[ZnO] based Hybrid Materials: Structural and Optical Studies

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ABSTRACT *The role of non-covalent interactions in structure-property-relationship of [ZnO] based inorganic-organic hybrid materials has been studied in a series of compounds which were analyzed through single crystal X-ray crystallographic data. The XRD data were simulated for molecular dynamics through computational systems to calculate the non-covalent interactions in series of ZnO hybrid composites. The structural frameworks depict that the non-covalent interactions are holding the organic moieties within the inorganic components through X-H…A, C-H…π, π… π, halogen-halogen and metallophilic type of 1D, 2D and 3D patterns. The different structural motifs from 1D chain, 2D ribbons and 3D dimmer patterns are responsible for structure stability of these materials. The IR and Raman spectra tensors were calculated for the selected series of derivatives which indicates that IR, Raman and Hyper-Raman modes are dominant in ZnO based derivatives as compared to other type of similar hybrid materials. The structural and spectroscopic parameters reveal that such non-covalent interactions plays in important role to design the materials with optical and spectroscopic applications.*

Keywords:

I. Introduction

The functional hybrid materials had played an important role in advanced applications of materials science in today's technocratic society. The hybrid materials are being used as energy storage devices such as in hybrid batteries and solar cells. The advanced applications of the hybrid materials in photo-voltaic devices has made them very important class of materials for solar energy devices. ZnO is a group II-VI compound semiconductor material, with a direct wide bandgap of 3.37 eV and a large exciton binding energy of 60 meV [1]. This binding energy is significantly high, 2.4 times the room temperature thermal energy which permits the fabrication of ZnO based photoelectronic devices possessing high optical efficiency, while the wide bandgap eases the application of ZnO thin films for short wavelength optoelectronic devices. The unique physical properties of ZnO has numerous advantages for the electronic device due to the improved carrier confinement in one-dimension, increased junction area and hole transport. The conjugated polymer has higher hole mobility while the ZnO has higher electron mobility. When ZnO mixed with other materials, it makes good electronic properties. ZnO has impressive electronic and optical properties. Due to these properties, ZnO has received a considerable attention in a wide range of applications such as transparent conductive oxide, optoelectronic, and piezoelectric devices. Recently, ZnO has attracted increasing interest in organic and amorphous semiconductor for plastic electronic, LEDs, photodetector (PD), solar cells (SCs), and transparent thin film transistors[2]. During the past decade the hybrid materials were developed on a very large scale with desired properties. The clubbing of two different components i.e. inorganic and organic into single composite form the hybrid compound. The hybrids are classified into different types as per the mode of combining these two different moieties into single composite. Class I hybrid materials are made up by the non-covalent interactions in which organic moieties are held together the inorganic layers through the secondary interactions. The non-covalent interactions are responsible for holding the organic and inorganic moieties together into single hybrid composite. The role of these interactions is the key point to study the structural and optical behaviour of hybrid materials [3].

II. EXPERIMENTAL DATA:

The hybrid materials are the class of functional materials with desired properties for the modern industrial applications, as they are the future of nano-materials science due to combination of two different solid state sciences into single hybrid composite. The structural and optical studies of these materials are an important aspect of their properties and hence the applications of such materials in industry. To analyze the structural parameters of hybrids, the XRD data of a series of [ZnO] inorganic-organic hybrid derivatives were selected from international union of crystallography, U.K.. The crystallographic open data base (COD), of international union of crystallography, U.K. has been used to collect the available zinc based metal-organic molecules XRD structural data in crystallographic information file format. The structural and molecular

dynamics simulations to analyze the weak interactions were performed with DIAMOND-Crystal and molecular structure visualization and function program [4].

III. RESULTS AND DISCUSSION:

The hydrogen bond geometry for ZnO derivatives indicates that the acceptor bond length lies in the range of 1.78Å to 2.97Å and the donar-acceptor length exist in between 2.616(2)Å to 3.910(3)Å and H-centered D-A angle has values from 101° to 177°. The range of hydrogen bond distances and angles in Zinc based hybrid materials is given in Table 3.3. For $ZnCl_2$ the range of H…A bond distance is 1.78 to 2.97(Å), for $ZnBr_2$ it is 1.84 to 3.08(Å) and for ZnI_2 And ZnF_2 the range of bond distance is 2.22 to 3.09(Å) and 1.71 to 2.92(Å) respectively. Similarly the range of bond angles for $ZnCl_2$, $ZnBr_2$, ZnI_2 and ZnF_2 are 101 to 177 (°), 82 to 179 (°), 72 to 167 (°) and 94 to 173(°) respectively as described in table 3.3 below.

