Supporting Information

Enhancing Charge Carrier Delocalization in Perovskite Quantum Dot Solids with Energetically Aligned Conjugated Capping Ligands

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Experimental:

Materials

All chemicals were used without further purification, which include: toluene (spectroscopic grade, Fisher Scientific), N,N-Dimethylformamide (DMF) (spectroscopic grade, Fisher Scientific), PbBr₂ (99.99%, Alfa Aesar), MABr (Greatcellsolar), butylamine (BTYA) (99%, Oakwood Chemical), 3,3-diphenylpropylamine (DPPA) (98%, Combi-block), valeric acid (VA) (99%, Alfa Aesar), trans-cinnamic acid (TCA) (99%, Alfa Aesar), trans-4-(trifluoromethyl) cinnamic acid (TFCA) (99%, Oakwood Chemical), trans-2,3,4,5,6-pentafluorocinnamic acid (PFCA) (99%, Oakwood Chemical), trans-4-methoxycinnamic acid (MOCA) (99%, TCI), and oleic acid (OA) (97%, Alfa Aesar).

Spectroscopy and Microscopy

Absorption spectra were measured with an Agilent Technologies Cary 60 UV-Vis spectrophotometer. Fluorescence spectra were measured using a HORIBA Jobin Yvon Fluoromax-3 spectrofluorometer. Transmission electron microscopy images were obtained using a FEI monochromated F20 UT Tecnai. Scanning electron microscopy image was obtained using a FEI Quanta 3D Dual beam microscope.

Absolute PLQY

Newport 819C-SF-4 Integrating Sphere with an optical setup consists of two mirrors, the integrating sphere, a focusing lens and collimating lens, an optical fiber, a 450 nm short pass filter,

a 470 nm long pass filter, a PicoQuant PDM series single photon avalanche diode (SPAD) for detection and a Coherent 405 nm continuous wave diode laser for excitation. Silicon wafers (with and without samples on them) were glued to clean glass slides, which are then placed into the holder at one end of the integrating sphere. The laser light is incident on the sample and reflects inside the integrating sphere, transmitting through the optical fiber where it is collimated and refocused onto a SPAD. The filters are switched out to measure the laser counts being absorbed/emitted from the sample. Next, the calibration slide (silicon wafer + blank glass slide) is placed into the holder and the laser is turned on to measure the amount of counts reflected off the calibration slide. Then, we measure the counts absorbed by the sample by replacing the calibration slide with a sample slide, along with the short pass filter. Once these counts are recorded, the



Figure S1. Diagram of integrated sphere for measuring absolute PLQY

emission is measured by switching out the short pass filter with the high pass filter. **Figure S1** is a diagram of the measurement.

BTYA-VA,-TCA,-TFCA,-PFCA, and -MOCA MAPbBr₃ Synthesis

MAPbBr₃ PQDs were synthesized using a solvent reprecipitation method under ambient conditions. CH₃NH₃Br (80 mol, 9.0 mg), PbBr₂ (0.20 mmol, 73 mg), and VA (0.16 mmol, 16 μ L), TCA (0.16 mmol, 24 mg), TFCA (0.16 mmol, 35 mg), PFCA (0.16 mmol, 38 mg), or MOCA (0.16 mmol, 29 mg) and 400 μ L DMF was added to a borosilicate 7.0 mL vial and the solution was sonicated and heated until all solid dissolved. Next, BTYA (81 μ mol, 8.0 μ L) was added to

the solution and sonicated for 30 sec. 100 μ L of the precursor solution was injected at a fast rate to 5.0 mL toluene stirring at 1,600 rpm in a 7.0 mL borosilicate vial. The bright yellow PQD solution was purified first by centrifugation at 5,500 rpm for 5 min. (3 times), collecting the solid and discarding supernatant. Then, the solid was re-dispersed in 7.0 mL toluene and filtered using a loosely packed cotton-plug. Finally, the PQD solution was centrifugated again at 5,500 rpm and liquid was discarded. Films (borosilicate glass) were prepared using 100 μ L of a 40 mg/mL PQD in toluene solution and spin coating at 1,000 rpm for 60 sec.

