Halide Directed Synthesis of Indium Derived Metal-Organic Frameworks

by

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ABSTRACT

Herein I report the thesis work on halide directed synthesis of indium derived metal-organic frameworks (MOFs). Building upon work done by a previous graduate student, conditions to produce phase-pure MOFs were investigated by varying temperature and concentration of salt-additives. A phase table was compiled and data trends were observed, showing MOF isomerism between In-derived MOFs YCM-31 and YCM 32, as well as ZJU-28 and an isomer of ZJU-28.

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I.Introduction

Metal Organic Frameworks (MOFs)

Metal-organic frameworks (MOFs) are coordination polymers that are defined as macromolecular scaffold structures consisting of organic linkers and metal ion clusters commonly referred to as secondary building units (SBUs) (**Figure 1.**).[1, 2] From the vast number of metals and linkers, the potential combinations of MOFs could be almost infinite.

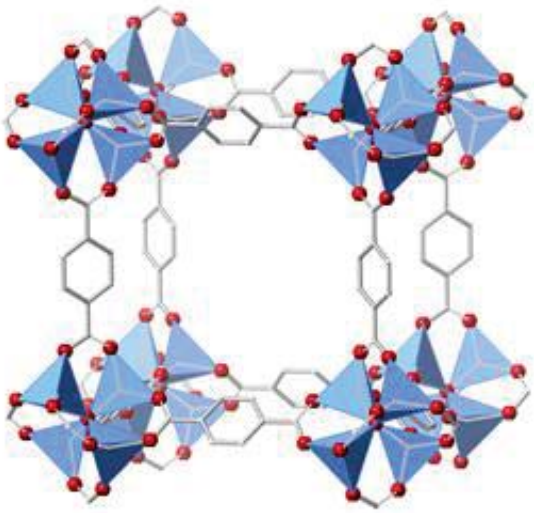


Figure 1. Generic MOF Structure. Purple area represents the metal cluster and the white sticks represent the organic linker

The first researchers to use the term metal-organic frameworks were Yaghi and his colleagues.[1, 2] From this research, the idea of creating crystalline materials that are linked through covalent bonds that have potential for a wide variety of applications was realized.[3] One of the attractive features of these new materials was their porosity, which makes them similar to porous inorganic materials (e.g., zeolites). Some MOFs have recorded surface areas that exceed their zeolite counterparts, such as NU-100, with a reported Brunauer-Emmet-Teller theory (BET) surface area of 6143 m^2/g.[3-6] High surface area and permanent

porosity allows MOFs to take up large amounts of materials suggesting that MOFs have potential applications for gas separation, water purification, etc.[3, 7-9]

Traditionally MOFs are synthesized in a one-pot procedure, which is often developed through extensive trial and error. Early MOFs were made using divalent metals and had excellent porosity leading to the promise for a variety of applications, although they were found to be unsuitable due to their lack of long-term stability in ambient conditions.[6, 10] Researchers such as Yaghi and colleagues created procedures to produce stable MOFs (MOF-5) when the solvent was removed from its pores using trivalent and tetravalent metal centers as well as by Lillerud and Ferey.[9, 11, 12] The stability of the bond between the metal and the organic linkers is a vital part of maintaining the integrity of the MOF. For practical applications, the MOF and its metal-organic linker would need to be more stable and resistant to hydrolysis.[13] These trivalent and tetravalent metals tend to have greater stability because of the decreased lability of the metal-oxygen bonds.[9, 14-16] Thus further investigation into more stable trivalent/tetravalent metal centered MOFs is needed.

Isomeric MOFs

MOFs are synthesized from the combination of metal clusters and organic linkers; the same building units can potentially combine in diverse ways to make different structures. These different structures are called 'framework isomers.[17] There are three classifications of framework isomers: orientation, conformational, and interpenetrated isomers (**Figure 2.**) [17-19] Orientation isomers are identical in all aspects, but the orientation of the ligand or SBU within the crystal may be different, creating isomers.[17-19] Conformational isomers are frameworks that are chemically the same but structurally distinct from one another by having different connectivity.[17] The final classification of framework isomers is interpenetrated, these isomers have an original structure that is noninterpenetrated, and the same framework interpenetrates itself and creates an isomer.[17]

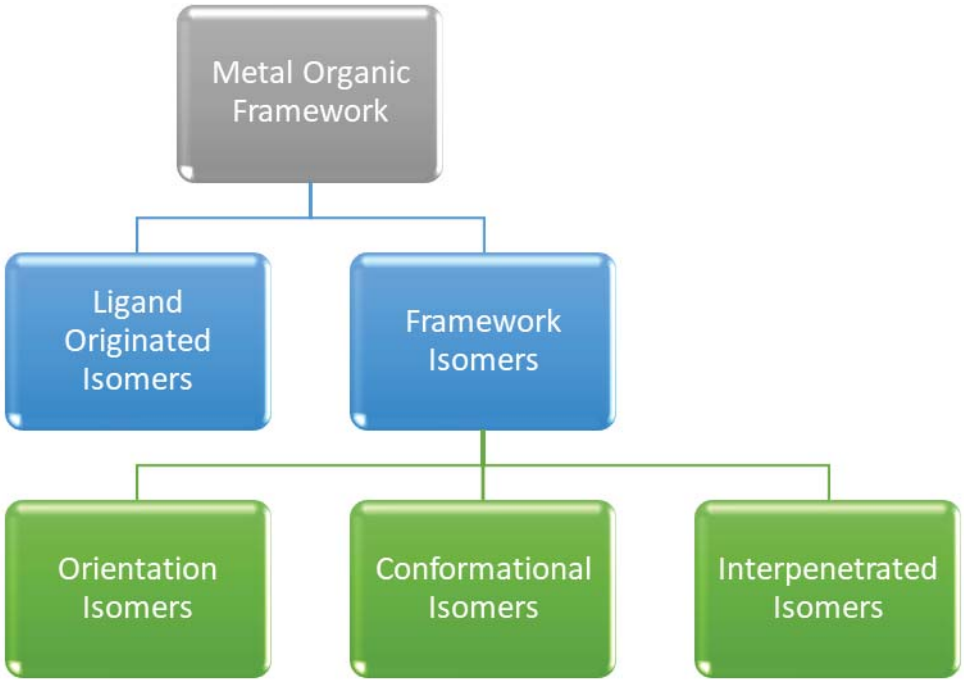
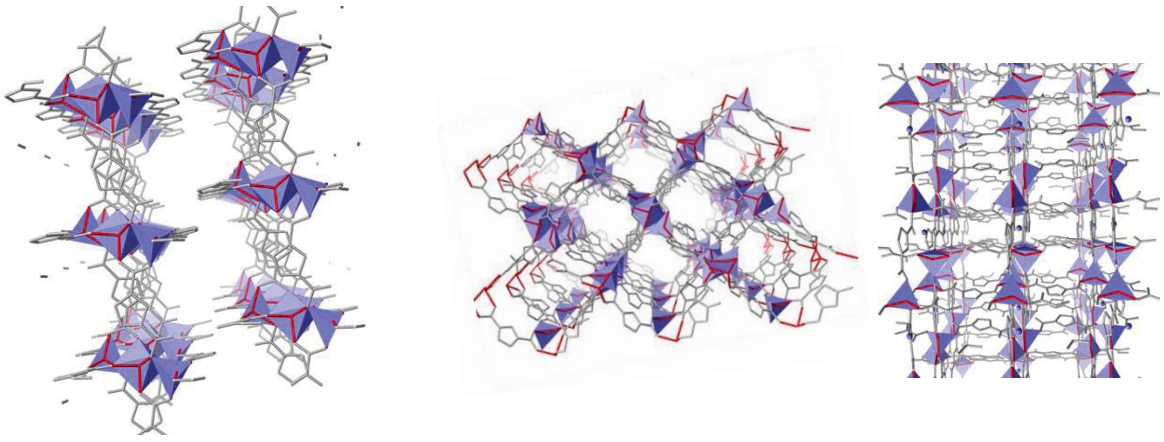


Figure 2. Hierarchy of isomerism as it applies to MOFs

Interpenetration refers to MOFs that have separate frameworks but are interwoven to create one extended network.[20]

A variety of factors can influence the way a framework forms; solvent, pH, concentrations, and temperature are a few factors. In 2012, the Ghosh research group investigated how temperature variation would affect the structure of the MOF synthesized.[21] They aimed to explore how constant reaction conditions with varying temperature would influence topology, different dimensionality, and unique properties of the anionic porous MOFs, synthesized from Zn(II), 2,5-furan dicarboxylic acid (H_2FDA), and DMF.[21] By simply varying the reaction temperature three MOFs were formed, $[Zn_{1.5}(FDA)_2(Me_2NH_2)]$ at 90 °C (**Figure 3A**), $[Zn_3(FDA)_4(Me_2NH_2)_2]$ at 120 °C (**Figure 3B** and $[Zn_{1.5}(FDA)_2(Me_2NH_2)]$ at 160 °C (**Figure 3C.**).[21] Sharing a general formula of



A B C

Figure 3. MOF structures, A$[Zn_{1.5}(FDA)_2(Me_2NH_2)]$, B $[Zn_3(FDA)_4(Me_2NH_2)_2]$, C $[Zn_{1.5}(FDA)_2(Me_2NH_2)]$

$[Zn_{1.5}(FDA)_2(Me_2NH_2)]_n$, all three MOFs are considered to be isomers of one another. [21] Interestingly once these MOFs were desolvated, a phase change occurred increasing the difficulty of classification and phase purity.[21]

Another example of metal-organic framework isomers is MIL-88 and MIL-101, investigated by Zou in 2013.[22] MIL-88 and MIL-101 are also topological framework isomers: they are both made from trinuclear metal−carboxylate nodes and 1,4-benzenedicarboxylate (BDC) linkers but their connectivity is different.[22] These distinct frameworks can be heated in ethanol to 200 °C to isomerize into MIL-47.[22] Zou's group went beyond temperature variation and explored how an additive may affect the solvothermal synthesis itself. MIL-47 is synthesized from vanadium chloride, BDC, ethanol, and HCl at 200 °C. [22] However, if the reaction temperature is lowered to 120 °C, MIL-88 is produced. If the temperature remains at 120 °C and HCl is not added MIL-101

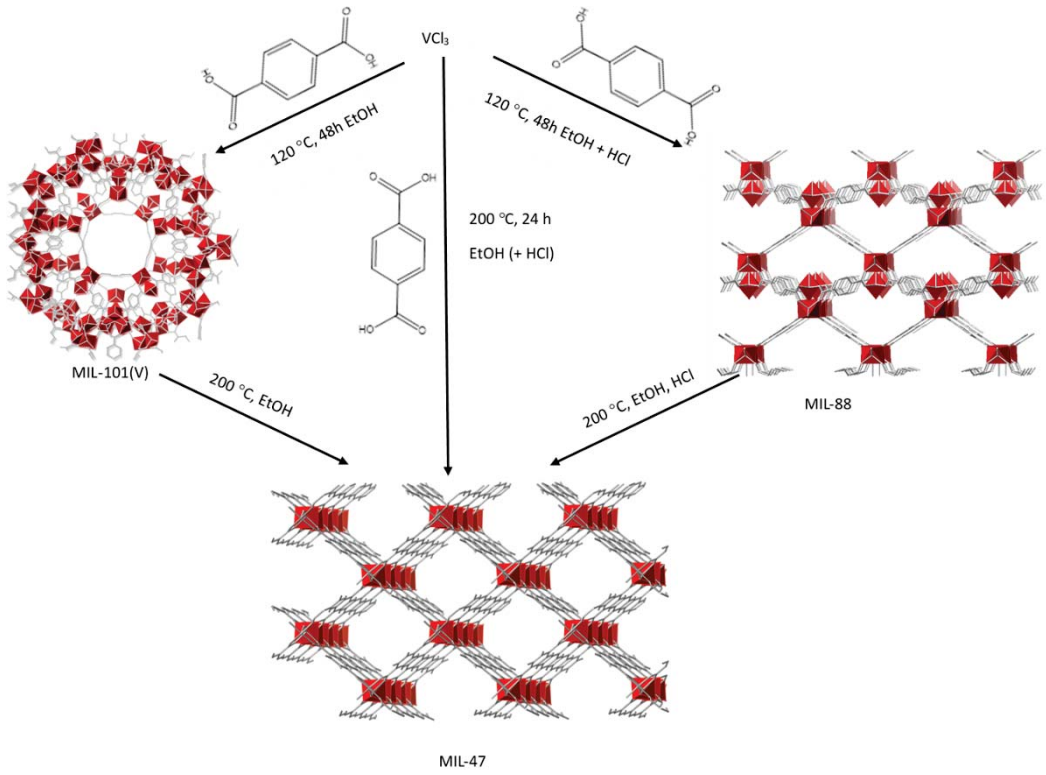


Figure 4. Schemes showing synthesis for MIL-101(V), MIL-88 and MIL-47

is produced (**Figure 4.**)[22] Isomerism is another possible pathway for manipulation of MOFs.

Indium MOFs

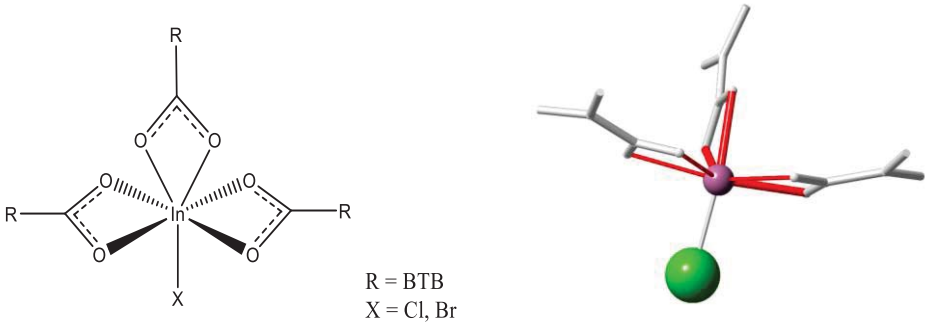


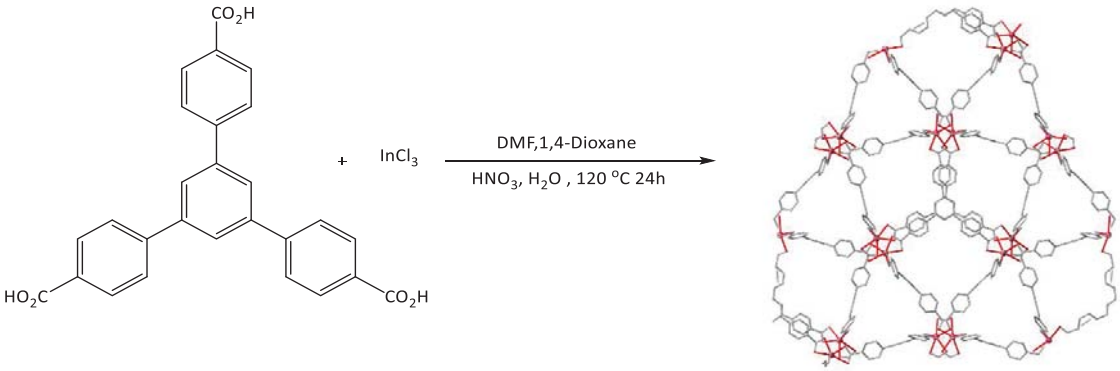
Figure 5. 2D and 3D representation of the Indium Node

There is a significant amount of reported porous and non-porous metal-organic frameworks that use transition metals as their inorganic component.[23] Although there has been a large number of reported MOFs that have divalent metal centers, comparatively there are less that incorporate heavier main group trivalent metals such as In(III).[23-25] As more MOF structures are reported in the literature, an increased understanding of how to control the macromolecular scaffold structure has become a more predominant issue.

Indium is a highly versatile element with respect to coordination abilities: it can bind up to seven X-type ligands and hold a formal charge of negative four (**Figure 5**)[26] Thus with this range of possible coordination, a vast combination of structures and overall formal charges can be obtained within the MOF. In addition to being anionic, indium-derived MOFs can also be neutral and cationic.[26, 27] One such example of an anionic 3-D interpenetrated indium MOF is ZJU-28 (**Scheme 1.**).[28] ZJU-28 is synthesized using benzene tribenzoic acid (H_3BTB) as the organic linker and indium chloride as the metal

source for the produced MOF. ZJU-28's largest pore size is ~9 Å, and the secondary building unit of ZJU-28 is pseudo-tetrahedral with the indium metal coordinating to four BTB linkers producing the 3-D framework.[28] By changing the indium center and inhibiting the binding of one or more carboxylates, there is potential to form new MOFs.

Halogenated MOFs



Scheme 1. The ZJU-28 Reaction Mixture and Crystal Structure

Metal-organic frameworks having two key parts, the organic linker and metal node, gives them the ability to be tuned and adjusted on either part. Halogenation on MOFs can be done in a few diverse ways, at the metal center or on the organic linkers.

In 2011, Allendorf and colleagues investigated monohalogenated metal-organic frameworks specifically monohalogenation on the organic linkers of IRMOF-2, using fluorine, chlorine, bromine and iodine as the halogens.[29] Halogens can help investigate how polarizability can effect adsorption into the pores.[29] Allendorf showed that IRMOF-2 could be synthesized isostructurally with functionalized organic linkers that had different halogens.[29]

In 2013, Van Der Voort and colleagues published a report about partially fluorinated MIL-47 and Al-MIL-53 through solvothermal synthesis using halogenated linkers.[30] Both MIL-47 and Al-MIL-53 are composed of 1,4-benzenedicarboxylate and metals nodes of Al for MIL-53 and V for MIL-47.[30] It has previously been shown that Al-MIL-53's organic linker can be functionalized with chloride and bromide. Through this study, it was found that MIL-47's rigid framework and Al-MIL-53's flexible framework could be partially functionalized with fluorine.[30] Halogenation of the organic linker can increase moisture stability, hydrophobicity, and adsorption ability.[30] Halogenation can sometimes alter the topology of a given framework. For example Al-MIL-53, when halogenated at the linker the aluminum metal center maintains a 3+ oxidation state. [30] MIL-47 with halogenated linkers undergoes oxidation at the vanadium metal center and topology is not affected when guest molecules are removed.[30] Having the ability to retain the topology of a MOF based on the presence or absence of guest molecules implies that halogenation can influence the breathing behavior.[15, 16, 31] Breathing is the expansion and contraction of the unit cell when the pore of a MOF is occupied and unoccupied by guest molecules.[16, 31, 32] Varying halogenation positions or types of halogenation would allow for different interactions with guest molecules and effects on topology.

