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Review

Recent advances of covalent organic frameworks in electronic and optical applications

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ABSTRACT

Covalent organic frameworks (COFs) as an emerging class of porous materials have achieved remarkable progress in recent years. Their high surface area, low mass densities, highly ordered periodic structures, and ease of functionalization make COFs exhibit superior potential in gas storage and separation, optoelectronic device and catalysis. This mini review gives a brief introduction of COFs and highlights their applications in electronic and optical fields.

1. Introduction

Covalent organic frameworks (COFs) are crystalline organic porous materials connected by strong covalent bonds. Since the first examples of COFs reported by Yaghi et al. in 2005 [1], the research of COFs has evoked an immense amount of recent interest and progressed significantly [2]. Generally, according to the dimensions of their structural features, COFs can be divided into two-dimensional (2D) and three-dimensional (3D) frameworks. 2D COFs usually consist of either single layer structure or multi-layer stacking structure assembled with the aid of π–π interactions (e.g. COF-5 and ZnP-COF, Fig. 1a and b). The layered structures with periodic and infinite topology are formed by covalently linking of multi-functional building blocks. 3D COFs generally expand the network framework to three-dimensional space through tetrahedrally-structured building blocks (e.g. COF-105 and COF-108, Fig. 1c and d).

Compared with other crystalline porous materials, COFs with high surface area, adjustable pore size and tunable internal chemical environment possess many unique advantages: (1) unlike metal-organic frameworks or coordination polymers [3], COFs are usually composed of only light elements, such as B, C, H, N and O, resulting in low mass densities of COFs (e.g. 0.17 g cm^{-3} for COF-108, 0.18 g cm^{-3} for COF-105 [2a]); (2) diversities of organic building blocks and synthetic organic reactions facilitate to design and synthesize COFs with specific structures and functions; (3) COFs are constructed from organic building units linked by robust covalent bonds, endowing COFs with high thermal stability, and except for boron linked COFs, most of COFs also have good chemical stability; (4) easy to introduce additional functional groups by post-synthetic modification; (5) possessing highly ordered periodic structures, not only beneficial to study the specific physical and chemical behavior from atomic and molecular level, but also helpful to improve the performance. These advantages make COFs as promising candidates for gas storage and separation [2i,4], catalysis [5], optoelectronics [2e,6] and energy storage [7] applications. In recent years, some pioneering works have also explored their potential applications in drug delivery [8], water capture [9], trypsin immobilization [10] and high-resolution chromatographic separation [11].

The research in the COFs can be roughly classified into structural-oriented and functional-oriented protocols. For the structural design, researchers often focus on creating crystalline porous materials with the different topologies, arrangements of building units and pore shapes and sizes using reticular chemistry by changing the geometry of building blocks and the symmetry of reactive groups, combined with new synthetic methodologies. For the functional-oriented protocol, the strategies include the design of functional building units, post-synthetic modification, and the encapsulation of particular small molecules into the pores. There is

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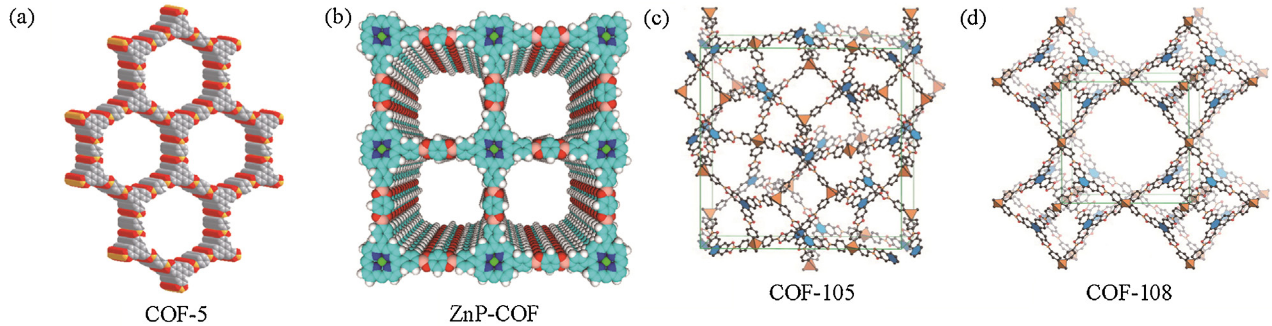

