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Probing Reactive Platinum Sites in UiO-67 Zirconium Metal-organic Frameworks

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2. Linker synthesis

1.1. Synthesis of H_2bpydc

H_2bpydc was prepared following the literature method reported by Constable¹ consisting in the oxidation of 5,5'-dimethyl-2,2'-bipyridyl with $K_2Cr_2O_7$ in concentrated sulfuric acid. 5,5'-dimethyl-2,2'-bipyridyl (5.00 g, 27.1 mmol) was dissolved in 125 mL concentrated sulfuric acid in a 250 mL round bottom flask. Potassium dichromate (24.0 g, 81.6 mmol) was added over approximately 30 minutes. The reaction is very exothermic, and thus the reaction vessel was cooled by an ice bath if the temperature exceeded 80°C in order to prevent further oxidation and unwanted byproducts. When the reaction was complete, the contents of the flask were poured into a 1 L beaker filled with ice and water. The crude product was isolated by filtration, washed five times in 100 mL portions of cold water and once in 100 mL acetone. The product was dried in air at 60°C. The final product weight was 6.24 g (Yield: 94 %) $PtCl_2(H_2bpydc)$. White solid: 1H NMR (300 MHz, DMSO- d_6) δ 13.52 (s, 2H), 9.20 (dd, J = 2.1, 0.8 Hz, 2H), 8.57 (dd, J = 8.3, 0.8 Hz, 1H), 8.45 (dd, J = 8.3, 2.2 Hz, 2H).

1.2. Synthesis of $PtCl_2(H_2bpydc)$

K_2PtCl_4 (1005 mg, 2.42 mmol) and 65 % HNO_3 (2.0 mL, 29 mmol) were dissolved in 200 mL water in a 250 mL round bottom flask. H_2bpydc (505 mg, 2.07 mmol) was added, but was only suspended in the solution due to its poor solubility in acidic solution. The reaction was heated and stirred under reflux for 40 hours. The precipitated red powder was isolated by filtration and washed three times with water and once with 2-propanol. The powder was dried in air at 60° C, where it changed color to dark brown. It regained the red color upon rehydration and dissolved readily in hot DMF and DMSO, creating a clear, yellow solution. The final product weight was 800 mg (Yield in respect to starting H_2bpydc : 77 %). Dark red solid. 1H NMR (300 MHz, DMSO- d_6) δ 14.30 (s, 2H), 10.01 (d, J = 1.7 Hz, 2H), 8.85 – 8.71 (m, 4H).

1.3. Synthesis of $PtCl_4(H_2bpydc)$

$Na_2PtCl_6 \cdot 6H_2O$ (600 mg, 1.07 mmol), KNO_3 (1.00 g, 9.89 mmol) and KOH (90 mg, 1.38 mmol) were dissolved in 45 mL water in a 50 mL round bottom flask. H_2bpydc (250 mg, 1.03 mmol) was added, but was only suspended in the solution due to its poor solubility even in basic aqueous solution. The reaction was heated and stirred under reflux for four days. The precipitated yellow powder was isolated by filtration and washed three times with water and once with 2-propanol. The powder was dried in air at 60° C. The final product weight was 366 mg, or a yield of 61 % in respect to starting H_2bpydc . $PtCl_4(H_2bpydc)$, pale yellow solid. 1H NMR (300 MHz, DMSO- d_6) δ 9.97 – 9.83 (m, 2H), 9.19 (d, J = 8.5 Hz, 2H), 9.00 (d, J = 8.4 Hz, 2H).

1.4. Synthesis of $PtBr_4(H_2bpydc)$

$PtBr_4(H_2bpydc)$ was generated in situ by adding one drop of Br_2 to the NMR tube containing a DMSO solution of $PtCl_2(H_2bpydc)$. In another experiment, a few drops of Br_2 were added to a solution of $PtCl_2(H_2bpydc)$ in DMF. After a few days, crystals of $PtBr_2(H_2bpydc)$ precipitated out, presumably due to light-mediated reduction with DMF.

Full 1H NMR spectra are shown in Figure S1. $PtBr_2(H_2bpydc)$, orange solid. 1H NMR (500 MHz, DMSO- d_6) δ 10.26 (s, 2H), 8.73 (dd, J = 8.2, 1.8 Hz, 2H), 8.67 (d, J = 8.3 Hz, 2H). $PtBr_4(H_2bpydc)$, orange solution in DMSO- d_6 . 1H NMR (500 MHz, DMSO- d_6) δ 10.03 – 9.76 (m, 2H), 9.26 (d, J = 8.4 Hz, 2H), 9.05 – 8.84 (m, 2H).