DPPA-VA,-TCA,-TFCA,-PFCA, and -MOCA MAPbBr₃ Synthesis

MAPbBr₃ PQDs were synthesized using a solvent reprecipitation method under ambient conditions. CH₃NH₃Br (80 µmol, 9.0 mg), PbBr₂ (0.20 mmol, 73 mg), and VA (0.40 mmol, 40 µL), TCA (0.40 mmol, 59 mg), TFCA (0.34 mmol, 73 mg), PFCA (0.29 mmol, 68 mg), or MOCA (0.34 mmol, 60 mg) and 400 µL DMF was added to a borosilicate 7.0 mL vial and the solution was sonicated and heated until all solid dissolved. Next, DPPA (0.17 mmol, 35 µL) was added to the solution and sonicated for 30 sec. 100 µL of the precursor solution was injected at a fast rate to 5.0 mL toluene stirring at 1,600 rpm in a 7.0 mL borosilicate vial. The bright yellow PQD solution was purified first by centrifugation at 5,500 rpm for 5 min. (three times), collecting the solid and discarding supernatant. Then, the solid was re-dispersed in 7.0 mL toluene and filtered using a loosely packed cotton-plug. Finally, the PQD solution was centrifugated again at 5,500 rpm and liquid was discarded. Films (borosilicate glass) were prepared using 100 µL of a 40 mg/mL PQD in toluene solution and spin coating at 1,000 rpm for 60 sec.

BTYA-OA and DPPA-OA MSC Synthesis

MAPbBr₃ MSCs were synthesized using a solvent reprecipitation method under ambient conditions. CH₃NH₃Br (80 μ mol, 9.0 mg), PbBr₂ (0.20 mmol, 73 mg), and 400 μ L DMF was added to a borosilicate 7.0 mL vial and the solution was sonicated and heated until all solid dissolved. Next, DPPA (1.5 mmol, 300 μ L) or BTYA (2.0 mmol, 200 μ L) was added to the solution and sonicated for 30 sec. Then, OA (1.0 mmol, 250 μ L) was added to the solution and sonicated for 30 sec. Then, OA (1.0 mmol, 250 μ L) was added to the solution and sonicated for 30 sec. Then precursor solution was injected at a fast rate to 5.0 mL toluene stirring at 1,600 rpm in a 7.0 mL borosilicate vial. The clear MSC solution was then diluted in toluene, 1.0 mL toluene was added to 2.0 mL MSC solution. The MSC (2:1) solution produces bright blue photoluminescence under a UV lamp.

Fourier Transform-Infrared Spectroscopy

FT-IR spectra were obtained using a PerkinElmer Spectrum One FT-IR Spectrometer. FT-IR spectra of each MAPbBr₃ PQD with identifying TCA, TFCA, PFCA, or MOCA peaks are displayed in **Figure S2.** In the range 900 to 600 cm⁻¹ several monosubstituted aromatic C-H is observed for each MAPbBr₃ PQD. In the range 1700 to 1525 cm⁻¹ a new C=O stretching is observed for each MAPbBr₃ QD except for DPPA-TFCA and DPPA-PFCA, however, from 1500 to 900 cm⁻¹ C-F stretching is observed in the FT-IR spectra of these MAPbBr₃ PQDs.



Figure S2. FT-IR spectra of each MAPbBr₃ PQD in ranges with characteristic TCA, TFCA, PFCA, or MOCA peaks.

Ligand Exchange of BTYA-OA and DPPA-OA MSCs with TCA

5.0 mL of the MSC (2:1) solution (BTYA-OA or DPPA-OA) was added to a 7.0 mL borosilicate vial containing a magnetic stir bar and TCA (2.0 mmol, 296 mg). The ligand exchange solution was set to stir (1,000 rpm) in the refrigerator (5 °C) for 24 hours. As a control, 5.0 mL of MSC (2:1) solution (BTYA-OA or DPPA-OA) without TCA was set to stir (1,000 rpm) in the refrigerator (5 °C) for 24 hours. The sizes of the MSCs were estimated using the Brus equation:¹

$$E_{g(MSC)} = E_{g(bulk)} + \frac{h^2 \pi^2}{8r^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{4\pi \varepsilon \varepsilon_0 r}$$
(1)

where $E_{g(MSC)}$ is the bandgap of the MSC [BTYA-OA, before ligand exchange ($E_{g(MSC)} = 2.92 \ eV$) and after ligand exchange ($E_{g(MSC)} = 2.89 \ eV$); DPPA-OA, before ligand exchange ($E_{g(MSC)} = 3.00 \ eV$) and after ligand exchange ($E_{g(MSC)} = 2.81 \ eV$)], $E_{g(bulk)}$ is the bandgap of the bulk material (2.30 eV),² h is Planck's constant, r is the radius, m_e is the effective mass of the electron, m_h is the effective mass of the hole, e is electronic charge, ε is the relative permittivity, and ε_0 is permittivity of vacuum. Using this relation and the size (r) and the MAPbBr₃ PQD bandgap ($E_{g(PQD)}$) from a previous report ($r = 1.55 \ nm, E_{g(PQD)} = 2.64 \ eV$),³ the effective mass of the used to calculated the size of BTYA-OA and DPPA-OA MSCs before and after ligand exchange.

