学 位 論 文 の 要 約

博士の専攻分野の名称　博士（総合化学）　　氏名　シェルスター　バスティアン　ビェルケム

学 位 論 文 題 名

Theoretical Study on Formation and Reactivity of Coordination Compounds Employing AFIR
（人工力誘起反応法を用いた配位化合物の生成と反応性に関する理論的研究）

Coordination compounds have emerged as an intriguing class of functional materials due to their desirable properties for a variety of applications, including gas storage and separation, catalysis, drug delivery and biological imaging and sensing. In this Thesis, two different subclasses of coordination compounds, namely metal-organic frameworks (MOFs) and transition metal (TM) complexes, are surveyed by means of quantum chemical calculations to evaluate their early-stage self-assembly mechanisms and catalytic properties, respectively.

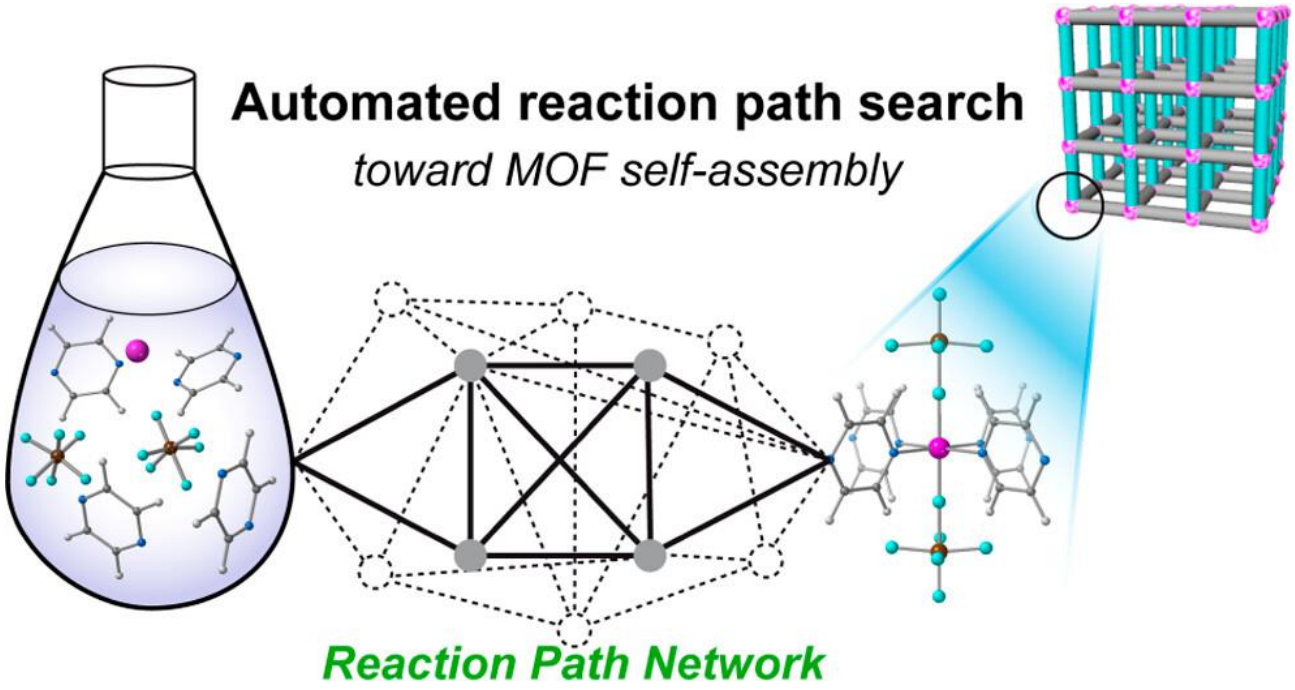
Metal-Organic Framework Formation

Synthesis of new MOFs relies on chemical intuition and serendipity, as their mechanisms of formation are poorly understood at present. As an attempt to bridge the gap, and enable targeted synthesis of MOFs with desired properties, a general workflow based on the artificial force induced reaction (AFIR) method is devised to analyze the formation of MOF units through automated reaction path exploration and kinetic simulations enabling identification and analysis of the dominating pathways of assembly.

The developed workflow is applied to study the formation of the SIFSIX-3-Zn MOF node $[Zn(pyz)_4(SiF_6)_2]^{2-}$ (pyz = pyrazine), finding that assembly proceeds in a stepwise manner, in which the organic pyz ligands coordinate to the inorganic core structure one at a time, while the coordination of the SiF_6–Zn–SiF_6 unit flexibly changes to accommodate for the incoming organic ligands. Moreover, interconvertibility between reaction intermediates and competing reaction pathways likely operating simultaneously are observed, providing a plausible explanation for stochastic processes believed to be key in MOF formation.

