Supporting Information

Synthetic control of coincidental formation of N-heterocyclic carbene-copper(I) complex and imidazolium cations within metal-organic frameworks

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Materials and methods

Copper chloride, copper perchlorate hexahydrate, methanol, ether, dimethyl sulfoxide, xylene, *N*-methyl-2-pyrrolidone, 4-bromophenyl, (bis(pinacolate)diboron (B_2Pin_2), sodium *tert*-butoxide, acetone (HPLC grade) and dodecane (anhydrous) were purchased from commercial sources and used as received without further purification. Tetrahydrofuran was distilled over sodium benzophenone ketyl and stored in molecular sieves (4 Å) prior to use. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III (Ultrashield Plus 400 MHz magnet) spectrometer for ^{1}H. Electrospray ionization mass spectrometry (ESI-MS) spectra were measured by using a LTQ Orbitrap Velos™ mass spectrometer (Thermo Scientific, USA). Elemental analysis (EA) for C, H, and N were conducted using Flash 2000 (Thermo Fisher Scientific Inc.). Thermogravimetric analysis (TGA) were measured in a nitrogen stream using a Scinco TGA N-1000 with a heating rate of 10 ℃ min^{-1}. Powder X-ray diffraction (PXRD) were carried out using Rigaku SmartLab (Cu Kα, λ = 1.5418 Å) at room temperature. The low pressure N_2 gas adsorption/desorption experiments were conducted on nanoPOROSITY-XQ (Mirae scientific instruments Inc.) at 77 K. The low pressure CO_2 adsorption/desorption gas experiments were performed using AUTOSORB-iQ-C (Quantachrome Corporation) and BELSORP-max (BEL Japan, Inc.) at 195 and 273 K. Single crystal X-ray diffraction (SC-XRD) data were collected on a Bruker D8 VENTURE diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) or synchrotron radiation of 2D-SMC at the Pohang Accelerator Laboratory (PAL, Korea) using an ADSC Quantum-210 detector furnished with a silicon (111) double crystal monochromator (DCM) at 100 K. A gas chromatography mass spectrometry (GC–MS) were measured using a 5977A series GC system and analyzed using the Agilent GC/MSD ChemStation Software package (Agilent Technologies).

X-ray Crystallographic Analysis

Table S1. Crystal data and structure refinement for **Im-MOF-1**.

Empirical formula	$C_{30.50}\ H_{32.50}\ Cl\ Cu\ N_4\ O_{10}$	
Formula weight	714.09	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.2442(4) Å	α = 90°
	b = 26.9115(13) Å	β = 90.408(2)°
	c = 13.1670(7) Å	γ = 90°
Volume	3275.5(3) $Å^3$	
Z	4	
Density (calculated)	1.448 Mg/m^3	
Absorption coefficient	0.810 mm^{-1}	
F(000)	1478	
Crystal size	0.200 x 0.100 x 0.050 mm^3	
Theta range for data collection	2.330 to 25.252°.	
Index ranges	-9<=h<=11, -32<=k<=32, -15<=l<=15	
Reflections collected	15166	
Independent reflections	5856 [$R_{(int)}$ = 0.0725]	
Completeness to theta = 25.242°	98.70%	
Absorption correction	Empirical	
Max. and min. transmission	0.9866 and 0.9734	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5856 / 93 / 489	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R_1 = 0.0628, wR_2 = 0.1370	
R indices (all data)	R_1 = 0.1057, wR_2 = 0.1583	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.728 and -0.719 $e.Å^{-3}$	

Table S2. Crystal data and structure refinement for **Im-MOF-2**.

Empirical formula	C_{20} H_{20} Cl Cu N_3 O_{10}	
Formula weight	561.38	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 6.6863(11) Å	α = 90°
	b = 33.340(4) Å	β = 107.156(5)°
	c = 11.3250(19) Å	γ = 90°
Volume	2412.3(6) $Å^3$	
Z	4	
Density (calculated)	1.075 Mg/m^3	
Absorption coefficient	0.810 mm^{-1}	
F(000)	1148	
Crystal size	0.100 x 0.050 x 0.020 mm^3	
Theta range for data collection	1.221 to 25.252°.	
Index ranges	-8<=h<=8, -28<=k<=40, -11<=l<=13	
Reflections collected	19083	
Independent reflections	4362 [$R_{(int)}$ = 0.1145]	
Completeness to theta = 25.242°	100%	
Absorption correction	Empirical	
Max. and min. transmission	0.979 and 0.900	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4362 / 11 / 326	
Goodness-of-fit on F^2	1.009	
Final R indices [I>2sigma(I)]	R_1 = 0.0632, wR_2 = 0.1388	
R indices (all data)	R_1 = 0.1387, wR_2 = 0.1696	
Extinction coefficient	0.0050(7)	
Largest diff. peak and hole	0.846 and -0.538 $e.Å^{-3}$	

Table S3. Crystal data and structure refinement for **Im-MOF-3**.

