Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Construction of a PolyMOF using a Polymer Ligand bearing the Benzenedicarboxylic Acid Moiety in the Side Chain

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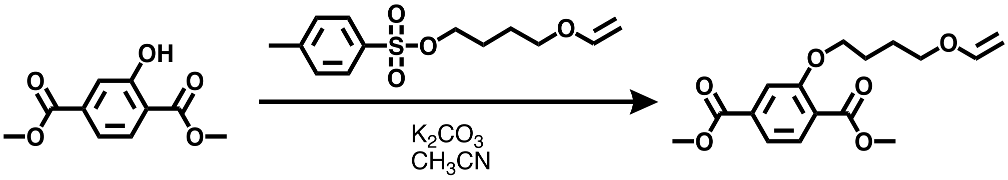
Materials and methods

NMR: Bruker AVANCEIII-HD (500 MHz), ESI-TOF MS: Bruker micrOTOF II, FT-IR: JASCO FT-IR-4200, XRD: Rigaku SmartLab.

Solvents and reagents: TCI Co. Ltd., Wako Pure Chemical Industries Ltd., Kanto Chemical Co. Inc., Sigma-Aldrich Co., and Cambridge Isotope Laboratories Inc. 4-(Tolylsulfonyl)butyl vinyl ether was synthesized according to previously reported procedures (C. Hellermark, U. W. Gedde, A. Hult, *Polymer* **1996**, *37*, 3191-3196).

Synthesis of monomer 1



Dimethyl 2-hydroxyterephthalate (3.2673 g, 15.545 mmol), 4-(tolylsulfonyl)butyl vinyl ether (4.7445 g, 17.550 mmol), K_2CO_3 (11.242 g, 81.345 mmol), and acetonitrile (ca. 200 mL) were added to a 500 mL glass flask containing a magnetic stirring bar. The mixture was stirred at 80 ºC for 1 day and then concentrated under reduced pressure. After the addition of water, the crude product was extracted with diethyl ether. The obtained organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by gel permeation chromatography to afford monomer **1** as a pale-yellow oil (4.1035 g, 13.308 mmol, 86% yield).

^{1}H-NMR (500 MHz, $CDCl_3$, r.t.): δ 7.79 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.61 (s, 1H), 7.48 (dd, J = 14.5, 7.0 Hz, 1H), 4.18 (dd, J = 14.5, 7.0 Hz, 1H), 4.13 (t, J = 6.0 Hz, 2H), 3.99 (dd, J = 7.0, 2.0 Hz, 1H), 3.93 (s, 3H), 3.90 (s, 3H), 3.76 (t, J = 6.0 Hz, 2H), 1.99-1.87 (m, 4H). ^{13}C-NMR (125 MHz, $CDCl_3$, r.t.): δ 166.4(C_q), 166.4(C_q), 158.2(C_q), 152.0(CH), 134.4(C_q), 131.5(CH), 124.6(C_q), 121.3(CH), 113.9(CH), 86.5(CH), 68.7(CH), 67.5(CH), 52.6(CH), 52.4(CH), 25.9 (CH), 25.8(CH). FT-IR (KBr, cm^{-1}): 2953, 2878, 1728, 1616, 1578, 1501, 1489, 1389, 1294, 1233, 1198, 1114, 1082, 1006, 964, 818, 756. HR MS (ESI-TOF; CH_3CN): *m/z* Calcd. 331.1152, Found 331.1149 [**1** + Na]$^+$.

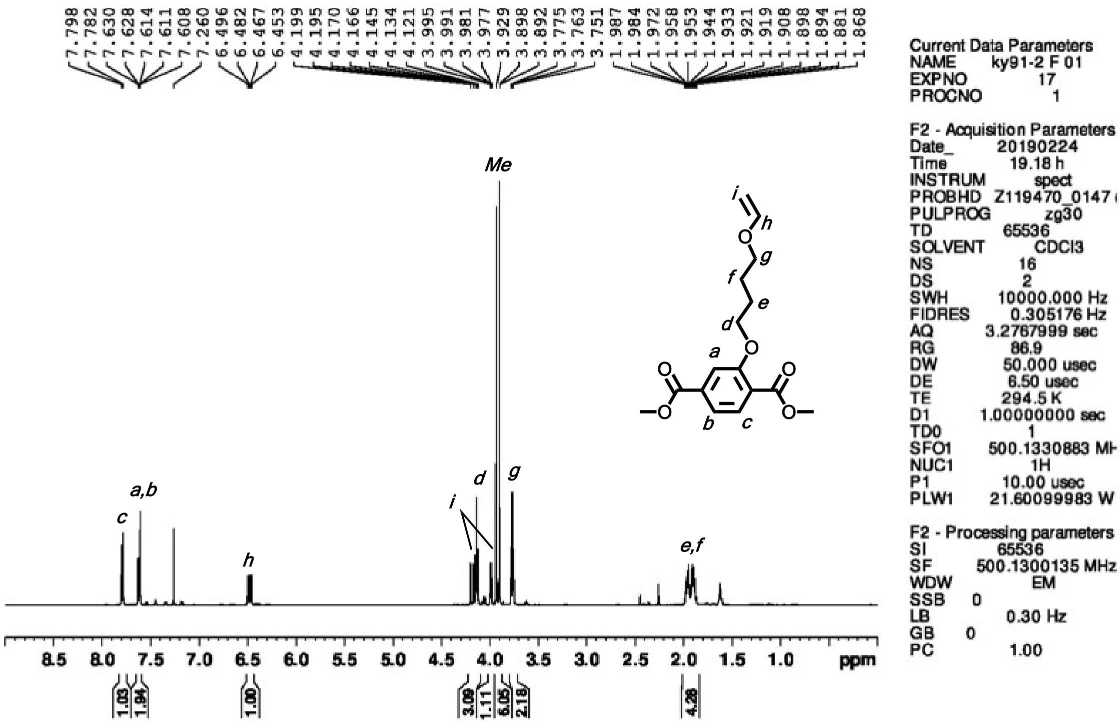


Figure S1. ^{1}H-NMR spectra (500 MHz, CDCl$_3$, r.t.) of **1**.

