# Supporting Information

## Molecular Understanding for the Adsorption of Water and Alcohols in Hydrophilic and Hydrophobic Zeolitic Metal–Organic Frameworks

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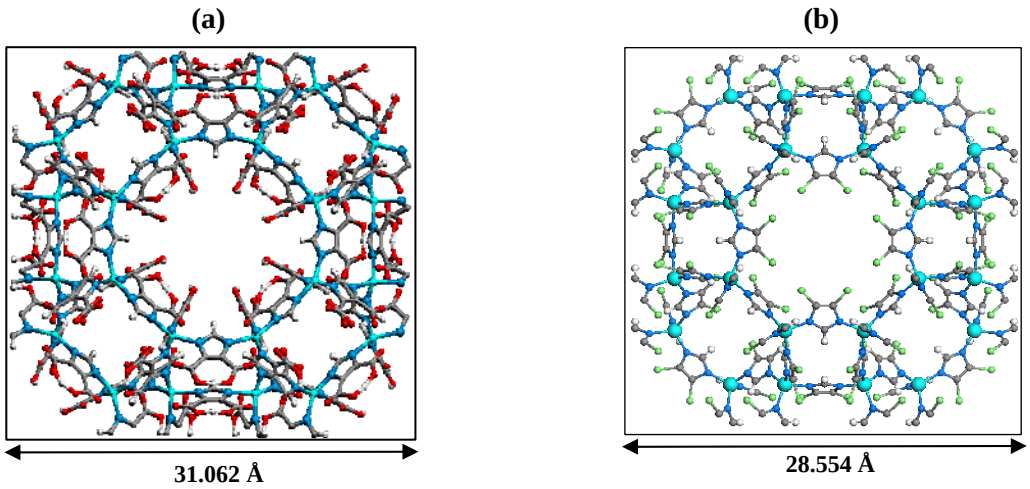


**Figure S1.** Unit cells of (a) *rho*-ZMOF and (b) ZIF-71. Color code: In/Zn, cyan; N, blue; C, grey; O, red; Cl, green; and H, white. The nonframework $Na^+$ ions in *rho*-ZMOF are not shown.

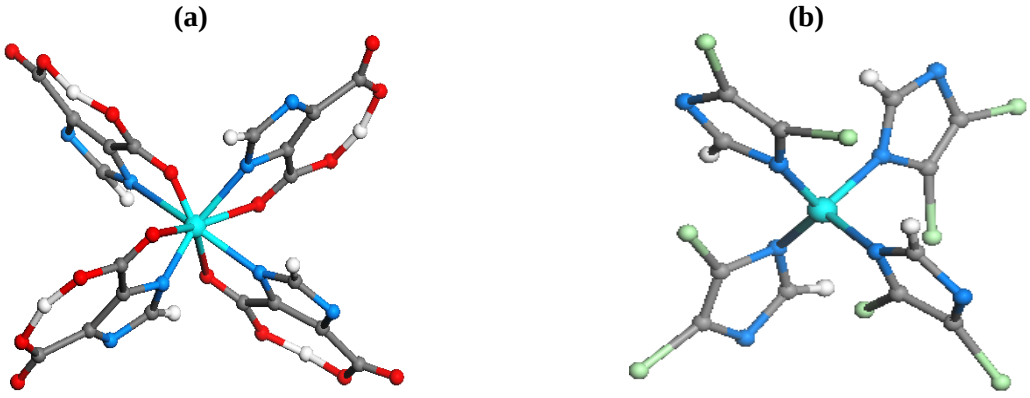


**Figure S2.** (a) Eight- and (b) four-coordinated molecular building blocks in *rho*-ZMOF and ZIF-71. Color code: In/Zn, cyan; N, blue; C, grey; O, red; Cl, green; and H, white.


**Figure S3.** Zeolite-analogue representation of (a) Na-*rho*-ZMOF and (b) ZIF-71. Two types of binding sites exist for $Na^+$ ions in Na-*rho*-ZMOF, in which site I (pink) is at the single eight-membered ring (S8MR) and site II (yellow) is in the $\alpha$-cage. The two S8MRs form a double eight-membered ring (D8MR).

