

## Supplementary Information

### *Two-Dimensional Metal–Organic Layers Constructed from Hf<sub>6</sub>/Hf<sub>12</sub>- oxo Clusters and Trigonal Pyramidal Phosphine Oxide Ligand*

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## 1. Materials and Methods

Reagents were commercially available and used without further purification. The powder X-ray diffraction (PXRD) data were collected on Rigaku IV diffractometers using Cu K $\alpha$  radiation sources ( $\lambda = 1.54178 \text{ \AA}$ ) using a step size of  $1^\circ$ . Transmission electron microscopy (TEM) images were obtained on a JEOL 1400 (120kV) and JEOL 2100 (200kV) transmission electron microscopy. High-angle annular dark field (HAADF) images were acquired in Tecnai F20 (200kV) and Tecnai F30 (300kV) scanning transmission electron microscopy (STEM, Philips-FEI). Crystal data were collected on a Rigaku Diffraction XtaLAB Synergy diffractometer with a Rigaku Hypix detector using Cu K $\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ). Atomic force microscopy (AFM) images were taken on Asylum Research Cypher S atomic force microscopy with tapping mode. N<sub>2</sub> sorption isotherm was performed using a Micrometrics ASAP 2460 instrument at 77 K.

<sup>1</sup>H NMR and <sup>31</sup>P NMR spectra were recorded on a Bruker 500 MHz DRX spectrometer. <sup>13</sup>C NMR spectra was recorded on a Bruker 400 MHz DRX spectrometer. <sup>31</sup>P MAS NMR spectra was collected on a Bruker 400MHz Avance III SS-NMR. The spin-lattice relaxation time (T<sub>1</sub>) of HCOO<sup>-</sup> and TPO were determined by <sup>1</sup>H NMR using a variable delay list. The T<sub>1</sub> relaxation time for the formyl proton is  $7.790 \pm 0.014 \text{ s}$ .<sup>1</sup> The T<sub>1</sub> relaxation time for the two kinds of the phenyl proton of TPO are  $2.215 \pm 0.003 \text{ s}$  and  $1.772 \pm 0.004 \text{ s}$ , respectively. Thus, the D<sub>1</sub> relaxation delay of spectral acquisition is set to 30 s for NMR quantification of the digested Hf-TPO-MOL.

Thermogravimetric analysis (TGA) was performed in air using a Shimadzu TGA-50 equipped with an alumina pan and heated at a rate of 10 °C per minute. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) measurements were undertaken on a ThermoFisher iCap 7000 instrument. Electrospray ionization mass (ESI-MS) spectrum were performed on Agilent 1290-6545XT quadrupole TOF mass spectrometry in positive ion mode, automatic sample injection was used in the ESI-MS test and the mobile phase is methanol. Fourier transform infrared (FTIR) spectra were obtained using a Nicolet iS50 infrared spectrometer.

The proposed structural model of Hf-TPO-MOL was built by using Materials Studio 2017 software combined with the information of its larger unit cell and related crystal structure.

## 2. Synthesis and characterization of TPO ligand

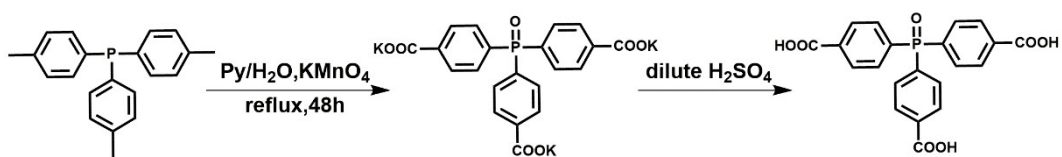


Fig. S1 Synthesis of TPO ligand.

Tris(4-carboxylphenyl)phosphine oxide (TPO) was synthesized according to the reported literature.<sup>2,3</sup> To a solution of tris(4-methylphenyl)phosphine (2 g, 6.58 mmol) in pyridine (16 mL) and water (32 mL), solid  $\text{KMnO}_4$  (20 g, 126.6 mmol) was slowly added in batches. The mixture was heated to 110 °C and refluxed for more than 48 h. After the reaction, the suspension was filtered and washed with hot water. The pH of the filtrate was adjusted to  $\text{pH} < 5$  using dilute  $\text{H}_2\text{SO}_4$  to give light yellow solid precipitates. The precipitates were filtered and then dissolved in a small amount of NaOH aqueous solution. The aqueous solution was washed with ethyl acetate three times and then acidified with dilute  $\text{H}_2\text{SO}_4$  to obtain a white solid. After filtration and drying in vacuum drying oven, the white powder weighted 1.794 g, corresponding to a yield 66.5%.

**$^1\text{H}$  NMR** (500 MHz,  $\text{DMSO}-d_6$ )  $\delta$  8.10 (dd,  $J = 8.3, 2.3$  Hz, 6H), 7.79 (dd,  $J = 11.6, 8.4$  Hz, 6H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{DMSO}-d_6$ )  $\delta$  166.98 , 137.14 , 136.14 , 134.69 , 132.37 (d,  $J = 10.2$  Hz), 130.01 (d,  $J = 12.2$  Hz).

**$^{31}\text{P}$  NMR** (202 MHz,  $\text{DMSO}-d_6$ )  $\delta$  24.56.

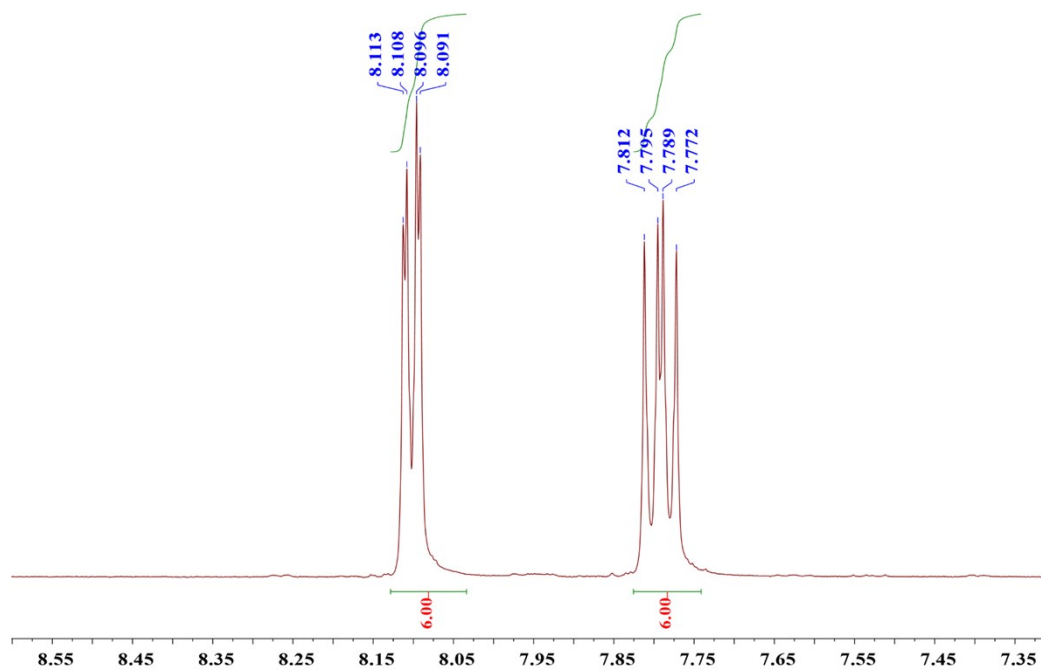


Fig. S2  $^1\text{H}$  NMR spectra of TPO ligand in  $\text{DMSO-}d_6$  (500 MHz).