Table 1: Hydrogen bonding geometry of Zinc based hybrid materials

Zinc based hybrid material	Range H---A(Å)	Range X---A(Å)	Range X-H---A(°)
$ZnCl_2$	1.78 – 2.97	2.616 – 3.910	101 – 177
$ZnBr_2$	1.84 – 3.08	2.732 – 3.915	82 – 179
ZnI_2	2.22 – 3.09	2.774 – 3.904	72 – 167
ZnF_2	1.71 – 2.92	2.677 – 3.771	94 – 173

The d-θ scatter plot for hydrogen bonding interactions shows that most of the data points exist in H…A distance range of 1.8 to 2.9 Å and X-H…A angle ranges from 100° to 175° in the selected series of metal-organic compounds which indicate these interactions are moderate type of hydrogen bonds as shown in Figure 1.

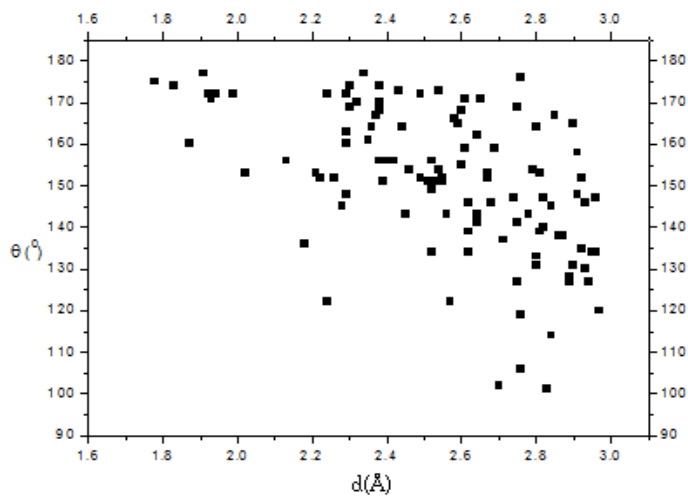

Figure 1: d (H…A) and θ (X-H…A) scatter plot for $ZnCl_2$ based metal-organic derivatives.

The π-interactions were constructed by selecting the centeriod of two phenyl rings and their corresponding distances and torsion angles were calculating, which shows that the minimum value of π…π distance in zinc chloride is 3.590(7)Å for compound $ZnCl_{18}$ with torsion angle 63.45(1)° having symmetry position x,1+y,z and the maximum π…π interaction is 3.676(7)Å for compound $ZnCl_{17}$ with torsion angle 66.53(2)° having symmetry position 1-x,2-y,-z. The minimum value of π…π interactions in zinc bromide is 3.512(7)Å for compound ZnBr29 with torsion angle 180.0(4)° having symmetry position 1-x,-y,1-z, and 1.5-x,-0.5+y, 0.5-z and the maximum π…π interaction is 3.881(2)Å for compound ZnBr23 with torsion angle 180.0(2)° having symmetry position 1-x,1-y,1-z as shown in Table 2. The minimum value of π…π interactions in zinc floride is 3.644(2)Å for compound ZnF4 with torsion angle 64.03(2)° having symmetry position -x,1-y,-z, and the maximum π…π interaction is 3.811(1)Å for compound ZnF5 with torsion angle 121.14(2)° having symmetry position 1-x, 1-y, 1-z as shown in Table 2.

Table 2: *π*…π interactions in selected series of metal-organic compounds.

Zinc based hybrid material	π…π (Å) Distance range	Max. torsion angle (°) π…π
$ZnCl_2$	3.590(7) - 3.706(1)	C18- π…π-C20= 63.48(2)
$ZnBr_2$	3.512(7) - 3.881(2)	C15-π…π-C15= 180.00(2)
ZnF_2	3.644(2) - 3.811(1)	C11-π…π-C12= 121.14(2)

Different structural pattern were obtained within the organic moiety through π-interactions such as a 1D chain of C-H…π interaction is observed in ZnCl19 derivative in which π acts as acceptor of H23 atom of organic moiety of the metal-organic derivatives linking the organic components in 1D chain of C-H…π interactions.

Table 3: C-H…π interactions in selected series of metal-organic compounds.

Zinc based hybrid material	H…π (Å) Distance range	Range C-H…π (°)
$ZnCl_2$	3.279(1) - 3.669(5)	71.82(1) - 140.12(2)
$ZnBr_2$	2.800(4) - 3.617(3)	52.07(2) - 145.62(2)
ZnI_2	2.912(2) - 3.729(2)	85.43(2) - 155.48(3)
ZnF_2	2.895(8) - 3.727(2)	86.004(3) - 138.23(1)

The d-Θ scatter plot [Fig. 1] for hydrogen bonding interactions shows that most of the data points exist in H…A distance range of 2.2 to 2.9 Å and X-H…A angle ranges from 120 to 170° in the selected series of metal-organic compounds which indicate these interactions are moderate type of hydrogen bonds [5].

