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Supplementary Material (Revised Manuscript)

PMO[KIT-5]-n: Synthesis of highly ordered three-dimensional periodic mesoporous organosilicas with Fm3m symmetry

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See http://www.rsc.org/suppdata/cc/b0/b000000a/

Experimental

General

1,2-bis(triethoxysilyl)ethane (BTEE) and hexadecyl-trimethylammonium bromide ($C_{16}TABr$) from Aldrich were used as the organosilica precursor and as an SDA, respectively. NaOH was obtained from Merck-Schuchardt. These reagents were used as received without further purification. Divalent surfactants *N*-(3-trimethylammoniumpropyl)-hexadecylammonium-dibromide, and $[CH_3(CH_2)_{15}NMe_2(CH_2)_3NMe_3]^{2+}2Br^-$ ($C_{16\text{-}3\text{-}1}$) and *N*-(3-trimethylammoniumpropyl)-octadecylammoniumdibromide, and $[CH_3(CH_2)_{17}NMe_2\text{-}(CH_2)_3NMe_3]^{2+}2Br^-$ ($C_{18\text{-}3\text{-}1}$) were synthesized according to the literature by reacting hexadecyldimethylamine or octadecyldimethylamine with (3-bromopropyl)trimethylammonium bromide, respectively (see ref. 19).

Syntheses of mesoporous organosilicas

Synthesis of Material 4 (PMO[KIT-5]-4)

A mixture of $C_{16\text{-}3\text{-}1}$ (2.45 g) and NaOH (0.73 g) in 55 g warm deionized water was stirred to form a clear solution. Then, BTEE (2.82 g) was added and the stirring was continued for 24 h at ambient temperature. Thus obtained clear solution was heated at 95°C for 7 h upon which a white precipitate formed. The suspension was transferred into a polypropylene bottle and aged at 80 °C for 24 h without stirring. The final molar composition of the gel was 1 BTEE : 0.60 $C_{16\text{-}3\text{-}1}$: 2.35 NaOH : 396 H_2O. The warm solid product was recovered by suction filtration without washing and dried at ambient temperature.

The synthesis of materials **2**, **3**, **5-8** was similar to that of material **4**, taking into account the reaction details given in Table 2.

