Supporting Information

Experimental

Materials: Ethanol (anhydrous, 99%, was purchased from Sigma-Aldrich (St. Louis, MO). Polybead® Carboxylate Microspheres (2.73% Solids-Late) were purchased from Polysciences, Inc. (Warrington, PA) and separated from water by centrifugation at 4000 RPM for 10 minutes and were allowed to dry overnight. $Mn_{12}O_{12}(O_2CCH_3)_{16}4H_2O$ was synthesized in our lab according to the literature. [9]

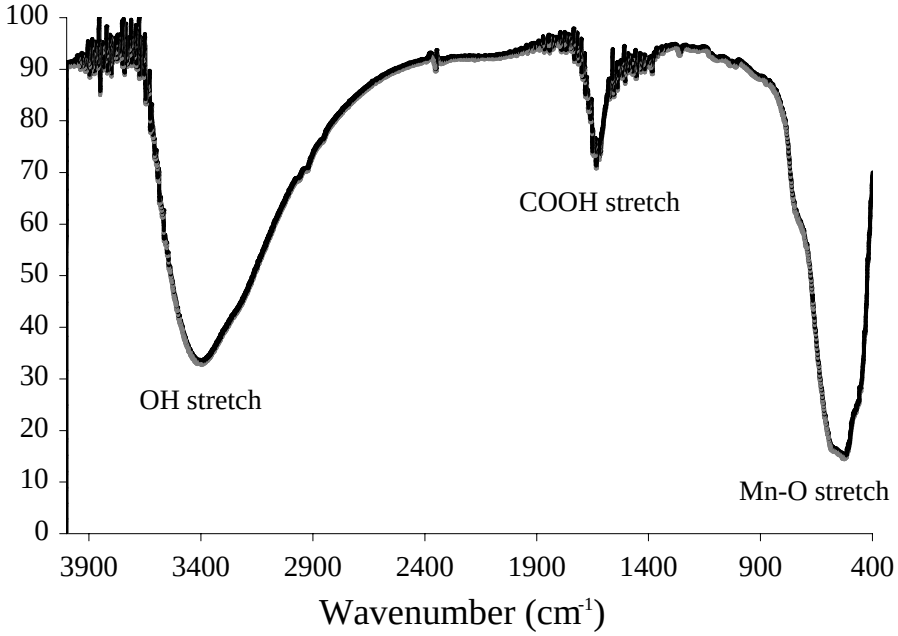
Polystyrene beads coated with $Mn_{12}O_{12}(O_2CCH_3)_{16}$. Dry polystyrene beads were suspended in dry ethanol and soaked for 24 hours prior to surface attachment. A solution of $Mn_{12}O_{12}(O_2CCH_3)_{16}$ in ethanol (2mM) was filtered and added to the ethanolic solution of beads and this mixture was stirred for 2 hours. The Mn-12 coated beads were removed from solution by centrifugation at 4000 RPM for 10 minutes. The beads were washed with ethanol and centrifuged and isolated 3 times. The FTIR of the beads matched that of polystyrene. Based on monolayer coverage (assuming 177 ng/cm^2 from QCM data of thin films), the theoretical [Mn] for 47 nm, 120 nm, 209 nm, 489 nm beads were 7.0%, 3.1%, 1.9% and 0.83% and based on atomic absorption the [Mn] was 1.7 ± 0.1%, 2.3 ± 0.1%, 0.5 ± 0.07% and 0.2 ± 0.04% respectively. The actual concentration of Mn by atomic absorption was used in determining the relaxivity reported. These results were reproduced 4 times, although we do not yet understand why the surface coverage is not linear with surface area.

Characterization. FTIR experiments were recorded in the range 4,000-450 cm^{-1}, from pressed pellets in KBr on a Nicolet FTIR. Atomic absorption was measured using a BUCK Scientific Model 200A Atomic Absorption Spectrophotometer. Instrument detection limits for the AA are calculated to be 0.099 ppm by calculating 3 times the 95% confidence level. A calibration curve was prepared from solutions of Mn(II) acetate in DI H_2O and samples were prepared for analysis by dissolution of surface bound cluster in an aqueous solution of HCl (to remove the polystyrene bead).

