Electronic Supplementary Material (ESI) for Nanoscale Horizons.

Supporting information

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

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Experimental section

Fabrication of PbS QD solid films: Colloidal PbS QD was firstly synthesized by using our previously reported method.[1] Then PbS QD solid films were deposited onto glass substrates by a typical layer-by-layer method. Briefly, as-prepared colloidal PbS-OA (original ligand of PbS is OA) QDs was spin cast onto glass substrate at 2500 rpm for 15 s. Then, a MAA ligand solution in methanol (10 mM) was dropped on the substrate and spun dry after a 15 s wait. The substrate was finally rinsed twice with methanol. The entire process was iterated 10 times to obtain smooth nm-thick films with QDs bound to the MAA ligand.

The UV-vis-NIR absorption spectra of PbS QD solid films were recorded using a spectrophotometer (JASCO, V-670). The Fourier transform infrared absorption (FTIR) spectra (Thermo Scientific, Nicolet 6700) of the PbS QD solid films were measured to verify that the as-synthesized ligand (OA) on PbS QDs were successfully exchanged by MAA ligands. The interparticle distance between PbS QDs was determined by high resolution transmission electron microscope (HRTEM, JEOL, JEM-2100F). Ultrafast transient absorption (TA) spectra were examined by using a fs-TA system. The laser source was a Ti/sapphire laser (CPA-2010, Clark-MXR Inc.) with a wavelength of 775 nm, a pulse width of 150 fs, and a repetition rate of 1 kHz. To avoid PbS QD degradation, PbS QD solid film was sealed into a transparent quartz cuvette (size: 60mm × 10mm × 40mm) filled with Ar gas, and the excitation positions of sample were moved during the measurement using a XY translational stage. The TA measurements were performed at 20 ℃ (room humidity: 30%).

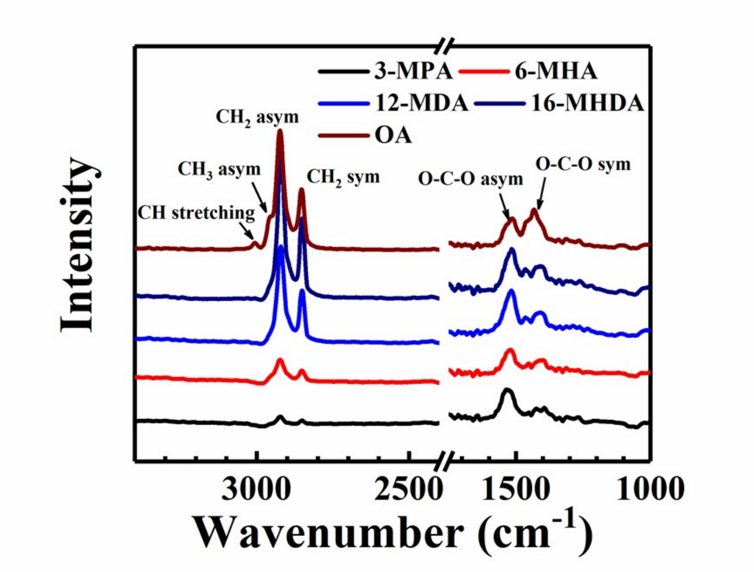

Fig. S1 FTIR spectra of PbS QD films with various MAA surface ligands.

The weak peak at 3006 cm^{-1} and peak at 2955 cm^{-1} are specifically assigned to the CH (-C=C-H) stretch and asymmetric CH_3 stretch of oleic acid. After exchange with MAA ligand, both above peaks disappeared. Peaks at 2923 cm^{-1} and 2853 cm^{-1} which belong to the C−H bending vibration of the hydrocarbon chains, and two sets of peaks in the range of 1551−1515 cm^{-1} and 1463−1415 cm^{-1} which belong to carboxylate stretches have been detected in all films.[2] These results show that MAA group replaces the oleic acid successfully. It is known that there is a peak at ~2600 cm^{-1} corresponding to SH stretching mode in the MAA ligands.[3] But the peak at ~2600 cm^{-1} cannot be observed in the MAA ligand treated PbS QD films, which suggests that sulfur atoms of thiols were bonded with unsaturated lead atoms on QD surfaces.

