Surface energetics mediated charge transfer and exciton transfer in cation-adsorbed rubrene/PbS nanocrystal hybrids

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Abstract
Organic molecule and inorganic nanocrystal (NC) hybrids have become a promising platform for photon energy conversion. Although surface energetics modification has proven effective in promoting triplet energy transfer, singlet energy transfer and charge transfer have been barely investigated. Here, we systematically clarify the photophysical dynamics of charge, singlet exciton, and triplet exciton within the energy conversion process based on hybrids of rubrene and Cd\(^{2+}\)-adsorbed PbS NCs. It is found that a considerable number of charges in rubrene molecules can be transferred to cation-induced surface states in the ~2 ps time scale with high efficiency to trigger a delayed biexciton effect, which provides a novel approach to uncover the intermediate role of NC surface states. For the triplet exciton, strong interaction with surface states is investigated with a recycling energy transfer of around 14% efficiency, which is found to be insensitive to changes in NC surface energetics. As a result, the maximum photoluminescence lifetime of PbS NCs was enhanced by about 38%. This work reveals the neglected photo-physical dynamics in the transfer process between organic molecules/inorganic NCs and validates the capability of the surface state in sensitization of organic charges and excitons.

1. Introduction

Hybrids composed of organic acene molecules and inorganic nanocrystals (NCs) have emerged as the promising platform for photon energy transfer in achieving efficient light up- or down-conversion. Under high-energy excitations, the photons are absorbed by acene molecules to initiate singlet fission (SF), a spin-allowed multiple exciton generation processes, during which a photoexcited spin-singlet exciton converts into two spin-triplet excitons with approximately half of the original energy. The energy of these triplets can be transferred to inorganic NCs and eventually be radiated as two lower-energy photons to support optoelectronic devices such as photovoltaic cells and light-emitting diodes [1−5]. For the reverse process, the excitons in semiconductor NCs excited by near-infrared (NIR) photons can be transferred to triplet state in acene molecules, and sequentially, re-form a high-energy singlet exciton through triplet−triplet annihilation to realize the emission of visible photons [6−9]. The down-conversion provides a multiple-photon-amplification strategy for effective triplet energy collection and the up-conversion is attractive in NIR solar irradiance utilization [10, 11], which is low-cost and weak excitation adaptable.
compared to lanthanide-based materials [12]. This photon conversion platform exhibits strong applicability, since its probing and emitting wavelength can be easily manipulated by changing the structure of the organic molecules or the size of the NCs, and the energy transfer direction is controllable by adjusting the energy level of the concerned states.

Both up- and down-conversion are closely correlated to energy transfer between organic molecules and inorganic NCs. As the transfer dynamics are affected by the interconnection manner and interfacial regions between the donor and acceptor, it is crucial to modify the NCs surface energetics to obtain efficient energy collection. Growing interest has been focused on surface energetics manipulation to improve energy transfer efficiency, especially optimizing the Dexter-type triplet energy transfer (TET) between organic molecules and inorganic NCs [13, 14]. The first report of the application of NCs as SF-induced triplet acceptors proposed a hole transfer mediated TET dynamics in PbS NC-pentacene bilayers films [15]. Klimov et al. reported an intermediate surface state formation rather than direct TET from PbS NCs to TIPS-pentacene ligand [16]. Rao et al. reported that using SF molecules as ligands for NCs allows injection of the triplets to enhance the NC NIR emission quantum efficiency [17, 18]. Te molecular ligand shell on a NC surface has been reported to be an effective method to provide a 'bridge' state located at the NCs' surface for efficient TET in SF-generated triplet excitons harvest [18] and NIR photon up-conversion [6, 8]. The heterostructure at the NC surface is another effective method for energy transfer enhancement, due to defect passivation and energetics modulation. Ehler et al. combined core–shell PbS–CdS NCs with a tetracene derivatives ligand to absorb a NIR photon and emit visible light at 560 nm, reaching an up-conversion quantum yield of 8.4 ± 1.0% [8]. Ma et al. used femtosecond pump-probe spectroscopy and directly observed SF in a rubrene single crystal [19]. Mahboub et al. reported a mid-gap defect state introduced by surface adsorbed Zn and Cd in PbS NCs promotes the TET-based up-conversion efficiency, reaching an up-conversion quantum yield of 21% [20, 21].

