# SOME GENERAL CONCEPTS OF ORGANIC PHOTOVOLTAIC SOLAR CELLS - A POTENTIAL CLEAN ENERGY FOR FUTURE

MỘT SỐ KHÁI NIỆM CHUNG VỀ PIN NĂNG LƯỢNG MẶT TRỜI HỮU CƠ -Nguồn năng lượng sạch tiềm năng cho tương lai

### ABSTRACT

Photovoltaic technology is the technique in which the sunlight is converted directly into electricity. This technique is considered as one of the most effective ways to address global energy crisis using a renewable resource. While the high cost production and environmental issues reduced the using of inorganic solar cells in life; low-cost, low energy budgets, solution processing, flexible solar cells, are the keywords associated with organic solar cells, led to improve the attention of scientists to this area. The power conversion efficiencies of organic photovoltaics now reached the record of 11.7% for organic solar cell used polymer and fullerene derivative in a bulk - heterojunction (reported by H. Yan's group), and 13.2% for an organic photovoltaics multi-junction cell (reported by Heliatek R&D teams at Dresden, Germany). However, this research area is quiet young in Vietnam. In this paper, we would like to briefly introduce to organic photovoltaic regarding to history, principle and the main strategies of this technique. This information may be useful for research in organic solar cells in Vietnam.

Keywords: Organic solar cell, photovoltaic, efficiency.

#### TÓM TẮT

Kỹ thuật quang điện là công nghệ mà trong đó ánh sáng mặt trời được biến đổi trực tiếp thành điện năng. Đây được coi là một trong những phương án hiệu quả nhất để giải guyết cuộc khủng hoảng năng lượng toàn cầu bằng cách sử dụng nguồn tài nguyên thiên nhiên có thể tái tao được. Nếu các vấn đề về chi phí cao, tác động mội trường làm giảm bớt phần nào ứng dung của pin năng lượng mặt trời vô cơ thì chi phí thấp, vốn đầu tư thấp, phù hợp với các địa hình và hình dạng là các từ khoá liên guan đến pin năng lượng mặt trời hữu cơ, làm cho lĩnh vực này thu hút được rất nhiều sự quan tâm chú ý của các nhà khoa học. Theo các nghiên cứu trên thế giới, hiệu suất chuyển đổi năng lượng của các tế bào quang điện hữu cơ đã đạt giá trị cao nhất tính đến thời điểm hiện tại là 11,7% đối với các pin năng lượng mặt trời hữu cơ sử dụng hợp phần polymer: fullerene (theo công bố của H. Yan và các công sư tai Đai hoc khoa hoc và công nghê Hồng Kông); và 13,2% đối với pin quang điện hữu cơ kết hợp (báo cáo bởi Heliatek R & D tai Dresden, Đức). Tuy nhiện, lĩnh vực nghiên cứu này vẫn còn khá non trẻ ở Việt Nam. Trong bài báo này, chúng tôi xin giới thiệu khái quát về pin quang điện hữu cơ, bao gồm lịch sử phát triển, nguyên tắc hoạt đông và các hướng nghiên cứu chính của kỹ thuật này. Các thông tin trong bài báo sẽ hữu ích cho việc nghiên cứu các pin năng lượng mặt trời hữu cơ ở Việt Nam.

Từ khóa: Pin năng lượng mặt trời hữu cơ, quang điện, hiệu suất.

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#### **1. INTRODUCTION**

Photovoltaics (PVs) are among the most promising collections for clean and renewable resources. Until now, inorganic energy photovoltaics, which are using Silicon-based (mono-Si, multi-Si, ribbon-Si) and then thin-film (such as cadmium-telluride, gallium-arsenide, etc) - corresponding to first and second generations of PV technologies, have been being available in commercial market. However, they are currently too expensive to compare to fossil fuels and also cause some environmental issues when they come to recycling and disposal. To dissolve these problems, organic photovoltaics (OPV), referred to as a third generation of PV technology has been attached attention of scientists with many advantages such as: low-cost production, low energy budgets, solution processing, flexible solar cells. A result of searching the phrase "Organic soler cells(s)" on scifinder - the important searching tool of researchers - is shown in Figure 1. It can be seen that the interest of scientists in this area is significantly increased year by year corresponding to the increasing of publications.



