SINGLE CRYSTAL GROWTH, X-RAY STRUCTURE ANALYSIS, OPTICAL BAND GAP, RAMAN SPECTRA, STRAIN TENSOR AND PHOTOLUMINSCENCE PROPERTIES IN $[HgCl_4]^-[R]^+$ AND $[ZnCl_4]^-[R]^+$ (R = 2-AMINO-5-CHLOROPYRIDINE) HYBRID MATERIALS

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ABSTRACT

Single crystal growth of tetrachloromercurate (II) [HM-1] and tetrachlorozincate (II) [HM-2] with 2-amino-5-chloropyridine has been performed by slow cooling (SC) crystal growth technique of solution growth method. The crystal structures of these hybrid materials have been studied by X-ray diffraction, experimental and computational techniques, which depict that $N-H^{\delta+}...Cl^{\delta-}$, Hg...Hgand Cl...Cl interactions are stabilizing the structures in 3D pattern. UV-vis absorption spectra illustrate the change in opticalband gap from 3.01eVto 3.42eV on replacing the metal halide group.Raman and Hyper-Raman tensors calculations were performed based on single crystal X-ray data and the Lagrangian strain tensor calculations show the degree of lattice distortion = 1.794 between [HM-1]and[HM-2].The photoluminescence emission spectra peaks lie in the visible range for both materials.

Keywords: Single crystal growth; structure analysis; optical E_g; Raman spectra; strain tensor and lattice distortion.

1. INTRODUCTION

The single crystal growth and materials characterization of inorganic-organic hybrid materials is a recent, very significant and prolific enterprise [1]. Pyridine derivatives have photochemical, electrochemical and catalytic applications and possess nonlinear optical (NLO) properties [2-9]. Recently, the pyridine molecule has been used in combination with different metal transitions such as Hg, Cd, Zn, etc. to characterize new complexes containing organic and inorganic parts [10-12]. The Hg(II), Cd(II) and Zn(II) based hybrid materials having combined desirable physical properties of both organic and inorganic components within the single composite [13] build up through secondary interactions [14]. These hybrids are of interest due to their self-assembled organic-inorganic layered structures which causes variation in their structural, magnetic, optical and electrical properties, particularly since these can be modified by replacement of the metal halide, or amine [15, 16]. Hybrid materials with non linear optical (NLO) properties [17] are currently attracting considrable attention because of their potential applications in optoelectric devices, optical switching and tetrahertz (THz) wave generation [18]. As part of our ongoing research on single crystal growth and characterization of inorganic-organic hybrid materials with an aim of optical properties of these materials, two hybrid materials were studied in this paper.

2. RESULTS AND DISCUSSION

The 3D view depicting molecular geometry and atomic numbering schemes employed for 2-amino-5-chloropyridine tetrachloromercurate(II) and 2-amino-5-chloropyridine tetrachlorozincate(II) are illustrated in figure 1(a) and figure 1(b), respectivelywith thermal ellipsoids were drawn at 50% probability level. Single crystal XRD data were used to refine the structural parameters upto R-factor of 0,029 for HM-1 and 0.051% for HM-2. The detailed single crystal structural data for [HM-1] & [HM-2] has been given in in Table-1.

