Poster Presentation

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Vernier structures of metal benzenedicarboxylats MIL-47 and MIL-53

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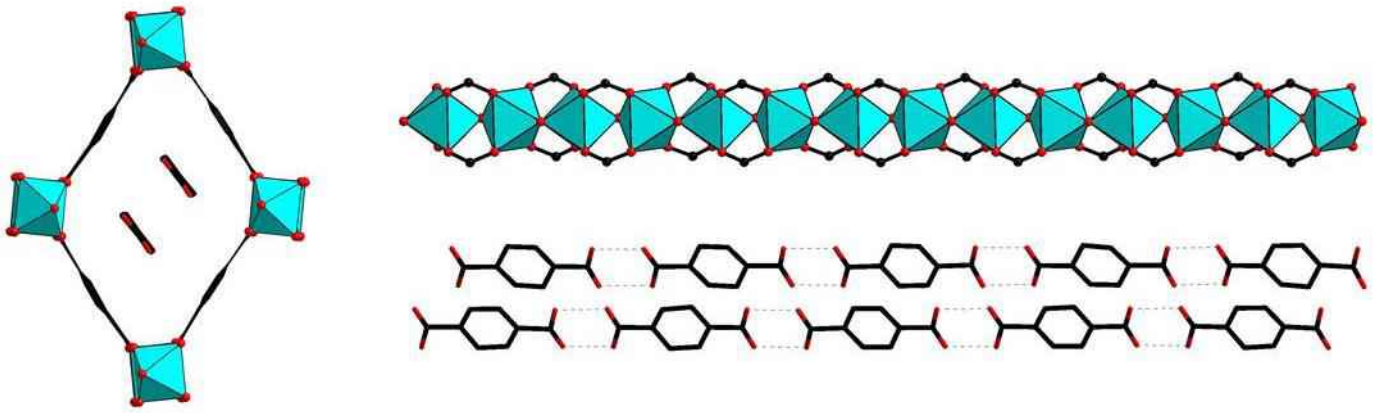
The nanoporous frameworks VO(bdc), MIL-47, and M(OH)(bdc), MIL-53, bdc = 1,4-benzenedicarboxylate, can absorb various guest species in their 1D channels. As synthesized, the channels are filled with H_2bdc molecules that have been reported to be disordered, except for In(OH)bdc·0.75H_2bdc which has a Vernier structure with H_2bdc molecules forming an ordered sublattice.[1] We have found similar Vernier structures in other members of the family based on X-ray data from large single crystals. The MO(bdc) framework consists of single chains of MO_6 octahedra that share trans corners and are bridged by bdc ligands. The guest H_2bdc molecules form double columns in each channel parallel to the octahedral chains. Commensurate superstructures are observed, which result from mismatch between the basic periodicities of the guest and host sublattices, for [VO(bdc)]$(H_2bdc)_5/_7$, (1), (293 K, $P2_1$, a=23.903, b=17.191, c=25.722 Å, β=105.91°), [Ga(OH)(bdc)]$(H_2bdc)_{12}/_{17}$, (2), (100 K, $P2_1$, a=17.707, b=11.730, c=114.639 Å, β=90.48°), and [Al(OH)(bdc)]$(H_2bdc)_{11}/_{16}$, (3), (293 K, orthorhombic, a=12.278, b=17.059, c=105.488 Å). Different simple fractional numbers of H_2bdc molecules per framework metal cation result from change in the basic periodicity of the octahedral chains due to different metal cation sizes. The octahedral chains are parallel to [201] in (1), and to [001] in (2) and (3). Remarkably, all atoms in (2) are observed to show significant transverse sinusoidal modulation along [001] direction. We thank the Robert Welch Foundation for financial support (Grant No. E-0024).

[1] *E. V. Anokhina, M. Vougo-Zanda, X. Wang, A. J. Jacobson, J. Am. Chem. Soc., 2005, 127, 15000.*



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