

Supporting Information

Copper-Coordination Induced Fabrication of Stimuli-Responsive Polymersomes from Amphiphilic Block Copolymer Containing Pendant Thioethers

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Synthesis of phenylboronate containing N-hydroxysuccinimide ester (C1). The phenylboronate containing N-hydroxysuccinimide ester (C1) was prepared according to the reported method with minor modification.¹ Di(N-succinimidyl) carbonate (DSC) (6.53 g, 25.5 mmol) was dissolved in dry acetonitrile (70 mL) and the solution of 4-(hydroxymethyl) benzeneboronic acid pinacol ester (3.98 g, 17 mmol) in 30 mL of dry acetonitrile and triethylamine (TEA) (4.7 mL, 34 mmol) were added dropwise. After the mixture was stirred for 7 h under Ar atmosphere at room temperature, the reaction solution was diluted with 200 mL chloroform (CHCl₃) and washed with deionized water (150 mL × 3). The organic layer was collected, dried over anhydrous Na₂SO₄ and filtered. The filtrate was concentrated to dryness and the residue was purified by column chromatography (dichloromethane: ethyl acetate = 20:1.5, v/v) to obtain C1 (3.65 g, 44%) as a white solid. ¹H NMR (Fig. S1, 400 MHz, CDCl₃): δ = 1.33 (a, 12H, s), δ = 7.81 (b, 2H, d), δ = 7.36 (c, 2H, d), δ = 5.31 (d, 2H, s), δ = 2.81 ppm (e, 4H, s).

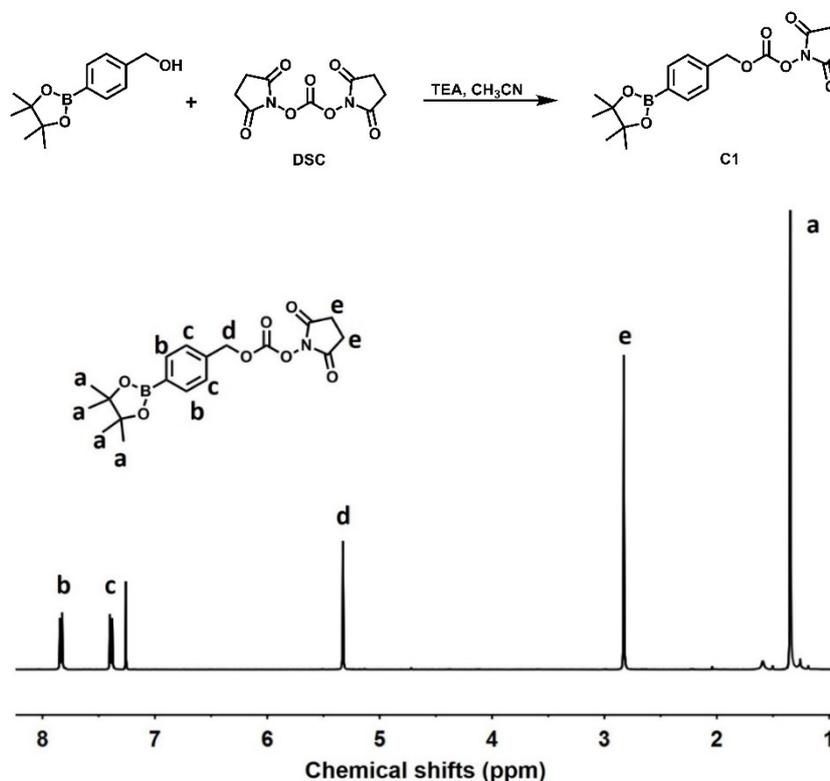


Fig. S1 ¹H NMR spectrum of C1.

