Supporting Information

Why Does Enzyme Not Leach from Metal-Organic Frameworks? Unveiling the Interactions between an Enzyme Molecule and a MOF

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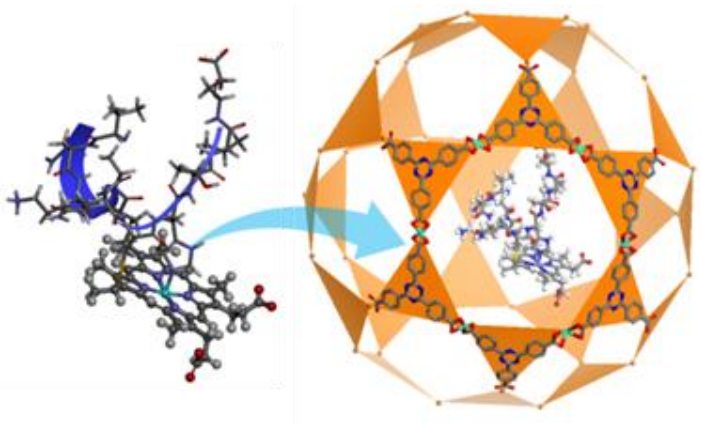
Experimental section

Immobilization of MP-11. Typically, 5.0 mg of Tb-mesoMOF was immersed in pH7.5 HEPES buffer (12hours) for solvent exchange and then immersed into 0.6 mL MP-11 (223μM) aqueous solution and incubated at 37°C until saturation (~50hours). The MP-11 concentration in the supernatant was determined at different time points using the JASCO V-670 UV Spectrometer (λ_{max} = 400, ε=176 $mM^{-1}cm^{-1}$)[1] in order to track the uptake profile. For the encapsulation of MP-11 into MCM-41 (5.0 mg), the same procedure and conditions were followed except an initial MP-11 concentration of 4mM and incubation time of 97 hours to achieve saturation. For each preparation, a sample of the initial MP-11 solution was also incubated under the same conditions and was used to determine the reference concentrations and spectra. The saturated samples were then washed with fresh HEPES buffer solution (0.1 M) several times till the supernatant became colorless to fully remove the surface adsorbed MP-11. In order to load detectable MP-11 into MCM-41 for Raman studies, the concentration of MP-11 used during the preparation for MCM-41 is 18 times higher than that for Tb-mesoMOF, however, the loading amount of MP-11@MCM-41 was still relatively low (~5.4μmol/g) compared to MP-11@Tb-mesoMOF (~20μmol/g)

Raman spectroscopy measurements. All the Raman experiments were carried out using Confocal Raman Microscope purchased from Horiba Jovin Yvon, equipped with an Argon and Krypton laser (Coherent, Innova 70C series). A laser at 514 nm was used with a power of 78 mW at room temperature. The Raman shift was calibrated using silicon wafer. All samples were placed in a HEPES buffer solution during Raman measurements. Three accumulations were employed to all samples. The spectrograph grating was 600 grooves/mm and a 20X objective was used.

In order to obtain optimal intensities of the samples, different exposure times were applied: 5 s for buffer solution and Tb-mesoMOF, 10 s for MP-11@Tb-mesoMOF, 15 s for MP-11 sample, and 30 s for MP-11@MCM-41. All experiments have been repeated at least three times to check the reproducibility. Raman spectra in the range from 200 to 3600 cm^{-1} were collected and only the region with interesting peaks was shown and discussed here.



(a) (b)

Scheme 1. (a) Magnified images of MP-11 structure. (b)MP-11 encapsulated into Tb-mesoMOF.

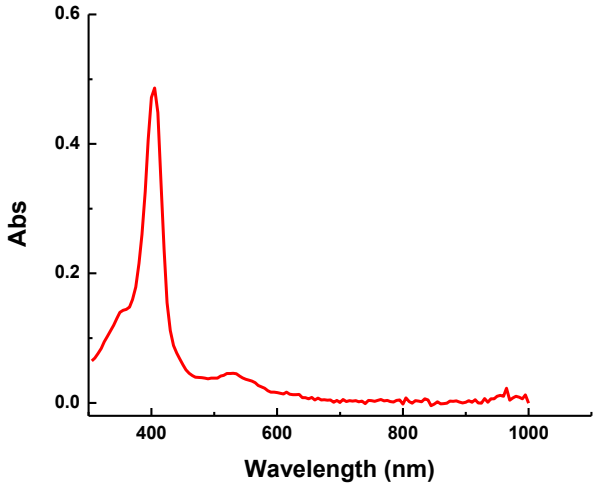


Figure S1. UV-Vis spectrum of the supernatant for MP-11@MCM-41 assay indicating severe leaching of MP-11(after 4hours in HEPES buffer). (The saturated MP-11@MCM-41 sample was taken out of solution, and then washed with fresh pH7.5 HEPES buffer solution (0.1 M) 9 times till the supernatant became colorless to fully remove the surface adsorbed MP-11. The washed sample was then placed into fresh pH7.5 HEPES buffer (0.1 M) for releasing test, and the supernatant was tracked by UV-vis to check the leaching of MP-11).

