Supporting Information

Tailoring Bifunctional Periodic Mesoporous Organosilicas for Cooperative Catalysis

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**Materials.** All chemicals and reagents were used without further purification. Triblock copolymer EO$_{20}$PO$_{70}$EO$_{20}$ (Pluronic P123), hydrochloric acid (37%), sodium chloride, thioacetic acid, hydrogen peroxide ($\text{H}_2\text{O}_2$, 30 wt%) and ethanol were obtained from Aldrich. For the catalytic test, acetone and Amberlyst-15 were purchased from Aldrich, whereas phenol was provided by Merck. LC grade methanol was purchased from VWR Chemicals. 4,4´-Bisphenol A (p,p´-BPA) was obtained from Fluka and isotopically labelled 4,4´-Bisphenol A ($^{13}\text{C}_{12}$-BPA, 100 mg L$^{-1}$ in acetonitrile) from IS Cambridge Isotope Laboratories. 2,4´-Bisphenol A (o,p´-BPA) and 2,2´-Bisphenol A (o,o´-BPA) were synthesised by Toronto Research Chemicals. Individual stock solutions of BPA-isomer (10 g L$^{-1}$) and $^{13}\text{C}_{12}$-BPA (1.2 mg L$^{-1}$) were prepared in methanol and stored at -18 °C. For UV-irradiation a Metallight Classic UV irradiation chamber fitted with twelve 360 nm UV-lamps was used.

**Synthesis of 1-thiol-ethylene-bridged PMO (SH-PMO)$^1$.** In a typical synthesis, 0.42 g of P123 and 2.1 g of KCl were added to 14.76 mL of water and 2.1 mL of HCl (35%) and stirred overnight at 45 °C. After complete dissolution of the surfactant, 1-thiol-1,2-bis(triethoxysilyl)ethane (compound 2) was added, and the mixture was stirred at 45 °C for 24 h, followed by another 24 h at 100 °C under static conditions. The white solid was filtered, washed thoroughly with water and ethanol. The polymeric surfactant was removed by refluxing 0.5 g of as-synthesized material with 150 mL of ethanol and 4 mL of HCl (35%) for 24 h. After repeating this process twice, the resulting solid was filtered, washed with ethanol and dried under vacuum at 120 °C.

**Synthesis of sulfonic acid-functionalized ethane PMO (in-situ SO$_3$H-ethane PMO)$^2$.** In a typical synthesis, 0.42 g of P123 and 2.1 g of KCl were added to 14.76 mL of water and 2.1 mL of HCl (35%) and the solution was vigorously stirred overnight at 45 °C. To the resulting clear solution, an equimolar mixture of 1,2-bis(triethoxysilyl)ethane and 1-thiol-1,2-bis(triethoxysilyl)ethane was then added dropwise. The synthesis mixture was kept under stirring at 45 °C for 3 h and then, 1.5 mL of H$_2$O$_2$ (30 wt%) was added to the solution. The resulting solution was stirred at 45 °C for 24 h and subsequently aged at 100 °C for 24 h under static conditions. After cooling down, the solid was recovered by filtration and washed thoroughly with water and ethanol, and finally dried. The surfactant was removed by solvent extraction as described previously.

**Analysis of BPA isomers.** Separation and quantitation of BPA isomers was accomplished by using a hybrid triple quadrupole/linear ion trap (Applied Biosystems MSD Sciex 4000QTRAP, Foster City, CA, USA) coupled to a liquid chromatograph (Agilent HP 1200 series, Palo Alto, CA, USA) with a TurbolonSpray (TIS) interface operating in the negative ion mode. The stationary phase was an ACE C18-PFP column (3 mm, 150 mm x 3.0 mm) from Advanced Chromatography Technologies (Aberdeen, UK). It was preceded by a guard cartridge (ACE C18-PFP; 3 mm, 10 mm x 3 mm) in order to protect the analytical column. The injection volume was 10 µL and the temperature for the analytical column was set at 40 °C.

All data were acquired and processed using the Analyst 1.5.1 Software. The mobile phase consisted of water and methanol at a flow rate of 0.3 mL min$^{-1}$. The elution program was as follows: isocratic conditions (15 % methanol) for 2 min, then linear gradient up to 85 % of methanol for 13 min, followed by linear gradient for 1 min up to reaching 100 % methanol, which
was kept for 2 min. Finally, linear gradient for 2 min to decrease methanol proportion up to 15%
and keeping this condition for 22 min for column stabilization.

