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Tetrazole-Functionalized Zirconium Metal–Organic Cages for Efficient C₂H₂/C₂H₄ and C₂H₂/CO₂ Separations

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Abstract: Isoreticular functionalization is a well-elucidated strategy for pore environment tuning and the basis of gas separation performance in extended frameworks. The extension of this approach to discrete porous molecules such as metal-organic cages (MOCs) is conceptually straightforward but hindered by synthetic complications, especially stability concerns. We report the successful isoreticular functionalization of a zirconium MOC with tetrazole moiety by bottom-up synthesis. The title compound (ZrT-1-tetrazol) shows promising C_2H_2/CO_2 and C_2H_2/C_2H_4 separation performance, as demonstrated by adsorption isotherms, breakthrough experiments, and density functional theory calculations. The design analogy between MOFs and highly stable MOCs may guide the synthesis of novel porous materials for challenging separation applications.

The acetylene (C_2H_2) gas market is poised to grow by 105.13 million tons during 2020-2024, corresponding to a compound annual growth rate (CAGR) of 3% during the forecast period.^[1] High-purity C₂H₂ is one of the most commonly used chemical raw materials for synthetic chemicals, such as synthetic α -ethynyl alcohols and acrylic acid derivatives.^[2] C₂H₂ is mainly produced from the cracking of hydrocarbons or through the partial combustion of methane, coexisting with ethylene (C_2H_4) or carbon dioxide (CO₂).^[3] However, based on the structure of unsaturated carbon-carbon and carbon-oxygen bonds, their molecular sizes, boiling points, and electronegativity are very close. Therefore, the separation of C₂H₂ from C₂H₂-containing mixtures (e.g., C₂H₂/C₂H₄, C₂H₂/CO₂) is an important but challenging industrial separation task.^[4] Prevailing technologies for C₂H₂ removal typically rely on cryogenic rectification or liquid absorbents, with high energy consumption and cost.^[5] In contrast, non-thermally driven approaches such as adsorption or membrane separation may provide alternatives with lower energy penalties.

The performance of adsorptive separation is driven to a large extent by the sorbent properties. Significant progress has been made for $C_2H_2/C_2H_4^{[6]}$ and $C_2H_2/CO_2^{[7]}$ separations by metalorganic frameworks (MOFs), as well as other framework-type sorbents such as covalent organic frameworks (COFs, assembled by covalent bonds)^[8] and hydrogen-bonded organic frameworks (HOFs, assembled by hydrogen bonds).^[9] The effective separation of C_2H_2 using these materials leverages

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Figure 1. (a) Structural regulation of MOCs (ZrT-1, ZrT-1-NH₂, and ZrT-1-tetrazol). (b) ESI-TOF-MS spectra of ZrT-1-tetrazol in acetonitrile/water solutions with various pH values.

various design strategies. In particular, the acidity of the alkyne hydrogens in C_2H_2 is an intuitive sorption target, which may be addressed by the deliberate installation of polar (Lewis-basic) groups. Differing strengths of the adsorptive interactions form a basis for appreciable thermodynamic selectivities in the thus-decorated materials.^[10] It should be noted that the intensity of the introduced active site should be moderate, as overly high adsorption strength will lead to higher adsorption energy and, accordingly, higher regeneration energy consumption.^[11]

Metal-organic cages (MOCs) are discrete molecules selfassembled from organic linkers and metal ions or clusters.^[12] MOCs differ from extended porous frameworks, i.e., MOFs and COFs, in the sense that their extended periodicity arises from a multitude of weak interactions instead of strong coordination or covalent bonding. Their molecular nature grants processability advantages, which are difficult to achieve in their higherdimensional counterparts. Meanwhile, owing to their modular chemistries, MOCs may, in principle, be rationally designed by well-elucidated reticular chemistry principles toward numerous applications. However, the application-driven development of MOCs remains limited by a smaller pool of available structures meeting specific prerequisites. In particular, for successful rational design, the MOC platform must (1) remain isoreticular during the modification process, and (2) maintain stability in the intended operating conditions. MOC-based membranes have demonstrated performance in CO₂ separation,^[13] but MOCs as adsorbents have not yet achieved a breakthrough in gas separation, especially for hydrocarbon separation. Previously, we have reported zirconium-based MOCs, namely ZrT-1 and ZrT-1-

