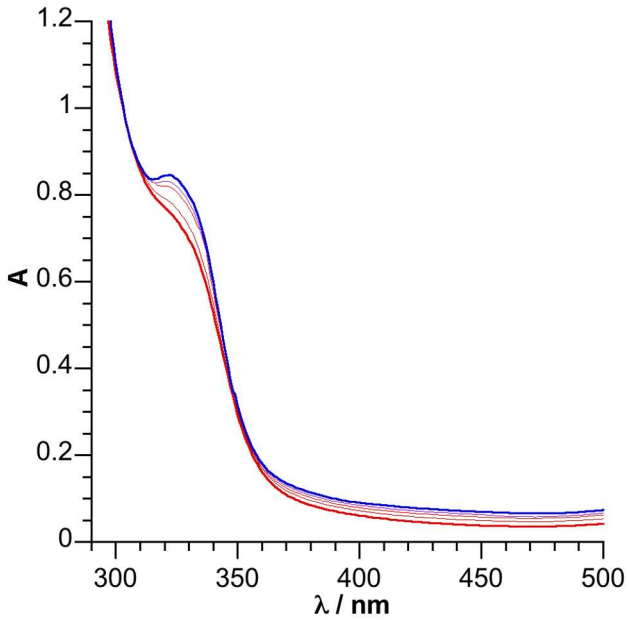
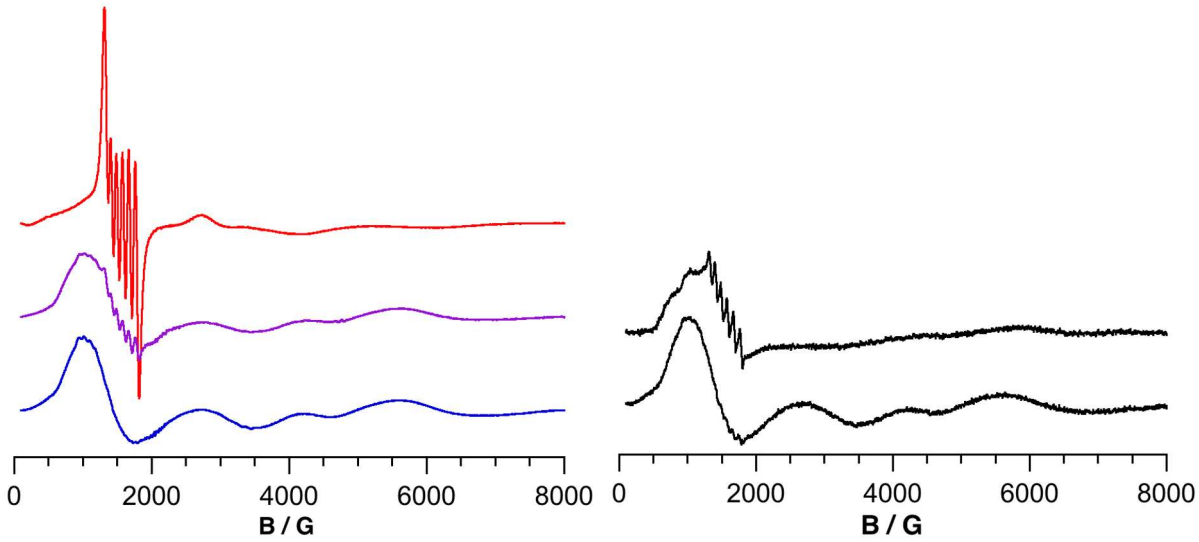
Supporting Information

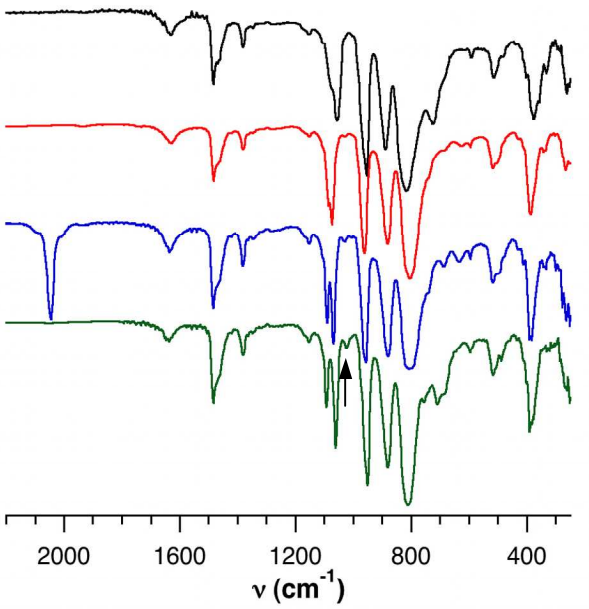


Effect of temperature on the absorbance spectral profile for **TBA-2(N_3)** in butyronitrile. Spectra were recorded from room temperature (red curve) to 140 K (blue curve).

