

Supporting Information for

**Aptamer-conjugated Mn₃O₄@SiO₂ Core-Shell Nanoprobes for Targeted
Magnetic Resonance Imaging**

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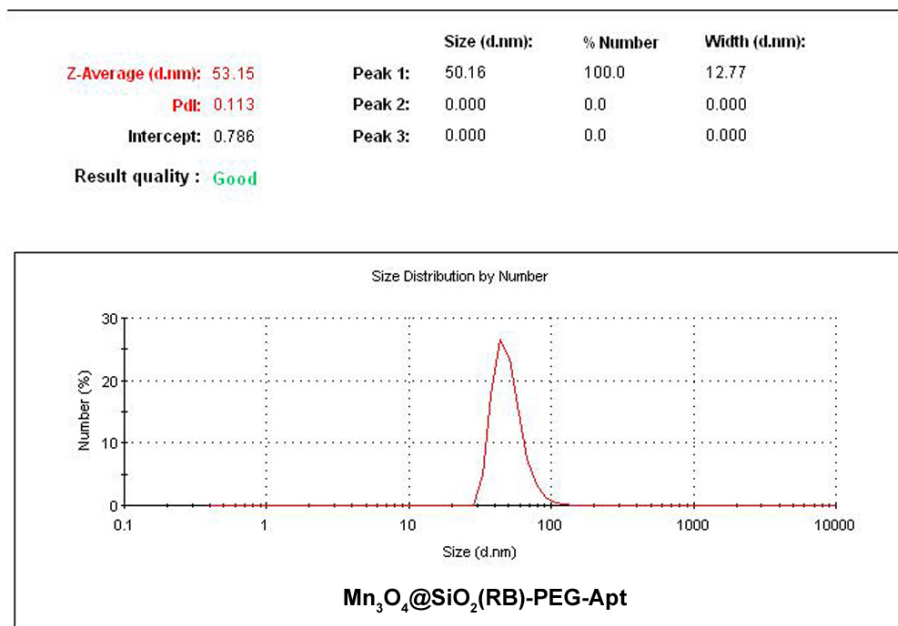
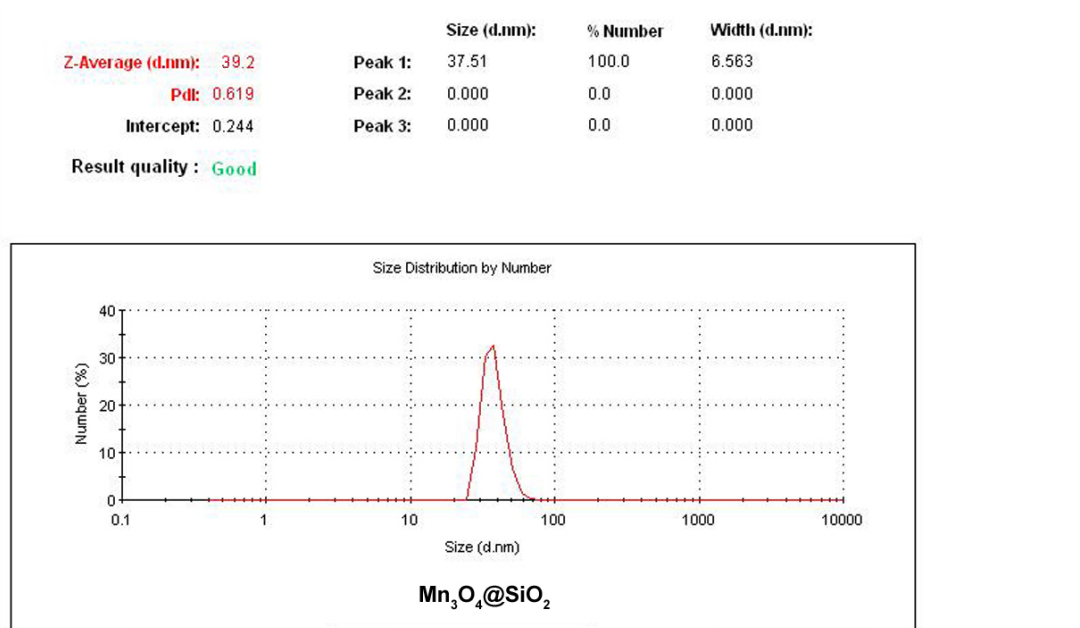