The mass spectrometer was operated in the multiple reaction monitoring (MRM) mode. MRM
transitions were (m/z) 227 / 212 (quantifier ion) and 227 / 133 (qualifier ion) for p,p’-BPA; (m/z)
227 / 93 (quantifier ion) and 227 / 133 (qualifier ion) for o,p’-BPA; (m/z) 227 / 93 (quantifier ion)
and 227 / 133 (qualifier ion) for o,o’-BPA; and (m/z) 239 / 224 (quantifier ion) and 239 / 139
(qualifier ion) for $^{13}$C$_{12}$-BPA. The dwell time was set up at 100 ms. The TIS source parameters
were adjusted as follows: probe vertical y-axis position, 2 mm; probe horizontal y-axis position,
6 mm; curtain gas (N$_2$), 27 psi; nebulizer gas, 70 psi; turbo gas, 50 psi; temperature of the turbo
gas, 600 °C; ion spray voltage, 4.500 V; entrance potential, 10 V; and declustering potential, 95
V. Parameter values for the analyzer were as follows: 1.0 unit resolution for the first and third
quadrupoles; collision gas, 2.3 x 10$^{-5}$ Torr; collision energy, 26 V; and collision cell exit potential,
5 V. The procedure followed was:

1) Standards isomers commercially obtained were baseline separated by chromatography.
Retention times were p-p’-BPA: 13.2 min, o-p’-BPA: 16.8 min and o-o’-BPA: 17.6 min.
2) For each chromatographically separated standard isomer, the parent ion, two ion transitions
(two fragment ions) and the intensity ratio between both fragment ions were obtained.
3) The presence of isomers in samples was considered positive as the following requirements
were met:
   a) Retention time for the isomer in the sample was within ±0.1 min compared to the
      retention time of the respective standard isomer.
   b) The parent ion and the two fragment ions were identical to those of the respective
      standard isomers.
   c) The intensity ratio of fragment ions for each isomer was below the maximum permitted
tolerances defined in European Commission Decision 2002/657/EC.

According to this procedure, four identification points (1 point for precursor ion and 1.5 points
for each fragment ion) were used for each isomer, which surpasses the requirements for
compound identification (3 identification points are required for confirmatory methods).

Calibration curves were run using the standard addition method. For this purpose, appropriate
volumes of the individual stock solutions were added to the diluted synthesis solutions to give
concentrations of each BPA isomer in the range 4·10$^{-5}$-10 mg L$^{-1}$ and a constant concentration
of $^{13}$C$_{12}$-BPA (0.8 mg L$^{-1}$). Correlation between BPA isomer/internal standard peak area ratios
and concentrations of BPA isomers was determined by linear regression and 1/x weighted
calibration.

(1) Esquivel, D.; Van Den Berg, O.; Romero-Salguero, F. J.; Du Prez, F.; Van Der Voort, P.
100% Thiol-Functionalized Ethylene PMOs Prepared by “Thiol Acid-Ene” Chemistry.

(2) López, M. I.; Esquivel, D.; Jiménez-Sanchidrián, C.; Romero-Salguero, F. J.; Van Der
https://doi.org/10.1016/j.jcat.2015.04.008.
Figure S1. $^1$H NMR of 1,2-(E)-bis(triethoxysilyl)ethane.
Figure S2. $^1$H NMR of 1-thioacetic-1,2-(E)-bis(triethoxysilyl)ethane (1).
Figure S3. $^1$H NMR of 1-thiol-1,2-(E)-bis(triethoxysilyl)ethane (2).
Figure S4. $^{13}$C DEPT NMR spectra of 1-thiol-1,2-(E)-bis(triethoxysilyl)ethane (2).
Figure S5. Powder X-ray diffraction patterns of in-situ PMO (left) and SH-PMO (right).
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**Figure S7.** TEM images of in-situ SO$_3$H-ethane PMO (left) and SH-PMO (right).
Figure S8. TEM images of hexagonally structured bifunctional PMO materials: 
$\text{SH}_{25}/\text{SO}_3\text{H}_{75}@\text{PMO}$ (a), $\text{SH}_{50}/\text{SO}_3\text{H}_{50}@\text{PMO}$ (b) and $\text{SH}_{75}/\text{SO}_3\text{H}_{25}@\text{PMO}$. 