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

Hieu T. Hoang,† Ha L. Nguyen,*‡,§ Thang B. Phan,† Sareeya Bureekaew,§ Yoshiyuki Kawazoe,‖ Duc Nguyen-Manh,⊥ and Hung M. Le,*†

1†Center for Innovative Materials and Architectures (INOMAR), Vietnam National University, Ho Chi Minh City 721337, Vietnam 2‡Center for Research Excellence in Nanotechnology (CENT), King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia 3§Department of Chemical and Biomolecular Engineering, School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Rayong 21210, Thailand 4‖New Industry Creation Hatchery Center, Tohoku University, Sendai 980-8579, Japan 5⊥Culham Centre for Fusion Energy, United Kingdom Atomic Energy Authority, Culham Science Centre, Abingdon OX14 3DB, United Kingdom

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 inorganic 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. 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. Gas storage and selective separation of CO₂ from a mixture of gas (biogas, flue gas stream) is an emerging application 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).
It should be noted that designing new ZIFs for CO₂ capture and separation still remains a challenging task because of the limit of organic linkers used in the synthesis, in which imidazole derivatives are set to react with bivalent metal sites. To overcome this circumstance, the geometrical structure of linking units needs to be varied or modified to produce various kinds of points of extension. 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). 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 complex (Scheme 1) to react with 4-

Scheme 1. Synthetic Procedure of Square-Planar Complex of Cu(Im)₄²⁺ Acting as the SBU Reactant for New ZIF Construction

<table>
<thead>
<tr>
<th>topology</th>
<th>vertices</th>
<th>edges</th>
<th>geometrical node</th>
</tr>
</thead>
<tbody>
<tr>
<td>css</td>
<td>2</td>
<td>1</td>
<td>tetrahedron + tetrahedron</td>
</tr>
<tr>
<td>dia-b</td>
<td>2</td>
<td>1</td>
<td>tetrahedron + tetrahedron</td>
</tr>
<tr>
<td>icd</td>
<td>2</td>
<td>1</td>
<td>tetrahedron + tetrahedron</td>
</tr>
<tr>
<td>ics-b</td>
<td>2</td>
<td>1</td>
<td>tetrahedron + tetrahedron</td>
</tr>
<tr>
<td>hvt-b</td>
<td>2</td>
<td>1</td>
<td>square + square</td>
</tr>
<tr>
<td>nbo-b</td>
<td>2</td>
<td>1</td>
<td>square + square</td>
</tr>
<tr>
<td>pth</td>
<td>2</td>
<td>1</td>
<td>tetrahedron + square</td>
</tr>
<tr>
<td>pts</td>
<td>2</td>
<td>1</td>
<td>tetrahedron + square</td>
</tr>
<tr>
<td>ast</td>
<td>2</td>
<td>1</td>
<td>tetrahedron + square</td>
</tr>
<tr>
<td>bte-b</td>
<td>2</td>
<td>1</td>
<td>tetrahedron + tetrahedron</td>
</tr>
<tr>
<td>rhr-b</td>
<td>2</td>
<td>1</td>
<td>square + square</td>
</tr>
<tr>
<td>sod-b</td>
<td>2</td>
<td>1</td>
<td>tetrahedron + tetrahedron</td>
</tr>
<tr>
<td>ssa</td>
<td>2</td>
<td>1</td>
<td>square + square</td>
</tr>
<tr>
<td>ssb</td>
<td>2</td>
<td>1</td>
<td>square + square</td>
</tr>
<tr>
<td>ssc</td>
<td>2</td>
<td>1</td>
<td>square + square</td>
</tr>
</tbody>
</table>

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 ZIF-pts. (c) Crystal structures of corresponding ZIFs are presented to show various kinds of pores.

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.
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>14/mmm</td>
<td>a = b = 19.19; c = 19.02</td>
<td>12.0</td>
</tr>
<tr>
<td>pth</td>
<td>hexagonal</td>
<td>P6,22</td>
<td>a = b = 9.25; c = 21.74</td>
<td>7.5</td>
</tr>
<tr>
<td>pts</td>
<td>tetragonal</td>
<td>P4/2/mmc</td>
<td>a = b = 10.08; c = 13.80</td>
<td>11.5</td>
</tr>
</tbody>
</table>

"For convenience, we use the name of topology and a number to indicate the network type with each (M₁, M₂) identity.

and are found to spread in a wide range from 110 to 160°. For those structures with the pts topology, there are 2 M₁ and 2 M₂ in a primary unit cell containing 68 atoms, with the M₁–M₂ Im–M angle 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 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 participating atom. The consideration of the 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. Semi-consistency is considered 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 (M₁ and M₂ having similar spin alignment), nonmagnetic, and ferrimagnetic (M₁ and M₂ 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$^+$ site (pth-5), 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 Cu$^{2+}$ contributes a small magnetic moment of 0.5 $\mu_B$ and has a tendency to resist the magnetic alignment of the M$^+$ sites (if it does exist).

