

Supporting Information: PbS Nanocrystal Emission is Governed by Multiple Emissive States

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This supporting information is divided into three parts. In the first section, we show the Photoluminescent Excitation (PLE) spectra and Transmission Electron Microscopy for PbS NCs. We then derive Solution Photon Correlation Fourier Spectroscopy (S-PCFS) and our approach to fitting spectral linewidths from the spectral correlation measured using S-PCFS. We then derive and discuss the model used to fit the temperature dependent photoluminescence in the main text.

Photoluminescent Emission Spectroscopy

In figure S1a we show photoluminescent excitation spectra (PLE) collected on a NIR sensitive spectrometer (Ocean Optics) using a Fluoromax (Horiba Jobin Yvon) as an excitation

source. Transmission electron microscopy was conducted using an FEI Tecnai Electron Microscope. PLE shows that size heterogeneity contributes at least 30 meV to the observed linewidth, however even upon size selective excitation, the emission linewidth is still over 150 meV consistent with S-PCFS measurements shown in figure 2d (center spectrum). TEM demonstrates significant size and shape heterogeneity within the limited resolution available for imaging sub 2-nm particles.

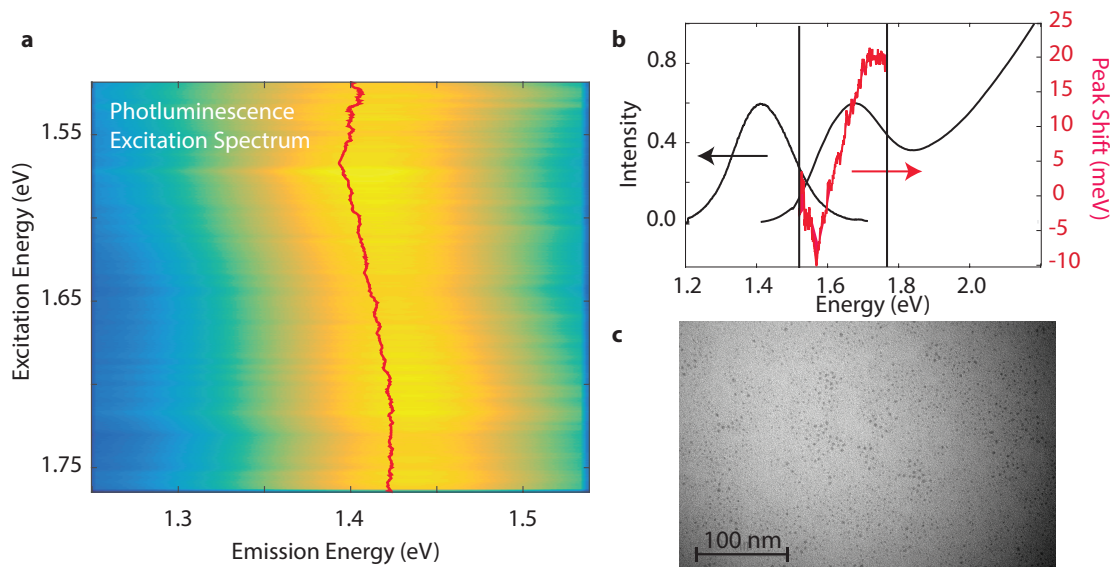


Figure S 1: a) The two dimensional excitation-emission spectrum of a PbS quantum dot sample (plotted in the center of figure 2d). b) Ensemble absorption and emission spectra (black) plotted with the peak shift from the central energy (red). The peak shift is plotted against wavelength of excitation. c) TEM of nanoparticles studied shows size polydispersity, though contrast is poor for sub-2nm particles.

