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ZIF-8 gate tuning via terminal group modification: a computational study

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Abstract

Tuning the pore structure of zeolitic imidazolate frameworks (ZIFs) enables unique control of their material properties. In this work, we used computational methods to examine the gate structure of ZIF-8 tuned by substitution terminal groups. The substitution position and electron affinity of the added groups were shown to be key factors in gate size. Electrostatic interactions are responsible for the variation in gate opening. These results suggest that the post-modification of terminal group in ZIFs can be used to finely tune the pore gate, opening up new strategies in the design of ZIFs with desired properties.

1. Introduction

Zeolitic imidazolate frameworks (ZIFs), composed of tetrahedral metal nodes bridged by imidazolate (IM) linkers, combine the desirable features of conventional zeolites and metal-organic frameworks (MOFs), making them attractive candidates for a wide range of applications including separation and purification, drug delivery, and catalysis [1-7]. Although different ZIFs can be synthesized directly from differently-functionalized organic linkers, post-synthesis modification of ZIFs is an increasingly important means of producing new framework properties [8-10].

To that end, significant recent efforts have been made in exploring post-synthesis modification. New crystalline ZIF structures (ZIF-91 and -92) [10] and functionalized ZIFs with enhanced properties [9, 11] have been obtained using post-synthesis strategies. And Karagiari *et al.* employed the solvent-assisted linker exchange (SALE) strategy to synthesize new ZIFs (SALEM-1 and -2) [12-13]. Only rarely however have researchers been able to both maintain the integrity of the original crystal structure and achieve a uniform distribution of the modified groups [8-9, 12-13]. In most post-modifications, only a local area can be functionalized without altering the original structural integrity [14-15]. The resulting heterogeneous regions, called defects, can significantly alter the material performance in some applications [9, 14, 16-17]. Comprehensive understanding of the connection between MOF post-modification and the resulting material properties would yield considerable benefits. Such a broad experimental investigation however would be intractable [16]. Theoretical and computational methods can therefore more readily provide a microscopic understanding of the post-modification defect framework [18-21]. Density functional theory (DFT) calculations have, independent of force field parameters, contributed significantly to a better understanding of the post-modified framework structure [17, 22]. Schmidt *et al.* for example showed that post-modification via missing elementary linkers and metals in ZIFs impose only a small energy penalty, making their appearance thermodynamically unsurprising [22]. In other work, post-modified ZIFs have been shown to exhibit strong Lewis acidity, having a potentially outsized impact on guest molecule adsorption and hence catalytic properties [17, 22]. In a few limited examples, post-modification has been shown to alter gate size [16, 23], an essential characteristic in guest transfer for chemical separation and drug delivery applications [24-26]. Study shows that the diffusivity drops remarkably by 10 orders of magnitude over molecular diameter difference of merely 1.0 Å

(from C₃H₆ to *iso*-C₄H₁₀ in ZIF-8), mainly indicating the extreme important of gate size [27]. Certainly, the gate-opening behavior of ZIFs resulting from the flexibility in the swing of the organic linkers is also important, as allows large guest molecules to pass through the narrow gates of ZIFs [21, 24-25, 27].

In this letter, we used DFT calculations to investigate the ability of post-modification of organic linker terminal groups to control a ZIF gate. We used ZIF-8 as a prototypical model. To alter the ZIF-8 gate size, the position of the methyl group was varied. By analyzing the relationship between atomic interactions and gate size, we distinguished the geometric and electrostatic effects of the methyl group. The electrostatic dependence of gate size was elucidated by replacing the methyl group with electron withdrawing or donating groups. The electron affinity of the terminal group was used to finely control the ZIF-8 gate. As an easily-implemented modification, this strategy is especially helpful in the design of new ZIFs with desired properties.

