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Construction of Solvent Mediated Supramolecular Templated Assembly of Metal Organophosphonate via Crystal-Amorphous-Crystal Transformation

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ABSTRACT

Three 0D Cu(II) based organophosphonate i.e., two molecular cationic complexes $[Cu_2(\mu_2\text{-}L)_2(^{2,2'}BPy)_2(H_2O)_2](NO_3)_2.S$ (**1**), $[Cu(L)(^{2,2'}BPy)_2].NO_3.(H_2O)_2$ (**3**), and one neutral complex, $[Cu_2(\mu_2\text{-}L)_2(^{2,2'}BPy)_2(NO_3)_2].MeOH$ (**2**), assembled by phosphonomonoester, **L** ((ethylhydrogen(anthracen-9-ylmethyl)phosphonate)) and an auxillary bidendate ligand 2,2'-Bipyridine ($^{2,2'}$BPy) have been synthesized. Single crystal X-ray diffraction analysis reveals that complex **1** comprised of a dimer unit arranged supramolecularly with nitrate anion and these layers are further assembled via π···π interactions, which results in the formation of porous supramolecular architecture. Interestingly, the cationic complexes **1** and **3** showed supramolecular templated assembly by just altering the solvent, responsible for the change in architecture. Moreover, the remarkable change of cationic complex to neutral one via the formation of amorphous solid, **1a** (crystal-amorphous crystal transformation) is observed when the crystals of **1** was allowed to heat at 90°C under vacuum. It is hypothesized that the compound showed the mobility of uncoordinated nitrate ion from the lattice to the metal, hence, resulting in the transformation of cationic metal complex to neutral metal complex and furthermore, these complexes manifest luminescent behavior.

Introduction

In last few years, researchers have established a great interest in the synthesis of metal organophosphonates bearing variety of different organic groups accountable for potential application such as sorption[1], catalysis[2], proton conductivity[3] and magnetic materials[4] etc. The rational way of controlling the functions as well as the dimensions of the channels ascertained in the open framework is to make right choice of interlinking organic group on phosphonic acid[5-6] whereas the coordination geometry and the charge on the framework is chiefly controlled by inorganic groups.[7] Moreover, In particular, the modular coordination compounds, associated with dynamic and flexibility, changes their structure in response to external stimuli for instance heat, light, solvent etc and hence, exhibits solid state transformation.[8-9] Materials, with switchable nature to another material on external stimuli, display the potential application[10-12] in molecular capture, sensing, switches etc. owing to the presence of intermolecular interactions such as hydrogen bonds, π–π stacking, vander Waals forces, and others.

On one hand, rational design and controlled synthesis of supramolecular complexes with similar composition and to the other hand, supramolecular templated assembly facilitated by the solvent have attracted the attention of the researchers as it has resulted in the production of potential materials.[13-15] It is well known that the solvent molecule is one of the paramount structure-directing agents, which particularly affords different coordination metal complex in contrast to the one formed in its absence that may not only result in different crystalline solids but may have tendency to show solid state transformation. However, the latter have led towards the strategy of switching one material to another on external incentive in potential application.[16-19] Nonetheless, this dynamic behavior of the system is fostered by the non-covalent interactions such as $\pi\cdots\pi$ interaction and aids in the synthesis of adaptive materials in respond to any external stimuli.[20-22] Additionally, the propensity of solid structure to access this strategy, has led to the reversible solid state transformation i.e., single crystal to single crystal transformation (SC-SC), single crystal to amorphous or amorphous to crystal.[23-25] Many reports have been found on the solid transformation of 1D, 2D and 3D coordination complex[26-28] and many on Cu(II) phosphonates with their molecular analogues[29-34] but to the best of our knowledge, rarely any report has been found on the reversible transformation of low-dimensional (0D) material involving phosphonomonoester.

However, the predilection of organophosphonate to show multidenticity in metal complex has often confronted obstacle for crystallizing the phosphonate as the formation of insoluble compound take place. In this context, various strategies[35-41] have been attempted in order to overcome this solubility issue to tailor the molecular metal phosphonate such as 1) use of sterically hindered phosphonic acid; 2) use of chelating ligand and 3) controlled degree of protonation i.e. the exploitation of phosphonic acid as the source of monoanionic in bidentate chelation mode. Nevertheless of this, the report on the formation of molecular metal complexes of phosphonates is still scarce as compare to the overburdened carboxylates.[42-46] At this end, we have constructed a molecular metal phosphonate from newly synthesized anthracene based phosphonomonoester and a chelating ligand i.e., 2,2'-bipyridine keeping the aforementioned strategies in mind. With the expertise available till now, the monoester has been employed for the first time in the formation of molecular phosphonate, which subsequently reduces the possibility of coordinating to the metal ion. Subsequently, it increases the solubility of the compound and in turn enhances the probability of getting it crystallized.

