

Electronic Supplementary Information

Squeezing the box: Isoreticular contraction of pyrene-based linker in a Zr-based metal–organic framework for Xe/Kr separation

Rodrigo R. Maldonado, Xuan Zhang, Sylvia Hanna, Xinyi Gong, Nathan C. Gianneschi, Joseph T. Hupp, Omar K. Farha

Department of Chemistry and International Institute of Nanotechnology, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208

Corresponding author email: j-hupp@northwestern.edu o-farha@northwestern.edu

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Section 1 Starting Materials

All starting materials and solvents were purchased from commercial suppliers and used without further purification. Methanol (99.8), N,N-dimethylformamide (DMF, 99.9%), acetone (99.5), and hydrochloric acid (36.5-38.0%) were purchased from Fisher Chemical. Xantphos (97%), palladium (II) acetate (98%), formic acid (>98%), sodium hydroxide pellets (>97%) and zirconyl chloride octahydrate (98%) were purchased from Millipore-Sigma. N-formylsaccharin (NFS, 98%) was purchased from TCI Chemical. Potassium fluoride (99%) was purchased from Alfa Aesar, and 1,3,6,8-tetrabromopyrene (98%) was purchased from ChemSoon. Biphenyl-3,3',5,5'-tetracarboxylic acid (98%) was purchased from Combi-Blocks. Anhydrous DMF (99.8%) was purchased from EMD Millipore. The water used in experiments was deionized water.

Section 2 Ligand Synthesis

Synthesis of 1,3,6,8-pyrene tetracarboxylic acid (Py-TC)¹

Palladium (II) acetate (158 mg) and Xantphos (602 mg) were added to a high-pressure flask (with large stir bar) inside the glovebox. 75 mL of anhydrous DMF were added. Tetrabromopyrene (3 g), Potassium Fluoride (3.48 g), and NFS (6.12 g), were added to vessel in that order. Once NFS was added, the flask was immediately sealed to avoid loss of carbon monoxide. (Synthesis has been prepared in the past with 1.5 g of Tetrabromopyrene. In this case, the solid reagents were halved as well; however, 75 mL of DMF was used).

To purify, the Py-TC solution was cooled to room-temperature. For a 3 g synthesis, 12 mL of triethylamine and 20 mL of water were added to the flask, then left to stir overnight. The contents were dried under vacuum using a rotovap. The crude material was suspended, vacuum filtered, and washed with copious amounts of water (about 800-900 mL). 1 g batches of the material were each dissolved in separate 250 mL 1M NaOH (aq.) solutions. Each solution was filtered 3-4 times until precipitate was completely removed. Solutions were then acidified with 2M HCl (aq.) until pH = 5 or 6, vacuum filtered, and then washed further with small amounts of cold water. When dried, precipitate forms dark brown/red sheets that stick to filter paper. Material was carefully scratched off the filter paper, dissolved in minimal DMF, and then precipitated with MeOH to form a powder. The powder was then washed with copious amounts of acetone, yielding an orange product (42 % yield). ¹H-NMR shifts (ppm): 9.14 (2 H, s), 9.41 (4 H, s).