Solution-Photon Correlation Fourier Spectroscopy

The technique Solution-Photon Correlation Fourier Spectroscopy (S-PCFS) allows us to measure the spectral correlation of photon pairs arriving from an ensemble of emitters diffusing through a focal volume.¹⁻⁴ It accomplishes this by mapping these photons probabilistically to the outputs of a Michelson interferometer with a variable path length difference (δ) based on their energies. By measuring the photon stream on each leg of the interferometer (defined

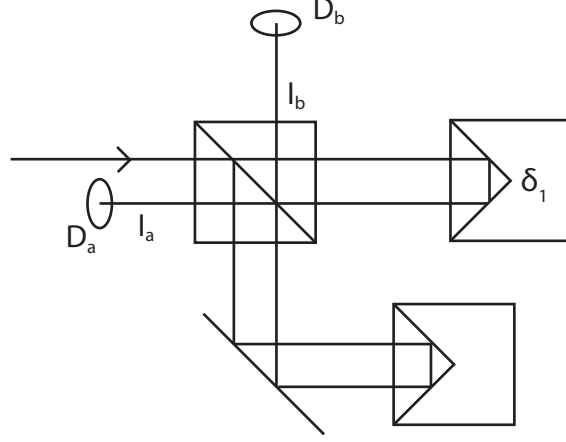


Figure S 2: Traditional photon correlation Fourier spectroscopy utilizes two detectors on either end of a Michelson Interferometer. By varying δ over different distances, photons are mapped to D_a and D_b with different probabilities. The cross-correlation signal between detectors can be used to study intraphoton energy gaps as a function of time.

as a and b in figure S2), the second order intensity correlation g^2 , encodes both single emitter diffusion information as well as spectral information, allowing us to combine fluorescence correlation spectroscopy (FCS) with Fourier spectroscopy to obtain *average* single molecule linewidths.⁵ Below, we provide a derivation (taken in part from references 4 and 5) of how to extract an average single molecule spectrum from an S-PCFS interferogram.

In figure S2 we show the setup for a typical PCFS experiment. From reference 5, each interferometer output (denoted a , b) has an electric field as follows:

$$E_a(t) = \mathcal{R}\mathcal{R}E(t) + \mathcal{T}\mathcal{T}E(t + \delta/c) \quad (1)$$

$$E_b(t) = \mathcal{R}\mathcal{T}E(t) + \mathcal{T}\mathcal{R}E(t + \delta/c) \quad (2)$$

Where c is the speed of light and $\mathcal{R}/\mathcal{T}$ represents reflection or transmission of the electric

field. The detected intensity $I_a(t)$ is the square of the electric field at detector a

$$\begin{aligned}
I_a(t) &= \frac{1}{2}\epsilon_0 c |E_a(t)|^2 = \\
&\frac{1}{2}\epsilon_0 c [\mathcal{R}^* \mathcal{R}^* E^*(t_1) + \mathcal{T}^* \mathcal{T}^* E^*(t_1 + \delta/c)] [\mathcal{R} \mathcal{R} E(t_1) + \mathcal{T} \mathcal{T} E(t_1 + \delta/c)] = \\
&\frac{1}{2}\epsilon_0 c |\mathcal{R}|^2 |\mathcal{T}|^2 (|E(t_1)|^2 + |E(t_1 + \delta/c)|^2 + 2 * \text{Re}[E^*(t_1) E(t_1 + \delta/c)]) \quad (3)
\end{aligned}$$

Taking the time averaged value of $I_a(t)$ and changing $\delta/c = \tau_g$

$$\langle I_a(t) \rangle = \epsilon_0 c |\mathcal{R}|^2 |\mathcal{T}|^2 \langle |E(t)|^2 \rangle \left(1 + \left\langle \text{Re} \frac{E^*(t_1) E(t_1 + \tau_g)}{|E(t)|^2} \right\rangle \right) \quad (4)$$

Here we have utilized the assumption that the fields are *stationary*. In other words, the time averaged intensity is identical to the statistical average over an ensemble of emitters. This allows us to assert that $\langle E(t_1) \rangle = \langle E(t_1 + \tau_g) \rangle = \langle E(t) \rangle$. We can analyze the response of the field as a function of time separation τ between photon arrivals. The second term in equation 4 can be expressed as follows,

$$\left\langle \frac{\text{Re}[E(t_1) E^*(t_1 + \tau_g)]}{|E(t)|^2} \right\rangle = \frac{\text{Re}[\langle E^*(t_1) E(t_1 + \tau_g) \rangle]}{\langle |E(t)|^2 \rangle} = g^{(1)}(\tau_g). \quad (5)$$

