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Organic light emitting diodes with a solution processible organic bulk heterojunction electroluminescent layer

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Efficient organic light emitting diodes with an electroluminescent layer composed of the blends of p-type and n-type organic semiconductors, which undergo nanoscale phase separation to form a bulk heterojunction with percolated hole and electron transport channels, are reported.

The development of organic lighting and signage technologies stimulated research on solution processible organic light emitting diodes (OLEDs).[1,2] Solution-based technologies allow for the high throughput and low cost production of flat and flexible electroluminescent panels, which are expected to find extensive applications for indoor and outdoor lighting.[3]

White light emitting diodes are suitable for conventional illumination.[4] Nevertheless, blue, green, yellow, orange and red OLEDs are also required for decorative lighting, advertising and signage applications.[5,6] It is a common belief that only triplet phosphorescent emitters can afford high efficiencies in OLEDs.[7] However, cheap fluorescent emitters can also be used for the fabrication of OLEDs with an exceptionally high power efficacy of 31.2 lm W^{-1}, which is more than sufficient for lighting applications.[8] A big research effort has been made in the design of conjugated polymers which are considered as the most promising materials for solution-processible OLEDs.[9–13] Energy-transfer systems comprising quantum dots of inorganic semiconductors,[14] organic dyes[15,16] and phosphorescent metal complexes[17] as light emitters were designed. Power efficiencies above 25 lm W^{-1} have been realized recently using light-emitting conjugated polymers.[18] At the same time, power efficiencies of ~50 lm W^{-1} have been achieved for OLEDs based on solution processible low-molecular-weight compounds comprising triplet dopants.[19,20]

According to the basic principles of OLED operation, both types of charge carriers (holes and electrons) have to be injected from the opposite electrodes to the electroluminescent layer with equal efficiency (or equal rates) thus providing the balanced generation of excitons. Therefore, an ideal electroluminescent material should behave as an ambipolar organic semiconductor with similar hole and electron mobilities. In addition, both electrodes in an OLED device should provide ohmic contacts with the electroluminescent layer for the barrierless injection of holes and electrons. It is well known that the vast majority of common electroluminescent materials are represented by p-type and n-type semiconductors which normally do not exhibit ambipolar transport properties. In the case of p-type semiconductors, the injection of holes dominates over the injection of electrons; therefore, recombination takes place near the cathode/organic layer interface, which results in significant non-radiative losses. For n-type semiconductors, the same problem occurs at the anode/organic layer interface since the injection of electrons in this case dominates over the injection of holes. To overcome the problem of the unbalanced injection of charge carriers in OLEDs, one might apply special hole/electron injecting and hole/electron transport layers.[21] This approach can be easily performed in multilayer devices fabricated using vacuum deposition techniques. However, it is hardly suitable for solution processible OLEDs.

Photovoltaic cell is another type of organic electronic devices, which have reversed functionality compared to the light emitting diode. It is known that optimized solution processible fullerene-polymer solar cells are capable of efficient charge generation, balanced charge transport and charge extraction at the electrodes.[22] The advanced performance of these devices is related to the existence of three-dimensional percolated networks of p-type and n-type materials forming a bulk heterojunction.[23,24]

Here, we applied the same bulk heterojunction concept to the construction of OLED devices. Both types of charge carriers are injected to the composite of p-type and n-type electroluminescent materials forming a bulk heterojunction electroluminescent layer. Electrons are transported in the phase of n-type material, while holes are moving in the phase of p-type semiconductor. Recombination takes place at the interfaces between the nanoclusters of p-type and n-type semiconductors in the whole volume of the electroluminescent composite layer (Figure 1). A similar idea was pursued but not realized in hybrid organic/inorganic quantum dot OLEDs.[25]

To demonstrate the feasibility of the proposed concept, we used simple materials such as commercially available polyfluorene PF8 and fluorescent small molecular emitter bis-TPBIIN (Figure 2).[26,†] Cyclic voltammetry measurements were performed for bis-TPBIIN in a mixture of 1,2-dichlorobenzene and acetonitrile (2 : 1, v/v) using 0.1 M Bu_4NPF_6 solution as a supporting electrolyte and a glassy carbon working electrode. The test material showed an irreversible oxidation wave with E_{onset} = 1.1 V *vs.* Fc/Fc^+ and

