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Efficient hybrid colloidal quantum dot/organic solar cells mediated by near-infrared sensitizing small molecules

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Solution-processed semiconductors are promising materials to realize optoelectronic devices that combine high performance with inexpensive manufacturing. In particular, the exploitation of colloidal quantum dots (CQDs) capable of harvesting infrared photons, in conjunction with visible-absorbing organic chromophores, has been demonstrated as an interesting route. Unfortunately, CQD/organic hybrid photovoltaics have been limited to power conversion efficiencies (PCEs) below 10% due to chemical mismatch and difficulty in facilitating charge collection. Here we devise a hybrid architecture that overcomes these limitations by introducing small molecules into the CQD/organic stacked structure. The small molecule complements CQD absorption, creates an exciton cascade with the host polymer, thus enabling efficient energy transfer and also promoting exciton dissociation at heterointerfaces. The resulting hybrid solar cells exhibit PCEs of 13.1% and retain over 80% of their initial PCE after 150 hours of continuous operation unencapsulated, outperforming present air-processed solution-cast CQD/organic

photovoltaics.

Solution-processed semiconductors such as perovskites[1], organics[2], and colloidal quantum dots[3] are materials that, with their distinctive photophysical and optoelectronic properties, enable the realization of next-generation photodetectors, light-emitting diodes, and solar cells exhibiting programmable characteristics.[4]

Colloidal quantum dots (CQDs) can be tuned in absorption across the solar spectrum via size-dependent quantum confinement. Advances in the last decade in CQD chemistry, surface passivation, film assembly, and device architecture have led to the demonstration of CQD solar cells with certified power conversion efficiencies (PCEs) of 12%.[5] Present-day best CQD solar cells use a depleted heterojunction architecture consisting of a halide solution-exchanged CQD photoactive layer and a hole transport layer comprised of a thiol-exchanged CQD film.[6]

In organic semiconductors, bulk-heterojunction (BHJ) architectures are often employed. Donor and acceptor molecules are intermixed at the nanoscale to generate heterojunctions throughout the active layer. This is required to overcome short exciton diffusion lengths within disordered polymers and small-molecule-based materials.[2] These diffusion lengths are usually limited to tens of nm – well below the absorption length of light in these materials.

Since hybrid CQD/organic solar cells were proposed,[7] various strategies for CQD/organic heterostructures have been studied with the goal of combining the advantages of the two classes of materials and thereby achieving higher PCE and stability.[8] Many of these hybrid structures demonstrated complementary absorption spectra; but failed to exploit this to improve performance in optoelectronic devices due to poor charge transfer and carrier extraction efficiencies, limiting PCEs to below 10%.[8]

We revisited the CQD/polymer architecture with the goal of overcoming these challenges. Here, we sought to modify the polymer layer by mixing in a low-bandgap non-fullerene small molecule. The introduction of a small molecule bridge into the polymer layer allowed us to increase the efficiency of exciton dissociation and funneling – as revealed using ultrafast transient absorption and photoluminescence excitation spectroscopies, as well as external and internal quantum efficiency measurements – and thereby enabled improved charge extraction efficiencies exceeding 90% across the visible and near-infrared. Due to absorption that is complementary in the host polymer vs. the CQD film, photocurrents in hybrid devices are also

improved.

Using this architecture, we achieve a PCE of 13.1%, which is the most efficient organic/CQD hybrid solar cell reported. In addition, we demonstrate devices having continuously stable operation (80% of initial PCE, t_{80}) of 150 hours at their maximum power point, relying neither on a UV filter nor on encapsulation, outperforming prior air- and solution-processed CQD/organic photovoltaics.

Small-molecules as a bridge between the CQD and the polymer

We began by considering architectures that could accommodate a CQD/polymer hybrid material configuration. CQD/polymer BHJ structures have been widely investigated to this end[8] and have exploited PDPPTPD[9], PDTPBT[10], P3HT[11,12], PDTPQx[13] and si-PCPDTBT[14] paired with various CQDs. In a bilayer configuration, on the other hand, a polymer layer is stacked vertically on a CQD film. With the goal of constructing an efficient CQD/polymer hybrid, we screened a range of *p*-type polymers and explored their combinations with CQDs both in BHJ and bilayer configurations. (Fig. 1a) We sought low-bandgap polymers[15-17] with absorption bands between 550 ~ 850 nm that could complement those of the PbS CQDs and improve light harvesting (Supplementary Fig. 1).