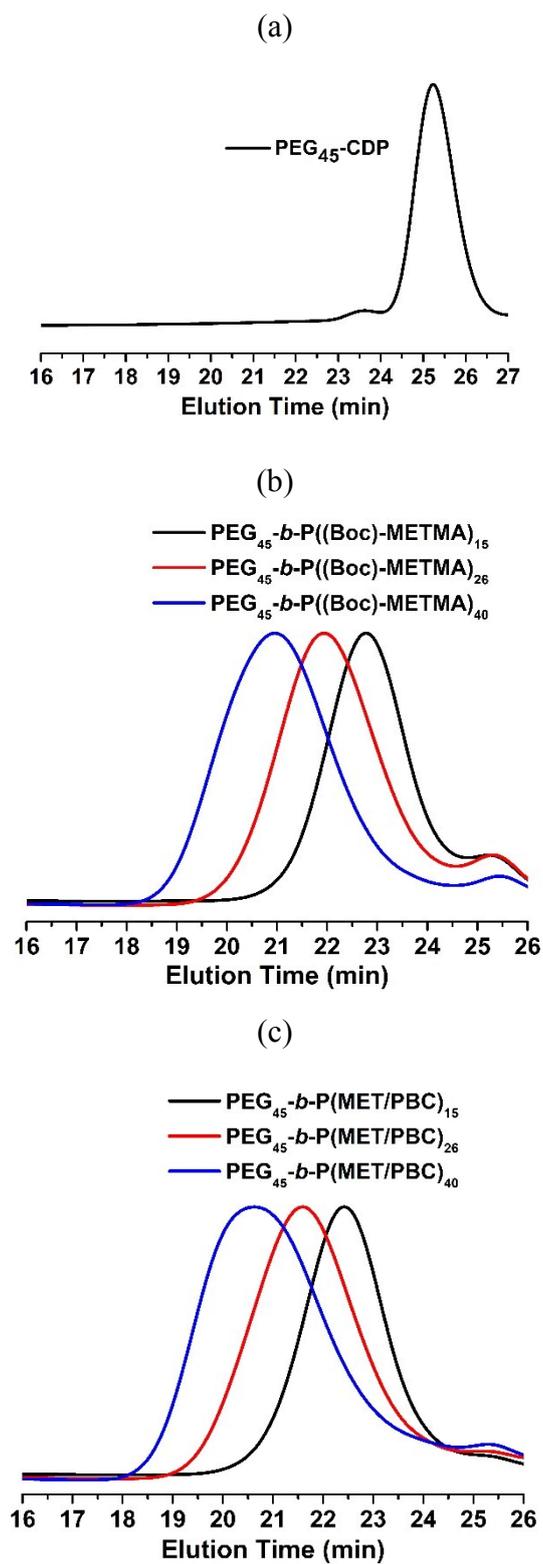


Fig. S2 GPC traces of PEG₄₅-CDP (a), PEG₄₅-*b*-P((Boc)-METMA)_n diblock copolymers (b), and PEG₄₅-*b*-P(MET/PBC)_n diblock copolymers (c).

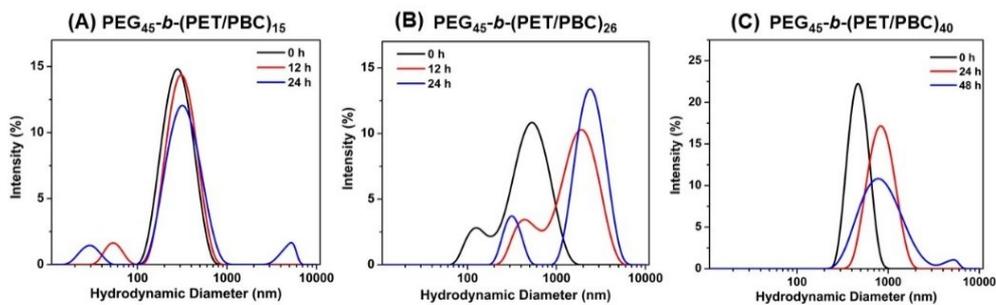


Fig. S3 DLS curves of PEG₄₅-*b*-P(MET/PBC)_n self-assemblies in the aqueous solution after incubation with H₂O₂ (10 mM) at 37°C.

