Installation of Organic Functional Groups into Titanium-Oxo Molecular Clusters for Efficient Catalyst

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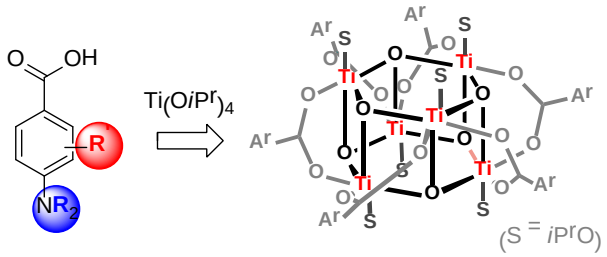
Titanium(IV) is earth abundant early transition metal, and it has been widely studied for various organic transformations as a organometallic reagent or catalyst (e.g., Sharpless Asymmetric Expoxidation). Since the titanium(IV) ion has very high oxo-philic character and proper size to form the molecular cluster, titanium(IV) carboxylate molecular clusters have many attentions from inorganic and catalyst communities.[1,2] However, reported porous or non-porous titanium-molecular cluster or metal-organic frameworks (MOFs) are very limited up to date. And very recently, starting from the titanium(IV) carboxylate molecular clusters, 3-dimentional supramolecular structure was prepared using covalent-organic framework (COF) strategy.[3]

Even thought, titanium-based molecular clusters, and MOFs are emerging materials, the functionalizations of titanium materials are also very limited. The work herein, we have designed and synthesized various functionalized benzoic acid ligands, and applied them to the titanium(IV) carboxylate molecular cluster synthesis. Various amino group, hydroxyl, alkoxy, halogens were successfully installed into titanium-oxo molecular clusters. In addition, the functional group tolerances for titanium-oxo molecular clusters extensively studied. These functionalization titanium-oxo molecular clusters could be applied to various organic transformations as a catalyst, and selective absorbents for CO2, and photoredox catalysis.



$Ti_6O_6(L)_6(^iPrO)_6$

Fig.1 Synthesis of Functionalized Titanium-Oxo Molecular Clusters.

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