Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supplementary Information

Unusual ligand substitution of a metal-organic framework with distorted metal-ligand coordination

Hikaru Sakamoto, Akitaka Ito, and Masataka Ohtani[†,*]

[†] School of Environmental Science and Engineering, Kochi University of Technology

185 Miyanokuchi, Tosayamada, Kami, Kochi 782-8502, Japan

E-mail: ohtani.masataka@kochi-tech.ac.jp (M.O.)

Table of Contents

1. Materials S2

2. Experimental Procedure S2

3. Supporting Figures S4

1. Materials

All the reagents and chemicals used were obtained from commercial sources and used as received, unless otherwise noted. Methanol (MeOH), *N*,*N*-dimethylformamide (DMF), 2-propanol, hexane, zinc (II) acetate hexahydrate ($Zn(OAc)_2 \cdot 6H_2O$), ortho-phthalic acid (*o*-H_4PA), triethylamine (TEA) and para-tetrafluorohthalic acid (*p*-F_4PA) were purchased from Wako Pure Chemical Industries Co. Ltd (Japan). Ortho-tetrafluorophthalic acid (*o*-F_4PA) was obtained from Sigma Aldrich.

2. Experimental Procedure

2.1 Synthesis of Zn-phthalate metal-organic framework [Zn(*o*-H_4P)-MOF]

$Zn(OAc)_2 \cdot 6H_2O$ (0.2 mmol) and ortho-phthalic acid (1 mmol) were dissolved in MeOH (50 mL). The resultant precursor solution was stirred for 5 min and transferred to an autoclave reactor of 100 mL inner volume. The sealed precursor solution was heated at a rate of 2 ºC/min to 100 ºC in a bead bath, held at 100 ºC for 4 days and then cooled to room temperature. The obtained crystals were centrifuged, washed several times with MeOH, and dried under vacuum (30 ºC, 1 day) to give a product (25 mg, 53%).

2.2 Ligand substitution reaction of Zn(*o*-H_4P)-MOF with *o*-F_4PA

Zn(*o*-H_4P)-MOF (100 mg) was dissolved in 10 mL of DMF in a centrifuge tube, and then 0.43 mmol of *o*-F_4PA was added to reach a molar ratio of 1:1:130 (Zn(*o*-H_4P)-MOF/*o*-F_4PA /DMF). After that, the reaction tube was left to stand at room temperature for 3 days.

2.3 Ligand substitution reaction of Zn(*o*-H_4P)-MOF with *p*-F_4PA

Zn(*o*-H_4P)-MOF (150 mg) was dissolved in 10 mL of DMF and 50 μL of H_2O in a centrifuge tube, and then 0.8 mmol of *p*-F_4PA was added to reach a molar ratio of 1:1:2.7:130 (Zn(*o*-H_4P)-MOF/ *o*-F_4PA /H_2O/DMF). After that, the reaction tube was left to stand at room temperature for 3 days.

2.4 Synthesis of Zn(*o*-F_4P)$_{6.5}$(*o*-H_4P)$_{3.5}$

$Zn(OAc)_2 \cdot 6H_2O$ (1 mmol) and phthalic acid (2.5 mmol), *o*-F_4PA (2.5 mmol), TEA (0.5 mmol) were dissolved in MeOH (50 mL). The resultant precursor solution was stirred for 5 min and transferred to an autoclave reactor of 100 mL inner volume. After that, the precursor was heated at a rate of ca. 2 ºC/min to 100 ºC in a bead bath, held at 100 ºC for 1 day and then cooled to room temperature. The obtained crystals were centrifuged, washed several times with MeOH, and dried

under vacuum (30 ºC, 24 hour) to give a product (178 mg, 64%).

To observe the structural transition from Zn(*o*-F_4PA)$_{0.65}$(*o*-H_4P)$_{0.35}$ to Zn(*o*-F_4P)-MOF, Zn(*o*-F_4PA)$_{0.65}$(*o*-H_4P)$_{0.35}$ was dispersed in DMF without any additional ligands for 1 day at room temperature.

