

Supporting Information for

Pt Nanoparticles@Photoactive Metal-Organic Frameworks: Efficient Hydrogen Evolution via Synergistic Photo-excitation and Electron Injection

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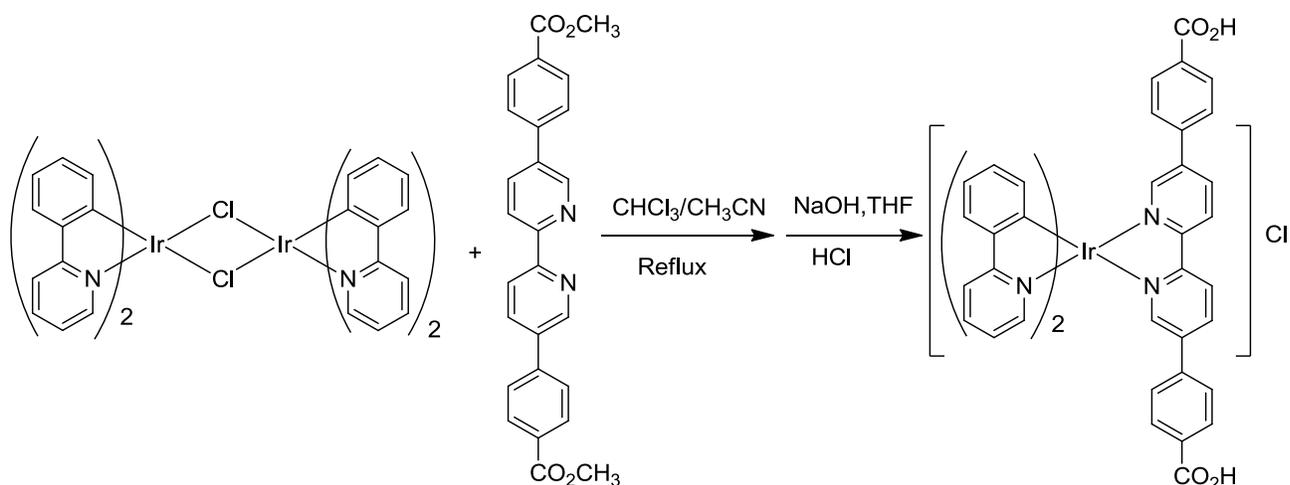
**To whom correspondence should be addressed. E-mail: wlin@unc.edu*

1. Materials and Methods. All starting materials were purchased from Aldrich and Fisher, unless otherwise noted, and used without further purification. ^1H -NMR and ^1H - ^1H COSY spectra were recorded on Bruker NMR 400 NB and 400 DRX Spectrometers at 400 MHz and referenced to the proton resonance resulting from incomplete deuteration of deuterated chloroform (δ 7.26). Mass spectrometric analyses were conducted using positive-ion electrospray ionization on a Bruker BioTOF Mass Spectrometer. Thermogravimetric analysis (TGA) was carried out on a Shimadzu TGA-50 equipped with a Pt pan. Single crystal and powder X-ray diffraction was carried out on a Bruker SMART Apex II CCD-based X-ray diffractometer system equipped with a Cu α -target X-ray tube and operated at 1600 watts. A Varian 820-MS Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) was used to determine metal loadings in the samples. Scanning electron microscopy (SEM) was used to image the samples, using a Hitachi 4700 field emission scanning electron microscope. Energy dispersive X-ray spectroscopy (EDS) was used to determine elemental composition of the particles, using an Oxford 7200 IncaPentaFET-x3 Energy Dispersive X-ray Spectrometer. Low-resolution transmission electron microscopy (TEM) was obtained on a JEOL 100CX-II Transmission Electron Microscope, and high-resolution TEM (HRTEM) was obtained on a JEOL 2010F-FasTEM. Nitrogen adsorption experiments were performed with a Quantachrome Autosorb-1C. Steady-state and time-resolved emission spectra were recorded on an Edinburgh FLS 920 spectrometer. Amounts of H_2 generated in the photocatalysis experiments were determined by gas chromatography (GC) using an SRI 8610C Gas Chromatograph.

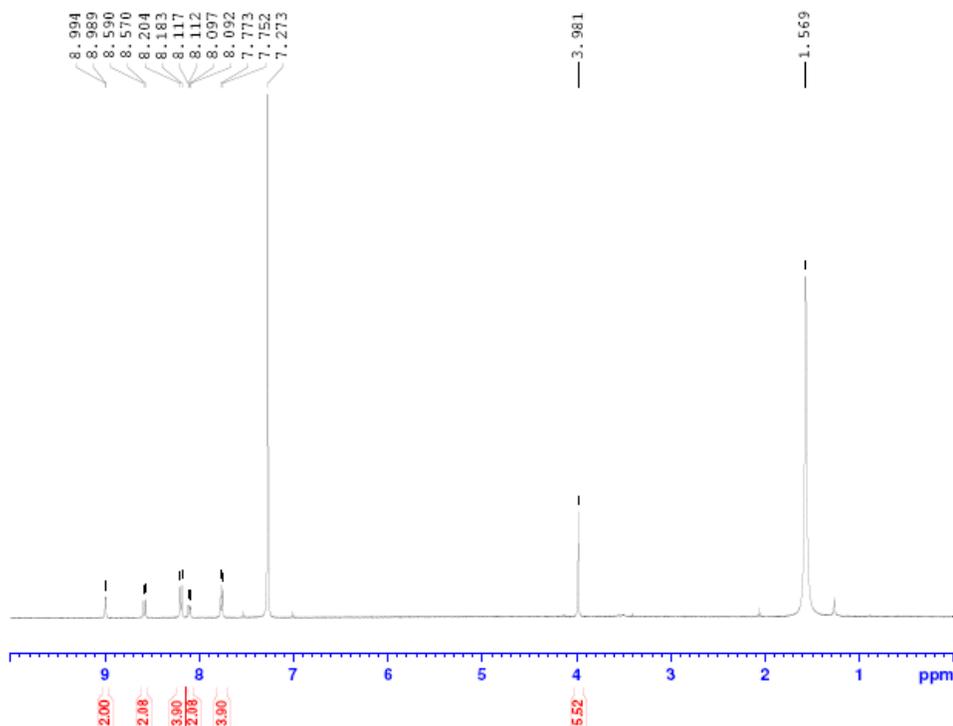
2. Synthesis and characterization of ligands H_2L_1 and H_2L_2 .

2.1. Synthesis of ligand H_2L_1 . Ligand L_1 was synthesized as previously reported.¹

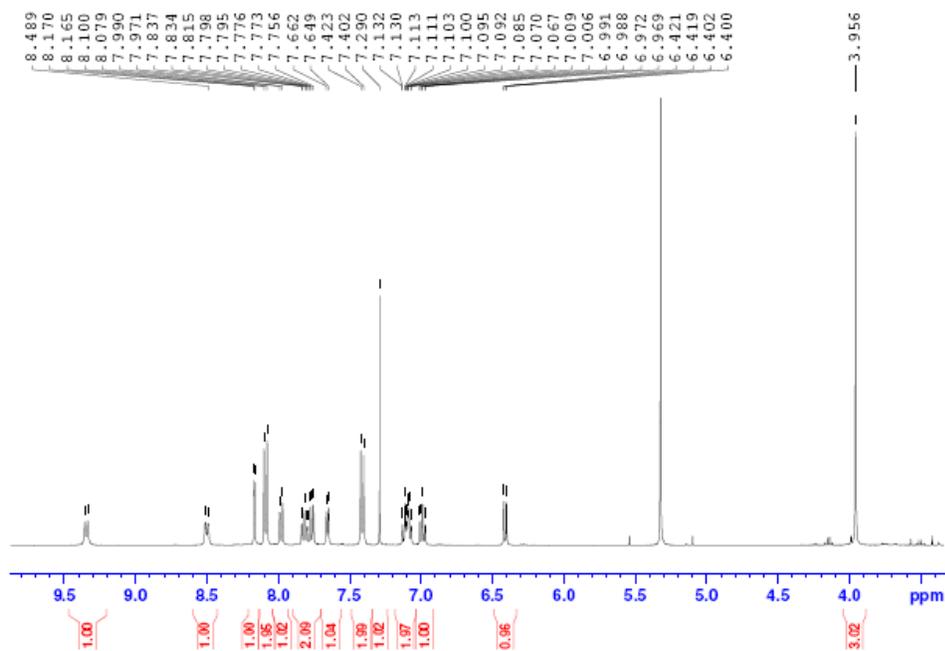
2.2. Synthesis of ligand H_2L_2 .

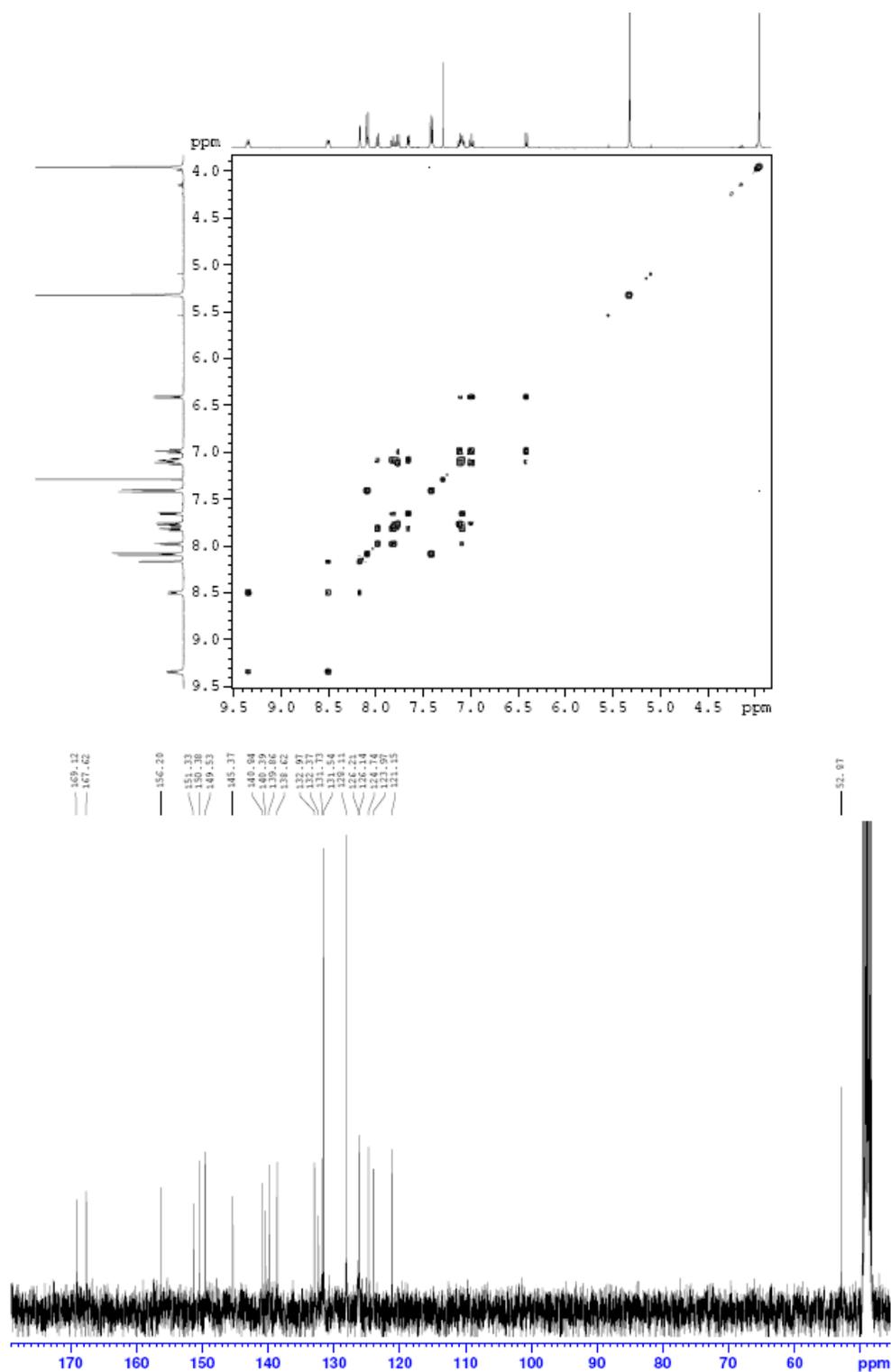


Synthesis of dimethyl 2,2'-bipyridine-5,5'-dibenzoate. A solution of 5,5'-dibromo-2,2'-bipyridine (0.5 g, 1.7 mmol) and 4-(methoxycarbonyl)phenylboronic acid (0.9 g, 5.0 mmol) in ethylene glycol dimethyl ether (DME) (35 mL) was degassed for 15 min. An aqueous solution of saturated NaHCO_3 (15 mL) and $\text{Pd}(\text{PPh}_3)_4$ (70 mg) were added to this solution. The reaction vessel was sealed and the reaction mixture was stirred at $100\text{ }^\circ\text{C}$ for 3 days. After cooling to room temperature, the solid was obtained by filtration. The solid was then subjected to Soxhlet extraction with chloroform overnight. The chloroform was removed by rotary evaporation to afford pure dimethyl 2,2'-bipyridine-5,5'-dibenzoate. Yield: 0.5 g (70 %). $^1\text{H NMR}$ (400 MHz, CDCl_3): 8.992 (d, 2H, $J=2\text{Hz}$), 8.80 (d, 2H, $J=8\text{Hz}$), 8.194 (d, 4H, $J=8.4\text{Hz}$), 8.105 (dd, 2H, $J_1=2\text{Hz}$, $J_2=8\text{Hz}$), 7.763 (d, 4H, $J=8.4\text{Hz}$) 3.981 (s, 6H).



