Review

Metal-organic frameworks in chromatography

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ABSTRACT

Metal-organic frameworks (MOFs) emerged approximately two decades ago and are the youngest class of porous materials. Despite their short existence, MOFs are finding applications in a variety of fields because of their outstanding chemical and physical properties. This review article focuses on the applications of MOFs in chromatography, including high-performance liquid chromatography (HPLC), gas chromatography (GC), and other chromatographic techniques. The use of MOFs in chromatography has already had a significant impact; however, the utilisation of MOFs in chromatography is still less common than other applications, and the number of MOF materials explored in chromatography applications is limited.

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1. Introduction

Metal-organic frameworks (MOFs) are crystalline, highly ordered framework systems synthesised via the self-assembling combination of organic ligands and inorganic metals or metal-oxo units (secondary building units, SBUs) using strong bonds to form a permanent, porous open crystalline framework [1,2]. The inorganic part of MOFs could be selected with various dimensionalities, creating chains (1D), layers (2D) and frameworks (3D) [3].

The term coordination polymers (coordination networks) was previously used to describe MOFs [4–8] due to their similarity with coordination chemistry, especially the polyhedral inorganic parts [3]. The differences in vocabulary are usually due to the researchers who created the structures, although they are almost using the same types of materials [9]. However, Tranchemontagne et al. identified distinct differences between coordination polymers and MOFs [10]. Since the term "MOF" was introduced in 1995 by Yaghi and co-workers [11], there has been intensive research that led to approximately 20,000 different MOFs over the past two decades [1].

In comparison to conventional porous inorganic frameworks, such as zeolites or carbon-based materials, the active surface areas of MOFs are considerably large, reaching $7140 \, m^2 \, g^{-1}$ [12]. Inorganic frameworks also have limited diversity because they accept only a few cations [13–19], mostly limited to Al, Si and chalcogens [20], whereas MOFs exist with almost all possible cations up to tetravalent atoms [3]. The variety of elements used in MOFs, along with the large choice of organic linkers, provides a substantial number of possibilities for creating new MOFs.

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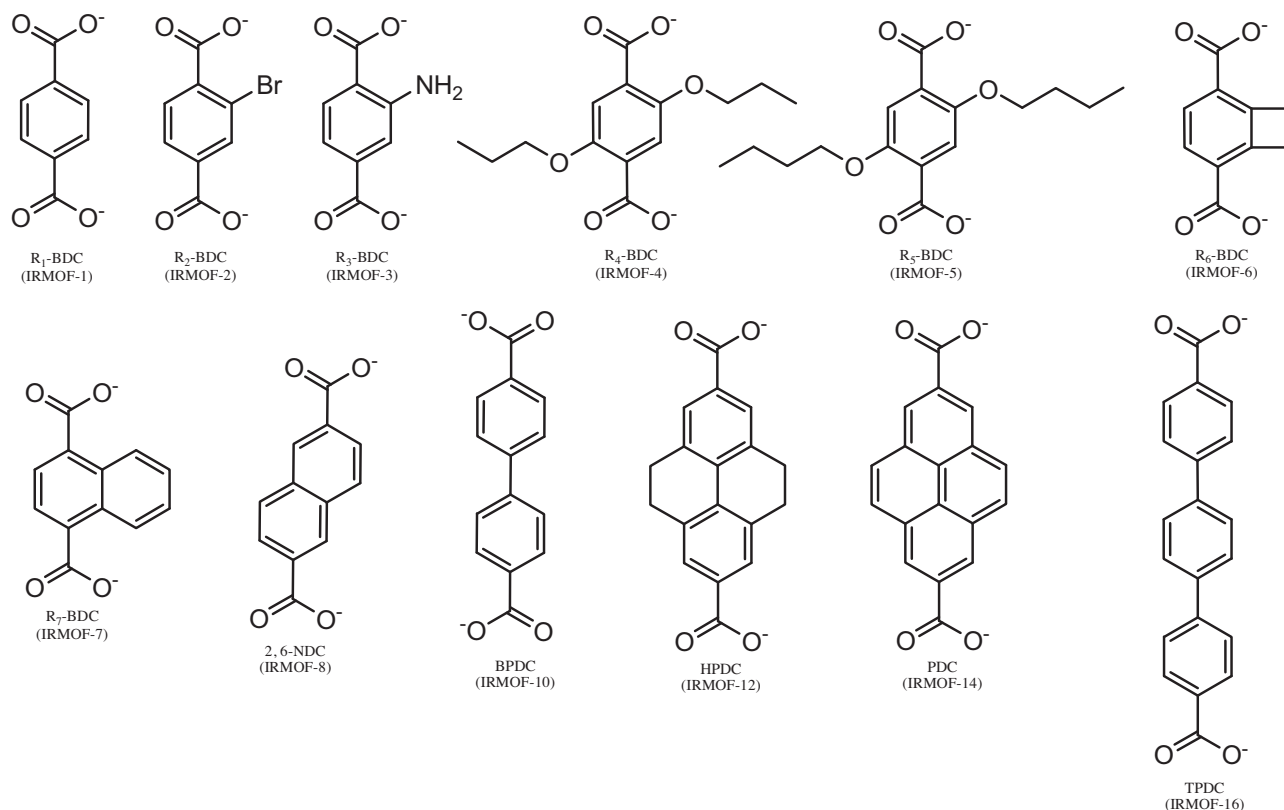(K. Yusuf).

