

Electronic Supplementary Information (ESI) for

**Cu-In-Te and Ag-In-Te colloidal nanocrystals with tunable composition  
and size**

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## Experimental section

### General remarks

Copper (I) chloride (anhydrous, ≥99.99%), indium (III) chloride (anhydrous, 99.999%), selenium (99.99%) tellurium (broken ingots, 99.999%), and tri-*n*-octylphosphine (TOP, 97%) were purchase from STREM; silver (I) iodide (anhydrous, 99.999%), and indium (III) iodide (anhydrous, 99.999%) from Alfa-Aesar; 1-dodecanethiol (DDT, ≥98%), diethylzinc (1.0 M in hexane), oleic acid (techn. 90%), toluene (99.7%), ethanol (99.9%), and methanol (99.9%) from Sigma-Aldrich; lithium bis(trimethylsilyl)amide (LiN(SiMe<sub>3</sub>)<sub>2</sub>, 95%) and oleylamine (80-90%) from Acros. LiN(SiMe<sub>3</sub>)<sub>2</sub> was recrystallized from a hexane solution at -20°C; other chemicals were used as received.

Stock solutions of CuCl, InCl<sub>3</sub>, AgI, InI<sub>3</sub> (0.25 M), Se stock solution (1 M, denoted as TOP:Se), and Te stock solution (1 M, denoted as TOP:Te) were prepared in the glove box by dissolving 0.247 g of CuCl in 10 mL of TOP, 0.553 g of InCl<sub>3</sub> in 10 mL of TOP, 0.587 g of AgI in 10 mL of TOP, 1.239 g of InI<sub>3</sub> in 10 mL of TOP, 7.896 g of Se in 100 mL of TOP, and 12.760 g of Te in 100 mL of TOP, respectively. It is suggested to use anhydrous metal halides as well as tellurium ingots (not a powder) for the stock solutions. Volume change upon dissolution was negligible for all. The stock solution of LiN(SiMe<sub>3</sub>)<sub>2</sub> was prepared by dissolving 4.2 g of lithium amide in 10 mL of TOP. The volume of obtained solution was approximately 15.6 mL of solution and the concentration of the LiN(SiMe<sub>3</sub>)<sub>2</sub> stock solution was calculated to be 1.6 M. All stock solutions were stable for at least 3 weeks.

### Synthesis of Cu-In-Te nanocrystals

In typical synthesis of 5.5 nm Cu<sub>2</sub>In<sub>4</sub>Te<sub>7</sub> nanocrystals (NCs), 1 mL of CuCl stock solution (0.25 M) was mixed with 1 mL of InCl<sub>3</sub> stock solution (0.25 M) and 6 mL of TOP in the glovebox. The mixture was transferred to the 25 mL three-neck flask, connected to the Schlenk line set-up and pumped for 30 min at 100°C. Afterwards, reaction flask was filled with N<sub>2</sub> and heated to 260°C. At 260°C, the injection mixture, consisting of 1 mL of TOP:Te stock solution (1 M) and 1.5 mL of LiN(SiMe<sub>3</sub>)<sub>2</sub> stock solution (1.6 M), was swiftly added to the mixture. The reaction solution turns brown-black, indicating fast formation of Cu-In-Te NCs. After 3 min of growth, the solution was cooled down with a water bath.

To purify the Cu-In-Te NCs, a crude solution was mixed with 10 mL of toluene. Then, 60 mL of ethanol and 20 mL of methanol were added. The mixture was centrifuged at 6000 rpm during 5 min. Precipitated NCs were dissolved in 2 mL of toluene and 0.5 mL of DDT and then precipitated once again with 8 mL of methanol and centrifugation at 6000 rpm for 5 min. Obtained NCs formed long-term colloiddally stable solutions in toluene or hexane, and were stored in the glove box.

To obtain other sizes of Cu<sub>2</sub>In<sub>4</sub>Te<sub>7</sub> NCs, different growth times were applied. The growth time of 3 min provided optimal size distributions of Cu<sub>2</sub>In<sub>4</sub>Te<sub>7</sub> NCs.

