IRIS AperTO

UNIVERSITÀ DEGLI STUDI DI TORINO

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

Probing reactive platinum sites in uio-67 zirconium metal-organic frameworks

This is the author's manuscript

Original Citation:

Availability:

This version is available http://hdl.handle.net/2318/1534311 since 2017-11-13T17:48:01Z

Published version:

DOI:10.1021/cm504362j

Terms of use:

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)

28 April 2024

Supporting information for

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

Sigurd Øien,[1] Giovanni Agostini,[2,3] Stian Svelle,[1] Elisa Borfecchia,[2] Kirill A. Lomachenko,[2,4] Lorenzo Mino,[2] Erik Gallo,[2,3] Silvia Bordiga,[2] Unni Olsbye,[1] Karl Petter Lillerud,[1,*] Carlo Lamberti[4,5,*]

[1] inGAP Centre for Research Based Innovation, Department of Chemistry, University of Oslo, P.O. Box 1033, N-0315 Oslo, Norway.
[2] Department of Chemistry, NIS and INSTM Reference Centers, University of Torino, Via Quarello 15, I-10135, Torino, Italy.
[3] European Synchrotron Radiation Facility (ESRF), 6 Rue Jules Horowitz, BP 220 38043, Grenoble Cedex 9, France.
[4] Southern Federal University, Zorge Street 5, 344090 Rostov-on-Don, Russia.
[5] Department of Chemistry, CrisDi Centre for crystallography, University of Torino, Via Giuria 7, I-10125 Torino, Italy.

Content

[*] Corresponding authors: C. Lamberti Tel: +39011-6707841 Fax: +39011-6707855; e-mail: carlo.lamberti@unito.it
K.-P Lillerud: Tel: +4722855457; e-mail: k.p.lillerud@kjemi.uio.no

2. Linker synthesis

1.1. Synthesis of H_2bpydc

H_2bpydc was prepared following the literature method reported by Constable[1] 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: ^{1}H NMR (300 MHz, DMSO-d6) 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. ^{1}H NMR (300 MHz, DMSO-d6) 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. H2bpydc (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 H2bpydc. $PtCl_4(H_2bpydc)$, pale yellow solid. ^{1}H NMR (300 MHz, DMSO-d6) 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, e 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 ^{1}H NMRspectra are shown in Figure S1. $PtBr_2(H_2bpydc)$, orange solid.^{1}H 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. ^{1}H 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).