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Figure 2. Gas sorption and separation performance of ZrT-1-tetrazol: (a) N_2 sorption isotherms at 77 K (filled symbols, adsorption; open symbols, desorption), the inserted is pore size distribution; (b) Single-component adsorption (ads) and desorption (des) isotherms of C_2H_2 , C_2H_4 , and CO_2 at 298 K; (c) IAST calculations for C_2H_2/C_2H_4 (50/50, 1/99) and C_2H_2/CO_2 (50/50) mixtures at 298 K; (d) Breakthrough curves of equimolar C_2H_2/C_2H_4 and C_2H_2/C_2 mixtures at 298 K and 1 bar (C_A/C_0 , outlet concentration/feed concentration); (e) Separation cycling test of equimolar C_2H_2/C_2H_4 mixtures; (f) Breakthrough curves for C_2H_2/C_2H_4 (1/99) mixtures.

NH₂,^[14] demonstrating the requisite stability for efficient synthetic design. Herein, we report the successful bottom-up synthesis of derivative, tetrazole functionalized ZrT-1-tetrazol. This isostructural congener exhibits superior C₂H₂ recognition properties relative to its parent MOCs owing to the tetrazole moiety, as evidenced by gas sorption experiments, density functional theory (DFT) calculations, Grand Canonical Monte Carlo (GCMC) simulations, and comparisons to control MOF samples prepared in this work (UiO-66-tetrazol, CAU-1-tetrazol, and MIL-101-tetrazol). The results establish Zr-MOCs as a promising sub-class of molecular porous materials with significant potential in gas separation applications.

Starting from the 2-aminoterephthalic acid ligand of ZrT-1- NH_{2} ,^[14] the tetrazole-appended ligand 2-(1H-tetrazol-1vl)terephthalic acid (BDC-tetrazol) was synthesized bv heterocyclic reaction (Scheme S1 and Figure S1,2). The one-pot combination of BDC-tetrazol and zirconocene dichloride (Cp₂ZrCl₂) in N,N'-dimethylacetamide (DMA) and H₂O yielded crystals of ZrT-tetrazol (Figure 1a). Although we have obtained large single crystals (Figure S3,4), the structure analysis failed due to weak X-ray diffraction. Therefore, the structure and molecular formula of ZrT-1-tetrazol were confirmed by powder Xray diffraction (PXRD) and high-resolution electrospray ionization mass spectrometry (ESI-TOF-MS). PXRD shows that the peak positions of ZrT-1-tetrazol and ZrT-1-NH₂ (simulated and experimental) are consistent, indicating that they have the same framework structures (Figure S9). The ESI-TOF-MS spectra verified the existence of cage molecules in the solution (Figure 1b and Figure S10,11). The continuous change of the charge state peaks from +1 to +4 is attributed to the continuous loss of

hydrogen from μ_2 -OH and the loss of counterion (Cl⁻). To be specific, the ion peaks at m/z of 1766.7993, 1178.2098, and 883.9152 correspond to [M-4Cl-2H]²⁺, [M-4Cl-H]³⁺, and [M-4Cl]⁴⁺ ions, respectively. After m/z deconvolution, the average measured molecular weight of the component is 3677 Da, comparable to that of ZrT-1-tetrazol (3677 Da). Compared with the molecular formula of ZrT-1-NH₂, only the functional group on the ligand is different in ZrT-1-tetrazol. The molecular weight difference between the two MOCs is 318 Da (3677-3359), which exactly corresponds to the molecular weight difference of the functional groups on the six ligands in MOC (53 Da, [M(N₄CH)-M(NH₂)]), further confirming the structure similarity between ZrT-1-tetrazol and ZrT-1-NH₂.

Although ZrT-1, ZrT-1-NH₂, and ZrT-1-tetrazol have similar structures and the same cavity size (7.05 Å), the aperture size gradually decreases (4.01, 3.73, and 3.65 Å for ZrT-1, ZrT-1-NH₂, and ZrT-1-tetrazol, respectively, Figure S5), and the polarity of the pore surface gradually increases. This feature allows the gradual tuning of the host-guest interactions between the framework and gas molecules, thereby facilitating gas separation. ESI-TOF-MS analysis indicates that ZrT-1-tetrazol remains stable in acetonitrile/water solutions with variable pH values between 2.0 and 10.0. The excellent stability of ZrT-1-tetrazol originates from the strong Zr-O bonds, promising for multitudinous applications, including C_2H_2 storage and separation.