Fig. 1. Schematic representation of 2D and 3D COFs.
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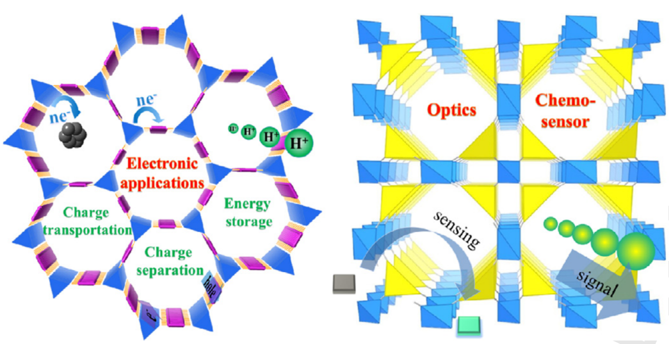
a very close structure-function relationship in COFs, varying structural features always result in distinct performance, and imparting COFs with special functions requires intentionally design of structures. The structural features, synthetic reactions, and formation mechanisms of COFs and their applications in gas storage and separation have been well summarized in several pioneering reviews [2b,2c,2g–i]. In this mini review, we focus on the recent advances of COFs in electronic and optical applications (Scheme 1) and hope this work could promote further development for COF-based optical-electronic systems.



Scheme 1. Schematic illustration of COFs' applications in electronic and optical fields.

2. Electronic and optical properties

2.1. Semiconduction and photoconduction

In 2D COFs, periodic polymer sheets with different topologies, such as hexagonal or tetragonal geometric shapes, are usually constructed from aromatic building blocks through strong covalent bonding, and the extensive π–π interaction between these sheets drives to form layered stacking structures. Aromatic building units are self-sorted to constitute periodic and vertical columnar arrays that are favored for charge carrier and photoexcited exciton transportation, endowing COFs with semiconductive and photoconductive behaviors. Moreover, simultaneously incorporating donor and acceptor into one framework or introducing one component into the framework and another into the pores offer great opportunities for photoexcited charge transfer and ambipolar transportation capability, which is of vital importance for photoelectronic applications.

Jiang and co-workers pioneered in this area and firstly reported semiconductive and photoconductive COFs, TP-COF [12] and PPy-COF [13], via co-condensation or self-condensation of highly ordered π-conjugated pyrene derivative. TP-COF (Fig. 2a) shows semiconducting characters and strong blue light emission ability, while PPy-COF (Fig. 2b) is able to harvest

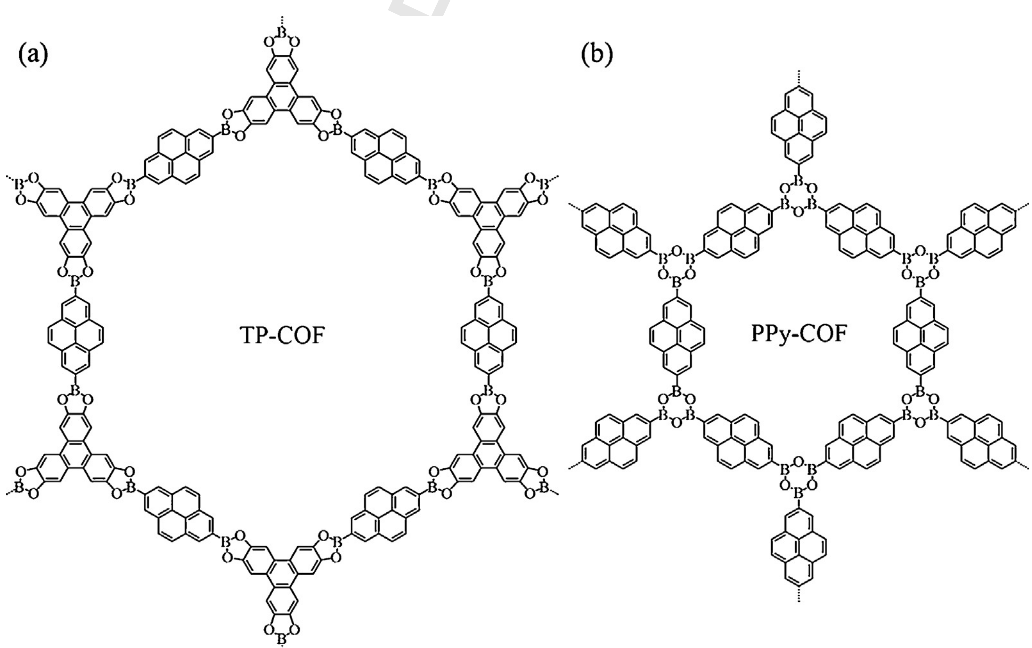


Fig. 2. Schematic representation of TP-COF and PPy-COF.