As the energy cascade exists in all photon conversion systems, the resonance energy transfer from singlet exciton and charge transfer between donor and acceptor are unavoidable and crucial for both energy transfer direction and efficiency. Although previous studies on TET dynamics have proposed several models to illustrate surface states that mediate TET, the research on the accompanying charge and singlet transfer is insufficient and fragmentary. Moreover, the interrelationship between surface manipulation strategies and charge behavior is still ambiguous. The lack of a clear understanding of excited-state dynamics besides triplet exciton impedes the further improvement of the efficiency of energy collection in photon conversion platforms. Encouraged by these research gaps, here we investigate the dynamics of charge transfer, singlet energy transfer, and TET, and the effects of surface energetics manipulation based on Cd$^{2+}$ adsorbed rubrene/PbS NCs hybrids. Through femtosecond and nanosecond transient absorption (fs- and ns-TA) spectroscopies, it was found that the introduced surface states have intensive interaction with the charges that support fast transfer dynamics with efficiency beyond 50%. The occupation of cation-induced surface states from charge transfer generates a delayed biexciton effect (DBE) in NC TA spectra, which provides a novel approach to interpreting the transfer kinetics and comprehending the intermediate role of NC surface states. For triplet exciton, triplet photo-induced absorption (PIA) and DBE reveal the recycling energy transfer between triplet exciton and surface state. However, singlet energy transfer efficiency is investigated with a stable value of about 13% – 15% in the systems with and without changes in NCs surface energetics, indicating an unaffected transfer mechanism. As a result, the fluorescence lifetime of NCs is increased by a maximum of about 38%.

2. Results and discussion

Rubrene is a widely studied organic semiconductor in applications of photovoltaic and light emission due to its efficient SF dynamics [5, 21, 22]. The absorption response and photoluminescence (PL) spectra of rubrene in toluene solution are shown in figure 1(a). The absorbance exhibits prominent vibronic features with 0–0 peak at 532 nm, 0–1 peak at 469 nm, and relative 0–2 peak at 467 nm, and PL spectrum exhibits two vibronic signals at 565 nm and 595 nm in both neat rubrene solution and rubrene/NC hybrids. The singlet state ($S_1$) energy of rubrene is about 2.23 eV higher than the ground state in comparison with 1.14 eV of the triplet state ($T_1$), indicating an endothermic SF process following the energy condition of $E(S_1) < 2E(T_1)$ [21, 23].

The synthesis of PbS NCs and cation adsorption procedures are summarized in supporting information. Previous research has proven that NCs' surfaced bound cations, especially Cd$^{2+}$, contribute to adequate triplet sensitization through trap passivation and defect states generation [19, 21]. The surface states stem from non-stoichiometric composition, and surface dangling bonds of NCs can not only form an energy cascade, but possess enhanced spin-triplet characteristics that reduce the spin-forbidden effect. Here, we applied Cd$^{2+}$ with various adsorption ratios to modify the surface energetics of PbS NCs as its effectiveness
has been proven in the up-conversion process [21]. The molar ratio of Pb and Cd atoms in cation-adsorbed NCs was measured by inductively coupled plasma-mass spectrometry (table S1). Three kinds of NCs obtained from cation adsorption possess Pb/Cd molar ratios of about ~50, ~25, and ~10 and were marked as PbS-1, PbS-2, and PbS-3, respectively. The unchanged oleic acid ligand coverage was confirmed through the uniform Fourier transform infrared spectra after the cation adsorption (figure S1). To realize an efficient TET, the NCs need to be tuned to a suitable size since the bandgap of NCs is size-dependent, and TET is affected by the energetics of both rubrene T and NC band-edge state (X). Transmission electron microscopy images show the PbS NCs before and after cation adsorption are synthesized with the diameter ranging from 3.7 to 3.9 nm (figure S2). Absorption spectra in figures 1(a) and S3 exhibit absorption peaks at ~1240 nm, where the bandgap of original PbS NCs and cation-adsorbed NCs is 1.02 eV and 1.04 eV, respectively. Remarkably, we observed a blue shift in the absorption of PbS NC after the adsorption of Cd$^{2+}$ ion. As the adsorption ratio increases, a slight red shift of absorption can be noticed in various PbS NCs. This arises from either the contraction of PbS during cation exchange or the formation of an alloy structure [21, 24, 25].

