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Framework Isomerism in a Series of btb-Containing In-Derived Metal−Organic Frameworks

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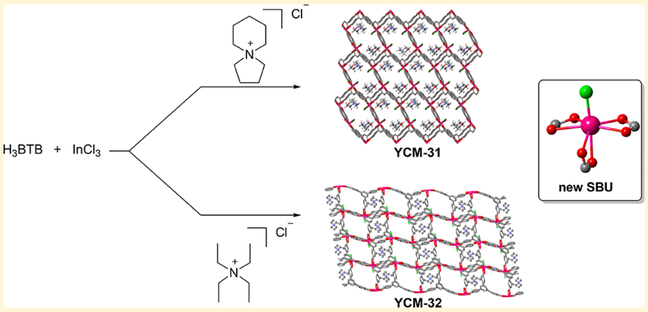
Supporting Information

ABSTRACT: The discovery of new inorganic building units for metal−organic framework (MOF) synthesis remains challenging. We hypothesized that incorporation of X-type halogen capping ligands on indium-building units would yield a series of previously unknown frameworks and the placement of the halogen could lead to framework isomerism. Herein we report the synthesis of three new MOFs; two (YCM-31 and YCM-32) contain an $[In(CO_2R)_3Cl]^-$ secondary building unit (SBU) and are framework isomers of each other. A third new MOF, ZJU-28′, contains an $[In(CO_2R)_4]^-$ SBU and is a framework isomer of the known MOF ZJU-28. The conditions to control the syntheses of these isomers through ammonium-cation templation, along with the rationale for their formation are discussed.



The synthesis of metal−organic frameworks (MOFs) is a constantly evolving art.[1−6] Derived from an organic linker and an inorganic node, there are nearly infinite possible self-assembly outcomes.[7] However, each linker-node combination often leads to a single privileged structure. Recently, there have been several reports of linker-node combinations that lead to multiple, condition-controlled, framework isomers.[8−11] The term framework isomerism is often confused with polymorphism. The two terms differ in that polymorphs have identical chemical composition but pack in the solid-state in different ways. MOF framework isomers must have the same chemical composition of the architectural network, but the guest molecules that reside within the structure (i.e., solvent, cations, etc.) can vary and thus would prohibit the strict use of the term polymorphism even when discussing frameworks that have identical architectural formulas that pack in different ways. We have adopted the following definition of framework isomers as described by Zhou as "MOFs constructed from the same ligand and metal species that display different network structures."[12] Identifying the existence of these framework isomers and then controlling their selective synthesis is a nontrivial task that requires extensive condition screening once the privileged structure has been identified.[8,13,14]

Traditionally, the tools for manipulating framework isomerism have been temperature, solvent/templating molecule, reactant concentration, and pH.[15] Wu and Hou have shown that three unique framework isomers of Co-derived frameworks can be isolated depending on the mole fraction of 1,4-dioxane or THF added to a $CH_3CN/CH_3OH/H_2O$ solvent mixture.[16] Serra-Crespo and Gascon[17] and Hu[18] independently demonstrated the temperature dependence of lanthanide-derived MOFs, where the more densely packed (enthalpically favored) framework isomers form as the reaction temperature increases. Zou has shown a pH dependence on the synthesis of MIL-101(V) (at high pH) and MIL-88B(V) (at low pH).[19] We have previously reported the synthesis of framework isomers of anionic In-derived MOFs as a function of charge balancing guest cation, where the $Me_2NH_2^+$ counterion led to the three-dimensional interpenetrated framework ATF-1, while Et_4N^+ yielded the two-dimensional architecture YCM-21-TEA (YCM = Youngstown Crystalline Material).[20] The challenge in controlling MOF isomerism is most apparent when examining the Zn-zeolitic imidazolate frameworks (ZIFs), where to date 14 different framework isomers containing the chemical formula $Zn(Im)_2$ (Im = imidazolate) have been independently synthesized.[21] Achieving phase-pure synthesis of these isomers has been challenging and has been achieved in select cases using additives,[22,23] complex solvent mixtures,[24] and mechanochemistry.[21]

