

Luminescence Blinking of a Reacting Quantum Dot

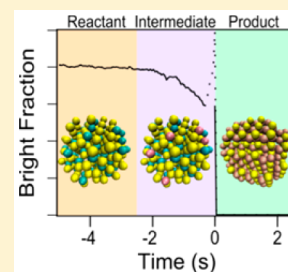
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S Supporting Information

ABSTRACT: Luminescence blinking is an inherent feature of optical emission from individual fluorescent molecules and quantum dots. There have been intense efforts, although not with complete resolution, toward the understanding of the mechanistic origin of blinking and also its mitigation in quantum dots. As an advance in our microscopic view of blinking, we show that the luminescence blinking of a quantum dot becomes unusually heavy in the temporal vicinity of a reactive transformation. This stage of heavy blinking is a result of defects/dopants formed within the quantum dot on its path to conversion. The evolution of blinking behavior along the reaction path allows us to measure the lifetime of the critical dopant-related intermediate in the reaction. This work establishes luminescence blinking as a single-nanocrystal level probe of catalytic, photocatalytic, and electrochemical events occurring in the solid-state or on semiconductor surfaces.

KEYWORDS: Single-molecule fluorescence, cation exchange, emission, cadmium selenide

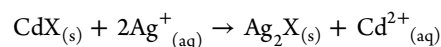


Single emitters blink. The luminescent emission from an individual photoexcited fluorescent molecule or quantum dot is not continuous but is interspersed by periods of darkness.^{1–3} There is random switching between bright, emissive (ON) and dark, nonemissive (OFF) states. The precise origins of luminescence blinking are still being resolved via studies on quantum dots.⁴ One widely accepted theory is that the dark state is a charged state of the quantum dot, produced by photoexcitation.^{5–8} In particular, multiphoton excitation can cause an electron or hole to be ejected from the quantum dot, leaving the quantum dot charged. In this charged state, photogenerated excitons recombine nonradiatively via an Auger recombination process rather than by radiative emission, thereby rendering the quantum dot nonemissive.⁹ Eventually, when the charge on the quantum dot is neutralized, the emissive state is restored.

Apart from mechanistic investigations, important work in the area has focused on eliminating blinking or at least reducing the prevalence of the nonemissive state, so as to produce imaging labels with steady emission.^{10–13} In this Letter, we show the usefulness of quantum dot blinking as a dynamic signature of the chemical state of the quantum dot. Our demonstration relies on our discovery that in the temporal vicinity of a reactive transformation, the blinking behavior of a quantum dot is significantly altered. In particular, the OFF state becomes more prevalent as one approaches the time-instant of the reactive transformation. We take advantage of this finding to identify a dopant/defect-related intermediate formed in the reaction path and also to measure the millisecond-time scale reaction dynamics within a semiconductor nanocrystal (NC).

The reaction studied was cation exchange, which is the place-exchange of all the cations of an ionic solid with foreign cations.^{14–18} A classic example is the cation exchange of a CdX

(where X = S, Se) NC with silver ions (Ag⁺) to form a silver chalcogenide (Ag₂X) NC (Figure 1, top).



A related reaction is the reverse exchange of Ag₂X NCs with Cd²⁺ to form CdX NCs.¹⁴

We used fluorescence nanoscopy to monitor individual CdSe/CdS NCs undergoing forward and reverse exchange reactions in a microfluidic reaction cell.^{19–24} The monitoring was possible because unlike CdSe/CdS NCs Ag₂Se/Ag₂S NCs exhibit no visible photoluminescence.²⁵ Single-NC level photoluminescence spectra (Figure 1, bottom) demonstrate that we were able to perform such single-NC level probing with a high degree of fidelity; after a full cycle of forward and reverse exchange, the photoluminescence spectrum of the NC is fully recovered with a peak maximum identical to the starting spectrum, indicating that the CdSe/CdS NC recovers its original composition and size.^{26,27} It must be noted, however, that after a full cycle of exchange, the average photoluminescence intensity per NC is lower, by ~14% (±9% std. dev.) as determined from representative experiments. Also, it is found in representative experiments that ~57% (±18% std. dev.) of NCs are recovered after a full cycle. The CdSe/CdS NCs recovered after a full cycle do not necessarily maintain their initial locations, either due to some mobility of NCs on the substrate or because a unique subset of the NC population is permanently dark at the initial and final stages.

