Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supplementary Information

Introducing Alkyl Chains to Realize the Construction of Superhydrophobic/Superoleophilic MOFs and the Transformation from Three-Dimensional to Two-Dimensional Structure

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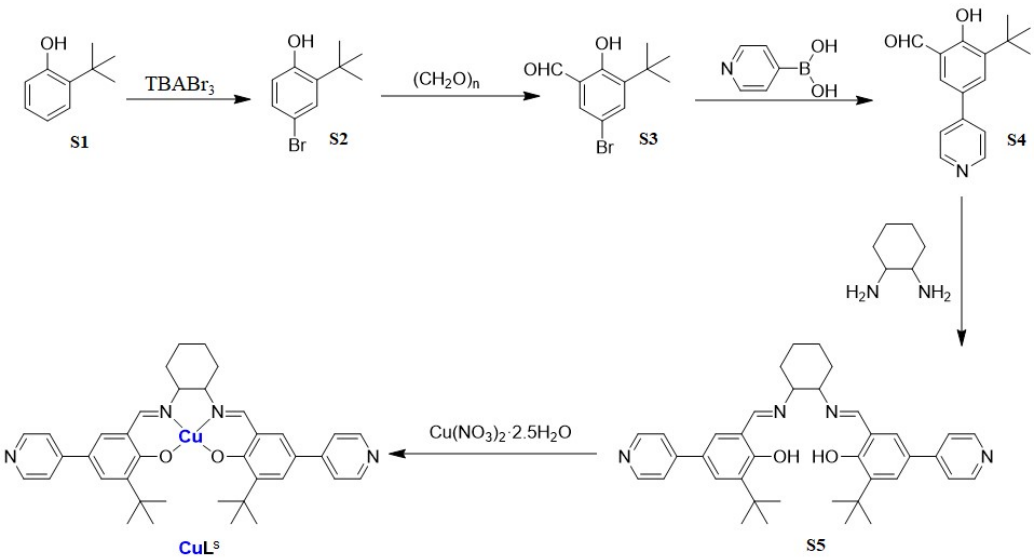
Content

SI-1 Experimental section

Synthesis of CuL^s



Scheme S1 Schematic diagram of synthesis of **CuL^s**.

Synthesis of **S2** (4-Bromo-2-tert-butylphenol)

S2 was synthesized according to the literature,[1] but slightly modified. **S1** (3.75 g, 25 mmol) was dissolved in dichloromethane (200 mL). Tetra-n-butyl ammonium tribromide ($TBABr_3$, 14.47 g, 30 mmol) was slowly added and the solution was stirred for 3 h at room temperature. The solvent was removed by rotary evaporation and the crude product was partitioned between ethyl acetate and water. The ethyl acetate (EA) layer was washed sequentially with 1 M HCl (2 × 30 mL) and brine (2 × 30 mL). The organic layer was separated and dried over Na_2SO_4. The solvent was evaporated and the crude product was purified by chromatography on silica gel to afford clear yellow oil. Yield: 5.20 g (90.8 %). ^{1}H NMR (400 MHz, Chloroform-d, δ): 7.37 (s, 1H, Ar H), 7.17 (dd, J = 8.4, 2.5 Hz, 1H Ar H), 6.56 (d, J = 8.4 Hz, 1H, Ar H), 5.19-5.06 (m, OH), 1.40 (s, 9H, *t*-Bu).

Synthesis of **S3** (5-bromo-3-(tert-butyl)-2-hydroxybenzaldehyde)

S3 was synthesized according to the literature.[2] In a dry two-necked flask, a solution of **S2** (15.2 g, 66.3 mmol), $MgCl_2$ (21.0 g, 221 mmol), and Et_3N (55 mL) in 174 ml of anhydrous CH_3CN were

stirred at room temperature for 30 minutes. Then, 22.3 g (791 mmol) of paraformaldehyde was added and the reaction mixture was stirred at 85 °C for 4 h. After cooling at room temperature, the mixture was diluted with EA (100 mL) and washed with HCl 1M (3 x 50 mL), H2O (3 x 50 mL), brine (3 x 50 mL). The organic phase was dried over Na_2SO_4 and filtered. The crude was purified by chromatographic column on flash silica gel. Yield: 12.35 g (72.1 %). ^{1}H NMR (400 MHz, Chloroform-d, δ): 11.72 (s, 1H, OH), 9.81 (s, 1H, CHO), 7.58 (d, J = 2.5 Hz, 1H, Ar H), 7.51 (d, J = 2.5 Hz, 1H, Ar H), 1.40 (s, 9H, *t*-Bu).

Synthesis of **S4** (3-tert-butyl-5-(4-pyridyl)-2-hydroxybenzaldehyde)

S4 was synthesized according to the literature.[3] A mixture of **S3** (2.5 g, 9.72 mmol), 4-pyridinylboronic acid (1.31 g, 10.69 mmol), Na_2CO_3 (1.55 g, 14.58 mmol), and $Pd(PPh_3)_4$ (1.13 g, 0.98 mmol) was refluxed in 1,4-dioxane and H_2O (3:1 v/v, 60 mL, degassed with N_2) at 102 °C for 1 h. After cooling to room temperature, the reaction contents were poured into water (50 mL). The aqueous mixture was extracted with CH_2Cl_2 (50 mL), and the combined extracts were dried over Na_2SO_4 before being concentrated under reduced pressure. The crude was purified by chromatographic column on flash silica gel to afford a pale yellow solid. Yield: 1.23 g (53.2 %). ^{1}H NMR (400 MHz, Chloroform-d, δ): 11.94 (s, 1H, OH), 9.98 (s, 1H, CHO), 8.66 (d, J = 5.5 Hz, 2H, Ar H), 7.80 (d, J = 2.3 Hz, 1H, Ar H), 7.69 (d, J = 2.4 Hz, 1H, Ar H), 7.53-7.48 (m, 2H, Ar H), 1.48 (s, 9H, *t*-Bu).

Synthesis of **S5** (3,3ˈ-Diaminocyclohexanediylbis(nitromethylidine)bis [3-tert-Butyl2-hydroxy-5-(4-pyridinyl)-benzald ehyde)

S5 was synthesized according to the literature.[3] **S4** (3.92 g, 15.4 mmol) was dissolved in methanol (50 mL). A solution of (1,2)-diaminocyclohexane (860 mg, 7.58 mmol) in methanol (10 mL) was added dropwise and the solution turned bright yellow. The solvent was evaporated. The crude compound

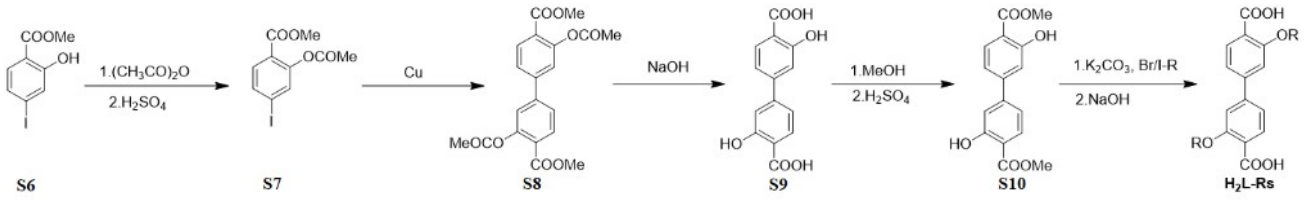
was purified by flash chromatography on silica gel with EA to get a yellow solid. Yield: 3.48 g (78.1 %) ^{1}H NMR (400 MHz, Chloroform-d) δ 14.18 (s, 2H, OH), 8.61-8.53 (m, 4H, Ar H), 8.36 (s, 2H, CHO), 7.51 (d, J = 2.3 Hz, 2H, Ar H), 7.38-7.32 (m, 4H, Ar H), 7.27 (d, J = 1.9 Hz, 2H, Ar H), 3.44-3.36 (m, 2H, CH), 1.97-1.92 (m, 2H, CH_2), 1.89-1.82 (m, 2H, CH_2), 1.83-1.74 (m, 2H, CH_2), 1.56-1.50 (m, 2H, CH_2), 1.44 (s, 18H, *t*-Bu).

Synthesis of **CuL^s**

A solution of **S5** (588 mg, 1 mmol) in MeOH (20 mL) was added dropwise to $Cu(NO_3)_2{\cdot}2.5H_2O$ (232.6 mg, 1 mmol) in MeOH (5 mL). The reaction mixture was stirred at 60 ℃ for 3 h. The dark purple powder precipitate of **CuL^s** was collected by filtration, washed with MeOH, and dried under reduced pressure. Yield: 0.60 g (92.2 %).

Synthesis of H_2L-Rs (R = ethyl, n-butyl, n-hexyl, n-octyl)

H_2L-Rs was synthesized according to the literature.[4]



Scheme S2. Schematic diagram of synthesis of H_2L-Rs.

Synthesis of **S7** (methyl 2-acetoxy-4-iodobenzoate)

Concentrated H_2SO_4 (85 uL) was added to **S6** (methyl 2-hydroxy-4-iodobenzoate) (2.0 g, 7.2 mmol) in acetic anhydride (3 mL) and the mixture was stirred at 80 ℃ overnight. After cooling to room temperature, water (15 mL) was added and the solution was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic extracts were passed through a plug of silica and washed with saturated $NaHCO_3$ solution, dried over Na_2SO_4, filtered and the solvents removed in vacuo to give a white solid.

Synthesis of **S8** (dimethyl 3,3'-diacetoxy-[1,1'-biphenyl]-4,4'-dicarboxylate)

S7 (1.60 g, 13.70 mmol), copper powder (3.00 g, 46.0 mmol), and DMF (4 mL) were mixed under N_2 atmosphere and then heated to 155 ℃ for 10 h. After the reaction mixture was filtered while it was still hot, the filtrate was collected, poured into water (40 mL), and stirred vigorously. The formed precipitate was collected by filtration and dried under reduced pressure at 60 ℃ overnight to afford a white solid.

Synthesis of **S9** (3,3'-dihydroxy-[1,1'-biphenyl]-4,4'-dicarboxylic acid)

S8 (1.16 g, 3 mmol) was dissolved in a mixed solution of methanol (30 mL) and THF (tetrahydrofuran 30 mL), then added to a 100 mL one-neck flask equipped with a condenser and a magnetic stirrer. After that 6 mL 2 M NaOH solution was added drop by drop, and the reaction mixture was refluxed overnight. After cooling to room temperature, the reaction mixture was concentrated in vacuo to remove some organic solvent. 50 mL water was added to the residue, the aqueous layer was acidified with concentrated HCl until a pH < 3 was attained and the resulting precipitate was collected by filtration, washed with ample H_2O, and dried to obtain a white powder.

