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学位論文題目 Design and Functions of Imine-Linked Covalent Organic Frameworks

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論文内容の要旨  
Summary of thesis contents

Covalent organic frameworks (COFs) are a class of crystalline porous polymers that enable the atomically precise integration of building blocks into two- or three-dimensional (2D or 3D, respectively) periodicities. In 2D COFs, the building blocks for the vertices and edges are covalently linked to form extended 2D polygon sheets that stack to constitute layered frameworks. This covalently linked and topologically crystallized 2D architecture merges two structural characters, i.e., periodic  $\pi$  arrays and ordered one-dimensional channels. The 2D COFs offer a unique platform for constructing periodic columnar  $\pi$  arrays of arenes, porphyrins, phthalocyanines, and thiophenes, which exhibit remarkable light-emitting, semiconducting, photoconductive, charge-transferring, and charge-separating properties. In addition, 2D COFs provide ordered one-dimensional (1D) channels whose size and shape can be tailored for gas adsorption and guest encapsulations.

If catalytic active sites can be successfully integrated into the frameworks, the highly ordered skeletal alignment and open-channel structure of 2D COFs provide an intriguing motif for exploring well-defined nanoreactors. Two strategies can be used for constructing catalytic COFs. Incorporating building blocks that possess catalytic sites constitute the direct method. However, this technique requires a tedious solvothermal synthesis. Particularly, if the catalytic site is bulky, forming a crystalline porous COF structure becomes difficult. Another methodology for constructing catalytic COFs involves the post-synthetic integration of catalytic sites into a crystalline COF skeleton. This approach can reduce the influence of the bulky catalytic sites on the COF scaffold crystallinity and the undesired effect of harsh solvothermal conditions on the catalytic sites. The construction of a covalently linked, yet highly active catalyst remains a synthetic challenge in the field.

Most of heterogeneous organocatalysts are using linear polymers as catalyst supporters, which however, give low activity as a result of inefficient access to catalytic sites. Polymer particles could enhance the reaction interface on surface; however, they involve complicated surface modification while the inner part of the particles is unavailable for catalysis. To overcome this issue, metal-organic framework (MOF)-based organocatalysts have been developed, utilizing coordination chemistry to introduce the catalytic sites into the open frameworks. However, the MOF-based organocatalysts are problematic in terms of pore size, enantioselectivity and diastereoselectivity, and reusability.

In my doctoral work, I developed a general strategy for the design and synthesis of chiral covalent organic frameworks and demonstrated their functions as unique platform for designing heterogeneous asymmetric organocatalysts. I introduced a surface engineering approach that allows for post-synthetic integration of chiral catalytic sites onto the channels walls of the imine-based 2D COFs. To develop catalytic systems, chemical stability of the 2D COFs thus far reported are not robust

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enough to maintain crystallinity and porosity in different solvents and under heating, acidic, or basic conditions. I explored a new stable structure for 2D covalent organic frameworks, which retain high crystallinity and large porosity in different solvents, strong acid and base, and even under heating conditions (100 °C in water). Based on these two major achievements, I created a series of chiral 2D COFs as asymmetric catalysts for Michael addition reactions.

In Chapter 2, I developed a pore surface engineering strategy for the controlled functionalization of imine-linked COFs using a three-component condensation system in conjunction with click chemistry. I introduced the ethynyl- group into the building blocks and optimized the solvothermal conditions to create a serious ethynyl-modified COFs. These COFs shows good crystallinities and BET surface area about 1000 m<sup>2</sup>/g, based on this, I introduced the azide modified organocatalytic active sites (S)-2-(Azidomethyl)pyrrolidine into the pore walls via click reaction at room temperature. This postsynthesis strategy preserved the crystallinity of the COF skeletons which ensure the open channels accessible for the reactants; meanwhile, the ambient condition of the click reaction largely maintained the activity and selectivity of the organocatalytic active sites. Engineering pyrrolidine units onto the pore walls creates COF based heterogeneous organocatalysts, which showed significantly improved activity because of the ordered nano-channel structure and the high surface area. Utilize these features, this COF-based catalyst was further employed as the filler of the column (1 cm bed height), such catalyst column maintained a 100% conversion and its stereoselectivities for more than 48 h under continuous flow conditions.

In Chapter 3, I will introduce a novel mesoporous imine COF which combines high crystallinity, porosity and excellent stabilities. COFs are designed and synthesized utilizing the reversible formation of covalent bonds that can be formed, broken, and reformed under the principle of dynamic covalent chemistry. Consequently, the reversible reaction nature makes the high crystallinity and large porosity seem to be incompatible with a robust stability in COF materials. In this chapter, I challenge this contradiction by a synthetic discovery of highly-crystallized imine-COF which owns a chemical robust nature but shows high crystallinity. The intense main peak (135 x 10<sup>3</sup> cps) together with five detailed minor peaks suggests that this COF material has a highly ordered crystalline structure; besides, the experimental BET surface area is nearly identical to the theoretical surface area, which indicates its high crystallinity nature, since only the ideal structure could offer efficient access to guest molecules and result a theoretical porosity. The highly ordered crystalline structure benefits the porosity and also endow this COF with an exceptional stability: this COF could perfectly maintain its crystallinity and porosity in different organic solvents and strong acid (12 M HCl), strong base (14 M NaOH), and even at heating conditions (boiling water) for 1 week. This discovery makes a breakthrough in the field of crystalline frameworks, providing an efficient solution to the contradiction of high performance with high stability.

