Even in some of the most heavily studied materials, a careful structural analysis can solve stubborn mysteries. The first part of my talk focuses on cesium lead iodide (CsPbI$_3$), an inorganic halide perovskite of interest for solar energy conversion that is unstable at room temperature. I use X-ray diffraction measurements to reveal that the Cs atom rattles within its coordination polyhedron, causing the material’s thermodynamic instability. Next, I demonstrate the remarkable emergence of chirality in the self-assembled molecular material C$_{60}$(SnI$_4$)$_2$, despite the very high icosahedral and tetrahedral symmetry of its constituent molecules. These results demonstrate that almost any molecular, nanocrystalline, or engineered precursor can be considered when designing chiral assemblies, allowing new classes of optical devices, asymmetric catalysts, and biological sensors to be imagined.