Table 1. Crystal data and structural refinement for *[HM-1]* and *[HM-2]*

Parameters	*[HM-1]*	*[HM-2]*
Emperical formula	$(C_5H_6ClN_2)_2[HgCl_4]$	$(C_5H_6ClN_2)_2[ZnCl_4]$
Formula weight(g/mol)	436.51	466.33
Temperature (K)	294(2)	110(0)
Crystal system	Monoclinic	Monoclinic
Space group	$P\,2_1/c$	$P\,2_1/c$
Unit cell dimensions		
$a(\text{Å})$	3.984(3)	13.317(1)
$b(\text{Å})$	34.317(3)	14.817(2)
$c(\text{Å})$	23.030(2)	8.571(1)
$\beta(°)$	94.669(1)	92.923(9)
$V\,(\text{Å}^3),\,Z$	3138.0(5), 12	1689.0(3), 4
μ (Mo-Kα) (mm^{-1})	15.684	2.399
$F(000)$	2376	928
θ Range	1.07-26.25°	3.35-29.54°
Measured reflections	6283	4360
Unique reflections	5441	3553
Refined parameters	337	190
Goodness-of-fit on F^2	1.103	1.023
R_1 (on F, $I > 2\sigma(I_o)$)	0.029	0.051
wR_2 (F^2, all data)	0.061	0.099
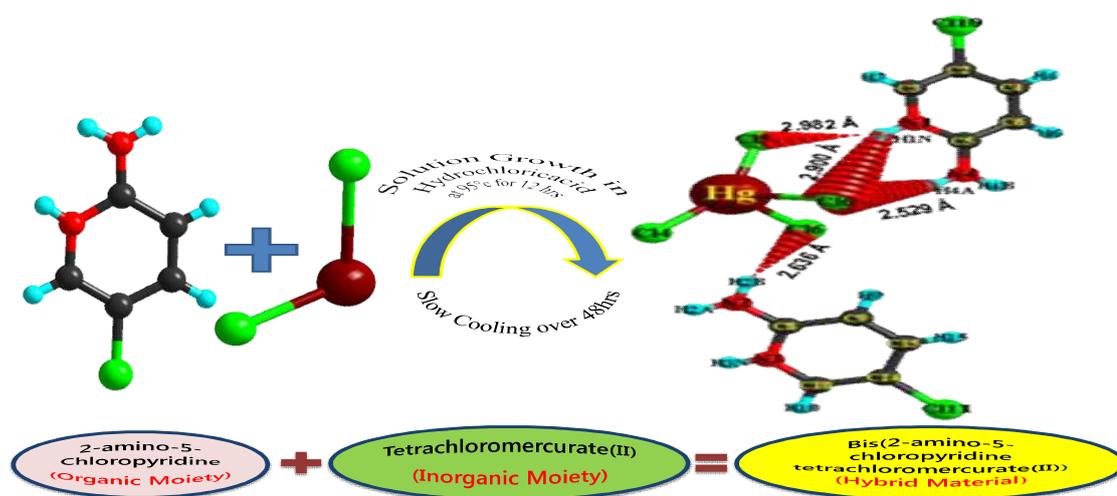
Fig.1.a. Chemical scheme for HM-1 showing the atomic numbering
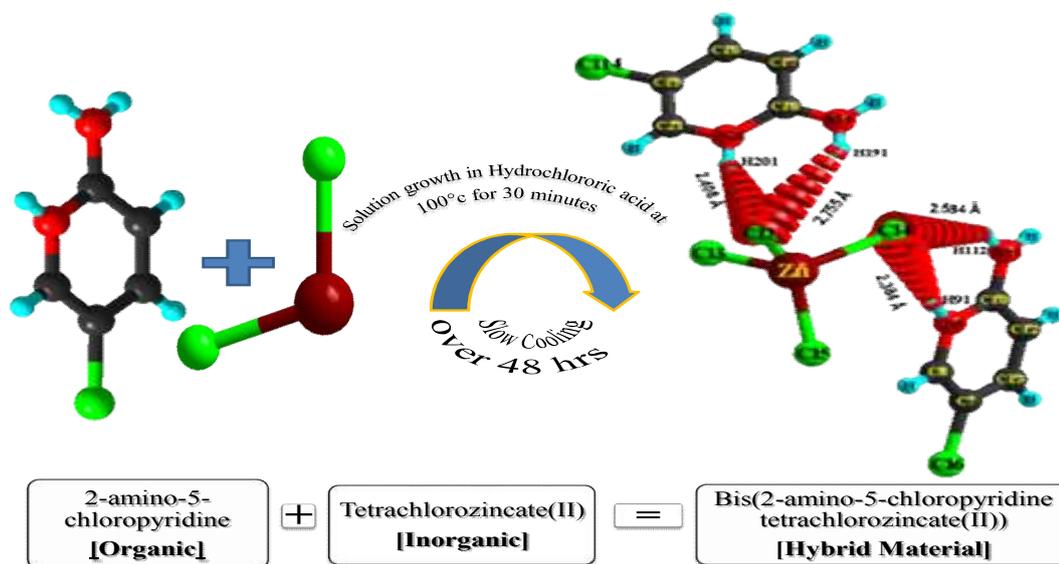
Fig.1.b. Chemical scheme for HM-2showing the atomic numbering

