

Supporting Information

Synthesis of Biotinylated α -D-Mannoside or *N*-Acetyl β -D-Glucosaminoside Decorated Gold Nanoparticles – Study of Their **Biomolecular** Recognition with Con A and WGA Lectins

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Materials. All chemicals were purchased from Sigma-Aldrich or Acros Chemicals. EZ-Link™ Biotin PEO-Amine, ((+)-Biotinyl-3,6-dioxaoctanediamine, Pierce), and other materials were used without further purification.

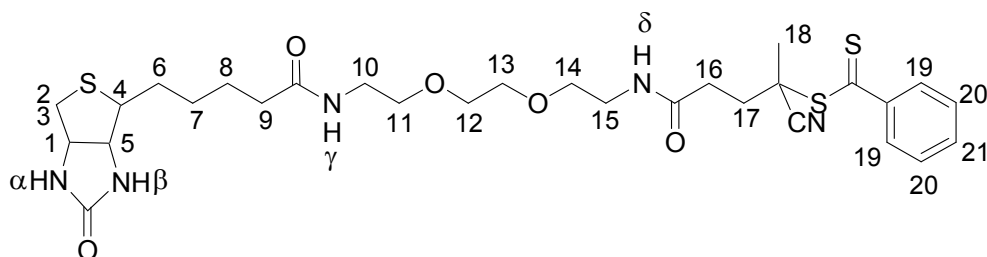
Synthesis of *N*-[8-((+)-biotinamido)-3,6-dioxaoctyl]-2-[[2-phenyl-1-thioxo]thio]-4-cyanopentanoate (BCBDBA). The biotin-CTA (BCBDBA) was synthesized from a precursor RAFT agent, the succinimido-4-[[2-phenyl-1-thioxo]thio]-4-cyanopentanoate(1,2), and a commercial biotin derivative, EZ-Link™ Biotin PEO-Amine.

In a 100 mL round-bottomed flask equipped with a magnetic stirrer, the precursor RAFT agent (0.113 g, 0.300 mmol) was dissolved in chloroform (20 mL). A solution of EZ-Link™ Biotin PEO-Amine (0.112 g, 0.300 mmol) in 25 mL of chloroform was prepared. The latter was added dropwise to the solution of RAFT agent during 2 h at 30°C. Then, the organic phase was washed five times with 60 mL of distilled water

and dried over anhydrous magnesium sulfate. After solvent removal, a column chromatography (Silica gel 60, Merk) was performed (dichloromethane/ethanol: 90/10 v/v) to afford a very viscous red oil (0,093 g, yield 49%).

Fast Atom Bombardment (FAB) mass spectrometry: characteristic ion $[M + Na^+]$: $C_{29}H_{41}N_5NaO_5S_3$; calculated 658.22; found 658.21.

1H NMR 500MHz ($CDCl_3$, RT, ppm) (see structure below for proton assignment): 7.90 (2 H, d, H_{19}); 7.55 (1 H, dd, H_{21}); 7.39 (2 H, dd, H_{20}); 7.11 (1 H, t, H_2); 6.61 (1 H, t, H_3); 6.36 (1 H, d, H_β); 5,37 (1 H, s, H_α); 4.47, 4.30 (2 H, ddd, H_2 and H_3); 3.64-3.43 (12 H, m, from H_{10} to H_{15}); 3.13 (1 H, dt, H_4); 2.88 (1 H, ddd, H_1); 2.72 (1 H, dd, H_5); 2.58 (2 H, t, H_{16}); 2.42 (2 H, t, H_{17}); 2.22 (2 H, t, H_9); 1.94 (3 H, s, H_{18}); 1.71-1.64 (4 H, m, H_7 and H_8); 1.44 (2 H, dt, H_6).



References.

- (1) Bathfield, M., D'Agosto, F., Spitz, R., Charreyre, M.-T., and Delair, T. (2006)
Versatile precursors of functional RAFT agents. application to the synthesis of
bio-related end-functionalized polymers. *J. Am. Chem. Soc.* 128, 2546-2547.
- (2) Gody, G., Boullanger, P., Ladavière, C., Charreyre, M.-T., and Delair, T. (2008)
Biotin α -end-functionalized gradient glycopolymers synthesized by RAFT
copolymerization. *Macromol. Rapid Commun.* 29, 511-519.

