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High propylene/propane adsorption selectivity in a copper(catecholate)-decorated porous organic polymer

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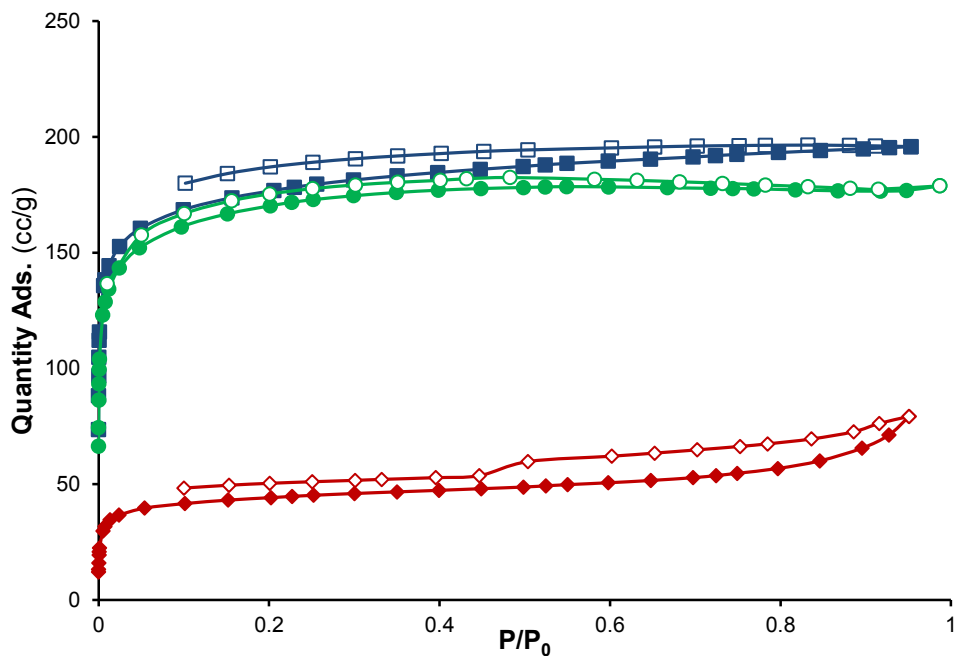## Table of Content

S1. Materials and methods.

Unless otherwise stated, all chemicals and solvents were purchased from Aldrich Chemicals Co. (Milwaukee, WI) and used without further purification. For reaction work up and adsorption isotherm measurements, 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). Materials $A_{10}B_1$, $CuA_{10}B_1$, and CuA_2B_1 were synthesized following previously reported procedures.[S1, S2]

Trace-metal analysis was performed using inductively coupled plasma optical emission spectroscopy (ICP-OES) conducted on a Varian Vista-MDX model ICP-OES spectrometer (Varian, Walnut Creek, CA) that was equipped with a CCD detector and an argon plasma to cover the 175-to-785 nm spectral range. 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) in a Biotage (Uppsala, Sweden) SPX microwave reactor (software version 2.3, build 6250) at 180 °C for 20 min or until the solution became clear. An aliquot of this concentrated acid solution was diluted to 8.0 vol% in ultrapure deionized H_2O (18.2 MΩ·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 that were prepared from commercially available ICP standard solutions.
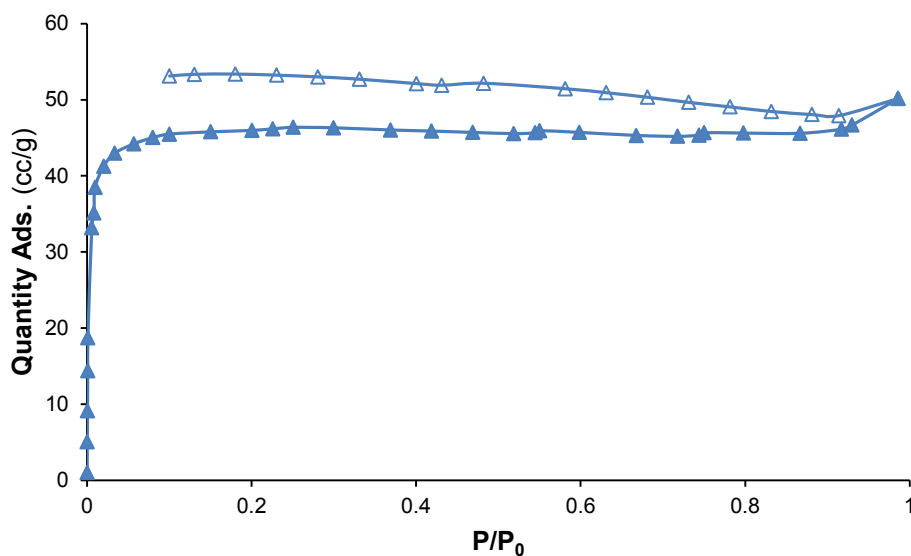
All N_2 adsorption and desorption measurements were performed on a Micromeritics Tristar 3020 system (Micromeretics, Norcross, GA). Between 20-80 mg of samples were employed in each measurement and the data was analyzed using the Tristar II 3020 V1.03 software (Micromeretics, Norcross, GA). N_2 adsorption and desorption isotherms were measured at 77 K. The specific surface areas for N_2 were calculated using the Brunauer-Emmet-Teller (BET) model in the range of $0.01 < P/P_0 < 0.1$. The pore size distributions were calculated from the adsorption-desorption isotherms by density functional theory (DFT) in the range of $5.0 \times 10^{-5} < P/P_0 > 0.95$ using the slit-pore N_2-DFT model.

