

POLYMER BASED PHOTOVOLTAICS: NOVEL CONCEPTS, MATERIALS AND STATE-OF-THE ART EFFICIENCIES

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ABSTRACT: A summary is given of the multidisciplinary research efforts in the Netherlands in the field of polymer-based photovoltaics (PV) between 1997 and 2005. It has been shown that different types of bulk heterojunctions namely *polymer:fullerene*, *polymer:polymer* and *polymer:metal-oxide* cells can be made in a laboratory environment with relatively simple and new low temperature deposition techniques using conjugated polymers as the primary absorber. State-of-the art efficiencies have been achieved for all polymer based solar cell concepts.

Keywords: Fundamentals, Organic Solar Cells, Polymer film

1 INTRODUCTION

In the past decade, there is a growing interest for new generations of PV technologies and conversion concepts aiming at either very low cost or very high efficiency or a combination of both. It has been recognized that organic based PV can be considered as such a high risk-high potential option since it has many attractive features like:

- Flexibility and light weight
- Semi-transparency
- Low-cost fabrication via high-throughput, low temperature printing techniques
- Easy integration in a wide variety of devices
- Tunable properties of organic materials
- It may profit from experiences in the development/commercialization of organic electronics like Light Emitting Displays (LEDs) and Field Effect Transistors (FETs)

A multitude of device concepts have been investigated to date like liquid and solid state versions of the dye sensitized oxide solar cells, molecular as well as polymer organic solar cells [1]. The research focus is on understanding the working principles and improving efficiency and stability, which are all necessary to show the potential of organic based PV for commercial applications.

Semiconducting polymers have shown to be interesting candidates for Light Emitting Displays (LEDs) and Field Effect Transistors (FETs) and PV cells for reasons mentioned above. When applied in PV cells, two properties of semiconducting polymers, i.e. the exciton diffusion length and the absorption coefficient, put stringent constraints on the device structure as will be outlined below. An overview on three types of polymer based PV, namely *polymer:fullerene*, *polymer:polymer* and *polymer:metal-oxide* cells will be presented in this paper. The investigations described in this contribution are the result of an ongoing multidisciplinary research program on polymer based PV in the Netherlands initialized in 1997 and carried out by a consortium of universities, research institutes and industry.

2 THE NEED FOR A BULK HETEROJUNCTION

One of the main differences between inorganic and organic semiconductors (here conjugated polymers) is the magnitude of exciton binding energy. An exciton is defined as an electron-hole pair created upon excitation of the semiconductor across the bandgap. For most inorganic semiconductors, the exciton binding energy is small compared to the thermal energy at room temperature ($kT \sim 25$ meV). Therefore, free charges are generated under ambient conditions. Organic semiconductors, on the other hand, typically have exciton binding energies exceeding kT by more than an order of magnitude. As a consequence, excitons are formed upon excitation instead of free charges. This fundamental difference between inorganic and organic semiconductors is of critical importance for the design of organic based PV devices. Whereas in conventional, inorganic solar cells free charges are created upon light absorption, organic solar cells need an additional mechanism to dissociate the excitons.

A successful method to dissociate excitons in organic semiconductors is at a so-called donor/acceptor heterojunction interface. This interface is formed between two organic semiconductors with dissimilar valence (VB) and conduction bands (CB).

If an exciton is created in the donor and reaches the donor/acceptor interface, the electron will be transferred to the acceptor material and the hole will recede in the donor material (similarly, a hole will be injected in the donor material after excitation of the acceptor material). An exciton created in either the donor or acceptor will reach the interface within its lifetime only if it is created within a slab of material around the interface with a thickness less than the exciton diffusion length, which is limited to about 10 nm for organic semiconductors. Since the absorption coefficient of most of these organic semiconductors is $\sim 10^7$ m⁻¹, a layer of 100-300 nm is required to absorb all the visible light. In order to solve this dilemma, efficient polymer solar cells require a nano-scale interpenetrating bicontinuous network of donor and acceptor materials within the whole photoactive layer to ensure an efficient dissociation of

photogenerated excitons and transport of the charges to the electrodes. This so called bulk heterojunction (BHJ) solar cell is shown schematically in Figure 1.

