

Electronic Supplementary Information

Mn₁₂ Single-Molecule Magnet Aggregates as Magnetic Resonance Imaging Contrast Agents

Yinglin Wang,^a Wen Li,^a Shengyan Zhou,^b Daliang Kong,^b Haishan Yang,^b

*and Lixin Wu^{*a}*

^a State Key Laboratory of Supramolecular Structure and Materials, Jilin University,
Changchun 130012, P. R. China.

^b Radiology Department, China-Japan Union Hospital of Jilin University, Changchun,
Jilin, P. R. China

* To whom correspondence should be addressed. E-mail: wulx@jlu.edu.cn

Materials: CH₃(CH₂)₁₇(OCH₂CH₂)_nOH (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 N₂ 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 °C 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 $\text{mM}^{-1}\text{ s}^{-1}$. 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 Mn_{12} ($\text{Mn}_{12}\text{-C}_{18}$): A mixture of $\text{Mn}_{12}\text{-Ac}$ (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 °C, which was then filtrated and concentrated. Toluene was added and then evaporated to remove free $\text{CH}_3\text{CO}_2\text{H}$. To make the acetic acid ligands completely substituted, this procedure was repeated four times. The results brown solid was dissolved in hot methanol (65 °C), 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 $\text{Mn}_{12}\text{-C}_{18}$: IR (KBr, cm^{-1}) $\nu = 2920, 2850, 1583, 1569, 1531, 1468, 1455, 1443, 1429, 1380, 1317, 1261, 1098, 1025, 868, 804, 721, 705, 673, 641, 610, 585$. LDI-TOF mass spectra of $\text{Mn}_{12}\text{-C}_{18}$ show the presence of $[\text{Mn}_{12}\text{O}_{12}(\text{OOCCH}_3)_4(\text{OCC}_{17}\text{H}_{35})_{11}]^-$ ion at $m/z = 4206.4$, and fragments resulting from the stepwise loss of several $\text{C}_{17}\text{H}_{35}\text{CO}_2$ units ($\Delta m/z = 283$) and CH_3CO_2 units (Δ

$m/z = 59$). Anal. Calcd for $\text{Mn}_{12}\text{-C}_{18}$ ($\text{C}_{208}\text{H}_{402}\text{O}_{45}\text{Mn}_{12}$, 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, $\text{Mn}_{12}\text{-C}_{18}$ should correspond to the formula of $\text{Mn}_{12}\text{O}_{12}(\text{OOCCH}_3)_5(\text{OCC}_{17}\text{H}_{35})_{11}\text{H}_2\text{O}$.

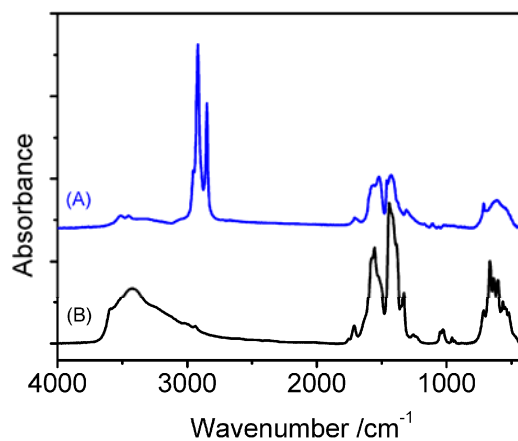


Fig. S1 IR spectra of (A) $\text{Mn}_{12}\text{-C}_{18}$ and (B) $\text{Mn}_{12}\text{-Ac}$ in solid state.

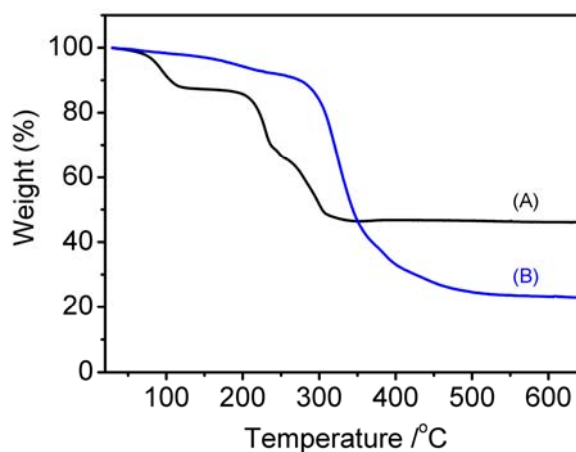


Fig. S2 TGA graphs of (A) $\text{Mn}_{12}\text{-Ac}$ and (B) $\text{Mn}_{12}\text{-C}_{18}$.

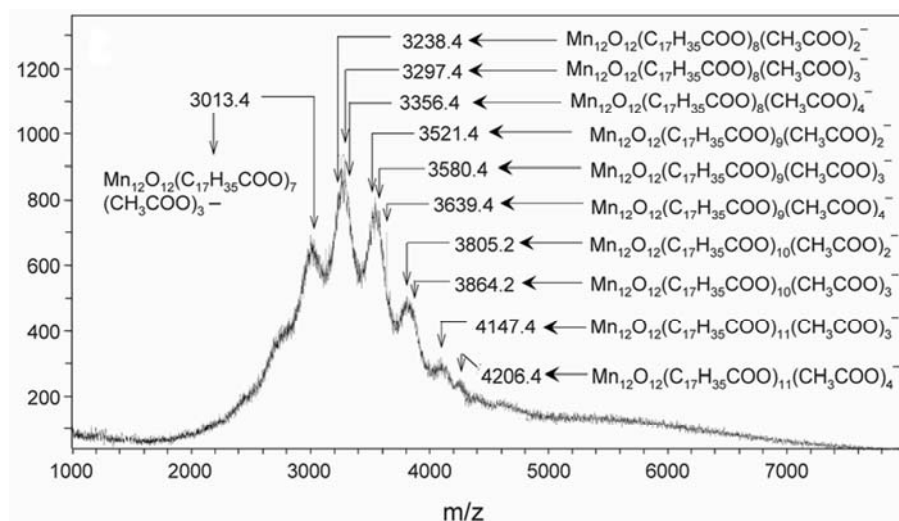


Fig. S3 High mass region of the negative mode LDI-TOF mass spectrum of $\text{Mn}_{12}\text{-C}_{18}$.