Representative current density-voltage (*J-V*) curves and photovoltaic parameters of various CQD/polymer hybrids are shown in Fig. 1b and Supplementary Table 1, respectively. In these devices, active layers consisted of CQDs passivated with 1-ethyl-3-methylimidazolium iodide (EMII) ligands. PCEs ca. 10% were obtained for CQD control devices using a top (hole transporting) layer of CQDs treated with 1,2-ethanedithiol (EDT), a commonly used CQD bilayer architecture. When polymers are used instead of an EDT-CQD layer, all CQD/polymer bilayer combinations exhibited significantly lower performance, with PCEs below 5%. The short-circuit current (J_{sc}) reached only half of that of the CQD reference devices despite a similar total absorption. The external quantum efficiency (EQE) of the hybrid devices is particularly low in the wavelength range corresponding to absorption in the polymer, suggesting that photogenerated excitons fail to dissociate at polymer/CQD boundaries, and so carriers are not extracted efficiently[18] (Supplementary Fig. 1c). We also explored a suite of BHJ structures with the goal of overcoming limitations in exciton diffusion, dissociation and charge extraction. (Fig. 1b) However, hybrid BHJ devices exhibited a lower performance than the bilayer structures, which we attributed to a poor CQD/polymer interpenetration network

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arising from the large surface energy difference between inorganic CQDs and polymers (Supplementary Fig. 2),[19] interfacial defect recombination at the CQD surface,[20] rapid geminate recombination at the halide CQD:polymer interface.[21]

These findings led us to posit that introducing an auxiliary *n*-type organic semiconductor into the polymer could potentially reduce geminate recombination and assist charge transport to the CQD-polymer boundary by dissociating strongly bound excitons into free charge carriers. Hybrid *p*-type CQD/polymer structures employing PCBM have been studied previously;[22,23] however, this approach failed to achieve high PCEs and resulted in poor stability due to the narrow absorption band of PCBM, the large driving energy for exciton separation at the CQD/PCBM interface (which severely limited V_{oc})[24,25], and oxidation or dimerization of PCBM.

Ideally, well-designed molecular additives would exhibit an acceptor-like behavior that would induce faster exciton dissociation at interfaces and establish an energy gradient that could facilitate cascading energy transfer of excitons and electrons toward the *n*-type CQD film, acting as a bridge between the two materials. Recently, non-fullerene small molecules suitable for this application – exhibiting a low bandgap, distinctive absorption bands in the NIR, and compatibility with *p*-type polymers – have been reported.[2] We selected the small-molecule acceptor bridge (hereafter called SM-bridge) (2,2 '- ((2Z, 2'Z) - ((5,5'-bis (4,4,9,9-tetrakis) - 4,9-dihydro-s-indaceno [1,2-b: 5,6-b '] dithiophene-2,7-diyl) bis (4- (2-ethylhexyl) oxy) thiophene-diyl) bis (methanylylene)) bis- (3-oxo-2,3-dihydro-1H-indene-2,1-diylidenene) dimalononitrile (IEICO)).[26] (Fig. 1c) With its 1.34 eV bandgap, the SM-bridge absorbs light between 600 and 900 nm and thus complements the absorption of the CQD/polymer hybrids (Fig. 1d). For the host *p*-type polymer, we selected PBDTTT-E-T, a copolymer of benzo[1,2-b:4,5-b']dithio-phene (BDT) and thieno[3,4-b]thiophene (TT), because of the previously-reported high-quality morphology of mixed solids of PBDTTT-E-T and IEICO.[2]

In order to evaluate the energy levels of each material and verify that the proposed SM-bridge has a favorable band alignment with the polymer and CQD components, we performed ultraviolet photoelectron spectroscopy (UPS) on its individual constituents (Supplementary Fig. 3). Halide-treated CQD films exhibit an *n*-type behavior and a deeper conduction band (-3.90 eV) than that of the SM-bridge. The SM-bridge exhibits a HOMO level of -5.23 eV and a LUMO level of -3.84 eV, straddled by the valence band of the CQDs and the LUMO level of

the polymer (Fig. 1e). In this energy landscape, electrons photoexcited at the polymer and SM-bridge sites transport toward the CQD layer.

