

Conductive Organic Polymer Based Inorganic-Organic Hybrid Composite: Synthesis and Characterization

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Abstract

Inorganic organic (IO) hybrids where inserted conducting organic polymers (COP) imprint their polymeric nature onto the hybrid material are one of the most promising candidates for solving many technological problems of modern technocratic society. The Inorganic-Organic hybrid material of para toluidine (organic) and mercuric chloride (inorganic) was synthesized by using "instant-heating and slow-cooling" technique. Some light orange coloured plate-like crystals were obtained. XRD patterns of the grown crystal were analysed which shows that crystal has been grown into monoclinic crystal system in which $a \neq b \neq c$ [$10.061(4) \text{ \AA} \neq 4.317(2) \text{ \AA} \neq 12.987(5) \text{ \AA}$] and $\alpha = \gamma = 90^\circ \neq \beta$ [$\alpha = \gamma = 90^\circ$, $\beta = 104.322(7)^\circ$] and belongs to space group $P2_1$. Analysis of secondary interactions shows that such material has potential application in opto-electronics.

Keywords: *Conducting organic polymers, inorganic-organic hybrids, secondary interactions, slow cooling, optoelectronic devices, non-covalent weak interactions, hydrogen bond*

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INTRODUCTION

There is always a great need for better materials with predetermined multifunctional response. In this context, recent researches on inorganic-organic hybrid materials have shown that these materials have tremendous potential for solving various technological issues [1-5]. This is mainly due to the existence of innumerable possible combinations of organic and inorganic components with the purpose of tailoring resultant hybrid material's properties. Among all these possibilities, combination of conducting organic polymer with various inorganic components on the molecular scale has shown huge potential in various applications including energy storage, light sensitizer, solar cell and other optoelectronic applications [6-8]. In such hybrids, two species are linked through various intermolecular interactions including weak electrostatic interactions, hydrogen bonding, non-covalent bonding, covalent bonding, ionic

bonding etc. These interactions play predominant role in defining the structure and the properties of the resultant hybrid material [9]. There are mainly two categories of such hybrid materials [10]. First is Organic-Inorganic (OI) hybrid materials where the organic phase acts as host to an inorganic guest. In an organic-inorganic (OI) hybrid, conducting organic polymer (COP) acts as the host or major component and provides structural support to inorganic molecules to form hybrid structure. However inorganic component contributes in terms of its chemical activity. In OI hybrids, organic and inorganic components are linked together through covalent bonds. Second is Inorganic-Organic (IO) materials, with inorganic hosts and organic guests. In IO hybrids, inorganic component generally fulfils the task of structure formation, whereas inserted conducting organic polymer (COP) is for imprinting their polymeric nature into the

resultant hybrid formed. In spite of the fact that organic components have relatively large molecular weight, their role as intercalated guest molecule within Vander Waal gaps of layered or channel inorganic phases is highly recognized for structural stability of the resultant hybrid structure. Here we report the synthesis of para toluidine based hybrid material while taking mercuric chloride as inorganic component. Intermolecular secondary interaction analysis of the synthesized hybrid shows its potential application in optoelectronics [11-13].

EXPERIMENTAL WORK

0.097 g, i.e., 0.357 mmol of mercuric chloride and 0.102 g, i.e., 0.333 mmol of para toluidine has been weighed out in a vial. 10 ml (30%) of hydrochloric acid was added in the vial. Precipitates were formed and the sample was submerged in an ultrasonic bath but failed to form properly dissolved solution at room temperature. Vial was then heated in oil bath. The temperature of the oil bath was set to 90°C through programmable temperature controller provided with the oil bath. The temperature equals 90°C was kept constant for 4 h. After then all precipitates were dissolved. A polytop lid sealing was made on the sample and finally vial height in the oil bath was adjusted. It was made in such a way that only filled part of the vial is immersed in the oil bath. After about 48 h, slow cooling in the oil bath leads to the formation of crystals in the vial mostly on the

upper half of the vial. Crystals were thin plate shaped and light orange in colour. Successfully prepared crystals were then extracted using filter paper. Philip PW 1315 powder diffractometer and CRYSFIRE programs has been used for obtaining X-Ray diffraction pattern and indexing of the pattern respectively [14-16].

