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Review

Semiconducting covalent organic frameworks: a type of two-dimensional conducting polymers

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ABSTRACT

In recent years, as a new class of two-dimensional polymer, covalent organic frameworks (COFs) have attracted intensive attention and developed rapidly. This review provides an overview of a type of COFs which can be utilized as organic semiconductors. Carefully choosing monomers as the building blocks will bestow different types of semiconducting character on COFs. We summarize the p-type, n-type and ambipolar semiconducting COFs and highlight the effects of π-functional building blocks on the photoconductive behaviors of the semiconducting COFs.

1. Introduction

Covalent organic frameworks (COFs) are a class of porous crystalline materials which consist of organic building blocks orderly linked by strong covalent bonds [1], and it can also be defined as a type of two-dimensional polymer. According to the principles of reticular chemistry, the porosity and composition of COFs can be well controlled. That they are composed of light-weight elements bestows the character of low mass density on COFs, and covalent bonds linkages endow COFs with thermal stabilities. Combining the advantages of permanent porosity and high surface area makes COFs a perfect candidate material for gas storage [2], gas separation [3], catalysis [4], and proton conductivity [5]. Moreover, another significant feature of COFs is that their functionality can be tuned by carefully choosing the type of the building blocks, resulting in potential applications in various fields. Polymers with π-conjugated functional groups usually possess fluorescent and photoconductive property [6]. Similarly, if we use π-conjugated molecules as the monomers, COFs with photoconductive properties can be obtained as well [7]. Fig. 1 summarizes the π-functional molecules which can be used for synthesizing the semiconducting COFs. In this short review, we summarize the recent advance in this field.

2. Fundamentals and motivation

COFs can be developed into two-dimensional (2D) or three-dimensional (3D) frameworks based on the structure of building blocks. In 2005, the first 2D COFs were designed and synthesized through the condensation reaction of boronate ester [1]. To improve the crystallization, the organic reaction for synthesizing COFs need have a good reversibility [8], and till now the reactions include the formation of B–O (boronate, boroxine, and borosilicate) [9], C=N (imine, hydrazine, and squaraine) [10], C–N (triazine and imide) [11], B–N (borazine) [12], and N=N (azodioxide) [13] bond linkages (Fig. 2).

In 2D COFs, organic building blocks are orderly linked to form 2D sheets with regular pores which then stack together by π–π interaction of the building blocks in a face-to-face way. So, there are periodically aligned columns developed by building blocks in 2D COFs. Such a well-organized structure will benefit 2D COFs applied as organic semiconductors when selecting π-functional molecules as building blocks, because the charge carriers excited from the building blocks will transport along the discrete and periodic columns [14]. These unidirectional pathways for charge carrier transport definitely improve the charge carrier mobility of 2D COFs as semiconductor. That is a great advantage compared with traditional organic semiconductors or polymer semiconductors which are amorphous.

