Supporting information for

## Halide Directed Synthesis of an In-derived Metal-organic Framework with Two Unique Metal Centers and Isolation of its Potential Synthetic Precursor

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#### **Experimental details**

#### **General Considerations**

Tetraethylammonium chloride, tetraethylammonium bromide, and tetraethylammonium tetrafluoroborate were purchased from Sigma Aldrich and used as received. Biphenyl-4,4<sup>-</sup>- dibarboxylic acid was purchased from TCI and used as received. InCl<sub>3</sub> was received as a generous gift from the University of Toledo – Department of Chemistry and used as received.

NMR data were collected on a 400 MHz Bruker Avance NMR Spectrometer.

#### **X-ray Powder Diffraction**

Powder XRD patterns of small samples were collected on a Bruker AXS X8 Prospector CCD single crystal diffractometer using the "pilot" plugin for collection of multicrystalline XRD patterns. The instrument is equipped with a copper IµS microsource with a laterally graded multilayer (Goebel) mirror for monochromatization ( $\lambda = 1.54178$  Å, beam size 0.1-0.2 mm) and an ApexII CCD area detector. Powder samples were thoroughly ground to assure a representative number of crystallites to be present in the X-ray beam. Powder samples were mixed with small amounts of mineral oil and mounted onto a 0.4 mm diameter Mitegen micromesh mount for data collection. Samples were centered in the beam using the instrument's mounting microscope video camera. Data were collected in an emulated theta-2theta setup using the Apex2 software package of Bruker AXS. The sample mount was aligned horizontally ( $Chi = 0^{\circ}$ ) and theta angles were set to eight different angles between 12 and 96° to cover a range equivalent to a 0 to 110° range of a powder X-ray diffractometer operated in Debye Scherrer mode (omega angles of each run were set to half the theta values). Samples were rotated around the mount's spindle axis during measurement (360 rotation around phi), typical exposure times were 30 seconds per frame collected. The eight individual patterns taken were corrected for unequal sample to detector surface distance ("unwarped") and were combined into one continuous pattern using the "pilot plugin" software embedded in the Apex2 software package. Data were integrated over 2theta, converted in powder XRD patterns in Bruker "raw" format and were further processed with standard powder XRD software packages.

#### Synthesis of YCM-41

To a premixed solution of DMF (18 mL) and dioxane (12 mL) was added InCl<sub>3</sub> (0.114 g, 0.500 mmol, 1.00 equiv). To this solution, tetraethylammomium (TEA) X (X = Cl: 0.170 g, 1.00 mmol, 2.00 equiv; Br: 0.216 g, 1.00 mmol, 2.00 equiv: BF<sub>4</sub>: 0.224 g, 1.00 mmol, 2.00 equiv) was added and the flask was swirled. Biphenyl-4.4'-dicarboxylic acid (0.298 g, 1.23 mmol) was added to the flask and the solution was sonicated for 15 minutes. Following sonication, the solution was filtered through a GE 25 mm PVDF syringe filter (0.45  $\mu$ m) in 6 mL portions into individual 20 mL scintillation vials. Each vial was sealed with Teflon-lined caps and heated in an oven at 120 °C for 6 days. At this time, the vials were removed from the oven and cooled to room temperature. The contents of each individual vial were combined and washed with 40 mL (4 × 10 mL) DMF. The DMF was decanted and the crystals were dried *in vacuo* yielding 78 mg of MOF in 21% yield relative to In.



**Figure S1.** X-ray powder diffraction pattern of the experimental YCM-41 (red) and calculated YCM-41 (black).

### **Digestion of YCM-41**

NMR digestion analysis was performed by treating 20 mg isolated YCM-41 with 1%  $HNO_3$  in DMSO-D<sub>6</sub> (0.75 mL).



**Figure S2.** <sup>1</sup>H NMR spectrum (DMSO-d<sub>6</sub>, ambient temperature) of YCM-41 following digestion of MOF with three drops of nitric acid.

### **Stability Studies**

To a 20 mL vial charged with YCM-41 (30 mg) that was previously desolvated under reduced pressure at room temperature, was added the solvent of study (5 mL). The vial was sealed with a Teflon-lined cap and shaken on a ThremoFisher MaxQ orbital shaker at 100 rpm for one week at room temperature. The solvent was decanted off and the MOF was then analyzed via PXRD.