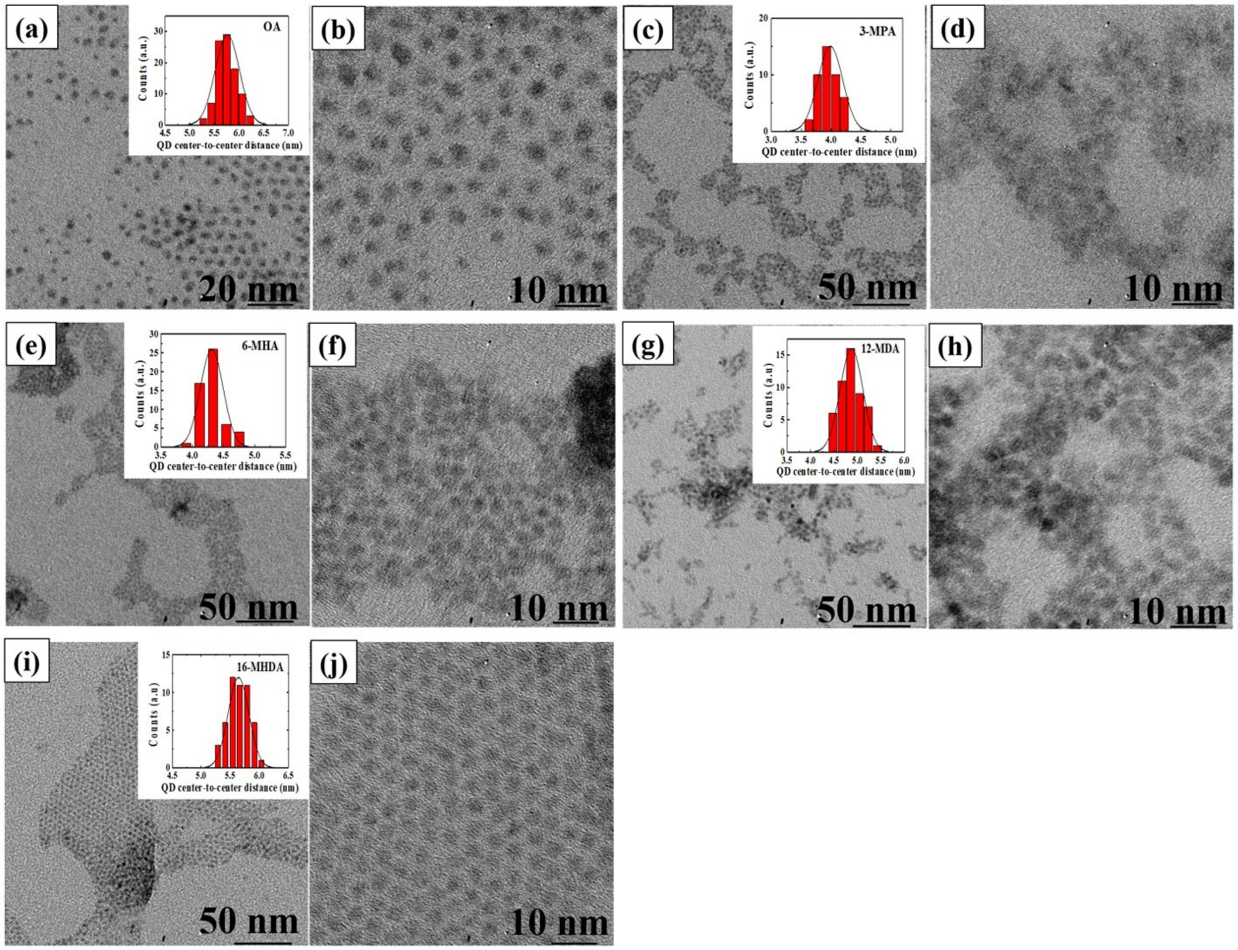

Fig. S2 TEM images of chemically treated PbS QD films with different ligands: (a, b) OA; (c, d) 3-MPA; (e, f) 6-MHA; (g, h) 12-MDA and (i, j) 16-MHDA. The inset Figures are the histograms of the QD center-to-center distances.

