From Reticular Chemistry Design to Density Functional Theory Modeling for New Zeolitic Imidazolate Framework Topologies: Mechanical Stability, Electronic Structure, and CO₂ Selectivity

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Supporting Information

ABSTRACT: Adopting the knowledge and resource of reticular chemistry, we introduce a series of new zeolitic imidazolate framework (ZIF) structures within three topological categories, pth, pts, and ast, constructed by the square-planar and tetrahedral building blocks. Systematic metalation is considered with various cations (i.e., Ni²⁺, Cu²⁺, Mn²⁺, Co²⁺, Zn²⁺). Utilizing the advantage of density functional theory (DFT) calculations, we observe that the imidazole linking units suffer severe deformation in the ast and pts networks, as pointed out by the negative phonon modes. The mechanical stability is then verified by analyzing the elastic tensors (Cij), and we conclude four structures to acquire mechanical stability: pth-1 (NiMn), pth-2 (NiCo), pth-3 (NiZn), and pth-6 (CuZn). Electronic structure analysis suggests the first two structures to exhibit strong magnetism, whereas the latter are weakly or even nonpolarized, which establishes good agreement with the ligand-field theory prediction. The band gaps of those structures fall in the range of 0.74 to 1.78 eV, as estimated by conventional DFT calculations. Finally, we investigate the CO₂ selectivity over N₂ within pth-1 and pth-3 by conducting grand canonical Monte Carlo simulations for gas adsorption. For the pth-1 (NiMn) and pth-3 (NiZn) cases, the load of CO₂ dominantly exceeds the uptake of N₂ at the pressure up to 1 bar, indicating those structure to be promising in CO₂ capture and selectivity.

I. INTRODUCTIONS

Zeolitic imidazolate frameworks (ZIFs) are a subclass of metal–organic frameworks (MOFs), hybrid materials composed of metal organic metal secondary building units (SBUs), and organic linkers based on the carboxylate links. They are fundamentally composed of the tetrahedral building units of Zn²⁺, Cu²⁺, or Co²⁺ and imidazole-based linkers.¹ Not only are ZIFs regarded as a highly porous materials whose organic and inorganic nodes can be designed, modified, and functionalized to form targeted structures for certain applications, but also they have been found to be more chemically and thermally stable than MOFs because of covalent bonding owing to the linkage of tetrahedral metal ions and heteroatom (N)-based imidazole ring in the 3D network.² Gas storage and selective separation of CO₂ from a mixture of gas (biogas, flue gas stream) is an emerging application³ exploiting the capabilities of ZIFs such as high porosity, strong affinity of framework with adsorbent, and, the most pivotal factor, the suitable pore size and shape affording gas molecules to tightly interact with adsorbate. In addition, when considering the gas separation under high humidity and regeneration process, ZIFs can be reckoned as a potential candidate compared with MOFs, zeolites, and activated carbon due to their high stability under harsh working conditions (boiling water, acidic medium, high temperature) as well as low energy for the recyclability (the regeneration process requires no heating power).⁴

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imidazole derivatives are set to react with bivalent metal sites.4 To overcome this circumstance, the geometrical structure of linking units needs to be varied or modified to produce various kinds of points of extension.5 This point is directly related to the phenomenon of conceptual reticular chemistry.

Reticular chemistry has evolved during the last few decades and has become an exceptionally intellectual methodology for materials science research, especially in the field of porous structures, that is, MOFs, ZIFs, and covalent organic frameworks (COFs).6 In this context, we utilize the knowledge of reticular chemistry to derive three different kinds of ZIF topology, which include ast, pth, and pts. Those topologies are discussed for the first time in the ZIF chemistry, when we use four-coordination point of extension (4-c) generated from the Cu(Im)₄²⁺ square-planar complex7 (Scheme 1) to react with 4-

c of Zn²⁺ tetrahedral SBUs. The postsynthetic metalation (PSM) is used to exchange the Cu open sites with Ni, which is due to the challenge of Ni-imidazolate-based square-planar complex, and Zn sites with Co or Mn to form 18 new ZIF structures in total. It is noted that PSM is applied to lead experimental research in the near future to produce the multivariate metal-based ZIFs. The main purpose of this study is to employ quantum-mechanical computational modeling techniques to classify the most realistic structures among those 18 ZIFs. Subsequently, the properties of designed materials based on multivariate metal clusters are to be systematically investigated with the following highlighted aspects: geometrical and mechanical stability and full understanding of the electronic configuration by first-principles modeling, leading to our obtaining four stable structures of the pth network, which eventually are found to be selective for CO₂ uptake.

II. STRUCTURE DESIGN AND COMPUTATIONAL METHOD

II.1. Structural Design. It should be noted that the modification of the linking units plays a crucial role in the design and synthesis of new topological structure in the ZIF chemistry. Indeed, ZIFs mimic the nature of zeolite-type topology. To our knowledge, there are around 20 topologies found for ZIF structures compared with almost 200 networks of zeolites.5,11 Mixed linker systems, or abundantly bulk functionalities of imidazole-based linkers, were successfully introduced to achieve new kinds of structures in ZIFs.3–5 To get a full picture of using the modified linking units for ZIF construction, we use the precursor linker that contains four coordinations, which is the square-planar complex of Cu(Im)₄²⁺. Such a linking unit was reportedly utilized to form two kinds of new ZIF topology, which are ntn and thl.1 By adopting the principle of topological deconstruction governed by the Reticular Chemistry Structure Resources (RCSR) database, when connecting one kind of edge and two kinds of vertices whose coordination numbers are 4, we can find 15 possibilities of topology (see Table 1). We then consider the geometry of the precursor, square-planar Cu(Im)₄²⁺, and the tetrahedral SBUs of Zn²⁺, leading to our finally getting the well-known pth and pts topologies that are constructed by the combination of square and tetrahedral nodes with the 1:1 ratio. We also change the ratio of square/tetrahedral SBUs to 1:2 to build up the ast network (Figure 1).