Synthesis of **S10** (dimethyl 3,3'-dihydroxy-[1,1'-biphenyl]-4,4'-dicarboxylate)

S9 (0.55 g, 2 mmol) was dissolved in methanol (40 mL) and added to a 100 mL one-neck flask equipped with a condenser and a magnetic stirrer. After that 800 uL concentrated H_2SO_4 was added drop by drop, and the reaction mixture was refluxed 24 h. After cooling to room temperature, the reaction mixture was concentrated in vacuo to remove MeOH. 50 mL water was added to the residue after the solution was filtered, the precipitate was dried under vacuum and a white powder was obtained.

Synthesis of **H_2L-R**s

S10 (302 mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol), and DMF (5 mL) were added to a 50 mL one-neck

flask equipped with a condenser and a magnetic stirrer, Br-R (R = ethyl, n-butyl, n-hexyl, n-octyl) (2.5 mmol) was added dropwise to the mixture. The reaction mixture was heated at 85 ℃ for 3 h. After cooling to room temperature, the reaction mixture was concentrated in vacuo to remove DMF. After that, a mixed solution of methanol (10 mL) and THF (10 mL) was added, and 2 mL 2 M NaOH solution was added drop by drop to the reaction mixture and refluxed overnight. After cooling to room temperature, the reaction mixture was concentrated in vacuo to remove organic solvent. Water (50 mL) was added to the residue, the aqueous layer was acidified with concentrated HCl until a pH < 3 was attained and the resulting precipitate was collected by filtration, washed with ample H_2O, and vacuum-dried to obtain a white powder.

SI-2 Crystal data and structure refinement details

Tab. S1 Crystal data and structure refinement details of **1**, **2,** and **1-Oct.**

Complex	**1**	**2**	**1-Oct**
Formula	$C_{52}H_{50}CdCuN_4O_6$	$C_{55}H_{56}CuZnN_5O_7$	$C_{128}H_{147}Cd_2Cu_2N_8O_{16}$
formula weight, fw	1002.90	1027.95	2405.41
Temperature, *T* [K]	296.15(10)	296.15	293.15
crystal system	*orthorhombic*	*orthorhombic*	*triclinic*
space group	*Pbca*	*Pbca*	*P1*
a [Å]	26.966(2)	13.7150(6)	11.2898(9)
b [Å]	13.9127(10)	25.9845(8)	13.6418(11)
c [Å]	26.3405(14)	26.6380(11)	23.3580(19)
α [°]	90	90	103.862(7)
β [°]	90	90	97.472(7)
γ [°]	90	90	104.800(7)
V [Å^3]	9882.3(12)	9493.2(6)	3306.0(5)
Z	8	8	1
ρ [g cm^{-3}]	1.348	1.438	1.208
μ [mm^{-1}]	0.912	1.014	0.695
θ range	2.1540-18.8990	2.291-24.438	2.7450-22.2700
F(000)	4120	4288	1253
goodness-of-fit, GOF	0.990	1.144	1.032
R_1[a] [I > 2σ (I)]	0.0601	0.0759	0.1169
wR_2[b] (all data)	0.1569	0.2264	0.2835

[a] $R_1 = ||F_o| - |F_c|| / |F_o|$. [b] $wR_2 = [w(|F_o^2| - |F_c^2|)^2 / w|F_o^2|^2]^{1/2}$.

SC-XRD of **1**, **2,** and **1-Oct** were tested on a Bruker D8 Venture using Mo Kα radiation. The empirical absorption correction was performed using the Crystal Clear program. The structure was solved by direct methods and refined on F^2 by the full-matrix least-squares technique using the SHELXL program package. Table S1 shows the refinement details of **1**, **2,** and **1-Oct**.

SI-3 N_2 adsorption data

Tab. S2 BET surface area, pore volume and porosity of **1**, **2**, **1-NH$_2$**, **1-Et**, and **1-Oct**.

Sample	S_{BET} ($m^2\ g^{-1}$)	V_t (cc g^{-1})	P (%)
1	94.812	133.8184	16.5
2	23.154	81.8093	16.1
1-NH$_2$	0.913	2.7987	
1-Et	189.174	52.8486	
1-Oct	4.392	2.7678	13.1

S_{BET} is the BET surface area. V_t stands for the single point total pore volume determined by using the adsorption branch of the N_2 isotherm at $P/P_0 = 0.99$. P stands for porosity calculated by the PLATON program.

SI-4 Elemental analyses by EDS

Tab. S3 Elemental analyses by EDS of PDMS/**1-Oct**@MS.

Element	Intensity (c/s)	Conc.	Units
C	830.73	30.809	wt. %
N	208.32	17.179	wt. %
O	599.11	26.106	wt. %
Si	2,404.29	20.661	wt. %
Cu	19.91	1.878	wt. %
Cd	69.32	3.367	wt. %

Tab. S4 Elemental analyses by EDS of PDMS/**1-Oct**@MS after 50 cycles.

Element	Intensity (c/s)	Conc.	Units
C	1,270.12	29.786	wt. %
N	403.36	23.454	wt. %
O	822.25	29.011	wt. %
Si	2,262.88	14.902	wt. %
Cu	23.98	1.731	wt. %
Cd	30.51	1.116	wt. %

SI-5 Structure and characterization

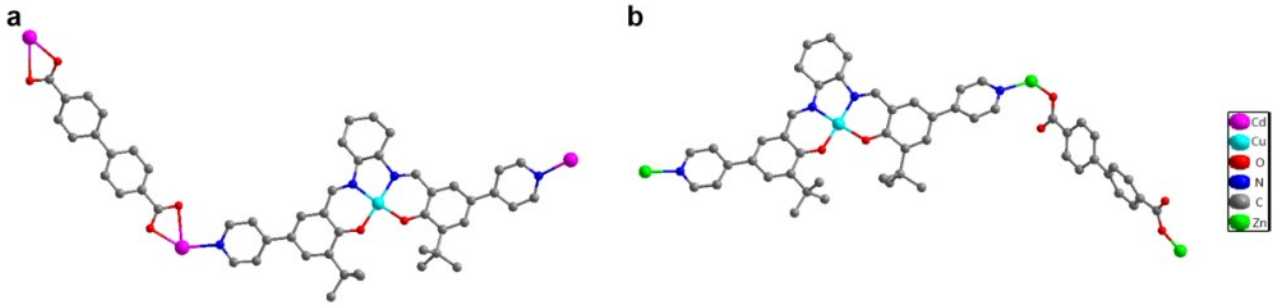


Fig. S1 Asymmetric units of **1** and **2**.

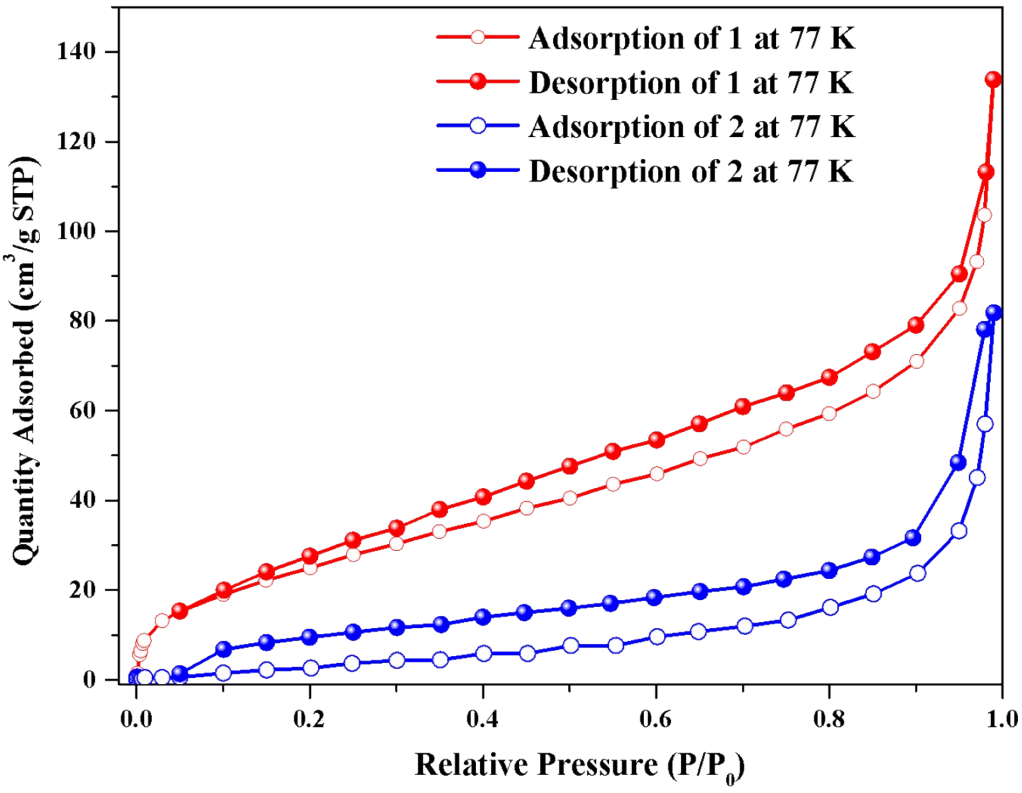


Fig. S2 N_2 adsorption-desorption isotherms of **1** and **2**.

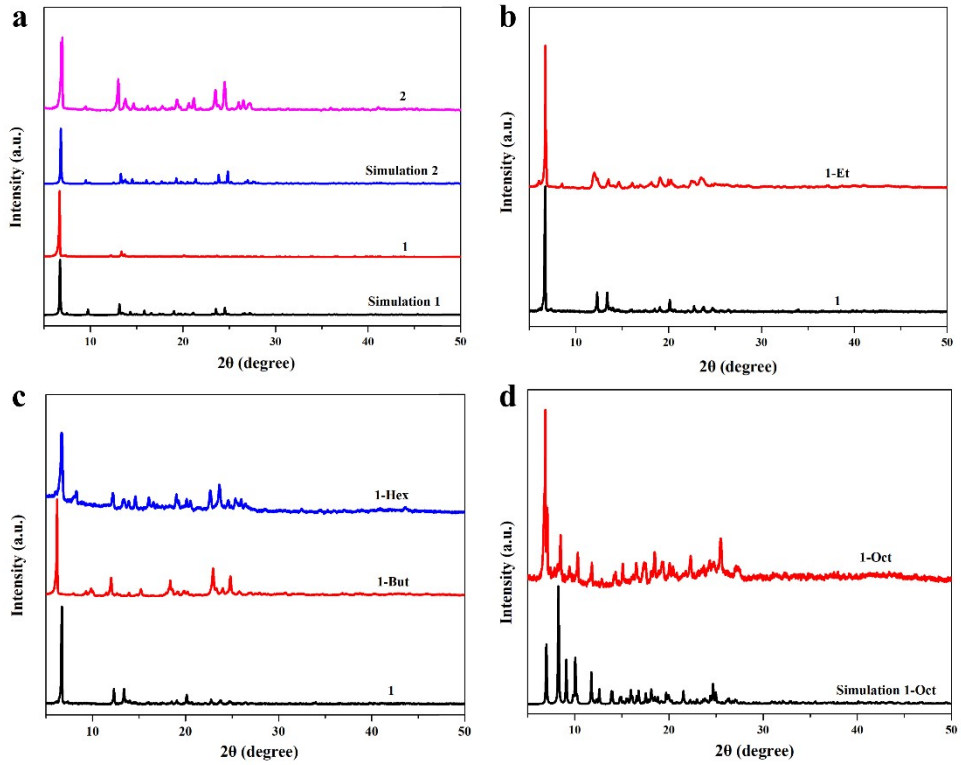


Fig. S3 PXRD patterns of **1** and **2** (a), **1-Et** (b), **1-But** and **1-Hex** (c), and **1-Oct** (d).

