

Supporting Information

Trace of Molecular Doping in Metal-Organic Frameworks: Drastic Change of
Electronic Band Structure with Preserved Topology and Porosity

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S1 Chemicals

2,5-thiophenedicarboxylic acid (H₂TDC), terephthalic acid (BDC), benzene 1,3,5-tricarboxylic acid (TMA) and m-methyl red (MR) were purchased from Admas. Zirconium (IV) chloride (ZrCl₄) was purchased from J&K Co. Ltd. H₂PtCl₆·6H₂O, hemin (HE), 1,5-dihydroxyanthraquinone (1,5-DHAD) and poly(vinylpyrrolidone) (PVP, MW = 55,000) were purchased from Energy Chemical Co. Ltd. Tetrakis (para-hydroxylphenyl) porphyrin (THPP), p-methyl red (PR), tetrahydroxyquinone (THQN), 2,6-naphthalenedicarboxylate (2,6-NDC), 7,7,8,8-tetracyanoquinodimethane (TCNQ) were purchased from TCI. Tetrakis (para-hydroxylphenyl) porphyrin (THPP) was purchased from Frontier Co. Ltd. Sodium hydroxide (NaOH), Cu(NO₃)₂·3H₂O, Zn(NO₃)₂·6H₂O, N,N-dimethylformamide (DMF), N,N-diethylformamide (DEF), N-methyl pyrrolidone (NMP), acetonitrile (CH₃CN), triethanolamine (TEOA), triethylamine (TEA), ethylene glycol, acetone, acetic acid (HAc), formic acid (HCOOH) and benzoic acid were purchased from Sinopharm. [5,10,15,20-Tetrakis(4-carboxyphenyl)porphyrinato]-Ni(II) (TCPP(Ni)) and [5,10,15,20-Tetrakis(4-carboxyphenyl)porphyrinato]-Mn(III) Chloride (TCPP(Mn)) were synthesized according to the procedure in the literature.¹ All chemicals and solvents purchased are analytical grade and used without further purification.

S2 Instruments

The powder X-ray diffraction patterns (PXRD) were recorded by a Rigaku Miniflex 600 Benchtop equipped with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) at room temperature and taken in a 2θ range of 3° - 45° . The UV-Vis absorption spectra were recorded on a PerkinElmer Lambda950 spectrophotometer in transmission mode at room temperature using BaSO₄ as a reference. N₂ adsorption-desorption isotherms were performed in the ASAP 2460 system at 77 K. Samples were activated by solvent exchange (in several cycles using fresh acetone), followed by degassing at elevated temperature (130 °C) for 10 h. X-ray photoelectron spectroscopy (XPS) measurements were performed with the use of a ESCALAB 250Xi spectrometer equipped with an Al-K α X-ray source (1486.6 eV). Energy dispersive X-ray spectroscopy (EDX) elemental mapping images were acquired on a JSM6700-F scanning electron microscope at an accelerating voltage of 15 kV equipped with an energy dispersive detector. Fourier transform infrared spectroscopy (FTIR) spectra were obtained on a Bruker Spectrum in the range of 4000–250 cm⁻¹ mixed with KBr pellet. Raman spectra were measured using LabRAM HR evolution with excitation wavelength of 325 nm. ¹H NMR spectra were recorded using a Bruker Avance III (400 MHz) spectrometer. Scanning electron microscope (SEM) measurements were performed on FEI NANO 450 and energy dispersive X-ray spectroscopy (EDX) was carried out by Oxford Aztec Xmax 50 system equipped with X-ray mapping. TEM images were taken on a JEM-2100F field-emission high-resolution transmission electron microscope. Atomic absorption spectroscopy (AAS) was performed on ContrAA700. The solid-state fluorescent spectra were measured at room temperature on an Edinburgh-instruments FS5 fluorescence spectrophotometer. In a standard three-electrode system, Mott-Schottky experiments were carried out on an electrochemical analyzer (Zahner, Germany) at frequencies of 1000, 1500 and 2000 Hz. The synchrotron x-ray absorption spectra measurements were conducted at the beam line BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), operated at 3.5 GeV with injection currents of 140-210 mA. The station was operated with a Si(111) double crystal monochromator.

S3 Synthetic procedures

Synthesis of DUT-67

DUT-67 was prepared following a modified procedure as described in literature.² In a typically experiment, 42 mg of

ZrCl₄ and 20 mg of 2,5-thiophenedicarboxylic acid (H₂TDC) were dissolved in the mixture of DMF (2.2 mL) and NMP (2.2 mL) by sonication for 10 min. Following that, 1.6 mL acetic acid was added, then sealed and put into a preheated oven at 120 °C for 48 h. Product was collected by centrifugation and washed several times with DMF and acetone until the supernatant became colorless. Finally, DUT-67 was activated by removing the solvent under vacuum at 130 °C overnight.

Synthesis of X MR⊂DUT-67 (X = 0.71 %, 1.59 %, 1.94 % or 3.14 %)

X MR⊂DUT-67 was prepared following the above method with slight modifications. Typically, 42 mg of ZrCl₄, 20 mg of 2,5-thiophenedicarboxylic acid (H₂TDC) and X mg of m-methyl red (X = 4, 10, 16 or 24) were dissolved in the mixture of DMF (2.2 mL) and NMP (2.2 mL) by sonication for 10 min. Following that, 1.6 mL acetic acid was added, and then sealed and put into a preheated oven at 120 °C for 48 h. Product was collected by centrifugation and washed several times with DMF and acetone until the supernatant became colorless. Finally, DUT-67 was activated by removing the solvent under vacuum at 130 °C overnight.

Synthesis of X⊂DUT-67 (X = PR, HE, THQN, TCNQ or 1, 5-DHAD)

The above method for synthesis of 0.71 % MR⊂DUT-67 was used with 8 mg of X (X = PR, HE, THQN, TCNQ or 1,5-DHAD) instead of 4 mg of m-methyl red in the reaction mixture.

Synthesis of TCPP(X)⊂DUT-67 (X = Mn or Ni)

The above method for synthesis of 0.71 % MR⊂DUT-67 was used with 3 mg of [5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin]-X (X = Mn(III) or Ni(II)) instead of 4 mg of m-methyl red in the reaction mixture.

Synthesis of THPP⊂DUT-67

The above method for synthesis of 0.71 % MR⊂DUT-67 was used with 3 mg of tetrakis (para-hydroxyphenyl) porphyrin (THPP) instead of 4 mg of m-methyl red in the reaction mixture.

Synthesis of UiO-66

UiO-66 was prepared following the similar procedure as described in literature.³ ZrCl₄ (30 mg, 0.129 mmol), BDC (20 mg, 0.120 mmol) and benzoic acid (600 mg, 4.918 mmol) in 2 mL of DMF were ultrasonically dissolved in a Pyrex vial. The mixture was heated in an oven at 120 °C for 48 h. Product was collected by centrifugation and washed several times with DMF and acetone. Finally, UiO-66 was activated by removing the solvent under vacuum at 130 °C overnight.

Synthesis of MR⊂UiO-66-120

MR⊂UiO-66-120 was prepared following the UiO-66 method with slight modifications. ZrCl₄ (30 mg, 0.129 mmol), BDC (20 mg, 0.12 mmol), m-methyl red (10 mg, 0.037mmol) and benzoic acid (600 mg, 4.918 mmol) in 2 mL of DMF were ultrasonically dissolved in a Pyrex vial. The mixture was heated in an oven at 120 °C for 48 h. Product was collected by centrifugation and washed several times with DMF and acetone until the supernatant became colorless. Finally, MR⊂UiO-66-120 was activated by removing the solvent under vacuum at 130 °C overnight.

Synthesis of MR⊂UiO-66-180

MR⊂UiO-66-180 was prepared by the above method except that the reaction was under 180 °C.

Synthesis of MR-PS⊂DUT-67

Typically, 40 mg of DUT-67 and MR (20 mg) were immersed in the DMF (5 mL), and then allowed to react at 120 °C for six days without stirring. The yellow precipitates were collected by centrifugation and washed several times with DMF and acetone until the supernatant became colorless. Finally, MR-PS⊂DUT-67 was activated by removing the solvent under vacuum at 130 °C overnight.

Synthesis of X-HCOOH (X= 0.6 mL, 1.0 mL or 1.6 mL)

In a typical synthetic process, 42 mg of ZrCl₄, 20 mg of 2,5-thiophenedicarboxylic acid (H₂TDC) and 4 mg of m-methyl red (MR) were dissolved in the mixture of DMF (2.2 mL) and NMP (2.2 mL) by sonication for 10 min. Following that, formic acid (0.6 mL, 1.0 mL or 1.6 mL) was added in the glass vials, and then sealed and put into a preheated oven at 120 °C for 48 h. Product was collected by centrifugation and washed several times with DMF and acetone until the

supernatant became colorless. Finally, the obtained materials were activated under vacuum overnight at 130 °C to remove the solvent.

Synthesis of HKUST-1

HKUST-1 was prepared following a modified procedure as described in literature.⁴ In a typically experiment, 75 mg of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 44.6 mg of TMA were mixed with 1.25 mL EtOH/ H_2O ($V_{\text{EtOH}}:V_{\text{H}_2\text{O}} = 1:1$), and put into a preheated oven at 120 °C for 48 h. Product was collected by centrifugation and washed several times with acetone. Finally, HKUST-1 was activated by removing the solvent under vacuum at 80 °C overnight.

Synthesis of TCPP(Mn)@HKUST-1

75 mg of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 44.6 mg of TMA and 3mg of TCPP(Mn) were mixed with 1.25 mL EtOH/ H_2O ($V_{\text{EtOH}}:V_{\text{H}_2\text{O}} = 1:1$) and put into a preheated oven at 120 °C for 48 h. Product was collected by centrifugation and washed several times with acetone until the supernatant became colorless. Finally, TCPP(Mn)@HKUST-1 was activated by removing the solvent under vacuum at 80 °C overnight.

Synthesis of MOF-5

MOF-5 was prepared following a modified procedure as described in literature.⁵ $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (120 mg) and BDC (33.4 mg) were dissolved in DMF (4 mL). TEA (220 μL) was slowly added drop by drop to the solution with stirring for 1 h under atmospheric condition. The white powder was washed with DMF and acetone, and finally dried at 80 °C for 3 h in an oven.

The single crystal was obtained using the following procedure. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (73 mg) and BDC (13 mg) were dissolved in 2 mL of DEF, and put into a preheated oven at 100 °C for 24 h.

Synthesis of TCPP(Mn)@MOF-5

The powder and crystal of TCPP(Mn)@MOF-5 were prepared by the above method except 3mg of TCPP(Mn) was added into the reaction, respectively.

Synthesis of Pt NPs

Typically, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (50.75 mg, 0.098 mmol) was dissolved in 20 mL of ethylene glycol with 222 mg of poly(vinylpyrrolidone) (PVP, MW = 55,000) in a round bottomed flask. The mixture was heated at 180 °C for 10 min, during which the color of the solution turned from yellow to black. The as-synthesized PVP-protected Pt NPs were precipitated by acetone and then collected by centrifugation at 12,000 rpm for 10 minutes. The sample was then washed with acetone and hexane to remove excess free PVP, and re-dispersed in DMF to give a colloidal solution of Pt NPs with the concentration of about 1 mg/mL.

Synthesis of Pt@DUT-67

42 mg of ZrCl_4 and 20 mg of 2,5-thiophenedicarboxylic acid (H_2TDC) were dissolved in the mixture of DMF (0.7 mL) and NMP (2.2 mL). Following that, 1.6 mL acetic acid and 1.5 mL Pt NPs solution (~ 1 mg/mL) were added, then sealed and put into a preheated oven at 130 °C for 48 h. Product was collected by centrifugation and washed several times with DMF and acetone until the supernatant became colorless. Finally, the obtained materials were activated under vacuum overnight at 80 °C to remove the solvent.