Charge carrier dynamics in the CQD/polymer:SM-bridge systems

We next sought to understand charge and energy transfer dynamics among the various organic and CQD components using a suite of spectroscopic techniques. (Fig. 2a,b) In photoluminescence (PL) emission experiments, photoexciting the polymer:SM-bridge mixed layer leads to increased emission from the SM-bridge (~870 nm), accompanied by reduced emission from the polymer donor (~760 nm), consistent with energy transfer from the polymer donor to the SM-bridge.[27,28] The spectral overlap of the SM-bridge emission and CQD absorption suggests energy transfer from the SM-bridge to the CQDs should also be favorable.[28] Normalized PL spectra show a shift in emission toward the CQD bandgap, indicative of energy transfer (Supplementary Fig. 4 and Supplementary Note 1).[29] This indicates that the SM-bridge helps to form an energy funnel that facilitates transfer of excitons photogenerated in the polymer domains to the CQD layer.

To evaluate more clearly if energy transfer occurs from the organic to CQD domains, we carried out photoluminescence excitation (PLE) spectroscopy on bilayer films comprised of polymer/CQDs and SM-bridge/CQDs, photoexciting the top surface of the stack (Fig. 2b). We prepared the CQD layer using larger sized dots (excitonic peak: ~1050 nm) and monitored the PL emission at 1200 nm, thus avoiding PL from the organics themselves. By photoexciting at wavelengths across the absorption range (500 – 950 nm), we recover the shape of the static absorption spectrum of each organic molecule, revealing energy transfer from the molecules to the underlying CQD layer. (Fig. 2c) Notably, in the normalized PLE spectra, we find that when we compare the ratio of the peak amplitude for emission originating from exciting the organic molecule (between 600 – 800 nm), compared to direct excitation of the CQDs (near 500 nm), this ratio is greater for the SM-bridge than for the polymer, indicating that energy transfer to the CQDs from the SM-bridge is more efficient compared to the polymer (Supplementary Fig. 4).

The type-II band alignment between the organic and the CQD layers indicates that excitons and electrons migrate from the organics to CQDs, and that hole transfer must occur from CQDs to organics (Fig. 1e). We probed this process using ultrafast transient absorption spectroscopy

(TAS). TA spectra for hybrid/CQD films are shown in Fig. 2d. The generation of an excited state population in the CQDs (evidenced by the CQD bandedge exciton bleach at 900 nm) is followed by the build-up of bleach signal at ~730 nm from the polymer (Supplementary Fig. 11), which appears at early delay times and becomes larger in amplitude over 100s of picoseconds (Fig. 2d). This is consistent with hole transfer from photoexcited CQDs into the polymer layer (Supplementary Fig. 10 and Supplementary Table 2). Global fitting of the TA data with three decay associated spectra (DAS) and associated time constants and gives an approximate hole transfer time of 270 ps (Fig. 2g). Similar TAS experiments on SM-bridge/CQD films show the absence of hole transfer from CQDs to SM-bridge (Supplementary Fig. 5,8,9), and bleaching of only the polymer component is observed in the same experiment for polymer:SM-bridge/CQD films, indicating the hole-transporting role of polymer domains (Supplementary Note 2).

In addition to exciton funneling, another important role of the SM-bridge is to serve as an electron acceptor at the polymer:SM-bridge interfaces. In the absence of the SM-bridge, energy transfer will be the dominant carrier migration mechanism in the polymer film. Due to the short exciton diffusion length within the disordered polymer film,[30] the majority of excitons will be quenched before reaching the polymer/CQD interface (Supplementary Fig. 1). Acceptor-like molecules can help overcome this limitation by facilitating charge separation of the exciton at donor:acceptor interfaces through interfacial charge transfer (CT) states, generating longer-lived free electrons and holes.