To confirm the energy levels of X state and cation-induced surface state, we employed the previously reported analysis based on asymmetry PL spectra and temperature-dependent emission spectra [26, 27]. Figures 1(b) and S4 plot the PL spectra of applied NCs. It can be found that all PL spectra exhibit asymmetric features and match well with two-species emission. We fit the PL spectra into two Gaussians with the following equation:

$$PL(E) = C_A e^{-(E-E_A)^2/2\sigma_A^2} + C_B e^{-(E-E_B)^2/2\sigma_B^2},$$

in which $E_{A,B} = 1240/\lambda_{A,B}$ are the average energy and $\sigma_{A,B}$ are the standard deviation. It shows that the PL spectra are composed of a short-wavelength centered peak A and a relatively long-wavelength centered wake emission peak B. The peak center and energy offset between peak A and B are summarized in table S2, showing a 33.9 meV offset in PbS NC, while beyond 60 meV in cation-adsorbed NCs. We further investigate the temperature dependence of NCs emission spectra (figure 2) to confirm the origination of the two fitted species. As the temperature decreases from 320 K to 78 K, all NCs emissions exhibit a red-shift that varies from 24.8 nm to 53.6 nm. The result is consistent with the reported model of multiple emissive states [4]. For PbS NCs with a size larger than 3.0 nm, the defect states sit lower than the band edge. When the temperature decreases, the conversion between defect states and X is impeded, resulting in an enhanced band-edge feature in PL spectra and a red-shift of the emission peak. Therefore, we can, moreover, ascribe peak B to the emission of the defect and surface states, while peak A we ascribe to the X emission. In figure 2, we employ the average energies acquired at 300 K to fit the PL spectrum at various temperatures (black curves). These
results confirm that the cation-induced surface states locate lower than the NC band-edge, with a nearly double offset of \( \sim 65 \) meV in comparison to that of the original defect states in PbS NCs, about \( \sim 34 \) meV. Moreover, we also measured the temperature dependence plots of the A and B peaks, confirming that the A peak is the X1 emission and the B peak is the defect surface state (figure S5). An ultraviolet photoelectron spectrometer was applied to determine the valence band of NCs (figure S6). The results indicate a valence band of \(-4.68\) eV for PbS NCs and \(-4.78\) eV for PbS-2 NCs. Combined with the bandgap, the energy level diagram of applied NCs can be depicted as shown in figure 1(c).

Femtosecond and nanosecond TA spectroscopy was applied to investigate the dynamics of excited states in the photon energy conversion hybrids. Figure S7 displays the 2D TA spectra of neat rubrene solution excited at the wavelength of 470 nm. The negative peak centered at 540 nm represents the ground state bleaching (GSB), the positive response at 510 nm is the PIA of triplet exciton. The positive signal at \( \sim 1000 \) nm might arise from the PIA of S1 state due to the similar dynamics compared to GSB [21, 23]. TA 2D maps of neat NCs (figure S8) and rubrene/NC hybrid solutions (figure S9) in the NIR region are measured at the excitation wavelength of 470 nm and probed in the region of 1100–1550 nm. Figures 3(a)–(c) display the spectra recorded at various delay times of PbS, PbS-2 NCs and rubrene/PbS-2 hybrids. Immediately after the excitation, a distinctive negative signal rises at 1250 nm, which corresponds to the X1 bleaching. Along with the rising of X1 bleaching signal, two PIA signals appear at both the low-energy and high-energy sides. For the short-wavelength side, it can be attributed to the inter-band transient of the photoexcited NC [28, 29]. For the long-wavelength side, the origin of the low-energy PIA signal detected right after excitation can be explained by the energy shift on account of the biexciton effect, as schematically illustrated in figure 4 [30–33].

