



AFRL-AFOSR-JP-TR-2017-0073

Magnetic field effect in conjugated molecules-based devices

Tzung-Fang Guo
NATIONAL CHENG KUNG UNIVERSITY

10/23/2017
Final Report

DISTRIBUTION A: Distribution approved for public release.

Air Force Research Laboratory
AF Office Of Scientific Research (AFOSR)/ IOA
Arlington, Virginia 22203
Air Force Materiel Command

REPORT DOCUMENTATION PAGE				<i>Form Approved</i> OMB No. 0704-0188	
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Executive Services, Directorate (0704-0188). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.</p>					
1. REPORT DATE (DD-MM-YYYY) 15-11-2017		2. REPORT TYPE Final		3. DATES COVERED (From - To) 22 Jul 2014 to 21 Jul 2017	
4. TITLE AND SUBTITLE Magnetic field effect in conjugated molecules-based devices				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER FA2386-14-1-4012	
				5c. PROGRAM ELEMENT NUMBER 61102F	
6. AUTHOR(S) Tzung-Fang Guo				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) NATIONAL CHENG KUNG UNIVERSITY 1, TA HSUEH RD., TAINAN CITY, 70101 TW				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AOARD UNIT 45002 APO AP 96338-5002				10. SPONSOR/MONITOR'S ACRONYM(S) AFRL/AFOSR IOA	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-AFOSR-JP-TR-2017-0073	
12. DISTRIBUTION/AVAILABILITY STATEMENT A DISTRIBUTION UNLIMITED: PB Public Release					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT This project with TF Guo has been an very successful basic research project to identify Magnetic field effect in conjugated molecule-based devices. The final year of the project had a collaboration with Professor Bin Hu at the University of Tennessee, Knoxville. In this work, the researchers were able to identify that the magneto-photocurrent becomes negligible and appreciates towards short-circuits and open circuit conditions, revealing an increase on charge dissociation under the influence of the NiOx layer. This 3 year study highlighted the fundamental aspect in NoOx transport layer to modulate the magneto-photocurrent in perovskite-based photovoltaic cells.					
15. SUBJECT TERMS magnetic activity, organic and polymeric optica devices, organic materials					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 20	19a. NAME OF RESPONSIBLE PERSON CHEN, JERMONT
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			

**Report for AOARD Grant FA2386-14-1-4012
(AOARD-14-4012)**

10/20/2017

Magnetic field effect in conjugated molecules-based devices

07/22/2016 ~ 07/21/2017

Name of Principal Investigator: Tzung-Fang Guo

E-mail address: guotf@mail.ncku.edu.tw, guotf023@gmail.com

Institution: Department of Photonics, National Cheng Kung University

Mailing address: No. 1 Ta-Hsueh Rd., Tainan 701, Taiwan

Phone: +886-6-2757575 ext. 63914

FAX: +886-6-2747995

Co-investigators (names and institutions): Ten-Chin Wen

**Department of Chemical Engineering, National Cheng Kung University, Tainan 701,
Taiwan**

Contents

I. Abstract	3
II. Progress summaries	3
III. Summary of Accomplishments	5
IV. Magnetic field effect of perovskite-based photovoltaics with NiO_x transport layer	7
V. Conclusions and Future work	17

I. Abstract

In this period of project, we focus on the effects of NiOx transport layer on internal photovoltaic processes in perovskite solar cells [ITO/HTL/CH₃NH₃PbI₃/PC₆₀BM/PEIE/Ag] based on magneto-photocurrent, transient and field-dependent photoluminescence. This is a joint research work between NCKU with Prof. Bin Hu in University of Tennessee Knoxville. NCKU team had supported one Ph.D. student, Miss Pei-Ying Lin, to study under Prof. Bin Hu in University of Tennessee Knoxville from March 2016 to February 2017. We had disclosed that the magneto-photocurrent becomes negligible and appreciable towards short-circuit and open-circuit conditions, revealing an increase on charge dissociation under the influence of the NiOx layer. The transient photoluminescence indicates that the NiOx/CH₃NH₃PbI₃ interface leads to an enlarged lifetime (~20 ns), suggesting a reduction on non-radiative recombination and increasing excitons available for photovoltaic actions. The field-dependent photoluminescence measured alternatively at short-circuit and open-circuit conditions show that the NiOx can also suppress the radiative recombination, boosting the photovoltaic actions from available excitons. Our studies had highlighted the fundamental aspects in NiOx transport layer to modulate the magneto-photocurrent in perovskite-based photovoltaic cells.

II. Progress summaries

- The unique MC responses tetracene-based diodes by the singlet fission reaction and the photovoltaic application

We had verified that the singlet fission reactions of tetracene molecules would determine MC responses of the photocurrent. However, the blend of C₆₀ with tetracene generates the charge transfer complexes at C₆₀/tetracene interfaces under the photo illumination and suppresses the fission reaction. We concluded that the kinetic response of the charge transfer at the acceptor/donor interfaces is higher than that of the fission reaction in tetracene molecules, which markedly limits the fission reaction to generate multiple carriers in photovoltaic application. Accordingly, we had to design an efficient hole transport layer (HTL)/active layer for fission reaction/electron transport layer (ETL) system for the extraction of multiple carriers by the fission reaction under the photoillumination, which is a currently ongoing subject.

