University of Groningen

Polymer tandem solar cells

Hadipour, Afshin

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2007

Citation for published version (APA):
Hadipour, A. (2007). *Polymer tandem solar cells*. s.n.

Chapter 2
A Review on Tandem (multi-junction) Organic Solar Cells[a]

Abstract

Many methods and device structures have been realized in the last decade for organic tandem or multi-junction solar cells. Because of this great variety a general review of all organic tandem and multi-junction solar cells reported by different groups from 1990 until recent is given. The device structures are divided into three different classes; First, the tandem (or multi-junction) solar cells are mentioned that are based on small organic molecules. The second group is that of hybrid solar cells, in which the sub cells are fabricated from both small weight organic molecules and blend of polymers with PCBM. As final group, the tandem (or multi-junction) solar cells are discussed that are fully based on polymers and PCBM.

2.1   Introduction

In the last decades, solar cells (converting the sunlight into electricity) have attracted much attention as a proper candidate for the main energy source in the future. In order to produce low-cost and large-area solar cells, many new device structures and materials are being developed. For the first time in the 1950s photoconductivity was reported in organic crystals, such as anthracene.[9,45,10,11] The first highly conductive polymer was reported in 1977, chemically doped polyacetylene.[12] Since then, organic molecules and semiconducting polymers are being increasingly used in (opto)electronic devices. In the last years, the use of organic materials as active layer in photovoltaic devices has attracted more and more attention and the total conversion efficiency of those cells has increased rapidly.[26,46,29,47] First, small (low molecular weight) organic molecules[48,49] and later also semi-conducting polymers[28,50] were incorporated into solar cells. In general, illumination of an organic semiconductor leads to the creation of excitons [51] with a binding energy of about 0.4 eV [20,21,22], instead of free charges. The exciton can be separated when it reaches the interface between suited donor (D) and acceptor (A) materials, where the difference in the electron affinities and the ionization potentials between those two (A & D materials) are sufficiently large to overcome the exciton binding energy. The hole and electron are still Coulombically bound across the D/A interface, even though the opposing charges reside in different organic materials. After breaking the Coulomb binding between the electron in the acceptor and the hole in the donor, the electrons and holes are subsequently transported through the acceptor and donor phase, respectively, to the electrodes of the device. However, the low mobility of electrons and holes, together with relatively narrow absorption spectra of the organic materials, lead to a relatively low performance of the organic solar cells. The efficiency typically amounts to 4–5%, which limits them for practical applications. Excellent reviews have appeared in literature regarding these so-called single active layer or mono junction solar cells.[47,52,53,54,55,56] To improve the absorption of the solar radiation by organic solar cells, materials with a broad absorption band have to be designed and produced, or different narrow band absorbers have to be stacked or mixed in

multiple junctions.[49] When two (or more) donor materials with partially non-overlapping absorption spectra are used in a tandem (or multi-junction) solar cell, a broader range of the solar spectrum (whole visible and part of the IR range) can be covered. There are several approaches for organic tandem (multiple) cells reported in the last years, depending on the materials used for the active layer and the proper separation or recombination layer(s). All layers can be different in each architecture or approach. In general, the multiple organic solar cells, reported until today, can be divided in three classes;

A) Tandem (or multi-junction) organic solar cells in which low molecular weight molecules are used for both the bottom (front) and the top (back) cells,

B) Hybrid tandem organic solar cells in which the bottom cell is processed from polymers by solution-processing, while the top cell is made of vacuum-deposited low molecular weight molecules,

C) Fully solution-processed tandem or multi-junction organic solar cells in which both the bottom and the top cells are made of polymers.

An overview of the chemical structures of organic materials presently used in organic tandem and multi-junction solar cells is given in Figure 2.1. Depending on which kinds of materials are being used for the active layers, different separating layers are fabricated and reported. In the following sections, the different types of organic tandem and multi-junction photovoltaic cells are described and recent results obtained by various groups are presented.
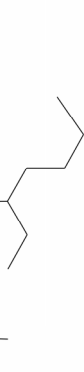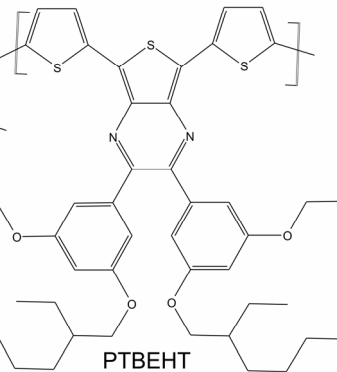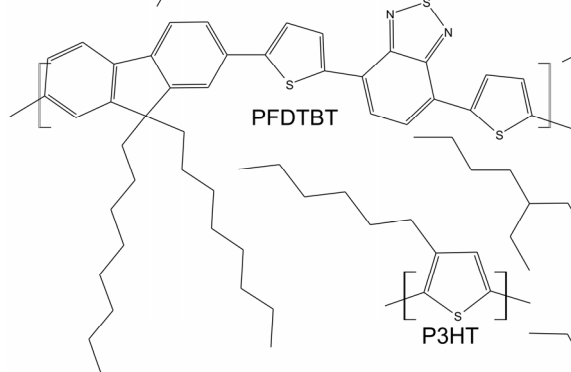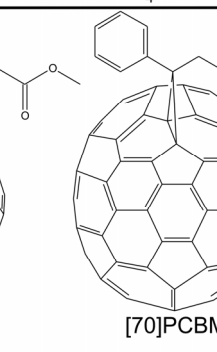
CuPc: M = Cu
ZnPc: M = Zn

