Supporting Information

Multiresponsive Nanoprobes for Turn-On Fluorescence/^{19}F-MRI Dual-Modal Imaging

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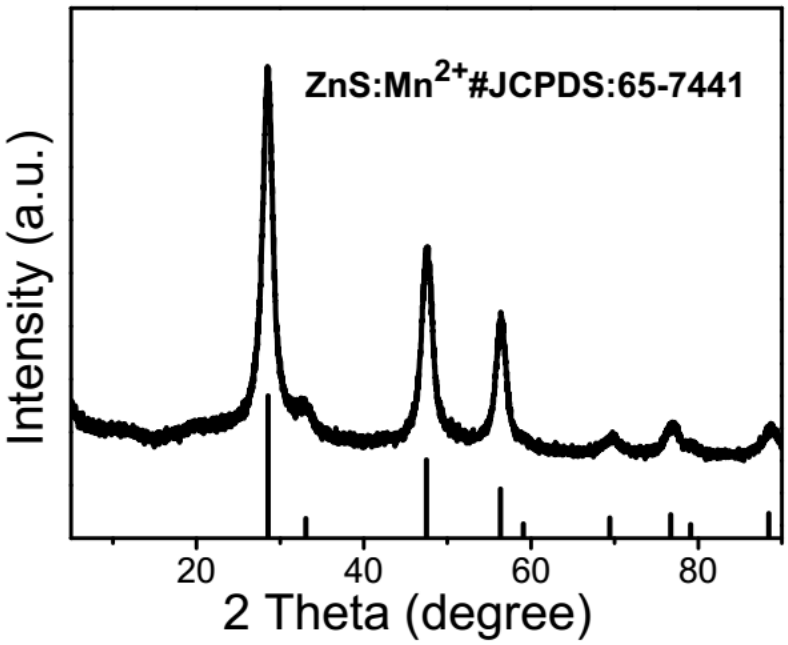


Figure S1. XRD pattern of ZnS:Mn^{2+} QDs.

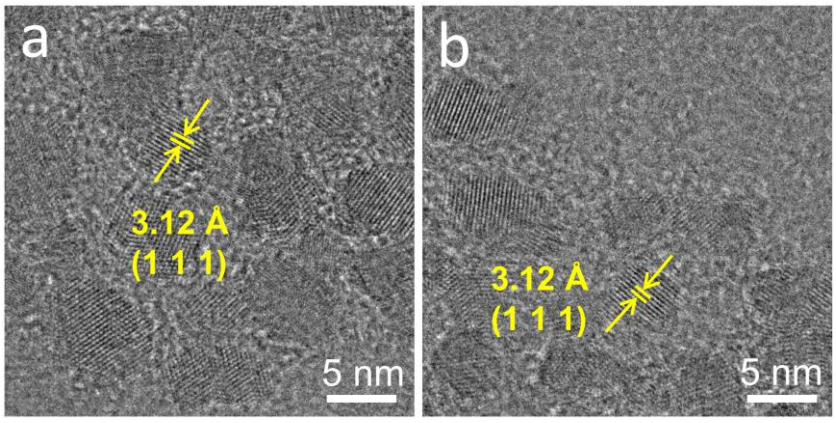


Figure S2. HRTEM images of ZnS:Mn^{2+}-F-$Mn(OA)_2$@PSI_{OAm} nanoprobe before (a) and after (b) reaction with GSH (10 mM, at pH 6.0).

