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Influence of Linker Design in Geometrically Frustrated Reticular Materials

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Covalent organic frameworks (COFs) are a class of reticular materials known for their tailorable pores and crystallinity, which results from the careful nucleation of monomers forming elongated layers that stack horizontally. Geometric frustration occurs when building blocks can't fit together perfectly due to conflicting interactions. This prevents the formation of a uniform structure, as multiple incompatible arrangements are favoured simultaneously, making it impossible to propagate a single preferred pattern throughout the system [1]. To introduce structural complexities and study these frustrated materials in more details, we planned on synthesizing a linker which might induce Geometric frustration in its respective materials.

Geometric frustration, introduced by using incompatible symmetries, affects the stability and crystallinity of COFs. This study highlights the challenges and potential of incorporating geometric frustration in COFs, offering insights into their design, synthesis, and characterization. In this study, three new COFs (THPD, THCH, and THBZ) were synthesized using a common aldehyde linker (THAL) combined with three different amine linkers of varying flexibility. The flexibility of the amine linkers introduces internal strain, leading to rapid decomposition as observed in the PXRD. The peculiar 72-degree angle between each connectivity distinguishes it from a typical C4 linker.

We also attempted to synthesize Metal organic frameworks using an analogous thiophene based carboxylic acid linker. So far, we synthesized an interesting cobalt-based MOF using a bipyridine linker as a pillar linker. Here, the angles between each connectivity do not follow the same order as the linker alone. This might be due to the geometric frustration that causes the distortion in linker connectivity in this Co-based MOF. This distortion in the SBU was previously reported in the Cu-based MOF using a pseudo C5 linker named PLH5 [2]. This study explores the synthesis and characterization of covalent organic frameworks (COFs) and metal-organic frameworks (MOFs) with geometric frustration, highlighting the challenges and

potential of incorporating incompatible symmetries to induce structural complexities and internal strain.

References:

1 [1] Grason, G. M. **2016**, *J. Chem. Phys.*, 145 (11), 110901.

2 [2] Haase, F.; Craig, G. A.; Bonneau, M.; Sugimoto, K.; Furukawa, S. **2020,** *J. Am. Chem. Soc.*, 142 (32), 13839–13845.