

Final Progress Report

a. DOE Award # and Name of the Recipient (Institution)

DOE Award #:

DE-SC0014902

Name of the Recipient:

Prof. Shenqiang Ren

Temple University

College of Engineering

1947 N. 12th St.

Philadelphia, PA 19122

b. Project Title and Name of the PI

Project Title:

“Collaborative Research: Polymeric Multiferroics”

Name of the PIs:

Dr. Shenqiang Ren (Temple University), PI

c. Date of the report and research period covered by the report

Date of the Report:

04/12/2017

Research Period Covered by the Report:

08/14/2015 ~ 02/14/2017

d. Description of Accomplishments

This collaborative project addresses the novel physical properties of a new type of organic multifunctional materials, as polymeric multiferroics. Our collaboration on this project (Dr. Manfred Wuttig at the University of Maryland, and Dr. Shenqiang Ren at Temple University) has constructed a unique organic multiferroic material system with the understanding of room temperature organic magnetism, magneto-transport, magnetic field effects and magnetoelectric coupling, which could have potential impacts on the flexible electronics, and potentially high T_c organic superconductors.

Synopsis:

The goal of this project is to investigate room temperature magnetism and magnetoelectric coupling of polymeric multiferroics. A new family of molecular charge-transfer crystals has been emerged as a fascinating opportunity for the development of all-organic electrics and spintronics due to its weak hyperfine interaction and low spin-orbit coupling; nevertheless, direct observations of room temperature magnetic spin ordering have yet to be accomplished in organic charge-transfer solids. Furthermore, room temperature magnetoelectric coupling effect hitherto known multiferroics, is anticipated in organic donor-acceptor complexes because of magnetic field effects on charge-transfer dipoles, yet this is also unexplored. The PI seeks to fundamental understanding of the control of organic crystals to demonstrate and explore room temperature multiferroicity. The experimental results have been verified through the theoretical modeling. By tuning external magnetic field, light, electric field and thermal field on organic multiferroics, some **key findings** are observed as follow:

- Room temperature ferroelectricity, magnetism, magnetoelectric coupling and magnetic field effects in molecular charge-transfer crystals.
- The coupling between spin resonance and transport behaviors with the temperature dependence of polymeric multiferroics.
- The density functional theory (DFT) modeling confirms the magnetism origin of polymeric multiferroics from charge transfer and ordering at the interfaces between donor and acceptor.
- Multifunctional organic charge-transfer crystals through the coupling among the assembly crystallization, charge-spin-lattice interactions, and multiferroic properties.

Impact of Findings:

The invention of polymeric multiferroics opens up the development of all-organic nanoferronics, which include the ferroic ordering (such as, organic ferroelectrics and magnets), and magnetoelectric coupling at room temperature. The potential contribution of this study includes:

- 1) a novel magnetoelectric coupling mechanism of polymeric multiferroics.
- 2) magnetic anisotropic characteristics of polymeric multiferroics, resulted from the orientation effect of spin cone and electron-phonon coupling within organic crystalline lattice.
- 3) room temperature magnetic field effects (the tunability of electric current and dielectric constant by magnetic field) for flexible magnetic field sensors and energy transduction systems.

Key Findings:

Finding 1: A free-standing molecular spin-charge converter for ubiquitous magnetic-energy harvesting (Advanced Materials, 29, 8, 2016)

