A Targeted Approach towards Efficient Semitransparent Organic Photovoltaics for Next-Generation Energy-Efficient Buildings

Introduction

Organic Photovoltaics (OPVs) harvest energy directly from sunlight. They comprise a molecular or polymeric carbon-based donor:acceptor blend (bulk heterojunction or BHJ) in between two electrodes.[1,2] OPVs underwent tremendous progress in the past few years, now reaching Power Conversion Efficiencies (PCEs) of over 19%.[3–6] In contrast to their well-established inorganic counterparts, OPVs are lightweight, thin, and flexible, and they can be tuned on the molecular level, allowing the modification of color and transparency.[7–11] These unique properties render OPVs ideal candidates for integrated energy harvesting solutions. Their optical tunability and solution-processability are, for example, favorable for integration into buildings, greenhouses, or displays.[7,8] However, to date, OPVs do not meet the requirements for a widespread commercialization. A systematic in-depth understanding of the structure-property relationships is absent and semitransparent OPVs (ST-OPVs) still suffer from poor performances even though theoretical calculations predict high PCEs even for systems with 100% average visible transmittance (AVT).[12] This work has aimed to improve the in-depth understanding of OPVs, facilitate the study of OPVs, and make progress toward ST-OPVs with sufficient transparency and PCE.

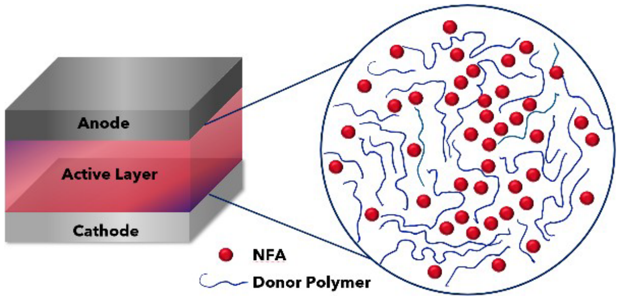

Figure 1. Schematic structure of an Organic Solar Cell with a semitransparent active layer, composed of a carbon-based polymeric donor material and a molecular non-fullerene acceptor (NFA), that is comprised between anode and cathode.

Results and Impact

The work supported by the Link Foundation has focused on the understanding the current limitations of OPVs through a multidimensional and targeted approach, including both experimental and simulation-based methods. Aiming to provide a more in-depth understanding of the device physics of narrow band gap OPVs, which are prime candidates for integrated energy harvesting solutions, we have studied the interfacial recombination processes in such devices.[13] Interfacial recombination is a performance-limiting process that occurs at the interface of the BHJ active layer and the electrodes. Charge carriers recombine (annihilate each other) through interfacial trap states, thus reducing the performance of the devices. In this framework, we have studied OPV devices with ZnO and with PFN-Br-functionalized ZnO front

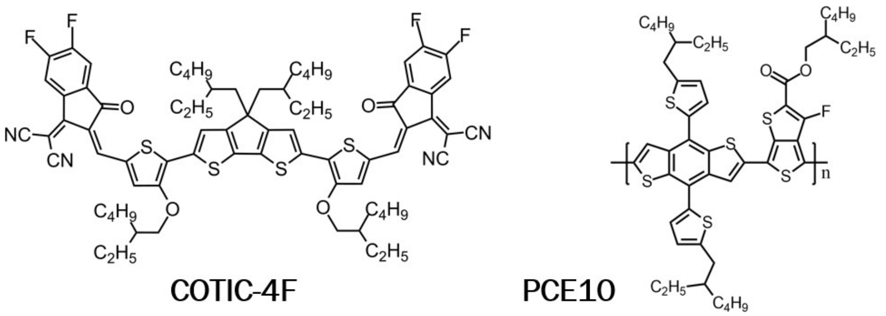

Figure 2. Molecular Structures of the narrow band gap (1.1 eV) NFA COTIC-4F and the donor polymer PCE10. This blend system is suitable for ST-OPVs.

