Gas adsorption and separation: tuning the channel electrostatics for CO_2.

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Metal-Organic frameworks (MOFs) and porous molecular materials represent a new platform for achieving and exploring high-performance sorptive properties and gas transport. The key lies in the modular nature of these materials, which allows for *tuning and functionalization towards improved gas capture*.

Self-assembly of polyfunctional molecules containing multiple charges, namely, tetrahedral tetra-sulfonate anions and bi-functional linear cations, resulted in a permanently porous crystalline material in which the channels are decorated by double helices of electrostatic charges that governed the association and transport of CO_2 molecules (Fig. 1). These channels *electrostatically compliment the CO_2 molecules* and forms strong interactions of 35 kJ mol^{-1}, ideal for CO_2 capture/release cycles.[1]

The CO_2 adsorption properties were modulated for an isoreticular series of Fe-MOFs by varying the decoration of fluorine atoms within their channel (Fig. 2). A host of complementary experimental and computational techniques gives a holistic view of the host-CO_2 properties towards the potential selective removal of CO_2 from other gases. GCMC and DFT were employed for a detailed description of the CO_2 diffusion and interactions in the porous materials. CO_2–matrix adsorption enthalpies of 33 kJ mol−1 was accurately measured *in-situ* by simultaneous acquisition of micro-calorimetric and volumetric-isotherm data. *Direct measurements of adsorption heats are not common and such data helps to validate mathematical models and protocols for sorption-derived adsorption enthalpies.* [2]

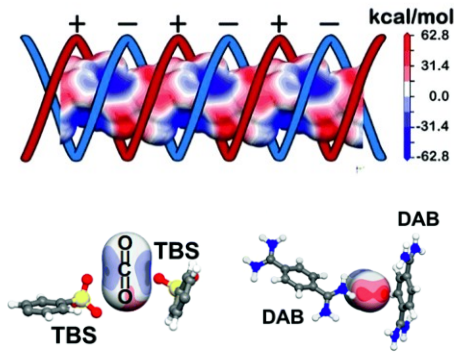

Figure 1. Channel with helical positive and negative electrostatics and the interactions of such a channel with CO_2.

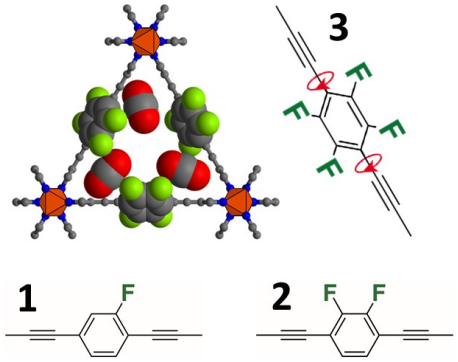

Figure 2. Fe-MOF triangular channels decorated by fluorine atoms and occupied with CO_2. The three different ligand spacers with increasing number of fluorine atoms are shown.

[1] Xing, G.; Bassanetti, I.; Bracco, S.; Negroni, M.; Bezuidenhout, C.; Ben, T.; Sozzani, P.; Comotti, A., *Chemical Science* **2019,** *10* (3), 730-736.

[2] Perego, J.; Bezuidenhout, C. X.; Pedrini, A.; Bracco, S.; Negroni, M.; Comotti, A.; Sozzani, P., *Journal of Materials Chemistry A* **2020,** *8* (22), 11406-11413.

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