

A beryllium-selective microcantilever sensor modified with benzo-9-crown-3 functionalized polymer brushes

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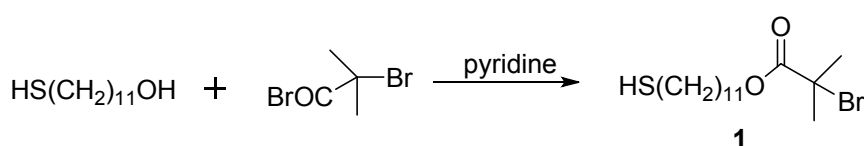


Figure S1. Synthetic procedure of **1**

Preparation of **1**¹:

In a 100 mL round-bottom flask, mercaptoundecanol (0.6 g, 2.94 mmol), pyridine (0.22 mL, 3.04 mmol), and dry dichloromethane (20 mL) were added. The solution was cooled to 0 °C. Then, ice-cold bromoisobutyryl bromide (0.33 mL, 2.69 mmol) in 1 mL CH₂Cl₂ with 5 mg 4-dimethylaminopyridine (DMAP) was dropwise added in the flask. After stirring at 0 °C for 1 h, the reaction continued for 16 h at room temperature. The solution was then extracted with toluene (3 × 50 mL). The organic phase was separated and solvent was removed by rotary evaporation. The resulting crude extract was dissolved in ether (40 mL) and washed with a saturated NH₄Cl solution (3 × 40 mL), and dried over anhydrous Na₂SO₄, elution with 1 : 10 CH₂Cl₂ : petroleum ether, yielded 0.46 g (46%) compound **1**. ¹H NMR (400 MHz, CDCl₃) δ 4.15 (t, *J* = 6.6 Hz, 2H), 2.50 (dd, *J* = 14.7, 7.4 Hz, 2H), 1.91 (s, 6H), 1.68 – 1.57 (m, 4H), 1.41–1.25 (m, 15H), EI-MS: *m/z* calcd for C₁₅H₂₉O₂SBr: 352.11 found: 352.12 [M]⁺, 273.17 [M-Br]⁺.

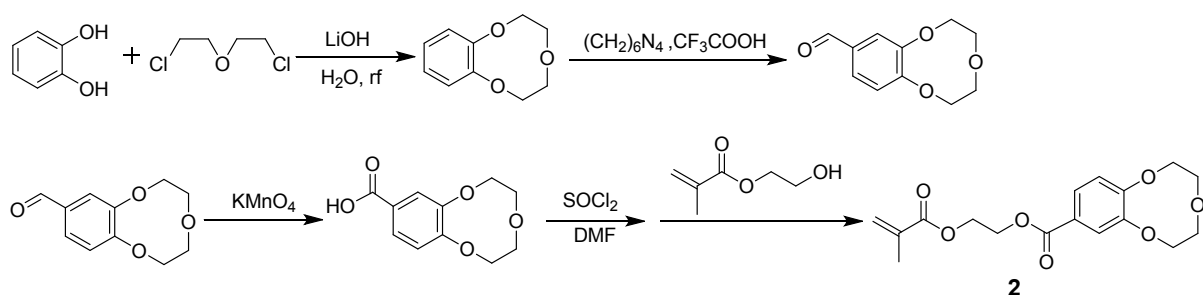


Figure S2. Synthetic procedures of 2

Preparation of benzo-9-crown-3²:

Catechol (8.15 g, 0.074 mol), water (850 mL), and LiOH (6.2 g, 0.148 mol) were added in a 1 L round-bottom flask, and the solution was stirred for 5 min. 2,2'-dichlorodiethylether (10.35 g, 0.074 mol) was added dropwise and the solution was then refluxed for 3.5 days. Upon cooling, dilute H₂SO₄ was added to acidify the solution until pH 2. The solution was extracted with CH₂Cl₂ (3 × 100 mL) and washed with 5% NaOH (3 × 100 mL), saturated NaCl (100 mL), and water, respectively. After drying over anhydrous Na₂SO₄, solvent was removed to yield a reddish slurry. , elution with 10 : 1 CH₂Cl₂ : ethyl acetate on silica gel column chromatography yielded 3.2 g (24%) Benzo-9-crown-3. ¹H NMR (400 MHz, CDCl₃) δ 7.04 - 6.93 (m, 4H), 4.40 - 4.31 (m, 4H), 3.96 - 3.89 (m, 4H). EI-MS: m/z calcd for C₁₀H₁₂O₃: 180.08, found: 180.07[M]⁺.

