Unraveling the effects of linker substitution on structural, electronic and optical properties of amorphous zeolitic imidazolate frameworks-62 (a-ZIF62) glasses: a DFT study

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I. Computational Details

To ensure the high accuracy of the a-ZIF-62 models, we have fully relaxed all structures using Vienna Ab Initio Simulation Package (VASP). [1] The projector augmented wave (PAW) [2] method with the Perdew-Burke-Ernzerhof (PBE) [3] potential for exchange correlation functional together within the generalized gradient approximation (GGA) are adopted. For the electronic relaxation, a high energy cutoff of 600 eV is used with the electronic convergence criterion set at $1.0*10^{-4}$ eV. For ionic relaxation, we set the force convergence criteria to be $5*10^{-2}$ eV/Å. A single k-point at the zone center is sufficient for a large glassy model. For electronic structure and interatomic bonding calculations, we us the first principles orthogonalized linear combination of atomic orbitals (OLCAO) method based on the VASP-relaxed structures. [4] The OLCAO method uses atomic orbitals for basis expansion which is more efficient in the calculation of physical properties. The combination of these two DFT-based methods has demonstrated to be highly effective in the study or large complex systems including non-crystalline solids [5-10] and liquids [11], large organic crystals [12] and biomolecules [13, 14]. The evaluation of effective charges Q_α^* and each atom and bond order (BO) values (overlap population), $\rho_{\alpha\beta}$, between any pair of atoms (α, β) based on Mulliken population analysis, [15, 16] and localization index (L_n) are of central importance. [4] L_n values range from 1.0 for a completely localized state on a single orbital to 1/N where N is the dimension of the secular matrix for a completely delocalized state in which the eigenvector coefficients are evenly distributed over all orbital components.

$$Q_\alpha^* = \sum_i \sum_{\substack{n \\ occ}} \sum_{j,\beta} C_{i\alpha}^{m*} C_{j\beta}^m S_{i\alpha,j\beta} \tag{1}$$

$$\rho_{\alpha\beta} = \sum_{\substack{n \\ occ}} \sum_{j,\beta} C_{i\alpha}^{*n} C_{j\beta}^n S_{i\alpha,j\beta} \tag{2}$$

$$L_n = \sum_{i,\alpha} \left[\sum_{j,\beta} C_{i\alpha}^{*n} C_{j\beta}^n \right]^2 \tag{3}$$

Here, i, j label the orbital quantum number and n the band index, $C_{j\beta}^n$ are the eigenvector coefficients of the wave function and $S_{i\alpha,j\beta}$ is the overlap matrix between atoms α and β. The BO value $\rho_{\alpha\beta}$ is a direct quantitative measure of strength between a pair of atoms. Although BO is not a quantum observable, it is far more accurate and concise than pure geometric criteria or other parameters such as coordination numbers. It should be pointed out that Mulliken scheme is basis dependent and its application must be confined to a specific method and a well-defined basis set. It is most effective when a more localized minimal basis set is used. In the present work, the BO is calculated using a minimal basis (MB) set whereas for the self-consistent potential and the electronic structure calculation, a full basis (FB) set is used. [4] Although there are other more elaborate methods to calculate BO values, they are usually limited to simpler molecules or crystals

and based on numerical evaluation on a dense 3-dimensional mesh. They are less efficient in analyzing multi-component materials with complex structures and large number of atoms. The total bond order density (TBOD) and partial bond order density (PBOD) is obtained as the cumulative BO from all unique bond pairs divided by the cell volume. The use of TBOD and PBOD as quantum mechanical metric in characterizing interatomic bonding in a variety of materials has been demonstrated in recent publications. [17-21].

The MOF materials are envisioned to have many interesting functional applications. The optical properties calculation within the one-electron application calculated in the form of the frequency-dependent complex dielectric function and the refractive index n which are important for opt-electronic applications. For the calculation of inter-band optical properties, the imaginary part of the dielectric function ε_2 is evaluated first, using [22]:

$$\varepsilon_2(\hbar\omega) = \frac{e^2}{\pi m\omega^2} \int_{BZ} dk^3 \sum_{n,l} \left| \left\langle \psi_n(\vec{k},\vec{r}) \right| -i\hbar\vec{\nabla} \left| \psi_l(\vec{k},\vec{r}) \right\rangle \right|^2 f_l(\vec{k}) \left[1 - f_n(\vec{k}) \right] \delta\left(E_n(\vec{k}) - E_l(\vec{k}) - \hbar\omega \right)$$

(4)

Here $E = \hbar\omega$ is the photon energy, ℓ and n label the occupied and unoccupied states respectively. $\psi_n(\vec{k},\vec{r})$ is the wave function for the nth state with energy $E_n(\vec{k})$ at Brillouin zone point k. $f(\vec{k})$ is the Fermi distribution function. The momentum matrix elements (MME) $\left\langle \psi_n(\vec{k},\vec{r}) \left| \vec{P} \right| \psi_l(\vec{k},\vec{r}) \right\rangle$ are explicitly calculated from the *ab initio* wave functions. In the present study of a large glass model, only the $k = (0,0,0)$ is used. The real part of the dielectric function ε_1 is obtained from the imaginary part ε_2 via Kramers–Kronig transformation:

$$\varepsilon_1(\hbar\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{s\varepsilon_2(\hbar\omega)}{s^2 - \omega^2} ds \qquad (5)$$

From the complex dielectric function, n can be estimated from the square root of ε_1 at zero frequency, or $n = \sqrt{\varepsilon_1(0)}$. Also obtained is the energy loss function ELF ($\hbar\omega$):

$$ELF(\hbar\omega) = IM\left\{ -\frac{1}{\varepsilon(\hbar\omega)} \right\} = \frac{\varepsilon_2(\hbar\omega)}{[\varepsilon_1^2(\hbar\omega) + \varepsilon_2^2(\hbar\omega)]}. \qquad (4)$$

The program PLATON is used for all structures to calculate the porosity of the a-ZIF models with "VOID" algorithm. [23] When we construct the a-ZIF models, the bIm linkers were distributed randomly by the computer. Based on the original amorphous ZIF model, we label all the Im ligands, then generate several numbers in a python script to choose those substituted with bIm. The bIm linkers are distributed as isotropically as possible.

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