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Device modeling of solution-processed organic solar cells, photodiodes and photo-resistances

Invited paper

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Abstract—This paper reviews the state of the art of organic photodetectors, used for large area sensors as well as CMOS imagers applications, both in the visible and near infra-red range. Device modeling issues related to this technology are also discussed. A comparison between the expected performances of photodiodes versus photo-resistances is presented, as an example of device modeling application.

Keywords—organic electronics, imagers, CMOS imagers, Infra Red, modeling.

I. INTRODUCTION

Organic electronics is a technology employing organic semiconductors to produce (opto-)electronics devices^[1]. Some of these materials (small molecules essentially) can be deposited by evaporation, requiring clean room facilities. Others can be solution-processed in air, using “roll to roll”^[2] or “sheet to sheet” printing technology (polymers, but not exclusively). Both approaches allow producing large area, potentially flexible (depending on substrate used) devices at low cost. These devices can also be co-integrated with CMOS devices, in an “above IC” approach essentially. Both for fundamental and process-dependent reasons, most of these materials however suffer from poor transport properties compared to inorganic semiconductors (even organic crystals used for organic transistors^[3] $\mu \sim 1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), low temperature processing ($<150^\circ\text{C}$) and poor air stability, limiting their range of applications. However, these technologies can make a difference in some specific applications such as wearable electronics, bio-electronics, OLED display and imaging. This paper addresses in particular this latter field of application, presenting both the state of the art of organic photodetectors, and their challenges in terms of device modeling.

II. ORGANIC PHOTODETECTORS : STATE OF THE ART

A. Organic Photodiodes : introduction.

The first difficulty in building photodetectors with organic materials consists in dissociating the strong excitons generated by light absorption to induce electron-holes pairs. This challenge has been solved in part using the concept of Bulk Hetero-Junction^[4] where light absorbing organic semiconductors are mixed with acceptor molecules (mostly fullerene based) able to dissociate excitons thanks to the

bandgap mismatch at their interface. This concept has been extensively used for solar cell applications^[5]. Together with the introduction of new electrodes, new small molecule acceptor and low bandgap polymers^[6], the power conversion efficiency of organic solar cells has reached the record value of 13 %^[7]. Although the research for printed large area solar cell is now also driven by the promising perovskite technology, there is still an interest for organic solar cell based on Green or ‘Sustainable’ materials, or for in-door applications (organic cells being more efficient than silicon cells to collect artificial light at low irradiance^[8]).

B. Organic Photodiodes for large area image sensors.

In the meantime, organic photodiodes have been also investigated for imaging applications. Several academic teams have recently demonstrated that it is possible to produce solution processed photodiodes operating in the visible range, as efficient as silicon devices in term of sensitivity, dark currents and detectivity^{[9][10]}. Such devices of course require suitable encapsulation, being highly sensitive to oxygen and water^[11]. Their bandwidth however remains low ($<100 \text{ kHz}$), but sufficiently high for most imaging applications. Large area organic photodiode matrices have been successfully produced, essentially for fingerprint sensor applications, or for replacing amorphous silicon matrix in X ray detectors based on scintillators^{[12][13]}. Finding a suitable readout integrated circuit remains an open question, as the conventional TFT backplane on glass are non-flexible and fragile but still more efficient than organic or IGZO based devices on flexible substrate.

C. Organic Photodiodes integrated into CMOS imagers : visible range.

Several teams including Panasonic^[14] and Samsung^[15] have proposed to deposit organic light sensitive layers on the top of CMOS imagers^[16]. The expected advantages are to improve the fill factor and viewing angles^[17], removing the need for micro-lenses. Also, as the charge can be stored in the floating diffusion node and no longer in the photodiode itself, the dynamics of the sensor can be extended^[14]. Moreover, it is also possible to design color sensitive photodiodes^{[15][18]}, removing the need for a Bayer filter, known to induce aliasing and optical losses. However, the integration of these layers on the top of a silicon read out

circuit only allows designing 3T pixels, known to suffer from reset noise. Even if sophisticated solutions have been proposed^[19], this concern penalizes the integration of these original solutions.

D. Organic Photodiodes integrated in CMOS imagers : Near Infra-Red (NIR) range.

There is currently a growing interest for CMOS imagers capable of taking a NIR image in addition to the visible one^[20]. As silicon is poorly efficient above 1000 nm of spectral range, new materials are investigated for this particular application. Germanium would be an excellent option up to 1600 nm, as epitaxial growth processes are compatible with both front- and back-end Si CMOS fabrication technologies. However, the leakage current of Germanium photodiodes ($> 10 \mu\text{A}/\text{cm}^2$) currently remains too high^[21].