Figure S1. X-ray powder diffraction patterns from stability studies of YCM-41.

#### Single Crystal Structure Analyses

Data were collected using a Bruker Quest CMOS diffractometer with Mo-K $\alpha$  radiation ( $\lambda$  =

0.71073 Å) with an IµS microsource and laterally graded multilayer (Goebel) mirrors for monochromatization. Single crystals were mounted on Mitgen micromesh mounts using a trace amount of mineral oil and cooled in situ to 100(2) K for data collection. Frames were collected, reflections were indexed and processed, and the structures were solved by direct methods using APEX3.<sup>1</sup> The space groups were assigned and the structures were solved by direct methods using XPREP within the SHELXTL suite of programs<sup>2</sup> and refined by full matrix least squares against  $F^2$  with all reflections using Shelx12018<sup>3</sup> and the graphical interface Shelxle.<sup>4</sup> H atoms attached to carbon and nitrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with carbon hydrogen bond distances of 0.95 Å for alkene and aromatic C-H, 1.00, 0.99, and 0.98 Å for aliphatic CH, CH<sub>2</sub>, and CH<sub>3</sub>, and 0.88 Å for N-H moieties, respectively. Methyl H atoms were allowed to rotate, but not to tip to best fit the experimental electron density. Uiso(H) values were set to a multiple of U<sub>eq</sub>(O/C/N) with 1.5 for CH<sub>3</sub> and 1.2 for CH, CH<sub>2</sub>, and NH units, respectively. Details of disorder and other special considerations for each structure are given in the below and in the Crystallographic Information Files. Complete crystallographic data, in CIF format, have been deposited in the Cambridge Crystallographic Data Centre (CCDC). CCDC 1954267-1954270 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Local name: cjt\_1\_34d\_0m\_sq

# Table S1. Experimental details for YCM-41(Cl)

Crystal data	
Chemical formula	$C_{70}H_{40}Cl_{2}In_{3}O_{20} \cdot C_{8}H_{20}N \cdot C_{8}H_{17}N$
M <sub>r</sub>	1873.85
Crystal system, space group	Orthorhombic, <i>P</i> 222 <sub>1</sub>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	15.3566 (11), 9.3863 (6), 34.022 (2)
$V(\text{\AA}^3)$	4904.0 (6)
Ζ	2
Radiation type	Μο Κα
$\mu$ (mm <sup>-1</sup> )	0.82
Crystal size (mm)	0.2  imes 0.09  imes 0.08
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan SADABS 2016/2 <sup>3</sup>
$T_{\min}, T_{\max}$	0.655, 0.745
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	129451, 10080, 8384
R <sub>int</sub>	0.116
$(\sin \theta / \lambda)_{\text{max}} (\text{\AA}^{-1})$	0.626
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.047, 0.102, 1.04
No. of reflections	10080
No. of parameters	549
No. of restraints	118
H-atom treatment	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.0415P)^2 + 10.0224P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \text{ Å}^{-3})$	0.61, -1.31
Absolute structure	Refined as an inversion twin.

Absolute structure parameter	0.05 (4)
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Computer programs: Apex3 v2018.7-2,<sup>1</sup> SAINT V8.38A,<sup>5</sup> SHELXS97,<sup>2</sup> SHELXL2018/3,<sup>6</sup> SHELXLE Rev915.<sup>4</sup>

Refinement details:

Refined as a 2-component inversion twin.

For the disordered tetraethylammonium ion, a restraint (SIMU in Shelxl) was applied to the U<sup>ij</sup> components of disordered atoms, for those atoms closer than 2.0 Å (N2-C47). Equivalent bond distances involving the ethyl groups attached to nitrogen were restrained to be similar (SADI in Shelxl).

Carbon atom C22 is affected by disorder with a very minor halogen component that affect the position and ADP of C22, but that were too low in occupancy for full refinement. Instead, the distance C22 to C23 was restrained to a target value of 1.52(2) Å, and the ADPs of C22 and C23 were constrained to be identical.

The structure contains three solvent accessible voids of 645 Å<sup>3</sup> each (1285 Å<sup>3</sup> combined). The residual electron density peaks are not arranged in an interpretable pattern. The hkl file was instead corrected using reverse Fourier transform methods using the SQUEEZE routine<sup>7, 8</sup> as implemented in the program Platon. The resultant files were used in further refinement. (The FAB with details of the SQUEEZE routine is appended to the cif). The Squeeze procedure corrected for 431 electrons within the solvent accessible voids.

