Research article

Xiaochun Liu, Haifeng Zhao, Linfeng Wei, Xinjian Ren, Xinyang Zhang, Faming Li, Peng Zeng* and Mingzhen Liu*

Ligand-modulated electron transfer rates from CsPbBr₃ nanocrystals to titanium dioxide

<https://doi.org/10.1515/nanoph-2020-0631>

Received November 29, 2020; accepted January 21, 2021;

published online February 26, 2021

Abstract: In most perovskite nanocrystal (PeNC)-based optoelectronic and photonic applications, surface ligands inevitably lead to a donor–bridge–acceptor charge transfer configuration. In this article, we demonstrate successful modulation of electron transfer (ET) rates from all-inorganic CsPbBr₃ PeNCs to mesoporous titanium dioxide films, by using different surface ligands including single alkyl chain oleic acid and oleylamine, cross-linked insulating (3-aminopropyl)triethoxysilane and aromatic naphthoic acid molecules as the ligand-bridge. We systematically investigated the ET process through time-resolved photoluminescence spectroscopy. Calculations verified the ligand-bridge barrier effect of the three species upon the ET process. Transient absorption measurements excluded carrier-delocalization effect of the naphthoic acid ligands and confirmed the bridge-barrier effect. Our work provides a perspective for composable and appropriate ligands design for diverse practical purposes.

Keywords: bridge-barrier effect; CsPbBr₃ nanocrystals; electron transfer; ligand-bridge.

1 Introduction

Over the past decade, metal halide perovskites have risen to prominence in optoelectronic and photovoltaic fields for their outstanding properties that resulted in a rocketing progress in device performance [1, 2]. Recent research focus has also been directed toward low-dimensional metal halide perovskites with expectation for their unique photonic and electrical properties under quantum confinement and surface effects [3–8]. Quasi-zero-dimensional all-inorganic CsPbX₃ (X=Cl, Br, I) perovskite nanocrystals (PeNCs) soon distinguished themselves as a new family of photonic and optoelectronic materials for their narrow emission width with color tunability [9], high optical gain [4] and reduced fluorescence blinking [10]. Particularly, their unusual antibonding nature of electronic band structure endows CsPbX₃ PeNCs higher tolerance to surface defects than conventional II–VI semiconductor nanocrystals [11–13]. The latter usually perform limited photoluminescence quantum yields due to defect-induced PL quenching. Therefore, together with their low-cost and ease of synthesis, CsPbX₃ PeNCs are perceived as potential candidates for low-threshold lasers [7, 14], high dynamical displays [15], light-emitting diodes [8, 16] and photovoltaics [6, 17, 18].

Surface ligands are necessary and crucial to PeNCs in stability of the lattice structure and control of crystal growth [19–24]. Inevitably, in most PeNC-based optoelectronic and photonic applications, it leads to a donor–bridge–acceptor charge transfer (CT) system, in which the anchoring ligands act as a linking bridge. Therefore, it is of significant importance to carefully choose appropriate ligands in order to tune the CT rates and thus achieve the desired performance of PeNC-based devices.

So far it has been one of the focuses to investigate the ligand-bridge effect on the CT process and find composable and appropriate ligands for diverse practical purposes [25, 26]. Ligands with high potential barriers for either electrons or holes may notably hinder the CT process, which is necessary to some photonic applications that need

Xiaochun Liu and Haifeng Zhao are Co-first authors.

***Corresponding authors: Peng Zeng and Mingzhen Liu**, School of Materials and Energy, University of Electronic Science and Technology of China, Chengdu 611731, P. R. China; and Center for Applied Chemistry, University of Electronic Science and Technology of China, Chengdu 611731, P. R. China, E-mail: peng.zeng@uestc.edu.cn (P. Zeng), mingzhen.liu@uestc.edu.cn (M. Liu). <https://orcid.org/0000-0001-8017-9706> (M. Liu)

Xiaochun Liu, Haifeng Zhao, Linfeng Wei, Xinjian Ren, Xinyang Zhang and Faming Li, School of Materials and Energy, University of Electronic Science and Technology of China, Chengdu 611731, P. R. China; and Center for Applied Chemistry, University of Electronic Science and Technology of China, Chengdu 611731, P. R. China. <https://orcid.org/0000-0001-9039-7811> (H. Zhao)

restrained photon-induced charge losses to surroundings, such as in lasers and displays [27]. Low-potential barrier ligands are in contrary. They boost the CT rates by acting as a conductive bridge between the NCs and carrier acceptors/donors, and this is crucial to charge extraction purpose [25, 26, 28]. One limiting case is that the ligand possesses a potential close or even lower than that of the NCs donating level, so-called carrier-delocalizing ligands. There is thus a possibility that the ligand performs as charge carrier acceptors rather than the bridge, leading to carrier trapping effect on the ligand which may potentially reduce the carrier extraction efficiency [29].

