

Effect of ZnO Electron Extraction Layer on Charge Recombination and Collection Properties in Organic Solar Cells

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4 **Effect of ZnO Electron Extraction Layer on Charge Recombination and Collection**
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7 **Properties in Organic Solar Cells**
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51 CELIV, Organic Solar Cells
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Abstract

The effect of zinc oxide (ZnO) electron extraction layer (EEL) on charge recombination and collection properties in bulk-heterojunction (BHJ) organic solar cells (OSCs), based on poly[[4,8-bis[(2-ethylhexyl)oxy] benzo [1,2-b:4,5-b'] dithiophene-2,6- diyl] [3-fluoro-2-[(2-ethylhexyl)carbonyl] thieno [3,4-b] thiophenediyl]] (PTB7):3'H-Cyclopropano[8,25][5,6]fullerene-C70-D5h(6)-3'- butanoicacid, 3'-phenyl-, methyl ester (PC₇₀BM) blend system, has been analyzed using the transient photo-current (TPC) and photo-induced charge extraction by linearly increasing voltage (photo-CELIV) measurements. The TPC and photo-CELIV results indicate that the trap-limited bimolecular recombination can be strongly suppressed by interposing a 20 nm thick ZnO EEL between the BHJ and cathode, leading to a 9.4% increase in power conversion efficiency. The presence of ZnO EEL is beneficial in efficient operation of OSCs in two ways: (1) suppressing trap-limited bimolecular recombination and (2) enhancing the charge collection at the organic/cathode interface.

Introduction

Remarkable progresses have been made in the development of high performing organic solar cells (OSCs) due to their characteristic advantages of flexibility, light weight and large-area solution fabrication capabilities.¹⁻³ Considerable efforts have been devoted to increase the power conversion efficiency (PCE) and the stability of OSCs through improved understanding of the impacts of the morphology, vertical stratification in bulk heterojunction (BHJ) on built-in potential (V_{bi}) in the devices.⁴ Encouraging progresses made in OSCs with a PCE of >15% have been reported.⁵ In a recent work, we show that maintaining a stable and high V_{bi} across BHJ through interfacial modification favors the efficient and stable operation of OSCs.⁶ The charge transport properties have a profound impact on charge recombination and charge collection in OSCs, which are the critical factors limiting the efficient operation of OSCs.⁷ It is crucial to understand the charge transport, interfacial engineering and thus overcome the limitations for attaining high-performing and stable OSCs.

The loss of photo-generated carriers due to recombination includes monomolecular and bimolecular recombination processes. Monomolecular recombination, also known as the geminate recombination, is considered as the first order recombination process, where the charge transfer (CT) states originate from the same singlet excitons.^{8,9} It was shown that the dissociation of the CT excitons is weakly dependent on the electric field in high performing OSCs.^{10,11} With internal quantum efficiency approaching unity under short-circuit condition, it indicates that the bimolecular recombination process is a major loss mechanism in high-performance OSCs.¹²⁻¹⁶

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4 Bimolecular recombination, or nongeminate recombination, is the recombination process
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6 that occurs between the photo-generated free electrons and holes before charge extraction,
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8 affecting especially the fill factor (FF).^{17,18} It has been demonstrated that bimolecular
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10 recombination process is closely associated with the low charge carrier mobility in the
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12 disordered organic semiconductors and the charge trap states at the organic/electrode interface,
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14 leading to the buildup of space charges in BHJ, thus reducing the effective charge extraction
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16 probability.¹⁹⁻²³
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23 Interfacial engineering is one of the effective approaches for suppressing interfacial defects
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25 and improving the energy level alignment at the BHJ/electrode interfaces. This helps to
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27 minimize the recombination losses in OSCs.²⁴⁻²⁷ The use of appropriate charge extraction
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29 interlayers also facilitates desired ohmic contact at the organic/electrode interface, avoiding the
30
31 formation of unfavorable interface dipoles and carrier traps.^{28,29} Various efforts have been
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33 devoted on the design of both electron extraction layer (EEL) (e.g., ZnO, LiF and poly[(9,9-
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35 bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] and hole
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37 extraction layer (HEL) (e.g., poly(3,4-ethylenedioxythiophene):poly(styrene sulphonate
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39 (PEDOT:PSS), WO₃, V₂O₅ and MoO₃). Among different EEL choices, ZnO is one of the most
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41 attractive materials due to its high optical transparency, high electron mobility and
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43 environmentally friendly attributes. It is also easy to synthesis and can be processed by cost-
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45 effective solution fabrication process.^{30,31} There have been reports illustrating the great impact
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47 of ZnO morphology and surface properties on the cell performance.^{32,33} The performance of
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49 OSCs is also dependent on the deposition of the ZnO EEL, including ZnO solution
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51 formulation,³⁴ process condition,³⁵ and post-deposition treatment.³⁶ However, much research
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4 effort is desired to improve the understanding of charge recombination and collection
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6 properties for efficient and stable operation of OSCs.
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10 In this work, the effect of ZnO EEL on charge collection and recombination properties has
11 been analyzed systematically with a combination of photo-induced charge extraction by
12 linearly increasing voltage (photo-CELIV), transient photo-current (TPC) and light intensity
13 dependent current density–voltage ($J-V$) characteristic measurements. It shows that a 9.4 %
14 increase in PCE of poly[[4,8-bis[(2-ethylhexyl)oxy] benzo [1,2-b:4,5-b'] dithiophene-2,6- diyl]
15 [3-fluoro-2-[(2-ethylhexyl)carbonyl] thieno [3,4-b] thiophenediyl]] (PTB7):3'H-
16 Cyclopropa[8,25] [5,6]fullerene-C70-D5h(6)-3'- butanoicacid, 3'-phenyl-, methyl ester
17 (PC₇₀BM)-based OSCs with a 20 nm thick ZnO EEL as compared to a control OSC without a
18 ZnO EEL. Our results suggest that the use of the ZnO EEL enables suppressing bimolecular
19 recombination and unfavorable interfacial exciton dissociation, and thereby facilitating the
20 sufficient charge extraction in OSCs.
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39 **Device fabrication**