Synthesis of bis(4-phenyl-2-pyridine)(5,5'-dimethoxyl(4-carboxyl-phenyl)-2,2'-bipyridine)-iridium(III) chloride (Me₂L₂). [Ir(ppy)₂Cl₂]₂ (383 mg, 0.35 mmol) and dimethyl 2,2'-bipyridine-5,5'-dibenzoate (320 mg, 0.75 mmol) were suspended in 20 mL 1:1 MeCN/CHCl₃ under nitrogen. After refluxing overnight, evaporation of the solvent under reduced pressure yielded a red solid. The crude product was purified by silica gel column chromatography. After flushing the column with CHCl₃, CH₂Cl₂ and EtOAc, CH₃OH/CHCl₃ (1/10 v/v) solution was used to wash down a reddish band. Afterward, the organic solvent was removed under vacuum to afford the pure product. Yield: 356 mg (51%). ¹H NMR (400 MHz, CDCl₃): 9.335 (d, 2H, J=8Hz), 8.496 (d, 2H, J=7.6Hz), 8.168 (d, 2H, J=2Hz), 8.090 (d, 4H, J=8.4Hz), 7.981(d, 2H, J=7.6Hz), 7.815 (t, 2H, J=8.0 Hz), 7.766 (d, 2H, J=7.6Hz), 7.656 (d, 2H, J=5.2hz), 7.413 (d, 2H, J=8.4Hz), 7.132-7.067 (m, 4H), 6.990 (td, 2H, J₁=7.2Hz, J₂=1.2 Hz), 6.411 (dd, 2H, J₁=7.6Hz, J₂=0.8Hz), 3.956 (s, 6H). ¹³C NMR (CDCl₃): 169.12, 167.62, 156.20, 151.33, 150.38, 149.53, 145.37, 140.84, 140.39, 139.86, 138.62, 132.97, 132.37, 131.73, 131.54, 128.11, 126.21, 126.14, 124.74, 123.97, 121.15, 52.87. MS (ESI): 925.10 m/Z, (expected 925.24 m/Z for [C₄₈H₃₆O₄N₄Ir]⁺).





Synthesis of bis(4-phenyl-2-pyridine)(5,5'-di(4-carboxyl-phenyl)-2,2'-bipyridine)iridium(III) chloride (H₂L₂). A solution of Et₂L₁ (300 mg) in tetrahydrofuran (THF) (10 mL), ethanol (10 mL), and 3 M aqueous NaOH (10 mL) was refluxed at 70 °C overnight. The solution was cooled to room temperature, acidified to a pH of 1, and extracted with ethyl acetate/H₂O. The organic layer was dried

over Na₂SO₄ and the solvent was evaporated under reduced pressure to give the pure product. Yield: 270 mg (93%). ¹H NMR (400MHz, MeOD-*d*₄): 8.845 (d, 2H, J=8.8Hz), 8.548 (dd, 2H, J₁=8.8Hz, J₂=2Hz), 8.284 (d, 2H, J=1.6Hz), 8.189 (d, 2H, J=8Hz), 8.084 (d, 4H, J=8Hz), 7.965-7.851 (m, 6H), 7.514 (d, 2H, J=8Hz), 7.152-7.114 (m, 4H), 7.003 (t, 2H, J=7.6Hz), 6.455 (d, 2H, J=7.6Hz).

3. Synthesis and characterization of MOFs 1 and 2

3.1. Synthesis of 1. ZrCl₄ (10.0 mg, 0.043 mmol), biphenyldicarboxylic acid (H₂bpdc) (9.0 mg, 0.037 mmol), H₂L₁ (2.0 mg, 0.004 mmol), and glacial acetic acid (25 μL, 0.437 mmol) were dispersed in DMF (1.5 mL), sealed in a vial, and placed in an oven. The temperature was kept at 100 °C for 24 hours. After cooling down to room temperature, the resulting solid was isolated by centrifugation, and was washed with DMF and methanol repeatedly before being dried under vacuum. Yield: 15 mg (75%). The Ir-complex (L₁) content in MOF-1 was determined by ICP-MS to be 2.0 wt%. Molar doping level [mol L₁/(mol bpdc+ mol L₁)] was calculated from the ICP-MS result to be 1.0%. Different amounts of acetic acid were added to the reaction mixture to control the size of the MOF nanocrystals.

3.2. Synthesis of 2. ZrCl₄ (1.0 mg, 0.0043 mmol), H₂L₂ (3.9 mg, 0.0043 mmol), and trifluoroacetic acid (5 μL, 0.0875 mmol) were dissolved in DMF (0.25 mL), sealed in a vial, and placed in an oven. The temperature was kept at 100 °C for 72 hours. Crystalline films formed on the glass wall of the vial. After cooling down to room temperature, the resulting solid was isolated by decanting the supernatant solution. The crystalline solid was then washed with DMF, methanol and water repeatedly, and stored in water. Yield: 3.5 mg (25%). Formula of **2**: [Zr₆(μ₃-O)₄(μ₃-OH)₄(IrC₄₆H₃₂O₄N₄)₆(O₂CCF₃)₆·64DMF], expected DMF weight percentage: 41.0% (observed 41.1% from ¹H-NMR, 44.2% from TGA), expected trifluoroacetate weight percentage: 6.0% (observed 7.4% from TGA, 5.7% from ¹⁹F-NMR), expected residue mass after TGA: 18.3% (observed 18.4%). Powdery samples of **2** were obtained at 120 °C.

3.3 Characterization of MOF-1

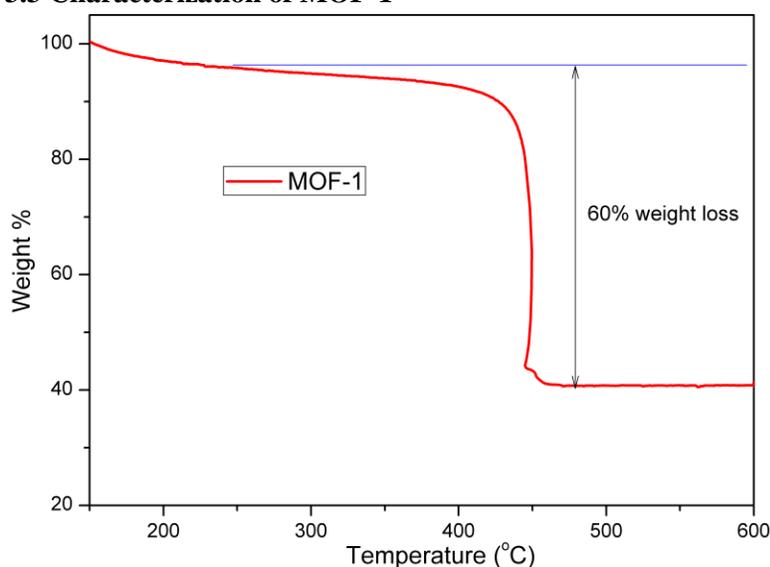


Figure S1. TGA of **1**. The 60% weight loss of organic linker in the structure agrees with the proposed formula.

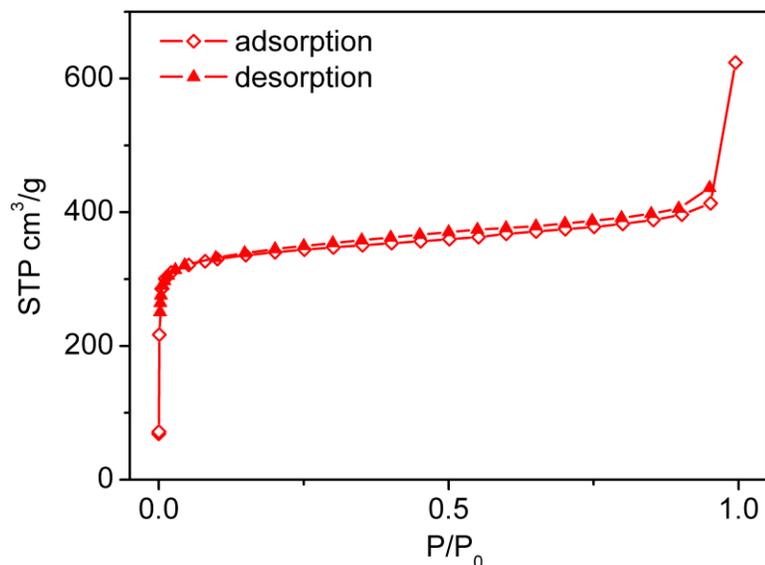


Figure S2. Nitrogen adsorption isotherm of **1** at 77K. BET surface area is 1194 m²/g.

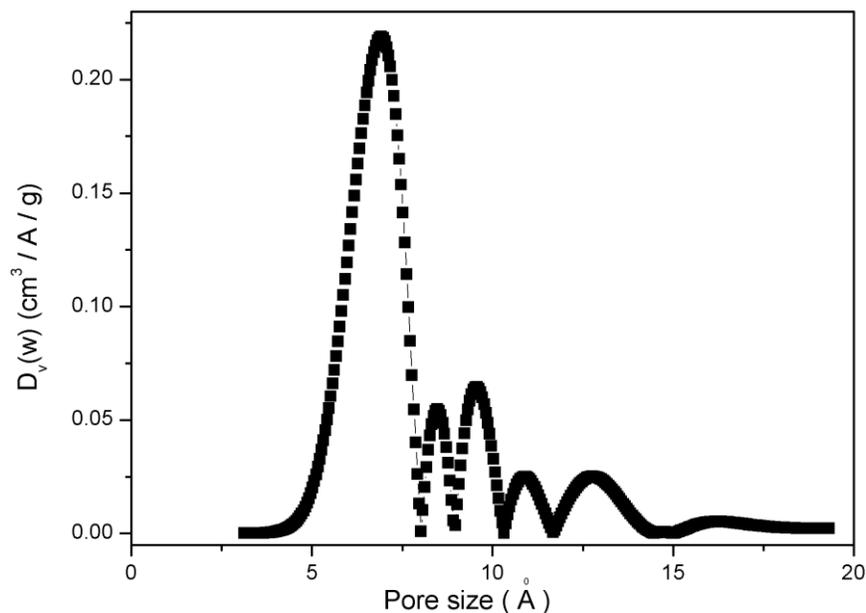


Figure S3. Pore size distribution of **1**, calculated from nitrogen adsorption data using the HK method. The major peak centered at 6.7 Å agrees well with the pore size from the structural model.

3.4 Determination of solvent content and counterions in **2**

A known amount of MOF crystals (20.03 mg) was immersed in 1mL MeOD overnight to exchange out the solvent molecules in the MOF channel. After removing the MOF solid, 10 μ L of mesitylene was added to the solution as an internal standard for ¹H-NMR. Integrations of peaks in the ¹H-NMR spectrum were used to quantify the amount of DMF in the MOF channels. The weight percentage of DMF in the

crystal was calculated to be 41.1%. ^{19}F -NMR of the MeOD solution was also taken but no fluorine signal was visible, indicating that no trifluoroacetic acid came out of the channels during the washing procedure.

To figure out if trifluoroacetate (TFA) exists in the channels as a counterion, a known amount of MOF crystals (5.23 mg) was dissolved in 1 mL of a mixed solution of $\text{H}_2\text{O}/\text{EtOH}/1\text{M NaOH}$ (10/1/1). After removing the ZrO_2 solid, 10 μL of a triflic acid stock solution was added as internal standard (stock: 85.1 mg triflic anhydride in 2 mL aqueous solution). 10% of D_2O was also added to the solution for the purpose of signal locking. Integrations of peaks in the ^{19}F -NMR spectrum were used to quantify the amount of TFA in the MOF channels. The weight percentage of TFA in the crystal is calculated to be 5.77%.

The calculated formula of **2**, $[\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{IrC}_{46}\text{H}_{32}\text{O}_4\text{N}_4)_6(\text{O}_2\text{CCF}_3)_6 \cdot 64\text{DMF}]$, was further confirmed by TGA.

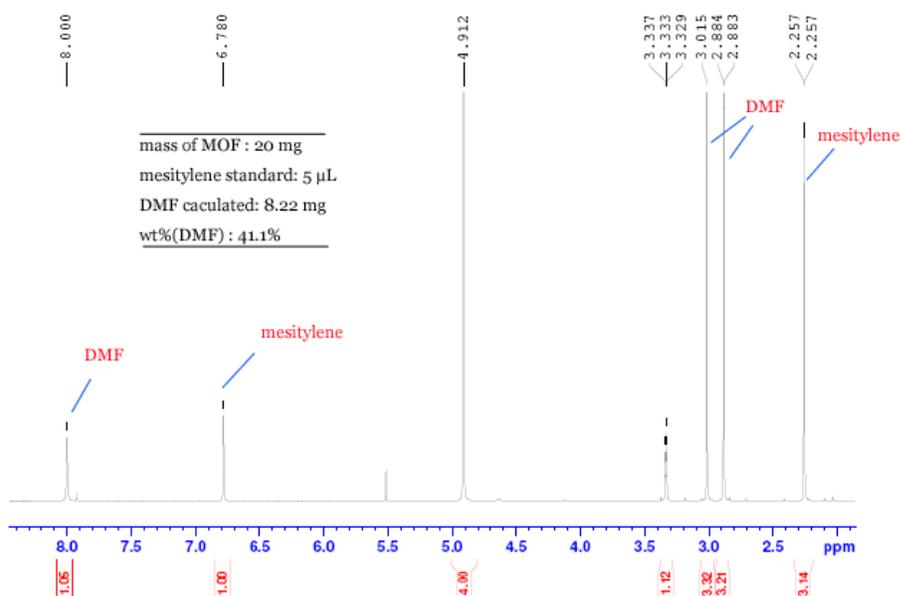


Figure S4. ^1H NMR (methanol- d_4) spectroscopic determination of solvent content in **2** (20.03 mg), 10 μL mesitylene (Mes) was added as an internal standard.