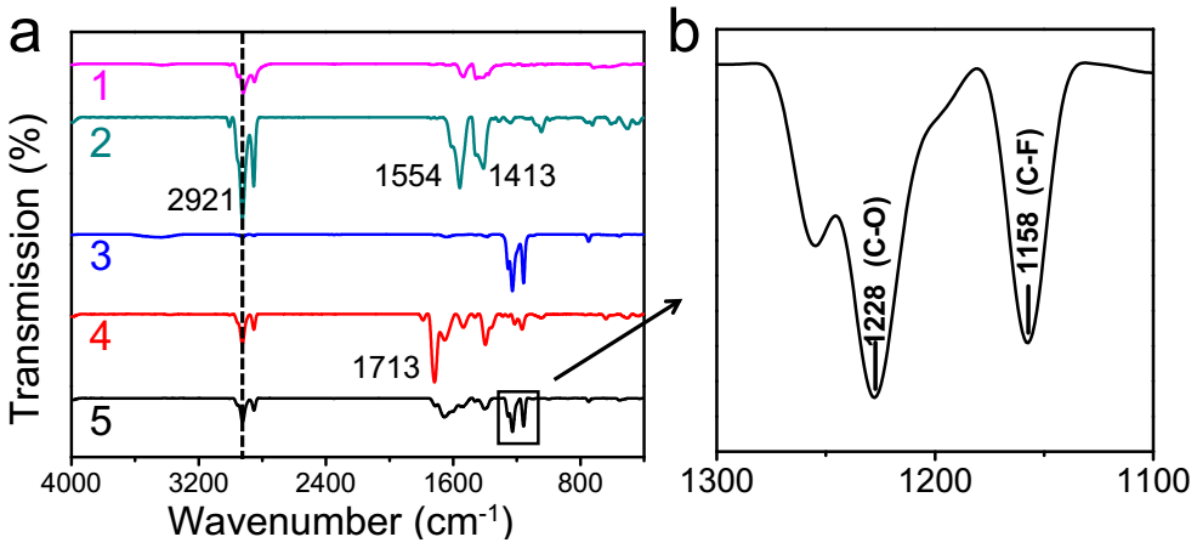


Figure S3. FT-IR spectra of different materials (1. ZnS:Mn^{2+} QDs, the ligand is oleic acid; 2. $Mn(OA)_2$; 3. PFCE; 4. PSI_{OAm}; 5. ZnS:Mn^{2+}-F-$Mn(OA)_2$@PSI_{OAm}).

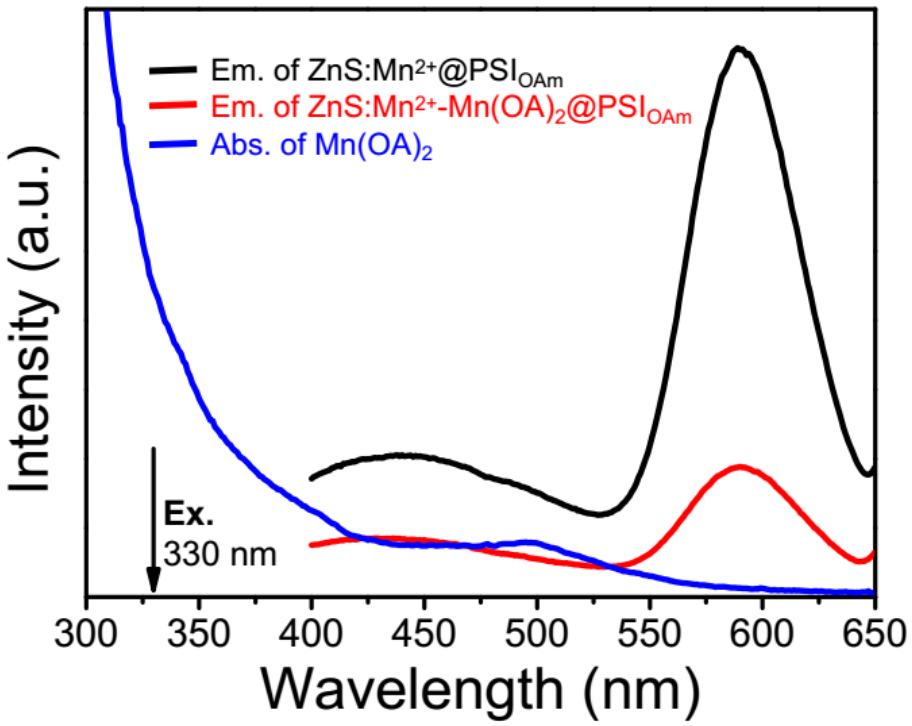


Figure S4. UV-Vis absorption spectrum of $Mn(OA)_2$, fluorescence spectra of ZnS:Mn^{2+}@PSI_{OAm} and ZnS:Mn^{2+}-$Mn(OA)_2$@PSI_{OAm}, respectively. Ex = 330 nm.