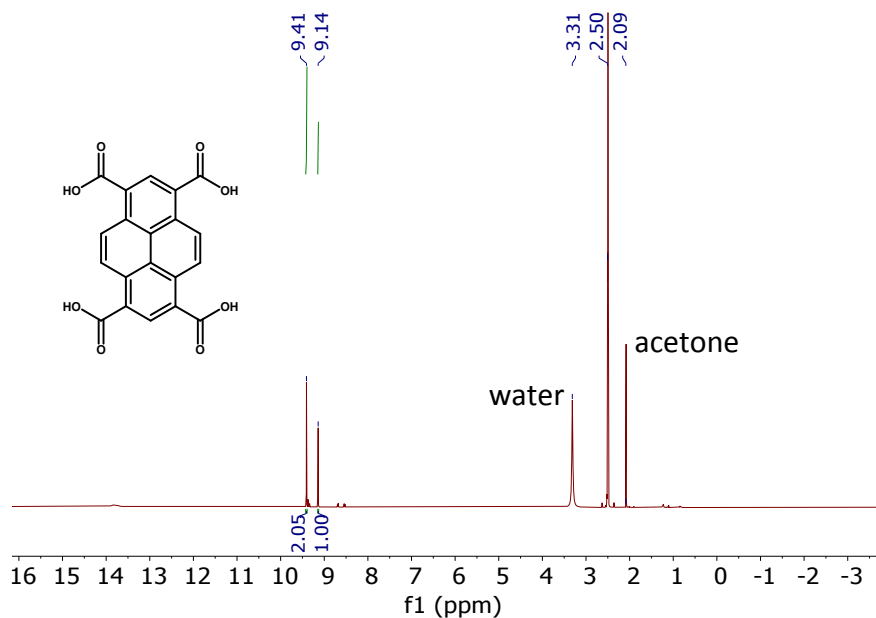


Figure S1. ¹H-NMR of Py-TC in DMSO. Shifts (ppm): 9.14 (2 H), 9.41 (4 H), 2.09 (acetone), 3.31 (water)