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42 The ZnO nanoparticles with a diameter around 5.0 nm were synthesized following the
43 processes described in a previous work.³⁷ The ZnO nanoparticle solution was formulated by
44 mixing the ZnO particles in methanol (10 mg/ml). The PTB7:PC₇₀BM solution was formulated
45 by dissolving PTB7 (*1 Material*) and PC₇₀BM (*Nano C*), mixed in a weight ratio of 1:1.5, in
46 chlorobenzene (CB) solvent (Sigma-Aldrich, 99.8%), with a 3% 1, 8-Diiodooctane (DIO)
47 (Sigma-Aldrich) additive. The donor/acceptor mixture solution was stirred overnight at 60 °C
48 for better dissolution.
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4 OSCs comprising a layer configuration of ITO/PEDOT:PSS(30 nm)/PTB7:PC₇₀BM(90
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6 nm)/ZnO(20 nm)/Al(100 nm) were prepared. A 30 nm thick PEDOT:PSS (Baytron PVP
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8 AI4083) was prepared on the pre-cleaned ITO substrate using spin-coating at a rotation speed
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10 of 2500 rpm following a post-annealing at 140°C in air for 10 min. A 90 nm thick
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12 PTB7:PC₇₀BM blend layer was then formed on the surface of PEDOT:PSS, prepared using the
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14 PTB7:PC₇₀BM mixture solution by spin-coating at 2000 rpm for 120 s inside the glovebox,
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16 having oxygen and moisture levels <0.1 ppm. After drying at room temperature for ~1h, a 20
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18 nm thick ZnO layer was then overlaid on the PTB7:PC₇₀BM active layer by spin-coating at
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20 2500 rpm for 120 s. Finally, samples were transferred to an adjacent vacuum evaporator for
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22 the deposition of a 100 nm thick Al top contact. The control cells without the ZnO interlayer
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24 were also made for comparison studies.
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33 In the TPC measurements, an Nd:YAG pulsed laser with a pulse duration of 5 ns and the
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35 wavelength of 355 nm was used. A set of devices comprising layer configurations of
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37 ITO/PEDOT:PSS(30 nm)/PC₇₀BM(400 nm)/Al (30 nm) (control) and ITO /PEDOT:PSS(30
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39 nm)/PC₇₀BM(400 nm)/ZnO(20 nm)/Al (30 nm) were prepared for the photo-physics studies.
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41 The use of the 400 nm thick PC₇₀BM layer helps suppressing the drift current, generated in the
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43 bulk of the PC₇₀BM layer, allowing for analyzing the interfacial exciton dissociation process
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45 occurred at the organic/electrode interface. The use of a 30 nm thick semitransparent top Al
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47 contact enables analyzing the interfacial exciton dissociation process at the organic/Al
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49 interface.^{38,39}
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58 In the photo-CELIV measurements, a short laser pulse is used to create free charge carriers
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4 in an organic active layer, followed by the extraction of free charge carriers using a linear
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6 voltage ramp.^{40, 41} A set of devices comprising layer configurations of ITO/PEDOT:PSS(30
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8 nm)/PTB7:PC₇₀BM(90 nm)/Al(100 nm) and ITO/PEDOT:PSS(30 nm)/PTB7:PC₇₀BM(90
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10 nm)/ZnO(20 nm)/Al(100 nm) were prepared for the photo-CELIV studies. An offset voltage
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12 (U_{offset}) of 0.6 V was applied to compensate V_{bi} for offsetting the internal electric field.
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17 **Results and discussion**

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21 The J - V characteristics measured for OSCs with a ZnO EEL and a control cell under AM
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23 1.5G illumination (100 mW/cm²) are plotted in Fig. 1(a). The absorption spectrum of the ZnO
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25 layer is shown in the Inset in Fig. 1(a). A summary of the cell parameters, averaged from more
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27 than 10 cells, is listed in Table 1. A higher FF of 0.73 was obtained for OSCs with a ZnO EEL,
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29 which is obviously higher than that of an optimized control cell (0.67), leading to a PCE of
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31 7.69±0.2 %, with a 9.4% increase as compared to the control cell (7.03±0.2 %). As shown in
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33 Table 1, OSCs with a ZnO EEL also exhibit a relatively lower R_{S} and higher R_{SH} compared to
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35 a control cell, revealing the efficient charge transport and extraction properties in the cell. The
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37 use of the ZnO EEL also improved contact quality at the active layer/Al interface, leading to
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39 an obvious reduction in the leakage current, as shown in Fig. 1(b).
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48 Fig. 2 shows the double logarithmic plot of the photocurrent (J_{ph})– effective voltage (V_{eff}),
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50 $J_{\text{ph}}-V_{\text{eff}}$, characteristics measured for OSCs, where $J_{\text{ph}}= J_{\text{l}}-J_{\text{d}}$, J_{l} is current measured under
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52 illumination, J_{d} is the dark current, with J_{sat} being the saturation photocurrent. V_{eff} is the
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54 effective voltage across the cell, defined as the difference between the built-in potential V_{bi} and
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56 the applied bias. Almost all the photo generated carriers can be collected at a high V_{eff} . The
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4 charge recombination increases with decrease in V_{eff} , therefore not all the photo-generated
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6 carriers can be collected at low V_{eff} . The charge collection efficiency P is a function of the
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8 intensity of the incident light, I and V_{eff} , and can be expressed as follows:⁴²
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$$P(I, V_{\text{eff}}) = \frac{J_{\text{ph}}(I, V_{\text{eff}})}{J_{\text{ph,sat}}(I)} \quad (1)$$

