2D matrix engineering for homogeneous quantum dot coupling in photovoltaic solids

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sharp and asymmetric PL emission (peak $\lambda \approx 520$ nm, full-width at half-maximum ~16 nm) of hybrid-amine films is a signature of the independent and substantially homogeneous population of PbI$_2$ monolayers. Such PL features have typically been observed in layered 2D perovskite single crystals$^{28}$ and layered PbI$_2$ single crystals under cryogenic conditions$^{29}$. The emission spectra for BTA films are much broader and darker (Supplementary Fig. 2). We ascribe this to the presence of less self-similar and/or less-confined layered structures. In contrast, the random 3D growth habit of DMF films yields negligible emission, due to the numerous defects at the grain surfaces and the mutual quenching effect$^{30,31}$.

We noticed that the PL linewidth (~16 nm) of the PbI$_2$–hybrid-amine films is comparable to that of 2D perovskite single crystals (~16 nm) and is superior to that of 2D perovskite films (>40 nm (Supplementary Fig. 3)). This near-single-crystalline feature motivated crystallographic measurements that employed grazing incidence wide-angle X-ray scattering (GIWAXS). Conventional DMF films exhibited no detectable layered features (Fig. 2c). By contrast, sharp and discrete Bragg spots along the $q_z$ axis were observed in hybrid-amine films (Fig. 2d and Supplementary Fig. 4), which reveals a high-quality 2D monolayer structure with long-range ordering and orientation. This finding indicated the potential to enhance the 2D confinement of the PbI$_2$ matrix component by leveraging the hybrid-amine coordination.

We used Fourier transform infrared (FTIR) spectroscopy to gain a further mechanistic understanding of the PbI$_2$–amine complex in CQD films (Fig. 2c). First, the coordination effect of amines on PbI$_2$ is confirmed by the consistent shift of the N–H stretch mode ($3,170$ cm$^{-1}$) and N–H scissor mode ($1,560$ cm$^{-1}$) in PbI$_2$–amine complexes compared with those in reference solvents of the amines (Supplementary Fig. 4)$^{22}$. This signature of 2D PbI$_2$–amine complexes is present identically both in PbI$_2$ films and in PbI$_2$-capped CQD films prepared using amines (Fig. 2e and Supplementary Figs. 5 and 6c). Moreover, when the matrix-to-CQD ratio is tuned, the spectral signature of the 2D PbI$_2$–amine complex in CQD films is retained in the FTIR measurements (Supplementary Fig. 7d). Its lattice pattern was also identified using GIWAXS (Supplementary Fig. 7b). In contrast, such features are absent both in PbI$_2$ films and in CQD films prepared using DMF (Fig. 2e and Supplementary Figs. 6f and 7h). This comparison indicates that the mechanism for CQD surface functionalization is inherited from the PbI$_2$–amine 2D coordination in the matrix, rather than from the PbS CQD bare surfaces.

The signatures of the PbI$_2$–hybrid-amine complexes shown in the CQD films are consistent with those presented in pure 2D layered perovskite films$^{28}$. This, again, indicates a confined monolayer configuration for the PbI$_2$ matrix stabilized by the hybrid-amine ligands, consistent with conclusions drawn from absorption spectra, PL signals and GIWAXS patterns (Fig. 2a–d). Overall, the photophysics and crystallography studies reveal a reduction of the dimensionality during the PbI$_2$ crystallization process associated with the incorporation of longer amines. These open up opportunities to suppress CQD fusion and the formation of thicker PbI$_2$ regions between CQDs. Consistent with this view, the hybrid-amine devices exhibited $V_{oc}$ values higher than those of the best control devices made using BTA and DMF inks (Supplementary Fig. 8).
The PbI$_2$–hybrid-amine matrix leads to CQD inks with an improved colloidal stability (Supplementary Fig. 9) that benefit from the enhanced steric repulsion$^{14,24}$ of the longer amine surfactants (hexylamine). We also observed narrower PL peaks and higher PL quantum yields from hybrid-amine inks (Supplementary Fig. 10), which indicate high-quality surfaces stabilized in the solution phase. We propose that, compared with control BTA inks, this new matrix mediates a less-disruptive CQD-densification process during the transition from the solution to the solid phase. In this regard, in situ spectroscopic ellipsometry, absorption and thermogravimetric analyses were used to study the evolution of the CQD film thickness, absorption and mass, respectively, during the postannealing (Supplementary Fig. 11). We found that 40–50% increases in film density occur, and these are associated with remarkable reductions of film thickness and the amount of volatile amine species. These changes are quantitatively much more appreciable than the near-imperceptible changes of the control BTA CQD films subjected to the same postannealing conditions. After the postannealing process, hybrid-amine films are PV-quality films. This sol–gel-like solidification process of the PbI$_2$–hybrid-amine matrix is reminiscent of sol–gel solidification processes reported in lead halide perovskites$^{15,20}$.