Propylene, propane, ethylene, ethane, and water vapor adsorption isotherms were performed on a VTI MB-300G Gravimetric Analyzer (now part of TA Instruments, Schaumburg, IL) and measured at 298 K. Unless otherwise noted in the manuscript, all samples (between 4-10 mg) were degassed at 200 °C under high vacuum ($<10^{-3}$ bar) for 120 min or until weight equilibration (<0.0010 wt% change over 5 min). Data was logged at 2 min intervals or every 0.200 wt% change while samples were allowed to equilibrate for 45 min for each step or <0.0010 wt% change over 5 min.

S2. Sorption isotherms and pore size distributions.

Figure S1. Nitrogen isotherms for $A_{10}B_1$ (blue squares), CuA_2B_1 (green circles), and $CuA_{10}B_1$ (red diamonds) measured at 77 K. Closed symbols, adsorption; open symbols, desorption.

Figure S2. Nitrogen isotherms measured at 77K for $CuA_{10}B_1$ after exposure to an atmosphere of 80% RH (~20 Torr of water vapor pressure) and mild activation at 80 °C under vacuum (10^{-3} Torr). Closed symbols, adsorption; open symbols, desorption.
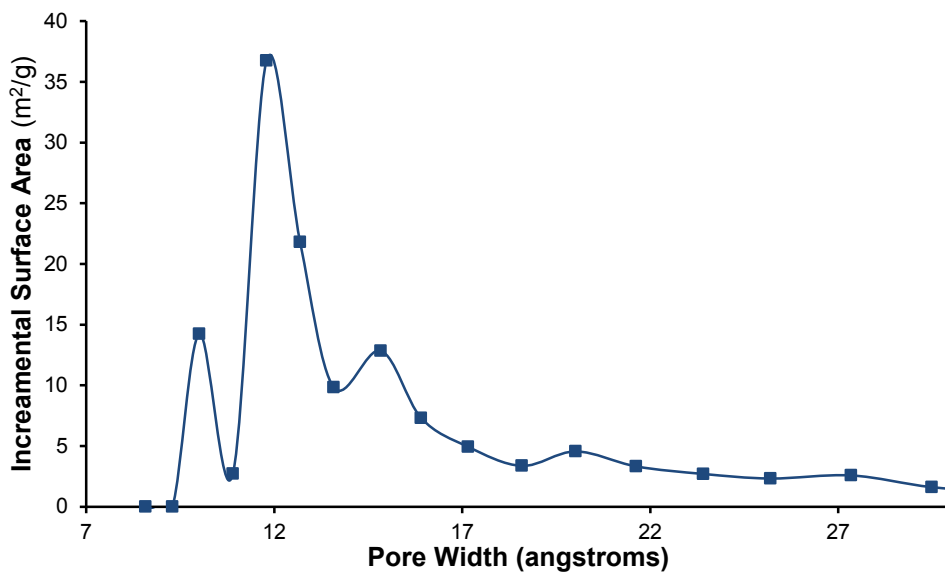
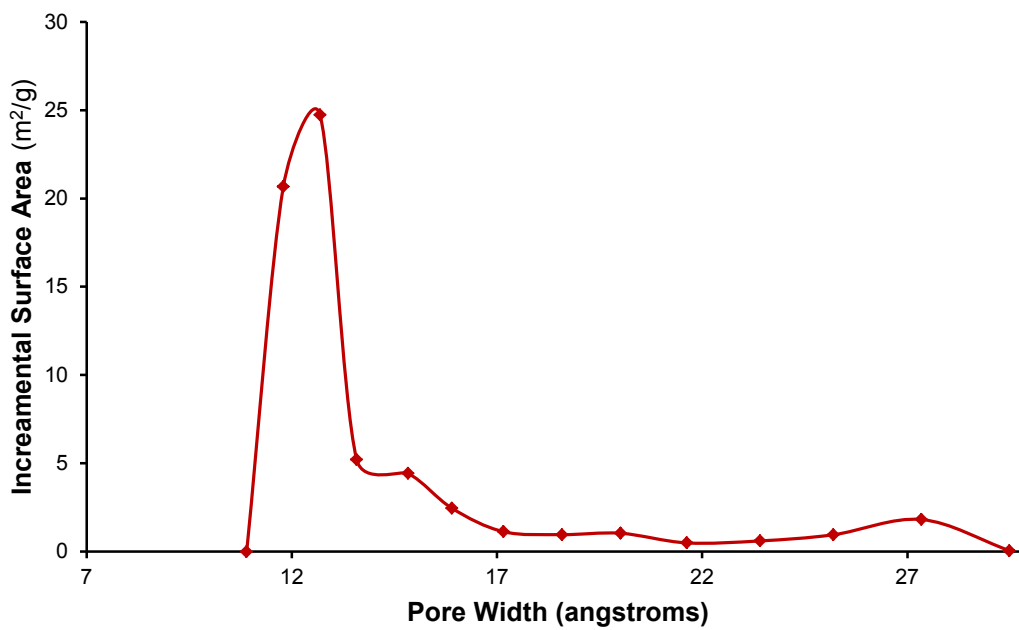**Figure S3**.　　　Pore size distribution based on DFT calculations for $A_{10}B_1$.
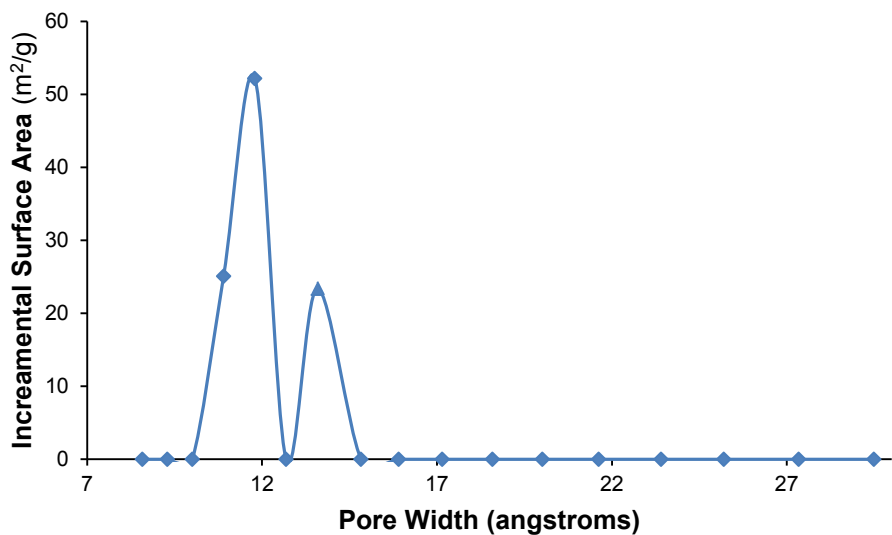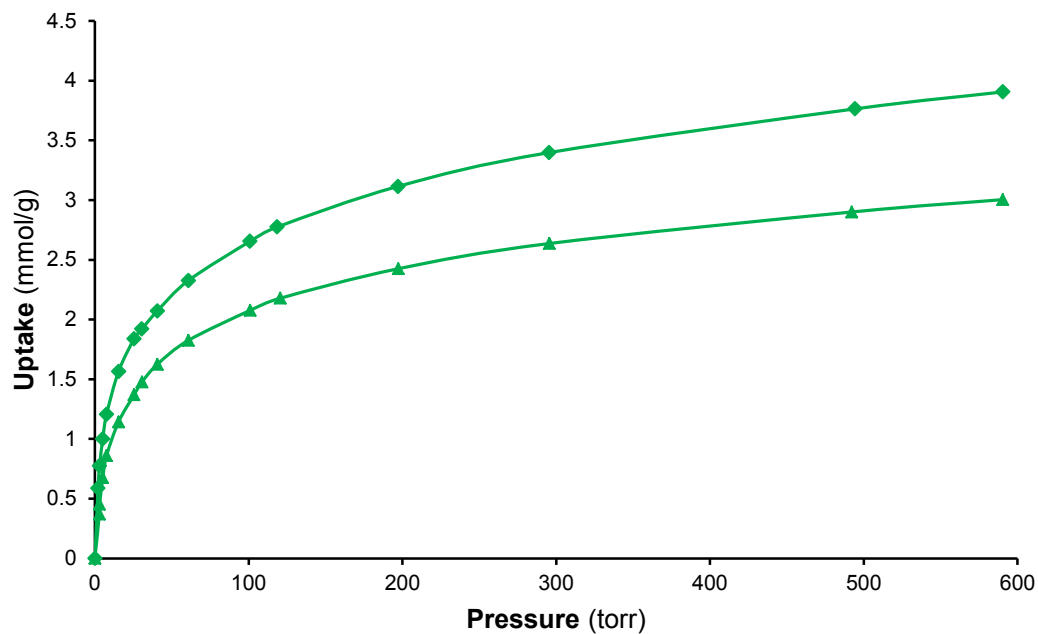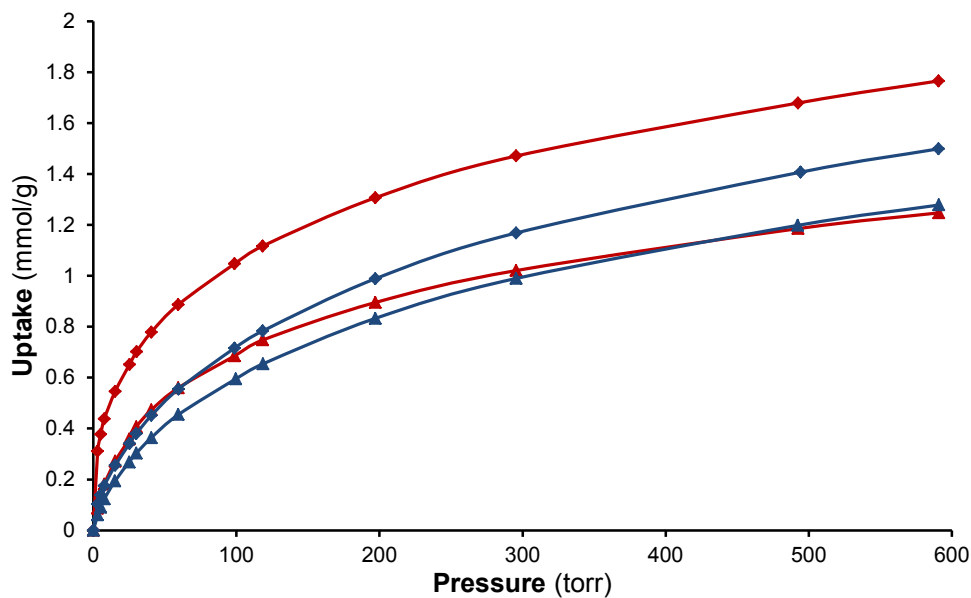

