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Triplet Energy Transfer from $CsPbBr_3$ Nanocrystals Enabled by Quantum Confinement

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Supporting Information Placeholder

ABSTRACT: Spectral properties of lead halide perovskite nanocrystals (NCs) can be engineered by tuning either their sizes *via* quantum confinement effect or their compositions using anion and/or cation exchange. So far, the latter is more frequently adopted due primarily to the ease of ion exchange for lead halide perovskites, making quantum confinement effect seemingly redundant for perovskite NCs. Here we report that quantum confinement is required for triplet energy transfer (TET) from perovskite NCs to polycyclic aromatic hydrocarbons (PAHs). Static and transient spectroscopy measurements on $CsPbBr_3$ NC-pyrene hybrids showed that efficient TET only occurred for small-size, quantum confined $CsPbBr_3$ NCs. The influences of size-dependent driving force and spectral overlap on TET rates were found to be negligible. Instead, TET rates scaled linearly with carrier probability densities at the NC surfaces, consistent with a Dexter-type TET mechanism requiring wavefunction exchange between NC donors and pyrene acceptors. Efficient TET funnels the excitation energy generated in strongly light-absorbing perovskite NCs into long-lived triplets in PAHs, which may find broad applications such as photon upconversion and photoredox catalysis.

Lead halide perovskite nanocrystals (NCs) have become attractive light harvesting and emitting materials for many applications,[1-3] owing to their strong light absorption and high emission quantum yields (QYs). One of their unique advantages is also the facile tunability of their absorption edges and emission colors *via* anion and/or cation exchange reactions.[4-5] For example, synthesis of ~10-nm-diameter $CsPbBr_3$ NCs followed by continuous exchange of Cl and I for Br enables the accessibility of any emission wavelength in between 410 and 700 nm. Traditional NCs, such as CdSe quantum dots (QDs), require considerable size tuning in order to cover the whole visible spectrum *via* the so-called quantum confinement effect.[6] As such, from a practical standpoint, the emission colors of perovskite NCs are often tuned by halide compositions rather than sizes, rendering quantum confinement, the most fascinating part for traditional NCs, seemingly unnecessary for this class of materials.

Efficient emission from perovskite NCs is partially enabled by their strong and fast band edge transitions.[7] The radiative lifetime of these NCs is a few ns at room temperature, which is further accelerated to 100s ps at low temperature.[7] This property, on the other hand, could limit their applications in charge and energy transfer related applications. Recently, triplet energy transfer (TET) to polycyclic aromatic hydrocarbons (PAHs) has been developed as an effective means to store the excitation energy of NCs in long-lived molecular triplets.[8-13] These triplets have a broad scope of applications such as photon upconversion across various spectral ranges[8, 11, 14] and photoredox catalysis[15-17]. In principle, merging perovskite NCs with PAHs *via* efficient TET would take full advantage of the strong light-harvesting capability of these NCs and meanwhile overcome the issue associated with their short emission lifetime. Photon upconversion based on $CsPbBr_3$-PAH hybrids was recently demonstrated[18] but with an upconversion QY of only ~1.3% which lags behind the value achieved with CdSe QDs (>12%)[19] by almost an order of magnitude, implying low-efficiency TET at the $CsPbBr_3$/PAH interface. It remains unclear why TET from $CsPbBr_3$ NCs is inefficient and how to improve the efficiency.

In this work, we study TET dynamics from $CsPbBr_3$ NCs of varying sizes to pyrene using transient absorption spectroscopy. We found that quantum confinement was required for efficient TET: while TET efficiency is almost zero for commonly-used bulk-like $CsPbBr_3$ NCs, it can be enhanced to ~99% for strongly-confined NCs with TET rate up to 9.1 ± 0.1 ns^{-1}. Driving force and spectral overlap were found to be insignificant on TET rate; rather, the TET rate scaled linearly with carrier probability density at the NC surface calculated from wavefunction. This is consistent with the Dexter-type TET mechanism relying on donor-acceptor wavefunction overlap. Our study demonstrates that for applications involving TET process, quantum confinement is still needed for perovskite NCs.

Cube-shaped CsPbBr$_3$ NCs of varying edge lengths (L) were synthesized according to literature methods;[20] see Supporting Information (SI) for details. Figure S1 shows their representative transmission electron microscopy (TEM) images, according to which L is tuned from 3.5 to 11.2 nm for these NCs (Figure S2); as a reference, the Bohr exciton diameter of CsPbBr$_3$ is ~7 nm.[3] Due to the quantum confinement effect, the lowest energy absorption peak is blue-shifted from 509 to 454 nm when L decreases from 11.2 to 3.5 nm (Figure 1a; see also Table S1). 1-pyrenecarboxylic acid (PCA) molecules, the triplet acceptor, were grafted on to NC surfaces *via* the carboxyl group using a simple ligand-exchange procedure (see SI). The absorption spectra of NC-PCA complexes contain not only features of NCs but also those of PCAs in the <400 nm range (Figure 1a). Based on the size-dependent extinction coefficients of CsPbBr$_3$ NCs and that of PCA, the PCA:NC ratio in these samples was controlled to be similar; see SI for details.

