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achieve solution-processable hybrid semiconductors**

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## ARTICLE

## Making coordination networks ionic: a unique strategy to achieve solution-processable hybrid semiconductors

Xiuze Hei<sup>a, b</sup> and Jing Li<sup>\*, b, a</sup>

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The development of high-performance, solution-processable semiconducting materials is crucial for the advancement of emerging clean-energy technologies such as light-emitting diodes and photovoltaics. While hybrid perovskites have shown considerable promise for implementation in these technologies, their rely on toxic metals and relatively low stability towards moisture and chemical environment remain to be addressed. In this Chemistry Frontiers article, we describe a unique strategy to build nontoxic, robust and solution-processable hybrid semiconductors based on copper halide by incorporating ionic bonds in coordination complexes (molecular or extended network structures). Specifically, these compounds are made of anionic copper(I) halide and cationic organic ligands that form both coordinate and ionic bonds at the inorganic/organic interfaces and are referred to as all-in-one (AIO)-type structures. The unique bonding nature renders the AIO-type structures greatly enhanced solubility, excellent optical tunability and remarkable framework stability, all highly desirable for thin-film based optoelectronic devices. We will highlight the most recent progress in the development of the this material group, including their design strategies, important properties and potential for clean-energy related applications. We will also briefly discuss the existing challenges and future outlook of these materials.

### Introduction

Crystalline inorganic-organic hybrid structures represent an importance class of functional materials. Such materials consist of both inorganic and organic motifs and thus possess a wide range of intriguing properties, not only those intrinsic to each individual component but also new features extrinsic to both as a result of their synergetic interplay.<sup>1, 2</sup> Due to the extraordinary tunability of their structures and properties, crystalline inorganic-organic hybrid materials have been extensively investigated for various applications.<sup>3</sup> Among them, high-performance solution-processable semiconductors suitable for emerging clean-energy related technologies such as light-emitting diodes (LEDs), and photovoltaics (PVs) have been one of the most targeted material classes.<sup>4, 5</sup>

Despite of their superior optoelectronic properties, the utility of many conventional inorganic semiconductors in high-end thin-film based devices is often hampered due to their very poor solution processability. Designing new semiconducting materials that are solution-processable is critical for the device industries.<sup>6</sup> Hybrid perovskites, an important class of crystalline inorganic-organic hybrid structures, represent a good example. Having excellent solubility in polar aprotic solvents, cost-effective and high-quality thin films of these materials can be fabricated via various solution processing methods, including screen printing, spin/spray coating, and inkjet printing.<sup>6, 7</sup>

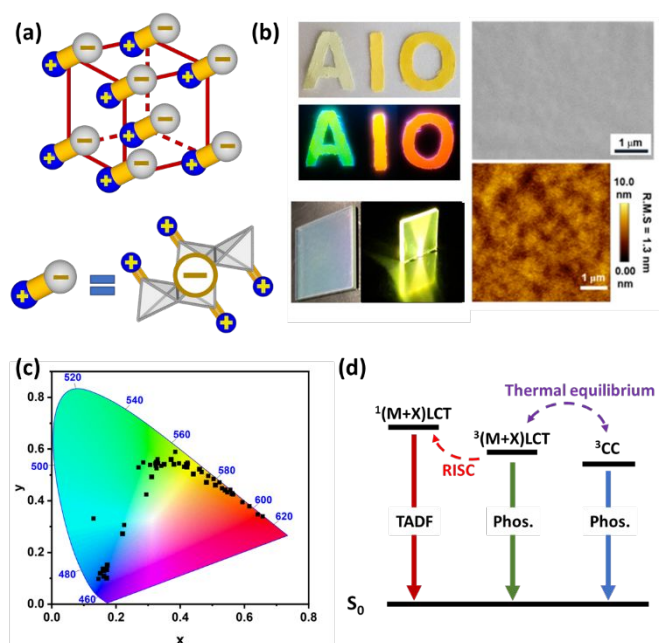
Optoelectronic devices (e.g. LEDs and PVs) based on hybrid perovskite thin-films have achieved competitive performance. Nevertheless, these materials suffer generally from their toxicity and instability.<sup>8, 9</sup> Though applaudable progresses have been made to improve their stability, the search for alternative semiconductors that are nontoxic, robust, and solution-processable represents an important research objective which may impact the field significantly.

