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Electronic and optical properties of zinc based hybrid organic-inorganic compounds

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Abstract

There is significant interest in hybrid organic-inorganic (HOI) compounds since these materials offer multiple functionalities and properties that can be tailored at the mesoscopic and nanoscale levels. HOIs investigated for photovoltaic applications typically contain lead or mercury. There is considerably less work done on Zn-based HOIs. These could potentially be considered in biomedical applications due to presence of organic components and the biocompatibility of Zn cations. Using a systematic materials selection approach, we have carried out a detailed search of Zn-HOIs compounds in two comprehensive experimental crystallographic repositories: Inorganic Crystal Structure Database and American Mineralogist Crystal Structure Database. Thirteen Zn-HOIs compounds are discovered: CuZnO\textsubscript{2}(CO\textsubscript{3})\textsubscript{1.85}, Zn(C\textsubscript{2}O\textsubscript{4})\textsubscript{1.9}, (CH\textsubscript{3})\textsubscript{2}NH\textsubscript{2}Zn\textsubscript{3}(PO\textsubscript{4})\textsubscript{1.6}, (CH\textsubscript{3}NH\textsubscript{2})\textsubscript{2}(HPO\textsubscript{4})\textsubscript{2}Zn\textsubscript{4}(PO\textsubscript{4})\textsubscript{3}, Zn(N(CH\textsubscript{2}PO\textsubscript{3}H)\textsubscript{3})(H\textsubscript{2}O)\textsubscript{1.6}, (CH\textsubscript{3}NH\textsubscript{2})Zn(HCO\textsubscript{3})\textsubscript{2}, Zn\textsubscript{4}(CO\textsubscript{3})\textsubscript{2}, Zn\textsubscript{6}(HPO\textsubscript{4})\textsubscript{1.6}(C\textsubscript{2}H\textsubscript{8}N)\textsubscript{2}, Zn\textsubscript{8}(CO\textsubscript{3})\textsubscript{2}, (Mg\textsubscript{2}Zn\textsubscript{4})(CO\textsubscript{3})\textsubscript{1.2}(OH), Zn\textsubscript{2}(CO\textsubscript{3})\textsubscript{2}(OH)\textsubscript{10}, Ca\textsubscript{1}Zn\textsubscript{3}(PO\textsubscript{4})\textsubscript{3}(OH)\textsubscript{2}H\textsubscript{2}O, and Zn(CO\textsubscript{3})\textsubscript{2}. We have then performed first principles calculations via density functional theory with hybrid functional treatment to determine the electronic band gap and optical response of these materials. Our computations show that eleven of the thirteen compounds have insulating properties with band gaps ranging from 2.8 eV to 6.9 eV. Ten of these are found to have a high absorbance in the far ultra-violet (FUV) region of 200–112 nm wavelength. For example, the absorption coefficient of (CH\textsubscript{3}NH\textsubscript{2})Zn(HCO\textsubscript{3})\textsubscript{2} is \(\sim0.75 \times 10^{5}\) cm\(^{-1}\) for F\textsubscript{2} excimer laser energy (wavelength \(\sim157\) nm) which is more than three orders higher than the average tissue absorbance (\(\sim10^{1.5}\) cm\(^{-1}\)) and the refractive index of 1.85 is larger than typical biological matter which is in the range 1.36–1.49. These results suggest that Zn-HOIs could potentially find applications in photothermolysis and UV protection.

1. Introduction

Hybrid organic-inorganic (HOI) materials offer the ability to tailor brand-new functionalities by adjusting composition on the atomic/molecular scale. A combination of organic–inorganic character provides an opportunity to design interesting properties from the ground up and thereby the realization of a new group of materials specifically conceived for many innovative applications in diverse fields ranging from optics, electronics, photovoltaics, energy storage, sensors and catalysis [1–5]. The wide chemical space of hybrid materials is often accompanied by rich structural forms and polymorphism. This increases adjustability of the material for desired physicochemical properties and has been rightly emphasized. The dynamic properties of HOI materials are related to the nature of the bonding between the organic and the inorganic components. HOIs are subclassified into two categories: class I and class II. Weak van der Waals or hydrogen bonding link the
organic and inorganic interfaces of class I hybrids. Class II HOI materials are associated with strong covalent or ionic-covalent chemical bonds [6] and provide stronger structural integrity and stability.