Based on our recent success in CsPbBr₃ PeNCs synthesis with varied ligands, we demonstrate herein a control of the electron transfer (ET) process using single alkyl chain, cross-linked insulating and aromatic ligands. These ligand species correspond to conventional acid-base coordinated oleic acid (OA) and oleylamine (OAm), (3-aminopropyl)triethoxysilane (APTES) and naphthoic acid (NCA), respectively. Tuning the potential barrier by use of different ligands, we realized modulation of the ET rates from CsPbBr₃ PeNCs to electron-accepting mesoporous titanium dioxide (TiO₂) substrates spanning a range of fivefolds, as revealed by time-resolved PL spectroscopy. Calculations of the ligand molecule frontier orbitals verified the bridge-barrier effect on the changes of ET rates. Especially, the successful anchoring of NCA ligands revealed an appropriate potential barrier leading to the most significant ET rates with no obvious charge delocalization effect, which may be detrimental to quantum yields of the NCs.

2 Experimental section

2.1 Materials

All chemicals were used without further purification, which include: lead(II) bromide (PbBr₂, 98%) and (3-aminopropyl)triethoxysilane (APTES, 98%) were purchased from Alfa Aesar; cesium carbonate (Cs₂CO₃, 99.9%), octadecene (ODE, 90%), oleylamine (OAm, 70%), oleic acid (OA, 90%) were purchased from Sigma-Aldrich; octane (C₈H₁₈, 99%) were purchased from Adamas Reagents; 1-naphthoic acid (NCA, 98%) was purchased from TCI; methyl acetate (MeAC, 98.0%) were purchased from Greagent.

2.2 Synthesis of CsPbBr₃ PeNCs with various ligands

The preparation of OA/OAm-CsPbBr₃ and OA/APTES-CsPbBr₃ PeNCs were conducted following a well-established synthesis process as

reported by Zhao and coworkers [30]. In brief, the Cs-oleate precursor solution was prepared by mixing 0.18 g Cs₂CO₃, 0.75 mL OA and 7.5 mL ODE into a 50 mL three-necked round-bottomed flask. With being stirred, the mixture was degassed at 120 °C under vacuum for 20 min. In order to remove moisture and O₂ in the mixture, the flask was purged with Ar by switching on a double-row-pipe and subsequently degassing under vacuum for three times at 60 and 90 °C, respectively. Then, the reactant was heated to 150 °C under Ar flow until the solution turned clear which indicated a complete reaction of Cs₂CO₃ and OA. The Cs-oleate precursor was kept at 100 °C to avoid solidification before injection.

Taking OA/OAm-CsPbBr₃ PeNCs as an example, a mixture of 0.1 g PbBr₂, 0.75 mL OA, 0.75 mL OAm and 7.5 mL ODE were dried in a three-necked flask under vacuum, and then were heated to 120 °C with magnetic stirring. During the rise of temperature, the system was rinsed under Ar and vacuum in turn for three times at 60 and 90 °C, respectively. After PbBr₂ was completely dissolved, the atmosphere was switched from vacuum to Ar, and the reaction temperature was elevated to 170 °C. Then 0.75 mL of the prepared Cs-oleate precursor was swiftly injected into the reaction mixture. The reaction was rapidly quenched down in an ice-water bath after mixing for 5 s. The crude solution was first washed by adding MeAC with a 3-times greater volume, and then was centrifuged at 10,000 rpm for 1 min to collect the as-synthesized OA/OAm-CsPbBr₃ PeNCs. In the end, the products were dispersed in octane and centrifuged again at 10,000 rpm for 3 min. The supernatant was collected for all spectroscopic investigations reported here. OA/APTES-CsPbBr₃ PeNCs were prepared using the same reaction procedure as the OA/OAm-CsPbBr₃ PeNCs except for replacing 0.75 mL OAm with 0.75 mL APTES and lowering the inject temperature to 150 °C. For OA/OAm-capped NCs and OA/APTES-capped NCs, both the synthesis and washing procedure were performed under the same conditions, and the same amount of OA was added during the reaction. Thus it is rational to assume similar ligand densities in both OA/OAm- and OA/APTES-CsPbBr₃ systems. For the case of NCA/OAm-CsPbBr₃ PeNCs, they were obtained by a ligand treatment procedure, in which 0.25 mg NCA was added into 1 mL OA/OAm-CsPbBr₃ PeNCs stock solution. The ligand treatment reaction was stirred for 5 min followed by centrifuging at 10,000 rpm for 3 min in order to remove the unbounded ligands. For NCA/OAm-CsPbBr₃ NCs obtained through a well-established and mild ligand-treatment reaction, the total acid-ligand density (including OA and NCA) was also reasonably assumed to be similar to that of the pristine OA/OAm-CsPbBr₃ system.

2.3 Preparation of CsPbBr₃ PeNC films

About 0.05 mL of CsPbBr₃ PeNC solution in octane was spin-coated at 1500 rpm for 30 s onto a mesoporous TiO₂ layer deposited onto a fluorine-doped tin oxide (FTO)-coated glass substrate, and a poly-methyl methacrylate (PMMA) layer on a glass substrate, respectively. Films were for time-resolved PL and transient absorption (TA) measurements. For the mesoporous TiO₂ layer, mesoporous TiO₂ precursor was spin-coated on the substrates at 3800 rpm for 30 s, followed by annealing at 180 °C for 20 min and then annealing at 500 °C for 50 min in air. For the PMMA layer, PMMA dissolved in chlorobenzene was spin-coated on the substrates at 3000 rpm for 30 s, followed by annealing at 60 °C for 10 min in air.