In the resultant CQD films, an enhanced packing density and uniformity, and therefore a reduced structural disorder, were also indicated in a suite of microscopic studies (Fig. 3). Ex situ force-indentation curves measured with an atomic force microscope (AFM) were used to study differences in the mechanical characteristics of CQD films that stemmed from different traits of the matrix materials. In agreement with observations from the in situ studies, the hybrid-amine films without postannealing are characteristically soft, and feature much lower elastic moduli and larger hysteresis in the force–height response compared to control BTA films (Supplementary Fig. 12). After CQD rearrangement and densification during postannealing, the hybrid-amine films exhibited concurrent improvements (~20%) of the elastic modulus and hysteresis compared with the control BTA films (Fig. 3a,b). In addition, tapping-mode topographic AFM analysis of the film morphology showed that the local and global smoothness can be greatly improved by using hybrid-amine inks (Fig. 3c and Supplementary Fig. 13). For the progressively increasing field of views (5×5 to 30×30 µm$^2$), hybrid-amine films retain a surface roughness of ~0.6 nm, whereas control BTA films’ roughness increases from 1.4 nm to ~2 nm (Fig. 3d). The enhanced elastic modulus, in conjunction with improved smoothness, implies a simultaneous optimization of the CQD packing density and uniformity. Enhanced packing uniformity has recently been recognized as greatly benefiting the carrier transport in CQD assemblies$^{19,14,31,13,28}$.

Further analysis using grazing-incidence small-angle X-ray scattering (GIXS) confirmed the structural enhancement both in density and uniformity$^{29}$. The localized diffraction pattern indicates the orientational in-plane ordering of CQDs in hybrid-amine films (Fig. 3e and Supplementary Fig. 6b). This feature is absent in CQD films prepared using DMF (Supplementary Fig. 6e). Compared with control BTA films (Supplementary Fig. 10), we can clearly identify an additional ~10% densification in the planar direction and an average ~6–7% densification of the interdot spacing from azimuthal integration$^{30}$ of the diffraction pattern (Fig. 3f). The enhanced denstification during postannealing, the hybrid-amine films exhibited concurrent improvements (~20%) of the elastic modulus and hysteresis compared with the control BTA films (Fig. 3a,b). In addition, tapping-mode topographic AFM analysis of the film morphology showed that the local and global smoothness can be greatly improved by using hybrid-amine inks (Fig. 3c and Supplementary Fig. 13). For the progressively increasing field of views (5×5 to 30×30 µm$^2$), hybrid-amine films retain a surface roughness of ~0.6 nm, whereas control BTA films’ roughness increases from 1.4 nm to ~2 nm (Fig. 3d). The enhanced elastic modulus, in conjunction with improved smoothness, implies a simultaneous optimization of the CQD packing density and uniformity. Enhanced packing uniformity has recently been recognized as greatly benefiting the carrier transport in CQD assemblies$^{19,14,31,13,28}$.

