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Site-Selective Cyclometalation of a Metal-Organic Framework

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Supplementary Information

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MOFs Synthesis.

Starting materials and solvents were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, Alfa Aesar, EMD, TCI, Cambridge Isotope Laboratories, Inc., and others). 2-Phenylpyridine-5,4'-dicarboxylic acid (dcppy), DMOF-1-dcppy, and BMOF-1-dcppy were synthesized as previously reported.[1]

Synthesis of UiO-67-dcppy. Dcppy (85 mg, 0.35 mmol), $ZrCl_4$ (82 mg, 0.35 mmol), and acetic acid (~600 uL, 10.5 mmol) were dissolved in *N,N*-dimethylformamide (DMF, 4 mL) in a Teflon-lined Parr stainless steel vessel (20 mL). The vessel was sealed and placed in a preheated oven at 120 °C for 24 h. After cooling to room temperature, the reaction mixture was separated from the white crystalline powder by centrifugation and the remaining solid was washed with DMF (3×10 mL). The solvent was then exchanged for dichloromethane (CH_2Cl_2, 3×10 mL) where the powder were left for 3 d, replacing the solution with fresh CH_2Cl_2 every 24 h.

Cyclometallation of UiO-67-dcppy with $[Ir(COD)(OCH_3)]_2$ or $[Rh(COD)(Cl)]_2$. A solution of $[Ir(COD)(OCH_3)]_2$ (COD = 1,5-cyclooctadiene) (172 mg, 0.26 mmol) or $[Rh(COD)(Cl)]_2$ (128 mg, 0.26 mmol) was prepared in tetrahydrofuran (THF, 8 mL). UiO-67-dcppy (~50 mg, 0.13 mmol dcppy) was then placed in a scintillation vial containing a solution of the Ir(I) or Rh(I) source. The vial was then transferred into a pre-heated isotherm oven at 55 °C for 1 d. The cyclometallated UiO-67-dcppy were washed with DMF (3×10 mL) for 3 d. The solvents was then exchanged for THF (3 ×10 mL) where the powder were left for 3 d, replacing the solution with fresh THF every 24 h.

Cyclometallation of DMOF-1-dcppy with $[Ir(COD)(OCH_3)]_2$ or *$[Rh(COD)(Cl)]_2$.* DMOF-1-dcppy (~60 mg, 0.17 mmol dcppy) was washed with CH_2Cl_2 (3×10 mL) for 3 d. A solution of $[Ir(COD)(OCH_3)]_2$ (226 mg, 0.34 mmol) or $[Rh(COD)(Cl)]_2$ (168 mg, 0.34 mmol) was prepared in CH_2Cl_2 (8 mL). DMOF-1-dcppy was then placed in a scintillation vial containing a solution of the Ir(I) or Rh(I) source. The vial was then transferred into a pre-heated isotherm oven at 55 °C for 1 d. The cyclometallated DMOF-1-dcppy were washed with DMF (3×10 mL) for 3 d.

The solvents was then exchanged for CH_2Cl_2 (3 ×10 mL) where the crystals were left for 3 d, replacing the solution with fresh CH_2Cl_2 every 24 h.

Cyclometallation of BMOF-1-dcppy with [Ir(COD)(OCH$_3$)]$_2$ or [Rh(COD)(Cl)]$_2$. BMOF-1-dcppy (~100 mg, 0.26 mmol dcppy) was washed with THF (3×10 mL) for 3 d. A solution of $[Ir(COD)(OCH_3)]_2$ (344 mg, 0.52 mmol) or $[Rh(COD)(Cl)]_2$ (256 mg, 0.52 mmol) was prepared in THF (8 mL). BMOF-1-dcppy was then placed in a scintillation vial containing a solution of the Ir(I) or Rh(I) source. The vial was then transferred into a pre-heated isotherm oven at 55 °C for 1 d. The cyclometallated BMOF-1-dcppy were washed with DMF (3×10 mL) for 3 d. The solvents was then exchanged for THF (3 ×10 mL) where the crystals were left for 3 d, replacing the solution with fresh THF every 24 h. Identical reactions were performed with BMOF-1-dcppy using 0.25, 0.5, and 1.0 equivalent of $[Ir(COD)(OCH_3)]_2$.

MOFs Characterization.

Powder X-ray Diffraction. For cyclometalated UiO-67-dcppy, approximate 20-30 mg MOFs were dried under vacuum at room temperature for ~2 mins prior to PXRD analysis. For cyclometalated DMOF-1-dcppy and BMOF-1-dcppy, approximately 20-30 mg of MOF material was dried in air for less than 1 min prior to PXRD analysis. PXRD data was collected at ambient temperature on a Bruker D8 Advance diffractometer using a LynxEye detector at 40 kV, 40 mA for Cu Kα (λ= 1.5418 Å), with a scan speed of 1 sec/step, a step size of 0.02^o, 2θ range of $5\text{-}45^o$.