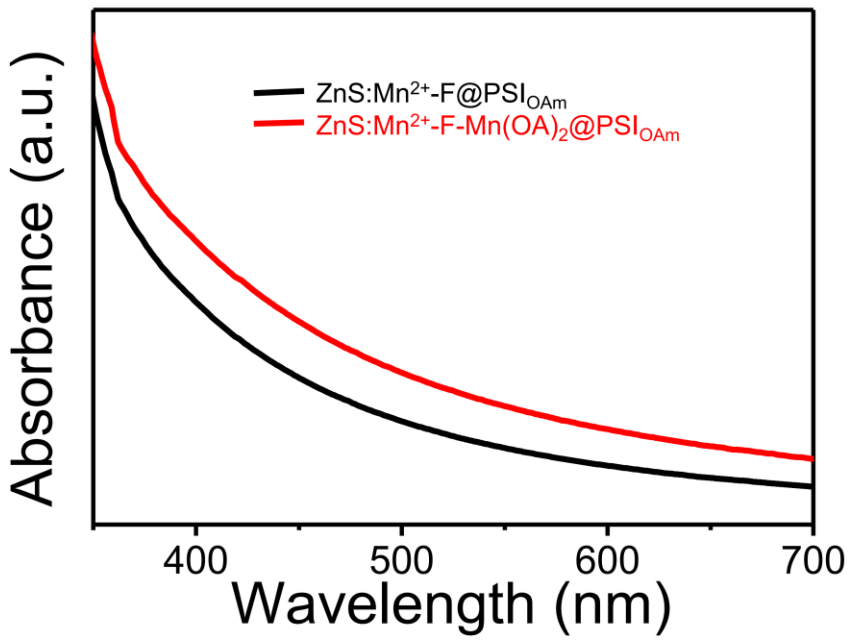


Figure S5. UV-Vis absorption spectra of ZnS:Mn^{2+}-F@PSI_{OAm} and ZnS:Mn^{2+}-F-$Mn(OA)_2$@PSI_{OAm}.

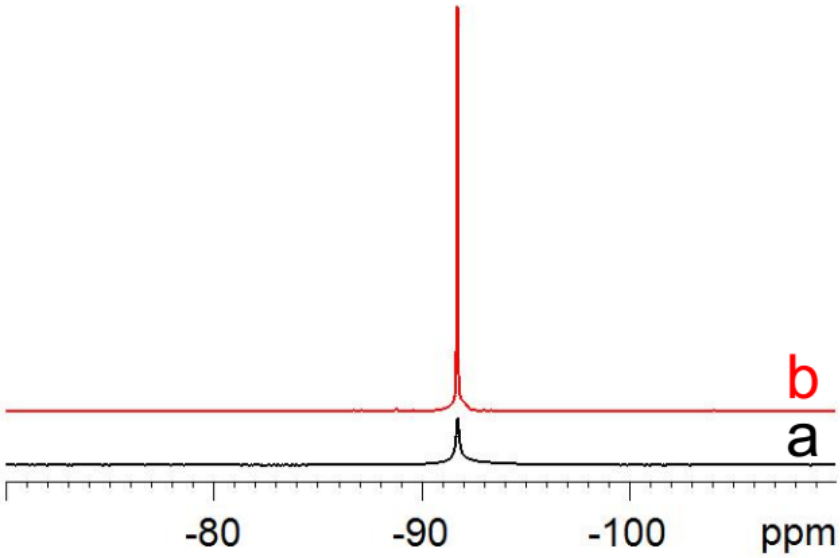
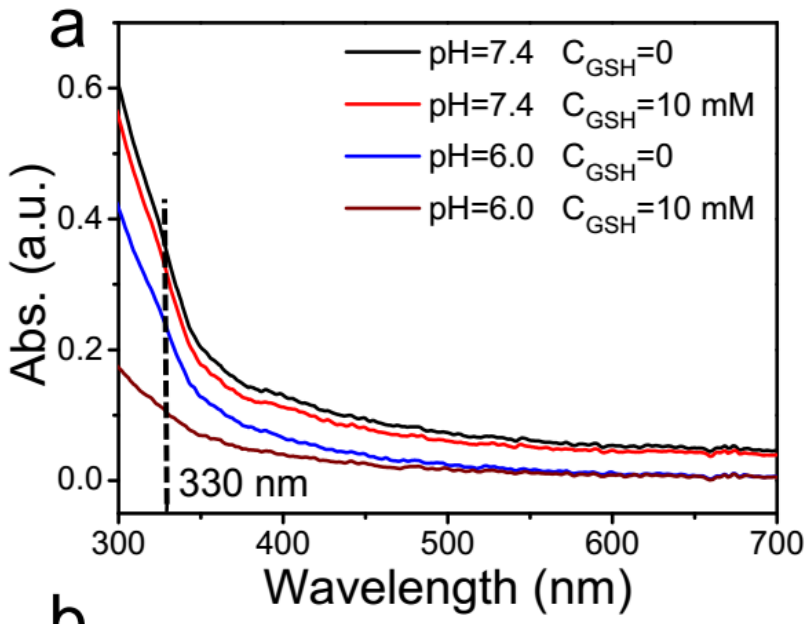


