Letter

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ACS Energy Lett., **Just Accepted Manuscript** • DOI: 10.1021/acsenergylett.8b00460 • Publication Date (Web): 03 May 2018

Hybrid Tandem Quantum Dot/Organic Solar Cells with Enhanced Photocurrent and Efficiency *via* Ink and Interlayer Engineering

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Notes

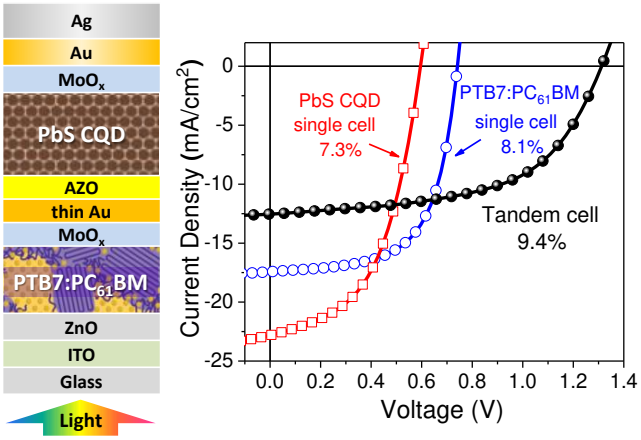
The authors declare no competing financial interest.

ABSTRACT

Realization of colloidal quantum dot (CQD)/organic photovoltaic (OPV) tandem solar cells that integrate the strong infrared absorption of CQDs with large photovoltages of OPVs is an attractive option toward high-performing, low-cost thin film solar cells. To date, monolithic hybrid tandem integration of CQD/OPV solar cells has been restricted due to the CQD ink's catastrophic damage to the organic subcell, thus forcing the low bandgap CQD to be used as front cell. This sub-optimal configuration limits the maximum achievable

photocurrent in CQD/OPV hybrid tandem solar cells. In this work, we demonstrate hybrid tandem solar cells employing a low-bandgap CQD back cell on top of an organic front cell thanks to a modified CQD ink formulation and a robust interconnection layer (ICL) which together overcome the long-standing integration challenges for CQD and organic subcells. The resulting tandem architecture surpasses previously reported current densities by ~20-25% and yields a state-of-the-art power conversion efficiency (PCE) of 9.4%.

TOC GRAPHICS



Organic and colloidal quantum dot (CQD) light absorbers are attractive solution-processed materials for thin film photovoltaics (PV), enabling roll-to-roll manufacturing of cost-effective lightweight modules at low temperature.[1-8] Individual materials are currently limited to ca. 13% certified power conversion efficiency (PCE) in single-junction solar cells.[9-12] Multi-junction solar cell architectures can harvest a larger portion of the solar spectrum.[13-19] CQD solids benefit from a size-tunable bandgap that allows absorbing a wide range of wavelengths from visible to near infrared.[4-8,11] Meanwhile, organic absorbers tend to have a narrower spectral absorption compared to quantum dot solids,[1,2,9,10,20] making them especially attractive for multi-junction CQD and organic solar cells, especially if materials are selected to

exhibit complementary light absorption properties. In recent years, CQD/organic hybrid tandem solar cells have been monolithically integrated and reported by several groups.[21-26] However, one noteworthy limitation in all the reports has been the unusual placement of the low bandgap CQD subcell as the front cell, namely on the transparent electrode-coated glass substrate, limiting the ability of the tandem to generate higher photocurrent. The primary reason constraining researchers to this architecture is the incompatibility of the CQD ink solvents with underlayers, including the bulk heterojunction (BHJ) organic photoactive layer and the interconnection layers (ICL).[22-25] The secondary, yet still important reason, is the need for repeated solid state ligand exchange in many legacy recipes for CQD active layer or for the CQD hole transporting layer (HTL).[4,5,8,11] Ligand exchange, which significantly densifies the CQD film, has been shown to cause additional chemical damage and stress-induced cracking of underlayers.[22-24] Tong *et al.* have suggested top-illumination in CQD/organic hybrid tandem solar cells using transparent indium-doped tin oxide (ITO) bottom and PEDOT:PSS top electrodes, respectively.[24] However, illuminating from the top still resulted in poorly performing devices, since the illumination direction strongly affects the light harvesting by the depleted heterojunction (DHJ) CQD subcell.[27,28] This favors illumination through the n-type electron transporting layer (ETL), which is typically at the bottom of n-p and n-i-p CQD solar cells, placing additional constraints on the subcell and hybrid tandem configurations. We have taken the view that overcoming these challenges and successfully integrating solution-processed low bandgap CQD solar cells on top of the organic front cell is crucial to realize highly efficient tandem solar cells which surpass the performances of state-of-the-art single-junction CQD or organic solar cells. Indeed, two-terminal hybrid tandem solar cells are predicted to achieve a 30% higher photocurrent for the same active materials simply by switching the CQD subcell to the back and placing the OPV subcell at the front (**Figure 1**).

