Multifunctional Periodic Mesoporous Organosilicas with Bridging Groups Formed via Dynamic Covalent Chemistry

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Experimental

1. Materials. (3-aminopropyl)triethoxysilane (99% APTES, Aldrich) and 4-(trimethoxysilyl)aniline (90% TMA, Gelest) were used as amine sources and triethoxysilyl butyraldehyde (90% TEBA, Gelest) was used as an aldehyde-containing organosilica source. 1,2-bis(triethoxysilyl)ethane (96% BTEE, Aldrich), 1,4-bis(triethoxysilyl)benzene (96% BTEB, Aldrich) and 2,5-bis(triethoxysilyl)thiophene (96% BTET, JSI silicone) were used as bridged organosilanes. Organosilica precursors were used as purchased without further purification. Silver nitrate ($AgNO_3$, Fisher Scientific), hydrogen peroxide (35 wt% H_2O_2, Acros) and acetonitrile (CH_3CN, Fisher Scientific) were used for oxidation of aldehydes to carboxylic acids inside the PMO materials. Poly(ethylene oxide)-poly(DL-lactic acid-co-glycolic acid)-poly(ethylene oxide), $EO_{16}(L_{29}G_7)EO_{16}$, triblock copolymer (LGE538, M_n (GPC) = 5310, M_n (NMR) = 4220, polydispersity index (PI) = 1.28, and fraction Φ_{PEO} = 0.38) was synthesized through a ring opening polymerization. LGE538 triblock copolymer was used as a soft template for hexagonal mesostructure.

2. Preparation of Multifunctional Periodic Mesoporous Organosilicas. The multifunctional LBMA-PMOs were synthesized by self-assembly of LGE538, BTEB, APTES and TEBA under 0.1 M HCl acidic conditions. The 1:1 molar ratio of APTES and TEBA was used in the synthesis of LBMA-PMOs by varying the composition of reactive organosilanes in relation to BTEB as follows: ([APTES] + [TEBA]):[BTEB]) = 10:90, 20:80, 30:70, 40:60, and 100:0. The relative molar compositions of the synthesis gel studied were: BTEB : (APTES + TEBA) : LGE538 : H_2O : C_2H_5OH : HCl = 15.1-19.6 : 2.8-10.0 : 1.0 : 12850.2 : 115.4: 23.7.

The thiophene-silica-based LTMA-PMOs were prepared using LGE538, BTET, APTES and TEBA under 0.05 - 0.1 M HCl acidic conditions. The ethanesilica-based LENA-PMOs were prepared using LGE538, BTEE, TMA and TEBA under 1 M HCl acidic conditions. The total molar ratios (10, 20 and 30 mol%) of the reactive organosilane precursors used in the synthesis of LTMA- and LENA-PMOs were adjusted similarly as in the case of the LBMA-PMO samples. In a typical synthesis of multifunctional PMO (e.g., LBMA30 in Table 1), 0.5 g of LGE538 triblock copolymer was dissolved in a mixture of 0.5 g of ethanol and 21.78 g of distilled water at 40 °C. After stirring the polymer solution for 1 h, 0.22 g of HCl (37 wt %, Aldrich) was added. After 2 h additional stirring, the mixture of BTEB (0.636 g), APTES (0.0749 g), and TEBA (0.0793 g) was added. White precipitates were obtained after stirring the mixture for about 1-2.5 h at 40 °C followed by ageing for 24 h at 100 °C. 60 g of acetone was used as a washing solvent under magnetic stirring for 5 h at 56 °C to remove the block copolymer template and to make mesoporous

materials accessible for gas adsorption. Finally, the product was washed with distilled water using a suction flask and dried at 100 °C for 1d.

3. Oxidation of Aldehydes to Carboxylic Acids. The aldehyde-containing LTMA-PMOs were oxidized with 35% H_2O_2 and $AgNO_3$ in acetonitrile solution as described elsewhere.[8] In a typical experimental procedure, 70 mg of the LTMA20 sample and 8.5 mg of $AgNO_3$ were mixed in 5 mL CH_3CN solution and 0.25 mL of 35% H_2O_2 was added in the mixture at 50 °C. The reaction mixture was stirred for 5 h maintaining the reaction temperature at 50 °C. The final product was obtained by the filtration with distilled water using a suction flask.

