Supporting Information for

Implementation of High School Level Laboratory Experiments Demonstrating Nanoscale Porosity in Metal–Organic Frameworks

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Synthesis of HKUST-1

To synthesize HKUST-1, 1,3,5-benzene tricarboxylic acid (H_3btc; 2.0 g, 9.5 mmol) was stirred (~400 rpm) in ethanol (46 mL) for 10 minutes until fully dissolved. Next, copper (II) hydroxide (1.0 g, 10 mmol) was dissolved in 18 mL cold water (which had been chilled in an ice bath) under moderate stirring (~400 rpm) in an ice bath for 10 minutes. The H_3btc solution was then added to the chilled copper (II) hydroxide solution and allowed to stir for an additional 10 minutes (while still on ice). The resulting blue precipitate (HKUST-1) was then placed on a vacuum filtration apparatus and washed with ethanol (150 mL). The sample was then stored in an 85 °C oven for activation (a minimum of 45 minutes before proceeding to the CO_2 adsorption experiments).

Synthesis of AlF

To synthesize the aluminum fumarate MOF (AlF), aluminum sulfate (1.670 g, 2.5 mmol) was dissolved in distilled water (6 mL). Then, fumaric acid (0.600 g, 5.17 mmol) was suspended in distilled water (6 mL). Sodium hydroxide (Approximately 3 mL, 1 M) was then added to the fumaric acid solution until the contents were fully dissolved. The deprotonated fumaric acid solution was then added dropwise to the aluminum sulfate solution at 90 °C over a period of five minutes under constant stirring. The resulting white precipitate was then placed on a vacuum

filtration apparatus and washed with ethanol (150 mL). The sample was then stored in an 85 °C oven for activation (a minimum of 45 minutes before proceeding to the CO_2 adsorption experiments).

CO_2 Adsorption experiments

The CO_2 adsorption experiments were performed identically for both HKUST-1 and AlF. Dry ice (approximately 5-6 pellets) was added into an empty 1 L plastic bottle and allowed to displace the air within the bottle for ca. 5 minutes. A balloon was then fastened to the neck of the bottle, which was then filled by the CO_2 generated from sublimation of the dry ice at room temperature. After the balloon was full (ca. 15 minutes), the balloon was carefully removed from the bottle (being sure not to let any CO_2 gas escape by pinching the balloon shut) and then attached to the neck of an empty 22 mL glass vial. The vial was placed in a beaker to prevent it from falling over. The CO_2 in the balloon was allowed to displace the air within the vial for about 15 minutes. This step helps account for the background CO_2 present within the vial during adsorption. After 15 minutes, the balloon was carefully removed, and the vial was quickly recapped (to ensure a minimal amount of CO_2 was lost). The mass of the empty vial (now containing CO_2 from the sublimed dry ice) was recorded. The MOF (Approximately 0.150 g of either HKUST-1 or AlF) was quickly added to the vial, which was promptly recapped. The mass of the vial (now containing both the MOF and background CO_2) was recorded. The cap was once again removed, and the balloon was quickly resecured onto the vial to begin adsorption. The vial was again placed in a beaker to prevent from falling over. After 30 minutes of adsorption, the balloon was removed and the vial was quickly recapped and weighed. The calculations to determine the quantity of CO_2 adsorbed is given below:

$$m_{MOF} = m_{MOF+vial+background\ CO2\ (pre\ adsorption)} - m_{vial+CO2}$$

$$m_{CO2\ adsorbed} = m_{MOF+vial+CO2\ (post\ adsorption)} - m_{MOF+vial+background\ CO2\ (pre\ adsorption)}$$

$$V_{CO2\ adsorbed} = \frac{m_{CO2\ adsorbed}}{\rho_{CO2}}$$

$$PV = nRT$$

$$n_{CO2\ adsorbed} = \frac{PV_{CO2\ adsorbed}}{RT}$$

Where P is the atmospheric pressure (1 atm), T is the ambient temperature in K, and R is the gas constant ($0.0821\ \frac{\text{L·atm}}{\text{K·mol}}$)