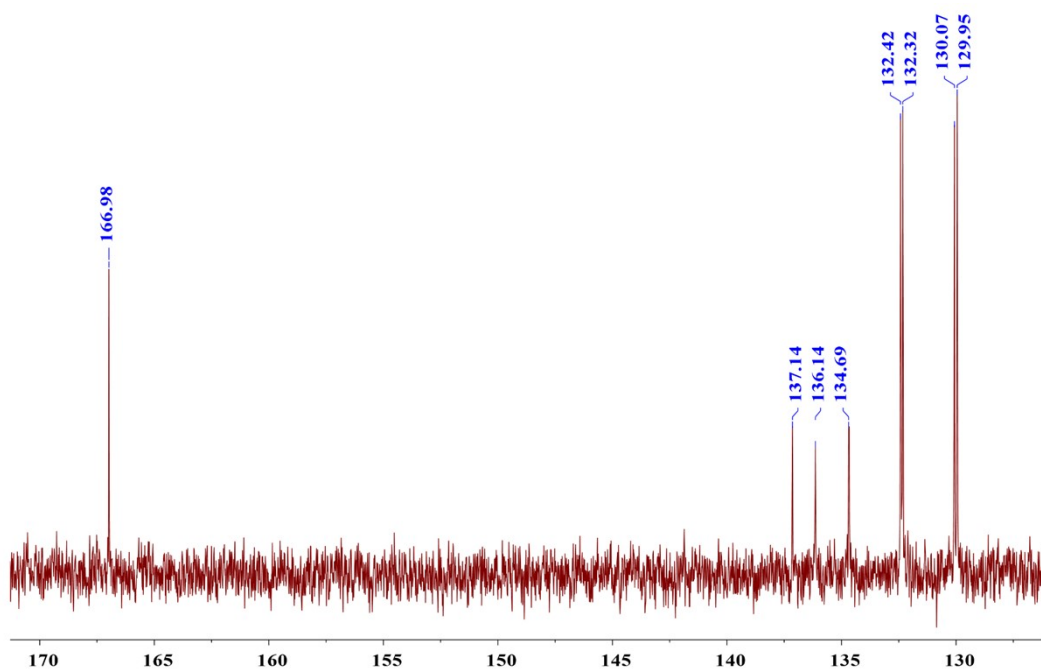


Fig. S3  $^{13}\text{C}$  NMR spectra of TPO ligand in  $\text{DMSO-}d_6$  (101 MHz).

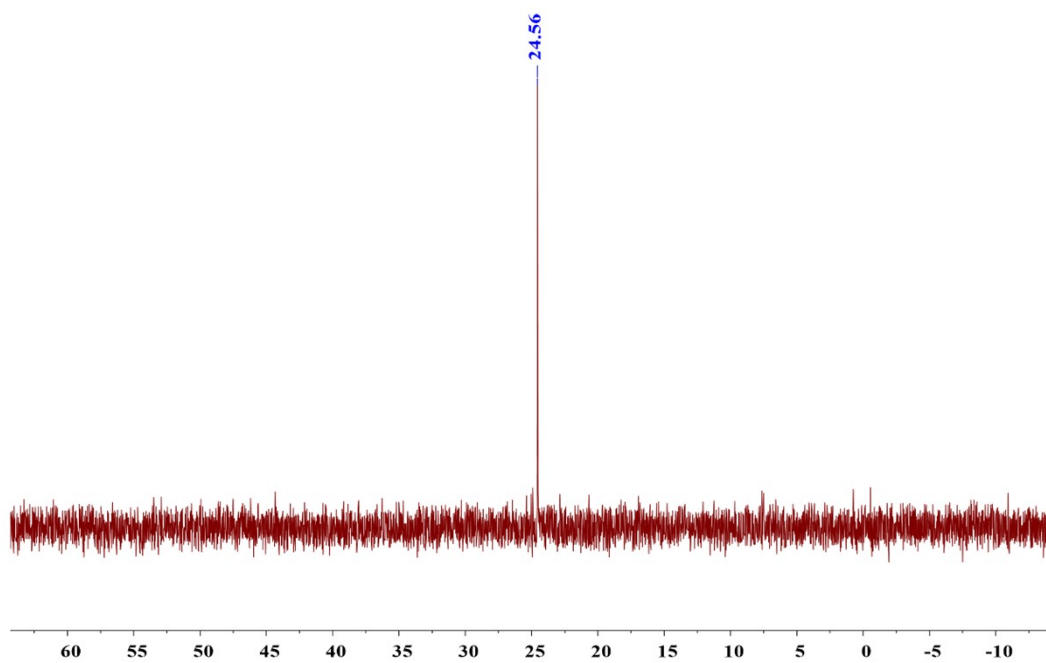


Fig. S4  $^{31}\text{P}$  NMR spectra of TPO ligand in  $\text{DMSO-}d_6$  (202 MHz).

### **3. Synthetic Conditions for Hf-TPO-MOL and Zr-P MOF**

#### **Synthesis of 2D Hf-TPO-MOL.**

TPO (24.0 mg, 0.06 mmol) and HfCl<sub>4</sub> (24.0 mg, 0.075 mmol) were dissolved in a mixture of 1.466 mL of DMF and 0.05 mL of H<sub>2</sub>O, and then HCOOH (0.46 mL) was added into the system. The mixed solution was sealed in a glass vial and heated at 120 °C for 2 days. The reaction system was cooled slowly to room temperature. After centrifugation and washing with DMF and acetone more than 3 times, white precipitates were finally obtained.

#### **Synthesis of Zr-P MOF crystal.**

ZrOCl<sub>2</sub>·8H<sub>2</sub>O (16.0 mg, 0.05 mmol) and TPO (21.7 mg, 0.05 mmol) were dissolved in a mixture of DMF (2.5 mL) and HCOOH (1.4 mL). The mixed solution was sealed in a Teflon-lined autoclave and heated at 120 °C for 2 days. Colourless block crystals were obtained.