To clarify the pore properties of ZrT-1-tetrazol, we obtained gas sorption isotherms with the optimum activated porous samples. N₂ (77 K) sorption measurement gives a type I isotherm, typical for microporous solids. The adsorption capacity is 207.1 cm³ g⁻¹ (1 bar, Figure 2a). The Brunauer–Emmett–Teller (BET)

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Figure 3. DFT-calculated binding configurations of (a) C_2H_2 , (b) C_2H_4 , and (c) CO_2 in ZrT-1-tetrazol (green dotted lines represent the interaction between gas molecules and the cage; purple dotted lines represent the interaction between gas molecules).

surface area was calculated to be around 636.7 m² g⁻¹ by utilizing the non-local density functional theory (NLDFT) based on the N₂ sorption isotherm. The distribution of pore size localizes between 5.9 and 11.8 Å, corresponding to the intrinsic porosity and the extrinsic porosity resulting from crystalline packing, respectively (Figure S6). The BET and pore size distribution did not change after breakthrough stability testing, indicating that the internal and external porosity is stable (Figure S56).

The permanent porosity and weakly basic pore surface of ZrT-1-tetrazol prompted us to study its storage and separation of acidic C₂H₂ against its typical separands (C₂H₄ and CO₂, Figure 2b). The uptake of ZrT-1-tetrazol for C_2H_2 is 57.7 cm³ g⁻¹ (298 K, 1 bar), which is 130% higher than that of ZrT-1-NH₂. Meanwhile, the uptakes of C_2H_4 and CO_2 increased by 21.4% and 54.6%, respectively, upon tetrazole functionalization. This is because C_2H_2 is more acidic than C_2H_4 and CO_2 .^[15] At the same time, the C₂H₂ adsorption of ZrT-1-tetrazol is higher than some of the adsorbents studied for C₂H₂/CO₂ and C₂H₂/C₂H₄ separations, such as PAF-110 (49.9 cm 3 g 1),^[8a] PAF-120 (50.8 cm 3 g 1),^[8b] HOF-1a (57.1 cm³ g⁻¹),^[9a] HOF-3a (47 cm³ g⁻¹),^[9b] HOF-21a (44.4 cm³ g⁻¹),^[9c] and ECUT-HOF-30a (43.7 cm³ g⁻¹).^[9d] To evaluate the affinity of ZrT-1-tetrazol to gas molecules, Clausius-Clapeyron equation was used to calculate the heat of adsorption (Q_{st}). The C₂H₂ Q_{st} in ZrT-1-tetrazol is 33.27 kJ mol⁻¹ at zero coverage, higher than that of C₂H₄ (29.87 kJ mol⁻¹) and CO₂ (29.89 kJ mol⁻ ¹), indicating that the framework of ZrT-1-tetrazol possesses a higher affinity to C₂H₂ than C₂H₄ and CO₂. Notably, the C₂H₂ Q_{st} of ZrT-1-tetrazol is lower than that of PAF-110 (38.4 kJ mol⁻¹),^[8a] PAF-120 (37.5 kJ mol⁻¹),^[8b] SIFSIX-2-Cu-i (41.9 kJ mol⁻¹),^[16] HOF-1a (58.1 kJ mol⁻¹),^[9a] and NKMOF-1-Ni (60.3 kJ mol⁻¹),^[4a] indicating easy regeneration due to reversible physisorption. To evaluate the separation performance of ZrT-1-tetrazole, we used the ideal adsorbed solution theory (IAST) to calculate the selectivities for C₂H₂/C₂H₄ (50/50, 1/99) and C₂H₂/CO₂ (50/50) mixtures of ZrT-1-tetrazol at 298 K (Figure 2c). The selectivity of ZrT-1-tetrazol to C_2H_2/C_2H_4 is 4.05, which is comparable to that of PAF-110 (3.9)^[8a] and PAF-120 (4.1),^[8b] but higher than CTF-PO71 (2.8),[8c] M'MOF-2a (1.93),[17] NOTT-300 (2.17),[6b] and Fe-MOF-74 (2.08).^[6a] The selectivity of ZrT-1-tetrazol to C₂H₂/CO₂ is 2.83, higher than that of M'MOF-2a (1.89).^[17] The low C_2H_2 Q_{st} , high C₂H₂ uptake, and moderate separation selectivity highlight that ZrT-1-tetrazol is a promising candidate for C2H2/C2H4 and C_2H_2/CO_2 separations with low regeneration energy.

