

# A Low-Bandgap Semiconducting Polymer for Photovoltaic Devices and Infrared Emitting Diodes\*\*

By Christoph J. Brabec, Christoph Winder,\* N. Serdar Sariciftci,\* Jan C. Hummelen, Anantharaman Dhanabalan, Paul A. van Hal, and René A. J. Janssen

A novel low-bandgap conjugated polymer (PTPTB,  $E_g \approx 1.6$  eV), consisting of alternating electron-rich *N*-dodecyl-2,5-bis(2'-thienyl)pyrrole (TPT) and electron-deficient 2,1,3-benzothiadiazole (B) units, is introduced for thin-film optoelectronic devices working in the near infrared (NIR). Bulk heterojunction photovoltaic cells from solid-state composite films of PTPTB with the soluble fullerene derivative [6,6]-phenyl  $C_{61}$  butyric acid methyl ester (PCBM) as an active layer shows promising power conversion efficiencies up to 1% under AM1.5 illumination. Furthermore, electroluminescent devices (light-emitting diodes) from thin films of pristine PTPTB show near infrared emission peaking at 800 nm with a turn on voltage below 4 V. The electroluminescence can be significantly enhanced by sensitization of this material with a wide bandgap material such as the poly(*p*-phenylene vinylene) derivative MDMO-PPV.

## 1. Introduction

Conjugated polymer-based photonic devices show promising application potential.<sup>[1]</sup> As prominent examples of optoelectronic devices using semiconducting conjugated polymers, electroluminescence-based light-emitting diodes (LEDs) and photovoltaic elements can be listed.

Polymer LEDs are already entering display markets and much effort is dedicated to this area by optoelectronics manufacturers worldwide. An important wavelength area for LED devices is the near infrared (NIR) where the telecommunication frequency windows are located. A polymer LED in these NIR frequencies would be important as a pump source for telecommunications devices.

Polymer photovoltaics, on the other hand, offers great technological potential as a renewable, alternative source for elec-

trical energy. The demand for inexpensive renewable energy sources is the driving force for new approaches in the production of low-cost polymer photovoltaic devices. In the last couple of years, the development of solar cells based on organic molecules<sup>[2–4]</sup> and conjugated polymers<sup>[5–9]</sup> has progressed rapidly. Semiconducting polymers in combination with electron-accepting fullerenes have been found to show an ultrafast photoinduced charge-transfer reaction<sup>[10,11]</sup> at the donor-acceptor interface, which results in a metastable charge-separated state. Utilizing the nanoscopic interpenetrating network of the two constituents (donor/acceptor) in such a “bulk heterojunction” composite allows the construction of a large interfacial area and ensures a homogenous, efficient charge generation throughout the sample. Power conversion efficiencies exceeding 2.5% under AM1.5 illumination have been reported<sup>[5]</sup> for bulk heterojunction plastic solar cells (PSCs) recently.

One of the limiting parameters in these plastic solar cells is the mismatch of their absorption to the terrestrial solar spectrum. At present substituted poly(*p*-phenylene vinylene)s (PPVs) and polythiophenes are typically used in the construction of PSCs. The optical bandgap of these conjugated polymers ( $E_g = 2.0\text{--}2.2$  eV) is not optimized with respect to the solar emission, which has a maximum photon flux around 1.8 eV. The use of low-bandgap polymers ( $E_g < 1.8$  eV) to expand the spectral region of bulk heterojunction solar cells is a viable route to enhance the number of photons absorbed.

In this paper, we demonstrate the implementation of the recently synthesized low-bandgap polymer poly-*N*-dodecyl-2,5-bis(2'-thienyl)pyrrole, 2,1,3-benzothiadiazole (PTPTB)<sup>[12]</sup> into plastic solar cells and LEDs. Bulk heterojunction solar cells of PTPTB with [6,6]-phenyl  $C_{61}$  butyric acid methyl ester (PCBM) were demonstrated recently by van Duren et al.<sup>[13]</sup> Photophysical results evidencing photoinduced charge transfer using PCBM are observed. Prototype PV devices have been realized with improved white light power efficiencies of around 1%.