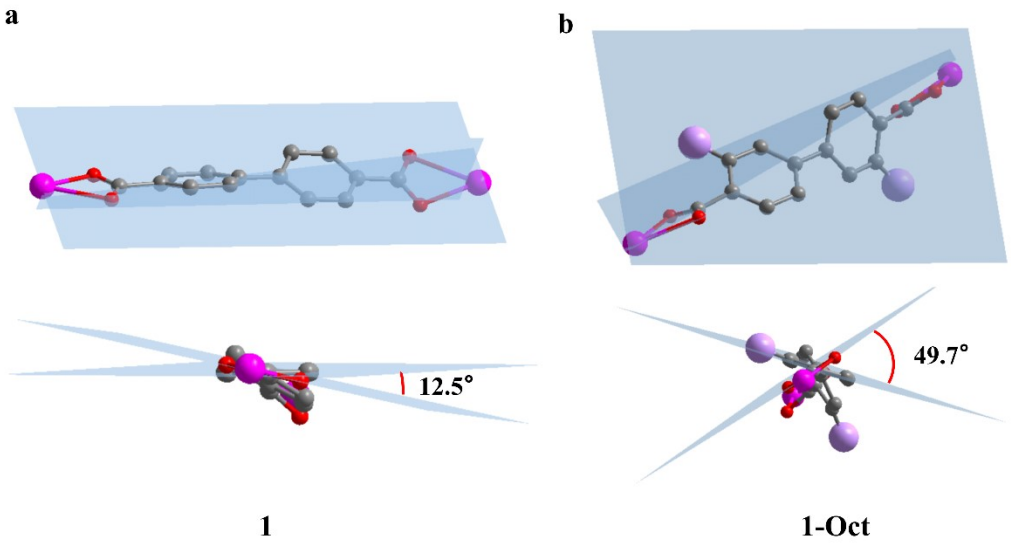


Fig. S4 The dihedral angle formed by a carboxyl group and the connected benzene ring in **1**(a) and **1-Oct** (b).

SI-6 Stability analysis

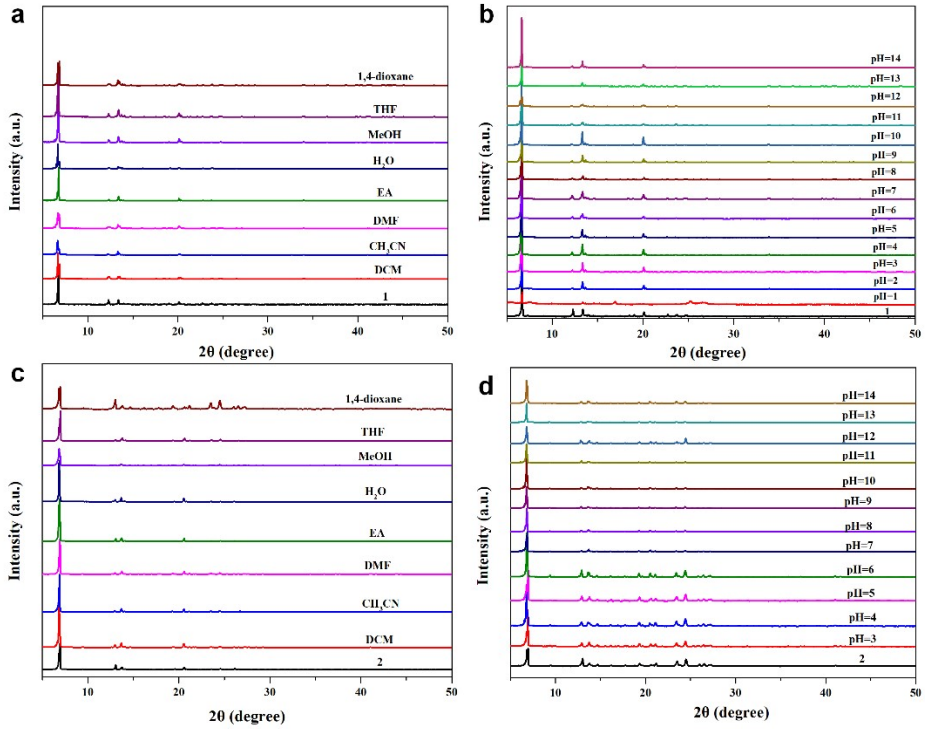


Fig. S5 (a) PXRD patterns after soaking **1** in different solvents (dichloromethane (DCM), acetonitrile (CH_3CN), DMF, ethyl acetate (EA), H_2O, methanol (MeOH), tetrahydrofuran (THF), 1,4-dioxane) for 60 days. (b) PXRD patterns after soaking **1** in aqueous solutions of different pH for 48 hours. (c) PXRD patterns after soaking **2** in different solvents for 60 days. (d) PXRD patterns after soaking **2** in aqueous solutions of different pH for 48 hours.

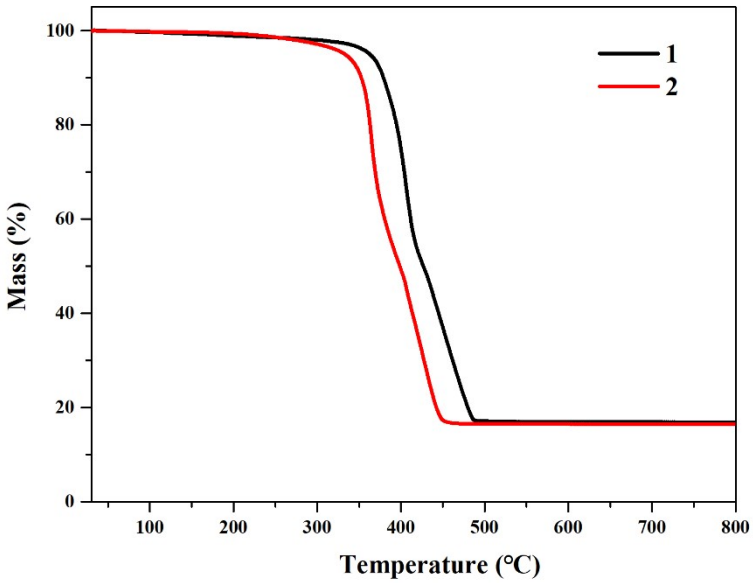


Fig. S6 The thermogravimetric analyses of **1** and **2.**

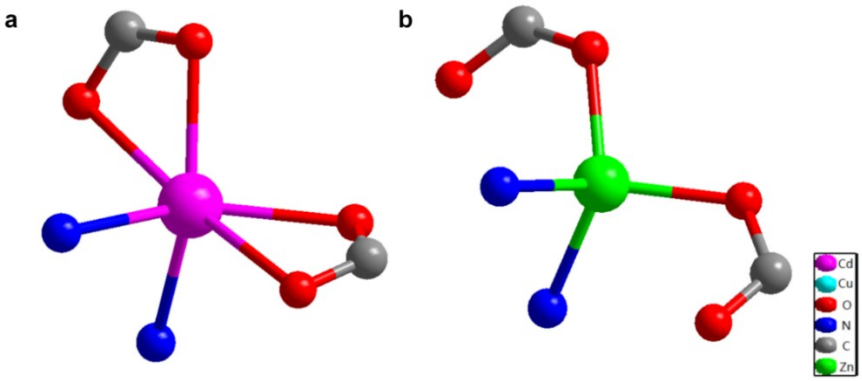


Fig. S7 Coordination modes of metal atoms in the secondary building units (SBUs) of **1** (a) and **2** (b).

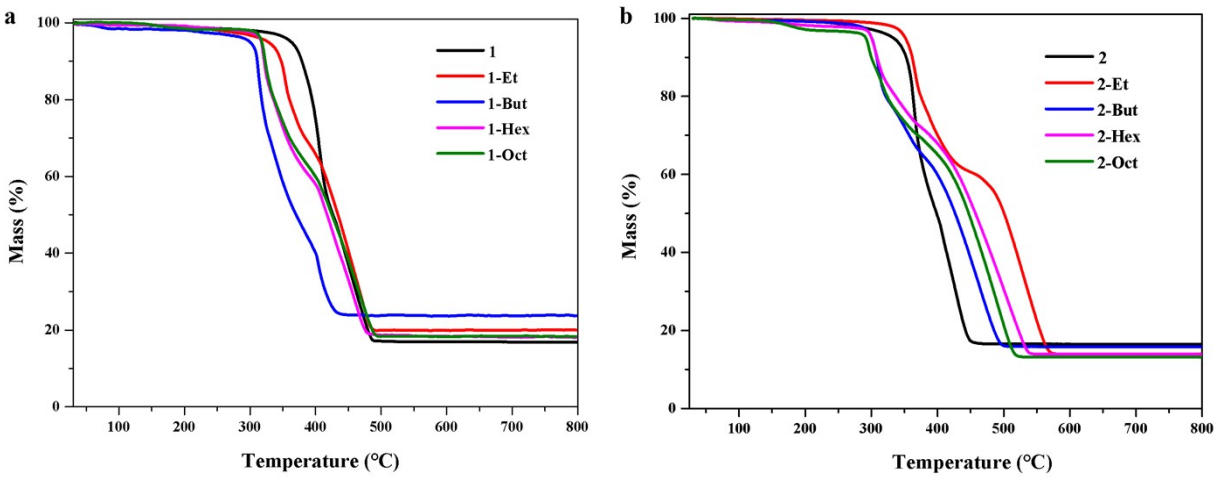


Fig. S8 The thermogravimetric analyses of **1-R**s (a) and **2-R**s (b).