2.5 Scanning Electron Microscopy

Scanning electron microscopy (SEM) images were measured on a Hitachi FE-SEM SU-8020 scanning electron microscope. A specimen was prepared by directly placing the bulk powder on a conducting carbon tape.

2.6 Powder X-ray diffraction (XRD) measurement

Powder X-ray diffraction (XRD) measurements were performed using a Rigaku SmartLab SE diffractometer with graphite-monochromatized Cu-K_α radiation (X-ray wavelength: 1.5418 Å) in steps of 0.01° over the 2θ range of 5−60°. A sample was set in a standard glass holder or a non-refractive silicon holder (Overseas X-Ray Service, Saitama, Japan).

2.7 Optical microscopy

Optical microscopy was carried out with a Kenis Zoom Stereomicroscope TF50-B with a digital camera attached. For the preparation of the specimen, the powdery MOF sample was dispersed in solvent DMF with sonication. The resultant dispersion was drop-casted on a glass plate. The solvent was vaporized under dry or wet air conditions.

2.8 Single-crystal X-ray diffraction measurement

Data collection for X-ray crystal analysis was performed on Rigaku/XtaLAB Synergy-S/Mo (Mo K_α = 0.71073 Å) diffractometers. The X-ray diffraction measurement was performed at –150°C. The structures were solved by direct methods (SHELXT) and refined through full-matrix least-squares techniques on F2 using SHELXL and OLEX2 crystallographic software packages. All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were placed at calculated positions and refined “riding” on their corresponding carbon atoms.

