Electronic Supplementary Information

Microgravimetric lectin biosensor based on signal amplification using carbohydrate-stabilized gold nanoparticles

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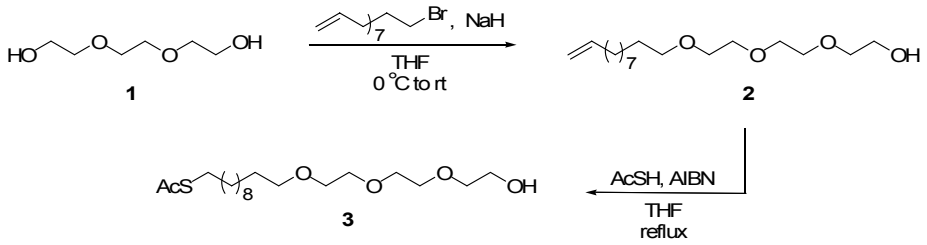
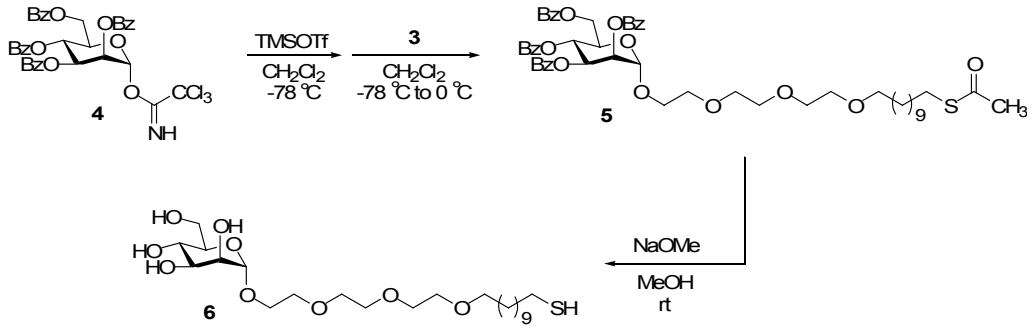
Synthesis and characterization of a thiol-modified mannoside



Compound **3** was prepared starting from compound **1** by way of compound **2** according to the known procedure (Jungkyu K. Lee; Young Shik Chi; Insung S. Choi *Langmuir* **2004**, *20*, 3844-3847).



In order to prepare compound **5**, a solution of mannosyl trichloroacetimidate **4** (412 mg, 0.556 mmol) and alcohol **3** (250 mg, 0.667 mmol, 1.2 equiv) in dry CH_2Cl_2 (7 mL) in the presence of 4Å molecular sieves was stirred for 15 min at -78 °C. After addition of TMSOTf (20 μm, 0.111 mmol, 0.2 equiv) to the solution, the reaction mixture was stirred at -78 °C for further 10 min and allowed to warm over 1 h to 0 °C. The reaction mixture was quenched with saturated aqueous $NaHCO_3$, and the organic phase was washed with brine, dried ($MgSO_4$), concentrated, and purified by silica gel flash column chromatography to give the compound **5** (500 mg, 94%): R_f = 0.15 (33% ethyl acetate in hexane); $[\alpha]_D^{20}$ = 43.7 (c = 0.47, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) 1.20–1.31 (m, 14 H), 1.50–1.59 (m, 4 H), 2.32 (s, 3 H), 2.85 (t, *J* = 7.4 Hz, 2 H), 3.41 (t,