BET Surface Area and Gas Sorption Analysis. Between 30-100 mg of MOF material was evacuated under vacuum for ~2 min at room temperature. Samples were then transferred to a pre-weighed sample tube and degassed at 105 °C on a Micromeritics ASAP 2020 Adsorption Analyzer for a minimum of 12 h or until the outgas rate was <5 mmHg/min. The sample tube was re-weighed to obtain a consistent mass for the degassed MOF. Brunauer-Emmett-Teller (BET) surface area (m^2/g) measurements were collected at 77 K with N_2 on a Micromeritics ASAP 2020 Adsorption Analyzer using a volumetric technique. The samples were then manually degassed for at least 2 h prior to N_2 isotherm at 77 K.

Thermalgravimetric Analysis. Approximately 10-15 mg of MOF materials were used for thermogravimetric analysis (TGA) measurements, immediately after collection of gas sorption data (i.e. activated samples). Samples were analyzed under a stream of N_2 (10 ml/min) using a TA Instrument Q600 SDT running from room temperature to 600 °C or 800 °C with a ramping rate of 5 °C/min.

Inductive-couple Plasma Mass Spectroscopy Analysis (ICP-MS). Approximately 10-30 mg of MOF material was dried under vacuum at 120 °C overnight prior to ICP-MS analysis. The samples were dissolved with 50% H_2O_2 (2 mL) and HNO_3 (1 mL). These solutions were diluted with 5% HNO_3 in H_2O (15 mL) before analysis. Five standard samples (10, 100, 250, 500, and 1000 ppb) were used to prepare a calibration curve. The samples were analyzed using Thermoquest Finnegan ICP-MS instrument.

Single Crystal X-ray Diffraction. Single crystals of BMOF-1-dcppy exposed to 2.0 equivalent of $[Ir(COD)(OCH_3)]_2$ or $[Rh(COD)(Cl)]_2$ taken from THF were mounted on nylon loops with paratone oil and placed under a nitrogen cold stream (230 K). Data was collected on a Bruker Apex diffractometer using Cu Kα (λ= 1.5418 Å) radiation controlled using the APEX 2010 software package. A multi-scan method utilizing equivalents was employed to correct for absorption. All data collections were solved and refined using the SHELXTL software suite.[2] Structures of cyclometalated BMOF-1-dcppy were treated with the "SQUEEZE" protocol in PLATON[3] to account for partially occupied or disordered solvent (e.g. THF) within the porous frameworks.

Single crystals of DMOF-1-dcppy exposed to 2.0 equivalent of $[Ir(COD)(OCH_3)]_2$ or $[Rh(COD)(Cl)]_2$ taken from CH_2Cl_2 were mounted on nylon loops with paratone oil and placed under a nitrogen cold stream (250 K). Data was collected on a Bruker Apex diffractometer using Mo Kα (λ= 0.71073 Å) radiation controlled using the APEX 2010 software package. A multi-scan method utilizing equivalents was employed to correct for absorption. All data collections were solved and refined using the SHELXTL software suite.[2] Structure of cyclometalated DMOF-1-dcppy was treated with the "SQUEEZE" protocol in PLATON[3] to account for partially occupied or disordered solvent (e.g. CH_2Cl_2) within the porous frameworks.

Data for all structures were collected at high temperature (>200 K) due to the instability of the single crystals at low temperature. DMOF-1-Irdcppy and BMOF-1-Irdcppy were refined isotropically due to weak diffraction and severe disorder (e.g. dabco ligands, phenylpyrdine moiety). Because of the low occupancy of Ir or Rh atoms in the structures, other ligands that coordinated to the Ir or Rh atoms were not determined. Additional refinement details are listed under _refine_special_details in cif files.

References

1. *P. V. Dau, M. Kim, S. J. Garibay, F. H. L. Muench, C. E. Moore and S. M. Cohen, Inorg. Chem., 2012,* ***51****, 5671-5676.*
2. *G. M. Sheldrick, Acta Cryst. , 2008,* ***A64****, 112.*
3. *A. L. Spek, Acta Cryst., 2009,* ***D65****, 148-155.*

Fig. S1 Picture of DMOF-1-Irdcppy (right, containing 8.3 wt% of Ir) and DMOF-1-Rhdcppy (left, containing 7.4 wt% of Rh).