Figure S6. ^{19}F NMR spectra of ZnS:Mn^{2+}-F-$Mn(OA)_2$@PSI_{OAm} aqueous solution before (a) and after (b) reaction with GSH (10 mM) at pH 6.0, respectively.



b

Conditions	pH=7.4 C_{GSH}=0	pH=7.4 C_{GSH}=10 mM	pH=6.0 C_{GSH}=0	pH=6.0 C_{GSH}=10 mM
C_{Mn}/ppm	0.85	0.46	0.26	16.67

Figure S7. UV-Vis absorption spectra of ZnS-$Mn(OA)_2$@PSI_{OAm} colloidal solution at different conditions (a) and ICP-OES measurements of the Mn content (b) in the supernatants accordingly.

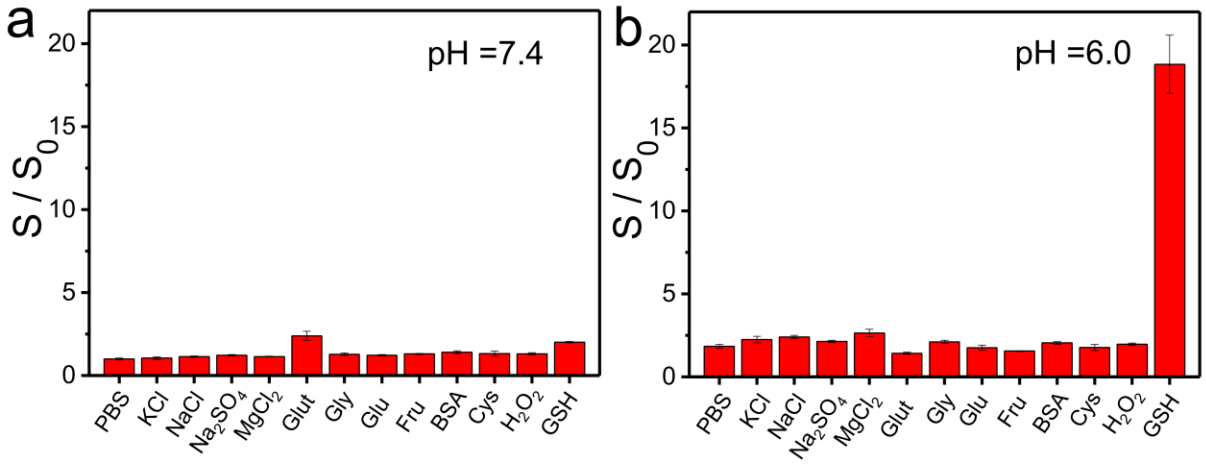


Figure S8. ^{19}F NMR response (relative intensity, S/S_0) of ZnS:Mn^{2+}-F-$Mn(OA)_2$@PSI_{OAm} toward various interference species under pH 7.4 (a) and pH 6.0 (b), respectively. The concentration of bovine serum albumin (BSA) was 1.0 mg/mL, the others were 10 mM. Glut, Gly, Glu, Fru, and Cys refer to glutamic acid, glycine, glucose, fructose, and cysteine, respectively. For each group, three independent parallel experiments were carried out (n = 3).

