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energetic alignment between the highest occupied molecular orbitals (HOMO) of PTC and the highest density-of-states in the valence band-edge of CdSe QDs. In other studies, the effect of PbS QD surface modification on exciton delocalization was investigated using trans-cinnamic acid (TCA) derivatives as capping ligands.^{34–36} Functionalizing the TCA molecule with electron-withdrawing or electron-donating groups profoundly affects the band-edge positions, bandgap, and optical absorption enhancement of PbS QDs. Furthermore, energetic alignment between the orbitals of exciton-delocalizing ligands (EDLs) and the band-edges of QDs can affect charge carrier cooling, which is sensitive to the ligand binding configuration.³⁷ Therefore, in addition to energetic alignment, specific EDL binding on the QD surface can significantly affect QD–QD electronic coupling and, thereby, charge transport in QD solids.

Using EDLs to increase QD–QD electronic coupling has also been reported for MAPbBr₃ PQDs. An LED device fabricated using MAPbBr₃ PQDs passivated with EDLs resulted in 22-fold higher conductivity and carrier mobility than MAPbBr₃ PQDs with long alkyl-chain capping ligands.²² Additionally, in our previous work, MAPbBr₃ PQDs passivated with EDLs were observed to have higher conductivity and charge mobility along with longer excitonic recombination lifetime and faster charge transport time.²³ However, to achieve greater QD–QD electronic coupling for PQD solids, it is critical to energetically align the related molecular orbitals of the ligands with the band-edges of the PQD core.

In this work, MAPbBr₃ PQDs were synthesized by surface passivating with valeric acid (VA), TCA, *trans*-4-(trifluoromethyl) cinnamic acid (TFCA), *trans*-2,3,4,5,6-pentafluorocinnamic acid (PFCA), and *trans*-4-methoxycinnamic acid (MOCA) to vary their energy levels with respect to the band-edges of the PQD core, as well as butylamine (BTYA) and 3,3-diphenylpropylamine (DPPA), to stabilize the conjugated carboxylate ions or alter their binding geometry on the PQD surface. Optical and photoelectrochemical, as well as time-resolved optical and electrical measurements, have confirmed that conjugated ligands with HOMO or lowest unoccupied molecular orbital (LUMO) closest to the band-edges of the MAPbBr₃ PQDs increases charge delocalization on the PQD surface when passivated in combination with DPPA. DPPA's π – π stacking intermolecular interaction in conjunction with TCA, TFCA, or MOCA, generates PQD solid films with enhanced optical and electronic properties, as well as produces bright electroluminescent LED devices with low turn-on voltages.

MAPbBr₃ PQDs were synthesized by following a previously reported procedure.²³ Precursor solution consisting of PbBr₂, MABr, DPPA, or BTYA and VA, TCA, TFCA, PFCA, or MOCA is dissolved in *N,N*-dimethylformamide (DMF) and rapidly injected into a vigorously stirred toluene antisolvent. A detailed description of the synthesis is in the [Supporting Information \(SI\)](#). Absolute PLQY data were obtained using an integrating sphere, a diagram of the measurement is displayed in [Figure S1](#). Absolute PLQY for each MAPbBr₃ PQD sample is shown in [Table 1](#). DPPA-TCA MAPbBr₃ PQDs are observed to have the highest absolute PLQY at 90%. Among the PQDs synthesized with BTYA, BTYA-MOCA MAPbBr₃ PQDs were observed to have the highest PLQY at 72%. The UV–vis absorption and photoluminescence (PL) spectra of each MAPbBr₃ PQD sample is displayed in [Figure 1a](#) and [b](#). Each MAPbBr₃ PQD sample was tuned to have an exciton

Table 1. Absolute PLQY of MAPbBr₃ QDs and Molecular Structure of (a) TCA, (b) TFCA, (c) PFCA, (d) MOCA, (e) VA, (f) BTYA, and (g) DPPA

MAPbBr ₃ PQD	PLQY(%)
BTYA-VA	18
BTYA-TCA	52
BTYA-TFCA	30
BTYA-PFCA	18
BTYA-MOCA	72
DPPA-VA	36
DPPA-TCA	90
DPPA-TFCA	46
DPPA-PFCA	46
DPPA-MOCA	58

a)	b)	c)	d)
e)	f)	g)	

absorption peak between 510 and 525 nm and PL peak between 515 and 530 nm to accurately compare optical and electronic properties among different PQD samples.

