

Pore Engineering Enables MOFs to Capture Trace Benzene Vapor

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Volatile organic compounds (VOCs) are a class of air pollutants.^[1] Particularly, benzene is a Group A carcinogen, and longtime exposure to benzene vapor even at very low concentrations is of high risk for mankind.^[2-3] One of the most widespread sources of benzene in indoor air is cigarette smoke, rendering benzene vapor being everywhere.^[4] Around the world, acceptable indoor benzene limits are in the range of 3-100 $\mu\text{g}/\text{m}^3$.^[3] Some indoor environments, however, have benzene in concentrations much higher than these limits. Driven by non-covalent interactions between sorbates and sorbents, physisorption is attractive for benzene removal because of the advantage in facile adsorbent regeneration. Many porous materials including activated carbons, zeolites, and metal-organic frameworks (MOFs, also known as porous coordination polymers) have been investigated for benzene sorption as physisorbents.^[5-8] However, the study on benzene adsorption at ultra-low pressures has been overlooked, hindering to capture low-concentration benzene from polluted air. For trace benzene capture, adsorption

capacity and selectivity, as well as the stability of adsorbents should be taken into accounts when developing relevant sorbents. So far, rational design of the adsorbents with high performance in the removal of trace benzene from ambient air remains challenging.

The modular nature of MOFs allows for tailoring their structures and functions for desired properties at the molecular or even atomic level, namely pore engineering, by rationally choosing the organic and inorganic building blocks.^[9,10] A series of interesting metal-dipyrzolate frameworks (termed as BUT-53 to BUT-58) reported in *Nature Materials*—by Jian-Rong Li, Zuo-Ren Nie, Michael J. Zaworotko, and co-workers—show double-walled pore structures. Those MOFs are composed of divalent metal ions and dipyrzolate ligands with different symmetry, length, and functionality showing varying benzene sorption performance.^[11] In that work, multiple merits including tunable pore, high stability, high adsorption selectivity and capacity have been integrated into those hydrophobic MOFs. Even at ultra-low pressures (<



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10 Pa) and room temperature, those MOFs can exhibit high benzene uptakes ($2.47\text{--}3.28\text{ mmol g}^{-1}$).

