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Metallophilic interactions and structure-stability relationship with secondary interactions in $[ZnX]^-$ based hybrid derivatives

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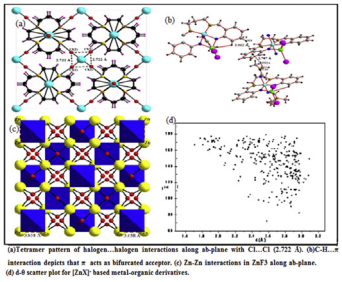
HIGHLIGHTS

- Inorganic-Organic Hybrid Materials.
- Non-Covalent Interactions.
- π-Interactions, Halogen···Halogen Interactions, Metallophilic (M … M) Interactions.
- Structure stability relationship of inorganic-organic hybrid material.
- Industrial applications of hybrid material.

GRAPHICAL ABSTRACT



(a) Tetramer pattern of halogen…halogen interactions along ab-plane with Cl…Cl (2.722 Å). (b)C–H…π interaction depicts that π acts as bifurcated acceptor. (c) Zn-Zn interactions in ZnF3 along ab-plane. (d) d-d scatter plot for $[ZnX]^-$ based metal-organic derivatives.

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ABSTRACT

To scrutinize the role of the weak interactions in structure-stability of zinc based metal-organic compounds a series of seventy derivatives were analyzed through single crystal X-ray crystallographic data obtained from IUCr. The structural parameters obtained from the cif file were simulated for molecular dynamics to calculate the weak interactions in series of zinc chloride, zinc bromide, zinc iodide and zinc fluoride 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 secondary interactions. The different structural motifs from 1D chain, 2D ribbons and 3D dimmer patterns were observed in the selected series. The comprehensive structural statistics results that the average Zn-X bond distance = 2.375 (4)Å [$ZnCl_2$ = 2.465 (4)Å, $ZnBr_2$ = 2.396 (4)Å, ZnI_2 = 2.557 (6)Å, ZnF_2 = 2.019 (5)Å] and X-Zn-X bond angles lie in the range of 64.77–126.45° in these compounds. The X–H … A hydrogen bond calculations result the average H … A bond length = 2.38 Å [$ZnCl_2$ = 2.37 Å, $ZnBr_2$ = 2.44 Å, ZnI_2 = 2.65 Å, ZnF_2 = 2.28 Å] and the average X–H … A bond angle = 125.5° [$ZnCl_2$ = 139°, $ZnBr_2$ = 130.5°, ZnI_2 = 119.5°, ZnF_2 = 133.5°]. This indicates that these hydrogen interactions are in the category of strong to moderate type of hydrogen bonds. The minimum value of H … π = 2.800 (4) Å is observed in ZnBr*17* at symmetry position -x, 1-y, 1-z shows that such interactions are stabilizing the organic moieties within the metal-organic derivatives. It is observed that the minimum value of halogen … halogen weak interaction is 2.382 (2)Å for ZnF*1* at symmetry position -x, 0.5-y, 0.5-z and the minimum value of metallophilic interaction distance is observed as 2.508 (6)Å in ZnBr*32* at symmetry position,1 + x, y, z, which are linking the inorganic components of metal-organic derivatives. 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 $ZnCl_2$ based

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derivatives as compared to $ZnBr_2$, ZnI_2 and ZnF_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]. An organic moiety containing a functional group that allows the attachment to an inorganic network, acts as a network modifying compound because in the final structure the inorganic network is only modified by the organic group. One example for such a material is the combination of inorganic clusters or particles with organic polymers lacking a strong (e.g. covalent) interaction between the components. In this case a material is formed that consists of an organic moiety with entrapped discrete inorganic derivatives in which, depending on the functionalities of the components, the weak cross-linking occurs by the entrapped units through weak non-covalent interactions. If an inorganic and an organic network interpenetrate each other without strong chemical interactions, so called interpenetrating networks (IPNs) are formed [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 non-covalent interactions are responsible for holding the two chemical branches, inorganic and organic, together into a single composite. To achieve the desired properties such as opto-electric applications the role of non-covalent interactions is highly important as their influence to understand the intrinsic structure-property relationships in highly ordered molecular assemblies has been underscored by developments in inorganic-organic hybrid electro-optic materials [4,5].

The self-assembly methods continue to hold a lot of promise in achieving desired architectures of organic assemblies with inorganic moieties. The desire to guide molecular assembly into hierarchical macro-structures have been propelled by the realization that specific molecular geometries favor specialized functions, such as the nonlinear optical (NLO) effects observed in asymmetrically ordered multilayer's [6]. These studies demonstrate a way of formation of structures through the control of non-covalent interactions. Tuning non-covalent interactions within such assemblies is important for controlling the internal morphology, which in turn will determine bulk properties such as structural and optical nonlinearity, as well as the mechanical properties of the assembly [7]. 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. Another driving force in the area of these materials is the possibility to create multifunctional materials. Functional organic molecules can add third order nonlinear optical (NLO) properties in such materials for electronic and optoelectronic applications include light-emitting diodes, photodiodes, solar cells, gas sensors and field effect transistors [2,6]. 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 long term 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 and computational molecular dynamics

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 database (COD), of the international union of crystallography, U.K. was used to gather the available zinc based metal-organic molecules structural data in the crystallographic information file format. The crystal structure data with IUPAC name for selected series of hybrid derivatives has been deposited in supplementary data with codes ZnCl*1* [12], ZnCl*2* [13], ZnCl*3* [14], ZnCl*4* [15], ZnCl*5* [16], ZnCl*6* [17], ZnCl*7* [18], ZnCl*8* [19], ZnCl*9* [20], ZnCl*10* [21], ZnCl*11* [22], ZnCl*12* [23], ZnCl*13* [24], ZnCl*14* [25], ZnCl*15* [26], ZnCl*16* [27], ZnCl*17* [28], ZnCl*18* [29], ZnCl*19* [30], ZnCl*20* [31], ZnBr*1* [32], ZnBr*2* [33], ZnBr*3* [34], ZnBr*4* [35], ZnBr*5* [36], ZnBr*6* [37], ZnBr*7* [38], ZnBr*8* [39], ZnBr*9* [40], ZnBr*10* [41], ZnBr*11* [42], ZnBr*12* [43], ZnBr*13* [44], ZnBr*14* [45], ZnBr*15* [46], ZnBr*16* [47], ZnBr*17* [48], ZnBr*18* [49], ZnBr*19* [50], ZnBr*20* [51], ZnBr*21* [52], ZnBr*22* [53], ZnBr*23* [54], ZnBr*24* [55], ZnBr*25* [56], ZnBr*26* [57], ZnBr*27* [58], ZnBr*28* [59], ZnBr*29* [60], ZnBr*30* [61], ZnBr*31* [62], ZnBr*32* [63], ZnBr*33* [64], ZnBr*34* [65], ZnI*1* [66], ZnI*2* [67], ZnI*3* [68], ZnI*4* [69], ZnI*5* [70], ZnI*6* [71], ZnI*7* [72], ZnI*8* [73], ZnI*9* [74], ZnF*1* [75], ZnF*2* [76], ZnF*3* [77], ZnF*4* [78], ZnF*5* [79], ZnF*6* [80], ZnF*7* [81]. The molecular dynamics simulations for studying the physical evaluations of weak interactions were performed with DIAMOND-Crystal and molecular structure visualization and function program [8].

3. Results and discussion

The structural parameters were calculated by Crystal and molecular structure visualization and function programs which were