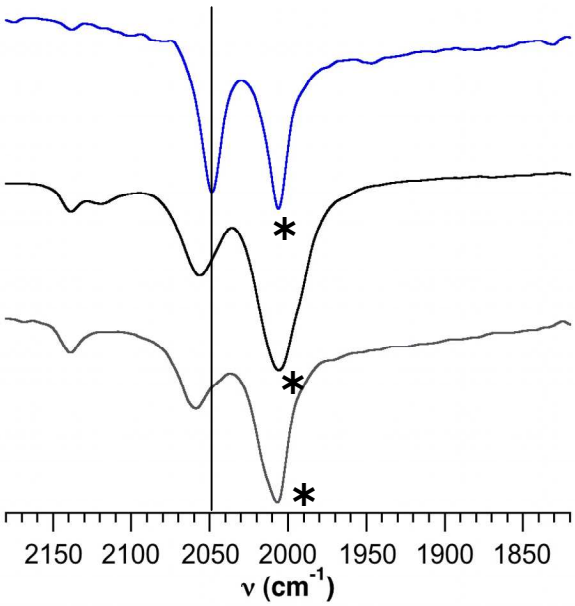


Left: Evolution of the EPR spectrum (X band) of **TBA-1(OH_2)** (red) upon addition of increasing amounts of **$TBAN_3$** in CH_3CN (77 K). The blue plot corresponds to the signal of **TBA-1(N_3)** while the purple one corresponds to a mixture of **TBA-1(OH_2)** and **TBA-1(N_3)**.

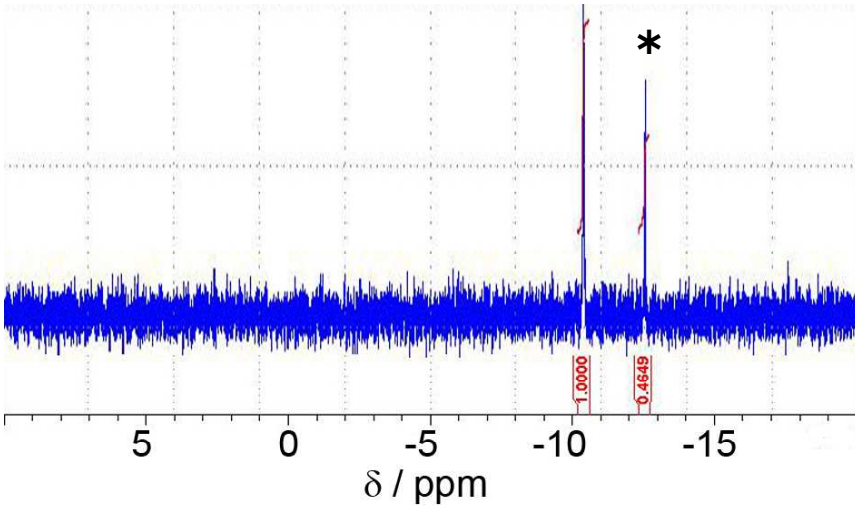
Right up: EPR spectrum (X band) of a photolysed solution (room temperature, λ_{exc} = 335 nm) of **TBA-2(N_3)** (0.5 mM, 2 eq. of $TBAN_3$ per Mn^{III}) in CH_3CN. Right down: same sample after addition of an excess of $TBAN_3$.



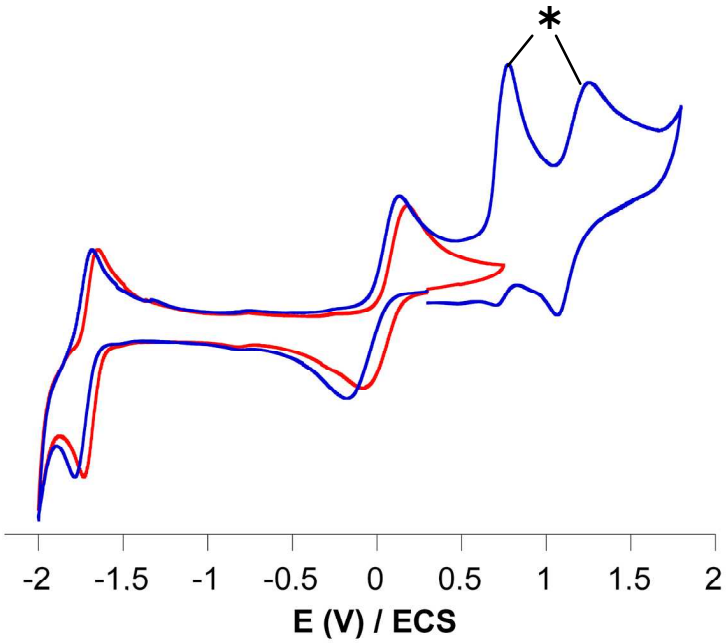
IR spectra of **TBA-1(OH_2)** (black), **TBA-2(OH_2)** (red), **TBA-2(N_3)** (blue) and **TBA-3** in KBr (the arrow indicates the very weak band at 1023 cm^{-1} that was assigned to the Mn-N stretch).