3. Supporting Figures

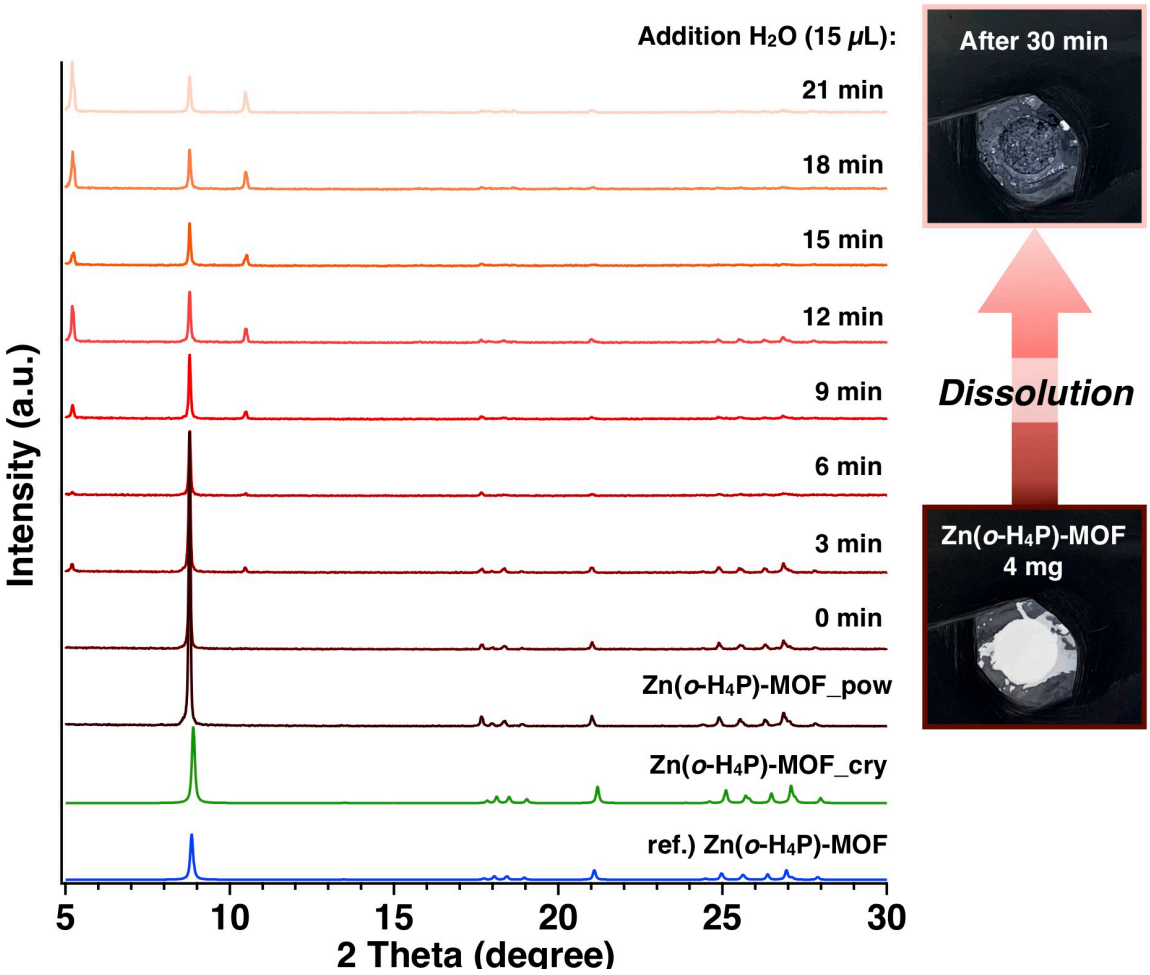

Figure S1. Comparison of XRD patterns: (blue) calculated XRD pattern from the cif file (CCDC-908149), (green) as-prepared Zn(*o*-H_4P)-MOF crystal, and time-course change in PXRD patterns of Zn(*o*-H_4P)-MOF powder upon adding H_2O (15 μL). Photographs of powdery samples before and after adding H_2O.