SI-7 Component analyses of 1-Rs and 2-Rs

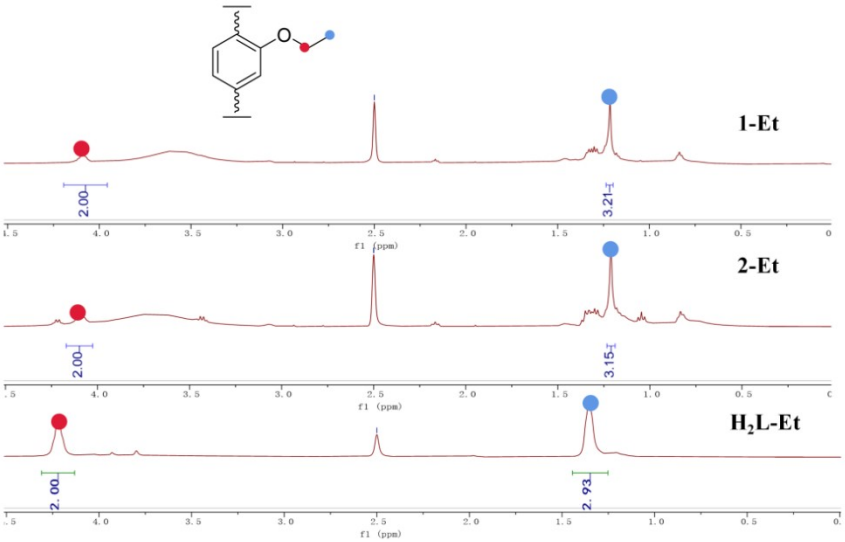


Fig. S9 The ^{1}H NMR spectra of digested **1-Et**, **2-Et** and H_2L-Et.

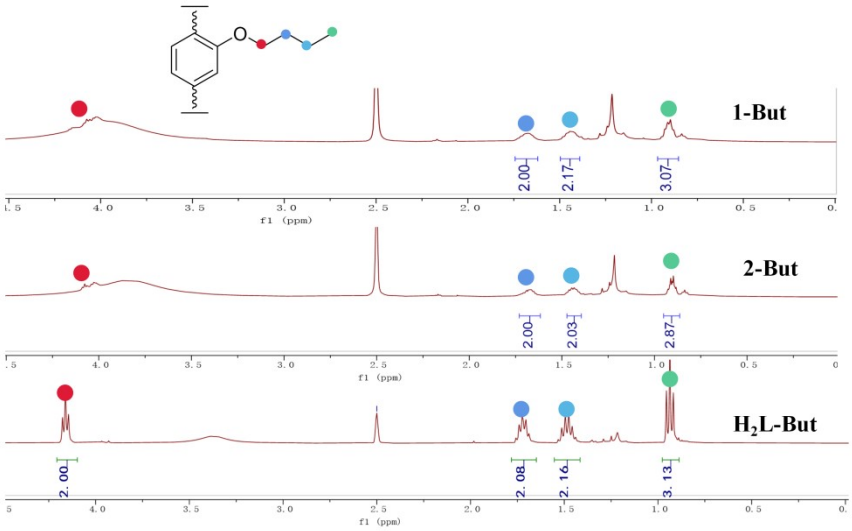


Fig. S10 The ^{1}H NMR spectra of digested **1-But**, **2-But** and H_2L-But.

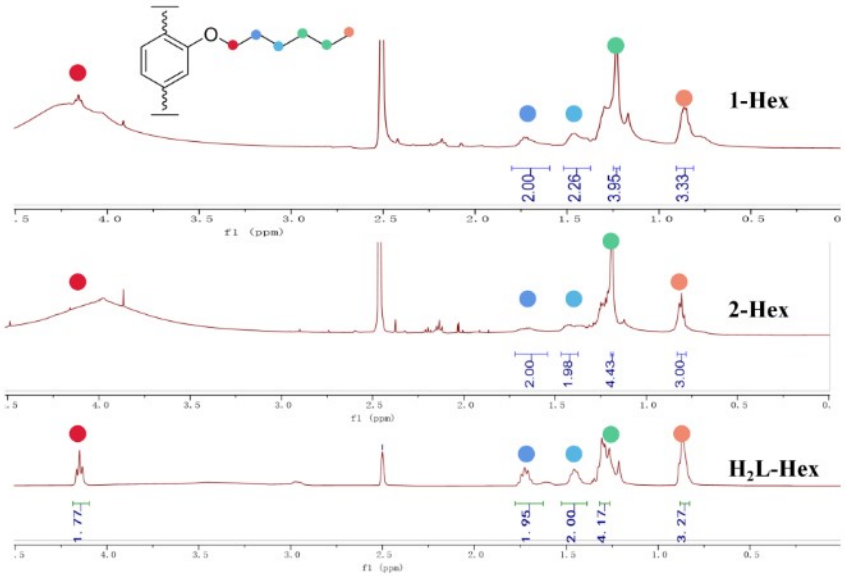


Fig. S11 The ^{1}H NMR spectra of digested **1-Hex**, **2-Hex** and H_2L-Hex.

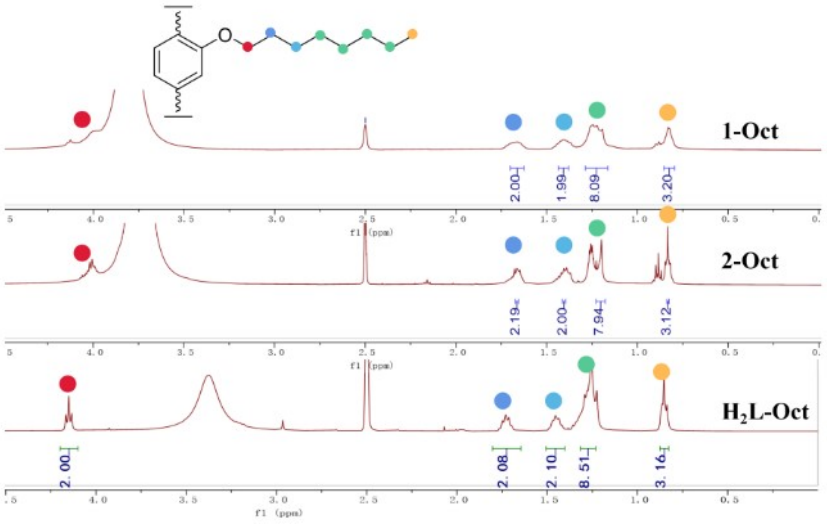


Fig. S12 The ^{1}H NMR spectra of digested **1-Oct**, **2-Oct** and H_2L-Oct.

Digested process: 100 mg **1-R**s and **2-R**s were added to 10 mL aqua regia ($V_{HCl(Conc.)}$: $V_{HNO3(Conc.)}$) by ultrasound for 10 minutes. Then the mixed solution was extracted with ethyl acetate (20 × 3 mL), the collected organic phase was washed with saturated salt water (20 × 3 mL), dried with anhydrous Na_2SO_4, concentrated in a vacuum, and white solids were collected.

SI-8 Study on hydrophobicity of 1-Rs

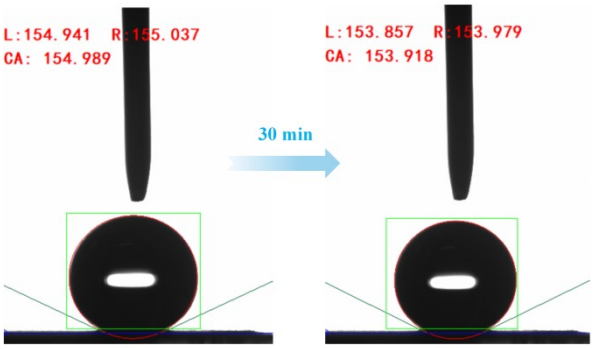


Fig. S13 The WCAs of **1-Oct** and **1-Oct** after standing for 30 minutes.

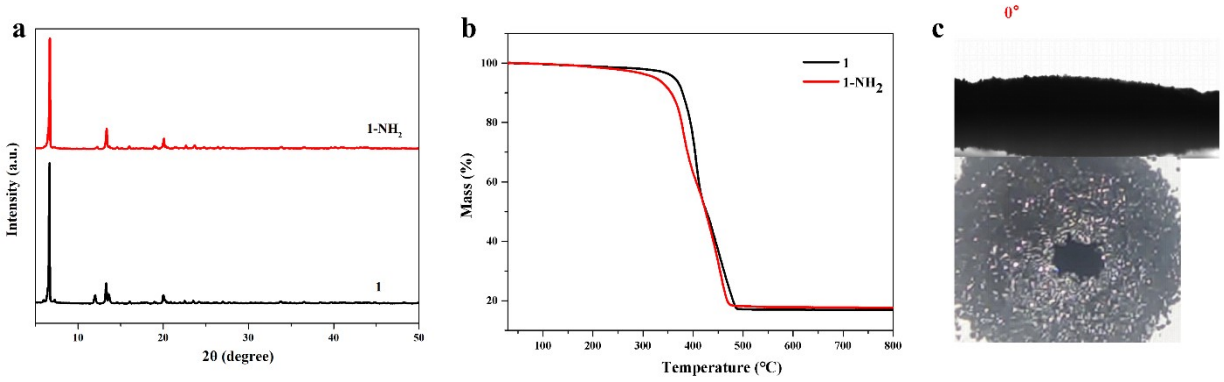


Fig. S14 The PXRD patterns (a), thermogravimetric analyses (b), WCAs and digital photograph (c) of **1-NH$_2$**.

H_2L-NH_2 (2-Amino-[1,1'-biphenyl]-4,4'-dicarboxylic acid) was obtained through commercial purchase replaced H_2L as ligand to synthesize **1-NH$_2$**. The PXRD patterns demonstrate correct crystal structure and high phase purity of **1-NH$_2$**. The thermogravimetric analyses reflect the thermal stability of **1-NH$_2$**. The WCA shows the superhydrophilicity of **1-NH$_2$**.