Empirical formula	C_{32} H_{39} Cl Cu_2 N_5 O_8	
Formula weight	784.21	
Temperature	100(2) K	
Wavelength	0.62998 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.1080(18) Å	α = 90°
	b = 25.909(5) Å	β = 96.69(3)°
	c = 14.588(3) Å	γ = 90°
Volume	3419.0(12) $Å^3$	
Z	4	
Density (calculated)	1.523 Mg/m^3	
Absorption coefficient	0.992 mm^{-1}	
F(000)	1620	
Crystal size	0.050 x 0.050 x 0.010 mm^3	
Theta range for data collection	2.333 to 20.510°	
Index ranges	-9<=h<=9, -28<=k<=28, -16<=l<=15	
Reflections collected	14913	
Independent reflections	4513 [$R_{(int)}$ = 0.0575]	
Completeness to theta = 25.242°	91.7 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9869 and 0.9367	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4513 / 25 / 439	
Goodness-of-fit on F^2	0.969	
Final R indices [I>2sigma(I)]	R_1 = 0.0645, wR_2 = 0.1752	
R indices (all data)	R_1 = 0.0809, wR_2 = 0.1878	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.193 and -0.839 $e.Å^{-3}$	

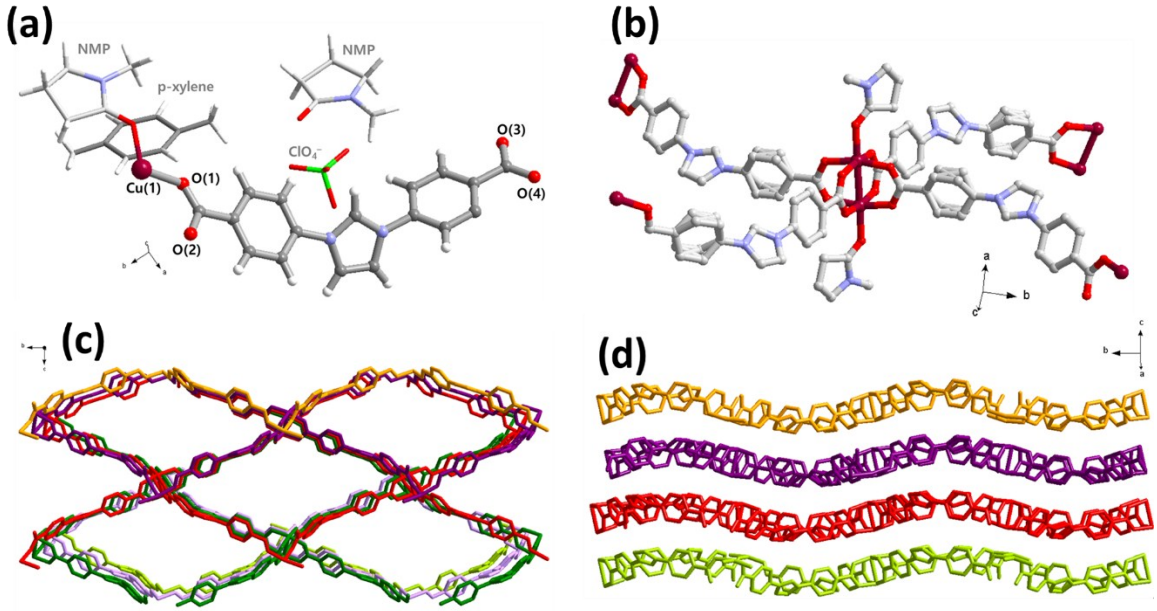


Figure S1. (a) Asymmetric unit of **Im-MOF-1**. (b) Cu(II) paddle-wheel cluster and coordination environment. Perspective views from the top (c) and side (d) of **Im-MOF-1**. Hydrogen atoms, anion and solvent molecules have been omitted for clarity.

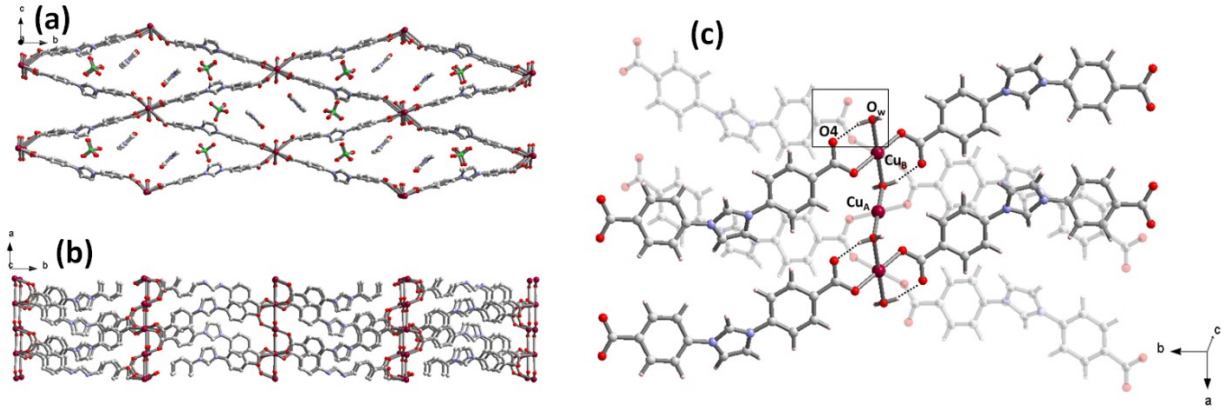


Figure S2. Crystal structure of **Im-MOF-2** (not activated) viewed along a- (a) and c-axis (b). Hydrogen atoms, perchlorate anion (ClO_4^-) and DMF solvents have been omitted for clarity. (c) Infinite SBUs representing interactions between bridging water molecules and monodentate carboxylates.

