

The Chemistry of Covalent Organic Frameworks

School of Materials Science, Japan Advanced Institute of Science and Technology

Sasanka Dalapati and Donglin Jiang*

Introduction

Materials with permanent pores constitute a unique class of materials that enable the creation and utilization of nanometer-scale pores for achieving specific properties and functions that would be impossible with nonporous materials. The progress in chemistry and materials science over the past century has generated a series of classes of porous materials, showing general trends in structural evolution from inorganic compositions to organic components, from small pores to large pores, from rigid frameworks to soft dynamic skeletons, and from three dimensions to two dimensions. Covalent organic frameworks (COFs) are a class of porous polymers that enable precise integration of organic building blocks into extended structures with periodic skeletons and ordered pores.^[1,2] One distinct feature of COFs is that a unique topology diagram for structural guidance based on reticular chemistry is available, facilitating the design of both skeletons and pores. This topological strategy directs the growth of the frameworks in a predictable manner and thus allows for the predesign of not only the primary-order structure but also high-order structure. Consequently, in principle, the geometry and dimensions of the organic building blocks and linkages should determine the structures of the resulting COFs. Indeed, the diversity of organic units, variety of linkages, and scope of topology diagrams endow COFs with structural diversity, accuracy, predictability, and controllability in both their skeletons and pores. As a result, COFs represent a unique class of porous polymers that enable the total design and control of the primary and high-order structures; this structural designability is attractive and difficult to achieve using other porous materials.

Their well-defined structures make COFs an emerging platform for the creation of desired functions on a molecular basis. From a chemistry perspective, COFs are unique because their skeletons and pores are totally predesignable. Additionally, from a physics perspective, COFs offer a platform for mechanistic studies of correlated organic π -systems in which the confined space triggers interactions with excitons, electrons, holes, spins, ions, and molecules. Finally, from a materials science perspective, COFs enable functional design at three different levels: skeletons, pores, and their combination. Specifically, COFs can be designed to trigger synergistic effects between the skeletons and pores to achieve specific functions. Their outstanding abilities, including CO₂ capture, semiconduction, proton conduction, light emission, catalysis, and energy conversion and storage, have been explored and show great potential for practical implementation.^[1-2] Herein, we discuss our recent

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Field of Environment and Energy, School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi 923-1292, Japan. E-mail: djiang@jaist.ac.jp, Phone: 0761-51-1540

advancements in the structural design and functional explorations of highly luminescent COFs.^[3-6]

Results and Discussion

Although various luminescent and π -systems have been integrated into the skeletons of COFs, the synthesis of COF-based luminescent materials remains challenging. Indeed, almost all of the COFs reported to date are not luminescent because their π - π stacked layer structures quickly dissipate excitation energy. Exploring the layered structures to develop highly emissive COFs is key to further advancing this application. Thus, the development of a strategy that takes advantage of the layer structures for light emitting is of fundamental significance. Recently, we developed a new mechanism based on aggregation-induced emission (AIE) has been explored for the design of highly luminescent COFs. Tetraphenylethene (TPE) is an AIE active molecule and adopts C_2 symmetry. By using a $C_2 + C_2$ topology diagram, a TPE-based boronate ester-linked COF (TPE-Ph-COF) has been successfully synthesised (Figure 1). The TPE-Ph-COF consists of TPE vertices in a kagome-type dual-pore 2D skeleton that stacks via π - π interactions. This layered structure suppresses the rotation of the phenyl units of the TPE vertices and triggers strong blue luminescence at 500 nm upon excitation at 390 nm. Because the boronate ester linkages form complexes with ammonia via Lewis acid-base interactions, the TPE-Ph-COF acts as a fluorescence sensor for ammonia. The luminescence is substantially quenched by ammonia, and the COF can detect ammonia at sub-ppm level.

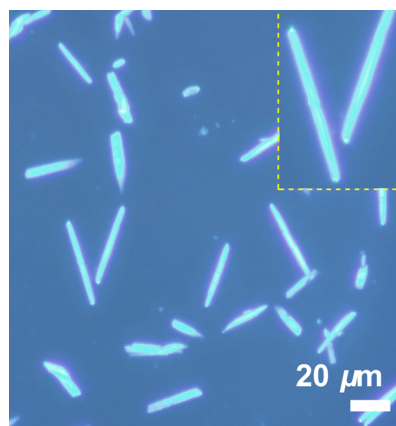
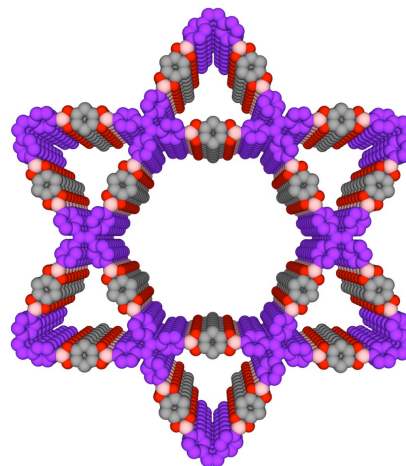


Figure 1. A luminescent COF.

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