It is of our particular interest to study the structural dynamism resulting from change in chemical environment available to the framework. Here, we envisaged that the synthesized ligand, on one hand, with the introduction of the $\pi\cdots\pi$ interaction in the extended supramolecular architecture,[47-53] might be responsible for being soft porous and on the other hand, might display emission property owing to the presence of the fluorescent organic group on the phosphonomonoester. Herein, we report three 0D Cu(II) complexes **1**-**3** based on a newly synthesized ethyl hydrogen(anthracen-9-ylmethyl)phosphonate (**L**) in the presence of a chelating agent 2,2'-bipyridine ($^{2,2'}$BPy) (Scheme 1). The cationic framework (**1**) with extra framework nitrate ions held together via dynamic non-covalent interaction, hence shows crystal-to-amorphous transformation upon desorption of solvent, which further on resorption in methanol resulted in a different complex, $[Cu_2(\mu_2\text{-}L)_2(^{2,2'}BPy)_2(NO_3)_2]$.MeOH (**2**). However, the latter complex is a neutral framework with methanol molecule present in the lattice, as deduced by thermogravimetric analysis (TGA), powder X-ray diffraction (PXRD) and single crystal XRD.

Result and Discussion

Three metal phosphonate supramolecular solids, **1**-**3**, were produced with monophosphonate, $^{2,2'}$BPy and $Cu(NO_3)_2$ in addition to one more supramolecular solid, **4**, that is formed by the depletion of phosphonomonoester (L) from the solid complex to mother liquor. Hence, blue colored solid complex, **4**, was detected when the green crystals of **1** in mother liquor were allowed to stand at room temperature for 10-15 days. These metal organophosphonate features different structure as characterized by IR, PXRD, and single crystal XRD. Notably, the complex **1** show reversible transformation of crystalline to amorphous and the latter remodels itself back into the crystalline phase **1'**, as characterized by single crystal XRD.

It may be noted that the presence of triethylamine is essential for the synthesis of this system otherwise it might have been possible to acquire slightly modified molecular system. Basically, the nature of the framework is altered by the slight change in the reaction condition.[32,54]

Herein to gain the information of interest here, the dinuclear molecular systems have been accomplished with the change in solvent. As a result, solvent mediated supramolecular templated assembly of metal organophosphonate were obtained enduring stacked $\pi\cdots\pi$ interaction between organic moiety and the auxiliary ligand over each other which ended up into porous/non-porous extended 3D supramolecular framework.

Description of crystal structure 1: Single crystal X-ray diffraction analysis revealed that **1** is crystallized in the triclinic space group, *P-1*. The asymmetric unit contains one crystallographically Cu(II) ion, one molecule each of monoester and auxiliary ligand: $^{2,2'}$BPy, one coordinated water molecule and an uncoordinated distorted nitrate anion along with distorted solvent molecules (Fig. 1a). The five-coordinated copper ion lies on a crystallographic two-fold axis and hence, resulting in the formation of the dinuclear assembly. This dimer assembly represents a composite building unit for the resulting supramolecular network and it lies about an inversion centre in the solid state. However, the coordination environment around the Cu(II) atom is displayed in Fig. S1a [see ESI†] representing that the Cu atom exhibits a distorted square pyramidal coordination with N_2O_3 donor set. The equatorial plane endures two nitrogen-coordinating sites from same bidendate ligand, the two sites are occupied by the two oxygen of the monoester and the fifth site is engaged by the oxygen of the water molecule, which is nearly perpendicular to the plane. The Cu(II)–N1, Cu(II)–N2, Cu(II)–O1, Cu(II)–O3 and Cu(II)–O4(water) distances are in agreement with those reported for other Cu(II) phosphonate compounds such as 2.004(15), 2.015(9), 1.945(13), 1.932(14) and 2.245(13) Å respectively.[32,55] Each of two bipyridine moieties and monoester altogether are holding the dinuclear assembly where the latter is bridged isobidentatly to the metal atom resulting in the formation of a chair shaped single eight membered ring ($Cu_2O_4P_2$). Its resemblance to the S8R building units of zeolites is the remarkable feature of this molecule.[56] Crystallographic data and other pertinent information for complexes **1−4** and ligand, L are tabulated in Table S1 [see ESI†]. The selected bond lengths and angles for **1**-**4** are listed in Table S2 [see ESI†].

