



Metal-organic materials derived from Amino P(V) ligands and investigation of their potential as Ferroelectric materials

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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.¹ 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.² 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.³ Metal-organic materials which show novel structural topologies have also been utilized for many applications in fields like selective binding and reactive molecule trapping ⁴, gas and solvent storage and separation ⁵. 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.⁶ 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.⁷ Also to obtain dynamic architectures with tunable properties, peripherally functionalized phosphoramides provides an essentially ideal platform. For example, the 3-pyridyl 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.⁸

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.⁹ 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.⁹ More importantly, the noncentrosymmetric assemblies were found to be a potential ferroelectric materials and exhibited high remnant polarization and dielectric constant values.⁹ 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).

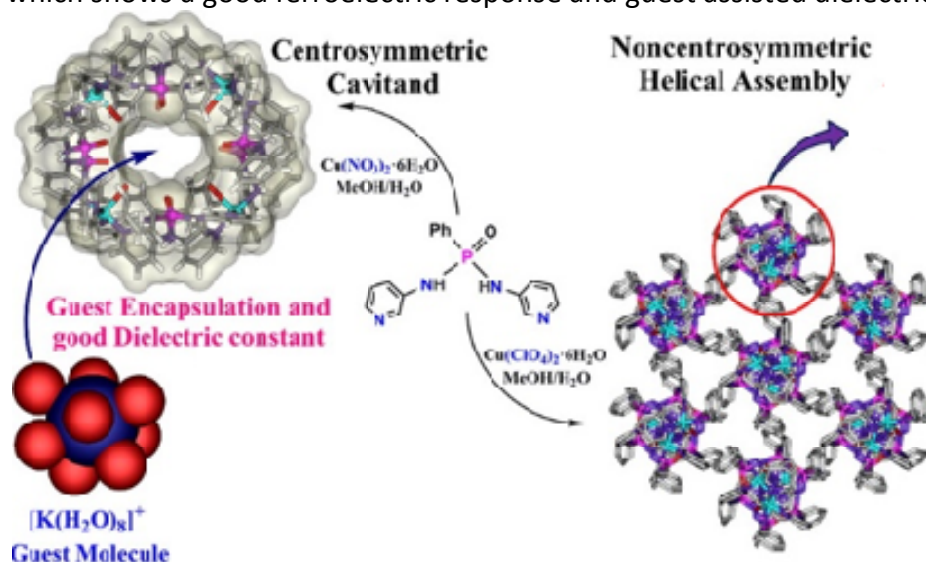


Figure : Synthesis of anion driven ferroelectric material based on L^2 (Ref. 9)

Noncentrosymmetric helical assembly generates by treating L with excess of copper perchlorate ions in MeOH/ H_2O as a solvent (shown in Figure below). These noncentrosymmetric helical assemblies show trigonal cavity. Perchlorate ions and solvate ions reside in these trigonal cavities.

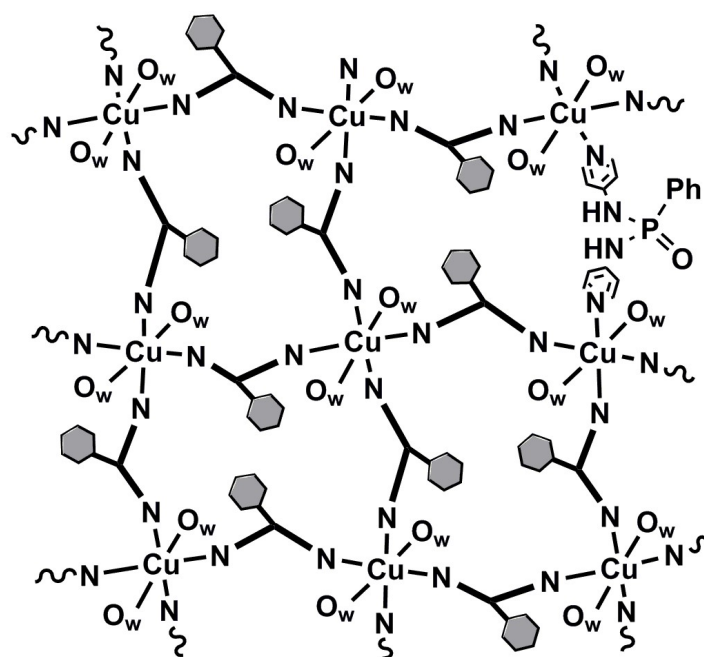


Figure : Structure of a 2D-framework materials based on a 4-pyridyl functionalized dipodal phosphoramidate ligand.



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 propagating along the axis forms a left handed strand.⁹ 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.¹⁰

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.^{10,11}

The most prevalent ferroelectric materials are perovskites, specifically Barium Titanate (BTO) and Lead zirconate titanate (PZT).¹¹ 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.^{7,11}

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 $(\text{p-cresol})\text{PO}(\text{NH}^3\text{Py})_2$ in its pure form. Further, we have successfully deduced crystal structure of newly synthesized $(\text{p-cresol})\text{PO}(\text{NH}^3\text{Py})_2$ 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 AgClO_4 . Interestingly, the 3D-framework is crystallized in the non-centrosymmetric space group and thus could be a potential ferroelectric material.