For this particular application and others, several organic materials^[20] have been investigated, polymers (PTT, PDDTT, PBTTT, DTBTT ...) as well as small molecules (Porphyrin-based, Lead phthalocyanine (PbPc), Heptamethine salts ...). There are however only few examples of quantum efficiency higher than few % above 1000 nm wavelength. Recently, the team of Fred Wudl at University of California has reported a solution processed full organic photodiode operating up to 2500 nm^[22], with leakage currents as low as $10^{-6} \text{ A}/\text{cm}^2$, proving that there is still room for improvements for NIR organic photodetectors.

Several elegant solutions have been proposed for turning a broadband organic photodiode into a spectrally selective NIR photodetectors. One approach consists in using a thick (2 μm) organic layer, where only NIR generated electrons-holes will be collected, as they are generated in the full volume, and not only close to the contact (charge collection narrowing^[23]). Another approach consists in enhancing the weak intermolecular charge transfer absorption (between polymer and fullerene) using an optical resonant cavity, allowing to tune the peak of spectral response up to 1100 nm^[24]. Panasonic has also recently presented a 2.1 Mpixel double organic layer imager capable of taking both a visible and IR image, up to 900 nm^[25].

In this context, colloidal nanocrystals may appear currently as a more mature solution^[26]. Using PbS quantum dots, it is already possible to deposit a spectrally sensitive thin layer by a solution-processed approach^[27]. Indeed, by playing on the quantum dot diameter (the size dispersion being as low as 5%), these layers are light-sensitive from the visible up to the NIR range (up to 2000 nm). Several authors have reported photodiodes integrated on silicon featuring a quantum efficiency $\sim 10\%$ for wavelength above 1000 nm^{[28][29]}. However, it remains difficult to extract photo-generated carriers from dots because of the presence of isolating ligands between them. Delicate successive steps of "ligands exchanges" are needed to find a suitable trade-off between improving mobility without degrading dots interface and overall layer integrity. Moreover, little is known so far about the reliability and scalability of this technology.

III. DEVICE MODELING OF ORGANIC PHOTODIODES

A. Models and challenges.

In this context, device modeling can be a powerful tool to evaluate and optimize device performances^[30]. Indeed, several relevant issues can be addressed by device modeling: selection of materials composing each layers^[31] (and the role of doping^{[32][33]} if any), analysis of performances (such as dark currents^[34], bandwidth^[35] ...), impact of traps^{[36][37]}, analysis of electrical measurement and parameter extraction^[38], selection of potential device architecture^[23], impact of contamination^{[11][39]}, compact modeling^[40] and circuit simulations ...

Most of the device modeling works have been done so far using the Drift Diffusion approach^[41], which handles efficiently heterojunctions (including, if needed, the bulk heterojunction itself^[42]), impact of contacts and trapping, and time or frequency dependent simulations. The main limitation of this approach is the excessive simplicity of the physical description of transport in organic materials, forcing to calibrate simulations with experimental temperature and field dependent mobility (which requires delicate experiments^[43]). More sophisticated models can be used, ranking from phenomenological hopping models^[44] to quantum chemistry^{[45][46]}. This latter approach, combining density functional theory, molecular dynamics, and transport via kinetic Monte Carlo simulations, is certainly promising, but has to face the complexity of transport in a large variety of organic materials, interfaces, and disorder configuration.

