Supplementary Information for:

Synthesis of Macrocyclic Polyphenol Resin by Methylene Crosslinked Calix[4]arene (MC-[4]H) for The Adsorption of Palladium and Platinum Ions

Yoga Priastomo, Shintaro Morisada, Hidetaka Kawakita, Keisuke Ohto, and Jumina

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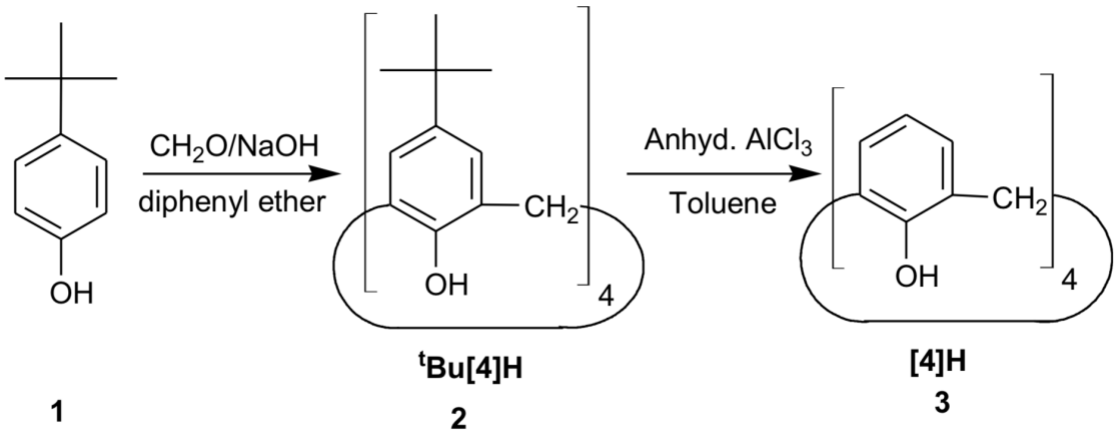


1 ^{t}Bu[4]H 2 [4]H 3

Scheme S1 The synthetic route of **3** ([4]H)

5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene(^{t}Bu[4]H) (2)

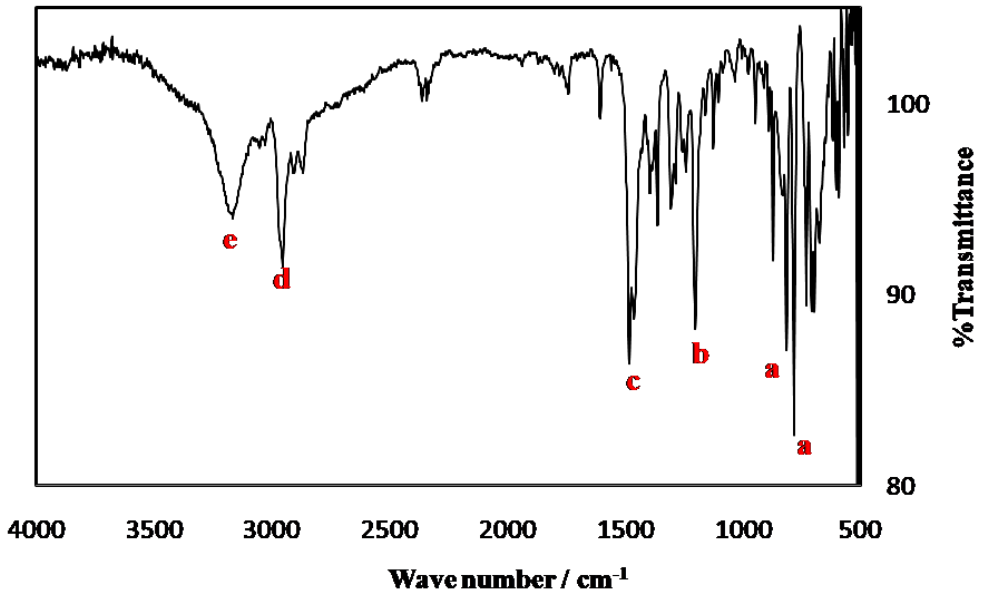


Figure S1 FT-IR spectra of ^{t}Bu[4]H (**2**)

Table S1 FT-IR interpretation of ^{t}Bu[4]H (**2**)

FT-IR	Wave number / cm^{-1}	Assignment
KBr	781 & 815	aromatic C-H (**a**)
	1201	methylene bridge CH_2 (**b**)
	1480	aromatic C=C (**c**)
	2956	alkyl C-H sp^3 (**d**)
	3192	O-H (**e**)

