Origins of Stokes Shift in PbS Nanocrystals

Oleksandr Voznyy,[†] Larissa Levina,[†] Fengjia Fan,[†] Grant Walters,[†] James Z. Fan,[†] Amirreza Kiani,[†] Alexander H. Ip,[†] Susanna M. Thon,[‡] Andrew H. Proppe,[†] Mengxia Liu,[†] and Edward H. Sargent*,[†]

[†]Department of Electrical and Computer Engineering, University of Toronto, 10 King's College Road, Toronto, Ontario M5S 3G4, Canada

[‡]Department of Electrical and Computer Engineering, Johns Hopkins University, 3400 North Charles Street, Baltimore, Maryland 21218-2608, United States

S *Supporting Information*

ABSTRACT: Stokes shift, an energy difference between the excitonic absorption and emission, is a property of colloidal quantum dots (CQDs) typically ascribed to splitting between dark and bright excitons. In some materials, e.g., PbS, CuInS$_2$, and CdHgTe, a Stokes shift of up to 200 meV is observed, substantially larger than the estimates of dark−bright state splitting or vibronic relaxations. The shift origin remains highly debated because contradictory signatures of both surface and bulk character were reported for the Stokes-shifted electronic state. Here, we show that the energy transfer among CQDs in a polydispersed ensemble in solution suffices to explain the excess Stokes shift. This energy transfer is primarily due to CQD aggregation and can be substantially eliminated by extreme dilution, higher-viscosity solvent, or better-dispersed colloids. Our findings highlight that ensemble polydispersity remains the primary source of the Stokes shift in CQDs in solution, propagating into the Stokes shift in films and the open-circuit voltage deficit in CQD solar cells. Improved synthetic control can bring notable advancements in CQD photovoltaics, and the Stokes shift continues to provide a sensitive and significant metric to monitor ensemble size distribution.

KEYWORDS: *Stokes shift, colloidal quantum dots, nanocrystals, energy transfer, aggregation*
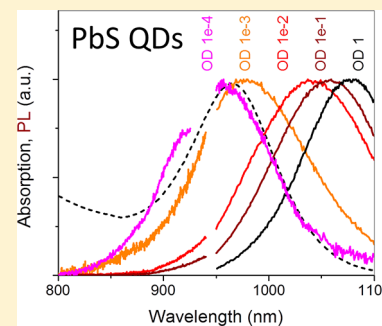
The Stokes shift in colloidal quantum dots (CQDs) is usually ascribed to excitonic fine structure: the manifold of closely spaced optical transitions, some of which are forbidden by parity and spin selection rules. The resulting optically passive (dark) excitons are undetectable in absorption spectra[1−5] and typically lie lowest in energy and thus produce and dominate photoluminescence, albeit with extended photoluminescence lifetime due to low transition oscillator strength. The resulting shift between absorption (bright excitons) and emission (dark excitons) spectra is the Stokes shift, analogous to the behavior of molecular emitters, albeit mechanistically distinct.

Controlling the Stokes shift in CQDs is of significant applied importance. Light-emitting diodes benefit from a thermally populated bright ground state (i.e., small dark−bright level splitting) with a strong transition oscillator strength and, thus, short radiative lifetime that competes efficiently with nonradiative processes. In contrast, in luminescent solar concentrators and lasers, a Stokes shift large enough to eliminate light reabsorption is desired.[6,7] In photovoltaics, the difference between optical and electronic bandgaps leads to losses in the open-circuit voltage and should desirably be minimized.[8] Lead sulfide is a material that has shown notable performance progress in CQD solar cells, yet today, it is particularly prone to a large Stokes shift whose origin remains unresolved.[9−12]

Theoretical models of exciton fine structure based on effective mass,[3,13−15] tight-binding,[1,4,16] and pseudopoten-tial[2,17] approximations reliably predict the Stokes shift in CdSe CQDs. However, they fail dramatically in PbS, where shifts reaching 200 meV for ∼3 nm diameter CQDs are observed. Estimations of the Franck−Condon shift[18] and exchange interaction[2,14] predict, at most, a Stokes shift of 20 meV, suggesting that a different, yet not uncovered, mechanism is responsible for the majority of the shift. In the absence of a better explanation, large Stokes shift is often ascribed to surface trap states[10] or to symmetry-forbidden optical transitions.[19] Such uncertainty impedes further progress in CQD optoelectronics.

