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Supporting Information for

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Figure S1. TEM images of Ag₂Se nanocrystals synthesized by a direct reaction between AgTFA and TOPSe in (A) and with addition of tin (II) bis[bis(trimethylsilyl)amide] (B).



Figure S2. Absorbance and PL spectrum for Ag₂Se nanocrystals, synthesized with addition of tin (II) bis[bis(trimethylsilyl)amide]



Figure S3. Absorbance (A), and EDX spectrum (B) of Ag nanocrystals. The vertical lines in B give the theoretical positions of the chalcogene lines which are clearly not present in our colloidal solution. Inset (A): photo of the Ag NC solution.



Figure S4. Absorption spectra of differently sized Ag_2Se nanocrystals. Inset: linear dependence of the absorbance peak position in respect to the Ag/Se molar ratio, evidencing a size control by the Ag/Se molar ratio.



Figure S5. PL spectra of samples with different growth times (synthesis at 70 °C), evidencing a size focusing with time.



Figure S6. PL spectra of Ag₂Se (black lines) and Ag₂Se/ZnSe core/shell nanocrystals (gray lines), measured after synthesis (A) and after 6 months of storing (B).



Figure S7. Selected area electron diffraction (SAED) of Ag₂Se nanocrystals, suggesting the presence of the low-temperature α -Ag₂Se crystal structure (solid arcs), and an absence of high-temperature α -Ag₂Se (dashed arcs).^{1,2}



Figure S8. Theoretical atom arrangement in β -type (low temperature modification) Ag₂Se (as simulated for Figure 2C).



Figure S9. EDX spectra of (A) Ag₂Se nanocrystals, and (B) Ag₂Se/ZnSe core shell nanocrystals with quantifications of elemental contents.



Figure S10. Wide angle X-ray scattering (WAXS) spectrum of the 2.0 nm Ag₂Se nanocrystals compared to theoretical spectrum for bulk Ag_2Se (low-temperature phase).¹



Figure S11. SAXS spectra of the 2.0 nm Ag₂Se nanocrystals (black dots), and 2.2 nm Ag₂Se/ZnSe core/shell nanocrystals (gray dots), together with fits (red lines).



Figure S12. Absorption spectum of PCBM solution in chlorobenzene (A), and photoresponse of PCBM film deposited on interdigitate gold electrodes (B).



Figure S13. EDX spectra of (A) Ag₂S nanocrystals, and (B) Ag₂Te nanocrystals with quantifications of elemental contents (silicon was used as substrate).



Figure S14. TEM images of (A) Ag₂S nanocrystals, and (B) Ag₂Te nanocrystals synthesized with addition of lithium bis(trimethylsilyl)amide.



Figure S15. Size histograms for Ag₂S (A-B), and Ag₂Te nanocrystals (C) taken from TEM images, and fitted by Gauss distributions.

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- Billetter, H.; Ruschewitz, U. Structural Phase Transitions in Ag₂Se (Naumannite). Z. Anorg. Allg. Chem. 2008, 634, 241-246.
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