SI-9 Synthesis and characterization of small size 1-Oct (s1-Oct)

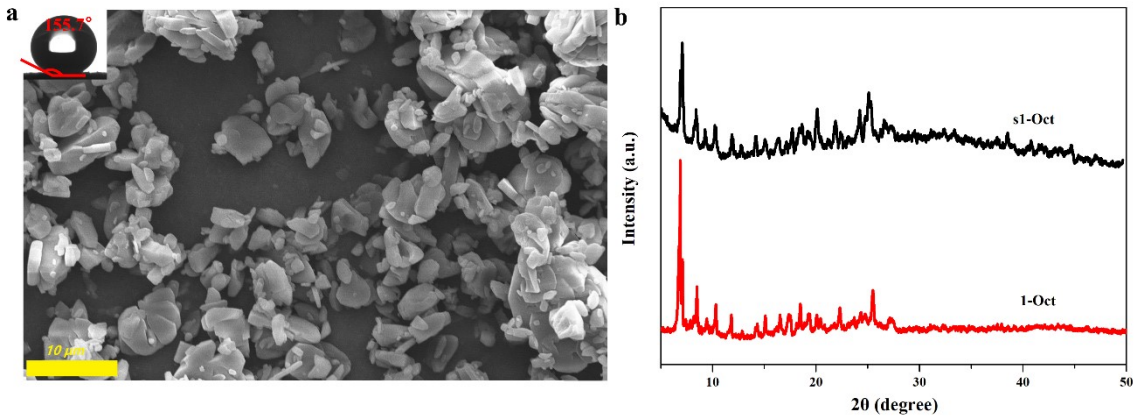


Fig. S15 (a) The SEM and WCA images of s**1-Oct**. (b) The PXRD patterns of **1-Oct** and s**1-Oct**.

SI-10 Analysis of 1-Oct load in PDMS/1-Oct@MS

Tab. S5 The average and standard deviation of MS of 1x1x1 cm^3 and coated MS of 1x1x1 cm^3 with PDMS or/and **1-Oct**.

Weight (mg) / Sample	M_M	$\bar{x}_M$	M_{PM}	M_P	$\bar{x}_P$	S_P	M_{POM}	M_{PO}	$\bar{x}_{PO}$	S_{PO}	$\bar{x}_O$
1	7.9	7.7	39.8	31.9	31.9	2.5					6.6
2	7.4		43.1	35.7							
3	6.8		39.4	32.6							
4	8.6		38.5	29.9							
5	6.7		36.2	29.5							
6	6.9						43.1	36.2	38.5	2.2	
7	8.1						49.3	41.2			
8	8.0						48.3	40.3			
9	7.3						44.1	36.8			
10	8.2						46.3	38.1			

M_M, M_{PM}, M_P, M_{POM}, and M_{PO}, stand for the weight of MS, PDMS/MS, loaded PDMS, PDMS/**1-Oct**@MS, and loaded PDMS/**1-Oct**, respectively (mg). $\bar{x}_M$, $\bar{x}_P$, and $\bar{x}_{PO}$ are the averages of MS, loaded PDMS, and loaded PDMS/**1-Oct**, respectively (mg); S_P and S_{PO} stand for the standard deviation values of loaded PDMS and loaded PDMS/**1-Oct**, respectively; $\bar{x}_O$ (mg) is obtained by subtracting $\bar{x}_{PO}$ from $\bar{x}_P$.

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n} \quad \text{(Eq. 1)}$$

$$S = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2} \quad \text{(Eq. 2)}$$

$\bar{x}$ is the average value (mg); S is the standard deviation value (%); n stands for total number of samples; i stands for serial number of samples.

SI-11 Morphology characterization and composition analysis of PDMS/1-Oct@MS

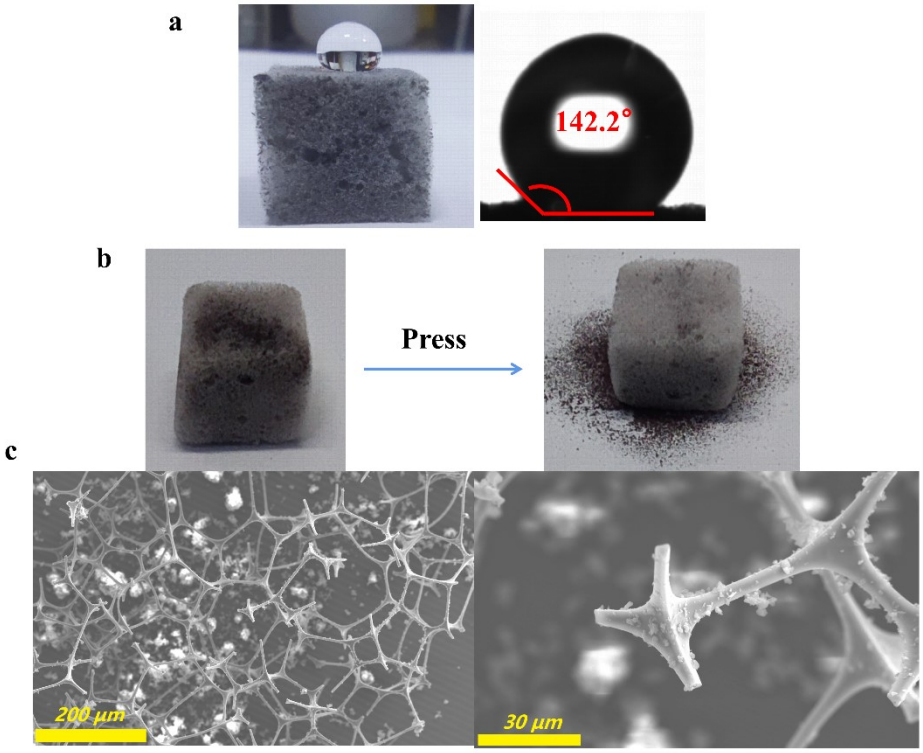


Fig. S16 (a) The hydrophobicity analysis of **1-Oct**@MS. (b) The shedding of **1-Oct** in **1-Oct**@MS after pressing. (c) The SEM images of **1-Oct**@MS.

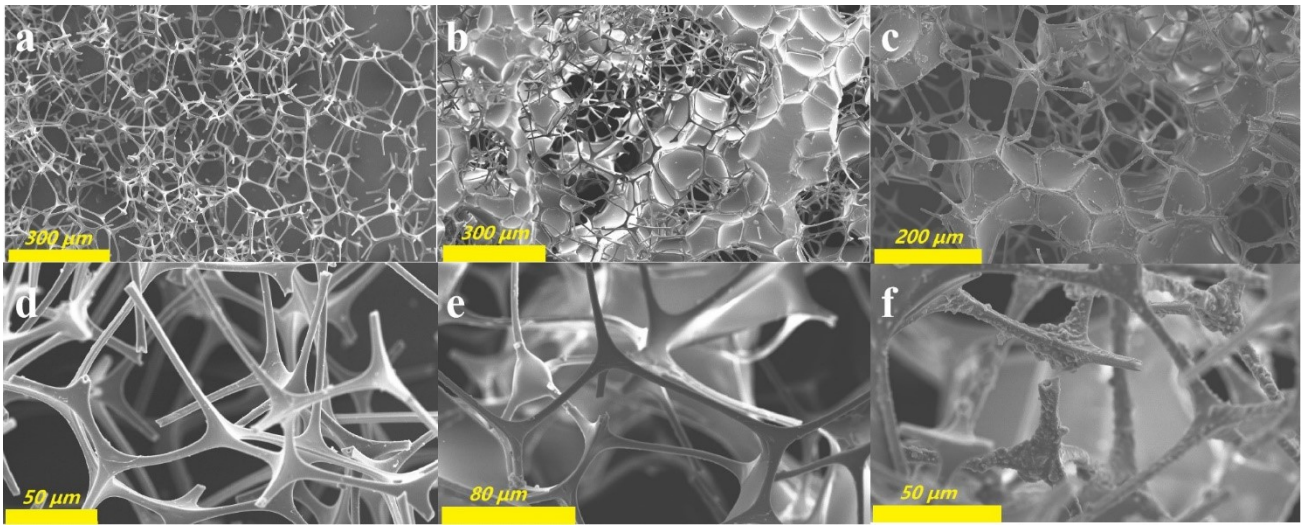


Fig. S17 The SEM images of MS (a and d), PDMS/MS (b and e), and PDMS/**1-Oct**@MS (c and f).

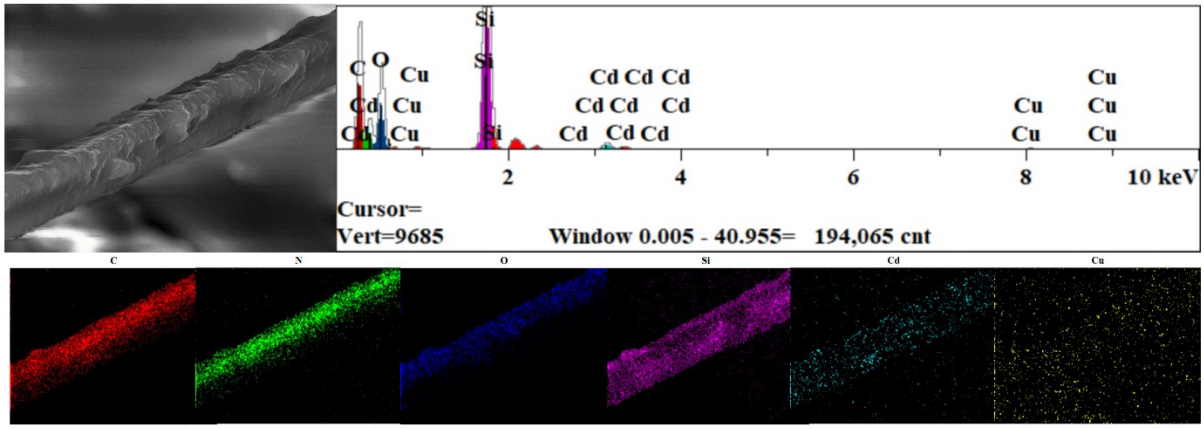


Fig. S18 EDS-mapping images of PDMS/**1-Oct**@MS.

