# [Electronic Supporting Information to accompany *Chem. Commun.* manuscript CC-COM-01-2013-040475] **Removal of Toxic Chemicals by Porous Organic Polymers Containing Metal-Catecholates**

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## **Table of Content**

S1. Materials and methods	S1
S2. Synthesis of POPs $ZnA_1B_1$ and $CuA_2B_1$	S2
S3. Breakthrough curves of POPs	S3
S4. TGA profiles	S5
Author contributions audit	S5
References	<i>S5</i>

### S1. Materials and methods.

Unless otherwise stated, all chemicals and solvents were purchased from Aldrich Chemicals Co. (Milwaukee, WI) and used without further purification. Water was obtained from a deionized water source provided by Northwestern University. Deuterated solvents were purchased from Cambridge Isotope Laboratories (Andover, MA) and used as received. All the gases used for the adsorption/desorption were ultra high purity grade 5 and were obtained from Airgas Specialty Gases (Chicago, IL). Material  $A_2B_1$  was synthesized following previously reported procedures.<sup>S1</sup>

Trace-metal analysis was performed using inductively coupled plasma optical emission spectroscopy (ICP-OES) conducted on a Varian Vista-MDX model ICP-OES spectrometer with simultaneous CCD detector (Varian, Walnut Creek, CA) that was equipped to cover the spectral range from 175 to 785 nm. The instrument was controlled by ICP expert software (version 4.1.0). Activated POP samples (3-7 mg) were digested in conc.  $H_2SO_4$ : $H_2O_2$  (35 wt% in  $H_2O$ ) (3:1 v/v) at 180 °C for 20 min using microwave irradiation. An aliquot of this concentrated acid solution was diluted to 8.0 vol% in ultrapure deionized  $H_2O$  (18.2 M $\Omega$ ·cm resistivity), which was obtained from a Millipore Milli-Q Biocel A10 instrument (Millipore Inc., Billerica, MA). The instrument was calibrated using ultrapure deionized water and mixtures containing 2, 5, 10, 20, and 30 ppm of Cu, and Zn that were prepared from commercially available ICP standard solutions. ). TGA data were obtained with a Mettler-Toledo TGA/DSC1 Star<sup>e</sup> thermal analyzer (Mettler-Toledo, Columbus OH) at a heating rate of 10 °C min<sup>-1</sup> under nitrogen flow.

All N<sub>2</sub> adsorption and desorption measurements were performed on a Micromeritics Tristar 3020 system (Micromeretics, Norcross, GA). Between 20-80 mg of samples were employed in each measurement and the data was analyzed using the Tristar II 3020 V1.03 software (Micromeretics, Norcross, GA). N<sub>2</sub> adsorption and desorption isotherms were measured at 77 K. The specific surface areas for N<sub>2</sub> were calculated using the Brunauer-Emmet-Teller (BET) model in the range of  $0.01 < P/P_0 < 0.1$ .

Breakthrough testing was conducted on a milligram scale using an apparatus and method described previously.<sup>S2</sup> Materials were activated at 250 C under vacuum to remove any labile coordinated solvent/water molecules and so that an accurate sample weight can be obtained prior to breakthrough measurements. Briefly, a small-scale breakthrough system was constructed capable of evaluating milligram quantities of sorbent. A feed stream is delivered to a diluent stream at rates necessary to achieve the required challenge concentrations and relative humidity conditions. For ammonia, cyanogen chloride, and sulfur dioxide, the feed stream consists of a pressurized ballast; for octane, a saturated vapor is used. Moisture level (humidity) is also controlled by a saturated vapor method using a saturator cell submerged in a temperature controlled water bath. Under ambient humid conditions, we assume that the metal sites in the POPs are coordinating to solvent/water molecules in addition to potential interactions with the TICs. Electronic Supplementary Material (ESI) for Chemical Communications This journal is © The Royal Society of Chemistry 2013

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The mixed stream is delivered to a nominal 4 mm internal diameter fritted glass tube in which the sorbent is packed to a height of approximately 4 mm. The feed concentration is measured by first bypassing the tube; the effluent concentration is continuously monitored using Hewlett Packard 5890 Series II gas chromatographs equipped with flame ionization detectors (cyanogen chloride, octane), a flame photometric detector (sulfur dioxide), and a photoionization detector (ammonia). Table S1 summarizes the conditions of the testing.

