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Supporting Information

A self-crosslinking nanogel scaffold for enhanced catalytic efficiency and stability

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Scheme S1. Synthetic pathways of NSN-NCA and NAG-NCA monomers.



Scheme S2. Synthetic route of the homopolymer PNSN and block copolymer PEG-*b*-PNSN.



Scheme S3. Synthetic pathway of the self-crosslinking nanogels from photoresponsive polypeptoid copolymers.



Scheme S4. Synthetic route of the side chain modification of photoresponsive polypeptoid copolymers.



Figure S1. ¹H NMR spectra of (a) NSN-NCA (CDCl₃, δ , ppm): 2.74 (t, 2H), 3.55 (t, 2H), 4.11 (s, 2H), 4.17 (s, 2H), 7.43-7.50 (m, 2H), 7.59 (t, 1H), 7.97 (d, 1H); (b) NAG-NCA (CDCl₃, δ , ppm): 3.95 (d, 2H), 4.01 (s, 2H), 5.27 (d, 2H), 5.72 (m, 1H). *indicates solvents.



Figure S2. FTIR spectra of NSN-NCA and PEG-*b*-PNSN₁₀.



Figure S3. GPC traces of the copolymers.



5.0 4.5 4.0 3.5 Chemical Shift (ppm) 8.5 7.5 0.5 8.0 7.0 6.5 6.0 5.5 3.0 2.5 2.0 1.5 1.0





р ehm a bcd 0 3.5 8.0 5.0 4.5 4.0 3.5 Chemical Shift (ppm) 7.5 7.0 6.5 6.0 5.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0



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Figure S4. ¹H NMR spectra of the graft polypeptoids (a) 1a in CDCl₃, (b) 1c, (c) 1d and (d) 1e in DMSO. *indicates solvents.





3.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0. Chemical Shift (ppm)





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Figure S5. ¹H NMR spectra of the graft polypeptoids (a)**2a**, (b)**2b**, (c)**2c** and (d)**2e** in DMSO. *indicates solvents.



Figure S6. GPC traces of the PEG-*b*-PNSN-*co*-PNAG with non-irradiation (red line) and 10 h irradiation (black line).



Figure S7. (a) Plots of transmittance as a function of temperature for the aqueous solution (2 mg/mL) of **1a**. (b) Transmittance of **1a** aqueous solution at a concentration of 2 mg/mL *vs* 3 heating and cooling cycles between 20 and 60 °C.

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Figure S8. The D_h distributions of PEG-*b*-PNSN-*co*-PNAG without irradiation (a) and with 10 h UV irradiation (b).

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Figure S9. Absorption spectra of the nanogels@Au and the AuNPs.



Figure S10. Time-dependent UV-vis spectra for the reduction of 4-nitrophenol.



Figure S11. (a) UV-vis spectra of the catalytic hydrolysis process of 4-nitrophenyl palmitate (*pNPP*) by native lipase and irradiated lipase. (b) UV-vis spectra of native lipase and PEG-*b*-PNSN-*co*-PNAG.



Figure S12. The relationship between the concentration of *p*-nitrophenol and the absorbance recorded at 400 nm.