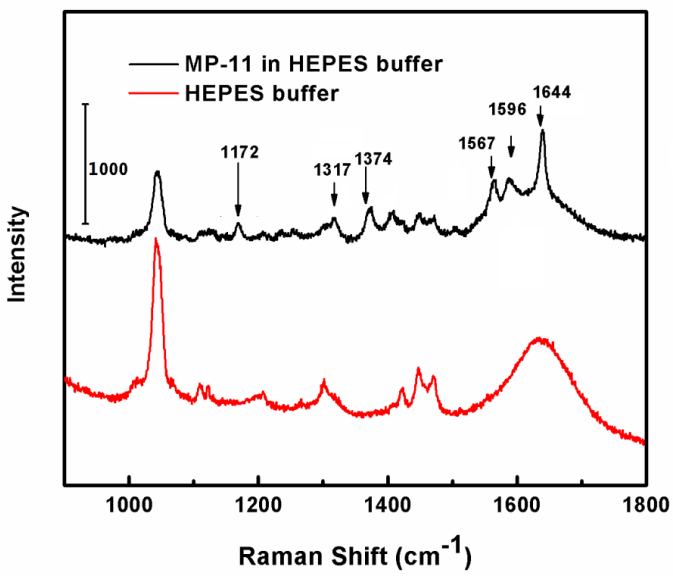


Figure S2. Raman spectra of 50 μM MP-11 dissolved in HEPES buffer (black) and the HEPES buffer solution (red).

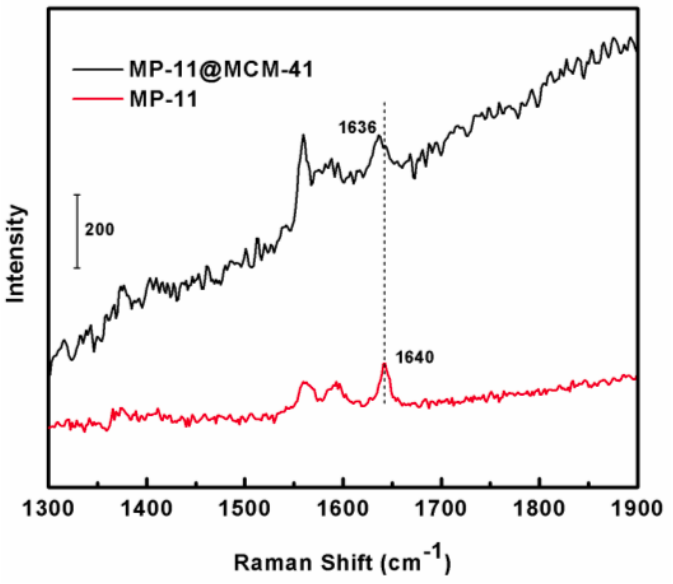


Figure S3. Raman spectra of MP-11@MCM-41 (black) and 0.8 mM MP-11 in HEPES buffer solution (red). (Please note: The concentration of MP-11 in Figure S3 is 15 times higher than that in Figure S2, which causes peak shifts of MP-11 compared to Raman spectrum of the low concentrations of MP-11 in Figure S2)

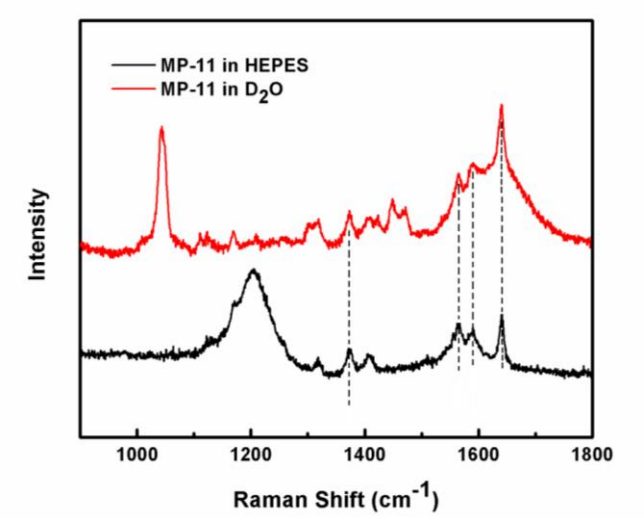


Figure S4. Raman spectra of 50 μM MP-11 in HEPES (red) and in D_2O (black): These Raman spectra indicate MP-11 is not involved to the interaction with HEPES, which confirms that the peak shifts of MP-11 in Tb-MOF is originated from the interaction between MP-11 with the ligands of Tb-MOF.

