Investigating the role of solvents in metal-organic frameworks with molecular dynamic simulations

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The modular assembly of metal-organic frameworks (MOFs) from metal nodes and organic linkers offers unprecedented opportunities for materials design.[1] Yet, this flexibility also presents a major challenge: polymorphism,[2] where the same building blocks can form multiple distinct crystal structures with differing properties. Zeolitic imidazolate frameworks (ZIFs), based on unsubstituted imidazole, offer an excellent model system for studying this phenomenon, with over 18 experimentally reported topologies[3] for Zn**Im**$_2$. Recently, we showcased[4] that mechanochemical synthesis, combined with the use of various structure-directing liquid additives (LAs), can selectively access 12 unique polymorphs of Zn**Im**$_2$. In this study, periodic density functional theory (DFT) calculations were employed to demonstrate how various LAs can stabilize each Zn**Im**$_2$ via thermodynamics; however, DFT inherently provides only static snapshots of energy landscapes, making it difficult to account for dynamic, solvent-driven templating effects that is crucial to specific ZIF polymorph formation.

To address this limitation, we now apply molecular dynamics (MD) simulations to capture the dynamic interactions between ZIFs and LAs. Our methodology[5,6] involves constructing Zn**Im**$_2$ supercells first, followed by populating the pores with LA molecules. Consequently, MD simulations were performed to evaluate the energetic effects of guest incorporation over time. By systematically simulating all experimentally used LAs across experimentally obtained ZIFs with different topologies, we can quantify dynamic stabilization effects and better rationalize the experimental outcomes of mechanochemical synthesis. These results highlight how MD simulations, in conjunction with the previously shown[4] DFT calculations, can provide more insights into solvent-mediated polymorph selection and open pathways for more computationally-aided MOF design strategies.

[1] Ejsmont, A., Andreo, J., Lanza, A., Galarda, A., Macreadie, L., Wuttke, S.; Canossa, S.; Ploetz, E.; Goscianska, J. (2021). *Coord. Chem. Rev.*, **430**, 213655.

[2] Aulakh, D., Varghese, J. R., Wriedt, M. (2015). *Inorg. Chem.*, **54** (17), 8679–8684.

[3] Guo, S., Li, H.-Z., Wang, Z.-W., Zhu, Z.-Y., Zhang, S.-H., Wang, F., Zhang, J. (2022). *Inorg. Chem. Front.*, **9** (9), 2011–2015.

[4] Brekalo I., Lisac K., Ramirez J. R., Pongrac P., Xu Y., Ferguson M., Marrett J. M., Arhangelskis M., Friščić T., Holman K. T. (2025). *ChemRxiv*, Preprint, DOI: 10.26434/chemrxiv-2025-65t1h.

[5] Ejsmont, Thompson, A. P., Aktulga, H. M., Berger, R., Bolintineanu, D. S., Brown, W. M., Crozier, P. S., in 't Veld, P. J., Kohlmeyer, A., Moore, S. G., Nguyen, T. D., Shan, R., Stevens, M. J., Tranchida, J., Trott, C., Plimpton, S. J. (2022). *Comput. Phys. Comm.*, **271**, 108171.

[6] Weng, T., Schmidt, J. R. (2019). *J. Phys. Chem. A.*, **123** (13), 3000–3012.