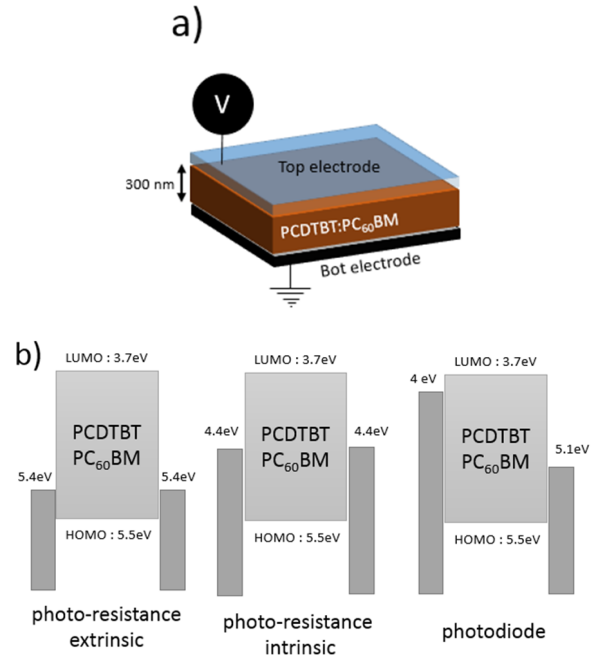


Fig. 1. Schematic drawing of vertically stacked photoresistance and photodiodes (a), and corresponding band diagram (b).

B. An example of device modeling : investigation of photo-multiplication in organic photoresistances.

Organic photodiodes typically use two different electrodes^[10], one with a high work function to collect holes

(typically PEDOT:PSS), and one with a low work function to collect electrons (for instance ITO functionalized with PEIE). However, it is also possible, and by some extent even easier, to use the same electrode for both contacts. In this case, the photo-detector is no longer a photodiode, but a photo-resistance (see Fig. 1).

As bulk PbS photo-resistance (also called photo-conductive cell or light-dependent resistor) are quite common low cost NIR sensors, the advantages and drawbacks of this device compared to photodiodes have been known for a long time: high sensitivity due to gain (photo-multiplication), low detectivity due to high dark current, and low bandwidth^[47]. Interestingly, this question has recently found a renewed interest, both in organic based and quantum dots based photodetectors, due to the unexpected high levels of gain (more than 1000) that have been obtained empirically in several papers^{[48][49][50]}, and sometimes attributed to the presence of traps. If the pros and cons of this device seem similar to the one of old fashion bulk photo-resistance, we believe that the physics involved is in fact quite different. Indeed, devices of interest are vertically stacked devices (where contacts are located on the front and the back of the active layer, see fig.1) and not longitudinal devices (where contacts are lateral) as in conventional photo-resistances. To investigate the operation of this new type of device and its performance, Drift-Diffusion simulations have been performed, considering an active layer of PCDTBT:PC₆₀BM, a material extensively investigated in our group in the photodiode configuration^{[10][11]}. Simulations were found in excellent agreement with experiments (see Fig. 2). In these simulations, traps parameters were not used as fitting parameter, but extracted on previous experiments based on photodiodes using the same active layer materials.

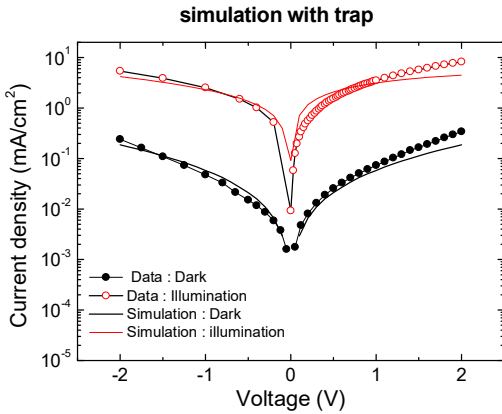


Fig. 2. Comparison between theory and experiments in dark and illuminated I-V PCDTBT:PC₆₀BM photoresistance

Simulation results have revealed a more complex physics than expected according to the classical photo-resistance theory. First of all, it has been found that it is possible in principle to obtain a (modest) gain even in absence of traps in vertically stacked extrinsic photo-resistance (but not in intrinsic photo-resistance, nor photodiodes). Secondly, in the presence of traps, the gain has been found significant only at low levels of irradiance. This may not be an issue in principle, as the gain is needed to detect low-level optical

signals. However, it implies that there is no perfect linearity in this type of device, which complicates the practical use of this photodetector. Finally yet importantly, these results are not in agreement with the formula from the theory of gain in classical photo-resistance.

A deeper analysis has shown that the photo-multiplication requires the breakdown of the quasi neutrality approximation, i.e. that electric fields in dark and illuminated conditions differ. It is indeed the case in P-only photo-resistance with electron acceptor traps for instance, the capture by trapping of photo-generated electrons inducing a significant electric field modification. This change of electric field triggers hole injection by the contacts. This observation explains why low dark current devices, such as photodiodes and intrinsic photo-resistances does not show any photo-multiplication.

