

Supporting Information for

One-Temperature Synthesis of Doped and Alloyed Zn-Cd-Se Nanocrystals

Yonghui Liu, Jingzhi Lu, Jin Zhu*

Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, State Key Laboratory of Coordination Chemistry, Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing 210093, China

Corresponding Author. Phone: +86-25-83686291; Fax: +86-25-83317761; Email: jinz@nju.edu.cn.

Materials and Measurements. ZnO (99.99%), CdO (99.99%), Se (99.99%), oleic acid (OA, 90%), oleylamine (OLA, 90%), 1-octadecene (ODE, 90%) were obtained from Alfa Aesar. Trioctylphosphine (TOP, 97%) was from Sigma-Aldrich. Methanol (AR), ethanol (AR), and hexane (AR) were from Sinopharm. UV-vis absorption spectra were obtained on a Shimadzu UV 3600 facility. Room-temperature luminescent (RTL) spectra were obtained on a Perkin Elmer LS-55 facility. Excited state lifetimes were measured on a Edinburgh FLS920 fluorescence spectrometer. Temperature-dependent luminescent spectra were obtained on an Ocean Optics OE65000-FL facility. Inductively coupled plasma atomic emission spectra (ICP-AES) were measured on a Perkin Elmer Optima 5300 DV facility. X-ray photoelectron spectra (XPS) were obtained on a VG ESCALAB MK II facility. X-ray diffraction (XRD) spectra were measured on a Bruker D8 Advance X-ray diffractometer. High-resolution transmission electron microscopy (HRTEM) was performed on a JEOL JEM-2100 LaB₆ microscope.

Synthesis of High-Temperature Luminescent (HTL) Zn-Cd-Se Nanocrystal. The synthesis of HTL nanocrystal can be achieved at a ZnO/CdO mole ratio between 12:1 and 1.8:1, with the total amount of 0.2 mmol. The change of ZnO/CdO mole ratio allows for the tuning of emission maximum. The synthetic procedure, by taking a 3:1 ZnO/CdO mole ratio sample as an example, is described as follows: **1. Preparation of the precursor solution for Zn and Cd.** ZnO (0.0122 g, 0.15 mmol) and CdO (0.0064 g, 0.05 mmol) were placed in a three-necked flask. To the flask were further added oleic acid (OA, 1 mL), oleylamine (OLA, 3 mL), and 1-octadecene (ODE, 5 mL). The mixture was subjected to three cycles of pump (30 min)-fill (5 min, with argon) operation at 100 °C. A further heating at 235 °C for 5 min enabled the complete dissolution of precursor species.

2. Preparation of the precursor solution for Se. Se powder (0.0320 g, 0.4 mmol) was loaded in a Schlenk flask and subjected to repeated cycles of pump-fill (with argon) operation at room temperature. To the flask was added 1 mL of trioctylphosphine (TOP). The dissolution of Se powder was carried out by stirring of the mixture for 20 min. **3. Preparation of the HTL nanocrystal.** The as-prepared precursor solution for Zn and Cd was heated to 230 °C. To the solution was swiftly injected the as-prepared precursor solution for Se. A hand-held UV lamp (365 nm) was used to monitor the progress of the reaction by enabling the visualization of luminescence. Depending on the ZnO/CdO mole ratio, luminescence could be observed after merely 1 to 3 min. An aliquot of solution (0.2 mL) was taken out regularly from the reaction mixture and placed in 1.8 mL of hexane. The sample was then examined for its luminescent property. When no further shift of the emission maximum could be observed, the whole system was quenched with 5 mL of hexane. **3. Purification of the HTL nanocrystal.** The nanocrystal solution was allowed to be cooled to room temperature. To the solution was added a solvent mixture of methanol/ethanol (25 mL, 1/1 v/v) as the precipitant. The mixture was then centrifuged at 15000 rpm for 20 min. The supernatant was discarded and the precipitate was redispersed in 3 mL of hexane. The centrifugation-redispersion step was repeated for two more times. The precipitate was finally dispersed in 3 mL of hexane.