[\*] C. Winder, Dr. C. J. Brabec,<sup>[†]</sup> Prof. N. S. Sariciftci  
Linz Institute for Organic Solar Cells (LIOS)  
Physical Chemistry, Johannes Kepler University of Linz  
Altenbergerstrasse 69, A-4040 Linz (Austria)  
E-mail: Christoph.Winder@jku.at

Prof. J. C. Hummelen  
Stratingh Institute and Materials Science Center, University of Groningen  
Nijenborgh 4, NL-9747 AG Groningen (The Netherlands)

Dr. A. Dhanabalan, P. A. van Hal, Prof. R. A. J. Janssen  
Laboratory of Macromolecular and Organic Chemistry  
Eindhoven University of Technology  
PO Box 513, NL-5600 MB Eindhoven (The Netherlands)

[†] Current address: Siemens AG, CT MM1, D-91052 Erlangen, Germany.

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We further demonstrate electroluminescence from PTPTB in the near IR peaking at 800 nm and sensitization of the PTPTB light-emitting diodes via energy transfer from poly-(2-methoxy, 5-(3,7-dimethyloctyloxy))-*p*-phenylene-vinylene (MDMO-PPV). Reports on IR emission from conjugated polymers are rare<sup>[14,15]</sup> due to a lack of materials. Therefore, the possibility of obtaining a light source working at telecommunications wavelengths and/or for medical treatment applications, together with the functionality of the same material for photovoltaic devices as demonstrated in this work is promising.

## 2. Results and Discussions

The synthesis and characterization of PTPTB was described earlier.<sup>[12,16]</sup> The structure is presented, together with that of MDMO-PPV and PCBM in Figure 1.

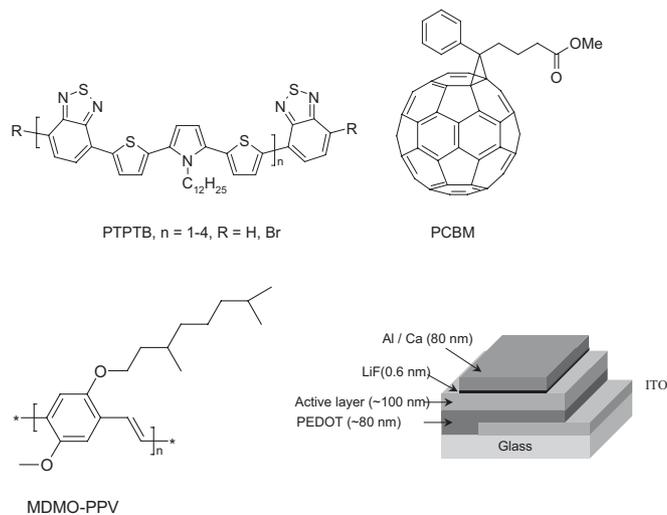


Fig. 1. Chemical structures of PTPTB, MDMO-PPV, and PCBM, together with the scheme for the photovoltaic and electroluminescent diodes, with blend and neat polymer active layers, respectively. Thin-film diodes were prepared on cleaned glass/ITO/PEDOT:PSS substrates by spin coating the photoactive layer from solutions in chlorobenzene, for the LED, or toluene, for the PV diodes. PTPTB and PTPTB/PCBM films are rather thin (< 70 nm), determined by a step profiler. The rather low film thickness is a consequence of the low molecular weight of the polymer. As top electrode, a LiF/Al (6 Å/80 nm for PSC) electrode was thermally deposited in a two step evaporation process as described earlier [27]. The insertion of a LiF layer between the metal and the organic semiconductor enhances the formation of contacts with low contact resistivities.

The bandgap and the energetic position of the band edges of PTPTB were determined via cyclic voltammetry in CH<sub>2</sub>Cl<sub>2</sub> solution. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the polymer were estimated to lie at ~5.5 eV vs. vacuum ( $E_{ox1} = 0.53$  V vs. SCE) and ~3.73 eV vs. vacuum ( $E_{red} = -1.24$  V vs. SCE), respectively. The electrochemical bandgap of 1.77 eV is slightly higher than the optical gap, which is determined to be approximately 1.6 eV.

