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Conjugated polymer blends: linking film morphology to performance of light emitting diodes and photodiodes

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Abstract

Blending is a technique known in polymer technology that takes advantage of the processibility of polymers to produce new solid materials or composites with specific structural and physical properties, distinct from the ones of their components. In thin films of polymer blends interesting morphologies are formed because of phase separation. For conjugated polymers, i.e. solution-processible semiconductors, blending also opens a way to optimize the performance of opto-electronic devices, bringing about technological benefits. It is therefore crucial to achieve understanding of the effect film morphology has on the device performance, and, ultimately, to achieve control over the phase separation in a blend, so that structures can be designed that yield the desired device performance. Light-emitting diodes (LEDs) made of polymer blends have shown strongly enhanced electroluminescence (EL) efficiencies, as compared to pure homopolymers. Colour conversion, white light emission, polarized light emission, emission line narrowing, and voltage-tunable colours are other effects that have been observed in blends containing light-emitting polymers. Although the enhanced EL efficiency is attributed to Förster-type energy transfer in numerous reports, the exciton dynamics behind this effect is not well understood. Here we review the formation and morphology of thin films of conjugated polymer blends, as well as modern microscopic and spectroscopic techniques to study them. Furthermore, we attempt to link the film morphology to the electronic performance of electroluminescent and photovoltaic devices and discuss energy and charge transfer phenomena at the interfaces. We also report some new results, specifically for polyfluorene blends in LEDs.

(Some figures in this article are in colour only in the electronic version)

1. Background

Semiconductors are traditionally viewed as inorganic crystalline materials with well defined optical and electrical properties, such as bandgap, electron affinity, conductivity, mobility and surface properties. Thanks to semiconductors such as silicon and gallium arsenide we have seen an explosive growth of electronic applications in the 20th century. They have, however, one limitation that has plagued physicists and engineers over the years. The properties of this rather small group of materials can only adopt a discrete number of possible values, unlike organic molecules, which are available in a wide variety and can be synthesized with a set of desired properties. To some extent a semiconductor's properties can be modified externally during or after growth of the solid. By doping a semiconductor with an appropriate dopant, for instance, its conductivity can be changed over a wide range and its type of conductivity (n-type or p-type) manipulated. For instance, In_2O_3 is doped with Sn to obtain the conducting transparent material ITO, used widely in optoelectronics. While these modifications of semiconductors are very important for their value in device applications, mixing and doping solid inorganic materials requires high-temperature and rather sophisticated methods.

To exploit the wide variety of available materials, molecular materials have become increasingly popular as replacements for inorganic semiconductors. The idea of replacing silicon technology by molecular electronics has found additional incentive in the reports of single-molecule devices with rectifying, storage and switching properties [1], as well as in the successful integration of molecular materials in some particularly visible fields of technology. One of these fields is display technology [2], where both vacuum-deposited molecular layers (so-called small molecule technology) [3, 4] and spin-coated conjugated polymers (polymer technology) [5, 6] have clearly made their entry during the last two decades, and appear strongly competitive in performance with the more established single-crystalline semiconductor LED technology.

The first reports of electronic conduction in conjugated polymers date from the 1970s [7, 8], and electroluminescence (EL) in polymers was observed for the first time in 1989 [9]. The use of conjugated polymers—polymers with a conjugated π - π system—in optoelectronic devices, in particular in LEDs, has grown fast since then [10]. Today light-emitting polymers (LEPs) are at the verge of being commercialized in full-colour active matrix displays. The reasons for the success of LEP displays are their flexibility, adaptability, high performance and low cost. Display technology is not the only field where molecular materials in general, and conjugated polymers in particular, appear to have a bright future. Solar cells [11–13], transistors [14–16], lasers [17–21], memories [22], and all-polymer integrated circuits [23, 24] are other examples.

One additional advantage of molecular materials, apart from the immense variety available, is their ability to be mixed. The possibility of simply mixing materials with different properties at room temperature, and obtaining a new material with tuned electronic properties, is a strong merit of molecular materials in electronics. Solution-processible conjugated polymers offer this advantage. Copolymerization and blending are two alternative ways to give birth to new material properties, designed to yield efficient devices.

2. Blending polymers and film formation

Blending is an established strategy in polymer technology where two or more polymers are mixed in order to achieve specific structural and physical properties of the polymeric mixture in the solid state, without the synthesis of new polymers. Traditionally immiscible blends of insulating polymers, such as polystyrene (PS), polybutadiene (PB), polymethylmethacrylate (PMMA) and polyvinylalcohol (PVA), are studied because of their technological interest.

The combined properties of their components and their potential for enhanced mechanical strength, if prepared under specific conditions (e.g. under flow), make them useful in everyday applications. Research in the field of the morphology of insulating polymer blends has developed strongly since the late 1980s, particularly the issues of thermodynamics of thin film formation and the phenomenon of phase separation. The polymer blend film morphology has been studied in great detail for binary and ternary blends. We first present a brief overview of the formation of thin films of traditional polymer blends before we move on to the particular case of conjugated polymers.

2.1. Phase separation

When two different polymers are blended together, phase separation is likely to occur [25]. The driving force is thermodynamical, namely when long polymer chains are mixed, they do not gain enough entropy to yield a negative free energy of mixing (enthalpy of mixing is positive, entropy positive but small), and thus mixing does not happen spontaneously. Given enough time to reach equilibrium, the immiscible polymer blend demixes and forms separate coexisting phases, with different compositions, consisting dominantly of one of the blend components. However, when the polymer blend is not given enough time to complete the phase separation, an intermediate state of mixing is frozen into the solid state, giving rise to the typical morphology of a blend. There are two main ways to effect phase separation in a polymer blend: temperature quenching and solvent quenching. Temperature quenching means that a homogeneous mixture of polymers is driven into the two-phase region of the phase diagram by variation of the temperature, corresponding to temperatures above the glass transition temperature, T_g , of the components. In solvent quenching, the polymers are dissolved in a common solvent and form a homogeneous solution, which phase separates when the solvent evaporates from the solution. The latter is what happens during the preparation of thin films of polymer blends.

