Computational Design of new Non-Isoreticular MOF Families with Paddlewheel-Type SBUs

Maxim Peskov1, Mikhail Suyetin2

1Samara Center For Theoretical Materials Science, Samara, Russian Federation, 2King Abdullah University of Science and Technology, Jeddah, Saudi Arabia
E-mail: maxim.peskov@gmail.com

Developing metal organic frameworks (MOFs) with high storage capability is promising for limiting greenhouse gas emissions. One of the main properties of interest in the design of MOFs is the diffusion characteristics of gas molecules in the structure. In this work, we design in silico MOFs belonging to new MOF series, and investigate their physical properties as well as diffusion behaviour by MD simulations.

To establish a topological pattern for the MOFs to be designed, we address the nets occurring in the previously reported paddlewheel based coordination polymers. We perform a complete screening of the Cambridge Structural Database (version 5.36, May 2015) and compile a list of 697 coordination polymers by employing the TOPOS package [1]. Afterwards we search in the Reticular Chemistry Structure Resource [2] for uninodal nets not appearing in this list with the local vertex geometry closely resembling the plane square coordination of the metal atoms in paddlewheel cluster. Construction of the MOFs and their pre-optimization is done with molecular mechanics and universal force-field. As organic ligand, we use two ditopic linkers: 1,4-benzenedicarboxylic and biphenyl-4,4′-dicarboxylic acid. We optimize the unit cells by performing a set of density-functional theory calculations.

The nets qzd, rhr, and tcb are chosen as blueprints for building three new non-isoreticular MOF families (a-c). The MOF structures have paddlewheel clusters in few orientations. For establishing the connectivity, at least two kinds of linkers with rotated carboxylates are required.

Grand canonical Monte Carlo simulations are employed to investigate the methane sorption properties and working capacity (gravimetric and volumetric) at different temperatures (240 K, 258 K, 273K, 298K) and pressures (up to 90 bar). The adsorption isotherms of the gas molecules are obtained from a series of fixed pressure simulations over a fugacity range from 0 to 5 MPa. One of the proposed candidates can compete well with all existing MOFs with respect to the gas storage capacity due to high porosity (2.2 cm3/g pore volume) and calculated surface area (3656 m2/g BET surface area). The CO2 storage capacity of 44.8 mmol/g, for example, comes close the record of 54.5 mmol/g.

The proposed MOFs are distinguished by very high diffusivities, which typically, though depending on the specific gas and temperature, are at least one order of magnitude higher than in the existing MOFs. They are able to retain a remarkable amount of CO2, CH4 and CO molecules that can be attributed to their high porosity with good accessibility to channels and the existence of aromatic rings in the organic linkers.


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