

# **Metal- Organic Materials Derived From Amino P(V) Ligands**



A thesis submitted towards partial fulfillment of  
**BS-MS Dual Degree Programme**

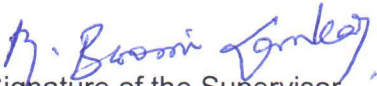
By  
**KIRAN DADASAHEB GAJHANS**  
**(Reg. no. 20121032)**

Under the guidance of

**Dr. R. BOOMI SHANKAR**  
**Department of Chemistry**  
**Indian Institute of Science Education and research, Pune**

## Certificate

This is to certify that this dissertation entitled “**Metal-organic materials derived from Amino P(V) ligands**” towards the partial fulfillment of **BS-MS Dual Degree Programme** at Indian Institute of Science Education and Research, Pune represents the research carried out by **Kiran Dadasaheb Gajhans** under the guidance of **Dr. R. Boomi Shankar**, Associate Professor at IISER Pune during the academic year 2016-2017.

  
Signature of the Supervisor

**Dr. R. Boomi Shankar**

*Department of Chemistry*

*IISER Pune*

Date: 23/03/2017

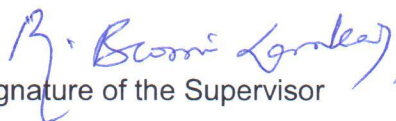
  
**Kiran Dadasaheb Gajhans**

(Reg. no. 20121032)

IISER Pune

## Declaration

I hereby declare that the matter embodied in the thesis titled “**Metal-organic materials derived from Amino P (V) ligands**” are the results of the investigations carried out by me at the Department of Chemistry, IISER Pune under the guidance of Dr. R. Boomi Shankar and the same has not been submitted elsewhere for any other degree.



Signature of the Supervisor

**Dr. R. Boomi Shankar**

*Associate Professor*

*Department of Chemistry*

*IISER Pune*

*Email: [boomi@iiserpune.ac.in](mailto:boomi@iiserpune.ac.in)*

*Phone: 020-2590-8208*

**Date:** 23/03/17



**Kiran Dadasaheb Gajhans**

**(Reg. no. 20121032)**

IISER Pune

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## Abbreviations

L <sup>1</sup>	(p-cresol)PO(NH- <sup>3</sup> Py)
L <sup>2</sup>	PhPO(NH- <sup>3</sup> Py)
L <sup>3</sup>	(p-cresol)PO(NH- <sup>3</sup> Py)
IR	Infrared
UV	Ultraviolet
NMR	Nuclear magnetic resonance
Ph	Phenyl
Py	Pyridyl
Eq.	Equivalent
EtOH	Ethanol
SC-XRD	Single crystal X-ray diffraction
PXRD	Powder X ray diffraction
MeOH	Methanol
ACN	Acetonitrile
MALDI-TOF	Matrix-Assisted laser desorption/ionization-time of flight
DMF	Dimethyl sulfoxide

## Abstract

Herein, we report the synthesis and metallation chemistry of dipodal pyridyl functionalized phenyl and p-cresol substituted pyridyl phosphoramidate ligands. The crystal structures of the p-cresol containing pyridyl phosphoramidate ligands have been reported. The metallation reaction of the p-cresol functionalized dipodal ligands are not successful. Reactivity of the ligand  $L^2$  (phenyl phosphoramidate ligand backbone) with silver salts results in the isolation of two different 1D- and 3D-frameworks. The non-centrosymmetric nature of the 3D-framework indicates the potential of this material as a possible ferroelectric material.



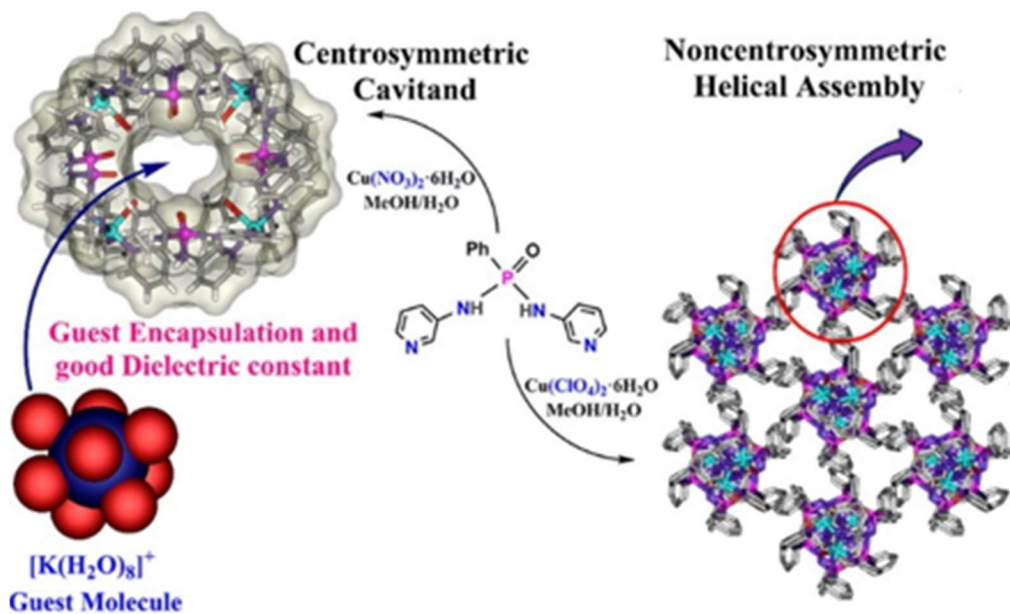
## Introduction

Past few decades have witnessed developments in coordination driven self-assemblies topic of research in area of supramolecular chemistry owing to their easy synthesis, novel applications and ability to display unique structure driven properties.<sup>1</sup> Organic ligand moieties offer tunable structural features depending on its shape- coordination angles, size- length and bulkiness of ligand and functionality whereas, the inorganic part- metal centers in such self-assemblies invoke thermal and mechanical stabilities and exhibit interesting magnetic, electric and nonlinear optical properties.<sup>2</sup> It is possible to get novel crystalline structures which range from zero dimensional discrete and well-define molecules, one-dimensional helices or chains, two dimensional layers grids as well as three dimensional frameworks and polyhedral assemblies with the help of self-assembly approach.<sup>3</sup> Metal-organic materials which show novel structural topologies have also been utilized for many applications in fields like selective binding and reactive molecule trapping <sup>4</sup>, gas and solvent storage and separation <sup>5</sup>. In order to achieve the above mentioned applications, the specific attributes of metal-organic materials such as metal ions, their coordination geometries, counter anions, ligand backbones, guest present in their voids and the topology of the obtained network needs to be controlled with accurate precision. Specifically, earlier reports from our group and others have shown that the P(V) centered ligand motifs, viz. phosphonate monoesters, phosphine- carboxylates, phosphine oxides, phosphonium salts and phosphoramides have received recent attention as they have shown to provide both rigid and flexible ligand platforms depending on the substituents around central phosphorous atom.

