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Monolithic column incorporated with lanthanide metal-organic framework for capillary electrochromatography

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ABSTRACT

A new lanthanide metal-organic frameworks NKU-1 have successfully incorporated into poly (BMA-co-EDMA) monolith and evaluated by capillary electrochromatography (CEC). Lanthanide metal-organic frameworks [Eu₂(ABTC)_{1.5}(H₂O)₃(DMA)] (NKU-1) were synthesized by self-assembly of Eu(III) ions and 3,3',5,5'-azo benzene tetracarboxylic acid ligands have been fabricated into poly(BMA-co-EDMA) monoliths. 1-Butyl-3-methylimidazolium tetrafluoroborate and *N,N*-dimethylformamide were developed as binary porogen obtaining homogeneous dispersibility for NKU-1 and high permeability for monolithic column. The successful incorporation of NKU-1 into poly(BMA-co-EDMA) was confirmed and characterized by FT-IR spectra, scanning electron microscopy, X-ray diffraction, energy dispersive spectrometer area scanning, and transmission electron microscopy. Separation ability of the NKU-1-poly (BMA-co-EDMA) monoliths was demonstrated by separating four groups of analytes in CEC, including alkylbenzenes, polycyclic aromatic hydrocarbon, aniline series and naphthyl substitutes. Compared with bare monolithic (column efficiency of 100,000 plates/m), the NKU-1-poly (BMA-co-EDMA) monoliths have displayed greater column efficiency (maximum 210,000 plates/m) and higher permeability, as well as less peak tailing. The results showed that the NKU-1-poly (BMA-co-EDMA) monoliths are promising stationary phases for CEC separations.

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1. Introduction

Monolithic columns prepared by in situ polymerization have extensively been found in various applications in gas or liquid chromatography due to high resolution, low-cost preparation, long service life, good stability and other advantages. Up to date, the polymer-based monoliths exhibit obvious merits in separation of large organic molecules with outstanding column efficiency. In contrast, separation of small molecules in ordinary polymer monoliths is difficult owing to intricate morphology, small specific surface area as well as lacking of mesopores and adequate interaction sites. Improving separation performance by incorporation nano materials into polymer monolith is a valid manner for small molecules due to increased surface area of the polymer monolith. For example,

graphene oxide (GO) [1], carbon nanotube (CNT) [2] and C60-fullerene [3] have been incorporated into polymer monoliths.

Metal-organic frameworks (MOFs) are attractive crystalline solids constructed from chains or clusters of inorganic metal ions connected by organic ligands due to exceptional artistic architectures and potential applications, e.g., catalysis [4], molecular recognition [5], gas storage [6], and sensors [7]. Syntheses of MOFs can be used in the separation area and have become one of the hot topic due to their outstanding merits, such as versatile framework composition, high specific surface areas, size-controllable pores and apertures [8–10]. As a new family of mesoporous materials, MOF (such as MIL-53(Al) [Al(OH)(BDC)(H₂BDC)_{0.7}] [11], MIL-101(Cr) [Cr₃F(H₂O)O(BDC)₃-nH₂O] [12], HKUST-1 [Cu₃(BTC)₂(H₂O)₃] [13])-organic polymer monolithic columns have been fabricated for HPLC, CLC and CEC. Combination of MOFs and organic polymer exhibited additional advantages of large specific surface area, sufficient mesoporous and high permeability. Specially, MOFs-polymer monolithic column has shown excellent separation in small organic molecule with high column efficiency and enhancing resolution.

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Compared with transition ions used mostly in MOFs, lanthanide (Ln) ions have higher affinity for donor atoms and ligands including oxygen as well as hybrid oxygen-nitrogen atoms, in particular multicarboxylate ligands [14]. The carboxyl group oxygen atoms in multicarboxylate ligands could adopt various binding modes and geometrical configurations to provide unique structures in the construction of coordination polymers. What's more, lanthanide ions have higher coordination numbers and connectivities than transition metal ions, which are favorable to stabilize the frameworks. In addition, the lanthanide ions hold unique optical, electron, and magnetic properties arising from 4f electrons [15,16]. Ln-MOFs are characterized with better dispersive property, thus they combine easily with small molecules with no loss in intrigue framework architectures and topologies.

By our knowledge, Ln-MOFs-incorporated monolithic column has not been reported. Among lanthanide ions, Eu^{3+} is one of the most essential luminescent centers [17,18]. In the present study, a new 3D metal-organic frameworks $[\text{Eu}_2(\text{ABTC})_{1.5}(\text{H}_2\text{O})_3(\text{DMA})]$ (NKU-1) were synthesized by self-assembly of Eu(III) ions and aromatic multicarboxylate ligands 3,3',5,5'-azo benzene tetracarboxylic acid (ABTC) under solvothermal reaction conditions. Afterwards, NKU-1 was employed as doping materials to prepare an organic-inorganic hybrid stationary phase. Binary porogen, a mixture of 1-butyl-3-methylimidazolium tetrafluoroborate and *N,N*-dimethylformamide was developed to allow homogeneous dispersibility of NKU-1 and form monolithic column incorporated with Ln-MOFs with high permeability. Four kinds of small organic molecules, alkylbenzenes, polycyclic aromatic hydrocarbon (PAHs), aniline series and naphthyl substitutes, were used as analytes to investigate the separation ability of the resulting NKU-1-poly (BMA-co-EDMA) monolith in CEC modes.