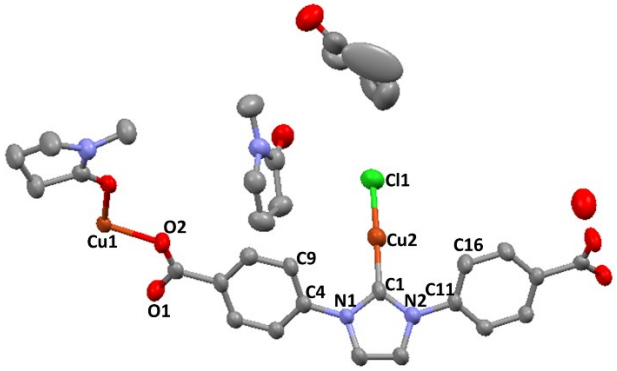


Figure S3. Asymmetric unit of **Im-MOF-3** with the thermal ellipsoid probability drawn at 50%. Selected experimental X-ray analysis [DFT calculated at the B3PW91/6-31G(d,p) for the optimized structure B] bond lengths [Å] and angles [°]. C4–N1 1.4409(3) [1.426], C11–N2 1.4285(2) [1.426], C1–N1 1.3599(2) [1.365], C1–N2 1.3627(3) [1.365], Cu(2)–C(1) 1.8855(3) [1.881], Cu(2)–Cl(1) 2.1064(4) [2.111] N1–C1–N2 103.057(2) [103.661], C1–N2–C11–C16 40.939(3) [45.354].

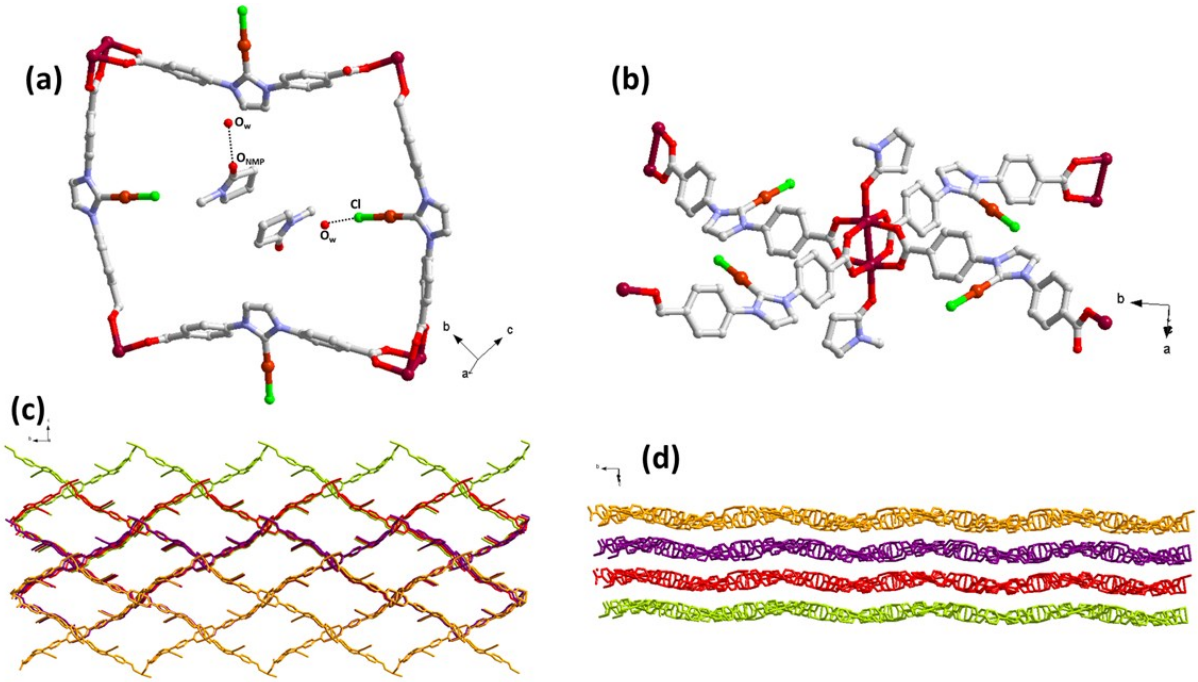


Figure S4. Crystal structure of **Im-MOF-3**. (a) Distorted square segment. (b) Cu(II) paddle-wheel cluster and coordination environment. Perspective views from the top (c) and side (d). Hydrogen atoms, anion and solvent molecules have been omitted for clarity.