With the information on those topologies in hand, we further model the crystal structures of ZIF-ast, ZIF-pth, and

<table>
<thead>
<tr>
<th>Table 1. Collecting of the Statistic Information for the Topological Formation12</th>
</tr>
</thead>
<tbody>
<tr>
<td>topology</td>
</tr>
<tr>
<td>---------------</td>
</tr>
<tr>
<td>css</td>
</tr>
<tr>
<td>dia-b</td>
</tr>
<tr>
<td>icd</td>
</tr>
<tr>
<td>ics-b</td>
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<tr>
<td>pts</td>
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</tr>
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<td>rhr-b</td>
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<tr>
<td>sod-b</td>
</tr>
<tr>
<td>ssa</td>
</tr>
<tr>
<td>sbb</td>
</tr>
<tr>
<td>ssc</td>
</tr>
</tbody>
</table>

Figure 1. (a) Strategy of topological deconstruction: The combination of mixed SBUs, square-planar Cu(Im)₄²⁺, and tetrahedral ZnN₄ to form three possibilities of new ZIF networks. (b) Augmented topological structures of ast, pth, and pts. (c) Crystal structures of corresponding ZIFs are presented to show various kinds of pores.
ZIF-pts on the basis of mixed metal cations (Table 2). After evaluating the possible nets including pts, pth, and ast, the
simplified network, which contains the node of vertices and edges based on the RCSR database, was constructed with Materials Studio. The square-planar complex of Cu-imidazolate (Cu(Im)_4^{2+}) was built in the GaussView graphical interface, which can identify the suitable resonance geometries. The plausible nets were initially comprised by connecting Cu-imidazolate, acting as a 4+ point of extension to the Zn^{2+} SBUs (points of extension or vertices). Those structures are subsequently optimized using the geometrical optimization functionality with the Universal Force Field (UFF) in the Materials Studio software. The ZIF-pts structure crystallized in the tetragonal lattice system with the maximum space group of the pts topology is found to be P4_4_2_2, leading to constraint of the geometrical vibration of Cu(Im)_4^{2+} linking parts in a planar plane. The linking of Cu^{2+} square SBUs to Zn^{2+} tetrahedral SBUs provides a square channel whose pore size is ~11.5 Å (shown in Figure 1c). In the case of pth topology, the hexagonal lattice is found with the space group of P6_3,22 which does not affect the constraint of the imidazole link. Thus the imidazole linking units are twisted by a certain angle to form stable geometry, resulting in the distortion of square-planar units linked to the tetrahedral building block of Zn^{2+} generating four- and eight-membered rings (Figure 1), in which the channels through four rings possess a square window of 7 Å and the pore constructed by the combination of both of four- and eight-membered rings is found to possess a 7.5 Å diameter. The largest diameter of the cage is attributed to the ZIF-ast structure is 12 Å, covered by 6 of the four-membered rings and 12 of the six-membered rings (Figure 1).

Considering the similarity in binding coordination of metal cations, we explore the possibility of replacing the first metal cation site (Cu^{2+}) of the square-planar SBUs by Ni^{2+} and the cations, we explore the possibility of replacing the

Table 2. Crystallographic Data of Initially Constructed ZIF-ast, ZIF-pth, and ZIF-pts

<table>
<thead>
<tr>
<th>topology</th>
<th>lattice</th>
<th>space group</th>
<th>unit-cell parameter (Å)</th>
<th>pore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ast</td>
<td>tetragonal</td>
<td>P4_4_2_2</td>
<td>a = b = 19.19; c = 19.02</td>
<td>12.0</td>
</tr>
<tr>
<td>pth</td>
<td>hexagonal</td>
<td>P6_3.22</td>
<td>a = b = 9.25; c = 21.74</td>
<td>7.5</td>
</tr>
<tr>
<td>pts</td>
<td>tetragonal</td>
<td>P4_4_2_2</td>
<td>a = b = 10.08; c = 13.80</td>
<td>11.5</td>
</tr>
</tbody>
</table>

and are found to spread in a wide range from 110 to 160°. For those structures with the pts topology, there are 2 M^1 and 2 M^2 in a primary unit cell containing 68 atoms, with the M-Im-M angles initially optimized in the range of (95°; 155°). In the next stage, we carry out first-principles calculations to examine the structural and mechanical stability of the so-designed ZIFs.

