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Supplementary Information for

Observation of Indentation Induced Shear Bands in a Metal-Organic Framework Glass

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Supplementary methods

In order to assess the structure of the obtained ZIF-62 glass and possible differences in structure due to application of pressure during melting (in hot-press method), we performed powder X-ray diffraction (P-XRD) and Fourier-transform infrared spectroscopy (FT-IR). We compared the hot-pressed glass with a standard melt-quenched one. The latter was obtained by melting and quenching the ZIF-62 crystal in ambient pressure in a Netzsch STA 404C differential scanning calorimeter (DSC) with heating and cooling rates of 10 K/min and maximum temperature of 460 ^{o}C. PANalytical empyream XRD with Cu $K_{\alpha 1}$ radiation (λ = 1.54098 Å) machine was used to collect XRD data in the range of 5 to 50° (step size 0.013°). FT-IR data was collected in absorbance mode on a Bruker Tensor II equipped with platinum ATR in range of 400-4000 cm^{-1} wavenumber. In order to assess the ligand stability during hot pressing, liquid-state nuclear magnetic resonance (L-NMR) measurement was performed on Bruker DPX600 Advance (at 600 MHz frequency) spectrometer at 298 K. Samples were digested in DCl/D_2O/DMSO-d6 solution.

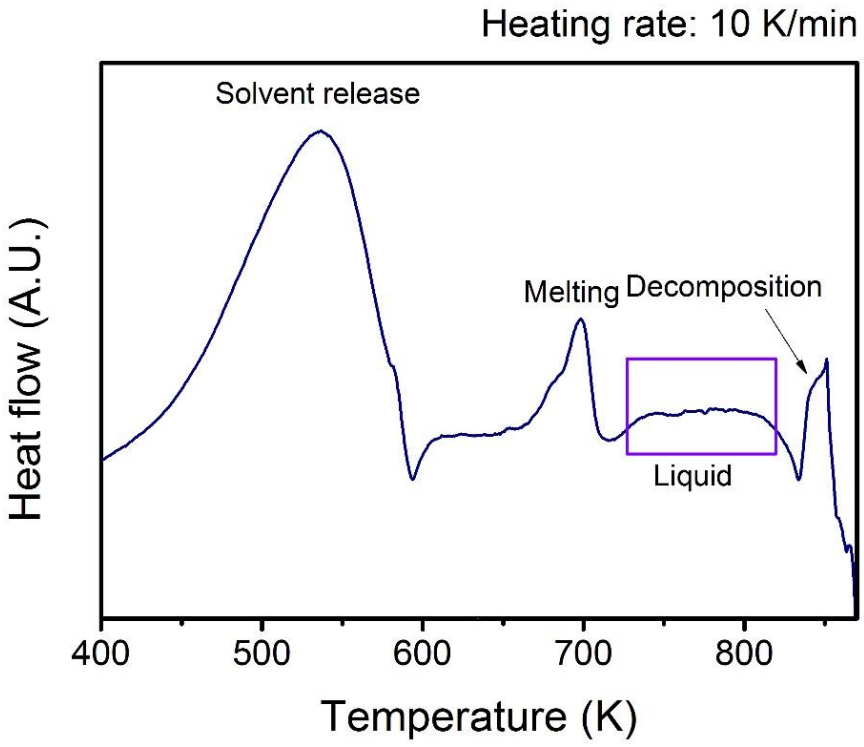

Fig. S1. Differential scanning calorimetry (DSC) measurement of crystalline ZIF-62, showing heat flow dependence on temperature during heating at 10 K/min. With increasing temperature, we first observe the release of remaining solvent after the synthesis (from the pores in the framework), then melting of ZIF-62, and finally the beginning of its decomposition. The sample is thermally stable in the liquid state in the temperature range between melting and decomposition events.