Where $g^{(1)}(\tau_g)$ is the *degree of first-order temporal coherence of light*. The Wiener-Khintchine theorem maps $g^{(1)}(\tau_g)$ to the frequency spectrum of the emitted light

$$g^{(1)}(\tau_g) = \int_{-\infty}^{\infty} s(\omega) \exp(2\pi i \omega \tau_g) d\omega = FT[s(\omega)]_{\tau_g} \quad (6)$$

Leaving us with the time averaged intensity relationship

$$\langle I_a(t) \rangle = \frac{1}{2} \langle I(t) \rangle (1 \pm \text{Re}\{FT[S(\omega)]_{\tau_g}\}) \quad (7)$$

Where $I(t) = 1/2\epsilon_0 c |E(t)|^2$ and $|\mathcal{R}|^2 = |\mathcal{T}|^2 = 1/2..$

From equation 7 we can now begin to evaluate correlation functions. First, let us assert a form for $S(\omega)$, the spectral function, which represent the distribution of photon frequencies (energies) from the emissive sample.

$$S(\omega) = \delta(\omega[t]) \quad (8)$$

In this equation, δ represents delta function in frequency and $\omega[t] = \omega_0 + \Delta(t)$, where ω_0 is a central carrier frequency and $\Delta(t)$ is a time varying fluctuation in the central energy of a single emitter such that $\langle \Delta(t) \rangle = 0$. Plugging this into equation 7 we get a time averaged intensity function for path a ,

$$\langle I_{a/b}(t) \rangle = \frac{1}{2} \langle I(t) \rangle (1 \pm \langle \text{Re}\{FT[\delta(\omega[t])]\} \rangle) = \frac{1}{2} \langle I(t) \rangle (1 \pm \langle \cos(\tau_g \omega[t]) \rangle) \quad (9)$$

While the choice of sign is arbitrary, due to conservation of energy, it must be the opposite for each detector.

Given this, let us evaluate the intensity cross correlation function across detectors

$$g^{ab} = \frac{\langle I_a(t) I_b(t + \tau) \rangle}{\langle I_a(t) \rangle \langle I_b(t + \tau) \rangle} \quad (10)$$

$$g^{(ab)}(\tau) = \frac{\frac{1}{4} \langle I(t)(1 + \cos(\tau_g \omega[t]) I(t + \tau)(1 - \cos(\tau_g \omega[t + \tau])) \rangle}{\frac{1}{4} \langle I(t) \rangle \langle I(t + \tau) \rangle} \quad (11)$$

Making the assumption that frequency fluctuations are independent of intensity fluctuations we can simplify equation 10:

$$g^{(ab)}(\tau) = \frac{\langle I(t) I(t + \tau) \rangle \langle (1 + \cos(\tau_g \omega[t])(1 - \cos(\tau_g \omega[t + \tau])) \rangle}{\langle I(t) \rangle \langle I(t + \tau) \rangle}. \quad (12)$$

Expanding the binomial yields

$$\begin{aligned} \langle (1 + \cos(\tau_g \omega[t]))(1 - \cos(\tau_g \omega[t + \tau])) \rangle = \\ \langle (1 + \cos(\tau_g \omega[t]) - \cos(\tau_g \omega[t + \tau]) - \cos(\tau_g \omega[t])\cos(\tau_g \omega[t + \tau])) \rangle. \end{aligned} \quad (13)$$

In the implementation of PCFS, we "dither" (oscillate) a stage over several optical periods ($1/\omega_0$) while measuring the correlation function such that any term which oscillates at an optical frequency averages to zero, for example

$$\langle \cos(\tau_g \omega[t]) \rangle = \int_0^T \cos(\tau_g(\omega_0 + \Delta(t))) d\tau_g \approx 0 \quad (14)$$

