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Complete List of Authors:	Matsubara, Keigo; Kyoto University, Watabe, Yoshiyuki; Research Center, Shimadzu General Service, Inc K-Yamada, Sayaka; Kyoto Prefectural University Hosono, Nobuhiko; The University of Tokyo, Applied Chemistry Uemura, Takashi; The University of Tokyo, Applied Chemistry Kubo, Takuya; Kyoto Prefectural University, ; Kyoto University,

Metal-organic frameworks (MOFs) based separation columns: fundamental study for molecular recognitions and potential for separation of linear polymers with close terminal structure

Keigo Matsubara,[1] Yoshiyuki Watabe,[2,3] Sayaka Konishi-Yamada,[2] Nobuhiko Hosono,[4] Takashi Uemura,[4] Takuya Kubo*,[1,2]

[1] *Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan*

[2] *Graduate School of Life and Environmental Science, Kyoto Prefectural University, 1-5 Shimogamo Hangi-cho, Sakyo-ku, Kyoto 606-8522, Japan*

[3] *Research Center, Shimadzu General Service, Inc, 1, Nishinokyo, Kuwabara-cho, Nakagyo-ku, Kyoto 604-8511, Japan*

[4] *Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, Tokyo 113-8654, Japan*

Corresponding author

Prof. Dr. Takuya Kubo

E-mail: tkubo@kpu.ac.jp

Tel: +81-75-703-5629

ABSTRACT

We report stationary phases using metal-organic frameworks (MOFs) composed of metal ions and organic ligands in HPLC. We mainly applied $[Zn_2(1,4\text{-ndc})_2ted]_n$ (ZnJAST4) (ndc: naphthalenedicarboxylate, ted: triethylenediamine) for the stationary phase. To inspect how metal ions and organic ligands affect retention behavior, three different types of MOF, $[Cu_2(1,4\text{-ndc})_2ted]_n$ (CuJAST4) substituted from zinc ions of ZnJAST4 to copper ions, $[Zn_2(1,4\text{-bdc})_2ted]_n$ (ZnJAST1) (bdc: benzenedicarboxylate) substituted from a part of naphthalene of ZnJAST4 to benzene, and ZnJAST4 were packed to columns, and then HPLC using benzene derivatives was conducted to evaluate the recognition ability toward functional groups and shapes of molecules using hexane as the mobile phase. The result revealed that the retention behavior depended on various factors such as halogen bonding, π stacking, molecular shapes, and molecular sizes.

Furthermore, to evaluate retention selectivity toward functional groups, HPLC analyses were conducted with a ZnJAST4 packed column in a mobile phase, *N,N*-dimethylformamide (DMF), using poly(ethylene glycol) (PEG) derivatives, which have different polar terminal groups, as analytes. The result showed that when the polarity was low, the retention to ZnJAST4 decreased, and the retention behavior was affected by the molecular weight of the PEG.

1. Introduction

In recent years, polymer chemistry has been remarkably developed, while synthesized macromolecules are mixtures having disorganized distributions of a molecular weight and unstable structures, which is one of the challenges in this field. Precise syntheses of macromolecules have been enthusiastically examined since living radical polymerization has been reported in 1990s.[1, 2] While the precise syntheses of macromolecules having single chemical compositions and their structures has not been artificially realized yet, they are easily generated *in vivo*.

Instead of precise synthesis, separation and purification methods are preferred to obtain synthesized single polymers because these methods enable to efficiently obtain target single polymers in bulk. Methods such as distillation, recrystallization, and extraction for purification of low-molecular weight compounds are not applicable for separation of macromolecules. Chemical compositions and structures of a macromolecule are mostly the same, and slight difference of chemical structures hardly affect properties of a whole molecule, so that single polymers cannot be isolated.

