Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Diffusion Mechanism of Water in Conductive Metal-Organic Frameworks: Supplementary Information

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1 Details of MD simulations

The table below include the information of the water box dimension in the first stage of simulation. The water box simulation of MOF is performed to calculate the average number of water molecules N_{ave} in each MOF tube, which is also tabulated. Table S2 records the Lennard-Jones potentials of the elements in the MOFs (adopted from the universal force field). Interatomic potentials are calculated using the arithmetic rule.

Table S1: Details of the MD simulations

MOF type	Water box dimension ($x \times y \times z$, Å^3)	N_{ave}
M-HAB	$46.24 \times 47.921 \times 94.61$	N/A
$M_3(HITP)_2$ AA	$54.91 \times 57.70 \times 93.29$	435
$M_3(HITP)_2$ AB	$55.82 \times 59.25 \times 92.69$	407
$M_3(HITN)_2$	$63.32 \times 67.91 \times 96.04$	1123

Table S2: 12-6 Lennard-Jones potentials of elements in MOFs

Interaction	σ (Å)	ϵ (kcal mol^{-1})
C-C	3.851	0.105
N-N	3.660	0.069
Ag-Ag	3.148	0.036
Cr-Cr	3.023	0.015
Cu-Cu	3.495	0.005
Fe-Fe	2.912	0.013
Ni-Ni	2.834	0.015
Pd-Pd	2.899	0.048

2 Fitting of MSD curves

Figure S1 shows an example of the the least squares fitting of the a MSD with respect to the simulation time curve. Only the MSD between 5 to 25 ns of the simulation is used for the fitting (Orange line in the Figure S1).

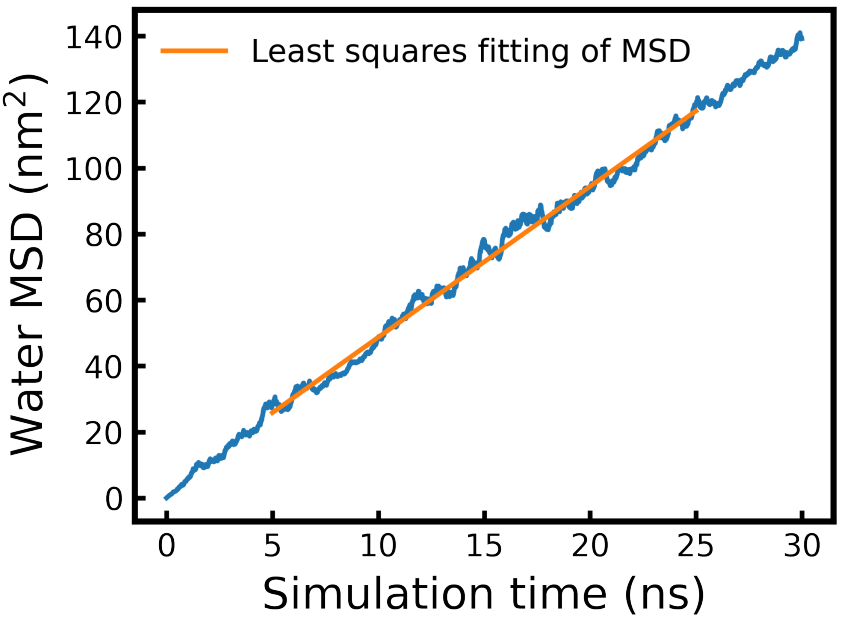

Figure S1: The least squares fitting of MSD to calculate the z-direction diffusion coefficient (D_z). Only the MSD between 5 ns to 25 ns of the simulation is used to fit the value of D_z.

3 Rare case of non-Fickian diffusion in $M_3(HITP)_2$ AA

In very rare situations (roughly 2-4 runs out of the 48 runs of the $M_3(HITP)_2$ AA tube simulations), the water MSD curve shows non-linear relationship with respect to simulation time at the beginning of the simulation. Here, two of the example are shown. The $Ag_3(HITP)_2$ AA run 4 (blue curve) shows ballistic-type diffusion during 4-9 ns of the simulation, and the $Cu_3(HITP)_2$ AA run 7 (orange curve) during the 4-8 ns. Although the MSD curve over the entire 30 ns simulation can still be considered as Fickian-type diffusion, they are the major source of the high standard deviation of the D_z of the $M_3(HITP)_2$ AA.

