

Supporting Information

Single-molecule magnet behaviour in metal-organic nanospheres generated by simple precipitation of Mn₁₂O₁₂ clusters

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1. TEM micrographs and EELS (Electron Energy Loos Spectrometer) Mn-O mapping of Mn₁₂-based nanospheres.

Images were obtained with a JEOL JEM 2010F transmission electron microscope coupled to an Electron Energy Loos Spectrometer. One drop of a solution of the materials was deposited on a carbon coated copper grid, left to dry under high vacuum, and the observation was performed at room temperature at a voltage of 200 kV.

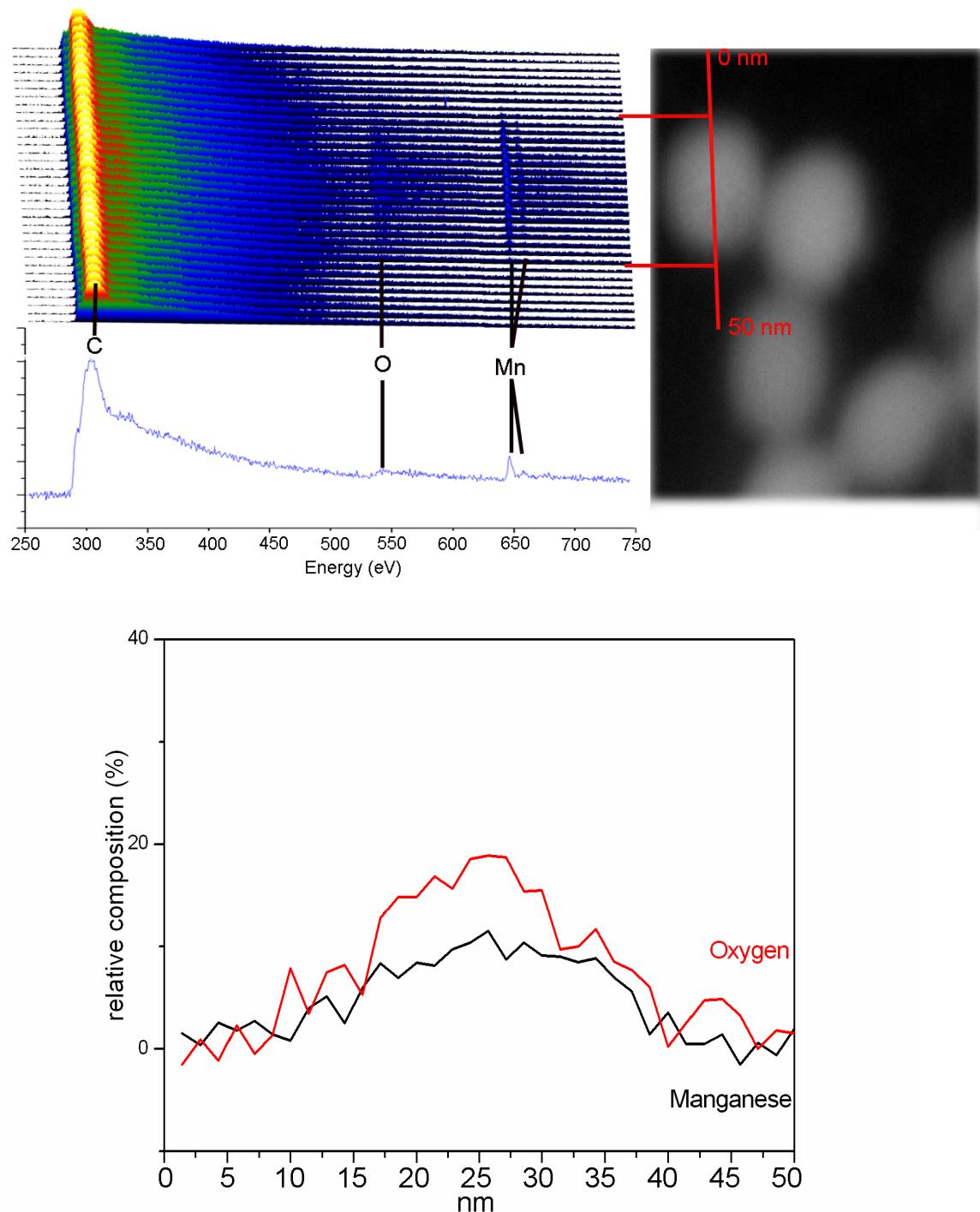


Figure 1S. (top) Two-dimensional EELS spectra representation (down) Mn and O relative composition in the analyzed zone calculated from EELS spectra.