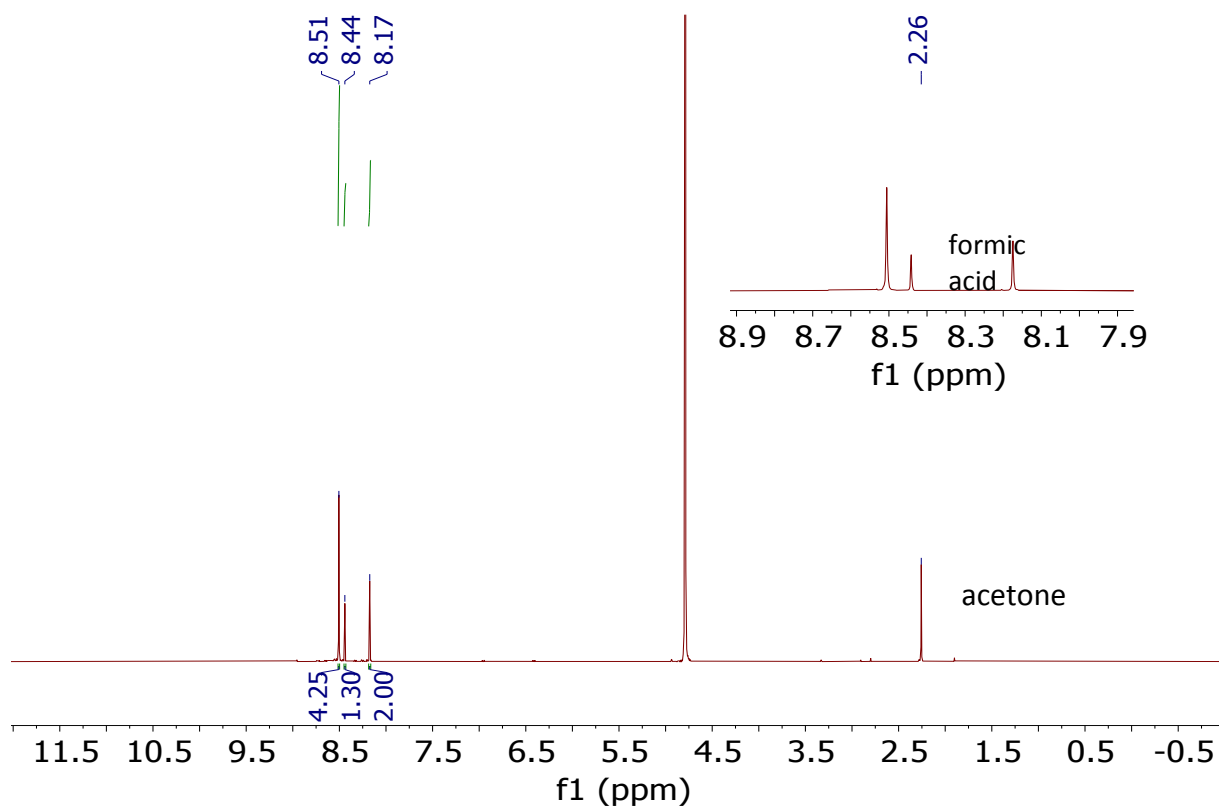
Section 3 MOF Synthesis and Preparation

NU-1106 ($Zr_6(\mu_3-O)_4(\mu_3-OH)_4(Py-TC)_3$) Synthesis

The synthesis for **NU-1106** follows a protocol similar to that set out by Wang *et al.* for the biphenyl version of the MOF.² Zirconyl chloride octahydrate (32.2 mg, 0.1 mmol) was dissolved in DMF (2.5 mL); formic acid (5 mL) was then added. Py-TC (18.9 mg, 0.05 mmol) was added to 2.5 mL of DMF and heated until the powder fully dissolved. The two solutions were combined, and the new solution was heated to 130 °C for 2 days. MOF was washed in a hot DMF bath for 2 days (130 °C), each day collected by centrifugation and washed again with fresh DMF. Then washed with methanol for 3 days under Soxhlet (70% yield).

To activate, the MOF was heated under vacuum at 300 °C overnight.

The biphenyl version (BPTC) of the MOF was synthesized using the same protocol but with a different linker (1,3,6,8-biphenyl tetracarboxylate) at equal mole amounts as the zirconyl chloride octahydrate (33.0 mg, 0.1 mmol) and activated the same.



Fig

ure S2. ¹H-NMR of **NU-1106**. **NU-1106** (1 mg) was digested in 6-8 drops of 1 M NaOD and diluted in D₂O. Shifts (ppm): 8.17 (s, 2 H), 8.51 (s, 4 H), 2.26 (s, acetone), 8.44 (s, formic acid).

Section 4 Material Characterization

Powder X-ray Diffraction (PXRD): For room temperature experiments, PXRD patterns were obtained by using a STOE-STADI P powder diffractometer. The instrument was operated at 40 kV and 40 mA using Cu-K α 1 X-ray radiation ($\lambda = 1.54056 \text{ \AA}$). Data for variable-temperature experiments were obtained with a STOE-STADI MP powder diffractometer using similar current and voltage, and identical radiation. For a single sample, multiple PXRD patterns were taken at increasing temperatures, starting at 150 °C and ending at 400 °C. Ten PXRD patterns were measured for a single temperature, one every 6 minutes. The temperature was then increased by 10 °C, followed by the next set of ten measurements.

Thermogravimetric Analysis (TGA): TGA measurements were conducted on a TA Instruments Discovery TGA under flow of air (20% O₂/80% N₂, 20 mL/min) at a heating rate of 10 °C/min from room temperature to 600 °C.

Adsorption Experiments: MOFs were activated at 300 °C overnight on the Micromeritics Smart Vac Prep. Adsorption was measured on a Micromeritics 3Flex instrument. Nitrogen isotherms were taken at 77 K (using liquid nitrogen). BET analysis was applied to data obtained over the range from $P/P^0 = 0.005$ to 0.07. Krypton and xenon experiments were run at 25 °C with the temperature being fixed with a Micromeritics Isocontroller.

¹H Nuclear Magnetic Resonance (NMR): For MOFs, NMR samples were prepared by dissolving approximately 1 mg of material in eight drops of 0.1 M NaOD solution using a sonicator. About 0.6 mL of D₂O was added to the solution. NMR measurements were taken on a Bruker Avance III 500 MHz equipped with a DCH CryoProbe.

High-resolution Transmission Electron Microscopy (HR-TEM): TEM images were collected on a TEM JEOL ARM300F using a Gatan OneView-IS camera, which is equipped with a CMOS electron sensor. The accelerating voltage was 300 kV and the emission current 15 μ A. The electron dose for each image was approximately 10 e/($\text{\AA}^2 \cdot \text{s}$).