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The CQD packing density in the control BTA films was previously characterized as being the densest compared with other state-of-art PV-quality films (for example, tetrabutylammonium halide salt-exchanged CQD films and metal–halide perovskite-exchanged CQD films$^{9}$). Attempts to densify the BTA films further with annealing typically deteriorated the V$_{OC}$ (Supplementary Figs. 8 and 14), a finding we attributed to the increased inhom-
Fig. 3 | Enhanced packing density and uniformity, and reduced structural disorder in CQD solids for solar cells. a, Mechanical characteristics of hybrid-amine films (force–indentation curves) measured by an AFM. Arrows indicate the tip approach and retraction. b, Elastic moduli and plastic deformation (calculated from the slope and its hysteresis in the linear rising region of force–indentation curves) between hybrid-amine films (before and after postannealing) and best-performing control films. Postannealed hybrid-amine films are PV-quality films and are characterized in c–f. c, Topographic AFM morphology analysis of hybrid-amine films, which show a surface roughness (RMS) of ~0.6 nm. d, Over progressively increasing field of views (5 × 5 to 30 × 30 µm²), the hybrid-amine films (red) exhibit a greatly reduced roughness compared with the best control films (grey). e, The GISAXS 2D pattern of the hybrid-amine films. The vertical black line on the lower left is the beam stop and the horizontal black line is due to the Pilatus 200k detector. The localized diffraction peak indicates the orientational in-plane ordering of the CQD assembly. f, Azimuthally integrated intensities of the diffraction peak. They show the distribution of interdot d spacing (d ≈ d), Azimuthally integrated intensities of the diffraction peak. They show the distribution of interdot d spacing (d ≈ d), which overcomes a long-lasting compromise that has been the focus of research. The enhanced resistance to heterogeneous fusion during CQD densification suggests that the CQD surface is greatly preserved with the aid of PbI₂-hybrid-amine complexes.

This preservation of CQD surfaces is supported by an investigation of the energetic disordering in films (Fig. 4). As observed in PL studies (Fig. 4a), additional postannealing induces a visible redshift and broadening of the peak for the best control BTA films, which indicates degradation of the energetic ordering. In contrast, in the hybrid-amine films subjected to the same postdensification process, the PL features were retained (Supplementary Fig. 15) and exhibited a sharper and slightly blueshifted PL peak relative to that of BTA films, which corresponds to an increased energetic ordering. In agreement with the above film-level studies, we also characterized the energetic disordering at the device level by highly sensitive techniques. In the energetic range of the band tail (Fig. 4b), in agreement with the PL results, the band tails of devices using hybrid-amine films are steeper than those of the best control BTA devices, and BTA films subjected to postannealing failed to preserve the bandtail sharpness.

Encouragingly, the suppression of structural and energetic disordering in the denser CQD solids successfully enhances the JSC and VOC simultaneously in the CQD PV devices (Supplementary Fig. 14), which overcomes a long-lasting compromise that has been the focus of many previously attempted strategies. In addition to the structural and energetic analyses, we also directly characterized the electronic parameters to quantify the enhancements to the photocarrier diffusion length for the optimized matrix. In the standard field effect transistor (FET) spectroscopy analysis, the hybrid-amine films exhibit higher n-type electronic mobility, associated with a sharper slope in the LDE = V DS response (Fig. 4c). From FET sub-threshold slope state density spectroscopy (Supplementary Fig. 16), hybrid-amine films also showed a reduction in sub-bandgap state densities (6.3 × 10¹⁵ cm⁻³) by one order of magnitude compared with the best BTA control films (5.7 × 10¹⁵ cm⁻³).

We also conducted an analysis under contact-free and photocactive conditions. We employed the donor–acceptor scheme of free charge carriers dominate the photophysical dynamics in these thick and highly coupled CQD films (Supplementary Fig. 18), a fact we attribute to rapid exciton dissociation. Acceptor emission contributed from exciton diffusion and trion recombination is negligible due to low inclusion ratio (< 0.1%) in films and low excitation intensity (< 1 Sun). The PL ratio (PL emission intensity of acceptors over that of donors in a film) increases when there are more acceptors included, for a shorter diffusion distance is required for carriers to reach the acceptors. The enhancement of mobility in hybrid-amine films is quantitatively confirmed by a twofold increase in the slope of the PL

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The advantages of hybrid-amine CQD solids enable the realization of thickened PV devices that offer to enhance simultaneously the \( J_{sc} \) and \( V_{oc} \). When we increased the absorber thickness from 250 nm to 600 nm, the full-spectrum EQE exhibited progressive broadband enhancement (Fig. 5a), with excitonic peak values of ~80% and integrated \( J_{sc} \) densities that approached 32 mA cm\(^{-2}\), a record level in a high-efficiency CQD PV. The retained high flat response in the blue region (<800 nm) and red excitonic region (>900 nm) in 600 nm thick films indicates a collection efficiency free of degradation for photocarriers at both the front and rear contacts, respectively. The experimentally acquired internal quantum efficiencies (Supplementary Fig. 20) are spectrally flat over the absorption region and indicate a near-unity charge generation and collection efficiency within these thick planar devices. They rule out energy-dependent charge generation and also argue against a strong quantitative influence of hot exciton or carrier effects.