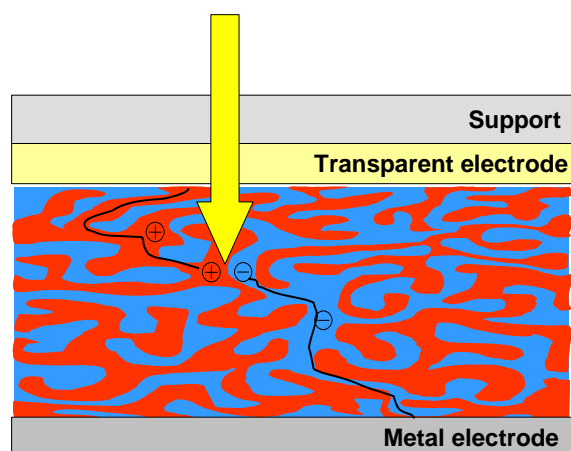


Figure 1. Schematic representation of a BHJ solar cell.

3 RESULTS AND DISCUSSION

3.1 Polymer-Fullerene BHJ

The first proof-of-principle of the BHJ concept was successfully demonstrated by the group of Alan Heeger in 1995 for a blend of a soluble polyphenylenevinylene (PPV) polymer acting as an electron donor and a fullerene derivative (C60-PCBM, see chart 1) as molecular electron acceptor [2]. A PV device based on this material combination showed an estimated efficiency of almost 1 %. This promising result triggered many groups worldwide to start extensive research in this direction with increasing support from industry and public finance.

It was until 2001 that a breakthrough to truly appealing efficiencies of around 2.5 % under simulated AM1.5 illumination was realized on a lab scale for BHJ solar cells using a blend of a slightly different polymer (MDMO-PPV, see chart 1) than originally used by the group of Heeger [3,4] and C60-PCBM. The photoactive composite is sandwiched between two electrodes with different workfunctions: a transparent front electrode

consisting of a transparent conducting oxide (ITO) on a glass or plastic support covered with a conducting polymer, abbreviated as PEDOT for hole collection and a metal back electrode consisting of a very thin (~1nm) layer of LiF covered with Al for electron collection.

One of the crucial parameters in the optimization of the device performance was the creation of a suitable morphology of the photoactive composite facilitating both photoinduced charge generation and transport of the charge carriers to the external electrodes. By tuning the nanomorphology with a number of suited solvents, best devices were obtained for a 1:4 (w:w) blend of MDMO-PPV and C60-PCBM, using chlorobenzene as the solvent for spincoating. This material combination functioned as a workhorse to generate deeper understanding of these BHJ solar cells. Investigations into the morphology, electronic structure and charge transport have provided detailed understanding of the degree and dimensions of the phase separation in the active layer [5], parameters that determine the origin of the open-circuit voltage [6], the influence of electrode materials [7] and the magnitude of electron and hole mobilities [8]. These studies revealed that C60-PCBM has high electron mobility ($\sim 10^{-3}$ cm²/Vs), as compared to many other organic, or polymer materials. It was further shown that, next to morphology, the main origin of the relatively high External Quantum Efficiency (EQE) and obtained efficiencies is the enhancement of the hole mobility in the MDMO-PPV, when blended with C60-PCBM as compared to the pristine polymer [9]. This enhancement results in a better balance of the hole and electron transport, which prevents the built-up of space charge. This allows for fill factors up to 65 % to be reached. These insights have led to the development of a quantitative model describing the PV characteristics under illumination, which serves as a guide for new developments [10]. This device model in combination with morphology studies has firmly established the relation between composition, morphology and solar cell performances.

Although reasonably high EQE's (up to 55 %) could be reached for MDMO-PPV:C60-PCBM devices, the short circuit current densities (J_{sc}) at 1 sun (~ 5 mA/cm²) are still low, limited mainly by a poor match between the absorption spectrum of the photoactive materials and the solar spectrum. An increase of the layer thickness should lead to absorption of more photons but this has not resulted in improved current densities so far due to too

