Supporting information

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

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Table of Contents

Chemicals

Unless otherwise specified, reagents were used as received.

Distilled Water, N,N-dimethylformamide (DMF), Dichloromethane, Trimethyl amine, Hydrochloric acid, Terephthalic acid, Chlorobenzene, Bromobenzene, Nitrobenzene, o-xylene, 1,2-dichlorobenzene, 1,3- dichlorobenzene, 1,2,4- trychlorobenzene, Naphthalene, Copper acetate (II) monohydrate and solvents including Methanol, Hexane, Chloroform, Toluene, 2-prooanol were purchased from Nacalai Tesque inc. (Kyoto, Japan). Propionyl chloride, Zinc nitrate hexahydrate, 1,4-Naphthalenedicarboxylic acid, Propylbenzene, 1-phenylpentane, 1-phenylhexane, 1-phenylheptane, 1-phenyloctane, 1-phenylnonane, 1-phenyldecane, anisole (methoxybenzene), iodobenzene, m-xylene, p-xylene, 1,2-diethylbenzene, 1,4-diethylbenzene, 1,4-dichlorobenzene, o-terphenyl, Pentafluorochlorobenzene, Pentafluorobromobenzene, Phenanthrene, and Benzene were Wako pure chemical industries, Ltd. (Osaka, Japan). Valeryl chloride, Butylbenzene, Phenetole (ethoxybenzene), Fluorobenzene, 1,3-diethylbenzen, 1,2-dimethoxybenzene, 1,3-dimethoxybenzen, 1,4-dimethoxybenzene, 1,2-diethoxybenzene, 1,3-diethoxybenzene, 1,4-diethoxybenzene, 1,2-difluorobenzene, 1,3-difluorobenzene 1,4-difluorobenzene, 1,2-difluorobenzene, 1,3-dibromobenzene, 1,4-dibromobenzene, 1,2-diiodobenzene, 1,3-diiodobenzene, 1,4-diiodobenzene, 1,4-dinitrobenzene, 1,2,3-trifluoromethylbenzene, 1,2,4-trifluoromethylbenzene, 1,3,5-trifluoromethylbenzene, 1,2,3-trichlorobenzene, 1,3,5-trichlorobenzen, 1,2,3-tribromobenzene, 1,2,4-tribromobenzene, 1,3,5-tribromobenzene, Hexafluorobenzene, Hexachlorobenzene, Hexabromobenzene, Pentafluoroiodobenzene, Anthracene, Naphthacene, Benz[a]anthracene, Chrysene (benzo[a]phenanthrene), Triphenylene, and Coronene were Tokyo chemical industry Co., Ltd. (Tokyo, Japan). Acetyl chloride, ethyl benzene, 1,2-dinitrobenzene, p-terphenyl, Hexaphenylbenzene, Pyrene, and 1,3-dinitrobenzen were Sigma-Aldrich Japan Co. (Tokyo, Japan). m-Terphenyl was Honeywell International Inc. (Charlotte, NC). 1,3,5-Triiodobenzene was Angene Co. (London, UK). Corannulene was Kanto Chemical Co. (Tokyo, Japan). m-PEG-OH (*M*w=2000) was from BroadPharm. (San Diego, CA). Column for HPLC was SHIMADZU VP-ODS (150×2.0 mm i.d.) Shimadzu Co. (Kyoto, Japan).