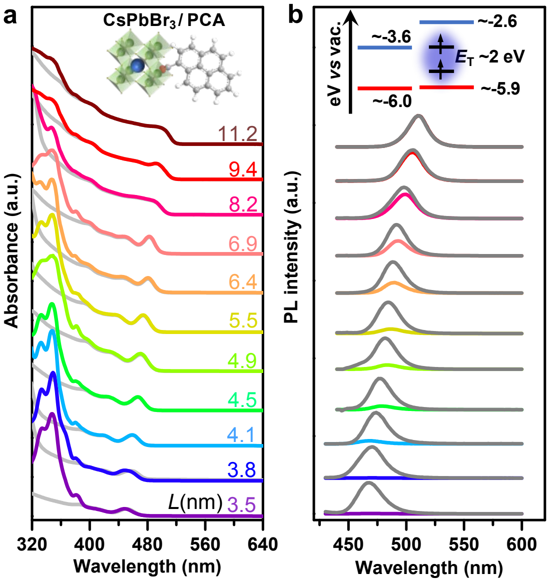

Figure 1. (a) Absorption spectra of CsPbBr$_3$ NCs (gray solid lines) and NC-PCA complexes (colored solid lines) with varying NC sizes (edge length L indicated) dispersed in hexane. The difference between them is due to PCA absorption. Inset are the schematic structures of NCs and PCAs. (b) PL spectra of CsPbBr$_3$ NCs (gray solid lines) and NC-PCA complexes (colored solid lines) excited at 420 nm. Inset is the schematic energy level alignment between NCs and PCAs.

The photoluminescence (PL) of these NC-PCA complexes, excited which 420 nm light which selectively pumped NCs, are quenched to different extents as compared to their respective free NCs (Figure 1b). The quenching efficiency increases from ~0.6% for 11.2-nm, bulk-like NCs to 99% for 3.5-nm, strongly-confined NCs (Table S1). Based on the schematic energy level alignment between bulk CsPbBr$_3$[21] and PCAs[16] shown in Figure 1b inset, TET from NCs to PCAs should be the dominant quenching mechanism for NC excitons. Hole transfer from NCs is also likely energetically-allowed, but its contribution should be negligible according to our TA experiments to be described later.

TA was used to directly monitor TET dynamics from NCs to PCAs; see SI for experimental details. The pump pulse was tuned to 470 nm to selectively excite NCs and the pump energy densities were maintained to be low such that the average exciton number per NC ($<N>$) was <<1 in these experiments to exclude complications from multiexcitonic effects. Figure 2a shows the TA spectra of 4.9-nm NC-PCA complexes at selective delays following excitation, which are dominated by the exciton bleach (XB) feature of NCs due to state-filling effects;[22-23] TA spectra of corresponding free NCs are shown in Figure S3. The kinetics of XB in free NCs and NC-PCA complexes are plotted in Figure 2b for comparison. Compared with free NCs, the XB lifetime is significantly shortened in NC-PCA complexes. Accompanying the ultrafast decay of XB is the complementary formation of a weak yet discernible absorptive feature around 430 nm that can be assigned to the $T_1 \rightarrow T_n$ transition of PCA triplets.[9] Thus, the ultrafast quenching of NC exciton is due to TET from NCs to PCAs. In contrast, if hole transfer was the dominant mechanism, no molecular triplet formation would be expected and the XB should only show partial decay due to contribution of both electrons and holes to the XB feature. By simultaneously fit XB and triplet kinetics, the TET rate (k_{TET}) for this sample was calculated to be 1.6±0.1 ns^{-1}; see SI for fitting details. The generated PCA triplets are long-lived as expected (Figure S4). We notice that a recent study reported ultrafast hole transfer from CsPbBr$_3$ NCs (L ~ 8 nm) to 1-aminopyrene (AMP).[24] The difference likely results from the sensitive dependence of the redox potential of molecules on their functional groups. It was reported the oxidation potential of AMP was ~0.8 V more negative than that of PCA,[25] resulting in large driving force for hole transfer from CsPbBr$_3$ NCs to AMP.