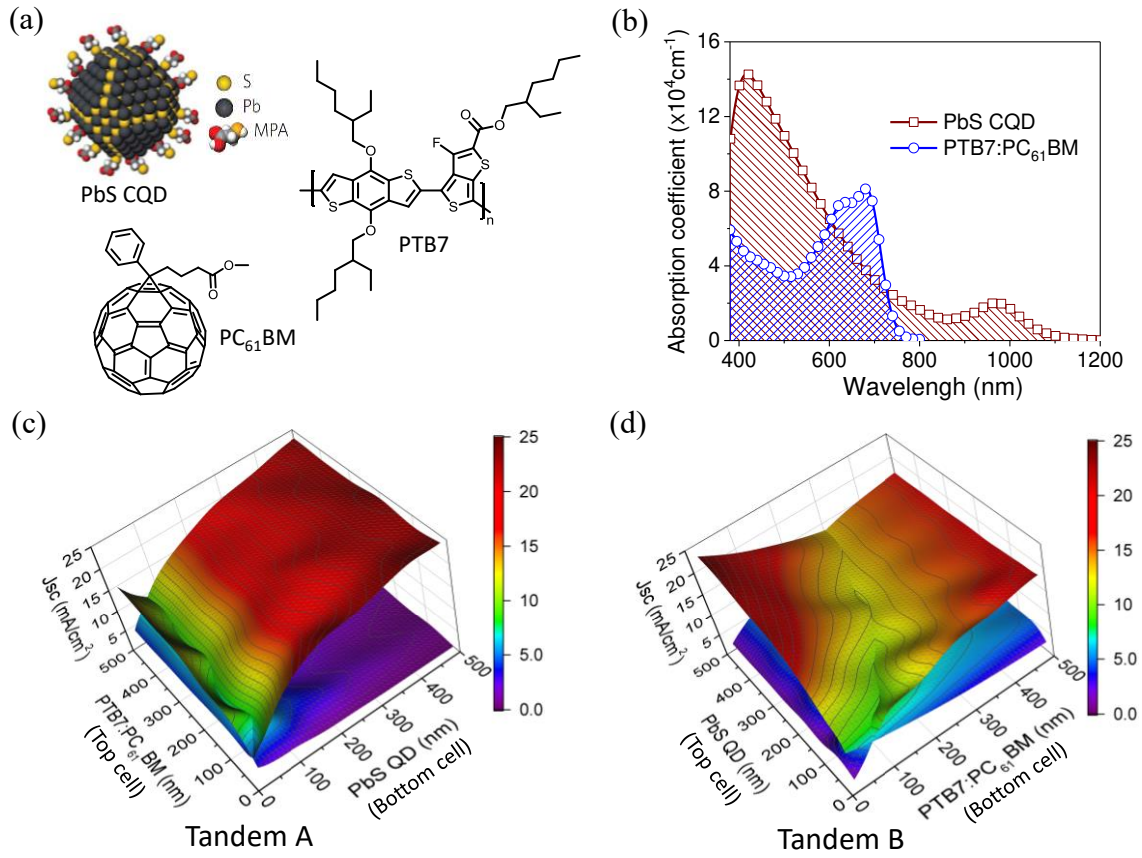


Figure 1. (a) Materials chart: PbS quantum dots after ligand exchange, the polymer donor PTB7 and the fullerene acceptor $PC_{61}BM$. (b) Absorption coefficients of the PbS CQD and the PTB7:$PC_{61}BM$ active layers. Simulated J_{SC} of the hybrid tandem solar cells depending on the device structures: (c) PbS CQD active layer as front cell, while organic active layer as back cell (Tandem A), (d) PbS CQD active layer as back cell, while organic active layer as front cell (Tandem B). The cross-matched intersection of the surface plot shows the current matched values achievable in each case, giving a 30% advantage to Tandem B. The contour is drawn with 1 mA/cm^2 increments.

In this letter, we successfully overcome the challenges of monolithic integration of a low bandgap CQD subcell directly on top of a high bandgap organic front cell to achieve state-of-the-art PCE for hybrid tandem CQD/OPV solar cells by experimentally achieving a 20-25% increase of the photocurrent as compared to the previously reported values to date.[21-23, 25,26] To do so, we have designed a modified CQD ink formulation and a robust electrical ICL which

are compatible and preserve the integrity of the underlying OPV front cell. The reformulated CQD ink utilizes hexane,[25] which reduces damage to the delicate organic BHJ layer and cuts the number of steps required for CQD layer deposition, better preserving the integrity of all underlayers, including the ICL. The tandem's open circuit voltage (V_{OC}) of 1.31 V is equal to the sum of subcell voltages, while the photocurrent of 12.5 mA/cm^2 and the PCE of 9.4% are the highest reported to date in CQD/organic hybrid tandem solar cells.[21-26] The tandem PCE significantly surpasses those of the organic (8.1%) and CQD (7.3%) subcells, highlighting the success of the integration approach. This successful demonstration is an important milestone for the monolithic integration of state-of-the-art CQD and organic solar cells into tandem devices that can outperform the best single-junction solar cells in each field.

In **Figure 1(a)** we show the material systems used in this study: the chemical structures of the polymer donor, thieno[3,4-b]thiophene/benzodithiophene (PTB7), and fullerene acceptor, [6,6]-phenyl-C_{60}-butyric acid methyl ester ($PC_{61}BM$),[29-31] as well as a PbS CQD with an organic 3-mercaptopropionic acid (MPA) ligand.[32,33] The high-resolution transmission electron microscopy (TEM) image of PbS CQDs before ligand exchange is shown in **Figure S1** (average CQD size: ~ 3.5 nm). PTB7 was used in conjunction with $PC_{61}BM$ to form the polymer:fullerene organic bulk heterojunction subcell. The absorption coefficients of the PTB7:$PC_{61}BM$ and PbS CQD active layers are shown in **Figure 1(b)**. The CQD layer shows relatively strong absorption in the short-wavelength visible range and weaker absorption in the red and NIR with an exciton peak at 970 nm, while the PTB7:$PC_{61}BM$ subcell transmits, to some extent, the visible spectrum at around 500 nm and then absorbs effectively in the red regions (up to 750 nm), compensating for the CQD layer's weaker absorption in the red regions. The spectral responses of the two active layers are thus reasonably complementary.[25]

In previous reports on CQD/organic hybrid tandem solar cells, the device architectures have been configured such that the CQD subcell is located at the bottom on the transparent

substrate, while the organic subcell is fabricated above.[21-26] This forces the incident light to be absorbed first by the low bandgap CQD layer with the remaining light transmitted through the ICL, and then absorbed by the organic active layer. [21-23, 25,26] Importantly, the J_{SC} of the tandem device is limited in this configuration, despite the partial spectral complementarity of the active layers, limiting, in turn, the achievable PCE by the tandem as compared to the individual CQD and organic single-junction cells. Optical simulations were performed to compare the two CQD/organic hybrid tandem architectures, with tandem A (**Figure S2(a)**) placing the CQD subcell at the bottom side,[22,23,25,26] and tandem B (**Figure S2(b)**) placing it at the top side. The device structures, layer thicknesses, and optical constants are depicted in **Figure S2**. The simulated current densities of tandem A and B are shown in **Figure 1(c)** and **1(d)**, respectively, for active layer thicknesses ranging from 0 to 500 nm, with light incidence from the glass substrate side in both scenarios. The simulations predict a J_{SC} as high as ca. 10 mA/cm^2 for tandem A and ca. 13 mA/cm^2 for tandem B, and identify optimal subcell thicknesses for these scenarios, clearly showing a 30% advantage for tandem B. Hence, the complementary absorption by the two active layers is more effective in tandem B than in tandem A. The ca. 30% advantage of tandem B in terms of in J_{SC} motivates its fabrication, but poses serious challenges from the monolithic integration perspective. In particular, the bottom organic active layer is easily dissolved or damaged by some of the solvents typically used for CQD coating and/or ligand exchange, imposing important restrictions on the CQD ink and its coating process.[21-26] We have set out to investigate alternative CQD ink solvents and robust ICLs which can survive the CQD coating process and provide protection for all underlayers.

