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Article

Ionic covalent organic frameworks for highly effective catalysis

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ABSTRACT

As an emerging class of crystalline porous materials, covalent organic frameworks (COFs) have been widely used as catalysts or catalyst supports. Flexible regulation of the pores and easy introduction of functional active sites onto the skeleton of COFs make them promising platforms for many catalysis applications. However, only a single function is generally observed in these COFs. Herein, we synthesized a negatively charged ionic COF (I-COF) and successfully incorporated functionalized counter ions, that is, metallic Mn^{2+} and a coordination complex of manganese(II) bipyridine complexes ([Mn(bpy)$_2$]$^{2+}$), via a simple ion exchange process. The resulting I-COFs can act as effective heterogeneous catalysts for epoxidation reactions. We envisage that with this type of ionic architecture, a variety of other functional cations could be exchanged into the frameworks, thus making the COF a versatile platform for different applications.

1. Introduction

Covalent organic frameworks (COFs) are a series of crystalline porous materials composed of light elements (e.g., C, H, N, B, O) [1–4]. COFs have been extensively studied in recent years because of their potential applications in various areas, such as gas storage/separation [5–9], sensing [10,11], and energy conversion [12–19]. Moreover, flexible regulation of the pores and easy introduction of functional active sites onto the skeleton of COFs make them promising platforms for many catalysis applications. Thus, many efforts have been focused on either post-synthetic modification or a bottom-up strategy that was shown to be successful in the introduction of catalytic active sites [20–27]. In contrast to post-synthetic modification, the bottom-up strategy generally requires a tedious solvothermal condition, particularly if a bulky catalytic site is attached to building units, it will be difficult to obtain crystalline COFs. Post-synthetic modification is relatively easy and simple, but this strategy generally endows the resulting COFs with only a certain function. To optimize a COF for use in a wide variety of different applications, it is important to be able to tailor its functionality in a straightforward fashion.

Nanosized pores in ionic architectures exhibit unique properties in terms of adsorption and separation of gas molecules [28,29]. This charged nature also enables ionic materials to permanently incorporate, through ion exchange, other extra-framework counter ions, thus making it possible to obtain special properties, such as those useful in chemical sensing, photonics, and catalysis, to realize many unconventional applications [30]. Ionic COFs (I-COFs) have recently been reported, and these ionic frameworks exhibit exceptional proton/ion conduction, electrolyte performance, and removal of pollutants

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[31–34]. However, little research has been done on the utilization of I-COFs for catalysis by far. It is known that many positively charged species, including metal ions and coordinated metal complexes, exhibited excellent catalytic performance, and their high catalytic activity remained when they were loaded within the ionic framework as counter ions. Therefore, we expect that I-COFs can be used as versatile catalysts that maintain the high catalytic activity of either metal ions or coordinated metal complexes. Moreover, the high porosity, designable topology, and easy modification of I-COFs make them ideal materials for catalysis applications.

Herein, we report the synthesis of a negatively charged I-COF through a post-synthetic modification strategy. A chemically stable imine-based COF, DhaTab, was first constructed by the condensation reaction of 2,5-dihydroxyterephthalaldehyde (Dha) and 1,3,5-tris(4-aminophenyl)benzene (Tab) [35]. The ring-opening reaction of 1,3-propane sultone with phenolic hydroxyl on the skeleton of DhaTab affords a sulfoacid-based COF material. In the presence of a dilute NaOH solution, two different counter ions, metallic Mn^{2+} and a coordination complex of manganese(II) bipyridine complexes ($[Mn(bpy)_2]^{2+}$), were successfully incorporated via a simple ion exchange process (Scheme 1). The resulting I-COFs, as heterogeneous catalysts, exhibited excellent catalytic activities in epoxidation reactions. The proposed I-COF strategy provides a promising platform for the development of versatile materials for catalysis.