Figure 1. A result of searching "organic solar cell(s)" done on Scifinder (updated until Jan-2018)

The efficiency of a polymer solar cells is proportional to the short-circuit current ( $J_{sc}$ ), open-circuit voltage ( $V_{oc}$ ) and the fill factor (FF). To reach power conversion efficiency (PCE) of organic photovoltaics (OPVs) in range of 10-15%, which can be competed with inorganic solar cells, these values need to be optimized via both device optimization and designing new photo-harvesting materials.

## 2. THE DEVELOPMENT AND PRINCIPLE OF ORGANIC PHOTOVOLTAICS

The first successful OPV was reported by Tang and Albrecht in 1975, who incorporated chlorophyll-a as the photoactive layer between two electrodes with a PCE of about 0.001% [1]. The organic photovoltaic solar cells with a single-component active layer exhibited very low PCE because of poor charge carrier generation and unbalanced charge transport [2]. To improve the photocurrent of solar cell devices, a bilayer heterojunction configuration containing a p-type (D, donor material) layer for hole transport and an n-type (A, acceptor material) layer for electron transport has been developed by Tang [3]. The working mechanism of D-A heterojunction solar cells involves four distinct events[4] as shown in Figure 2. First, the photoexcitation in the D material happens, leading to the formation of an electron-hole pair, namely an exciton. Second, the exciton diffuses to the D-A interfaces. If the distance it has to travel is longer than the maximum diffusion length (max  $L_D$ , generally around 10 nm in organic materials,[5-9] this excited stated will be quenched, exciton will recombine to ground state, inhibiting any further process. Third, the dissociation of the exciton at the D-A interface occurs through an electron-transfer process, in which hole and electron remain in the donor and acceptor phases, respectively. Finally, the charge transport and collection to the respective electrodes in the opposite direction with the aid of the external electric field. This process leads to generate the photocurrent and photovoltage, which can be converted into useful work.



ohole

Figure 2. Working mechanism for D-A heterojunction solar cells [4]

Due to the short diffusion length and small area of D-A interface for charge generation, the exciton created from D material in bilayer heterojunction device is recombined before reach the A material, leads to limit PCE. To overcome this issue, a BHJ was introduced by Yu et al [10]. By blending D and A materials together, the large D-A

interfacial area can be achieved via controlling the phase separation of two components in bulk. The formation of the bicontinuous interpenetrating network increase the chance for exciton dissociates, resulting in efficient charge separation. To date, the BHJ-structured active layer is the most successful structure for OPVs. The general structure of single layer and heterojunction solar cells using an aluminum cathode and a transparent indium tin oxide (ITO) anode is illustrated in Figure 3.



Figure 3. Schematic diagram of single layer and heterojunction solar cell structures

To evaluate the performance of an OSC and compare it to another, the PCE is the most commonly parameter used. The conditions under which PCE is measured must be controlled similarly in all researches. In general, the OSCs are measured under illumination of AM 1.5G, 100 mW cm<sup>-2</sup>, at a temperature of 25°C. The PCE is defined as the ratio of energy output ( $P_{out}$ ) from the solar cell to input energy ( $P_{in}$ ) from the sun and expressed in following equation[11]:

$$PCE(\eta) = \frac{P_{out}}{P_{in}} = FF. \frac{J_{sc}.v_{oc}}{P_{in}}$$
(1)

$$FF = \frac{J_{max} \cdot V_{max}}{J_{sc} \cdot V_{oc}}$$
(2)

where  $V_{oc}$  is the open-circuit voltage,  $J_{sc}$  is the shortcircuit current; and FF is the fill factor. The  $V_{oc}$ , the photovoltage at zero current density, depends on the offset between the highest occupied molecular orbital (HOMO) of the donor material and the lowest unoccupied molecular orbital (LUMO) of the acceptor material; [12, 13] the  $J_{sc}$ , photocurrent at zero bias, is influenced by the photon absorbance (determined mainly by the band gap and the thickness of active layer), charge separation and mobility; and the FF is affected by the balanced charge transport and recombination properties of active layer [14, 15].