#### 4. Morphology of Hf-TPO-MOL

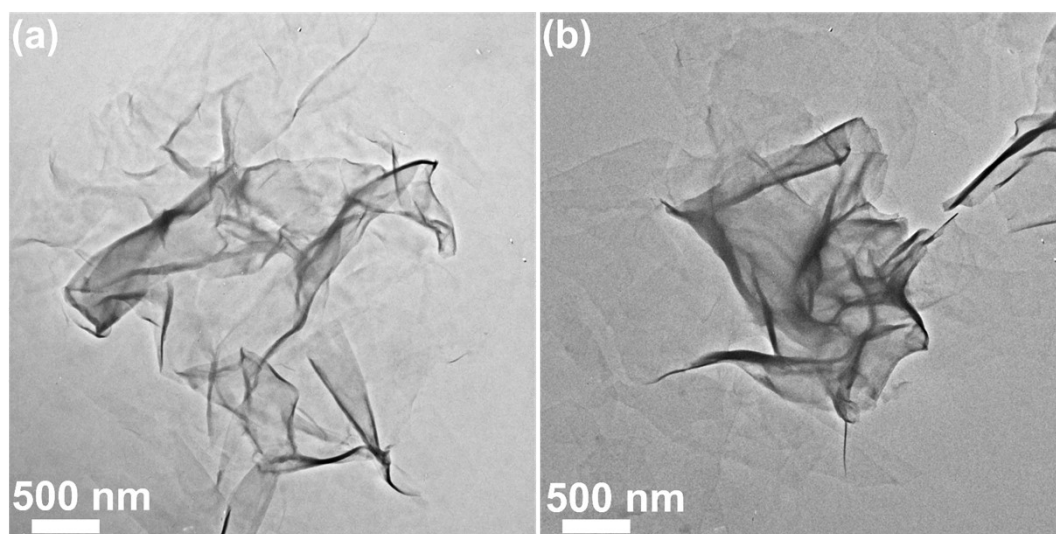


Fig. S5 (a, b) TEM images of Hf-TPO-MOL.



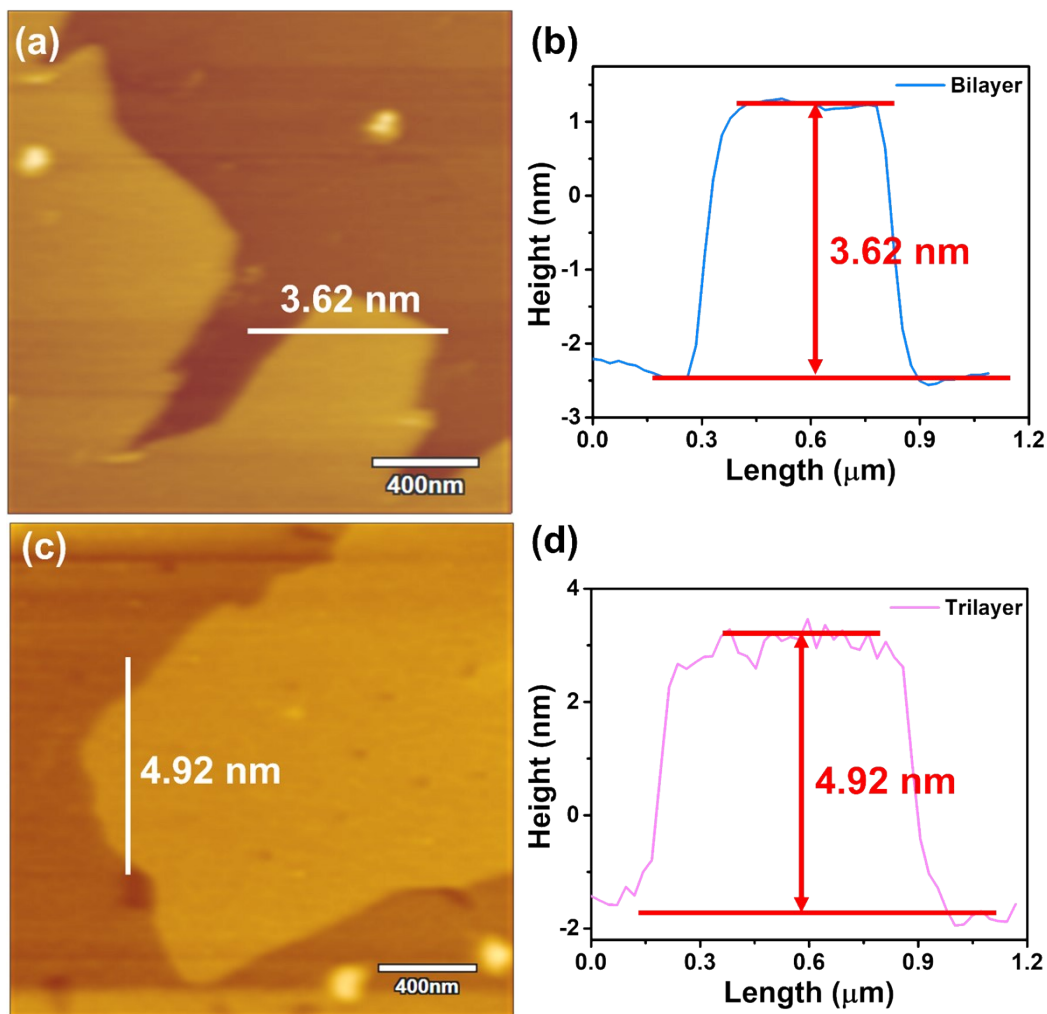


Fig. S6 Tapping-mode AFM images of the bilayer and trilayer of Hf-TPO-MOL with height profile along the white line. This  $\text{Hf}_{12}$  cluster in the TPO-MOL is tilted, so the AFM is not measuring the long axis of the cluster. If the  $\text{Hf}_{12}$ -oxo cluster vertices are capped with formate in the proposed structure, the expected height of the MOL is 2.12 nm. But if the SBUs are capped with hydroxyl or water, the height is about 1.85 nm. The AFM measurement is not far from the expected height of the tilted  $\text{Hf}_{12}$  cluster capped with hydroxyl or water.

## 5. Structural analysis of Hf-TPO-MOL

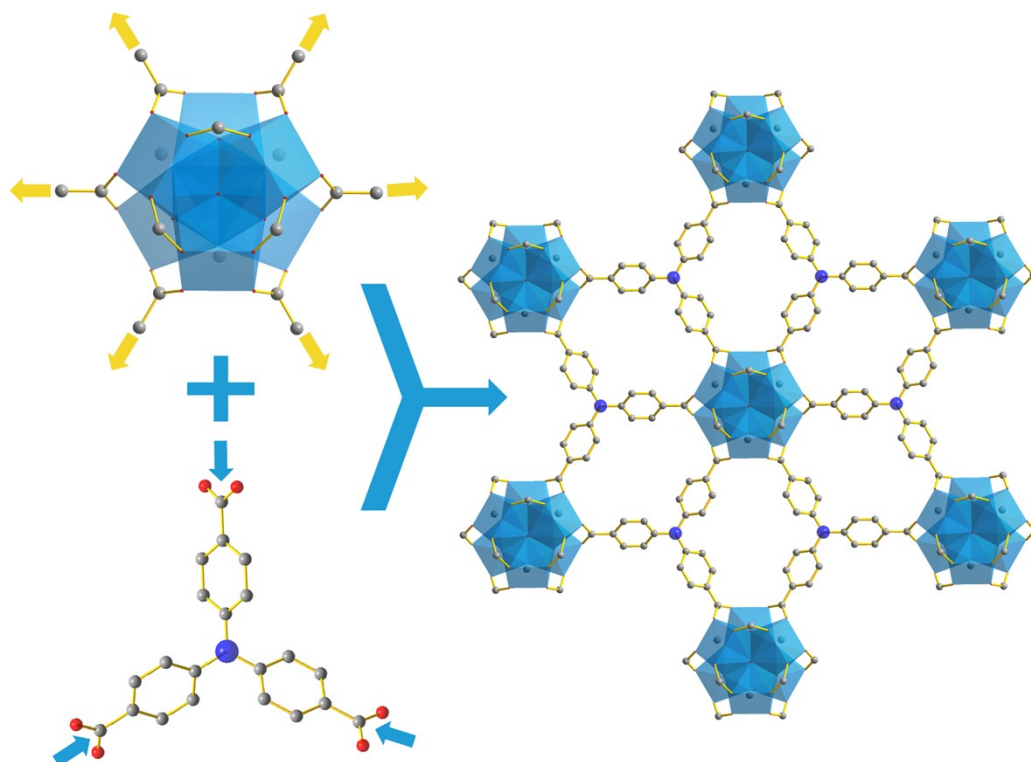


Fig. S7 Structure of Hf-NTB-MOL with 2D *kgd* topology from 6-connected site in equatorial plane of Hf<sub>6</sub> SBUs and 3-connected NTB ligands. Hf blue (polyhedral), C gray, N dark blue, O red.

