Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPORTING INFORMATION

Hydrophobic and Moisture-Stable Metal-Organic Frameworks

Carlos A. Fernandez,* Satish K. Nune,* Harsha V. Annapureddy, Liem X. Dang, , B. Peter McGrail, Feng Zheng, Evgueni Polikarpov, David L. King, Charles Freeman and Kriston P. Brooks

Number of tables: 1

Number of Figures: 8

No. of videos: 2 (Attached Separately)

Table S1. Contact angle values for unmodified and P1-modified MOFs

Sample name	Contact angle at t=0	Droplet life time, s
MIL101	0	0
P1-MIL101	~25°	~35
Ni-MOF-74	~7°	~1
P1-Ni-MOF-74	~22°	~30

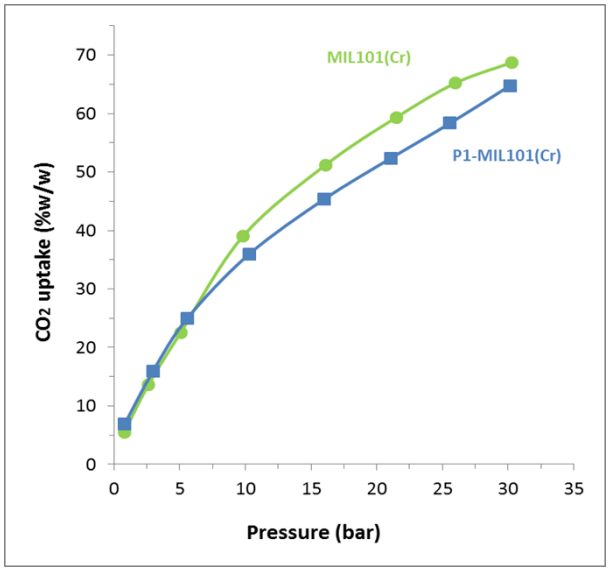


Figure S1. High pressure RT CO2 sorption in unmodified and P1-modified MIL101(Cr)

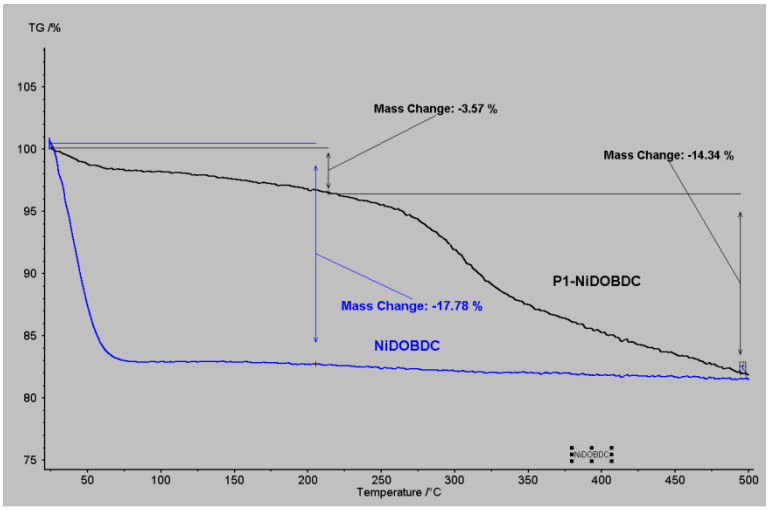


Figure S2. RT water sorption on unmodified as well as P1-treated MIL101(Cr) showing no change on capacity after three activation/exposure cycles.