### 3. PHOTOACTIVE MATERIALS FOR ORGANIC PHOTOVOLTAICS

In general, active layer of BHJ OSCs use two distinct materials, a donor is an electron-donating conjugated polymer or small molecule (Figure 4) (D material) and an acceptor is an electron-accepting material (A material) which is mostly a fullerene derivative (Figure 5).



R: 3,7-dimethylocthyl; HD: 2-hexyldecyl; EH: 2-ethylhexyl; OEH: 2-ethylhexyloxy; OD: 2-octyldodecyl; OHD: 2-hexyldecyloxy

Figure 4. Structure of some donor materials



Figure 5. Structure of some acceptor materials

For conjugated polymers or small molecules to be used in OPVs, they would ideally exhibit

➢ Low band gap to harvest as much as possible of the photons from sunlight

Good charge mobility

> Suitable energy levels to enhance the value of  $V_{oc}$  and allow efficient electron transfer to acceptor

> Excellent solubility to ensure their solutionprocessability.

The most successful strategy in designing low band gap materials is the coupling a conjugated electron-donating unit and a conjugated electronwithdrawing unit in the same backbone to obtain alternative D-A polymer. Because a synthesized alternative D-A polymer has HOMO and LUMO energy levels are largely localized on the electron-donating and electronaccepting units, respectively, the HOMO and LUMO, therefore, band gap of polymer, can be tuned by carefully design and select the donor or acceptor units for polymerization [16].

Till now, fullerene derivatives are dominating as the acceptor materials for high efficiency OPVs. The fullerene derivatives, such as PC<sub>60</sub>BM and PC<sub>70</sub>BM (Figure 5), show not only strong electron affinity but also exhibit good solubility, high crystallinity for using in active layer of OPVs. However, because of several drawbacks, including poor light absorption and hiah-cost production and purification, [17, 181 recently, some novel accepting materials which can be easily tuned electronic and optical properties have been developed. Electrochemical and photovoltaic properties of several materials were synthesized recently, exhibiting high efficiencies are summarized in Table 1.

There are some challenges of this field recently:

- Synthesis of new materials and optimization device structure

of cells to obtain long term stability of organics solar cells

- Synthesis of new materials which can be exhibited higher PCE

- Optimization the conditions (materials, solvents, additives, etc.) to fabricate in large area of devices which still get high PCE in compared to that of small area devices.

#### 4. CONCLUSION

From the first time of discovery of OSC with noncertificated performance of 0.001%, the performance of