2. Computational Method

In order to reduce the computational cost, a rhombohedral cell of ZIF-8, converted from the original cubic system (space group $I\bar{4}3m$), with a periodic boundary condition, lattice parameters of $a=b=c=14.71$ Å, and angles of $\alpha=\beta=\gamma=109.47^\circ$ was chosen. Current model owns one complete six-member ring gate irrespective of symmetry (Figure 1). No symmetry constrains was applied within the rhombohedral cell for the calculations. Geometry optimization was carried out with DFT to obtain an equilibrium structure, followed by energy calculations on the relaxed structure. DFT calculations were performed using Dmol³ code [28-29]. The exchange correlation energy was described by the PW91 functional under a generalized gradient approximation (GGA-PW91) [30]. DFT Semi-core pseudo-potentials for all atoms were used. Double-numeric basis with polarization functions (DNP) were used for all atoms. We used a k-point sampling scheme of a $3\times 3\times 3$ Monkhorst–Pack grid and Methfessel–Paxton smearing of 0.005 hartrees. A global real space orbital cutoff of 4.8 Å of the atomic basis sets was assumed. Spin polarization was used to calculate the energies and structural parameters of all models. The convergence criteria for structure optimization and energy calculations were 1.0×10^{-6} for SCF, 1.0×10^{-5} au for energy, 2.0×10^{-3} au for maximum force, and 5.0×10^{-4} nm for maximum displacement. The k-point and orbital cutoff values were obtained via a series of trial calculations. In DFT calculations we used both of relaxed and fixed lattice parameters (Table 1). From table 1, the two models show small

difference (<1.2%) in the computation of ZIF-8 gate size and represent the same law of gate size variation due to terminal group modification. This can be attributed to the stable ZIFs framework, as is supported by the experimental results that the post-modified ZIFs (SALEM-1 and SALEM-2) owns their parents' topology and ignorable cell size variation [12-13].

3. Results and discussion

We computed the 6 member-ring (6MR) gate size of ZIF-8 using geometries obtained both from X-Ray Diffraction (XRD) experiments and DFT geometry optimization. The computational model for the gate is shown in Figure 2(a). The van der Waals (VDW) radius (r_v) of a hydrogen atom is 1.1 Å. The final gate size is therefore calculated as $2 \times (r - r_v)$ (Table 1). Comparison of the calculated value with the XRD measurement (Table 1) shows that the calculation error is small, supporting the reliability of our geometry calculations.

Koros *et al.* proposed the effective aperture sizes to define where molecular sieving is truly realized [27, 31]. According to their reports, the effective aperture size of ZIF-8 for molecular sieving is in the range of 4.0 to 4.2 Å, which is significantly larger than the nominal ZIF-8 pore size of around 3.4 Å. There are two points to note in their study. One, the polycrystalline ZIFs were used in their experiment and then the inter-crystal space enhanced the gate size. Another, the gate size depends on the diameter of guest molecule, i.e. larger guests, bigger host gate [32]. Their tests used adsorbate ranging from C_3H_6 to *iso*- C_4H_{10} (> 4.0 Å), thus obtained large gate size.

The C2-C2 distance (Figure 2b) was used to characterize the 6MR gate size. A series of ZIF-8 geometry models with different gate sizes were constructed in accordance with gate-opening processes, i.e. linker swing (Figure 1). Stretching of the C2-C2 long-range bonds was used to describe the swing of the linkers. Employing the harmonic formula from our previous work [35]:

$$E_{\text{bond}} = K_b(b - b_0)^2 \quad (1)$$

Where K_b is the force parameter and b and b_0 are the C2-C2 bond length and its equilibrium value, respectively.

This model produces two important pore gate parameters: the equilibrium gate size (b_0) and the strength of gate opening (K_b). The former is especially important to understanding small guest molecule diffusion. H_2 for example has a kinetic diameter of ~2.9 Å, which compared to

the ZIF-8 pore gate size of 3.4 Å allows it to pass through even a closed gate. By comparison, inter-cage diffusion of larger guests, such as CH₄ (kinetic diameter: ~3.8 Å), require that the ZIF-8 gate open, making the strength of gate opening (K_b) a critical property.

Four models (Figure 3) were constructed to investigate the effect of organic linker methyl groups on ZIF-8 gate. The numbers of methyl groups present were 0, 1, and 2 in case 1, case 3, and case 2, respectively. From the un-modified ZIF-8 to case 3, the position of the methyl group was changed from C1 to C2. In order to model gate-opening, a series of structures were prepared in which the 3 linkers gradually open the gate. One typical gate-opening structure is shown in Figure 1. The prepared structures were optimized by freezing all Zn atoms and the C2 atoms located on the rotating linkers (the red atoms in Figure 1).