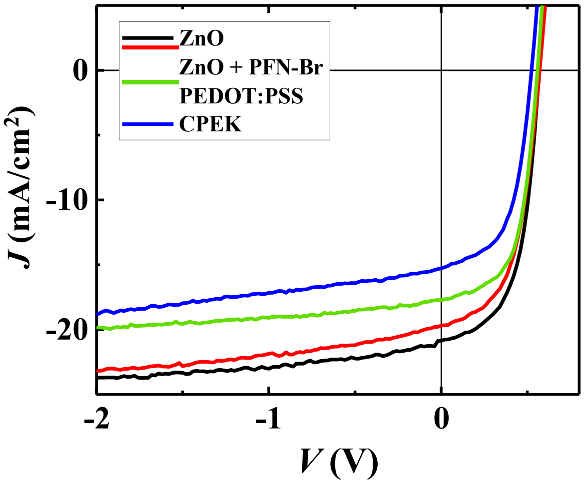

Figure 3. Current-voltage characteristics of PCE10:COTIC-4F devices with different electrodes.

electrodes and devices with PEDOT:PSS and CPE-K front electrodes. Specifically ZnO and PEDOT:PSS are common electrode materials. In the case of opaque OPVs, which have been studied extensively, ZnO is known to cause surface recombination and thus limit the performance. However, for the narrow band gap PCE10:COTIC-4F system, we have found the performance trend ZnO > ZnO/PFN-Br > PEDOT:PSS > CPE-K. With that, ZnO is the most suitable electrode among the tested configurations for the narrow band gap PCE10:COTIC-4F system, thanks to low interfacial recombination rates, efficient charge extraction, beneficial energy level alignment, and lower energetic disorder in comparison to those in the conventional device architecture. Similarly, low interfacial recombination rates and no further reduction in surface traps were observed, when PFN-Br functionalized ZnO was used instead. The devices based on PEDOT:PSS showed high rates of interfacial recombination and reduced photogeneration in the active layer, resulting in lower performance. This negative effect of the surface traps can be mitigated and reduced by nearly 70% when PEDOT:PSS is replaced with the polyelectrolyte CPE-K. These results encourage further exploration of the surface trap passivation effect of CPE-K in other OPV systems. In summary, our findings highlight that interfacial recombination can play a significant role in narrow band gap OPVs and that ZnO is a suitable electrode choice for these narrow systems, contrasting the rules established for opaque OPVs.

Employing the most suitable electrode configuration, we then focused on increasing the transparency of the photoactive layer.[14] A high average visible transmittance (AVT) is a prerequisite for ST-OPVs for integrated energy harvesting solutions such as window-integrated photovoltaics.

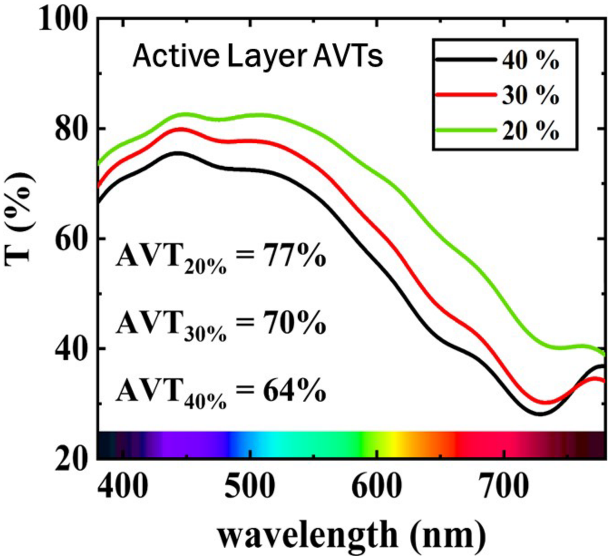

Figure 4. Systematically increased AVT for dilute donor OPVs based on PCE10:COTIC-4F.

To achieve an increased AVT, we applied the ‘dilute donor’ concept to PCE10:COTIC-4F, systematically reducing the donor and increasing the acceptor concentration. The acceptor PCE10 absorbs in the visible range, while COTIC-4F has an absorption maximum around 1000 nm in the infrared. To date, efficient donor polymers that absorb outside the visible range are absent and therefore undesired donor absorption in the visible range is a bottleneck for ST-OPVs. We prepared three PCE10:COTIC-4F active-layer systems with donor concentrations of 40%, 30%, and 20% and found that these provide exceptionally high AVTs of 64% to 77%. We found that the donor:acceptor ratio impacts the nanoscale morphology and the domain sizes, however, efficient charge extraction ($\eta > 90\%$)

is maintained in all systems. The obtained PCEs of 7.0%, 6.5%, and 4.1% follow a clear trend with decreasing donor content due to reduced short-circuit currents, which originate from reduced charge-carrier generation, reduced lifetime, and increased bulk trap-assisted recombination, as our in-depth device analysis revealed. Higher degrees of intermixing in the 30% devices and an unaltered effective charge carrier mobility explain why only a moderate PCE drop is observed when the donor content is reduced from 40% to 30%. We further found very low bimolecular recombination contributions and low charge-carrier densities in all devices, causing trap-assisted recombination channels to be dominant. While surface trap contributions remain constant, an increase in bulk trap-assisted recombination with decreased donor content may be due to morphological changes such as isolated donor islands. In summary, we have outlined how the dilute donor approach can be applied to narrow band gap OPV systems with donor polymers that absorb in the visible range to tune the PCE and AVT based on the transparency requirements for a specific application.