To determine the size and shape, high-resolution transmission electron microscopy (HRTEM) was performed, as shown in [Figure 1c](#) and [d](#). The average diameter for the PQDs synthesized with BTYA and VA, TCA, TFCA, PFCA, or MOCA is 6.1 ± 1.5 nm, while PQDs synthesized with DPPA and each respective acid is slightly larger at 6.8 ± 1.3 nm. Shown in the inset of [Figure 1c](#) and [d](#) are images of lattice spacing, which is measured to be 0.29 nm for each MAPbBr₃ PQD sample, corresponding to the (002) crystal face of cubic CH₃NH₃PbBr₃.³⁸

To confirm the presence of each capping ligand, Fourier transform-infrared (FT-IR) spectroscopy was conducted for each PQD sample, as shown in [Figure S2](#). Monosubstituted aromatic C–H in the regions 770–730 and 720–680 cm^{−1} is observed for each MAPbBr₃ PQD, indicating the presence of TCA, TFCA, PFCA, or MOCA from each respective MAPbBr₃ PQD.

The extent of charge carrier delocalization from passivating with conjugated capping ligands was determined from a ligand exchange using MAPbBr₃ magic-sized clusters (MSCs) capped with BTYA and oleic acid (OA), as well as DPPA and OA. BTYA-OA and DPPA-OA MAPbBr₃ MSCs were synthesized following a previously reported procedure.³⁹ Detail of the synthesis is in [SI](#). MSCs were chosen for ligand exchange because they are in a very strong confinement regime and more strongly confined charge carriers will have a greater sensitivity to increases to extra delocalization volume. The sizes of BTYA-

