Supporting Information

3D Metal-Organic Frameworks Based on Functionalized Tetracarboxylate Linkers: Synthesis, Structures, and Gas Sorption Studies

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1. Quantitative determination of solvent molecules in compound 5-8.

Compound **5-8** are easily lose solvent molecules once they leave the mother liquid, and present a significant challenge to precisely determine the solvent contents based on X-ray crystallography (due to the disorder) and elemental analysis. We have used ^{1}H NMR and TGA results to deduce the solvent content quantitatively. To minimize the experimental inconsistency, each sample is treated in exactly the same way for ^{1}H NMR and TGA experiments. A typical procedure is as follows. Fresh crystals were harvested by quick filtration, dried on filter paper for 2 minutes, and then loaded into pre-weighted NMR tube or the sample tray in TGA. To the weighted sample in the NMR tube, 10 μL mesitylene (as an internal standard) and 0.6 mL Acetone-d_6 were added. After four hours of soaking, the ^{1}H NMR spectrum was taken on a 400 MHz Bruker NMR spectrometer.

The crystals of **5-8** are grown in DMF/H_2O. Since the DMF is miscible in acetone-d6, it is convenient to calculate their exact amount against the internal standard. The percentage of solvent for **5-8** can be obtained by TGA. Thus the amount of water molecules can be calculated by subtracting DMF from the total solvent amount.

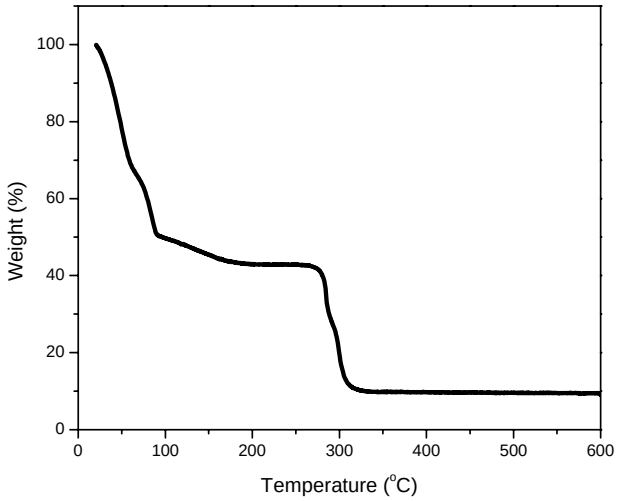

Figure S1. TGA curve for **5**. The sample was heated to 600 °C at the heating rate of 3 °C/min.

