

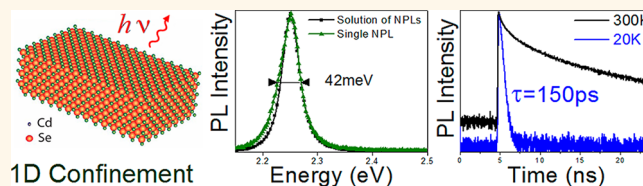
Spectroscopy of Single CdSe Nanoplatelets

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The spectroscopy of a single molecule has led to the observation of new effects^{1–3} and to direct measurements of the influence of the molecule's environments.⁴ Semiconductor single nanoparticle spectroscopy is limited because the nanoparticles observed so far, as quantum dots or nanorods, have slightly different composition, shape, or surface atoms. These differences prevent a complete decoupling between fluctuations due to the nanoparticle composition from the ones due to the environment. Recently, semiconductor nanoplatelets (NPLs) with a thickness controlled to atomic precision have been synthesized.^{5–7} These colloidal objects have 1D confinement, and they show identical thickness and composition at least in the direction of highest confinement. These NPLs thus offer an interesting opportunity to study the effect of the environment on the nanoparticle fluorescence emission, independently of the particle composition. The 1D confined nanoparticles with two different crystal structures, wurtzite and zinc blende, have been synthesized. Wurtzite crystal type structures have the shape of nanoribbons and have been obtained by an amine-rich reaction pathway through a lamellar assembly growth mechanism.^{8,9} The top and bottom faces of these wurtzite nanoribbons are terminated with a mixture of anions and cations. These structures have, in general, large lateral dimensions (~ 100 nm), tend to aggregate in solution, and single ribbon spectroscopy is a difficult task.¹⁰ On the other hand, zinc blende crystal type structures have their thickness in the 100 direction, and their top and bottom surfaces are uniformly terminated with cadmium atoms, passivated with carboxylate alkyl groups. These NPLs have tunable lateral dimensions from a few nanometers to a few tens of nanometers,¹¹ and they can be dispersed in hexane in low concentration without noticeable aggregation. These NPLs have recently been synthesized in CdSe, CdS, and CdTe with different thicknesses for

ABSTRACT



We collect and resolve spectrally and temporally the photoluminescence of single CdSe nanoplatelets. The emission intensity of single nanoplatelets at room temperature shows ON and OFF periods with a usual blinking statistics, while at 20 K, their emission intensity can be extremely stable in time. At room temperature, the emission spectra of single nanoplatelets are similar to ensemble measurements with a full width at half-maximum of 40 meV. At 20 K, we obtain a resolution-limited spectral line width (<0.4 meV). The fluorescence lifetime of single nanoplatelets decreases when the temperature decreases to reach 200 ps at 20 K. This lifetime shortening is concomitant with an increase of the nanoplatelets' emission intensity.

KEYWORDS: single nanocrystals · quantum wells · photoluminescence · lifetime · blinking

each material.⁶ Their quantum yield can reach 50%.

In this work, we have used zinc blende type NPLs with an emission peaking at 551 nm. These NPLs have been synthesized as described in Ithurria *et al.*⁶ A transmission electron microscope image of these NPLs is presented in Figure 1a. Their lateral dimensions are 8 ± 2 nm by 35 ± 5 nm, their thickness is ~ 2 nm, and their quantum yield in solution is close to 50%. Such high quantum yield confirms that the surface of these NPLs is well-passivated by the carboxylate ligands. Emission and absorption spectra in solution are presented in Figure 1b. The absorption spectrum is similar to the one expected for colloidal quantum wells with infinite barriers. The first two transitions, respectively, at 551 and 520 nm correspond to the heavy hole and the light hole transitions. The emission spectrum of these NPLs is maximum at 551 nm with full width at half-maximum (fwhm) of 8.5 nm (35 meV). The emission Stokes shift is very small

