



Metal–Organic Frameworks

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An Ultrastable Metal Azolate Framework with Binding Pockets for Optimal Carbon Dioxide Capture

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Abstract: In the evolution of metal-organic frameworks (MOFs) for carbon capture, a lasting challenge is to strike a balance between high uptake capacity/selectivity and low energy cost for regeneration. Meanwhile, these man-made materials have to survive from practical demands such as stability under harsh conditions and feasibility of scale-up synthesis. Reported here is a new MOF, Zn(imPim) (aka. MAF-stu-1), with an imidazole derivative ligand, featuring binding pockets that can accommodate CO₂ molecules in a fitlike-a-glove manner. Such a high degree of shape complementarity allows direct observation of the loaded CO₂ in the pockets, and warrants its optimal carbon capture performances exceeding the best-performing MOFs nowadays. Coupled with the record thermal (up to 680°C) and chemical stability, as well as rapid large-scale production, both encoded in the material design, Zn(imPim) represents a most competitive candidate to tackle the immediate problems of carbon dioxide capture.

Modern studies in adsorption of gas molecules into porous solids experienced a renaissance with the advent of metalorganic frameworks (MOFs).^[1,2] Essentially, it is the ease of design down to their molecular building blocks and underlying topologies for this new class of crystalline porous materials that guarantees a broad spectrum of applications,^[3–5] especially for addressing utilitarian concerns such as storage for alternative fuels and separation for clean air (for example carbon dioxide capture).^[6,7] To satisfy the urge

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the author(s) of this article can be found under: https://doi.org/10.1002/anie.201909046. of achieving both high uptake capacity/selectivity and low energy penalty, significant advances are made concerning the development of two important types of MOF adsorbents in the recent decade.^[8-15]

First, the success of MOF-74 (CPO-27) and related materials brought forward the role of open metal sites in efficient carbon capture.^[8-11] The strong interaction with CO₂ molecules is the key to high selectivity in gas separation, especially when the exposed metal sites are appended with amines (as in mmen-Mg₂(dobpdc))^[10] or hydroxide (as in MAF-X25ox).^[11] However, the large energy penalty associated with the desorption process, even up to the extent of chemisorption, is a critical drawback. Second, later on, a family of pillared-square-grid metal-organic materials, namely SIFSIX-n and analogues, were developed by taking advantage of pore size selectivity in gas separation.^[12-15] In the cases of SIFSIX-3-Cu^[13] and Qc-5-Cu-sql-β,^[15] the pore sizes were judiciously engineered to achieve ultrahigh selectivity and also lower the energy costs for regeneration, but a compromise in uptake capacity is inevitable. Furthermore, the related NbOFFIVE-1-Ni was demonstrated to be stable toward moisture and highly efficient for CO₂ capture under fuel gas stream^[7] and direct air capture conditions.^[14]

A third, sporadic type of MOF adsorbents also exhibited excellent ability for carbon dioxide capture, which was mainly attributed to their collective binding sites, as exemplified by Zn₂(Atz)₂(ox),^[16] NOTT-300,^[17] UTSA-16,^[18] and MAF-23.^[19] The cooperation of multiple weak interaction sites to achieve binding specificity is reminiscent of biomolecules which evolve towards shape-oriented binding domains rather than rely on autonomous sites: a cavity on the surface or in the interior of a protein that possesses the ability of binding a substrate is usually referred to as a binding pocket.^[20,21] Compared with the situation for flexible MOFs (that is, induced fit),^[22,23] it is more challenging to accomplish shape complementarity for rigid MOFs (that is, fit like a glove). The existence of periodic binding pockets will also facilitate the direct observation of loaded guests in MOFs through singlecrystal X-ray diffraction (SCXRD) or neutron scattering techniques.^[24,25]

Since the discovery of the Zn^{II}-imidazolate frameworks with zeolitic **sod** (aka. ZIF-8 or MAF-4), **ana**, and **rho** topologies,^[26] a large amount of efforts were paid to the construction of zeolitic imidazolate frameworks.^[27-29] Recently, we found that deliberate introduction of chelating groups in imidazole-based ligands could afford unusual zeolitic nets (for example, **gie** and **uks**),^[30,31] because the chelating sites occupying two of the four coordination vacancies would force the metal nodes to deviate from the ideal tetrahedral geometry substantially. Meanwhile, the

