Bruker / MIT Symposium 2020

SHAPE PERSISTENT MACROCYCLES AS "0D" POROUS MOLECULAR SOLIDS AND TEMPLATES FOR POLYMORPHIC METAL-ORGANIC FRAMEWORKS

K. Travis Holman, Georgetown University, e-mail: kth7@georgetown.edu

There is much contemporary interest in the development of new micro/nanoporous materials for gas capture/sequestration, separation, sensing, *etc.* Efforts have largely been directed toward molecule-derived materials that exhibit permanent "open" pores (*e.g.*, metal-organic frameworks (MOFs), covalent organic frameworks (COFs), polymers with intrinsic microporosity (PIMs), and even certain kinds of porous molecular solids (PoMoSs)). Much less is understood about the properties of porous materials that, in the static view of their structures, do not appear to exhibit interconnected pores, but nonetheless offer appreciable space in the form of "0D pores" or isolated cavities. As will be discussed, such structures are ubiquitous, yet have gone largely unrecognized and little studied due to various experimental biases. Various families of shape persistent macrocycles, however, provide many new examples of 0D PoMOSs and these materials can offer several advantages, including: i) impressive thermodynamic and chemical stability, ii) solubility and trivial assembly, and/or disassembly, and iii) low cost, easy synthesis. Moreover, by offering pores that completely encapsulate putative sorbates, they have the potential to optimize thermodynamic selectivity with respect to sorbate capture. Additionally, the kinetics of substrate uptake and/or release can vary enormously, are largely dependent upon molecular and crystalline structure, and can be engineered. The presentation will highlight studies in our laboratory concerning the design and widely varying properties of 0D PoMoSs derived from shape persistent macrocycles,[1-2] container molecules,[3] hydrogen bonded frameworks,[4] and the exploitation of these compounds for the templation of novel MOF architectures.[5] The intrinsic 0D pores of these materials have been exploited for the capture, sorption, kinetic separations, and/or extreme kinetic confinement of commodity gases and other small molecules.

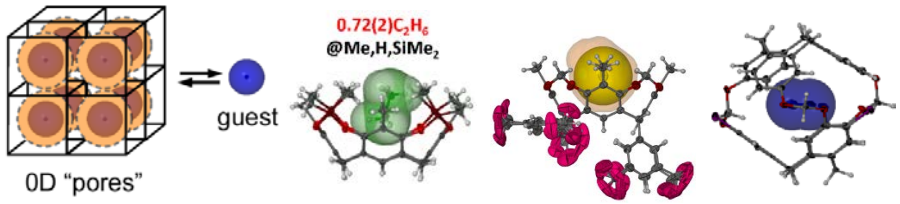

Figure 1. Various 0D PoMoSs and their gas-occupied (C_2H_6, Xe N_2, respectively) structures.

1. C. M. Kane, A. Banisafar, T. P. Dougherty, L. J. Barbour, K. T. Holman *J. Am. Chem. Soc.*, **2016**, *138*, 4377.
2. C. M. Kane, O. Ugono, L. J. Barbour, K. T. Holman *Chem. Mater.*, **2015**, *27*, 7337.
3. A. I. Joseph, S. H. Lapidus, C. M. Kane, K. T. Holman *Angew. Chem. Int. Ed.* **2015**, *54*, 1471.
4. Brekalo, I.; Deliz, D. E.; Barbour, L. J.; Ward, M. D.; Friščić, T.; Holman, K. T. *Angew. Chem. Int. Ed.* **2020**, *59*, 1997–2002.
5. Brekalo, I.; Kane, C. M.; Ley, A. N.; Ramirez, J. R.; Friščić, T.; Holman, K. T. *J. Am. Chem. Soc.* **2018**, *140*, 10104–10108.