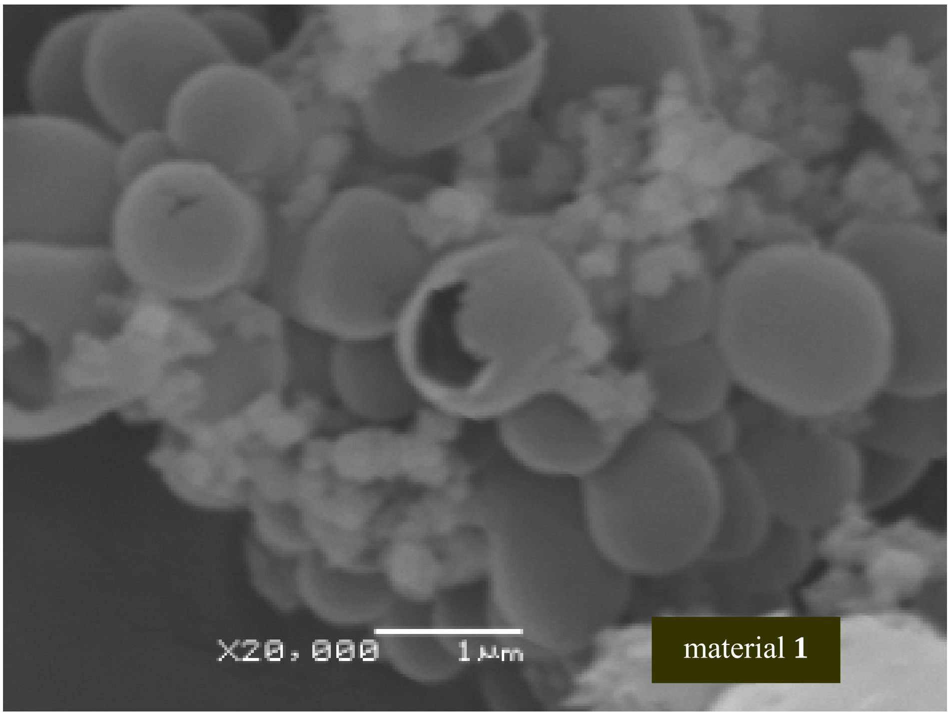
Surfactant removal

For all of the as-synthesized materials **1**–**8**, the surfactant molecules were removed by solvent extraction using a Soxhlet apparatus. In a typical extraction process, 1.0 g of an as-synthesized mesoporous organosilica material was stirred in a solvent mixture of 150 ml ethanol and 4 ml 37% hydrochloride acid for 6 h at 60 ~ 70 °C. The final product was further extracted into a hydrochloride acidified ethanol solution for 24 h by using a Soxhlet apparatus.