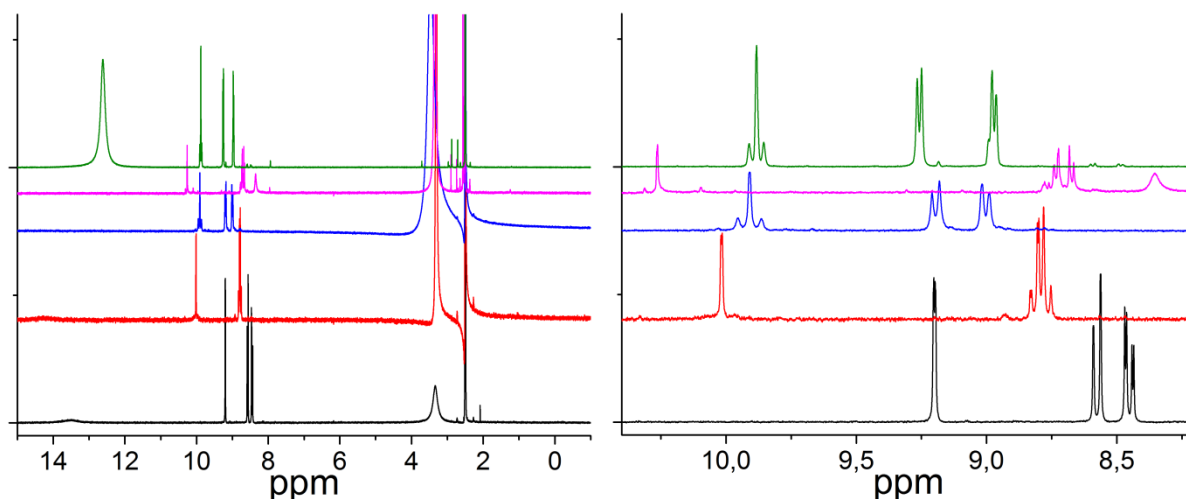


Figure S1. ^1H NMR spectra of (from the top) $\text{PtBr}_4(\text{H}_2\text{bpydc})$, $\text{PtBr}_2(\text{H}_2\text{bpydc})$, $\text{PtCl}_2(\text{H}_2\text{bpydc})$ and H_2bpydc . $\text{PtBr}_4(\text{H}_2\text{bpydc})$ (green) was made in situ and contains a lot of HBr (12.6 ppm, s) due to the reaction between Br_2 and water, and some DMF. $\text{PtBr}_2(\text{H}_2\text{bpydc})$ has an impurity of dimethylammonium (8.35 ppm, s) due to cocrystallization from DMF.

2. Single crystal X-ray diffraction of crystallized linkers

Single crystals of $\text{PtCl}_2(\text{H}_2\text{bpydc})$ (yellow prisms) and $\text{PtBr}_2(\text{H}_2\text{bpydc})$ (orange plates) were obtained by recrystallizing the prepared powder in DMF solution, into which water was allowed to diffuse by vapor, as described by Spingler and coworkers.² Single crystals of $\text{PtBr}_4(\text{H}_2\text{bpydc})$ (orange plates) were grown from a solution of $\text{PtCl}_2(\text{H}_2\text{bpydc})$ in DMSO to which a drop of Br_2 was added. Crystals of $\text{Pt}(\text{tdt})(\text{H}_2\text{bpydc})$ (dark blue-green prisms) were grown from a DMF solution of $\text{PtCl}_2(\text{H}_2\text{bpydc})$ to which a small amount of 3,4-toluene dithiol (H_2tdt) was added.

Table S1. Summary of crystal structure refinements for the Pt-linkers.