Against this background, one study posed the possibility that metal-organic frameworks (MOFs) can be helpful as precise molecular recognition sites for polymers.[3] MOFs are coordination polymers composed of metal ions and organic ligands, having appealing properties: the pore size and chemical structures inside of pores can be freely designed by changing combination of metal ions and organic ligands, which is different from existing porous materials.[4-6] Because of these features, MOFs are of great interest to apply for preservation and separation of gas molecules,[7-9] catalyst of reactions[10-12] and sensors.[13-15] In addition, they have been submitted to the use of optical analysis of gas not involving crystal structures and liquid molecules.[16] Recent studies have revealed that linear polymers such as poly(ethylene glycol)s (PEGs), linear alkynes, and polythiophenes are spontaneously introduced in the pores of MOFs.[17]

MOFs are promising candidates as separation media for polymers since the study has reported that poly(ethylene glycol)s (PEGs) are installed in the pores of MOF. To date, size exclusion separations based on various types of terminal functional groups of PEG by designing the size of a pore[18, 19] and separations based on linear PEG and cyclic PEG[20] have been reported.

According to these studies, applications of MOFs have drawn attention as separations media in liquid phase. Some researches have shown separations based on various terminal functional groups of PEG chains[18] and liquid phase separations based on various PEG shapes[21], and that in HPLC separations[22], MOF modified silica monolith capillary columns involve superior separation efficiency to traditional MOF crystal particle packed columns[23], which are clearly inferior to the conventional HPLC columns.

In this study, we explored molecular recognition ability using MOF as a stationary phase in liquid phase and better separation efficiency of MOF columns.

2. Materials and methods

2.1 Synthesis of MOFs and their column packing

To examine molecular recognition when MOF was applied to the stationary phase in HPLC, two types of MOF besides ZnJAST4, CuJAST4, ZnJAST1, were synthesized[24]. After observing with SEM, three types of MOF columns were fabricated by packing each MOF (Table 1). MOFs were fabricated following procedures: (i) Adding starting materials shown in Table 1 in a 100 mL eggplant flask and implementing sonification for 5 min, (ii) mixing at 120 °C for 48 h (When the temperature inside of the flask reached around 120 °C, it was sealed and heated.), (iii) After heating, washing with DMF and drying in vacuum. The amount of all the prepared MOFs were more than 3 g. Each MOF was observed with SEM, and then MOFs (about 500 mg) were wet-packed with DMF as a slurry solvent to columns of 100 mm×2.0 mm i.d. The wet packing was implemented under the following condition: 0-5 min: 200 kgf/cm^2, 5-15 min: 500 kgf/cm^2

Table 1. The composition of the components for MOFs.

	Metal	Acidic ligand	Basic ligand	Solvent
ZnJAST4	$Zn(NO_3)_2 \cdot 6H_2O$ (3.49 mmol)	1,4-Na (3.37 mmol)	TEDA (1.66 mmol)	DMF (40 mL)
CuJAST4	$Cu(CH_3COO)_2 \cdot H_2O$ (3.36 mmol)	1,4-Na (3.39 mmol)	TEDA (1.71 mmol)	DMF (40 mL)
ZnJAST1	$Zn(NO_3)_2 \cdot 6H_2O$ (3.36 mmol)	1,4-Be (3.41 mmol)	TEDA (1.71 mmol)	DMF (40 mL)

(1,4-Na): 1,4-Naphthalenedicarboxylic acid, (1,4-Be): 1,4-benzenedicarboxylic acid, (TEDA): triethylenediamine

2.2 HPLC evaluations with MOFs packed columns

The retention behavior in the mobile phase, hexane, was analyzed with the column fabricated in 2.3 using monosubstituted benzenes as analytes. The retention coefficient k was evaluated as elution time of hexane, t_0 and retention time of analyte, t_R. $\underline{k = (t_R - t_0) / t_0}$

HPLC conditions: column: ZnJAST4 (100 mm×2.0 mm i.d.), CuJAST4 (100 mm×2.0 mm i.d.), ZnJAST1 (100 mm×2.0 mm i.d.), mobile phase: hexane, flow rate: 0.2 mL/min (ZnJAST4, ZnJAAST1), 0.1 mL/min (CuJAST4), temperature: 40 ˚C, injection volume: 5 μL, detection: UV (254 nm).