- Triplet-triplet annihilation to Fluorescence in polymer light emitting diodes

We apply the magnetoconductance (MC) and magneto-electroluminescence (MEL) measured under low and high current density to identify the triplet-triplet annihilation process (TTA) process in charge-balanced polymer light emitting diode (PLED) containing a super yellow poly-(phenylene vinylene) (SY-PPV) material. TTA process possibly generates the singlet from triplet excitons to enhance the quantum efficiency in fluorescent organic light emitting diodes (OLEDs). We confirm our assumption by measuring MC and MEL under different temperature and found that the MEL response decreases at the high magnetic field in the low temperature regime. This observation verifies the contribution of TTA process to the fluorescence at the high current density. Our results demonstrate a clear correlation between TTA process and current density as well as temperature in charge-balanced SY-PPV-based PLEDs.

- Magnetic field effect of perovskite-based photovoltaics with NiO_x transport layer

NCKU team had supported one Ph.D. student, Miss Pei-Ying Lin, to study in Prof. Bin Hu's lab at University of Tennessee Knoxville from March 2016 to February 2017. We focused on the magneto-photocurrent responses of hybrid perovskite solar cells of NiO_x hole transport layer. We had found that the magneto-photocurrent becomes negligible and appreciable towards short-circuit and open-circuit conditions, revealing an increase on charge dissociation under the influence of the NiO_x layer. We disclose the mechanisms for the improvement of J_{sc} and V_{oc} towards the high photovoltaic parameters with the appropriate charge transport layer.

III. Summary of Accomplishments

Publications to date;

1. “Modulations in line shapes of magnetoconductance curves for diodes of pentacene:fullerene charge transfer complexes” *Org. Electron.* **15**, 3076 (2014). **(AOARD-14-4012)**
2. “The origins in the transformation of ambipolar to n-type pentacene-based organic field-effect transistors” *Org. Electron.* **15**, 1759 (2014). **(AOARD-14-4012)**
3. “Conversion efficiency improvement of inverted $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells with room temperature sputtered ZnO by adding the C_{60} interlayer” *Appl. Phys. Lett.* **107**, 253301 (2015). **(AOARD-14-4012)**
4. “Functional p-type, polymerized organic electrode interlayer in $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite/fullerene planar heterojunction hybrid solar cells” *ACS Appl. Mater. Inter.* **7**, 24973 (2015). **(AOARD-14-4012)**
5. “Oxidized Ni/Au transparent electrode in efficient $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite/fullerene planar heterojunction hybrid solar cells” *Adv. Mater.* **28**, 3290 (2016). **(AOARD-14-4012)**
6. “ NiO_x electrode interlayer and $\text{CH}_3\text{NH}_2/\text{CH}_3\text{NH}_3\text{PbBr}_3$ interface treatment to markedly advance hybrid perovskite-based light-emitting diodes” *Adv. Mater.* **28**, 8687 (2016). **(AOARD-14-4012)**
7. “Simultaneously enhancing dissociation and suppressing recombination in perovskite solar cells by using NiO_x transport interlayer” *Nano Energy* **36**, 95 (2017). **(AOARD-14-4012)**
8. “Magneto conductance responses of singlet fission reaction in tetracene-based diodes” submitted (2016). **(AOARD-14-4012)**
9. “Angle dependent magnetoconductance responses for diodes based-on intermolecular charge transfer complexes” submitted (2016). **(AOARD-14-4012)**
10. “Modulating the magnetoconductance line-shape by triplet exciton-charge reaction in polymer light emitting diodes” in preparation (2016). **(AOARD-14-4012)**
11. “Triplet-triplet annihilation to Fluorescence in polymer light emitting diodes” in preparation (2016). **(AOARD-14-4012)**

Presentations (conferences, workshops, general/invited);

1. **T. –F. Guo*** 2016 International symposium on Next-Generation Solar Cells and Solar Energy Conversion, Hsin-Chu, Taiwan (Nov. 2016). **(Invited presentation)**
(AOARD-14-4012)

2. **T. –F. Guo*** *2016 International Workshop in Magneto-optic studies for novel molecular materials and devices*, Beijing (Dec. 2016). (**Invited presentation**)
(AOARD-14-4012)
3. **T. –F. Guo*** *2016 SPSJ Symposium on Electrical and Electronic Properties of Polymer and Organics*, Kyoto, Japan (Dec. 2016). (**Invited presentation**)
(AOARD-14-4012)
4. **T. –F. Guo*** *MRS Spring Meeting*, Phoenix City, USA (Apr. 2017). (**Invited presentation**) **(AOARD-14-4012)**
5. **T. –F. Guo*** *2nd International Workshop on Luminescence and Optoelectronic Materials and Devices*, Beijing, China (Oct. 2017). (**Invited presentation**)
(AOARD-14-4012)

IV. Magnetic field effect of perovskite-based photovoltaics with NiO_x transport layer

1. Introduction

Interface engineering has led to remarkable photovoltaic developments in organo-metal halide perovskite solar cells (PSC) ¹⁻⁷. Initially, the Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) has been used as a hole-transport layer (HTL) in PSCs with an inverted device structure⁸⁻¹¹. However, the PEDOT:PSS possesses hydrophilic and acidic nature^{12, 13}, which is detrimental to the long-term device-operation stability^{14, 15}. Recently, it has been found that the NiO_x can replace the PEDOT:PSS, functioning as an important HTL, to improve device photovoltaic performance¹⁶⁻²². However, it remains as un-addressed issue to reveal how the NiO_x HTL can influence the internal photovoltaic processes in PSCs. Revealing the effects of NiO_x HTL on charge dissociation, recombination, and collection can provide an insightful understanding on rational design of interface engineering towards further advancement of photovoltaic actions in organo-metal halide perovskites.