Majority of the work on the development of HOI materials for electronic technology research is focused on perovskite HOIs with the general chemical formula ABO$_3$. Common examples include, CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbBr$_3$, which are actively investigated for their photovoltaic properties [6]. HOIs have been stabilized with various organic functional groups, such as halides, formates, dianides, dicyanamides, amides and dicyanometallates [1, 7, 8]. Ferroelectric properties have been explored for [(CH$_3$)$_2$NH$_3$]$_2$[M(HCOO)$_2$]$_3$ with M = Mg, Fe, Co, Ni, Cu, or Zn, where polarizations in the range 0.6 μC cm$^{-2}$–6 μC cm$^{-2}$ have been observed [9–13]. The magnitude of polarization is not as high as prototypical ferroelectric oxides, e.g., 50 μC cm$^{-2}$ and 66 μC cm$^{-2}$ for Bi$_4$Ti$_3$O$_{12}$ and PbTiO$_3$, respectively [14, 15], yet might be promising for bio-imaging applications. More importantly, environmental and sustainability issues motivate the reduction of elements such as Pb from technologies and products. Many existing HOI materials have Pb and Hg as a constituent cation, which are toxic to the environment and pose a health risk to living organisms. There is a drive to remove hazardous materials from the economy chain through design of safe, yet smart materials substitutions. Furthermore, successful integration of organic blocks with a nontoxic cation would increase the applicability of HOI materials for a wider variety of uses in areas such as life sciences and medicine. Thus, the need to develop stable and non-toxic HOI perovskite materials is a priority.

A significant amount of research efforts in put into developing HOI compounds as bioactive materials in biochemical engineering [16, 17]. For example, Ca based bioactive glasses and glass-ceramics have been developed for healing fractures in living bone [18, 19]. Some studies on HOI compounds have been undertaken for their optical properties for potential applications, such as metacycloxypropyltrimetoxisilan (MEMO) and Zn(OPr)$_3$ being used as waveguides for integrated optics, short wavelength reflective gratings, and for optical communications [20–22]. First-principles theoretical tools have been applied to better understand the physiochemical interaction of anticancer and anthelmintic drugs gatifloxacin and mebendazole at the atomic level with a purpose of improving effectiveness of the drug [23]. *Ab initio* techniques and molecular dynamics have also been used to investigate the influence of cation doping on hydroxyapatite (HAP), a chemical base for drug carrier, where it is shown that Zn doping enhances the adsorption capacity of macromolecular drugs such as doxorubicin on HAP [24]. The success of HOI compounds in biomedical applications depends on proper choice, combination and spatial disposition of the external components in the supporting bioenvironment [25].

**Zinc** is a widely used biocompatible element. It is a component of many bio-enzymes and plays an important role in metabolizing nucleic acids, thus in assisting in cell replication, tissue repair and growth in living organisms [26, 27]. The simplest inorganic oxide of zinc, ZnO, is an intriguing material due to its large bandgap, high excitonic binding energy, high optical absorbance for ultraviolet (UV) light, and high chemical stability [28–30]. ZnO finds applications in light emitting diodes, optical sensors, piezoelectric devices for energy harvesting and in the biomedical field, for such uses as bioimaging, drug delivery and biosensors [31, 32]. Therefore, incorporating organic units and zinc oxides into a single system would considerably expand the use of these materials use towards bio-applications while the functionalities of inorganic components could still be preserved. This further emphasizes the need for further research on the development of Zn based HOI materials. We note that there are only a few Zn-HOIs compounds that have been synthesized so far. The discovery of new materials and their development have typically required a bit of intuition, chance, and extensive experimental work. This process takes a relatively long time, a lot of manual labor at an enormous cost. Programs such as the Materials Genome Initiative (MGI) aim to accelerate materials discovery and development using a combination of techniques including data analysis/curation, computational methodologies at multiple length scales, and judicious experimental work [33, 34]. In line with some of these ideas, we present here a novel targeted approach that identifies stable class II Zn-HOIs. Specifically, we mine and then analyze existing experimental databases, followed by high accuracy computations to describe structural, electronic, and optical properties using first principles approaches. Our results show that there are thirteen experimentally synthesized Zn-HOIs out of which several could potentially lend themselves to UV applications in biological systems. The descriptors used here are the electronic band gap, the optical absorption coefficient, and the refractive index. It is our hope that this study will motivate more theoretical and experimental work in the development of Zn-HOI materials for potential applications in biotechnology. More generally, we show here using this particular example that such an approach can be adopted to systematic searches of existing databases such as the Organic Materials Database [35–39], the Open Quantum Materials Database [40], the Materials Project [41], Computational 2D Materials Database [42], 2DMetPedia [43], the Novel Materials Discovery (NOMAD) [44], Computation-Ready Experimental Metal-Organic Framework (CoRE MOF) [45], Crystallography Open Database [46], Polymer Dataset (Khazana) [47], with a specific set of physical and chemical properties in mind.
2. Computational methodology