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chelate effect can contribute to the thermodynamic stability, thus improving the thermal and chemical (in particular, hydrolytic) stabilities of MOFs, which are crucial for practical demands.^[32,33] On the other hand, chelation is kinetically favored overwhelmingly, which is beneficial for rapid, scaleup synthesis and high product purity, which are key requirements toward industrial production of MOF materials.^[34]

We report herein a new metal azolate framework (MAF),^[35] namely Zn(imPim) (also known as MAF-stu-1), based on an imidazole derivative ligand 2-(1H-imidzol-2-yl)-3H-imidazo[4,5-c]pyridine (H₂imPim), which can be obtained by solvothermal reaction for high-quality single crystals, and also by rapid synthesis for gram-scale samples with a high yield (70%; Supporting Information, Experimental Details and Figures S1-S3). The single-crystal structure shows each Zn^{II} ion, adopting a highly distorted tetrahedral geometry, is chelated by two imidazolyl-N of a deprotonated ligand and extended through one imidazolyl-N and one pyridine-N from two imPim²⁻ ligands (Figure 1a; Supporting Information, Figure S4 and Tables S1–S4). The remaining imidazolyl-N of imPim²⁻ is uncoordinated, rendering it an exposed Lewis base site, which interacts weakly with the Zn^{II} center (Zn…N ca. 2.92 Å). The extending angle defined by linking three adjacent Zn^{II} nodes with one rigid imPim^{2–} ligand is 68.25°, severely deviating from that of an ideal tetrahedron (109.47°). Topologically, simply connecting all Zn^{II} nodes with shortest links passing the ligands leads to an unusual 4-coordinated (4-c) **usf** net (point symbol 6⁵.8; Figure 1c),^[36,37] which is a potential uninodal zeolite net. Alternatively, if one views both the metal and ligand as 3-c nodes, the deconstruction results in a uninodal 3-c net, known as **etf.**^[37]

When projected into the *ab* plane, the overall framework of Zn(imPim) (crystal void volume $0.19 \text{ cm}^3 \text{g}^{-1}$, 27.8%; total pore volume $0.256 \text{ cm}^3 \text{g}^{-1}$ calculated from Ar sorption isotherm at 87 K)^[38,39] is composed of two types of triangular channels with the edge lengths of ca. 9.6 and 14.0 Å, respectively (Figure 1b). The effective pore apertures are narrower, estimated to be ca. 4–5 Å (Supporting Information, Figure S5), because the wider channels are gated by imidazolyl groups, and the corners of the narrower triangular channels are inaccessible.^[40] The most interesting structural



Figure 1. Structure of Zn(imPim). a) Coordination environment of Zn^{II} ion, showing the highly distorted tetrahedral geometry imposed by a 5-memberred ring formed from the chelating site of imidazole derivative ligand. b) Perspective view down the *c* direction of the framework (H omitted), showing the triangular channels and narrow apertures. c) Topological representation of the underlying net, **usf** (6⁵.8), in which the characteristic 8- and 6-cycles are delineated in red and green, respectively. d) Connolly surface representation (meshed, probe radius 1.0 Å) integrated with the framework backbone (in green), highlighting the helicoidal channels with pocket-like terminals.



Figure 2. Stability of Zn(imPim). a) Comparison on thermal stability, indicated by thermogravimetric curves (under N₂ atmosphere, heating rate 5 °Cmin⁻¹), of Zn(imPim), ZIF-8 (MAF-4) and UiO-66 prepared from stirring methods, as well as that of MOF-5 and HKUST-1 (⁺ from literatures). b) Chemical stabilities of Zn(imPim) from large-scale synthesis, indicated by powder X-ray diffraction (PXRD) patterns, suspended in boiling water (9 days), acidic/basic aqueous solutions (pH 2–13) and common organic solvents (room temperature, 3 days).

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feature is the interconnecting regions between the wider and narrower channels are surrounded by the organic part, forming pocket-like cavities for docking substrates. From the Connolly surface representation (commonly used for visualizing protein surfaces),^[20,21] it is clear there exist three-fold helicoidal channels with pocket-like terminals propagating along the *c* direction of the titled crystalline material (Figure 1 d).