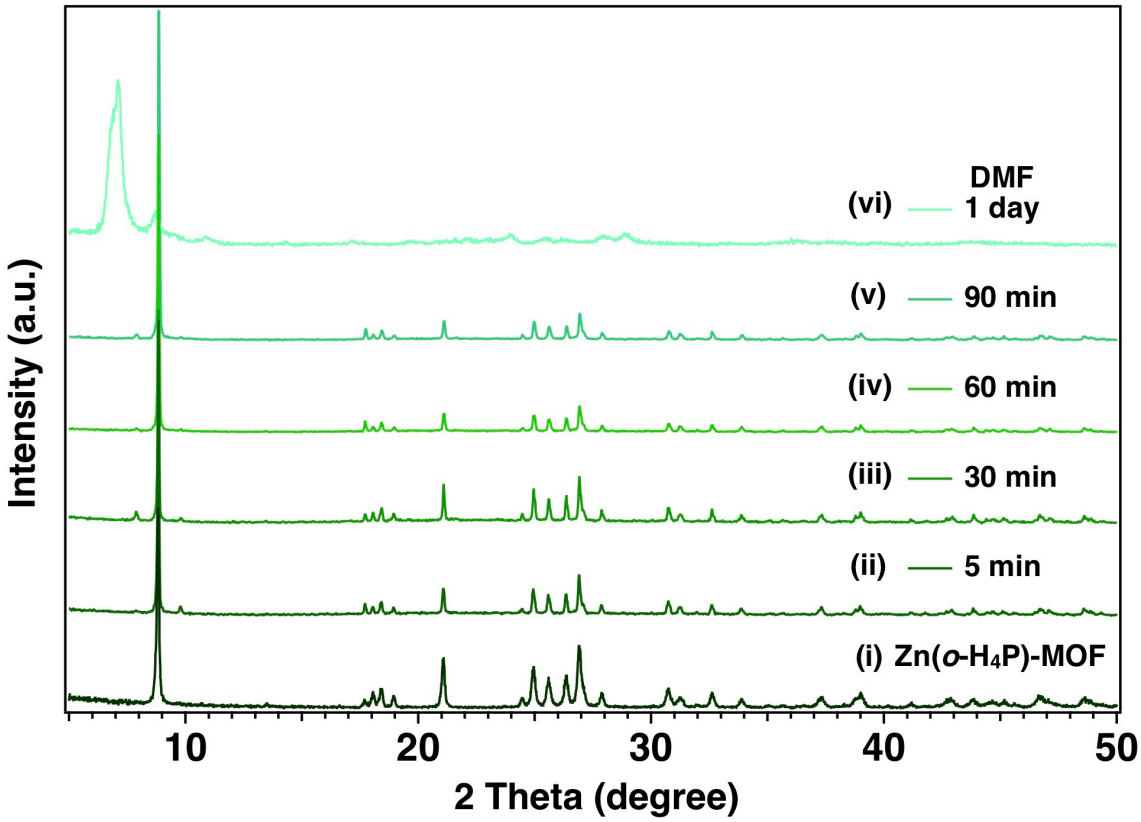

Figure S2. XRD patterns of samples with different dispersion time in DMF: (i) as-prepared Zn(*o*-H_4P)-MOF, (ii) 5 min, (iii) 30 min, (iv) 45 min, (v) 60 min, (vi) 1 day.

