

Azolate Coordination Networks for Adsorptive Purification of Light Hydrocarbons

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State-of-the-art for commodity purifications, *e.g.*, cleaning commodity chemicals, air, and water is highly energy-intensive. Traditional physisorbents, including zeolites, and >100,000 metal-organic frameworks (MOFs, composed of organic ligands) can reduce this energy footprint, but are limited by cost, performance and/or stability issues.[1] To address this, our group is developing a new class of energy-efficient azolate coordination networks that feature “*the best of both Worlds*”: A) inorganic ligands and azolates-derived hybrid compositions that offer electrostatically strong binding sites for gas sorbates like carbon dioxide and light hydrocarbons (*e.g.*, acetylene, propyne); B) ultramicropores, *i.e.*, narrow pore sizes < 0.7 nm, ideal for tightly binding to the foregoing sorbates of relevance.[2] Amenability to bottom-up design approaches along both aspects, following the first principles of crystal engineering is poised to deliver (and control) several high-volume gas/water purifications.[3] In this context, we have developed an isostructural family of four previously unreported azolate coordination networks, ACNs,[4] and examined their CO₂ and C₂H₂ affinities through gas adsorption studies. Built from a tetrazole-pyridyl ligand, MF₆²⁻ (M' = Si, Ge, Ti, and Zr) anionic pillars, and Cu(II), these three-dimensional (3D) *pcu* topology ACNs demonstrate transient porosity.[5, 6] Despite the absence of guest-accessible channels along their structures, the activated ACNs exhibit A) clear temperature-independent microporosity to CO₂; B) temperature-dependent microporosity to C₂H₂ (only under ambient conditions, but not under cryogenic conditions). The latter anomalous sorption trend for C₂H₂, alongside the rare example of transient porosity renders this case study an ideal potential blueprint to design temperature-regulated transiently porous and/or nonporous sorbent analogues of the future, by simply tweaking their compositions at will. On top of this, ongoing solid-state ¹³C CP/MAS NMR results and molecular dynamics calculations have complemented our findings thus far. Further, three new families of ACNs were developed from an azole-pyridyl mixed series of ligands: an imidazole, a triazole, and a tetrazole, a series along which nitrogen atoms were purposely increased one at a time. Whereas our in-house Cambridge structural database (CSD) survey suggests all three ligands are new,[7] all the resulting 3D ACNs exhibited high efficiency in light hydrocarbon separations, such as in C₃H₄/C₃H₆, C₃H₆/C₃H₈ and C₃H₆/C₂H₄ respectively. Thanks to the isorecticular ACN platform, light hydrocarbon separation performances were further optimised by modulating pore chemistry through anion variation. To this end, substitution of methyl (CH₃) and fluorine (F) functionalities near the coordinating metal centres was found to directly control the ACNs' dimensionality, affording 1D and 0D structures, respectively. Whereas the findings establish azole-pyridyl ligands' versatility in the crystal engineering of coordination networks, the foregoing examples entail a profound control of sorption properties stemming from direct control of their structures. This, in essence, underpins the vision of modern crystal engineering: controlling the functions by leveraging the control over forms.[2, 8]

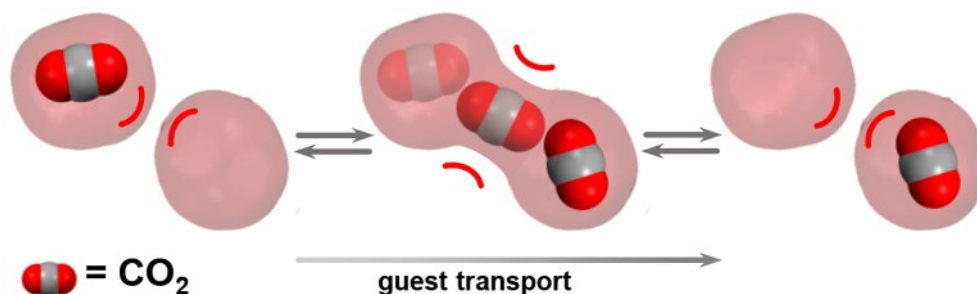


Figure 1. Porosity “*without pores*”: we uncover a crystal engineering strategy with potential to enable the design of transient porosity in an array of underexplored coordination networks.[3]

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