As expected, Zn(imPim) exhibited exceptional thermal, hydrothermal, and chemical stabilities. In particular, the thermal stability of up to $680 \,^{\circ}$ C under N₂ atmosphere (Figure 2a, up to ca. 750 $^{\circ}$ C monitored by in situ PXRD measurements; Supporting Information, Figures S6–S8) sets a new record for MOF materials,^[32,33] surpass-

ing Zr⁴⁺-based UiO-66^[41] and imidazolatebased ZIF-8 (MAF-4),^[26] which are wellknown for their remarkable stabilities, let alone the iconic MOF-5^[42] and HKUST-1.^[43] The maintained crystallinity, indicated by unaltered PXRD patterns (Figure 2b), after immersing the bulk samples in boiling water (9 days), acidic/basic solutions or various organic solvents also suggested Zn(imPim) might be suitable for capturing CO₂ from flue gas, an industrial environment typically under high temperature and containing moisture and acid gases.^[6,7]

In the adsorption experiments (Supporting Information, Figure S9), Zn(imPim) showed a typical type-I isotherm for CO₂ at room temperature, exhibiting a steep uptake increase below 150 mbar. This is similar to the situation for a few MOFs with collective binding sites, for example, Zn₂(Atz)₂(ox),^[16] NOTT-300^[17] and UTSA-16,^[18] which prompted us to study the direct observation of CO2 loaded in Zn-(imPim). A simple apparatus was set up to demonstrate the carbon dioxide capture can be achieved at ambient environment (Figure 3a). After exposing the activated Zn(imPim) in CO_2 gas for 5 days, the crystal structure of the adsorbed phase can be determined through SCXRD analyses, showing 18 CO2 molecules in each unit cell (Figure 3b). Further unrestrained refinement revealed the site occupancy of CO₂ molecules to be 0.6 (Supporting Information, Figure S10a), corresponding to a formula of $Zn(imPim) \cdot 0.6 CO_2$ (that is, $10.8 CO_2$ per unit cell). Note that no constraint was imposed on the geometries or thermal parameters to minimize the influence of thermal motion and disorder, and the CO₂ guests showed no positional or orientational disorder.^[24] In comparison, the direct observation of CO2 was managed within a sealed capillary backfilled with 850 mbar CO₂ for SCXRD analysis in the case of $Zn_2(Atz)_2(ox)$,^[16] while for NOTT-300^[17] and UTSA-16,^[18] the visualization of guest molecules was implemented with the aid of neutron scattering techniques. $^{\left[25\right] }$

Unlike the situation in $Zn_2(Atz)_2(ox)$,^[16] in which two observed CO₂ binding sites interfere with each other in a complicated manner, the CO₂ binding pockets within Zn(imPim) have only one crystallographically independent position. It can be seen that within one pocket (Figure 3 c), it is the cooperation of a number of weak C–H···O and π – π interactions that is responsible for fixing a single CO₂ molecule, rather than the exposed imidazolyl-N Lewis base sites (N···CO₂ separation ca. 4.2–5.7 Å). The reduced density gradient analysis,^[44] a powerful tool for identifying intricate noncovalent interactions among interfaces in proteins and



Figure 3. Periodic CO₂ binding pockets of Zn(imPim). a) A simple apparatus for capturing CO₂ at room temperature and ambient pressure, giving b) the single-crystal structure of Zn(imPim)·0.6CO₂, in which c) a binding pocket perfectly isolate an individual CO₂ guest shown in space-filling mode (Zn cyan, N blue, C gray, O red; π - π interactions, orange dashed lines; C-H···O interactions, green dashed lines; for details see the Supporting Information, Figure S10b and Table S5). d) Reduced density gradient isosurfaces (isovalue = 0.5 a.u.) around a trapped CO₂ molecule within the pocket. The color scale (in a.u.) indicates a range of interaction strength from strong attraction (blue), close to van der Waals radii (green) to strong repulsion (red). e) Side view of the Connolly surface integrated with the gloved CO₂ molecules, highlighting adsorbent–adsorbate shape complementarity.

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Figure 4. Carbon dioxide capture and separation performances of Zn(imPim). a) Adsorption and desorption isotherms for N₂ (298 K) and CO₂ (195, 273, and 298 K). b) Isosteric adsorption enthalpy ($-Q_{st}$), compared with GCMC simulated plot, and change of entropy (ΔS) calculated from CO₂ sorption isotherms (273–303 K). c) Five cycles (running from 0–100 kPa for each cycle) of CO₂ adsorption and desorption performed at 298 K. d) CO₂/N₂ (15:85, v/v) adsorption selectivity at 298 K predicted by IAST. e) Column breakthrough experiment results for a 15:85 CO₂/N₂ (v/v) mixture gas flow (2 mLmin⁻¹, 500 mg sample) performed at 298 K. f) Five cycles (running for 2000 s for each cycle) of breakthrough experiments by using a faster gas flow (10 mLmin⁻¹) and with He-gas-purging reactivated samples (1 g) performed at 298 K.

solids, indicated the weak interactions between the binding pockets and the gloved CO_2 are neither attractive nor repulsive (Figure 3d). That is to say, pocket-substrate shape complementarity^[20,21] is mainly responsible for the efficient CO_2 capture of Zn(imPim), as confirmed by the Connolly surface analysis (Figure 3e). In contrast to previously reported pocket-like cavities in MOFs,^[17,45,46] which were not fully encompassing ones, the binding pockets in Zn(imPim) can fully accommodate CO_2 molecules without the assist of open metal sites or polarizing organic groups.