PTCBI

Me-PTC

BCP

H₂Pc

m-MTDATA

C₆₀

F₄-TCNQ

MDMO-PPV

MEH-PPV

[60]PCBM

[70]PCBM

PFDTBT

P3HT

PTBEHT
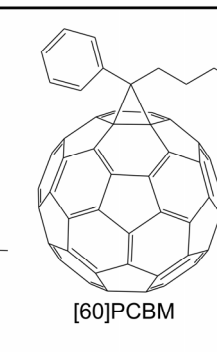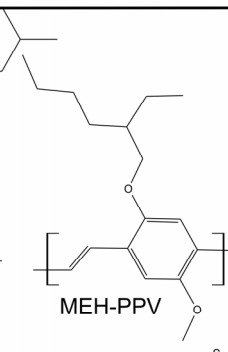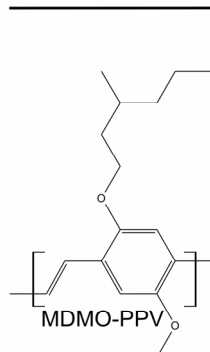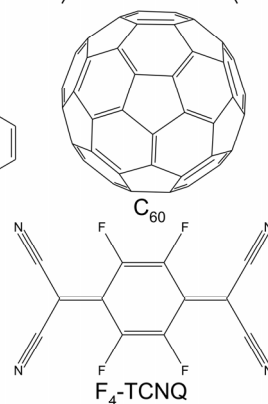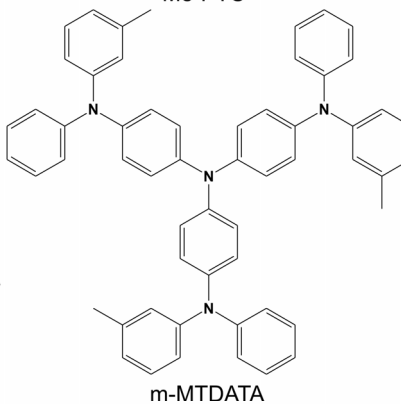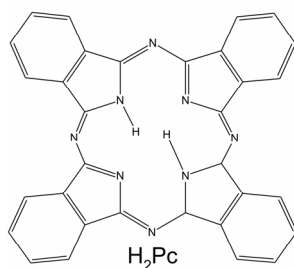
Figure 2.1. The chemical structures of the donor and the acceptor materials used in organic tandem and multi-junction solar cells. The molecules above the solid line are frequently used in multi-junction photovoltaic cells fabricated by vapor deposition, whereas the polymers and molecules depicted below the solid line are used in solution-processed multi-junction solar cells.

2.2   A. Tandem and multilayer organic solar cells based on low molecular weight molecules

The main advantage of using low molecular weight or small molecules for tandem structures is that different layers of donor and acceptor (or mixed layers) materials can be evaporated (or co-evaporated) with sharp interfaces on top of each other, without affecting the already existing layers. A disadvantage of such structures is the relatively low evaporation rate of active materials, which limits the processing speed for large-area applications. The first organic tandem (double junction) cell was realized by Hiramoto, Suezaki and Yokoyama and was constructed from two identical bilayers.[57] Each bilayer consisted of H_2-phthalocyanine (50 nm) and a perylene tetracarboxylic derivative (70 nm), and the two bilayer cells were separated by a thin interstitial layer (2 nm) of Au. This first organic tandem solar cell resulted in almost a doubling of the open-circuit voltage (V_{OC}) to 0.78 V.

Yakimov et al. presented the first multiple-heterojunction solar cells by stacking two, three or five vacuum-deposited ultrathin organic bilayer photovoltaic cells in series.[58] All single thin heterojunction cells[59] (bottom and top cell) were made of Cu-phthalocyanine (CuPc) as   donor and 3,4,9,10 perylenetetracarboxylic bis-benzimidazole (PTCBI) as an acceptor. The device was processed on an indium-tin-oxide (ITO) substrate covered by 30 nm poly(3,4-ethylene dioxythiophene) : polystryrenesulfonic acid (PEDOT:PSS), which served as anode of th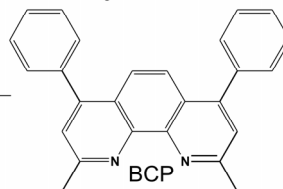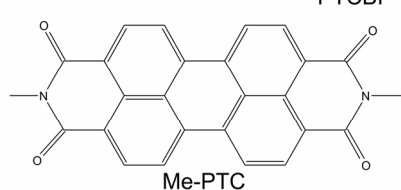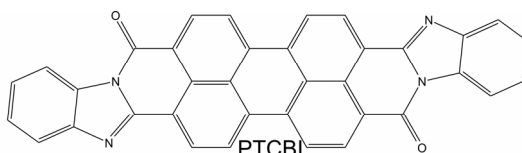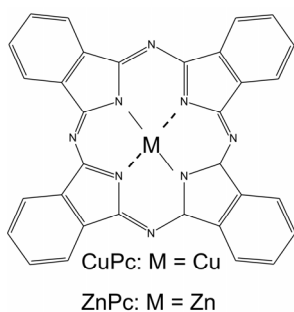e device. The sub cells were deposited by thermal evaporation in vacuum of ~10^{-6} Torr, starting with the donor material (CuPc) and followed by the acceptor material (PTCBI). A thin layer of silver clusters (0.5 nm) was deposited between the two sub cells as recombination layer and finally 80 nm Ag was thermally deposited for the cathode of the device. Generally, the built-in voltage of a single heterojunction cell is given by the difference in the Fermi levels of the donor and the acceptor materials used.[26] This means that for a well-performing tandem cell, consisting of two (or more) series-connected heterojunction single cells, the open-circuit voltage of the tandem cell should be equal to the sum of the built-in voltages of the individual

cells. However, deposition of the sub cells in series without a separation layer in between them will cause the formation of an inverse heterojunction between the donor layer of the top (back) cell and the acceptor of the bottom (front) cell. Yakimov et al. have placed a very thin and discontinuous layer of silver (0.5 nm Ag) between each sub cell. The Ag clusters then serve as charge recombination sites. The electrons and the holes arriving from the bottom and the top cell, respectively, can recombine at this separating layer. The structure of the small molecule tandem cell is shown in Figure 2.2.
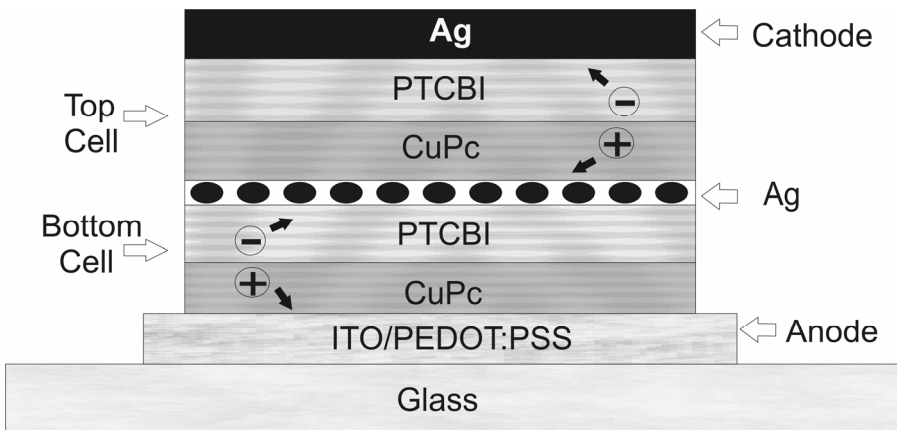
Figure 2.2. The structure of an organic tandem solar cell based on the small molecules CuPc (donor) and PTCBI (acceptor) as described in ref. [58]. The 0.5 nm Ag separation layer provides recombination sites for the free charges arriving from the bottom and top cell.