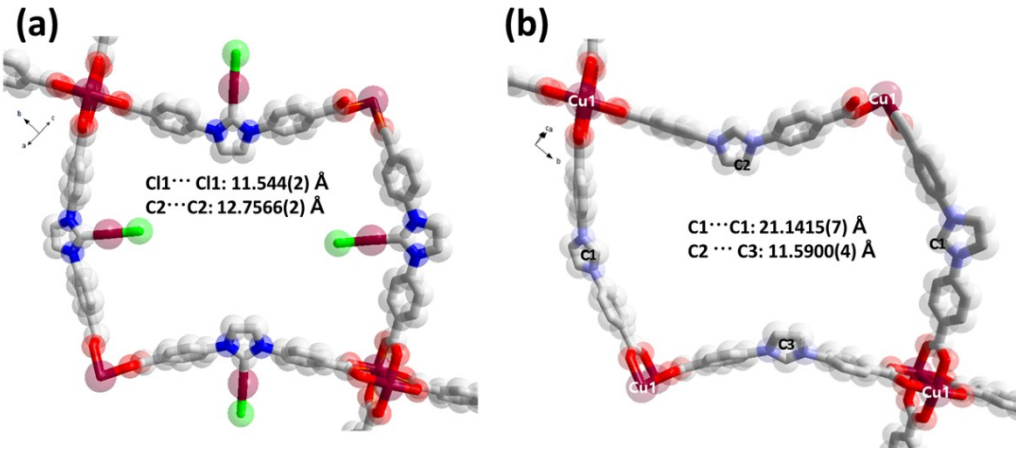


Figure S5. Perspective views of Im-MOF-**3** (a) and Im-MOF-**1** (b)