Synthesis of Pt@TCPP(Mn)@DUT-67

42 mg of ZrCl_4 , 20 mg of 2,5-thiophenedicarboxylic acid (H_2TDC) and 3 mg of TCPP(Mn) were dissolved in the mixture of DMF (0.7 mL) and NMP (2.2 mL). Following that, 1.6 mL acetic acid and 1.5 mL Pt NPs solution (~ 1 mg/mL) were added, then sealed and put into a preheated oven at 130 °C for 48 h. Product was collected by centrifugation and washed several times with DMF and acetone until the supernatant became colorless. Finally, the obtained materials were activated under vacuum overnight at 80 °C to remove the solvent.

Synthesis of DUT-52

DUT-52 was synthesized according to the documented method.⁶ ZrCl_4 (23 mg, 0.103 mmol) and 2,6-naphthalenedicarboxylate (2,6-NDC) (21.6 mg, 0.1 mmol) were dissolved in 5 mL of DMF. 0.1 mL of acetic acid were

added and the mixture was sonicated for additional 5 minutes. The reaction mixture was heated in an oven at 120 °C for 48 h. The obtained crystalline powder was washed several times with DMF and acetone.

Synthesis of Pt@DUT-52

The photocatalyst Pt@DUT-52 was synthesized according to the modified procedure as described in literature.⁷ In a typical experiment, ZrCl₄ (23 mg, 0.103 mmol) and 2,6-naphthalenedicarboxylate (2,6-NDC) (21.6 mg, 0.1 mmol) were dissolved in 5 mL of DMF. Following that, 0.4 mL of acetic acid and 1.5 mL Pt NPs solution (~ 1 mg/mL) were added and the mixture was sonicated for additional 5 minutes. The reaction mixture was heated in an oven at 120 °C for 48 h. The product was collected by centrifugation and washed several times with DMF and acetone until the supernatant became colorless. Finally, the obtained materials were activated under vacuum overnight at 80 °C to remove the solvent.

Synthesis of Pt@TCPP(Mn)@DUT-52

ZrCl₄ (23 mg, 0.103 mmol), 2,6-naphthalenedicarboxylate (2,6-NDC) (21.6 mg, 0.1 mmol) and 3 mg of TCPP(Mn) were dissolved in 5 mL of DMF. Following that, 0.3 mL of acetic acid and 1.5 mL Pt NPs solution (~ 1 mg/mL) were added and the mixture was sonicated for additional 5 minutes. The reaction mixture was heated in an oven at 120 °C for 48 h. The product was collected by centrifugation and washed several times with DMF and acetone until the supernatant became colorless. Finally, the obtained materials were activated under vacuum overnight at 80 °C to remove the solvent.

S4 Power X-ray diffraction (PXRD) patterns

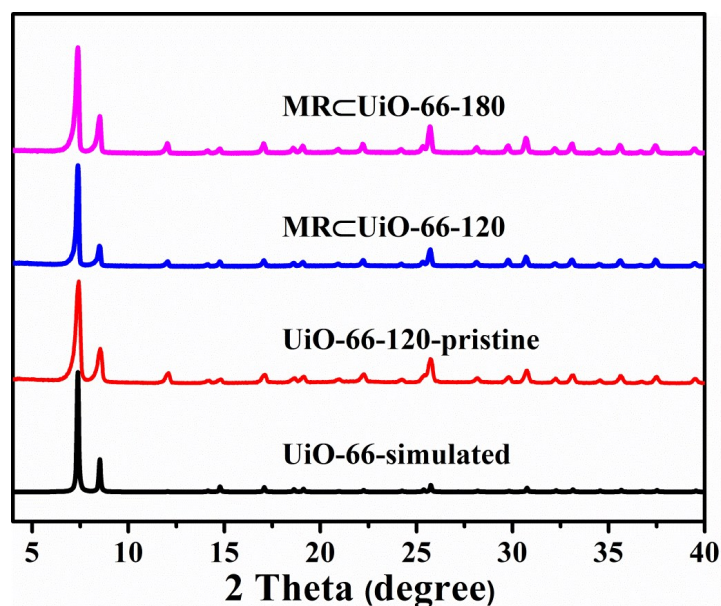


Figure S1. PXRD analyses for UiO-66-120, MR@UiO-66-120 or MR@UiO-66-180

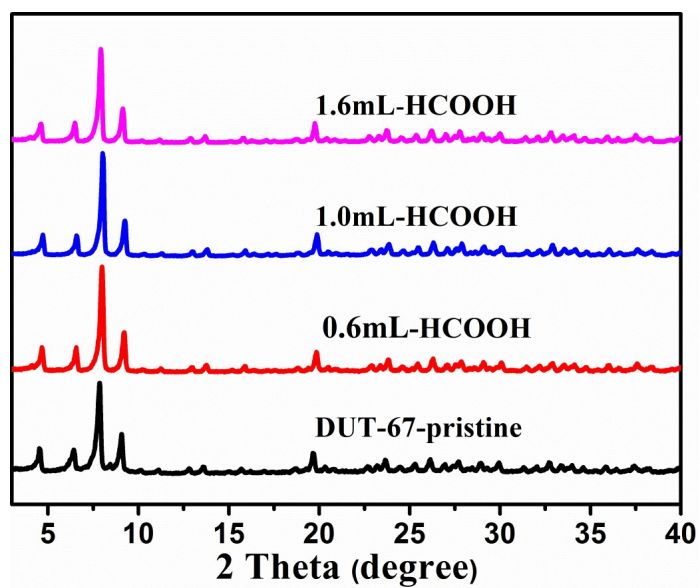


Figure S2. PXRD analyses for X-HCOOH (X= 0.6 mL, 1.0 mL or 1.6 mL)

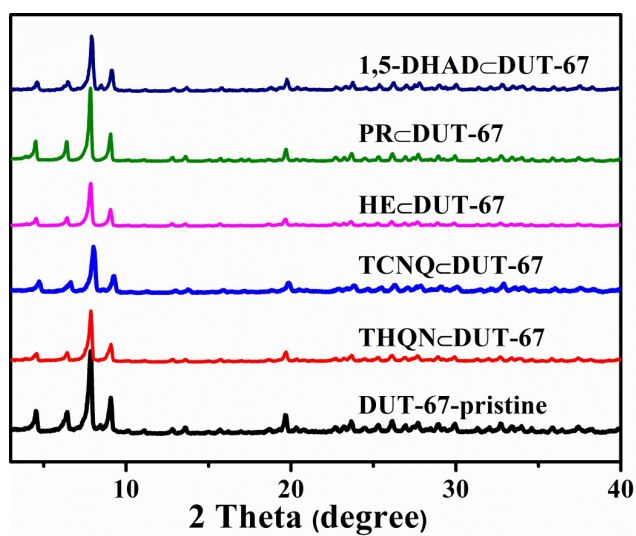


Figure S3. PXRD analyses for X@DUT-67 (X=1,5-DHAD, PR, HE, TCNQ or THQN)

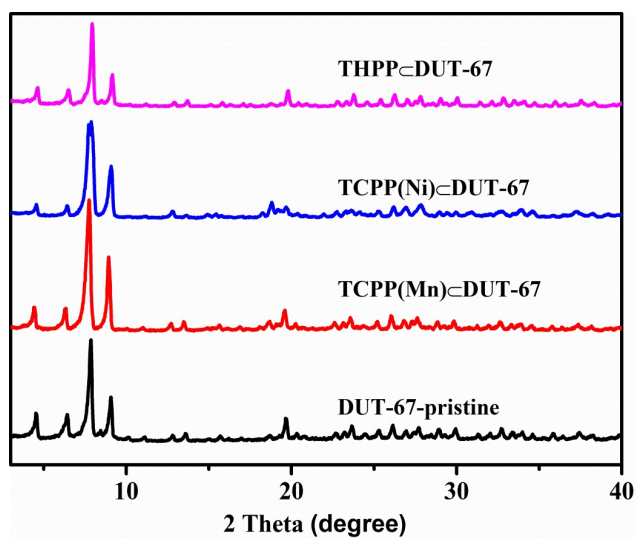


Figure S4. PXRD analyses for X@DUT-67 (X=THPP, TCPP(Ni) or TCPP(Mn))

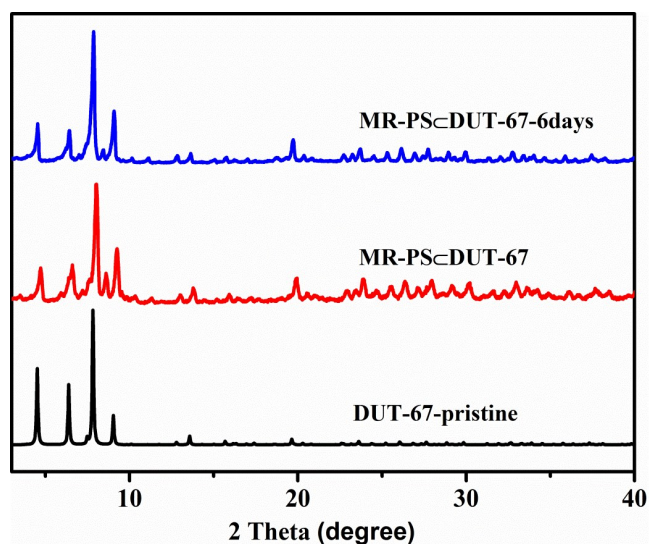


Figure S5. PXRD analyses for MR-PS@DUT-67 and MR-PS@DUT-67 after being treated in DMF at 60 °C for six days.

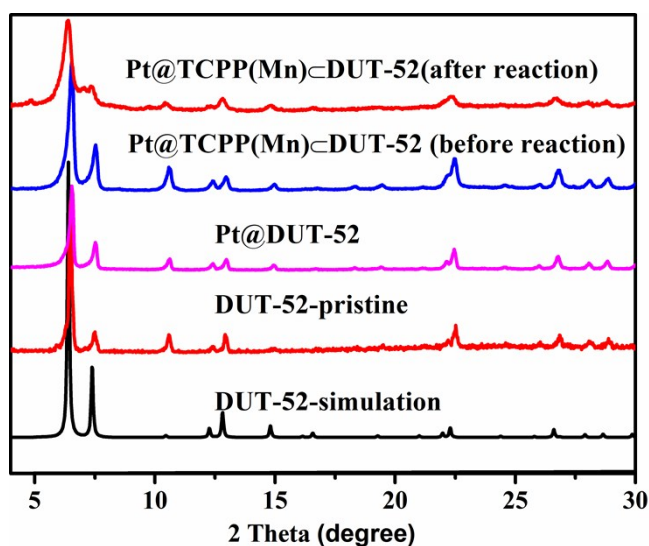


Figure S6. PXRD analyses for DUT-52, Pt@DUT-52 and Pt@TCPP(Mn)@DUT-52 before and after photocatalytic reaction.

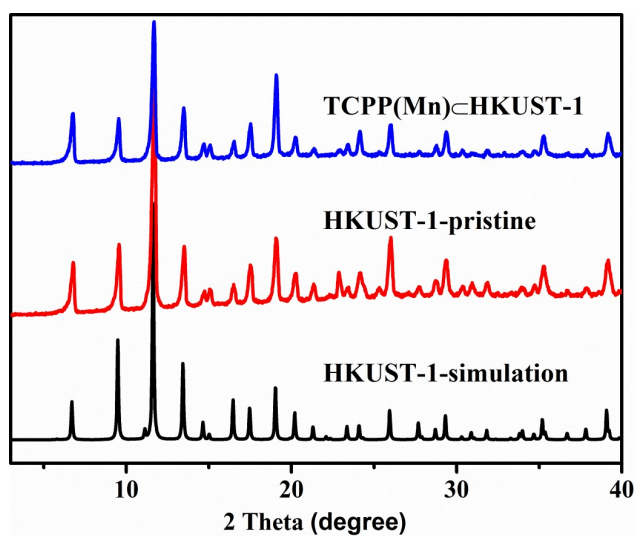


Figure S7. PXRD analyses for HKUST-1 and TCPP(Mn)@HKUST-1.

