# Supplementary Information

### Heat-Driven Acoustic Phonons in Lamellar

# Nanoplatelet Assemblies

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#### **Materials and Methods**

*Materials*. Cadmium acetate hydrate ( $\geq$ 99.99 %, Aldrich), cadmium chloride (99.99%, Aldrich), , selenium (99.99 %, powder, ~100 mesh, Aldrich), 1-octadecene (90 %, technical grade, Aldrich), oleic acid (90 %, technical grade, Aldrich), trioctylphosphine (90 %), cadmium nitrate (97 %, Aldrich), and sodium myristate (>98 %, Aldrich) were sourced from commercial suppliers and used as received. Solvents used were sourced from commercial suppliers and were ACS grade or higher.

Synthesis. Synthesis of CdSe nanoplatelets (NPLs) was performed using standard literature recipes with minor modifications to produce NPLs of different thicknesses and lateral dimensions.<sup>1-4</sup> Cadmium myristate was synthesized by dissolving 1.5 g sodium myristate in methanol (via sonication) and then adding 600 mg of cadmium nitrate under stirring. The methanolic solution immediately becomes cloudy and was allowed to stir under air for 4 hours, then the white solid was isolated by centrifugation at 5000 rpm. The white precipitate was re-dispersed in methanol and precipitated two more times, then once using acetone. Cadmium myristate was isolated after vacuum drying for 16 hours at 60 °C. 3.5 monolayer (ML) NPLs were synthesized by mixing 240 mg of cadmium acetate, 150 µL oleic acid, and 15 mL of octadecene. The mixture was held under vacuum for 1 hour at 80 °C, then heated under nitrogen to 180 °C, whereupon a 150 µL solution of 1 M selenium dissolved in trioctylphosphine was rapidly injected. The reaction was held at 180 °C under nitrogen for 10 minutes, then cooled to room temperature and precipitated with isopropanol and re-dispersed in methylcyclohexane. Multiple films were made after single and multiple iterative washing steps, but in no instance were oscillatory optical signals observed experimentally. The general procedure for 4.5 ML NPLs is as follows: in a flask are mixed 12 mg selenium powder, 170 mg cadmium myristate, 15 mL octadecene, which are held under vacuum at room temperature for 1 hour, then heated under nitrogen to 240 °C. At 195 °C, under nitrogen counterflow, 40 mg of finely-ground cadmium acetate was added rapidly. For smaller lateral dimensions, an aliquot of the reaction medium is removed at 225 °C via syringe and plunged into a hexane solution. After reactions were completed, the heating mantle was removed and 2 mL of oleic acid was injected followed, at ~100 °C with 10 mL of toluene. NPLs were precipitated from the reaction medium by centrifugation at 15000 rpm. For drop-cast samples prepared in optical studies, all samples were additionally washed by precipitation with ethanol, redispersion in methylcyclohexane, and drop-casting. For other sizes, the time of the reaction at 240 °C was varied from 2 minutes to 15 minutes. Synthesis of 5.5 ML NPLs was achieved by mixing 170 mg cadmium myristate in 14 mL octadecene, holding under vacuum for 1 hour at room temperature, then heated under nitrogen to 250 °C. At 250 °C, a dispersion of 12 mg selenium in 1 ML octadecene (dispersed with sonication and vigorous mixing) was rapidly injected, followed, after 1 minute, by addition of 90 mg cadmium myristate with nitrogen counterflow. The reaction proceeded for an additional 15 minutes. After removal of the heating mantle, 2 mL of oleic acid was injected followed, at ~100 °C with 10 mL of toluene before being cooled to room temperature by removal of the heating mantle. Samples were isolated by centrifugation of the reaction mixture at 15000 rpm, with the sample redispersed and stored in methylcyclohexane. Preparation of the sample for optical measurement consisted of an additional precipitation with ethanol followed by drop-casting from a methylcyclohexane dispersion. 6.5 ML NPLs were prepared by mixing 170

mg cadmium myristate and 14 mL octadecene, held under vacuum for 30 minutes at 85 °C, then heating under nitrogen to 250 °C. At 250 °C, a dispersion of 12 mg selenium in 1 ML octadecene (dispersed with sonication and vigorous mixing) was rapidly injected, followed, after 20 seconds, by addition of 60 mg cadmium myristate with nitrogen counterflow. The reaction proceeded for an addition 60 seconds, then a dropwise injection of 0.15 mL 0.5 M cadmium chloride in water over two minutes. After an additional 3 minutes, the reaction was cooled by removing the heating mantle. At 150 °C, 2 mL oleic acid and 15 mL methylcyclohexane was injected. The reaction medium was centrifuged to precipitate a mixture which contains 6.5 ML NPLs, thinner NPLs, and other small particles, which were separated by size-selective precipitation of methylcyclohexane dispersions.

