Supporting Information

Prediction of the Glass Transition Temperatures of Zeolitic Imidazolate Glasses through Topological Constraint Theory

Yongjian Yang[1], Collin J. Wilkinson[1], Kuo-Hao Lee[1], Karan Doss[1], Thomas D. Bennett[2], Yun Kyung Shin[3], Adri C. T. van Duin[1,3] and John C. Mauro[1*]

[1] Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, USA

[2] Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, CB3 0FS, UK

[3] Department of Mechanical and Nuclear Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, USA

Corresponding Author: *jcm426@psu.edu

Computational details

To calculate the standard deviation of each type of atomic constraint, a recently published ReaxFF forcefield[1] has been used to simulate ZIF-4 [$Zn(Im)_2$] and ZIF-62 [$Zn(Im_{2-x}bIm_x)$] using LAMMPS[2]. A timestep of 0.25 fs is used for the integration of the trajectory. The initial structure of ZIF-4, ZIF-62 are extracted from CSD[3] (The Cambridge Structural Database) and are equilibrated at 10 K using a Berendsen thermostat. Both ZIF-4 and ZIF-62 are heated from 10 K to 1500 K in 15 ps with the temperature and the pressure controlled using a Nosé-Hoover thermostat/barostat[4–6] in the isothermal-isobaric ensemble (NPT). A tolerance of 10^{-6} for the charge equilibrium[7–9]is used. The pressure of the system is kept at approximately 1 atm. The sample contains 2176 atoms and 2368 atoms for ZIF-4 and ZIF-62, respectively. Properties of the two systems including atomic structure, density, thermal properties, and pore morphology can be found in Ref [1]. One of the important findings in Ref [1] is that ReaxFF simulation shows that the melting temperature of ZIF-62 is lower than that of ZIF-4 by ~100 K, which is consistent with the experimental result of ca. 150 K[10]. Because the dynamics of the liquid is very slow[11], it will be difficult to get a realistic glass structure with mostly 4-coordinated Zn[10] via melt-quench using MD, as already seen in our previous simulations[1]. Therefore, we have relied on the structural change of ZIF-4 and ZIF-62 crystals upon heating to deduce the bond constraint difference between Im and bIm. Atomic configurations of the two systems are extracted at different temperatures. Based on the atom position, the standard deviation of different types of constraints such as radial bonds: Zn-N/N-C/C-C and angular bonds: N-Zn-N/Zn-N-C/C-C-N/C-N-C/C-C-C are calculated. To get better statistics, the results are averaged for every 7 consecutive trajectories whose temperatures are close. The bond cutoffs used to search for the Zn-N, C-N and C-C bond pairs are 2.5 Å, 1.75 Å and 1.85 Å, respectively. These cutoffs correspond to the first minimum of the partial radial distribution function for each atomic pair. No bond dissociation between C-N and

C-C is found at temperature below ~1100 K and only a few transient C-C pairs (<0.6%) appear at $T > 1100$ K with pair distances a little above the cutoffs.

Over-counting of constraint in Im and bIm

Referring to Figure 1 in the main text, one can see that both Im and bIm contain a 5 membered ring (imidazolate-type ring) in which only 4 out of the 5 angles are independent from geometry. Meanwhile, the bIm contains two rings (a 5 membered and a 6 membered rings) sharing one edge and among the two N-C2-C3 angles on both ends of the edge, one is redundant. Therefore, in Table 1, the total number of constraint in Im has been deducted by one and that of bIm has been deducted by two.

Angular constraint of C-N-C, N-C-N and N-Zn-N

Figure S1a shows that both the C-N-C angle and the N-C-N angle in the 5-membered ring are quite rigid and similar between Im and bIm in the range of temperature explored. Now let us consider the angular constraint N-Zn-N contained in the a_gZIF-62 [$Zn(Im_{1.75}bIm_{0.25})$] system, i.e. the β angle in Figure 1. Hu *et al.*[12,13] have developed a force field from DFT calculations for ZIF-8 which consists of Zn atoms connected by 2-methylimidazolate groups (mIm) shown in Figure S1b. It is found that the elastic constants associated with the N-Zn-N angular constraint is much weaker (<18%) than the N-C-N angle and the C-N-C angle. Reverse Monte Carlo results of the a_gZIF-4 $[Zn(Im)]_2$ glass by Beake *et al.*[14] show that the tetrahedral angle N-Zn-N has a large standard deviation (23~25°) in the glass even at low temperature (implying a broken constraint). From our MD simulations of ZIF-4 (and similarly for ZIF-62), as shown in Figure S1c, we have found a large relative standard deviation (or 15-20°) for all of the six bond angles in the ZnN_4 tetrahedral. In their analysis of silica glass, Bauchy and Micoulaut[15] have used a std of ~19° to delimit the rigid O-Si-O tetrahedral bond angle (whose standard deviation is around 5°) and the other floppy bond angles. It can be seen that the standard deviation of the N-Zn-N tetrahedral angle is much larger than that of the other angular constraints; therefore, it is reasonable to deduce that the N-Zn-N angular bond is not rigid.