The interaction with PCBM was investigated by photoluminescence (PL) and by photoinduced absorption (PIA) measurements. The PL of pristine PTPTB is quenched by more than two orders in magnitude upon addition of PCBM.<sup>[13,16]</sup>

Figure 2 shows the *I*-*V* characteristics of a device prepared with a 1:3 (w/w) mixture of PTPTB and PCBM. The device structure for PV and LED devices is shown in Figure 1. It is interesting to note that while the bandgap of PTPTB is ~0.6 eV

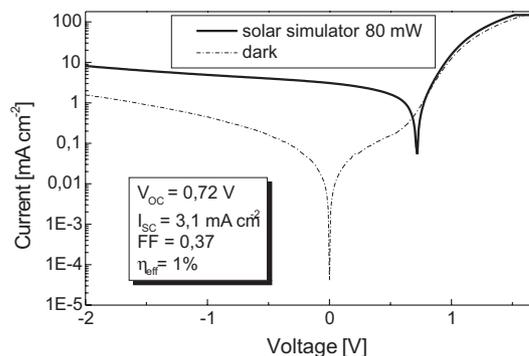


Fig. 2. *I*-*V* characteristics of the ITO/PEDOT/PTPTB:PCBM (1:3)/LiF/Al device under 80 mW cm<sup>-2</sup> AM1.5 illumination (full line) and in the dark (dashed line) recorded by a Keithley 2400 source meter in inert atmosphere at ~55 °C using a Steuernagel solar simulator (KH 575).

less than that of other donor polymers used for plastic solar cells (e.g., MDMO-PPV<sup>[5]</sup> or P3OT<sup>[9]</sup>) with comparable oxidation potentials, the  $V_{oc}$  of the PTPTB/PCBM devices is found to be only ~0.1 V lower. This result becomes clear if the effective bandgap is regarded as the difference of donor HOMO and acceptor LUMO, of the PTPTB/PCBM blend, which is in the same range as for MDMO-PPV/PCBM and polythiophene/PCBM blends.

While the observed photocurrent is satisfyingly high, the low fill factor (FF) of the device limits the overall performance. From the outstanding high injection currents at low voltages (Fig. 2) the presence of a large serial resistance can be excluded as being responsible for the limitation of the FF. We propose two possible underlying mechanisms that are relevant to this observation. First, the rather low molecular weight of the polymer (~5–16 repeating units) is likely to result in thin films of relatively low quality. Accompanied by an unfavorable morphology within the polymer/fullerene blend these factors may lead to significant shunts. Second, the close energetic proximity of the donor and acceptor LUMO (~3.7 eV for PTPTB and ~4 eV for PCBM potentials determined from solution electrochemistry) may diminish the selectivity of the metal electrode contacts, lowering the diode quality by loss mechanisms such as enhanced interface recombination or tunnel injection under reverse bias. Nevertheless, at present the relevant mechanism for the low FF is not fully understood, making further investigation to improve the FF necessary.

Spectral photocurrent measurements, presented in Figure 3 in comparison with the optical absorption, were performed to analyze the wavelength regions contributing to the photocurrent in the devices. The relationship between absorption and spectrally resolved photocurrent is generally divided into two categories, either sybatic (good correlation between absorption and spectrally resolved photocurrent) or antibatic behavior (missing correlation between absorption and spectrally resolved photocurrent). Excellent sybatic behavior is found

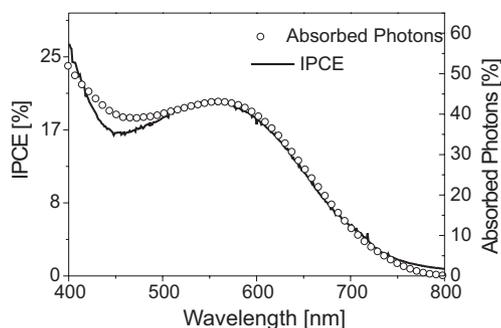


Fig. 3. IPCE spectrum (full line) of an ITO/PEDOT/PTPTB:PCBM (1:3)/LiF/Al device and the percentage of absorbed photons in a reference device of comparable thickness, measured in reflection geometry by an integrating sphere, accounting for scattering (open circles). Spectrally resolved photocurrent measurements were recorded by the lock-in technique, illuminating the device with  $\sim 0.1 \text{ mW cm}^{-2}$  monochromatized and modulated light from a Xe arc lamp on top of white light background illumination. The IPCE was calculated versus a calibrated Si photodiode.