To regulate the composition of Cu-In-Te NCs, the initial ratio of metal halides was adjusted. The total amount of chloride ions, however, has to be kept constant ([Cl<sup>-</sup>] = 1 mmol). To calculate the expected

$$R_{Cu:In} = 0.18 + 0.42 \frac{n_{CuCl}}{n_{InCl_3}}$$

composition, the experimental dependence can be used (where  $R_{Cu:In}$  is an atomic Cu:In ratio in the Cu-In-Te composition,  $n_{CuCl}$  is total amount of CuCl, in mol, and  $n_{InCl_3}$  is total amount of InCl<sub>3</sub>, in mol).

Further remarks: reaction conditions for Figures 2a,b are  $T_{inj} = 260^{\circ}\text{C}$ ,  $[\text{LiN}(\text{SiMe}_3)_2] = 2.4 \text{ mmol}$ ,  $[\text{Cl}^-] = 1 \text{ mmol}$ ; reaction conditions for Figure 3a are  $T_{inj} = 260^{\circ}\text{C}$ ,  $[\text{LiN}(\text{SiMe}_3)_2] = 2.4 \text{ mmol}$ ,  $[\text{CuCl}]:[\text{InCl}_3] = 1$ ,  $[\text{Cl}^-] = 1 \text{ mmol}$ .

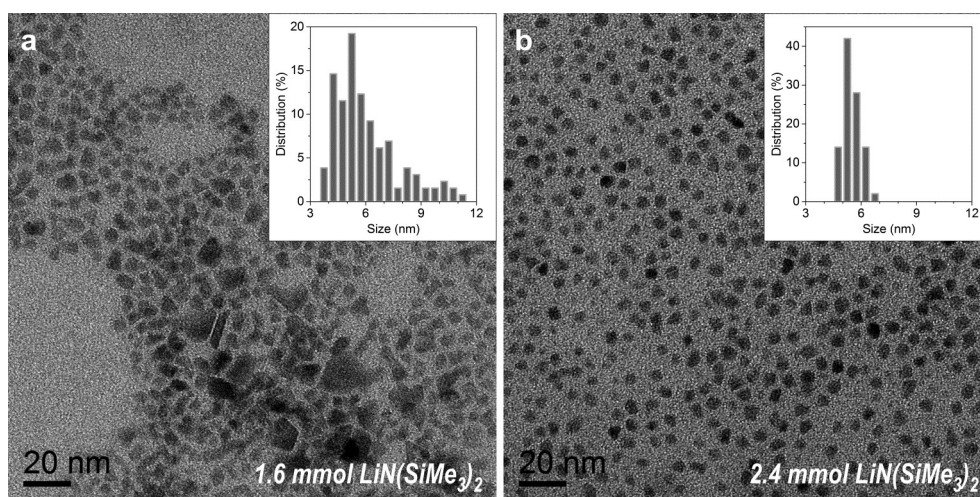


Figure S1. TEM images of Cu-In-Te NCs, synthesized at same conditions except for the amount of introduced lithium amide: (a) with 1.6 mmol of  $\text{LiN}(\text{SiMe}_3)_2$  and (b) with 2.4 mmol of  $\text{LiN}(\text{SiMe}_3)_2$  in total. Reaction conditions:  $T_{\text{inj}} = 260^\circ\text{C}$ ,  $t_{\text{growth}} = 2$  min,  $[\text{CuCl}]:[\text{InCl}_3] = 1$ ,  $[\text{Cl}^-] = 1$  mmol.

