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A focus on microporous perovskites: new tricks for an old dog

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Hybrid organic–inorganic perovskites (HOIPs) are widely studied for their potential in optoelectronic devices due to their unique semiconductor features. Porous HOIPs are extremely rare, with (APOSS) [CuCl₄]₄ being one of the very few examples, featuring 12 Å pores within its lattice. Reed and coworkers (C. W. Dalton, P. M. Gannon, W. Kaminsky and D. A. Reed, *Chem. Sci.*, 2025, DOI: <https://doi.org/10.1039/D4SC04378B>) have recently shed light on the structure of this interesting material and demonstrated that these pores can incorporate large electroactive molecules such as ferrocene (Fc) and tetracyanoethylene (TCNE). Further, they showed that the ability to incorporate molecules within the pores also enables the synthesis of new crystalline phases and unlocks numerous applications, including gas sensing and photocatalysis, among others.

Hybrid organic–inorganic perovskites (HOIPs) have been attracting considerable interest due to their versatile application potential in light emitting diodes (LEDs),¹ solar cells,^{2–4} photocatalysis⁵ and beyond.^{6–10} Most of these applications are possible thanks to their extended, two- or three-dimensional network of overlapping orbitals, which collectively form the electronic structure characteristic of a semiconductor. As an intense orbital overlap is needed, close packing is usually a prerequisite, making porous semiconductors exceptionally rare. In fact, there is only one report of a permanently porous HOIP: (APOSS)[MCl₄]₄ (where APOSS is an octylammonium polyhedral oligomeric silsesquioxane and M = Cu, Mn or Pb). Originally reported by Kataoka and collaborators,¹¹ (APOSS)[MCl₄]₄ showed an impressive surface area of up to 205 m² g^{−1}. However, Kataoka and colleagues were

unable to obtain a reliable crystal structure or to show if this porosity could accommodate molecules larger than dinitrogen.

In a recently published article, Reed and coworkers,¹² have been able to obtain a high-quality single-crystal X-ray structure of (APOSS)[CuCl₄]₄, revealing a structure with a unique arrangement of POSS groups that shift to create 12 Å pores (Fig. 1).

Beyond characterizing the structure, the authors demonstrated that electroactive molecules like ferrocene (Fc) and tetracyanoethylene (TCNE) can be introduced by simply soaking the material in

a solution of either molecule or by exposing it to Fc vapors. Remarkably, Fc adsorption turns the originally yellow crystals a deeper yellow, a color change that persists after washing, suggesting successful incorporation of Fc into the perovskite lattice. The presence of TCNE and Fc was confirmed *via* several techniques, indicating that more than one Fc molecule per pore can be retained within the material. Additionally, Reed and coauthors found that the loading amount is tunable based on the duration of Fc exposure, with significant structural adjustments occurring when larger quantities are introduced. Experimental analyses showed that TCNE molecules

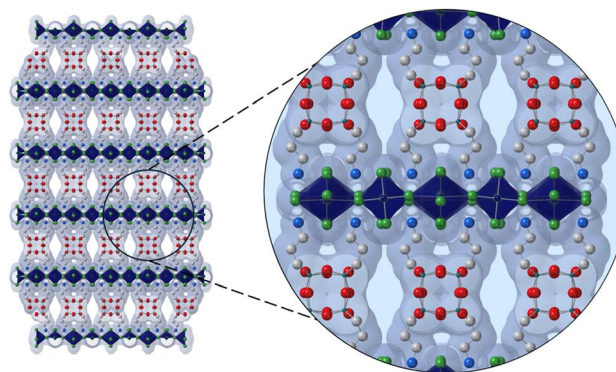
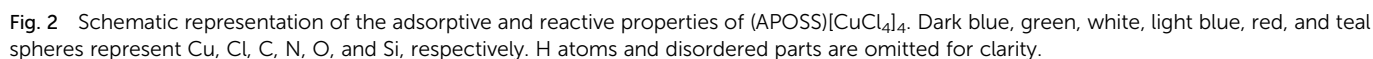


Fig. 1 Structure of (APOSS)[CuCl₄]₄. Dark blue, green, white, light blue, red, and teal spheres represent Cu, Cl, C, N, O, and Si, respectively. H atoms and disordered parts are omitted for clarity.

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