Time-Correlated Single Photon Counting Spectroscopy

Time-resolved PL (TRPL) were taken at room temperature using a 200 MHz Ti:Sapphire laser (790-820 nm) with an output of 350 mW, which passed through a Conoptics pulse picker that was set to select 500 kHz pulse train and a BiBO crystal to generate a second harmonic pulse. The second harmonic pulse was centered at 405 nm (4.0 μ J) was used to excite the sample. The sample's emission was collected 90° using an ID100 avalanche photodiode. The instrument response function was determined to be 50 ps. The time-resolved PL (TRPL) lifetimes were fitted using the following double-exponential function:

$$L = A_1 e^{\left(-\frac{t}{\tau_1}\right)} + A_2 e^{\left(-\frac{t}{\tau_2}\right)}$$
(2)

where A_1 and A_2 are the amplitude of the fast and slow decay components, and τ_1 and τ_2 are the lifetime of the fast and slow decay components, respectively. The slow decay component is mostly contributed to PL emission from the exciton as it is mostly associated with the longer timescale. Additionally, since non-radiative transitions occur on a much faster timescale than radiative transitions, a shorter fast component with higher ⁽³⁾ amplitude may indicate that vibrational relaxation is the dominate mechanism. The average lifetime ($\langle \tau \rangle$) of photogenerated charge carriers was calculated using the following equation:

 $\langle \tau \rangle = \frac{A_1 {\tau_1}^2 + A_2 {\tau_2}^2}{A_1 \tau_1 + A_2 \tau_2}$

The radiative decay rate (τ_r) was calculated using the equation:

$$\tau_r = \frac{\langle \tau \rangle}{PLQY} \tag{4}$$

and the non-radiative decay rate (τ_{nr}) was calculated using the equation:

$$\tau_{nr} = \frac{\langle \tau \rangle}{1 - \frac{\langle \tau \rangle}{\tau_r}} \tag{5}$$

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Table S1. Non-radiative and radiative		
lifetimes of each MAPbBr ₃ PQD		
calculated using absolute PLQY.		
MAPbBr ₃ PQD	$\tau_r(ns)$	$\tau_{nr}(ns)$
BTYA-VA	124.7	27.8
BTYA-TCA	16.5	17.8
BTYA-TFCA	66.8	27.9
BTYA-PFCA	154	29.7
BTYA-MOCA	91.5	16.5
DPPA-VA	116	65.8
DPPA-TCA	29.1	248
DPPA-TFCA	74.9	64.6
DPPA-PFCA	62.1	53.3
DPPA-MOCA	38.8	53.0

Shown in Table S1 is a summary of the calculated non-radiative and radiative lifetimes of each

Calculation of Relevant

MAPbBr₃ PQD.

Energy Levels for the

Ligands

The bandgap and band edge positions of the PQD core are assumed to be similar to that of bulk film and are obtained from a previous report ($E_{HOMO} = -3.3 \text{ eV}$, $E_{LUMO} = -5.6 \text{ eV}$).² The HOMO and LUMO energy levels for TCA ($E_{HOMO} = -3.2 \text{ eV}$, $E_{LUMO} = -6.3 \text{ eV}$), TFCA ($E_{HOMO} = -3.8 \text{ eV}$, $E_{LUMO} = -6.9 \text{ eV}$), PFCA ($E_{HOMO} = -4.3 \text{ eV}$, $E_{LUMO} = -7.5 \text{ eV}$), and MOCA ($E_{HOMO} = -3.1 \text{ eV}$, $E_{LUMO} = -6.1 \text{ eV}$) were calculated using Materials Studio DMol³ version 2017 with

Density Functional Theory Electronic Structure Program (B3LYP density functional method).⁴

These calculated energy levels are compared to values from previous reports: TCA ($E_{HOMO} = -$ 3.0 eV, $E_{LUMO} = -6.1$ eV), TFCA ($E_{HOMO} = -3.4$ eV, $E_{LUMO} = -6.5$ eV), PFCA ($E_{HOMO} = -3.0$ eV, $E_{LUMO} = -7.6$ eV), and MOCA ($E_{HOMO} = -$ 3.1 eV, $E_{LUMO} = -6.1$ eV).^{5,6} Figure S3 summarizes energy levels of PQD core compared to TCA, TFCA, PFCA, and MOCA ligands.



Figure S3. Diagram of energy levels between PQD core and ligands TCA, TFCA, PFCA, and MOCA. Solid lines are values from references 5 and 6, and dashed lines are calculated results from this work.

