

Enhancing of CO uptake in Metal-Organic Frameworks by linker functionalization; A Multi-scale theoretical study

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MOFs are one of the most promising materials for gas adsorption, owing their big scientific interest to their intrinsic properties such as their large surface areas and porosity. The purpose of this study was to propose new materials for high Carbon Monoxide (CO) adsorption. Initially, the interaction strength of CO with a set of 42, strategically selected, functionalized benzenes was calculated in the MP2/6-311++G** level of theory [1]. Our results reveal that phenyl hydrogen sulfate (-OSO₃H) showed the highest interaction with CO (-19.5 kJ/mol), approximately 3 times stronger compared with the unfunctionalized benzene (-5.3 kJ/mol) [2]. Moreover, the three top-performing functional groups (-OSO₃H, -OPO₃H₂, -SO₃H) were selected to modify the organic linker of IRMOF-8 and test their ability to capture CO at 298K for a wide pressure range. Our Grand Canonical Monte Carlo (GCMC) simulations showed a significant increase in the CO uptake in the functionalized MOFs, compared with the parent IRMOF-8. Distinctive is that for the volumetric uptake a 60x increase was observed at 1 bar and 2x at 100 bar. The proposed functionalization strategy can be applied for improving the CO uptake performance not only in MOFs but also in various other porous materials.

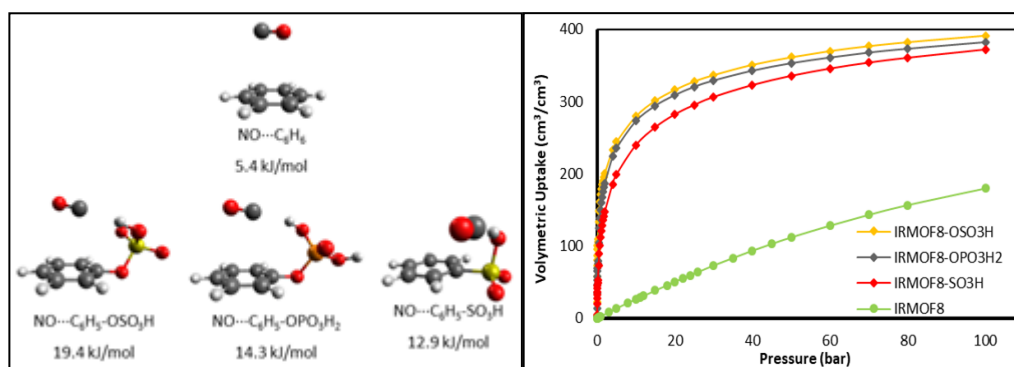


Figure 1: Left: Optimized geometries and the corresponding binding energies of the C₆H₅-X (X: -H, -OSO₃H, -OPO₃H₂, -SO₃H) calculated at the MP2/6-311++G** level of theory, Right: Absolute Volumetric isotherms for IRMOF8 and IRMOF8-n (n: -OSO₃H, -OPO₃H₂, -SO₃H) at T=298 K and pressure ranges up to 100 bar

References

- [1] C. Møller and M. S. Plesset, Phys. Rev. 46, 618 (1934).
- [2] C.G. Livas, E. Tylianakis, G.E. Froudakis Chemistry 4, 603-614 (2022).

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