4. Measurements. The small angle X-ray scattering experiments were performed using a Synchrotron radiation with λ = 1.608 Å at the 4C1 lines of Pohang Accelerator Laboratory in POSTECH. The distance between each sample and detector was 50 cm and the sample exposure time was 10 s per sample. The SAXS patterns were obtained by collecting signals scattered on a 2D detector using 2D data processing software. The TEM images were obtained with an FE-TEM (JEOL JEM2100F) operated at an accelerating voltage of 200 kV. The samples were sonicated for 30 min in an adequate quantity of acetone and 5 drops of the solution was taken onto a porous carbon film on a copper grid and then dried.

Nitrogen adsorption-desorption isotherms were measured on a Micromeritics 2020 analyzer. The samples were degassed at 150 °C to achieve vacuum below 30 µmHg. The BET (Brunauer–Emmet–Teller) specific surface area was calculated from the adsorption data in the relative pressure range from 0.03 to 0.15. The total pore volume was evaluated from the amount adsorbed at a relative pressure of 0.99. The PSD curves were calculated from the adsorption branches of the isotherms by using the improved KJS (Kruk–Jaroniec–Sayari) method. The pore width (diameter) was estimated at the maximum of PSD.

The quantitative analysis of organic moieties in the solid powders was performed using a Flash EA 1112 series elemental analyzer (CE Instruments). Thermogravimetric profiles were recorded under air or nitrogen flow in the range from 30 to 800 °C on a TA Instruments TGA 2950 analyzer using a high-resolution mode with a heating rate of 10 °C/min.

An attenuated total reflection Fourier transform infrared spectrometer (ATR-FTIR, Bruker IFS-66/S, Bruker) was used over a frequency range of 600 - 4000 cm^{-1} to identify the imine groups of the samples.

The solid-state ^{13}C cross-polarization magic angle spinning (CP MAS) NMR experiments were performed on an AVANCE II$^+$ 400 MHz spectrometer (Bruker BioSpin GmbH, Germany) using a double-resonance (H-X) MAS probe equipped with a 4-mm rotor. The resonance radio frequencies for ^1H and ^{13}C NMR were 400.1 and 100.6 MHz, respectively. The sample rotor at the magic angle was spun at 13 kHz. A pulse repetition delay of 3 sec and a CP period of 2 ms, a proton pulse length of 4.2 µs corresponding to 90° flip were used for all the NMR experiments in this work. Adamantane (Sigma-Aldrich, U. S. A.) was used as the external standard for referencing the solid-state ^{13}C (38.3 ppm for CH carbons) chemical shifts. The final spectra were obtained after the 14216, 118896, 109340, and 138198 scans for BMA, LBMA10, LBMA20, and LBMA30 samples, respectively.
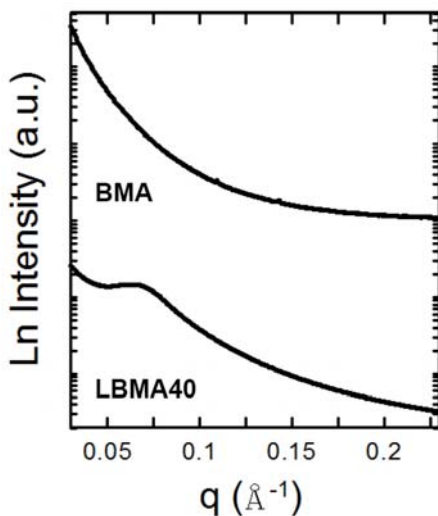
Supporting Figures