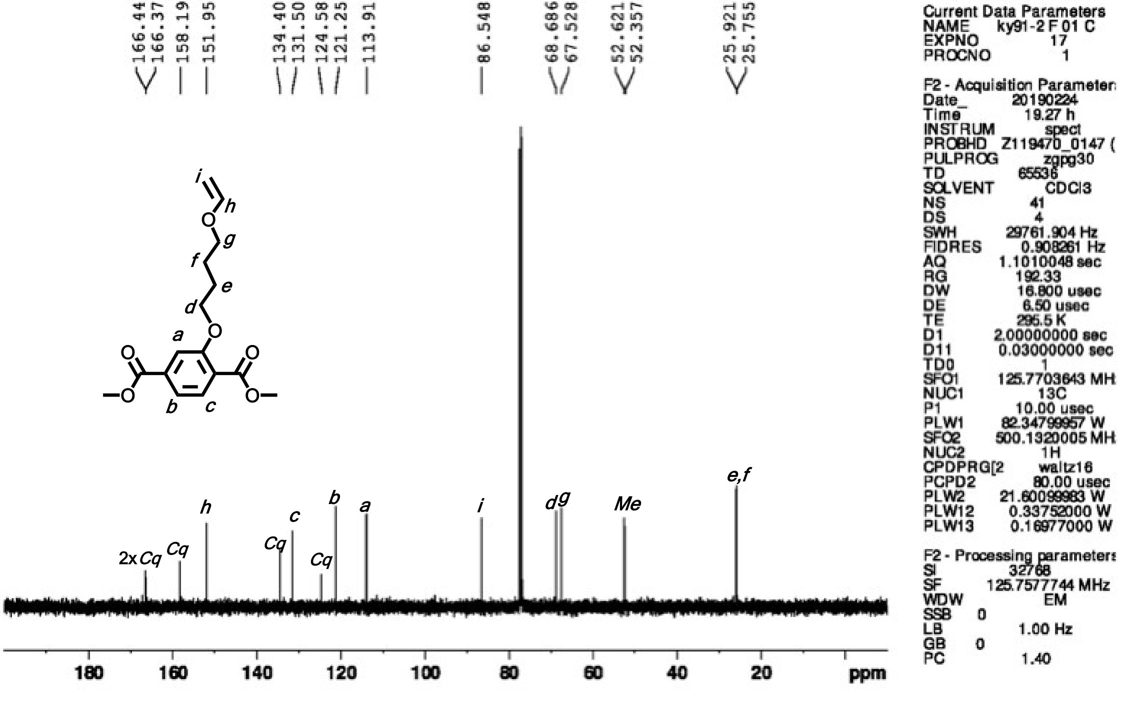


Figure S2. ^{13}C-NMR spectra (500 MHz, CDCl$_3$, r.t.) of **1**.

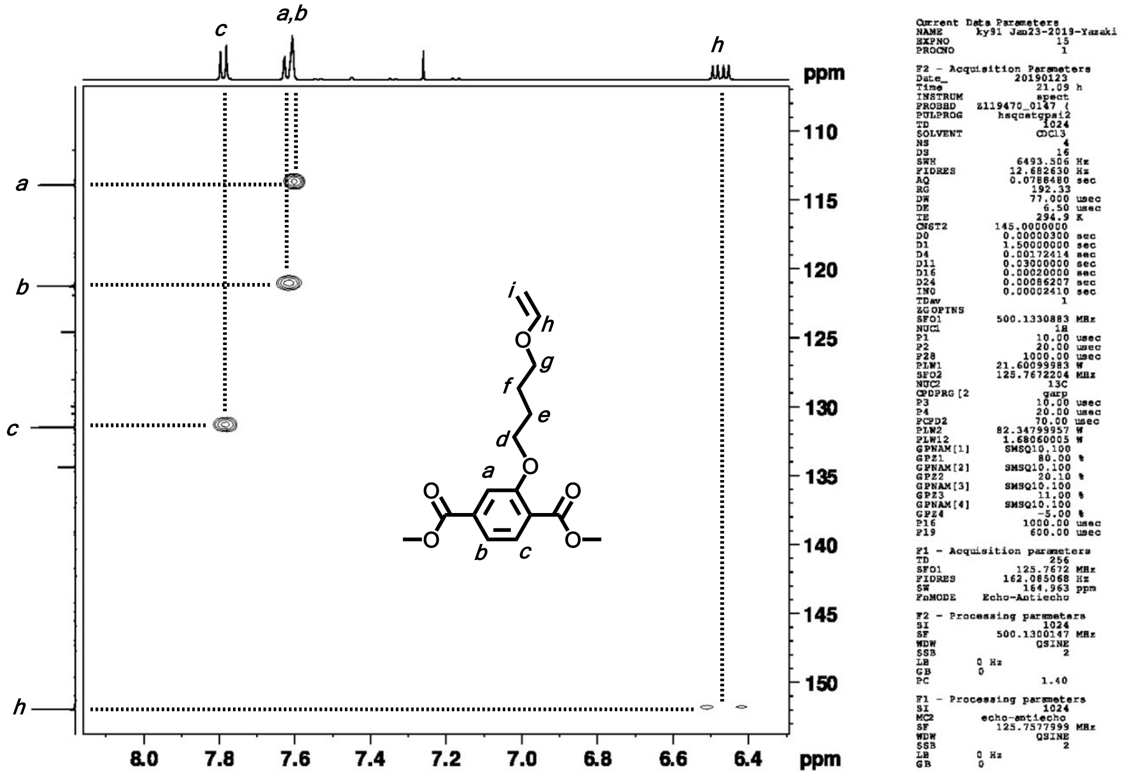


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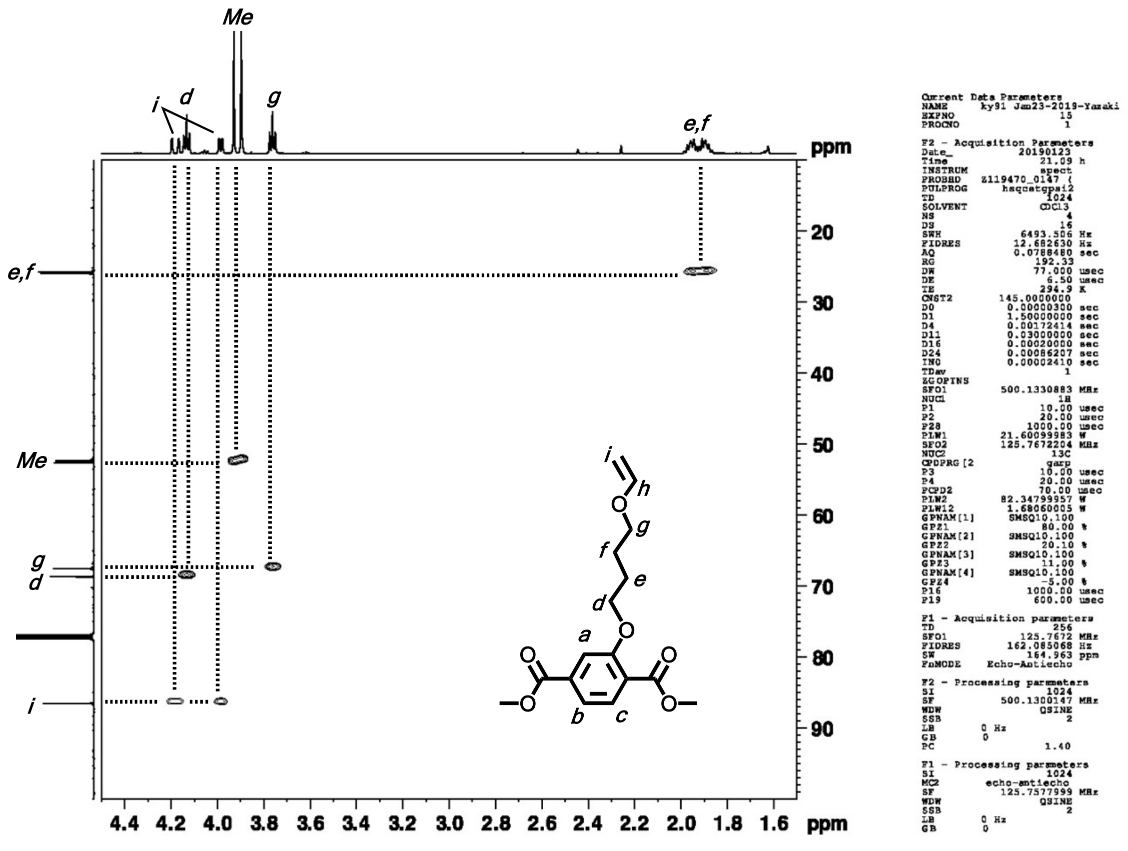
Figure S3. HSQC NMR spectra (500 MHz, $CDCl_3$, r.t.) of **1** (aromatic region).