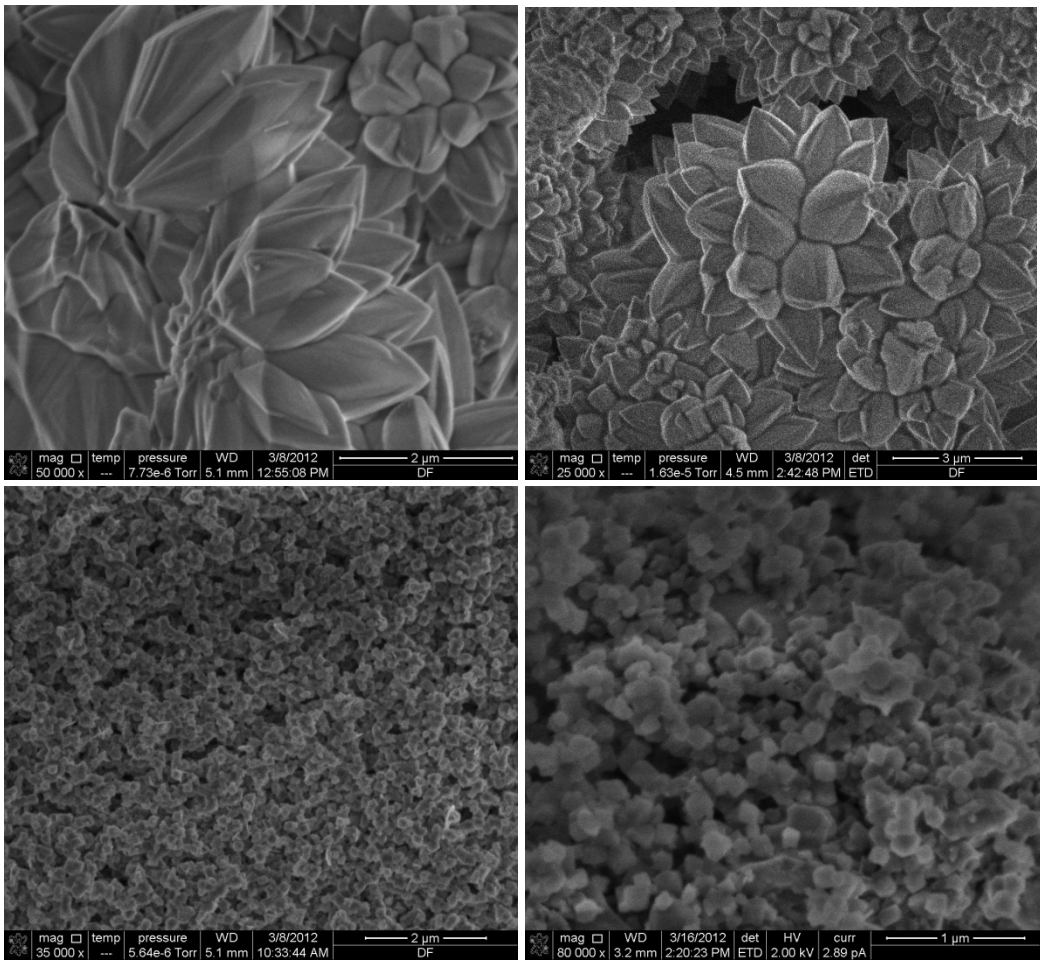


Figure S3. Top. SEM micrographs of unmodified (top left) and P1-modified NiDOBDC (top right). Bottom. SEM micrographs of unmodified MIL101(Cr) and P1-modified MIL101(Cr).