The \( J_{sc} \) of devices with different thicknesses, measured under standard AM 1.5G solar illumination conditions (Fig. 5b), agree quantitatively with the EQE measurements. No sign of \( J_{sc} \) saturation appeared when the absorber thickness was increased from 250 nm to 600 nm. In contrast, the devices using the best-published control films showed an optimal \( J_{sc} \) (~27 mA cm\(^{-2}\)) and PCE (~11%) at the optimal thickness of ~350 nm (Fig. 5c). In agreement with previous reports, control devices with thicker absorbers exhibited losses in \( V_{oc} \) (from 0.62 V to 0.6 V) and FF, which we attribute to insufficient carrier diffusion lengths\(^{9,11}\).

The optimal devices using hybrid-amine CQD solids (excitonic peak at ~950 nm in a synthetic solution) can be achieved with thicknesses of ~500 nm. The devices showed a reproducible high performance with a champion PCE = 12.48% (Fig. 5d). One of our devices measured by an accredited PV laboratory (Newport Technology and Application Center, PV Lab) was found to display very similar figures of merit (\( V_{oc} = 0.647 \pm 0.009 \) V, \( J_{sc} = 29.04 \pm 0.60 \) mA cm\(^{-2}\), FF = 63.8 ± 1.3%) with PCE = 12.01 ± 0.26% (Fig. 5d and Supplementary Fig. 21), the highest certified PCE reported for a CQD solar cell. This further verified the stability and reproducibility of our new strategy of matrix engineering.

We also demonstrate large-area (1.1 cm\(^2\)) devices (Supplementary Fig. 22). The spatial and electrical uniformity of CQD films are verified by an excellent agreement among the EQE spectra measured at different locations across the large-area devices. The large-area devices exhibited \( V_{oc} \) and \( J_{sc} \) values that agree well with those of...
small-area (0.049 cm^2) devices. The somewhat lower PCE in large-area devices relative to small-area devices majorly resides in the FF due to the limited series resistance (R_s) of the transparent conductive oxide. We believe that strategies such as integrating metal grids onto indium tin oxide (ITO) can reduce the R_s limit in large-area CQD devices.

The evolution of device performance with progressively increasing matrix-to-CQD ratios (Supplementary Fig. 23) reveals the sensitivity with respect to the matrix size. The reduced J_sc × FF associated with the thicker matrix indicates the loss of interdot carrier hopping or tunnelling. This observation supports the type-I band alignment between CQD and the matrix composition in our films (Fig. 1c).

Overall, this work showcases a matrix engineering strategy that allows significant improvements in the photocarrier diffusion length in CQD solids. The enhanced structural and energetic ordering in densified CQD films allows us to overcome the long-lasting compromise between devices’ Voc and J_sc, and therefore fulfill the advantage of building a thick device with record performance. More broadly, this study reveals the hidden sensitivity and flexibility of matrices’ microscopic nature in CQD solids, and provides a means to tune material properties within the wide scope of CQD applications, such as printable devices, tandem cells, photodetectors and light-emitting diodes.

Methods
Methods, including statements of data availability and any associated accession codes and references, are available at https://doi.org/10.1038/s41565-018-0117-z.

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References


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Author contributions

J.X. conceived the idea and contributed to most experimental work. E.H.S. supervised the project. O.V. and S.O.K. co-supervised the project. Mengxia Liu assisted in the device fabrication and experiment design. S.H. assisted in the devices certificate and experiment design. A.R.K., M.A. and A.A. performed the in situ measurements of film formation. R.M., M.S. and A.R.Q. performed the GIWAXS/WAXS measurements. G.W. and M.W. performed the AFM and PL measurements. A.H.P. performed the TA measurements. R.B. carried out the FET measurements. O.V. and O.O. carried out the device simulations. Min Liu carried out microscopic studies. O.V. facilitated the RBS analysis. J.X., O.V. and E.H.S. wrote the manuscript. All the authors assisted in the experiments and provided comments on the text.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information is available for this paper at https://doi.org/10.1038/s41565-018-0117-z.

