Supporting Information

Self-crosslinking Assemblies with Tunable Nanostructures from Photoresponsive Polypeptoid-based Block Copolymers

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Scheme S1. Synthetic route of photoresponsive NSN-NCA monomer.



Fig. S1 ¹H NMR spectra of S-(o-nitrobenzyl)-cysteamine (CDCl₃, δ, ppm): 2.29 (b, 2H), 2.60 (t, 2H), 2.89 (m, 2H), 4.08 (s, 2H), 7.43 (t, 1H), 7.50 (d, 1H), 7.57 (t, 1H), 7.98 (d, 1H). * indicates solvents.



Fig. S2 ¹H NMR spectra of 2-(S-(o-nitrobenzyl)-thioethyl amino) acetic acid hydrochloride (DMSO, δ , ppm): 2.75 (t, 2H), 3.13 (m, 2H), 3.86 (m, 2H), 4.09 (s, 2H), 7.56 (t, 1H), 7.71 (m, 2H), 8.04 (d, 1H), 9.41 (b, 1H). * indicates solvents.



Fig. S3 ¹H NMR spectra of 2-(S-(o-nitrobenzyl)-thioethyl-tert-butoxycarbonyl) acetic acid (DMSO, δ , ppm): 1.34 (s, 9H), 2.58 (t, 2H), 3.30 (t, 2H), 3.81 (s, 2H), 4.06 (s, 2H), 7.52-7.71 (m, 3H), 7.99 (d, 1H), 12.55 (s, 1H). * indicates solvents.



Fig. S4 ¹³C NMR spectra of *N*-(S-(o-nitrobenzyl)-thioethyl)-*N*-carboxyanhydride (CDCl₃, δ, ppm): 33.35, 42.61, 48.46, 49.86, 125.58, 128.82, 132.19, 133.37, 133.49, 148.65, 152.32, 165.41.* indicates solvents.



Fig. S5 ¹H NMR spectra of (a) PEG-*b*-PNSN₁₁, (b) PEG-*b*-PNSN₂₂ and (c) PEG-*b*-PNSN₅₁ in CDCl₃. * indicates solvents.



Fig. S6 DSC thermograms of PEG-*b*-PNSN₁₁ and PEG-*b*-PNSN₅₁ (a), and TGA profiles of PEG*b*-PNSN₁₁ (b).







Fig. S7 ¹H NMR spectra of (a) PEG-*b*-PNSN₁₁, (b) PEG-*b*-PNSN₂₂, (c) PEG-*b*-PNSN₄₁ and (d) PEG-*b*-PNSN₅₁ with different UV irradiation time.



Fig. S8 The photocleavage ratio of copolymers with different UV irradiation time.



Fig. S9 AFM images of PEG-*b*-PNSN₁₁ with non-irradiation (a) and with 6h irradiation (b), PEG*b*-PNSN₂₂ with non-irradiation (c) and with 6h irradiation (d), PEG-*b*-PNSN₄₁ with non-irradiation (e) and with 6 h irradiation (f), PEG-*b*-PNSN₅₁ with non-irradiation (g) and with 6 h irradiation (h). The inset images are the corresponding height profiles.



Fig. S10 TEM images of PEG-*b*-PNSN₄₁ (a) and PEG-*b*-PNSN₅₁ (b) (negatively stained) with non-irradiation; PEG-*b*-PNSN₁₁ (c), PEG-*b*-PNSN₂₂ (d), PEG-*b*-PNSN₄₁ (negatively stained) (e) and PEG-*b*-PNSN₅₁ (f) with 6h irradiation.



Fig. S11 The D_h distribution of PEG-*b*-PNSN₂₂ without UV irradiation (a), with 6 h UV irradiation (b) and in the presence of GSH (10 mM) after 6 h UV irradiation (c); PEG-*b*-PNSN₄₁ without UV irradiation (d), with 6 h UV irradiation (e) and in the presence of GSH (10 mM) after 6 h UV irradiation (f); PEG-*b*-PNSN₅₁ without UV irradiation (g), with 6 h UV irradiation (h) and in the presence of GSH (10 mM) after 6 h UV irradiation (i) at different concentration.