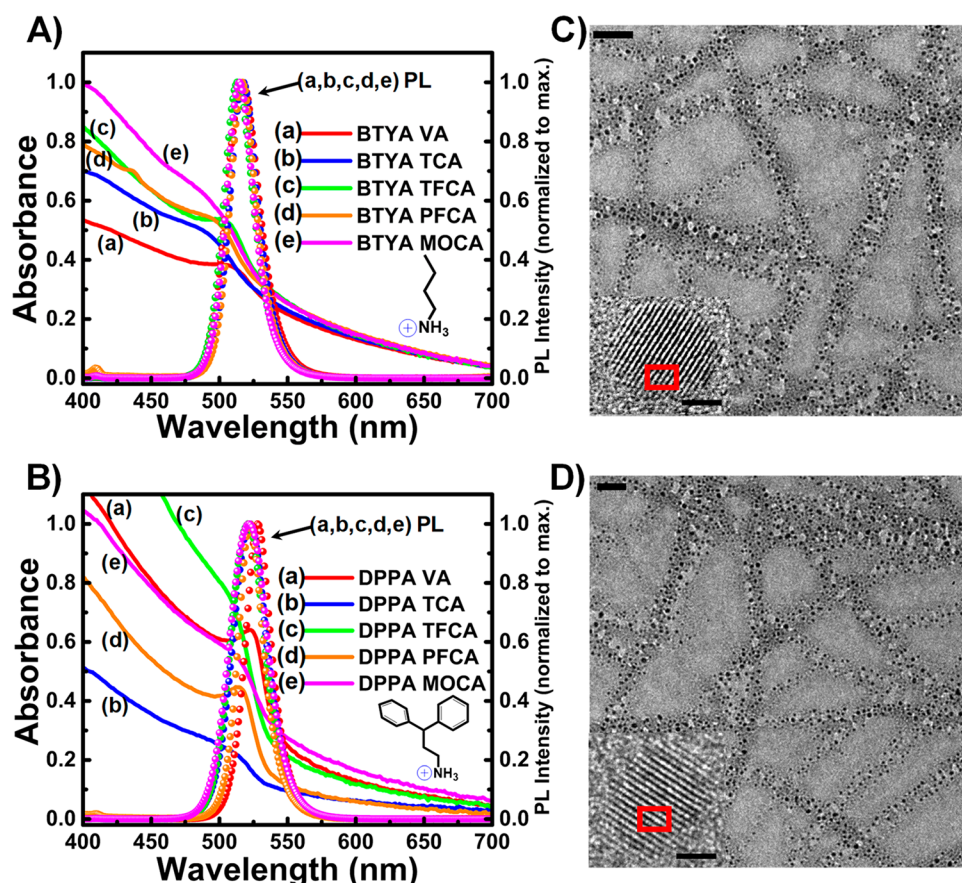


Figure 1. UV-vis absorption (solid line) and PL spectra (dotted line) of (A) BTYA-VA (a, red), -TCA (b, blue), -TFCA (c, green), -PFCA (d, orange), and -MOCA (e, magenta) and (B) DPPA-VA (a, red), -TCA (b, blue), -TFCA (c, green), -PFCA (d, orange), and -MOCA (e, magenta) MAPbBr₃ PQRDs suspended in toluene. (C) HRTEM image of MAPbBr₃ PQRDs passivated with DPPA-TCA (scale bar 10 nm). The lower left inset is image of lattice spacing (scale bar 2 nm). (D) HRTEM image of BTYA-TCA MAPbBr₃ PQRDs (scale bar 10 nm), and the lower left inset is lattice spacing image (scale bar 2 nm). HRTEM images are similar with respect to BTYA or DPPA amine with each acid.

OA and DPPA-OA MSCs were estimated using the Brus equation developed for QDs.⁴⁰ Because of their molecular-like structures, TEM images of the MSCs could not be obtained.^{39,41} These calculated values are used as estimates and may not reflect the true size. Detail of the calculation and ligand exchange procedure is in SI. Before ligand exchange with TCA, the BTYA-OA and DPPA-OA MSC sizes were calculated to be 2.89 and 2.65 nm, respectively. After exchanging OA ligands with TCA ligands, a 4 nm redshift in exciton absorption peak and 4 nm red-shift in PL peak was observed for the BTYA-TCA MSC solution, equivalent of an increase in size to 2.99 nm, as shown in Figure 2a. The delocalization radius was estimated by subtracting the calculated MSC size before and after ligand exchange.³¹ On the basis of the bandgap shift, this corresponds to an increase in delocalization radius of 0.05 nm. For the DPPA-OA MSC solution, exchanging OA ligands for TCA ligands resulted in a 27 nm redshift of the absorption peak and 49 nm redshift in PL peak, as displayed in Figure 2b. This translates to a calculated size of 3.30 nm. Therefore, the increase in delocalization radius for DPPA-TCA MSC solution is calculated to be 0.33 nm. The larger increase in delocalization radius upon ligand exchange for the DPPA-OA MSC solution could be due to stabilization of the TCA ligands on the PQD surface from the π - π stacking interactions between the aromatic rings in the DPPA and TCA molecules. This could enable more TCA molecules to adsorb

to the PQD lattice or orient TCA to have more geometric orbital overlap.

Furthermore, the PLQY before and after ligand exchange was measured. Before ligand exchange the PLQY of BTYA-OA and DPPA-OA MSC solution was calculated to be $18 \pm 4\%$ and $12 \pm 3\%$ (vs quinine sulfate, 58%), respectively. After ligand exchange, the PLQY of BTYA-TCA and DPPA-TCA MSC solution was $11 \pm 3\%$ and $36 \pm 5\%$, respectively. This enhancement in PLQY has been previously observed in CdSe QDs upon ligand exchange with an EDL, which can be attributed to stabilization of the excitonic state and increased probability of band-edge transitions.³³

To determine the extent of ligand interaction with the PQD core, FT-IR spectroscopy was performed before and after ligand exchange. As shown in Figure 2c, the most noticeable changes in the FT-IR spectra for the BTYA-OA MSCs upon ligand exchange with TCA is the appearance of strong monosubstituted aromatic C-H at 773 and 688 cm⁻¹. In addition, a strong peak at 733 cm⁻¹ and shoulder peak at 716 cm⁻¹ appear in the FT-IR spectrum after ligand exchange, which may also be indicative of different bound states of the TCA ligand on the PQD lattice.⁴²⁻⁴⁴ For the DPPA-OA MSC ligand exchange with TCA, due to the aromatic DPPA molecule, multiple aromatic C-H is observed before ligand exchange at 770, 750, 737, and 702 cm⁻¹, as shown in Figure 2d. After ligand exchange, peaks in this region become stronger in intensity, sharper, and slightly shifted. Peaks after ligand