2. InfraRed spectra of Mn₁₂-based nanospheres.

Methods for FT-IR: FT-IR spectra were collected on a Perkin Elmer spectrometer in the range of 400-4000 cm⁻¹ on ATR.

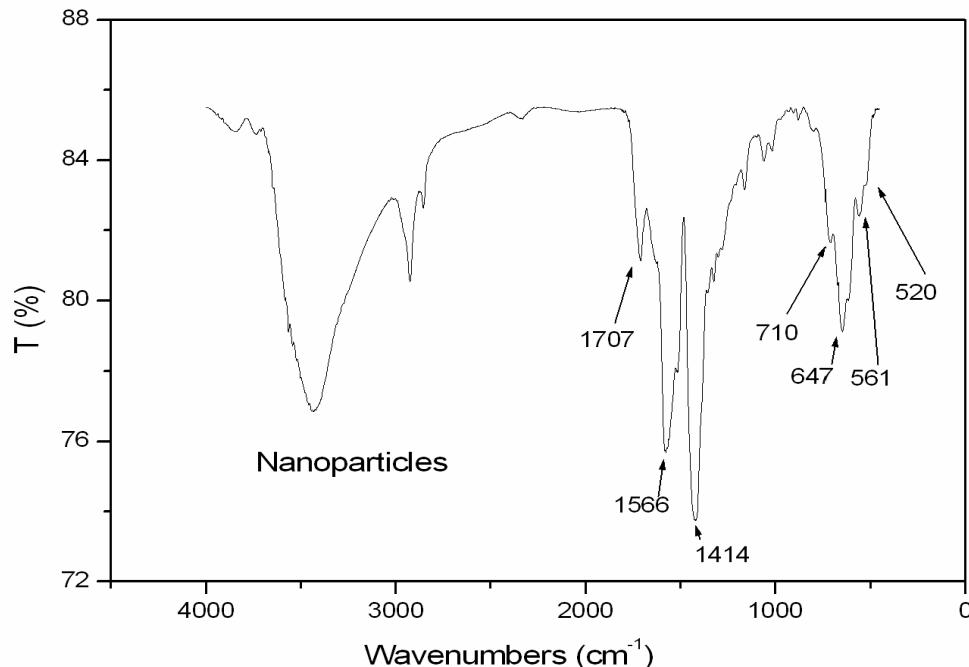


Figure 2S. IR spectra of Mn₁₂-based nanospheres.

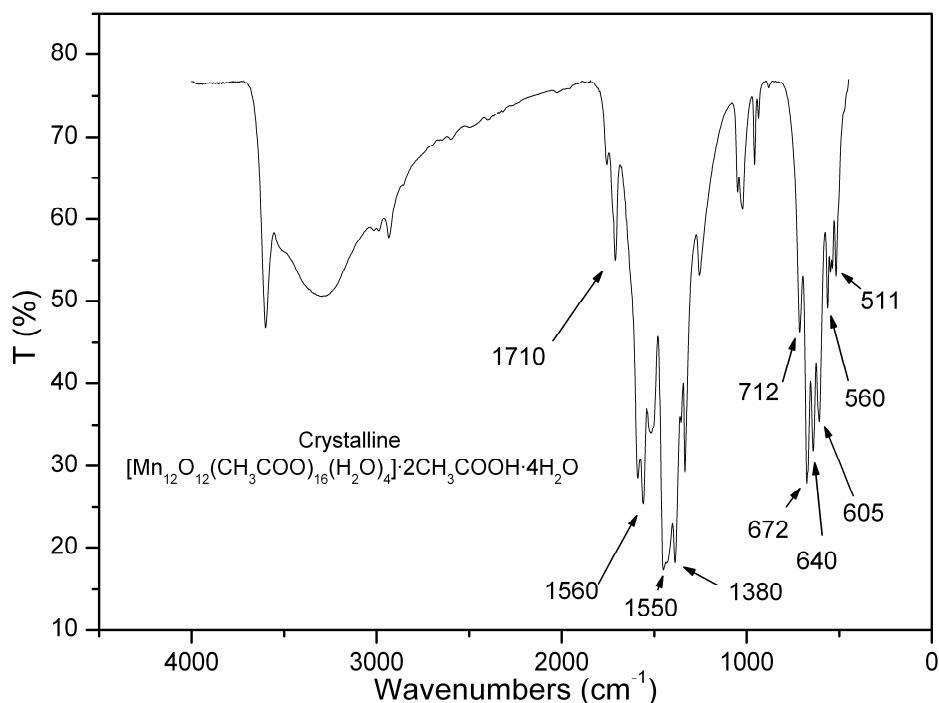


Figure 3S. IR spectra of [Mn₁₂O₁₂(CH₃COO)₁₆(H₂O)₄] · 2CH₃COOH · 4H₂O.

