Supporting information for

Poly(acrylic acid)-block-poly(vinyl alcohol) Anchored Maghemite
Nanoparticles Designed for Multi-stimuli Triggered Drug Release

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**Figure S1.** $^1$H NMR spectrum of FA-labelled PVOH-$b$-PAA copolymer, insert: the partially enlarged spectra in the range of 6 ~ 8 ppm, and assignment of the protons; a grafting degree of ca. 1.4 mol. % (PAA-FA blocks out of overall PAA blocks) was confirmed. The spectrum was recorded in D$_2$O at room temperature with a 250 MHz Bruker spectrometer.

**Figure S2.** TGA traces of the $\gamma$-Fe$_2$O$_3$ nanoparticles before and after coating with PAA-$b$-PVOH macromolecules, and a polymer fraction of 12 wt.% was estimated. Experiments were performed from 20 to 600°C at a heating rate of 20°C/min under air with a TA Q100 Instrument.
Figure S3. Calibration curve: methylene blue (MB) absorbance at 665 nm as a function of concentration. A good linear fitting was observed with $R^2 = 0.9994$.

Figure S4. (a) TEM image of the $\gamma$-Fe$_2$O$_3$ NPs (scale bar: 50 nm) (insert: statistical size distribution histogram from $ca.$ 200 particles), and (b) size distribution of the bare $\gamma$-Fe$_2$O$_3$, $\gamma$-Fe$_2$O$_3$@PAA-\textit{b}-PVOH and $\gamma$-Fe$_2$O$_3$@PAA-\textit{b}-PVOH@MB NPs suspension as determined by DLS.
Figure S5. (a) XRD patterns of the $\gamma$-Fe$_2$O$_3$@PAA-b-PVOH NPs and (b) evolution of zeta potential vs. pH for the bare $\gamma$-Fe$_2$O$_3$ NPs (the solid lines just serve to guide the eye). X-ray diffraction was performed on a Philips PW1700 diffractometer with CuK$\alpha$ radiation ($\lambda = 1.5418 \, \text{Å}$).

Figure S6. XPS spectra of the $\gamma$-Fe$_2$O$_3$@PAA-b-PVOH NPs: fitted C 1s (a) and Fe 2p spectra (b). The C1s XPS spectrum (a) of the $\gamma$-Fe$_2$O$_3$@PAA-b-PVOH NPs can be fitted into 5 component peaks centered at 288.6, 287.2 and 286.2, 285.1 and 284.0 eV, representing the carbon atoms of COOR, C=O, C-O, C-CO and C-C units, respectively. The C1s peak (COOR) strongly supports the presence of the PAA-b-PVOH copolymer. Peaks at 709.1 (Fe 2p3/2) and 722.6 eV (Fe 2p1/2) were also observed for iron oxides components (b). In addition, weak satellite peak (717.2 eV) on their high binding energy side was also observed. Such a spectrum is typical of iron oxides ($\alpha$- and $\gamma$-Fe$_2$O$_3$ polymorphs). XPS experiments were performed with a VG Scientific 220 i-XL ESCALAB spectrometer, equipped with a non-monochromatised MgK$\alpha$ source ($h\nu = 1253.6 \, \text{eV}$) at 100 W (10 kV and 10 mA). A pressure of $10^{-7} \, \text{Pa}$ was maintained in the chamber during analysis. The analysed area was ca. 150 μm in diameter. The full spectra ($0 \sim 1150 \, \text{eV}$) were obtained with constant pass energy of 150 eV and high-resolution spectra at constant pass energy of 40 eV. Charge neutralization was required for insulating samples. The peaks were referenced to C1s peak at 284.7 eV. High-resolution spectra were fitted using the AVANTAGE software provided by ThermoFisher Scientific.
**Figure S7.** SQUID curves of the $\gamma$-Fe$_2$O$_3$@PAA-b-PVOH NPs and bare $\gamma$-Fe$_2$O$_3$ NPs at 300 K (insert: magnified SQUID curves in the range of -600 to 600 Oe).

**Figure S8.** UV/vis spectra of the $\gamma$-Fe$_2$O$_3$@PAA-b-PVOH NPs, pure methylene blue, $\gamma$-Fe$_2$O$_3$@PAA-b-PVOH@MB NPs and FA-labeled $\gamma$-Fe$_2$O$_3$@PAA-b-PVOH NPs.
Figure S9. FACS measurement of untreated MEL-5 cells (red) and cells after incubation with FA-labelled γ-Fe₂O₃@PAA-b-PVOH NPs (50 μg/mL, 3-h incubation, green), and plotting log of FITC intensity (GFP-A on x-axis) against the number of cells (counts on y-axis).

References