The biexciton effect arises from the Coulomb interaction between the hot exciton in the higher excited states generated by the pump and the band edge exciton generated by the probe. Under the existence of a hot exciton, the optical transition gap \( E_g \) changes with an extra biexciton binding energy \( \Delta_{XX} \), compared to the situation without hot exciton occupation. This change arises from a shift in the TA spectrum as the depressed lowest–optical transition can only respond to the probe at a red-shifted wavelength, resulting in a positive PIA signal (‘0 ps < t < 2 ps’). As shown in figure 4(b), the PIA and X1 bleaching can be observed in the overlapping spectrum when a hot exciton exists. After the relaxation of the hot exciton, only bleaching appears around the band edge, since the shift of \( \Delta_{XX} \) is not pronounced and PIA is restricted by the state-filling effect (‘2 ps < t < 10 ps’), resulting in the corresponding TA spectra in figure 4(c) [33]. The TA spectra in figures 3(a) and (b) show prominent biexciton effect peaks centered at 1316 nm in PbS solution.
Figure 3. Femtosecond TA spectra in the NIR region of (a) neat PbS NC solution, (b) neat PbS-2 NC solution, (c) rubrene/PbS NC hybrid. (d) TA dynamics of neat rubrene GSB and biexciton effect in neat PbS and PbS-2 NCs. Comparisons between TA dynamics of rubrene.

and 1366 nm in PbS-2 solution, respectively. The biexciton effect in all neat NC solutions lasts for about 2 ps, indicating a fast relaxation dynamic for the hot exciton generated by the initial excitation (figure S8) [30, 31, 34]. However, when we investigated the TA spectra in hybrid systems, a positive PIA emerges again at the low-energy side with a blue-shifted peak compared to the initial biexciton effect. The PIA is detected with a peak at 1282 nm in the rubrene/PbS-2 hybrid (figure 3(c)) and 1293 nm in the rubrene/PbS hybrid (figure S9). The dynamics of rubrene GSB and the delayed signal at the biexciton effect wavelength are compared to confirm the origination of the delayed NC PIA. In figure 3(d), GSB of neat rubrene solution shows a fast but weak amplitude drop followed by a long-lived decay. The initial drop may be ascribed to the fast charge recombination in the rubrene molecule. However, when blended with NCs, as shown in figures 3(e), (f) and S10, the initial fast decay of rubrene GSB is found with a larger fall in amplitude. Rubrene GSB decay kinetics are fitted with the double-exponential function, and the lifetimes are summarized in table S3. For the fast component, neat rubrene has a charge recombination time of about 6 ps, while the lifetime of the initial decay decreases from 8.50 ps to 4.09 ps, as the cation adsorption ratio increased in the hybrids containing NCs. The long-lived component has a lifetime of 18.90 ns in neat rubrene solution and also decreases as rubrene is blended with NCs with a high Cd\textsuperscript{2+} adsorption ratio, from 18.63 ns to 12.15 ns. We further employed time-resolved PL spectroscopy to investigate the emission dynamics of the rubrene S\textsubscript{1} state (figure S11). Fitted by the single-exponential function, the PL lifetime of rubrene in each system is almost identical to the lifetime of the slow decay component of rubrene GSB (table S3). Since the GSB signal in the TA spectrum is contributed to by all charges, while PL only records the recombination of bonded charge pairs, i.e., excitons, the unique decay process in the initial dynamics of rubrene GSB represents a fast charge decay channel. Compared with the NC PIA kinetics, the fast decay dynamics are temporally overlapped with the rising of the reproduced PIA (figures 3(e) and (f)). Therefore, we ascribe the fast decay to the charge transfer from rubrene molecules to the NCs intrinsic defect or induced surface states, and the long-lived blue-shifted peaks to a charge transfer triggered DBE. For PbS NCs, the defect state is ∼34 meV lower than X\textsubscript{1}. Once the defect states are occupied by transferred charges, the following excited NC excitons are affected by an extra Coulomb interaction, and TA spectra of NCs exhibit a DBE signal, leading to the circumstance of '0 ps < t < 2 ps' in figure 4(a). For cation-adsorbed NCs, the Cd\textsuperscript{2+} ion-induced surface state is located ∼65 meV lower than the X\textsubscript{1} state. With the increase of ion ratio, the charge transfer rate is enhanced as the GSB decay lifetime of rubrene decreases from 8.12 ns in the PbS-1 hybrid to 4.09 ns in the PbS-3 hybrid. The charge transfer ratio can be estimated by the amplitude of rubrene GSB, which shows that 38.6% of charges are transferred in the rubrene/PbS hybrid, and 50.3%, 59.2%, and 60.0% for the PbS-1, PbS-2, and the PbS-3 hybrid, respectively. In addition, the rising dynamics of DBE have fitted with a lifetime of about 21.3 ps in rubrene/PbS, which decreases to 9.6 ps in rubrene/PbS-3, as the Cd\textsuperscript{2+} adsorption ratio is increased. The amplitude of DBE peaks achieves an obvious increment in the cation-adsorbed system, which also implies an
enhanced transfer efficiency. In comparison to the intrinsic surface defect state in PbS NCs, the cation-induced high-lying surface states are favorable for sensitizing charge in the rubrene molecule.

