This is the published version of a paper published in *Chemistry - A European Journal*.

Citation for the original published paper (version of record):

The First One-Pot Synthesis of Metal-Organic Frameworks Functionalised with Two Transition-Metal Complexes.
*Chemistry - A European Journal*, 21(2): 861-866
https://doi.org/10.1002/chem.201403909

Access to the published version may require subscription.

N.B. When citing this work, cite the original published paper.


Permanent link to this version:
http://urn.kb.se/resolve?urn=urn:nbn:se:diva-113542
Metal–Organic Frameworks

The First One-Pot Synthesis of Metal–Organic Frameworks Functionalised with Two Transition-Metal Complexes

Ana E. Platero-Prats,[a, b, c] Antonio Bermejo Gómez,[a, b] Louise Samain,[c] Xiaodong Zou,[a, c] and Belén Martín-Matute*[a, b]

Abstract: The synthesis of a metal–organic framework (UiO-67) functionalised simultaneously with two different transition metal complexes (Ir and Pd or Rh) through a one-pot procedure is reported for the first time. This has been achieved by an iterative modification of the synthesis parameters combined with characterisation of the resulting materials using different techniques, including X-ray absorption spectroscopy (XAS). The method also allows the first synthesis of UiO-67 with a very wide range of loadings (from 4 to 43 mol%) of an iridium complex ([IrCp*(bpydc)(Cl)Cl]22+; bpydc = 2,2'-bipyridine-5,5'-dicarboxylate, Cp* = pentamethylcyclopentadienyl) through a pre-functionalisation methodology.

Introduction

Metal–organic frameworks (MOFs) are modular and crystalline materials[1] amenable to chemical modification[2] that can be used in a wide range of applications.[3] When the intrinsic properties of MOFs are combined with those of transition metal complexes,[4] crystalline materials with multiple potential uses, including catalysis, are created. MOFs were originally functionalised by introducing organic fragments into their linkers.[5] Recently, a multivariate (MTV) functionalisation was reported, through which a large number of diverse linkers bearing different organic functional groups were incorporated into MOF-5.[6] Another versatile approach is the linker-exchange method, for example, post-synthetic exchange (PSE) and solvent-assisted linker exchange (SALE).[7]

MOFs can be functionalised with transition metal complexes through post- or pre-functionalisation strategies. Examples of post-functionalisation include metal impregnations and metallo-linkers with matching length and connectivity was incorporated into the same MOF.[10] Cohen, Ott, and co-workers have recently reported similar results using the PSE protocol.[11]

Despite great efforts, the synthesis of transition-metal-functionalised MOFs still presents a challenge. This is partly due to decomposition of transition metal complexes under the reaction conditions needed for MOF synthesis. The controlled synthesis of these materials functionalised with a wide range of loadings of a transition metal or with more than one transition metal complex is difficult but desirable. Furthermore, little is known about how functionalisation may change the structure of MOFs. Herein, we report the first one-pot synthesis of MOFs functionalised with one or simultaneously two transition metal complexes from their basic components (i.e., transition metal precursors, linkers, and structural metal salts) (Figure 1). The method is exemplified with the ZrIV MOF UiO-67[12] and transition metal complexes LM1 = [IrCp*(bpydc)(Cl)Cl]22+, LM2 = [Pd(bpydc)Cl]22+, and LM3 = [RhCp*(bpydc)(Cl)Cl]22+ (L = bpydc = 2,2'-bipyridine-5,5'-dicarboxylate).[13]