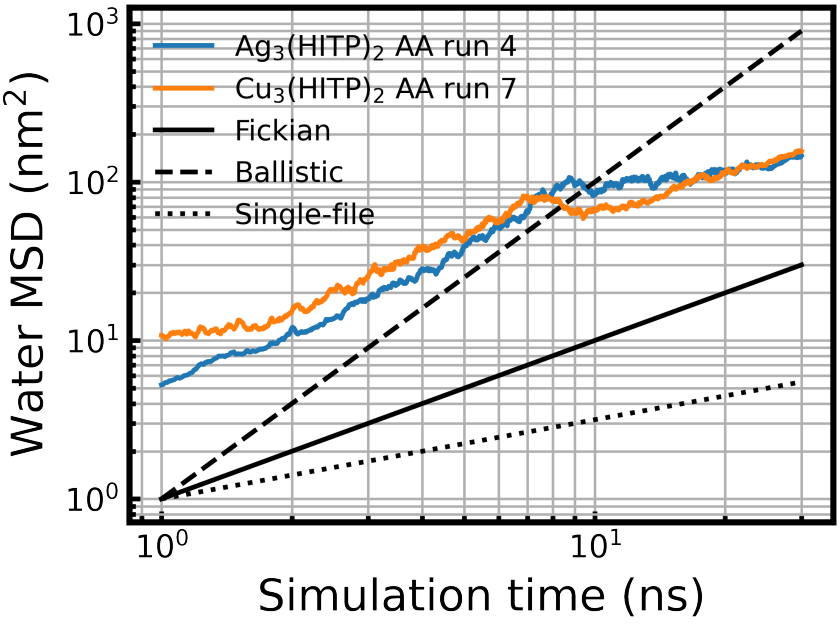

Figure S2: Example of partially non-Fickian type of diffusion in some $M_3(HITP)_2$ AA simulations.

4 Effect of metal type on water structure

Shown in Figure S3, the type of metal center does not have impact on the water structure inside of $M_3(HITP)_2$ AA MOF tube.

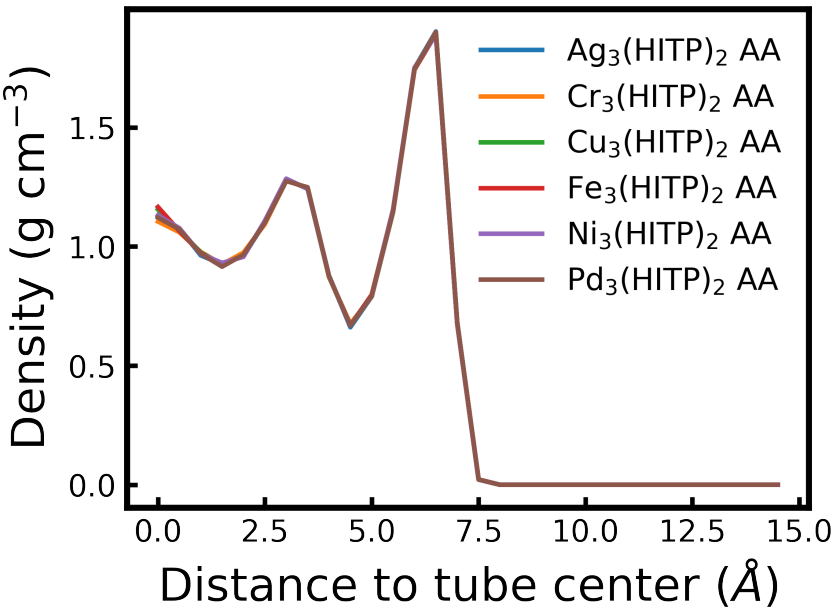

Figure S3: The comparison between the radial density profiles of water between metal center types of $M_3(HITP)_2$ AA

5 Snapshot of water molecules trapped in $M_3(HITP)_2$ AB

A close look at a typical situation when a water molecule is trapped by the angled ridge area in the $M_3(HITP)_2$ AB tube. We can notice that the water molecule is sandwiched by two layers of MOF (translucent in Figure S4). It has to bypass those MOF layers in order to move in the z-direction, which hinders it's diffusion.