3. Dynamic Light Scattering (DLS) measurements of Mn₁₂-based nanospheres.

Methods for DLS: DLS measurements were obtained with a Malvern Zetasizer Nano-ZS differential light scattering.

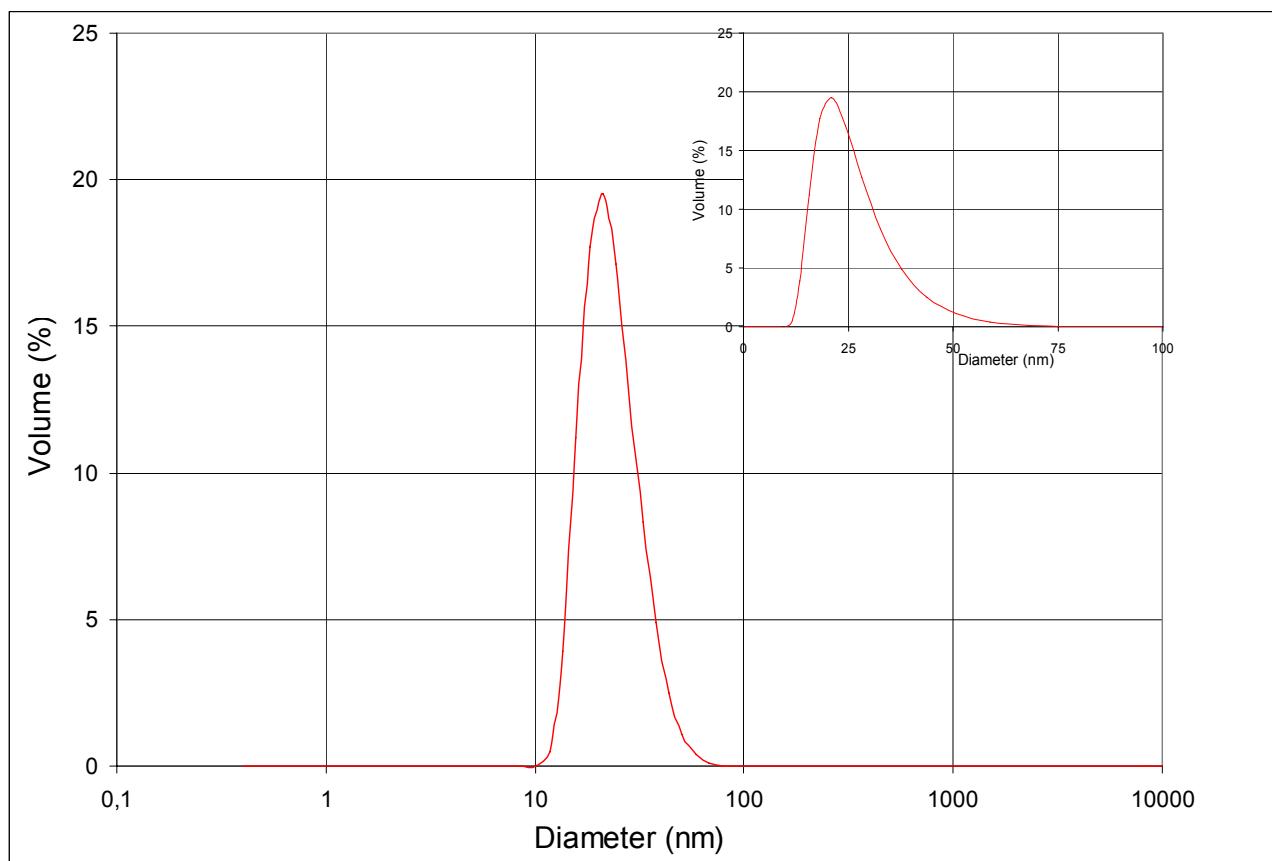


Figure 4S. Dynamic Light Scattering (DLS) measurements of Mn₁₂-based nanospheres dispersed in toluene.

4. Field Emission Scanning Electron Micrographs (FE-SEM) of Mn₁₂-based nanospheres

Methods for FE-SEM: FE-SEM images were performed on a scanning electron microscope (Strata DB235 FEI Company) at acceleration voltages of 10–15 kV. Aluminium was used as support.