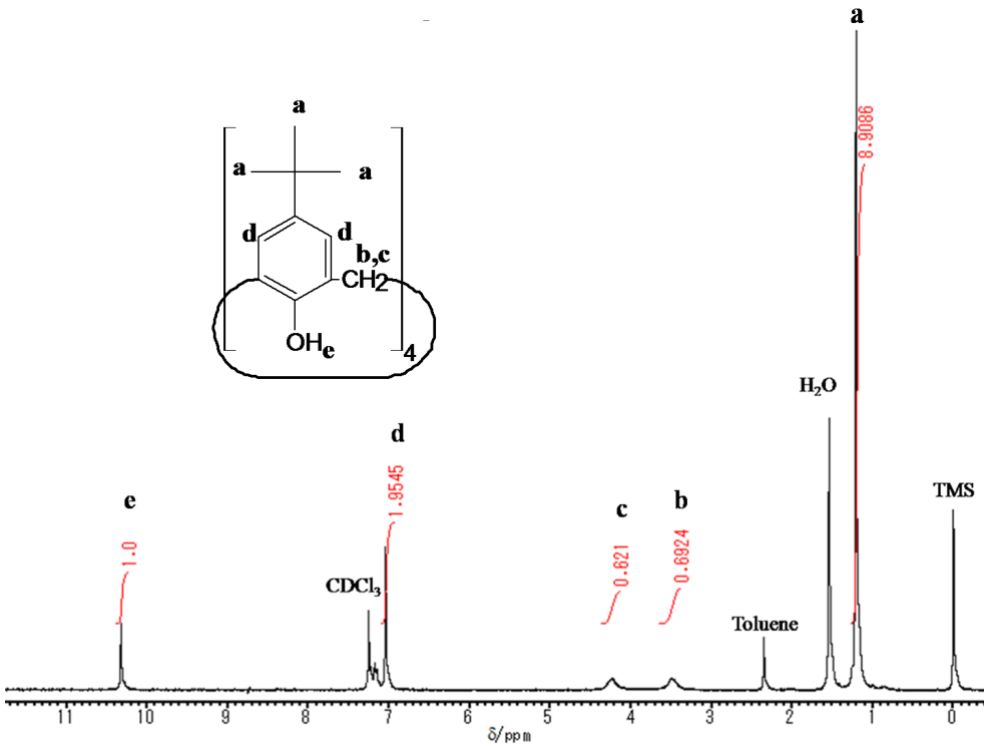


Figure S2 ^{1}H-NMR spectra of ^{t}Bu[4]H (**2**)

Table S2 ^{1}H-NMR interpretation of ^{t}Bu[4]H (**2**)

^{1}H-NMR	***δ*(ppm)**	**Assignment**	**Multiplicity**	**Integral ratio**
300 MHz	1.26	a	s	8.91 (36H)
$CDCl_3$	3.64	b	s	0.69 (4H)
TMS	4.34	c	s	0.62(4H)
	7.05	d	s	1.95 (8H)
	10.3	e	s	1.00 (4H)

25,26,27,28-tetrahydroxycalix[4]arene (3)

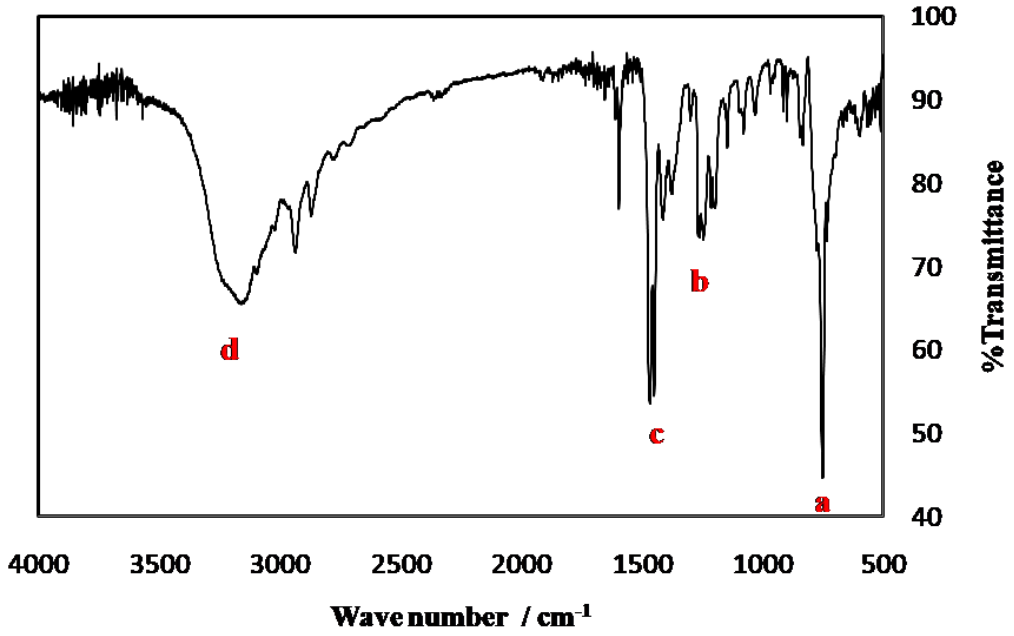


Figure S3 The FT-IR spectra of [4]H (**3**)

Table S3 FT-IR interpretation of [4]H (**3**)

