

Quantitative measurement of ligand exchange on iron oxide nanoparticles via radiolabeled oleic acid

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Supporting Information

Nuclear Magnetic Resonance (NMR) was performed to verify the synthesized polymers. Proton NMR was performed using a JEOL 300 MHz NMR instrument. The samples were dissolved in deuterated chloroform and analyzed using 64 scans. The NMR spectra of PEG-COOH and PEG-nitroDOPA are shown below. Peaks for PEG-COOH include 2.65 ppm ($\text{O}=\text{C}-\text{CH}_2-\text{CH}_2-\text{C}=\text{O}$, addition of succinic anhydride), 3.4 ppm ($\text{O}-\text{CH}_3$, methoxy end group), 3.67 ppm ($\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$, PEG). Peaks for PEG-nitroDOPA include 2.65 ppm ($\text{O}=\text{C}-\text{CH}_2-\text{CH}_2-\text{C}=\text{O}$, addition of succinic anhydride), 2.88 and 2.95 ppm (CH_2-CH_2 , DOPA), 3.4 ppm ($\text{O}-\text{CH}_3$, methoxy end group), 3.7 ppm ($\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$, PEG), 8.0 ppm (CH , ring, DOPA).

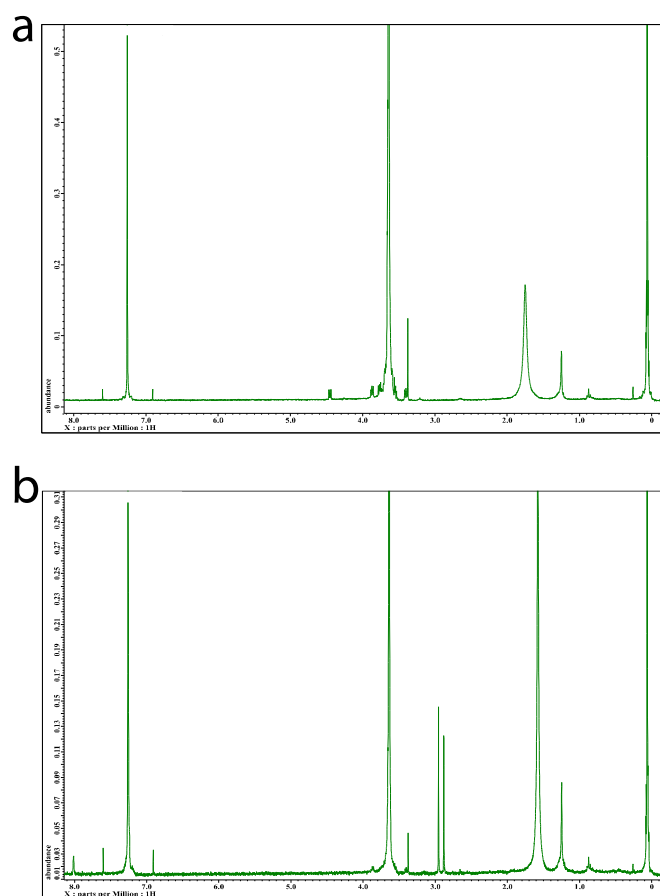


Figure S1. NMR spectra of PEG-COOH (a) and PEG-nitroDOPA (b). The polymers were dissolved in deuterated chloroform with TMS.

The NMR spectra of PEG-Phosphonate and PEG-DOPA are shown below. Peaks for the PEG-Phosphonate include 1.9 ppm ($\text{CH}_2\text{-P(=O)(OH)}_2$), 2.7 ppm ($\text{O=C=CH}_2\text{-CH}_2\text{=C=O}$, addition of succinic anhydride), 4.15 ppm (HO-), 3.4 ppm (O-CH_3 , methoxy end group), 3.7 ppm ($\text{O-CH}_2\text{-CH}_2\text{-O}$, PEG). Peaks for the PEG-DOPA include 2.65 ppm ($\text{O=C=CH}_2\text{-CH}_2\text{=C=O}$, addition of succinic anhydride), 2.9 and 2.95 ppm ($\text{CH}_2\text{-CH}_2$, DOPA), 3.4 ppm (O-CH_3 , methoxy end group), 3.65 ppm ($\text{O-CH}_2\text{-CH}_2\text{-O}$, PEG), 8.0 ppm (CH , ring, DOPA).

