Supporting Information

Characterizations

Nuclear Magnetic Resonance (NMR) spectra were recorded on Varian Inova 600 (^1H: 600 MHz, ^{13}C: 150 MHz). Solvent signals were used as internal standards for chemical shifts (^1H: $\delta = 2.50$ ppm and ^{13}C: $\delta = 40.45$ ppm for DMSO, ^1H: $\delta = 7.26$ ppm and ^{13}C: $\delta = 77.16$ ppm for $CDCl_3$).

High resolution mass spectrometry (HRMS) analyses were performed with an Agilent LC-MS TOF 1260-6224.

Single crystallographic data were collected by a Bruker SMART APEX CCD (MOF before activation: 1820169; MOF after activation: CCDC 1819935).

Powder crystallographic data was collected by an X-ray diffractometer D/MAX-IIIC.

Melting point was measured with a WRS-2A digital melting point instrument.

The optical microscopy (OM) measurements were performed with a transflective polarized microscope (Tuming CP-602C).

The Raman spectroscopy measurement was conducted with an Invia Raman spectroscope ($\lambda = 532$ nm).

For the Infrared (IR) spectra, Materials were mixed with KBr and measured with a Nicolet iS10 Infrared spectroscope.

The TG analysis was performed with Perkin elmer Diamond TG/DTG under a nitrogen atmosphere.

The atomic force microscopy (AFM) measurements were performed under ambient conditions with an NT-MDT microscope. The cantilever was a Budget Tap300Al-G (Resonant Freq. 300 KHz, Force Constant 40 N/m). The substrate was muscovite mica (EMS Muscovite mica-V1). Samples were drop-cast on to the freshly cleaved mica substrate and then the solvent was removed by natural evaporation following high vacuum. The images were obtained using the tapping mode.

For the scanning electron microscopy (SEM) measurements and *in-situ* energy dispersive spectroscopy (EDS) measurements, (1) sheets in solution were drop-cast on TEM grids, which was stuck on the sample stage by conducting tapes (2) crystals were directly stuck on the conducting tapes on the sample stage. Samples were measured with Zeiss GEMINI500, Zeiss SIGMA500 or JEOL JSM7100F. All SEM images were captured with a secondary electron (SE) mode.

Copper and lacey-carbon-coated copper TEM grids were purchased from Beijing Daji Technology (D11012).

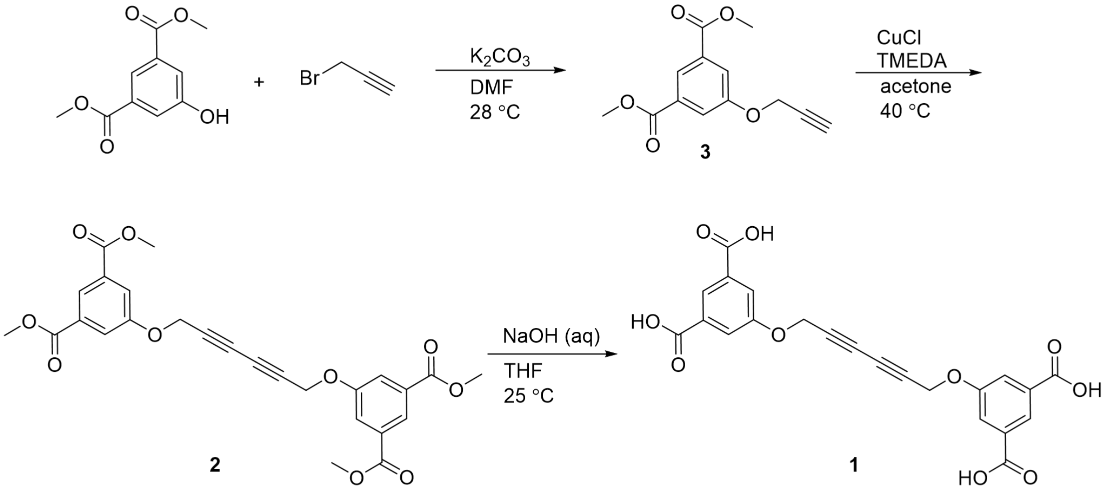
The transmission electron microscopy (TEM), High-resolution TEM (HRTEM) and selected area electron diffraction (SAED) measurements were performed with Quanta 3D FED Titan FP2023/32 (300 kV).

The XPS measurements were performed with Thermo Fisher Escalab 250Xi.

Materials

All starting reagents were purchased from Aladdin and Sinoreagent, and used without further purification.

Synthesis procedure, analytical data and original spectra of compounds are shown as follows.



Scheme S1. Synthetic procedure of the integrated ligand **1**.

Known compound **3**

A 250 mL round-bottom flask was charged with dimethyl 5-hydroxyisophthalate (9.46 g, 45 mmol), potassium carbonate (15.53g, 112.5 mmol) and DMF (60 mL). The mixture was stirred for 0.5 h and then 3-bromoprop-1-yne (15.74 g, 132 mmol) was added in drop-wise. The reaction was allowed to conduct at 28 °C for 11 h. After reaction, the mixture was filtered to remove inorganic salts, and the solution was dropped into water to get the white precipitate. After vacuum-filtration and dry, compound **3** was obtained as a white solid (10.84 g, 97 %). M.p. : 118.8 – 119.5 °C

^{1}H NMR ($CDCl_3$，600 MHz) δ/ppm: 8.33 (s, 1H, Ph); 7.83 (s, 2H, Ph); 4.79 (s, 2H, CH_2); 3.95(s, 6H, CH_3); 2.55 (s, 1H, -C≡CH)

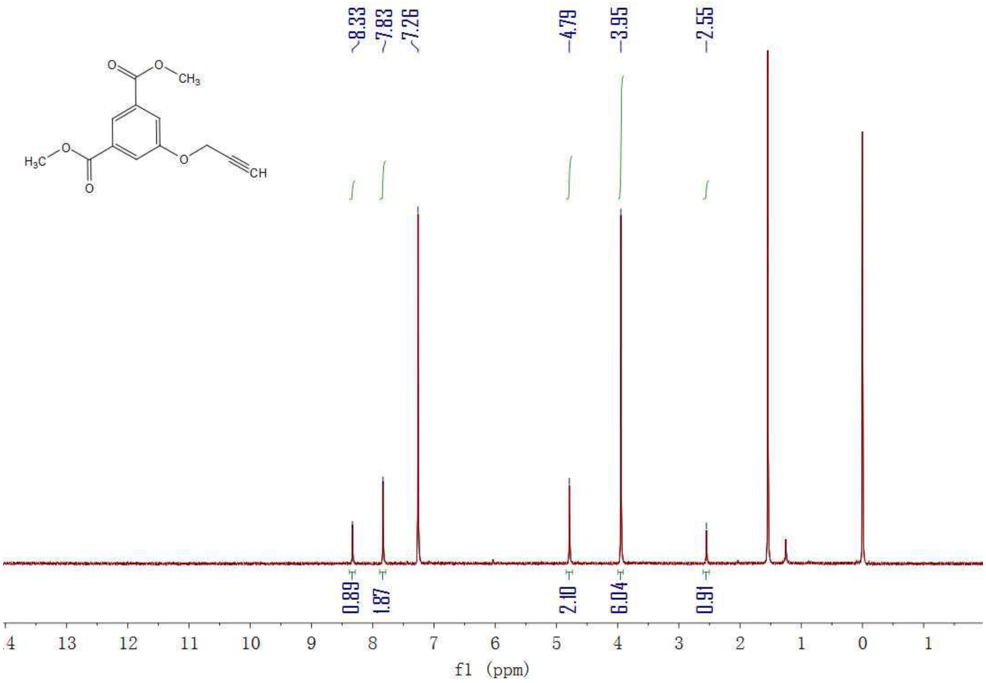


Figure S1. ^{1}H-NMR spectrum of compound **3**

Compound **2**

Under air atmosphere, CuCl (0.27 g, 2.7 mmol), Tetramethylethylenediamine (TMEDA) (0.39 g, 3.4 mmol) and 10 mL acetone were added in a 250 mL beaker. After stirred for 10 min at room temperature (r.t.), compound **3** (2.48 g, 10 mmol) in 70 mL acetone was added in. The mixture was stirred at 40 °C for 35.5 h. After reaction, the mixture was cooled to r.t. and acetone was removed by rotary evaporation. The remaining solid was passed a plug of silica gel (eluent: CH_2Cl_2) to afford compound **2** as a white solid (2.23 g, 90.3 %). M. p.: 192.2 – 193.0 °C.

