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

**Abstract:** Metal-organic layers (MOLs) serve as an ideal platform for enzyme-mimetic modification through post-synthetic functionalization. This study systematically investigates the coordination exchange reactions at secondary building units (SBUs), focusing on surface modification patterns and thermodynamic principles. We demonstrate that the exchange process between carboxylic acids and formate capping groups proceeds readily under mild conditions. However, modification levels consistently fall below theoretical maximums. It is possible that the majority MOLs are not single layer, so that some of the “surface sites” are buried under layer stacking and not accessible to capping agent or modifier for replacement. Through comprehensive experiments with various carboxylic acids, we establish a clear correlation between acid strength and modification thermodynamics, following the principle of stronger acids displacing weaker ones. These findings provide fundamental insights into coordination exchange reactions on MOLs, offering valuable guidance for the rational design and surface engineering of these materials for catalytic and sensing applications. However, we are still puzzled about the underlying model and formula governing the adsorption. We have some trials of fitting for the data but the fitting formula are not supported by clear physical model.

**Keywords:** Metal-organic layers (MOLs), Post-modification functionalization, Thermodynamic equilibrium

Enzyme catalysis is renowned for its exceptional efficiency and selectivity, which are intrinsically linked to the coordination environment of the active center and the structural arrangement of proximal amino acids or cofactors. Additionally, non-covalent interactions provided by the secondary coordination sphere play a crucial role. In recent years, numerous researchers have developed various biomimetic catalysts through enzyme-inspired design, including cyclodextrin inclusion complexes, supramolecular cages, and metal-organic frameworks (MOFs) etc. Among these, metal-organic layers (MOLs), as two-dimensional counterparts of MOFs, have emerged as highly competitive candidates in heterogeneous catalysis due to their high dispersion and fully exposed surfaces. The functional ligands on MOLs can chelate active metal ions, while the coordination exchange reactions at secondary building units (SBUs) enable molecular modification, facilitating the construction of catalytic pockets and making them ideal platforms for enzyme-mimetic modification (Figure 1). However, our experimental investigations have revealed that the coordination exchange reactions at SBUs are more complex than anticipated. We observed that the modification of small molecules often fails to reach saturation, potentially compromising the efficiency of catalytic active sites. Here in, using the classical BTB-MOL as a model system, we have systematically investigated the influencing factors of SBU coordination exchange reactions to gain deeper insights into the reaction mechanism, which will facilitate the design and synthesis of highly efficient catalysts.



**Figure 1.** Schematic diagram of coordination exchange and catalytic pocket construction on MOL surface

The 3,6-connected two-dimensional network structure BTB-MOL with kagome dual (kgd) topology can be successfully synthesized under solvothermal conditions. This two-dimensional ultrathin material has the molecular formula Hf6(μ3-O)4(μ3-OH)4(HCO2)6(BTB)2 (where BTB is benzenetribenzoate). According to the theoretical model, each Hf6 cluster coordinates with six distinct BTB ligands through the six sites within the same plane, while the remaining six sites at both the upper and lower positions are capped by formate groups. By systematically adjusting the ratio of formic acid and water during the synthesis of MOL (Table S1), we consistently obtained well-crystallized MOL products (Figure 2). Nuclear magnetic resonance (NMR) analysis of the digested samples revealed that the formate content remained relatively constant across different synthesis conditions, consistently reaching approximately half of the theoretical value (Figure 2). Specifically, each secondary building unit (SBU) was found to be capped by approximately three formate groups.

We initiated our investigation by systematically examining the modification of benzoic acid (BA) on the MOL. Our findings revealed that the BA modification amount remained consistent across MOL samples synthesized under various conditions, with an average BA/SBU ratio of approximately 2.5 (Figure 2). Furthermore, the BA modification level exhibited negligible variation when altering key reaction parameters, including solvent type, temperature, BA concentration, and reaction duration (Table S2). Notably, the BA modification reached near-saturation levels within 0.5 hours of reaction time, indicating a rapid coordination exchange kinetics in this system.



**Figure 2.** PXRD of BTB-MOL synthesized under different conditions (left) and its FA content and BA modification amount (right).