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16 J_{ph} becomes independent of the applied voltage and saturates at a high V_{eff} (>0.5 V), where
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18 P approaches unity and gives rise to almost 100% collection of the photo-generated charges.⁴³
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20 In this regime, recombination is negligible while it becomes increasingly important at low V_{eff} .
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22 As shown in Fig. 2, P decreases much slower in a ZnO modified device than that in a control
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24 cell at $V_{\text{eff}} < 0.5$ V, revealing enhanced charge collection efficiency.
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31 Light intensity dependent J - V characteristics measured for OSCs with a ZnO EEL and the
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33 control cell are investigated. There is a power law dependence of the photocurrent on light
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35 intensity, e.g., $J_{\text{ph}} \propto I^\alpha$.^{44,45} The value of the exponent α is associated with the recombination
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37 loss. α is usually approaching unity in OSCs with an efficient charge collection process, while
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39 the loss of the photo-generated charges through recombination generally results in a smaller α .
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41 As shown in Fig. 3, a unity α was obtained at high V_{eff} , suggesting an excellent charge
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43 collection process. As the charge mobility in organic materials is field dependent, less efficient
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45 charge extraction and collection would occur at low V_{eff} , leading to the charge recombination
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47 due to the space charge accumulation, and thereby a decrease in α can be observed in the $J_{\text{ph}}-I$
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49 characteristics. As shown in Fig. 3, α of 0.67 was obtained for the control device at a low V_{eff}
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51 of 0.085 V, while a higher α of 0.87 could still be remained in OSCs with a ZnO EEL at the
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53 same V_{eff} due to the reduced charge recombination, and thereby attaining higher charge
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4 extraction.

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7 OSCs with a ZnO EEL and the control cell possess the identical anode/organic contact.
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10 The charge extraction behaviors at the BHJ/anode in both types of OSCs can be considered
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12 identical. Hence, the change in the variations in the $J_{\text{ph}}-V_{\text{eff}}$ and $J_{\text{ph}}-I$ characteristics can be
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14 considered mainly due to the difference in charge extraction behaviors at the organic/cathode
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16 interfaces in both types of OSCs. The results reveal that OSCs with a ZnO EEL had a much-
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18 reduced recombination loss as compared to the control cell at the organic/cathode interface.
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20 The effect of the ZnO EEL on internal electric field, charge recombination and extraction
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22 processes in OSCs was analyzed using the TPC and photo-CELIV measurements.
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29 The exciton dissociation processes at the organic/cathode interfaces, a critical factor
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31 determining the performance in OSCs, was analyzed.^{46,47} The transient photocurrent includes:
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33 (1) the field dependent drift current formed under the internal electric field, and (2) current
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35 generated due to the interfacial exciton dissociation at the organic/electrode interfaces, which
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37 is independent on the electric field. To better understand the exciton dissociation process, the
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39 drift current due to the exciton dissociated at the donor/acceptor interface is offset by applying
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41 an opposite external bias to compensate the internal field. Therefore, the information of kinetics
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43 of photo-generated carriers at organic/electrode interface can be analyzed by measuring the
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45 transient photocurrents (I_{TPC}) at different biases.
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53 I_{TPC} measured for the devices comprising layer configurations of
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55 ITO/PEDOT:PSS/PC₇₀BM(400 nm)/Al(30 nm) and ITO/PEDOT:PSS/PC₇₀BM(400
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57 nm)/ZnO(20 nm)Al(30 nm) at different biases, with light incident from the semitransparent Al
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4 contact, are plotted in Fig. 4 (a) and (b). The positive I_{TPC} decays measured without external
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6 bias are always observed for both types of devices, which is predominantly contributed by the
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8 drift current. However, very unique I_{TPC} behaviors are observed when a positive bias is applied.
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10 V_{bi} decreases when a positive bias was applied to the devices. Therefore, the contribution in
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12 I_{TPC} from the drift current will decrease, while that originated from the exciton dissociation will
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14 increase. A clear rapid negative signal for the control device is observed with the reverse bias
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16 from 0.3 V to 0.5 V, and then followed with a slower positive photocurrent. The negative
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18 transient current originates from exciton dissociation at the PC₇₀BM/Al interface, which is very
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20 sensitive to the interfacial properties. While the slower positive photocurrent comes from the
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22 photo-generated carriers that drift with V_{bi} and decreases with the increase of the reverse bias.
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24 This negative I_{TPC} suggests that the direction of the transient current created by the exciton
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26 dissociation at the PC₇₀BM/Al contact is opposite to that of the drift current. Thus, these photo-
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28 generated electrons must be compensated preferentially before the drifted electrons are
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30 collected by the cathode. The negative transient photocurrent comes from the exciton
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32 dissociation which is unfavorable for electron collection. However, with the presence of a ZnO
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34 EEL between PC₇₀BM and Al, the rapid negative transient current due to the unfavorable
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36 interfacial exciton dissociation at the organic/Al interface can be eliminated, only a rapid
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38 positive transient current is observed at an external bias of 0.9V. The TPC results reveal clearly
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40 that the use of a ZnO EEL helps to remove the unfavorable interfacial exciton dissociation, and
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42 thereby enhances of the electron collection efficiency.³⁹

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57 TPC measured for the devices comprising different layer configurations of ITO/Al(10
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59 nm)/PC₇₀BM/MoO₃/Ag and ITO/Al(10 nm)/ZnO(20 nm)/PC₇₀BM/MoO₃/Ag was also