The composite building units are further assembled through π–π stacking interactions, mainly responsible for the extension of 0D structure into a 3D supramolecular network. On scrutiny, it was observed that the 1D chain of the composite unit and the uncoordinated nitrate ion runs parallel to the *bc*-plane, linked via hydrogen bond between the coordinated water molecule and uncoordinated nitrate ion (O4-H4A···O5, 1.932 Å). These 1D chains runs parallel to each other and glued together via C-H···O and C-H···N interactions along *ac*-plane resulting in interdigited structure [Fig. S2, see ESI†]. Further, these discrete 2D sheets stacked over one another along *b*-axis, thereby resulting in a porous supramolecular framework ending in 1D channel along *a*-axis, accommodated by disordered nitrate and disordered solvent molecules (Fig. 2b). The strength of the complete framework is based on array of π-π stacking between the π electron cloud of the anthryl group and the $^{2,2'}$Bpy.

In the crystal lattice, a disordered nitrate anion is present and the presence of some residual electron density observed by X-ray crystallography, which validates the presence of few disordered solvent molecules. In addition, there is a potential disordered solvent void of 153.1 Å^3 containing 70 electrons/unit cell as determined by the PLATON[57] and the residual electron density was removed by SQUEEZE program.

Description of crystal structure 2:

The neutral complex, $[Cu_2(\mu_2\text{-}C_{15}H_{12}PO_3)_2(^{2,2'}BPy)_2(NO_3)_2]$.MeOH (**2**) is formed from cationic complex, **1** via solid state transformation (crystal-amorphous-crystal). The coordination environment around Cu(II) remain unchanged with a same N_2O_3 donor set in both complexes but differs in the crystal system, the unit cell parameters and the space group, which changed from triclinic (*P*-1) to monoclinic ($P2_1/c$). Structurally, the coordinated water molecule in **1** is substituted by nitrate ion in complex **2**, thereafter, changing the cationic framework to neutral framework. The bond lengths and angles around Cu(II) were observed close to the bond lengths found in complex **1**. However, its asymmetric unit consisted of the neutral composite unit along with the extra-framework solvent molecule, methanol (Fig. 1b). Similar to **1**, the dimeric unit in **2** lies about an inversion centre in the solid state and the formation of S8R ring (Fig. S1b, ESI†]) with the extension to 2D framework, and which assembled further to generate 3D network, remain unchanged. Evidently, these intermolecular non-covalent interactions such as π-π stacking are responsible for increasing the dimensionality of the framework from zero dimensional structure to three dimensional network.

Structural study showed that the composite unit of compound **2** forms 1D chain along *b*-axis, that further stitched together by π-π stacking between $^{2,2'}$BPy and anthracene ring of the two different composite units. This 1D chain is extended to 2D via C12–H12···O6 interaction between anthranyl C–H to nitrate anion of another layer along *a*-axis, thereby leading to the formation of a sheet (Fig. 2c). Moreover, the 2D sheets are further assembled into 3D supramolecular polymer through π-π interactions in *ac*-plane (Fig. 2d). The offset π-π (centroid-centroid) distance in interlayer and intralayer are 3.202 and 3.625Å respectively and, the π-rings are displaced by 1.253 Å in interlayer and 1.375 Å in intralayer (Fig. S3, ESI†) as calculated by Olex2 (version 1.2.2).[58] Various non-classical interactions such as C-O and C-N are involved in interlayer sheets [see ESI†]. The crystallographic data and selected bond distances of **2** are given in Table S1 and S2 respectively.

Description of crystal structure 3:

X-ray diffraction analysis reveals that complex **3** is also a zero dimensional dinuclear structure with the different asymmetric unit comprising of one Cu(II) center coordinated by one and two molecules of phosphonomonoester and $^{2,2'}$BPy respectively, along with one nitrate and two water molecules in its lattice (Fig. 1c). The metal ion is penta-coordinated by two bidentate $^{2,2'}$BPy and one phosphonomonoester displaying distorted square pyramidal coordination geometry with N_4O donor set. Unlikely, in complexes **1** and **2**, the complex **3** comprised of mononuclear unit, which is linked supramolecularly to another unit via H-bonding O–H···O between nitrate anion and water molecule as shown in Fig. 3a [Fig. S4, see ESI†]. Further this H-bonded unit is extended to 2D sheet via C–H···O and C–H···π interaction as shown in Fig. 3b and in Fig. S5 [see ESI†].