Material	номо	LUMO	Device structure	Voc	J <sub>sc</sub>	FF	PCE	Def
	[eV]	[eV]	Device structure		[mA cm <sup>-2</sup> ]	[%]	[%]	Ker.
PTB7	-5.15	-3.51	ITO/PFN/PTB7:PC <sub>71</sub> BM/ MoO <sub>3</sub> /Al, Ag	0.74	17.2	72	9.15	[19]
PTB7-Th	-5.22	-3.64	ITO/ZnO-C60/PTB7-Th:PC <sub>71</sub> BM/MoO <sub>3</sub> /Ag	0.80	15.73	74.3	9.35	[20]
PBDT-TS1	-5.33	-3.52	ITO/PEDOT:PSS/PBDT-TS1:PC <sub>71</sub> BM/Mg/AI	0.8	17.46	67.9	9.48	[21]
PTIPSBDT-DPP	-5.44	-4.00	ITO/PEDOT:PSS/PTIPSBDT-DPP:PC <sub>71</sub> BM/Ca/AI	0.76	16.21	0.65	8.00	[22]
PBDT-BT	-5.45	-3.65	ITO/ZnO/PCBE-OH/PBDT-BT:PC71BM/MoO3/Ag	0.92	15.4	66	9.4	[23]
PffBT4T- 20D	-5.34	-3.69	ITO/ZnO/PffBT4T-20D: TC <sub>71</sub> BM/MoO <sub>3</sub> /Al	0.77	18.8	75	10.8	[24]
PPDT2FBT	-5.45	-3.69	ITO/PEDOT:PSS/ PPDT2FBT:PC <sub>70</sub> BM/AI	0.79	16.3	73	9.39	[25]
PDTP-DFBT	-5.26	-3.61	ITO/ZnO/PDTP-DF BT:PC <sub>71</sub> BM/MoO <sub>3</sub> /Ag	0.68	17.8	65	7.9	[26]
PNT4T-20D	-5.24	-3.71	ITO/ZnO/PNT4T-20D: PC <sub>71</sub> BM/MoO <sub>3</sub> /AI	0.76	19.8	68	10.1	[24]
PBDT- DTNT	-5.19	-3.26	ITO/ZnO/PFN-Br/PBDT-DTNT:PC71BM/MoO3/Ag	0.75	17.4	61	8.4	[27]
PBDTTPD (2EH/C7)	N.A	N.A	ITO/PEDOT:PSS/PBDTTPD(2EH/C7):PC71BM/Ca/AI	0.97	12.6	70	8.5	[28]
PTPD3T	-5.55	-3.73	ITO/ZnO/PTPD3T:PC <sub>71</sub> BM/MoO <sub>x</sub> /Ag	0.795	12.5	79.6	7.90	[29]
PBDT-TFQ	-5.52	-3.30	ITO/PEDOT:PSS/PBDT- TFQ:PC <sub>71</sub> BM /Ca/AI	0.76	17.9	57.6	8.0	[30]
PBDTT-FID	-5.64	-3.98	ITO/ZnO/PNFBr/PBDTT-FID:PC <sub>71</sub> BM/MoO <sub>3</sub> /Ag	0.92	11.30	68	7.04	[31]
PTNT	-5.94	-3.57	ITO/PEDOT:PSS/ PTNT:PC71BM/LiF/AI	0.90	8.1	0.63	4.6	[32]
p-DTS (FBTTh <sub>2</sub> ) <sub>2</sub>	-5.12	-3.34	ITO/PEDOT:PSS/p-DTS (FBTTh <sub>2</sub> ) <sub>2</sub> :PC <sub>71</sub> BM/Ca/AI	0.773	14.74	72.4	8.24	[33]
DR3TSBDT	-5.07	-3.30	ITO/PEDOT:PSS/DR3TS BDT:PC71BM/ETL-1/AI.	0.91	14.45	73	9.95	[34]
IC <sub>60</sub> BA	-5.67	-3.74	ITO/s-W03/P3HT:IC <sub>60</sub> BA/ Ca/Al	0.84	10.60	69	6.14	[35]
IC <sub>70</sub> BA	-5.61	-3.72	ITO/s-W03/P3HT:IC <sub>70</sub> BA/ Ca/AI	0.84	10.85	69.8	6.36	[35]
SF-PDI <sub>2</sub>	-5.90	-3.83	ITO/ZnO/PffBT4T-2DT:SF-PDI <sub>2</sub> /V <sub>2</sub> O <sub>5</sub> /AI	0.98	10.7	57	6.3	[36]
P(NDI20D-T2)	-5.45	-4.0	ITO/ZnO/PEIE/BFS4: P(NDI20D-T2)/MoO <sub>x</sub> /Ag	0.90	9.2	52	4.3	[37]
FBR	-5.70	-3.57	ITO/ZnO/P3HT:FBR/ MoO <sub>3</sub> /Ag	0.82	7.95	63	4.11	[38]

Table is summanization of chergy leters and photororate properties of several aonor and acceptor materials	Table 1. Summarization of energy	levels and photovolta	ic properties of several donor ar	d acceptor materials
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organic photovoltaic devices has been significantly increasing with the certificated performance of over than 11%. Although many issues still remain needed to be addressed, the meaningful progress of this research area makes scientists interested in this technique are confident that practical uses will be found for OPVs in the near future.

#### REFERENCES

[1]. C.W. Tang, A.C. Albrecht, 1975. *Photovoltaic effects of metal-chlorophyll a-metal sandwich cells*. J. Chem. Phys., 62, 2139-2149.