Using 50 ms frame-resolution video microscopy (also see Supporting Movies M3), we obtained time-trajectories of the

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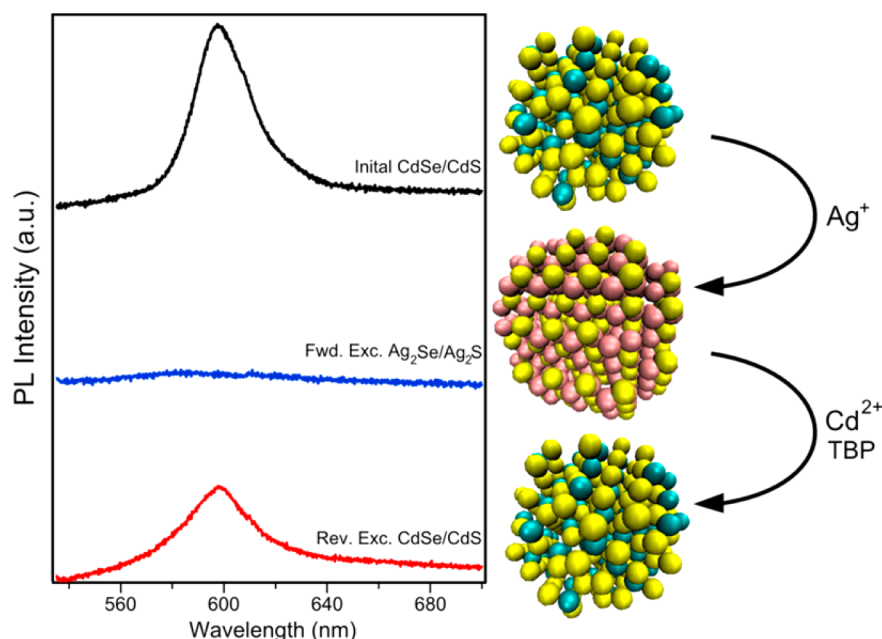


Figure 1. (Right) A cartoon of the cation exchange reactions studied. A CdSe/CdS NC, upon treatment with Ag^+ , is converted from brightly luminescent CdSe/CdS to nonluminescent $\text{Ag}_2\text{Se}/\text{Ag}_2\text{S}$. The reaction can be reversed by treatment with Cd^{2+} , whereby a luminescent CdSe/CdS NC is recovered. (Left) The forward and reverse exchange reactions are monitored on the single-NC level using photoluminescence imaging/spectroscopy, as shown by single-NC emission spectra (averaged over a handful of representative NCs). The distinct excitonic emission of an initially CdSe/CdS NC (black line) is completely lost (blue line) upon forward exchange. Upon reverse exchange, the CdSe/CdS NC is recovered and excitonic emission is restored with the same peak maximum (red line). For reasonable S/N, spectra shown are averaged over 9, 9, and 6 individual NCs for black, blue, and red lines, respectively. The photoluminescence intensity was normalized by the number of NCs sampled.