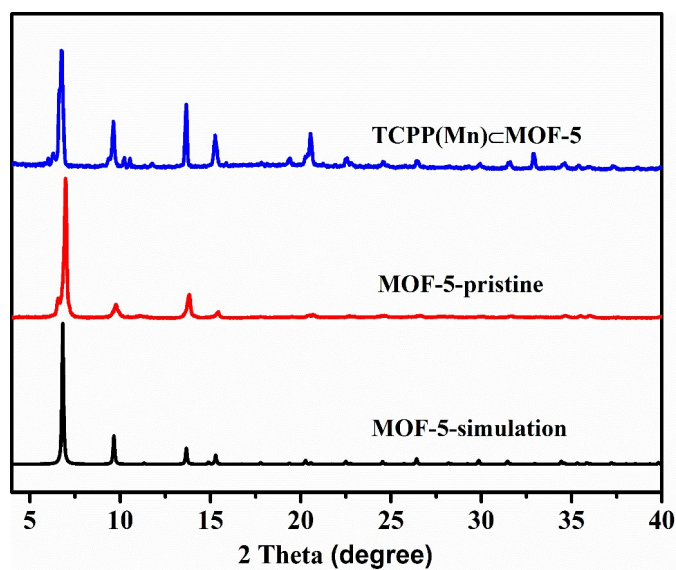


Figure S8. PXRD analyses for MOF-5 and TCPP(Mn)@MOF-5.

S5 ^1H NMR spectra

15 mg doped DUT-67 samples and 20 mg NaOH were digested in a solution of 0.5 mL D_2O and sonicated for 15 min. The supernatant was obtained by centrifugation and analyzed by ^1H NMR. The weight ratio of H_2TDC : MR is based on the integral areas of H_2TDC and MR. The peak derived from H_2TDC ligand is designated as “a” in all the figures.

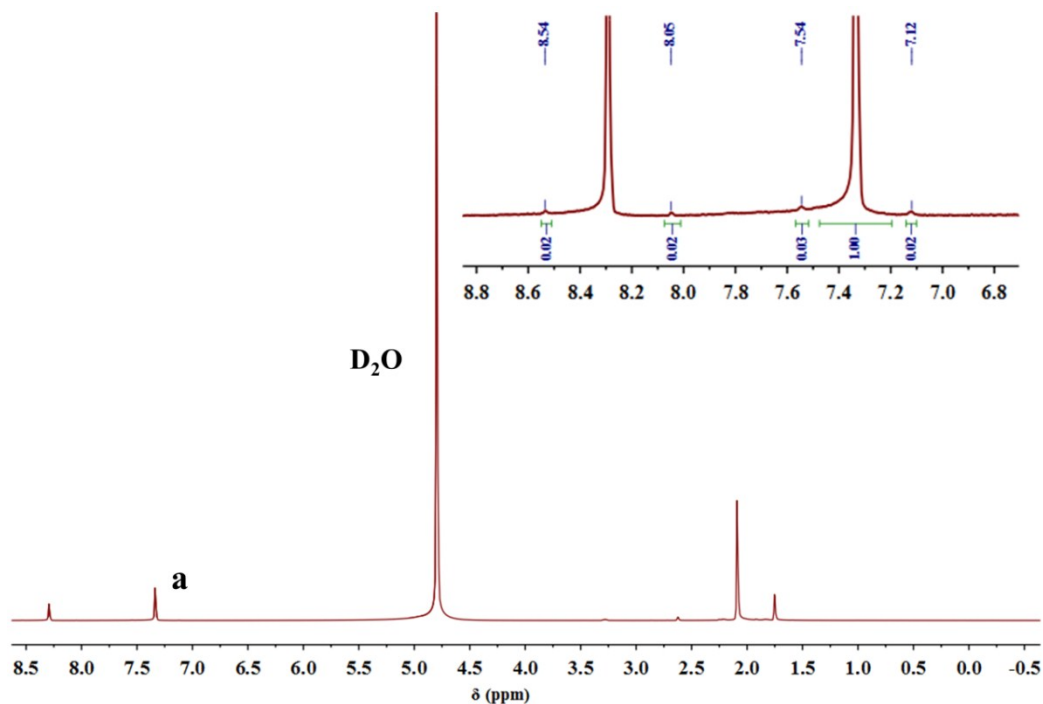


Figure S9. ^1H NMR spectrum of digested 1.59% MR@DUT-67 ligand in D_2O . The signals in aromatic region (inset) show the presence of 1.59 % MR (in weight percent) in DUT-67.

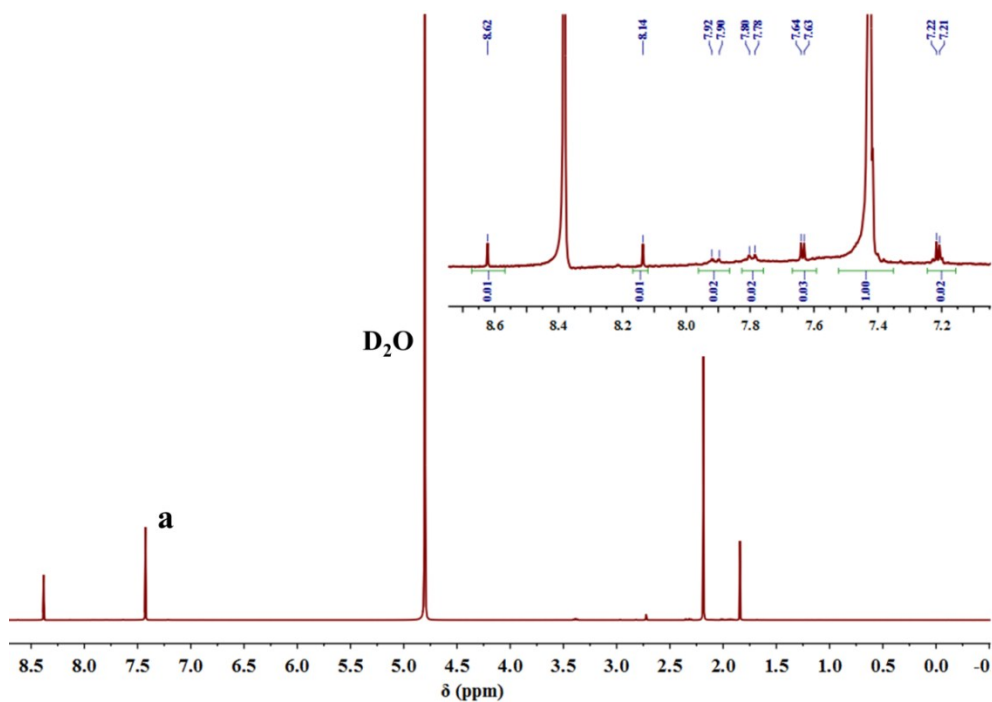


Figure S10. ¹H NMR spectrum of digested **1.94% MR-DUT-67** ligand in D₂O. The signals in aromatic region (inset) show the presence of 1.94% MR (in weight percent) in **DUT-67**.

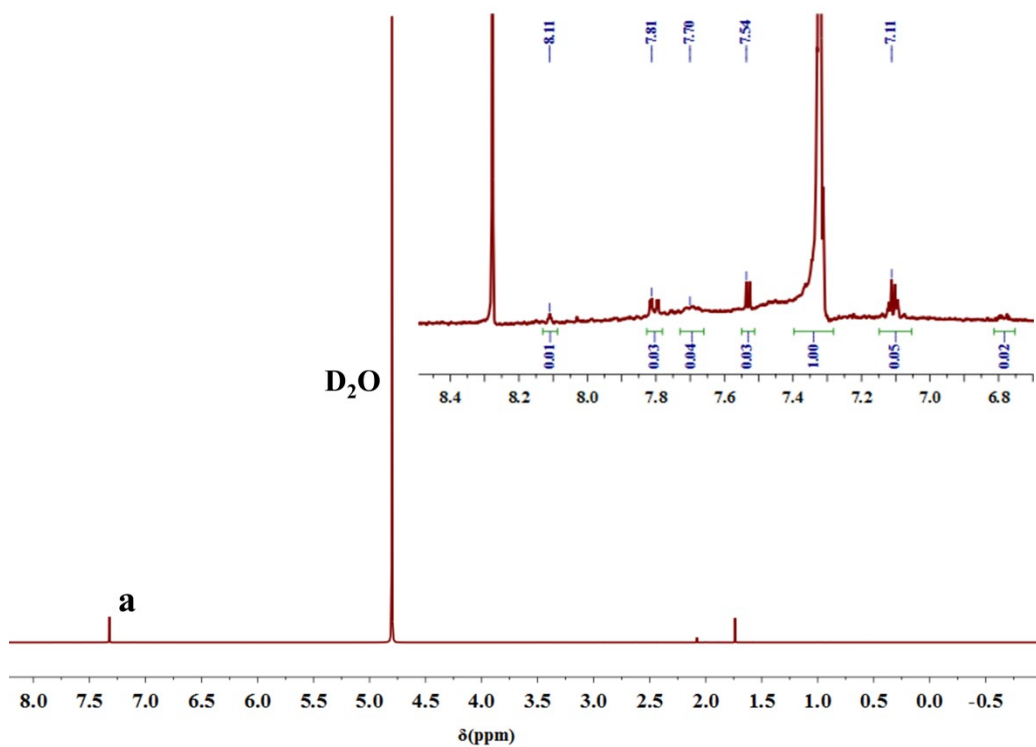


Figure S11. ¹H NMR spectrum of digested **3.14% MR-DUT-67** ligand in D₂O. The signals in aromatic region (inset) show the presence of 3.14% MR (in weight percent) in **DUT-67**.

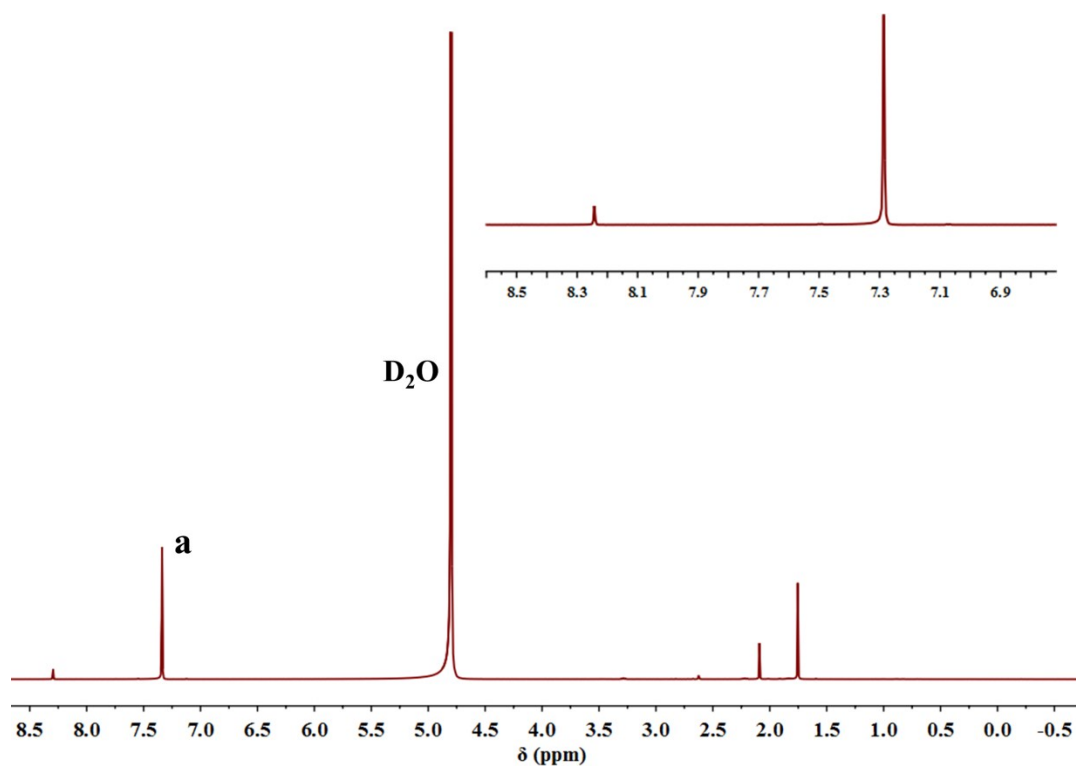


Figure S12. ^1H NMR spectrum of digested DUT-67 in D_2O .