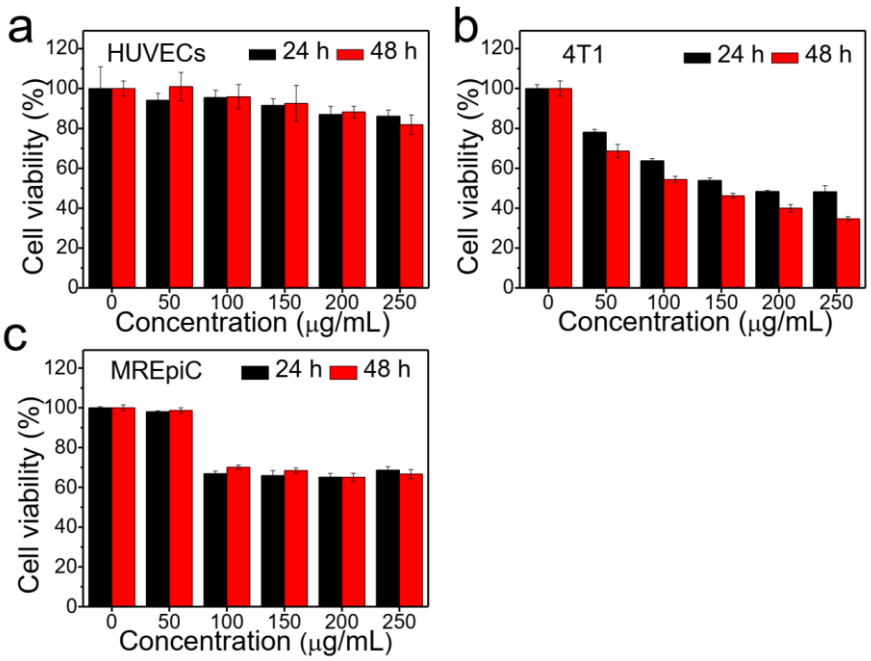


Figure S9. Cytotoxicity tests of ZnS:Mn^{2+}-F-$Mn(OA)_2$@PSI_{OAm} colloids after incubation with HUVECs cells (a), 4T1 cells (b) and MREpiC cells (c) for 24 h and 48 h, respectively. For each concentration level, six independent parallel experiments were carried out (n = 6).

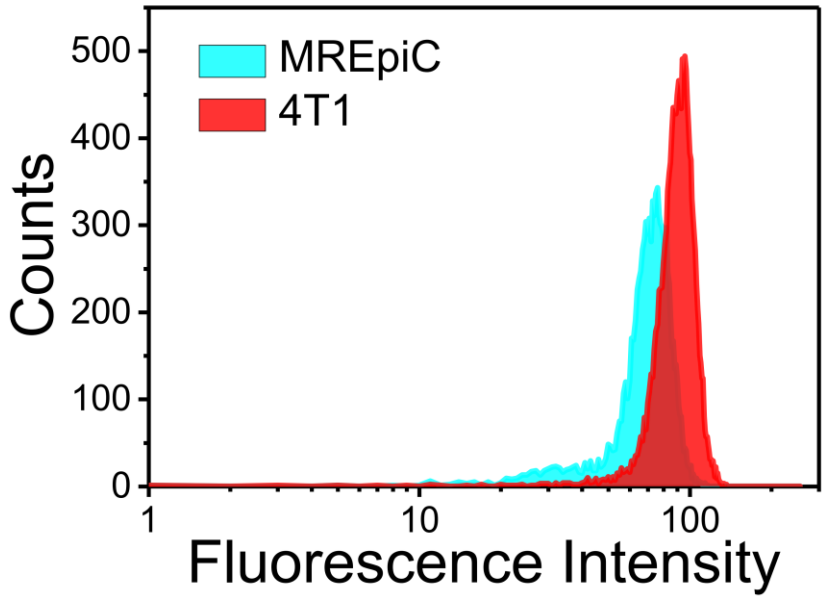


Figure S10. Flow cytometry analysis of MREpiC and 4T1 cells incubated with ZnS:Mn^{2+}-F-NLR-$Mn(OA)_2$@PSI_{OAm} for 4 h. The excitation and emission wavelengths were 488 nm and 630 nm, respectively. (Note: Nile red (NLR) loading was required because its excitation wavelength (~480 nm) also lies in the range of the absorption of $Mn(OA)_2$, meanwhile suitable for FC analysis).