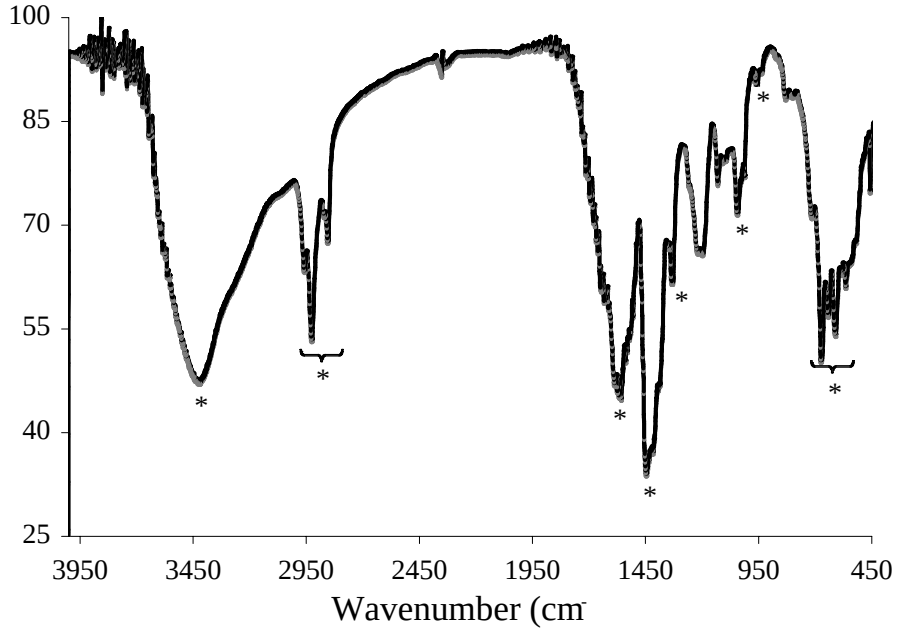
NMR Experiments. Fresh samples for NMR measurements were prepared immediately prior to use. The cluster and the cluster coated beads were dissolved in a solution of 60% acetic acid in D_2O and D_2O, respectively. These solutions were filtered via syringe filter, although no noticeable solid material was present. T_1 measurements were measured using the inversion recovery pulse sequence, in a field of 300 MHz or 500 MHz, at room temperature with a least squares fit to 10 data points. The T_2 was obtained using a conventional spin echo sequence on a 300 MHz spectrometer and using Carr-Purcell-Meiboom-Gill (CPMG) sequence on 500 MHz Bruker spectrometer. Relaxivity was determined from the slope of a plot of $1/T_1$ or $1/T_2$ versus concentration of Mn-12 and Mn-12 coated beads. The cluster concentration was determined by atomic absorption of Mn.

Stability Experiments. The stability of the cluster coated beads was studied by stirring a sample of the beads (20mg) in DI H_2O (10mL) for 24 hours. The solid was removed by centrifugation, and the supernatant was analyzed for Mn content by atomic absorption. No Mn was detected in the supernatant for these experiments.

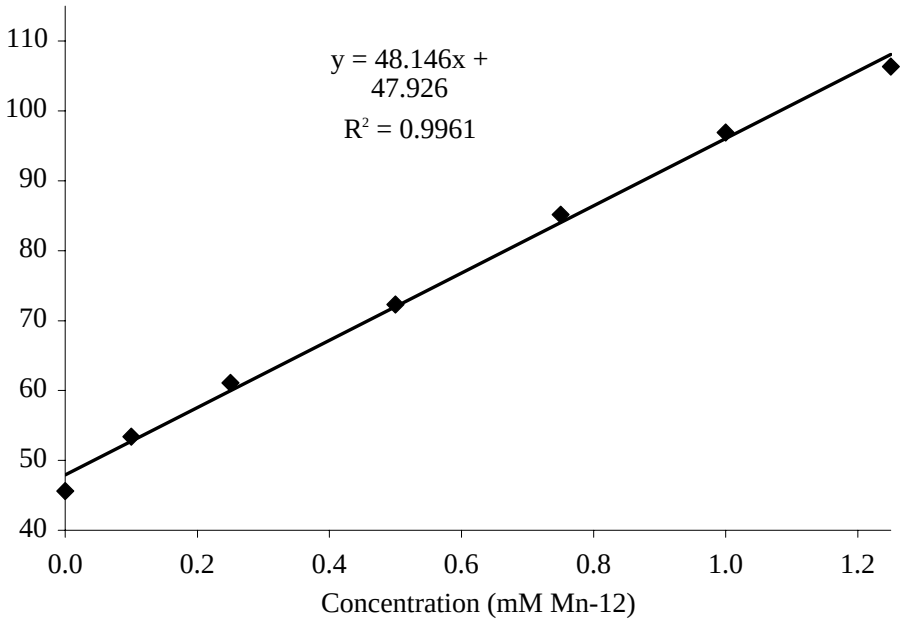
S1. FTIR of precipitate formed from $Mn_{12}O_{12}(Ac)_{16}$ from aqueous solutions. *Although the material is amorphous and it was not possible to obtain a powder X-ray diffraction pattern, the Mn-O, O-H, and COOH peaks are clearly visible.*



