

# Transformable periodic mesoporous organosilica materials

Steven E. Dickson and Cathleen M. Crudden\*

Department of Chemistry, Queen's University, 90 Bader Lane, Kingston Ontario Canada  
K7L 3N6

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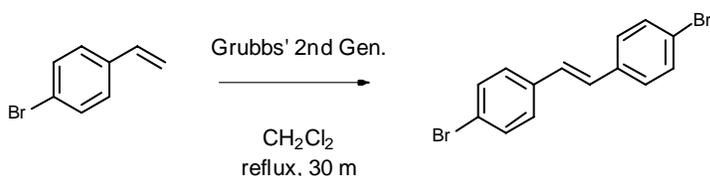
## 1. General Information

4-Bromostyrene and Grubbs' 2<sup>nd</sup> Generation Catalyst were purchased from Aldrich and used without further purification. Triethoxysilane was purchased from TCI America. CH<sub>2</sub>Cl<sub>2</sub> was obtained dry from a solvent purification system fitted with alumina columns. THF was freshly distilled from sodium/benzophenone ketyl. Triethylamine was purchased from Aldrich and distilled fresh from CaH<sub>2</sub> prior to use. *N,N*-Dimethylformamide (DMF) was purchased dry from EMD and used without any further treatment. *n*-BuLi was freshly titrated before use with *N*-benzylbenzamide in dry THF. Gas sorption experiments were performed using a Micromeritics ASAP 2010 physisorption analyzer with nitrogen gas as the adsorbate at 77 K. Samples were degassed at 80 °C for at least 8 hours and until 10<sup>-3</sup> mm Hg pressure was maintained. Solid-state CP MAS <sup>13</sup>C and <sup>29</sup>Si NMR measurements were recorded on a Bruker Avance 600 spectrometer operating at 150.9 and 119.2 MHz for <sup>13</sup>C and <sup>29</sup>Si, respectively, and using a Bruker 5 mm CP MAS probe. A typical spinning rate for CP MAS experiments is 11 kHz. A 2 ms cross polarization contact time was used to acquire <sup>29</sup>Si and <sup>13</sup>C CP MAS spectra with a repetition delay of 2 s. The number of scans was in excess of 600 and 2400 for <sup>13</sup>C and <sup>29</sup>Si respectively to obtain sufficient signal. <sup>13</sup>C and <sup>29</sup>Si MAS spectra were referenced to tetramethylsilane. Infrared spectra were acquired with a Varian 1000 FT-IR spectrometer. TEM images were obtained using a 200keV JEOL 2010 STEM operated in both transmission and STEM modes. In STEM mode a Gatan High Angle Annular Dark Field Detector was used to image the sample. Elemental maps and spectra were generated using an EDAX (Genesis) Energy Dispersive X-ray system. The sample was prepared by placing a small amount of powder in ethanol and sonicating for 5 minutes. 20  $\mu$ l of the solution was pipetted onto a carbon coated, 200 mesh copper grid. Raman spectra were acquired with a Jobin-Yvon/Horiba (Edison, NJ) microRaman Spectrometer (Model: LabRam) with a spectrum resolution capability of 2-3 cm<sup>-1</sup>, equipped with a 632 nm He/Ne laser source, 1800 1/nm

grating and an Olympus BX41 microscope system. Collection of the spectra was performed in backscattered mode at room temperature under the following conditions: x100 microscope objective, 1100  $\mu\text{m}$  pinhole size, 300  $\mu\text{m}$  slit width, and 60 s exposure time. Each spectrum represents the average of two measurements. Powder X-ray diffraction measurements were run on an automated Siemens/Bruker AXS D5000 diffractometer. The system is equipped with a high power line focus Cu- $k\alpha$  source operating at 50 kV/35mA. A solid-state Si/Li Kevex detector was used for removal of k-beta lines. The diffraction patterns were collected on a theta/2-theta Bragg-Brentano reflection geometry with fixed slits. The slits were set up appropriately for both low- and wide angle ranges in order to ensure the optimal quality of the diffraction patterns. A step scan mode was used for data acquisition with step size of  $0.02^\circ$  2-theta and counting time of 3.0 s per step for low-theta scans and 1.0 s per step for the wide range scans.