*Preparation of thin-film samples.* Samples for static and time-resolved spectroscopy and X-ray diffraction measurements were prepared by drop-casting methylcyclohexane dispersions of NPLs in air at room temperature on to various substrates. Sapphire windows were used for temperature-resolved spectroscopy; coverglass was used for room temperature X-ray measurements; thin (70-80 µm) double-polished silicon was used for temperature-dependent X-ray measurements.

*Microscopy*. Transmission electron microscopy (TEM) was performed using a JEOL-2100 operated at 200 keV.

*Static Optical Spectroscopy*. Static absorption spectra were collected at different temperatures on solid films on sapphire in a helium cryostat by focusing a white light lamp output through the sample, collected by a fiber and analyzed with an Ocean Optics spectrometer.

*Time-resolved Spectroscopy*. Infrared pump, electronic probe (IPEP) measurements were performed with an infrared pump beam centered at 3500 nm and a visible white light probe. The white light probe was generated by focusing the fundamental 800 nm output of a 2 KHz 30 fs Ti: sapphire laser (Spectraphysics) through a sapphire plate. Pump and probe were spatially overlapped and a mechanical chopper was used to block the pump at 1 KHz to generate pump on/pump off data for transient absorption. The power of the infrared pump beam was maintained at 5 mW (1 kHz, ~300 µm diameter spot) for all measurements unless specifically stated otherwise.

X-ray Scattering. Small-angle X-ray scattering (SAXS) measurements were performed on SAXSLab Ganesha instrument equipped with a Pilatus 300K detector using Cu K $\alpha$  radiation. All measurements were performed in the transmission mode. For the room temperature measurements, the colloidal solutions of NPLs were drop-casted on a thin glass slide. The *in situ* heating/cooling experiments on 4.5 ML NPL stacks were performed using a Linkam stage. For these experiments the colloidal solution of 4.5 ML NPLs was drop-casted on a thin Si wafer (thickness 70-80  $\mu$ m) to ensure good thermal contact with the Linkam stage. The sample was allowed to equilibrate for 300 s at each temperature before the measurement.

*Resolution of SAXS measurements.* The apparent absence of any change in temperature-dependent measurements of CdSe NPLs (except for the formation of scattering ice crystals at low temperature) highlights the importance of SAXS resolution. A silver behenate standard was run to estimate the resolution in *q* of the measurement, which is approximately  $\Delta q = 0.0085$ . Based upon reported (volumetric) thermal expansion coefficients of ~6×10<sup>-6</sup> K<sup>-1</sup> for CdSe, the measured 187

K change in temperature would yield only static 0.1 % change in the CdSe lattice contributing  $< 10^{-4} \text{ Å}^{-1}$  change in the lamellar reflection (considering that the CdSe represents only a ~20% volume fraction of the total solid). Thermal expansion coefficients of solid aliphatic material, such as the ligands, is typically much larger than for inorganic compounds:  $100-200\times10^{-6} \text{ K}^{-1}$  for polyethylene of various densities near room temperature. Heating through a glass transition typically increases the thermal expansion coefficient of polymers.<sup>5</sup> Volume of the ligands may change in volume by 2% over the measured temperature range; the contribution of an isotropic volume expansion of that magnitude to the lamellar reflection would be 0.7% of the distance contributed by the ligand, estimated to be  $6\times 10^{-4} \text{ Å}^{-1}$ . Based upon these measurements and estimates, any change in the lattice spacing which occurs is most likely smaller than can be reliably differentiated, which is why no change is clearly observed.