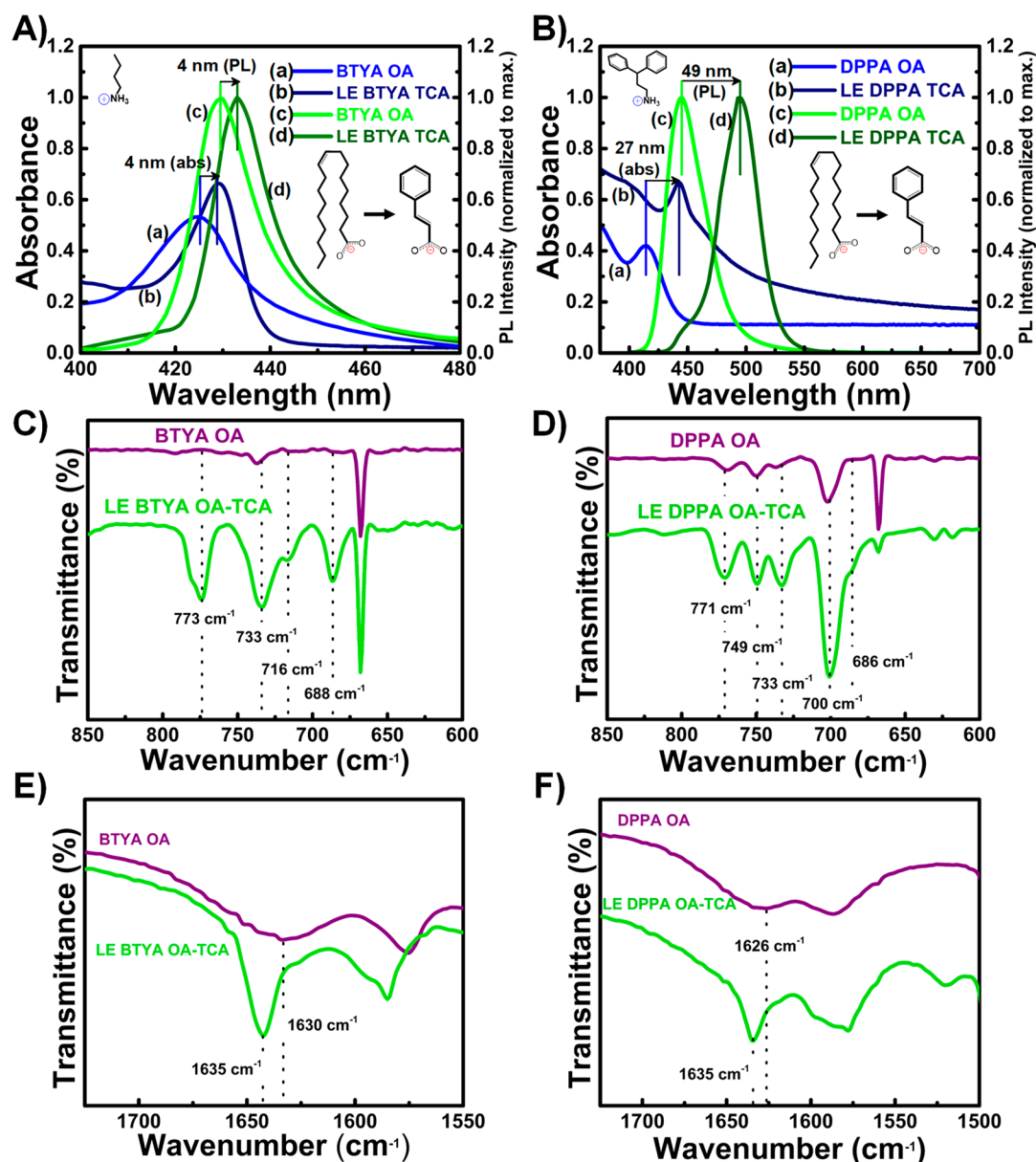


Figure 2. UV-vis absorption spectra of (A) BTYA-OA and (B) DPPA-OA MSCs before and after ligand exchange with TCA. FT-IR spectra of (C) BTYA-OA and (D) DPPA-OA MSCs before and after ligand exchange with TCA in the C-H aromatic region, and (E) BTYA-OA and (F) DPPA-OA MSCs before and after ligand exchange with TCA in the C=O stretching region.

exchange in the monosubstituted aromatic C-H region are at 771, 749, 733, and 700 cm^{-1} , as well as the appearance of a 686 cm^{-1} shoulder peak. Shown in Figure 2e and f is the C=O stretching before and after ligand exchange. Before ligand exchange for BTYA-OA and DPPA-OA MSCs, there is weak and broad C=O stretching at 1630 and 1626 cm^{-1} , respectively, corresponding to OA. After ligand exchange, these peaks disappear, and there is an appearance of a strong and sharp at peak 1635 cm^{-1} for both MSC solutions, which is assigned to the C=O stretching of TCA. Therefore, it may be concluded that TCA ligands significantly or completely replaced OA ligands.