	$\text{PtCl}_2(\text{H}_2\text{bpydc})$	$\text{PtBr}_2(\text{H}_2\text{bpydc})$	$\text{PtBr}_4(\text{H}_2\text{bpydc})$	$\text{Pt}(\text{tdt})(\text{H}_2\text{bpydc})$
Space group	$\text{P2}_1/\text{c}$	$\text{P2}_1/\text{c}$	$\text{P}\bar{1}$	$\text{C2}/\text{c}$
Cell dimensions				
a (Å)	17.3214(11)	15.4705(8)	12.4323(4)	21.3954(11)
b (Å)	7.2698(4)	7.6230(4)	13.2777(4)	17.3795(8)
c (Å)	17.6866(10)	17.7505(9)	23.5825(8)	14.3340(6)
α (°)	90	90	94.6600(12)	90
β (°)	105.259(2)	114.0660(10)	96.4670(12)	92.3600(14)
γ (°)	90	90	103.3430(12)	90
Crystal sizes (mm)	0.23 × 0.12 × 0.07	0.28 × 0.10 × 0.03	0.26 × 0.23 × 0.02	0.15 × 0.10 × 0.04
Pt first shell mean bond lengths				
Pt – X (X = Cl or Br) (Å)	2.2935(8) Å	2.4206(6)	2.4277(4) Equatorial 2.4511(4) Axial	2.259(3)
Pt – N	2.009(3) Å	2.022(3)	2.052(3)	2.071(6)
Θ_{max} (°); d_{min} (Å)	28.3; 0.75	29.13°; 0.73	30.5°; 0.70	25.2; 0.84
radiation	Mo K α	Mo K α	Mo K α	Mo K α
Reflections/parameters/restraints	5326/291/0	5144/312/0	22821/856/0	4796/356/0
R_1 & wR_2 [$I > 2\sigma$]	0.026 0.040	0.018 0.037	0.029 0.066	0.043 0.087
R_1 & wR_2 all	0.042 0.043	0.023 0.038	0.041 0.070	0.059 0.092

The diffraction data was recorded on a Bruker D8 Venture diffractometer, with a Photon 100 CMOS detector and fixed χ goniometer. Bruker's software suite *APEX2* (v2013.6–2) was used for data collection and unit cell determination. (Bruker AXS, Madison, Wisconsin, USA, 2014) *SAINT* and *SADAB* (Bruker AXS, Madison, Wisconsin, USA, 2014) were used for integration and scaling, respectively. *SHELXS2013* and *SHELXL2013* were used for solving and refining the structure,³ utilizing both *ShelxLE*,⁴ and *Olex2*⁵ as GUI. Molecular graphics were made using *Diamond v4.0.1* (Brandenburg, K., Crystal Impact GbR, Bonn, Germany. 2014). The CIF files were edited in *publCIF*⁶ and *enCIFer* v1.4.⁷ Table S1 summarizes the main results of this crystallographic study, while the refined structures can be observed in Figure S2, where also the anisotropic thermal parameter for each atom can be appreciated.