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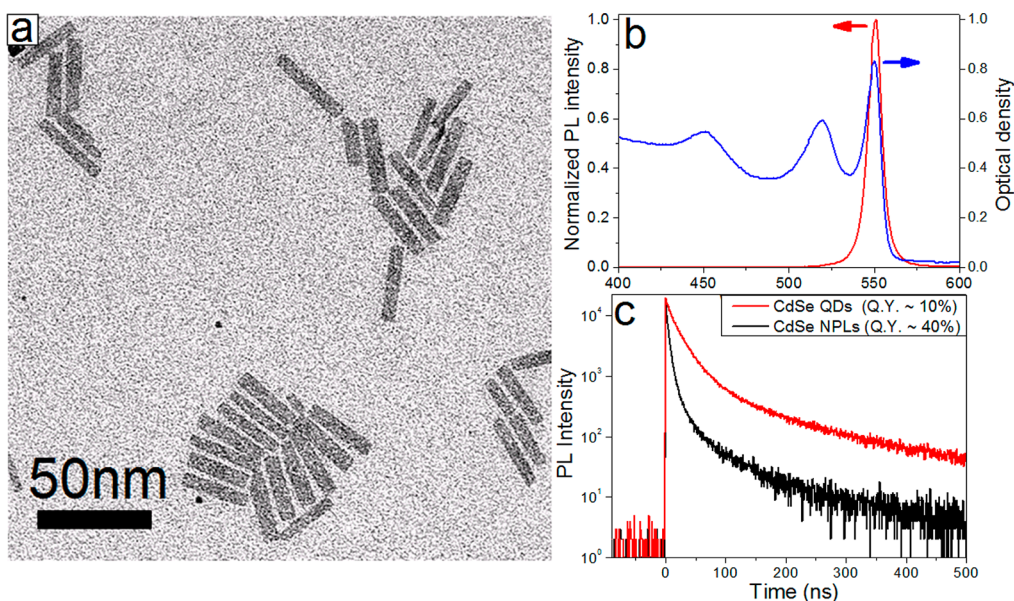


Figure 1. (a) Transmission electron microscopy image of NPLs with homogeneous thickness. (b) Absorption (blue) and PL spectrum (red) of a solution of NPLs. (c) Intensity decay of CdSe QDs emitting at 545 nm with 10% quantum yield and of the CdSe NPLs emitting at 551 nm with 40% quantum yield. All measurements were done at room temperature in hexane.

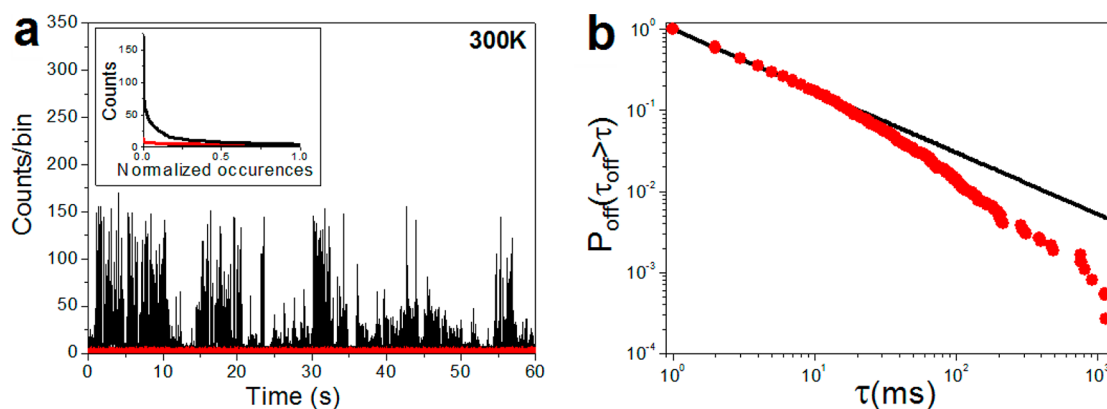


Figure 2. (a) Emission time trace of a single NPL at room temperature (black) and corresponding background noise (red). The time trace is binned at 1 ms. Excitation intensity = $250 \text{ W} \cdot \text{cm}^{-2}$, repetition rate = 5 MHz. Inset: Normalized intensity distribution for the NPL time trace (black) and the background noise (red). (b) Corresponding cumulative distributions of OFF times in a logarithmic scale (red points). The solid line is a power-law distribution of parameter 0.76.

(~ 1 nm) compared to quantum dots (~ 10 nm). Interestingly, the fluorescence lifetime of these NPLs with 40% quantum yield is much shorter than the one of CdSe spherical quantum dots with 10% quantum yield (see Figure 1c). We evaluated the NPLs' absorption cross section at 400 nm in hexane to $\sim 2.5 \times 10^{-13} \text{ cm}^2$ (see Supporting Information), a value 1 order of magnitude larger than that for spherical CdSe QDs emitting at the same wavelength.¹² The high quantum yield and the good dispersion of our NPLs suggested that single NPL spectroscopy is possible.