In solid state, 2-amino-5-chloropyridine tetrachloromercurate(II), self-assemble into structures consisting of alternating organic layers, made up of 2-amino-5-chloropyridine and inorganic layers made up of tetrachloromercurate. Crystal structure analysis of a single crystal of compound Bis(2-amino-5-chloropyridine tetrachloromercurate(II)) [HM-1]revealed that the inorganic part of the structure contains four chlorine atoms annexed with mercury to form a tetrahedron, in which all the Hg-Cl bond lengths are different [Hg2-Cl4=2.319(1)Å, Hg2-Cl5=2.339(1)Å and Hg2-Cl6=2.772(1)Å and Hg2-Cl6=2.753(1)Å]. The Cl-Hg-Cl bond angle ranges from 92.30(4)° to 153.23(5)° with an average value of 102.36(1)°. The minimum

distance between Hg-Hg atoms is 3.984(5)Å [Fig.2(a)] which is in comparison with the literature value [19][Fig.4] and hence, there is mercurophilic (Hg...Hg) interactions in this compound *[HM-1]* as proposed by Das et al. [20].
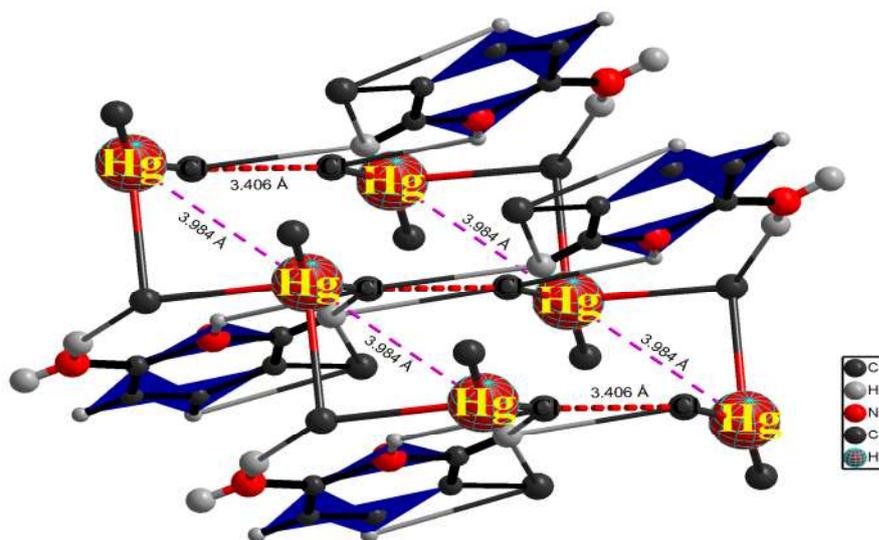
Fig.2.a. Packing diagram of *[HM-1]* depicting the Hg…Hg and Cl...Cl interactions

There is also an interesting phenomenon of Cl...Cl halogen bonding [symmetry positions: 1-x, -y, 1-z; x, -y, 0.5+z] having distance of 3.406(2)Å [Fig.2(a)] and Hg-Cl...Cl angle of 163.38(6)°.The organic and inorganic layers are linked to one another through N-H...Cl hydrogen bonds. N1 and N4 are the donor atoms whereas the three chlorine atoms [Cl4, Cl5 and Cl6] act as proton acceptors. These results are analogous to the analysis of 6624 crystallographically characterized hydrogen bonds containing M-Cl, C-Cl or Cl$^-$ and either HO or HN groups shows that M-Cl moieties are good, anisotropic hydrogen-bond acceptors forming hydrogen bonds similar in length to those of the chloride anion, while C-Cl moieties are very poor hydrogen-bond acceptors [21].All the three hydrogen atoms of N1 and N4 are involved in intra and intermolecular interactions [Fig.1(a)]. H1N atom at symmetry position x, -y+3/2, z+1/2 is shared by two chlorine atoms [Cl5 at symmetry position: x, -y+3/2, z+1/2 and Cl6 at symmetry position: x-1, -y+3/2, z+1/2] and thus acts as bifurcated hydrogen atom with bifurcated hydrogen bond angle of 82.73(2)°.