FT-IR	Wave number / cm^{-1}	Assignment
KBr	751	aromatic C-H (**a**)
	1268	Methylene bridge CH_2 (**b**)
	1595	aromatic C=C (**c**)
	3208	O-H (**d**)

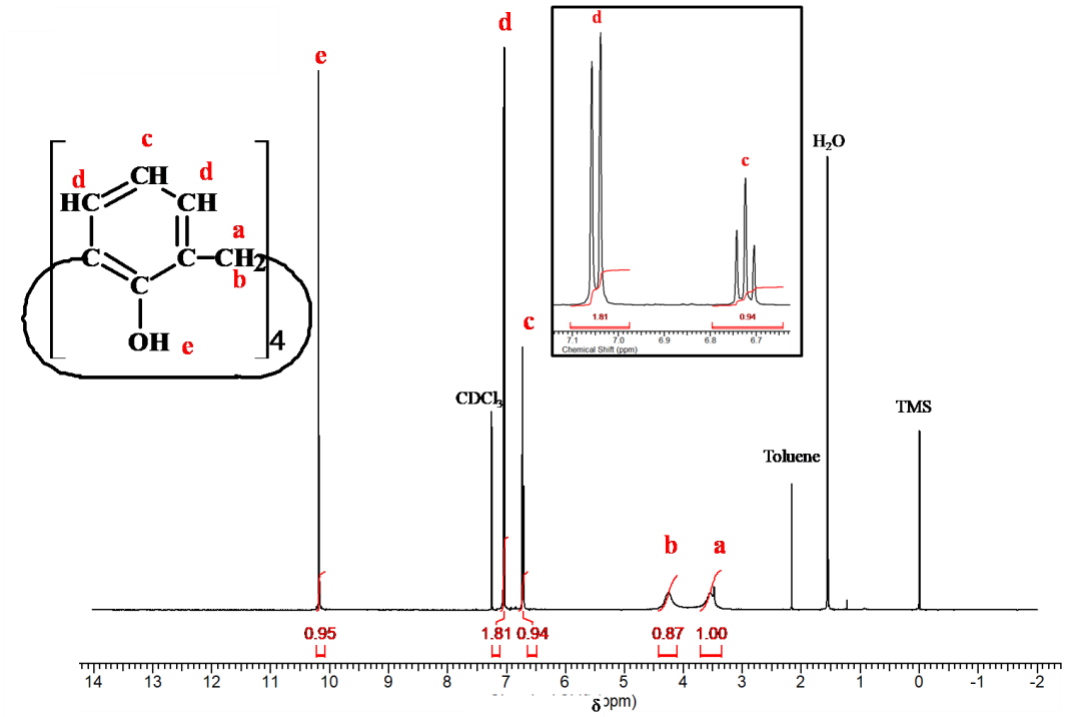


Figure S4 ^{1}H-NMR spectra of [4]H (**3**)

Table S4 ^{1}H-NMR interpretation of [4]H (**3**)

^{1}H-NMR	***δ*(ppm)**	**Assignment**	**Multiplicity**	***J* (Hz)**	**Integral ratio**
400 MHz $CDCl_3$ TMS	3.53	a	s	0	1.00 (4H)
	4.23	b	s	0	0.87 (4H)
	6.72	c	t	8.00 & 8.00	0.94 (4H)
	7.04	d	d	8.00	1.81 (8H)
	10.8	e	s	0	0.95 (4H)