2.3 Elution behavior in the ZnJAST4 column with etherified terminal of PEGs

We examined elution behavior of PEG ethers with various numbers of alkyl carbons in the ZnJAST4 column using *N, N*-dimethylformamide (DMF) as a mobile phase. MeO-PEG-OH (*M*n=2000), single-end type of analytes (mPEG-OR) synthesized from MeO-PEG-OH (*M*n=2000), and dual-end type of analytes (RO-PEG-OR) synthesized from mPEG-OR were utilized.[18] ZnJAST4 was packed in a column, and elution behavior of either etherified or not etherified terminal PEGs in the mobile phase, DMF, was evaluated. HPLC conditions were follows; column: ZnJAST4 packed column, injection volume of analytes: 5 μL, measurement temperature: 25, 40, 60 °C, flow rate: 0.2 mL/min, detector: evaporate light scattering detector for HPLC. As analytes, etherified terminal of PEGs (mPEGOCOR, R = methyl, ethyl, and butyl) were simply synthesized from PEG monomethyl ether (mPEGOH) (*M*n=2000). The detailed procedures are described in Supporting Information (Scheme S1, Table S1).[17]

2.4 Elution behavior of esterified terminal of PEGs in the ZnJAST4 column

We conducted analyses using mPEGOH and preparative purified mPEGOCOBu as analytes in the ZnJAST4 crystal packed column. HPLC conditions are below; column: ZnJAST4 (100 mm × 2.0 mmm i.d.), mobile phase: DMF, flow rate: 0.2 mL/min, temperature: 40 ˚C, detection: RI, injection volume of analytes: 10 μL, analytes: mPEGOH (raw material). mPEGOCOR (10 mg/mL each)

3. Results and discussion

3.1 Synthesis of MOFs and their column packing

Fig. 1 shows the SEM of obtained crystals after synthesis, revealing that the particle size of CuJAST4 was smaller than that of ZnJAST4 and ZnJAST1. After packing them to HPLC column, the back pressure was measured. Since back pressure of CuJAST4 column was higher than the others, the flow rate for further evaluations of CuJAST4 column was reduced to half compared to others in HPLC.

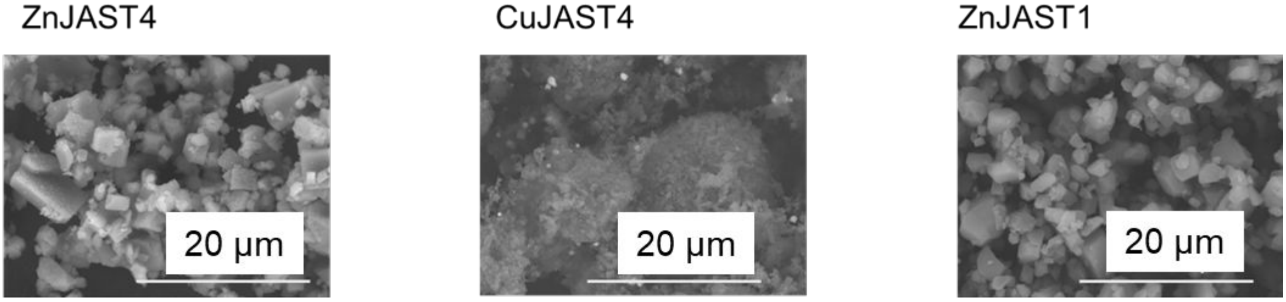

Fig. 1. The SEM of the prepared MOFs crystals.

3.2 Evaluation of the retention behavior of monosubstituted benzenes

Table S2 shows the retention coefficient, *k* of monosubstituted benzenes with each column. Strong retention was observed with the all columns when using nitrobenzene. This is because carboxyl groups in the ligand of the MOF structures and nitro groups have similar electronic property and, temporarily nitro groups are grabbed into the MOF structure.