Figure S1. SAXS patterns for the BMA and LBMA40 samples prepared in this study.
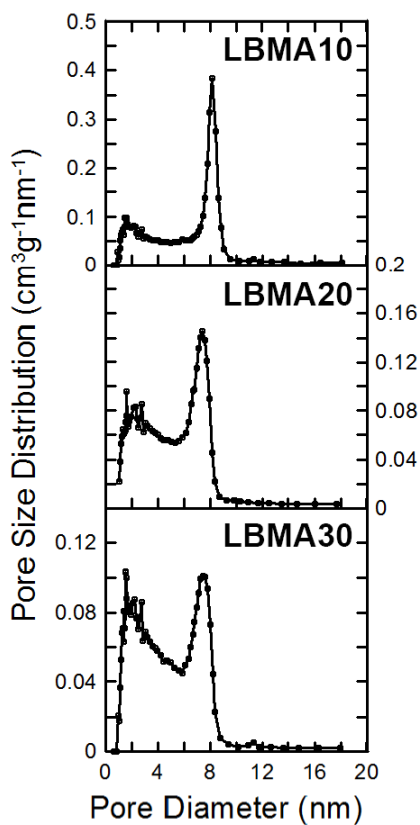

Figure S2. Pore size distributions for the LBMA10, LBMA20 and LBMA30 samples calculated from the adsorption branches of the isotherms by using the improved KJS (Kruk–Jaroniec–Sayari) method.
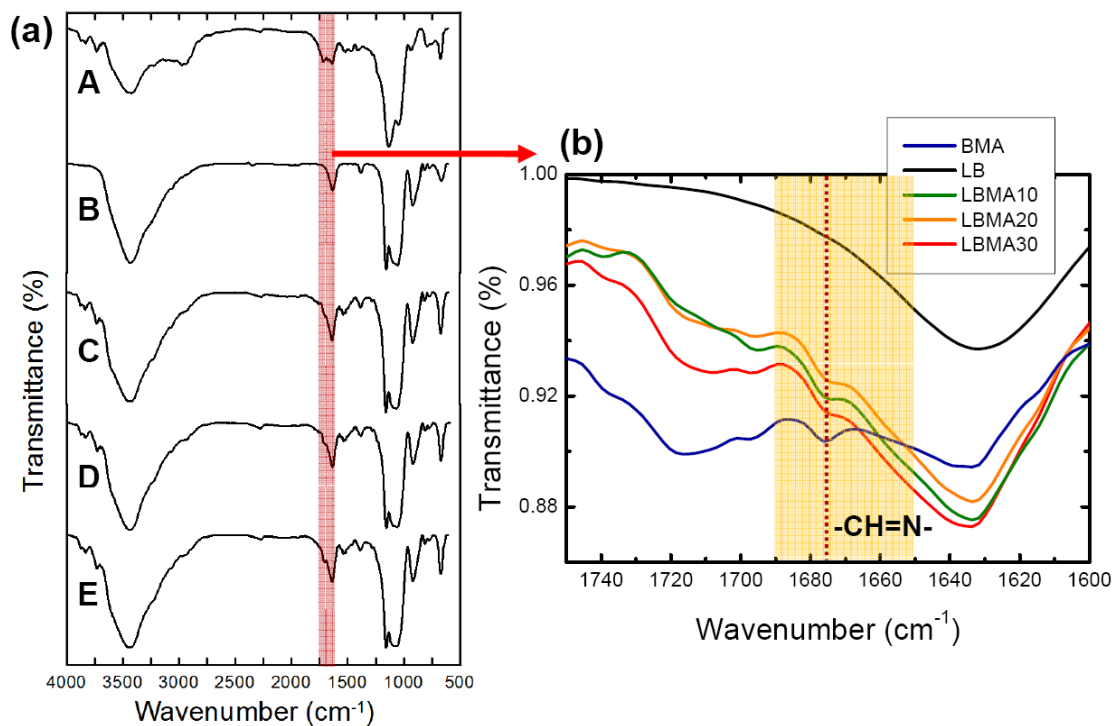
Figure S3. FT-IR spectra (a) for the BMA (A), pure mesoporous benzene-silica without reactive organosilicas (B), LBMA10 (C), LBMA20 (D) and LBMA30 (E) samples. Enlarged IR spectra (b) represent the trace (~1675 cm^{-1}) of imine group formed during the synthesis except for pure mesoporous benzene-silica (LB).
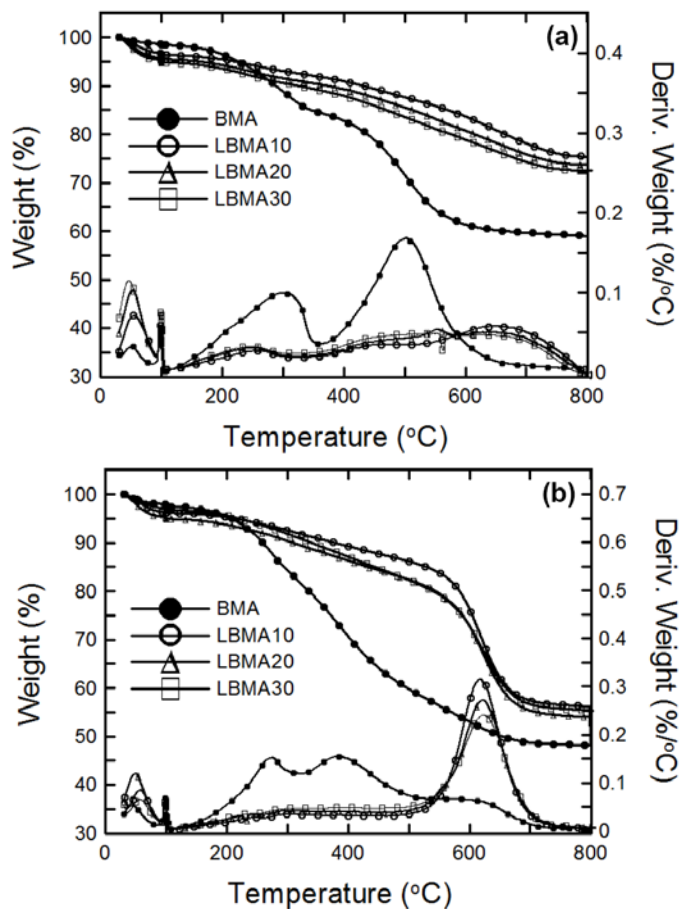
Figure S4. Thermogravimetric analysis of the BMA, LBMA10, LBMA20 and LBMA30 samples prepared under acidic conditions. The TG weight changes and the corresponding DTG curves were obtained in flowing nitrogen (a) and air (b), respectively. The TG weight loss under 100 °C reflects thermodesorption of residual solvents such as acetone and water; the weight loss (12-15 wt%) for the BMA sample from 100 to 350/320 °C (nitrogen/air flow) corresponds mainly to amine and aldehyde groups with attached propyl chains;* and 25-30 wt% weight loss for BMA from 350 to 700 °C refers to the remaining organic groups.*