Results and Discussion

The molecular formula of UiO-67 is [Zr6O4(OH)4(bpdc)6], with six unique linkers (bpdc = 4,4'-biphenyldicarboxylate) per octahedral (O6) cavity. Functionalised analogues can then be defined as [Zr6O4(OH)4(bpdc)6–(LM1)y], in which y is the number of metallo-linkers (LM1) per O6 cavity (Figure 2). As an example, 33 mol% functionalisation would be represented by y = 2 (Figure 2). The parameter y is then defined as the intended number of metallo-linkers per O6 cavity (see the Experimental
linkers are represented as black rods and the bpydc = carboxylate linkers as black rods with white dots. (from Zr IV salts, H₂bpdc, and H₂Chem. Eur. J. 2015 LM1 rarameters in the preparation of UiO-67 functionalised with Section). First, we evaluated the effect of several synthetic parameters in the preparation of UiO-67 functionalised with LM1 (from Zr²⁺ salts, H₄bpdc, and H₄LM1) with the aim of obtaining materials with a wide range of iridium loadings. We found that the crystallinity of UiO-67 functionalised with LM1 (y = 1) is highly dependent on the amount of water used in the synthesis. By varying the number of equivalents of water (from 3 to 150 equiv per ZrCl₄), we found that 5 equiv gave crystalline samples (Figure 3 and Table 1, entry 2; y = 0.36; Supporting Information). Water was needed to form the Zr cluster. Although 1.3 equiv per Zr would be theoretically sufficient (in agreement with the molecular formula \(\left[\text{Zr}_6\text{O}_4\text{(OH)}_4\right]\left(\text{bpdc}\right)\text{(LM1)}\)), a slight excess of H₂O was needed to obtain good reproducibility. The use of ZrOCl₂ instead of ZrCl₄ resulted in poorer crystallinity (see the Supporting Information). In addition, decomposition of the iridium complex was observed when different additives (e.g., formic acid or potassium carbonate) were used. To obtain a methodology that would allow higher iridium loadings, different LM1 concentrations and synthesis temperatures (100 °C, Method A; 140 °C, Method B) were then tested. In all cases (Table 1, entries 1–8), crystalline materials were obtained (Figure 4). ICP-AES showed that the iridium contents were systematically lower at higher temperatures (Table 1, entries 1–4 vs. 5–8). The amount of LM1 was determined by analysing the samples by ¹H NMR spectroscopy after digestion under optimized conditions (i.e., \(\text{D}_2\text{DMSO/DOPO}_{4}\)), see the Supporting Inf-

![Figure 1](image1.png)  
**Figure 1.** One-pot synthesis of UiO-67 functionalised with a) one metal complex or b) simultaneously multifunctionalised with two. The grey spheres correspond to different metal complexes. The bpdc = 4,4'-biphenyl dicarboxylate linkers are represented as black rods and the bpdc = 2,2'-bipyridine-5,5'-dicarboxylate linkers as black rods with white dots.

![Figure 2](image2.png)  
**Figure 2.** The UiO-67 composition is described as \(\left[\text{Zr}_6\text{O}_4\text{(OH)}_4\right]\text{(bpdc)}\text{(LM1)}\text{(bpdc)}\). Among the six linkers (L) are (6 – x) bpdc linkers, (x – y) demetalled LM1 linkers (i.e., bpdcy), and y functionalised metalo-linkers LMMy (m = 1 – 3, 1 = Ir, 2 = Pd, 3 = Rh). The composition of the Oₓ cavity in UiO-67 is \(\left[\text{Zr}_{6-3m}\text{O}_{12-3m}\text{(OH)}_{4-3m}\right]\text{(LM1)}\text{(bpdcy)}\). Each linker is shared by two Oₓ cavities and the number of metalo-linkers per Oₓ cavity is represented by y.

![Figure 3](image3.png)  
**Figure 3.** Linker composition per Oₓ cavity.