RESULTS AND DISCUSSION

We first studied the emission intensity of CdSe single NPLs at room temperature. The NPLs were diluted in a mixture of 90% hexane/10% octane, drop-casted on a microscope cover slide, and observed on an inverted

fluorescence microscope. With a mercury lamp for the excitation, and a suitable set of fluorescent filters (see Materials and Methods), single NPLs could easily be visualized with bare eyes through the microscope ocular (see Figure 2a). The first observation is that the intensity emission of single NPLs *versus* time fluctuates between complete dark states, so-called OFF states, and emitting states, or ON states, with a large range of intensities. This blinking of the emission intensity has been reported for a wide range of inorganic nanoparticles,¹³ as well as organic molecules¹⁴ when observed at the single particle level. The observation that the NPL emission blinks confirms that we are observing single NPLs on a glass surface. A typical intensity trace of single NPL is reported Figure 2b. During a 60 s observation time, the single NPL displays bursts of fluorescent emission spaced with dark periods. The emission

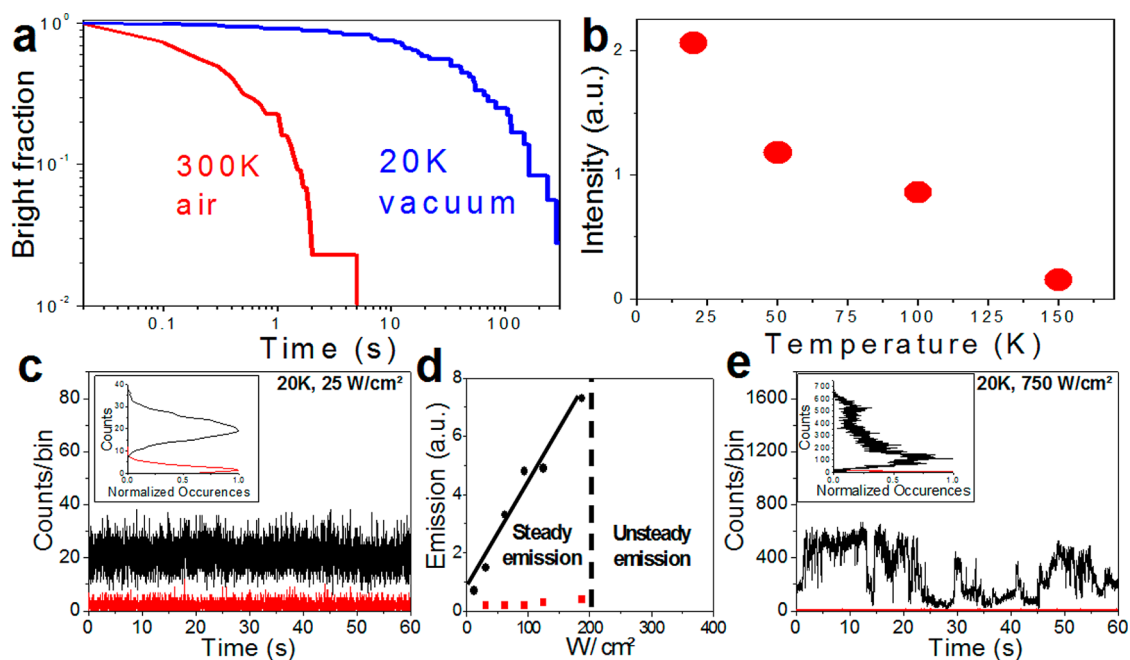


Figure 3. (a) Global bright fraction in a log–log scale of a sample of 34 NPLs at 20 K (blue line) and of a sample of 33 NPLs at 300 K (red line). Excitation power = $10 \text{ W} \cdot \text{cm}^{-2}$. (b) Temperature dependence of the intensity of NPLs averaged over ~ 50 NPLs. Under vacuum, the NPLs' emission intensity is too weak to be measured under the same condition for temperatures higher than 150 K. (c) Emission time traces and corresponding normalized intensity distribution (inset) of a NPL at 20 K excited with a pulsed diode at $25 \text{ W} \cdot \text{cm}^{-2}$. (d) Red points: emission intensity vs excitation power of a single NPL. Black square: background noise. (e) Same as in c, with an excitation power of $750 \text{ W} \cdot \text{cm}^{-2}$. The time traces are binned at 10 ms. Laser repetition rate: 40 MHz. Black color is for NPL signals, and red color is for background noises in the same experimental conditions.

