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## Tiny pores turning the tide

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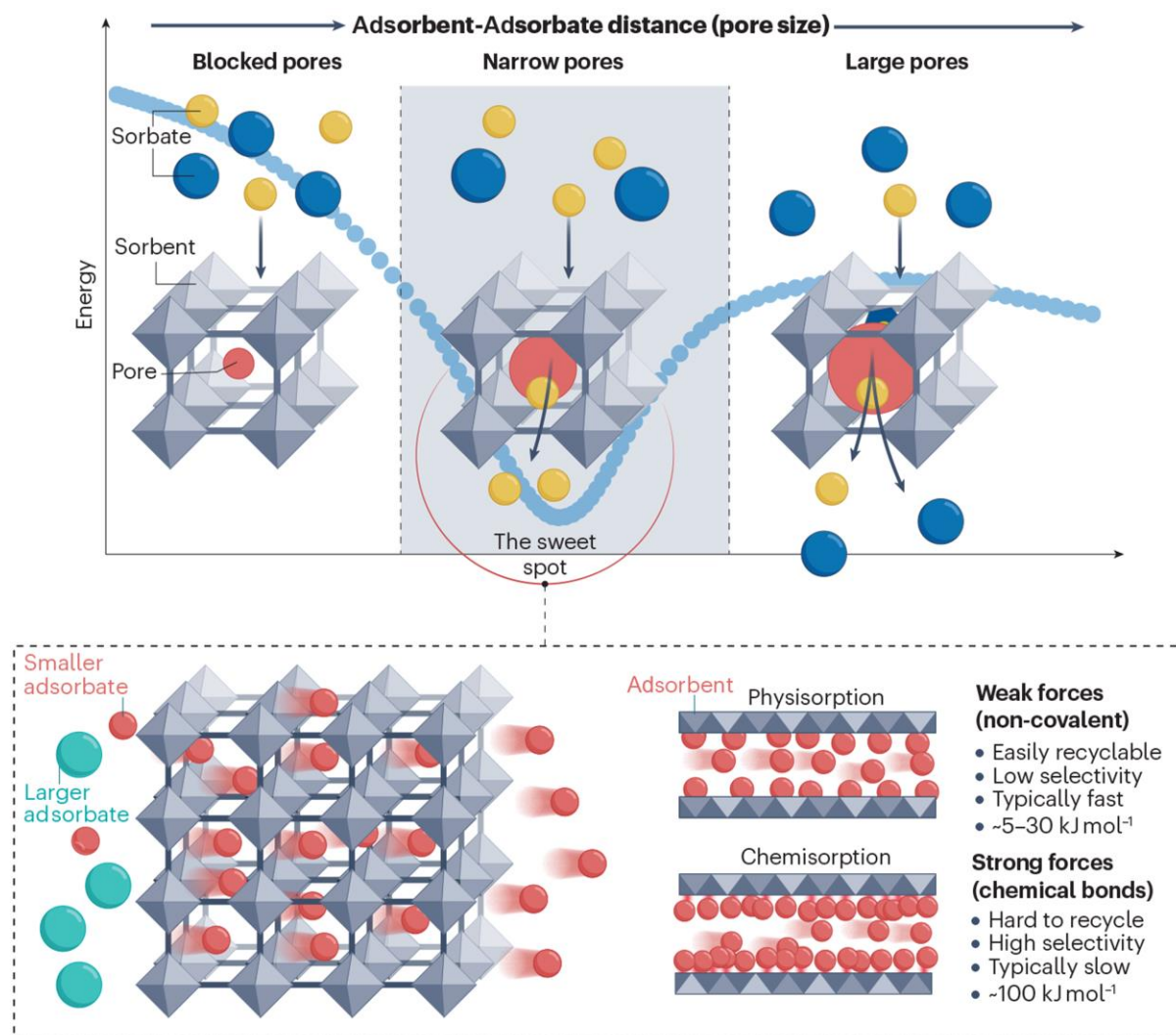
*A decade ago, Zaworotko and co-workers engaged the principles of crystal engineering to demonstrate that narrow-pore (< 0.7 nm) coordination networks are ideal sorbent platforms for small-molecule sorbates. This approach transformed sorbent design for such separations and has provided several performance benchmarks in trace gas capture-enabled purifications.*