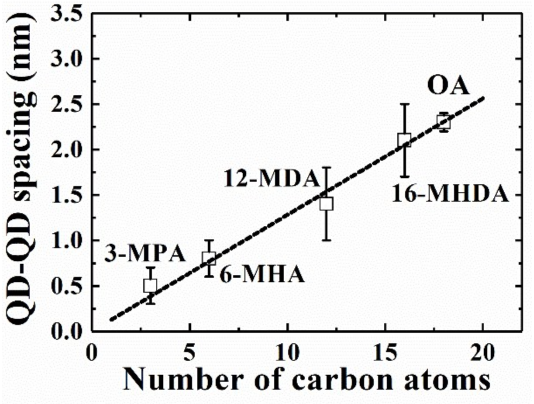

Fig. S3 The linear relationship between the QD-QD interparticle spacing and the number of carbon atoms of capping ligands.

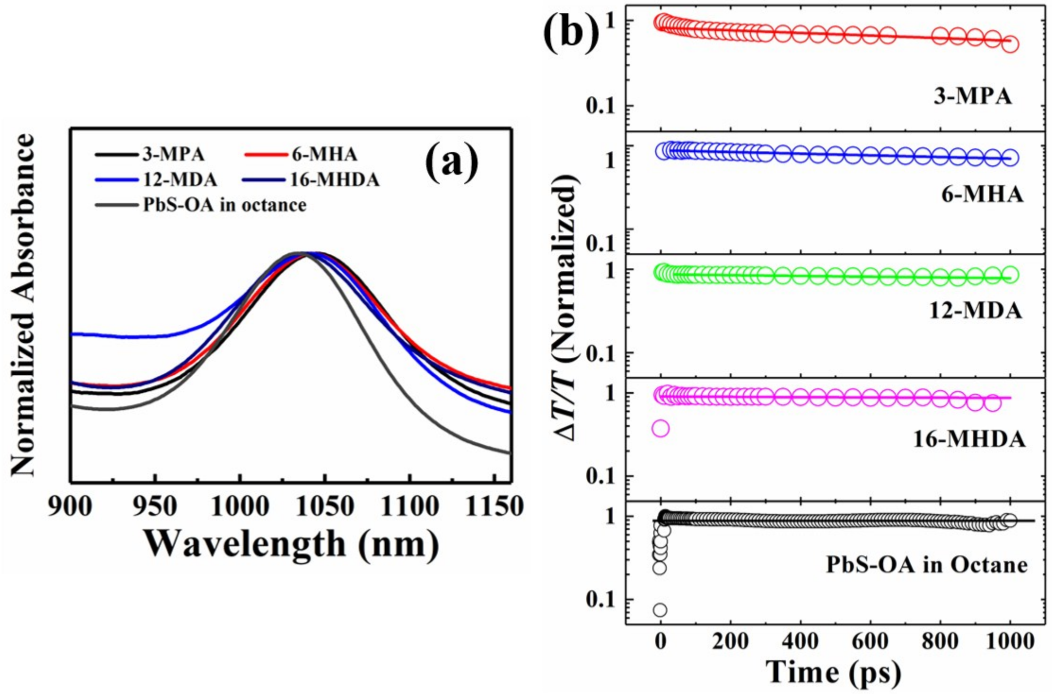

Fig. S4 (a) Absorption spectra of PbS QD films capped by different MAA ligands and PbS QDs capped by OA in Octane. (b) TA time decay curves of PbS QD films capped by different MAA ligands and PbS QDs capped by OA in Octane solutions. TA signal intensities were normalized at 5 ps. The solid lines are the fitting results.

