Nongeminate Radiative Recombination of Free Charges in Cation-Exchanged PbS Quantum Dot Films

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Abstract:

Using photoluminescence (PL) spectroscopy we explore the radiative recombination pathways in PbS quantum dots (QDs) synthesized by two methods. We compare conventionally synthesized PbS from a PbO precursor to PbS synthesized using cation-exchange from CdS QDs. We show that strongly coupled films of PbS QDs from the cation-exchange luminesce with significant efficiency at room temperature. This is in stark contrast to conventional PbS QDs, which have exceedingly weak room temperature emission. Moreover, the power dependence of the emission is quadratic, indicating bimolecular recombination, a feature previously unreported in coupled PbS QD films. We interpret these results in terms of a greatly reduced defect concentration for cation-exchanged QDs that mitigates the influence of trap-assisted recombination. Cation-exchanged QDs have recently been employed in highly efficient and air-stable lead chalcogenide QD devices, and the reduced number of trap states inferred here may lead to improved current collection and higher open circuit voltage.

Keywords

photoluminescence, PbS, quantum dots, nanocrystals, bimolecular recombination

Introduction

One of the keys to optimal solar cell performance is to approach the so-called “radiative limit,” which dictates that at open-circuit the primary recombination mechanism should be radiative decay at or very near the band gap energy.[1] For GaAs solar cells, the limit is approached due to the near-unity internal emission efficiency, and optimization of the external PL efficiency is a performance metric.[2] Although the photoluminescence (PL) of colloidal quantum dots (QDs) is often reported in order to show band gap energy, size distribution, and reasonably effective surface passivation, the emission from processed QD films relevant for solar cells is much less often reported. We have found that the PL at room temperature from a strongly coupled QD film is most often exceedingly weak ($\ll 1\%$) even in cases where the PL efficiency of the colloidal QDs is high prior to film formation (10-60%).[3–5] We recently characterized PL in a series of PbS QD films with varying degrees of coupling and conclusively showed that the PL quantum yield (PLQY) vs. temperature directly informs about charge transport.[4] The charge carrier mobility and PLQY for most lead chalcogenide QD films are inversely related using conventional QD synthesis and film formation procedures. Photogenerated charge-carriers in coupled QD arrays can sample a large number of QDs at high temperatures, inevitably leading to strongly quenched PL even with a relatively low concentration of defects.[5]

QD solar cells are on a reasonably steep trajectory of power conversion efficiency (PCE) vs. time,[6] but the recent incremental gains involve improvements not clearly related to defect passivation, for example using structured TiO_2 in order to trap light more efficiently.[7] Often,

the fill factor (FF) appears to be the most improved feature of champion solar cells, as opposed to the open-circuit voltage (V_{OC}), which is far below its theoretical limit. The FF has a complicated dependence on device characteristics and can depend on factors not related to the material quality, while the V_{OC} is more directly influenced by defect states. In order to steepen the efficiency vs. time curve, a better defined methodology for reducing defect density would be helpful for improvements in V_{OC} and for enabling the use of thicker active layers that can approach nearly ideal J_{SC} values.

Performing ligand exchanges changes the electronic characteristics of the QDs, in some cases providing improved defect passivation and surface protection against photooxidation or other forms of degradation.[8] A variety of chemical methodologies have been used to control the QD surface chemistry, these include, but are not limited to, *in situ* passivation during the synthesis of the QDs,[9–12] using shorter ligands to replace native ligands that can also provide additional passivation or protection to QDs in films,[13–15] or adding a second metal chalcogenide material to encapsulate the QD in a core-shell structure. Core-shell structures have been shown to reduce the number of surface traps in lead chalcogenide QDs, revealing improved PL in solution and resulting in improved V_{OC} in QD devices.[16,17] The apparently reduced defect density is presumably due to replacing atoms likely to have dangling bonds with a shell material that is less prone to forming inter-gap energy states (i.e., a type-I structure). The dual benefits of reduced dangling bonds and protection from oxygen make this strategy attractive. However, a wide-bandgap shell can limit the short-circuit current in a device by confining carriers within the core due to the band offset between the core and the shell.

A modified core-shell type approach that utilizes a thin layer of lead halide instead of a metal chalcogenide has been demonstrated computationally and experimentally to be beneficial.