To investigate whether the incorporation of the SM-bridge into the polymer domains leads to such dynamics, we performed additional TAS experiments on the organic blends (photoexciting at 730 nm) (Fig. 2e,f) and again performed global analysis to extract DAS spectra,[31] shown in Fig. 2h,i. We observe photoinduced absorption (PIA) signals for the blend that are longer-lived and redshifted compared to the unblended individual polymer and SM-bridge components, an observation that is characteristic of CT states in organic blends. (Supplementary Fig. 11,12 and Supplementary Note 3,4). We also found that this PIA signal is larger in amplitude when the organic blend is formed atop the CQD layer, attributable to additional CT state formation at the organic/CQD interface (Fig. 2f and Supplementary Fig. 13).[32] A similar PIA amplitude increase is also observed for the individual SM-bridge and polymer components when they are interfaced with the CQDs (Supplementary Fig. S12). The formation of these interfaces should favor exciton dissociation, enabling improved charge

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extraction under solar cell operation (Supplementary Fig. 11,14). We propose that the SM-bridge, in addition to serving as an exciton relay, serves as electron acceptor from the polymer, diminishing exciton quenching within the polymer domains. (Supplementary Note 4,5)

Absorption and charge extraction enhancement

We then sought to take advantage of the auspicious photoinduced carrier dynamics in the CQD/SM-bridge:polymer hybrids to build improved photovoltaic devices (Fig. 3a). CQD solids and polymer layers were sequentially deposited, forming the CQD/polymer heterostructure. SM-bridges were mixed into the polymer prior to its deposition. Atomic force microscopy (AFM) revealed rod-shaped grains of several tens of nanometers in polymer:SM-interfaces (Supplementary Fig. 15).[33] Cross-sectional transmission electron microscopy (TEM) shows the structure and thickness of each layer in the complete device: ZnO (30 nm) / CQDs (150 nm) / polymer (with or without SM-bridge, 65 nm) / MoO_3 (10 nm) / Ag (150 nm) (Figure 3a). The elemental depth profiling measured via time of flight-secondary ion mass spectroscopy (ToF-SIMs) agrees with the imaged structure (Supplementary Fig. 16).

Next, we characterized the solar cells under simulated solar irradiation and found that the resulting device performance depends heavily on the use of the SM-bridge (Supplementary Fig. 17). Notably, short-circuit current (J_{sc}) was significantly enhanced, from 13 to 23 mA·cm^{-2}, upon incorporation of the SM-bridge. To investigate the origins of the observed J_{sc} enhancement, we studied the spectral response of our CQD/polymer hybrid devices (Fig. 3b-d). The EQE of CQD/polymer without the SM-bridge lies below 40% for wavelengths longer than 600 nm. Incorporation of the SM-bridge led to a two-fold enhancement in EQE in this wavelength region, in which the organics contribute significantly to photocurrent.

To gain additional insight into the origins of the observed enhancement in EQE, we measured the total absorption and internal quantum efficiency (IQE) spectra. CQD/polymer films without the SM-bridge showed a similarly high absorption up to 700 nm, corresponding to the absorption peak of the polymer. (Fig. 3d) Near-infrared absorption increases significantly near 800 nm in samples including the SM-bridge, consistent with the absorption peak of the SM-bridge (Fig. 1d).

To determine the contribution of each material to the total absorption, we calculated the net absorption of both CQDs and organic layers using the transfer matrix formalism (TMF) (Fig.

3e,f). CQD/polymer devices without the SM-bridge exhibit broadband CQD absorption spanning from 300 to 1000 nm and strong polymer absorption between 550 nm and 750 nm. Samples including the SM-bridge show improved total absorption from 750 to 900 nm due to the contribution of the SM-bridge. From these results, we estimated the current density corresponding to the calculated absorption at perfect charge extraction conditions (i.e. IQE = 100%) and observed a 1.6-fold increase in J_{sc} from the polymer (from 5 to 8 mA·cm^{-2}) upon insertion of the SM-bridge.