Moreover, we have summarized the state of the ST-OPV field in a review, covering relevant synthetic strategies to narrow the band gap of organic semiconducting molecules, transparent electrodes, and considerations that are unique to ST-OPVs and the device engineering of ST-OPVs.[15] We have highlighted that fundamental device physics considerations should be taken into account to guide the design of ST-OPVs. For example, high-purity and morphologically optimized active layers with low trap density are required due to the increased importance of bulk traps in ST-OPVs.

Optical simulations have been employed in the above-mentioned projects to give insights into narrow band gap OPV systems. These simulations have been applied to TiN/CdZnTe heterojunction photodiodes in a cross-functional collaboration.[16] Such photodiodes are of relevance for nuclear safety or space applications. Lastly, OPVs have been considered for space applications, and the donor polymer molecular weight dependence of OPVs has been studied.

Outlook

Further research aiming to better understand the requirements for ST-OPVs and how they differ from traditional opaque devices in the photoelectronic processes, as well as applied research promoting the material development specifically on the donor side, are expected to move the field forward quickly. Besides exploring different transparent back-electrodes, a future direction might also involve ternary systems to improve the PCE and AVT of the present blend system further. Overall, more synthetic efforts to obtain high-performing ultranarrow-bandgap NFAs with bandgaps of ≈1.12 eV are desirable to overcome the low AVT bottleneck and establish OPV blends with high AVTs >70%. As with opaque OPVs, long-term stability must be addressed for successful commercialization.

Publications Acknowledging Link Foundation Support:

1. **Schopp, N.**, Sabury, S., Chaney, T., Zhang, J., Wakidi, H., Kim, B. M., Sankar, R., Luong, H. M., Therdkatanyuphong, P., Brus, V. V., Marder, S., Toney, M. F., Reynolds, J. R., Nguyen, T.-Q. Organic Photovoltaic Performance Resiliency: Role of Molecular Weight in a PM7 Derivative. *Submitted.*
2. **Schopp, N.**, Abdikamalov· E., Mostovyi, A. I., Parkhomenko E. A., Bazan, G. C., Nguyen, T.-Q., Smoot, G. F., Brus, V. V. Interstellar Photovoltaics. *Submitted.*
3. Schopp, N. (2023). *Understanding the Limitations of Organic Photovoltaics*. University of California Santa Barbara.
4. **Schopp, N.**, Akhtanova, G., Panoy, P., Arbuz, A., Chae, S., Yi, A., Kim, H. J., Promarak, V., Nguyen, T.-Q., & Brus, V. V. (2022). Unraveling Device Physics of Dilute-Donor Narrow-Bandgap Organic Solar Cells with Highly Transparent Active Layers. *Advanced Materials*, *34*(31), 2203796. https://doi.org/10.1002/adma.202203796
5. **Schopp, N.**, & Brus, V. V. (2022). A Review on the Materials Science and Device Physics of Semitransparent Organic Photovoltaics. *Energies*, *15*(13), 4639. https://doi.org/10.3390/en15134639
6. **Schopp, N.**, Luong, H. M., Luginbuhl, B. R., Panoy, P., Choi, D., Promarak, V., Brus, V. V., & Nguyen, T.-Q. (2022). Understanding Interfacial Recombination Processes in Narrow-Band-Gap Organic Solar
7. Schopp, N. (2023). *Understanding the Limitations of Organic Photovoltaics* [University of California Santa Barbara]. 10.13140/RG.2.2.17015.50089
8. Solovan, M. M., Mostovyi, A. I., Parkhomenko, H. P., Kaikanov, M., **Schopp, N.**, Asare, E. A., Kovaliuk, T., Veřtát, P., Ulyanytsky, K. S., Korbutyak, D. V., & Brus, V. V. (2023). A High-Detectivity, Fast-Response, and Radiation-Resistant TiN/CdZnTe Heterojunction Photodiode. *Advanced Optical Materials*, *11*(2), 2202028. https://doi.org/10.1002/adom.202202028