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4 analyzed. The measured transient photocurrents are plotted in Fig. 5. It is clear that the rapid
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6 negative peak, indicating an unfavorable exciton dissociation at the Al/PC₇₀BM interface, was
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8 not seen in devices with a reverse configuration, which is independent on the ZnO EEL. This
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10 indicates that the interfacial exciton dissociation behaviors at the organic/Al interface are
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12 dependent on formation of the organic/metal interface, e.g., the depositing sequences of the
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14 organic layer and Al. When the organic/metal interface is formed by depositing the organic
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16 layer on the Al layer, a relatively clear metal/organic interface is expected. However, the
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18 interfacial defects and traps occurred when the organic/Al interface was formed by depositing
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20 Al on organic surface using thermal evaporation. The sub-gap states induced by the interfacial
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22 defects may allow electron transfer from Al to PC₇₀BM, caused by the unfavorable interfacial
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24 exciton dissociation. The presence of the ZnO EEL also serves as a good hole-blocking layer
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26 at the organic/Al interface, preventing the undesired exciton dissociation at the PC₇₀BM/Al
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28 interface. Schematic diagrams illustrating the processes of exciton dissociation at the PC₇₀BM
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30 /Al and PC₇₀BM /ZnO/Al interfaces are presented in Fig. 6 (a) and (b).
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41 The influence of the ZnO EEL on bimolecular recombination process is analyzed using
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43 photo-CELIV measurements. Photo-CELIV is a powerful technique to investigate both the
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45 carrier mobility and recombination dynamics.^{48,49} Fig. 7 presents the schematic illustration of
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47 the photo-CELIV method. A laser pulse is introduced to generate the photo-carriers. An offset
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49 bias (U_{offset}) is applied to compensate the built-in potential, forcing the charge carriers to remain
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51 in the device and recombine. After an adjustable delay of the laser pulse, the remaining charge
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53 carriers are extracted under the linearly increasing voltage pulse with a rising speed A , which
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55 is defined as $A = dU/dt$.
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The maximum current due to photoexcitation (Δj) and the time taken to reach the extraction current maximum (t_{\max}) can be estimated using the photo-CELIV transient currents. The charge mobility (μ) can then be calculated using equation (2):

$$\mu = \frac{2d^2}{3At_{\max}^2 \left[1 + 0.36 \frac{\Delta j}{j(0)} \right]} \quad (2)$$

Equation (2) is corrected for the electric field re-distribution during the charge extraction process. The photo-CELIV transients are recorded for OSCs with a thin ZnO EEL and the control cell over a delay time range from 5 μ s to 1000 μ s. U_{offset} was set at -0.6V, which is very close to V_{bi} in the cell. Fig. 8 presents the typical photo-CELIV transients measured for OSCs using a delay time of 5 μ s. The carrier mobility results, calculated with Equation (2), show that the effective carrier mobility μ in the device with a ZnO/Al cathode ($2.0 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) is a little higher than that of the control cell ($9.7 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$). This reveals the efficient carrier transport in OSCs with a ZnO EEL.

According to the theory of dispersive recombination dynamics, the delay time dependent density of electrons $n(t)$, and density of holes $p(t)$, can be expressed by:⁵⁰

$$n(t) = p(t) = \frac{n(0)}{1 + (t / \tau_B)^\gamma} \quad (3)$$

where $n(0)$ is the initial carrier density, t is the delay time and $\tau_B = \left[\frac{\gamma}{n(0)\beta_0} \right]^{1/\gamma}$ is the bimolecular recombination lifetime. The parameter γ ($0 < \gamma < 1$) is denoted as the dispersion parameter, which is around 1 for a non-dispersive recombination. The dispersive recombination process often results in a smaller γ . Fig. 9(a) exhibits the delay time-dependent carrier density

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4 characteristics, obtained by integrating the photo-CELIV transients over time. Solid curves in
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6 Fig. 9 (a) are the theoretical results calculated using equation (3), indicating that $n(t)$ derived
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8 by photo-CELIV measurements are in good agreement with the results obtained by the
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10 theoretical recombination model. The values of $n(0)$, τ_B and γ , calculated for different cells,
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12 are summarized in Table 2. The carrier density includes the extracted photo-generated charge
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14 carriers remained after the recombination losses. The number of the extracted carriers varies
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16 with the delay time that was used in the photo-CELIV measurements.
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23 Two particularities can be attained from the delay time dependent carrier density results.
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25 First, the density of extracted charge carriers decreases with increase in the delay time for both
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27 devices. This reflects that less photogenerated carriers were collected when longer delay time
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29 is applied due to the recombination processes. Second, the two devices exhibit very different
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31 delay time-dependent carrier density characteristics. The fitting data suggest the power law
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33 dependence of the carrier density on delay time for the control device. While for OSCs with a
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35 ZnO EEL, $n(t)$ exhibits a much faster decay with increasing delay time, suggesting a higher
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37 order delay time dependence on carrier density. A smaller dispersive parameter γ value ($\gamma=0.26$)
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39 implies that a highly dispersive recombination process dominates in the control cell, indicating
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41 a high loss due to the trap-limited charge recombination. Whereas a high γ of 0.98 manifests
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43 an almost non-dispersive or trap-free recombination in OSCs with a ZnO EEL.
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52 According to the delay time-dependent bimolecular recombination relation
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54 $\frac{dn}{dt} = \frac{dp}{dt} = -\beta(t)np$, the bimolecular recombination coefficient $\beta(t)$ as a function of carrier
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56 density $n(t)$ can be expressed as follows:
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$$\beta(t) = \frac{dn(t)/dt}{n^2(t)} \quad (4)$$

Combining equations (3) and (4), $\beta(t)$ can also be expressed as:

$$\beta(t) = a\gamma n_0^{-1} (at)^{\gamma-1} \quad (5)$$

where $a=1/\tau_B$, τ_B is the “effective” bimolecular recombination lifetime ($\tau_B = \left\{ \frac{\gamma}{[n(0)\beta_0]} \right\}^{1/\gamma}$), and γ ($0 < \gamma \leq 1$) is the dispersion parameter.