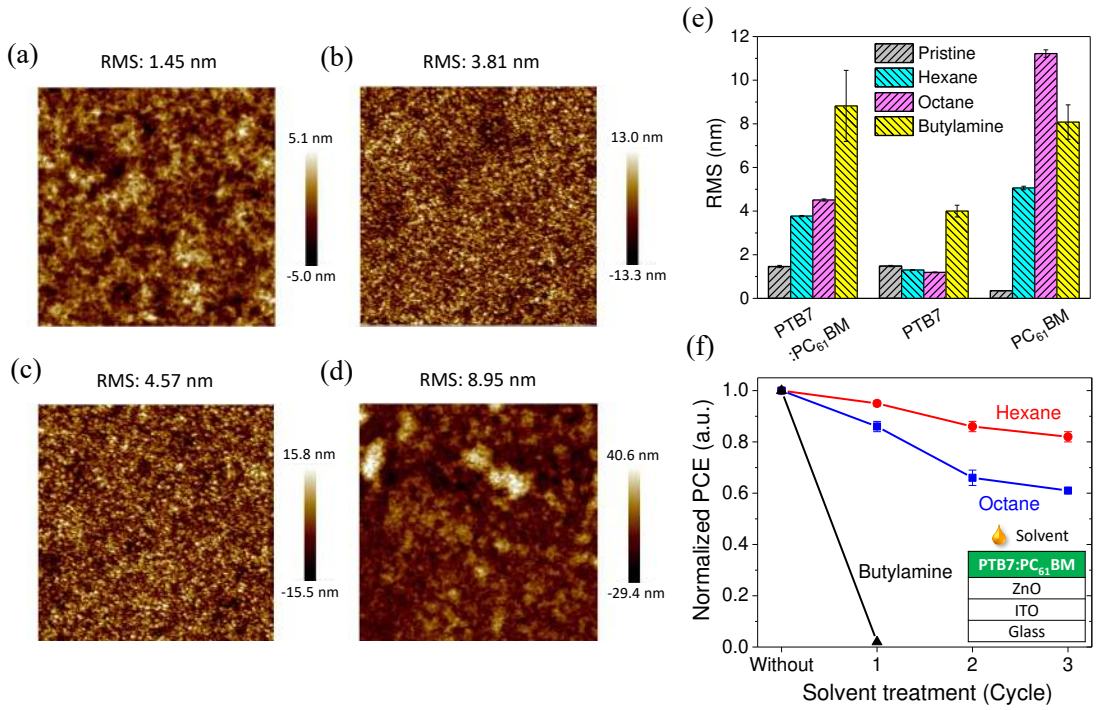


Figure 2. AFM images of PTB7:$PC_{61}BM$ surface topography, (a) before the solvent treatment, treated with (b) hexane, (c) octane, and (d) butylamine, respectively. The scan size is 5 µm x 5 µm. (e) Summary of RMS surface roughness of solvent-treated organic thin films of PTB7:$PC_{61}BM$, only PTB7, and only $PC_{61}BM$, respectively. (f) Normalized PCE of organic single-junction cells without and with direct solvent-treatment of the photoactive layers (without a protective ICL).

Octane and butlyamine are the two most commonly used solvents for conventional PbS CQD solar cells.[4-8,11,25,32,33] In **Figure 2**, we investigate and compare the effects of exposure to the two common CQD solvents (octane and butylamine) on the morphology of the organic BHJ layer and the operational stability of a single-junction organic solar cell. For this purpose, we have exposed the PTB7:$PC_{61}BM$ BHJ layers directly to blank solvents, which were cast and spun off of the organic photoactive layers in a manner which simulates CQD coating conditions. The solvent treatments were performed in the absence of the ICL in order to simulate the worst case scenario of solvent damage. We assess the solvent effects on BHJ morphology by performing atomic force microscopy (AFM) measurements of the surface

topography before and after exposure to each solvent. We subsequently fabricated single-junction organic solar cells using similarly solvent-treated photoactive layers (see experimental section of supporting information about the solvent treatment method). In **Figure 2(a)** we see AFM images of the surface morphology of an as-prepared PTB7:$PC_{61}BM$ active layer, exhibiting a root mean squared (RMS) roughness of 1.45 nm. Micrographs in **Figures 2(b, c, d)** show that the BHJ layer roughens moderately in the case of octane and very significantly in the case of butylamine, indicative of significant solvent-BHJ interactions. We summarize in **Figure 2(e)**, the RMS surface roughness of pristine PTB7, $PC_{61}BM$, and PTB7:$PC_{61}BM$ blend layers and after solvent treatment. AFM images of PTB7 and $PC_{61}BM$ before and after solvent treatment are presented in **Figure S3**. The data attribute the increasing RMS roughness of the PTB7:$PC_{61}BM$ blend to partial solubility of $PC_{61}BM$ in octane, whereas butylamine dissolves both the PTB7 and $PC_{61}BM$.

These changes to the active layer's morphology understandably impact the operation of organic solar cells. We plot the normalized PCE of the solvent-treated PTB7:$PC_{61}BM$ single-junction cells with respect to the number of solvent treatments in **Figure 2(f)**. A one-time exposure to butylamine is sufficient to render the solar cell inoperable, whereas octane exposure is less invasive, but reduces efficiency by 40% after three treatments. Even when butylamine solvent treatment was applied indirectly through the ICL (see below for detailed selection criteria of ICL) in a simulated solar cell stack (glass/ITO/PTB7:$PC_{61}BM$/MoO_x/thin Au/AZO) (**Figure S4(b-c)**) it caused significant damage by dissolving the organic layer. Octane had a far less dramatic, but non-negligible effect. Fortunately, 3-mercaptopropionic acid (MPA) in acetonitrile (ACN) treatment used to simulate the CQD ligand exchange did not show negative effect on organic device performance (**Figure S4(a)**).[33] We therefore conclude that the latest, most modern CQD inks based on butylamine are particularly difficult to apply at this stage in the tandem B architecture, with octane emerging as a better choice, but one

which is still unacceptable since it reduces the operational performance of the OPV subcell through the protective ICL.

Addressing these issues requires a solvent which can disperse CQDs and minimize harmful interactions with the underlying OPV subcell and the ICL. We propose hexane as an alternative solvent since it is considered a marginal solvent for many organic semiconductors. Hexane also has the advantage of a much lower boiling point (68 ºC) than octane (125 ºC), allowing it to dry much faster and minimize liquid-OPV interactions during CQD spin-coating. Indeed, we show in **Figure 2** that hexane appears to induce the smallest morphological changes to the organic photoactive layer among all three solvents. Hexane is also found to have minimal effect on the ICL compared to octane and butylamine (**Figure S4(b-d)**). Importantly, hexane exposure shows the smallest loss on OPV devices, with a 5% drop in PCE after a single direct treatment and 20% drop in PCE after three cycles of solvent treatment. These losses should be mitigated further by the protective ICL.

The fast-drying solvent has an additional mitigating benefit by reducing the number of CQD coating steps. CQD films coated using octane and hexane-based inks of identical concentration (50 mg/mL) result in a final CQD thickness (after MPA ligand exchange) of 40 nm (2500 rpm) when using octane,[22] and 100 nm (3000 rpm) when using hexane. This difference is ascribed to the rapid drying and solidification of the ink, which reduces the time window within which the ink can be ejected during the spin-up and outflow regimes of spin-coating.[34] The ability of hexane to decrease the number of CQD coating cycles required to achieve thicker films required for the tandem B architecture can thus significantly reduce the potential damage to underlayers compared to octane by a combination of reduced interaction strength and interaction time. The choice of hexane forces the use of a legacy CQD DHJ top cell using a hexane-based ink and MPA ligand exchange as the most suitable approach for successful monolithic integration of a CQD back cell on top of the OPV front cell.