Here, we demonstrate efficient energy transfer between CQDs in solution in ensembles that exhibit a typical distribution in nanoparticle sizes. In a manner that is then further emphasized by the effect of long photoluminescence lifetimes and CQD aggregation, this transfer of carrier population suffices to account for the observed excess Stokes shift. In support of this proposed mechanism, we show that Stokes shift can be nearly eliminated via dilution and by improving the colloidal stability.

Typical absorption and photoluminescence spectra for PbS CQDs of ∼3 nm in diameter (exciton peak 930−990 nm) are shown in Figure 1a. Samples are sufficiently dilute (optical
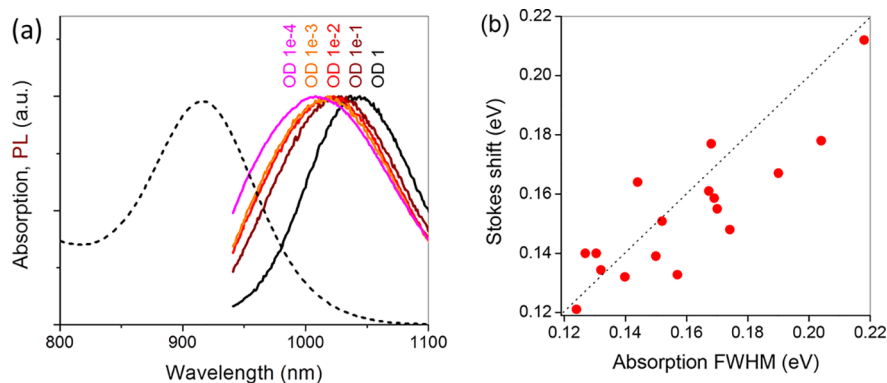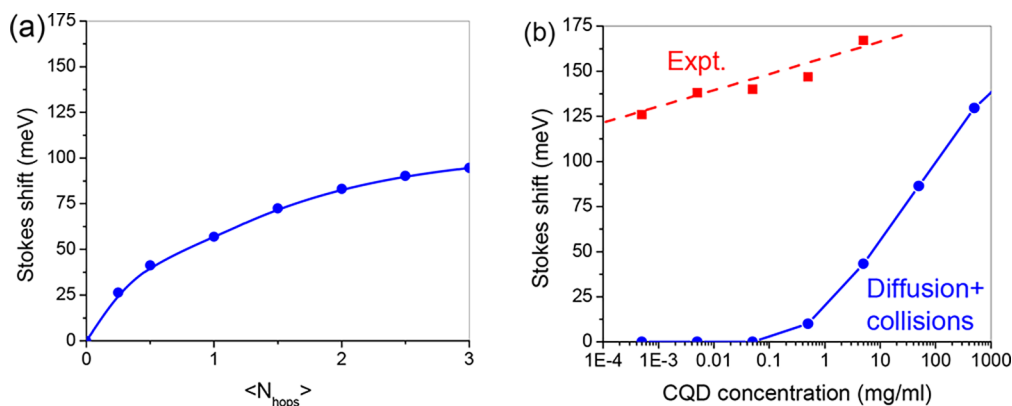
Figure 1. Stokes shift in PbS CQD solutions. (a) Absorption and emission spectra at 10×−100 000× dilutions. (b) Correlation between the Stokes shift and exciton absorption line width in different PbS CQD batches in the 930−990 nm range diluted 100× (OD 0.1 in a 1 mm cuvette). Representative spectra are shown in Figure S5.


Figure 2. Monte Carlo modeling of energy transfer. (a) Stokes shift vs number of energy-transfer hops in an ensemble with Gaussian size distribution. (b) Stokes-shift dependence on CQD concentration compared with experimental values.

density (OD) of less than 0.01 (transmittance 98%) at exciton peak in a 1 mm cuvette) to avoid optical reabsorption (Figure S1), which otherwise screens the blue side of the peak, resulting in an apparent peak red-shifting and narrowing. Nevertheless, the Stokes shift value has not saturated, even at the lowest concentration. A similar effect is observed for larger CQDs (Figure S2). This hints that the Stokes shift could be further reduced by diluting even more. At such low CQD concentrations, however, photoluminescence measurements become problematic due to extremely low signal strength. Stability of the CQD surface is a concern at such high dilutions due to a gradual loss of the lead oleate ligands and consequent etching.[20] We thus verified that the absorbance of the samples has not changed on the time scale of the experiment (Figure S3).

