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Revealing the Relationship Between the Microstructure and the Optoelectronic Properties of Donor-Acceptor Thin Films

Abstract

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Contents

Keywords

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Abstract

In the last decade, conjugated polymers have received special attention because of their use in a very extensive field of applications ranging from organic energy devices [1-3], to energy storage [4], to thermoelectrics and bioelectronics [5, 6], to batteries [7], to photonics [8], etc. Although the efficiency of organic solar cells, for example, is reported to increase every year [9-12], there is still a tremendous challenge to clearly understand how different factors related to material processing and/or to specific physical mechanisms influence conversion of light into electricity. Generally, in photovoltaic active layers, an electron donor conjugated polymer is blended with an electron accepting material, most commonly fullerenes. Resulting blends form interpenetrating bulk heterojunction networks with increased donor:acceptor interfacial area [13] that can boost, for instance, the exciton dissociation [14] and, that can influence other internal physical phenomena [15, 16]. In the same time, light absorption and emission properties are also known to be microstructure dependent [17, 18]. As a result, power conversion efficiency is essentially depending on the microstructure of bulk heterojunction [19]. Thus, the need of conjugated polymer films comprised of a microstructure exhibiting specific absorption properties [20], good hole transport mobility [21], high crystallinity [22], controllable morphology and aggregation [23] is well justified.

Generally, films exhibiting an optimized microstructure can be obtained by exposing conjugated polymers [15, 22, 24, 25] to a variety of material processing methods [26]. For instance, molecular packing and aggregation in thin polymer films can be manipulated at some extent by varying the deposition speed of the spin-coater [27]. In comparison, convective self-assembly (CSA) is a blade-coating type of technique that was shown to be efficient in fabricating uniform and structured films of conjugated polymers [17]. This is mainly due to the possibility to precisely vary the deposition speed, i.e. the time that polymer molecules can use to adopt their almost final molecular conformations during film formation.

In this thesis, we work with mixtures of different organic polymers as electron donors and fullerenes as electron acceptors to find the most ideal ingredients and experimental/environmental conditions for the production of the active material of optoelectronic devices using processing techniques such as spin casting and CSA. As we will see, this objective is not straightforward, as organic matter is highly sensitive to a variety of processing parameters. One such parameter is the dissolution temperature, as most polymer solutions need to be heated for several hours to obtain a homogeneous solution. In addition, the casting temperature is not negligible either [28]. Furthermore, careful selection of the solvent is also an important step because the evaporation time of the solvents affects the final structure of the thin film. Often good and poor solvents can be combined to optimize the resulting film microstructure [29].

Each conjugated polymer crystallizes differently and mixes differently with fullerenes, so several combinations were tested during this work. It is very important that the donor and acceptor pairs contact each other on the largest possible surface, as they play an important role in charge separation, but in the same time they should still form rather ordered/interconnected structures through the whole film. This is because charge separation does take place most efficiently at the donor-acceptor interface [30], while charges need to be able to travel through the films towards electrodes. Therefore, the technique used to prepare thin active films is of paramount importance as it is influencing the final film microstructure, and thus the optoelectronic properties of the active layer [31].

Our work introduces two novelties to the scientific world, one of which is the use of a thin film making technique: the convective self-assembly. Using this casting “doctor-blade” type technique we have managed to create thin active layers with controlled microstructure and to induce changes in their resulting optoelectronic properties. The other novelty is related to experiments performed on a polyfullerene system that were, to the best of our knowledge, first of their kind. This new polyfullerene material was blended with known semiconductor polymers to form active layers with the goals to better control structure formation processes in such layers and to study their puzzling optoelectronic properties.

Furthermore, we have shown that fully intercalated co-crystalline polymer:fullerene microstructure can be obtained when depositing thin films using the convective self-assembly technique. Moreover, this microstructure appears to be dependent, under specific film casting conditions, on the fullerene size. Use of slightly bigger fullerenes is leading to a multi-phase microstructure comprised of neat polymer domains, fullerene aggregates and co-crystalline polymer:fullerene structure.