Powder X-ray Diffraction Data

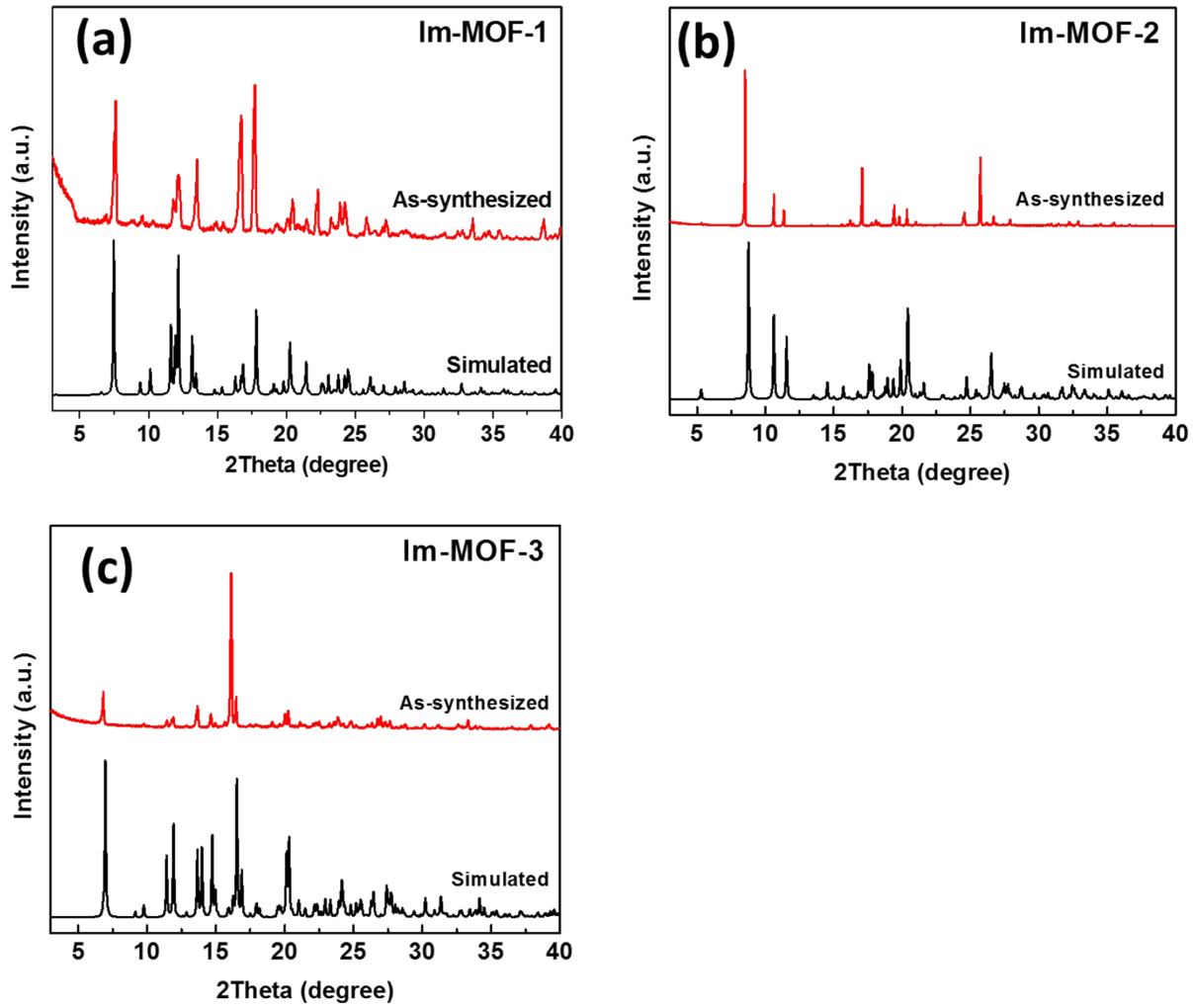


Figure S6. PXRD patterns of **Im-MOF-1** (a), **Im-MOF-2** (b) and **Im-MOF-3** (c)

Gas adsorption/desorption isotherm

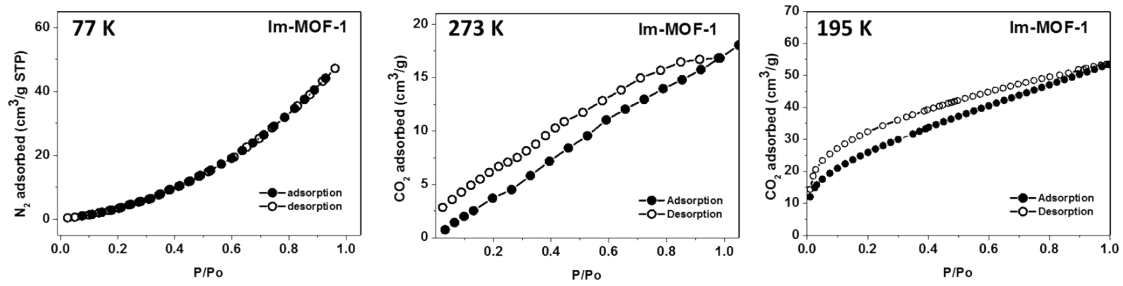


Figure S7. (a) The N_2 gas adsorption isotherm measured at 77 K (b) The CO_2 gas adsorption isotherm measured at 273 K and (c) at 195 K of **Im-MOF-1**.

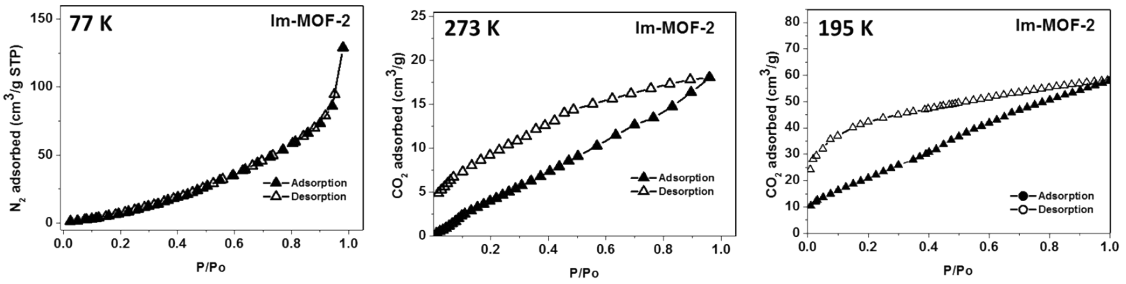


Figure S8. (a) The N_2 gas adsorption isotherm measured at 77 K (b) The CO_2 gas adsorption isotherm measured at 273 K and (c) at 195 K of **Im-MOF-2**.

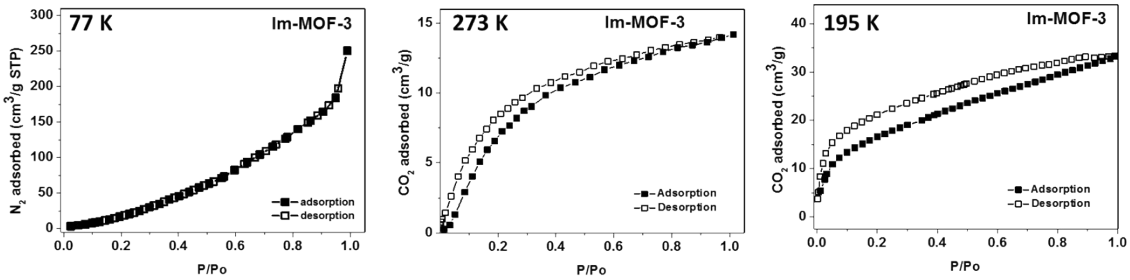
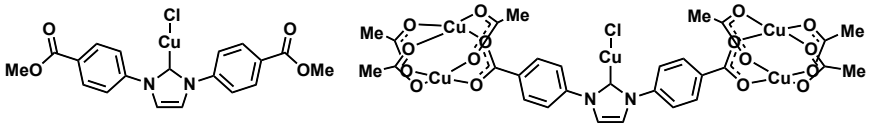


Figure S9 (a) The N_2 gas adsorption isotherm measured at 77 K (b) The CO_2 gas adsorption isotherm measured at 273 K and (c) at 195 K of **Im-MOF-3**.