The photogenerated charge carrier dynamics of each MAPbBr₃ PQD sample was investigated in solid films using time-correlated single-photon counting (TCSPC). Details of the measurements are described in SI. Comparing the valence band (VB) and conduction band (CB) edges of the PQD core

with the HOMO and LUMO energy levels of each conjugated acid, based on calculations using density functional theory (DFT/B3LYP), as well as values from previous reports,^{35,45,46} TCA's HOMO and LUMO orbitals are both near the VB and CB edges of the PQD core, while TFCA has LUMO more aligned to the CB edge and MOCA has its HOMO more aligned to the VB edge. The relevant energy levels are summarized in Figure S3. Therefore, TCA, TFCA, and MOCA are more likely to facilitate delocalization of photogenerated charge carriers in the PQD core than VA and PFCA. However, the strong interaction between the orbitals of EDLs and PQD core may facilitate trapping of charge carriers if the EDL is bound in a particular binding geometry.³⁷ On the surface of the PQD core, the intermolecular interaction of adjacent BTYA and EDL ligands is relatively weaker than the π - π stacking intermolecular interaction between adjacent DPPA and EDL ligands. Because of the stronger π - π stacking

intermolecular interactions between adjacent DPPA and EDL ligands, vibration and rotation of the EDLs may be more restrained than with BTYA. Therefore, charge carriers delocalizing into EDLs may have less nonradiative recombination in the company of DPPA than BTYA. As shown in Figure 3a and b, this may contribute to the shorter or similar

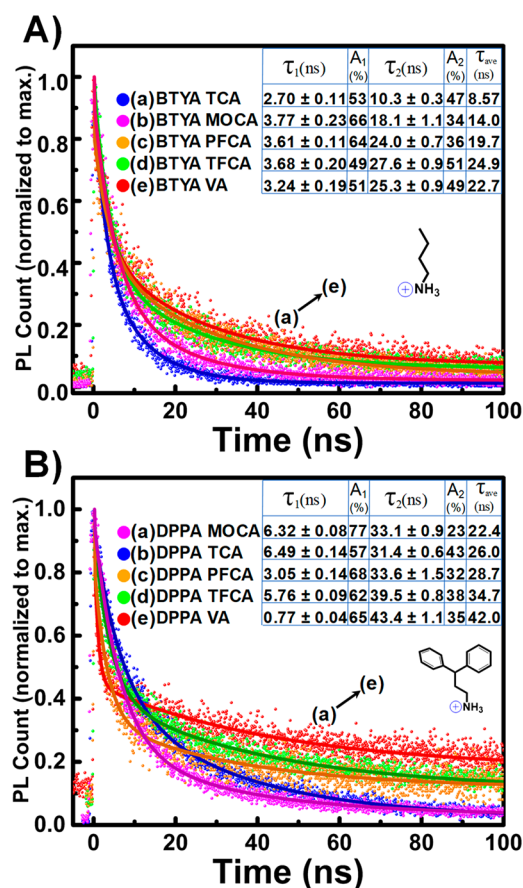


Figure 3. Time-resolved PL spectra of (A) BTYA-VA (e, red), -TCA (a, blue), -TFCA (d, green), -PFCA (c, orange), and -MOCA (b, magenta) and (B) DPPA-VA (e, red), -TCA (b, blue), -TFCA (d, green), -PFCA (c, orange), and -MOCA (a, magenta) MAPbBr₃ PQD film on borosilicate glass substrate. Inset displays τ_1 , τ_2 , A_1 , A_2 , and τ_{ave} representing the fast and slow decay component lifetime and amplitude, and average PL lifetime, respectively.

PL lifetimes of BTYA-TCA, BTYA-TFCA, and BTYA-MOCA MAPbBr₃ PQD films compared to the PL lifetimes of BTYA-VA and BTYA-PFCA MAPbBr₃ PQD films, which contain insulating and not energetically aligned ligands, respectively. In contrast, significantly longer fast decay component lifetimes are observed in DPPA-TCA, DPPA-TFCA, DPPA-MOCA MAPbBr₃ PQD films, at 6.5 ± 0.1 , 5.8 ± 0.1 , and 6.3 ± 0.1 ns, respectively, compared to DPPA-VA and DPPA-PFCA MAPbBr₃ PQD film at 0.77 ± 0.04 and 3.05 ± 0.14 ns, respectively. This opposite trend from passivating with BTYA compared to DPPA may be due to DPPA's π - π stacking interaction, which could restrict the molecular motion of the EDLs to a greater extent than BTYA. By restricting the molecular motion of the EDLs, a dampening of nonradiative pathways slow the rate of nonradiative recombination resulting in longer PL lifetime.