II.2. Computational Detail for Electronic Structure Calculations. First-principles density functional theory (DFT) calculations for the periodic ZIF structures are performed using the Vienna Ab Initio Simulation Package (VASP). The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional is employed with the projector-augmented wave (PAW) method in constructing electronic wave functions. For relatively large periodic systems, we choose the standard cutoff energy of 400 eV, which is sufficient for plane-wave expansion of the participant atoms. Upon the consideration of hexagonal unit-cell vectors, we choose the k-point mesh of (5 × 5 × 2) for the pth unit cells. For the pts and ast structures, we choose the k-point meshes of (5 × 5 × 4) and (3 × 3 × 3), respectively. Self-consistency is set to achieve an energy criterion of 10^-5 eV, which is good enough for large systems with more than 100 atoms. Spin-polarization is activated to validate the spin states of metal cation sites. In each structural optimization, the unit cell and atoms are simultaneously relaxed by adopting the conjugate-gradient algorithm with an energy convergence criterion of 10^-5 eV/Å. For the treatment of long-range van der Waals interactions, we use the semiempirical Grimme correction (D3) in our calculations.

III. QUALIFICATION TESTS FOR NEW ZIF STRUCTURES

III.1. Structural Optimizations. Various optimizations with different magnetic initializations are performed to figure out all of the possibilities of different spin states and make judgment of the energetic favorability based on total energy intuition. For each compound, at least three different calculation trials are executed, in which we consider the alignment of ferromagnetic (M^1 and M^2 having similar spin alignment), nonmagnetic, and ferrimagnetic (M^1 and M^2 having partially opposite spin alignment).
III.1.1. pth Topology. We first examine the initially built structure given by empirical optimization. For the case of CuZn (pth-6), only one spin state is found with a total magnetic moment of 3 \( \mu_B \)/cell. By analyzing the partial magnetic contribution, we find that the three Zn\(^{2+}\) cations do not prefer to exhibit spin polarization. In other words, the 3d orbitals of Zn do not possess unpaired electrons. Cu, on the contrary, is found to contribute a dominant magnetic moment of 0.55 \( \mu_B \) whereas Im\(^-\) also exhibits a small positive magnetic contribution.

For the case of CuMn (pth-4), two magnetic states are examined: (Cu, Mn) to have analogous spin direction (ferromagnetic, FM) and opposite spin direction (antiferromagnetic, AFM). Adopting the same magnetic behavior as seen in pth-6, Cu would prefer to establish one unpaired electron. In general, Mn\(^{2+}\) is a strongly polarized cation. In particular, we observe that in this case when M\(^{2+}\) is surrounded by four Im\(^-\) anions, each Mn\(^{2+}\) preferably establishes a very strong magnetic moment of 4.2 \( \mu_B \). More interestingly, Cu\(^{2+}\) and Mn\(^{2+}\) are found to align with opposite spin directions. In total, a magnetic moment of 12 \( \mu_B \) is found. For the last pth candidate involving Cu\(^{2+}\) as the M\(^1\) site (pth-S), a total magnetic moment of 6 \( \mu_B \) is found, in which we again conceive a contradicting magnetic alignment of Cu\(^{2+}\) and Co\(^{2+}\). It is not surprising that each of the Cu\(^{2+}\) cations contributes a small resisting moment of 0.5 \( \mu_B \), whereas each Co\(^{2+}\) cation exhibits 2.4 \( \mu_B \). Overall, as we attempt to optimize various magnetic states of each pth structure involving Cu\(^{2+}\), all variations arrive at a particular spin alignment, in which Co\(^{2+}\) contributes a small magnetic moment of 0.5 \( \mu_B \) and has a tendency to resist the magnetic alignment of the M\(^2\) sites (if it does exist).

Subsequently, we move on to the Ni\(^{2+}\) pth derivatives (pth-1, pth-2, pth-3). Within the pth category, pth-1 (involving Ni\(^{2+}\) and Mn\(^{2+}\)) is the only structure that exhibits two different magnetic behaviors. When considering magnetic moments with similar direction for both metal cations (FM), we obtain a magnetism of 15 \( \mu_B \). In this case, Mn\(^{2+}\) is reported to have four unpaired electrons (4.3 \( \mu_B \)/metal site), whereas Ni\(^{2+}\) contributes a less significant amount. For the AFM states, Mn\(^{2+}\) again exhibits four unpaired electrons, whereas each Ni\(^{2+}\) cation gives a resisting moment of \(-1.4\) \( \mu_B \). Actually, the total energy difference of 1.28 eV clearly indicates the favorability of the FM state. The pth-2 structure with the participation of Ni\(^{2+}\) and Co\(^{2+}\) has only one magnetic state of 9 \( \mu_B \) in which each Co\(^{2+}\) cation contributes 2.4 \( \mu_B \). The pth-3 structure does not exhibit a magnetic moment due to almost fully occupied 3d subshells. In fact, this structure is the only nonmagnetic ZIF in the pth topology.

III.1.2. pts Topology. The first structure pts-1 exhibits two magnetic states, 10 \( \mu_B \) (high spin) and 4.59 \( \mu_B \) (low spin), with the high-spin structure being more energetically stable by only 0.02 eV/unit cell, which indicates the tendency to switch between the two spin states. In the high-spin state, Ni\(^{2+}\) and Mn\(^{2+}\) align ferromagnetically with magnetic moments of 1.2 \( \mu_B \) and 3.3 \( \mu_B \) respectively. In the low-spin state (AFM), the magnetic moments of the two metal cation sites are very similar in magnitude compared with those given in the FM state, but their directions are opposite. A similar behavior is seen in pts-2, where the energy gap between FM (4 \( \mu_B \)/cell) and AFM (3.72 \( \mu_B \)) states is 0.03 eV. In this particular case, pts-2 prefers to align antiferromagnetically, in which a Ni\(^{2+}\) site contributes 1.36 \( \mu_B \) and a Co\(^{2+}\) site contributes \(-2.58\) \( \mu_B \). For pts-3, we observe only one magnetic state (3.95\$/cell).