Instruments

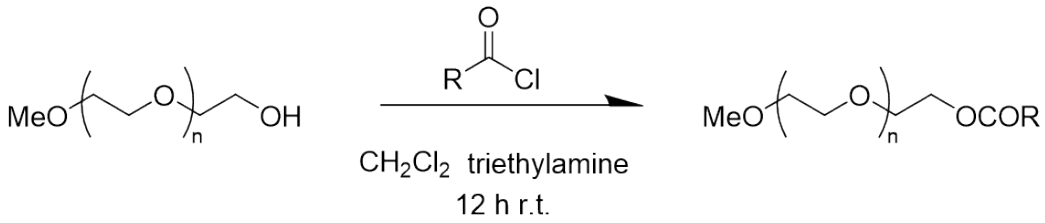
SEM: Miniscope TM-1000 (HITACHI), FT-IR: Nicolet iS5 ATR (Thermo Fisher Scientific Inc.), HPLC/MS consisted of pump: LC-30AD , column oven: CTO-20AC, MS: LCMS-8030 (SHIMADZU Co.). Or, Pump: LC-40B x3, Autosampler: SIL-40C x3, column oven: CTO-40S (SHIMADZU Co.), PDA: SPD-M40 (SHIMADZU Co.). For preparative separation, HPLC device consisted of Pump: LC-20AB, column oven: CTO-20A, RI: RI-104 (Shodex Co.).

Synthesis of esterified terminal of PEGs

Elution behavior of esterified terminal of PEGs assumes that retention may change depending on polar terminal groups. Thus, we synthesized the esterified terminal of PEGs, conducting the analysis using ZnJAST4 crystal packed columns. Synthesis of PEG esters was carried out based on the reference.[17] Scheme 1 shows the chemical reaction and the composition is shown in Table 2. Dichloromethane of 5 mL dissolved PEG monomethyl ether (mPEGOH) (*M*n=2000) and triethylamine was shaken in an ice bath, and dichloromethane of 5 mL dissolved various types of acyl chlorides was dropped. Then it was shaken for more than 12 h at room temperature. After quenching with water of 50 mL, extraction using dichloromethane (ca. 20 mL×3) was implemented. The obtained dichloromethane solution was washed with 10 mM HClaq (ca. 10 mL×3). The solvent was removed from the organic layer, and dried in a vacuum for a day. The synthesized analytes were qualitatively analyzed using FT-IR, HPLC-MS.

Purification of esterified terminal of PEGs

We attempted purification of crude products using an ODS column. Preparative purification was conducted using a SHIMADZU VP-ODS column as separation medium. Separation conditions are below; column: SHIMADZU VP-ODS (150 mm×4.6 mm i.d.), mobile phase: water/ethanol=35/65, temperature: 40 ˚C, detection: RI, analytes: mPEGOH (raw material), mPEGOCOR crude products (100 mg/mL each)



Scheme S1. Synthesis of mPEGOCOR

Table S1. Composition for synthesis of mPEGOCOR

mPEGOH (*M*w = 2000)	Triethylamine	RCOCl
1.0 g 0.50 mmol	348 μL, 2.5 mmol	R = Methy, 2.5 mmol
		R = Ethyl, 2.5 mmol
		R = Buthyl, 2.5 mmol

HPLC/MS conditions, column: N/A, mobile phase: MeOH, flow rate: 0.2 mL/min, temperature: 40 ˚C, Injection volume of analytes: 5 μL, detection: MS-TIC (positive, m/z=10-2000), Analyte: mPEGOH, three types of products (50 mg/L).

Table S2. The retention coefficient of monosubstituted benzenes in the mobile phase, hexane

	X =	ZnJAST4	CuJAST4	ZnJAST1
Ph-X	H	0.79	0.54	0.88
	CH_3	0.53	0.35	1.81
	C_2H_5	0.82	0.40	1.46
	OCH_3	1.64	0.82	2.60
	OC_2H_5	1.43	0.76	0.86
	F	0.97	0.59	1.27
	Cl	0.98	0.56	2.79
	Br	1.25	0.68	3.26
	I	1.91	1.05	2.72
	NO_2	6.67	3.22	8.79