In this report, we use three major experimental measurements, (i) magneto-photocurrent (magneto-Jsc) under external bias, (ii) transient and field-dependent photoluminescence (PL) studies to address how the NiO_x HTL affects the dissociation, recombination in both non-radiative and radiative regimes, and interfacial charge collection based on the inverted device [ITO/HTL/CH₃NH₃PbI₃/PC₆₀BM/PEIE/Ag] with an efficiency of 17.53% (16.15% averagely between 10 devices). Interestingly, the magneto-Jsc shows a negligible value in the NiO_x-based device, suggesting a sufficient dissociation in the NiO_x-based device at short-circuit condition. However, applying a forward bias to weaken the built-in field can recover the magneto-Jsc: changing the magneto-Jsc from negligible to appreciable value, implying an in-sufficient dissociation upon decreasing the built-in field. As a reference, the PEDOT:PSS-based device exhibits an appreciable magneto-Jsc, suggesting an in-sufficient dissociation at short-circuit condition. But, applying a reverse bias to strengthen the built-in field leads to a negligible magneto-Jsc in the PEDOT:PSS-based device, presenting a sufficient dissociation upon increasing the built-in field. Therefore, the bias-dependent magneto-Jsc provides the first evidence that the built-in field associated with the NiO_x HTL plays an important role on internal charge dissociation in the PSCs. Furthermore, the transient PL measurement shows that the NiO_x/CH₃NH₃PbI₃ interface yields a much enlarged lifetime up to 20 ns while the PEDOT:PSS/CH₃NH₃PbI₃ interface yields a much shorter lifetime of ~ 6 ns. This PL lifetime study provides an experimental confirmation that the NiO_x HTL can suppress the non-radiative

recombination, leading to more excitons available for generating photovoltaic actions in the perovskite layer. Furthermore, the NiOx HTL causes a larger PL difference between J_{sc} and V_{oc} conditions as compared to the PEDOT:PSS HTL, revealing that the NiOx HTL also decrease the radiative recombination within the available excitons, enhancing the photovoltaic actions in the NiOx-based device. Moreover, the photoinduced capacitance directly confirms that the NiOx HTL generates a stronger built-in field in the PSCs. With a stronger built-in field, the NiOx HTL results in a less interface-accumulation of photogenerated carriers, shown as a lower CV peak shift with increasing the photoexcitation intensity. Consequently, the NiOx HTL enhances the J_{sc} and V_{oc} towards the photovoltaic enhancement in the PSCs.

2. Experimental

Device Fabrication: The solar cells were fabricated onto the pre-cleaned ITO/glass substrates. PEDOT:PSS (4083, Heraeus, filtered with 0.45 μ m PVDF filter) was spin-coated onto ITO substrates at 4000 rpm for 60 s and then thermally annealed in air at 150 °C for 25 minutes. Nickel oxide (NiOx) was prepared by solution processing method according to the previous publications^{16, 23}. In particular, an ethylene glycol solution containing 0.5 M nickel formate dihydrate ($\text{CH}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$) with 1 molar equivalents of ethylenediamine (EN) was stirred overnight at room temperature and then filtered with 0.45 μ m nylon filters before using. The solution was spin-cast on ITO substrates at 4000 rpm for 90 seconds and then annealed at 300 °C in air for 60 minutes. The precursor solution of $\text{CH}_3\text{NH}_3\text{PbI}_3$ was prepared by dissolving 1 mmole $\text{CH}_3\text{NH}_3\text{I}$ and 1mmole PbI_2 in 1 mL mixture solvent of γ -butyrolactone (GBL):dimethyl sulfoxide (DMSO) (7:3, v/v) at 60 °C for 12 h inside the nitrogen-filled glove box. The perovskite films were spin-cast by a consecutive two-step process at 1000 rpm and 4000 rpm for 20 s and 40 s, respectively. Additionally, 400 μ L toluene was dropped on the top of the perovskite films at the 20th second of the second step. The as-cast films were immediately annealed at 100 °C for 10 minutes. After cooling down, Phenyl- C_{61} -butyric acid methyl ester (PCBM, 20 mg/mL in chlorobenzene) was spin-cast on top of perovskite layers at 1000 rpm for 60 s and followed by drying in covered Petri-dish for 45 minutes at N_2 atmosphere. Afterwards, an interface-modifying layer (PEIE) (0.02 wt% in anhydride 2-Propanol) was spin-cast on top of PCBM layer at 5000 rpm for 60 s. Finally, the 100 nm thick silver electrodes were deposited on the PEIE with the area of the 0.1 cm^2 under the vacuum of 6×10^{-6} torr.

