

Coupled HgSe colloidal quantum wells through a tunable barrier: a strategy to uncouple optical and transport band gap

Eva Izquierdo^{1,2}, Marion Dufour^{1,2}, Audrey Chu^{1,2,3}, Clément Livache^{1,2,3}, Bertille Martinez^{1,2,3}, Dylan Amelot³, Gilles Patriarche⁴, Nicolas Lequeux^{1,2}, Emmanuel Lhuillier³, Sandrine Ithurria^{1,2*}

¹ LPEM, ESPCI Paris, PSL Research University, CNRS, 75005 Paris, France

² Sorbonne Université, CNRS, LPEM, 75005 Paris, France

³ Sorbonne Université, CNRS, Institut des NanoSciences de Paris, INSP, F-75005 Paris, France

⁴ Centre de Nanosciences et de Nanotechnologies, CNRS - Université Paris Sud, Université Paris Saclay, route de Nozay, 91460 Marcoussis

*To whom correspondence should be sent: sandrine.ithurria@espci.fr

| | |
|---|----|
| 1. Absorption and TEM | 2 |
| 2. X-ray diffraction | 7 |
| 3. Energy dispersive X-ray..... | 8 |
| 4. Numerical simulation..... | 10 |
| 5. Transport measurements | 11 |
| 6. Transport properties of a mixture..... | 13 |
| 7. Time resolved measurements..... | 14 |
| 8. References..... | 15 |

1. Absorption and TEM

- Absorption spectroscopy

UV-visible spectrum have been acquired from a Shimadzu UV-1800 spectrometer.

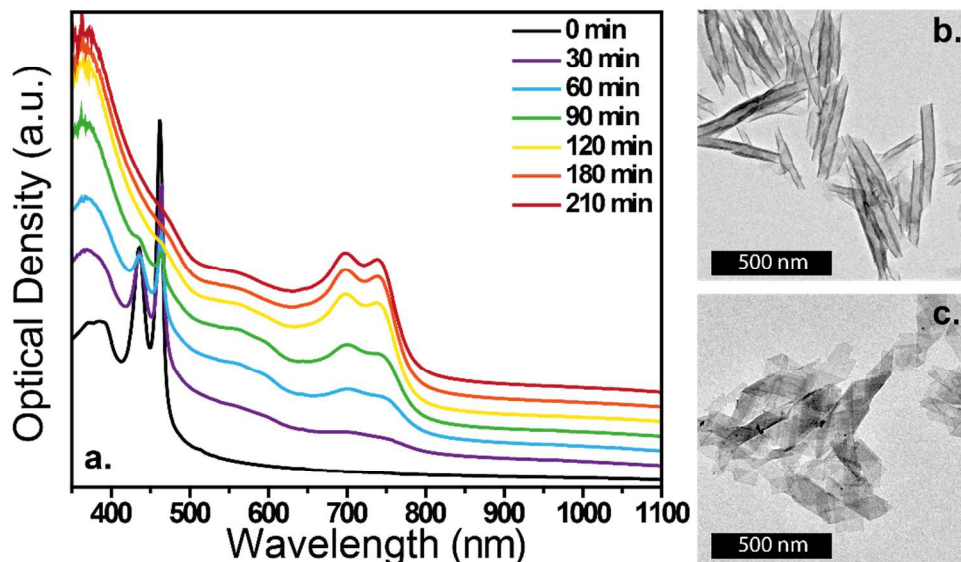


Figure S1: (a.) Absorption spectra from CdSe to HgSe NPLs cation exchange. (b.) TEM image of CdSe NPLs before cation exchange. (c.) TEM image of HgSe NPLs after cation exchange.

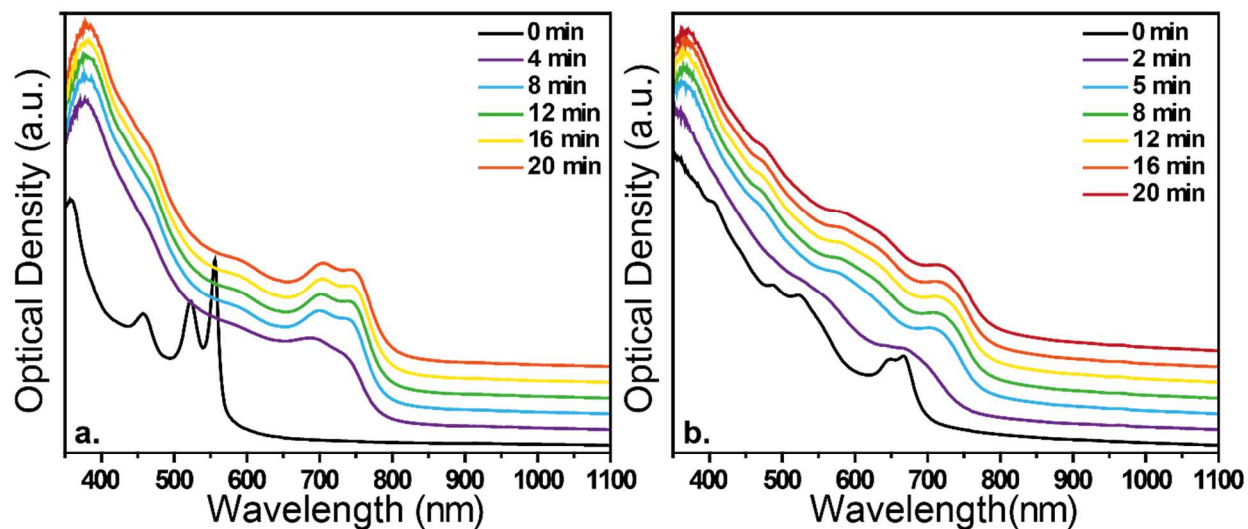


Figure S2: Absorption kinetics of cation exchange on (a.) 5 MLs CdSe NPLs and (b.) 11 MLs CdSe NPLs.

For each population of CdSe NPLs (from 3 MLs to 11 MLs), the cation exchange is monitored by absorption spectroscopy. In order to obtain the optical features and their error bar on both red and blue structure, we did as on the Figure S3.