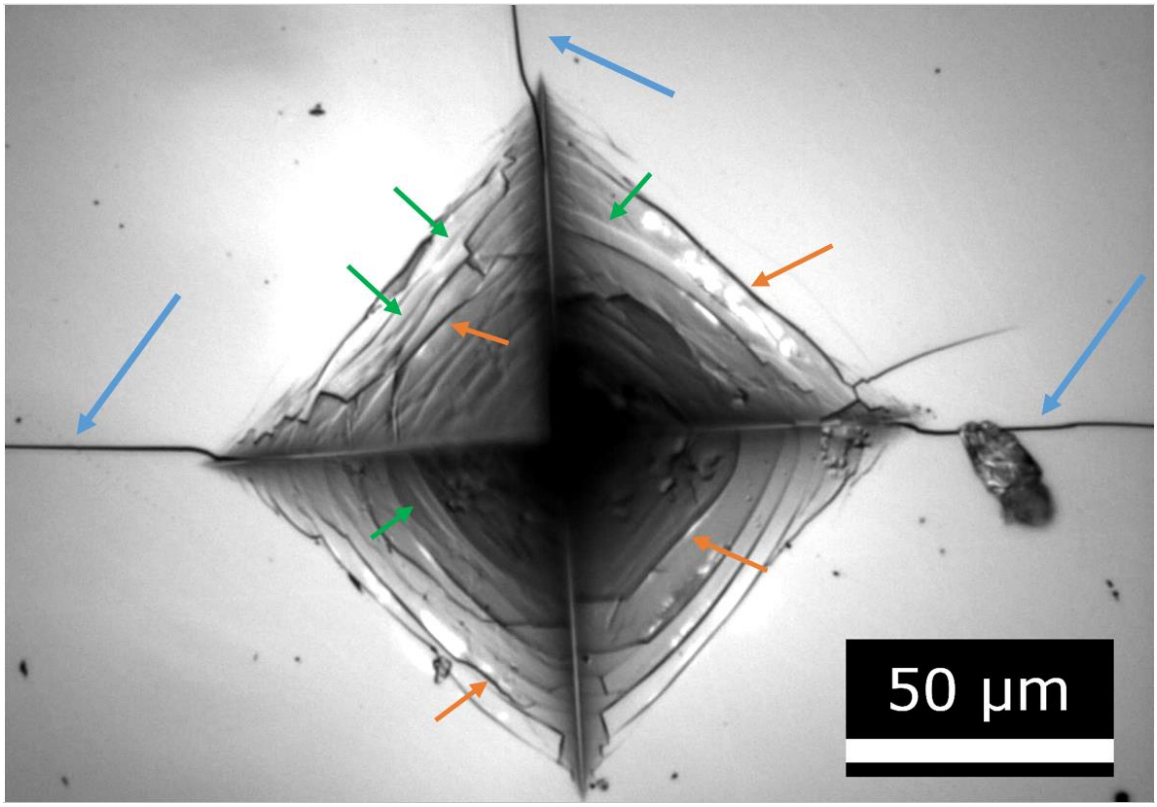

Fig. S2. Close-up on top view of indent on ZIF-62 glass. Radial crack (blue arrows) and two types of cracking features: edge cracks (examples shown with orange arrows) and shear bands (examples shown with green arrows) are visible.

