Cooperative gas adsorption without a phase transition in metal-organic frameworks

Cooperative adsorption of gases by porous frameworks permits more efficient uptake and removal than does the more usual non-cooperative (Langmuir-type) adsorption. Cooperativity, signaled by a step-like isotherm, is usually attributed to a phase transition of the framework. However, the class of metal-organic frameworks mmen-M_2(dobpdc) exhibit cooperative adsorption of CO_2 but show no evidence of a phase transition. Here we show how cooperativity emerges in these frameworks in the absence of a phase transition. We use a combination of quantum and statistical mechanics to show that cooperativity results from a sharp but finite increase, with pressure, of the mean length of chains of CO_2 molecules that polymerize within the framework. Our study provides microscopic understanding of the emergent features of cooperative binding, including the position, slope and height of the isotherm step, and indicates how to optimize gas storage and separation in these materials.