The design and selection of the ICL to connect the CQD back cell to the underlying organic front cell was also significantly constrained by the same stringent requirements posed by the CQD deposition and ligand exchange on top of the ICL and organic underlayers. These constraints are as follows: (1) sensitivity to solvents used in the CQD layer deposition,[22,24] (2) sensitivity to heat as PTB7 (and many related donor materials) does not fare well under thermal annealing or high temperature deposition,[35] and (3) sensitivity to mechanical stresses induced by solid-state ligand exchange.[36] The low-temperature processing requirement excludes the use of popular interlayers, such as sol-gel ZnO and TiO_2 as ETL and PEDOT:PSS as HTL due to their thermal annealing requirements.[13,37-40] The mechanical stress resistance requirement also excludes most organic interlayers and films processed by thermal evaporation at the expense of sputtering at low-temperature. However, organic semiconductors are easily damaged by sputtering, requiring the first layer of the ICL in direct contact with the organic BHJ layer to be vacuum-evaporated instead and be sufficiently robust to withstand subsequent sputtering.[41] For these reasons, we have opted for a tri-layer ICL with vacuum-evaporated MoO_x on the organic side and a metal oxide ETL on the CQD side.[18,19,23,41-44] The central layer of the ICL was an ultrathin (0.5 nm) Au layer which breaks up into islands acting as effective recombination sites,[42-44] as will be discussed below. We have opted for Al-doped ZnO (AZO) deposited by RF-sputtering as the n-type ETL.[25] The conductivity of the AZO layer used here was $\leq 10^{-7}$ S/cm. **Figure S5** shows the significant damage to metal oxide nanoparticle (NP) layers based on solution-processed AZO and ZnO NPs instead of sputtered AZO. Therefore, the compact and dense AZO produced by sputtering was preferred over solution-processed nanocrystal metal oxides such as AZO, TiO_2 and ZnO, etc., as these often yield less compact films which can be easily permeated by or delaminated the CQD ink and/or be harmed by the mechanical stress build-up in the CQD overlayer after ligand exchange. The oleic acid capped PbS CQD active layer deposited from the hexane-based formulation was ligand-exchanged

using a 3-mercaptopropionic acid (MPA) in acetonitrile (ACN) and was repeated until the desired thickness was reached. The tandem stack was completed by vacuum evaporation of MoO_x as HTL and Au/Ag as the anode.[25,33]

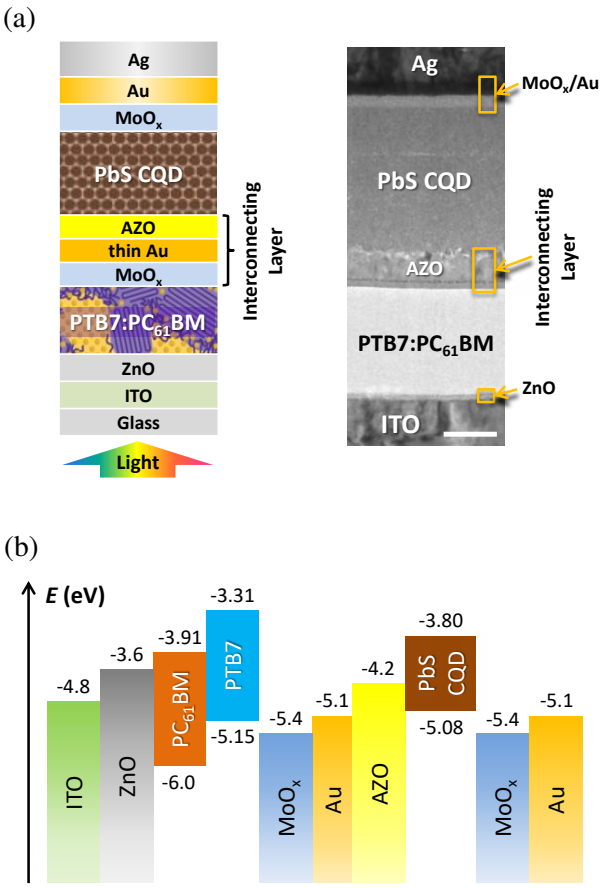


Figure 3. (a) Hybrid tandem solar cell configuration and TEM cross-sectional image of the corresponding device. Scale bar is 100 nm. (b) Energy level diagram of the hybrid tandem solar cell.

In **Figure 3(a)** we present the hybrid tandem B device schematic and show a cross-sectional transmission electron microscopy (TEM) image of the actual device based on a 200 nm thick PTB7:$PC_{61}BM$ bottom active layer and a 300 nm PbS CQD (3 layers) active layer. The device includes a ZnO/ITO cathode, a MoO_x/Au/Ag anode and the tri-layer MoO_x/thin Au/AZO ICL. The energy level diagram of the hybrid tandem device is presented in **Figure 3(b)**. The PTB7:$PC_{61}BM$ active layer was spin-cast on top of a sol-gel ZnO layer prepared by spin-coating on ITO-coated glass. The ICL consists of a stack of MoO_x/thin Au/AZO. MoO_x

was vacuum-deposited on PTB7:$PC_{61}BM$ to form the HTL. An ultrathin Au layer (0.5 nm) was deposited by thermal evaporation with careful thickness monitoring. As shown in **Figure 3(b)**, the Au layer forms an asymmetric work function within the ICL which grades the work function from high on the MoO_x side – to promote hole injection from the organic photoactive layer into the ICL – to low work function on the AZO side – to promote electron injection from the CQD photoactive layer into the ICL.[18,19,23] The ultrathin Au layer forms nano-islands, as seen in SEM and AFM measurements (**Figure S6**). These act as efficient recombination sites and reduce the accumulation of photo-excited charges in the photoactive layers and near the ICL.[18,19,23,41-44] The fill factor (FF) and thus the performance of tandem cells benefits strongly from the presence of Au nano-islands,[18,19,23,25] as shown in **Figure S7(a)** of tandem solar cells prepared without and with Au nano-islands within the ICL. **Figure S7(b)** compares the conductance of ICL including a thin Au layer as compared to an ICL without Au and shows that the inclusion of Au reduces the series resistance of the ICL.[18,19,23,25] The device structures used for conductance measurements were the isolated interlayer stacks, including glass/ITO/MoO_x/Au (0.5 nm)/AZO/Al and glass/ITO/MoO_x/AZO/Al.

