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Dynamic adaptive adsorption as a strategy to reconfigure crystals

Adsorption has widely been studied in porous materials but the mechanism remains a mystery for nonporous systems. Now, nonporous polymeric crystals have been demonstrated to absorb molecules by coupling dynamic boron-nitrogen bonding and host-guest binding.

Strategies for adsorption in nonporous polymers using existing mechanisms are limited due to their naturally low specific surface areas. However, it is known that interfacial interactions between sorbents and sorbates drive adsorption, instead of the surfaces themselves. Now, writing in *Angewandte Chemie*, Huang, Stoddart, Li, and colleagues demonstrate a model system for nonporous polymers to adsorb molecules from solution and recrystallize as thermodynamically favoured crystals, with the process denoted as adaptisorption[1].

There have already been reports of nonporous materials that can adsorb guest species despite the absence of atomic-scale channels, such as in nonporous adaptive crystals. However, these materials possess prefabricated cavities. "For the next generation of nonporous adsorption materials, we want to propose a novel adsorption strategy that eliminates the need for intrinsic voids in nonporous materials," says Huang.

The team strategized that the system utilizing dynamic B–N bond-containing polymers and host-guest binding units can serve as kinetic and thermodynamic components, respectively (Fig. 1). This allows the ring guests to thread through the dynamic B–N bonds of the nonporous polymer and become trapped by strong host-guest binding with the pre-designed unit of the polymer. "We drew inspiration from the phenomenon in crystal engineering: thermodynamic crystals replace metastable ones by maintaining the dissolution-recrystallization balance. Consequently, we speculated that nonporous polymers with efficient recognition units and highly dynamic linkages could adsorb molecules in solution, and then undergo recrystallization as thermodynamically favoured crystals to achieve adsorption with nonporous polymers," explains Huang.

Adaptisorption not only extends the family of adsorption mechanisms but can also be used as a preparation method to access nanomaterials with precise architectures and integrated functions. Huang comments: "The facile preparation we show here to construct crystalline mechanically interlocked molecules by adsorption is meaningful for the research of molecular machines."

The researchers are interested in continuing to prepare new systems that utilize adaptisorption. "Theoretically, any nonporous polymer that combines matched thermodynamic and kinetic components has the potential to display adaptisorption," concludes Huang. "We plan to adsorb molecules of higher utility value, such as pharmaceutical molecules and gas molecules, or to further explore multifunctional adaptisorption."

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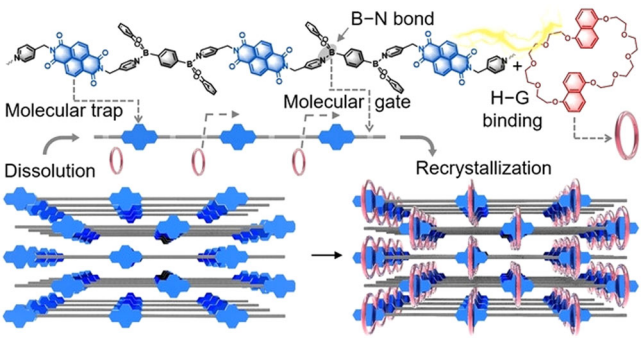

Fig. 1 | Adaptisorption of nonporous polymer crystals. The making and breaking of dynamic B–N bonds allow for host-guest binding between naphthalene diimide units of the polymer with 1,5-dinaphtho[38]crown-10 ring guests. Adapted from ref. 1 (https://doi.org/10.1002/anie.202317947) Used with permission of Wiley-VCH GmbH, from Adaptisorption of Nonporous Polymer Crystals, Shan, T. et al., Angew. Chem. Int. Ed., 63, e202317947, 2024.

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1. Shan, T. et al. Adaptisorption of nonporous polymer crystals. *Angew. Chem. Int. Ed.* **63**, e202317947 (2024).