



The interparticle distance limit for multiple exciton dissociation in PbS quantum dot solid films

Journal:	<i>Nanoscale Horizons</i>
Manuscript ID	NH-COM-10-2018-000341.R1
Article Type:	Communication
Date Submitted by the Author:	14-Nov-2018
Complete List of Authors:	<p>Nakazawa, Naoki; The University of Electro-Communications Zhang, Yaohong; The University of Electro-Communications, Liu, Feng; Institute of Plasma Physics Chinese Academy of Sciences, Key Laboratory of Novel Thin Film Solar Cells Ding, Chao; The University of Electro-Communications Hori, Kanae; The University of Electro-Communications Toyoda, Taro; University of Electro-communications, Engineering Science yao, yingfang; Nanjing University, College of Engineering and Applied Sciences Zhou, Yong; Nanjing University, Hayase, Shuji; Kyushu Institute of Technology, Graduate School of Life Science and Systems Engineering Wang, Ruixiang; Beijing Engineering Research Centre of Sustainable Energy and Buildings Zou, Zhigang; Nanjing University, Physics Shen, Qing; University of Electro-communications, Department of Engineering Science</p>

Conceptual insights

In this study, we report the interparticle distance dependent multiple exciton dissociation behaviour in quantum dot (QD) solid films for the first time, and we systematically investigate the complex multiple exciton charge transfer behaviour in PbS QD solid films by using ultrafast transient absorption spectroscopy. We found that the charge transfer rate constant k_{et} of single exciton, biexciton and triexciton within the QD solid film is exponentially enhanced as the interparticle distance between the QDs decreases, where the charge transfer occurs via tunneling effect between the neighboring QDs. More importantly, when the QD center-to-center distance is smaller than 4.3 nm (or QD-QD spacing is smaller than 0.8 nm), multiple excitons can be rapidly extracted before the occurring of Auger recombination. This result reveals the reason why over 100% incident photon to current conversion efficiency (IPCE) only could be observed in short surface ligand treated QD based devices to date. Our finding points out a vital condition for using the multiple exciton in QD solid films and will be beneficial for using multiple exciton generation (MEG) of QDs in turning to improve the performance of quantum dot solar cells and could have important implications in the development of this technology.

The interparticle distance limit for multiple exciton dissociation in PbS quantum dot solid films

Naoki Nakazawa, ^a Yaohong Zhang, ^{*a} Feng Liu, ^a Chao Ding, ^a Kanae Hori, ^a Taro Toyoda, ^a Yingfang Yao, ^b Yong Zhou, ^b Shuzi Hayase, ^c Ruixiang Wang, ^d Zhigang Zou, ^b and Qing Shen^{*a}

^a *Faculty of Informatics and Engineering, The University of Electro-Communications, Tokyo 182-8585, Japan. E-mail: yhzhang1021@live.com (Y.Z.); shen@pc.uec.ac.jp (Q.S.)*

^b *Ecomaterials and Renewable Energy Research Center, Jiangsu Key Laboratory for Nano Technology, National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China*

^c *Faculty of Life Science and Systems Engineering, Kyushu Institute of Technology, Fukuoka 808-0196, Japan.*

^d *Beijing Engineering Research Centre of Sustainable Energy and Buildings, Beijing University of Civil Engineering and Architecture, Beijing 102616, China.*

ABSTRACT

Understanding the behaviour of multiple exciton dissociation in quantum dot (QD) solid films is of fundamental interest and paramount importance for improving the performance of quantum dot solar cells (QDSCs). Unfortunately, the charge transfer behaviour of photogenerated multiple exciton in QD solid films is not clear to date. Here, we systematically investigate the multiple exciton charge transfer behaviour in PbS QD solid films by using ultrafast transient absorption spectroscopy. We observe that multiple exciton charge transfer rate within QD ensembles is exponentially enhanced as the interparticle distance between QDs decreases. The biexciton and triexciton dissociation between adjacent QDs occur via charge transfer tunneling effect just like single exciton, and charge tunneling constants of single exciton ($\beta_1: 0.67 \pm 0.02 \text{ nm}^{-1}$), biexciton ($\beta_2: 0.68 \pm 0.05 \text{ nm}^{-1}$) and triexciton ($\beta_3: 0.71 \pm 0.01 \text{ nm}^{-1}$) are obtained. More importantly, for the first time, interparticle distance limit ($\leq 4.3 \text{ nm}$) of multiple exciton charge transfer between adjacent QDs is found for extracting the multiple exciton rapidly before the occurrence of Auger recombination. This result points out a vital and necessary condition for using the multiple exciton produced in PbS QD films especially for their applications in QDSCs.

Introduction

Quantum dot solar cells (QDSCs) are considered to be one of the most promising candidates for the new-generation photovoltaics due to multiple exciton generation (MEG) in QDs.¹⁻¹⁰ In the MEG process, a single high energy photon can generate more than two excitons (electron-hole pairs) across the band gap, which is potentially vital for improving the photocurrent and thus the energy conversion efficiency of the solar devices. The MEG process is known as the inverse Auger recombination (AR) process,¹ in which the electron (e) - hole (h) recombination energy is transferred to a third charge (e or h) that is re-excited to a higher-energy state.¹¹ Quantum confinement of exciton in QD enhances exciton-exciton interactions which leads to MEG and AR processes.¹² Thus, a detailed and deep understanding of the dynamics of multiple exciton, including generation and dissociation, is very important for applying MEG to enhance the photovoltaic performance of QDSCs.

The mechanism of MEG and AR processes in colloidal QD has been studied using ultrafast transient absorption (TA) spectroscopy.^{2, 11-13} The probability of MEG and AR can be greatly enhanced due to carrier confinement and increased e - h Coulomb interaction.^{4, 14} It is known that MEG has been observed not only in solution but also in closely packed QD solid films such as PbS and PbSe QD films as the excitation photon energy exceeds 2.7 times E_g .^{2, 4, 15-23} and improvement of the incident-photon-to-current efficiency (IPCE) of over 100% has also been experimentally demonstrated.^{24, 25} Surface passivation and modification of QDs is significantly important to enhance the photovoltaic performance of QDSCs.^{5, 26-42} Designed

surface treatment of QDs can improve the mobility of carriers and reduce the non-radiative carrier recombination.^{39, 43-52} In particular, in the QD solid films, the interparticle distance between the QDs can be controlled by the length of surface ligand of the QDs.⁵³ It was reported that QD solid film treated with short ligands has strong electronic interaction between QDs which can improve the carrier mobility.^{45, 54} However, to date, the deeper reason behind this result has not been revealed and the charge transfer mechanism of multiple exciton between adjacent QDs is not fully understood. Thus, the study of dynamics of multiple exciton in QD solid films is essential to realize the extraction of excitons and high performance of QDSCs based on MEG.