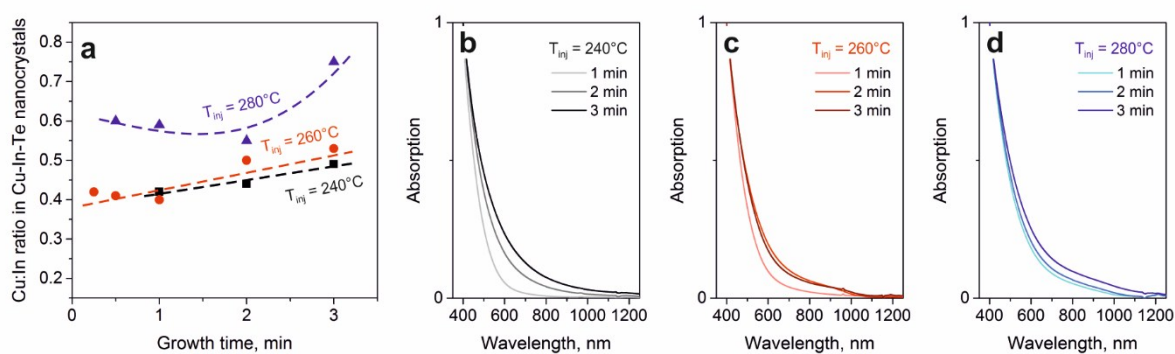


Figure S2. Syntheses of Cu-In-Te NCs at different injection temperatures ( $T_{\text{inj}}$ ). EDX and absorption spectroscopies were used to measure composition (a) and optical properties (b-d) of Cu-In-Te products at the different growth times. Reaction conditions:  $[\text{LiN}(\text{SiMe}_3)_2] = 2.4$  mmol,  $[\text{CuCl}]:[\text{InCl}_3] = 1$ ,  $[\text{Cl}^-] = 1$  mmol.

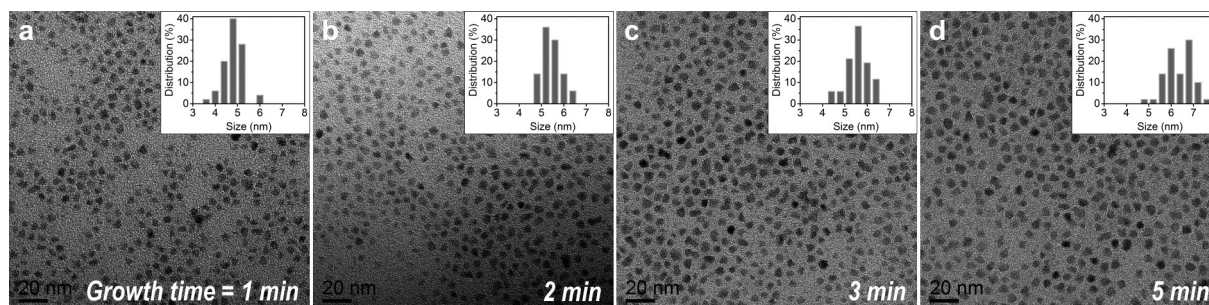


Figure S3. TEM images of Cu-In-Te NCs, prepared using different growth times. Reaction conditions:  $T_{\text{inj}} = 260^\circ\text{C}$ ,  $[\text{LiN}(\text{SiMe}_3)_2] = 2.4$  mmol,  $[\text{CuCl}]:[\text{InCl}_3] = 1$ ,  $[\text{Cl}^-] = 1$  mmol.

## Synthesis of Ag-In-Te nanocrystals

In a typical synthesis of 5.1 nm  $\text{Ag}_2\text{In}_4\text{Te}_7$  nanocrystals (NCs), 0.3 mL of AgI stock solution (0.25 M) was mixed with 1 mL of  $\text{InI}_3$  stock solution (0.25 M) and 6 mL of TOP in the glovebox. The mixture was transferred to the 25 mL three-neck flask, connected to the Schlenk line set-up and pumped for 30 min at 100°C. Afterwards, the reaction flask was filled with  $\text{N}_2$  and heated to 240°C. At 240°C, injection mixture, consisting of 1 mL of TOP:Te stock solution (1 M) and 2 mL of  $\text{LiN}(\text{SiMe}_3)_2$  stock solution (1.6 M), was swiftly added to the mixture. The reaction solution turned brown-black, indicating fast formation of Ag-In-Te NCs. After 30 s of growth, the solution was cooled down with a water bath.