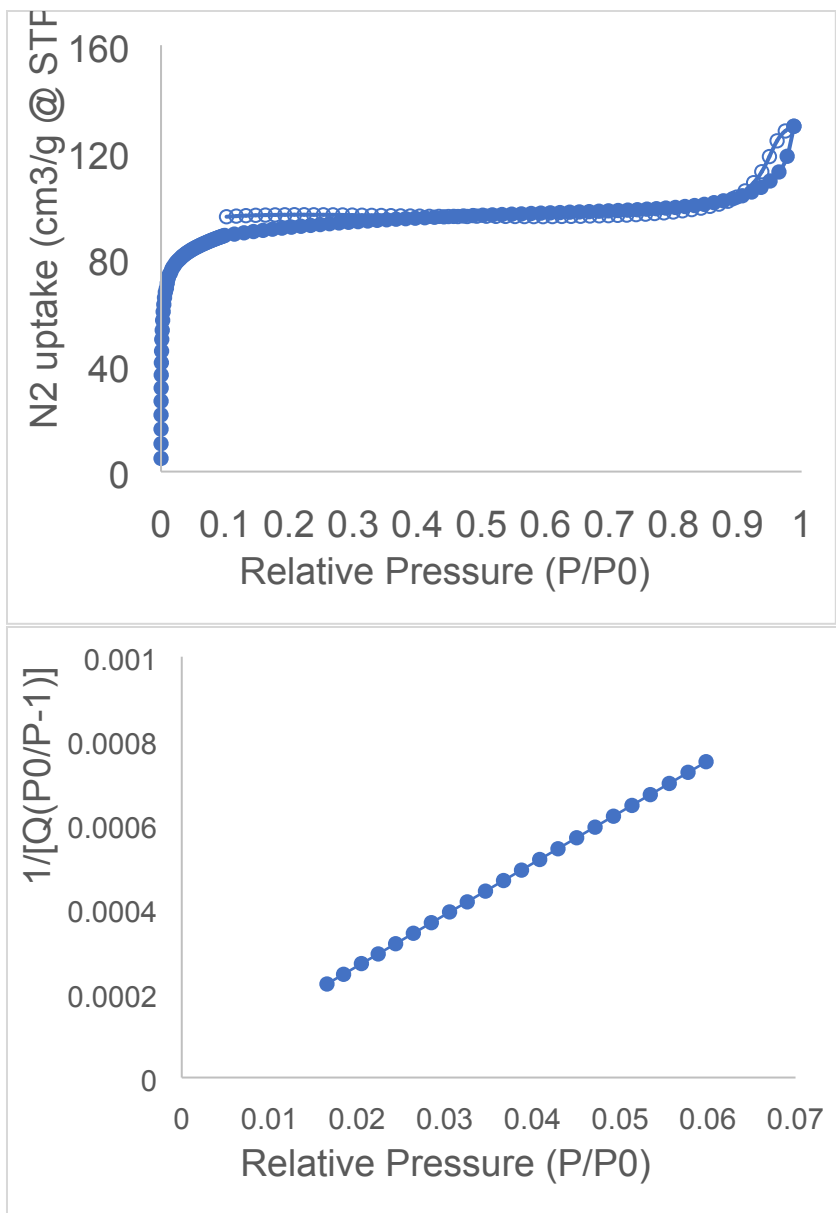


Figure S3. Nitrogen Isotherm (top) and BET linear plot (bottom) of NU-1106.

