Electronic Supplementary Information

Mn$_{12}$ Single-Molecule Magnet Aggregates as Magnetic Resonance Imaging Contrast Agents

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Materials: CH$_3$(CH$_2$)$_{17}$(OCH$_2$CH$_2$)$_n$OH (average $M_n = 711$) was a product from Aldrich. Bovine serum Albumin (BSA) was obtained from Dingguo Biotechnology (Beijing, China).

Instrument: The mass spectrum (MS) was recorded using an autoflex TOF/TOF (Bruker, Germany) mass spectrometer, equipped with a nitrogen laser (337 nm, 3 ns pulse). The mass spectrometer was operated in the negative ion reflector mode. Elemental analysis was performed on the Flash EA1112 from ThermoQuest Italia S.P.A. Thermogravimetric analysis (TGA) was performed on Perkin-Elmer7 series thermal analysis system in a N$_2$ flow with a heating rate of 10 °C min$^{-1}$. The inductive couple plasma-optical emission spectrometer (ICP-OES) was performed on Thermo
Scientific iCAP ICP-OES 6000 Series. FT–IR spectra were recorded on a Bruker Vertex 80v FT–IR spectrometer equipped with a DTGS detector (32 scans) with a resolution of 4 cm⁻¹ on a KBr pellet. Hydrodynamic diameters were determined on Nano-ZS instrument (Malvern Instruments). TEM images were carried out on Hitachi H8100 electron microscope. Magnetization hysteresis data were collected at 2 K, between +5 T and –5 T, cooling the samples at zero field with a magnetometer (Quantum Design MPMSXL-5) equipped with a SQUID sensor. ¹H NMR spectra were recorded on a Bruker Ultrashield 500 MHz spectrometer, and all the relaxation times were recorded on the same instrument, at 25 ºC with a least square fitting to 16 data points. $r_1$ and $r_2$ are defined as the changes in $1/T_1$ and $1/T_2$ normalized to the concentration of metal ion, with unit of mM⁻¹ s⁻¹. The $r_1$ and $r_2$ values can be calculated as the slopes of the lines $1/T_1$ and $1/T_2$ versus the CA concentration. All the MRI experiments were performed in a clinical 1.5 T MRI instrument (Signa HDx 1.5 T Series) at room temperature: 32 echoes; repetition time (TR): 1000 ms; echo times (TE): 6–67 ms.

**Preparation of stearic acid modified Mn₁₂ (Mn₁₂–C₁₈):** A mixture of Mn₁₂-Ac (0.1 mmol) and stearic acid (3 mmol) was dissolved in 50 ml of 1:1 (v:v) solution of toluene and dichloromethane. The mixture was stirred for 24 h at 50 ºC, which was then filtrated and concentrated. Toluene was added and then evaporated to remove free CH₃CO₂H. To make the acetic acid ligands completely substituted, this procedure was repeated four times. The results brown solid was dissolved in hot methanol (65 ºC), filtered and washed with hot methanol five times to remove the superfluous stearic acid. The obtained brown product was dried under vacuum.

**The characterization of Mn₁₂–C₁₈:** IR (KBr, cm⁻¹) ν = 2920, 2850, 1583, 1569, 1531, 1468, 1455, 1443, 1429, 1380, 1317, 1261, 1098, 1025, 868, 804, 721, 705, 673, 641, 610, 585. LDI–TOF mass spectra of Mn₁₂–C₁₈ show the presence of $[\text{Mn}_{12}\text{O}_{12}(\text{OOCCCH}_3)_{4}(\text{OOCC}_{17}\text{H}_{35})_{11}]^-$ ion at m/z = 4206.4, and fragments resulting from the stepwise loss of several C₁₇H₃₅CO₂ units ($\Delta$ m/z = 283) and CH₃CO₂ units ($\Delta$...
m/z = 59). Anal. Calced for Mn$_{12}$–C$_{18}$ (C$_{208}$H$_{402}$O$_{45}$Mn$_{12}$, 4282.65): C, 58.33; H, 9.45. Found: C, 57.99; H, 8.99. The TGA at range of 30–150 °C corresponds to the loss of crystallized water (0.52 %), and the calculated number of crystallized water is ca. 1. Combining the MS, TGA and elemental analysis, Mn$_{12}$–C$_{18}$ should correspond to the formula of Mn$_{12}$O$_{12}$(OOCCH$_3$)$_5$(OOCC$_{17}$H$_{35}$)$_{11}$H$_2$O.

**Fig. S1** IR spectra of (A) Mn$_{12}$–C$_{18}$ and (B) Mn$_{12}$–Ac in solid state.

**Fig. S2** TGA graphs of (A) Mn$_{12}$–Ac and (B) Mn$_{12}$–C$_{18}$.
**Fig. S3** High mass region of the negative mode LDI–TOF mass spectrum of Mn_{12–C_{18}}.

**Fig. S4** The magnetization hysteresis loop measured at 2 K for Mn_{12–C_{18}}.

**Fig. S5** Photograph of Mn_{12–C_{18}/C_{18}EO_{10}} aqueous solution extracted by chloroform and n-hexane.
Fig. S6 Magnetization hysteresis loop at 2 K for Mn\textsubscript{12}–C\textsubscript{18}/C\textsubscript{18}EO\textsubscript{10} complexes.

Fig. S7 Plots of hydrodynamic diameter of Mn\textsubscript{12}–C\textsubscript{18}/C\textsubscript{18}EO\textsubscript{10} aggregates versus different (a) NaCl concentration, (b) pH conditions, and (c) temperature.

Fig. S8 The longitudinal relaxation rate 1/T\textsubscript{1} changes against time.