MSc Departmental Seminar – Chem 6001

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Thursday, November 21 2024, at 1:00p.m. (Rm: CSF-1302)

Title:

Puzzling Together the Self-Assembly of Metal-Organic Frameworks: An Exercise in ^{2}H-NMR

Abstract:

Metal-organic frameworks (MOFs) are highly porous materials formed via the self-assembly of organic bridging ligands to metallic nodes. MOFs have many potential applications in areas such as separation[1,2] and catalysis,[3,4] and yet very little is understood about their self-assembly. Time-resolved in-situ ^{1}H-NMR would be the ideal methodology for following MOF synthesis, but the deuterated form of the prototypical solvent for MOF formation (*N,N*-dimethylformamide; DMF)[5] is costly in its deuterated form (DMF-d_7). To prepare and perform 10 ^{1}H-NMR experiments under reasonable analytical precision, the price of DMF-d_7 alone would exceed $4000. As such, this analytical method has been underutilized.

Time resolved solution-phase deuterium NMR (^{2}H-NMR) would alleviate these challenges by allowing the use of regular protonated solvents, and only requiring small amounts of deuterated analyte(s). Approximately 800 MOFs use 1,4-benzenedicarboxylate (BDC^{2-}) as their organic linker,[6] making BDC-containing MOFs ideal candidates for time-resolved NMR analysis. The cost of using H_2BDC-d_4 for ^{2}H-NMR is orders of magnitude lower than that of DMF-d_7 for equivalent ^{1}H-NMR experiments.

In this work, solution-phase ^{2}H-NMR was utilized to follow the self-assembly of UiO-66 (a zirconium and BDC-based MOF). The synthesis of UiO-66 can be influenced by the use of non-bridging carboxylic acids (coordinating modulators) or other strong acids (non-coordinating modulators);[7] this work looks at acetic acid, hydrochloric acid, and benzoic

acid. By utilizing and following either $H_2BDC\text{-}d_4$, for information regarding linker consumption, or D_2O, for information regarding acidity and chemical exchange, defining features of the synthesis were observed. Between different rate constants, induction periods, changes in acidity (or lack thereof), and non-NMR experiments such as porosimetry and time resolved solid formation, a broader picture of the mechanism of self-assembly of UiO-66 was elucidated.

References:

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(2) Daglar, H.; Keskin, S. Recent Advances, Opportunities, and Challenges in High-Throughput Computational Screening of MOFs for Gas Separations. *Coordination Chemistry Reviews* **2020**, *422*, 213470. https://doi.org/10.1016/j.ccr.2020.213470.

(3) A. Goetjen, T.; Liu, J.; Wu, Y.; Sui, J.; Zhang, X.; T. Hupp, J.; K. Farha, O. Metal–Organic Framework (MOF) Materials as Polymerization Catalysts: A Review and Recent Advances. *Chemical Communications* **2020**, *56* (72), 10409–10418. https://doi.org/10.1039/D0CC03790G.

(4) Li, L. Titanium-Based MOF Materials: From Crystal Engineering to Photocatalysis. *Small Methods* **2020**, *4*. https://doi.org/10.1002/smtd.202000486.

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(6) Cambridge Crystallographic Data Centre. *Cambridge Structural Database*. https://library.bath.ac.uk/chemistry-software/ccdc (accessed 2024-06-30).

(7) Forgan, R. S. Modulated Self-Assembly of Metal–Organic Frameworks. *Chemical Science* **2020**, *11* (18), 4546–4562. https://doi.org/10.1039/D0SC01356K.