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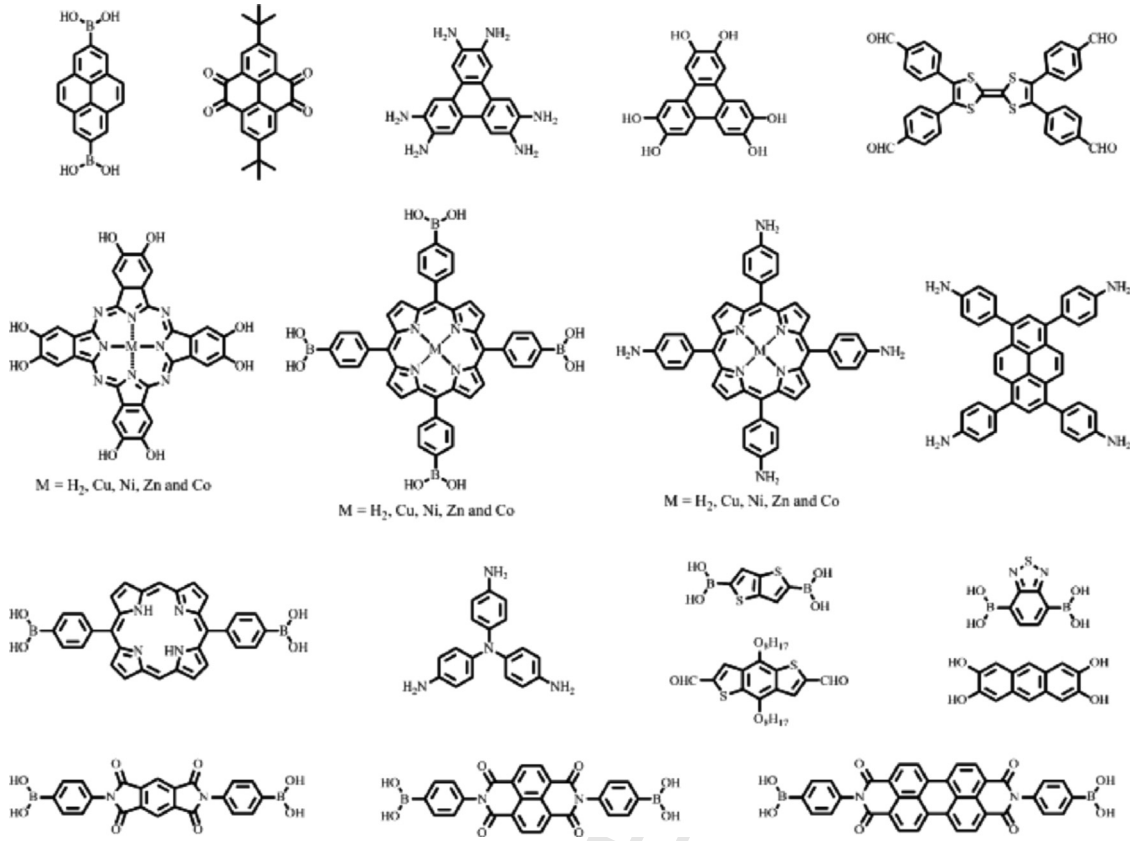

Fig. 1. π-functional molecules used for synthesizing semiconducting COFs.

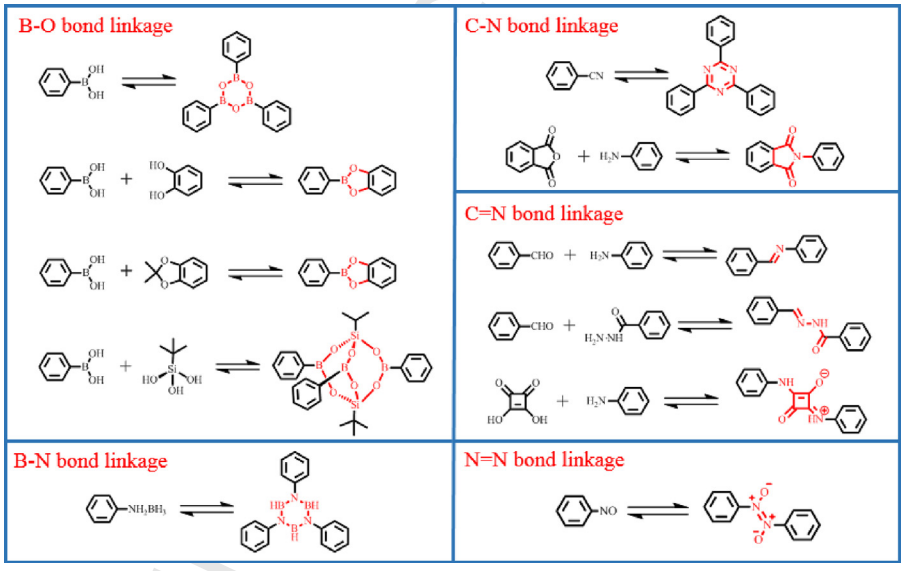

Fig. 2. Linkages and organic reactions used for synthesizing COFs.

3. *P*-type semiconducting COFs

Utilizing π-functional organic molecules especially with electron-rich feature to construct COFs which will form an extended π-conjugated system, renders the COFs p-type semiconducting behavior. In 2008, Jiang et al. reported the first example of semiconducting TP-COFs, with a pore size of 3.14 nm, by condensation reaction of 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) and pyrene-2,7-diboronic acid (PDBA) (Fig. 3a) [15]. The specific surface area and pore volume values of TP-COFs were 868 $m^2 g^{-1}$ and 0.7907 $cm^3 g^{-1}$, respectively. The electrical conductivity of TP-COFs was measured by a two-probe method. The homogenous acetone dispersion of TP-COF was casted onto the Pt electrodes with the width of 10 μm. The *I-V* profile of TP-COF was linear in the air at 25 °C, while the gap itself was silent which meat TP-COF had a semiconductor character. After TP-COF was

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