2.2. Film formation

Spin-coating (also called spin-casting) is one of the methods that are commonly used for the preparation of thin polymer films, where the coating solution is dispensed onto a substrate, which is subsequently set to rotate at about 1000–4000 rpm in the surface plane. During the spin-coating process a number of processes take place sequentially [26]. First, at the beginning of the rotation, the main part of the polymer solution is slung off from the substrate (which makes spin-coating a waste generating process). In a second step a thin liquid film is formed. In a third step, the solvent evaporates further and the viscosity of the film rises [27]. It is in this last step that the structure of the blend film is formed. There are several theories that explain the formation of the typical blend structures and strong surface topographic structure in thin spin-coated films [28–30]. When no blend component wets the surface or substrate, lateral phase domains are formed, accompanied by surface undulations. Phase domains may be circular or extended, and are usually formed of one phase in a homogeneous background of the other phase. The domains either protrude out of the surface (islands) or form wells into the surface. Walheim *et al* [28] have explained this structure for a binary blend as driven by the solubility differences of the components in the common solvent. During spin-coating, the domains that are rich in the least soluble component solidify first and form ‘walls’, while the remaining solution, which is rich in the most soluble component, resides between the walls. When the solvent continues to evaporate, the second domain collapses in the wells formed between the walls, which often includes some shrinkage because the polymer was swollen in the solvent. The theory has been expanded to ternary blends [31, 32].

The morphology and domain size is strongly influenced by the blend ratio, i.e. the relative polymer mass fraction. The rate of solvent evaporation is determined by the solvent properties, solvent–polymer interactions and the spin-coating conditions (spin speed, temperature etc). The more time the solvent has to evaporate, the longer time the film has to form phase-separated domains and to let them grow. Slowly evaporating solvents, higher polymer concentrations, higher molecular weights, lower spin speeds and lower temperatures will thus yield larger domains, as a general rule. The larger the domains, the less polymer–polymer interface area there is in a certain sample volume. Phase-separated blends will tend to minimize their interface area.

Moreover, external factors, such as the nature of the substrate surface and the addition of a compatibilizer can affect the resulting film morphology strongly. Block copolymers with two blocks, each made of one of the components of the immiscible blend, are efficient compatibilizers that will tend to reside at the interface between the two phases, lowering its energy, and hence decreasing the size of the domains. By modifying the substrate surface, e.g. by self-assembling monolayers with specific tail groups, the substrate surface energy can be altered and phase separation affected [33]. This surface-induced phase separation has been utilized on patterned surfaces to externally induce one-dimensional structures in the polymer film by pattern replication [34–39].

2.3. One-step process

Probably the most important benefit of blending solution-processible polymers is the simplified formation of thin films. Two or more different materials can be deposited together from solution in one single processing step, provided they can be dissolved in the same solvent. The unique polymer property of solution processibility offers thus a simple and inexpensive method to form a solid thin film of mixed composition and with tailored material properties. Hence, blend film processing avoids a problem common in multilayer processing, where the solvent used in the spin-coating process of a second polymer layer may partly dissolve the previously coated polymer layer underneath, unless the underlying layer was treated thermally [40]. This property can, however, be found useful in some cases, e.g., in so-called stratification [37, 41]. Such stratified multilayers have for instance been used for photodiodes [42].

3. Conjugated polymer blends

3.1. Sorts of blend for conjugated polymers

After the discovery in the 1970s, which was awarded the Nobel Prize in Chemistry 2000 [43–45], that polymers can be made conductive, an interesting new branch in polymer blend technology was created. Blends of conjugated (conducting or semiconducting) polymers do not only have interesting structures and mechanical advantages, but also offer a handle for optimizing electrical properties, and yield enhanced efficiency—as compared to the homopolymers—when used in devices, such as photodiodes and light-emitting devices.

For completeness, we differentiate here between three possible kinds of blending partner for a conjugated polymer that have been described in the recent literature. A first group consists of single molecules, macromolecules, oligomers, dyes etc and is mainly used as molecular dopants, colour converters [46, 47], phosphorescent emitters [48, 49] or emission line narrowing additives [46, 50], but also in photovoltaic cells [51]. The idea behind colour conversion, i.e. the addition of red and green dyes into a blue-emitting polymer, in order to absorb the blue light emitted by the polymer and convert it to red and green light, is also used successfully in full-colour vacuum-deposited ‘small molecule’ OLED displays [52, 53].

A second group of compounds that have been used in blends with conjugated polymers since the early days is inorganic and organic nanoparticles, in particular fullerenes [11, 54, 55]. Polymers have been blended with C_{60} , and a C_{60} derivative, (phenyl-(6, 6')- C_{61})-butyric acid methyl ester (PCBM) [13, 56, 57], but also with CdSe nanoparticles [58, 59], TiO_2 [18, 60, 61] and SiO_2 [61] for the fabrication of efficient polymeric solar cells, and lasers. One reason for the popularity of n-type nanoparticles as blend components is the lack of a wide range of n-type (electron transporting) conjugated polymers.