We have demonstrated by spectroscopic and microscopic methods that the molecular arrangement of various semiconductor polymers and polymer-fullerene mixtures can be controlled by the CSA method. By varying the CSA speed, thin films with different conformation from nano- to macroscale were projecting. These morphological changes involve changes in the optoelectronic properties of thin films, as seen in the absorption and photoluminescence spectra. In our work, we investigated several electron donor and electron acceptor using CSA and spin casting film-making methods. Since PL quenching is a measure of exciton separation at the donor – acceptor interfaces, which greatly contributes to improve the efficiency of solar cells, we have therefore paid close attention to it. However, we also experimented a new polyfullerene material, PPCBMB. The best result, *i.e.* the highest PL quenching, was obtained with a blend of PCE11 donor and PPCBMB acceptor. A 6 g/l solution was prepared in chlorobenzene, the donor and acceptor substances were present in the solution in a 1:1 ratio, the solution was spin-cast on a UV-ozone treated glass substrate, thin films were also formed by the CSA method as well. At low CSA speeds, the PL quenching of the PCE11:PPCBMB blend was 65%, in spin casting case it was only 25%. This difference in PL quenching was also detected in other donor: acceptor pairs and it was due to close molecular mixing.

In the case of PBTTT:[C60]PCBM and PBTTT:[C70]PCBM blends created by low CSA speed, we showed significant changes in the absorption spectra due to more ordered aggregates and fully intercalated co-crystalline PBTTT:[C60] PCBM and PBTTT:[C70]PCBM domains, which are also evidenced by the AFM images. In thin films made with the CSA technique, the

FLIM showed a shorter fluorescence average lifetime than those made with the spin casting technique due to the optimized film microstructure.

REFERENCES

1. Li, G., R. Zhu, and Y. Yang, *Polymer solar cells.* Nature Photonics, 2012. **6**: p. 153.
2. Oh, J.Y., et al., *Intrinsically stretchable and healable semiconducting polymer for organic transistors.* Nature, 2016. **539**: p. 411.
3. Boroumand, F.A., P.W. Fry, and D.G. Lidzey, *Nanoscale Conjugated-Polymer Light-Emitting Diodes.* Nano Letters, 2005. **5**(1): p. 67-71.
4. Moia, D., et al., *Design and evaluation of conjugated polymers with polar side chains as electrode materials for electrochemical energy storage in aqueous electrolytes.* Energy & Environmental Science, 2019. **12**(4): p. 1349-1357.
5. Søndergaard, R.R., et al., *Practical evaluation of organic polymer thermoelectrics by large-area R2R processing on flexible substrates.* Energy Science & Engineering, 2013. **1**(2): p. 81-88.
6. Goel, M., et al., *Principles of Structural Design of Conjugated Polymers Showing Excellent Charge Transport toward Thermoelectrics and Bioelectronics Applications.* Macromolecular Rapid Communications, 2019. **40**(10): p. 1800915.
7. Miroshnikov, M., et al., *Power from nature: designing green battery materials from electroactive quinone derivatives and organic polymers.* Journal of Materials Chemistry A, 2016. **4**(32): p. 12370-12386.
8. Tuncel, D., *π-Conjugated nanostructured materials: preparation, properties and photonic applications.* Nanoscale Advances, 2019. **1**(1): p. 19-33.
9. Green, M.A., et al., *Solar cell efficiency tables (Version 45).* Progress in Photovoltaics: Research and Applications, 2015. **23**(1): p. 1-9.