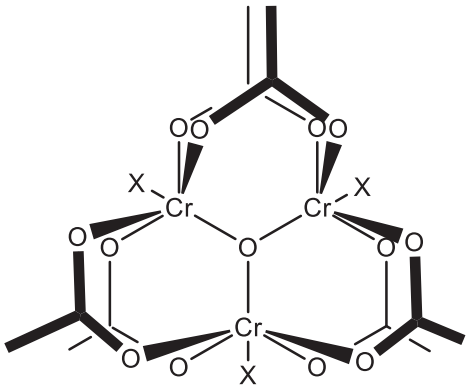


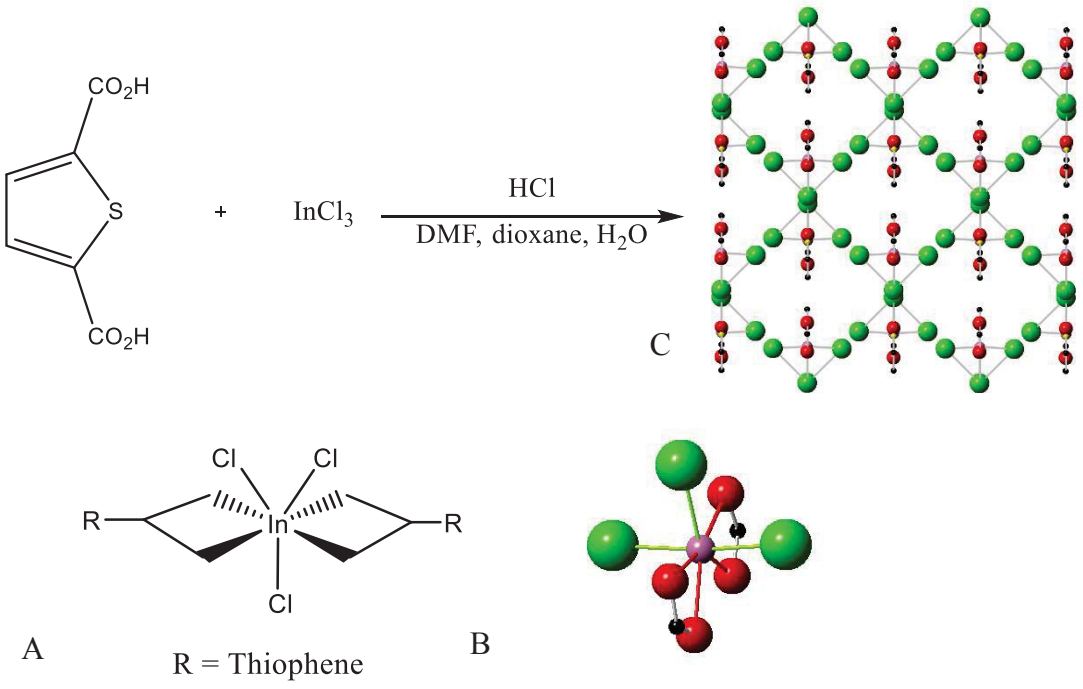
Figure 6. Cr-MIL-101 metal node

Both above examples are MOFs that have halogenation on the organic linker. An example of a MOF containing a halogen at the metal center would be Cr-MIL-101.[31] Cr-MIL-101 can be synthesized using $CrCl_3$ and terephthalic acid in water to produce a halogenated chromium node (**Figure 6.**).[31] The halogenation of the metal center opens the MOF up to the possibility of post-synthetic modification. Like the effects of halogenation, post-synthetic modification can affect stability, framework resistance to hydrolysis, and breathing behavior. Having a point on the metal node that can be replaced or can influence the overall stability of the MOF can be beneficial for tuning and synthesizing better MOFs that can be more applicable. Adding functional groups or halogens that can alter the polarity of the framework can increase desirable features such as framework resistance to hydrolysis that would cause decomposition.

Fan and colleagues recently reported in the literature a 1D indium chain that could hydrogen bond to create more complex supramolecular structures.[33] This indium chain was synthesized from a mixture of benzimidazole-5,6-dicarboxylic acid (H_3bidc) and indium chloride in acetonitrile, nitric acid, and water.[33] The reaction was heated to 120 °C for 24

hrs and then subsequently cooled to room temperature, producing crystals.[33] The neutral indium centers produced have four coordinating carboxylates, one water molecular and one chloride ion.[33] The 1D chains can interact with one another through hydrogen bonding of the chloride (nonclassical hydrogen bonds) with the H-N of the imidazole creating 2D layers.[33] Classical hydrogen bonds of the benzimidazole rings and carboxyls can then connect 2D layers creating a 3D structure.[33] This research shows that an indium center with single point halogenation can be synthesized.

Previous graduate student, Joseph J. Mihaly, synthesized and fully characterized halogenated@In-derived MOFs YCM-21 and YCM-31. YCM-21 has an indium center with three chlorides (**Scheme 2.**) and a connecting carboxylate group, and YCM-31 has one halogen and three carboxylates. YCM-21 has been published, YCM-31 and other

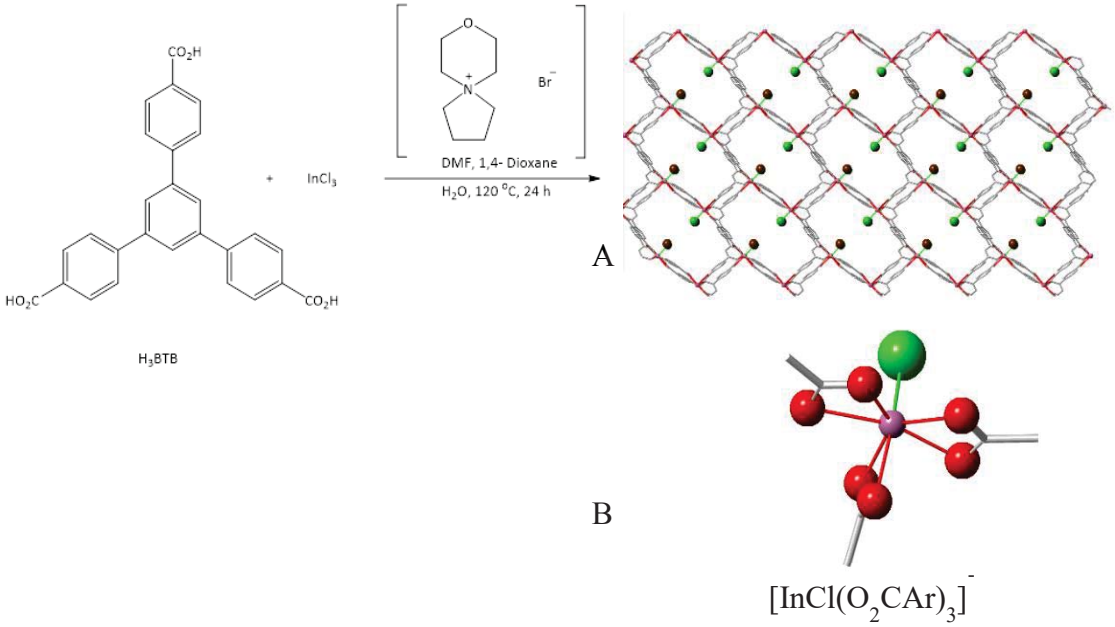


Scheme 2. YCM-22 reaction scheme, framework, and node, A) Chemdraw figure of the node in YCM-21, B) a 3D model of the node, C) the crystal structure of YCM-21

indium centers like it are novel for 2D and 3D frameworks.[27] Building upon this work and expanding the scope of investigation for YCM-31, I herein report the results for an exploration of how the concentration of different ammonium salt additives and temperature affect the formation of indium derived partially halogenated metal-organic frameworks.

II. Results and Discussion

YCM -31-spMPBr



Scheme 3. Original YCM 31 synthesis, A) The crystal structure of YCM-31-spMPBr, B) the indium node of YCM-31-spMPBr

Mihaly identified two MOF structures. The first being YCM-31, which can be synthesized through the treatment of indium chloride and H_3BTB were dissolved in a mixture of DMF and 1,4-dioxane, to the original mixture a solution of water and spirocyclic morpholinium bromide (spMPBr) were added, (**Scheme 3**). For this synthesis BTB was the organic linker and indium chloride the metal source. YCM-31 is a 2-D anionic MOF and has an A-B-A-B sheet pattern; this framework has the spirocyclic cations inside the pore of the MOF.[34] MOF sheets are different layers of a 2-dimensional MOF that repeat to create patterns such as A-A-A-A, A-B-A-B, etc (**Figure 7.**). YCM-31's SBU has a pseudo-square planar geometry due to the In-In-In *trans* bond angles of 180.00° and *cis* In-In-In

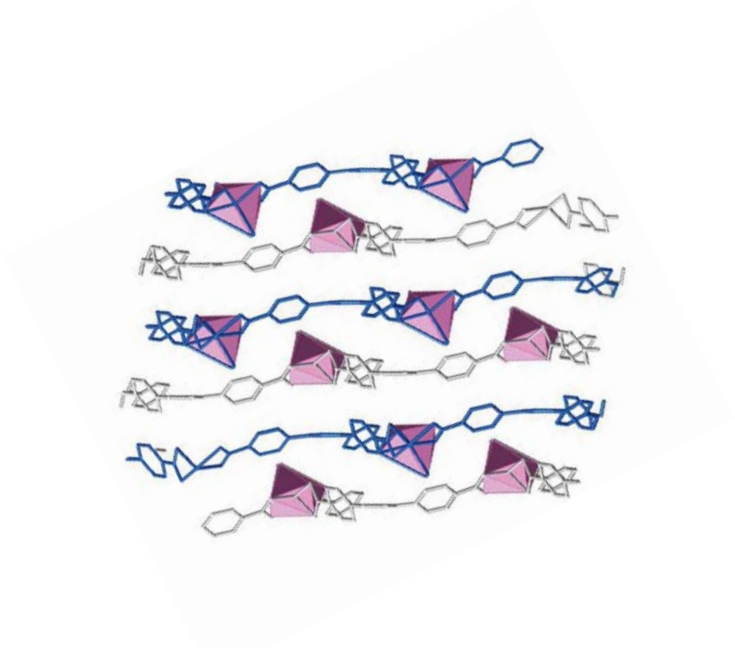
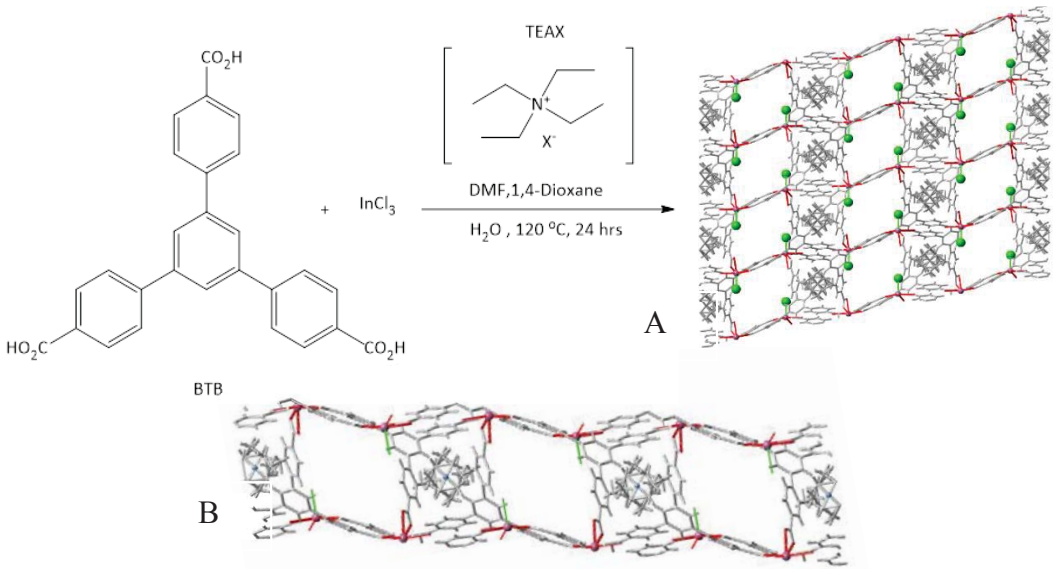


Figure 7. Crystallographic view over A-B-A-B sheet pattern

bond angles of 74.45° and 105.55°.[34] The pore size of YCM-31 is 17.72 Å x 8.83 Å, with the distance between sheets A-B when measuring from In-In being 9.0 Å and B-A being 11.3 Å.[34] YCM-31 has a single halogen connected at the indium node, this halogen is directed into the aperture.

YCM-32 TEACl



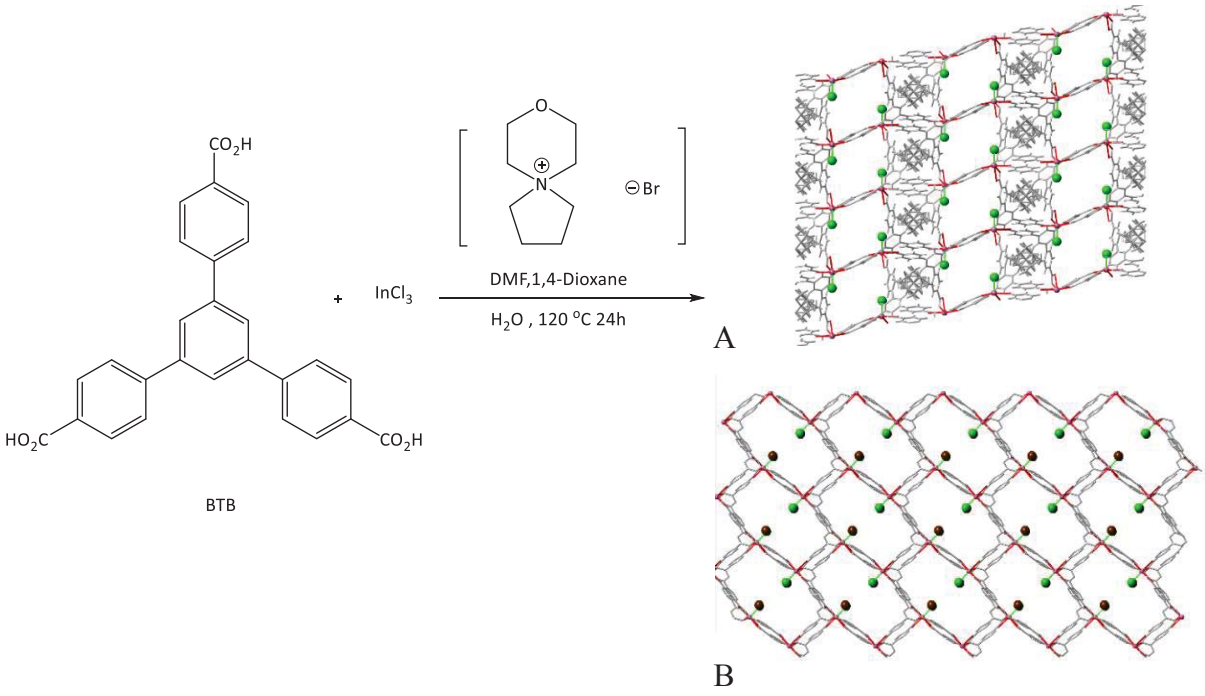
Scheme 4. Original YCM 32 synthesis, A) Crystal structure of YCM-32-TEACl, B) close view of the pore of YCM-32-TEACl

The second MOF synthesized by Mihaly was YCM-32 (**Scheme 4.**). Treatment of $InCl_3$ with H_3BTB in the presence of tetraethylammonium chloride (TEACl) yields a new 3D 2-periodic structure with a pore size of 9.3 Å by 9.0 Å, YCM-32. Unlike YCM-31 where crystallographically every pore contains the ammonium cation, there is a systematic absence in every other pore. Simple charge balancing suggested there was another crystallographically silent tetraethylammonium cation,[34] the presence of which has been confirmed via ^1H NMR analysis of the digested MOF. Also, like YCM-31, all indium centers are halogenated with chlorine.

One difference between YCM-31 and YCM-32 is the accessibility of the chlorine. The chlorine of YCM-31 points straight into the pore which is different from its isomer YCM 32. Because YCM 31 and YCM 32 are two MOFs that are chemically the same but

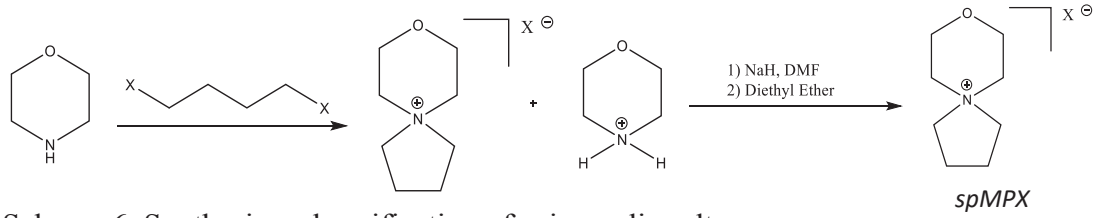
structurally distinct, they are considered conformational isomers of one another. Initially it was noted that YCM-32-TEA was confirmed crystallographically but when a bulk PXRD was taken the results showed that YCM-32-TEA represented only a small portion of the bulk sample. This was also found to be true with YCM-31-spMPBr: when single crystal data was taken it was not representative of the bulk sample. The main goal of the reported research was to reproduce these MOFs and to find conditions to produce phase pure MOFs that are consistently reproducible.

spMPX



Scheme 5. The YCM-3X-spMPX reaction, Crystallographic structures of potential outcomes from exploratory research A YCM-32 B YCM-31

Initially, attempts to reproduce YCM-31-spMPBr were unsuccessful (**Scheme 5.**), through a closer examination of each individual component it was found an impurity was hindering the synthesis. The original synthesis of YCM-31-spMP was difficult to reproduce due to the presence of the stoichiometric impurity, *N,N*-dihydro morpholinium



Scheme 6. Synthesis and purification of spirocyclic salts

halide in the salts used for synthesis. The impurities stopping MOF growth necessitated the development of a purification protocol. Treatment of the impure salts with sodium hydride

led to deprotonation of the dihydro-form, which could then be separated from the desired salt **(Scheme 6.).**

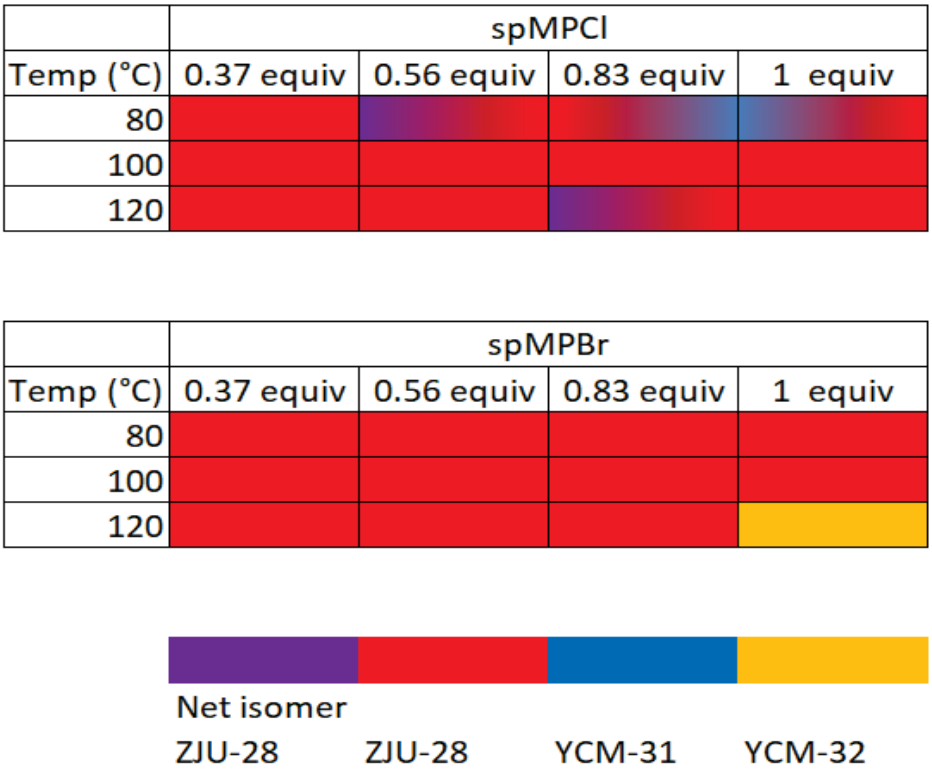
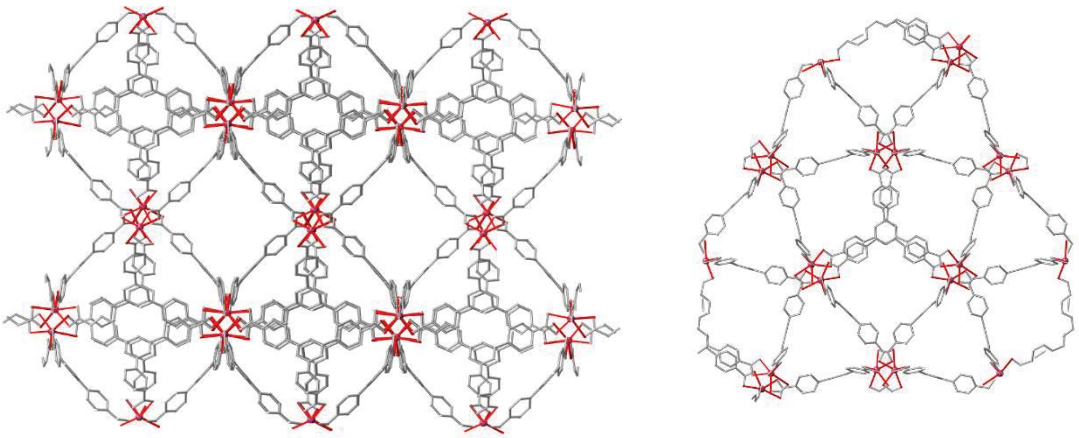


Figure 8. spMPX sections from phase table

After purifying the spirocyclic salt, spMPBr was used to reproduce the original reaction, 0.83 equivalents (relative to indium) at 120 °C. The treatment of indium chloride and H_3BTB in a DMF and 1,4 dioxane mixture with spMPBr salt and water was heated to 120 °C. However, there was no formation of halogenated MOF, only ZJU-28 was synthesized (**Figure 8.**). Decreasing salt concentration while remaining at 120 °C continues to produce ZJU-28. Changing the temperature over the varying concentrations of salt produces the same result of ZJU-28. When salt concertation is increased the shift in reaction conditions produces YCM-32-spMPBr in a phase pure.