Finally, a third group of blending partners for conjugated polymers consists of other polymers: conjugated polymers, non-conjugated polymers, and even conjugated/non-conjugated block copolymers [62]. There are several incentives for blending conjugated polymers with other polymers. Conducting polymers were mixed with insulating polymers [63–67] to tune the conductivity [65, 68], to externally induce order for the generation of polarized emission [64, 66, 69, 70], or to dilute the polymer in order to decrease aggregation [71, 72] or to study the electron transfer between individual polymer chains [67, 73]. It was found that as little as 1% of conducting polyaniline (PANI) in PMMA is needed to make the blend PANI/PMMA conducting. The reason was that because of phase separation a fractal-like conducting network is formed upon solvent evaporation [68, 74]. Polydiocylfluorene (F8) is a popular light-emitting polymer with high mobility [75] and blue emission colour [76], but aggregation and thermal crystallization of F8 result in an undesired absorption in the red [71, 77–80]. Weinfurter *et al* [81] reported that the low molecular weight parts of the polymer are responsible for the aggregation. It was found that this aggregation can be eliminated by blending F8 with PS, yielding molecularly dispersed F8 for 1% of F8 in PS [71].

In section 6 we will specifically concentrate on the morphology and performance of semiconducting, conjugated polymer blends in devices. But before that, we will first, in section 4, summarize some methods to study the morphology of polymer/polymer blends, and then, in section 5, discuss charge and energy transfer aspects in blends of semiconducting polymers.

4. Methods for morphology studies of blends

Modern microscopic and spectroscopic methods have been used to evaluate the morphology of spin-coated thin films of phase-separated polymer blends. We can classify them into two groups: those methods applicable to polymer blends in general and those specifically useful for LEP blends. Furthermore, they can also be divided into methods for investigating the in-plane morphology (various types of microscopy), and methods for depth profiling. We refer to earlier reviews [82, 83] for a more complete coverage of relevant techniques.

The in-plane morphology of thin films of two- and three-component polymer blends [31, 32] has been studied primarily by atomic force microscopy (AFM) in contact mode [28, 31, 32, 84] and Tapping ModeTM [28] and lateral force microscopy (LFM) [32, 85, 86], as well as force modulation microscopy [87]. The materials in the blend can be distinguished either by differences in their mechanical properties [34, 85, 87] or by removal of one of the phases by a selective solvent [28, 31–33, 38, 88]. Scanning electron microscopy (SEM) [63], environmental SEM (ESEM) [183], transmission electron microscopy (TEM) [12, 66, 89–91] and photoemission electron microscopy (PEEM) [92] have been used occasionally to image the structure of the phase-separated domains. Optical microscopy, such as fluorescence microscopy, is a simple alternative useful in the case of LEP blends, provided that the domains are of micrometre size. The latter is particularly useful in addition to AFM topographic images, for identifying the polymer components, if they have different emission spectra. Near-field scanning optical microscopy (SNOM) has shown great potential

in monitoring fluorescence emission intensity with a high spatial resolution (~ 100 nm) for polymers [93, 94] and fluorescent polymers [95–97, 162, 163, 184]. The composition of the domains can also be analysed by (micro-)Raman spectroscopy [98–100]. Other techniques, which map the phase separation by probing lateral compositional differences, are near-edge x-ray absorption fine structure (NEXAFS) [101–103], and the mapping mode of secondary ion mass spectroscopy (SIMS) [104].

The distribution of polymer material, perpendicular to the film surface, i.e. investigation of vertical phase separation, are traditionally investigated by nuclear reaction analysis (NRA) [105–107], neutron scattering and reflectometry [108–110]. SEM-techniques [183] and the profiling mode of dynamic SIMS [102, 104] have recently shown to be powerful tools. In dynamic SIMS low energy ions (5 keV) sputter the sample, exposing successive layers, and the secondary ions, identified by mass spectroscopy, are monitored as a function of sputtering time (profiling). In the mapping mode, the focused ion beam is scanned over an area and at each point the secondary ions are collected and give a compositional map. By collecting compositional maps recorded for subsequently exposed layers, dynamic SIMS offers a novel way to obtain a three-dimensional picture of the phase domain structure with a depth resolution of 20 nm and lateral resolution of at most 120 nm [104]. In a similar way, AFM images collected for subsequent layers, exposed either by plasma etching [111] or selective dissolution [28, 38], can yield high resolution three-dimensional information of the phase domain structure.

In the case of semiconducting polymers, photoluminescence (PL) and EL spectroscopy [112, 113] can indirectly give information about the proximity of the blend components, based on evaluation of energy transfer processes between the blend components and resulting emission colour. These techniques were found to be superior to AFM when separations on the length scale of the exciton diffusion length are concerned [112, 113]. Time-resolved fluorescence spectroscopy is used to study the exciton dynamics and energy transitions between the blend components on an ultra-short timescale [114–116].

Finally, we also mention the surface potential microscopy technique, which allows the mapping of work function differences on the surface scanned by a metal-coated AFM-tip [117]. This technique has recently shown to be able to distinguish the components of a blend of semiconducting polymers based on their differences in work function [118–120]. For this measurement the substrate has to be electrically connected to the grounded base plate of the AFM instrument. The work function is mapped using a two-pass technique, also called Lift ModeTM. During a first pass of the tip, the topography of the sample surface is measured. Then the tip is lifted to a selected height and held at this constant distance above the surface during the second pass, tracking the measured topography. During this second pass a potential is applied to the tip with respect to the substrate. The potential is modulated and the phase shift caused by the contact potential difference between the tip and the sample, is annihilated at each point of the scanned surface. This technique has a slightly lower resolution than AFM.

5. Energy and charge transfer in blends

5.1. Structure of efficient devices

For conjugated polymer blends the formation of domains in a thin film has more than only morphological consequences. If the blend consists of polymers with preferential electron- or hole-transporting abilities, then the electronic structure and behaviour of such a blend film can be very complex. For electronic devices, the interface between the different functional polymers is crucial for the performance. It is not uncommon that the use of blends in technological applications is met with scepticism, precisely for this reason, and the synthesis of (co)polymers with new properties is preferred.

