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Supporting Information

Insight into the Effect of Ligand-exchange on Colloidal $CsPbBr_3$ Perovskite Quantum Dot/mesoporous-TiO_2 Composite-based Photodetectors: Much Faster Electron Injection

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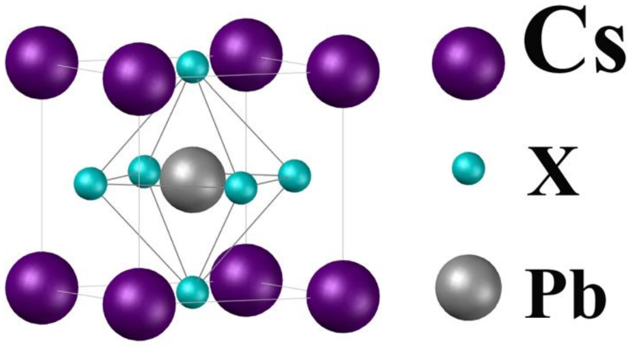


Fig. S1 Cubic perovskite structure of $CsPbX_3$ QDs: Large purple spheres in the cubic corners: Cs; Small cyan spheres in the centers of the cubic faces: X; Medium gray sphere in the center of the cubic: Pb.

Sample	τ_1 (ns)	Ratio1	τ_2 (ns)	Ratio2	τ_3 (ns)	Ratio3	$\tau_{ave}^{\#}$
$CsPbCl_3$ QDs	1.0	29.5%	6.0	39.2%	32.2	31.3%	12.73ns
$CsPbBr_3$ QDs	12.3	21.3%	42.4	56.4%	189.0	22.3%	68.68ns
$CsPbI_3$ QDs	92.3	40.4%	261.1	59.6%	-	-	192.90ns

$^{\#}\tau_{ave}$ = Ratio1*τ_1+ Ratio2*τ_2+ Ratio3*τ_3

Table S1. Values for TRPL characteristics (**Fig. 2**e) of $CsPbX_3$ (X=Cl, Br, or I) QDs in n-hexane solution.

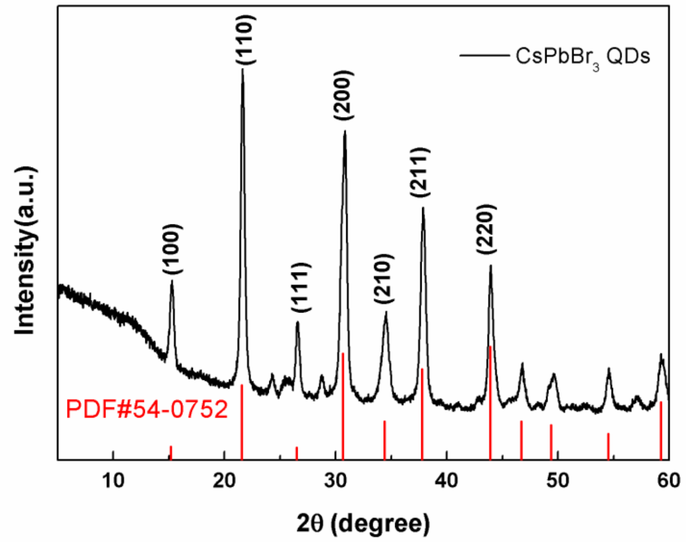
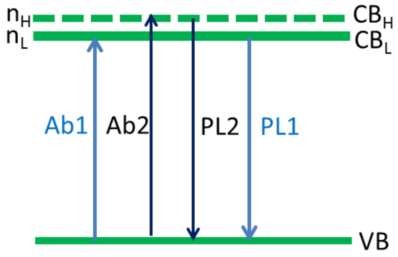


Fig. S2 Powder XRD pattern of $CsPbBr_3$ QDs (black) and the corresponding reference (red, PDF#54-0752).