Previously we reported the synthesis of YCM-22, an In-derived one-dimensional coordination polymer containing a dianionic $[InCl_3(\kappa^2\text{-}O_2CAr)_2]^{2-}$ SBU.[20] This unprecedented polyhalogenated In-center inspired us to pursue the synthesis of other In-X (X = halogen)-containing coordination polymers,

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specifically MOFs, and to explore their isomeric possibilities. In 2009, Bu reported the synthesis of a two-dimensional MOF containing the anionic $[\mathrm{In}(\kappa^2\text{-}O_2CAr)_2(\kappa^1\text{-}O_2CAr)Cl(OH_2)]$ building unit.[25] Wang and Fan, in 2018, reported the synthesis of a neutral one-dimensional coordination polymer containing an $\mathrm{In}(\mu\text{-}O_2CAr\text{-}\kappa O{:}\kappa O')_4(OH_2)Cl$ center.[26] Recently Liu and Ma reported MOFs containing $[\mathrm{InX_2(CO_2R)_2}]^-$ (X = halide) building units.[27] To this end, the monochlorinated $[\mathrm{In(CO_2R)_3Cl}]^-$ SBU was targeted for the synthesis of a two- or three-dimensional MOF. While the proposed In-center is tetracoordinate allowing for the adoption of a pseudotetrahedral or pseudosquare planar coordination geometry, it is only tritopic (due to the halogen ligand occupying one of the coordination sites on In), which would allow for either a trigonal pyramidal or T-shaped connectivity within the framework respectively (Figure 1). Our successful efforts to synthesize such building units and their role in framework isomerism are described herein.

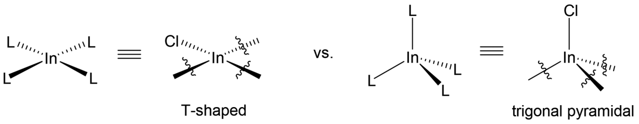

Figure 1. Coordination modes of tetracoordinate tritopic In. Squiggle lines indicate that In is bound to ligands connecting the rest of the framework.

Successful synthesis of the $[\mathrm{In(CO_2R)_3Cl}]^-$ SBU was first realized when $\mathrm{InCl_3}$ (1.00 equiv) was treated with 4,4′,4″-benzene-1,3,5-triyl-tribenzoic acid ($\mathrm{H_3BTB}$) (0.47 equiv) and the spirocyclic ammonium cation spPP**Cl** (1.00 equiv) in a mixture of DMF, dioxane, and water at 120 °C yielding the new MOF YCM-31-spPP (Figure 1). Note that the term YCM-31 is the descriptor for the anionic framework of molecular formula $C_{27}H_{15}ClInO_6$ only and does not contain information about guest cations or solvent. YCM-31 is a two-dimensional framework comprised of *hcb* nets with an A,B repeating pattern and 13.3 Å × 7.2 Å channels. The anionic inorganic node in YCM-31-spPP is charge-balanced by the spPP ammonium cation, which participates in cation-π interactions with the arene closest to the carboxylate of the BTB linker. The SBU has an average C−In−C angle of 114°(where C is the carbon of the carboxylate linker), indicating a distorted trigonal pyramidal geometry.

Strikingly, when a fresh reaction batch of $\mathrm{InCl_3}$ (1.00 equiv), $\mathrm{H_3BTB}$ (0.47 equiv), and spPP**Br** (1.00 equiv) in a mixture of DMF, dioxane, and water was heated to 120 °C, the new MOF YCM-32-spPP was synthesized (Figure 3). Note that the term YCM-32 is the descriptor for the anionic framework of molecular formula $C_{27}H_{15}ClInO_6$ only and does not contain information about guest cations or solvent. YCM-32 is a three-dimensional, periodic structure comprised of 3L5 net repeating units, containing the targeted $[\mathrm{In(CO_2R)_3Cl}]^-$ SBU. The periodic layers of YCM-32 are not interpenetrated but are discrete frameworks with 7.6 × 7.2 Å pores perpendicular to the planes of the layers. In YCM-32-spPP, each anionic center is counterbalanced with a $[\mathrm{spPP}]^+$ cation that also participates in cation-π interactions with the arenes of the BTB linker. Like YCM-31, the SBU has an average C−In−C angle of 114° (where C is the carbon of the carboxylate linker), indicating a distorted trigonal pyramidal geometry. The key difference between the two structures is that in YCM-31, the In−Cl bond always points in the same direction leading to a continuous flat sheet, while in YCM-32 the In−Cl bond points in alternatingly opposite directions allowing for the sheet to wrap around on

