Supporting Information for

Anchoring and Post-Depositional Growth Enables Matrix Manipulation of PbS

QD Inks and Efficient Solar Cells

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1. Experimental details

1.1 Direct Synthesis of PbS CQD Inks.

For the synthesis of control PbS CQD inks, 6 mmol PbI₂ and 1 mmol DPhTA were dissolved in 8 mL and 1 mL DMF with stirring under nitrogen at room temperature, respectively. When all the solids were dissolved, 1 mL BA was quickly injected, after that DPhTA was injected. The solution immediately turned black. After adding toluene as an anti-solvent, the PbS CQDs were centrifuged for 5 min at 8000 rpm. The obtained solids were stored in the glovebox. The TT CQD inks were synthesized by adding 0.25 mmol TT molecules in 1Ml BA. The purification was the same as the control one.

1.2. Synthesis of ZnO Nanoparticles.

ZnO nanoparticles were synthesized according to the literature with some modifications¹. 2.95 g of zinc acetate dihydrate (ZnAc₂·H₂O) was added to 125 mL methanol (MeOH) in a three-necked bottle. 1.48 g potassium hydroxide (KOH) was dissolved in 60 mL MeOH and dropwise added to the zinc acetate solution under vigorous stirring at 63.5 $^{\circ}$ C for 3 h. After cooling down, ZnO nanocrystals were extracted from their mother solution via centrifugation and washed twice with methanol. Finally, 10 mL of chloroform (CF) and 10 mL MeOH were added to the precipitates and the solution was filtered with a 0.45 µm filter.

1.3 Device Fabrication.

ITO glass was cleaned in sequence using industrial acetone, detergent, isopropyl alcohol, and acetone again for 15 min, respectively. The substrates were treated with oxygen plasma for 30 min before spin coating. ZnO nanoparticle solution was spin-coated on ITO glass at 2500 rpm for 20 s. The ZnO film was used without thermal annealing. The PbS CQD ink solution (1000 mg mL⁻¹) was spin-coated at 2000 rpm for 40 s in an inert atmosphere, followed by annealing at 80 °C for 10 minutes. For the interface layer, 5 mg mL⁻¹ PbS-OA CQDs in hexane were spin-coated at 2500 rpm for 20 s, followed by MPA/methanol solution (v:v = 1:50) treatment for 30 s and methanol rinsing twice. For the hole transport layer, 5 mg mL⁻¹ PBDB-T was spin-coated at 2500 rpm for 40 s in an inert atmosphere. After that, a 5 nm thick MoO₃ film and 80nm silver were thermally evaporated through a shadow mask to prepare devices with a total active area of about 0.0725 cm². The active area was determined by the overlap of ITO and silver electrodes, which was further verified by the microscope. Devices were stored in ambient air (relative humidity around 30%) for the air stability test.

2. Characterization

UV-vis NIR spectra were recorded on a Perkin Elmer model Lambda 750. PL spectra and PL lifetime of CQDs solution were measured by a FluoroMax-4 spectrofluorometer (HORIBA

Scientific). IR spectra were recorded by an FTIR spectrometer (Bruker HYPERION). The TAS was carried out on an fs-TA system, including a Pump-probe spectrometer (Harpia, Light Conversion), Fundamental laser (PHAROS-PH2, Light Conversion), Optical parameter amplifier (OPA, ORPHEUS-HP, Light Conversion). The pump wavelength and pump power were set to be 600 nm and 9.1 mW, respectively. PL spectra of the CQD solution were obtained on FluoroMax-4 spectrofluorometer (HORIBA Scientific) with excitation at 750 nm. Current density-voltage (J-V) characteristics of the devices were measured under ambient air using a programmable Keithley 2401 source meter under a simulated AM 1.5G solar irradiation of 100 mW cm⁻². (Newport, Class AAA solar simulator, 94023A-U) The light intensity is calibrated by a certified Oriel Reference Cell (91150V) and verified with an NREL-calibrated Hamamatsu S1787-04 diode. The ITO/electrode overlap area is 0.0725 cm². The devices are measured with shadow mask, determining the active area of 0.04 cm². Voltage swept from -0.8V to 0.8V with a speed of 0.01 V per point and a dwell time of 10 ms. For the magneto-photocurrent (MPC) test, the device was placed in an Oxford Optistat BLV cryostat. The air pressure inside the cavity was controlled below 10⁻⁴ mBar using a molecular pump, and the temperature was adjusted as required. The device was irradiated with a standard AM1.5 light source. A self - written LabVIEW program was used to control the Keithley 2450 source meter and the electromagnet power supply. First, the source meter was controlled to apply the required bias voltage to the device. Then, the current of the electromagnet power supply was controlled to sweep the magnetic field. During the field - sweeping process, the device current was recorded by the source meter simultaneously. For the obtained raw field - sweeping data, a self - written Python script was used to calculate the magnetic field effect to obtain the result.



