

Instilling flexibility in rigid MOFs through strain field engineering: A case study on crumple zones to relieve stress in UiO-66

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Traditionally, metal-organic frameworks (MOFs) and other framework materials are classified as either flexible when they can undergo large-amplitude crystalline-to-crystalline transitions, or rigid otherwise.¹ However, this historical picture does not take into account the spatial heterogeneity in MOFs, such as those introduced at the crystal surface or near defect regions.^{2,3} This heterogeneity may introduce flexibility in otherwise rigid MOFs, as well as rigidity in otherwise flexible MOFs, explaining for instance the growing number of crystal-size dependent phenomena.^{4,5} The question remains, however, how to design a MOF's local flexibility or rigidity for specific applications.

Herein, we present the concept of strain field engineering to quantify the impact building block alterations have on the local and overall flexibility in MOFs as well as to design MOFs for specific applications. Strain fields are local and time-dependent tensor quantities that describe a material's deviation from its equilibrium structure under external triggers, thereby constituting an important fingerprint for (local) flexibility. As a case study, we focus on UiO-66,⁶ a material that can withstand pressures of 1.5 GPa and above in its defect-free form.^{7,8,9} Any treatment exceeding this pressure leads to an almost complete loss of crystallinity and porosity. However, this rigid behaviour can be fundamentally impacted by introducing linker vacancies in such a way as to introduce shear-susceptible crumple zones in the material. While this lowers the pressure the strain-engineered material can withstand before undergoing a phase transition, the induced transition no longer leads to a total loss of crystallinity and porosity. Instead, the crumple zones introduce flexibility in the material and spatially localise the externally applied strain so that the crystallinity and porosity of the

material is retained locally. As a result, the here designed material can be used under harsher conditions than its regular counterpart.

References

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