[2]. D. Woehrle, D. Meissner, 1991. *Organic solar cells*. Adv. Mater. (Weinheim, Fed. Repub. Ger.), 3, 129-138.

[3]. C.W. Tang, 1986. *Two-layer organic photovoltaic cell*. Appl. Phys. Lett., 48, 183-185.

[4]. Y.-J. Cheng, S.-H. Yang, C.-S. Hsu, 2009. *Synthesis of Conjugated Polymers for Organic Solar Cell Applications*. Chem. Rev. (Washington, DC, U. S.), 109, 5868-5923.

[5]. J.J.M. Halls, K. Pichler, R.H. Friend, S.C. Moratti, A.B. Holmes, 1996. *Exciton diffusion and dissociation in a poly(p-phenylenevinylene)/C60 heterojunction photovoltaic cell*. Appl. Phys. Lett., 68, 3120-3122.

[6]. M. Theander, A. Yartsev, D. Zigmantas, V. Sundstrom, W. Mammo, M.R. Andersson, O. Inganas, 2000. *Photoluminescence quenching at a polythiophene/C60 heterojunction*. Phys. Rev. B: Condens. Matter Mater. Phys., 61, 12957-12963.

[7]. A. Haugeneder, M. Neges, C. Kallinger, W. Spirkl, U. Lemmer, J. Feldmann, U. Scherf, E. Harth, A. Gugel, K. Mullen, 1999. *Exciton diffusion and dissociation in conjugated polymer/fullerene blends and heterostructures*. Phys. Rev. B: Condens. Matter Mater. Phys., 59, 15346-15351.

[8]. T. Stubinger, W. Brutting, 2001. *Exciton diffusion and optical interference in organic donor-acceptor photovoltaic cells*. J. Appl. Phys., 90, 3632-3641.

[9]. D.E. Markov, E. Amsterdam, P.W.M. Blom, A.B. Sieval, J.C. Hummelen, 2005. *Accurate Measurement of the Exciton Diffusion Length in a Conjugated Polymer Using a Heterostructure with a Side-Chain Cross-Linked Fullerene Layer.* J. Phys. Chem. A, 109, 5266-5274.

[10]. G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, 1995. *Polymer photovoltaic cells: enhanced efficiencies via a network of internal donor-acceptor heterojunctions*. Science (Washington, D. C.), 270, 1789-1791.

[11]. R.S. Kularatne, H.D. Magurudeniya, P. Sista, M.C. Biewer, M.C. Stefan, 2013. *Donor-acceptor semiconducting polymers for organic solar cells*. J. Polym. Sci., Part A: Polym. Chem., 51, 743-768.

[12]. C.J. Brabec, C. Winder, N.S. Sariciftci, J.C. Hummelen, A. Dhanabalan, P.A. Van Hal, R.A.J. Janssen, 2002. *A low-bandgap semiconducting polymer for photovoltaic devices and infrared emitting diodes*. Adv. Funct. Mater., 12, 709-712.

[13]. M.C. Scharber, D. Muehlbacher, M. Koppe, P. Denk, C. Waldauf, A.J. Heeger, C.J. Brabec, 2006. *Design rules for donors in bulk-heterojunction solar cells-towards 10 % energy-conversion efficiency*. Adv. Mater. (Weinheim, Ger.), 18, 789-794.

[14]. X. Guo, N. Zhou, S.J. Lou, J. Smith, D.B. Tice, J.W. Hennek, R.P. Ortiz, J.T.L. Navarrete, S. Li, J. Strzalka, L.X. Chen, R.P.H. Chang, A. Facchetti, T.J. Marks, 2013. *Polymer solar cells with enhanced fill factors*. Nat. Photonics, 7, 825-833.

[15]. L. Yang, J.R. Tumbleston, H. Zhou, H. Ade, W. You, 2013. *Disentangling the impact of side chains and fluorine substituents of conjugated donor polymers on the performance of photovoltaic blends*. Energy Environ. Sci., *6*, 316-326.