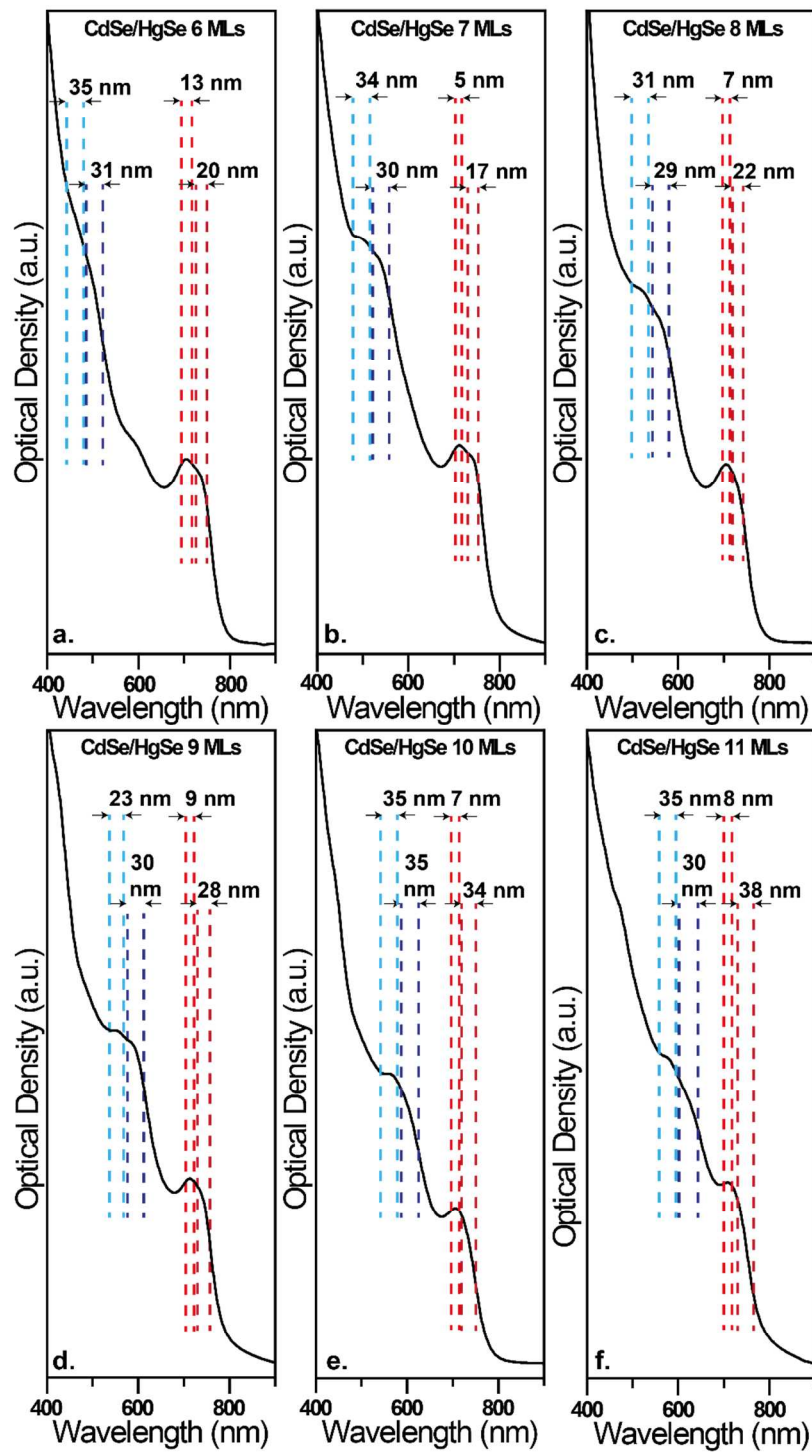


Figure S3: (a.-f.) Absorption spectra from 6 MLs to 11 MLs of CdSe/HgSe NPLs with error bars for first two peaks of two structures (blue and red).

- Transmission electronic microscopy (TEM)

For transmission electron image, the nanoparticles are dispersed in hexane and dropcast on a copper TEM grid. The grids are then degassed overnight under secondary vacuum. Images are acquired on a JEOL 2010 microscope operated at 200 kV. For the HAADF pictures, the TEM is a Titan Themis. The TEM images of 5, 7, 9 and 11 MLs CdSe and CdSe/HgSe NPLs are given on Figure S54. A preservation of the morphologies during the c-ALD and the cation exchange is observed. On 10 MLs CdSe/HgSe NPLs TEM BF image (respectively TEM HAADF-STEM image), 2 planes in each external side of the NPLs are darker (respectively brighter), corresponding to 2 planes of Hg (Figure S5).