Compared with the previous nonmagnetic pth-3 structure, it is seen in this case that by adopting a different topology the electronic configurations of Ni\(^{2+}\) and Zn\(^{2+}\) yield different numbers of unpaired electrons.

The pts-4 and pts-6 structures have no more than one stable ground state. For pts-4, a magnetic moment of 7.20 \( \mu_B \)/cell is observed, whereas pts-6 exhibits a weak magnetism of 1.04 \( \mu_B \)/cell. In pts-4, Mn\(^{2+}\) is strongly polarized (3.4 \( \mu_B \)) and dominates the magnetic contribution, whereas Cu\(^{2+}\) gives only an insignificant resisting (negative) magnetic moment. Two spin states are observed for pts-5 with the participation of Cu\(^{2+}\) and Co\(^{2+}\), that is, 4.00 \( \mu_B \)/cell (FM, stable) and 2.54 \( \mu_B \)/cell (AFM, less stable by 0.05 eV). In both cases, each Co\(^{2+}\) cation exhibits a magnetic moment of 1.3 \( \mu_B \) whereas Cu\(^{2+}\) contributes a small amount of \(-0.3\) \( \mu_B \) (this amount is positive in the FM state or negative in the AFM state).

III.1.3. ast Topology. In the ast structures, the number of M\(^2\) sites (eight cations) is dominant and is four times the number of M\(^1\) sites (two cations). Therefore, we find large magnetic moments of 40 \( \mu_B \)/cell and 24 \( \mu_B \)/cell for the case of ast-1 and ast-2, in which Ni\(^{2+}\) is almost nonpolarized. Mn\(^{2+}\) (from ast-1) and Co\(^{2+}\) (from ast-2) contribute significant magnetic moments of 4.3 \( \mu_B \) and 2.4 \( \mu_B \)/cell, respectively. For ast-3, no spin polarization is found, as all electrons pair up in the 3d shells of Ni\(^{2+}\) and Zn\(^{2+}\).

With the involvement of Cu\(^{2+}\), the resultant magnetic moments of ast-4, ast-5, and ast-6 noticeably decrease in comparison with the previous corresponding cases. Among those three cases, ast-4 exhibits the largest magnetism of 38 \( \mu_B \)/cell, in which Mn\(^{2+}\) contributes 4.2 \( \mu_B \) and Cu\(^{2+}\) contributes an opposite magnetic moment of \(-0.39\) \( \mu_B \). The ast-5 possesses a strong magnetic moment of 2S \( \mu_B \)/cell, whereas ast-6 possesses a weak magnetic moment of 2 \( \mu_B \)/cell, which mainly comes from the weak polarization of Cu\(^{2+}\). For those particular cases, we find only one stable spin state for each of the (M\(^2\), M\(^1\)) cationic pairs.

III.2. Stability Verification Based on Formation Energy, Phonon Vibration, and Elastic Tensor Qualification Tests. III.2.1. Formation Energy. The first stability verification step is simply carried out by computing formation energies for all resultant ZIF structures. Let us consider a net reaction for the formation of ZIF

\[ \text{xM}^0\text{Cl}_2 + \text{yM}^0\text{Cl}_3 + (2x + 2y)\text{Im} \rightarrow \text{ZIF} + (2x + 2y)\text{HCl} \]  

In the above net chemical reaction of imidazole with M\(^0\)Cl\(_2\) and M\(^0\)Cl\(_3\) (chloride salts of M\(^1\) and M\(^2\), respectively), a new ZIF structure and HCl are formed. Therefore, the formation energy per unit cell is calculated as

\[ E_t = [E_{\text{ZIF}} + 2(x + y)E_{\text{HCl}}] - [xE_{(M\text{Cl}_2)} + yE_{(M\text{Cl}_3)} + 2(x + y)E_{\text{Im}}] \]  

where \( E_{\text{ZIF}} \), \( E_{\text{HCl}} \), \( E_{(M\text{Cl}_2)} \), \( E_{(M\text{Cl}_3)} \), and \( E_{\text{Im}} \) are the total energies of the ZIF structure, isolated HCl, M\(^0\)Cl\(_2\), M\(^0\)Cl\(_3\), and imidazole, respectively. A negative value of formation energy is indicative of energetic stability. All pth structures have negative formation energies (from \(-4.55 \text{ to } -0.85 \text{ eV}\)), which confirms the energetic stability of the suggested pth ZIF structures. For the pts structures, we obtain positive formation energies, an indication of thermodynamic instability (from \(5.88 \text{ to } 9.12 \text{ eV}\)). For the ast structures, ast-2, ast-3, and ast-5 have negative
formation energies (−4.47, −0.17, and −3.15 eV, respectively), whereas the other three structures have positive formation energies (unstable).

It is obvious that each topology has a unique number of metal cations and Im⁻ anions in the unit cell; therefore, to make a comparison among structures, it is more beneficial to adopt the average stabilization energy per one imidazole molecule

$$E_{\text{stabilize}} = E_i / (2x + 2y) \quad (3)$$

A plot of stabilization energy is presented in Figure 2 for comparison purposes. It is clearly seen that the pth structures of the structure. Therefore, all six pth structures are regarded as stable according to the second test. As we continue to observe the phonon DOS of the pts structures (presented in Figure 4), two negative wavenumbers are clearly found, which are associated with the abnormal “shaking vibration” of C–H linkages and bond stretching of M’-imidazole because Im⁻ suffers severe bending within the pts network.

