



Citation: P. C. Dastoor, W. J. Belcher (2019) How the West was Won? A History of Organic Photovoltaics. *Substantia* 3(2) Suppl. 1: 99-110. doi: 10.13128/Substantia-612

Copyright: © 2019 P. C. Dastoor and W. J. Belcher. This is an open access, peer-reviewed article published by Firenze University Press (<http://www.fupress.com/substantia>) and distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The Author(s) declare(s) no conflict of interest.

How the West was Won? A History of Organic Photovoltaics

PAUL C. DASTOOR, WARWICK J. BELCHER

Centre for Organic Electronics, University of Newcastle, University Drive, Callaghan NSW 2308, Australia

E-mail: paul.dastoor@newcastle.edu.au

Abstract. The history of organic photovoltaics has been characterised by the complex interplay between fundamental research, large scale manufacture and commercialization activities. In addition, the field is highly interdisciplinary; ranging across physics, chemistry and engineering. This environment has resulted in a frontier character to the field, with researchers constantly expanding into new areas and confronting new challenges as the area has developed. This article seeks to chart the developments in organic photovoltaic research, with emphasis on the last two decades, to provide some historical context to current status of the field.

Keywords. Photovoltaics, Conjugated Polymers, Renewable Energy, Flexible Electronics, Roll-to-Roll Printing, Bulk Heterojunction.

*Come forth into the light of things,
Let Nature be your Teacher.*
—William Wordsworth

*We have dominated and overruled nature,
and from now on the earth is ours, a
kitchen garden until we learn to make our
own chlorophyll and float it out in the sun
inside plastic membranes.*
—Lewis Thomas

1. GO WEST YOUNG MAN (SETTING THE SCENE)

The interaction of light with matter has framed existence since the Earth was first formed some 4.5 billion years ago, with the key step in abiogenesis being the synthesis of complex organic molecules occurring via photochemical processes. Ultimately, the creation of the biosphere via photosynthesis and the consequent development of our entire ecosystem has, of course, been driven by light-matter interactions. More recently, the expansion of human

civilization has been enabled by the energy resources contained within fossil fuel sources; representing the historically stored effects of ancient photochemical processes.

The direct generation of electrical energy from light is a much more recent phenomenon. Photoelectrochemical effects were first reported in 1839, with the French physicist Alexandre Edmond Becquerel (1820–1891) observing the photovoltaic (PV) effect via an electrode in a conductive solution exposed to light.^{1,2} In 1876 William Grylls Adams (1836–1915) and his student, Richard Evans Day, observed the photovoltaic effect in solidified selenium, and published a paper; ‘The action of light on selenium’ in the Proceedings of the Royal Society.³ In 1883 the American inventor Charles Fritts (1850–1903) developed the first selenium wafer based solar cells. These cells, which were typically around 2 x 2.5 inches in size, had a power conversion efficiency of around 1% and employed an extremely thin layer of gold as a transparent electrode.⁴

The history of the modern silicon solar cell (Figure 1) is much more recent. On April 25, 1954, Bell Labs announced the invention of the first practical silicon solar cell. Shortly afterwards, they were shown at the National Academy of Science Meeting. These cells had about 6% efficiency. The New York Times forecast that solar cells may eventually lead to “the beginning of a new era, leading eventually to the realization of one of mankind’s most cherished dreams – the harnessing of

the almost limitless energy of the sun for the uses of civilization.”⁵ Since then there has been an enormous development of silicon (and other inorganic) solar cell, technologies. Early work determined that the maximum theoretical efficiency of a single junction cell is 33.16%, the Shockley-Queisser limit⁶, and maximum values of 27% have been reached for single junction crystalline Si cells⁷, with four junction cell efficiencies of 39% achieved.⁸

Perhaps surprisingly, the history of photoelectrical processes in organic molecules is almost as long as that of inorganic materials. The photoconductivity of anthracene was first studied by the Italian physical chemist Alfredo Pochettino (1876–1953) at Sassari, Italy in 1906⁹ and later by Max Volmer (1885–1965) at Leipzig in 1913.¹⁰ In 1958 the Nobel Laureate Melvin Calvin (1911–1997) and his student David Kearns worked with magnesium phthalocyanines (MgPc), measuring a photovoltage of 200 mV.¹¹ This early work suggested that a photovoltaic effect could be observed if a sandwich cell consisting of a low work function metal, an organic layer and a high work function metal (or conducting glass) is illuminated. Throughout the 1960s and onwards many organic dyes and biomolecules were discovered to exhibit photoconductivity and a photovoltaic effect, however it was not until the mid-1970’s that this phenomenon would be utilized to generate electrical currents.

2. RIDING THE RANGE (THE FIRST DEVICES)

The first true organic photovoltaic (OPV) devices were developed in the 1970’s and incorporated small organic molecules with porphyrins being a natural place to start given their fundamental role in photosynthesis. In 1975 Ching W. Tang (b. 1947) and Andreas C. Albrecht (1927–2002) at Cornell University showed that chlorophyll-a (Chl-a) from green spinach (Figure 2) could be sandwiched between metal electrodes and under optimal conditions (Cr/Chl-a/Al) had a power conversion efficiency (PCE) of 0.01%; orders of magnitude better than other organic devices at the time (which had efficiencies of around 10^{-6} %) and arguably the first working example of an organic solar cell.¹² In 1978 Larry R. Faulkner (b. 1944) and his student Fu-Ren OPV Fan (b. 1946) demonstrated the generation of short circuit photocurrent in zinc and free base phthalocyanines (ZnPc and Pc, respectively) when sandwiched between an ohmic contact (Au) and a blocking contact (Al or In).¹³ In 1979 Geoffrey Chamberlain and Peter Cooney of Shell Research Ltd observed similar effects in Al/CuPc/Au cells.¹⁴

In 1983 Chamberlain published “Organic Solar Cells: A Review” proclaiming that “remarkable progress

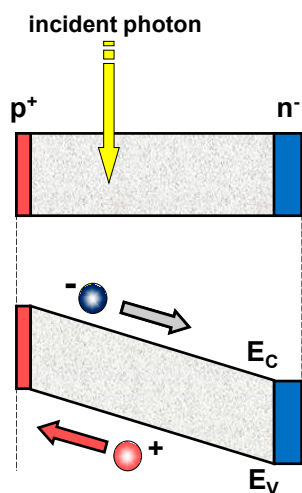


Figure 1. Schematic of modern silicon solar cell. Light absorbed in intrinsic region and creates free electron-hole pairs. The built-in electric field separates charges with holes migrating to the p-doped region and electrons migrating to the n-doped region; resulting in a tilting of the conduction (E_C) and valence (E_V) energy bands in the material.

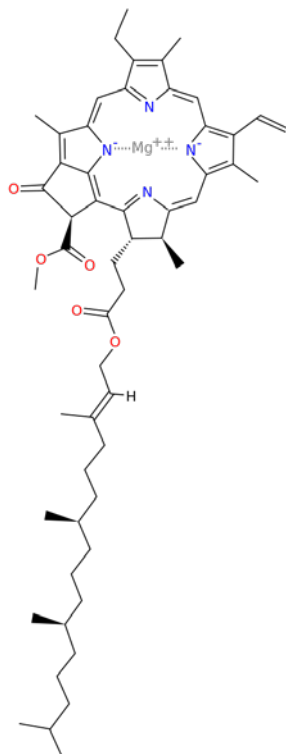


Figure 2. Structure of chlorophyll-a (Chl-a).

has been made in recent years in improving the sunlight efficiency from about 0.001 % in the early 1970s to about 1% recently” and describing the range of porphyrin, phthalocyanines and other small molecules which had been observed to produce photovoltaic effects.¹⁵ Interestingly, even in these early days of organic photovoltaic research Chamberlain noted that “it is generally accepted, however, that cell efficiencies must be as high as possible and at least 5% to offset area-related costs arising from encapsulation materials, support structures etc.”; beginning an efficiency-based bias which has haunted the OPV field ever since.

