

*Computational exploration of interesting gas adsorption/separation in MOFs*Renjith S. Pillai¹, Guillaume Maurin¹¹Institut Charles Gerhardt Montpellier UMR 5253 CNRS UM ENSCM, Université Montpellier, Montpellier, France
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Adsorption-based phenomena are important in gas separations, such as the treatment of greenhouse-gas and toxic-gas pollutants, and in water-adsorption-based heat pumps for solar cooling systems. The ability to tune the pore size, shape and functionality of crystalline porous coordination polymers--or metal-organic frameworks (MOFs)--has made them attractive materials for such adsorption-based applications. The flexibility and guest-molecule-dependent response of MOFs give rise to unexpected and often desirable adsorption phenomena. Common to all isothermal gas adsorption phenomena, however, is increased gas uptake with increased pressure. Here we report our computational approach that combined with a series of advanced experimental tools evidenced a negative gas adsorption behaviour of a MOF (DUT-49) that is, spontaneous desorption of gas (methane and n-butane) occurs during pressure increase in a defined temperature and pressure range controlled by a sudden hysteretic structural deformation and pore contraction of the MOF, which releases guest molecules. These findings may enable technologies using frameworks capable of negative gas adsorption for pressure amplification in micro- and macroscopic system engineering [1].

We further report an unprecedented capture of N₂ for both natural gas upgrading and air separation using a mesoporous Metal-Organic Framework material containing accessible Cr(III) sites. A combination of advanced experimental and computational tools revealed that the separation mechanism for both N₂/CH₄ and N₂/O₂ gas mixtures is driven by the presence of these unsaturated Cr(III) that allows a much stronger binding of N₂ vs CH₄ and O₂. This concept opens new horizons to address several challenges in chemistry, such as the removal of nitrogen or the design of heterogeneous biomimetic catalysts through nitrogen fixation [2].

[1] Krause, S. et al. (2016) Nature 532, 348-352.

[2] Yoon, J.W. et al. (2017) Nat. Mater., accepted.

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