Figure S1. XRD patterns of Control and TT PbS CQD.



Figure S2. FTIR measurements of control and TT CQD films with different amounts of TT.



Figure S3. a) Photographs of the PbI₂(1 mmol), BA(0.03 mL) and TT(0.1 mmol) dispersed in DMF(5 mL) at Romtemperature and 60, 80 °C.



Figure S4. UV-vis absorption spectra of Control (a) and TT (b) CQD inks and films.



Figure S5. TRPL measurements of control and TT CQD inks.



Figure S6. The shift of peak position of PIB over the time.



Figure S7. Cross-section SEM image of the PbS CQD photovoltaic device used in this study.



Figure S8. J-V² curve of space charge limited current (SCLC) device of control and TT-PbS CQD films. Device structure: ITO/ZnO/PbS-ink/ZnO/LiF/Ag



Figure S9. Transient photocurrent (TPC) decay spectroscopy of the control and TT CQD devices



Magnetic power source

Figure S10. Schematic diagram of the MPC testing equipment.



Figure S11. Stability test of unencapsulated devices stored in air.

Table S1. TRPL measur	ement of control	and TT	CQD in	ıks.
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	A ₁	τ_1 (µs)	A ₂	$\tau_2(\mu s)$	$\tau_{avg}(\mu s)$
Control	0.38	0.08	0.40	1.67	0.9
TT	0.21	0.13	0.53	2.35	1.74

Table S2. Photovoltaic parameters of devices based on Control CQD film with different absorptions.

	V _{OC} (V)	J _{SC} (mA/cm ²)	FF(%)	PCE(%)
Control-885nm	0.69	25.97	67.41	12.08
Control-946nm	0.62	27.63	65.01	11.13

Supplementary Note 1: Experimental setup and characterization methodology of MPC test.

I. Sample Environment Control System

1. Device Electrical Interconnection:

The device under test (DUT) is securely mounted on a PCB board, establishing stable electrical interconnections through designed contact interfaces.

2. Cryogenic Signal Transmission:

The PCB interfaces with the cryostat's internal terminals via oxygen-free copper contacts with gold-plated surfaces. External electrical connections are achieved using vacuum feedthrough components, which route signals to a Keithley 2450 source meter.

II. Photocurrent Detection System

1. Optical Excitation:

Standard AM1.5G solar spectrum illumination (100 mW/cm²) is delivered through the cryostat's quartz optical window using a xenon lamp source equipped with an AM1.5G filter.

2. Signal Acquisition:

Photocurrent signals are collected by the Keithley 2450 source meter via shielded vacuum feedthrough cables, operating in zero-bias voltage mode.

3. Synchronized Control:

A custom LabVIEW program coordinates the magnetic field sweep and photocurrent measurement sequences, ensuring temporal synchronization with a timing resolution <50 ms.

- III. Magneto-Photocurrent (MPC) Characterization
- 1. Testing Protocol:

(1) Under zero-bias conditions, perform magnetic field sweeps (-200 mT \rightarrow +200 mT) at discrete temperatures (140–

260 K, $\Delta T = 20$ K).

- (2) Record the steady-state photocurrent I(B) synchronously with each applied field strength B.
- (3) Calculate MPC response:

$$MPC(B) = \frac{I(B) - I(0)}{I(0)} \times 100\%$$

where I(0) and I(B) denote photocurrent values at zero field and field B, respectively.

2. Data Analysis:

- (1) Fit MPC-B curves at each temperature to the Lorentzian function.
- (2) Extract MPC values at 200 mT and analyze thermal activation behavior using the Arrhenius model:

$$MPC \propto \exp\left(-\frac{E_a}{k_{BT}}\right)$$

where E_a represents the activation energy and k_B is the Boltzmann constant.