intensity histogram of a single NPL (inset of Figure 2b) shows that the NPL has a continuous distribution of intensities for the ON states, and that it spends most of its time close to the noise level, that is, close to the dark state. This broad intensity distribution has also been observed for other shapes of nanoparticles, including CdSe QDs,¹⁵ nanorods,¹⁶ or quantum wires,¹⁷ and has been interpreted by a broad distribution of energy for the surface trap states. The intermittency of a single nanocrystal emission can be characterized more precisely with the statistical properties of the duration τ_{off} of dark periods.¹⁵ The cumulative distribution of the duration of dark states, that is, the probability $P_{\text{off}}(\tau_{\text{off}} > \tau)$ of detecting a dark period of duration greater than τ , is plotted Figure 2c. A NPL is considered to be in a dark state if its intensity drops below $\langle M \rangle + 4\sigma$, where $\langle M \rangle$ is the average intensity of a region without NPLs and σ its standard deviation. The cumulative distribution of OFF states follows a heavy-tailed power-law distribution, $P_{\text{off}}(\tau_{\text{off}} > \tau) \propto 1/(\tau^\mu)$, with $\mu = 0.76$. This statistical behavior is similar to the one reported for other semiconductor structures^{15,18} and is explained using fast Auger processes with charges that are close to the nanoparticle surface and that quench the fluorescence emission. We have studied the blinking behavior of several tens of single NPLs at room temperature, and the OFF state statistics are always described with a heavy-tailed power-law distribution. The fraction of single NPLs that do not blink once decreases rapidly. Under continuous excitation,

after 1 s of excitation, more than 90% of the NPLs have blinked at least once (Figure 3a). We conclude from these experiments that the blinking behavior of single CdSe nanoparticles is similar, regardless of their geometry (sphere,^{4,15} rod,¹⁶ or NPL).

The fluorescent emission of single NPLs at 20 K is presented Figure 3. For low-temperature measurements, the NPLs are first spread on a sapphire coverslip and observed at room temperature in air. The coverslip is then mounted on an oxford cryostat. We first observe the NPLs with the cryostat filled with air. The NPLs are clearly visible and blink as reported in Figure 2. When we pump the air out of the cryostat, the NPLs' fluorescence intensity strongly decreases and cannot be detected even with our CCD camera. This gas-dependent fluorescence quenching can be connected to the influence of water and/or oxygen on the trapping/detrapping of the surface states.¹⁹ It is reversible: when the cryostat is filled again with air, the NPLs' fluorescence can be detected again. The fluorescence intensity of single NPLs starts to be detectable on our set up at 150 K. From 150 down to 20 K, the average NPL fluorescence emission intensity, averaged for ~ 50 single NPLs, increases steadily and almost linearly with temperature (Figure 3b). At 20 K, NPLs are bright and their blinking behavior has dramatically changed. For example, the bright fraction of NPLs decreases 100 times slower at 20 K than at 300 K (Figure 3a). Some NPLs have very stable fluorescence emission intensity for at