Figure S1. The effective hydrodynamic diameter of the core-shell Mn₃O₄@SiO₂ and Mn₃O₄@SiO₂(RB)-PEG-Apt measured by dynamic light scattering (DLS).

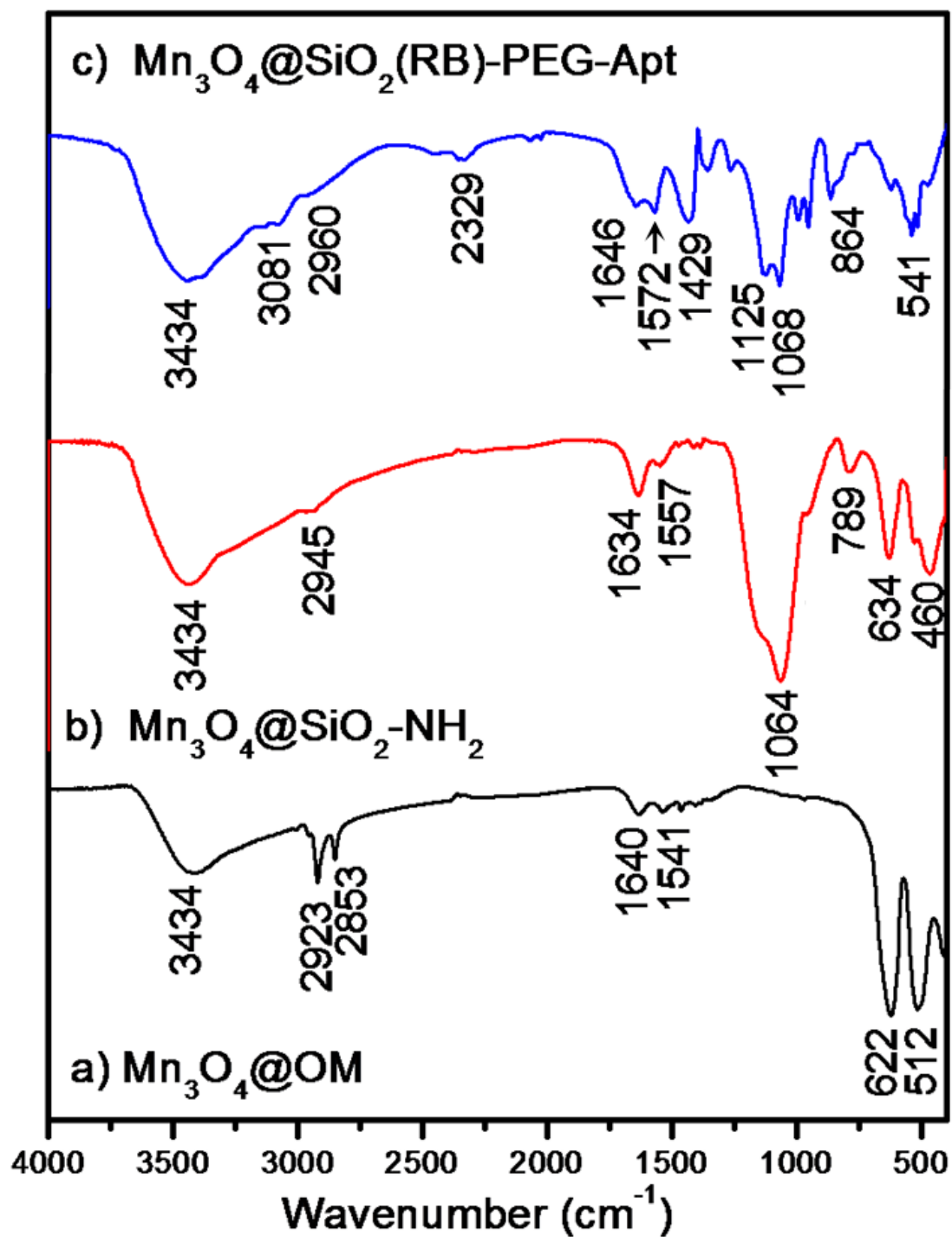


Figure S2. FTIR spectra of A) Mn₃O₄ NPs, B) Mn₃O₄@SiO₂-NH₂ core-shell nanocomposites and c) Mn₃O₄@SiO₂(RB)-PEG-Apt.

The broad band at around $\nu = 3434 \text{ cm}^{-1}$ corresponds to the -N-H and O-H stretching vibrations are observed from the as-prepared sample. As shown in Figure S2a, the peaks at 2923 and 2853 cm^{-1} are assigned to the asymmetric (ν_{as}) and symmetric (ν_s) stretching vibrations of methylene (-CH_2) in the long alkyl chain of OM. The peaks at 1640 , 1541 , 622 , and 512 cm^{-1} should be attributed to the Mn-N or Mn-O absorption band. After silica coating (Figure S2b), the strong and broad band in the range of $1230 \sim 1010 \text{ cm}^{-1}$ and a relative weak peak at 460 cm^{-1} , corresponding to the Si-O-Si asymmetric (ν_{as}) stretching vibration from the SiO_2 matrix. The transmission bands at $\nu = 2945$, 789 , and 634 cm^{-1} assign to the asymmetric (ν_{as}) and symmetric (ν_s) stretching vibrations of methylene (CH_2) from the hydrolysis and condensation of $\text{-Si-(CH}_2)_2\text{-NH}_2$ of APTES, respectively. The characteristic absorption peak at 1634 cm^{-1} can be assigned to N-H deformation vibrations. After the core-shell nanoparticle further conjugated with RBITC, PEG and Aptamer (Figure S2c), the large amount of organic ligands on the surface of the NPs resulting the stretching vibrations of methylene (CH_2) (around $\nu = 3081$, 2960 , and 864 cm^{-1}) increased dramatically. the new peaks at $\nu = 2329$, 1646 , 1572 and 1640 cm^{-1} attributed to the vibration of imide-bond appear in aptamer molecular and formation between the amines and carboxylic acid of PEG. the strong and broad band in the range of $1230 \sim 1010 \text{ cm}^{-1}$ is slightly different from the silica coated Mn_3O_4 NPs is due to the overlap of the C-O-C stretching vibration from the PEG and Si-O-Si asymmetric (ν_{as}) stretching vibration from the SiO_2 matrix.