Local name: jjm\_3\_112\_d\_0m\_sq

# **Table S2.** Experimental details for YCM-41(Br).

Crystal data	
Chemical formula	$C_{70}H_{40}Br_2In_3O_{20} \cdot 2(C_8H_{20}N)$
$M_{ m r}$	1965.80
Crystal system, space group	Orthorhombic, <i>P</i> 222 <sub>1</sub>
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.3894 (19), 15.536 (4), 34.201 (7)
$V(\text{\AA}^3)$	4988.9 (18)
Ζ	2
Radiation type	Μο Κα
$\mu$ (mm <sup>-1</sup> )	1.55
Crystal size (mm)	$0.40 \times 0.20 \times 0.20$
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	SADABS <sup>3</sup>
$T_{\min}, T_{\max}$	0.485, 0.746
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	80376, 13363, 7492
R <sub>int</sub>	0.194
$(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$	0.715
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.100, 0.283, 0.99
No. of reflections	13363
No. of parameters	545
No. of restraints	605
H-atom treatment	H-atom parameters constrained
	$w=1/[\sqrt{\sigma^2(Fo^2)} + (0.1748P)^2]$
	where $P = (Fo^2 + 2Fc^2)/3$
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} \ (e \ \text{\AA}^{-3})$	2.88, -1.98
Absolute structure	Refined as an inversion twin.

Absolute structure parameter	0.12 (3)
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Computer programs: Apex2 v2014.11,<sup>9</sup> SAINT V8.34A,<sup>5</sup> SHELXS97,<sup>2</sup> SHELXL2014/7,<sup>6</sup> SHELXLE Rev714.<sup>4</sup>

Refinement notes: The structure consists of a relatively well defined metal-ligand framework, and interstitial areas filled with tetraethyl ammonium cations and solvate molecules. One ammonium cation is relatively well resolved, another is disordered and ill defined, and the third cation as well as solvate molecules are not resolved.

Due to the low data quality a global rigid body restraint was applied for all C, N and O atoms (RIGU in Shelxl). For the disordered tetraethyl ammonium cation an additional similarity restraint was applied.  $U^{ij}$  components of ADPs were restrained to be similar if closer than 2.0 Å. The C-C distances between carboxylate and ipso carbon atoms of phenyl rings were restrained to be 1.45 Å. The distances of the carboxylate C atoms to the next indium atom were refined to be all similar. Neighboring C atoms C22 and C23 were constrained to have identical ADPs. The two moieties of the disordered tetraethylammonium ion were restrained to be similar to the not disordered tetraethylammonium cation, and to have approximate local tetrahedral geometry around the nitrogen atom. A weak anti-bumping restraint was applied to keep atoms of the disordered moieties from approaching the main framework too closely. Subject to these conditions the occupancy ratio if the disordered cation refined to 0.56(3) to 0.44(3).

The structure contains two additional solvent and cation accessible voids of 649 Å<sup>3</sup> each. No substantial electron density peaks were found in the solvent accessible voids (less than two electron per cubic Angstrom) and the residual electron density peaks were not arranged in an interpretable pattern. The hkl file was thus corrected for using reverse Fourier transform methods using the SQUEEZE routine<sup>7, 8</sup> implemented in the program Platon.

The resultant files were used in the further refinement. (The FAB file with details of the Squeeze results is appended to the cif file). The Squeeze procedure corrected for 342 electrons within each of the two solvent accessible voids.

### Local name: CJT-1-01B

# **Table S3.** Experimental details for YCM-42.

Crystal data	
Chemical formula	$C_{14}H_8Cl_2InO_4 \cdot C_8H_{20}N$
$M_{ m r}$	556.17
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>
Temperature (K)	191
a, b, c (Å)	8.1788 (7), 19.2590 (16), 15.5205 (14)
β (°)	102.436 (3)
$V(\text{\AA}^3)$	2387.4 (4)
Ζ	4
Radiation type	Μο <i>Κ</i> α
μ (mm <sup>-1</sup> )	1.24
Crystal size (mm)	$0.1 \times 0.05 \times 0.05$
Data collection	· ·
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan SADABS 2016/2 <sup>3</sup>
$T_{\min}, T_{\max}$	0.413, 0.746
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	27201, 7323, 5859
R <sub>int</sub>	0.065
$(\sin \theta / \lambda)_{\text{max}} (\text{\AA}^{-1})$	0.719
Refinement	· ·
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.052, 0.136, 1.08
No. of reflections	7323
No. of parameters	275
H-atom treatment	H-atom parameters not defined
	W =1/[ $\sigma^2(Fo^2)$ + (0.0694P) <sup>2</sup> + 1.3185P] where P = (Fo <sup>2</sup> + 2Fc <sup>2</sup> )/3
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} \ (e \ \text{\AA}^{-3})$	0.85, -1.64