Interestingly, the green crystals of complex **1** changes to blue after 10-15 days when exposed to air due to the loss of phosphonomonoester and deforms into complex **4**. It comprised of two bidentate $^{2,2'}$BPy and nitrate anion coordinated to metal ion along with one molecule each of nitrate ion and water molecule in its lattice with N_4O donor set in distorted square pyramidal geometry [Fig. S6, see ESI†]. Structural analysis revealed that 1D chain is formed through continuous H-bonding between nitrate anion and water molecule [Fig. S7, see ESI†] and which is extended to 2D sheet via C–H···O weak interaction [Fig. S8, see ESI†].

Solid state transformation (Crystal-amorphous-crystal (CAC)):

In this paper, we report a porous supramolecular solid, **1**, produced by the supramolecular assembly of a dinuclear unit and nitrate anion in the presence of polar aprotic solvent, acetonitrile. A remarkable effect was observed when crystals of **1** resulted in green solid powder, **1a**, with lost crystallinity on heating under vacuum for 1 day and subsequently, the latter does not show any diffraction pattern when it was diffracted by X-rays. Moreover, the complex, **1a**, was characterized later and found to be amorphous as supported by PXRD and elemental analysis (Anal. Calcd: C, 55.81; H, 4.16; N, 7.23 %. Found: C, 55.96; H, 4.30; N, 7.15 %). The solvent mediated structural transformation was accomplished when the amorphous solid, **1a**, was kept in methanol, it deforms into different dimer unit in crystalline form i.e., complex **2** as confirmed by single crystal analysis. It exhibits different cell parameters from **1** and structural analysis revealed that a new compound **2** was formed by replacing the coordinated water molecule per Cu(II) by the extra framework nitrate anion. Hence, new non-porous supramolecular polymer was established from porous supramolecular polymer. Although, the geometry of the metal centre remains unchanged; but the size, shape of the cavity was altered and hence, the overall structural change supports the dynamic behavior for complex **1**. A number of sets was planted for the synthesis of complex **2** directly from phosphomonoester and $^{2,2'}$BPy, but the attempts were fruitless. However, on the other hand, when the amorphous solid, **1a**, was immersed in the methanol and acetonitrile mixture, it triggered back to the original crystalline form (say **1'**).

Another interesting case was observed, when the green crystals of **1** transmuted to blue crystals, i.e., hitherto reported complex[59] **4**, $[Cu(^{2,2'}BPy)_2.(NO_3)].NO_3.\ H_2O$, on exposure to air for 10-15 days led to the loss of phosphonomonoester unit from the complex to the mother liquor as evidenced by single crystal XRD. Though, the destabilization of complex **1** in presence of moisture has not been clearly understood but the structural transformation due to architecture destabilization have been apprehended by the change in color and by single crystal XRD studies.[60-62] On the other hand, another supramolecular solid i.e., complex **3** but this time mononuclear unit was observed in the absence of acetonitrile and sustained by weak interactions such as H-bonding, π···π, C–H···π etc.

On probing the supramolecular complexes **1**-**3**, it was found that the solvent plays an important role in the synthesis and transformation of these supramolecular solids as it controls the crystal structure, dynamic and flexibility of the network involving the crystal-amorphous-crystal transformation. Thereafter, it was inferred that acetonitrile, as a solvent, is playing an important role in synthesizing dimer complex of phosphonomonoester otherwise it would end up with the monomeric unit. However, the stability of flexible complexes has been studied by TGA, elemental analysis, PXRD, and IR spectra. The complex **1** loses methanol and coordinated water molecule in a range of 80-110 °C (found: 6.77%; anal. calc. 7.22%) as deduced by TGA profile and produces the dehydrated complex **1a**, $[Cu_2(C_{15}H_{12}PO_3)_2(^{2,2'}BPy)_2].(NO_3)_2$ (fig. 4b). As the removal of water breaks the interlayer H-bonding and it is anticipated that these molecules arrange themselves such as it led to the formation of amorphous state.[63] This was also supported by IR, which shows the peak for coordinated water is absent in IR spectra of complex **1a** (fig. 4a). The characteristic IR absorption band in complex **2** with medium intensity of M-OH appeared at 3765 cm^{-1} and that of N-O at 1370 cm^{-1} corresponding to the coordinated water molecule and free nitrate anion respectively. Moreover in complex **2**, the broad absorption band at 2920 cm^{-1} exemplifies the presence of hydrogen bonded O-H present in methanol molecule and the corresponding absorption band for coordinated N-O from nitrate displayed at 1320 cm^{-1}. On the other hand, PXRD clearly shows that complexes **1** and **1'** are same as the peak observed in latter well matches with the peaks correspond to former. However, the PXRD pattern of complex **1a** with absence of peaks demonstrates that the complex **1a** is in an amorphous phase (fig. 5a).

