Electronic Supplementary Material (ESI) for Analyst.

Supporting Information for:

Efficient Extraction of Glycopeptides by Supramolecular Nanoassemblies that Use Proximity-Assisted Covalent Binding

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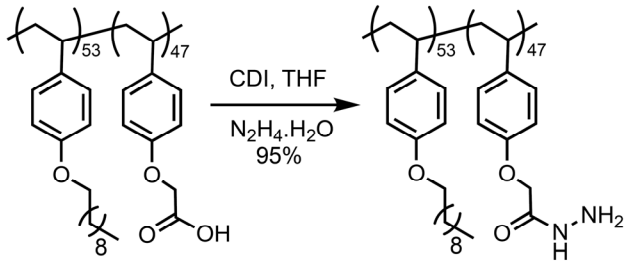
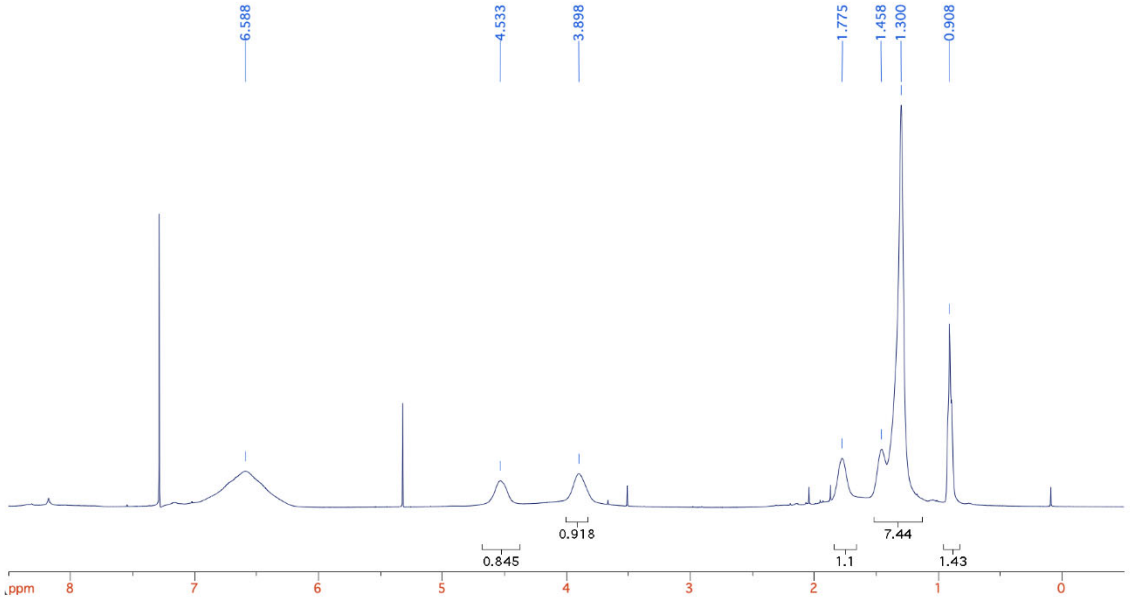
Polymer synthesis and characterization



P0 **P1**

Scheme S1. Synthesis of amphiphilic random copolymer **P1**.

Synthesis of random copolymer P1: Polymer **P0** was prepared according to previous procedures.[1] **P0** (100 mg) and carbonyldiimidazole (61 mg, 2 equivalents of carboxylate group) were dissolved in 5 mL tetrahydrofuran and stirred at room temperature for 2 hours. Then, this mixture was added to a hydrazine monohydrate/THF (2 mL/2 mL) solution dropwise and allowed to reflux overnight. The solvent was removed by a rotavapor, and the crude oil was purified by precipitating it 3 times in methanol. Yield: 90%, GPC (THF) Mn: 11.5 K. Đ: 1.08. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.57-6.2, 4.53, 3.89, 1.77, 1.48-1.26, 0.90. ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 128.5, 114.2, 67.9, 31.9, 29.6, 29.3, 29.1, 26.2, 25.5, 22.7, 14.1. From ^{1}H NMR, integration of the proton peaks at 0.90 ppm and 4.53 ppm confirmed the molar ratio of these two components to be 53:47.



The hydrazide functional group attachment was confirmed by IR (**Figure S1**) showing a broad peak at 3319 cm^{-1} corresponding to N-H bond, C=O bond shift from 1731 cm^{-1} to 1693 cm^{-1} due to the conversion of -OH to -$NHNH_2$.

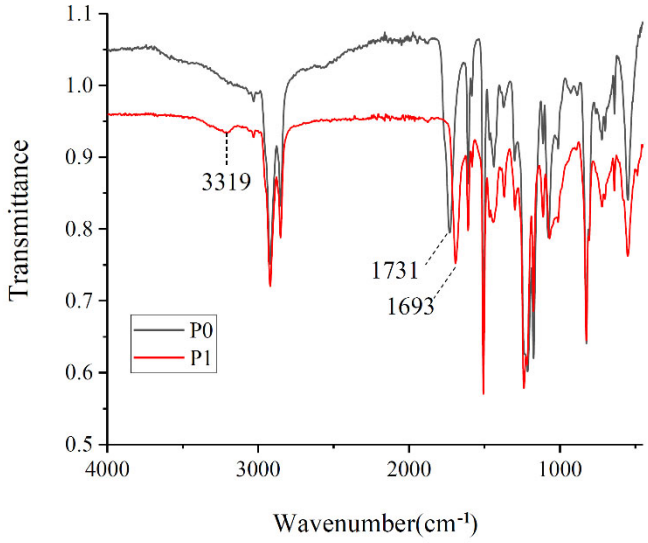


Figure S1. FT-IR of polymer carboxylate polymer **P0** and hydrazide polymer **P1**.