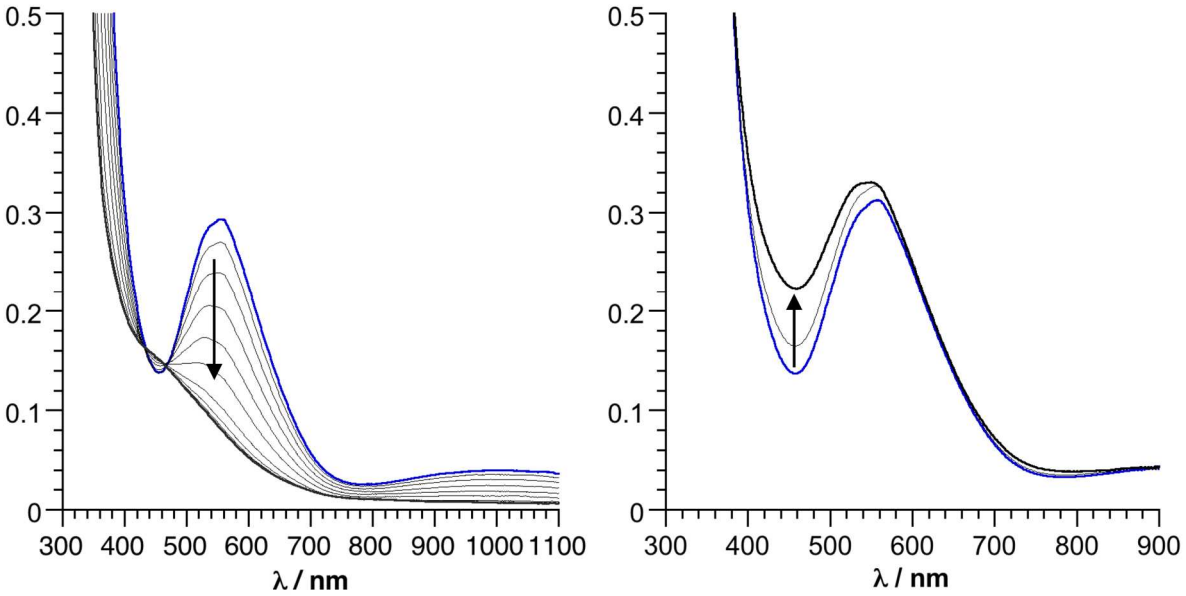
1800-2200 cm^{-1} region of the IR spectra of solutions of **TBA-2(N_3)** (0.5 mM, 2 eq. of $TBAN_3$ per Mn^{III}) in MeCN (blue), **TBA-1(N_3)** (1 mM, large excess of $TBAN_3$) in MeCN (black) and photolysed solution (room temperature, λ_{exc} = 335 nm) of **TBA-2(N_3)** (0.5 mM, 5 eq. of $TBAN_3$ per Mn^{III}) in CH_3CN (grey). The peaks marked by ✱ corresponds to the free N_3^- present in solution.



^{31}P NMR (CD_3CN/CH_3CN, 121.5 MHz) spectrum of a solution of **TBA-3** obtained by photolysis at -30°C with λ_{exc} = 313 nm of **TBA-2(N_3)** (1.0 mM, 4 eq. of $TBAN_3$ per Mn^{III}). The peak marked by ✱ corresponds to $TBA_3[PW_{12}O_{40}]$ (0.5 mM) used as internal reference.



Cyclic voltammograms of **TBA-2(OH_2)** (1 mM, red) and **TBA-2(N_3)** (1.0 mM, 2 eq. of $TBAN_3$ per Mn^{III}, blue) in CH_3CN with 10^{-1} M $TBABF_4$ as supporting electrolyte versus SCE (scan rate 100 $mV.s^{-1}$). The waves marked by ✱ correspond to the oxidation of free N_3^-.



Left: spectral changes observed during the photolysis of **TBA-2(N_3)** (1 mM) in CH_3CN solution with λ_{exc} = 365 nm at room temperature. The photolysis was complete within 1 hour. Right: same experiment carried out at -30°C. After 1 hour of photolysis, (black bold curve) the reaction was still far from completion.