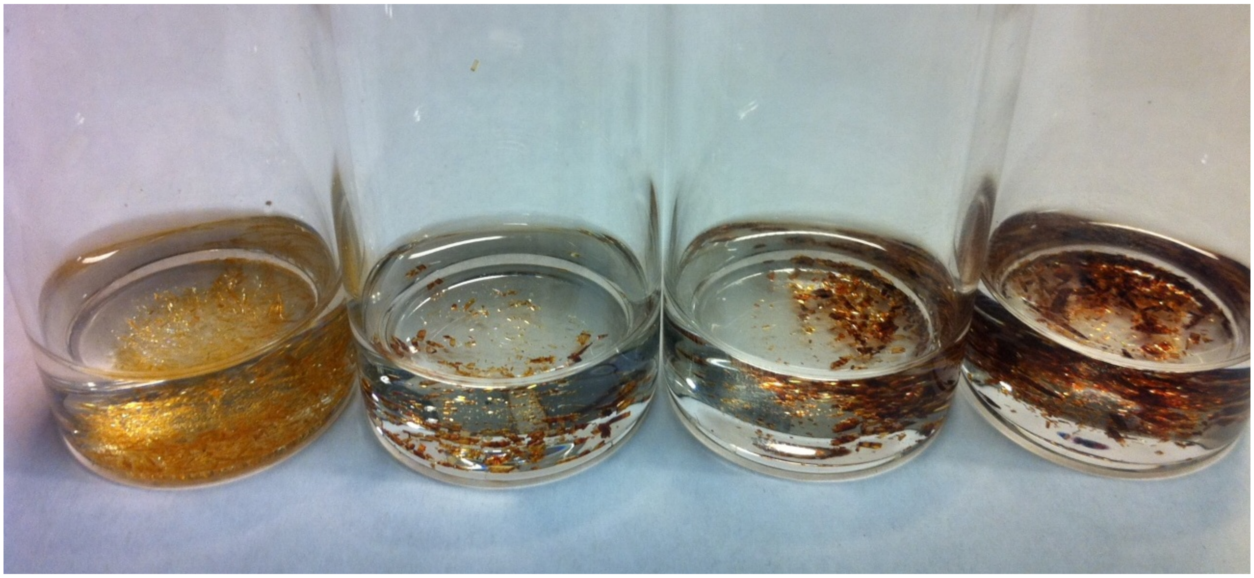

Fig. S2 Picture of BMOF-1-Irdcppy (left to right: containing 0.6 wt%, 2.6 wt%, 3.4 wt%, and 7.1 wt% of Ir, respectively).

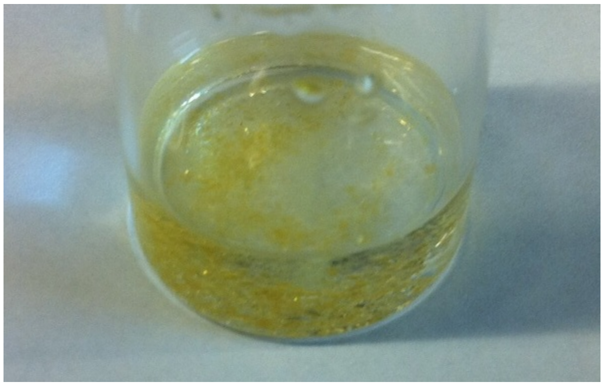

Fig. S3 Picture of BMOF-1-Rhdcppy (containing 6.9 wt% of Rh).

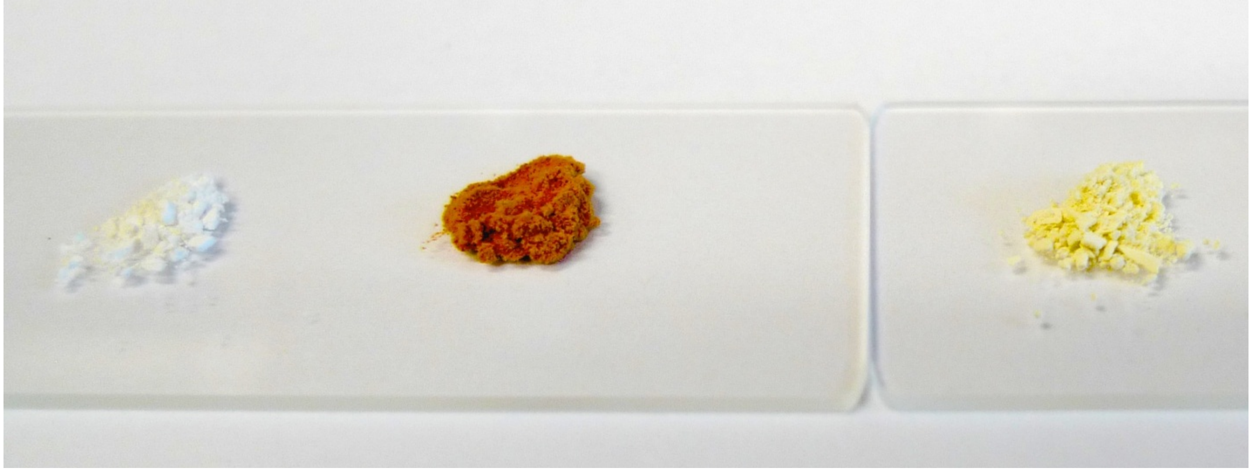

Fig. S4 Picture of UiO-67-dcppy (left), UiO-67-Irdcppy (middle, containing 7.7 wt% of Ir), and UiO-67-Rhdcppy (left, containing 5.4 wt% of Rh).