Colorimeter Apparatus and App Set-Up for Dye Adsorption Experiments

The free app *Color Meter* by VisTech Projects (downloaded from the Google Play Store on Android OS) was used for all dye adsorption experiments. To prepare the colorimeter apparatus, a flat carboard box was used. The box was laid flat, and the back panel was cut off. Approximately 1 inch from the (now exposed) back of the box, a hole was cut to the size of a 22 mL vial (the solution container being used). A small square was cut on the front panel of the box matching with the height and camera placement of the phone to be used in this experiment. The apparatus was placed against a wall so that colored paper could be held in place on the open panel of the box. Additional supports (such as books) were used as necessary to keep the phone in place during the experiment.

Excel Set-Up for Dye Adsorption Experiments

Prior to conducting dye adsorption experiments, an Excel data workbook was prepared as follows. Nine columns were prepared, (referred to as columns A-I). In cell A1, the name of the MOF being observed (either HKUST-1 or AlF) was recorded, and cells A2-A6 were left blank. Cell B1 was labeled as "Time (min)". Cell C1 was labeled as either "Red Value" (if using methylene blue and red colored paper in the colorimeter apparatus) or "Blue Value" (if using the

potassium iodide/ iodine solution and blue colored paper in the colorimeter apparatus). Cells D1-G1 were left blank. Cell H1 was labeled either "Avg. Red Value" (if using methylene blue and red colored paper) or "Avg. Blue Value" (if using the potassium iodide/ iodine solution and blue colored paper). Cell I1 was labeled "Conc. (M) = (signal -b)/m". The time at which the experiment starts (when the MOF was dispersed into the dye-containing solution) was recorded in cell A7. Going down column A, from cells A8 and down, the time was recorded in 5-minute increments for a total of 30 minutes. In column B, the time (in minutes) that elapsed from the beginning of recording the red/ blue values was recorded, starting at 0. The red/blue value was read and recorded five times at each time interval before adding the MOF and then entered into cells C2-G2. The next reading was then entered in cells C3-G3, then C4-G4, and so on. Column H was used to calculate the average of the 5 readings. Once all data has been recorded for the dye adsorption, a plot was generated with time (minutes) on the x-axis and concentration (M) on the y-axis. An example data table is provided in Table S3.

Preparation of the Methylene Blue Dye for Adsorption Experiments

A 3.1 mM stock solution of methylene blue in DI water was prepared by dissolving methylene blue (0.200g, 0.62 mmol) in 200 mL of DI water. For the dye adsorption experiments, a 0.138 mM solution of methylene blue was prepared using 0.090 mL of the 3.1 mM stock solution and 19.91 mL of water.

Preparation of the Potassium Iodide/ Iodine solution for Adsorption Experiments

A 0.0744 M stock solution of potassium iodide/ iodine was prepared by dissolving KI (10 g, 60.2 mmol) and I_2 (2.5 g, 9.8 mmol) in 400 mL of DI water. For the dye adsorption experiments, a 1.163 mM solution of potassium iodide/iodine was prepared using 0.313 mL of the 0.0744 M stock solution and 19.687 mL of water.

Calibration Curve of Color Meter Application

For the methylene blue calibration curve, dilutions were made using the 3.1 mM stock solution (prepared above). A 19-point calibration curve was generated by preparing 19 dilutions ranging from 0.098 mM to 0.00020 mM. A line of regression was calculated for the linear range of the plot of red values vs. concentration to produce an equation of the calibration curve as seen in Figure S3.

For the potassium iodide/iodine calibration curve, dilutions were similarly made using the 0.0744 M stock solution (prepared above). A 13-point calibration curve was generated by preparing 12 dilutions (including the stock solution) ranging from 0.0186 M to 0.00454 M. A line of regression was calculated for the linear range of the plot of blue values vs. concentration to produce and equation of the calibration curve. The concentration was plotted on the *x*-axis in logarithmic scale, as seen in Figure S4.

