Journal of Chromatography A, xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Homochiral zeolite-like metal-organic framework with DNA like double-helicity structure as stationary phase for capillary electrochromatography enantioseparation

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ARTICLE INFO

Article history:
Received 1 December 2017
Received in revised form 29 January 2018
Accepted 6 February 2018
Available online xxx

Keywords:
Homochiral metal-organic framework
DNA like double-helicity structure
Capillary electrochromatography
Enantioseparation

ABSTRACT

In recent years, artificial materials with double helix structure have attracted widespread attention due to their unique properties such as the DNA like double-helicity, intrinsic chirality and diverse functional groups. Developing novel chiral stationary phases (CSPs) for capillary electrochromatography enantioseparation is of intriguing interest. Herein, a novel homochiral zeolite-like metal-organic framework (ZMOF) JLU-Liu23 with unique DNA like double-helicity structure was firstly utilized as the CSP in open tubular capillary electrochromatography (OT-CEC) for enantioseparation of chiral monoamine neurotransmitters and analogues. Owing to the unique DNA like double-helicity structure of the homochiral ZMOF JLU-Liu23, the good enantioseparation of four monoamine neurotransmitters and analogues was achieved on the prepared homochiral ZMOF JLU-Liu23 coated capillary column. The relative standard deviations (RSDs) of the analytes migration time for intra-day, inter-day and column-to-column were in the range of 0.3–0.6%, 0.8–2.2% and 3.5–6.5%, respectively.

1. Introduction

The double helix structure is one of the most amazing geometrical structures in nature. Helical structures can be either right-handed or left-handed depending on the direction of rotation. From the structure it can be deduced that the materials with double helix structure possess the chirality property. In 1953, the double helical structure of deoxyribonucleic acid (DNA) was discovered by Watson and Crick [1]. Since then, researchers began to synthesize some materials with DNA-like double helix structures. The prepared materials possess the chirality property and specific double-helicity structures similar with DNA. More importantly, the prepared double helical materials have the advantages of good chemical and thermal stability and flexible functional groups, which are favorable for further applications. Up to now, researchers have prepared some materials with double-helicity structure. Firstly, the artificial double-stranded DNAs were successfully built from metal-mediated base pairs, exhibiting better thermal stability than DNAs [2–4]. After that, few inorganic double helical materials were designed and synthesized, such as double-helical carbon nanotubes [5,6], double-helical nitrogen-doped carbon nanotubes [7], double-helical silicon microtubes [8], double-helical SnIP [9] and double-helical Au-Ag alloy nanowire [10]. The prepared inorganic double helical materials exhibit good mechanical stability. More recently, organic-inorganic hybrid material homochiral metal organic frameworks (HMOFs) with unique DNA like double-helicity structure and intrinsic chirality were successfully fabricated, which both possess the characteristics of MOFs and the DNA like double-helicity structure [11,12]. Moreover, the preparation process of the HMOFs is relatively simple. Considering the described characteristics above, the DNA like HMOFs should be effective candidates for enantioseparation.

Capillary electrochromatography (CEC), a hybrid technique that combines the high selectivity of high performance liquid chromatography (HPLC) with the high efficiency of capillary electrophoresis (CE) system, is a powerful enantioseparation technique. DNA, owing to its intrinsic chirality, has been utilized as chiral stationary phase for CEC enantioseparation [13]. Though good enantioseparation has been achieved by using DNA as CEC chi-

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https://doi.org/10.1016/j.chroma.2018.02.015
0021-9673/

ral stationary phase, the existing of some problems such as easy denaturation limits its further applications in enantioseparation in a certain degree. Therefore, choosing an artificial material which both possesses DNA-like double-helicity structure and good chemical stability for CEC enantioseparation will be a good choice.

Homochiral metal-organic frameworks (HMOFs), a novel class of organic-inorganic hybrid materials built from clusters or chains of metal ions and organic ligands, have attracted increasing attention in enantioseparation fields in recent years. For example, various HMOFs have been explored as stationary phases for high performance liquid chromatography (HPLC) [14–18] and gas chromatography (GC) enantioseparation [19–23]. Besides, HMOFs have also been revealed to be promising stationary phase for CEC enantioseparation recently [24–29]. For example, Yuan et al. developed a dynamic coating method to fabricate chiral MOF $[Zn_2(D\text{-}Cam)_2(4,4'\text{-}bpy)]_n$ as chiral stationary phase (CSP) for open tubular capillary electrochromatography (OT-CEC) separation of chiral drugs and positional isomers [24]. Our groups also prepared a homochiral MOF AlaZnCl coated capillary column [26] and a homochiral MOF $[Zn(s\text{-}nip)_2]_n$ coated capillary column [27] by using in situ fabrication approach and applied them in the OT-CEC enantioseparation of monoamine neurotransmitters. Although HMOFs have a few applications in OT-CEC enantioseparation, the flexible structures and specific properties of HMOFs promote researchers to further explore the applications of HMOFs in enantioseparation. Therefore, fabricating functional HMOFs with specific structures as CSPs for OT-CEC enantioseparation will be a prospective field.

