

Electronic Supplementary Information for:

Probing the Pore Structure of a Chiral Periodic Mesoporous Organosilica Using Liquid Crystals

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A. SYNTHESIS AND CHARACTERIZATION OF CHIRAL PMO MATERIALS

All mesoporous silicas were synthesized using an RCT basic (IKA) hotplate stirrer equipped with an oil bath using brand new 4 dram vials (VWR) and Teflon coated magnetic stir bars. The monomers 4,4'-bis-(triethoxysilyl)biphenyl (**2**) and (*rac*)-, (*R*)- and (*S*)-3,3'-bis-(triethoxysilyl)-2,2'-dimethoxy-1,1'-binaphthyl (**4**) were synthesized according to published procedures.^{1,2}

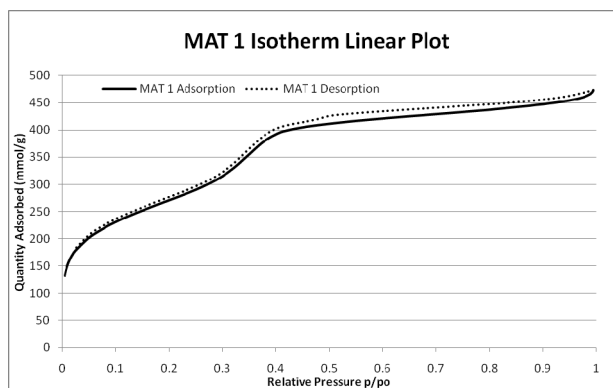
Preparation of Samples for N₂ adsorption. Analysis was carried out with a Micromeritics ASAP 2010 (Accelerated Surface Area and Porosimetry System). A clean dry sample tube with cap was measured accurately 4 times and the average weight recorded. Approximately 80-100 mg of material was carefully loaded into the tube which was then evacuated and backfilled with nitrogen. The mass was then accurately measured 4 times and averaged. The sample was then analyzed using standard methods.

Preparation of Samples for Transmission Electron Microscopy. A small amount of sample was placed in a glass vial and ~50cc of ethanol was added. The solution was sonicated for 15 minutes; 20 mL of the solution was removed using a micropipette and dropped onto a carbon coated 200 mesh copper EM grid. The grid was left to dry overnight. The sample was examined using a JEOL 200keV STEM. Images were collected on a 4 x 4k Gatan digital camera, using Digital Micrograph to acquire and analyze the data.

(*rac*)-15-QPMO1-*ex* (using Brij 76/HCl)

Brij 76 (0.467 g), deionized H₂O (13.7 g) and 37% aq HCl (1.0 g) were stirred together at 60 °C for 1 h; NaCl (1.32 g) was then added and stirred (speed 4) at 60 °C for an additional 3 h. EtOH (1.2 g), **2** (629 mg) and (*rac*)-**4** (126 mg) were premixed and added at 60 °C, the vial was capped and stirred for 20h (speed 4). The material was aged under static conditions at 80 °C for 24h. Solids were recovered by filtration and washed with 400 mL of deionized water. The surfactant was removed by Soxhlet extraction with a solution of 200 mL EtOH and 2 mL of 37% aq HCl for 72 h. After drying for 24 h under vacuum at room temperature, 0.451g of a fine colorless powder is recovered.

Fig.1. (*rac*)-15-QPMO1-*ex* (using Brij 76/HCl): N₂ adsorption/desorption isotherm