Dye Adsorption experiments (using Methylene Blue or potassium iodide/iodine solutions)

The adsorption of methylene blue was carried out with both HKUST-1 and AlF, whereas the adsorption of the potassium iodide/iodine solution was only carried out with AlF. The dye adsorption experiments were carried out similarly to each other: the only differences were the MOFs being tested (HKUST-1 or AlF), the dyes being used (methylene blue for HKUST-1 and AlF, and potassium iodide/iodine for just AlF), and the color of the paper used behind the colorimeter apparatus depending on the dye being used (red colored paper for methylene blue, and blue colored paper for potassium iodide/iodine).

The free mobile application *Color Meter* by VisTech Projects (which can be downloaded from the Google Play Store on devices running Android OS) was used for these experiments. The colorimeter apparatus was set up as described above, being sure not to move the phone throughout

the duration of the experiment. A 25 mL glass vial containing the dye was placed in the designated slot in the apparatus. Depending on the dye solution being used, the appropriate colored paper was placed behind the colorimeter apparatus (red colored paper for methylene blue or blue colored paper for potassium iodide/iodine). Both the *Color Meter* app and the Excel data workbook were prepared as outlined above. The colorimeter was then calibrated by taking the reading of the red value (for methylene blue) or the blue value (for potassium iodide/ iodine) five times every five seconds over the course of 30 seconds. This was repeated a total of five times, totaling 25 readings over 2.5 minutes.

The MOF (0.060 g of either HKUST-1 or AlF) was weighed out and quickly poured into the vial containing the dye. Immediately after addition of the MOF, five readings on the colorimeter were taken and recorded in the Excel workbook. Readings were then taken every five minutes (five readings each time) for the remainder of the experiment (approximately 45 minutes). The concentration of the dye solution was determined at each time point by using the previously generated calibration curve for either methylene blue or potassium iodide/ iodine (see Figures S3 and S4 for example calibration curves). Once the concentration of the dye solution was determined, a plot of dye concentration (M) vs. time (minutes) was generated (see Figure 6).

Supporting Figures

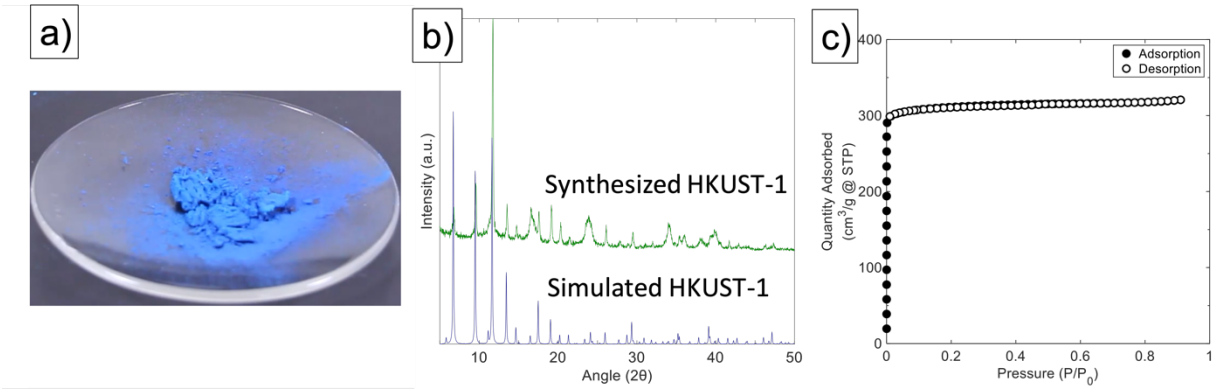

Figure S1. a) Photograph of HKUST-1 synthesized in this work after drying at 85 °C for 45 minutes. b) Powder X-ray diffractogram (λ = 1.5406 Å) of synthesized HKUST-1 compared with that simulated from the crystallographic model[1] of HKUST-1. c) Nitrogen gas sorption isotherm for HKUST-1 obtained at 77 K.