Use of spMPCl was done to investigate the role of the counteranion of the additive on MOF formation; phase-pure synthesis of YCM-3X cannot be achieved. Although when higher concentrations (0.83 and 1.0 equiv) of spMPCl are used at a reaction temperature of 80 °C there is a mixed phase of ZJU-28 and YCM-31. At higher temperature (120 °C), with a mid-range equivalent of salt (0.56 and 0.83) there begins to form a net-isomer of ZJU-28 (**Figure 9.)**. Conditions to synthesize the ZJU-28 net isomer in phase-pure form are not yet known, but it does appear in significant quantities with ZJU-28 under the above conditions.



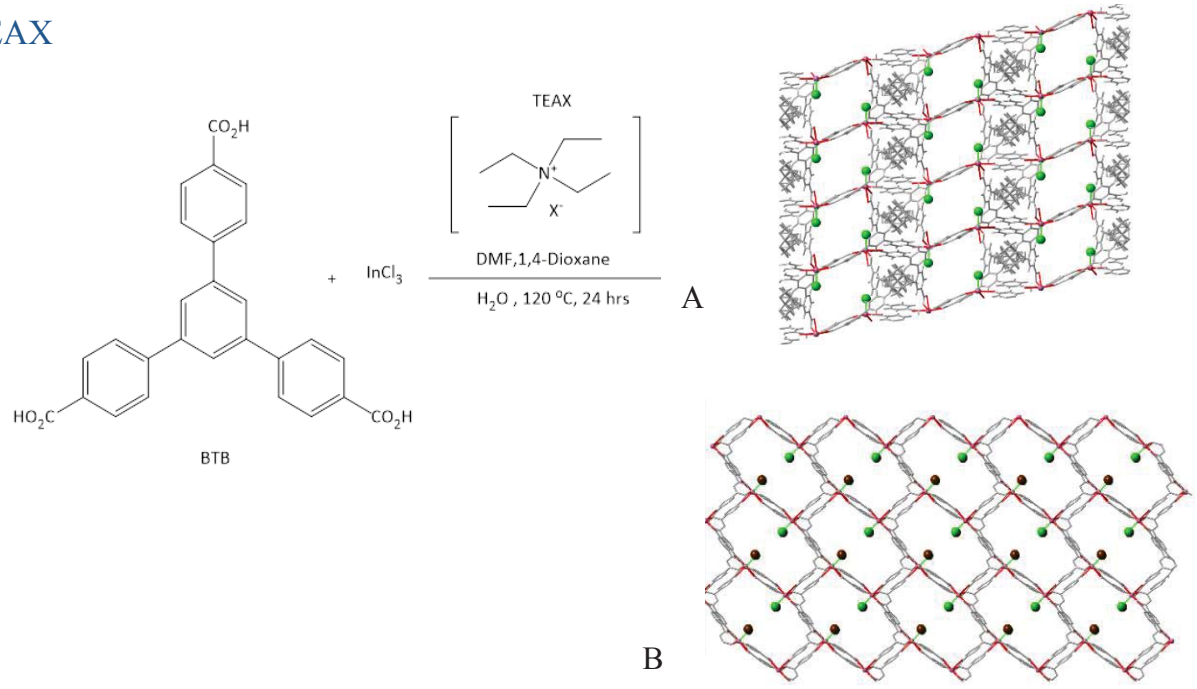
ZJU-28 isomer ZJU-28

Figure 9. Side by side comparison of ZJU-28 and its net isomer.

However, while phase-pure YCM-31 could not be synthesized using a spMP salt, YCM-32-spMPBr formed at the higher concentration and temperature that were used, allowing for the possibility that another increase could reveal more conditions for growing. The use of spMPCl has some similar results in the aspect that high salt concentrations are needed to form YCM-31 but at lower temperatures. Lowering the temperature to 60 °C produced some results but with increased reaction times (7-14 days). These reaction

conditions were not viable as prolonged reaction times often led to the precipitation of purely inorganic salts in the form of higher order InX species. The use of the phase table and variation of reaction conditions assisted in the confirmation that YCM-31-spMPBr was only a minor product when synthesized initially and that under these conditions YCM-32 is the favored halogenated@In-derived-MOF.

TEAX



Scheme 7. The YCM-3X-TEAX reaction, Crystallographic structures of potential outcomes from exploratory research A YCM-32 B YCM-31

Using the conditions for the second synthesized MOF by Mihaly, indium chloride and H_3BTB in DMF and 1,4-dioxane were treated with TEACl and heated to 120 °C (**Scheme 7.**). Through this reaction, it was found that a phase-pure sample of YCM-31-TEACl *not* YCM-32 could be formed. Examining the phase diagram sections for TEAX it shows similar results to the spMPCl (**Figure 10.**). Chloride of both salts only forms YCM-31. However, TEACl has a much more extensive range of conditions for synthesis. TEACl

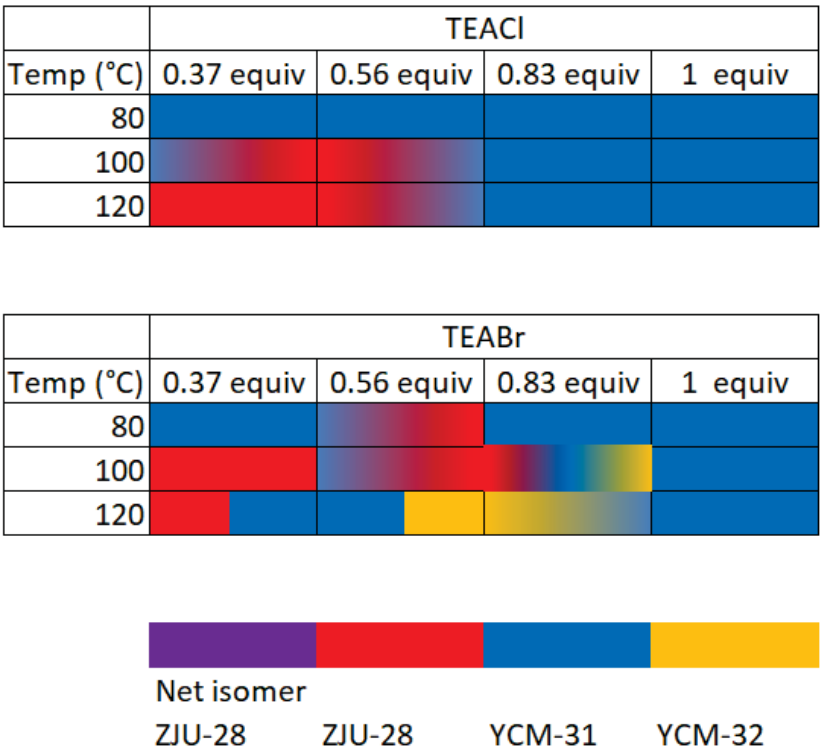
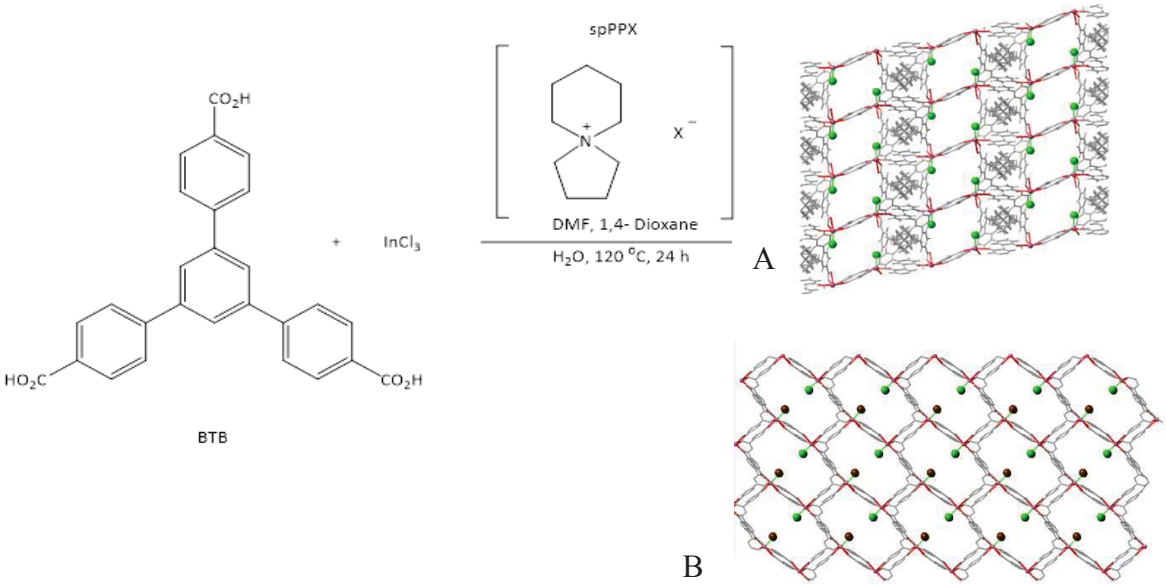


Figure 10. TEAX sections from phase table

also produces phase pure YCM-31-TEACl at high concentrations of salt (0.83 and 1 equiv) under all three reaction temperatures and at a lower concentration (0.37-0.56 equiv) under low reaction temperatures. When using TEABr as the salt, three different MOFs can be formed. Using 1.0 equiv of salt phase pure YCM-31-TEABr can be synthesized at all three temperatures. If the mole fraction is lowered to 0.83 equivalents, at 120 °C a mixed phase of both isomers YCM-31-TEABr and YCM-32-TEABr is observed. Lowering the temperature to 100°C allows for the formation of ZJU-28. At 0.83 equivalents and 100 °C, two possible outcomes are observed: one is YCM-31-TEABr mixed with YCM-32-TEABr and YCM-31-TEABr and ZJU-28. Lowering the mole fraction to 0.56 equivalents removes a mixed phase product and produces two separate phases at high concentration. As the temperature is lowered to 100 °C and 80 °C YCM-31-TEABr is the preferred isomer but

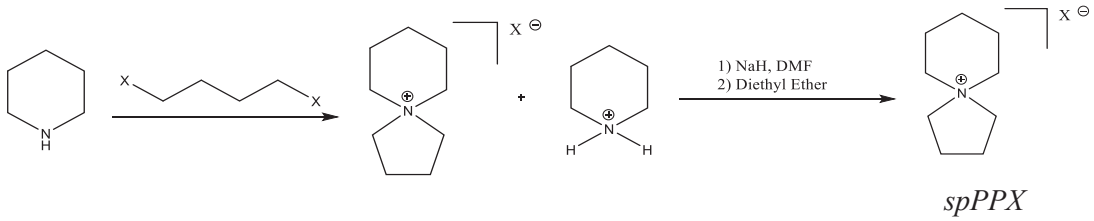
is not phase pure it contained ZJU-28. At the 0.37 equivalents, separate phases of YCM-31-TEABr and ZJU-28 form at 120 °C and as the temperature lowers to 100 °C and 80 °C one phase is preferred. Further expansion toward both higher concentration of salt and temperature may reveal a set of conditions for pure YCM-32-TEAX.

spPPX



Scheme 8. The YCM-3X-spPPCl reaction, Crystallographic structures of potential outcomes from exploratory research A YCM-32 B YCM-31

After finding success with the spirocyclic morpholinium salt and tetraethylammonium salts, the role of the salt in MOF formation was further investigated if structure of the spirocyclic salt was enough to promote YCM-32 formation. This was done by using spirocyclic piperidinium X, a salt structure like spMPX but has electronics similar to TEAX which is known to promote YCM-31 formation. (**Scheme 8.**). The spirocyclic piperidinium salts (spPPX) were then used as the salt for MOF growth; spirocyclic piperidinium shares a similar structure to spMPX having six and five-member rings connected at the nitrogen. Similar to spMPX, initial synthesis of the piperidinium salt



Scheme 9. Synthesis and purification of spirocyclic salts

had a 50:50 mixture of desired salt and protonated impurity. Using the same procedure for purification that was used for the spMPX salts, the clean spPPX salts were synthesized and purified (**Scheme 9**).

When using spPPX, it appears to have trends similar to the spMPBr and TEABr sections of the phase diagram (**Figure 11.)**. Unlike the other two salts, the use of spPPX can lead to phase-pure syntheses of both YCM-31 and YCM-32. The chloride salt has three

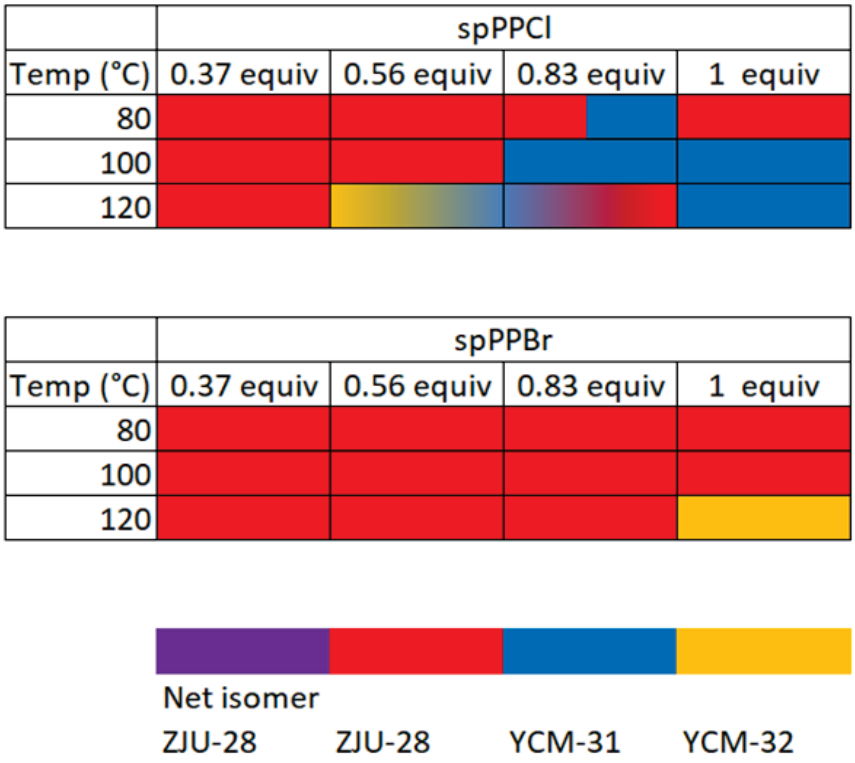


Figure11. spPPX sections from phase table

MOFs that can be formed at high temperatures and concentrations. YCM-31-spPPCl was formed using at least 0.83 equiv. of spPPCl; lower concentrations led to almost exclusive formation of ZJU-28. Interestingly, at 0.56 equivalents and 120 ºC a mixed phase of YCM-31-spPPCl and YCM-32-spPPCl formed. Increasing temperature at this concentration may overcome an energy threshold to produce phase pure YCM-32-spPPCl. The bromide salt shares a lot of similarities with the spMPBr synthesis. Halogenated MOF is only formed at the highest concentration and temperature. The similarity between spMPBr and spPPBr may suggest that the structure of the salt play an influential role in the formation of YCM-32.

It is worth noting that the purity of the salt plays an influential role in determining the structure. If the spPPX salt has impurities or is "wet" from being outside of a desiccator and soaking up moisture, only YCM-32 will form at a reaction temperature of 120 °C, and 0.83 equivalents, ZJU-28 will form for the remaining concentrations and temperatures.

Post Synthetic Modification

One pathway that was explored with YCM-31 and YCM-32 was post synthetic modification. The halogenated nodes of YCM-3X are points of access for modification to the framework. The halogen could be displaced by other functional groups or removed to create an open coordination site so that the framework can sequester materials. The accessibility of YCM-31's halogen that points directly into its pore made this framework a prime candidate for modification.

The first attempts to displace the halogen were a direct displacement of the chloride for benzoic acid. The MOF was synthesized and dried under reduced vacuum to remove

any solvent remaining. After drying, 30 mg of the MOF was suspended in a DMF solution containing 5 equivalents of benzoic acid and was then either heated at 85 °C or kept at room temperature. The reaction was kept at a lower temperature to avoid any possible framework changes or decomposition. Incorporation of the benzoic acid into the framework was unsuccessful and confirmed through NMR digestion.

The second set of attempts to post-synthetically modify the YCM-31 framework started with a different approach. Instead of working to displace a chloride with a bond strength of 102 kcal/mol when bonded to indium, it was hypothesized that by using a framework that had indium bromide bonds (92 kcal/mol) the displacement would be easier.[35] Synthesizing a full bromide framework proved not to be a viable route. Frameworks did not form, which may be due to the lability of the indium bromide bond. During formation ZJU-28 is favored over YCM-31, and the indium carboxylate bond is more stable with a higher bond energy of 720 kcal/mol.[35]

The final attempts to post-synthetically modify YCM-31 deployed salts to promote the displacement of the chloride. The MOF was synthesized and dried under reduced vacuum to remove guest molecules. After drying, 30 mg of the MOF was added to a DMF solution containing 5 equivalents of salt. The salts used were sodium benzoate, sodium terephthalate, and sodium tetrafluoro terephthalate. The sodium salts were hypothesized to promote chloride displacement in favor of sodium chloride formation. These reactions were all unsuccessful, except when using sodium benzoate. NMR showed that after 3 washes with fresh DMF, there was still benzoate in the MOF. This could be the incorporation of the benzoate, or it could be residual benzoate stuck to the surface of the

MOF. During the reaction, crystallinity is lost, and conformation by single crystal diffraction was not possible.