The physical properties of the compounds are obtained from electronic structure calculations based on first-principles density functional theory (DFT). The plane-wave pseudopotential approach implemented in the Vienna *ab initio* simulation package (VASP) \([48, 49]\) was used. DFT with local-density or generalized-gradient approximation for exchange-correlation treatment provides reasonably accurate description of electronic properties and total energies at zero Kelvin. However, the band gap is underestimated in these methods which have direct consequences for optical properties. To overcome the limitation, we have adopted the screened hybrid functional (SHF) method as proposed by Heyd-Scuseria-Ernzerhof \([50–52]\) with the exact exchange and generalized-gradient exchange mixed in the ratio 1:3 is employed to treat the inter-atomic potentials. Thus, the SHF method is a more valid method for optical properties of materials \([53]\). The ion-electron interaction was treated with the projector augmented wave (PAW) method \([54]\). Kinetic energy cut-off for the plane waves was set to 500 eV. For geometrical optimization the Perdew-Burke-Ernzerhof parametrized generalized gradient approximation (GGA) functional is used with the energy tolerance of \(10^{-6}\ \text{eV}\), which is sufficiently accurate for structural properties \([55]\). The geometrical optimization is performed with no constraints on the unit cell vectors and atomic coordinates. A high-density \(k\)-points grid was used to span the reciprocal space. The total energy tolerance was set to \(10^{-7}\ \text{eV}\).

The ground state calculations are followed by calculations of the frequency dependent dielectric function, the imaginary part of which is given by (see \([56]\))

\[
e^{\text{Im}}_{\alpha\beta}(\mathbf{q}, \omega) = \frac{4\pi^2\epsilon_0}{\Omega} \lim_{\epsilon \to 0} \frac{1}{q^2} \sum_{\epsilon, \mathbf{k}} 2W_k \delta(\epsilon_{\mathbf{k}} - \epsilon - \omega) \langle u_{\mathbf{k}+\mathbf{q}}|u_{\mathbf{k}}\rangle \langle u_{\mathbf{k}}|u_{\mathbf{k}+\mathbf{q}}\rangle,
\]

where \(\epsilon\) and \(\nu\) are the conduction band and valence band states, respectively, \(u_{\mathbf{k}}\) is the cell periodic part of the orbitals at the \(k\)-point \(\mathbf{k}\). The Bloch vector of the incident wave represented as \(\mathbf{q}\) and the normalized \(k\)-points weight given by \(W_k\). The real part of the dielectric function is obtained from the imaginary part by the Kramers-Kronig transformation as

\[
e^{\text{Re}}_{\alpha\beta} = 1 + \frac{2}{\pi} \int_{0}^{\infty} \frac{e^{\text{Im}}_{\alpha\beta}(\omega')\omega'}{\omega'^2 - \omega^2 + i\eta}\ d\omega'.
\]