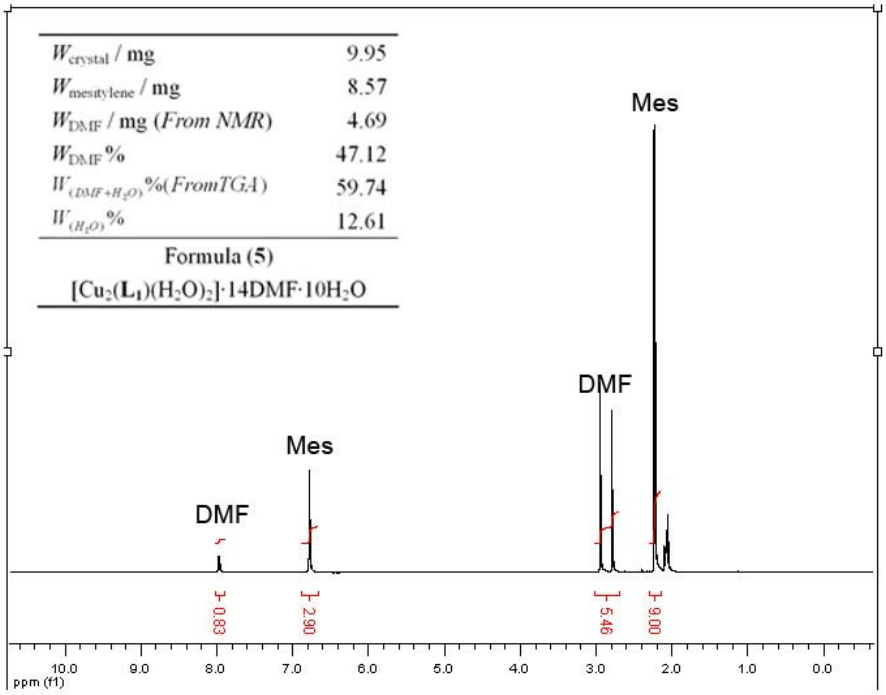

Figure S2. 1H NMR spectroscopic determination of solvent content in **5**, mesitylene (Mes) was added as an internal standard.

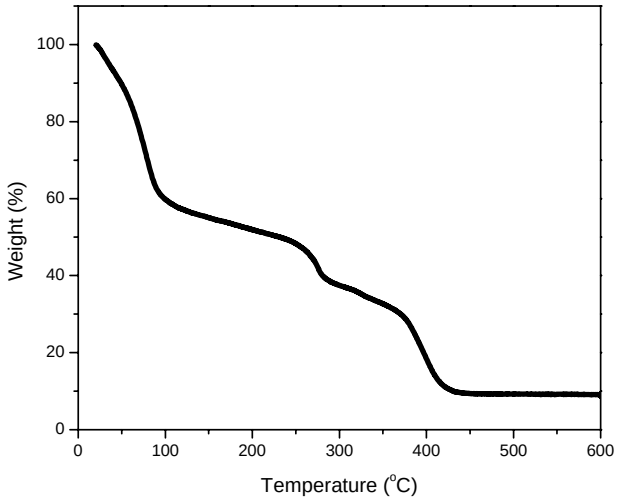

Figure S3. TGA curve for **6**. The sample was heated to 600 °C at the heating rate of 3 °C/min.

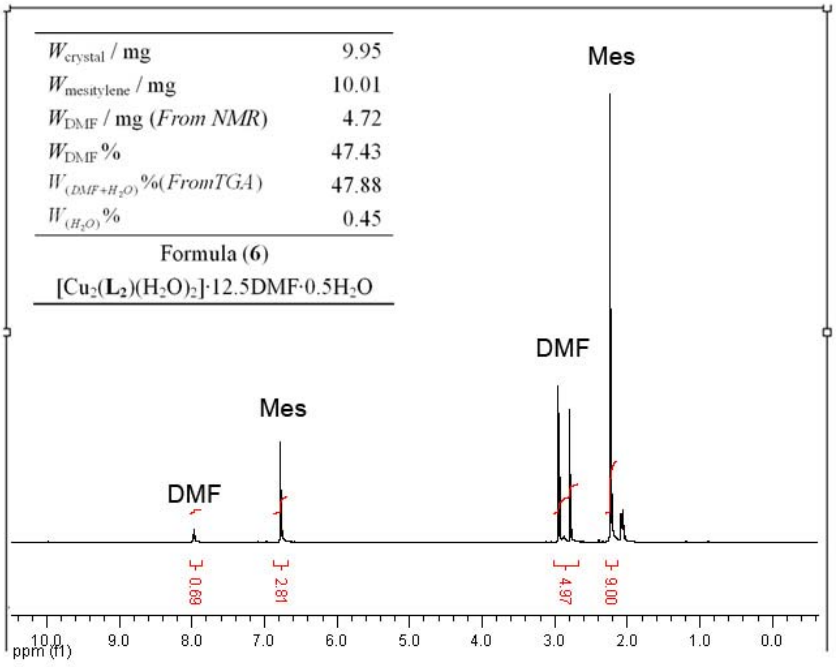

Figure S4. 1H NMR spectroscopic determination of solvent content in **6**, mesitylene (Mes) was added as an internal standard.