Synthesis of High-Temperature Non-Luminescent (HTNL) Zn-Cd-Se Nanocrystal. The synthesis of HTNL nanocrystal can be achieved at a ZnO/CdO mole ratio between 1.6:1 and 1:1, with the total amount of 0.2 mmol. The change of ZnO/CdO mole ratio allows for the tuning of emission maximum. The synthetic procedure was identical to that for HTL nanocrystal except with a different ZnO/CdO ratio.

Recording of Temperature-Dependent Luminescent Images. 1. Thermal stability of

HTL nanocrystal. An aliquot of HTL nanocrystal hexane solution (10 μ L) was placed in a 1 cm quartz cuvette. To the cuvette were added a solvent mixture of 0.1 mL OA, 0.3 mL OLA, 0.5 mL ODE, and 0.1 mL TOP. The temperature of HTL nanocrystal solution was raised to 200 $^{\circ}$ C in a heating mantle. The sample was then cooled down to room temperature. The thermally treated HTL nanocrystal solution was placed side by side with an otherwise identical HTL nanocrystal solution except without the thermal treatment. The two cuvettes were then heated to 110, 140, 170, and 200 $^{\circ}$ C, respectively. The cuvettes were kept at each temperature for 5 min before the recording of luminescent images under the irradiation of a hand-held UV lamp (365 nm) with a digital camera. **2.**

Comparison of temperature-dependent luminescent properties for HTL and HTNL

nanocrystals. An aliquot of each of HTL and HTNL nanocrystal hexane solutions (10 μ L) was placed side by side in two 1 cm quartz cuvettes. To each cuvette were added a solvent mixture of 0.1 mL OA, 0.3 mL OLA, 0.5 mL ODE, and 0.1 mL TOP. The two cuvettes were then heated to 110, 140, 170, and 200 $^{\circ}$ C, respectively. The cuvettes were kept at each temperature for 5 min before the recording of luminescent images under the irradiation of a hand-held UV lamp (365 nm) with a digital camera.

Measurement of Temperature-Dependent Emission Spectra. 1. Background

calibration. To a 50 mL three-necked flask were added 1 mL OA, 3 mL OLA, 5 mL ODE, and 1 mL TOP. The mixture was subjected to a pump (30 min)-fill (5 min, with argon)-pump (15 min)-fill (5 min, with argon) operation at 100 $^{\circ}$ C. The optical fiber probe was then placed through a side neck at \sim 1 cm above the nanocrystal solution. The emission intensity was measured by using a 455 nm light-emitting diode laser as the

excitation source. The resulting emission value was recorded as the background. A software was used to automatically calibrate the background emission as zero. **2. Sample preparation.** An aliquot of nanocrystal hexane solutions (2 mL) was placed in a 50 mL three-necked flask. To the flask were added 1 mL OA, 3 mL OLA, 5 mL ODE, and 1 mL TOP. The mixture was subjected to a pump (30 min)-fill (5 min, with argon)-pump (15 min)-fill (5 min, with argon) operation at 100 °C. The optical fiber probe was then placed through a side neck at ~ 1 cm above the nanocrystal solution. **2. Emission spectrum measurement.** The nanocrystal solution was first cooled to room temperature. The emission spectrum was recorded by using a 455 nm light-emitting diode laser as the excitation source. The sample was then heated to 110, 140, 170, 200, and 230 °C and kept for 2 min before the measurement of emission spectrum at each temperature.