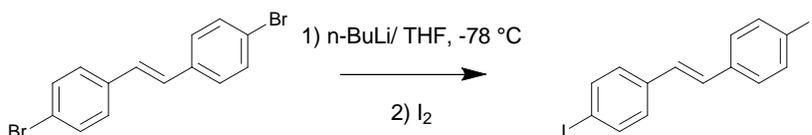
## 2. Synthetic Procedures

### 4,4'-dibromo-*trans*-stilbene:



To a flame-dried 250 mL round bottom flask, containing a stirbar, was added *p*-bromostyrene (25 g, 137 mmol). The flask was flushed with Ar and dry  $\text{CH}_2\text{Cl}_2$  (150 mL) was cannulated in to dissolve the aryl bromide. Finally, Grubbs' 2<sup>nd</sup> Generation catalyst (23.8 mg, 0.02 mol %) was weighed into a vial in a glovebox and transferred quickly to the solution. A reflux condenser was fitted to the flask and refluxed for 17 h. The resulting white precipitate was vacuum filtered using a Buchner funnel and washed with cold  $\text{CH}_2\text{Cl}_2$  until colourless (~50 mL). Colourless flakes (22.85 g, 99 %) were obtained and used subsequently without further purification.

### 4,4'-Diiodo-*trans*-stilbene:

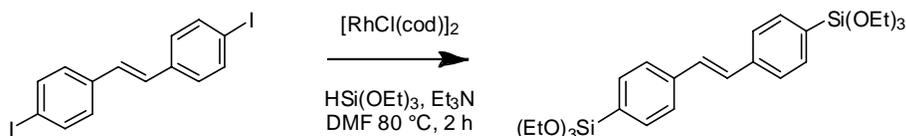


Adapted from reference<sup>1</sup>:

In a 500 mL flame-dried round bottom flask containing a stirbar was added 4,4'-dibromo-*trans*-stilbene (15.6 g, 37.8 mmol) and dry THF (250 mL). The solid was allowed to dissolve and cool in a dry ice/ <sup>1</sup>PrOH bath to  $-78^\circ\text{C}$  before *n*-BuLi (2.3 eq, 87.0 mmol), was added dropwise over 20 m. The mixture was allowed to stir cold for 30 m before solid  $\text{I}_2$  chips (24.1 g, 95.0 mmol) were added. The mixture was allowed to warm to room

temperature and stirred overnight. Saturated Na<sub>2</sub>SO<sub>3</sub> solution was added and the mixture was transferred to a separatory funnel. The aqueous layer was extracted 3 x 50 mL Et<sub>2</sub>O, and the organic layers combined, dried over MgSO<sub>4</sub>, filtered and concentrated to impure solid. The crude product was dissolved in MeOH and kept cold overnight. An equal volume of H<sub>2</sub>O was added to yield precipitate which was vacuum filtered to an off-white solid (14.6 g, 76 %).

**4,4'-Bis(triethoxysilyl)*trans*-stilbene BTETS or  
(*E*)-1,2-bis(4-(triethoxysilyl)phenyl)ethene (1):**

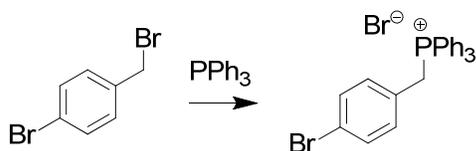


As described in reference<sup>2</sup>:

To a flame-dried 100 mL round bottom flask containing a stirbar, was added (*E*)-1,2-bis(4-iodophenyl)ethane (859 mg, 1.99 mmol) and [RhCl(cod)]<sub>2</sub> (29.2 mg, 0.0592 mmol, 3 mol %). The solids were briefly flushed with Ar and DMF (15.8 mL) was added. Et<sub>3</sub>N (1.65 mL, 11.8 mmol) and triethoxysilane (1.46 mL, 7.90 mmol) were added via dry needle and syringe and the mixture was stirred for 2 h at 80 °C. The mixture was concentrated *in vacuo* at 50-60 °C under high vacuum. The black residue was filtered through a short plug of silica, using 5:1 Hex:EtOAc, concentrated to a yellow oil and purified by column chromatography using a Biotage Flash chromatograph, with an elution of 2 % EtOAc in hexanes increasing to 20 % EtOAc over 1 L total volume. Collected R<sub>f</sub> 0.24 (10: 1 Hex: EtOAc) and concentrated to obtain 557 mg, 55 % yield of white solid.

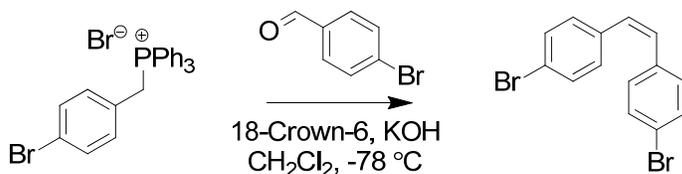
<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) (500 MHz) δ 1.33 (t, *J*= 7.0 Hz, 18H), 3.96 (q, *J*= 7.0 Hz, 12H) 7.28 (s, 2H) 7.64 (d, *J*= 8.0 Hz, 4H) 7.76 (d, *J*= 8.0 Hz, 4H); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>) (500 MHz) δ 18.5, 59.1, 126.4, 129.7, 131.3, 135.6, 139.4; exact mass calculated for C<sub>26</sub>H<sub>40</sub>O<sub>6</sub>Si<sub>2</sub> m/e 504.2363, found m/e 504.2368.