Dynamic transient breakthrough experiments were conducted under ambient conditions to assess the actual separation performance of the C₂H₂/CO₂ and C₂H₂/C₂H₄ mixtures in ZrT-1tetrazol. In these experiments, the gas mixture flowed through the packed column under a total flow rate of 2 mL min⁻¹. Figure 2d implies that the ZrT-1-tetrazol exhibits a highly efficient separation of equimolar C₂H₂/C₂H₄ and C₂H₂/CO₂ mixtures. C₂H₄ and CO₂ eluted first because of their weak affinity toward the adsorbent, whereas C₂H₂ retained in the column for a remarkable period until its saturated sorption and breakthrough. The C₂H₂ retention time of ZrT-1-tetrazol for C₂H₂/C₂H₄ (50/50) reached 26 min g⁻¹ and without any noticeable change in the separation performance after six adsorption/desorption cycles, indicating its good recyclability and stability (Figure 2e). The easy desorption of C_2H_2 and C₂H₄ suggests that the adsorbent can be facilely regenerated (Figure S23). In addition, C_2H_2 can retain in the column for 48 min g^{-1} , and the productivity of highly pure C₂H₄ (> 99.99%) can reach 4.24 mol kg⁻¹, calculated based on the C_2H_2/C_2H_4 (1/99) breakthrough curve, indicating that ZrT-1-tetrazol can capture trace amounts of C_2H_2 to obtain high purity C_2H_4 (Figure 2f).

First-principle DFT calculations and GCMC simulations were conducted to elucidate the host-guest interactions and to better understand the adsorption behaviors of C₂H₄, C₂H₂, and CO₂ in ZrT-1-tetrazol at the molecular level.^[18] The optimized structures, as well as the corresponding adsorption energies, are presented in Figure 3a. The highly polar hydrogen of C₂H₂ is bound with the electronegative or basic tetrazole N sites on the cage surface through strong C=C-H····N electrostatic interactions with very short distances between 2.38 and 2.75 Å, implying strong interactions between C₂H₂ and the cage. Each ZrT-1-tetrazol cage contains six exposed N atoms and can bind three C2H2 molecules. The distance between neighboring adsorbed C₂H₂ molecules is ideal for them to synergistically interact with each other through multiple $C^{\delta} \cdots H^{\delta+}$ dipole-dipole interactions, further enhancing the adsorption energy. The calculated adsorption energy (ΔE) of C₂H₂ is -44.67 kJ mol⁻¹, higher than that of C₂H₄ (-29.72 kJ mol⁻¹) and CO₂ (-31.64 kJ mol⁻¹, Figure 3b,c), indicating weaker interactions of C2H4-ZrT-1-tetrazol and CO₂-ZrT-1-tetrazol compared with that of C₂H₂-ZrT-1-tetrazol. GCMC simulation results show that the main preferred gas sorption sites of ZrT-1-tetrazol are the internal surface of the cage (tetrazole groups and benzene rings), and the density



Figure 4. Single-component adsorption (ads) and desorption (des) isotherms of C_2H_2 , C_2H_4 , and CO_2 for UiO-66-tetrazol (a), CAU-1-tetrazol (c), and MIL-101-tetrazol (e) at 298 K. Breakthrough curves of equimolar C_2H_2/C_2H_4 and C_2H_2/CO_2 mixtures in an absorber bed packed with UiO-66-tetrazol (b), CAU-1-tetrazol (d), and MIL-101-tetrazol (f) at 298 K and 1 bar.

distributions of C_2H_2 are stronger than that of C_2H_4 and CO_2 (Figure S27).