In Bis(2-amino-5-chloropyridine tetrachlorozincate(II))*[HM-2]*, the minimum distance between Zn-Zn atoms is 6.632(1)Å [Fig.2(b)] which is more than sum of their van der Waals

radii [19]. Hence, there is no metallophilic Zn...Zn interaction in this compound as proposed by Das et al. [20], whereas the minimum distance between two Chlorine atoms is 3.357(2)Å [Fig.2(b)] which shows that the halogen-halogen interactions can be anticipated in this compound and Zn-Cl...Cl angle is 145.99(5)°.
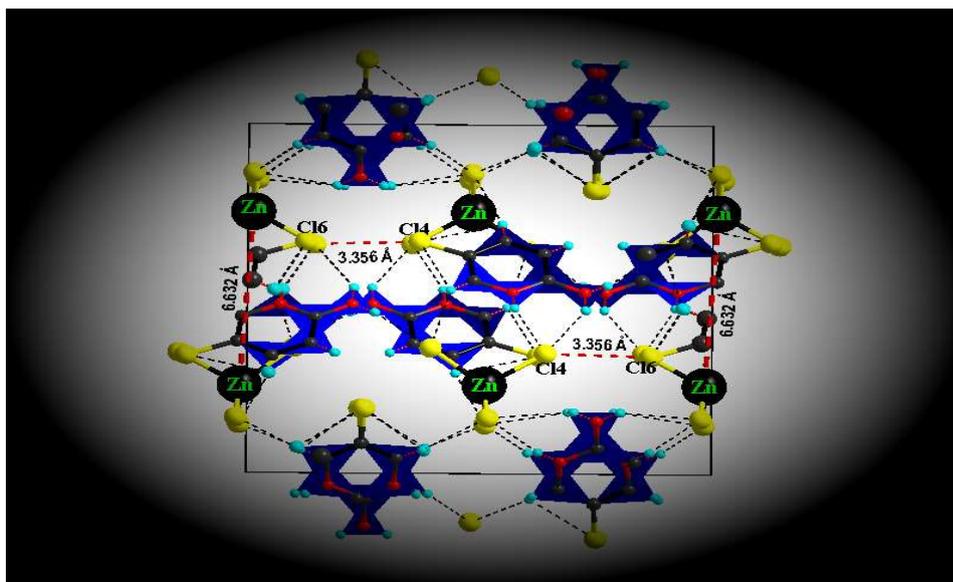
Fig.2.b. Packing diagram of *[HM-2]* down c-axis depicting the values of Zn…Zn and Cl...Cl interactions

On comparison with other $[HgCl_4]^-$ based hybrid materials [22], it is observed that inorganic layers are connected to one another through Cl...Cl secondary interactions. The scatter plot [Fig.3] for Cl...Cl bond length for different compounds [23]shows that most of the data points lie in the range of 3.6 to 3.9Å. The Cl...Cl bond length (3.406Å) and linearity in Hg-Cl...Cl bond angle conclude the strong secondary interactions in such compounds and hence is considered as an important tool to study the structure-property-relationship in hybrid materials.
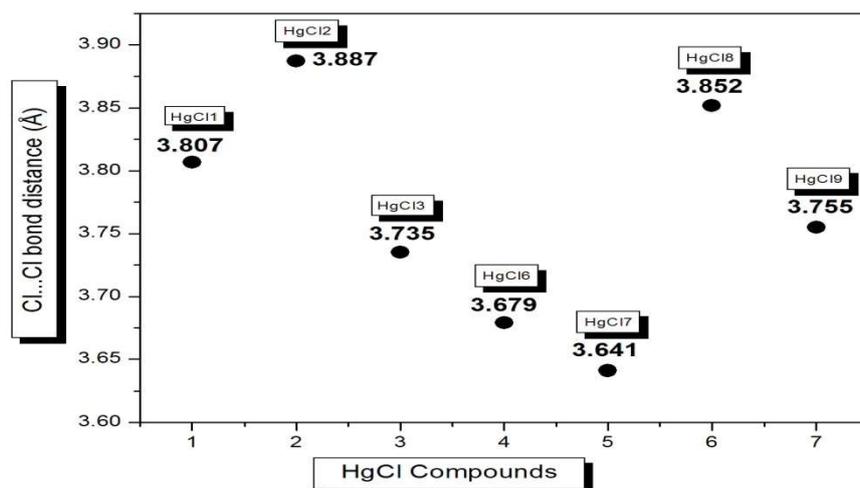
Fig.3. d-scatter plot for Cl...Cl interactions in HgCl derivatives
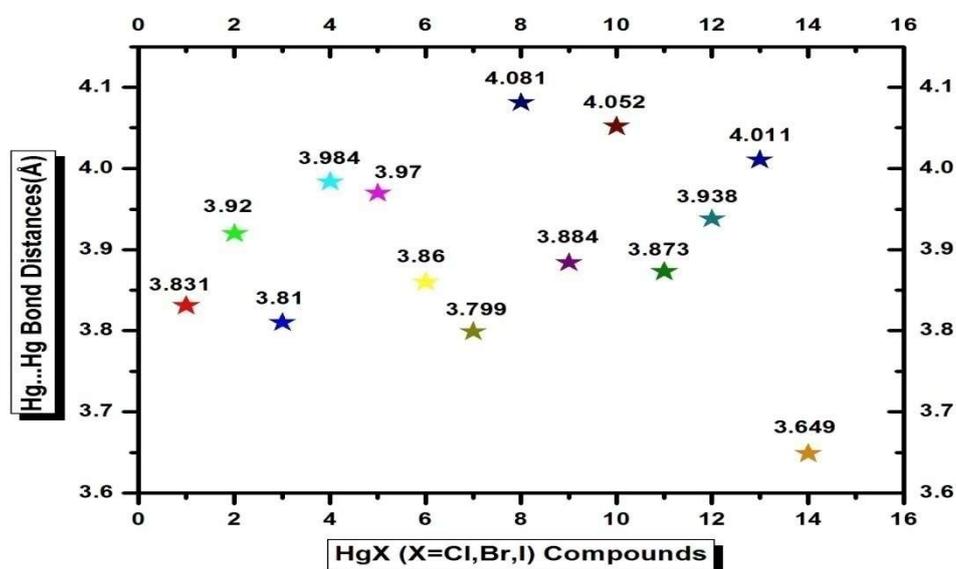
Fig.4. d-scatter plot for Hg...Hg interactions in HgX (X = Cl, Br and I) derivatives