Calculations suggest that a thin PbI_2 layer surrounds PbSe QDs after iodide salt treatment, which passivates surface states and makes QDs oxidatively stable.[18] Similar results have been reported for chloride salt treatments on PbSe QDs, leaving them more air stable and with higher PLQYs than their all-organic capped counterparts.[12] These photophysical observations have translated to improved performance in recent QD devices, primarily through passivation protection from oxidation.[19] In fact, all recent record efficiency PbS QD devices have used some form of halide treatment during fabrication of the QD absorber layer.[7,9,14,19] Protection from oxidation and the removal of intrinsic surface-related inter-gap defect levels are interconnected variables in most device studies with lead chalcogenide QDs, thus the microscopic origins of improved performance remain unclear. In fact a recent study of different iodide PbS QD treatments found that the defect density was always higher in iodide treated films compared to EDT treated films.[20]

In addition to PL measurements, transient absorption (TA) spectroscopy is often used to characterize excited state lifetimes and elucidate recombination mechanisms. For isolated QDs, a model including quantum confined Auger recombination involving multiexcitons can successfully reproduce the TA data as a function of pump fluence.[21,22] For coupled QDs, the same model can be employed and produces results that reasonably reproduce the data, but important parameters, such as the biexciton lifetime, change considerably and appear to depend on the film conductivity, calling into question the validity of the exciton model. Especially problematic would be the presence of separated charge carriers within the film.[23,24] Moreover, the lifetime observed at low pump fluence, typically greater than 100 ns for uncoupled QDs, decreases significantly with increased QD coupling, further complicating the analysis. In many cases, there is a clear inverse relationship between the degree of QD coupling

and the low fluence lifetime measured by time-resolved terahertz or TA. The shortened lifetime is further evidence for increased deleterious defect densities that exists after most ligand-exchanges that leads to trap-assisted recombination hastened by a high charge-carrier or exciton mobility.[25,26]

In order to analyze data sets that may span large ranges of temperatures, excitation densities, and unknown strengths of inter-QD coupling (and exciton binding energies), we begin with a general model that encompasses both bulk recombination of free-charge carriers and excitonic recombination. The model includes terms that are linear, quadratic, and cubic in the excited state population. The linear terms involve geminate electron-hole radiative or nonradiative recombination and trap-assisted nonradiative decay, (often via a Shockley-Read Hall (SRH) mechanism), with rate constants k_X^r , k_X^n , and k_A^n , respectively. The quadratic terms include nongeminate electron-hole radiative recombination (C_B^r) and exciton-exciton nonradiative (C_{XX}^n) recombination coefficients. The latter term is often associated with an Auger mechanism. The cubic term describes nonradiative Auger recombination of free carriers (C_A^n).[27] This model is expressed in equation 1 as a change in excited state population density (N_t) vs. time. The superscripts on each rate constant/coefficient denote if it is radiative (r) or nonradiative (n).

$$N_t' = -(k_A^n + k_X^r + k_X^n)N_t - (C_B^r + C_{XX}^n)N_t^2 - C_A^n N_t^3 \quad (1)$$

Under conditions of strong QD coupling and low fluence, the linear term involving charges (k_A^n) dominates at room temperature. The other linear term involving excitons (k_X^r, k_X^n) are relevant only in weakly coupled films or at low temperatures where exciton dissociation is negligible. At higher excitation density, quadratic terms become important, with the C_B^r pathway commonly

observed in high performing solar cells, including PbMAI₃ perovskite films.[28] We note that the nonradiative pathway involving bimolecular charge-carrier recombination is often seen in organic solar cells with low dielectric constant (i.e., via a Langevin or related mechanism).[29] The quadratic term with coefficient C_{XX}^n is negligible at room temperature for systems with small exciton binding energy (i.e. most bulk inorganic semiconductors). For QDs in a film, the term is only relevant when the barrier to exciton dissociation is similar to or larger than $k_B T$. At even higher photon fluxes or in film regions where charges accumulate (i.e. at a junction under open circuit), the cubic Auger term can dominate, typically leading to fast and mobility dependent nonradiative decay.

With uncertainty about the degree to which each term in equation 1 contributes, extracting the rate constants/coefficients from a direct time-resolved measurement can be challenging.