A similar workflow is used to investigate formation of paddlewheel structures, one of the most common motifs in MOFs, finding that axially coordinating ligands play a crucial role in stabilizing reaction intermediates as well as the assembled structures. In Zn-based paddlewheels, assembly is facilitated by axially coordinating ligands, which stabilize the paddlewheel structure. Cu-based structures, on the other hand, depend to a lesser extent on the stabilization by axial ligands, implying that open metal site formation, of importance to catalysis and adsorption, is more accessible. Four structures, $[Zn_2(OAc)_4] \cdot 2\ H_2O$, $[Zn_2(OAc)_4] \cdot 2$ py, $[Cu_2(OAc)_4]$ and $[Cu_2(OAc)_4] \cdot 2\ H_2O$ (OAc = acetate, py = pyridine), are found to form through a single phase directly from the reaction mixture, whereas $[Cu_2(OAc)_4] \cdot 2$ py forms *via* two

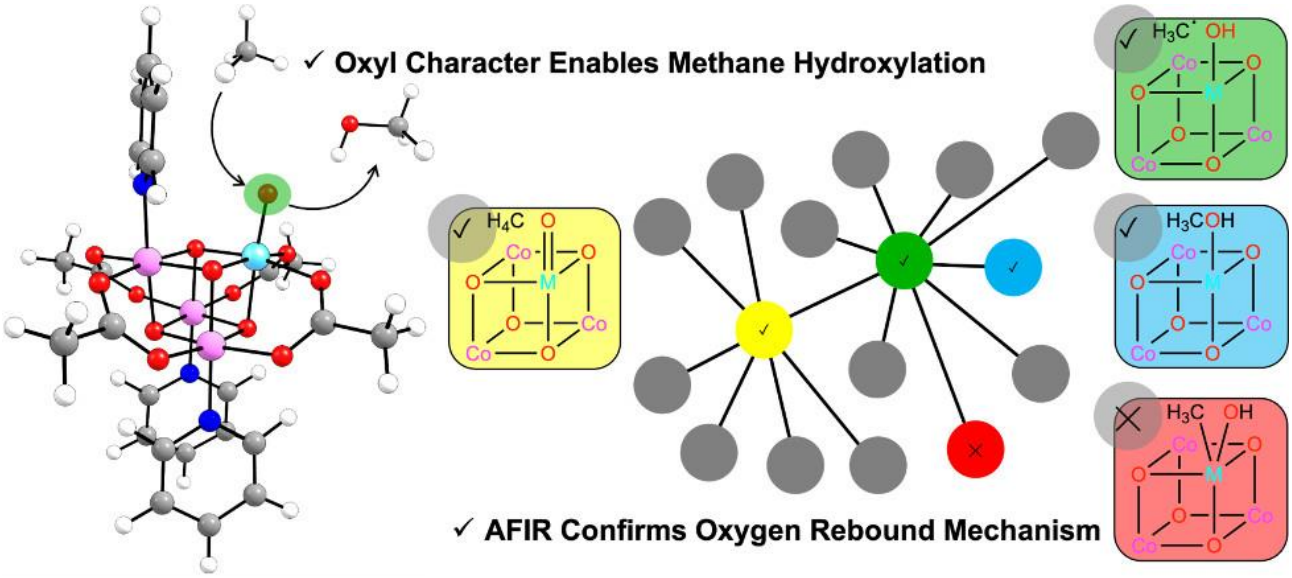
phases. Despite formation of $[Cu_2(OAc)_4] \cdot 2$ py through a single phase being thermodynamically conceivable, as it is the global minimum of the AFIR calculation, it is kinetically inaccessible as demonstrated by the kinetic simulation. Instead, $[Cu_2(OAc)_4] \cdot 2\ H_2O$ must first be formed, and through ligand exchange where H_2O is replaced by py, $[Cu_2(OAc)_4] \cdot 2$ py is formed. This rationalizes the experimental synthesis procedure, which is also performed in two steps.



Transition Metal Catalysis

Methane has the highest gravimetric energy density of all hydrocarbons, but its low density leads to a poor volumetric energy density. Hydroxylation to methanol is a promising strategy to increase its density, of interest to chemical industry, however no 3d TM catalyst capable of selectively oxidizing methane to methanol is currently known. In this Thesis, the electronic and reactive properties of TM-doped cobalt–oxo cubane complexes are studied, enabling design principles for the development of new methane hydroxylation catalysts to be established.

The electronic properties of $[M(O)Co_3O_4(OAc)_4(py)_3]$ (M = Cr, Mn, Fe, Mo, Tc, Ru, Rh) are studied, and based on the high terminal oxyl spin density of the Fe-based cubane, it is proposed as a catalyst for alkane hydroxylation and compared to the experimentally known Ru-doped cubane. Hydroxylation of methane is found to be feasible for the Fe cubane, over a rate-determining H atom abstraction barrier of 24.6 kcal/mol. AFIR calculations provide further evidence for the validity of the oxygen rebound mechanism for methane hydroxylation as the operating lowest-energy mechanism for heterometallic oxo cubanes.


✓ Oxyl Character Enables Methane Hydroxylation
✓ AFIR Confirms Oxygen Rebound Mechanism