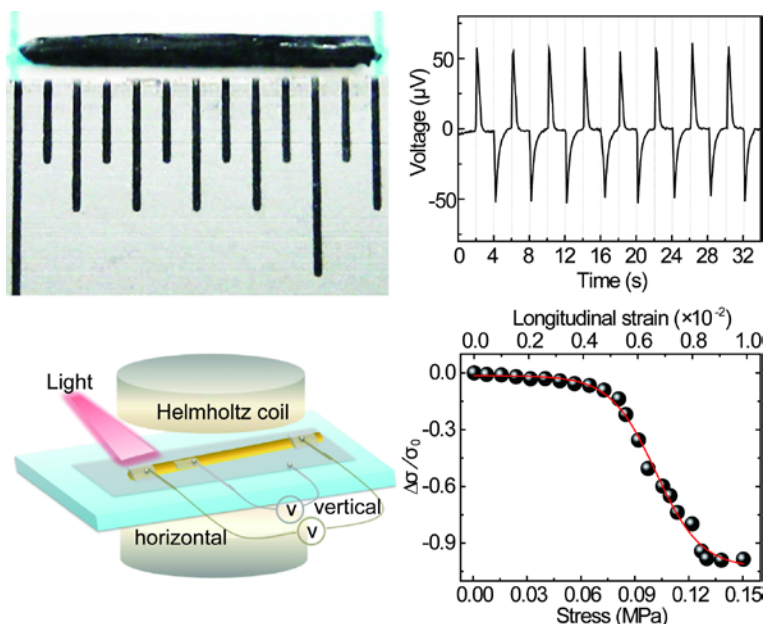


Figure 1. The centimeter-sized molecular charge-transfer crystals, as a new spin-charge converter, for magnetic energy harvesting and sensing.

electronics. However, it still remains a great challenge to convert magnetic energy into electrical energy, and transduce multiple stimuli into a coupled signal in non-integrated organic semiconductors. In this work, we demonstrate magnetic energy harvesting ability from centimeter-sized free-standing organic single crystal semiconductor prepared by solution process (Fig. 1). The largest output voltage and current reaches $\sim 67 \mu\text{V}$ and $\sim 62 \text{ pA}$ at a magnetic field of 2000 Oe. The functional properties of these crystals are then rationalized through the nature of their charge transfer process using experimental measurements and quantum mechanical density functional theory (DFT) calculations. The simulation confirms the strong intermolecular charge transfer interaction. By controlling the intrinsic intermolecular charge transfer state and carrier transport through external magnetic field, heat and strain, the capacitance and conductivity can be modulated in a large scale, enabling the semiconductor with sensitive optical, thermal, mechanical sensing ability. The crystal shows an excellent temperature sensitivity of $< 0.01 \text{ K}$ as well as good photoresponse. Moreover, the anisotropic molecular stacking enables the crystals with obvious anisotropy. The self-powered sensing performance, together with its solution processability and flexibility, endow it with the capability to drive a new generation of non-contact magnetic energy harvesting and sensing technologies.

Finding 2: Multifunctional charge-transfer single crystals through supramolecular assembly (Advanced Materials, 28, 26, 2016)

Self-powered organic conjugated materials with multiple sensing ability are of vital importance for the development of micro/nanosystems for next-generation, flexible, and fully-integrated energy, sensing, personal healthcare systems, and artificial intelligence technologies.¹ Among them, the most rapidly developing technologies is energy harvesting and sensing from the ubiquitous distributed magnetic field of the earth, human brain and heart, and high-voltage power lines. Compared with inorganic materials, the lightweight, flexible, solution processable ability endows organic materials with multiple freedom for flexible

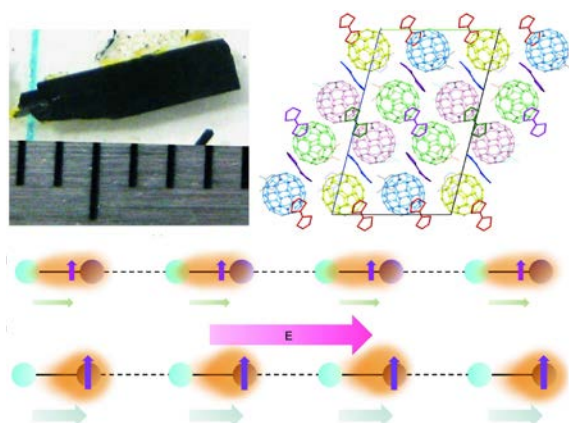


Figure 2. Centimeter-sized segregated stacking TTF- C_{60} single crystals are crystallized by mass-transport approach combined with solvent vapor evaporation for the first time. The intermolecular charge transfer interaction in the long-range ordered superstructure enables the crystals to demonstrate external stimuli-controlled multifunctionalities and angle/electrical potential dependent luminescence.