Therefore, the middle terms of equation 13 are experimentally eliminated using the dither described by equation 14. The outside term can be expressed using the trigonometric identity $\cos(u)\cos(v) = \frac{1}{2}(\cos(u - v) + \cos(u + v))$ yielding

$$\begin{aligned} \langle \cos(\tau_g \omega[t])\cos(\tau_g \omega[t + \tau]) \rangle &= \frac{1}{2} \langle \cos(\tau_g(\omega[t] - \omega[t + \tau])) + \cos(\tau_g(\omega[t] + \omega[t + \tau])) \rangle = \\ &= \frac{1}{2} \langle \cos(\tau_g(\Delta(t) - \Delta(t + \tau))) + \cos(\tau_g(2\omega_0 + \Delta(t) + \Delta(t + \tau))) \rangle = \\ &= \frac{1}{2} \langle \cos(\tau_g(\Delta(t) - \Delta(t + \tau))) \rangle. \end{aligned} \quad (15)$$

The final expression in (15) comes from eliminating the components that oscillate at twice the optical frequency. We now express the cross correlation signal as follows:

$$g^{(ab)}(\tau) = g^{(2)}(1 - \frac{1}{2} \langle \cos(\tau_g(\Delta(t) - \Delta(t + \tau))) \rangle) \quad (16)$$

$$g^{ab}(\tau) = g^{(2)}(\tau) \left(1 - \frac{1}{2} \text{Re}\{FT[p(\zeta, \tau)]\} \right) \quad (17)$$

$$\text{Re}\{FT[p(\zeta, \tau)]\} = 2 \left(1 - \frac{g^{ab}(\tau)}{g^{(2)}(\tau)} \right) \quad (18)$$

After Fourier transform over the a range of path length distances, δ , we obtain the the *auto-*

correlation of the fluorescence spectrum $S(\omega)$ the spectral correlation. Here $p(\zeta, \tau)$ describes the relative emission frequencies.

$$p(\zeta, \tau) = \frac{1}{\tau} \int_0^T \int_{-\infty}^{\infty} S^*(\omega, t) S(\omega + \zeta, t + \tau) d\omega dt \quad (19)$$

It is straightforward to extend this result to ensemble spectral correlations in solution.^{2,3} In this case, we arrive at the governing equation

$$Re\{FT [(g^2(\tau) - 1)p_{single}(\zeta, \tau) + p_{ens}(\zeta, \tau)]\} = 2(g^2(\tau) - g^{ab}(\tau)) = \tilde{g}^2(\tau) \quad (20)$$

Using the fact that an ensemble of emitters will have Poissonian statistics, and that the single molecule contribution decays to zero after the particle diffuses out of the focal volume t_D , ($g_{ens}^2(\tau) = 1$ and $g_{single}^2(\tau > \tau_D) = 0$) we arrive at the single molecule contribution to the spectral correlation.

$$Re\{FT [p_{single}(\zeta, \tau)]\} = \frac{2(g^2(\tau) - g^{ab}(\tau)) - \tilde{g}^2(\tau > \tau_D)}{(g^2(\tau) - 1)} \quad (21)$$

This technique allow us to monitor spectral fluctuations of individual molecules across a diverse set of correlation time-scales. In this paper we average the signal over the from 10 μ s to 1 ms. S-PCFS probes the spectral correlation, or the intraphoton energy gaps, losing information about the absolute energy. This makes it impossible to directly invert the spectral correlation to arrive at the time resolved fluorescence spectrum. To arrive at the spectra plotted in figure 2d we use a spectral model (two displaced Gaussians) to arrive at a spectral correlation expression. We detail this procedure below.