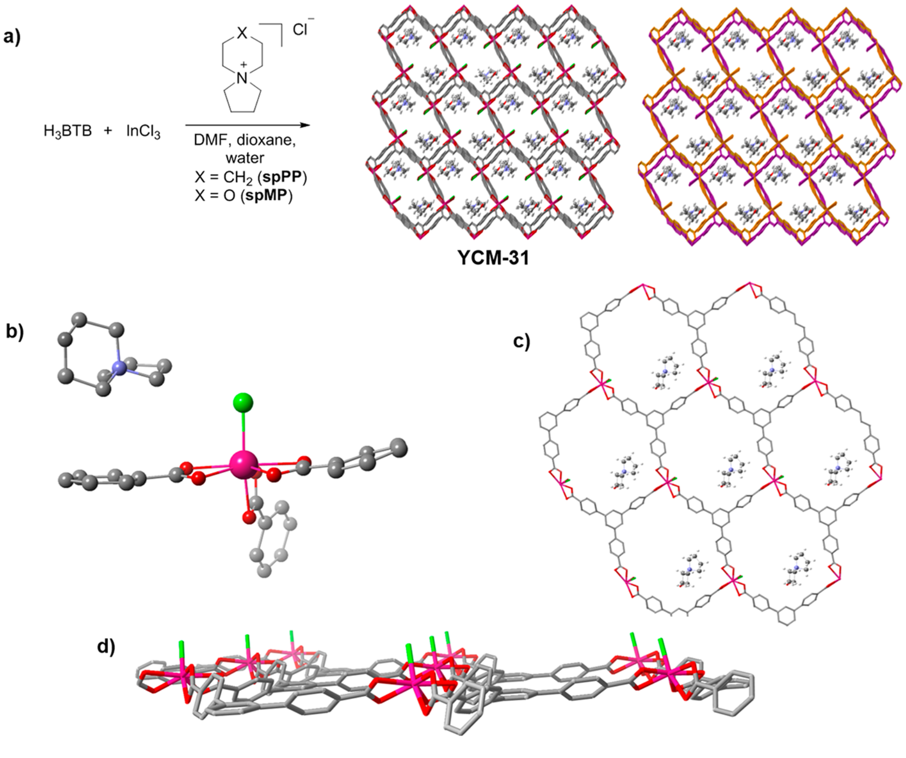

Figure 2. (a) Synthesis and structure of YCM-31 along with individual frameworks color-coded purple and orange, (b) single node of YCM-31 with spPP cation, (c) Single *hxl* sheet of YCM-31 with spMP cation, (d) single sheet of YCM-31 rotated 90, cation deleted for clarity.

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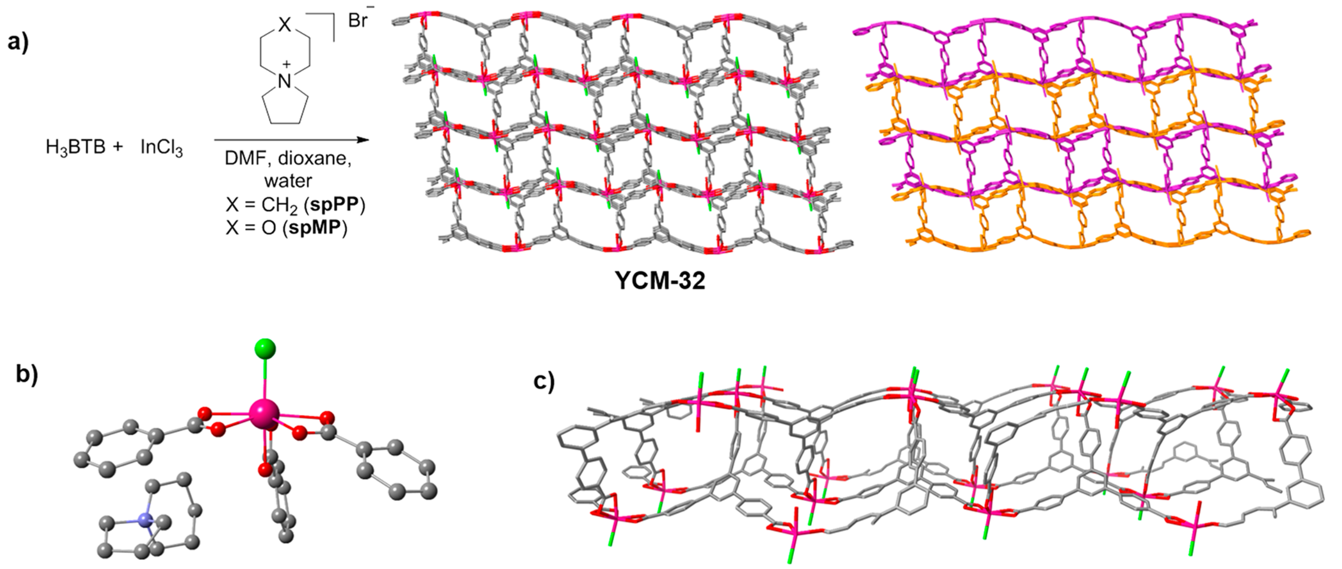