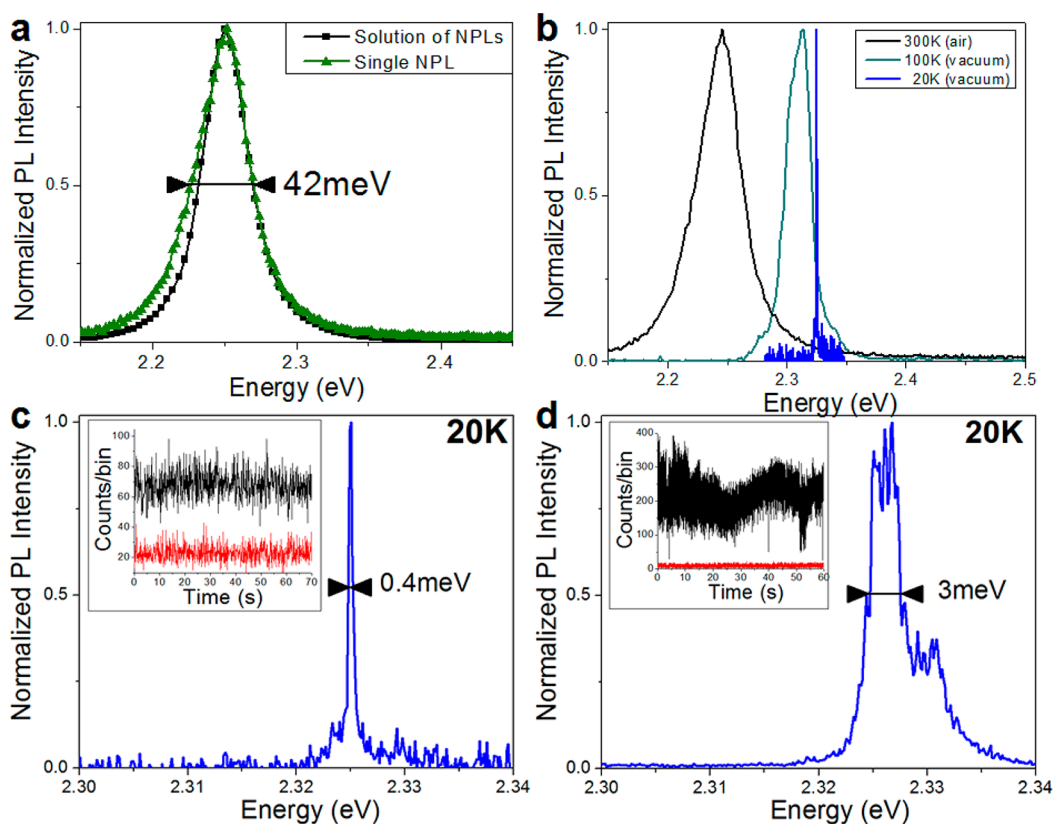


Figure 4. (a) Room temperature photoluminescence spectra of a solution of NPLs and of a single NPL under air on a glass substrate excited at $250 \text{ W} \cdot \text{cm}^{-2}$. (b) Evolution with temperature of the photoluminescence spectrum of single NPLs between 300 and 20 K. (c) PL spectrum of a single NPL excited at $20 \text{ W} \cdot \text{cm}^{-2}$. Inset: Corresponding emission time trace binned at 10 ms. (d) PL spectrum of the same single NPL as in Figure 3c excited at 1250 W/cm^2 . Inset: Corresponding emission time trace binned at 10 ms.

least 60 s when pumped at low intensity ($25 \text{ W} \cdot \text{cm}^{-2}$) (Figure 3c). Similar behavior has been observed for quantum dots.²⁰ The emission intensity histogram of these NPLs is well-fitted with a Poissonian distribution, which further suggests that these NPLs are in one emitting state only. The emission intensity of this kind of NPL increases linearly with the excitation intensity up to a threshold that depends on the NPL observed. In Figure 3d, the NPL observed has a steady emission for excitation powers ranging from 10 to $200 \text{ W} \cdot \text{cm}^{-2}$. At higher excitation power, the emission intensity of the NPL starts to fluctuate, indicating that several emitting states are visited during its emission.²¹ The appearance of these fluctuations points to a photoactivated process that may be related to the generation of multiple excitons in the NPL and/or to the photo-oxidation of some of its surface ligands. For some NPLs, the OFF state is never visited at low temperature. For others, even at the lowest possible excitation power, unsteady emission was observed (Figure S1 in the Supporting Information). These differences between the time traces for single NPLs at low temperature suggest that, although the NPLs all have exactly the same thickness and roughly the same lateral dimensions, their ligand coverages and/or the atoms at their rim fluctuate from one NPL to the other. These slight changes in surface passivation are

sufficient to induce important differences in the NPL emission time trace.

We compared at room temperature the emission spectrum of our CdSe NPLs suspended in hexane in a quartz cuvette with the emission spectrum of a single NPL on a glass surface in air (Figure 4a). Interestingly, the emission spectrum of the single NPL coincides very well with the ensemble measurement. The full width at half-maximum (fwhm) of the ensemble spectrum is 35 meV, the one of a single NPL is 42 meV; both have the same emission maximum. In the case of spherical CdSe/ZnS core/shell QDs, the fwhm of a single QD has been measured to be around 50 meV,²² while ensemble measurements routinely give a fwhm of around 100 meV.²³ Surprisingly, the fwhm of a single NPL is larger than the ensemble measurement. This suggests that, under air, a single NPL has several emitting states with different positions of the emission maximum. These various emitting states can result from ligand rearrangements, from neighboring charge relocation² (Stark effect), from reversible interaction of the NPL surface with H_2O and/or O_2 ,¹⁹ or from the photo-oxidation of the NPL under intense excitation.²² The emission spectra of more than 30 NPLs from the same sample were recorded. We found emission spectra similar to the one presented in Figure 4a with slight