A fundamental difference between copolymers and blends is that the active functional units reside on one single polymer chain (intra-chain) in a copolymer, while in a blend they may be on different chains, which are less or more separated from each other, depending on the blend morphology. Blending electron-transporting (n-type) and hole-transporting (p-type) polymers has particular advantages, and the complex structure, provided it can be controlled, is a flexible tool for optimizing the device performance. This type of self-ordering in the polymer blend film can be exploited to create an interpenetrating network [11, 13, 121], where the contact area between the n- and p-type polymer is maximized. This morphology has appeared to be particularly favourable for photovoltaic devices. The maximized interface area is beneficial for the solar energy conversion efficiency, provided that a continuous path is maintained in each phase for the appropriate charge carrier to travel to the electrode (figure 1(a)). Indeed, for solar cells the electron-hole-pair (exciton) is generated by light in one of the polymers, usually the polymer with the narrowest bandgap (the absorber), and diffuses to the polymer/polymer interface, where it can dissociate into an electron and a hole. The electron and hole are then separated and transported to the opposite electrodes. In the context of photodiodes, the polymer through which the electron is transported is often called the (electron-)acceptor polymer, and the one that transports the hole the (electron-)donor. The exciton generation has to happen in the vicinity of an interface, i.e. within a distance comparable to the exciton diffusion length. The active region for photogeneration of excitons that can contribute to the current extends therefore only to 10 nm from the polymer/polymer interface [122–124]. An additional requirement for current generation is that the carriers can be collected efficiently at the electrodes, which means that the contacts should be ohmic. Ideally, the work function of the cathode should match the LUMO of the electron-accepting polymer closely while the work function of the anode matches the HOMO of the (electron-)donor polymer. This, together with the requirement that one electrode needs to be transparent, limits the choice of electrode materials. For an updated overview of organic solar cells and more details about dispersed heterojunctions, see also [185].

For an efficient LED structure the requirements are complementary. It is beneficial for the charge injection efficiency if a hole-transporting (p-type) polymer is preferentially located near the hole-injecting electrode (high work function anode), and an electron transporting (n-type) polymer near the electron-injecting electrode (low work function cathode) (figure 1(b)). Moreover, as in the case of photovoltaic devices, an LED structure needs to have continuous paths through these polymers from the electrodes to the place for exciton generation. Furthermore, the light-emitting component (which can be one of these previously named polymers, or a third component) should ideally be located such that the electron and hole reach it simultaneously, and so that the exciton is formed and recombines as far away from the electrodes as possible, to avoid luminescence quenching. Exciton formation will occur near an interface where electron and hole meet. For light to be emitted, the exciton energy then has to be transferred to the light-emitting component. This component needs therefore to be situated within the exciton diffusion length from the place where the exciton was generated.

The art of producing efficient devices depends, hence, not only on the choice of polymers and their intrinsic properties (energy levels, mobility), but also has to do with adjusting the processing conditions so that an optimal structure is obtained for a particular device.

5.2. Charge transfer versus energy transfer

The fate of an exciton formed at or near a polymer/polymer interface is determined largely by the positions of the energy levels in each polymer. The main possibilities are

- (1) dissociation of the exciton into an electron and a hole with subsequent transfer of one of them to the other side of the interface
- (2) exciton energy transfer to the lowest bandgap polymer, followed by radiative recombination
- (3) non-radiative recombination.

Exciton dissociation is favourable when the difference in electron affinities and ionization potentials between the polymers is large, i.e. larger than the exciton binding energy.

Halls *et al* [123] demonstrated that charge transfer occurs at the interface between poly(2-methoxy-5-(2'-ethylhexoxy)-1,4-phenylenevinylene) (MEH-PPV) and the cyano-substituted polyphenylenevinylene (PPV) derivative, CN-PPV, making the MEH-PPV:CN-PPV blend an efficient photodiode [11, 12], whereas energy transfer occurs at the interface between PPV and CN-PPV, as well as between a silyl-substituted PPV, DMOS-PPV, and CN-PPV, making these couples useful for LED applications [125, 126]. PL quenching is used as an indication for efficient charge transfer. Generalization of these results, supported by quantum chemical calculations, led to the conclusion that large bandgap differences between two polymers favour energy transfer, and thus the use in efficient LEDs, while small bandgap differences favour charge transfer, and hence the use in efficient photovoltaic devices [123]. Among other investigations of p-n heterojunction photodiodes which are in agreement with this finding we can mention, for instance, the report of Onoda *et al* [127] of efficient charge transfer in photovoltaic devices of an n-type polymer, poly(*p*-pyridyl vinylene) (PPyV), with poly(3-hexylthiophene) (P3HT) with bandgaps of 2.4 and 2.2 eV, respectively, as well as that of Jenekhe and Yi [128] for photodiodes of PPV and the new n-type polymer poly(benzobisimidazolebenzophenanthroline) ladder (BBL), with bandgaps of 2.4 and 1.9 eV, respectively.

5.3. Energy transfer in blends

Exciton transfer between two polymers with different optical and electronic properties can happen according to the Förster-type energy transfer mechanism from the large bandgap polymer to the lower bandgap polymer [129, 130]. This mechanism is based on 'long range' dipole-dipole interaction and the energy transfer rate depends on R^{-6} , where R is the distance between the dipoles. The interaction range can be calculated and is usually only of the order of 10 Å. Two fundamental requirements for energy transfer via the Förster mechanism are

- (1) a good spectral overlap between the emission spectrum of the (energy) donor and the absorption spectrum of the (energy) acceptor, and
- (2) uniform mixing of the two species.