[16]. H. Zhou, L. Yang, W. You, 2012. *Rational design of high performance conjugated polymers for organic solar cells*. Macromolecules (Washington, DC, U. S.), 45, 607-632.

[17]. Y. He, Y. Li, 2011. *Fullerene derivative acceptors for high performance polymer solar cells*. Phys. Chem. Chem. Phys., 13, 1970-1983.

[18]. A. Anctil, C.W. Babbitt, R.P. Raffaelle, B.J. Landi, 2011. *Material and Energy Intensity of Fullerene Production*. Environ. Sci. Technol., 45, 2353-2359.

[19]. Z. He, C. Zhong, S. Su, M. Xu, H. Wu, Y. Cao, 2012. *Enhanced power-conversion efficiency in polymer solar cells using an inverted device structure*. Nat. Photonics, 6, 593-597.

[20]. S.-H. Liao, H.-J. Jhuo, Y.-S. Cheng, S.-A. Chen, 2013. Fullerene Derivative-Doped Zinc Oxide Nanofilm as the Cathode of Inverted Polymer Solar Cells with Low-Bandgap Polymer (PTB7-Th) for High Performance. Adv. Mater. (Weinheim, Ger.), 25, 4766-4771.

[21]. L. Ye, S. Zhang, W. Zhao, H. Yao, J. Hou, 2014. *Highly Efficient 2D-Conjugated Benzodithiophene-Based Photovoltaic Polymer with Linear Alkylthio Side Chain*. Chem. Mater., 26, 3603-3605.

[22]. J.-H. Kim, M. Lee, H. Yang, D.-H. Hwang, 2014. *A high molecular weight triisopropylsilylethynyl (TIPS)-benzodithiophene and diketopyrrolopyrrole-based copolymer for high performance organic photovoltaic cells*. J. Mater. Chem. A, 2, 6348-6352.

[23]. J. Subbiah, B. Purushothaman, M. Chen, T. Qin, M. Gao, D. Vak, F.H. Scholes, X. Chen, S.E. Watkins, G.J. Wilson, A.B. Holmes, W.W.H. Wong, D.J. Jones, 2015. *Organic Solar Cells Using a High-Molecular-Weight Benzodithiophene-Benzothiadiazole Copolymer with an Efficiency of 9.4%*. Adv. Mater. (Weinheim, Ger.), 27, 702-705.

[24]. Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade, H. Yan, 2014. *Aggregation and morphology control enables multiple cases of high-efficiency polymer solar cells*. Nat. Commun., 5, 5293.

[25]. T.L. Nguyen, H. Choi, S.J. Ko, M.A. Uddin, B. Walker, S. Yum, J.E. Jeong, M.H. Yun, T.J. Shin, S. Hwang, J.Y. Kim, H.Y. Woo, 2014. *Semi-crystalline photovoltaic polymers with efficiency exceeding 9% in a ~300 nm thick conventional single-cell device*. Energy Environ. Sci., 7, 3040-3051.

[26]. J. You, L. Dou, K. Yoshimura, T. Kato, K. Ohya, T. Moriarty, K. Emery, C.-C. Chen, J. Gao, G. Li, Y. Yang, 2013. *A polymer tandem solar cell with 10.6% power conversion efficiency*, Nat. Commun., 4, ncomms2411, 2410 pp.

[27]. T. Yang, M. Wang, C. Duan, X. Hu, L. Huang, J. Peng, F. Huang, X. Gong, 2012. *Inverted polymer solar cells with 8.4% efficiency by conjugated polyelectrolyte*. Energy Environ. Sci., 5, 8208-8214.

[28]. C. Cabanetos, A. El Labban, J.A. Bartelt, J.D. Douglas, W.R. Mateker, J.M.J. Frechet, M.D. McGehee, P.M. Beaujuge, 2013. *Linear Side Chains in Benzo*[1,2-b:4,5-b']dithiophene-Thieno[3,4-c]pyrrole-4,6-dione Polymers Direct Self-Assembly and Solar Cell Performance. J. Am. Chem. Soc., 135, 4656-4659.