BJH Pore Diameter Å

Surface Area m²/g

Pore Volume cm³/g

22.7

978

0.676

Fig. 2. (*rac*)-15-QPMO1-*ex* (using Brij 76/HCl): CP-MAS ²⁹Si NMR

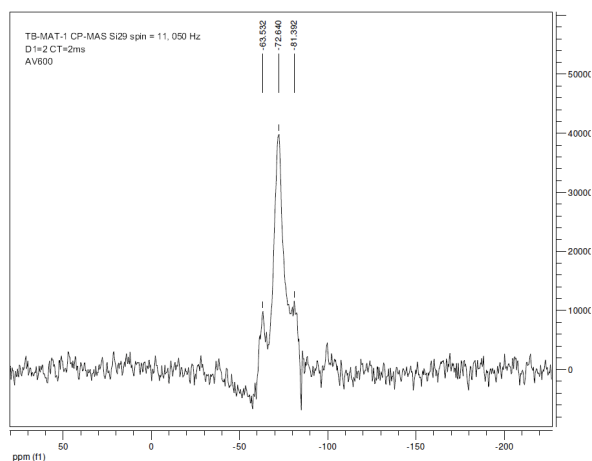


Fig. 3. (*rac*)-15-QPMO1-*ex* (using Brij 76/HCl): CP-MAS ¹³C NMR

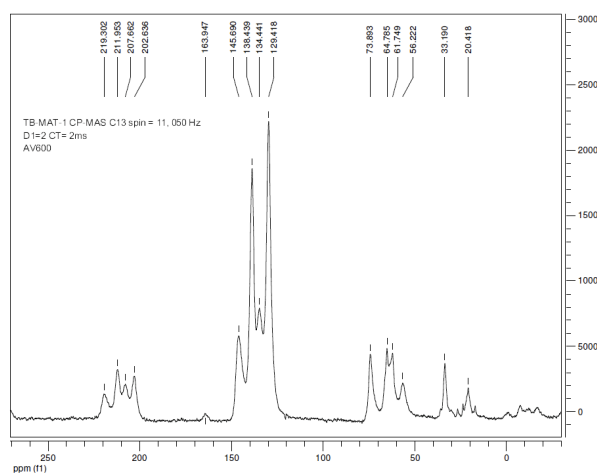
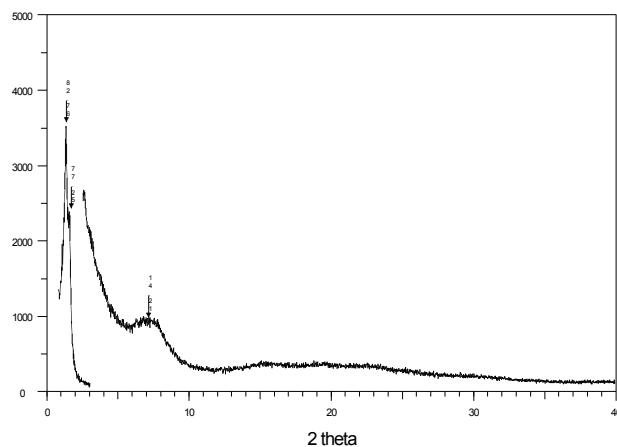


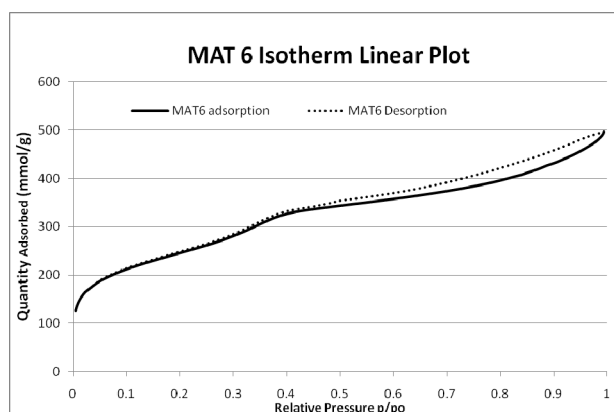
Fig. 4. (*rac*)-15-QPMO1-*ex* (using Brij 76/HCl): Powder X-ray diffraction profile



(*R*)-5-QPMO1-*ex*

Brij 76 (0.23 g), deionized H₂O (6.8 g) and 37% aq HCl (0.5 g) were stirred together at 60 °C for 1 h; NaCl (0.66 g) was then added and stirred (speed 4) at 60 °C for an additional 3 h. EtOH (0.6 g), **2** (460 mg) and (*R*)-**4** (27.6 mg) were premixed and added at 60 °C, the vial was capped and stirred for 20h (speed 4). The material was aged under static conditions at 80 °C for 24h. Solids were recovered by filtration and washed with 200 mL of deionized water. The surfactant was removed by Soxhlet extraction with a solution of 200 mL EtOH and 2 mL of 37% aq HCl for 72 h. After drying for 24 h under vacuum at room temperature, 0.231 g of a fine colourless powder is recovered.