Our group has been actively synthesizing dipodal and tripodalphosphoramide ligands exhibiting various physical and chemical properties.<sup>6</sup> Amino-P(V) ligands containing peripheral pyridyl functionalities tend to offer flexible platform and their reactivity towards transition metal ions and lead to materials that exhibit structures with cluster, cage and functional framework architectures.<sup>7</sup> Also to obtain dynamic architectures with tunable properties, peripherally functionalized phosphoramides provides an essentially ideal platform. For example, the 3-pyridyly substituted phosphoric triamide ligand can lead to

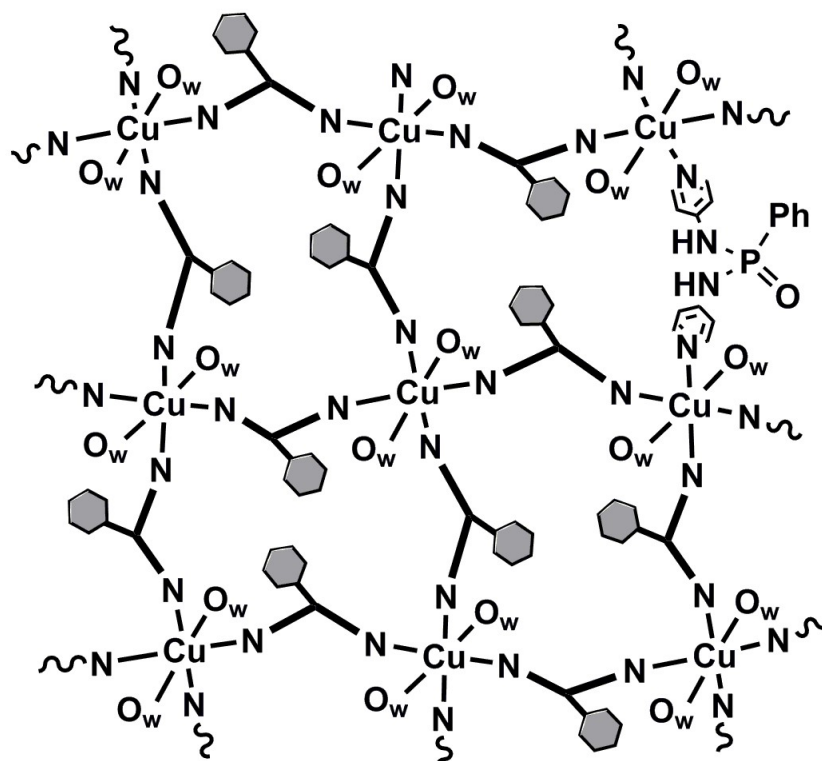
$M_6L_8$  nanocages with structurally different conformations and the anionic ligand  $[PO(NH^4Py)_2]^-$  can generate dynamic coordination polymers by changing the reaction conditions, temperature, etc.<sup>8</sup>

Interestingly, it has been reported from our group that dipodal ligands based on phenyl phosphoramides  $PhPO(NHPy)_2$  [  $Py = 2$ -pyridyl ( ${}^2Py$ ) or  $3$ -pyridyl ( ${}^3Py$ ) ] backbone can generate  $\{Cu^II L_2\}_n$  assemblies exhibiting both centrosymmetric and noncentrosymmetric crystal geometries.<sup>9</sup> However, both these classes of assemblies have shown interesting properties. The centrosymmetric assemblies  $\{Cu^II L_2\}_n$  has the structure of a cavitand and form the host-guest complexes with hydrated alkali-metal cations.<sup>9</sup> More importantly, the noncentrosymmetric assemblies were found to be a potential ferroelectric materials and exhibited high remnant polarization and dielectric constant values.<sup>9</sup> Utilizing a similar backbone as that of  $L^2$  but with  $4$ -pyridyl substituents a  $2D$ - $\{Cu^II L_2\}_n$  framework was reported which shows a good ferroelectric response and guest assisted dielectric anomaly (Figure 1).



**Figure 1:** Synthesis of anion driven ferroelectric material based on  $L^2$  ( Ref. 9)

Noncentrosymmetric helical assembly generates by treating L with excess of copper perchlorate ions in MeOH/H<sub>2</sub>O as a solvent (shown in Figure 2). These noncentrosymmetric helical assemblies show trigonal cavity. Perchlorate ions and solvate ions reside in these trigonal cavities.



**Figure 2 :** Structure of a 2D-framework materials based on a 4-pyridyl functionalized dipodal phosphoramidate ligand.

Focussing on a single unit in this noncentrosymmetric helical assembly each ligand can be assumed as a part of separate chain. These separate chains while propogating along the axis forms a left handed strand.<sup>9</sup> As we know, ferroelectricity is described by presence of permanent dipole in a material that can be reversed by applying an external magnetic field. Transfer of charge from a donor molecule to acceptor molecule allow them to go from neutral to ionic state breaking the centrosymmetric nature and leads to the creation of polarization.<sup>10</sup>

This process is energy driven in order to stabilize the molecule pair, thus giving a permanent dipole. Ferroelectric materials are highly desirable for making electronic memory devices.<sup>10,11</sup>

The most prevalent ferroelectric materials are perovskites, specifically Barium Titanate (BTO) and Lead zirconate titanate (PZT).<sup>11</sup> However, they are rigid and heavyweight, and require high temperature processing, which limits their application in certain field. Also, high lead content in PZT is a major environmental concern. In this regard, molecular ferroelectrics are drawing huge attention recently because of advantages associated with them such as lightness, flexibility, non-toxic and facile synthesis.<sup>7,11</sup>

Since, centrosymmetric helical assemblies do not contain any dipole moment. On the other hand transferring of a charge from donor molecule to acceptor molecule in the case of noncentrosymmetric assemblies lead to formation of polarization. Hence, noncentrosymmetric assemblies exhibit ferroelectric properties.

Despite the progress that has been made in recent years, the field of molecular and metal-organic ferroelectrics is still in its infancy. Phosphoramidate ligands are being explored and gave hope to explore this molecular treasure. Inspired from our previous work, we started with subtly varying the ligand backbone, metal ions and counter anions in order to obtain a family of noncentrosymmetric metal-organic assemblies.

In this effort, we have synthesized a ligand similar to  $\text{PhPO}(\text{NH}^3\text{Py})_2$  by employing a bulkier p-cresol moiety in place of phenyl ring. Herein, we have shown synthesis of a ligand  $(p\text{-cresol})\text{PO}(\text{NH}^3\text{Py})_2$  in its pure form. Further, we have successfully deduced crystal structure of newly synthesized  $(p\text{-cresol})\text{PO}(\text{NH}^3\text{Py})_2$  ligand and have utilized the ligand in reaction with various transition metal salts, in view to obtain noncentrosymmetric metal-organic assemblies. In another effort, the previously reported ligand  $\text{PhPO}(\text{NH}^3\text{Py})_2$  gave an interesting 1D- and 3D-frameworks upon treatment with  $\text{AgClO}_4$ . Interestingly, the 3D-framework is crystallized in the non-centrosymmetric space group and thus could be a potential ferroelectric material.

## Experimental

### General remarks

All manipulations involving phosphorus halides and reactions are performed under a dry nitrogen atmosphere in standard Schlenk glassware. 3-Aminopyridine, POCl<sub>3</sub>, Triethylamine were purchased from Aldrich and used as received. PhPOCl<sub>2</sub> was purchased from Acros-Organics and used as received. The solvent Toluene was dried using sodium. p-cresol was purchased from Alfa-aesar. Tetrabutylammonium nitrate, Copper perchlorate salts were purchased from Aldrich, and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O was purchased from Merck and used as received. NMR spectra were recorded on a Jeol 400 MHz spectrometer (<sup>1</sup>H NMR: 400.13 MHz; <sup>13</sup>C{<sup>1</sup>H} NMR, 100.62 MHz; <sup>31</sup>P{<sup>1</sup>H} NMR, 161.97 MHz) at room temperature using SiMe<sub>4</sub> (<sup>1</sup>H, <sup>13</sup>C) and H<sub>3</sub>PO<sub>4</sub> as external standards. MALDI-TOF spectra were obtained on an Applied Biosystem MALDI-TOF/TOF spectrometer. The powder X-ray diffraction (PXRD) data were obtained from a Bruker-D8 Advance diffractometer. FT-IR spectra were taken on a PerkinElmer spectrophotometer with samples prepared as KBr pellets.

### Synthesis

**S<sup>1</sup>:** In a two neck RB, p-cresol (1.6ml, 40mmol, 1 eq. ) was dissolved in 40 ml of dry diethyl ether under an inert atmosphere. The solution was then cooled further to -78°C using dry ice and acetone. After stirring for 10 minutes, POCl<sub>3</sub> ( 1.5ml, 40mmol, 1eq. ) was injected slowly to the mixture. Triethylamine was then added to the reaction mixture dropwise. Now, the reaction mixture was kept for stirring for 12 hours at room temperature. A white colored precipitate was formed. This mixture was then filtered using FRIT. Filtrate was concentrated using rotor evaporator. The resulting compound was further characterized by MALDI-TOF, <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR and it confirms the formation of S<sup>1</sup>.