In this work, we report the interparticle distance dependent multiple exciton dissociation in PbS QD solid films. Here, PbS QD solid films were fabricated by a layer-by-layer method using different mercaptoalkanoic acid (MAA) such as 3-mercaptopropionic acid (3-MPA), 6-mercaptophexanoic acid (6-MHA), 12-mercaptophexanoic acid (12-MDA) and 16-mercaptophexadecanoic acid (16-MHDA) to replace original surface ligands (i.e. oleic acid (OA)) of colloidal PbS QDs. Based on this design, the interparticle distance between PbS QDs was well controlled by the length of MAA.⁵³ Using the same binding structure of these MAA ligands to QDs, we can observe the mere dependency of the exciton dissociation dynamics of PbS QD solid films on the QD center-to-center distance. We find that the biexciton and triexciton dissociation between adjacent QDs can occur rapidly via charge transfer tunneling effect just like single exciton, and the obtained charge tunneling constants of single exciton

(β_1), biexciton (β_2) and triexciton (β_3) are $0.67 \pm 0.02 \text{ nm}^{-1}$, $0.68 \pm 0.05 \text{ nm}^{-1}$ and $0.71 \pm 0.01 \text{ nm}^{-1}$, respectively. More importantly, we discover that when the QD center-to-center distance between the PbS QDs is smaller than 4.3 nm (or interparticle spacing is smaller than 0.8 nm), multiple exciton can be rapidly extracted before the occurrence of Auger recombination. This result reveals the reason why over 100% IPCE only has been observed in short surface ligand treated QD based devices to date.^{24, 25} Our finding points out a necessary condition for using the multiple exciton in QD solid films and will be beneficial for using MEG of QDs in turning to improve the performance of QDSCs.

Results and discussion

We firstly investigated PbS QDs surface chemistry using Fourier transform infrared absorption (FTIR) spectroscopy. Fig. S1 shows the FTIR spectra of PbS QD solid films before and after MAA ligand exchanges. FTIR results confirm that new MAA ligand can be capped on the QDs surface after ligand exchange. In order to evaluate interparticle distance between adjacent PbS QDs which are capped by different MAA ligands, monolayer PbS QDs are deposited on ultrathin carbon film and characterized by high resolution transmission electron microscope (HRTEM). Fig. S2 shows the HRTEM images of PbS QD ensembles with various MAA ligands. It can be obviously found that the size of PbS QD is about 3.5 nm and the borderlines of MAA treated QDs are more distinct than that of OA-capped PbS QD film, which are in good agreement with the removal of OA ligands from QDs surface. The averaged QD center-to-center distance was calculated as $4.0 \pm 0.3 \text{ nm}$, $4.3 \pm 0.4 \text{ nm}$, 4.8 ± 0.3

nm and 5.6 ± 0.4 nm for 3-MPA, 6-MHA, 12-MDA and 16-MHDA ligand treated QDs, respectively. And the averaged QD-QD spacing was calculated as 0.5 ± 0.2 nm, 0.8 ± 0.4 nm, 1.3 ± 0.4 nm and 2.1 ± 0.4 nm for 3-MPA, 6-MHA, 12-MDA and 16-MHDA ligand treated QDs, respectively. Interestingly, the averaged QD center-to-center distance and averaged QD-QD spacing in these MAA treated films were found to be linearly increase from 4.0 nm to 5.8 nm and from 0.5 nm to 2.3 nm with the number of carbon atoms of corresponding ligands increasing from 3 to 18 as shown in Fig. 1 and Fig. S3, respectively.

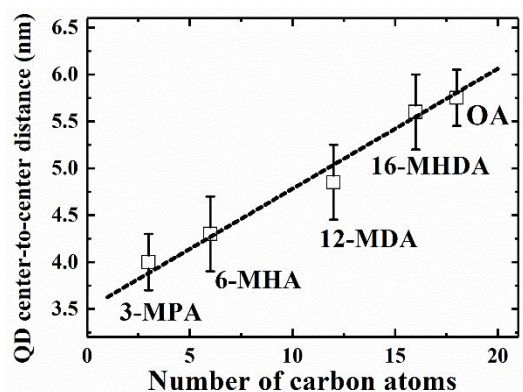


Fig. 1 The linear relationship between the QD center-to-center distance and the number of carbon atoms of capping ligands.

Optical absorbance spectra of the four types of MAA ligand treated PbS QD solid films and isolated OA-capped PbS QDs solution are shown in Fig. S4a. We investigated the exciton relaxation dynamics of the four types of PbS QD solid films by using TA measurements. In Fig. 2a, as an example, the spectro-temporal TA map together with the ground-state absorption spectrum of 6-MHA treated PbS QD solid film are shown. It can be obviously observed that the optical absorption peak and TA bleach peak around 1035 nm of the 6-