In Chapter 4, I combined the pore surface engineering strategy with the highly

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crystallized mesoporous imine COF to create a high-performance heterogeneous asymmetric organocatalyst. The stability renders the COFs able to be chemically functionalized while retaining crystallinity and porosity; the chiral COF catalysts engineered with active sites on the channel walls were synthesized in a facile yet controlled manner. The crystalline structure of the resulting COF catalyst was perfectly preserved and lead to a BET surface area as high as 1960 m<sup>2</sup>/g. The mesoporous nature together with highly ordered 1D nano-channels and extremely high surface area endow this crystalline catalyst a number of striking features, including enhanced activity, high enantioselectivity, excellent stability and cycle performance and environmental benignity; these advantages offer a plausible solution to long-standing challenges for real application of organocatalysts. Therefore, these advancements open new perspectives in the design of heterogeneous catalysts for the sustainable production of chemicals and fuels; the utilization of stable open framework architectures may facilitate the design of other functions and applications.

Summary of the results of the doctoral thesis screening

共有結合性有機骨格構造は、高分子シートの結晶化によって構築され、周期的な $\pi$ カラム構造及び規則正しく配列した一次元ナノチャンネル構造をつくりだす。このような高度な特性を有す有機構造は、これまでの非共有結合で形成される超分子や共有結合で連結した高分子では実現できない。共有結合性有機骨格構造は、開かれた多孔構造を有するため、触媒骨格として魅力的である。触媒として機能するためには、安定でかつ高い結晶性と多孔性を有することが不可欠である。しかしながら、これまで報告された構造は、安定性と結晶性及び多孔性を持ち合わせることが困難であった。本研究では、化学的に安定な共有結合性有機骨格構造の構築に着眼し、結晶性と多孔性を兼備した種々共有結合性有機骨格構造の設計・合成を通じて、有機分子触媒として機能する共有結合性有機骨格構造を開拓した。さらに、構造制御と共に、機能発現メカニズムを解明し、触媒機能の向上と制御に成功した。

第一章は2次元有機骨格構造に関して、これまでの分子設計原理、合成反応、ガス貯蔵、触媒作用、光電子機能について記述している。第二章はポルフィリン骨格を有するアミン誘導体とジアルデヒド類をモノマーとして開拓し、重合反応を用いてイミンで連結した2次元共有結合性有機骨格構造の合成について記述している。さらに、3成分からなる縮合反応システムを開拓し、クリック反応を用いて共有結合性有機骨格構造に有機分子触媒活性点を制御して導入することを可能としている。これらの2次元共有結合性有機骨格構造の結晶構造、多孔構造、熱安定性、溶媒安定性、及び触媒機能について検討し、2次元有機骨格構造は再利用可能な触媒として機能することを明らかにしている。第三章は安定な2次元共有結合性有機骨格構造の合成、構造同定及び安定性について記述している。トリフェニルベンゼンをベースとした一連のイミン連結2次元有機骨格構造を合成し、結晶構造、多孔構造、及び安定性について検討した。これらの2次元有機骨格構造は、極めて高い結晶性と大きな表面積を有し、強酸・強塩基下にも安定に存在することを明らかにしている。第四章は前章で開拓した安定構造をベースに、メソポアを有するキラル有機触媒骨格構造の合成と機能開拓について記述している。これらの有機分子触媒は、水を溶媒として用いることができ、高い触媒活性やエナンチオ選択性、立体選択性を示した。触媒の再利用を検討したところ、高いエナンチオ選択性と立体選択性を維持したまま反応を促進できることを明らかにしている。第五章は全体まとめと展望について記述している。

本論文は、2次元共有結合性有機骨格構造に関して、結晶構造を安定化させる設計原理を開拓した。この原理に基づいて、安定性、結晶性、及び多孔性を兼備した新奇な共有結合性有機骨格構造を合成した。これらの結果をベースに、種々の2次元共有結合性有機骨格構造の合成を通じて、特異な規則正しい一次元チャンネル構造を用いた触媒システムの開拓を行った。さらに、表面積やポアサイズ、触媒活性サイト密度の影響を検討し、高い触媒機能を有する骨格構造を見いだしている。特に、安定な2次元有機骨格構造の創製はこ

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れまでに困難であった応用への展開に新しい分子設計戦略を与えるものとして大きな意義を持つ。以上のことから、審査委員会は出願論文が博士（理学）の授与に値すると全員一致で判断した。