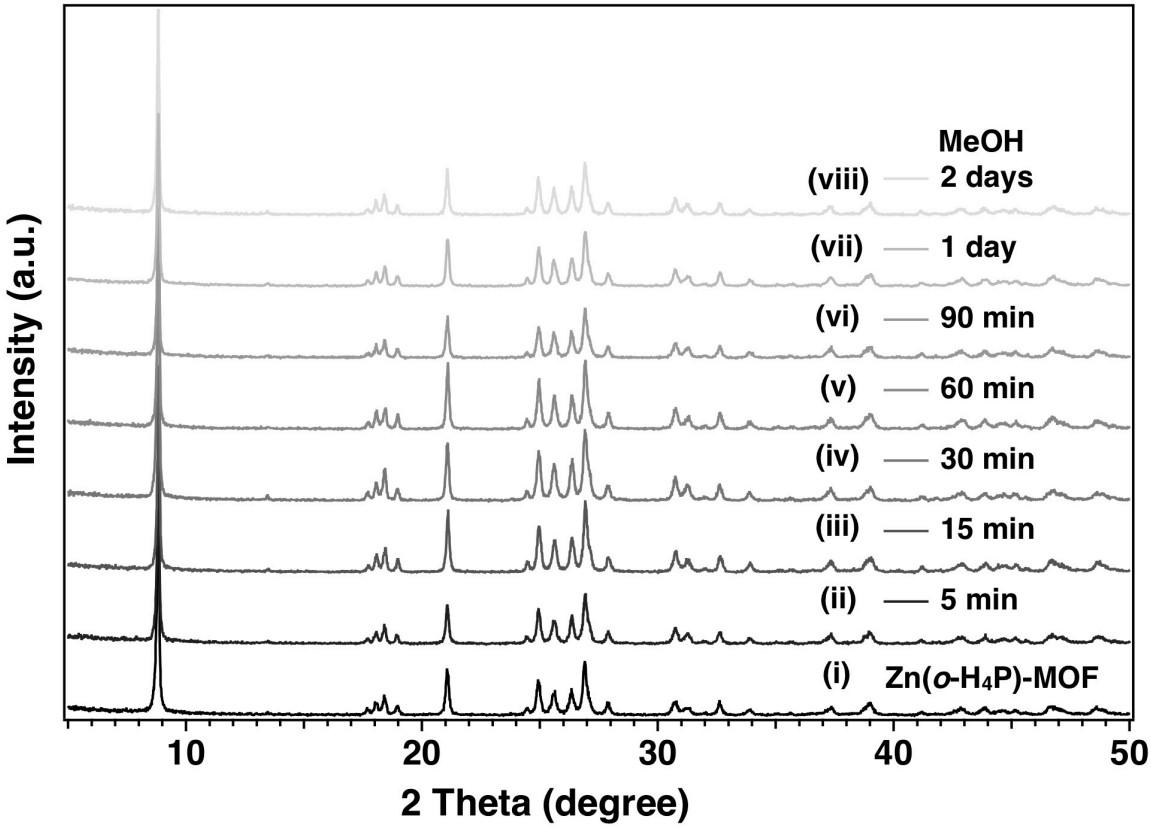

Figure S3. XRD patterns of samples with different dispersion time in MeOH: (i) as-prepared Zn(*o*-H_4P)-MOF, (ii) 5 min, (iii) 30 min, (iv) 45 min, (v) 60 min, (vi) 90 min, (vii) 1 day, (viii) 2 days.

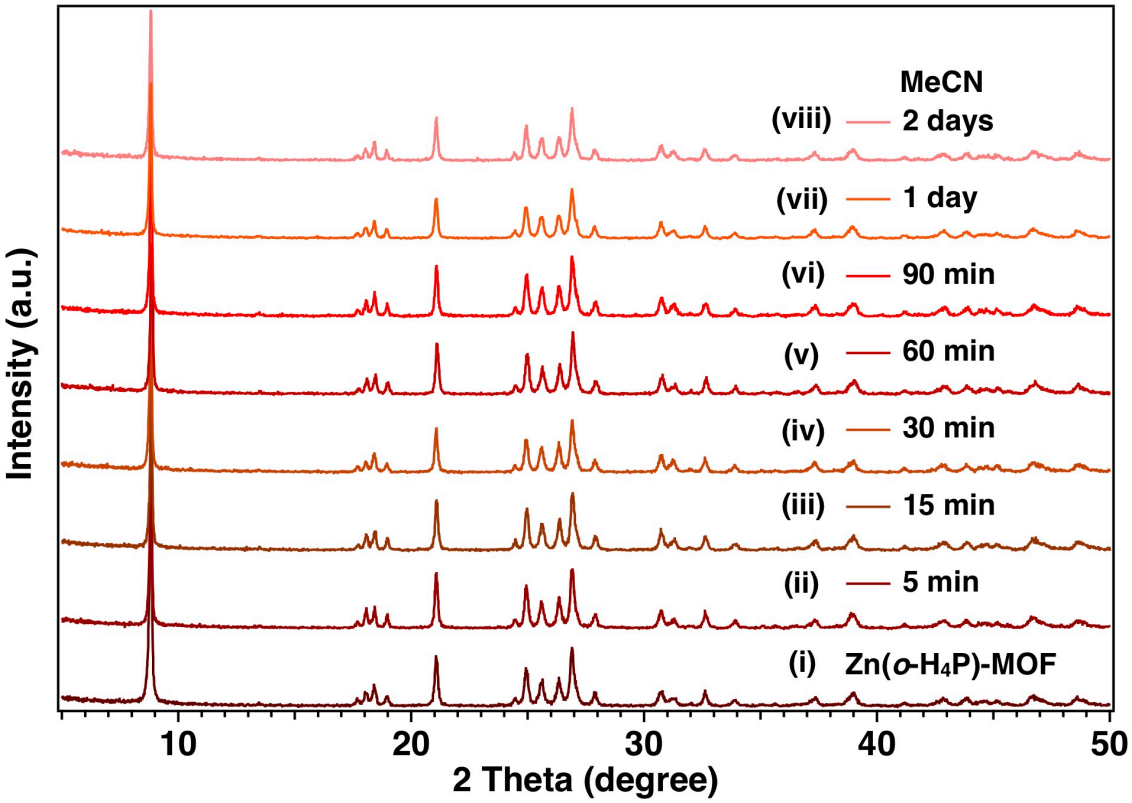

Figure S4. XRD patterns of samples with different dispersion time in MeCN: (i) as-prepared Zn(*o*-H_4P)-MOF, (ii) 5 min, (iii) 30 min, (iv) 45 min, (v) 60 min, (vi) 90 min, (vii) 1 day, (viii) 2 days.