Experimental

Synthesis

S¹: In a two neck RB, p-cresol (1.6ml, 40mmol, 1eq.) 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_3 (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, ^1H , ^{13}C and ^{31}P NMR and it confirms the formation of S¹.

L¹: 3-Aminopyridine (4.5gm, 48mmol, 4eq.) was dissolved in dry acetonitrile under an inert atmosphere. To this solution, **S¹** (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, ¹H, ¹³C and ³¹P NMR. MALDI-TOF, ¹H, ¹³C and ³¹P NMR confirms the formation of **L¹** in pure form which is discussed in results and discussion part. Crystal of **L¹** was obtained from its methanolic solution in which **L¹** was dissolved.

¹H NMR (400 MHz, d₆-DMSO): δ = 8.77-8.80 (2H), 8.39 (2H), 8.10-8.11 (2H), 7.49-7.52 (2H), 6.95-7.27 (6H) ppm. ³¹P NMR (161.97 MHz, D₆-DMSO): δ = -2.10 ppm. MALDI-TOF m/z = 342 [M+H]⁺, 362.99 [M+Na]⁺, 378.96 [M+K]⁺. ¹³C NMR (100.62 MHz, D₆-DMSO): δ – 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 (cm⁻¹): 3405, 3130, 2940, 1579, 1494, 1467, 1396, 1330, 1272, 1212, 1165, 1127, 1098, 1016, 979, 947, 808, 748, 698, 609, 557, 492.

Results and Discussion

The ligand **L¹** was synthesized by reaction of 3-aminopyridine with (p-cresol)POCl₂ in presence of triethylamine. The ligand was characterized by mass spectroscopy, ¹H, ³¹P and ¹³C NMR. The reaction scheme and conditions for the formation of **L¹** are (shown in figure 3).

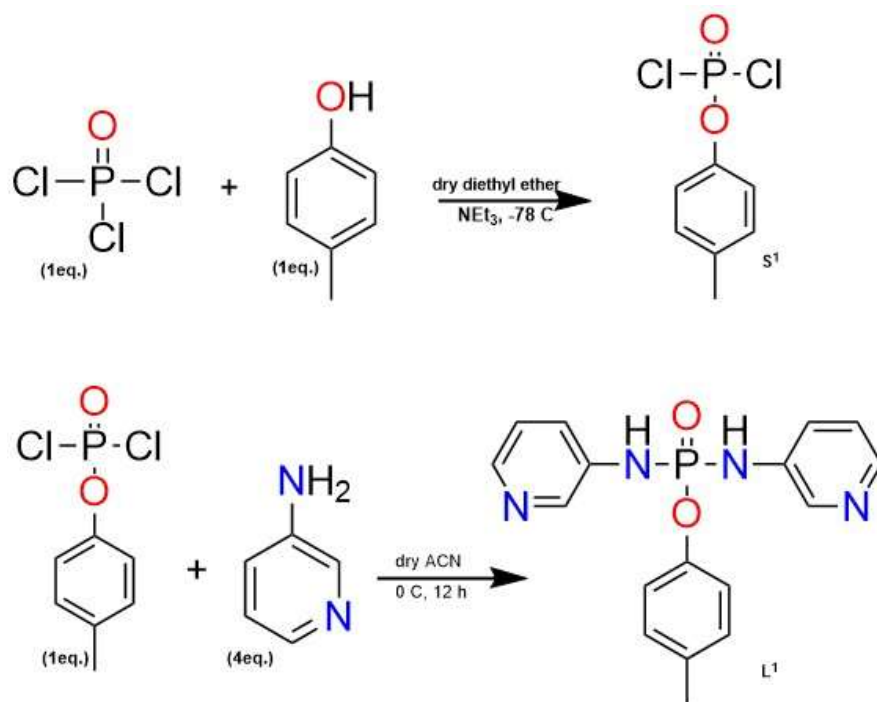


Figure : Reaction scheme and condition for formation of **L¹**

Crystal structure of **L¹**(C₁₇H₁₇N₄O₂P):

Ligand **L¹** crystallizes in monoclinic crystal system space group P2₁. P-N bond distance is 1.64 Å, while P-O bond distance is 1.56 Å.