Individual single-junction cells were first fabricated employing organic or CQD photoactive layers with different thickness using the same ETL and HTL as in the tandem B architecture. The configurations for the PbS CQD and organic single cells were glass/ITO/AZO/PbS CQD/MoO_x/Au/Ag and glass/ITO/ZnO/PTB7:$PC_{61}BM$/MoO_x/Ag, respectively. In **Figure 4(a)** we show current density-voltage (*J-V*) curves obtained for CQD and organic single-junction cells depending on active layer thickness ranging from 100 to 500 nm for the former and 145 to 210 nm for the latter. The summary of statistical device parameters of the organic and CQD single-junction cells is presented in **Figures S8** and **S9**, respectively, while all parameters are summarized in **Table 1**. The organic active layer thickness was varied by changing the spin-coating speed, whereas the CQD active layer

thickness was varied by repeating the CQD coating and ligand exchange processes, which incremented the thickness by 100 nm per cycle. In organic cells, increasing the active layer thickness leads to higher J_{SC} at the expense of FF, with the PCE showing a small drop due to the trade-off between J_{SC} and FF within the thickness range studied (**Table 1**). The single-junction CQD cells also show a similar trend, with higher J_{SC} in thicker active layers with the FF and PCE showing maximum values for a 300 nm thickness (**Table 1**). Looking into the V_{OC} of PbS CQD single-junction cells, CQDs are known for exhibiting significant energetic losses that lead to poor output voltages corresponding to the band gap. Fundamentally, the voltage loss mechanism in CQDs is directly related to the significantly large number of surface atoms (due to the high surface-to-volume ratio), which result in a high density of band tails. The solid-state ligand exchange further enhances these band tails due to an increased morphological disorder. Guyot-Sionnest has theoretically suggested that the extent of band tails currently found in legacy CQD solids (obtained by solid-state ligand exchange) limits the maximum achievable output voltage to 50% of the CQD band gap.[45] Therefore, ~ 0.58 V output voltage for our CQD cells employing PbS CQDs with *ca.* 1.2 eV band gap is close to the theoretical optimum.

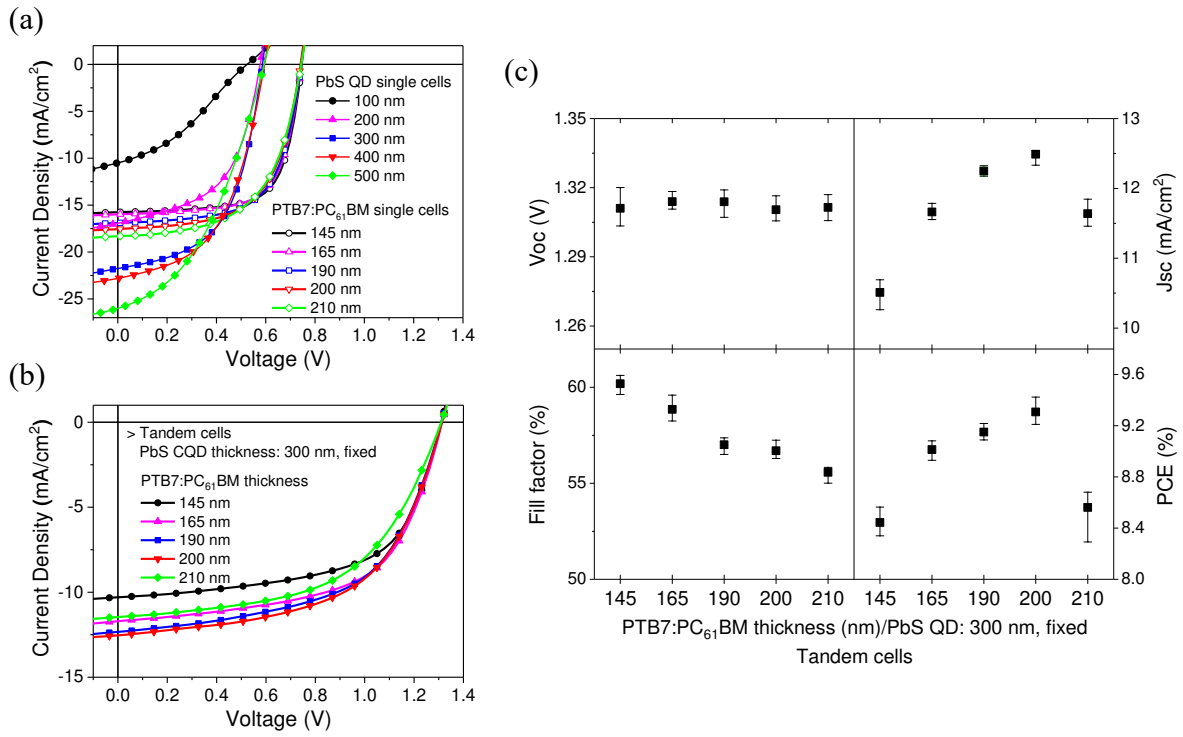


Figure 4. (a) Representative *J-V* curves of PTB7:PC_{61}BM, and PbS CQD single-junction cells depending on their active layer thicknesses. (b) *J-V* characteristics of hybrid tandem solar cells of various PTB7:PC_{61}BM layer thicknesses, fixing PbS CQD layer with 300 nm thick, and (c) statistical parameter summary of these tandem solar cells.

Table 1. Averaged device parameters of PTB7:PC_{61}BM, PbS CQD single-junction cells and hybrid tandem solar cells depending on active layer thicknesses. Average values based on 20 devices.

Device structure	Active layer	Thickness	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)	Best PCE (%)
Single cell	PTB7:PC_{61}BM	145 nm	0.75	15.8	69.4	8.2	8.3
		165 nm	0.75	15.9	68.1	8.1	8.2
		190 nm	0.75	16.9	64.0	8.1	8.2
		200 nm	0.74	17.4	60.8	7.9	8.1
		210 nm	0.74	18.3	58.0	7.9	8.1
	PbS CQD	100 nm	0.51	10.6	34.9	1.9	2.1
		200 nm	0.58	16.9	54.0	5.3	5.9
		300 nm	0.58	21.8	54.7	7.0	7.3
		400 nm	0.60	22.6	50.2	6.5	7.0

		500 nm	0.59	25.9	44.0	6.4	6.9
Tandem cell	PTB7:$PC_{61}BM$ /PbS CQD	145 nm /300 nm	1.31	10.5	60.2	8.4	8.6
		165 nm /300 nm	1.31	11.7	58.9	9.0	9.1
		190 nm /200 nm	1.31	11.1	58.6	8.6	8.7
		190 nm /300 nm	1.31	12.3	57.0	9.2	9.2
		190 nm /400 nm	1.30	12.6	54.7	8.9	9.0
		190 nm /500 nm	1.30	12.6	53.7	8.8	8.9
		200 nm /300 nm	1.31	12.5	56.7	9.3	9.4
		210 nm /300 nm	1.31	11.6	55.6	8.6	8.7

Based on the experimental results for single-junction organic and CQD cells with re-engineered CQD ink, we have monolithically integrated CQD/organic subcells into the tandem B architecture shown in **Figure 3(a)**, namely glass/ITO/ZnO/PTB7:$PC_{61}BM$/MoO_x/ultrathin Au/AZO/PbS CQD/MoO_x/Au/Ag. The thicknesses of both CQD and organic active layers were varied to maximize current matching and achieve the highest PCE. Fixing the organic active layer thickness to 190 nm, the FF decreased and the J_{SC} saturated with increasing CQD active layer thickness up to 500 nm (**Figure S10**, **Table 1**). By contrast, fixing the CQD layer thickness to 300 nm and increasing the organic active layer thickness up to 210 nm, the FF decreased while J_{SC} peaked at a thickness of 200 nm (**Figure 4(b,c)**, **Table 1**). Importantly, the V_{OC} was nearly constant without significant photovoltage drops, independent of either active layer thicknesses. This is significant as it indicates that the ICL and the organic subcell can survive up to five repeated CQD coating and ligand exchange steps without serious damage to the device.