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**Methods**

**Ligand exchange in solution.** PbS CQDs (bandgap ~1.3 eV) capped with oleic acid and dispersed in octane (50 mg ml\(^{-1}\)) were used. The solution-exchange process was modified from that of our previous report. The precursor solution for ligand exchange was made from lead halides (lead iodide 100 mM and lead bromide 40 mM) in DMF, with ammonium acetate (60 mM) to improve the solubility. The ligand exchange was performed in a centrifuge tube in air. PbS CQD octane solution (2.5 ml, 50 mg ml\(^{-1}\)) was first diluted in 10 ml octane and then added to a 20 ml precursor solution in DMF. These were mixed vigorously for ~2 min until the CQDs were totally transferred from the octane phase to the DMF phase. The CQDs in the DMF phase were washed three times using octane and then precipitated by adding toluene (~50–60% in a volume ratio compared with DMF). After centrifugation, the CQDs were separated and then dried in vacuum for 30 min to obtain PbS-capped CQD solid powders.

**Matrix engineering and film formation.** The hybrid amine was prepared by mixing BTA, amylamine and hexylamine (volume ratio 10:3:2). The hybrid amine was prepared by mixing BTA, amylamine and hexylamine (volume ratio 10:3:2). The hybrid amine was used to functionalize the surface of the as-prepared PbI\(_2\)-capped CQD solid powders. These were mixed vigorously for ~2 min until the CQDs were totally transferred from the octane phase to the DMF phase. The CQDs in the DMF phase were washed three times using octane and then precipitated by adding toluene (~50–60% in a volume ratio compared with DMF). After centrifugation, the CQDs were separated and then dried in vacuum for 30 min to obtain PbS-capped CQD solid powders.

**CQD planar solar cell fabrication.** The ZnO nanoparticle dispersion in methanol and chloroform (1:1 by volume ratio) was spin cast on ITO to form an electron-transport layer (ETL) (~100–150 nm in thickness). The ZnO nanoparticle dispersion in methanol and chloroform (1:1 by volume ratio) was spin cast on ITO to form an electron-transport layer (ETL) (~100–150 nm in thickness). The ZnO nanoparticles were synthesized following a published recipe. The CQD active absorber (~250–600 nm in thickness) was deposited on the ZnO layer using the fresh PV ink. The ZnO layer was formed by a postannealing step as described above. Then the hole-transport layer (HTL) (~50 nm in thickness) was deposited on the ZnO layer by a postannealing step as described above. Then the hole-transport layer (HTL) (~50 nm in thickness) was deposited on the ZnO layer. The pristine films were glassy and soft. A postannealing at 75 °C for ~15 min in an N\(_2\)-filled glovebox was performed to solidify the matrix and densify the CQD films. In control films, BTA or DMF was used to disperse the CQD solid powder to prepare the PV ink. In best-performing BTA films, however, the postannealing step needed to be eliminated as in previous reports. To tune the matrix-to-CQD ratio in the films, additional PbI\(_2\) was dissolved in the solvent (hybrid amine, BTA or DMF) to disperse the CQD solid powder.

**AM 1.5G solar efficiency measurement.** The active area (0.049 cm\(^2\)) was determined by the aperture placed between the solar cell and the AM1.5G solar simulator (Sciencetech class A). Through this aperture, the light intensity (1 sun, 100 mW cm\(^{-2}\)) was calibrated using a Mellers–Griot broadband power meter. The spectral mismatch was calibrated using a reference solar cell (Newport). The J–V curve was measured by a Keithley multimeter by scanning the bias forward (−0.7 V to 0.1 V) and backward (0.1 V to −0.7 V) to estimate the hysteresis effect. The steady-state PCE was then measured by fixing the bias at the maximum power output point determined from J–V curves (Supplementary Fig. 24).

**RBS.** RBS measurements were performed at the Tandetron facility at the University of Western Ontario. CQD films of ~300 nm thickness were deposited on Si substrates to avoid overlaps with the main elements in CQD films. All the samples were measured with a 3.7 MeV He\(^{+}\) beam (non-Rutherford resonance for nitrogen) and a dose of 10\(^{16}\) cm\(^{-2}\).