**(4-Bromobenzyl)triphenylphosphonium bromide:**



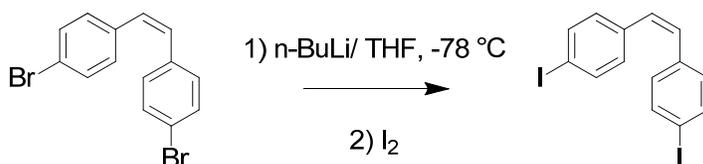
Prepared as previously reported<sup>3</sup>.

**4,4'-dibromo-*cis*-stilbene:**



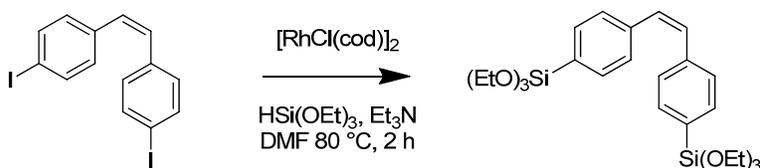
Prepared as previously reported<sup>4</sup>.

#### 4,4'-diiodo-*cis*-stilbene:



A similar procedure to that reported for the synthesis of 4,4'-diiodo-*trans*-stilbene was used.

#### 4,4'-Bis(triethoxysilyl)*cis*-stilbene BTECS or (Z)-1,2-bis(4-(triethoxysilyl)phenyl)ethene (2):



To a flame-dried 100 mL round bottom flask containing a stirbar, was added (Z)-1,2-bis(4-iodophenyl)ethane (859 mg, 1.99 mmol) and [RhCl(cod)]<sub>2</sub> (29.2 mg, 0.0592 mmol, 3 mol %). The mixture was briefly flushed with Ar and DMF (15.8 mL) was added. Et<sub>3</sub>N (1.65 mL, 11.8 mmol) and triethoxysilane (1.46 mL, 7.90 mmol) were added and the mixture was stirred for 2 h at 80 °C under Ar. The mixture was concentrated *in vacuo* at 50-60 °C under high vacuum. The black residue was filtered through a short plug of silica, using 5:1 Hex:EtOAc, concentrated to a yellow oil and purified by column chromatography using a Biotage Flash chromatograph, with an elution of 2 % EtOAc in hexanes increasing to 20 % EtOAc over 1 L total volume. Collected R<sub>f</sub> 0.27 (10: 1 Hex: EtoAc) and concentrated to clear oil to obtain 448 mg, 45 % yield.

<sup>1</sup>H NMR (CDCl<sub>3</sub>) (400 MHz) δ 1.27 (t, *J* = 6.9 Hz, 18H), 3.99 (q, *J* = 6.9 Hz, 12H) 6.63 (s, 2H) 7.28 (d, *J* = 7.9 Hz, 4H) 7.55 (d, *J* = 7.9 Hz, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) (400 MHz) δ 18.2, 58.8, 128.3, 129.8, 130.7, 134.7, 139.1; exact mass calculated for C<sub>26</sub>H<sub>40</sub>O<sub>6</sub>Si<sub>2</sub> m/e 504.2363, found m/e 504.2383.

### 3. Material Preparation

#### **PMO-1/4<sup>H+</sup>**:

Molar Ratios : (BTEBP: BTETS (**1**): Brij 76: H<sub>2</sub>O: HCl: NaCl)  
(0.85: 0.15: 0.534: 600: 8.05: 19.0)

In a typical procedure, 0.199 g of Brij 76, 5.67 g d. H<sub>2</sub>O and 0.428 g c. HCl (36 wt %) were combined in a capped 30 ml polypropylene Nalgene bottle with stirbar and allowed to stir to homogeneity at 60 °C for 1 hr at which point 0.582 g of NaCl was added and recapped to stir at 60 °C for 3 more hours. BTEBP (0.213 g) and BTETS (**1**) (0.040g) were added and the mixture was stirred for 20 h at 60 °C. The stirbar was removed and the white precipitate was allowed to age statically at 80 °C for 24 h. The bottle was removed from the oil bath, cooled to room temperature and filtered. The powder was washed with 200 ml d. H<sub>2</sub>O and allowed to air dry. The template was extracted by stirring in an acidic ethanol solution (0.45 g c. HCl, 30 mL EtOH, 95 %) for 6 h at 60 °C. The mesoporous material was filtered, washed with 250 mL EtOH and air dried.