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NUC1                    1H
P1                   10.00 usec
P2                   20.00 usec
P28                1000.00 usec
PLW1           21.60099983 W
SFO2           125.7672204 MHz
NUC2                   13C
CPDPRG[2              garp
P3                   10.00 usec
P4                   20.00 usec
PCPD2                70.00 usec
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PC                    1.40

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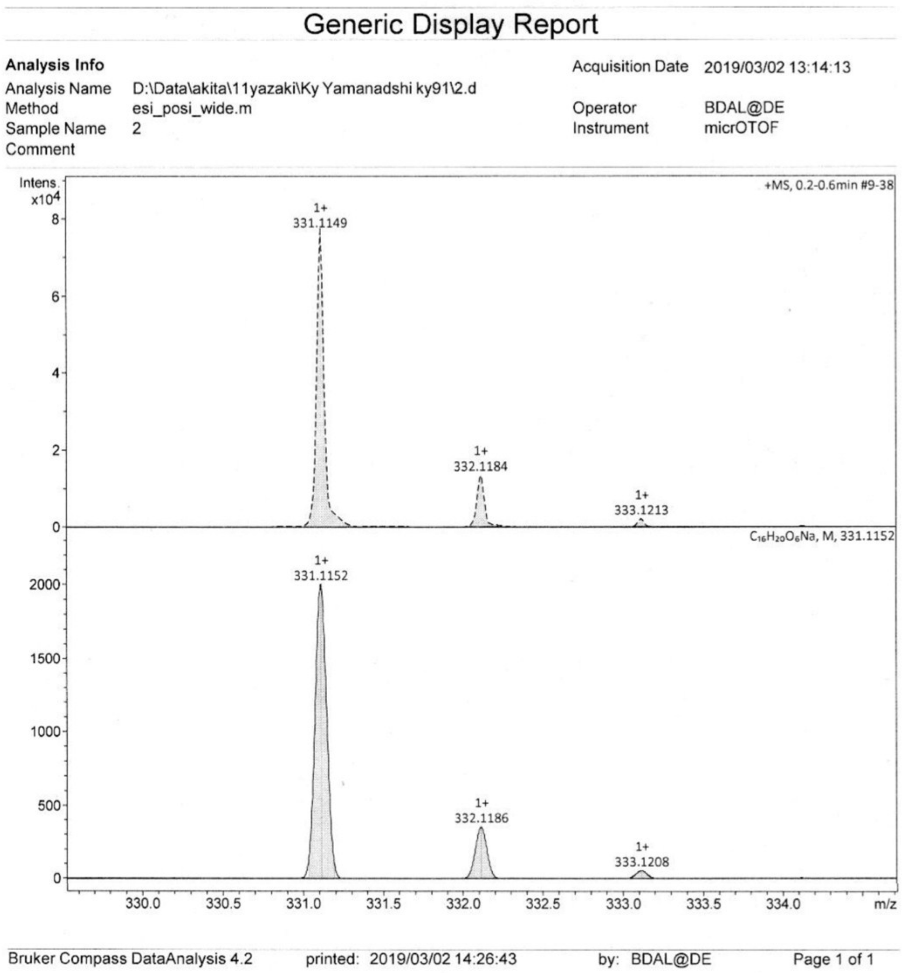
Figure S4. HSQC NMR spectra (500 MHz, $CDCl_3$, r.t.) of **1** (aliphatic region).



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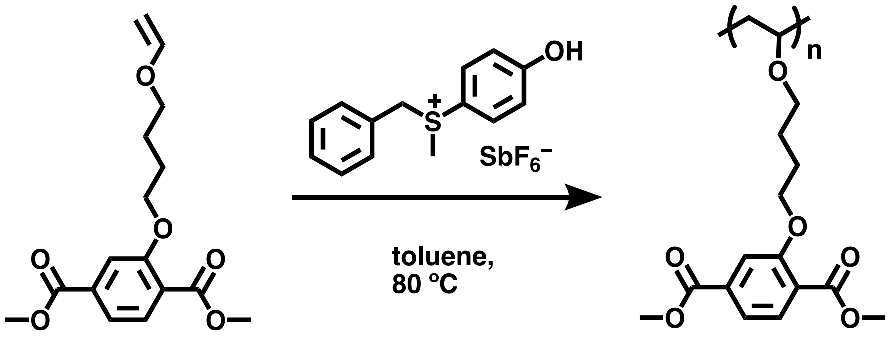
Operator BDAL@DE
Instrument micrOTOF

Bruker Compass DataAnalysis 4.2 printed: 2019/03/02 14:26:43 by: BDAL@DE Page 1 of 1

Figure S5. HR MS spectra (ESI, CF_3CO_2Na as an internal standard) of **1**.

Synthesis of polymer 2



Monomer **2** (7.5951 g, 24.633 mmol), thermal cationic polymerization initiators (55.6 mg, 0.119 mmol), and toluene (50 mL) were added to a 200 mL two-necked glass flask filled with N_2. The mixture was stirred at 80 °C for 14 h and poured into excess methanol to obtain a highly viscous brown liquid. This product was dissolved in CH_2Cl_2 and dropped into methanol. The obtained viscous brown liquid was dried under reduced pressure to obtain the target polymer **2'** (4.7530 g, 63% yield).

^{1}H-NMR (500 MHz, DMSO-d_6, r.t.): δ 7.87-7.31 (br, 3H), 4.16-3.92 (br, 2H), 3.92-3.71 (br, 6H), 3.71-3.25 (br, 3H), 2.00-1.34 (br, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$, r.t.): δ 166.1(C_q), 158.2(C_q), 134.2(C_q), 131.4(CH), 124.3(C_q), 121.1(CH), 113.7(CH), 73.8(CH), 52.5(CH), 52.2(CH), 27.1(CH), 26.5(CH). FT-IR (KBr, cm^{-1}): 2949, 2860, 1726, 1581, 1575, 1452, 1438, 1294, 1226, 1109, 1080, 1003, 962, 878, 816, 791, 754, 696.

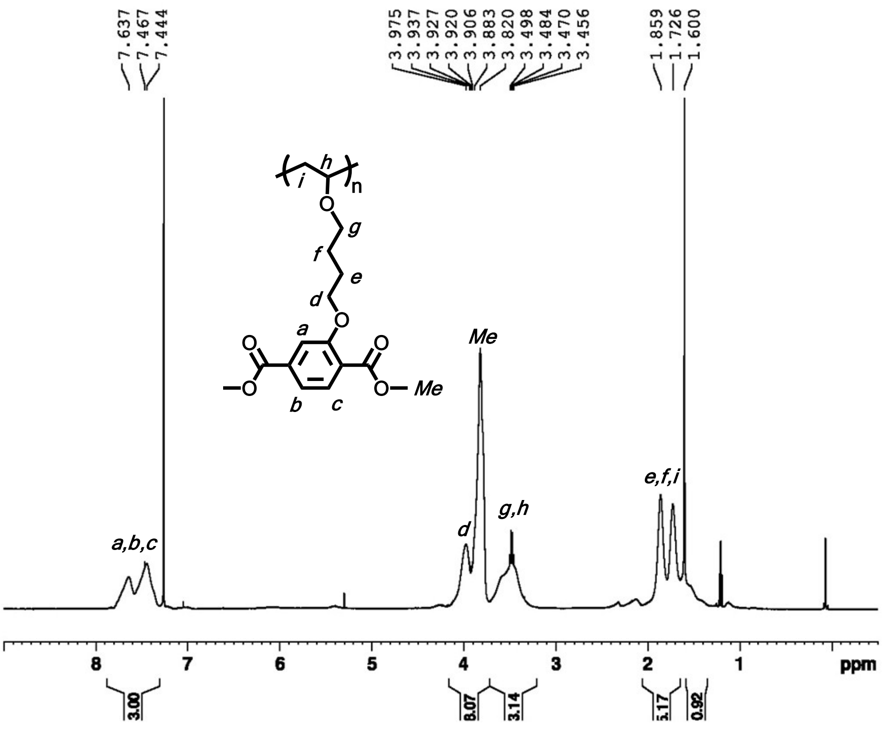


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Figure S6. ^{1}H-NMR spectra (500 MHz, CDCl$_3$, r.t.) of **2**.