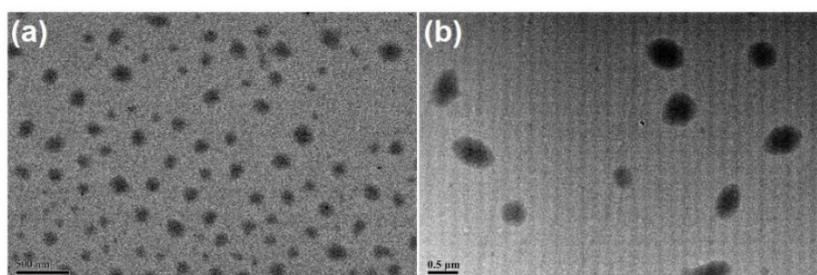


Fig. S4 TEM images of PEG₄₅-*b*-P(MET/PBC)₁₅ micelles (a) and PEG₄₅-*b*-P(MET/PBC)₁₅/Cu²⁺ co-assemblies (b).

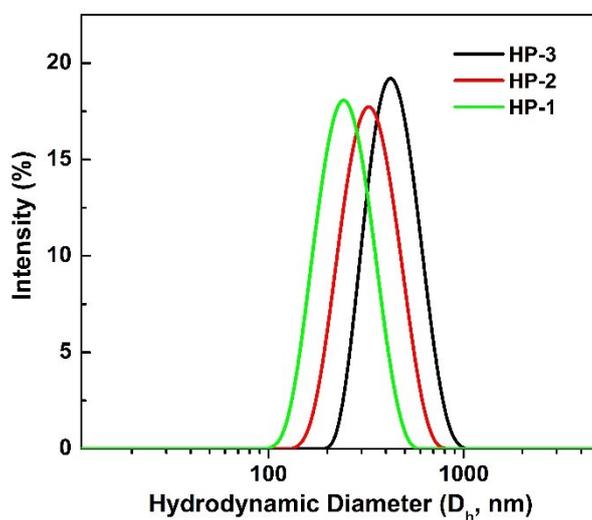


Fig. S5. DLS curves of PEG₄₅-*b*-P(MET/PBC)₂₆/Cu²⁺ co-assemblies prepared at various feeding ratios of Cu²⁺/thioether (HP-1: 0.5/1 (mol/mol); HP-2: 1/1 (mol/mol); HP-3: 2/1 (mol/mol)).

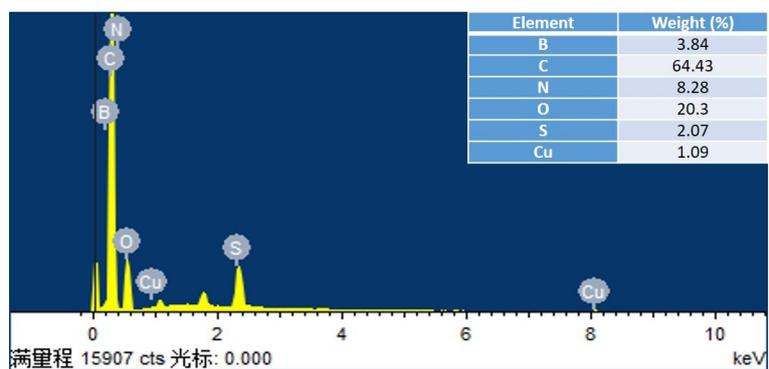


Fig. S6 EDS data of HP-3 polymersomes.