If gain and dark currents are correlated, is there a possible trade-off to reach a significant detectivity? Fig. 3 is an attempt to answer this question (considering only one type of volume traps and no additional layers). Indeed, theoretical detectivities (ignoring the additional source of noise induced by the presence of traps) of photo-resistances and photodiodes are plotted. As expected, device featuring no gain, such as photodiodes and intrinsic photo-resistance, are only penalized by traps, while extrinsic photo-resistances shows a better detectivity at high trap concentration due to gain. However, even in the best case, the detectivity of extrinsic photo-resistances would never exceed the level of detectivity experimentally achieved in record photodiodes PD(Rp)^[10]. Considering also that traps respond slowly to light time variation, these conclusions suggests that photodiodes always outperform high gain photo-resistances. This conclusion may differ if, for some reasons such as poor material quality or poor contacts for instance, photodiodes suffer for excessive dark currents.

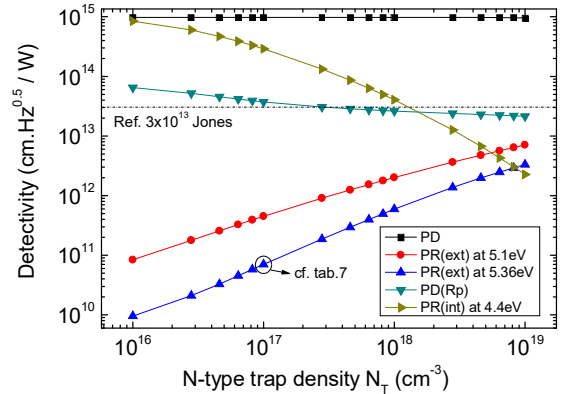


Fig. 3. Calculated detectivity versus volume trap density for ideal photodiode with no traps (PD), intrinsic photoresistance (PR (int.)), photodiode with traps and shunt resistance (PD(Rp)) as in^[10], and extrinsic photoresistance (PR(ext.)) with two levels of contact work function.

IV. CONCLUSIONS

Organic electronics is a promising technology for large area, flexible and low cost imager (as required for fingerprints or X ray medical imaging applications for

instance). In the visible range, thanks to the progress in terms of materials, contacts, processes and encapsulation, organic photodiodes now show similar performances to silicon devices in term of sensitivity, dark currents and detectivity. There is also currently an interest for introducing photosensitive organic layers into CMOS imagers and taking advantage, for instance, of their spectral selectivity, in the visible RGB range, as well as in the Near Infra-Red range. Reset noise remains a concern. Drift Diffusion simulations, carefully calibrated with experiments, is a powerful platform to investigate the steady state and time dependent performances of these devices. The intriguing phenomena of trap-assisted photo-multiplication in solution-processed photo-resistances has been successfully investigated by this approach, providing interesting insights on its physical origin and device implications.