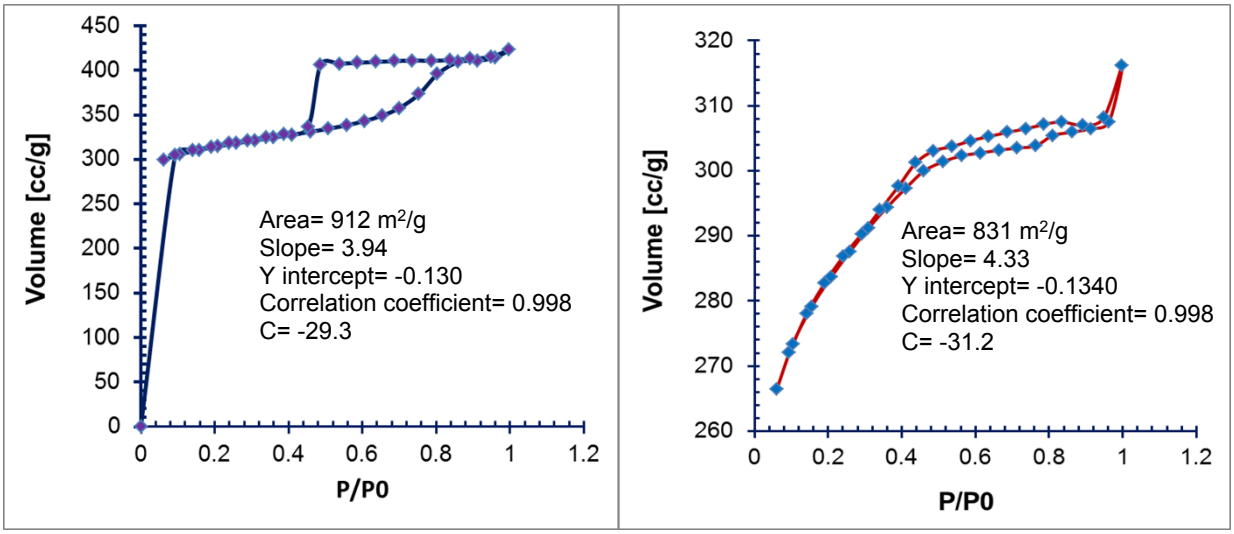


Figure S4. Nitrogen isotherms at 77 K and BET surface area calculated for unmodified