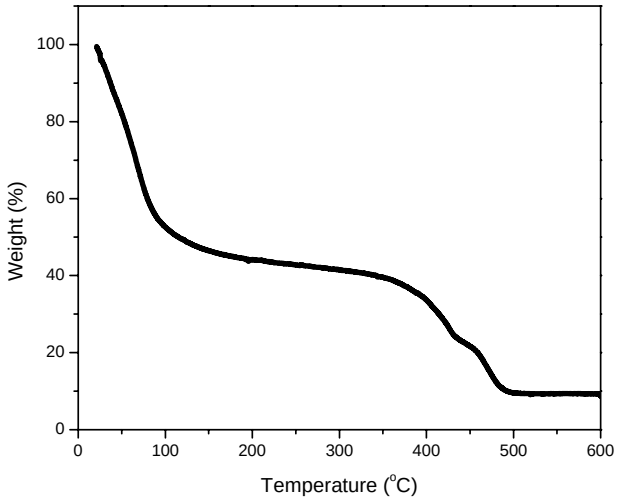

Figure S5. TGA curve for **7**. The sample was heated to 600 °C at the heating rate of 3 °C/min.

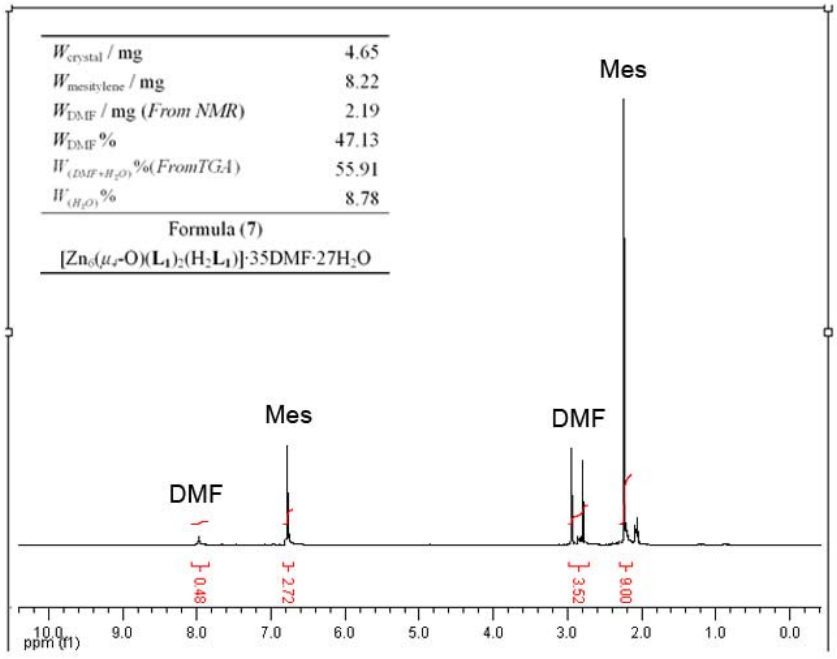

Figure S6. 1H NMR spectroscopic determination of solvent content in **7**, mesitylene (Mes) was added as an internal standard.

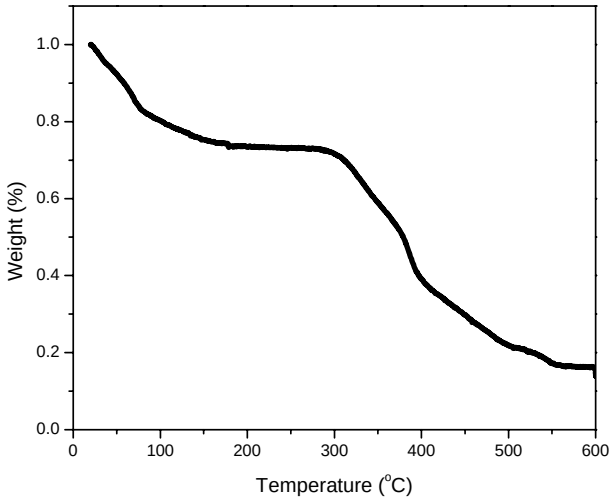

Figure S7. TGA curve for **8**. The sample was heated to 600 °C at the heating rate of 3 °C/min.