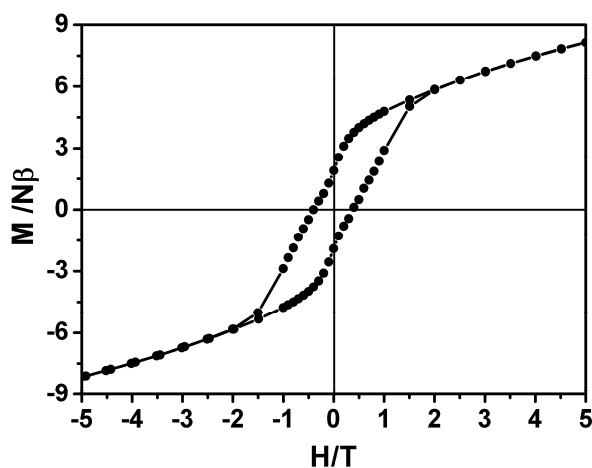


Fig. S4 The magnetization hysteresis loop measured at 2 K for $\text{Mn}_{12}\text{-C}_{18}$.



Fig. S5 Photograph of $\text{Mn}_{12}\text{-C}_{18}/\text{C}_{18}\text{EO}_{10}$ aqueous solution extracted by chloroform and *n*-hexane.

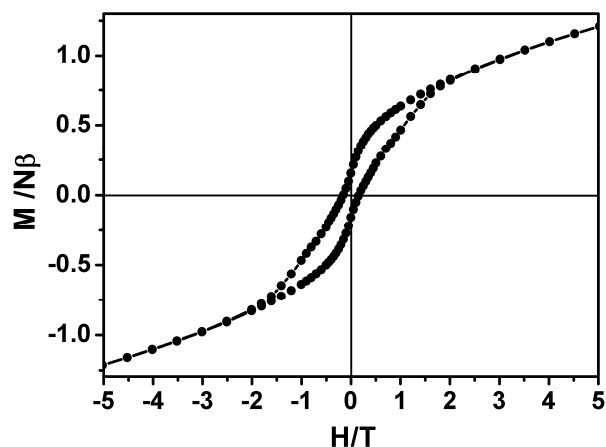


Fig. S6 Magnetization hysteresis loop at 2 K for $\text{Mn}_{12}\text{-C}_{18}/\text{C}_{18}\text{EO}_{10}$ complexes.

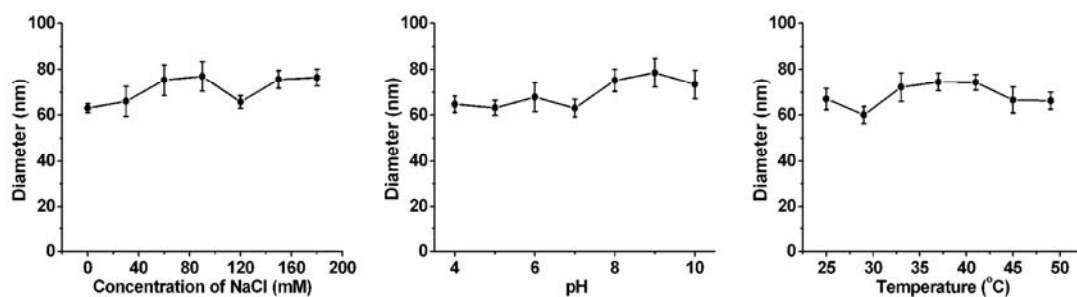


Fig. S7 Plots of hydrodynamic diameter of $\text{Mn}_{12}\text{-C}_{18}/\text{C}_{18}\text{EO}_{10}$ aggregates versus different (a) NaCl concentration, (b) pH conditions, and (c) temperature.

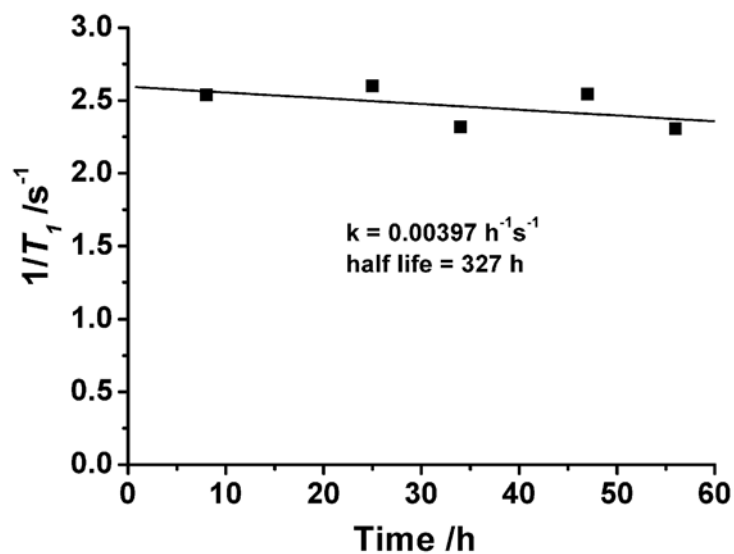


Fig. S8 The longitudinal relaxation rate $1/T_1$ changes against time.