We then calculated the IQE spectrum of CQD/polymer hybrids with and without SM-bridge (Fig. 3c). The CQD/polymer hybrids show a wavelength-dependent IQE particularly in the 600 to 750 nm range, corresponding to the absorption band of the polymer. CQD/SM-bridge:polymer samples, on the other hand, show a consistently higher IQE throughout the entire wavelength range 300 - 1000 nm, with an average IQE of 90% as mentioned above. In particular, the IQE dip between 600 - 750 nm disappears, which we ascribe to improved energy transfer and charge extraction dynamics at organic boundaries, as attested to by spectroscopic investigations.

Performance of CQD/organic hybrid photovoltaics

We optimized the CQD/SM-bridge:polymer hybrid composition to maximize light harvesting efficiency and photovoltaic performance. The CQD layers were prepared by using a solution-phase ligand exchange, resulting in improved performance compared to typical solid-state layer-by-layer exchange processes.[34] We achieved a PCE of 13.1% for CQD/SM-bridge:polymer hybrids, significantly higher than organic-only (polymer:SM-bridge BHJ) (8.0%) and CQD-only (CQD/EDT-treated CQD) (10.4%) reference devices (Fig. 4a). This represents the most efficient organic/CQD hybrid structure reported (Supplementary Fig. 19 and Supplementary Table 3). The PCE histogram of hybrid devices displays an average efficiency of 12.4% (Fig. 4b). Optimized devices exhibit a J_{sc} of 30 mA·cm^{-2} for this CQD bandgap, highlighting the benefits of using CQDs and organics together to improve light harvesting. The EQE exceeds 80% in the visible range and reaches 60% in the near infrared (Fig. 4c). In addition, the hybrid structure also showed higher a V_{oc} (0.66 V) compared to the CQD-only (0.64 V) and CQD/polymer without SM-bridge (0.60 V) devices (Supplementary Table 1), attributable to improved charge separation and hole extraction which in turn suppress recombination − consistent with our observations from TAS (Fig. 2), IQE (Fig. 3) and

impedance spectroscopy (Supplementary Fig. 20 and Supplementary Note 6).[35] The hybrid devices also exhibit good stability, with a certified PCE of 12.3% after 1500 h of shelf storage under ambient conditions without encapsulation (Supplementary Fig. 21), retaining over 90% of their initial PCE even after 3500 h (Fig. 4d).

Encouraged by the enhanced shelf stability of the proposed hybrid platform, we then sought to evaluate their stability in more demanding conditions. We tracked the performance under continuous illumination at the maximum power point (MPP), with neither encapsulation, UV-filter, nor controlled atmosphere (Fig. 4e). The operating lifetime of hybrid devices outperformed organic- and CQD-only devices by a factor of 100 and 5, respectively, retaining over 80% of the initial performance after 150 h. Photo oxidation of organic molecules due to high energy UV photons is well known to hinder the stable operation of organic solar cells.[36] In this hybrid architecture, high-energy photons are absorbed in the CQD film prior to reaching the organic materials, thereby significantly reducing this photodegradation mechanism. The hybrid structures also showed higher stability than CQD-only devices because of efficient oxygen and moisture blocking by the organic layers covering the CQD layer.[37] In addition, the SM-bridge organic layer has a superior stability compared to prior PCBM-CQD hybrids, which exhibited limited photostability due to the oxidation and dimerization of PCBM under irradiation.[38,39] The resulting MPP stability (t_{80} ~ 150 hr, PCE of 13.1%) of the hybrid structure is the highest among organic (t_{80} ~ 90 hr, PCE of 7.7%) and CQD-based solar cells reported to date.[36,40] The hybrid structure presented herein circumvents the need to rely on filters and highly controlled atmospheres, making it a competitive photovoltaic platform for commercially viable solar energy harvesting.

Conclusions

In this work, we demonstrate a CQD/polymer hybrid platform that outperforms CQD and organic PV devices in both PCE and stability. We achieved this by introducing a SM-bridge in the polymer layer that improves NIR absorption and charge separation. This combination leads to a maximum PCE of 13.1% and a certified value of 12.3% following 1500 h of unencapsulated storage, outperforming previously reported CQD and organic (and hybrid) PV cells. In addition, hybrid devices exhibited excellent stability even under demanding operating conditions. We demonstrated that hybrid devices retain more than 80% of their initial performance after 150 h of continuous operation at MPP under one sun illumination in air, with

neither UV filter nor encapsulation. This joint advance in PCE and stability highlights the potential of this hybrid technology to realize inexpensive, air-processed, efficient and stable solution-processed photovoltaics.