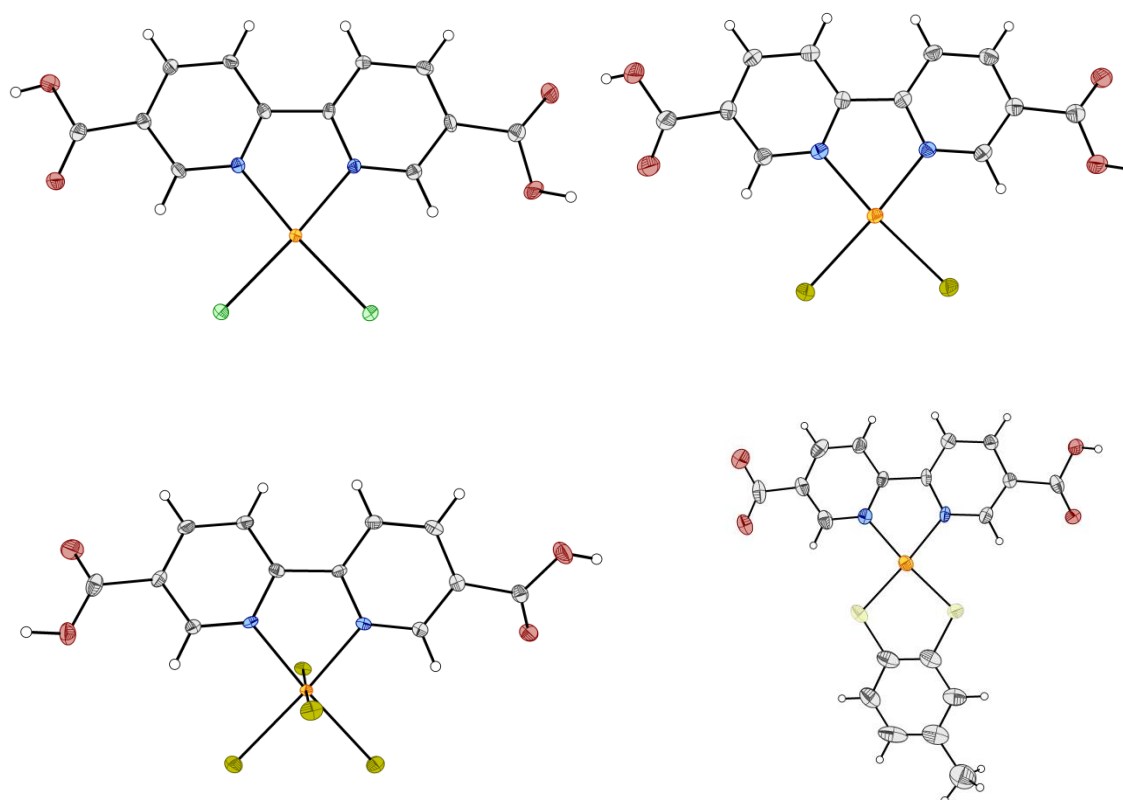


Figure S2. Structural models of $\text{PtCl}_2(\text{H}_2\text{bpydc})$ (top left), $\text{PtBr}_2(\text{H}_2\text{bpydc})$ (top right), $\text{PtBr}_4(\text{H}_2\text{bpydc})$ (bottom left) and $\text{Pt}(\text{tdt})(\text{H}_2\text{bpydc})$ (bottom right).

3. MOF synthesis and sorption measurements

The UiO-67 materials were synthesized by reacting ZrCl_4 with a mixture of H_2bpdC and $(\text{H}_2\text{bpydc})/\text{PtCl}_x(\text{H}_2\text{bpydc})$; the ratio between the linkers being 9:1, and equal molar quantity of ZrCl_4 and linker) in a solution of DMF. 5 molar equivalents of benzoic acid was added to obtain a modulator effect, which resulted in a porous MOF with monodispersed particles and well-defined crystallinity. Attempts of making UiO-67-Pt(II/IV) without using benzoic acid resulted in poorly crystalline, nonporous material. Assuming the platinum chloride will selectively coordinate to bipyridine, whereas zirconium will bind to the carboxylate groups, all methods should yield the same product. However, the OPS synthesis method did not give reproducible results. The BET surface areas were calculated according to the principles outlined by Walton and Snurr.⁸

3.1. Synthesis and BET data for UiO-67-bpy (10% functionalized)

ZrCl₄ (602 mg, 2.58 mmol) and H₂O (61 µL, 3.4 mmol) were dissolved in 100 mL DMF while stirring. The solution was heated, and benzoic acid (1.58 g, 12.9 mmol), H₂bpydc (63 mg, 0.26 mmol) and H₂bpdc (563 mg, 2.33 mmol) were added. A clear, colorless solution was obtained after a few minutes of stirring. The solution was kept at 95 °C for 4 days. The solution was decanted off, and a white crystalline powder was recovered. The powder was then washed 3 times in 15 mL portions of anhydrous DMF and 3 times in 15 mL portions of 2-propanol, before it was dried in air at 60 °C. The product weight was 1.30 g, and the solvent fraction was found to be 41 % by thermogravimetric analysis. Thus the dry product mass was estimated to 764 mg and the final yield to 83 % (Yieldmax: 921 mg).

Table S2. Adsorption data for UiO-67-bpy

Starting point	3	
End point	19	
Slope	0,001932	
Intercept	9,2408E-07	
Correlation coefficient	1	
V _m	517,34	[cm ³ (STP) g ⁻¹]
a _{s,BET}	2251,7	[m ² g ⁻¹]
C	2091,8	
Total pore volume ($p/p_0=0.990$)	0,916	[cm ³ g ⁻¹]
Average pore diameter	1,6273	[nm]