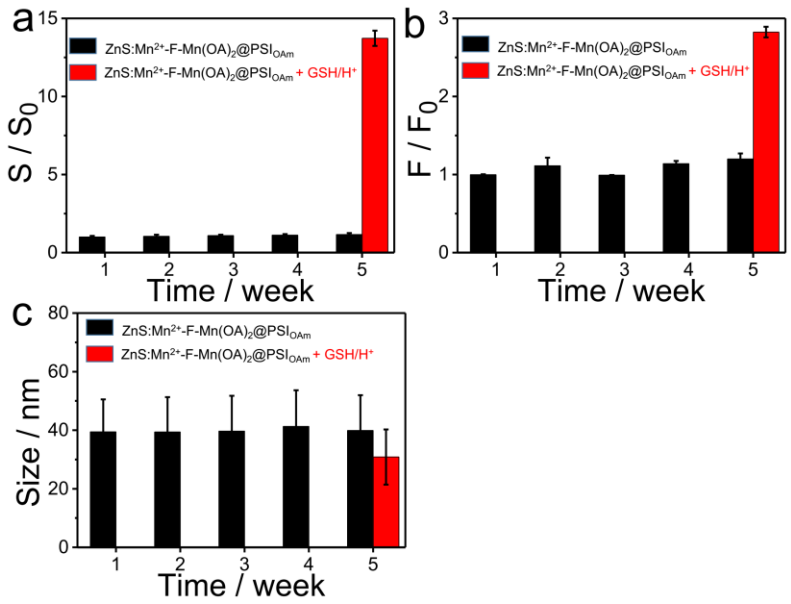


Figure S11. Stability evaluation of ZnS:Mn^{2+}-F-$Mn(OA)_2$@PSI_{OAm} colloids by observing the evolution of ^{19}F MR signal (a), fluorescence (b) and DLS size (c) versus time, respectively. S_0 and F_0 refer to ^{19}F MR signal and fluorescence intensity of the first measurement, namely, the freshly prepared sample solution (pH 7.4). For each measurement, 400 μL of the sample solution was mixed with 500 μL of PBS buffer solution with different pH values (pH 6.0 for GSH groups, otherwise pH = 7.4). C_{GSH} = 10 mM. For each time interval, three independent parallel experiments were carried out (n = 3).