Copper(I) halide (CuX, X = Cl, Br, I) based inorganic-organic hybrid semiconductors, especially those made of Cu-L (L = ligand) coordinate bonds, have attracted substantial interests in luminescence-related applications due to their numerous desired features including excellent structural/optical tunability, strong photoluminescence (PL), high resistance towards heat/moisture/chemical environment, and low cost, facile synthesis.<sup>10-12</sup> However, a main issue that limits their applications, especially in the optoelectronic devices, is their generally poor solubility. To address this issue, we have recently developed a new subclass of CuX based hybrid semiconductor materials, namely the all-in-one (AIO) type structures.<sup>13-15</sup> The AIO-type structures differ from the CuX(L) family in that their inorganic motifs are not neutral CuX, but anionic (Cu<sub>m</sub>I<sub>m+n</sub>)<sup>n-</sup> and likewise, their organic ligands are not neutral L, but cationic L<sup>k+</sup>. The inorganic anions and organic cations are further connected via Cu-L coordinate (dative) bonds to complete the bonding within the structure, as depicted in Fig. 1a. The unique multi-fold bonding at the inorganic/organic interface renders AIO-type structures integrated properties from both coordinate bonds (e.g., structural/optical tunability, strong luminescence) and ionic bonds (e.g., solubility and stability), greatly raising their potential for applications in optoelectronic devices.

<sup>a</sup> Hoffmann Institute of Advanced Materials, Shenzhen Polytechnic, 7098 Liuxian Blvd, Nanshan District, Shenzhen, 518055 People's Republic of China.

<sup>b</sup> Department of Chemistry and Chemical Biology, Rutgers University, 123 Bevier Road, Piscataway, New Jersey, 08854 USA.

\* Email: jingli@rutgers.edu



**Fig. 1** (a) Schematic illustration of AIO structures. Color scheme: blue: organic ligand; gray: inorganic motif; yellow rod: coordinate bond. Reproduced with permission from ref. 15 from the Royal Society of Chemistry. (b) Left: selected AIO-type compounds coated on soft fabric and glass substrate under daylight and UV light; Right: Top-view of the SEM (top) and AFM (bottom) image of the as-made thin film sample of a selected AIO compound. Reproduced with permission from ref. 13 and 18, from American Chemical Society. (c) Color chromaticity of all AIO-type compounds reported to date. (d) Schematic energy diagrams of different emission mechanisms of AIO compounds (Phos. = phosphorescence).

## Structures and physical properties

**Synthesis and structures.** To obtain a typical AIO structure, the ligand must be designed to contain (i) cationic center to ensure the ionic interactions with the anionic inorganic motif, and (ii) available coordination sites to allow the subsequent formation of Cu-L dative bonds. The ionic feature of the ligand is generally realized by the alkylation of a tertiary amine or phosphine to yield a quaternary N or P cation that does not interfere with the coordination active sites. The active binding sites are typically N, P atoms that have strong coordination affinity towards Cu atoms. Besides the typical AIO structures, there are also structural variants inspired by the AIO approach. Examples include compounds made of coordinated  $\text{Cu}_m\text{X}_n(\text{L}_k)$  anions and free charge-balancing cations;<sup>16</sup> as well as compounds containing  $[\text{Cu}_x\text{I}_y]^{2-}$  anions and  $\text{Cu}^+$  cations, separated in space by a Janus head ligand.<sup>17</sup>

Since the success in systematic construction of the first group of the AIO-type structures in 2017,<sup>14</sup> great efforts by us and others have been devoted to the design of new AIO structures and 60+ AIO compounds have been synthesized to this date.<sup>13, 14, 16-26</sup> Their structures range from molecular species (zero-dimension, 0D) to one-dimensional (1D) chains and two-dimensional (2D) layers. A variety of inorganic anionic modules from the smallest  $\text{CuI}_2^-$  monomer to infinite 2D network of  $\text{Cu}_8\text{I}_{10}^{2-}$  have been identified, revealing excellent structural diversity of this interesting material class. To gain

insight into the ligand effects in these structures, which is crucial to guide the structure modification and property optimization, comprehensive studies have been carried out on different aspects, including coordination affinity,<sup>13, 23</sup> steric effect,<sup>20, 22</sup> connectivity<sup>19</sup> and hybridization.<sup>21</sup> The structure formation of AIO-typed compounds may also be influenced by the synthesis conditions. By controlling the ratios of the reagents, different types of AIO structures may result even with the same ligand.

