Breathing Mixed-ligand MOFs – solvent exchange and sorption studies

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Metal-organic frameworks (MOFs) have attracted widespread attention for their porosity and potential applications in separation chemistry, catalysis, molecular sensing and gas storage. [1] This class of materials are coordination polymers and may be 1-periodic, 2-periodic or 3-periodic. Firstly, we report a partially-fluorinated, 2-periodic MOF, $[Zn(hfipbb)(bpt)]_n \cdot n(C_3H_7NO)_2 \cdot n(H_2O)$ where H_2hfipbb = 4,4′-(hexafluoroisopropylidene)bis(benzoic acid) and bpt = 4-amino-3,5-bis(4-pyridyl)-1,2,4-triazole. This framework undergoes single-crystal-to-single-crystal in solvent exchange with ethanol, dichloromethane and N,N'-dimethylacetamide, respectively. The solvent-induced 'breathing' of the 2-periodic frameworks results in potential void spaces varying from 15.2-35.4%.[2] In addition, we report the synthesis of a pair of isoreticular mixed-ligand MOFs, $[Zn(\mu_2\text{-ia})(\mu_2\text{-bpe})]_n \cdot n$DMF and $[Zn(\mu_2\text{-mia})(\mu_2\text{-bpe})]_n \cdot n(C_3H_7NO)$, where ia = isophthalate, mia = 5-methoxyisophthalate and bpe = 1,2-bis(4-pyridyl)ethane.[3] Both structures consist of doubly interpenetrated 2-periodic frameworks. Despite a lower void space, one of the activated MOFs exhibits significantly higher sorption of carbon dioxide at 195 K, illustrating that small changes in functional groups, even in structurally similar MOFs, may have a large effect on sorption properties.

[1] Zhou, H.; Long, J. R.; Yaghi, O. M. Introduction to Metal-Organic Frameworks. *Chem. Rev.* **2012***, 112*, 673-674.

[2] Chatterjee, N. and Oliver, C.L., Cryst. Growth Des. **2018**, 18, 7570−7578.

[3] Gcwensa, N., Chatterjee, N., Oliver, C.L., Inorg. Chem. **2019**, 58, 2080−2088.

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