#### **PMO-1/4<sup>OH-</sup>**:

Molar Ratios : (BTEBP: BTETS (**1**): C<sub>18</sub>TAMCl: H<sub>2</sub>O: NaOH)  
(0.85: 0.15: 1.28: 1320: 12100)

In a typical procedure, 0.186 g octadecyltrimethylammonium chloride, 0.85 mL 6 N NaOH and 9.93 g d.H<sub>2</sub>O were combined in a 4 dram glass vial with stirbar. The mixture was stirred until homogeneous. 0.170 g BTEBP and 0.032 g BTETS (**1**), were then added with vigorous stirring and allowed to stir at room temperature for 20 h. The vials were then heated without stirring at 95 °C for 22 h. After heating, the precipitate was recovered and washed with 100 mL of d. H<sub>2</sub>O. The template was extracted with 40 mL of acidic EtOH solution (500 mL EtOH (anhydrous), 10.3 g 2 M HCl).

#### **PMO-2/4<sup>H+</sup>**:

Molar Ratios : (BTEBP: BTECS (**2**): Brij 76: H<sub>2</sub>O: HCl: NaCl)  
(0.85: 0.15: 0.534: 600: 8.05: 19.0)

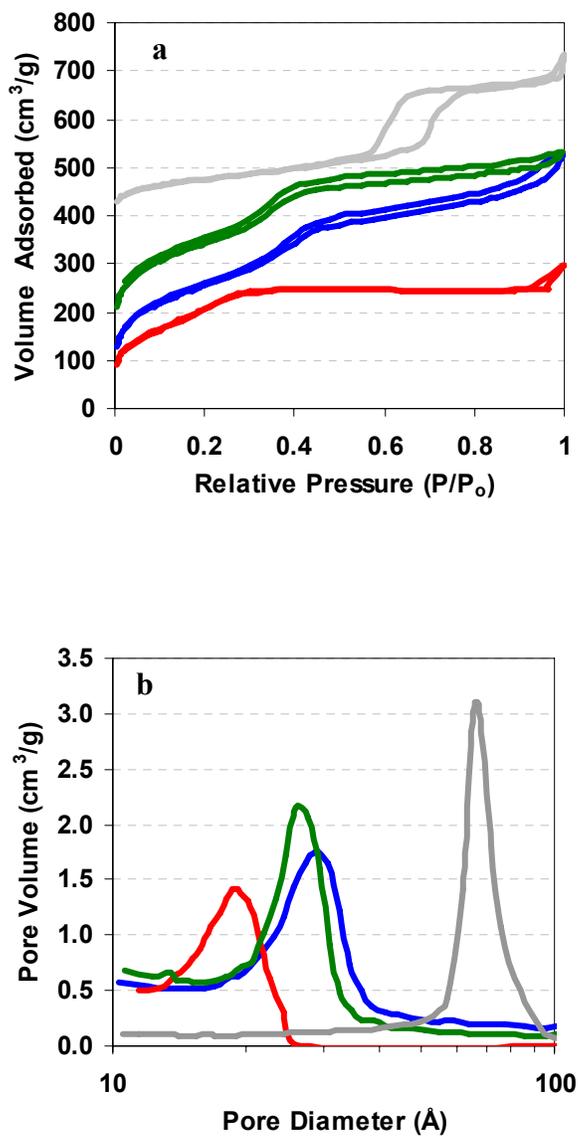
As Material **PMO-1/4<sup>H+</sup>** using BTECS (**2**).