<table>
<thead>
<tr>
<th>Sample (Method)</th>
<th>Ir²⁺</th>
<th>bpydc⁰²</th>
<th>LM1/wt %</th>
<th>Isolated yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 a (A)</td>
<td>5.53</td>
<td>0.33</td>
<td>0.14</td>
<td>12.2 %</td>
</tr>
<tr>
<td>2 a (A)</td>
<td>5.08</td>
<td>0.56</td>
<td>0.36</td>
<td>6.4 %</td>
</tr>
<tr>
<td>3 a (A)</td>
<td>4.24</td>
<td>0.95</td>
<td>0.81</td>
<td>8.5 %</td>
</tr>
<tr>
<td>4 a (A)</td>
<td>2.41</td>
<td>1.34</td>
<td>2.25</td>
<td>16.8 %</td>
</tr>
<tr>
<td>5 b (B)</td>
<td>5.50</td>
<td>0.50</td>
<td>0</td>
<td>0.22 %</td>
</tr>
<tr>
<td>6 b (B)</td>
<td>5.51</td>
<td>0.85</td>
<td>0</td>
<td>0.51 %</td>
</tr>
<tr>
<td>7 b (B)</td>
<td>4.41</td>
<td>1.59</td>
<td>0</td>
<td>1.74 %</td>
</tr>
<tr>
<td>8 b (B)</td>
<td>3.64</td>
<td>2.36</td>
<td>0</td>
<td>5.81 %</td>
</tr>
<tr>
<td>9 c (C)</td>
<td>5.50</td>
<td>0.25</td>
<td>0.25</td>
<td>1.00 %</td>
</tr>
<tr>
<td>10 c (C)</td>
<td>5.22</td>
<td>0.39</td>
<td>0.39</td>
<td>1.00 %</td>
</tr>
<tr>
<td>11 c (C)</td>
<td>4.49</td>
<td>0.72</td>
<td>0.79</td>
<td>1.10 %</td>
</tr>
<tr>
<td>12 c (C)</td>
<td>2.34</td>
<td>1.09</td>
<td>2.57</td>
<td>2.36 %</td>
</tr>
<tr>
<td>LM1 ≡ (</td>
<td>\text{Ir}^+\text{(bpdc)}\text{(Cl)}</td>
<td>) ≡ (</td>
<td>\text{Ir}^+\text{(bpdc)}\text{(Cl)}</td>
<td>)</td>
</tr>
</tbody>
</table>

[a] Method A: 100 °C, Teflon autoclave reactors using dry DMF as the solvent and 5 equiv of H₂O. Method B: 140 °C, Teflon autoclave reactors using dry DMF as the solvent and 5 equiv of H₂O. Method C: 100 °C, sealed microwave tube in an oil bath with stirring using dry DMF as the solvent and 5 equiv of H₂O. [b] Intended LM1 amounts (y') for samples 1a–1c, 2a–2c, 3a–3c, and 4a–4c were 0.5, 1, 2, and 4, respectively. [c] Determined by ¹H NMR spectroscopic analysis of the digested samples. [d] Number of metalo-linkers (LM1) per Oₓ cavity (y). [e] The value LM1/bpydc was consistent for different batches. [f] Determined by ICP-AES analysis.

Table 1. LM1 and bpydc contents determined by ¹H NMR spectroscopy for MOFs synthesised using Methods A, B, and C, in terms of degree of functionalisation per Oₓ cavity (y).
formation). Surprisingly, H₂bpydc was found in all digested samples. Free bpydc was formed by demetallation of LM1 during the synthesis of the MOFs, lowering the iridium metal-lo-linker content in the products (Table 1).\[14\] Furthermore, although samples 1b–4b contained iridium (as confirmed by ICP-AES), no LM1 was found in the digested samples by ¹H NMR spectroscopy (Table 1, entries 5–8). Iridium is thus not present as Ir III coordinated to bpydc but as other species, which was further confirmed by XAS (see below).

Next, we explored the effect of stirring during the synthesis of the MOF, with the aim of decreasing demetallation of LM1 and increasing the yield. The reaction mixtures were stirred in sealed vials and heated in an oil bath at 100 °C (Method C).

Stirring resulted in a more homogeneous reaction mixture, preventing both high local concentrations of acidic species (e.g., HCl) and local overheating,\[20\] which may have resulted in reduced demetallation. Indeed, ¹H NMR spectroscopic analysis after digestion of the samples showed that 1c–4c had undergone significantly lower demetallation compared to the products obtained without stirring at the same temperature (1a–4a) and, importantly, their crystallinity was not affected. The LM1/bpydc ratios were 1.00, 1.00, 1.10, and 2.36 for 1c–4c (Table 1, entries 9–12; Supporting Information), compared to 0.42, 0.64, 0.85, and 1.68 for 1a–4a (Table 1, entries 1–4). This represents increases in the LM1/bpydc ratio by 138, 56, 29, and 40%, respectively. Furthermore, not only was the degree of functionalisation better controlled, but the yields were considerably higher (by 10–30%). PXRD showed that Methods A and C gave UiO-67 materials with good crystallinity and a wide degree of functionalisation (y = 0–2.25) (Figure 4; Supporting Information). Interestingly, synthesis with stirring (1c–3c) led to sharper PXRD peaks than without stirring, although significant peak broadening was observed for the highest functionalisation (4c, y = 2.57). This could be explained by the formation of defects in the crystal structure of the MOF (e.g., domains).