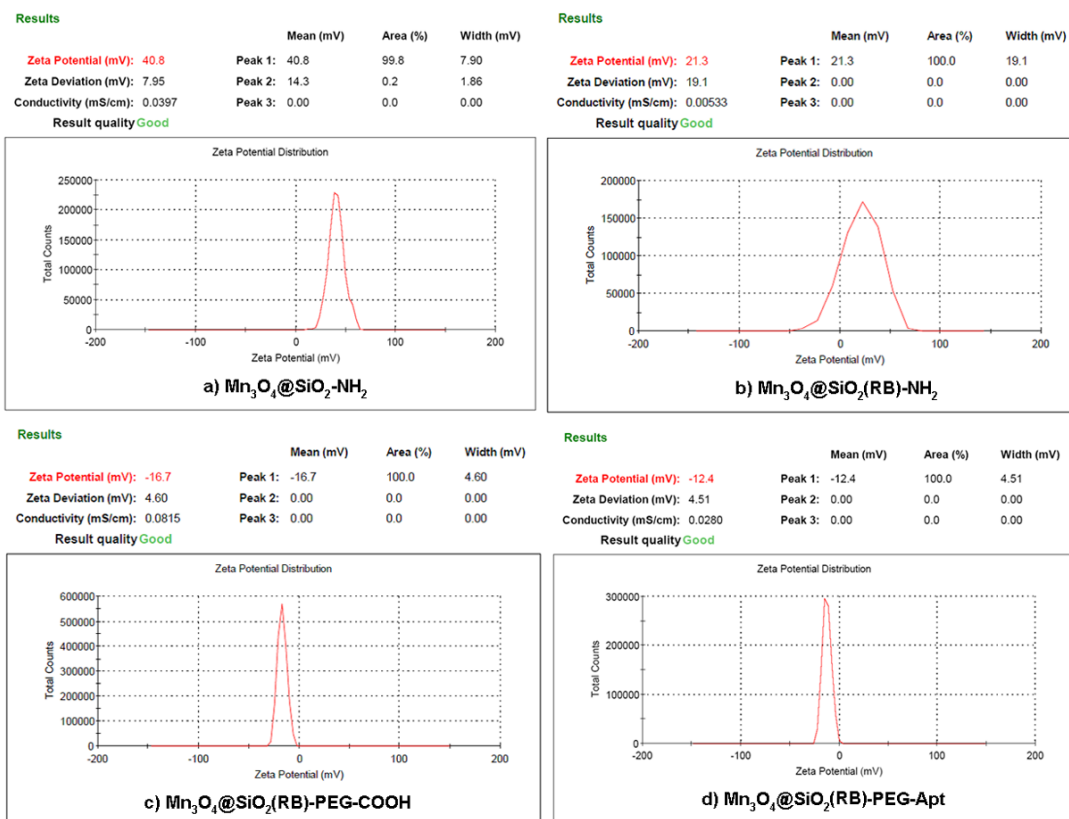


Figure S3. The surface zeta potential of a) Mn₃O₄@SiO₂-NH₂, b) Mn₃O₄@SiO₂(RB)-NH₂, c) Mn₃O₄@SiO₂(RB)-PEG-COOH, d) Mn₃O₄@SiO₂(RB)-PEG-Apt.

As well known, the surface zeta potential of pure SiO₂ hollow spheres was about -49 mV, while the amine-functionalized Mn₃O₄@SiO₂ core-shell nanocomposites were increased to +40.8 mV, and the value was reduced to +20.3 mV after one-third of amines conjugated with RBITC, and the value was reduced to -16.7 mV after PEG-COOH conjugated with the remaining amines. After formation of the final Mn₃O₄@SiO₂(RB)-PEG-Apt products, the zeta potential was -12.4 mV.