Subsequently, we move on to the Ni$^{2+}$ pth derivatives (pth-6, pth-7, etc.). 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, Ni$^{2+}$ 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$^{3+}$ site contributes ~2.58 $\mu_B$. For pts-3, we observe only one magnetic state (3.95$\mu_B$/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$^+$ sites (eight cations) is dominant and is four times the number of M$^-$ 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 Ni$^{2+}$ 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 25 $\mu_B$/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$^+$, M$^-$) 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

$$xM^+Cl_2 + yM^2Cl_2 + (2x + 2y)\text{Im} \rightarrow \text{ZIF} + (2x + 2y)\text{HCl}$$

(1) 319

In the above net chemical reaction of imidazole with M$^+Cl_2$ and M$^2Cl_2$ (chloride salts of M$^+$ and M$^2$, respectively), a new ZIF structure and HCl are formed. Therefore, the formation energy per unit cell is calculated as

$$E_f = [E_{\text{ZIF}} + 2(x + y)E_{\text{HCl}}] - [xE_{(M^+Cl_2)} + yE_{(M^2Cl_2)}]$$

$$+ 2(x + y)E_{\text{Im}}$$

(2) 324

where $E_{\text{ZIF}}$, $E_{\text{HCl}}$, $E_{(M^+Cl_2)}$, $E_{(M^2Cl_2)}$, and $E_{\text{Im}}$ are the total energies of the ZIF structure, isolated HCl, M$^+Cl_2$, M$^2Cl_2$, and Im$^-$, respectively. A negative value of formation energy is indicative of energetic stability. All pth structures have negative formation energies (from ~4.55 to ~0.85 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 to 9.12 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

$$E_{\text{stabilize}} = E_f / (2x + 2y)$$

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

III.2.2. Phonon Analysis. As various metal cations are employed as building bridges to connect imidazole, it is obvious that different bond lengths and angles would be established because of the identity of the engaging metal. As a result, the unit cell of a particular topology involving different metals has unique cell parameters. In some cases, imidazole might be slightly or severely distorted. By saying “distorted”, we refer to compressed, stretched, or bent. Unfortunately, those behaviors cannot be justified by formation energy analysis. Therefore, we carry out phonon analysis to study the vibrational modes of the designed ZIF structures and thereby re-evaluate their mechanical stability. A ZIF structure is regarded as unstable when at least one negative vibrational mode exists.

For all pth structures, we conceive that all vibrational wavenumbers are positive, which qualifies the six pth structure for the phonon test. In the phonon density of states (DOS) (Figure 3), the broad peak around 3150 cm$^{-1}$ is attributed to the vibration of C–H stretching. Part of the broad peak below 350 cm$^{-1}$ is negative due to calculation uncertainty, which reflects the translational motions in three Cartesian dimensions are associated with the abnormal “shaking vibration” of C–H linkages and M$^-$imidazole stretch because Im$^-$ suffers severe bending within the pts network.

The negative phonon vibrational modes are also observed in the ast structures, as shown in Figure 6, and the ast structures are therefore disqualified from our mechanical stability test. In

![Figure 2](image)  
Figure 2. Stabilization energy per one imidazole molecule for the proposed ZIF structures.

![Figure 3](image)  
Figure 3. Phonon DOS of the six pth structures. All vibrational modes 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.

![Figure 4](image)  
Figure 4. Phonon DOS of the six pts structures. Two modes around −500 and −100 cm$^{-1}$ are attributed to the “shaking vibration” of C–H linkages and M$^-$imidazole stretch because Im$^-$ suffers severe bending within the pts network.
In 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 $-20\text{ cm}^{-1}$) 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,24 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

$$C_{11} > |C_{12}|$$

$$2C_{13}^2 < C_{33}(C_{11} + C_{12})$$

$$C_{44} > 0$$

$$C_{66} = (C_{11} - C_{12})/2$$

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

<table>
<thead>
<tr>
<th>pth</th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{13}$</th>
<th>$C_{15}$</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>$-66.4$</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></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pth-6</td>
<td>35.4</td>
<td>20.1</td>
<td>33.7</td>
<td>72.6</td>
<td>4.7</td>
<td>7.7</td>
<td>35.4</td>
<td>20.1</td>
<td>7.2</td>
</tr>
</tbody>
</table>
Figure 7. Occupation of 3d electrons in the degenerate orbital states of tetrahedral Mn\textsuperscript{2+}, Co\textsuperscript{2+} and square-planar Ni\textsuperscript{2+}, Cu\textsuperscript{2+} using ligand-field-theory interpretation.

Figure 8. Electronic PDOS of pth-1 and pth-2.