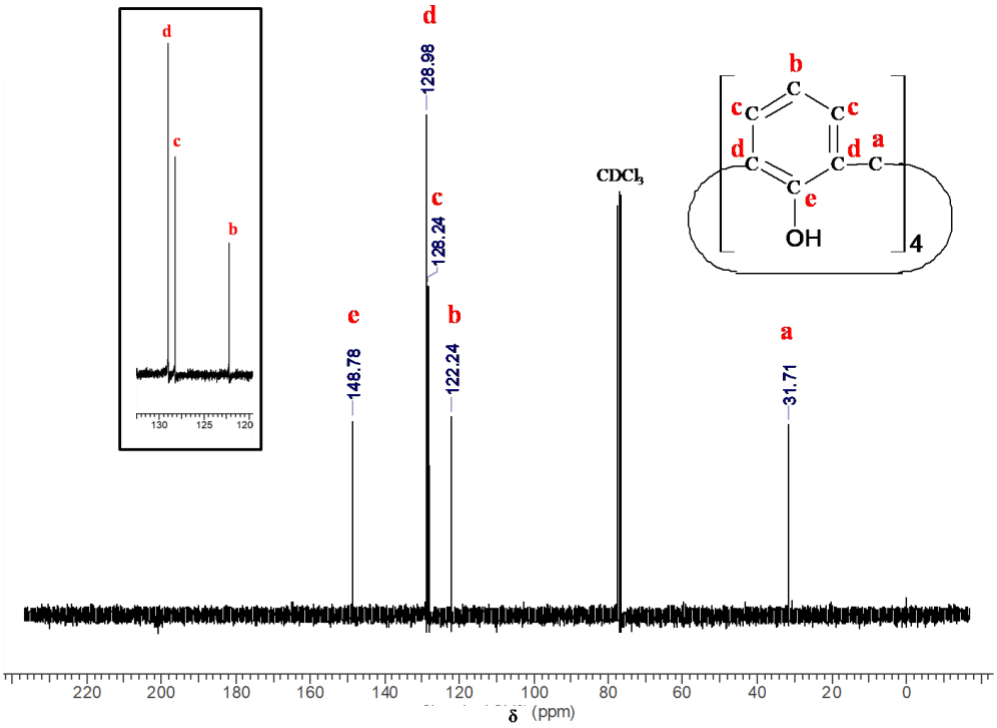


Figure S5 ^{13}C-NMR spectra of [4]H (**3**)

Table S5 ^{13}C-NMR interpretation of [4]H (**3**)

^{13}C-NMR	***δ*(ppm)**	**Assignment**
100 MHz $CDCl_3$ TMS	31.7	a
	122	b
	128	c
	129	d
	149	e

25,26,27,28-tetramethoxy calix[4]arene (4)

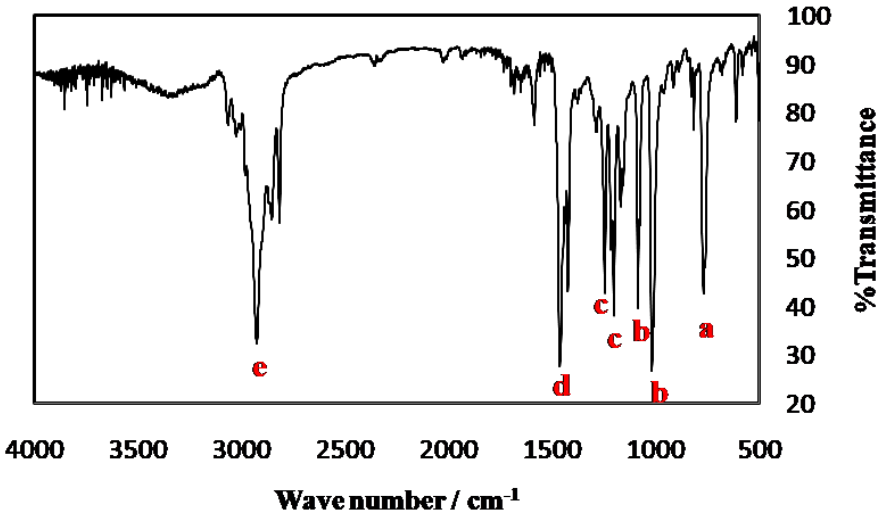


Figure S6 FT-IR spectra of [4]CH_3 (**4**)

Table S6 FT-IR interpretation of [4]CH_3 (**4**)

FT-IR	Wave number / cm^{-1}	Assignment
KBr	772	aromatic C-H (**a**)
	1022 & 1085	ether C-O (**b**)
	1204 & 1247	methylene bridge CH_2 (**c**)
	1466	aromatic C=C (**d**)
	2932	alkyl C-H sp^3 (**e**)