The transfer depends strongly on the orientation of the dipoles. Interchain interactions can however play a role, as discussed elsewhere in this issue [137]. The latter are very sensitive to film morphology and the solvent used during film formation [131].

The mechanism behind the enhanced EL efficiency observed in blends is not well understood. In numerous reports it is attributed to Förster-type energy transfer [62, 132–136]. Some fundamental problems, however, exist with the application of the Förster interpretation. For instance, in the blend of two phenylquinoline derivatives, poly(2,2'-(2,5-thienylene)-6,6'-bis(4-phenylquinoline)) (PTPQ) and poly(2,2'-(biphenylene)-6,6'-bis(4-phenylquinoline)) (PBPQ) negligible energy transfer is observed, and EL enhancement is instead assigned to spatial confinement of excitons in the dispersed minority component, which leads to enhanced exciton stability and electron-hole recombination efficiency [138]. Buckley *et al* [139]

showed by time-resolved PL spectroscopy that exciton migration to the nearest neighbour sites contributes to the dynamics governing the energy transfer in a polyfluorene blend.

6. Literature overview of conjugated polymer blend devices

One of the limiting factors for the application of polymer blends in devices is that few suitable n-type polymers are available, because they are hard to synthesize. It was perhaps for this reason that blends of polymers with nanoparticles, in particular C₆₀, were the first to be applied in photodiodes in the early 1990s [11, 54, 55, 140]. The use of polymer/polymer blends in photodiodes was reported shortly after that [12, 121, 132]. In both cases phase separation was observed [12, 13], and enhanced energy conversion efficiency was reported compared to single or multilayer devices [12, 121, 141, 142]. Both types of photodiode, the polymer/C₆₀ type as well as the polymer/polymer type, are under continuous further development.

In 1994, a few years after EL in conjugated polymers was discovered, polymer/polymer blends were applied for the first time in LEDs [40, 143]. In one report, a blue-emitting blend of poly(*p*-phenylphenylene vinylene) (PPPV) and poly(9-vinylcarbazole) (PVK) was used [40]. The advantage of the simplified preparation technique is pointed out and a maximum EL efficiency of 0.16% photons/electron is reported for 2% PPPV in PVK. In another report, various conjugated polymers were blended and a voltage-tunable EL colour was observed [143]. Enhanced EL efficiency compared to the homopolymers was also observed in many blends [62, 90, 132, 144–148]. Later, polymer blends were also successfully used in the quest for white light EL [19, 149–153], based on a cascading effect of energy transfer between polymers with different bandgaps [19, 152]. Colour tuning is particularly important for display applications, such as full-colour television and computer screens, and matching the emission spectrum with the standard PAL colours is a specific challenge.

For laser applications polymer/polymer blends have also shown some benefits. Blending PPV derivatives resulted in the lowering of the threshold for amplified spontaneous emission by more than an order of magnitude, as compared to the homopolymers [20].

6.1. Morphology

6.1.1. Conjugated polymer blends for LEDs. Phase separation has been observed in several conjugated polymer/polymer blends.

To the best of our knowledge morphological studies of conjugated polymer blends, by AFM, were first reported in 1994 by Berggren and coworkers [143]. EL with voltage-controllable emission colours was observed when two poly(3-alkyl)thiophene derivatives, selected from the following series, were blended together: poly(3-cyclohexyl 2-methylthiophene) (PCHMT), poly(3-cyclohexylthiophene) (PCHT), poly(3-(4-octylphenyl)-2, 2'-bithiophene) (PTOPT) and poly(3-octylphenylthiophene) (POPT), synthesized by side-chain substitution yielding systematic control over bandgaps and conjugation lengths. To try to understand this phenomenon, the thin films of the spin-cast blends were studied spectroscopically and microscopically. Absorption spectra showed features from both polymers in the blend. PL spectroscopy gave evidence for a partial exciton transfer from the high bandgap polymer to the low bandgap polymer, while the efficiency varied with the fraction. By optical and luminescence microscopy, no microstructure was observed in the blend fraction. However, by AFM, evidence of phase separation was observed. From the comparison of samples with different mole fractions, the phases were identified. The diameter of the minority phase is 50–200 nm, depending on blend and blend ratio. At this point, based on the incomplete exciton transfer, the conclusion is drawn that at least one of the phases is pure homopolymer. Later, this was restated [149] as that the possibility is ruled out for a major

fraction of the film to be a molecular blend, and that phase separation must occur on a small scale. The height differences in the films are 5 nm (film thickness 30–100 nm). SEM was also used and confirmed the phase separation in the blend films. In this early work, SNOM is already mentioned as an interesting technique for future blend characterizations [149].

Similar polythiophene derivatives were used for the fabrication of a white-emitting diode, namely poly(3-methyl-4-octylthiophene) (PMOT), PCHT and PTOPT, together with an inert matrix polymer of PMMA to partially block the efficient exciton transfer between the high and low bandgap polymers [150]. Morphological studies by Tapping-Mode AFM were reported for blends of PCHT and PCHT:POPT in an inert polymer, poly(2, 6-dimethyl-1, 4-phenylene oxide), PPO [154]. Enhanced EL efficiency was also reported for blends of poly(3-hexylthiophene) (P3HT) with MEH-PPV as compared with the homopolymers in the same device structure with a Ca cathode and ITO anode [132]. Only EL and PL have been investigated and no morphological studies were included here either. In a similar way the blend of P3HT with poly(9-vinylcarbazole) (PVK) was investigated, and the EL efficiency was also here enhanced by blending, with an optimized value of 0.2% photons/electron for 2% P3HT in PVK [144].