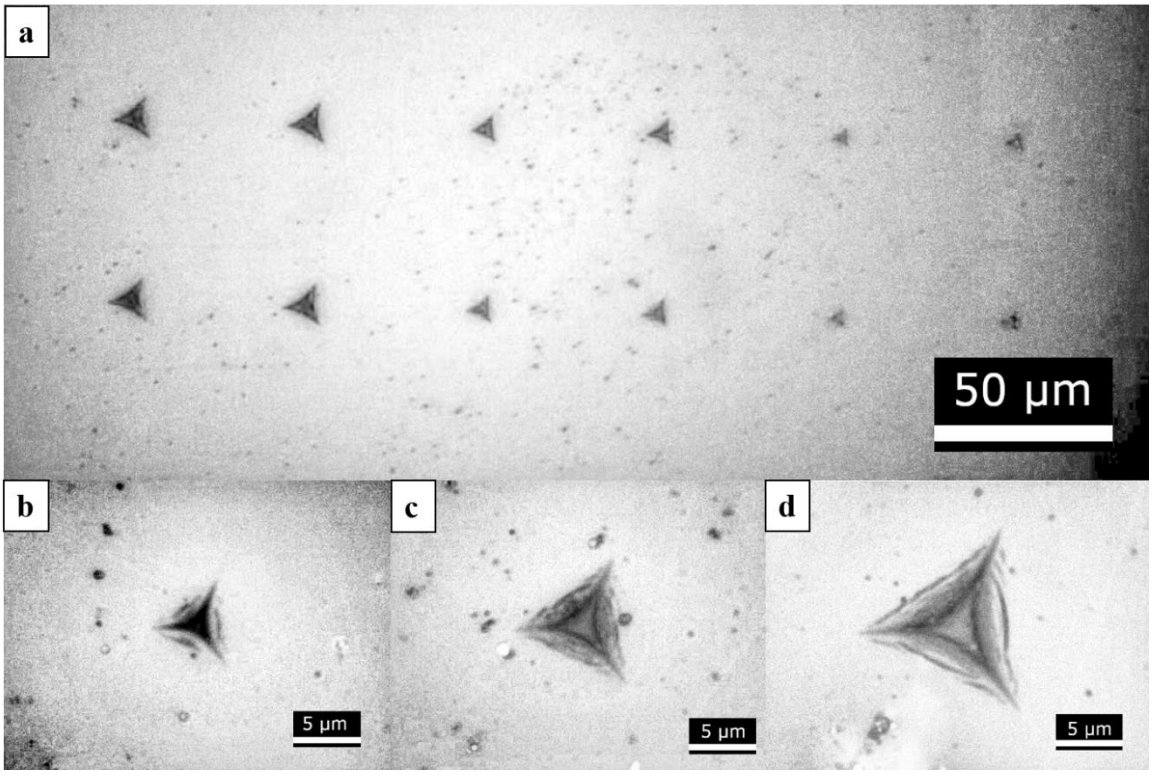

Fig. S3. Indent images obtained for nanoindentation measurements: (a) an example of an area with indents created with 3 loads used, from the highest on the left (40 mN), the middle (20 mN) to the lowest (10 mN) on the right, (b – d) close-ups of examples of indent impressions after measurements with 3 loads: (b) 10 mN, (c) 20 mN, (d) 40mN.

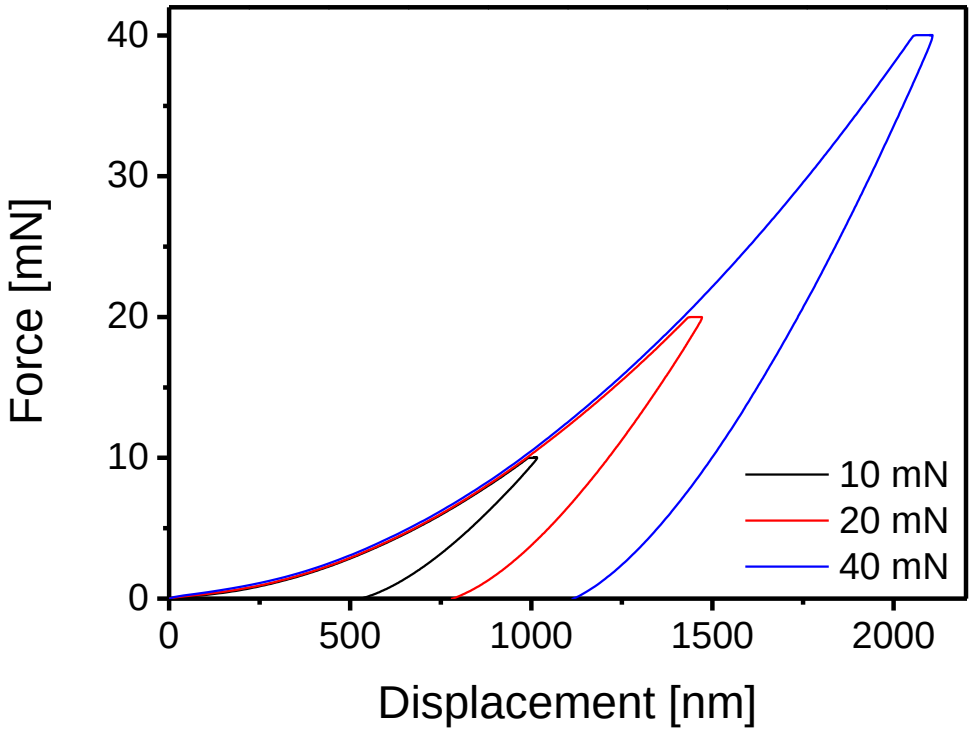

Fig. S4. Force-displacement curves for nanoindentation on ZIF glass with changing maximum load. Black line represents the curve obtained for 10 mN maximum load; red curve – 20 mN, and blue curve – 40 mN respectively.