Figure 3. (a) Synthesis and structure of YCM-32 along with individual frameworks color-coded purple and orange, (b) a single node of YCM-32 with the spPP cation, (c) single periodic unit of YCM-32.

itself making a three-dimensional layer (Figure 2d vs Figure 3c). Since both the frameworks of YCM-31 and YCM-32 have identical chemical formulas and the geometrical difference (i.e., different nets) between the two architectures is dictated by orientation of the In-node, YCM-32 can be considered a framework isomer of YCM-31 (Table 1).

Table 1. Formulaic Comparison of btb-Containing In-derived MOFs

MOF	chemical formula[a]	node	net[b]
ZJU-28	$C_{36}H_{20}InO_8$	$[In(CO_2R)_4]^-$	jcy
ZJU-28′	$C_{36}H_{20}InO_8$	$[In(CO_2R)_4]^-$	ofp
YCM-31	$C_{27}H_{15}ClInO_6$	$[In(CO_2R)_3Cl]^-$	hcb
YCM-32	$C_{27}H_{15}ClInO_6$	$[In(CO_2R)_3Cl]^-$	3L5

[a] Formula are of the anionic network only. [b] Nets were determined via cif file submission to TOPOSPro at www.topospro.com.

Consistent with the behavior of other anionic In-derived MOFs, both YCM-31 and YCM-32 decompose in the presence of polar protic solvents such as H_2O, ethanol, 1 M NaOH, 1 M HCl, and acetic acid. However, these materials are stable in polar aprotic solvents such as DMF, acetonitrile, dioxane, and dichloromethane.

This subtle balance between YCM-31 and YCM-32 prompted us to explore this chemistry more fully by examining the roles of temperature, concentration, and source of the ammonium halide on the outcome of the reaction. The results are summarized in Table 2. Chloride and bromide salts of $[spPP]^+$, $[spMP]^+$, and $[Et_4N]^+$ were examined from 0.37 to 1.0 equiv relative to $InCl_3$. Each set of experimental conditions was screened at 60, 80, 100, and 120 °C and repeated at least three times. After 5 days at 60 °C, none of these experimental conditions consistently produced any MOF, and thus those results are not included in the table. Additionally, under many of the test conditions and when no ammonium cation is used (data not in table), the previously reported $[In(CO_2R)_4]^-$-derived MOF ZJU-28 was synthesized.[28] When additional cations *N*-butylpyridinium (**1**), *N*-benzyl-triethylammonium (**2**), cinchonium (**3**), diisopropylethylammonium (**4**), and *N*-butyl-*N*-methylmorpholinium (**5**) (Figure 4) were screened only the formation of ZJU-28 was observed.

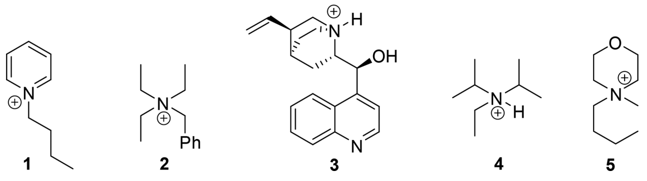

Figure 4. Structure of additional cations screened.