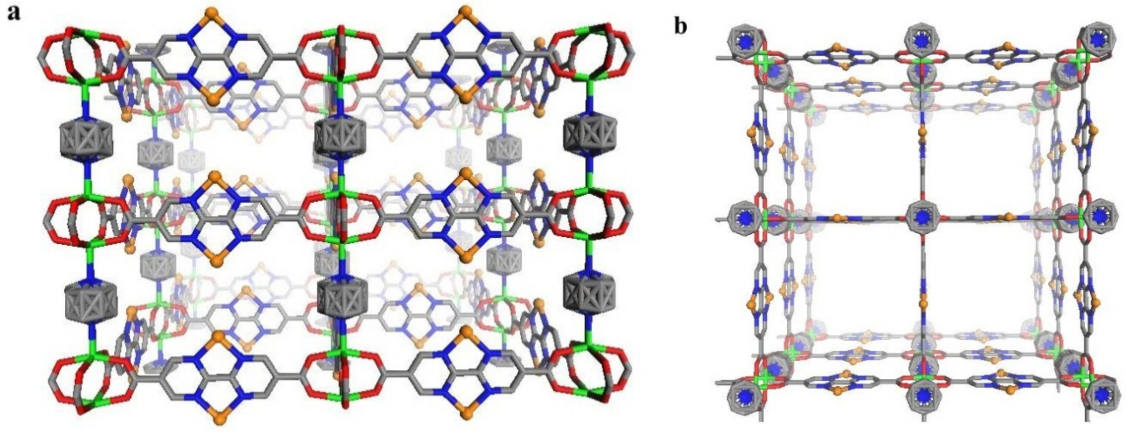

Fig. S5 Structure of DMOF-1-Rhdcppy. View along crystallographic *c*-axis (a); view along crystallographic *a*-axis (b). Rh atoms were refined as disordered over two positions with occupancy of ~6%. Color scheme: C (gray), N (blue), O (red), Rh (orange), and Zn (green).

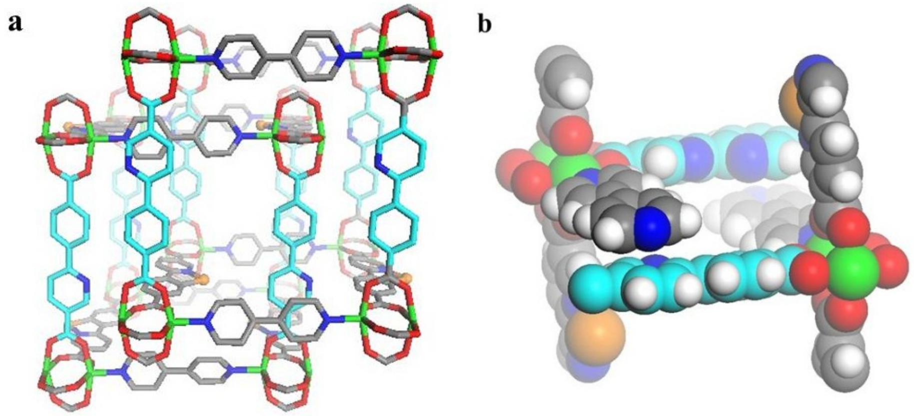

Fig. S6 Structure of BMOF-1-Rhdcppy. View of a section of the interpenetrated framework, unmodified dcppy ligands are highlighted in cyan (a); view of the inter-ligand interaction between the two interpenetrated nets (b). Rh atoms were found to have occupancy of ~7.5%. Color scheme: C (gray), N (blue), O (red), Rh (orange), and Zn (green).