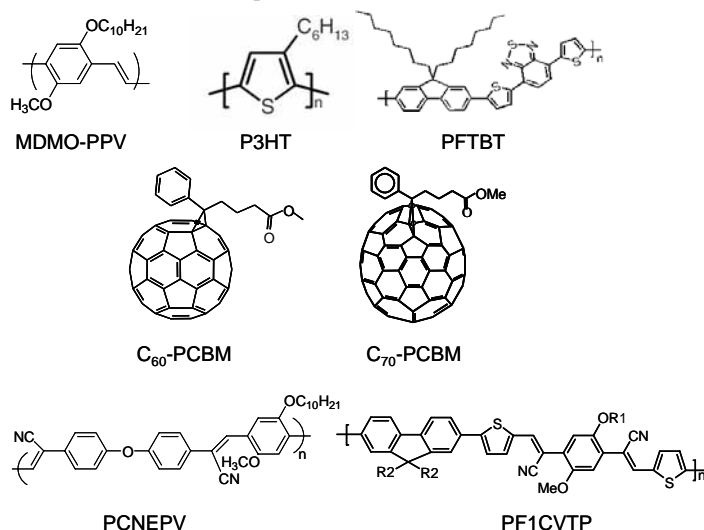


Chart 1. Donor and acceptor materials used in polymer BHJ cells.

low charge carrier mobilities and lifetimes. The strategy is thus to engineer materials with lower energy band gaps and higher charge carrier mobilities.

We first considered modifying the acceptor material. C60-PCBM, which amounts to 75 wt. % of the photoactive layer, but has a very low absorption coefficient in the visible region of the spectrum and, hence, a relatively small contribution to the photocurrent. The low absorption is due to its high degree of symmetry that makes many of the low-energy transitions formally dipole-forbidden. When the C60 moiety is replaced by a less symmetrical fullerene, such as C70, these transitions become allowed and a drastic increase in light absorption is observed. Consequently, when C70-PCBM (see chart 1) instead of C60-PCBM is used in a PV cell in combination with MDMO-PPV, 50 % higher J_{sc} (7.6 mA/cm² compared to 5 mA/cm²) is obtained with a power conversion efficiency measured under standard test conditions of 3.0 % (see figure 2) [11].

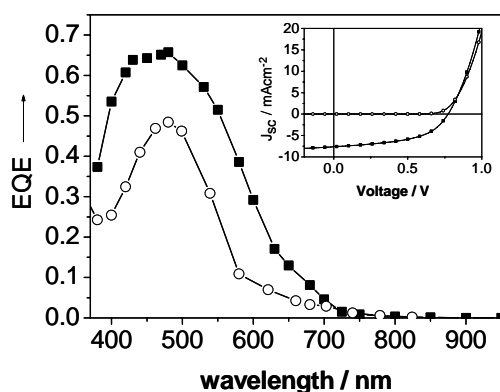


Figure 2. EQE of C70-PCBM/MDMO-PPV cells, spincoated from ortho-dichlorobenzene (closed squares) and C60-PCBM/MDMO-PPV devices spincoated from chlorobenzene (open circles). Inset: Current-Voltage characteristics of C70-PCBM/MDMO-PPV devices, spincoated from ODCB, in the dark (open circles) and under illumination (AM1.5, 100 mW/m², closed squares).

It should be noted that by changing the acceptor material from C60 to C70-PCBM, different processing conditions had to be used to optimize the efficiency. This stresses the importance that for each new material combination, optimal processing conditions should be found to get the desired morphology for maximum device performance.

Another strategy, which is currently followed by many researchers, is the design and preparation of low band gap, high mobility, processable polymers. This is not trivial since application of low band gap materials can lead to a loss in voltage and/or efficiency of charge separation. P3HT (see chart 1), a polythiophene derivative, is known as a semi-crystalline polymer with a higher charge carrier mobility and reduced band gap as compared to MDMO-PPV. Optimized EQE's close to 80 % have been reported for devices based on P3HT and C60-PCBM [12]. This corresponds to a maximum J_{sc} value of around 11 mA/cm² which is significantly larger compared to the maximum J_{sc} values obtained for MDMO-PPV:C60-PCBM devices. However, a simultaneous loss in open circuit voltage (V_{oc}) from 0.87

to 0.6 V leads to a relatively small increase of the power conversion efficiency from 2.5 % up to 4 % under optimized conditions. By more careful positioning of the HOMO and LUMO energy levels of donor and acceptor it should be possible to increase the current density while maintaining a high V_{oc} . In that respect, PFTBT (see chart 1) is a promising material since it has a bandgap comparable to P3HT but gives V_{oc} ~1 V when blended with C60-PCBM due to a favorable energy level alignment [14,15]. The EQE's and fill factors are still too low (<50 %) to reach efficiencies beyond 5 % for this latter combination but further device optimization and modelling should reveal whether this can ever be reached.