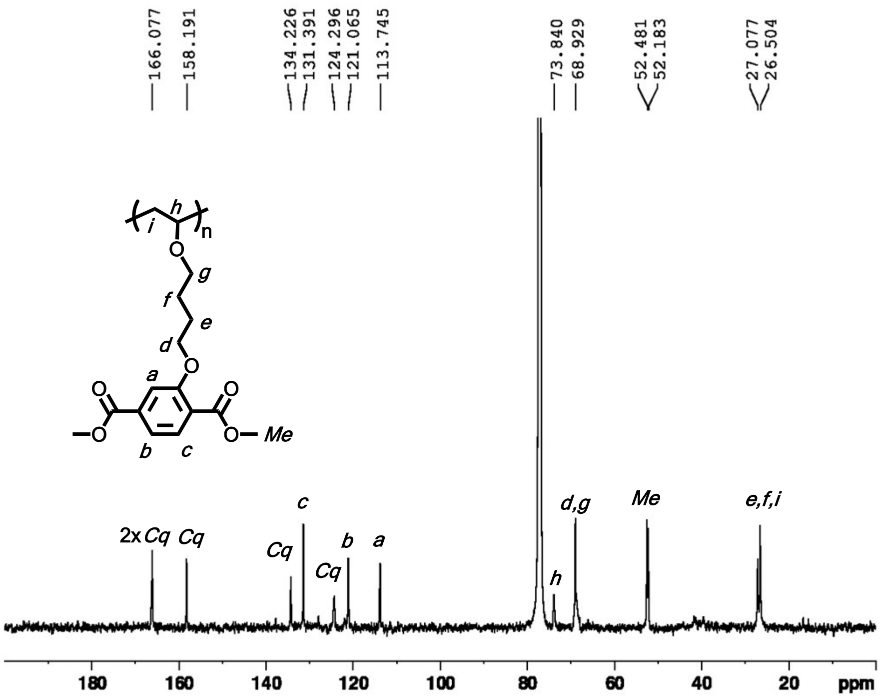

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Figure S7. ^{13}C-NMR spectra (500 MHz, CDCl$_3$, r.t.) of **2**.

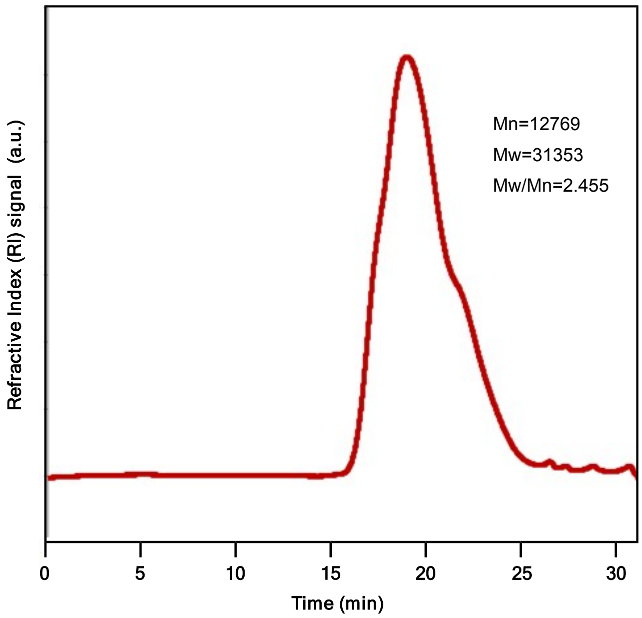
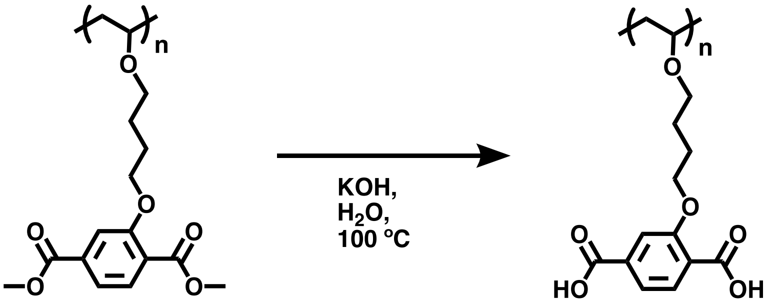


Figure S8. SEC chromatograms of polymer **2** (solvent: THF, reference: polystyrene standards).

Synthesis of polymer ligand 3



Polymer **2** (3.6618 g), KOH (15.1642 g, 0.5247 mmol), and H_2O (50 mL) were added to a 100 mL vessel. The mixture was stirred at 100 °C for 48 h and then poured into an aqueous HCl solution to obtain a brown solid. This product was washed with H_2O and methanol and dried under reduced pressure to obtain the target polymer ligand **3** (3.1431 g, 94% yield).

^{1}H-NMR (500 MHz, DMSO-d_6, r.t.): δ 13.00 (s, 2H), 7.76-7.34 (br, 3H), 4.20-3.72 (br, 2H), 3.72-2.95 (br, 3H+DMSO), 1.89-1.11 (6H). ^{13}C-NMR (125 MHz, DMSO-d_6, r.t.): δ 167.0(C_q), 166.6(C_q), 156.9(C_q), 134.4(C_q), 130.3(CH), 125.6(C_q), 1120.8(CH), 113.4(CH), 73.1(CH), 68.3(CH), 26.3(CH), 25.9(CH).

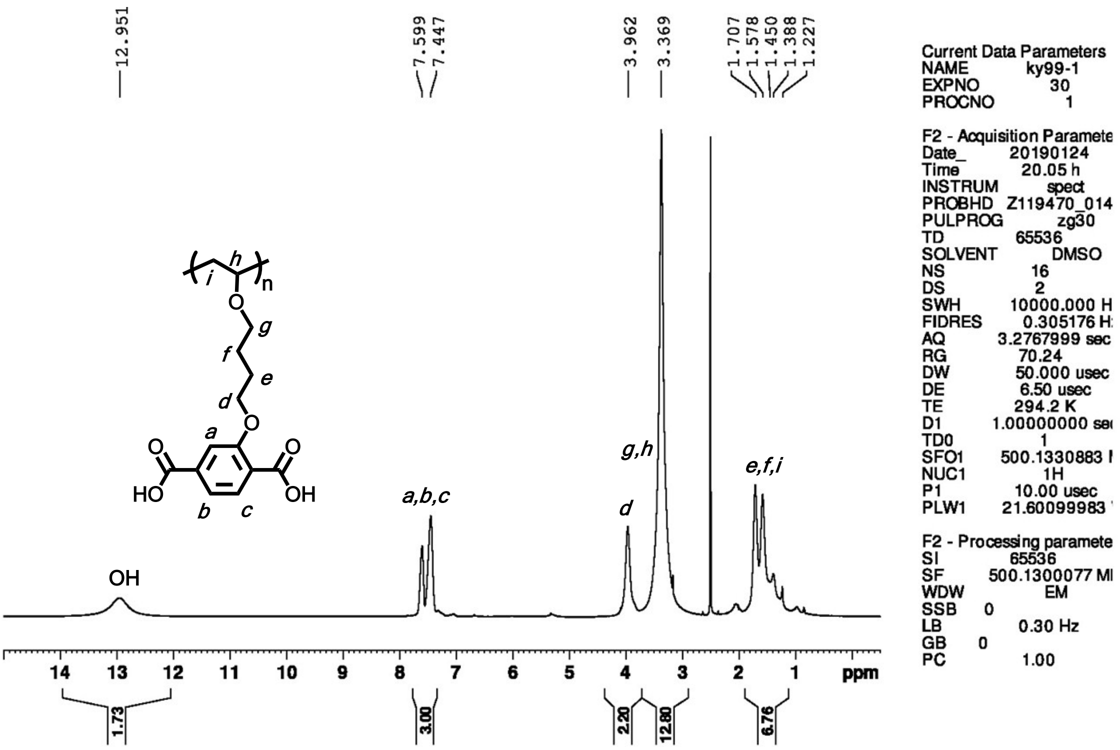


Figure S9. ^{1}H-NMR spectra (500 MHz, DMSO-d_6, r.t.) of **3**.