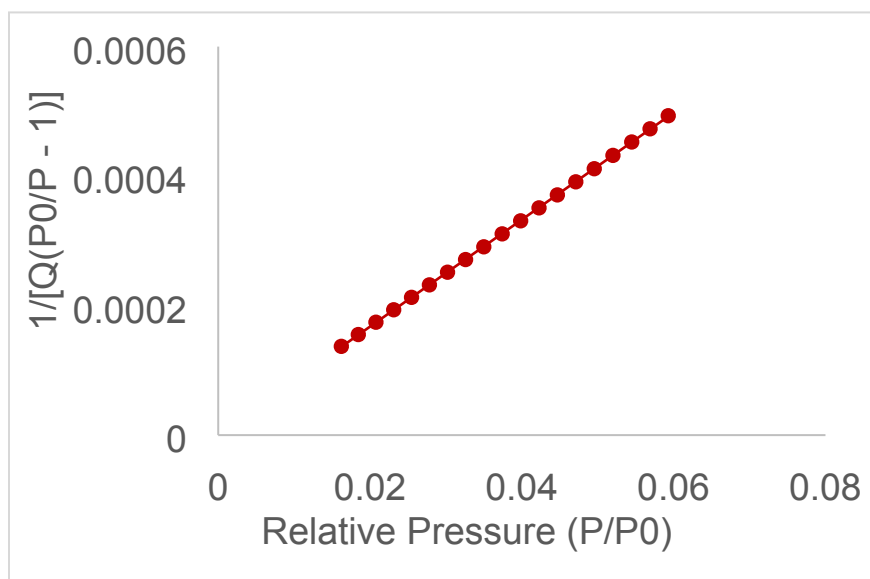
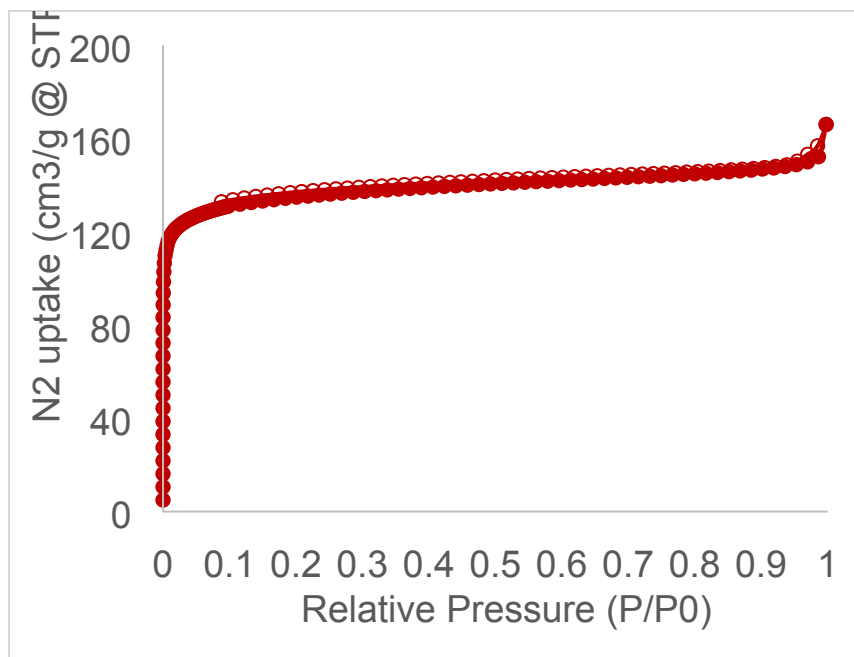


Figure S4. Nitrogen Isotherm (top) and BET linear plot (bottom) of the Zr-BPTC *ftw* MOF.