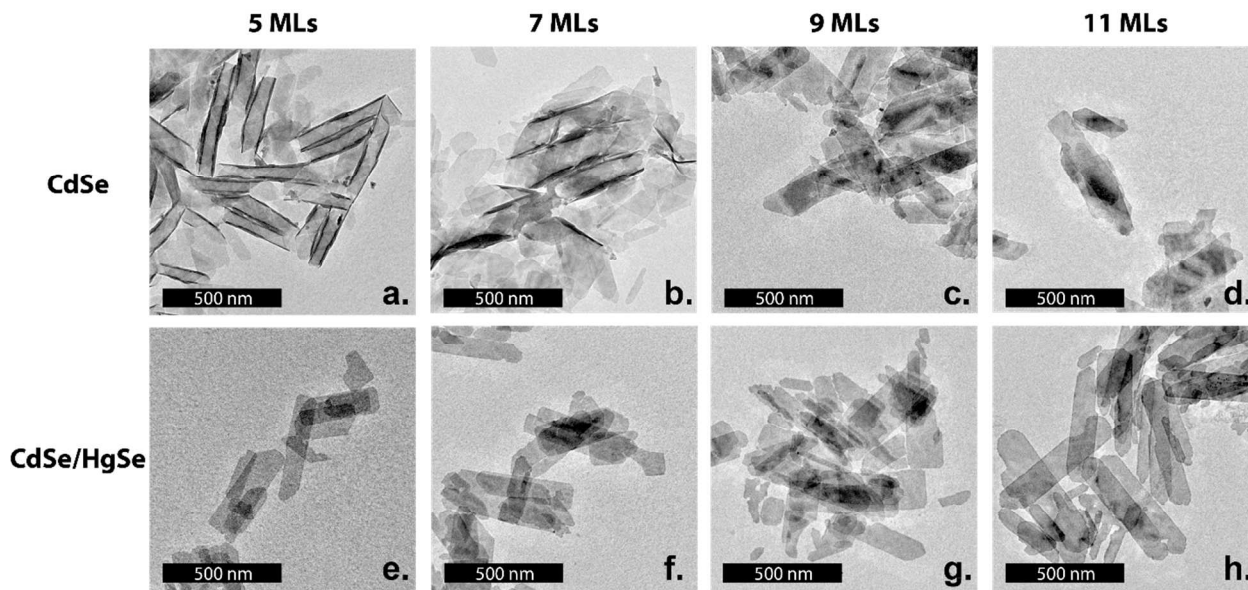
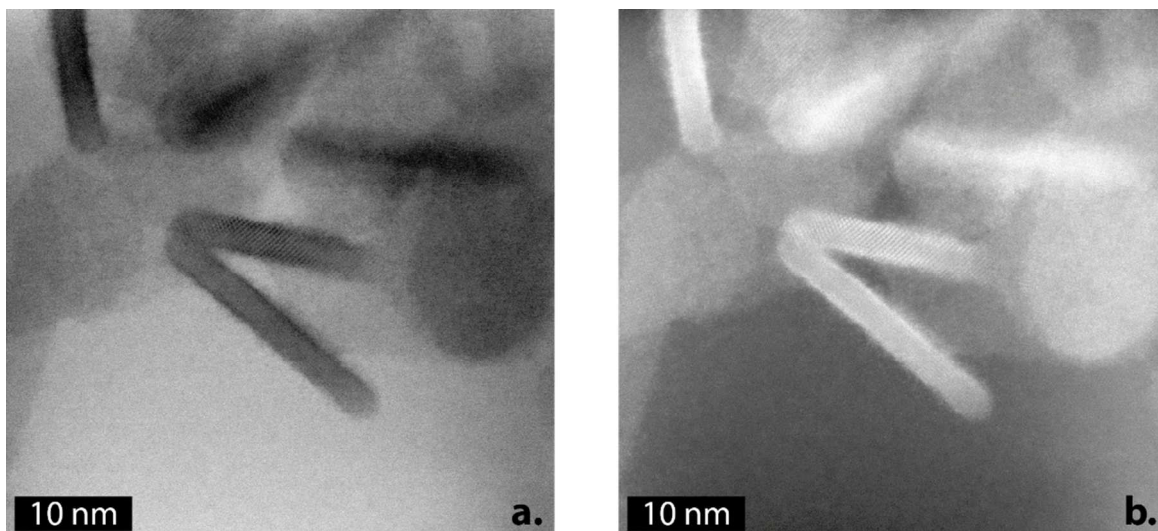
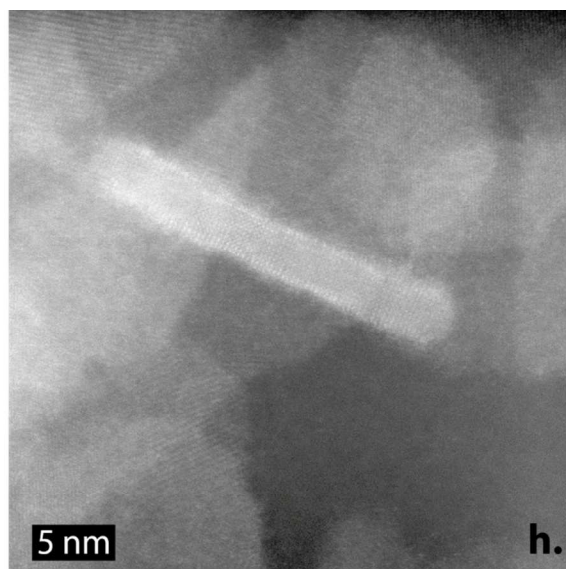
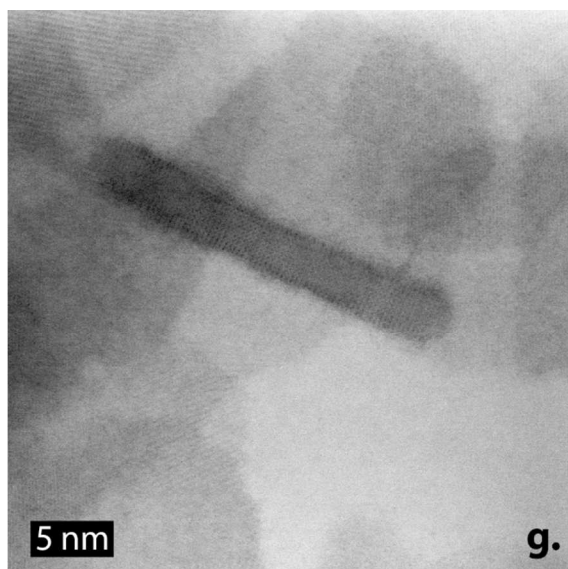
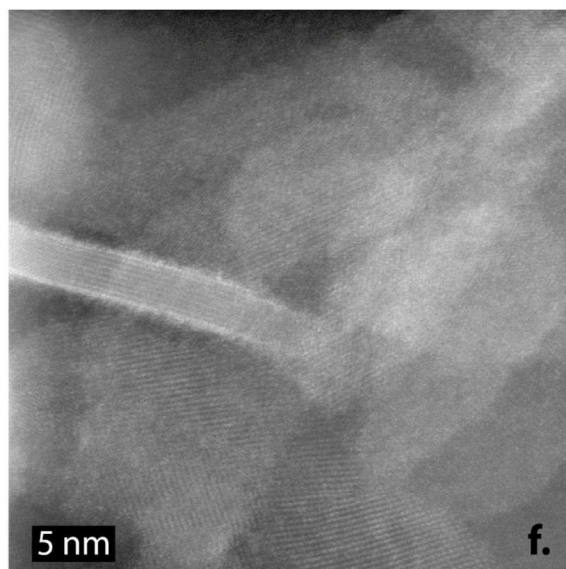
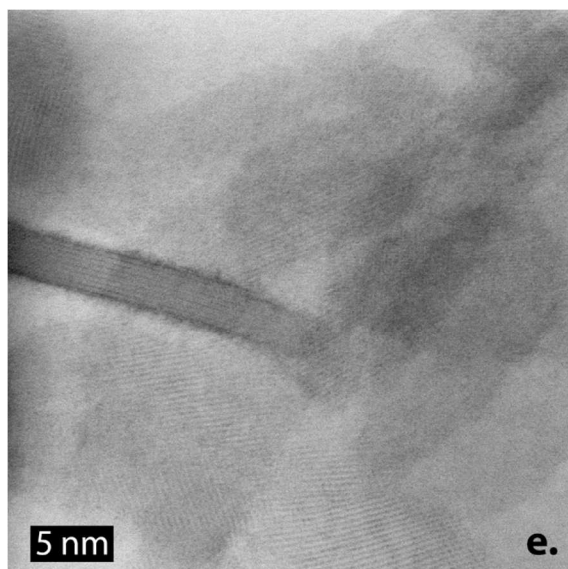
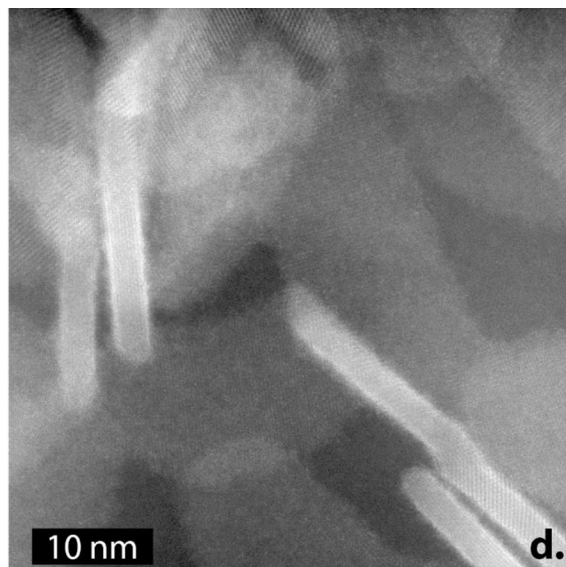
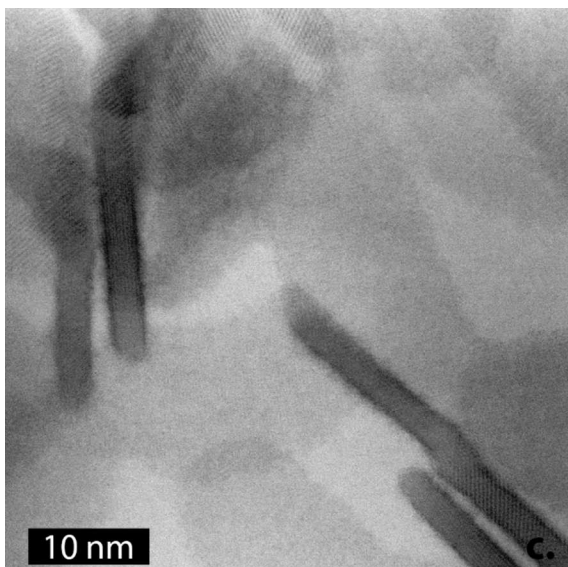