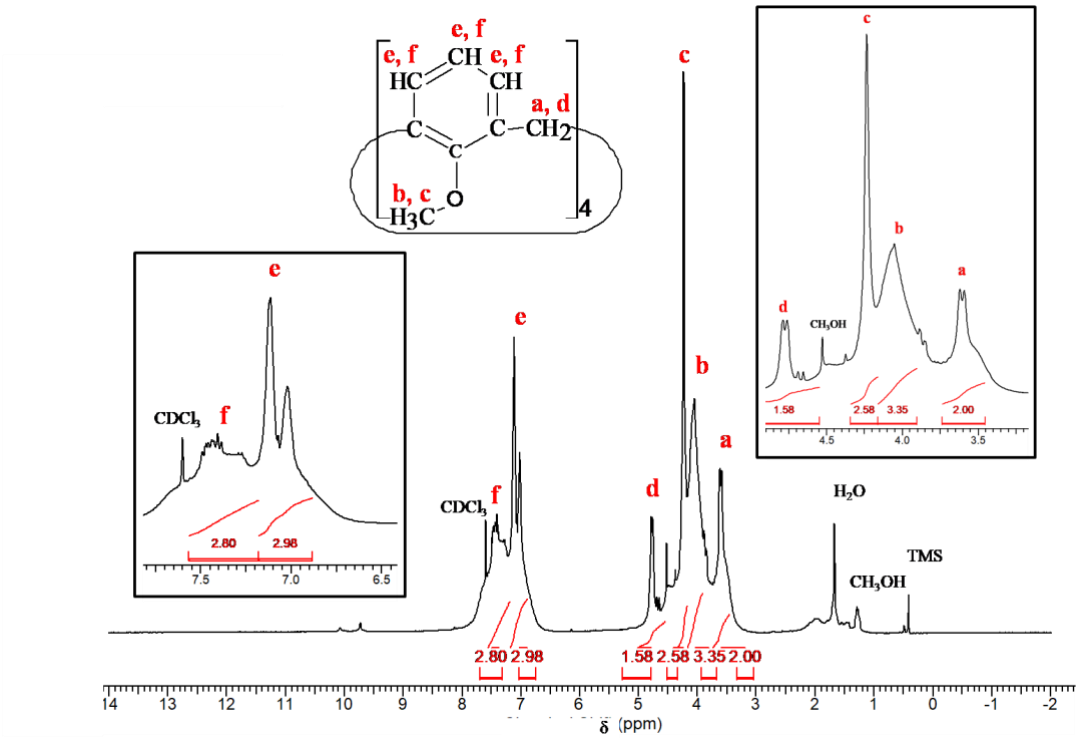


Figure S7 ^{1}H-NMR spectra of [4]CH_3 (**4**)

Table S7 ^{1}H-NMR interpretation of [4]CH_3 (**4**)

^{1}H-NMR	***δ*(ppm)**	**Assignment**	**Multiplicity**	**Integral ratio**
400 MHz	3.59	a	s	2.00 (4H)
$CDCl_3$	4.05	b	s	3.35 (6H)
TMS	4.24	c	s	2.58 (6H)
	4.79	d	s	1.58 (4H)
	7.12	e	d	2.98 (6H)
	7.41	f	m	2.80 (6H)

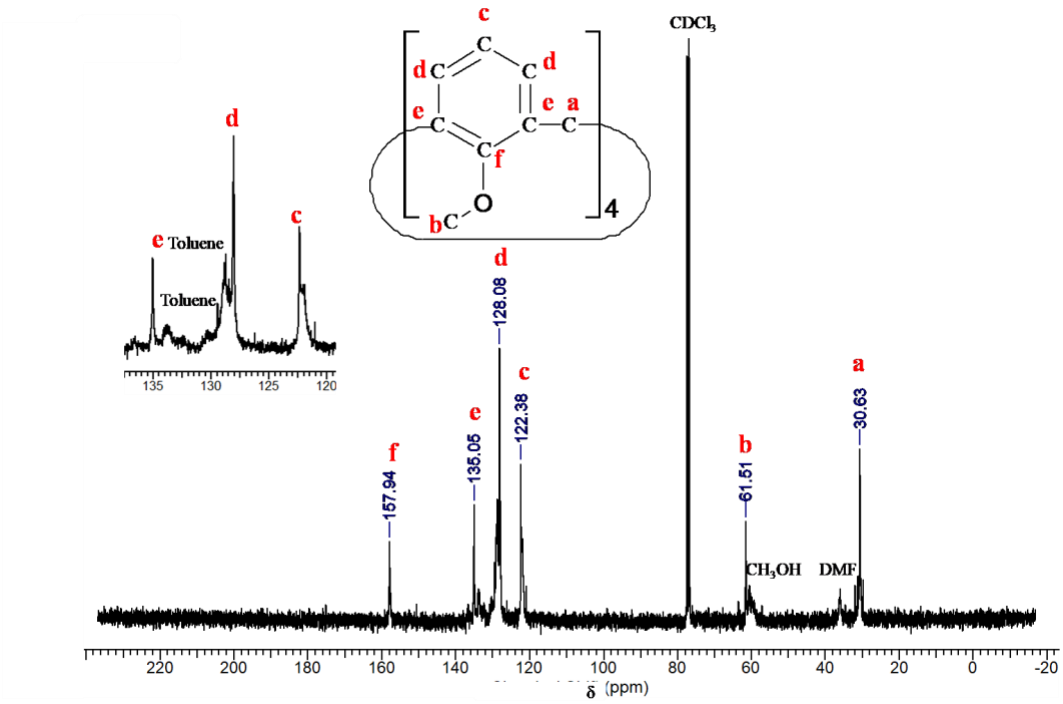


Figure S8 ^{13}C-NMR spectra of [4]CH_3 (**4**)

Table S8 ^{13}C-NMR interpretation of [4]CH_3 (**4**)

^{13}C-NMR	***δ*(ppm)**	**Assignment**
100 MHz $CDCl_3$ TMS	30.6	a
	61.5	b
	122	c
	128	d
	135	e
	158	f