However, by measuring steady-state PL intensity vs. incident excitation intensity (proportional to N_t), we can extract the mechanism of radiative recombination by determining the order of the kinetic process (i.e., linear or quadratic). We find that in cation-exchanged QD films the radiative recombination regime switches from linear to quadratic with increased temperature and that PL is not strongly quenched. This is in stark contrast to conventionally synthesized PbS QDs of the same size that show greater than two orders of magnitude quenching above ~ 200 K.[3] In addition, TA analysis suggests that at very low fluence within the linear recombination regime the excited state lifetime is increased significantly (i.e., k_A^n is reduced) when the cation-exchange method is used to synthesize the QDs. Taken together, these observations imply that greatly improved surface passivation enables carriers to undergo many more phonon-assisted tunneling events without nonradiative decay, leading to the opportunity for radiative decay at room temperature and open circuit. This improvement should have a direct impact on V_{OC} as

well as the maximum thickness of QD films that can be employed in order to capture a higher fraction of available solar flux.

Results and Discussion

In Figure 1 are shown PL spectra of 3 nm diameter PbS QDs synthesized by cation exchange from CdS QDs, with a first

exciton at 930 nm (~ 1.3 eV), cast

into a film on a sapphire

substrate using dip-coating with

1,2-ethanedithiol (EDT) to

replace the native oleic acid

(OA) ligands. The room

temperature Stokes shift of ~ 0.15

eV is typical for small PbS QDs

when fast energy transfer within

the distribution competes with

PL.[4,30] The inset highlights the peak PL energy as a function of temperature, showing an

initial red shift, then a strong blue shift as the temperature increases.

The initial red-shift of the PL peak energy as the temperature is raised is indicative of band-tail behavior,[3,31,32] while the general blue-shift is consistent with previous literature which shows an increase in bandgap with increased temperature.[3] More notably, the EDT-treated PbS QDs made by cation exchange show significant emission at room temperature. Strong emission at room temperature is also observed in uncoupled QDs, such as QDs capped with OA or long-

Figure 1: PL of 3 nm diameter PbS QDs synthesized by cation exchange, cast into a film using EDT. Dashed line is room temperature absorption spectrum. Inset: PL peak position vs. temperature.

chain thiol ligands, because the excitons are not dissociated regardless of the temperature,[4] and intra-QD excitonic radiative recombination is competitive with nonradiative recombination. However, coupled PbS QD films have previously shown 2-3 orders of magnitude of quenching at room temperature compared with ~20 K. This is thought to be due to deep trap states on the surfaces of QDs, which charge carriers readily find when they are able to sample a large number of QDs during hopping transport through the film. The reasonably strong room temperature emission of these cation-exchanged QD films suggests that the trap state density normally responsible for quenching emission has significantly decreased.

In order to prove that the QD films are not composed of isolated QDs, Fourier transform infrared spectroscopy (FTIR) measurements were performed to demonstrate a complete ligand exchange. FTIR spectra show complete removal of the OA peaks (Figure S2) to within the instrument sensitivity. Field-effect transistors (FET) were fabricated in order to further demonstrate strong electronic coupling in the films. Current-voltage scans (Figure S3) reveal an n-type film with a mobility of $3.8 \times 10^{-3} \text{ cm}^2/\text{Vs}$, which is similar to or slightly higher than mobility values determined for conventional PbS QDs of a similar size ($2.7 \times 10^{-3} \text{ cm}^2/\text{Vs}$, Table S2). Literature values of mobilities for PbS QDs treated only with short-chain organic molecules typically fall in the range $\sim 1\text{-}2 \times 10^{-3} \text{ cm}^2/\text{Vs}$. [9,33,34] FETs are majority carrier devices and generally should be insensitive to the presence of intragap states because the high gate bias quickly fills those states and thus should not contribute to the FET measurement, but shallow defects would impact the mobility. The improvements in the FET mobility and the improved PL at room temperature suggest that the cation exchanged QDs have less mid-gap deep defects and fewer shallow defects. The n-type behavior suggests that the normally anion-rich EDT-capped PbS[35] surface has become more stoichiometric or slightly cation-rich. This may be due to residual Cd^{2+} from

the cation exchange process binding to surface sulfur sites.[15] Chloride ions may also be adding electron density to the lattice if they replace surface sulfur.[9,36] Furthermore, a lower EDT packing density due to fewer available Pb^{2+} binding sites may reduce the density of thiolate groups at the surface that might otherwise lead to p-type behavior. The chemistry of the surface, including the locations and densities of Cl^- and Cd^{2+} , is not fully understood and requires further theoretical and experimental studies.