Using the absolute PLQY and the average PL lifetime, the radiative and nonradiative lifetimes were calculated. Detail of the calculation is included in SI. As shown in Table S1, coupling DPPA ligand with TCA or MOCA ligands enhances its radiative rate of decay with respect to its nonradiative rate. While for BTYA ligand, when coupled with EDLs, the radiative decay is comparable or significantly slower than its non-radiative decay. The increase in radiative decay rate and PLQY in DPPA passivated PQDs could be attributed to EDL's ability to stabilize photoexcited charge carriers generated in the PQD core by forming newly available interfacial states that could enhance the probability of band-edge transitions.³³ Whereas, for BTYA passivated PQDs, these interfacial states may trap charge carriers and increase nonradiative recombination.

To investigate the effect of EDLs on the conductivity and charge transport properties of PQD films, electrochemical impedance spectroscopy (EIS) was conducted. Details of the EIS measurements are supplied in SI. Figure 4a and b shows

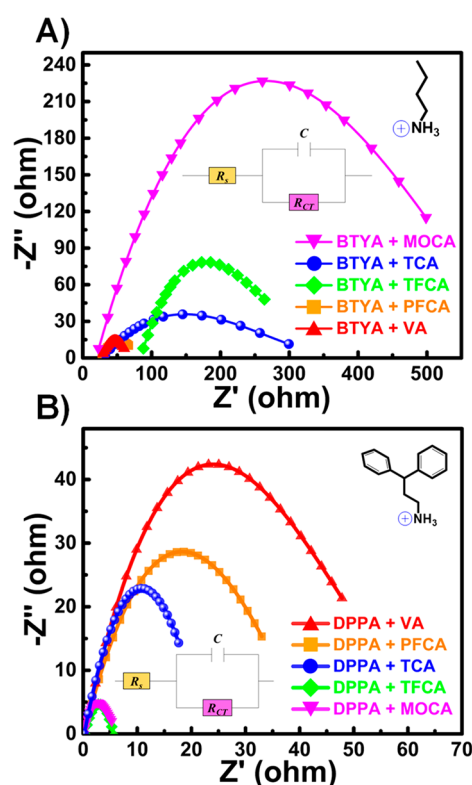


Figure 4. Nyquist spectra of (A) BTYA-VA, -TCA, -TFCA, -PFCA, and -MOCA and (B) DPPA-VA, -TCA, -TFCA, -PFCA, and -MOCA MAPbBr₃ PQD film on FTO substrate under one sun illumination (100 mW/cm^2). Inset displays equivalent circuit.

the Nyquist spectra of PQD films passivated with BTYA and DPPA with each acid, respectively. Table 2 provides a summary of the series resistance (R_s) and charge transport resistance (R_{CT}), determined by the first and second intercepts on the real axis, respectively, as well as the lifetime of charge transfer calculated using the constant-phase element (CPE) and R_{CT} .⁴⁷ The films containing DPPA passivated PQDs have consistent R_s near 0.195 ohm, while BTYA passivated PQD films have much larger R_s ranging from 30.1 to 78.8 ohm. However, the R_{CT} and τ_{rel} for BTYA-VA and DPPA-VA MAPbBr₃ PQD films is similar. Therefore, DPPA ligand by itself may not have significant conductivity advantages. The

Table 2. Series Resistance (R_s), Charge Transport Resistance (R_{CT}), and Charge Transfer Lifetime (τ_{rel}) of Each MAPbBr₃ PQD Film on FTO Substrate

MAPbBr ₃ PQD	R_s (ohm)	R_{CT} (ohm)	τ_{rel} (ms)
BTYA-VA	30.1	67.5	3.20
BTYA-TCA	33.0	341	16.1
BTYA-TFCA	78.8	328	15.5
BTYA-PFCA	30.1	80.8	3.83
BTYA-MOCA	30.1	645	30.5
DPPA-VA	0.195	60.5	2.97
DPPA-TCA	0.195	21.9	1.04
DPPA-TFCA	0.195	2.67	0.12
DPPA-PFCA	0.195	40.2	1.90
DPPA-MOCA	0.195	7.18	0.34

conjugated acids that are more energetically aligned with the PQD core; TCA, TFCA, and MOCA are observed to have the highest R_{CT} and slowest τ_{rel} for BTYA-passivated PQD films. This appears counterintuitive as the energetically aligned ligands should have strong PQD-ligand electronic coupling that increases surface charge carrier density. However, because of the instability and lack of π - π stacking intermolecular interaction, the strong PQD-ligand coupling may enhance trapping of charge carriers and is consistent with the TRPL