Figure S4: TEM images of (a.) 5 MLs CdSe NPLs, (b.) 7 MLs CdSe NPLs, (c.) 9 MLs CdSe NPLs, (d.) 11 MLs CdSe NPLs, (e.) 5 MLs CdSe/HgSe NPLs, (f.) 7 MLs CdSe/HgSe NPLs, (g.) 9 MLs CdSe/HgSe NPLs and (h.) 11 MLs CdSe/HgSe NPLs.





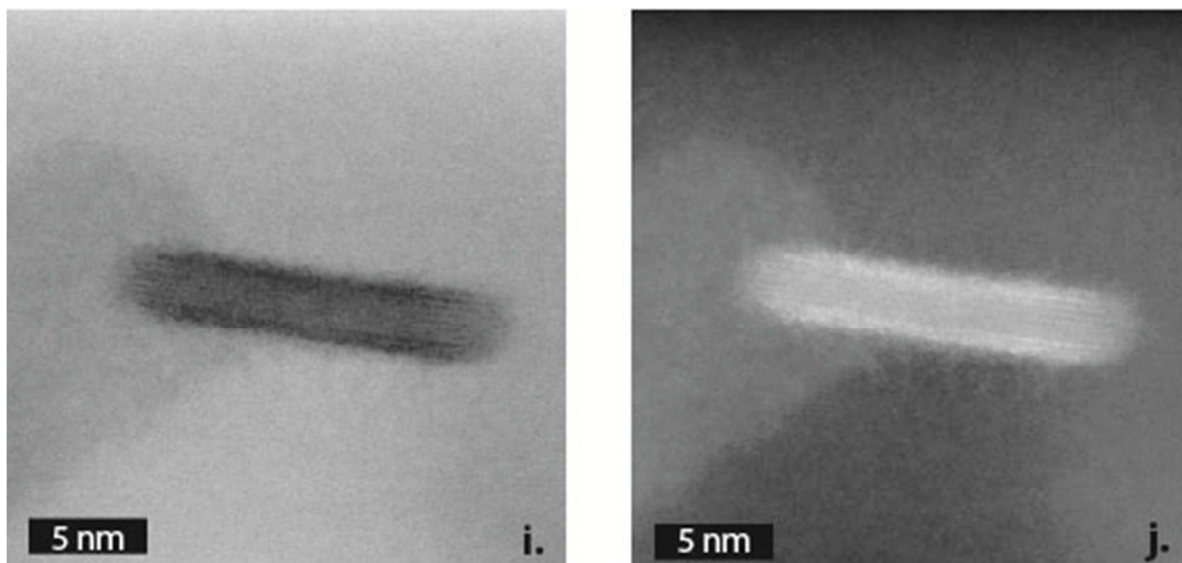


Figure S5: TEM bright-field (a., c., e., g., i.) and HAADF-STEM (b., d., f., h., j.) of 10 MLs CdSe NPLs

2. X-ray diffraction

X-ray diffraction is obtained by dropcasting the considered solution of NPLs on a Si wafer. The diffractometer is a Philips X'Pert based on the emission of the Cu K_α line at $\lambda=0.154$ nm, operated at 40 kV and 40 mA.

The XRD data are consistent with a zinc blende structure for both core and core-shell structure, see Figure S6. The diffraction peaks get narrower while the NPLs get thicker which is consistent with an increase of the crystallite size.