J = 6.8 Hz, 2 H), 3.53–3.60 (m, 2 H), 3.62–3.68 (m, 2 H), 3.68–3.74 (m, 4 H), 3.74–3.80 (m, 2 H), 3.80–3.85 (m, 1 H), 3.93–4.01(m, 1 H), 4.44–4.54 (m, 2 H), 4.70 (dd, *J* = 2.0, 11.6 Hz, 1 H), 5.14 (d, *J* = 1.6 Hz, 1 H), 5.70–5.75 (m, 1 H), 5.93 (dd, *J* = 3.2, 10.2 Hz, 1 H), 6.12 (t, *J* = 10.0 Hz, 1 H), 7.22–7.62 (m, 12 H), 7.80–8.13 (m, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$) 26.2, 29.0, 29.26, 29.3, 29.6(5), 29.7, 29.8, 30.8, 63.0, 67.1, 67.8, 69.0, 70.2, 70.24, 70.3, 70.6, 70.9, 71.0, 71.7, 97.95, 128.4(3), 128.6(4), 128.7(3), 129.9(3), 129.96(4), 130.0(3), 133.2, 133.3, 133.5, 133.6, 165.5, 165.6(2), 166.3, 195.98; HRMS Calcd for $C_{53}H_{64}O_{14}S$ $(M+Na)^+$: m/z 979.3914. Found 979.3912.

In order to prepare compound **6**, a solution of the compound **5** (450 mg, 0.470 mmol) and sodium methoxide (5.10 mg, 0.0940 mmol, 0.2 equiv) in MeOH (5 mL) was stirred at room temperature for 5 h. The reaction mixture was neutralized with DOWEX® MAC-3 ion exchange resin, filtered through Celite®, and concentrated. The residue was purified by column chromatography on Iatrobeads® to give the compound **6** (220 mg, 94%): R_f = 0.33 (25% methanol in chloroform); ^{1}H NMR (400 MHz, CD_3OD) 1.27–1.43 (m, 14 H), 1.51–1.61 (m, 2 H), 1.62–1.72 (m, 2 H), 2.64–2.71 (m, 2 H), 3.44–3.49 (m, 2 H), 3.55–3.73 (m, 16 H), 3.78–3.86 (m, 3 H), 4.79 (s, 1 H); ^{13}C NMR (100 MHz, CD_3OD) 27.2, 29.4, 30.2, 30.3, 30.6(3), 30.7, 39.8, 63.0, 67.8, 68.6, 71.2, 71.4, 71.6(4), 72.1, 72.4, 72.6, 74.6, 101.8; HRMS Calcd for $C_{23}H_{46}O_9S$ $(M+Na)^+$: m/z 521.2760. Found 521.2756.

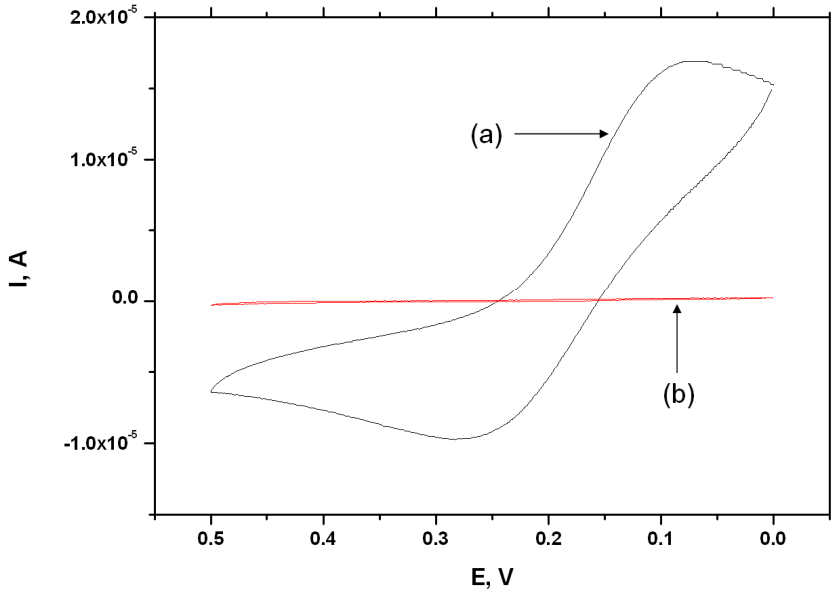


Figure S1. Cyclic voltammograms of 1.0 mM $K_3Fe(CN)_6$ on a bare gold QCM electrode (a) and a mannose SAM-modified gold QCM electrode (b) at a scan rate of 50 mV/s.