

Synthesis of UiO-66 Metal Organic Frameworks

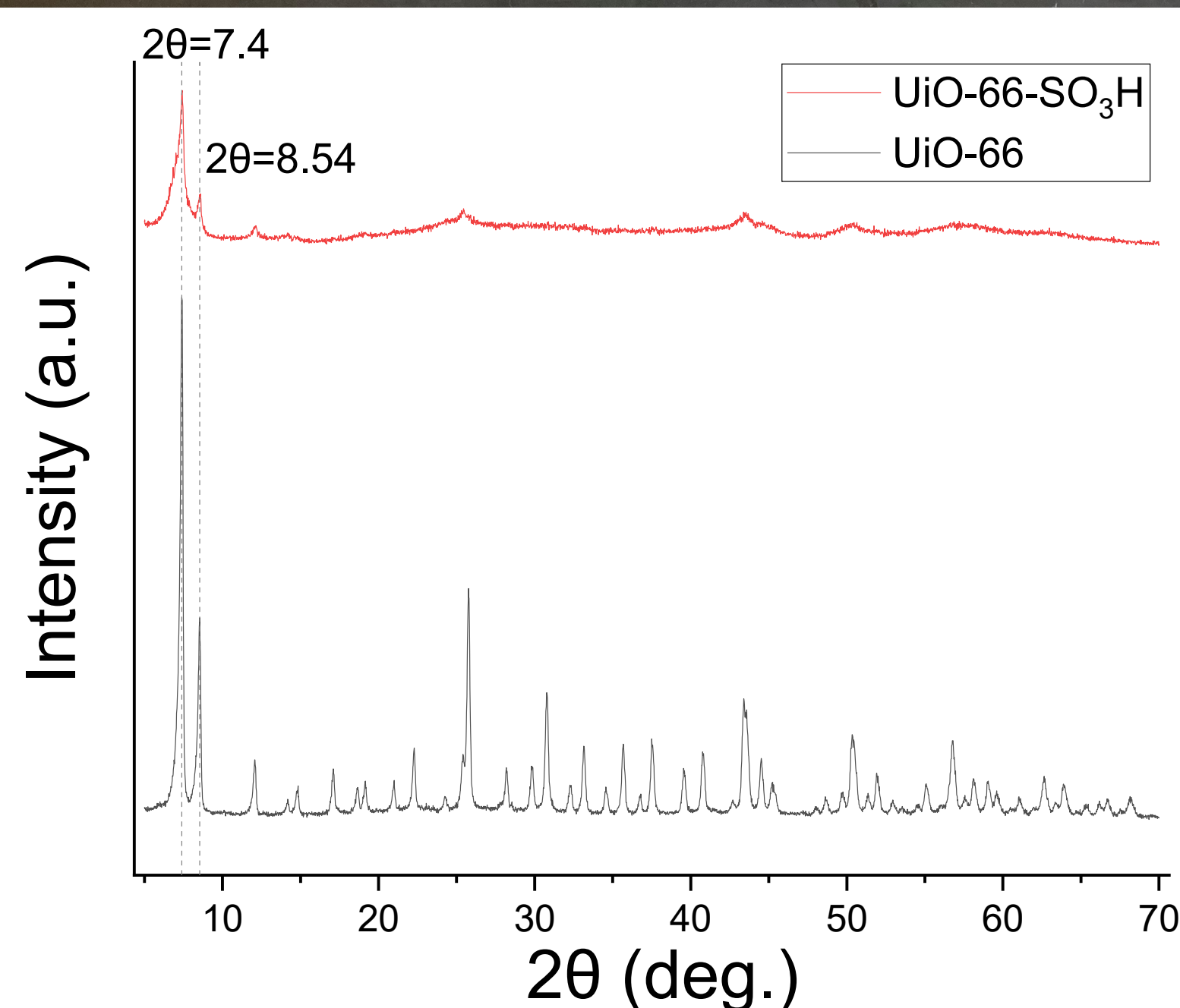
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Introduction

- Metal organic frameworks are composed of a regular array of positively charged metal ions surrounded by organic molecules called linkers. The metal ions act as nodes which bind the linkers together. The structure of a MOF is hollow, which results in a large internal surface area.
- MOFs are currently being studied for CO₂ capture based on its structure, stability, selectivity, and excellent adsorption capacity. In an industrial environment with several other gases, these characteristics make MOFs a viable option.
- Two MOF candidates were synthesized and analyzed: one established for over a decade, UiO-66, and UiO-66-SO₃H, a newer MOF with minimal research for CO₂ capture.

Experimental

- UiO-66 was synthesized by dissolving equimolar amounts of ZrCl₄ and terephthalic acid in dimethylformamide or DMF. This mixture was then heated for 24 hours at 120°C. The resulting solid was dissolved within DMF, centrifuged several times, and dried overnight in a vacuum oven at 90°C.
- UiO-66-SO₃H was synthesized by mixing ZrCl₄ and 2-sulfoterephthalic acid where both of which were previously dissolved in DMF. 1 mL of acetic acid was added, and the mixture was placed into an autoclave and heated at 120°C for 40 hours. The precipitate was then centrifuged within DMF twice and methanol once, and placed in a vacuum oven overnight at 100°C.
- The final product: UiO-66 is on the left and UiO-66-SO₃H is on the right.