After absorption of the incident light in such a structure, excitons are created in both the donor (D) and acceptor (A) material. Only excitons that are created very close (in range of the exciton diffusion length, ~10 nm)[60] to the D/A interface can be separated into charges. Then, the electrons and the holes travel through the acceptor (PTCBI) and donor (CuPc) layers, respectively, to the contacts of the device. The holes of the bottom cell and the electrons of the top cell are extracted from the device, whereas the electrons of the bottom cell recombine with the holes of the top cell at the metallic interlayer (Ag nanoclusters). It was demonstrated that for a thickness of about 11 nm for the donor and also 11 nm for the acceptor layer (22 nm heterojunction) the open-circuit voltage (V_{OC}) and short-circuit current (J_{SC})

are maximized.[58] The V_{OC} and J_{SC} of tandem cells with two stacked sub cells and varying thickness for the metallic interlayer (Ag) are summarized in Table 2.1.

Ag thickness [nm]	0	0.5	1.5	3
V_{OC} [Volt]	0.45	0.9	0.9	0.9
J_{SC} [A/m^2]	26	63	52	39

Table 2.1. Data extracted from reference [58]: For a Ag interlayer with a thickness of 0.5 nm, the tandem cell has the highest V_{OC} and J_{SC}. For a thinner Ag interlayer, both open-circuit voltage and short-circuit current drop. For a thicker Ag interlayer the V_{OC} has the same values while J_{SC} drops.

As the data in Table 2.1 show, the use of a thicker Ag interlayer leads to a much lower photocurrent, while the V_{OC} is the same. The high absorption coefficient of the silver interlayer leads to a reduction of the light intensity at the top cell and therefore the top cell generates a lower current for a thicker Ag interlayer. The sub cells were connected in series, meaning that the current of the tandem cell is limited by the lower current of the two sub cells, which is the top cell. With the same donor and acceptor materials, Yakimov et al. demonstrated also triple and fivefold heterojunction solar cells measured at different light intensities. A summary of their results of V_{OC} and power conversion efficiency (η) of different cells under 1 and 10 sun illumination is given in Table 2.2.

Stack cells:	V_{OC} [volt] (1 sun)	V_{OC} [volt] (10 sun)	η [%] (1 sun)	η [%] (10 sun)
Single cell	0.45	0.43	1.0	0.5
Tandem cell	0.90	0.90	2.5	1.8
Triple cell	1.20	1.40	2.3	2.6
Fivefold cell	1.23	1.70	1.0	1.4

Table 2.2. The open-circuit voltage (V_{OC}) and power conversion efficiency (η) of single and multilayer cells under different light intensities are extracted from reference [58]. Under 1 sun illumination condition, the dual structure (tandem cell) has the best performance. At higher light intensity of 10 sun, the triple cell reaches the highest efficiency.

In order to explain the results mentioned above we have to note that the total current extracted from the tandem structure is directly dependent on how efficient charges can recombine at the metallic interlayer (0.5 nm Ag). All sub cells have to generate the same amount of photocurrent (current matching), since they are connected in series. If one of the individual cells generates much more current than the other(s), charges will pile-up at the very thin Ag interlayer such that the effective bias of the sub cells will be far off from their best performance. In addition, in a single bilayer heterojunction cell the excitons must be generated sufficiently close to the D/A interface in the range of L_D ~10 nm [60] such that exciton dissociation can take place. Therefore, the performance of organic bilayer devices is limited by their exciton diffusion length (L_D ~10 nm), which is much shorter than the thickness needed to absorb all incident light (L_A ~150 nm). Stacking of cells in a tandem structure is the way to overcome this limitation. A problem that remains when three or five identical cells are stacked is that under 1 sun illumination the absorption of light by the first two sub cells leads to a reduction of the photocurrent of the following cells, limiting the total current extracted from the whole device. At higher light intensity (10 sun),

the triple cell (instead of the tandem cell) shows the maximum efficiency, but again the light intensity is decreased for the following sub cells limiting the performance of the complete 5 layer (penta junction) device. Similar experiments using CuPc and PTCBI in combination with ultrathin Ag and Au interlayer were performed by Triyana and co-workers to produce tandem and triple junction solar cells.[61]