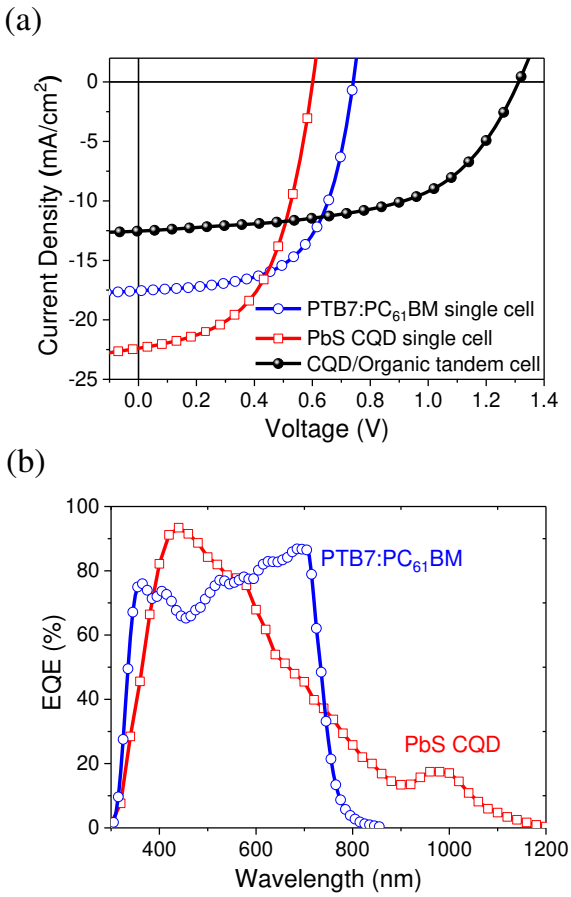


Figure 5. (a) *J-V* curves of optimized hybrid tandem and the single-junction cells with the same active layer thicknesses, (b) EQE spectra of the PTB7:$PC_{61}BM$ and PbS CQD single-junction cells, which were applied for the optimized tandem cells.

The optimized hybrid tandem solar cell yielded a V_{OC} of 1.31 V, a FF of 56.7%, and a J_{SC} of 12.5 mA/cm^2 with high current matching, leading to a PCE of 9.3% on average, and a best PCE value of 9.4%. This is achieved with a 200 nm thick organic active layer and a 300 nm thick CQD active layer. The photocurrent is the highest achieved to date and surpasses by ~20-25% the previous reported photocurrent values,[21-23,25,26] in reasonably good agreement with optical simulations reported in **Figure 1**. The shunt and series resistances of the optimized tandem and their single cells are summarized in **Table S1**.

In **Figure 5(a)** we show the *J-V* characteristics of single-junction and tandem cells with the same active layer thicknesses. **Figure 5(b)** shows the external quantum efficiency (EQE)

for the single-junction CQD and organic cells with the thickness employed in the optimized tandem cell. The CQD cell harvests the solar spectrum in the short wavelength region (UV/blue regions), but the EQE drops significantly from its peak at 440 nm and up to 880 nm, showing a second increase at around 970 nm, corresponding to the CQD exciton peak position before the band edge near 1200 nm. The EQE of the PTB7:$PC_{61}BM$ cell is particularly pronounced from the green to red region, for 500 nm < λ < 750 nm showing complementary EQE spectra with CQD cell. The optimized tandem solar cells exhibit significantly higher PCE than the best performing single-junction organic (8.3%) and CQD (7.1%) cells. The tandem open circuit voltage (V_{OC}) of 1.31 V is equal to the sum of two single-junction cell voltages. The FF (56.7%) of the optimized tandem was found to be at an intermediate level as the single-junction organic (60.8%) and CQD (54.7%) cells with the same active layer thickness. These results prove that the organic and CQD subcells are effectively connected and current-matched.

In conclusion, we demonstrated the implementation of a tandem solar cell with a solution-processed PbS CQD back cell monolithically integrated through connection in series with an underlying PTB7:$PC_{61}BM$ front cell. This tandem solar cell with the CQD back cell and an OPV front cell achieves higher current matching and PCE compared to previous reports. The primary enabling breakthrough was the development of a CQD ink formulation which minimizes chemical and structural damage to the underling OPV subcell and ICL. The secondary enabling development was the design of a robust trilayer ICL which survives the chemical and mechanical stresses induced by CQD coating and ligand exchange steps whilst itself not damaging the delicate organic subcell. To date, this is the most efficient CQD/organic hybrid tandem structure and far exceeds the PCEs of individual subcells. This work is expected to pave the way for further successful integration of hybrid tandem OPV/CQD solar cells with PCE which can one day surpass the state-of-the-art PCE of each individual field.

ASSOCIATED CONTENT

Supporting Information.

Experimental methods of device fabrication, electrical characterization. AFM, TEM, SEM images.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by the King Abdullah University of Science and Technology (KAUST), and the Ontario Research Fund - Research Excellence program. M.L. acknowledges support from the Hatch Research Scholarship. The authors thanks E. Palmiano for support in the synthesis of quantum dots.

REFERENCES

(1) Heeger, A. J. 25th Anniversary Article: Bulk Heterojunction Solar Cells: Understanding the Mechanism of Operation. *Adv. Mater.* **2014**, *26*, 10-28.

(2) Beaujuge, P. M.; Fréchet, J. M. Molecular Design and Ordering Effects in π-Functional Materials for Transistor and Solar Cell Applications. *J. Am. Chem. Soc.* **2011**, *133*, 20009-20029.

(3) Finn III, M.; Martens, C. J.; Zaretski, A. V.; Roth, B.; Søndergaard, R. R.; Krebs, F. C.; Lipomi, D. J. Mechanical Stability of Roll-to-Roll Printed Solar Cells under Cyclic Bending and Torsion. *Solar Energy Mater. Sol. Cells* **2018**, *174*, 7-15.

(4) Kim, J. Y.; Voznyy, O.; Zhitomirsky, D.; Sargent, E. H. 25th Anniversary Article: Colloidal Quantum Dot Materials and Devices: A Quarter-Century of Advances. *Adv. Mater.* **2013**, *25*, 4986-5010.

