Electronic Supplementary Information

Molecularly imprinted mesoporous silica particles showing a rapid kinetic binding

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Materials and measurements. 3-(Triethoxysilyl)propyl isocyanate, dibutyltin dilaurate (DBDU), tetraethyl orthosilicate (TEOS), cetyltrimethylammonium bromide (CTAB), (3-aminopropyl)triethoxysilane, bisphenol-A, 4,4'-biphenol, and hydroquinone were obtained from Aldrich. (E)-Diethylstilbestrol (DES) was purchased from Sigma. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker Avance DPX-300 spectrometer. FT-IR spectra were recorded on a Perkin-Elmer Spectrum 2000 spectrometer. Elemental analyses were carried out on a Flash EA 1112 elemental analyzer. Transmission electron microscopy (TEM) images were obtained by a CM-20 instrument operating at 200 kV. Scanning electron microscopy (SEM) images were taken by a JEOL JSM6330F microscope. Surface area was measured by using a Belsorp-Max (BEL Japan, Inc.) analyzer. Ultra-high purity grade N_2 was used for all adsorption measurements. X-ray diffraction (XRD) patterns were recorded by a Bruker Xps GADDS diffractometer (Cu Kα radiation, λ = 1.54 Å).The solid-state ^{13}C CP/MAS NMR spectra were obtained on a Bruker Avance DSX-400 (400 MHz) spectrometer equipped with a CP-MAS probe. Samples were spun in air at approximately 7 kHz. Reverse phase HPLC analysis was carried out using a M930 solvent delivery system, a M720 UV-vis detector (Young Lin Instrument Co., Ltd., Korea), a MetaSil 5u ODS column from Metachem

(Torrance, Canada) with methanol as an eluent at a rate of 1.0 mL/min at room temperature. For each analysis 20 mL of sample was injected, and the column effluent was monitored at 254 nm.

Synthesis of DES-Si. Diethylstilbestrol (3.0 g, 11 mmol) and 3-(triethoxysilyl)propyl isocyante (6.08 g, 24 mmol) were dissolved in THF (50 mL). To the solution, catalytic amount of dibutyltin dilaurate was added at room temperature. The reaction mixture was stirred for 24 h at 75 ^{o}C. After the solvent evaporation, the product was obtained by recrystallization from methanol. Yield: 47%. Anal. Calcd. (in wt%) for $C_{38}H_{62}N_2O_{10}Si_2$: C, 59.81; H, 8.19; N, 3.67. Found: C, 59.95; H, 8.01; N, 3.55. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.17 (d, *J* = 8.4 Hz, Ar-H, 4H), 7.11 (d, *J* = 8.7 Hz, Ar-H, 4H), 5.36 (t, *J* = 6 Hz, -NH-, 2H), 3.85 (q, *J* = 6.9 Hz, O-CH_2-CH_3, 12H), 3.29 (q, *J* = 6.3 Hz, N-CH_2-CH_2, 4H), 2.12 (q, *J* = 7.5 Hz, C-CH_2-CH_3, 4H), 1.73 (m, CH_2-CH_2-CH_2, 4H), 1.25 (t, *J* = 6.9 Hz, OCH_2-CH_3, 18H), 0.78-0.67 (m, overlap, Si-CH_2-CH_2, CCH_2-CH_3, 10H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 154.9, 149.8, 139.2, 129.7, 121.3, 58.7, 43.8, 28.7, 23.4, 18.5, 13.5, 8.0. IR (KBr pellet, cm^{-1}): 3313, 2973, 2933, 2889, 1716, 1546, 1499, 1260, 1208, 1079, 954.

Synthesis of imprinted mesoporous silica particles. To a solution of CTAB (1.00 g, 2.74 mmol) in deionized water (480 mL) was added NaOH (aq) (2.00 M, 3.50 mL). A solution of TEOS (5.45 g, 26.1 mmol) and **DES-Si** (0.8 g, 1.04 mmol) in THF (10 mL) was added dropwise to the CTAB solution. The reaction mixture was stirred for 3 h at 60 ^{o}C. The precipitated silica particles were isolated by filtration, washed with deionized water and methanol, and dried in vaccum. To remove CTAB, the silica particles (1.0 g) were stirred for 3 h in a mixture of concentrated HCl (10 g) and methanol (200 g) at room temperature. The silica particles were isolated by filtration, washed with deionized water and methanol, and dried in vaccum. To extract the template molecules, the silica particles were refluxed in a

mixture of 1,4-dioxane and water (7/1 v/v). The process of extraction was monitored by UV spectroscopy. For the synthesis of control mesoporous silica particles, (3-aminopropyl)triethoxy silane was used instead of **DES-Si**.

Rebinding test. In specific binding test, the imprinted silica or the control silica particles (100 mg) were added to a solution of DES, 4,4'-biphenol, bisphenol-A, or hydroquinone in THF (3 mM, 50 mL). After incubating for 2 h at room temperature, the silica particles were isolated by filtration. The filtrate was concentrated to dryness by evaporation of the solvent before HPLC analysis.

In kinetic test, the imprinted or the control silica particles (100 mg) were added to a solution of DES in THF (3 mM, 50 mL). Then 0.5 mL of the mixture was taken at regular time and filtrated. The filtrate was concentrated to dryness by evaporation of the solvent before HPLC analysis.