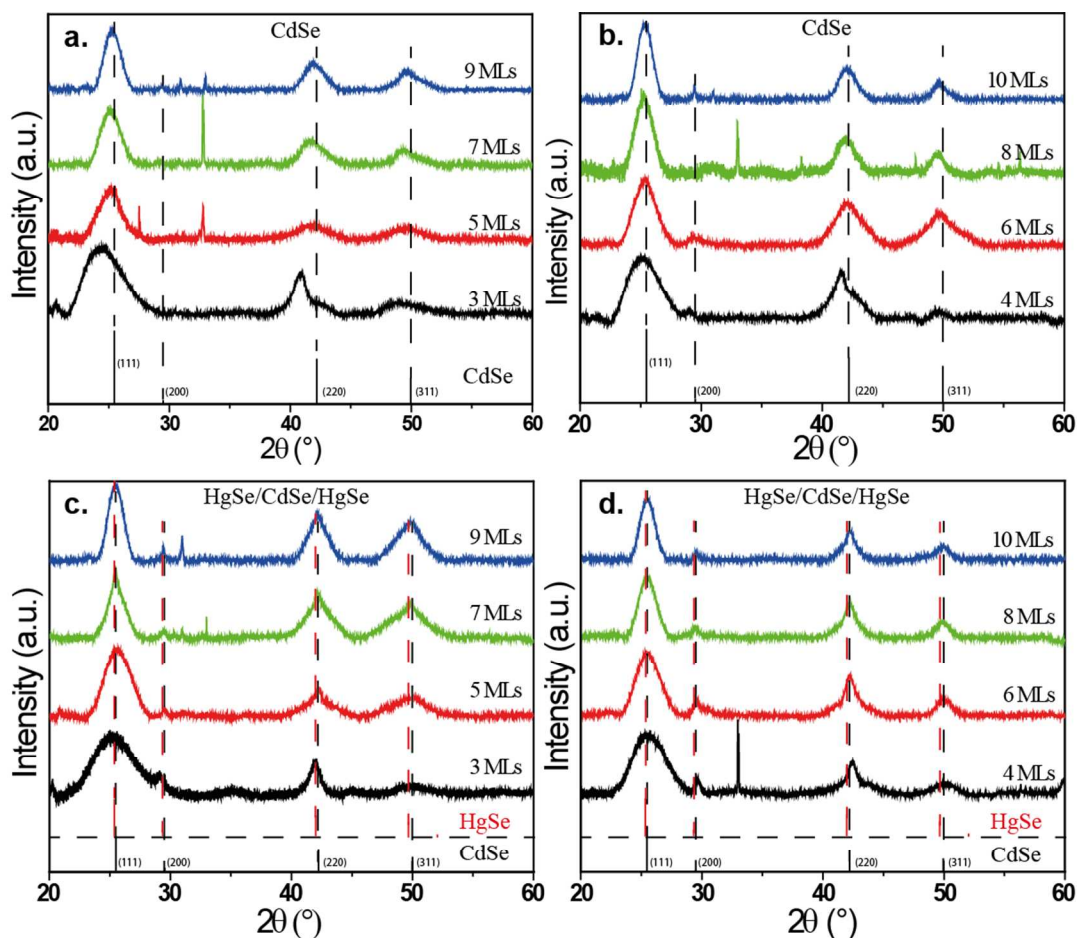


Figure S6: X-ray powder diffractograms of (a.) 3, 5, 7 and 9 MLs CdSe NPLs, the 5, 7 and 9 MLs are coming from the growth by c-ALD on 3 MLs CdSe NPLs, (b.) 4, 6, 8 and 10 MLs CdSe NPLs, the 6, 8 and 10 MLs CdSe are coming from the growth by c-ALD on 4 MLs CdSe NPLs, (c.) 3 MLs HgSe NPLs and 5, 7 and 10 MLs HgSe/CdSe/HgSe and (d.) 4, 6, 8 and 10 MLs HgSe/CdSe/HgSe NPLs.

3. Energy dispersive X-ray

Energy dispersive X-ray (EDX) analysis is conducted by depositing a solution of NPLs onto a conductive carbon patch. The sample is then introduced into a FEI Magellan scanning electron microscope and brought under secondary vacuum. The current of the beam is adjusted to 1.6 nA and the operating bias is set to 20 kV. The EDX analysis is obtained from an Oxford EDX probe. The EDX spectrum of 11 MLs CdSe and CdSe/HgSe NPLs thin films are obtained (see respectively Figure S7 a. and b.). The Table S1 summarizes the measured Cd/Hg stoichiometry of the 3 MLs HgSe NPLs and different CdSe/HgSe NPLs films. When the size of the starting CdSe NPLs increases, the ratio of Cd and Hg also increases. By using N MLs CdSe NPLs, the Cd:Hg ratio is N-4:4, corresponding to 2 planes of Hg on the external sizes of NPLs.

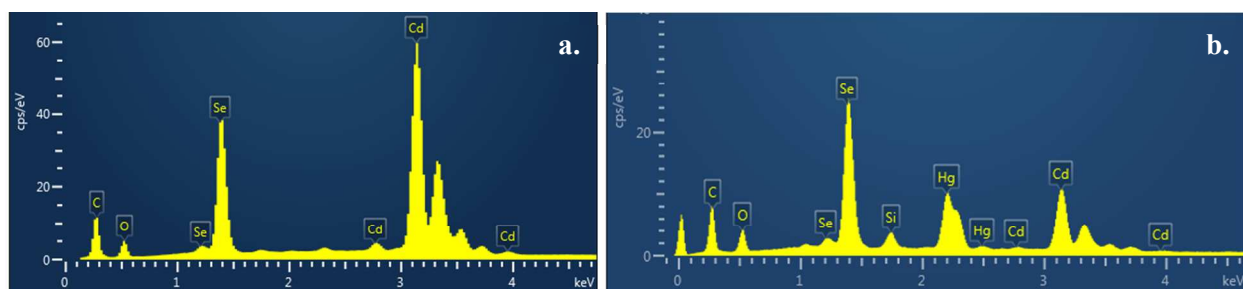


Figure S7: EDX spectrum of 11 MLs CdSe NPLs film before (a.) and after (b.) cation exchange.

| Sample | Cd ratio on cations content (%) | Hg ratio on cations content (%) | Experimental Cd:Hg ratios | Theoretical Cd:Hg ratios |
|------------------|---------------------------------|---------------------------------|---------------------------|--------------------------|
| HgSe 3 MLs | undetectable | 100 | 0:4 | 0:4 |
| CdSe/HgSe 4 MLs | 20 ± 2 | 80 ± 2 | 1(2):4 | 1:4 |
| CdSe/HgSe 5 MLs | 33 ± 2 | 67 ± 2 | 2(3):4 | 2:4 |
| CdSe/HgSe 6 MLs | 47 ± 2 | 53 ± 2 | 3.5(3):4 | 3:4 |
| CdSe/HgSe 7 MLs | 54 ± 2 | 46 ± 2 | 4.7(3):4 | 4:4 |
| CdSe/HgSe 8 MLs | 56 ± 2 | 44 ± 2 | 5.1(4):4 | 5:4 |
| CdSe/HgSe 9 MLs | 60 ± 2 | 40 ± 2 | 6(5):4 | 6:4 |
| CdSe/HgSe 11 MLs | 69 ± 2 | 31 ± 2 | 8.9(6):4 | 8:4 |

Table S1: Quantitative composition analysis on 3 MLs HgSe NPLs and CdSe/HgSe NPLs with different sizes of CdSe barrier thin films made from EDX.

4. Rutherford Backscattering Spectrometry (RBS)

Rutherford Backscattering Spectrometry has been used as a complementary analysis to EDX to determine the Hg/Cd stoichiometry on 5 MLs HgSe/CdSe/HgSe NPLs. To do so the SAFIR source of INSP was used with He^+ as ion accelerated under 1.8 MeV. The beam size is 1.5 mm^2 and the collection angle 165° . The He^+ beam current is operated at 50 nA. The energy calibration is done using a Bi implanted Si wafer with a $6.10^{15} \text{ cm}^{-2}$ dose.

From the backscattered yield, R is determined:

$$R = \frac{A_{\text{Cd}}}{A_{\text{Hg}}} \left(\frac{Z_{\text{Hg}}}{Z_{\text{Cd}}} \right)^2$$

A_{Hg} denotes the area of the peak resulting from backscattering at Hg atoms, A_{Cd} equals the area of the Cd peak, and Z_{Hg} and Z_{Cd} are the atomic number of Hg and Cd, respectively.

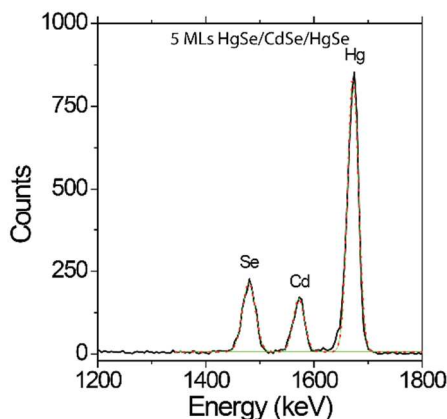


Figure S8: RBS spectrum of 5ML HgSe/CdSe/HgSe NPLs

| Sample | RBS Cd :Hg ratio | EDX Cd :Hg ratio | Theoretical Cd:Hg ratios |
|-----------------|---------------------|---------------------|-----------------------------|
| CdSe/HgSe 5 MLs | 2.22:4 | 2(3):4 | 2:4 |

Table S2: Quantitative composition analysis on 5 MLs HgSe/CdSe/HgSe NPLs and comparison with EDX results.

