

## TEMPLATING EFFECT OF ORGANIC LIGANDS ON THE STABILIZATION OF ZIFS AND ON THEIR ADSORPTION PROPERTIES FOR CO<sub>2</sub>

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### Abstract:

One of the technological problems that face society today is the environmentally friendly and economically favourable separation, capture and storage of gases. The use of nanoporous sorbents (e.g. zeolites) embedded in membranes to remove impurities and/or as a possible technology for CO<sub>2</sub> capture has been proposed by various researchers. Such materials would be far less costly, as well as being chemically more benign than amine units. However some drawbacks of conventional zeolitic membranes are insufficient selectivity and flux, poor thermal cycling behavior and non-facile synthesis involving long calcinations. In this context, Metal Organic Frameworks (MOFs) [1] have been recently proposed in the field as potentially interesting materials for CO<sub>2</sub> adsorption and separation purposes [2]. The rational construction of hybrid open-frameworks, with controlled-size cavities and periodic intraframework organic functionality, is an ongoing synthetic challenge and is attracting exceptional scientific and technological interest. It already offers great potential for innovative applications pertaining to strategic gas (H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>) processing [3,4,5,6].

More recently the synthesis of Zeolitic Imidazole Framework (ZIFs) has gained considerable attention, due to their spectacular nanoporous architecture. Using high-throughput synthesis techniques, ZIFs have been recently recognized as potentially interesting materials for CO<sub>2</sub> capture and CO<sub>2</sub>/CH<sub>4</sub> selective adsorption [7,8]. Rotation and substitution of imidazoles might have a major impact on sorption properties and thermodynamic stabilities of ZIFs structures. We have recently performed periodic boundary conditions DFT including vdW contributions and Monte Carlo simulations in order to study the ZIF-8 framework. We have investigated the effect of imidazole substitution on the rotational energy landscape. A very exciting finding is the existence of a two-minima potential following the imidazole-methyl substituent rotation around the N-N axis which does not appear in the original ZIF (pure imidazole). Shoulders on the potential curves at 160°±360° are due to the short distances (2.23 Å) between the Zn<sup>2+</sup> ions and the two H atoms at the bottom of the imidazoles in the 4- and 6-membered rings. While shoulders at -70°±360° appear only in the case of the imidazole- methyl substituent and correspond to short distances (2.22 Å) between H atoms of the methyl groups and those at the bottom of the imidazole of the neighbor imidazole in 6-membered rings. Potential barriers at 60°±360° correspond to molecular overlap between the imidazoles' methyl groups in 4-membered rings. While potential barriers at 230°±360° are a result of molecular overlap between the imidazoles' bottom H atoms in 4-membered rings,

At the potential energy minima (i.e 0° for pure imidazole, and (0°,100° for methyl substituent), we performed DFT calculations of global relaxations of cell parameters, and geometries. We then compared the final cell volumes, and the resulting adsorption energies per unit formula (i.e per imidazole and per Zn atom). We found that the structure with methyl-imidazole substituent at 100° is the most stable, it might hence correspond to a new polymorph that has not yet been identified experimentally (under publication [9]).

### REFERENCES:

- [1] C. Lee, W. T. A. Harrison, C. Mellot, B. Slater, J. Wu, C. N. R. Rao and A. K. Cheetham, *Chem. Comm.* p. 2687, 2006.
- [2] H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Nature*. vol. 453, p. 207, 2008.
- [3,4] Yaghi et al. *Science*. vol. 300, p. 1127, 2003 and. vol. 295, p. 469, 2002.
- [5] Yaghi et al, *Nature*. vol 427, p. 523, 2004.
- [6] Yaghi et al, *J. Am. Chem. Soc.* Vol. 127, p. 7110, 2005.
- [7] X. C. Huang et al, *Angew. Chem. Int. Ed.* Vol. 45, p. 1557, 2006.
- [8] B. Wang, A. P. Côté, H. Furukawa, M. O'Keeffe, O.M. Yaghi, *Nature*. Vol. 453, p. 20, 2008.
- [9] B. Kerkeni, A. Torrisi, R. Galvelis, C. Mellot-Draznieks, *J. Phys. Chem. B*, 2011.