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Removal of airborne toxic chemicals by porous organic polymers containing metal–catecholates[†]

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Porous organic polymers bearing metal-catecholate groups were evaluated for their ability to remove airborne ammonia, cyanogen chloride, sulphur dioxide, and octane by micro-breakthrough analysis. For ammonia, the metal-catecholate materials showed remarkable uptake under humid conditions.

While microporous materials such as metal-organic frameworks (MOFs), porous organic polymers (POPs), and covalent organic frameworks (COFs) have been extensively evaluated for a wide range of applications such as gas storage,¹⁻⁶ chemical separations,7-10 chemical sensing,11 and catalysis,12-17 their potential for chemical protection has been underexplored.¹⁸⁻²² Given their porous nature and tailorable micropore environments, MOFs, POPs, and COFs are attractive high-capacity materials for use in sorptive protection against toxic industrial chemicals (TICs) such as ammonia, cyanogen chloride, sulphur dioxide, and octane. Although MOFs have been explored for this application, the labile nature of the metal-ligand bonds in these materials often render them unstable under humid conditions, especially in the presence of acid- (SO₂ and CNCl) or base-generating (NH₃) chemicals.²³ On the other hand, POPs comprising chemically stable carbon-carbon bonds should not suffer from such framework degradation. Herein, we report the capability of a family of chemically stable catecholdecorated POPs to purify airborne toxic gases under both dry and humid conditions. Notably, the adsorption capacities of these materials for ammonia can be tuned by modifying the catechol units in the POP pore with Lewis-acidic metal centers.

Using a cobalt-catalyzed acetylene trimerization strategy,^{24–28} we have previously reported the copolymerization of orthoesterprotected diethynyl **A** with T_d -directing tetrakis(4-ethynyl)methane monomer **B** to form of a family of robust POPs that possess high densities of isolated catechol moieties and surface areas (1050 m² g⁻¹) that are comparable to activated carbon, the standard workhorse materials in the sorptive protection field (Scheme 1).²⁹ We hypothesize that these micropore-isolated catechol units can hydrogen bond to several of the aforementioned TICs and increase the sorptive capacity.³⁰ Furthermore, their stoichiometric metallation should provide Lewis-acidic mono-catecholate metal moieties with high degrees of coordinative unsaturation²⁹ useful for the binding of Lewis basic TICs such as ammonia. For this study, we choose Zn^{II} and Cu^{II} given their good Lewis acidity, good oxidative stability, and ease of metallation from readily available starting metal precursors.²⁹

As expected, the catechol groups in A_2B_1 can be metallated with ease using commercially available ZnEt₂ or Cu(OAc)₂, affording ZnA₂B₁ (550 m² g⁻¹) or CuA₂B₁ (645 m² g⁻¹), respectively (Scheme 1; Fig. 1a; Table 1). We attribute the slightly higher-than-expected zinc loading in ZnA₂B₁ (Table 1) to a small amount of prevalent zinc oxide entrapped in the pores, which agrees with its relatively lower gravimetric nitrogen BET surface area compared to CuA₂B₁.

We carried out micro-breakthrough measurements to obtain both retention and maximum capacity of the sorbent material for each of the TICs of interest under dynamic dry and high humidity (80% relative humidity (RH)) conditions; the former represents ideal adsorption conditions, while the latter mimics ambient atmospheric conditions (see ESI[†] for breakthrough



Scheme 1 Synthesis of POPs A₂B₁, ZnA₂B₁, and CuA₂B₁

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Fig. 1 Nitrogen isotherms (a) and water vapor isotherms (b) for A₂B₁ (blue triangles), CuA2B1 (red diamonds), ZnA2B1 (green circles). Closed symbols adsorption; open symbols desorption.

Surface area and porosity measurements of catechol POPs

POP	Metal qty., theor. (wt%)	Metal qty., actual (wt%)	BET surface area $(m^2 g^{-1})$	Pore volume $(cm^3 g^{-1})$
A_2B_1			1050	0.51
CuA ₂ B ₁	14.9	13.8	645	0.28
ZnA_2B_1	15.2	16.3	550	0.20

measurement procedures). A typical adsorbent composed of a zinc oxide- and amine-impregnated porous activated carbon material, ZnO/BPL/TEDA,18 was used as a comparison (see ESI+ for further description).

Under both dry and high humidity conditions, ammonia begins breaking through and reaches half-saturation much earlier for A_2B_1 (~410 and ~825 min g⁻¹, respectively) than



Fig. 2 Ammonia breakthrough results of A₂B₁ (blue; solid), CuA₂B₁ (red; dashed), and $ZnA_{2}B_{1}$ (green; dotted) under dry (a) and humid (b) conditions. (C/C₀ is the ratio of the concentration of ammonia in the breakthrough stream to a predefined challenge concentration C_0 (see ESI⁺)). After saturation is reached, the column was then purged with air under the same RH to evaluate retention, and the C/C_0 profiles began to return to 0

Table 2 Saturation loading of TICs

TICs	RH%	Loading (mol kg ⁻¹)				
		A_2B_1	ZnA ₂ B ₁	CuA ₂ B ₁	ZnO/BPL/TEDA	
NH ₃	0	0.70	1.36	2.10	0.69	
	80	1.31	3.32	4.32	0.45	
CNCl	0	0.80	0.81	0.81	1.22	
	80	0.04	0.04	0.16	2.14	
SO_2	0	0.02	0.13	0.04	0.30	
	80	0.03	0.07	0.30	0.82	
Octane	0	2.32	1.68	1.47	3.30	
	80	0.22	0.08	0.19	2.88	

for ZnA_2B_1 (~1110 and ~2650 min g⁻¹, respectively), with CuA_2B_1 being the most retentive (~1575 and ~2800 min g⁻¹, respectively) of the three materials (Fig. 2 and Table 2). All three saturated samples exhibit desorption under a flow of air at the same RH, indicating that at least some of the ammonia uptake is reversible (see below). As expected for a structure possessing acidic protons, a significant amount of ammonia was adsorbed by A₂B₁ comparable to typical zinc oxide- and amine-impregnated porous carbon (ZnO/BPL/TEDA).¹⁸ For A_2B_1 , the ammonia uptake can be explained by interactions between the basic ammonia and the acidic catechols as well as by simple adsorption and pore filling. It is, however, clear that the additional Lewis acid-Lewis base interactions available in the metallated materials were primarily responsible for their high affinities for ammonia, a remarkable fact considering their lower total pore volumes compared to that of the parent A_2B_1 material.