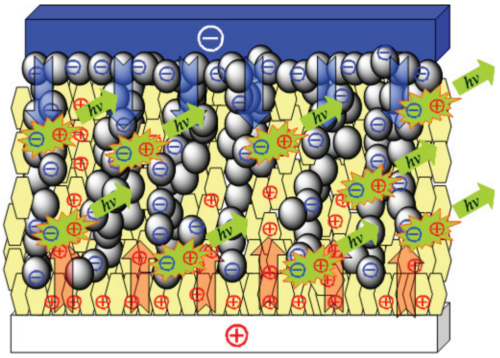


Figure 1 Schematic illustration of a bulk heterojunction OLED.

[†] For experimental details, see Online Supplementary Materials.

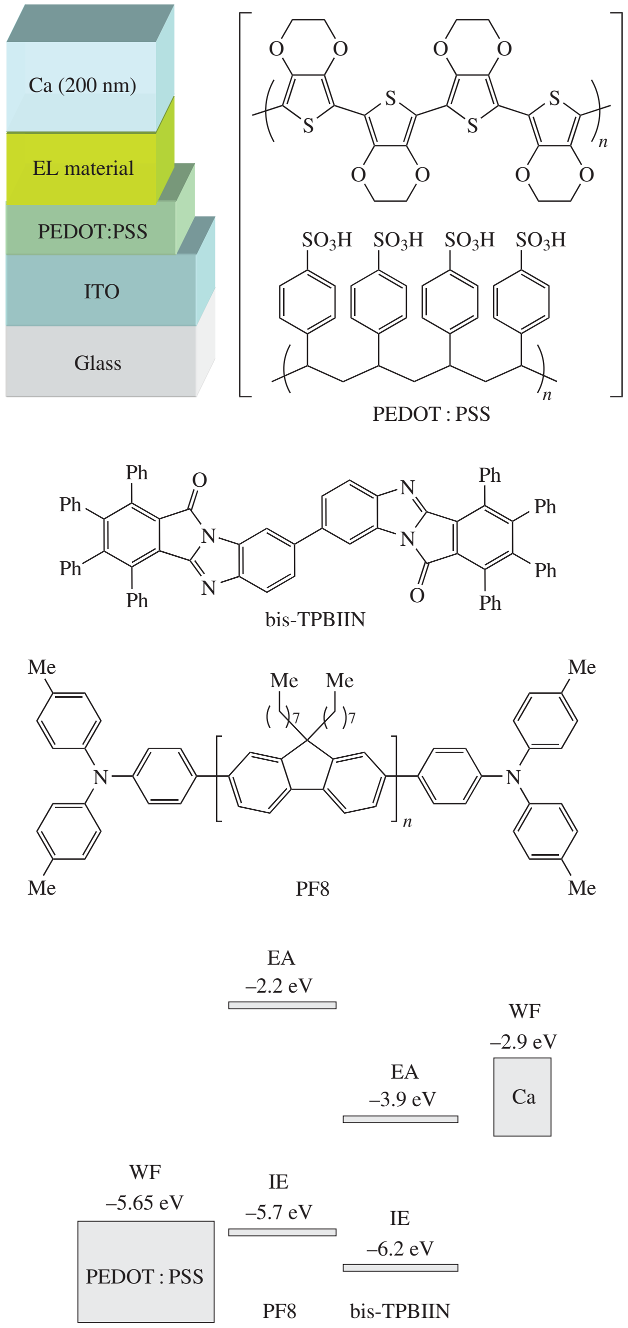


Figure 2 Architecture of the OLED device, the molecular structures of used materials and the alignment of their energy levels. Work functions (WF), ionization energies (IE or HOMO) and electron affinities (EA or LUMO) are provided based on published data (PEDOT : PSS, PF8, Ca) and the experimental results of this work (bis-TPBIIN).

a partially reversible reduction wave with $E_{\text{onset}} = -1.23$ V *vs.* Fc/Fc$^+$, which corresponded to the electrochemical band gap of 2.33 eV. This value was somewhat lower than the optical band gap of 2.5 eV obtained from the offset of the absorption band.

