Unique gas adsorption properties of the first Porous Ionic Packings (PIPs)

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We present a new class of materials composed of large cations and/or anions that assemble into close-packed structures containing isolated pores, named Porous Ionic Packings (PIPs). This study focuses on the synthesis, characterization, and gas sorption properties of selected PIPs, particularly $(NMe_4)_2B_{12}H_{12}$ (TMAD) and $(PMe_4)_2B_{12}H_{12}$ (TMPD), offering new insights into their potential applications in gas storage and separation. TMAD was successfully synthesized in a face-centered cubic (fcc) porous phase using ionic exchange in water. Similarly, TMPD was found to crystallize in both a porous fcc phase and a non-porous monoclinic phase, with thermal stability exceeding that of TMAD.

Gas sorption studies revealed that TMAD and TMPD can absorb various small gas molecules. Gas diffusion was found to be hindered by the lack of pore connectivity, likely governed by the rotational dynamics of ions. Significant amounts of CO_2 are retained inside the pores of TMAD, and the resulting materials are stable in air. Localization of CO_2 and its thermal desorption was studied by synchrotron X-ray powder diffraction.

Hydrogen adsorption in dodecaborane-based PIPs is another important focus of our research, given the fact that the hydridic nature of the pore surface has been shown recently to help packing H_2 molecules very densely inside the pores [1]. The $H^{\delta-}\ldots H_2$ interaction may help to bring the absorption enthalpies of hydrogen in hydridic small pore systems to substantial values, thus allowing hydrogen storage closer to ambient temperature.

PIPs exhibit properties distinct from classical porous materials, with their slow adsorption kinetics offering potential for tunable gas uptake. Future research will explore external stimuli, such as electromagnetic or vibrational energy, to control sorption behavior, potentially enabling applications in controlled gas storage and separation. Furthermore, modifying the ion size and chemistry, such as substitutions on $B_{12}H_{12}^{2-}$, could allow for precise tailoring of pore size and surface properties, paving the way for a versatile new class of functional materials. This work opens new avenues in materials science, demonstrating that large ionic assemblies can form porous structures capable of selective gas sorption.

[1] Oh, H., Tumanov, N., Ban, V., Li, X., Richter, B., Hudson, M., Brown, C., Iles, G., Wallacher, D., Jorgensen, S., Daemen, L., Balderas-Xicohtencatl, R., Cheng, Y., Ramirez-Cuesta, A., Heere, M., Posada-Perez, S., Hautier, G., Hirscher, M., Jensen, T. & Filinchuk, Y. (2024). *Nature Chem.* **16**, 809.