^{1}H NMR ($CDCl_3$，600 MHz) δ/ppm: 8.33 (s, 2H, Ph); 7.83(s, 4H, Ph); 4.84 (s, 4H, CH_2); 3.94(s, 12H, CH_3)

^{13}C NMR ($CDCl_3$, 150 MHz) δ/ppm: 165.9; 157.4; 132.0; 124.1; 120.2; 73.9; 71.5; 56.6; 52.5.

HRMS (LC-MS TOF, Formic acid) calcd. for $C_{26}H_{22}O_{10}$ $[M+Na]^+$ 517.1105, found 517.1104.

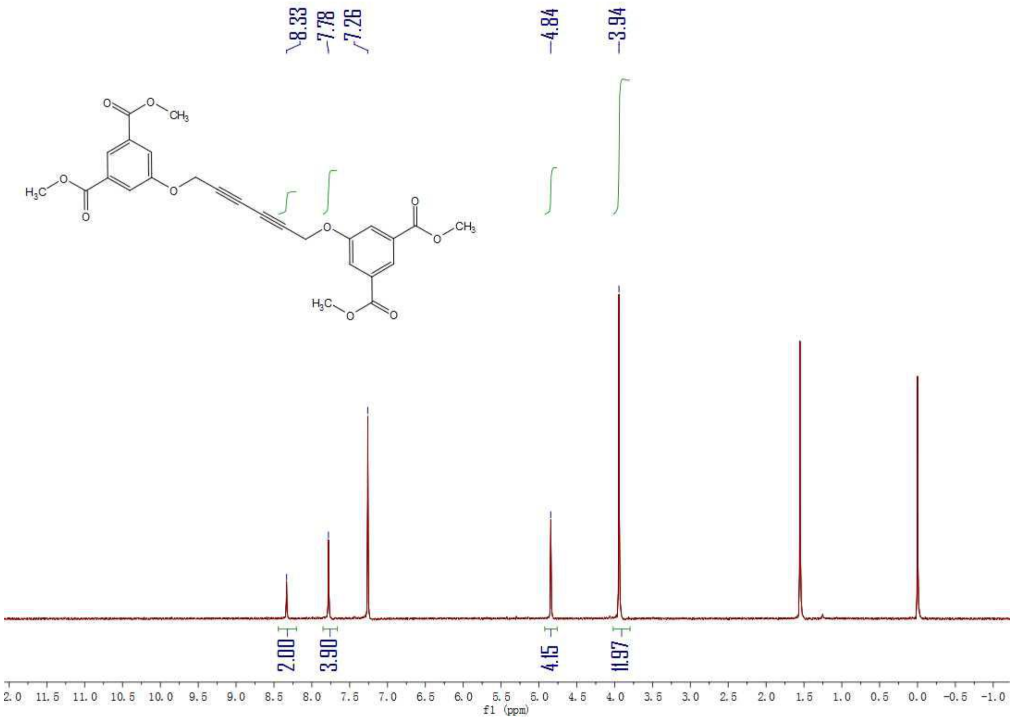


Figure S2. ^{1}H-NMR spectrum of compound **2**

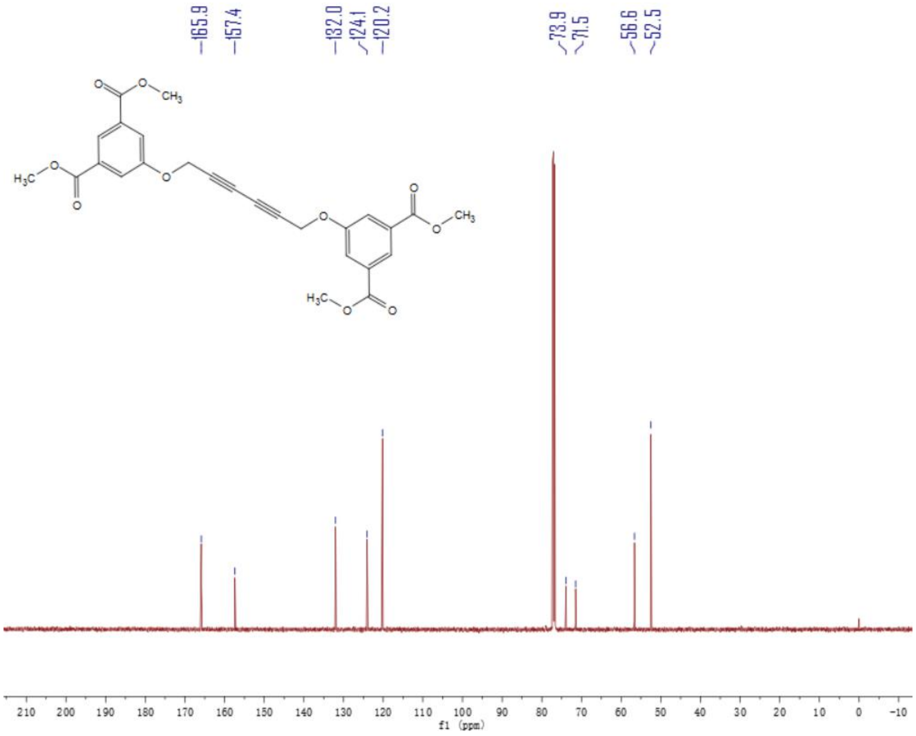


Figure S3. ^{13}C-NMR spectrum of compound **2**.

Compound **1**

Compound **2** (0.50 g, 1 mmol) and 50 mL THF were added in a 250 mL round bottom flask. NaOH (0.32 g, 8 mmol) was dissolved in 15 mL deionized water and then slightly added in. The system was stirred at 25 °C for 2.5 h. After reaction, THF was removed by rotary evaporation. The yellow solution was acidized by HCl (2 M) and diluted by pure water. After filtration, 250 mL ethyl acetate (EA) was added in the yellow solid so as to dissolve product under ultrasound. Then the mixture was filtrated and dried by anhydrous $MgSO_4$ to give a clear EA solution. After removal of EA by rotary evaporation, the solid was washed by CH_2Cl_2 and dried to yield compound **1** as white solid (0.36 g, 82.1 %). M. p. > 250 ^oC.

^1H NMR (DMSO-d_6, 600 MHz) δ/ppm: 8.12 (s, 2H, Ph); 7.70(s, 4H, Ph); 5.14 (s, 4H, CH_2)

^{13}C NMR (DMSO-d_6, 150 MHz) δ/ppm: 166.8; 157.7; 133.3; 123.7; 120.0; 76.2; 70.8; 56.9.

HRMS (LC-MS TOF, Formic acid) calcd. for $C_{22}H_{14}O_{10}$ $[M-H]^-$ 437.051, found 437.047.