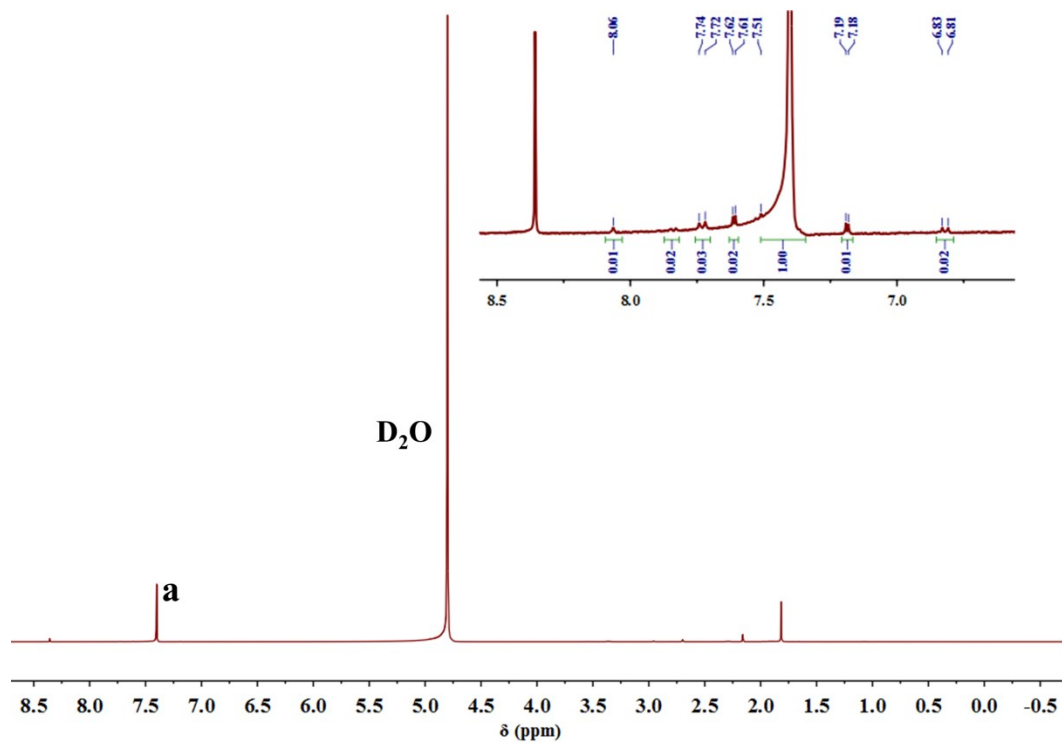


Figure S13. ^1H NMR spectrum of digested **physical mixture** of MR (1 mg) and DUT-67 (50 mg) in D_2O , closing to the 1.94% MR<DUT-67. The signals in aromatic region (inset) show the presence of 1.94 % MR in **physical mixture**.

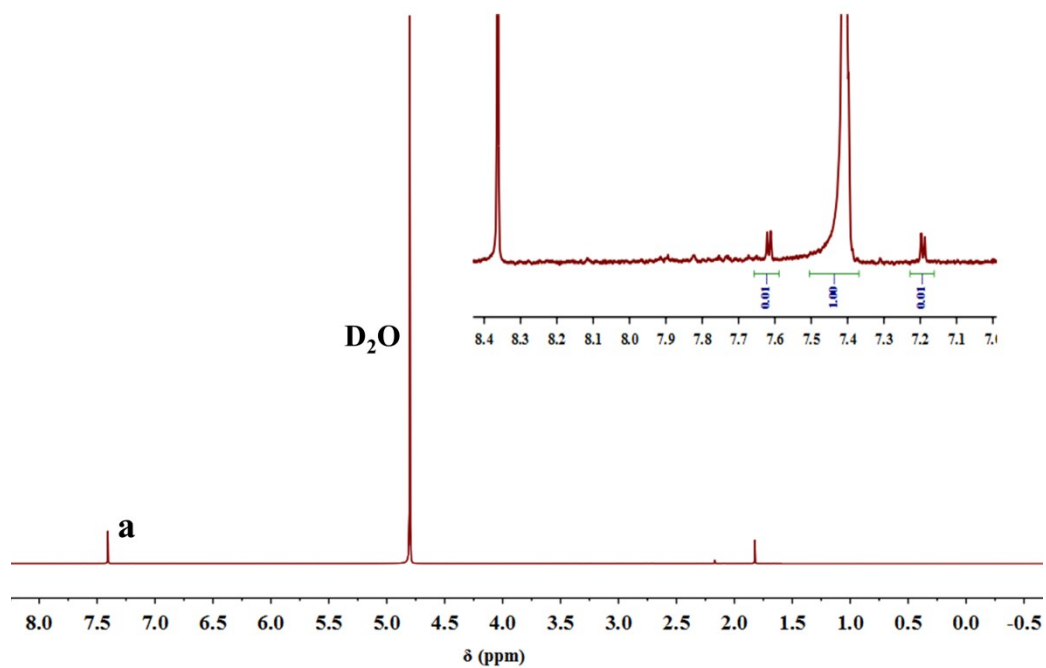


Figure S14. ^1H NMR spectrum of digested 0.36 % PR in DUT-67 in D_2O . The signals in aromatic region (inset) show the presence of 0.36 % (in weight percent) PR in DUT-67.

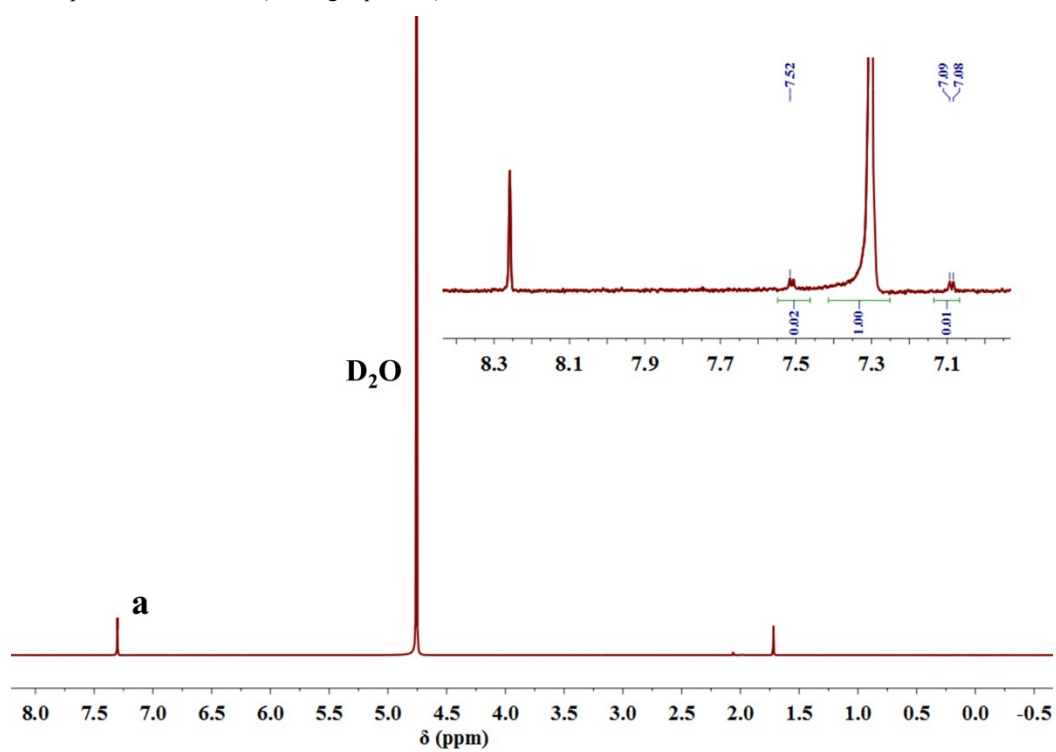


Figure S15. ^1H NMR spectrum of digested 2.11 % THQN in DUT-67 in D_2O . The signals in aromatic region (inset) show the presence of 2.11 % (in weight percent) THQN in DUT-67.

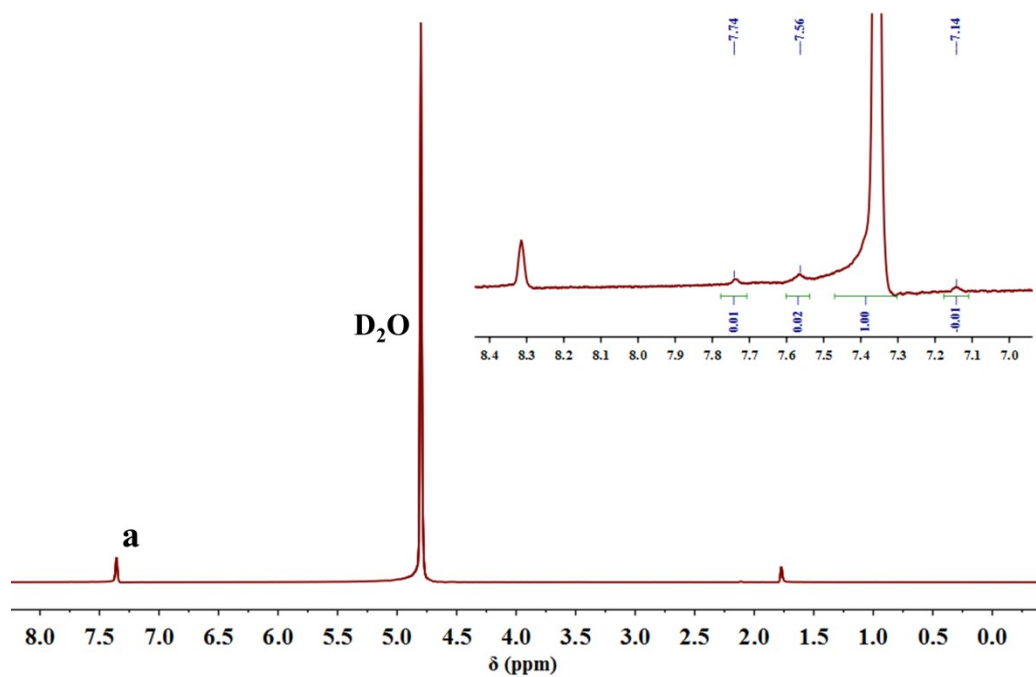


Figure S16. ^1H NMR spectrum of digested TCNQ-DUT-67 in D_2O . The signals in aromatic region (inset) show the presence of 1.42 % (in weight percent) TCNQ in DUT-67.

