How does water move in MOF-303 and MOF-333?

Diffusion of water in the metal-organic frameworks MOF-303 and MOF-333

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In Short

- Several billion people live in water-stressed regions, emphasizing the need for innovative solutions; modern metal-organic frameworks offer exciting opportunities for adsorbing water from air;
- We plan to use density functional theory (DFT) to investigate diffusion of water in the two metal-organic frameworks MOF-303 and MOF-333;
- This project will guide and accelerate the knowledge-driven design of water harvesting materials and devices.

Addressing the worsening global water crisis is of paramount importance given the large populations living in water-stressed regions.[1] Existing solutions, such as water transfer and desalination, have high costs and environmental impacts that hinder their widespread adoption. However, the invention of water-harvesting metal-organic frameworks (MOFs) represents a promising avenue.[2] These porous materials are capable of efficiently capturing and releasing atmospheric water. MOF-based water harvesting devices demonstrate operational flexibility over diverse temperature and humidity ranges and require minimal maintenance while producing clean drinking water.[3]

In recent years, there has been a focus on elucidating the crystal structures and chemical properties of water-harvesting MOFs to improve our understanding of their performance. Studies show that metal oxide clusters mostly ensure MOF stability, while organic linkers influence water-harvesting behavior.[4,5] In addition, studies have shown that the introduction of vinyl groups to the PZDC linker increases pore size and water uptake by 50%.[5] These advances in linker design are significant for more efficient water uptake. A MOF-303-based device can harvest 1.3 liters of water per kg of MOF per day using only sunlight. In the Mojave Desert, it collected 0.7 L-kg MOF^{-1}-day^{-1} of clean water without electricity.[6] While this partially meets an average person's daily water needs, it is insufficient for domestic and agricultural use. To advance water-harvesting materials, understanding water adsorption and the movement of water molecules within the MOF is critical.

The HLRN grant significantly advanced our project by expanding the study of diffusion pathways, including interpore diffusion. We used the CI-NEB technique in our in-house program MonaLisa [7,8] to study water diffusion in MOF-303. Positions of water molecules from XRD structures were optimized to create different structures to connect key sites for water diffusion and to compare barriers.

We focused on two water loadings: approximately 4 and 8 water molecules per asymmetric unit, representing important clustering situations. We classified water jumps into intracluster, intercluster, and interpore categories. These calculations allowed us to draw the energy diagrams showing the diffusion barriers and the stability of intermediate structures. An example of such a diagram is shown in Figure 1. In addition, we performed barrier decomposition to understand the interactions affecting water diffusion. The knowledge gained is crucial for the development of water-harvesting materials. The goals for the first year have been met, with the remaining tasks focused on refinement.

Throughout the project, the results obtained will be compared with available experimental data from the collaborative group of Prof. Dr. Yaghi at UC Berkley. This will verify the reliability and accuracy of our results. In addition, we are collaborating with the group of Prof. Dr. Gagliardi at UC Chicago. The combination of their molecular dynamics simulations with our results will help to establish a comprehensive understanding of water diffusion in MOFs. The results obtained will also be used as input for Grand Canonical Monte Carlo (GCMC) and Kinetic Monte Carlo (kMC) methods. The ultimate goal of the project is to contribute to the development of improved water-harvesting materials and to gain a comprehensive understanding of the molecular-level phenomena involved.

In the extension proposal, we will shift our focus from MOF-303 to MOF-333 (Figure 2), another state-of-the-art water-harvesting material differentiated by its furane-based linker. This new system will allow us to explore water harvesting under different ratios of hydrophobicity/hydrophilicity in the material. Based on test calculations using VASP 6.4.2. on HLRN resources with specific settings (PBE+D3(BJ), 520 cutoff, Γ point, standard POTCARs), we have determined that the total amount of computational resources will be approximately 6.5M core hours.

More Information

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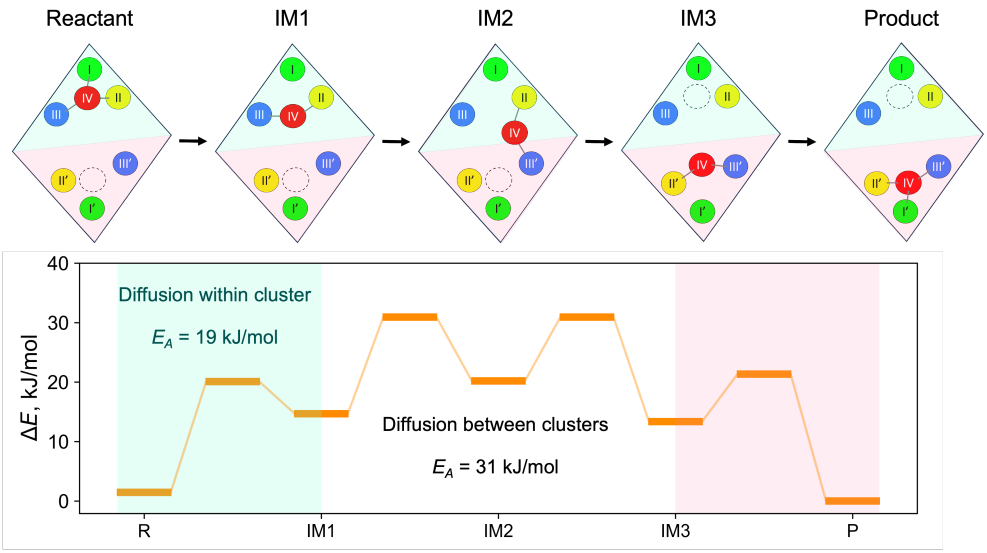

Figure 1: *Schematic water diffusion pathway and the corresponding energy profile. Water adsorption sites I-IV are shown in different colours. Water molecule transitions from top to bottom cluster via three intermediates.*

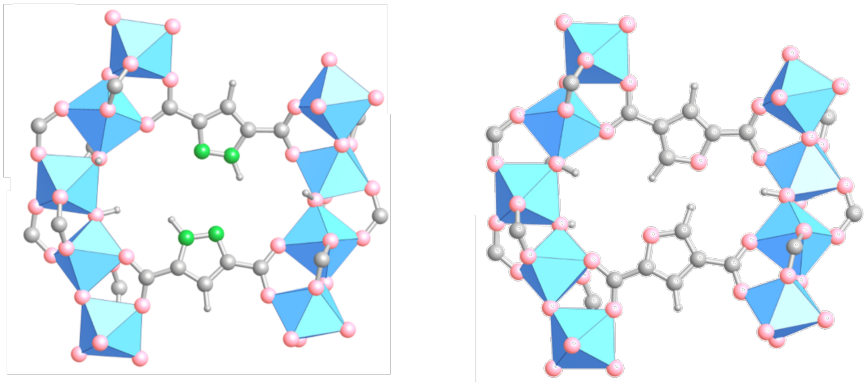

Figure 2: *XRD structures of modern water-harvesting materials MOF-303 (left) and MOF-333 (right). Picture adapted from ref. 9*

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