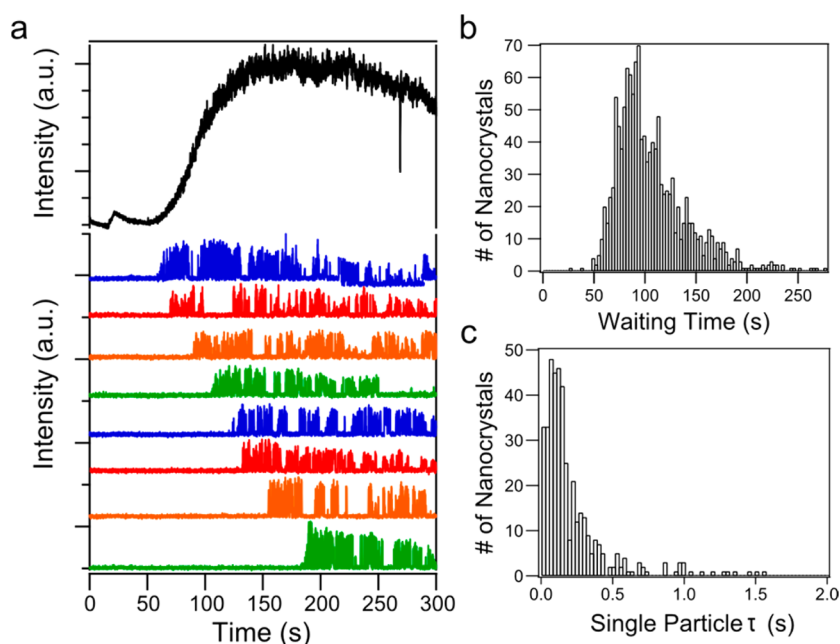


Figure 2. (a, top) A gradual increase in the wide-field intensity with time is indicative of the conversion of the ensemble of nonluminescent $\text{Ag}_2\text{Se}/\text{Ag}_2\text{S}$ NCs, subject to a 50 $\mu\text{L}/\text{min}$ flow of a 27 mM $\text{Cd}^{2+}/0.1$ M TBP solution in acetonitrile, to luminescent CdSe/CdS NCs. The intensity reaches a plateau when all NCs are converted, beyond which a small intensity decrease due to photobleaching is seen. The small intensity bump at $t = 25$ s is due to the reaction solution front entering the field of view and momentarily causing scattering of laser light. $t = 0$ s corresponds to the point of injection of the reaction solution. (a, bottom) Intensity trajectories of representative single $\text{Ag}_2\text{Se}/\text{Ag}_2\text{S}$ NCs show that an individual NC makes a rather sharp transition to the luminescent CdSe/CdS form. The instant of time (referred to as the waiting time) when such a transition occurs is distinct for each NC. (b) A histogram of the waiting times has a peaked distribution spanning tens of seconds in width while (c) the time-constant for the sharp transition of individual NCs is ca. 300 ms.

photoluminescence intensity for several individual $\text{Ag}_2\text{Se}/\text{Ag}_2\text{S}$ NCs undergoing exchange to CdSe/CdS. The wide-field

intensity over the field-of-view gradually increased over ca. 100 s as the ensemble of NCs converted from nonluminescent

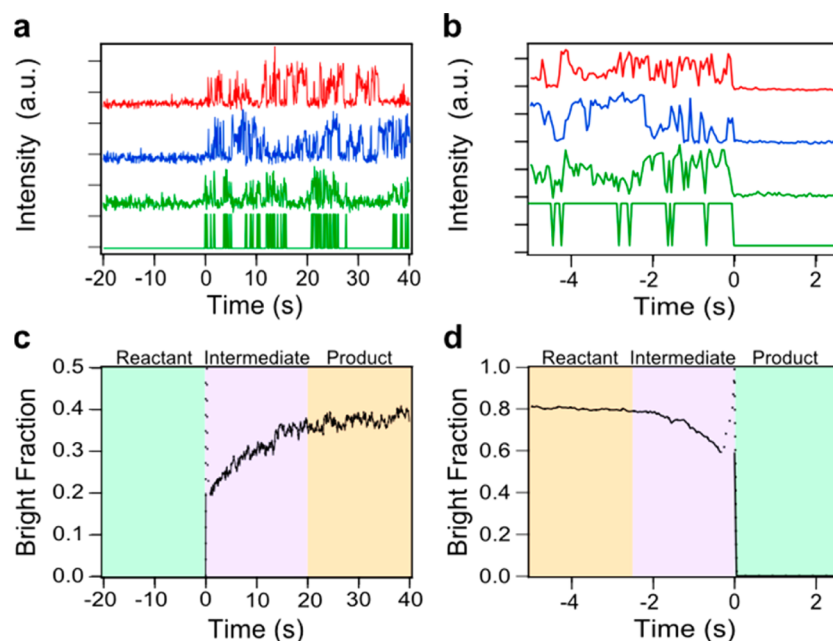


Figure 3. Three representative single NC trajectories for the reverse (a) and forward (b) exchange reactions. NC trajectories shown have been temporally aligned such that the time-instant of the reactive transition was coincident across all NCs and set to $t = 0$ s. For the third trajectory (green) in both (a) and (b), the equivalent binary ON/OFF trajectory has been shown immediately below. Gray states are considered to be emissive. It must be noted that even though CdSe/CdS nanocrystals exhibit multistate emission, we do not attempt to distinguish between these different intensity levels of emission. The bright fraction determined for a large ensemble of such “in phase” binary trajectories is shown as a function of time for the reverse (c) and forward (d) reactions. The procedure for digitization of trajectories to a binary form, temporal alignment of single NC trajectories, and determination of bright fraction are described in detail in the Supporting Information. The feature at $t = 0$ s in (c,d), marked by a dotted curve, is an artifact of the alignment procedure: at that instant, every NC is in the ON state by definition, either for the first time (reverse exchange) or for the last time (forward exchange).

