

# Carbohydrate Recognition by Porphyrin-Based Molecularly Imprinted Polymers

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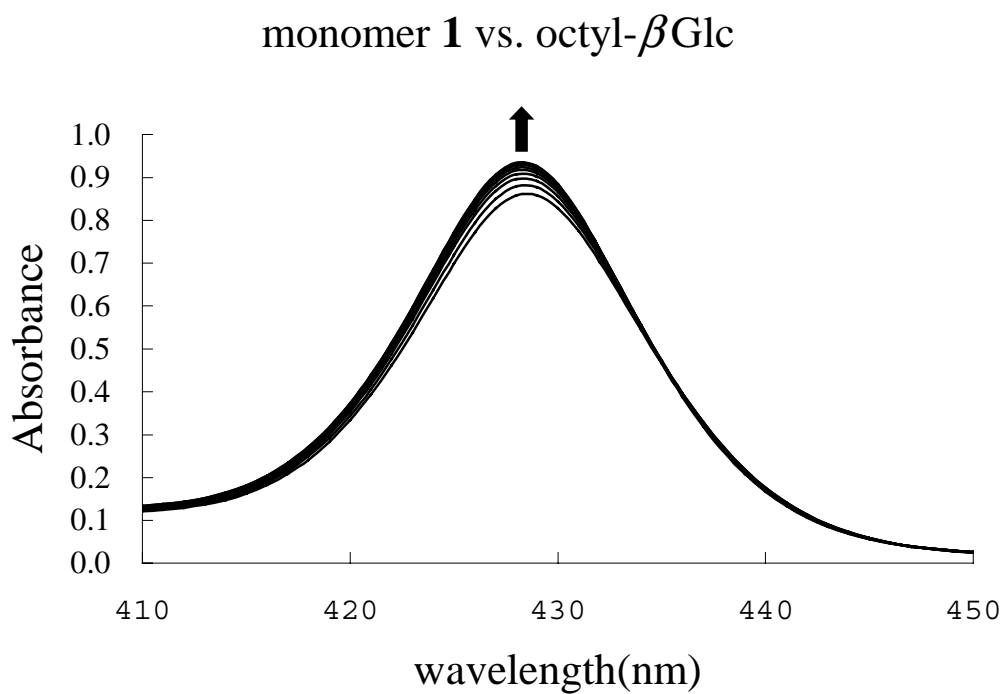
## Contents

Synthesis of monomer <b>1</b> .....	S2
Spectral change of monomer <b>1</b> in the presence of <i>n</i> -octyl- $\beta$ -D-glucopyranoside.....	S3
UV-visible titration curves.....	S3
Preparation of polymers.....	S4