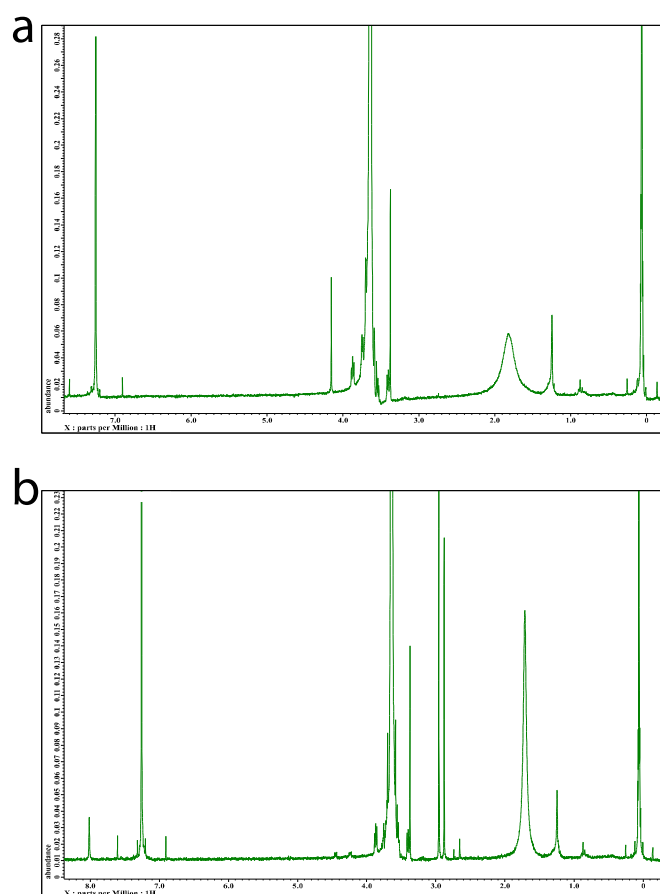


Figure S2. NMR spectra of PEG-Phosphonate (a) and PEG-DOPA (b). The polymers were dissolved in deuterated chloroform with TMS.

The NMR spectra for PEG-NH₂ is shown below. Peaks for PEG-Phosphonate include 2.4 ppm (CH₂-NH₂, protons next to amine end group), 3.3 ppm (CH₂-OH, protons next to hydroxyl end group), and 3.7 ppm (O-CH₂-CH₂-O, PEG).

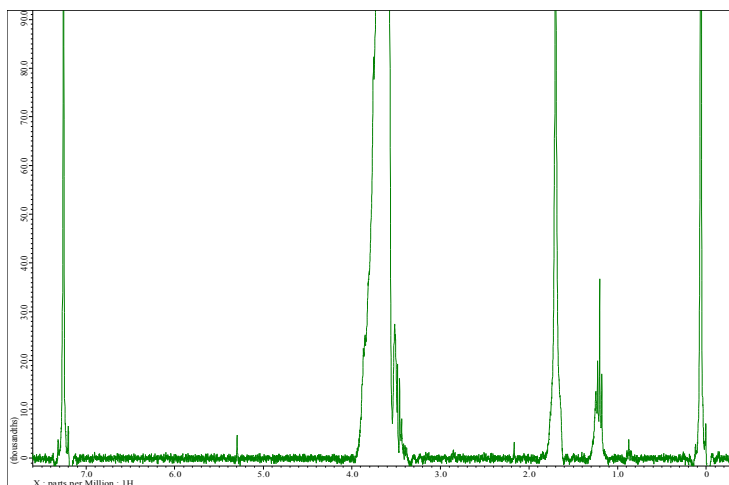


Figure S3. NMR spectra of PEG-NH₂. The polymer was dissolved in deuterated chloroform.