MHA treated PbS QD solid film correspond to the lowest-energy excitons in the PbS QD solid film. In order to gain the single exciton (1 $e-h$ pair) relaxation dynamics in the MAA treated PbS QD solid films, the TA spectra were measured under low excitation fluences ($\sim 10 \mu\text{J}/\text{cm}^2$, which will be discussed in detail later) which is the condition for minimizing the Auger recombination and maintaining signal-to-noise ratio during the TA measurement. Fig. S4b shows the TA responses of the lowest energy exciton in the 3-MPA, 6-MHA, 12-MDA and 16-MHDA treated PbS QD solid films and isolated OA-capped PbS QDs in octane solution. In the TA measurements, all samples are pumped by 470 nm (2.64 eV) laser pulse of which the photon energy is about 2.2 times of E_g , where E_g is the peak energy of the lowest-energy exciton in each PbS QD solid film. The photoinduced transmission changes $\Delta T/T$ of all samples are positive, representing the bleach of the lowest exciton state. As shown in Fig. S4b, no obvious decay of TA signal intensities for 16-MHDA treated film and isolated PbS QDs in solution can be observed in the timescale up to 1 ns. It suggests that there is no exciton dissociation, i.e. no charge transfer from one QD to the neighbouring QD in both samples. This is because the QD center-to-center distance is too large for the charge transfer between two neighbouring QDs. In contrast, for 3-MPA, 6-MHA and 12-MDA treated films, the TA signal intensities decay faster than that of 16-MHDA treated film under the same excitation fluence. This indicates that an efficient charge transfer (1 $e-h$ pair relaxation) channel appears in those three short ligands (3-MPA, 6-HMA and 12-MDA) treated films. Then we can calculate the charge transfer rate constant k_{1et} , i.e. the exciton lifetime τ_1 ($1/k_{1et}$) by fitting the TA decay curves with a single exponential function (Table S1). As

shown in Fig. S4b (solid lines), the fitting results reproduced the experimental results well. Interestingly, as shown in Fig. 2b, the relationship between the averaged QD center-to-center distance d and the charge transfer rate constant k_{1et} of 1 $e-h$ pair can be well fitted by a single exponential decay function as reported in our earlier report.⁵⁵ This behaviour can be explained very well by Marcus theory in which charge transfer rate constant k_{et} (i.e. the k_{1et} here) corresponds to the following model:⁵⁶

$$k_{et} = k_0 e^{(-\beta d)} \quad (1)$$

where β is the charge tunneling constant and d is the donor-acceptor distance which is the averaged QD center-to-center distance here.⁵⁷ And as shown in Fig. S5, the relationship between the averaged QD-QD spacing and k_{1et} can also be well fitted by eq.(1). This result strongly indicates that behaviour of the charge transfer of 1 $e-h$ pair in MAA-capped PbS QD solid films is dominated by the tunneling mechanism, and shorter ligands lead to a faster charge transfer rate. The value of the charge tunneling constant for 1 $e-h$ pair (i.e. single exciton), namely β_1 , can be extracted from eq. (1) as $0.67 \pm 0.02 \text{ nm}^{-1}$.

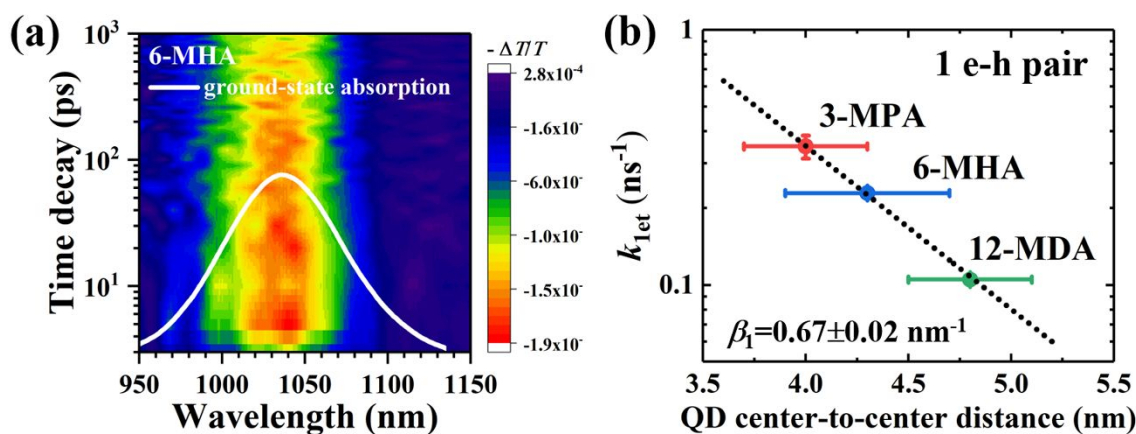


Fig. 2 (a) Spectro-temporal TA map together with the ground-state absorption spectrum of 6-MHA treated PbS QD solid film. The negative signal in the changes of absorption (i.e., the positive value of ΔT) indicates the photobleaching of exciton state. (b) Correlation between averaged QD center-to-center distance (d) and charge transfer rate constant (k_{1et}) of 1 $e-h$ pair which calculated from exciton lifetimes in Fig. S4b. Single exponential decay fit (eq. (1)) (dotted line) indicates that the charge transfer occurs via tunneling of charge.

Next, to explore interparticle spacing dependent multiple exciton relaxation dynamics in the closely packed PbS QD solid films, TA decay behaviours of the PbS QD solid films capped by different ligands were investigated under various excitation fluences of the pump light with the same wavelength of 470 nm (i.e., the photon energy of 2.64 eV). Fig. 3a and 3b show the TA responses of 16-MHDA and 3-MPA treated PbS QD solid films under various excitation fluences. As the excitation fluence increases, fast-decay components can be observed in the both of 16-MHDA and 3-MPA treated PbS QD solid films. Fig. 3c and Fig. 3d show the excitation fluence dependence of TA signal intensities at a delay time of 1 ns (after AR finished) for 16-MHDA and 3-MPA treated films, respectively. For the 16-MHDA treated films, the TA signal intensity at 1 ns increases as the excitation fluence increases and saturates at about $150 \mu\text{J}/\text{cm}^2$. Since AR occurs at fast timescale from a few tens to hundreds picosecond in the photoexcited QDs, almost all photoexcited QDs include only one single exciton at a longer time such as 1 ns after the AR is finished. Thus, the TA signal intensities at the longer time correspond to the initial number of the photoexcited QDs. It is known that

the probability of initial generation of the multiple exciton ($e-h$ pairs) in a QD can be expressed with a Poisson distribution, $P_n(\langle N_0 \rangle)$, where n is the number of the $e-h$ pairs in a QD and $\langle N_0 \rangle$ is the average number of the $e-h$ pairs per QD immediately after photogeneration, respectively.^{47, 58} $\langle N_0 \rangle$ is described by the product of the photon fluence J_p and the absorption cross section σ ($\langle N_0 \rangle = J_p \sigma$).⁵⁹ Hence, TA signal intensities at 1 ns are given by:⁶⁰

$$\Delta T/T(t = 1 \text{ ns}) \propto \sum_{n=1}^{\infty} P_n(\langle N_0 \rangle) = 1 - e^{(-J_p \sigma)} \quad (2)$$

As shown in Fig. 3c, the fitting results by eq. (2) can reproduce the experimental results very well, which verifies that the multiple exciton relaxation in 16-MHDA treated film is dominated by AR. The value of σ is obtained to be $9.9 (\pm 0.5) \times 10^{-15} \text{ cm}^2$. The dependence of the TA signal intensity at 1 ns versus the photon fluence of the pump light for the 16-MHDA treated films, i.e., the decay behaviour of the multiple exciton is very similar to that of the isolated QD solution (Fig. S6e) which confirms that the electronic interactions between the adjacent QDs in 16-MHDA treated film is negligible.