*Estimation of bathochromic shifts due to minibands.* Based upon Figure 1a in Movilla et al.,<sup>6</sup> the *change* in bathchromic shift due to change in interparticle spacing of NPLs is estimated to be ~5 meV nm<sup>-1</sup> at the 4 nm distance typical for oleic acid coated platelets, also confirmed by SAXS measurements. To achieve a red-shift of 200  $\mu$ eV, this requires a decrease in spacing of 0.04 nm, or -1 %. This is approximately 100 times greater than the anticipated bathochromic shift due to expansion of the NPL short lattice direction and therefore unlikely to contribute substantially to the observed signal, although both effects may contribute.

### **Supporting Data and Figures**



Figure S1. Spectrum of the IR pump used in time-resolved experiments.



Figure S2. TEM micrographs of (a) 3.5 ML, (b) 4.5 ML, (c), 5.5 ML, and (d) 6.5 ML CdSe NPL samples.



Figure S3. Fluence-dependence of IPEP signal of 4.5 ML CdSe NPL sample. The low power trace is shown in open red circles; the higher-power trace is shown in a solid black line. Both measurements were collected at 6 K.



Figure S4. Temporal line-cuts of IPEP data for 4.5 ML nanoplatelets from the heavy hole increased and decreased absorption features, collected at 6 K. Data in open symbols ( $HH_{+}$ ) and closed symbols ( $HH_{-}$ ) are fitted with monoexponential functions shown in solid lines.



Figure S5. TEM micrographs of 4.5 ML CdSe NPLs with average dimensions of (a) 4.8 nm  $\times$  8.3 nm, (b) 9.1 nm  $\times$  16.1 nm, (c) 9.8 nm  $\times$  15.4 nm, and (d) 9.2 nm  $\times$  28.9 nm. (d) is the same sample as appears in Figure S2b above.



Figure S6. Sine wave frequency of damped exponential fits to 4.5 ML sample residuals in Figure 3a. Data are given for both the heavy hole increased and decreased absorption features.

Table S1. Structural data on size and stacking distances of NPL samples

Sample (thickness,	TEM Size (nm)	SAXS Reflection (q)	Spacing (nm)	Face-to-Face
nm)				Spacing (nm)

3.5 ML (1.1)	39.4 × 21.5	N/A	N/A	N/A
4.5 ML – 1 (1.4)	$4.8 \times 8.3$	0.123	5.1	3.7
4.5 ML – 2 (1.4)	9.1 × 16.1	0.116	5.4	4.0
4.5 ML – 3 (1.4)	$9.8 \times 15.4$	0.119	5.3	3.9
4.5 ML – 4 (1.4)	$9.2 \times 28.9$	0.125	5.0	3.6
5.5 ML (1.7)	$8.3 \times 28.2$	0.109	5.8	4.1
6.5 ML (2.0)	13.8 × 13.8	0.104	6.0	4.0



Figure S7. SAXS data of 4.8 nm  $\times$  8.3 nm 4.5 ML CdSe NPL solid. The data show higher-order lamellar reflections at multiples of 0.123 Å<sup>-1</sup>. Higher-order diffraction of the peak at 0.068 Å<sup>-1</sup> is not observed.



Figure S8. (a) Transient kinetics at the heavy-hole increased and decreased absorption features for a 4.5 ML CdSe NPL sample collected at 6 K for a sample as prepared then cooled (<3 hours between preparation and measurement) and subsequently aged for 4 weeks at room temperature. (b) Corresponding SAXS data for the same sample as prepared and after aging.



Figure S9. Normalized absorption spectra of solid film and methylcyclohexane dispersion of 5.5 ML CdSe NPLs.



Figure S10. (a) Measured frequencies of for phonon oscillations of all measured samples displaying such a feature. The dashed line indicates the expected change in frequency for a fixed k, based upon the average value of the 4.5 ML samples. (b) Estimated values of k for the oscillations from all measured samples. (c) k estimated for single unit cell columns, having exactly defined mass. The values are given per unit cell surface. (d) Temperature-dependent estimates of k for a sample of 4.5 ML CdSe NPLs.



Figure S11. SAXS patterns of 4.5 ML CdSe NPL sample collected at specified temperatures.



Figure S12. SAXS pattern of silver behenate.



Figure S13. Kinetic traces of the heavy-hole induced absorption and heavy-hole bleaching feature at several temperatures. Dashed lines indicate an exponential rise fit to the data.

### References

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