

Supporting information for

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**Ligand exchange upon Oxidation of a Dinuclear Mn complex – Detection of Structural Changes by FT-IR Spectroscopy and ESI-MS**

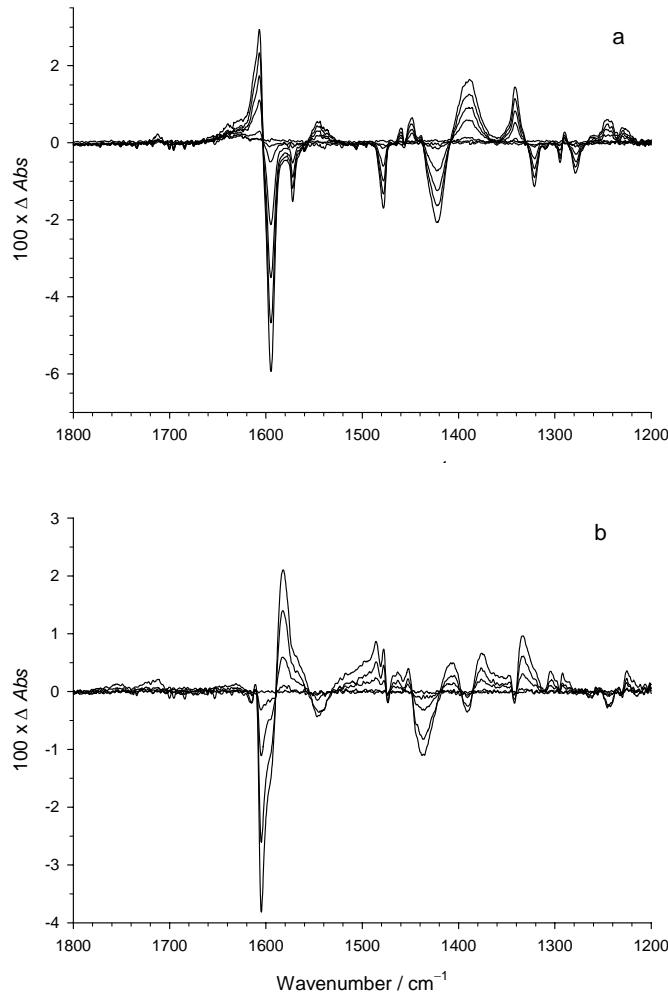
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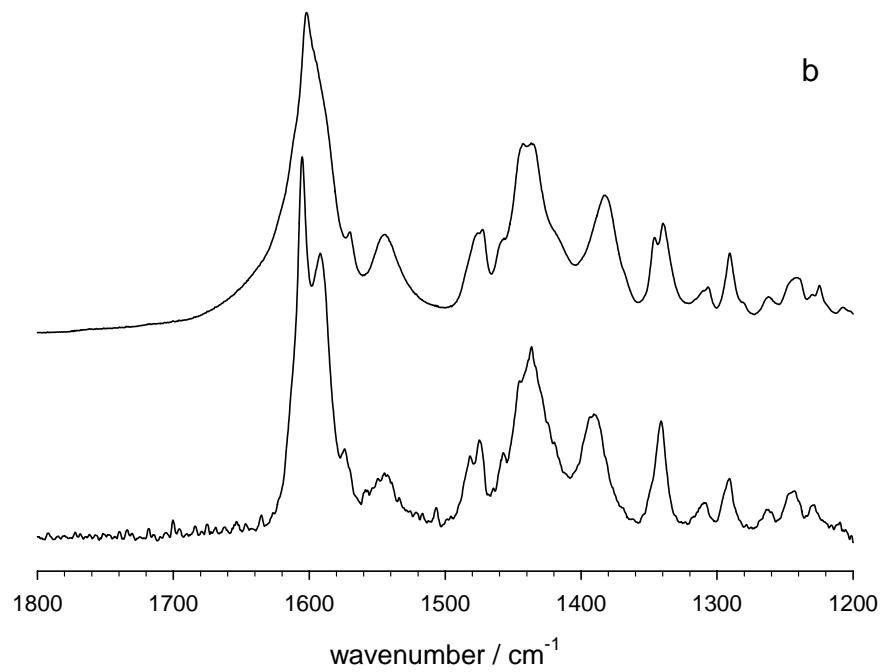
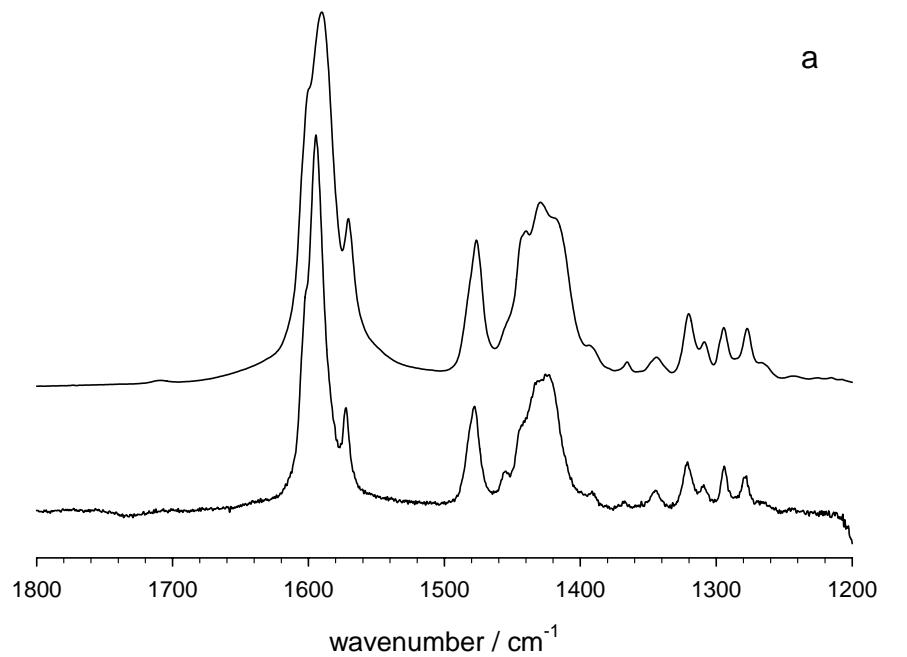
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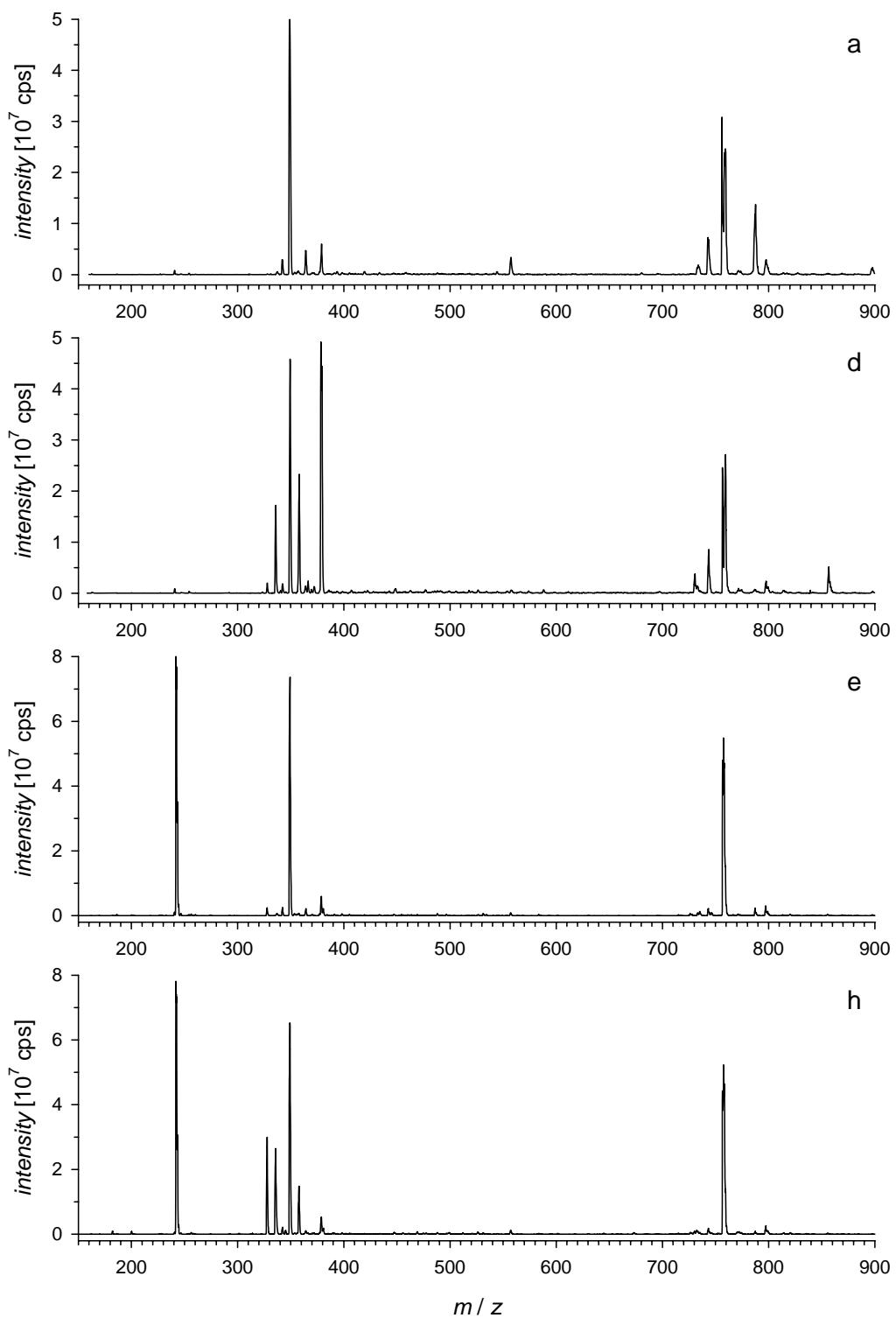