In Figure 2 the integrated PL across the relevant spectral region ($\sim 0.8\text{-}1.4$ eV) is plotted on a log-log scale as a function of incident laser power. In all cases, the power is kept far below the threshold for multiphoton absorption in a single QD ($\langle N_{\text{abs}} \rangle \ll 1$). The black squares show data for uncoupled QDs at room temperature, revealing a slope of 0.95. A slope near one is indicative of geminate recombination of the initially created electron-hole pair. At low temperature (blue circles), the slope for a coupled QD film is also ~ 1 due to excitonic recombination resulting from minimal thermal energy available for exciton dissociation. At room temperature (red squares), however, the slope changes to 1.9, indicating that nongeminate bimolecular recombination of free charges, the second term in equation 1, is now dominating the radiative decay.

Figure 2: Integrated PL intensity vs. incident laser power and calculated intensity at 514 nm for a film of OA-capped PbS QDs at room temperature and the same QDs after exchange of OA with EDT at two different temperatures.

Figure 3 displays the integrated PL intensity over the entire relevant spectral range vs. temperature for two samples, conventional PbS QDs and cation exchanged PbS QDs, both subsequently ligand-exchanged with EDT. The notable differences between the two curves are the slopes of PL quenching at intermediate temperatures and the strength of persistent emission as room temperature is approached. We note that there are no substantial differences in overall PLQY or temperature dependence for isolated QDs made by the different synthetic methods (data not shown). The first term in equation 2 is the previously developed model of PL quenching, derived by Zhang et al [4]. This term expresses the kinetic competition between excitonic radiative decay and exciton dissociation leading to PL quenching. We note that exciton dissociation by itself is not a decay mechanism (and thus does not appear in equation 1), but is a potential mechanism for PL quenching in the presence of defects, thus justifying its

presence in equation 2. The model fits the conventional PbS QD PL vs. temperature well, but deviates from the cation-exchanged QD PL considerably. The second term in equation 2 is an additional pathway to radiative recombination for free charge-carriers that were born from exciton dissociation via the first term.

$$\Phi_{PL}(T, N) = \frac{k_X^r}{k_X^r + k_{CT}(T) + k_X^n} + \Phi_{PL}^{bi}(N) \frac{k_{CT}(T)}{k_X^r + k_{CT}(T) + k_X^n} \quad (2)$$

, where $k_{CT}(T)$ is the exciton dissociation rate constant, expressed in equation 3. We previously confirmed that the exciton dissociation rate constant can be equated with the temperature-dependent hopping rate constant used in dark transport measurements, thus the form follows as:

$$k_{CT}(T) = \alpha \exp\left(-\left(\frac{T^*}{T}\right)^\nu\right) \quad (3)$$

, where α is the attempt frequency, T^* is the characteristic temperature, and the exponent ν is related to the transport regime.[37] Here, for simplicity we have assumed $\nu = 1$, which represents nearest-neighbor hopping.

The bimolecular radiative recombination yield (Φ_{PL}^{bi}) as a function of carrier density N is given by:

$$\Phi_{PL}^{bi}(N) = \frac{C_B^r}{C_B^r + k_A/N + NC_A^n} \quad (4),$$

which expresses the competition between rates of radiative bimolecular decay, $C_B^r N^2$, vs. the sum of the rates of relevant processes ($C_B^r N^2$ itself, unimolecular trapping, k_A , and Auger decay, $C_A^n N^3$).

Using Equation 2 to fit the data for cation-exchanged QDs, we find that the bimolecular recombination term is non-zero since the PL does not strongly quench at high temperature. The

non-zero value for bimolecular recombination shows that carriers are able to recombine with each other radiatively before being trapped and non-radiatively decaying. We note that the term Φ_{PL}^{bi} is excitation power dependent as expected (Figure 3 inset), following a roughly quadratic dependence at low fluence before exhibiting saturation at high fluence due to the influence of higher-order nonradiative recombination (e.g., Auger decay).