Because reabsorption is negligible at the lowest concentrations, we hypothesized that energy transfer within a polydisperse ensemble could contribute to the Stokes shift. Indeed, if such an energy transfer were present, carriers would funnel into the lowest-energy tail of the distribution, as happens in coupled CQD films.[21−26] This hypothesis is consistent with a strong correlation between the CQD size distribution (assessed via the exciton peak width) and the Stokes shift in multiple measured CQD batches in solution (Figure 1b), also observed previously.[27] Stokes shift in solution is only 20 meV smaller than in drop-cast CQD films (Figure S4). Despite being well-documented in CQD films with strong interdot coupling, energy transfer in solution was quite unexpected.

Indeed, Forster resonance energy transfer and tunneling transfer efficiencies decay extremely fast with distance.[26] This excludes the possibility of long-range transfer across the solvent and requires that CQDs collide for energy transfer to happen. To describe the probability of such collisions in diluted solutions, we performed kinetic Monte Carlo simulations of CQDs under continuous illumination, with an ensemble size distribution comparable to the experimental one (150 meV; see details in Supporting Information). We found that two or three energy-transfer events (hops) are sufficient to shift the photoluminescence by 100 meV (Figure 2a). Given the long radiative lifetime of PbS CQDs (2.5 μs), CQD migration and rare collisions are feasible, at least in the highest-concentration regime.

A more-accurate estimate of the collision lifetime for 10 000× dilution (0.05 mg/mL, OD 0.001), however, is in the range of 3 ms, significantly longer than the photoluminescence lifetime, thus resulting in essentially zero Stokes shift (Figure 2b). Moreover, even the slope of the Stokes shift concentration dependence is found to deviate from the one dictated by the diffusion equation $L_d = \sqrt{D\tau}$, where L_d is the CQD diffusion length (related to CQD concentration), D is the diffusion coefficient (constant), and τ is the lifetime (constant). We thus conclude that there should be a fraction of CQDs remaining in close contact despite the extreme dilution. Dynamic light scattering (DLS) qualitatively supports this hypothesis, showing large CQD aggregates at lower dilutions (Figure S6).
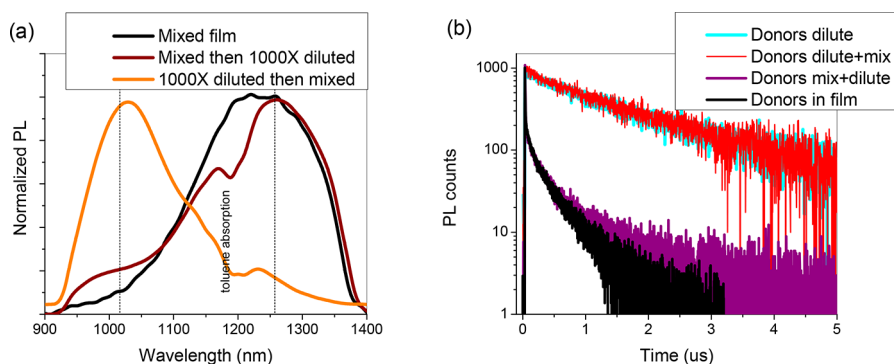
Figure 3. Energy transfer in donor−acceptor CQD mixtures. (a) Redistribution of photoluminescence intensities between donors and acceptors. Dotted lines show the donor and acceptor emission peaks at high concentrations and where photoluminescence decays were measured. (b) Photoluminescence decays of donor CQDs showing that energy transfer happens only in the presence of CQD aggregation.

To explicitly test energy transfer and the crucial role of CQD aggregation, we mixed in equal proportion (Figure S7) two CQD batches emitting at different wavelengths and monitored the redistribution of their photoluminescence (Figure 3a). Photoluminescence decays of the donors (Figure 3b) are used as a signature of energy transfer (Figures S8 and S9). Samples were diluted 1000× (0.05 mg/mL, OD of 0.01 in a 1 mm cuvette) to avoid reabsorption. When donor and acceptor CQDs are diluted first and then mixed together, no energy transfer can be observed (Figure 3). However, when CQDs are mixed at 50 mg/mL and then diluted 1000×, energy transfer on a tens of nanoseconds time scale, comparable to that in drop-cast films, is clearly detectable, suggesting that at high concentrations, the dots collide and aggregate, and these aggregates remain intact even after dilution.