Fig. 5. (*R*)-5-QPMO1-*ex*: N₂ adsorption/desorption isotherm



(*S*)-5-QPMO1-*ex*

Brij 76 (0.23 g), deionized H₂O (6.8 g) and 37% aq HCl (0.5 g) were stirred together at 60 °C for 1 h; NaCl (0.66 g) was then added and stirred (speed 4) at 60 °C for an additional 3 h. EtOH (0.6 g), **2** (300 mg) and (*S*)-**4** (15.6 mg) were premixed and added at 60 °C, the vial was capped and stirred for 20h (speed 4). The material was aged under static conditions at 80 °C for 24h. Solids were recovered by filtration and washed with 200 mL of deionized water. The surfactant was removed by Soxhlet extraction with a solution of 200 mL EtOH and 2 mL of 37% aq HCl for 72 h. After drying for 24 h under vacuum at room temperature, 0.168 g of a fine colourless powder is recovered.

Fig. 6. (S)-5-QPMO1-ex: N₂ adsorption/desorption isotherm

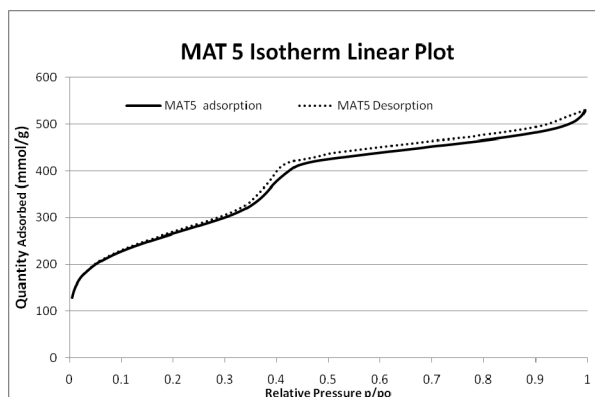
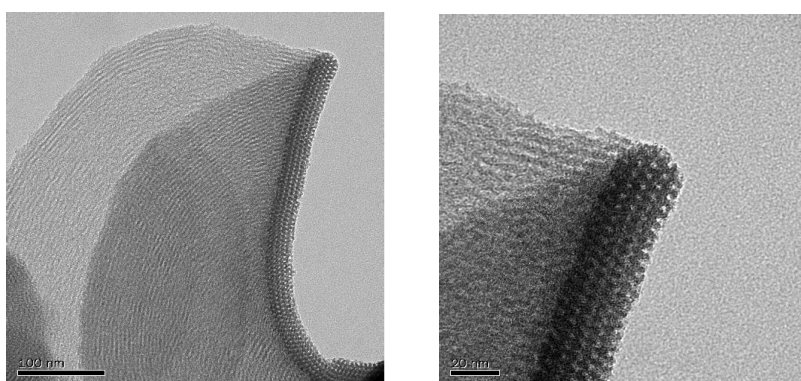