Various methods have been developed to grow high-quality single crystals of AIO-type compounds. Layered diffusion method is one of the most efficient approaches, wherein the reactants are dissolved in different solvents first and then transferred to a reaction vessel as two separated layers to allow slow diffusion to reduce the nucleation rate. In most cases, a middle buffer layer between the two reactant layers is used to further control the reaction rate. For the phases that require high temperatures, solvothermal method is generally used, in which the solvent system plays an important role in the determination of the resulting structures. Additionally, this synthetic method sometimes involves in situ generation of the cationic ligands when alcohols are used as solvents, which can act as alkylating reagents at high temperature.

**Solution processability.** Unlike most conventional coordinated networks of  $n\text{D-CuX(L)}$  ( $n = 1-3$ ) that are insoluble in all common solvents,<sup>27, 28</sup> the AIO-type compounds demonstrate good to excellent solubility in polar aprotic solvents in most cases. Specifically, depending on the structure and composition their solubility in DMSO varies between 40 to 420 mg/ml at room temperature. For example, 420 mg of  $1\text{D-Cu}_4\text{I}_6(\text{bttmp})_2$  made of  $[\text{Cu}_4\text{I}_6]^{2-}$  1D chain can be readily dissolved in 1 ml of DMSO at room temperature, comparable to hybrid perovskites and inorganic salts.<sup>18, 29, 30</sup> The extraordinary solubility of AIO compounds allows facile pin-hole-free thin-film fabrication by simple spin-coating methods (Fig. 1b), making their use possible in solution processed thin-film based optoelectronic devices.

The intriguing solvation behavior of the AIO compounds has been studied in detail and the results suggest it is a direct result of introducing ionic bonds between neutral inorganic motifs ( $\text{CuX}$ ) and organic ligands ( $\text{L}$ ).<sup>13, 20</sup> Because of the unique bonding characteristics, the solvation of AIO compounds involves the structure complexation in DMSO to generate soluble small fragments, similar to those of hybrid perovskites.<sup>15, 31, 32</sup> The dissolved species were identified as anionic  $\text{CuX}$  clusters which remain coordinated to the cationic ligands via dative bonds by NMR and mass spectrometry.<sup>20, 21</sup>

**Optical tunability.** Compared to the  $\text{CuX}$ -based hybrid compounds made of pure ionic bonds, which are also well solution processable, the major advantage of the AIO compounds lies in their remarkable optical tunability.<sup>10</sup> As shown in Fig. 1c, strong photoluminescence (with the highest internal quantum yield >90%)<sup>14, 16-18</sup> and emission maxima ranging from 430 nm to 630 nm has been achieved, covering the entire visible spectrum. In addition, our recent effort has successfully resulted in a number of AIO structures with low bandgaps of  $\sim 1.3-1.7$  eV. This further illustrates the potential of

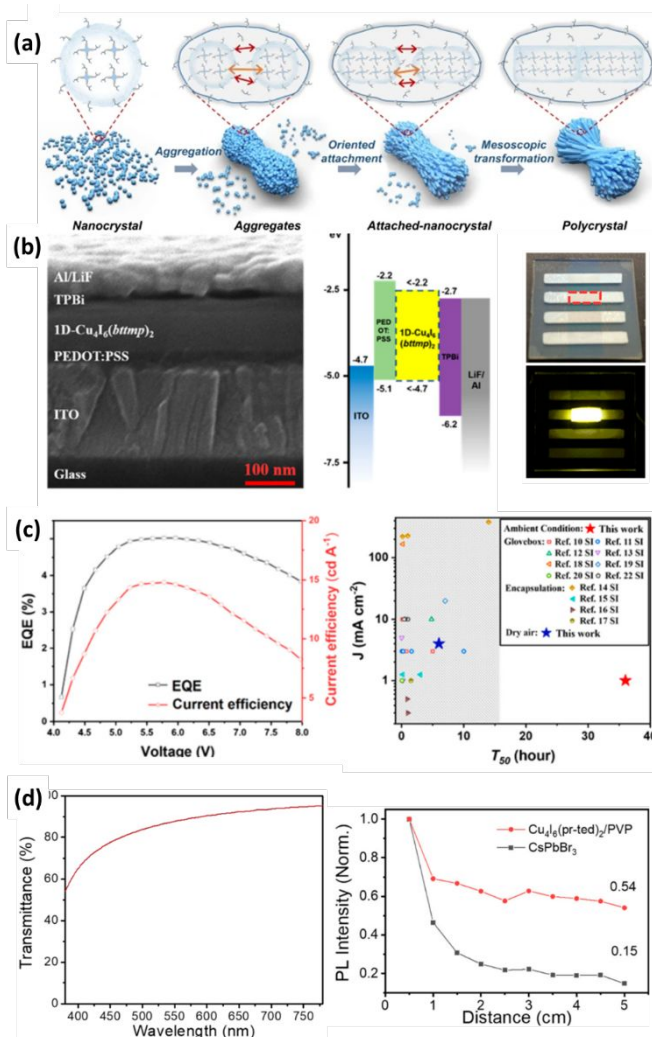
this intriguing material class for NIR emission related applications and their optical tunability.