NiDOBDC (left) and P1-modified NiDOBDC (right).

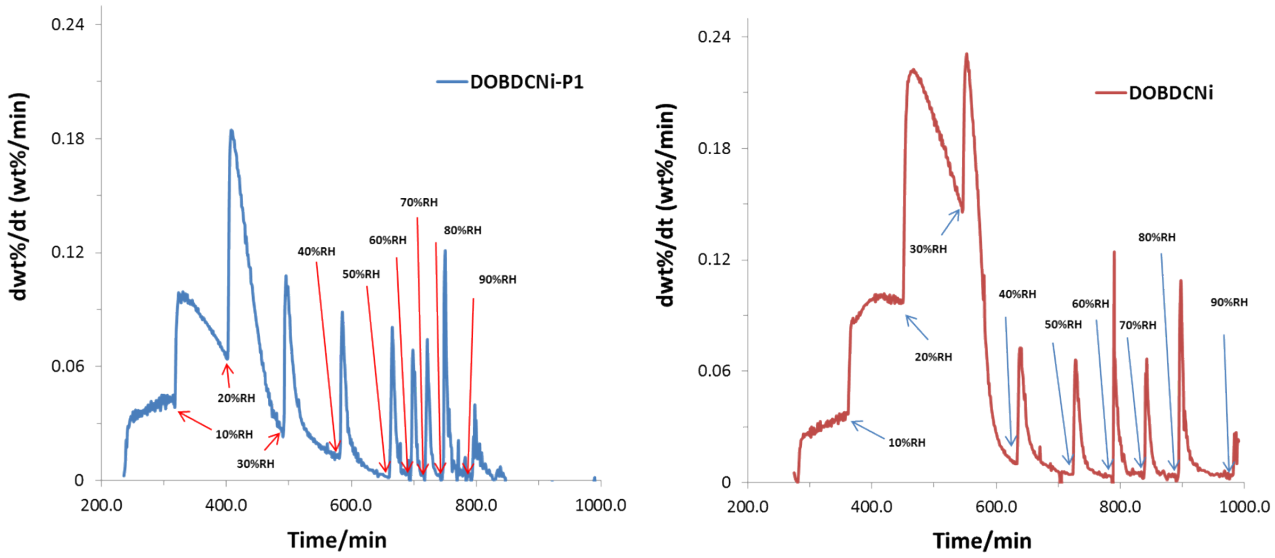
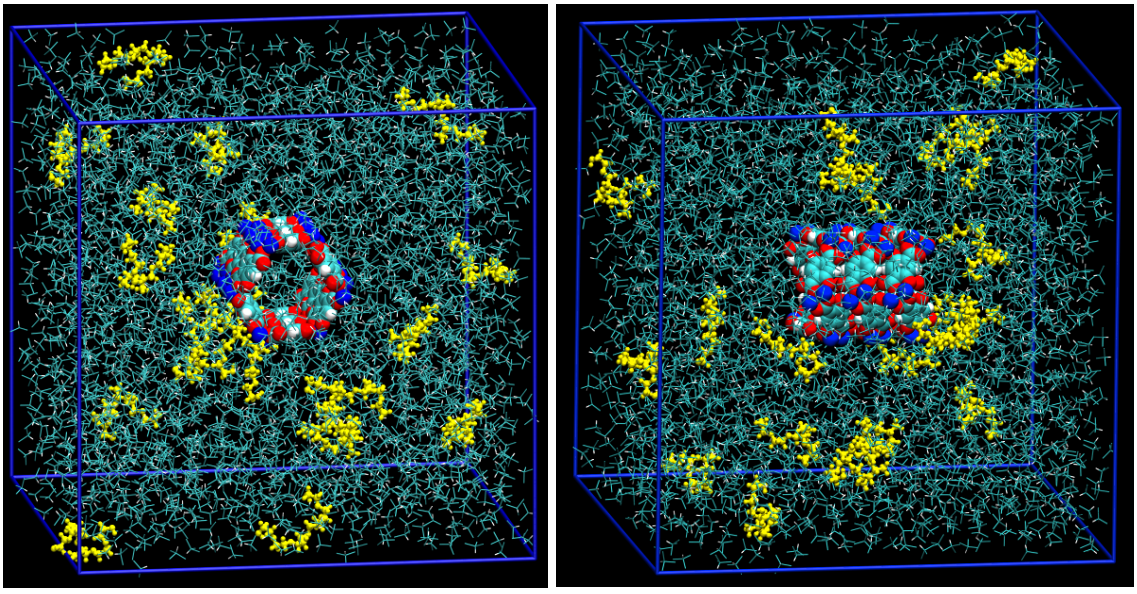


