Supporting Information

In situ fabrication of PHEMA-BSA core-coronae biohybrid particles

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AGET ATRP of HEMA initiated by BSA macroinitiator in the absence of N,N'methylene diacrylamide.



BSA macroinitiator (30 mg, 2.32×10^{-4} mmol), HEMA (100 mg, 0.77 mmol) and 3 mL of ultrapure water were added into a 10 mL Schlenk flask. After six freeze-pumpthaw cycles, 7.5 µL of catalyst solution (5.53 mg of CuBr₂ and 12.0 mg of bipy in 1.25 mL of deoxygenated water) and 7.5 µL of ascorbic acid solution (13.57 mg of ascorbic acid in 1.25 mL of deoxygenated water) were added, the Schlenk flask was placed in an oil bath at 35 °C. After the polymerization, the mixture was exposed to air to stop the polymerization and dialyzed (MWCO = $12 \sim 14$ KDa) against water to remove traces of reagents (monomer, copper, bipy). After centrifugation at 3,000 rpm for 3 min, the particles were collected and redispersed in 2.0 mL of ultrapure water.

Cleavage of PHEMA from protein for ¹H NMR and GPC measurement.

Isolated BSA-PHEMA core-corona particles prepared in the absence of cross-linker were freeze dried, and then redispersed in DMF with excess DTT. After stirring at 45 $^{\circ}$ C for 48h, the solution was centrifuged at 10,000 rpm and supernatant was collected and filtered with a 0.22 μ m filter. PHEMA was precipitated in diethyl ether, dried under vacuum prior to ¹H NMR and GPC analysis.



Fig. S1 ¹H NMR spectrum of hydroxyethyl-mercaptopyridine in CDCl₃.



Fig. S2 ¹H NMR spectrum of 2-(2-pyridinyldithio)ethyl 2-bromo-2-methylpropionate in CDCl₃.



Fig. S3 (a) UV-vis spectra of 2-mercaptopyridine in 20 mM PBS at pH=7.0 at

different concentrations. (b) Calibration curve for 2-mercaptopyridine determined by plotting the UV-vis absorbance at 343 nm against concentration.



Fig. S4 (a) UV-vis spectra of BSA at different concentrations in water. (b) Calibration curve for BSA determined by plotting the UV-vis absorbance at 278 nm against concentration.



Fig. S5 ¹H-NMR spectrum (a) and GPC trace (b) of PHEMA after cleavage of disulfide bonds between BSA and PHEMA particles prepared in the absence of cross-linker.



Fig. S6 TEM image (a), DLS curve (b) and AFM image (c) of NP-1; TEM image (d), DLS curve (e) and AFM image (f) of NP-3.