Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Electronic Supporting Information

# Deformation mechanism of a metal-organic framework glass under indentation

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**Supporting Methods**

*Preparation of the ZIF-62 crystals*

The crystalline ZIF-62 was synthesized by using the solvothermal method. 1.7326 g $Zn(NO_3)_2 \cdot 6H_2O$ (99.99%, Sigma), 5.3527 g imidazole (99.5%, Sigma) and 1.0321 g benzimidazole (99%, Sigma) were mixed and dissolved in 50 ml N,N-dimethylformamide (DMF, 99.9%, Sigma). After magnetic stirring for 1 hour, the solution was moved to a sealed glass jar (100 ml) and placed in an Oven for 96 hours at 403 K. The derived powder were washed three times in DMF and then dried at 373 K for 4 hrs.

*Powder X-ray diffraction (XRD) measurements*

Room-temperature XRD data ($2\theta$=5−40°) were collected with a PANalytical Empyream diffractometer using Cu $K_\alpha$ (λ=1.540598 Å) radiation.

*Calorimetric measurements*

The Differential Scanning Calorimetry (DSC) characterizations of all the samples were performed using a Netzsch STA 449 F1 instrument. The samples were placed in a platinum crucible situated on a sample holder of the DSC at room temperature. The samples were held for 5 min at an initial temperature of 313 K, then heated at 10 K/min to the 773 K, and then cooled back to 473 K at 10 K/min. After natural cooling to room temperature, the second upscan was performed using the same procedure.

*Atomic packing ratio calculation*

Atomic packing ratio ($C_g$) of glass is defined as the ratio between the volume occupied by the atoms and the corresponding effective volume of glass. It is an indicator for the free volume in the glass. For oxide glasses, the $C_g$ can be calculated based on the density as follow:

$$C_g = \rho \frac{\sum f_i V_i}{\sum f_i M_i}$$

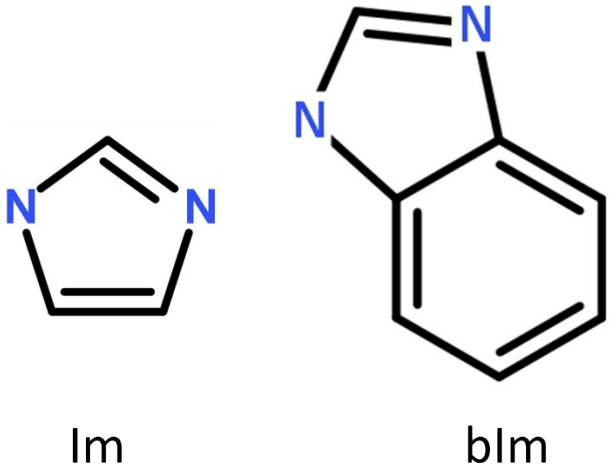
$$V_i = \frac{4}{3}\pi N_a (x r_A^3 + y r_B^3)$$

where $\rho$ is the density of glass, $f_i$ is the molar fraction of formula $A_xB_y$, $V_i$ is theoretical volume, $M_i$ the molar mass, $r_A$ and $r_B$ are the atomic radii and $N_a$ is Avogadro's number.

However, due to the fact that the ZIF glass is constituted by metal ions and organic ligands, the organic ligands should be treated as an integral unit. Therefore, for ZIF-62 glass ($Zn(Im)_{1.75}(bIm)_{0.25}$), the $C_g$ should be calculated as follow:

$$C_{g,ZIF-62\ glass} = \rho_{ZIF-62\ glass}\frac{V_{zn} + 1.75V_{Im} + 0.25V_{bIm}}{M_{ZIF-62\ glass}}$$

where the atomic radii of Zn is 0.74 Å[1], the molecular volume of Im and bIm ligands were calculated based on their precise geometry[2,3] and the covalent radii of atoms (C, N and H)[4]. The $C_g$ value of ZIF-62 glass is found to be 0.03, much lower than that of other oxide glasses as listed in Table S1.




Im bIm

**Supporting Figures**

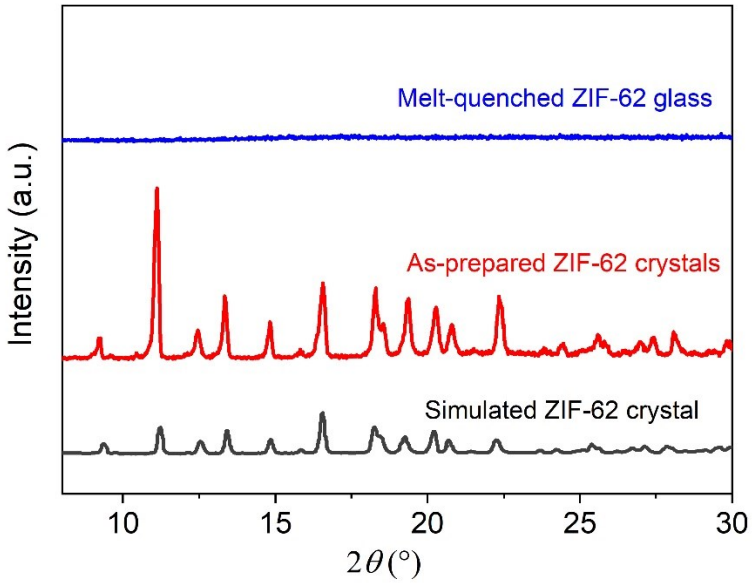



Figure S1. XRD patterns of as-prepared ZIF-62 by solvothermal method and melt-quenched ZIF-62.