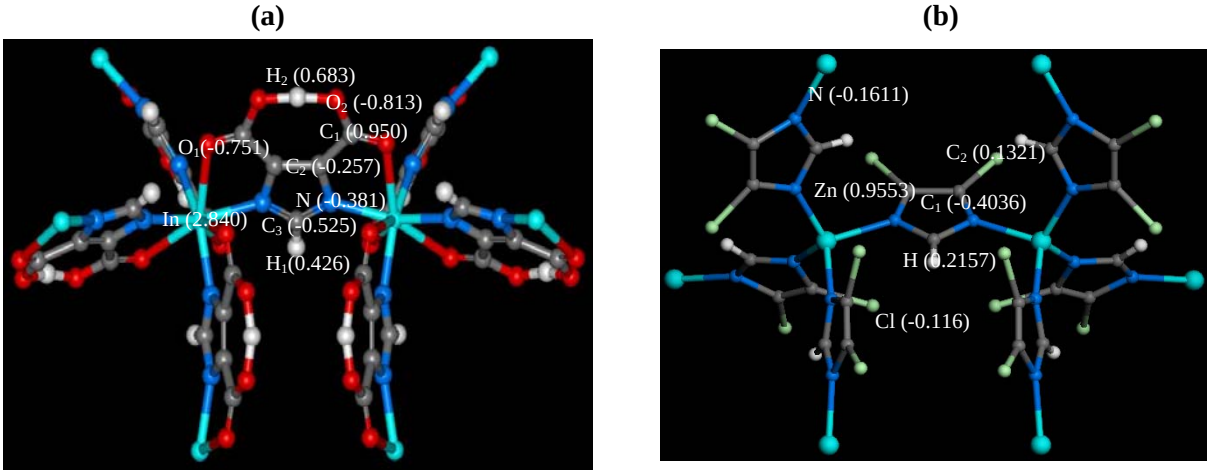


**Figure S4.** Atomic charges in the fragmental clusters of (a) *rho*-ZMOF and (b) ZIF-71. Color code: In/Zn, cyan; N, blue; C, grey; O, red; Cl, green; and H, white.

**Table S1.** Lennard-Jones parameters of the framework atoms in *rho*-ZMOF and ZIF-71.

| Atom | $\sigma$ (Å) | $\varepsilon$ (kJ/mol) |
|---|---|---|
| In | 3.976 | 2.504 |
| Zn | 2.461 | 0.519 |
| N | 3.260 | 0.288 |
| O | 3.118 | 0.251 |
| C | 3.431 | 0.439 |
| H | 2.571 | 0.184 |
| Cl | 3.516 | 0.949 |

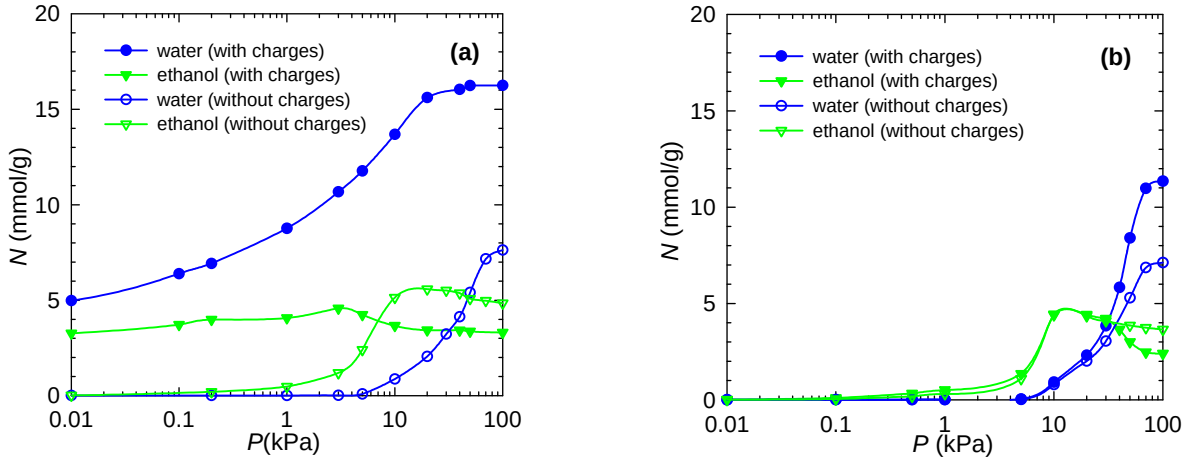


**Figure S5.** Adsorption isotherms for the equimolar mixture of water/ethanol in (a) Na-*rho*-ZMOF and (b) ZIF-71 with and without the framework charges. The framework charges have a substantial effect on adsorption in hydrophilic Na-*rho*-ZMOF, but a small effect in hydrophobic ZIF-71. The isotherms in Na-*rho*-ZMOF without the framework charges behave like in ZIF-71.