Explanation about Stokes shift of $CsPbBr_3$ QDs decrease in Fig. 4a



As shown above, we divide the electrons on conduction band (CB) into two parts simply. One part is lower energy state electrons (n_L) on CB_L, the other is higher energy state electrons (n_H) on CB_H. Then, the absorption and PL also can be divided into two parts (Ab1, Ab2; PL1, PL2). When the $CsPbBr_3$ QDs is modified by MPA, n_L on CB_L is easier to transfer to MPA. Hence, empty states on CB_L are increased, while n_L is decreased. It means the MPA treatment will promote Ab1 process and suppress PL1 process. Compared to the QDs without MPA, lower energy absorption (Ab1) will occupy more percentage in whole absorption process, which can result in the absorption red-shifted; higher energy PL (PL2) will occupy more percentage in whole PL process, which can result in the PL blue-shifted. In the end, the Stokes shift of $CsPbBr_3$ QDs is decreased.

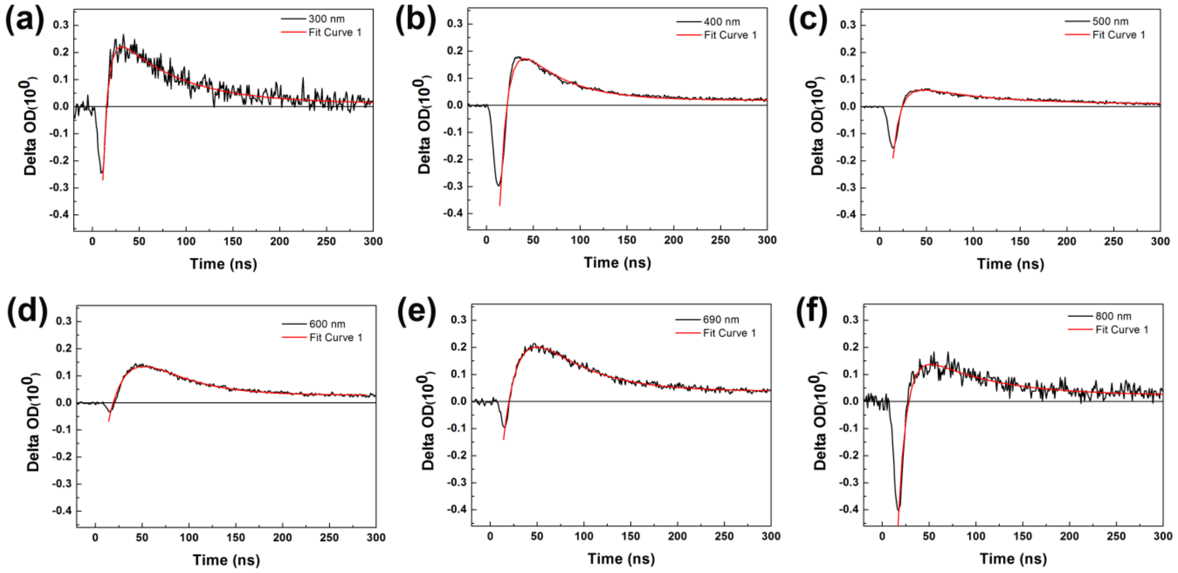


Fig. S3 The corresponding transient decays of transient absorption at a) 300, b) 400, c) 500, d) 600, e) 690 and f) 800 nm for **Fig. 4b**. Concentration: 10^{-4}~10^{-5} M.

λ	τ_1 (ns)/A_1	Ratio1	τ_2 (ns)/A_2*	Ratio2
300 nm	67.81 / 0.36	51.8%	5.83 / 3.90	48.2%
400 nm	47.53 / 0.44	40.1%	8.67 / 3.60	59.9%
500 nm	82.14 / 0.10	39.4%	8.43 / 1.50	60.6%
600 nm	42.69 / 0.73	55.0%	21.86 / 1.17	45.0%
690 nm	53.88 / 0.58	56.5%	16.17 / 1.49	43.5%
800 nm	72.42 / 0.27	34.1%	9.41 / 4.02	65.9%

*Transient kinetics of $CsPbBr_3$ QDs were fitted with the following equation:
$S(t) = y_0 + A_1 e^{-t/\tau_1} - A_2 e^{-t/\tau_2}$, where τ_1 is the lifetime of the ESA (positive) signal, and τ_2 is the lifetime of the GSB/SE (negative) signal.