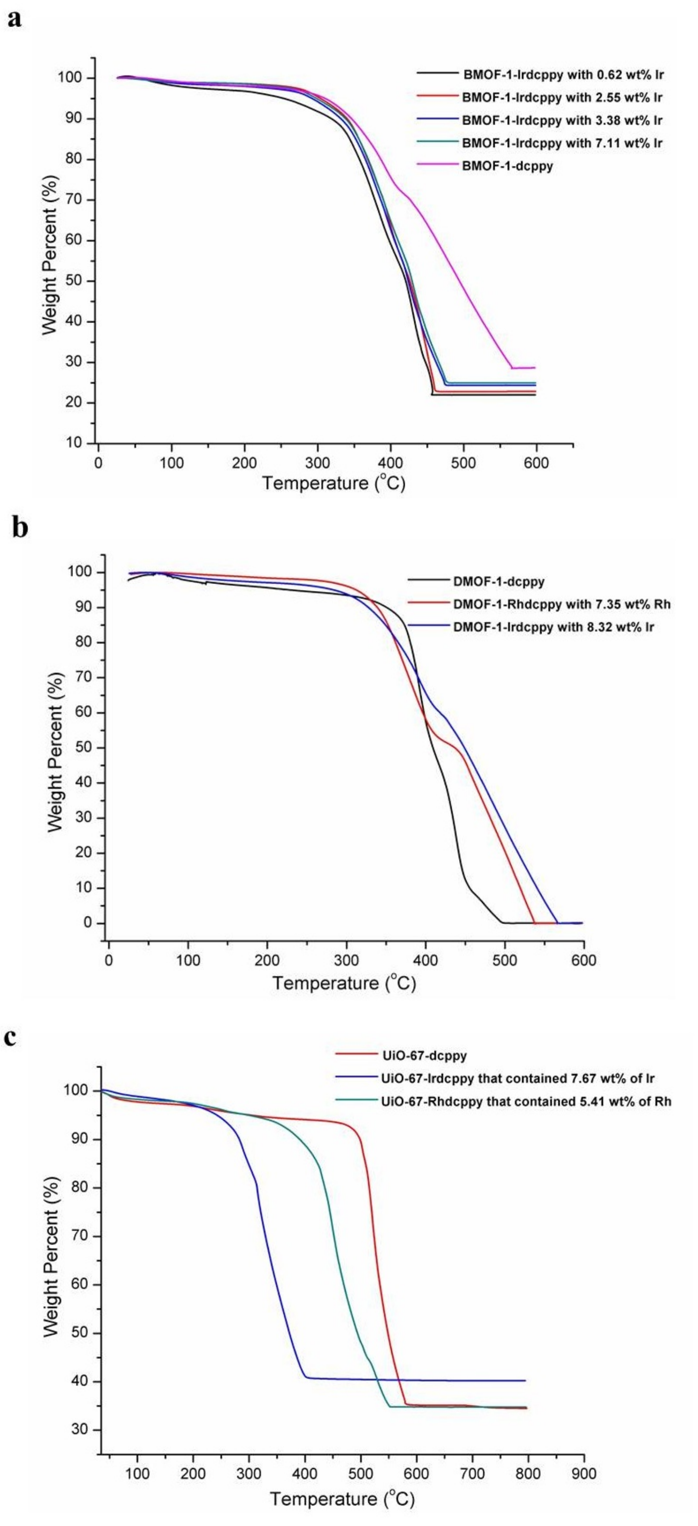

Fig. S7 Thermogravimetric analysis (TGA) of (a) BMOF-1-dcppy, (b) DMOF-1-dcppy, and (c) UiO-67-dcppy.

