Supplementary Information

Framework Flexibility of ZIF-8 Under Liquid Intrusion: Discovering Time-Dependent Mechanical Response and Structural Relaxation

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1. Experimental methods

1.1 Liquid intrusion tests

The liquid intrusion tests were conducted using the stainless-steel cylindrical chamber illustrated in Figure S1, driven by Instron 5582 (for 0.5 mm/min) or Instron 8872 (for 50 mm/min). 25 mg ZIF-8 powder and 0.1 mL liquid were combined in the chamber with precisely fitted sealing rings. The pistons on the chamber can be compressed by the Instron machine to apply mechanical pressure onto the ZIF-8/liquid system inside. Once the pressure has reached 56 MPa (1.58 kN), the piston reversed its direction but maintaining the speed. For the systems with higher intrusion pressure (e.g., Figure 3a), the peak pressure was increased accordingly so as to observe the complete intrusion process before unloading. The force F and displacement d data from the loading and unloading process were recorded and used to plot the P-ΔV curves. The initial length and volume of the specimen were around 4.0 mm and 0.11 mL, with a cross-sectional area of the piston A = 28.26 mm^2. The nominal pressure P is defined as $P = F/A$, and the specific volume change ΔV is defined as $\Delta V = (A \cdot d)/m$, with m being the mass of ZIF-8 powder. When glycerol or other alcohols were introduced into the liquid phase, the solution mixtures were prepared first and then combined with ZIF-8 powder in the chamber.

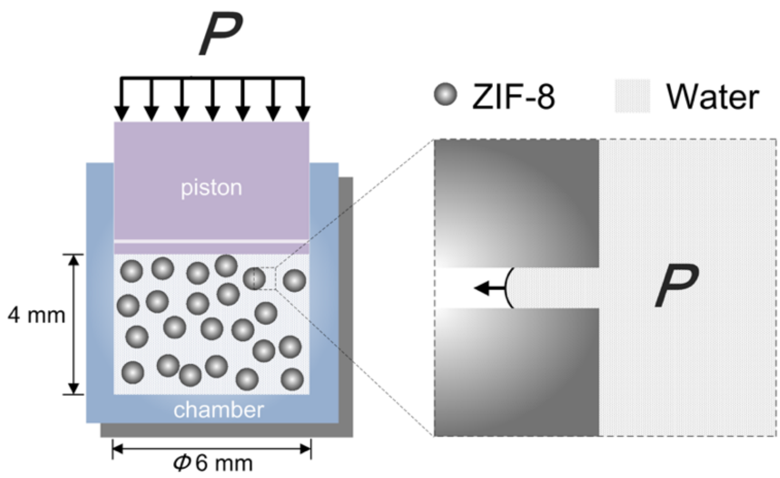

Figure S1. Schematic of the liquid intrusion setup to measure the P-ΔV curves under compression. The diameter of the piston is 6 mm.

1.2 Materials characterization

Powder X-ray diffraction (XRD) patterns were recorded on the Rigaku Miniflex 600 using CuKα radiation (15 mA and 40 kV) at a scan rate of 2°/min using a 2θ step-size of 0.01°.