Table S2**.** Kinetic parameters of the transient absorption (Fig. S3) for the $CsPbBr_3$–MPA systems.

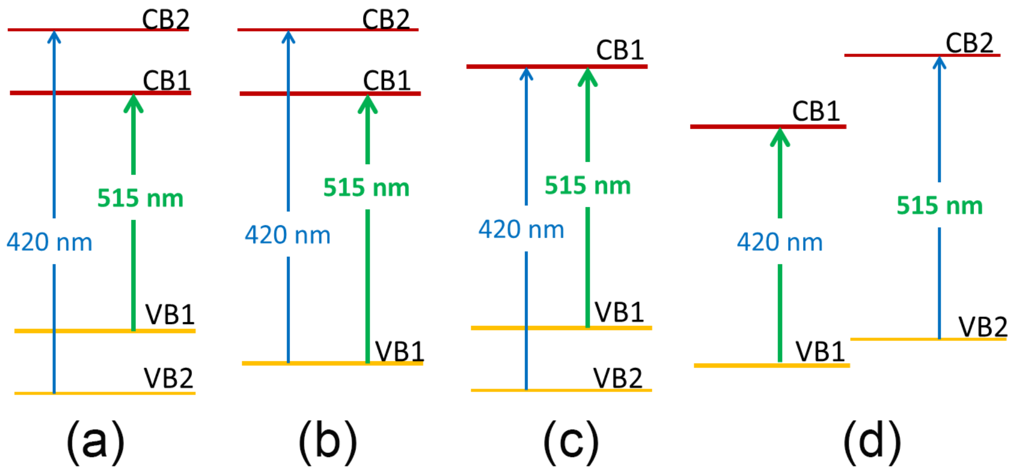


Fig. S4 Energy level schematics showing the four possible scenarios for the two peaks (negative signal at 420 nm and 515 nm) observed in the linear absorption and TA spectra. (a): separate valence bands to separate conduction bands transitions; (b) common valence band to separate conduction bands transitions; (c) separate valence bands to common conduction band transitions; and (d) a mixture of two photo-systems with independent transitions.

Interpretation for negative signal peaks at 420 nm and 515 nm[28]

Scenario a: The long-lived nanosecond GSB transient measured at 420 nm would exclude this situation because hot carrier relaxation to the lower levels would occur on a much faster picoseconds timescale.

Scenario d: It is well known that $CsPbBr_3$ QDs don’t have this kind of energy band structure.[22-23]

Differentiating Scenario b and c: In Scenario b, the transition at 420 nm does not depend on the electron populations at CB1 since the hot electron at CB2 decays within 1ps. But in Scenario C, the transition at 420 nm strongly depends on the electron populations at CB1.

For the QDs-MPA system, the dynamics originating from the electron populations at CB1 will be affected. Compared to the bleach peak at 515 nm, the MPA has little effect on the bleach peak at 420 nm in the first 15 ns. It indicates that the CB2 is participating in the 420 nm transitions. This eliminates Scenario c and confirms Scenario b.

Sample	λ_{peak}	Height (a.u.)	FWHM
pure QDs film	521.5 nm	43800	19.8 nm
QDs on mp-TiO_2	518.5 nm	9500	19.8 nm
QDs on mp-TiO_2 with MPA	519.4 nm	1400	18.0 nm

Table S3. The corresponding parameters of PL in **Fig. 6**b.