Spectral correlation from asymmetric lineshapes

In previous S-PCFS implementations, the spectral correlation is fit to a set of symmetric Gaussian functions, which describes the emission from single quantum dots in solution and

enables the direct extraction of linewidth.³ In this paper, we assert that PbS nanocrystals emit from two states which interchange at room temperature. Given this, we observe a slightly asymmetric lineshape ensemble lineshape. To fit the S-PCFS data, we have implemented a modified model, which explicitly accounts for lineshape asymmetry by fitting to two Gaussian functions with a displacement a and standard deviations σ .

$$G_{tot}(\omega; C_1, C_2, a, \sigma_1, \sigma_2) = C_1 \exp\left(\frac{\omega^2}{2\sigma_1^2}\right) + C_2 \exp\left(\frac{(\omega - a)^2}{2\sigma_2^2}\right) \quad (22)$$

We then take the autocorrelation of the G_{tot} , G_{AC} , which can be analytically expressed as follows

$$G_{AC} = \int_{-\infty}^{\infty} G_{tot}(\omega) * G_{tot}(\omega + \omega_1) d\omega_1$$

$$\sqrt{\pi} \left(\frac{C_1^2 e^{\frac{-\omega^2}{4\sigma_1^2}}}{\sqrt{\frac{1}{\sigma_1^2}}} + \frac{\sqrt{2} C_1 C_2 e^{\frac{-a^2 + \omega^2}{\sigma_1^2 + \sigma_2^2}} \left(e^{\frac{(a-\omega)^2}{2(\sigma_1^2 + \sigma_2^2)}} + e^{\frac{(a+\omega)^2}{2(\sigma_1^2 + \sigma_2^2)}} \right)}{\sqrt{\frac{1}{\sigma_1^2} + \frac{1}{\sigma_2^2}}} + \frac{C_2^2 e^{\frac{-\omega^2}{4\sigma_2^2}}}{\sqrt{\frac{1}{\sigma_2^2}}} \right). \quad (23)$$

The Fourier transform of G_{AC} is a function as follows.

$$\text{ReFT}[G_{AC}] = \sqrt{2\pi} \left(C_1 \sigma_1^2 e^{\sigma_1^2 \delta^2} + C_2 \sigma_2^2 e^{\sigma_2^2 \delta^2} + C_1 C_2 e^{\frac{1}{2}(\sigma_1^2 + \sigma_2^2) \delta^2} (\sigma_1^2 \sigma_2^2) \sqrt{\frac{1}{\sigma_1^2} + \frac{1}{\sigma_2^2}} \sqrt{\frac{1}{\sigma_1^2 \sigma_2^2}} \right) \quad (24)$$

from this equation we extract a FWHM of the emission profile and plot the two Gaussian fit for comparison in figure 2e of the main text.

Model of Multi-State PbS Emission

We invoke the model shown in figure 4a-b to explain the emissive properties of PbS nanocrystals. Here state A represents band-edge emission while state B is a defect state. We modulate the population of each state using temperature. The initial populations of A and B are C_A

and C_B respectively. Transitioning from A to B is governed by an activation barrier with forward and reverse rates k_1 and k_2 . States A and B will also relax irreversibly to the ground state with rates k_A and k_B .



The time dependence the populations of A and B are reflected in the following differential equations,

$$A' = -k_1 A - k_A A + k_2 B \quad \text{and} \quad B' = -k_2 B - k_B B + k_1 A. \quad (26)$$

We recast (26) as a second-order homogeneous differential equation in A,

$$\underbrace{A''}_a + \underbrace{(k_1 + k_2 + k_A + k_B)}_b A' + \underbrace{(k_1 k_B + k_2 k_b + k_A k_B)}_c A = 0, \quad (27)$$

leading to a characteristic polynomial with the discriminant $D = b^2 - 4ac$

$$D = (k_1 + k_2 + k_A + k_B)^2 - 4(k_1 k_B + k_2 k_b + k_A k_B) = (k_1 - k_2 + k_A - k_B)^2 + 2k_1 k_2. \quad (28)$$