Figure S5. Water sorption change rate ($\delta wt\%/\delta t$) as a function of time on unmodified NiDOBDC (right) and on P1-modified NiDOBDC (left) showing the times at which water sorption at a new %RH takes place. Note the higher rates observed for unmodified NiDOBDC at low %RH and the very high rates observed in the first few minutes of a new RH% condition followed by exponential rates decay in both materials.



Front View Side View

Figure S6: Simulation snapshot of a NiDOBDC fragment and 20 molecules of P-123 solvated in chloroform during the process of MOF functionalization with P-123.

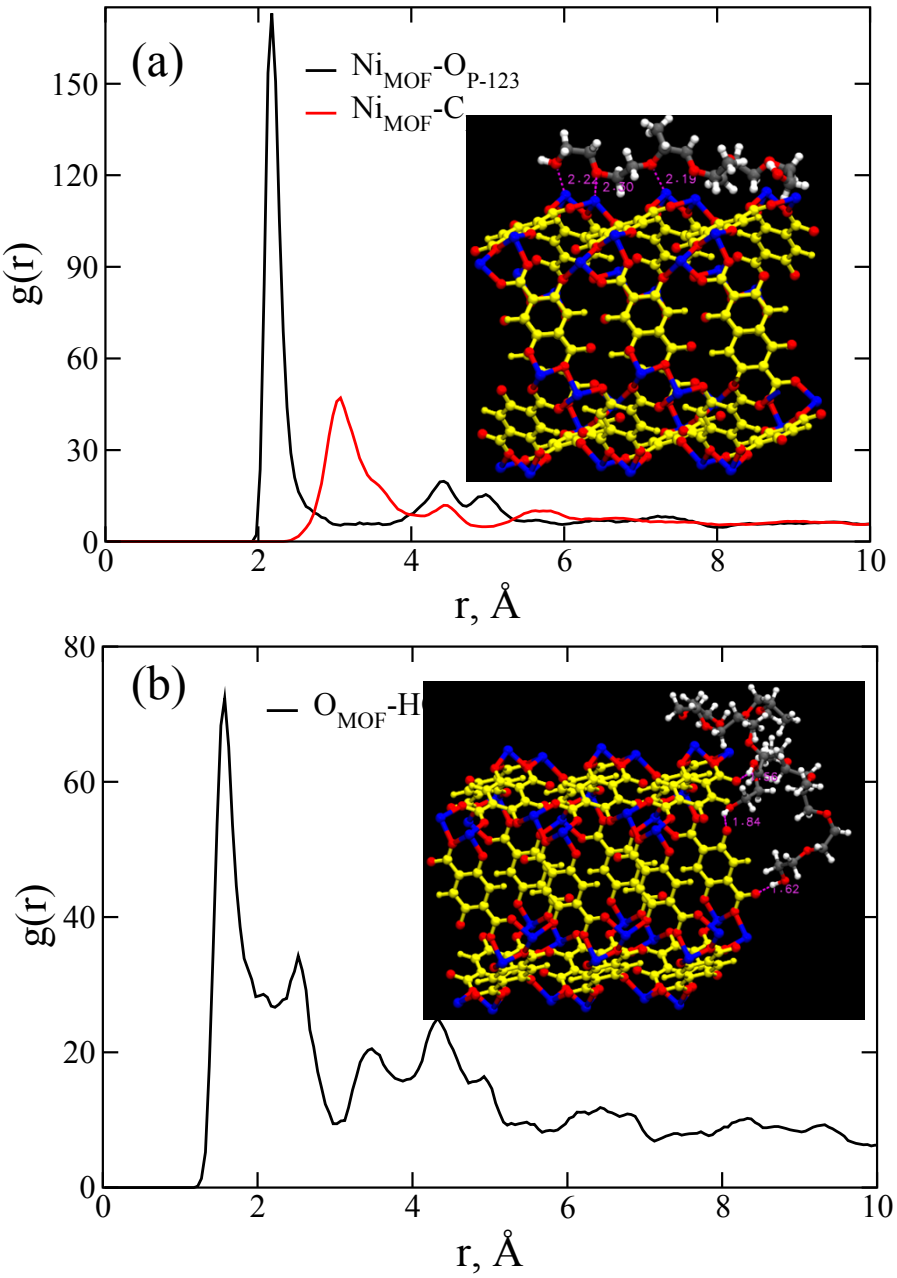


Figure S7: (a) Radial distribution function between the Ni atoms of NiDOBDC and the oxygen atoms of the P-123. (b) Radial distribution functions between the Oxygen atoms of NiDOBDC and the terminal Hydrogen atoms of P-123. In inset we show the snapshot illustrating the corresponding interactions between P-123 and MOF.