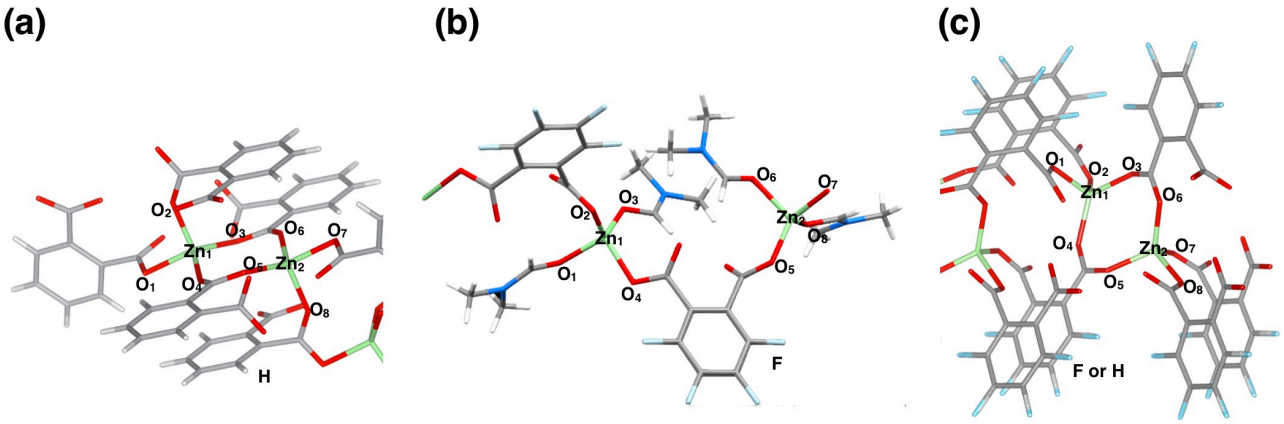

Figure S5. The fragments of each crystal with numbering scheme: (a) Zn(*o*-H_4P)-MOF, (b) Zn(*o*-F_4P)-MOF, and (c) Zn(*o*-F_4P)$_{6.5}$(*o*-H_4P)$_{3.5}$. *Zn atoms, light green sticks; O atoms, red sticks; C atoms, grey sticks; N atoms; blue sticks; F atoms, light blue; H atoms, white sticks*

Table S1. Selected average angles (°) and standard deviation

Bite angle (°)	Zn(*o*-H_4P)-MOF	Zn(*o*-F_4P)-MOF	Zn(*o*-F_4P)$_{6.5}$(*o*-H_4P)$_{3.5}$
O_1-Zn_1-O_2	116.06(9)	110.171(3)	106.60(12)
O_1-Zn_1-O_3	109.64(8)	113.335(3)	110.61(13)
O_1-Zn_1-O_4	127.63(10)	118.305(2)	107.09(14)
O_2-Zn_1-O_3	107.54(9)	95.611(3)	109.25(14)
O_2-Zn_1-O_4	96.44(9)	104.635(3)	101.94(14)
O_3-Zn_1-O_4	96.74(9)	111.939(3)	120.31(15)
O_5-Zn_2-O_6	127.63(10)	118.305(2)	126.72(14)
O_5-Zn_2-O_7	96.74(9)	113.335(3)	103.65(14)
O_5-Zn_2-O_8	96.44(9)	110.171(3)	101.39(14)
O_6-Zn_2-O_7	109.64(8)	111.939(3)	108.23(12)
O_6-Zn_2-O_8	116.06(9)	104.635(3)	103.29(14)
O_7-Zn_2-O_8	107.54(9)	95.611(3)	112.37(13)
Average	109.008	108.999	109.287
standard deviation	10.859	7.230	7.268