2.4 Characterization

Absorption spectra were measured with an UV-vis spectrometer (type, PerkinElmer). Steady-state and time-resolved PL spectra were obtained by a time-correlated single photon counting instrument (FT300, PicoQuant) with a 454 nm ps pulse laser as the excitation source. Transmission electron microscope (TEM) measurements were conducted with G2F20 S-Twin Tecnai. X-ray diffraction (XRD) patterns were taken at a voltage of 40 kV and current of 40 mA on an X-ray diffractometer (D8 Advance, Bruker) with Cu K α 1/2 source and Vantec-1 detector in 2θ -Omega model. Fourier transform infrared spectra (FTIR) were obtained using a PerkinElmer Spectrum Two FTIR Spectrometer with a diamond attenuated total reflection kit. Scanning electron microscope (SEM) images were collected by an FEI Inspect F50 electron microscope with an electron energy of 10 kV.

TA measurement was carried out on a home-built femtosecond time-resolved pump-probe system using a regeneratively amplified laser source (Solstice, Spectra-Physics). In detail, a portion of 800 nm output beam with a repetition rate of 1 kHz was frequency-doubled in a BBO crystal for the generation of 400 nm pump beam. After sending through a computer-controlled delay stage, the pump beam was chopped by a chopper synchronized to 500 Hz. The continuum white-light probe beam covering a wavelength range from 440 to 800 nm was generated by focusing a portion of 800 nm beam into a 3-mm-thick sapphire window. The pump and probe pulses were spatially overlapped in a quartz cell of CsPbBr₃ PeNC solution, or on the coated CsPbBr₃ PeNC film side. Then pump-induced variations in absorbance of the samples at different delay times were recorded by a synchronized fiber spectrometer. The IRF (instrument response function) width of 150 fs was determined by 800 nm autocorrelation measurements at the sample position.

CsPbBr₃ PeNC samples dispersed in octane were excited at a low pump flux of 16 nJ/pulse, in order to avoid any multiple-exciton-induced effects. The estimated exciton number per particle is provided in Supplementary Information (SI). All measurements were conducted at room temperature.

2.5 DFT calculations

All calculations were accomplished using density functional theory (DFT) with the Gaussian 09 program suit [31]. The electronic structure was obtained by Kohn-Sham density functional calculations using B3LYP (Beckethree-Lee-Yang-Parr) as the exchange-correlation functional and 6-311 + $G(d,p)$ as the basis set [32].

3 Results and discussion

Our synthesis procedure was based on the conventional hot-injection method incorporating OA and OAm precursors. For OA/APTES-CsPbBr₃ PeNCs, the APTES was introduced as a substitute for OAm. Its dangling silane groups are able to form cross-linked Si-O-Si via the mutual hydrolysis process. Based on our previous work [30], by a mild self-hydrolysis of the APTES precursor, we herein

obtained highly uniform OA/APTES-CsPbBr₃ PeNCs, in which particles remained in an individual cubic shape and were wrapped with thin silicone layers (see Figure S1 in SI). For NCA/OAm-CsPbBr₃ PeNCs, a post-reaction of ligand-treatment procedure based on OA/OAm-CsPbBr₃ PeNCs was introduced, which was able to maintain the same morphology and size of the nanoparticles.

Consistent particle size circumvents the intrinsic size-dependent properties of PeNCs and allows significative discussion of ligand-bridge effect on the CT process. Herein, synthesis of CsPbBr₃ PeNCs with different ligand composites was carefully controlled through adjusting hot injection temperature (see the synthesis part), in order to obtain similar-sized PeNCs. Particle sizes were further certified by TEM, as shown in Figure 1A. All CsPbBr₃ PeNCs exhibit characteristic cubic shapes, and the average edge lengths are 11.2 ± 1.1 nm for OA/APTES-CsPbBr₃ PeNCs, 11.3 ± 1.4 nm for OA/OAm-CsPbBr₃ PeNCs, and 11.3 ± 1.3 nm for NCA/OAm-CsPbBr₃ PeNCs (see Figure S2 in SI). As shown in Figure 1B, the absorption spectra for all CsPbBr₃ PeNCs possess similar absorption onsets close to 510 nm, meanwhile, the photo-excited PL emission peak of OA/APTES-CsPbBr₃ PeNCs is centered at 511 nm, close to that of OA/OAm-CsPbBr₃ and NCA/OAm-CsPbBr₃ PeNCs at 514 nm, implying comparable size-dependent photonic properties for all three CsPbBr₃ PeNC systems. The absorption spectra of APTES, OA, OAm and NCA solution in ethanol all show no absorption band features above 400 nm (see Figure S3). We accordingly clarify that only CsPbBr₃ PeNCs were selectively excited in the following spectroscopic measurements. It is also worth noting that, after the ligand treatment and washing procedure, the distinctive absorption onset close to 350 nm in NCA-CsPbBr₃ PeNCs was consistent with that of the NCA solution, indicative of likely successful linkage of NCA ligands onto CsPbBr₃ PeNCs.