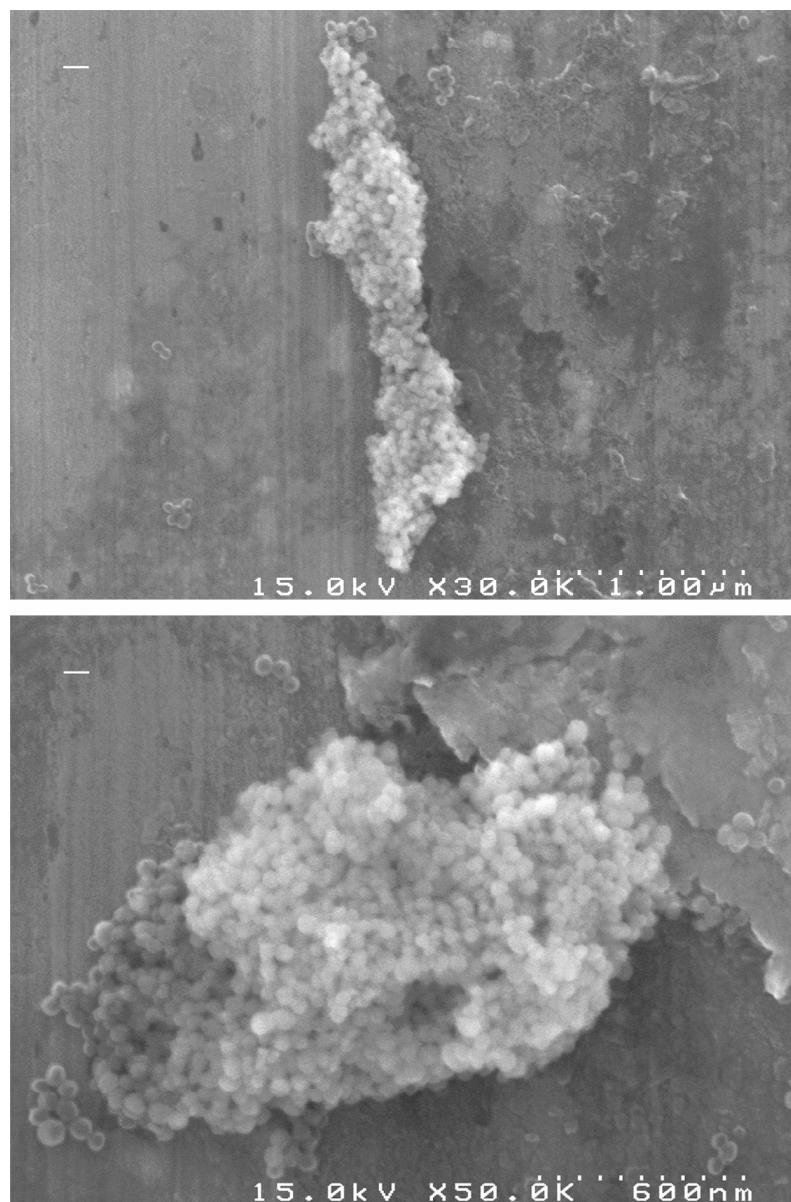


Figure 5S. FE-SEM images of Mn₁₂-based nanospheres.

5. Transmission Electron micrographs of Mn₁₂-based nanospheres

Methods for TEM: TEM images were performed on a JEOL model JEM-1010 transmission electron microscope. One drop of a solution of the materials was deposited on a carbon coated copper grid, left to dry under high vacuum, and the observation was performed at room temperature at a voltage of 100 kV.