Ag₂Se/Ag₂S to luminescent CdSe/CdS (Figure 2a, top). Representative single-NC trajectories (Figure 2a, bottom), however, show that the conversion of an individual NC from Ag₂Se/Ag₂S to CdSe/CdS is rather sharp compared to the ensemble kinetics, typically taking $\tau = 300$ ms (Figure 2c).

One experimental limitation is that single-NC photoluminescence emission possibly probes only a portion of the entire conversion process in a NC. In forward exchange,²⁰ the loss of emission is possibly complete before the NC is fully converted to Ag₂Se/Ag₂S. Likewise, in the reverse reaction the emission possibly recovers only when a significant fraction of Ag₂Se/Ag₂S inclusions have been removed. Fortunately, from a separate study²⁸ cation exchange in this system is known to follow co-operative switching-like dynamics; therefore the “nonproportional” dependence of emission intensity on the extent of conversion does not severely limit the use of photoluminescence for following the conversion dynamics within a single NC. Nevertheless, the measured time constant τ is likely to be a close lower limit for the actual time scale of conversion of a single NC.

Recent experiments^{26,28} and theory²⁹ point to the formation of dopant and vacancy-related intermediates along the reaction pathway. However, intensity trajectories have limited information for further resolution of the reaction dynamics around the transition point. Single-NC photoluminescence emission spectra can be more informative in this regard because spectra can be expected to be sensitive to the doping of the NC^{28,30–32} or to changes in the crystallite size^{33,34} as the solid-state exchange ensues. However, the collection of spectra requires several seconds-long acquisition times, which is too slow for elucidating subsecond-scale temporal dynamics. We, therefore,

decided to inspect the luminescence blinking behavior of the NC, which is rich in information and from past work is known to be sensitive to the charge state/environment/surface passivation of the NC.^{10,35–39} In particular, we asked the question if the blinking behavior of a NC changes in the temporal vicinity of its reactive transformation.

In order to address this question, we analyzed the time-evolution of the blinking behavior of NCs undergoing cation exchange. Such temporal dynamics is not obtainable from conventional analyses of luminescence blinking, wherein ON and OFF time distributions and averages are typically extracted from tens to hundreds of seconds long single-NC intensity trajectories.^{38,40–42} Therefore, we adopted a modified strategy taking advantage of the ergodic principle: instead of using hundreds of time-points of single-NC emission intensity, we utilized emission information from hundreds of similar NCs from each frame. Using the latter information, we determined a transient bright fraction, which is the ratio of NCs that are ON in a given frame to the known total number of NCs. The bright fraction provides a frame-by-frame measure of the average blinking behavior of the NCs, the evolution of which can be followed with a time-resolution of 50 ms, the frame acquisition time. Because we were interested in the evolution of blinking behavior relative to instant of the reactive transition, all individual NC trajectories were temporally aligned so as to make the instant of the reactive transition (set to $t = 0$ s) coincident for all NCs (Figure 3a). From an ensemble of such “in-phase” single-NC trajectories, the bright fraction was determined as a function of time.

Such a time-resolved blinking analysis is shown for the reverse cation exchange reaction in Figure 3c. Prior to the