intermolecular contacts between asymmetric TTFs and multi-orientational C_{60} molecules lead to spin and charge order within the crystal structure. These crystals are found to exhibit spontaneous and hysteretic polarization, potential-dependent luminescence, and magnetoelectric properties owing to the presence of spin-charge composite ferroic ordering in the long-range ordered TTF- C_{60} lattice solids. In combination with their relatively simple crystallization process and broad chemical flexibility, molecular charge-transfer crystals promote the material-by-design paradigm towards the development of multifunctional all-organic nanoferronics. This work provides, for the first time, the evidence that molecular stacking and orientational ordering regulate the charge, spin and photonic orders within organic molecular CT single crystals. In this work, we report on the observation of the centimeter-sized three-dimensional supramolecular assembly of alternating π -electron tetrathiafulvalene donor and fullerene acceptor as the prototypical π -conjugated supramolecular charge-transfer single crystal, which is solved by high resolution synchrotron diffraction.

Finding 3: All-polymeric control of nanoferronics (Science Advance, e1501264, 2015)

In the search of light and flexible nanoferronics, a significant research effort is geared towards discovering the coexisting magnetic and electric orders in crystalline charge-transfer complexes.

Organic molecular charge-transfer solids have attracted tremendous interest in contemporary materials science, where the charge, spin and lattice degrees of freedom are all strongly entangled to promote new properties (superconductivity, ferroelectricity, quantum spin liquid state, etc.) for flexible and lightweight multifunctional materials.^{2, 3} There is a great deal of interest and excitement recently in understanding the role of charge transfer and stacking arrangement in multifunctional supramolecular assembly networks for efficient optoelectronics and molecular electronics.⁴ Historically, the invention of each new kind of organic charge-transfer (CT) complex initiates a technological revolution. Here, we report external stimuli-controlled multifunctionalities of molecular charge-transfer single crystals, in which electron donor tetrathiafulvalene (TTF) and acceptor fullerene (C_{60}) build a charge-transfer network in the crystalline lattice solid (Fig. 2). The

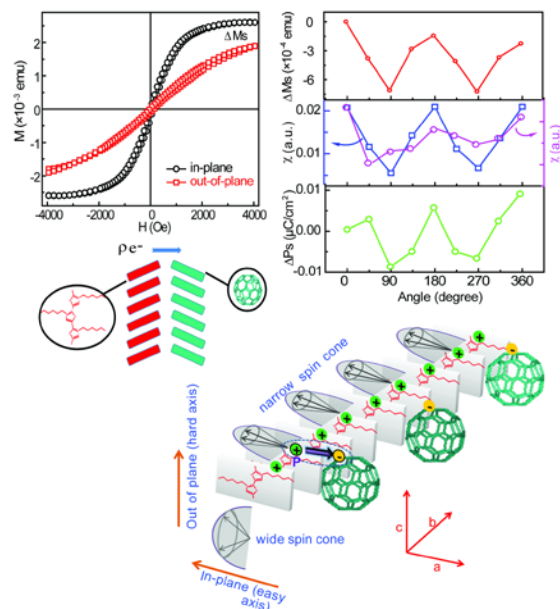


Figure 3. Magnetic hysteresis loops of polymeric nanoferronics in the in-plane and out-of-plane directions. Angle dependent saturation magnetization (above), experimental (middle left) and calculated spin susceptibility (middle right), and saturation polarization (below). The spin cone distribution along the long axis (b axis) of the CTTC and the polarization induced by charge ordering and charge transfer at the interface. The direction and width of the spin cone depend on the spin direction and the charge-lattice coupling extent.

charge-transfer crystals will constitute a new direction for solution-processable all organic ferroic devices. In this respect, this work defines a research avenue for alternative materials to those studied extensively in recent years such as inorganic multiferroic oxides and organic spintronics, and opens a search for suitable carbon-based charge transfer materials with yet untapped potential for efficient ferroic devices. The principal of using crystalline CT compounds offers a broad design flexibility, which leads to a great potential for the development of room temperature organic magnetoelectric multiferroics.