In 1986, Ching Tang was able to show (by fabricating a bilayer device with copper phthalocyanine and a perylene tetracarboxylic derivative) that the interfacial region was responsible for the generation of photocharges and therefore, for determining the devices photovoltaic properties. Exciton dissociation is known to be efficient at interfaces between materials with different electron affinities and ionization potentials, where the electron is accepted by the material with larger electron affinity and the hole by the material with lower ionization potential. A significant advantage of this device architecture over the prevalent single material devices was that charge generation was no longer dependent on

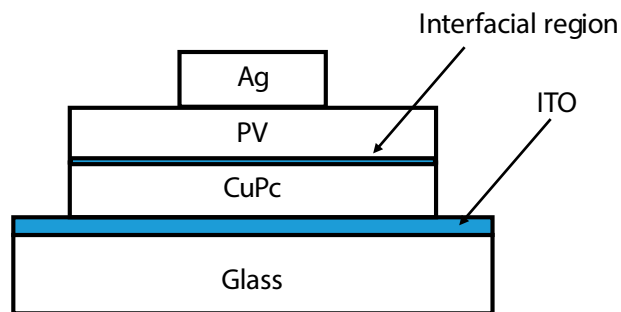


Figure 3. Schematic of Tang's bilayer device using copper phthalocyanine (CuPc) and a perylene tetracarboxylic derivative (PV).

the electric field but rather the work functions of the two layer materials. A PCE of ~1% was achieved.¹⁶

The process of photosynthesis (the conversion of solar energy into chemical energy) involves two protein complexes, photosystem I (PSI) and photosystem II (PSII), that drive photoinduced electron separation. Interestingly, and despite decades of research, by 2017 the best solid-state solar cell device based on photosystem I (PSI) still has a PCE of only 0.069%.¹⁷ However, in 2018 Shengnan Duan fabricated devices by combining Chl-a as the PSI simulator (electron acceptor) with Chl-D as the PSII simulator (electron donor) in an indium tin oxide (ITO)/ZnO/Chl-a/(Chl-Ds)/MoO₃/Ag structure which mimicked the pathway of photoinduced electron transport from photosystem II (PSII) to photosystem I (PSI) in nature (Figure 4).¹⁸ The optimized devices had a PCE of 1.30%, much higher than devices based on PSI alone.

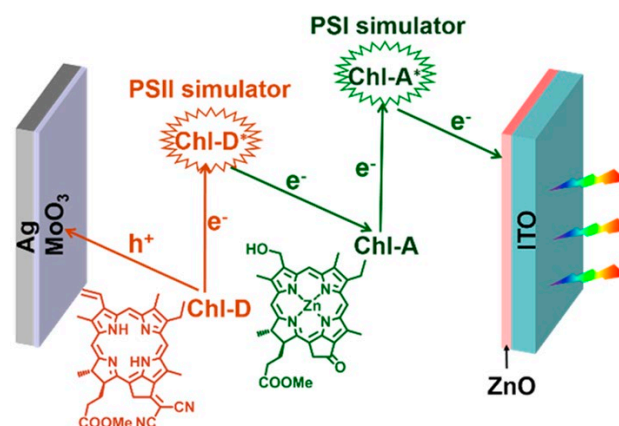


Figure 4. Schematic of indium tin oxide (ITO)/ZnO/Chl-a/(Chl-Ds)/MoO₃/Ag devices mimicked the pathway of photoinduced electron transport from photosystem II (PSII) to photosystem I (PSI) in nature. Reprinted with permission from 18. Copyright (2018) American Chemical Society.

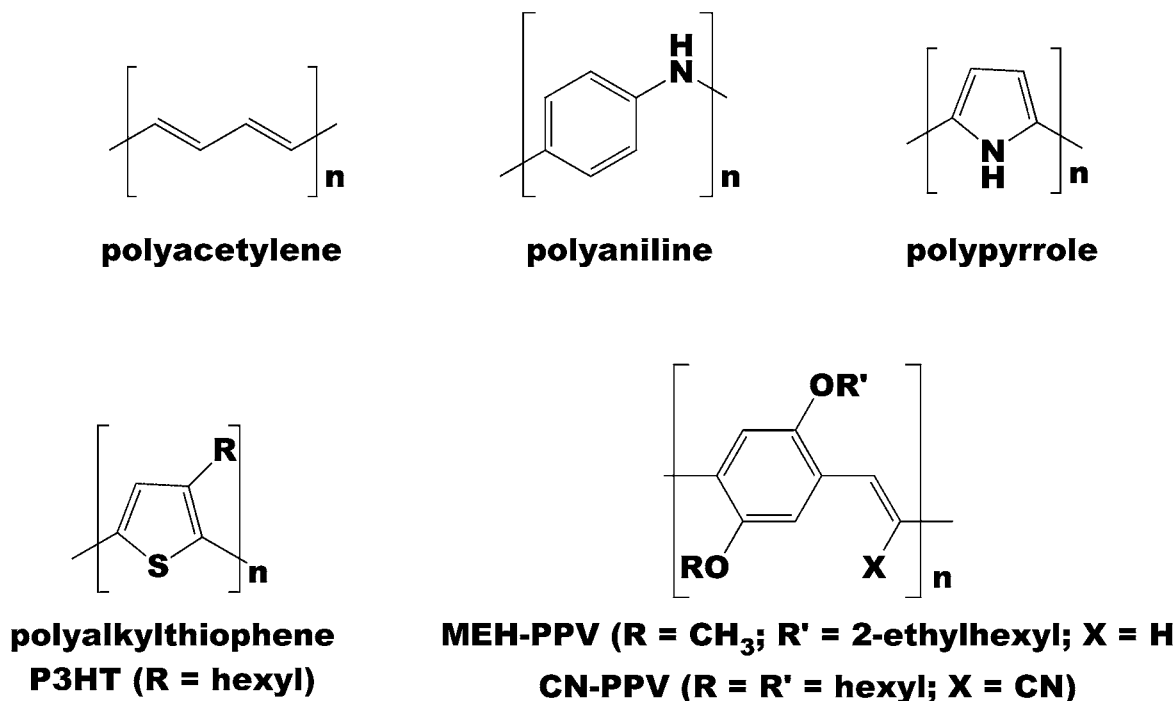


Figure 5. Chemical structures of some common conducting polymers.