Yang *et al* [89] investigated the morphology of a large number of blends based on MEH-PPV by TEM and found structures of nanoscale size (10–100 nm). Ding *et al* [136] blended two polymers (called I and II) and observed phase separation with AFM. Blend ratio variation resulted in roughness changes of the films, spin-coated in chloroform. When used in an LED device, all blend ratios gave pure green emission from polymer II, through complete energy transfer by the Förster mechanism, except in the blend with a higher minority fraction, where incomplete energy transfer is observed. This is interpreted as due to the presence of larger domains of pure polymer I. The energy transfer in a blend of a conjugated–nonconjugated multiblock copolymers (CNMBC), poly(1, 3-propane-dioxy-1, 4-phenylene-1, 2-ethenylene(2, 5-bis(trimethyl-silyl)-1, 4-phenylene)-1, 2-ethenylene-1, 4-phenylene) (DSiPV), with MEH-PPV led to enhanced emission of MEH-PPV. An EL efficiency improvement of 500-fold was observed for some blend ratios [62]. However, no phase separation was observed in the MEH-PPV-based blends with DSiPV [131, 145]. Finally, we mention that phase separation was also imaged by AFM in a three-component conjugated polymer blend, with PVK as the major component, which acted as the inert matrix as well as excitation energy donor [153].

6.1.2. Polymer/C₆₀ photodiodes. Blends of poly(2-methoxy-5(3', 7'-dimethyloctyloxy)-1, 4-phenylene vinylene) (MDMO-PPV) as electron donor and C₆₀ or the highly soluble methanofullerene (phenyl-(6, 6')-C₆₁)-butyric acid methyl ester (PCBM) as electron acceptor were studied by AFM and show phase separation. The phase separation depends strongly on the solvent (toluene and chlorobenzene) used [13]. In blends of MDMO-PPV with C₆₀ a strong dependence was observed of the photocurrent and open circuit voltage of the photodiodes on the solvent. Non-aromatic solvents (tetrahydrofuran and chloroform) yielded smaller photocurrents and higher open circuit voltages than devices made with aromatic solvents, such as xylene. This difference is ascribed to the solvation-induced polymer morphology, which was imaged by AFM [155]. PCBM and C₆₀ were also studied in blends with the donors poly(3-octylthiophene) (P3OT) and MDMO-PPV, spin-coated from xylene solutions. The images are compared and the conclusions are that MDMO-PPV:PCBM (1:3) formed a rather homogeneous film without pinholes (though regular structure can be observed in the images), while P3OT:PCBM (1:2) blends form strongly phase separated films (several micrometres) in which pinholes (~30 nm deep) were observed. However, P3OT:C₆₀ (1:1) formed pinhole free and homogeneous films on the sub-micron scale [156].

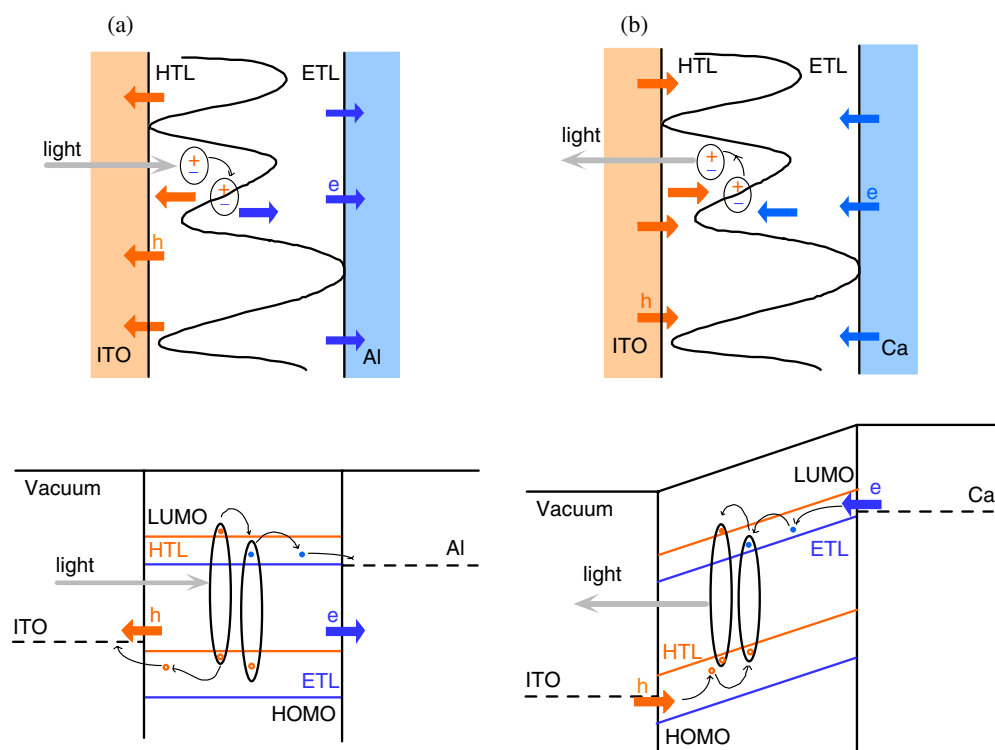


Figure 1. (a) Schematic representation of a polymer thin film photovoltaic device, made of an electron-transporting (ETL) and a hole-transporting (HTL) polymer, with an arbitrarily chosen mixing profile, an ITO anode and an Al cathode: (top) film cross section; (bottom) energy diagram. An exciton is generated by light in one of the polymers, here the lowest bandgap HTL. The exciton separates to a nearby interface, where it separates into an electron and a hole. The electron is transferred to the polymer with the largest electron affinity (ETL) and transported to the metal cathode. The hole is transported in the polymer with the lowest ionization potential (HTL) to the ITO anode. (b) Schematic representation of a polymer thin film LED, made of an electron-transporting (ETL) and a hole-transporting (HTL) polymer, with an arbitrarily chosen mixing profile, an ITO anode and a Ca cathode: (top) film cross section; (bottom) energy diagram. An exciton is formed at the interface between the two polymers. The exciton energy is then transferred to the lowest bandgap polymer, where it can recombine and emit light.