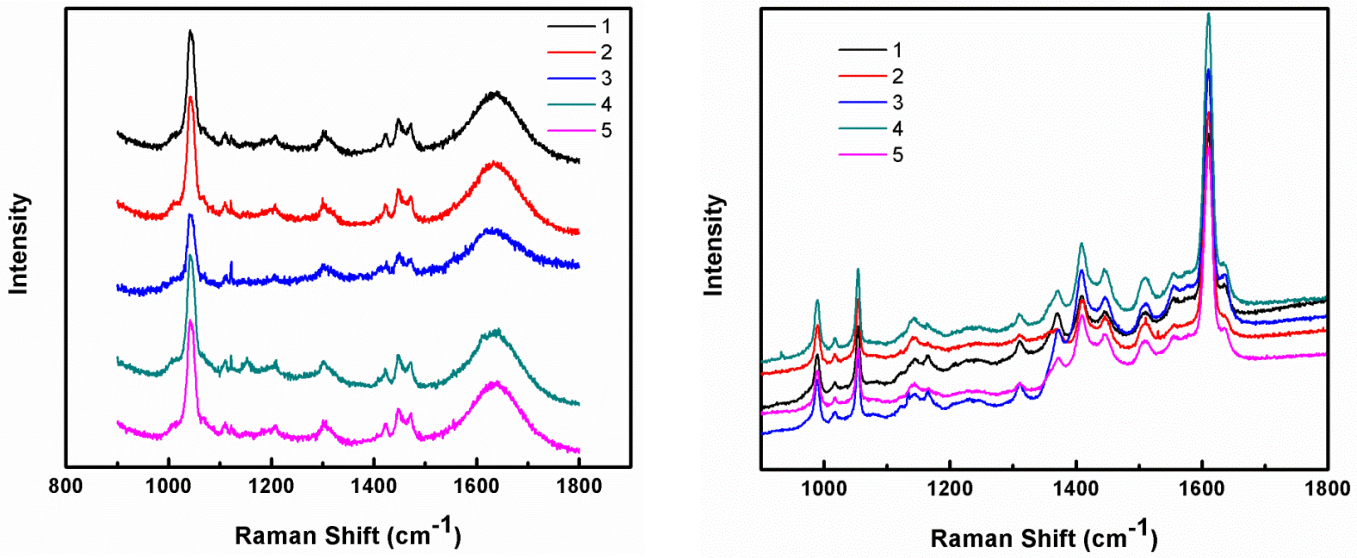


Figure S5. Raman spectra of HEPES buffer solution (left) and MP-11@Tb-MOF in HEPES solution (right): each of HEPES buffer spectra was collected from MP-11@Tb-MOF sample by changing confocal distance to focus the laser in the bulk buffer solution after Raman measurement of Tb-MOF sample in HEPES solution as the internal standard. This process was repeated 5 times as the number shown in the Figure.

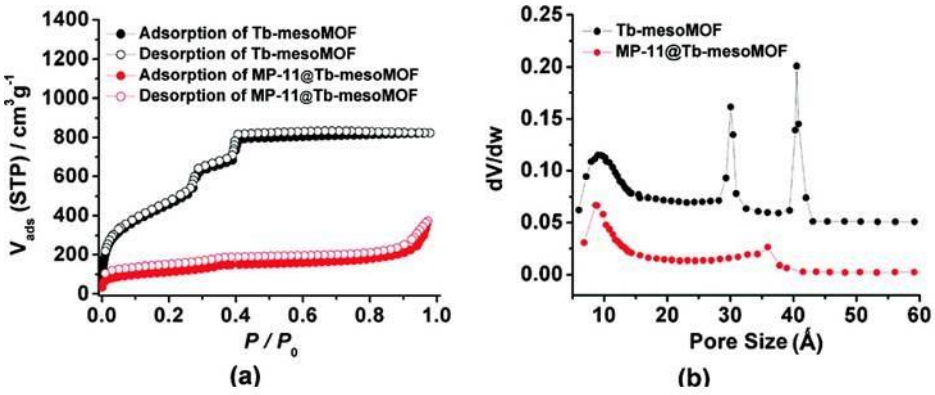


Figure S6. (a) N_2 sorption isotherms, and (b) pore size distributions of Tb-mesoMOF and MP-11@Tb-mesoMOF. A significant decrease of surface area and disappearance of ~3and 4nm nanoscopic pores was observed.

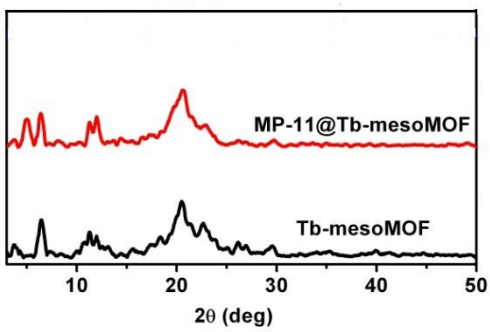


Figure S7. PXRD patterns for Tb-mesoMOF and MP-11@Tb-mesoMOF.

Reference:

1. Nakamura, S.; Mashino, T.; Hirobe, M.; *Tetrahedron Lett.* **1992**, 33, 5409.