The elution order of analytes showed the resembling trend and the retention of halogen became stronger in order of the atomic number with ZnJAST4 and CuJAST4, while the different trend was observed and the retention of bromine was largest with ZnJAST1. Additionally, NO_2 substituted benzene was strongly retained in all the MOFs. In these results, although the detailed interaction modes were not evaluated, several interactions including dipole-dipole, halogen bonding, π stacking, and size effect were contributed.[25] In any case, molecular recognition in MOF might be affected more by difference of acid ligands and their pore sizes than that of metallic ions.

3.3 Evaluation of the retention behavior of alkylbenzenes on MOF columns

The retention coefficient, *k* of alkylbenzenes with each column was plotted toward the carbon number of alkyl chains (0: benzene) as shown in Fig. 2 (a). The elution order of ZuJAST4 and CuJAST4 showed similar trend; as the carbon number increased, the retention became longer. ZnJAST1 showed different trend from them; the retention of toluene and ethylbenzene were comparatively large but as the carbon number increased, the retention became smaller. According to these results, while insertion of the alkyl chain into the pore occurred in the structure of JAST4, the pore size may be too large to stabilize the alkyl chain inside of the pore in the structure of JAST1 in hexane. The consideration is corresponding to the size of the MOFs, which was previously reported (Fig. 2 (b)).[18, 26] The repeated length of the structure itself is almost the same in ZnJAST4 and ZnJAST1, but due to steric hindrance of the acidic ligands, the pore diameters of the voids in the MOF structure are significantly different, at 5.7 Å and 7.5 Å, respectively.

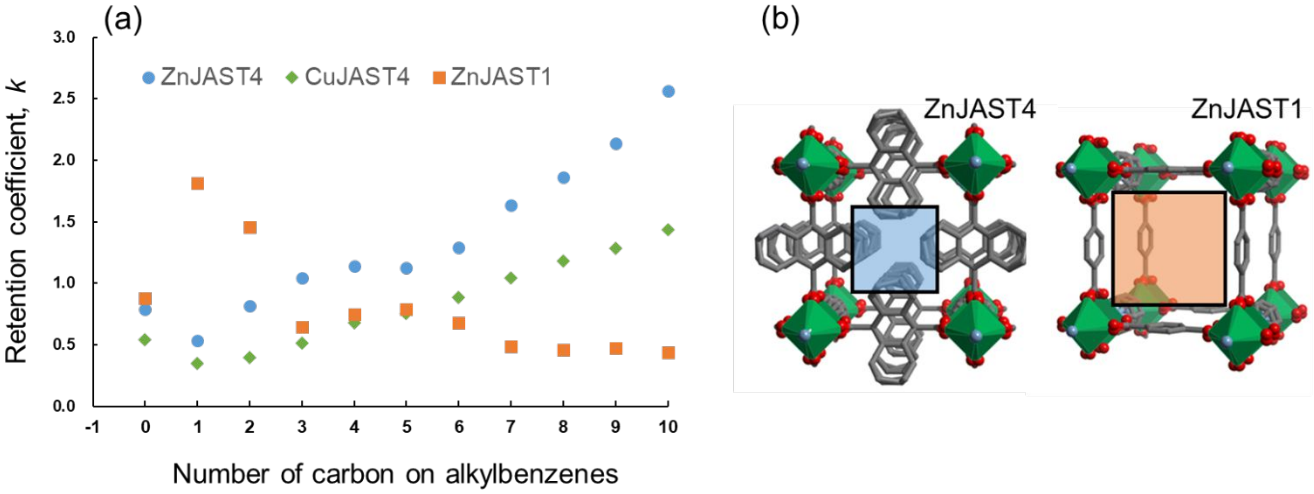

Fig. 2. (a) The retention behavior of alkylbenzene with the MOF column, and (b) schematic structures of ZnJAST4 and ZnJAST1

