Supporting Information for
Composition and size controlled I-V-VI semiconductor nanocrystals

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**Figure S1.** Energy dispersive X-ray (EDX) quantifications of Ag-Sb-Se nanocrystal samples, presented as a function of amounts of initial metal halide salts. Dashed vertical line demarcates the two-phase region \((\text{Ag}_2\text{Se} + \text{AgSbSe}_2)\) and the \(\text{Ag}_{1-x}\text{Sb}_{1+x}\text{Se}\) solid solution.

**Figure S2.** An average size of \(\text{Ag}_{1-x}\text{Sb}_{1+x}\text{Se}\) nanocrystals, prepared at 90°C during 30 min (variable AgI:SbCl₃ molar ratio).

**Figure S3.** Transmission electron microscopy image and size distribution histogram of AgSbSe₂ nanocrystals, prepared at 90°C during 30 min.
Figure S4. A lattice constant of rock salt structure of Ag$_{1-x}$Sb$_{1+x}$Se nanocrystals, as calculated from the peak position of (002) Bragg reflection on X-ray diffractograms.

Figure S5. Transmission electron microscopy images of Sb$_2$Se$_3$ nanocrystals, prepared at T$_{\text{growth}}$ = 90°C and t$_{\text{growth}}$ = 30 min.

Figure S6. (a) Exemplar transmission electron microscopy images of AgSb$_2$Se$_3$ nanocrystals. (b) X-ray diffractograms of AgSb$_2$Se$_3$ nanocrystals, prepared at different temperatures, but otherwise same reaction conditions. (c) A size map for AgSb$_2$Se$_3$ nanocrystals in coordinated of injection temperature and reaction time.
**Figure S7.** Average sizes of Ag$_{1-x}$Sb$_{1+x}$Se nanocrystals, extracted from transmission electron microscopy images and X-ray diffractograms (Scherrer formula), and schematics of extracted sizes.

![Graph showing the relationship between size from TEM and XRD for Ag$_{1-x}$Sb$_{1+x}$Se nanocrystals.](image1.jpg)

**Figure S8.** Absorption spectra of Cu$_3$SbSe$_4$ nanocrystals, synthesized at 80°C and different reaction times. Plasmonic feature, peaking at 1400 nm, indicates the presence of Cu$_{2-x}$Se binary byproduct.

![Absorption spectra graph for Cu$_3$SbSe$_4$ nanocrystals.](image2.jpg)

**Figure S9.** Arrhenius plot, illustrating reactivity of metal halides in the synthesis of I-VI colloidal nanocrystals, qualitatively.

![Arrhenius plot graph showing the reactivity of metal halides.](image3.jpg)
Figure S10. Crystal structures of bulk AgBiSe$_2$, CuBiSe$_2$, Cu$_3$SbSe$_4$, and CuSbSe$_2$ semiconductor materials, indicating the atomic arrangements as arrays of Se polyhedra. AgBiSe$_2$ belongs to rhombohedral crystal system and can be seen as distorted rock-salt structure (see Figure 1a, inset), having a space-filling arrangement of Se octahedra. Cu$_3$SbSe$_4$ structure belongs to a family of tetrahedral semiconductors, in which all atoms have a coordination number of 4 (the other examples being e.g., zinc blende, chalcopyrite, III-V semiconductors, etc.). The structures of CuBiSe$_2$ and CuSbSe$_2$ are similar, exhibiting low-symmetry orthorhombic lattices, formed from distorted tetrahedra and tetragonal prisms. This non-conventional coordination environment for Se atoms can be explained by the fact that Sb and Bi typically have coordination numbers of 5, whereas Cu atoms remain tetrahedrally coordinated.
Figure S11. Absorption spectra and Tauc plots for AgSbSe$_2$ nanocrystals with different average sizes.
Figure S12. Absorption spectra and Tauc plots for AgSb₂Se₃ nanocrystals with different average sizes.
Figure S13. Absorption spectra and Tauc plots for CuSbSe$_2$ nanocrystals with different average sizes.

Figure S14. Absorption spectra and Tauc plots for AgBiSe$_2$ and for CuBiSe$_2$ nanocrystals.
Figure S15. Absorption spectrum and Tauc plots for thin film of Cu$_3$SbSe$_4$ nanocrystals, cross-linked with 1,2-ethanedithiol.