**L<sup>1</sup>:** 3-Aminopyridine (4.5gm, 48mmol, 4eq.) was dissolved in dry acetonitrile under an inert atmosphere. To this solution, S<sup>1</sup> (12mmol, 1eq.) was introduced dropwise at 0°C. The reaction mixture was stirred for 10 hours. A white colored (light pink) precipitate was formed. Now, the remaining solvent in the mixture was evaporated and the residue was

washed 2-3 times with distill water and dried. The resulting phosphoramidate compound was characterized using MALDI-TOF,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR. MALDI-TOF,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR confirms the formation of  $\text{L}^1$  in pure form which is discussed in results and discussion part. Crystal of  $\text{L}^1$  was obtained from its methanolic solution in which  $\text{L}^1$  was dissolved.

$^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO):  $\delta$  = 8.77-8.80 (2H), 8.39 (2H), 8.10-8.11 (2H), 7.49-7.52 (2H), 6.95-7.27 (6H) ppm.  $^{31}\text{P}$  NMR (161.97 MHz,  $D_6$ -DMSO):  $\delta$  = -2.10 ppm. MALDI-TOF  $m/z$  = 342  $[\text{M}+\text{H}]^+$ , 362.99  $[\text{M}+\text{Na}]^+$ , 378.96  $[\text{M}+\text{K}]^+$ .  $^{13}\text{C}$  NMR (100.62 MHz,  $D_6$ -DMSO):  $\delta$  – 148.17, 142.19, 139.70, 137.76, 134.64, 130.63, 124.41, 120.57, 120.53 ppm. FT-IR data in KBr pellet ( $\text{cm}^{-1}$ ): 3405, 3130, 2940, 1579, 1494, 1467, 1396, 1330, 1272, 1212, 1165, 1127, 1098, 1016, 979, 947, 808, 748, 698, 609, 557, 492.

## General procedure for the metallation reactions of $\text{L}^1$ :

**I:** To a solution of  $\text{L}^1$  ( 0.05mmol ) in MeOH (2 ml) was added a solution of  $\text{M}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.025mmol) (Here M = Cu, Cd, Zn, Co and Ni) in  $\text{H}_2\text{O}$  (2 ml). The reaction mixture was mixed for 4 hours using stirrer. The solution was filtered through caelite. and kept for crystallization.

## Preparation of Ag(I) compounds 1 and 2:

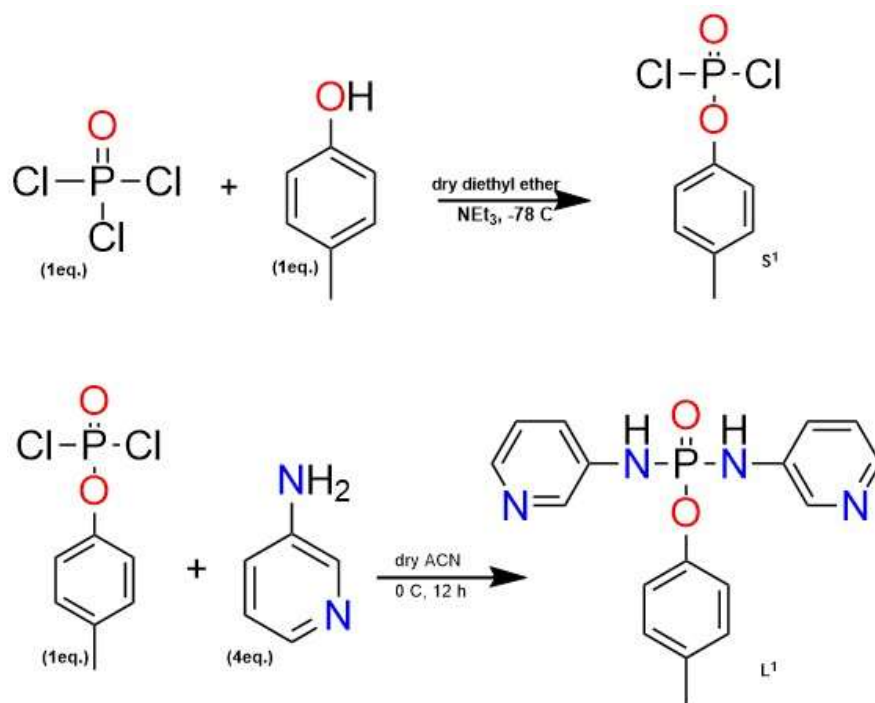
Compounds **1** and **2** were prepared by layering method using toluene.

**1:** Single crystals of Ag(I) ions  $\text{L}^2$  were synthesized by reacting  $\text{AgClO}_4$  (0.1 mmol, 20.7 mg),  $\text{L}^2$  (0.1 mmol, 31 mg) in Toluene (3 mL) and MeOH (3mL) in a 10ml layering tube at room temperature. The tube was then kept at 300 K until crystallization/ crystals were formed. The colorless crystals were observed after 4 days .

**2:** Single crystals of Ag(I) ions  $\text{L}^2$  were synthesized by reacting  $\text{AgClO}_4$  (0.1 mmol, 20.7 mg),  $\text{L}^2$  (0.2 mmol, 62.1 mg) in Toluene (3 mL) and MeOH (3mL) in a 10ml layering tube at room temperature. The tube was then kept at 300 K until crystallization/ crystals were formed. The colorless crystals were observed.

## Results and Discussion

The ligand  $L^1$  was synthesized by reaction of 3-aminopyridine with (p-cresol)POCl<sub>2</sub> in presence of triethylamine. The ligand was characterized by mass spectroscopy, <sup>1</sup>H, <sup>31</sup>P and <sup>13</sup>C NMR. The reaction scheme and conditions for the formation of  $L^1$  are (shown in figure 3).



**Figure 3:** Reaction scheme and condition for formation of  $L^1$

### Characterization of $L^1$

To confirm the formation of  $L^1$ , MALDI-TOF spectra was taken which is shown below. The MALDI spectra shows the peak corresponding to the expected mass i.e. 341. Peaks at 342, 362, 378 relate to  $[M+H]^+$ ,  $[M+Na]^+$ ,  $[M+K]^+$  respectively which shows the formation of  $L^1$ .

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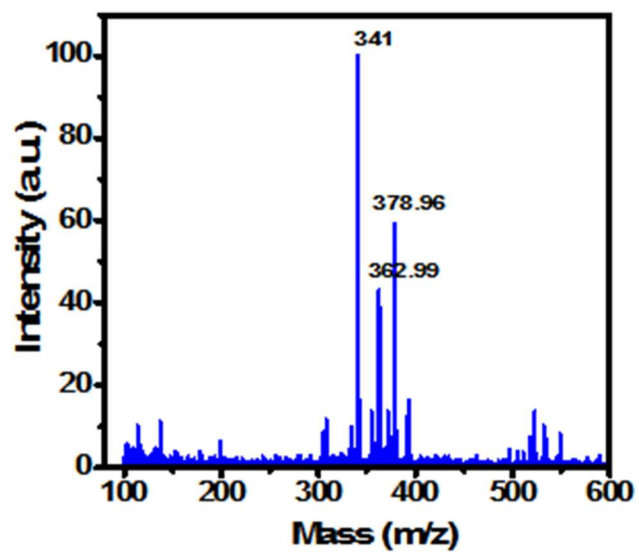


