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Breathing layered metal–organic frameworks based on 1,3-bis(imidazolyl)propane

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1 Introduction.

Today, most MOFs are created based on rigid aromatic carboxylic acids and N-donor ligands. Ligands with flexible aliphatic bridges can provide conformational mobility to the ligand, which may be promising when modeling new MOFs with unusual structures and properties.

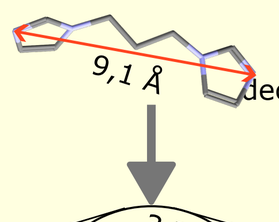
Layered MOFs have an important feature - the absence of bonds between the layers. The layers are usually held together only by weak hydrogen or π-π interactions, which allows the MOF to "breathe", i.e., to shift the layers relative to each other.

2 Aim.

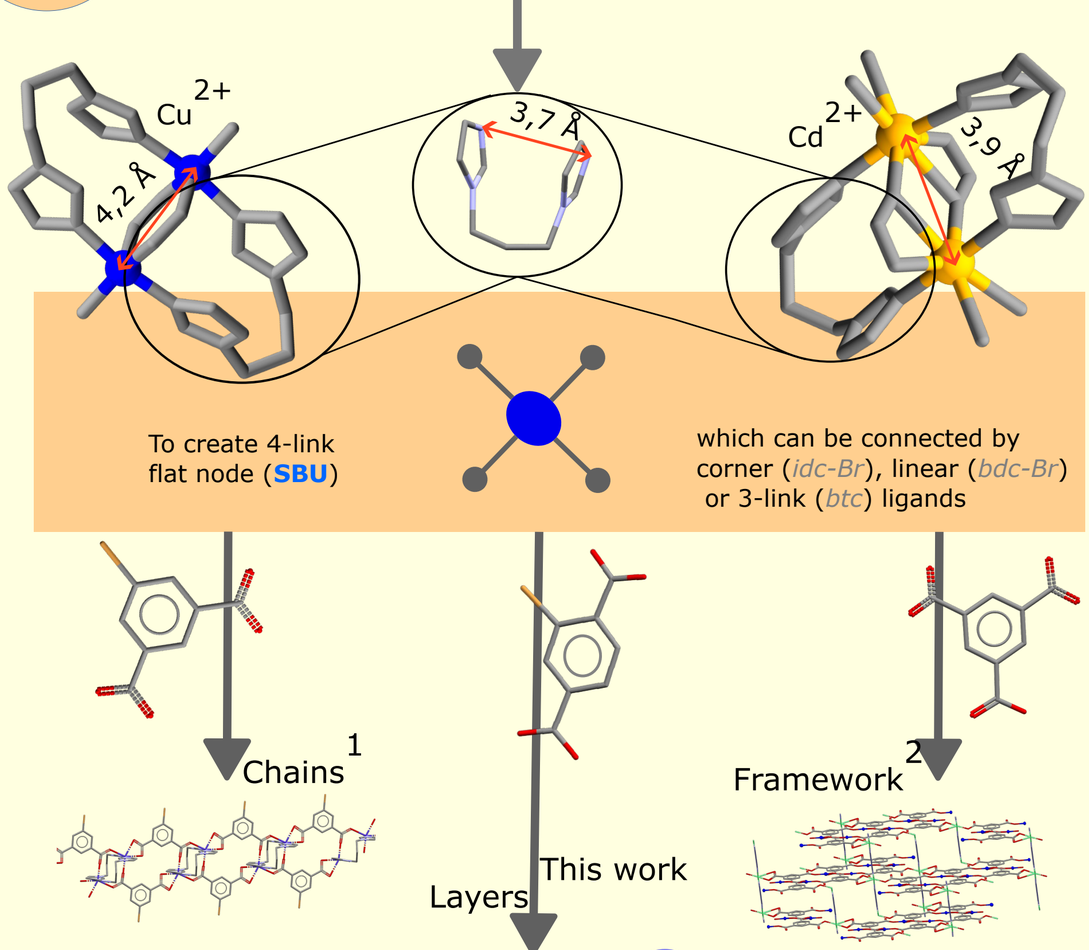
Our work is devoted to the study of layered MOFs based on 1,3-bis(imidazolyl)propane (bip) containing a -C_3H_6- alkyl group. Due to its conformational mobility, bip acts as a bridging ligand that connects two metal atoms into one secondary building block (SBU). Secondary building blocks M $(bip)_2^{2+}$ (M = Cd, Cu) form a layered mobile structure with the help of functionalized terephthalic acids (bdc-NO_2, bdc-Br).