By comparison, the history of conjugated and conducting polymers also dates back to the early 19th century.¹⁹ Beginning in 1834, various forms of oxidized polyaniline were produced by Friedlieb Ferdinand Runge (1794–1867) via the oxidation of aniline, although the structure of these materials was not determined until 1920.²⁰ In 1963 an important breakthrough in the field occurred when Donald Eric Weiss (1924–2008) and coworkers at CSIR, Australia identified iodine doped derivatives of polypyrrole (Figure 5) with resistivities down to 0.1 $\Omega\cdot\text{cm}$.^{21–23} Until this time, other than conductive charge transfer complexes, organic molecules were still considered insulating materials. However, publishing in the Australian Journal of Chemistry, the initial results were not widely recognized or known. Nevertheless, a new class of compounds was born and gradually additional reports of conducting polymers encompassing new examples of oxidized polyacetylenes,²⁴ polyanilines,^{25–28} and polypyrroles²⁹ surfaced. Finally, in 1977 Alan J. Heeger (b. 1936), Alan G. MacDiarmid (1927–2007) and Hideki Shirakawa (b. 1936) reported highly conductive, doped polyacetylene.³⁰ Following their award of the 2000 Nobel Prize in Chemistry for “the discovery and development of conductive polymers”, this developing field became widely recognized and conducting polymer research exploded.

2.1 Single layer junctions – the earliest polymer OPVs

Interest in conjugated polymers as photovoltaic materials really commenced in 1994 when Heeger and co-authors fabricated photodiodes of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV; Figure 5) between indium tin oxide and calcium electrodes. The open circuit voltage (V_{OC}) and short circuit current (I_{sc}) under 20 mW/cm^2 were 1.05 V and 1.1 $\mu\text{A}/\text{cm}^2$, respectively, and the sensitivity and the quantum yield at -10 V were 5 \times 10 mA/W and 1.4% el/ph (electrons per photon).³¹

Schottky cell devices fabricated from other conjugated polymers at the time (such as polyacetylene³² and poly(alkylthiophenes)³³) showed similar (low) efficiency photovoltaic behavior. In 1996 Lewis J. Rothberg (b. 1956) and coworkers, working on PPV diode devices^{35,36}, showed that a significant issue associated with simple single material organic diodes and solar cells is that exciton dissociation must occur at the dye/polymer electrode interface since the built in electric field imposed by the electrode materials is insufficient to drive charge separation. This limitation severely restricts the charge generation efficiency of the device and increases the likelihood of recombination of separated charges. In 1996 Richard Friend (b. 1953), Andrew Holmes (b. 1943) and co-workers produced bilayer MEH-PPV/ C_{60} OPV



Figure 6a. Chemical structure of phenyl-C61-butyric acid methyl ester (PCBM).

devices. They showed that excitons generated in the MEH-PPV layer had a diffusion length of 7 ± 1 nm and that photocurrent was only generated by excitons formed within this distance of the MEH-PPV-fullerene interface. Devices with a PCE of $\sim 1.5\%$ were achieved.³⁷

2.2 Bulk heterojunctions – altering the paradigm of polymer OPVs

However, one of the most significant advances in polymer OPV research occurred in 1995 when Richard Friend, Andrew Holmes and co-workers applied the principles observed by Ching Tang in 1986 to produce highly efficient photodiodes from interpenetrating networks of MEH-PPV and poly(2,5,2',5'-tetrahexyloxy-7,8'-dicyano-p-phenylene vinylene (CN-PPV; Figure 5). Phase separation of the two materials led to the spatially distributed interfaces necessary for efficient charge photogeneration, as well as the connected domains required to collect both the electrons and holes.³⁹

Coincidentally, also in 1995, Fred Wudl (b. 1941) and co-workers overcame a major barrier to the use of fullerenes in OPV devices by reporting the synthesis of a range of soluble methanofullerene derivatives suitable for solution deposition of active layers.⁴⁰

Previous work by Alan Heeger, Fred Wudl and co-workers in 1992 had demonstrated picosecond charge transfer from photo-excited conducting polymers (MEH-PPV) to fullerene (C_{60}).³⁸ Alan Heeger, Fred Wudl and co-workers then combined these ideas, taking advantage of the near perfect charge transfer between conducting polymers and fullerene by blending MEH-PPV with one of these methanofullerenes (phenyl-C61-butyric acid methyl ester or PCBM; Figure 6) together in an OPV device active layer with a 1:4 ratio. The resultant bicontinuous network (or bulk heterojunction; BHJ) resulted in devices with a PCE of 2.9%, more

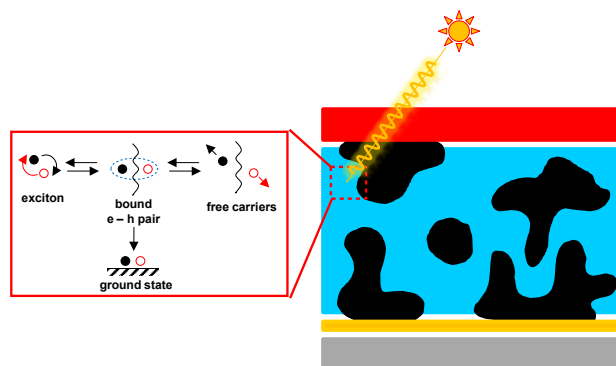


Figure 6b. Schematic of bulk heterojunction (BHJ) structure and charge generation process in OPV devices. An incident photon generates a coupled electron-hole pair (exciton) which diffuses to a donor (polymer) – acceptor (fullerene) interface to form a bound electron-hole pair. This bound state can then either recombine or separate into free charge carriers to generate a photocurrent.

than two orders of magnitude higher than devices of MEH-PPV alone.⁴¹

Subsequently, N. Serdar Sariciftci (b. 1961), Jan C. Hummelen and coworkers showed that control of blend morphology in MDMO-PPV:PCBM devices was critical to optimized device performance.⁴² Interestingly, the authors proposed that the PCE of 2.5 % achieved in these devices “approaches what is needed for the practical use of these devices for harvesting energy from sunlight”. Indeed, the BHJ active layer morphology has remained the basis for the majority of OPV devices to this day.

2.3 The Focus on Metrics – the millstone around the neck of OPVs

From the first days of OPV there has been an arguably disproportionate focus on PCE as the key metric for device performance. From 1993, Martin Green (b. 1948) has published regular (biannual) sets of solar cell and module efficiency tables summarizing the highest independently confirmed results for different technologies in *Progress in Photovoltaics*. As well as keeping researchers informed of the state-of-the-art in the field, a stated aim of these tables is “the encouragement of researchers to seek independent confirmation of research results and the further simulation of intercomparison of measurements between designated cell test centres”.⁴³

Unfortunately, despite the importance of this topic and the clear necessity for rigorous characterization of devices in the field, independent confirmation of device performance (and in particular PCE) is still not com-

monplace. Whilst the highest performing devices are routinely tested by certified laboratories, such as the National Renewable Energy Laboratory (NREL), logistics and expense prohibit the vast majority of devices in published reports from being tested outside of the reporting laboratory.