Luminescence Properties:

The solid state emission for ligand and complexes **1-3** has been investigated at room temperature as shown in fig. 5b. The fluorescent spectra of these complexes display maximum emission wavelengths (λ) at 516, 482, and 492 nm with excitation wavelengths at 215 nm in the solid state. However, the ligand shows emission as located at 433 nm upon excitation at 350 nm, which can be assigned to π—π^* transition.[64] After probing the results, it was anticipated that the emission of the complexes **1-3** in the solid state is mainly due to metal-to-ligand charge transfer (MLCT) transition. It was observed that the fluorescence spectra of the Cu(II)organophosphonates complexes exhibit a red shift compared with that of the ligand probably due, on one hand, to back-coupling π-bond between the metal and the ligand, which further directed the increase in mobility of electron transition and, on the other hand, to the enhancement in the π–π^* conjugation length on coordination of ligand with metal attributable to the formation of five membered ring and as a consequence, resulting in the conformational co-planarity and which further reduces the energy gap between the π and π* molecular orbital of the ligand.[65] The enhancement of conformational rigidity in the molecule structure with the introduction of metal ion causes the metal complex to emit fluorescence.

Conclusion

It is hypothesized that the compound shows the mobility of uncoordinated nitrate from the lattice to the metal, hence, resulting in modification of cationic molecular complex to neutral one via the amorphous state. The dynamic nature of supramolecular complex **1** has the propensity to reversibly switch to another supramolecular solid **2** via passing through amorphous state and also convert back to its original form in the presence of CH_3OH/CH_3CN mixture. However, the importance of acetonitrile was observed when it resulted in different crystalline form in methanol as characterized by IR, PXRD and single crystal XRD. In addition, the solid state emission of three complexes **1-3** was studied at room temperature, and the results suggest that compounds exhibit good luminescence properties due to metal-to-ligand charge transfer (MLCT) transition.

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ESI†, Supporting Information. Structure solution and refinement procedures, experimental details for ligand synthesis and complexes **1-4**, supplementary figures, including tables of crystallographic data, CIF files, and anisotropic thermal ellipsoids for complexes **1–4** reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) for the structures and ligand reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as deposition Nos. CCDC 1042812-1042815, 1433403 and 1044127.

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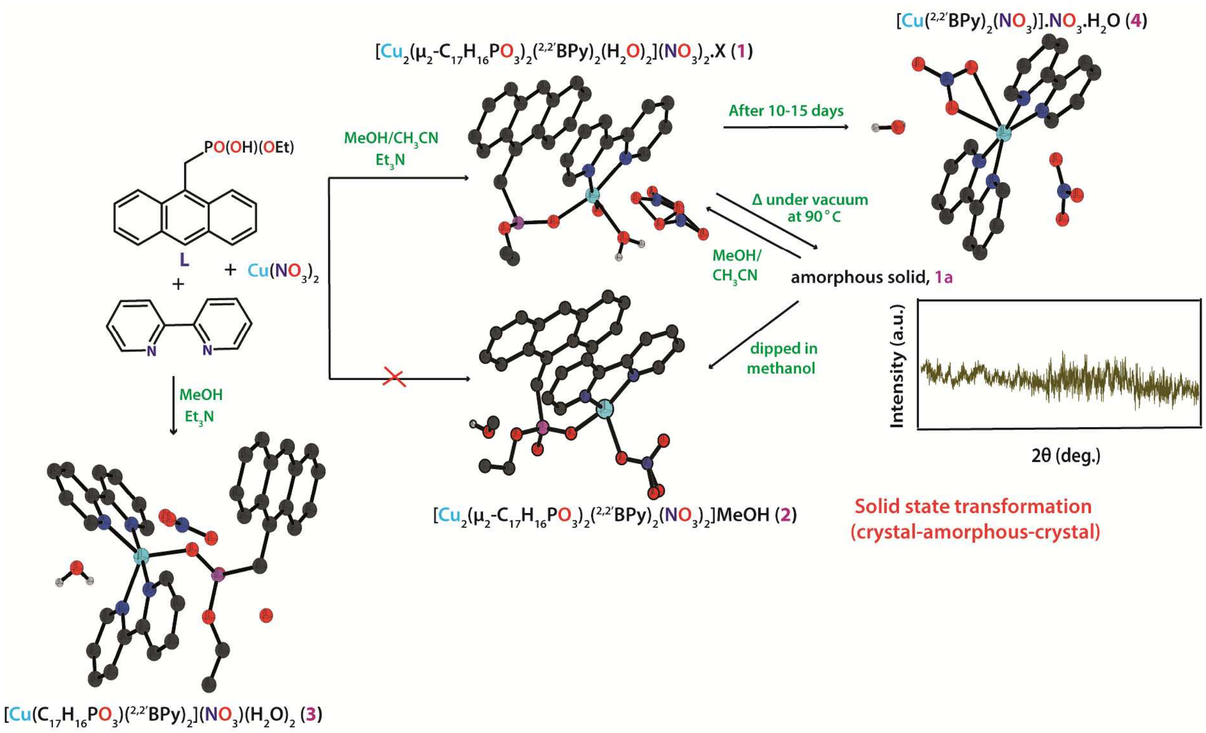
Graphics



