$[AgSePh]_\infty$: A Self-Assembled Bulk 2D Semiconductor

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The electronic properties of semiconductor monolayers such as transition metal dichalcogenides (TMDs) have attracted interest for a variety of device applications. However, exploiting monolayers technologically is complicated by the strict requirement for physical isolation.

Here, we report the synthesis, characterization, and electronic structure of a semiconductor that retains 2D electronic properties in the bulk. Silver benzeneselenolate, [AgSePh]∞, is an air-stable metal-organic crystal comprised of ultrathin silver selenide layers, decoupled by covalently linked organic spacers.

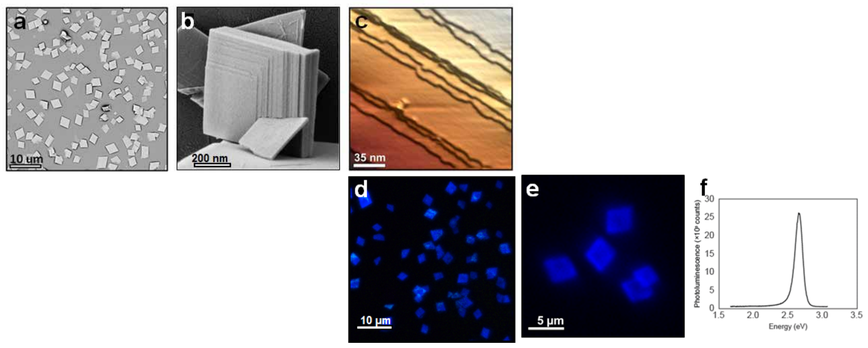
This material:

... self-assembles in one step from small-organic building blocks at ambient temperature and pressure,

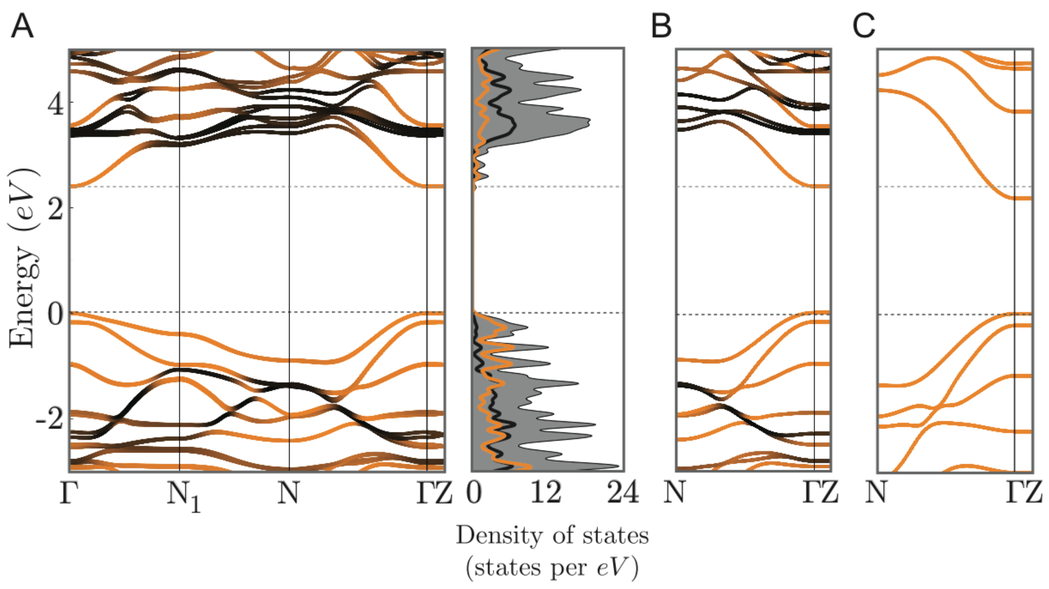
...is a direct band gap semiconductor with intense blue fluorescence at 467 nm,

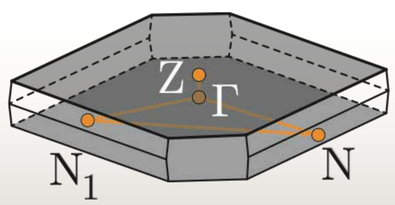
... and requires no physical exfoliation to exhibit its 2D properties.

Ab initio calculations confirm that the layers in the bulk crystal are direct band gap semiconductors and electrically isolated. Furthermore, ab initio calculations show that ligand design may present opportunities for manipulating the optoelectronic properties of a new class of hybrid vdW solids, the metal-organic chalcogenide assemblies.