for the PTPTB/PCBM devices in the wavelength region between 400 and 800 nm, proving the efficient photogeneration of charge carriers over the whole spectral region. The wavelength dependence of the internal photocurrent efficiency confirms the low bandgap of PTPTB through its contribution to the photocurrent for wavelengths up to 800 nm (Fig. 3).

The simplest and most widely used polymer LED structure is a metal–insulator–metal (MIM) tunnel diode with metal electrodes of asymmetrical workfunction, forming selective contacts for electron injection at the cathode and hole injection at the anode. The rectifying diode characteristics of such MIM devices can be accompanied by radiative recombination channels of the injected electrons and holes within the molecular solid; the result is a light-emitting diode.<sup>[17–21]</sup> If photoinduced free charge carrier generation is allowed at the same time (with or without an acceptor), the same device structure can be utilized for solar cells and photodetectors (dual function).<sup>[22]</sup> Figure 4 compares the room-temperature photoluminescence of PTPTB with the electroluminescence from a thin-film device. This emission is located in the near IR, ranging down to 950 nm (1.3 eV). The onset for the light detection of the LED is at 3 V, the emission increases up to 7 V and saturates.

The light emission of the PTPTB diode is very low compared to a MDMO-PPV device. For technical application, it is desir-

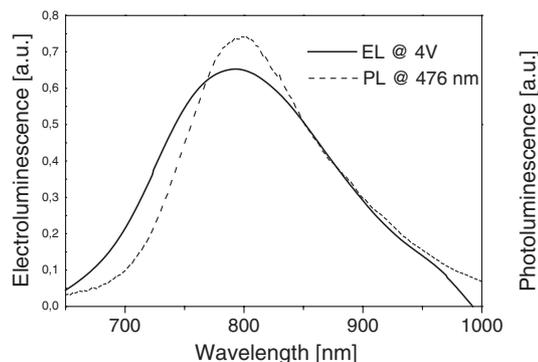


Fig. 4. Electroluminescence spectrum (full line) of thin-film ITO/PEDOT/PTPTB/LiF/Ca diodes (at 4 V) compared to the room-temperature photoluminescence of a PTPTB thin film excited at 476 nm (dotted line).

able to enhance the efficiency. One possible mechanism is sensitization of the luminescence of a low-bandgap polymer<sup>[23,24]</sup> or dye<sup>[25,26]</sup> via energy transfer.

Figure 5 shows the PL from thin films of MDMO-PPV, PTPTB, and different blends. At the laser wavelength of 514 nm, presumably the MDMO-PPV is excited. In the blends, strong quenching of the photoluminescence of MDMO-PPV around 600 nm and a shift in emission to the far red is observed.

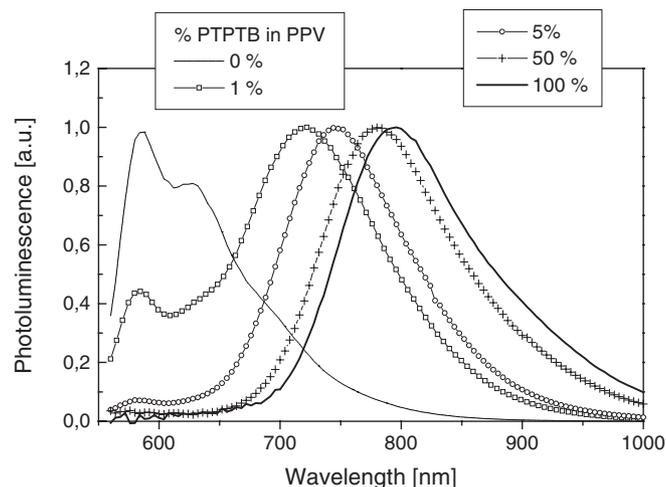


Fig. 5. Photoluminescence for MDMO-PPV (thin line), PTPTB (thick line), and blends of the materials, 1 % PTPTB (open squares), 5 % (open circles), and 50 % (crosses) at room temperature and excitation at 514 nm with 40 mW of a laser spot of 4 mm diameter.