RESULTS AND DISCUSSION

Crystal data of synthesized material showed that the grown crystal belongs to monoclinic crystal system in which $a \neq b \neq c$ [$10.061(4) \text{ \AA} \neq 4.317(2) \text{ \AA} \neq 12.987(5) \text{ \AA}$] and $\alpha = \gamma = 90^\circ \neq \beta$ [$\alpha = \gamma = 90^\circ, \beta = 104.322(7)^\circ$] and belongs to space group $P2_1$ as shown in Table 1. Sharp peaks of the powder diffraction pattern, as shown in Figure 1, confirms the crystallinity of the grown hybrid material. For inorganic part of the hybrid structure, mercury atoms and chlorine atoms are interconnected such that Hg1-Cl1 bond length is 2.354(2) Å, Hg1-Cl2 bond length is 2.352(1) Å and Hg1-Cl3 bond length is 2.925(7) Å. The bond length with Cl3 is larger than rest of the two by the distance of 0.57 Å which is quite significant distance. Also from the bond angle values for Hg1^a-Cl3-Hg1 equals 95.4(1)° shows that Cl3 is acting as bifurcated acceptor so that inorganic part of the crystal structure forms a unique zig-zag pattern. Cl1-Hg-Cl2 bond angle value is 173.2(1). Thus Cl1 and Cl2 are joined quite linearly through respective mercury atom. However all the angles with Cl3 are close to 90° as shown in Figure 2.

Table 1: Crystal Data of Synthesized Material.

| Components of the Hybrid | Paratoluidine (Organic), Mercuric Chloride (Inorganic) |
|------------------------------------|--|
| Empirical formula | C ₇ H ₁₀ NHgCl ₃ |
| Formula weight | 415.10 |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic with unit cell parameters as |
| a=10.061(4) Å | $\alpha=90^\circ$ |
| b=4.317(2) Å | $\beta=104.322(7)^\circ$ |
| c=12.987(5) Å | $\gamma=90^\circ$ |
| Space Group | P2 ₁ |
| Absorption coefficient | 14.761 mm ⁻¹ |
| Crystal size | 30x28x27 mm |
| θ range for data collection | 1.62 to 26° |
| Miller Indices Limited to | -12 ≤ h ≤ 12, -5 ≤ k ≤ 5, 0 ≤ l ≤ 16 |
| Reflections collected/unique | 2164/2164 [R(int)=0.0001] |
| Completeness to Theta =25.00 | 99.9% |
| Refinement Method | Full-matrix least-squares on F ² |

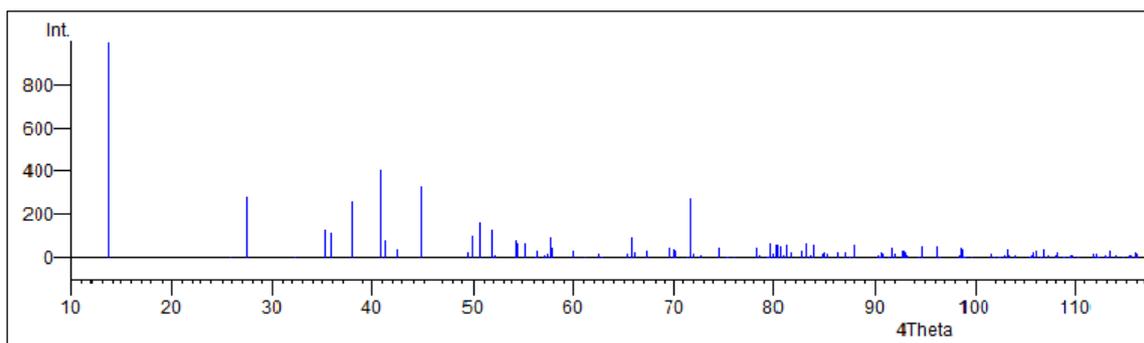


Fig. 1: Powder Diffraction Pattern of Synthesized Hybrid Material.