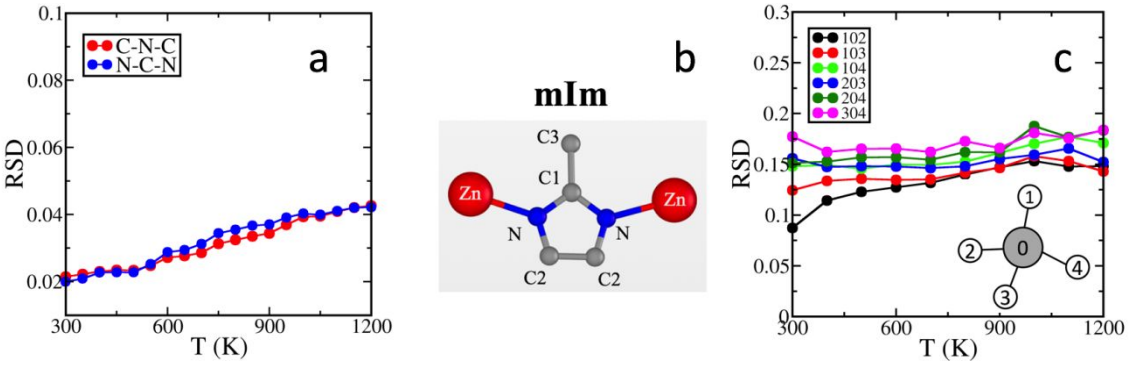

Figure S1. (a) Relative standard deviation (RSD) for the atomic angular constraints in ZIF-62: C-N-C and N-C-N. (b) The mIm organic ligand appearing in ZIF-8. (c) RSD of the atomic angular constraint N-Zn-N in ZIF-4. In the analysis of N-Zn-N, the four N atoms are ranked according to their distances to the Zn atom from the closest to the farthest as shown in the inset of (c).

REFERENCES

(1) Yang, Y.; Shin, Y. K.; Li, S.; Bennett, T. D.; van Duin, A. C.; Mauro, J. C. Enabling Computational Design of ZIFs Using ReaxFF. *J. Phys. Chem. B* **2018**, *122*, 9616–9624.
(2) Plimpton, S. Fast Parallel Algorithms for Short-Range Molecular Dynamics. *J. Comput. Phys.* **1995**, *117* (1), 1–19.
(3) Allen, F. H. The Cambridge Structural Database: A Quarter of a Million Crystal Structures and Rising. *Acta Crystallogr. B* **2002**, *58* (3), 380–388.
(4) Nosé, S. A Unified Formulation of the Constant Temperature Molecular Dynamics Methods. *J. Chem. Phys.* **1984**, *81* (1), 511–519.
(5) Hoover, W. G. Canonical Dynamics: Equilibrium Phase-Space Distributions. *Phys. Rev. A* **1985**, *31* (3), 1695–1697.
(6) Hoover, W. G. Constant-Pressure Equations of Motion. *Phys. Rev. A* **1986**, *34* (3), 2499.
(7) Rappe, A. K.; Goddard III, W. A. Charge Equilibration for Molecular Dynamics Simulations. *J. Phys. Chem.* **1991**, *95* (8), 3358–3363.
(8) Nakano, A. Parallel Multilevel Preconditioned Conjugate-Gradient Approach to Variable-Charge Molecular Dynamics. *Comput. Phys. Commun.* **1997**, *104* (1–3), 59–69.
(9) Aktulga, H. M.; Fogarty, J. C.; Pandit, S. A.; Grama, A. Y. Parallel Reactive Molecular Dynamics: Numerical Methods and Algorithmic Techniques. *Parallel Comput.* **2012**, *38* (4–5), 245–259.
(10) Bennett, T. D.; Yue, Y.; Li, P.; Qiao, A.; Tao, H.; Greaves, N. G.; Richards, T.; Lampronti, G. I.; Redfern, S. A.; Blanc, F.; et al. Melt-Quenched Glasses of Metal–Organic Frameworks. *J. Am. Chem. Soc.* **2016**, *138* (10), 3484–3492.
(11) Gaillac, R.; Pullumbi, P.; Beyer, K. A.; Chapman, K. W.; Keen, D. A.; Bennett, T. D.; Coudert, F.-X. Liquid Metal–Organic Frameworks. *Nat. Mater.* **2017**, *16* (11), 1149.
(12) Hu, Z.; Zhang, L.; Jiang, J. Development of a Force Field for Zeolitic Imidazolate Framework-8 with Structural Flexibility. *J. Chem. Phys.* **2012**, *136* (24), 244703.
(13) Zhang, L.; Hu, Z.; Jiang, J. Sorption-Induced Structural Transition of Zeolitic Imidazolate Framework-8: A Hybrid Molecular Simulation Study. *J. Am. Chem. Soc.* **2013**, *135* (9), 3722–3728.
(14) Beake, E.; Dove, M.; Phillips, A.; Keen, D.; Tucker, M.; Goodwin, A.; Bennett, T.; Cheetham, A. Flexibility of Zeolitic Imidazolate Framework Structures Studied by Neutron Total Scattering and the Reverse Monte Carlo Method. *J. Phys. Condens. Matter* **2013**, *25* (39), 395403.
(15) Bauchy, M.; Micoulaut, M. Atomic Scale Foundation of Temperature-Dependent Bonding Constraints in Network Glasses and Liquids. *J. Non-Cryst. Solids* **2011**, *357* (14), 2530–2537.