This situation has led to some controversy in the field. In 2007 Rene Janssen (b. 1959) published a rebuttal of a paper by Wong et al. (July 2007 issue of *Nature Materials*) that presented a new platinum metallopolyene donor polymer (P1) with a bandgap of 1.85 eV that provided a photovoltaic power-conversion efficiency, η , of up to 4.93% in combination with a C60 fullerene derivative (PCBM) as acceptor. This high efficiency represented an important step towards the development of more efficient plastic solar cells. Rene Janssen argued, however, that the optical properties of the new polymer presented in the paper were incompatible with the published high efficiency and that — based on the optical data — the efficiency was unlikely to exceed 2%.⁴⁴ In response, in 2008 the journal *Solar Energy Materials and Solar Cells* resorted to using an editorial to provide a guide on how efficiency data should be reported, especially whenever power conversion efficiencies require external quantum efficiencies (EQE) values above 50% over a large range of wavelengths or when reported power conversion efficiencies exceed 2.5%. In particular they stated that “extra care should be taken in submitted manuscripts to document the measurement’s quality, relevance and independent verification”.⁴⁵

In 2011, the International Summit on OPV Stability (ISOS) published a series of generally agreed test conditions and practices to allow ready comparison between laboratories and to help improve the reliability of reported values.⁴⁶ In 2012 Henry Snaith (b. 1978) published “The perils of solar cell efficiency measurements”, a critique on the use of PCE for characterising OPV devices.” He pointed out that PCE as a performance metric has become so influential and has such a high level of perceived importance that it is now widely used as a key parameter for assessing the value or worth of an entire solar technology, particularly for new and emerging solar technologies, which must constantly justify their existence. Furthermore, in the specific field of OPV, ignorance and negligence are frequently causing solar cells to be mischaracterized, and invalid efficiency results have been reported in a number of journals.⁴⁷

Unfortunately, little has changed since this time. Independent certification of “record” devices is now essentially mandatory for publication, but routine certification of published device performance is not com-

monplace. In light of the import which is placed upon OPV device efficiency by researchers and reviewers this oversight is a major problem and poses a significant barrier to the transfer of knowledge between practitioners.

3. THE TAMING OF THE OLD WEST (THE NEW MILLENNIUM AND THE MATURING OF THE FIELD)

In 2002, Pavel Schilinsky (b. 1974) reported the characterization of new poly(3-hexylthiophene):methanofullerene [6,6]-phenyl C61 butyric acid methyl ester (P3HT:PCBM) solar cells, with a PCE of 2.8% and began a fascination with this material system which dominated the OPV research scene for a decade, and has continued to this day.⁴⁸ The appeal of the P3HT:PCBM system is not hard to see. Even the initial Schilinsky publication highlighted the excellent interpenetrating “bulk heterojunction” phase morphology, ideal for efficient photovoltaic performance.

Monochromatic (550 nm, the absorption maximum) external quantum efficiencies of up to 76% and internal quantum efficiencies of close to unity were reported and recombination of photoinduced carriers was negligible when operated in the photovoltaic mode. As a polymer, P3HT was easy to synthesize at large scale,^{49–54} considerably more soluble and oxidatively stable than the PPV-based polymers which had been studied previously⁵⁵ and P3HT’s semi-crystalline nature meant that thermal^{56, 57} and solvent-annealing⁵⁸ of the blended active layer could be readily used to optimize donor and acceptor domain sizes and crystallinity.

Consequently, P3HT:PCBM solar cells became the “Best Seller in Polymer Photovoltaic Research” with Guillaume Wantz (b. 1977) and co-workers reviewing 579 papers published between 2002 and 2010 alone. The PCE of the P3HT:PCBM solar cells reported in these publications is moderate at best, with a wide range of reported values averaging around 3% and approaching 5% at best.⁵⁹ Nonetheless, P3HT remains a key model polymer for research in organic solar cells. However, as pointed out by Darren Lipomi (b. 1983) and co-workers, P3HT is structurally and morphologically very different from the majority of new generation polymers in OSC research. Consequently, the validity and value of transferring design and processing knowledge from the P3HT material system must be questioned.⁶⁰ Ultimately, however, the relatively poor overlap between the absorption of P3HT and the sun’s irradiance spectrum prohibits significantly higher PCEs and this mismatch has driven the development of polymers with lower bandgaps which better match the sun’s irradiation.⁶¹

3.1 Lower Band gap materials

In polymer:fullerene solar cells the primary light absorbing component is the polymer, since most fullerenes do not absorb strongly in the visible and near-IR, where terrestrial solar intensity is at its greatest. Indeed, Paul Dastoor (b. 1968) and coworkers have shown that PCBM contributes only ~13% of the photocurrent in a P3HT: PCBM device under AM 1.5 illumination.⁶² Consequently, over the last decade or so, attention has been focused at tuning and reducing the optical bandgap, E_g , of the polymer to increase device light absorption.⁶³

The bandgap which determines light absorption in a conjugated polymer is a result of overlap and delocalization of π -orbitals along the polymer backbone. Increasing the planarity of this backbone maximizes the p-orbital overlap and extends the π -delocalization, lowering the bandgap.

A range of both structural and electronic methods have been employed to alter polymer planarity and/or π -delocalization.⁶⁴ Structurally, fused ring systems (either fully aromatic or using bridging atoms) and the use of steric peripheral groups on the backbone are both routinely used to enhance polymer planarity. Increasing the quinoidal nature of linked ring systems breaks aromaticity (and thus electron confinement to the ring), which allows more extensive delocalization. This last effect is particularly prevalent in polythiophene polymers, in part explaining their success in the OPV field.

Planarity of the polymer backbone is not the whole story however. P3HT itself can form ordered microcrystalline domains in which the polymer backbone is highly planar,⁶⁵ but has a wide bandgap of ~1.8 eV (which means it has a maximum solar photon absorption of ~ 46 %).⁶⁶

The optical bandgap can be further reduced by alternating electron rich (donor, D) and electron poor (acceptor, A) subunits along the polymer backbone. The resulting molecular orbital mixing and intermolecular charge transfer between the D and A moieties produces a new set of hybrid molecular orbitals with a bandgap that can be lower than either of the subunits alone. In addition, it has been proposed that alternation of the donor and accepting components increases the double bond character between the units, which could enhance planarity and further decrease the bandgap.⁶⁷

In 2006 Paul Blom (b. 1965) and co-workers presented model calculations for the potential for polymer: fullerene solar cells. They predicted that lowering the band gap of the polymer would result in devices exceeding 6% and that, ultimately, with optimized level tuning, band gap, and balanced mobilities polymeric: fuller-

ene solar cells could reach power conversion efficiencies approaching 11%.⁶⁸ The first truly low bandgap polymer, poly(isothianaphthene) was reported by Fred Wudl in 1984, with a bandgap of ~1.0 eV,⁶⁹ but initially the synthesis of suitable, soluble low band gap materials proved difficult.⁷⁰ However, in 2002 Christoph Brabec (b. 1966) et al. reported ~1% efficient devices from the recently synthesized poly(N-dodecyl-2,5-bis(2'-thenyl)pyrrole-alt-2,1,3-benzothiadiazole) (PTPTB) with PCBM. PTPTB consists of alternating electron-rich N-dodecyl-2,5-bis(2'-thenyl)pyrrole (TPT) and electron deficient 2,1,3-benzothiadiazole (B) units and is the first example of the use of a molecularly engineered lower bandgap material in OPV devices. The electrochemical bandgap of the polymer was determined to be 1.77 eV, placing just within the range of low bandgap materials as defined by the authors ($E_g < 1.8\text{eV}$) but higher than the official definition as set in the Handbook of Conducting Polymers. ($E_g < 1.5\text{eV}$).⁷¹

Since these humble beginnings, a wide range of donor-acceptor low band gap polymers have been synthesized from a growing catalogue of donor and acceptor building blocks.

