Synthesis of single-crystal two-dimensional covalent organic frameworks

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Polymerizing monomers into periodic two-dimensional (2D) networks provides structurally precise, layered macromolecular sheets that exhibit desirable mechanical, optoelectrotronic, and molecular transport properties. 2D covalent organic frameworks (COFs) offer broad monomer scope but are generally isolated as powders comprised of aggregated nanometer-scale crystallites. Here we control 2D COF formation using a two-step procedure, in which monomers are added slowly to pre-formed nanoparticle seeds. The resulting 2D COFs are isolated as single-crystalline, micron-sized particles. The resulting COF nanoparticles are of exceptional and unprecedented quality, isolated as single crystalline materials with micron-scale domain sizes. Stabilization as colloidal particles allows for high-quality optical characterization for the first time, which demonstrates that through space electronic communication unlocks emergent opto-electronic behaviour in these materials. These findings advance the controlled synthesis of 2D layered COFs and enable a broad exploration of synthetic 2D polymer structures and properties.