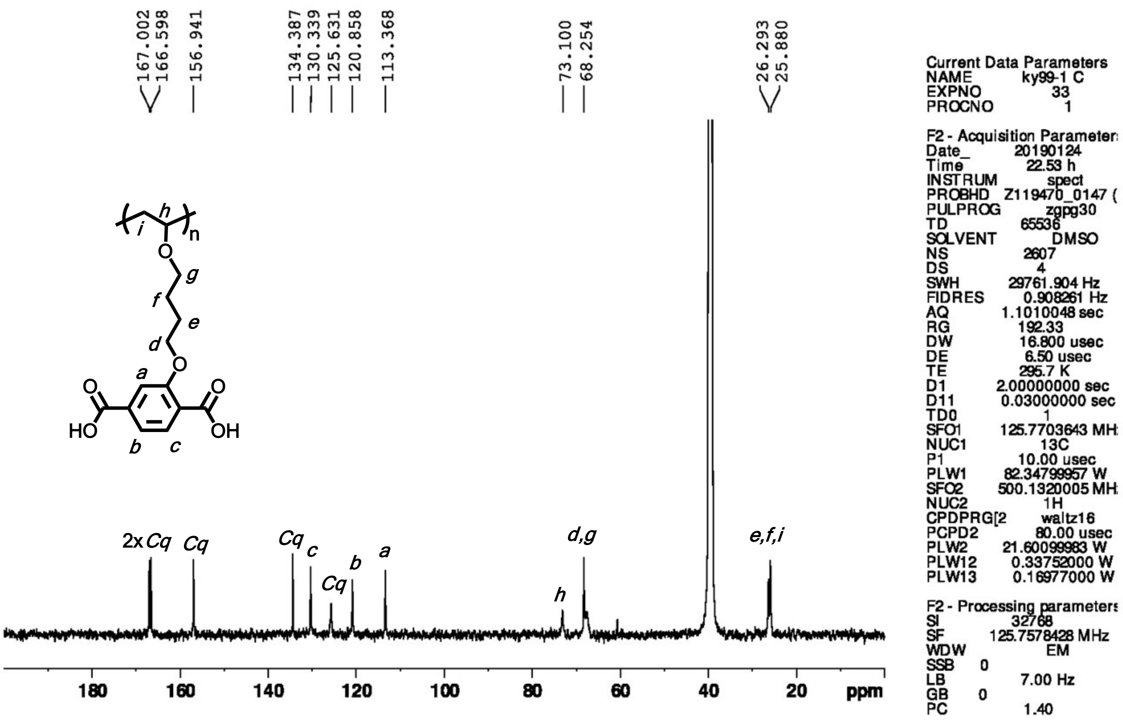


Figure S10. ^{13}C-NMR spectra (125 MHz, DMSO-d_6, r.t.) of **3**.

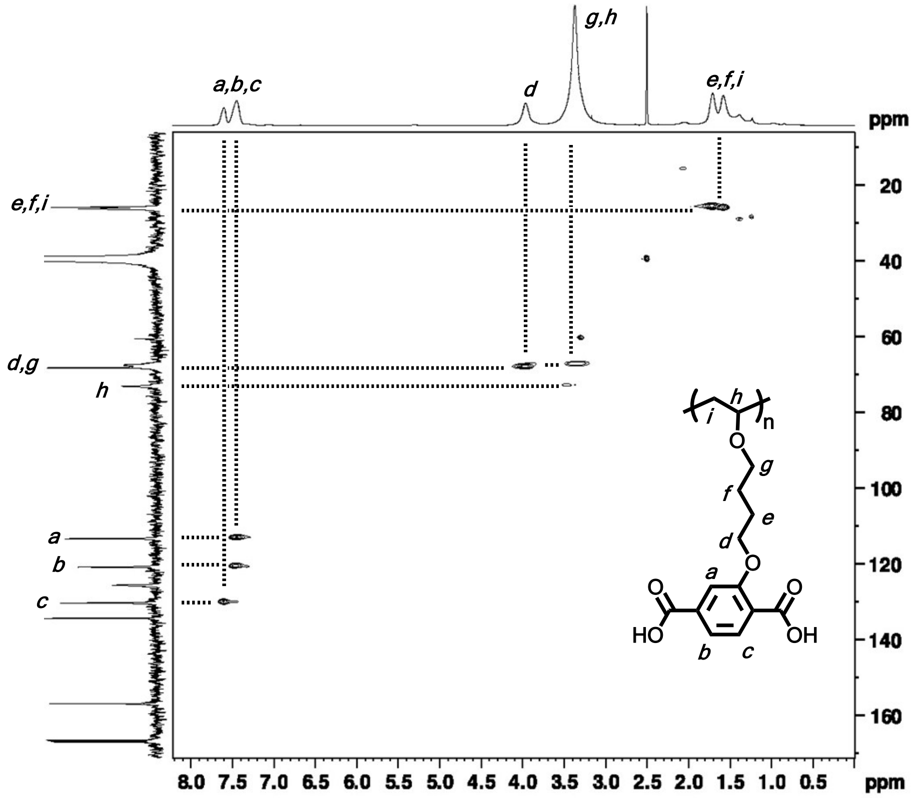


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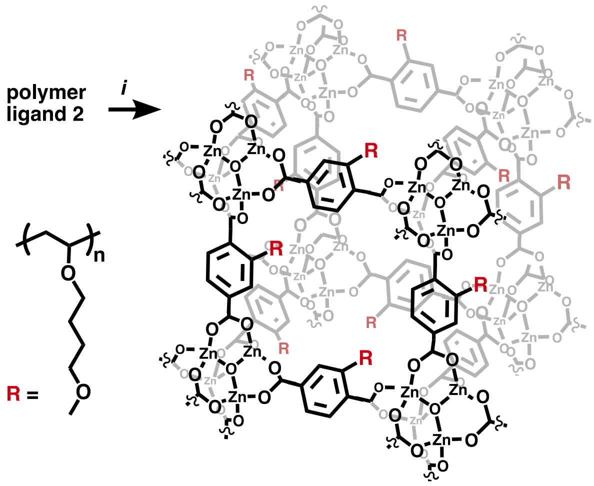
Figure S11. HSQC NMR spectra (500 MHz, $CDCl_3$, r.t.) of **3**.

Synthesis of polyMOF 4



Polymer ligand **3** (566.2 mg), $Zn(NO_3)_2\cdot 6H_2O$ (4.032 g), and DMF (ca. 40 mL) were added to a 50 mL glass vial. The mixture was heated to, and maintained at, 100 ºC for 4 days. A pale brown film appeared at the bottom of the vial. The product was washed with DMF and $CHCl_3$ to obtain polyMOF **4** (1.049 mg).