In this model, $k_x > 0$, making $D > 0$ allowing the solution of (27) to be two exponentials,

$$A(t) = C_+ e^{-r(+)t} + C_- e^{-r(-)t} \quad (29)$$

Where r is the solution to the characteristic polynomial of the differential equation. We fit to equation 29 in the manuscript. Given the initial conditions $A(0) = C_A$ and $B(0) = C_B$

the time evolution of states A and B is as follows:

$$F_{i,j,k,l} = C_k(k_1 - k_2 + k_A - k_B) - 2C_l k_j \quad (30)$$

$$A(t) = \frac{1}{2\sqrt{D}} \left((F_{1,2,A,B} + C_1\sqrt{D})e^{\frac{-1}{2}(b+\sqrt{D})t} + (-F_{1,2,A,B} + C_1\sqrt{D})e^{\frac{-1}{2}(b-\sqrt{D})t} \right) \quad (31)$$

$$B(t) = \frac{1}{2\sqrt{D}} \left((F_{2,1,B,A} + C_2\sqrt{D})e^{\frac{-1}{2}(b+\sqrt{D})t} + (-F_{2,1,B,A} + C_2\sqrt{D})e^{\frac{-1}{2}(b-\sqrt{D})t} \right) \quad (32)$$

Our spectroscopic observables are a) The total population dynamics as a function of temperature $C(t; T) = A(t; T) + B(t; T)$, and b) The relative contribution of states A and B to the total emission at different temperatures. The total population is as follows,

$$C(t) = \frac{1}{2\sqrt{D}} \left(\left(C_A(-m + n + \sqrt{D}) + C_B(-m - n + \sqrt{D}) \right) e^{\frac{-1}{2}(b+\sqrt{D})t} + \left(C_A(m - n + \sqrt{D}) + C_B(m + n + \sqrt{D}) \right) e^{\frac{-1}{2}(b-\sqrt{D})t} \right), \quad (33)$$

with $m = k_1 + k_2$ $n = k_A - k_B$. We measure equation 33 through time resolved photoluminescence. We assert that transport between states A and B is mediated by a fixed activation energy E_a and a total energy difference E_{AB} as shown:

$$k_1 = A_p e^{-\beta E_a} \quad k_2 = A_p e^{-\beta(E_a + E_{AB})}. \quad (34)$$

With $\beta = 1/K_{boltz}T$ and A_p representing an attempt rate. In figure 3, we fit the total population dynamics to equation (29), and plot observed rates (in this case $r_{(-)}$) in figure 4a. That rate can be best fit to the following equation:

$$r_{(-)} = (b - \sqrt{D})/2 = (k_A + k_B + A_p e^{-E_a\beta} + A_p e^{-(E_a + E_{AB})\beta} - \sqrt{2A_p^2 e^{-(2E_a + E_{AB})\beta} + (k_A - k_B + A_p(e^{-E_a\beta} - e^{-(E_a + E_{AB})\beta}))^2}). \quad (35)$$

We fit this rate this equation to the temperature dependence of the slow-rate in figure 5a.

We also compare the model, to the temperature dependent relative $Rel_{qy}(T)$. We collect all spectra with equal laser power and only varying the temperature and normalize to the 77 K spectrum. Assuming the radiative and nonradiative rates stay constant we can fit the normalized QY to

$$Rel_{qy}(T) = \frac{\int_0^\infty C(t; \beta) dt}{\int_0^\infty C(t; 77K) dt} \quad (36)$$

$$\int_0^\infty C(t; \beta) dt = \frac{4((k_1 + k_2 + k_A)C_B + (k_1 + k_2 + k_B)C_A)}{b^2 - D}. \quad (37)$$

We plot the results in figure 5b. To further confirm the model in supplemental figure S3 a-c we plot the same data from figure 3a, but normalized to integrated intensity, which shows the observed change in spectral character as a function of temperature. We fit each spectra to two Gaussians (equation 1 in the main text), varying the intensity and linewidth as a function of temperature. In figure S3d, we plot the ratio of State A to the total spectrum. Using the parameters in table 1 of the main text we overlay the following equation in figure S3d

$$\frac{\int_0^\infty A(t) dt}{\int_0^\infty C(t) dt} = \frac{(b^2 - D)(C_B k_2 + C_A(k_2 + k_B))}{(2(k_2 k_A + k_2 k_B + k_A k_B)(C_B(m + n - b) + C_A(m - n - b)))} \quad (38)$$

We observe good agreement to the data, however, the large dots show more spectral character from the defect at low-temperatures than expected from the model.