Lowering the amount of spPPBr used to less than 1.00 equiv relative to $InCl_3$ led to exclusive formation of $[In(CO_2R)_4]^-$ containing ZJU-28. Similar results were obtained when the temperature was lowered below 120 °C. These results revealed that YCM-32-spPP could only be accessed using 1.00 equiv of spPPBr at 120 °C. However, YCM-31-spPP could be accessed under a more diverse set of conditions; however, routinely obtaining phase-pure YCM-31 could only be achieved with 1.00 equiv of spPPCl at 120 or 0.75 equiv of spPPCl at 100 °C. All other conditions yielded either phase-pure ZJU-28 or batches would inconsistently form phase-pure vials of either YCM-31 or YCM-32.

When the morpholine derived $[spMP]^+$ cation was deployed, YCM-32 could only be synthesized using 1.00 equiv of the bromide salt at 120 °C. Using spMPBr under any other of our conditions yielded solely ZJU-28. Deployment of spMPCl also led primarily to ZJU-28, although occasionally the material was contaminated with YCM-31 or a previously unknown framework isomer of ZJU-28 (Figure 5) referred to as ZJU-28′. Single-crystal X-ray diffraction revealed that ZJU-28′ is a three-dimensional 2-fold interpenetrated structure containing an $[In(CO_2R)_4]^-$ node. Both ZJU-28 and ZJU-28′ have molecular formulas of $C_{36}H_{20}InO_8$. However, ZJU-28 is comprised of two interpenetrated jcy nets, while ZJU-28′ is comprised of two interpenetrated ofp nets. The two frameworks differ further in that ZJU-28′ is porous along two Cartesian coordinates, while ZJU-28 is a channel MOF and is porous only along one single axis. Unfortunately, efforts to find

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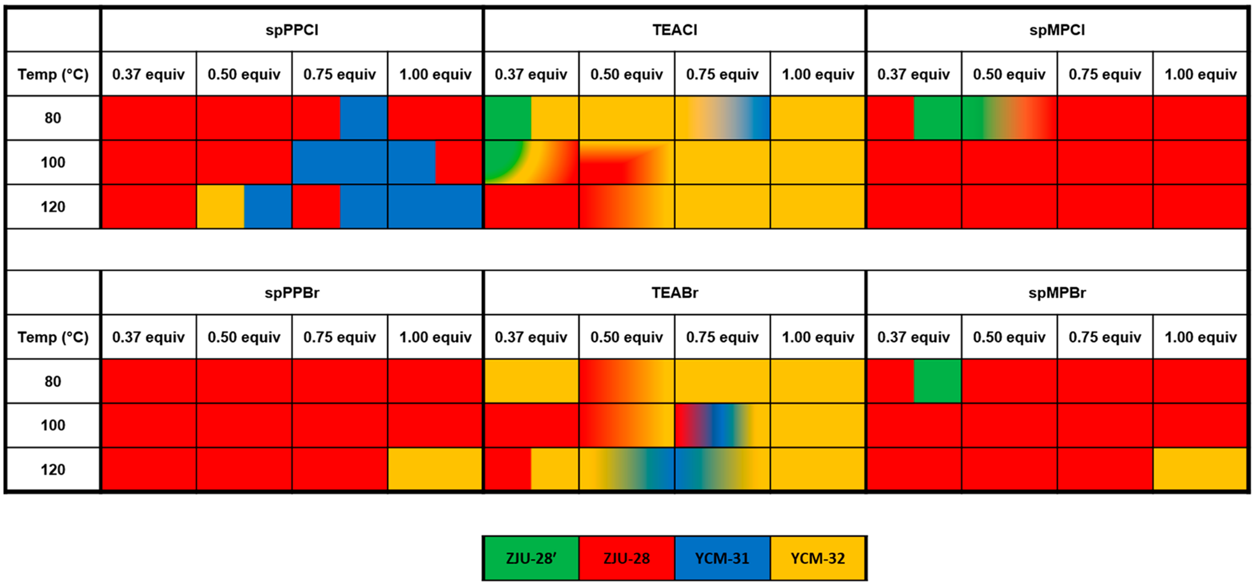
Table 2. Summary of Synthesis Conditions[a]