To reduce aggregation, we replaced toluene with octadecene, a nonpolar solvent that can provide stronger van der Waals interactions with the CQDs. This allowed the further suppression of the Stokes shift despite a noticeable CQD etching (Figure S10).

We also noted that, even in toluene, improving the surface passivation by increasing chloride ligands[28] led to similar improvements (Figure 4). Stronger concentration dependence without changing the solvent viscosity indicates that it is the aggregation rather than diffusion that was most affected by
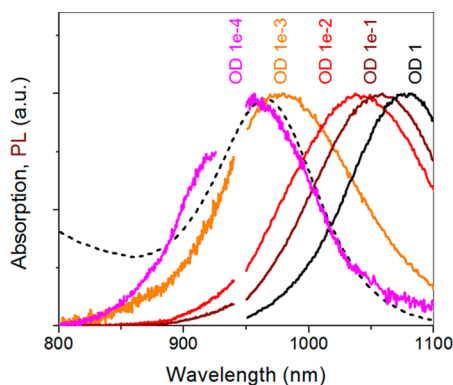
Figure 4. Absorption and emission spectra of PbS CQDs passivated with chloride ligands at 10× to 100 000× dilutions. The cutout at 950 nm is the spectral range not covered by the visible and NIR photodetectors. Absorption peak remains stable down to an OD of 1×10^{-3} (Figure S3), whereas some etching and blue-shifting cannot be excluded at an OD of 1×10^{-4}.

passivation. We note, however, that aggregation and the ensuing energy transfer are not completely eliminated but only suppressed because the photoluminescence peak remains broader than the excitonic peak in the absorption spectrum, and a discrepancy remains with the theoretical diffusion model in which the latter predicts elimination of the Stoke shift already at 1000× dilution (OD of 0.01).

The role of Cl in suppressing aggregation will require further studies. At this moment, several hypotheses can be suggested: chloride-treated CQDs may possess better surface coverage by ligands that could protect from aggregation; alternatively, the origin of aggregation and oriented attachment may relate to internal dipoles,[29] recently attributed to PbS lattice distortion.[30] Chloride passivation could potentially reduce this dipole.

Our findings reveal efficient energy transfer between CQDs in a polydisperse solution-phase ensemble, amplified by a long photoluminescence lifetime. This energy transfer and the resulting Stokes shift reveal the true extent of the polydispersity, making it a useful metric for assessing the ensemble quality.

We recently reported the role of bandtails arising from broad size distribution in photovoltaic CQD films.[8] Because the majority of the carrier population resides in the bandtails, their energy defines the solar cell open-circuit voltage as well as the efficiency of charge injection into electrodes. Preservation of the Stokes shift from solution to films implies that the exchange procedure to conductive ligands does not deteriorate the CQD properties significantly. It has thus been concluded that a major breakthrough in CQD solar cell open-circuit voltage will require the elimination of the Stokes shift component arising already in the solution phase. The origin of the Stokes shift in solution, however, has been so far debated.[9−12] Here, we uncover that the Stokes shift in solution can be fully accounted for by polydispersity, pinpointing where to focus the efforts that could pay off as a 25% improvement in photovoltaic performance. Improvements in the size distribution of the ensemble will require developing better syntheses via, e.g., fine-tuning of synthetic parameters[31] or changing precursors to engineer reactivity more finely.[32]

Lastly, a large Stokes shift is also observed in other materials, such as $CuInS_2$[33] and CdHgTe.[34] It is interesting to note that the photoluminescence lifetime of these materials is also long, and monodispersity is poor.[35] Moreover, even in $CsPbBr_3$ CQDs with photoluminescence lifetimes in the tens of nanoseconds range, there is a strong dependence of the Stokes shift on CQD size and polydispersity;[36] in CdSe, resonant and

ensemble Stokes shifts are known to deviate.[15] The same energy-transfer mechanism could play a role in their Stokes shifts, and our preliminary data indeed show the decrease of the Stokes shift of $CuInS_2$ with dilution (Figure S11). The applicability of these materials in optoelectronics could also potentially be improved with better synthetic control.