To purify Ag-In-Te NCs, the crude solution was mixed with 10 mL of toluene. Then, 60 mL of ethanol and 20 mL of methanol were added. The mixture was centrifuged at 6000 rpm for 5 min. Precipitated NCs were dissolved in 2 mL of toluene and 0.5 mL of DDT and then precipitated once again with 8 mL of methanol and centrifugation at 6000 rpm for 5 min. Obtained NCs formed long-term colloiddally stable solutions in toluene or hexane, and were stored in the glove box.

To obtain other sizes of  $\text{Ag}_2\text{In}_4\text{Te}_7$  NCs, different growth times were applied. The growth time of 30 s provided optimal size distributions of  $\text{Ag}_2\text{In}_4\text{Te}_7$  NCs.

To regulate the composition of Ag-In-Te NCs, the initial ratio of metal halides was adjusted. The total amount of iodide ions, however, has to be kept constant ( $[\text{I}^-] = 0.825 \text{ mmol}$ ). To calculate the expected

$$R_{\text{Ag:In}} = 1.35 \frac{n_{\text{AgI}}}{n_{\text{InI}_3}}$$

composition, the experimental dependence

$R_{\text{Ag:In}}$  can be used (where  $R_{\text{Ag:In}}$  is an atomic Ag:In ratio in the Ag-In-Te composition,  $n_{\text{AgI}}$  is total amount of AgI, in mol, and  $n_{\text{InI}_3}$  is total amount of  $\text{InI}_3$ , in mol).

Further remarks: reaction conditions for Figures 2c,d are  $T_{\text{inj}} = 240^\circ\text{C}$ ,  $[\text{LiN}(\text{SiMe}_3)_2] = 3.2 \text{ mmol}$ ,  $[\text{I}^-] = 0.825 \text{ mmol}$ ; reaction conditions for Figure 3b are  $T_{\text{inj}} = 240^\circ\text{C}$ ,  $[\text{LiN}(\text{SiMe}_3)_2] = 1.6 \text{ mmol}$ ,  $[\text{AgI}]:[\text{InI}_3] = 0.3$ ,  $[\text{I}^-] = 0.825 \text{ mmol}$ .