In order to obtain the gate size parameters, the gate opening process was followed via the length variation of the C2-C2 distance, as in our previous work [32]. In each model, the system energy was calculated at every C2-C2 distance as well as during the swing of organic linker. Those energy values (Figure 3e and f) represent the correlation between the system energy and the ZIF-8 gate size. From Figure 3, it can be seen that the existence and position of methyl groups on the IM linker affect the equilibrium gate size and opening force. Both properties decrease in the absence of any methyl group (case 1). The data in Figure 3e were fitted to Equation 1, yielding $K_b = 0.87 \text{ kcal}\cdot\text{mol}^{-1}\cdot\text{\AA}^{-2}$ and $b_0 = 4.95 \text{ \AA}$ for case 1, compared to $K_b = 1.68 \text{ kcal}\cdot\text{mol}^{-1}\cdot\text{\AA}^{-2}$ and $b_0 = 5.15 \text{ \AA}$ for the original ZIF-8. In case 2, the second methyl group on C2 produces a significant increase in b_0 (5.29 Å) and a small rise in K_b (2.08 kcal·mol⁻¹·Å⁻²). In case 3 (Figure 3f), where the methyl group is moved to C2, the system energy varies irregularly with increasing C2-C2 bond length, most likely due to the overall unstable chamber structure.

To understand these results, we analyzed the contributions of atomic interactions to the gate parameters. We focused on non-bonded interactions (electrostatic and VDW) because the gate size is a function of the relative position of the adjacent linkers, which have only non-bonded interactions. The contribution of the C2-C2 interaction force was excluded due to its high length (~5.0 Å). The non-bonded forces between linkers comprising the tetrahedron geometry of Zn(IM)₄ were the primary contributors to gate size. We identified (Figure 4a) two representative non-bonded forces (C1-C2 and C2-C3, with equilibrium lengths of ~3.9 Å and ~3.8 Å, respectively) that correlate to the gate size of ZIF-8. In order to better understand the relationship between the characteristic lengths in Figure 4a and the ZIF-8 gate size, we plotted the C1-C2 or

C2-C3 length vs. gate size (Figure 4b). The negative correlation shows that shortening the characteristic length reflects ZIF-8 gate-opening.

We then focused on the variation of C1-C2 and C2-C3 non-bonded interactions with post-modification of ZIF-8. The electrostatic force, depending on the charge distribution, is especially important in controlling the gate size. Figure 5 shows the charge distribution on our different models. Both the C1 and C2 atom have partial positive charges, producing repulsive electrostatic interactions. The terminal hydrogen is also positively charged. After replacing the hydrogen terminal with a methyl group (Figure 5b), there is an attractive force between the C2 and C3 atoms, shortening the adjacent C2-C3 or C1-C3 distance and enhancing the gate opening force. That explains the larger b_0 and K_b for original ZIF-8 compared to case 1 (Figure 3e). Further post-modification was performed by grafting a methyl group onto the C2 atom (Figure 5c). This new methyl group makes the two C2 atoms in one linker different: the C2 atom bonded H atom becomes slightly negative ($-0.002e$) while the C2 atom bonded methyl group becomes significantly positive ($+0.111e$). The net effect however due to the repulsive and attractive interactions can be close to zero. The repulsive force among terminal H atoms from adjacent linkers (Figure 5d) contributes significantly to the larger equilibrium gate size in observed in Figure 3e. Further, the steric hindrance makes gate opening more difficult (larger K_b).

We have investigated the effect of post-modification position (C1 or C2) on ZIF-8 gate size (Figure 3e). The new terminal group on the C2 position changes the gate size via variation of the ring shape. Contrary to experimental expectations, the structure is distorted; even collapse could be induced (Figure 3f). By comparison, it is believed that post-modification of the C1 position can tune the gate size via electrostatic interactions without creating an unstable geometry. In particular, the electrostatic attractive force can open the gate while the repulsive force makes the gate smaller. In order to confirm this observation, we investigated the effect of introducing electron withdrawing and donating groups on ZIF-8 gate size.