Finally, in figure S4a-c we plot emission energy resolved spectra for 3.1 nm QDs. In S4a, we plot the spectra of QDs at room and 77 K, along with the 5 band pass filters used to collect spectra 1-5. In S4b-c we plot emission lifetimes for all 5 filters, at 300 K and 77 K. As expected, we observe a significant increase in the lifetime as we scan from “defect” dominated emission to (blue) to band-edged dominated emission (red). We observe bi-exponential behavior reflective of two states as discussed in the main text, with slower dynamics and interchange between states at 77 K (figure S4c).

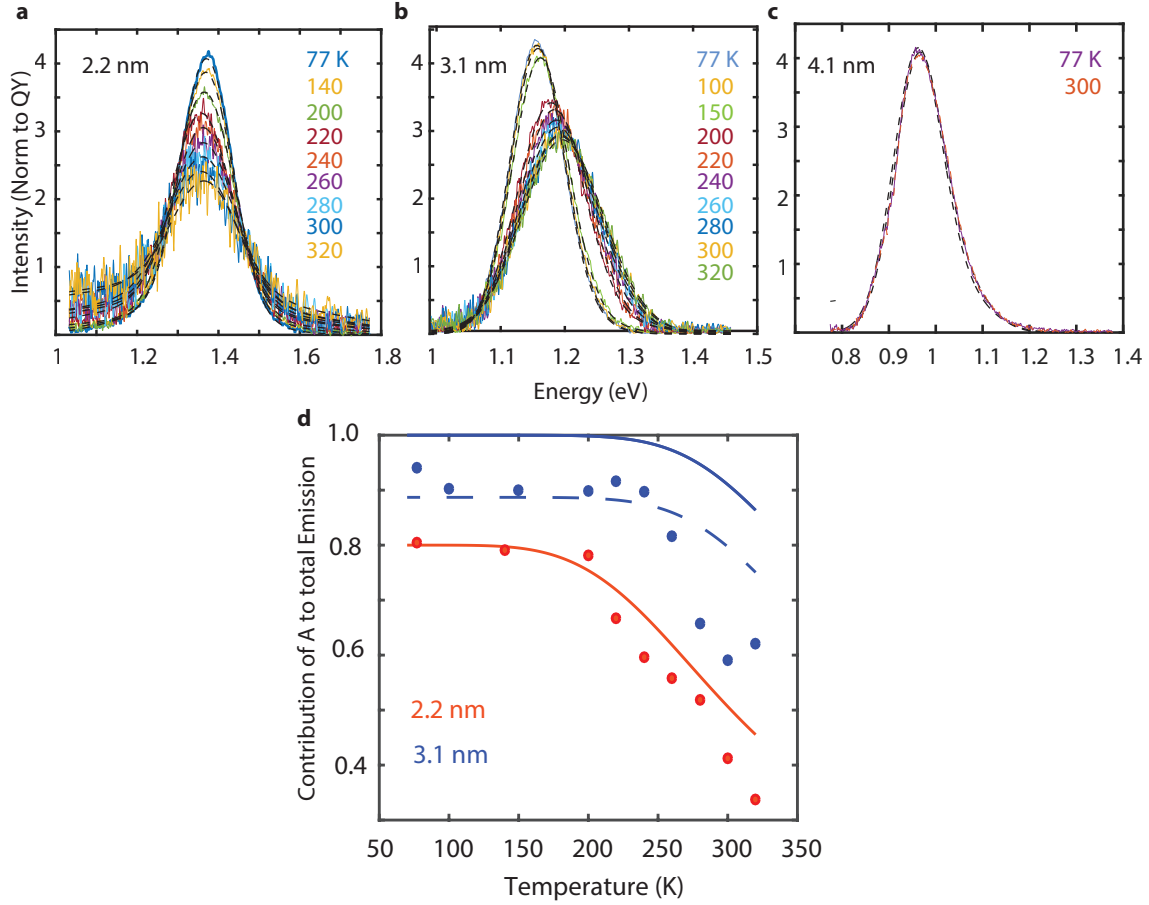


Figure S 3: a) Temperature-Dependent PbS NC emission, for 2.2(a), 3.1(b) and 4.1(c) nm nanocrystals to their total area for temperatures ranging from 77 to 320 K. We fit each spectra to two