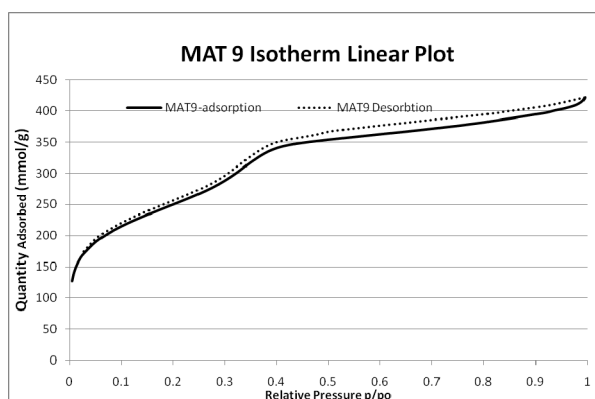
Fig. 7. (S)-5-QPMO1-ex: TEM images



(R)-15-QPMO1-ex

Brij 76 (0.23 g), deionized H₂O (6.8 g) and 37% aq HCl (0.5 g) were stirred together at 60 °C for 1 h; NaCl (0.66 g) was then added and stirred (speed 4) at 60 °C for an additional 3 h. EtOH (0.6 g), **2** (314 mg) and (*R*)-**4** (65 mg) were premixed and added at 60 °C, the vial was capped and stirred for 20h (speed 4). The material was aged under static conditions at 80 °C for 24h. Solids were recovered by filtration and washed with 200 mL of deionized water. The surfactant was removed by Soxhlet extraction with a solution of 200 mL EtOH and 2 mL of 37% aq HCl for 72 h. After drying for 24 h under vacuum at room temperature, 0.187 g of a fine colourless powder is recovered.

Fig. 8. (R)-15-QPMO1-ex: N₂ adsorption/desorption isotherm



(S)-15-QPMO1-ex

Brij 76 (0.23 g), deionized H₂O (6.8 g) and 37% aq HCl (0.5 g) were stirred together at 60 °C for 1 h; NaCl (0.66 g) was then added and stirred (speed 4) at 60 °C for an additional 3 h. EtOH (0.6 g), **2** (314 mg) and (*S*)-**4** (65 mg) were premixed and added at 60 °C, the vial was capped and stirred for 20h (speed 4). The material was aged under static conditions at 80 °C for 24h. Solids were recovered by filtration and washed with 200 mL of deionized water. The surfactant was removed by Soxhlet extraction with a solution of 200 mL EtOH and 2 mL of 37% aq HCl for 72 h. After drying for 24 h under vacuum at room temperature, 0.193 g of a fine colourless powder is recovered.

Fig. 9. (*S*)-15-QPMO1-ex: N₂ adsorption/desorption isotherm

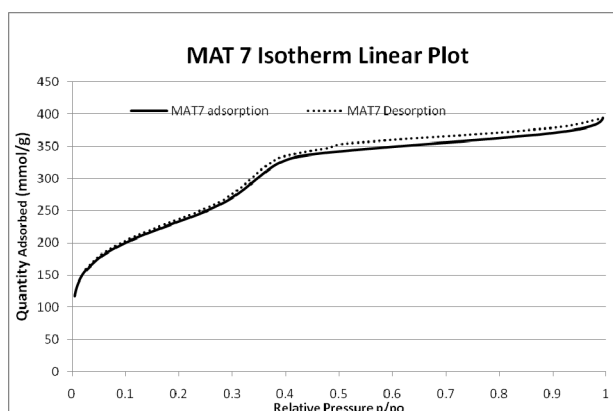
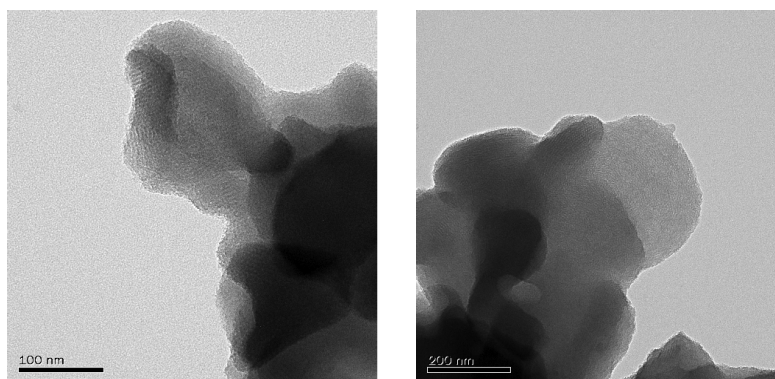