To improve the efficiency of stacked solar cells, Xue and Forrest applied several modifications to the structure of the device mentioned above.[62] First, they used C_{60} as acceptor since it has a longer exciton diffusion length of $L_D \sim 40$ nm as compared to the previous acceptor PTCBI.[49] Secondly, they incorporated a mixed donor-acceptor layer (bulk heterojunction) sandwiched between pure donor and pure acceptor layers. The homogenous layers of C_{60} and PTCBI serve as electron transport layer (ETL) and hole transport layer (HTL), respectively. The device is called hybrid planar-mixed heterojunction (PM-HJ) device.[62,63] Instead of a very thin Ag interlayer for the recombination sites (separating layer between two sub cells), they used Ag nanoclusters with a typical thickness of 0.5 nm but buried in a 5 nm thick $4,4^{'},4^{''}$-tris(3-methyl-phenyl-phenyl-amino)triphenylamine (m-MTDATA), which was p-doped with 5 mol % tetrafluoro-tetracyano-quinodimethane (F_4-TCNQ).[62] The reason for using an additional layer of p-doped m-MTDATA is not explained by the authors. Clearly, advantages are found when using doped transport layers namely:[64,65] doping of this interlayer increasing the conductivity of this layer and reduces Ohmic losses, quenching processes at the electrode are avoided since excitons created in the active layer cannot enter the wide-gap transport layer, the thickness of the highly conductive interlayer can be tuned to optimize the optical field distribution in the solar cell, and the increase in overall thickness of the devices allows higher stability and a lower probability for short circuiting the device. It has to be noted that silver particles also serve as scattering centers for incident light. The scattering of light in the middle of the device improves the optical absorption of the active layers of the sub cells. Finally, thin layers of bathocuproine (BCP)[59] and (PTCBI) are used as the exciton-blocking layer (EBL) in the top (back) sub cell and bottom (front) sub cell, respectively. The structure of the whole device is depicted in Figure 2.3.
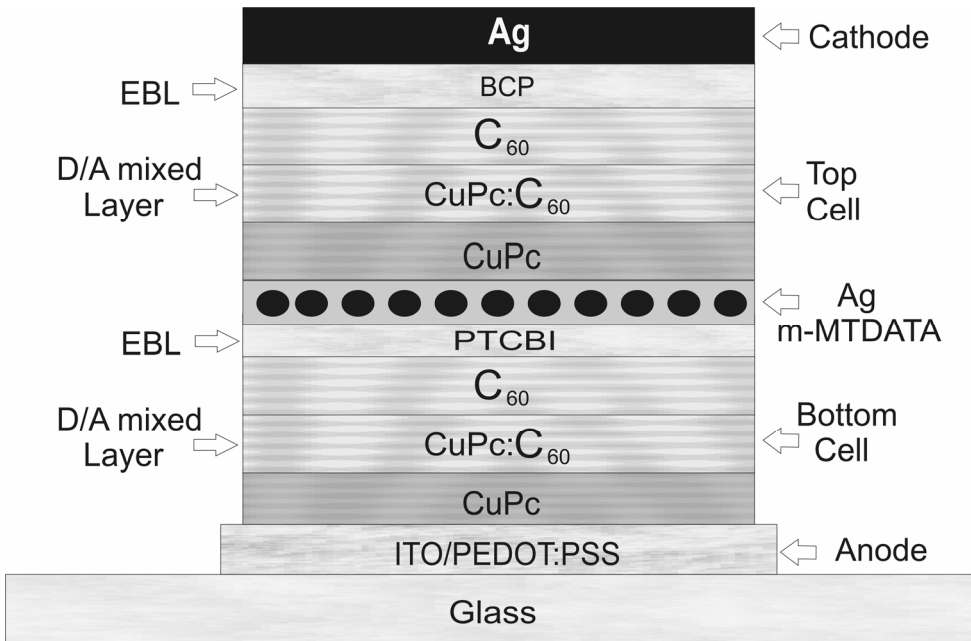
Figure 2.3. The complete stacked structure of PM-HJ tandem organic solar cell as described in reference [62].

The exciton blocking layers (EBL) serve in three different ways:

(a) for the top cell it prevents damage of the active layer caused by evaporation of a (hot) metallic cathode (hot Ag particles),

(b) it eliminates diffusion of Ag particles, which act as exciton quenching sites, into the active layer,

(c) the EBL layers provide an optical spacer between the active layer and the reflecting cathode of each sub cell.

In this way, the light intensity can be tuned to be maximized at the D/A interface (or at the mixed donor-acceptor layer), which leads to an improved optical absorption in these devices. Because of the low thicknesses of the active layers (limited by the short exciton diffusion length) optical interference between the transmitted light through the active layer of the device and the reflected light at cathode of the device has a significant effect on the total absorption of each sub cell. By using different

thicknesses for the active layers, the optical profiles can be tuned inside the device. The donor material CuPc absorbs incident light between 550 nm and 750 nm wavelengths, while the acceptor material C_{60} has very high absorption between 300 nm and 400 nm and relatively lower absorption between 400 nm and 600 nm with a maximum at 550 nm. Using a thicker homogeneous CuPc layer and thinner homogeneous C_{60} layer in the bottom cell as compared to the top cell (keeping the thickness of mixed donor-acceptor layer fixed), the absorption of the bottom cell is shifted to longer-wavelengths relatively to the absorption of the top cell. Such an asymmetric absorption of both sub cells leads to an improved spectral overlap with the sunlight. For current matching, the thicknesses of the homogeneous layers of CuPc and C_{60} and mixed layers have to be further optimized. It is also important to realize that molecular intermixing (mixed layer of each sub cell) leads to significantly lower charge carrier mobilities compared to those in polycrystalline homogeneous layers (CuPc and C_{60} layers), whereas the exciton separation efficiency is much higher in the mixed layer as compared to pure CuPc or C_{60} layers. The power conversion efficiencies of PM-HJ tandem cells using different thicknesses for the active regions are summarized in Table 2.3. All thicknesses are in nm beginning with the bottom cell followed by the top cell.

Cell	CuPc	CuPc:C_{60}	C_{60}	PTCBI	CuPc	CuPc:C_{60}	C_{60}	BCP	η [%]
1	10	18	2	5	2	13	25	7.5	5.4
2	7.5	12.5	8	5	6	13	16	7.5	5.7
3	9	11	0	5	5	10	21	10	5.0

Table 2.3. Layer thicknesses in nanometers and efficiencies (%) of various PM-HJ tandem organic solar cells from reference [62]. The effect of thickness variations for the active layers is shown. Cell 2 has the best performance because the thicknesses used are the best tradeoff between the electrical and optical properties.