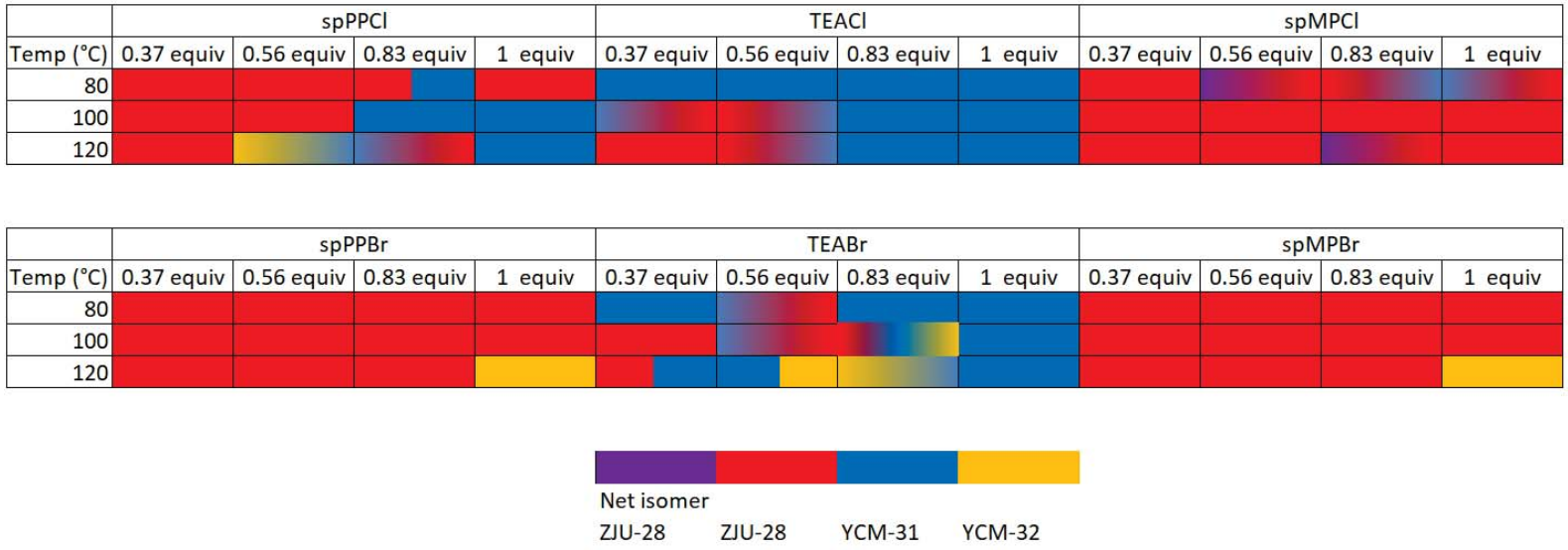


Figure 12. Phase Table, showing the resulting MOFs from variation of temperature

Starting from the conditions under which Mihaly had initially synthesized minor products YCM-31-spMPBr and YCM-32-TEACl, a table of MOF growing conditions was proposed (**Figure 12.**) varying both temperature and concentration of the respective additives. The results of this undertaking led to the phase diagram shown as **Figure 12** and will be discussed in detail (*vide infra*).

One major trend as displayed in the phase diagram is that all three salts can produce at least two different MOFs. Another big trend of the diagram is that YCM-32 forms more frequently when using the bromide version of the salts, whereas YCM-31 is formed more often when the chloride salt is used. Phase impurity is a large concern when synthesizing these MOFs; all three salts have a transition point where the temperature and concentration reach the threshold between two phases producing a mixed phase result. Since YCM-32 is formed more in the bromide sections of the table, it is possible that weaker interactions between the spirocycle and the bromide of the salt allow for faster dissociation. Free cation could play a vital role for intermediate formation and building of the SBU. The breaking up of the bromide salt ion pair due to weaker interactions than chloride, would occur more rapidly when in solution, as the faster ion separation could facilitate the growth of the 3D 2-periodic structure of YCM 32.

Assignments of the phase purity were different for the YCM-3X isomers. Being that the isomers are chemically the same and only marginally structurally different from one another, their crystallography patterns were very similar. Overall this table shows that all isomers can be produced in phase pure or mixed phase. Both major and minor products were identified by single crystal X-ray diffraction and powder X-ray diffraction.

Conclusions

After determining the MOFs, YCM-31 and YCM-32 were originally synthesized and characterized as minor products, the phase table was constructed and completed. From the data displayed on the phase table it can be concluded that the interactions between the ion pairs of the salt additive used plays a determining factor in MOF formation. Weaker ion pairs produce YCM-32 whereas the stronger ion pairs produce YCM-31. ZJU-28 is very predominant on the phase table but increasing temperature and concentration of salt additive may provide further conditions to synthesize YCM-31 and YCM-32. The main goal of this research was to find conditions that both YCM-31 and YCM-32 could be synthesized phase pure, this was done by varying temperature and the salt additive. YCM-32 can be synthesized phase pure at 1 equivalent at 120 °C using spPPBr and spMPBr. YCM-31 can be synthesized using TEACl, TEABr, and spPPCl at 1 equivalent at 100 °C and 120 °C. YCM-31 can also be synthesized using the same salts at different concentrations and temperatures.

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III. Experimental

Reagents and Instrumentation

Morpholine, piperidine, sodium hydride, 1-bromobutane, and 1,4-dibromobutane were purchased from Sigma-Aldrich, and the chemicals were used as received.

TGA data were collected on a TA Instruments TGA Q50 from 40 °C to 600 °C at a rate of 10 °C per minute. NMR data were collected on a 400 MHz Bruker Avance NMR Spectrometer.

Spirocyclic piperidinium bromide (spPPBr)

To a 20 mL scintillation vial equipped with a stir bar was added piperidine (1.78 mL, 18.0 mmol, 1.00 equiv.) and 1,4-dibromobutane (2.15 mL, 18.0 mmol, 1.00 equiv.) dropwise via syringe. The resulting mixture was stirred at room temperature for 24 hours (caution: initial reaction is highly exothermic!). In a 250 mL Erlenmeyer Flask, the resulting precipitate was then dissolved in DMF with the addition of a stoichiometric amount of sodium hydride (216 mg , 9.0 mmol). After 48 hours the mixture was filtered to remove the solids and collect the solution, and the pure salts precipitated from the filtered solution using diethyl ether (100 mL). The final salt was dried under vacuum for 24 hrs. ^{1}H NMR ($CDCl_3$, 400 MHz) 1.6808 (q, J = 6.13 Hz), 1.8311 – 1.9341 (bm), 2.1065 – 2.2235 (bm), 3.3615 (t, J = 5.64 Hz), 3.5332 (t, J = 6.73 Hz)

Spirocyclic morpholinium bromide (spMPBr)

To a 20 mL scintillation vial equipped with a stir bar was added morpholine (1.55 mL, 18.0 mmol, 1.00 equiv) and 1,4-dibromobutane (2.15 mL, 18.0 mmol, 1.00 equiv) dropwise via syringe. The resulting mixture was stirred at room temperature for 24 hours (caution: initial reaction is highly exothermic!). In a 250 mL Erlenmeyer Flask, the resulting precipitate was then dissolved in DMF with the addition of a stoichiometric amount of sodium hydride (216 mg, 9.0 mmol). After 48 hours the mixture was filtered to remove the solids and collect the solution, and the pure salts precipitated from the filtered solution using diethyl ether (100 mL). The final salt was dried under vacuum for 24 hrs. ^{1}H NMR (D_2O, 400 MHz) 2.171 – 2.256 (bm), 3.5067 (t, J = 4.80 Hz), 3.663 (t, J = 7.18 Hz), 3.985 – 4.078 (bm)

Spirocyclic piperidinium chloride (spPPCl)

To a 20 mL scintillation vial equipped with a stir bar was added piperidine (1.78 mL, 18.0 mmol, 1.00 equiv) and 1,4-dichlorobutane (2.28 mL, 18.0 mmol, 1.00 equiv) dropwise via syringe. The resulting mixture was stirred at room temperature for 24 hours (caution: initial reaction is highly exothermic!). In a 250 mL Erlenmeyer Flask, the resulting precipitate was then dissolved in DMF with the addition of a stoichiometric amount of sodium hydride. After 48 hours the mixture was filtered to remove the solids and collect the solution, and the pure salts precipitated from the filtered solution using diethyl ether (100 mL). The final salt was dried under vacuum for 24 hrs. ^{1}H NMR ($CDCl_3$, 400 MHz) 1.814 (q, J = 5.8 Hz), 1.874 – 1.967 (bm), 2.2383 – 2.328 (bm), 3.7595 (t, J = 5.71 Hz), 3.898 (t, J = 6.92 Hz)

Spirocyclic morpholinium chloride (spMPCl)

To a 20 mL scintillation vial equipped with a stir bar was added morpholine (1.55 mL, 18.0 mmol, 1.00 equiv) and 1,4-dichlorobutane (2.28 mL, 18.0 mmol, 1.00 equiv) dropwise via syringe. The resulting mixture was stirred at room temperature for 24 hours (caution: initial reaction is highly exothermic!). In a 250 mL Erlenmeyer Flask, the resulting precipitate was then dissolved in DMF with the addition of a stoichiometric amount of sodium hydride. After 48 hours the mixture was filtered to remove the solids and collect the solution, and the pure salts precipitated from the filtered solution using diethyl ether (100 mL). The final salt was dried under vacuum for 24 hrs. ^{1}H NMR ($CDCl_3$, 400 MHz) 2.2597 – 2.3866 (bm), 3.8346 (t, J = 4.62), 3.9772 – 4.1475 (bm)

Synthesis of YCM 31-spMPCl

To a premixed solution of DMF (18 mL) and dioxane (12 mL) was added benzene tribenzoic acid ($BTBH_3$) (275 mg, 0.620 mmol, 1.00 equiv) and $InCl_3$ (291 mg, 1.32 mmol, 2.13 equiv). In a separate vial, spMPCl (178 mg, 1.10 mmol, 1.77 equiv) was dissolved in 2.0 mL of deionized water. The aqueous solution was added to the DMF mixture, and the resulting mixture was sonicated for 5 minutes. The resulting solution was then filtered through a GE 25 mm PVDF syringe filter (0.45 μm) in 5.33 mL portions into six individual 20 mL scintillation vials. The vials were sealed with Teflon-lined caps and heated in an oven at the reported temperature (80, 100, or 120 °C, see Figure 29) for the reported time (24, 48, 72). The vials were removed from the oven and were cooled to room temperature. The contents of each individual vial were combined and washed with 30 mL (3 × 10 mL) of fresh DMF.

Synthesis of YCM 32-spMPBr

To a premixed solution of DMF (18 mL) and dioxane (12 mL) was added benzene tribenzoic acid ($BTBH_3$) (275 mg, 0.620 mmol, 1.00 equiv) and $InCl_3$ (291 mg, 1.32 mmol, 2.13 equiv). In a separate vial, spMPBr (272 mg, 1.32 mmol) was dissolved in 2.0 mL of deionized water. The aqueous solution was added to the DMF mixture, and the resulting mixture was sonicated for 5 minutes. The resulting solution was then filtered through a GE 25 mm PVDF syringe filter (0.45 μm) in 5.33 mL portions into six individual 20 mL scintillation vials. The vials were sealed with Teflon-lined caps and heated in an oven at the reported temperature (80, 100, or 120 °C, see Figure 33) for the reported time (24, 48, 72). The vials were removed from the oven and were cooled to room temperature. The contents of each individual vial were combined and washed with 30 mL (3 × 10 mL) of fresh DMF.

Synthesis of YCM 31-spPPCl

To a premixed solution of DMF (18 mL) and dioxane (12 mL) was added benzene tribenzoic acid ($BTBH_3$) (275 mg, 0.620 mmol, 1.00 equiv) and $InCl_3$ (291 mg, 1.32 mmol, 2.13 equiv). In a separate vial, spPPCl (173 mg (1.10 mmol, 1.77 equiv) was dissolved in 2.0 mL of deionized water. The aqueous solution was added to the DMF mixture, and the resulting mixture was sonicated for 5 minutes. The resulting solution was then filtered through a GE 25 mm PVDF syringe filter (0.45 μm) in 5.33 mL portions into six individual 20 mL scintillation vials. The vials were sealed with Teflon-lined caps and heated in an oven at the reported temperature (80, 100, or 120 °C, see Figure 13) for the reported time (24, 48, 72 hours). The vials were removed from the oven and were cooled to room

temperature. The contents of each individual vial were combined and washed with 30 mL (3 × 10 mL) of fresh DMF.

Synthesis of YCM 32-spPPBr

To a premixed solution of DMF (18 mL) and dioxane (12 mL) was added benzene tribenzoic acid ($BTBH_3$) (275 mg, 0.620 mmol, 1.00 equiv) and $InCl_3$ (291 mg, 1.32 mmol, 2.13 equiv). In a separate vial, spPPBr (267 mg, 1.32 mmol) was dissolved in 2.0 mL of deionized water. The aqueous solution was added to the DMF mixture, and the resulting mixture was sonicated for 5 minutes. The resulting solution was then filtered through a GE 25 mm PVDF syringe filter (0.45 μm) in 5.33 mL portions into six individual 20 mL scintillation vials. The vials were sealed with Teflon-lined caps and heated in an oven at the reported temperature (80, 100, or 120 °C, see Figure 17) for the reported time (24, 48, 72 hours). The vials were removed from the oven and were cooled to room temperature. The contents of each individual vial were combined and washed with 30 mL (3 × 10 mL) of fresh DMF.

Synthesis of YCM 31-TEAX

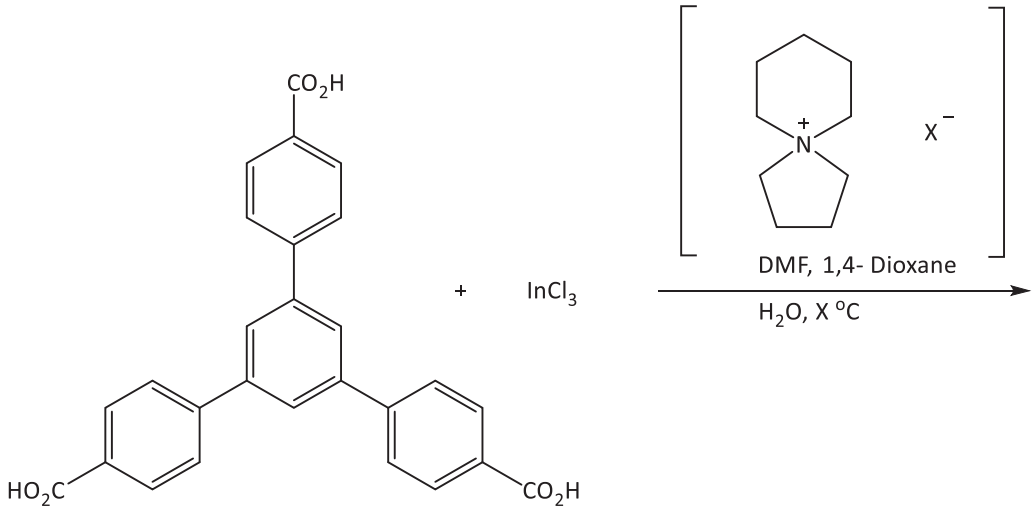
To a premixed solution of DMF (18 mL) and dioxane (12 mL) was added $BTBH_3$ (275 mg, 0.620 mmol, 1.00 equiv) and $InCl_3$ (291 mg, 1.32 mmol, 2.13 equiv), followed by tetraethylammonium X (X = Cl (219 mg); X = Br (277 mg) 1.10 mmol) and 2 mL of deionized water. The resulting mixture was sonicated for 5 minutes. The resulting solution was then filtered through a GE 25 mm PVDF syringe filter (0.45 μm) in 5.33 mL portions into six individual 20 mL scintillation vials. The vials were sealed with Teflon-lined caps

and heated in an oven at the reported temperature (80, 100, or 120 °C, see Figure 21) for the reported time (24, 48, 72 hours). The vials were removed from the oven and were cooled to room temperature. The contents of each individual vial were combined and washed with 30 mL (3 × 10 mL) of fresh DMF.

Synthesis of YCM 32-TEABr

To a premixed solution of DMF (18 mL) and dioxane (12 mL) was added $BTBH_3$ (275 mg, 0.620 mmol, 1.00 equiv) and $InCl_3$ (291 mg, 1.32 mmol, 2.13 equiv), followed by tetraethylammonium bromide (158mg, 0.75 mmol) and 2.0 mL of deionized water. The resulting mixture was sonicated for 5 minutes. The resulting solution was then filtered through a GE 25 mm PVDF syringe filter (0.45 μm) in 5.33 mL portions into six individual 20 mL scintillation vials. The vials were sealed with Teflon-lined caps and heated in an oven at the reported temperature (80, 100, or 120 °C, see Figure 23) for the reported time (24, 48, 72 hours, see figure X). The vials were removed from the oven and were cooled to room temperature. The contents of each individual vial were combined and washed with 30 mL (3 × 10 mL) of fresh DMF.