2. Experimental

2.1. Materials

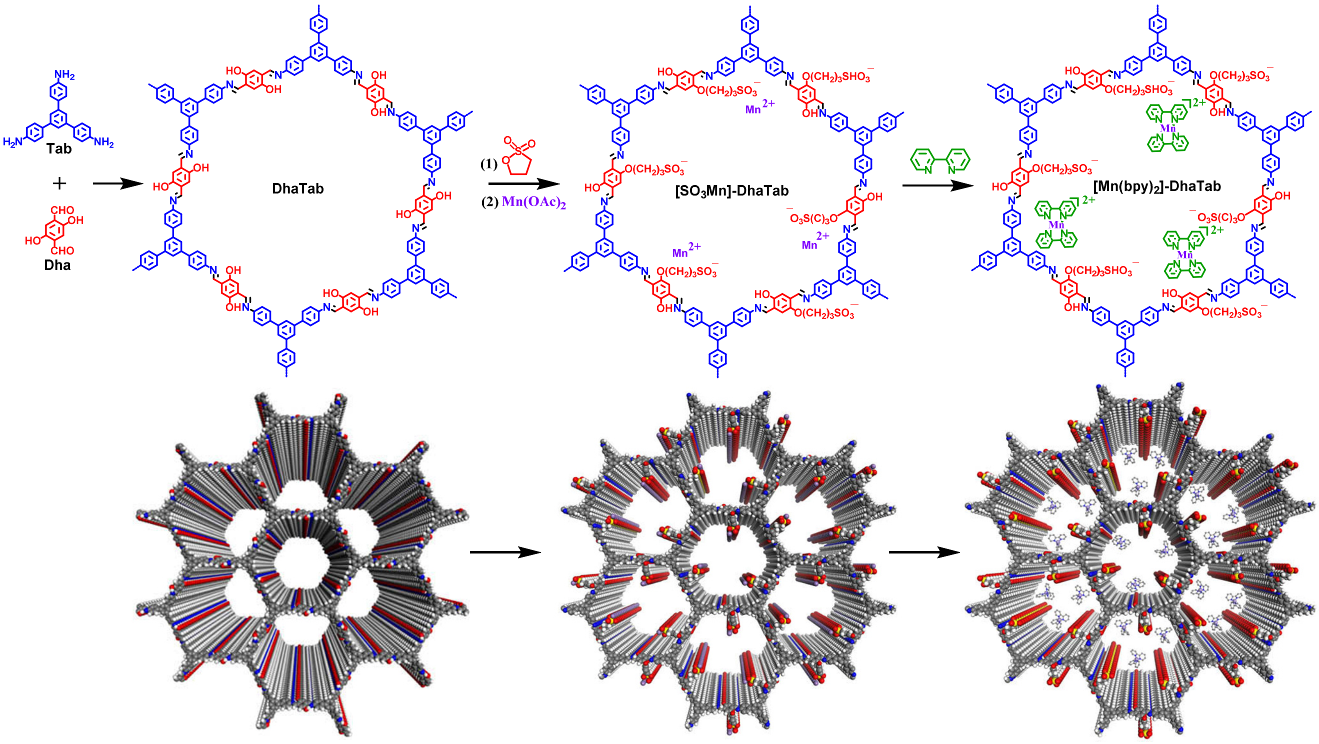
All starting materials and solvents, unless otherwise specified, were obtained from commercial sources and used without further purification. Dha was synthesized according to a previously published procedure [36]. All reactions were performed under ambient laboratory conditions, and no precautions were taken to exclude oxygen or atmospheric moisture, unless otherwise specified.

2.2. Synthesis of DhaTab COF

A pyrex tube was charged with Tab (0.16 mmol, 56 mg) and Dha (0.24 mmol, 32 mg), 1.0 mL of *ortho*-dichlorobenzene (*o*-DCB), 1.0 mL of *n*-butanol, and 0.2 mL of 6 mol L^{-1} acetic acid. This mixture was sonicated for 5 min and then flash-frozen at –196 °C (liquid N_2 bath) and degassed by three freeze-pump-thaw cycles. The tube was sealed off and then heated at 120 °C for 3 d. A yellowish precipitate appeared and was collected by filtration. The solid was then thoroughly washed with dimethylacetamide (DMAc), water, and then ethanol. The collected powder was solvent-exchanged with ethanol three times and then dried at 100 °C under vacuum overnight to give a yellowish powder in ca. 80% (38 mg) isolated yield. Elemental analysis (%) calcd. for $C_{60}H_{48}N_6O_6$: C (75.92), H (5.06), N (8.86); found C (73.36), H (4.51), N (7.69).

2.3. Synthesis of [SO_3H]-DhaTab COF

To 10.0 mL of a toluene suspension of DhaTab (10 mg) was added 5.0 mL of 1,3-propane sultone. The reaction was refluxed for 6 h, and the solid was filtered and then thoroughly washed with DMAc, then water, and then ethanol. The solid



Scheme 1. Synthesis of DhaTab, [SO_3Mn]-DhaTab, and [$Mn(bpy)_2$]-DhaTab COFs.