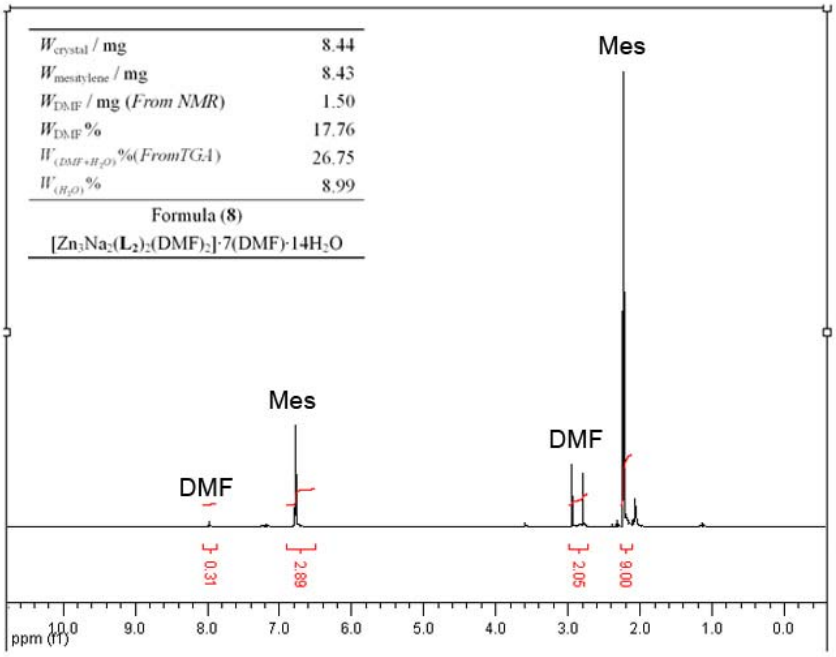

Figure S8. 1H NMR spectroscopic determination of solvent content in **8**, mesitylene (Mes) was added as an internal standard.

2. X-ray powder diffraction studies.

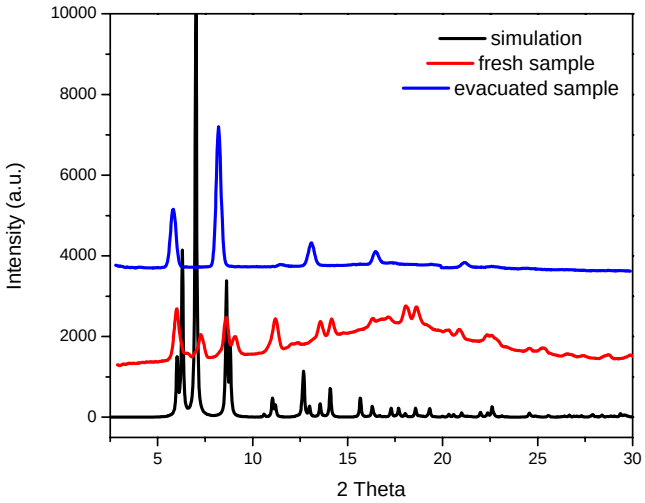

Figure S9. The X-ray powder diffraction patterns for **5**.

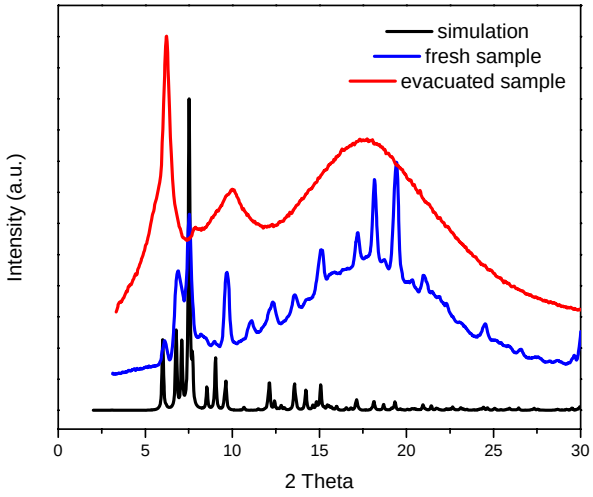

Figure S10. The X-ray powder diffraction patterns for **6**.

