

Electronic Supplementary Information for

Highly selective recognition of acetate and bicarbonate by thiourea-functionalised inverse opal hydrogel in aqueous solution

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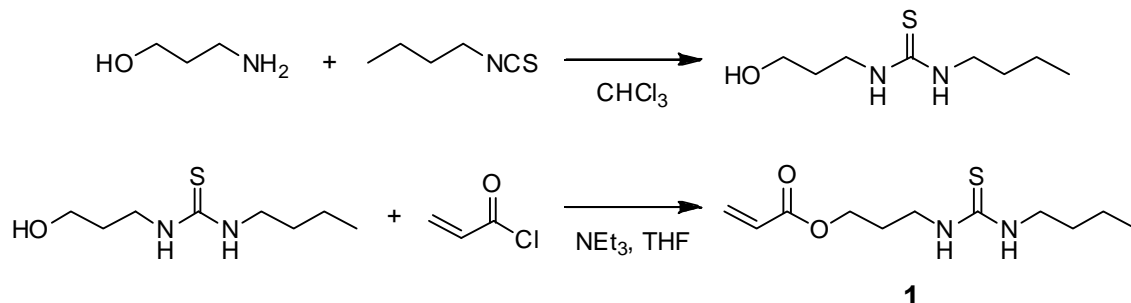
Materials

All the chemicals were commercially available. Acrylamide was purified by recrystallisation from ethyl acetate. AIBN was purified by recrystallisation from methanol. DMSO used as a solvent of pre-gel solutions was distilled under reduced pressure. Other chemicals were used as received without any purification. Silica nanoparticles (about 200 nm in diameter) provided by Nissan Chemical Industries, Ltd. (Japan) were used to prepare the silica colloidal crystals according to the literature.[S1]

Measurements

NMR spectra were obtained with JEOL JNM-ECA 400 spectrometer (400 MHz) in CDCl₃ solution with tetramethylsilane as an internal standard. IR spectra were recorded with JASCO FT/IR-420 spectrometer. Reflection spectra of inverse opal hydrogels were measured with a spectrophotometer (USB4000, Ocean Optics Inc.) equipped with a light source (DH-2000, Ocean Optics Inc.) and a fibre probe, which was kept in a perpendicular position to the hydrogel surface. The obtained reflection spectra were subjected to the background correction based on subtraction of the base line signal from the original spectra, if necessary.

Synthesis



Scheme S1 Synthesis of thiourea-functionalised monomer.

Synthesis of 3-(*N'*-butylthioureido)propanol

To a stirred solution of 3-aminopropanol (7.62 g, 0.101 mol) in 250 mL of chloroform in an ice bath was added *n*-butyl isothiocyanate (11.5 g, 0.100 mol), and the reaction mixture was stirred for 3.5 h at 0 °C. Then, the mixture was stirred for additional 2 h at room temperature. The solvent was removed *in vacuo*, and the residue was washed with water. The crude product was recrystallised from ethyl acetate to give the thiourea-alcohol (14.2 g, 75 %) as a white solid. m.p. 74 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.94 (3H, t, *J* = 7 Hz), 1.39 (2H, m), 1.59 (2H, m), 1.80 (2H, m), 3.64 (6H, m), 6.13 (2H, d).

Synthesis of 3-(*N'*-butylthioureido)propyl acrylate, compound **1**

To a stirred solution of 3-(*N'*-butylthioureido)propanol (3.43 g, 18.0 mmol) and triethylamine (3.23 g, 31.9 mmol) in 100 mL of dry THF was added acryloyl chloride (1.71 g, 18.9 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 20 h and then filtered. The solvent was removed *in vacuo*, and ethyl acetate (100 mL) and water (100 mL) were added to the residue. The organic layer was separated and washed with water (100 mL x 5), and then evaporated. The crude product was purified by silica gel column chromatography (1 : 1, hexane-ethyl acetate) to afford compound **1** (0.79 g, 18 %) as a slightly yellow viscous liquid. ¹H NMR (400 MHz, CDCl₃) δ 0.95 (3H, t, *J* = 7 Hz), 1.38-1.42 (2H, m), 1.56-1.63 (2H, m), 1.97-2.03 (2H, m), 3.32-3.35 (2H, br m), 3.61-3.63 (2H, br m), 4.29 (2H, t, *J* = 6 Hz), 5.88 (1H, dd, *J* = 10, 1 Hz), 5.94 (1H, br s), 6.13 (1H, dd, *J* = 17, 10 Hz), 6.22 (1H, br s), 6.44 (1H, dd, *J* = 17, 1 Hz); IR(KBr) 3357, 3257, 3069, 2958, 2932, 2872, 1724, 1711, 1636, 1618, 1555, 1409, 1295, 1274, 1195, 1062, 984, 811 cm⁻¹; Anal. Calcd. for C₁₁H₂₀N₂O₂S: C, 54.07; H, 8.25; N, 11.46. Found: C, 53.66; H, 8.30; N, 11.40.

