Electronic Supplementary Information

Highly nanoporous silicas with pore apertures near the boundary between micro- and mesopores through an orthogonal selfassembly approach

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Experimental Section

Synthesis of SDAs: The first step was performed under a flow of nitrogen by using standard Schlenk techniques, while the following hydrolysis reaction was performed under ambient atmosphere. Reaction scheme for the synthesis of **BC4** is shown in Scheme S1. Typically, 1,3,5-trihydroxybenzene dehydrate (TCI, 1.9 g, 15 mmol) was dissolved in dehydrated acetone (Wako, 50 mL). The resulting solution was then added into a mixture of anhydrous K₂CO₃ (Wako, 26 g, 90 mmol) and 18-crown-6 (TCI, 0.11 mg, 0.42 µmol). After the mixture was stirred at room temperature for 10 min, ethyl 4-bromobutyrate (TCI, 11 g, 66 mmol) was added and then the reaction was carried out by heating at reflux temperature for 8 days. The reaction solution was cooled to room temperature, filtered, evaporated, and purified by gradient, flash chromatography on a silica column (eluted with *n*-hexane/acetone = x: 1; x varied from 5 to 2) to afford a colorless transparent oil. In the hydrolysis step, the oil was boiled with 10% KOH (Wako, 19 g, 33 mmol) aqueous solution for 4 days and the reaction system then became homogeneous. After the reaction mixture was cooled to room temperature, HCl (Wako, conc., ~36%) was slowly added until reaching pH 1. A resulting white solid was filtered and dried to afford BC4 (2.1 g, 37% yield) as a white powder. ¹H NMR (269.7 MHz, methanol- d_4 , TMS): δ (ppm) 6.08 (s, 3H), 3.95 (t, 6H, J = 6.2 Hz), 2.46 (t, 6H, J = 7.3 Hz), 2.02 (dt, 6H, J = 6.7 Hz). ¹³C NMR (67.7 MHz, methanol- d_4 , TMS): δ (ppm) 177.0, 162.1, 95.0, 67.9, 31.3, 25.7. ESI-MS (m/z): $[M+H]^+$ calcd for C₁₈H₂₄O₉, 385.1493; found, 385.1472.

Synthesis of **BC5** (23% yield) was conducted by the similar procedure using ethyl 5bromopentaonate (TCI). ¹H NMR (269.7 MHz, methanol-*d*₄, TMS): δ (ppm) 6.06 (s, 3H), 3.93 (t, 6H, J = 7.3 Hz), 2.37 (t, 6H, J = 6.9 Hz), 1.81–1.21 (m, 12H). ¹³C NMR (67.7 MHz, methanol-*d*₄, TMS): δ (ppm) 177.4, 162.3, 95.0, 68.6, 34.6, 29.8, 22.8.

BC6 was synthesized by the similar procedure using ethyl 6-Bromohexaonate (TCI) in 41% yield. ¹H NMR (269.7 MHz , methanol- d_4 , TMS): δ (ppm) 6.07 (s, 3H), 3.91 (t, 6H, J = 7.3 Hz), 2.32 (t, 6H, J = 7.1 Hz), 1.81–1.41 (m, 18H). ¹³C NMR (67.7 MHz, methanol- d_4 , TMS): δ (ppm) 177.6, 162.4, 94.9, 68.8, 30.1, 26.8, 25.9.



Scheme. S1 Synthesis of BC4.

Synthesis of silicas: The synthesized aromatic compound (**BC***n*) was dispersed in deionized water while stirring at 60 °C. A mixture of 3-aminopropyltrimethoxysilane (TCI) and tetraethyl orthosilicate (Wako, 95%) was slowly added to the solution while stirring at 60 °C. The final molar composition were 0.05 **BC***n*: *x* **APS**: (1-x) **TEOS**: 90 H₂O. The synthesis mixture was stirred for 24 hours at 60 °C and then kept without stirring at the same temperature for 4 days. The resulting solid was filtered and washed with deionized water and dried under 60 °C. The as-made white powder was either calcined at 550 °C for 6 hours or washed (extracted) with ethanolic solution of ammonium acetate. For the extraction, 2 g of ammonium acetate (Wako) and 0.1 g of as-made sample was dispersed in 100 mL ethanol (Wako). The suspension was heated at 95 °C overnight. Then, the solid was recovered by filtration and washed with ethanol. The process was repeated twice. Finally, the product was dried at 60 °C.

Characterization: Solid-state NMR spectra were obtained from an ECA 500 spectrometer (JEOL). ²⁹Si MAS NMR spectra were recorded at 99.3 MHz with a pulse width of 5.0 µs, a recycle delay of 60 s, and a spinning frequency of 10 kHz. $^{1}H^{-13}C$ CP/MAS NMR spectra were obtained at 125.8 MHz with a contact time 5.0 ms, a pulse width of 2.75 µs, a recycle delay of 5.0 s, and a spinning frequency of 10 kHz. Solution-state ¹H and ¹³C NMR spectra were obtained from an EX270 spectrometer (JEOL) at 269.7 MHz and 67.7 MHz, respectively. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultra IV with CuK α radiation (40 kV, 40 mA). The 2 θ values were ranged from 1° to 6° with a scan speed of 0.6° min⁻¹ and a scanning step of 0.01° . Gas sorption analysis was performed using an Autosorb-iQ2-MP (Quantachrome). Nitrogen sorption was carried out at 77 K in a liquid nitrogen bath, while argon sorption isotherms were collected at 87 K in a liquid argon bath. Pore size distributions were evaluated with a non-local density functional theory (NL-DFT) method where nitrogen molecules are adsorbed onto cylindrical pores of silica with equilibrium model or where argon molecules are adsorbed onto spherical/cylindrical pore of zeolite/silica with equilibrium model. UV-Vis spectra were collected on a JASCO V-670 instrument. ESI-MS analyses were performed on a Bruker maXis. Scanning electron microscopy (SEM) image was obtained with a JSM-7000F (JEOL). Transmission electron microscopy (TEM) observations of the calcined sample on carbon-coated copper grids were performed on a JEM 2000EXII (JEOL) operated at 200 kV. Carbon, hydrogen, and nitrogen (CHN) elemental analyses were performed on a CE-440 (Exeter Analytical). Thermogravimetric (TG) analyses were performed on a PU 4K (Rigaku) with a heating rate of 10 K min⁻¹ using a mixture of 10% O₂ and 90% He as the carrier gas.