Fig. 1. Organic linkers of IRMOF-*n* (*n* = 1 through 7, 8, 10, 12, 14, and 16) labelled appropriately.

Conversely, inorganic frameworks often utilise a variety of templates or structure-directing compounds. These templates are removed via oxidation, and as a consequence, the removal of the template can result in the collapse of the framework. In MOFs, the framework template is directed by the SBU and the organic ligands [21,22].

MOFs hold the world records for the most porous materials with the largest pore aperture (98 Å) [23], the highest specific surface area ($10,400\,m^2\,g^{-1}$) [12] and the lowest density ($0.13\,g\,cm^{-3}$) [24]. MOF structures have synthetic flexibility to change their size and nature without changing their topology, which is called the isoreticular principle (from the Greek term *iso* meaning same and the Latin term *reticulum* meaning net). The isoreticular character allows MOFs to hold macromolecules, such as vitamins and proteins, and to increase the interaction space within the pores. The ability of adding functional groups into the framework also give MOFs another advantage over other porous materials by allowing post-synthetic modification [1]. The designable structures of MOFs, along with their unique physical, thermal and chemical properties, have led to their utilisation in numerous applications, including chromatographic applications.

2. Structural overview

Metal-organic frameworks consist of two main components: a metal-containing component (cationic part) and an organic component (anionic part) that combine through strong bonding to produce a well-defined highly ordered framework [25]. One of the main properties of MOFs is self-assembly, which affords the desired structure framework. Self-assembly is defined by George Whitesides as "a process where pre-designed components assemble in a determined structure without the intervention of human operators" [26]. The important characteristics of the metal-containing part are their coordination numbers and geometries, which play an

important role in directing the MOF structures. The other important property is the organic linkers, which have a great influence over the shape of the constructed MOF. The organic linkers (or ligands) generally contain coordinating functional groups, such as carboxylates, phosphates, sulphonates, amines, or nitriles, which serve an essential function in locking the metal ions strongly into their positions. Fig. 1 shows some examples of such organic linkers in MOFs [27].

It is difficult, but not impossible, to obtain such MOF structures from simple metal ions and organic linkers because the ions provide little directionality [27]. This limited directionality results in mobility around the metal ion and more than one possible structure, which yields generally inconsistent results, as exemplified by the frameworks based on Cu ions and bipyridine and related linkers [28–35].

To design a network molecular structure such as a MOF, we can start with well-defined and rigid molecular building blocks (MBBs) that will maintain their structure during the construction process [36,37]. Alternatively, the use of well-defined reaction conditions to form these building blocks in situ is an equally applicable method to design this type of extended structure, which is called reticular synthesis [37]. Yaghi et al. described reticular synthesis as "the process of carefully designing a rigid molecular building blocks into stable highly ordered networks, which are held together by strong bonding" [27]. Reticular chemistry [38] – sometimes referred to as 'crystal engineering' – is concerned with the design and synthesis of compounds formed from finite SBUs joined by strong chemical bonds [27]. SBU is an abbreviation that refers to the geometry of the building units defined by the points of extension and describes either the organic or inorganic part of the MOF structure [27]. In reticular synthesis, the metal-containing (cationic) SBUs cannot be isolated, so they have to be constructed in situ with careful control over the reaction conditions, including the mixing stoichiometry, reaction temperature and time, solvent system, ionic strength and