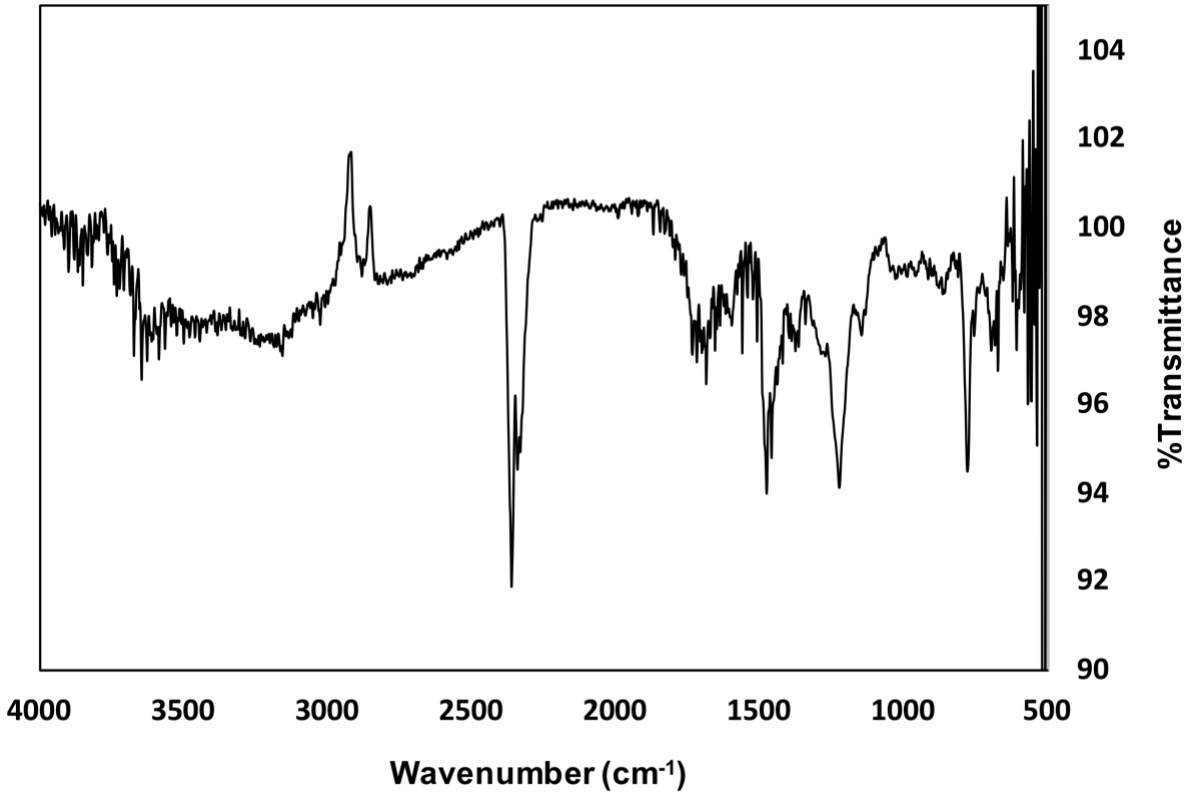
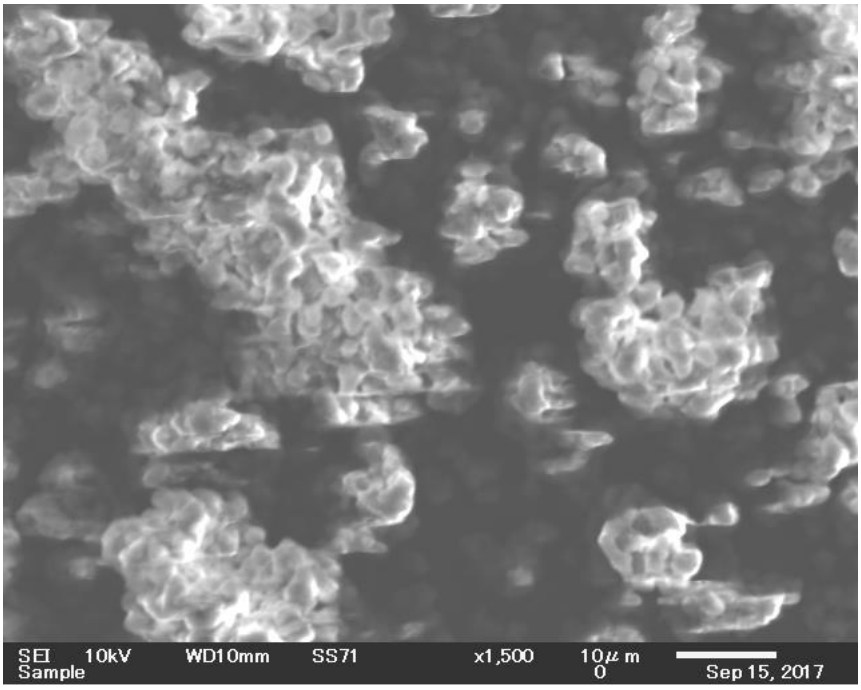
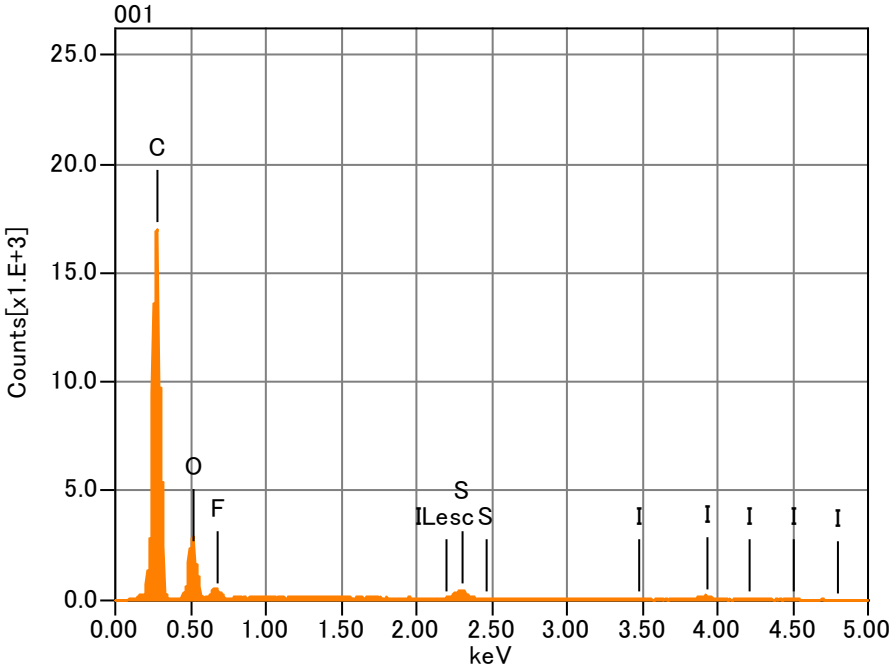