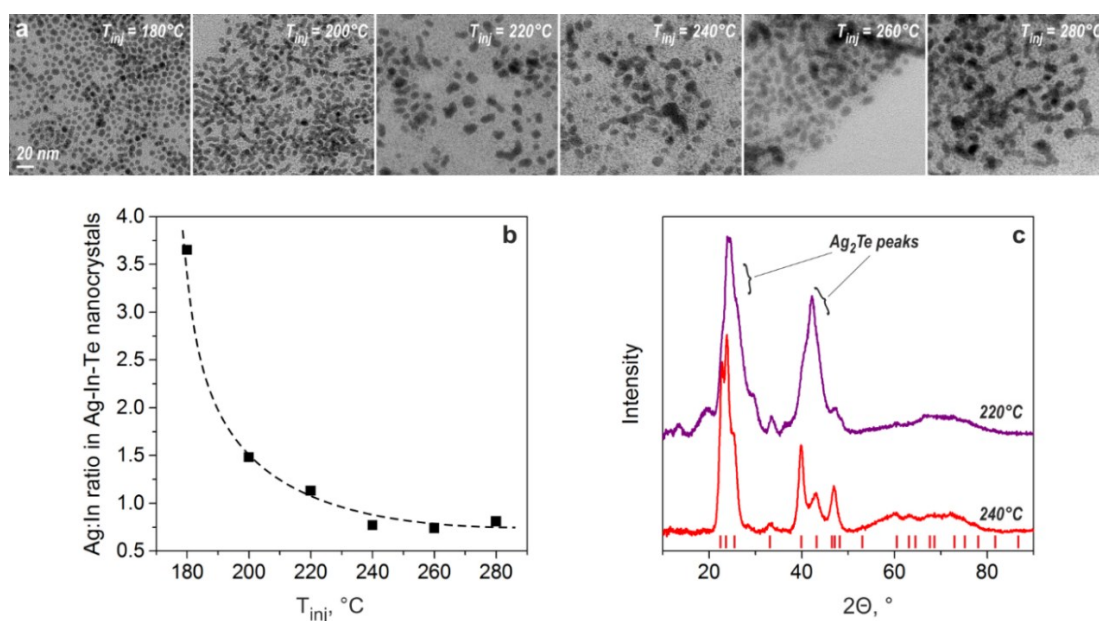


Figure S4. Syntheses of Ag-In-Te NCs at different injection temperatures ( $T_{\text{inj}}$ ): (a) TEM images, (b) composition (EDX), and (c) structure of obtained materials (XRD). X-ray diffraction spectra in (c)

illustrate presence of  $\text{Ag}_2\text{Te}$  phase<sup>[S1]</sup> at  $T_{\text{inj}} = 220^\circ\text{C}$  and single phase Ag-In-Te sample at  $T_{\text{inj}} = 240^\circ\text{C}$ .  
Reaction conditions:  $t_{\text{growth}} = 1 \text{ min}$ ,  $[\text{LiN}(\text{SiMe}_3)_2] = 1.6 \text{ mmol}$ ,  $[\text{AgI}]:[\text{InI}_3] = 0.75$ ,  $[\text{I}^-] = 0.937 \text{ mmol}$

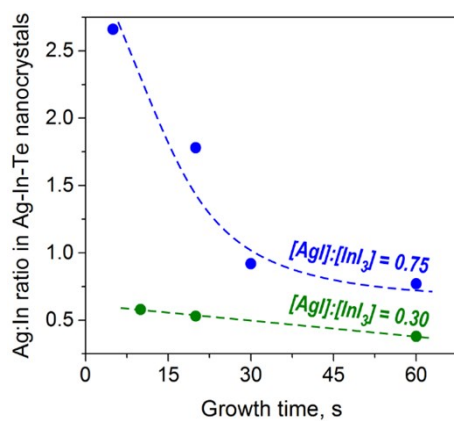


Figure S5. Syntheses of Ag-In-Te NCs with different metal halide initial ratios. Reaction conditions:  $T_{inj} = 240^{\circ}\text{C}$ ,  $[\text{LiN}(\text{SiMe}_3)_2] = 1.6 \text{ mmol}$ ,  $[\text{InI}_3] = 0.25 \text{ mmol}$ .