FTIR spectroscopy was further employed to confirm the existence of cross-linked APTES and NCA molecules in the CsPbBr₃ PeNC complexes, respectively. As shown in Figure 1C, for OA/OAm-CsPbBr₃ PeNCs, vibrations of C=O and NH₃⁺ from OA and OAm ligand appear at 1536 and 1644 cm⁻¹, respectively [33]. Two additional peaks at 1033 and 1109 cm⁻¹ are observed for OA/APTES-CsPbBr₃ PeNCs, corresponding to the vibration of Si-O-Si and Si-O-C for the wrapping of APTES on CsPbBr₃ nanoparticles which are in line with our previous work [30]. The former clearly verified the formation of cross-linked APTES ligands through the hydrolysis process which resulted in a wrapping silicone layer outside the nanoparticles. As for

Figure 1: (A) TEM images, (B) UV-Vis absorption and PL emission spectra, (C) FTIR spectra and (D) XRD patterns of OA/APTES-CsPbBr₃ (green), OA/OAm-CsPbBr₃ (blue) and NCA/OAm-CsPbBr₃ (orange) PeNCs. Scale bars are 50 nm.

NCA/OAm-CsPbBr₃ PeNCs, vibrations of the conjugate structure C=C observed at 1512, 1573 and 1592 cm⁻¹ are indicative of the presence of NCA molecules, as well as the vibrations of the C=O group observed at 1672 and 1623 cm⁻¹ [34].

XRD patterns (Figure 1D) verified that the cubic phase remains unchanged for all species upon introduction of various ligands. Noticeably, a significant change was observed, that is, after partially replacing OA with NCA, the split of (100) diffraction peak centered at 15.11° for OA/OAm-CsPbBr₃ PeNCs was suppressed, indicating that NCA conduces to more excellent crystallinity.

With the successful anchorage of the ligands, we investigated the ET process from CsPbBr₃ PeNCs to the electron-accepting TiO₂ with different ligand systems. In a typical electron donor-acceptor system, the PL of the electron donors is quenched, and its lifetime is accordingly shortened as the ET process provides an additional depopulation channel for the photoinduced charge carriers. Hence, the ET, or electron extraction rate in the CsPbBr₃-TiO₂ system here can be derived by comparing the PL lifetimes between CsPbBr₃ PeNCs assembled with PMMA and TiO₂ [35]:

$$k_{\text{ET}} = \frac{1}{\tau_{\text{CsPbBr}_3, \text{TiO}_2}} - \frac{1}{\tau_{\text{CsPbBr}_3, \text{PMMA}}} \quad (1)$$

where $\tau_{\text{CsPbBr}_3, \text{TiO}_2}$ and $\tau_{\text{CsPbBr}_3, \text{PMMA}}$ are the PL lifetimes for CsPbBr₃ PeNCs casted on conductive mesoporous TiO₂ with FTO-coated glass as substrates and on insulating polymethyl methacrylate (PMMA) with glass as substrates, respectively. As PMMA is insulating and thus able to inhibit carrier leakage, CsPbBr₃ PeNCs coated on the PMMA layer

provides a meaningful reference of the quenched PL decays. Here, TCSPC measurements were applied to monitor the PL decays of CsPbBr₃ PeNCs, whereby the average lifetimes $\tau_{\text{CsPbBr}_3, \text{TiO}_2}$ and $\tau_{\text{CsPbBr}_3, \text{PMMA}}$ were accessible through multiexponential fittings to the time-resolved PL dynamics following the intensity-weighting calculation [36]:

$$\tau_{\text{av}} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i} \quad (2)$$

The collected PL decays, measured at the emission peak wavelengths for all CsPbBr₃ PeNCs complexes attached to PMMA and TiO₂ are presented in Figure 2A–C. The time-resolved PL decays were well fitted by using a triexponential model (solid lines in Figure 2A–C). Table 1 summarizes the fitting parameters and the average lifetimes. Both of the two faster decay components, τ_1 and τ_2 on a time scale shorter than 10 ns, are assigned to trap-mediated charge recombination; and the slow component τ_3 longer than 10 ns is attributed to the intrinsic carrier radiative recombination [37]. For CsPbBr₃ PeNCs with no TiO₂, the incorporation of APTES and NCA ligands both exhibited remarkable suppression of the trap-mediated charge recombination, and consequently induced an elongated PL lifetime as compared with OA/OAm-CsPbBr₃ PeNCs (Figure 2D). It suggests a significant surface passivation effect from APTES and NCA than traditional OA and OAm, in line with previously reported results [30].

When CsPbBr₃ PeNCs were assembled with the TiO₂ substrate, the PL decayed faster than that on the PMMA insulating layer especially for the cases of OA/OAm- and NCA/OAm-capped PeNCs, indicating the occurrence of the

Figure 2: (A–C) PL decays of OA/APTES-CsPbBr₃, OA/OAm-CsPbBr₃ and NCA/OAm-CsPbBr₃ PeNCs attached to PMMA (green) and TiO₂ (orange) films. Insets: schematic diagram presenting the capping ligand on CsPbBr₃ PeNCs, (D) comparison of decay curves of all three CsPbBr₃ PeNCs-ligand systems coated on PMMA.

Table 1: Multiexponential fitting parameters for PL decays of CsPbBr₃ PeNCs on TiO₂ and PMMA.