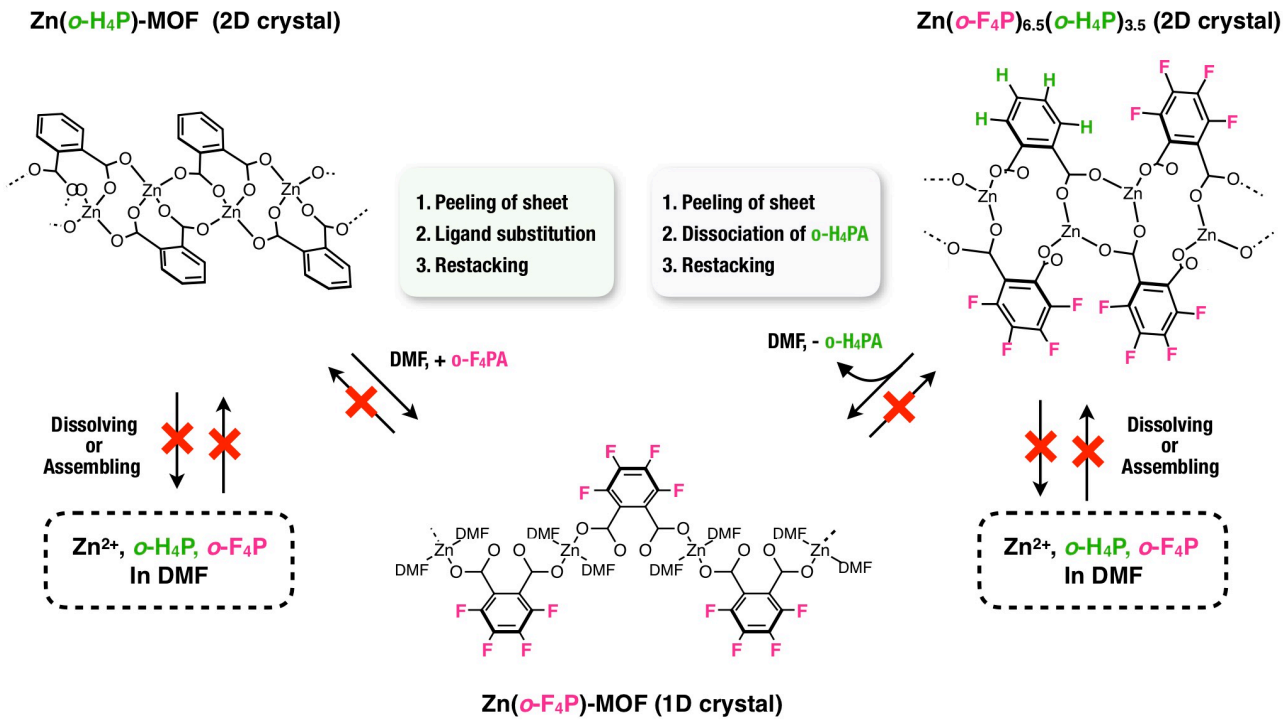

Figure S6. Schematic illustration of structural transition pathway of Zn(*o*-H_4P)-MOF and Zn(*o*-F_4P)$_{6.5}$(*o*-H_4P)$_{3.5}$-MOF.

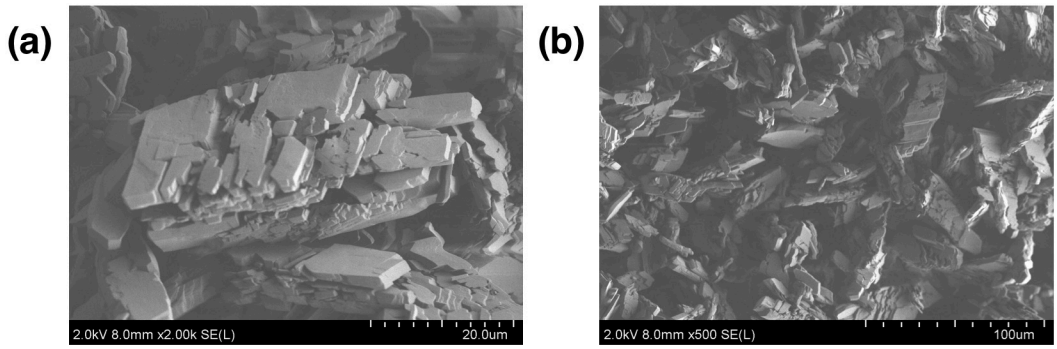

Figure S7. SEM images of Zn(*p*-F_4P)-MOF: (a) high magnification, (b) low magnification.