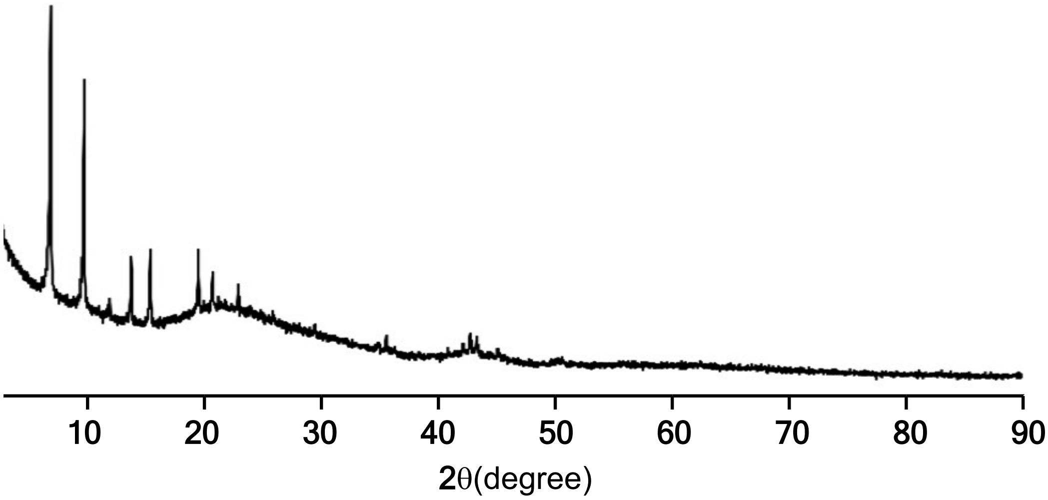


Figure S12. PXRD pattern of **4**.

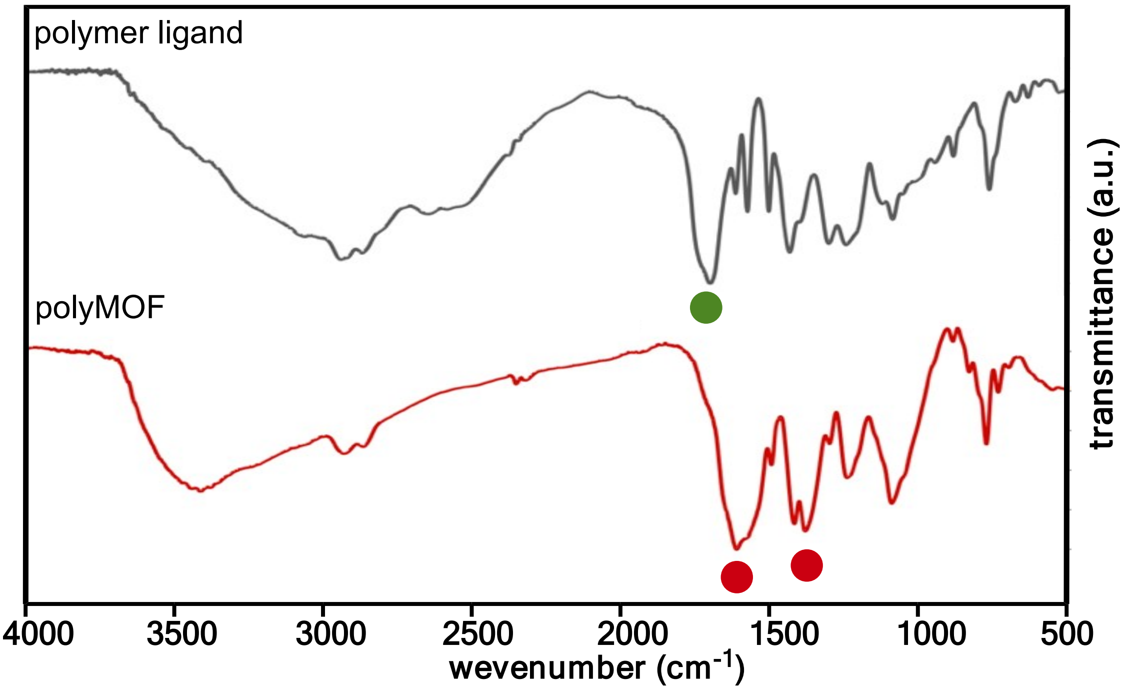


Figure S13. FT-IR spectra (KBr method) of (d) polymer ligand **3** and polyMOF **4** (the broad signal at 3000–3600 cm^{-1} represents absorbed water).

Solvent-exchange process of polyMOF 4

PolyMOF **4** (ca. 50 mg) was stored in a series of solvents ($CHCl_3$, CH_2Cl_2, pentane, and diethyl ether) in a 50 mL glass vial for 5 days. Each day the solvent was changed. The obtained samples were air-dried for 10 min, and subjected to PXRD analysis to confirm the crystal structure.

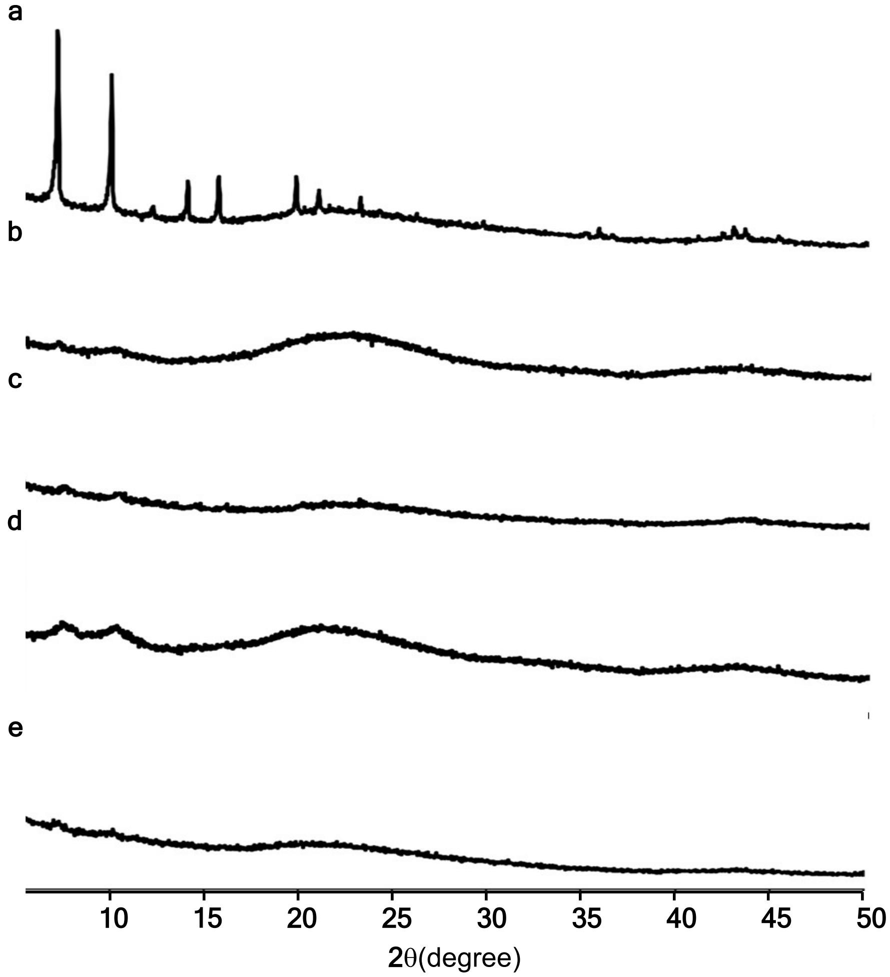


Figure S14. PXRD patterns of **4** a) before solvent exchange, and stored in b) diethyl ether, c) CH_2Cl_2, d), pentane, and e) $CHCl_3$.