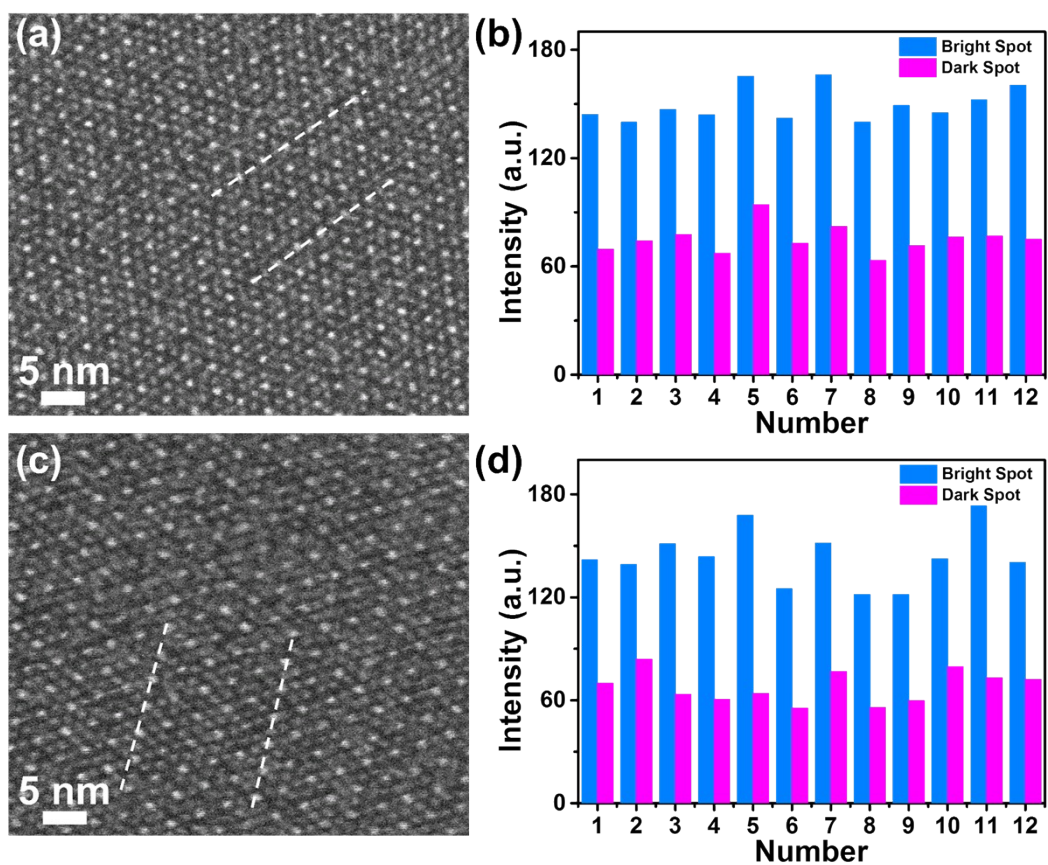


Fig. S8 (a, c) STEM-HAADF images of Hf-TPO-MOL and corresponding (b, d) contrast statistics of the white spots along the white line.

## 6. Analysis of Zr-P MOF crystal structure.

Zr-P MOF crystal data were collected on a Rigaku Diffraction XtaLAB Synergy diffractometer with a Rigaku Hypix detector using Cu K $\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ). Crystal data were tested at 100 K in a nitrogen flow. The data reduction and absorption correction were performed using the CrysAlisPro software.<sup>4</sup> The structures were solved by direct methods ShelXT<sup>5</sup> and refined by a full-matrix least-squares method using ShelXL<sup>6</sup> on the OLEX2<sup>7</sup>. The SQUEEZE subroutine of the PLATON software<sup>8</sup> was utilized to remove disorder solvent molecules in a void space. All non-hydrogen atoms were refined anisotropically.

Table S1 The crystal data and structure refinement for Zr-P MOF.

Name	Zr-P MOF
CCDC	2159729
Empirical formula	C <sub>51</sub> H <sub>41</sub> NO <sub>36</sub> P <sub>2</sub> Zr <sub>6</sub>
Formula weight	1853.11
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> / $\text{\AA}$	21.8571(3)
<i>b</i> / $\text{\AA}$	17.8537(2)
<i>c</i> / $\text{\AA}$	26.4192(6)
$\alpha$ / $^\circ$	90
$\beta$ / $^\circ$	114.129(2)
$\gamma$ / $^\circ$	90
Volume/ $\text{\AA}^3$	9408.8(3)
Z	4
$\rho_{\text{calc}}/\text{g/cm}^3$	1.308
$\mu/\text{mm}^{-1}$	6.177
F(000)	3648.0
Crystal size/ $\text{mm}^3$	0.1 $\times$ 0.1 $\times$ 0.05
Radiation	Cu K $\alpha$ ( $\lambda = 1.54184$ )

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2 $\theta$ range for data collection/ $^{\circ}$	6.16 to 149.108
Index ranges	$-20 \leq h \leq 27$ , $-18 \leq k \leq 21$ , $-32 \leq l \leq 33$
Reflections collected	64914
Independent reflections	18175 [ $R_{\text{int}} = 0.0614$ , $R_{\text{sigma}} = 0.0585$ ]
Data/restraints/parameters	18175/972/903
Goodness-of-fit on $F^2$	1.035
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0507$ , $wR_2 = 0.1191$
Final R indexes [all data]	$R_1 = 0.0655$ , $wR_2 = 0.1254$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	1.73/-1.45