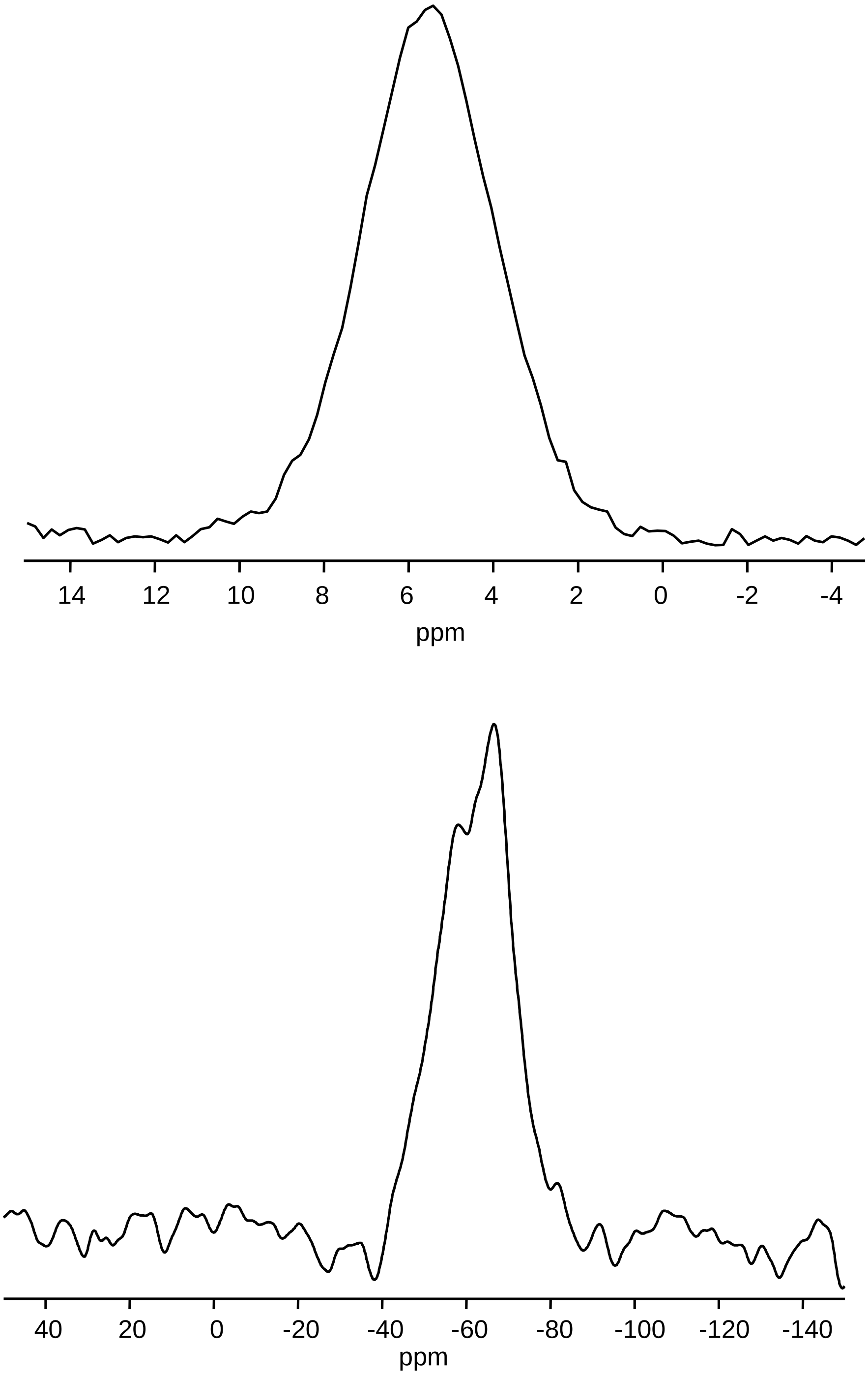
Characterization

Powder X-ray diffraction (PXRD) patterns were recorded on a Philips X'pert PRO instrument in the step/scan mode (step width: 0.00856, accumulation time: 54.61 s/step, range (2θ): 0.51–9.997°) using monochromatic C-K_α radiation ($\lambda = 0.15418$ nm). Scanning electron microscopy (SEM) images were recorded on a JEOL 840A microscope operated at an accelerating voltage of 10-20 kV. Transmission electron micrographs (TEM) were obtained using a JEOL JEM2010 operated at 120 kV.

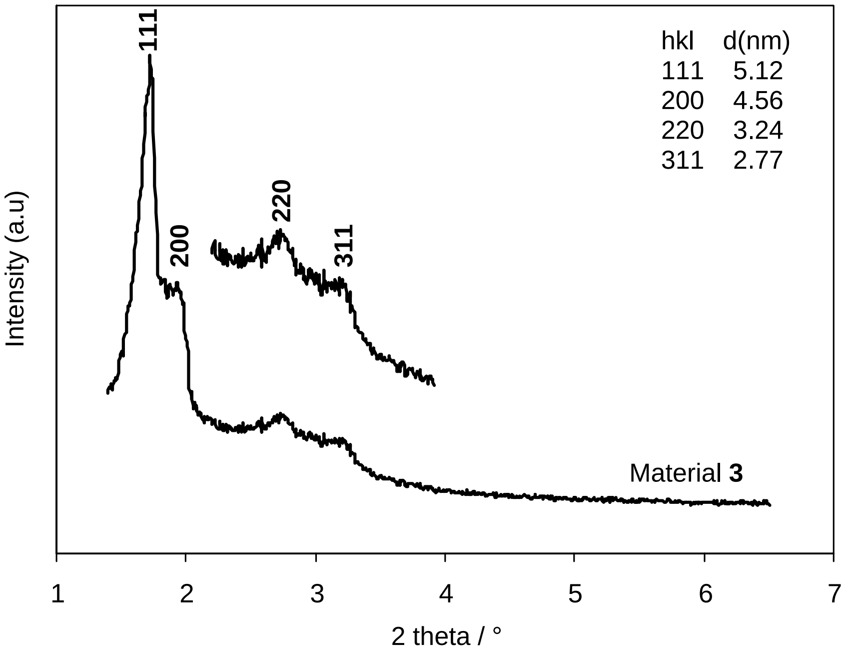
^{13}C and ^{29}Si NMR spectra were obtained at room temperature on a Bruker AV300 instrument in a magnetic field of 7.04 T (the resonance frequencies were 300.13, 75.46, and 59.63 MHz), using 4 mm (^{1}H and ^{13}C) and 7 mm (^{29}Si) standard MAS probes. The ^{13}C spectra were recorded using cross polarization and proton decoupling and referenced to adamantane (^{1}H: 1.76 and 1.87 ppm; ^{13}C 28.46 and 37.85 ppm to adamantane). The following conditions were used in the measurements: ^{13}C, pulse repetition 10.0 s, $\pi/2$ pulse, spinning speed 7 kHz. The ^{29}Si NMR spectra were obtained by the application of single-pulse excitation with high-power proton decoupling at spinning speed of 7 kHz. The spectra were referenced to $Si[Si(CH_3)_3]_4$ (^{29}Si: δ 9.8 ppm). Nitrogen adsorption–desorption isotherms were recorded on an ASAP 2020 volumetric adsorption apparatus (Micromeritics) at 77.4 K for relative pressures from 10^{-2} to 0.99 [$a_m(N_2$, 77 K$)=0.162$ nm^2]. Prior to analysis the samples were outgassed in the degas port of the adsorption analyzer at 523 K for at least 4 h. The BET specific surface area was obtained from the nitrogen adsorption data in the relative pressure range from 0.04 to 0.2. The pore size and pore volumes were calculated from the adsorption and desorption branches of the isotherm using the Kelvin equation and *Barrett–Joyner–Halenda* (BJH) method. Herein, we made use of this method to determine the pore diameter of mesoporous organosilicas.