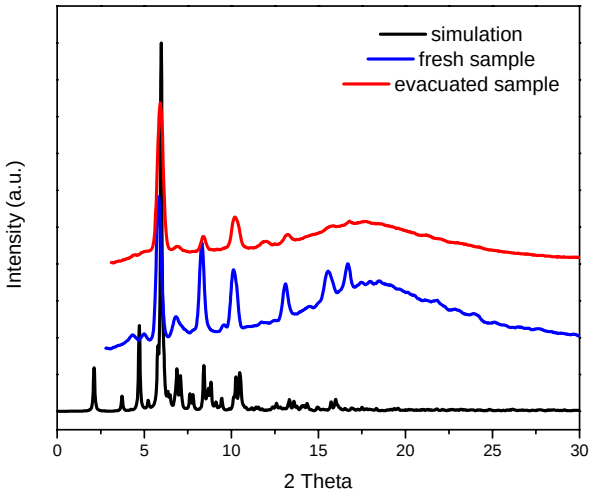

Figure S11. The X-ray powder diffraction patterns for **7**.

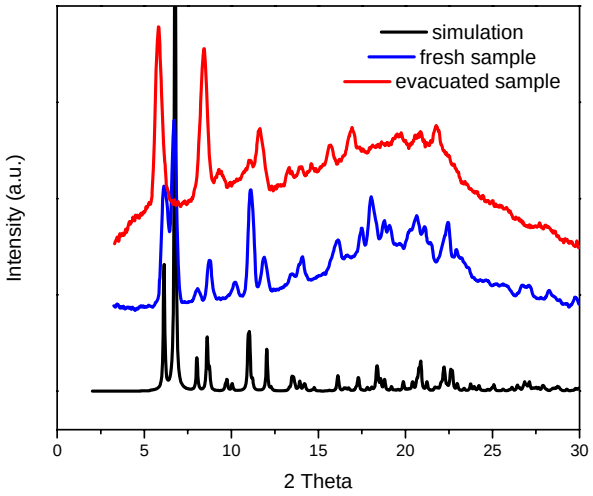

Figure S12. The X-ray powder diffraction patterns for **8**.

3. X-ray single crystal studies for the crown ether groups in 6.

Positional disorder often occurs in the biphenol system. Because of the free rotation along the pivot of the biphenyl group, the dihydroxy, diethoxy, and crown ether group exhibit positional disorder in **5**-**7**. In the case of disorder for **5** and **7**, the dihydroxy groups possess two well-defined energetically similar conformations. However, the case of crown ether group in **6** is

more complicated. The crown ether groups in the framework structure not only are disordered along the rotate axis of the central biphenyl group, but also exhibit flexible fluctuation (up and down) on the crown ether plane. As discussed in main text, there are crystallographically unique $\mathbf{L_{2a}}$, $\mathbf{L_{2b}}$, and $\mathbf{L_{2c}}$. The crown ether group in $\mathbf{L_{2b}}$ possesses two sets of similar conformations. The same situation exists in $\mathbf{L_{2c}}$. The crown ether group in $\mathbf{L_{2a}}$ behaves differently. Because the dihedral angle for the central biphenyl rings of three different $\mathbf{L_{2a}}$ ligands is 89.55°, the positional disorder of crown ether group become equally in four directions. As a result, the crown ether group possesses four sets of similar conformations, which shown in Figure S13 as four different colors. However, due to low quality of the X-ray single crystal dataset, the exact location of each atom becomes difficult to locate. In many ways, the crown ether groups behave just like the highly disordered solvent molecules which can only be accurately determined with a combination of TGA and ^{1}H NMR analyses.