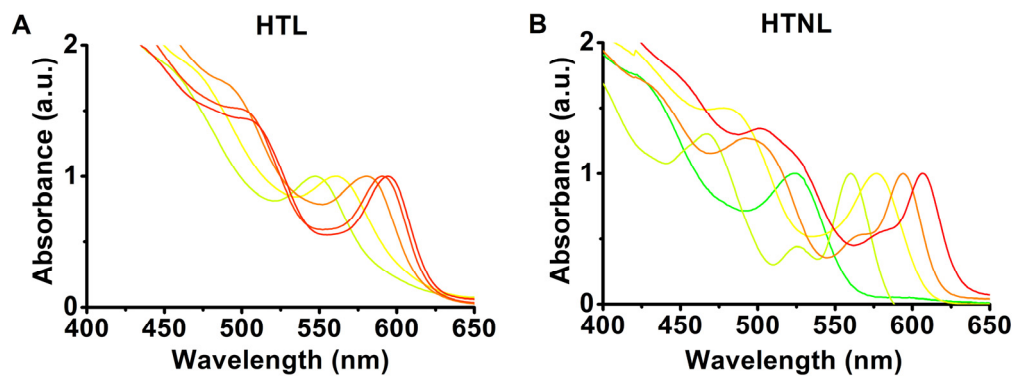


Fig. S1 UV-vis absorption properties of HTL and HTNL nanocrystals. (A) UV-vis absorption spectra of HTL nanocrystals synthesized with varied ZnO/CdO ratios (left to right: 3:1, 2.3:1, 5.7:1, 9:1, 12:1). (B) UV-vis absorption spectra of HTNL nanocrystals synthesized with varied ZnO/CdO ratios (left to right: 1.6:1, 1.4:1, 1.2:1, 1.5:1, 1:1).

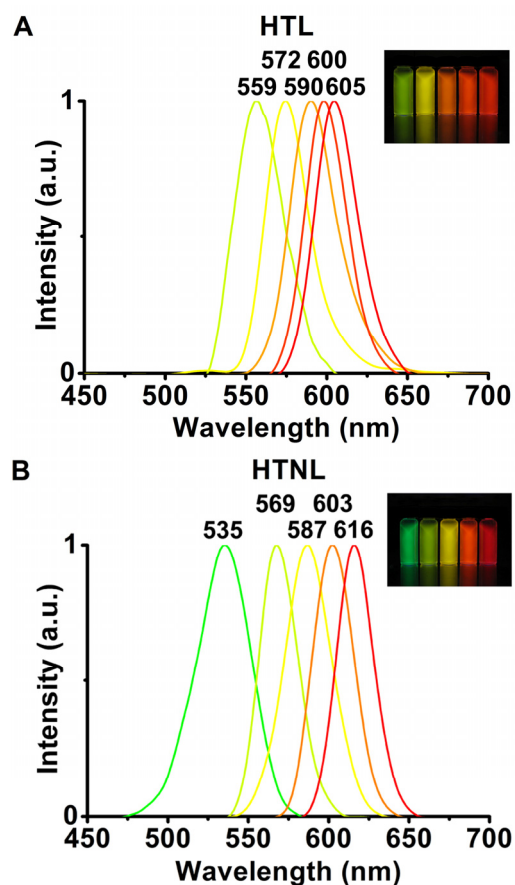


Fig. S2 RTL properties of HTL and HTNL nanocrystals. (A) Emission spectra of HTL nanocrystals synthesized with varied ZnO/CdO ratios (559 nm, 3:1; 572 nm, 2.3:1; 590 nm, 5.7:1; 600 nm, 9:1; 605 nm, 12:1). Excitation wavelength: 365 nm. Inset: RTL images of the corresponding HTL nanocrystals excited by a hand-held UV lamp (365 nm). (B) Emission spectra of HTNL nanocrystals synthesized with varied ZnO/CdO ratios (535 nm, 1.6:1; 569 nm, 1.4:1; 587 nm, 1.2:1; 603 nm, 1.5:1; 616 nm, 1:1). Excitation wavelength: 365 nm. Inset: RTL images of the corresponding HTNL nanocrystals excited by a hand-held UV lamp (365 nm).