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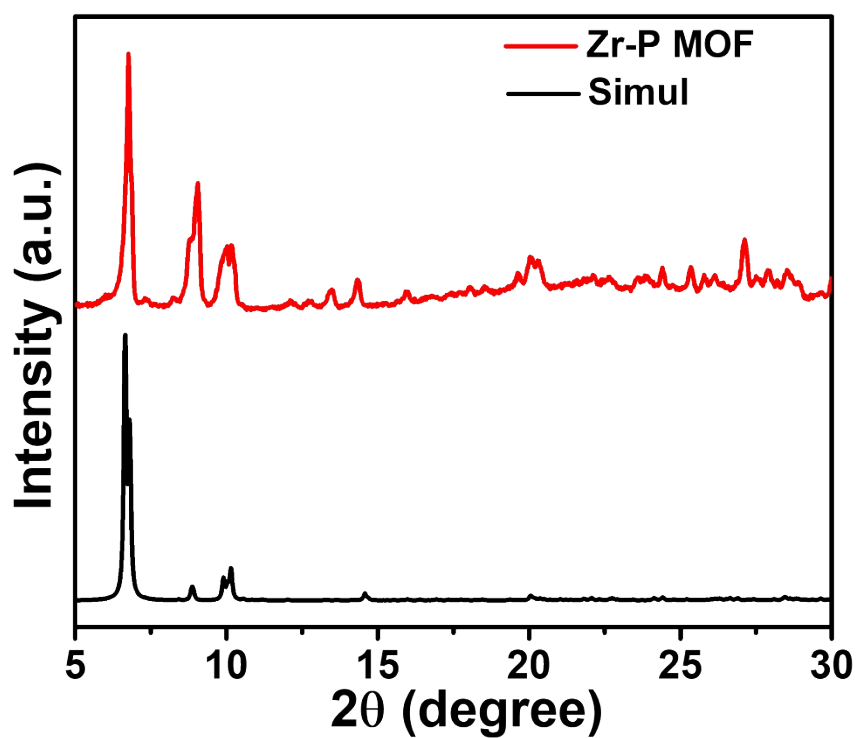


Fig. S9 PXRD pattern of Zr-P MOF.

## **7. Simulation of diffraction data.**

A simulated PXRD pattern was obtained by a previously developed Matlab codes using CIF files as structural input (<https://github.com/Wang-Group/2D-XRD-Modelling>).<sup>9</sup>

## 8. N<sub>2</sub> sorption isotherm of Hf-TPO-MOL

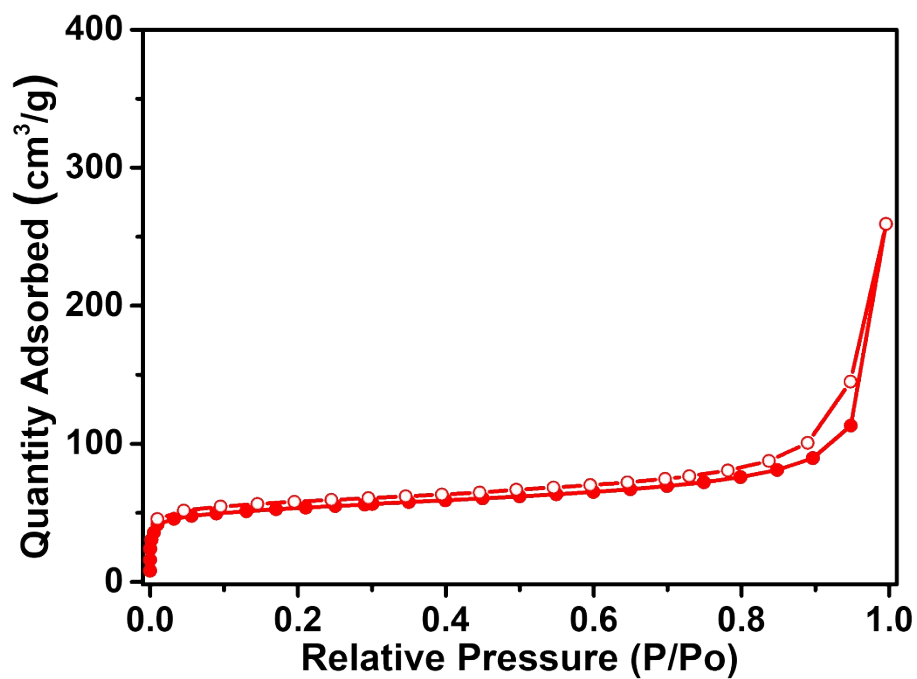


Fig. S10 (a) N<sub>2</sub> adsorption isotherm of Hf-TPO-MOL.

## 9. Analysis of chemical composition

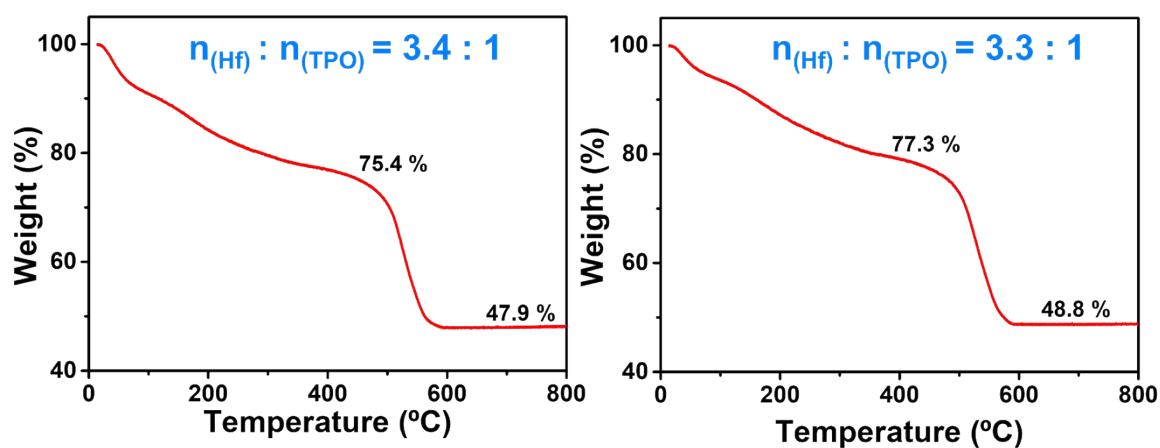


Fig. S11 TGA of Hf-TPO-MOL (two repeated experiments). The molar ratio of Hf : TPO is  $3.4 \pm 0.2$ .

Table S2 The Hf content of the MOL measured by ICP-OES and TGA.

Note	Hf (wt%)
ICP-OES (raw)	$36.1 \pm 0.7$
ICP-OES (mass correction)*	$41.0 \pm 0.8$
TGA	$42.3 \pm 1.5$
In the structure model	49.2

\* Mass correction means that the absolute content of Hf is calculated by excluding the proportion of water and solvent (12 wt%) based on TGA data.



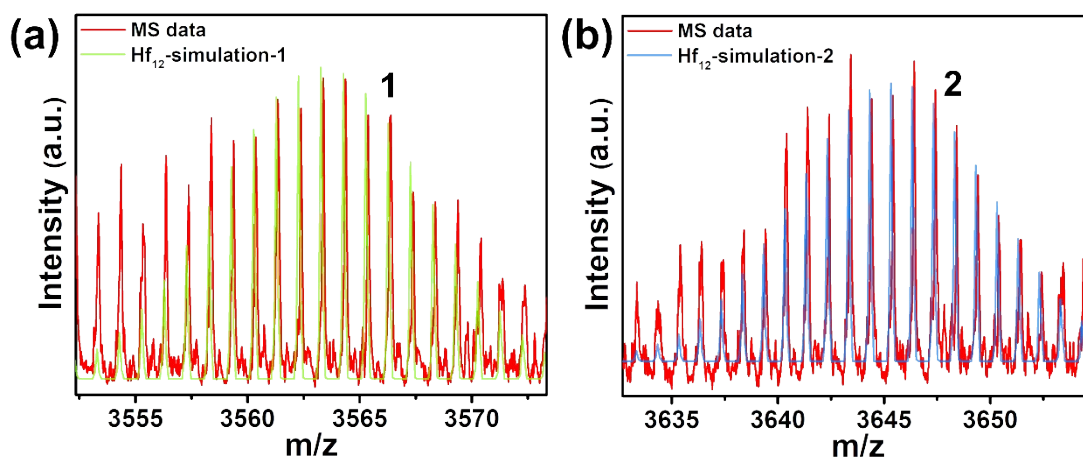


Fig. S12 ESI-MS data of the reaction solution without ligand added under synthesis conditions of Hf-TPO-MOL. Species in the solution with the higher  $m/z$  value, which can be assigned as the  $\text{Hf}_{12}$  clusters with formula of  $\text{Hf}_{12}\text{O}_{16}\text{H}_8(\text{HCOO})_{23}(\text{H}_2\text{O}\cdot\text{OH})(\text{CH}_3\text{OH})_2$  and  $\text{Hf}_{12}\text{O}_{16}\text{H}_8(\text{HCOO})_{23}(\text{H}_2\text{O}\cdot\text{OH})(\text{DMF})_2$ .