TGA curves of the unlabeled, unmodified, oleic acid coated nanoparticles are shown below. The nanoparticles before dialysis (a) showed a weight loss of 59.85%, and the nanoparticles after dialysis showed a 51.21% weight loss. This indicates that the dialysis in chloroform was not successful in removing any excess oleic acid that may be present on the surface of the nanoparticles. The increase in weight loss after dialysis can be attributed to manual step analysis of the curves via the TGA software.

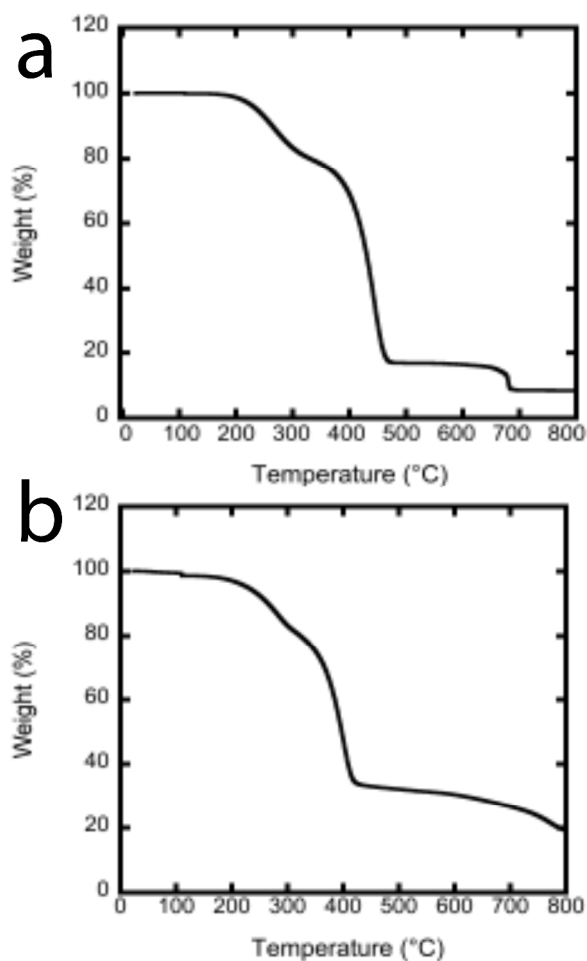


Figure S4. TGA curves of unlabeled, oleic acid coated iron oxide nanoparticles before dialysis (a) and after dialysis in chloroform (b). The samples were heated to 800°C.

TGA curves of the PEG-nitroDOPA and PEG-DOPA coated nanoparticles are shown below. The TGA of the PEG-nitroDOPA modified nanoparticles revealed a 74.17% weight loss. The TGA of the PEG-DOPA modified nanoparticles revealed a 90.34% weight loss. This data corresponds well to the trend seen in the LSC data.