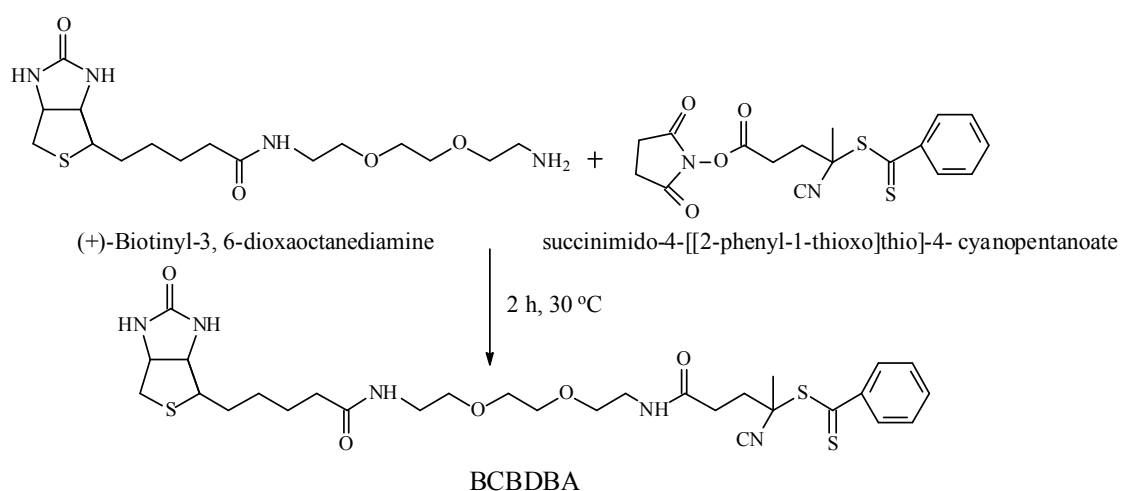


Figure S1. Synthetic route to the preparation of *N*-[8-((+)-biotinamido)-3,6-dioxaoctyl]-2-[[2-phenyl-1-thioxo]thio]-4-cyanopentanoate (BCBDBA).

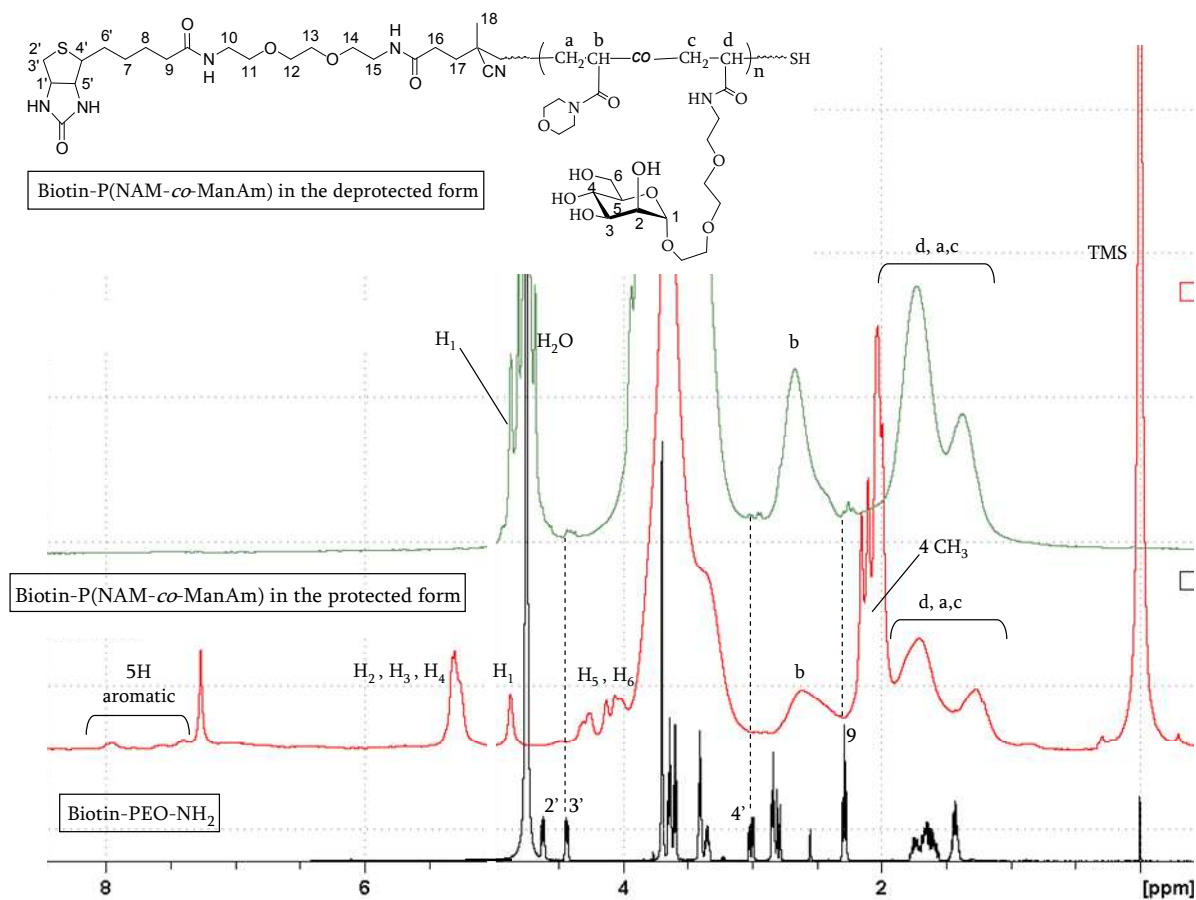


Figure S2. Comparison of the NMR spectra before ($CDCl_3$) and after (D_2O) deprotection of the P(NAM-co-ManAm) copolymer with that of Biotin-PEO-amine (D_2O).