Methods

CQD:organics hybrid device fabrication: Oleic acid-capped lead sulfide (PbS) CQDs (first excitonic peak at 850 - 930 nm) were prepared as previously described.[34] For the fabrication of hybrid devices, a ZnO sol-gel solution, mixture of zinc acetate dihydrate:ethanolamine = 1:0.28 wt% dissolved in 10 ml of methoxyethanol, was spin-cast onto a pre-cleaned ITO substrate and dried at 200°C for 10 min, forming a 30 nm-thick layer. Five layers of the EMII-treated PbS CQDs were coated using a layer-by-layer (LBL) process (Fig. 1-3).[41] For the hybrid CQDs layer (Fig. 4), we used solution-processed ligand exchange processes instead of LBL process as previously reported.[34] Briefly, oleic-capped PbS CQDs are exchanged by the PbX$_2$/AA solution-phase ligand-exchange process. (PbI$_2$: 0.1 M and PbBr$_2$: 0.02 M and AA (NH$_4$Ac): 0.04 M). Exchanged dots are precipitated and dried in a vacuum chamber for 10 min. The final CQDs were dispersed in butylamine (BTA), forming a CQD ink at a concentration of 250 mg/ml and spin-coated at 2500 rpm for 30 sec. After one day of air drying, a prepared solution of (PBDTTT-E-T:IEICO=1:1, 15mg/ml in chlorobenzene:1,8-diiodoctane=98:2 wt%) was spin-coated at 3000rpm for 60 sec. Organic molecules were purchased from 1-materials. All films were coated onto the substrate under ambient conditions. Subsequently, the film was dried at 100°C for 5 min. Finally, the MoO$_3$ (10 nm) / Ag (150 nm) electrode was deposited using thermal evaporation under high vacuum (<10^{-6} torr) through a shadow mask.

CQD/polymer bilayer solar cells: For the fabrication of CQD/polymer devices, a ZnO sol-gel solution was spin-cast onto pre-cleaned ITO substrates and dried at 200°C for 10 min. Five layers of the EMII-treated PbS CQDs were coated using a LBL process. After one day of air drying, the various polymer solutions (10 mg/ml in chlorobenzene) were spin-coated at 3000 rpm for 30 sec. Subsequently, the films were dried at 100°C for 5 min. Finally, MoO$_3$ (10 nm) / Ag (150 nm) electrodes were deposited using thermal evaporation. All films were coated on substrate under ambient conditions.

CQD/polymer BHJ solar cells: For the fabrication of CQD/polymer BHJ devices, a ZnO sol-

gel solution was spin-cast onto pre-cleaned ITO substrates. Oleic acid-capped PbS CQDs were mixed with polymer solutions (5 mg/ml in chloroform) and spin-coated at 3000 rpm for 30 sec under ambient conditions. The resultant films were treated using the EMII ligand and dried in ambient conditions. Finally, the MoO_3 (10 nm) / Ag (150 nm) electrodes were deposited using thermal evaporation.

Transient absorption measurement: Femtosecond laser pulses (1030 nm, 5 kHz repetition rate) were produced using a regeneratively amplified Yb:KGW laser (PHAROS, Light Conversion). The majority part of the fundamental beam was used to pump an optical parametric amplifier (ORPHEUS, Light Conversion) while the minority part was focused into a sapphire crystal to generate a white-light continuum probe. The pump pulse duration was estimated to be ~200 fs. Both the pump and probe pulses were directed into a commercial transient absorption spectrometer (Helios, Ultrafast). Delaying the probe pulse relative to the pump provides a time window of up to 8 ns. Measurements were performed using an average power less than 50 μW with a spot size of ~0.40 μm^2 at wavelengths of 730 or 930 nm. These fluences are sufficiently low to avoid Auger recombination in the directly photoexcited CQDs or exciton-exciton annihilation in the organics.[42]