Appendix 1 - PXRD



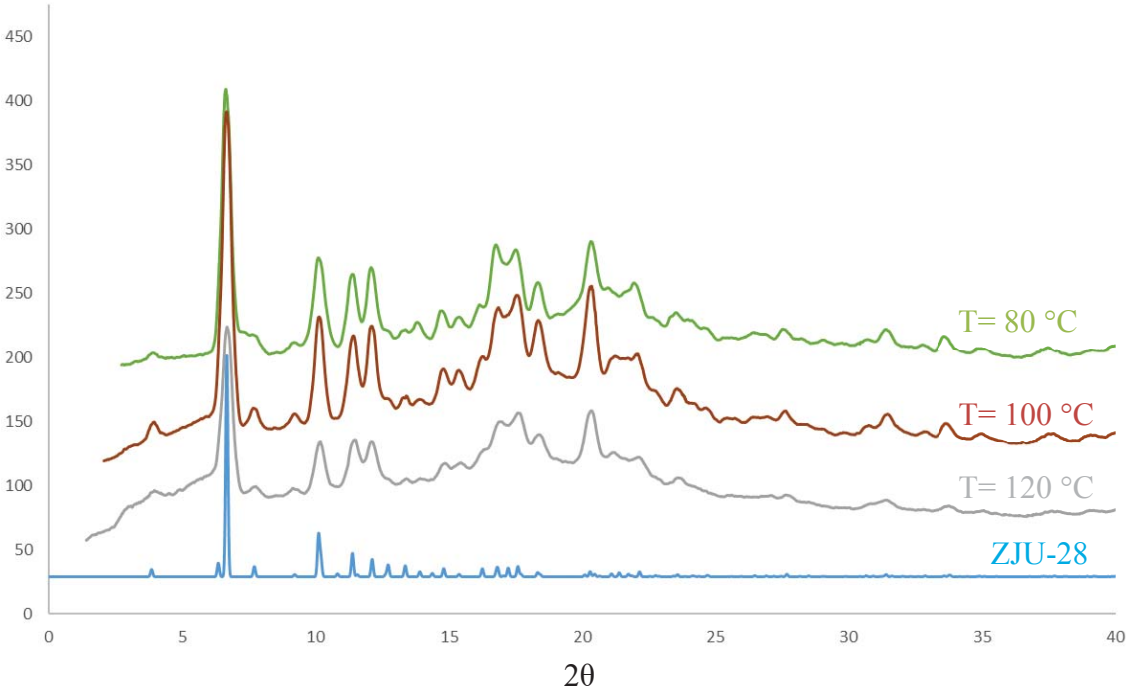


Figure A1 - 1. 0.37 equivalents spPPCl

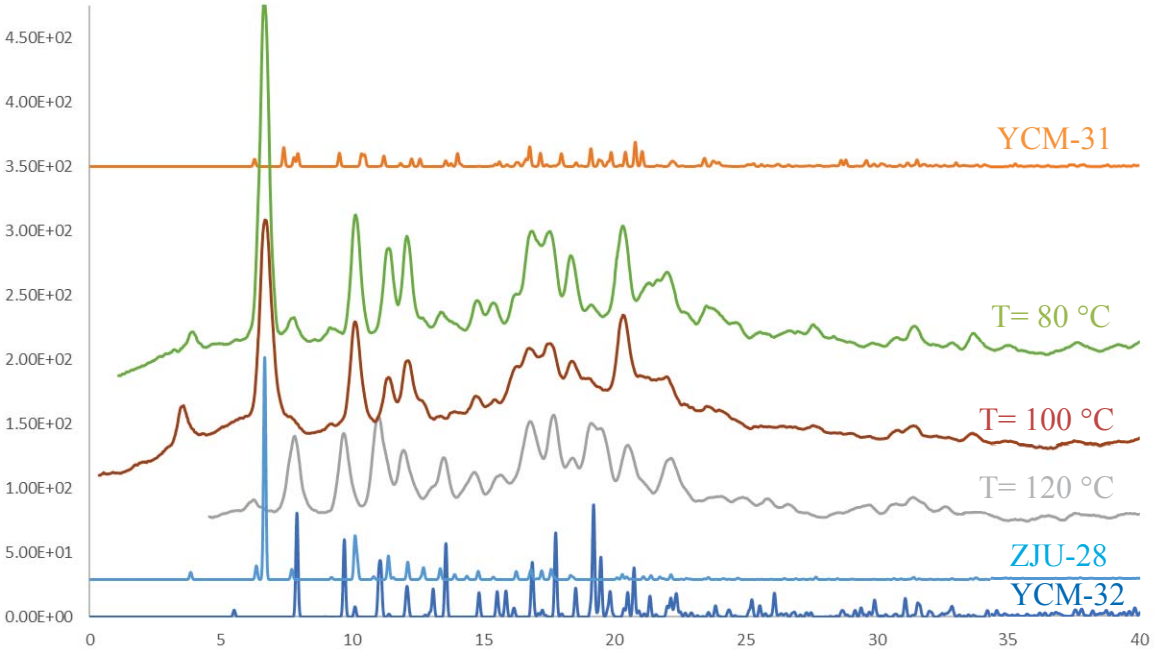


Figure A1 - 2. 0.56 equivalents spPPCl

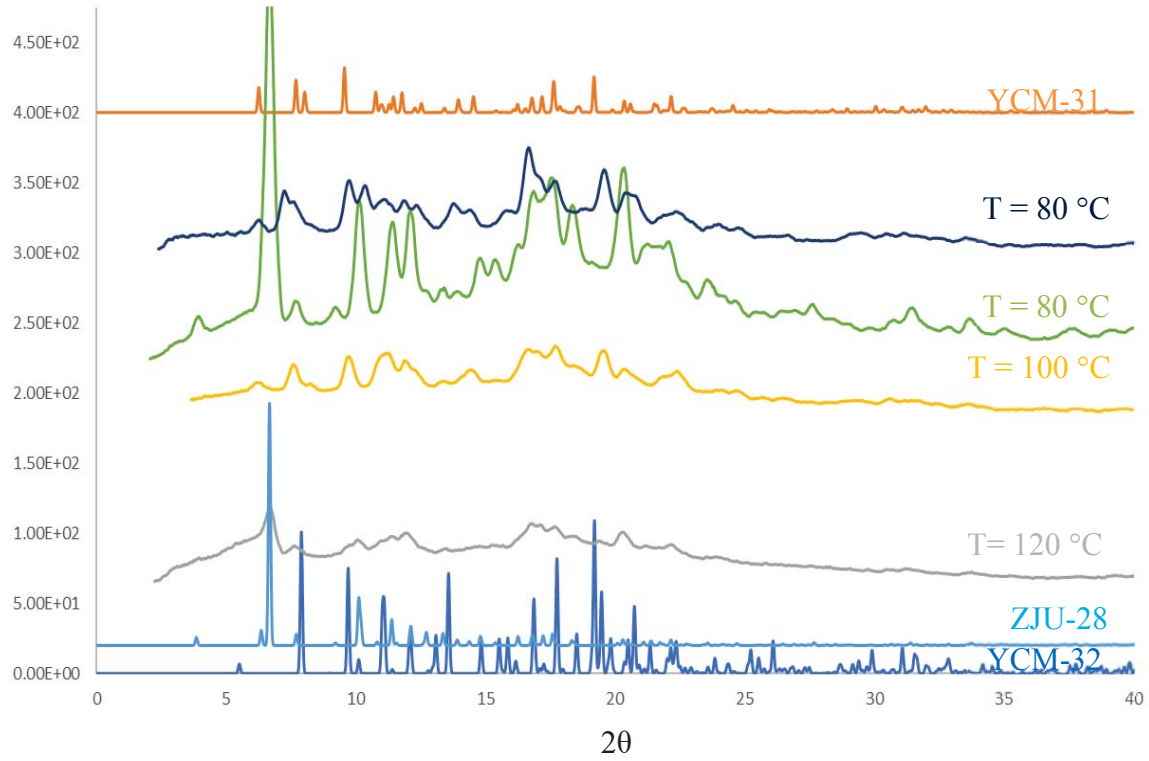


Figure A1 - 3. 0.83 equivalents spPPCl

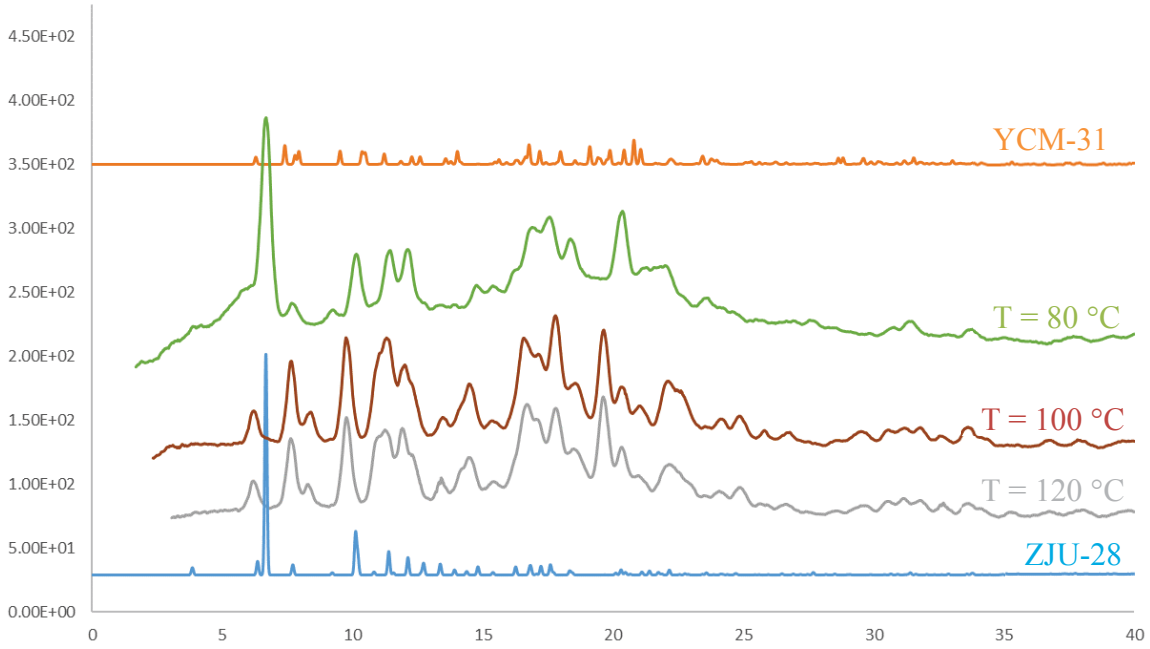


Figure A1 - 4. 1.0 equivalent spPPCl

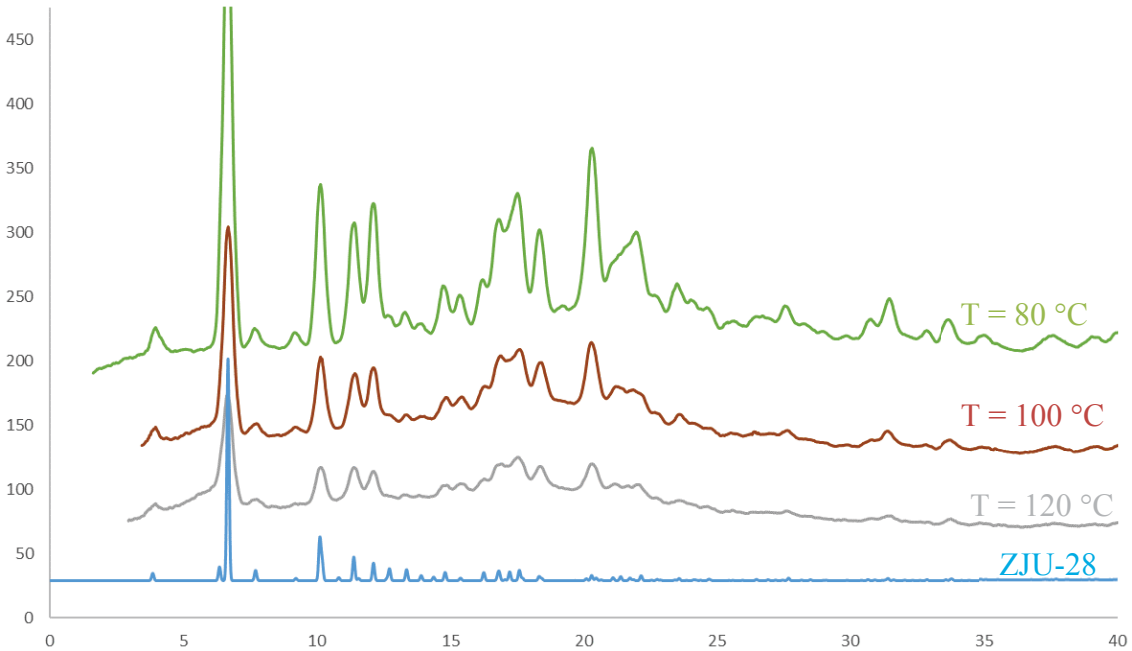


Figure A1 - 5. 0.37 equivalents spPPBr

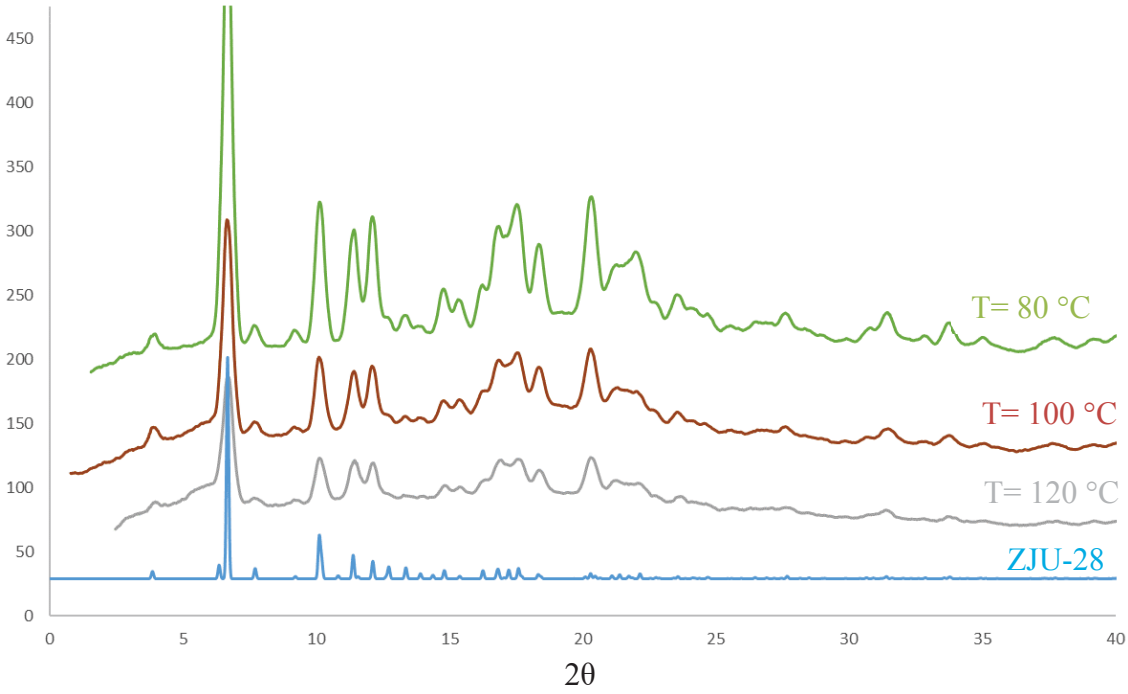


Figure A1 - 6. 0.56 equivalents spPPBr

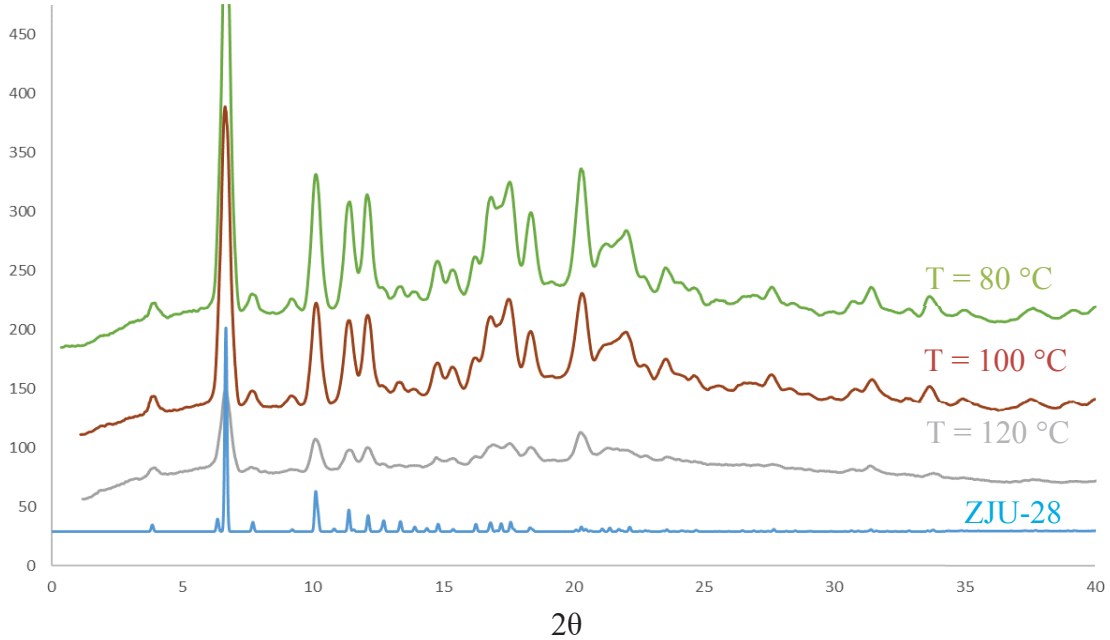


Figure A1 - 7. 0.83 equivalents spPPBr

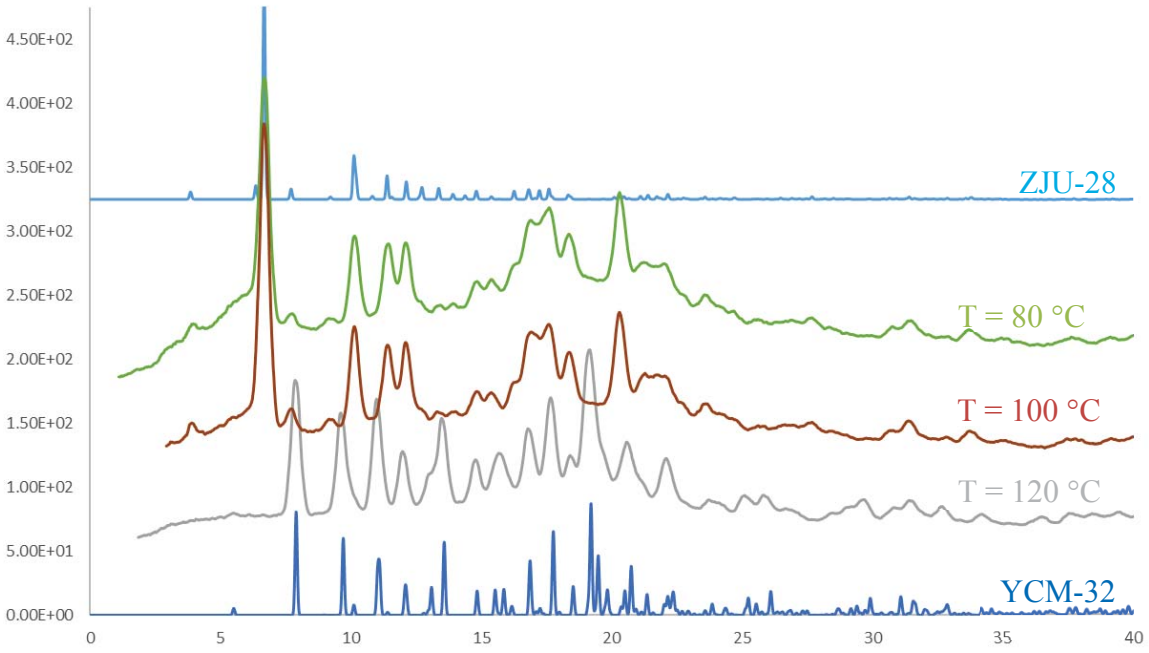
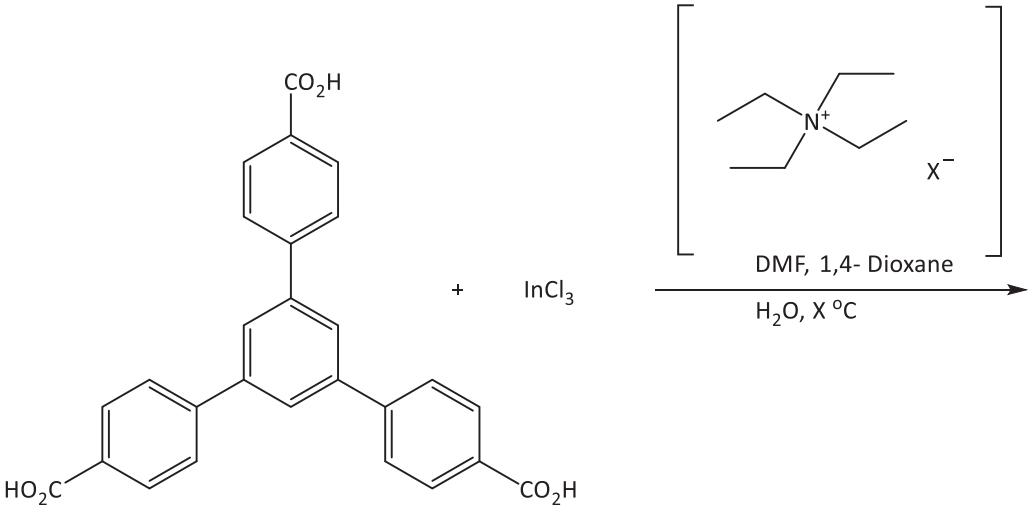