Table S1. Fitted lifetime (τ_1) and charge transfer rate constant (k_{1et}) of single exciton by fitting the TA decay curves of MAA-PbS QD films with a single exponential function.

PbS QD Films	**τ_1 (ns)**	**k_{1et} ($1/\tau_1$, ns^{-1})**
3-MPA	2.86±0.29	0.35±0.04
6-MHA	4.36±0.15	0.23±0.01
12-MDA	9.52±0.22	0.11±0.01

16-MHDA	11.3±1.2	0.009±0.001

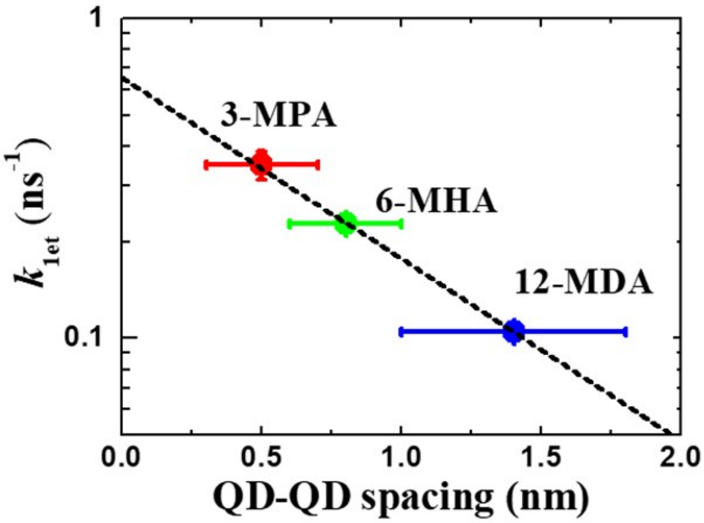

Fig. S5 Correlation between averaged QD-QD interparticle spacing and charge transfer rate constant (k_{1et}) of 1 *e*-*h* pair which calculated from exciton lifetimes in Fig. S4b. Single exponential decay fit (eq. (1)) (dotted line) indicates that the charge transfer occurs via tunneling of charge.