3.4 Evaluation of the retention behavior of disubstituted benzenes

Table 2 shows the retention coefficient, *k* of disubstituted benzenes with each column. The analytes at *ortho* position tended to be retained stronger in JAST4. ZnJAST1 showed higher retention toward the analytes at *para* position was mostly high, but there were a number of exceptions such as Br and I. The strong retention of dinitrobenzene was observed with each column; especially the retentions at *ortho* and *para* position was stronger. The retention of terphenyl was strongest at *para* position with the all columns. This may be correlated to how easily insertion into the pore occurs. Fig. S1 shows the chromatograms of ZnJAST4 and ZnJAST1 when using divinylbenzene (mixture of *ortho*, *meta*, and *para*) as an analyte. Three peaks were observed with both of them, while the elution orders were different because of the peak shapes. When chloroform was added to hexane as mobile phase, the retention of most analytes decreased. In the case of a halogen substitution, thus, halogen bond may contribute to the retention to MOF. However, in the case of a nitro group substitution, the elution orders were back and forth, that is, inexplicable behavior was observed. Regarding this phenomenon, further study is required.

Table 2. The retention coefficient of disubstituted benzene in the mobile phase, hexane

	position	ZnJAST 4	CuJAST 4	ZnJAST 1		position	ZnJAST 4	CuJAST 4	ZnJAST 1
CH_3	*ortho*	0.35	0.27	4.97	F	*ortho*	1.14	0.73	0.99
	meta	0.35	0.23	1.65		*meta*	0.90	0.53	1.12
	para	0.43	0.27	1.79		*para*	1.76	0.71	4.11
C_2H_5	*ortho*	0.38	0.22	8.33	Cl	*ortho*	0.99	0.69	7.43
	meta	0.87	0.38	.045		*meta*	0.78	0.48	3.63
	para	1.33	0.63	.041		*para*	2.21	0.69	12.7
OCH_3	*ortho*	3.98	1.58	18.2	Br	*ortho*	1.35	0.91	17.6
	meta	2.34	1.25	5.90		*meta*	1.34	0.76	17.6
	para	3.81	1.34	7.98		*para*	3.43	1.17	11.4
OC_2H_5	*ortho*	1.96	1.30	2.16	I	*ortho*	2.17	1.48	21.4
	meta	2.05	1.04	1.19		*meta*	3.01	1.86	3.46
	para	3.89	1.44	1.24		*para*	6.13	2.70	3.22
NO_2	*ortho*	26.4	9.67	109	Phenyl	*ortho*	0.02	0.03	0.32
	meta	18.2	7.94	53.7		*meta*	5.09	1.47	0.83
	para	29.9	16.6	94.8		*para*	30.3	5.01	14.2

3.5 Evaluation of retention behavior of polysubstituted benzenes

Table S3 shows the retention coefficient, *k* of polysubstituted benzenes, more than tri-substitution, with each column. 1,3,5-trihalogenated benzenes were barely retained. This can be explained that halogen bonding effectively works for 1,3,5-trihalogenated benzenes but hydrogen bonding and π stacking mainly work for dihalogenated benzens described in our previous study.[25, 27] Besides, the retention of Br substitution was larger than that of other halogens.

It proposes that ZnJAST1 should specifically retain to bromine. With the ZnJAST4 column, the retention coefficient of hexamethylbenzene and hexaphenylbenzene was $k<0$, which may be influenced by size exclusion effect.

3.6 Evaluation of the retention behavior of PAHs

Table 3 shows the retention coefficient, *k* of PAHs with each column. Comparing benzene, naphthalene, anthracene, and naphthacene, all of them consist of linearly fused benzene rings, the retention became stronger in line with increase in the number of π electron. Comparing analytes having the same number of π electron, stronger retention was observed with ones having bent structures than with ones having linear structures. There should be thus another factor, such as polarity of analytes, affecting retention other than insertion to pores. Especially, in the case of ZnJAST1, corannulene, which is larger than the pore size, was strongly retained. This is because only corannulene involves high polarity vertically standing toward a curved structure.[28-30] When these analytes were measured in the mobile phase, toluene, using the ZnJAST4 and the ZnJAST1 columns, none of the analytes were retained with the ZnJAST4 column, and triphenylene and corannulene were slightly retained with the ZnJAST1. Therefore, the retention in the mobile phase, hexane, was affected by π electron, and certain molecular recognition toward bulky molecules may likely have occurred.