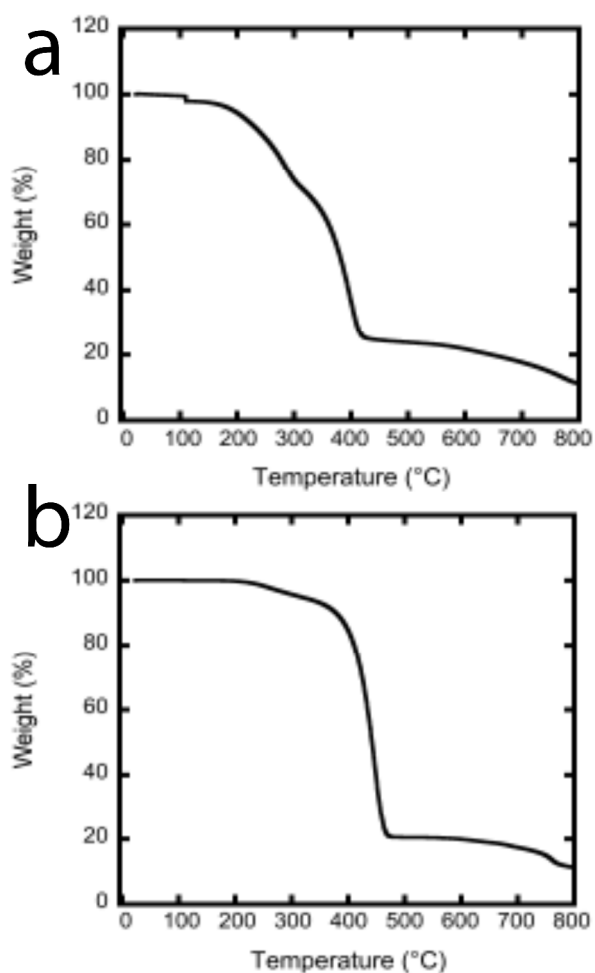


Figure S5. TGA curves of PEG-nitroDOPA modified nanoparticles (a) and PEG-DOPA modified nanoparticles (b). The samples were heated to 800°C.

TGA curves of the PEG-Phosphonate and PEG-COOH coated nanoparticles are shown below. The TGA results reveal a 76.86% weight loss for the PEG-Phosphonate nanoparticles and a 37.87% loss for the PEG-COOH particles. This data agrees with the trend in surface coverage of oleic acid as determined by LSC.

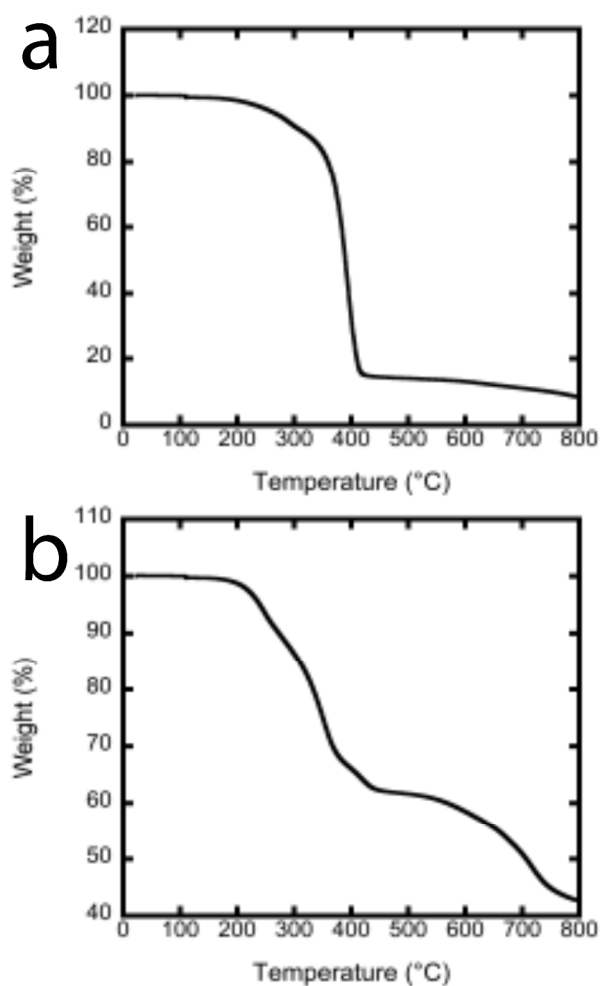


Figure S6. TGA curves of PEG-Phosphonate modified nanoparticles (a) and PEG-COOH modified nanoparticles. The samples were heated to 800°C.

The TGA curve of the PEG-NH₂ coated particles is shown below. The results reveal a weight loss of 40.17%. This weight loss is much lower indicating poor surface coverage of the PEG ligand.