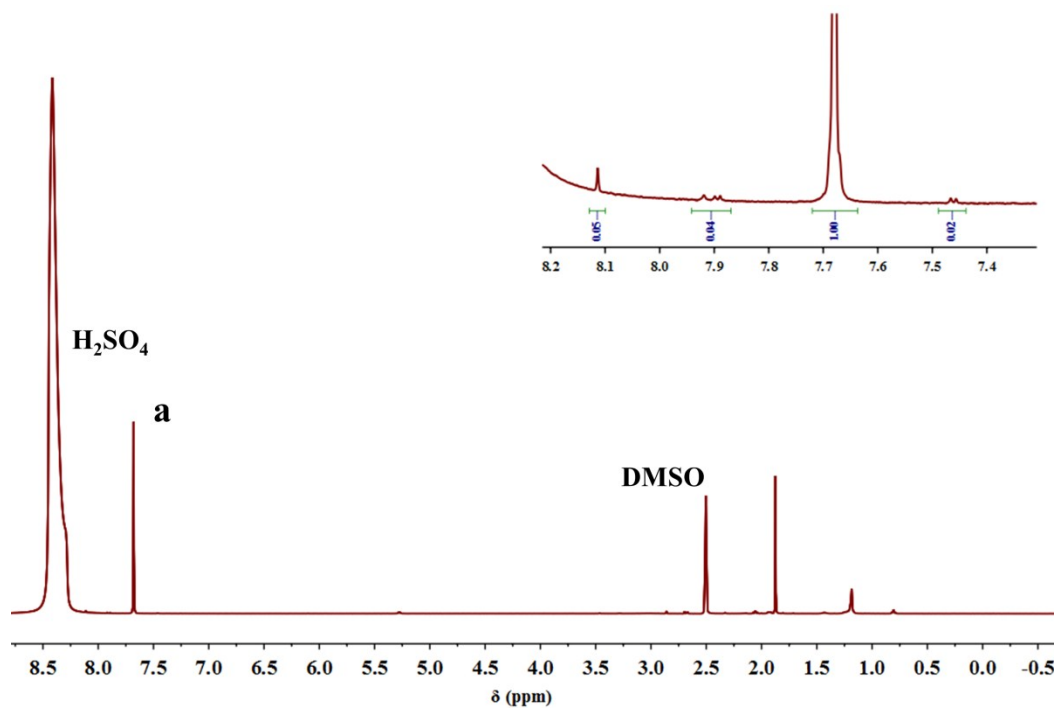


Figure S17. ^1H NMR spectrum of digested 1,5-DHAD-DUT-67 in DMSO. The signals in aromatic region (inset) show the presence of 2.3 % (in weight percent) 1,5-DHAD in DUT-67.

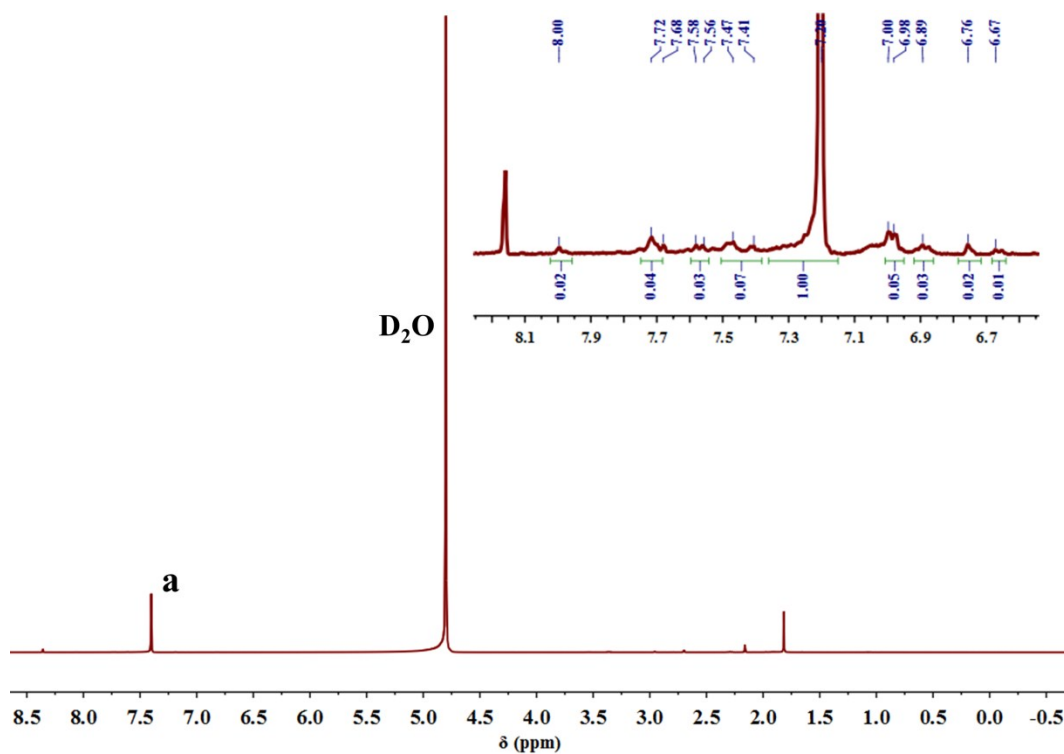


Figure S18. ^1H NMR spectrum of digested MR-PS@DUT-67 in D_2O . The signals in aromatic region (inset) show the presence of 4.64 % (in weight percent) MR in DUT-67.

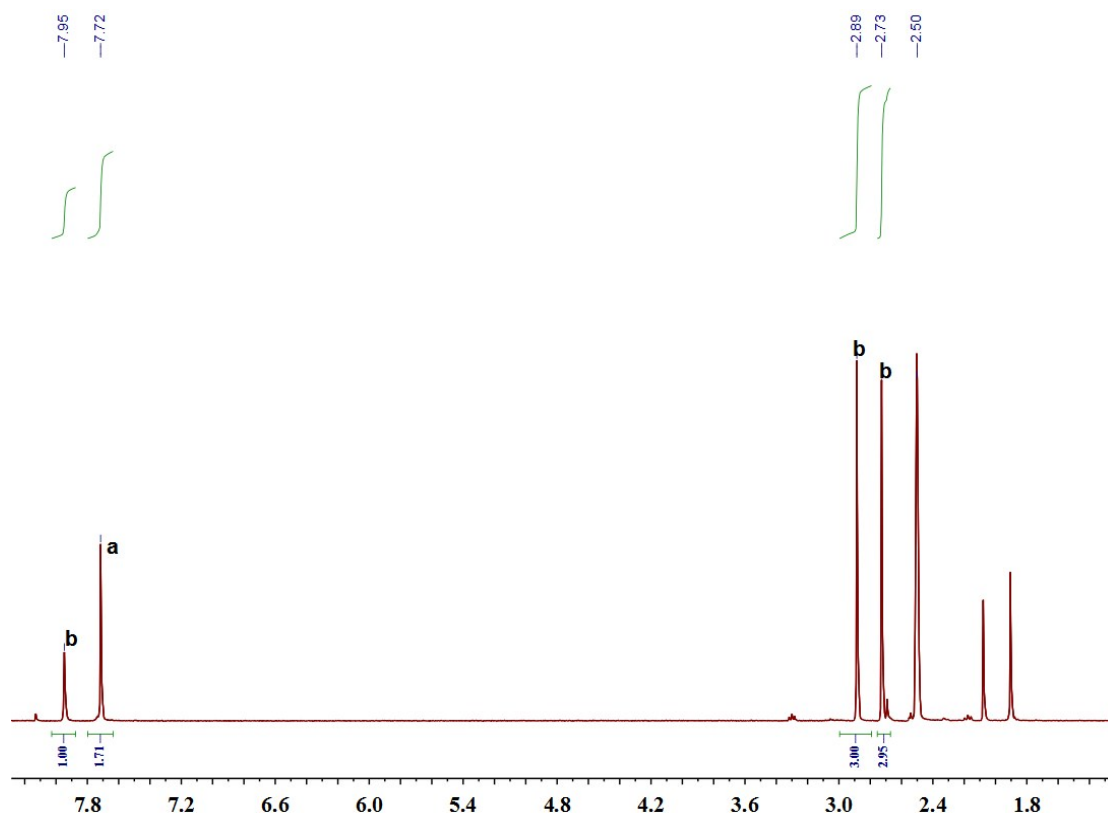


Figure S19. ^1H NMR spectrum of digested DUT-67 before activation in DMSO. The peaks designated as “b” are assigned to DMF.

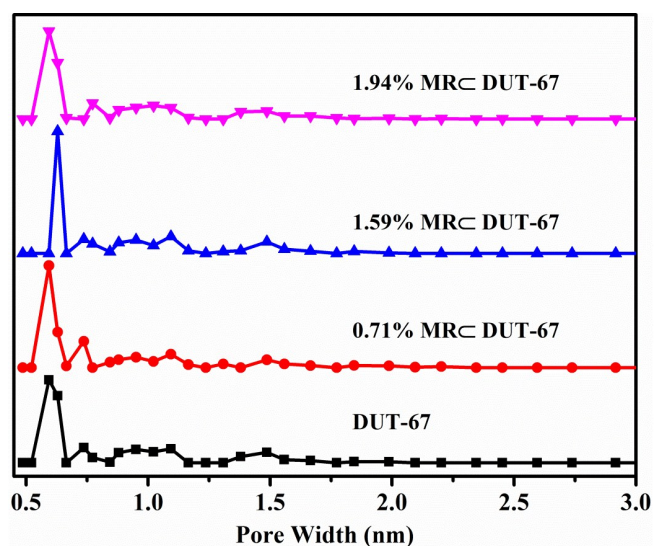


Figure S20. DFT pore size distribution of 0.71 % MRcDUT-67, 1.59 % MRcDUT-67 and 1.94 % MRcDUT-67 deduced from the corresponding N₂ isotherms.

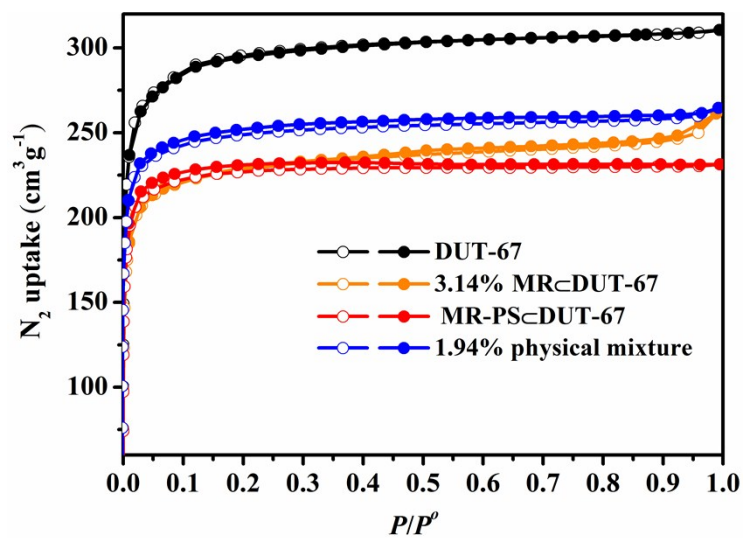


Figure S21. N₂ isotherms of pure DUT-67 and 3.14 % MRcDUT-67, MR-PScDUT-67 and 1.94% physical mixture.

S7 Photoluminescence spectroscopy

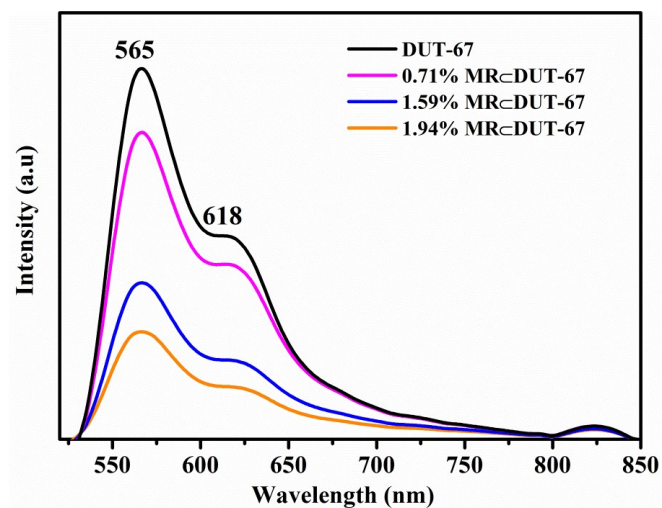


Figure 22. PL emission spectra (excited at 275 nm) for DUT-67, 0.71 % MR_cDUT-67, 1.59% MR_cDUT-67 and 1.94% MR_cDUT-67.

