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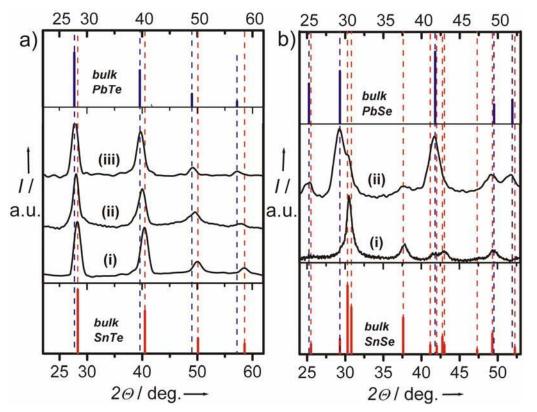
### **Supporting Information for**

# Quasi-seeded growth of ligand-tailored PbSe nanocrystals through cation-exchange mediated nucleation

Maksym V. Kovalenko<sup>\*,†</sup>, Dmitri V. Talapin<sup>‡</sup>, Maria Antonietta Loi<sup>§</sup>, Fabrizio Cordella<sup>§</sup>, Günter Hesser<sup>†</sup>, Maryna I. Bodnarchuk<sup>†</sup>, and Wolfgang Heiss<sup>†</sup>

 <sup>†</sup>Institute of Semiconductor and Solid State Physics, Johannes Kepler University Linz, A-4040 Linz, Austria
<sup>‡</sup>Department of Chemistry, University of Chicago, Chicago, IL 60637 (USA)
<sup>§</sup>Zernike Institute for Advanced Materials, University of Groningen, 9747 AG Groningen (The Netherlands)

E-mail: maksym.kovalenko@jku.at, mvkovalenko@uchicago.edu



*Figure S1.* Evolution of powder XRD spectra as a result of the cation-exchange during the treatment of Tin chalcogenide NCs by PbCl<sub>2</sub> in OLA at 120°C. Fig. S1a represent powder XRD patterns of (i) as-synthesized SnTe NCs [SnTe]=0.5 mmol, (ii) the same sample treated with 0.1 mmol of PbCl<sub>2</sub> and (iii) with another 0.4 mmol of PbCl<sub>2</sub>. Fig. S1b represent powder XRD patterns of (i) as-synthesized SnSe and (ii) the same sample treated with equimolar amount of PbCl<sub>2</sub>. Details of the synthesis of SnTe and SnSe NCs can be found in our previous report (Ref. 11f).

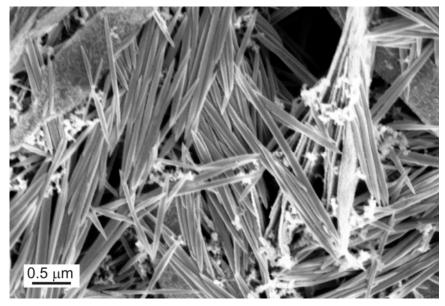
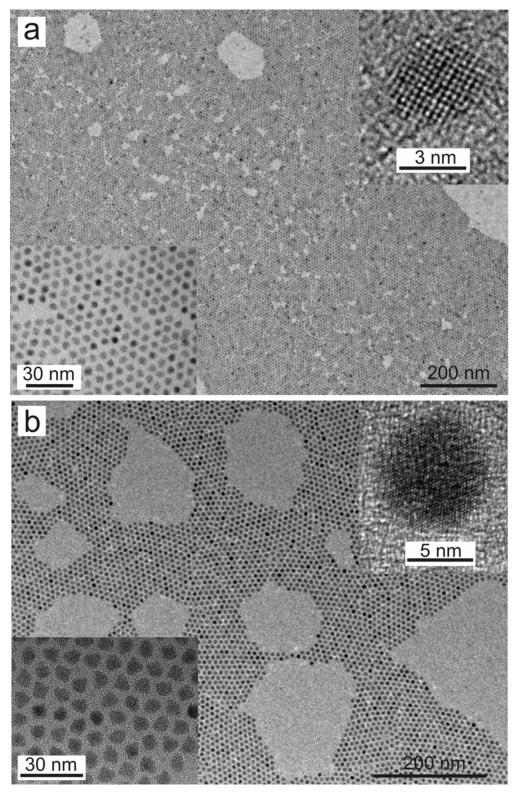
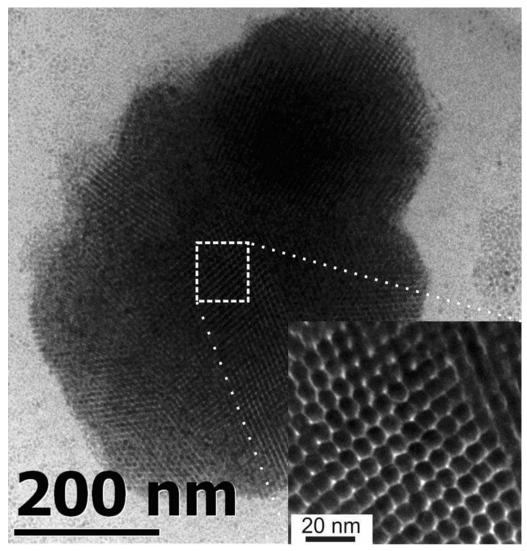