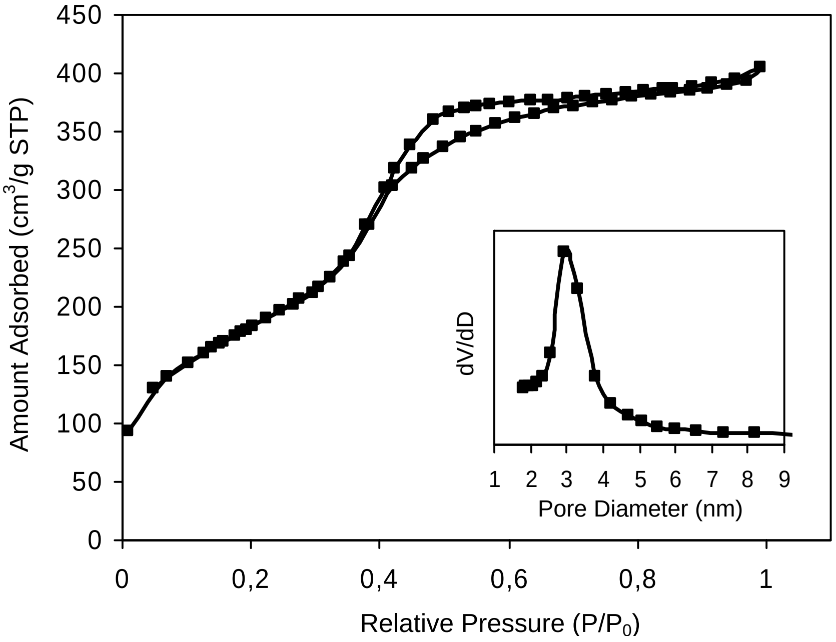
S1. Scanning electron microscopy image of material **1**.