2.3 B. Hybrid tandem organic solar cell

In order to improve the optical absorption of a single organic solar cell Dennler et al. have stacked a solar cell made of the small molecules zinc phthalocyanine:C_{60} (ZnPc:C_{60}) on top of a heterojunction polymer solar cell based on a mixed layer of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM).[66] For the two sub cells two different classes of materials (low molecular weight molecules and polymer) were used, which require different processing techniques, namely vapor deposition and spin coating. Therefore, this structure is called a hybrid tandem organic solar cell. The tandem cell was processed onto indium-tin-oxide (ITO) coated glass covered by a 90 nm thick layer of PEDOT:PSS. A layer (clusters) of 1 nm gold (Au) was used as intermediate layer between the two sub cells, which served as a recombination center. The P3HT polymer was dissolved in chlorobenzene and PCBM was dissolved in dichloromethane. The layer of P3HT was spin coated first followed by spin coating of the PCBM layer. This structure is called a diffused bilayer[66] or stratified bilayer.[67] The rest of the device was processed by thermal evaporation under vacuum (10^{-6} mbar). First, 10 nm C_{60} was evaporated serving as electron transport layer (ETL) for the bottom cell. Then, 1 nm Au was evaporated to enhance the recombination of hole and electrons from the top and bottom cell, respectively. The top cell was subsequently fabricated by thermal evaporation of 10 nm of zinc phthalocyanine (ZnPc), 40 nm of a mixture of ZnPc and C_{60} and 15 nm of C_{60}. The device was completed by evaporation of 5 nm of chromium (Cr) and 95 nm of aluminum (Al), which acts as the cathode of the device. In this way, the bottom cell was not affected or damaged during the processing of the top cell. The structure of the device is shown in Figure 2.4.
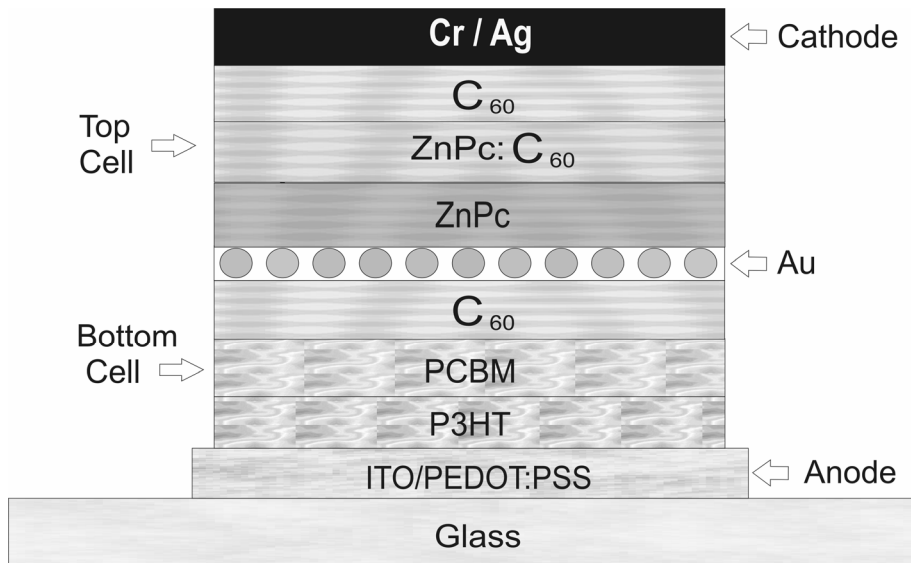
Figure 2.4. The structure of a hybrid tandem organic solar cell. The top cell, made of small molecules, is evaporated on top of the bottom cell based on a diffused bilayer of the conjugated polymer P3HT and the fullerene PCBM, which is processed from solution.

In order to compare the performance of the tandem cell with the single sub cells, Dennler et al. have also processed two reference single cells. They used ITO/P3HT:PCBM/Al processed as diffused bilayer as a reference for the bottom cell and ITO/ZnPc/ZnPc:C_{60}/C_{60}/Cr/Al as a reference for the top cell. The bottom cell has its main absorption between 375 and 630 nm, while the top cell mainly absorbs in the range of 600 to 800 nm. As a result, the tandem cell covers the whole visible range of the solar spectrum (from 400 to 800 nm). The measured performances of the tandem device and reference sub cells under 1 sun simulated light are summarized in Table 2.4.

Cell	J_{SC} [A/m^2]	V_{OC} [volt]	FF [%]	η [%]
Ref. bottom	85	0.55	55	2.6
Ref. top	93	0.47	50	2.2
Tandem	48	1.02	45	2.3

Table 2.4. Performance of the hybrid tandem organic solar cell [66]. The performance of the tandem cell is compared with the reference bottom and the reference top cells.

The results in Table 2.4 confirm the successful coupling of the two sub cells in series using the 1 nm Au recombination layer, since the V_{OC} of the tandem cell was equal to the sum of the V_{OC} of the bottom and the top cell. However, the performance of the tandem cell was limited by the lower photocurrent and fill factor (FF) extracted from the device. The thicknesses of the active layers of the sub cells were not yet optimized. Also the photocurrent of the tandem, reference bottom and reference top cells were measured under monochromatic light as a function of wavelength. By using monochromatic incident light the J–V characteristics of each individual sub cell can be measured and compared with the performance of the tandem cell, as summarized in Table 2.5.

Cell	J_{SC} [mA/W] λ = 500 nm	J_{SC} [mA/W] λ = 600 nm	J_{SC} [mA/W] λ = 700 nm
Ref. bottom	138	120	10
Ref. top	32	100	110
Tandem cell	8	51	2

Table 2.5. The J_{SC} of the tandem cell, reference bottom and reference top cell measured under monochromatic light with different wavelength [66].

Table 2.5 demonstrates that the tandem cell is only efficient when both sub cells perform properly. If one of the individual cells generates a low current, the current extracted from the tandem device is limited due to the series connection. As mentioned above, the main advantage of hybrid tandem organic solar cells is the absence of solvents for the processing of the top cell since the top cell has to be vapor deposited. However, using both processing methods may lead to higher costs of producing tandem (multiple) solar cells for commercial applications.

2.4   C. Solution-processed tandem organic solar cells

Semiconducting polymers are appropriate materials for developing low-cost technologies for large-area solar cells, since polymers can be deposited from solution using simple methods as spin coating and ink-jet printing.[7,8] The main problem to fabricate polymer tandem cells is the stack integrity: deposition of the top cell might dissolve or damage the earlier deposited bottom cell, especially when similar solvents as chlorobenzene and chloroform are used. Therefore, a separating layer (middle contact) is required that has to be thick enough (a closed layer) to protect the bottom cell from dissolving during spin coating (processing) of the top cell. At the same time, the middle contact has to be as transparent as possible to transmit light efficiently to the top cell. In order to overcome the stack integrity problem different structures and methods have been reported recently. In Chapter 3 the first solution-processed polymer tandem solar cell is reported in which sub cells have different optical absorption properties. In Chapter 4 a 4-electrode polymer tandem solar cell is considered using an optical spacer, which is the only 4-electrode structure reported until today. Recent alternative approaches to solution processed organic tandem cells are discussed in the following sections.

