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Experimental comparison of chiral metal-organic framework used as stationary phase in chromatography

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ABSTRACT

Chiral metal-organic frameworks (MOFs) are a new class of multifunctional material, which possess diverse structures and unusual properties such as high surface area, uniform and permanent cavities, as well as good chemical and thermal stability. Their chiral functionality makes them attractive as novel enantioselective adsorbents and stationary phases in separation science. In this paper, the experimental comparison of a chiral MOF $[In_3O(obb)_3(HCO_2)(H_2O)]$ solvent used as a stationary phase was investigated in gas chromatography (GC), high-performance liquid chromatography (HPLC) and capillary electrochromatography (CEC). The potential relationship between the structure and components of chiral MOFs with their chiral recognition ability and selectivity are presented.

1. Introduction

Metal-organic frameworks (MOFs) are a type of novel inorganic–organic porous hybrid material constructed from metal ions or metal clusters and organic bridging linkers (primarily aromatic acids or bases) via molecular assembly and crystal engineering methods. MOFs are typically synthesized using mild reaction conditions, which should allow for the facile construction of ideal MOF crystals by systematic design and tuning of their structures and properties on a molecular level. Recently, MOFs have attracted considerable interest, owing to their diverse structures and unusual properties, such as high surface area, versatile framework topologies, uniformly structured nanoscale cavities, the availability of in-pore functionality and outer-surface modification, as well as good chemical and thermal stability. To date, a large number of MOFs have been synthesized and have displayed a wide range of potential applications in gas storage [1,2], catalysis [3–5], separations [6,7], molecular magnetism [8], drug delivery [9], sensing [10], and membranes [11]. In particular, they have great potential in analytical applications [12–14] such as in-field sampling, solid-phase extraction (SPE), solid-phase microextraction (SPME), gas chromatography (GC), high performance liquid chromatography (HPLC) and capillary electrophoresis (CE).

As an important subclass of MOFs, chiral MOFs can be generated from chiral building blocks or using achiral ligands under spontaneous resolution without any chiral sources. Ideally, they can possess chiral functionalities that are accessible via the open channels or cavities present in the MOFs. Also, chiral MOFs have currently aroused a great deal of attention due to their unique applications in asymmetric heterogeneous catalysis, nonlinear optical materials and enantioselective separations, which is attributed to their intriguing helical topologies, molecular chirality and porous functionality. However, the applications of chiral MOFs have been primarily focused on the enantioselective adsorption of chiral compounds. Recently, a great deal of effort has been made by our group and others to explore chiral MOFs as chiral stationary phases (CSPs) for chromatographic applications [15–30].

As a new class of separation media, MOFs have shown good selectivity and separation performance toward various chemicals, and the process and mechanism of their separations mainly depends on multiple interactions between the MOFs and guest molecules, which are related to the structural features of MOFs such as pore size, open metal sites, functional groups and polarity [31–34]. Also, the pore size of chiral MOFs can significantly affect the enantioselectivity of the separation of chiral molecules. For example, a homochiral MOF $\{[ZnLBr]\cdot H_2O\}_n$ (the aperture size: ~9.8 Å) can afford outstanding separation of some chiral molecules, including (±)-ibuprofen (7.4 Å), (±)-1-phenyl-1-propanol (7.4 Å),

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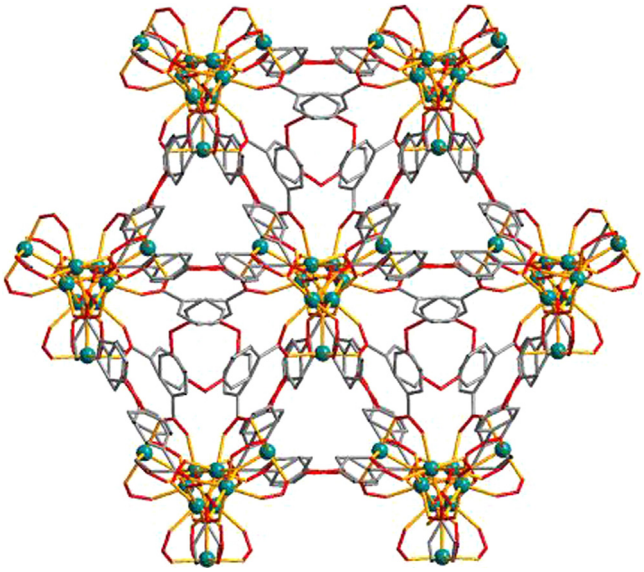

Fig. 1. The 3D structure of $[In_3O(obb)_3(HCO_2)(H_2O)]$ solvent (In – green, O – red, C – gray).

(±)-phenylethylamine (7.4 Å), and (±)-benzoin (9.2 Å), which are able to enter and readily go through the chiral channels. However, separation of larger molecules such as DL-ketoprofen (9.4 Å) and (±)-naproxen (9.7 Å), which finds it difficult to access the chiral channels of the MOF are not separated [21]. Evidently, the selectivity and recognition ability for guest molecules was attributed to the structure and properties of the MOFs.

In this article, a chiral MOF, $[In_3O(obb)_3(HCO_2)(H_2O)]$ solvent, was prepared, which is composed of an infinite polytrimer $\{In_3O(O_2CR)_6(HCO_2)(H_2O)\}_\infty$ chain (helical structure) built from trimeric $\{In_3O(O_2CR)_6(H_2O)_3\}$ clusters (Fig. 1). The unique structure, excellent chemical, and solvent and thermal stability of $[In_3O(obb)_3(HCO_2)(H_2O)]$ solvent make it a promising chromatographic stationary phase for use in GC, HPLC and CEC. Herein, we will compare the chiral recognition abilities of the chiral MOF, $[In_3O(obb)_3(HCO_2)(H_2O)]$ solvent used as a stationary phase in GC, HPLC and CEC, respectively.

