

Structural-Spectroscopic-Relationship in a Series of $[\text{CdX}_2]^-$ based Metal-organic Materials

Ajit Kumar^{1,2}, Bikram Singh¹, Dinesh Jasrotia^{1*}, Sanjay K. Verma¹,
Ritu Sihotra¹, P. A. Alvi and ²Mukesh Kumar¹

¹Materials Physics Laboratory, G.G.M. Science College, Jammu-180006, India
²Department of Physics and Material Science, Banasthali University, Newai, Rajasthan
E-mail: *ugcggm@gmail.com

Abstract—To scrutinize the role of the weak interactions in structure-property-relationship of zinc based metal-organic materials, a series of compounds were analyzed through single crystal X-ray crystallographic data. The structural parameters were simulated for molecular dynamics to calculate the weak interactions in series of CdCl_2 , CdBr_2 , CdI_2 and CdF_2 based metal-organic composites. The structural frameworks depict that the metal halides are holding the organic moieties within the inorganic patterns through X-H...A, C-H... π , π ... π , halogen-halogen and metallophilic weak interactions. The different structural motifs from 1D chain, 2D ribbons and 3D dimmer patterns were observed. 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 CdCl_2 based derivatives as compared to CdBr_2 , CdI_2 and CdF_2 based metal-organic compounds. The structural and spectroscopic parameters reveal that such weak interactions can be used to design the materials with spectroscopic applications.

1. INTRODUCTION:

Since, many of the acquitted industrially important materials, such as metals, ceramics or plastics cannot fulfill all the technological desires for the various new applications. Scientists and engineers realized early on that the mixtures of materials can show superior properties as compared with their pure counterparts [1]. It became evident that decreasing the size of the inorganic units to the same level as the organic building blocks could lead to more homogeneous materials that allow a further fine tuning of materials properties on the molecular and structural scale level, generating novel materials that either show characteristics in between the two original phases or even new properties[2]. Inorganic-organic hybrids are classified based on the possible interactions connecting the inorganic and organic species. *Class I* hybrid materials are those which shows non-covalent interactions between the two phases, such as hydrogen bonding, π ... π interactions, halogen...halogen interactions, metallophilic interactions, etc. *Class II* hybrid materials are those that show strong chemical interactions between the components such as covalent, ionic bonds, etc. [3]. The most obvious advantage of metal-organic hybrids is that they can favorably combine the

often dissimilar properties of organic and inorganic components in one material and because of the many possible combinations of components this field is very creative, since it provides the opportunity to invent an almost unlimited set of new materials with a large spectrum of known and unknown properties. While most of these devices can also be produced as fully organic polymer-based systems, the composites with inorganic moieties have important advantages such as the improvement of longterm stability, the improvement of electronic properties by doping with functionalized particles and the tailoring of the band gap by changing the size of the particles [3].

2. EXPERIMENTAL DATA:

Motivated by the industrial applications of metal-organic materials, as they are the future of nanotechnology of materials science due to combination of two different branches of solid state sciences such as organic and inorganic, in which the properties of two different materials can be clubbed together into single composite, a series of seventy number of zinc based metal-organic molecules were selected from international union of crystallography, U.K. to analyze the role of secondary interactions in the structure-stability and structure-property relationship. The crystallographic open data base (COD), of international union of crystallography, U.K. was used to gather the available zinc based metal-organic molecules structural data in crystallographic information file format. The molecular dynamics simulations for studying the physical evolutions of weak interactions were performed with DIAMOND-Crystal and molecular structure visualization and function program [4].