* (a) A. S. M. Chong et al., *J. Phys. Chem. B.*, 2003, **107**, 650. (b) X. Wang et al., *J. Phys. Chem. B.*, 2005, **109**, 1763. (c) L. Zhang et al., *Micropor. Mesopor. Mater.*, 2008, **109**, 172.)
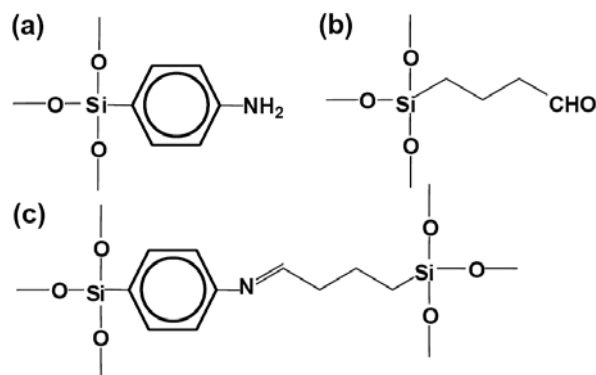
Figure S5. Chemical molecular structures of (a) 4-(trimethoxysilyl)aniline (TMA) and (b) TEBA reactive organosilanes used for the synthesis of the LENA-PMO samples, and (c) a bridged imine group formed by in-situ reaction in LENA-PMOs.
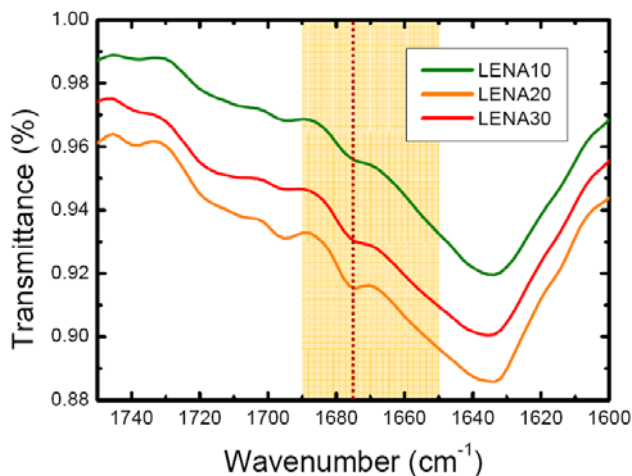