Since the energy of $S_1$ in the rubrene molecule is higher than $X_1$ in the PbS NC, the singlet energy transfer from rubrene to NCs must be taken into consideration. Focusing on the fitted PL lifetime in table S3, neat rubrene solution has a PL lifetime of about 18.10 ns while the lifetime in hybrids decreases to around 15.50 ns [35]. It can be noticed that the lifetime in the original NCs and cation adsorbed NCs show no noticeable difference, with a relatively stable singlet transfer efficiency estimated between 13% and 15%. We therefore conclude that singlet energy transfer in these systems occurs from the energy cascade between rubrene and PbS NCs and is rather affected by the introduced cation and energetics changes.

Based on the TA spectra, biexciton energy $\Delta_{XX}$ can be calculated to clarify the origination of DBE and the effects of cation adsorption. We adopt the model of the biexciton effect reported by Klimov et al.
transition energy, and $\Delta$ between (\text{in neat NC solutions and } (2) is the normalized detuning from the $X$ energy of both initial and DBEs represents the $X$ transition, $E_{1s}$ is the energy of the $X$ transition, and $\Gamma_{1s}$ stands for the $X$ absorption line width. Here $\Delta_{XX}$ in neat NC solutions and $\Delta_{XX}$ of both initial and DBEs in hybrid solutions are calculated using this model (parameters and results are summarized in table S4). All results are acquired with a positive value indicating an exciton–exciton attraction [4]. For the initial biexciton effect in neat NC solutions, $\Delta_{XX}$ is calculated with 14.9 meV, while the values in adsorbed NCs are approximately 15.5 meV. This difference can be attributed to the energetics variety induced by CdS formation at the NC surface. In hybrid solutions, the initial biexciton effects have $\Delta_{XX}$ between 14.1–14.8 meV. This slight difference may arise from the Coulomb effect of the exciton in rubrene molecules, and it is reasonable to ascribe the initial biexciton effects in hybrid systems to the identical occupation of hot excitons that occurred in neat NCs [36]. For the DBE peaks, the $\Delta_{XX}$ values of hybrids with cation adsorbed NCs reduce to around 9.2 meV. The apparent decrease compared with the initial effect combined with the shift of biexciton effect peaks in TA spectra indicates that the DBE rises from different high-energy state occupations. Considering the changes in NCs energetics after cation adsorption, we believe the cation-induced surface states with lifted energy levels more easily accept transferred charges in comparison with intrinsic defects in NCs, which leads to the variation in biexciton binding energy [37, 38].