Sample	τ_1 (ns)	A_1	τ_2 (ns)	A_2	τ_3 (ns)	A_3	τ_{av} (ns)
OA/APTES-PMMA	2.60	0.55	8.60	0.43	40.16	0.02	10.90
OA/APTES-TiO ₂	2.80	0.60	8.54	0.39	34.60	0.01	9.14
OA/OAm-PMMA	1.15	0.62	3.88	0.36	17.53	0.02	5.09
OA/OAm-TiO ₂	0.92	0.51	3.22	0.45	10.06	0.04	3.81
NCA/OAm-PMMA	2.67	0.69	7.41	0.29	41.83	0.02	11.60
NCA/OAm-TiO ₂	0.77	0.57	3.90	0.39	14.94	0.04	5.44

ET to TiO₂. We applied the donor–bridge–acceptor model in which the surface ligands act as a transition bridge between the nanoparticle and TiO₂. Comparing to the alkyl chain OA/OAm bridge, the quenching of the PL decay was inconspicuous with the cross-linked APTES ligand-bridge, while it became evidently enhanced with the incorporation of the aromatic NCA ligand-bridge. Based on Equation (1), we calculated the ET rates which were 6.6×10^7 , 1.8×10^7 and $9.7 \times 10^7 \text{ s}^{-1}$ for OA/OAm-CsPbBr₃, OA/APTES-CsPbBr₃ and NCA/OAm-CsPbBr₃ PeNCs, respectively. The aromatic NCA ligands resulted in a boosted ET rate while the cross-linked APTES significantly suppressed the extraction of electrons by a factor of over threefolds, in comparison to the commonly used long alkyl chain ligands.

The configuration of CsPbBr₃ PeNCs terminated with different surface ligands leads to an indirect contact

interface between the nanoparticles and the electron-accepting TiO₂. This was visualized by SEM measurements from which CsPbBr₃ nanoparticles adsorbed onto the mesoporous scaffolding of TiO₂ (See SEM images and elemental mapping images presented in Figure S4 and S5). As a result, the interparticle bridging molecules can be modeled as the potential barrier that electrons have to tunnel through in the ET process. We seek to further understand our experimentally determined k_{ET} trends by modeling the lowest unoccupied molecular orbital (LUMO) level of the ligand-bridge as a barrier potential with respect to the conduction band (CB) of the nanoparticle [38] and the electron accepting level of TiO₂ (Figure 3A) [39]. By using DFT calculations, the highest occupied molecular orbitals (HOMOs) and LUMOs of the four anchored surface ligands were compared. All LUMO levels place higher than the CB levels of both nanoparticle and TiO₂, which confirms the potential barrier effect between the nanoparticle donor and TiO₂ acceptor in our work. On the other hand, from the difference between LUMO and HOMO energy levels (Figure 3B), it can be inferred that the absorption peaks of APTES, OA, OAm and NCA are theoretically located at 196, 193, 197 and 291 nm, respectively. We indeed observed absorption peaks of these ligand molecules at 200, 199, 198 and 292 nm, respectively, which were in good consistency with the theoretical calculations. It suggests that the basis set and functional method chosen in our DFT calculation were reasonable.

Figure 3: (A) Schematic illustration of the ET process for CsPbBr₃ PeNCs-Bridge-TiO₂ system. (B) Energetic and spatial distribution of frontier orbits of ligand-bridge molecules APTES, OA, OAm and NCA. VB, valance band; CB, conduction band; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital.

Both OA and OAm possess similar LUMOs. Crossed-linked APTES (dimer) exhibits the highest-lying LUMO energy level resulting in the highest potential among the four ligand species. Correspondingly, APTES leads to the slowest ET rate which was indeed experimentally observed. In contrast, NCA possesses the lowest barrier potential, consequently gave rise to the ET rate. Additionally, from the electron density distribution of HOMO and LUMO for NCA illustrated in Figure 3B, it shows a pronounced frontier orbital delocalization across the entire molecule as a result of the aromatic group; whereas the OA/OAm and APTES ligands both exhibit intensively localized frontier orbitals which are commonly insulating for charge transition. The former is more conductive and favorable to charge transition across the molecule, thus the resulted system shows a noticeably enhanced ET rate. The APTES exhibit more insulating property with high barrier potential, preventing electrons from extraction by TiO₂. It should be addressed here that a dimer model of the cross-linked APTES was applied in the calculation to simulate the mild hydrolytic polymerization condition in our synthesis. In fact, more significantly high barrier potential is expected for heavily dense cross-linked APTES, which leads to further reduction in electron tunneling and subsequent transfer probability.

One concern may be raised regarding the possible delocalization of electrons caused by the NCA ligands as they exhibit low LUMO level. As discussed above, the carrier-delocalization is detrimental to the carrier extraction efficiency through the ligand-induced carrier trapping effect. We carried out ultrafast TA spectroscopy measurements to reveal the carrier delocalization effect.