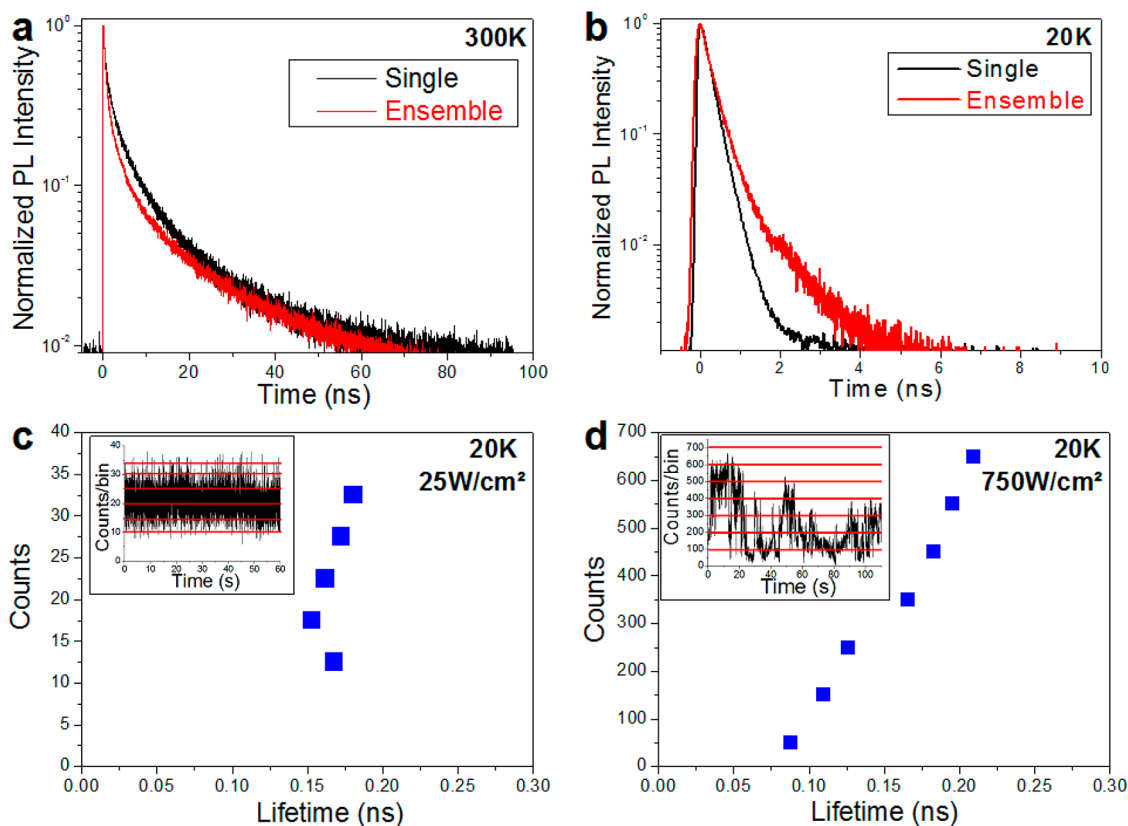


Figure 5. (a) Time dependence of the fluorescence intensity of an ensemble of NPLs (red) and a single NPL (black) at room temperature. Single NPL was excited at $250 \text{ W} \cdot \text{cm}^{-2}$ with a repetition period of 100 ns. Density of energy per pulse: $20 \mu\text{J} \cdot \text{cm}^{-2}$. (b) Same as in a, at 20 K. The single NPL was excited at $750 \text{ W} \cdot \text{cm}^{-2}$ with a repetition period of 25 ns. Density of energy per pulse: $19 \mu\text{J} \cdot \text{cm}^{-2}$. (c,d) Average fluorescence lifetimes vs emission intensity. The time trace of the single NPL is presented in the inset. The photon of each trace is binned in 5 intervals (c) or 7 intervals (d). The time traces are binned at 10 ms. The laser repetition rate is 40 MHz. The excitation power is (c) $25 \text{ W} \cdot \text{cm}^{-2}$ in and (d) $750 \text{ W} \cdot \text{cm}^{-2}$.