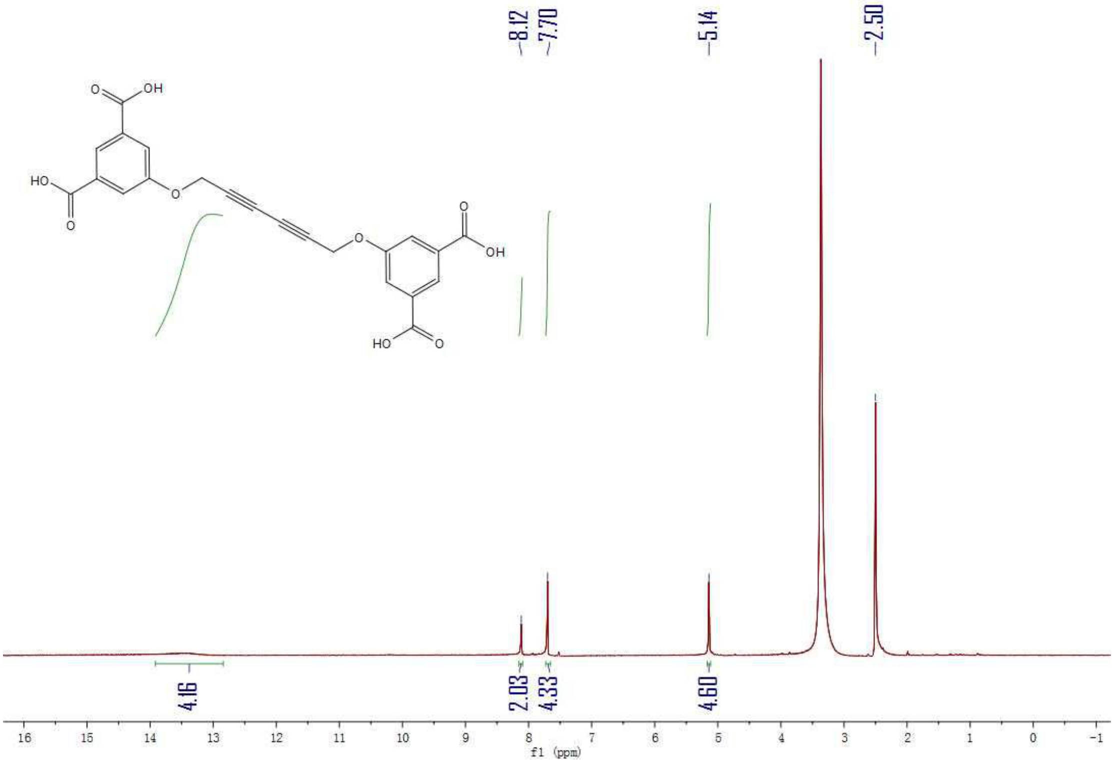


Figure S4. ^1H-NMR spectrum of compound **1**

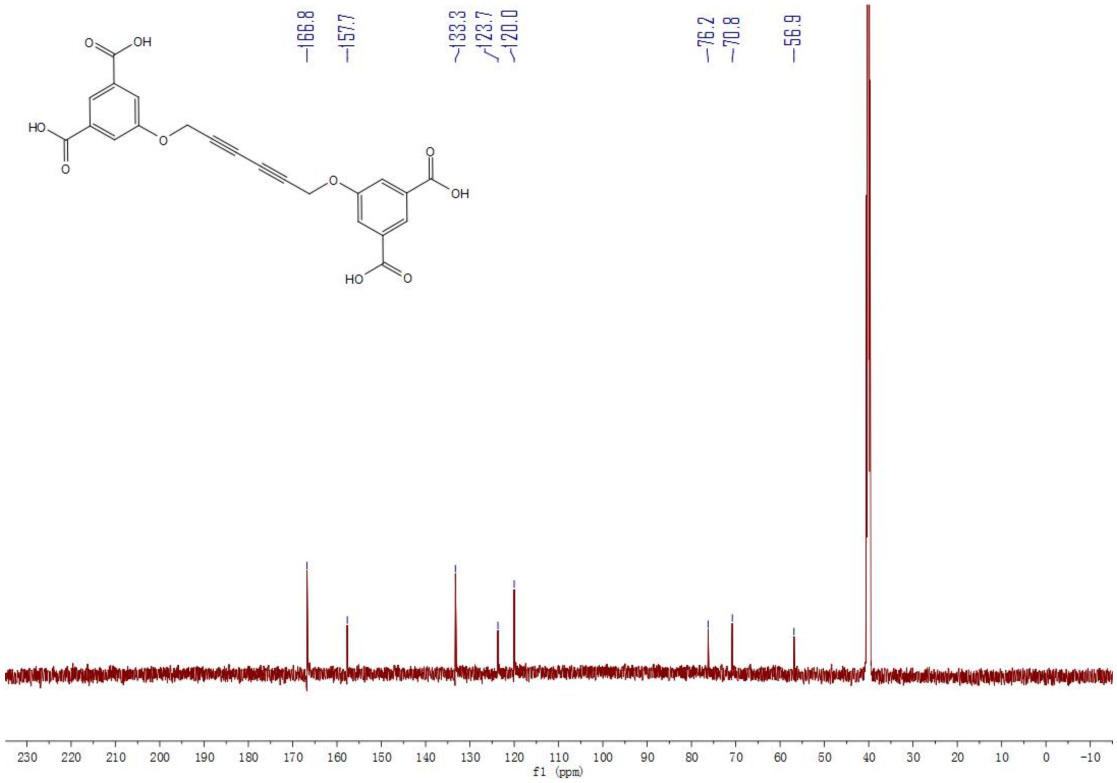


Figure S5. ^{13}C-NMR spectrum of compound **1**.

Preparation of MOF crystals

Compound **1** (47.4 mg, 0.108 mmol) and $Co(NO_3)_2$•$6H_2O$ (0.063g, 0.216mmol) in a mixture of DMF/C_2H_5OH (2.5 ml/1.5 ml) were placed in a 25 mL Teflon lined sealed tube. The tube was heated at 100 ^{o}C for 20 h, and then cooled gradually to r.t. for 20 h, yielding purple-red crystals (70.7 mg, 0.096 mmol, 89%)

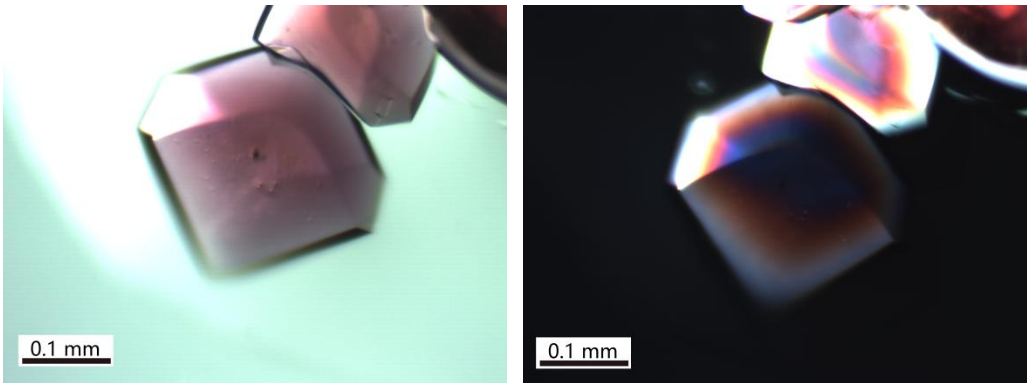


Figure S6. Optical microscope images of MOF crystals (right: polarized light).