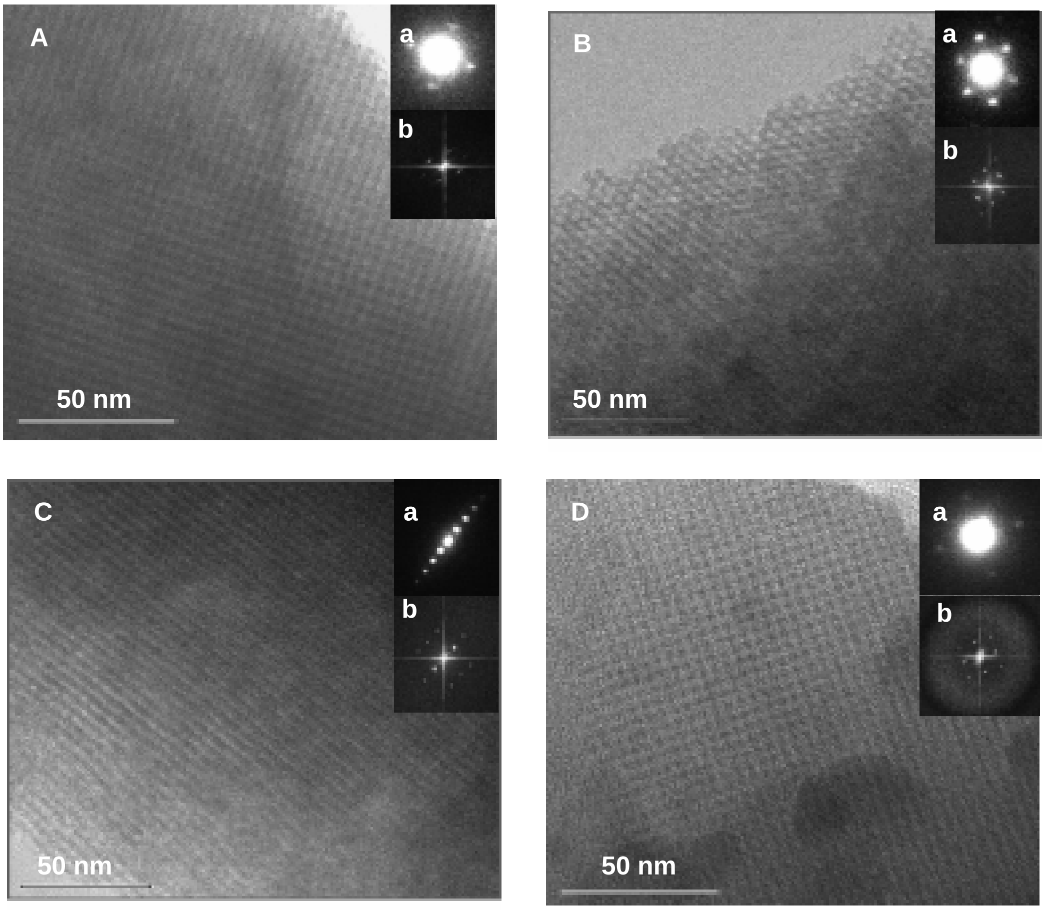
S2. ^{13}C CP MAS NMR spectrum (top) and ^{29}Si MAS NMR spectrum (bottom) for material **1**.



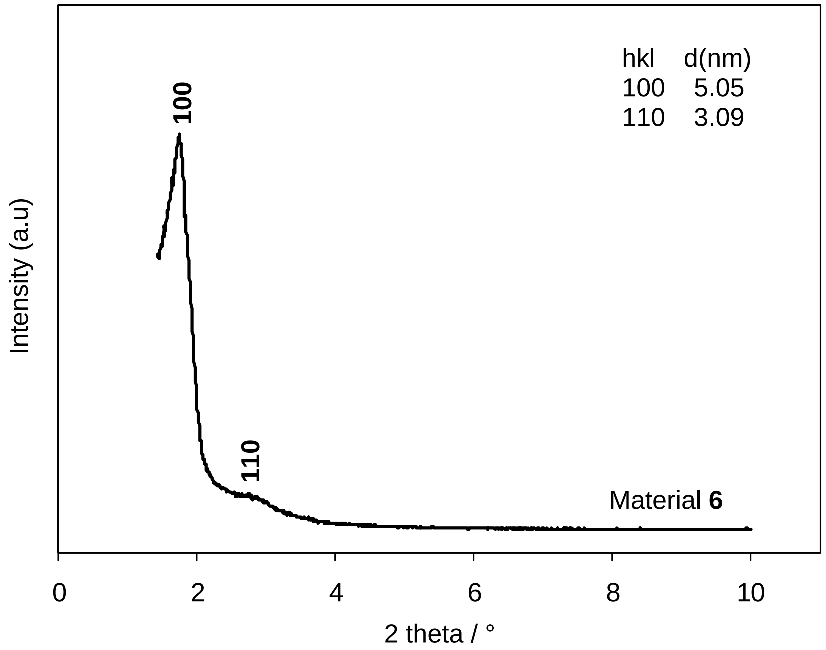
S3(a). Powder x-ray diffraction pattern for material **3**. It was prepared by using hexadecyltrimethylammonium bromide (C_{16}TABr) as an SDA under basic conditions. The molar ratio was 1 BTEE : 0.60 C_{16-3-1} : 2.35 NaOH : 396 H_2O. Aging temperature and aging time were 95 °C and 24 h, respectively. This material displays a cubic structure with Fm3m space group.