Homochiral zeolite-like metal-organic framework (ZMOF) JLU-Liu23, which was prepared from achiral precursors, is an attractive homochiral ZMOF with specific DNA-like double-helicity structure and permanent chiral porosity [11]. The homochiral ZMOF JLU-Liu23 encloses two interpenetrated chiral structures: (i) a chiral three-periodic zeolitic framework composed of four-connected $[Cu_4I_4]$ clusters bridged by 1,4-diazabicy-clo[2.2.2]-octane (dabco) ligands and formulated as $[Cu_4I_4(dabco)_2]_n$, and (ii) a chiral DNA-like double-helical chain based on Cu(I) ions linked by 1,3-bis(2-benzimidazol)-benzene (H_2bbimb) ligands and formulated as$[Cu_2(bbimb)]_n$. In addition, the synthesis process of the JLU-Liu23 is not complicated and the required organic ligands can be bought directly without further modification. The unique DNA-like double-helicity structure, chirality property, permanent porosity and relatively simple synthesis process of the homochiral ZMOF JLU-Liu23 make it an attractive candidate for enantioseparation.

Herein, the possibility of homochiral ZMOF JLU-Liu23 used for enantioseparation was investigated by utilizing JLU-Liu23 as chiral stationary phase for OT-CEC. As neurotransmitters play a crucial role in control and regulation of a variety of functions in central and peripheral nervous system [30], three monoamine neurotransmitters epinephrine, isoprenaline and synephrine and their analogue terbutaline were used as model analytes to evaluate the enantioseparation ability of the homochiral ZMOF JLU-Liu23 coated capillary column. The enantioseparation conditions such as the composition of buffer solution and the concentration of the coating material JLU-Liu23 were optimized. Furthermore, the stability and reproducibility of the prepared homochiral ZMOF JLU-Liu23 coated capillary columns were also investigated.

2. Experimental section

2.1. Chemicals and materials

NaOH and HCl were obtained from Chengdu Kelong Chemical Co., Ltd. (Chengdu, China). Methanol, ethanol, N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO) and HNO_3 were commercially available from Tianjin Guangfu Co., Ltd. (Tianjin, China). 1,3-bis(2-benzimidazol)benzene, CuI, tetramisole hydrochloride, 2-hydroxy-2-phenylacetophenone, verapamil hydrochloride, trans-stilbene oxide, norepinephrine and 1,4-diazabicyclo[2.2.2]-octane were purchased from ENERGY CHEMICAL Co. Ltd. (Shanghai, China). Borate was purchased from Xi'an Chemical Plant (Xi'an, China). Sodium silicate was available from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Isoprenaline and synephrine were bought from J&K Scientific LTD. (Beijing, China). Terbutaline and epinephrine were purchased from National Institutes for Food and Drug Control (Beijing, China). Chemical structures of the model analytes were shown in Fig. 1. Unless otherwise stated, all chemicals and reagents used were analytical grade and used without further purification. The ultrapure water used throughout the experiments was purified through an 18202V AXL water purification system (Chongqing, China).

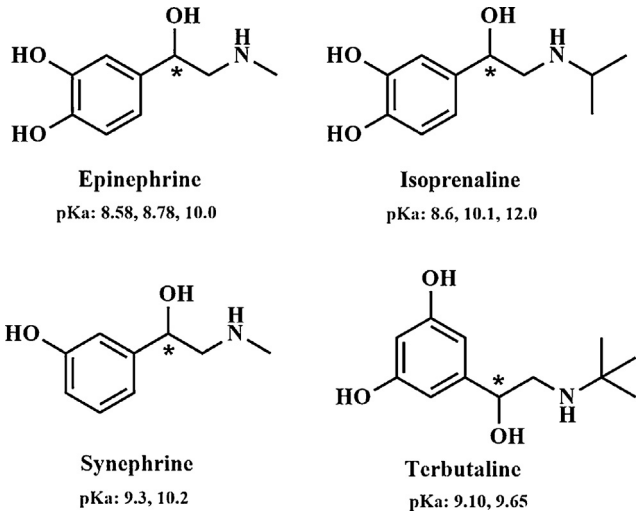

Fig. 1. Chemical structures of the four model analytes.

2.2. Apparatus and characterization

Scanning electron microscopy (SEM) images were recorded on a JSM-5600LV emission scanning electron microscope (JEOL, Japan). Powder X-ray diffraction (XRD) patterns were performed on a D/max 82400 X-ray powder diffractometer (Rigaku, Japan) with Cu Kα radiation (λ = 0.154056 nm). Transmission electron microscopy (TEM) images were recorded on a Tecnai G2F30 instrument (Hitachi, Japan). Thermogravimetric analysis curve was measured on a STA PT1600 instrument (Linseis, German). Circular dichroism (CD) spectra were recorded on a JASCO J-815 spectropolarimeter (JASCO, Japan).

2.3. Synthesis of homochiral zeolite-like metal-organic framework JLU-Liu23

The homochiral ZMOF JLU-Liu23 was synthesized according to the literature[11]. Typically, a mixture of 1,3-bis(2-benzimidazol)benzene (0.003 g, 0.01 mmol), CuI (0.008 g, 0.04 mmol), 1,4-diazabicyclo[2.2.2]-octane(0.01 g, 0.089 mmol), HNO_3 (2.7 M in DMF) and DMF (0.75 mL) was sealed in a 20 mL vial, heated at 105 °C for 12 h, and then cooled to room temperature. The yellow block crystals were collected, washed with DMF and dried in a vacuum oven.

The synthesized homochiral ZMOF JLU-Liu23 was dispersed in methanol and 10 mM borate buffer at room temperature for 24 h, respectively. Then the suspensions were centrifuged at 10000 rpm

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