The local environment and oxidation state of iridium was investigated by XAS. Figure 5 a shows the iridium L₃-edge X-ray absorption near-edge structure (XANES), which confirms incorporation of LM1 in MOFs 3a and 4a (3a, y = 0.81; 4a, y = 2.25) and MOFs 3c and 4c (3c, y = 0.79; 4c, y = 2.57). The extended
X-ray absorption fine structure (EXAFS) data for H₂LM1 were fitted using the structure model determined by single-crystal X-ray diffraction (see the Supporting Information). EXAFS analyses on 3a, 4a, 3c, and 4c confirmed incorporation of iridium exclusively in the form of LM1 (Figure 5b). In contrast, XANES and EXAFS spectra of 4b showed the presence of IrO₂ as the major phase, as well as other iridium species such as IrCl₃ (see the Supporting Information).

PXRD data of the samples prepared by Method C (1c–1d, 3c) revealed a framework contraction upon functionalisation, which correlated well with the degree of functionalisation y (Figure 5c and Table S6.3.1). A minor cell contraction (≤0.2%) occurred in samples with low LM1 contents (low y values) (1c–3c, y < 0.8), whereas a significant cell contraction (2.1%) was observed for the highest degree of functionalisation with the iridium metallo-linker (4c, y = 2.57), as given in Table S6.3.1. This framework contraction can be explained by: (i) the different lengths of the bpdc, bpydc, and LM1 linkers, and (ii) the presence of intermolecular interactions among the LM1 subunits within the MOF (C–H···π and C–H···O, see the Supporting Information).

Attenuated total reflection Fourier-transform infrared (ATR/FTIR) spectra of solid samples were collected for UiO-67, H₂LM1, and MOFs 1c–4c, as well as for a physical mixture of UiO-67 and H₂LM1. The aromatic C–H stretching band of the iridium metallo-linker shifted from 810 (H₂1c) to 795 cm⁻¹ in the functionalised MOFs. This can be attributed to the different electronic environment of LM1 when coordinated to the zirconium clusters in the MOF (Figure 5d). Additionally, thermal gravimetric analysis (TGA) confirmed that LM1 has a different thermal decomposition profile when incorporated into MOFs 1c–4c (see the Supporting Information). N₂ adsorption measurements confirmed that MOFs 1c–4c remained porous despite functionalisation with LM1.

Having demonstrated the beneficial effect of adding 5 equiv of water and synthesising the iridium-functionalised MOFs under stirring at 100 °C, we then attempted their synthesis by a one-pot procedure starting from the basic components (Method D, Figure 6, Table 2). The synthesis starting from commercially available [Ir(Cp*)Cl₂]₂ and H₂bpdc was successfully accomplished (see the Experimental Section) and afforded MOF 1d (Table 2, entry 1, y = 0.36) with higher crystallinity than when Method C was used, and in excellent isolated yield (74%). This procedure is much simpler and more cost-effective, since isolation of the metallo-linker is no longer needed. The framework composition was determined as [Zr₆O₄(OH)₄(bpdc)₅.28(bpydc)₀.36] (Table 2, entry 1), similar to that of the MOF synthesised by Method C [Zr₆O₄(OH)₄(bpdc)₃.18(bpydc)₀.36] (Table 1, entry 10).

Taking advantage of this successful methodology, we applied the sequential one-pot route to synthesise for the first time MOFs functionalised simultaneously with two transition metal complexes, LM₁ + LM₂ (2d, Ir + Pd) (Table 2, entry 2), and LM₁ + LM₃ (3d, Ir + Rh) (Table 2, entry 3). Using the commercially available metal precursors [Ir(Cp*Cl)₂], PdCl₂, and [Rh(CpCl₂)₂] (Table 2), crystalline dual-functionalised materials were obtained in excellent yields (2d, 84%; 3d, 71%). The compositions were determined after digestion as [Zr₆O₄(OH)₄(bpdc)₅.18(bpydc)₀.13] for 2d and [Zr₆O₄(OH)₄(bpdc)₄.4(bpydc)₀.33] for 3d (Table 2). ATR/FTIR and TGA data confirmed coordination of the metallo-linkers to the zirconium clusters in MOFs 1d–3d, and the BET surface areas of these materials indicated good porosity (see the Supporting Information).