The conjugated polymer PF8 is a typical polyfluorene with characteristic HOMO and LUMO energies of –5.7 and –2.2 eV, respectively.[27] Thermally annealed PEDOT : PSS is known to have a high work function of 5.65 eV, which enables the formation of an ohmic contact with PF8 and facilitates the injection of holes.[28] At the same time, a calcium cathode with the low work function of 2.9 eV should form an ohmic contact with bis-TPBIIN required for the efficient injection of electrons (Figure 2).

Polyfluorenes are typical p-type organic semiconductors which do not undergo reversible n-type doping under electrochemical conditions. This means that positive charge carriers (holes) can be injected in PF8 thin films, while the electrons will get stuck near the cathode, which will lead to significant non-radiative losses. Indeed, simple OLED devices possessing the glass/ITO/PEDOT : PSS/PF8/Ca configuration demonstrated rather poor performance: turn-on voltages of 4–6 V, maximal brightness of 300 cd m^{-2} and efficiency of 0.3–0.5 cd A^{-1}.

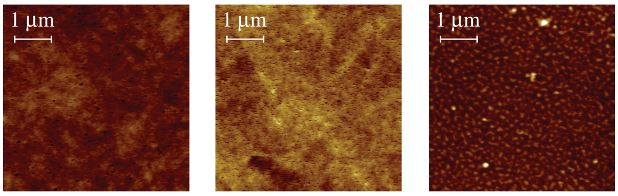
The fluorescent small molecular emitter bis-TPBIIN is an n-type material.[17] Therefore, the injection of electrons to bis-TPBIIN will strongly dominate over injections of holes. The recombination will take place in a close proximity to the anode, which will result in strong non-radiative losses. This hypothesis is confirmed by the poor performance of OLED comprising bis-TPBIIN as an electroluminescent material (glass/ITO/PEDOT : PSS/bis-TPBIIN/Ca), which showed the following characteristics: turn-on voltages of 5–6 V, maximal brightness of 200 cd m^{-2} at 13 V and efficiency of 0.1 cd A^{-1}.

The performance of OLEDs was dramatically enhanced when PF8 was combined with bis-TPBIIN in the electroluminescent layer of the device. The best performing devices comprising 40 wt% bis-TPBIIN showed a turn-on voltage of 2–3 V, a maximal brightness of 7000–11000 cd m^{-2} (at 10–12 V) and an efficiency of 3.0–5.0 cd A^{-1}. The devices with lower (25–30%) or higher (90%) weight concentrations of bis-TPBIIN exhibited inferior but still comparable characteristics. The observed remarkable improvement in the performance of light emitting diodes based on the PF8/bis-TPBIIN blends is clearly related to the combination of p-type and n-type materials in the electroluminescent layer.

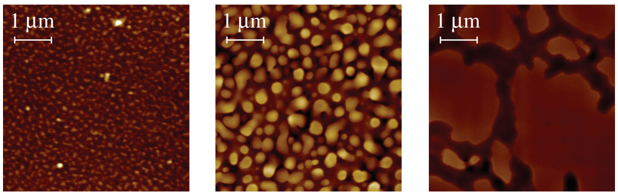
Reference glass/ITO/PEDOT:PSS/PF8/bis-TPBIIN/Ca planar heterojunction devices fabricated for comparison reasons by the evaporation of 30 nm of bis-TPBIIN on the top of solution processed PF8 films (50–60 nm) provided inferior characteristics: turn-on voltage of 5 V, maximal brightness of 400–500 cd m^{-2} (at 8–9 V) and the efficiency below 1.0 cd A^{-1}. These results fit well to the model of bulk heterojunction OLED discussed above.

The proposed concept of a bulk heterojunction OLED is based on the assumption that PF8 and bis-TPBIIN undergo nanoscale phase separation in composites and form interpenetrated networks of p-type and n-type charge transporting channels. In order to support this assumption experimentally, we investigated the topography of PF8/bis-TPBIIN composite films using atomic force microscopy (AFM) (Figure 3).