The relationship between $\beta(t)$ and t can then be obtained by substituting $n(0)$, τ_B and γ into equation (5), which is presented in Fig. 9(b). Results reveal different power law dependences between $\beta(t)$ and delay time for the two cells. $\beta(t)$ is almost independent on the delay time in ZnO modified device, with a constant value around $1.1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. While for the control device, it declines quickly with an increase in the delay time. $\beta(t)$ decreased by two orders of magnitude when the delay time increased from 5 μs to 100 μs .

The disparate behaviors of delay time-dependent carrier concentration and bimolecular recombination coefficient can be explained with the multi-trapping model as illustrated in Fig. 10. For the control cell, Al was evaporated directly onto the surface of organic layer. The weak van der Waals interaction between molecules in the organic layer can be perturbed by the incoming flux of high energetic Al clusters during the thermal evaporation, inducing undesired interfacial traps due to the formation of the structural and energetic disorders in the organic layer. The incoming flux of the energetic Al clusters may also penetrate into the organic active layer, resulting in complex interfacial properties.³⁹ These influences will bring more interfacial defects and much deeper trap states in the active layer. The trapping and de-trapping processes

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4 are responsible for the trap-limited bimolecular recombination.
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7 Both the deep traps and shallow traps the charge carriers at a high carrier density trap.
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9 While, at a low carrier density, charge carriers trapped by the deep traps are more difficult to
10 release. The charge carriers release from the shallow traps are mainly responsible for
11 bimolecular recombination followed by the charge carriers de-trapped from the deep traps. The
12 presence of the deeper traps or energy barriers at the organic/Al interface can lead to the buildup
13 of the space charge, reducing the effective recombination rate. When a solution-processed ZnO
14 layer is deposited before the thermal evaporation of Al, it can help to protect the active layer
15 by reducing the numbers of the interfacial defects, which is beneficial for the trap-free
16 bimolecular recombination with constant recombination rate.
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31 **Conclusions**

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35 The effect of ZnO EEL on charge collection and recombination processes in
36 PTB7:PC₇₀BM-based OSCs with a ZnO EEL has been analyzed systematically using a
37 combination of photo-CELIV, light intensity dependent $J-V$ characteristic and TPC
38 measurements. It shows that the use of the ZnO EEL favors the efficient operation of OSCs in
39 two ways: (1) it helps to suppress the trap-limited bimolecular recombination, and (2) it enables
40 to illuminate the unfavorable interfacial exciton dissociation at the organic/ cathode interface.
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8 Fig. 1: (a) $J-V$ and (b) dark $J-V$ characteristics measured for OSCs with a ZnO EEL and a
9 control cell. Inset in Fig. 1(a): Absorption spectrum of the ZnO layer.
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14 Fig. 2: Double logarithmic plots of $J_{\text{Ph}}-V_{\text{eff}}$ characteristics obtained for OSCs with a ZnO
15 EEL and a control cell.
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20 Fig. 3: Double logarithmic plots of the photocurrent density as a function of light intensity
21 measured for (a) the OSC with a ZnO EEL and (b) a control cell under different effective
22 voltages.
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29 Fig. 4: Transient photocurrents measured for devices comprising layer configurations of (a)
30 ITO/PEDOT:PSS/PC₇₀BM/Al and (b) ITO/PEDOT:PSS/PC₇₀BM/ZnO/Al under different
31 external biases.
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37 Fig. 5: Transient photocurrents measured for devices comprising layer configurations of (a)
38 ITO/Al/PC₇₀BM/M₂O₃/Ag and (b) ITO/Al/ZnO/PC₇₀BM/M₂O₃/Ag under different external
39 biases.
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46 Fig. 6: Schematic diagrams illustrating the processes of interfacial exciton dissociation at the
47 (a) organic/Al and (b) organic/ZnO/Al interfaces.
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51 Fig. 7: Schematic illustration of the photo-CELIV method.
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54 Fig. 8: Typical photo-CELIV transients measured for the OSC with a ZnO EEL and a control
55 cell with a delay of 5 μs .
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4 Fig. 9: Double logarithmic plots of delay time-dependent (a) carrier concentration and (b)
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6 bimolecular recombination coefficient obtained for the OSC with a ZnO EEL and a control
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12 Fig. 10: Schematic diagram illustrating the multi-trap model and the distribution of the
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14 interfacial defects and traps formed at the organic/Al interface that is formed by depositing Al
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16 on (a) organic layer, and (b) on ZnO EEL-protected organic layer.
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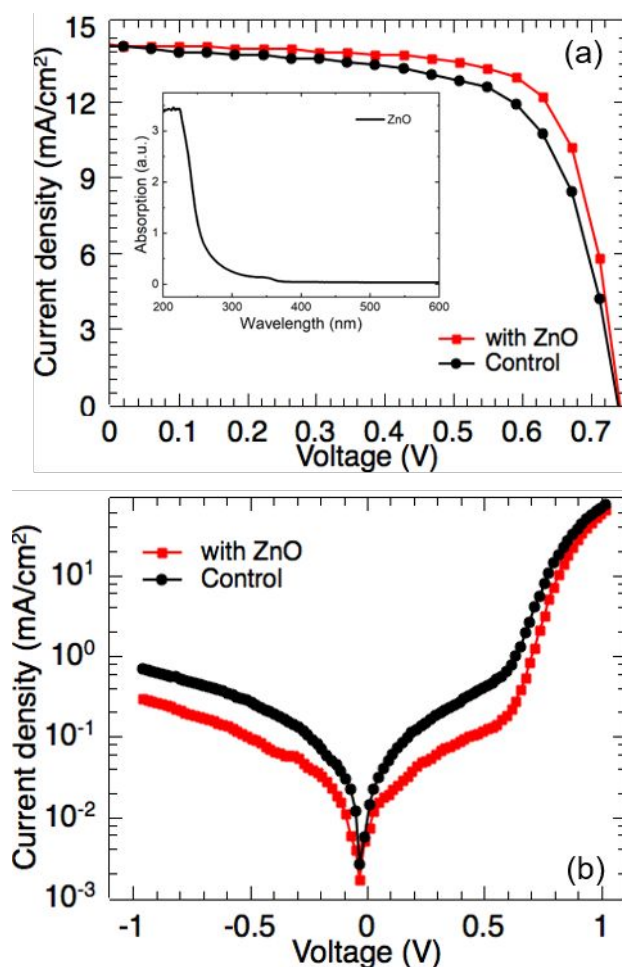