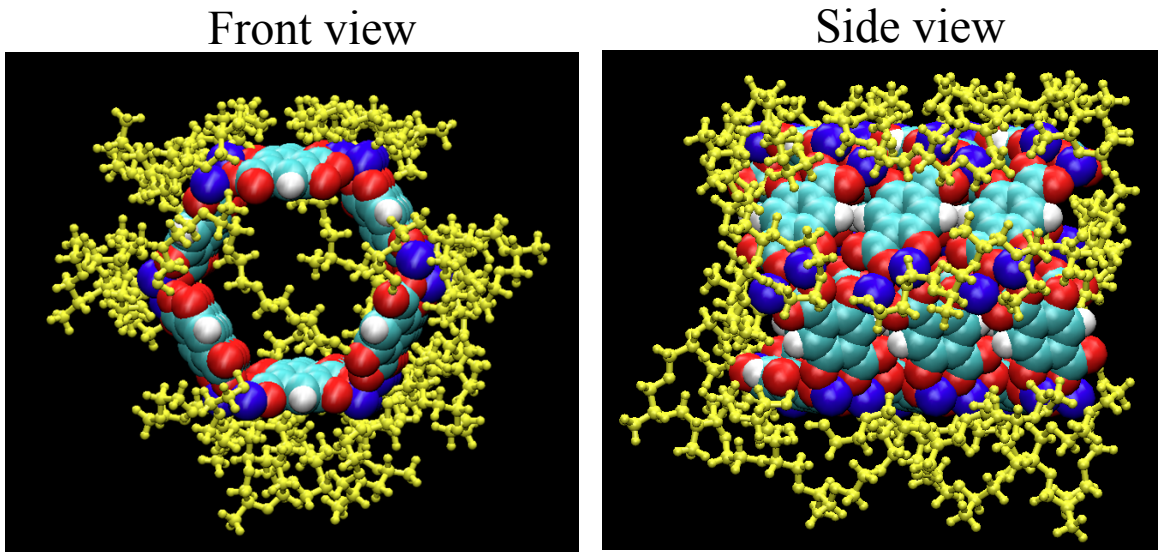
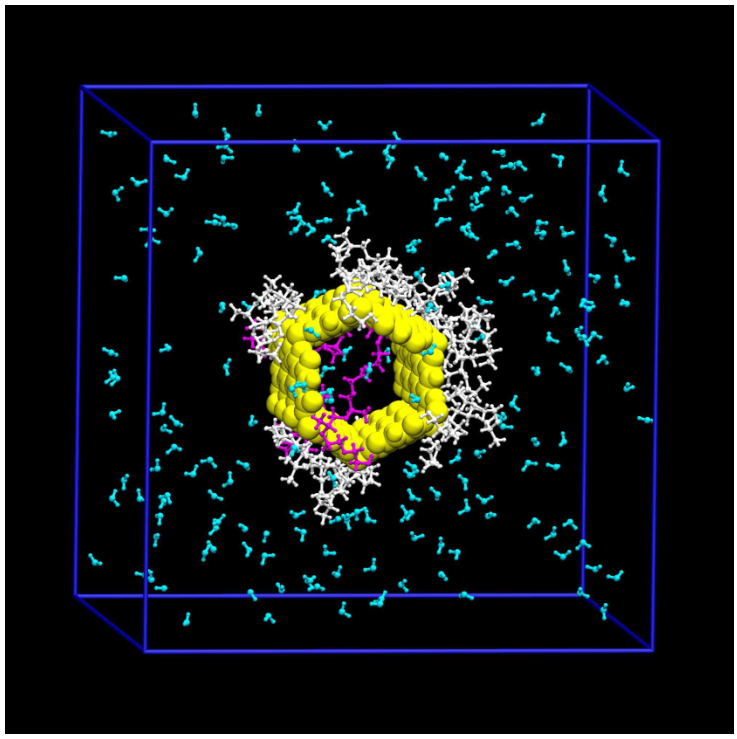
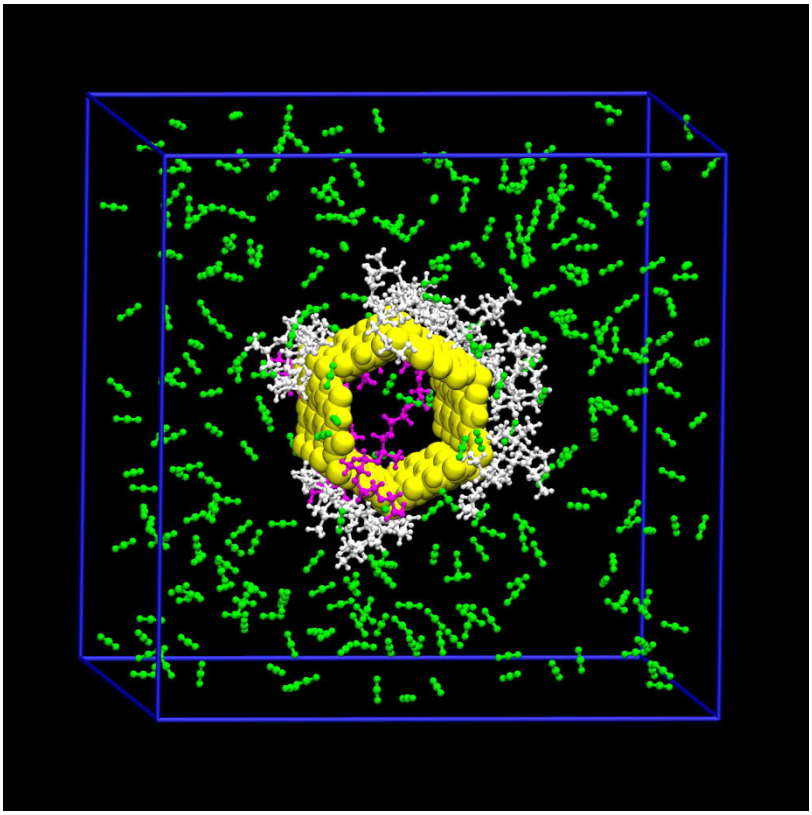


Figure S8: Front and side views of a NiDOBDC fragment with P-123 wrapped round it.