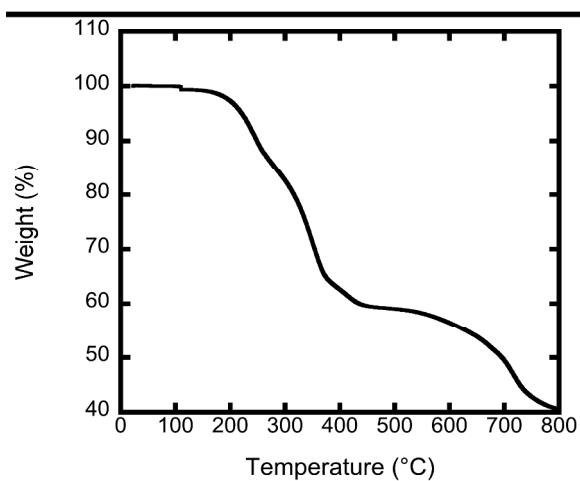


Figure S7. TGA curve of PEG-NH₂ modified nanoparticles. The sample was heated to 800°C.

TGA curves of the unlabeled, unmodified, oleic acid coated nanoparticles and iron oleate precursor are shown below. The nanoparticles passed through the GPC column (a) showed a weight loss of 35.79%. This illustrates that the GPC column was more useful than dialysis in removing much of the excess oleic acid on the surface of the nanoparticles. The TGA curve of the iron oleate reveals a weight loss between 200°C and 300°C. This same weight loss or step transition can be seen in the oleic acid coated particles indicating the presence of residual iron oleate from synthesis.

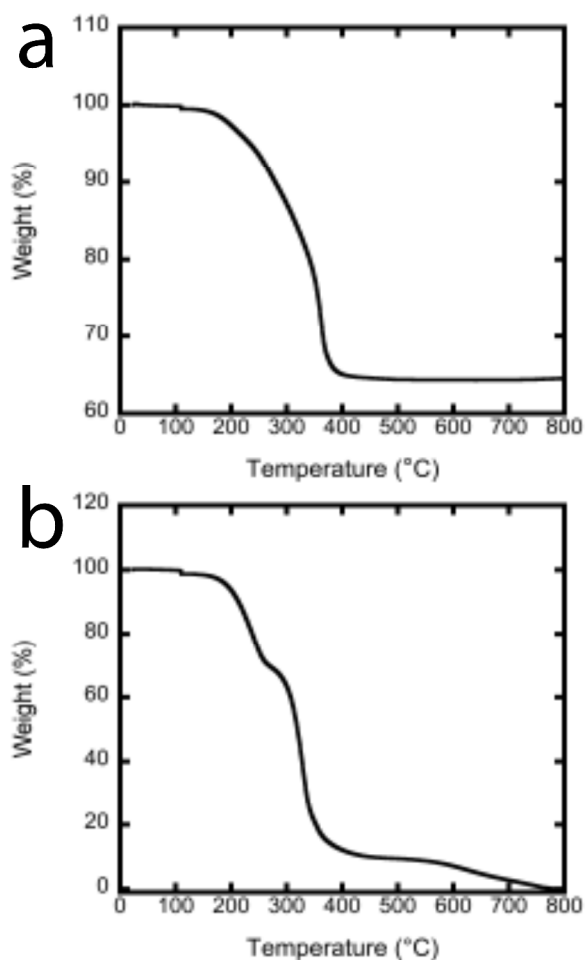


Figure S8. TGA curve of unlabeled, oleic acid coated iron oxide nanoparticles passed through a GPC column (a) and iron oleate precursor (b). The samples were heated to 800°C.

VSM was performed to verify that the nanoparticles are magnetic and to understand their magnetic behavior. The figure below shows a hysteresis loop across a 3T field (large loop) and a smaller loop to indicate coercivity, which is below the sensitivity of the instrument. The saturation magnetization observed is 66.85 emu/g.