variations of the emission maximum position. These slight variations probably result from variations of the lateral dimensions of the NPLs we observed. The 2D Bohr radius of the CdSe NPL is $(3/8)^{0.5} a_{3D} = 3.5 \text{ nm}$, where $a_{3D} = 5.6 \text{ nm}$ is the Bohr radius of bulk CdSe.²⁴ As a consequence, NPLs with at least one lateral dimension close to 7 nm have excitons that are also slightly confined laterally, in addition to the confinement in the thickness direction. This lateral confinement produces larger fwhm on ensemble measurements and slightly changes the emission maximum position.¹¹ When the temperature decreases from 300 to 20 K, the emission maximum of a single NPL shifts to higher energy from 2.25 to 2.33 eV (Figure 4b). A similar blue shift has been observed in ensemble measurements of NPLs emitting at 551 nm.⁵ This shift is well-described with the relation introduced by Varshni.²⁵ $E_g(T) = E_g(0) - \alpha T^2 / (T + \beta)$, with $\alpha = 4.5 \times 10^{-5} \text{ eV} \cdot \text{K}^{-1}$ and $\beta = 200 \text{ K}$. This relation was already observed in CdSe QDs, nanorods, as well as tetrapods with similar parameters,^{26,27} which further confirms that the temperature dilatation of the CdSe lattice and the interaction of the electron with the lattice are roughly independent of the CdSe nanoparticle shape. When the temperature decreases from 300 to 20 K, the fwhm of the emission spectrum decreases

from 42 to 0.4 meV, a value close to the resolution of our spectrophotometer. The evolution of the fwhm with temperature has already been observed on colloidal QDs and is attributed to the decrease of the exciton–phonon coupling strength when the temperature decreases.^{26,28,29} At 20 K, we measured the emission spectrum of single NPLs in two conditions, under low excitation power where the NPL trace is steady (Figure 4c) and under high excitation power where the NPL has a highly fluctuating trace (Figure 4d). We connect the larger fwhm observed at high pump power with the spectral diffusion linked to the Stark effect already observed in quantum dots² and observed also with the NPLs (Figure S2).

At 300 K, the fluorescence intensity decay of an ensemble of NPLs is highly multiexponential. This multiexponential decay could result from different fluorescence decay dynamics from one NPL to the other. However, all of the single NPL fluorescence decays we have measured, an example of which is shown Figure 5a, exhibit the same multiexponential behavior. When superposed, single NPLs have similar fluorescence decay than an ensemble of NPLs. This shows that several emitting states are present in a single NPL at room temperature and that the multiexponential decay observed

in ensemble measurements is not a consequence of the lifetime dispersity from one NPL to the other. The fluorescence decay of a single NPL can be reasonably fitted with three exponentials. Although such a fit is arbitrary and hard to interpret, it nevertheless suggests that 30% of the emitted photons have a lifetime around 1.1 ns, 40% around 7.7 ns, and 20% around 60 ns. The fluorescent lifetimes measured for NPLs are much shorter than the ones measured for spherical quantum dots. At 20 K, the fluorescence intensity decay of a single NPL is extremely rapid and can be well-fitted with a single exponential decay. A typical average lifetime, measured on 10 single NPLs of the same sample, is about 200 ps after deconvolution with the impulse response function (Figure S3). At the same temperature, quantum dots have a lifetime of about 20–80 ns.¹⁹ The single NPL lifetime we measure is slightly lower than the lifetime measured on an ensemble of NPLs, which is close to 300 ps (Figure 5b). The shortening of the fluorescence decay time with temperature of a single nanoparticle is usually associated with the opening of nonradiative recombination pathways for the exciton and thus with a decrease of the fluorescence intensity. In the case of a single NPL, the opposite is observed; the fluorescence lifetime shortening when the temperature decreases is concomitant with an increase of the fluorescence intensity (Figure 3b). This behavior is highly unusual and has already been observed on the ensemble measurement.⁶ It was interpreted as the appearance of a giant oscillator strength transition.^{30–32}

We have analyzed the correlation between the fluctuation in the emission trace of a single NPL and its lifetime at 20 K (Figure 5c,d). When the single NPL is excited at low intensity so that its emission trace is constant in time, the lifetimes of all of the photons emitted by the NPL are identical. On the contrary, when the same single NPL is excited at higher intensity, its

emission trace displays large intensity fluctuations. The photons emitted during the low intensity period have a shorter lifetime than the ones emitted during the high intensity periods. This observation is very similar to the one performed in Zhang *et al.*,²¹ and its possible interpretations are similar. These continuous fluctuations are inconsistent with a discrete model and suggest that we should consider a distribution of emissive states model. While the broad-band emission could result from photoinduced reorganization of molecular absorbates at the surface,³³ it could also result from variation of characteristics of the trapping state to vary as a function of time.³⁴