Figure A1 - 8. 1.0 equivalents spPPBr



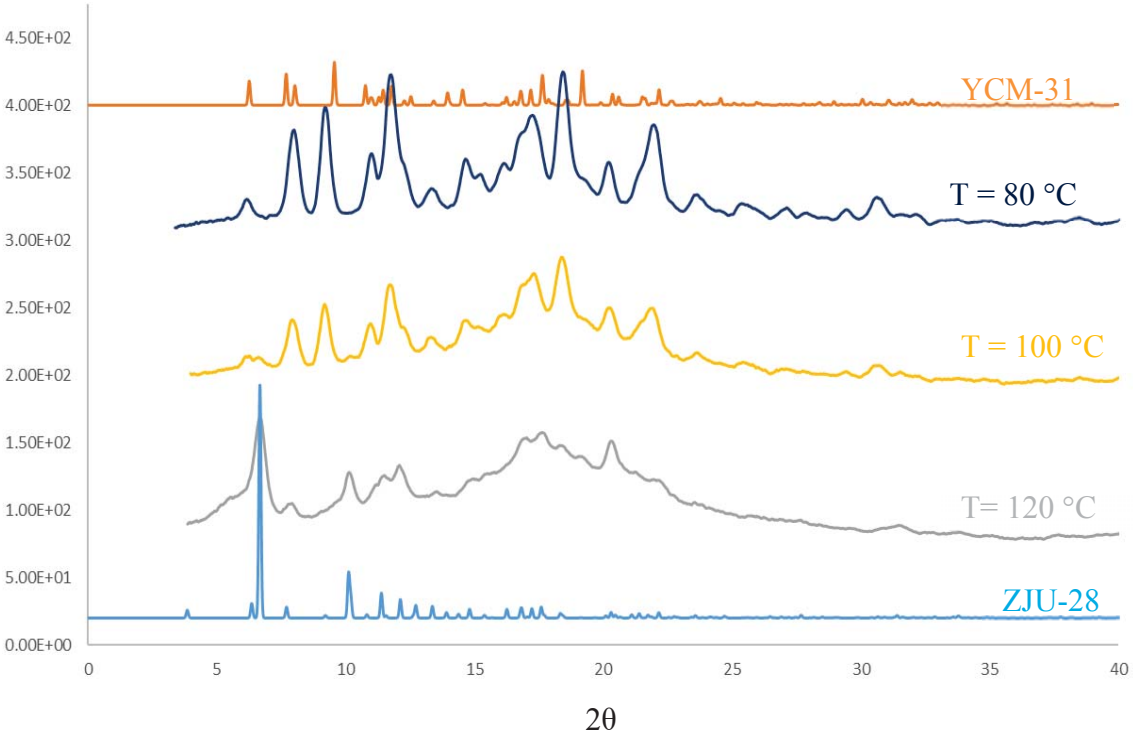


Figure A1 - 9. 0.37 equivalents TEACl

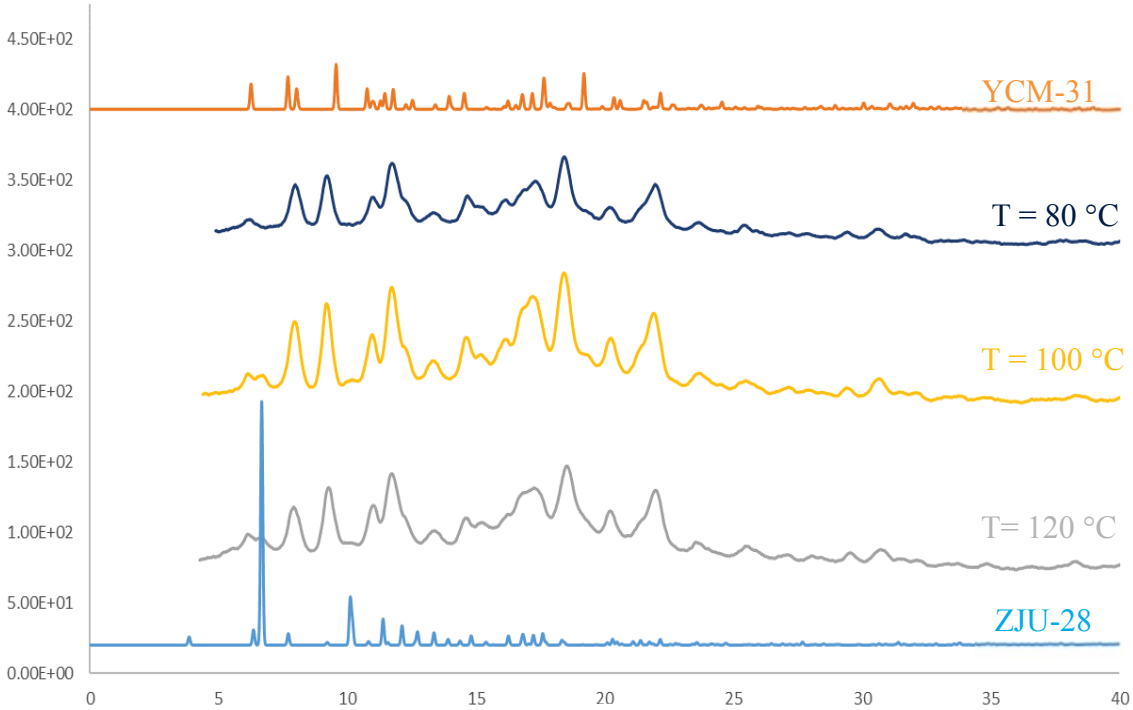


Figure A1 - 10. 0.56 equivalents TEACl

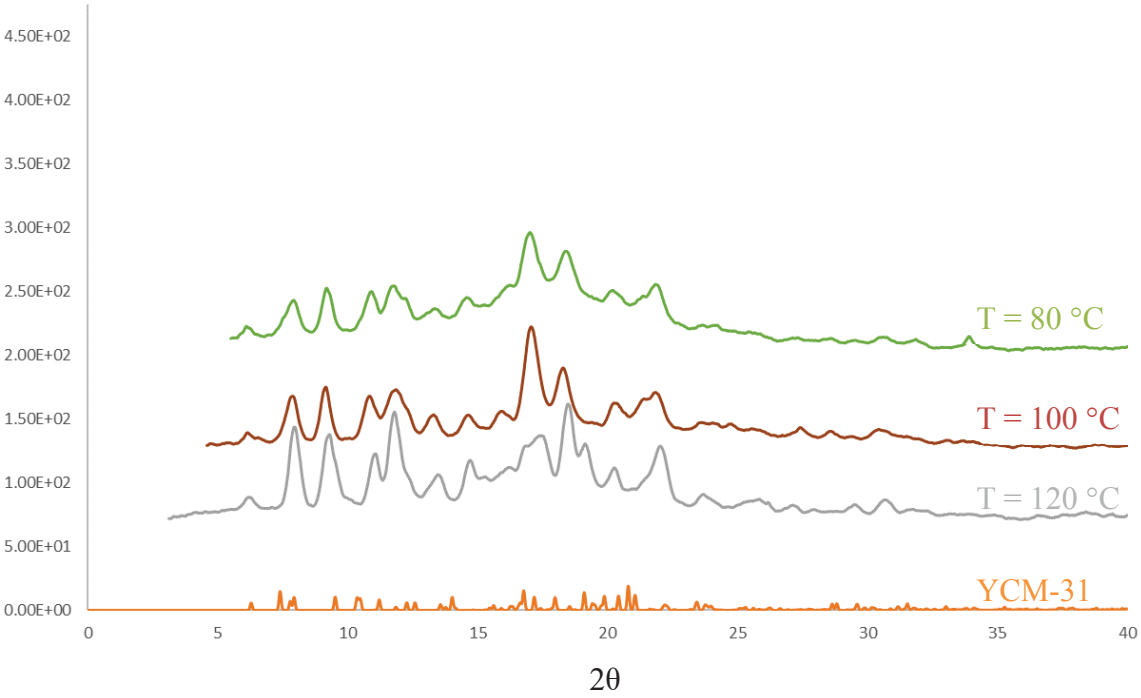


Figure A1 - 11. 0.83 equivalents TEACl

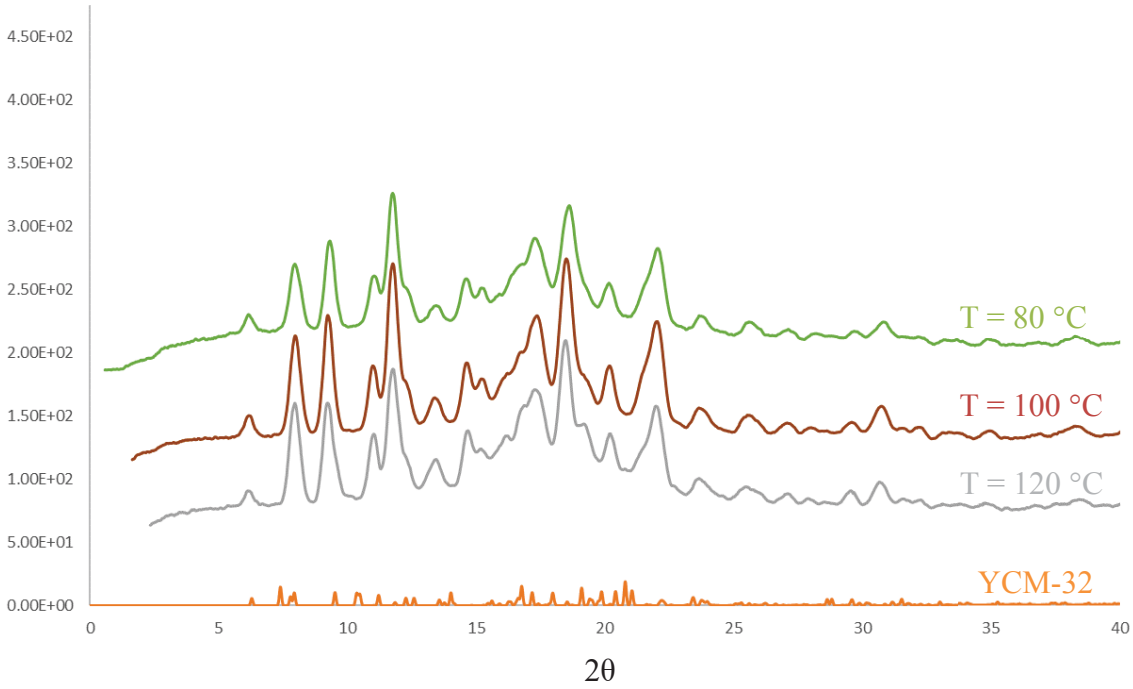


Figure A1 - 12. 1.0 equivalents TEACl

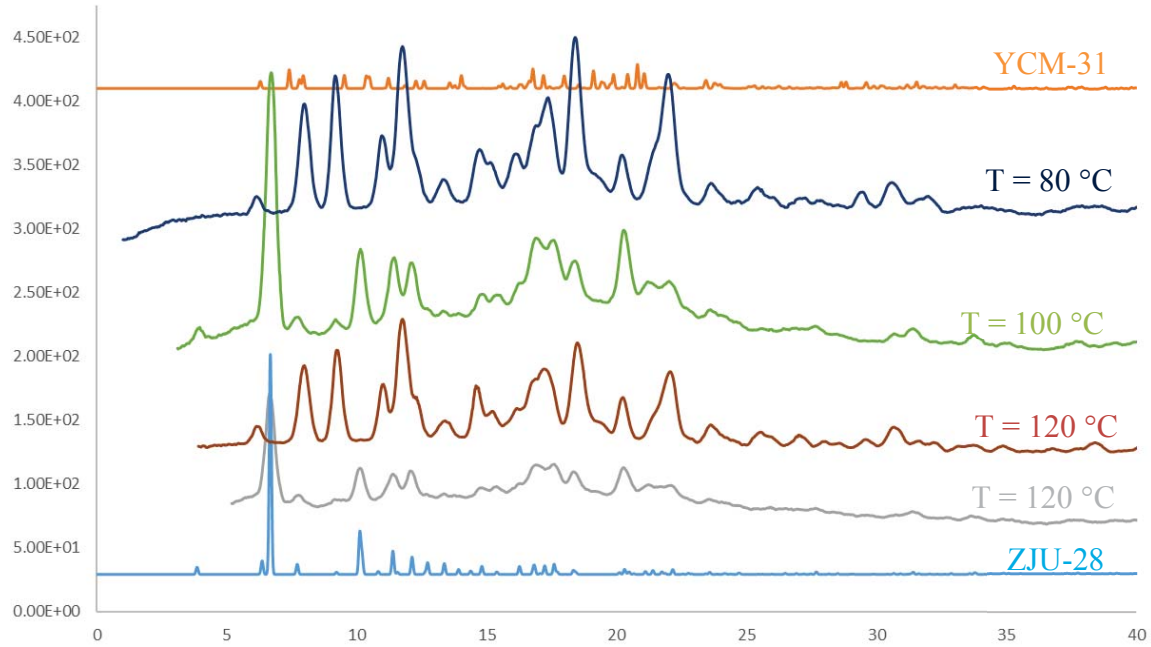


Figure A1 - 13. 0.37 equivalents TEABr

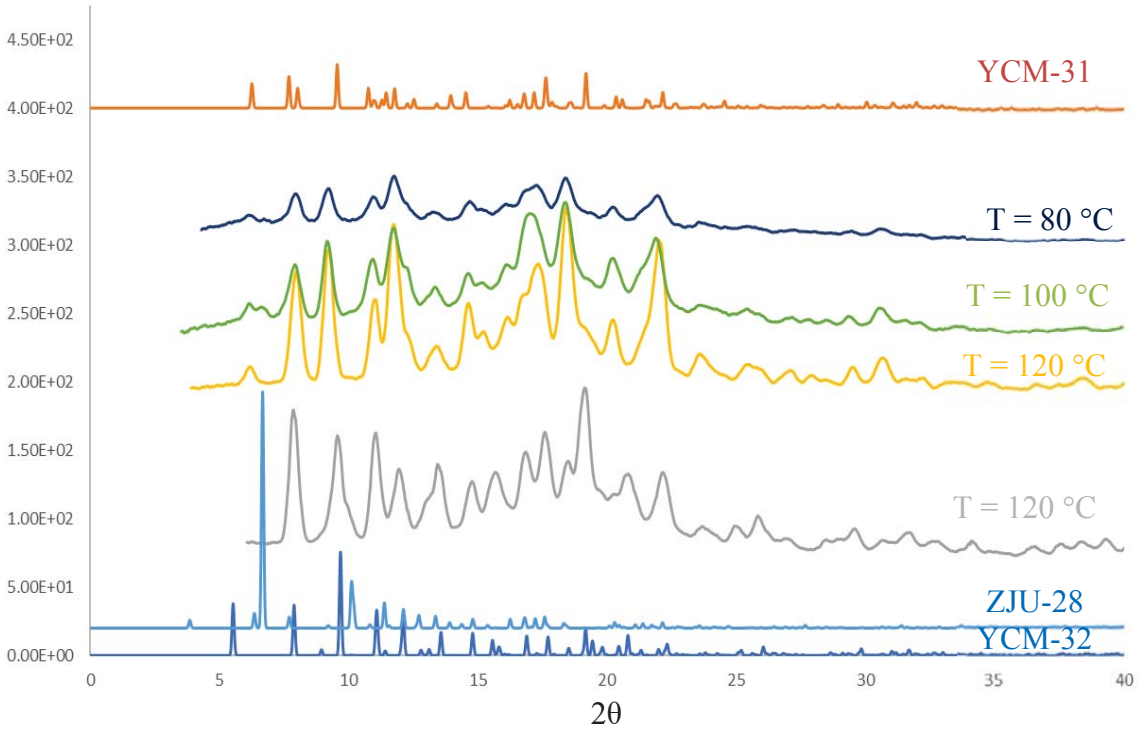


Figure A1 - 14. 0.56 equivalents TEABr

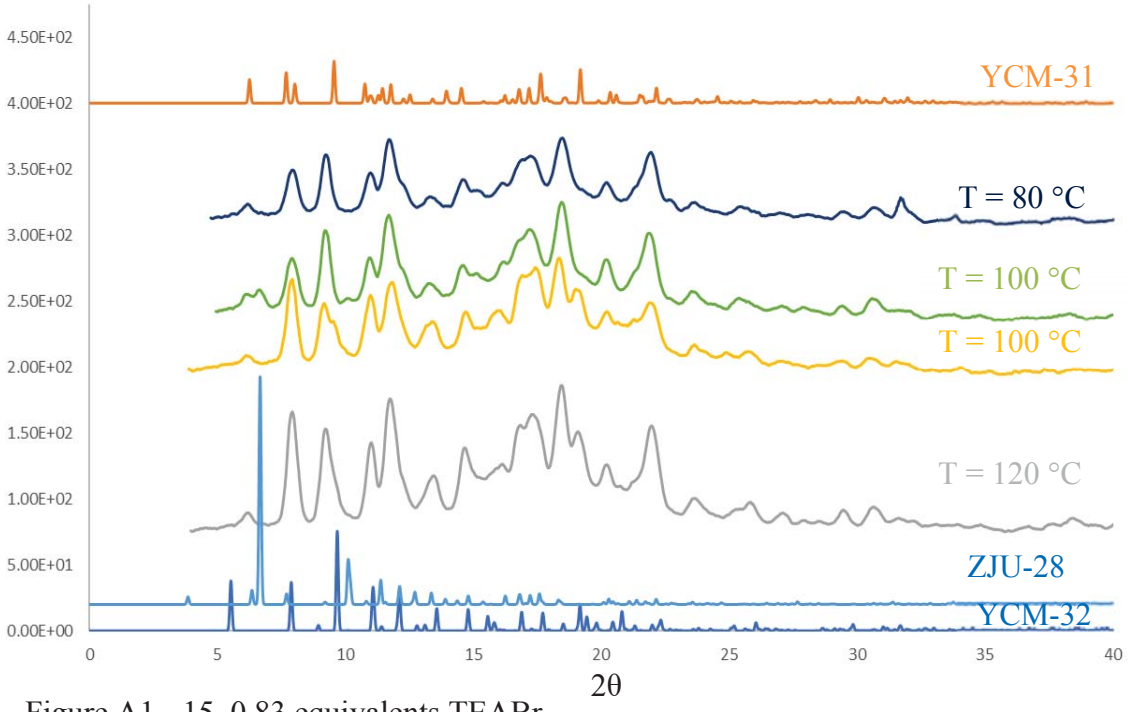


Figure A1 - 15. 0.83 equivalents TEABr

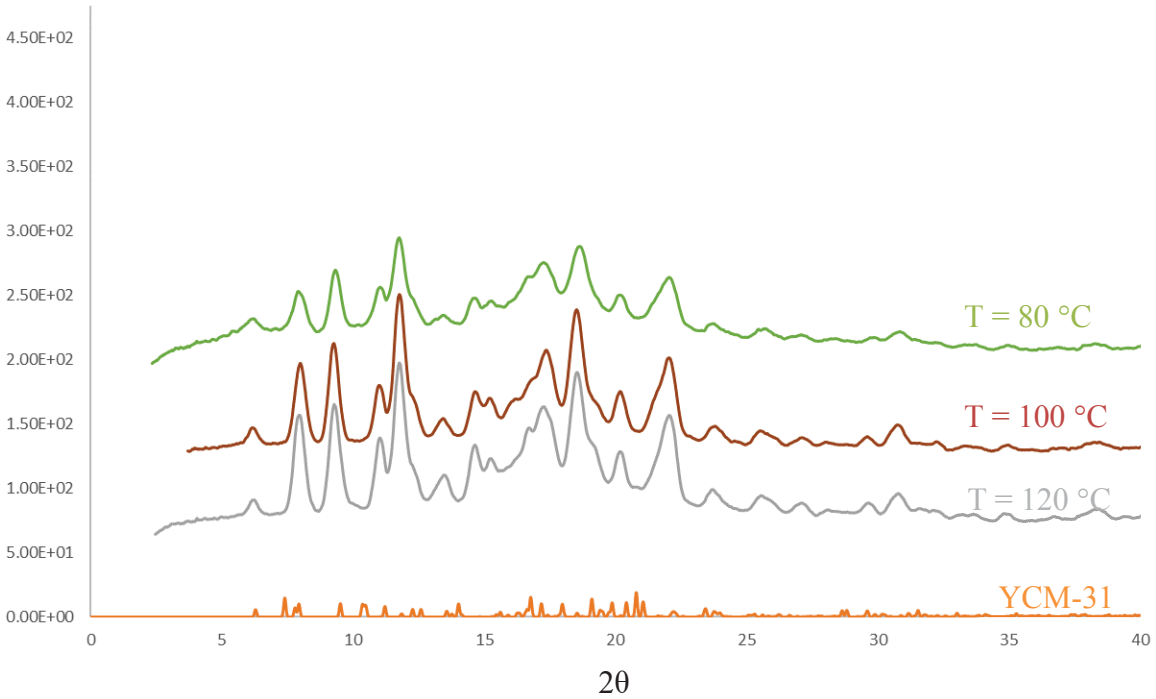
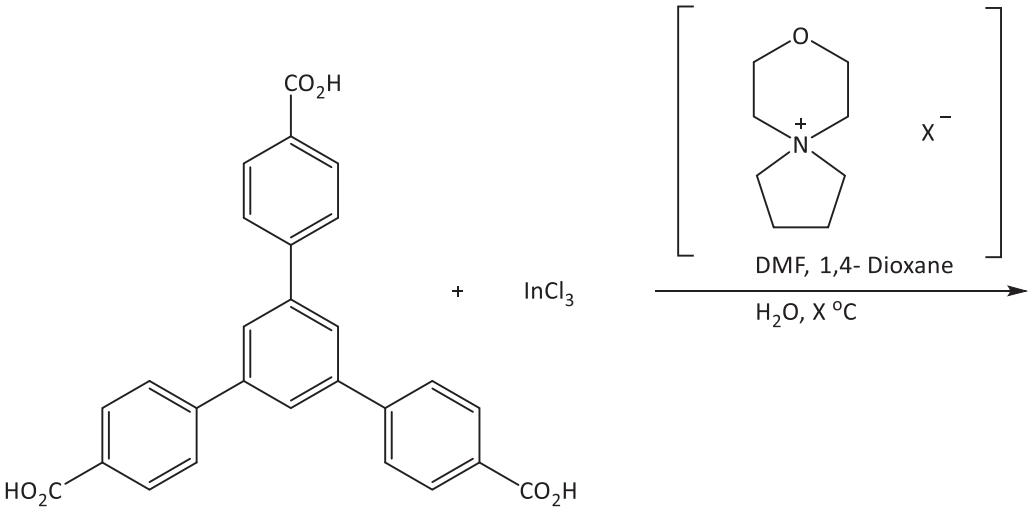