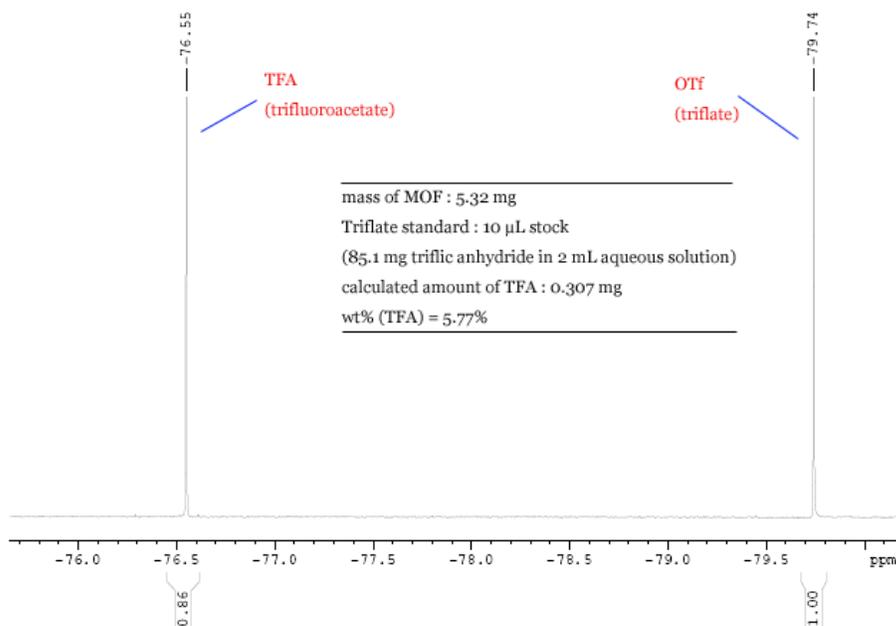


Figure S5. ^{19}F NMR ($\text{H}_2\text{O}/\text{D}_2\text{O}=10/1$) spectroscopic determination of the counter ion in **2** (5.32 mg). The MOF was dissolved to release the trifluoroacetate counter ion. 10 μL of triflic acid stock solution was added as internal standard (stock: 85.1 mg triflic anhydride in 2 mL aqueous solution).

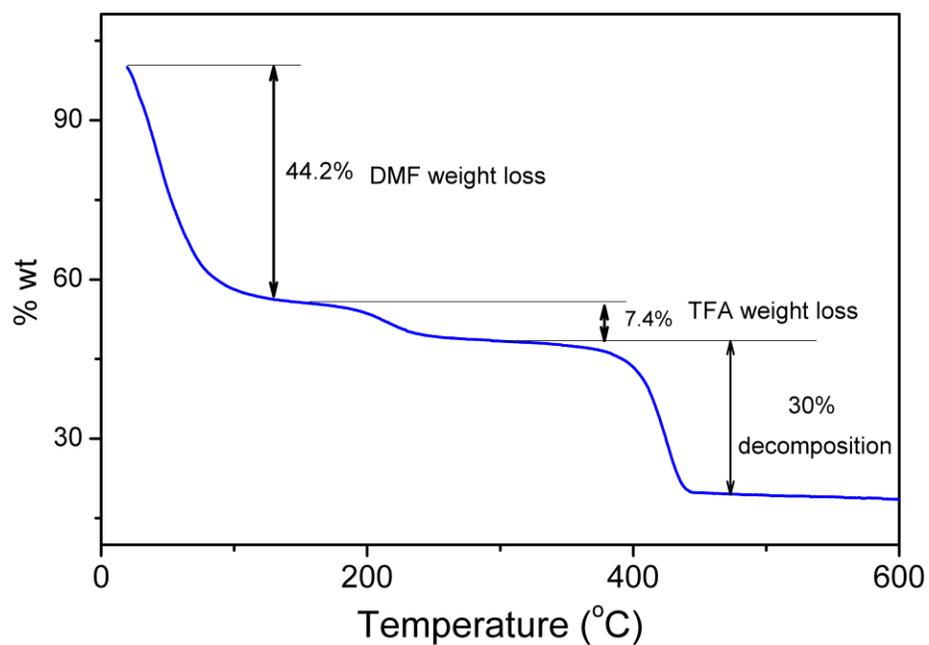


Figure S6. TGA curve for **2**. The sample was heated to 600 °C under air at a heating rate of 5 °C/min.

3.5 N₂ adsorption measurement of **2**

2 was activated using the freeze-drying protocol.² After decanting all the mother liquid, freshly prepared crystals of **2** were washed with methanol, then CH₂Cl₂ several times. The resulting crystals were washed with benzene several times and then soaked in benzene overnight before loading into a BET sample cell. About 1 mL of benzene was left in the sample cell, and the sample cell was then frozen at 0 °C. After three freeze-thaw cycles, the sample cell was placed in an ice/H₂O bath and evacuated under a dynamic vacuum for 24 h. The ice/H₂O bath was removed and the sample was kept under vacuum at room temperature for another 12 h, and then heated under vacuum at 60 °C for 10 h. The resulting freeze-dried **2** was used to perform gas uptake measurements.

Framework distortions were expected during the BET measurement, a phenomenon commonly observed for MOFs with large open channels.⁴ These framework distortions can reasonably account for the low value of N₂ uptake and irregular adsorption/desorption curves.

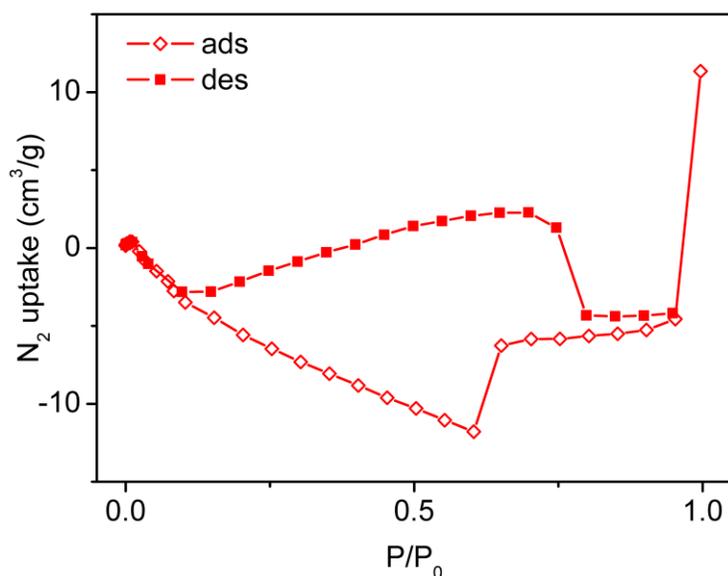


Figure S7. N₂ adsorption isotherms (77K) of **2**.

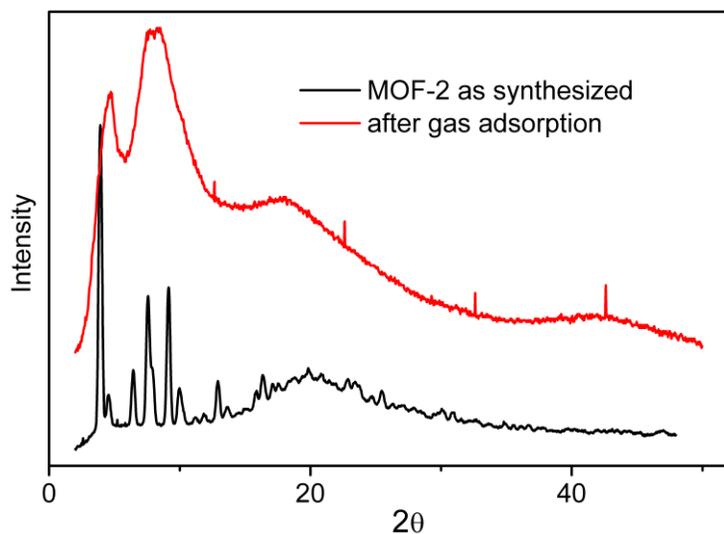


Figure S8. PXRD of **2** after gas adsorption measurement

3.6 General procedure for dye uptake measurements of **2**

Fresh crystals of **2** (2 mg) were briefly dried on filter paper, and then soaked in a methanol solution of Brilliant Blue R-250 (BBR-250) or Crystal Violet (24 mM, 2 mL) overnight. The resulting dark blue or purple crystals were washed with water thoroughly until the washings became colorless. Water was used to wash the BBR-250 dye on the external surfaces of the crystals. The channels of MOFs are hydrophobic so water cannot easily get in the channels to wash out the dye molecules inside the channels. After drying, TGA was performed on the crystals. The TGA data of the dye-loaded crystals are normalized to the same residue mass as that of the as-synthesized crystal. The additional weight loss at the ligand decomposition temperature of the dye-loaded MOFs is attributed to the decomposition of dye molecules in the MOF channels. For both BBR-250 and Crystal Violet, around 75 weight % dye is found to be included in the MOF channels/cavities.

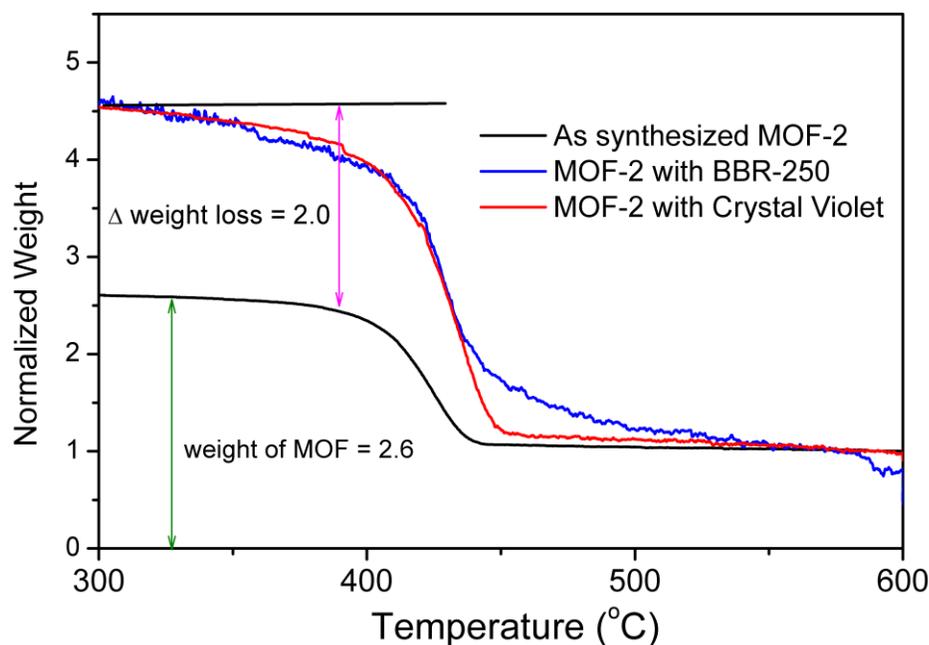


Figure S9. TGA of dye-loaded crystals. Data normalized to the same residue mass as that of the as-synthesized crystals.

4. Single Crystal X-ray Diffraction Determination of **2**

All crystallographic measurements were made on a Bruker SMART Apex II CCD-based X-ray diffractometer system operated at 1600 watts (Cu-target X-ray tube). The crystals were mounted inside a capillary tube (0.7 mm ID) with a small amount of mother liquid to prevent solvent loss from the crystal frameworks. The frames were integrated with the Bruker SAINT© build in APEX II software package using a narrow-frame integration algorithm, which also corrects for the Lorentz and polarization effects. Absorption corrections were applied using SADABS. Structures were solved by direct methods and refined to convergence by least squares method on F2 using the SHELXTL software suite.

Structure solution using the direct method gives the coordinates of the $Zr_6(\mu_3-O)_4(\mu_3-OH)_4(CO_2)_{12}$ cluster and Ir metal at two positions as a result of rotational disorder of the linear dicarboxylate ligand. Other parts of the organic ligands can be identified from the electron density difference map, which exhibited electron density residues at positions that connect the adjacent Zr_6 clusters. However, because of the low resolution of the dataset, the organic ligand cannot be resolved at the atomic level, and they are added manually into the structural model using Materials Studio. The identified positions of Zr_6 clusters and Ir metals in the structure verified that **2** adopts a non-interpenetrated structure with the **fcu** topology.