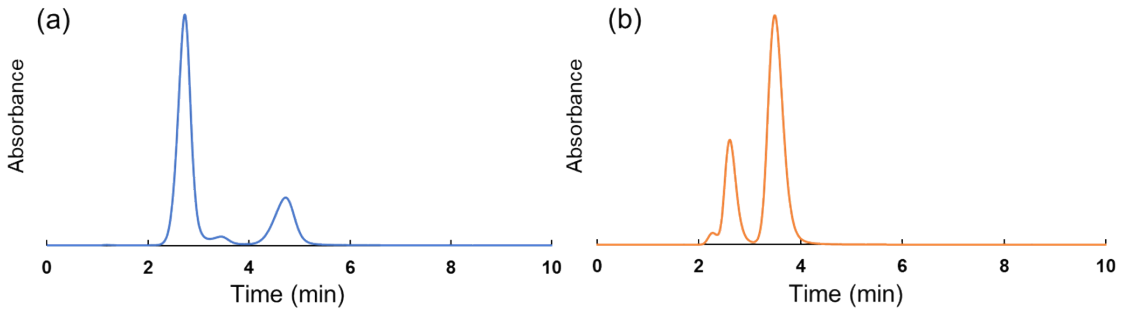


Fig. S1. The chromatograms of divinylbenzene in the mobile phase, hexane

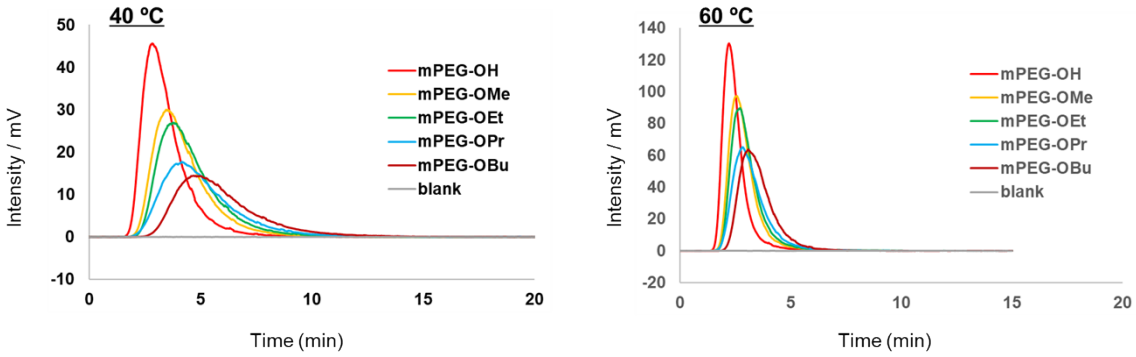
(a) ZnJAST4 column (b) ZnJAST1column

Table S3. The retention coefficient of polysubstituted benzenes in the mobile phase, hexane

3X	position	ZnJAST4	ZnJAST1	6X	ZnJAST4	ZnJAST1
F	1,3,5	0.58	0.77	5F1Cl	0.53	1.66
	1,2,3	1.28	0.98	5F1Br	0.50	1.95
	1,2,4	1.17	1.74	5F1I	0.86	2.89
Cl	1,3,5	0.19	2.16	6F	1.10	1.23
	1,2,3	1.35	14.7	6Cl	0.03	1.75
	1,2,4	0.90	6.03	6Br	0.30	17.5
Br	1,3,5	0.24	1.28	6CH3	------	0.73
	1,2,3	3.48	52.3	6Phenyl	------	0.56
	1,2,4	1.60	6.42			
I	1,3,5	0.20	0.47			

