MS33-P01 | TUNABLE POLAR LINKER DYNAMICS IN METAL-ORGANIC FRAMEWORKS

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Among the numerous interesting properties of metal–organic frameworks (MOFs), the rotational flexibility afforded by the organic linkers is especially captivating, and has been shown to drastically impact gas adsorption/separation.[1] The use of linkers with polar side groups is particularly interesting, since the dynamics of the resulting rotors could in principle be controlled by an external electric field.[2] Nevertheless, few studies of functionalized linker mobility are available,[3] and the techniques that have been used lack specificity, amounting to an incomplete understanding of the type of motions and the effect of different functionalities. In this work, we present the first comprehensive characterization of linker rotation dynamics in the amino- and nitro-functionalized forms of the renowned MOF MIL-53.

A combined experimental-computational study including broadband dielectric spectroscopy and density functional theory showed that the amine-functionalized linkers are mostly static within the framework, while the nitro-functionalized linkers undergo rotational motions. Both behaviors differ drastically from the dynamics observed in unfunctionalized MIL-53, where phenylene rings perform complete rotations about their axis. The functionalization of MOF linkers thus proves to be an effective strategy to tune their framework dynamics, which could provide a handle to tune several properties of practical importance for future applications.

[1] Yan et al. JACS 139, 13349 (2017).
[2] Namsani & Yazaydin O. Mol. Syst. Des. Eng. 3, 951 (2018).
[3] Damron et al. Angew. Chemie 57, 8678 (2018). Devautour-Vinot et al. Chem. Mater. 24, 2168 (2012). Morris et al. J. Mol. Struct. 1004, 94–101 (2011). Winston et al. Phys. Chem. Chem. Phys. 10, 5188–5191 (2008).