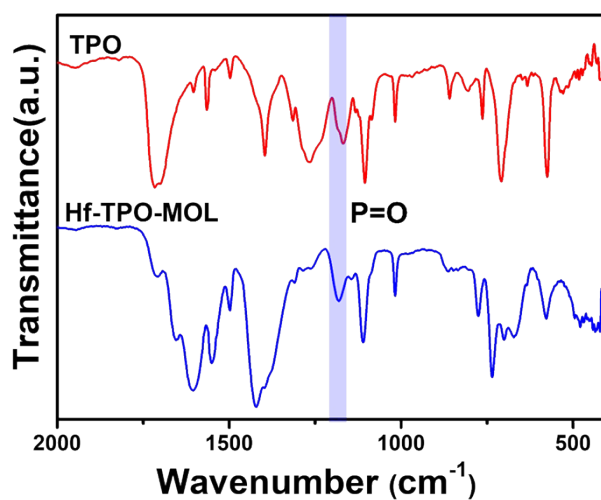


Fig. S13 FTIR analysis of Hf-TPO-MOL and TPO ligand. The peak of  $\sim 1170\text{ cm}^{-1}$  is referred to as a P=O bond of TPO.

## 10. Reduction of Hf-TPO-MOL

The Hf-TPO-MOL was reduced using the method modified from the reported work.<sup>10</sup> The operation was carried out in a glove box under N<sub>2</sub> atmosphere.

The gel-like MOL (< 96 mg vs TPO, 0.24 mmol) after solvent exchange was suspended in dry and degassed toluene (10 ml). HSiCl<sub>3</sub> (1.08 mL, 10.7 mmol) as reducing agent was added to the schlenk tube. The tube was sealed and heated at 130 °C for 72 h. And then the product was centrifuged out of viscous suspension and washed with degassed toluene and DMF, respectively. The solvated samples was used for PXRD test.

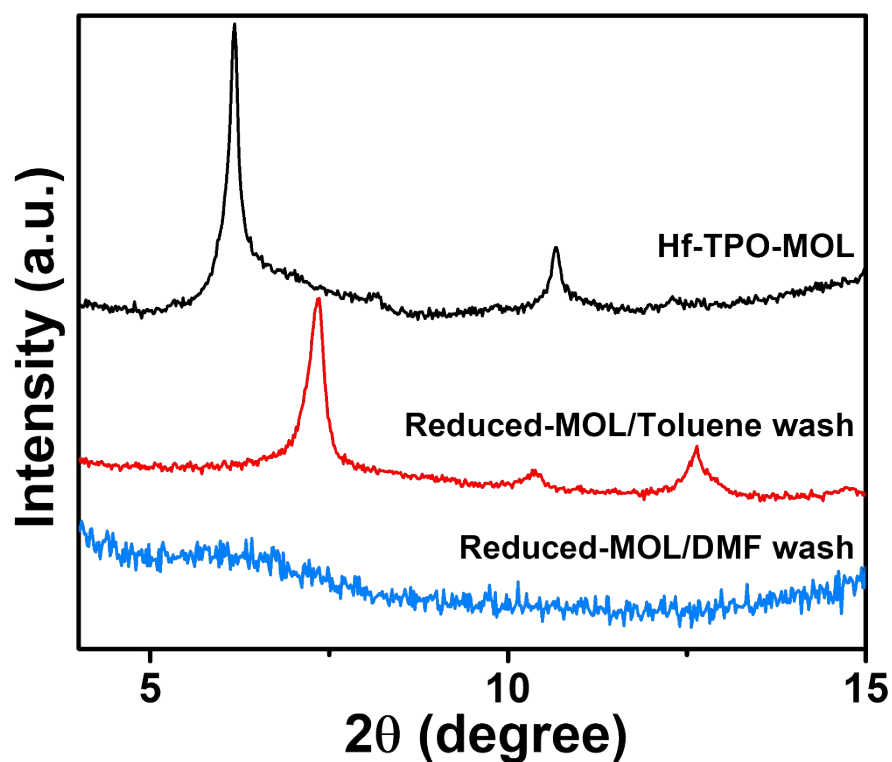


Fig. S14 (a) PXRD patterns of the Hf-TPO-MOL and the reduced product washed with degassed toluene and DMF, respectively.

## 11. Synthesis of TPP ligand and Hf-TPP-MOL

### Synthesis of TPP ligand

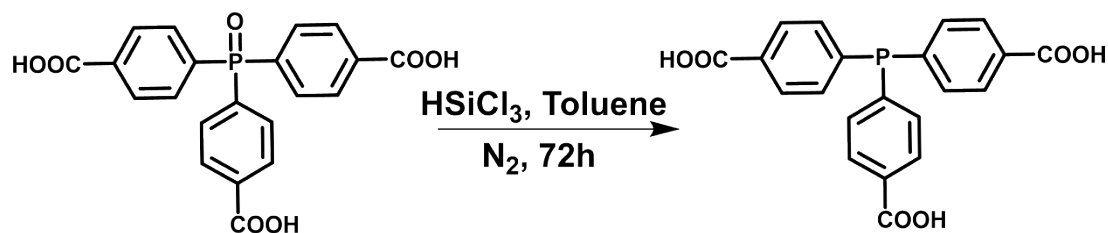


Fig. S15 Synthesis of TPP ligand.

Tris(4-carboxylphenyl)phosphine (TPP) was synthesized according to literature.<sup>10</sup> Tris(4-carboxylphenyl)phosphine oxide (200 mg, 0.48 mmol) was suspended in dry and degassed toluene (3.4 mL).  $\text{HSiCl}_3$  (2.2 mL, 21.8 mmol) as reducing agent was added to the schlenk tube. The suspension was heated at 130 °C for 72 h under  $\text{N}_2$  atmosphere. After the reaction, the volatiles were removed via evaporation. Degassed concentrated  $\text{NH}_3$  solution was added to dissolve solid precipitation. The aqueous phase containing the product was separated. The filtrate was acidified with degassed dilute  $\text{HCl}$  to obtain a white solid. After washing with degasses  $\text{H}_2\text{O}$  and dried in vacuum drying oven, we obtained white powder weighted 135 mg, corresponding to a yield 70.3%.