Scheme 1: Representation of various complexes **1-4**

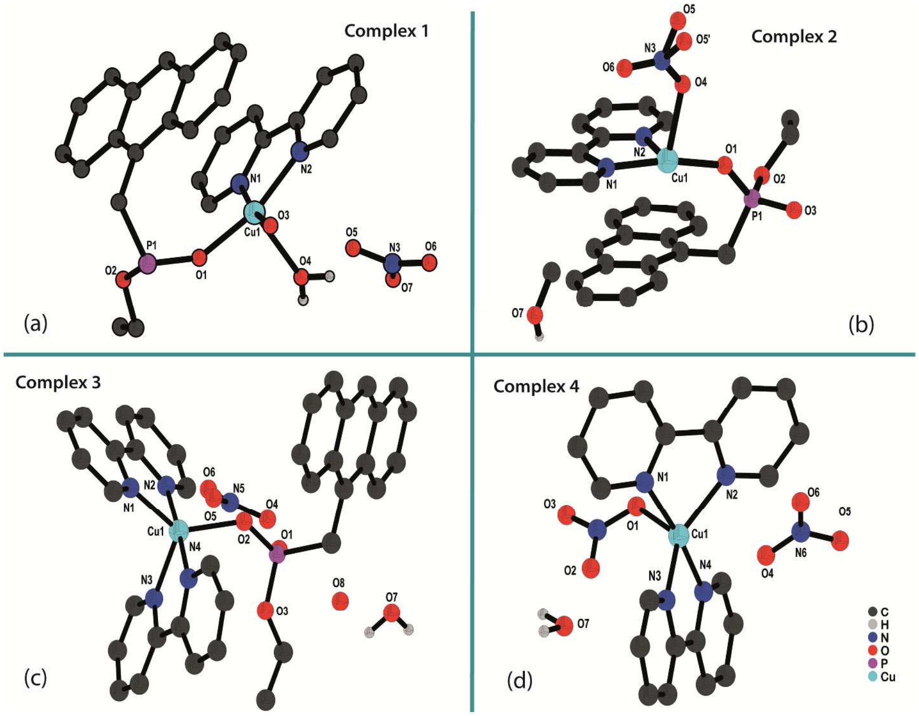


Fig. 1: Crystal structures of (a) complex **1;** (b) complex **2;** (c) complex **3**; (d) complex **4** (C-H bonds are not shown for clarity)