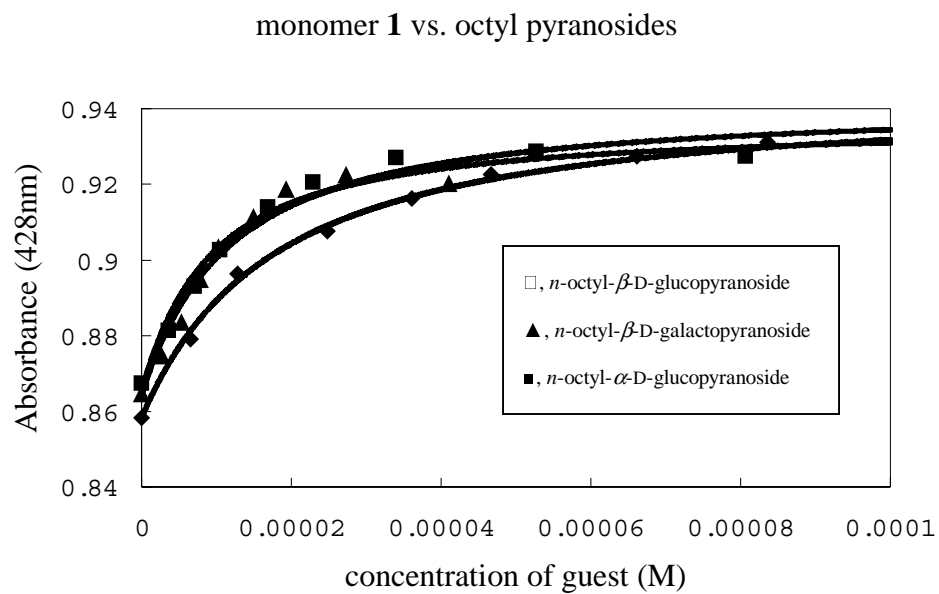
## Synthesis of monomer **1**

$\alpha,\alpha,\alpha,\alpha$ -5,10,15,20-tetrakis(2-aminophenyl)-21*H*,23*H*-porphine (835 mg, 1.24 mmol) was dissolved in 30 mL of distilled dichloromethane, and then 2-isocyanatoethylmethacrylate (from Aldrich, 1.75 mM, 12.4 mmol) was added slowly to the solution. After the reaction mixture was stirred overnight at room temperature under N<sub>2</sub>, solvent was evaporated under reduced pressure to give the crude product, which was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/methanol = 20:1, R<sub>f</sub> = 0.35) eluting with CH<sub>2</sub>Cl<sub>2</sub>/methanol = 40:1). Next, the product was dissolved in 15 mL of chloroform, followed by the addition of a solution of zinc acetate dihydrate dissolved in methanol. The resulting solution was stirred under nitrogen for 24 hours. Water was added, the mixture stirred for 30 minutes and organic layer separated. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, evaporated and purified by flash chromatography (CH<sub>2</sub>Cl<sub>2</sub> / methanol = 40:1) to yield **1** (640 mg, 38 % overall yield): UV-vis. (CHCl<sub>3</sub>)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 428 nm (5.57), 558 nm (4.24), 596 nm (3.52); <sup>1</sup>H NMR (300 MHz, acetone-*d*<sub>6</sub>): 1.54 (s, 12H), 3.00 (m, 8H), 3.75 (t, J = 5.7 Hz, 8H), 5.24 (s, 4H), 5.63 (s, 8H), 6.31 (s, 4H), 7.47 (t, J = 7.1 Hz, 4H), 7.77 (t, J = 8.1 Hz, 4H), 8.00 (d, J = 7.5 Hz, 4H), 8.29 (d, J = 7.8 Hz, 4H), 8.78 (s, 8H); <sup>13</sup>C NMR (100.6 MHz, acetone-*d*<sub>6</sub>): 17.44, 38.56, 63.52, 116.05, 121.97, 122.24, 125.06, 129.27, 131.91, 133.56, 135.03, 136.15, 140.23, 150.48, 155.40, 166.52; HRMS calcd for C<sub>72</sub>H<sub>69</sub>N<sub>12</sub>O<sub>12</sub>Zn *m/z* 1357.4449, found 1357.4398.

**Figure-S1.** Spectral change of monomer **1** in the presence of *n*-octyl- $\beta$ -D-glucopyranoside



**Figure-S2.** UV-visible titration curves



## Preparation of polymers

**General procedure for the preparation of MIP1.** All of the commercially available compounds such as azobisisobutyronitrile (AIBN), divinylbenzene (DVB), and methacrylic acid (MAA) were used without further purification. To a solution of monomer **1** (136 mg, 0.1 mmol) and *n*-octyl- $\beta$ -D-glucopyranoside (29.2 mg, 0.1 mmol) were added MAA (25  $\mu$ L, 0.3 mmol), DVB (0.84 mL) and AIBN (25.6 mg, 5 mol%). The solution was sonicated for 5 min. The polymerization was photoinitiated at 20°C with a Hanovia medium-pressure 450 W mercury arc lamp. The reaction was allowed to proceed for 20 h. After the monolith was ground, Soxhlet extraction followed three times; the first with methanol, the second with acetonitrile-methanol (v/v = 4/1) and the third with chloroform. Drying under vacuum afforded particles, which were used for rebinding studies.