In conclusion, we have uncovered a previously under-appreciated source of the Stokes shift in CQDs in solution. It is related to energy transfer that arises from severe CQD aggregation, even in dilute samples. We prove this mechanism using photoluminescence studies on donor–acceptor CQD mixtures and by demonstrating that the Stokes shift in CQDs in solution can be nearly eliminated. Our findings provide an insight into open-circuit voltage loss mechanism in CQD photovoltaics: carrier population redistribution in CQD solid films originates from as-synthesized ensemble polydispersity without the need to resort to optically dark states, either in the core or on the surface of CQDs. Thus, a path forward will require focusing on synthetically improving the ensemble monodispersity.[27,32]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.7b01843.

> CQD synthesis experimental details and additional absorption and photoluminescence measurements, and a diffusion model description. Figures showing the scaling of the PL intensity, reduction of the Stokes shift, absorbance, correlations of the Stokes shift with ensemble polydispersity, absorption and emission spectra, DLS results, photoluminescence and absorption measurements, and Stokes shifts. (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ted.sargent@utoronto.ca.

ORCID Ⓘ

Oleksandr Voznyy: 0000-0002-8656-5074
James Z. Fan: 0000-0002-1594-865X
Susanna M. Thon: 0000-0002-1003-2650
Mengxia Liu: 0000-0002-1676-705X