[29]. M. Hafezi, S. Mittal, J. Fan, A. Migdall, J.M. Taylor, 2013. *Imaging topological edge states in silicon photonics*. Nat. Photonics, 7, 1001-1005.

[30]. H.-C. Chen, Y.-H. Chen, C.-C. Liu, Y.-C. Chien, S.-W. Chou, P.-T. Chou, 2012. Prominent Short-Circuit Currents of Fluorinated Quinoxaline-Based Copolymer Solar Cells with a Power Conversion Efficiency of 8.0%. Chem. Mater., 24, 4766-4772.

[31]. Y. Yang, R. Wu, X. Wang, X. Xu, Z. Li, K. Li, Q. Peng, 2014. *Isoindigo fluorination to enhance photovoltaic performance of donor-acceptor conjugated copolymers*. Chem. Commun. (Cambridge, U. K.), 50, 439-441.

[32]. R. Kroon, A. Diaz de Zerio Mendaza, S. Himmelberger, J. Bergqvist, O. Backe, G.C. Faria, F. Gao, A. Obaid, W. Zhuang, D. Gedefaw, E. Olsson, O. Inganas, A. Salleo, C. Muller, M.R. Andersson, 2014. *A New Tetracyclic Lactam Building Block for Thick, Broad-Bandgap Photovoltaics*. J. Am. Chem. Soc., 136, 11578-11581.

[33]. D.H. Wang, A.K.K. Kyaw, V. Gupta, G.C. Bazan, A.J. Heeger, 2013. Enhanced Efficiency Parameters of Solution-Processable Small-Molecule Solar Cells Depending on ITO Sheet Resistance. Adv. Energy Mater., 3, 1161-1165.

[34]. B. Kan, Q. Zhang, M. Li, X. Wan, W. Ni, G. Long, Y. Wang, X. Yang, H. Feng, Y. Chen, 2014. *Solution-Processed Organic Solar Cells Based on Dialkylthiol-Substituted Benzodithiophene Unit with Efficiency near 10%*. J. Am. Chem. Soc., 136, 15529-15532.

[35]. Z.a. Tan, L. Li, C. Cui, Y. Ding, Q. Xu, S. Li, D. Qian, Y. Li, 2012. Solution-Processed Tungsten Oxide as an Effective Anode Buffer Layer for High-Performance Polymer Solar Cells. J. Phys. Chem. C, 116, 18626-18632.

[36]. J. Zhao, Y. Li, H. Lin, Y. Liu, K. Jiang, C. Mu, T. Ma, J.Y. Lin Lai, H. Hu, D. Yu, H. Yan, 2015. *High-efficiency non-fullerene organic solar cells enabled by a difluorobenzothiadiazole-based donor polymer combined with a properly matched small molecule acceptor*. Energy Environ. Sci., 8, 520-525.

[37]. K.D. Deshmukh, T. Qin, J.K. Gallaher, A.C.Y. Liu, E. Gann, K. O'Donnell, L. Thomsen, J.M. Hodgkiss, S.E. Watkins, C.R. McNeill, 2015. *Performance, morphology and photophysics of high open-circuit voltage, low band gap all-polymer solar cells*. Energy Environ. Sci., 8, 332-342.

[38]. S. Holliday, R.S. Ashraf, C.B. Nielsen, M. Kirkus, J.A. Rohr, C.-H. Tan, E. Collado-Fregoso, A.-C. Knall, J.R. Durrant, J. Nelson, I. McCulloch, 2015. *A Rhodanine Flanked Nonfullerene Acceptor for Solution-Processed Organic Photovoltaics*. J. Am. Chem. Soc., 137, 898-904.

[39]. J. Zhao, Y. Li, G. Yang, K. Jiang, H. Lin, H. Ade, W. Ma, H. Yan, 2016. *Efficient organic solar cells processed from hydrocarbon solvents*. Nature Energy, 1, 15027.

[40]. W. Zhao, S. Li, H. Yao, S. Zhang, Y. Zhang, B. Yang, J. Hou, 2017. *Molecular Optimization Enables over 13% Efficiency in Organic Solar Cells*. Journal of the American Chemical Society, 139, 7148-7151.