Considering the diffusion model of SF in solution, the triplet exciton related dynamics should occur at a relatively later temporal region [39, 40]. Therefore, by applying ns-TA spectroscopy, we compare the decay dynamics of DBE and triplet PIA at 510 nm in corresponding spectra, as shown in figures 5(a) and (b), respectively. In hybrid solutions, a $\sim$300 ns DBE signal is observed in the rubrene/PbS hybrid, while the rubrene/PbS-2 hybrid shows a long-lived feature from about 30–5000 ns. Identical slow dynamics can also be detected in the hybrid containing PbS-1 and PbS-3 NCs (figure S12). Table 1 summarizes the decay lifetimes of the DBE fitted by the double-exponential function, including a $\sim$10 ns fast decay process and a slow process. As the Cd$^{2+}$ amount increases, the lifetime of the slow dynamics grows from 910 ns to 1070.6 ns in contrast to 68.2 ns in the rubrene/PbS solution. For the triplet PIA dynamics in figure 5(b), in the solution of neat rubrene, the triplet exciton is observed with a lifetime of 961.6 ns fitted by the singlet-exponential function [6, 12]. In the rubrene/PbS solution, the PIA dynamics show a distinct quenching with a short lifetime of 100.3 ns, accompanied by a longer decay process of 916.6 ns. However, in hybrids containing cation-adsorbed NCs, we observed rising kinetics at about 100 ps after a fast signal dropping and followed by a slow decay (figure S12). The rise and decay times are fitted by the exponential function (table 1). As the Cd$^{2+}$ ratio is increased, the rising kinetics become faster with time reduced from $\sim$40 ps to $\sim$20 ps. Previous research indicated that SF in solution is a diffusion-driven process with a relatively slow mechanism, in contrast with that in solid systems [13]. Here, we find that both the surface state-related DBE and triplet PIA dynamics in cation-adsorbed hybrids show an extra slow decay process after 100 ps of evolution, which temporally matches the triplet generation process of SF in solution. Since the PbS NCs process strong spin–orbit coupling and surface states stemmed from the non-stoichiometric composition and dangling...
bonds on the NCs surface may acquire significant triplet character for sensitizing a triplet exciton \([7]\), the extra dynamics can be assigned to the recycling of the triplet exciton between the rubrene molecule and the PbS NCs \([5]\). After generation in rubrene molecules, \(T_1\) excitons tend to transfer onto the cation-induced surface states in comparison with defect states in the original PbS NCs. Note that the introduced surface states are located in the resonance domain of rubrene \(T_1\) \((1.14 \text{ eV})\) \([10]\), the reverse TET channel from NCs to \(T_1\) is accessible once an adequate number of surface states are occupied. Figure 5(c) shows the \(X_1\) bleaching dynamics in PbS and PbS-2 NC solutions and the hybrid solutions, respectively. Compared with PbS NCs, NCs with adsorbate have a slightly longer \(X_1\) exciton lifetime of 824.5 ns, which can be ascribed to the passivation of the intrinsic surface defects \([2, 9]\). When blended with rubrene molecules, both PbS and PbS-2 possess a longer bleaching lifetime and hybrids containing PbS-2 NCs exhibit a 38% lifetime elongation of 1183.2 ns, in comparison to 824.5 ns for the rubrene/PbS solution \([8]\). This manifests that the cation-induced surface state is effective as the intermediate state to collect triplet exciton energy and enhance NCs emission in NIR region. The magnetic field dependence of fluorescence in the rubrene/PbS-2 hybrid (figure S13) was examined to further confirm the existence of TET from rubrene \(T_1\) to NCs \(S_1\), as the number of triplet excitons can be adjusted by external magnetic field through regulation of the permissible triplet states in SF \([1, 11]\).