Figure 4: MALDI-TOF spectra of L<sup>1</sup>

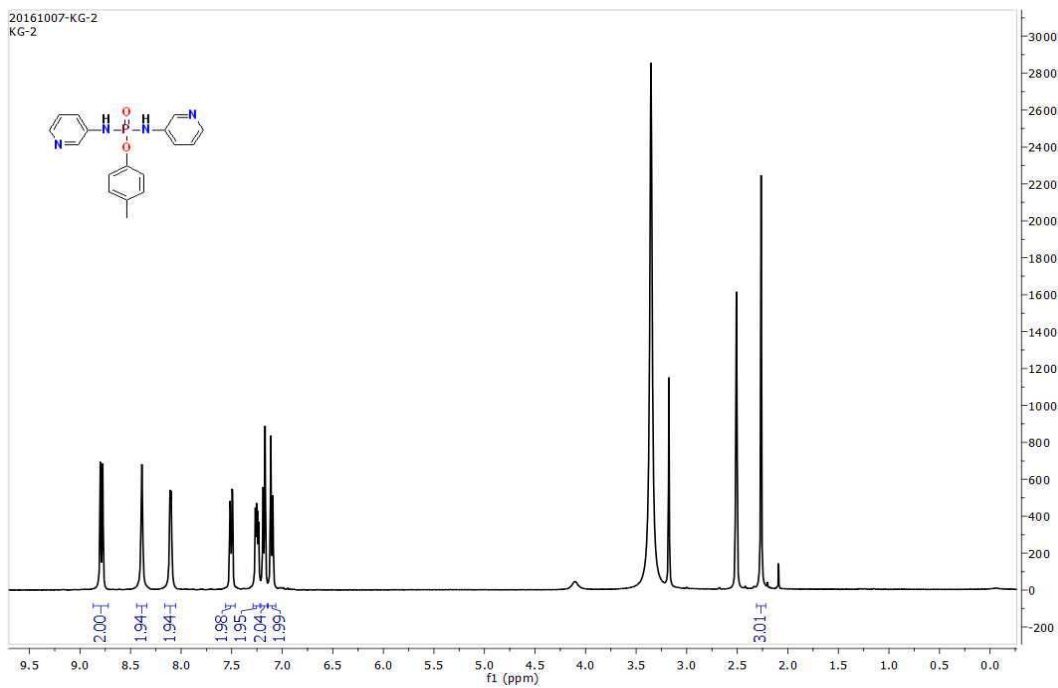


Figure 5: <sup>1</sup>H NMR spectra of L<sup>1</sup>



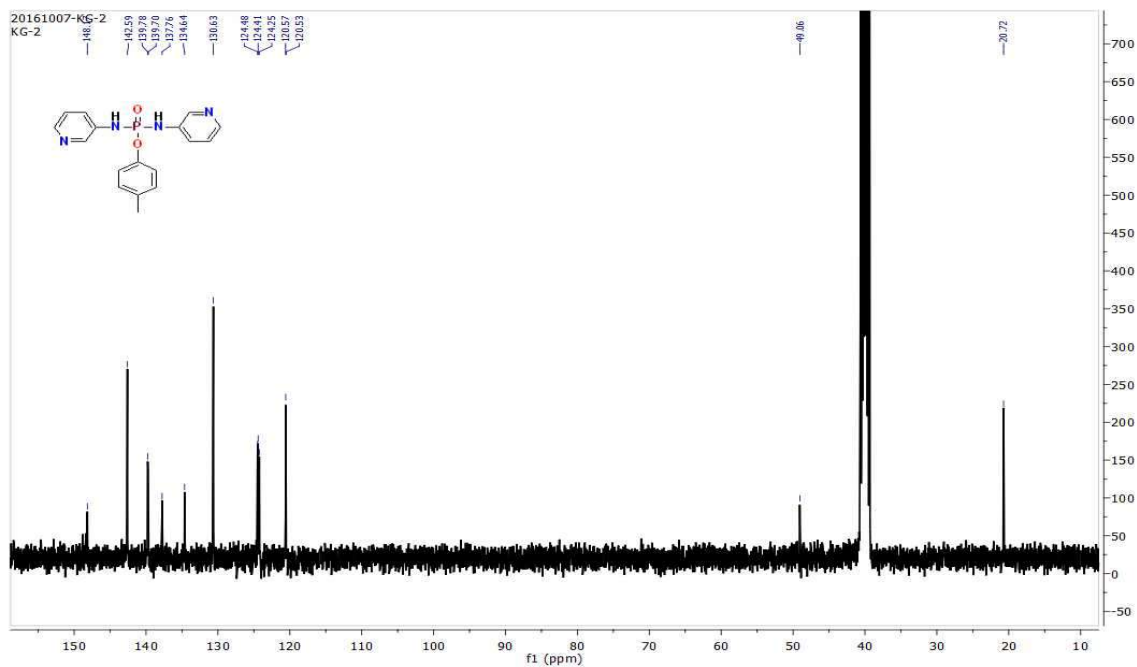


Figure 6:  $^{13}\text{C}$  NMR spectra of  $L^1$

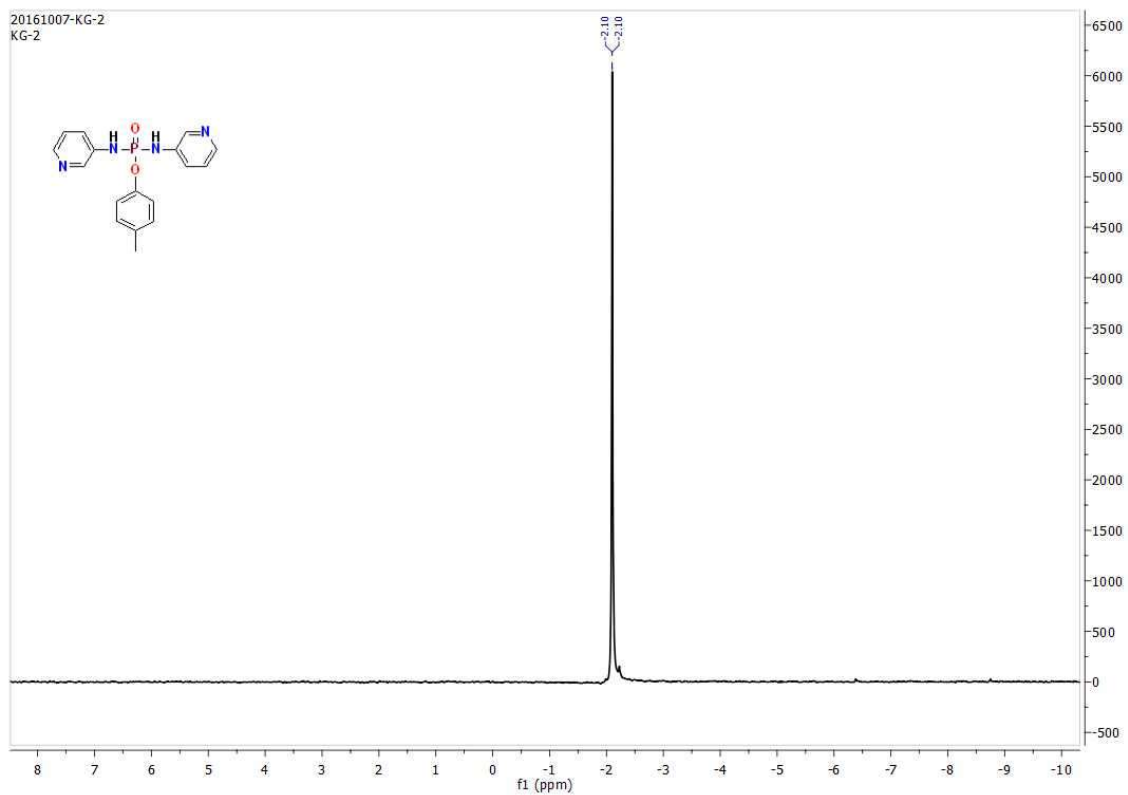


Figure 7:  $^{31}\text{P}$  NMR spectra of  $L^1$

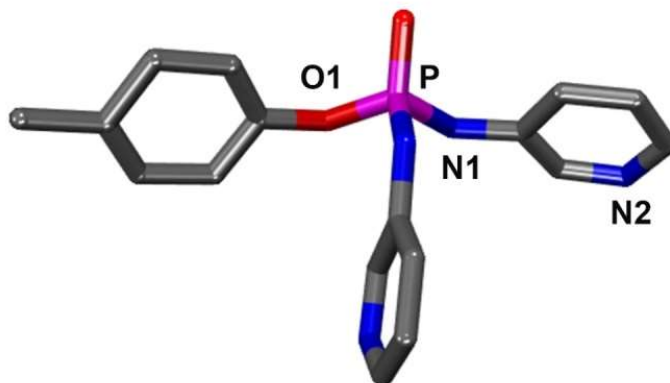
In  $^1\text{H}$  NMR, the proton next to nitrogen (and tertiary carbon) in pyridyl ring is most deshielded and hence comes upfield in region at  $\delta = 8.04$  ppm. The next peak in the NMR spectra corresponds to the other protons next to nitrogen in pyridyl ring comes as a doublet at  $\delta = 7.92$  ppm. The other protons of pyridyl ring appear at  $\delta = 7.36$  ppm. As it can be seen from NMR, there are merged peaks giving integration as 6. These 6 protons correspond to the aromatic protons of p-cresol ring. The singlet peak at 2.25 ppm is the methyl proton of p-cresol ring.