(5) Wang, R.; Shang, Y.; Kanjanaboos, P.; Zhou, W.; Ning, Z.; Sargent, E. H. Colloidal Quantum Dot Ligand Engineering for High Performance Solar Cells. *Energy Environ. Sci.* **2016**, *9*, 1130-1143.

(6) MacDonald, B. I.; Martucci, A.; Rubanov, S.; Watkins, S. E.; Mulvaney, P.; Jasieniak, J. J. Layer-by-Layer Assembly of Sintered $CdSe_xTe_{1-x}$ Nanocrystal Solar Cells. *ACS Nano* **2012**, *6*, 5995-6004.

(7) Crisp, R. W.; Panthani, M. G.; Rance, W. L.; Duenow, J. N.; Parilla, P. A.; Callahan, R.; Dabney, M. S.; Berry, J. J.; Talapin, D. V.; Luther, J. M. Nanocrystal Grain Growth and Device Architectures for High-Efficiency CdTe Ink-based Photovoltaics. *ACS Nano* **2014**, *8*, 9063-9072.

(8) Chuang, C.-H. M.; Brown, P. R.; Bulović, V.; Bawendi, M. G. Improved Performance and Stability in Quantum Dot Solar Cells through Band Alignment Engineering. *Nat. Mater.* **2014**, *13*, 796-801.

(9) Li, S.; Ye, L.; Zhao, W.; Zhang, S.; Mukherjee, S.; Ade, H.; Hou, J. Energy-Level Modulation of Small-Molecule Electron Acceptors to Achieve over 12% Efficiency in Polymer Solar Cells. *Adv. Mater.* **2016**, *28*, 9423-9429.

(10) Zhao, W.; Li, S.; Yao, H.; Zhang, S.; Zhang, Y.; Yang, B.; Hou, J. Molecular Optimization Enables over 13% Efficiency in Organic Solar Cells. *J. Am. Chem. Soc.* **2017**, *139*, 7148-7151.

(11) Liu, M.; Voznyy, O.; Sabatini, R.; de Arquer, F. P. G.; Munir, R.; Balawi, A. H.; Lan, X.; Fan, F.; Walters, G.; Kirmani, A. R.; et al. Hybrid Organic-Inorganic Inks Flatten The Energy Landscape in Colloidal Quantum Dot Solids. *Nat. mater.* **2017**, *16*, 258-263.

(12) Sanehira, E. M.; Marshall, A. R.; Christians, J. A.; Harvey, S. P.; Ciesielski, P. N.; Wheeler, L. M.; Schulz, P.; Lin, L. Y.; Beard, M. C.; Luther, J. M. Enhanced Mobility $CsPbI_3$ Quantum Dot Arrays for Record-Efficiency, High-Voltage Photovoltaic Cells. *Sci. Adv.* **2017**, *3*, eaao4204.

(13) Kim, J. Y.; Lee, K.; Coates, N. E.; Moses, D.; Nguyen, T.-Q.; Dante, M.; Heeger, A. J. Efficient Tandem Polymer Solar Cells Fabricated by All-Solution Processing. *Science* **2007**, *317*, 222-225.

(14) Hadipour, A.; de Boer, B.; Blom, P. W. Organic Tandem and Multi-Junction Solar Cells. *Adv. Funct. Mater.* **2008**, *18*, 169-181.

(15) Li, G.; Chang, W.-H.; Yang, Y. Low-Bandgap Conjugated Polymers Enabling Solution-Processable Tandem Solar Cells. *Nat. Rev. Mater.* **2017**, *2*, 17043.

(16) Cui, Y.; Yao, H.; Gao, B.; Qin, Y.; Zhang, S.; Yang, B.; He, C.; Xu, B.; Hou, J. Fine Tuned Photoactive and Interconnection Layers for Achieving over 13% Efficiency in a Fullerene-free Tandem Organic Solar Cell. *J. Am. Chem. Soc.* **2017**, *139*, 7302−7309.

(17) Wang, X.; Koleilat, G. I.; Tang, J.; Liu, H.; Kramer, I. J.; Debnath, R.; Brzozowski, L.; Barkhouse, D. A. R.; Levina, L.; Hoogland, S.; et al. Tandem Colloidal Quantum Dot Solar Cells Employing a Graded Recombination Layer. *Nat. Photonics* **2011**, *5*, 480-484.

(18) Choi, J. J.; Wenger, W. N.; Hoffman, R. S.; Lim, Y. F.; Luria, J.; Jasieniak, J.; Marohn, J. A.; Hanrath, T. Solution-Processed Nanocrystal Quantum Dot Tandem Solar Cells. *Adv. Mater.* **2011**, *23*, 3144-3148.

(19) Shi, G.; Wang, Y.; Liu, Z.; Han, L.; Liu, J.; Wang, Y.; Lu, K.; Chen, S.; Ling, X.; Li, Y. Stable and Highly Efficient PbS Quantum Dot Tandem Solar Cells Employing a Rationally Designed Recombination Layer. *Adv. Energy Mater.* **2017**, *7*, 1602667.

(20) Moreels, I.; Lambert, K.; Smeets, D.; De Muynck, D.; Nollet, T.; Martins, J. C.; Vanhaecke, F.; Vantomme, A.; Delerue, C.; Allan, G. Size-Dependent Optical Properties of Colloidal PbS Quantum Dots. *ACS Nano* **2009**, *3*, 3023-3030.

(21) Speirs, M.; Groeneveld, B.; Protesescu, L.; Piliego, C.; Kovalenko, M.; Loi, M. Hybrid Inorganic–Organic Tandem Solar Cells for Broad Absorption of The Solar Spectrum. *Phys. Chem. Chem. Phys.* **2014**, *16*, 7672-7676.

(22) Kim, T.; Gao, Y.; Hu, H.; Yan, B.; Ning, Z.; Jagadamma, L. K.; Zhao, K.; Kirmani, A. R.; Eid, J.; Adachi, M. M.; et al. Hybrid Tandem Solar Cells With Depleted-Heterojunction Quantum Dot and Polymer Bulk Heterojunction Subcells. *Nano Energy* **2015**, *17*, 196-205.

(23) Aqoma, H.; Azmi, R.; Oh, S.-H.; Jang, S.-Y. Solution-Processed Colloidal Quantum Dot/Organic Hybrid Tandem Photovoltaic Devices with 8.3% Efficiency. *Nano Energy* **2017**, *31*, 403-409.

(24) Tong, J.; Yang, X.; Xu, Y.; Li, W.; Tang, J.; Song, H.; Zhou, Y. Efficient Top-Illuminated Organic-Quantum Dots Hybrid Tandem Solar Cells with Complementary Absorption. *ACS Photonics* **2017**, *4*, 1172-1177.

(25) Kim, T.; Palmiano, E.; Liang, R.-Z.; Hu, H.; Murali, B.; Kirmani, A. R.; Firdaus, Y.; Gao, Y.; Sheikh, A.; Yuan, M.; et al. Hybrid Tandem Quantum Dot/Organic Photovoltaic Cells with Complementary Near Infrared Absorption. *Appl. Phys. Lett.* **2017**, *110*, 223903.