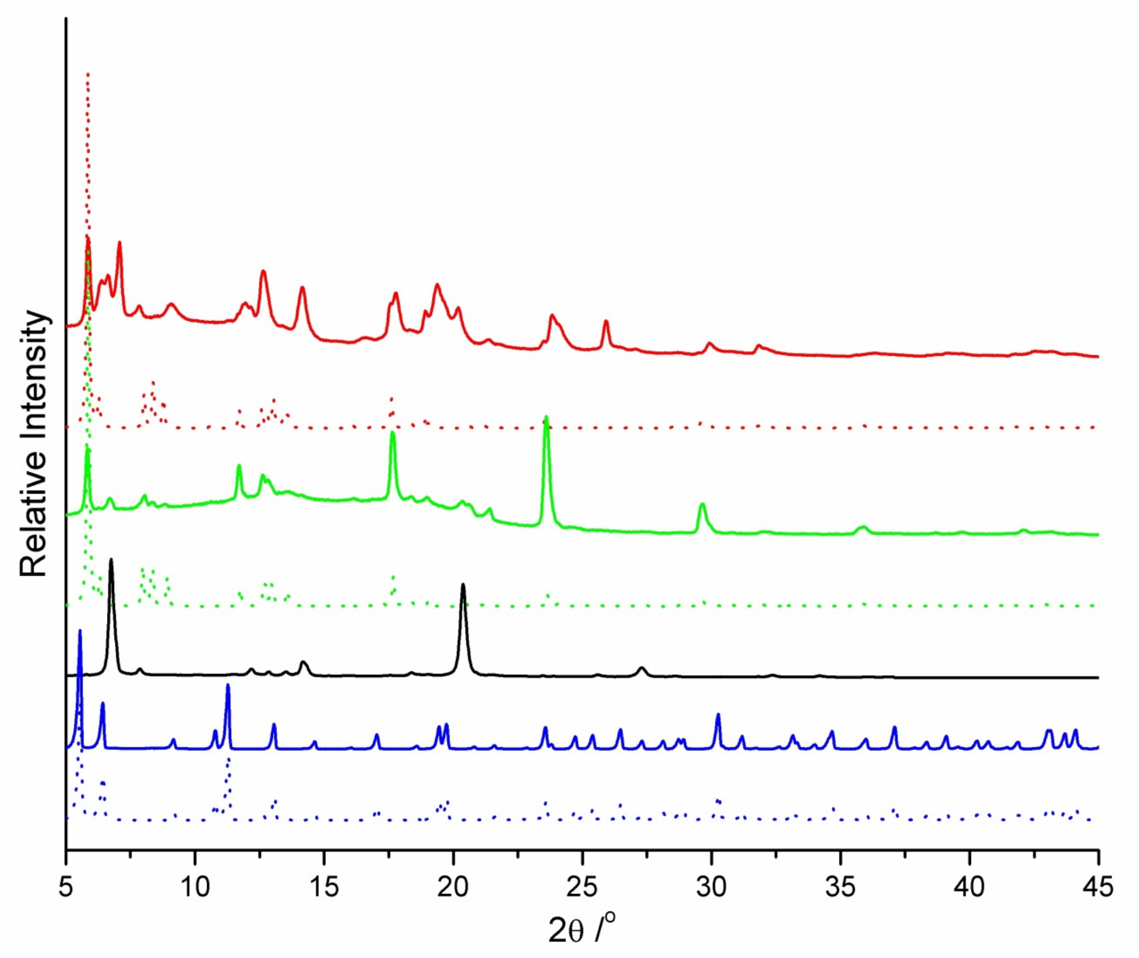

Fig. S8 PXRD patterns of cyclometalated MOFs. From bottom to top: UiO-67-dcppy (blue dot), UiO-67-Rhdcppy (blue line), BMOF-1-dcppy (black line), simulated BMOF-1-Irdcppy (green dot), BMOF-1-Irdcppy (green line), simulated BMOF-1-Rhdcppy (red dot), and BMOF-1-Rhdcppy (red line).