In previous work on conventional PbS QDs we have demonstrated that higher mobility, correlated with higher α via the Einstein-Smoluchowski equation ($\mu = (e/2kT) d^2 \alpha$), leads to faster trap-assisted nonradiative recombination.[4] However, we have shown here that both the mobility and room temperature PLQY of the cation-exchanged films are higher than those of the conventional QD films, thus invalidating the previously established inverse relationship between those quantities. From the relationship between α and μ , one might expect higher α for cation-exchanged films; however, the opposite is true, as α tends to be smaller than for conventional QDs ($\sim 10^8 \text{ s}^{-1}$ to $\sim 10^9 \text{ s}^{-1}$) despite the fact that the inter-QD distance d should be identical. This likely reflects the fact that the films of cation-exchanged QDs are n-type instead of p-type, and thus the mobilities of holes, being the minority carriers, are probed. Hole mobilities tend to be roughly an order of magnitude smaller than electron mobilities for QDs of this size.[38] Because the parameters α and Φ_{PL}^{bi} have a similar effect on the shape of the quenching curves (higher Φ_{PL}^{bi} mimics lower α), their influences are difficult to separate from each other. For this reason, α is held fixed for determination of Φ_{PL}^{bi} vs. power. More complex behavior may not be captured by the temperature-dependent PL data and thus other experiments are necessary to elucidate the full dynamical picture.

Figure 3: Integrated PL as a function of temperature for conventional PbS QDs (■) and for cation-exchanged PbS QDs (●). Inset: Log-Log plot of the power dependence of Φ_{PL}^{bi} .

The transient absorption curves shown in Figure 4 were collected at various excitation densities; calculated $\langle N_{abs} \rangle$ values are shown at the right of the figure, where $\langle N_{abs} \rangle$ is calculated from the measured pump fluence and the absorption cross section.[23] A trace at similarly low $\langle N_{abs} \rangle$ values is shown for an EDT-treated PbS QD film of a similar size but made by conventional synthesis (dashed curve). At the lowest excitation densities (black curves), only terms linear in the photoexcited carrier density contribute to the decay, and thus the nonradiative trap-assisted recombination term, involving k_A^n , dominates. The rate constant is at least one order of magnitude smaller for the cation-exchanged QDs with PbCl_2 than with conventional QDs, which further underscores the reduction in deleterious trapping that occurs in the cation-exchanged QDs. We attempted to simultaneously fit the series of power dependent decay curves to a model

of either quantum-confined Auger decay, free-carrier /bulk-like Auger decay, or a generic model including linear, quadratic, and cubic decay terms. None of these models fitted the full data set satisfactorily, although the bulk Auger decay model was a reasonable fit through most excitation densities. Inclusion of the quadratic term improved the fit slightly, but given our prior estimate of the yield of bimolecular decay (at most a few percent), it is not surprising that the fit was not greatly improved. Further investigation of the appropriate kinetic scheme for this situation is ongoing.

The TA measurements further reveal that the onset of a power dependent sub-ns decay occurs well below the $\langle N_{\text{abs}} \rangle = 1$ value. This is also observed in the steady-state PL power dependence, where saturation of the quadratic behavior occurs at excitation intensities of about 200 mW/cm², higher than solar intensities but far below the regime of multiple photon absorption per QD. This is likely due to diffusion assisted Auger recombination of charge-carriers, similar to that proposed by Gao *et al*[39] and reported in several investigations of coupled QD film dynamics.[23,25]

Figure 4: Transient absorption at the peak of the lowest exciton bleach signal (~930 nm) for various excitation powers at 800 nm for a cation-exchanged PbS QD film. The calculated

average exciton occupancy is shown at right. The dashed curve shows the bleach recovery for low excitation intensity of a film of conventional PbS QDs, also at 930 nm.

The connection between V_{OC} and radiative recombination of free carriers is expressed in

Equation 5:

$$qV_{OC} = qV_{OC-Ideal} - kT|\ln \eta_{ext}| \quad (5),$$

, where q is the elementary charge, V_{OC} is the open-circuit voltage, $V_{OC-Ideal}$ is the theoretical V_{OC} , k is Boltzmann's constant, T is the temperature, and η_{ext} is the external luminescence efficiency.[1] The V_{OC} loss for conventionally synthesized PbS QDs would be expected to be > 0.25 V since η_{ext} is $< 10^{-4}$. For cation-exchanged PbS QDs, the bimolecular recombination efficiency was found to be as high as ~ 0.02 , but at solar intensities it is ~ 0.005 . Using $\eta_{ext} = 0.005$, the V_{OC} loss, from Eq. 5, is around 0.14 V, or at least 0.1 V smaller than with conventional QDs. It should be pointed out that this is the minimum loss because η_{ext} is defined as only PL exiting from the front of the solar cell, which is inevitably lower than the η_{int} measured here by reference to absolute PLQY measurements. Whereas other loss mechanisms contribute to the ~ 0.5 V V_{OC} deficit now commonly measured for QD solar cells, the clear observation of bimolecular radiative recombination signifies the approach of the regime achieved by other high-performing solar cells for which PL at open circuit is an important metric.