Electrochemical Impedance Spectroscopy

FTO substrates were first sonicated with liquinox solution for 10 minutes and rinsed with DI water, followed by sonication with DI water for 10 minutes and washed with isopropanol, followed by sonication with isopropanol for 10 minutes and washed with ethanol, and finally sonicated with ethanol for 10 minutes and dried with N₂. Next, the PQDs were spin-coated using 100 μ L of 40 mg/mL PQD solution at 1,000 rpm for 60 sec. Films were annealed on a hot plate for 2 minutes at 70 °C. EIS was conducted similar to a previous report.⁷ The spectroelectrochemical setup consists of a three-electrode cell (counter, reference, and working) in 0.10 M Bu₄NPF₆/dichloromethane solution connected to a potentiostat/galvanostat (SI 1280B). The counter electrode was Pt (6) wire and Ag/AgCl wire as pseudoreference electrode. The measurements were conducted in the frequency range of 1.0 MHz to 0.10 Hz at open circuit voltage. A xenon lamp irradiated film (1.0 cm²) at 1 sun illumination (100 mW/cm²). The lifetime of the charge transfer (τ_{rel}) was calculated using the following equation:⁸

$$\tau_{rel} = R_{CT} \times CPE$$

where *Rct* is the charge transport resistance obtained from the second x-intercept in the Nyquist plot (Figure 4), and *CPE* is the chemical-phase element obtained from the circuit fitting results.

Photoelectrochemical Measurements

Transient photocurrent density measurements were conducted under the same conditions as the EIS measurements. At open circuit voltage, xenon lamp (one sun illumination, 100 mW/cm²) irradiated PQD film (1.0 cm^2) in on/off cycles every 25 sec. for 375 sec. and photocurrent density

was measured as a function of time (I-t curve). **Figure S4** shows the transient photocurrent response (I-t curve) for each MAPbBr₃ PQD film.



Figure S4. Transient photocurrent response of (a) BTYA-VA,-TCA,-TFCA,-PFCA, and -MOCA and (b) DPPA-VA,-TCA,-TFCA,-PFCA, and -MOCA MAPbBr₃ PQD films on FTO substrate. Every 25 sec. PQD films were exposed to one sun illumination (100 mW/cm²).

Transient Photovoltage and Photocurrent Measurements

Local transient photovoltage (TPV) and transient photocurrent (TPC) decays were acquired using Agilent 5500 conductive atomic force microscopy (AFM) in contact mode. The excitation source was a green laser pulse with 532 nm wavelength generated by MGL-I-532 DPSS. In contact with

the surface of film was a platinum/iridium coated silicon conductive tip (Budget Sensors ContE-G; force constant of 0.20 N/m; resonance frequency of 14 kHz). Transient data were obtained by Agilent MSOX4154A oscilloscope. Connected to the oscilloscope was an Agilent Breakout Box (N9447A) for receiving signal from the AFM controller. The oscilloscope input impedance was set to 1.0 M Ω for TPV and 50 Ω for TPC. The charge carrier lifetime and transport time (7) of the film was calculated using a mono-exponential decay equation:

$$X(t) = X_0 e^{\frac{-t}{\tau}}$$

where X_0 is the photocurrent or photovoltage before excitation, X(t) is the photocurrent or photovoltage after excitation at time t, and τ is the charge carrier lifetime or transport time.

PQD-based LED Fabrication

Prepatterned ITO slides were cleaned by sonication in alconox solution (10% conc.), deionized water, 2-propanol, and ethanol, respectively, for 15 min. at 60°C and dried using compressed nitrogen gas. A TiO₂ blocking layer (30 nm) (Solaronix Ti-nanoxide BL/SP) was prepared using a draw down method and scotch tape. This layer was heated at 125°C on a hotplate for 5 min., then at 500°C in an oven for 30 min. The PQD layer (250 nm) was prepared by 50 µL of a 40 mg/mL PQD solution in toluene spin coated at 1,500 rpm 3 times. Next, 30 µL Spiro-OMeTAD (150 nm) was spun at 3000 rpm for 30 sec. and placed in a dry box for 12 hours. The gold electrode (100 nm) was thermally evaporated. The current density-voltage (*J-V*) curve of DPPA-TCA and DPPA-VA PQD-based LEDs constructed in the configuration ITO/TiO₂/PQD/Spiro-MeOTAD/Au is shown in **Figure S5.** A representative EL spectrum of DPPA-TCA MAPbBr₃ PQD-based LED is shown in **Figure S6**.



Figure S5. Current density-voltage (*J-V*) curve of DPPA-TCA and DPPA-VA MAPbBr₃ PQD-based LEDs. Inset is SEM cross-



Figure S6. Electroluminescence spectra of DPPA-TCA MAPbBr₃ PQDbased LED.

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