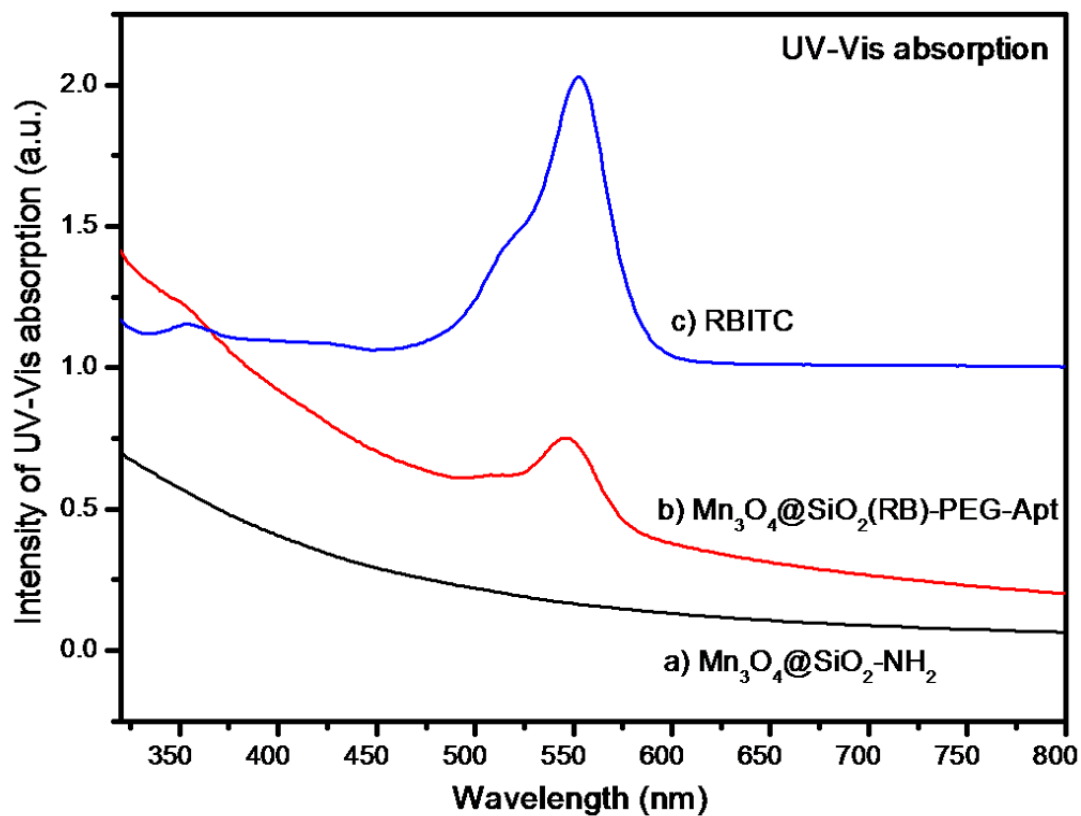


Figure S4. UV-vis spectra of A) $\text{Mn}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$ nanocomposites, B) $\text{Mn}_3\text{O}_4@\text{SiO}_2(\text{RB})\text{-PEG-Apt}$ and C) pure RBITC in PBS buffer. It is clear that $\text{Mn}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$ nanocomposites do not show any prominent absorption peaks, and the characteristic bands at 550 nm correspond to the absorption of the dye Rhodamine B.