3.2. Synthesis and BET data for UiO-67-Pt(II)-PMLS

ZrCl₄ (602 mg, 2.58 mmol) and H₂O (61 µL, 3.4 mmol) were dissolved in 100 mL DMF while stirring. The solution was heated, and benzoic acid (1.58 g, 12.9 mmol), H₂bpdc (563 mg, 2.33 mmol) and PtCl₂(H₂bpydc) (132 mg, 0.258 mmol) were added. A clear, yellow solution was obtained after a few minutes of stirring. The solution was kept at 95 °C for 4 days. The solution was decanted off, and a yellow crystalline powder was recovered. The powder was then washed 3 times in 15 mL portions of anhydrous DMF and 3 times in 15 mL portions of 2-propanol, before it was dried in air at 60 °C. The product weight was 833 mg, and the solvent fraction was found to be 42 % by thermogravimetric analysis. Thus the dry product weight was estimated to 481 mg and the final yield to 52 % (Yieldmax: 921 mg).

Table S3. Adsorption data for UiO-67-Pt(II)-PMLS

Starting point	1	
End point	14	
Slope	0.0019559	
Intercept	2.6652 E-06	
Correlation coefficient	1	
V _m	510.58	[cm ³ (STP) g ⁻¹]
a _{s,BET}	2222.3	[m ² g ⁻¹]
C	734.87	
Total pore volume ($p/p_0=0.990$)	1.1022	[cm ³ g ⁻¹]
Average pore diameter	1.9839	[nm]

3.3. Synthesis and BET data for UiO-67-Pt(II)-OPS

ZrCl₄ (602 mg, 2.58 mmol) and H₂O (61 µL, 3.4 mmol) were dissolved in 100 mL DMF while stirring. The solution was heated, and benzoic acid (1.58 g, 12.9 mmol), H₂bpydc (63 mg, 0.26 mmol), H₂bpdc (563 mg, 2.33 mmol) and K₂PtCl₄ (107 mg, 0.258 mmol) were added. A clear, yellow solution was obtained after a few minutes of stirring. The solution was kept at 95 °C for 4 days. The solution was decanted off, and a yellow crystalline powder was recovered. The powder was then washed 3 times in 15 mL portions of anhydrous DMF and 3 times in 15 mL portions of 2-propanol, before it was dried in air at 60 °C. The product weight was 553 mg, and the solvent fraction was found to be 44 % by thermogravimetric analysis. Thus the dry product weight was estimated to 310 mg and the final yield to 34 % (Yieldmax: 921 mg).

Table S4. Adsorption data for UiO-67-Pt(II)-OPS

Starting point	8	
End point	18	
Slope	0.0028916	
Intercept	2.0903 E-06	
Correlation coefficient	1	
V _m	345.58	[cm ³ (STP) g ⁻¹]
a _{s,BET}	1504.1	[m ² g ⁻¹]
C	1384.3	
Total pore volume ($p/p_0=0.990$)	0.625	[cm ³ g ⁻¹]
Average pore diameter	1.6621	[nm]

3.4. Synthesis and BET data for UiO-67-Pt(IV)-PMLS

ZrCl₄ (602 mg, 2.58 mmol) and H₂O (61 µL, 3.4 mmol) were dissolved in 100 mL DMF while stirring. The solution was heated, and benzoic acid (1.58 g, 12.9 mmol), H₂bpydc (563 mg, 2.33 mmol) and PtCl₄(H₂bpydc) (150 mg, 0.258 mmol) were added. A clear, yellow solution was obtained after a few minutes of stirring. The solution was kept at 95 °C for 4 days. The solution was decanted off, and a yellow crystalline powder was recovered. The powder was then washed 3 times in 15 mL portions of anhydrous DMF and 3 times in 15 mL portions of 2-propanol, before it was dried in air at 60 °C. The product weight was 1.22 g, and the solvent fraction was found to be 37 % by thermogravimetric analysis. Thus the dry product weight was estimated to 763 mg and the final yield to 83 % (Yieldmax: 921 mg).