For the structural refinement of **2**, SQUEEZE subroutine of the PLATON software suite was applied to remove the scattering from the highly disordered guest molecules. The resulting new HKL4 files were used to further refine the structures. Due to the relatively weak diffraction and low resolution (2.1 Å), which is not uncommon for this kind of framework with very large solvent accessible void space, restraints (SIMU and DELU) on displacement parameters, and DFIX for bond lengths are applied, and all the phenyl rings are constrained to ideal six-membered rings. Non-hydrogen atoms are refined isotropically.

Table S1. Single Crystal X-ray Structure Refinement of 2

<i>Compound</i>	2
Empirical formula	[Zr ₆ (μ ₃ -O) ₄ (μ ₃ -OH) ₄ (IrC ₄₆ H ₃₂ O ₄ N ₄) ₆ (O ₂ CCF ₃) ₆ ·64DMF]
Temperature (K)	296
Wavelength (Å)	1.54178
Crystal system	Cubic
Space group	<i>F</i> 23
Unit cell dimensions	a = b = c = 38.7410(2)
Volume (Å ³)	58145.0(9)
Z	4
Density (calcd. /cm ³)	0.670
Absorption coeff.(mm ⁻¹)	3.680
F(000)	11128.0
Crystal size (mm)	0.02×0.02×0.02
Crystal color & shape	Orange cuboctahedron
Radiation source	Cu Kα
θ range data collection	2.0 – 21.3
Limiting indices	-15 < h < 18 -16 < k < 14 -18 < l < 14
Reflections collected	1841
Independent reflections	517
R(int)	0.249
Refinement method	Full-matrix least-square on F ²
Data/restraints/parameter	517/22/131
Goodness-of-fit on F ²	2.17
Final R indices	R1 = 0.21
[I > 2σ(I)] ^{a,b}	wR2 = 0.36
R indices (all data)	R1 = 0.27 wR2 = 0.39

5. Structural Figures for MOFs 1 and 2

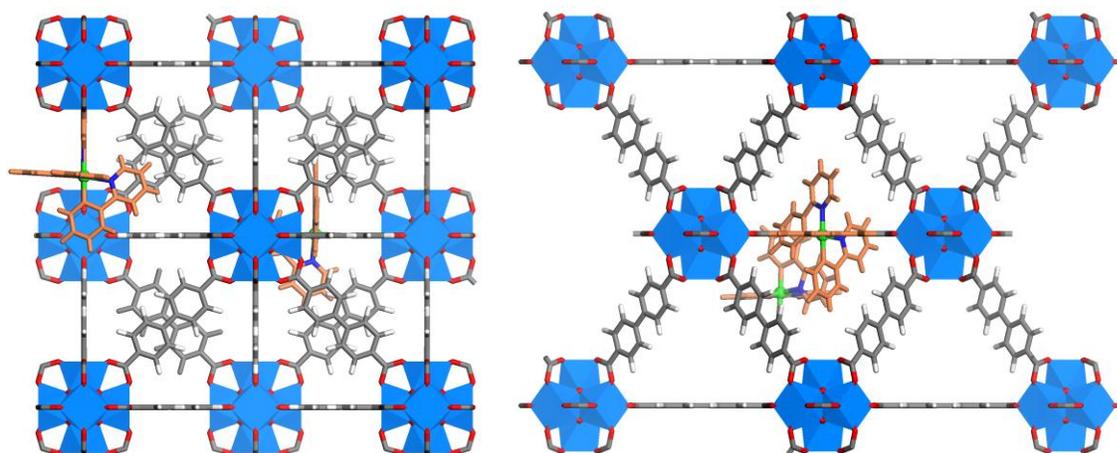


Figure S10. Structural model of **1**. (a) viewed along the [100] direction. (b) viewed along the [110] direction.

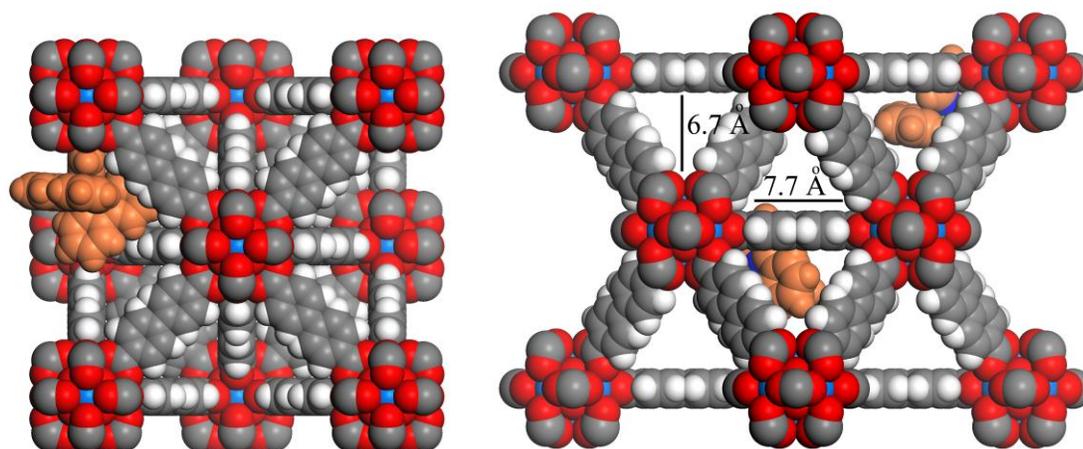


Figure S11. Space-filling model of **1**. (left) viewed along the [100] direction. (right) viewed along the [110] direction.

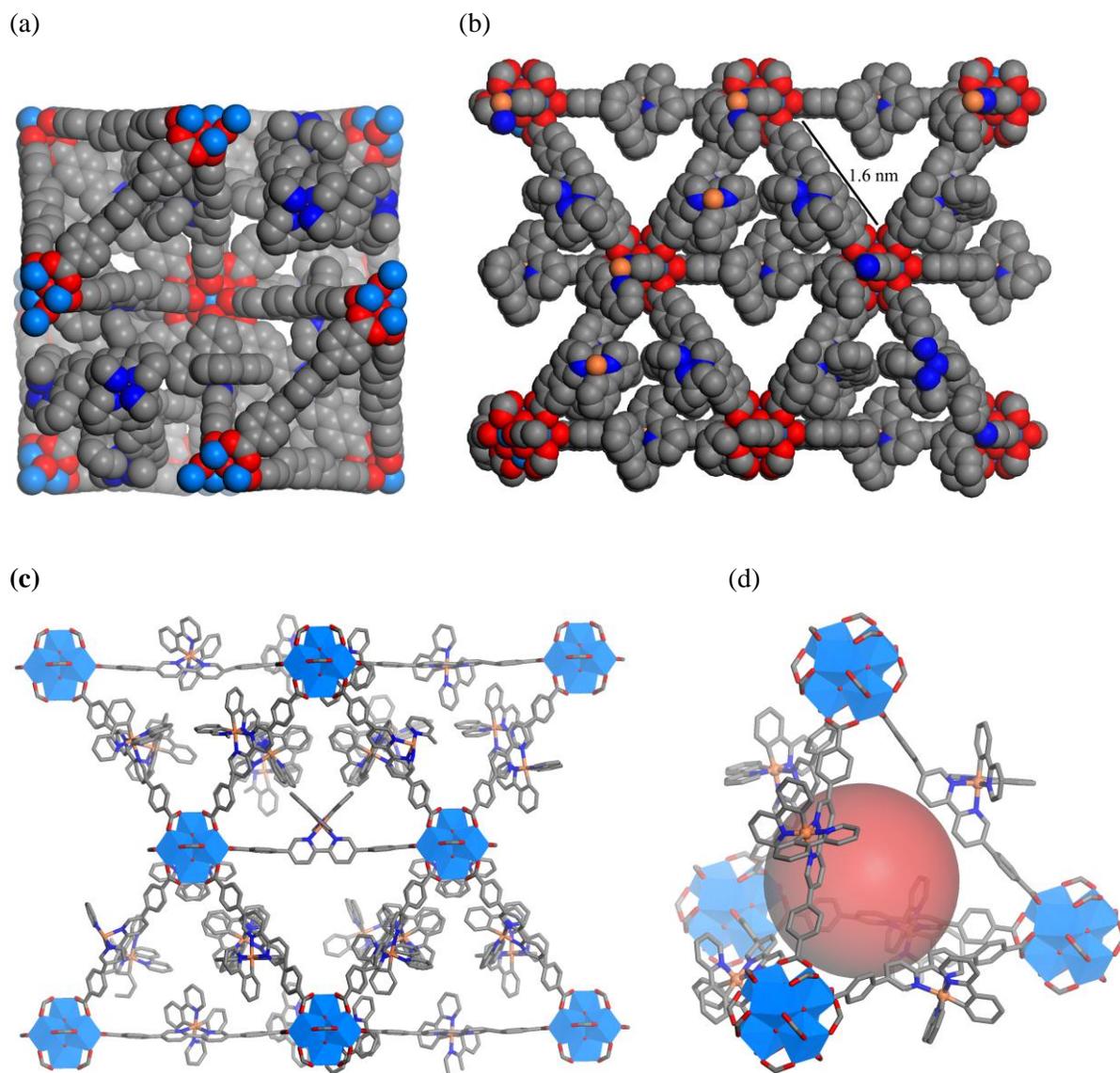


Figure S12. Space-filling model of **2**. (a) viewed along the [100] direction (b) viewed along the [110] direction. (c) Stick-polyhedron model of the crystal structure of **2** (a) viewed along the [110] direction; (d) showing a tetrahedral cavity, represented by a red ball with a diameter of 0.6 nm.

6. PXRD patterns of **2** in different solvents

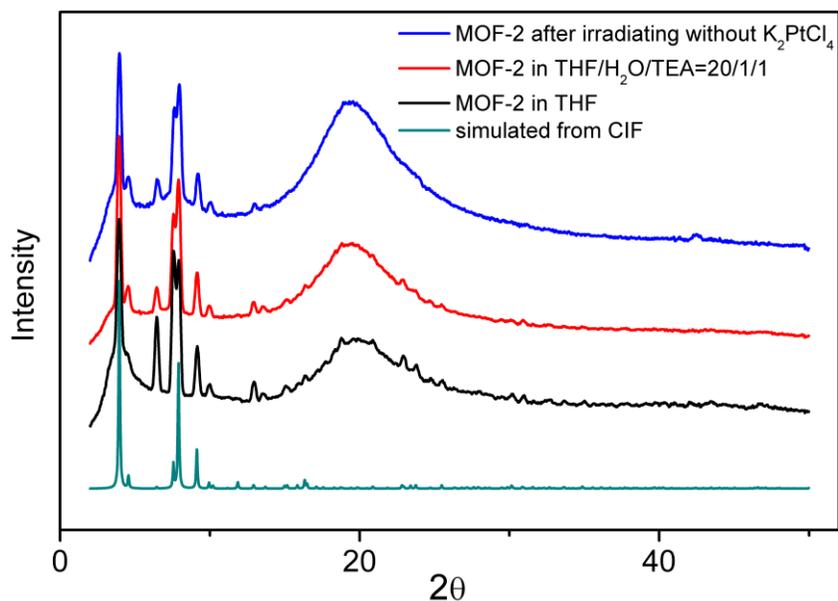
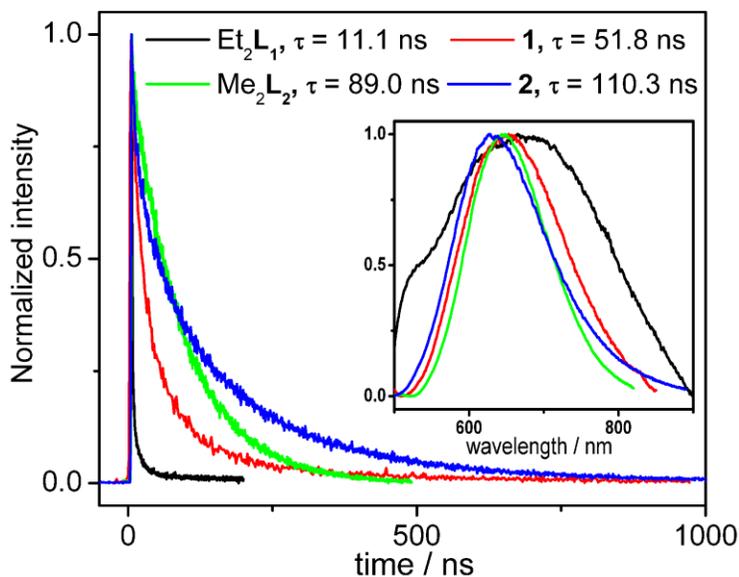


Figure S13. PXRD patterns of **2**: simulated from the CIF (green), in THF (black), in THF/H₂O/TEA (20/1/1) solution (red), in THF/H₂O/TEA (20/1/1) solution and irradiated with 450 W Xe-lamp for 6 hours without adding K₂PtCl₄ (blue). The broad peak around 20° comes from the glass capillary tube sample holder. All the PXRD patterns are taken when samples are sealed in capillary tubes with solvent to avoid sample desolvation. The majority of the peaks are preserved when putting the MOF in the experimental solvent with irradiation. This proves the stability of the framework under these experimental conditions.

