Revealing the Structure Modification-Gas Diffusivity Correlation in Zeolitic-Imidazolate Frameworks (ZIFs) with a Data Mining Strategy

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Zeolitic-imidazolate frameworks (ZIFs) have the potential to make highly selective gas separation membranes, due to their functionalization capabilities that can take place on the molecular level and affect considerably their performance. These modifications can greatly affect gas diffusivity in the pore network and thus enhance their sieving properties, which determines the separation performance. However, in practice the application of ZIFs in gas separations is limited due to our lack of knowledge on the modification-diffusivity correlation.

Our approach is based on the premise that the aperture connecting the cages of ZIFs controls the diffusion rate of guest species. In our recent works we showed that the aperture's size and flexibility can change and directly affect the ZIF's diffusion-based selectivity, by replacing the organic linker, the metal center or the functional group of the framework.[1,2,3,4] This knowledge shapes a chemical basis which we used in a novel machine learning (ML) tool towards developing a comprehensive modification/diffusivity correlation. We have built numerous new ZIFs of finely discretized aperture sizes, by replacing various units, and simulated the diffusion of guest molecules of varying in size (He, H_2 up to n-butane) in these structures, based on force fields developed with density functional theory (DFT). The simulations account for the flexibility of the structure, assessing thus the framework's response as a function of the gas penetrant's size. Then we trained a supervised ML model on readily available descriptors, such as the mass and size of the basic building units and the penetrant's size. The comparison of our ML model (Figure 1) with simulations highlights the high predictive power of our approach.

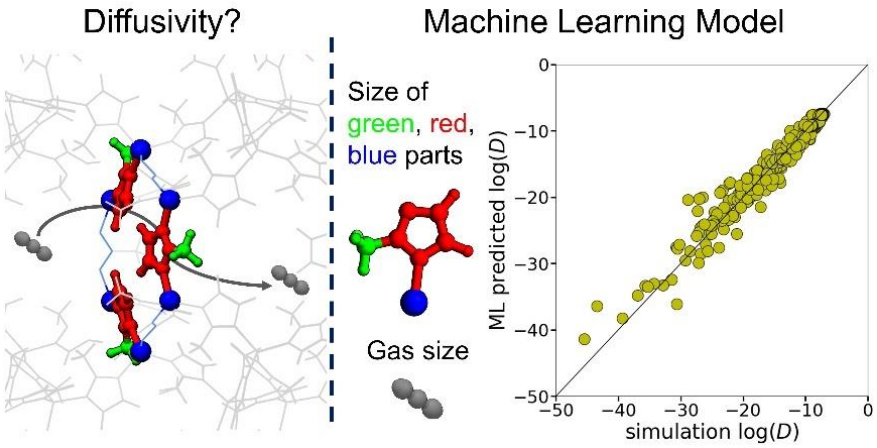

Figure 1. The ML algorithm: its principle and its performance.

Our ML model constitutes the first computational tool to predict the diffusivity of gases in nanoporous crystalline solids, based on their framework sub-units.[5] A researcher can consider a new ZIF functionalization, bypass time-expensive computations (DFT calculations and atomistic-level simulations), and directly obtain a good estimation of the diffusivity of different penetrants (and thus the structure's selectivity potential) through a simple two-step ML model.

References

1. Krokidas, P.; Moncho, S.; Brothers, E. N.; Castier, M.; Jeong, H. K.; Economou, I. G. *ACS Appl. Mater. Interfaces* **2018**, *10*, 39631–39644.

2. Krokidas, P.; Moncho, S.; Brothers, E. N.; Castier, M.; Economou, I. G. *Phys. Chem. Chem. Phys.* **2018**, 20, 4879–4892.

3. Krokidas, P.; Moncho, S.; Brothers, E. N.; Economou, I. G. A*CS Appl. Mater. Interfaces* **2020**, 12, 20536–20547.

4. Hillman, F.; Hamid, M. R. A.; Krokidas, P.; Moncho, S.; Brothers, E. N.; Economou, I. G.; Jeong, H. K. *Angew. Chemie - Int. Ed.* **2021**, *133*, 10191–10199.

5. Krokidas, P.; Karozis, S.; Moncho, S.; Giannakopoulos, G.; Brothers, E. N.; Kainourgiakis, M. E.; Economou, I. G. and Steriotis, T. A., *under review*