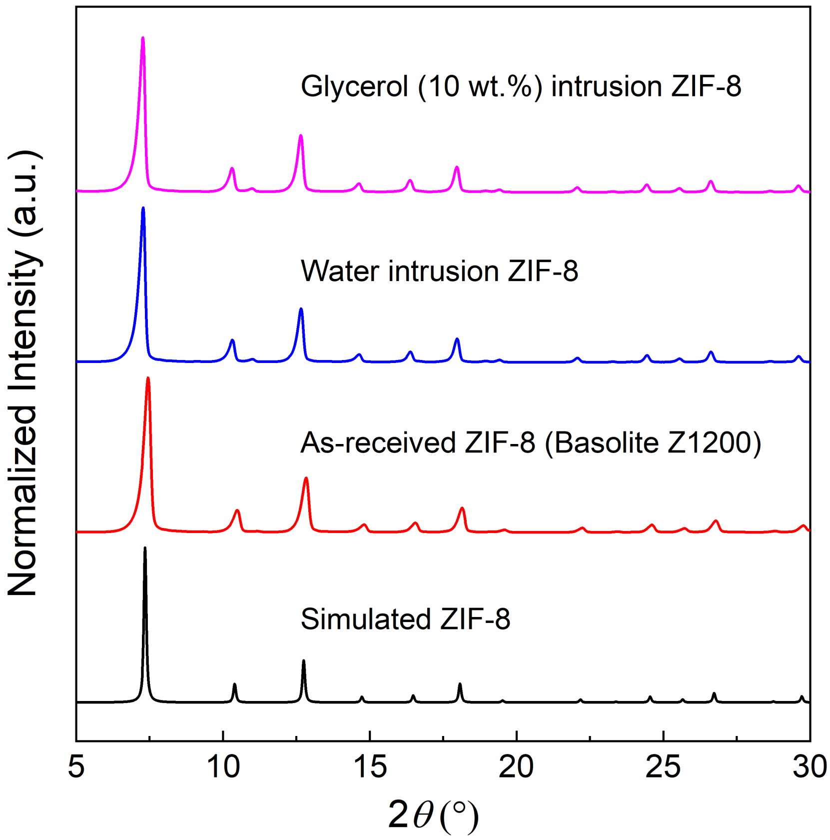

Figure S2. XRD of ZIF-8 sample in the as-received condition, ZIF-8 after water intrusion, and ZIF-8 after intrusion of 10 wt.% glycerol solution, showing the intact crystalline structure after multicycle liquid intrusion tests. The XRD data are consistent with the retained level of accessible pore volume for liquid intrusion, as evidenced from the P-ΔV curves (see Figure 1 in manuscript). The XRD intensities have been normalized (a.u.) with respect to the highest peak of each spectrum.

2. Energy dissipation analyses associated with liquid intrusion into ZIF-8

It is worth noting that the pressure-induced liquid intrusion into ZIF-8 dissipates substantial mechanical energy.[1-2] For all the liquids investigated here, their energy dissipations associated with their intrusions into ZIF-8 were calculated according to the areas enclosed by the loading and unloading curves on the P-ΔV plots (see Table S1). We found that the quasi-static intrusion of pure water into ZIF-8 can dissipate 2.98 J/g. Due to the increase of intrusion pressure along with the change of extrusion performance, the addition of glycerol enhances energy dissipation significantly, with 10 wt.% glycerol having 5.71 J/g and 50 wt.% glycerol soaring up to 12.35 J/g. Our results show that other kinds of polyhydric alcohols, i.e., ethylene glycol, erythritol and xylitol (at 10 wt.%) do not create notable changes on energy dissipations, all of which are around 3 J/g.

Table S1. Energy dissipation associated with the intrusion of various kinds of liquid into ZIF-8, for the first loading cycle under a quasi-static condition of 0.5 mm/min.

Intrusion liquid (wt.%)	Pure Water	Gly10 + Water	Gly20 + Water	Gly50 + Water	EG10 + Water	Eryt10 + Water	Xyli10 + Water
Energy dissipated (J/g)	2.98	5.71	7.58	12.35	2.97	3.04	3.15

Upon cyclic loading, the energy dissipation of water intrusion into ZIF-8 experiences a slight change due to the gate-opening phenomenon, which recovers after 24 hours of relaxation time, as shown in Figure S3(a). The intrusion of glycerol-water solutions exhibits the same trend, but the variation among different loading cycles is amplified due to the effect of glycerol molecules on the intrusion pressure and extrusion performance, and importantly, their transition from intrusion *inhibitors* to *promoters* once gate-opening is triggered by cyclic loading. As expected, this effect is enhanced by increasing the glycerol concentration (Figure S3(b)). However, at a higher loading rate (50 mm/min in Figure S3(c)), we have a relatively stable level of energy dissipation (around 4 J/g) throughout all loading cycles, due to the absence of gate-opening under a short loading duration (corresponding to a high deformation rate). Glycerol molecules are thus kept outside the framework, acting as intrusion inhibitors, and all the loading cycles have almost identical intrusion and energy dissipation performance. Similar result can be obtained by using larger molecules (erythritol and xylitol) at quasi-static conditions, as shown in Figure S3(d).