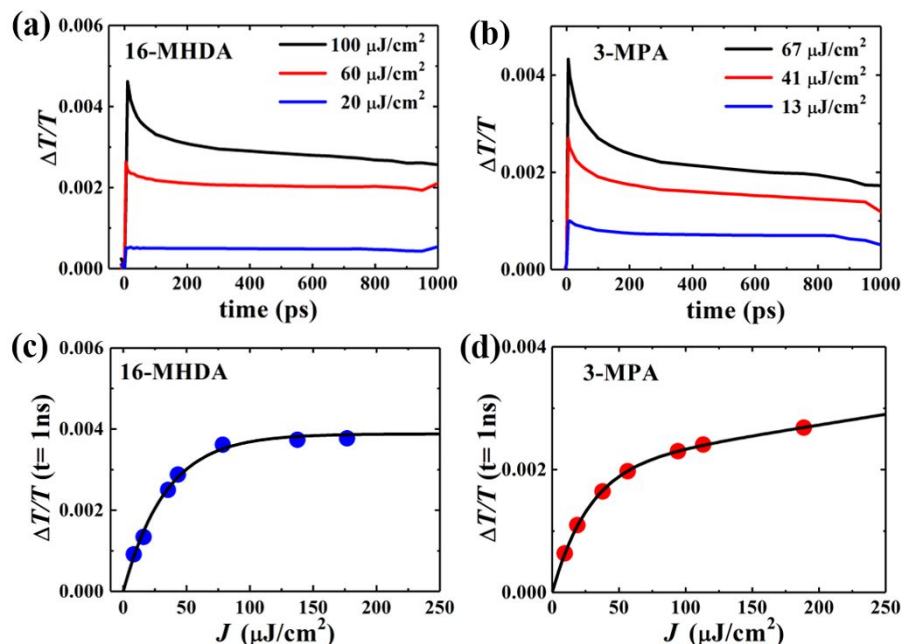


Fig. 3 Excitation-fluences dependent TA time decay curves of (a) 16-MHDA and (b) 3-MPA treated films. TA signals of (c) 16-MHDA and (d) 3-MPA treated films vs the excitation fluence (J) at delay time of 1 ns. The solid curves are the fitting results.

In contrast, for 3-MPA, 6-MHA and 12-MHDA treated films, the excitation-fluence dependent TA signal intensities at 1 ns of these three films are different from those of 16-MHDA treated film and isolated QDs in solution (Fig. S6). These results indicate that besides AR relaxation process, other relaxation processes of the multiple exciton occurred in the closely packed films. One possible process is the multiple exciton dissociation through charge transfer between the neighbouring QDs in the closely packed films, because the averaged QD center-to-center distance of the 3-MPA, 6-MHA and 12-MHDA treated films is shorter than that of 16-MHDA treated film: biexciton and triexciton in a single QD can transfer to the adjacent QDs like a single exciton as discussed above. According to the report of Kanemitsu

and co-workers,^{60, 61} the influence of this charge transfer process can be expressed by modifying eq. (2) for the TA signal intensities in the closely paced films at 1 ns as follows:

$$\Delta T/T(t = 1 \text{ ns}) \propto (1 - K) \sum_{n=1}^{\infty} P_n(\langle N_0 \rangle) + K \sum_{n=1}^{\infty} n P_n(\langle N_0 \rangle) = (1 - K)(1 - e^{(-J_p \sigma)}) + K J_p \sigma \quad (3)$$

where K is the probability of the charge transfer occurrence. In eq. (3), the first and second terms belong to the AR and the dissociation of multiple exciton caused by charge transfer, respectively. When the charge transfer in a single QD including n excitons generates n QDs including a single exciton, the TA signal intensity resulting from the charge transfer should be $K n P_n(\langle N_0 \rangle)$ at 1 ns.⁶⁰ Thus the TA signal intensity at 1 ns shows no saturation behavior with excitation fluence increasing. As shown in Fig. 3c and 3d and Fig. S6, the solid curve is the fitting result by using eq. (3), which reproduces the experimental result very well. The values of the carrier transfer possibility K and absorption cross section σ obtained from the fitting results are summarized in Table 1. As the averaged QD center-to-center distance decreases, the carrier transfer possibility K increases, because the increase of overlap of the wave functions of each QD results in rapid carrier transfer into adjacent QDs.

Table 1. Summary of carrier transfer probability K , and absorption cross section σ of different MAA ligands treated films and OA-capped PbS QDs in octane.