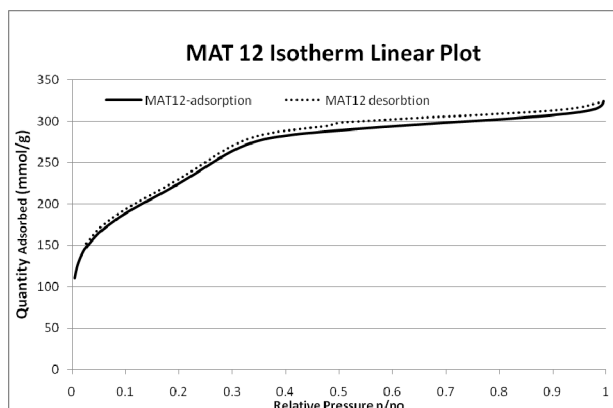
Fig. 10. (*S*)-15-QPMO1-ex: TEM images



(R)-30-QPMO1-ex

Brij 76 (0.23 g), deionized H₂O (6.8 g) and 37% aq HCl (0.5 g) were stirred together at 60 °C for 1 h; NaCl (0.66 g) was then added and stirred (speed 4) at 60 °C for an additional 3 h. EtOH (0.6 g), **2** (266 mg) and (*R*)-**4** (114 mg) were premixed and added at 60 °C, the vial was capped and stirred for 20h (speed 4). The material was aged under static conditions at 80 °C for 24h. Solids were recovered by filtration and washed with 200 mL of deionized water. The surfactant was removed by Soxhlet extraction with a solution of 200 mL EtOH and 2 mL of 37% aq HCl for 72 h. After drying for 24 h under vacuum at room temperature, 0.187 g of a fine colourless powder is recovered.

Fig. 11. (R)-30-QPMO1-ex: N₂ adsorption/desorption isotherm



(S)-30-QPMO1-ex

Brij 76 (0.23 g), deionized H₂O (6.8 g) and 37% aq HCl (0.5 g) were stirred together at 60 °C for 1 h; NaCl (0.66 g) was then added and stirred (speed 4) at 60 °C for an additional 3 h. EtOH (0.6 g), **2** (200 mg) and (*S*)-**4** (85 mg) were premixed and added at 60 °C, the vial was capped and stirred for 20h (speed 4). The material was aged under static conditions at 80 °C for 24h. Solids were recovered by filtration and washed with 200 mL of deionized water. The surfactant was removed by Soxhlet extraction with a solution of 200 mL EtOH and 2 mL of 37% aq HCl for 72 h. After drying for 24 h under vacuum at room temperature, 0.187 g of a fine colourless powder is recovered.

Fig. 12. (S)-30-QPMO1-ex: N₂ adsorption/desorption isotherm

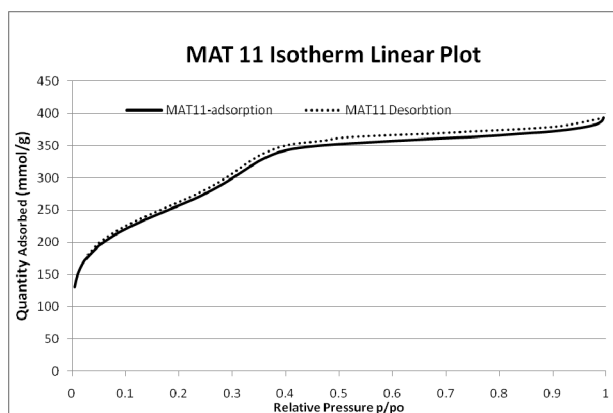
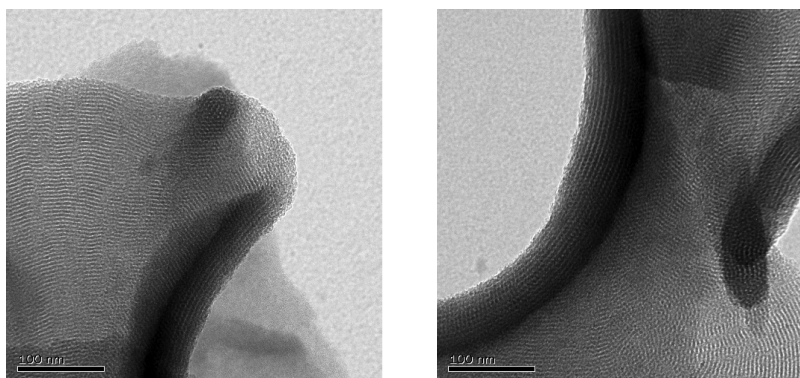