#### **PMO-1/3<sup>H+</sup>**:

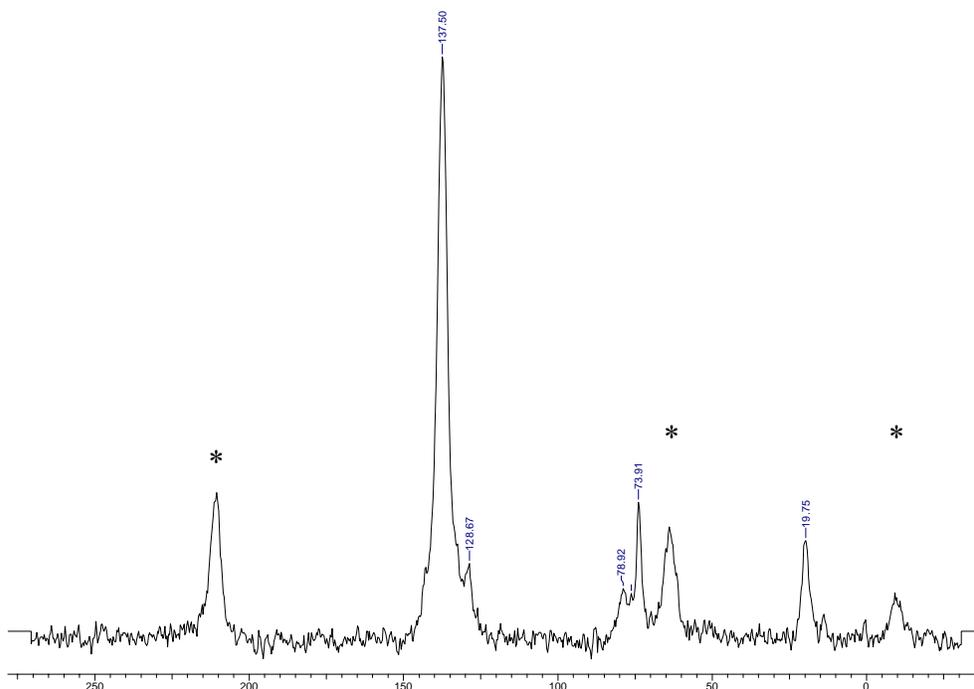
Molar Ratios : (BTEB: BTETS (**1**): P123: c. HCl: H<sub>2</sub>O)  
(0.85: 0.15: 0.068: 0.944: 800)

In a typical procedure, 0.625 g of P123, 22.7 mL of distilled water, and 126 μL of hydrochloric acid (36 wt %) are added to a capped 60 mL polypropylene bottle with stirbar. The mixture is stirred until homogeneous and cooled to 0 °C. BTEB (0.542 g) and BTETS (**1**) (0.120 g) are added and the mixture was stirred for 1 h cold. After stirring for 20 h at 39 °C, the white material is filtered, washed with water, and then heated in a closed polypropylene bottle of water statically at 100 °C for 3 d to improve mesoscale order. Finally, the white precipitate is filtered, and the template was extracted with ethanol at 60 °C for 16 h with stirring.