Table S1. Breakthrough system parameters.

Parameter	Value
Temperature	20°C
RH	0% (-40°C dew point), 80% RH
Adsorbent mass	~15-40 mg
Adsorbent volume	55 mm <sup>3</sup>
Flow rate	20 mL/min
Challenge concentration $(C_0)$	1,000 mg/m <sup>3</sup> (ammonia, sulfur dioxide)
	4,000 mg/m <sup>3</sup> (cyanogen chloride, octane)

For each test, the chemical was challenged to the packed bed until the effluent concentration equaled the feed concentration, resulting in saturation of the sorbent. At this point, the chemical feed was terminated and air was purged through the system to evaluate chemical retention. The effluent curve was then integrated to determine the mass balance for the system and calculate the loading at saturation, in mol/kg. Graphs are presented in normalized time on the x-axes to account for variations in mass and density of the samples. Calculated loadings deviate due to system error by approximately  $\pm 10\%$ .

## S2. Synthesis of POPs ZnA<sub>1</sub>B<sub>1</sub> and CuA<sub>2</sub>B<sub>1</sub>.

 $ZnA_2B_1$ . In an 8 dram vial  $A_2B_1$  (550 mg, ~1.50 mmol of catechol moieties) was activated at 170 °C under static vacuum (~100 millitorr) for 6 h, which was cooled, loaded in a nitrogen glovebox, suspended in dry toluene (10 mL), and  $Zn(Et)_2$  (1.0 M in hexanes, 3.22 mL, 3.22 mmol) was added dropwize. This suspension was stirred overnight at rt in the glovebox, flitered directly into a Soxhlet extraction apparatus, and washed with dry THF for 16 h under a N<sub>2</sub> atmosphere. The remaining black material was filtered and activated at 250 °C under vacuum overnight prior to measuring nitrogen isotherms.

 $CuA_2B_1$ .  $Cu(OAc)_2$ ·H<sub>2</sub>O (643 mg, 3.22 mmol) was added to a suspension of  $A_2B_1$  (550 mg, ~1.50 mmol of catechol moieties) in methanol (15 mL). This mixture was stirred at 50 °C for 18 h, filtered directly into a Soxhlet extraction apparatus, and washed with methanol for 16 h. The remaining black material was filtered and activated at 250 °C under vacuum overnight prior to measuring nitrogen isotherms.

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# S3. Breakthrough curves of POPs



Fig. S1 Ammonia breakthrough of  $CuA_2B_1$  in humid conditions (80% RH) first cycle (blue) and after re-activation (red). (In this test, a smaller amount of  $CuA_2B_1$  was used as compared to the initial results shown in Fig. S2, and therefore ammonia begins eluting earlier.)



Fig. S2 Cyanogen chloride breakthrough results of  $A_2B_1$  (blue, solid),  $CuA_2B_1$  (red, dashed), and  $ZnA_2B_1$  (green, dotted) under dry (a) and humid (b) conditions.

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Sulfur dioxide breakthrough results of  $A_2B_1$  (blue; solid),  $CuA_2B_1$  (red; dashed), and  $ZnA_2B_1$  (green; dotted) under dry (a) and humid (b) conditions.



Fig. S4 Octane breakthrough results of  $A_2B_1$  (blue; solid),  $CuA_2B_1$  (red; dashed), and  $ZnA_2B_1$  (green; dotted) under dry (a) and humid (b) conditions.

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Fig. S5 TGA profiles of  $CuA_2B_1$  (red; solid), and  $ZnA_2B_1$  (green; dashed).

Author contributions audit: M.H.W. and O.K.F. conceived the experiments presented herein. M.H.W. synthesized and characterized (including ICP and gas sorption measurements)  $A_2B_1$ ,  $CuA_2B_1$ , and  $ZnA_2B_1$ . M. A. B, and P. J. performed all the breakthrough measurements and G.W.P. carried out the data analysis for these experiments. O.K.F., J.T.H., and S.T.N. supervised the project. M.H.W. and G.W.P. wrote the initial draft of the paper with inputs from O.K.F. M.H.W. and S.T.N. finalized the manuscript.

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