Figure 6 shows the relative electroluminescence for the same blends from LED devices. A strong enhancement of the PTPTB electroluminescence is observed via sensitization from MDMO-PPV.

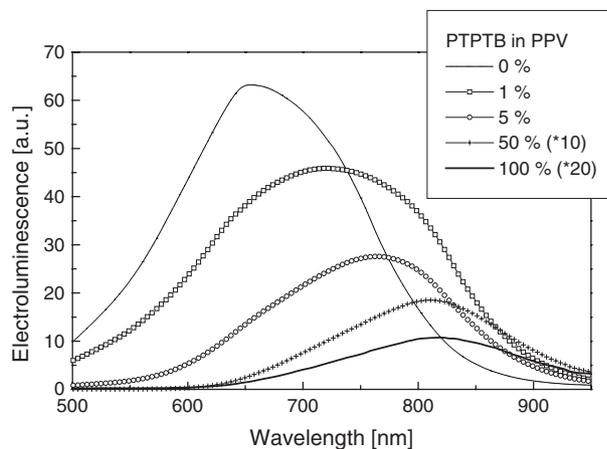


Fig. 6. Electroluminescence spectrum for thin-film diodes ITO/PEDOT/active layer/LiF/Al: pristine MDMO-PPV (thin line), pristine PTPTB (thick line), and different blends with 1 % (open squares), 5 % (open circles), and 50 % PTPTB (crosses); the spectrum for 50 % PTPTB and pristine PTPTB are enhanced by a factor 10 and 20, respectively, for comparison. The LEDs with pristine MDMO-PPV and PTPTB concentration up to 5 % were measured at +5 V and current densities of  $\sim 400 \text{ mA cm}^{-2}$ . The thickness of the devices ranges between 120 and 150 nm. The devices with 50 % PTPTB and pristine PTPTB were measured at 7 V, above saturation of the observed electroluminescence intensity. The current densities are  $\sim 1 \text{ A cm}^{-2}$ .

Further, the film quality is improved significantly in the blends compared to the neat PTPTB devices.

### 3. Conclusion

PTPTB is, to the best of our knowledge, the first low-bandgap conjugated polymer for which efficient photovoltaic activity in conjunction with a proper electron acceptor (PCBM) as well as near IR electroluminescence was demonstrated. The efficient photoinduced charge transfer to PCBM allowed the construction of bulk heterojunction solar cells with 1 % AM1.5 efficiency for a 70 nm photoactive layer. The efficiency of PTPTB light-emitting diodes can be significantly enhanced by sensitization with MDMO-PPV.

### 4. Experimental

Absorption spectra from thin spin-coated films were recorded with a HP 8453 spectrometer. Photoluminescence was measured on a homemade setup with excitation at 476 or 514 nm. Photovoltaic cells and LEDs were made in the sandwich geometry shown in Figure 1. A layer of PEDOT:PSS (Baytron P) was spin-coated on precleaned ITO. Afterwards the active layer was spin-coated from toluene or chlorobenzene. For the cathode, a 6 Å LiF layer followed by 60 nm Al was evaporated. *I*-*V* curves were recorded under illumination from a Steuernagel solar simulator with 80 mW, to simulate AM1.5 conditions. The spectral photocurrent (IPCE) was detected with a lock-in amplifier after monochromatic illumination. Calibration of the incident light was done with a monocrystalline silicon diode. The electroluminescence was measured with an Avantes spectrometer; the spectra were corrected for the detector sensitivity.

PTPTB and PTPTB/PCBM films were rather thin (<70 nm), determined by a step profiler. The rather low film thickness is a consequence of the low molecular weight of the polymer. As top electrode, a LiF/Al (6 Å/80 nm for PSC) electrode was thermally deposited in a two-step evaporation process as described earlier [27]. The insertion of a LiF layer between the metal and the organic semiconductor enhances the formation of contacts with low contact resistance.

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