Table S4. Elution time of each analyte

analyte	(min)	analyte	(min)
t_0	1.47	mPEG-OH(60 ˚C)	2.22
mPEG-OH(25 ˚C)	3.74	mPEG-OMe(60 ˚C)	2.55
mPEG-OMe(25 ˚C)	4.98	mPEG-OEt(60 ˚C)	2.65
mPEG-OEt(25 ˚C)	5.40	mPEG-OPr(60 ˚C)	2.84
mPEG-OPr(25 ˚C)	5.75	mPEG-OBu(60 ˚C)	3.08
mPEG-OBu(25 ˚C)	7.46	HO-PEG-OH(60 ˚C)	2.14
HO-PEG-OH(25 ˚C)	3.36	MeO-PEG-OMe(60 ˚C)	2.78
MeO-PEG-OMe(25 ˚C)	6.00	EtO-PEG-OEt(60 ˚C)	3.04
mPEG-OH(40 ˚C)	2.84	PrO-PEG-OPr(60 ˚C)	3.60
mPEG-OMe(40 ˚C)	3.44	BuO-PEG-OBu(60 ˚C)	4.19
mPEG-OEt(40 ˚C)	3.76		
mPEG-OPr(40 ˚C)	4.10		
mPEG-OBu(40 ˚C)	4.82		
HO-PEG-OH(40 ˚C)	2.67		
MeO-PEG-OMe(40 ˚C)	4.09		



HPLLC condition
column, JAST4(100 mm × 2.0 mm i.d.); injection volume, 5 μL; mobile phase,DMF; temperature,25 ºC, 40 ºC, 60 ºC; detection, ELSD; flow rate, 0.2 mL/min

Fig. S2. Chromatograms of single-end type of analytes at 40 ºC and 60 ºC

Determination of synthesis of esterified terminal of PEGs

Crude products reacted acetyl chloride, propionyl chloride, and pentanoyl chloride were 939 mg (brownish yellow), 1053 mg (white), and 1099 mg (white), respectively. Fig. S3 shows the result of IR, and then the peak of each product appeared at around 1700 cm^{-1}, and before and after reactions, broad peak area at around 3500 cm^{-1} reduced. The peak at 1700 cm^{-1} and the reduced peak area were caused by stretches of C=O bond in the ester part and decreased OH groups by esterification, respectively. The peak of the starting materials, and the final products at around 2900 cm^{-1} derived from stretches of C-H bond included in PEG. Obvious difference of other peak positions was not observed. These IR results assume that esterification may be progressed.

Fig. S4 shows MS spectra, m/z value of 900-1100, obtained from the starting material and the final products. Repetitive structures representing the peaks at the equal distance of 22 with all analytes were observed. What we observed at around m/z = 1000 should be the protonated divalent ion since the average molecular weight of the starting material is 2000, and the molecular weight of PEG repeating units is 44 g/mol. The peak positions of the starting material and the final products were different. As to each product, the values of theoretical molecular weight similarly changed, and the same peaks of MS spectrum were obtained. It can conclude that reactions of three products progressed.