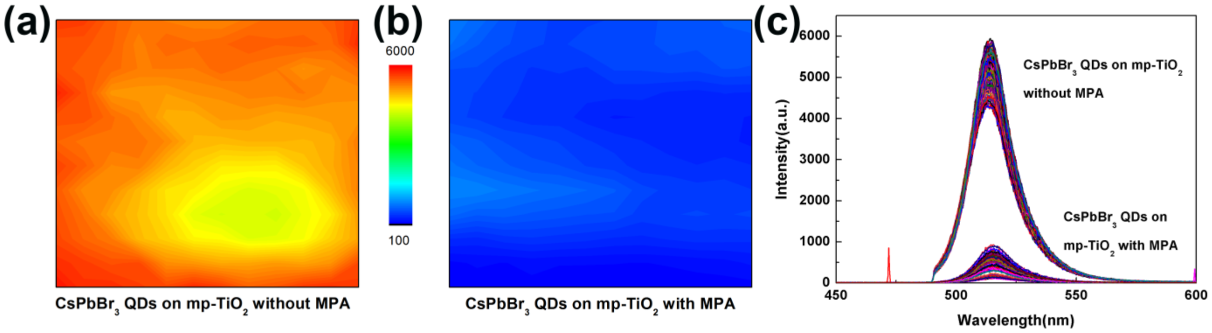


Fig. S5 PL mapping of $CsPbBr_3$ QDs on mp-TiO_2 a) without MPA or b) with MPA, and c) corresponding PL spectra upon excitation at 488 nm.

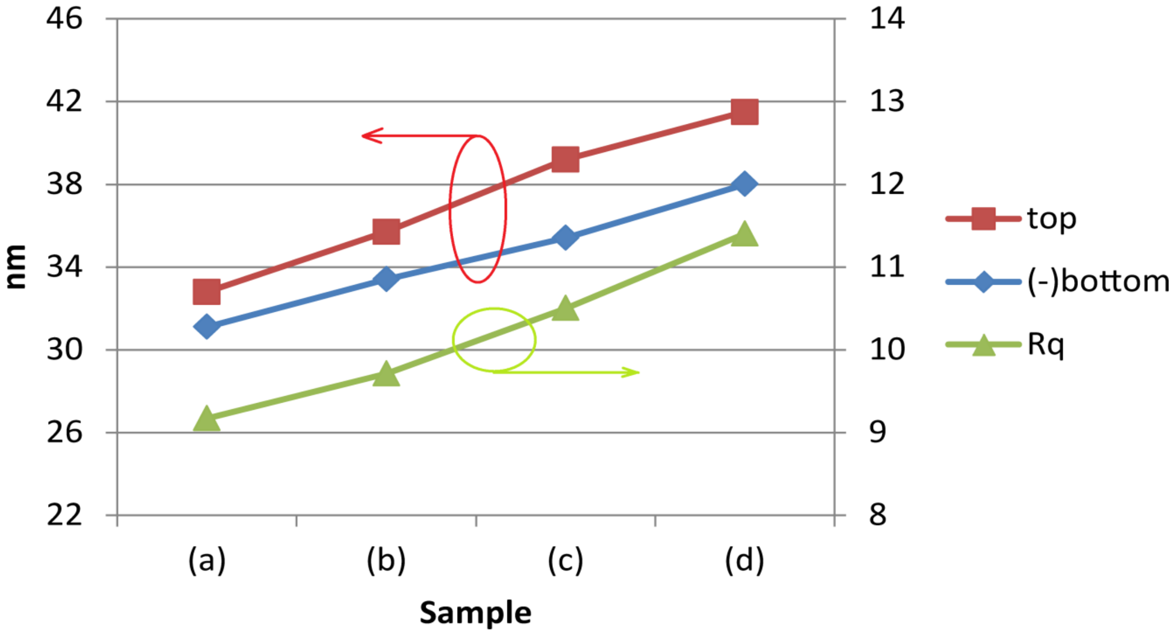


Fig. S6 The date scale and RMS roughness chart corresponding to **Fig. 6**.