S8 Fourier transform infrared spectroscopy (FTIR)

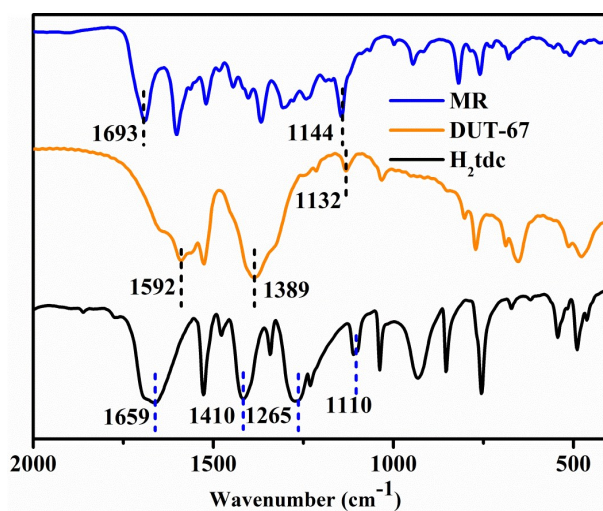


Figure 23. FTIR spectra of MR, DUT-67 and H₂TDC.

S9 Ultraviolet-Visible (UV-Vis) spectroscopy

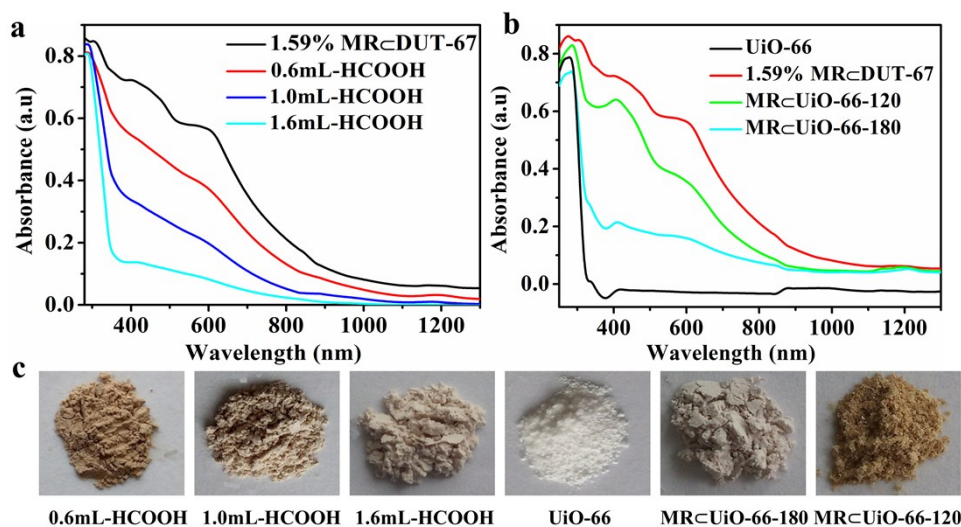


Figure S24. a) Absorption spectra of X-HCOOH (X = 0.6 mL, 1.0 mL or 1.6 mL) compared to 1.59% MR@DUT-67. b) Absorption spectra of MR@UiO-66-120 and MR@UiO-66-180 compared to 1.59% MR@DUT-67. c) Photographs of X-HCOOH (X=0.6 mL, 1.0 mL or 1.6 mL), UiO-66 and MR@UiO-66-X (X= 120 or 180).

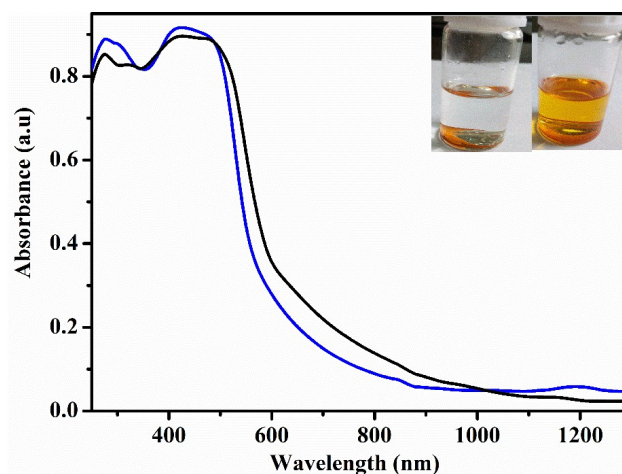


Figure S25. Absorption spectra of MR-PS@DUT-67 (black) and MR-PS@DUT-67 after being treated in DMF at 60 °C for six days (blue). Inset: photographs of MR-PS@DUT-67 (left) and being treated in DMF at 60 °C for six days (right). After soaked in DMF for six days, the solution turned to light red, indicating that some MR molecules leaching out from DUT-67 framework.

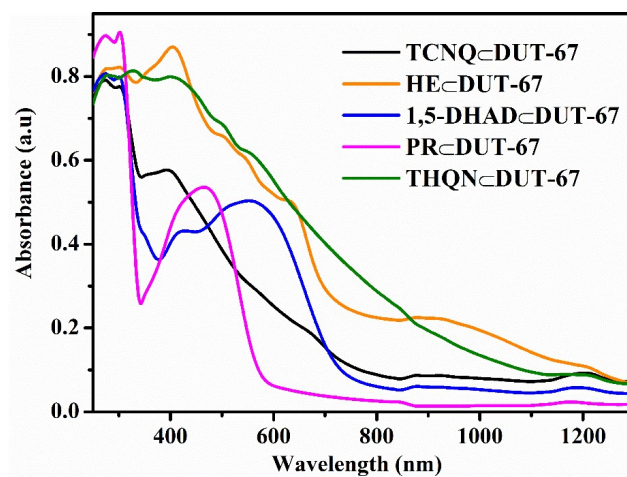


Figure S26. Absorption spectra of XcDUT-67 (X = TCNQ, HE, 1,5-DHAD, PR or THQN).

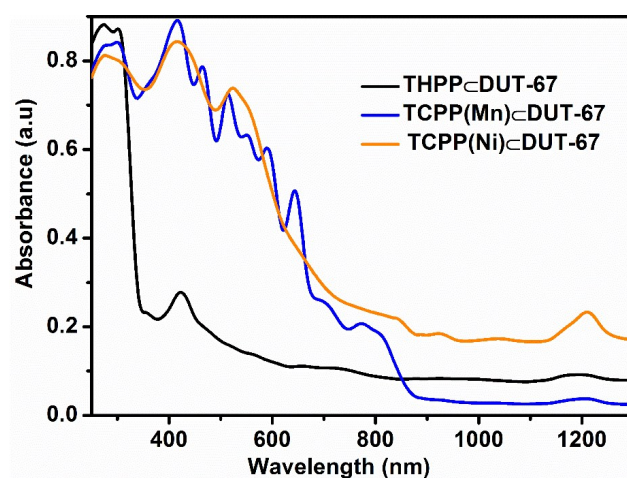


Figure S27. Absorption spectra of XcDUT-67 (X = THPP, TCPP(Mn) or TCPP(Ni)).

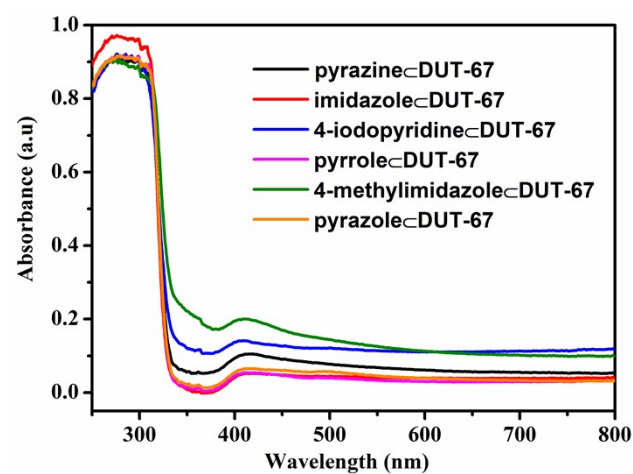


Figure S28. Absorption spectra of XcDUT-67 (X = pyrazine, imidazole, 4-iodopyridine, pyrrole, 4-methylimidazole or pyrazole).

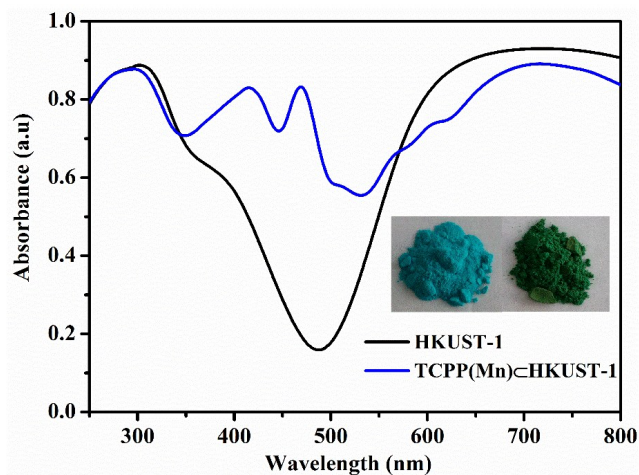


Figure S29. Absorption spectra of TCPP(Mn)@HKUST-1 compared to pristine HKUST-1. Inset: photographs of HKUST-1 (left) and TCPP(Mn)@HKUST-1 (right).

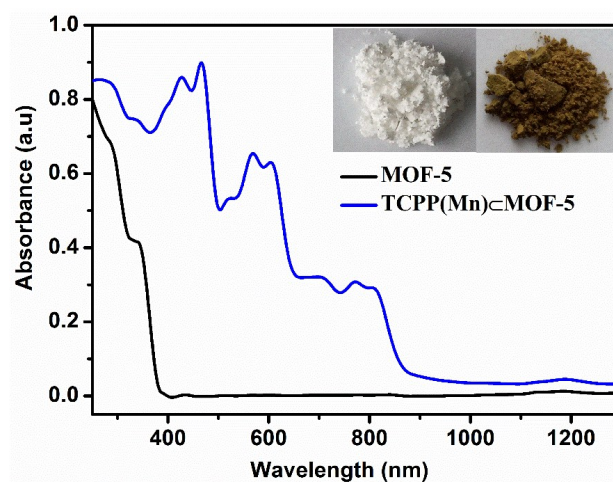


Figure S30. Absorption spectra of TCPP(Mn)@MOF-5 and pristine MOF-5. Inset: photographs of MOF-5 (left) and TCPP(Mn)@MOF-5 (right).

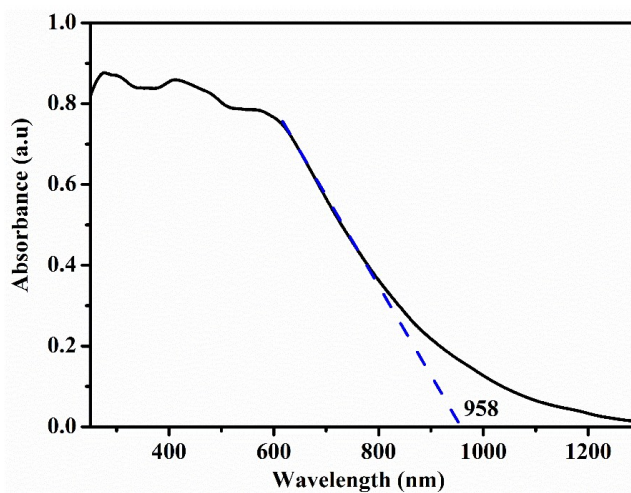


Figure S31. Absorption spectrum of 3.14 % MR@DUT-67.