Fig. 1: (a) J - V and (b) dark J - V characteristics measured for OSCs with a ZnO EEL and a control cell. Inset in Fig. 1(a): Absorption spectrum of the ZnO layer.

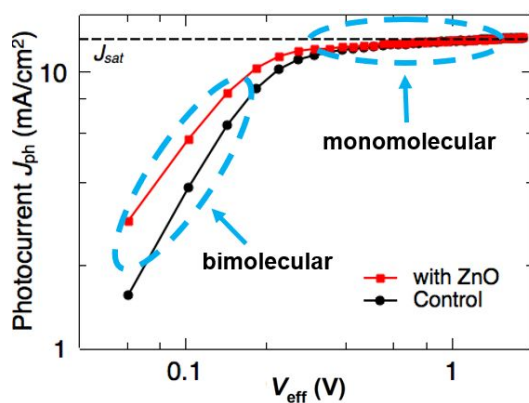


Fig. 2: Double logarithmic plots of $J_{\text{ph}}-V_{\text{eff}}$ characteristics obtained for OSCs with a ZnO EEL and a control cell.

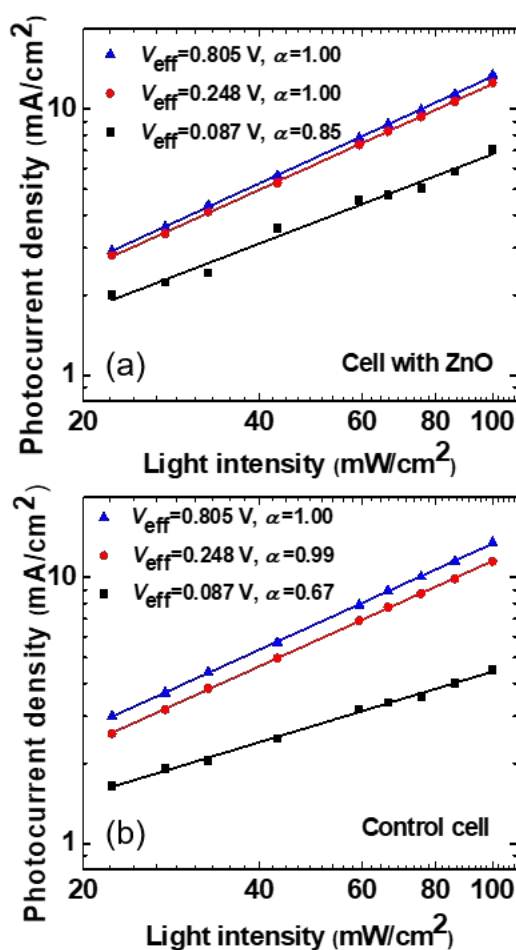


Fig. 3: Double logarithmic plots of the photocurrent density as a function of light intensity measured for (a) the OSC with a ZnO EEL and (b) a control cell under different effective voltages.