6.1.3. Polymer/polymer photodiodes. In the first reported studies of polymer/polymer blends for photodiodes MEH-PPV and the cyano-substituted PPV derivative CN-PPV were used [12, 121, 132]. Phase separation on the scale of 10–100 nm was observed in this blend made of 100 nm thin films spin-coated from a chloroform solution. The films were examined by TEM after selective staining with FeCl_3 [12]. Increased conversion efficiency has also been demonstrated in this blend photodiode, compared to single- or multilayer devices [12, 121, 157]. Next, blends of MEH-CN-PPV and a regioregular phenyl-octyl-substituted polythiophene, POPT, were studied [121, 158]. The morphology of these blends has been investigated by AFM, showing the phase separation on a length scale of 200–400 nm. After cross-sectioning of the spin-coated layer also the vertical phase separation has been imaged by AFM [158]. Blends of PPV derivatives, such as PPV:CN-PPV, MEH-PPV:CN-PPV and DMOS-PPV:CN-PPV, were investigated further and compared in terms of their PL and photovoltaic efficiencies [123]. This study deepened the understanding significantly of the exciton dynamics at the polymer/polymer interface in blends. In blends with a large bandgap difference, the exciton more likely transfers

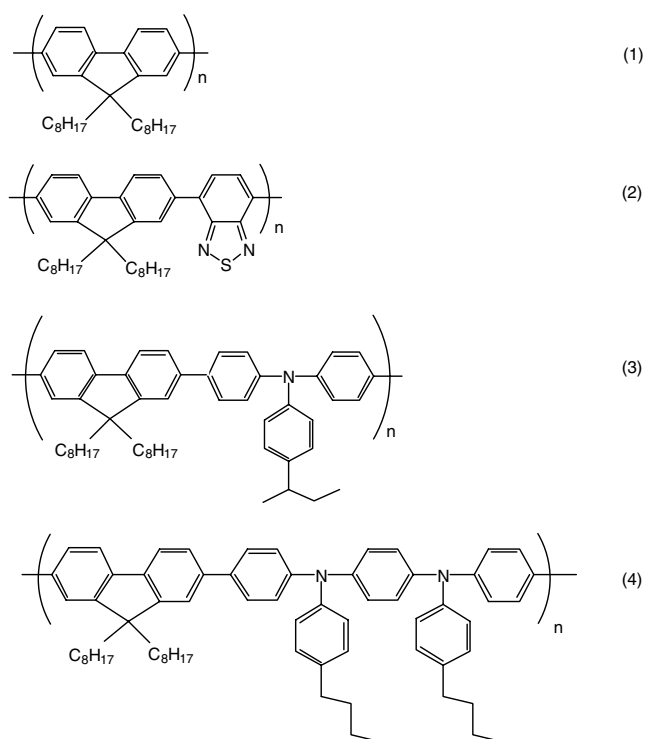


Figure 2. Chemical structures of poly(dioctylfluorene) and poly(dioctylfluorene) copolymers: (1) F8, (2) F8BT, (3) TFB and (4) PF8BT (see full names in the text).

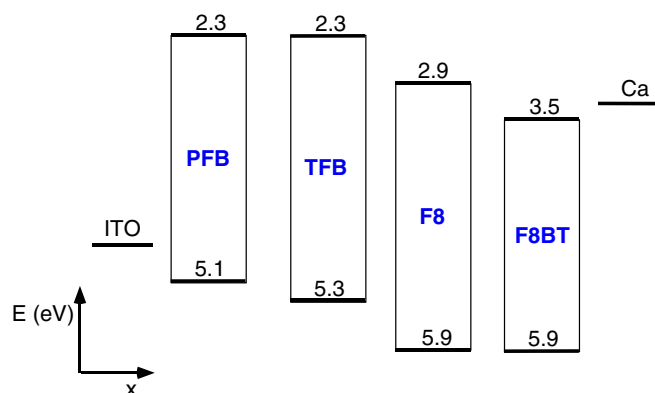


Figure 3. Energy diagram of the poly(dioctylfluorene) and poly(dioctylfluorene) copolymers: PF8, TFB, F8 and F8BT, giving their HOMO and LUMO positions.

its energy to the other blend component, without separation of charges, while in blends with small bandgap difference, excitons are more likely to undergo charge separation and transfer of one charge across the polymer/polymer interface. No further morphological studies were reported here for these blends. Onoda *et al* have also reported improvement of photovoltaic effects in poly(3-blends of alkylthiophene) (P3AT) and cyano-substituted poly(*p*-phenylene vinylene) (CN-PPV), originated from fractal network geometry and interfacial photoinduced