Table S5. Adsorption data for UiO-67-Pt(IV)-PMLS

Starting point	5	
End point	31	
Slope	0.002248	
Intercept	2.8812 E-06	
Correlation coefficient	0.9999	
V _m	444.28	[cm ³ (STP) g ⁻¹]
a _{s,BET}	1933.7	[m ² g ⁻¹]
C	781.21	
Total pore volume ($p/p_0=0.990$)	0.8682	[cm ³ g ⁻¹]
Average pore diameter	1.7959	[nm]

3.5. Synthesis and BET data for UiO-67-Pt(IV)-OPS

ZrCl₄ (120 mg, 0.517 mmol) and H₂O (12 μ L, 0.67 mmol) were dissolved in 20 mL DMF while stirring. The solution was heated, and benzoic acid (315 mg, 2.59 mmol), H₂bpydc (13 mg, 0.052 mmol), H₂bpdc (113 mg, 0.465 mmol) and K₂PtCl₆ (25 mg, 0.052 mmol) were added. A clear, yellow solution was obtained after a few minutes of stirring. The solution was kept at 95 °C for 4 days. The solution was decanted off, and a yellow crystalline powder was recovered. The powder was then washed 3 times in 15 mL portions of anhydrous DMF and 3 times in 15 mL portions of 2-propanol, before it was dried in air at 60 °C. The product weight was 203 mg, and the solvent fraction was found to be 39 % by thermogravimetric analysis. Thus the dry product weight was estimated to 124 mg and the final yield to 67 % (Yieldmax: 184 mg).

Table S6. Adsorption data for UiO-67-Pt(IV)-OPS.

Starting point	12	
End point	28	
Slope	0.0018131	
Intercept	1.4314 E-06	
Correlation coefficient	1	
V _m	551.11	[cm ³ (STP) g ⁻¹]
a _{s,BET}	2398.7	[m ² g ⁻¹]
C	1267.6	
Total pore volume ($p/p_0=0.990$)	0.9762	[cm ³ g ⁻¹]
Average pore diameter	1.6278	[nm]

3.6. Synthesis and BET data for UiO-67-Pt(II)-PSF

300 mg UiO-67-bpy (approximately 0.050 mmol bpy sites with a solvent loading of 41 %) was suspended in 15 mL anhydrous DMF in a 50 mL Erlenmeyer flask. K₂PtCl₄ (22 mg, 0.053 mmol) was added and dissolved under stirring. The suspension was heated to 100 °C and left overnight. A yellow powder was recovered, washed 3 times in 15 mL portions of 2-propanol and dried in air at 60 °C. The dry powder was weighed and stored in a desiccator. The product weight was 288 mg, and the solvent fraction was found to be 25 % by thermogravimetric analysis. Thus the dry product weight was estimated to 170 mg and the final yield to 96 % (Yieldmax: 177 mg).

Table S7. Adsorption data for UiO-67-Pt(II)-PSF.

Starting point	0	
End point	32	
Slope	0.0020896	
Intercept	0	
Correlation coefficient	0.9985	
V _m	478.56	[cm ³ (STP) g ⁻¹]
a _{s,BET}	2082.9	[m ² g ⁻¹]
C		
Total pore volume($p/p_0=0.990$)	0.865	[cm ³ g ⁻¹]
Average pore diameter	1.6611	[nm]

3.7. Synthesis and BET data for UiO-67-Pt(II)(tdt)-PSF

300 mg UiO-67-Pt(II)-PMLS (approximately 0.050 mmol PtCl₂ sites with a solvent loading of 42 %) was suspended in 15 mL 2-propanol in a 25 mL Erlenmeyer flask. H₂tdt (11 mg, 0.071 mmol) was added and dissolved under stirring. The powder in suspension was kept stirring at 25 °C and, changed color from yellow to blue in two hours, but left overnight to let the reaction go to completion. A blue powder was recovered, washed 3 times in 15 mL portions of 2-propanol and dried in air at 60 °C. The dry powder was weighed and stored in a desiccator. The product weight was 160 mg, and the solvent fraction was found to be 19 % by evacuation. Thus the dry product weight was estimated to 129 mg and the final yield to 65 % (Yield_{max}: 177 mg). This unexpected loss of sample can be due to incomplete recovery of product, e.g. if some crystals are very small.

Table S8. Adsorption data for UiO-67-Pt(IV)(tdt)-PSF

Starting point	21	
End point	34	
Slope	0.0017758	
Intercept	1.0881 E-06	
Correlation coefficient	1	
V _m	562.79	[cm ³ (STP) g ⁻¹]
a _{s,BET}	2449.5	[m ² g ⁻¹]
C	1633.1	
Total pore volume (<i>p</i> / <i>p</i> ₀ =0.990)	1.1065	[cm ³ g ⁻¹]
Average pore diameter	1.8069	[nm]

4. Elemental analysis

In a SEM equipped with EDX detector, suitable single crystals were chosen for elemental analysis. The electron beam was focused stationary on the crystal for 50 seconds. EDX spectra show platinum inside of MOF crystals (Figure S3).