5. Numerical simulation

The shooting method is a numerical resolution of the Schrodinger equation and is extensively described in the book by Harrison¹ and applied to 2D NPL in ref^{2,3}. The basic idea of the method is to start from the

time independent Schrödinger equation $\left[-\frac{\hbar^2}{2} \frac{d}{dz} \frac{1}{m^*(z)} \frac{d}{dz} + V(z) \right] \psi(z) = E \psi(z)$, with \hbar the reduced

Planck constant, $m^*(z)$ the mass profile, $V(z)$ the potential profile of the considered band, E the eigen energy and $\psi(z)$ the wavefunction magnitude. The equation is then spatially discretized choosing a small step (0.1 nm in our case)

$$\frac{\psi(z+dz)}{m^*(z+dz/2)} = \left[\frac{2}{\hbar^2} dz^2 (V(z) - E) + \frac{1}{m^*(z+dz/2)} + \frac{1}{m^*(z-dz/2)} \right] \psi(z) - \frac{\psi(z-dz)}{m^*(z-dz/2)}$$

From this equation we can determine the wavefunction magnitude at position z if we know its value at the two previous step. Additionally we set $\psi(0) = 0$ which means that the wavefunction is null outside of the confined structure and $\psi(1) = 1$. This second condition is arbitrary and the value of 1 will then be corrected by normalizing the wavefunction.

The external environment of the NPL is modeled as a tunnel barrier. Its band offset with the HgSe is set at 4 eV both for conduction and valence band. The length of this barrier is 2 nm.

The HgSe hole effective mass is set at $m_h^* = 0.78 m_0$ according to literature value.⁴ The electron effective mass is known to be smaller in HgSe than the hole mass, thus its determination is more critical. Here the electron effective mass is determined, in order that using the described environment and hole effective mass, the obtained theoretical value for the first energy transition leads to the best experimental fit, we obtain a value of $m_e^* = 0.107 m_0$. Then, this model is neglecting any non parabolicity effect.³ Similarly the model neglects dielectric confinement, charge mirror effect and strain effect.

6. Transport measurements

- Electrode fabrication

Electrodes are fabricated using standard optical lithography methods. Briefly the surface of a Si/SiO₂ (400 nm thick) wafer is cleaned by sonication in acetone. The wafer is rinsed with isopropanol and finally cleaned using a O₂ plasma. AZ5214 resist is spin-coated and baked at 110°C for 90 s. The substrate is exposed under UV through a pattern mask for 1.5 s. The film is further baked at 125°C for 2 min to invert the resist. Then a 40 s flood exposure is performed. The resist is developed using a bath of AZ726 for 32 s, before being rinsed with pure water. We then deposit a 5 nm Cr layer and a 80 nm gold layer using a thermal evaporator. The lift-off is performed by dipping the film for 1 h in acetone. The electrodes are finally rinsed using isopropanol and dried by air flow. The electrodes are 2.5 mm long and spaced by 20 μ m. These electrodes are used for DC measurements (IV curves and transistor measurements).

- Electrolyte preparation

50 mg of LiClO₄ are mixed with 230 mg of PEG on a hot plate in an Ar filled glove box at 170°C for 2 h.

- Transistor fabrication

We start from a solution of HgSe NPLs (or HgSe/CdSe NPLs) capped with oleylamine ligands. To exchange the ligands on the surface, 30 μ L of a solution of S²⁻ (NaSH in NMF at 0.1 M) is added to the NPLs. The solution is vigorously stirred up to the complete precipitation of the NPLs. Then 500 μ L of NMF are added to resuspend the precipitated NPLs. These one in NMF phase should be limpid however if it's not the case, sulfur solution should be added to the biphasic medium. After removing the hexane phase, the NPLs in NMF are washed with hexane. Finally, the NPLs are precipitated and suspend in 350 μ L of NMF.

In an air free glove box, the solution is dropcasted onto the electrodes on a hot plate at 100°C. Once the film is dried, the warm electrolyte (hot plate at 100°C for 3 minutes) is brushed on the film. The device is let cooled down until the electrolyte get whitish. Then, a metallic grid is deposited and used as a top gate.

- Transistor measurements

Electrical measurements are conducted in air using two Keithley 2400 as source-meters. To investigate the influence of CdSe barrier size on electronic properties, the drain-current (I_{DS}) as a function of gate-source voltage V_{GS} is measured. Transistor measurements are conducted by biasing the drain source under low bias (100 mV). The gate step bias is 1 mV.s⁻¹ for electrolyte gating. More V_{GS} is negative (respectively positive), more the Fermi level energy increases (respectively decreases) and electrons (respectively holes) are injected in the system. The transfer curves obtained for CdSe/HgSe heterostructure with various sizes of CdSe barrier in the core are given in Figure S9. For all populations after cation exchange, the conductance increases as electrons are injected (as n-type channel). However, more the CdSe barrier size in NPLs increases, more the threshold increases.

- DC transport

Electrical measurements are obtained in air from a Keithley 2400 which controls the drain bias (V_{DS}) between -10 and + 10 V with a step of 50 mV and measures the associated current (I_{DS}). This measurement is made in the dark and under illumination (green diode, 532 nm, 0.13 mW).