**Conclusion**

In conclusion, we have presented here the first one-pot synthesis of a metal–organic framework (UiO-67) pre-functionalised with one or simultaneously two transition metal complexes. This efficient methodology uses commercially available metal precursors ([Ir(Cp*Cl)₂], PdCl₂, and [Rh(CpCl₂)₂]), and requires neither isolation nor purification of the metallo-linkers, resulting in shorter synthesis times and lower costs. This has been achieved by evaluating how the experimental parameters

---

**Table 2. Sequential one-pot synthesis and characterisation of MOFs functionalised simultaneously with one or two transition metal complexes.**

<table>
<thead>
<tr>
<th>Sample (Method D)</th>
<th>bpdc</th>
<th>bpydc</th>
<th>LMM⁺[Ir]</th>
<th>Isolated yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1d</td>
<td>5.28</td>
<td>0.36</td>
<td>0.36LM₁</td>
<td>74</td>
</tr>
<tr>
<td>2d</td>
<td>5.29</td>
<td>0.12</td>
<td>0.19LM₁ + 0.40LM₂</td>
<td>84</td>
</tr>
<tr>
<td>3d</td>
<td>4.86</td>
<td>0.34</td>
<td>0.44LM₁ + 0.36LM₃</td>
<td>71</td>
</tr>
</tbody>
</table>

[a] Method D, sequential one-pot synthesis: 1) dry DMF, rt, 24 h; 2) 5 equiv of H₂O, 100 °C, 40 h. (b) Determined by 1H NMR spectroscopic analysis of the digested samples. (c) Number of metallo-linkers (LMM⁺) per O₈ cavity (y).
(water content, temperature, and stirring) influence the MOF synthesis by means of complementary characterisation techniques (PXRD, $^1$H NMR, ICP-AES, XAS, TGA, and ATR/FTIR). Additionally, the optimised procedure allows the synthesis of UIO-67 containing an unprecedentedly wide range of iridium loadings (4–43 mol%). This study has also shown that demetallated linkers are part of the MOF structure, and that a framework contraction occurs upon functionalisation.

On the basis of the presented advantages, this sequential one-pot methodology is expected to be broadly applicable for the synthesis of new MOFs functionalised with different transition metal complexes.

Experimental Section

Synthesis of multi-functionalised UIO-67 MOFs

Synthesis of UIO-67 functionalised with LM1 (Method C): ZrCl$_4$ (46.6 mg, 0.2 mmol, 1 equiv), H$_2$LM1 (2 mmol), and H$_2$bpdc (0.2–2 mmol) were placed in a vial, dry DMF (9 mL) and water (18 mL, 1 mmol, 5 equiv) were added, and the vial was sealed. The mixture was stirred at room temperature for 10 min, and then it was heated with stirring at 100 °C in an oil bath for 72 h. The reaction mixture was then allowed to cool down to room temperature. The solid was separated by centrifugation, activated by washing sequentially with DMF (15 mL), MeOH (15 mL), water (15 mL), and acetone (15 mL), and dried at 80 °C in vacuum (0.1 mmHg) for 10 h. Note: the value z is y expressed in mmol for a reaction carried out on a 0.2 mmol scale.

One-pot synthesis (Method D): The transition metal complex precursor(s) (0.033 mmol) and H$_2$bpdc (0.033 mmol) were placed in a microwave tube, dry DMF (9 mL) was added, and the tube was sealed. The mixture was stirred at rt for 24 h. ZrCl$_4$ (0.2 mmol, 1 equiv), H$_2$bpdc (0.167 mmol), and water (1 mmol, 5 equiv) were then added. The mixture was first stirred at room temperature for 10 min, and then heated under stirring at 100 °C in an oil bath for 72 h. After cooling, the solid was separated by centrifugation, washed sequentially with DMF (15 mL), MeOH (15 mL), water (15 mL), and acetone (15 mL), and dried at 80 °C in vacuum (0.1 mmHg) for 10 h.