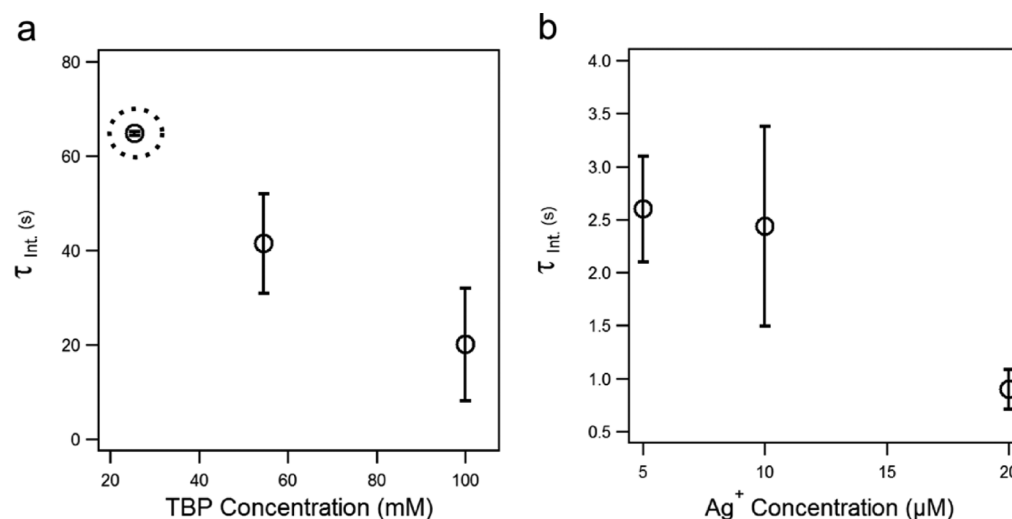


Figure 4. Intermediate state relaxation time/lifetime τ_{int} is dependent upon the reactant concentration. An increase in the TBP concentration results in a decrease in the relaxation time of the dopant-related intermediate state in the reverse exchange reaction (a). A similar decrease in the intermediate-state lifetime is seen for the forward exchange reaction (b) when the Ag^+ concentration is increased. Each data point represents an average of multiple trials. Supporting Information Table S1 shows results of individual trials. The error bars represent the standard deviation of a set of trials, except for the data-point for the 25 mM TBP trial (dotted circle) in which case the error bar represents a fitting error because only one trial was performed.

reaction ($t < 0$ s), all NCs are in the nonluminescent $\text{Ag}_2\text{Se}/\text{Ag}_2\text{S}$ state and therefore the bright fraction is zero, which characterizes the reactant state. Long after the reactive transition has taken place ($t > 20$ s), the bright fraction is observed to be steady in time, which characterizes the stable CdSe/CdS product state. However, immediately following the transition, newly formed CdSe/CdS NCs exhibit a much more prevalent nonemissive OFF state, as indicated by the low value of the bright fraction. However, over a few seconds following the transition point, the OFF state becomes less and less prevalent, indicated by the increase in the bright fraction, until the bright fraction eventually stabilizes to the steady-state value. This time-evolution of the blinking behavior following the reactive transition point represents the slow structural/compositional relaxation of an intermediate state of the postexchange NC.

What is the nature of this *intermediate state*? Past work has shown that NCs following exchange can contain defects like stacking faults,^{14,26} incomplete ligand passivation, and most prominently, leftover dopant impurities corresponding to the outgoing cation²⁶ in this case Ag^+ . The latter in particular can form long-lived deep traps for charge carriers,^{28,43–45} serving as a potential mechanism for B-type blinking.⁹ The presence of interstitial Ag^+ impurities is likely compensated by the presence of Cd^{2+} lattice/surface vacancies, one for every two Ag^+ impurities.²⁸ These vacancies may also serve as long-lived traps for carriers and give rise to the prevalent OFF state behavior.

Thus, our results suggest that a fast ($\tau \sim 300$ ms, Figure 2c) reactive transition results in the formation of an Ag-doped, defective CdSe/CdS NC, which exhibits prevalent OFF state behavior in its emission. On a slower time-scale ($\tau_{\text{int}} \sim 12$ s, Figure 3c), this doped, defective NC expels out remnant impurities and stabilizes to a more pure, less defective CdSe/CdS NC with higher quality emission characterized by lower prevalence of OFF state behavior. In fact, the conditions of our experiment, that is, the presence of tributyl phosphine (TBP), match the conditions under which monovalent dopant cations

are known to be expelled out of the NC.²⁶ Such purification is assisted by complexation of these ions of soft acid character by the soft base TBP. A study of the effect of the TBP concentration (Figure 4a) provided further credence for the picture of reaction dynamics invoked above. As the TBP concentration was increased, the relaxation time τ_{int} of the intermediate state was found to decrease. In other words, at a lower TBP concentration complexation-assisted expulsion of Ag^+ impurities is slower, resulting in the longer relaxation times. On the other hand, the time constant for the fast step does not exhibit any systematic change with the TBP concentration and stays in the 200–300 ms range (see Supporting Information Table S1).