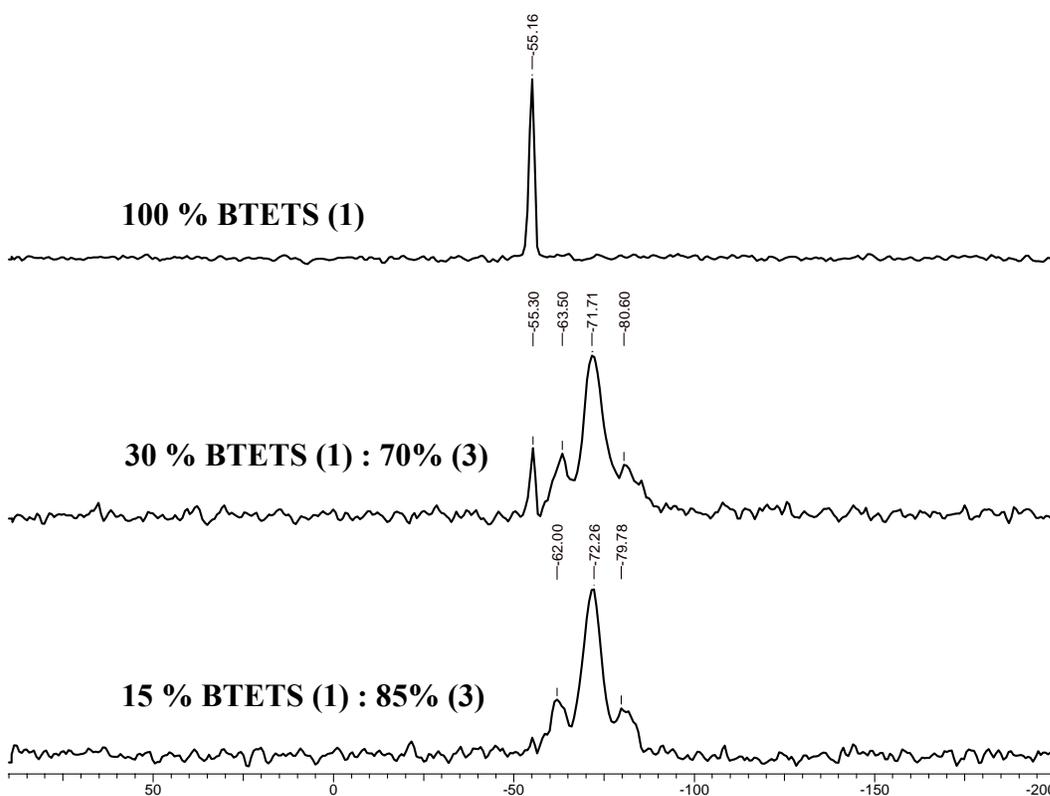
#### 4. Material Characterization



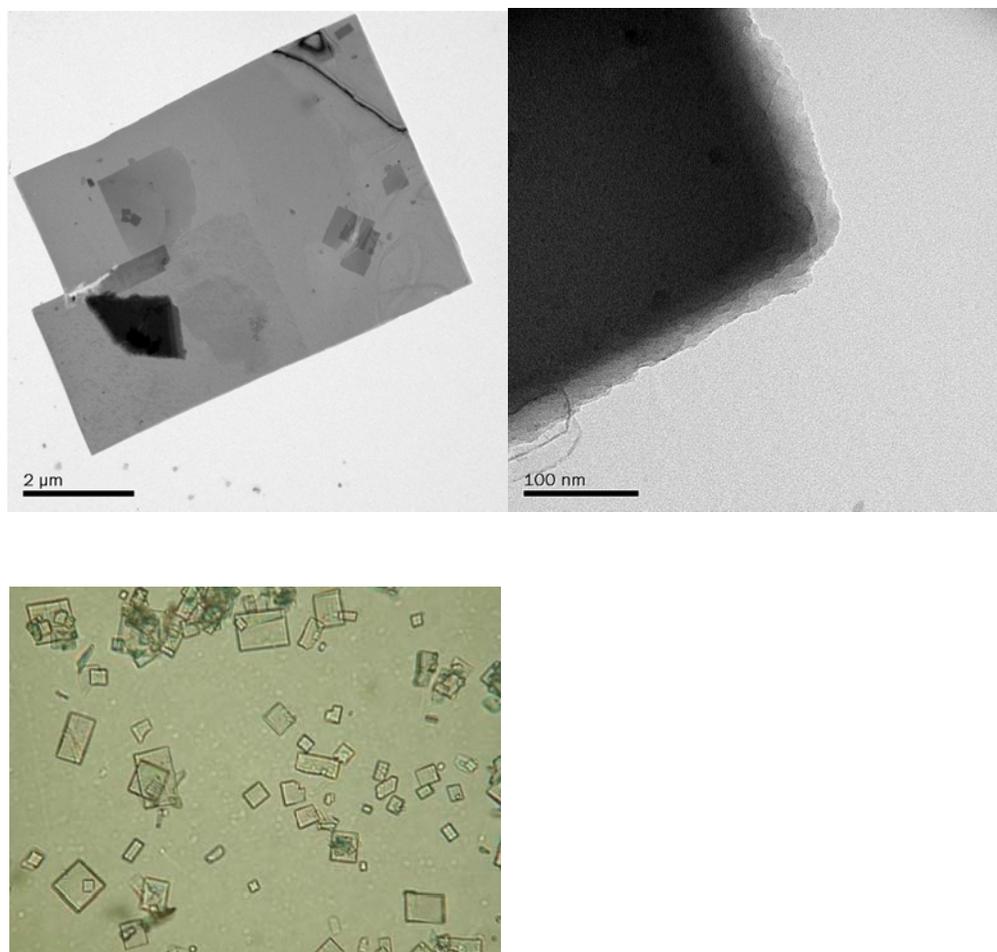
**Fig. S-1** (a) N<sub>2</sub> adsorption-desorption isotherms and (b) BJH pore size distribution curves of PMOs. **PMO-1/4<sup>H+</sup>**-blue, **PMO-1/4<sup>OH-</sup>**-red, **PMO-2/4<sup>H+</sup>**-green, **PMO-1/3<sup>H+</sup>**-grey. **PMO-2/4<sup>H+</sup>** and **PMO-1/3<sup>H+</sup>** are raised on the y-axis of (a) by 75 and 400 cm<sup>3</sup>g<sup>-1</sup> respectively for clarity.



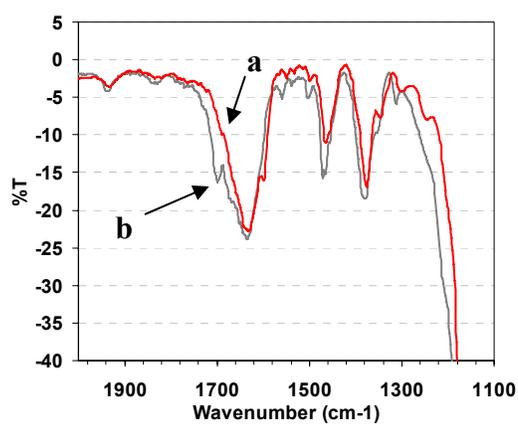
**Fig. S-2** CP MAS  $^{13}\text{C}$  NMR of **PMO-1/3 $\text{H}^+$** . The peak from **3** is seen at 137.5 ppm and the peaks from **1** are seen overlapping with **3** from 129 to 142 ppm. ‘\*’ Denotes spinning side bands. Other peaks are due to residual ethoxy groups or P123 polymer.