Finding 4: Chemically driven interfacial coupling in charge-transfer mediated functional superstructures (Nano Letters, 16, 2851, 2016)

The mixing of conductivity and ferroic orders in functional materials could lead to numerous technological advances, such as ferroic field-effect transistors and magnetoelectric tunnel junctions.^{5, 6} However, the ferroic orders are related to the interaction of localized electrons while the conduction is determined by the movement of electrons; thus, simultaneous conducting and ferroic orders remains challenging in conventional materials. Materials-by-design and assembly principle provides a unique and exciting opportunity, as it allows us to design novel multifunctional organic materials that combine two or more physical properties in the same crystal lattice, which are difficult or impossible to achieve in continuous inorganic crystalline solids. In this work, we shed light on the impact of chemically driven side-chain engineering on correlated

Here, we report the first example of multiferroicity in the centimeter-sized crystalline polymeric charge-transfer superstructures that grow at the liquid-air interface and are controlled by the regioregularity of the polymeric chain. The charge-order-driven ferroic mechanism reveals spontaneous and hysteretic polarization and magnetization at the donor-acceptor interface. The charge transfer and ordering in the ferroic assemblies depends critically on self-organizing and molecular packing of electron donor and acceptor. Charge transfer and ordering at interfaces enables the appearance of simultaneous room temperature anisotropic ferroic orders and their coupling along the stacking axis of the crystalline CT superstructures. The giant anisotropic behavior is largely resulted from packing structure along different crystal growth direction, which leads to the unique optical properties, extraordinary anisotropic electric and magnetoelectric coupling behaviors. Theoretical simulation uncovers a structural and interfacial mechanism on the crystal structure, energy level fluctuation and wavefunction distribution of CT superstructures. The invention described here not only represents a new coupling mechanism of magnetic and electric ordering, but also stands for a new class of the emerging all-organic nanoferronics. The large-sized freestanding

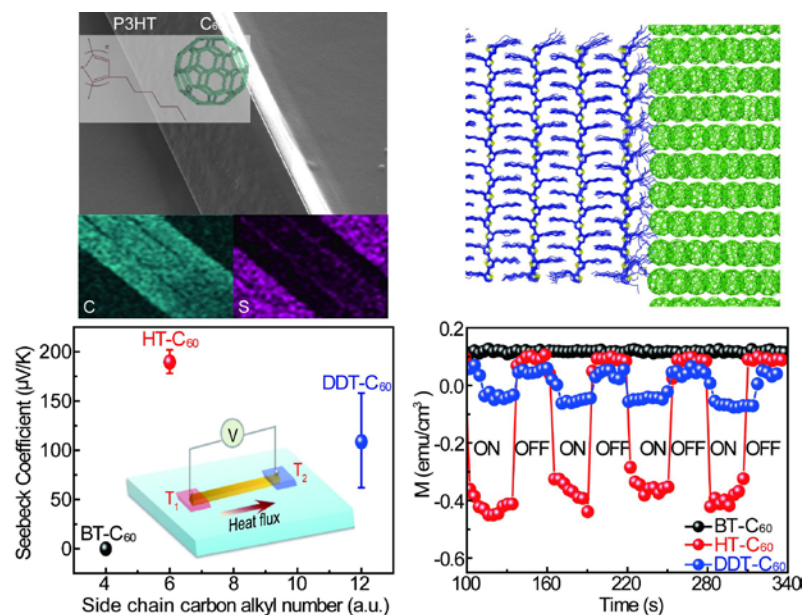


Figure 4. The control of organic crystallization and interfacial electron coupling are keys to dictate external stimuli responsive behaviors in organic charge-transfer superstructures. The integrated experimental and computational study reveals the importance of chemically driven interfacial coupling in organic charge-transfer superstructures.

such CT superstructures are among the highest reported for polymeric thermoelectric materials.

optical, thermal, electric and magnetic properties of CT superstructures using a combined experimental and theoretical approach (Fig. 4). The CT superstructures with crystallization between fullerene (C₆₀) acceptor and polythiophene donor with varying alkyl side chains were chosen as prototype systems since exceptional optoelectronic response and optical characteristics have been observed in these π -conjugated systems. Our results suggest that the essential strategy for side-chain design to dictate external stimuli responsive behavior is control over polymer crystallization and interfacial electron coupling. Moreover, the Seebeck coefficients observed in

e. A List of Papers

Published:

- 1) B. Xu, H. Chakraborty, R. C. Remsing, M. L. Klein, and S. Ren, A free-standing molecular spin-charge converter for ubiquitous magnetic-energy harvesting and sensing, **Advanced Materials**, 29, 8 (2017)

Acknowledgment

Work at Temple University (S.R.) was supported by the Army Research Office - Young Investigator Program (W911NF-15-1-0610, material design/self-assembly), U.S. Department of Energy-Basic Energy Sciences Award No. DE-SC0014902 (organic synthesis and physical property measurement). H.C., R.C.R., and part of the computational resources were supported as part of the Center for the Computational Design of Functional Layered Materials, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award #DE-SC0012575. A portion of the computations were performed on resources provided by the National Science Foundation through major research instrumentation grant number CNS-09-58854. H.C., R.C.R, and M.L.K. also acknowledge discussions and interactions with Prof. U.V. Waghmare.

- 2) Z. Zhang, B. Xu, B. Xu, L. Jin, H. Dai, Y. Rao and S. Ren, External stimuli responsive two-dimensional charge transfer polymers, **Advanced Materials Interfaces**, 4, 2 (2016)

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Work at the Temple University (S.R.) was supported by the Army Research Office Young Investigator Program (W911NF-15-1-0610, material design/self-assembly of carbon photovoltaics) and Department of Energy Basic Energy Sciences Award No. DE-SC0014902 (organic synthesis and physical property measurement). Y.R. and H.L.D acknowledge the seed funding from an Energy Frontier Research Center at Temple University funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC0012575, a Targeted Research Grant from the Temple University Office of the Vice Provost for Research.

- 3) Z. Zhang and S. Ren, Colloidal Excimer Superstructures, **Angewandte Chemie International Edition**, 10.1002/anie.201608845 (2016)

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- 6) B. Xu, Z. Luo, A. J. Wilson, K. Chen, W. Gao, G. Yuan, H. Chopra, X. Chen, K. A. Willets, Z. Dauter, and S. Ren, Multifunctional charge-transfer single crystals through supramolecular assembly, **Advanced Materials**, 28, 26 (2016)

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Work at Temple University (S.R) was supported by the Army Research Office - Young Investigator Program (W911NF-15-1-0610, material design/self-assembly of carbon photovoltaics), U.S. Department of Energy-Basic Energy Sciences Award No. DE-FG02-13ER46937 (organic synthesis and physical property measurement). Work at Temple University (A.J.W. and K.A.W.) was supported by the Department of Energy (DOE), Office of Science, Basic Energy Science (BES) under Award #DE-SC0010307. H.D.C. gratefully acknowledge support of National Science Foundation DMR-Condensed Matter Physics grant 1541236 (previously 1309712) and Temple University's OVPR's Infrastructure Grant. Diffraction data were collected at the SER-CAT beamline 22BM at the Advanced Photon Source, Argonne National Laboratory. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38. The authors also thank Temple Materials Institute and Dr. X. Xi for the AFM measurements.

- 7) B. Xu, H. Li, H. Li, A. J. Wilson, L. Zhang, K. Chen, K. A. Willets, F. Ren, J. C. Grossman, S. Ren, Chemically driven interfacial coupling in charge-transfer mediated functional superstructures, **Nano Letters**, 10.1021/acs.nanolett.6b00712 (2016)

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- 8) B. Xu, Z. Luo, W. Gao, A. J. Wilson, C. He, X. Chen, G. Yuan, H. Dai, Y. Rao, K. Willets, Z. Dauter, and S. Ren, Solution-processed molecular opto-ferroic crystals, **Chemistry of Materials**, 10.1021/acs.chemmater.6b00836 (2016)

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- 9) B. Xu, H. Li, A. Hall, W. Gao, M. Gong, G. Yuan, J. Grossman and S. Ren, All-polymeric control of nanoferronics, **Science Advances**, 1, e1501264 (2015)

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- 10) W. Qin, X. Chen, J. Lohrman, M. Gong, G. Yuan, M. Wuttig and S. Ren, External Stimuli Controlled Multiferroic Charge Transfer Crystals, **Nano Res**, 10.1007/s12274-015-0975-8 (2015)

Acknowledgment

S.R thanks the Army Research Office - Young Investigator Program (W911NF-14-1-0443, material design/self-assembly of carbon magnetoelectrics) and Department of Energy-Basic Energy Sciences Award No. DE-FG02-13ER46937 (organic synthesis and physical property measurement), and M. W thanks the financial support from US Department of Energy (DOE DESC0005448).