CONCLUSION

In summary, we have made the first optical study of single CdSe NPLs. We have shown that the spectroscopic characteristics and the fluorescence lifetime of a single NPL are very similar to ensemble measurements, both at room temperature and at 20 K. This study confirms that the NPLs are atomically flat with all of the same thickness, controlled with atomic precision. It also confirms that as far as the NPL lateral dimensions are larger than the NPL 2D Bohr radius, there is no inhomogeneous broadening in the NPL ensemble emission spectra. At the single molecule level, the NPLs blink at room temperature. The blinking can be completely suppressed at 20 K at low intensity excitation. It would be interesting to see if the blinking in CdSe/CdS core/shell NPLs can be suppressed at room temperature, as is the case for CdSe/CdS quantum dots,^{35,36} but the synthesis of these core/shell NPLs remains to be done. In this article, we also confirmed the interesting behavior already seen for an ensemble of NPLs: an ultrafast lifetime of about 200 ps at cryogenic temperature and a decrease of the exciton lifetime with decreasing temperature. This unusual behavior may be the signature of a giant oscillator strength transition.³⁰

MATERIALS AND METHODS

Chemicals. Cadmium nitrate dihydrate, cadmium acetate tetrahydrate $\text{Cd}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$, technical grade 1-octadecene, myristic acid sodium salt, and selenium in powder were purchased from Sigma Aldrich. Methanol, ethanol, and hexane were purchased from VWR.

Synthesis of Cadmium Myristate. Cadmium nitrate (1.23 mg) was dissolved in 40 mL of methanol. Then, 3.13 mg of sodium myristate was dissolved in 250 mL of methanol (1 h with strong stirring). After complete dissolution, the two solutions were mixed. It gave a white precipitate. This precipitate was filtered and washed on buchner (vacuum flask) and dried under vacuum for about 12 h.

Nanoplatelet Synthesis. $\text{Cd}(\text{myr})_2$ (170 mg, 0.3 mmol) and 14 mL of ODE were introduced in a three-neck flask and were degassed under vacuum. The mixture was heated under argon flow at 250 °C. A solution of 12 mg (0.15 mmol) of Se dispersed in 1 mL of ODE were quickly injected. One minute later, 120 mg of $\text{Cd}(\text{Ac})_2$ (0.45 mmol) were introduced. The mixture was

heated for 10 min at 250 °C. This synthesis produced 7 ML NPLs and also some QDs. The NPLs were separated from the QDs using selective precipitation. The NPLs were then dispersed in hexane.

Optical Characterization. The NPLs in hexane solution were diluted to nanomolar concentration in a mixture of 90% hexane/10% octane and deposited by drop-casting on a glass substrate. The sample is visualized using an inverted fluorescent microscope. An area of the sample containing several NPLs is excited using a Hg lamp, and the emitted light is collected with an oil objective (100 \times , NA = 1.4) and adapted filters (426–60 nm for the excitation 535–50 nm for the emission). The emitted light of the sample can be observed on a CCD camera (Cascade 512B, Roper Scientific) or directly through the microscope eyepiece with the naked eyes. NPLs are considered unique if they are clearly separated from each other and if we could distinguish non-emissive periods. To investigate in more details the emission of single NPLs, we record the fluorescence intensity emission of a unique NPL with a confocal microscope

(Microtime 200, Picoquant) and a Hanbury Brown and Twiss setup based on two avalanche photodiodes (SPAD PDM, MPD, time resolution 160 ps). The photodetection signal was recorded by a HydraHarp 400 module (Picoquant). In this configuration, the studied nanocrystal is excited with a pulsed diode emitting at 402 nm. To obtain a single NPL spectrum, a part or the totality of the collected photons is sent to a homemade spectrometer. The dispersion system is a prism, and the detector is a CCD camera (Cascade 512B, Roper Scientific). The resolution of this spectrometer is 10 meV. Spectra with a better resolution were obtained using a Triax (Jobin-Yvon) with a 1200 L/mm grating and a resolution of ~ 0.4 meV. To make measurements at cryogenic temperature, the solution of NPLs was deposited on a sapphire substrate. The sample is placed in a cryostat (optistat CF-V, Oxford Instruments), and the emitted light is collected with an air objective ($60\times$, NA = 0.7). To reach a cryogenic temperature, the sample is subjected to a vacuum of less than 10^{-6} mbar. With this setup, the sample can be cooled to 20 K.

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: Estimation of the absorption cross section. Emission time traces at 20 K. Observation of spectral diffusion due to Stark effect. Impulse response function of the setup. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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