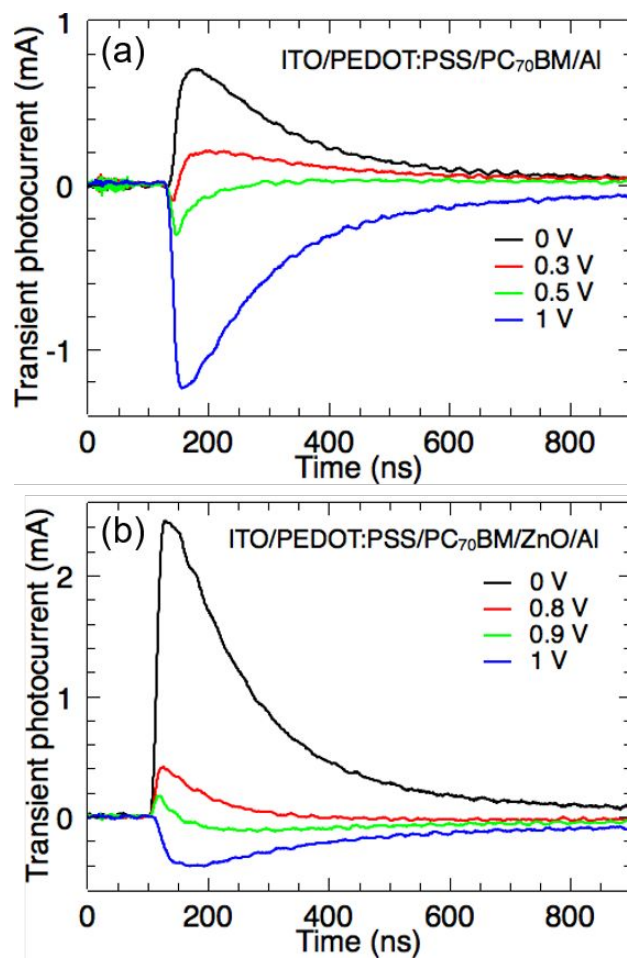


Fig. 4: Transient photocurrents measured for devices comprising layer configurations of (a) ITO/PEDOT:PSS/PC₇₀BM/Al and (b) ITO/PEDOT:PSS/PC₇₀BM/ZnO/Al under different external biases.

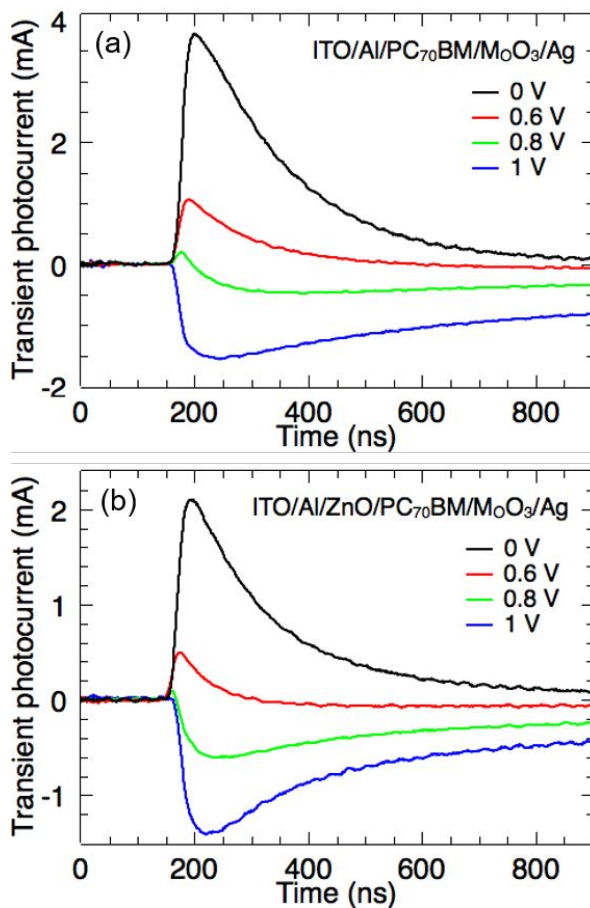


Fig. 5: Transient photocurrents measured for devices comprising layer configurations of (a) ITO/Al/PC₇₀BM/MoO₃/Ag and (b) ITO/Al/ZnO/PC₇₀BM/MoO₃/Ag under different external biases.

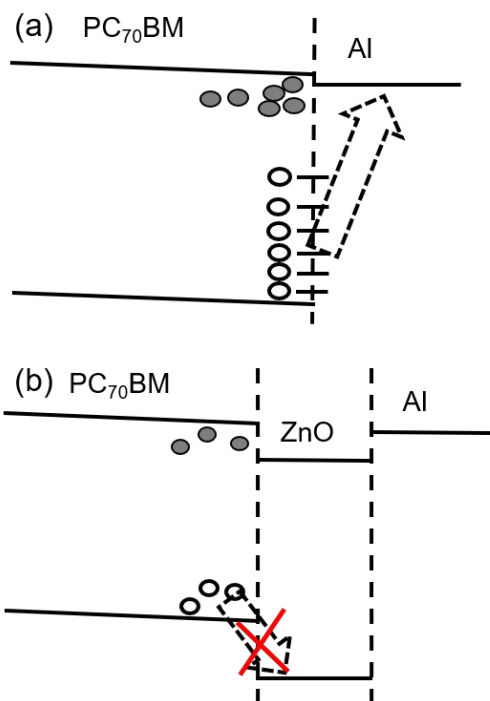


Fig. 6: Schematic diagrams illustrating the processes of interfacial exciton dissociation at the (a) organic/Al and (b) organic/ZnO/Al interfaces.

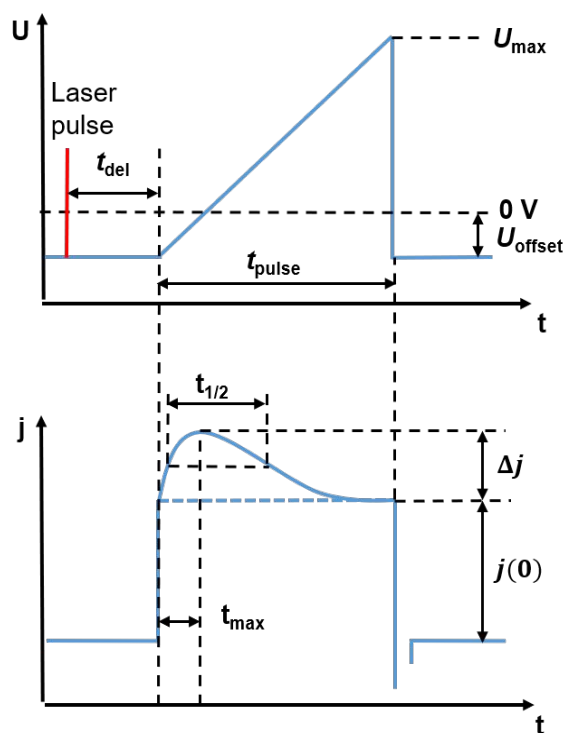


Fig. 7: Schematic illustration of the photo-CELIV method.