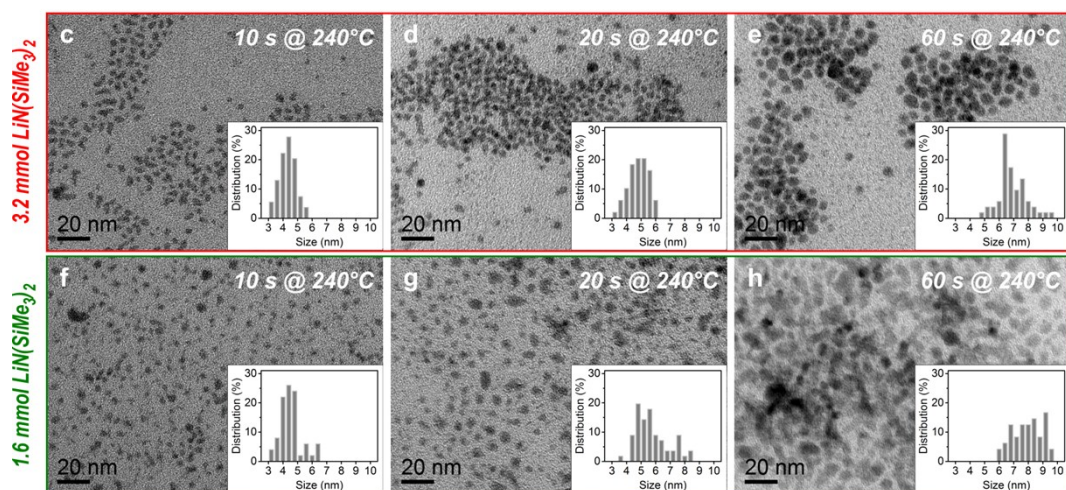
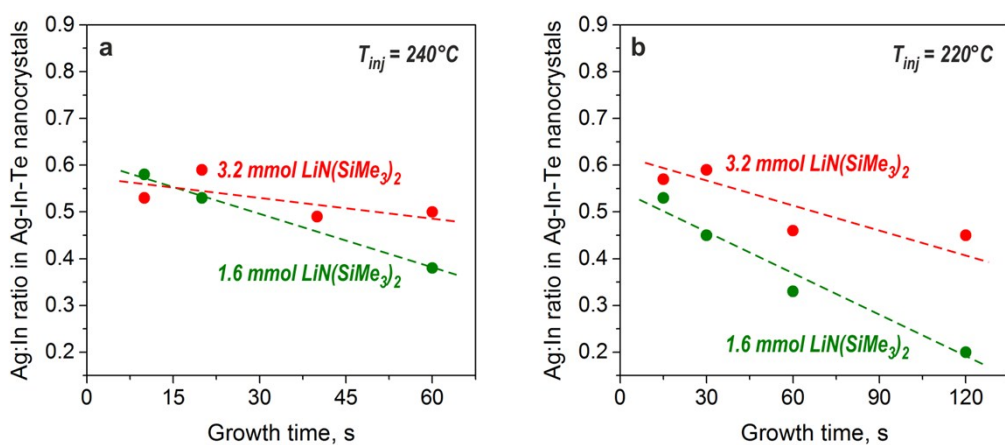


Figure S6. Syntheses of Ag-In-Te NCs with different amounts of  $\text{LiN}(\text{SiMe}_3)_2$  at (a)  $T_{inj} = 240^{\circ}\text{C}$  and (b)  $T_{inj} = 220^{\circ}\text{C}$ ; (c-h) TEM images of syntheses in (a). Reaction conditions:  $[\text{AgI}]:[\text{InI}_3] = 0.3$ ,  $[\text{I}^-] = 0.825 \text{ mmol}$

## Characterization

Absorption was measured with an Agilent Cary 5000 spectrophotometer. Photoluminescence spectra were taken by exciting colloidal solutions with 532 nm CW laser and collecting the emission with an Ocean Optics QE65000 spectrometer. Energy dispersive X-ray spectroscopy (EDX) was carried out on FEI Quanta 200 FEG (30 kV). X-ray diffraction measurements were made with Rigaku SmartLab 9 kW System with rotating Cu anode and 2D solid state detector HyPix-3000 SL. Lattice parameters were extracted from full-range fits, using FullProf Suite software. Transmission electron microscopy was performed on a Philips CM12 (100kV) and Tecnai F30 (300kV) instruments. Size distributions were determined using ImageJ software. Mean diameters were extracted from size histograms, compiled by measuring the size of 50-100 stand-alone NCs for each sample. For elongated NCs, the smallest dimension was considered as the size (i.e., thickness).

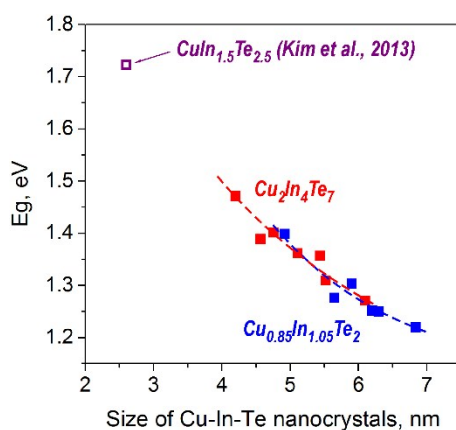


Figure S7. Optical band gaps of Cu-In-Te NCs with different compositions. Data for  $CuIn_{1.5}Te_{2.5}$  NCs from [S2].