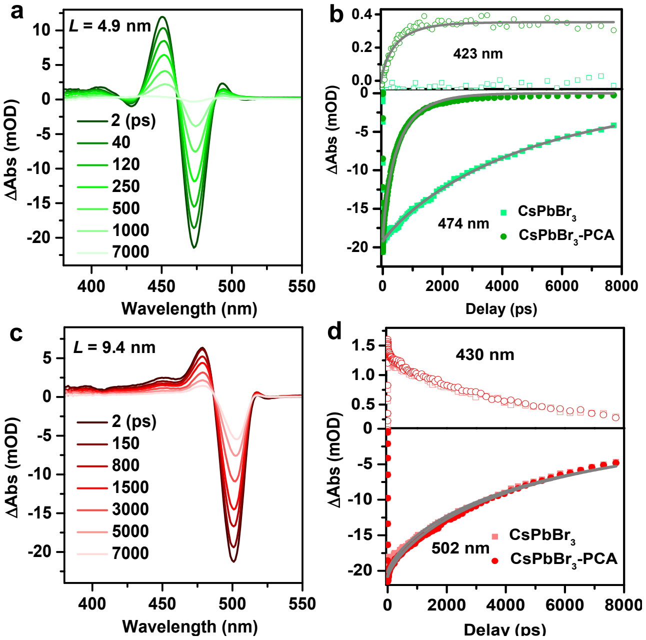

Figure 2. (a) TA spectra of L = 4.9 nm NC-PCA complexes probed at indicated time delays following the excitation by a 470 nm pulse. (b) TA kinetics probed at the exciton bleach (XB)

center (~474 nm; solid symbols) and probed at the PCA triplet absorption (~423 nm; open symbols) of L = 4.9 nm NCs (squares) and NC-PCA complexes (circles). The gray solid lines are their fits using stretched-exponential functions. (c,d) Similar plots as (a) and (b) for L = 9.4 nm NC-PCA complexes.

In stark contrast to the ultrafast TET observed for strongly-confined NCs, the 9.4-nm, bulk-like NCs shows negligible TET (Figure 2c and 2d). The XB lifetime is similar in free NCs and NC-PCA complexes and no triplet absorption feature was detected (Figure 2d). The dramatically different behaviors between small and large size NCs highlight the importance of quantum confinement effect in facilitating TET. Indeed, when we plot the XB decay kinetics in all NC-PCA samples together (Figure 3a; TA spectra and kinetics shown in Figures S5-S7), we find a clear trend that TET rates increase with decreasing NC sizes. The fitted TET rates (k_{TET}) increase from almost zero for 11.2-nm NCs to 9.1±0.1 ns^{-1} for 3.5-nm NCs (Table S1) and are plotted in Figure 3b.

Quantum confinement mainly affects energetics (driving force and spectral overlap) and electronic coupling[26] involved in TET process if TET occurs through the well-accepted Dexter mechanism[27]. The TET driving force for all NCs is sufficiently large (~0.44 to 0.73 eV), which cannot explain the above observations. Spectral overlap between NC and PCA triplets is difficult to determine due to the "dark" nature of triplets. We evaluated the impact of these two factors on TET using several $CsPbBr_{3-x}Cl_x$ NCs with similar sizes (L ~ 10 nm) but different emission peaks from 465 to 497 nm controlled by the parameter x (Figure S8). As shown in Figures S9 and S10, NC-PCA complexes with different x parameters show very similar XB recovery kinetics, suggesting that TET kinetics should also be similar (see Figure S10 for details) and that spectral overlap and driving force play negligible roles in TET for this system. Therefore, quantum confinement should affect TET primarily *via* electronic coupling. It has been established that smaller NCs with stronger quantum confinement effect have higher carrier probability densities at their surfaces which leads to stronger electronic coupling with attached acceptors.[28-30]

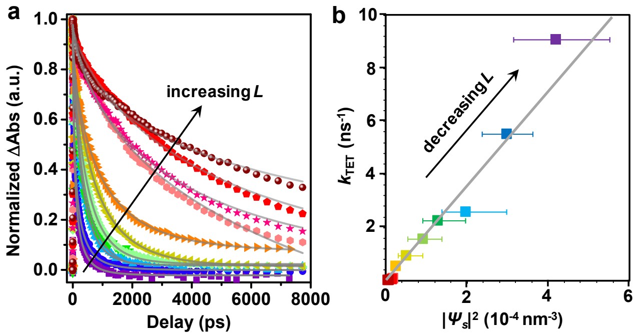

Figure 3. (a) Normalized TA kinetics probed at the XB of NC-PCA complexes with varying NC sizes (colored symbols). The gray solid lines are their fits. (b) Size-dependent triplet energy transfer rate (k_{TET}) plotted as a function of carrier probability densities at NC surfaces ($|\Psi_s|^2$) for varying NC sizes (colored symbols). The gray solid line is a linear fit.