$^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  13.13 (s, 3H), 7.98 (d,  $J = 7.8$  Hz, 6H), 7.40 (t,  $J = 7.6$  Hz, 6H).

$^{31}\text{P NMR}$  (202 MHz,  $\text{DMSO-}d_6$ )  $\delta$  -6.38.

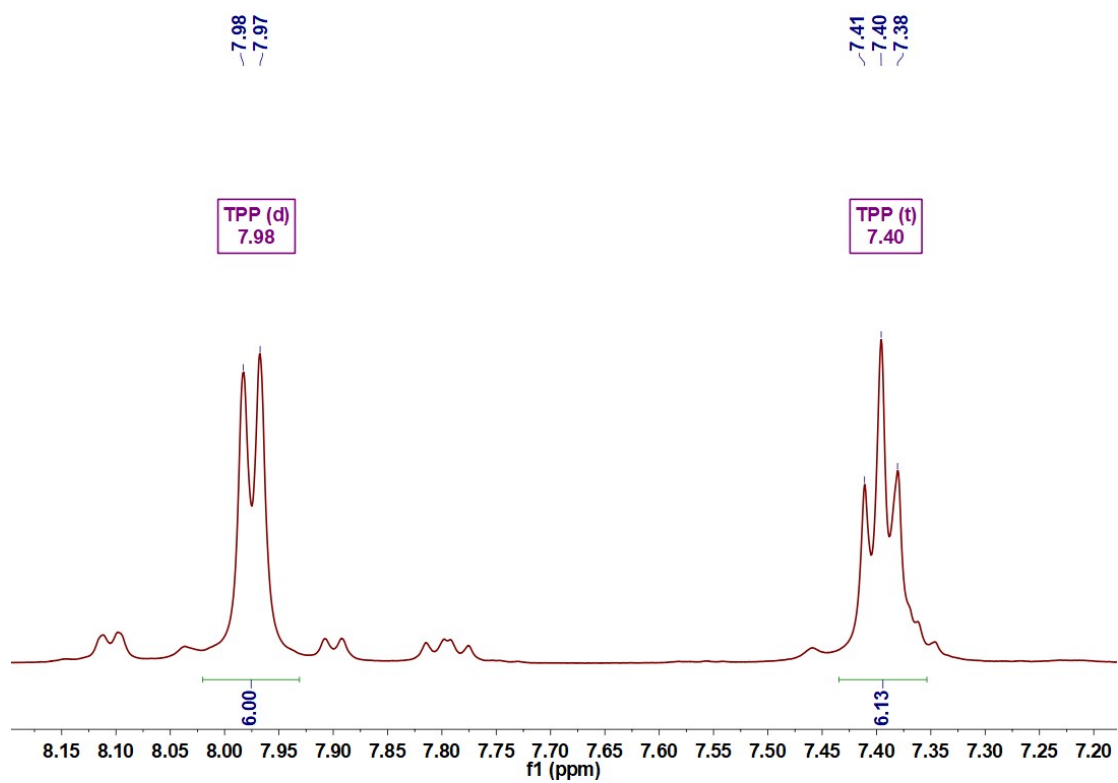


Fig. S16  $^1\text{H}$  NMR spectra of TPP ligand in  $\text{DMSO-}d_6$  (500 MHz).

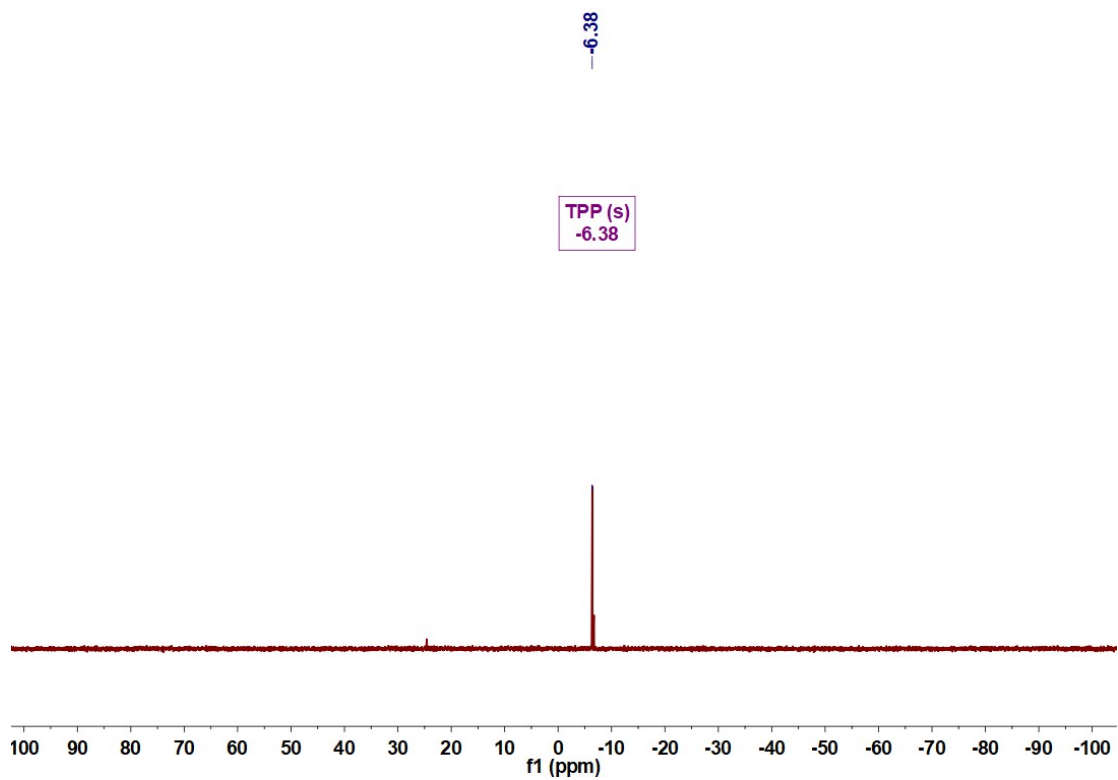


Fig. S17  $^{31}\text{P}$  NMR spectra of TPP ligand in  $\text{DMSO-}d_6$  (202 MHz).

## Synthesis of Hf-TPP-MOL

The experimental operation was carried out under N<sub>2</sub> atmosphere using a glove box. Hf-TPP-MOL was synthesized using a synthetic condition similar to that of the Hf-TPO-MOL. The mixed solution was sealed in a pressure-resistant bottle and heated at 120 °C for 2 days under N<sub>2</sub> atmosphere. White powders were obtained by centrifugation.