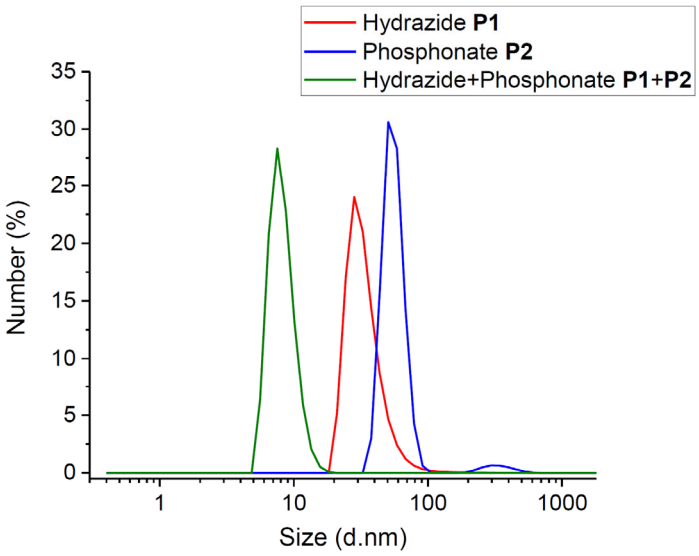


Figure S2. Dynamic light scattering data for nanoassemblies formed by polymers **P1**, **P2** and **P1**+**P2**.

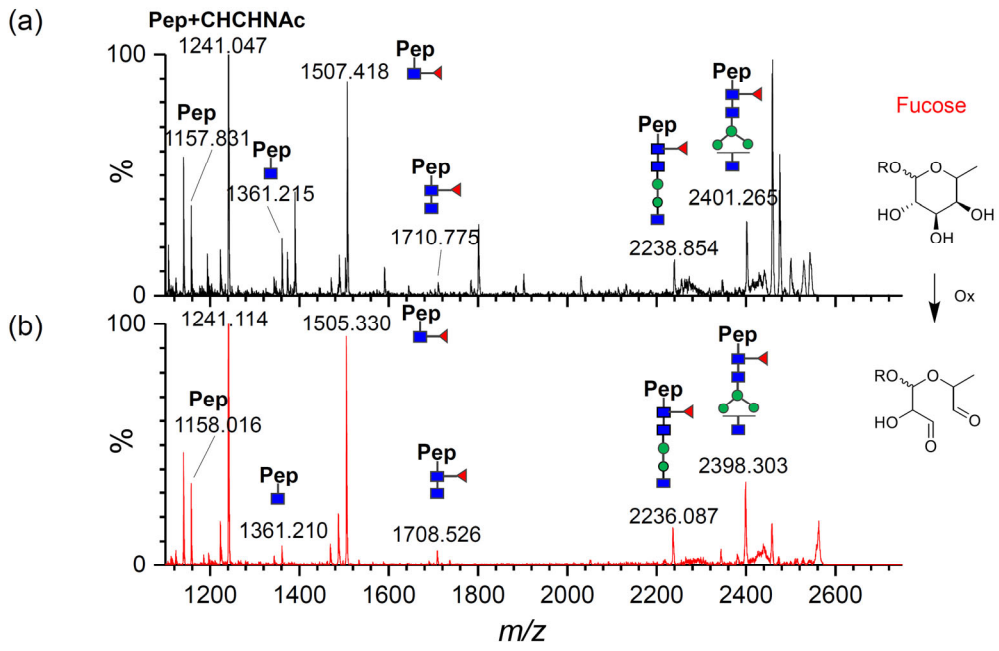


Figure S3. Glycopeptide analysis before and after enrichment with polymer **P1**. (a) Tandem mass spectrum of the precursor ion at *m/z* 2602.1 from the IgG1 digest and (b) Tandem mass spectrum of m/z 2600.4 after oxidation and enrichment (b). Symbol: (■) GlcNAc (●) Mannose (◀)Fucose.

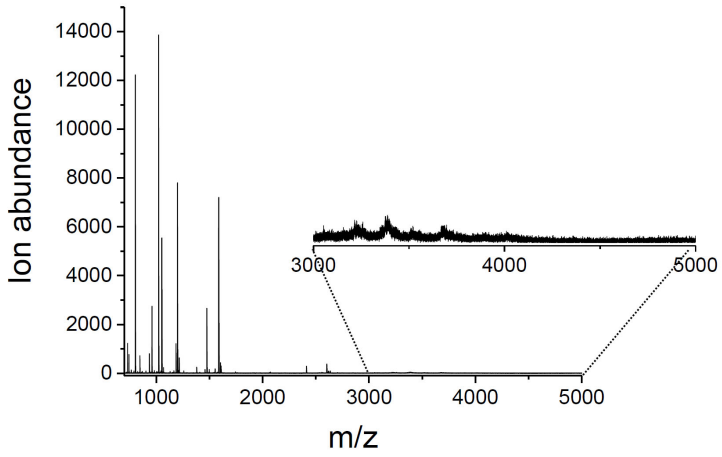


Figure S4. MALDI spectrum of oxidized HRP digests before enrichment. No glycopeptides are detected.

Reference

1 B. Zhao, J. Zhuang, M. A. C. Serrano, R. W. Vachet and S. Thayumanavan, *Macromolecules*, 2017, **50**, 9734–9741.