**GISAXS and GIWAXS.** GISAXS was carried out at the Cornell High Energy Synchrotron Source. The wavelength of the X-ray beam was 1.17 Å. A wide band-pass (1.47%) double-bounce multilayer monochromator was employed. The incident angle was set to 0.5° with respect to the sample plane. The exposure time was ~3 s. GISAXS and GIWAXS were also conducted using a SAXSLab Ganesha at the South Carolina SAXS Collaborative. A Xenocs GeniX 3D microfocus source was used with a copper target to produce monochromatic beam with a 0.154 nm wavelength. The instrument was calibrated just prior to the measurement using National Instrument of Standard and Technology reference material 640c. A Pilatus 300K detector (Dectris) was used to collect the 2D scattering pattern with a nominal pixel dimension of 172 x 172 µm. GISAXS data were acquired with an incident X-ray angle (α) of 0.5° with respect to the substrate using an X-ray flux of ~21.4 M photons per second upon the samples. Likewise, GIWAXS data were collected with α = 2° and an X-ray flux of ~36.3 M photon per second. The sample-to-detector distance was maintained at 452.1 and 112.1 mm for GISAXS and GIWAXS measurements, respectively.

**Long-time TA (flash photolysis).** Pump pulses were generated with a regenerative amplified ytterbium:potassium–gadolinium–tungstate laser at a 5 kHz repetition rate (PHAROS (Light Conversion)). The 1,030 nm fundamental was sent through an optical parametric amplifier (OrpheusLight Conversion), and the second harmonic of the idler was chosen for the 750 nm pump pulse. The probe was generated by a continuous-wave 1,310 nm laser diode (LPM1310-05E (Newport)). Both beams were focused onto the sample, and the probe was coupled to an InGaAs-amplified detector (PDA101D (Thorlabs)). The lifetime response was measured using a 1 GHz oscilloscope (DSO8104A (Agilent)), which was triggered by the pump laser.

**AFM.** The AFM study was done with an Asylum Research Cypher AFM equipped with AC240TM-R3 probes (resonant frequency 70 kHz, spring constant 2 N m\(^{-1}\)). Nanomechanical force spectroscopy was conducted with a trigger indentation force of 8 nN loaded at a rate of 2 nN s\(^{-1}\). Topographic imaging was performed in the tapping mode.

**Other characterizations.** Fourier transform infrared spectroscopy (FTIR) measurements were done using a Bruker Vertex 80 (4,000 to 600 cm\(^{-1}\), resolution 4 cm\(^{-1}\)) in the top configuration (attenuated total reflection (ATR)). Steady-state PL was carried out using an HORIBA Fluorolog-3 spectrofluorometer equipped with UV–vis–NIR photomultiplier tube detectors and a monochromatized xenon lamp excitation. UV–vis–infrared absorption was carried out on a PerkinElmer LAMBDA 950 spectrophotometer. EQE spectra measurements were carried out following a previously published process\(^{7}\).

**Reporting Summary.** Further information on experimental design is available in the Nature Research Reporting Summary linked to this article.

**Data availability.** The authors declare that the data supporting the findings of this study are available within the paper and its supplementary information files. The data that support the findings of this study are also available from the corresponding authors upon reasonable request.
Experimental design

Please check: are the following details reported in the manuscript?

1. Dimensions
   - Area of the tested solar cells
     - Yes
     - No
     - Certified device with small area ~0.049 cm² (Supplementary Figure S21). Large-area device 1 cm² (Supplementary Figure S22).
   - Method used to determine the device area
     - Yes
     - No
     - See the Methods (AM1.5 solar efficiency measurement). Optical aperture is used to define the active area.