3. Structure determination

Here, we use the Inorganic Crystal Structure Database (ICSD) \([57]\) and the American Mineralogist Crystal Structure Database (AMCSD) \([58]\) for data mining purposes. The combination of these two comprehensive databases gives us access to several hundred thousand of experimentally synthesized inorganic and organo-inorganic compounds. The library of compounds is filtered with additive search strings as zinc and carbon—carbon being the fundamental component of an organic-block. Other strings like hydrogen, oxygen, nitrogen, and phosphorus were also included in the search to match the scope of molecules common to organic matter. Through this process, we have identified thirteen distinct compounds that can reasonably be classified as Zn-HOI materials. The compounds are named as samples Z3–Z15 and are summarized in table 1, wherein we also list the ICSD/AMCSD repository identity tag, the functional group, and the crystal structure. The identity tags can be used to find the synthesis and experimental characterization references of compounds in the corresponding database.

The crystal structure information supplied in the databases provide experimentally determined positions of pure and mixed compound samples. Particularly for mixed components, some of the site positions are assigned multiple elements with the weight of occupancy proportional to the concentration. Since the plane-wave DFT calculations require structural information with atomic sites assigned explicitly with individual element types, a composition shift towards the Zn-rich side was felt necessary keeping in mind the motivation for Zn-HOI compounds. The residual inter-atomic forces were minimized through geometrical optimization before the properties were calculated. The geometrically optimized crystal structures are provided in the supplemental material is available online at stacks.iop.org/MRX/7/035701/mmedia.

It is observed that the organic building blocks of Zn-HOI are acceptor groups \([\text{CO}_3]^{2–}, [\text{C}_2\text{O}_4]^{2–}, [\text{HCO}_3]^{–}, [\text{PO}_4]^{3–}, [\text{HPO}_4]^{2–}, \) and \([\text{N(CH}_3\text{HPO}_3]^{–}\) or donor groups \([\text{CH}_3\text{NH}_2]^{+}\) and \([\text{CH}_3\text{NH}_2]^{–}\). Some of these organic blocks are known to have bio-functionalities. For example, \([\text{CO}_3]^{2–}\) is responsible for maintaining the pH balance of physiological reactions and \([\text{PO}_4]^{3–}\) ion is a functional moiety of hydroxyapatite which is a primary component of bones in vertebrates \([59]\). The phosphate group is also a major component of adenosine diphosphate and adenosine triphosphate that play an important role in the energy cycle in the living cells. These examples suggest a greater possibility of sustaining Zn-HOI materials for bio-applications.
**Table 1.** List of Zn-HOI compounds derived from ICSD and AMCSD repositories. The repository identity tag, organic functional group(s), crystal space group in Hermann–Mauguin (H–M) notation, corresponding and bandgap (eV) values obtained from SHF method are also shown. The bandgap and crystal structure space group of ZnO and ZnO2 are shown for reference purpose.