**Fig. S-3** CP MAS  $^{29}\text{Si}$  NMR of **PMO-1/3 $\text{H}^+$**  materials based on BTETS **1**. Silanetriol appearing at -55 ppm is not observed at 15 % loading of **1**.



**Fig. S-4** TEM and optical microscope images of 100 % **1**, showing non-porous, bis(silanetriol) plate-like crystals.



**Fig. S-5** FT-IR spectra of (a)  $\text{PMO-1/3}^{\text{H}^+}$  (red), and (b)  $\text{PMO-1/3}^{\text{H}^+}\text{-O}_3$  (grey) showing evolution of a new peak at  $1700\text{ cm}^{-1}$  following ozonolysis.

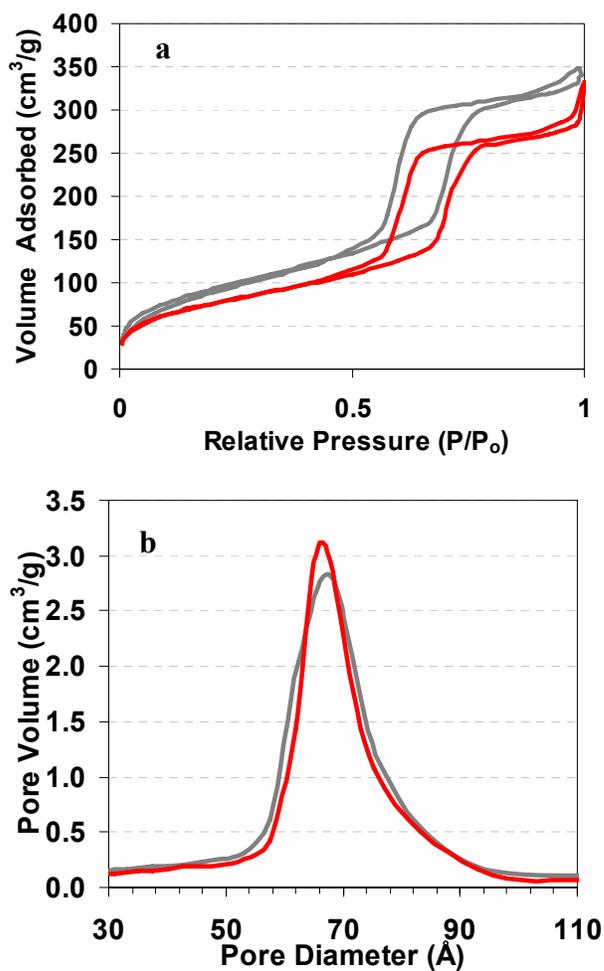
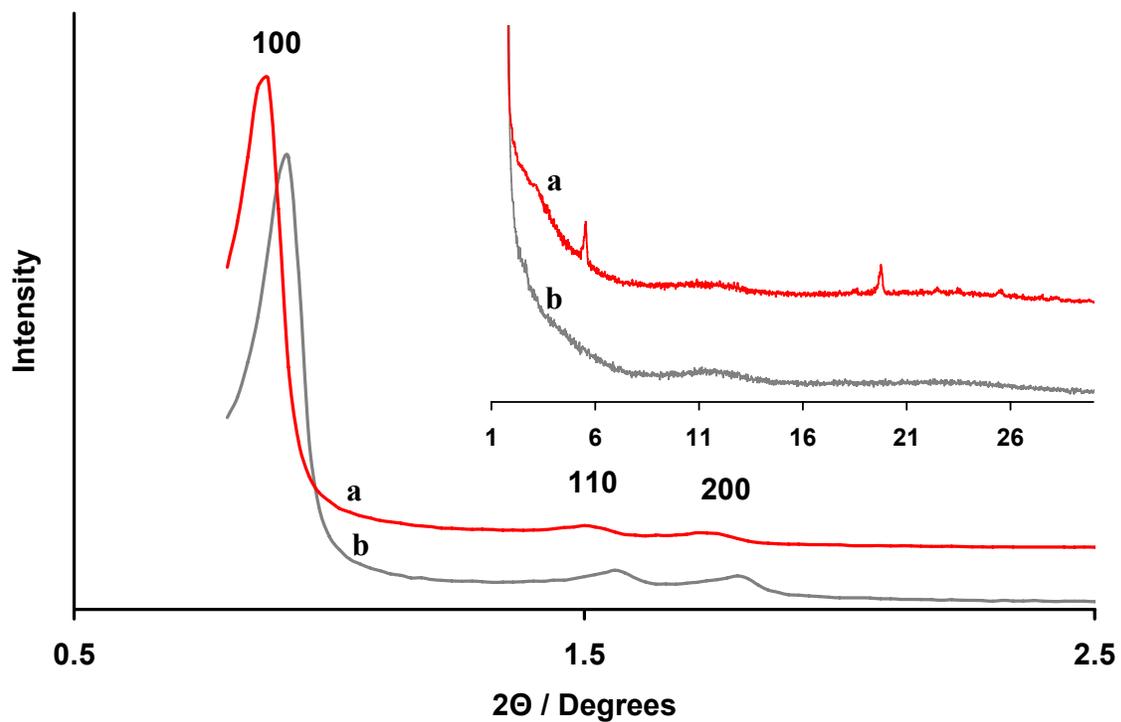