measurements. As observed in TRPL measurements, BTYA and DPPA capped PQDs have the opposite trend in EIS measurements. For DPPA-passivated PQDs, EDL-capped PQDs have the lowest R_{CT} and fastest τ_{rel} . The fastest τ_{rel} is measured to be 0.12 ms for DPPA-TFCA MAPbBr₃ PQD film. Our previous work using benzylamine (BZA) and benzoic acid (BA) delocalizing ligands have a τ_{rel} of 0.63 ms,²³ which is more than five times the lifetime of DPPA-TFCA MAPbBr₃ PQD film. Therefore, energy level alignment, as well as surface stabilization between the EDL and the PQD core, is crucial for increasing surface charge carrier density and charge transport in PQD solid film.

To examine the photogenerated current density, the transient photocurrent response ($I-t$ curve) was measured for each PQD solid film. Details of the measurements are in SI. As shown in Figure S4, the photogenerated current density measurements are consistent with the TRPL and EIS measurements. PQDs passivated with BTYA and the most energetically aligned ligands TCA, TFCA, and MOCA produce less photocurrent density than the VA and PFCA ligand, while the opposite is observed for DPPA passivated PQDs. Therefore, when the average ligand binding geometry facilitates charge trapping, the EDL diminishes photocurrent

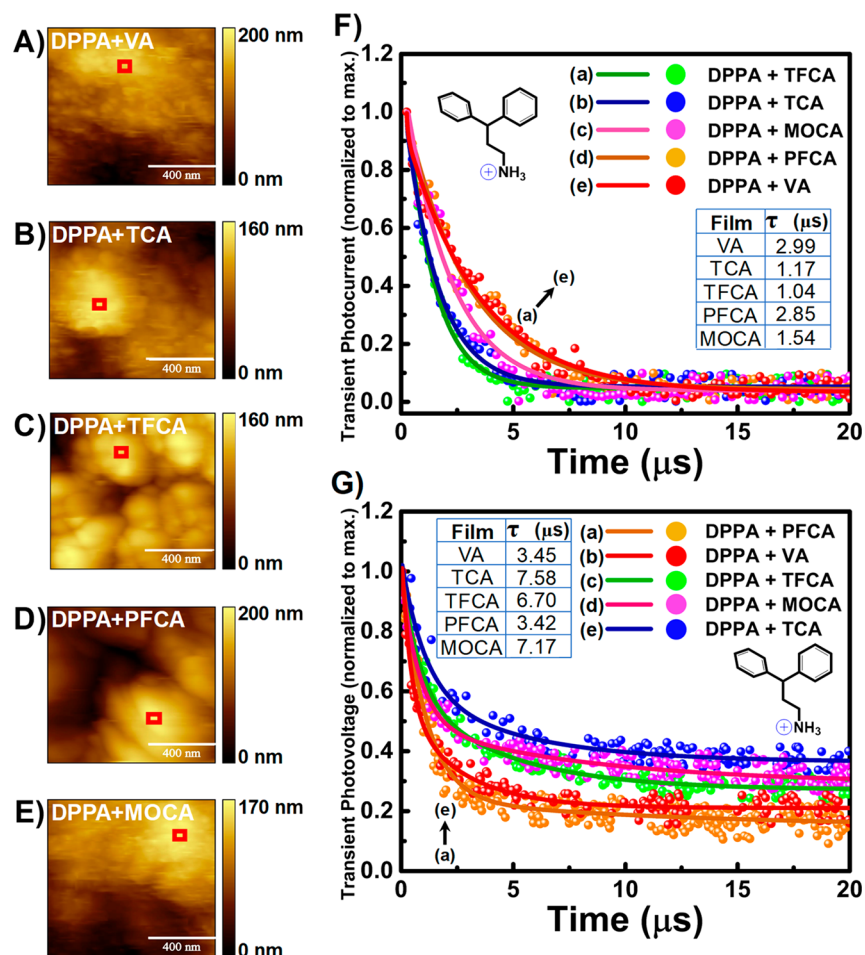


Figure 5. AFM topography images of (A) DPPA-VA, (B) DPPA-TCA, (C) DPPA-TFCA, (D) DPPA-PFCA, and (E) DPPA-MOCA MAPbBr₃ PQD films on FTO substrate. The area in the red square is where films were measured for TPC and TPV. (F) TPC decay curves of DPPA-VA (e, red), -TCA (b, blue), -TFCA (a, green), -PFCA (d, orange), and -MOCA (c, magenta) MAPbBr₃ PQD films. (G) TPV decay curves of DPPA-VA (b, red), -TCA (e, blue), -TFCA (c, green), -PFCA (a, orange), and -MOCA (d, magenta) MAPbBr₃ PQD films.

density even further than using an insulating capping ligand, such as VA.