Characterization: The current density-voltage (J - V) curves, were measured inside a nitrogen-filled glovebox by using Keithley 2602 source meter under standard one sun

AM 1.5G (100 mW/cm²) from Thermal Oriel 96000 300 W solar simulator. The magneto-Jsc were obtained by measuring photocurrent (Jsc) as a function of magnetic field parallel to device plane. The PL lifetimes were characterized by time-resolved fluorescence measurements using Streak camera (HAMAMATSU C10627). The samples were excited at 515 nm from the second harmonic of an Yb-doped fiber laser (TANGERINE, Amplitude System) with the fluences of 5 μJ/cm², and repetition rate of 50 kHz. In order to resolve the full dynamics with the best possible resolution and high signal-to-noise ratio, the dynamics of the fluorescence were recorded on several time windows, from 5 ns up to 500 ns with the time resolution of 0.5% for each time window. The photoexcitation for PL and magneto-Jsc measurements was used the 532 nm CW laser beam at the intensity of 415 mW/cm² perpendicularly applied on the devices through transparent ITO (indium-tin-oxide) electrodes.

3. Result and Discussion

Figure 1 (a and b) presents the device structure with the NiO_x and PEDOT:PSS HTLs with the inverted design [ITO/HTL/CH₃NH₃PbI₃/PCBM/PEIE/Ag] and the related energy diagram. **Figure 1c** shows the current density-voltage (*J-V*) characteristics for the NiO_x and PEDOT:PSS based PSCs. The key photovoltaic parameters are summarized in **Table 1**. We can see that using the NiO_x to replace the PEDOT:PSS leads to a substantial enhancement on open-circuit voltage (V_{OC}) from 0.88 V to 1.01 V, and simultaneously an increase on the short-circuit current (Jsc) from 19.32 to 21.14 mA/cm², while a high fill factor (FF~0.75) can be readily achieved in all devices. As a result, the power conversion efficiency (PCE) is improved from 12.8% to 16.0% averagely. The efficiency of the optimized device with NiO_x HTL has reached 17.53%. Both NiO_x and PEDOT:PSS based devices do not show any hysteresis effect on the *J-V* characteristics, suggesting high-quality PSCs.

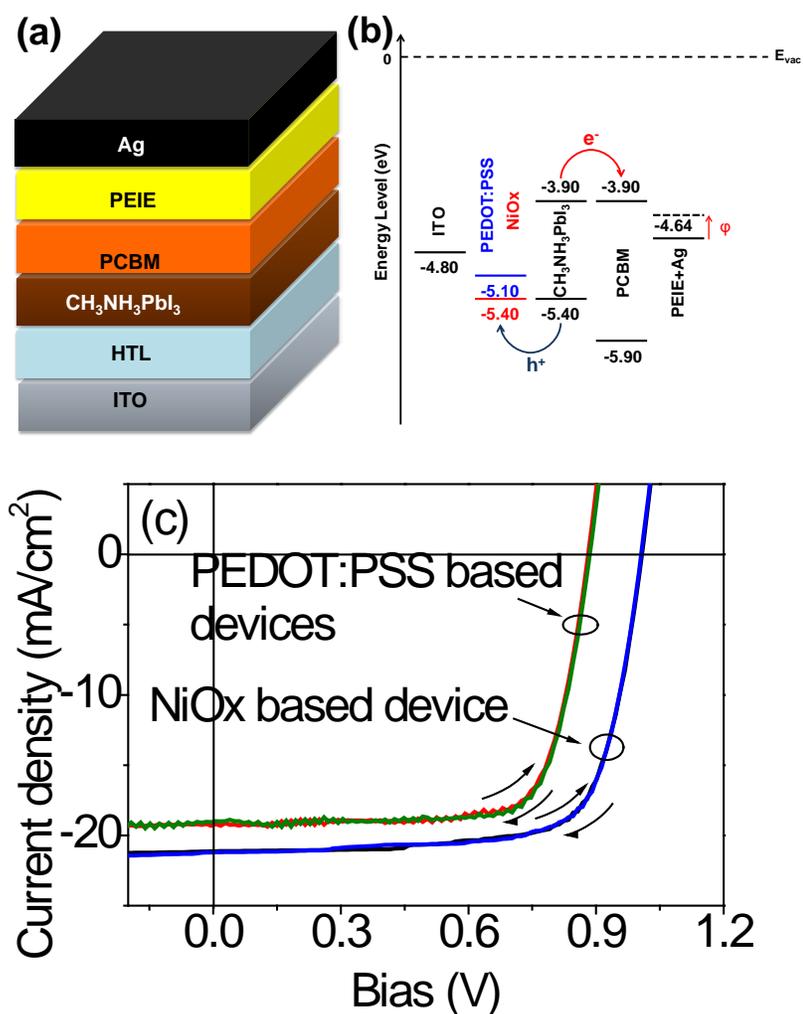


Figure 1. (a) Device architecture. The HTL refers to NiOx and PEDOT:PSS. (b) Energy diagram for fabricated devices [ITO/HTL/CH₃NH₃PbI₃/PC₆₀BM/PEIE/Ag]. (c) Current-voltage characteristics measured under forward and reverse scans.

Table 1. The photovoltaic parameters derived from current-voltage characteristics measured with forward and reverse scans for NiOx and PEDOT:PSS based devices.