10. Kwon, O.K., et al., *A High Efficiency Nonfullerene Organic Solar Cell with Optimized Crystalline Organizations.* Advanced Materials, 2016. **28**(5): p. 910-916.
11. Green, M.A., et al., *Solar cell efficiency tables (version 50).* Progress in Photovoltaics: Research and Applications, 2017. **25**(7): p. 668-676.
12. Green, M.A., et al., *Solar cell efficiency tables (version 52).* Progress in Photovoltaics: Research and Applications, 2018. **26**(7): p. 427-436.
13. Ganesamoorthy, R., G. Sathiyan, and P. Sakthivel, *Review: Fullerene based acceptors for efficient bulk heterojunction organic solar cell applications.* Solar Energy Materials and Solar Cells, 2017. **161**: p. 102-148.
14. Kularatne, R.S., et al., *Donor–acceptor semiconducting polymers for organic solar cells.* Journal of Polymer Science Part A: Polymer Chemistry, 2013. **51**(4): p. 743-768.
15. Gehrig, D.W., et al., *The Impact of Donor–Acceptor Phase Separation on the Charge Carrier Dynamics in pBTTT:PCBM Photovoltaic Blends.* Macromolecular Rapid Communications, 2015. **36**(11): p. 1054-1060.
16. Poelking, C., et al., *Characterization of Charge-Carrier Transport in Semicrystalline Polymers: Electronic Couplings, Site Energies, and Charge-Carrier Dynamics in Poly(bithiophene-alt-thienothiophene) [PBTTT].* The Journal of Physical Chemistry C, 2013. **117**(4): p. 1633-1640.
17. Botiz, I., et al., *Convective self-assembly of π-conjugated oligomers and polymers.* Journal of Materials Chemistry C, 2017. **5**(10): p. 2513-2518.
18. Botiz, I. and N. Stingelin, *Influence of Molecular Conformations and Microstructure on the Optoelectronic Properties of Conjugated Polymers.* Materials, 2014. **7**(3).
19. Scharber, M.C. and N.S. Sariciftci, *Efficiency of bulk-heterojunction organic solar cells.* Progress in Polymer Science, 2013. **38**(12): p. 1929-1940.
20. Xu, Y.-X., et al., *Improved Charge Transport and Absorption Coefficient in Indacenodithieno[3,2-b]thiophene-based Ladder-Type Polymer Leading*

to Highly Efficient Polymer Solar Cells. Advanced Materials, 2012. **24**(47): p. 6356-6361.

21. Zhang, H., et al., *Low band-gap conjugated polymer based on diketopyrrolopyrrole units and its application in organic photovoltaic cells.* Journal of Materials Chemistry A, 2017. **5**(21): p. 10416-10423.
22. Liu, Y., et al., *Aggregation and morphology control enables multiple cases of high-efficiency polymer solar cells.* Nature Communications, 2014. **5**: p. 5293.
23. Hoppe, H., et al., *Nanoscale Morphology of Conjugated Polymer/Fullerene-Based Bulk- Heterojunction Solar Cells.* Advanced Functional Materials, 2004. **14**(10): p. 1005-1011.
24. Agostinelli, T., et al., *Real-Time Investigation of Crystallization and Phase-Segregation Dynamics in P3HT:PCBM Solar Cells During Thermal Annealing.* Advanced Functional Materials, 2011. **21**(9): p. 1701-1708.
25. Davidson, E.C. and R.A. Segalman, *Thermal Control of Confined Crystallization within P3EHT Block Copolymer Microdomains.* Macromolecules, 2017. **50**(20): p. 8097-8105.
26. Botiz, I., S. Astilean, and N. Stingelin, *Altering the emission properties of conjugated polymers.* Polymer International, 2016. **65**(2): p. 157-163.
27. Ma, W., et al., *Influence of Processing Parameters and Molecular Weight on the Morphology and Properties of High-Performance PffBT4T-2OD:PC71BM Organic Solar Cells.* Advanced Energy Materials, 2015. **5**(23): p. 1501400.
28. Dupont, S.R., et al., *Interlayer adhesion in roll-to-roll processed flexible inverted polymer solar cells.* Solar Energy Materials and Solar Cells, 2012. **97**: p. 171-175.
29. Zhao, J., et al., *Efficient organic solar cells processed from hydrocarbon solvents.* Nature Energy, 2016. **1**(2): p. 15027.
30. Kim, Y., et al., *A strong regioregularity effect in self-organizing conjugated polymer films and high-efficiency polythiophene: fullerene solar cells*, in *Materials for Sustainable Energy*. 2010, Co-Published with Macmillan Publishers Ltd, UK. p. 63-69.

31. Krebs, F.C., *Fabrication and processing of polymer solar cells: A review of printing and coating techniques.* Solar Energy Materials and Solar Cells, 2009. **93**(4): p. 394-412.