In conclusion, we have found cation-exchanged PbS QDs to possess a much smaller deleterious trap state density than traditionally synthesized PbS QDs. This allows coupled films of PbS QDs to emit fairly strongly (PLQY $\sim 1\%$) at room temperature through bimolecular charge-carrier recombination, previously not seen in PbS QD films. The presence of halide and residual Cd^{2+} ions during the cation exchange process may result in improved surface defect passivation.

Improving the external luminescence efficiency will increase the V_{OC} in devices made from PbS

QD films, which has been one of the major limiting factors to increasing the efficiency in QD solar cells. Combining cation-exchanged QDs with additional surface treatments under development should lead to even better luminescence efficiency at open circuit and more efficient QD solar cells. Such PL measurements should be used as a metric for the development of new surface treatments with the caveat that the PL should scale with the light intensity as shown in Fig. 2.

Experimental

All chemicals were purchased from Sigma-Aldrich and used as received. PbS QDs were synthesized following the previously published procedure of cation exchange of CdSe to PbSe.[40] The only differences are the injection temperature and solvent. PbCl₂ (3 mmol) was mixed with 10 mL oleylamine (technical grade, 95%), degassed, and heated to 140°C for 30 min. The reaction was then cooled to 90°C and 2.5 mL of previously prepared CdS QDs (366 nm first exciton, 126 mg/mL in toluene)[41] was injected. The reaction was allowed to run for 1 minute before being quenched in a water bath. The QDs were washed twice by dissolving/precipitating with the solvent/non-solvent pair hexane/ethanol. The resulting QDs were dissolved in hexane and centrifuged at 7500 RPM for 10 min, then filtered through a 0.2 µm filter to remove any excess salts.

Films for PL and TA experiments were deposited on sapphire substrates by dipcoating with the QD in hexane solution and 1 mM EDT in acetonitrile. The sapphire substrate was submerged in the QD solution then removed slowly. After all hexane had dried the substrate was submerged in the EDT solution for about 2 seconds and then removed slowly. This process was repeated 20-30

times in order to build up an optically dense film with an OD $\sim$ 0.1-0.2 at the lowest energy exciton peak.

Pump-probe data were collected using a femtosecond transient absorption spectrometer (Helios, Ultrafast Systems). The laser source was a 4 W Ti-sapphire amplifier (Libra, Coherent), operating at 1 kHz and 100 fs pulse width. The fundamental beam at 800 nm was split, and a small portion (< 5 mW) was used to generate the near-infrared continuum (800 – 1700 nm) in a 1 cm thick sapphire rod. Another portion was attenuated with neutral density filters and used as the excitation source after being modulated at 500 Hz. The spot size was approximately 1 mm and 300 μ m for the pump and probe beams, respectively. The probe beam was split equally and directed to two different InGaAs array detectors. The portion that did not traverse the sample was used to cancel out laser fluctuations while the beam sent through the sample was collected and binned as either “pump on” or “pump off”, depending on the timing with respect to the 500 Hz excitation beam. The time delay was varied with an exponential distribution of time points out to 5 ns and averaged for 1 sec at each delay. Between two and ten scans were subsequently averaged. Fitting was performed in Igor Pro using a variety of kinetic schemes. The calculated $\langle N_{\text{abs}} \rangle$ values are determined from the pump fluence, the absorption cross section at 800 nm, and the measured spot size.

For temperature dependent PL experiments, the films were mounted in a closed loop He flow cryostat (18 K – 325 K) fitted with sapphire windows that was evacuated to 1×10^{-4} Torr. The sample was cooled to 18 K and then heated slowly in 20 K steps, with an equilibration time of 10 minutes at each temperature. Collecting PL spectra during cooling instead of heating produced the same results. The 514 nm line of an Ar-ion laser was used to excite the sample, with a beam size of approximately 2.5 mm and power varying from 0.5 to 150 mW. Each spectrum required

roughly one minute of exposure time. The excitation beam was modulated at 500 Hz, and the sample emission was routed through a monochromator with a 300 groove/mm grating blazed at 1250 nm. A dual, balanced Ge photodiode was used in concert with a lock-in amplifier to detect the signal. The spectral sensitivity of the entire system was determined with a calibrated tungsten lamp, and PL spectra were corrected accordingly.

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