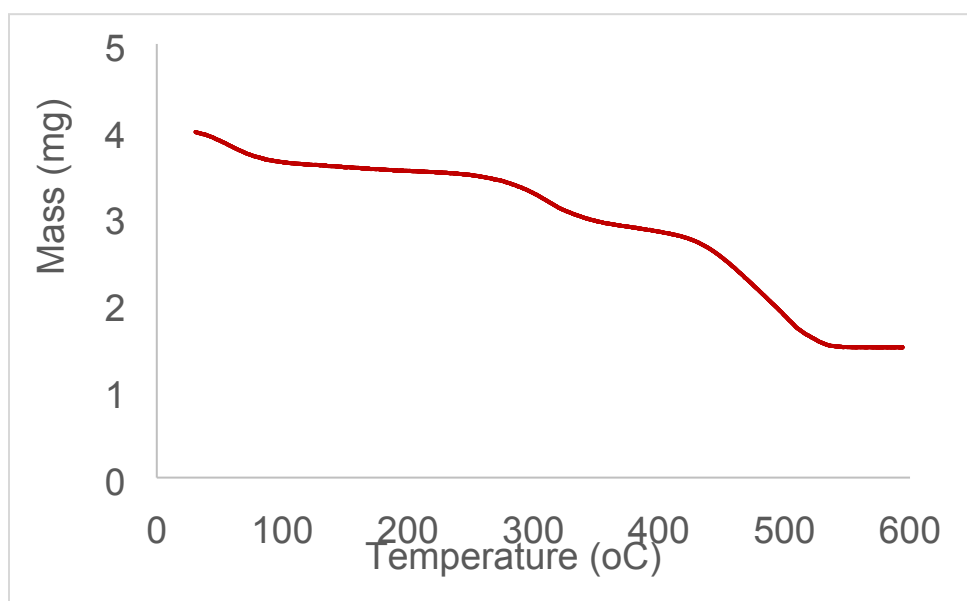
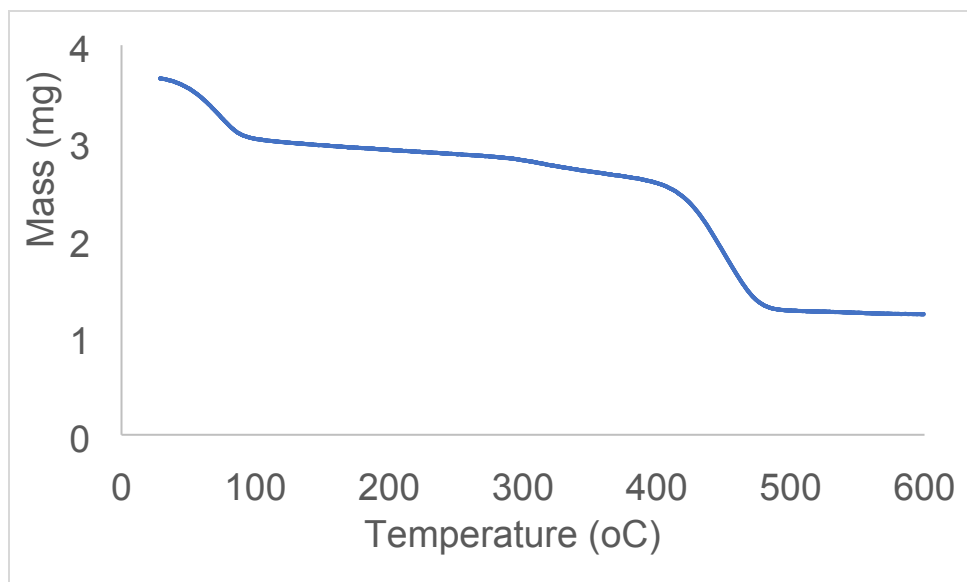


Figure S5. TGA measurements of NU-1106 (top, blue) and the Biphenyl derivative (bottom, red). Mass loss was measured at approximately 410 °C for both the MOFs, and both MOFs showed the same defect density of 2.2 linkers per Zr_6 node.