Preparation of 4-formylbenzo-9-crown-3³:

Benzo-9-crown-3 ether (2.8 g, 15.5 mmol), hexamethylenetetramine (2.17 g, 15.5 mmol) and trifluoroacetic acid (20 mL) were added in a 100 mL round-bottom flask. The solution was heated at 90°C under nitrogen for 12 h. The mixture was poured onto 40 g of ice and extracted with CH₂Cl₂ (3 × 100 mL). After washing with water (3 × 100 mL) dried over anhydrous Na₂SO₄, the organic solvent was removed by rotary evaporation. Elution with 10:1 CH₂Cl₂ : petroleum ether yielded 2.4 g (74.4%) 4-formylbenzo-9-crown-3. ¹H NMR (400 MHz, CDCl₃) δ 9.82 (s, 1H), 7.57 - 7.43 (m, 2H), 7.04 (d, *J* = 8.2 Hz, 1H), 4.65 - 4.59 (m, 2H), 4.29 - 4.24 (m, 2H), 3.93 - 3.85 (m, 4H). EI-MS: m/z calcd for C₁₁H₁₂O₄: 208.07, found: 208.08[M]⁺.

Preparation of 4-carboxybenzo-9-crown-3³:

4-formylbenzo-9-crown-3 (2.12 g, 0.01 mol), water (200 mL) in a 250 mL round-bottom flask was heated at 75°C. KMnO₄ (2.15 g, 0.01 mol) in water was added dropwise. The reaction continued for 4 h and then concentrated KOH solution was added until the solution was basic. The mixture was stirred for 30 min and filtered while it was still hot. The precipitates was washed with water (3 × 100 mL). The cooled filtrates were acidified with H₂SO₄. The as-formed white crude product was filtered, washed with cold water and recrystallized from water to yield 1.62 g (72.3%) 4-carboxybenzo-9-crown-3. ¹H NMR (400 MHz, CDCl₃) δ 7.84 - 7.67 (m, 2H), 7.00 (d, *J* = 8.4 Hz, 1H), 4.72 - 4.53 (m, 2H), 4.28 (dd, *J* = 5.2, 3.6 Hz, 2H), 3.92 (m, 4H). EI-MS: m/z calcd for C₁₁H₁₂O₅: 224.07, found: 224.07[M]⁺.

Preparation of 2:

A solution of 4-carboxybenzo-9-crown-3 (0.67g, 3 mmol) , SOCl₂ (0.2 mL, 15 mmol) , DMF (1 mL), 20 mL CH₂Cl₂ (20 mL) in a 50 mL round-bottom flask was stirred for 4 h at room temperature. Most of the solvent was removed by rotary evaporation, then 2-Hydroxyethyl methacrylate (0.7 mL, 6 mmol) and DMAP (5 mg, 0.04 mmol) was added. The reaction continued for 12 h and the resulting product was extracted with CH₂Cl₂ (3 × 50 mL) and dried over anhydrous Na₂SO₄. Elution with 20 : 1 CH₂Cl₂ : ethyl acetate yielded 0.5 g (49.6%) 2. ¹H NMR (400 MHz, CDCl₃) δ 7.75 - 7.61 (m, 2H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.14 (s, 1H), 5.64 - 5.51 (m, 1H), 4.62 - 4.42 (m, 6H), 4.27 (dd, *J* = 5.2, 3.6 Hz, 2H), 3.90 (m, 4H), 1.95 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.30, 165.69, 155.89, 150.64, 136.12, 126.34, 126.19, 125.72, 124.84, 122.07, 75.20, 72.83, 72.52, 71.98, 62.66, 62.59, 18.41. EI-MS: m/z calcd for C₁₇H₂₀O₇: 336.12, found: 336.09[M]⁺.

References

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