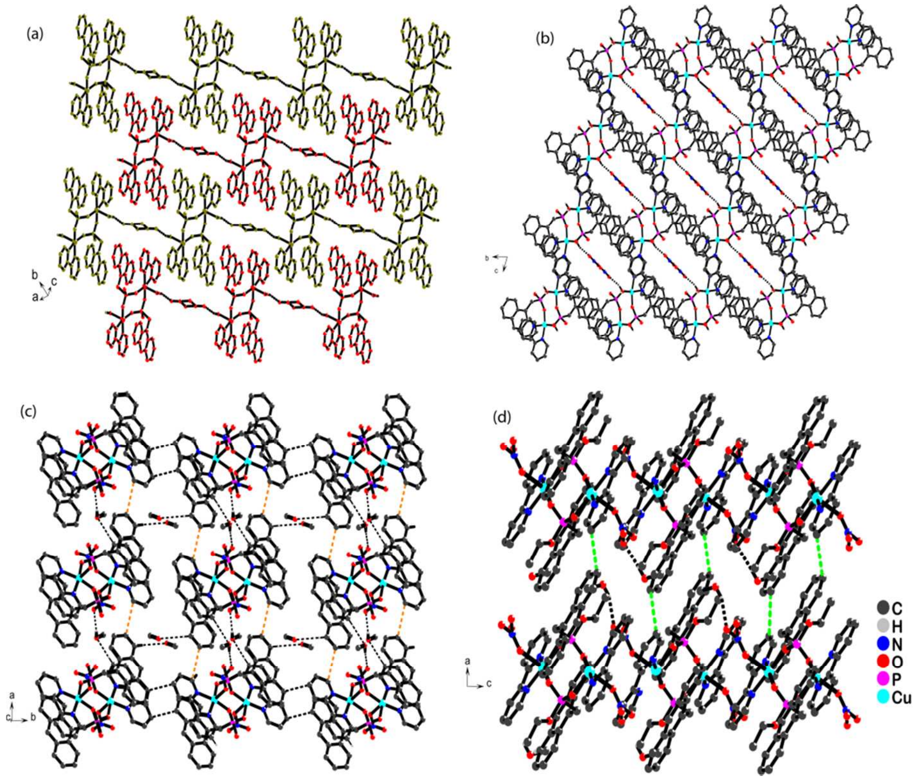


Fig. 2: (a) View of interdigitated parallel 1D chains of composite unit and nitrate anion in *ac*-plane; (b) 3D extended framework in *bc*-plane displaying the porous framework with uncoordinated nitrate anion inside the pores in **1**; (c) View of 2D sheet representing the interaction of methanol molecule with the framework along *c*-axis in **2**; (d) 3D representation of **2** in *ac*-plane displaying the π···π interaction between the anthracene moiety and $^{2,2'}$BPy units of neighboring 2D sheets.

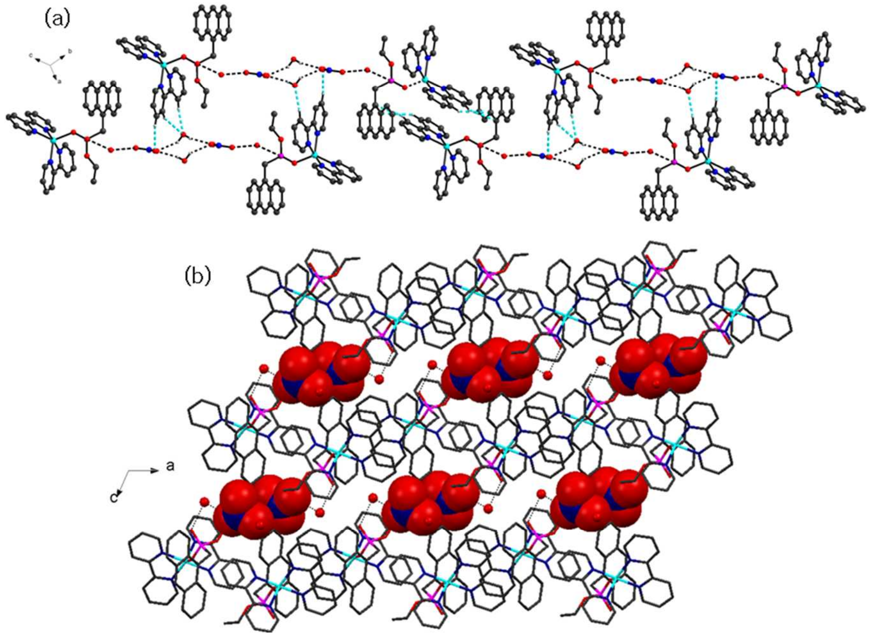


Fig. 3: (a) Discrete chain of the dimer unit with nitrate anion and water molecule in **3**; (b) Representation of 2D sheet in **3**