Photoluminescence (PL) and PL excitation measurements: PL characterization was performed using a Horiba Fluorolog system. Static PL was collected by illuminating the samples using a monochromatic Xe lamp. The excitation wavelength was 633 nm and emission was scanned from 700 nm to 1200 nm. For PLE measurements, PL signals were detected at 1200 nm to probe only CQD PL. Excitation wavelengths were scanned from 500 nm to 950 nm in 5 nm steps. The PL signal of the organics was negligible beyond 1100 nm, (Supplementary Fig. 23) implying that PLE signal solely originated from CQDs. Larger-sized (smaller-bandgap) CQD (excitonic peak: ~ 1050 nm) films were used for PLE measurements to obtain a clear, non-overlapping PL feature near 1200 nm (Supplementary Fig. 23). All films were prepared on the glass substrates using same method as in device fabrication.

Time-Resolved Photoluminescence (TRPL) measurement. For the TRPL measurements, a Hamamatsu C9300 streak camera with a time resolution of 15 ps system was employed. The excitation source for the TRPL was a Libra 1 kHz femtosecond Ti:sapphire regenerative amplifier system with a central wavelength of 780 nm and an 80 fs pulse duration. About 95% of the laser beam was sent to a Coherent TOPAS Prime optical parametric amplifier (OPA) to

be used as a tunable beam. TRPL traces were measured in the wavelength region of 750 − 850 nm under 700 nm excitation.

Solar cell characterizations: The *J-V* curves of the photovoltaic devices were characterized using a Keithley 2400 sourcemeter under 1-sun illumination with AM 1.5G solar spectrum (Sciencetech, class AAA) from an Xe lamp (Solar Light Company Inc.). The irradiance was calibrated using a reference Si solar cell (Newport, Inc.) to 100 mW·cm^{-2}, and the aperture size of each device was 0.0625 cm^2. The external quantum efficiency (EQE) was measured using a spectral measurement system (K3100 IQX, McScience Inc.). The spectral reflection of the solar cells was measured immediately after the EQE measurement at the same position.

Stability tests: Shelf lifetime was obtained from devices stored in air without encapsulation. For the operating lifetime at MPP, the device was held at V_{mpp}. The unencapsulated device was under 1 sun illumination. All devices were characterized under ambient conditions and the humidity and temperature were typically in the range of 30-50% and 27-30°C. Stability was characterized for devices with the best PCE in the various configurations depicted in Fig. 4a.

Optical calculations: For the calculations, all refractive indices were obtained by variable angle spectroscopic ellipsometric (VASE) and a homemade MATLAB code was used to implement TMF.[43] (Supplementary Fig. 18) Thicknesses were obtained from TEM images. We assumed that each layer was flat and considered no scattering effects. Note that the current density as described in Fig. 3d corresponds to the assumption of a maximum value perfect carrier extraction (i.e. IQE = 100%).

Absorbance measurements: Absorbance spectra were measured using a UV-vis-IR spectrophotometer (Lambda 950).

SEM ,TEM and TOF-SIMs: The cross-section electron microscope image of the hybrid device was obtained by focused-ion-beam (FIB, Helios 450 F1) and field-emission TEM (300 keV). TOF-SIMs (TOF-SIMS5, ION-TOF GmbH) was measured to clarify the device structure.

AFM measurements: AFM imaging (BRUKER, multimode 8) was performed in scanasyst mode with 1 Hz scanning speed.

Ultraviolet photoelectron spectroscopy: UPS (Sigma Probe, Thermo VG Scientific) was performed to characterize the energy level of each material.

Data availability

The authors declare that the main data supporting the findings of this study are available within the article and its Supplementary Information. Extra data are available from the authors upon request.