(26) Li, Y.-L.; Yeh, P.-N.; Sharma, S.; Chen, S.-A. Promotion of Performances of Quantum Dot Solar Cell and its Tandem Solar Cell with Low Bandgap Polymer (PTB7-Th): PC_{71}

BM by Water Vapor Treatment on Quantum Dot Layer on its Surface. *J. Mater. Chem. A* **2017**, *5*, 21528-21535.

(27) Pattantyus-Abraham, A. G.; Kramer, I. J.; Barkhouse, A. R.; Wang, X.; Konstantatos, G.; Debnath, R.; Levina, L.; Raabe, I.; Nazeeruddin, M. K.; Grätzel, M. Depleted-Heterojunction Colloidal Quantum Dot Solar Cells. *ACS Nano* **2010**, *4*, 3374-3380.

(28) Barkhouse, D. A. R.; Kramer, I. J.; Wang, X.; Sargent, E. H. Dead Zones in Colloidal Quantum Dot Photovoltaics: Evidence and Implications. *Opt. Express* **2010**, *18*, A451-A457.

(29) He, Z.; Zhong, C.; Su, S.; Xu, M.; Wu, H.; Cao, Y. Enhanced Power-Conversion Efficiency in Polymer Solar Cells using an Inverted Device Structure. *Nat. Photonics* **2012**, *6*, 591-595.

(30) Lu, L.; Yu, L. Understanding Low Bandgap Polymer PTB7 and Optimizing Polymer Solar Cells Based on It. *Adv. Mater.* **2014**, *26*, 4413-4430.

(31) Foster, S.; Deledalle, F.; Mitani, A.; Kimura, T.; Kim, K. B.; Okachi, T.; Kirchartz, T.; Oguma, J.; Miyake, K.; Durrant, J. R.; et al. Electron Collection as a Limit to Polymer:PCBM Solar Cell Efficiency: Effect of Blend Microstructure on Carrier Mobility and Device Performance in PTB7:PCBM. *Adv. Energy Mater.* **2014**, *4*, 1400311.

(32) Ip, A. H.; Thon, S. M.; Hoogland, S.; Voznyy, O.; Zhitomirsky, D.; Debnath, R.; Levina, L.; Rollny, L. R.; Carey, G. H.; Fischer, A.; et al. Hybrid Passivated Colloidal Quantum Dot Solids. *Nat. Nanotechnol.* **2012**, *7*, 577-582.

(33) Kirmani, A. R.; Carey, G. H.; Abdelsamie, M.; Yan, B.; Cha, D.; Rollny, L. R.; Cui, X.; Sargent, E. H.; Amassian, A. Effect of Solvent Environment on Colloidal-Quantum-Dot Solar-Cell Manufacturability and Performance. *Adv. Mater.* **2014**, *26*, 4717-4723.

(34) Zhao, K.; Wodo, O.; Ren, D.; Khan, H. U.; Niazi, M. R.; Hu, H.; Abdelsamie, M.; Li, R.; Li, E. Q.; Yu, L.; et al. Vertical Phase Separation in Small Molecule:Polymer Blend Organic Thin Film Transistors Can Be Dynamically Controlled. *Adv. Funct. Mater.* **2016**, *26*, 1737-1746.

(35) Derue, L.; Dautel, O.; Tournebize, A.; Drees, M.; Pan, H.; Berthumeyrie, S.; Pavageau, B.; Cloutet, E.; Chambon, S.; Hirsch, L. Thermal Stabilisation of Polymer–Fullerene Bulk Heterojunction Morphology for Efficient Photovoltaic Solar Cells. *Adv. Mater.* **2014**, *26*, 5831-5838.

(36) Diroll, B. T.; Ma, X.; Wu, Y.; Murray, C. B. Anisotropic Cracking of Nanocrystal Superlattices. *Nano Lett.* **2017**, *17*, 6501-6506.

(37) Jagadamma, L. K.; Abdelsamie, M.; El Labban, A.; Aresu, E.; Ndjawa, G. O. N.; Anjum, D. H.; Cha, D.; Beaujuge, P. M.; Amassian, A. Efficient Inverted Bulk-Heterojunction Solar Cells from Low-Temperature Processing of Amorphous ZnO Buffer Layers. *J. Mater. Chem. A* **2014**, *2*, 13321-13331.

(38) Jagadamma, L. K.; Al-Senani, M.; El-Labban, A.; Gereige, I.; Ndjawa, N.; Guy, O.; Faria, J. C.; Kim, T.; Zhao, K.; Cruciani, F.; et al. Polymer Solar Cells with Efficiency >10% Enabled via a Facile Solution-Processed Al-Doped ZnO Electron Transporting Layer. *Adv. Energy Mater.* **2015**, *5*, 1500204.

(39) Mali, S. S.; Hong, C. K.; Inamdar, A.; Im, H.; Shim, S. E. Efficient Planar n-i-p Type Heterojunction Flexible Perovskite Solar Cells with Sputtered TiO_2 Electron Transporting Layers. *Nanoscale* **2017**, *9*, 3095-3104.

(40) Kim, T.-S.; Na, S.-I.; Oh, S.-H.; Kang, R.; Yu, B.-K.; Yeo, J.-S.; Lee, J.; Kim, D.-Y. All-Solution-Processed ITO-Free Polymer Solar Cells Fabricated on Copper Sheets. *Solar Energy Mater. Sol. Cells* **2012**, *98*, 168-171.

(41) Schmidt, H.; Flügge, H.; Winkler, T.; Bülow, T.; Riedl, T.; Kowalsky, W. Efficient Semitransparent Inverted Organic Solar Cells with Indium Tin Oxide Top Electrode. *Appl. Phys. Lett.* **2009**, *94*, 243302.

(42) Gupta, D.; Wienk, M. M.; Janssen, R. A. Indium Tin Zxide-Free Tandem Polymer Solar Cells on Opaque Substrates with Top Illumination. *ACS appl. Mater. Interfaces* **2014**, *6*, 13937-13944.

(43) Zheng, Z.; Zhang, S.; Zhang, M.; Zhao, K.; Ye, L.; Chen, Y.; Yang, B.; Hou, J. Highly Efficient Tandem Polymer Solar Cells with a Photovoltaic Response in the Visible Light Range. *Adv. Mater.* **2015**, *27*, 1189-1194.

(44) Martínez-Otero, A.; Liu, Q.; Mantilla-Perez, P.; Bajo, M. M.; Martorell, J. An Extremely Thin and Robust Interconnecting Layer Providing 76% Fill Factor in a Tandem Polymer Solar Cell Architecture. *J. Mater. Chem. A* **2015**, *3*, 10681-10686.

(45) Guyot-Sionnest, P. Electrical Transport in Colloidal Quantum Dot Films. *J. Phys. Chem. Lett.* **2012**, *3*, 1169-1175.