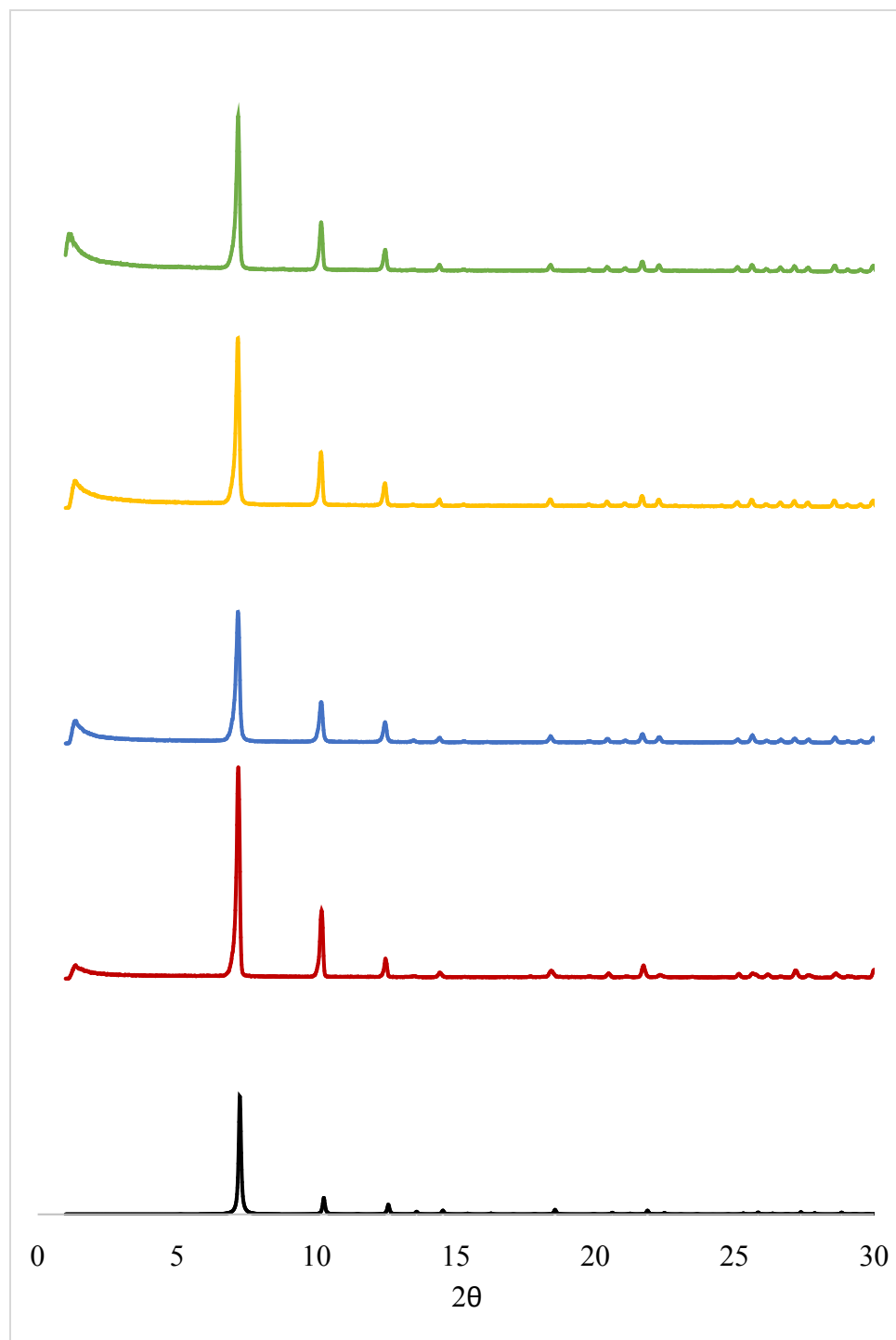


Figure S6. PXRD of the as-synthesized MOFs and after exposure to water. Both the as-synthesized NU-1106 (blue) and biphenyl version (red) follow the same pattern of the simulation (black). There is no change in PXRD when NU-1106 is exposed to water for 2 weeks at room temperature (yellow) or 24 hr at 80 °C (green).

References

1. T. Ueda, H. Konishi and K. Manabe, *Org Let*, 2013, **15**, 5370-5373.
2. H. Wang, X. Dong, J. Lin, S. J. Teat, S. Jensen, J. Cure, E. V. Alexandrov, Q. Xia, K. Tan, Q. Wang, D. H. Olson, D. M. Proserpio, Y. J. Chabal, T. Thonhauser, J. Sun, Y. Han and J. Li, *Nat Commun*, 2018, **9**, 1745.