2. Experimental

2.1. Reagents and chemicals

All reagents and chemicals used in experiment were at least analytical grade. Acetone, toluene and *N,N*-dimethylformamide (DMF) were from Jiangtian Chemical Reagent (Tianjin, China). Acetophenone, butyrophenone, 2,5-dihydroxyacetophenone, butylbenzene and ethylbenzene were obtained from Alfa Aesar (Tianjin, China). Propylbenzene naphthalene, fluorene, anthracene and 2,2-azobis (2-isobutyronitrile) (AIBN) were purchased from J&K Scientific Co. Ltd. (Beijing, China). Acenaphthylene, fluoranthene, pyrene, benzo(a)anthracene, benzo(b)fluoranthene, acetanilide, 4-fluoroaniline, 2-nitroaniline, 1-naphthylamine, 1-naphthol, 1-methylnaphthalene, 1-choronaphthalele, 1-bromonaphthalele were purchased from Aladdin (Shanghai, China). Butyl methacrylate (BMA) was from Tianjin Bodi Chemical (Tianjin, China). 2-Acrylamido-2-methyl-1-propanesulfonic acid (AMPS) and ethylene glycol dimethacrylate (EDMA) were obtained from Sigma-Aldrich (St. Louis, MO, USA). 1-Butyl-3-methylimidazolium tetrafluoroborate ($[\text{BMIM}]\text{BF}_4$) was purchased from Shanghai Chengjie Chemical Reagent (Shanghai, China). 3-(Trimethoxysilyl) propyl methacrylate (γ -MPS) was obtained from Acros (Geel, Belgium). Acetonitrile (ACN, HPLC grade) was purchased from Fisher (Fair Lawn, NJ, USA). Bare fused-silica capillaries with 100 μm I.D. and 375 μm O.D. were obtained from Xinnuo Optic Fiber Plant (Hebei, China).

2.2. Synthesis of NKU-1

Metal-organic framework NKU-1 was synthesized by hydrothermal method. Typically, $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.2 mmol), H_4ABTC (0.1 mmol) were dissolved in 8 mL of dimethylacetamide

Table 1

Porogen composition and metal-organic frameworks content for preparing NKU-1-poly(BMA-co-EDMA) monoliths.

Column	[BMIM]BF ₄ (μL)	DMF (μL)	NKU-1 (wt/wt%)
1	86	10	10
2	76	20	10
3	66	30	10
4	56	40	10
5	46	50	10
6	36	60	10
7	26	70	10
8	46 ^a	50	10
9	46 ^b	50	10
10	46 ^c	50	10
11	46	50	5
12	46	50	20

^a The amount of 1-hexyl-3-methylimidazolium tetrafluoroborate, $[\text{HMIM}]\text{BF}_4$.

^b The amount of 1-octyl-3-methylimidazolium tetrafluoroborate, $[\text{OMIM}]\text{BF}_4$.

^c The amount of 1-decyl-3-methylimidazolium tetrafluoroborate, $[\text{DMIM}]\text{BF}_4$.

(DMA), 4 mL of H_2O and 0.8 mL HNO_3 in 25 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and placed in an oven at 130 °C for 48 h, then cooled down to room temperature. The resultant orange crystals were washed with water via centrifugation-redispersion cycles to remove the unreacted H_4ABTC from NKU-1 pores. The product was dried at 150 °C in vacuum for 12 h. Then NKU-1 was characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and nitrogen adsorption/desorption isotherm (Fig. S1).

2.3. Preparation of NKU-1-poly (BMA-co-EDMA) monolithic columns

A bare fused-silica capillary was rinsed with 1 mol/L NaOH followed by water for at least 30 min. Next, a 0.4% (v/v) solution of γ -MPS in 0.006 mol/L acetic acid solution was pumped through the capillary for at least 1.5 h. After silanization modification by γ -MPS, the capillary was rinsed with acetone, dried in a steam of nitrogen, and left at room temperature overnight.

Pre-polymerization mixture was composed of $[\text{BMIM}]\text{BF}_4$, *N,N*-dimethylformamide, BMA (15 μL , functional monomers), EDMA (4.5 μL , cross-linking monomers), 1% (wt/wt%) AIBN (radical initiator) and 1% (wt/wt%) AMPS (electroosmotic flow provider) (Table 1). After purged with nitrogen for 5 min, metal-organic frameworks NKU-1 were then added into the pre-polymerization mixture and sonicated for another 15 min to suspend homogeneously and remove oxygen before introduced into the pre-treated capillaries. Both ends of the capillary were sealed with rubber septum before putted into water bath. Following polymerization at 63 °C for 30 min, the resulting monolithic column was rinsed with acetonitrile before CEC analysis. A detection window was fabricated by burning 2–3 mm segment of the polyimide outer coating at a distance of 9 cm from the outlet of monolith. The corresponding reference capillary was prepared in the absence of NKU-1.

2.4. Capillary electrochromatography

CEC was carried out on a K1050 system of capillary electrophoresis (Kaiao, Beijing, China) equipped with ultraviolet detector and CXT-3000 chromatographic workstation. The total length of the capillary was 41 cm and effective length (stationary phase) was 32 cm. The sample was introduced hydrodynamically for 3.0 s with 20 cm height difference between inlet and outlet. The electrolyte was composed of different ratios of ACN and sodium acetate buffer solution. All the buffers were prepared with buffer composed of acetic acid and sodium acetate (HPLC grade), and filtered with

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