Table 3. The retention coefficient of PAHs in the mobile phase, hexane

Analyte	ZnJAST4	CuJAST4	ZnJAST1
benzene	0.84	0.55	0.88
naphthalene	1.72	1.00	3.75
acenaphthene	1.08	1.24	3.50
anthracene	6.09	2.15	5.07
phenanthrene	5.62	2.65	6.61
naphthacene	7.76	1.44	42.9
benz[a]anthracene	8.08	3.30	24.0
chrysene	3.61	0.82	46.7
triphenylene	0.09	0.12	13.8
o-terphenyl	0.02	0.03	0.32
o-terphenyl	5.09	1.47	0.83
o-terphenyl	30.3	5.01	14.2
pyrene	3.10	2.30	11.0
coronene	0.17	0.48	0.31
corannulene	0.67	0.38	73.8

3.7 Elution behavior of etherified terminal of PEGs in the ZnJAST4 column

Fig. 3 shows chromatograms of etherified terminal of PEGs at 25 °C, and elution times of each analyte are listed in Table S4. When the number of terminal alkyl chains in ether groups increased, retention time became longer. It suggests that the raised number of terminal carbons increases affinity with MOF. At the same time, retention time decreased by raising temperature (Fig. S2). This may be described that intensified molecular motion of PEG as temperature increased hampered interaction with MOF. In comparison with mPEG-OMe and MeO-PEG-OMe, the latter had longer retention time. As they involve the same terminal structures, this difference of the molecular weight may derive from starting materials. If reaction ideally progressed, the average molecular weight of single-end type of Me (Mn=2014) and dual-end type of Me (Mn=2078) would be different by 64 g/mol. The increased molecular weight, that is, the expanded repetitive structures of MOF increased affinity with MOF. This trend corresponds to previous study.[31]

