

# Volatile Hybrid Organic/Inorganic Copper (I) Iodides/Polyiodides for Efficient Thin-Film Deposition of CuI

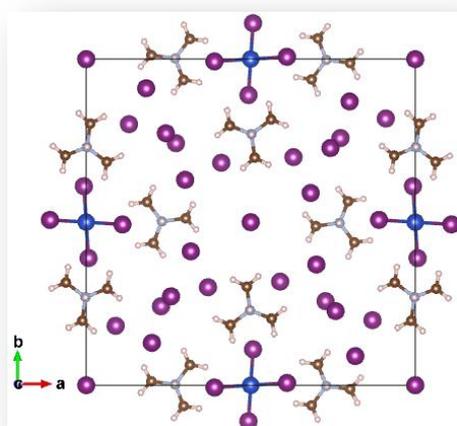
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P-type inorganic semiconductors are remarkably scarce when compared to their n-type counterparts, with notable examples found in the late 3d transition metal monoxides (i.e. Ni<sub>1-x</sub>O) or the group 14 metal monochalcogenides (e.g. Sn<sub>1-x</sub>Se). Among them, Cu(I) compounds, particularly the halides and the pseudohalides, stand out having been repeatedly employed as viable replacements to the best-performing organic p-type semiconductors, (*I*) based on triarylamine (e.g. PTAA) or thiophene (e.g. PEDOT:PSS) molecules commonly employed in photovoltaics.<sup>(2)</sup> One of the most notable difficulties encountered in the use Cu(I) based compounds, however is their notorious insolubility in common solvents, thus making its solution processability limited.

In this work, we propose of a viable method of preparing high concentration precursor solutions in non-polar solvents than can subsequently be used for efficient deposition of CuI via standard spincoating techniques. Towards this end we have synthesized a series of hybrid organic/inorganic copper (I) iodides and polyiodides with diammonium cations (A = H<sub>3</sub>N-(CH<sub>2</sub>)<sub>x</sub>-NH<sub>3</sub>)<sup>2+</sup>) with general formulae A<sub>x</sub>Cu<sup>I</sup>(I)<sub>y</sub>(I<sub>n</sub>)<sub>z</sub> (Figure 1) with the aim of dissociating the insoluble sphalerite-type CuI lattice into smaller fragments that can be easily solution processed. Moreover, the presence of the organic ammonium cation, as well that of the polyiodides further assists in the increase of solubility due to the enhancement of non-polar interaction between the solvents and the solids. The excess of these components in the films can be easily removed during the post-deposition heating stage of the spincoating process, due to the volatile nature of the said components. Relevant to the perovskite solar cells, CuI shares the same halogen atom, which in turn is designed to facilitate the formation of a smooth interface between the active perovskite-layer and the p-type hole transporting layer.

Several hybrid organic/inorganic compounds have been synthesized and extensively characterized,



both morphologically and spectroscopically, including the determination of the crystal structure via single-crystal X-ray diffraction. The thermal decomposition of the materials as well as their solubility tests in common organic solvents have also been performed. Ongoing work addresses the suitability of the materials as precursors in the CuI solution deposition process and evaluates their applicability in perovskite solar cells.

Figure 1. The crystal structure of the multicomponent hybrid organic/inorganic polyiodide iodocuprate based on the 1,4-diazabicyclo[2.2.2]octane dication.

## References

1. N. Arora *et al.*, Perovskite solar cells with CuSCN hole extraction layers yield stabilized efficiencies greater than 20%. *Science* **358**, 768-771 (2017).
2. L. Calió, S. Kazim, M. Grätzel, S. Ahmad, Hole-Transport Materials for Perovskite Solar Cells. *Angew. Chem., Int. Ed.* **55**, 14522-14545 (2016).