Figure A1 - 16. 1.0 equivalents TEABr



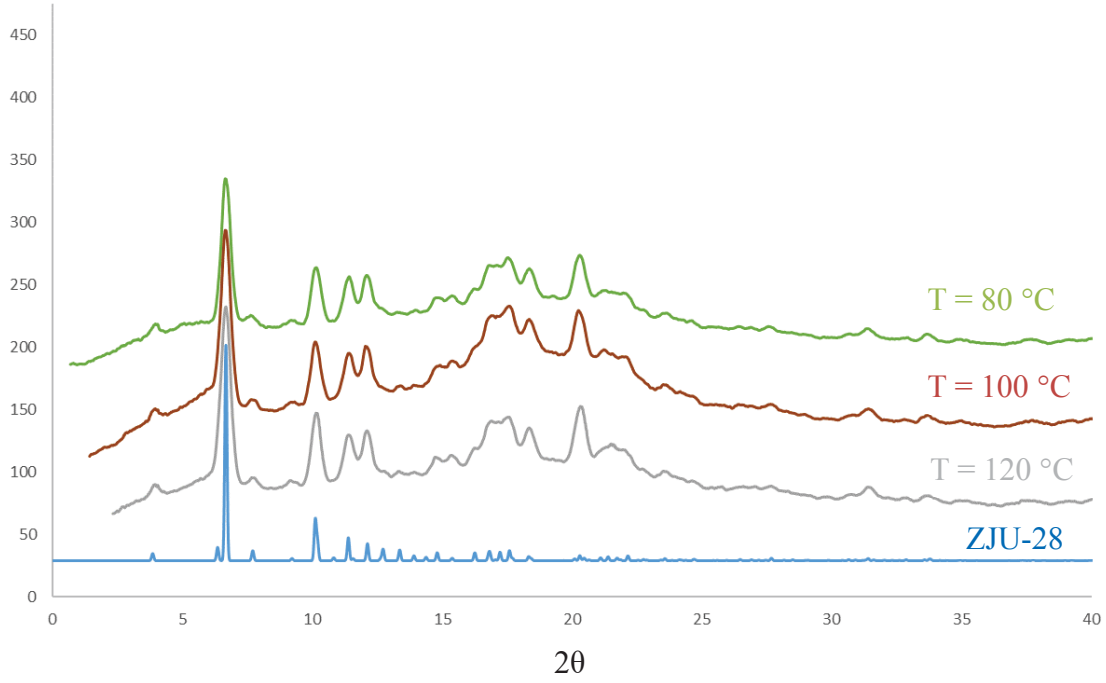


Figure A1 - 17. 0.37 equivalents spMPCl

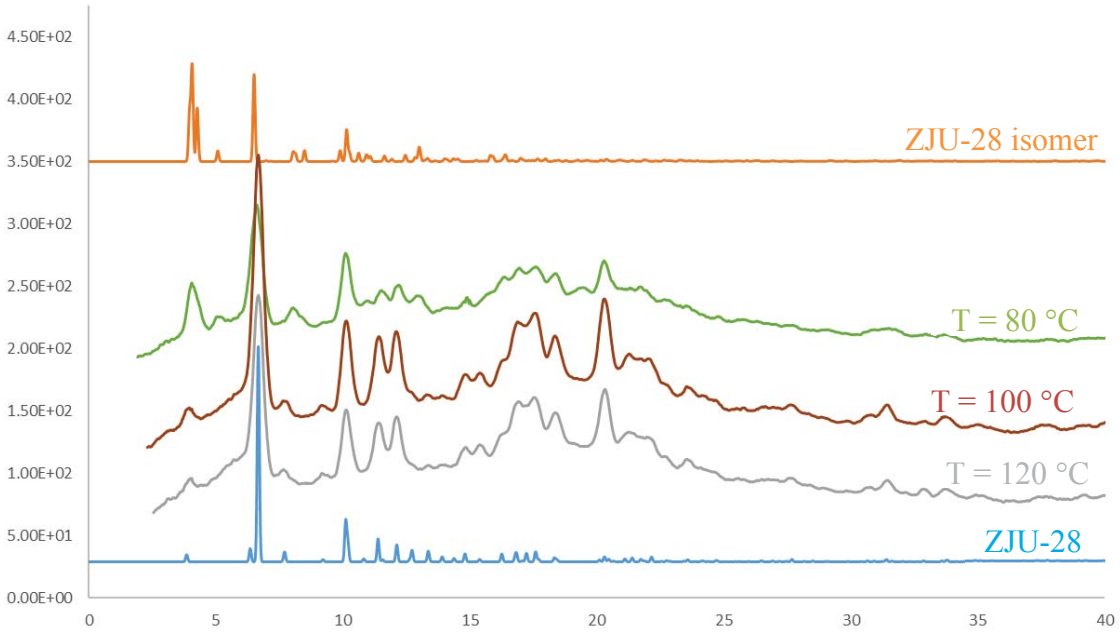


Figure A1 - 18. 0.56 equivalents spMPCl

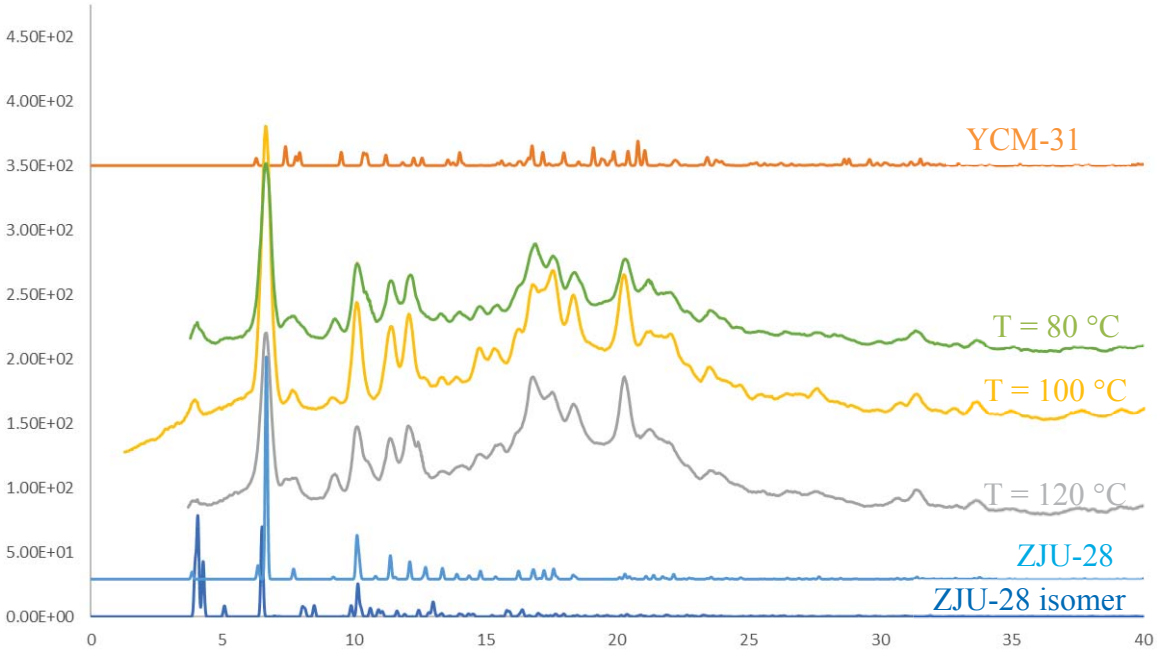


Figure A1 - 19. 0.83 equivalents spMPCl

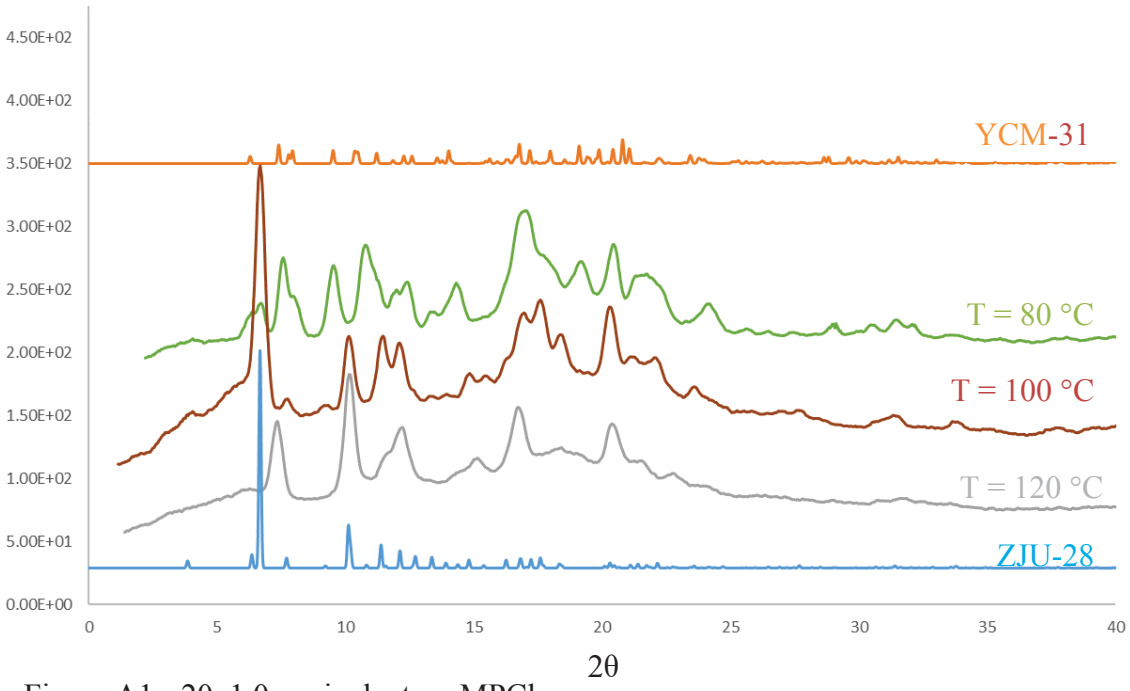


Figure A1 - 20. 1.0 equivalents spMPCl

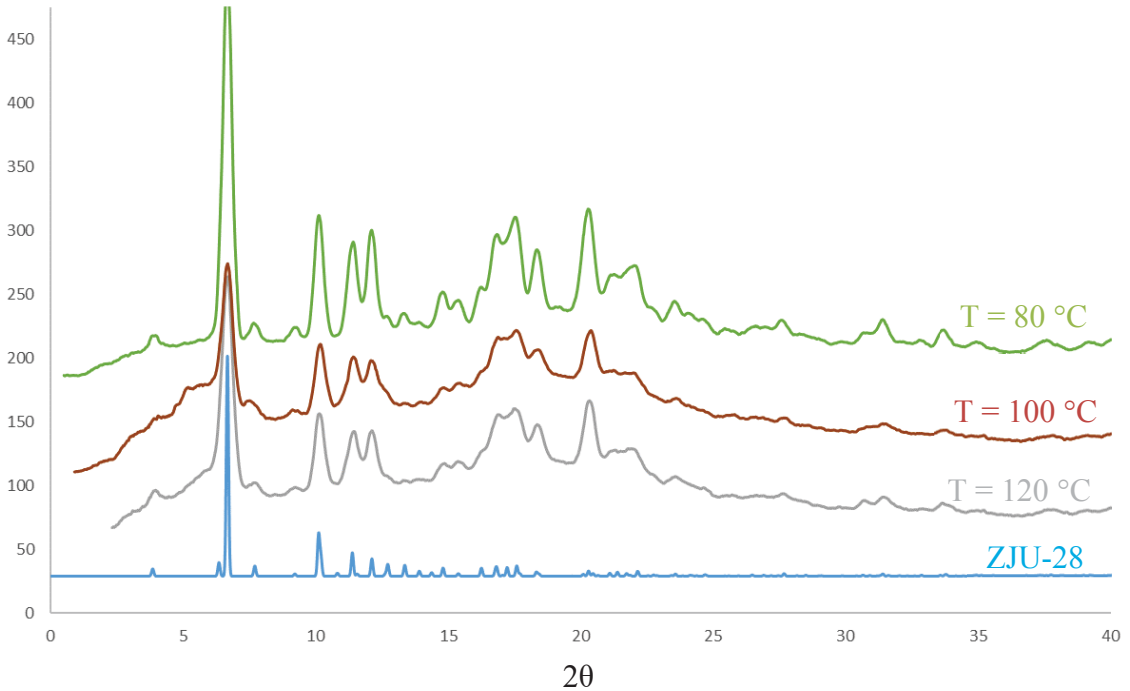


Figure A21. 0.37 equivalents spMPBr

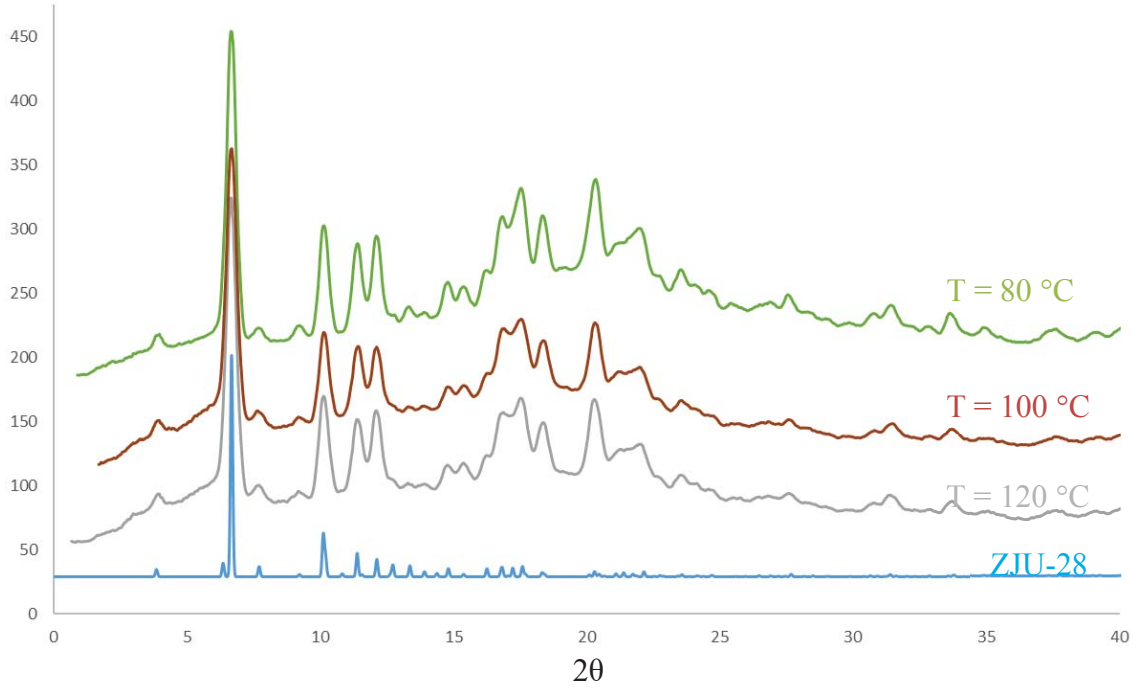


Figure A1 - 22. 0.56 equivalents spMPBr

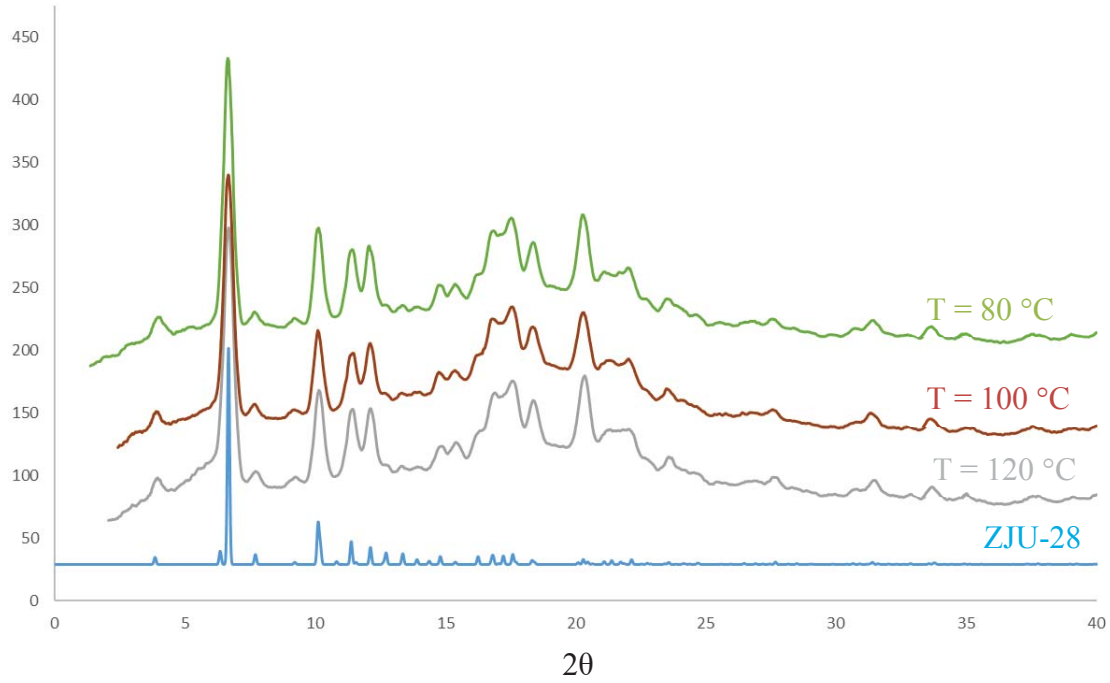


Figure A1 - 23. 0.83 equivalents spMPBr

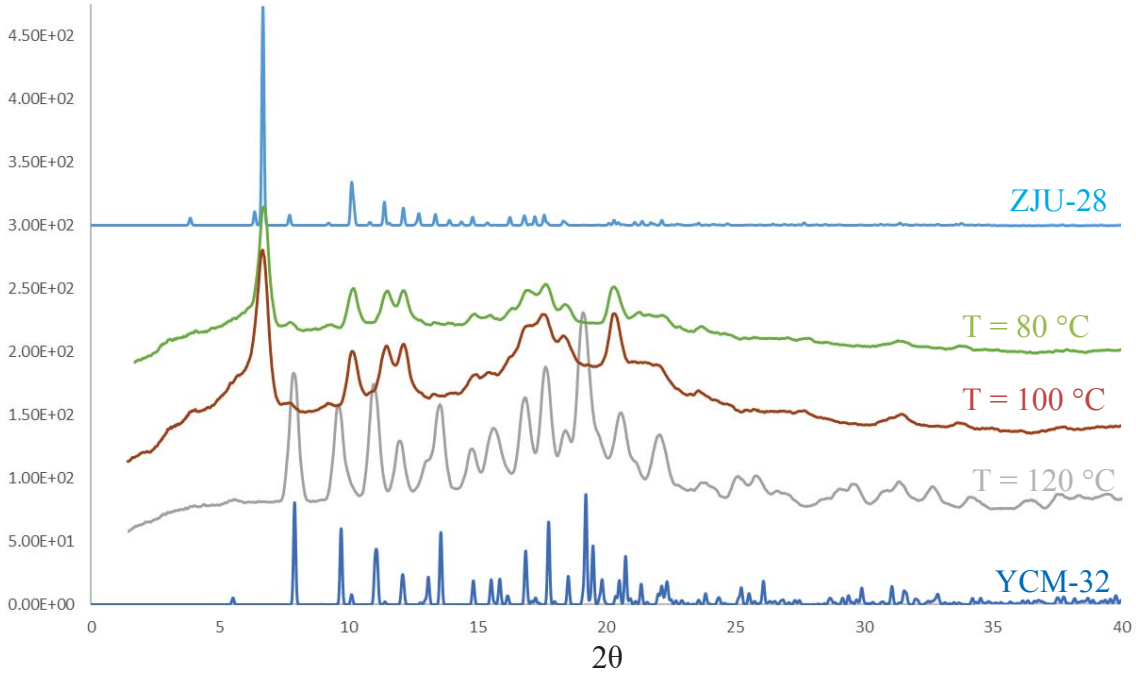


Figure A1 - 24. 1.0 equivalents spMPBr

Appendix 2 - Crystallographic Data Tables

Table A2 - 1. YCM-31-spPPCl

Crystal data	
Chemical formula	$C_{27}H_{15}ClInO_6 \cdot C_9H_{18}N \cdot 0.71(C_5H_{10}N) \cdot 0.617(C_3H_7NO)$
M_r	830.68
Crystal system, space group	Triclinic, *P*1
Temperature (K)	100
a, *b*, *c* (Å)	11.1033 (6), 12.1967 (7), 15.1510 (8)
α, β, γ (°)	69.9052 (17), 83.0639 (18), 89.6343 (18)
V (Å^3)	1911.44 (18)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.74
Crystal size (mm)	0.50 × 0.20 × 0.20
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan *SADABS* 2014/5
T_{min}, T_{max}	0.647, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	51251, 8457, 7948
R_{int}	0.046
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.643
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.054, 0.148, 1.21