| Sample | Compound                  | Repository identity tag | Functional group | Space group | Bandgap |
|--------|---------------------------|-------------------------|------------------|-------------|---------|
| Z1     | ZnO                       | —                       | —                | P6\textsubscript{3}mc | 2.4     |
| Z2     | ZnO\textsubscript{2}      | —                       | —                | Pa\textsubscript{3} | 4.3     |
| Z3     | CuZnO\textsubscript{2}(CO\textsubscript{3}) | ICSD-109166, AMCSD-001132 | [CO\textsubscript{3}]\textsuperscript{2−} | C2/c | 5.0     |
| Z4     | Zn(C\textsubscript{2}O\textsubscript{4}) | ICSD-109665, AMCSD-0019967 | [CO\textsubscript{3}]\textsuperscript{2−} | C2/c | 5.0     |
| Z5     | (CH\textsubscript{3})\textsubscript{2}NH\textsubscript{2}Zn\textsubscript{3}(PO\textsubscript{4})(HPO\textsubscript{4})\textsubscript{2} | ICSD-110594 | [(CH\textsubscript{3})\textsubscript{2}NH\textsubscript{2}]\textsuperscript{2+}, [HPO\textsubscript{4}]\textsuperscript{2−} | P2\textsubscript{1}/c | 5.9     |
| Z6     | (CH\textsubscript{3})\textsubscript{2}NH\textsubscript{2}Zn\textsubscript{4}(PO\textsubscript{4})| ICSD-170961 | [CH\textsubscript{3}NH\textsubscript{2}]\textsuperscript{2+}, [PO\textsubscript{4}]\textsuperscript{3−} | P6\textsubscript{3}m | 5.6     |
| Z7     | Zn(N(CH\textsubscript{2}PO\textsubscript{3})\textsubscript{2})\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2} | ICSD-172319 | [Ni(CH\textsubscript{3}HPO\textsubscript{3})\textsubscript{3}]\textsuperscript{2+} | P1 | 2.8     |
| Z8     | (CH\textsubscript{3})\textsubscript{2}NH\textsubscript{2}Zn\textsubscript{2}(HCO\textsubscript{3})\textsubscript{2} | ICSD-186753 | [CH\textsubscript{3}NH\textsubscript{2}]\textsuperscript{2+}, [HCO\textsubscript{3}]\textsuperscript{−} | Cm | 6.2     |
| Z9     | Zn\textsubscript{2}(CO\textsubscript{3})\textsubscript{2} | AMCSD-0009883 | [CO\textsubscript{3}]\textsuperscript{2−} | C2/c | 0.0     |
| Z10    | Zn\textsubscript{2}(HPO\textsubscript{4})\textsubscript{2}(C\textsubscript{2}H\textsubscript{4}N\textsubscript{2}) | AMCSD-0012625 | [(CH\textsubscript{2})\textsubscript{2}NH\textsubscript{2}]\textsuperscript{2+}, [PO\textsubscript{4}]\textsuperscript{4−} | C\textsubscript{2} | 6.9     |
| Z11    | Zn\textsubscript{2}(CO\textsubscript{3})\textsubscript{2} | AMCSD-0009288 | [CO\textsubscript{3}]\textsuperscript{2−} | C\textsubscript{2} | 4.9     |
| Z12    | (Mg\textsubscript{2}Zn\textsubscript{3})(CO\textsubscript{3})\textsubscript{2}(OH\textsubscript{8}) | AMCSD-0009744 | [CO\textsubscript{3}]\textsuperscript{2−} | P1 | 3.4     |
| Z13    | Zn\textsubscript{2}(CO\textsubscript{3})\textsubscript{2}(OH\textsubscript{8})\textsubscript{2} | AMCSD-0001284 | [CO\textsubscript{3}]\textsuperscript{2−} | P 1 | 4.9     |
| Z14    | Ca\textsubscript{2}Zn\textsubscript{3}(PO\textsubscript{4})\textsubscript{3}(OH\textsubscript{2})\textsubscript{2}H\textsubscript{2}O | AMCSD-0007259 | [CO\textsubscript{3}]\textsuperscript{2−}, [PO\textsubscript{4}]\textsuperscript{4−} | C\textsubscript{2} | 6.3     |
| Z15    | Zn\textsubscript{2}(CO\textsubscript{3})\textsubscript{2} | AMCSD-0000102 | [CO\textsubscript{3}]\textsuperscript{2−} | R − 3\textsubscript{c} | 5.7     |

*Figure 1.* Crystal structure of Zn-HOI compounds Z1–Z15 is shown in (a)–(o). The chemical formula and bandgap of each of the compounds is provided in table 1. The ZnO4 tetrahedral motif and ZnO6 octahedral motifs are shown as blue and gray colored polygons, respectively.