In the  $^{13}\text{C}$  NMR of  $\text{L}^1$ , the peak at 148.17 ppm is most deshielded carbon which corresponds to the tertiary carbon of p-cresol ring next to oxygen followed by the tertiary carbons of pyridyl ring. The next two carbons in C13 spectra are carbon next to nitrogen in pyridyl ring at 142 ppm and 139 ppm. The other tertiary carbon of p-cresol comes at 137 ppm, followed by the ortho carbons next to the methyl. The next peaks appearing at 134, 130 and 120 ppm are the protons of pyridyl ring. The most shielded proton is the methyl group attached with p-cresol ring which appears downfield at 20.72 ppm.

Also, the  $^{31}\text{P}$  NMR of  $\text{L}^1$  shows a single peak at  $\delta = -2.1$  ppm confirming the formation of ligand in its pure form and no other phosphorous impurity. Hence, all characterization techniques mentioned above clearly show formation of ligand  $\text{L}^1$ .

### Crystal structure of $\text{L}^1(\text{C}_{17}\text{H}_{17}\text{N}_4\text{O}_2\text{P})$ :

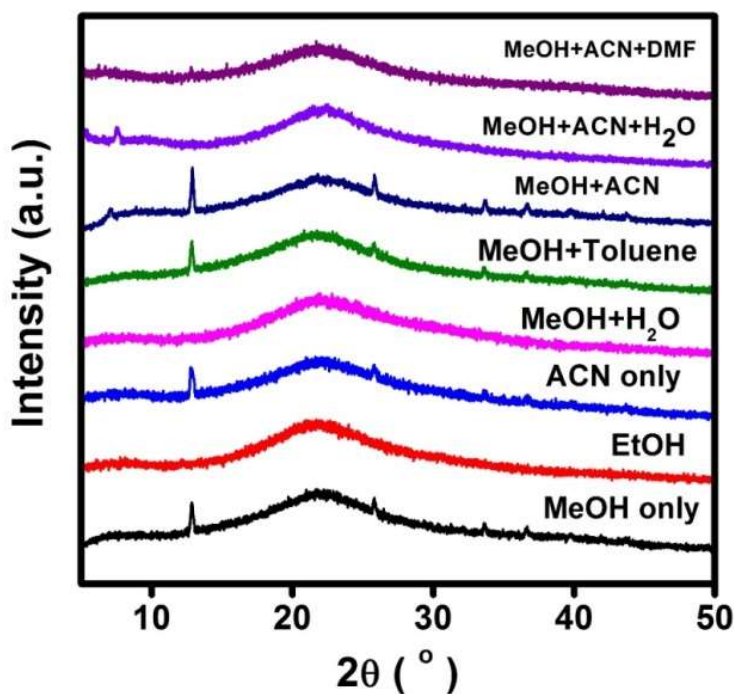
Ligand  $\text{L}^1$  crystallizes in monoclinic crystal system space group  $\text{P}2_1$ . P-N bond distance is 1.64 Å, while P-O bond distance is 1.56 Å.



**Figure 8:** Crystal structure of  $\text{L}^1$

## Metallation reactions and Analysis

We setup a number of metallation reactions with  $L^1$  with different metal salts in order to get a noncentrosymmetric complex so that we could further investigate its potential as ferroelectric material. In this process, we got many powders but could not get single crystal that can be examined by SC-XRD. So, in order to understand if the powder that we are getting has complex formed we proceeded to PXRD.



**Figure 9:** PXRD patterns for  $L^1$

Initially, we used MeOH solvent for metallation reactions and by looking at the PXRD pattern we can say that the complex formed. So, in order to obtain single crystal we thought of playing with different solvent combinations and used EtOH as a solvent for metallation reactions. As we can say from the plot, the complex which is formed is amorphous in nature as we see no sharp peak and hence we eliminated EtOH solvent from metallation reactions. Then, we used ACN solvent for metallation reactions.

Looking at the PXRD pattern of ACN solvent we can say that the complex formed is again not crystalline in nature. But if we compare this pattern with MeOH solvent PXRD pattern we find similarity in both.

Observing the patterns of different solvents, we increased polarity by adding H<sub>2</sub>O with MeOH thinking that we will get crystals. The pattern we got said that complex formed is amorphous in nature. Here, we can say that as water molecule is small in size it might not be acting as a good template in the reaction and complex can get squeezed. So, we used toluene instead of H<sub>2</sub>O along with MeOH as it is bigger in size and it will act as good template. But, when we observed the PXRD pattern we found it similar to that of MeOH PXRD pattern which means that the complex formed is similar crystalline but no expected cage crystals were formed.

Now, we further studied to use mixture of solvents and in turn we setup reactions using MeOH and ACN as solvents. PXRD pattern found was similar to that of MeOH. Now, we used H<sub>2</sub>O along with MeOH and ACN but the PXRD pattern suggests that the complex formed is amorphous in nature.

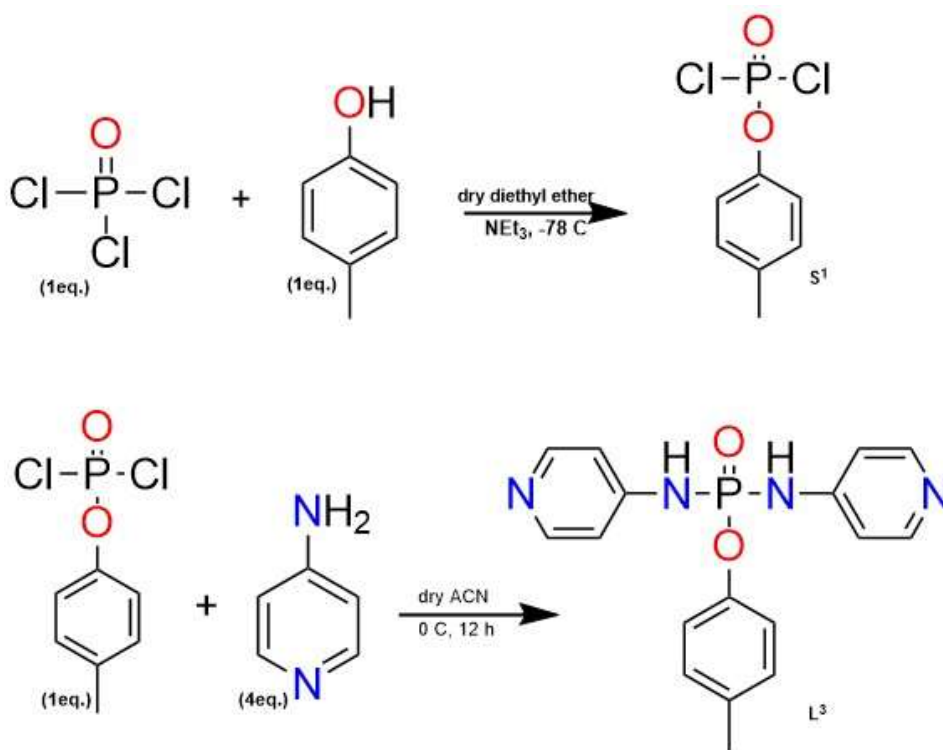
We further we use DMF solvent combination which has high boiling point and will take time to evaporate thereby helping in crystal formation. When we had a look at the PXRD pattern, we came to know that the complex formed is similar to earlier cases.

Therefore from all these studies we observed that polar solvents were helping to form high crystalline materials at room temperature but no expected single crystals were obtained. From all these inputs we further focused our studies using different polar-nonpolar, bulky- smaller, electron rich aromatic solvents as a templates combination at higher temperature via solvo-thermal reactions. Also, we attempted to prepare the 4-pyridyl analogue of the phosphoramidate ligand L<sup>1</sup>. The attempted synthetic procedure is described below.