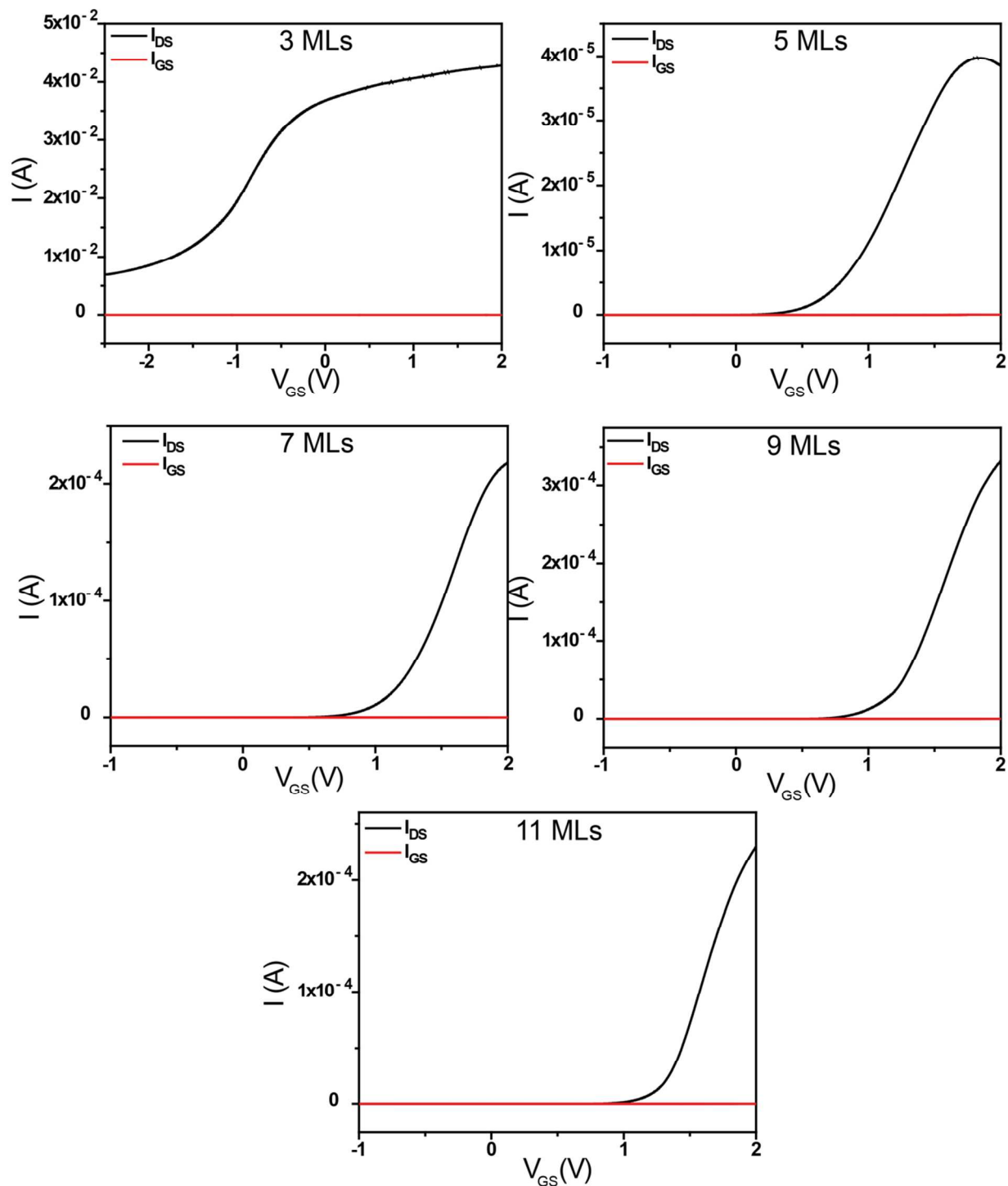


Figure S9: Transfer curves (drain current as a function of gate bias) for (a.) a 3 MLs HgSe NPLs thin film capped with S^{2-} and for (b.-e.) CdSe/HgSe NPLs (with an odd number of MLs) thin film capped with S^{2-} . NPLs films are used as an ion gel gated transistor ($V_{DS} = 100$ mV).

7. Transport properties of a mixture

One may wonder rather the transport properties of the heterostructure are the result of some effect at the single particle level or if actually a mixture of CdSe NPL and HgSe NPL with a similar ratio of the two material leads to similar results. We prepare a mixture made of 3 MLs HgSe and 3 MLs CdSe NPLs in a 1:1 ratio. The absorption spectrum associated to this mixture is given in Figure S10a in green. When it comes to transport, we observe that the mixture is actually behaving as pure HgSe with a very limited photoresponse ($G_{\text{light}}/G_{\text{dark}}$ between 1 and 2 while repeating the measurements over several samples, see Figure S10b) and a transistor curve with a negative threshold voltage, see Figure S10c. In this sense the mixture is behaving as if CdSe NPLs were not there, HgSe NPLs are the only active materials.

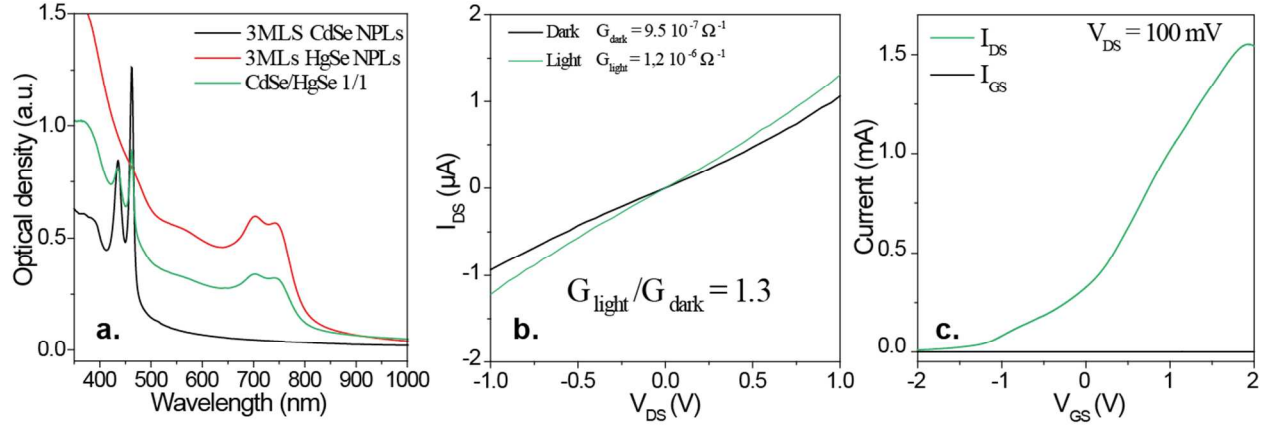


Figure S10: (a.) Absorption spectra of 3 MLs CdSe NPLs (black curve), 3 MLs HgSe NPLs (red curve) and a 1:1 ratio of 3 MLs CdSe and HgSe NPLs (green curve) (b.) IV curve under dark condition and under illumination for a film made of a 1:1 ratio of 3 MLs HgSe and CdSe NPLs mixture. (c.) Transfer curve (drain and gate current as a function of the applied gate bias) for a film made of a 1:1 ratio of 3 MLs HgSe and CdSe NPLs mixture. The applied drain source bias is 0.1 V. All measurements have been done in air at room temperature.

8. Time resolved measurements

- PET/ITO electrodes fabrication

The surface of a PET/ITO wafer is cleaned by rinsing with acetone and isopropanol. The AZ 5214E resist is spin-coated and baked at 110°C for 90 s. The substrate is exposed under UV through a pattern mask for 4 s. The resist is developed using a bath of AZ 326 for 45 s, before being rinsed in pure water. Then we proceed to the etching of the electrodes by dipping the substrate in 25% HCl for 10 s and rinsing with pure water to quench. Finally, the electrodes are rinsed using isopropanol and dried by an air flow. The electrodes are 1 mm long and spaced by 50 μm . These electrodes are used for transient photocurrent measurements. Transparent electrodes are used to avoid any heating effect of the photoresponse which tends to introduce drift.