In the twenty-first century, with concerns escalating over petroleum depletion, the value of gases — such as natural gas, biogas and ethylene — as commodity chemicals has skyrocketed. Indeed, the modern chemical industry contributes 7% of the world's GDP, amounting to US\$5.7 trillion annually<sup>1</sup>. These economic successes come at the expense of a high energy footprint. To mitigate this energy consumption in the 'age of gas'<sup>2</sup>, improving the energy efficiency has become crucial. Considering that the demand for these commodities is projected to triple by 2050<sup>2</sup>, it is evident that achieving energy-saving and highly efficient gas separation cannot be accomplished solely through incremental improvements in conventional (yet current) technologies, or the use of traditional porous materials, such as zeolites. Among non-traditional porous materials, a select few physisorbents (Fig. 1, bottom panel), exemplified by porous coordination networks (PCNs), which include metal–organic frameworks (MOFs), and porous coordination polymers<sup>3</sup>, exhibited early promise by offering task-specific molecular separation solutions. This is largely due to their low energy requirements for recycling and regeneration. Moving beyond Aristotle's postulate "Nature abhors a vacuum", the 'node-and-linker' approach<sup>4</sup> gave chemists the ability to control the structures of coordination networks, a strategy that evolved into the widely adopted reticular chemistry concept in 2003<sup>5</sup>. Combining supramolecular solid-state chemistry and their physicochemical properties, crystal engineering relies upon the knowledge of different intermolecular interactions to guide the design of solid-state architectures with desired properties. Crystal engineering blueprints of PCNs continue to support the ongoing transition from the high-throughput methods common in materials discovery. However, there remain a set of oft-encountered obstacles for PCNs to replace the existing separation technologies. These include cost and/or performance limitations, such as poor chemical stability, interference from water vapour, low selectivity, low working capacity and energy-intensive regeneration. Further, owing to low sorbate–sorbent affinity, most physisorbents (such as activated carbon or silica) exhibit binding energies on the order

of  $\leq 30$  kJ mol<sup>-1</sup>, whereas many PCNs suffer from mechanical, thermal and/or hydrolytic instability. Although chemisorbents often feature high selectivity, the energy needed to cleave sorbate-sorbent chemical bonds results in a high energy footprint of recycling and regeneration (Fig. 1), and their sorption kinetics tend to be slow for the removal of trace impurities. In essence, uptake and selectivity face a trade-off among most physisorbents, which are often mutually exclusive. Until 2012, activity in PCN research tended to focus upon high-surface-area sorbents, mostly microporous (<2 nm, including most MOFs) and mesoporous (>2 nm, including mesoporous silica and high-surface-area MOFs) variants, and these large pores resulted in weak sorbate binding. This led to low selectivity, even for binary equimolar mixture separations (Fig. 1). To overcome this challenge, in 2013, Zaworotko and co-workers identified the optimal combination of pore size and pore chemistry in a prototypical hybrid ultramicroporous material (HUM) as the key to achieving high adsorptive affinity towards small molecules<sup>6</sup>. In this study, the HUM Zn(pyrazine)<sub>2</sub>(SiF<sub>6</sub>) (SIFSIX-3-Zn) notched an ultrahigh selectivity of  $\sim 2,500$  for CO<sub>2</sub> over N<sub>2</sub> across its full loading (adsorption branch). This selectivity was at least an order of magnitude improvement compared with the previous carbon capture benchmarks, Zeolite 13X<sup>7</sup> and Mg-MOF-74<sup>8</sup>. The modular combination of metal nodes, organic ligands and inorganic pillars in SIFSIX-3-Zn enabled a framework with a tight pore of <4 Å, with sub-angstrom-level precision of pore size, as well as fine-tuning of pore chemistry. Thanks to the holistic success of this approach in setting new performance benchmarks, the modularity of HUM compositions enabled researchers to fine-tune the pore size and pore chemistry of ultramicroporous coordination networks. The resulting energetic 'sweet spots' serve as sorbate binding sites (Fig. 1) that can kill two birds with one stone; that is, they both lessen the high energy penalty of chemisorbents and increase selectivity by at least an order of magnitude compared with other physisorbents. This success arises as the narrow-pore HUMs present a high density of single-site, electrostatics-driven, strong (45–60 kJ mol<sup>-1</sup>) binding sites.

Now, 10 years since this discovery, the crystal engineering of ultramicroporous sorbents remains a watershed moment in the evolution of coordination networks suitable for adsorptive separations. The ultrahigh small-molecule selectivities demonstrated by HUMs stand alone amongst physisorbents and are only matched in performance by energy-intensive chemisorbents, such as liquid amines for CO<sub>2</sub> capture. A key criterion for performance was the matching of sorbent pore size and the sorbate van der Waals surface. This was instrumental in developing families of ultramicroporous materials with high selectivity for the industrially important C1–C4 gas molecules<sup>9</sup>. The recent success of commercially adopting a number of ultramicroporous coordination networks for applications, such as the ultramicroporous [Zn<sub>2</sub>(1,2,4-triazolate)<sub>2</sub>(oxalate)] (CALF-20) for carbon capture from flue gas<sup>10</sup>, has further demonstrated the profound impact of the crystal engineering blueprint introduced a decade ago. Importantly, the development of ultramicroporous sorbents, such as HUMs, has taught us that a high density of tight binding sites enabled by ultramicroporosity is a prerequisite for selective interactions

with C1, C2, C3 and noble gases. This is particularly timely in the context of the urgent need for a global commitment to a net-zero economy.



**Fig. 1 | A typical potential energy well that gives an edge to narrow-pore sorbents, typically ultramicroporous, for delivering selective affinity to its preferred sorbate.** Such sorbents can be designed at will, predicated upon existing and new-found crystal engineering approaches of recyclable physisorbent design. The bottom panel shows a comparison between physisorbents and chemisorbents.

## Competing interests

The authors declare no competing interests.

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