Fig. S1 Solution-state ¹³C NMR spectra of **BC4** (bottom), **BC5** (middle) and **BC6** (top) in methanol d_4 . The signals of carboxylic acid group (*ca.* 177 ppm), benzene ring (*ca.* 162 and 95 ppm), and alkyl chain (69–15 ppm) were observed.



Fig. S2 Illustrations of (a) **BC4**, (b) **BC5**, and (c) **BC6** optimized at B3LYP/6-31G(d) level with Gaussian 09 package.^{S1} Double-headed arrows represent the distance between the center of benzene ring and the proton on the carboxylic acid group.

Reference:

S1 Gaussian 09, Revision A. 02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.



Fig. S3 Solid-state ²⁹Si MAS NMR spectra of the as-made (top), extracted (middle), and calcined (bottom) silica-BC6 samples (x = 0.18). Signals from T³ (C<u>Si</u>(OSi)₃) were observed at *ca.* -66 ppm in the as-made and extracted samples. Q², Q³, and Q⁴ silicons (Q^{*a*} = <u>Si</u>(OSi)_{*a*}(OH)_{4-*a*}) were detected at *ca.* -91, -101, and -111 ppm, respectively.



Fig. S4 Solution-state ¹³C NMR spectrum of **BC6** in methanol- d_4 (top) and ¹³C CP/MAS NMR spectra of the as-made (middle) and extracted (bottom) silica-BC6 samples (x = 0.18). The assignment of **BC6** in methanol- d_4 is shown in Fig. S1. The signals of carboxylic acid group ($\delta = 183$ ppm), benzene ring ($\delta = 162$ and 95 ppm), and alkyl chain ($\delta = 71-12$ ppm) were observed in the spectrum of the as-made sample. An asterisk denotes spinning side band, detected at $\delta = 80$ ppm. Three peaks from carbon chain of **APS** were observed in the extracted sample ($\delta = 42$, 22, and 10 ppm) as indicated by dotted lines.



Fig. S5 UV-Vis spectra of the as-made, calcined, and, if any, extracted samples prepared with (a) **BC4**, (b) **BC5**, and (c) **BC6** (at x = 0.18) together with the spectra of the powder forms of **BC***n* molecules.



Fig. S6 (a) Powder XRD pattern, (b) nitrogen adsorption–desorption isotherms, and (c) NL-DFT pore size distribution of the silica product prepared without **BC***n*. The molar composition of the synthesis mixture was 0.18 **APS**: 0.82 **TEOS**: 90 H₂O.



Fig. S7 (a) Powder XRD patterns, (b) nitrogen adsorption–desorption isotherms, and (c) NL-DFT pore size distributions of the silica product prepared without **APS** (*i.e.*, x = 0).



Fig. S8 FE-SEM image of the calcined sample synthesized at x = 0.18 with **BC6** (calcined silica-BC6).



Fig. S9 Additional HRTEM images of the calcined sample synthesized at x = 0.18 with **BC6** (calcined silica-BC6). The sample is the same as that presenting in Fig. 3.



Fig. S10 (a, c) Nitrogen adsorption–desorption isotherms and (b, d) NL-DFT pore size distributions of the calcined silica-BC*n* samples synthesized at x = 0.10 (a, b) and 0.30 (c, d). The adsorption and desorption isotherms are presented as filled and empty symbols, respectively. In (a, c), the isotherms of the calcined silica-BC5 and calcined silica-BC6 were offset by 300 and 600 cm³ g⁻¹ STP, respectively.



Fig. S11 (a) Argon adsorption isotherms in a semi-log plot and (b) the corresponding histograms of NL-DFT pore size distributions of the calcined products synthesized at x = 0.18 with SDAs having different length of alkyl side chains and the extracted sample synthesized at x = 0.18 with **BC6**. In (a), the isotherms of the calcined silica-BC5, calcined silica-BC6, and extracted silica-BC6 were offset by 100, 200, and 300 cm³ g⁻¹ STP, respectively.



Fig. S12 (a) Powder XRD patterns, (b) nitrogen adsorption–desorption isotherms, and (c) NL-DFT pore size distributions of the extracted silica-BC6 (x = 0.18), in comparison with the calcined counterpart. The isotherms of the calcined sample were offset vertically by 300 cm³ g⁻¹ STP.

	BC6/APS molar ratio		Organic moieties/silica weight ratio	
	Experimental ^a	Ideal	Experimental ^a	Ideal
As-made silica-BC6	0.28	0.28 ^b	0.44	0.44 ^{<i>b</i>}
Extracted silica-BC6	0.06	0.00 ^c	0.18	0.17 ^c

Table S1 Composition of the as-made and extracted silica-BC6 samples (x = 0.18).

^{*a*} Determined by CHN elemental analysis.

^b Calculated based on the starting ratio of initial synthesis mixtures.

^c Calculated with the assumption that **BC6** is completely removed while all functional groups derived from **APS** remain in the material.