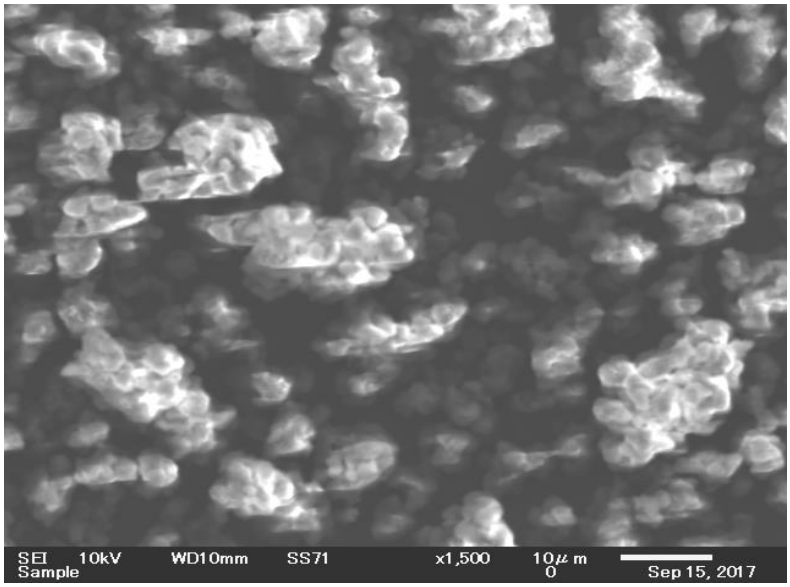
Figure S9 FT-IR Spectra of MC-[4]H (direct synthesis from **3** with *s*-trioxane)

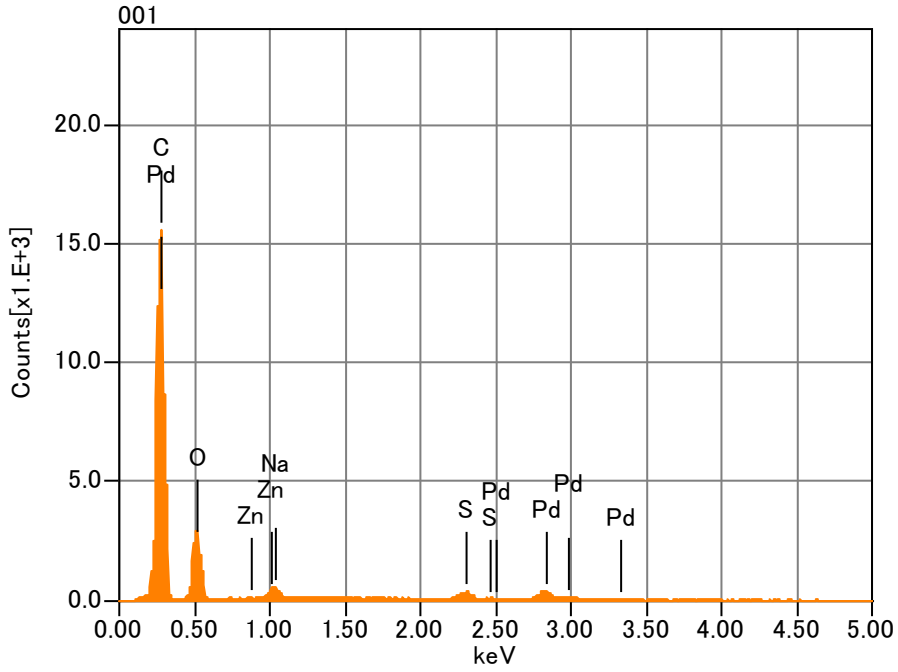




Chemical Formula	% Massa	% Atomic	σ	Integral intensity	Ratio K
C	74.20	84.29	0.02	434372	0.2090725
O	14.91	12.71	0.04	64916	0.0919040
F	2.05	1.47	0.03	10067	0.0248272
S	1.80	0.77	0.02	16155	0.0319447
I	7.05	0.76	0.12	14990	0.0993228
Total	100	100			