For all pth structures, we conceive that all vibrational wavenumbers are positive, which proves that all metal cations and Im⁻ anions settle in a nice minimum. The small negative part of each spectrum corresponds to the three translational modes, which arises from calculation uncertainty.
the following phonon calculations, we can only extract phonon data for ast-2, ast-3, and ast-6. For the other ast configurations, self-consistency in total energy calculations cannot be obtained when ionic positions are perturbed, which accordingly reveals the instability of those structures. As shown in Figure 6, we find that two negative vibrational modes (around $-220$ and $-20$ cm$^{-1}$) consistently appear in the phonon DOS spectra. Unsurprisingly, the motions of those two negative modes are associated with the internal vibrations of imidazole due to suffering from severe bending within the framework.

**III.2.3. Elastic Tensor Analysis.** From the phonon test, all pts and ast structures are disqualified. In the final test, we perform elastic tensor calculations to examine the mechanical stability of the pth network. To estimate the elastic tensors using the stress–strain relationship, structure perturbation with two degrees of freedom is performed. In total, six unit-cell deformations are executed on the unit-cell vectors. In addition, the contribution of ionic relaxation is also taken into account by perturbing the ionic position (six distortions for each ion in the 3D space, as previously done in the phonon calculations). With a hexagonal unit cell, each pth structure can be concluded to be stable if all four of the following conditions are satisfied

\[
C_{11} > |C_{12}|
\]

(4)

\[
2C_{13}^2 < C_{33}(C_{11} + C_{12})
\]

(5)

\[
C_{44} > 0
\]

(6)

\[
C_{66} = (C_{11} - C_{12})/2
\]

(7)

**Table 3. Calculated Elastic Modulus $C_{ij}$ (GPa) for All pth Structures**

<table>
<thead>
<tr>
<th></th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{13}$</th>
<th>$C_{33}$</th>
<th>$C_{44}$</th>
<th>$C_{66}$</th>
<th>$K$</th>
<th>$E$</th>
<th>$G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pth-1</td>
<td>32.2</td>
<td>19.1</td>
<td>29.6</td>
<td>62.9</td>
<td>11.1</td>
<td>6.5</td>
<td>31.5</td>
<td>24.7</td>
<td>9.0</td>
</tr>
<tr>
<td>pth-2</td>
<td>42.6</td>
<td>29.2</td>
<td>38.0</td>
<td>71.5</td>
<td>13.4</td>
<td>6.7</td>
<td>40.8</td>
<td>28.1</td>
<td>10.1</td>
</tr>
<tr>
<td>pth-3</td>
<td>39.9</td>
<td>26.3</td>
<td>34.4</td>
<td>65.6</td>
<td>11.6</td>
<td>6.8</td>
<td>37.3</td>
<td>25.9</td>
<td>9.4</td>
</tr>
<tr>
<td>pth-4</td>
<td>$-109.5$</td>
<td>$-120.3$</td>
<td>$-86.4$</td>
<td>$-33.7$</td>
<td>$-15.8$</td>
<td>5.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pth-5</td>
<td>3.9</td>
<td>$-10.6$</td>
<td>16.2</td>
<td>67.4</td>
<td>14.0</td>
<td>7.3</td>
<td>35.4</td>
<td>20.1</td>
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</tr>
<tr>
<td>pth-6</td>
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<td>20.1</td>
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<td>4.7</td>
<td>7.7</td>
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</table>
Condition 6 is a necessary condition to describe a hexagonal unit cell. According to our test, condition 7 is satisfied for all pth cases. However, because of largely negative $C_{11}$, pth-4 is disqualified because of the failure of inequality (eq 4). The elastic constants of pth-5 do not satisfy both inequalities (eqs 4 and 5); consequently, pth-5 is disqualified. The $C_{11}$, $C_{12}$, $C_{13}$, $C_{33}$, $C_{44}$, and $C_{66}$ elastic tensors for each structure are reported in Table 3.

From the elastic tensors $C_{ij}$ we are able to derive three important physical quantities using the Voigt–Reuss–Hill approximation: bulk (K), Young’s (E), and shear (G) moduli, which depict the ability to resist compression, linear stress, and shear of a particular material. Such moduli for the four stable pth structures are given in Table 4. The good stability is expressed by $K \sim 31–40$ GPa, equivalent to the bulk modulus of glass, which describes the capability to resist against uniform pressure.

### Table 4. Adsorption Energies (eV) for CO$_2$ and N$_2$

<table>
<thead>
<tr>
<th>pth</th>
<th>CO$_2$</th>
<th>N$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M'$</td>
<td>$M''$</td>
</tr>
<tr>
<td>pth-1</td>
<td>0.51</td>
<td>−1.03</td>
</tr>
<tr>
<td>pth-2</td>
<td>−0.27</td>
<td>n/a</td>
</tr>
<tr>
<td>pth-3</td>
<td>−0.01</td>
<td>−2.03</td>
</tr>
<tr>
<td>pth-6</td>
<td>−0.09</td>
<td>−2.41</td>
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</tbody>
</table>

The final test of mechanical stability by executing elasticity analysis finally eliminates pth-4 and pth-5 from our consideration. Therefore, from the initial set of 18 structures categorized in three different topologies (pth, pts, and ast), we conclude that pth-1 (NiMn), pth-2 (NiCo), pth-3 (NiZn), and pth-6 (CuZn) are stable according to phonon and elastic tensor analyses.