7. Steady-state luminescent spectra and time resolved transit decay of **1** and **2**

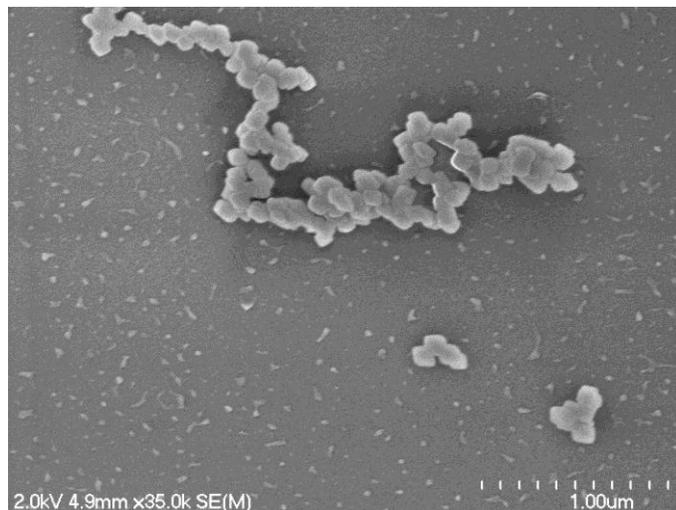


S14. Decay transients measured at 640 nm (with 445 nm excitation) in THF for Et₂L₁ (black), **1** (red), Me₂L₂ (green) and **2** (blue); The emission decays were fit to bi-exponential expression $A = A_1e^{-t/\tau_1} + A_2e^{-t/\tau_2}$

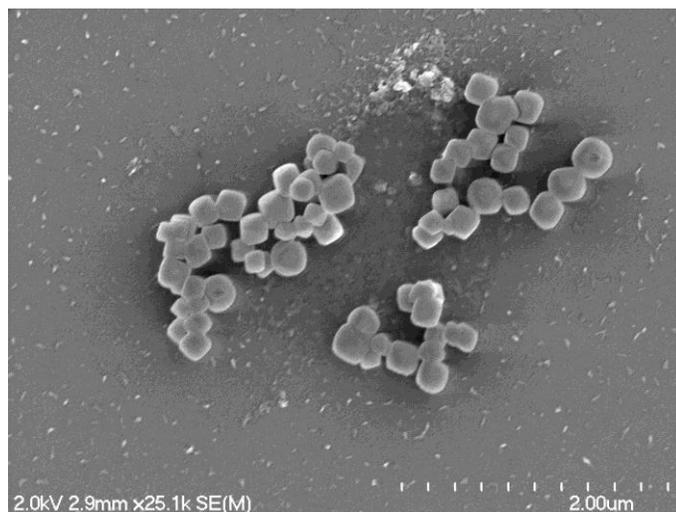
τ^2 . The reported lifetime τ is the weighted lifetime $\tau = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$. Inset: Steady-state emission spectra of Et₂L₁ (black), **1** (red), Me₂L₂ (green) and **2** (blue) with excitation at 485 nm.

8. SEM images of **1** and **2**

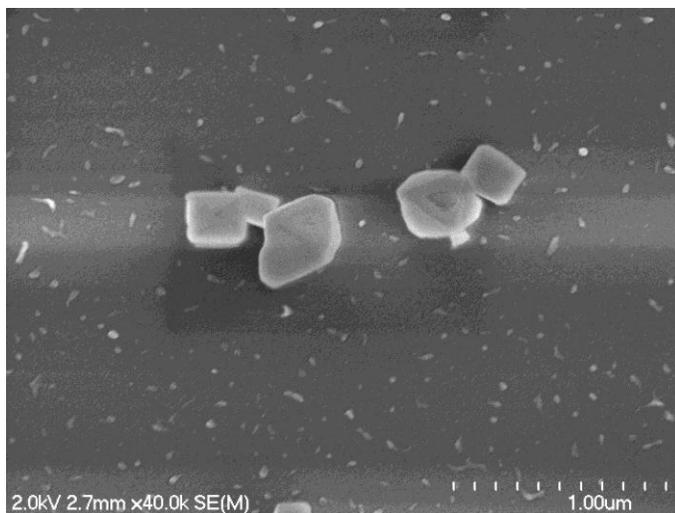
(a)



(b)



(c)



(d)

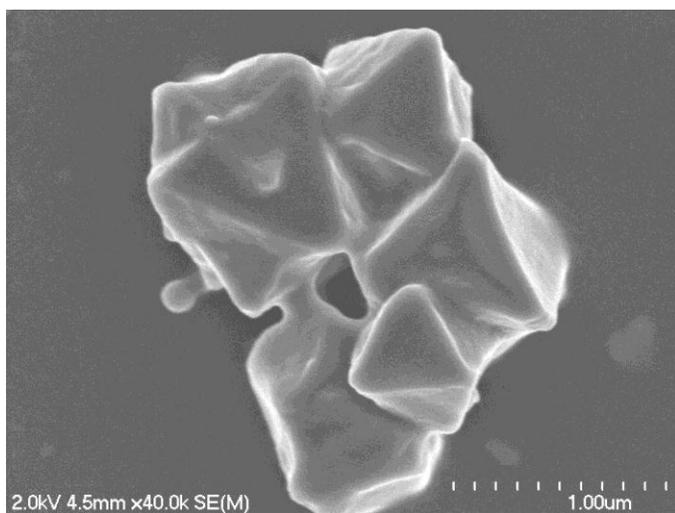
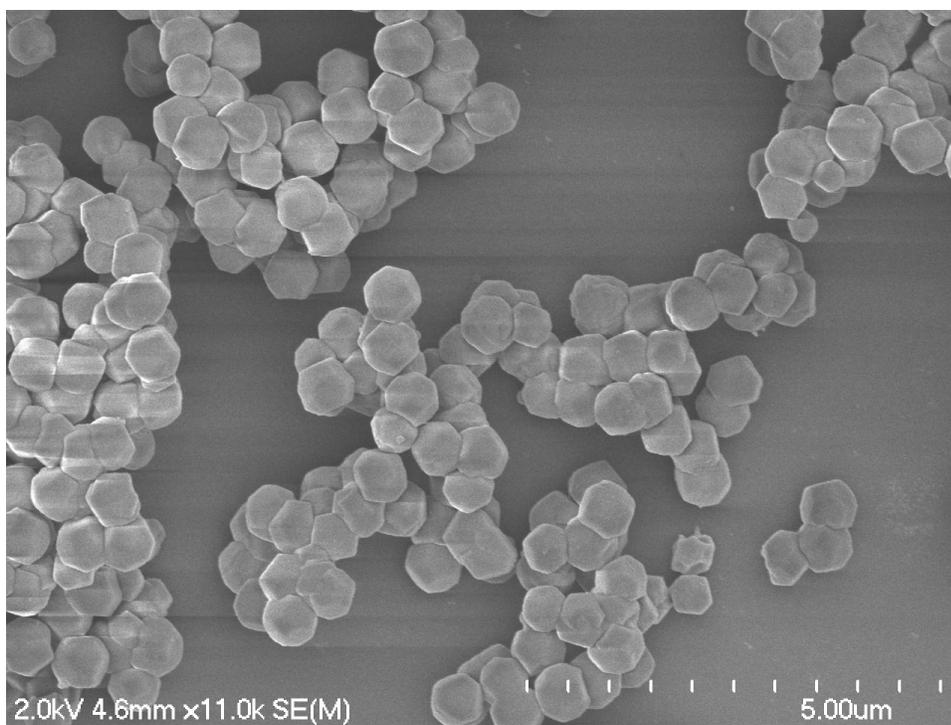


Figure S15. SEM images of **1** synthesized by adding different amounts of acetic acid: (a) 10 μL (b) 25 μL (c) 50 μL (d) 75 μL

(a)



(b)

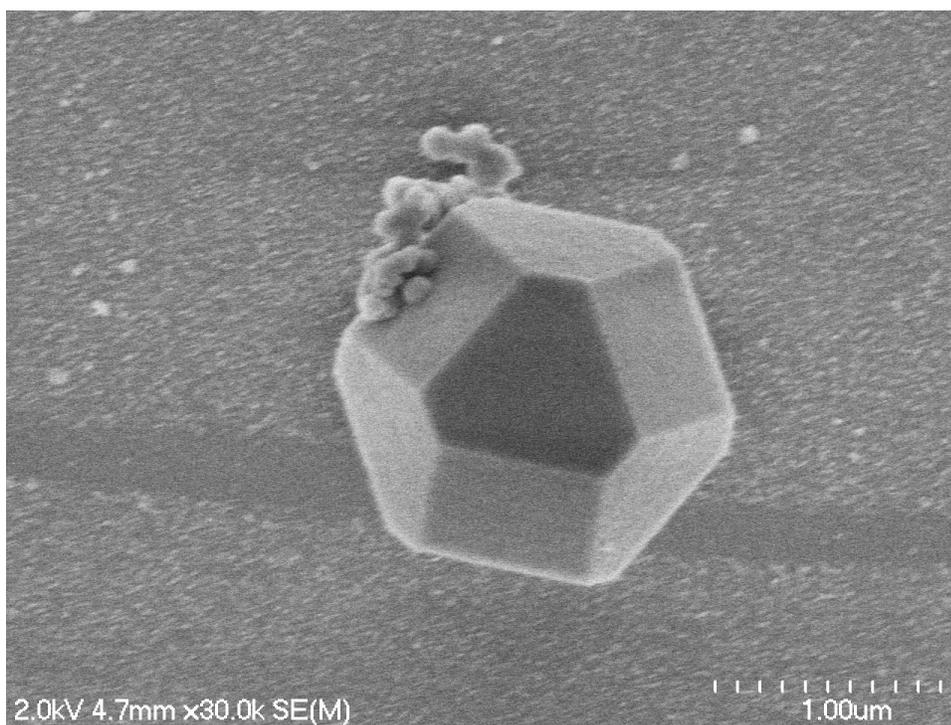
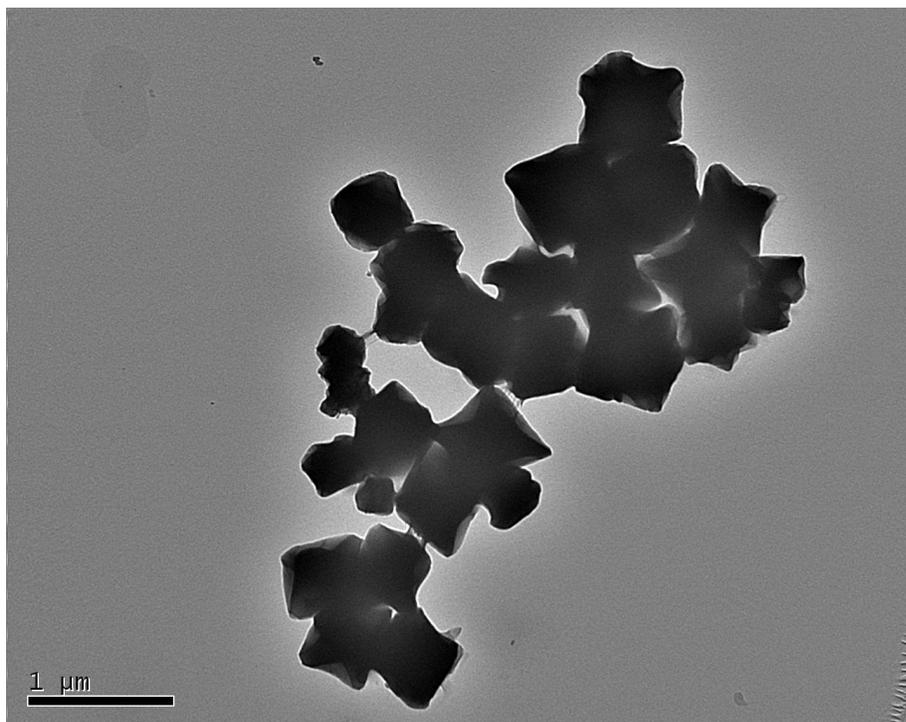


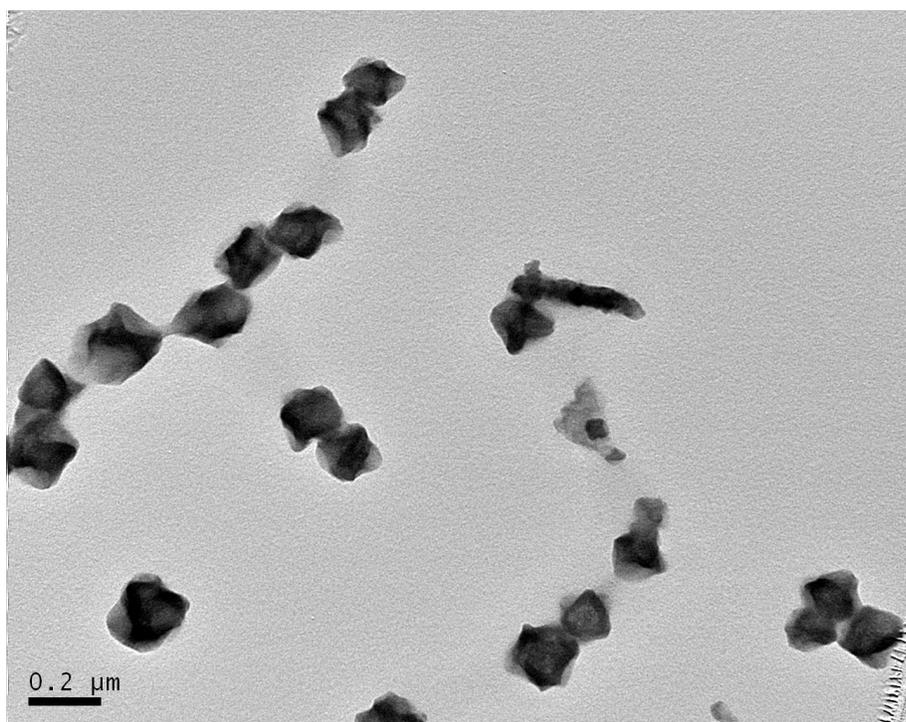
Figure S16. SEM images of a powdery sample of **2** showing (a) aggregated nanocrystals and (b) one crystal with a cuboctahedron shape.