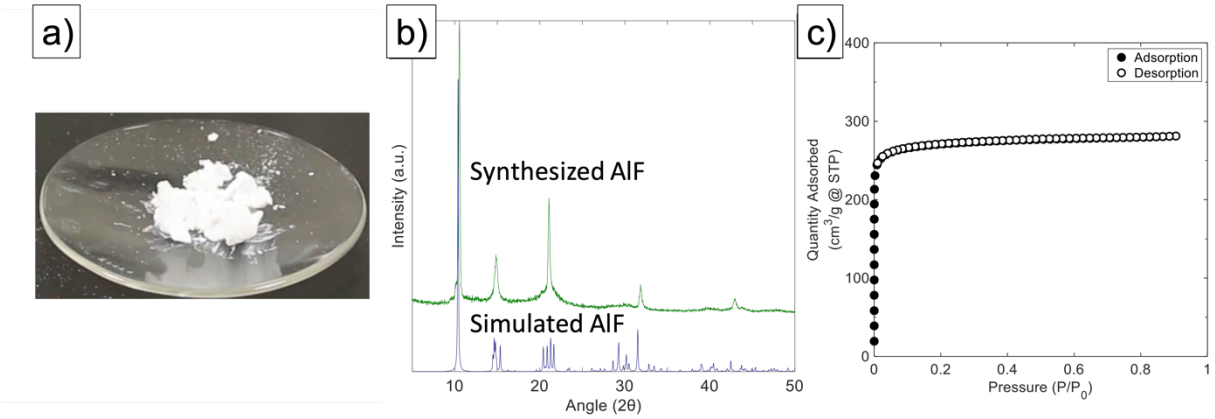

Figure S2. a) Photograph of AlF synthesized in this work after drying at 85 °C for 45 minutes. b) Powder X-ray diffractogram (λ = 1.5406 Å) of synthesized AlF compared with that simulated from the crystallographic model[2] of AlF. c) Nitrogen gas sorption isotherm for AlF obtained at 77 K.

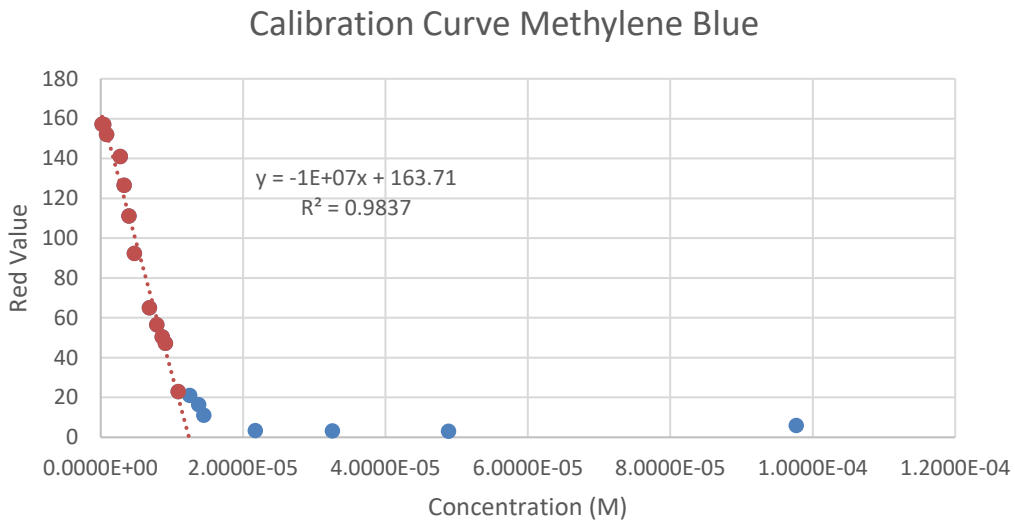

Figure S3. A plot of the calibration curve for methylene blue depicting red values (as read from the *Color Meter* colorimeter) vs. concentration (M). The linear region was fitted for a line of regression, giving an R^2 of 0.9837.