### IV. ELECTRONIC STRUCTURES AND GAS ADSORPTION CAPABILITY OF THE STABLE pth STRUCTURES

#### IV.1. Electronic Structure. The electronic structure of each stable structure, in terms of band gap and magnetic alignment, is important, as it is relevant to the excited state and number of unpaired electrons of the metal site if a particular ZIF structure in this study is used for future reaction catalysis. Therefore, we analyze the electronic gap between the highest occupied (HO) and lowest unoccupied (LU) states in conjunction with magnetic alignment of each stable pth structure by examining the partial density of states (PDOS) of $M'$, $M''$, and Im~. For pth-1, we have discussed in the previous section that the meromorphic state is preferred with a total magnetic moment of 15 $\mu_B$/cell. In particular, whereas three Ni$^{2+}$ sites contribute a fairly small magnetic sum (∼0.09 $\mu_B$), three Mn$^{2+}$ sites are highly polarized (4.26 $\mu_B$ for each cation). The total magnetic moment is 15 $\mu_B$/cell. On average, the presence of each tetrahedral Mn$^{2+}$ cation would produce a net magnetic moment of 5 $\mu_B$. Because Im~ anion is an intermediate-field ligand, the splitting energy between the $e_g$ and $t_{2g}$ states is relatively narrow. Hence, we can hypothesize that the five electrons of Mn$^{2+}$ ($d^5$ configuration) spread out to occupy the two $e_g$ and three $t_{2g}$ states in an adequate manner, as illustrated in Figure 7. The DOS of occupation can be seen in Figure 8a. The $\alpha$-spin of Mn$^{2+}$ seems to contribute significantly to constitute the HO state, whereas both $\alpha$- and $\beta$-spin of Ni$^{2+}$ take part in the formation of the HO-1 state. By examining the occupied and unoccupied eigenstates, we find that pth-1 possesses an indirect HO–LU gap of 1.21 eV. The LU state is, however, constituted by the 3d shells of Ni$^{2+}$ and Im~, and the contribution of Mn$^{2+}$ to this virtual state is very insignificant. Such PDOS occupation of electronic states helps to explain the indirect band gap behavior, as previously mentioned.

The pth-2 is another strongly polarized structure with a total magnetic moment of 9 $\mu_B$/cell. In this structure, Ni$^{2+}$ is observed to polarize very weakly. The total magnetic alignment of three Ni$^{2+}$ cations is ∼0.09 $\mu_B$, which is very similar to that found in the case of pth-1. Each Co$^{2+}$ site contributes 2.41 $\mu_B$, which is smaller than the magnetic alignment of Mn$^{2+}$ in pth-1. In this case, the presence of each tetrahedral Co$^{2+}$ cation with $d^7$ electron configuration induces a net magnetic moment of 3 $\mu_B$ which is in good agreement with our prediction based on the crystal-field theory. By examining the PDOS in Figure 8b, we observe that the HO and LU states are formed mainly with the $\beta$-spin electrons from the 3d orbitals of Co$^{2+}$. Literally, an indirect HO–LU gap of pth-2 is observed as 0.96 eV. At this point, for the two strongly polarized structures (pth-1 and pth-2), we observe that the $M''$ site actually plays an important role
in constituting the HO state. The Ni\textsuperscript{2+} site (d\textsuperscript{8}), however, would have two unpaired electrons if it adopts a tetrahedral bonding scheme or no unpaired electrons in the case of square-planar coordination. Actually, the optimized structures of pth-1 and pth-2 show that the square-planar coordination prevails, which is consistent with our initial design. Therefore, Ni\textsuperscript{2+} is nonmagnetic as a consequence.

In the two later cases (pth-3 and pth-6), the scenario in electronic structure is much different; that is, the M\textsuperscript{2} sites do not play a decisive role in the HO−LU gap anymore. In particular, for the nonmagnetic NiZn case (pth-3), both HO and LU states are jointly constituted by Zn\textsuperscript{2+} and Im\textsuperscript{−}, as revealed by the PDOS in Figure 9a. The role of M\textsuperscript{1} (i.e., Ni\textsuperscript{2+}) for the most suitable adsorption site. The binding strength can be verified by analyzing the energetic favorability between CO\textsubscript{2} and N\textsubscript{2} through total energy analysis. To be specific, the binding energy of a particular case will be computed as

$$E_{binding} = E_{ZIF} + E_{gas} - E_{adsorbed-gas}$$ (8)

In the equation above, \(E_{ZIF}\), \(E_{gas}\), and \(E_{adsorbed-gas}\) are the total energies of ZIF, isolated gas molecules (CO\textsubscript{2} or N\textsubscript{2}), and the complex system of a gas molecule encapsulated by ZIF. A positive value of adsorption energy is indicative of stable adsorption. In all adsorption cases, we notice that N\textsubscript{2} can hardly find a stable binding position to the metal sites on the framework. Initially, we place a nitrogen molecule close to either a M\textsuperscript{1} or M\textsuperscript{2} site. At the end of the optimization, N\textsubscript{2} is found to locate in the middle of a pore and establish minimal connection to the surrounding metals. In particular, the binding energies of N\textsubscript{2} to the M\textsuperscript{2} site in pth-3 and pth-6 are −2.41 and −2.03 eV, respectively, which clearly indicates strong repulsion. For pth-2, we even confront a divergent optimization with N\textsubscript{2} adsorption, whereas the M\textsuperscript{2} site in pth-1 is quite less repulsive to N\textsubscript{2} with an adsorption energy of −1.03 eV.