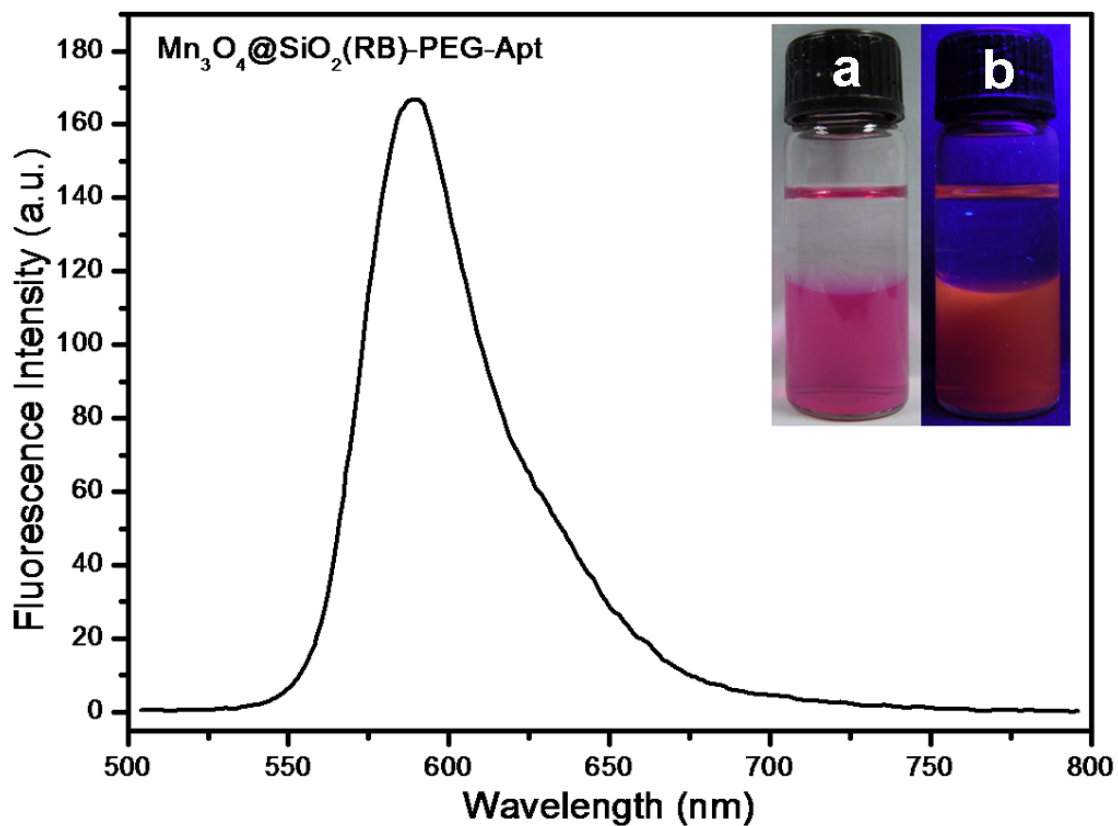


Figure S5. The room temperature photoluminescence (PL) spectra of $\text{Mn}_3\text{O}_4@\text{SiO}_2(\text{RB})\text{-PEG-Apt}$ with concentration of $100 \mu\text{g mL}^{-1}$ in aqueous excited at 488 nm. Insets: visual photographs of $\text{Mn}_3\text{O}_4@\text{SiO}_2(\text{RB})\text{-PEG-Apt}$ nanocomposites in a) PBS at the bottom (hexane at the upper layer), and the b) red emission of Rhodamine B under the 365nm portable UV lamp excitation.