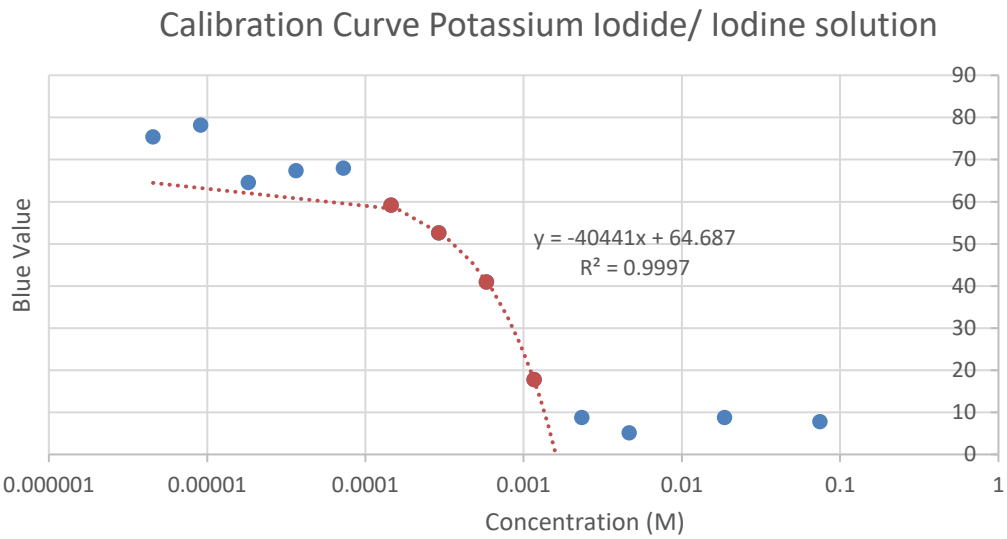

Figure S4. A plot of the calibration curve for the potassium iodide/ iodine solution depicting blue values (as read from the *Color Meter* colorimeter) vs. concentration (M). The concentration on the x-axis was plotted in a logarithmic scale. The linear region was fitted with a line of regression, giving an R^2 of 0.9997.

Supporting Tables

HKUST-1 CO_2 adsorption[a]	
HKUST-1 Sample	CO_2 Adsorbed (mmol/g)
1	0.7657
2	1.089
3	1.101
4	0.9392
5	0.9666
[a]Reported literature adsorption of CO_2 for HKUST-1 at 27 °C and 1 bar is 4.2 mmol/g.[3]	

Table S1. Representative CO_2 adsorption data for HKUST-1

AlF CO_2 adsorption[a]	
AlF Sample	CO_2 Adsorbed (mmol/g)
1	0.8763
2	0.8267
3	0.6026
4	0.7366
5	0.3865
[a]Reported literature adsorption of CO_2 for AlF at 303 K and 1 bar is 2.1 mmol/g.[4]	

Table S2. Representative CO_2 adsorption data for AlF

	A	B	C	D	E	F	G	H	I
1	.0673g AlF	Time (min)	Red Value					Avg. Red Value	Conc.(M) = (signal-b)/m
2		0	32	32	33	36	36	33.8	1.3E-05
3		0.5	33	31	33	31	32	32	1.3E-05
4		1	32	33	31	31	31	31.6	1.3E-05
5		2	30	36	29	32	30	31.4	1.3E-05
6		2.5	32	31	31	35	32	32.2	1.3E-05
7	MOF in @ 11:13 a.m.	3	26	23	11	19	18	19.4	1.4E-05
8	11:18	8	33	30	32	33	29	31.4	1.3E-05
9	11:23	13	40	40	37	38	34	37.8	1.3E-05
10	11:28	18	38	37	36	38	39	37.6	1.3E-05
11	11:33	23	39	45	46	40	40	42	1.2E-05
12	11:38	28	39	39	37	39	40	38.8	1.2E-05
13	11:43	33	35	40	40	38	39	38.4	1.3E-05
14	11:48	38	40	40	37	37	37	38.2	1.3E-05
15	11:53	43	40	36	42	40	40	39.6	1.2E-05
16	11:58	48	39	36	35	36	38	36.8	1.3E-05

Table S3. An example data table set up in Excel for the dye adsorption experiments.