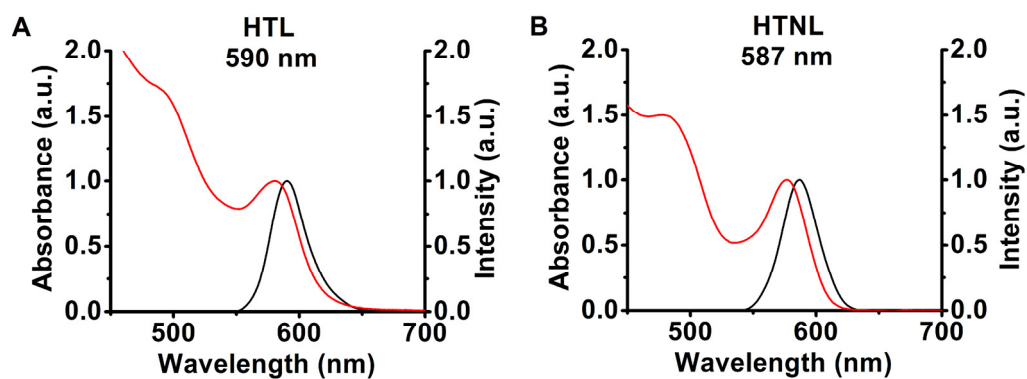


Fig. S3 Stokes shifts for HTL 590 and HTNL 587 nanocrystals. (A) UV-vis and emission (excitation wavelength: 365 nm) spectra of HTL 590 nanocrystal. Stokes shift: 10 nm. (B) UV-vis and emission (excitation wavelength: 365 nm) spectra of HTNL 587 nanocrystal. Stokes shift: 10 nm.

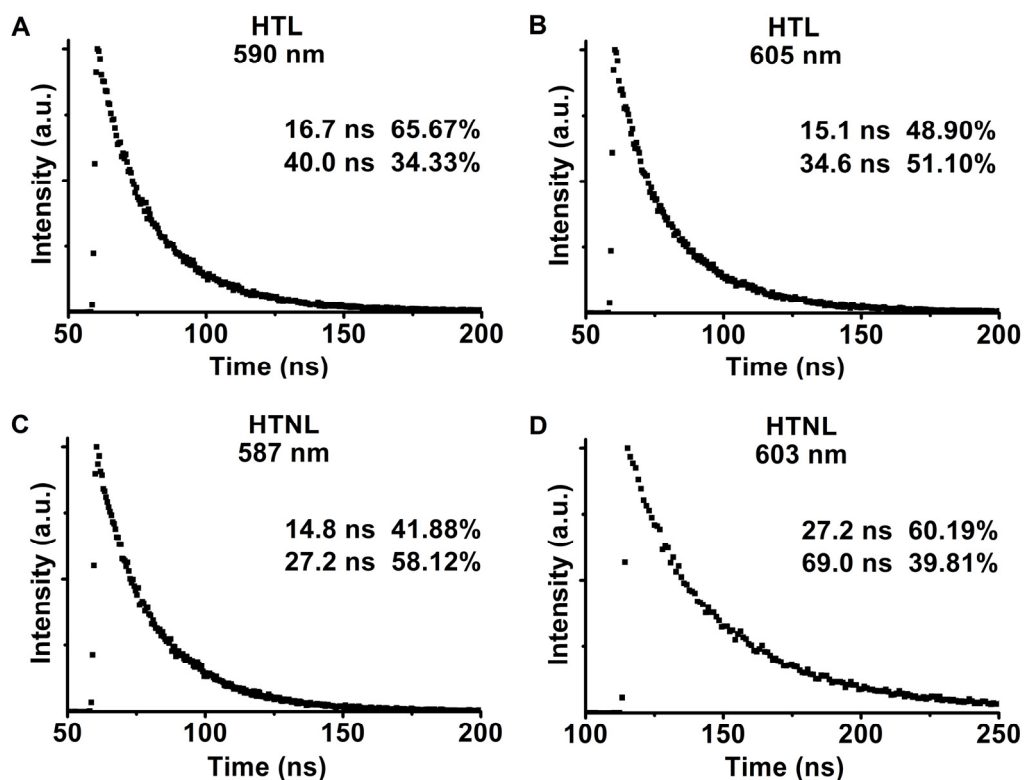


Fig. S4 Excited state lifetimes for HTL and HTNL nanocrystals. (A) Decay curve for HTL 590 nanocrystal. (B) Decay curve for HTL 605 nanocrystal. (C) Decay curve for HTNL 587 nanocrystal. (D) Decay curve for HTNL 603 nanocrystal. The excitation wavelength for all the measurements is 400 nm.

