Design and Synthesis of π-Electronic Covalent Organic Frameworks

Covalent Organic Frameworks (COFs) are a class of crystalline porous polymers that enable elaborate integration of organic building blocks into ordered structures with atomic precision. Because they are composed of lightweight elements linked by strong covalent bonds, COFs have low mass densities, possess high thermal stabilities, and provide permanent porosity. Depending on the geometry of building blocks, COFs can be categorized into either two- (2D) or three-dimensional (3D) COFs. 2D COFs consist of 2D sheets, which stack further to constitute layered structures, giving rise to periodically aligned columnar π arrays and ordered one-dimensional channels. The periodic columnar structure provides a powerful means to construct ordered π systems that are difficult to create via conventional covalent and/or noncovalent approaches. In contrast, 3D COFs consisting of three-dimensional network structure have high surface areas, possess numerous open sites, and have low densities making them ideal candidates for gas adsorption and storage. However, the limits on monomers and synthetic reactions for the preparation of COFs have impeded further advances in this emerging field. To advance this emerging field it is important to expand the scope of building blocks and the types of reactions. This thesis consists of seven chapters, whereas the first and last chapters are for General Introduction and Summary and Perspectives, respectively.

(1) Structural Control of Imine-Linked 2D COFs through Interlayer Molecular Interactions

Crystallinity and porosity are crucial for crystalline porous COFs. In chapter 2, the author reports the synthetic control over the crystallinity and porosity of COFs through managing interlayer interactions based on the self-complementary π-electronic force. Fluoro-substituted and non-substituted aromatic units at different molar ratios were integrated into the edge units that stack to trigger self-complementary π-electronic interactions in the COFs. The interactions improve the crystallinity and enhance the porosity through maximizing the total crystal stacking energy and minimizing the unit cell size. Consequently, the COF consisting of equimolar fluoro-substituted and non-substituted units shows the largest effect. These results suggest a new way to the design of COFs through managing the interlayer interactions.

(2) Structural Control of Imine-Linked 2D COFs through Intralayer Molecular Interactions

Chapter 3 describes a supramolecular approach using hydrogen-bonding interactions as a powerful means to control over the crystallinity, porosity, and π-electronic properties of imine-linked 2D porphyrin COFs. The hydrogen-bonding sites that are integrated into edge units of imine-linked COFs suppress the torsion of edge units and lock the polygon sheets in a planar conformation. As a result, hierarchical positive effects on structure and functions of both free-base and metalloporphyrin COFs were observed, including improved crystallinity, enhanced porosity, extended π conjugation, increased light-harvesting capability, and lowered band gap. By virtue of these features, these COFs are promising as photocatalysts for the molecular oxygen activation driven by visible light.

(3) The Scope of Edge Building Blocks for the Construction of Imine-Linked COFs

Chapter 4 describes the scope of edge building blocks for the construction of imine-linked porphyrin COFs. Edge units with different lengths and geometries were designed and synthesized for the preparation of imine-linked COFs. The effect of edge structure on the porosity and π electronic properties of COFs is systematically studied.

(4) Synthesis and Functions of Imine-Linked Pyrene COFs

Chapter 5 describes the synthesis and functions of a series of imine-linked two- and three-dimensional pyrene COFs. The edges units were tuned in both length and geometry. These pyrene COFs exhibit high porosities and discrete pore sizes. Owing to the imine linkages, these COFs show extended π conjugation over the molecular skeleton. The correlation of structure and luminescence property is investigated.

(5) A Squaraine Linkage for the Construction of Mesoporous COFs

Chapter 6 describes a new reaction for COF synthesis based on squaraine chemistry. A high-throughput protocol was established for the condensation reaction of squaric acid with porphyrin. The squaraine-linked COF features high crystallinity, inherent porosity, and robust solvent stability. The squaraine linkage is unique because it extends the π-conjugation over the 2D skeleton and provides a new molecular motif for π-cloud communications. Their improved light-harvesting capacity, lowered band gap, layered π-stacking porphyrin arrays, and open mesopores are useful properties for developing functional molecular systems, e.g. photocatalytic systems. This work expands the scopes of COFs and constitutes an important step toward porous crystalline organic architecture with predesigned π-conjugation and function.

As summarized above, through the three-year work, the author demonstrated that the 2D COFs with π conjugated skeletons together with well-defined nanopores enable the development of novel materials that are completely different from traditional linear conjugated polymers without porous structures and conventional porous materials lacking π correlations among the building blocks. Especially, the author has developed new principle and strategy for the molecular design of 2D imine- and squaraine-linked COFs.