A summary of state-of-the art power conversion efficiencies for PV devices based on the aforementioned materials combinations, as obtained in the laboratories of the authors, are listed in Table 1. It should be noted that in other laboratories higher efficiencies between 3 and 4 % were claimed for P3HT:C60-PCBM cells [12,13]

Table 1. Power conversion efficiencies (η (%)) measured under AM1.5 G, 100 mW/cm² at ECN Solar Energy for lab-scale devices with active areas in the range of 0.1-1 cm²

| Donor | Acceptor | I_{sc} mA/cm ² | V_{oc} mV | FF | η (%) |
|--------|----------|--------------------------------|----------------|------|------------|
| MDMOPP | C60PCBM | 4.9 | 870 | 0.60 | 2.5 |
| MDMOPP | C70PCBM | 7.6 | 770 | 0.51 | 3.0 |
| PFTBT | C60PCBM | 6 | 1000 | 0.50 | 3.0 |
| P3HT | C60PCBM | 7.6 | 610 | 0.61 | 2.9 |

Low-band gap polymers ($E_g < 1.8$ eV) have been synthesized to expand the spectral region of BHJ cells up to 900 nm [16]. These polymers, based on alternating electron rich/electron poor moieties, show in combination with C60-PCBM PV activity up to 900 nm but EQE's and subsequently current densities are still too low to increase the power conversion efficiencies beyond the 5% level.

3.2 Polymer: Polymer BHJs

At the same time as the introduction of the BHJ concept based on polymers and fullerenes, the group of Richard Friend reported on a blend of two conjugated donor and acceptor polymers as the photoactive layer in a PV device [17]. However, since this first report, the polymer:polymer BHJ have not attracted as much interest as the polymer:fullerene BHJ. This is quite remarkable since this concept may have certain advantages. In a polymer:polymer blend, both active materials can exhibit a high optical absorption coefficient and could cover complementary parts of the solar spectrum. On the other hand, polymer blends have an intrinsic tendency to phase separate. These phase-separated domains usually have dimensions of several microns and are thus not suitable for polymeric cells. The biggest challenge for this concept is to identify well-conducting n-type polymers, finding a combination in which the two polymers have complementary absorption spectra and the right morphology for efficient charge generation and collection. Our research on polymer:polymer BHJ started in 2001 in the frame of the Dutch Polymer Institute (DPI). We found a polymer blend based on MDMO-PPV

and PCNEPV (see chart 1) in which the typical dimensions of the domains could be tuned by varying the molecular weight of one of the two polymers. In this way, domains are obtained with a radius of ~ 200 nm, 20 nm or molecular dispersed (within the resolution of the electron microscope ~ 5 nm). The PV performance was considerably improved by a thermal treatment (annealing) altering the morphology of the photoactive layer. Device optimization yielded maximum EQE's of 23% at 500 nm and a power conversion efficiency of 0.75% (AM1.5G, 100 mW/cm²) [18]. Further material engineering has recently resulted in the application of a new acceptor polymer, PF1CVTP (see chart 1) in a photoactive blend with MDMO-PPV. With this polymer combination, a maximum EQE of 52 % at 530 nm and a power conversion efficiency of 1.5 % (AM1.5G, 100 mW/cm²) was obtained [19]. Even higher efficiencies up to 3 % were obtained at low incident light levels, mainly due to an increase of the fill factor. The progress in efficiency for polymer:polymer cells in a period of three years is nicely illustrated in figure 3. To our knowledge, the quantum and power conversion efficiencies reported here, are among the highest reported efficiencies for polymer:polymer PV cells.

An important challenge for this concept is design of light absorbing electron accepting polymers with sufficiently high electron mobilities up to a level that is common for fullerenes so that full profit can be made of the high potential of this concept.