Digestion and subsequent molecular analysis of the functionalised MOFs by $^1$H NMR spectroscopy: Samples were suspended in a 0.1 M solution of D$_2$PO$_4$ in D$_2$O/[D$_6$]DMSO and stirred at room temperature for 5 h to allow digestion of the MOFs. The solution was then transferred to an NMR tube. $^1$H NMR spectra were recorded at 500 MHz on a Bruker Avance spectrometer using a BBO S2 probe, 5 mm; with a z-gradient (BBO=broadband observe). In order to minimise the error, the parameters of the acquisition were as follows: number of scans (NS): 200, relaxation delay (D1): 5 s.

X-ray absorption spectroscopy: I$_\alpha$-edge XAS experiments were carried out at the I811 beamline, MAX IV Laboratory, Lund. The spectra were recorded in fluorescence mode because of the relatively low concentrations of I$_\alpha$ in the samples. Data processing and analysis were performed with the Athena and Artemis software package using IFEFFIT.[15,16] The background was removed using the AUTOBK and flattening algorithm implemented in Athena. The pre-edge background was linearly subtracted from 150 to 30 eV below the edge and a three-term polynomial function was used for the post-edge background subtraction over the range 150 to 900 eV above the edge. The frequency cut-off between the background and the data set was set at 1.2 Å. The pre-edge background-subtracted spectra were normalised to the edge jump, E0, which was taken as the energy of the first inflection point on the edge, that is, the first maximum in the derivative of the absorption. The EXAFS reduced data $\chi(k)$ were Fourier-transformed into R-space over the range 2–12 Å$^{-1}$ with a $k^2$ weighting factor and a Hanning window, where the window sill was set at 3 Å$^{-1}$. The EXAFS function ($\gamma(k)$) was then fitted to the ab initio multiple scattering XAS code FEFF in R-space.[17,18] The phase shifts and back-scattering amplitudes were obtained from FEFF6.0 calculations on the structure of metallo-linker H$_2$LM1 determined by single-crystal X-ray diffraction analysis. Detailed descriptions of the XAS analyses are given in the Supporting Information.

Powder X-ray diffraction: Powder X-ray diffraction (PXRD) was performed on a Panalytical X′Pert PRO diffractometer in Bragg–Brentano reflection geometry using Cu$_{\text{Kα}}$ radiation ($\lambda = 1.5418$ Å) at a power of 1800 W (45 kV, 40 mA). The PXRD data were collected using a silicon-based position-sensitive X′Celerator detector and programmed divergence and anti-scattering slits. Samples were suspended in 2-propanol and placed in zero-background sample holders. Optimised counting statistics were obtained by collecting data from the samples using a 0.017° 20 step scan from 5–35° with an exposure time of 100 s per step. All measurements were performed at room temperature and ambient pressure. Full-pattern profile-matching using the Pawley method[19] was conducted with Materials Studio using data in the range 20 = 5–35°. The background was first refined by applying a second-order polynomial function. The profile was calculated starting from the unit cell parameters of CCDC-889530 (a = 27.0942 Å, F23 space group). Unit cells and the zero-shift were first refined. The background was first refined by applying a tenth-order polynomial function. The patterns were then refined using a pseudo-Voigt profile, followed by refinement of peak asymmetry using the Finger–Cox–Jephcoat asymmetry function. Refinements of unit cell parameters, zero shift, peak asymmetry, and background were used to obtain the final profiles.

Acknowledgements

This project was supported by the Knut and Alice Wallenberg Foundation, the Swedish Research Council (VR), and the Swedish Governmental Agency for Innovation Systems (VINNOVA) through the Berzelii Center EXSELENT. B.M.-M. also thanks VINNOVA for a VINNMER grant. A.E.P.-P. was supported by the MATsynCELL project, Röntgen–Ångström Cluster. L.S. was supported by the Consortium for Crystal Chemistry (C3), Röntgen–Ångström Cluster. The authors acknowledge the MAX IV Laboratory, Lund, for the use of the synchrotron facilities (Proposal 20120319). In particular, we thank Dr. Stefan Carlson for his assistance in using the I811 beamline.

Keywords: functionalisation · metal–organic frameworks · microporous materials · synthesis design · transition metal complexes


Recently, bipyridyl linkers have been proved to act as Lewis basic sites: L. Li, S. Tang, C. Wang, X. Lv, M. Jiang, H. Wu, X. Zhao, Chem. Commun. 2014, 50, 2304–2307.

Received: June 11, 2014
Published online on November 3, 2014