S10 Extended X-ray absorption fine structure (EXAFS) analysis

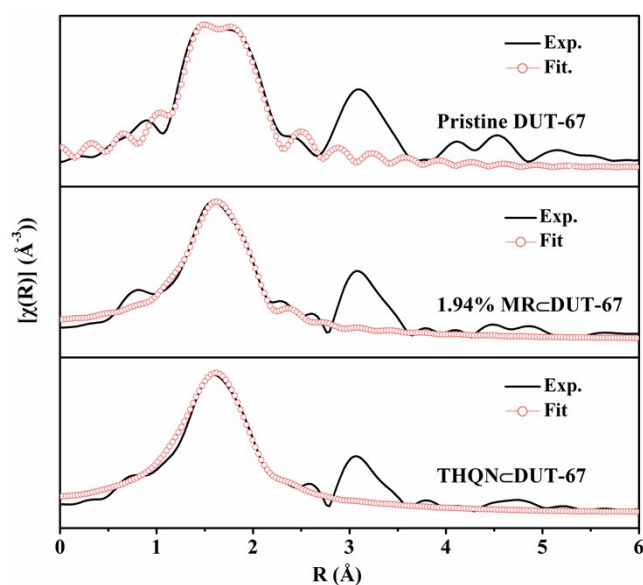


Figure S32. The corresponding EXAFS fitting curves of pristine **DUT-67**, **1.94 % MRcDUT-67** and **THQNcDUT-67** (the fitting results were listed in Table S1).

Table S1. Zr K-edge EXAFS curve fitting results of samples.

Samples	Path	CN	R (Å)	σ^2 (Å ²)	R factor
DUT-67	Zr-O(in face center)	4	2.13	-0.00166	0.02
	Zr-O(from H ₂ O)	2	2.25	-0.00933	
	Zr-O(from TDC)	2	2.38	-0.00856	
1.94 % MRcDUT-67	Zr-O(in face center)	4	2.16	0.00601	0.008
	Zr-O (from TDC)	2	2.31	0.00204	
THQNcDUT-67	Zr-O(in face center)	4	2.16	0.00241	0.023
	Zr-O (from TDC)	2	2.30	-0.00141	

CN, coordination number; R , distance between absorber and backscatter atoms; σ^2 , Debye-Waller factor (a measure of thermal and static disorder in absorber-scatter distances); R factor is used to value the goodness of the fitting.

S11 Scanning electron microscopy energy-dispersive X-ray spectroscopy (SEM-EDX)

The scanning electron microscope coupled with energy-dispersive X-ray spectroscopy was used to reveal the concentration of dopants. The intensities of Fe, Mn and Ni elements from HE, TCPP(Mn) and TCPP(Ni), respectively, were almost equal to the background noise, indicating the actual amount of dopant incorporated in DUT-67 was very low.

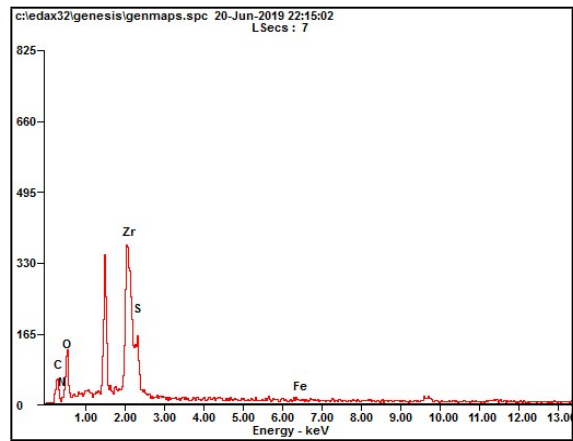


Figure S33. SEM/EDX analysis for HECDUT-67

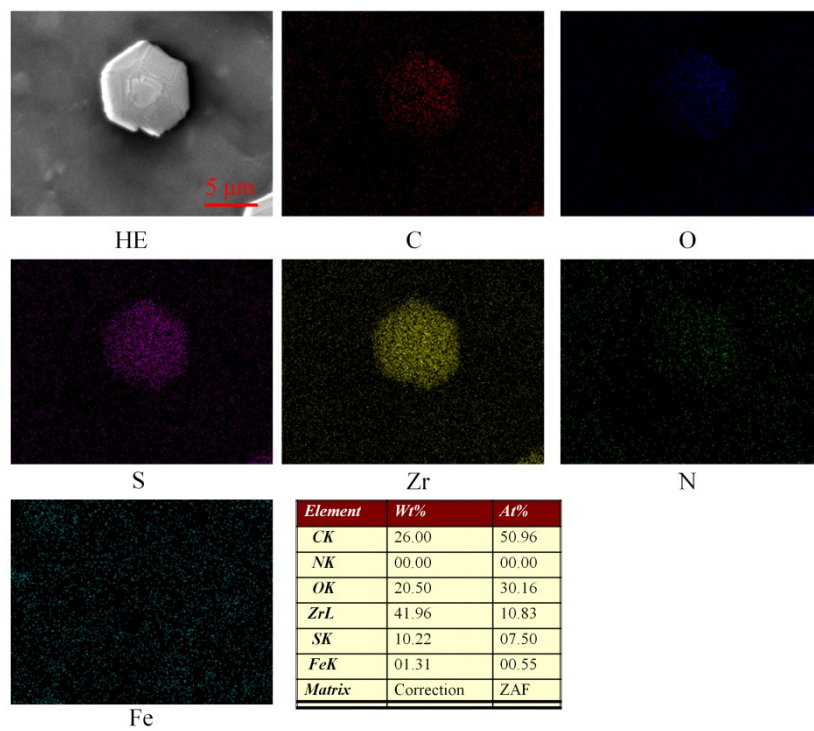


Figure S34. SEM image of HECDUT-67 crystal and the corresponding EDX-mappings.

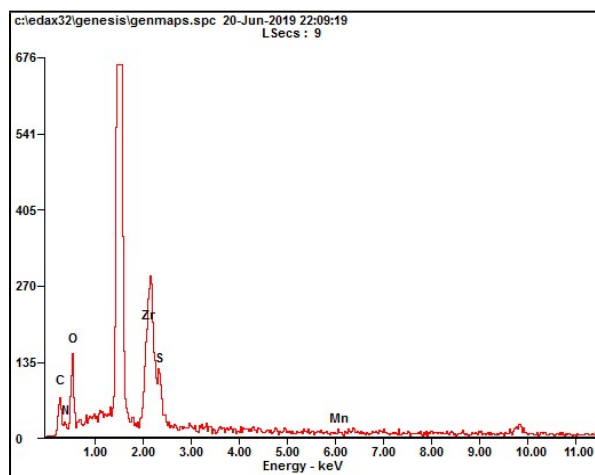


Figure S35. SEM/EDX analysis for TCPP(Mn)CDUT-67

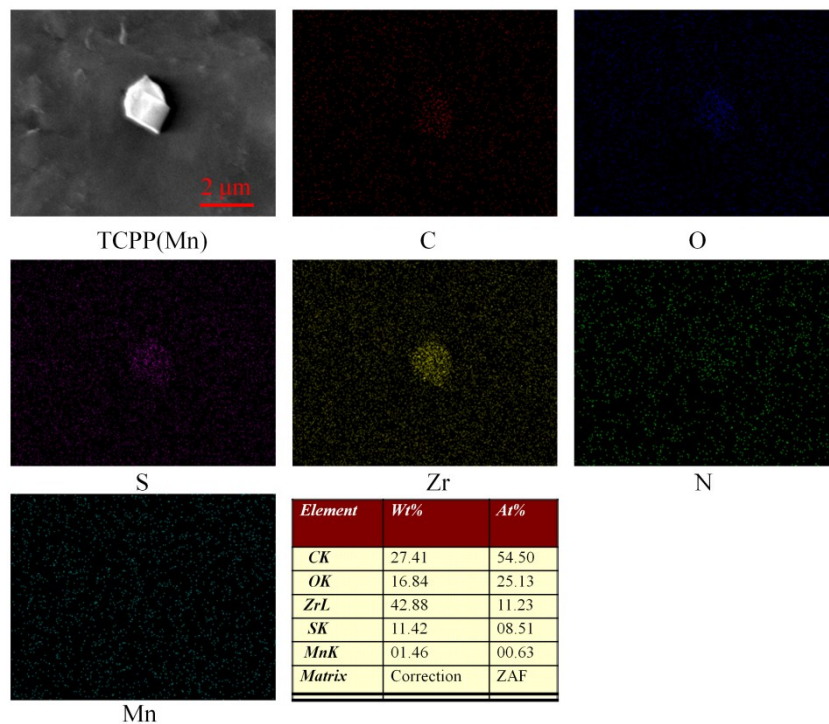


Figure S36. SEM image of TCPP(Mn)cDUT-67 crystal and the corresponding EDX-mappings.

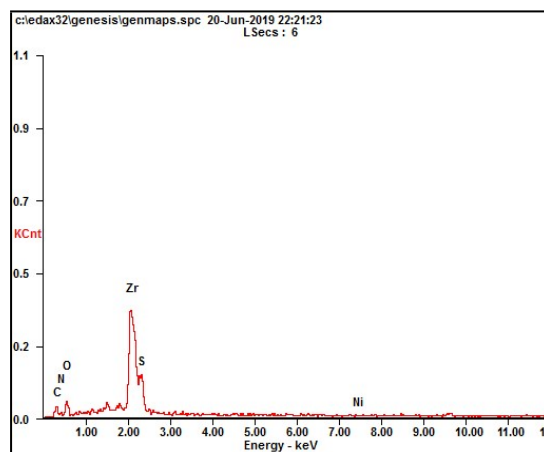


Figure S37. SEM/EDX analysis for TCPP(Ni)cDUT-67.

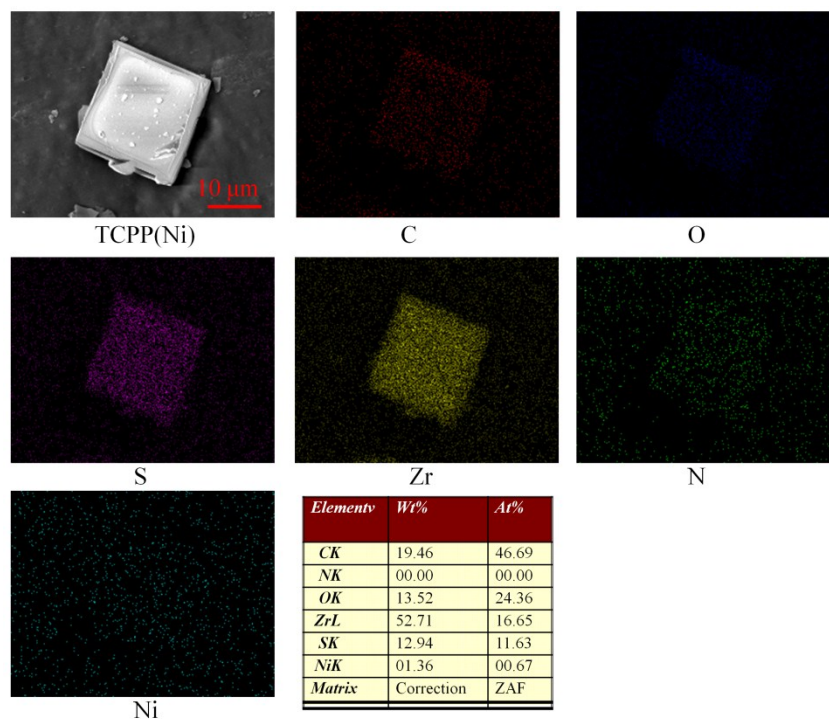


Figure S38. SEM image of TCPP(Ni)@DUT-67 crystal and the corresponding EDX-mappings.