In 2011 Mitsubishi Chemical announced the first certified single junction organic solar cell with a PCE of >10%.⁷² The device was certified at NREL, but no detail information on either the active layer composition or the device structure was given.

The first device to reach the $\eta > 10\%$ milestone published in a full peer review journal, was a polymer tandem solar cell with a PCE of 10.6% reported by Yang Yang (b. 1958) and coworkers in 2013.⁷³ The D-A polymer used was poly[(5,5-bis(3,7-dimethyloctyl)-5H-dithieno[3,2-b:2',3'-d]pyran-2,7-diyl)-alt-(5,6-difluoro-2,1,3-benzothiadiazole-4,7-diyl)] (PDTP-DFBT) with a reported bandgap of 1.38 eV, in conjunction with PC71BM. A single-junction device was also reported with a spectral response that extended to 900 nm and which had a PCE of 7.9%. Since then, progress in OPV development has been rapid, especially in terms of electrode interfacial layers, new active layers (ternary systems), and the synthesis of new low bandgap polymers. The current certified efficiency record for a single junction organic solar cell lies at $11.2 \pm 0.3\%$ by Toshiba.^{8, 74}

3.2 Understanding the Fundamental Physics

It was realized early on that the physical behavior of semiconducting polymers is dominated by their relatively low dielectric constant compared with that for inorganic semiconductors ($\epsilon_{\text{P3HT}} \sim 3$ vs $\epsilon_{\text{Si}} \sim 11$). Thus, there is much less screening in organic devices and so tightly bound

Frenkel excitons are formed upon light absorption rather than free electron-hole pairs. As a consequence, the energy levels in organic are localized and thus a band transport picture no longer holds. Instead exciton (and charge transport) occurs via a hopping mechanism. Finally, the picture for organic solar cells is further complicated by the fact that charge separation occurs via an intermediate charge-transfer state at the heterojunction.

The realization of these key differences has driven a re-evaluation of classical p-n junction theory and the development of new formalisms in understanding how organic solar cells work. Early work on different electrode materials suggested that V_{oc} depended on work function difference between electrodes.

However, work by Christoph Brabec on different acceptors in 2001 showed that changing the nature of the acceptor played a much bigger role than changing the work function. It was argued that Fermi level pinning through charged interface states between the n-type metal electrode and the fullerene reduction potential caused the insensitivity to work function.⁸⁰ Two possible origins for V_{oc} are either the HOMO-LUMO cross gap (V_{oc1}) or the electrode work function difference (V_{oc2}). In 2003, work by Blom's group showed that in the presence of non-ohmic contacts then V_{oc} could depend strongly on work function difference.⁸¹ A key driver for device design is to try to increase the V_{oc} to increase the power conversion efficiencies of OPVs. However, even when the HOMO-LUMO gap dominates we never observe V_{oc} equal to the calculated gap potential. In 2006, Scharber developed an empirical set of rules for determining the V_{oc} of a BHJ device with PCBM as the acceptor; arguing that there was always a general 0.3V loss in V_{oc} . For more than 26 different material combinations, no influence of the contact work function on the V_{oc} is observed. The 0.3V loss was postulated to be due to the dark current characteristics ($\sim 0.2V$) and the field driven nature of the charge separation process ($\sim 0.1V$) since the the open-circuit voltage depends on the slope of the field-driven current around the built-in voltage (V_{BI}).

In around 2008–2009 it was realized that electronic coupling at donor-acceptor interfaces, or in donor-acceptor blends, leads to the formation of an intermolecular charge-transfer complex that simultaneously influences the photogeneration of mobile charge carriers and the dark current due to thermal generation.⁸⁴⁻⁸⁶ Later work (2010) argued that for bilayers, there are relatively “flat” donor-acceptor (D/A) and metal-organic (M/O) interfaces. There is a large distance between D/A and M/O interfaces and a large barrier resulting in a low electric field at the M/O interface and Fermi-level pin-

ning. As such, unipolar transport dominates at interfaces and there is little effect of electrodes upon V_{oc} . For BHJ devices, however, intimate contact between D/A regions produces large field at M/O interface. In addition, it is possible to obtain an ambipolar carrier distribution at the electrodes. Both effects lower the barrier at the M/O interface and photogenerated carriers can no longer ‘pin’ electrode Fermi level.⁸²

So, the question remains – does the HOMO-LUMO cross gap or the electrode work function determine V_{oc} . The answer is that both can affect the open circuit voltage. In the case of non-ohmic (blocking) contacts then we see that the V_{oc} is dominated by the electrode work function. However, for ohmic contacts we see that electrons can flow into the M/O interface producing accumulated charges and leading to band bending and Fermi-level pinning. The device structure also affects the V_{oc} since the distance of the D/A interface can affect the electric fields at the M/O interface. Large distances result in unipolar charge distributions at the M/O interface (and little dependency of V_{oc} on work function) whereas for ambipolar distributions the opposite is true.

In polymer-fullerene systems (and building from earlier work in organic light emitting diodes (OLEDs) and dye-sensitized solar cells), charge recombination was identified as a major loss mechanism; whether geminate (electron hole-pair recombines while still bound) and non-geminate (electron hole-pair recombines after charges have been separated). It is widely understood that non-geminate recombination in the blended bulk phase dominates in BHJ devices.⁸⁷⁻⁹⁰

4. OF RANCHERS, FENCES AND RANGE WARS (INITIAL ATTEMPTS TO UPSCALE AND COMMERCIALIZE)

Attempts to commercialise the technology has featured early in the history of organic photovoltaics with numerous start-up companies founded, growing, merging, being acquired or going bankrupt. Moreover, the commercialization space has encompassed companies focused on materials and devices. However, given the commercially sensitive nature of establishing start-up companies, publications in the area are few and piecing together the history of OPV commercialization is challenging.

4.1 *The Early Promise*

One of the earliest companies in this space was Quantum Solar Energy Linz (QSEL), founded in 1997 on the back of advances made at the Linz Institute for

Organic Solar Cells (LIOS) under the leadership of N. Serdar Sariciftci. In 2001, Konarka Technologies, Inc. was founded in 2001 as a spin-off from the University of Massachusetts, Lowell. Named after the Konark Sun Temple in India and co-founded by, amongst others, the Nobel laureate Alan Heeger, the company initially decided to work on both solid-state polymer-fullerene solar cells and liquid dye-sensitized solar cells (DSSCs). In 2003, Konarka acquired QSEL, in a move that was described at the time as designed to “make the company the worldwide leader in organic photovoltaics”.

Meanwhile, again in the US, Plextronics was founded in 2002 in Pittsburgh as a spin-off company from Carnegie Mellon University primarily as a materials supply company based on the ability to synthesise regioselective P3HT developed by Richard McCullough (b. 1959). The business was aimed at supplying the anticipated market for conductive inks and process technologies with the advent of organic solar cells and organic light-emitting diode lighting. In the early days, Plextronics was extremely successful, highlighted as one of Pittsburgh's fastest growing companies in 2008 and raising over \$40 M in equity capital.

On the west coast of the USA, Solarmer Energy was founded in California in 2006. The company licensed OPV technology developed by Yang Yang at the University of California, Los Angeles and new semiconducting material technology developed at the University of Chicago. Solarmer established a facility in El Monte, California and initially worked on developing OPV with a goal to demonstrate commercial grade devices and indeed its devices held the record for OPV efficiency in 2009 and 2010. However, it rapidly focused on supplying advanced organic materials to the research community.