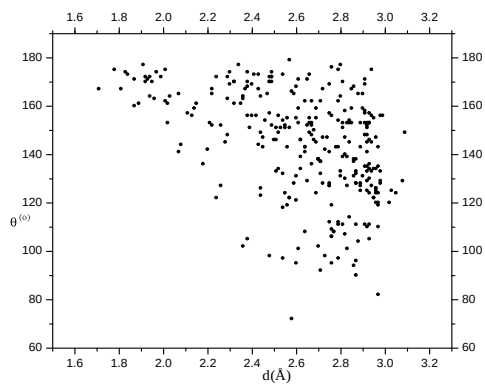

Fig.1. d (H...A) and Θ (X-H...A) scatter plot for zinc based metal-organic derivatives.

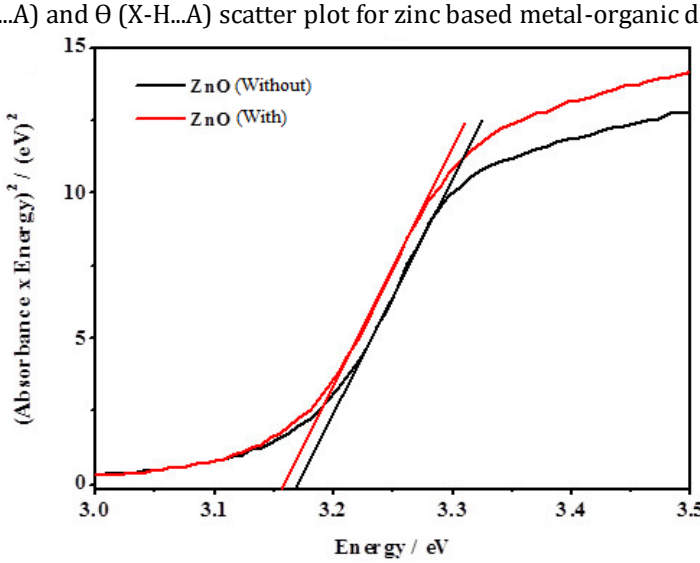

Fig.2. The energy vs absorbance UV-Vis spectra for optical band gap in hybrids with and without ZnO.

The variation in the optical band gap values such as 3.1, 3.15 and 3.2 eV for ZnO derivatives at room temperature have been reported by number of researchers and by comparing the optical properties of ZnO crystals using a variety of optical techniques it is concluded that the room temperature band gap lies between 3.1 and 3.2eV (as shown in Fig. 2) and that the other values are attributable to a valence band-donor transition at ~3.15 eV~3.15 eV that can dominate the optical absorption when the bulk of a single crystal has been probed. IR and Raman spectra tensors have been calculated by using fractional co-ordinates obtained from single crystal XRD data. In which the lattice

parameters and the fractional coordinates were used to study spectral active modes of IR and Raman spectra tensors in the SAM structural utility tool of Bilbao crystallographic server [6-7]. The quantitative comparison of the crystal structures of the selected series of metal-organic compounds through theoretically structural models shows that these compounds have the promising results for spectroscopic applications.

IV. CONCLUSIONS:

The analysis of non-covalent interactions such as C-H…Cl, C-H…Br, C-H…I, C-H…π, π…π, X…X and Zn…Zn in $[ZnX_4]^{2+}$ based hybrid materials shows that non-covalent interactions are responsible for holding the inorganic and organic moieties in single hybrid composite. The inorganic and organic components forms the different structural motifs through these non-covalent interactions. The organic moieties have the optical applications whereas the inorganic components produces the mechanical strength to these materials and the non-covalent interactions are responsible for combining the optical as well as mechanical properties of these materials. The optical studies for IR, Raman and Hyper-Raman tensors show that these materials can be used in junction diodes of hybrid solar cells in which the stability of the hybrid structure is maintained by the weak interactions.

References:

1. A.M. Nahhas, Amer.J. Nano. Res. & Appl., 6(2) (2018), 34-53.
2. P. Wu, J. Zhang, J. Lu, X. Li, C. Wu, R. Sun, L. Feng, Q. Jiang, B. Lu, X. Pan, and Z. Ye, IEEE Transactions on Electron Devices, 61, 1431-1435 (2014).
3. S. Bikram, T. Atul, K. Mukesh., Sanjay K. and Dinesh J. : Mat. Chem.and Phys.. 206, 34(2017).
4. G. Kickelbick, Hybrid Materials. Synthesis, Characterization & Applications (Wiley-VCH, Weinheim, **2005**) [in Germany].
5. K. Brandenburg and H. Putz, DIAMOND. Crystal Impact GbR, Bonn, Germany **(1999)**.
6. G. R. *Desiraju* and *T*. *Steiner*, The *Weak Hydrogen Bond* In *Structural Chemistry* and *Biology*, (IUCr, ***1999)*** [in UK].
7. G. de la Flor, D. Orobengoa, E. Tasci and M. I. Aroyo, et al., J. App. Crystallogr., **(2016)** 49, 653.