Supplementary Information

For

Magnetic nanomaterials with near-infrared pH-activatable fluorescence via iron-catalyzed AGET ATRP for tumor acidic microenvironment imaging†

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Fig. S1 Structures of benzo[a]phenoxazine-dotted Fe₃O₄@SiO₂@PPEGMA₄₇₅-co-PAA@Oxazine MNPs.

Fig. S2 XPS spectra of MNPs of (a) Fe₃O₄@SiO₂-NH₂, (b) Fe₃O₄@SiO₂-Br and (c) Fe₃O₄@SiO₂@PPEGMA₄₇₅-co-PtBA.
Fig. S3 XPS C 1s core-level spectra of Fe₃O₄@SiO₂@PPEGMA₄₇₅-co-PtBA.

Fig. S4 GPC curve and data of PPEGMA₄₇₅-co-PtBA grafted on the surface of Fe₃O₄@SiO₂@PPEGMA₄₇₅-co-PtBA. The sample was obtained by etching with hydrofluoric acid from corresponding MNPs.
Fig. S5 Absorption spectra of 3a (1, 2, 4, 6, 8, 10, 12, 14, 16 and 18 μg/mL) in Na2HPO4-citric acid buffer solution (pH 3.0); inset shows the linear fit of absorbance at 665 nm.

Fig. S6 Absorption spectra of PPEGMA_{475-c0-PAA}@Oxazine-2 (0.05, 0.09, 0.13, 0.17, 0.21, 0.25, 0.29, 0.33, 0.37 and 0.40 mg/mL) in Na2HPO4-citric acid buffer solution (pH 3.0); inset shows the linear fit of absorbance at 665 nm.
Fig. S7 Particle sizes of the as-prepared MNPs at different modification stages in water by DLS.

Fig. S8 Particle sizes of the as-prepared MNPs at different modification stages in water by DLS.
Fig. S9  Absorption properties of compound 3a (10 μM) toward different pH values in Na₂HPO₄-citric acid buffer solution with 10% DMSO as a co-solvent.

Fig. S10  Absorption properties of compound 3a (10 μM) toward different pH values in Na₂HPO₄-citric acid buffer solution with 10% DMSO as a co-solvent (λex = 600 nm).
**Fig. S11** Fluorescence intensity changes of compound 3a (10 μM) at 700 nm toward different pH values in Na₂HPO₄-citric acid buffer solution with 10% DMSO as a co-solvent.

**Fig. S12** Fluorescence intensity changes at 688 nm of Fe₃O₄@SiO₂@PPEGMA₄75-co-PAA@Oxazine-2 toward different pH values in Na₂HPO₄-citric acid buffer solution.
Fig. S13 Absorption properties of Fe$_3$O$_4$@SiO$_2$@PPEGMA$_{475}$-co-PAA@Oxazine-2 toward different pH values in Na$_2$HPO$_4$-citric acid buffer solution. (Iron concentrations is 0.025 mg/mL, $\lambda_{ex} = 600$ nm).

Fig. S14 Absorption spectra of grafted polymer PPEGMA$_{475}$-co-PAA@Oxazine-2 (0.25 mg/mL) toward different pH values in Na$_2$HPO$_4$-citric acid buffer solution. The polymer was collected from the hybrid Fe$_3$O$_4$@SiO$_2$@PPEGMA$_{475}$-co-PAA@Oxazine-2 MNPs after treated with HF to remove the Fe$_3$O$_4$@SiO$_2$ core.
**Fig. S15** Absorption properties of Fe$_3$O$_4$@SiO$_2$@PPEGMA$_{475}$-co-PAA@Oxazine-1 toward different pH values in Na$_2$HPO$_4$-citric acid buffer solution. (Iron concentrations is 0.025 mg/mL, $\lambda_{ex} = 600$ nm).

**Fig. S16** Emission properties of Fe$_3$O$_4$@SiO$_2$@PPEGMA$_{475}$-co-PAA@Oxazine-1 toward different pH values in Na$_2$HPO$_4$-citric acid buffer solution. (Iron concentrations is 0.025 mg/mL, $\lambda_{ex} = 600$ nm).
**Fig. S17** Absorption properties of Fe₃O₄@SiO₂@PPEGMA₄₇₅-co-PAA@Oxazine-3 toward different pH values in Na₂HPO₄-citric acid buffer solution. (Iron concentrations is 0.025 mg/mL, λex = 600 nm).

**Fig. S18** Emission properties of Fe₃O₄@SiO₂@PPEGMA₄₇₅-co-PAA@Oxazine-3 toward different pH values in Na₂HPO₄-citric acid buffer solution. (Iron concentrations is 0.012 mg/mL, λex = 600 nm).
**Fig. S19** Fluorescence intensity changes at 680 nm of Fe$_3$O$_4$@SiO$_2$@PPEGMA$_{475}$-co-PAA@Oxazine-3 toward different pH values in Na$_2$HPO$_4$-citric acid buffer solution.