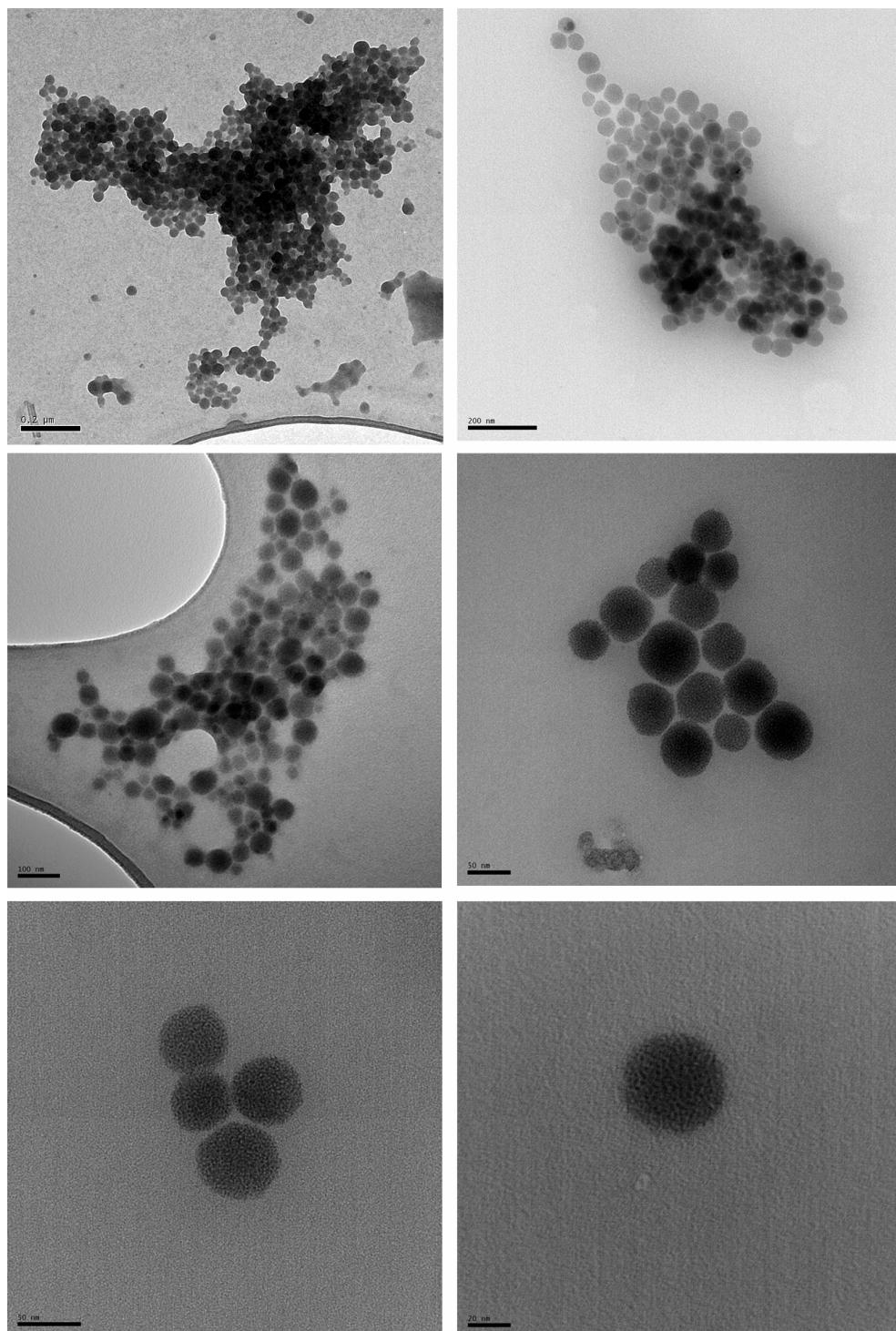


Figure 6S. TEM images of Mn₁₂-based nanospheres.

6. Experimental procedure for preparation of Mn₁₂-based nanoparticles

All HPLC quality solvents used were purchased from ROMIL, and used without further purification. [Mn₁₂O₁₂(CH₃COO)₁₆(H₂O)₄]·2CH₃COOH·4H₂O (Mn₁₂-Ac) was synthesized according to literature procedures.³⁰ The Mn₁₂-based nanoparticles were obtained by fast addition of a solution of Mn₁₂O₁₂(CH₃COO)₁₆(H₂O)₄] dissolved in acetonitrile into a toluene under vigorous stirring at room temperature. Firstly, a solution of Mn₁₂-Ac (20 mg, 0.01 mmol) is dissolved in 5 ml of acetonitrile. The resulting dark brown solution was filtered through a 5-7 µm filter to remove non-dissolved reactants. The Mn₁₂-Ac solution was then added into 30 ml of toluene at room temperature under vigorous stirring. A gradual opacity indicative of nanoparticles precipitation was observed. The brown nanoparticles were collected by centrifugation, washed several times with acetonitrile and toluene, and finally dispersed in toluene. The final colloidal solution was brown. Anal. (%) Calcd. For C₃₂H₅₆O₄₈Mn₁₂: C, 20.57; H, 3.02; Found: C, 19.97; H, 2.89; IR (ATR, cm⁻¹): 1707 (s), 1566 (s), 1414 (m), 710 (m), 647 (m), 561 (m), 520 (m).

30 T. Lis, *Acta Crystallogr., Sect. B*, 1977, **B33**, 2964