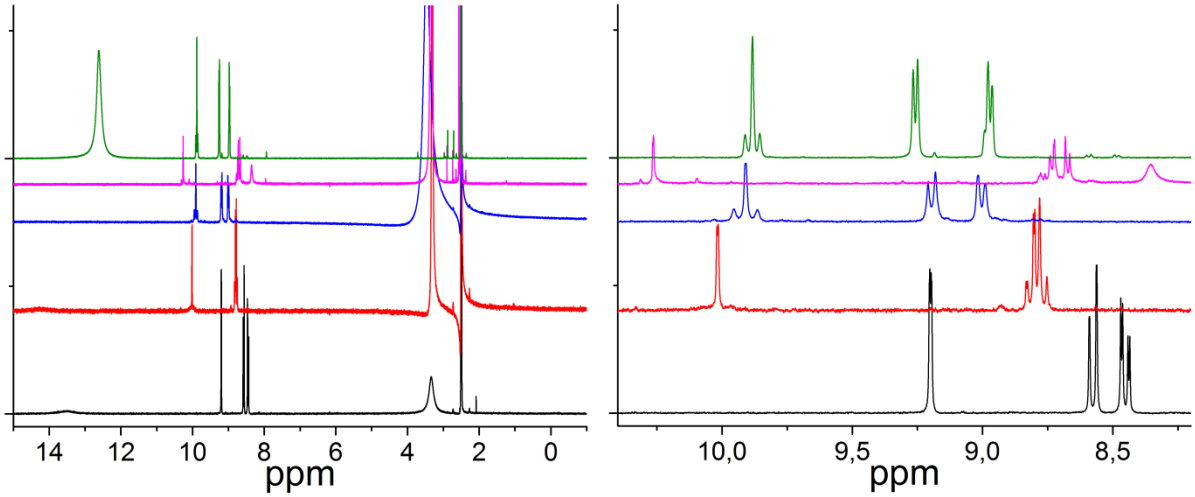


Figure S1. ^{1}H NMR spectra of (from the top) $PtBr_4(H_2bpydc)$, $PtBr_2(H_2bpydc)$ $PtCl_4(H_2bpydc)$, $PtCl_2(H_2bpydc)$ and H_2bpydc. $PtBr_4(H_2bpydc)$ (green) was made in situ and contains a lot of HBr (12.6 ppm, s) due to the reaction between Br_2 and water, and some DMF. $PtBr_2(H_2bpydc)$ has 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 $PtCl_2(H_2bpydc)$ (yellow prisms) and $PtBr_2(H_2bpydc)$ (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 $PtBr_4(H_2bpydc)$ (orange plates) were grown from a solution of $PtCl_2(H_2bpydc)$ in DMSO to which a drop of Br_2 was added. Crystals of Pt(tdt)(H_2bpydc) (dark blue-green prisms) were grown from a DMF solution of $PtCl_2(H_2bpydc)$ 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.

	$PtCl_2(H_2bpydc)$	**$PtBr_2(H_2bpydc)$**	**$PtBr_4(H_2bpydc)$**	**Pt(tdt)(H_2bpydc)**
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	C2/c
Cell dimensions				
a (Å) *b* (Å) *c* (Å)	17.3214(11) 7.2698(4) 17.6866(10)	15.4705(8) 7.6230(4) 17.7505(9)	12.4323(4) 13.2777(4) 23.5825(8)	21.3954(11) 17.3795(8) 14.3340(6)
α (°) β (°) γ (°)	90 105.259(2) 90	90 114.0660(10) 90	94.6600(12) 96.4670(12) 103.3430(12)	90 92.3600(14) 90
Crystal sizes (mm)	0.23 x 0.12 x 0.07	0.28 x 0.10 x 0.03	0.26 x 0.23 x 0.02	0.15 x 0.10 x 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 Kα	Mo Kα	Mo Kα	Mo Kα
Reflections/parameters/restraints	5326/291/0	5144/312/0	22821/856/0	4796/356/0
R_1 & $wR_{2\ [I>2sigma]}$	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.