Gas adsorption measurements of polyMOF 4

The BET adsorption experiment of polyMOF was measured using an BELSORP-max II instrument. A sample for gas adsorption measurements was stored in $CHCl_3$ for 4 days, heated to 100 °C under vacuum, and maintained at this temperature for 12 h. A sample (300 mg) was then added to a glass tube, and activated under preprocessing conditions (80 °C for 24 h under vacuum). The sample temperature during the gas adsorption experiment was maintained at 77 K using a liquid nitrogen bath.

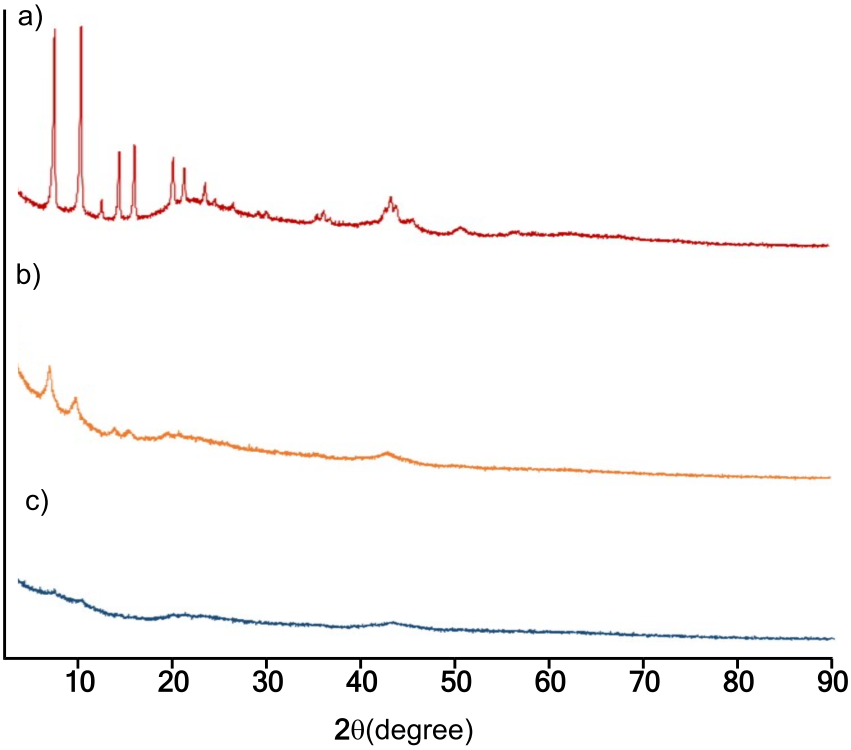


Figure S15. PXRD patterns of **4**. a) film form, b) stored in $CHCl_3$ then heated at 100 ºC for 12 h under vacuum, and c) after N_2 absorption (preprocessing condition is 80 ºC for 24 h under vacuum.)

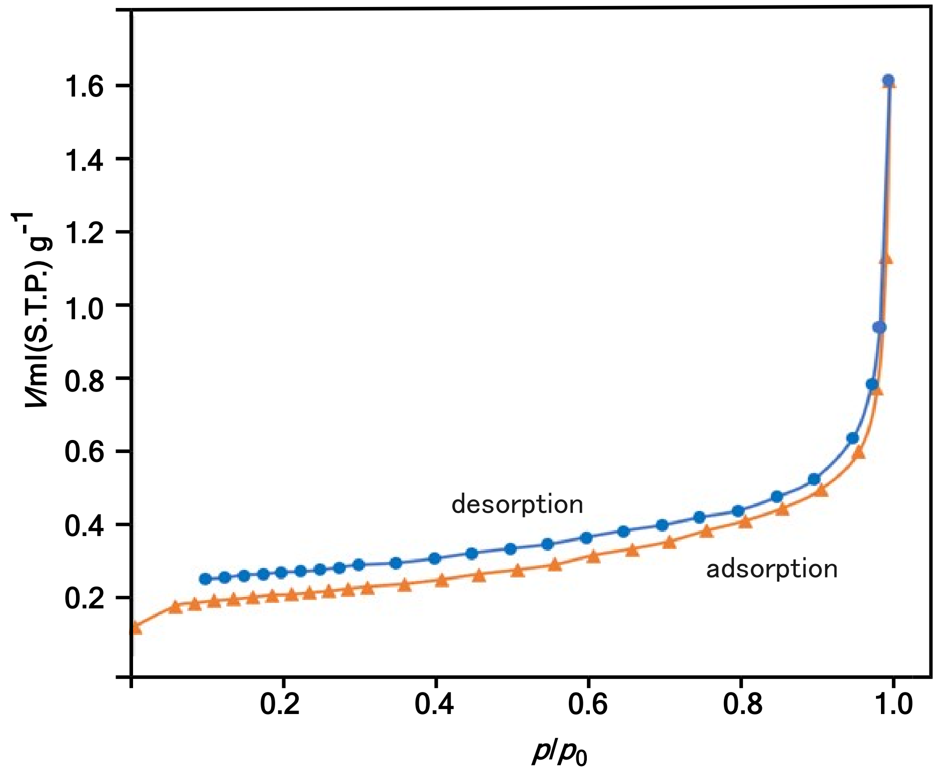


Figure S16. N_2 isotherms of decomposed **4**.

TGA Measurements of polyMOF 4

TGA was performed using a Shimazu DTG-60 instrument. A sample for TGA was stored in $CHCl_3$ for 5 days, and then air-dried for 30 min. A sample (38.3 mg) was placed in an alumina pan and heated at a rate of 0.2 °C min^{-1} from m 33 to 1000 °C with a purge gas (air) flow rate of 150 mL min^{-1}. PolyMOF $(C_{14}H_{14}O_6)_3Zn_4O)$ was converted to a white residue (5.71 mg). The weight loss that occurred between 100 and 235 ºC, ~26% (9.88 mg), corresponds to the evaporation of trapped solvent molecules. The weight loss between 235 and 1000 °C, ~59% (22.7 mg), is attributed to the decomposition of the free ligand the polyMOF structure. The white residue, ~15%, was ZnO (5.71 mg, 70.0 µmol). This amount of ZnO revealed that the ligand unit constituted 52.5 µmol of the MOF structure and 31.8 µmol of the free ligand unit. Therefore, 62% of the polymer ligand formed the MOF structure.