Figure S6. FT-IR spectra for the LENA10, LENA20 and LENA30 samples in the specified range (1600 – 1750 cm^{-1}) of wavenumber. The LENA-PMO samples were prepared using LGE538, BTEE, TMA and TEBA under 1 M HCl acidic conditions. The traces for imine groups are found at 1675 cm^{-1}.
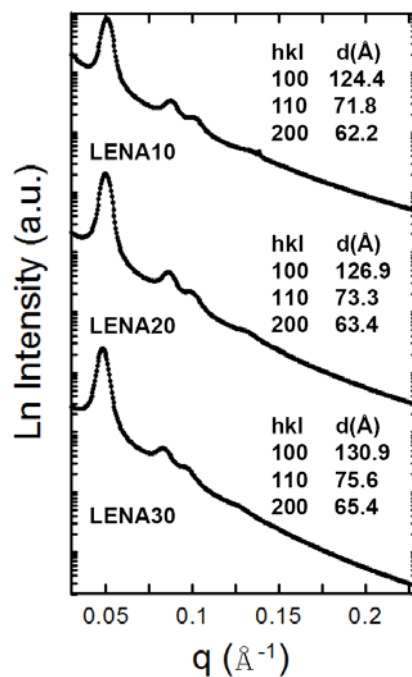
Figure S7. SAXS patterns for the LENA10, LENA20 and LENA30 samples prepared in this study. These samples show highly ordered hexagonal mesostructure. Bragg spacings are listed at each pattern.
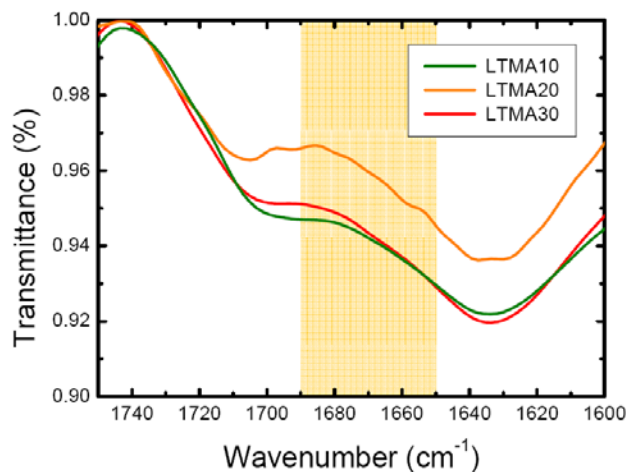