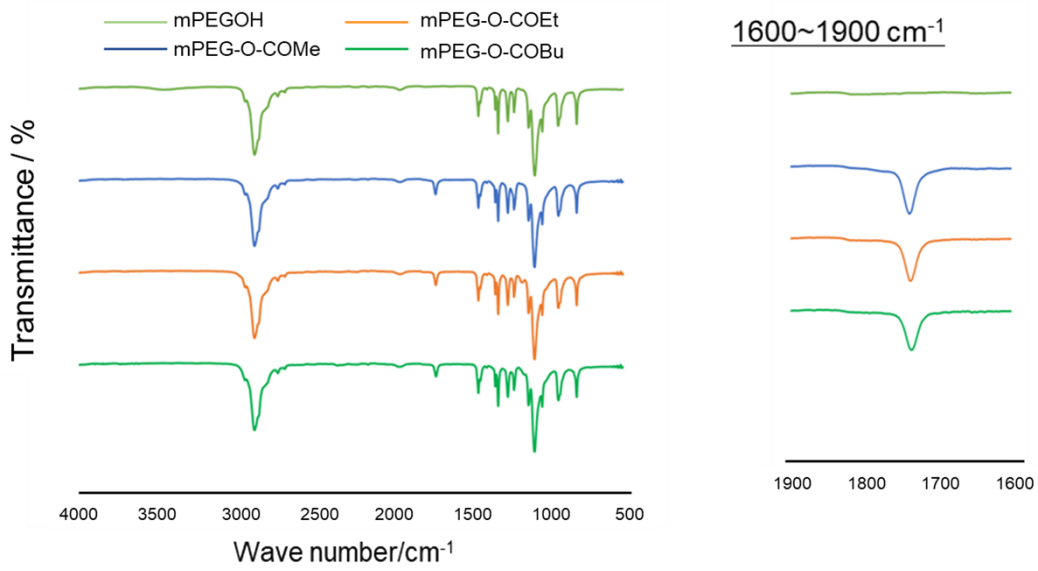


Fig. S3. IR spectra of the starting material and the final products

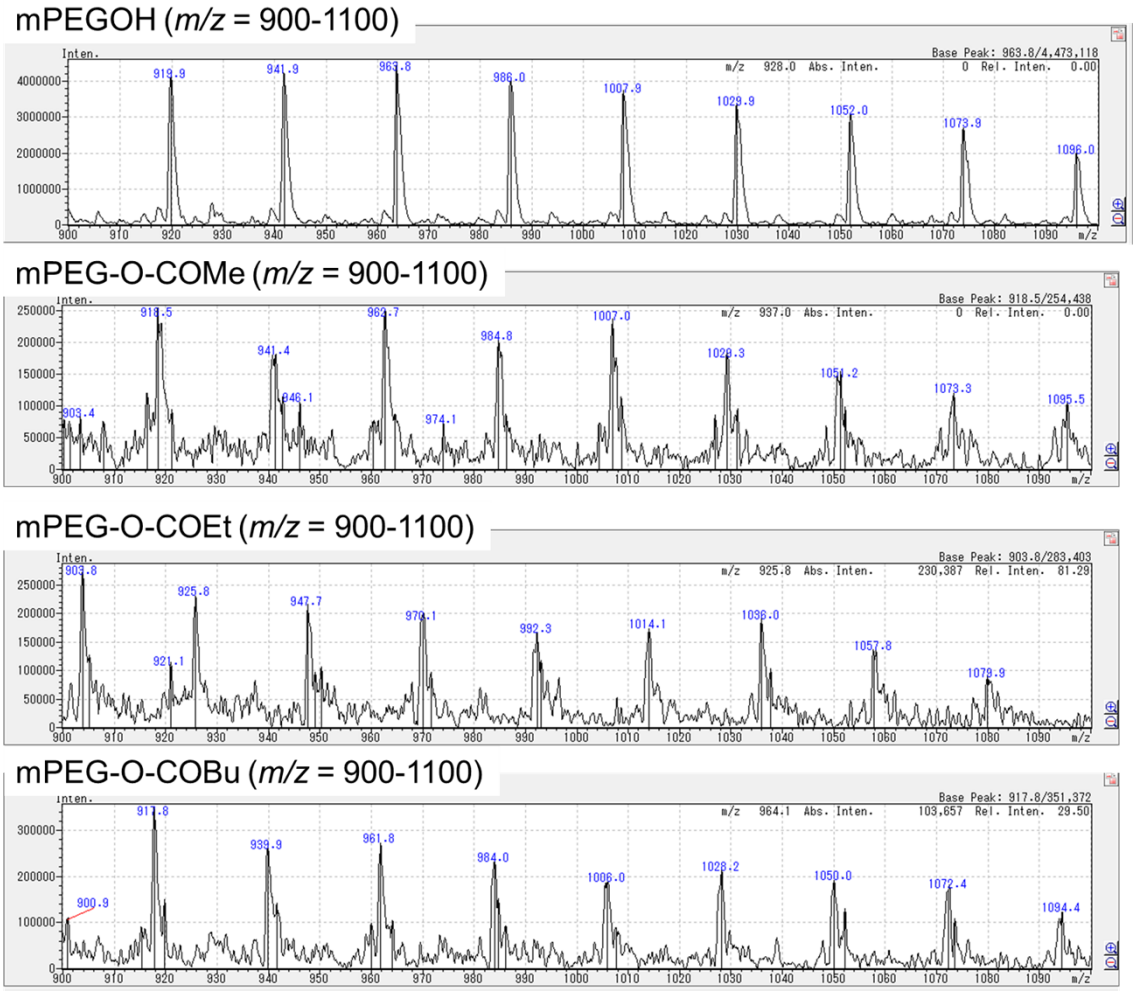


Fig. S4. MS spectra of the starting material and the final products (*m/z* = 900-1100).

