Supporting Information

ROS-responsive thermosensitive polypeptide hydrogels for localized drug delivery and improved tumor chemoimmunotherapy

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Scheme S1. Synthesis route of the mPEG-*b*-PMet.



Scheme S2. Oxidation route of the mPEG-*b*-PMet.



Figure S1. ¹H NMR spectra of different degrees of polymerization of three polymers.



Figure S2. Gel permeation chromatography (GPC) of different polymerization degree of polymers.

Table S1. T	he $M_{\rm n}$ and I	PDI of Gel	permeation	chromatography	(GPC) c	of different
polymerizatio	on degree of	polymers.				

Polymers	mPEG-PMet ₁₁	mPEG-PMet ₂₂	mPEG-PMet ₃₂
$M_{\rm n}({\rm Da})$	5511	5650	6320
PDI	1.12	1.11	1.16



Figure S3. The FTIR spectra of different degrees of polymerization of the copolymers.



Figure S4. The CD spectra of mPEG-*b*-PMet₁₁ A), mPEG-*b*-PMet₂₂ B), mPEG-*b*-PMet₃₂ C) at different temperature.



Figure S5. (A) SEM image of self-assembled nanoparticles of 1 mg/mL mPEG-*b*-PMet₂₂. (B) TEM image of self-assembled nanoparticles of 0.1 mg/mL mPEG-*b*-PMet₂₂. The scale bar in the TEM image represents 500 nm.



Figure S6. The representative pictures of sol-gel phase transitions of the 8.0 wt% mPEG-*b*-PMet₂₂ hydrogels *in vitro*



Figure S7. The FTIR spectra A) and the CD spectra B) of the post-oxidation copolymers.



Figure S8. The release behaviors of Cy3-IgG from the hydrogel formed by 8.0 wt% mPEG-*b*-PMet₂₂ evaluated hydrogen peroxide *in vitro* (n = 3).



Figure S9. Histological analysis of major organs of B16F10-bearing mice with different treatments at day 10. Scale bar = $100 \mu m$, G1: PBS, G2: Free Dox/R848/aPD-1, G3: Dox@Gel, G4: Dox/R848@Gel, G5: Dox/R848/aPD-1@Gel.



Figure S10. Immunohistochemistry images of CD11c⁺ cells and CD8⁺ T cells in tumor tissues via CSLM, (scale bar=2 μm), G1: PBS, G2: Free Dox/R848/aPD-1, G3: Dox@Gel, G4: Dox/R848@Gel, G5: Dox/R848/aPD-1@Gel.