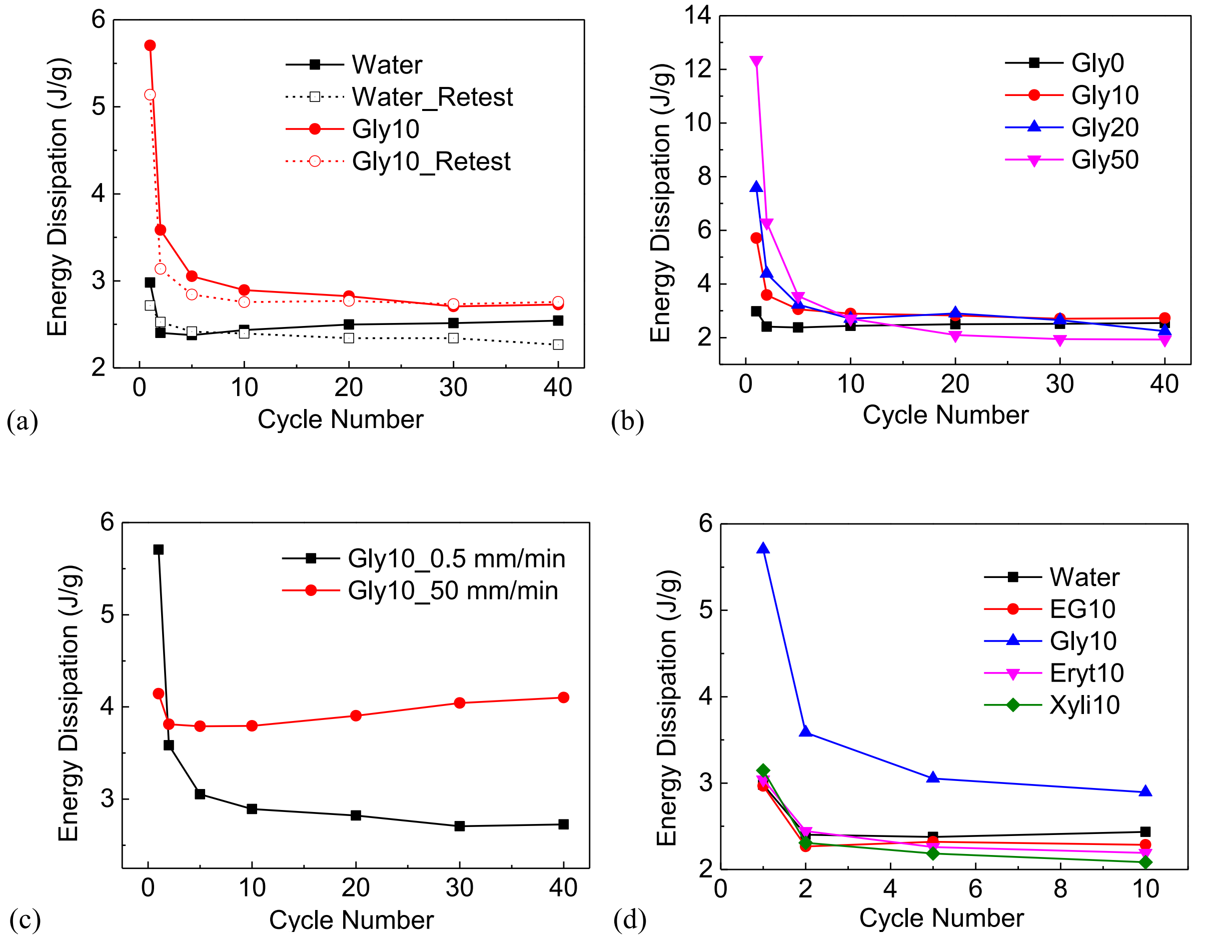

Figure S3. Mechanical energy dissipation associated with the liquid intrusion into ZIF-8 upon cyclic loading and unloading tests. (a) The quasi-static (0.5 mm/min) intrusion of pure water and 10 wt.% glycerol-water solution, showing two 40-cycle tests with a relaxation of 24h in between. (b) The quasi-static intrusion of glycerol-water solution at different concentrations. (c) The intrusion of 10 wt.% glycerol-water solution at different loading rates. (d) The quasi-static intrusion of various alcohol-water solutions (at the same concentration of 10 wt.%).

References

[1] G. Ortiz, H. Nouali, C. Marichal, G. Chaplais, J. Patarin. *Versatile energetic behavior of ZIF-8 upon high pressure intrusion–extrusion of aqueous electrolyte solutions*, J. Phys. Chem. C **118** (2014) 7321-7328.

[2] G. Ortiz, H. Nouali, C. Marichal, G. Chaplais, J. Patarin. *Energetic performances of the metal-organic framework ZIF-8 obtained using high pressure water intrusion-extrusion experiments*, Phys. Chem. Chem. Phys. **15** (2013) 4888-4891.