	Jsc(mA/cm²)	Voc(V)	FF(%)	PCE(%)
PEDOT:PSS (forward)	19.32	0.88	0.75	12.8
PEDOT:PSS (reversed)	19.10	0.89	0.77	13.02
NiOx (forward)	21.14	1.01	0.75	16.01
NiOx (revresed)	21.21	1.00	0.75	15.91

Now we discuss the effects of NiOx HTL on the charge dissociation occurring in the perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) layer. Recently, we have shown that magneto-Jsc combined with an external bias can be used as an in-situ measurement to elucidate the charge recombination in PSCs under device-operating condition²³. This experimental method is based on the following arguments. First, the electron-hole pairs are formed with both antiparallel and parallel spins through the Coulomb capture of photogenerated carriers in PSCs. Second, a magnetic field can shift the spin population between parallel and antiparallel electron-hole pairs, changing the Jsc based on the fact that the parallel and antiparallel spin pairs have higher and lower dissociation rates due to forbidden and allowed transitions. This generates a magneto-Jsc signal. Third, applying a bias can facilitate the dissociation of the electron-hole pairs, quenching the magneto-Jsc signal. As a result, monitoring the critical bias required to completely quench the magneto-Jsc provides a method to elucidate the dissociation of electron-hole pairs while operating PSCs.

Figure 2 shows the magneto-Jsc in NiOx and PEDOT:PSS-based devices. Surprisingly, the NiOx-based device presents a negligible magneto-Jsc while the PEDOT:PSS-based device shows an appreciable magneto-Jsc. Clearly, the negligible and appreciable magneto-Jsc imply that electron-hole pairs are sufficiently and in-sufficiently dissociated in NiOx-based and PEDOT:PSS-based devices at short-circuit condition, respectively. Interestingly, in the NiOx-based device weakening the built-in field by applying a forward bias (+1.0 V) changes the magneto-Jsc from negligible to appreciable value. On contrast, in the PEDOT:PSS-based device strengthening the built-in field by applying a reverse bias (-0.12 V) changes the magneto-Jsc from appreciable to negligible value. Clearly, this field-dependent magneto-Jsc provides the first evidence that the built-in field plays an important role on the charge dissociation in the PSCs. Using the NiOx HTL can enhance the charge dissociation through the built-in field, increasing the Jsc.

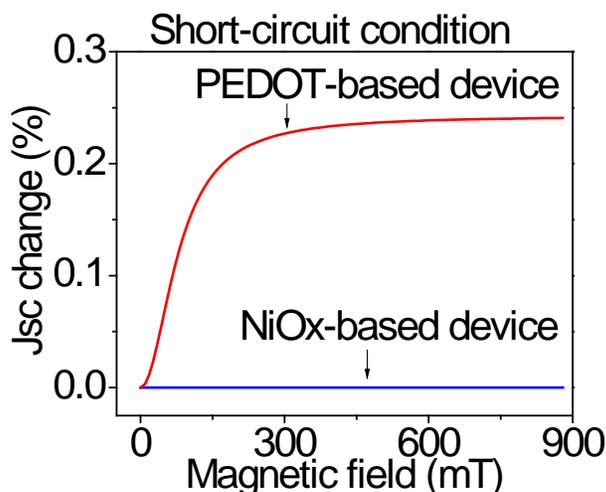
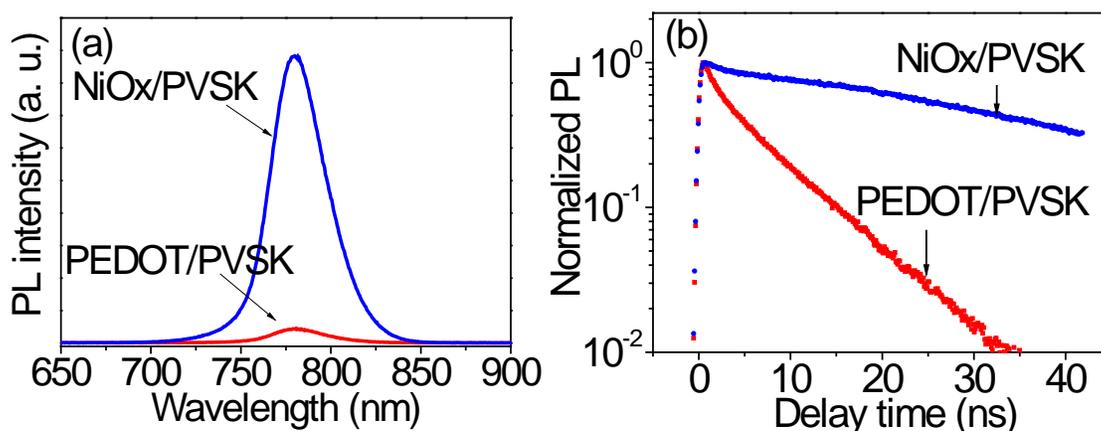


Figure 2. Magneto-Jsc becomes negligible and appreciable in NiOx and PEDOT:PSS based devices values at short-circuit condition (zero external bias). Negligible and appreciable magneto-Jsc correspond to sufficient and in-sufficient dissociation of electron-hole pairs in NiOx and PEDOT:PSS based devices, respectively.