DFT calculations

Model complexes: Due to the complexity of MOFs, two simplified structures were computed for analyzing the electronic structures of **Im-MOF-3**, mainly focusing on the NHC copper(I) chloride complex. One model (**A**) was designed to bear a methyl group on the carboxylate function and the other (**B**) was extended further to the structure having a copper(II) paddle-wheel structure without axial ligands at both carboxylate terminals.



model complex A model complex B

Scheme S1. Model complexes of **Im-MOF-3** for DFT calculation.

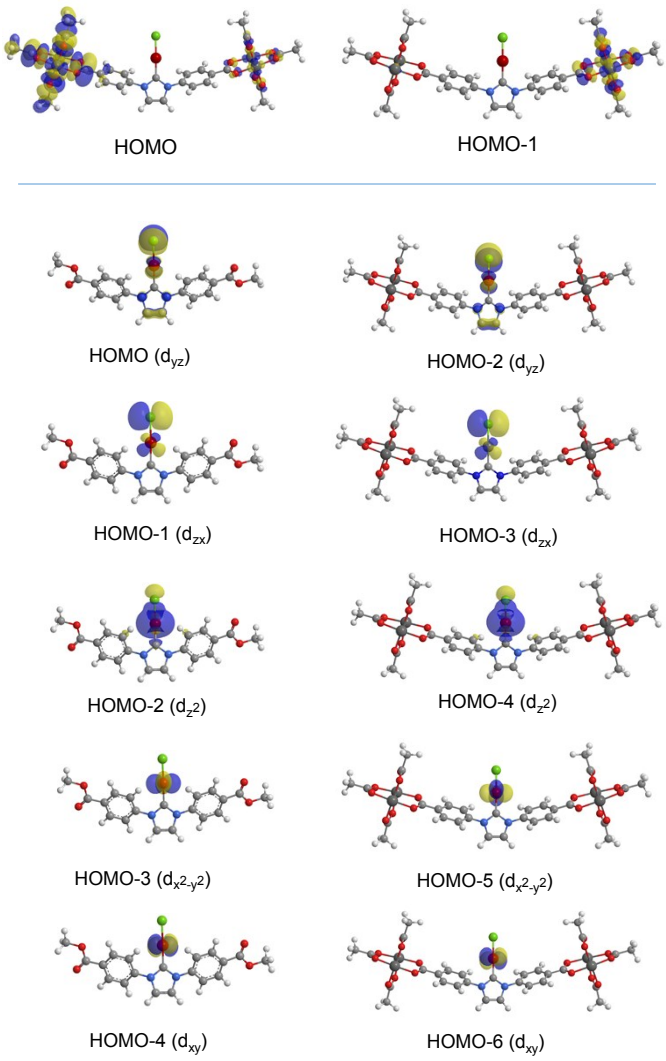
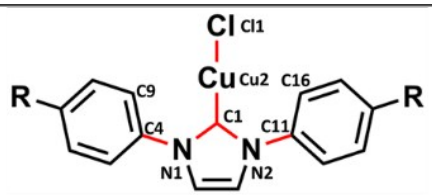
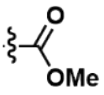
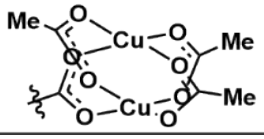


Figure S10. DFT calculation of frontier molecular orbitals (HOMO) of **Im-MOF-3** after optimization at the B3PW91/6-31G(d,p).

Table S4. Selected geometry parameters by X-ray structure and DFT calculation.



Method	MOF or –R
X-ray crystal structure	Im-MOF-3
B3PW91/BSI Model A	
B3PW91/BSI Model B	

Bond distances	X-ray	Model A	Model B
Cu(2)—Cl(1)	2.1064(4)	2.111	2.111
Cu(2)—C(1)	1.8855(3)	1.881	1.881
C(4)—N(1)	1.4409(3)	1.426	1.426
C(11)—N(2)	1.4285(2)	1.426	1.426
C(1)—N(1)	1.3599(2)	1.365	1.365
C(1)—N(2)	1.3627(3)	1.365	1.365

Bond angles	X-ray	Model A	Model B
C(9)—C(4)—N(1)	120.654(2)	120.107	120.158
N(1)—C(1)—N(2)	103.057(2)	103.688	103.661
Cl(1)—Cu(2)—C(1)	176.437(2)	177.672	178.352

Dihedral angles	X-ray	Model A	Model B
C(1)—N(2)—C(11) —C(16)	40.939(3)	45.090	45.354

Determination of GC yield

Calibration curve

GC-MS yield were calculated as follows. 1, 1, 2 and 3 µl of 4-biphenylboronic acid pinacol ester as product (C_p) and 1, 2, 1 and 1 µl of dodecane as internal standard (C_s) were added to 1 ml of acetone, respectively. Peak area of 4-biphenylboronic acid pinacol ester (A_P) and dodecane (A_S) were measured by conducting GC-MS analysis. Based on calibration data, a calibration curve was made by plotting the ratio of peak area versus standard concentration of the dodecane and 4-biphenylboronic acid pinacol ester.