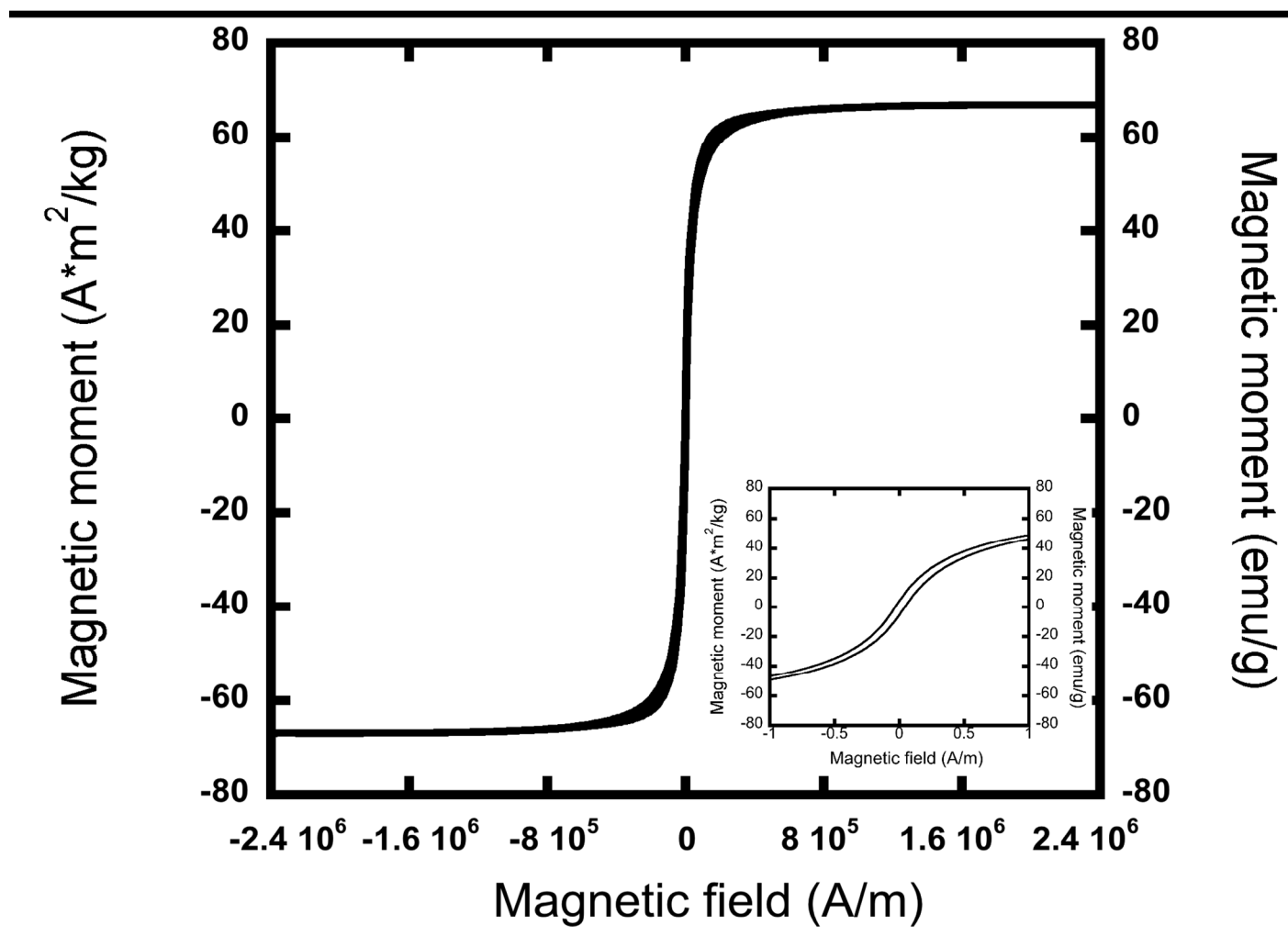


Figure S9. Hysteresis loop of the unlabeled nanoparticles. Magnetic moment is measured in SI units of $A \cdot m^2/kg$ of magnetite as determined by ICP-MS.