We synthesized tetrazole functionalized MOFs (UiO-66-tetrazol, CAU-1-tetrazol, and MIL-101-tetrazol) to further prove the role of tetrazole functionalization in improving C_2H_2 selectivity. PXRD and BET data confirmed the phase purity and porosity of the synthesized MOFs (Figure S28,29,30,34,40,46). The C_2H_2 uptakes of UiO-66-tetrazol, CAU-1-tetrazol, and MIL-101-tetrazol are 94.3, 97.5, and 77.4 cm³ g⁻¹ (298 K, 1 bar), respectively (Figure 4a, c, and e), representing increases of 30.6%, 26.6%, and 11.7% compared with that of UiO-66-NH₂, CAU-1-NH₂, and MIL-101-NH₂, respectively (Figure S33,39,45). The C_2H_2/C_2H_4 selectivities of UiO-66-tetrazol, CAU-1-tetrazol, and MIL-101-tetrazol are 2.34, 1.68, and 1.96, respectively; and the C_2H_2/C_2P_4 selectivities are 2.89, 3.78, and 3.17, respectively (Figure S49,50,51), suggesting that the tetrazole-functionalized MOFs

can improve the selectivity toward C₂H₂. During the breakthrough experiments, the C₂H₂ retention time of UiO-66-tetrazol, CAU-1tetrazol, and MIL-101-tetrazol for equimolar C₂H₂/C₂H₄ reached 29.2, 33.3, and 25.4 min g^{-1} , respectively; and the C₂H₂ retention time for equimolar C₂H₂/CO₂ reached 27.1, 81.8, and 14.0 min g⁻ ¹, respectively (Figure 4b, d, and f). It is worth noting that CAU-1tetrazole has a C₂H₂ adsorption capacity of 126 cm³ g⁻¹ for equimolar C₂H₂/CO₂ separation, which is higher than its static uptake (97.5 cm³ g⁻¹). On the other hand, the C_2H_2 uptake capacity of CAU-1-tetrazole obtained from the single-component breakthrough test (94.9 cm³ g⁻¹) is consistent with the static uptake (Figure S55), suggesting that the difference in C_2H_2 capacity of the mixed gas breakthrough test may originate from competitive adsorption. These data further confirm the actual separation performance of the tetrazole functionalized MOFs toward equimolar C_2H_2/C_2H_4 and C_2H_2/CO_2 mixtures. The selectivity and breakthrough performance of ZrT-1-tetrazol is similar, if not superior, to some of these stable MOFs. We anticipate that further exploration of reticular chemistry with stable MOCs may expand the relevance of these molecular materials in other demanding applications. In particular, performance enhancements to competitive levels may bring light to other valuable attributes such as materials processability.

In conclusion, we used isoreticular chemistry to synthesize a tetrazole-functionalized MOC (ZrT-1-tetrazol) with the same structure of ZrT-1 and ZrT-1-NH₂. The adsorption capacity of ZrT-1-tetrazol for C₂H₂ is increased by 130% (298 K) compared with ZrT-1-NH₂, and the IAST separation selectivities for C₂H₂/CO₂ and C₂H₂/C₂H₄ are increased to 2.83 and 4.08, respectively. Breakthrough experiments confirmed the selective adsorption of ZrT-1-tetrazol to C_2H_2 and the excellent separation cycle performance of C₂H₂/C₂H₄. DFT calculation revealed that ZrT-1tetrazol exerts a strong influence on C₂H₂ molecules through tetrazole N···H—C hydrogen bond and multiple C^{δ} ····H^{δ +} dipoledipole interactions. The selective separations of C₂H₂/CO₂ and C₂H₂/C₂H₄ by UiO-66-tetrazol, CAU-1-tetrazol, and MIL-101tetrazol confirmed the versatility of tetrazole functional sites for selective C₂H₂ adsorption in MOFs. Our work provides a benchmark for C₂H₂/CO₂ and C₂H₂/C₂H₄ separations of MOCs, and guides the design and synthesis of other porous materials for C₂H₂-selective adsorption.

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Conflict of interest

The authors declare no conflict of interest.

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We report using isoreticular chemistry to synthesize a tetrazolefunctionalized metal-organic cage (ZrT-1-tetrazole) with the same structure of ZrT-1 and ZrT-1-NH₂. The adsorption capacity of ZrT-1-tetrazol for C_2H_2 increases by 130% (298 K) compared with ZrT-1-NH₂, and it exhibits promising C_2H_2/CO_2 and C_2H_2/C_2H_4 separation performance.



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Tetrazole-Functionalized Zirconium Metal-Organic Cages for Efficient C₂H₂/C₂H₄ and C₂H₂/CO₂ Separations