- 11) M. Gong, T. A. Shastry, Q. Cui, R. R. Kohlmeier, K. A. Luck, A. Rowberg, T. J. Marks, M. F. Durstock, H. Zhao, M. C. Hersam, and S. Ren, Understanding Charge Transfer in Carbon Nanotube–Fullerene Bulk Heterojunctions, **ACS Appl. Mater. Interfaces**, 7, 7428 (2015).

Acknowledgment

Work at the University of Kansas (S.R) was supported by the Army Research Office - Young Investigator Program (W911NF-14-1-0443, material design/self-assembly of carbon heterojunctions), Department of Energy-Basic Energy Sciences Award No. DE-FG02-13ER46937 (organic synthesis and physical property measurement), and National Science Foundation - DMR Award No. 0954486 (H.Z., ultrafast pump–probe measurements). Work at Northwestern University (M.C.H. and T.J.M.) was supported as part of the Argonne–Northwestern Solar Energy Research (ANSER) Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award No. DE-SC0001059. T.A.S. and K.A.L. acknowledge graduate research fellowships from the National Science Foundation. R.R.K. thanks the National Research Council for the Postdoctoral Fellowship. UPS was performed in the NUANCE facility at Northwestern University, which is supported by the NSF-MRSEC (DMR-1121262), Keck Foundation, and State of Illinois.

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Acknowledgment

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- 13) Qin, W.; Chen, X.; Li, H.; Yuan, G.; Grossman, J.; Wuttig, M.; Ren, S.* Room temperature multiferroicity of charge-transfer crystals. **ACS Nano**, 9, 9373 (2015). Feature on Youtube: <https://www.youtube.com/watch?v=ugM9XVIJtT4>, and ACS Nano Podcast.

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S.R. acknowledges support from United States Department of Energy (DE-FG02-13ER46937) for carbon material synthesis and photoactivity measurement. Partial support from United States Department of Agriculture (USDA/NIFA Award 2011-10006-30362, for B. S and RV. C) is gratefully acknowledged. C.H. and X.J. acknowledge scholarship from China Scholarship Council. C.H. acknowledges financial support from Shihezi University and Key Project of Chinese Ministry of Education (2010250).

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Acknowledgment

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- 18) Qin, W.; Gong, M.; Chen, X.; Shastry, T.; Sakidja, R.; Yuan, G.; Hersam, M; Wuttig, M.; Ren, S.* Multiferroicity of carbon-based charge-transfer magnets. *Adv. Mater.* 2014, 27, 734.

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- 19) Gong, M.; Shastry, T.; Xie, Y.; Bernardi, M.; Jasion, D.; Luck, K.; Marks, T.; Grossman, J.; Ren*, S.; Hersam*, M. Polychiral Semiconducting Carbon Nanotube-Fullerene Solar Cells, *Nano Letters*, 14, 5308 (2014).

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fellowships through the National Science Foundation. Work at the Massachusetts Institute of Technology (M.B. and J.C.G.) was supported by an MITEI Seed Fund project. The authors thank P. Cizek and S. Christensen at NREL for their assistance with cell certification. UPS was performed in the NUANCE facility at Northwestern University, which is supported by the NSF-MRSEC (DMR-1121262), Keck Foundation, and State of Illinois.

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f. A List of People Working on the Project

Graduate Student: Ms. Jess Lohrman (20%), and Ms. Lin Zhang (20%)

Postdoc: Dr. Wei Qin (50%) and Dr. Beibei Xu (50%)

g. Estimated of the Unexpended Funds

N/A