	spPPCl				TEACl				spMPCl			
Temp (°C)	0.37 equiv	0.50 equiv	0.75 equiv	1.00 equiv	0.37 equiv	0.50 equiv	0.75 equiv	1.00 equiv	0.37 equiv	0.50 equiv	0.75 equiv	1.00 equiv
80	🟥	🟥	🟥🟦	🟥	🟩🟧	🟧	🟧→🟦	🟧	🟥🟩	🟩→🟥	🟥	🟥
100	🟥	🟥	🟦	🟦🟥	🟩→🟧→🟥	🟥→🟧	🟧	🟧	🟥	🟥	🟥	🟥
120	🟥	🟧🟦	🟥🟦	🟦	🟥	🟥→🟧	🟧	🟧	🟥	🟥	🟥	🟥

	spPPBr				TEABr				spMPBr			
Temp (°C)	0.37 equiv	0.50 equiv	0.75 equiv	1.00 equiv	0.37 equiv	0.50 equiv	0.75 equiv	1.00 equiv	0.37 equiv	0.50 equiv	0.75 equiv	1.00 equiv
80	🟥	🟥	🟥	🟥	🟧	🟥→🟧	🟧	🟧	🟥🟩	🟥	🟥	🟥
100	🟥	🟥	🟥	🟥	🟥	🟥→🟧	🟥→🟦→🟧	🟧	🟥	🟥	🟥	🟥
120	🟥	🟥	🟥	🟧	🟥🟧	🟧→🟦	🟦→🟧	🟧	🟥	🟥	🟥	🟧

🟩	🟥	🟦	🟧
ZJU-28′	ZJU-28	YCM-31	YCM-32

[a] The colors in the boxes indicate the synthetic outcomes of the given conditions (green = ZJU28′, red = ZJU-28, blue = YCM-31, orange = YCM-32). Note gradient coloring represents phase-impure samples. Boxes with two distinct colors are used when phase-pure vials of each sample could be isolated, but not in a controllable fashion. Phase identity was determined via powder X-ray diffraction. Phase impurity is purely qualitative.