The sorption characteristics of these compounds are of the greatest interest for research. As part of our work, we investigated the adsorption of industrially important hydrocarbons.

3 Synthetic idea.

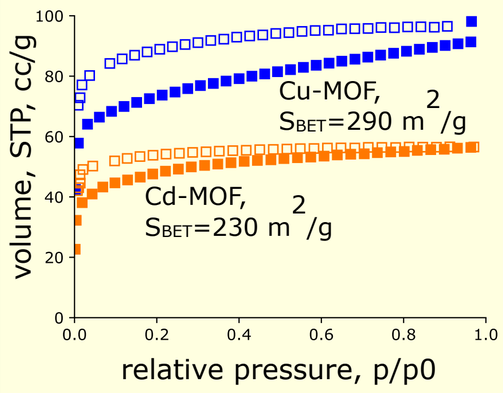


The ligand (*bip*) can be folded so that the N-N distance decrease from 9,1 is only to 3,7 Å.



4 Adsorption.

CO_2 isoterms at 195 K

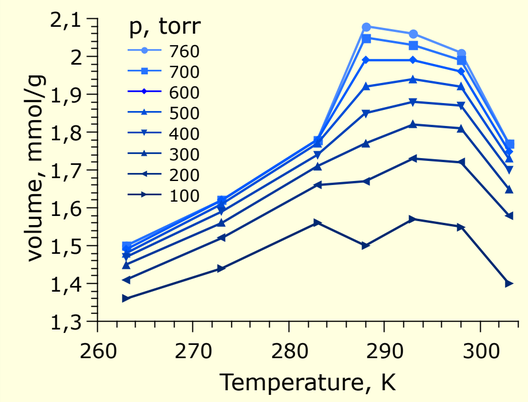


Amount of adsorbed gas (propane and propene) at different temperatures

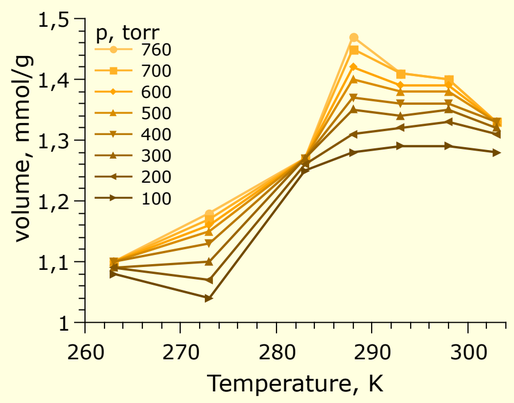
	Cu-MOF		Cd-MOF	
T, K	*C3H8, ml/g*	*C3H6, ml/g*	*C3H8, ml/g*	*C3H6, ml/g*
263	33		24	
273	36	44	26	32
283	40		28	
288	46	51	33	36
293	47	49	32	35
298	45	45	31	33
303	39		30	

Usually adsorption isobars decrease with increasing temperature, however, these compounds, due to their mobile structure, allow us to observe an increase in the amount of adsorbed gas, and then a more natural decrease in the temperature range of 283-303 K.

Cu-MOF, C_3H_8



Cd-MOF, C_3H_8



Apparently, gradual restructuring of the MOF gives a greater gain in adsorption capacity than an increase in temperature gives a loss.
This behavior is observed up to 288 K.

5 Conclusion.

We have obtained a series of layered MOFs based on 1,3-bis(imidazolyl)propane (*bip*). These MOFs are constructed based on $M_2(bip)_2$ fragments in such a way that the flexible ligand is folded in half so that the distance between the imidazole rings inside the ligand is only 3.6-3.9 A. Such secondary 4-linked building blocks are combined into layers using a rigid carboxylate ligand (bdc-Br), and are held together by the interaction of the same bent bip.

- Such a unique structure has a significant effect on the sorption characteristics of the compounds. In this work, we recorded an anomalous increase in adsorption with increasing temperature, which is associated with a change in the structure of the framework directly during the adsorption of C3 hydrocarbons.

6 Future work.

This behavior during adsorption requires careful further study to establish the relationship between the structure and the mechanism of its change during adsorption. In addition, it is interesting to study how this behavior will affect dynamic adsorption in breakthrough experiments.

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Literature:

[1]L.-F. Ma, X.-Q. Li, L.-Y. Wang, and H.-W. Hou, CrystEngComm, vol. 13, no. 14, p. 4625, 2011, doi: 10.1039/c1ce05308f.
[2]J.-F. Lu and Z.-H. Liu, Polyhedron, vol. 107, pp. 19–26, Mar. 2016, doi: 10.1016/j.poly.2016.01.018.