The carrier probability densities at $CsPbBr_3$ NC surfaces, *i.e.*, wavefunction squares ($|\Psi_s|^2$), were calculated using a simple effective mass approximation (EMA) model;[30] see SI for calculation details. Size-dependent k_{TET} is plotted against $|\Psi_s|^2$ in Figure 3b, which can be well fitted to a linear scaling. Thus, this simplest model already captures the physical essence of TET in this system: wavefunction exchange between $CsPbBr_3$ NCs and PCAs is the dominant factor controlling the rate of this Dexter-type TET process. Previous studies on photon conversion from CdSe QD-anthracene and PbS(Se) QD-rubrene systems also demonstrated strong enhancement of upconversion QYs with decreasing QD sizes.[31-32] Based on our results, this enhancement should also be contributed by size-dependent wavefunction overlap between QDs and PAHs.

The observation of linear scaling between TET rates and $|\Psi_s|^2$, although expectable from Dexter energy transfer theory, is enabled by the unique combination of electronic and optical properties of $CsPbBr_3$ NCs. To begin with, perovskite NCs have similar electron and hole wavefunction distributions due to similar electron and hole effective masses and relatively symmetric conduction and valence band structures near their edge, allowing us to calculate either one to represent the overall carrier probability densities at their surfaces. In contrast, CdSe QDs, for example, have very different electron and hole wavefunction amplitudes at their surfaces, making it difficult to quantify the overall wavefunction overlap factor involved in TET. PbS(Se) QDs have similar electron and hole effective masses. However, both PbS(Se) and CdSe core-only QDs, if not specially engineered, have relatively low PL QYs. For these QDs, it is not realistic to simply consider wavefunctions and energetics of band edge excitons for TET. Indeed, recent studies on PbS-acene system, for example, implied surface states mediated TET process.[33-34] In contrast, all the perovskite NCs used in our paper have QYs $\geq$ 60%, allowing us to consider the dominant role of band edge excitons in TET. The unique combination of the properties listed above allows us to observe the linear dependence of TET rates on $|\Psi_s|^2$ for the first time.

It is also interesting to examine the concept of "triplet" excitons for $CsPbBr_3$ NCs. For quantum confined NCs, spin is an ill-defined quantum number due to strong spin-orbital coupling and state mixing.[9] For CdSe QDs, it is well-established that an optically dark state with a total angular momentum $J = 2$ is located below a set of bright states;[35-36] the dark state carries features of triplet state and induces efficient TET. For $CsPbBr_3$ NCs, it was recently proposed that a dark state with $J = 0$ was located above three bright states with $J = 1$.[7] Regardless of their detailed exciton fine structures, because of the small bright-dark splitting (a few meVs) and fast spin flip in NCs, dark and bright states undergo rapid population exchanges at room temperature,[7] which enables "triplet" exciton extraction from these NCs.

At last, we would like to note that pyrene was chosen as the triplet acceptor in this work because it allows for a model study of TET from an extensive size series of $CsPbBr_3$ NCs. From a practical standpoint, however, it introduces significant energy losses due to large driving forces from $CsPbBr_3$ NCs to pyrene triplets. Our preliminary results indicate that quantum confinement in small-size $CsPbBr_3$ NCs can also enable TET to naphthalene which has triplet energy of 2.6 eV[16], with a driving force of only ~0.1 eV; see Fig. S11 for details. Naphthalene triplets can be used for visible-to-UV photon upconversion[14], or can be transformed to naphthalene anion radicals with very strong reducing power for photoredox catalysis[16].

To summarize, we measured triplet energy transfer (TET) dynamics in $CsPbBr_3$ NC-pyrene complexes with varying NC sizes (edge length from 3.5 to 11.2 nm) using static and time-resolved spectroscopy. We found that while TET efficiency was almost zero for commonly-used bulk-like $CsPbBr_3$ NCs, it could be enhanced to ~99% for strongly-confined NCs. The measured TET rates scaled linearly with the size-dependent carrier probability density at the $CsPbBr_3$ NC surfaces, consistent with the Dexter-type TET mechanism requiring donor-acceptor wavefunction exchange. This study not only directly demonstrates the linear scaling between TET rate and donor-acceptor wavefunction overlap for NC-PAH systems, but also shows that quantum confinement effect is essential for efficient TET from perovskite NCs for their applications ranging from photon upconversion, photoredox catalysis to photodynamic therapy.

ASSOCIATED CONTENT

Supporting Information. Figures S1-S11, Table S1, sample preparations, TA experiment set-ups, other supporting contents.

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Notes

The authors declare no competing financial interest.

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