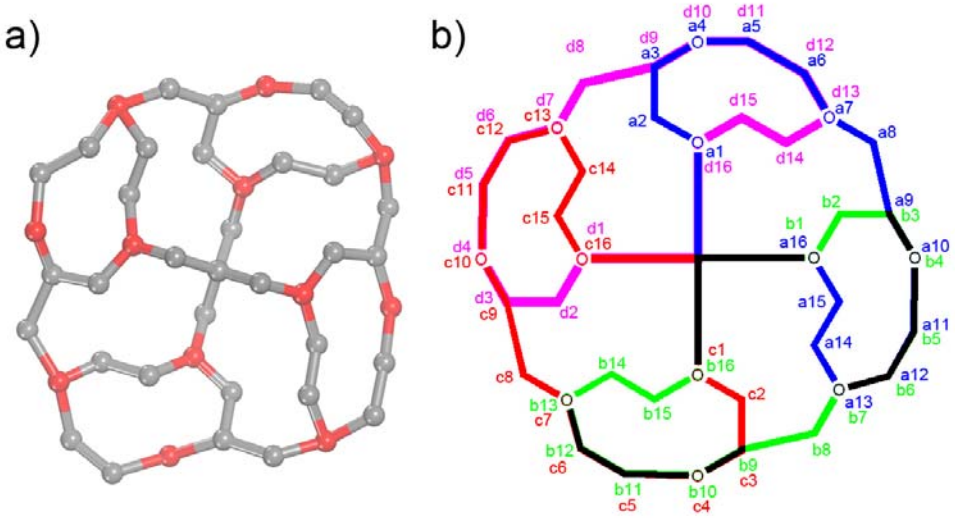

Figure S13. a) The representation of the disordered crown ether group as viewed down the axis of central biphenyl of $\mathbf{L_{2a}}$.. b) The schematic view of a). The color blue, green, red, and purple represent four sets of 16-member crown ether ring respectively.

4. Gas sorption studies.

The N_2 and H_2sorption experiments were taken at 77 K. The CO_2 sorption experiments were taken at 273 K. The fugacity were set from 0.05 to 100 kPa (for N_2 sorption), and 5.25 to 100

kPa (for H_2 and CO_2 sorption). The parameters for GCMC simulation of compound **5-8** are as follows: equilibrium steps: 500000, Production steps: 100000, Accuracy 0.0001 kcal/mol, and the creation versus destruction steps ratio are all about 1.0 for the data point selected.