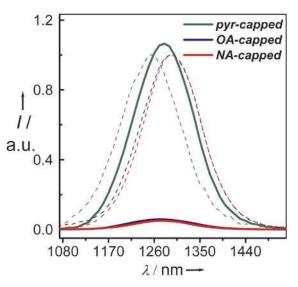
Figure S2. Elongated PbSe crystals formed upon the reaction between  $PbCl_2$  and TOPSe in OLA in the absence of  $Sn[N(SiMe_3)_2]_2$ .



*Figure S3.* TEM overview of monodisperse 4.5 nm (a) and 7.2 nm (b) PbSe NCs synthesized via cation-exchange mediated nucleation. No post-synthetic size-selection was applied.



*Figure S4.* TEM images of a typical 3D superlattice domain formed on carbon-coated TEM grid by 8.1 large PbSe NCs upon fast evaporation of relatively concentrated colloidal solutions in tetrachloroethylene.



*Figure S5.* Steady-state PL spectra from nonanoic acid (NA)-, oleic acid (OA)- and pyridine-capped PbSe NCs in solutions (dashed lines, normalized) and in films (solid lines, true intensities).

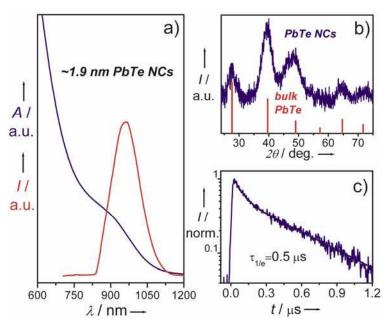


Figure S6. Optical and structural characterization of ~1.9 nm PbTe NCs synthesized via cation-exchange mediated nucleation. a) Optical absorption and emission spectra, b) powder XRD pattern and c) luminescence decay trace from the colloidal solution of PbTe NCs. For the synthesis of PbTe Ncs 50 μL of Sn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and 4 mL of TOPTe solution (10% referring to Te) were injected into 7 ml of OLA containing 0.19 g of PbCl<sub>2</sub> at 140°C. The reaction was terminated 2 min after the injection. The NC size of 1.9 nm is an average of the estimations based on i) the analysis of the width (fwhm) of the (220) XRD reflection peak using the Scherrer formula (according to Cademartiri et al. J. Am. Chem. Soc. 2006, 128, 10337-10346) and ii) the extrapolation of the empirical size-dependence of the PbTe bandgap energy (Ref. 11e) to the energy of 1.23 eV (975 nm).