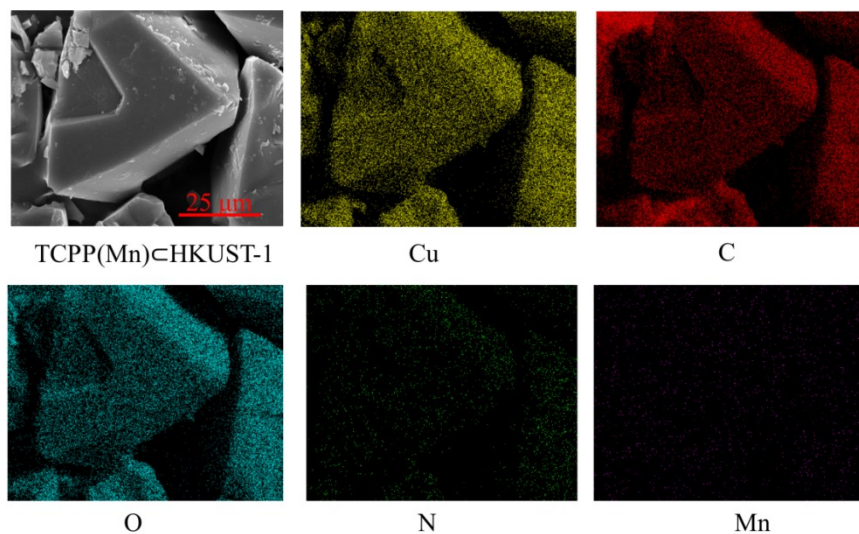


Figure S39. SEM image of TCPP(Mn)@HKUST-1 crystal and the corresponding EDX-mappings.

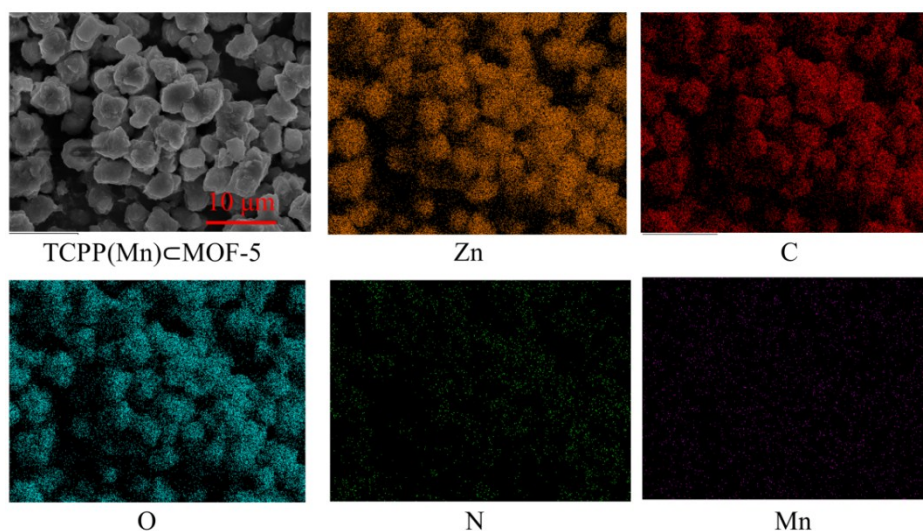


Figure S40. SEM image of TCPP(Mn)@MOF-5 crystal and the corresponding EDX-mappings.

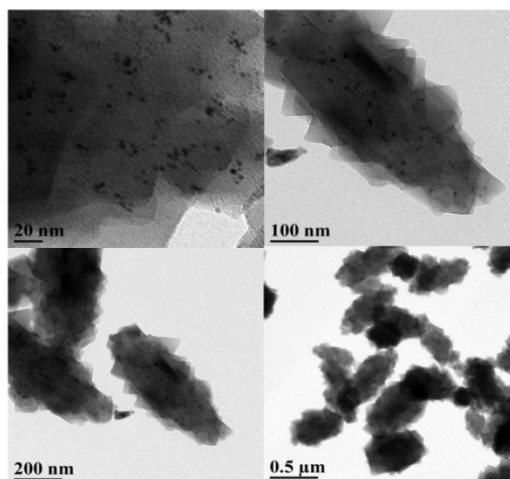


Figure S41. TEM images of Pt@TCPP(Mn)@DUT-52 crystal. The Pt content was estimated to be 0.821% by AAS analysis.

S12 Photocatalytic hydrogen production

The photocatalytic water splitting experiments were carried out in a 100 mL glass reaction cell with stirring at 20 °C within a water bath. 300 W Xe lamp equipped with an optical filter was used to cut off the light in the ultraviolet region. 13 mg of the photocatalyst was dispersed in 4 mL deionized water and 50 mL acetonitrile with 2 mL triethanolamine (TEOA) as a sacrificial reagent. The hydrogen production in the system was measured at an interval of 0.5 h with online gas chromatography.

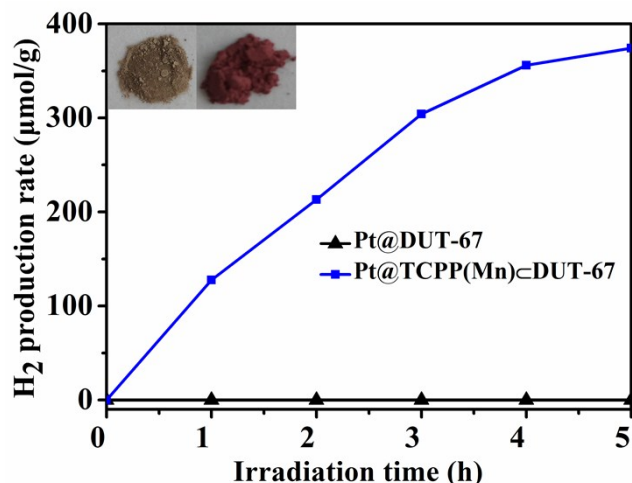


Figure S42. Photocatalytic hydrogen-production rates of Pt@TCPP(Mn)@DUT-67 compared with Pt@DUT-67. Inset (from left to right): photographs of Pt@DUT-67 and Pt@TCPP(Mn)@DUT-67.

S13 Single-crystal X-ray crystallography

Single-crystal X-ray diffraction data was collected at 100 K on an Oxford Diffraction SuperNova diffractometer equipped with Cu-K α radiation ($\lambda = 1.54178$). The structure was solved by direct method and refined using SHELXL-2014 software package.⁸⁻⁹ In addition, the “SQUEEZE” command was employed because large solvent accessible void existed in structure. Crystal data are summarized in Table S1.

Table S2 Crystal data of TCPP(Mn)@MOF-5 with reference to pristine MOF-5

Identification code	TCPP(Mn)@MOF-5	Pristine MOF-5
Empirical formula	C ₂₄ H ₁₂ O ₁₃ Zn ₄	C ₂₄ H ₁₂ O ₁₃ Zn ₄
Formula weight	769.82	769.75
Temperature/K	100.0(3)	100.0(4)
Crystal system	cubic	cubic
Space group	Fm-3m	Fm-3m
a/Å	25.6078(2)	25.6871(3)
b/Å	25.6078(2)	25.6871(3)
c/Å	25.6078(2)	25.6871(3)
α /°	90	90
β /°	90	90
γ /°	90	90
Volume/Å ³	16792.6(4)	16949.0(6)
Z	8	8
ρ_{calc} /cm ³	0.609	0.603
μ /mm ⁻¹	1.490	1.476
F(000)	3040.0	3040.0
Crystal size/mm ³	0.45 × 0.4 × 0.3	0.40 × 0.35 × 0.2
Radiation	CuK α ($\lambda = 1.54178$)	CuK α ($\lambda = 1.54178$)
2 θ range for data collection/°	11.46 to 146.346	11.424 to 143.95
Index ranges	-21 ≤ h ≤ 22, -31 ≤ k ≤ 21, -21 ≤ l ≤ 24	-30 ≤ h ≤ 28, -21 ≤ k ≤ 20, -30 ≤ l ≤ 13

Reflections collected	7244	3680
Independent reflections	879 [$R_{\text{int}} = 0.0170$, $R_{\text{sigma}} = 0.0090$]	862 [$R_{\text{int}} = 0.0214$, $R_{\text{sigma}} = 0.0125$]
Data/restraints/parameters	879/0/25	862/0/25
Goodness-of-fit on F^2	1.572	0.906
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.1106$, $wR_2 = 0.3483$	$R_1 = 0.0681$, $wR_2 = 0.1940$
Final R indexes [all data]	$R_1 = 0.1199$, $wR_2 = 0.3692$	$R_1 = 0.0850$, $wR_2 = 0.2217$

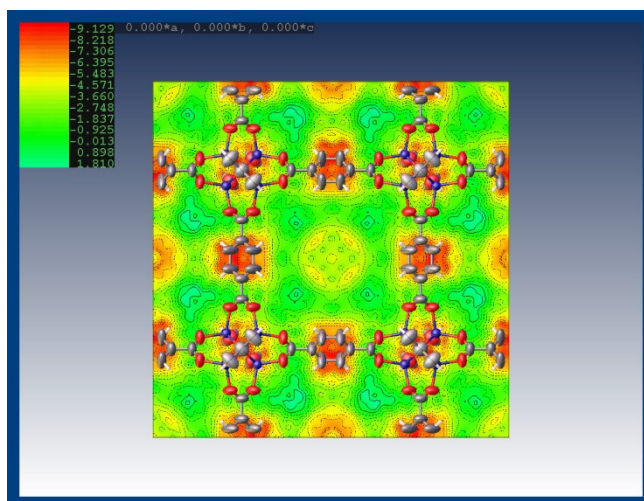


Figure S43. The differential electron density of MOF-5.

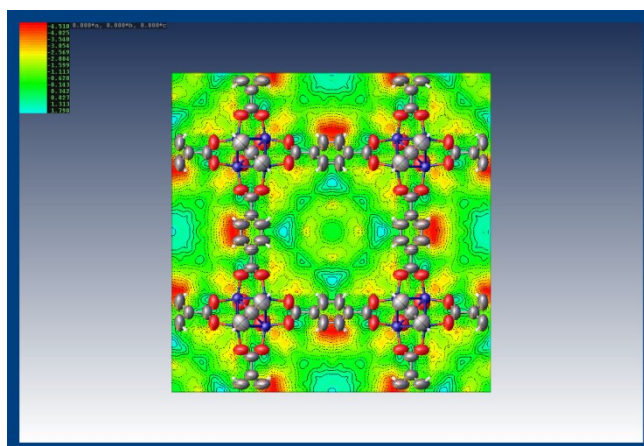


Figure S44. The differential electron density of TCPP(Mn)@MOF-5.

S14 Density functional theory (DFT) calculations

All periodic calculations were performed by using the Vienna ab initio Simulation Package (VASP). The projector augmented wave (PAW) method was used to describe the core–valence electron interactions. A $1 \times 1 \times 1$ k-point mesh was used, and we set the convergence criteria of 10^{-5} eV and 0.05 eV/Å. The pristine unit cell of DUT-67 has 396 atoms, including 36 metals, 144 O, 144 C, 24 S, and 48 H. To reduce the computational cost, electronic properties were obtained by using PBE exchange–correlation functional with a kinetic energy cutoff of 500 eV. Though the PBE functional may underestimate the energy band gap, it is still reliable to illustrate the variations of the band gaps and the relative activities of different photocatalysts.

S15 References

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