No. of reflections	8457
No. of parameters	657
No. of restraints	530
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.07, −0.96

Table A2 - 2. YCM-32-spPPCl

Crystal data	
Chemical formula	$2(C_{27}H_{15}ClInO_6)\cdot 2C_9H_{18}N\cdot C_4H_8O_2\cdot C_3H_7NO$
M_r	1613.00
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	100
a, *b*, *c* (Å)	32.798 (7), 11.9306 (15), 18.620 (3)
β (°)	102.042 (7)
V (Å^3)	7126 (2)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.79
Crystal size (mm)	0.10 × 0.10 × 0.05
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan *SADABS* 2014/5
T_{min}, T_{max}	0.662, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	50097, 8008, 5738
R_{int}	0.133
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.648
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.069, 0.175, 1.04
No. of reflections	8008
No. of parameters	686
No. of restraints	1163
H-atom treatment	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.0723P)^2 + 67.7656P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	3.36, −0.90

Appendix 3 – H NMR for Spirocyclic Salts

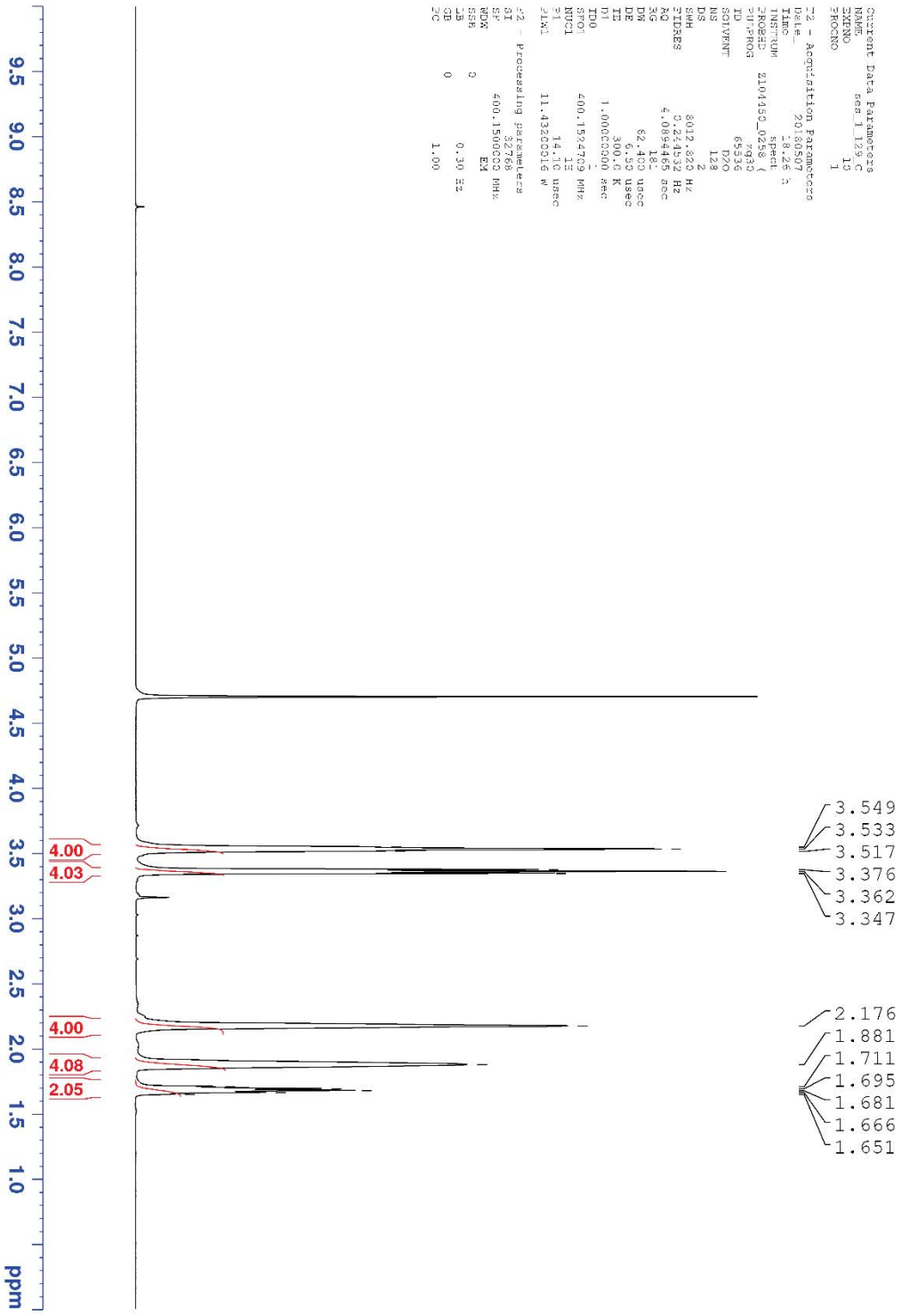


Figure A3- 1 H NMR of spPPBr

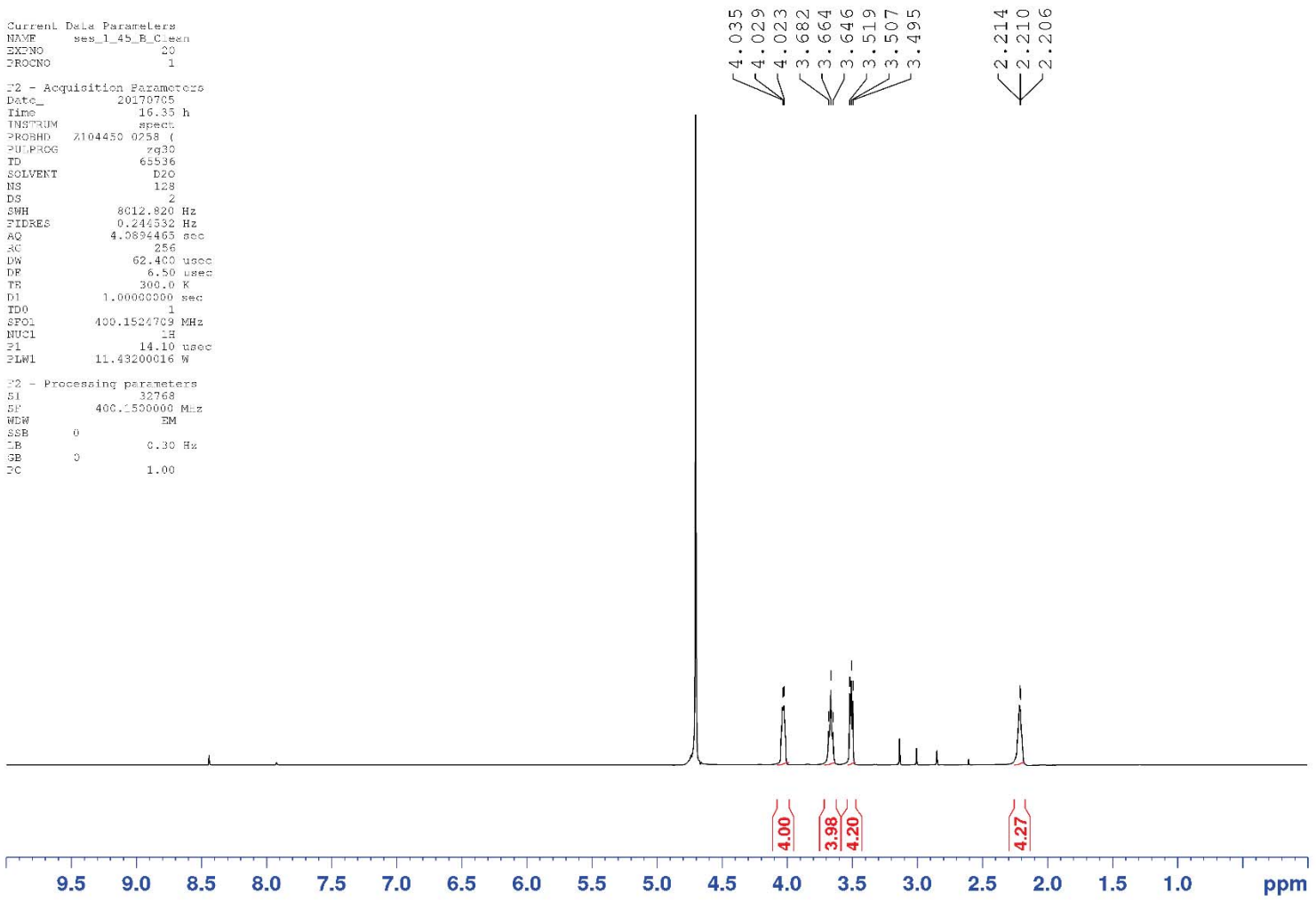


Figure A3- 2 H NMR of spMPBr

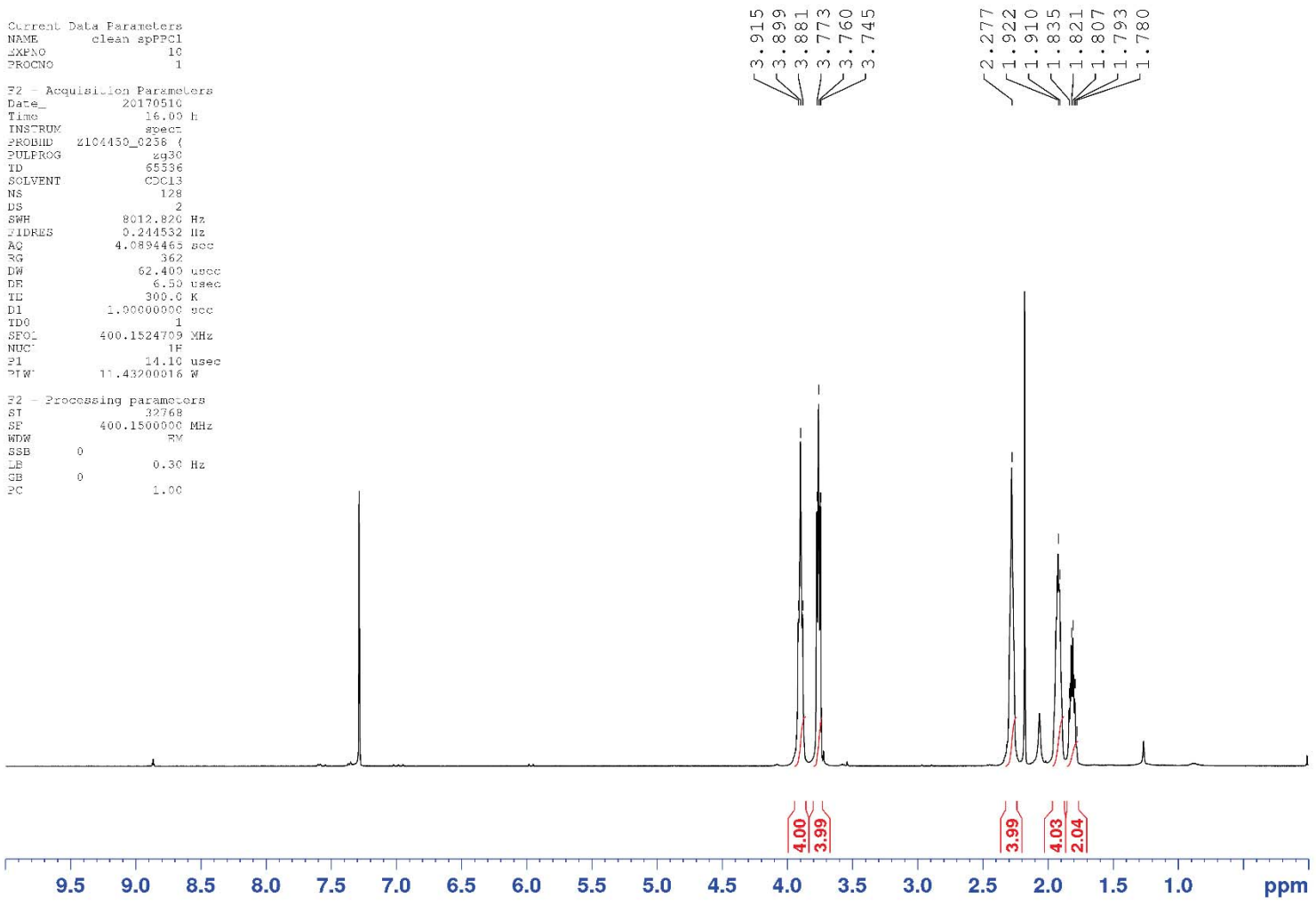


Figure A3- 3 H NMR of spPPCl

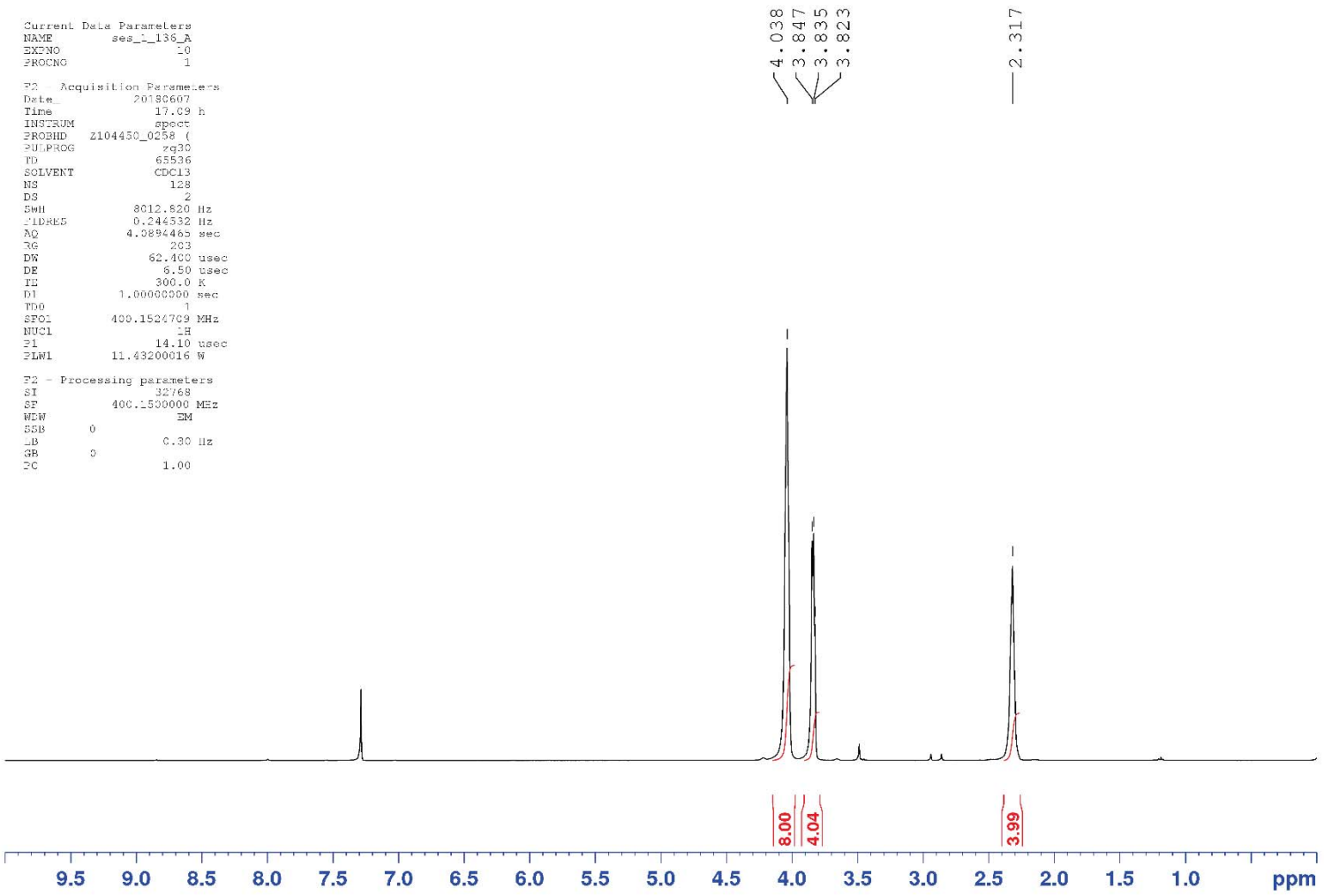


Figure A3- 4 H NMR of spMPCl

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