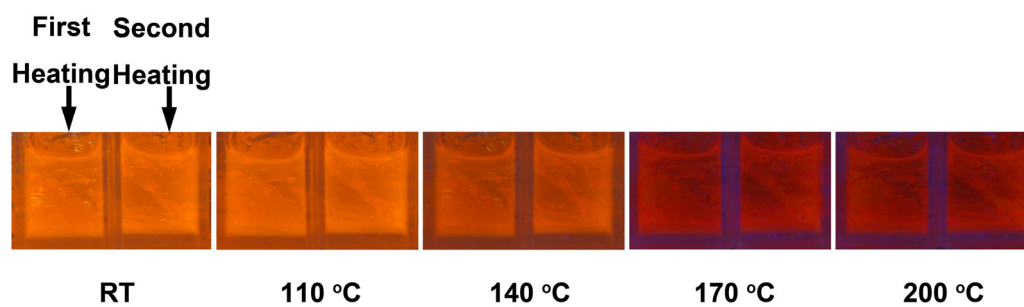


Fig. S5 Temperature-dependent luminescent properties of HTL nanocrystals. Luminescent images of HTL 590 nanocrystal at varied temperatures after first and second heating runs (excited by a 365 nm hand-held UV lamp).

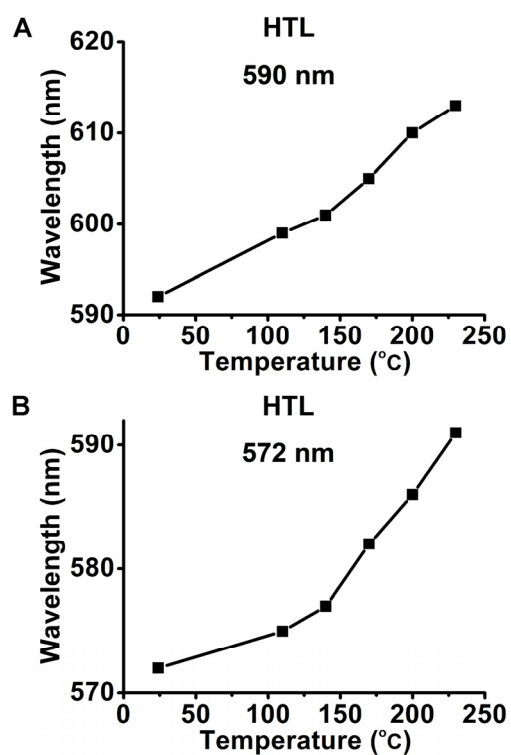


Fig. S6 Temperature-dependent luminescent properties of HTL nanocrystals. (A) Temperature-dependent emission peak position of HTL 590 nanocrystal (excitation wavelength: 455 nm). (B) Temperature-dependent emission peak position of HTL 572 nanocrystal (excitation wavelength: 455 nm).

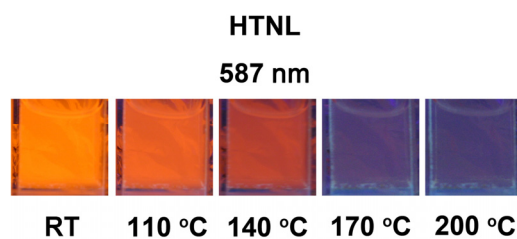


Fig. S7 Temperature-dependent luminescent properties of HTNL nanocrystals. Luminescent images of HTNL 587 nanocrystal at varied temperatures (excited by a 365 nm hand-held UV lamp).