Figure S6A–C presents the de-chirped TA spectra for OA/APTES-CsPbBr₃, OA/OAm-CsPbBr₃ and NCA/OAm-

CsPbBr₃ PeNC solution measured in 2 mm cuvettes, at different delay time following the 400 nm pulse excitation. Weak excitation power was delivered in order to circumvent multiexciton effect (see details in SI and Figure S8). At early stage, the spectra are dominated by a photoinduced bleach (PB) signal centered at 510 nm with two side-photoinduced absorption (PA) bands on both sides, which are consistent to the typical features of colloid CsPbBr₃ PeNCs TA spectra [40, 41]. The PB peaks agree well with the absorption onsets denoted in Figure 1A, therefore it is assigned to the state-filling effects and depicts the ground-state depopulation of both electrons and holes, as for perovskite the effective masses of both carriers are similar [41]. The above-bandgap absorption feature PA1 in the region of 440–480 nm is likely from the forbidden optical transitions activated by excitons, and the fast-recovering absorption ranging from 520 to 550 nm (PA2) was induced by the local fields produced by photoexcited carriers [42]. Figure 4A presents a comparison of normalized PB kinetic traces of all three CsPbBr₃ PeNC-ligand systems. Population, or the rising dynamics, of the PB feature at initial stage indicates the relaxation of excited electrons to the band-edge states in CsPbBr₃ PeNCs. Delocalization ligands may provide a competing channel for excited electron relaxation which leads to faster rising of the PB signal. Whereas we indeed found a similar rising of the PB feature in all three systems, which shows no obvious carrier delocalization effect caused by NCA ligands. In addition, both the depopulation of PB signals for OA/APTES-CsPbBr₃ and NCA/OAm-CsPbBr₃ PeNCs were slower than OA/OAm-CsPbBr₃ PeNCs, and again confirming obvious surface passivation effect from APTES and NCA than OA and OAm.

Figure 4: (A) Comparison of normalized PB kinetic traces of all three CsPbBr₃ PeNC-ligand solution systems measured in 2 mm cuvettes. (B–D) Normalized transient PB signal kinetics for OA/APTES-CsPbBr₃, OA/OAm-CsPbBr₃ and NCA/OAm-CsPbBr₃ PeNC films attached to PMMA and TiO₂. The gray curve in (A) represents instrument response functions of the TA instrument.

Meanwhile, TA measurements were also performed on CsPbBr₃ PeNC films attached to PMMA and TiO₂. Figure 4B–D shows the normalized PB kinetic traces of CsPbBr₃ PeNCs. There was no obvious difference in the recovery of PB signals for CsPbBr₃ PeNCs assembled with and without TiO₂ as the electron acceptors. These results suggest that the ET process occurs on a relatively longer time scale, beyond the detection window of our TA measurements (500 ps). Furthermore, global analysis results of the film TA dynamics supplemented to the conclusion. As indicated by the decay-associated spectra shown in Figure S7, although the noises were non-negligible, three exponential components with different lifetimes were yielded for all samples. Consistently, OA/OAm CsPbBr₃ PeNCs exhibit an overall fast decay as the poor passivation effect comparing to APTES and NCA. No obvious quenching of TA decays was observed in all CsPbBr₃ PeNC-TiO₂ systems indicating a relative long ET process.

4 Conclusion

In this work, we have investigated the ET process from CsPbBr₃ PeNCs to TiO₂ with single alkyl chain OA and OAm, cross-linked insulating APTES and aromatic ligands NCA as the linking bridge, respectively. It was found that the ET rates can be effectively tuned by anchored surface ligands, based on the ligand-bridge effect between PeNCs donor and oxide acceptor. By

modeling the LUMO energy level of the studied ligand-bridge with respect to the conduction band of the nanoparticle and the electron accepting level of TiO₂ as their potential barrier, it allows us to further understand experimentally determined ET rate k_{ET} trends. Meanwhile, TA measurements excluded the possibility of trapping carrier on the ligands as a consequence of the exciton-delocalizing effect. Our demonstration on bridge-barrier effect of the surface ligands provides possible options of ligands for different purposes of PeNC-based photonic and optoelectronic applications.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: This work was funded by the National Key R&D Program of China (2017YFA0207400), the National Natural Science Foundation of China (61604032 and 61905037), and the Fundamental Research Funds for the Central Universities of China (ZYGX2019J028), China Postdoctoral Science Foundation (2020M683281).

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

- [1] A. Kojima, K. Teshima, Y. Shirai, and T. Miyasaka, "Organometal halide perovskites as visible-light sensitizers for photovoltaic cells," *J. Am. Chem. Soc.*, vol. 131, pp. 6050–6051, 2009.