To gain further insight into the effect of passivating PQDs with DPPA and EDLs, local transient photocurrent (TPC) and transient photovoltage (TPV) decay measurements were conducted using conductive atomic force microscopy (AFM). Details of the TPC and TPV measurements are supplied in SI. Shown in Figure 5a–e are AFM topography images of each PQD film that contain a red square representing an area $100 \times 100 \text{ nm}^2$, where TPC and TPV measurements were performed with similar PQD film thickness on FTO substrate. Displayed in Figure 5f is the TPC decay curves, and the inset shows the charge transport times of each PQD film. This measurement is directly related to the conductivity and charge mobility of the PQD solid films. As shown, the PQDs passivated with energetically aligned ligands are observed to have up to 3-fold faster charge transport time than PQDs capped with insulating or not energetically aligned ligands. Our previous study of BZA-BA MAPbBr₃ PQD film was measured to have a charge transport time of $1.52 \mu\text{s}$.²³ Thus, our new PQD films with dual passivation using energetically aligned and π - π stacking ligands, outperform PQD film with insulating or not energetically aligned ligands, as well as our previously measured BZA-BA MAPbBr₃ PQD film.

TPV decays were collected to determine the charge carrier recombination lifetime of PQDs passivated with DPPA and each acid. Longer lifetimes represent a slower rate of exciton recombination and, hence, a greater probability of charge extraction. Shown in Figure 5g is the TPV decay curves and in the inset is the calculated charge carrier lifetimes. Dual passivation with EDLs and DPPA increases the charge carrier lifetime by two-folds with respect to using insulating or not energetically aligned ligands. Compared to $2.92 \mu\text{s}$ for BZA-BA MAPbBr₃ PQD film from our previous work,²³ the energetically aligned capping ligands coupled with DPPA shows major improvement in charge carrier lifetime.

To demonstrate applications of the MAPbBr₃ PQDs, DPPA-TCA and DPPA-VA PQD-based LEDs were constructed and successfully demonstrated in the configuration ITO/TiO₂/PQD/Spiro-MeOTAD/Au in a preliminary study. Details of the LED fabrication are in the SI. As shown from the current density–voltage (J - V) curve in Figure S5, DPPA-TCA MAPbBr₃ PQD-based LEDs generate much higher current density upon increasing voltage than DPPA-VA MAPbBr₃ PQD-based LEDs. DPPA-VA MAPbBr₃ PQD-based LEDs did not light up during the measurement; however, the DPPA-TCA MAPbBr₃ PQD-based LED generated bright electroluminescence (EL) with a turn-on voltage of 2.5 V. A representative EL spectrum is shown in Figure S6. MAPbBr₃ PQD-based LEDs with octylamine and oleic acid capping ligands have been recently reported to have turn-on voltages between 2.9 and 4.0 V.^{48–50} Therefore, DPPA-TCA MAPbBr₃ PQD-based LEDs show enhanced performance.

In summary, we report the synthesis and characterization of MAPbBr₃ PQDs using a combination of capping ligands that are energetically aligned and stabilized by π - π stacking. This results in higher PLQY, conductivity, and photocurrent density, as well as longer PL lifetime of charge carriers compared to PQDs with insulating ligands or EDLs not stabilized on the PQD surface. In addition, DPPA passivation increases PQD's charge carrier delocalization radius by more than 6-fold compared to BTYA passivation, as determined in

TCA ligand exchange with OA. Furthermore, TPC and TPV measurements confirm faster charge transport times and longer charge carrier lifetimes, respectively, for PQDs passivated with EDLs. In addition, DPPA-TCA MAPbBr₃ PQD-based LEDs are observed to have better performance than DPPA-VA MAPbBr₃ PQD-based LEDs with a low turn-on voltage of 2.5 V. This work has demonstrated that energetically aligned conjugated capping ligands coupled with a spatial orbital overlap facilitator can significantly increase surface charge carrier density for improving optical and electrical properties of PQD films for potential optoelectronic device applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsenerylett.0c00093>.

Experimental section and supplementary figures (PDF)

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Notes

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The authors declare no competing financial interest.

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