The presented data revealed the expected phase separation in PF8/bis-TPBIIN blends with the concentration of the latter component varying from 30 to 90%. The best performing blends with 40% bis-TPBIIN exhibited relatively small clusters (50–100 nm), which provided optimal charge transport and exciton generation



0% bis-TPBIIN 10% bis-TPBIIN 30% bis-TPBIIN



50% bis-TPBIIN 70% bis-TPBIIN 90% bis-TPBIIN

Figure 3 AFM images of the PF8/bis-TPBIIN composites with different weight concentrations of bis-TPBIIN.

properties. The AFM images showed a clear correlation between the morphology of the electroluminescent composite layers and their performance in OLEDs. Thus, we found that the bulk heterojunction concept might be very useful in solution processible OLEDs for achieving balanced injection of holes and electrons and providing efficient exciton generation and radiative recombination.

The spectral properties of OLEDs based on the PF8/bis-TPBIIN blends deserve special discussion. Figure S1 (see Online Supplementary Materials) shows the electroluminescence (EL) spectra of OLEDs based on pristine PF8, pristine bis-TPBIIN and their composites with minimal and maximal concentrations of the n-type component. It is somewhat surprising that the EL spectrum of OLEDs based on pristine bis-TPBIIN is very different from the photoluminescence (PL) spectrum of bis-TPBIIN in a solid state. Indeed, the EL spectrum is broader and it has two badly resolved maxima at ~510 and ~550 nm. The PL spectrum is narrower and it has a single maximum at 562 nm. It was shown previously that the solid state PL spectrum of bis-TPBIIN is represented by a single exciplex band.[26] Therefore, the difference between the EL and PL spectra can be attributed ever to the different mechanisms of the exciton formation or to different nature of exciplexes formed in the OLED (*e.g.*, bis-TPBIIN might form exciplexes with charge transporting layer PEDOT:PSS like it was shown for other systems previously[29]). This explanation is very plausible since excitons are generated at the PEDOT:PSS/bis-TPBIIN interface as a result of hindered hole injection to the bis-TPBIIN films.

The EL spectrum for OLED comprising 80% PF8 and only 20% bis-TPBIIN exhibited a minor band at 435 nm with a small shoulder at 422 nm, which might be attributed to the bands of PF8 emission with maxima at 422 and 437 nm. The low intensity of this band evidences a very efficient energy transfer channel from the polyfluorene PF8 to the acceptor bis-TPBIIN. The most intense band in the EL spectrum of 80% PF8 + 20% bis-TPBIIN has a maximum at 496 nm, and it can be attributed to some exciplex states formed together by the conjugated polymer and bis-TPBIIN. The second intense band at 550 nm overlaps completely with the EL band of bis-TPBIIN (Figure S1, Online Supplementary Materials).

The EL spectrum of an OLED with 10% PF8 and 90% bis-TPBIIN shows a very weak feature at ~430 nm, which might be attributed to the residual fluorescence of PF8. A more intense band with an undefined maximum at 510–512 nm closely resembles the EL spectrum of OLEDs based on pristine bis-TPBIIN. Taking into account the above considerations, one might suspect that this band is a signature of the exciplex states formed at the interface between bis-TPBIIN and PEDOT:PSS. The most intense band in the EL spectrum of 10% PF8 + 90% bis-TPBIIN (maximum at 562 nm) overlaps with the PL spectrum of solid bis-TPBIIN. This observation proves that the nature of excited states formed in the 10% PF8 + 90% bis-TPBIIN blends is very similar to the exciplex states formed in solid bis-TPBIIN under photoexcitation. Therefore, the band with the maximum at 562 nm is a signature of the exciplex states formed by aggregated bis-TPBIIN molecules and non affected by PEDOT:PSS or PF8 components. In other words, this band corresponds to the emission generated in the volume of the PF8/bis-TPBIIN blends owing to the existence of a well-developed bulk heterojunction.

In conclusion, we have demonstrated the feasibility of the bulk heterojunction OLED concept, which allows one to balance hole and electron injections to the electroluminescent layer by tuning the ratio between p-type and n-type components of the blend. The PF8/bis-TPBIIN composite systems provided highly efficient OLEDs with broad exciplex emission spectra. These devices generated yellowish white (warm white) emission, and they might be applied in the design of illumination devices. In general, the combination of two emitters (p-type and n-type) in a bulk heterojunction OLED device can be used for tuning the color of emitted light, which might contribute to the development of modern lighting technologies.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2014.02.006.

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