Acknowledgments

Author contributions

S.B., S.J., B.K. and A.H. P. equally contributed on this work. S. B., F. P. G. A., S. O. K., S. H. and O. V. developed the idea and prepared the manuscript. S. J., G. W., A. H. P., H. R. B. and M. S. J. studied and characterized carrier dynamics and C. K., B. K. optimized record device structure. J. K., J. S. and S. J. synthesized CQDs dots and characterized films. O. O. performed optical calculations. J. L. and E. H. S. supervised the project. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Figure Legends

Figure 1 | Hybrid CQD/polymer structure design strategy. a, Illustration of prior CQD/polymer (bilayer and bulk-heterojunction) and proposed CQD/polymer:SM-bridge structures. **b,** *J-V* curves of CQD/EDT-treated CQD control device (grey dashed line), CQD/PTB7 (yellow), CQD/PTB7-Th (red), CQD/PDTD-DFBT (orange) and CQD/PBDTTT-E-T (blue filled triangles) and CQD:PBDTTT-E-T (BHJ) (blue open triangles) under AM 1.5 illumination. **c,** Illustration and molecular structure of the PBDTTT-E-T polymer, the IEICO SM-bridge and the iodide-passivated PbS CQDs. **d,** Absorbance spectra of CQD (brown), polymer (yellow) and SM-bridge (red) films. **e,** Band alignment of polymer, SM-bridge, and CQD films.

Figure 2 | Photoinduced carrier dynamics in CQD:organics hybrid films. a, Static PL spectra of polymer (yellow), CQD/polymer (yellow dots), SM-bridge (red), CQD/SM-bridge (red dots), polymer:SM-bridge (blue), CQD/polymer:SM-bridge (blue dots) and CQD (brown) films under 633 nm excitation. **b,** Photoluminescence excitation (PLE) spectroscopy experiments. The detection wavelength is fixed at 1200 nm (corresponding to emission only from CQDs). The PLE spectra are of the polymer (yellow crosses), the SM-bridge (red crosses), polymer/CQD (yellow circles) and SM-bridge/CQD (red circles) bilayer films, respectively. Normalized absorbance spectra of CQDs (brown dashed line), polymer (yellow line) and SM-bridge (red line) layers are plotted. **c,** Schematics depicting energy transfer from organics to CQDs. Dark and light grey circles denote the electron and hole, respectively. **d,** Spectro-temporal TA maps and **g,** DAS for the CQD/polymer:SM-bridge with direct photoexcitation of the CQDs with NIR (930 nm) pump pulses. Inset illustrates hole transfer from CQD to polymer. Low excitation fluences were used in order to minimize Auger recombination in the photoexcited CQD layer.[42,44] **(e,f)** Spectro-temporal TA maps with a photoexcitation wavelength of 730 nm and their DAS **(h,i)** for films of polymer/CQD without **(e,h)** and with **(f,i)** SM-bridge.

Figure 3 | Structure and spectral response of hybrid solar cells. a, TEM cross-section of overall device structure. Scale bar: 50nm. **b,** EQE spectra of CQD/polymer device without

(yellow) and with (red) SM-bridge. **c,** IQE curves and **d,** experimentally measured absorption spectra of CQD/polymer devices without (yellow) and with (red) SM-bridge. Grey dashed lines in panels **b-d** depict relative EQE (**b**), IQE (**c**) or absorption (**d**) enhancement of the CQD/SM-bridge:polymer devices with respect to CQD/polymer devices. **e,** Calculated absorption spectra of CQD (brown), polymer (yellow) and CQD+polymer (red). **f,** Calculated absorption spectra of CQD (brown), polymer+SM-bridge (yellow) and CQD+organics (red). Black dashed line in panel **e,f** denote calculated total absorption of entire device. Brown and yellow dashed area in panel **e,f** describe the amount of photon collection of CQD and organics, respectively.

Figure 4 | Photovoltaic performance. a, Representative *J-V* curves of P:SM (polymer:SM-bridge BHJ, yellow), CQD (with EDT layer, brown) and CQD/P:SM (red). **b,** Statistical histogram of CQD/P:SM device. **c,** EQE spectra of CQD/P:SM device. **d,** Shelf lifetime of CQD/P:SM device. The devices were stored in ambient conditions without encapsulation. **e,** Operating lifetime of P:SM (yellow), CQD with EDT, (brown) and CQD/P:SM (red). All devices were stored in ambient conditions without encapsulation; nor filter was used; and ambient relative humidity was 30~50 %. The initial PCEs of the P:SM, CQD with EDT and CQD/P:SM devices were 7.9%, 10.5% and 12.7% respectively.

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