The blinking response of NCs in the course of a forward exchange reaction (Figure 3b,d) is similarly informative. In the forward reaction, at times significantly earlier than the instant of transition ($t < -3$ s) the bright fraction is steady in time, characterizing the stable CdSe/CdS reactant state. As a CdSe/CdS NC approaches its point of transition to $\text{Ag}_2\text{Se}/\text{Ag}_2\text{S}$, it begins to exhibit more and more prevalent OFF state behavior in its blinking. The latter is indicated by the continuously decreasing value of the blinking fraction in the $-2 \text{ s} < t < 0$ s region, which characterizes a doped-NC intermediate state. This decrease with time continues until the blinking fraction sharply drops to a value of zero at the point of transition to nonemissive $\text{Ag}_2\text{Se}/\text{Ag}_2\text{S}$, the product state. Mirroring the dynamics of the reverse reaction, the intermediate state in forward exchange is very likely a CdSe/CdS NC doped with surface/interstitial Ag^+ impurities with charge compensation by Cd^{2+} surface/lattice vacancies. Past chemical characterization on ensemble solution-phase CdSe NC samples²⁸ and electronic structure calculations²⁹ have both indicated that such Ag^+ doping is a critical precursor to cation exchange. The increase in the prevalence of the nonemissive OFF state as the transition point is approached signifies progressive doping of a NC; until at a critical number of dopants, the NC undergoes a rapid transition ($\tau \sim \text{few } 100 \text{ ms}$) to the $\text{Ag}_2\text{Se}/\text{Ag}_2\text{S}$ state limited only by mass transport of ions to the surface of the NC and/or

within the NC. The lifetime of the doped-NC intermediate state is found to be ca. 1 s, which is an order-of-magnitude faster than for the reverse reaction, under the reaction conditions employed in our studies (see Supporting Information Table S1).

There is significant variance in the measured lifetime over multiple trials at the same concentration. We believe this variance results from the finite ensemble size (few thousands of NCs) in each trial, limited S/N of single-NC emission that cause errors in the determination of the number of emissive NCs and reagent concentration variations from one trial to another. In addition, small variations in the surface chemistry of the glass substrate in the surface composition of the NC due to oxidation or hydroxylation and in the photochemical effect of the excitation laser light can lead to variations in the photoluminescence characteristics and reactivity of NCs.

Thus, despite the stochastic nature of luminescence blinking we find a systematic correlation between the blinking behavior of a quantum dot and its chemical/structural state. The finding of such a correlation is certainly not unreasonable when one considers the well-known role of chemical impurities and structural defects as long-lived nonradiative carrier traps and therefore easily culpable sources of OFF state behavior. Analogous to the role of quantum efficiency as a signature of optoelectronic quality of a bulk semiconductor sample,^{26,46} we establish luminescence blinking as a dynamic optical signature of the chemical/structural quality of a single NC. Atomic-level defects,^{47,48} impurities, charged species, and surface unsaturations are often formed dynamically in solid-state phenomena like charge transfer, surface photoelectrolysis, surface restructuring,⁴⁹ adsorption,⁵⁰ and catalysis. Although, these intermediates hold clues to atomistic mechanistics, these intermediates can be difficult to detect due to their fleeting nature and their subtlety on the bulk level. But the combination of single-NC monitoring and millisecond time-resolution achievable by dynamic blinking measurements, developed here, makes detection of such intermediates possible. In particular, from the point of view of reaction dynamics in the solid-state and on surfaces luminescence blinking can thus become a powerful, broadly applicable, information rich chemical/structural probe.

■ ASSOCIATED CONTENT

■ Supporting Information

Reagents and instrumentation; method of single-NC cation exchange studies, nanocrystal spectroscopy, and optical microscopy data analysis; transmission electron microscopy images of NC samples; effect of flow rate on single-NC reaction time constant; time evolution of blinking behavior for various reagent conditions; correlation of waiting times with spatial location of NC; effect of ON/OFF threshold on time-evolution of blinking; table of single-NC time-constant (τ), and intermediate lifetime (τ_{int}) under various reaction conditions for both the forward and reverse cation exchange reactions; representative single-NC spectra before forward exchange, in the Ag₂Se/Ag₂S state, and after reverse exchange; captions for supporting movies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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