

MS37-P11 Symmetry in MOF synthesis: A new network topology from a heterotritopic linker

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Metal-organic frameworks (MOFs) are crystalline materials, composed of inorganic clusters or coordination spheres (secondary building units, SBUs), connected by organic linkers through strong bonds. Most of the linkers employed in MOF synthesis are highly symmetric, leading to structures with only a few network topologies, aiming for a high network transitivity.^[1] A reason for this is that for linkers with identical functional groups, a pH exists that allows reversible bond formation to the metal centers, hence facilitating crystal growth. Here we report the use of a heterotritopic linker which leads to a stable, porous MOF (BET surface area 2140 m²g⁻¹) with a new network topology (named tto). MOF-910 crystallizes in the trigonal spacegroup *R*-3*c* with lattice parameters *a* = 47.239(2) Å and *c* = 27.1216(12) Å. The structure (Figure 1) consists of hexagonal channels 28 Å in diameter constructed from infinite helical SBUs of Zn²⁺ ions ligated by the oxygen and nitrogen atoms of the linker, which bears a benzoate, a semiquinonate and a pyridonate functional group.

The structure is achiral, as it contains an equal amount of left- and right-handed helical SBUs. The semiquinonate and the pyridonate group align together at the same SBU with the benzoate group bridging to the opposing SBU. The benzoate is disordered, showing two distinct conformations. Despite the differences of the pK_a values of the functional groups (benzoate: 4.2; catecholate: 9.5; pyridonate: 11),^[2,3] synthetic conditions could be derived which led to a homogeneous, stable product. These results show the potential of extending the variety of known MOFs constructed with new network topologies utilizing much higher complexity in the organic linker molecules than previously achieved.

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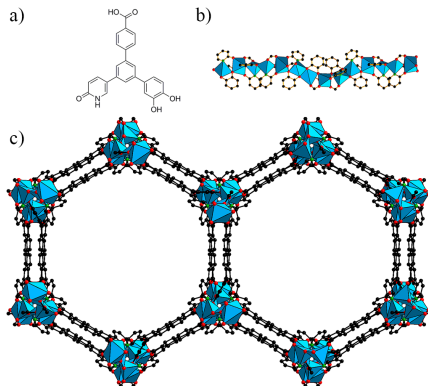


Figure 1. a) Heterotritopic linker. b) Section from helical SBU. c) Structure of MOF-910 viewed along the *c*-axis along the hexagonal channels. Color scheme: Zn, blue; C, black; O, red; N, green. Hydrogen atoms omitted for clarity.

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