2. Experimental

2.1. Chemicals and reagents

All chemicals were at least of analytical grade and used without further purification. $In(NO_3)_3$ (≥99.9%, Aladdin Reagent Co. Ltd., Shanghai, China), HNO_3 (≥99.7%, Guangdong Guanghua Chemical Reagent Technology Company, Guangdong, China), *N*,*N*-dimethylformamide (DMF) (≥99.5%, Tianjin Fengchuan Chemical Reagent Technology Company, Tianjin, China), and 4,4′-oxybisbenzoic acid (≥95%) (Adamas Reagent Co. Ltd., Basel, Switzerland) were used to synthesize the chiral MOF, $[In_3O(obb)_3(HCO_2)(H_2O)]$ solvent. NaH_2PO_4, Na_2HPO_4, Na_2SiO_3 and acetonitrile (ACN) were purchased from Tianjin Fengchuan Chemical Reagent Technology Company. HPLC-grade ethanol was obtained from Tedia (Ohio, USA). Ultrapure water (18.2 MΩ cm) was produced from a ELGA LabWater water purification system (High Wycombe, UK). All racemates were purchased from Sigma and Fluka (St Louis, MO, USA).

2.2. Synthesis of $[In_3O(obb)_3(HCO_2)(H_2O)]$ solvent

$[In_3O(obb)_3(HCO_2)(H_2O)]$ solvent was synthesized according to the procedure of Zheng et al. [35]. Typically, 4,4′-oxybisbenzoic acid (0.250 g), $In(NO_3)_3{\cdot}2H_2O$ (0.200 g), H_2O (0.50 g), HNO_3 (0.090 g) and DMF (3.5 g) were placed in a Teflon-lined bomb, which was heated at 120 °C in an oven for 5 days, and then cooled to room-temperature. The light yellow crystals were washed thoroughly with ethanol, and collected by centrifugation at 6000 rpm for 10 min.

2.3. Instrumentation

GC separations were carried out on a Shimadzu GC-2014 C (Kyoto, Japan) system equipped with a flame ionization detector (FID), split injection port and capillary control unit. Data acquisition and processing were controlled using an N-2000 chromatography data system (Zhida Information Engineering Co., Ltd., Zhejiang University, China).

The HPLC system consisted of a LabTech LC600 liquid delivery pump and LabTech UV–vis detector (Boston, MA, USA). A LabTech HPLC Workstation for the HPLC system was used to process the chromatographic data. An Auto science AT-330 column heater (±0.1 °C) was used to control the column temperature during HPLC separation.

CEC experiments were performed on a HPCE system (CL1020, Beijing Cailu Instrumental Co., Ltd., China) equipped with a UV detector (190–700 nm). Data acquisition and processing were controlled by a HW-2000 chromatography workstation (Qianpu Software, Shanghai, China).

Powder X-ray diffraction data (PXRD) were recorded on a Rigaku D/max-3B diffractometer (Tokyo, Japan) using $Cu_{K\alpha}$ radiation. Scanning electron microscopy (SEM) images were obtained using a S-3000N scanning electron microscope (Hitachi Science Systems, Japan). High-resolution transmission electron microscopy (HRTEM) images were recorded using a JEM-2100 transmission electron microscope (JEOL Ltd., Tokyo, Japan) operating at an accelerating voltage of 200 kV. Thermogravimetric analysis (TGA) was carried out using a heating rate of 10 °C min^{-1} in air with a ZRY-1P simultaneous thermal analyzer (Shanghai, China). The circular dichroism (CD) spectrum of the chiral MOF crystals was measured on a Chirascan Circular Dichroism Spectrometer (Applied Photophysics Ltd., Leatherhead, UK).

2.4. Preparation of MOF columns for GC, HPLC and CEC

Untreated fused silica capillary columns (2 m and 50 cm long × 75 μm i.d.) were sequentially rinsed with 1.0 M NaOH for 3 h, ultrapure water for 1 h, 0.1 M HCl for 1 h, and ultrapure water again until the outflow was neutral. Finally, the capillary was dried with a nitrogen purge for 6 h at 120 °C.

MOF-coated capillary columns for GC were fabricated using a dynamic coating method. A homogenous suspension of $[In_3O(obb)_3(HCO_2)(H_2O)]$ solvent in ethanol (2.0 mg mL^{-1}) was prepared. The suspension was used to fill the capillary column under gas pressure, and then pushed with N_2 at a rate of 40 cm min^{-1} to leave a wet coating layer on the inner wall of the capillary column. A 1 m long buffer tube was attached to the end of the capillary column as a restrictor to avoid acceleration of the solution plug near the end of the column. After coating, the capillary column was flushed with nitrogen for 3 h. Finally, the coated capillary column was conditioned using a temperature program consisting of heating at 30 °C for 10 min, increasing the temperature to 300 °C at a rate of 2 °C min^{-1} and being held at 300 °C for 6 h.

The MOF-packed column (25 cm long × 4.6 mm i.d.) for HPLC was prepared using a conventional high-pressure slurry packing procedure. Before packing, the MOF was crushed in ethanol by applying gentle pressure to obtain the desired MOF particles with the help of solvent suspension. A 4.5 g mass of the MOF prepared