Hydrochloric acid is commonly employed for the removal of formate capping groups from MOLs to facilitate subsequent modifications. To investigate the impact of this treatment on post-modification processes, we subjected BTB-MOL to formate removal procedures. The BTB-MOL samples were dispersed in either 1 M HCl or deionized water and maintained at 100°C. Both treatments effectively removed the majority of formate groups while preserving the crystallinity of the MOLs (Figure 3d-e). However, transmission electron microscopy (TEM) and thermogravimetric analysis (TGA) revealed distinct morphological changes (Figure 3b-c): HCl treatment resulted in significant structural degradation, as evidenced by fragmented morphology in TEM images and reduced hafnium content, whereas water treatment, while maintaining the metal-to-ligand ratio, led to the deposition of hafnium oxide particles on the MOL surface. Notably, despite these treatments, the benzoic acid (BA) modification level did not increase (Figure 3f) and was, in fact, lower than that observed in untreated samples.



**Figure 3.** TEM image of the BTB-MOL(a), BTB-MOL-HCl(b), BTB-MOL-H2O(c). (d) PXRD of MOLs along with the simulated PXRD pattern for BTB-MOL. (e) NMR spectra of digested MOLs. (f) NMR spectra of digested MOLs after BA modified.

To elucidate the thermodynamic characteristics of the coordination exchange reaction, we initially investigated the modification equilibrium between benzoic acid (BA) and formic acid (FA). This was achieved by examining the variation in the modification levels of these two carboxylic acids on the SBUs across solutions with different BA/FA concentration ratios (Table S3). The experimental results revealed that as the BA/FA ratio in the solution increased, the corresponding ratio on the MOL also increased, eventually reaching saturation (Figure 4a). The data can be fitted into an equation where Keq represents the equilibrium constant of the reaction. However, the equation is not on solid basis like a physical model. The equilibrium constant for BA was determined to be 3.8, indicating that the substitution of FA by BA is thermodynamically favorable. Notably, the Keq remained essentially unchanged when the concentrations of BA and FA in the solution were increased (Figure 4a, deeper).



**Figure 4.** (a) The variation of the BA/FA on the MOL as a function of the BA/FA in the solution, along with the corresponding fitting curve. (b) Table of pKa and K (modification equilibrium constant) of different carboxylic acid. (c) The relationship between pKa and K of different carboxylic acids.

Subsequently, we extended our investigation of benzoic acid to a series of carboxylic acids with varying pKa values to explore their coordination modification equilibria (Figure 4b) and elucidate the general principles governing this class of coordination exchange reactions. As illustrated in the experimental results, the modification of all carboxylic acids approached saturation with increasing molecular ratios (Figure S1). However, significant variations in equilibrium constants were observed, demonstrating a distinct negative correlation with pKa values (Figure 4c). Specifically, stronger acids (lower pKa) exhibited greater propensity to replace formate in metal coordination, suggesting that the acidity of the carboxylic acid plays a crucial role in determining the thermodynamic favorability of the coordination exchange process.

One big issue of the adsorption experiments is that the summation of the adsorbed acids are consistently below the theoretical maximum, which is 6 per SBU. A very possible reason for this is that the samples are not purely single layers. There are double layer and trilayers, which buried many sites for coordination. It is thus more meaningful to model the ratio between an acid and formic acid, which does not depend on the total amount of exposed sites.

In summary, we have gained significant insights into the coordination exchange reaction. Firstly, the reaction proceeds readily under mild conditions, requiring neither elevated temperatures nor high concentrations, and reaches near-completion within 30 minutes for most accessible sites. Secondly, even under more stringent reaction conditions or extended durations, the modification level of carboxylic acids fails to reach the theoretical maximum, indicating that the MOL surface may be not fully exposed with double layer and trilayer structures common in the samples. The coordination exchange reaction at SBUs follows the well-established principle of stronger acids displacing weaker ones, with the thermodynamic favorability increasing with the acidity of the carboxylic acid. These findings provide new perspectives for the field of coordination chemistry and materials science. The rapid kinetics and mild conditions of the exchange reaction suggest potential applications in dynamic materials and surface engineering. Furthermore, the established correlation between carboxylic acid acidity and exchange thermodynamics offers a predictive framework for designing functionalized MOLs with tailored properties, potentially advancing their applications in catalysis, sensing, and molecular recognition. Future research could explore the manipulation of these exchange processes through structural modifications of the MOL framework or the development of novel activation strategies to overcome the current limitations in modification efficiency. Importantly, a physical model with quantitation formula for the adsorption process was not obtained yet.