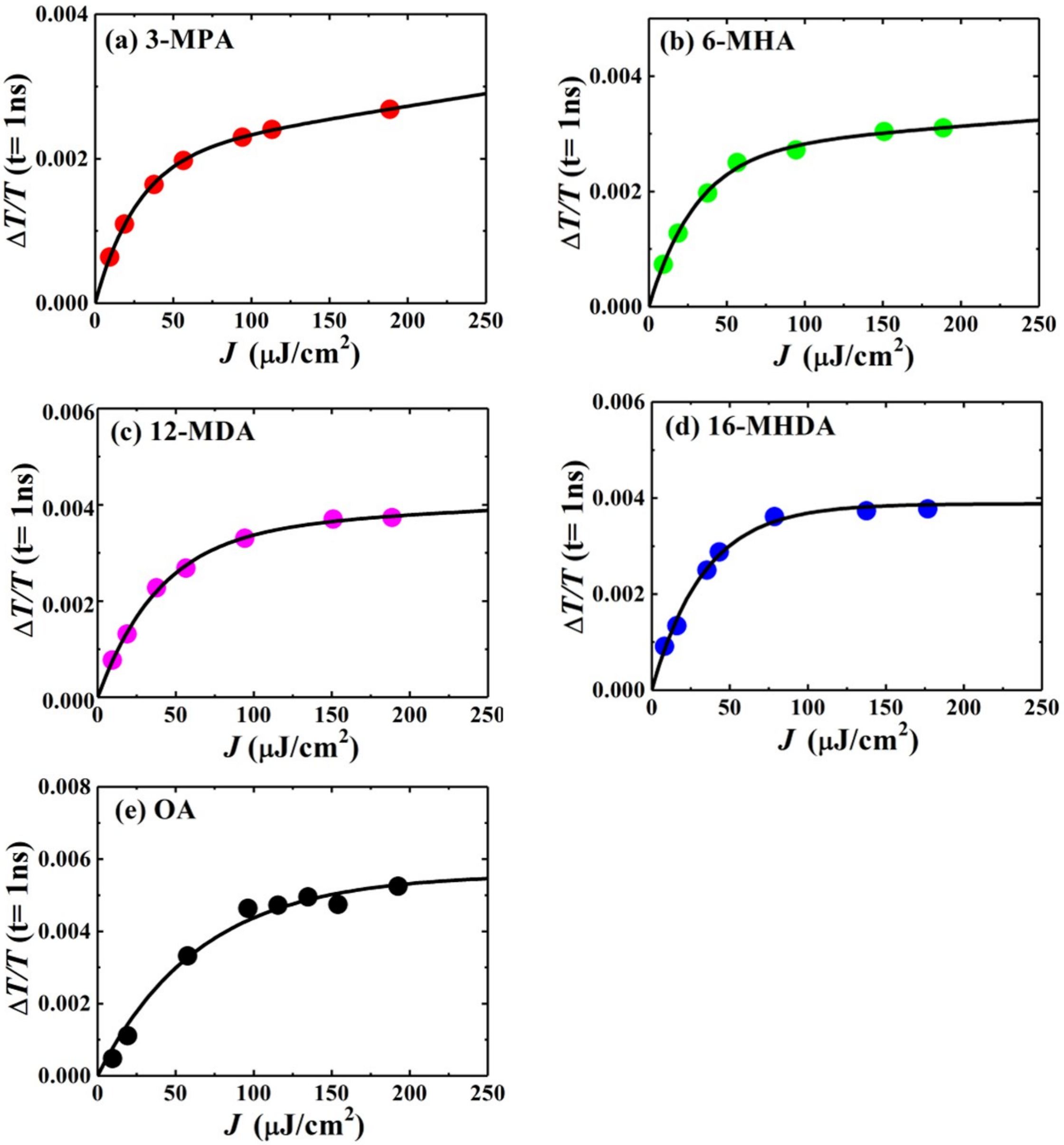

Fig. S6 TA signals of (a) 3-MPA, (b) 6-MHA, (c) 12-MDA and (d) 16-MHDA treated films and (e) OA-capped-PbS QDs in octane (isolated QDs) vs the excitation fluence (*J*) at delay time of 1 ns. The solid curves are the fitting results.

The solid curves of closely packed film treated 3-MPA, 6-MHA and 12-MDA are fitting curves using equation $\Delta T/T(t = 1\,ns) \propto (1 - K)\left(1 - e^{\left(-J_p\sigma\right)}\right) + KJ_p\sigma$.[4] The solid curves of 16-MHDA treated film and OA-capped PbS QDs in octane are fitting curves using equation: $\Delta T/T(t = 1\ ns) \propto 1 - e^{-J_p \sigma}$.[4]