Computer programs: Apex3 v2018.7-2,<sup>1</sup> *SAINT* V8.38A,<sup>5</sup> *SHELXS97*,<sup>2</sup> *SHELXL2018*/3,<sup>6</sup> SHELXLE Rev915.<sup>4</sup>

**Local name:** NA\_1\_65\_100

**Table S4.** Experimental details for YCM-51.

Crystal data		
Chemical formula	$C_8H_4Cl_2FInO_4 \cdot 2(C_2H_8N)$	
M <sub>r</sub>	461.02	
Crystal system, space group	Triclinic, $P\overline{1}$	
Temperature (K)	100	
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.9807 (5), 8.3911 (6), 16.7281 (12)	
$\alpha, \beta, \gamma$ (°)	76.835 (4), 89.407 (3), 68.085 (3)	
$V(\text{\AA}^3)$	882.13 (11)	
Ζ	2	
Radiation type	Μο Κα	
$\mu$ (mm <sup>-1</sup> )	1.67	
Crystal size (mm)	$0.6 \times 0.2 \times 0.2$	
Data collection		
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer	
Absorption correction	Multi-scan Twinabs 2012/1 <sup>10</sup>	
$T_{\min}, T_{\max}$	0.457, 0.747	
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	16864, 5457, 5152	
R <sub>int</sub>	0.106	
$(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$	0.714	
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.051, 0.139, 1.08	
No. of reflections	5457	
No. of parameters	205	
H-atom treatment	H-atom parameters constrained	
	w = $1/[\sigma^2(Fo^2) + (0.0582P)^2 + 5.3062P]$ where P = $(Fo^2 + 2Fc^2)/3$	
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \text{ Å}^{-3})$	2.07, -1.99	

Computer programs: Apex3 v2016.1-0,<sup>1</sup> SAINT V8.37A,<sup>5</sup> SHELXS97,<sup>2</sup> SHELXL2014/7,<sup>6</sup> SHELXLE Rev714.<sup>4</sup>

Refinement notes: The crystal under investigation was found to be a three domain nonmerohedric twin. The orientation matrices for the three components were identified using the program Cell\_Now,<sup>11</sup> with the second and third component related to the first by a 180° rotation around reciprocal (0 -1 1) and real (1 0 0), respectively. The three components were integrated using Saint and corrected for absorption using twinabs, resulting in the following statistics:

13435 data (3502 unique) involve domain 1 only, mean I/sigma 16.1
13424 data (3362 unique) involve domain 2 only, mean I/sigma 16.1
13890 data (3791 unique) involve domain 3 only, mean I/sigma 8.1
19405 data (6539 unique) involve 2 domains, mean I/sigma 17.1
4769 data (1863 unique) involve 3 domains, mean I/sigma 24.6

11 data (11 unique) involve 4 domains, mean I/sigma 8.3

The exact twin matrices identified by the integration program were found to be

Transforms h1.1(1)->h1.2(2)Transforms h1.1(1)->h1.3(3)-0.99964 -0.00081 0.000190.99672 0.00721 0.00024-0.68171 0.54311 -0.456360.90519 -0.99742 0.001440.68231 -1.54377 -0.543460.05835 -0.00595 -0.99930

Transforms h1.2(2)->h1.3(3) -1.00116 0.00282 -0.00316 -0.22381 -0.54462 0.45461 -0.73564 1.53941 0.54581

The structure was solved using direct methods with only the non-overlapping reflections of component 1. The structure was refined using the hklf 5 routine with all reflections of component 1 (including the overlapping ones), resulting in BASF values of 0.360(2) and 0.150(1).

The Rint value given is for all reflections and is based on agreement between observed single and composite intensities and those calculated from refined unique intensities and twin fractions (TWINABS).<sup>10</sup>

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