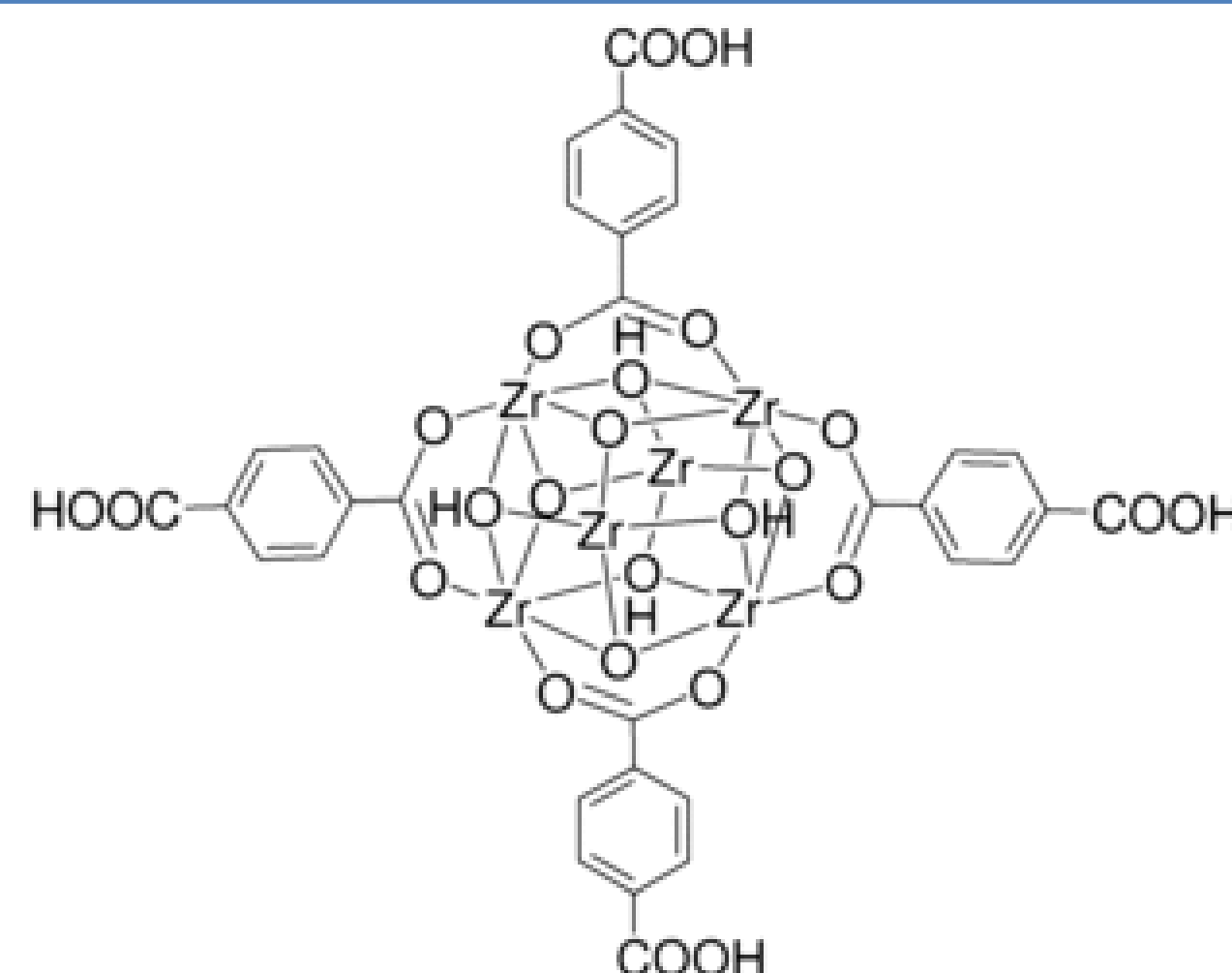


X-Ray Diffraction (XRD):