9. TEM images

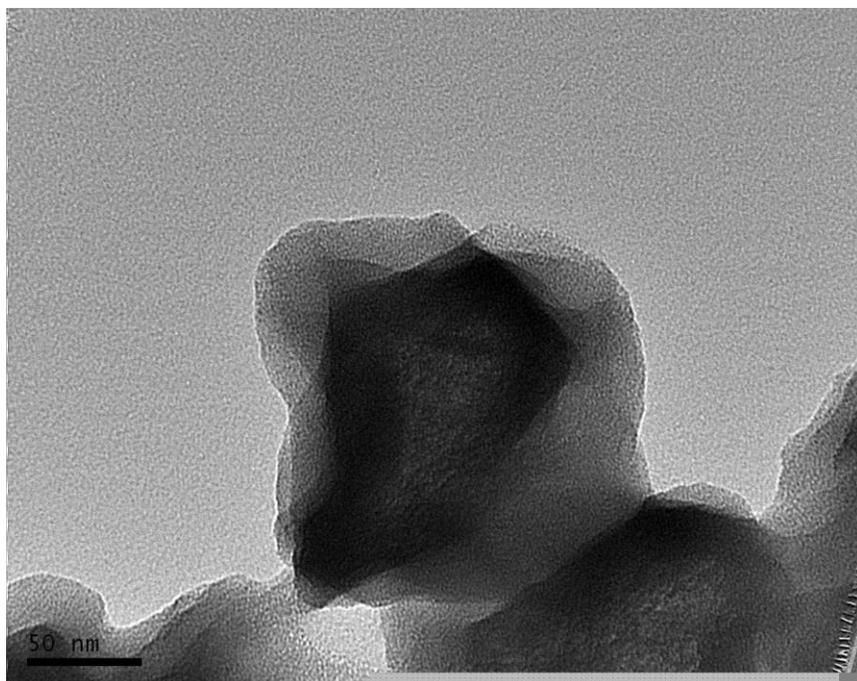
(a)



(b)



(c)



(d)

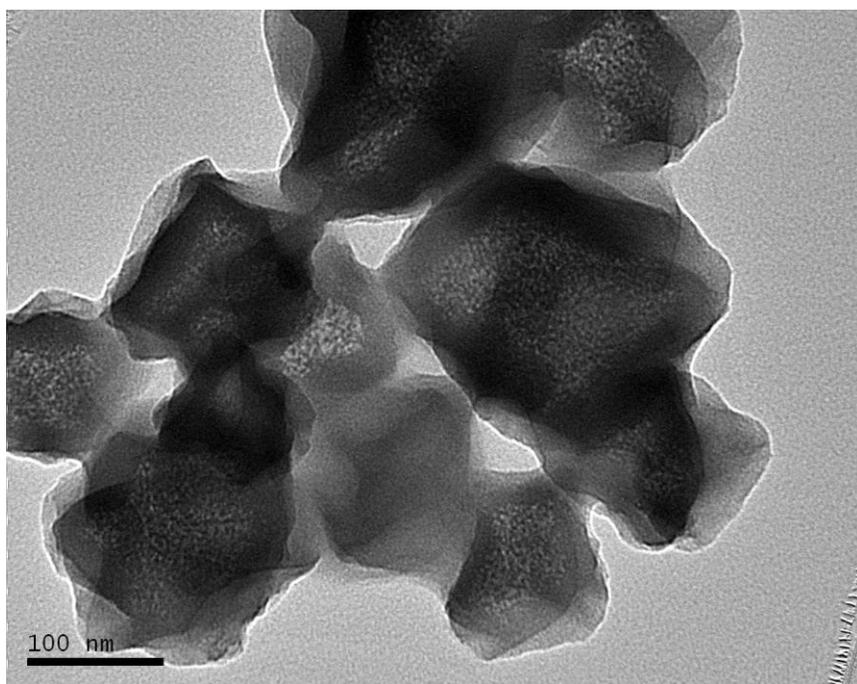
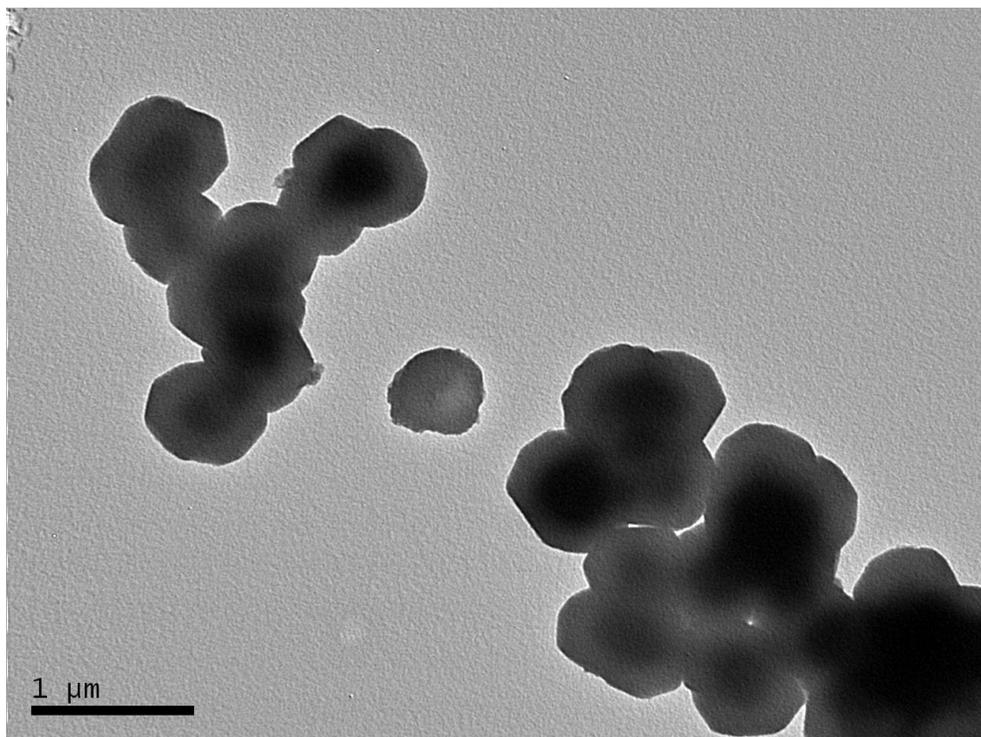
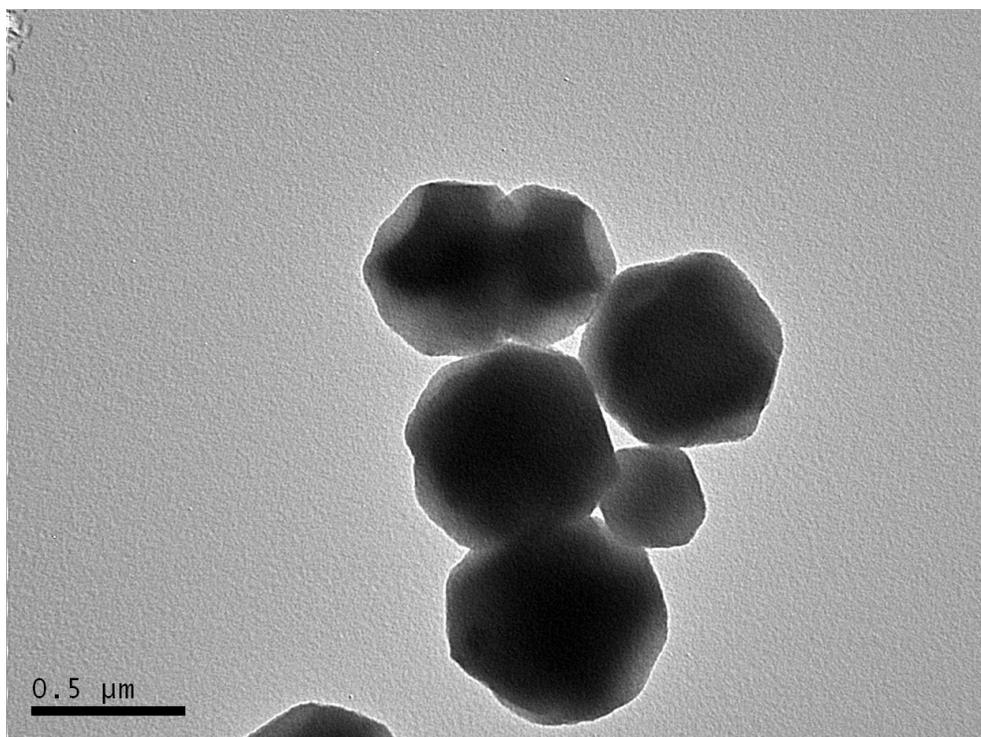


Figure S17. TEM images of a powdery sample of **1**.

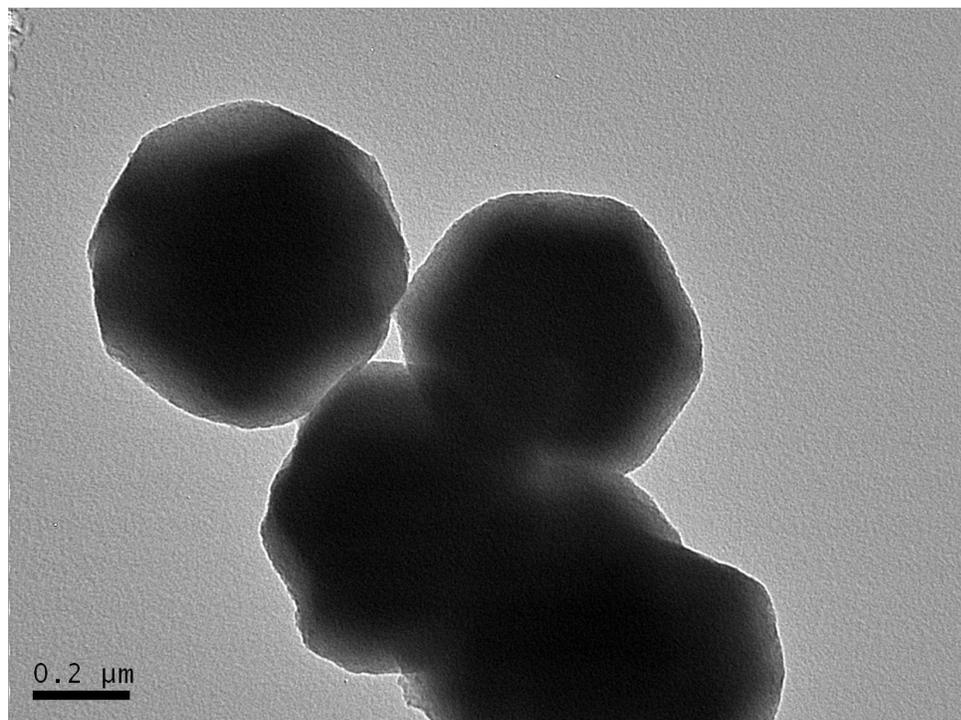
(a)



(b)



(c)



(d)