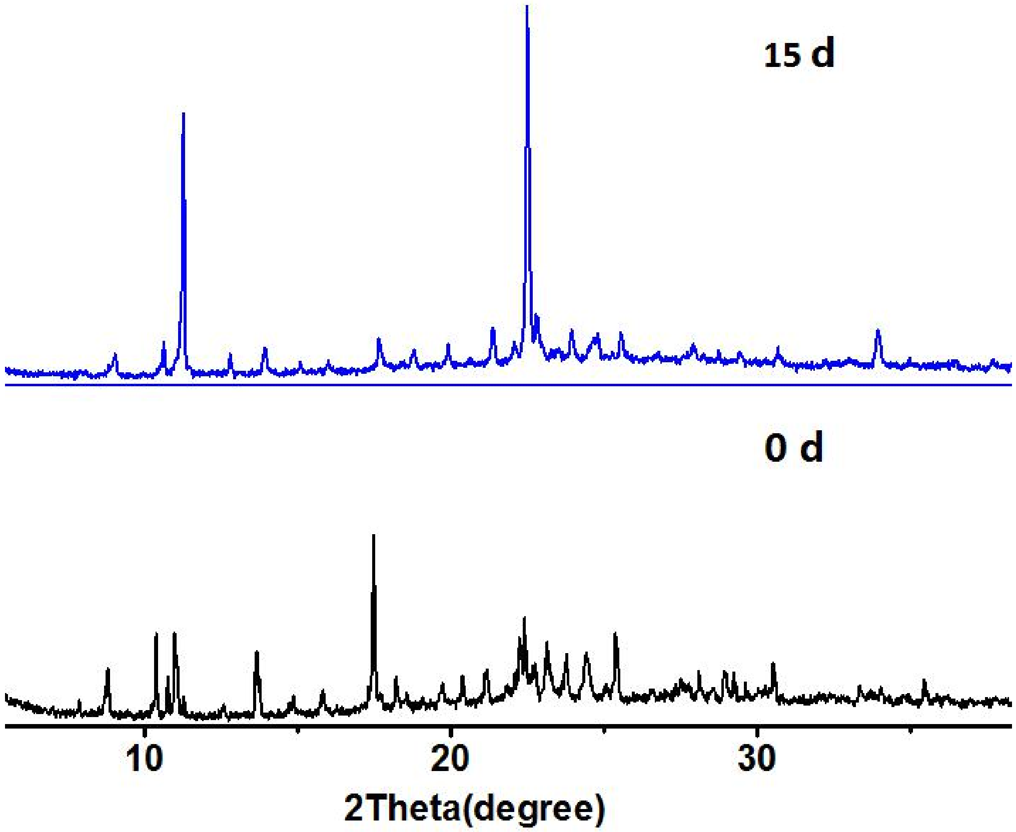
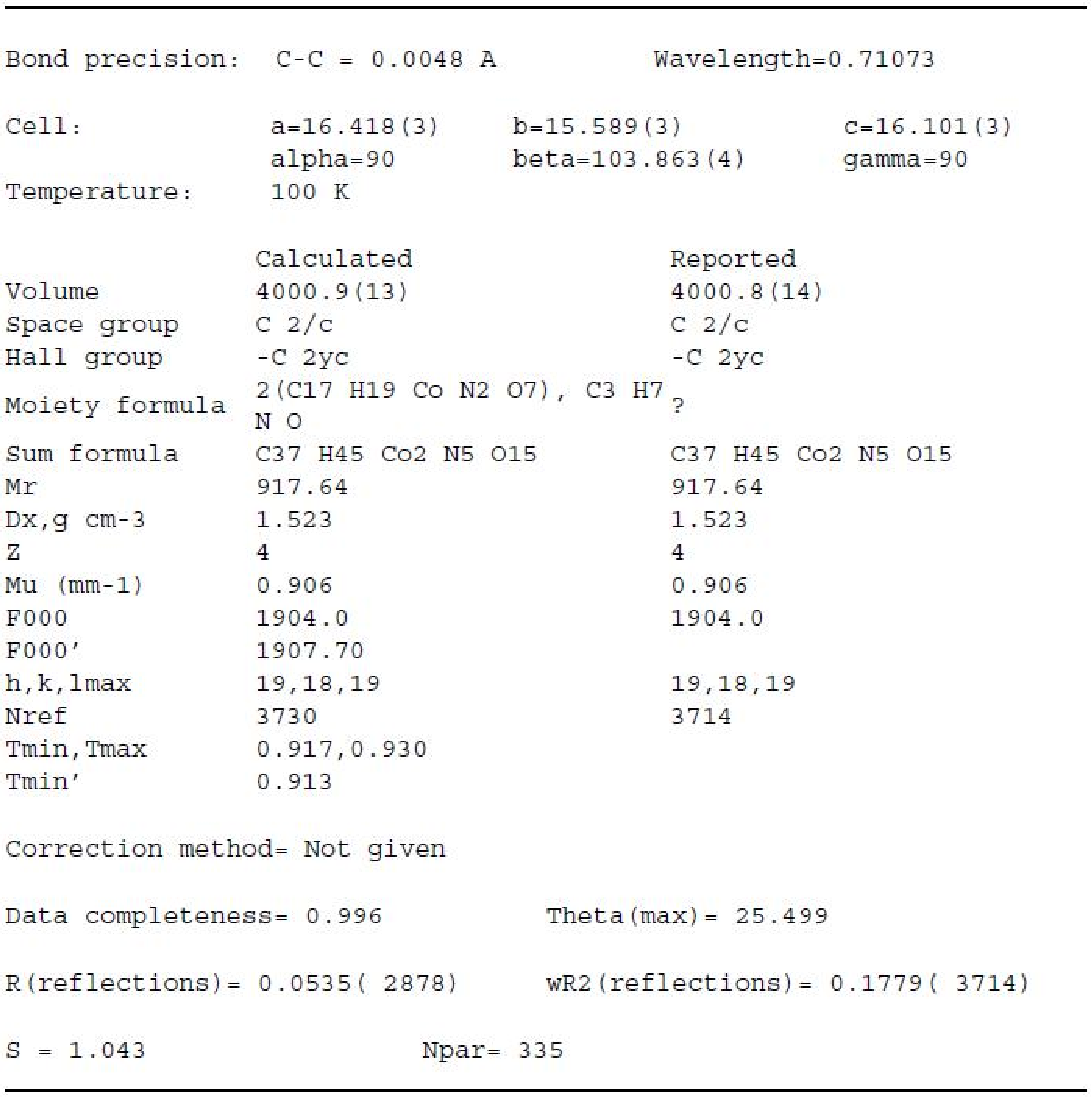


Figure S7. PXRD patterns of MOF crystals. After storage in air (moisture ~70%) at room temperature, peaks are still shape at the same region of the origin spectrum. Different intensity should result from that orientations of crystals are different during different measurements.

(a)



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Bond precision:   C-C = 0.0048 A          Wavelength=0.71073

Cell:             a=16.418(3)     b=15.589(3)          c=16.101(3)
                  alpha=90        beta=103.863(4)      gamma=90
Temperature:      100 K

                 Calculated                   Reported
Volume           4000.9(13)                   4000.8(14)
Space group      C 2/c                        C 2/c
Hall group       -C 2yc                       -C 2yc
Moiety formula   2(C17 H19 Co N2 O7), C3 H7   ?
                 N O
Sum formula      C37 H45 Co2 N5 O15           C37 H45 Co2 N5 O15
Mr               917.64                       917.64
Dx,g cm-3        1.523                        1.523
Z                4                            4
Mu (mm-1)        0.906                        0.906
F000             1904.0                       1904.0
F000'            1907.70
h,k,lmax         19,18,19                     19,18,19
Nref             3730                         3714
Tmin,Tmax        0.917,0.930
Tmin'            0.913

Correction method= Not given

Data completeness= 0.996           Theta(max)= 25.499

R(reflections)= 0.0535( 2878)      wR2(reflections)= 0.1779( 3714)

S = 1.043                   Npar= 335
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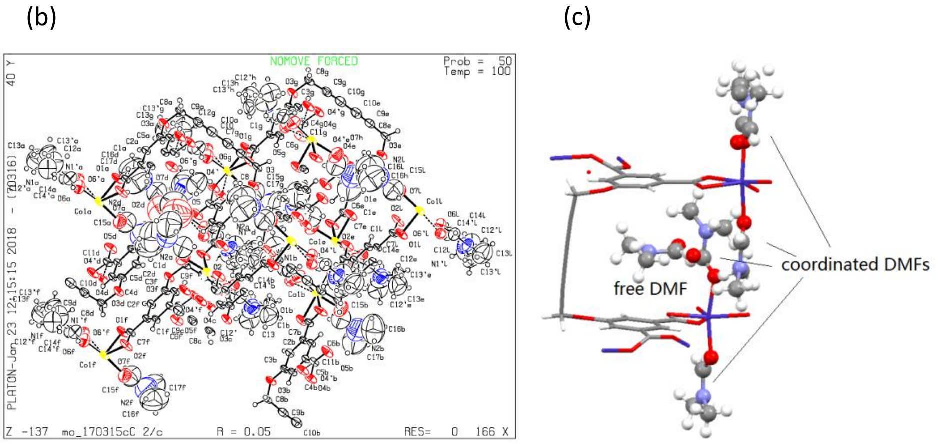


(b)

(c)

Figure S8. (a) CheckCIF and (b) Ellipsoid plot of the crystal structure of MOF crystals. (c) The free DMF molecule (there is a conformational disorder due to the rotation of C-N bond) and coordinated DMF molecules within the crystal. Some A alerts should result from disorders.

(a)

From crystal analysis, the formula of MOF crystals is $C_{37}H_{45}Co_2N_5O_{15}$:
$C_{22}H_{10}O_{10}$+1×DMF(free;C_3H_7NO)+2×DMF(coordinated)+2×DMF(coordinated)+2× Co^{2+}

Loss of the free DMF: (917.65-73.1)/917.65 = 92%

Loss of 3 DMF: (917.65-3×73.1)/917.65 = 76%

Loss of 5 DMF: (917.65-5×73.1)/917.65 = 60%

Loss of 5 DMF and decomposition of COO groups: (917.65-5×73.1-4×44.01)/917.65 = 41%

CoO remains: 149.86/917.65 = 16%

(b)