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.\textsuperscript{26–28} 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\textsuperscript{1}, M\textsuperscript{2}, and Im\textsuperscript{−}. For pth-1, we have discussed in the previous section that the ferromagnetic state is preferred against uniform pressure.

<table>
<thead>
<tr>
<th>Adsorptions in the Four Stable pth Structures</th>
<th>CO\textsubscript{2}</th>
<th>N\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>pth-1</td>
<td>M\textsuperscript{1}</td>
<td>M\textsuperscript{2}</td>
</tr>
<tr>
<td>pth-2</td>
<td>0.51</td>
<td>–1.03</td>
</tr>
<tr>
<td>pth-3</td>
<td>–0.27</td>
<td>n/a</td>
</tr>
<tr>
<td>pth-6</td>
<td>–0.09</td>
<td>–2.41</td>
</tr>
</tbody>
</table>

The Journal of Physical Chemistry C

DOI: 10.1021/acs.jpcc.8b07159

J. Phys. Chem. C XXXX, XXX, XXX–XXX

The Journal of Physical Chemistry C

DOI: 10.1021/acs.jpcc.8b07159

J. Phys. Chem. C XXXX, XXX, XXX–XXX
In constituting the HO state, the Ni$^{2+}$ site (d$^8$), 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$^{2+}$ 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$^2$ 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$^{2+}$ and Im$^+$, as revealed by the PDOS in Figure 9a. The role of M$^1$ (i.e., Ni$^{2+}$) in the bonding orbitals is very subtle. In fact, we observe that the orbitals of Ni$^{2+}$ occupy low-energy states around −2 eV. Whereas Zn$^{2+}$ (d$^{10}$) behaves as a nonmagnetic site, all 3d electrons of Ni$^{2+}$ 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 α- and β-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$^-$ in both HO and LU eigenstates. The 3d electron of Cu$^{2+}$ and Zn$^{2+}$, on the contrary, prefers to occupy a lower energy level, as shown in Figure 9b. Each Cu$^{2+}$ site exhibits a magnetic moment of 0.55 μ$_B$ whereas Zn$^{2+}$ remains almost non-polarized. Because of its contribution to the high occupation levels, Im$^-$ is found to be polarized as well. The net sum μ$_B$, which is somewhat remarkable considering the small indirect gap, is nearly 1 μ$_B$.

In this section, we validate the CO$_2$ and N$_2$ 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$^3$). The GCMC simulations using the μVT scheme are executed using the RASPA package, which has been used extensively to investigate the gas adsorption behavior in MOFs.

In the current simulation, we employ the semiempirical force field with pairwise Lennard-Jones potentials developed for MOF applications. 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$^4$ cycles of initial equilibration and 10$^5$ cycles of sampling. The net atomic electrostatic charge of the framework structure is computed using the

\[ E_{\text{binding}} = E_{\text{ZIF}} + E_{\text{gas}} - E_{\text{adsorbed-gas}} \]
The resultant isotherm curves are presented in Figure 10. In total, four cases are presented for \( \text{CO}_2 \) and \( \text{N}_2 \) adsorptions. For all \( \text{N}_2 \) cases, we observe that the uptake does not exceed 24.2 \( \text{cm}^3/\text{g} \). The \( \text{CO}_2 \) uptake levels of pth-1 and pth-3 at the maximum investigated pressure (1 bar) completely outreach the uptake of \( \text{N}_2 \). Those uptake quantities are 68.6 and 69.3 \( \text{cm}^3/\text{g} \), respectively. This is in good accordance from the binding energy analysis. In this study, adopting the power of reticular chemistry and first-principles DFT calculations with \( \mu \text{VT} \) ensembling at 25 \( ^\circ \text{C} \).

There is a graph showing isotherm curves for the \( \text{CO}_2 \) and \( \text{N}_2 \) uptakes within the pth-1 (NiMn) and pth-3 (NiZn) structures derived from GCMC calculations with \( \mu \text{VT} \) ensembling at 25 \( ^\circ \text{C} \).

**Figure 10.** Isotherm curves for the \( \text{CO}_2 \) and \( \text{N}_2 \) uptakes within the pth-1 (NiMn) and pth-3 (NiZn) structures derived from GCMC calculations with \( \mu \text{VT} \) ensembling at 25 \( ^\circ \text{C} \).
ACKNOWLEDGMENTS

H.L.N. expresses gratitude to Dr. Hiroyasu Furukawa (University of California, Berkeley) and Dr. Felipe Gándara (Materials Science Institute of Madrid, CSIC, Spain) for the initial discussion in this work. We acknowledge the technical discussion with Dr. Duc Nguyen-Manh ( Culham Centre for Fusion Energy, United Kingdom) and gratefully for the financial support from CSIC and the Institute for Material Research, Tohoku University. H.T.H. and H.L.N. are thankful for the financial support from Vietnam National University in Ho Chi Minh City under grant TX-2018-50-01.

REFERENCES


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