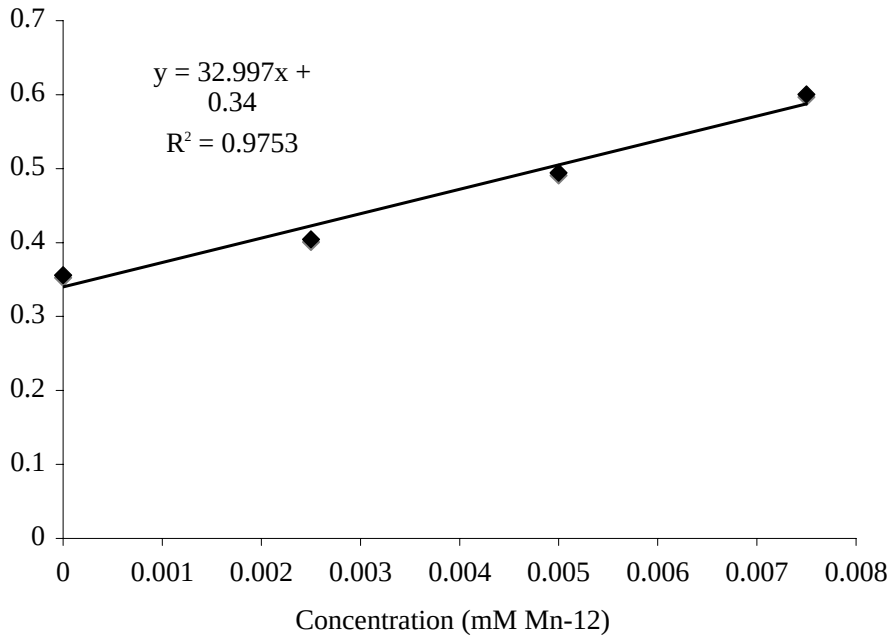
S2. FTIR of Mn-12 re-isolated after dissolution in acetic acid for 24 hours. *The stars (*) indicate peaks that match the literature values for Mn-12 (*see Eppely, *Inorganic Synthesis*; Wiley: NY, 2002, Vol. *33,* 61-66).



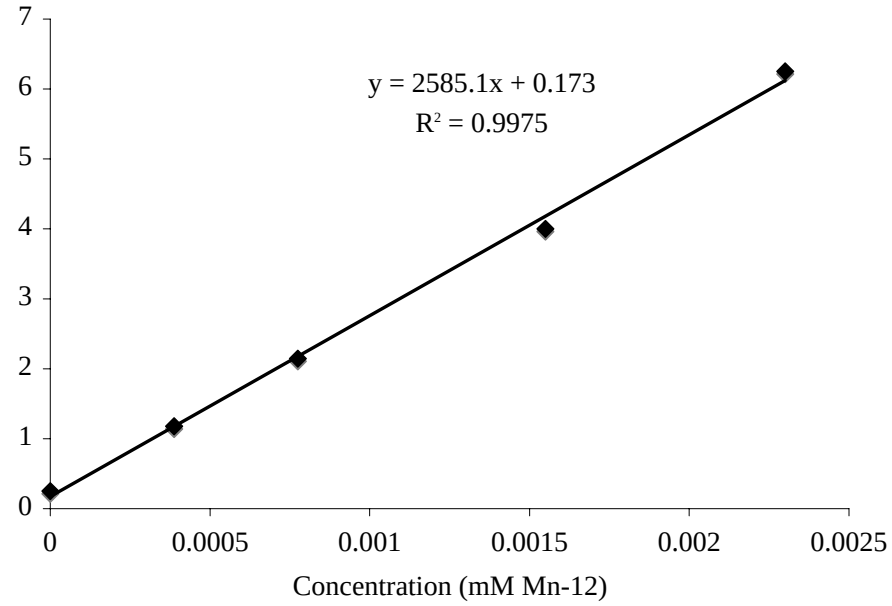
S3. Graph of $1/T_2$ versus concentration for Mn-12 complex in acetic acid (at 500 MHz).



S4. Graph of $1/T_1$ versus concentration for 209 nm Mn-12 coated beads (at 300 MHz).



S5. Graph of $1/T_2$ versus concentration for 209 nm Mn-12 coated beads (at 300 MHz).



S6. Graph of Ln (concentration of surface attached Mn-12) versus time for 209 nm Mn-12 coated beads.