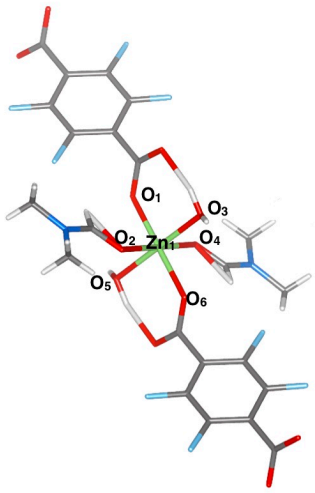

Figure S8. The fragments of Zn(*p*-F_4P)-MOF with numbering scheme.

Table S2. Selected average angles (°) and standard deviation.

Bite angle (°)	Zn(*p*-F_4P)-MOF
O_1-Zn_1-O_2	93.52(8)
O_1-Zn_1-O_3	92.17(9)
O_1-Zn_1-O_4	86.48(8)
O_1-Zn_1-O_5	87.83(9)
O_1-Zn_1-O_6	180.0000(0)
O_2-Zn_1-O_3	91.17(8)
O_2-Zn_1-O_4	180.0000(0)
O_2-Zn_1-O_5	88.83(8)
O_3-Zn_1-O_4	88.83(8)
O_3-Zn_1-O_5	180.0000(0)
O_4-Zn_1-O_5	91.17(8)
Average angle	90
Standard division	2.226942972

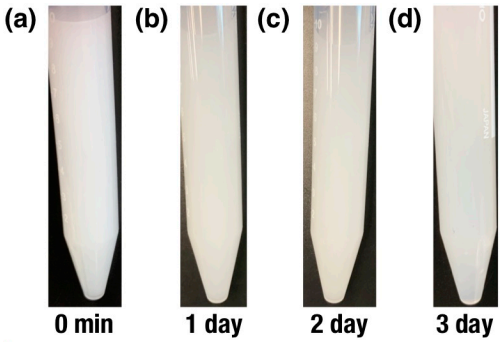

Figure S9. Photographs of the as-prepared Zn(*o*-H_4P)-MOF powder dispersed in DMF containing *p*-F_4P.

Table S3. Crystallographic data and structure refinement details for each sample

sample	Zn(*o*-H_4P)-MOF	Zn(*o*-F_4PA)-MOF	Zn(*o*-F_4PA)$_{6.5}$(*o*-H_4P)$_{3.5}$	Zn(*p*-F_4PA)-MOF
Formula	$C_8H_4O_4Zn$	$C_{14}H_{14}F_4N_2O_6Zn$	$C_{16}H_{2.88}F_{5.22}O_8Zn_2$	$C_{16}H_{14}F_4N_{0.5}O_8Zn$
Formula weight	229.48	447.64	551.04	482.65
T (K)	296	296	296	296
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$
a (Å)	10.5297(5)	8.5208(3)	13.8857(7)	5.2395(3)
b (Å)	5.2719(2)	16.3781(5)	4.77750(10)	10.1581(5)
c (Å)	13.8728(7)	12.7517(4)	25.5982(8)	16.8889(11)
α (Å)	90	90	90	90
β (Å)	109.266(5)	104.438(3)	100.241(4)	95.568(5)
γ (Å)	90	90	90	90
Z	4	4	4	2
D_x (g cm^{-3})	2.097	1.725	2.190	1.792
μ (mm^{-1})	3.348	1.502	2.975	1.459
F (000)	456	904	1076	487
Goodness-of-fit on F^2	1.063	1.054	1.101	1.047
R_1	0.0279	0.0287	0.0453	0.0359
wR_2	0.0726	0.0738	0.1240	0.0899