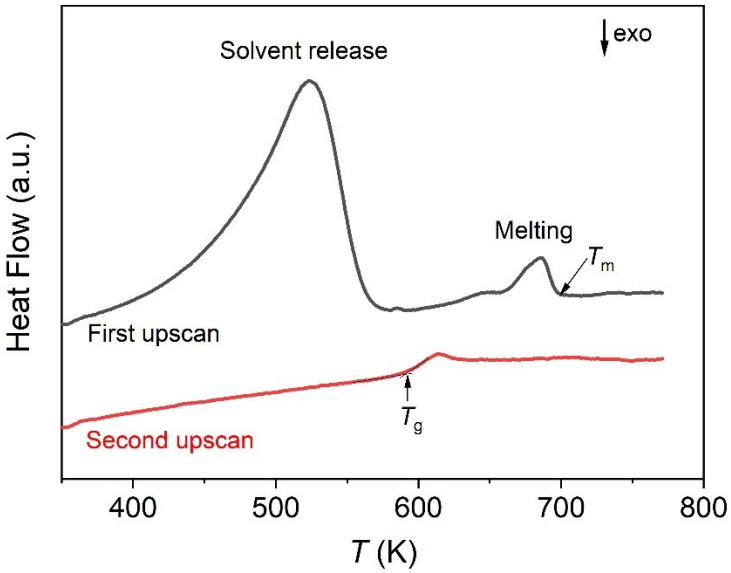



Figure S2. First DSC upscan curve (black line) for as-prepared ZIF-62 sample, showing two exothermic peaks assigned to solvent release and melting events respectively. After quenching from above melting point ($T_m$), second DSC upcan curve (red line) exhibits a clear glass transition

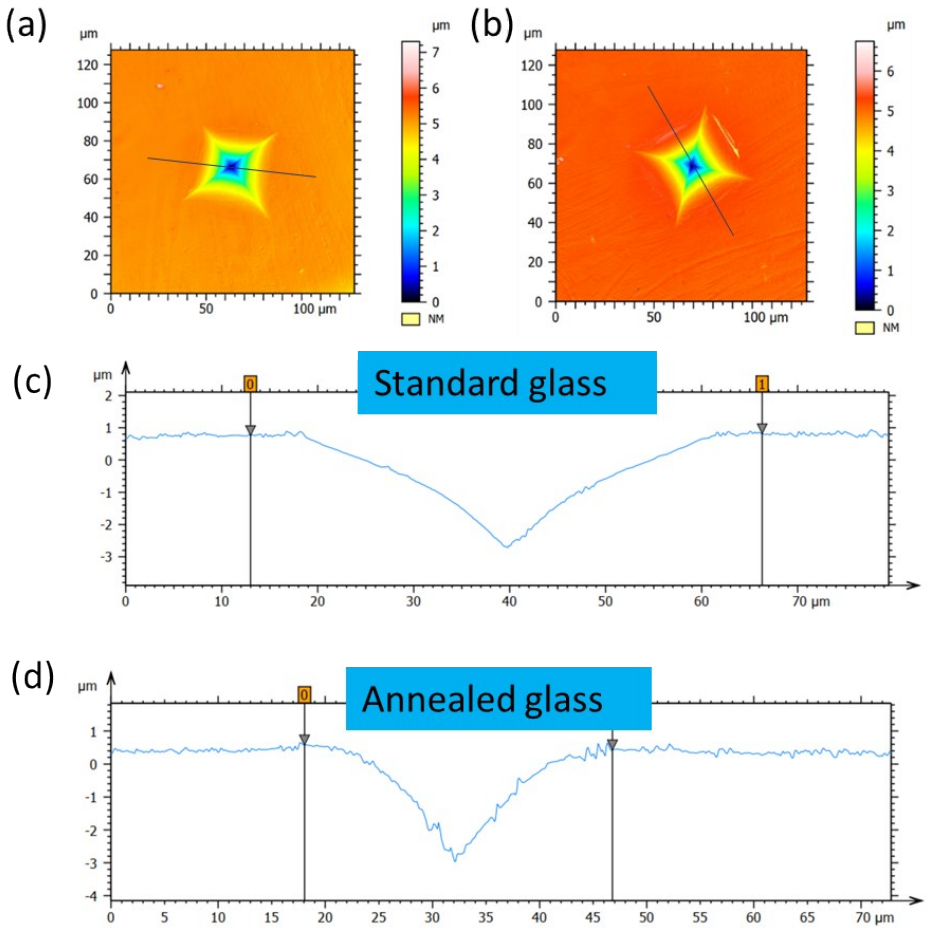



Figure S3. Laser microscopy images of Vickers indents in standard (a) and annealed (b) ZIF-62 glasses. Cross-section profiles derived from laser microscopy measurements for standard (c) and annealed (d) ZIF-62 glasses.

## Supporting Table

Table S1. Comparison of the atomic packing ratio ($C_g$) values for ZIF-62 glass and other glasses.

| Glass Composition | $C_g$ (-) | Refs |
|---|---|---|
| ZIF-62 | 0.03 | This work |
| Silica | 0.45 | SI Ref. 5 |
| Borosilicate | 0.49~0.75 | SI Ref. 6 |
| Ca-Zr-Silicates | 0.523 | SI Ref. 7 |
| Aluminoborates | 0.47~0.56 | SI Ref. 7 |
| Aluminoborosilicates | 0.50~0.56 | SI Ref. 7 |
| Zr-Cu-Al-Ni | 0.75 | SI Ref. 8 |
| Ge-Se | 0.64 | SI Ref. 8 |

## SI References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