Amino (electron donating) and nitril (electron withdrawing) groups were used to replace the terminal methyl group in ZIF-8. Each geometry was first optimized using DFT and then the system energy was calculated over the swing of the organic linker (Figure 6). The data in Figure 6 were fit to Equation 1, yielding $K_b = 1.54 \text{ kcal}\cdot\text{mol}^{-1}\cdot\text{\AA}^{-2}$ and $b_0 = 4.91 \text{ \AA}$ after the amino addition, compared to $K_b = 1.68 \text{ kcal}\cdot\text{mol}^{-1}\cdot\text{\AA}^{-2}$ and $b_0 = 5.15 \text{ \AA}$ for the original ZIF-8. Nitril modification produces a $K_b = 1.65 \text{ kcal}\cdot\text{mol}^{-1}\cdot\text{\AA}^{-2}$ and $b_0 = 5.29 \text{ \AA}$, i.e. a much larger gate. We

attribute this shift to the attractive interaction between the negative charge on the electron withdrawing group and the positive charge on the C2 atoms. The electron donating group in contrast still produces a repulsive force, which does not benefit gate-opening. Control over ZIF-8 gate size can be therefore be achieved by tuning the charge of the terminal group. While, the gate opening force (K_b) is almost independent of the type of the terminal group in ZIF-8.

4. Conclusion

In this work, we used DFT to investigate the effect of post-modification of ZIF-8 on its gate size and opening. The position of the methyl group was changed to the terminal positions of the C1 and C2 atoms (Figure 3) in the imidazolate ring. In the former case, the gate can be controlled via the electrostatic interactions between the adjacent linkers forming the tetrahedron geometry of $\text{Zn}(\text{IM})_4$. In the latter case, placing the methyl group on the C2 atoms makes the ZIF-8 gate open but distorts the structure significantly. We also investigated the substitution of electron donating and withdrawing groups for the C1 methyl group, resulting in, respectively, smaller and larger ZIF-8 gates. We show that the electron affinity of the terminal group can be used to tune the 6MR gate size in ZIF-8, informing the post-synthesis functionalization/modification ZIF-8 to produce desired pore structure and then properties. Future research will aim to study the post-modification of other metal-organic frameworks to understand and guide experimental design.

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Table 1 ZIF-8 (with and without post-modification) gate size obtained by experimental testing and DFT calculation. The values inside brackets were computed by using the experimental lattice parameters.

	Experiment ³³⁻³⁴	DFT calculations			
Gate structure
Gate size (Å)	3.42	3.46(3.50)	3.40(3.42)	3.32(3.35)	3.74(3.70)

Figure 1. DFT calculation model. Green denotes the C2-C2 distance defining the gate size.

Figure 2. (a) The model for calculating the size of the 6-member ring in ZIF-8. (b) Definition of the C2-C2 distance used to characterize the gate size irrespective of terminal group.

Figure 3. Study models: (a) original ZIF-8; (b) case 1; (c) case 2; (d) case 3. H atoms on methyl groups were hidden for visual clarity. (e) and (f) System energy vs. C2-C2 distance for each case.

Figure 4. (a) Tetrahedron geometry of $\text{Zn}(\text{IM})_4$, with H atoms omitted for clarity. (b) Evolution of the characteristic length during gate opening (C2-C2 distance). The characteristic length was defined in (a) as the length of C1-C2 or C2-C3.

Figure 5. Electron density on the gate surface and atomic partial charge distribution on one unit structure of (a) case 1, (b) original ZIF-8, and (c) case 2. All H atoms and their point charges were hidden for clarity. (d) The electrostatic repulsive interaction between terminal hydrogen atoms in case 2. The red numbers denote the point charge value; the green numbers denote the distance between two H atoms.

Figure 6. System energy vs. length of C2-C2 distance for three different terminal groups: NH_2^- , CH_3^- , and NO_2^- .

Figure1

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(a)

(b)

Figure 3

(a)

(b)

(c)

(d)

(e)

(f)

(a)

(b)

Figure 6

Graphical Abstract

ZIF-8 gate tuning via terminal group modification: a computational study

Highlights

1. The substitution position of the added groups tunes the ZIF-8 gate via steric effect.
2. The electron affinity of the terminal group can be used to finely control the ZIF-8 gate.
3. Electrostatic interactions between linkers comprising the tetrahedron geometry of $\text{Zn}(\text{IM})_4$ are responsible for the variation in ZIF-8 gate opening.