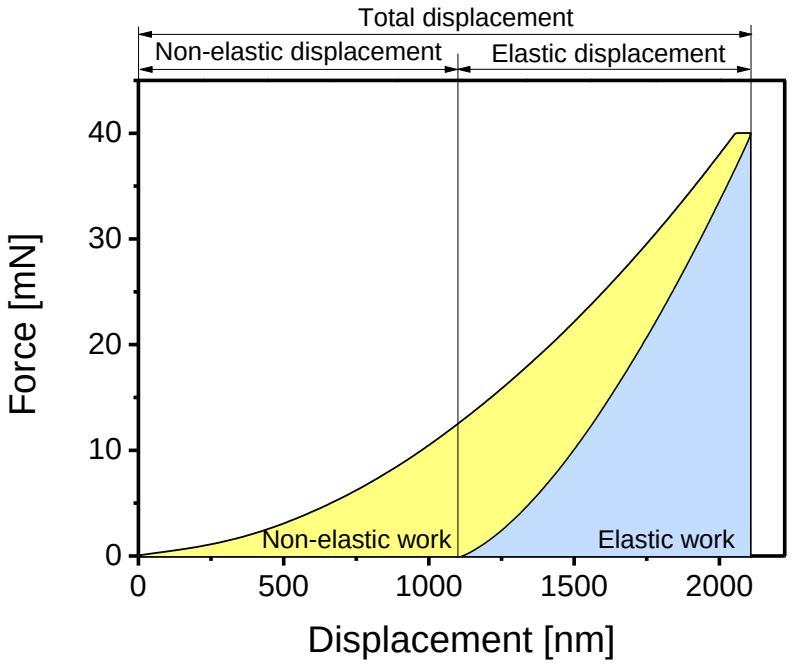

Fig. S5. Schematic representation of calculation methodology for parameters presented in Table S1. On the top of the figure, the displacement is shown; yellow area shows the non-elastic work; blue area refers to the elastic work during indentation. The shown curve has been obtained with a maximum load of 40 mN.