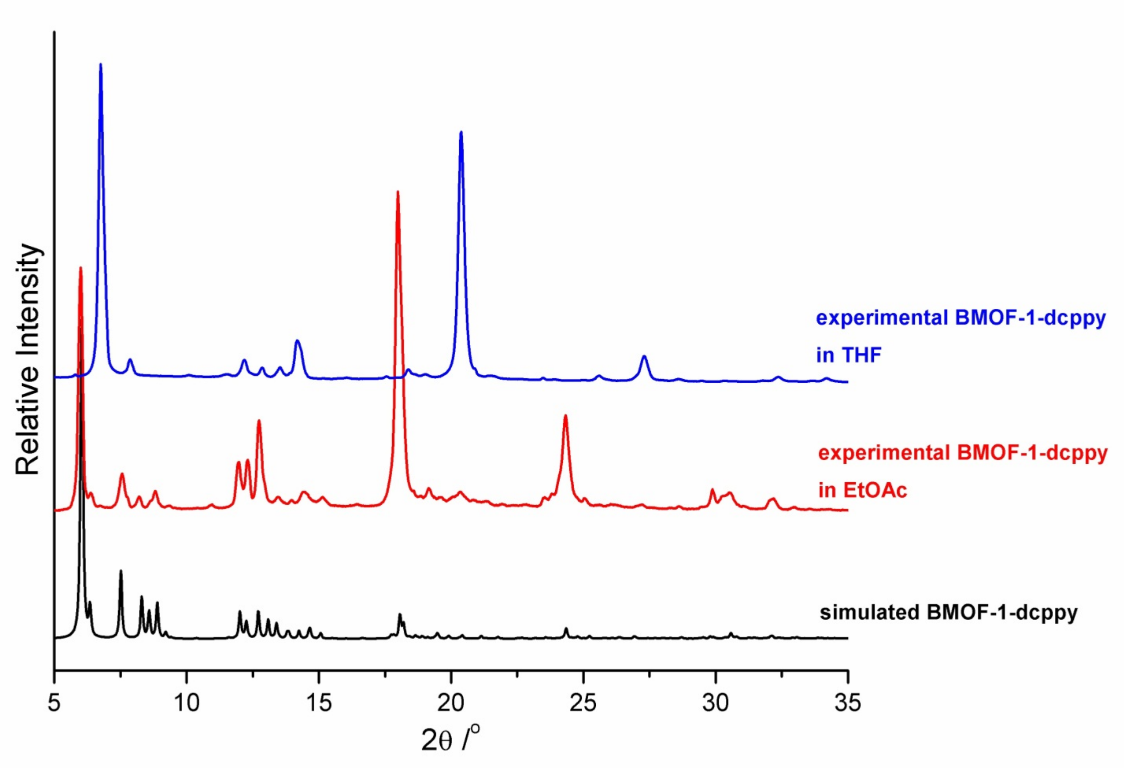

Fig. S9 PXRD patterns of BMOF-1-dcppy obtained in EtOAc (red) and THF (blue). The simulated pattern (black) was produced from single-crystal X-ray data from a crystal soaked in EtOAc. Note that the EtOAc simulated and experimental spectra agree very well; however, the experimental THF patterns differs significantly, indicative of framework flexibility.

Table S1 Summary of ICP-MS analysis of MOFs reported in this study.

	ICP-MS analysis of Ir (wt %) [a]	**Molar ratio between Ir and dcppy**	**ICP-MS analysis of Rh (wt %)** [a]	**Molar ratio between Rh and dcppy**
UiO-67-dcppy	<0.0001	N/A	<0.0001	N/A
UiO-67-dcppy exposed to 2.0 equiv of [Ir(COD)(OCH$_3$)]$_2$	7.7 [b]	0.16	<0.0001	N/A
UiO-67-dcppy exposed to 2.0 equiv of [Rh(COD)(Cl)]$_2$	<0.0001	N/A	5.4 [b]	0.20
DMOF-1-dcppy	<0.0001	-	<0.0001	-
DMOF-1-dcppy exposed to 2.0 equiv of [Ir(COD)(OCH$_3$)]$_2$	8.3 [b]	0.10	<0.0001	N/A
DMOF-1-dcppy exposed to 2.0 equiv of [Rh(COD)(Cl)]$_2$	<0.0001	N/A	7.4 [b]	0.28
BMOF-1-dcppy	<0.0001	N/A	<0.0001	N/A
BMOF-1-dcppy exposed to 0.25 equiv of [Ir(OCH$_3$)(COD)]$_2$	0.6 ± 0.1	0.012	<0.0001	N/A
BMOF-1-dcppy exposed to 0.5 equiv of [Ir(COD)(OCH$_3$)]$_2$	2.6 ± 0.2	0.052	<0.0001	N/A
BMOF-1-dcppy exposed to 1.0 equiv of [Ir(COD)(OCH$_3$)]$_2$	3.4 ± 0.4	0.072	<0.0001	N/A
BMOF-1-dcppy exposed to 2.0 equiv of [Ir(COD)(OCH$_3$)]$_2$	7.1 ± 0.9	0.16	<0.0001	N/A
BMOF-1-dcppy exposed to 2.0 equiv of [Rh(COD)(Cl)]$_2$	<0.0001	N/A	6.86 [b]	0.26

[a] The average and standard deviation were calculated from a total of four measurements on two independent samples (two measurements per sample).

[b] Only one sample was analyzed in duplicate – no standard deviation obtained.

Table S2 Summary of BET surface of cyclometaled MOFs.

MOFs	BET (m^2/g) [a]
UiO-67-dcppy	2458 ± 86
UiO-67-dcppy exposed to 2.0 equiv of $[Ir(COD)(OCH_3)]_2$	1586 ± 123
BMOF-1-dcppy	29 ± 15
BMOF-1-dcppy exposed to 0.25 equiv of $[Ir(OCH_3)(COD)]_2$	25 ± 6
BMOF-1-dcppy exposed to 0.5 equiv of $[Ir(COD)(OCH_3)]_2$	428 ± 98
BMOF-1-dcppy exposed to 1.0 equiv of $[Ir(COD)(OCH_3)]_2$	710 ± 107
BMOF-1-dcppy exposed to 2.0 equiv of $[Ir(COD)(OCH_3)]_2$	891 ± 136

[a] The average and standard deviation were calculated from three measurements on three independent samples.

Table S3 Crystal Data and structure refinement for DMOF-1-Irdcppy (Ir weight percent of 8.3%).

Identification code	DMOF-1-Irdcppy
Empirical formula	C_{24} H_8 $Ir_{0.29}$ N_6 O_8 Zn_2
Formula weight	694.07
Temperature	250(2) K
Wavelength	0.71073 Å
Crystal system	Tetragonal
Space group	P4/ m m m
Unit cell dimensions	a = b =15.093(6) Å c = 9.620(4) Å α = β = γ = 90°
Volume	2191.5(15) $Å^3$
Z	1
Density (calculated)	0.526 Mg/m^3
Absorption coefficient	0.997 mm^{-1}
F(000)	340
Crystal size	0.20 x 0.10 x 0.10 mm^3
Theta range for data collection	1.91 to 25.40°
Index ranges	-18<=h<=11, -18<=k<=17, -11<=l<=9
Reflections collected	7597
Independent reflections	1221 [R(int) = 0.0585]
Completeness to theta = 25.40°	99.1 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1221 / 0 / 29
Goodness-of-fit on F^2	1.250
Final R indices [I>2sigma(I)]	R1 = 0.1567, wR2 = 0.3555
R indices (all data)	R1 = 0.1677, wR2 = 0.3458
Extinction coefficient	not measured
Largest diff. peak and hole	1.872 and -1.641 $e.Å^{-3}$

Table S4 Crystal Data and structure refinement for BMOF-1-Irdcppy (Ir weight percent of 7.1%).