Ligand	K	σ (cm ²)
3-MPA	0.044(±0.002)	1.4(±0.3)×10 ⁻¹⁴

6-MHA	0.023(± 0.003)	1.2(± 0.1) $\times 10^{-14}$
12-MDA	0.018(± 0.003)	1.0(± 0.2) $\times 10^{-14}$
16-MHDA	0	9.9(± 0.5) $\times 10^{-15}$
OA	0	2.8(± 0.9) $\times 10^{-15}$

To gain a detailed understanding of multiple exciton relaxation dynamics, we used a simple subtractive procedure to characterize the relaxation of different multiple-pair QD states from the TA decay curves.⁶² Average number of photoexcited e - h pairs per QD is calculated by using $\langle N_0 \rangle = J_p \sigma$.^{59, 62} When the range of average number of e - h pairs per QD $\langle N_0 \rangle$ is changed from 0.5 to 2.5 (Fig. S7), the multiple exciton relaxation dynamics can be described by a triple exponential function:

$$\langle N(t) \rangle = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3} \quad (4)$$

where A_n is time-independent coefficients determined by the number of e - h pairs per QD and τ_n is the lifetime of the n -pair states.⁶² We subtracted TA decay curves measured at lower excitation fluence from those measured at higher excitation fluence to obtain single exponential curve. The lifetimes of τ_2 and τ_3 can be extracted by fitting the single exponential function to the TA decays which are obtained by subtracting the TA decay curve at $\langle N_0 \rangle < 1$ from that at $1 < \langle N_0 \rangle < 2$ and subtracting the TA decay curve at $1 < \langle N_0 \rangle < 2$ from that at $2 < \langle N_0 \rangle < 3$, respectively. Fig. 4 shows the TA decays derived from the subtractive procedure and the fitting results using a single exponential function (Fig. S7). The decay rate constants k_2 of biexciton ($2 e$ - h

pairs) and k_3 of triexciton (3 $e-h$ pairs), which are the inverse of the lifetimes τ_2 and τ_3 , are shown as a function of the QD center-to-center distance for each film in Fig. 5a. As the QD center-to-center distance decreases, the decay rate constants k_2 and k_3 of multiple exciton increases. From prior result of charge transfer possibility K , we can consider that that the increase of the multiple exciton decay rates resulted from the dissociation of multiple exciton due to charge transfer.

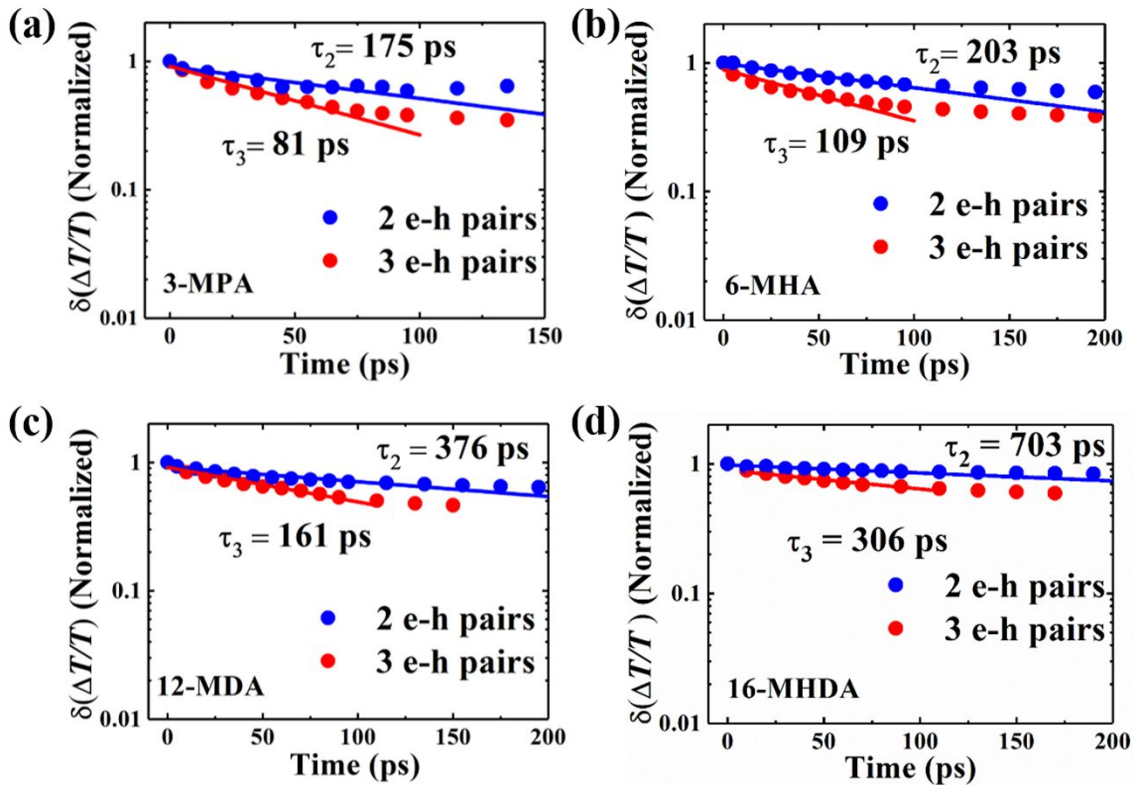


Fig. 4 Relaxation dynamics of 2 and 3 $e-h$ pair states of (a) 3-MPA, (b) 6-MHA, (c) 12-MDA and (d) 16-MHDA treated films by extracting the TA decay curve at $\langle N_0 \rangle < 1$ from that at $1 < \langle N_0 \rangle < 2$ and subtracting the TA decay curve at $1 < \langle N_0 \rangle < 2$ from that at $2 < \langle N_0 \rangle < 3$, respectively. The solid curves are fitting curves obtained by fitting the experimental data to a single exponential function.

We sought to gain further insight on the multiple exciton dissociation dynamics through charge transfer. To do so, we calculated charge transfer rate constants k_{2et} and k_{3et} of the 2 and 3 $e-h$ pairs, respectively. In 16-MHDA treated films, the multiple exciton relaxation dynamics is assumed to be only dominated by the AR process because of very weak electronic interactions between the QDs. Therefore, we can calculate the Auger recombination rate constants k_{2AR} and k_{3AR} , which are the inverse of the multiple exciton lifetimes τ_2 and τ_3 in the case of 16-MHDA treated film. Then, assuming that the Auger recombination rate constants k_{2AR} and k_{3AR} are the same in the PbS QD films treated by different MAA ligands in this study, we can calculate multiple charge transfer rate constants k_{2et} and k_{3et} from the measured exciton lifetimes of each MAA ligand-treated films via the following equation and the results are shown in Fig. 5b and 5c:

$$k_{et} = \frac{1}{\tau_{(3 - \text{MPA or } 6 - \text{MHA or } 12 - \text{MDA})}} - \frac{1}{\tau_{(16 - \text{MHDA})}} \quad (5)$$