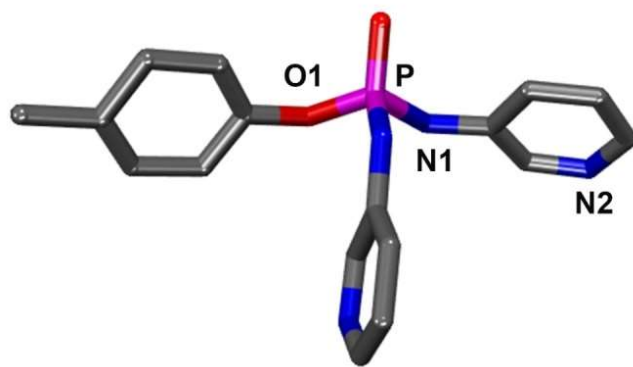


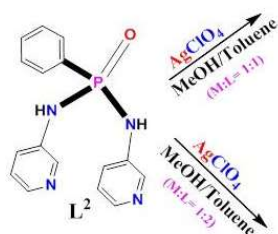
Figure : Crystal structure of L^1

Since, the metallation reactions of L^1 could not result in any structurally isolated compound, the analogous ligand 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. Since, the metallation reactions of L^1 could not result in any structurally isolated compound, the analogous ligand 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 L^2 with several other metal ions has been attempted. Notably reaction of L^2 with $AgClO_4$ gave interesting results (Scheme below).

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^2 segments. In the 3D-framework the $Ag(I)$ ions are positioned in a tetrahedral setting and contains four pyridyl associates from four different L^2 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.

Scheme : Formation of two $Ag(I)$ complexes based on L^2

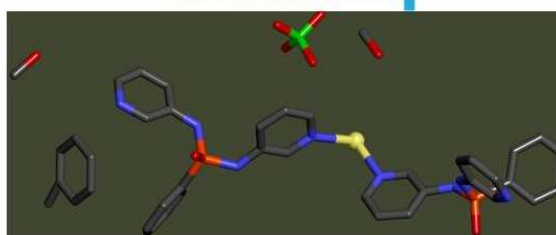
$a=11.20 \text{ \AA}$; $b=11.53 \text{ \AA}$; $c=19.95 \text{ \AA}$
 $\alpha=88.51$; $\beta=76.34$; $\gamma=70.93$
 $V=2351 \text{ \AA}^3$
 P-1



$a=15.16 \text{ \AA}$; $b=13.58 \text{ \AA}$; $c=20.31 \text{ \AA}$
 $\alpha=90$; $\beta=90.10$; $\gamma=90$
 $V=4183.59 \text{ \AA}^3$



1D-Chain



3D-Network

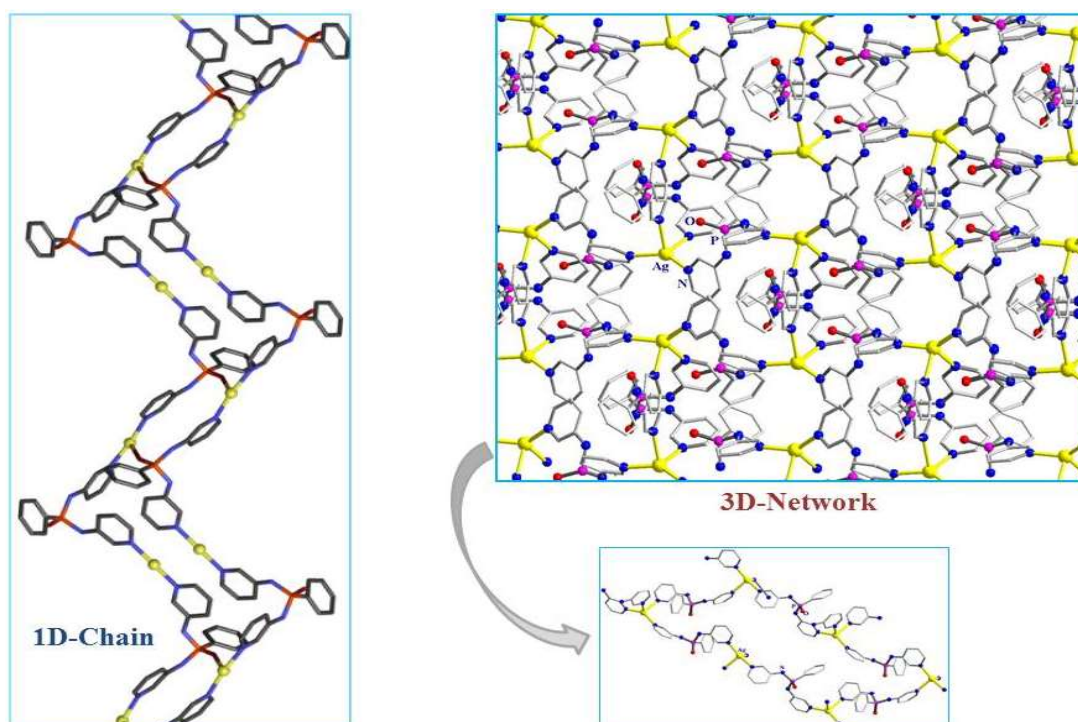


Figure : Crystal Structures of the 1D- and 3D-coordinations polymers **1** and **2** derived from Ag(I) ions and L^2 .

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.

Acknowledgements

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