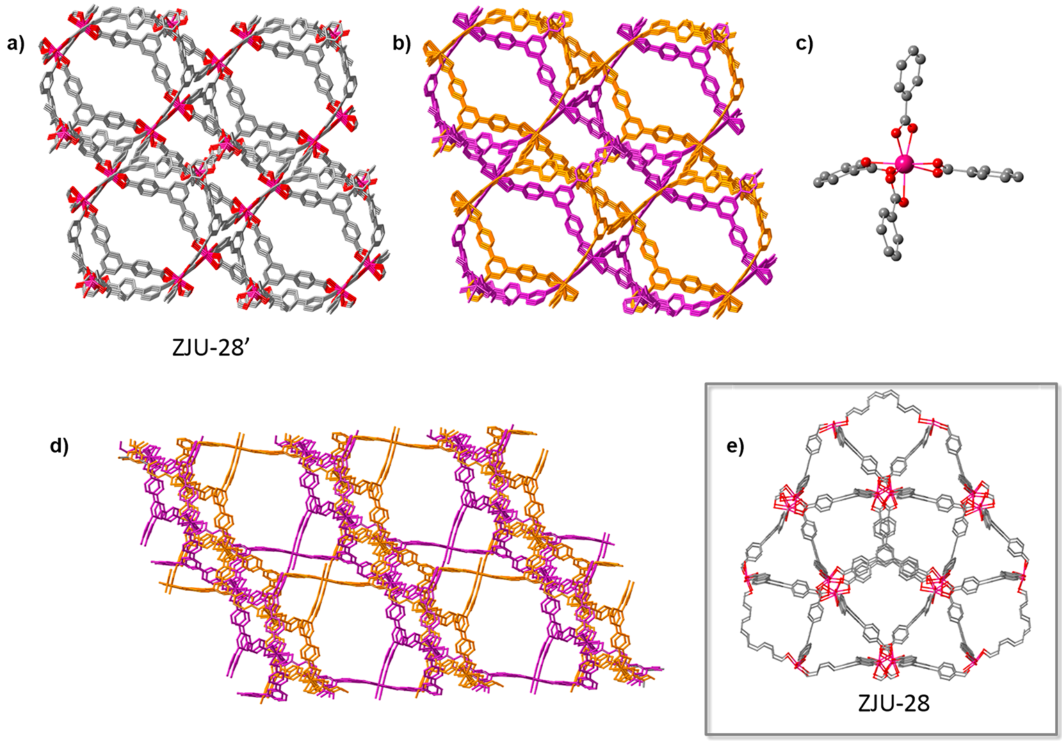


Figure 5. (a) Structure of ZJU-28′ (b) structure of ZJU-28′ with individual frameworks color-coded purple and orange. (c) Single node of ZJU-28′, (d) structure of ZJU-28′ with individual frameworks color-coded purple and orange rotated 90° (e) structure of ZJU-28.

conditions to routinely isolate phase-pure ZJU-28′ have been unsuccessful.

By contrast the use of $[Et_4N]^+$ yielded YCM-32 across several sets of synthetic parameters. Specifically, the use of Et_4NCl yielded YCM-32 exclusively with Et_4NCl loadings of as little as 0.37 equiv when the reaction was kept at 80 °C. However, it was very difficult to get consistent results when Et_4NBr was used as an additive, yielding mixtures of ZJU-28, YCM-31, and YCM-32. We attribute this lack of selectivity to the formation of reactive In−Br bonds that can be displaced by either Cl^- or RCO_2^- leading to a complex distribution of polymerizable In-centers.[29] While the YCM-32 architecture can be accessed using bromide salts of $[spPP]^+$, $[spMP]^+$, and $[Et_4N]^+$, energy dispersive X-ray spectroscopy (EDS) of bulk samples of YCM-32 indicates no incorporation of bromide. However, when the single-crystal structure of YCM-32-spPP was solved, 18% of the In-halide bonds were determined to be In−Br bonds. In conjunction with the EDS data, we posit that the 18% Br-content is only descriptive of that particular crystal and not indicative of the bulk material. Lastly, analysis by N_2 sorption at 77 K produced no evidence for accessible porosity in YCM-31-spPP or YCM-32-Et_4N. This finding is consistent with the expectation for densely packed anionic frameworks hosting guest cations.

It is worth noting that the powder X-ray diffraction patterns of bulk YCM-32-Et_4N did not perfectly align with the calculated pattern determined from the crystal structure. However, Pawley refinement against the crystallographic models of each compound shows that the phase-pure bulk samples identified in Table 2 most closely resemble YCM-32. Additionally the unit cell was determined for several unique crystals harvested from bulk samples identified as phase-pure YCM-32; all were consistent with the unit cell from the solved crystal structure.

The question of why YCM-31 forms with spPPCl and YCM-32 forms with Et_4NCl is difficult to answer. One could hypothesize that the increased degrees of freedom associated with the Et_4N cation allows it to pack more tightly during MOF formation, leading to a more densely packed MOF. Conversely, the rigidity of the spirocycles does not allow packing optimization, which would lead to a less densely packed MOF. Consistent with this rationale, guest-free (no solvent or ammonium cations) solvent accessible void volumes for YCM-31 and YCM-32 were calculated by PLATON to be 50% and 23%, respectively. However, the lack of additional YCM-31 and YCM-32 structures containing alternate ammonium cations makes it difficult to confirm our hypothesis fully. To summarize the more tightly packed YCM-32 forms most readily in the presence of the more tightly packing Et_4N cation. Lastly, the effect on isomerism caused by the counter halide to the ammonium cation remains unclear. Unfortunately, the limited number of conditions that can yield YCM-32 from spPPBr prevents development of any significant conclusions at this time.

In summary we report the synthesis of two new isomeric monohalogenated In-derived MOFs. To our knowledge YCM-31 and YCM-32 represent the first MOFs containing the $[In(CO_2R)_3Cl]^-$ SBU. The synthesis of these materials is influenced via a cation template effect, in which the degrees of freedom of the ion has the potential to control the isomeric outcome of the reaction. Notably cations with more rotational degrees of freedom (tetraethylammonium) yield the more densely packed YCM-32.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.9b00611.

> Experimental details, synthetic procedures, PXRD, NMR, and crystallographic information (PDF)

Accession Codes

CCDC 1898166−1898170 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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