From Fig. 5b, Fig. 5c, Fig. S8a and Fig. S8b, we find that the charge transfer rates of the 2 and 3 $e-h$ pairs are well described by a single exponential decay function of the QD center-to-center distance and the QD-QD spacing, similar to that of the 1 $e-h$ pair. The values of the charge transfer rate constants k_{2et} and k_{3et} and Auger recombination rate constants k_{2AR} and k_{3AR} are summarized in Table 2. In particular, when the QD center-to-center distance (or interparticle spacing) is smaller than 4.3 nm (or 0.8 nm) in the case of 3-MPA and 6-MHA treated PbS QD solid films, the charge transfer rate constants k_{2et} and k_{3et} are larger than the Auger recombination rate constants k_{2AR} and k_{3AR} of those samples. This result indicated that

in those samples, multiple exciton can be rapidly extracted before the occurring of Auger recombination. Moreover, we determined the charge tunneling constants β_2 and β_3 by fitting Fig. 5b and 5c to eq. (1). The extracted values of the charge tunneling constants β_2 and β_3 are $0.68 \pm 0.05 \text{ nm}^{-1}$ and $0.71 \pm 0.01 \text{ nm}^{-1}$ which are close to that of the single charge tunneling constants β_1 . Therefore, we find that the dissociation of multiple exciton in closely packed films occurs also via tunneling effect just like the behaviour of a single exciton in the QD films.

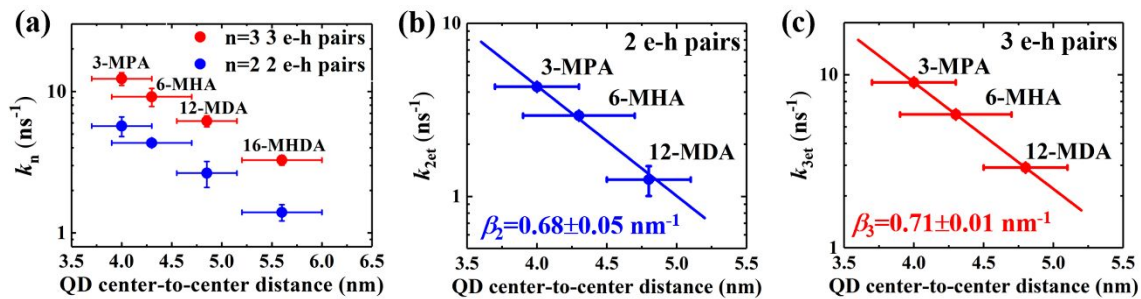


Fig. 5 Correlation between QD center-to-center distance and (a) the decay rate constant ($k = \tau^{-1}$), and charge transfer rate constants k_{2et} and k_{3et} of 2 $e-h$ pairs (b) and 3 $e-h$ pairs (c) for MAA ligands treated films. A single exponential decay fitting (dotted line) indicates that the carrier transfer occurs via tunneling of charge through a potential barrier.

Table 2. Summary of the charge transfer rate constants k_{2et} and k_{3et} and Auger recombination rate constants k_{2AR} and k_{3AR} .

QD center-to-center distance (nm)	$k_{2et} (ns^{-1})$	$k_{3et} (ns^{-1})$	$k_{2AR} (ns^{-1})$	$k_{3AR} (ns^{-1})$
4.0 ± 0.3 (3-MPA)	4.3 ± 0.2	9.0 ± 0.1	1.4 ± 0.1	3.2 ± 0.2
4.3 ± 0.4 (6-MHA)	2.9 ± 0.1	5.9 ± 0.2	1.4 ± 0.1	3.2 ± 0.2

4.8±0.3 (12-MDA)	1.2±0.2	2.9±0.2	1.4±0.1	3.2±0.2
5.6±0.4 (16-MHDA)	0	0	1.4±0.1	3.2±0.2

Conclusions

In summary, the interparticle distance between PbS QDs were well controlled by using different length MAA surface ligands, and the QD center-to-center distance in these MAA treated films was found to be linearly increase with the number of carbon atoms of corresponding ligands increasing. The evidence of interparticle distance dependent photogenerated multiple exciton dissociation in closely packed QD solid films has been shown for the first time. Our results show that the dissociation process of single exciton, biexciton and triexciton occur via tunneling of charges between neighboring QDs, and the obtained charge tunneling constants of single exciton (β_1), biexciton (β_2) and triexciton (β_3) are $0.67 \pm 0.02 \text{ nm}^{-1}$, $0.68 \pm 0.05 \text{ nm}^{-1}$ and $0.71 \pm 0.01 \text{ nm}^{-1}$, respectively. More importantly, for the first time, we found that the QD interparticle distance (or spacing) limit of multiple exciton extraction is 4.3 (or 0.8) nm, which clarifies one vital condition for using the multiple exciton in packed QD solid films before Auger recombination occurrence. This result reveals the reason why over 100% IPCE only could be observed in short surface ligand treated QD based devices to date. Our finding suggests that there is a large possibility to apply MEG in QDSCs. We consider that our results contribute to a further fundamental understanding of the improvement in the photovoltaic efficiency of QDSCs.

Supporting Information

Supplementary data includes: Experimental details, FTIR spectra, HRTEM images of PbS QDs, light absorption spectra, TA time decay curves and fitting data of single exciton, excitation-fluences dependent TA time decay curves.

Author Contributions

Naoki Nakazawa, Yaohong Zhang and Qing Shen conceived and designed the experiments; Naoki Nakazawa, Feng Liu, Chao Ding, Kanae Hori and Taro Toyoda performed the experiments; Yaohong Zhang, Yingfang Yao, Yong Zhou, Zhigang Zou and Qing Shen analyzed the data; Shuzi Hayase, Ruixiang Wang and Qing Shen contributed reagents/materials/analysis tools; Naoki Nakazawa and Yaohong Zhang wrote the paper; Qing Shen corrected the paper.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

This research was supported by the Japan Science and Technology Agency (JST) PRESTO and CREST programs, Beijing Advanced Innovation Center for Future Urban Design, Beijing University of Civil Engineering and Architecture (Grant UDC2018031121), and the MEXT KAKENHI Grant (Grants 26286013, 17H02736).