2.4.1   Tandem organic solar cell processed on separated substrates

One of the methods to overcome the processing difficulties was reported by Shrotriya et al..[68] Two identical bulk heterojunction single cells were fabricated onto different glass substrates and then positioned on top of each other. The sub cells were connected in series or in parallel outside the device. The bottom cell has a semitransparent cathode consisting of 1 nm thick lithium fluoride (LiF), 2.5 nm aluminum (Al) and 12.5 nm gold (Au) with a maximum transparency of about 74 % at 580 nm. Both sub cells were fabricated from a blend of poly(2-methoxy-5-(2′-ethyl)-hexyloxy)-1,4-phenylene vinylene (MEH-PPV) and PCBM with a 1:4 weight ratio. The thickness of the active layer of both the bottom and the top cell was about 70 nm. For PPV-based solar cells it is known that an increase of the active layer thickness does lead to an increased absorption, but not to an increased performance [69]. The absorption increase is cancelled by increased space-charge formation and recombination. Using two thin identical active layers for both sub cells is an attempt to effectively increase the absorption while maintaining the favorable electrical properties of thin devices. However, the coverage of the solar spectrum was not improved. The structure of the device from reference [68] is given in Figure 2.5. Furthermore, various semitransparent cathodes have been investigated. The highest transparency and best performance was obtained with the above-mentioned LiF/Al/Au cathode. Finally, it should be noted that the efficiency of ~2.5% of both the parallel and series tandem cell is equal to the efficiency of a single layer device with a thickness of 140 nm. Apparently, the coupling of two identical thin cells did not bring advantage as compared to a single cell with the same total active layer thickness. Shrotriya et al. have connected the sub cells in series and in parallel. They have compared the performance of the bottom, the top and the connected devices (series and parallel) under 1 sun simulated solar light. A summary of their results is given in Table 2.6.
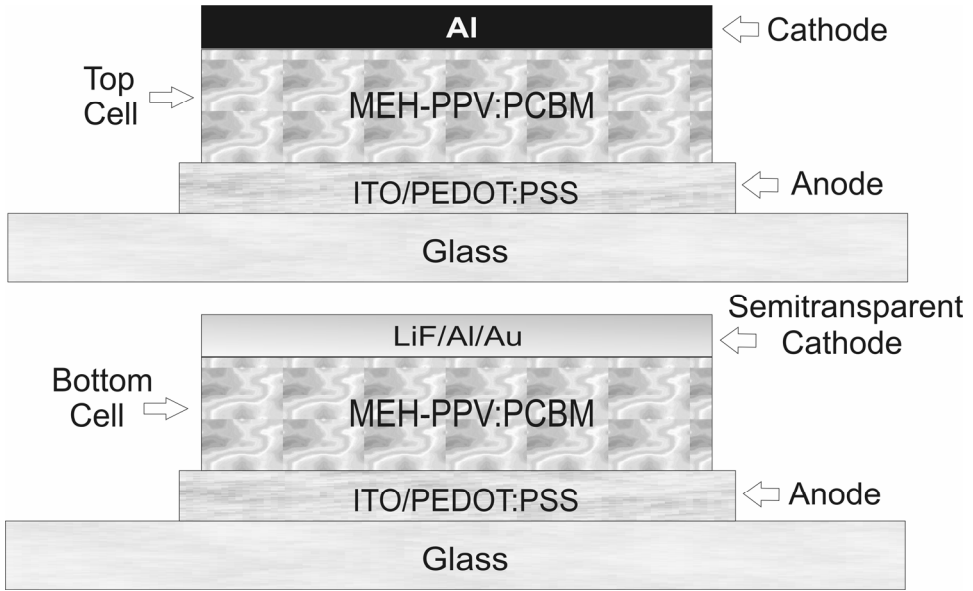
Figure 2.5. The separated sub cells positioned on top of each other as described in Ref [68]. The bottom cell has semitransparent cathode.

Cell	V_{OC} [Volt]	J_{SC} [A/m^2]	FF [%]	η [%]
Bottom	0.86	26	45	1.1
Top	0.86	32	45	1.3
Series connected	1.64	34	45	2.4
Parallel connected	0.84	63	45	2.5

Table 2.6. Performance of stacked organic solar sell processed on separated substrates [68]. For the measurements of the devices connected in series and in parallel, the bottom cell was positioned in front of the top cell, allowing the light to transmit through the bottom cell before reaching the active layer of the top cell.

2.4.2   Tandem organic solar cell with ITO as separating layer

Another polymer based tandem cell is recently reported by Kawano et al.. Two bulk heterojunction solar cells were electronically coupled with a interlayer of indium-tin-oxide (ITO)[70]. The stacked bulk heterojunction solar cells were both based on a 80 nm blend of poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV) and PCBM (1:4 weight ratio). As the separating layer, Kawano et al. deposited ITO by dc magnetron sputtering in 1 Pa of argon gas without substrate heating. The presence of argon gas into the deposition chamber prevented damaging of the active layer of the bottom cell during deposition of the ITO layer. The full structure of the device is given in Figure 2.6.
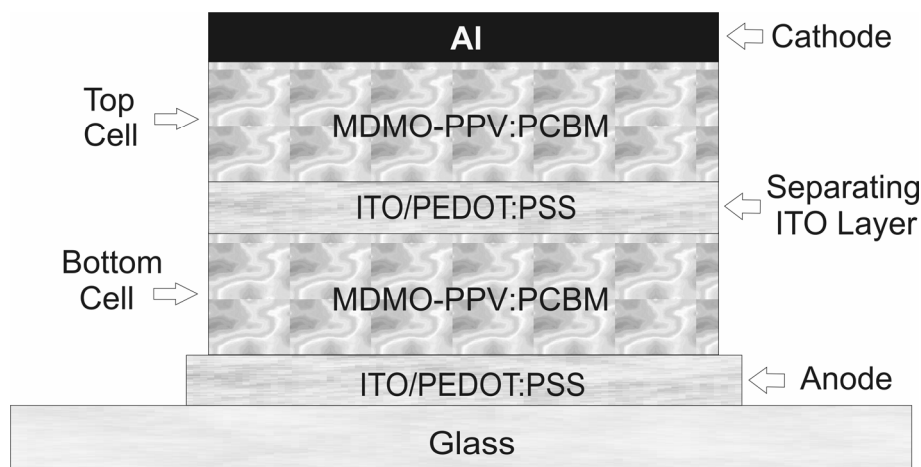
Figure 2.6. The structure of tandem cell as fabricated in Ref [70] is shown. A layer of transparent ITO separates the two sub cells.