Video 1: Simulation trajectory of P1-modified NiDOBDC with water



Video 2: Simulation trajectory of P1-functionalized NiDOBDC with CO_2

Molecular Dynamics (MD) Simulations. MD simulations were performed by using Amber 9 package. The radial distribution functions (RDFs) was computed to understand the interaction between the NiDOBDC fragments and P-123. Force field parameters for MOF were taken from previous work.[1,2] The SPC/E and the potential parameters for chloroform were taken from literature.[3,4] The molecular formula of polymer (P-123) unit used in our MD simulations is $(HO(CH_2CH_2O)_2(CH_2CH(CH_3)O)_2(CH_2CH_2O)_2H)$. Charges for the P-123 are computed using am1-bcc method implemented in the antechamber module of Amber 9 package. Lennard–Jones (LJ) and all the other intramolecular parameters such as bond, angle and torsion were obtained from general AMBER force field (GAFF).[5, 6]

A portion of a rigid fragment of MOF was taken from the NiDOBDC crystal structure. The MOF fragment is then centered in a box of size 80x80x80 Å. To this 20 units of P-123 were added and then solvated with chloroform. Snapshots of simulation box containing MOF + P123 solvated in chloroform are shown in Figure S9. Equilibration runs were carried out in a constant NPT (number of particles, pressure and temperature) ensemble to get the correct density, followed by a 20 ns of production run using canonical ensemble NVT (number of particles, volume and temperature)

using periodic boundary conditions applied in all three directions with a time step of 1 fs. The three-dimensional particle mesh Ewald summation technique was used to calculate the long-range electrostatic interactions.[7]

Figure S10 illustrates the radial density functions (RDF) computed between the Ni-atoms of MOF and the oxygen and carbon atoms of P-123. The Ni_{MOF}-$O_{P\text{-}123}$ RDF has sharp and intense peak at ~2.2 Å. As expected we observed strong interaction between the positive Ni-atoms of the MOF and the partially negative O-atoms of P-123. In Figure S10 we show the RDF between the oxygen atoms of MOF linker units and the terminal hydrogen atoms of P-123. This RDF has peak at ~1.7 Å, indicating strong O_{MOF}-$HO_{P\text{-}123}$ interactions. These two kinds of interactions are primary governing factors for binding of P-123 to MOF material.

Equilibrated MOF fragment with the polymer wrapped around it is taken and placed at the center of a simulation box of size 60x60x60Å (Figure S11). Two systems were prepared by randomly adding three hundred molecules of water and carbon dioxide respectively. MD simulations are performed for both the systems in an NVT ensemble at 298 K.

References

(1) Case, D. A.; Darden, T. A.; Cheatham III, T. E.; Simmerling, C. L.; Wang, J.; Duke, R. E.; Luo, R.; Merz, K. M.; Pearlman, D. A.; Crowley, M. *Amber 9*. University of California, San Francisco: 2006.

(2) Sun, X. Q.; Wick, C. D.; Thallapally, P. K.; McGrail, B. P.; Dang, L. X. Computational study of hydrocarbon adsorption in metal-organic framework Ni_2(dhtp). *Journal of Physical Chemistry B* **2011**, *115*, 2842-2849.

(3) Berendsen, H. J. C.; Griger, J. R.; Straatsma, T. P. T. The missing term in effective pair potentials. *J. Phys. Chem.*, 1987, *91*, 6269-6271.

(4) Jorgensen, W. L., Tirado-Rives, J. (1988). Energy Minimizations for Crystals of Cyclic Peptides and Crambin. *J. Am. Chem. Soc.* **110** (6): 1657–1666.

(5). Wang, J. M.; Wolf, R. M.; Caldwell, J. W.; Kollman, P. A.; Case, D. Development and testing of a general amber force field. *J. Comp. Chem.* **2004,** *25*, 1157-1174.

(6). Wang, J. M.; Wang, W.; Kollman, P. A.; Case, D. A. Automatic atom type and bond type perception in molecular mechanical calculations. *J. Mol. Graph Model* **2006,** *25*, 247-260.

(7) Essmann, U.; Perera, L.; Berkowitz, M. L.; Darden, T.; Lee, H. and Pedersen, L. G. A smooth particle mesh Ewald method. *J. Chem. Phys.* **1995,** *103*, 8577- 8593.