A little later, in the UK, Ossila was founded in 2009 by David Lidzey (b. 1967) and James Kingsley at the University of Sheffield. The focus of the company was on the supply of materials and equipment for organic electronics research. Meanwhile, in Cambridge, the company Eight19 was founded in 2010 to commercialise organic solar cell technology developed by Richard Friend at the Cavendish Laboratory of the University of Cambridge. The company was named after the time taken for light to travel to the Earth from the Sun and raised over \$7 million from the Carbon Trust and Rhodia to develop plastic organic solar cells.

4.2 The Crash

After nearly a decade of research and development, it became increasingly clear that the pathway to commercial scale OPV was challenging and unlikely to be

realized in the short term. The inability to deliver on its initial promises resulted in a number of these initial start-up companies filing for bankruptcy and closing down. Probably the most dramatic was in May 2012, when Konarka filed for Chapter 7 bankruptcy protection and laid off its approximately 80-member staff. This event sent shockwaves through the OPV community and was the subject of much discussion at OPV conferences around the world. This event was followed by Plextronics filing for Chapter 11 bankruptcy in January 2014.

4.3 Rising from the Ashes

The assets and rights of Konarka's German operations (Konarka Technologies GmbH) were acquired by Belectric, a Germany-based solar developer, financier, and construction firm in late 2012, who established Belectric OPV GmbH with the aim of manufacturing bespoke OPV devices for the building integrated PV, automotive and consumer electronics markets. Their approach was to overcome the short lifetime of OPV's by creating thin plastic laminates that could be readily integrated into a range of products. Commencing with consumer products (such as OPV based garden ornaments) by 2016, Belectric OPV had already showcased installations such as the German Pavilion at the World Expo in Milan in 2015. In 2017, Belectric OPV was renamed OPVIUS developing a range of OPV products based on small OPV modules encased in polycarbonate laminates.

In March 2014, Solvay SA, an international chemical group headquartered in Brussels, completed the acquisition Plextronics Inc. to bolster its OLED electronic display technology and launch a new development platform with a strong Asian foothold.

In 2016, and after 6 years of technological partnership with the major names of the global chemical industry and an investment of €40 million, the French company ARMOR launched industrial production of a new generation of photovoltaic material, designed and manufactured in France. Called ASCA[®], it is a OPV material based on combining the expertise of a number of different partners: CEA-INES France (devices and durability testing), CNRS-IMS France (materials and devices), CAMBRIOS Advanced Materials USA (silver nanowires), MERCK Germany (photoactive polymers and interface materials), LCPO France (organic polymers), AMCOR France (films and encapsulation), and ADHEX France (technical adhesives).

In May 2019, OPVIUS and ARMOR announced the decision to merge OPVIUS development, integration and marketing activities for flexible organic photovoltaic films with those of ARMOR. Their stated common

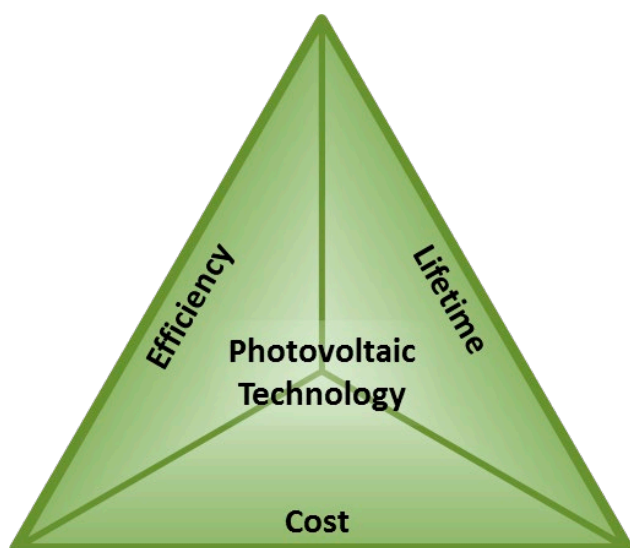


Figure 8. The three key parameters for successful photovoltaic technology: efficiency, lifetime, and cost.

objective was “to pool know-how in order to become the global benchmark company in flexible organic photovoltaic technology.”

In parallel with these commercialization activities there has been significant research effort undertaken in developing the scale-up technologies needed to mass manufacture OPV devices. Primarily based around roll-to-roll (R2R) printing⁹¹, one of the earliest pioneers of large scale manufacturing was Frederik Krebs who was originally based at the Riso National Laboratory, Denmark and subsequently went on to found InfinityPV, with a focus on providing materials and tools to the research community.

5. HIGH NOON (THE VERDICT)

Devices with PCEs in excess of 15 % are now possible, far in excess of the 5 % efficiency threshold proposed by Chamberlain 1983, so why is OPV not a commercially viable technology? The last decade of research and commercialization attempts have highlighted that the successful commercialisation of OPVs is governed by three key parameters: device efficiency, lifetime and cost (Figure 7). As identified in this review, the OPV research community has primarily been focussed on improving device efficiency with device lifetime becoming increasingly recognised as an important research topic. However, reducing the cost of OPV materials has thus far had much less attention, yet is an equally important scientific challenge that is crucial to the future development of

OPV. Indeed, it is the high cost of materials that is currently holding back scientific research at the large scale, and it is increasingly recognised that advances in the cost and scalability of organic photovoltaic (OPV) active materials are urgently required for the rapid industrial development of printed solar technologies.⁹²

More recent work has highlighted the development of low cost materials for OPV manufacture⁹³ and the importance of understanding how the cost of materials and upscaling material manufacture impacts upon the viability of OPV as an energy generating technology⁹⁴. However, one explanation for the fact that OPV has yet to become a viable commercial product is that R2R equipment is very costly to acquire, and as a consequence reports of large scale R2R processing are limited to very few research groups⁹⁵.

Looking to the future, it is clear that OPV is in the process of emerging from the classic “Valley of Death” commercialization phase with a number of restructured and consolidated companies developing large scale OPV products. Interestingly, those companies that have focused on supplying materials and tools to the research community appear to be those that have survived the “OPV crash” most successfully. Further development of the field requires the community to focus less on delivering ever higher efficiency OPV devices but rather to develop low cost efficient materials and architectures that can be manufactured at scale to deliver on OPV’s promise for a low cost sustainable energy technology.

REFERENCES

1. A.E. Becquerel, *Compt. Rend. Acad. Sci.* 9 (1839) 145.
2. A.E. Becquerel, *Compt. Rend. Acad. Sci.* 9 (1839) 561.
3. W.G. Adams, R.E. Day, *Proc. R. Soc. London* 25 (1876) 113.
4. C.E. Fritts, J. Franklin I., 119 (1885) 221.
5. D.M. Chaplin, C.S. Fuller, G.L. Pearson, U.S. Patent No. US2780765A (05 March, 1954).
6. W. Shockley, H. Queisser, *J. Appl. Phys.*, 32 (1961), 510.
7. K. Yoshikawa, H. Kawasaki, W. Yoshida, T. Irie, K. Konishi, K. Nakano, T. Uto, D. Adachi, M. Kanematsu, H. Uzu, K. Yamamoto, *Nature Energy* 2 (2017) 17032.
8. M.A. Green, Y. Hishikawa, E.D. Dunlop, D.H. Levi, J. Hohl-Ebinger, A.W.Y. Ho-Baillie, *Prog. Photovoltaics, Solar cell efficiency tables (version 54)*, 27 (2019), 565.