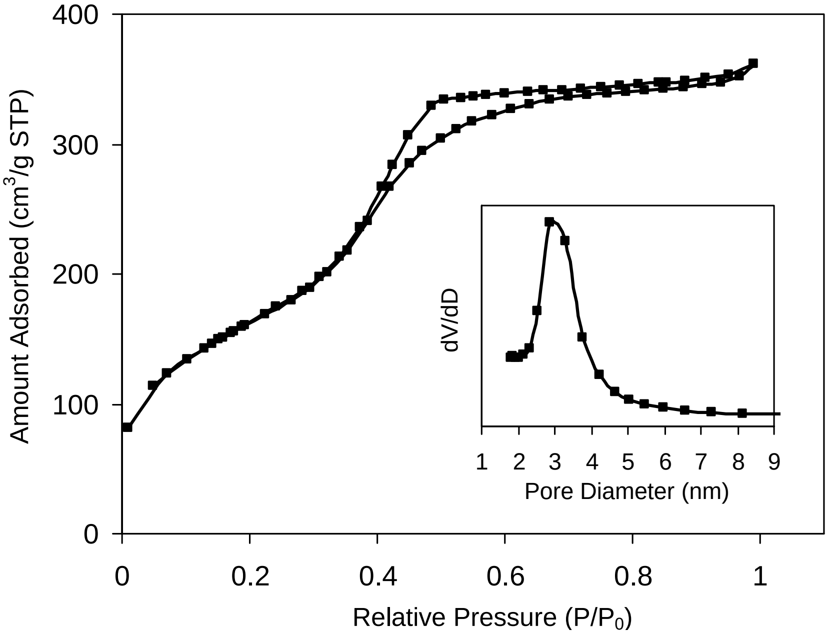
S3(b). N_2 adsorption and desorption isotherm for material **3**. Material **3** clearly indicates a type IV isotherm with H2 hysteresis loop. The inset shows the pore size distribution (PSD) calculated by the BJH method. A narrow PSD is observed. BET surface area: 670 m^2 g^{-1}, pore size: 2.9 nm, pore volume: 0.61 cm^3 g^{-1}.



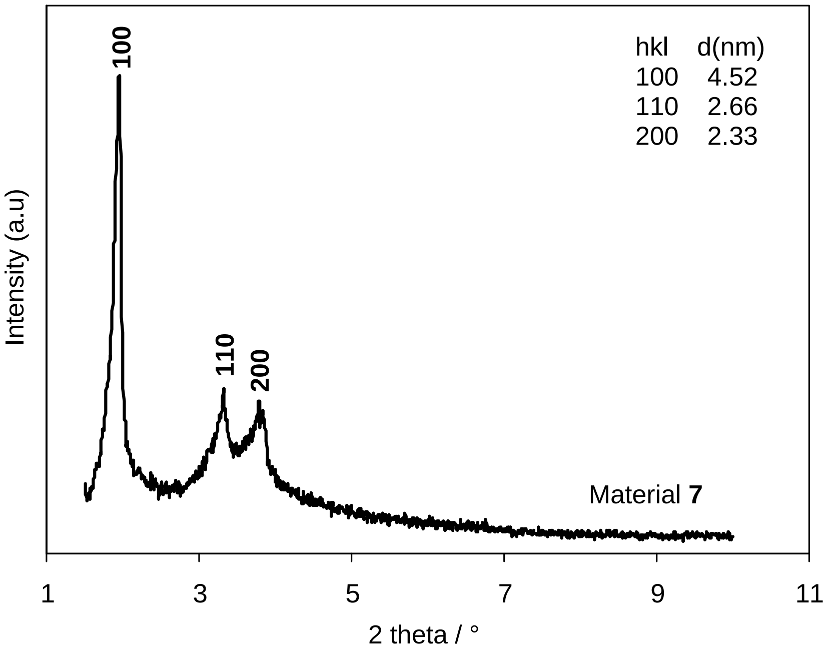
S4. TEM images of solvent-extracted material **4**. (A) PMO[KIT-5]-**4** particle viewed from [100] direction. The inset shows the electron diffraction pattern (a) and the respective Fourier diffractogram (b); (B) PMO[KIT-5]-**4** particle viewed from [110] direction. The inset shows the electron diffraction pattern (a) and the respective Fourier diffractogram (b); (C) PMO[KIT-5]-**4** particle viewed from [011] direction. The inset shows the electron diffraction pattern (a) and the respective Fourier diffractogram (b); (D) PMO[KIT-5]-**5** particle viewed along [100] direction. The inset shows the electron diffraction pattern (a) and the respective Fourier diffractogram (b).