**L<sup>3</sup>**: 4-Aminopyridine (4.5gm, 48mmol, 4eq.) was dissolved in dry acetonitrile under an inert atmosphere. To this solution, **S<sup>1</sup>** (12mmol, 1eq.) was introduced dropwise at 0°C. The reaction mixture was stirred for 10 hours. A white colored (light pink) precipitate was formed. Now, the remaining solvent in the mixture was evaporated and the residue was washed 2-3 times with distill water and dried.

The resulting phosphoramidate compound was then characterized using MALDI-TOF, <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR. Crystal of **L<sup>3</sup>** was obtained from its methanolic solution in which **L<sup>3</sup>** was dissolved.

The ligand **L<sup>3</sup>** was synthesized by reaction of 3-aminopyridine with p-crePOCl<sub>2</sub> in presence of triethylamine. The ligand was characterized by mass spectroscopy, <sup>1</sup>H, <sup>31</sup>P and <sup>13</sup>C NMR. The reaction scheme and conditions for the formation of **L<sup>1</sup>** are shown



**Figure 10:** Reaction scheme for formation of **L<sup>3</sup>**

## Characterization of L<sup>3</sup>:

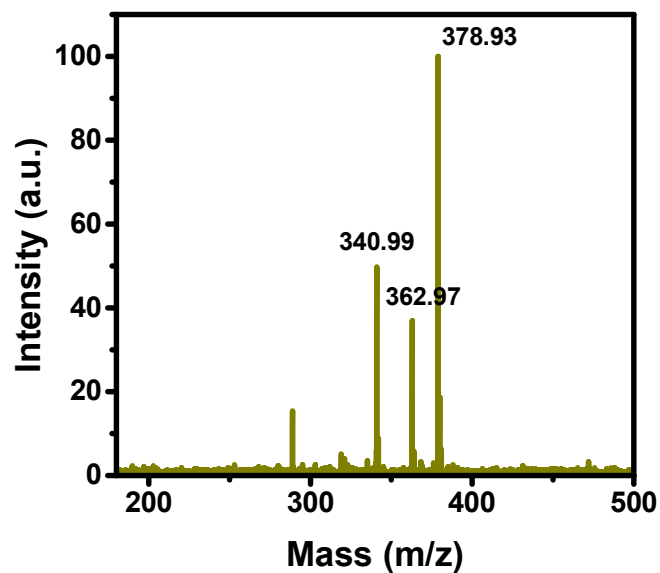


Figure 11: MALDI-TOF spectra of L<sup>3</sup>

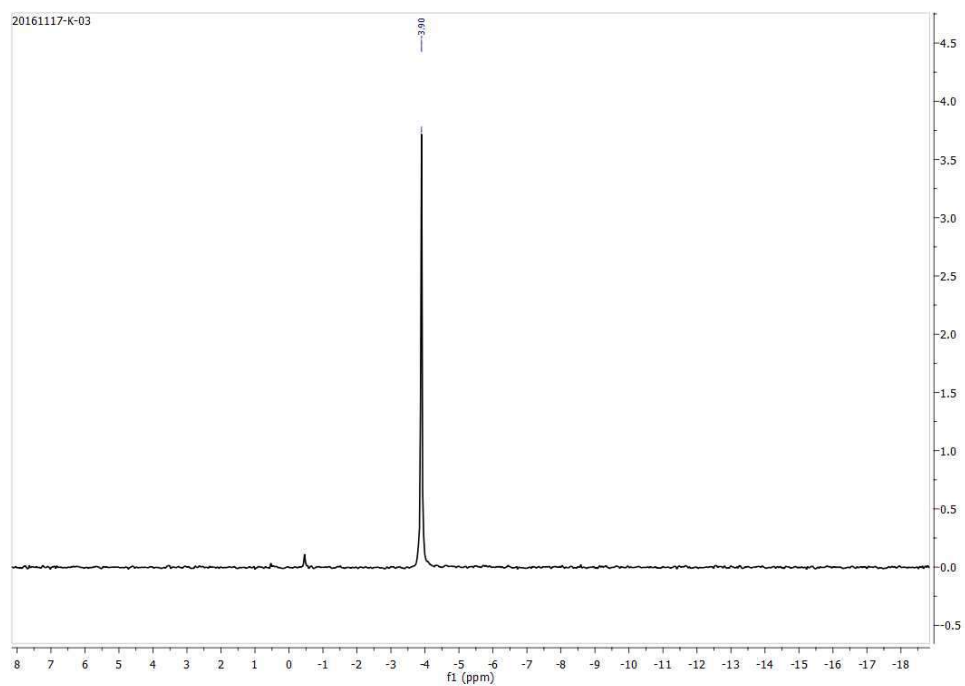
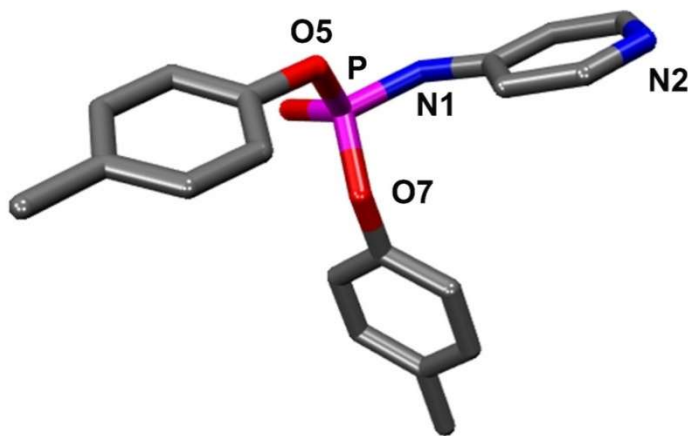


Figure 12 : <sup>31</sup>P NMR for L<sup>3</sup>

We got the expected mass spectra at 341, 362, 368 representing  $[M+H]^+$ ,  $[M+Na]^+$ ,  $[M+K]^+$  respectively and also  $^{31}\text{P}$  NMR peak at  $\delta = -3.9$  (reported). But we did not get  $^1\text{H}$  and  $^{13}\text{C}$  NMR.

## Crystal structure

**$\text{C}_{19}\text{H}_{19}\text{O}_3\text{N}_2\text{P}$**  : The crystal structure analysis revealed that the obtained compound contains two p-cresol groups and one pyridyl functionality. Hence, the synthetic procedure needs to be repeated to obtain the desired ligand. The ligand  $\text{L}^3$  crystallizes in monoclinic space group  $\text{P}2_1/c$ . The P-O bond distance is 1.46 Å. P-N bond distance is 1.632 Å.