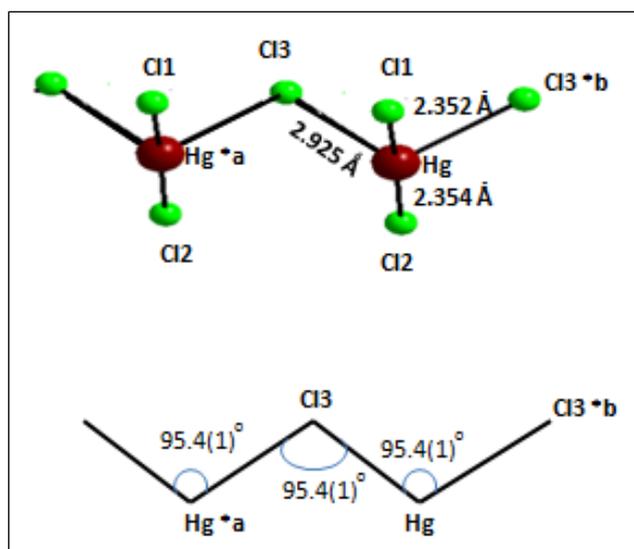


Fig. 2: Bond Angles and Bond Lengths Showing a Symmetric Zigzag Pattern Followed by Inorganic Moiety of the Hybrid Crystal.

The bond angles and bond lengths of the phenyl ring are quite comparable with the literature values. The torsion angle for (C1-C6) of phenyl ring is of value $0.003(6)^\circ$ which is quite sufficient for its planar confirmation.

Furthermore, organic and inorganic moieties of the synthesized hybrid material have been observed to be linked together through $N^+ \cdots H \cdots Cl^-$ hydrogen bond as shown in Figure 3(a) through pink coloured dashed lines. Moreover these moieties are linked together in a unique tetramer pattern i.e. two inorganic moieties are linked to two organic moieties through $N-H \cdots Cl$ hydrogen bond. Single nitrogen atom of the organic moiety is acting as hydrogen bond donor for the formation of three hydrogen bonds. Also chlorine atoms i.e. Cl3 (x, y, z) and Cl3 (x, y-1, z) are bifurcated acceptors for two hydrogen atoms and the bifurcated acceptor angle is H_A-

Cl3-H_B is $23.76(2)^\circ$. When seen along ac-plane, tetramer pattern have been observed to be extended along the diagonal of ac-plane. One tetramer pattern is linked to another through Hg-Cl metal halide weak interaction as depicted in Figure 2(b). Mercury atom Hg1 (-1+x, 3+y, z) is connected to chlorine atom Cl1 (1-x, 5/2y, z) via bond distance of $3.135(6) \text{ \AA}$. Since the sum of their Vander Waal radii is 3.30 \AA , therefore metal-halide weak interaction is confirmed. These secondary metal-halide interactions are of the kind dipole-dipole interaction, i.e., $Hg^+ \cdots Cl^-$ and the strength as calculated from the bond distance vs. bond valence model is just 5-10% of the Hg-Cl bond. This $Hg \cdots Cl$ weak interaction resulted into the formation of a symmetric dimer pattern of inorganic moiety. When minimum distance existing between the two mercury atoms is measured, it comes out to be $4.112(1) \text{ \AA}$.