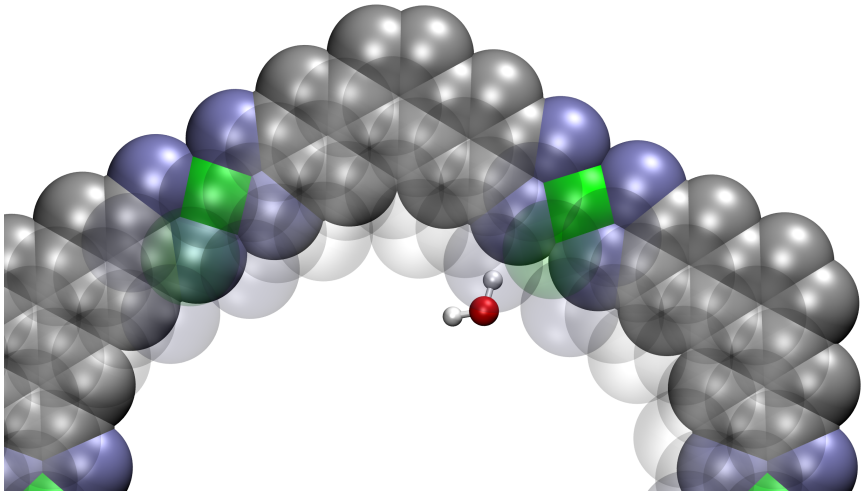

Figure S4: Snapshot of a water molecule being trapped in the upper right corner area of $M_3(HITP)_2$ AB tube. The layer of MOF on the same plane of the water molecules is shown in an opaque fashion, while the layers in front of and behind it are made translucent.

6 Snapshots of water translocation during NiHAB dehydration

The translocation of two water molecules in NiHAB tube during the dehydration process is shown in Fig. S5. Both of the water molecules locate at the left end of the tube and eventually moved out of the tube from the right end due to dehydration. The average z-direction force acting on the first and second water molecule is 0.120 and 0.159 N, respectively. Compared with the average z-direction force on all water molecules outside of the NiHAB tube, -0.003 N, the z-direction forces on the water molecules are orders-of-magnitude greater, which push them out from the right end of the tube thus causing dehydration.

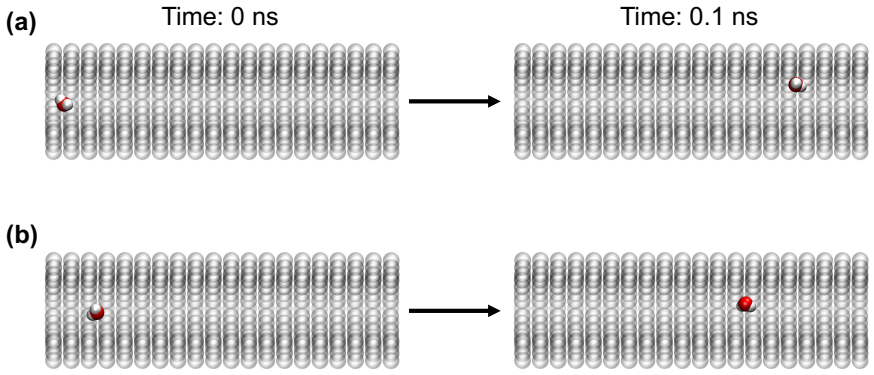

Figure S5: **(a)** and **(b)** shows the translocation of two water molecules in NiHAB MOF tube during dehydration.