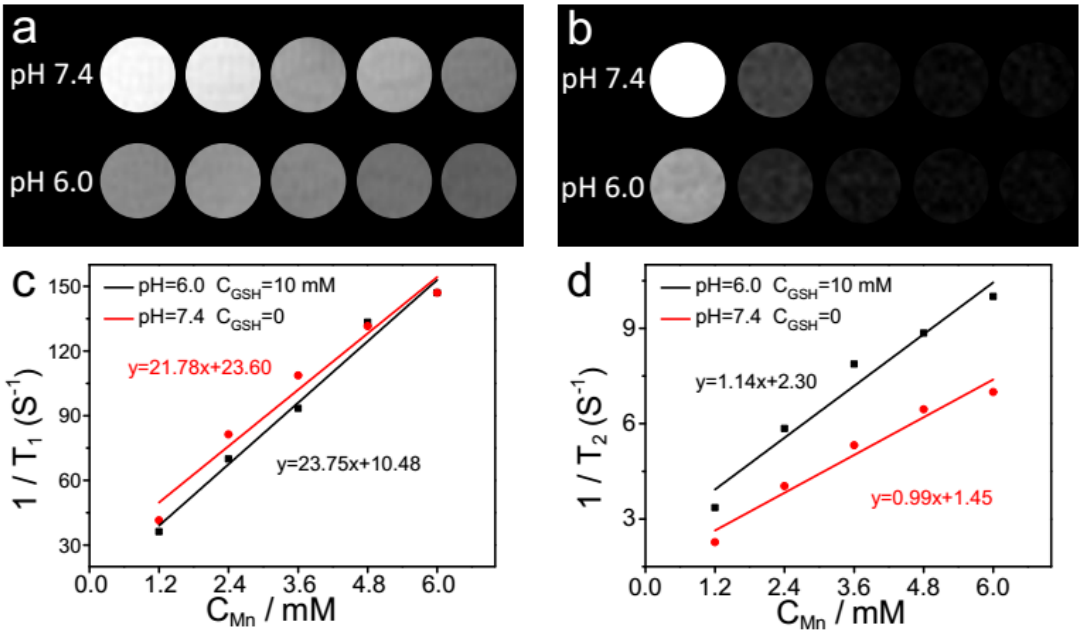


Figure S12. T_1-weighted (a) and T_2-weighted (b) ^1H MR imaging of ZnS:Mn^{2+}-F-$Mn(OA)_2$@PSI_{OAm} with different concentrations diluted from samples under pH 7.4, C_{GSH} = 0, and pH 6.0, C_{GSH} = 10 mM, respectively. The corresponding longitudinal (c) and transverse (d) relaxation rate evolution profile versus concentration of total Mn.

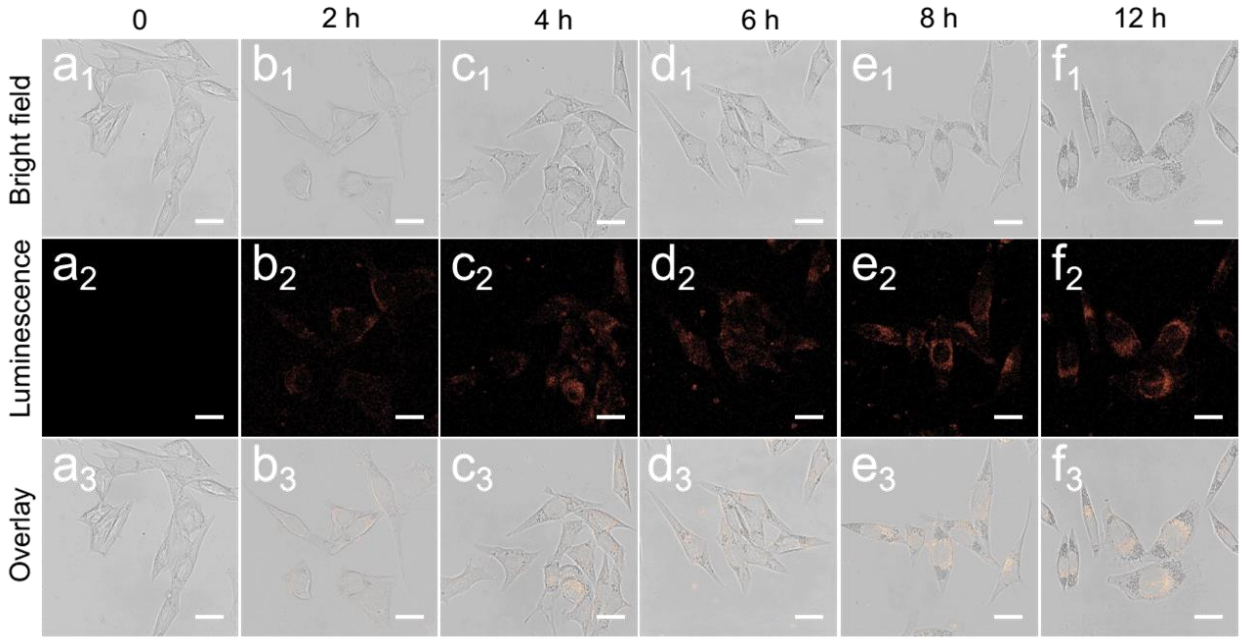


Figure S13. Fluorescence images of 4T1 cells cultured with ZnS:Mn^{2+}-F-$Mn(OA)_2$@PSI_{OAm} nanoprobes for different time. The scale bars in the figure are 25 μm.