In general, it should be noted that the M\textsuperscript{1} cationic site is less repulsive (in other words, more attractive) to both CO\textsubscript{2} and N\textsubscript{2} adsorptions than the M\textsuperscript{2} site, regardless of the metal identity. It is found for pth-2, pth-3, and pth-6 that N\textsubscript{2} possesses adsorption energies from −0.07 to −0.23 eV. In the case of pth-1, the adsorption energy is positive (0.45 eV), which indicates that N\textsubscript{2} finds a good settlement in the pore.

For CO\textsubscript{2} adsorption, the M\textsuperscript{2} site is more repulsive to the gas molecule than that seen in the N\textsubscript{2} adsorption case. The adsorption energies are found in the range of −1.03 to −2.41 eV. On the contrary, the M\textsuperscript{1} site seems to be more promising in capturing CO\textsubscript{2}. In particular, the M\textsuperscript{1} sites in pth-2, pth-3, and pth-6 possess quite negative adsorption energies from −0.01 to −0.27 eV. For pth-1, we obtain a positive adsorption energy of 0.51 eV, which is stronger than the adsorption of N\textsubscript{2} inside pth-1. We summarize the adsorption energies of CO\textsubscript{2} and N\textsubscript{2} within the four stable pth structures in Table 4.

Overall, in most cases, we observe that the M\textsuperscript{1} site is more attractive to both CO\textsubscript{2} and N\textsubscript{2}. Moreover, CO\textsubscript{2} is shown to be more favorable inside the ZIF structures in most cases (pth-1, pth-3, pth-6), except for the case of pth-2, as we conceive that the N\textsubscript{2} adsorption is slightly more favorable than the CO\textsubscript{2} adsorption. Among the four stable pth structures, pth-1 seems to be very promising in the application of CO\textsubscript{2} capture and selectivity.

To unveil the portrait of CO\textsubscript{2} and N\textsubscript{2} uptakes, we subsequently carry out a grand canonical Monte Carlo (GCMC) simulation for the adsorption of each type of gas in the pores of pth-1 and pth-3. It should be noted that because of the different choice of cationic pairs, pth-3 exhibits a larger volume by 8% in comparison with pth-1 (321 vs 297 Å\textsuperscript{3}). The GCMC simulations using the \(\mu\)VT scheme are executed using the RASPA package,\textsuperscript{30} which has been used extensively to investigate the gas adsorption behavior in MOFs.\textsuperscript{30,31} In the current simulation, we employ the semiempirical force field with pairwise Lennard-Jones potentials developed for MOF applications.\textsuperscript{32} The simulation temperature is fixed at 25 °C, whereas the pressure is varied in the range of [0; 1 bar]. For each simulation, we perform \(10^6\) cycles of initial equilibration and \(10^6\) cycles of assembling. The net atomic electrostatic charge of the framework structure is computed using the

![Figure 9](image-url). Electronic PDOS of pth-3 and pth-6.

in the bonding orbitals is very subtle. In fact, we observe that the orbitals of Ni\textsuperscript{2+} occupy low-energy states around −2 eV. Whereas Zn\textsuperscript{2+} (d\textsuperscript{10}) behaves as a nonmagnetic site, all 3d electrons of Ni\textsuperscript{2+} in this case also prefer to pair up, as consistently found in the previous cases of pth-1 and pth-2. As a consequence, the \(\alpha\) - and \(\beta\)-electrons prefer to jointly occupy the bonding eigenstates, which leads to the overall nonspin polarization for the whole structure. Like the previous cases, an indirect HO−LU gap is observed, in this case as 1.78 eV.

The pth-6 structure possesses a small indirect band gap of 0.74 eV. Interestingly enough, this is the sole case in the entire study in which we observe the major contribution of Im\textsuperscript{−} in both HO and LU eigenstates. The 3d electron of Cu\textsuperscript{2+} and Zn\textsuperscript{2+}, on the contrary, prefers to occupy a lower energy level, as shown in Figure 9b. Each Cu\textsuperscript{2+} site exhibits a magnetic moment of 0.55 \(\mu_B\), whereas Zn\textsuperscript{2+} remains almost non-polarized. Because of its contribution to the high occupation levels, Im\textsuperscript{−} is found to be polarized as well. The net sum magnetic contribution of all Im\textsuperscript{−} anions in the whole structure is nearly 1 \(\mu_B\), which is somewhat remarkable considering the total magnetization of 3.0 \(\mu_B/\text{cell}\) reported by our calculations. Overall, the presence of each tetrahedral Cu\textsuperscript{2+} cation induces a magnetic moment of 1 \(\mu_B\), which is in good agreement with the explanation using the crystal-field theory.

IV.2. CO\textsubscript{2} Selectivity. In this section, we validate the CO\textsubscript{2} adsorbing capability of the four stable pth structures. First, a gas molecule (either CO\textsubscript{2} or N\textsubscript{2}) is introduced into the ZIF structure near a specific metal site (M\textsuperscript{1} or M\textsuperscript{2}). Full structural optimizations with unit-cell relaxations are executed to search for
density derived electrostatic and chemical (DDEC6) method\cite{13-35} based on the DFT-optimized structure.