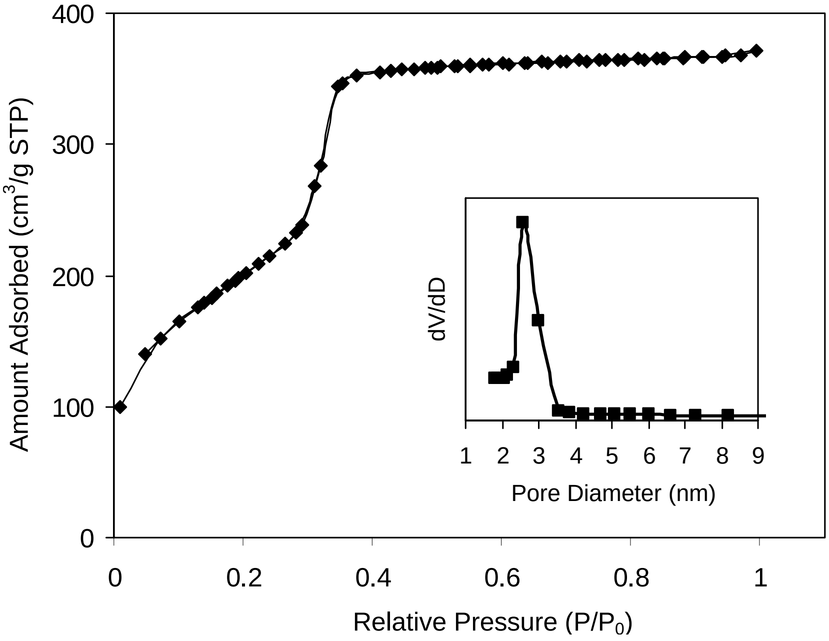
S5(a). Powder x-ray diffraction pattern for material **6**. It was prepared by using hexadecyltrimethylammonium bromide (C_{16}TABr) as an SDA under basic conditions. The molar ratio was 1 BTEE : 0.45 $C_{16\text{-}3\text{-}1}$: 2.35 NaOH : 396 H_2O. Aging temperature and aging time were 95 °C and 72 h, respectively. This material displays a hexagonal structure with P6mm space group.