Figure S4.　　　Pore size distribution based on DFT calculations for $CuA_{10}B_1$.
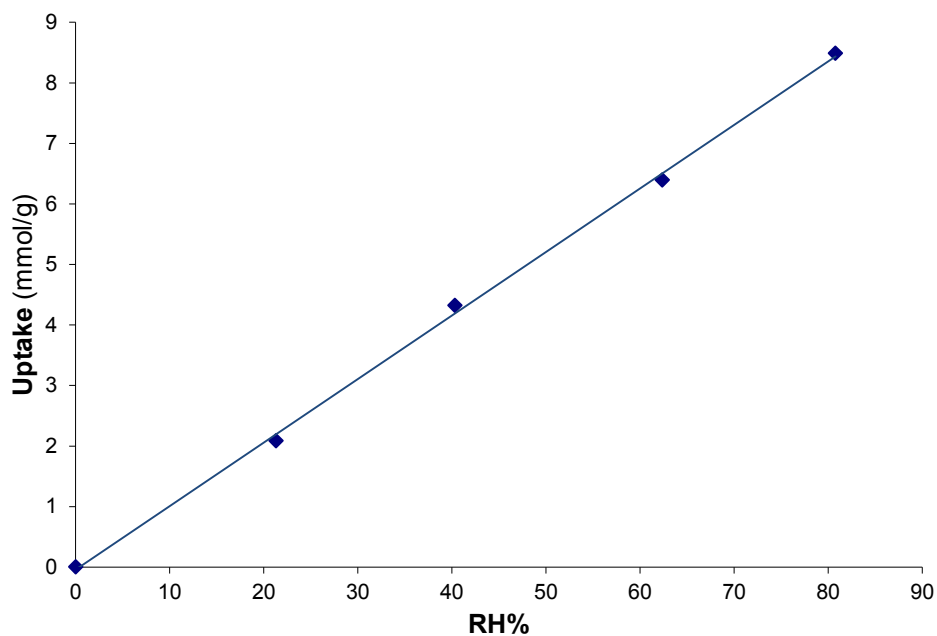
Figure S5.   Pore size distribution based on DFT calculations for $CuA_{10}B_1$ after exposure to an atmosphere of 80% RH (~20 Torr of water vapor pressure) and mild activation at 80 °C under vacuum (10^{-3} Torr).