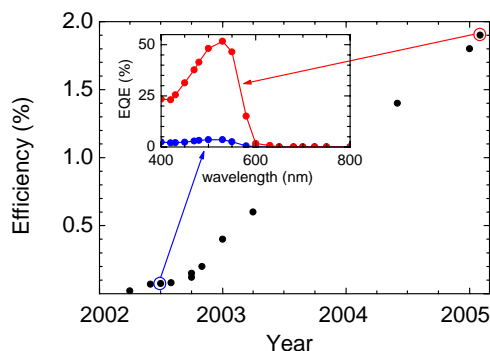


Figure 3. Progress in power conversion efficiency for polymer:polymer BHJ cells from 2002 until 2005. Inset: EQE of a low and high performance device

3.3 Polymer: metal oxide BHJ

A third approach towards a solution-processed BHJ PV device is based on the combination of conjugated polymers with *n*-type inorganic semiconductor nanoparticles. Such hybrid polymer:inorganic nanocomposite materials should combine the advantages of both types of materials: solution processing of polymer semiconductors and high electron mobility of inorganic semiconductors. Several hybrid polymer solar cells have been reported, using CdSe, TiO₂ or ZnO nanostructures. Ultimately, the use of a carefully nanostructured inorganic semiconductor may allow complete control over the desired morphology of the BHJ, but until now the highest efficiencies have been reached with random mixtures of conjugated polymers and inorganic nanoparticles. Finding a solvent that accommodates both nanoparticles and conjugated

polymers is not trivial. Hence, the processing window for such combinations of materials is quite narrow.

To overcome this problem we introduced the use of a molecular precursor for depositing the inorganic semiconductor. Because the precursor is readily soluble in organic media, it can be cast into a thin film together with the polymer from solution. Upon exposure to moisture from air, the precursor is converted into a metal oxide semiconductor within the polymer layer, ensuring intimate mixing and concomitantly efficient photoinduced charge generation. The validity of this approach was first demonstrated using titanium(IV) isopropoxide as precursor for TiO₂ and MDMO-PPV as semiconducting polymer [20,21]. However due to the ill-defined, amorphous nature of the formed TiO₂ phase, the power conversion efficiency of the resulting PV cells remained rather low at ca. 0.2%. Improvement can be expected from crystallization of TiO₂, but this would require high temperatures (> 350 °C) that are incompatible with the presence of the semiconducting polymer. Contrary to TiO₂, ZnO is known to crystallize at much lower temperatures. Moreover ZnO is an excellent *n*-type material in polymer solar cells, showing efficiencies up to 1.6 % for cells based on a blend of MDMO-PPV and ZnO nanoparticles [22]. Precursor-ZnO:polymer BHJ PV cells have been prepared by spin coating a solution containing an organozinc compound and a conjugated polymer, followed by thermal annealing at moderate temperature (~ 110 °C). The precursor is converted into the semiconductor, forming an intimately mixed blend layer with the polymer. By carefully optimizing the processing conditions, especially the donor:acceptor ratio and the relative humidity, a crystalline network of ZnO is obtained as was characterized by XRD. Clearly, such a structure fulfills the morphological requirements of a BHJ. Figure 4 shows the EQE of two cells made with such a layer fabricated from a ZnO precursor and MDMO-PPV under slightly different processing conditions. Both cells (active area 0.1-1 cm²) showed an overall power conversion efficiency of $\sim 1\%$, which is significantly higher compared to the amorphous precursor TiO₂:polymer cells [23].

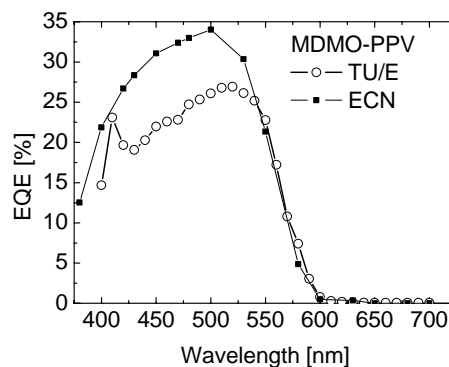


Figure 4. EQE at low illumination intensity of a ZnO:MDMO-PPV PV device (TU/e 15 vol.% ZnO; ECN: 26 vol.%) prepared at a R.H. of 35 % (TU/e) and 43 % (ECN) (device area: 0.1-1 cm²).