The most important aspect of this report is the method used to sputter the ITO onto the polymer surface without damaging it. The very high transparency of the ITO layer enhances the light intensity reaching the top cell resulting in an increased photocurrent of the top cell. A summary of the results achieved by the authors using a 20 nm ITO interlayer is given in Table 2.7.

Cell	V_{OC} [Volt]	J_{SC} [A/m^2]	FF [%]	η [%]
Reference	0.84	46	59	2.3
Tandem	1.34	41	56	3.1

Table 2.7. Performance of a tandem organic solar cell with 20 nm ITO as separating layer [70] is demonstrated. The performance of the tandem cell is compared to a reference BHJ single cell (using a ITO/PEDOT/80 nm MDMO-PPV:PCBM/Al structure).

As the data of Table 2.7 demonstrate, connection of the two sub cells in series leads in this case to a V_{OC} of 1.6 times higher than the reference cell, instead of the double value. The reason is that the high work function of ITO (~ 4.8–5.0 eV) limits the maximum V_{OC} of the bottom cell.[43,44] Thus, the absence of an Ohmic contact for electron extraction at the interface between the separating layer and the active layer of the bottom cell (LUMO of the PCBM in the blend) leads to a decrease of the V_{OC} of the bottom cell from 0.84 V (normal value when using an Ohmic contact) to 0.48 V, leading to a V_{OC} of the tandem cell of 1.34 Volt. Since in this study the same donor material (MDMO-PPV) was used for both sub cells the narrow absorption of the active layer was not improved. However, optimizing this structure using a transparent, low work function, metallic layer between the bottom cell and the ITO interlayer, in combination with donor materials with partially non-overlapping absorption band can lead to the fabrication of highly efficient tandem cells.

2.4.3   Multiple organic solar cell with solution-processed ZnO interlayer

One of the latest approaches to solution-processed organic tandem solar cell was reported by Gilot, Wienk and Janssen in which a solution-processed middle electrode (separating layer) was introduced.[71] These kinds of electrodes demonstrate the possibility to realize fully solution-processed solar cells (tandem or multiple cells) without using vapor-deposited contacts. For the fabrication of the

separating layer, ZnO nanoparticles were prepared,[72,73] dissolved in acetone, and spin coated. In order to create a high work function anode neutral pH PEDOT (ORGACON, pH = 7, 1.2 w%, Agfa Gevaert NV) was spin coated from a water-based suspension. The normal acidic PEDOT:PSS can not be used since the ZnO layer dissolves in an acidic solution. The ZnO layer serves as electron transporting layer (ETL), while the neutral PEDOT acts as hole transporting layer (HTL). The active layers were fabricated from a chlorobenzene solution of the donor materials MDMO-PPV or P3HT mixed with the acceptor material PCBM in a 1:4 and 1:1 ratio, respectively. The thicknesses of the active layers were 45 nm and 85 nm for the bottom and top cell of the tandem junction, and 45 nm, 65 nm and 85 nm for the bottom, middle, and top cell of the triple junction. The structure of this tandem device is given in Figure 2.7.
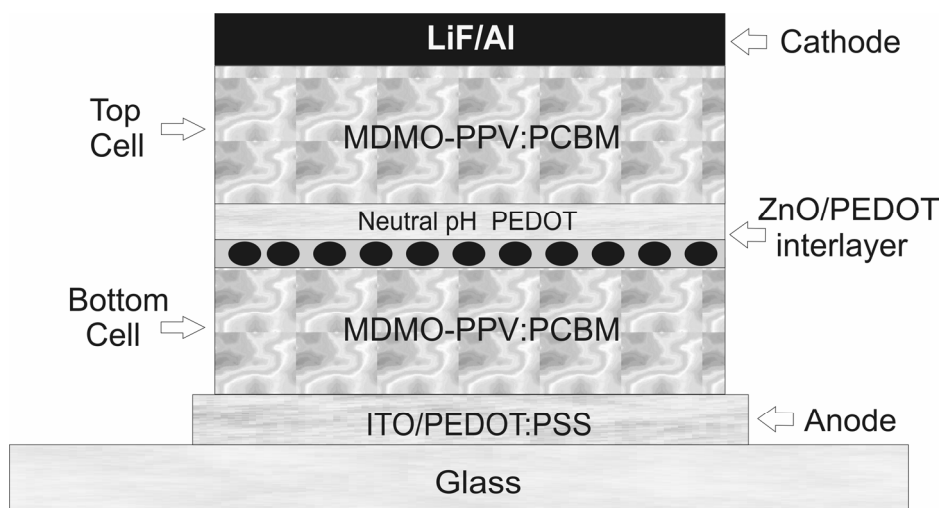

Figure 2.7. Structure of tandem solar cell based on ZnO/PEDOT as separating layer. The MDMO-PPV:PCBM (1:4) layers are 45 nm and 85 nm thick for the bottom and the top cell, respectively.

The recombination of charges across the interface between ZnO and neutral pH PEDOT is normally very poor, since a large energy offset exists at the interface between them. An Ohmic contact between ZnO and PEDOT is needed to prevent a voltage drop across the interface and allows the holes and the electrons to recombine efficiently. In order to increase the recombination probability, the two

materials have to be sufficiently doped or metallic clusters (0.5 nm Ag or Au) have to be deposited between them. In this study doping methods have been applied: The PEDOT is all p-doped, whereas the doping of the ZnO layer can be reached by exposure the layer to UV light (photo-doping) for a few seconds.[74,75] A summary of their results for tandem and triple solar cells using MDMO-PPV:PCBM for all active layers and photo-doped ZnO/neutral pH PEDOT layer is given in Table 2.8.

Cell	V_{OC} [Volt]	J_{SC} [A/m^2]	FF [%]
Single Cell	0.82	49	57
Tandem Cell	1.53	30	40
Triple Cell	1.92	24	33

Table 2.8. Performance of multi-junction organic solar cell with a solution-processed interlayer as taken from reference [71]. The tandem cell has a 45 nm active layer for the bottom and 85 nm layer for the top cell. The triple cell is based on 45 nm, 65 nm and 85 nm active layers for the bottom, the middle and the top cell, respectively.