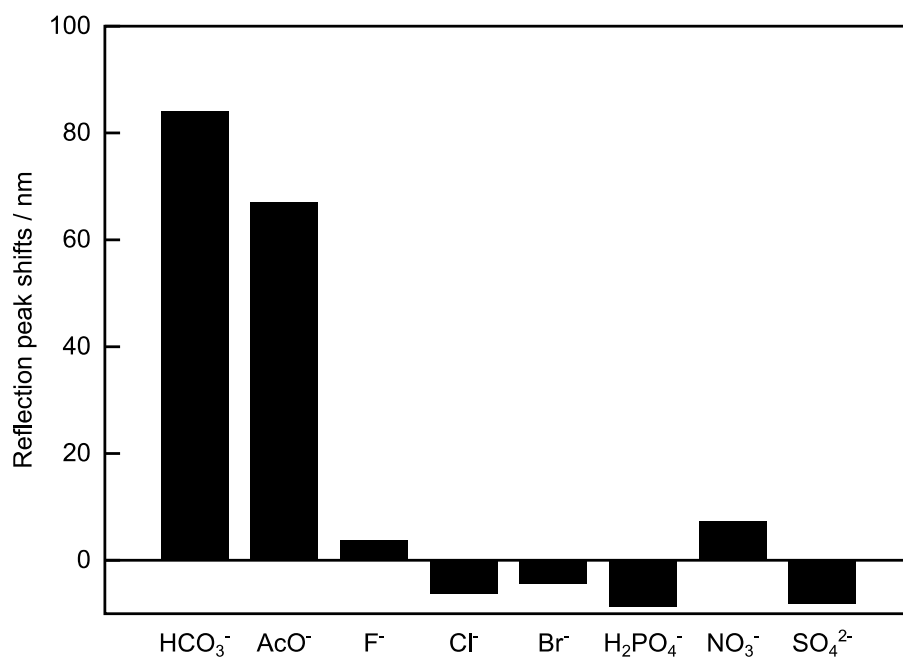


Fig. S1 Bar chart of reflection peak shifts of inverse opal hydrogel for various anions in water ([NaX] = 0.01 M).

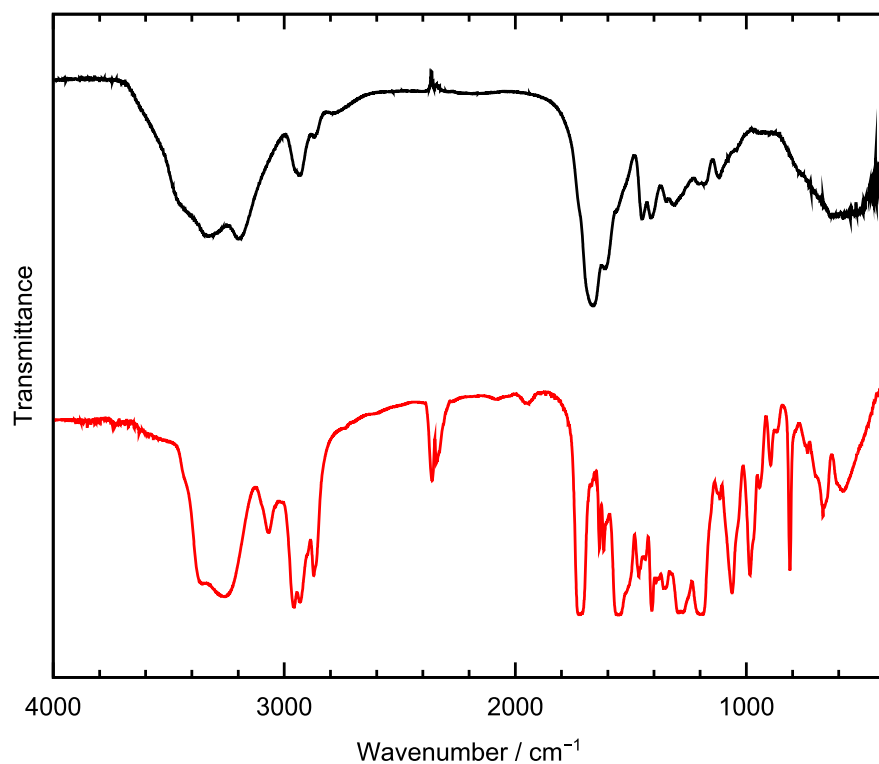


Fig. S2 FT-IR(KBr) spectra of (black) thiourea-functionalised hydrogel(in its dry state) and (red) the thiourea monomer. The peaks around 1200 cm⁻¹ in the both spectra can be assigned to C=S bond.

Reference

[S1] Y. Takeoka and M. Watanabe, *Adv. Mater.*, 2003, **15**, 199.