We should note that the photogenerated excitons can undergo non-radiative and radiative recombination in organo-metal halide perovskites. The non-radiative recombination is a fast process occurring in picoseconds caused by defects. Through non-radiative recombination the excitons can quickly annihilate into deeply trapped carriers prior to dissociation, forming a photovoltaic loss. The radiative recombination refers to a bimolecular behavior in which the excitons can be available for dissociation. Therefore, the non-radiative and radiative recombination dis-allows and allows the excitons for generating photovoltaic actions, respectively. Obviously, controlling the non-radiative/radiative recombination offers an important methodology to improve the photovoltaic actions in the PSCs. **Figure 3a** shows the PL quenching in the perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) layer upon applying the NiOx and PEDOT:PSS HTLs. We can see that the NiOx/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ interface leads to a weaker PL quenching but a stronger Jsc as compared to the PEDOT:PSS/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ interface (stronger PL quenching but a weaker Jsc). A similar phenomenon has been reported in PSCs. This puzzled phenomenon brings an important question on how the NiOx HTL can influence the non-radiative and radiative recombination in the PSCs. Our transient PL studies indicate that the NiOx/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ interface yields a much longer lifetime up to 20 ns while the PEDOT:PSS/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ interface gives a much shorter lifetime of ~ 6 ns, as illustrated in **Figure 3b**. This transient PL result provides the direct information that the NiOx/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ and PEDOT:PSS/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ interfaces exhibit lower and higher non-radiative recombination, respectively. Therefore, we can argue that the NiOx can suppress the non-radiative recombination in the perovskite layer and consequently increases the excitons available for generating photocurrent in PSCs.



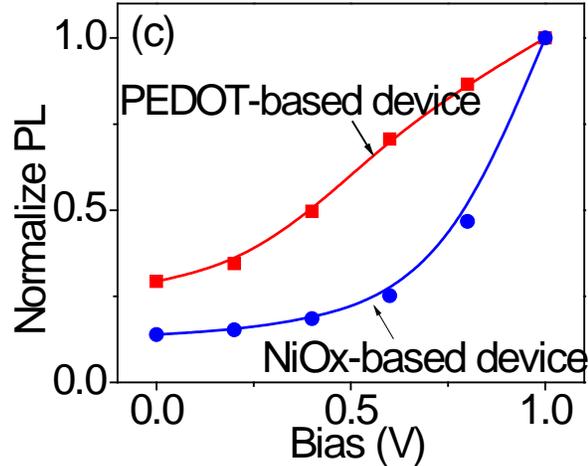


Figure 3. PL spectra measured for NiOx/PVSK and PEDPT:PSS/PVSK double-layer samples. PVSK refers to the perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$. (b) Transient PL lifetime for NiOx/PVSK and PEDPT:PSS/PVSK double-layer samples. (c) PL intensity is shown as a function of built-in potential by switching from short-circuit condition towards open-circuit condition in NiOx and PEDOT:PSS based devices.

We should further note that measuring field-dependent PL can evaluate radiative recombination in PSCs⁸. In particular, the perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) layer possesses low electron-hole binding energies ranging from 37 meV to 50 meV. With the low binding energies we can expect that changing the built-in field by applying an external bias can vary the exciton separation and consequently modifies the PL intensity. Essentially, stronger/weaker field-dependent PL reflects more/less radiative recombination. This method is based on the following arguments. First, the excitons involved in radiative recombination are available for generating photocurrent, noting that in the non-radiative recombination the excitons are not available for generating photovoltaic actions. Second, separating excitons is a field-dependent process in organo-metal halide perovskites due low binding energies, consequently leading to a field-dependent PL. Here, we measure the PL intensity alternatively towards short-circuit and open-circuit conditions to understand how the NiOx HTL affects the radiative recombination in the perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) layer. We can see in **Figure 3c** that the PL intensity difference measured at short-circuit and open-circuit conditions shows larger and smaller values in the NiOx-based and PEDOT:PSS-based devices, respectively. Specifically, the PL intensity is decreased by 86 % in the NiOx-based device but by 62 % in the PEDOT:PSS-based device when switching from open-circuit to short-circuit condition. Equivalently, the NiOx-based device shows a stringer field-dependent PL as compared to the PEDOT:PSS-based device. Therefore, we can suggest that the NiOx HTL can also

suppress the radiative recombination, increasing the photovoltaic actions within available excitons in the PSCs.

4. Summary

In summary, our bias-dependent magneto-Jsc results show that using the NiOx HTL can lead to a sufficient dissociation of electron-hole pairs in perovskite layer due to stronger built-in field in the NiOx-based PSCs. This study reveals that the built-in field plays an important role in controlling the charge dissociation in organo-metal halide perovskites. Furthermore, our transient measurement indicates that the NiOx HTL can enlarge the PL lifetime up to 20 ns. This PL lifetime study provides the direct information that the NiOx HTL can suppress the non-radiative recombination by decreasing interfacial traps at the NiOx/ CH₃NH₃PbI₃ interface. Suppressing the non-radiative recombination can essentially increase the excitons available for generating photocurrent. Furthermore, we observe that the NiOx HTL leads to a larger PL change in intensity upon alternatively measured at short-circuit and open-circuit conditions, presenting a stronger field-dependent PL in the NiOx-based device. This provides an experimental indication that the NiOx HTL can also suppress the radiative recombination through stronger built-in field, enhancing the photovoltaic actions within available excitons. Therefore, our studies had verified that by using NiOx HTL can lead to the modulation of the magneto-photocurrent and the enhancement of the photovoltaic parameters in Jsc and Voc in PSCs.