The crystal structures of Zn-HOI materials in ball-stick representation are displayed in figures 1(c)–(o). The binary zinc oxides, ZnO and ZnO2 are shown figures 1(a) and (b) for comparison as they are well known systems and have characteristic tetrahedral (ZnO4) and octahedral (ZnO6) motifs in their crystal structure, respectively. The tetrahedron and octahedron motifs are shown as blue and gray polygons, respectively, in figure 1. The tetrahedron motif is common for inorganic zinc oxides, but octahedral motif is atypical and have been reported only in dispersed medium [60–65] and in other complex oxides [66, 67]. Among Zn compounds highly electronegative components, such as KZnF\textsubscript{3} [68] and zinc peroxide (ZnO\textsubscript{2}), stabilize octahedral motifs. Among the listed Zn-HOI compounds, ((CH\textsubscript{3})\textsubscript{2}NH\textsubscript{2})Zn\textsubscript{3}(PO\textsubscript{4})(HPO\textsubscript{4})\textsubscript{2} (Z5), (CH\textsubscript{3})\textsubscript{2}NH\textsubscript{2}Zn\textsubscript{4}(PO\textsubscript{4})\textsubscript{3} (Z6), Zn\textsubscript{9}(HPO\textsubscript{4})\textsubscript{16} (C\textsubscript{2}H\textsubscript{4}N\textsubscript{2})\textsubscript{8} (Z10), (Mg\textsubscript{2}Zn\textsubscript{3})(CO\textsubscript{3})\textsubscript{2}(OH\textsubscript{8}) (Z12), and Ca\textsubscript{2}Zn\textsubscript{3}(PO\textsubscript{4})\textsubscript{3}(OH\textsubscript{2})\textsubscript{2}H\textsubscript{2}O (Z14) have explicit ZnO4
tetrahedral motifs and CuZnO$_2$(CO$_3$)$_2$ (Z3), Zn(C$_2$O$_4$)$_2$ (Z4), Zn(N(CH$_2$PO$_3$H)$_3$)(H$_2$O)$_2$ (Z7), (CH$_3$NH)$_3$Zn(HCO$_3$)$_2$ (Z8), and Zn(CO$_3$)$_2$ (Z15) have explicit ZnO$_6$ octahedral motifs. The compounds Zn$_6$(CO$_3$)$_2$ (Z9), Zn$_6$(CO$_3$)$_2$ (Z11) and Zn$_6$(CO$_3$)$_3$(OH)$_{10}$ (Z13) have mixed motifs with the number of tetrahedral to octahedral motifs in the ratio 1:4, 2:3, and 3:4, respectively.

The structural analysis carried out herein is thus useful to establish a classification scheme based on the local coordination of primary cation which has been applied for determination of certain physical properties [69]. For example, the arrangement of O-tetrahedra in zeolite (SiO$_4$) is central to improving the efficiency of their catalytic properties [70, 71]. The three-dimensional network of octahedra and tetrahedra provide the pathways for ion diffusion in electrolytes for all-solid-state lithium-ion batteries [72, 73]. Prototypical ceramic ferroelectrics such as BaTiO$_3$, PbTiO$_3$, and their solid solutions have typical TiO$_6$ motifs in their crystal structure [74]. The wide variety of functional properties in such materials (such as piezoelectricity and pyroelectricity) is associated with displacements and rotations of these octahedra. In superconducting materials, the correlation between the local structural motif, electronic configuration, and the critical temperature for the superconductor transition have been reported [75]. Furthermore, in the topic of point defects in solids, the local coordination of impurity atom plays a vital role in influencing the electronic structure and thus the conductivity of the system [76]. Determination of the structure-property relations of Zn-HOI materials would have significant impact if supplemented by extensive experimental research.