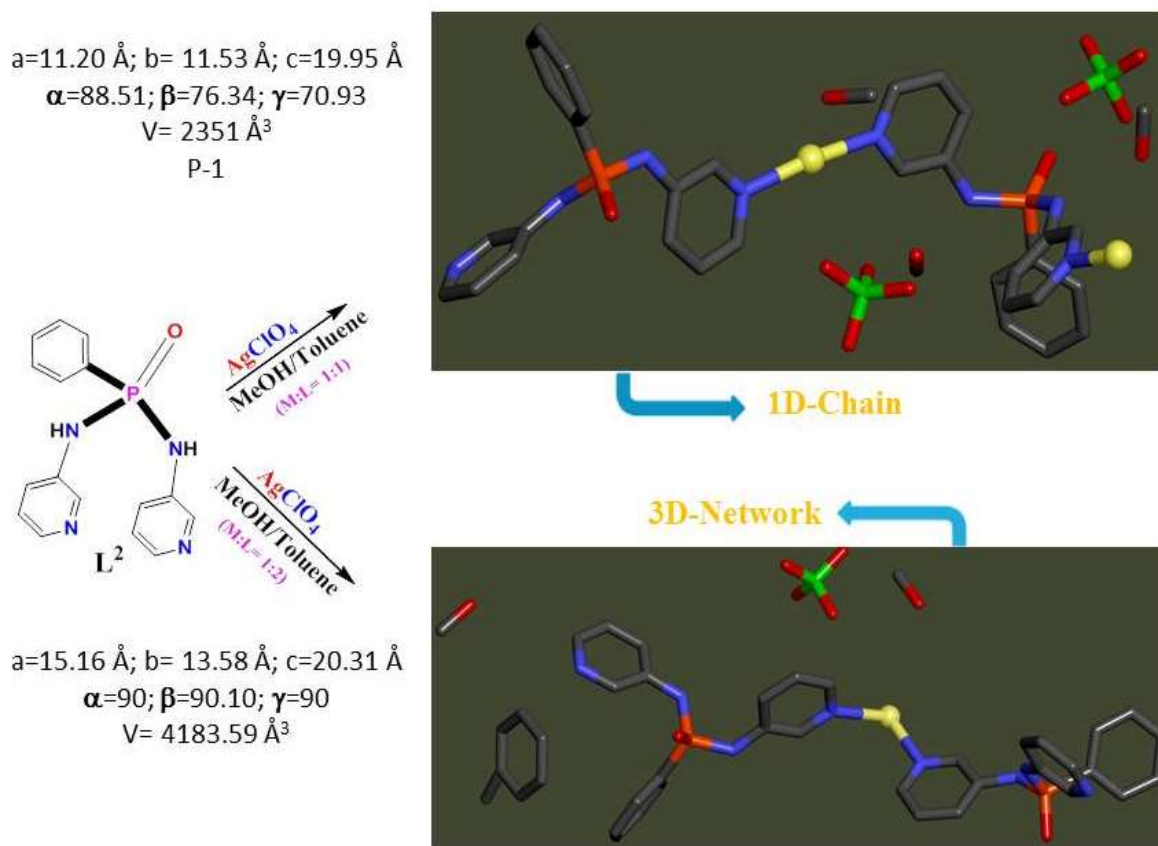


**Figure 13:** Crystal structure

Since, the metallation reactions of  $\text{L}^1$  could not result in any structurally isolated compound, the analogous ligand  $\text{L}^2$  which has already known to result in the formation of non-centrosymmetric metal-organic materials has been re-looked again for metallation reactions. Thus, treatment of  $\text{L}^2$  with several other metal ions has been attempted. Notably reaction of  $\text{L}^2$  with  $\text{AgClO}_4$  gave interesting results (Scheme below).

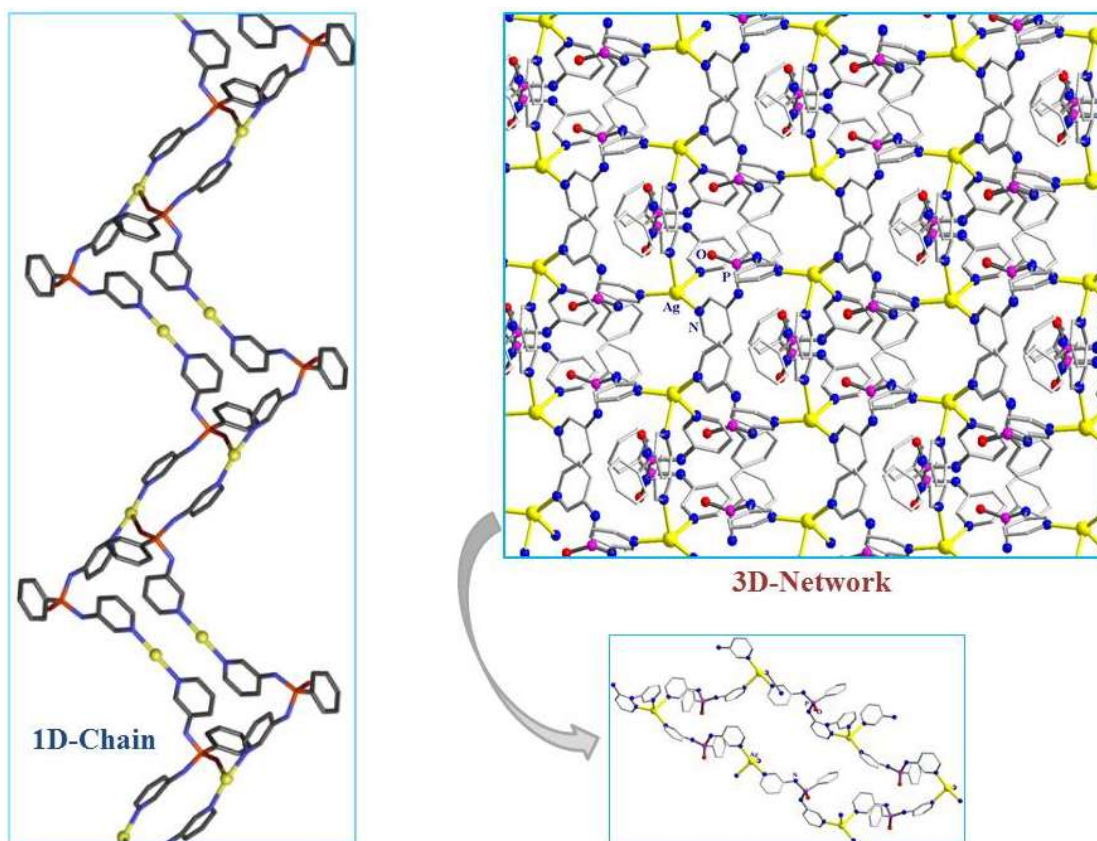
This reaction depending upon the stoichiometry of the reactants gave two new  $\text{Ag(I)}$  complexes as crystalline samples in small yields. X-ray diffraction investigation of these

single crystals showed the development of two new polymeric assemblies in 1D- and 3D- architectures. Owing to the poor yields of these compounds, other analytical characterizations have not been performed. However, it is believed that these reactions can be properly optimized to reproduce these results quantitatively.



**Scheme 1:** Formation of two Ag(I) complexes based on **L<sup>2</sup>**





**Figure 13:** Crystal Structures of the 1D- and 3D-coordinations polymers **1** and **2** derived from Ag(I) ions and L<sup>2</sup>

The molecular structures of these frameworks show that the Ag(I) ions exhibit variable coordination. In the 1D-framework it exists in a linear two-coordinate environment with two pyridyl contacts from two different L<sup>2</sup> segments. In the 3D-framework the Ag(I) ions are positioned in a tetrahedral setting and contains four pyridyl associates from four different L<sup>2</sup> segments. This arrangement is thus responsible for the extension of this framework in the three-dimension. Another interesting aspect of the structure of the 3D-framework lies in the crystal geometry. It crystallizes in the non-centrosymmetric framework and thus is suitable for investigation as a possible ferroelectric material.

## Conclusion

In conclusion, we examined the synthesis and coordination chemistry of dipodal pyridyl functionalized phosphoramidate ligands containing phenyl and p-cresol backbone moieties. The crystal structures of the p-cresol containing pyridyl phosphoramidate ligands have been reported. The metallation reaction of the p-cresol functionalized dipodal ligands are not successful so far and thus provides an opportunity to investigate its reactivity more closely. Reactivity of the ligand  $L^2$  (phenyl phosphoramidate ligand backbone) with silver salts results in the isolation of two different 1D- and 3D-frameworks. The non-centrosymmetric nature of the 3D-framework indicates the potential of this material as a possible ferroelectric material.