- [2] M. A. Green, E. D. Dunlop, D. H. Levi, J. Hohl-Ebinger, M. Yoshita, and A. W. Y. Ho-Baillie, "Solar cell efficiency tables (version 55)," *Prog. Photovoltaics*, vol. 28, pp. 3–15, 2020.
- [3] L. Protesescu, S. Yakunin, M. I. Bodnarchuk, et al., "Nanocrystals of cesium lead halide perovskites (CsPbX_3 , X = Cl, Br, and I): novel optoelectronic materials showing bright emission with wide color gamut," *Nano Lett.*, vol. 15, pp. 3692–3696, 2015.
- [4] Y. Wang, X. Li, J. Song, L. Xiao, H. Zeng, and H. Sun, "All-inorganic colloidal perovskite quantum dots: A new class of lasing materials with favorable characteristics," *Adv. Mater.*, vol. 27, pp. 7101–7108, 2015.
- [5] V. I. Korolev, A. P. Pushkarev, P. A. Obratsov, A. N. Tsyppin, A. A. Zakhidov, and S. Makarov, "Enhanced terahertz emission from imprinted halide perovskite nanostructures," *Nanophotonics*, vol. 9, pp. 187–194, 2020.
- [6] Q. A. Akkerman, M. Gandini, F. Di Stasio, et al., "Strongly emissive perovskite nanocrystal inks for high-voltage solar cells," *Nat. Energy*, vol. 2, p. 16194, 2017.
- [7] S. Yakunin, L. Protesescu, F. Krieg, et al., "Low-threshold amplified spontaneous emission and lasing from colloidal nanocrystals of caesium lead halide perovskites," *Nat. Commun.*, vol. 6, p. 8056, 2015.
- [8] J. Song, J. Li, X. Li, L. Xu, Y. Dong, and H. Zeng, "Quantum dot light-emitting diodes based on inorganic perovskite cesium lead halides (CsPbX_3)," *Adv. Mater.*, vol. 27, pp. 7162–7167, 2015.
- [9] Q. A. Akkerman, V. D'Innocenzo, S. Accornero, et al., "Tuning the optical properties of cesium lead halide perovskite nanocrystals by anion exchange reactions," *J. Am. Chem. Soc.*, vol. 137, pp. 10276–10281, 2015.
- [10] G. Raino, G. Nedelcu, L. Protesescu, et al., "Single cesium lead halide perovskite nanocrystals at low temperature: fast single photon emission, reduced blinking, and exciton fine structure," *ACS Nano*, vol. 10, pp. 2485–2490, 2016.
- [11] H. Huang, M. I. Bodnarchuk, S. V. Kershaw, M. V. Kovalenko, and A. L. Rogach, "Lead halide perovskite nanocrystals in the research spotlight: stability and defect tolerance," *ACS Energy Lett.*, vol. 2, pp. 2071–2083, 2017.
- [12] J. Kang and L. Wang, "High defect tolerance in lead halide perovskite CsPbBr_3 ," *J. Phys. Chem. Lett.*, vol. 8, pp. 489–493, 2017.
- [13] A. Swarnkar, R. Chulliyil, V. K. Ravi, M. Ifrullah, A. Chowdhury, and A. Nag, "Colloidal CsPbBr_3 perovskite nanocrystals: luminescence beyond traditional quantum dots," *Angew. Chem. Int. Ed.*, vol. 54, pp. 15424–15428, 2015.
- [14] A. S. Polushkin, E. Y. Tiguntseva, A. P. Pushkarev, and S. V. Makarov, "Single-particle perovskite lasers: from material properties to cavity design," *Nanophotonics*, vol. 9, pp. 599–610, 2020.
- [15] X. Li, Y. Wu, S. Zhang, et al., " CsPbX_3 quantum dots for lighting and displays: room-temperature synthesis, photoluminescence superiorities, underlying origins and white light-emitting diodes," *Adv. Funct. Mater.*, vol. 26, pp. 2435–2445, 2016.
- [16] H. Zhao, Z. Hu, L. Wei, et al., "Efficient and high-luminance perovskite light-emitting diodes based on CsPbBr_3 nanocrystals synthesized from a dual-purpose organic lead source," *Small*, vol. 16, p. 2003939, 2020.
- [17] M. V. Kovalenko, L. Protesescu, and M. I. Bodnarchuk, "Properties and potential optoelectronic applications of lead halide perovskite nanocrystals," *Science*, vol. 358, pp. 745–750, 2017.
- [18] L. Meng, X. Wu, S. Ma, et al., "Improving the efficiency of silicon solar cells using in situ fabricated perovskite quantum dots as luminescence downshifting materials," *Nanophotonics*, vol. 9, pp. 93–100, 2020.
- [19] A. Pan, B. He, X. Fan, et al., "Insight into the ligand-mediated synthesis of colloidal CsPbBr_3 perovskite nanocrystals: the role of organic acid, base, and cesium precursors," *ACS Nano*, vol. 10, pp. 7943–7954, 2016.
- [20] S. Sun, D. Yuan, Y. Xu, A. Wang, and Z. Deng, "Ligand-mediated synthesis of shape-controlled cesium lead halide perovskite nanocrystals via reprecipitation process at room temperature," *ACS Nano*, vol. 10, pp. 3648–3657, 2016.
- [21] F. Krieg, S. T. Ochsenbein, S. Yakunin, et al., "Colloidal CsPbX_3 (X = Cl, Br, I) nanocrystals 2.0: zwitterionic capping ligands for improved durability and stability," *ACS Energy Lett.*, vol. 3, pp. 641–646, 2018.
- [22] Z. Liu, Y. Bekenstein, X. Ye, et al., "Ligand mediated transformation of cesium lead bromide perovskite nanocrystals to lead depleted Cs_4PbBr_6 nanocrystals," *J. Am. Chem. Soc.*, vol. 139, pp. 5309–5312, 2017.
- [23] J. De Roo, M. Ibanez, P. Geiregat, et al., "Highly dynamic ligand binding and light absorption coefficient of cesium lead bromide perovskite nanocrystals," *ACS Nano*, vol. 10, pp. 2071–2081, 2016.
- [24] P. Zeng, L. Wei, H. Zhao, R. Zhang, H. Chen, and M. Liu, "Crystalline phase-controlled synthesis of regular and stable endotaxial cesium lead halide nanocrystals," *J. Mater. Chem. C*, vol. 8, pp. 9358–9365, 2020.
- [25] E. T. Vickers, T. A. Graham, A. H. Chowdhury, et al., "Improving charge carrier delocalization in perovskite quantum dots by surface passivation with conductive aromatic ligands," *ACS Energy Lett.*, vol. 3, pp. 2931–2939, 2018.
- [26] E. T. Vickers, E. E. Enlow, W. G. Delmas, et al., "Enhancing charge carrier delocalization in perovskite quantum dot solids with energetically aligned conjugated capping ligands," *ACS Energy Lett.*, vol. 5, pp. 817–825, 2020.
- [27] H. Wang, E. R. McNellis, S. Kinge, M. Bonn, and E. Canovas, "Tuning electron transfer rates through molecular bridges in quantum dot sensitized oxides," *Nano Lett.*, vol. 13, pp. 5311–5315, 2013.
- [28] J. Kim, B. Koo, W. H. Kim, et al., "Alkali acetate-assisted enhanced electronic coupling in CsPbI_3 perovskite quantum dot solids for improved photovoltaics," *Nanomater. Energy*, vol. 66, p. 104130, 2019.
- [29] V. A. Amin, K. O. Aruda, B. Lau, A. M. Rasmussen, K. Edme, and E. A. Weiss, "Dependence of the band gap of CdSe quantum dots on the surface coverage and binding mode of an exciton-delocalizing ligand, methylthiophenolate," *J. Phys. Chem. C*, vol. 119, pp. 19423–19429, 2015.
- [30] H. Zhao, L. Wei, P. Zeng, and M. Liu, "Formation of highly uniform thinly-wrapped CsPbX_3 @silicone nanocrystals via self-hydrolysis: suppressed anion exchange and superior stability in polar solvents," *J. Mater. Chem. C*, vol. 7, pp. 9813–9819, 2019.
- [31] P. Hohenberg and W. Kohn, "Inhomogeneous electron gas," *Phys. Rev.*, vol. 136, pp. B864–B871, 1964.
- [32] Y. Lee and Parr, "Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density," *Phys. B Condens. Matter*, vol. 37, pp. 785–789, 1988.
- [33] Z. Li, L. Kong, S. Huang, and L. Li, "Highly luminescent and ultrastable CsPbBr_3 perovskite quantum dots incorporated into a silica/alumina monolith," *Angew. Chem. Int. Ed.*, vol. 56, pp. 8134–8138, 2017.

