

A smart artificial glutathione peroxidase with temperature responsive activity constructed by host-guest interaction and self-assembly

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Synthesis of ADA-Te

ADA-Te was synthesized according to our previous synthesis method of bis-(3-acryloyloxypropyl)-telluride except acryloyl chloride was replaced by 1-adamantanecarbonyl chloride¹. Its structure was determined by Bruker 300MHz spectrometer using a TMS proton signal as the internal standard. ¹H NMR (300 MHz, CDCl₃) δ (ppm) 4.09 (t, 2 H), 3.71 (t, 2 H), 2.72 (t, 2 H), 2.66 (t, 2 H), 2.07 (m, 2 H), 2.00 (s, 3 H), 1.88 (s, 6 H), 1.71 (s, 6 H).

Synthesis of ADA-Arg

1-adamantanecarbonyl chloride (7.95 g, 0.040 mol) was dissolved in 30 mL anhydrous tetrahydrofuran and added dropwise to a stirred solution of L-Arginine (6.89 g, 0.040 mol) and triethylamine (5.55 mL, 0.040 mol) in anhydrous tetrahydrofuran (90 mL) at 0°C. After the addition was completed, the mixture was stirred for 3 h at room temperature. The precipitate triethylamine hydrochloride was filtered and the filtrate was concentrated under a vacuum. The product was purified by silica gel flash chromatography (methanol). After the removal of solvents, the product was isolated as colorless solid (yield, 72.5%). Its structure was determined by Bruker 300MHz spectrometer using a TMS proton signal as the internal standard. ¹H NMR (300 MHz, D₂O) δ (ppm) 4.25 (t, 1 H), 3.15 (t, 2 H), 1.97 (s, 3 H), 1.79 (s, 6 H), 1.72-1.51 (m, 10 H).

Synthesis of CD-Br

CD-Br was synthesized according to the preparing method of **triazol-CD monomer 2** in our previous report except acryloyl chloride was replaced by 2-bromopropanoic bromide². Its structure was determined by Bruker 300MHz spectrometer using a TMS proton signal as the

internal standard. ¹H NMR (300 MHz, D₂O) δ (ppm) 8.02 (s, 1 H), 5.07 (d, 7 H), 4.33 (t, 4 H), 4.24 (t, 2 H), 4.12 (m, 1 H), 3.67-3.86 (m 56H (14 H of glycol and 40 H of cyclodextrin)), 1.87 (d, 3 H)

Synthesis of CD-PNIPAM

CD-PNIPAM was synthesized according to the polymerization procedure reported by Masci et al³. The typical procedure was shown as follows: NIPAM (appropriate amount), Me₆TREN (115.1 mg, 0.5 mmol), water (5.0 mL) and DMF (5.0 mL) were introduced into a schlenk tube equipped with a magnetic stirring bar, followed by two freeze-pump-thaw cycle. Then, CuBr (71.7 mg, 0.5 mmol) was added under nitrogen and followed by two freeze-pump-thaw cycles. Finally, the initiator **CD-Br** (381.8 mg, 0.25 mmol) was dissolved in 1.0 mL DMF and added to the schlenk tube via a syringe to start the polymerization. The mixture was stirred for 12 h at 30°C. Then the mixture was exposed to air to terminate the polymerization and dialyzed against water for 2 d, a colorless polymer was obtained after the aqueous solution was freeze-dried. Herein, three kinds of **CD-PNIPAMs** were synthesized. The GPC analysis was like this: GPC analysis of one polymer revealed a Mn of 9815 and a polydispersity, Mw/Mn, of 1.50, the degree of polymerization (DPs) was estimated to be 73, this polymer was denoted as **CD-PNIPAM₇₃**; GPC analysis of one polymer revealed a Mn of 16344 and a polydispersity, Mw/Mn, of 1.61, the degree of polymerization (DPs) was estimated to be 130, this polymer was denoted as **CD-PNIPAM₁₃₀**; GPC analysis of one polymer revealed a Mn of 43871 and a polydispersity, Mw/Mn, of 1.45, the degree of polymerization (DPs) was estimated to be 374, this polymer was denoted as **CD-PNIPAM₃₇₄**.

References

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