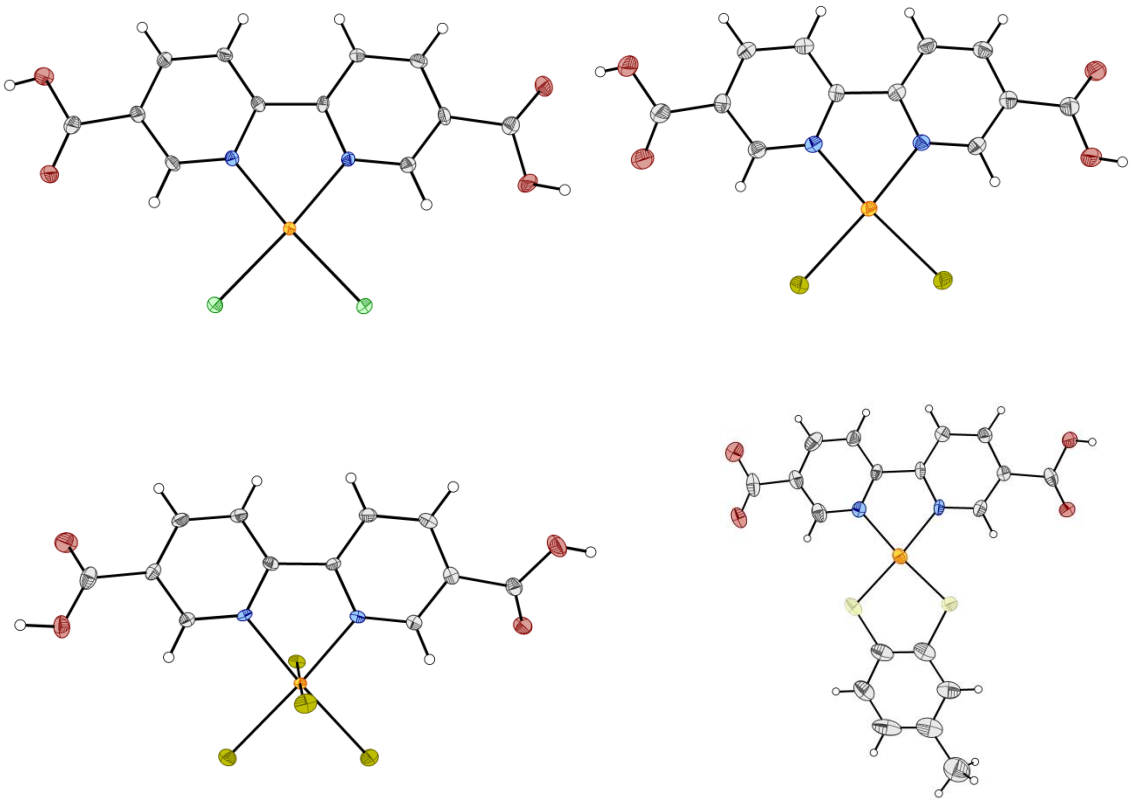


Figure S2. Structural models of $PtCl_2(H_2bpydc)$ (top left), $PtBr_2(H_2bpydc)$ (top right), $PtBr_4(H_2bpydc)$ (bottom left) and $Pt(tdt)(H_2bpydc)$ (bottom right).

3. MOF synthesis and sorption measurements

The UiO-67 materials were synthesized by reacting $ZrCl_4$ with a mixture of H_2bpdc and (H_2bpydc)/$PtCl_x(H_2bpydc)$; 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)

$ZrCl_4$ (602 mg, 2.58 mmol) and H_2O (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 H_2bpdc (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	
Slore	0,001932	
Intercept	9,2408E-07	
Correlation coefficient	1	
Vm	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

$ZrCl_4$ (602 mg, 2.58 mmol) and H_2O (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), H_2bpdc (563 mg, 2.33 mmol) and $PtCl_2$(H_2bpydc) (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	
Slore	0.0019559	
Intercept	2.6652 E-06	
Correlation coefficient	1	
Vm	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

$ZrCl_4$ (602 mg, 2.58 mmol) and H_2O (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), H_2bpdc (563 mg, 2.33 mmol) and K_2PtCl4 (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	
Slore	0.0028916	
Intercept	2.0903 E-06	
Correlation coefficient	1	
Vm	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

$ZrCl_4$ (602 mg, 2.58 mmol) and H_2O (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), H_2bpdc (563 mg, 2.33 mmol) and PtCl4(H_2bpydc) (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	
Slore	0.002248	
Intercept	2.8812 E-06	
Correlation coefficient	0.9999	
Vm	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

$ZrCl_4$ (120 mg, 0.517 mmol) and H_2O (12 µL, 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), H_2bpdc (113 mg, 0.465 mmol) and K_2PtCl6 (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	
Slore	0.0018131	
Intercept	1.4314 E-06	
Correlation coefficient	1	
Vm	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. K_2PtCl_4 (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	
Slore	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