Impact of the Link Energy Fellowship

The generous funding from the Link Energy Foundation has allowed me to pursue my research interest in ST-OPVs and carry out collaborations in this framework. Before receiving the fellowship, this area of research had not been actively pursued in my research group. Therefore, the fellowship shaped significantly the research direction of my Ph.D. Moreover, thanks to being able to focus on research full-time, I could work productively in my fourth and fifth year of the program without any teaching obligations. Prior to receiving the funding, teaching demanded 50% of my time and left little time for volunteer work, career development, and mentoring. The gained flexibility has been incredibly helpful for planning my experiments and for working on my own timeline. In addition, I was able to take part in career development opportunities, for example, through the IPS grant program from UCSB, which allowed me to gain insights into a career in consulting with a special interest in sustainability.

Towards the end of my Ph.D. program, the Link Foundation fellowship provided me with a head start in my job search, since I was able to schedule phone and in-person interviews as necessary, without having to consider any teaching schedules. Since the Link fellowship had enhanced my research experience, my job search was facilitated, allowing me to continue to do research on photovoltaics for sustainable energy harvesting solutions after graduation in industry. I am grateful for the support and the many outstanding opportunities the fellowship has given me.

References

[1] R. A. Street, *Advanced Materials* **2016**, *28*, 3814.

[2] A. Heeger, G. Bazan, T.-Q. Nguyen, F. Wudl, *Charge Recombination, Transport Dynamics, and Interfacial Effects in Organic Solar Cells*, Univ. Of California, Santa Barbara, CA (United States), **2015**.

[3] J. Yuan, Y. Zhang, L. Zhou, G. Zhang, H.-L. Yip, T.-K. Lau, X. Lu, C. Zhu, H. Peng, P. A. Johnson, M. Leclerc, Y. Cao, J. Ulanski, Y. Li, Y. Zou, *Joule* **2019**, *3*, 1140.

[4] Y. Cui, H. Yao, J. Zhang, T. Zhang, Y. Wang, L. Hong, K. Xian, B. Xu, S. Zhang, J. Peng, Z.Wei, F. Gao, J. Hou, *Nature Communications* **2019**, *10*, 1.

[5] Y. Cai, Y. Li, R. Wang, H. Wu, Z. Chen, J. Zhang, Z. Ma, X. Hao, Y. Zhao, C. Zhang, F. Huang, Y. Sun, *Advanced Materials* **2021**, *33*, 2101733.

[6] R. Sun, Y. Wu, X. Yang, Y. Gao, Z. Chen, K. Li, J. Qiao, T. Wang, J. Guo, C. Liu, X. Hao, H. Zhu, J. Min, *Advanced Materials* **2022**, *34*, 2110147.

[7] V. V. Brus, J. Lee, B. R. Luginbuhl, S.-J. Ko, G. C. Bazan, T.-Q. Nguyen, *Advanced Materials* **2019**, *31*, 1970219.

[8] A. Anctil, E. Lee, R. R. Lunt, *Applied Energy* **2020**, *261*, 114429.

[9] W. Cao, J. Li, H. Chen, J. Xue, *JPE* **2014**, *4*, 040990.

[10] Y. Cui, C. Yang, H. Yao, J. Zhu, Y. Wang, G. Jia, F. Gao, J. Hou, *Advanced Materials* **2017**, *29*, 1703080.

[11] Y. Li, X. Guo, Z. Peng, B. Qu, H. Yan, H. Ade, M. Zhang, S. R. Forrest, *Proc. Natl. Acad. Sci. U.S.A.* **2020**, *117*, 21147.

[12] R. R. Lunt, *Appl. Phys. Lett.* **2012**, *101*, 043902.

[13] N. Schopp, H. M. Luong, B. R. Luginbuhl, P. Panoy, D. Choi, V. Promarak, V. V. Brus, T.-Q. Nguyen, *ACS Energy Lett.* **2022**, *7*, 1626.

[14] N. Schopp, G. Akhtanova, P. Panoy, A. Arbuz, S. Chae, A. Yi, H. J. Kim, V. Promarak, T.-Q. Nguyen, V. V. Brus, *Advanced Materials* **2022**, *34*, 2203796.

[15] N. Schopp, V. V. Brus, *Energies* **2022**, *15*, 4639.

[16] M. M. Solovan, A. I. Mostovyi, H. P. Parkhomenko, M. Kaikanov, N. Schopp, E. A. Asare, T. Kovaliuk, P. Veřtát, K. S. Ulyanytsky, D. V. Korbutyak, V. V. Brus, *Advanced Optical Materials* **2023**, *11*, 2202028.