Fig. 13. (S)-30-QPMO1-ex: TEM images



(S)-100-QPMO1-ex

Brij 76 (0.47 g), deionized H₂O (13.7 g) and 37% aq HCl (1.0 g) were stirred together at 60 °C for 1 h; NaCl (1.32 g) was then added and stirred (speed 4) at 60 °C for an additional 3 h. EtOH (1.2 g) and (S)-4 (645 mg) were premixed and added at 60 °C, the vial was capped and stirred for 20h (speed 4). The material was aged under static conditions at 80 °C for 24h. Solids were recovered by filtration and washed with 200 mL of deionized water. The surfactant was removed by Soxhlet extraction with a solution of 200 mL EtOH and 2 mL of 37% aq HCl for 72 h. After drying for 24 h under vacuum at room temperature, 0.342g of a fine colourless powder is recovered.

Fig. 14. (S)-100-QPMO1-ex: N₂ adsorption/desorption isotherm

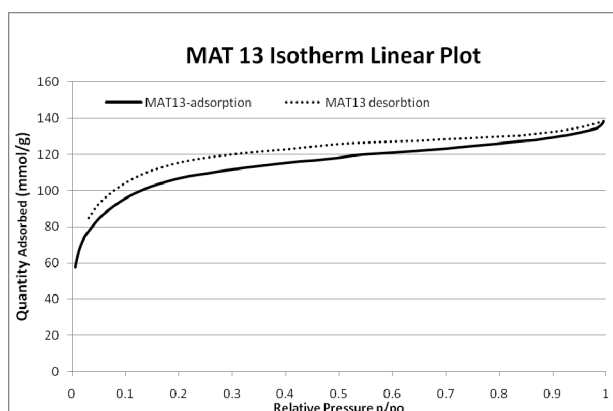
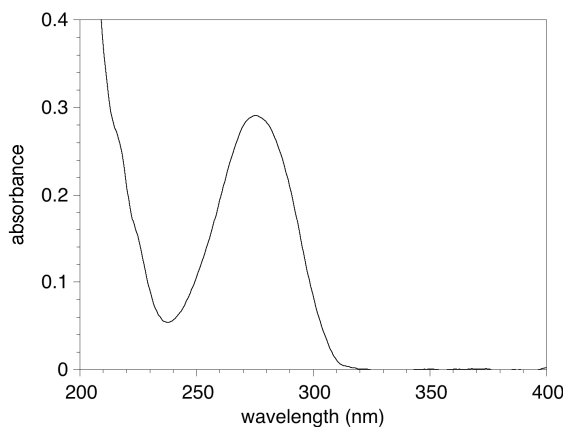


Fig. 15. UV spectrum of 5CB as a 1.1×10^{-5} M solution in hexanes.



References

1. S. MacQuarrie, M. Thompson, A. Blanc, N. Mosey, R. P. Lemieux and C. M. Crudden, *J. Am. Chem. Soc.*, 2008, **130**, 14099.
2. X. Wu, T. Blackburn, J. D. Webb, A. E. Garcia-Bennett and C. M. Crudden, *Angew. Chem. Int. Ed.*, 2011, **50**, 8095.