Identification code	BMOF-1-Irdcppy
Empirical formula	$C_{34} H_{18} Ir_{0.11} N_4 O_8 Zn_2$
Formula weight	761.45
Temperature	230(2) K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 14.0368(15) Å α = 85.358(6)° b = 15.1189(17) Å β = 85.555(5)° c = 15.1242(17) Å γ = 86.350(6)°
Volume	3184.2(6) $Å^3$
Z	2
Density (calculated)	0.794 Mg/m^3
Absorption coefficient	1.591 mm^{-1}
F(000)	764
Crystal size	0.10 x 0.10 x 0.08 mm^3
Theta range for data collection	2.94 to 58.91°.
Index ranges	-13<=h<=15, -16<=k<=16, -14<=l<=16
Reflections collected	15103
Independent reflections	8026 [R(int) = 0.0352]
Completeness to theta = 58.91°	87.8 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8026 / 0 / 220
Goodness-of-fit on F^2	1.337
Final R indices [I>2sigma(I)]	R1 = 0.1074, wR2 = 0.3089
R indices (all data)	R1 = 0.1356, wR2 = 0.3298
Extinction coefficient	not measured
Largest diff. peak and hole	1.500 and -0.847 $e.Å^{-3}$

Table S5 Crystal data and structure refinement for DMOF-1-Rhdcppy (Rh weight percent of 7.4%).

Identification code	DMOF-1-Rhdcppy
Empirical formula	$C_{26} H_8 N_{10} O_8 Rh Zn_2$
Formula weight	822.07
Temperature	250(2) K
Wavelength	0.71073 Å
Crystal system	Tetragonal
Space group	P4/ m m m
Unit cell dimensions	a = b =15.093(6) Å c = 9.620(4) Å $\alpha = \beta = \gamma = 90^{o}$
Volume	2191.5(15) Å^3
Z	1
Density (calculated)	0.623 Mg/m^3
Absorption coefficient	0.752 mm^{-1}
F(000)	403
Crystal size	0.60 x 0.30 x 0.30 mm^3
Theta range for data collection	1.91 to 25.40°.
Index ranges	-18<=h<=11, -18<=k<=17, -11<=l<=9
Reflections collected	7597
Independent reflections	1221 [R(int) = 0.0583]
Completeness to theta = 25.40°	99.1 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1221 / 0 / 53
Goodness-of-fit on F^2	1.100
Final R indices [I>2sigma(I)]	R1 = 0.0908, wR2 = 0.2529
R indices (all data)	R1 = 0.0998, wR2 = 0.2620
Extinction coefficient	not measured
Largest diff. peak and hole	1.218 and -0.641 e.Å^{-3}

Table S6 Crystal data and structure refinement for BMOF-1-Rhdcppy (Rh weight percent of 6.9%).

Identification code	BMOF-1-Rhdcppy
Empirical formula	$C_{36} H_{21} N_4 O_8 Rh_{0.15} Zn_2$
Formula weight	768.31
Temperature	230(2) K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 14.0869(13) Å α = 86.517(7)° b = 15.1333(17) Å β = 87.286(5)°. c = 15.1402(15) Å γ = 86.896(5)°.
Volume	3213.8(6) Å^{3}
Z	2
Density (calculated)	0.794 Mg/m^{3}
Absorption coefficient	1.481 mm^{-1}
F(000)	778
Crystal size	0.10 x 0.10 x 0.05 mm^{3}
Theta range for data collection	4.20 to 70.57°.
Index ranges	-17<=h<=17, -18<=k<=18, 0<=l<=18
Reflections collected	10145
Independent reflections	10145 [R(int) = 0.0000]
Completeness to theta = 70.57°	82.3 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^{2}
Data / restraints / parameters	10145 / 0 / 497
Goodness-of-fit on F^{2}	1.085
Final R indices [I>2sigma(I)]	R1 = 0.0518, wR2 = 0.1517
R indices (all data)	R1 = 0.0599, wR2 = 0.1572
Extinction coefficient	not measured
Largest diff. peak and hole	0.667 and -0.674 e.Å^{-3}