4. Electronic structure and energy gap

The electronic structure of the compounds are calculated using the SHF method. To establish a baseline, we note that the experimental bandgap of ZnO is reproduced by taking the exact exchange and GGA in the ratio 1:2 [77]. In the present calculations the ratio of 1:3 is retained as suggested in the rational for the SHF method [51] that allows to make comparison of results consistent across all the compounds. The optimum ratio can be decided by matching experimental results, which for most of the compounds is sparsely available. The results are still applicable because varying the ratio would vary the bandgap values, but the band dispersion and the pattern of density of states (DOS) would remain similar. Results show that among the list of thirteen Zn-HOI compounds, CuZnO$_2$(CO$_3$)$_2$ (Z3) and Zn$_6$(HPO$_4$)$_{10}$C$_2$H$_8$N$_4$ (Z10) are metallic while rest are semiconducting with wide bandgap. The numerical value of bandgap of each compound is listed in table 1. Four compounds with distinct features are taken to compare the electronic DOS. The distinct features are: ZnCO$_3$ (Z13) and Zn(C$_2$O$_4$)$_3$ (Z4) vary by the type of functional groups, i.e. [CO$_3$]$^{3-}$ and [C$_3$O$_2$]$^{5-}$, respectively, and Zn$_6$(CO$_3$)$_2$ (Z11) and Zn$_6$(CO$_3$)$_2$(OH)$_{10}$ (Z13) vary by the number of tetrahedral and octahedral motifs in their crystal structures. The energy gap of Z15, Z4, Z11 and Z13 are found to be 5.7 eV, 5.0 eV, 4.9 eV and 4.9 eV, respectively. The DOS figures for Z15, Z4, Z11 and Z13 are shown in figures 2(a)–(d), respectively, where the total DOS is compared with the DOS of Zn atoms with octahedral coordination (Zn$_{oct}$) and tetrahedral coordination (Zn$_{tet}$), and O atoms of octahedral (O$_{oct}$) and tetrahedral (O$_{tet}$) motifs, and O atoms common to both tetrahedral and octahedral (O$_{tet-oct}$) motifs. The scale of DOS is adjusted in order to bring out the hybridization features more prominently. The zero in the energy axis refers to the Fermi level. It is found that the occupied Zn d-bands have DOS weight in the energy range −8 eV and −4 eV. A small fraction of occupied Zn states spread across the valence band, which contain contributions mostly from O atoms. In general, the weight of occupied Zn states of Zn$_{oct}$ is found to be lower in energy than Zn$_{tet}$ implying that ZnO$_4$ tetrahedral units are more strongly bounded. The peak at −9 eV is attributed primarily to the C−O bond from CO$_3$ and appears in the DOS of ZnCO$_3$ (Z13), Zn$_6$(CO$_3$)$_2$ (Z11) and Zn$_6$(CO$_3$)$_2$(OH)$_{10}$ (Z13). The lower energy of C−O bonding state for CO$_3$ suggests that carbon-oxygen hybridization is relatively stronger in CO$_3$ HOI compounds than that containing C$_2$O$_4$ functional group. The antibonding state of CO$_3$ appears at 7 eV above the Fermi level, while the antibonding state of C$_2$O$_4$ falls within the bandgap region.

5. Optical properties

The optical excitation in semiconductors are from the occupied valency band to the unoccupied conduction band. Light frequencies below the energy gap energy is not absorbed. The value of energy gap together with the density of states and orbital selection rules for band-to-band transitions determine the optical properties. This is reflected in the dielectric function, which is a complex quantity with a real component ($\varepsilon^\Re(\omega)$) representing dispersion of light in the medium and an imaginary component ($\varepsilon^\Imag(\omega)$) describing the dissipation of energy into the medium. The absorption coefficient $\alpha(\omega)$ and the refractive index $n(\omega)$ as functions of the frequency $\omega$ can be calculated from the following relations:
We focus here on the isotropic magnitude of $\varepsilon$ by averaging the components of $\varepsilon^{\text{Re}}(\omega)$ and $\varepsilon^{\text{Im}}(\omega)$, which are then used to calculate the adsorption and refractive index. As an example, we provide here results for compound Z6, (CH$_3$NH$_3$)$_4$Zn$_4$(PO$_4$)$_2$. The crystal structure of Z6 and the corresponding DOS are shown in figures 3(a) and (b), respectively. The absorption coefficient and the refractive index of Z6 as a function of energy is shown in figure 3(c). The optical absorption coefficient is large in the energy range of 7–20 eV which is the energy range of UV radiation.

A similar analysis for other Zn-HOI compounds are carried out. The optical absorption coefficients and refractive indices for all the compounds with non-zero bandgap are plotted as a function of energy in figures 4(a) and (b), respectively. The energy range is restricted to the UV spectrum of 3.2–12.4 eV with a view of potential applications related to UV lasers. The UV spectrum is generally sub-classified into three energy regions, the near
UV (NUV) with energy (wavelength) in the range 3.10–4.13 eV (400–300 nm), the mid-UV (MUV) for 4.13–6.20 eV (300–200 nm), and the far UV (FUV) for 6.20–12.40 eV (200–122 nm). These ranges are marked as brown, orange and yellow regions in figure 4. The corresponding wavelength in nanometers is provided at the top horizontal axis. The optical adsorption spectra of figure 4(a) shows that all Zn-HOI compounds described herein have a relatively high absorbance capacity for FUV. This property is promising for applications such as UV coating of sensitive devices. But, the presence of Zn provides a compelling reason for potential use in bio-applications. The prospects of engineering bioactive materials for targeted tumor photothermal therapy and the mechanism behind it has been reviewed in [78]. In this regard, it is worth to review the effect of laser action on biological matter which involves either one or a combination of important phenomena; photothermal (involves...
photovaporization and photocoagulation) effect, photochemical (photoradiation and photoablation) effect, and photoionizing effect.