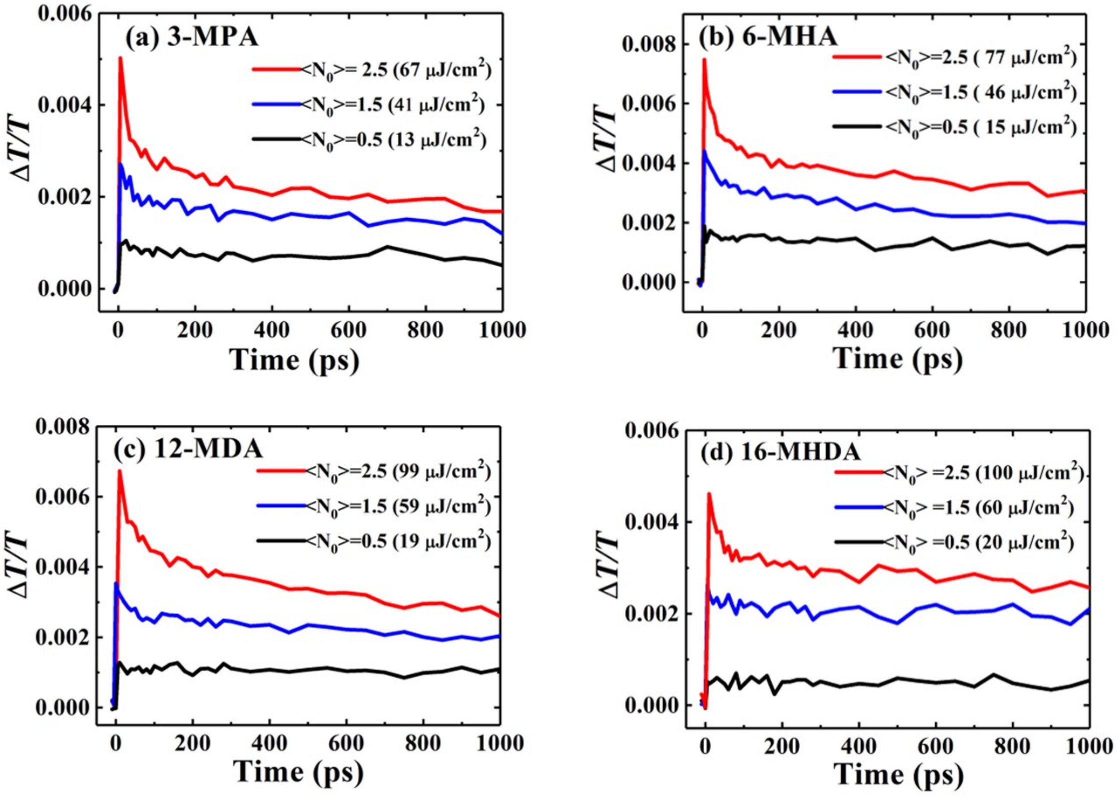

Fig. S7 Excitation-fluences dependent of TA curves of (a) 3-MPA, (b) 6-MHA, 12-MDA and 16-MHDA treated films. Average number of *e-h* pair per QD: $\langle N_0 \rangle = J_p \sigma$, [5, 6] where J_p and σ is photon fluence and absorption cross section, respectively.

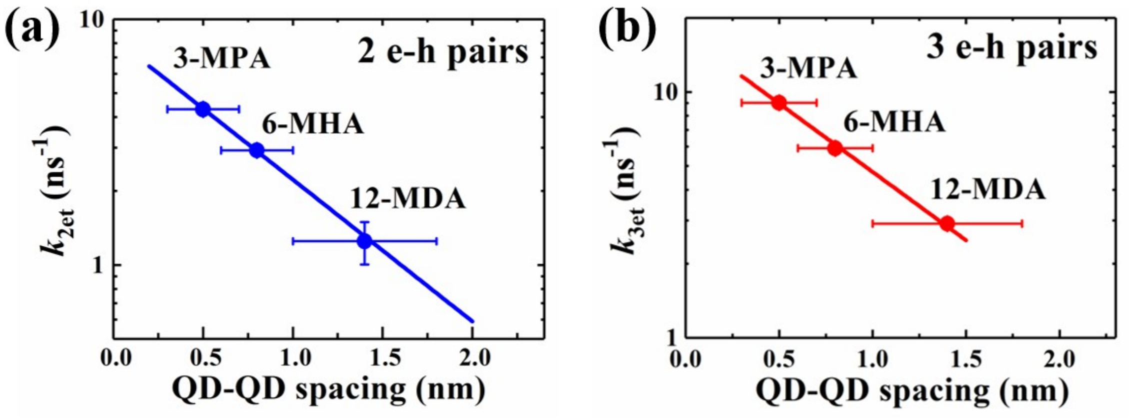

Fig. S8 Correlation between QD-QD spacing and charge transfer rate constants $k_{2\text{et}}$ and $k_{3\text{et}}$ of 2 *e-h* pairs (a) and 3 *e-h* pairs (b) for MAA ligands treated films. A single exponential decay fitting (dotted line) indicates that the carrier transfer occurs via tunneling of charge through a potential barrier.

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