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**Figure S1.** Spectroelectrochemical changes upon oxidation of  $[\text{Mn}_2^{\text{II,II}}(\text{bpmp})(\mu\text{-OAc})_2]^+$  (3 mM) in  $\text{CD}_3\text{CN}$  with 0.5 M  $\text{KPF}_6$ . Electrolysis at 0.32 V (a) and successive electrolysis at 0.82 V (b).



**Figure S2.** IR spectra of  $[\text{Mn}_2^{\text{II},\text{II}}(\text{bpmp})(\mu\text{-OAc})_2][\text{ClO}_4]$  (a) and  $[\text{Mn}_2^{\text{II},\text{III}}(\text{bpmp})(\mu\text{-OAc})_2][\text{ClO}_4]_2$  (b) as solid (top spectra) and in  $\text{CD}_3\text{CN}$  solution (bottom spectra).



**Figure S3.** Selected full range EC-ESI-MS spectra of  $[\text{Mn}_2^{\text{II},\text{II}}(\text{bpmp})(\mu\text{-OAc})_2]^+$  (45  $\mu\text{M}$ ) in  $\text{CH}_3\text{CN}$  without applied potential (a), and 1.2 V (d) applied to the EC cell. Mass spectra of  $[\text{Mn}_2^{\text{II},\text{II}}(\text{bpmp})(\mu\text{-OAc})_2]^+$  (97  $\mu\text{M}$ ) in  $\text{CH}_3\text{CN}$  with 10% (v:v)  $\text{H}_2\text{O}$  without applied potential (e) and with 0.6 V (h) applied to the EC cell.