From the isotherm for CO_2 at 298 K (Figure 4a), it can be calculated the pressure of loading 10.8 CO₂ into Zn(imPim) is about 145.2 mbar, which is close to the low partial pressure (0.15 bar) of CO_2 in post-combustion flue gas.^[6] The bulk samples prepared from scale-up synthesis were used for a comprehensive evaluation on the CO₂ uptake capacity, CO₂/ N_2 (15:85, v/v) selectivity, energy penalty for regeneration, stability, recyclability, and gas diffusion through adsorbent bed.^[7] The gravimetric and volumetric capacities for CO₂ of Zn(imPim) (3.54 mmol g^{-1} or 5.18 mmol cm⁻³) exceed those of SIFSIX-3-Zn $(2.51 \text{ mmol g}^{-1} \text{ or } 4.07 \text{ mmol cm}^{-3})$,^[12] SIFSIX-3-Cu $(2.58 \text{ mmol g}^{-1} \text{ or } 4.13 \text{ mmol cm}^{-3})^{[13]}$ and NbOFFIVE-1-Ni $(2.2 \text{ mmol g}^{-1} \text{ or } 3.88 \text{ mmol cm}^{-3})$,^[14] the most promising MOF candidates for post-combustion CO2 capture currently.^[7] Among the MOF adsorbents with collective binding sites, the CO₂ uptake of Zn(imPim) is lower than that of $Zn_2(Atz)_2(ox) = (3.67 \text{ mmol } g^{-1})$,^[16] NOTT-300 $(6 \text{ mmol } g^{-1})^{[17]}$ and UTSA-16 (4.3 mmol $g^{-1})^{[18]}$ at 1 bar, but the uptake at 0.15 bar for Zn(imPim) (2.445 mmolg⁻¹) is higher than that of these three (2.146, 1.7 and 2.37 mmol g^{-1} , respectively). Moreover, the uptake capacity of Zn(imPim) remains constant after five uptake-regeneration cycles (Figure 4c).

Another popular type of MOF adsorbents for carbon capture is the ones with open metal sites.^[8-11] Although the original Mg-MOF-74 set the record for CO₂ uptake capacity $(8.98 \text{ mmol g}^{-1})$,^[8] the uptake for the famous mmen-Mg₂-(dobpdc) was not that high $(3.86 \text{ mmol g}^{-1})$, and it also suffered from high energy cost for regeneration (71 kJ mol⁻¹).^[10] In comparison, Zn(imPim) exhibits a much lower zero-loading $-Q_{st}$ of ca. 35 kJ mol⁻¹ (Figure 4b; Supporting Information, Figures S11, S12), which is close to $Zn_2(Atz)_2(ox)$ (40.8 kJ mol⁻¹),^[16] NOTT-300 that of (27 kJ mol^{-1}) ,^[17] UTSA-16 $(34.6 \text{ kJ mol}^{-1})$,^[18] and lower than SIFSIX-3-Zn (45 kJ mol^{-1}) ,^[12] that of SIFSIX-3-Cu (54 kJ mol⁻¹)^[13] and NbOFFIVE-1-Ni (54 kJ mol⁻¹).^[14] Interestingly, the steady - $Q_{\rm st}$ values and declining ΔS values indicate the degree of disorder of the adsorbent-adsorbate system tends to decrease upon loading.