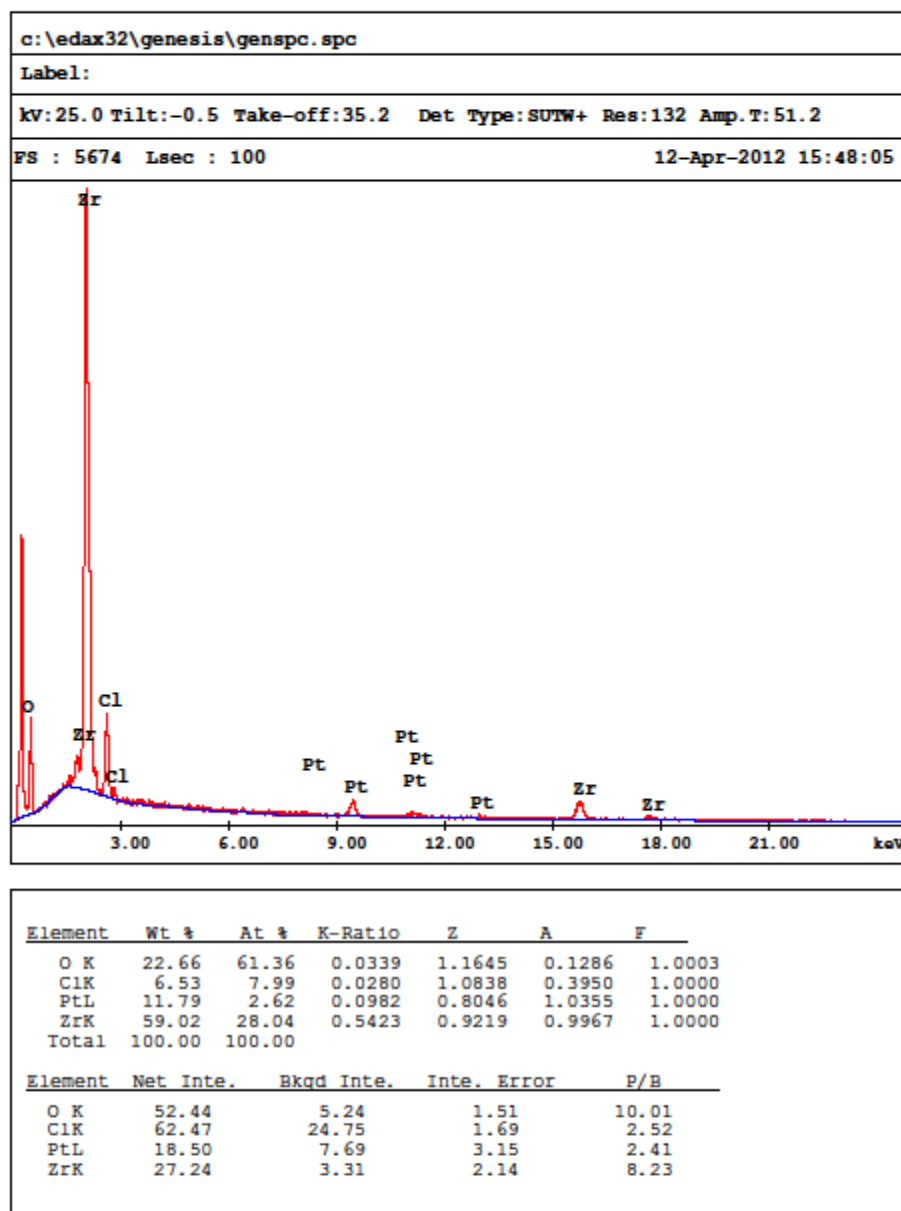


Figure S3. EDX spectrum of a single crystal of UiO-67-Pt(II)-PMLS.

5. SEM analysis

SEM micrographs were acquired for each sample. With the exception of Pt(II)-OPS, all samples consisted of well-defined powders with a defines particle morphology. Only Pt(II)-OPS samples showed no discernible morphology (Figure S4), in agreement with a lower surface area measured by BET.