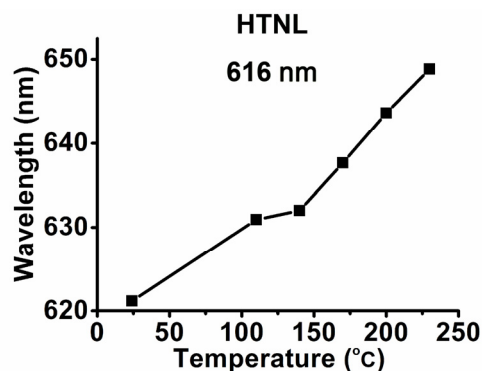


Fig. S8 Temperature-dependent luminescent properties of HTNL nanocrystals. Temperature-dependent emission peak position of HTNL 616 nanocrystal (excitation wavelength: 455 nm). Due to the use of a different spectrometer for temperature-dependent measurements, the peak position for RTL spectrum was slightly shifted.

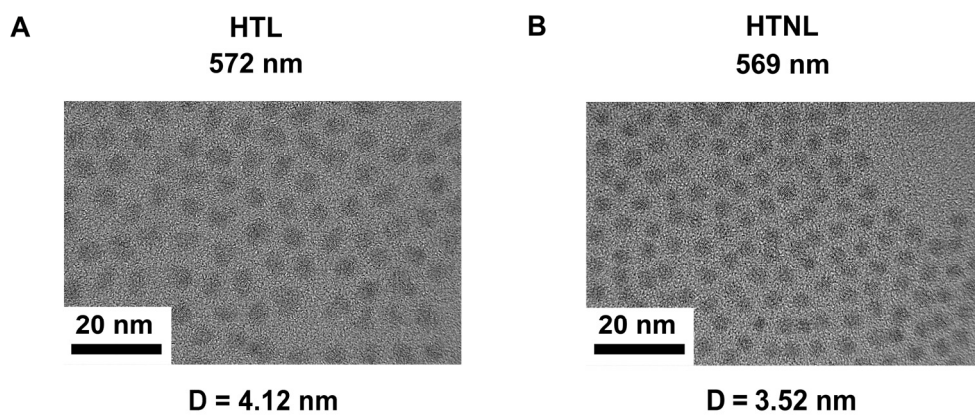


Fig. S9 Size measurements for HTL and HTNL nanocrystals. (A) TEM image for HTL 572 nanocrystal. (B) TEM image for HTNL 569 nanocrystal.

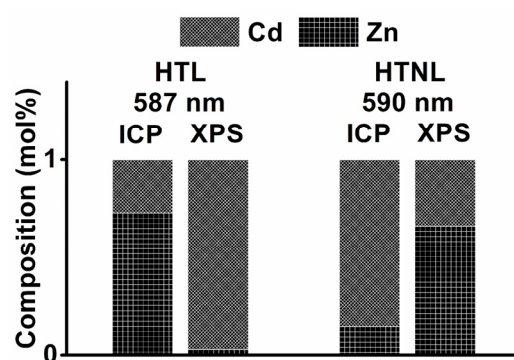


Fig. S10 Compositions for HTL and HTNL nanocrystals. (A) ICP-AES and XPS results for HTL 587 nanocrystal. (B) ICP-AES and XPS results for HTNL 590 nanocrystal.

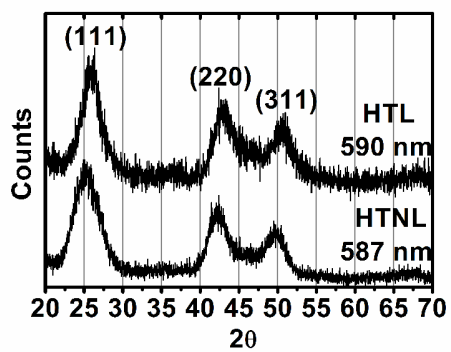


Fig. S11 XRD structural measurements for HTL and HTNL nanocrystals. XRD traces for HTL 590 and HTNL 587 nanocrystals.