2. Current-voltage characterization
   - Current density-voltage (J-V) plots in both forward and backward direction
     - Yes
     - No
     - See Methods (AM1.5 solar efficiency measurement) and Supplementary Figure S24.
   - Voltage scan conditions
     - Yes
     - No
     - Forward scanning (-0.7 V to 0.1 V) and backward (0.1 V to -0.7 V) with different speeds. No hysteresis was observed in all typies of CQD PV devices. Steady-state power conversion efficiency (PCE) is then measured by fixing the bias at the maximum power output point (VMPP). The PCE reported in main text was determined by the steady-state performance.
   - Test environment
     - Yes
     - No
     - NEWPORT certificate tested in N₂. Temperature 25°C.
   - Protocol for preconditioning of the device before its characterization
     - Yes
     - No
     - See Methods (AM1.5 solar efficiency measurement) and Supplementary Figure S24.
   - Stability of the J-V characteristic
     - Yes
     - No
     - Steady-state power conversion efficiency (PCE) is measured by fixing the bias at the maximum power output point (VMPP). The PCE reported in main text is determined by steady-state performance at maximum power point (MPP). Because there is no hysteresis in all CQD PVs, the PCE value from steady-state tests and J-V curves are identical.

3. Hysteresis or any other unusual behaviour
   - Description of the unusual behaviour observed during the characterization
     - Yes
     - No
     - No hysteresis was observed for all CQD PV devices, including both the control devices and hybrid-amine devices. The hysteresis-free behavior in CQD PVs is also widely-accepted in literature.
   - Related experimental data
     - Yes
     - No
     - Supplementary Figure S24.

4. Efficiency
   - External quantum efficiency (EQE) or incident photons to current efficiency (IPCE)
     - Yes
     - No
     - Figure 5 and Supplementary Figure S22.
   - A comparison between the integrated response under the standard reference spectrum and the response measure under the simulator
     - Yes
     - No
     - Figure 5 and Supplementary Figure S22.
   - For tandem solar cells, the bias illumination and bias voltage used for each subcell
     - Yes
     - No
     - Not applicable. No tandem device was involved in this work.
5. Calibration

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<td>Calculation of spectral mismatch between the reference cell and the devices under test</td>
<td>Yes</td>
<td>See Methods (AM1.5 solar efficiency measurement)</td>
</tr>
</tbody>
</table>

6. Mask/aperture

<table>
<thead>
<tr>
<th>Question</th>
<th>Yes/No</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size of the mask/aperture used during testing</td>
<td></td>
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<tr>
<td>Variation of the measured short-circuit current density with the mask/aperture area</td>
<td>Yes</td>
<td>See Methods (AM1.5 solar efficiency measurement) and Supplementary Figure S21. Aperture size 0.049cm² for small-area device. Aperture size 1cm² for large-area device.</td>
</tr>
</tbody>
</table>

7. Performance certification

<table>
<thead>
<tr>
<th>Question</th>
<th>Yes/No</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identity of the independent certification laboratory that confirmed the photovoltaic performance</td>
<td>Yes</td>
<td>See Methods (AM1.5 solar efficiency measurement) and Supplementary Figure S21. Certificate Performance from NEWPORT agrees with the value tested in our lab (Fig 5).</td>
</tr>
<tr>
<td>A copy of any certificate(s) Provide in Supplementary Information</td>
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</table>

8. Statistics

<table>
<thead>
<tr>
<th>Question</th>
<th>Yes/No</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of solar cells tested</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Statistical analysis of the device performance</td>
<td>Yes</td>
<td>Fig 5. In the thickness-dependent studies, for each thickness, 12 samples for each type (control and hybrid) fabricated in the same batch were tested.</td>
</tr>
</tbody>
</table>

9. Long-term stability analysis

<table>
<thead>
<tr>
<th>Question</th>
<th>Yes/No</th>
<th>Notes</th>
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</thead>
<tbody>
<tr>
<td>Type of analysis, bias conditions and environmental conditions For instance: illumination type, temperature, atmosphere humidity, encapsulation method, preconditioning temperature</td>
<td>Yes</td>
<td>As widely reported in the literature (see below references), the state-of-art CQD devices show no hysteresis and are stable in air. We found our devices are consistently hysteresis-free and air-stable, very similar with that reported for control devices. Ref 1. Chuang, C.-H. M., Brown, P. R., Bulović, V. &amp; Bawendi, M. G. Improved performance and stability in quantum dot solar cells through band alignment engineering, Nat Mater 13, 796–801 (2014). Ref 2. Liu, M. et al. Hybrid organic-inorganic inks flatten the energy landscape in colloidal quantum dot solids. Nat Mater 16, 258–263 (2016).</td>
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