Before activation

a=16.418 (3) Å, b=15.589 (3) Å, c=16.101 (3) Å

α=90 °, β=103.963 (4) °, γ=90 °

Volume=4000.9 (13) $Å^3$

After activation

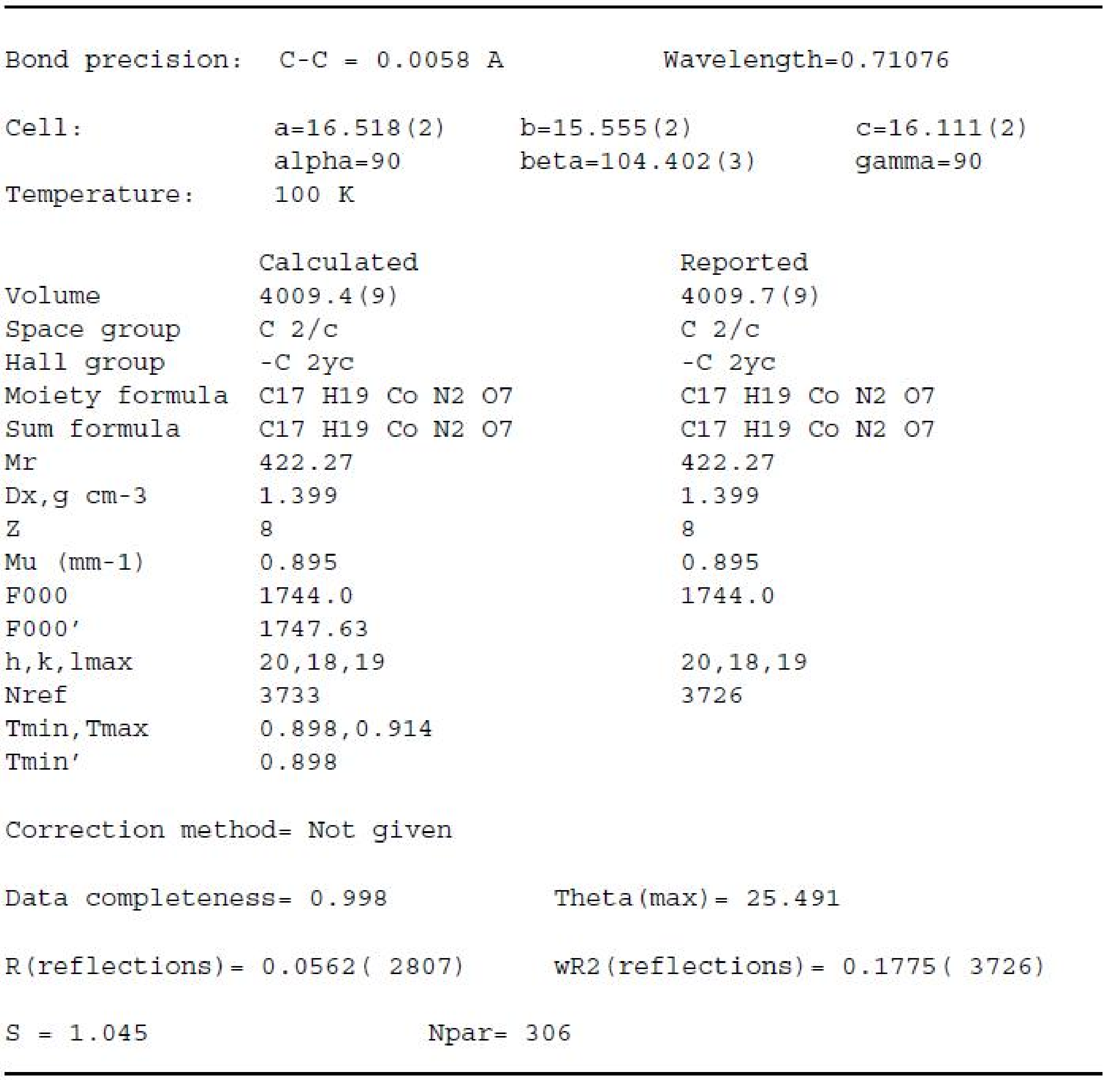
a=16.518 (2) Å, b=15.555 (2) Å, c=16.111 (2) Å

α=90 °, β=104.402 (3) °, γ=90 °

Volume=4009.4 (9) $Å^3$

Figure S9. (a) Calculation of the TG analysis of MOF crystals; (b) cell parameters of MOF crystals before and after activation at 140 °C.

(a)



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Bond precision:   C-C = 0.0058 A          Wavelength=0.71076

Cell:             a=16.518(2)     b=15.555(2)        c=16.111(2)
                  alpha=90        beta=104.402(3)    gamma=90
Temperature:      100 K

                 Calculated                  Reported
Volume           4009.4(9)                   4009.7(9)
Space group      C 2/c                       C 2/c
Hall group       -C 2yc                      -C 2yc
Moiety formula   C17 H19 Co N2 O7            C17 H19 Co N2 O7
Sum formula      C17 H19 Co N2 O7            C17 H19 Co N2 O7
Mr               422.27                      422.27
Dx,g cm-3        1.399                       1.399
Z                8                           8
Mu (mm-1)        0.895                       0.895
F000             1744.0                      1744.0
F000'            1747.63
h,k,lmax         20,18,19                    20,18,19
Nref             3733                        3726
Tmin,Tmax        0.898,0.914
Tmin'            0.898

Correction method= Not given

Data completeness= 0.998          Theta(max)= 25.491

R(reflections)= 0.0562( 2807)     wR2(reflections)= 0.1775( 3726)

S = 1.045                   Npar= 306
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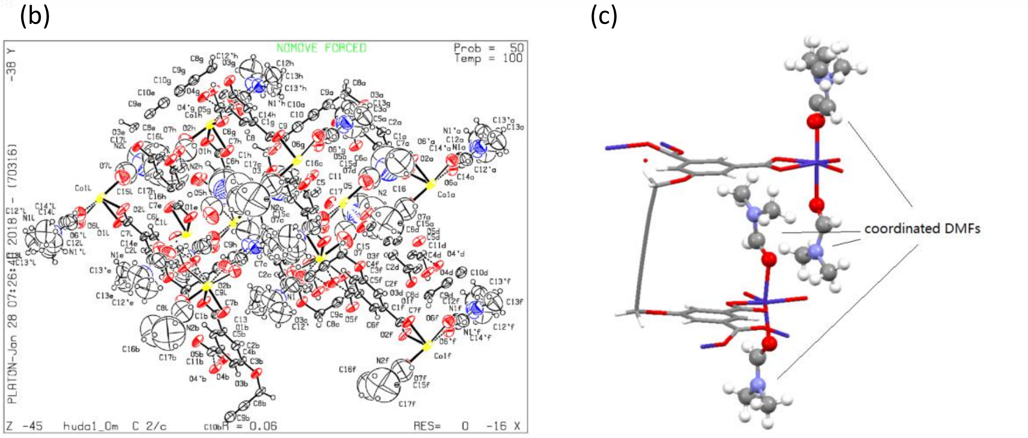


(b)

(c)

Figure S10. (a) CheckCIF and (b) Ellipsoid plot of the crystal structure of MOF crystals after activation at 140 °C. (c) The free DMF molecule disappeared within the void.