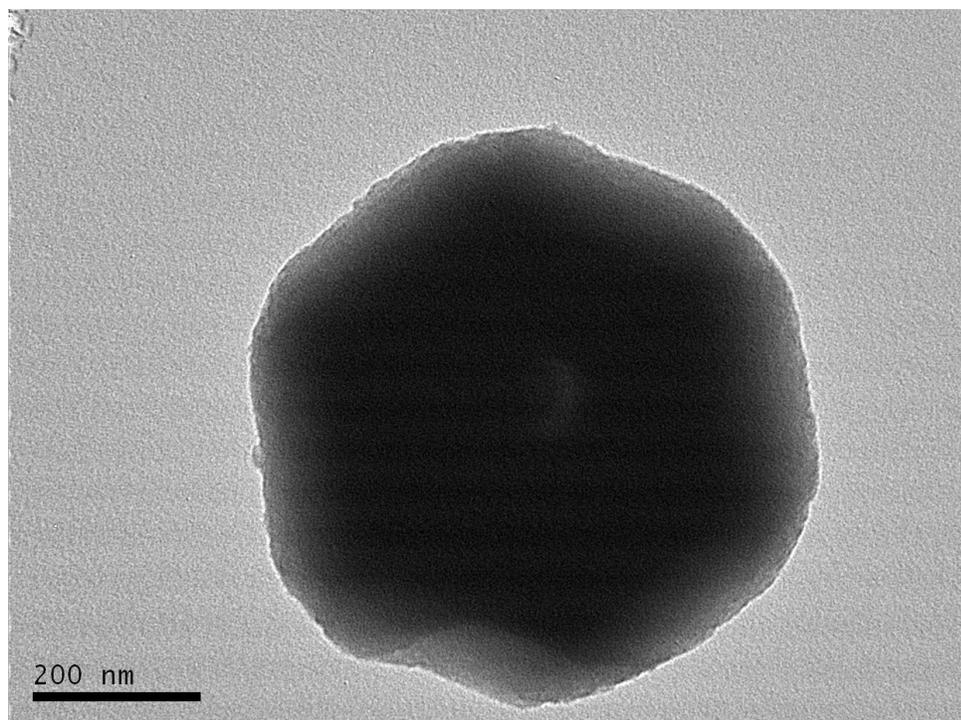
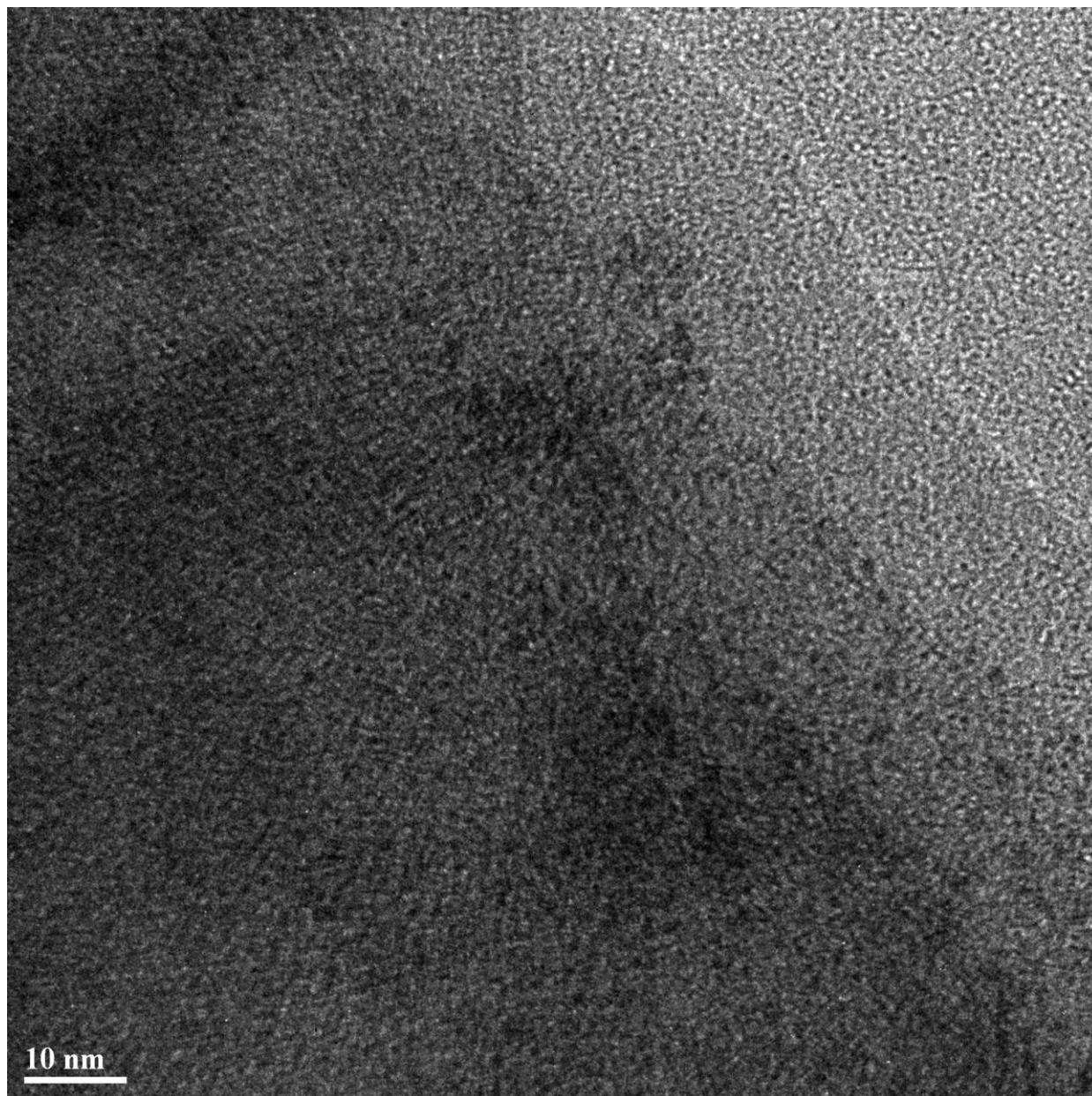


Figure S18. TEM images of a powdery sample of **2**.

10. HRTEM images of Pt@1 and Pt@2

(a)



(b)

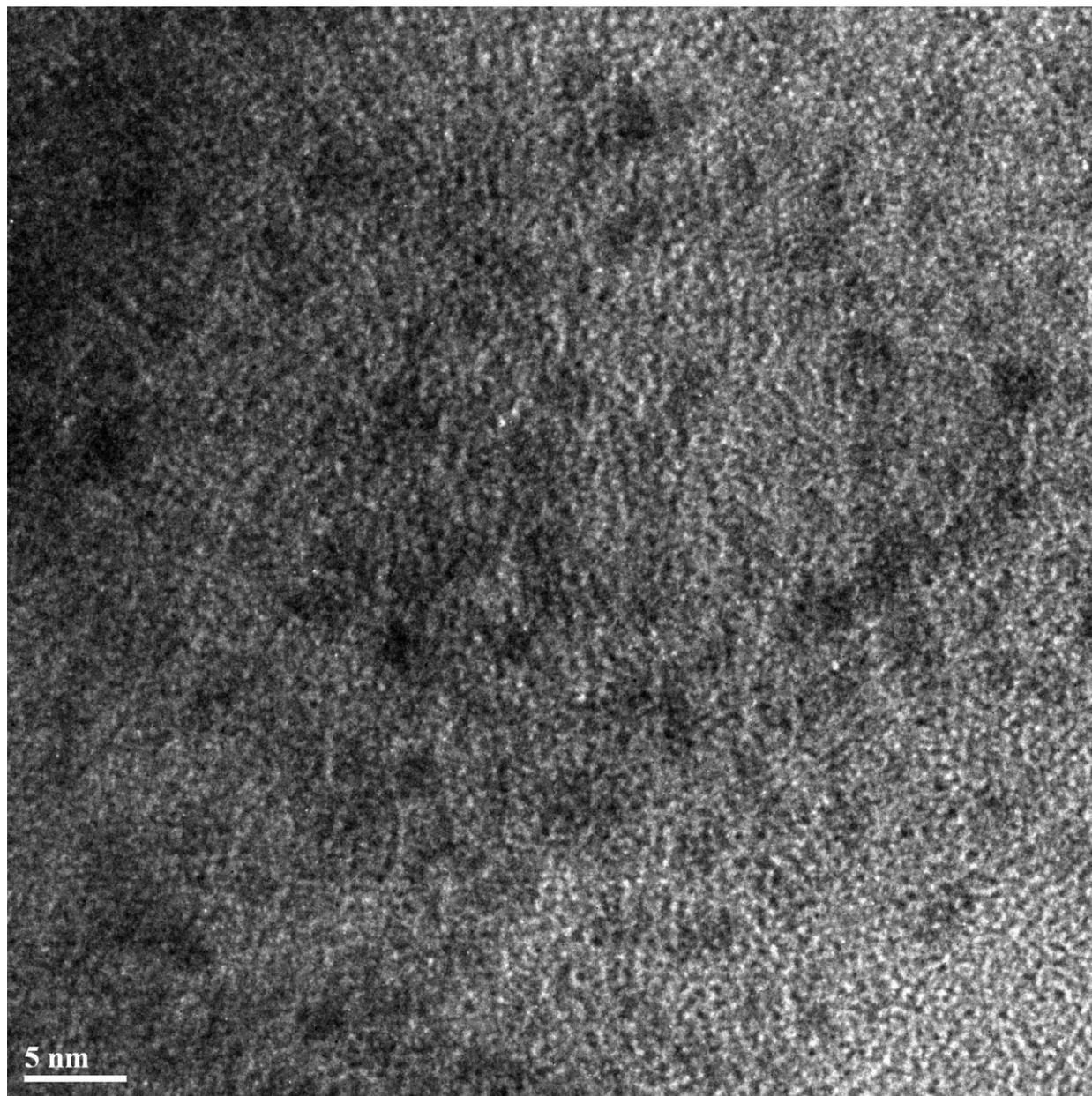
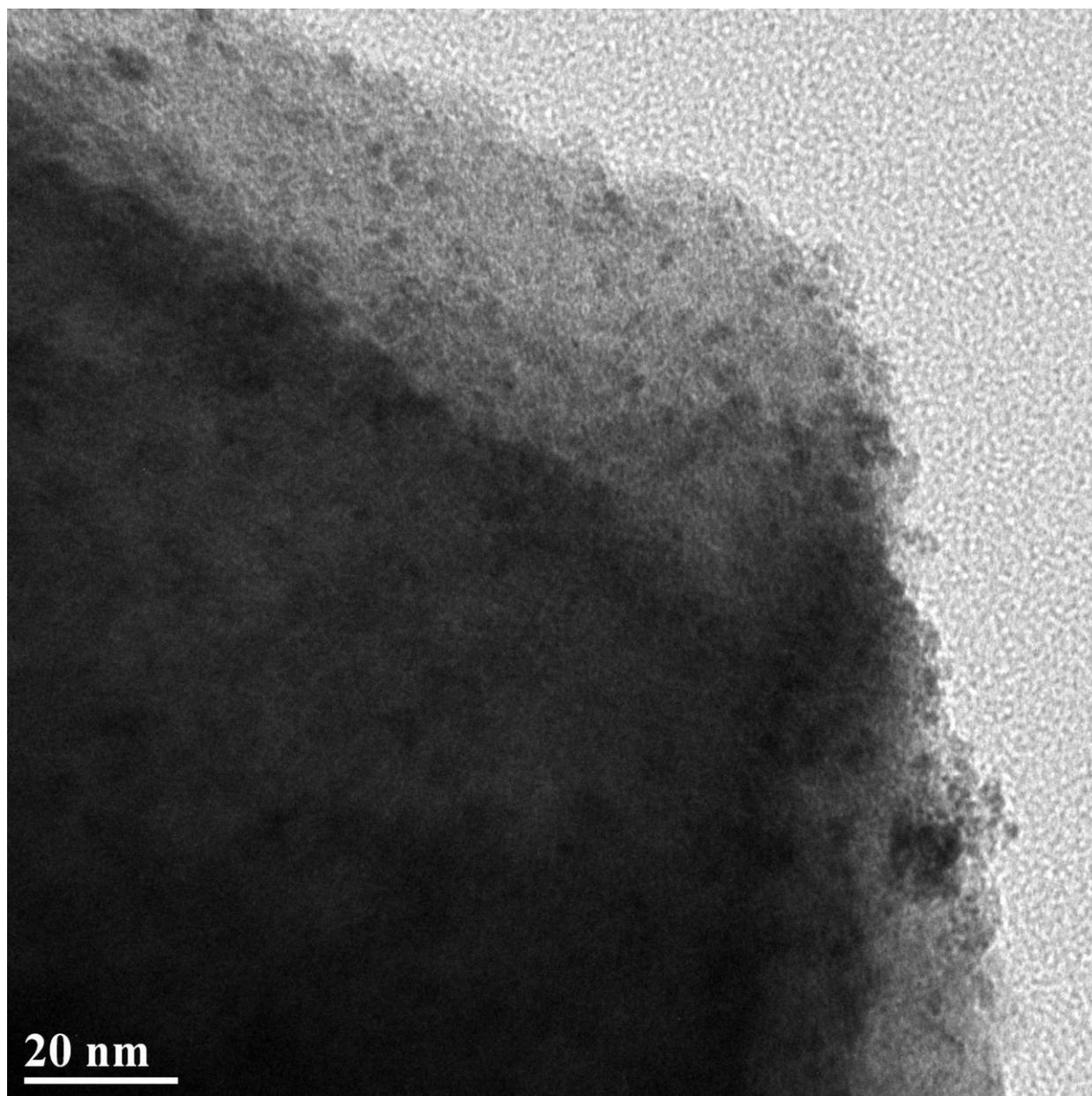
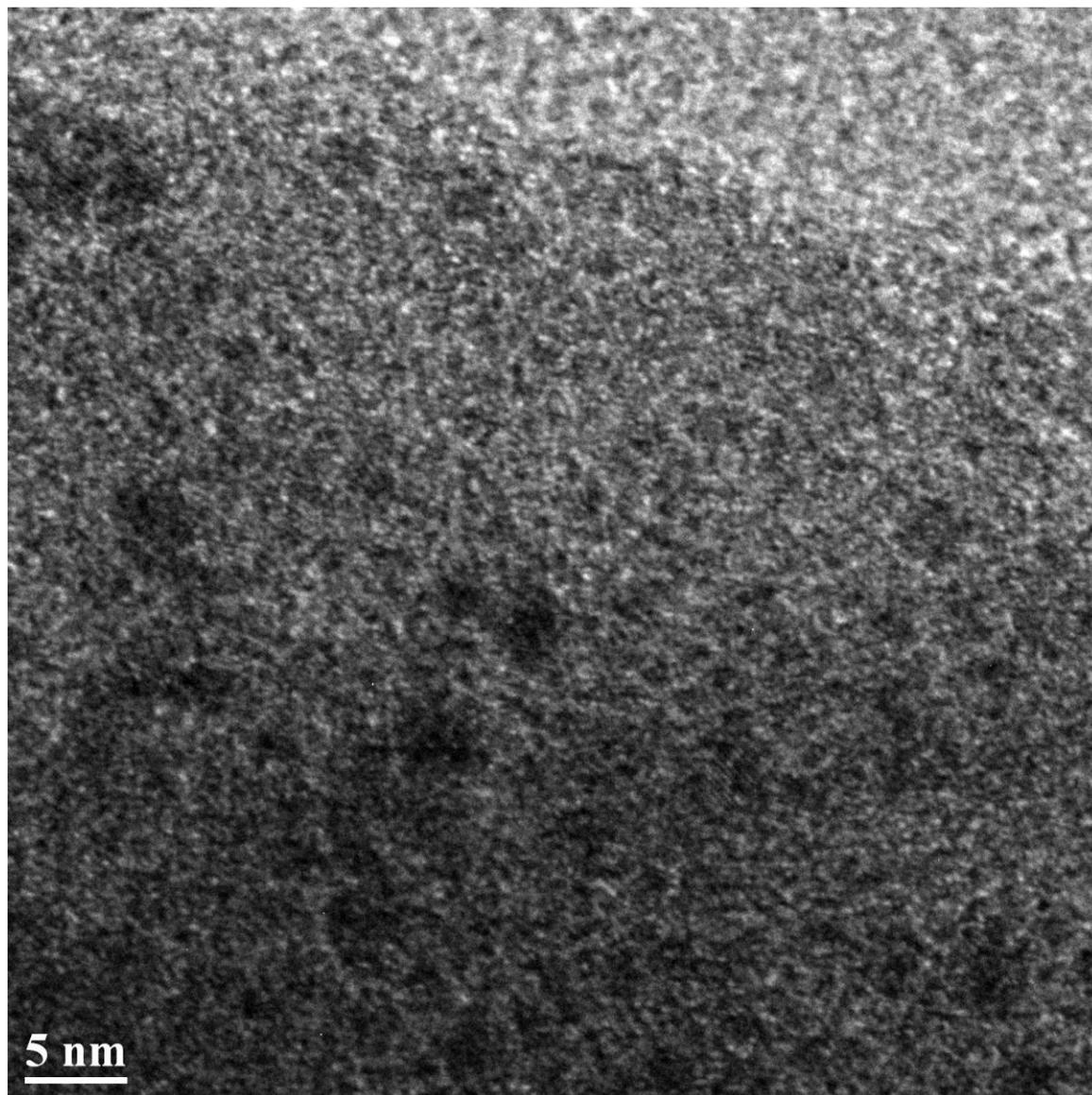