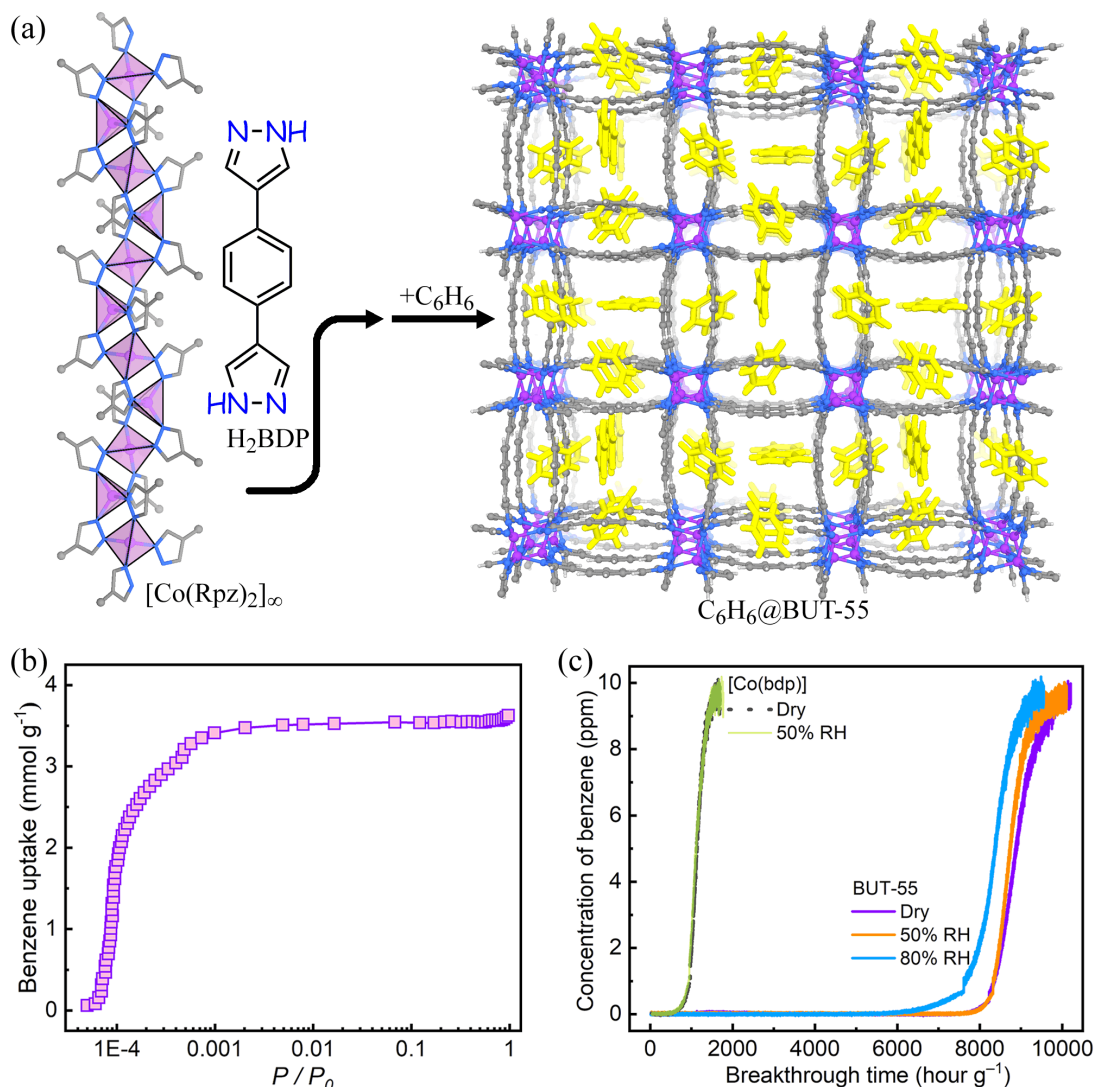


Figure 1. Schematic representation of benzene capture by BUT-55. (a), Structure of chain unit and ligand in BUT-55, and crystal structure of C₆H₆@BUT-55. (b), Benzene adsorption isotherm of BUT-55 at 298 K. (c), Benzene breakthrough curves for BUT-55 and Co(BDP) collected at different relative humidities at 298 K.

BUT-55 is a rod-packing structure with one-dimensional (1D) zigzag [Co(Rpz)]_∞ (Rpz denotes pyrazolate groups) chains that linked by double-layered linear BDP²⁻ (H₂BDP=1,4-di(1H-pyrazol-4-yl)benzene) linkers with π - π interactions of 3.7 Å (**Figure 1a**). The distortion of cobalt pyrazolate chains and BDP²⁻ linkers in BUT-55 results in undulating 1D pore channels with aperture size of about 8.0 Å in contrast to that of 13.2 Å in BUT-58 (also called CoBDP). Compared with previously reported benzene adsorbents, the optimal pore space endows BUT-55 to show relatively high benzene uptake at low-pressure region (3.28 mmol g^{-1} at 7.3 Pa, **Figure 1b**). Therefore, BUT-55 shows the

best-performing capture performance for trace benzene removal. Under both dry and humid (relative humidity of 50%) conditions, BUT-55 shows remarkably long retention time of $\sim 8000\text{ h/g}$ during the breakthrough experiments for a gas mixture that contains 10 ppm benzene (**Figure 1c**). Even upon exposure to more humid gas mixture like relative humidity of 80%, only slight decrease in the retention time of BUT-55 was observed. Notably, the residual benzene in purified outlet effluent by BUT-55 was determined to be $2.82\text{ }\mu\text{g m}^{-3}$ that is lower than acceptable indoor limits, implying the production of clean air from polluted air. After benzene capture, BUT-55 can be regenerated upon heating at

120 °C in nitrogen flow. For the adsorption mechanism, multiple C–H···X (X = N, O, π) interactions play a key role for the strong adsorption affinity and high sensitivity of BUT-55 toward benzene, which was verified by both single-crystal structures of benzene-loaded C₆H₆@BUT-55 (**Figure 1a**) and DFT calculations. Therefore, BUT-55 shows high benzene selectivity over water or other VOCs, including cyclohexane and ethanol. The separations of gas mixtures are important and energy intensive industrial processes,^[12] especially the separation of gases with similar structures and properties, as well as for the removal of some minor components for the air, including VOCs, water, etc. The performance of these porous metal dipyrzolate frameworks successfully demonstrates their high potential for benzene removal from polluted air. That study also illustrated a nice example on rational design of MOFs for on-demand adsorbents toward practical applications.

Meanwhile, it should be noted that there is still a long way to go for a benzene adsorbent to serve as real air cleaner. Scale-up, processing and cost of MOFs should be addressed before any further commercialization. The long-term durability of MOF adsorbents under practical deployment has also been concerned. The good point is that there are already a small number of MOFs holds the promise to work well under real conditions. Once upon solving challenges of cost and durability, it would be great opportunities to apply relevant techniques for air purification, environmental remediation, and industrial separations.

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