Evaluation of esterified terminal of PEGs

Fig. S5 shows MS-TIC chromatograms using a SHIMADZU VP-ODS column as a separation medium, revealing that the starting material, mPEGOH, exists in each crude product. The modification of terminal ester increased hydrophobicity, and the retention became longer in the case of involving the larger number carbon of terminal ester. With the crude products of mPEG-O-COMe and -COEt, the peaks of the products, and the starting material overlapped. Given molecular-weight distribution of the starting material, mPEGOH, and that larger molecular weight provides higher hydrophobicity, the retentions of the starting product with large number of the molecular weight and the products with smaller number of the molecular weight are close. To apply as analytes for the MOF column, preparative purification of the mPEG-O-COMe, -COEt with ODS columns may be difficult to conduct due to distribution of the molecular weight affecting retention behavior. Therefore, mPEG-O-COBu

crude products were applied for considering preparative condition. Preparative conditions were determined as below in accordance to the obtained results. Preparative conditions; column: SHIMADZU VP-ODS (150 mm×4.6 mm i.d.), mobile phase: Water/Methanol= 35/65, flow rate: 1.0 mL/min, temperature: 40 ˚C, detection: RI, injection volume: 50 µL, analyte: mPEGOCOBu crude product 100 mg/mL, preparative time: 7.0-20.0 min. Fig. S6 (a) shows chromatograms during preparative separation. To obtain the ester as pure as possible, eluate was fractionated during 7.0 min and 20 min. The preparative separation was conducted 16 times, and the solvent was removed using an evaporator, dried in vacuum. The white solid of 53.1 mg was obtained as shown in Fig. S6 (b). As a result, the final yield was 57 %.

Fig. S7 (a) shows IR spectrum of the crude products, mPEGOH, mPEGOCOBu, and the isolated product. The peak of the separated analyte appeared at around 1700 cm^{-1} similar to that of the crude product, mPEGOCOBu. This peak corresponds to stretching vibration of C=O bonds of ester groups. Fig. S7 (b) shows chromatograms obtained from HPLC under the same conditions as the fractionation above. In isolated product, the peak of the starting materials observed in the crude products was not detected. Therefore, preparative purification of mPEGOCOBu was succeeded.