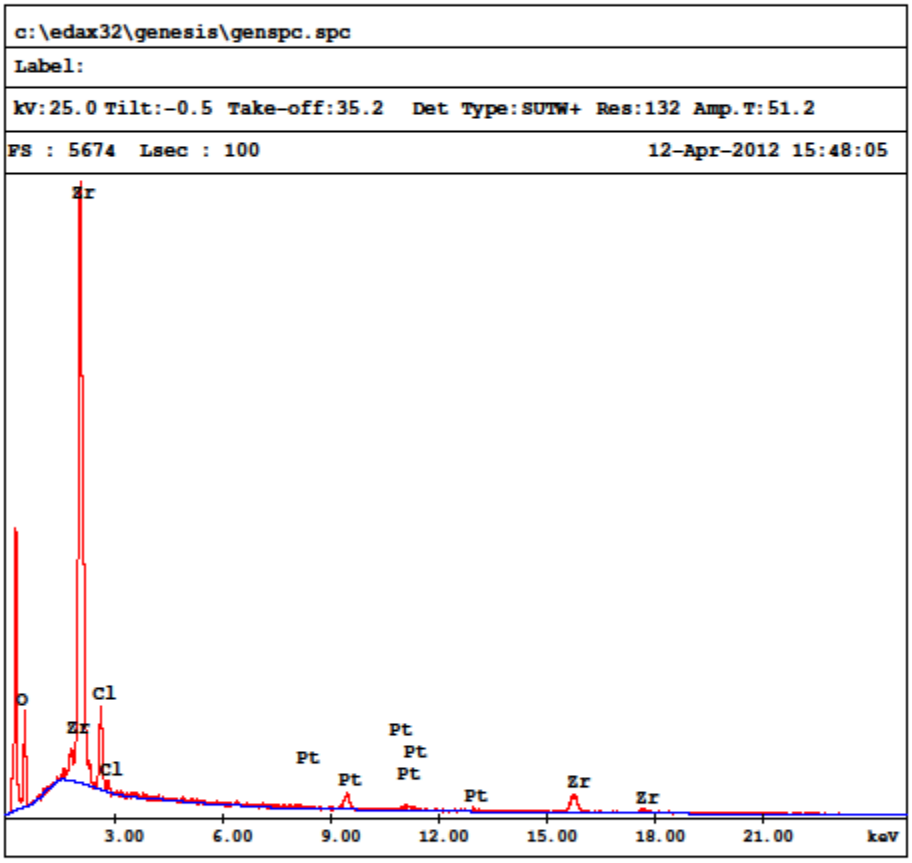
300 mg UiO-67-Pt(II)-PMLS (approximately 0.050 mmol $PtCl_2$ sites with a solvent loading of 42 %) was suspended in 15 mL 2-propanol in a 25 mL Erlenmeyer flask. H_2tdt (11 mg, 0.071 mmol) was added and dissolved under stirring. The powder in suspension was kept stirring at 25 °C and, changed color from 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(IiV)(tdt)-PSF

Starting point	21	
End point	34	
Slore	0.0017758	
Intercept	1.0881 E-06	
Correlation coefficient	1	
Vm	562.79	[cm^3(STP) g^{-1}]
$a_{s,BET}$	2449.5	[m^2 g^{-1}]
C	1633.1	
Total pore volume (p/p_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).



Element	Wt %	At %	K-Ratio	Z	A	F
O K	22.66	61.36	0.0339	1.1645	0.1286	1.0003
ClK	6.53	7.99	0.0280	1.0838	0.3950	1.0000
PtL	11.79	2.62	0.0982	0.8046	1.0355	1.0000
ZrK	59.02	28.04	0.5423	0.9219	0.9967	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
O K	52.44	5.24	1.51	10.01
ClK	62.47	24.75	1.69	2.52
PtL	18.50	7.69	3.15	2.41
ZrK	27.24	3.31	2.14	8.23

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.