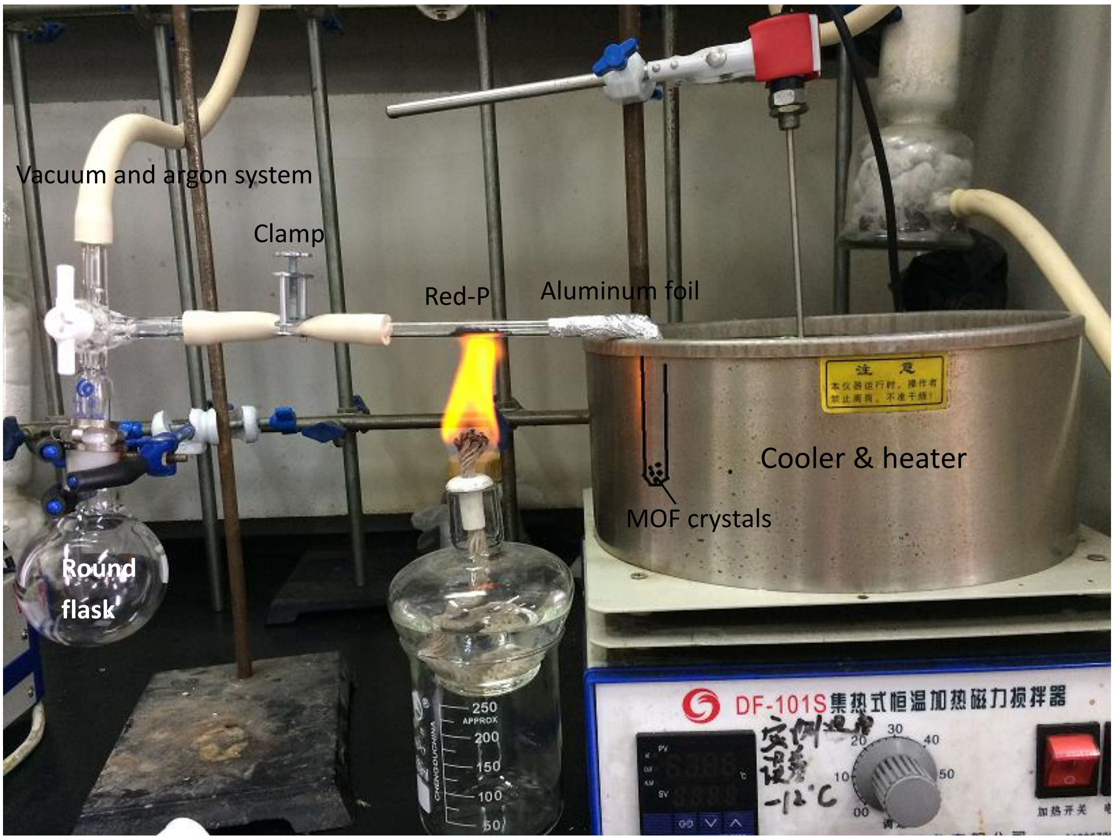


Figure S11. The self-made equipment for P_4 up-take into MOF crystals. Firstly, activated MOF crystals (MOF crystals were activated at 140 °C for 10 hours) and red-phosphorus were loaded in the system. Secondly, the whole system was vacuumed by an oil pump and then the clamp was closed. The round flask was filled with argon. Thirdly, P_4 gas was generated from red phosphorus by an alcohol burner and *in-situ* cooled to immerse MOF crystals. Fourthly, the alcohol burner was extinguished. Finally, the temperature was increased to 80 °C, and the vacuum system was intermittently open. After 10 hours, MOF crystals filled with P_4 (MOF@P_4) was obtained.

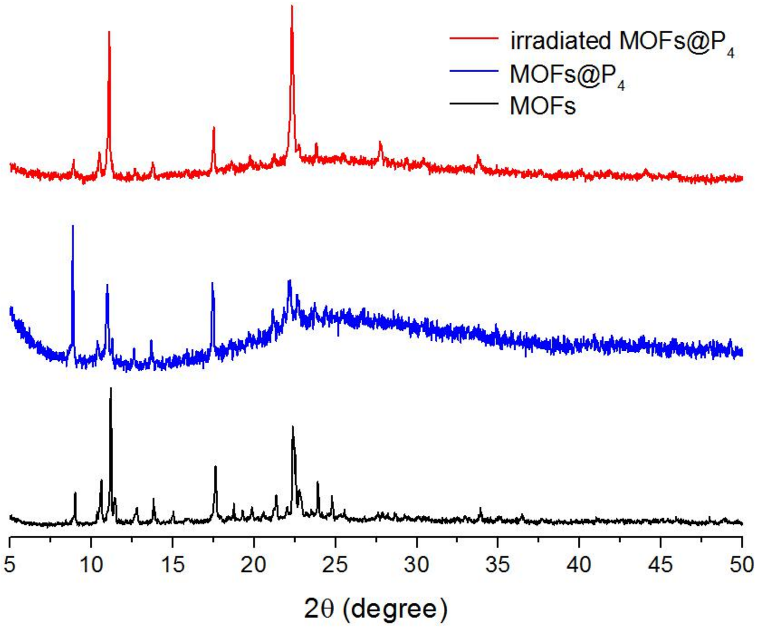


Figure S12. PXRD patterns a of MOFs, MOFs@P_4 and irradiated MOFs@P_4, respectively.

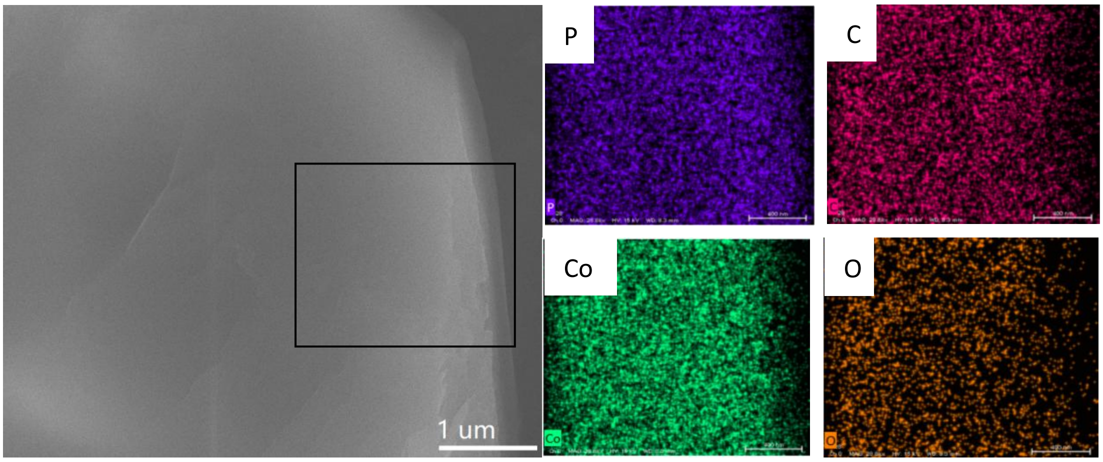


Figure S13. SEM image of the MOF crystals filled with P_4 (MOF@P_4), EDX mappings.

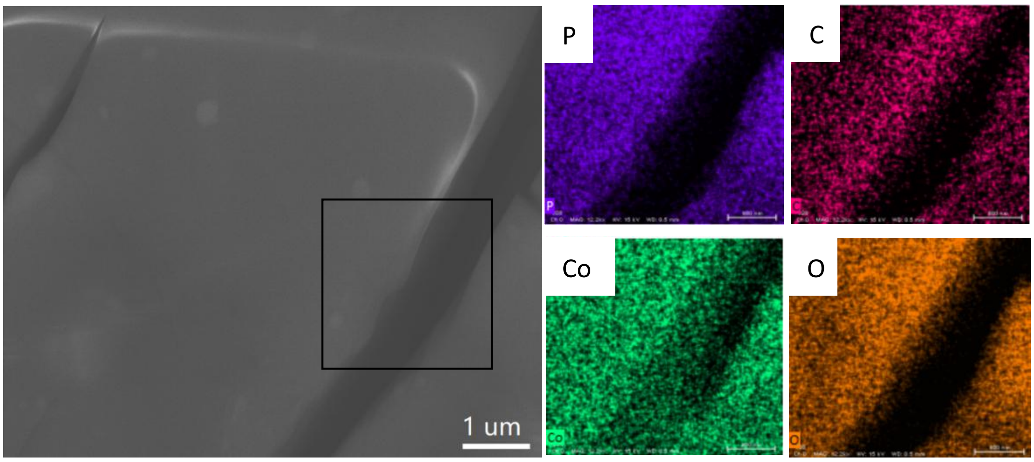


Figure S14. SEM image of the irradiated MOF@P_4 crystals, EDX mappings.

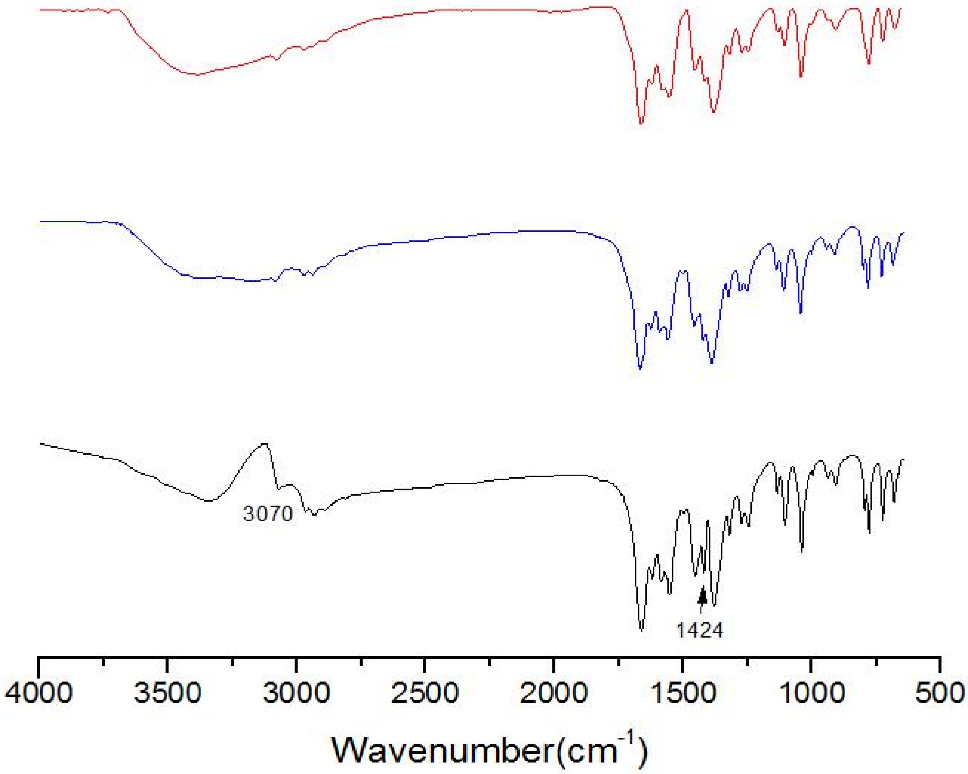


Figure S15. Infrared spectra of MOFs, MOFs@P_4 and irradiated MOFs@P_4, respectively.