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REFERENCES

- [1] J. S. Chang, A. F. Facchetti, R. Reuss, *IEEE J. Emerg. Sel. Top. Circuits Syst.* **2017**, 7, 7.
- [2] N. Palavesam, S. Marin, D. Hemmetzberger, C. Landesberger, K. Bock, C. Kutter, *Flex. Print. Electron.* **2018**, 3, DOI: 10.1088/2058-8585/aaaa04.
- [3] S. Fratini, D. Mayou, S. Ciuchi, *Adv. Funct. Mater.* **2016**, 26, 2292.
- [4] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, a. J. Heeger, *Science* (80-). **1995**, 270, 1789.
- [5] G. Dennler, M. C. Scharber, C. J. Brabec, *Adv. Mater.* **2009**, 21, 1323.
- [6] C. Liu, K. Wang, X. Gong, A. J. Heeger, *Chem. Soc. Rev.* **2015**, DOI: 10.1039/C5CS00650C.
- [7] W. Zhao, S. Li, H. Yao, S. Zhang, Y. Zhang, B. Yang, J. Hou, *J. Am. Chem. Soc.* **2017**, 139, 7148.
- [8] B. P. Lechêne, M. Cowell, A. Pierre, J. W. Evans, P. K. Wright, A. C. Arias, *Nano Energy* **2016**, 26, 631.
- [9] A. Pierre, I. Deckman, P. B. Lechêne, A. C. Arias, *Adv. Mater.* **2015**, 27, 6411.
- [10] M. Kiehar, O. Dhez, G. Pecastaings, A. Curutchet, L. Hirsch, *Sci. Rep.* **2016**, 6, srep39201.
- [11] M. Kiehar, M. Daanoun, O. François-Martin, B. Flament, O. Dhez, A. K. Pandey, S. Chambon, R. Clerc, L. Hirsch, *Adv. Electron. Mater.* **2018**, 4, DOI: 10.1002/aelm.201700526.
- [12] A. Kumar, D. Moet, J.-L. van der Steen, A. Tripathi, F. G. Rodriguez, J. Maas, M. Simon, W. Reutten, A. Douglas, R. Raaijmakers, P. E. Malinowski, K. Myny, U. Shafique, R. Andriessen, P. Heremans, G. Gelincik, *Proc. SPIE* 9137, *Org. Photonics VI*, **2014**, 9137, 91370Q.
- [13] S. F. Tedde, P. Buchele, R. Fischer, F. Steinbacher, O. Schmidt, *Tech. Dig. - Int. Electron Devices Meet. IEDM* **2015**, 2015-Febru, 10.4.1.
- [14] K. Nishimura, Y. Sato, J. Hirase, R. Sakaida, M. Yanagida, T. Tamaki, M. Takase, H. Kanehara, M. Murakami, Y. Inoue, in *2016 IEEE Int. Solid-State Circuits Conf.*, **2016**, pp. 110-112.
- [15] S. J. Lim, D. S. Leem, K. B. Park, K. S. Kim, S. Sul, K. Na, G. H. Lee, C. J. Heo, K. H. Lee, X. Bulliard, R. I. Satoh, T. Yagi, T. Ro, D. Im, J. Jung, M. Lee, T. Y. Lee, M. G. Han, Y. W. Jin, S. Lee, *Sci. Rep.* **2015**, 5, 1.
- [16] R. D. Jansen-van Vuuren, A. Armin, A. K. Pandey, P. L. Burn, P. Meredith, *Adv. Mater.* **2016**, 4766.
- [17] D. Baierl, L. Pancheri, M. Schmidt, D. Stoppa, G.-F. Dalla Betta, G. Scarpa, P. Lugli, *Nat. Commun.* **2012**, 3, 1175.
- [18] S. Aihara, H. Seo, T. Sakai, M. Kubota, N. Egami, M. Furuta, T. Hirao, *IEEE Electron. Device Meet.* **2011**, 15.
- [19] M. Ishii, S. Kasuga, K. Yazawa, Y. Sakata, T. Okino, Y. Sato, J. Hirase, Y. Hirose, T. Tamaki, Y. Matsunaga, Y. Kato, *VLSI Circuits (VLSIC), 2013 Symp.* **2013**, 8.
- [20] X. Liu, Y. Lin, Y. Liao, J. Wu, Y. Zheng, *J. Mater. Chem. C* **2018**, DOI: 10.1039/C7TC05042A.
- [21] A. K. Sood, J. W. Zeller, Y. R. Puri, M. O. Technologies, C. Park, *Int. J. Eng. Res. Technol.* **2017**, 10, 81.
- [22] L. Zheng, T. Zhu, W. Xu, L. Liu, J. Zheng, X. Gong, F. Wudl, *J. Mater. Chem. C* **2018**, 18.
- [23] A. Armin, R. D. Jansen-Van Vuuren, N. Kopidakis, P. L. Burn, P. Meredith, *Nat. Commun.* **2015**, 6, 1.
- [24] B. Siegmund, A. Mischok, J. Benduhn, O. Zeika, S. Ullbrich, F. Nehm, M. Böhm, D. Spoltore, H. Fröb, C. Körner, K. Leo, K. Vandewal, *Nat. Commun.* **2017**, 8, DOI: 10.1038/ncomms15421.