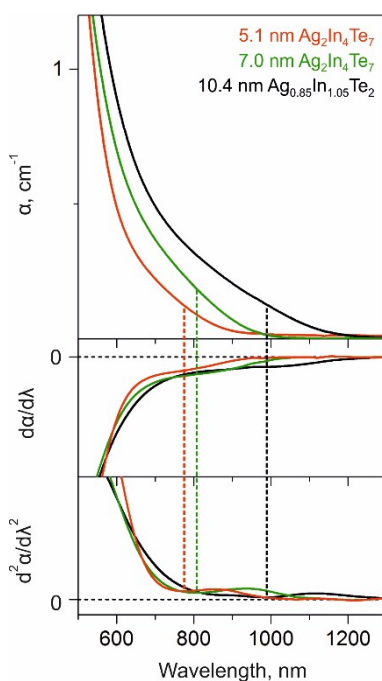


Figure S8. Absorption spectra of Ag-In-Te NCs with variable size and composition.



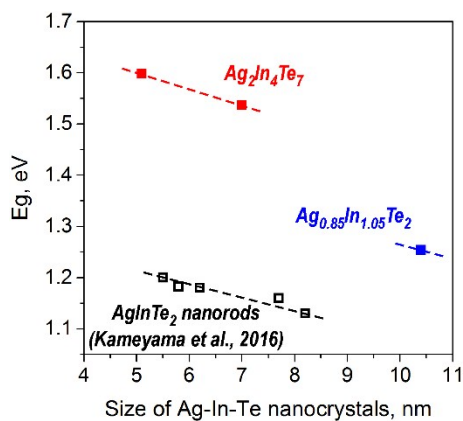


Figure S9. Optical band gaps of Ag-In-Te NCs with different compositions. Data for AgInTe<sub>2</sub> nanorods from [S3].

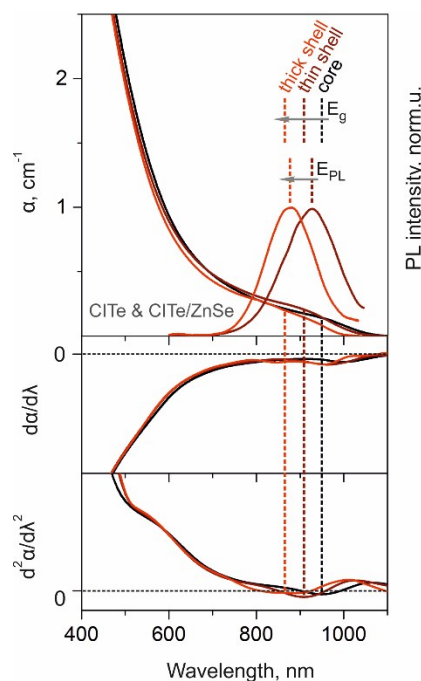


Figure S10. Absorption and photoluminescence spectra of Cu-In-Te NCs before and after ZnSe shell growth.

### References to the Electronic Supplementary Information

- [S1] Y.-W. Liu, D.-K. Ko, S. J. Oh, T. R. Gordon, V. Doan-Nguyen, T. Paik, Y. Kang, X. Ye, L. Jin, C. R. Kagan, and C. B. Murray, *Chemistry of Materials*, 2011, **23**, 4657.
- [S2] S. Kim, M. Kang, S. Kim, J.-H. Heo, J. H. Noh, S. H. Im, S. I. Seok, and S.-W. Kim, *ACS Nano*, 2013, **7**, 4756.
- [S3] T. Kameyama, Y. Ishigami, H. Yukawa, T. Shimada, Y. Baba, T. Ishikawa, S. Kuwabata, and T. Torimoto, *Nanoscale*, 2016, **8**, 5435.