3.1 UV-Vis SPECTROSCOPY

UV-Vis spectroscopic technique is used to calculate the optical energy band gap in these hybrid materials in which the absorption spectra has been recorded within the wavelength range of 200 to 800 nm with cut-off value of wavelength = 412.22 nm for [HM-1] as shown in Fig.5(a). The critical wavelength was determined from the spectrum using the slope of the linear region, and was determined to be equal to 412.22 nm. Using the linear cut Range 390 to 404 nm and equation of linear fitting profile, $y = p_0 + p_1 x$, the wavelength is calculated,

λ=412.22 nm and the optical energy gap = 3.01 eV. UV-Vis absorption spectra for [HM-2]has recorded the cut-off value of wavelength = 362.27 nm by using linear cut range 363 to 377 nm [Fig.5(b)]. The change in metal halide depicts the variation in optical energy gap = 3.42 eV which indicate the role inorganic moiety in optical properties of inorganic-organic hybrid materials. The direct and indirect energy band gaps were calculated by tauc plots which indicate the E_g value in close agreement as calculated by linear fit method.
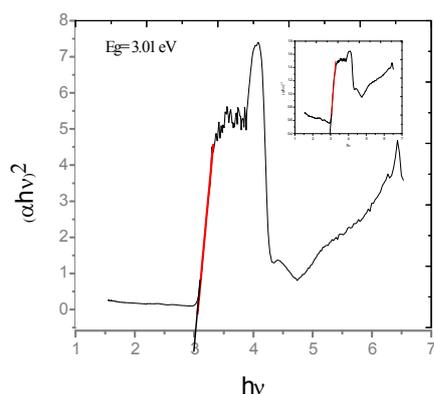
Fig.5.a. Direct and indirect optical E_g by tauc plot of UV-Vis spectra for (HM-1)
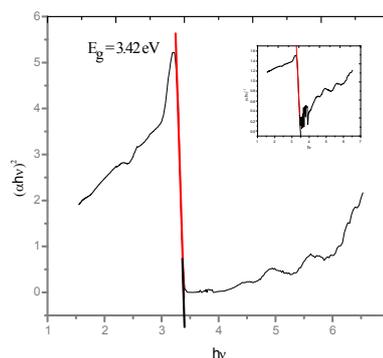
Fig.5.b. Direct and indirect optical E_g by tauc plot of UV-Vis spectra for (HM-2)

3.2 IR AND RAMAN SPECTRA

The IR, Raman and Hyper-Raman tensors are calculated for the Hybrid materials by using crystallographic computing programs [24] in which selected Wyckoff positions are chosen based on the crystal structure data. The initial Hyper-Raman tensors are calculated by selection rules. The relative intensities of the hyper-Raman (HR) lines of this as a function of the scattering geometry are calculated. The parameters $\partial\chi(2)ijl/\partial um(\kappa)$ in terms of a nonlinear bond-polarizability model are interpreted and it indicates the dominant role of the such hybrid materials in the nonlinear-optical response. It shows that the hyper-Raman tensors would be useful as a method for studying the band structure in solids through spectroscopic methods [25].