Gaussians as discussed in the main text. d) We plot the contribution of the band-edge Gaussian (A) to the total emission of 2.2 and 3.1 nm QDs. Solid lines are equation S38 using averaged fit values from table 1. The dashed line represents the solution of equation S38 shifted down for better comparison to the data. The offset may be attributed to a non-interconverting sub-ensemble of NCs.

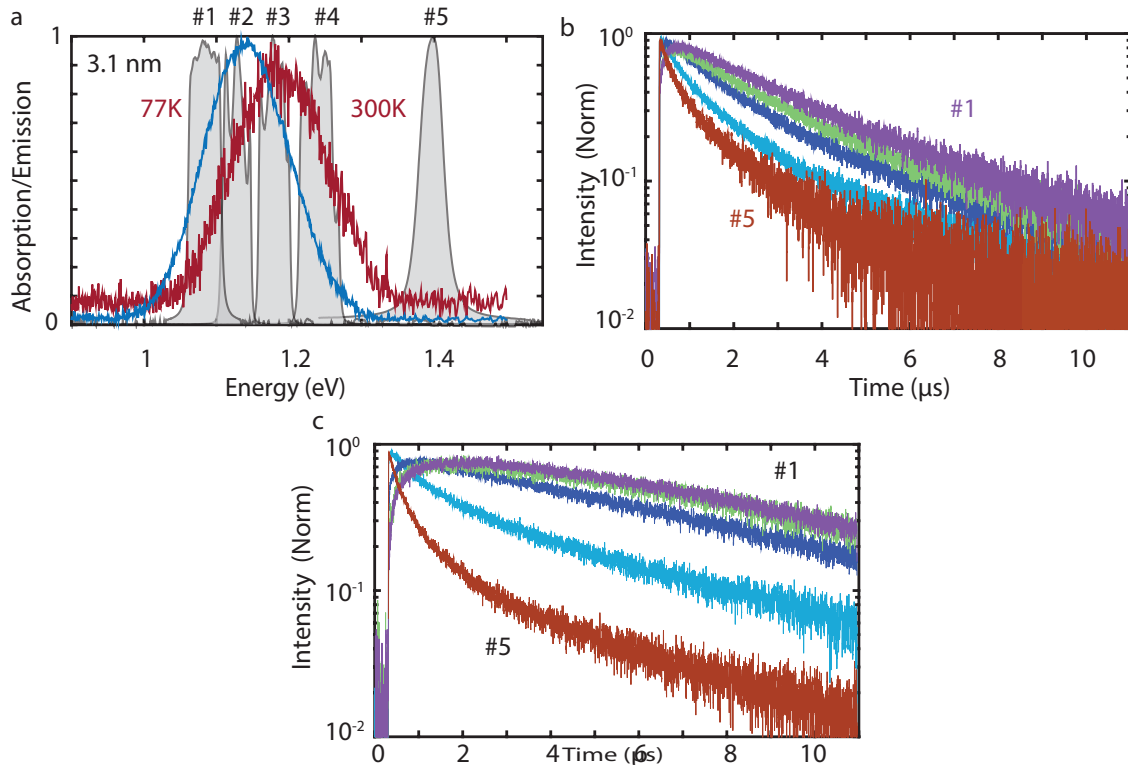


Figure S 4: a) The emission of 3.1 nm QDs at room temperature and 77 K, plotted against 5 band-pass emission filters. b-c) Time-resolved PL spectra for each filter at room temperature (b) and 77 K (c). The biexponential behavior is consistent with two slowly equilibrating states, where equilibration is slower at 77 K than at room temperature.

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