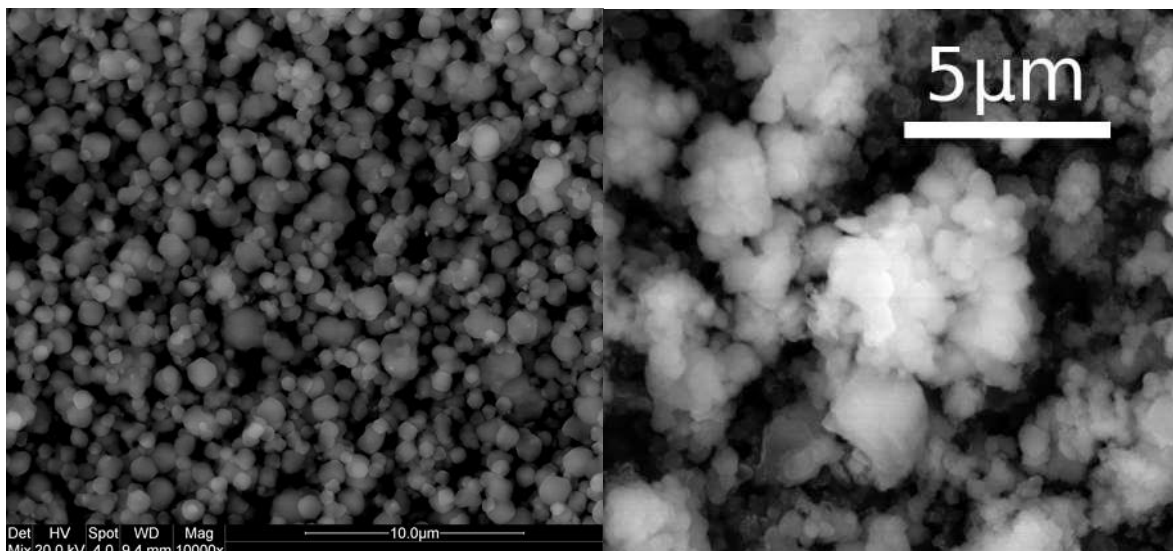


Figure S4. SEM micrographs of UiO-67-Pt(IV)-OPS (left) and UiO-67-Pt(II)-OPS (right).

6. Operando TPR-EXAFS experiment on UiO-67-Pt(II)-OPS

In the limited amount available before the end of our beamtime at I811 of the MAX-II storage ring in Lund we run a last operando TPR-EXAFS experiment on UiO-67-Pt(II)-OPS sample, at an higher heating gradient (of 10 K min^{-1} , with respect to 3 K min^{-1} used in the other experiments, see Figure 6 of the main text). Formally, for the UiO-67-Pt(II)_OPS material (Figure S5), no quantitative conclusions can be obtained. The fact that we have been forced to perform the EXAFS-TPR experiment with a gradient of 10 K min^{-1} , to reach the temperatures of interest before the beam shutdown implied that only 7 XAS spectra have been collected. However, on a qualitative ground the same conclusions can be reached: Pt–Cl bonds break before Pt–N bonds, at the end of the treatment most of the Pt species are still linked to the MOF framework. The Einstein temperatures $\Theta_E(\text{Pt–N})$ and $\Theta_E(\text{Pt–Cl})$ obtained from the parametric refinement described in Section 2.5.2, see Eq. (1) in the main text are compatible with those determined in the other cases, although determined with a much higher errors (more than twice than in the other cases).

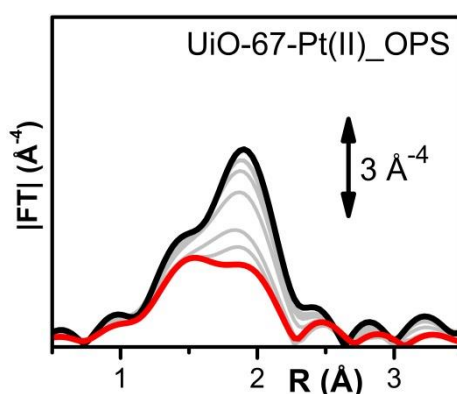


Figure S5. k^3 -weighted, phase uncorrected, FT of Pt L_3 -edge EXAFS spectra collected during the operando TPR experiments on UiO-67-Pt(II)_OPS. The experiment were performed adopting a temperature gradient of 10 K min^{-1}

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