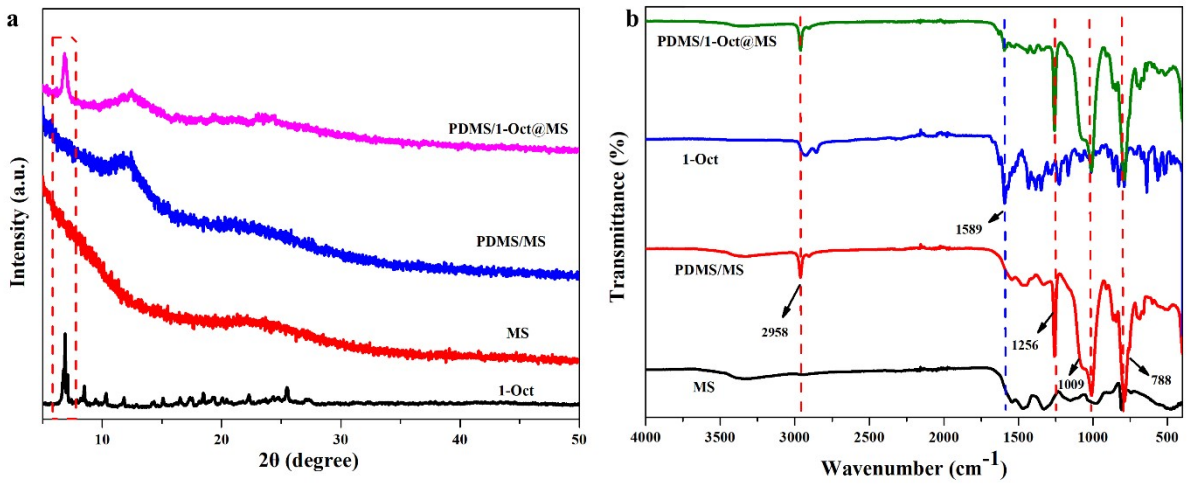


Fig. S19 The PXRD patterns (a) and FTIR spectra (b) of **1-Oct**, MS, PDMS/MS, and PDMS/**1-Oct**@MS.

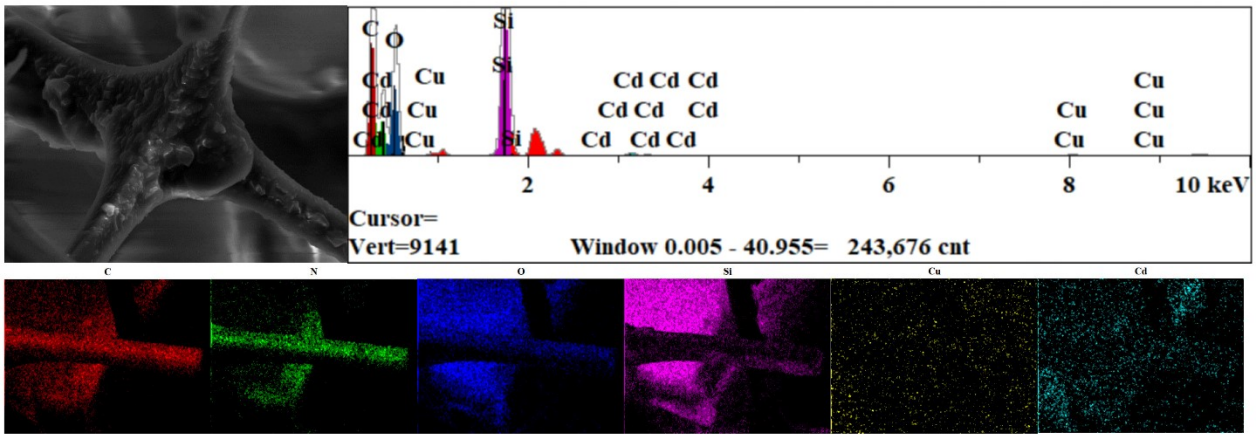


Fig. S20 EDS-mapping images of PDMS/**1-Oct**@MS after 50 cycles.

SI-12 Oil-water separation experiment

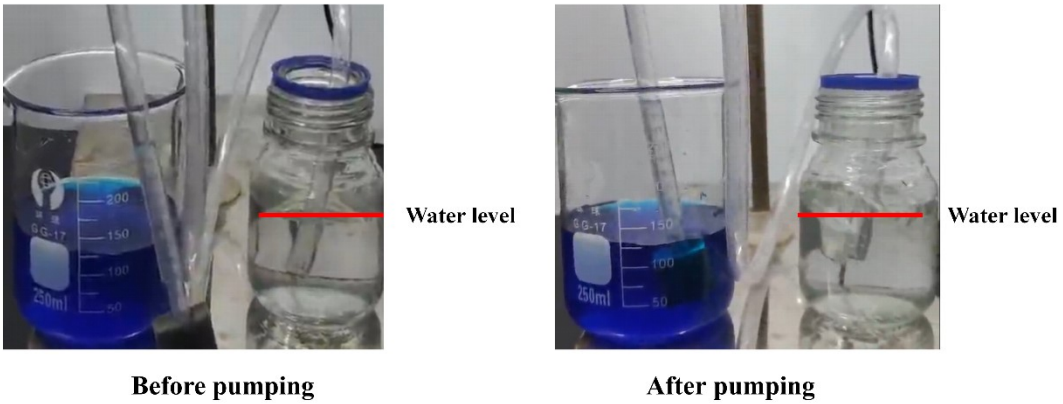


Fig. 21 Water level of outlet before and after pumping.

SI-13 The influence of functional groups on the N_2 adsorption

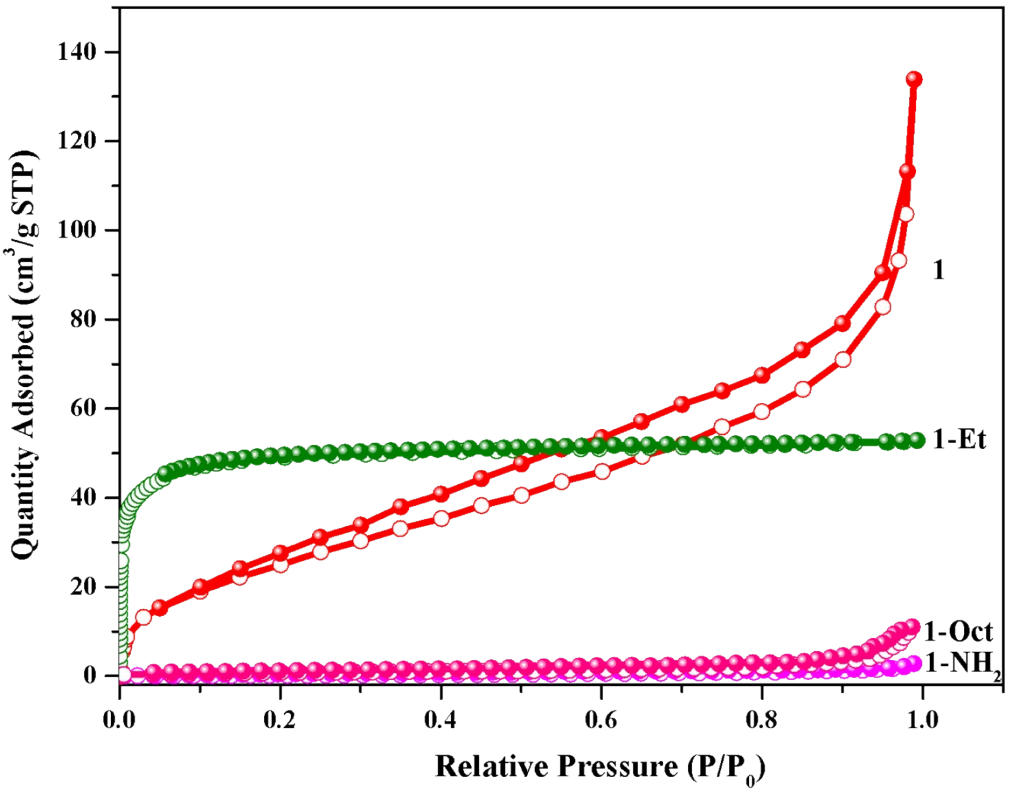


Fig. S22 N_2 adsorption-desorption isotherms of **1**, **1-NH$_2$**, **1-Et**, and **1-Oct** at 77 K (The hollow sphere stands for adsorption and the solid sphere stands for desorption).