Notes and references

1. A. J. Nozik, *Inorg. Chem.*, 2005, **44**, 6893-6899.
2. A. J. Nozik, M. C. Beard, J. M. Luther, M. Law, R. J. Ellingson and J. C. Johnson, *Chem. Rev.*, 2010, **110**, 6873-6890.
3. M. C. Beard, J. M. Luther, O. E. Semonin and A. J. Nozik, *Acc. Chem. Res.*, 2013, **46**, 1252-1260.
4. R. J. Ellingson, M. C. Beard, J. C. Johnson, P. Yu, O. I. Micic, A. J. Nozik, A. Shabaev and A. L. Efros, *Nano Lett.*, 2005, **5**, 865-871.
5. Y. Zhang, C. Ding, G. Wu, N. Nakazawa, J. Chang, Y. Ogomi, T. Toyoda, S. Hayase, K. Katayama and Q. Shen, *J. Phys. Chem. C*, 2016, **120**, 28509-28518.
6. Y. Zhang, J. Zhu, X. Yu, J. Wei, L. Hu and S. Dai, *Sol. Energy*, 2012, **86**, 964-971.
7. L. Hu, Z. L. Zhang, R. J. Patterson, Y. C. Hu, W. J. Chen, C. Chen, D. B. Li, C. Hu, C. Ge, Z. H. Chen, L. Yuan, C. Yan, N. Song, Z. L. Teh, G. J. Conibeer, J. Tang and S. J. Huang, *Nano Energy*, 2018, **46**, 212-219.
8. A. A. Chistyakov, M. A. Zvaigzne, V. R. Nikitenko, A. R. Tameev, I. L. Martynov and O. V. Prezhdo, *J. Phys. Chem. Lett.*, 2017, **8**, 4129-4139.
9. S. Jiao, J. Du, Z. Du, D. Long, W. Jiang, Z. Pan, Y. Li and X. Zhong, *J. Phys. Chem. Lett.*, 2017, **8**, 559-564.
10. C. Ding, Y. Zhang, F. Liu, Y. Kitabatake, S. Hayase, T. Toyoda, R. Wang, K. Yoshino, T. Minemoto and Q. Shen, *Nanoscale Horizons*, 2018, **3**, 417-429.

11. H. Htoon, J. A. Hollingsworth, R. Dickerson and V. I. Klimov, *Phys. Rev. Lett.*, 2003, **91**, 227401.
12. Y. Kanemitsu, *Acc. Chem. Res.*, 2013, **46**, 1358-1366.
13. S. Garakyaraghi, C. Mongin, D. B. Granger, J. E. Anthony and F. N. Castellano, *J. Phys. Chem. Lett.*, 2017, **8**, 1458-1463.
14. A. Shabaev, A. L. Efros and A. J. Nozik, *Nano Lett.*, 2006, **6**, 2856-2863.
15. J. M. Luther, M. C. Beard, Q. Song, M. Law, R. J. Ellingson and A. J. Nozik, *Nano Lett.*, 2007, **7**, 1779-1784.
16. R. D. Schaller and V. I. Klimov, *Phys. Rev. Lett.*, 2004, **92**, 186601.
17. M. C. Beard, A. G. Midgett, M. Law, O. E. Semonin, R. J. Ellingson and A. J. Nozik, *Nano Lett.*, 2009, **9**, 836-845.
18. L. A. Padilha, J. T. Stewart, R. L. Sandberg, W. K. Bae, W.-K. Koh, J. M. Pietryga and V. I. Klimov, *Acc. Chem. Res.*, 2013, **46**, 1261-1269.
19. Q. Shen, K. Katayama, T. Sawada, S. Hachiya and T. Toyoda, *Chem. Phys. Lett.*, 2012, **542**, 89-93.
20. Q. Shen, K. Katayama and T. Toyoda, *J. Energy Chem.*, 2015, **24**, 712-716.
21. S. Akhavan, A. F. Cihan, A. Yeltik, B. Bozok, V. Lesnyak, N. Gaponik, A. Eychmuller and H. V. Demir, *Nano Energy*, 2016, **26**, 324-331.
22. V. Sukhovatkin, S. Hinds, L. Brzozowski and E. H. Sargent, *Science*, 2009, **324**, 1542-1544.
23. J. B. Sambur, T. Novet and B. A. Parkinson, *Science*, 2010, **330**, 63-66.

24. O. E. Semonin, J. M. Luther, S. Choi, H.-Y. Chen, J. Gao, A. J. Nozik and M. C. Beard, *Science*, 2011, **334**, 1530-1533.
25. Y. Yan, R. W. Crisp, J. Gu, B. D. Chernomordik, G. F. Pach, Ashley R. Marshall, J. A. Turner and M. C. Beard, *Nat. Energy*, 2017, **2**, 17052.
26. C.-H. M. Chuang, P. R. Brown, V. Bulović and M. G. Bawendi, *Nat. Mater.*, 2014, **13**, 796-801.
27. J. Tang, K. W. Kemp, S. Hoogland, K. S. Jeong, H. Liu, L. Levina, M. Furukawa, X. Wang, R. Debnath, D. Cha, K. W. Chou, A. Fischer, A. Amassian, J. B. Asbury and E. H. Sargent, *Nat. Mater.*, 2011, **10**, 765-771.
28. W. Shi, S. W. H. Eijt, C. S. Suchand Sandeep, L. D. A. Siebbeles, A. J. Houtepen, S. Kinge, E. Brück, B. Barbiellini and A. Bansil, *Appl. Phys. Lett.*, 2016, **108**, 081602.
29. J. Y. Woo, S. Lee, S. Lee, W. D. Kim, K. Lee, K. Kim, H. J. An, D. C. Lee and S. Jeong, *J. Am. Chem. Soc.*, 2016, **138**, 876-883.
30. D. A. Hines and P. V. Kamat, *J. Phys. Chem. C*, 2013, **117**, 14418-14426.
31. R. W. Crisp, D. M. Kroupa, A. R. Marshall, E. M. Miller, J. Zhang, M. C. Beard and J. M. Luther, *Sci. Rep.*, 2015, **5**, 9945.
32. P. R. Brown, D. Kim, R. R. Lunt, N. Zhao, M. G. Bawendi, J. C. Grossman and V. Bulović, *ACS Nano*, 2014, **8**, 5863-5872.
33. J. Jean, T. S. Mahony, D. Bozyigit, M. Sponseller, J. Holovsky, M. G. Bawendi and V. Bulovic, *ACS Energy Lett.*, 2017, **2**, 2616-2624.