Reference

1. Zhou, H., Chen, Q., Li, G., Luo, S., Song, T.-B., Duan, H.-S., Hong, Z., You, J., Liu, Y. & Yang, Y. Interface engineering of highly efficient perovskite solar cells. *Science* **345**, 542–546 (2014).
2. Lim, K.-G., Kim, H.-B., Jeong, J., Kim, H., Kim, J. Y. & Lee, T.-W. Boosting the power conversion efficiency of perovskite solar cells using self-organized polymeric hole extraction layers with high work function. *Adv. Mater.* **26**, 6461–6466 (2014).
3. Chiang, T. -Y., Fan, G.-L., Jeng, J.-Y., Chen, K. -C. Chen, P., Wen, T. -C., Guo, T. -F. & Wong, K. -T., Functional p- type, polymerized organic electrode interlayer in CH₃NH₃PbI₃ perovskite/fullerene planar heterojunction hybrid solar cells. *ACS Appl. Mater. Interfaces* **7**, 24973–24981 (2015).
4. Liu, C., Su, Z., Li, W., Jin, F., Chu, B., Wang, J., Zhao, H., Lee, C. S., Tang, J. & Kang, B. Improved performance of perovskite solar cells with a TiO₂/MoO₃ core/shell nanoparticles doped PEDOT:PSS hole-transporter. *Org. Electron. : Phys. Mater. Appl.* **33**, 221-226 (2016).
5. Huang, X., Wang, K. Yi, C., Meng, T. & Gong, X. Efficient perovskite hybrid solar cells by highly electrical conductive PEDOT:PSS hole transport layer. *Adv. Energy Mater.* DOI: 10.1002/aenm.201501773 (2016).
6. Wang, K., Liu, C., Yi, C., Chen, L., Zhu, J., Weiss, R. A. & Gong, X. Efficient perovskite hybrid solar cells via ionomer interfacial engineering. *Adv. Funct. Mater.* **25**, 6875–6884 (2015).
7. Song, D., Wei, D., Cui, P., Li, M., Duan, Z., Wang, T., Ji, J., Li, Y., Mbengue, J. M., Li, Y., He, Y., Trevor, M. & Park, N.-G. Dual function interfacial layer for highly efficient and stable lead halide perovskite solar cells. *J Mater. Chem. A* **4**, 6091-6097 (2016).
8. Jeng, J. -Y., Chiang, Y. -F., Lee, M. -H., Peng, S. -R., Guo, T. -F., Chen, P. & Wen, T.-C. CH₃NH₃PbI₃ perovskite/fullerene planar-heterojunction hybrid solar cells. *Adv. Mater.* **25**, 3727–3732 (2013).
9. Liang, P. -W., Liao, C. -Y., Chueh, C. -C., Zuo, F., Williams, S. T., Xin, X. -K., Lin, J. & Jen, A. K.-Y. Additive enhanced crystallization of solution-processed perovskite for highly efficient planar-heterojunction solar cells. *Adv. Mater.* **26**, 3748–3754 (2014).
10. Xiao, Z., Bi, C., Shao, Y., Dong, Q., Wang, Q., Yuan, Y., Wang, C., Gao, Y. & Huang, J. Efficient, high yield perovskite photovoltaic devices grown by interdiffusion of solution-processed precursor stacking layers. *Energy Environ. Sci.* **7**, 2619–2623(2014).
11. Nie, W., Tsai, H., Asadpour, R., Blancon, J. -C., Neukirch, A. J., Gupta, G., Crochet, J. J., Chhowalla, M., Tretiak, S., Alam, M. A., Wang, H.-L. & Mohite, A. D. High-efficiency solution-processed perovskite solar cells with millimeter-scale grains. *Science* **347**, 522–525(2015).
12. De Jong, M. P., Van Ijzendoorn, L. J., de Voigt & M. J. A. Stability of the interface between indium-tin-oxide and poly (3,4-ethylenedioxythiophene)/poly (styrenesulfonate) in polymer light-emitting diodes. *Appl. Phys. Lett.* **77**, 2255 (2000).
13. Liu, T., Jiang, F. Tong, J., Qin, F., Meng, W. Jiang, Y., Lia, Z. & Zhou, Y. Reduction and oxidation of

- poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) induced by methylamine (CH₃NH₂)-containing atmosphere for perovskite solar cells. *J. Mater. Chem. A* **4**, 4305-4311(2016).
14. You, J., Meng, L., Song, T. -B., Guo, T.-F., Yang, Y, M., Chang, W.-H., Hong, Z., Chen, H., Zhou, H. Chen, Q. Chen, Y. Liu, De Marco, N. & Yang, Y. Improved air stability of perovskite solar cells via solution-processed metal oxide transport layers. *Nat Nano* **11**, 75–81 (2016).
15. Chen, W., Wu, Y., Yue, Y., Liu, J., Zhang, W., Yang, X., Chen, H., Bi, E., Ashraful, I., Grätzel, M. & Han L. Efficient and stable large-area perovskite solar cells with inorganic charge extraction layers. *Science* **350**, 944–998 (2015).
16. Chen, W., Wu, Y., Liu, J., Qin, C., Yang, X. Islam, A., Cheng, Y.-B. & Han, L. Hybrid interfacial layer leads to solid performance improvement of inverted perovskite solar cells. *Energy Environ. Sci.* **8**, 629–640 (2015).
17. Kim, J. H., Liang, P. -W., Williams, S. T., Cho, N., Chueh, C.-C., Glaz, M. S., Ginger, D. S., Jen, A. K.-Y. High-performance and environmentally stable planar heterojunction perovskite solar Ccells based on a Ssolution-processed copper-doped nickel oxide hole- transporting layer. *Adv. Mater.* **27**, 659–701 (2015).
18. Lai, W. -C. Lin, K. -W. Wang, Y. -T. Chiang, T. -Y. Chen, P. Guo, T.-F. Oxidized Ni/Au transparent electrode in efficient CH₃NH₃PbI₃ perovskite/fullerene planar heterojunction hybrid solar cells. *Adv. Mater.* **28**, 3290 (2016).
19. Jeng, J. -Y., Chen, K. -C., Chiang, T. -Y. Lin, P. -Y., Tsai, T. -D., Chang, Y. -C. Guo, T. -F., Chen, P., Wen, T. -C. & Hsu, Y.-J. Nickel oxide electrode interlayer in CH₃NH₃PbI₃ perovskite/PCBM planar-heterojunction hybrid solar cells. *Adv. Mater.* **26**, 4107 (2014).
20. Park, J. H., Seo, J., Park, S., Shin, S. S., Kim, Y. C., Jeon, N. J., Shin, H.-W., Ahn, T. K., Noh, J. H., Yoon, S. C., Hwang, C. S. & Seok, S. I. Efficient CH₃NH₃PbI₃ perovskite solar cells employing nanostructured p-type NiO electrode formed by a pulsed laser deposition. *Adv. Mater.* **27**, 4013 (2015).
21. Wang, K. -C., Jeng, J. -Y., Shen, P. -S., Chang, Y. -C., Diau, E. W.-G., Tsai, C.-H., Chao, T.-Y., Hsu, H.-C., Lin, P.-Y., Chen, P., Guo, T.-F. & Wen, T. -C. P-type mesoscopic nickel Oxide/organometallic perovskite heterojunction solar cells. *Sci. Rep.* **4**, 4756 (2014).
22. Seo, S., Park, I. J., Kim, M., Lee, S., Bae, C., Jung, H. S. Park, N. -G. Kim J. Y. & Shin, H. An ultra-thin, un-doped NiO hole transporting layer of highly efficient (16.4%) organic–inorganic hybrid perovskite solar cells. *Nanoscale* **8**, 11403-11412 (2016).
23. Hsiao, Y.-C., Wu, T., Li, M. & Hu, B. Magneto-optical studies on spin-dependent charge recombination and dissociation in perovskite solar cells. *Adv. Mater.* **27**, 2899–2906 (2015).

VI. Conclusions and Future work

The singlet fission reaction modulates the distribution of triplet excited states and causes the decreased and increased magnitude of MC responses at the low and high magnetic field, respectively. We had investigated the unique MFE on photocurrent for tetracene-based diodes. Although the singlet fission reaction of tetracene molecules germinates at the initial stage of excitation, the fast carrier transfer process at the donor/acceptor interface (the formation of CT complex molecules) quenches the fission reaction easily. As a result, the donor/acceptor heterojunction would NOT be the practical design to utilize the fission reaction to increase the numbers of multiple carriers for photovoltaic application. We had to design an efficient hole transport layer (HTL)/active layer for fission reaction/electron transport layer (ETL) system for the extraction of multiple carriers by the fission reaction under the photo illumination, which is a currently ongoing subject.

We studied the magnetic field effect on photocurrent (MC) and electroluminescence (MEL) for charge-balance SY-PPV based PLED. We are able to extract a negative component from the positive MEL response at the high bias current regime under the high magnetic field. We attributed the negative MEL component at high current density originates from the triplet-triplet annihilation process in SY-PPV layer. Since TTA process possibly generates the singlet from triplet excitons to enhance the quantum efficiency in fluorescent organic light emitting diodes (OLEDs), decreasing the temperature increases the lifetime of triplet and enhances TTA to effectively contribute the fluorescent emission. This observation verifies the contribution of TTA process to the fluorescence at the high current density. The concept we proposed about the application of TTA to generate the fluorescence would be important to reduce the efficiency droop of high power fluorescent OLEDs operated at the high current density regime.

As requested by Dr. Charles Lee to set up the real collaboration between the research groups at University of Tennessee Knoxville with NCKU. We focus on the effects of NiOx transport layer on internal photovoltaic processes in perovskite solar cells [ITO/HTL/CH₃NH₃PbI₃/PC₆₀BM/PEIE/Ag] based on magneto-photocurrent, transient and field-dependent photoluminescence. The studies about MFE by the alternative p-type charge transport layers would help us to understand the functionality and working mechanisms of the electrode interlayers in efficient perovskite-based photovoltaic cells. Based on the bilateral interaction, NCKU and University of Tennessee Knoxville had disclosed that the application of NiOx transport layer leads to the modulation of the magneto-photocurrent and the enhancement of the photovoltaic parameters in Jsc and Voc

in perovskite solar cells. We identified the functionalities of an appropriate electrode interlayer to effectively dissociate the charges and suppress the recombination of the opposite charges at the electrode interfaces. We have had a joint publication on this topic by NCKU and University of Tennessee Knoxville, published on a high impact journal, Nano Energy, in 2017. Currently, we also have the ongoing collaborations to continuously investigate the development of efficient perovskite-based light-emitting diodes. We realize the passivation of the perovskite crystalline boundaries would lead to the marked enhancement of the device performance. In addition, the ion migrations would modulate the efficiency of photoluminescence and electroluminescence and balance the injection of the opposite charge carriers. The initial results indicate that the passivation of perovskite crystalline interfaces by amphiprotic ionic additives significantly elevates the luminous efficiency by 2 orders of magnitude under the low current density regime. Our work poses the direction of perovskite LEDs for real application. The studies about the mechanisms resulting in such enhancement are ongoing.