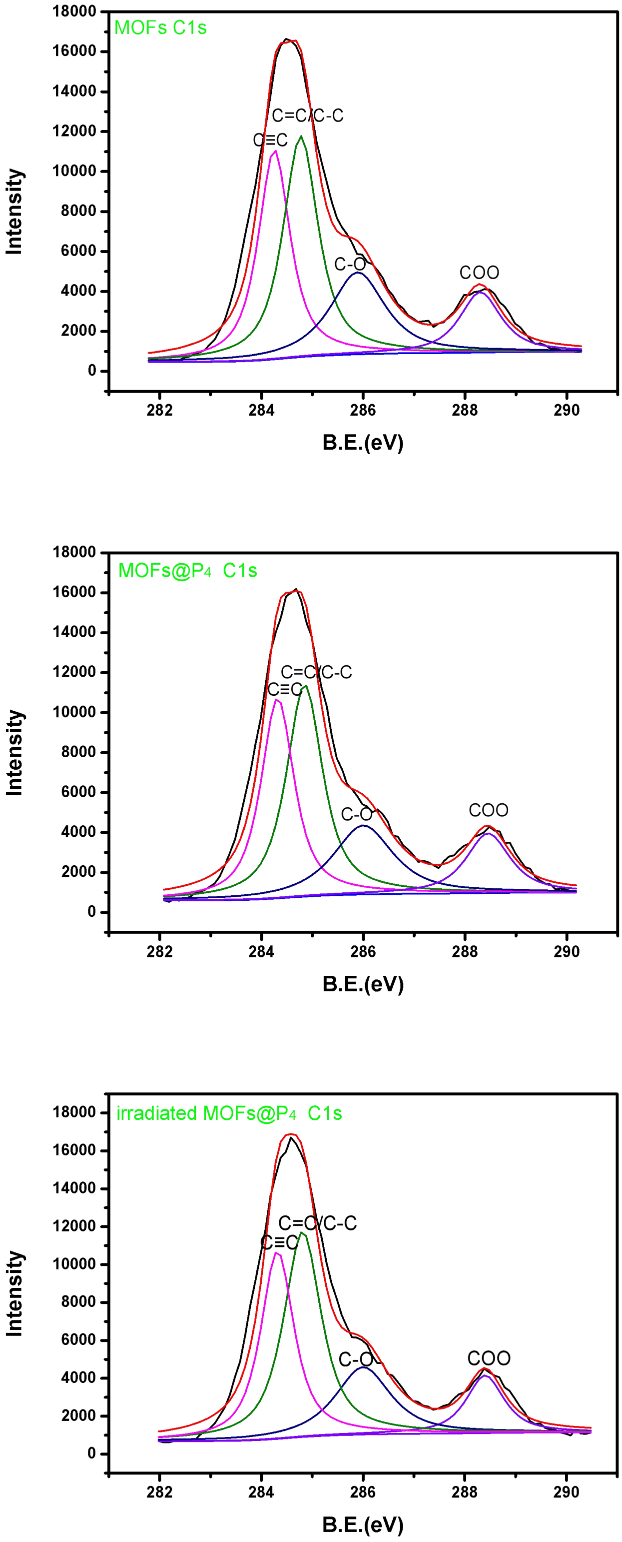


Figure S16. XPS spectra of C1s envelope of MOFs, MOFs@P$_4$ and irradiated MOFs@P$_4$. A should at the left side can be observed in all black curves, so it should not result from the P-C bond (283.5 eV). we tried to add a peak at 283.5 eV during deconvolution of these spectra, but it can not improve the fit of the black curve.

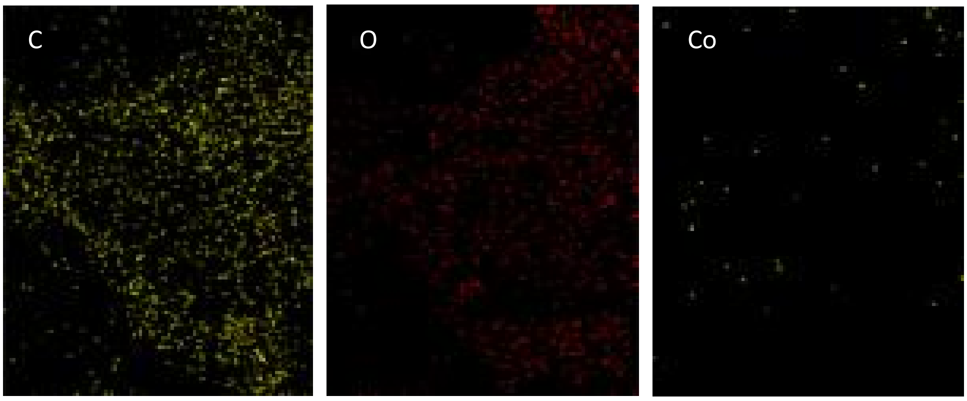


Figure S17 The EDX mapping of C, O and Co elements of the film observed by SEM (Figure 4b).

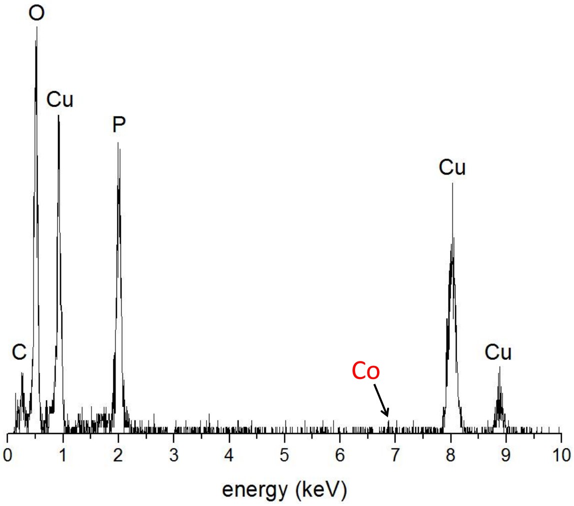


Figure S18. The EDX spectrum of the film observed by TEM.

