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Selectivity in adsorption of responsive metal-organic frameworks

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Flexible metal-organic frameworks (MOFs) that show reversible guest-induced phase transitions between closed and open pore phases have enormous potential for highly selective, energy-efficient separations, because they can selectively respond to external stimuli, adapting their pore size triggered by adsorption-induced gating or breathing.
The flexible framework DUT-8 is the focus of the present contribution. It consists of paddle wheels, 2,6-naphthalenedicarboxylate linkers, and 1,4-diazabicyclo(2.2.2)octane pillars forming a primitive cubic net. The composition of the metal node, crystal size, morphology, and conformation are used to effectively tune the responsivity of DUT-8.
The macrosized crystals of DUT-8 show selective guest responsivity associated with a pronounced cell volume change (~250%) upon gate opening. For DUT-8(Ni), an adsorption-induced transition from a closed-pore (cp) to an open-pore (op) phase can be triggered by nitrogen, carbon dioxide, or hydrocarbons at their standard boiling points, as well as by the majority of solvent vapors and CO2 at high pressure at room temperature. Nanocrystals of DUT-8 are rigid instead and show reversible uptake of gasses after desolvation. This is a behavior typical for conventional microporous solids.
The mechanism behind gate opening relies on the hinge energetics of the network nodes, balancing strain energy (favoring the open form) and linker-linker interactions (stabilizing the closed form). The guest molecules' interactions with the pore interior counteract these linker-linker interactions and induce gate opening. For gas separation, selective pore opening can induce colossal selectivity, which is a crucial aspect of energy-efficient separation processes.
DUT-8(Ni) is able to discriminate between CO2 and CH4 in the mixture of these gases at room temperature.1
It is also able to isotopolog-selective switching, demonstrating D2 over H2 selective responsivity.2
The macrocrystals of DUT-8(Zn) show selective reopening in the presence of dichloromethane (DCM) over alcohols, wherever the crystal downsizing to micron size unexpectedly reverses the gate opening selectivity, causing DUT-8(Zn) to open its nanosized pores for alcohols but suppressing the responsivity towards DCM.3
References:
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Primary author: SENKOVSKA, Irena

Co-authors: Dr ABYLGAZINA, Leila; MALIUTA, Mariia; KASKEL, Stefan (Technische Universität Dresden); BON, Volodymyr (Technische Universität Dresden)

Presenter: SENKOVSKA, Irena

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