**Broad-band luminescence involving fluconazole antifungal drug in a lead-free bismuth iodide perovskite: Combined experimental and computational insights**

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**1. Introduction (section 1)**

Lead-free zero-dimensional (0D) organic-inorganic metal halide perovskites have recently attracted increasing attention for their exceptional photoluminescence properties and chemical stability [1-7].

Among these hybrid materials, the halobismuthates have a substantial importance for their promising application in light-emitting devices [4-7]. This class of materials has the perovskite crystal structure, trend to constitute bi- or polynuclear anions in the crystalline state, where the basicMX6 octahedra share either corners, edges or faces. The infinite number of connections results in numerous polymeric or discrete units, starting with isolated octahedra (0D), through poly-anionic chains and layers (1D, 2D or 3D). Recently, it has been demonstrated that some halobismuthates can be used as the active layer in photovoltaic devices [8,9]. The majority of halobismuthates that have been tested for photovoltaic applications has a 0D structure [10,11]. However, controllable synthesis remains an important challenge in chemistry because the resulting structures are influenced by the ligand geometry, solvent, pH and reaction temperature [12-15]. For all that, the selection of polytopic fluconazole ligand, 2-(2,4-difluorophenyl)-1,3-bis(1H-124-triazol-1-yl)propan-2-ol is a key for the construction of unusual hybrid materials due to its flexible backbone [16-17]. Fluconazole is an antifungal drug containing two triazole rings and a fluorinated phenyl unit. Furthermore, the Fluconazole ligand has several available donors/acceptors (difluoro phenyl, triazole and hydroxyl groups) to form weak interactions (H-bonding function and π-π interaction) to stabilize the supramolecular frameworks [18,19]. A search in the Cambridge Structural Database (CSD version 5.40, November 2018)) showed 108 entrances relative to metal complexes including the Fluconazole against 14 entries concerning Fluconazole molecule directly linked to the metal, but only the structure reported here is the first organic-inorganic (linked by hydrogen bonds) salt base on bismuth-fluconazole. Herein, we describe the synthesis, molecular structure, vibrational (infrared), optical properties, and HOMO-LUMO transitions of a zero-dimensional bismuth-iodide-based compound: (C13H14N6F2O)2Bi2I10. DFT and TD-DFT calculations were carried out to investigate the electronic states, molecular orbitals and some parameters related to the global chemical reactivity of the presented material. The Hirshfeld surface analysis has been performed to clarify the intermolecular interactions predictable to contribute towards an understanding of the forces which ensure the crystal interconnection in this kind of hybrid material.

**2. Results**

The synthesis and characterization of a lead-free perovskite-type material, (C13H14N6F2O)2Bi2I10 is reported. It exhibits a zero-dimensional (0D) Bi2I104- octahedral unit, surrounded by a flexible tripodal antifungal ligand (H2Fluconazole)2+. The several intermolecular interactions of the independent cation and the bismuth iodide octahedra were tested via the Hirshfeld surface analysis. The detailed interpretation of the vibrational modes was

carried out. The band gap (Eg) of 2.10 eV agrees with the theoretical values. Upon photoexcitation, the crystals exhibit a broadband green emission peaked at 534 nm, which originates from electronic transitions within the inorganic cluster [Bi2I10]4-. The theoretical calculations were carried out using DFT and TD-DFT methods to appraise the molecular geometry, vibrational spectra, electronic absorption spectra, frontier molecular orbitals (FOMs) and global reactivity descriptors. Calculations reveal that the energy gap (Eg) and other chemical reactivity descriptors are primarily linked to the inorganic anion and the triazolium rings (A and B) of the organic cation reflecting their importance in the activity and the antioxidant ability of the molecule

 

Fig. 1: An ORTEP plot of the molecular entities of (H2Fluconazole)2Bi2I10, showing the

atom numbering scheme. Anisotropic displacement parameters are shown at the 50%

probability level. Symmetry code: i: 1-x, 1-y, 2-z.

Fig. 2: Room temperature photoluminescence spectrum upon excitation wavelength 400 nm of (H2Fluconazole)2Bi2I10 and the photoluminescence spectrum of fluconazole drug.

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