3. Conclusion

To summarize, the capability of NC surface energetics in influencing charge transfer and exciton energy transfer has been validated, based on Cd\(^{2+}\) adsorbed rubrene/PbS NCs hybrids. Charges in rubrene molecules tend to transfer rapidly to the cation-induced surface states and trigger a DBE due to the lower energy level of surface states in comparison with NCs band edge. Variation of biexciton binding energy reveals a different origination of the DBE compared to the original biexciton effect. The singlet energy transfer efficiency is estimated with a relatively stable value between 13% and 15%, indicating the transfer dynamics are insensitive to the changes in NCs’ surface energetics. For a triplet exciton, intensive spin–orbit coupling combining with weakening singlet feature of the surface state lead to a slow-decaying energy cycling between rubrene and NCs covering a temporal scale from \(~100\text{ ns}\) to a few microseconds. As a result, the lifetime of NC band-edge state is improved about 38%, from 824.5 ns to 1138.2 ns. This work highlights the applicability of NCs surface cation adsorption in sensitizing charge and the exciton of organic molecules, and provides new insight into the analysis and comprehension of the intermediate role of NCs’ surface state in energy transfer.

4. Experimental method

4.1. Materials and synthesis

Lead (II) acetate trihydrate (Pb(OAc)\(_2\)·2H\(_2\)O, 99.999%), oleic acid (OA, tech. grade, 90%), 1-octadecene (ODE, 90%), oleylamine (OLA, tech. grade, 70%), bis(trimethylsilyl) sulfide ((TMS)\(_2\)S), cadmium acetate hydrate (Cd(OAc)\(_2\)·2H\(_2\)O, 99.99%) were all purchased from Sigma-Aldrich.

PbS NCs were synthesized as follows. Briefly, Pb(OAc)\(_2\)·2H\(_2\)O (379.33 mg, 1 mmol), OA (1.2 ml), and ODE (10 ml) were combined and heated to 110 °C in a 50 ml three-neck flask under a 10\(^{-2}\) mbar vacuum for an hour to form Pb-oleate. Subsequently, the reaction flask was heated to 120 °C and the atmosphere was switched to nitrogen. Meanwhile, the sulfur precursor was prepared by mixing (TMS)\(_2\)S (210 \(\mu\)l) in anhydrous ODE (10 ml) in a nitrogen glovebox. The sulfur precursor was swiftly injected into the reaction flask and the heater was removed sequentially. Twenty seconds after the injection, the reaction was quenched by placing the flask into an ice-water bath and injection of cold hexane (10 ml). The crude product was quickly transferred to a nitrogen glove box and PbS NCs were isolated from the crude product by adding a 1:1 volume of hexane/acetone mixture for three washes followed by centrifugation at 7000 rpm for 5 min. The purified NCs were dispersed in toluene and stored in the dark in the nitrogen glovebox for future use.

The cation adsorption was carried out as follows. The cadmium precursor was prepared by combing Cd(OAc)\(_2\)·2H\(_2\)O (461 mg, 2 mmol) with ODE (5.37 ml) and OLA (1.24 ml) in a 10 ml three-neck flask, heated to 120 °C and degassed under a 10\(^{-2}\) mbar vacuum for 30 min to form a clear solution. The precursor was then transferred in to three 5 ml vials with volumes of 40 \(\mu\)l, 65 \(\mu\)l, and 160 \(\mu\)l, respectively, and followed by injection of 3 ml of 17 mg ml\(^{-1}\) PbS solution each and stirring at 90 °C. The temperature was set to 80 °C after the injection. Seven minutes later, 500 \(\mu\)l OA and 500 \(\mu\)l cold hexane were injected to quench the reaction. The mixtures were quickly transferred into the nitrogen glovebox for cleaning, once with acetone and twice with methanol followed by centrifuging at 7000 rpm for 5 min. The precipitation was
redissolved by the addition of 0.5 ml hexane each time after discarding the supernatant. The final NCs were dispersed in toluene and stored in the dark in glovebox for further use.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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Conflicts of interest

The authors declare no conflict of interest.

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