In pure ionic CuX hybrid structures, as the organic cations are generally far away from the anionic inorganic motifs with only weak interactions, their photoluminescence is typically cluster-centered (CC) emission. As such, their optical properties are mainly determined by the inorganic modules with negligible ligand effect in most cases, making the fine tuning of electronic structures difficult.<sup>33</sup> In contrast, having Cu-L dative bonds, the emission mechanisms of AIO compounds may include metal halide-to-ligand charge transfer [(M+X)LCT], CC and combination of the two (Fig. 1d), with a strong dependence on the Cu...Cu distances (an indicator of cuprophilic interaction). These variables can be altered to suit different application needs.

Generally, ligands with aliphatic binding sites afford AIO structures with relatively short Cu...Cu distances (<2.80 Å, twice the vdW radius of Cu atom) and CC emission mechanism. On the other hand, AIO compounds composed of ligands with aromatic binding sites often have longer Cu...Cu distance and follow (M+X)LCT emission mechanism. Electronic structure analysis shows that for this subgroup of structures, the valence band maximum (VBM) is populated mainly by the inorganic motifs while the conduction band minimum (CBM) is primarily made of the lowest unoccupied molecular orbital (LUMO) of the ligands. Therefore, by selecting ligands with different functional groups (e.g., electron donating or electron withdrawing groups), their LUMO energies, and consequently the bandgap and emission energy of the resultant AIO structures, can be systematically tuned. Interestingly, when the Cu...Cu distances approach ~2.80 Å, the two emission pathways <sup>3</sup>CC and <sup>3</sup>(M+X)LCT may couple and both are responsible for the photoluminescence of the hybrid structures.<sup>19</sup> As the higher lying excited state requires higher energy, its relative intensity can be varied by adjusting the excitation energy, including temperature and excitation wavelength, which is often associated with responsive color change of the compounds toward heat and excitation energy.

Moreover, AIO materials often exhibit efficient thermally activated delayed fluorescence (TADF), which is highly favored in harvesting excitons generated in LED devices.<sup>34</sup> The extensive (M+X)LCT character of their excited states generally induce distinct spatial separations of the frontier orbitals, leading to relatively small exchange integrals and, consequently, small energy gaps  $\Delta E(S_1-T_1)$  between the lowest singlet state  $S_1$  and the lowest triplet state  $T_1$ .<sup>35</sup> As a result, a fraction of the electrons can be thermally populated back to  $S_1$  from  $T_1$  via reverse intersystem crossing (RISC) and then follow  $S_1$  to  $S_0$  radiative transition, benefitting the harvesting of generated singlet and triplet excitons.

**Stability.** To be suitable for real-world applications, semiconductor materials must process high resistivity towards moisture, light, and heat. Compared to CuX hybrid structures composed of pure coordinate or ionic bonds at the inorganic/organic interfaces, the framework stability of AIO compounds is significantly enhanced as a result of the



**Fig. 2** (a) Schematic illustration of the non-classical crystallization process of chiral AIO nanocrystals. Reproduced with permission from ref. 25 from Springer Nature. (b) Left to right: Cross-sectional HeIM image of the prototype YLED device structure using 1D-Cu<sub>4</sub>I<sub>6</sub>(bttmp)<sub>2</sub> as the sole EML, overall energy band diagram and photographs of the fabricated device at "off" and "on" stages. (c) Left: EQE and current efficiency of the best-performing LED; right: T<sub>50</sub> values of the yellow LED device and those of PeLEDs. (b) and (c) are reproduced with permission from ref. 18 from American Chemical Society. (d) Light transmittance (left) and light propagation property of the fabricated AIO based LSC film. Reproduced with permission from ref. 26 from American Chemical Society.