The predicted CO_2/N_2 (15:85, v/v) selectivity (ca. 106, Figure 4d; Supporting Information, Figure S13) is not as extremely high as those with molecular sieving effect, for example, NbOFFIVE-1-Ni^[14] and Qc-5-Cu-sql- β (40000),^[15] but adequate for efficient post-combustion CO_2 capture. Breakthrough experiments of the gas mixture were performed by utilizing a packed bed adsorber filled with the activated bulk samples of Zn(imPim). It is showed that CO_2 can be retained for about an hour, allowing N₂ to break out

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first (Figure 4e). The recyclability was demonstrated to be excellent at a faster gas flow for five cycles (Figure 4 f; Supporting Information, Figures S14, S15). The simple reactivation method (He gas purging, without heating or vacuuming) here is also used for a most recently reported MOF, dptz-CuTiF₆,^[47] showing excellent carbon capture performance. Preliminary results of H₂O vapor sorption and SCXRD analysis after exposing activated Zn(imPim) under a wet CO₂ environment suggested its carbon dioxide capture ability was not influenced significantly at such condition (Supporting Information, Figures S19–S21 and Tables S6, S7).

A comprehensive comparison of Zn(imPim) with the best-performing MOF adsorbents^[7,48,49] is provided in the Supporting Information Table S8, showcasing the optimal carbon dioxide capture performance of Zn(imPim). This finding can be further rationalized by computational studies (Supporting Information, Computational Details). Grand canonical Monte Carlo (GCMC) simulations were performed to study the performance of $Zn(imPim) \cdot x \operatorname{CO}_2$ under different pressures. As shown in Figure 5 a, the simulated isotherm can



Figure 5. Computational evaluation of $Zn(imPim) \cdot xCO_2$ upon loading. a) Experimental and GCMC simulated CO_2 adsorption isotherms at 298 K. Inset: DFT optimized CO_2 binding pocket (see SCXRD structure in Figure 3 c). b) The CO_2 density profiles of at 1, 10, and 100 kPa from GCMC simulation.

almost reproduce the experimental plot (Supporting Information, Figure S16). Through comparing the density profiles at varied pressures (Figure 5b; Supporting Information, Figures S17, S18), it can be seen that the loaded CO_2 molecules tend to concentrate on a single independent location upon increasing pressure. Even at a low pressure (1 kPa), the statistical distribution of adsorption regions can match well with the CO_2 position determined by SCXRD (Figure 3b), suggesting the performance of the binding pockets would not vary significantly during the uptake process.

Density functional theory (DFT) calculation gave a CO_2 binding pocket geometry almost identical to that of SCXRD results (Figure 5a inset; Supporting Information, Table S5).

The overall binding energy (ΔE_{total}) for Zn(imPim)·CO₂ is calculated to be 71.69 kJ mol⁻¹, which can be divided into pocket–CO₂ interaction ($\Delta E_{\text{host-guest}} = 70.80 \text{ kJ mol}^{-1}$) and CO₂–CO₂ interaction ($\Delta E_{\text{guest-guest}} = 1.04 \text{ kJ mol}^{-1}$). The fact that the host–guest interaction contributes the vast majority of the binding energy has confirmed the decisive role of binding pockets in the optimal carbon dioxide capture.

Taken together, the advantages of the unusual (**usf** net) MOF, Zn(imPim), equipped with shape-complemented binding pockets, lie in the combination of rapid large-scale synthesis, record thermal (up to $680 \,^{\circ}$ C) and chemical stabilities, high CO₂ uptake capacity ($3.54 \,\mathrm{mmol}\,\mathrm{g}^{-1}$ or $5.18 \,\mathrm{mmol}\,\mathrm{cm}^{-3}$), high CO₂/N₂ ($15:85, \,\mathrm{v/v}$) selectivity (106), low energy cost for regeneration ($35 \,\mathrm{kJ}\,\mathrm{mol}^{-1}$), and convenient reactivation (inert gas purging), satisfying all the cuttingedge demands for carbon dioxide capture from flue gas and outperforming the most competitive MOF candidates nowadays.^[7,47] The outstanding CO₂ capturing performance at room temperature and ambient pressure, as well as at a wet condition, suggests Zn(imPim) may have prospect in direct capture of CO₂ from ambient air,^[50] which will be studied further in future.

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Conflict of interest

The authors declare no conflict of interest.

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Metall-organische Gerüstverbindungen

Z.-S. Wang, M. Li, Y.-L. Peng, Z. Zhang, W. Chen, X.-C. Huang* _____ **IIII**-**IIII**

An Ultrastable Metal Azolate Framework with Binding Pockets for Optimal Carbon Dioxide Capture



Passt perfekt: Die Protein-artige Komplementarität von Bindungstasche und Substrat in einem ultrastabilen MOF (siehe Bild) löst das Problem der Balance zwischen hoher Aufnahmekapazität/selektivität und niedrigem Energieaufwand für die CO₂-Absorption aus Brenngas.

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