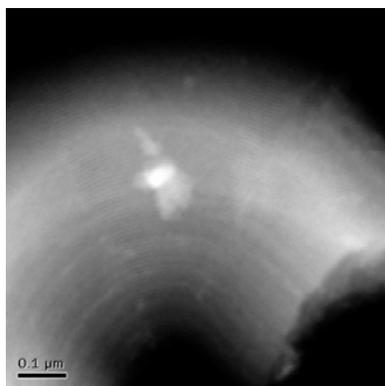
Fig. S-6 (a) N<sub>2</sub> physisorption isotherm and (b) pore size distribution for **PMO-1/3<sup>H+</sup>** (red) and **PMO-1/3<sup>H+</sup>-O<sub>3</sub>** (grey).



**Fig. S-7** Powder X-ray diffraction patterns of (a)  $\text{PMO-1/3}^{\text{H}^+}$  (red) and (b)  $\text{PMO-1/3}^{\text{H}^+}\text{-O}_3$  (grey) with 2d hexagonal index trio marked. The  $a_0$  lattice parameter increases from 112.2 Å in **a** to 116.9 Å in **b**.

## 5. Osmium staining of PMO

In a closed, glass chamber containing osmium tetroxide (**DANGER-Use only in fumehood with proper protection!**), 2-3 mg of PMOs were placed in separate vials and were exposed to the saturated vapour in the closed vessel for 4 h at room temperature. The PMOs were then placed under an Ar flow overnight to remove any physisorbed Os. The resulting materials were imaged by TEM.



**Fig. S-8.** HAADF TEM image of **PMO-1/3<sup>H+</sup>-Os** showing bright contrast for Os.

## 6. Ozonolysis of PMO-1/3<sup>H+</sup>

In a typical procedure, **PMO-1/3<sup>H+</sup>** (34 mg), was added to a 50 mL glass tube with ground joint and stirbar. Solvent was added (1 mL MeOH: 1 mL CH<sub>2</sub>Cl<sub>2</sub>) and the mixture was cooled to -78 °C in an isopropanol/dry ice bath. The ozonator line was fitted to an adapter with a stopcock and attached to the glass tube. A slow gas flow was led below the solvent level through a pipette which was fitted to the adapter. The O<sub>2</sub> pressure gauge was set to 9 PSI and the voltage to 0.9 V to initiate the O<sub>3</sub> production. After 20 m, the O<sub>3</sub> flow was terminated and the ozonide was quenched with anhydrous dimethylsulfide (0.2 mL). The mixture was allowed to warm up to room temperature over 1.5 h, and then the fine white powder was collected by centrifugation and subsequently resuspended (three times in EtOH and once in Et<sub>2</sub>O) to remove any soluble reagents. The solvent was removed from the powder (28 mg) in a vial under an Ar flow.

## 7. References

- <sup>1</sup> H.-K. Chang, S. Datta, A. Das, A. Odedra and R.-S. Liu, *Angew. Chem. Int. Ed.*, 2007, 4744.
- <sup>2</sup> M. Murata, M. Ishikura, M. Nagata, S. Watanabe and Y. Masuda, *Org. Lett.*, 2002, 4, 1843.
- <sup>3</sup> H. Hopf, J. Hucker and L. Ernst, *Eur. J. Org. Chem.*, 2007, 1891.
- <sup>4</sup> T. Bosanac and C. S. Wilcox, *Org. Lett.* 2004, 6, 2321.