C_p (µl/ml)[a]	C_S (µl/ml)	C_S/C_P (a.u.)	A_P (a.u.)	A_S (a.u.)	A_S/A_P (a.u.)
1	1	1.00	172464383	43598537	0.252797338
1	2	2.00	72377365	37284511	0.515140486
2	1	0.50	169436226	20385810	0.120315534
3	1	0.33	219261340	19648950	0.089614293

[a] Acetone was used as GC solvent

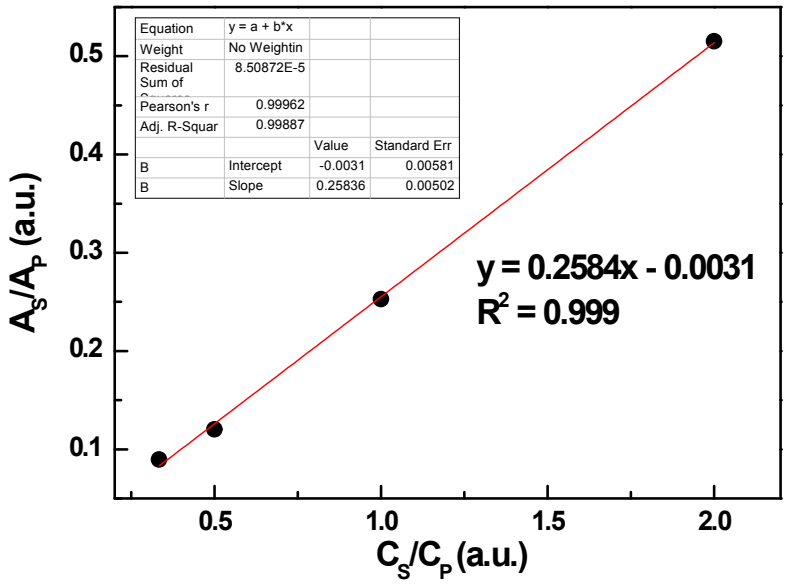


Figure S11. Calibration curve for determining GC yield.

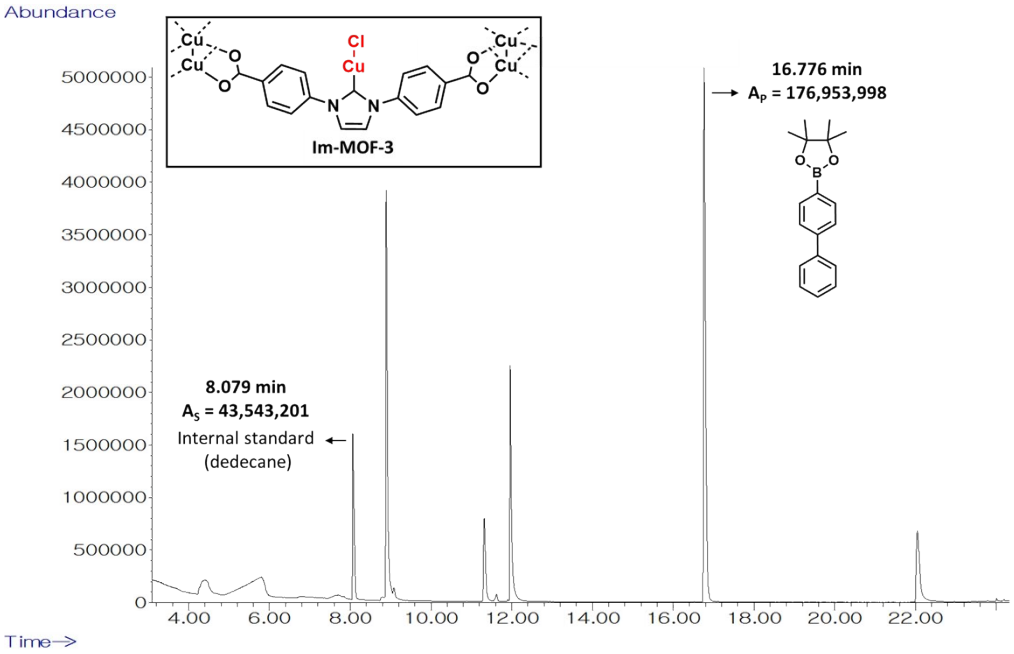
Yield determination of borylation reactions