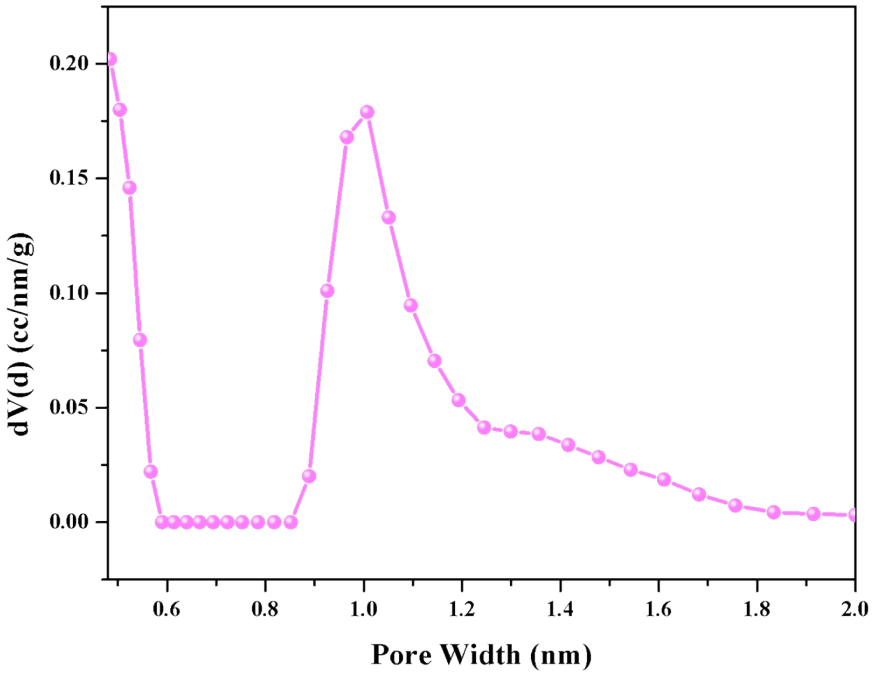
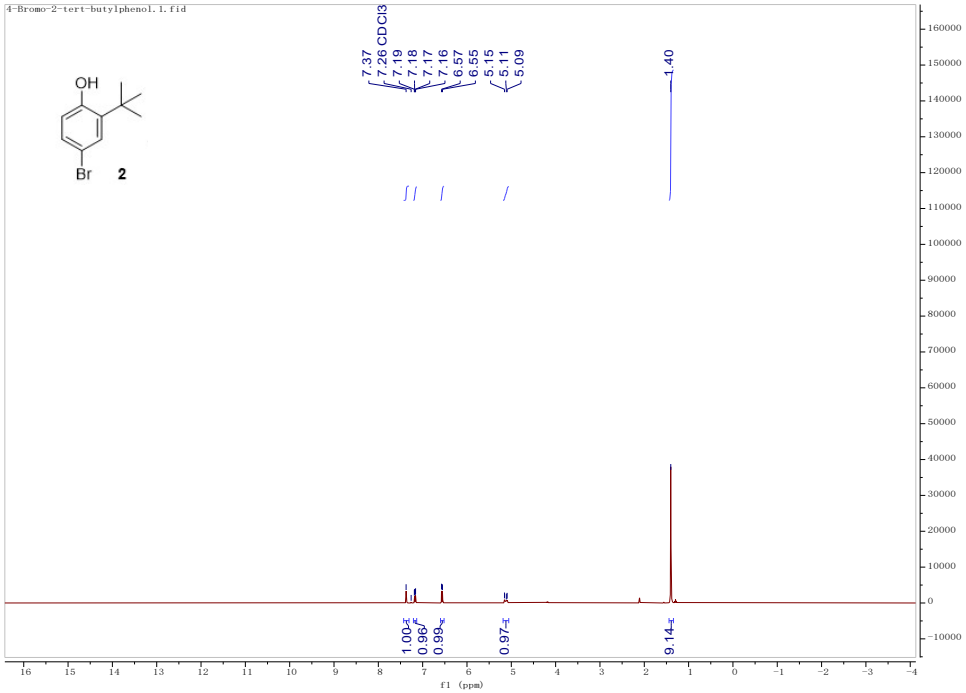
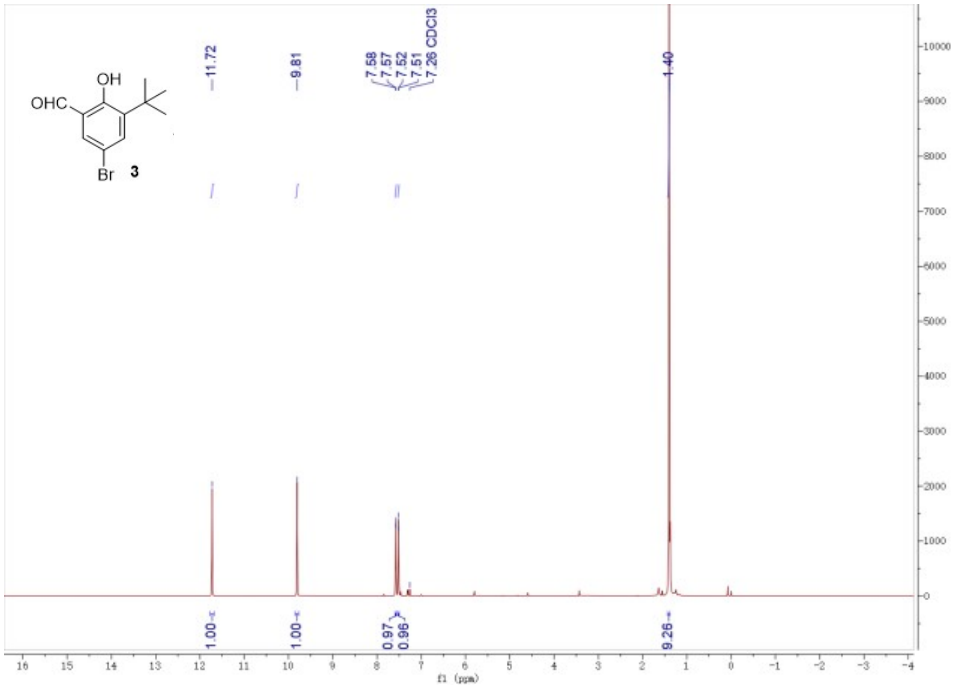
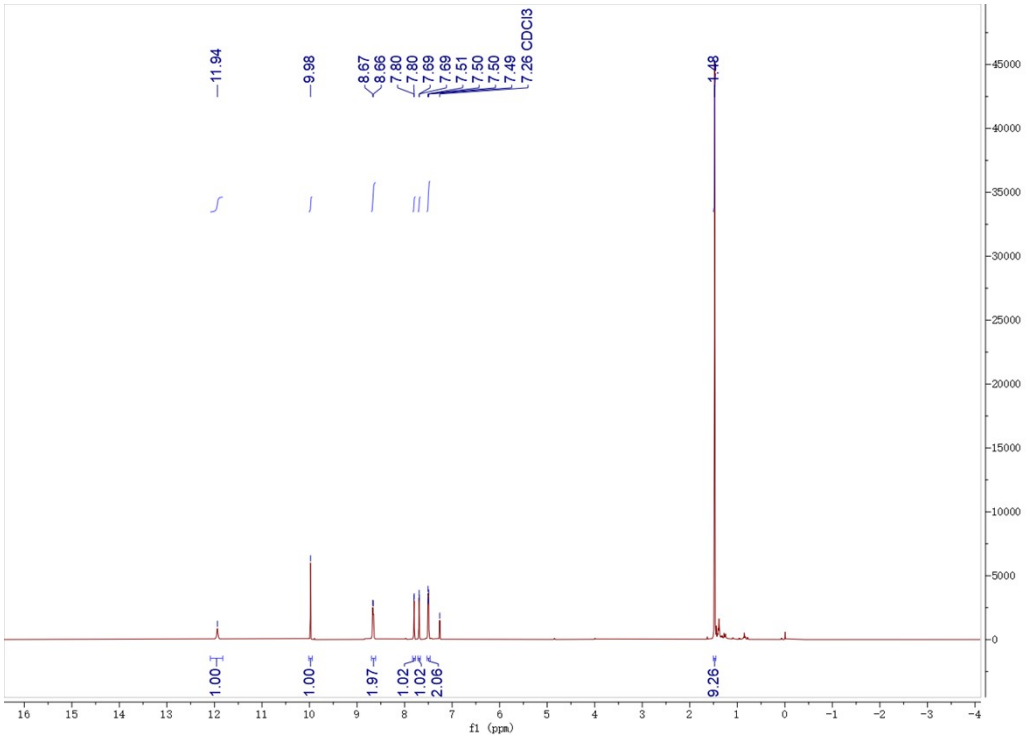


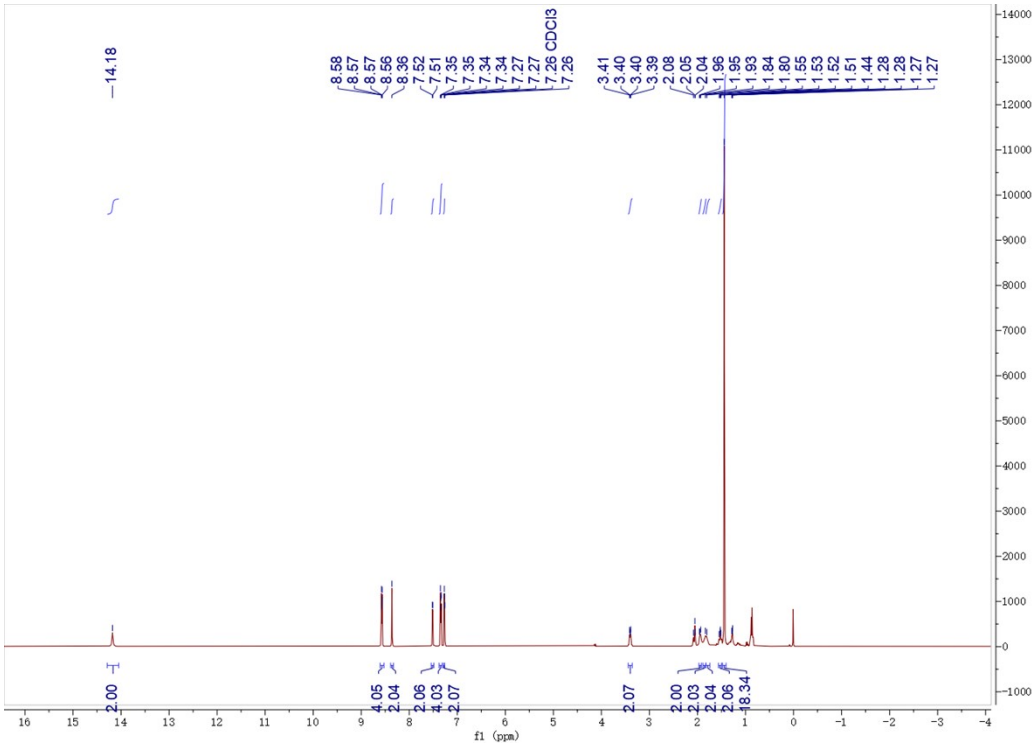
Fig. S23 Pore size distribution of **1-Et.**