Active Modes: ($\Gamma_{acoustic} = A_u + 2B_u$)

Different Modes Activity	A_g	A_u	B_g	B_u
Infrared[WP 3 = 2a, 2c and 4e]	0	3	0	5
[WP 5 = 2a, 2b, 2c, 2d and 4e]				
Raman [WP 1 = 4e]	1	0	1	0
Hyper-Raman[WP 3 = 2a, 2c and 4e]	0	5	0	4
[WP 5 = 2a, 2b, 2c, 2d and 4e]				

Where, '0' represents the modes which cannot be detected.

3.3   STRAIN TENSORS

The strain tensors and their corresponding eigenvalues have been calculated by computer program [19] in which the single crystal X-ray data parameters of two hybrid materials *[HM-1]* and *[HM-2]* are selected. The finite Lagrangian strain tensor was calculated according to the formula: $S = 0.5 (e + e^T + e^T e)$, where, $e = R_2 R_1^{-1} - I$ and R_1 and R_2 are the standard root tensors of [HM-1]and[HM-2].

Lagrangian Strain Tensor: [5.35 0.01 -0.03] [0.01 -0.41 0.01] [-0.25 0.01 -0.43]

Eigenvalues: -0.407 5.348 -0.432 and *Degree of lattice distortion* = 1.794.

3.4   PHOTOLUMINESCENCE:

The photoluminescence emission spectra peaks for material [HM1] were observed in the wavelength range of 371 to 598 nm with maximum peak intensity of 9.9 a.u. at 443 nm and 456 nm and photoluminescence excitation spectra peaks were observed in the wavelength range of 280 to 322 nm with maximum peak intensity of 8 a.u. at 284 nm and 285 nm shown in figure 6a.The photoluminescence emission spectra peaks for material [HM1] were observed in the wavelength range of 384 to 600 nm with maximum peak intensity of 9.9 a.u. at 442 nm and photoluminescence excitation spectra peaks were observed in the wavelength range of 280.5 to 350 nm with maximum peak intensity of 9.9 a.u. at 294 nm and 297 nm shown in figure
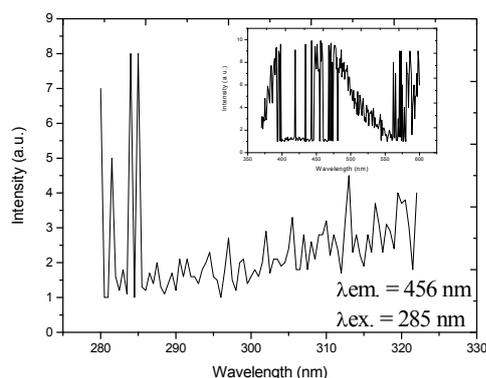
Fig.6.a. 2-Amino-5- Choloropyridine tetracholoromercurate(II) excitation and emission graph.
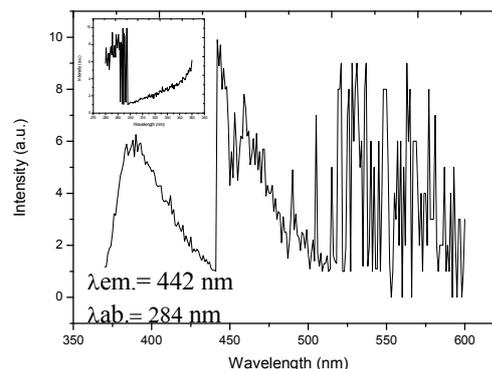
Fig.6.b. 2-Amino-5-choloropyridine tetracholorozincate(II) excitation and emission graph.