- [25] S. Machida, S. Shishido, T. Tokuhara, M. Yanagida, T. Yamada, M. Izuchi, Y. Sato, Y. Miyake, M. Nakata, M. Murakami, M. Harada, Y. Inoue, *IEEE J. Solid-State Circuits* **2018**, 53, 229.
- [26] R. Saran, R. J. Curry, *Nat. Photonics* **2016**, 10, 81.
- [27] Z. M. Beiley, A. Pattantyus-Abraham, E. Hanelt, B. Chen, A. Kuznetsov, N. Kolli, E. H. Sargent, in *Proc. SPIE*, **2017**, p. 101001B.
- [28] E. J. D. Klem, C. Gregory, D. Temple, J. Lewis, in *Proc. SPIE*, **2015**, p. 945104.
- [29] P. E. Malinowski, E. Georgitzikis, J. Maes, I. Vamvaka, F. Frazzica, J. Van Olmen, P. De Moor, P. Heremans, Z. Hens, D. Cheyns, *Sensors* **2017**, 17, DOI: 10.3390/s17122867.
- [30] R. Clerc, B. Bouthinon, M. Mohankumar, P. Rannou, J. Vaillant, T. Maindron, B. Racine, Y.-F. Chen, L. Hirsch, J. M. Verilhac, A. Pereira, A. Revaux, in *Tech. Dig. - Int. Electron Devices Meet. IEDM*, **2017**.
- [31] W. Tress, K. Leo, M. Riede, *Adv. Funct. Mater.* **2011**, 21, 2140.
- [32] S. Olthof, S. Mehraeen, S. K. Mohapatra, S. Barlow, V. Coropceanu, J.-L. Brédas, S. R. Marder, A. Kahn, *Phys. Rev. Lett.* **2012**, 109, 176601.
- [33] M. L. Tietze, L. Burtone, M. Riede, B. Lüssem, K. Leo, *Phys. Rev. B* **2012**, 86, 35320.
- [34] A. H. Fallahpour, S. Kienitz, P. Lugli, *IEEE Trans. Electron Devices* **2017**, 64, 2649.
- [35] B. V. Popescu, D. H. Popescu, P. Lugli, S. Locci, F. Arca, S. F. Tedde, M. Sramek, O. Hayden, *IEEE Trans. Electron Devices* **2013**, 60, 1975.
- [36] F. Arca, S. F. Tedde, M. Sramek, J. Rauh, P. Lugli, O. Hayden, *Sci. Rep.* **2013**, 3, 1324.
- [37] B. Bouthinon, R. Clerc, J. Vaillant, J.-M. Verilhac, J. Faure-Vincent, D. Djurado, I. Ionica, G. Man, A. Gras, G. Pananakakis, R. Gwoziecki, A. Kahn, *Adv. Funct. Mater.* **2015**, 25, DOI: 10.1002/adfm.201401633.
- [38] E. Knapp, B. Ruhstaller, *Appl. Phys. Lett.* **2011**, 99, 93304.
- [39] B. Bouthinon, R. Clerc, J. M. Verilhac, B. Racine, J. De Girolamo, S. Jacob, P. Lienhard, J. Joimel, O. Dhez, A. Revaux, *J. Appl. Phys.* **2018**, 123, DOI: 10.1063/1.5017030.
- [40] O. Marinov, M. J. Deen, U. Zschieschang, H. Klauk, *IEEE Trans. Electron Devices* **2009**, 56, 2952.
- [41] E. Knapp, R. Häusermann, H. U. Schwarzenbach, B. Ruhstaller, *J. Appl. Phys.* **2010**, 108, 54504.
- [42] B. Ray, M. a. Alam, *Sol. Energy Mater. Sol. Cells* **2012**, 99, 204.
- [43] M. Stephen, K. Genevicius, G. Juška, K. Arlauskas, R. C. Hiorns, *Polym. Int.* **2017**, 66, 13.
- [44] I. I. Fishchuk, a. K. Kadashchuk, J. Genoe, M. Ullah, H. Sitter, T. B. Singh, N. S. Sariciftci, H. Bässler, *Phys. Rev. B* **2010**, 81, 45202.
- [45] B. G. Sumpster, V. Meunier, *J. Polym. Sci. Part B Polym. Phys.* **2012**, 50, 1071.
- [46] K. Do, M. K. Ravva, T. Wang, J. L. Brédas, *Chem. Mater.* **2017**, 29, 346.
- [47] S. M. Sze, Kwok K. Ng, *Physics of Semiconductor Devices*, John Wiley & Sons, New York, **2006**.
- [48] F. P. García De Arquer, A. Armin, P. Meredith, E. H. Sargent, *Nat. Rev. Mater.* **2017**, 2, 1.
- [49] L. Li, F. Zhang, J. Wang, Q. An, Q. Sun, W. Wang, J. Zhang, F. Teng, *Sci. Rep.* **2015**, 5, 1.
- [50] L. Li, F. Zhang, W. Wang, Q. An, J. Wang, Q. Sun, M. Zhang, *ACS Appl. Mater. Interfaces* **2015**, 7, 5890.