9. A. Pochettino, *Acad. Lincei Rend.* 15 (1906) 355.
10. M. Volmer, *Ann. Physik* 40 (1913) 775.
11. D. Kearns, M. Calvin, *J. Chem. Phys.* 29 (1958) 950.
12. C.W. Tang, A.C. Albrecht, *J. Chem. Phys.* 62 (1975) 2139.
13. F.R. Fan, L.R. Faulkner, *J. Chem. Phys.* 69 (1978) 3341.
14. G.A. Chamberlain, P.J. Cooney, *Chem. Phys. Lett.* 66 (1979) 88.
15. G.A. Chamberlain, *Solar Cells* 8 (1983) 47.
16. C.W. Tang, *Appl. Phys. Lett.* 48 (1986) 183.
17. S. Kazemzadeh, G. Riazi, R. Ajeian, *ACS Sustainable Chem. Eng.* 5 (2017) 11.
18. S. Duan, C. Dall'Angnese, G. Chen, X.-F. Wang, H. Tamiaki, Y. Yamamoto, T. Ikeuchi, S. Sasaki, *ACS Energy Lett.* 3 (2018) 1708.
19. S.C. Rasmussen in *Handbook of Conducting Polymers*, 4th Ed. (Eds.: J.R. Reynolds, T. Skotheim, B. Thompson), CRC Press: Boca Raton, FL, 2019, pp. 1-35.
20. S.C. Rasmussen, *Substantia* 1 (2017) 99.
21. R. McNeill, R. Siudak, J. H. Wardlaw, D.E. Weiss, *Aust. J. Chem* 16 (1963) 1056.
22. B.A. Bolto, D.E. Weiss, *Aust. J. Chem* 16 (1963) 1076.
23. B.A. Bolto, R. McNeill, D.E. Weiss, *Aust. J. Chem* 16 (1963) 1090.
24. D.J. Berets, D.S. Smith. *Trans. Faraday Soc.* 68 (1968) 823.
25. M. Jozefowicz, L.T. Yu, *Rev. Gen. Electr.* 75 (1966) 1008.
26. L.T. Yu, M. Jozefowicz, *Rev. Gen. Electr.* 75 (1966) 1014.
27. R. De Surville, M. Jozefowicz, L.T. Yu, J. Pepichon, R. Buvet, *Electrochim. Acta.* 13 (1968) 1451.
28. M. Jozefowicz, L.T. Yu, J. Perichon, R. Buvet, *Proprietes Nouvelles des Polymeres Semiconducteurs. J. Polym. Sci., Part C: Polym. Symp.* 22 (1969) 1187.
29. A. Dall'Olio, G. Dascola, V. Varacca, and V. Bocchi. 1968. *C. R. Seances Acad. Sci., Ser. C* 267:433-435.
30. H. Shirakawa, E.J. Louis, A.G. MacDiarmid, C.K. Chiang, A.J. Heeger, *J. Chem. Soc., Chem. Commun.* 16 (1977) 578.
31. G. Yu, C. Zhang, A.J. Heeger, *Appl. Phys. Lett.* 64 (1994) 1540.
32. B.R. Weinburger, M. Akhtar, S.C. Gau, *Synth. Metals* 4 (1982) 187.
33. S. Glenis, G. Tourillon, F. Garnier, *Thin Solid Films* 139 (1986) 221.
34. J. Gilot, M.M. Wienk, R.A.J. Janssen, *Nature Materials* 6 (2007) 704.
35. L.J. Rothberg, M. Yan, S. Son, M.E. Galvin, E.W. Kwock, T.M. Miller, H.E. Katz, R.C. Haddon, F. Papadimitrakopoulos, *Synth. Metals* 78 (1996) 231.
36. L.J. Rothberg, M. Yan, F. Papadimitrakopoulos, M.E. Galvin, E.W. Kwock, T.M. Miller, *Synth. Metals* 80 (1996) 41.
37. J.J.M. Halls, K. Pichler, R.H. Friend, S.C. Moratti, A.B. Holmes, *Appl. Phys. Lett.* 68 (1996) 3120.
38. N.S. Sariciftci, L. Smilowitz, A.J. Heeger, F. Wudl, *Science* 258 (1992), 1474.
39. J.J.M. Halls, C.A. Walsh, N.C. Greenham, E.A. Marseglia, R.H. Friend, S.C. Moratti, A.B. Holmes, *Nature* 376 (1995) 498.
40. J.C. Hummelen, B.W. Knight, F. Lepec, F. Wudl, *J. Org. Chem.* 60, (1995) 532
41. G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, *Science* 270 (1995) 1789.
42. S.E. Shaheen, C.J. Brabec, N.S. Sariciftci, F. Padinger, T. Fromherz, J.C. Hummelen, *Appl. Phys. Lett.* 78 (2001) 841.
43. M.A. Green, K. Emery, *Prog. Photovoltaics* 1 (1993) 25.
44. J. Gilot, M.M. Wienk, R.A.J. Janssen, *Nat. Mater.* 6 (2007) 704.
45. G.P. Smestad, F.C. Krebs, C.M. Lampert, C.G. Granqvist, K.L. Chopra, X. Mathew, H. Takakura, *Sol. Energy Mater. Sol. Cells* 92 (2008) 371.
46. M.O. Reese, S.A. Gevorgyan, M. Jørgensen, E. Bundgaard, S.R. Kurtz, D.S. Ginley, D.C. Olson, M.T. Lloyd, P. Morvillo, E.A. Katz, A. Elschner, O. Hailant, T.R. Currier, V. Shrotriya, M. Hermenau, M. Riede, K.R. Kirov, G. Trimmel, T. Rath, O. Inganäs, F. Zhang, M. Andersson, K. Tvingstedt, M. Lira-Cantu, D. Laird, C. McGuinness, S. Gowrisanker, M. Pannone, M. Xiao, J. Hauch, R. Steim, D.M. DeLongchamp, R. Rösch, H. Hoppe, N. Espinosa, A. Urbina, G. Yaman-Uzunoglu, J.-B. Bonekamp, A.J.J.M. van Breemen, C. Girotto, E. Voroshazi, F.C. Krebs, *Sol. Energy Mater. Sol. Cells* 95 (2011) 1253.
47. H.J. Snaith, *Nat. Photonics* 6 (2012) 337.
48. P. Schilinsky, C. Waldauf, C.J. Brabec, *Appl. Phys. Lett.* 81 (2002) 3885.
49. R.D. McCullough, R.D. Lowe, *J. Chem. Soc., Chem. Commun.* 1 (1992) 70.
50. R.D. McCullough, R.D. Lowe, M. Jayaraman, D.L. Anderson, *Org. Chem.* 58 (1993) 904.
51. R.D. McCullough, S. Tristram-Nagle, S.P. Williams, R.D. Lowe, M.J. Jayaraman, *Am. Chem. Soc.* 115 (1993) 4910.
52. T.A. Chen, R.D. Rieke, *J. Am. Chem. Soc.* 114 (1992) 10087.
53. T.A. Chen, R.A. O'Brien, R.D. Rieke, Rieke, *Macromolecules* 26 (1993) 3462.
54. T.A. Chen, X. Wu, R.D. Rieke, *J. Am. Chem. Soc.* 117 (1995) 23.