As the data of Table 2.8 demonstrate, the V_{OC} of the multi-junction solar cells connected in series are slightly lower than the sum of the V_{OC}'s of the individual sub cells. The deviation of the V_{OC} from estimated values (two or three times the V_{OC} of the single cell) is probably caused by a small voltage drop at the interface between the ZnO and neutral pH PEDOT. The very high transparency of the ZnO/PEDOT interlayer in combination with the possibility to fabricate the whole multi-junction solar cell from solution makes this approach very useful and practical for future applications.

2.4.4 Tandem organic solar cell with solution-processed TiO$_x$ interlayer

The most recent and efficient tandem organic solar cell based on solution processing was reported by Kim et al.[76] In this tandem cell a highly transparent titanium oxide (TiO$_x$) layer was used to separate the two sub cells of the tandem device. This transparent middle electrode demonstrates the possibility to realize fully solution-processed solar cells (tandem or multiple cells) without using vapor-deposited contacts. The advantages of using oxides such as the above-mentioned ZnO or TiO$_x$ for the middle electrode is the optical transparency of the layer and the orthogonally compatible solvents used for processing all layers. In these cases, the separating layer does not significantly affect the light intensity. The increased light intensity at the top cell leads to a higher photocurrent generated by the top cell. Therefore, the efficiency of the tandem device is not limited any more by the lower current of the top cell as observed for tandem structures with a metallic interlayer. The cell was processed onto a glass/ITO substrate covered by a 40 nm thick layer of PEDOT:PSS (Baytron P). The transparent TiO$_x$ interlayer was fabricated by spin coating from methanol solution by means of sol-gel chemistry.[77] For the bottom BHJ cell a 130 nm thick layer of PCPDTBT:PCBM (1:3.6)[78] was used that was processed from chlorobenzene. The top BHJ cell was fabricated from a 170 nm thick P3HT:PC$_{70}$BM (1:0.7) blend, which was processed from chloroform. The two sub cells have complementary absorption spectra, which leads to coverage of the whole visible and part of the infrared of solar spectrum by the tandem device. On top of the TiO$_x$ interlayer layer, the highly conductive hole transport layer poly(3,4-ethylene dioxythiophene) : polystryrenesulfonic acid (PEDOT:PSS, Baytron PH500) was spin coated. The structure of the device is given in Figure 2.8.
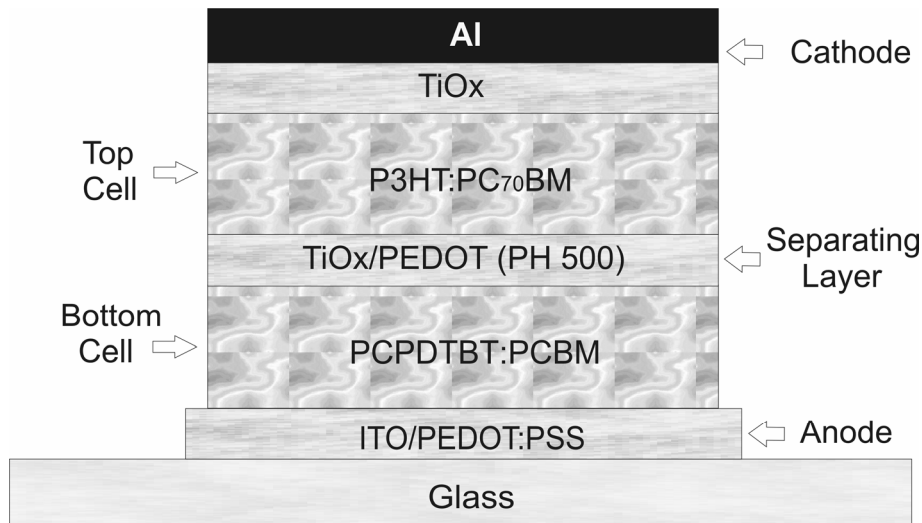
Figure 2.8. The structure of the tandem device from reference [76]. The two sub cells are separated by a highly transparent layer of TiO_x covered by the highly conductive PEDOT:PSS (PH 500).

The performance of the above-mentioned tandem device in the dark and under illumination with different light intensities was measured and the results of these measurements are summarized in Table 2.9.

Light intensity [W/m^2]	200	500	1000	2000
FF [%]	0.68	0.67	0.66	0.64
J_{SC} [A/m^2]	24	38	75	150
V_{OC} [volt]	1.15	1.2	1.25	1.28
η [%]	6.7	6.5	6.3	6.2

Table 2.9. The data extracted from reference [76]. An optimum tandem solar cell is measured under different light intensities.

As listed in Table 2.9, this all-solution processed tandem cell has the highest efficiency reported until now of all tandem organic solar cells. The power-conversion efficiency reaches more than 6 % at intensities above 200 milliwatts per

square centimeter. The main reasons for the high efficiency in this series tandem cell is the relatively high photocurrent of both the sub cells due to the transparent separating interlayer.

2.5 Summary

In order to achieve organic solar cells with higher performance, the narrowness of the optical absorption of the active layer has to be improved. By using two (or more) donor materials with partially non-overlapping absorption spectra in a tandem or multi-junction structure, the whole visible range of the solar light can be absorbed and even extended into the near IR. In addition to covering a larger part of the spectrum, tandem solar cells offer the distinct advantage that the photon energy is used more efficiently, because the voltage at which charges are collected in each sub cell is closer to the energy of the photons absorbed in that cell. In the various tandem structures the layer that separates both sub cells plays a very important role. The final efficiency of the tandem cell depends directly on the electrical (Ohmic contact and proper conductivity) and optical (transparency) properties of this middle electrode. In the series configuration, the middle contact serves as recombination site only and therefore does not have to be highly conductive. In the parallel configuration, the sheet-conductivity has to be high since the contact is also used to extract the charges from the device. This overview demonstrates that recently developed multi-junction photovoltaic cells with optimized materials and thicknesses lead eventually to higher efficiencies as compared to single layer solar cells. Recently, power-conversion efficiencies of more than 6 % have been reported using solution-processed organic bulk heterojunction tandem solar cells. The realization of working organic tandem and multi-junction photovoltaic cells is an important step forward to the improvement and finally commercialization of large-area organic solar cells.