The refractive index of Zn-HOI compounds are shown in figure 4(b) and compared with the range of refractive indices of mammalian tissues (1.36–1.49) [79, 80]. The vacuum refractive index is marked as a horizontal dashed line. Refractive index of Zn-HOI materials being larger than that of tissues would effectively confine the applied laser beam and reduce outward scattering. This is because light beam travelling from a rarer medium (lower refractive index, $n_1$) to a denser medium (higher refractive index, $n_2$) bends towards the normal at the interface. The angle of bending is proportional to the ratio of the refractive index ($n_2 / n_1$). This physical effect matters much in radiation therapy where securing the beam to a narrow confinement is of primary importance so that the scattered radiation does not excite the surrounding tissue. It is found that the absorption coefficient of Zn-HOI materials is three orders of magnitude larger than average tissue; a comparison is provided in figure 5. This implies that in an integrable environment most of the radiation energy would be absorbed by the Zn-HOI material. Depending on the requirements, this can be beneficial for protecting the underlying tissue from radiation damage or subjecting a targeted heat delivery to destroy the tissue as in selective photothermolysis therapy. The high UV absorption of these materials also make it attractive for UV detection and protection (such as skin care products, sunscreen lotions) applications. The applications projected in this study are based on the knowledge of properties and rationality, however it should be emphasized that practical experiments need to be performed to verify the performance (figure of merit, coefficient of performance, etc) and device strategies to overcome the challenges [81]. As in most computational materials research, our study is intended to provide the starting motivation for more rigorous experimental work in this direction [82, 83].

Figure 5. The absorption coefficient of Zn-HOI materials compared to the absorption spectra of proteins, hemoglobin, melanin, water and tissue. Zn-HOI materials is three times larger in magnitude than average tissues absorption of UV light. Part of the data adopted from [84]. Reproduced from [84]. © IOP Publishing Ltd. All rights reserved.
6. Conclusions

Zn-HOI compounds could be promising in biomedical technology due to the presence of biocompatible Zn ions and organic functional units. However, the scope of this class of compounds for bio-applications are yet to be discovered. We have thoroughly analyzed two existing experimental crystallographic repositories, ICSD and AMICSD, and successfully identified thirteen Zn-HOI compounds that have been experimentally synthesized. Electronic structure calculations using DFT with the screened hybrid functionals were then used to study the optical properties of these compounds. Our results show that many of these compounds possess wide electronic bandgaps and have a propensity for large absorption of light in the MUV and FUV range. The relatively high optical absorbance and the high refractive index of Zn HOIs are attractive properties for potential applications as protective coatings for UV radiation. The presence of non-toxic Zn and functional groups CH$_3$NH$_3$, CO$_3$$^2^-$, C$_6$O$_6$$^-$ and PO$_4$$^3^-$ which play prominent role in metabolic activities point towards applications in areas such as life sciences and medicine. We note that the list could be expanded with modern materials manipulation and processing techniques, such as chemical vapor deposition (CVD), pulsed laser deposition (PLD), atomic layer deposition (ALD), and molecular beam epitaxy (MBE), and adjusting the composition of HOIs to fine tune their properties. Discovery and development of functional materials for targeted applications present a major challenge which can be accelerated by combining theoretical, experimental and informatics research and forms the basis of rational design of materials.

Author contributions

TS conceived the original idea. SKN and TS performed the DFT calculations and lead the analysis efforts. TS, UAA, SPA and SKN contributed in preparing the manuscript.

Declaration of interest

None.

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