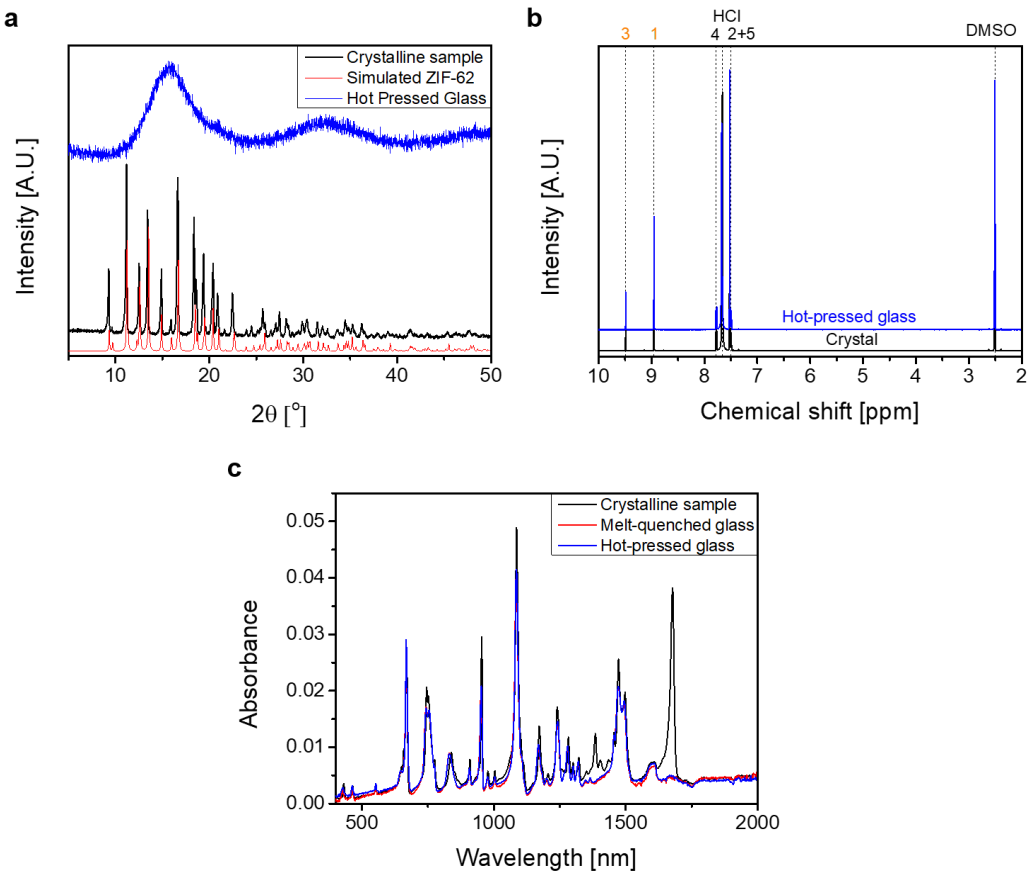

Fig. S6. Structural characterization of ZIF-62 in crystalline and glassy states. (a) P-XRD patterns for obtained ZIF-62 crystals, simulated ZIF-62 (1), and the hot-pressed glass. It is confirmed that the obtained phase is ZIF-62 and that the sample after hot pressing has a pattern characteristic for glassy samples (visible amorphous bump). (b) ^{1}H-L-NMR spectra measured for both the crystalline and hot pressed sample. The two spectra are found to be analogous to that of the crystalline sample, suggesting the amorphization does not have a pronounced effect on the organic ligands. Peaks corresponding to hydrogen 1 (imidazole) and 3 (benzimidazole) have been integrated in order to assess the ratio of ligands in the structure. By calculating the percentage of benzimidazole (where 100% is Im+bIm content), it was determined that benzimidazole accounts for around 15.1% of ligands in the crystalline sample and 15.4% of ligands in the hot-pressed glass. This suggests the ligand ratio stays nearly constant during melt-quenching under pressure. (c) FT-IR spectra obtained for the crystalline sample and both melt-quenched and hot-pressed glasses. Only some small differences are observed, as expected during amorphization. The additional peaks for the crystalline samples (around 1350-1440 cm^{-1} and at 1677 cm^{-1}) are due to the remaining solvent (DMF) in the crystals. Only small differences are seen between the two measured glasses, confirming the bonds are not changed significantly with the applied pressure during melting.

Table S1. Mechanical properties obtained from nanoindentation of the ZIF-62 glass as a function of the maximum load.

Maximum load (F_{max})	10 mN	20 Mn	40 mN
Hardness [GPa]	0.674 ± 0.007	0.641 ± 0.006	0.622 ± 0.005
Indentation modulus [GPa]	5.59 ± 0.02	5.47 ± 0.02	5.32 ± 0.03
Elastic work (unloading) [a)] [pJ]	1960 ± 20	5620 ± 20	16050 ± 50
Total work [a)] [pJ]	3640 ±160	10610 ± 100	31152 ± 80
Elastic work [a)] [%]	53.8	53.0	51.5
Elastic displacement [a)] [nm]	496 ± 6	713 ± 5	1022 ± 6
Total displacement [a)] [nm]	1019 ± 6	1473 ± 4	2116 ± 8
Elastic displacement [a)] [%]	48.7	48.4	48.3

[a)] The method for determining these properties is illustrated in Supplementary Fig. S4 in Supplementary Information.

SI References

1. R. Banerjee, *et al.*, High-throughput synthesis of zeolitic imidazolate frameworks and application to CO2 capture. *Science.* 319, 939–943 (2008).