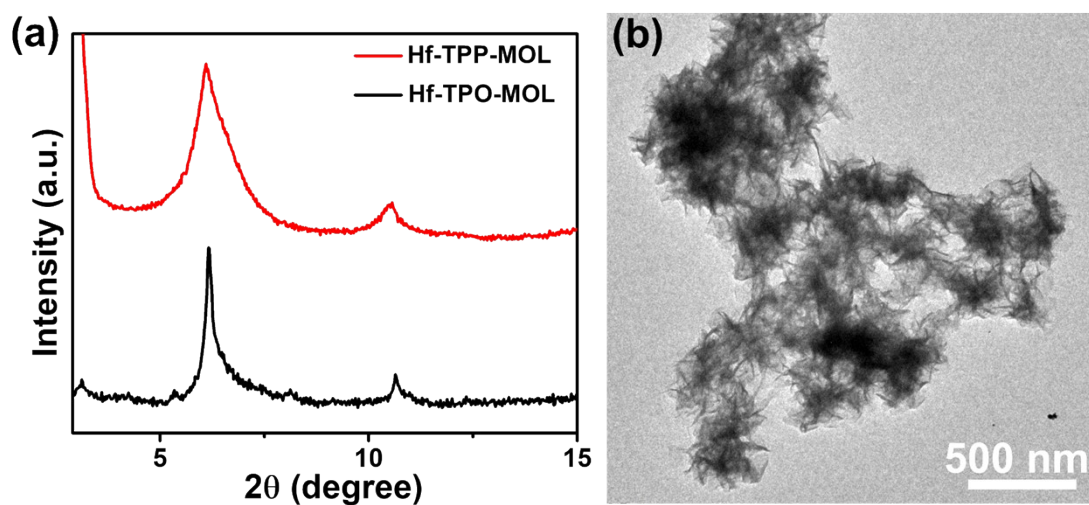


Fig. S18 (a) PXRD pattern of Hf-TPP-MOL compared with that of Hf-TPO-MOL. (b) TEM image of Hf-TPP-MOL.

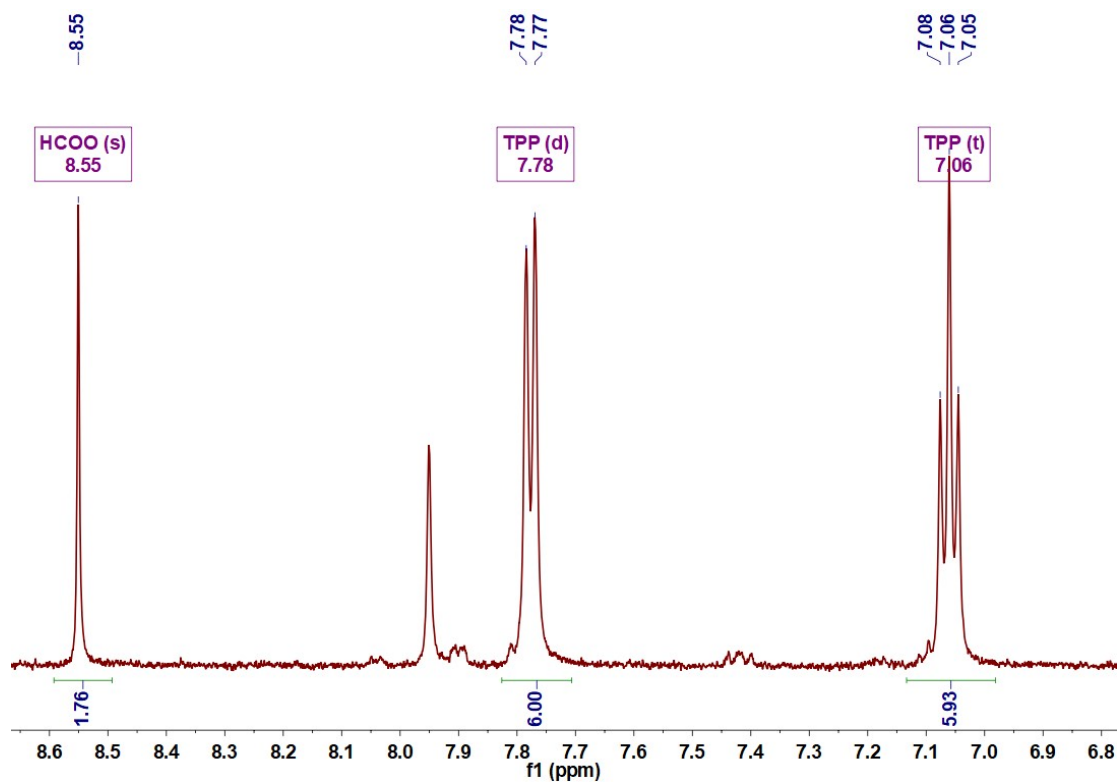


Fig. S19 <sup>1</sup>H-NMR spectra of the digested Hf-TPP-MOL by tetra-n-butylammonium fluoride (TBAF).

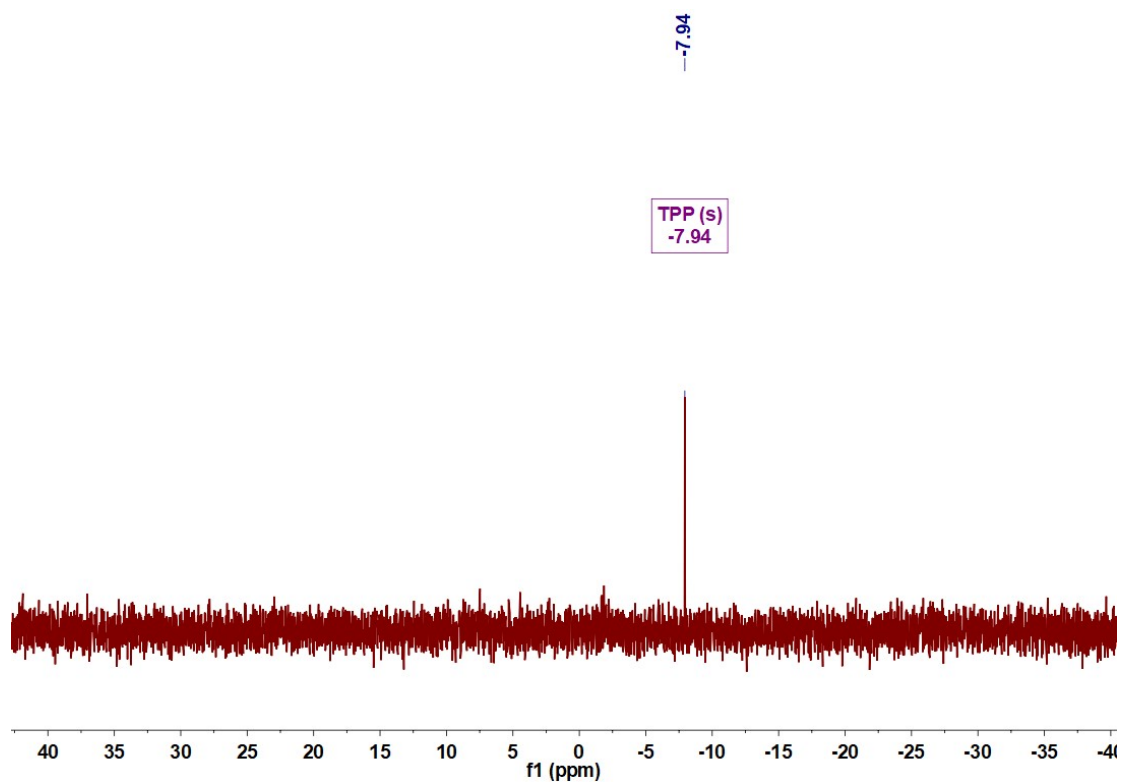


Fig. S20  $^{31}\text{P}$ -NMR spectra of the digested Hf-TPP-MOL by tetra-n-butylammonium fluoride (TBAF).

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