- [34] S. Chandra, H. Saleem, N. Sundaraganesan, and S. Sebastian, "The spectroscopic FT-IR gas phase, FT-IR, FT-Raman, polarizabilities analysis of naphthoic acid by density functional methods," *Spectrochim. Acta*, vol. 74, pp. 704–713, 2009.
- [35] A. Kongkanand, K. Tvrđy, K. Takechi, M. Kuno, and P. V. Kamat, "Quantum dot solar cells. Tuning photoresponse through size and shape control of CdSe-TiO₂ architecture," *J. Am. Chem. Soc.*, vol. 130, pp. 4007–4015, 2008.
- [36] E. Fiserova and M. Kubala, "Mean fluorescence lifetime and its error," *J. Lumin.*, vol. 132, pp. 2059–2064, 2012.
- [37] K. Zheng, K. Zidek, M. Abdellah, M. E. Messing, M. J. Al-Marri, and T. Pullerits, "Trap states and their dynamics in organometal halide perovskite nanoparticles and bulk crystals," *J. Phys. Chem. C*, vol. 120, pp. 3077–3084, 2016.
- [38] V. K. Ravi, G. B. Markad, and A. Nag, "Band edge energies and excitonic transition probabilities of colloidal CsPbX₃ (X = Cl, Br, I) perovskite nanocrystals," *ACS Energy Lett.*, vol. 1, pp. 665–671, 2016.
- [39] M. M. Byranvand, T. Kim, S. Song, G. Kang, S. U. Ryu, and T. Park, "P-type CuI islands on TiO₂ electron transport layer for a highly efficient planar-perovskite solar cell with negligible hysteresis," *Adv. Energy Mater.*, vol. 8, p. 1702235, 2018.
- [40] J. Butkus, P. Vashishtha, K. Chen, et al., "The evolution of quantum confinement in CsPbBr₃ perovskite nanocrystals," *Chem. Mater.*, vol. 29, pp. 3644–3652, 2017.
- [41] K. Wu, G. Liang, Q. Shane, Y. Ren, D. Kong, and T. Lian, "Ultrafast interfacial electron and hole transfer from CsPbBr₃ perovskite quantum dots," *J. Am. Chem. Soc.*, vol. 137, pp. 12792–12795, 2015.
- [42] N. Mondal and A. Samanta, "Complete ultrafast charge carrier dynamics in photo-excited all-inorganic perovskite nanocrystals (CsPbX₃)," *Nanoscale*, vol. 9, pp. 1878–1885, 2017.

Supplementary Material: The online version of this article offers supplementary material (<https://doi.org/10.1515/nanoph-2020-0631>).