55. R.L. Elsenbaumer, K.Y. Jen, R. Oboodi, *Synth. Met.* **15** (1986) 169.
56. W. Ma, C. Yang, X. Gong, K. Lee, A.J. Heeger, *Adv. Funct. Mater.* **15** (2005) 1617.
57. H. Kim, W.-W. So, S.-J. Moon, *Sol. Energy Mater. Sol. Cells* **91** (2007) 581.
58. G. Li, Y.S. Yao, H. Yang, V. Shrotriya, G. Yang, Y. Yang, *Adv. Funct. Mater.* **17** (2007) 1636.
59. M.T. Dang, L. Hirsh, G. Wantz, *Adv. Mater.* **23** (2011) 3602.
60. A.T. Kleinschmidt, S.E. Root, D.J. Lipomi, *J. Mater. Chem. A* **23** (2017) 11396.
61. P.R. Berger, M. Kim, *J. Renew. Sustain. Ener.* **10** (2018) 013508.
62. N.C. Nicolaidis, B.S. Routley, J.L. Holdsworth, W.J. Belcher, X. Zhou, P.C. Dastoor, *J. Phys. Chem C* **115** (2011) 7801.
63. S. Holliday, Y. Li, C.K. Luscombe, *Prog. Polym. Sci.* **70** (2017) 34.
64. J. Roncali, *Chem. Rev.* **97** (1997) 173.
65. H. Sirringhaus, P.J. Brown, R.H. Friend, M.M. Nielsen, K. Bechgaard, B.M.W. Langeveld-Voss, A.J.H. Spiering, R.A.J. Janssen, E.W. Meijer, P. Herwig, D.M. de Leeuw, *Nature*, **410** (1999) 685.
66. C. Soci, I.-W. Hwang, D. Moses, Z. Zhu, D. Waller, R. Gaudiana, C.J. Brabec, A.J. Heeger, *Adv. Funct. Mater.* **17** (2007) 632.
67. R.S. Kularatne, H.D. Magurudeniya, P. Sista, M.C. Biewer, M.C. Stefan, *Polym. Chem.* **51** (2013) 743.
68. L.J.A. Koster, V.D. Mihailetschi, P.W.M. Blom, *Appl. Phys. Lett.*, **88** (2006) 093511.
69. F. Wudl, M. Kobayahi, A.J. Heeger, *J. Org. Chem.* **49** (1984) 3382.
70. H. Hoppe, H.S. Sacriciftci, *J. Mater. Res.* **19** (2004) 1924.
71. S. Rasmussen (2015) Low-Bandgap Polymers. In: Kobayashi S., Müllen K. (eds) *Encyclopedia of Polymeric Nanomaterials*. Springer, Berlin, Heidelberg.
72. S. Aramaki, Solution-processable crystalline organic semiconductors for photovoltaic. MRS 2011 Fall Meeting. Symposium H: *Organic photovoltaic devices and processing*. Boston, USA. Materials Research Society. (2011, December).
73. J. You, L. Dou, K. Yoshimura, T. Kato, K. Ohya, T. Moriarty, K. Emery, C.-C. Chen, J. Gao, G. Li, Y. Yang, *Nat. Commun.* **4** (2013) 1446.
74. Toshiba Global. Retrieved 25 July, 2019; [available online](#).
75. N. Cooling, K.B. Burke, X. Zhou, S.J. Lind, K.C. Gordon, T.W. Jones, P.C. Dastoor, W.J. Belcher, *Sol. Energy Mater. Sol. Cells* **95** (2011) 1767.
76. P.C. Dastoor, C.R. McNeill, H. Frohne, C.J. Foster, B. Dean, C.J. Fell, W.J. Belcher, W.M. Campbell, D.L. Officer, I.M. Blake, P. Thordarson, M.J. Crossley, N.S. Hush, J.R. Reimers, *J. Phys. Chem. C* **111** (2007) 15415.
77. W.J. Belcher, K.I. Wagner, P.C. Dastoor, *Sol. Energy Mater. Sol. Cell*, **91** (2007) 447.
78. K.B. Burke, W.J. Belcher, L. Thomsen, B. Watts, C.R. McNeill, H. Ade, P.C. Dastoor, *Macromolecules* **42** (2009) 3098.
79. N.A. Cooling, X. Zhou, T.A. Sales, S.E. Sauer, S.J. Lind, K.C. Gordon, T.W. Jones, K.B. Burke, P.C. Dastoor, W.J. Belcher, *Sol. Energy Mater. Sol. Cells* **98** (2012) 308.
80. C.J. Brabec, N.S. Sariciftci, J.C. Hummelen, *Adv. Func. Mat.*, **11** (2001) 15.
81. V.D. Mihailetschi, P.W.M. Blom, J.C. Hummelen, M.T. Rispens, *J. Appl. Phys.* **94** (2003) 6849.
82. C. Zhang, S-W. Tong, C-Y. Jiang, E-T. Kang, D.S.H. Chan, *IEEE transactions of electronic devices*, **57** (2010) 2.
83. M.C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A.J. Heeger, C.J. Brabec *Adv. Mater.*, **18**, (2006) 789.
84. M.D Perez, C.Borek, S.R. Forrest, M.E.Thompson, *JACS* **131**, (2009) 9281.
85. W.J. Potscavage, S. Yoo, B. Kippelen, *Appl. Phys. Lett.*, **93** (2008) 193308.
86. K. Vandewal, K. Tvingstedt, A. Gadisa, O. Inganäs, J.V. Manca. *Nature Mat.*, **8** (2009) 904.
87. G.J.A.H. Wetzelaer, N.J. van der Kaap, J.A. Koster, P.W.M. Blom *Adv. Energy Mater.* **3** (2013) 1130.
88. G. Juška, K. Arlauskas, J. Stuchlik, R. Österbacka, *J. Non-Cryst. Solids* **352** (2006) 1167.
89. D. Credgington, J.R. Durrant *J. Phys. Chem. Lett.* **3** (2012) 1465.
90. C. Deibel, A. Wagenpfahl, V. Dyakonov *Phys. Rev. B* **80** (2009) 075203.
91. R.R. Søndergaard, M. Hösel, F.C. Krebs, *J. Polym. Sci. B: Polym. Phys.*, **51** (2013) 16.
92. M.-E. Ragoussia and T. Torres, *Chem. Commun.*, **2015**, **51**, 3957–3972.
93. N.A. Cooling, E.F. Barnes, F. Almyahi, K. Feron, M.F. Al-Mudhaffer, A. Al-Ahmad, B. Vaughan, T.R. Andersen, M.J. Griffith, A.S. Hart, A.G. Lyons, W.J. Belcher, P.C. Dastoor *J. Mater. Chem. A* **4** (2016) 10274.
94. F. Almyahi, T.R. Andersen, N. Cooling, N.P. Holmes, A. Fahy, M.G. Barr, D. Kilcoyne, W. Belcher, P.C. Dastoor, *Org. Elec.* **52** (2018) 71–78.
95. M.J. Griffith, N.A. Cooling, B. Vaughan, K.M. O'Donnell, M.F. Al-Mudhaffer, A. Al-Ahmad, M. Noori, F. Almyahi, W.J. Belcher, P.C. Dastoor, *Energy Technol.* **3**, (2015) 428.