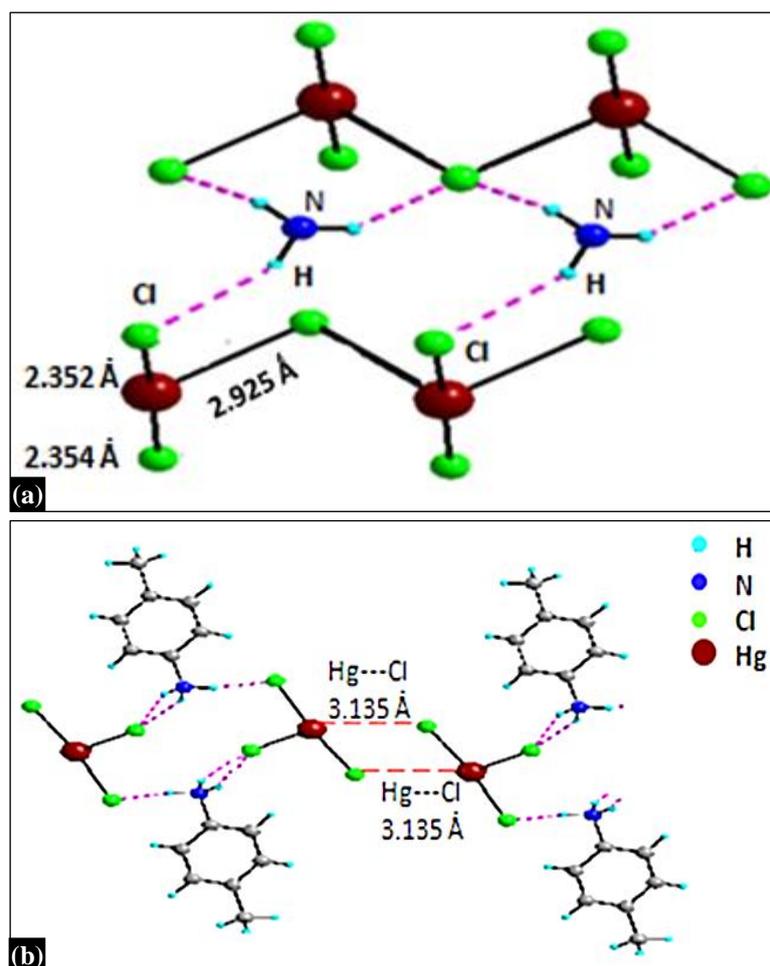


Fig. 3: Perspective View of (a) Hydrogen Bonding (Pink Dashed Line), (b) Metal Halide Secondary Weak Interaction (Red Dashed Line) through which Organic and Inorganic Components are Linked Together to Form a Single Composite.

However the sum of their Vander Waal radii is approximately 3.50 Å. Thus, non-existence of mercuriphilic interaction, i.e., Hg-Hg interaction in this compound is confirmed. Similarly there is no halogen-halogen interaction as the minimum Cl-Cl distance is 3.764(7) Å. Also the distance from the centroid of aromatic ring to the nearest hydrogen atom comes out to be 3.695(2) Å which is quite large for C-H $\cdots\pi$ interaction to exist [17-19].

CONCLUSION

The inorganic (mercuric chloride) organic (para-toluidine) hybrid material was synthesized by using slow cooling technique. The light orange coloured crystals were obtained. The powder diffraction peak profiles for the hybrid material shows that b-axis has

smaller value as compared to other two axes. The torsion angle of phenyl ring comes out to be 0.003(6) $^\circ$ which gives its planar confirmation for synthesized inorganic-organic hybrid material. Organic and inorganic moieties of the synthesized hybrid material are linked together through N $^+$ -H \cdots Cl $^-$ hydrogen bond. Two inorganic moieties are linked to two organic moieties through N-H \cdots Cl hydrogen bond to form unique tetramer pattern. Layers of inorganic and organic moieties are linked through Hg-Cl metal halide weak interaction. There is no metallophilic interaction as the minimum Hg-Hg distance comes out to be 4.112(1) Å which is quite large for any metallophilic interaction to exist. The minimum halide-halide distance is 3.764(7) Å which indicates that there is hardly any halogen-halogen interaction.

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