The resultant isotherm curves are presented in Figure 10. In total, four cases are presented for CO$_2$ and N$_2$ adsorptions. For all N$_2$ cases, we observe that the uptake does not exceed 24.2 cm$^3$/g. The CO$_2$ uptake levels of pth-1 and pth-3 at the maximum investigated pressure (1 bar) completely outreach the uptake of N$_2$. Those uptake quantities are 68.6 and 69.3 cm$^3$/g, respectively. This is in good accordance from the binding energy predicted by DFT (Table 4), which predicts that the adsorption of a single CO$_2$ is more favorable than the adsorption of N$_2$. The binding energy analysis points out that pth-3 would be less attractive to gas molecule than pth-1. However, both pth-1 and pth-3 seem to possess similar gas uptake capacity. As a result, we believe that the larger volume of pth-3 is helpful in gaining the uptake amount of CO$_2$ in the gas capture scheme. At 1 bar, the CO$_2$ working capacity in each case is ∼3.1 mmol/g, which is relatively good. For comparison purposes, one may consult the level of CO$_2$ working capacity in the hypothetical MOFs presented by Wilmer et al.\cite{36} Hence, we believe those two pth structures are good candidates for CO$_2$ capture and selectivity.

**V. SUMMARY**

In this study, adopting the power of reticular chemistry and RCSR database to combine two different kinds of SBUs including square-planar [Cu(Im)$_4$]$^{2+}$ complex and tetrahedral building block of Zn$^{2+}$, we have hypothesized developed a series of new ZIF structures within three topological categories: pth, pts, and ast. Those structural networks are systematically metalated to give a series of isoreticular structures with various metal SBUs (i.e., Ni$^{2+}$, Co$^{2+}$, Mn$^{2+}$) whose geometrical and mechanical stability are subsequently examined using first-principles DFT calculations. In addition, we carry out qualification tests to suggest the most stable candidates as a reference for future experimental syntheses. The phonon test points out that the imidazole linking units have to undergo severe deformation in the ast and pts networks. As a result, the internal vibrations of imidazole indicate that the linker is not in relaxation form; instead, it is in a saddle curvature as negative (imaginary) vibrational frequencies are obtained, which leads to the conclusion that the ast and pts topological networks are unstable.

The third test of elastic tensors actually eliminates two other candidates, which are pth-4 and pth-5. Finally, we conclude that four structures are stable: pth-1 (NiMn), pth-2 (NiCo), pth-3 (NiZn), and pth-6 (CuZn). Electronic configuration and band structure analyses suggest that pth-1 and pth-2 are strongly polarized due to the presence of Mn$^{2+}$ and Co$^{2+}$, respectively. In any case, the M$^2$ site (Ni$^{2+}$ or Cu$^{2+}$) is weakly polarized. Moreover, the participation of Zn$^{2+}$ at the M$^2$ position actually diminishes spin polarization. As for pth-3, we even conceive a nonmagnetic case, whereas pth-6 only exhibits a net magnetic moment of 3 $\mu_B$/cell. In terms of band gap, all four stables structures are found to possess indirect gaps in the range of 0.74 to 1.78 eV. Lastly, with those validated stable structures in hand, we further investigate if the CO$_2$ selectivity over N$_2$ displays a potential performance, as we expect for CO$_2$-selective capture. First, the DFT binding energies suggest that pth-1 and pth-3 favor CO$_2$ over N$_2$. Then, the GCMC simulation for CO$_2$ and N$_2$ adsorptions within pth-1 and pth-3 is executed to truly understand the gas uptake process. In general, we observe that the loads of CO$_2$ within pth-1 and pth-3 dominantly outreach the uptake of N$_2$. Such observation depicts pth-1 (NiMn) and pth-3 (NiZn) as promising candidates for CO$_2$ capture and selectivity.

In conclusion, we believe that our designed structures and the so-found properties based on molecular modeling can be a good reference to obtain new ZIF structures, which not only possess new topology but also endure harsh working conditions (high pressure, as shown by the bulk, Young’s, and shear moduli). In addition, the multivariate metalation active center in porous ZIF structures utilizing the open metal sites is designed for the first time in ZIF chemistry. Our final effort, at the end of the story, is subjected to extend further application of CO$_2$ capture and sequestration.

**ASSOCIATED CONTENT**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b07159.

- Optimized structure with the pth-1 topology (CIF)
- Optimized structure with the pth-2 topology (CIF)
- Optimized structure with the pth-3 topology (CIF)
- Optimized structure with the pth-4 topology (CIF)
- Optimized structure with the pth-5 topology (CIF)
- Optimized structure with the pth-6 topology (CIF)
- Optimized structure with the ast-1 topology (CIF)
- Optimized structure with the ast-2 topology (CIF)
- Optimized structure with the ast-3 topology (CIF)
- Optimized structure with the ast-4 topology (CIF)
- Optimized structure with the ast-5 topology (CIF)
- Optimized structure with the ast-6 topology (CIF)
- Optimized structure with the pts-1 topology (CIF)
- Optimized structure with the pts-2 topology (CIF)
- Optimized structure with the pts-3 topology (CIF)
- Optimized structure with the pts-4 topology (CIF)
- Optimized structure with the pts-5 topology (CIF)
- Optimized structure with the pts-6 topology (CIF)
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REFERENCES


(8) Materials Studio, version 6.0; Accelrys Software: San Diego, CA.