3.4 Stability

Any practical application of BHJ solar cells requires that the cells are stable. Similar to the polymer light emitting diodes, polymers based solar cells must be protected from ambient air to prevent degradation of the active layers and electrode materials by reaction with water and oxygen. Even with proper protection there are several degradation processes that need to be eliminated to ensure stability. Apart from device integrity, the materials must be photochemically stable and the nanoscale bicontinuous donor-acceptor network should be preserved. Recent studies revealed that MDMO-PPV/C60-PCBM solar cells show a significant degradation under accelerated lifetime testing conditions at increased temperatures [24]. This degradation is not so much associated with the chemical stability. At elevated temperatures, the PCBM molecules can diffuse through the MDMO-PPV matrix and form large crystals, thereby increasing the dimension and extent of phase separation [25]. This behavior has been observed for temperatures ~ 20 °C below the T_g of the polymer. Several strategies can be followed that may alleviate the limited thermal stability of the morphology. In general, high T_g (glass transition temperature) polymers will increase the stability of as prepared morphologies. An example has already been established for the combination of P3HT and C60-PCBM, where thermal annealing was used to produce and stabilize a nanoscale interpenetrating network with crystalline order for both components. Upon cooling to operating temperatures, it may be expected that no further changes occur in the morphology. In this respect it is important that for P3HT/PCBM blends the efficiency changed less than 20 % during 1000 hours of light soaking at 70 °C under an inert atmosphere (see Figure 5) [26]. This demonstrates that outstanding high stabilities are within reach.

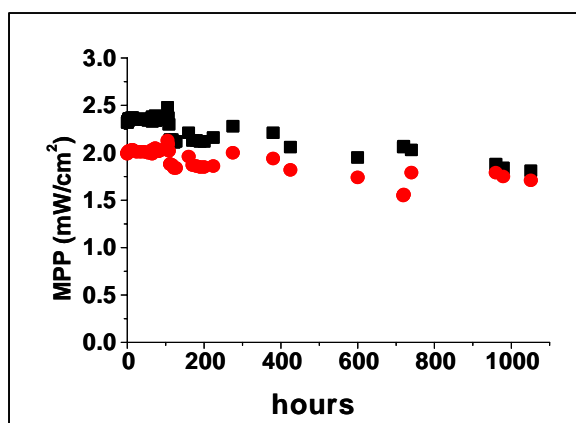


Figure 5. Stability test for two devices based on a P3HT:C60-PCBM blend under thermally accelerated aging at 70 °C and 1 sun equiv. illumination in N_2 atmosphere. MPP = Maximum Power Point.

4 CONCLUSIONS AND OUTLOOK

A summary is given of the multidisciplinary research efforts in the Netherlands in the field of polymer based solar cells between 1997 and 2005. It has been shown that different types of BHJ solar cells can be made in a

laboratory environment with relatively simple and new low temperature deposition techniques using a conjugated polymer as the donor material. The collaboration between universities and research institutes has led to comprehensive insights in the effect of crucial materials parameters in terms of purity, structure, band gap, morphology, energy levels, charge transport and electrode materials on cell parameters.

The polymer:fullerene concept has shown the highest efficiencies to date. Around 3 % efficiency on lab scale can routinely be obtained for a number of material combinations and some laboratories even claim efficiencies up to 4 %. Despite the progress made in this field, it is clear that Polymer PV is still in its early infancy. Several research issues must still be addressed before polymer PV will become a practical technology. These include a further understanding of operation (interfaces, charge transport, morphology control) and degradation of these cells while novel materials are needed for a better spectrum utilization (band gap engineering, new device architectures). This should ultimately lead to much higher power conversion efficiencies (>10 %), and lifetimes that are sufficiently long for practical use.

The prospect of lightweight, flexibility and low cost processing technology as well as the wider applicability of organic PV in areas that are inaccessible to conventional inorganic PV technologies have triggered a number of companies (for instance Konarka Technologies [27]) to start R&D on polymeric based solar cells. The short-term targets of these companies are to launch first applications most likely in the low power market segment of consumer products and portables, which have a relatively small share in the total market for PV. The restrictions on performance in terms of efficiency, lifetime and costs for this segment are more relaxed compared to the performance profile needed to enter the on-grid market, making them more suitable for polymer PV at this stage of development. Continued long term R&D by combining synthesis, processing and materials science with device physics and processing will reveal whether polymer PV will realize its potential to become a low cost, economically viable PV-technology with a significant impact.

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