ABSTRACT: Porous molecular crystals are a class of solid state porous materials which are composed of discrete molecules rather than extended polymeric structures. Their molecular nature makes them fundamentally interesting, as small molecules typically closely pack in the solid state, without leaving large voids. In addition, molecular crystals have higher solution and vapor phase processability which allows their easier incorporation into thin films and devices. Our recent work has identified two new classes of porous molecular crystals. The first is based on rigid fluorinated aromatic compounds which are terminated with pyrazole or tetrazole end groups. These termini are capable of hydrogen bonding and aromatic stacking and their solid-state assembly results in extrinsically porous structures with modular hexagonal pores. These pores have been shown useful in adsorption of Freons, hydrocarbons, and fluorinated anesthetics. The second class of molecular precursors are produced by the benzoin condensation of rigid aromatic dialdehydes into cyclic oligomers known as cyclobenzoins. Cyclobenzoins self-assemble into porous solid-state structures and offer rich derivatization chemistry that either takes advantage of their esterification or condensation with 1,2-phenylenediamines.