Figure S19. HRTEM images of a powdery sample of Pt@1.

(a)



(b)



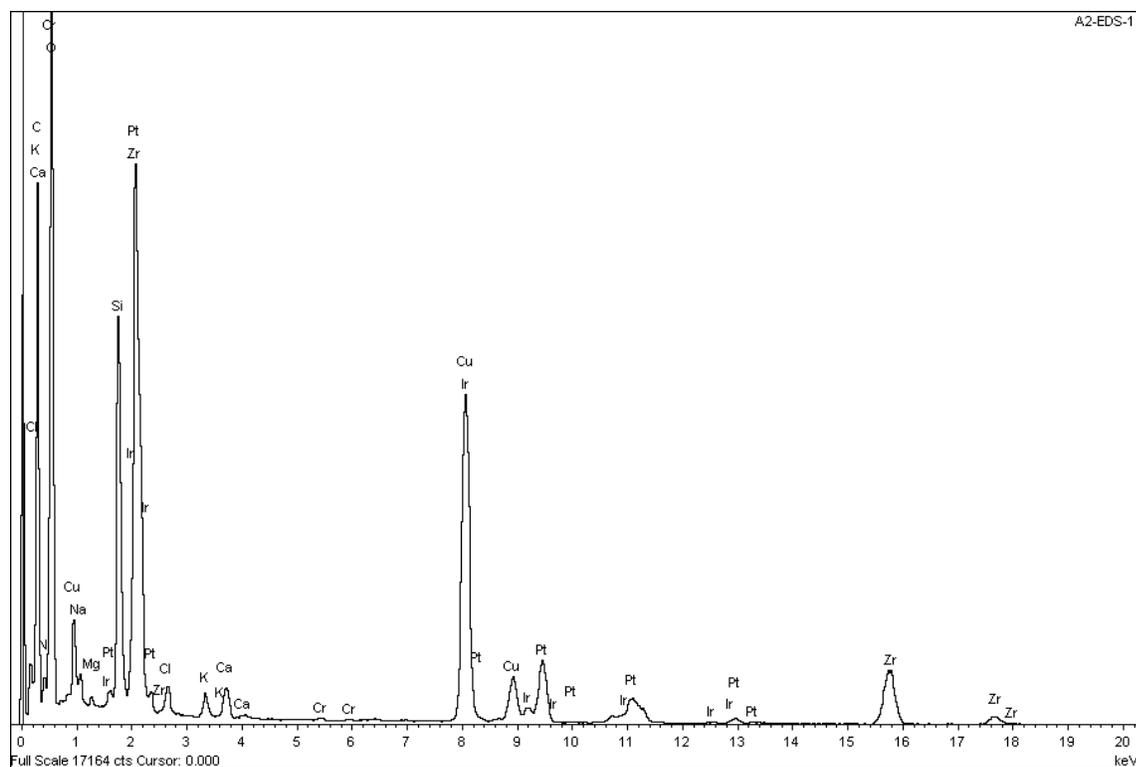


Figure S22. EDS of Pt@2.

12. General procedure for hydrogen production experiment

Samples for photocatalytic hydrogen production were prepared in 10 mL septum-sealed glass vials. Each sample was made up to a volume of 2 mL of THF. 0.1 mL of H₂O was added to serve as the proton source. 0.1 mL of TEA (triethylamine) was added, as the sacrificial reducing agent. Samples typically contained 0.04-0.05 μmol of the Ir- photosensitizer. Different amounts of K₂PtCl₄ were then added to the reaction mixture. Sample vials were capped and deoxygenated by bubbling nitrogen through them for 10 min. 50 μL of methane gas (1 atm, room temperature) was added to the vial as an internal standard. The vials were then placed in front of a 450 W Xe-lamp with a 420 nm cut-off filter and magnetic stirring. The hydrogen evolution reaction lasted for 6 hours, after which the gas in the headspace of the vial was analyzed by GC (SRI 8610C) to determine the amount of hydrogen generated.

Table S2. Pt@MOFs as photocatalyst for hydrogen evolution^[a]

	entry	Pt/Ir added in solution	Pt/Ir in Pt@MOF ^[b]	Ir-TON	Pt-TON	Ir-TON (recovered) ^[c]	Pt-TON (recovered) ^[c]
Pt@1	1	16.3	2.91	29.8	10.2	14.2	4.88
	2	51.2	12.5	163	13.0	79.1	6.32
	3	68.6	17.5	483	27.5	389	22.2
	4	86.0	18.6	730	39.2	633	34.0
	5	102	23.0	293	12.8	232	10.1
	6	121	32.2	294	9.13	244	7.58

	7	156	48.5	274	5.66	249	5.14
Pt@2	8	8.14	4.66	84.0	18.0	63.0	13.5
	9	16.3	8.21	530	64.6	550	66.9
	10	24.4	17.8	1620	90.9	1500	84.1
	11	33.7	21.8	318	14.6	218	10.0
	12	51.2	28.0	278	9.93	131	4.69
	13	86.0	31.8	310	9.75	285	8.97
	14	121	37.0	158	4.27	177	4.79
	15	156	41.0	182	4.44	101	2.45

[a] The hydrogen evolution reaction lasted for 6 hours using a 450 W Xe-lamp with a 420nm cut-off filter. Ir turnover number is defined as Ir-TON = $n(1/2H_2)/n(Ir)$. Pt turnover number is defined as Pt-TON = $n(1/2H_2)/n(Pt)$. [b] Pt/Ir ratio determined by ICP-MS. [c] the solids in the reaction mixture were recovered by centrifugation and added into 2 mL fresh THF/H₂O/TEA (20/1/1) solution without adding any more K₂PtCl₄. After degassing with N₂, the sample was put under light to perform a second run of the hydrogen generation reaction for another 6 hours.

Table S3. Control experiments for photocatalytic hydrogen evolution^[a]

Entry	Catalyst	Ir-TON ^[b]	Pt-TON ^[c]
1 ^[e]	1	0	N/A
2 ^[f]	K ₂ PtCl ₄ +1	0	0
3 ^[g]	K ₂ PtCl ₄ +1	0	0
4 ^[h]	K ₂ PtCl ₄	N/A	0
5 ^[i]	K ₂ PtCl ₄	N/A	4.3

^[a] Hydrogen evolution reactions were carried out for 6 hours using a 450 W Xe-lamp with a 420 nm cut-off filter. ^[b] Ir-based turnover number (Ir-TON) is defined as $n(1/2H_2)/n(Ir)$. ^[c] Pt-based turnover number (Pt-TON) is defined as $n(1/2H_2)/n(Pt)$. ^[d] The solids were recovered from the reaction mixtures via centrifugation and added to 2 mL fresh THF/H₂O/TEA (20/1/1). The mixture was degassed before reuse tests without adding K₂PtCl₄. ^[e] without adding K₂PtCl₄. ^[f] without adding TEA. ^[g] in the dark. ^[h] without adding Ir-phosphor using 420 nm cut-off filter. ^[i] without adding Ir-phosphor using 300 nm cut-off filter.

The GC analysis protocol

A valve rotation(G on/off) technique was used in the GC analysis of multiple gases in the headspace.

Operating conditions in a typical run:

Carrier gas: helium at 5 PSI

Column 1: RESTEK 15m, MXT-1

Column 2: 6' silica gel

Detector: Channel 1, HID

Event sequence in a typical run: 0.05 min, G-on; 7.00 min, G-off.

Column temperature sequence in a typical run: 0 min, keep at 40 °C; 4 min, 40 °C → 80 °C with 20 °C/min; 6 min, keep at 80 °C; 7min, cool down.

Under these operating conditions, the retention times are: 1.58-1.66 min for H₂, 2.29-2.44 min for O₂, 3.09-3.29 min for N₂, 5.52-5.59 min for CH₄.

In these experiments, the detected O₂ and N₂ came from residual air in the GC injector.

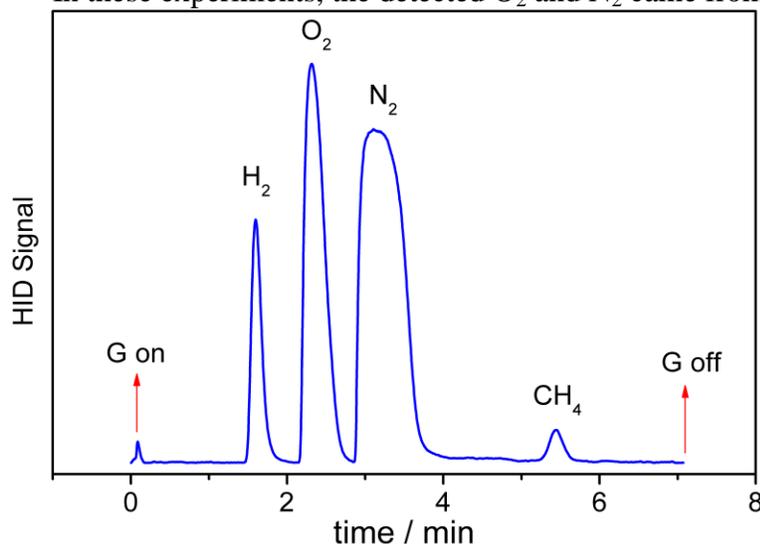


Figure S23. Representative GC trace of Pt@MOF catalyzed photocatalytic hydrogen evolution (from Pt@2 catalyzed reaction at the optimized condition running for 27 hours).

13. Determination of quantum yield of Pt@2 catalyzed reaction and homogeneous control.

The reaction mixture of **2** with K₂PtCl₄ in 20/1/1 THF/TEA/H₂O solution under the optimized condition was put in a septum-sealed cuvette and loaded onto a fluorometer after degassing with N₂. The excitation wavelength of the fluorometer was set to 440 nm with a slit width of 20 nm, and the reaction proceeded for 12 hours before analyzing the headspace gas using GC. The amount of hydrogen generated during the 12 hours was calculated to be 0.0935 μmol based on the GC data. Absorbance of the sample at the wavelength of 440 nm was measured to be A₄₄₀ = 0.268.

The light intensity of the fluorometer at 440 nm is then determined using potassium ferrioxalate as a chemical actinometer. Following a procedure in the literature³, using a 0.15 M solution of K₃Fe(ox)₃ in 0.1 M H₂SO₄, the light intensity of the fluorometer at 440 nm with slit width of 20 nm is determined to be (1.00±0.06)×10¹⁶ photons·s⁻¹·cm⁻². These measurements lead to a quantum yield of (5.6±0.4)×10⁻⁴ for the Pt@2-catalyzed hydrogen evolution.

A similar procedure was used for the homogeneous control using [Ir(ppy)₂(bpy)]Cl, except that the reaction time was elongated to 24 h to yield enough hydrogen gas for detection. 0.0949 μmol was detected from GC analysis and the absorbance of the sample at the wavelength of 440 nm was A₄₄₀ = 0.246, leading to a quantum yield of (3.0±0.3)×10⁻⁴ for [Ir(ppy)₂(bpy)]Cl-catalyzed hydrogen evolution.

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