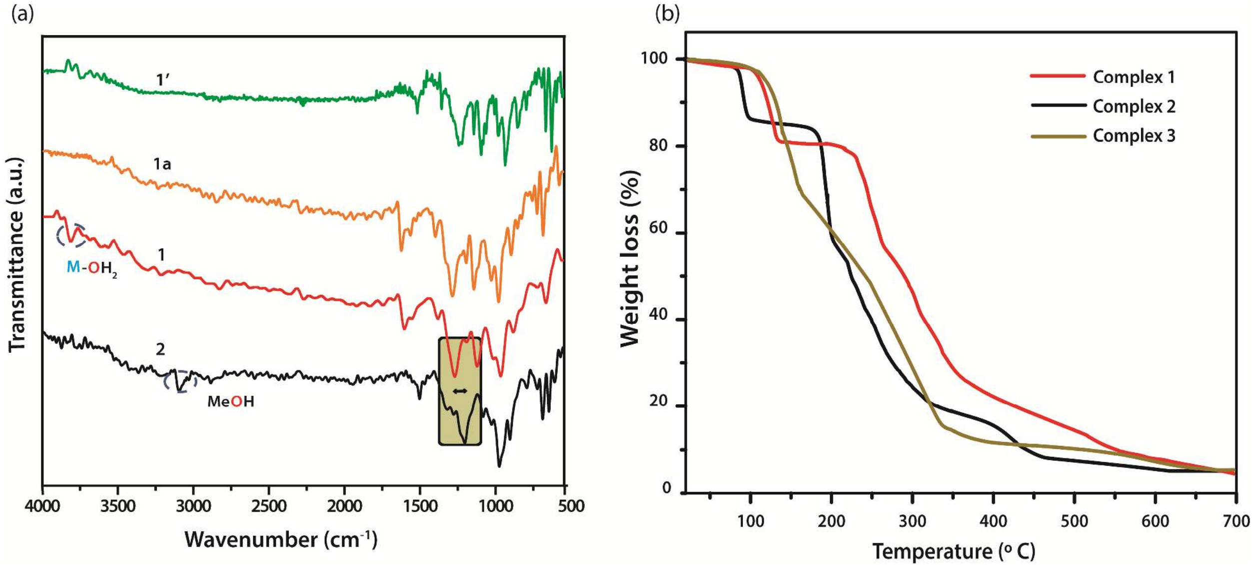


Fig. 4: (a) Illustration of IR spectra of complexes **1**, **1a**, **1'** and **2** confirming the reversibility of the complex; (b) TGA plots for complexes **1**-**3**.

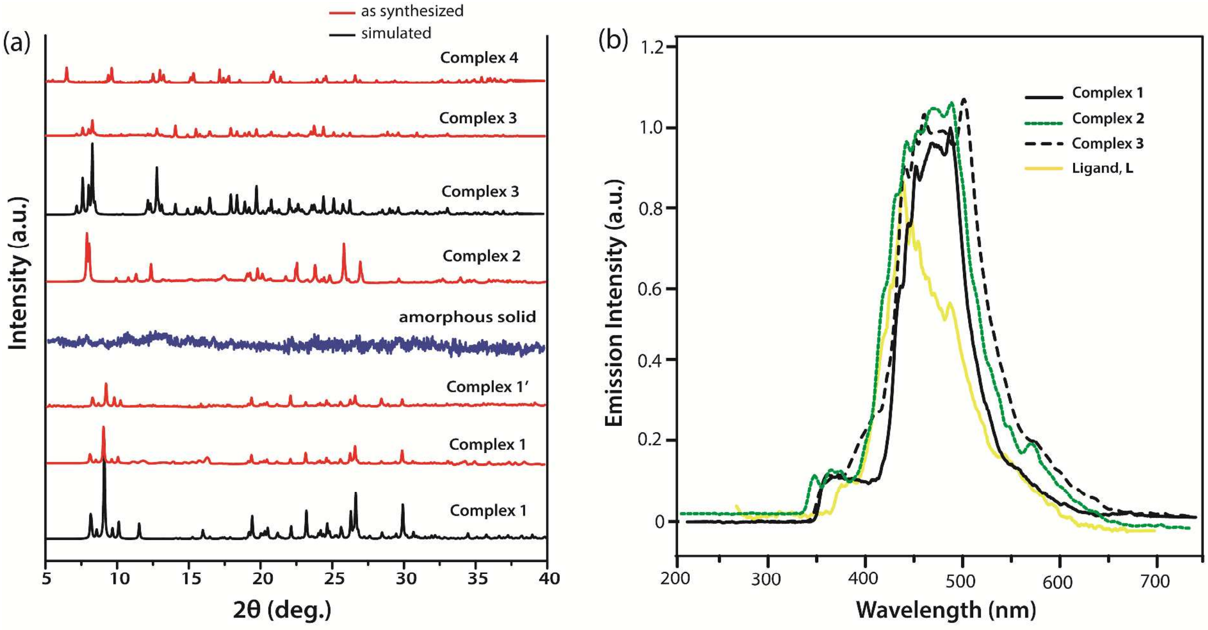


Fig. 5: (a) PXRD patterns of supramolecular isomers; (b) Emission spectra of the ligand, L and the complexes **1**-**3** in the solid state at room temperature.

Table of content:

Construction of Solvent Mediated Supramolecular Templated Assembly of Metal Organophosphonate via Crystal-Amorphous-Crystal Transformation

Three monophosphonoester based supramolecular assembly have been synthesized and fully characterized. These complexes demonstrated a reversible crystal-to-amorphous-to-crystal transformation with variation in emission.