synergistic effect of both bond types. With only a few exceptions, most AIO structures are stable over 200 °C, with some exceeding 300 °C. Moreover, many AIO compounds demonstrate stable PL performance against thermal and photo stress. For example, the IQY values of 0D-Cu<sub>4</sub>I<sub>6</sub>(pr-td)<sub>2</sub> and 0D-Cu<sub>4</sub>I<sub>6</sub>(tpp)<sub>2</sub>(btmm)<sub>2</sub> remain over 90% of their initial values after being exposed to hot air at 100 °C or to continuous UV irradiation (365 nm) for 20 days without protection.<sup>14</sup> In another example, the crystallinity of 1D-Cu<sub>4</sub>I<sub>6</sub>(bttmp)<sub>2</sub> remained nearly the same after being submerged in water for 2000 h.<sup>18</sup> Different approaches have been applied to further improve the stability of these compounds and proven to be successful. These approaches include: 1) Using ligands with higher connectivity to form multidentate structures; 2) Selecting ligands with electron

rich N, P or S sites, which can form particularly strong coordination bonds with Cu atoms; and 3) Building extended networks to increase structural rigidity.

## Applications

As discussed above, the strategy of incorporating both coordinate and ionic bonds in AIO structures serves as a general and powerful tool not only for the synthesis of very robust materials but also for the assembly of extended networks with greatly enhanced solubility. This enables thin-film fabrication of the AIO semiconductors by simple solution based processes, which are not possible to achieve for other types of CuX-based hybrids.

The AIO materials were first tested as phosphors in the phosphor-converted white LEDs (pc-WLEDs). Such WLEDs generate warm-white light by coating a blue LED chip with blue-excitable yellow phosphor or multiple (green-red) phosphors.<sup>36</sup> As phosphors currently dominating the pc-WLED market are made of rare-earth elements (REEs), which not only are subject to the potential supply and cost risks, but also cause severe environmental impact,<sup>37</sup> seeking eco-friendly and REE-free alternative phosphor materials would bring substantial benefits to the society. The AIO materials stand out as promising candidates due to the advantages mentioned in the previous section, coupled with their easily scalable synthesis, earth-abundance, and excellent blue-excitable.<sup>13, 14, 23</sup> Prototype LED bulbs using selected AIO compounds as phosphors have been assembled.<sup>14</sup> The findings imply that the molecular motions of compounds can be suppressed by the use of multidentate ligands, which effectively reduce nonradiative decay and lead to enhancements in IQYs.

Using chiral cationic ligands, a series of hierarchically structured noncentrosymmetrical AIO materials have been successfully synthesized via non-classical crystallization process involving nanocrystal nucleation, aggregation, oriented attachment and mesoscopic transformation (Fig. 2a). They show interesting circularly polarized luminescence (CPL).<sup>25</sup> The chiral AIO polycrystals assemble at nano- and micro-scales and yield significantly improved luminescence dissymmetry factor ( $g_{lum}$ ) of  $1.5 \times 10^{-2}$  without significant loss of its photoluminescence quantum yield (PLQY). Interestingly, the chiroptical properties of these AIO aggregates strongly hinge on the position of chiral centre in the ligand, which can substantially influence the interactions among chiral groups within the hierarchically structured polycrystals. These findings point to the possibility of using these compounds as efficient CPL active materials.

Recently, we successfully demonstrated the use of AIO materials as active emissive layer (EML).<sup>18</sup> A first-ever yellow LED (YLED) device using an AIO-type hybrid semiconductor 1D-Cu<sub>4</sub>I<sub>6</sub>(bttmp)<sub>2</sub> as the sole EML was fabricated (Fig. 2b). The spin-coated thin-film samples remain stable under harsh conditions (e.g., elevated temperature and high humidity) for over 2000 h without protection. The prototype YLED device achieves an external quantum efficiency (EQE) of 5.02%. Remarkably, the device demonstrates outstanding stability with its half-lifetime

( $T_{50}$ ) reaching 35.5 h under ambient conditions (Fig. 2c), while those of most hybrid perovskite-based LED devices are much shorter even tested under one form of protection (in glovebox, under dry air or being encapsulated).<sup>38, 39</sup> This work certainly demonstrates the potential of AIO compounds for the construction of robust and nontoxic LED devices.

