Supporting Information

How Can Proteins Enter the Interior of a MOF? Investigation of Cytochrome *c* Translocation into a MOF Consisting of Mesoporous Cages with Microporous Windows

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Materials Syntheses

Crystalline samples of the Tb-mesoMOF were prepared according to the procedures reported in ref. S1.

Cytochrome *c* uptake experiments

Typically 2.5 mg/mL of cytochrome *c* (Cyt *c*) from bovine heart (Sigma) was prepared in 2.0 mL 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer added into 5.0 mg of Tb-mesoMOF and incubated at 37°C for 75 hours. The protein concentration in the supernatant was determined at different time points using the BCA method of protein determination (Bicinchoninic Acid protein assay using bovine serum albumin as the standard) in order to establish the uptake of Cyt *c*.[S2]

N_2 sorption measurements

N_2 sorption isotherms of Tb-mesoMOF and Cyt *c*@Tb-mesMOF were collected using the surface area analyzer ASAP-2020. Before the measurements, the freshly prepared samples were thoroughly solvent-exchanged with methanol, and activated under dynamic vacuum first at room temperature overnight and then at 120 ^{o}C for two hours. The surface area of Tb-mesoMOF is comparable with that reported in ref. 10 for the sample activated at 80 ^{o}C.

ICP-MS and AA experiments

To quantify the amount of Cyt c protein in the MOF crystals, Cyt *c*@Tb-mesoMOF was dissolved by the mixture of perchloric acid (Acros organics), H_2O_2 (RICCA Chemistry) and DMA (EMD), and then diluted by DI water to the proper concentration for each test. Inductively coupled plasma-mass spectrometry (ICP-MS) was performed on a Perkin Elmer Elan II DRC instrument to determine the content of Fe and Tb in the sample, which was further measured by Atomic Adsorption Spectroscopy (Varian AA Spectr 100). Both ICP-MS and AA experiments revealed the Cyt *c* uptake amount of ~9.8 μmol/g, which is in good agreement with the loading amount determined by BCA method.

Fluorescent Spectroscopy Experiments

Steady state emission studies of Cyt *c*@Tb-mesoMOF were performed using samples of the solid material (5 mg) suspended in 2 mL of an aqueous buffered solution (50 mM HEPES,

pH 7.5) in a 1 cm quartz optical cuvette using an ISS PC1 spectrofluorimeter. The sample was continuously stirred during the measurements. Solution emission studies of Cyt *c* (50 mM HEPES, pH 7.2) and Cyt *c* in GdnHCl (50 mM HEPES, pH 7.2 + 6 M GdnHCl) were obtained using ~ 5μM protein in 2 mL of buffer. The excitation wavelength for all studies was 280 nm with a 0.5 mm slit width on both the excitation and emission monochrometers to minimize scatter. The Tb-mesoMOF crystals did not exhibit significant emission in the 290-400 nm spectra region.

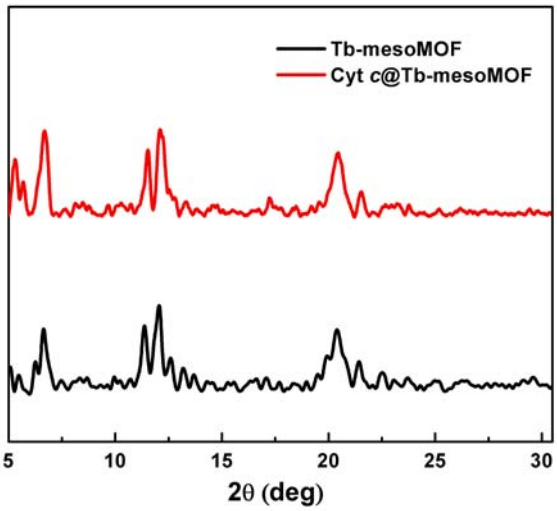

Figure S1. PXRD patterns of Tb-mesoMOF and Cyt *c*@Tb-mesoMOF.

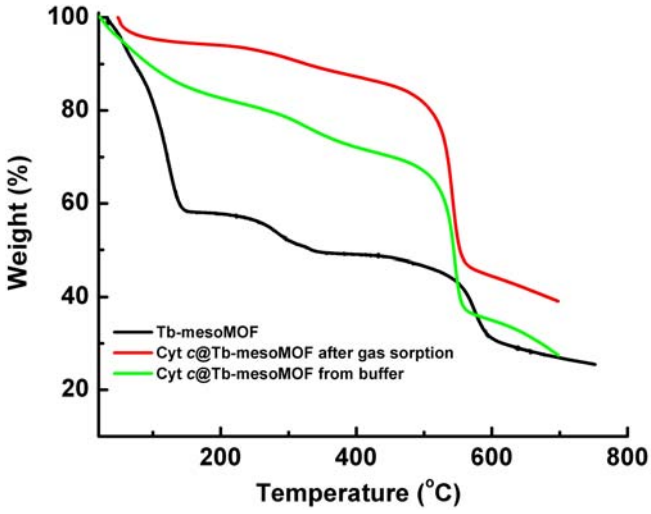

Figure S2. TGA plots of Tb-mesoMOF and Cyt *c*@Tb-mesoMOF.

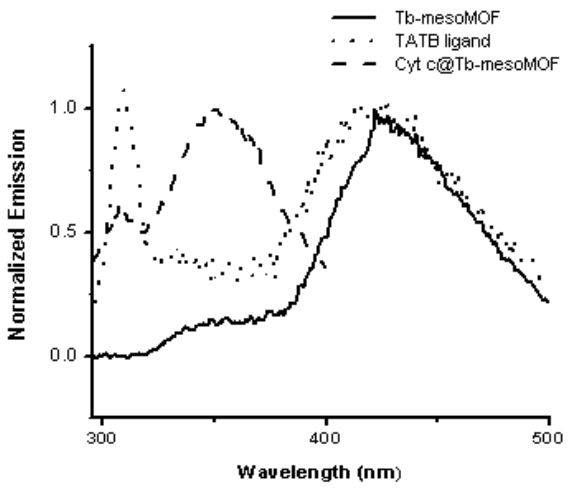

Figure S3. Fluorescent spectra of Tb-mesoMOF, TATB ligand and Cyt *c*@Tb-mesoMOF in HEPES buffer.

References

S1. Y. K. Park, S. B. Choi, H. Kim, K. Kim, B.-H. Won, K. Choi, J.-S. Choi, W.-S. Ahn, N. Won, S. Kim, D. H. Jung, S.-H. Choi, G.-H. Kim, S.-S. Cha, Y. H. Jhon, J. K. Yang and J. Kim, *Angew. Chem. Int. Ed*., 2007, **46**, 8230-8233.

S2. P. K. Smith, R. I. Krohn, G. T.Hermanson, F. H Gartner, E. K. Fujimoto, N. M. Goeke, B. J. Olson and D. C. Klenk, *Anal. Biochem*., 1985, **150**, 76-85.