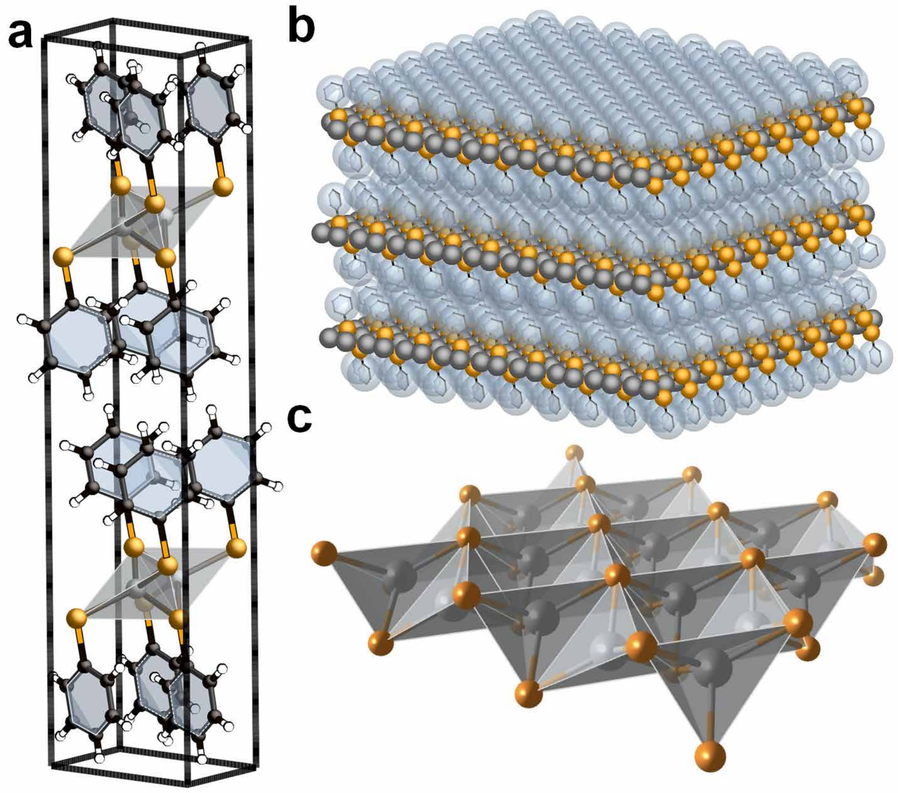


Images and emission spectrum of silver benzeneselenolate a) Silver benzeneselenolate crystals recovered from the immiscible liquid-liquid interface of organic and aqueous solutions of diphenyl diselenide and silver nitrate, respectively. Crystals of [AgSePh]∞ have edge lengths between 1 and 4 microns. b) Scanning electron micrograph of a silver benzeneselenolate silver crystal reveals the layered structure of the crystal. Each layer is comprised of a 2D inorganic silver selenolate polymer, uniformly functionalized at every selenium site with a benzene ring. c) Atomic force microscopy reveals highly uniform [AgSePh]∞ (001) terraces with measured step heights at 1.4 nm. d,e) Confocal micrographs showing the color uniformity of photoluminescence in [AgSePh]∞. f) A single, intense emission of the solid at 467 nm is attributed to a direct-gap electronic transition.

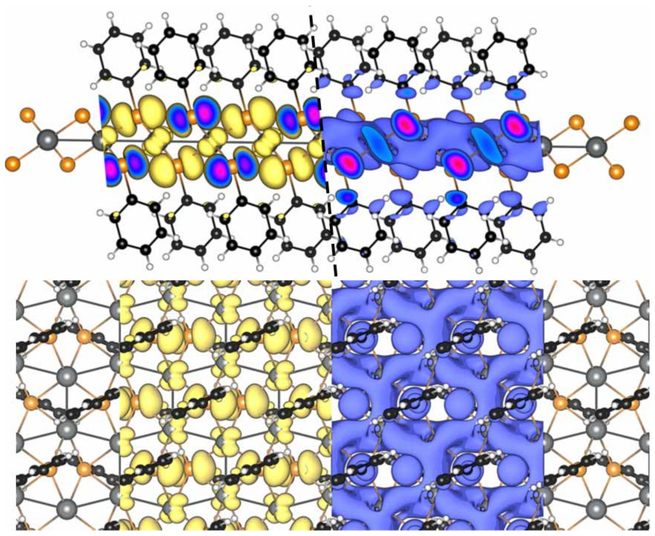




Band structures and density of states of bulk [AgSePh]∞, a single layer of [AgSePh]∞ and a single layer of [AgSePh]∞ with phenyl groups replaced with hydrogens a) DFT-HSE band structure and density of states of bulk [AgSePh]∞. Band color signifies the fractional contribution of states centered on inorganic (Ag and Se, orange) and organic (C and H, black) atoms in the crystal. The total density of states is shown in gray. b) DFT-HSE band structure of a single layer of [AgSePh]∞ c) DFT-HSE band structure of a single layer of [AgSePh]∞ with the phenyls replaced by hydrogen. The hydrogen positions have been relaxed with PBE; see Extended Data Figure 4. The near-band edge character remains relatively unchanged when the phenyls are replaced by hydrogen, suggesting that the degree of 2D quantum confinement is unchanged by 3D crystallization. d) The Brillouin zone for the primitive cell of [AgSePh]∞. The path in the Brillouin zone used for the band structure is identified by orange lines and k-point labels.



Single crystal structure of silver benzeneselenolate a) The monoclinic unit cell of solid silver benzeneselenolate contains two complete layers of hybrid metal-organic 2D polymer. Silver is coordinated tetrahedrally by four selenium atoms. b) The multilayered structure electrically isolates inorganic layers via the benzene moieties oriented above and below the silver monolayer. c) Each silver atom has four coordinating selenium atoms in a distorted tetrahedral configuration with three argentophillic Ag-Ag interactions. Silver is represented as the grey spheres, selenium in dark orange, and carbon in black. Aromatic rings are accented in blue.



Charge density associated with bulk [AgSePh]∞ conduction band minimum and valence band maximum states Depictions of side and top views of [AgSePh]∞ with overlain charge density maps. The DFT-HSE computed valence band maximum (VBM) and conduction band minimum (CBM) at Γ are accented in yellow and blue, respectively. The minimal but non-negligible participation of carbon in the CBM state suggests tailoring of electronic properties via synthetic modification of ligand.

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