4. MATERIALS AND EXPERIMENTAL METHOD

4.1 Physical Homogeneous Synthesis

The growth of these hybrid materials has been carried out by using the following reaction scheme: $MCl_2 + 2RNH_2 + 2HCl \rightarrow (RNH_3)_2MCl_4$

Where, M=Hg(II), Cd(II) and Zn(II); R = 2-amino-5-chloropyridine

The ratio of metal halide to monoamine to acid halide is 1:2:2. Single crystal growth has been achieved by using solution growth (SG) technique by slow cooling (SC) method [26] by using programmable heating and slow cooling apparatus. All compounds have been obtained commercially and used without further purification. The hybrid material of Bis(2-amino-5-chloropyridine tetrachloromercurate(II)) [HM-1] has been prepared by adding mercuric chloride [0.092g] and 2-Amino-5-chloropyridine [0.102g (0.333 mmol)]and 5ml of hydrochloric acid [33% HCl] into a glass sample vial. Precipitates were formed and solution did not dissolve at room temperature even being submersed in an ultrasound bath. The vial was heated in oil bath that is controlled by a programmable temperature controller. The oil bath was heated upto $95^{o}C$ and then held constant at that temperature for 10 hours as shown in test tube (T1) in Fig.5(a), until all the precipitates dissolved. The sample was sealed with its polytop lid and the height of the vial in the oil bath was adjusted such that only the vial is immersed upto the level of the solution inside the vial. Slow cooling over 48 hours was employed to obtain single crystal materials of the Hg(II) based hybrid material [Tube (T2) in

Fig.5(a)].

Fig.5.a. Needle shaped single crystals of the Hg(II) hybrid material.
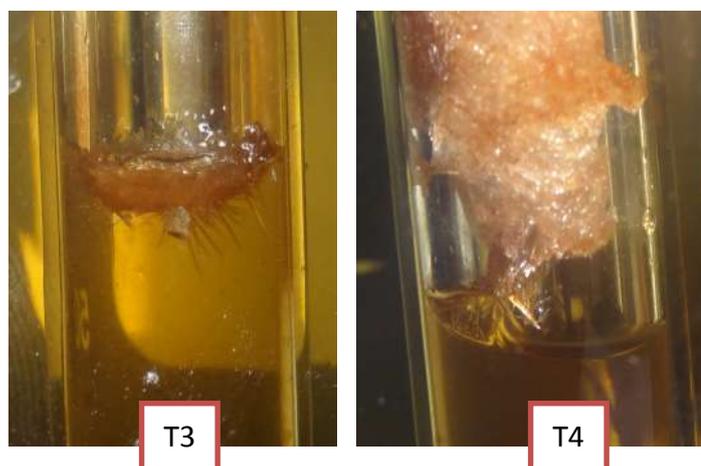
Fig.5.b. Needle shaped single crystals of the Zn(II) hybrid material in T3 and rectangular plate shaped crystals of Zn(II) hybrid material grown through solution growth (SG) and slow cooling (SC) method

The compound of Bis(2-amino-5-chloropyridine tetrachlorozincate(II)) [HM-2]has been prepared by zinc chloride [0.097g], 2-amino-5-chloropyridine [0.108g (0.333 mmol)] and 5ml of hydrochloric acid [33% HCl] by using the same technique. Single crystal materials of the Zn(II) based hybrid material obtained from (SG) and (SC) process are shown in tube T3 & T4 of Fig.5(b).

4.2 Structure Analysis

Single crystal X-ray crystallographic techniques have been employed for the crystal structure determination and refinement. Morphologically perfect single crystal has been selected for the

three-dimensional X-ray diffraction data by using X-calibur CCD diffractometer. Colourless crystals of [HM-1]having size (0.35 x 0.20 x 0.15) mm & [HM-2] having size (0.35 x 0.25 x15) mm were used for X-ray diffraction data.

The structure determination has been carried by SHELXS program [27]whereas the least-squares refinement has been contemplated by using SHELXL program [28] for the precise values of R-factor.

5. CONCLUSIONS

Analysis of charge assisted $N-H^{\delta+}...Cl^{\delta-}$ hydrogen bonds,metallophilic (Hg...Hg) and halogen-halogen (Cl...Cl) interactions in [HM-1] and [HM-2]elucidate the importanceof secondary interactions in structure-property-relationship of hybrid materials with optical properties.The change in metal halide group has altered the structural as well as optical properties of hybrid materialfrom 2D parallelogram pattern [HM-1] to antiparallel layer pattern in [HM-2] along b-axis and optical band gap from 3.01 eV for [HM-1] to 3.42 eV for [HM-2]. Photoluminescence properties show change in emission and excitation spectra due to metal halide variant.

6. ACKNOWLEDGEMENTS

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