**Supplementary Information**

**Coordination Exchange Chemistry on Metal-Organic Layers: Revealing Surface Modification Mechanisms and Thermodynamic Principles**

**S1. Materials and methods**

All reagents were commercially available and used without further purification. Powder X-ray diffraction (PXRD) patterns were performed on Rigaku IV diffractometer with Cu Kα radiation (λ = 1.54178 Å). Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-1400 (120kV). Thermogravimetric analysis (TGA) was measured by a Shimadzu TGA-50 in air equipped with an alumina pan and heated at a rate of 10 °C per minute. 1HNMR spectra were recorded on a Bruker 400 DRX spectrometer at 400 MHz and a Bruker 500 DRX spectrometer at 500 MHz.

**S2. Synthesis and Characterization of BTB-MOL**

**Synthesis of BTB-MOL.** To a 50 mL glass vial was added 5 mL of HfCl4 solution (109 μmol in N,N-dimethylformamide, DMF), 7.5 mL of 1,3,5-tris(4-carboxyphenyl)benzene (H3BTB) solution (73 μmol in DMF), followed by the addition of HCO2H (99%) and H2O (Table S1). The mixture was sonicated for 5 min, and kept at 120 °C oven for 2 days. The white precipitate was collected by centrifugation, and washed with DMF three times. BTB-MOL with a formula of (Hf6O4(OH)4(BTB)2(HCOO)6) was obtained in 58% yield and dispersed in DMF for further use.

|  |  |  |  |
| --- | --- | --- | --- |
| **Sample** | **FA (mL)** | **H2O (mL)** | **FA/H2O (mol)** |
| BTB-MOL-1 | 0.75 | 0.75 | 0.477 |
| BTB-MOL-2 | 2.25 | 1.5 | 0.716 |
| BTB-MOL-3 | 2.25 | 0.75 | 1.431 |
| BTB-MOL-4 | 3.1 | 1.0 | 1.479 |
| BTB-MOL-5 | 1.875 | 0.375 | 2.385 |
| BTB-MOL-6 | 3.1 | 0.375 | 3.944 |

**Table S1.** The amount of formic acid (FA) and H2O added under different MOL synthesis conditions.

**Synthesis of BTB-MOL-HCl.** BTB-MOL (25 μmol) was dispersed in 50 mL hydrochloric acid (1 M aqueous solution) and sealed in a 200 mL glass vial, followed by thermal treatment at 100°C oven for 48 hours. The white precipitate was collected by centrifugation, and thoroughly washed three times each with deionized water and acetonitrile.

**Synthesis of BTB-MOL-H2O.** BTB-MOL (25 μmol) was dispersed in 50 mL deionized water and sealed in a 200 mL glass vial, followed by thermal treatment at 100°C oven for 48 hours. The white precipitate was collected by centrifugation, and thoroughly washed three times each with deionized water and acetonitrile.

**S3. Post-modification of BTB-MOL**

**Modification of benzoic acid (BA).** BTB-MOL (2.5 μmol) was dispersed in 2 mL BA solution (144 μmol in N,N-dimethylformamide, DMF), and maintained at 55°C in oil bath for 18 hours. The white precipitate was collected by centrifugation, and thoroughly washed three times with DMF. As summarized in Table S2, systematic modification experiments were conducted by varying multiple reaction parameters for BA functionalization.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Entry** | **Sample** | **Temp. (℃)** | **Sol.** | **CBA (mM)** | **Reation time (h)** | **BA/SBU** |
| 1 | BTB-MOL-3 | 55 | DMF | 72 | 18 | 2.50 |
| 2 | BTB-MOL-5 | 55 | DMF | 72 | 18 | 2.88 **a** |
| 3 | BTB-MOL-6 | 55 | DMF | 72 | 18 | 2.58 **a** |
| 4 | BTB-MOL-6 | 55 | DMF | 72 | 0.5 | 2.86 **a** |
| 5 | BTB-MOL-6 | 55 | DMF | 72 | 72 | 3.16 **a** |
| 6 | BTB-MOL-3 | 55 | DMF | 144 | 18 | 2.38 |
| 7 | BTB-MOL-5 | 80 | DMF | 72 | 18 | 2.92 **a** |
| 8 | BTB-MOL-6 | 80 | DMF | 72 | 18 | 2.82 **a** |
| 9 | BTB-MOL-6 | 55 | THF | 72 | 18 | 2.64 |
| 10 | BTB-MOL-6 | 55 | CH3CN | 72 | 18 | 2.40 |
| 11 | BTB-MOL-6 | 55 | H2O(NaOH) | 72 | 18 | 2.42 |