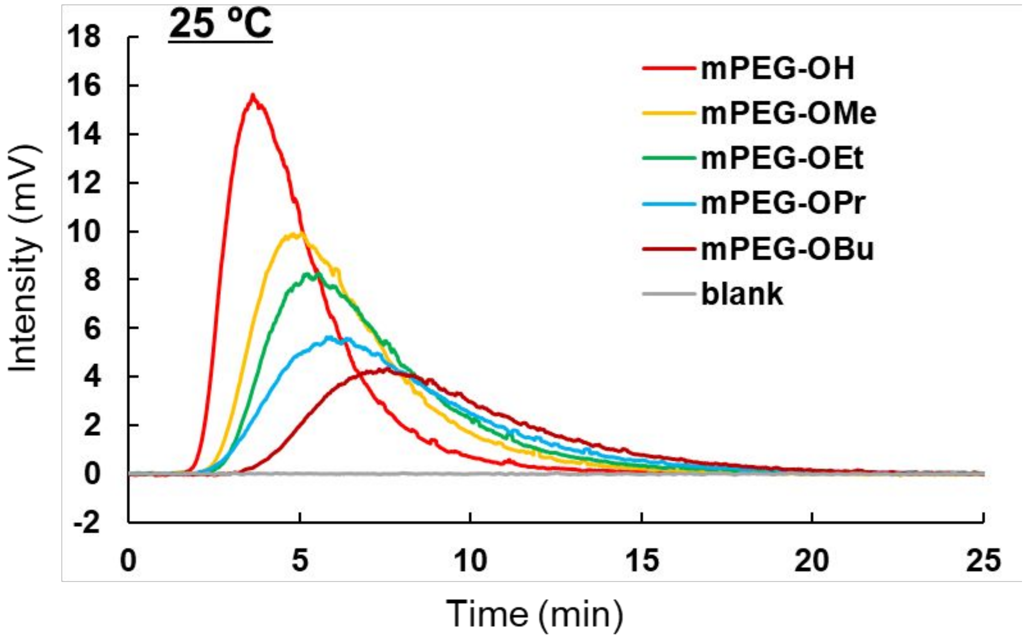

Fig. 3. Chromatograms of single-end type of analytes at 25 °C

3.8 Elution behavior of the esterified terminal of PEG using the ZnJAST4 column

The chromatograms shown in Fig. 4 indicates that the elution time of mPEGOCOBu increased compared with that of mPEGOH: each elution time was 2.96 min and 6.25 min, respectively. The separation factor (retention factor of mPEGOHOBu/retention factor of mPEGOH), $\alpha_{\text{mPEGOHOBu/mPEGOH}}$ was 2.73 as t_0=1.06 min, suggesting that affinity with ZnJAST4 increased due to low polarity caused by esterification of terminal groups and extended chain lengths.

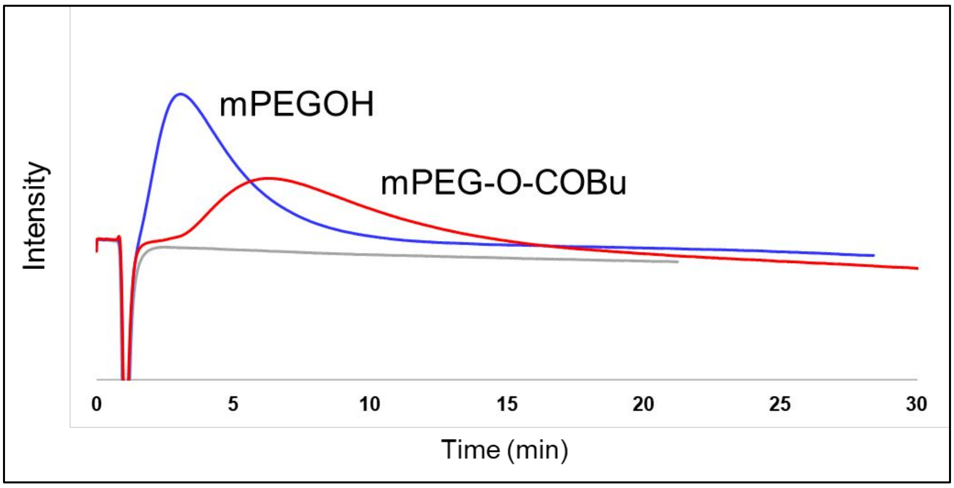

Fig. 4. Chromatograms of the esterified terminal of PEG using the ZnJAST4 column

4. Conclusion

In the first part, MOFs including ZnJAST4, CuJAST4, and ZnJAST1, which have different metallic ion and acidic ligand, were packed to the column, and benzene derivatives were analyzed. As a result, the retention behavior such as an authentic size exclusion chromatography was not observed, however, the gate size of MOF crystal was strongly contributed for the molecular recognition. Furthermore, the retention mechanisms conjugating hydrogen bonding, halogen bonding, π stacking, polarity, and size effect provided complicating separations. Additionally, in the second part, using PEGs with different end groups as samples, the possibility of separation based on terminal polarity and molecular weight was demonstrated. Further analysis for retention mechanisms may reveal correlation between the MOF structure and molecular recognition, which can make MOF effectively act toward substances hardly separated such as divinylbenzene and synthetic polymers

Author Contributions

All authors contributed to and have given approval for the final version of the manuscript. T. Kubo supervision, project administration, funding acquisition, conceptualization, methodology, writing-original draft, writing-review & editing; K. Matsubara, Y. Watabe, H. Hosono, T. Uemura conceptualization, data curation, formal analysis, S. K-Yamada writing-original draft, writing-review & editing.

Conflicts of interest

There are no conflicts to declare.

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KYOTO PREFECTURAL UNIVERSITY
Graduate School of Life and Environmental Science
1-5 Shimogamo Hangi-cho, Sakyo-ku, Kyoto 606-8522, Japan

Dr. Takuya KUBO
Professor
Analytical Chemistry of Functional Materials

Phone: +81-75-703-5629
E-mail: tkubo@kpu.ac.jp
(URL) https://kubo-lab-fmac.com/

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Data are available upon request from the authors.

Takuya KUBO, Ph.D