Figure S8. FT-IR spectra for the LTMA10, LTMA20 and LTMA30 samples in the specified range (1600 – 1750 cm^{-1}) of wavenumber. The numbers of 10, 20, and 30 in the sample codes represent the molar ratios of reactive organosilane precursors to the total number of moles of the organosilane used. The LTMA-PMO samples were prepared using LGE538, BTET, APTES and TEBA under 0.05 - 0.1 M HCl acidic conditions. The traces for imine groups are not found in these PMO materials except for a small trace (~ 1660 cm^{-1}) for LTMA20.
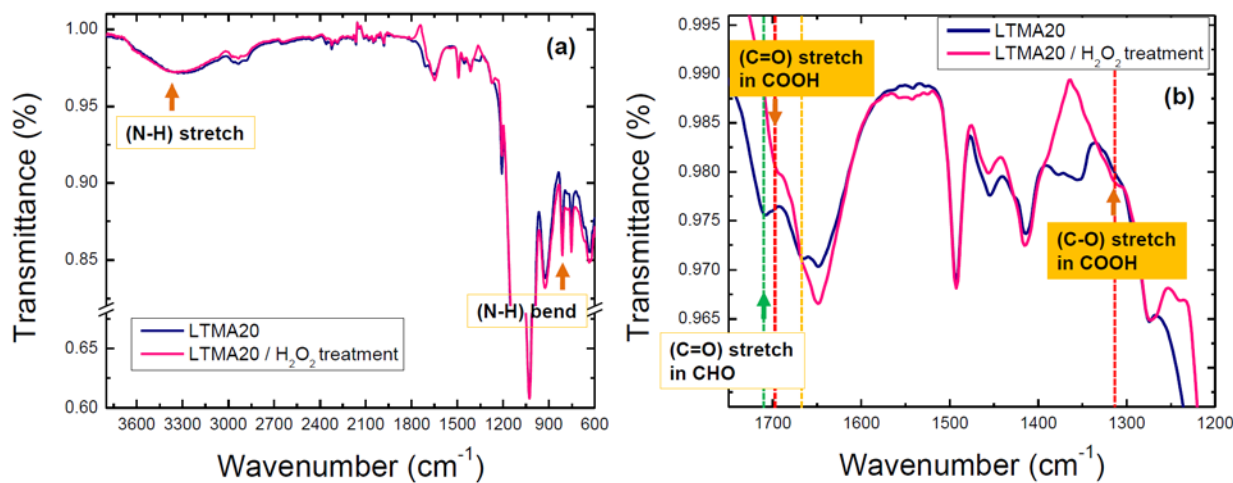
Figure S9. FT-IR spectra for LTMA20 and the oxidized LTMA20 sample treated with H_2O_2 in the full range (a) and the specified range (1200 – 1750 cm^{-1}) (b) of wavenumber. The C=O stretch (~ 1710 cm^{-1}) in aldehyde (CHO) group is shifted to the C=O stretch (~ 1700 cm^{-1}) in carboxylic group (COOH) and the C-O stretch (~ 1310 cm^{-1}) characteristic for carboxylic group (COOH) is visible. The traces for amine (~ 800 and ~ 3400 cm^{-1}) and imine groups (~ 1665 cm^{-1}) are still maintained for the oxidized LTMA20 sample.
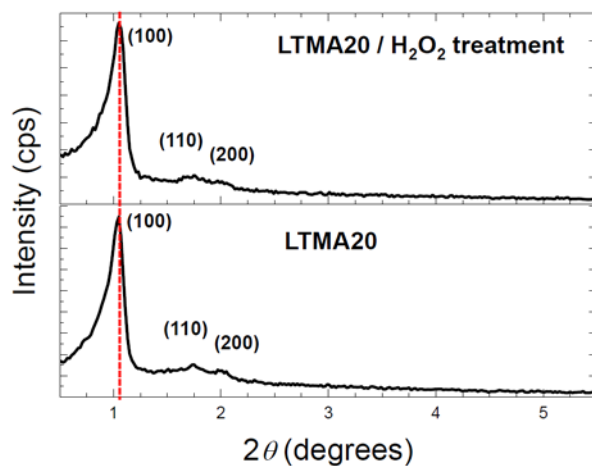

Figure S10. SAXS patterns for LTMA20 and the oxidized LTMA20 sample treated with H_2O_2 prepared in this study. The LTMA20-PMO samples show highly ordered hexagonal mesostructures and the *d*-spacing is still maintained for the oxidized LTMA20 sample. The powder SAXS data were obtained using the PANalytical X'Pert Pro instrument at 40 kV and 40 mA.