**Table S2.** Summary of reaction conditions and corresponding BA modification levels.

**Experiment of Modification equilibrium (BA as an example).** BTB-MOL (0.75 μmol) was dispersed in 1 mL BA and FA mixed solution (Table S3), and maintained at 55°C in oil bath for 3 hours. The white precipitate was collected by centrifugation, and thoroughly washed three times with acetonitrile. (BA and FA were prepared as stock solutions in acetonitrile at predetermined concentrations. Appropriate volumes of these solutions were mixed and diluted with additional acetonitrile to maintain a constant total reaction volume of 1 mL.)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Entry** | **mBA (mg)** | **VFA (mL)** | **CBA (mM)** | **CFA (mM)** |
| 1 | 22 | 1.7 | 180 | 45 |
| 2 | 16.5 | 3.4 | 135 | 90 |
| 3 | 13.8 | 4.2 | 112.5 | 112.5 |
| 4 | 11 | 5.1 | 90 | 135 |
| 5 | 6.8 | 6.4 | 56.25 | 168.75 |
| 6 | 5.5 | 6.8 | 45 | 180 |

**Table S3.** Concentration ranges of BA and FA solutions employed for modification equilibrium studies.

**Figure S1.** Modification equilibrium behavior and corresponding fitting curves for carboxylic acids with varying pKa values. Not that the formula used for the fittings are not based on solid physical model

**S4. A failed Trial to construct a physical model for the adsorption process on the MOLs**

**1. Problem Setup**

**Three types of molecules**: A is one carboxylate modifier, B is another carboxylate modifier, while S is the solvent. Their total numbers are , , in the system, respectively.

**Adsorption sites**:

* + There are distinguishable sites on the MOL.
  + Each site is one side of one SBU that can adsorb exactly 3 molecules (possibly of different or repeated types).
  + We denote the “composition” of a site by XYZ, for instance AAB, BSS, etc. Let *N*(*XYZ*) be the number of sites that have the composition XYZ.
  + The energy of a site with composition XYZ is U(*XYZ*). We also consider internal permutations of the 3 positions within a site.

**Solution (bulk) phase**:

* + Some fraction of A remains in solution, denoted . Similarly for B and for S.
  + The energy of one A in solution is ; similarly for B and for S.

**Particle-number conservation**:

**Site-number conservation**:

**Total energy**

**Goal**:

* + We want to find the most probable (i.e., most likely) distribution and that **maximizes** the total number of microstates W (or equivalently, ln W), subject to these constraints.

**2. Expression for the Total Number of Microstates WW**

From standard combinatorial arguments, for a system with distinguishable sites plus a solution phase, a common form for the total number of microstates is:

.

The first term is the site distribution; the second term is the degeneracy due to the order within the site; the third term is the solution distribution.

**Adsorption part**:

* + counts how to distribute distinguishable sites among various composition types XYZ.
  + accounts for permutations of the 3 adsorbed molecules *within* each site (if the 3 sub-positions in the site are distinguishable). If the site’s internal positions are indistinguishable, we omit this factor.

**Solution part**:

* + If we regard the solution as a set of discrete “slots,” or equivalently as an ideal mixture where each particle is distinguishable by position, then the factor counts all ways to place the three types of particles in the solution.
  + This does *not* imply that AA, BB, and SS are interconvertible; it is simply the standard multinomial count for distributing indistinguishable A’s, indistinguishable B’s, and indistinguishable S’s among a total of distinct “slots.”

In the thermodynamic (large-number) limit, we often maximize ln W.

**3. The Log of WW and Stirling’s Approximation**

For large values NN, we can use Stirling’s approximation ln⁡(n!)≈nln⁡n−n \ln (n!) \approx n \ln n - n. Hence,

etc.

Thus, for ln W one obtains a sum of terms like

**4. Lagrange-Multiplier Method**

To incorporate the constraints, we form a Lagrangian-like function:

Here, ,,,, are Lagrange multipliers enforcing each constraint.

In many physics treatments, and , , , , where is the chemical potential of species X or the site.

**4.1 Variation with respect to N(XYZ)**

We set

So

From

We can obtain that

So

**4.2 Variation with respect to**

Similarly,

We know that the amount of adsorbed molecules is negligible

So

This gives

So

Now expand

is the interaction term of adjacent sites.

Then

Let

We would like to know the ratio of A and B in the adsorption phase

First ignore interaction terms

If

Let , , which are the ratios of site occupation of the substrate to the solvent in the absence of interactions among adjacent sites.

Where

and are solution phase concentrations of A and B; and are activity coefficient, while K is their equilibrium constant in the absence of inter-site interactions.

In reality,

So

If only is prominent and let

4.2 Problem with this formula

The problem is that this formula, although technically sound, cannot fit the experimental data at all.

The simplistic formula form that can fit the data is

However, I have no idea how to reach a formula like that.