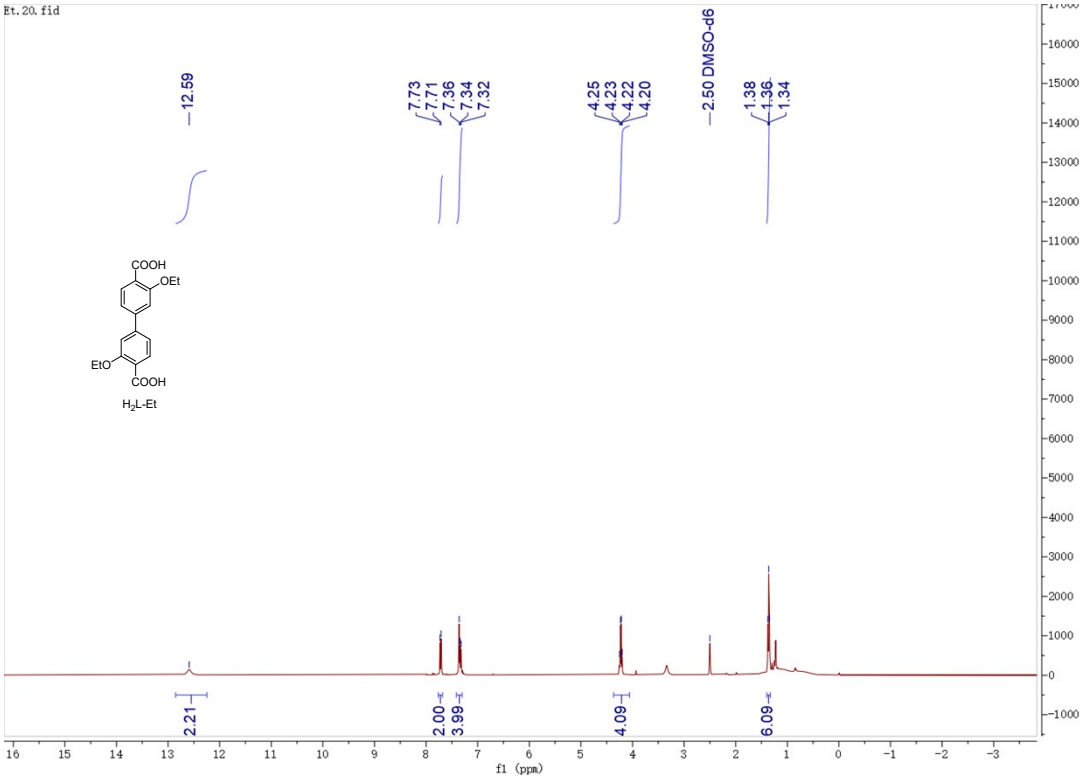
SI-14 ^{1}H NMR spectra

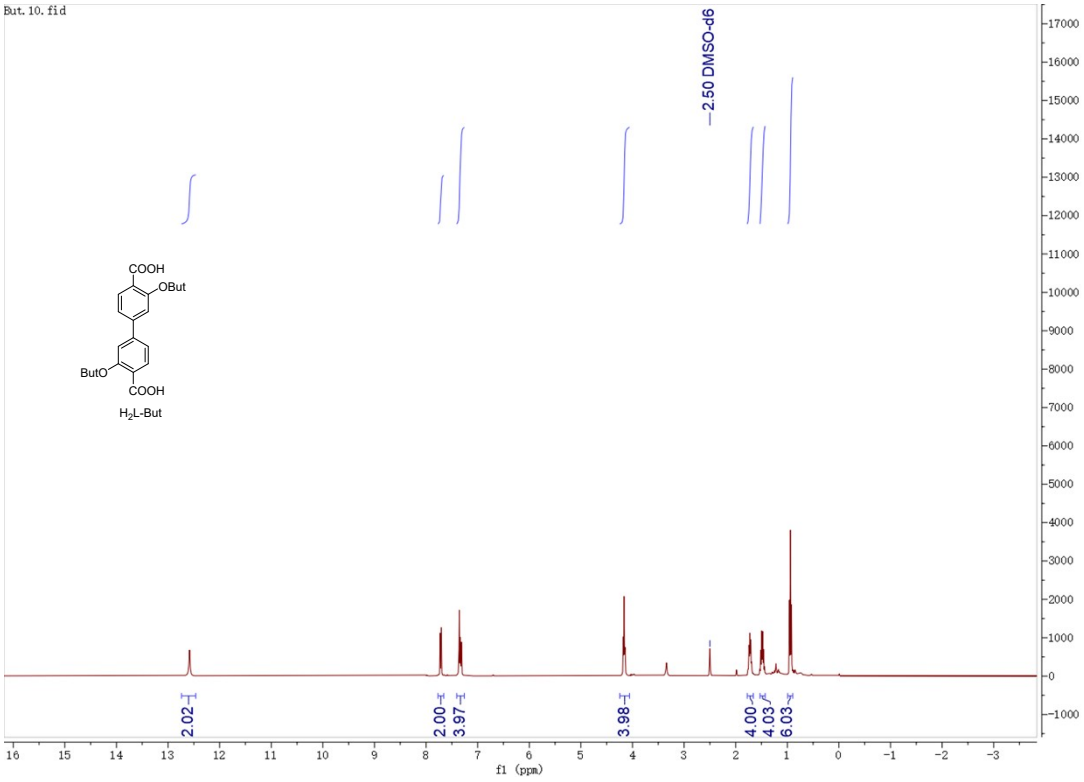


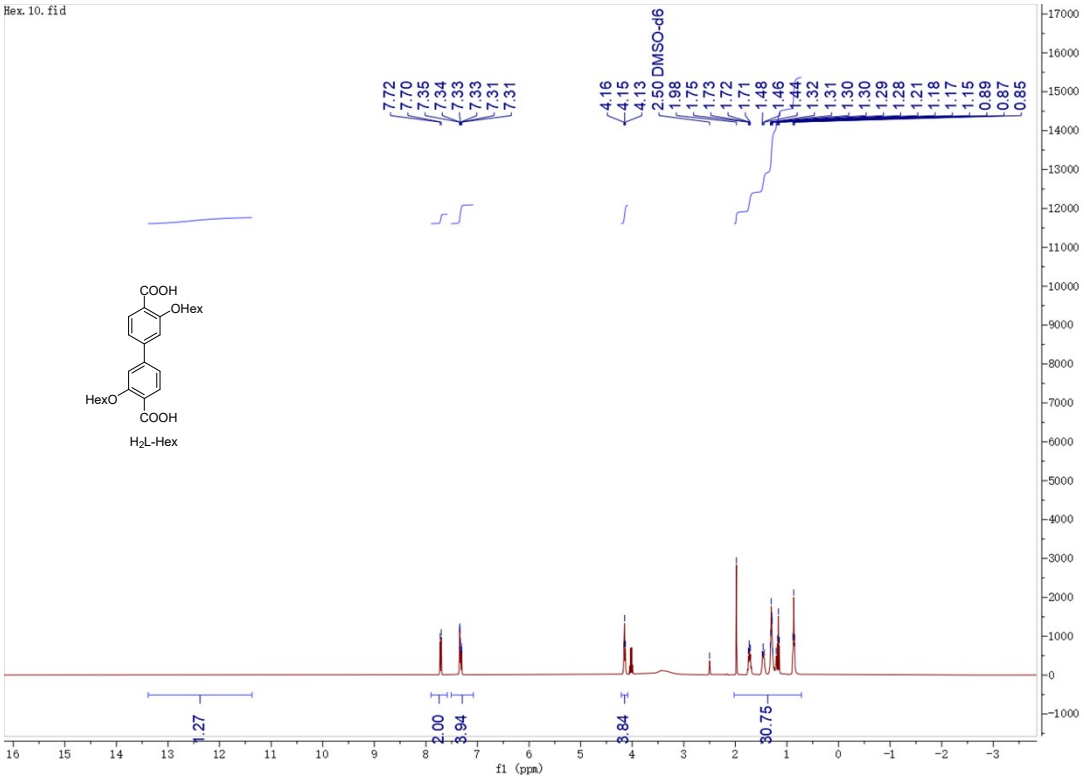


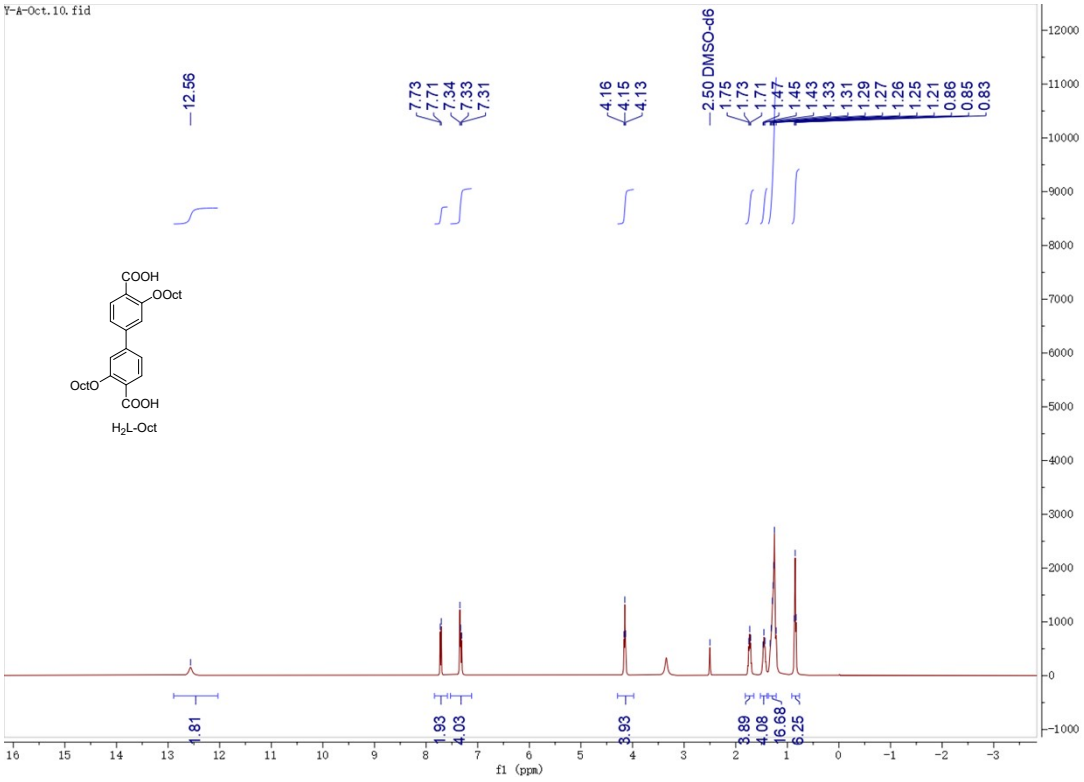

11.94
9.98
8.67
8.66
7.80
7.80
7.69
7.69
7.51
7.50
7.50
7.49
7.26 CDCl3
1.48
1.00
1.00
1.97
1.02
1.02
2.06
9.26
f1 (ppm)


14.18
8.58
8.57
8.57
8.56
8.36
7.52
7.51
7.35
7.35
7.34
7.34
7.27
7.27
7.26 CDCl3
7.26
3.41
3.40
3.40
3.39
2.08
2.05
2.04
1.96
1.95
1.93
1.84
1.80
1.55
1.53
1.52
1.51
1.44
1.28
1.27
1.27
2.00
4.05
2.04
2.06
4.03
2.07
2.07
2.00
2.03
2.04
2.06
18.34
f1 (ppm)


Et.20.fid
12.59
7.73
7.71
7.36
7.34
7.32
4.25
4.23
4.22
4.20
2.50 DMSO-d6
1.38
1.36
1.34
COOH
OEt
EtO
COOH
H2L-Et
2.21
2.00
3.99
4.09
6.09
f1 (ppm)


But.10.fid
2.50 DMSO-d6
COOH
OBut
ButO
COOH
H2L-But
2.02
2.00
3.97
3.98
4.00
4.03
6.03
f1 (ppm)


Hex.10.fid
7.72
7.70
7.35
7.34
7.33
7.33
7.31
7.31
4.16
4.15
4.13
2.50 DMSO-d6
1.98
1.75
1.73
1.72
1.71
1.48
1.46
1.44
1.32
1.31
1.30
1.29
1.28
1.21
1.18
1.17
1.15
0.89
0.87
0.85
COOH
OHex
HexO
COOH
H2L-Hex
1.27
2.00
3.94
3.84
30.75
f1 (ppm)


Y-A-Oct.10.fid
12.56
7.73
7.71
7.34
7.33
7.31
4.16
4.15
4.13
2.50 DMSO-d6
1.75
1.73
1.71
1.47
1.45
1.43
1.33
1.31
1.29
1.27
1.26
1.25
1.21
0.86
0.85
0.83
COOH
OOct
OctO
COOH
H2L-Oct
1.81
1.93
4.03
3.93
3.89
4.08
16.68
6.25
f1 (ppm)

SI-15 References

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