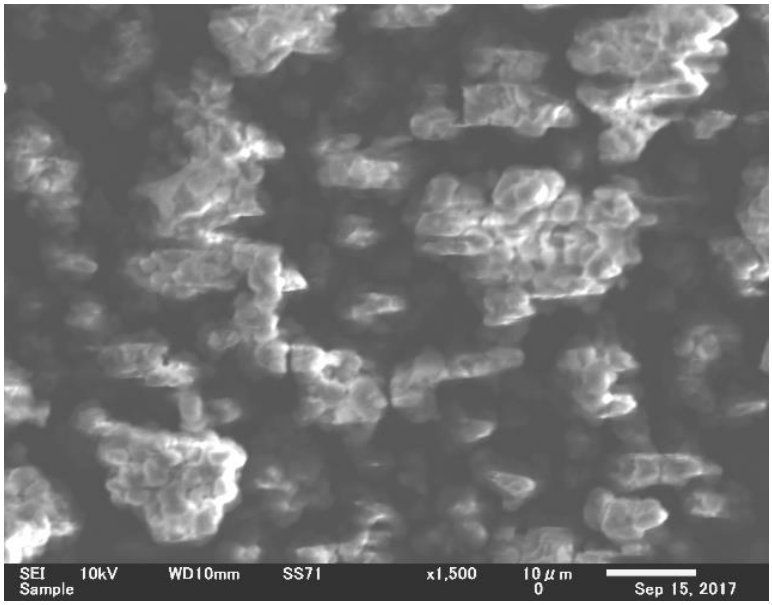
Figure S10 The SEM-EDX of MC-[4]H

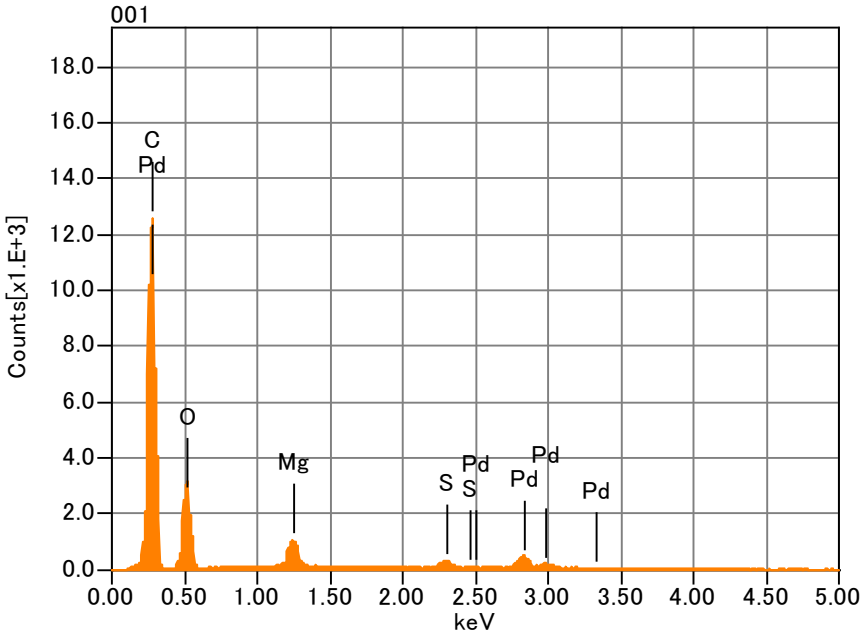




Chemical Formula	% Massa	% Atomic	σ	Integral intensity	Ratio K
C	72.33	82.26	0.02	395627	0.1904234
O	18.14	15.49	0.05	69063	0.0977741
Na	1.06	0.63	0.02	11518	0.0146870
S	1.52	0.65	0.02	12759	0.0252298
Zn	1.06	0.22	0.05	6535	0.0109805
Pd	5.88	0.76	0.09	19758	0.0750599
Total	100	100			

Figure S11 The SEM-EDX of complex MC-[4]H-Pd(II) (Low concentration of Pd(II))





Chemical Formula	% Massa	% Atomic	σ	Integral intensity	Ratio K
C	66.87	78.60	0.02	321772	0.1548754
O	20.24	17.86	0.05	72423	0.1025313
Mg	3.13	1.82	0.03	33257	0.0428476
S	1.40	0.62	0.02	10758	0.0212740
Pd	8.35	1.11	0.10	25764	0.0978793
Total	100	100			

Figure S12 The SEM-EDX of complex MC-[4]H-Pd(II) (High concentration of Pd(II))