3. RESULTS AND DISCUSSION:

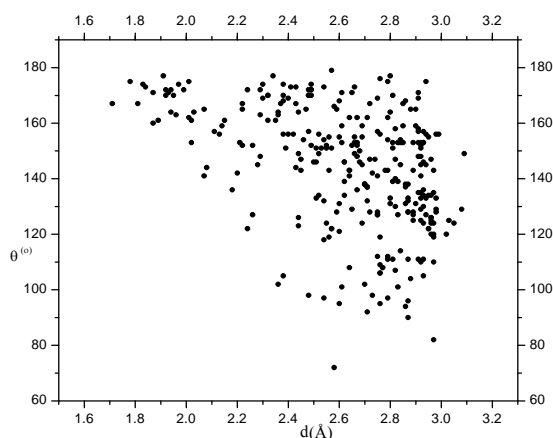
The hydrogen bond geometry for CdCl_2 derivatives indicates that the acceptor bond length lies in the range of 1.78Å to 2.97Å and the donor-acceptor length exist in between 2.616(2)Å to 3.910(3)Å and H-centered D-A angle has values from 101° to 177°.

Table 1: Hydrogen-Bonding Geometry (Å,°) in CdCl₂, CdBr₂, CdI₂ and CdF₂ based derivatives.

Code	D-H(Å)	H...A(Å)	D...A(Å)	D-H...A(°)
CdCl	0.90	2.37	3.247	139.0
CdBr	0.95	2.46	3.297	130.5
CdI	0.86	2.65	3.339	119.5
CdF	0.90	2.28	3.213	133.5

The hydrogen bond geometry for CdBr₂ derivatives indicates that the acceptor bond length lies in the range of 1.84Å to 3.08Å and the donar-acceptor length exist in between 2.732(7)Å to 3.915(7)Å and H-centered D-A angle has values from 82° to 179°. The hydrogen bond geometry for CdI₂ derivatives indicates that the acceptor bond length lies in the range of 2.22Å to 3.09Å and the donar-acceptor length exist in between 2.774(9)Å to 3.904(9)Å and H-centered D-A angle has values from 72° to 167°. The hydrogen bond geometry for CdF₂ derivatives indicates that the acceptor bond length lies in the range of 1.71Å to 2.92Å and the donar-acceptor length exist in between 2.677(7)Å to 3.771(6)Å and H-centered D-A angle has values from 94° to 173°.

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].

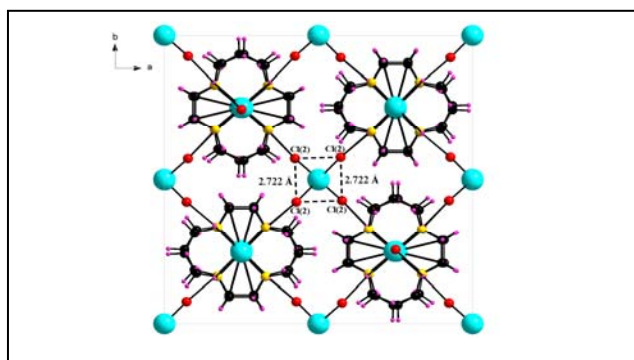
**Fig.1. d (H...A) and θ (X-H...A) scatter plot for zinc based metal-organic derivatives.**

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.

4. CONCLUSION

The analysis of weak interactions such as X-H...A, C-H... π , π ... π , halogen...halogen and Cd...Cd in zinc based metal-organic derivatives results that these interactions are responsible for holding the inorganic and organic moieties in single composite. The π ... π interactions are binding the organic moieties into dimmer patterns whereas the halogen-halogen and metallophilic interactions are holding the inorganic constituents into 1D chain and 2D layer patterns. The metallic constituents of these derivatives provide the mechanical strength to the composite whereas the organic moiety is responsible for its optical as well as spectroscopic properties. The spectroscopic 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 these weak interactions. Looking upon the industrial applications of hybrid material, they are the future of nanotechnology due to combination of two different branches of solid state sciences such as organic and inorganic in which the properties of two different scientific worlds were clubbed together into single composite material.

**Fig. 2. Tetramer pattern of metal-organic CdCl derivative along ab-plane with Cl...Cl (2.722 Å) interaction at symmetry position 1-y, x, 1-z and 1-x, 1-y, z.**

5. AKNOWLEDGEMENT

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