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Korkusinski, M.; Voznyy, O.; Hawrylak, P. Phys. Rev. B: Condens. Matter Mater. Phys. 2010, 82, 245304.
(2) Franceschetti, A.; An, J. M.; Zunger, A. Nano Lett. 2007, 7, 2129–2135.
(3) Nirmal, M.; Norris, D. J.; Kuno, M.; Bawendi, M. G.; Efros, A. L.; Rosen, M. Phys. Rev. Lett. 1995, 75, 3728–3731.
(4) Allan, G.; Delerue, C. Phys. Rev. B: Condens. Matter Mater. Phys. 2004, 70, 245321.
(5) Giansante, C.; Infante, I.; Fabiano, E.; Grisorio, R.; Suranna, G. P.; Gigli, G. J. Am. Chem. Soc. 2015, 137, 1875–1886.
(6) Liu, M.; Yao, W.; Li, C.; Wu, Z.; Li, L. RSC Adv. 2015, 5, 628–634.
(7) Meinardi, F.; McDaniel, H.; Carulli, F.; Colombo, A.; Velizhanin, K. A.; Makarov, N. S.; Simonutti, R.; Klimov, V. I.; Brovelli, S. Nat. Nanotechnol. 2015, 10, 878–885.
(8) Liu, M.; Voznyy, O.; Sabatini, R.; García de Arquer, F. P.; Munir, R.; Balawi, A. H.; Lan, X.; Fan, F.; Walters, G.; Kirmani, A. R.; Hoogland, S.; Laquai, F.; Amassian, A.; Sargent, E. H. Nat. Mater. 2016, 16, 258–263.
(9) Lewis, J. E.; Wu, S.; Jiang, X. J. Nanotechnology 2010, 21, 455402.
(10) Caram, J. R.; Bertram, S. N.; Utzat, H.; Hess, W. R.; Carr, J. A.; Bischof, T. S.; Beyler, A. P.; Wilson, M. W. B.; Bawendi, M. G. Nano Lett. 2016, 16, 6070–6077.
(11) Ushakova, E. V.; Litvin, A. P.; Parfenov, P. S.; Fedorov, A. V.; Artemyev, M.; Prudnikau, A. V.; Rukhlenko, I. D.; Baranov, A. V. ACS Nano 2012, 6, 8913–8921.
(12) Gaponenko, M. S.; Tolstik, N. A.; Lutich, A. A.; Onushchenko, A. A.; Yumashev, K. V. Phys. E 2013, 53, 63–65.
(13) Kang, I.; Wise, F. W. J. Opt. Soc. Am. B 1997, 14, 1632.
(14) Norris, D. J.; Efros, A. L.; Rosen, M.; Bawendi, M. G. Phys. Rev. B: Condens. Matter Mater. Phys. 1996, 53, 16347–16354.
(15) Efros, A. L.; Rosen, M.; Kuno, M.; Norris, D. J.; Nirmal, M.; Bawendi, M. G. Phys. Rev. B: Condens. Matter Mater. Phys. 1996, 54, 4843–4856.
(16) Goupalov, S. V. Phys. Rev. B: Condens. Matter Mater. Phys. 2009, 79, 233305.
(17) An, J. M.; Franceschetti, A.; Dudiy, S. V.; Zunger, A. Nano Lett. 2006, 6, 2728–2735.
(18) Franceschetti, A. Phys. Rev. B: Condens. Matter Mater. Phys. 2008, 78, 75418.
(19) Voznyy, O.; Fan, F.; Ip, A.; Kiani, A.; Thon, S. M.; Kemp, K. W.; Levina, L.; Sargent, E. H. arXiv:1608.05113. arXiv.org e-Print archive. https://arxiv.org/abs/1608.05113.
(20) Grisorio, R.; Debellis, D.; Suranna, G. P.; Gigli, G.; Giansante, C. Angew. Chem., Int. Ed. 2016, 55, 6628–6633.
(21) Kagan, C.; Murray, C.; Nirmal, M.; Bawendi, M. Phys. Rev. Lett. 1996, 76, 1517–1520.
(22) Gao, Y.; Talgorn, E.; Aerts, M.; Trinh, M. T.; Schins, J. M.; Houtepen, A. J.; Siebbeles, L. D. Nano Lett. 2011, 11, 5471–5476.
(23) Zhitomirsky, D.; Voznyy, O.; Hoogland, S.; Sargent, E. H. ACS Nano 2013, 7, 5282–5290.
(24) Kholmicheva, N.; Moroz, P.; Bastola, E.; Razgoniaeva, N.; Bocanegra, J.; Shaughnessy, M.; Porach, Z.; Khon, D.; Zamkov, M. ACS Nano 2015, 9, 2926–2937.
(25) Gilmore, R. H.; Lee, E. M. Y.; Weidman, M. C.; Willard, A. P.; Tisdale, W. A. Nano Lett. 2017, 17, 893–901.
(26) Choi, J. J.; Luria, J.; Hyun, B.-R.; Bartnik, A. C.; Sun, L.; Lim, Y.-F.; Marohn, J. a; Wise, F. W.; Hanrath, T. Nano Lett. 2010, 10, 1805–1811.
(27) Weidman, M. C.; Beck, M. E.; Hoffman, R. S.; Prins, F.; Tisdale, W. A. ACS Nano 2014, 8, 6363–6371.
(28) Ip, A. H.; Thon, S. M.; Hoogland, S.; Voznyy, O.; Zhitomirsky, D.; Debnath, R.; Levina, L.; Rollny, L. R.; Carey, G. H.; Fischer, A.; Kemp, K. W.; Kramer, I. J.; Ning, Z.; Labelle, A. J.; Chou, K. W.; Amassian, A.; Sargent, E. H. Nat. Nanotechnol. 2012, 7, 577–582.
(29) Cho, K.-S.; Talapin, D. V.; Gaschler, W.; Murray, C. B. J. Am. Chem. Soc. 2005, 127, 7140–7147.
(30) Bertolotti, F.; Dirin, D. N.; Ibáñez, M.; Krumeich, F.; Cervellino, A.; Frison, R.; Voznyy, O.; Sargent, E. H.; Kovalenko, M. V.; Guagliardi, A.; Masciocchi, N. Nat. Mater. 2016, 15, 987–994.
(31) Rempel, J. Y.; Bawendi, M. G.; Jensen, K. F. J. Am. Chem. Soc. 2009, 131, 4479–4489.

(32) Campos, M. P.; Hendricks, M. P.; Beecher, A. N.; Walravens, W.; Swain, R. A.; Cleveland, G. T.; Hens, Z.; Sfeir, M. Y.; Owen, J. S. *J. Am. Chem. Soc.* **2017**, *139*, 2296−2305.

(33) Shabaev, A.; Mehl, M. J.; Efros, A. L. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2015**, *92*, 35431.

(34) Gupta, S.; Zhovtiuk, O.; Vaneski, A.; Lin, Y.-C.; Chou, W.-C.; Kershaw, S. V.; Rogach, A. L. *Part. Part. Syst. Charact.* **2013**, *30*, 346−354.

(35) Zang, H.; Li, H.; Makarov, N. S.; Velizhanin, K. A.; Wu, K.; Park, Y.-S.; Klimov, V. I. *Nano Lett.* **2017**, *17*, 1787−1795.

(36) Brennan, M. C.; Zinna, J.; Kuno, M. *ACS Energy Lett.* **2017**, *2*, 1487−1488.