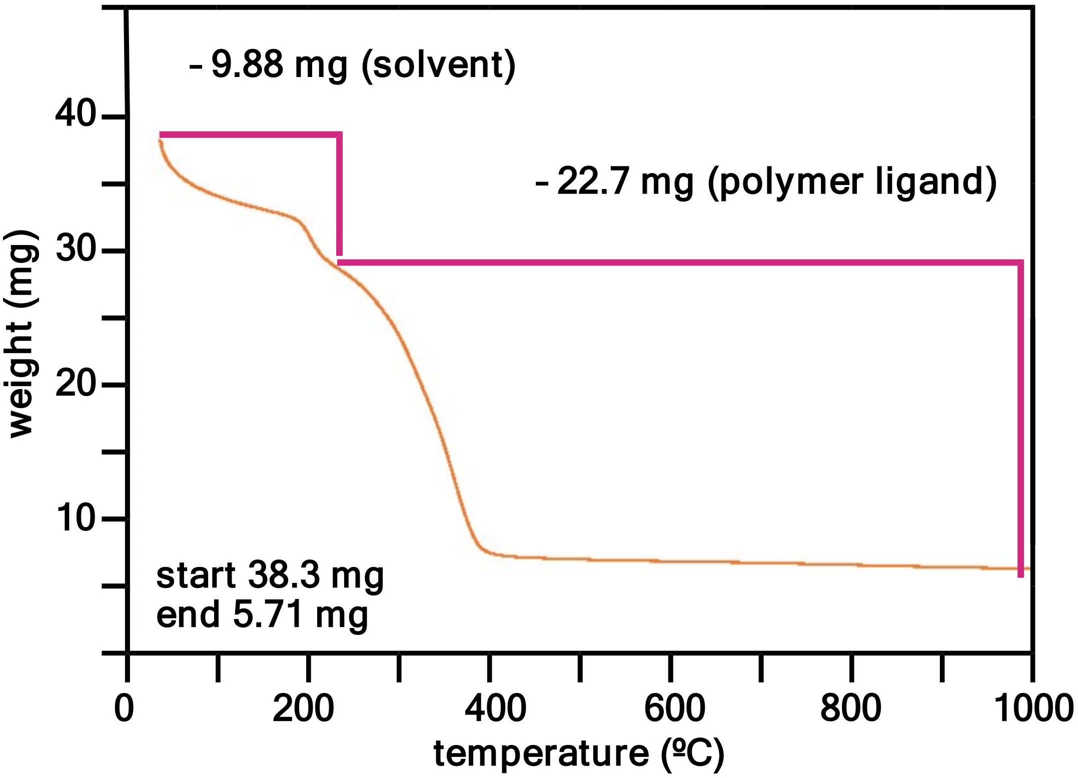
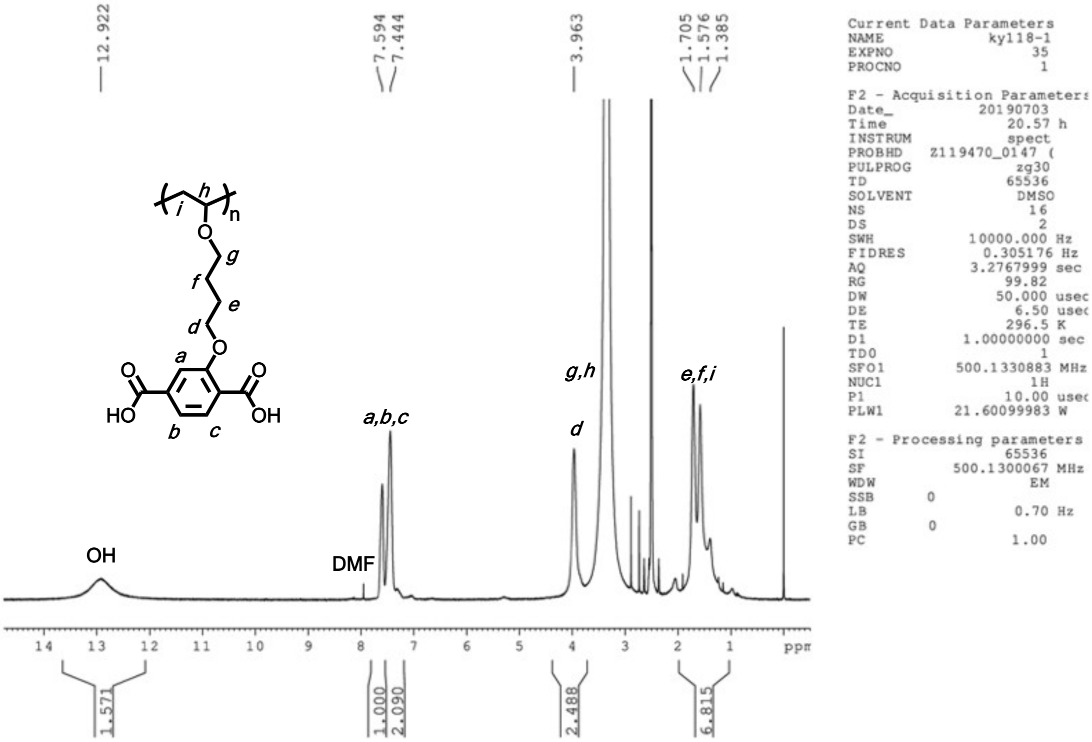


Figure S17. TGA of **4**.



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PULPROG            zg30
TD                65536
SOLVENT            DMSO
NS                   16
DS                    2
SWH          10000.000 Hz
FIDRES        0.305176 Hz
AQ           3.2767999 sec
RG                99.82
DW               50.000 usec
DE                 6.50 usec
TE                296.5 K
D1           1.00000000 sec
TD0                   1
SFO1        500.1330883 MHz
NUC1                 1H
P1                10.00 usec
PLW1        21.60099983 W

F2 - Processing parameters
SI                65536
SF          500.1300067 MHz
WDW                  EM
SSB        0
LB                 0.70 Hz
GB         0
PC                 1.00
```

Figure S18. ^{1}H-NMR spectra (500 MHz, DMSO-d_6, r.t.) of **2** obtained by disassembly of polyMOF **4**.

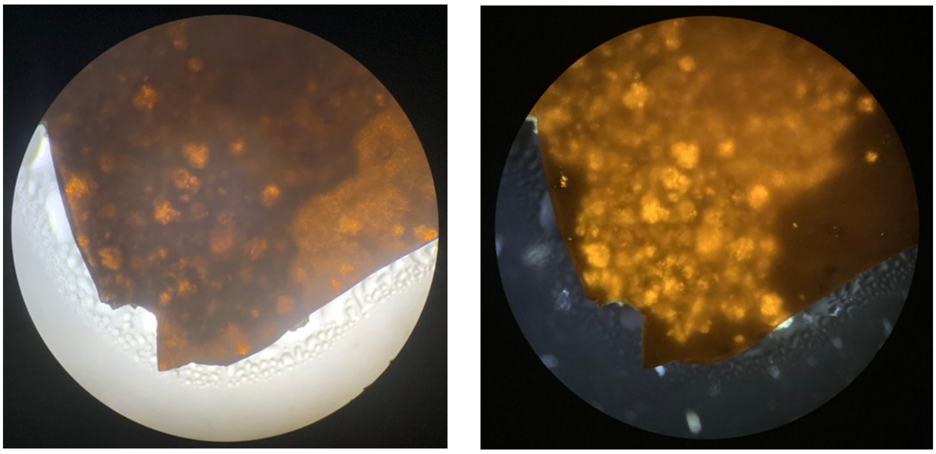

Figure S19. Transmission-type polarizing microscope images of **4** (magnification of 20); 0º (right) and 90º (left).

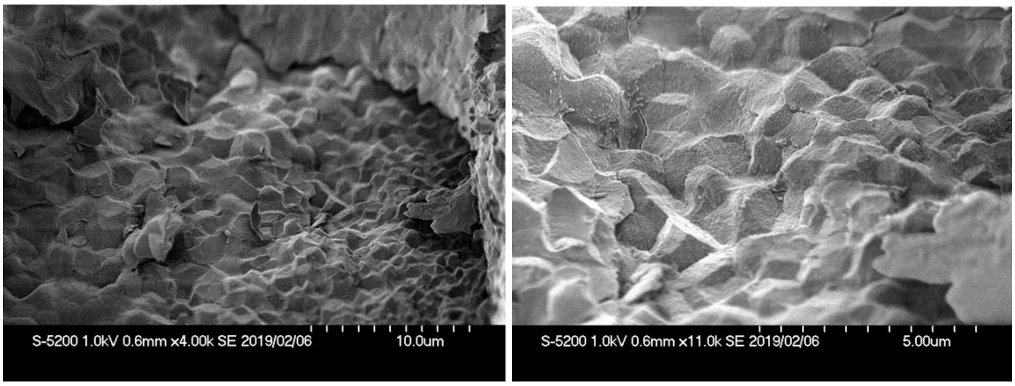

Figure S20. SEM image of polyMOF **4**.