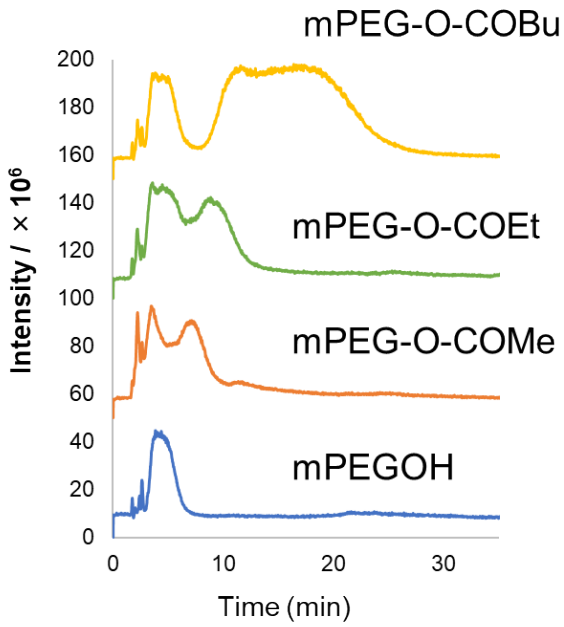


Fig. S5. MS-TIC analyzed each product using the ODS column

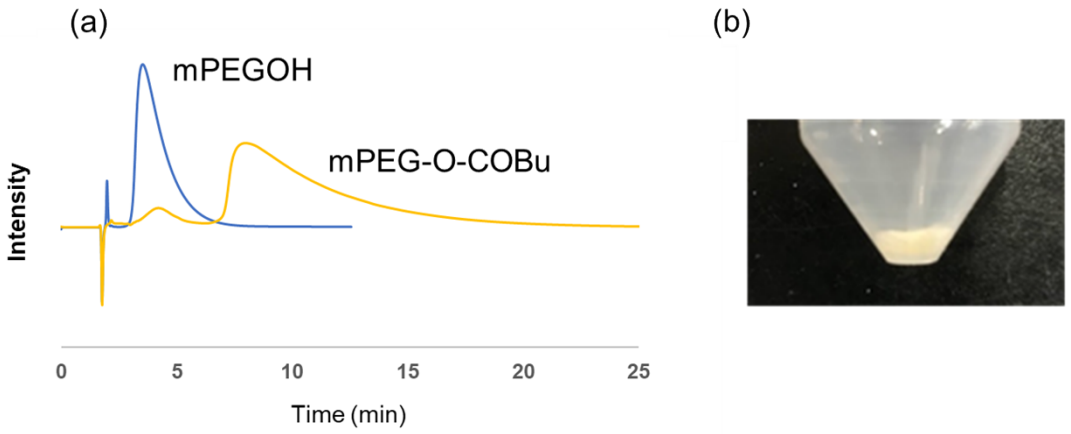


Fig. S6. (a) Chromatograms during preparative separation (b) Obtained white product after drying

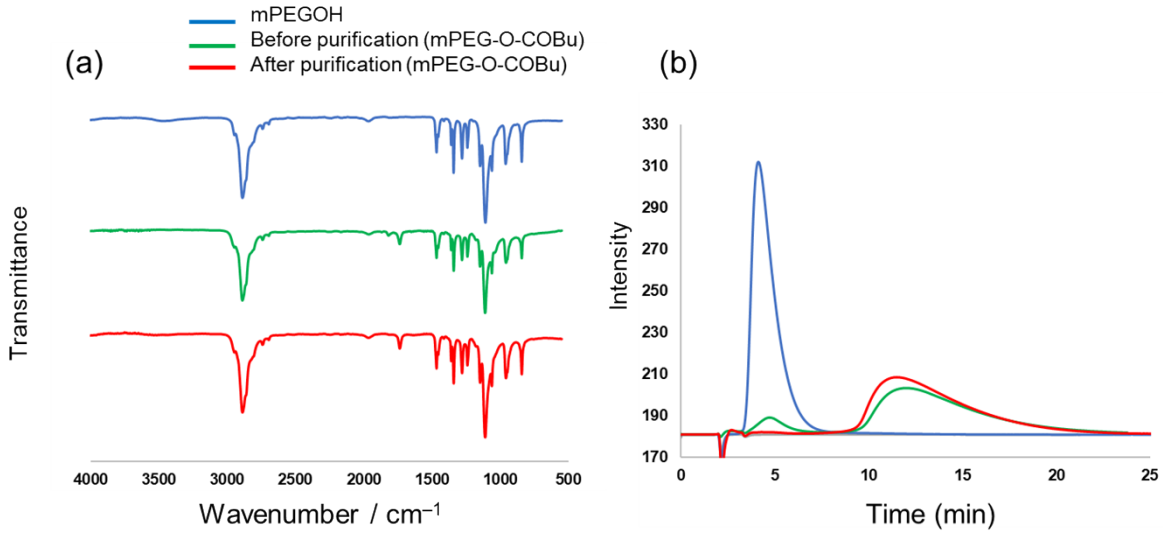


Fig. S7. (a) IR spectra of mPEGOH, mPEGOCOBu crude products and isolated products (b) Chromatograms analyzed them with an ODS column.