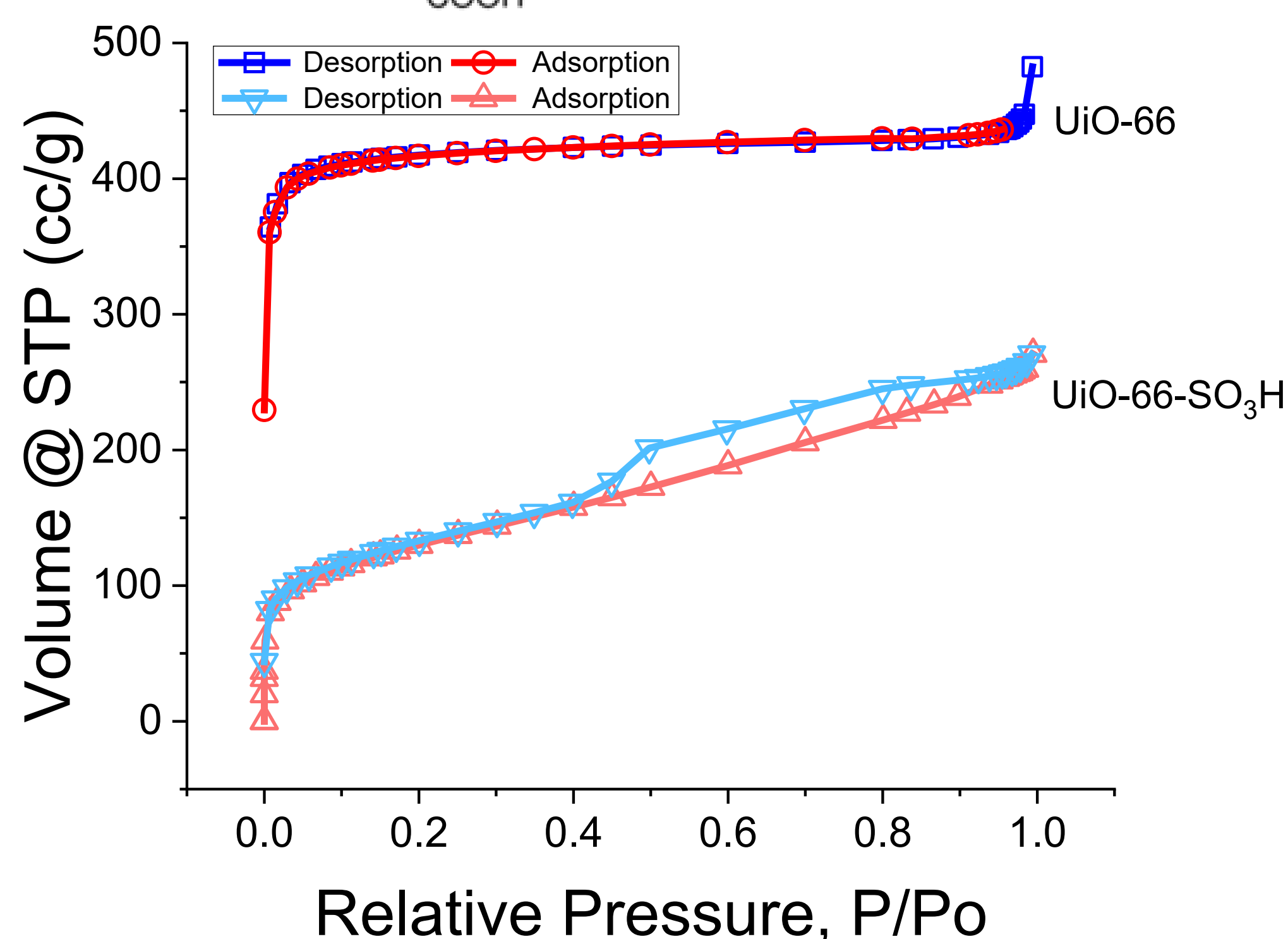
- The XRD data for UiO-66 and UiO-66-SO₃H was measured between 5° and 70° at a rate of .5° min.
- The peaks measured are consistent with the literature values, and the similarity of the first two peaks demonstrate that UiO-66-SO₃H is crystalline and maintained the UiO-66 structure.

References

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2. Olorunoyi, J. F., Liu, T., Ho, C.-K., Li, C.-Y. V., & Chan, K.-Y. (2021). Imparting UiO-66 with fast cation exchange property via sulfonating organic linkers for selective adsorption. *Separation and Purification Technology*, 260, 118219. <https://doi.org/https://doi.org/10.1016/j.seppur.2020.118219>
3. <https://www.strem.com/catalog/v/40-1108/85/zirconium>



Structure of UiO-66. UiO-66-SO₃H has the SO₃H molecule attached to each benzene ring.



Sample	DFT Surface area (m ² /g)	DFT Pore Volume (cc/g)	DFT Pore Radius (Å)
UiO-66	1362	.60	3.6
UiO-66-SO ₃ H	356.5	.37	7.0

- The two graphs above are N₂ adsorption and desorption isotherms and are used in calculating the data above.

Density Functional Theory (DFT)

- The tabular data is derived from DFT, an analysis method based on molecular modeling, and provides accurate values for microporous materials, the material type of the MOFs.

Conclusions

- UiO-66 and UiO-66-SO₃H were successfully synthesized.
- The significant reduction in surface area and pore volume is plausibly due to the sulfonation of UiO-66.

Future Research

- Varying the molar ratio of acetic acid to ZrCl₄ in the UiO-66-SO₃H synthesis has yet to have been done, and its impact undetermined.
- This new UiO-66-SO₃H could be superior in CO₂ capture applications, potentially due to improved adsorption capabilities from this change in the molar ratio.

Acknowledgements

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