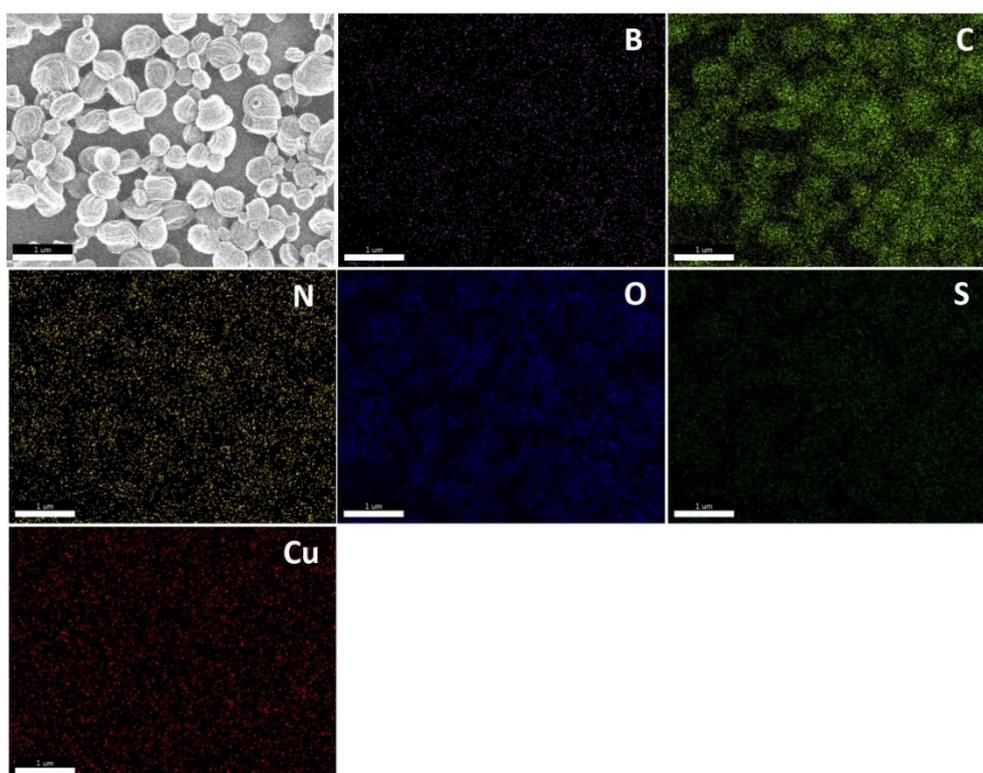


Fig. S7 SEM image and elemental mapping analysis (B, C, N, O, S, Cu) of HP-3 polymersomes.

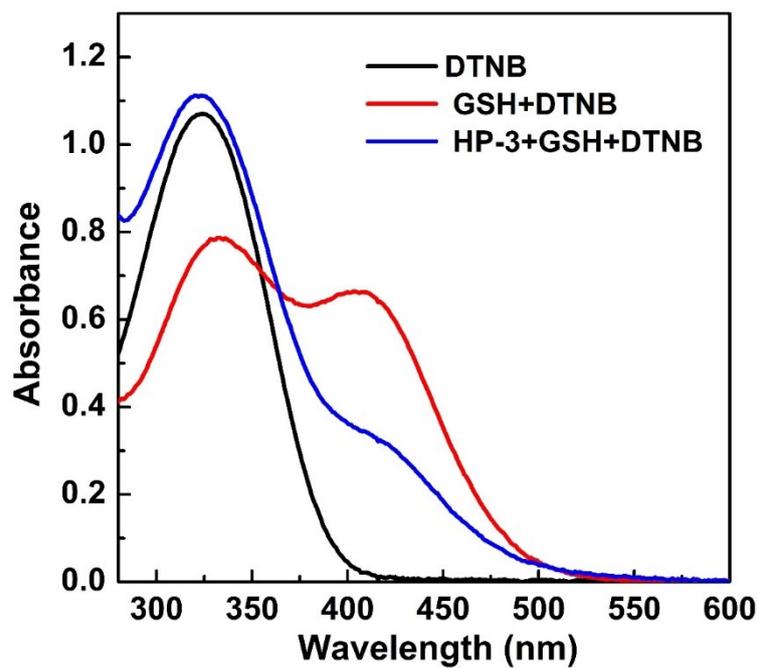


Fig. S8 UV-vis spectra of Ellman's assay for GSH with/without the HP-3 polymersomes.

References:

1. Ikeda, M.; Tanida, T.; Yoshii, T.; Hamachi, I., Rational molecular design of stimulus-responsive supramolecular hydrogels based on dipeptides. *Adv Mater* **2011**, *23* (25), 2819-22.