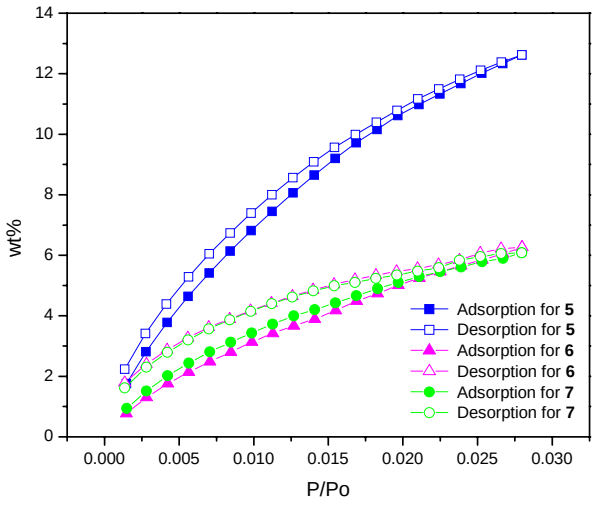

Figure S14. CO_2 adsorption isotherms for **5** – **7.**

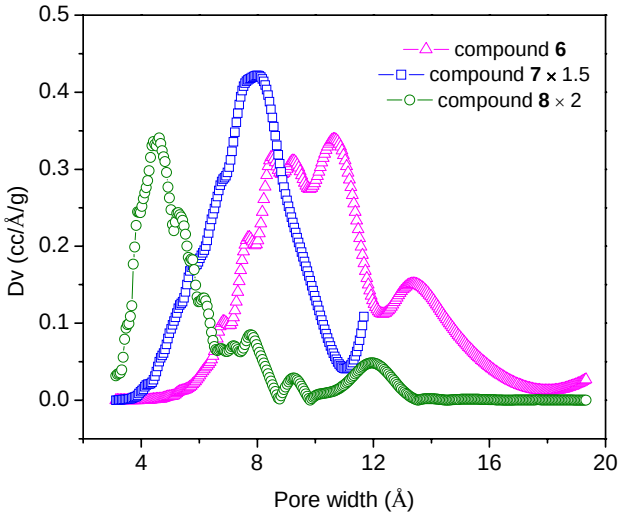

Figure S15. HK pore size distribution based on GCMC simulation datasets for **5** – **7.**

Table S1. The calculated pore sizes for compound **5-8** (using GCMC simulation results) by BJH and HK method.

Compound	BJH method (Å)	HK method (Å)	Crystal structure (Å)
5	7.94, 9.36, 10.75	7.57, 9.27, 10.97	10×10, 5×25

6	6.96, 7.94	7.7 ~ 8.1	8×8
7	7.93, 8.8, 10.72, 12.76	8.57, 9.37, 10.77, 13.52	10×14.5
8	6.69, 7.24, 8.34, 10.72~11.63	4.62, 7.87, 9.37, 12.17	5.5×9.7

5. Dye inclusion experiments.

Rhodamin 6G uptake by framework **5**. Freshly prepared crystal **5** (2.96 mg, 1.61 μmol) was briefly dried on a filter paper, and then soaked in a methanol solution of Rhodamine 6G (40 mM) overnight. The resulting red crystals were washed with water thoroughly until the washings became colorless. The samples were then digested by Na_2EDTA (0.05 M, 2 mL) and NaOH (6 M, 0.1 mL), the resultant solution with light red color was diluted to 125 mL. Absorption experiments were performed on a Shimadzu UV-2401PC UV-VIS spectrophotometer to estimate the amount of Rhodamin 6G uptaked by framework **5**. Uptake of Brilliant Blue R-250 by framework **5** was carried out in the same fashion (except that the pH of the resulting light blue solution was adjusted to pH=1.2).

Table S2. Summary of dye uptake by framework **5**.

	5 + Rdm6G	**5** + BBR250
Dye/Ligand	0.42	0.74
wt% dye/framework	42.5%	77.7%
est. molecular dimensions	1.3×1.6 nm	1.8×2.2 nm

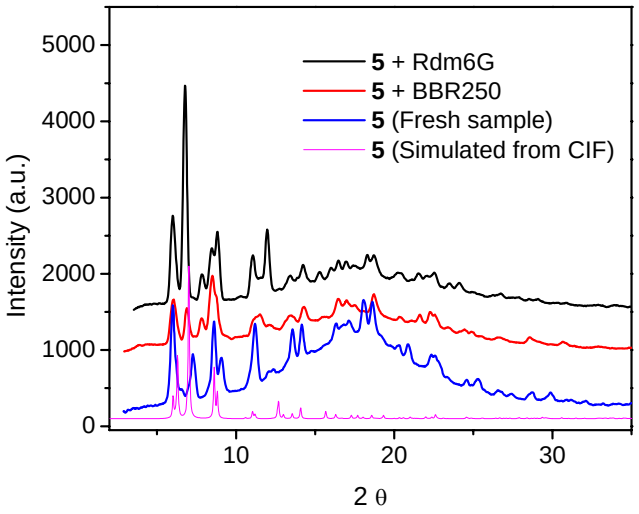

Figure S16. X-ray powder diffraction patterns of fresh sample **5**, **5**/Rodamine 6G, and **5**/Brilliant Blue R-250. Simulated pattern using the single crystal data is also shown (pink).