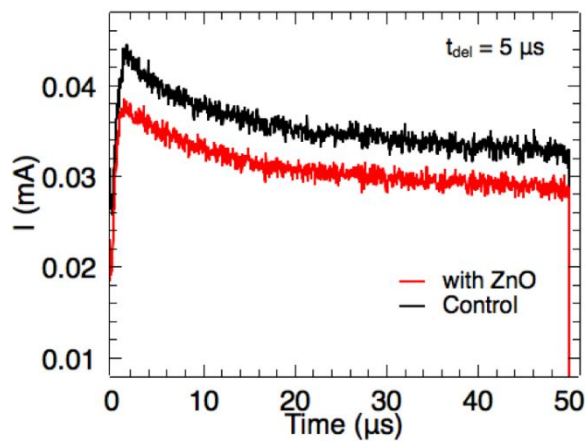


Fig. 8: Typical photo-CELIV transients measured for the OSC with a ZnO EEL and a control cell with a delay of 5 μs .

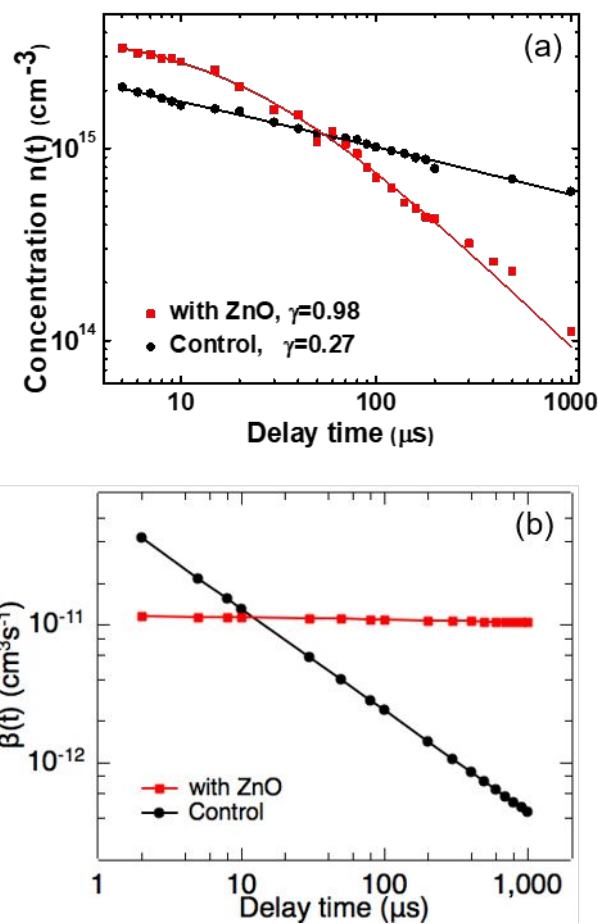


Fig. 9: Double logarithmic plots of delay time-dependent (a) carrier concentration and (b) bimolecular recombination coefficient obtained for the OSC with a ZnO EEL and a control cell.

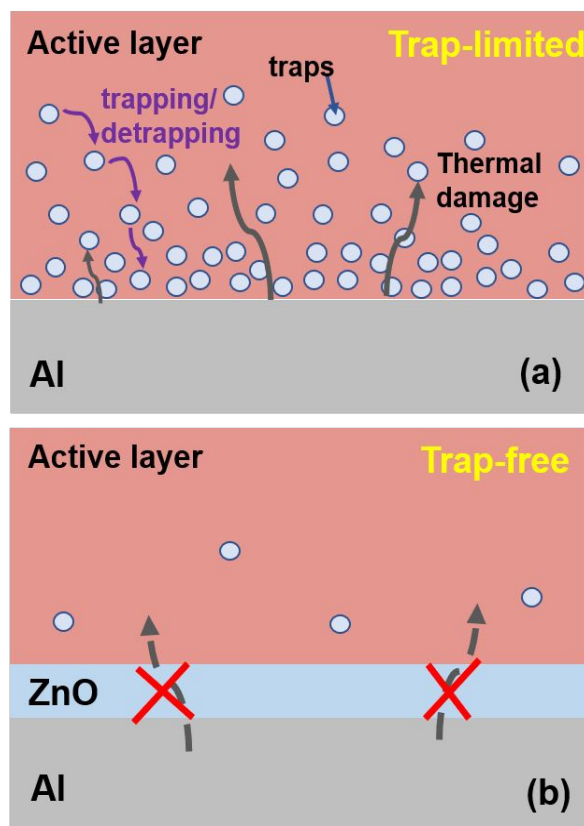


Fig. 10: Schematic diagram illustrating the multi-trap model and the distribution of the interfacial defects and traps formed at the organic/Al interface that is formed by depositing Al on (a) organic layer, and (b) on ZnO EEL-protected organic layer.

Table 1: Summary of the parameters obtained for OSCs made with and without a ZnO EEL.

	PCE	J_{SC}	FF	V_{OC}	R_S	R_{SH}
	(%)	(mA/cm ²)	(%)	(V)	($\Omega \cdot \text{cm}^2$)	($\Omega \cdot \text{cm}^2$)
with ZnO	7.69±0.2	14.22±0.1	72.94±0.2	0.74	4.8	1513.8
Control	7.03±0.2	14.13±0.2	67.23±0.1	0.74	5.9	987.1

Table 2: Summary of parameters calculated using equation (3).

	$n(0)$ (cm ⁻³)	γ	τ_B (μs)
ZnO/Al	4.12×10^{15}	0.98	21.41
Al	1.27×10^{15}	0.26	0.01