The possible use of AIO materials as luminescent solar concentrators (LSCs) was also investigated (Fig. 2d).<sup>26</sup> LSCs are transparent waveguide substrates that help to provide higher optical concentration to the attached solar cells and thus increase their power output. The higher energy portion of the sunlight (at which the solar cell has low absorption) first gets absorbed by the luminescent material in LSC and converted to the lower energy lights, and the reemitted lights then get directed to the solar cell.<sup>40</sup> A strongly luminescent film (9 cm × 4.5 cm) of 0D-AIO-Cu<sub>4</sub>I<sub>6</sub>(pr-td)<sub>2</sub>/PVP (polyvinylpyrrolidone) was fabricated by facile blade coating to evaluate the performance of this AIO material as LSC. The optimized film shows over 85% average transmittance in the visible light range and a high PLQY of 76.1%. In addition, it demonstrates much better waveguide property than CsPbBr<sub>3</sub>. The good performance, coupled with their high stability validate AIO materials as good candidates for LSCs.

## Conclusions and outlook

As an emerging subclass of copper halide-based crystalline hybrid semiconductors, the AIO-type structures represent a new addition to the solution-processable material family that are critical for the future advancement of optoelectronic devices. They possess excellent air, moisture and thermal stability as a result of forming both strong coordinate and ionic bonds at the inorganic/organic interfaces. Their intriguing modular nature enables systematic control of the binding mode, metal-ligand connectivity, ligand orbital energies and consequently, the electronic structures and bandgaps, which, in turn, leads to fine-tuning of their chemical and physical properties to suit different application needs. Most remarkably, making the extended coordination networks ionic significantly enhances the solubility of the AIO-type compounds, taking them from totally insoluble to well soluble in polar aprotic solvents such as DMF and DMSO. Therefore, various cost-effective solution processing technologies can be used to fabricate high quality thin films of AIO-type semiconductors. These important and advantageous features offer a considerable promise for their future use in the clean energy related technologies. However, addressing the existing challenges and issues through further research and development is crucial to fully realize the potential of these materials.

First of all, improving the performance and stability of the solution-processable blue-emitting LEDs (BLEDs), particularly deep blue-emitting LEDs, is of great interest to the lighting industries.<sup>41, 42</sup> The successful assembly of an ultrastable YLED device using AIO compound as sole EML may offer an alternative solution.<sup>18</sup> To do so, robust and efficient AIO emitters ( $\lambda_{em}$  at ~ 450 nm) with high photoluminescence and



good charge transport properties need to be developed. In addition, the research on AIO compounds as sole EML in LED devices is still in its infancy. Continuous and thorough investigations to further optimize and increase their EQE are vital to their ultimate implementation in general lighting technologies.

Secondly, the application of AIO semiconductors in the PV solar cells, one of the most important branches of optoelectronic devices, accounts for an important aspect of future research of these materials. Most recent work by us and others has yielded promising solution-processable low bandgap AIO compounds as efficient solar light absorbers. Although the photogenerated excitons may be somewhat localized due to the (M+X)LCT feature and can lead to low carrier mobility, a possible solution is to use ligands with strong  $\pi$ - $\pi$  stackings to facilitate charge transfer.<sup>43</sup> This is a very interesting new direction for the design of nontoxic and robust semiconductors targeted for PV solar cells.

Third, UV emissive AIO-type compounds represent an equally interesting subgroup but yet to be synthesized. These materials will be extensively explored in our future studies.

Furthermore, building AIO compounds composed of high-dimensional inorganic modules is much desirable. Most of the AIO compounds reported to date contain inorganic modules limited to 0D clusters to 1D chains, with only a few exceptions of 2D layers. AIO structure with 3D inorganic backbone remains to be discovered. Increasing the dimensionality of inorganic motifs would, presumably, largely enhance/improve some very important properties directly relevant to device performance (e.g., conductivity, carrier mobility, diffusion length).

Finally, as a general tool for the design of solution processable and stable hybrid semiconductors, the strategy of including ionic bonds within coordinate networks can be extended to other hybrid materials<sup>44</sup> beyond copper halide-based hybrid family. By applying the AIO approach to other hybrid systems, exciting new opportunities for discovering advanced functional semiconductors could be unlocked.

## Conflicts of interest

There are no conflicts to declare.

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