Surprisingly, under high humidity conditions, the ammonia uptake capacities for both CuA₂B₁ and ZnA₂B₁ improves by over 100% compared to that of A_2B_1 (Table 2), a highly desirable feature for humid ammonia adsorption.18 These values show higher increases in ammonia adsorption under humid conditions than those observed for MOF-74¹⁹ and HKUST²³ and many fold higher than that observed for the ZnO/BPL/TEDA standard. We attributed this to an improvement in the interactions of the metallated polymer matrix with ammonia in the presence of water molecules, which help to retain more ammonia in the micropore through a hydrogen-bonded network.³¹ For protective applications, the high chemical stability of the metal-catechol POPs in "wet" ammonia is particularly attractive: the appreciable amount of ammonium hydroxide formed under high humidity conditions would most likely degrade many MOFs.^{23,32} The formation of ammonium hydroxide under these conditions can partially explain the diminished uptake capacity of CuA2B1 for humidified ammonia upon being recycled (2.1 mol kg^{-1} , Fig. S1 in the ESI⁺), even after reactivation at 200 °C. Either the retention of this "salt" inside the pore (or the high ligation strength of the Cu^{II}-NH₃ bond) would certainly diminish the ability of Cu^{II} ion to ligate NH₃. We note that while recycling may be of interests in flue gas treatment, the initial capture capacity and rate are of primary importance in chemical protection.

Since water is capable of both hydrogen-bonding and Lewisbasic interactions with acidic metal sites, its presence under high RH conditions often interferes with the adsorption of the desired adsorbate, reducing the effectiveness of a sorbent. To evaluate the effect of water in the adsorption capacities of A_2B_1 ,

ZnA₂B₁, and **CuA₂B₁**, we measured their moisture uptake profiles (Fig. 1b) which turn out to be quite similar to those for a family of highly hydrophobic MOFs that has been examined for air purification.³³ At low relative humidity (below 30% RH), the metallated POPs have slightly higher affinity for water vapor than the parent material, not surprisingly due to the presence of polar metal–catecholates. Above 50% RH, A₂B₁ achieves moderately higher water loading that can be attributed to its greater pore volume (0.51 cm³ g⁻¹ for A₂B₁; 0.28 and 0.21 cm³ g⁻¹ for CuA₂B₁ and ZnA₂B₁, respectively). These data suggest that our materials can be considered as being overall moderately hydrophobic even though they possess a significant number of hydrophilic catechol and metal–catecholate groups.

Consistent with having only Lewis-acidic metal sites, CuA2B1 and ZnA₂B₁ both show negligible interactions with the Lewisacidic cyanogen chloride (CNCl, Table 2 and Fig. S2 in the ESI⁺) and sulfur dioxide (Table 2 and Fig. S3 in the ESI⁺). That the uptakes for both TICs by these metallated materials and A_2B_1 are similar under both dry and humid conditions suggests that the TICs are not strongly bound to the metal sites and that the primary interactions between them and the POPs are simply van der Waals. For all samples, breakthrough occurs immediately under dry conditions, and reaches saturation almost immediately under humid conditions. Adsorbates were also readily removed after feed termination, again supporting the lack of retention or affinity within the material. In comparison, the ZnO/BPL/TEDA standard performs better against both cyanogen chloride and sulfur dioxide since it contains both a Lewis acid and a Lewis base. This suggests that incorporating a Lewis-basic motif that does not interact with the Lewis-acidic sites of metal-catechol POPs might lead to better performance for cyanogen chloride and sulfur dioxide.

As expected for moderately hydrophobic materials, our POPs have good uptakes of octane (1.47–2.32 mol kg⁻¹) under dry conditions (Table 2 and Fig. S4 in the ESI[†]). The adsorption here is again essentially driven by van der Waals interactions between the aromatic framework and the hydrophobic octane. Interestingly, water uptake is preferred by the POPs under high humidity, presumably *via* hydrogen-bonding of water clusters to the catechol units, thus dropping the uptake of hydrophobic octane by almost an order of magnitude.

In summary, chemically stable porous organic polymers decorated with isolated Lewis-acidic metal-catecholate groups integrate hydrophobic interactions and Lewis acid-Lewis base interactions synergistically together in a microporous material for chemical protections. The Lewis-acidic sites found in CuA2B1 and ZnA_2B_1 result in high ammonia breakthrough capacities under dry conditions that outpace traditional carbon materials. Moreover, the tailored metal-catecholate micropore environments (not available for activated carbon) allow for the stabilization of Lewis-basic ammonia via hydrogen bonding with water molecules/clusters. As a result, the ammonia uptake is further enhanced under humid conditions, a trait which is rarely observed in similar ammonia breakthrough measurements for MOFs. Further modifications (i.e., incorporations of amphiphilic metal-catecholates or Lewis-basic motif that does not interact with the Lewis-acidic sites) may provide materials

with higher uptake for other chemical threats such as sulphur dioxide or cyanogen chloride.

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