Figure S6.   Propylene/propane adsorption isotherms for CuA_2B_1 (propylene, green diamonds; propane, green triangles) measured at 298 K.

Figure S7.   Ethylene/ethane adsorption isotherms for **CuA$_{10}$B$_1$** (ethylene, red diamonds; ethane, red triangles) and **A$_{10}$B$_1$** (ethylene, blue diamonds; ethane, blue triangles) measured at 298 K.

Figure S8.   Water vapor adsorption isotherm for **CuA$_{10}$B$_1$** measured at 298 K.

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Figure S9. TGA profile for $\mathbf{CuA_{10}B_1}$ after exposure to 80%RH (~20 Torr of water vapor pressure). The removal of physisorbed water (~12 wt% loss before the 80 °C activation temperature) can be clearly seen followed by the loss of chemisorbed water (~3 wt% in the 90-230 °C range). This is consistent with our assumption that the $\mathbf{CuA_{10}B_1}$ material can maintain the ligated water molecules after the mild activation conditions.

S3. IAST calculations.

IAST calculations were carried out following the protocol originally reported by Myers and Prausnitz[S3] for a binary system using 7 equations and 9 unknowns. (Note that equations S1 and S2 apply to each of the two components, yielding a total of 7 equations.) The equations are analogous to Raoult's law for vapor-liquid equilibrium and describe the equilibrium between the adsorbed phase and the gas phase, assuming the activity coefficients in the adsorbed phase are unity:

$$Py_i = P_i^{\circ} x_i \qquad \text{(S1)},$$

$$\pi_i^{\circ} = \frac{RT}{A} \int_0^{P_i^{\circ}} \frac{q_i(P)}{P} dP \qquad \text{(S2)},$$

$$\pi_1^{\circ} = \pi_2^{\circ} \qquad \text{(S3)},$$

$$x_1 + x_2 = 1 \qquad \text{(S4)},$$

$$y_1 + y_2 = 1 \qquad \text{(S5)},$$

Here, π_i° is the spreading pressure of component i, R is the universal gas constant, T is temperature, A is the surface area of the material, P_i° is the equilibrium pressure corresponding to spreading pressure π, $q_i(P)$ is the amount adsorbed of component i as a function of pressure (in other words, the pure component isotherm), P is pressure, y_i is the gas phase mole fraction of component i, and x_i is the adsorbed phase mole fraction of component i. Ultimately, due to the equilibrium condition of equal spreading pressures between the components (Eq S3), R, T, and A cancel out, leaving 9 unknowns. By specifying P and y_1, for instance, this set of equations may be solved and hence the composition of the adsorbed phase can be calculated.

S4. Author contributions audit. M.H.W., O.K.F., J.T.H., and S.T.N. conceived the experiments presented herein. M.H.W. synthesized and characterized $A_{10}B_1$, $CuA_{10}B_1$, and CuA_2B_1 and carried out all the sorption measurements. Y.J.C. and Y-S.B. carried out the IAST calculations with guidance from R.Q.S. S.J.G. carried out the BET and TGA characterization of $CuA_{10}B_1$ that was exposed to an atmosphere of 80% RH. O.K.F., J.T.H., and S.T.N. supervised the project. M.H.W. wrote the initial draft of the paper with inputs from all coauthors. M.H.W. and S.T.N. finalized the manuscript.

S5. References

S1.   M. H. Weston, O. K. Farha, B. G. Hauser, J. T. Hupp and S. T. Nguyen, *Chem. Mater.*, 2012, **24**, 1292-1296.

S2.   M. H. Weston, G. W. Peterson, M. A. Browe, P. Jones, O. K. Farha, J. T. Hupp and S. T. Nguyen, *Chem. Commun.*, 2013, **49**, 2995-2997.

S3.   A. L. Myers and J. M. Prausnitz, *AIChE J.*, 1965, **11**, 121-127.