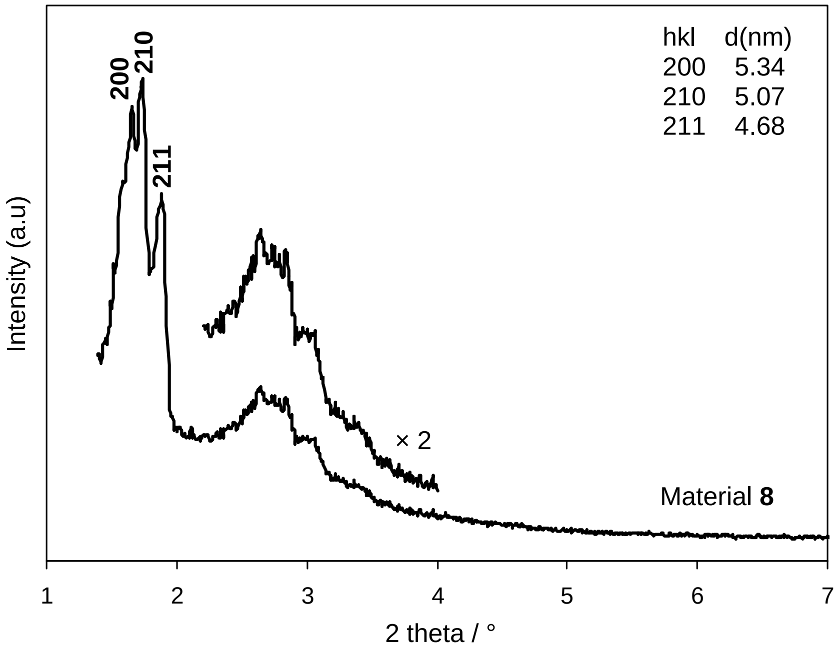
S5(b). N_2 adsorption and desorption isotherm for material **6**. Material **6** clearly indicates a type IV isotherm with H2 hysteresis loop. The inset shows the pore size distribution (PSD) calculated by the BJH method. A narrow PSD is observed. BET surface area: 600 m^2 g^{-1}, pore size: 2.9 nm, pore volume: 0.54 cm^3 g^{-1}.

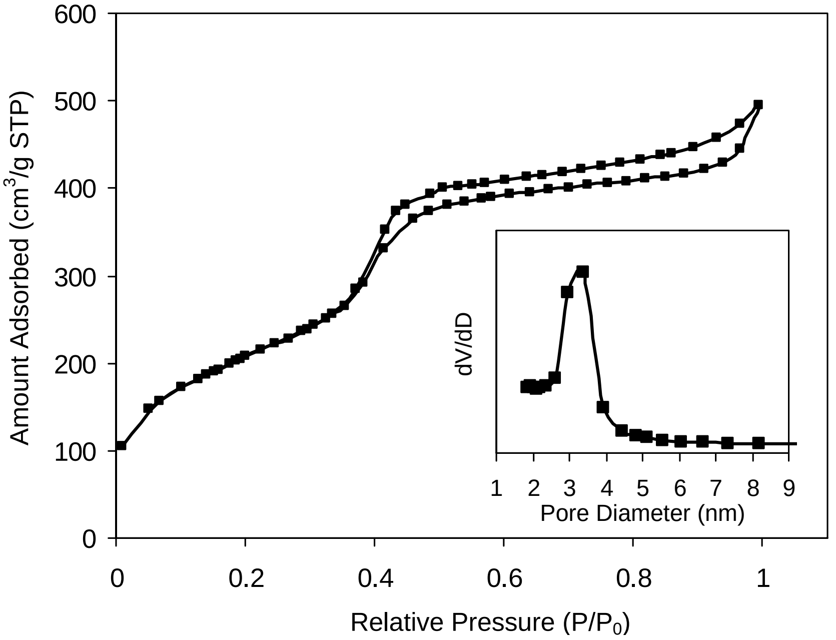


S6(a). Powder x-ray diffraction pattern for material **7**. It was prepared by using hexadecyltrimethylammonium bromide (C_{16}TABr) as an SDA under basic conditions. The molar ratio was 1 BTEE : 0.60 C_{16}TABr : 2.35 NaOH : 396 H_2O. Aging temperature and aging time were 80 °C and 24 h, respectively. This material displays a hexagonal structure with P6mm space group.



S6(b). N_2 adsorption and desorption isotherm for material **7**. Material **7** clearly indicates a type IV isotherm without hysteresis loop. The inset shows the pore size distribution (PSD) calculated by the BJH method. A narrow PSD is observed. BET surface area is 750 m^2 g^{-1}, pore size is 2.6 nm (adsorption branch), and pore volume is 0.57 cm^3 g^{-1}.





S7. PXRD pattern for material **8**(top); N_2 adsorption and desorption isotherm for material **8** (bottom). Material **8** clearly indicates a type IV isotherm with hysteresis loop. The inset shows the pore size distribution (PSD) calculated by the BJH method. A narrow PSD is observed.