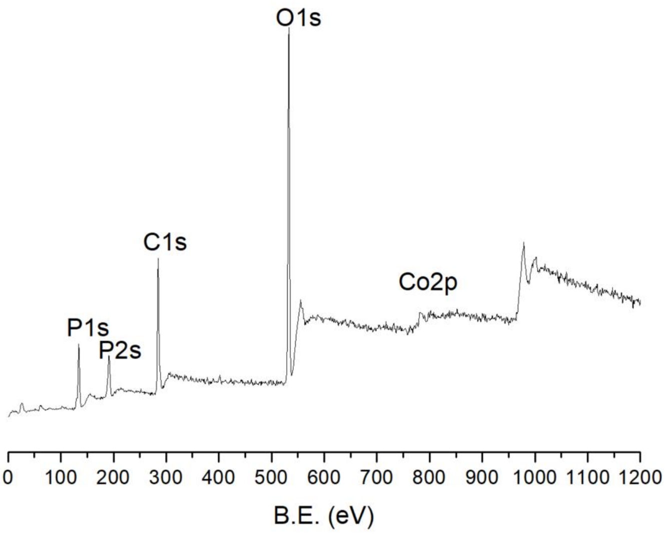
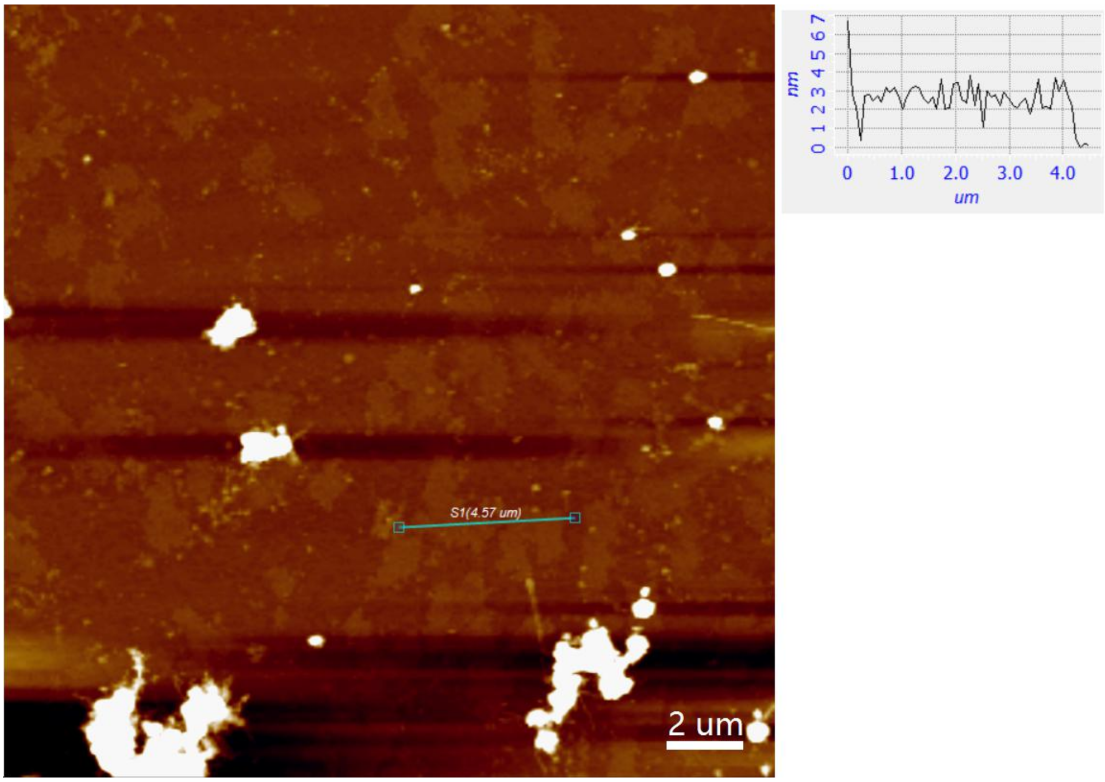


Figure S19. The EDX spectrum of the bulk sample of exfoliated films.



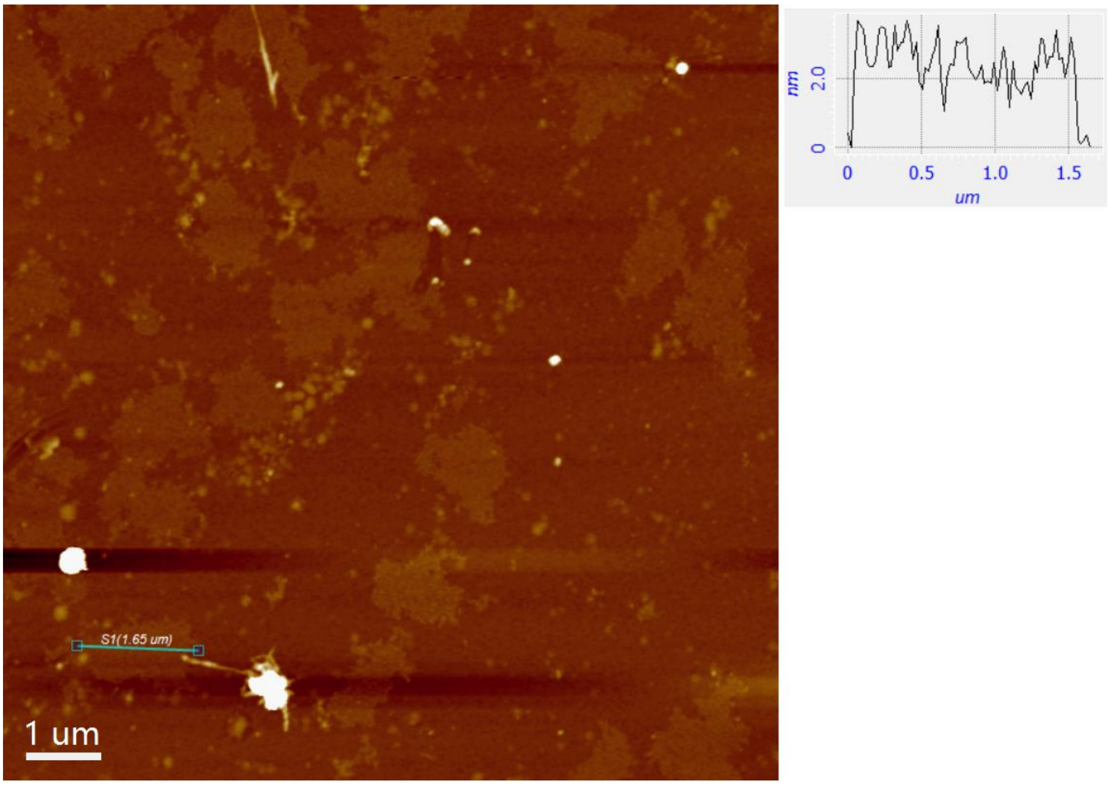
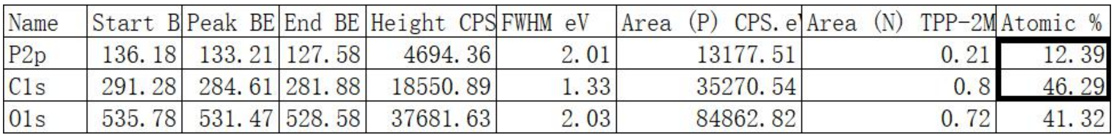


Figure S20. AFM image and height profiles (inserts) of thin sheets.



Name	Start B	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS. e	Area (N) TPP-2M	Atomic %
P2p	136. 18	133. 21	127. 58	4694. 36	2. 01	13177. 51	0. 21	12. 39
C1s	291. 28	284. 61	281. 88	18550. 89	1. 33	35270. 54	0. 8	46. 29
O1s	535. 78	531. 47	528. 58	37681. 63	2. 03	84862. 82	0. 72	41. 32

As a ligand has 22 carbon atom, the ratio between phosphorus atom and ligand is 12.39/(46.29/22) = 5.89 ≈ 6.

Figure S21. calculation of the ratio between phosphorus atom and ligand in phosphorus films based on the XPS atomic contents.

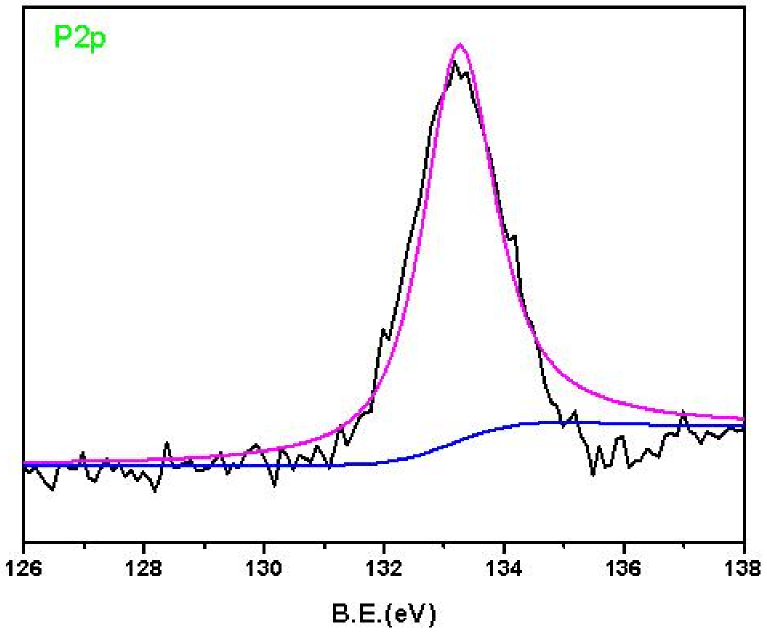


Figure S22. The XPS spectrum of the 2D phosphorus sample stored at r.t. for 15 d in air.