- Time-resolved measurements

To make these measurements, a pulsed laser (Crylas FTSS 355-50) at 355 nm are used. To prevent excessive heating of the sample which may lead to a drift of the photoresponse, the laser beam is around 1 mm in diameter (i.e., poorly focused). The pulse are 1 ns long and repeated every 10 ms (100 Hz). A photodiode is used to trigger the signal. The sample is placed in a vacuum chamber. The bias, 30 V is applied by a Keithley 2432b. The bias is higher than the applied electric field for transistor measurement in order to boost the signal. Nevertheless, the photoconductance of the system is bias independent, see Figure S11. An oscilloscope (Rohde & Schwarz, RTE 1102) acquired the outcoming signal through a 50 Ω resistor, which is proportional to I_{DS} .

The response of the film is measured at different time scales, normalized, on 3 MLs HgSe NPLs and CdSe/HgSe NPLs with different sizes of CdSe barrier. These obtained curves are plotted in log-log scales, see Figure S11 and S12, and the transient photocurrent decay time is extracted by a biexponential (Figure S512d.)

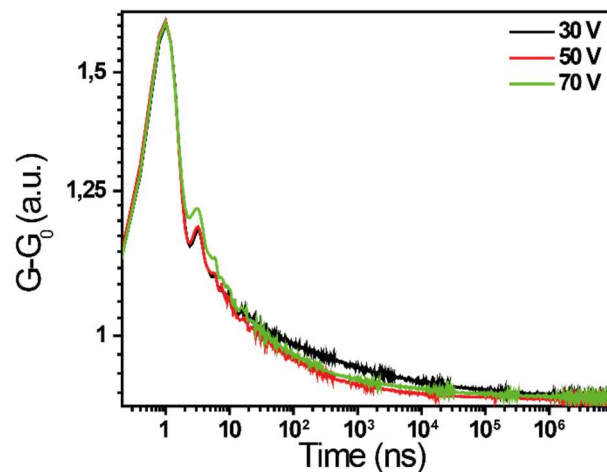


Figure S11: Influence of the bias (30 V, 50 V and 70 V) on the transient photocurrent on 3 MLs HgSe NPLs.

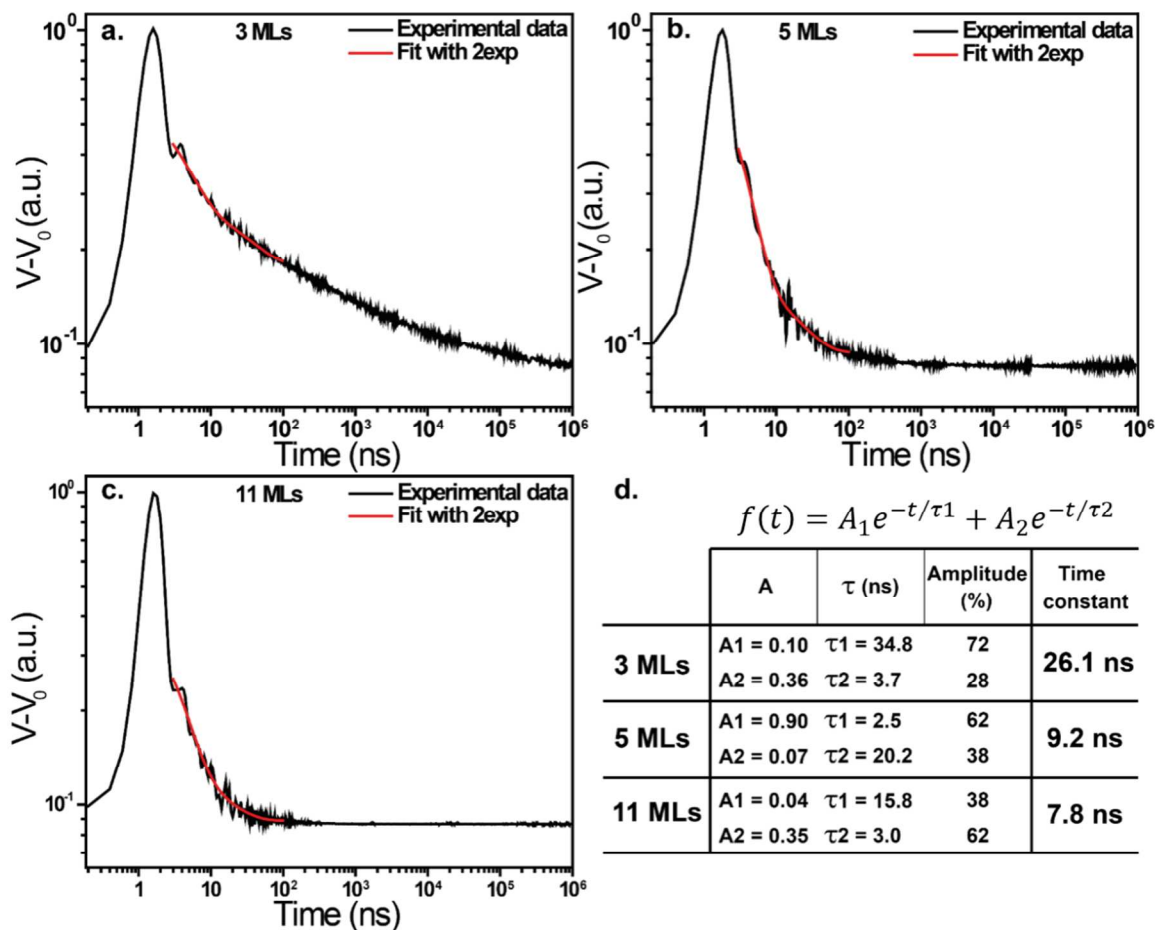


Figure S12: Typical conductance curves for films of (a.) 3 MLs HgSe NPLs, (b.) 5 MLs CdSe/HgSe NPLs and (c.) 11 MLs CdSe/HgSe NPLs capped S²⁻ as a function of time after its illumination by 1 ns pulse of light at 355 nm.

9. References

- (1) Harrison, P. *Quantum Wells, Wires and Dots*, 2nd Editio.; Wiley, 2005.
- (2) Chu, A.; Livache, C.; Ithurria, S.; Lhuillier, E. Electronic Structure Robustness and Design Rules for 2D Colloidal Heterostructures. *J. Appl. Phys.* **2018**, *123* (035701), 1–6.
- (3) Cruguel, H.; Livache, C.; Martinez, B.; Pedetti, S.; Pierucci, D.; Izquierdo, E.; Dufour, M.; Ithurria, S.; Aubin, H.; Ouerghi, A.; Lacaze, E.; Silly, M. G.; Dubertret, B.; Lhuillier, E. Electronic Structure of CdSe-ZnS 2D Nanoplatelets. *Appl. Phys. Lett.* **2017**, *110* (152103), 1–5.
- (4) Lehoczky, S. L.; Broerman, J. G.; Nelson, D. A.; Whitsett, C. R. Temperature-Dependent Electrical Properties of HgSe. *Phys. Rev. B* **1974**, *9* (4), 1598–1620.