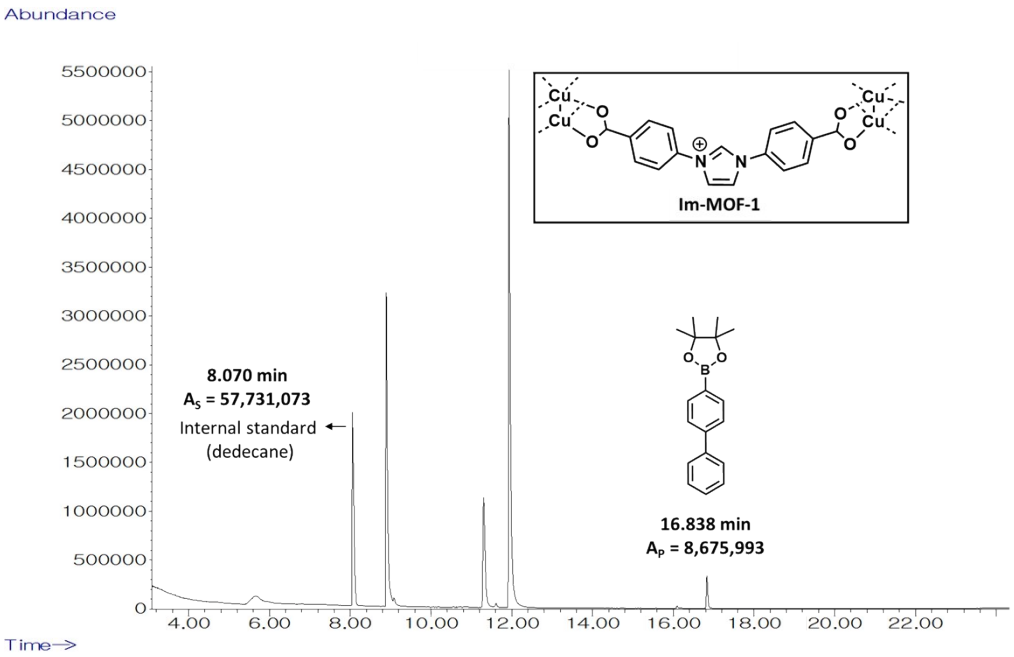
The reaction yield was calculated as shown below.

$$Yield = \frac{0.2584 \times x}{y + 0.0031} \times 100\% \quad \cdots \quad (1)$$

$$x = \frac{moles\ of\ internal\ standard}{moles\ of\ product}$$

$$y = \frac{Peak\ area\ of\ internal\ standard}{Peak\ area\ of\ product}$$


Abundance
Im-MOF-3
16.776 min
A_p = 176,953,998
8.079 min
A_s = 43,543,201
Internal standard
(dedecane)
Time


Abundance
Im-MOF-1
8.070 min
A_s = 57,731,073
Internal standard
(dedecane)
16.838 min
A_p = 8,675,993
Time

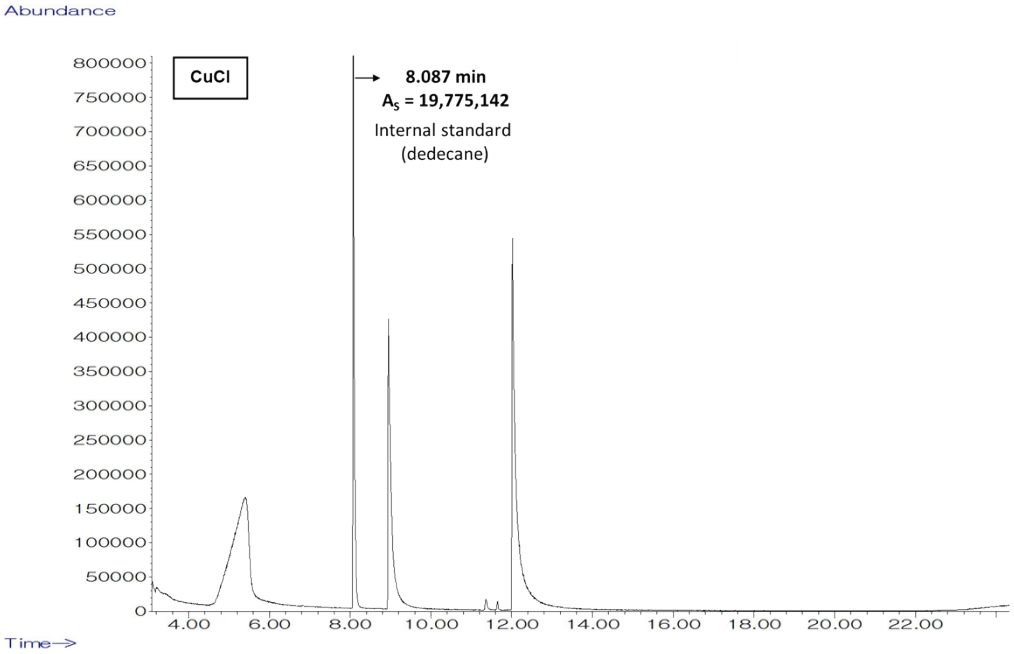


Table S5. Peak area of dodecane as an internal standard and 4-biphenylboronic acid pinacol ester as a product.

Reagent	Yield (%)	Area (Internal standard)	Area (Product)
Im-MOF-3	33.8	43543201	176953998
Im-MOF-1	1.3	57731073	8675993
CuCl	0.0	19775142	0