**Fig. S20** Confocal fluorescent images of fixed 293T cells incubated with Fe$_3$O$_4$@SiO$_2$@PPEGMA$_{475}$-co-PAA@Oxazine-2 and Hoechst 33342 at pH 5.0 (a-c), pH 6.0 (d-f), and pH 7.4 (g-i), respectively.
Fig. S21 Relative cell viability data of 4T1 cells incubated with a series of iron concentrations of Fe₃O₄@SiO₂@PPEGMA₄₇₅-co-PAA@Oxazine-2 measured by the MTT cell viability assay.

Fig. S22 Relative cell viability data of 293T cells incubated with a series of iron concentrations of Fe₃O₄@SiO₂@PPEGMA₄₇₅-co-PAA@Oxazine-2 measured by the MTT cell viability assay.
Fig. S23 $^1$H NMR (300 MHz) of 2a in DMSO-$d_6$. 

Fig. S24 $^1$H NMR (300 MHz) of 2b in DMSO-$d_6$. 

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Fig. S25 $^1$H NMR spectra (300 MHz) of 3a in DMSO-$d_6$.

Fig. S26 $^1$H NMR spectra (300 MHz) of 3b in DMSO-$d_6$. 
Fig. S27 $^1$H NMR (300 MHz) of 3c in DMSO-$d_6$.

Fig. S28 $^1$H NMR spectra (300 MHz) of 2a+$\text{H}^+$ in DMSO-$d_6$. 
Fig. S29 $^1$H NMR spectra (300 MHz) of 3a+H$^+$ in DMSO-$d_6$.

Fig. S30 $^1$H NMR spectra (300 MHz) of 3c+H$^+$ in DMSO-$d_6$. 

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Fig. S31 $^1$H NMR spectrum (300 MHz) of grafted PPEGMA$_{475}$-co-PAA in DMSO-$d_6$. The polymer was collected from Fe$_3$O$_4$@SiO$_2$@PPEGMA$_{475}$-co-PAA after treated with HF to remove the Fe$_3$O$_4$@SiO$_2$ core.

Fig. S32 $^1$H NMR spectrum (300 MHz) of grafted PPEGMA$_{475}$-co-PAA in DMSO-$d_6$. The polymer was collected from Fe$_3$O$_4$@SiO$_2$@PPEGMA$_{475}$-co-PAA after treated with HF to remove the Fe$_3$O$_4$@SiO$_2$ core.
**Fig. S33** $^1$H NMR spectrum of grafted polymer in DMSO-$d_6$. The polymer was collected from Fe$_3$O$_4$@SiO$_2$@PPEGMA$_{475}$-co-PAA@Oxazine-2 after treated with HF to remove the Fe$_3$O$_4$@SiO$_2$ core.

**Fig. S34** $^{13}$C NMR (75 MHz) of 2a in CDCl$_3$. 

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**Fig. S33** $^1$H NMR spectrum of grafted polymer in DMSO-$d_6$. The polymer was collected from Fe$_3$O$_4$@SiO$_2$@PPEGMA$_{475}$-co-PAA@Oxazine-2 after treated with HF to remove the Fe$_3$O$_4$@SiO$_2$ core.

**Fig. S34** $^{13}$C NMR (75 MHz) of 2a in CDCl$_3$. 

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Fig. S35 $^{13}$C NMR (75 MHz) of 2b in DMSO-$d_6$.

Fig. S36 $^{13}$C NMR (75 MHz) of 3a in DMSO-$d_6$. 
Fig. S37 ¹³C NMR (75 MHz) of 3b in DMSO-δ₆.

Fig. S38 ¹³C NMR (75 MHz) of 3c in DMSO-δ₆.
Fig. S39 $^{13}$C NMR (75 MHz) of 2a+$\text{H}^+$ in DMSO-$d_6$.

Fig. S40 $^{13}$C NMR (75 MHz) of 3a+$\text{H}^+$ in DMSO-$d_6$. 
Fig. S41 $^{13}$C NMR (75 MHz) of 3c+H$^+$ in DMSO-$d_6$.

Fig. S42 HRMS of 2a.
Fig. S43 HRMS of 2b.

m/z calcd for C_{25}H_{23}N_{4}O_2^+ 411.1821

Fig. S44 HRMS of 3a.

m/z calcd for C_{27}H_{27}N_{4}O^+ 423.2185
Fig. S45 HRMS of 3b.

Fig. S46 HRMS of 3c.
Fig. S47 FRTC of 2a.

Fig. S48 FRTC of 2b.
Fig. S49 FRTC of 3a.

Fig. S50 FRTC of 3b.
Fig. S51 FRTC of 3e.