## Reference

- (1) (a) Cariati, Elena, Machhi, R.; Roberto, D.; Ugo, R.; Galli, S.; Casati, N.; Machhi, P.; Sironi, A.; Bogani, L.; Caneschi, A. "Polyfunctional inorganic– organic hybrid materials: an unusual kind of NLO active layered mixed metal oxalates with tunable magnetic properties and very large second harmonic generation." *J. Am. Chem. Soc.* **2007**, 129, 9410-9420. (b) Horcajada, P., Serre, C., Vallet-Regí, M., Sebban, M., Taulelle, F., & Férey, G. (2006). Metal-organic frameworks as efficient materials for drug delivery. *Angew. Chem., Int. Ed.* **2006**, 45(36), 5974-5978. (c) Ma, L., Falkowski, J. M., Abney, C., & Lin, W. A series of isoreticular chiral metal– organic frameworks as a tunable platform for asymmetric catalysis. *Nat. Chem.*, **2010**, 2(10), 838-846. (d) Wang, M. S., Guo, S. P., Li, Y., Cai, L. Z., Zou, J. P., Xu, G., ... & Guo, G. C. A direct white-light-emitting metal– organic framework with tunable yellow-to-white photoluminescence by variation of excitation light. *J. Am. Chem. Soc.* **2009**, 131(38), 13572-13573.
- (2) (a) Batten, Stuart R., and Keith S. Murray. "Structure and magnetism of coordination polymers containing dicyanamide and tricyanomethanide." *Coord. Chem. Rev.*, **2003**, 246.1, 103-130. (b) Noveron, J. C., Lah, M. S., Del Sesto, R. E., Arif, A. M., Miller, J. S., & Stang, P. J. (2002). Engineering the structure and magnetic properties of crystalline solids via the metal-directed self-assembly of a versatile molecular building unit. *J. Am. Chem. Soc.* **2002**, 124(23), 6613-6625. (c) Wang, Xin-Yi, Zhe-Ming Wang, and Song Gao. "A pillared layer MOF with anion-tunable magnetic properties and photochemical [2+ 2] cycloaddition." *Chem. Commun.*, **2007**, 1127-1129.
- (3) (a) Furukawa, H., Cordova, K. E., O'Keeffe, M., & Yaghi, O. M. The chemistry and applications of metal-organic frameworks. *Science*, **2013**, 341(6149), 1230444. (b) Long, J. R., & Yaghi, O. M. The pervasive chemistry of metal–organic frameworks. *Chem. Soc. Rev.* **2009**, 38(5), 1213-1214. (c) Zou X, Ren H, Zhu G. Topology-directed design of porous organic frameworks and their advanced applications. *Chem. Commun.* **2013**, 49(38), 3925-36.

- (4) (a) Müller, C., Whiteford, J. A., & Stang, P. J. (1998). Self-Assembly, Chiroptical Properties, and Host– Guest Chemistry of Chiral Pt– Pt and Pt– Pd Tetranuclear Macrocycles. Circular Dichroism Studies on Neutral Guest Inclusion Phenomena. . *J. Am. Chem. Soc.*, **1998**, *120*(38), 9827-9837. (b) Cai, H., Li, M., Lin, X. R., Chen, W., Chen, G. H., Huang, X. C., & Li, D. (2015). Spatial, Hysteretic, and Adaptive Host–Guest Chemistry in a Metal–Organic Framework with Open Watson–Crick Sites. *Angew. Chem., Int. Ed*, **2015**, *127*(36), 10600-10605.
- (5) Ajami, D., & Rebek, J. Gas Behavior in Self-Assembled Capsules. *Angew. Chem., Int. Ed*, **2008**, *47*(32), 6059-6061.
- (6) (a) Gupta, Arvind K., Anant Kumar Srivastava, Indra Kumar Mahawar, and Ramamoorthy Boomishankar. "Discrete and Polymeric Cu (II) Complexes Derived from in Situ Generated Pyridyl-Functionalized Bis (amido) phosphate Ligands,[PO<sub>2</sub> (NHPy) <sub>2</sub>]-." *Cryst. Growth Des.* **2014**, 1701-1709. (b) Srivastava, Anant Kumar, B. Praveenkumar, Indra Kumar Mahawar, Pillutla Divya, S. Shalini, and Ramamoorthy Boomishankar. "Anion driven [CuII<sub>2</sub>] <sub>n</sub> frameworks: crystal structures, guest-encapsulation, dielectric, and possible ferroelectric properties." *Chem. Mater.* **2014**, *26*, 3811-3817. (c) Gupta, A. K., Yadav, A., Srivastava, A. K., Ramya, K. R., Paithankar, H., Nandi, S., ... & Boomishankar, R. A Neutral Cluster Cage with a Tetrahedral [Pd<sub>12</sub>II<sub>6</sub>] Framework: Crystal Structures and Host–Guest Studies. *Inorg. Chem.* **2015**, *54*(7), 3196-3202. (d) Li, N., Jiang, F., Chen, L., Li, X., Chen, Q., & Hong, M. From discrete octahedral nanocages to 1D coordination polymer: Coordination-driven a single-crystal-to-single-crystal transformation via anion exchange. *Chem. Commun.*, **2011**, *47*(8), 2327-2329. (e) Li, X. J., Jiang, F. L., Wu, M. Y., Zhang, S. Q., Zhou, Y. F., & Hong, M. C. (2012). Self-assembly of discrete M<sub>6</sub>L<sub>8</sub> coordination cages based on a conformationally flexible tripodal phosphoric triamide ligand. *Inorg. Chem*, **2012**, *51*(7), 4116-4122. (f) Yadav A.; Srivastava A. K.; Balamurugan A.; Boomishankar R.; Cationic copper(I) iodide cluster MOF exhibiting unusual ligand assisted thermochromism. *Dalton Trans.*, **2014**, *43*, 8166-8169.

- (7) Lin, Z. J., Lü, J., Hong, M., & Cao, R. Metal–organic frameworks based on flexible ligands (FL-MOFs): structures and applications. *Chem. Soc. Rev.* **2014**, *43*(16), 5867-5895.
- (8) Gupta, A. K., Nagarkar, S. S., & Boomishankar, R. Zn (II) coordination polymer of an in situ generated 4-pyridyl (4 Py) attached bis (amido) phosphate ligand, [PO<sub>2</sub> (NH<sub>4</sub> Py)<sub>2</sub>]<sup>-</sup> showing preferential water uptake over aliphatic alcohols. *Dalton Trans.*, **2013**, *42*(30), 10964-10970
- (9) Srivastava, A. K., Praveenkumar, B., Mahawar, I. K., Divya, P., Shalini, S., & Boomishankar, R. Anion driven [CuII<sub>2</sub>] n frameworks: crystal structures, guest-encapsulation, dielectric, and possible ferroelectric properties. *Chem. Mater.* **2014**, *26*(12), 3811-3817.
- (10) (a) Dawber, M., Rabe, K. M., & Scott, J. F. Physics of thin-film ferroelectric oxides. *J. F. Rev. Mod. Phys.*, **2005**, *77*(4), 1083-1130 (b) de Araujo, C. A. P., Cuchiaro, J. D., McMillan, L. D., Scott, M. C., & Scott, J. F. (1995). Fatigue-free ferroelectric capacitors with platinum electrodes. *Nature*, **1995**, *374*(6523), 627-629. (c) Lee, H. N., Christen, H. M., Chisholm, M. F., Rouleau, C. M., & Lowndes, D. H. Strong polarization enhancement in asymmetric three-component ferroelectric superlattices. *Nature*, **2005**, *433*(7024), 395-399. (d) Rijnders, G., & Blank, D. H. Materials science: Build your own superlattice. *Nature*, **2005**, *433*(7024), 369-370. (e) Scott, J. F., De Araujo, P., & Carlos, A. Ferroelectric memories. *Science (Washington, D. C.)*, **1989**, *246*(4936), 1400-1405.
- (11) (a) Lines, M. E., & Glass, A. M. *Principles and applications of ferroelectrics and related materials*. Oxford university press, New York, **2000**. (b) Uchino, Kenji. "Ferroelectric Devices-Marcel Dekker." *New York*, **2000**.
- (12) Malik, P., Chakraborty, D., & Ramkumar, V. New phosphoroamidate compounds: Synthesis, structural characterization and studies on ZnCl<sub>2</sub> assisted hydrolysis of the P–N bond. *Polyhedron*, **2010**, *29*(10), 2142-2148.

- (13) Boomishankar, Ramamoorthy, and Anant kumar Srivastava. "Functional metal-organic molecules and materials derived from rigid and flexible PN scaffolds." *Phosphorous, Sulfur and silicon related elements*, **2016**, 191.4, 618-623.
- (14) Ajami, D., & Rebek, J. Gas Behavior in Self-Assembled Capsules. *Angew. Chem., Int. Ed*, **2008**, 47(32), 6059-6061.
- (15) Lin, Z. J., Lü, J., Hong, M., & Cao, R. Metal–organic frameworks based on flexible ligands (FL-MOFs): structures and applications. *Chem. Soc. Rev.* **2014**, 43(16), 5867-5895.