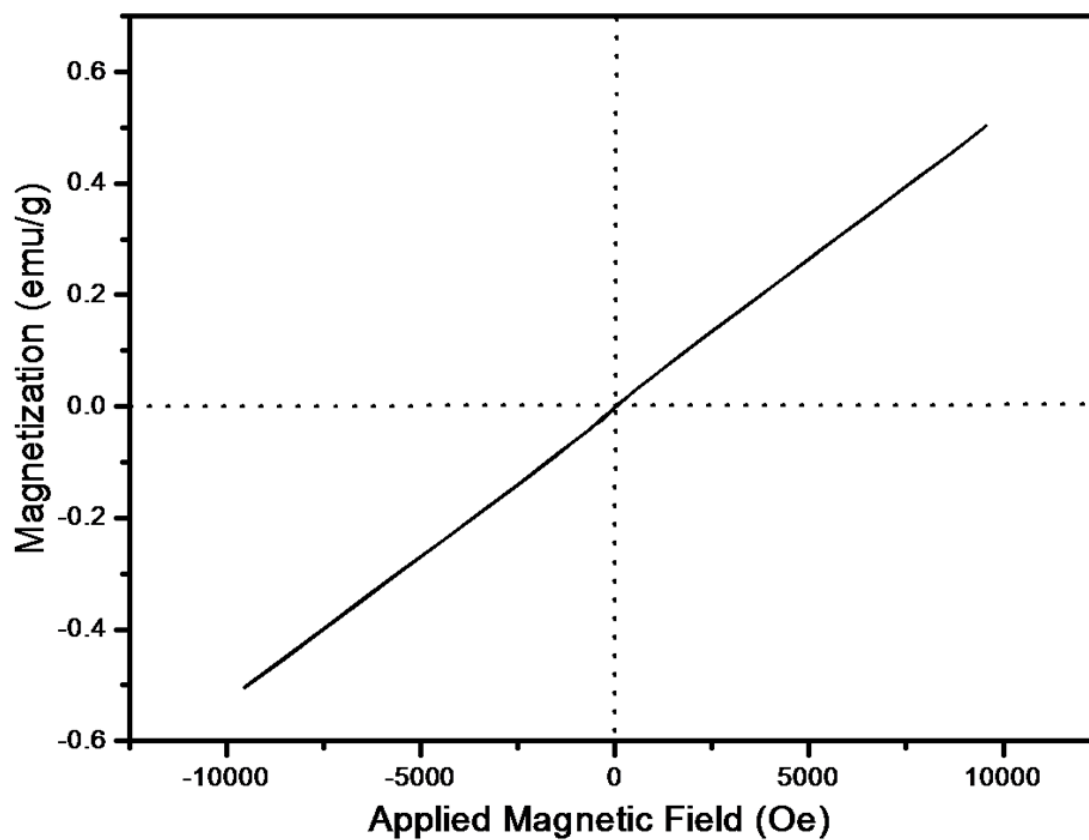


Figure S6. Hysteresis loops of $\text{Mn}_3\text{O}_4@\text{SiO}_2(\text{RB})\text{-NH}_2$ NPs at $T = 300$ k. They were paramagnetic at room temperature.

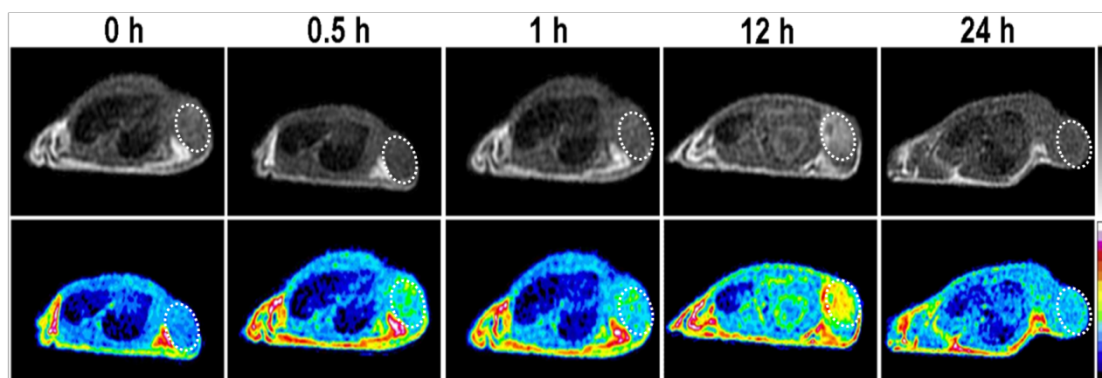


Figure S7. The target group of T_1 -weight MR images of a tumor bearing mouse model (inoculated with HeLa cells) injected with $\text{Mn}_3\text{O}_4@\text{SiO}_2(\text{RB})\text{-PEG-Apt}$ NPs, obtained at pre, 0.5, 1, 12, and 24 h post-injection. The upper panel shows the black and white images, the bottom panel shows the colored images (the color bar changing from black to white indicates the gradual increase in MR signal intensity).

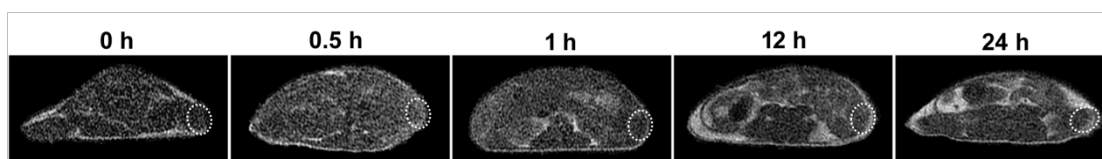


Figure S8. The control group of T_1 -weight MR images of a tumor bearing mouse model (inoculated with HeLa cells) injected with $\text{Mn}_3\text{O}_4@\text{SiO}_2(\text{RB})\text{-PEG}$ NPs, obtained at pre, 0.5, 1, 12, and 24 h post-injection. There were nearly no contrast enhancement in tumor throughout the observation time.