34. B. Sun, O. Voznyy, H. Tan, P. Stadler, M. Liu, G. Walters, A. H. Proppe, M. Liu, J. Fan, T. Zhuang, J. Li, M. Wei, J. Xu, Y. Kim, S. Hoogland and E. H. Sargent, *Adv. Mater.*, 2017, **29**, 1700749.
35. M. Ono, T. Nishihara, T. Ihara, M. Kikuchi, A. Tanaka, M. Suzuki and Y. Kanemitsu, *Chem. Sci.*, 2014, **5**, 2696-2701.
36. R. K. Capek, D. Yanover and E. Lifshitz, *Nanoscale*, 2015, **7**, 5299-5310.
37. C. R. Kagan, E. Lifshitz, E. H. Sargent and D. V. Talapin, *Science*, 2016, **353**, aac5523.
38. D. Asil, B. J. Walker, B. Ehrler, Y. Vaynzof, A. Sepe, S. Bayliss, A. Sadhanala, P. C. Y. Chow, P. E. Hopkinson, U. Steiner, N. C. Greenham and R. H. Friend, *Adv. Funct. Mater.*, 2014, **25**, 928-935.
39. Y. Gao, M. Aerts, C. S. S. Sandeep, E. Talgorn, T. J. Savenije, S. Kinge, L. D. A. Siebbeles and A. J. Houtepen, *ACS Nano*, 2012, **6**, 9606-9614.
40. P. Galar, P. Piatkowski, T. T. Ngo, M. Gutierrez, I. Mora-Sero and A. Douhal, *Nano Energy*, 2018, **49**, 471-480.
41. H. I. Wang, M. Bonn and E. Cánovas, *J. Phys. Chem. Lett.*, 2017, **8**, 2654-2658.
42. F. Liu, Y. Zhang, C. Ding, T. Toyoda, Y. Ogomi, T. S. Ripolles, S. Hayase, T. Minemoto, K. Yoshino, S. Dai and Q. Shen, *J. Phys. Chem. Lett.*, 2018, **9**, 294-297.
43. J. M. Luther, M. Law, Q. Song, C. L. Perkins, M. C. Beard and A. J. Nozik, *ACS Nano*, 2008, **2**, 271-280.
44. S. J. Oh, Z. Wang, N. E. Berry, J.-H. Choi, T. Zhao, E. A. Gaulding, T. Paik, Y. Lai, C. B. Murray and C. R. Kagan, *Nano Lett.*, 2014, **14**, 6210-6216.

45. Y. Liu, M. Gibbs, J. Puthussery, S. Gaik, R. Ihly, H. W. Hillhouse and M. Law, *Nano Lett.*, 2010, **10**, 1960-1969.
46. Y. Zhang, G. Wu, C. Ding, F. Liu, Y. Yao, Y. Zhou, C. Wu, N. Nakazawa, Q. Huang, T. Toyoda, R. Wang, S. Hayase, Z. Zou and Q. Shen, *J. Phys. Chem. Lett.*, 2018, **9**, 3598-3603.
47. H. Zhang, B. Hu, L. Sun, R. Hovden, F. W. Wise, D. A. Muller and R. D. Robinson, *Nano Lett.*, 2011, **11**, 5356-5361.
48. S. J. Oh, D. B. Straus, T. Zhao, J. H. Choi, S. W. Lee, E. A. Gaulding, C. B. Murray and C. R. Kagan, *Chem. Commun.*, 2017, **53**, 728-731.
49. Q. Lin, H. J. Yun, W. Liu, H.-J. Song, N. S. Makarov, O. Isaienko, T. Nakotte, G. Chen, H. Luo, V. I. Klimov and J. M. Pietryga, *J. Am. Chem. Soc.*, 2017, **139**, 6644-6653.
50. G. W. Guglietta, B. T. Diroll, E. A. Gaulding, J. L. Fordham, S. Li, C. B. Murray and J. B. Baxter, *ACS Nano*, 2015, **9**, 1820-1828.
51. M. T. Frederick, V. A. Amin and E. A. Weiss, *J. Phys. Chem. Lett.*, 2013, **4**, 634-640.
52. E. A. Weiss, *ACS Energy Lett.*, 2017, **2**, 1005-1013.
53. M. S. Kodaimati, C. Wang, C. Chapman, G. C. Schatz and E. A. Weiss, *ACS Nano*, 2017, **11**, 5041-5050.
54. C. S. S. Sandeep, S. Ten Cate, J. M. Schins, T. J. Savenije, Y. Liu, M. Law, S. Kinge, A. J. Houtepen and L. D. A. Siebbeles, *Nat. Commun.*, 2013, **4**, 2360.
55. J. Chang, Y. Ogomi, C. Ding, Y. H. Zhang, T. Toyoda, S. Hayase, K. Katayama and Q. Shen, *Phys. Chem. Chem. Phys.*, 2017, **19**, 6358-6367.

56. R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta, Rev. Biomembr.*, 1985, **811**, 265-322.
57. J. J. Choi, J. Luria, B.-R. Hyun, A. C. Bartnik, L. Sun, Y.-F. Lim, J. A. Marohn, F. W. Wise and T. Hanrath, *Nano Lett.*, 2010, **10**, 1805-1811.
58. V. I. Klimov, *J. Phys. Chem. B*, 2000, **104**, 6112-6123.
59. V. I. Klimov, D. W. McBranch, C. A. Leatherdale and M. G. Bawendi, *Phys. Rev. B*, 1999, **60**, 13740-13749.
60. T. Nishihara, H. Tahara, M. Okano, M. Ono and Y. Kanemitsu, *J. Phys. Chem. Lett.*, 2015, **6**, 1327-1332.
61. H. Tahara, M. Sakamoto, T. Teranishi and Y. Kanemitsu, *Nat. Commun.*, 2018, **9**, 3179.
62. V. I. Klimov, A. A. Mikhailovsky, D. W. McBranch, C. A. Leatherdale and M. G. Bawendi, *Science*, 2000, **287**, 1011-1013.