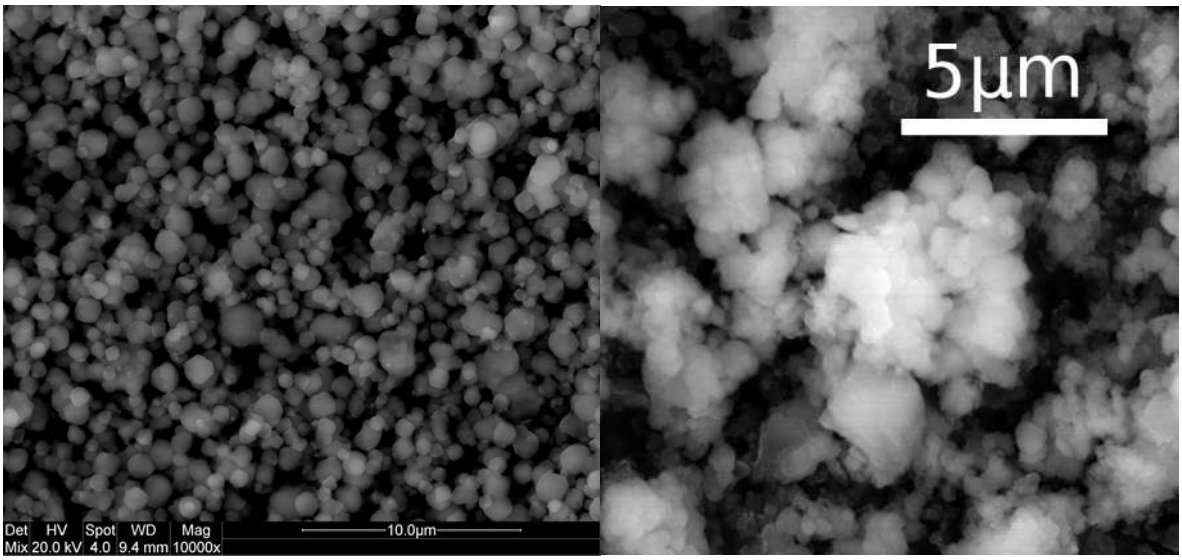


Figure S4. SEM micrographs of UiO-67-Pt(IV)-OPS (left) and UiO-67-Pt(II)-OPS (right).

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}, withe respect to 3 K min^{-1} used in he other experiments, see Figure 6 of the manin 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 breaks before Pt–N bonds, at at the end of the treatment most of the Pt species are still linked to the MOF framework. The Einstein temperatures Θ_E(Pt–N) and Θ_E(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).

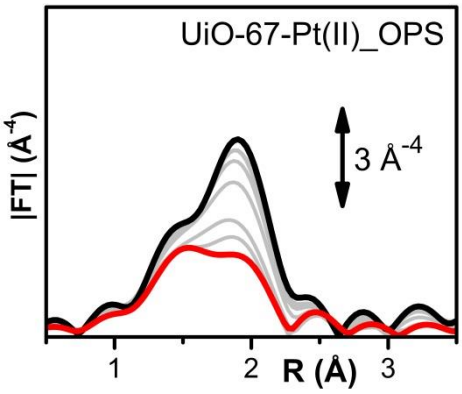


Figure S5. k^3-weighted, phase uncorrected, FT of Pt L_3-edge EXAFS spectra collected during the operando TPR experiments on UiO-67-Pt(II)_OPS. The experiment were performed adopting a temperature gradient of 10 K min^{-1}

References and Notes

1. Constable, E. C., *Adv. Inorg. Chem.* **1989,** *34*, 1-63.
2. Spingler, B.; Schnidrig, S.; Todorova, T.; Wild, F., *Crystengcomm* **2012,** *14*, 751-757.
3. Sheldrick, G. M., *Acta Crystallogr. Sect. A* **2008,** *64*, 112-122.
4. Hubschle, C. B.; Sheldrick, G. M.; Dittrich, B., *J. Appl. Crystallogr*. **2011,** *44*, 1281-1284.
5. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., *J. Appl. Crystallogr*. **2009,** *42*, 339-341.
6. Westrip, S. P., *J. Appl. Crystallogr.* **2010,** *43*, 920-925.
7. Allen, F. H.; Johnson, O.; Shields, G. P.; Smith, B. R.; Towler, M., *J. Appl. Crystallogr*. **2004,** *37*, 335-338.
8. Walton, K. S.; Snurr, R. Q., *J. Am. Chem. Soc.* **2007,** *129*, 8552-8556.