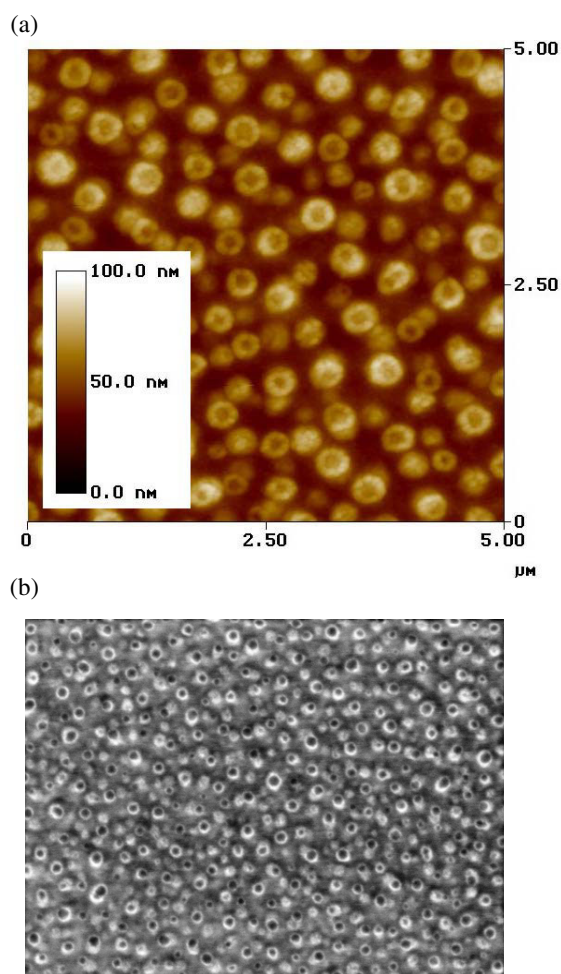


Figure 4. (a) Tapping-Mode AFM topographic image (Nanoscope IIIa Dimension 3100, Digital Instruments, Santa Barbara, USA) of a thin film of the blend F8:F8BT (75:25) spin-coated from a 14 g l^{-1} solution in xylene on a substrate of ITO, precoated with 70 nm poly(ethylene dioxythiophene) doped with PS sulfonic acid (PEDOT:PSS), also called Baytron P (Bayer, Ludwigshafen, Germany). (b) Field emission SEM image (LEO 1530) of a thin film of the same blend F8:F8BT (75:25) as in (a). The long side of the image is $16 \mu\text{m}$. Measurement conditions: In-Lens detector, acceleration voltage 2 kV, magnification $26\,000\times$, 7 mm working distance.

charge transfer between P3AT and CN-PPV. In this case, P3AT and CN-PPV acted as a donor and an acceptor, respectively [159].

SNOM has been used extensively to study the morphology of blends, and to identify the components by means of their luminescence behaviour. A considerable amount of work was reported by Hsu *et al* on PdOPV:PPV blends studied with SNOM [95, 160, 161]. Stevenson *et al* [162, 163] have reported similar studies for polyfluorene blends.

More recently, heterojunction photodiodes were reported, where a blend is used as the donor layer and C_{60} as the acceptor layer. These blends, made of a PPV derivative, BEHP-PPV, and various polythiophenes, e.g., PBOPT, yield higher efficiencies than a donor layer made of the corresponding homopolymers in devices with C_{60} as the acceptor layer. The blend does not show significant phase separation larger than the AFM instrument can resolve (10–20 nm).

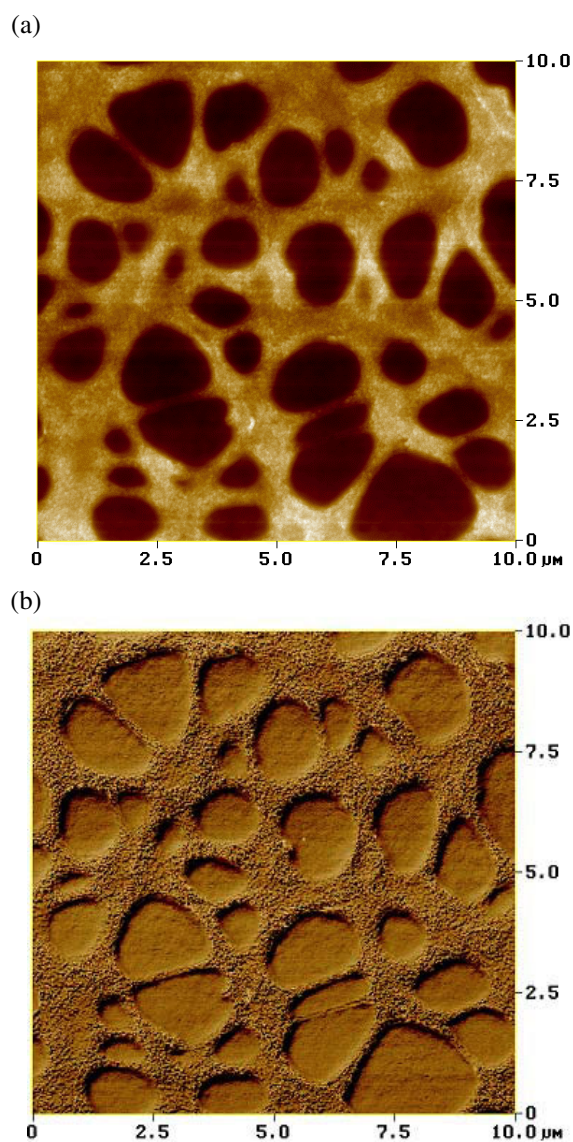


Figure 5. Tapping-Mode AFM images of a thin film of the blend F8BT:TFB (1:1) spin-coated from a 14 g l^{-1} solution in xylene on a substrate of ITO, precoated with 70 nm PEDOT:PSS (a) topography. (b) phase image.

This efficiency enhancement is interpreted as due to Förster transfer from the BEHP-PPV to the polythiophene and the fact that the latter has a more efficient charge separation at the interface with C_{60} than the former [164].

7. Polyfluorenes

Following the success of poly(9, 9-dioctylfluorene) (F8) as a highly efficient blue emitter [165], many reports on the synthesis of several polyfluorene copolymers [166–

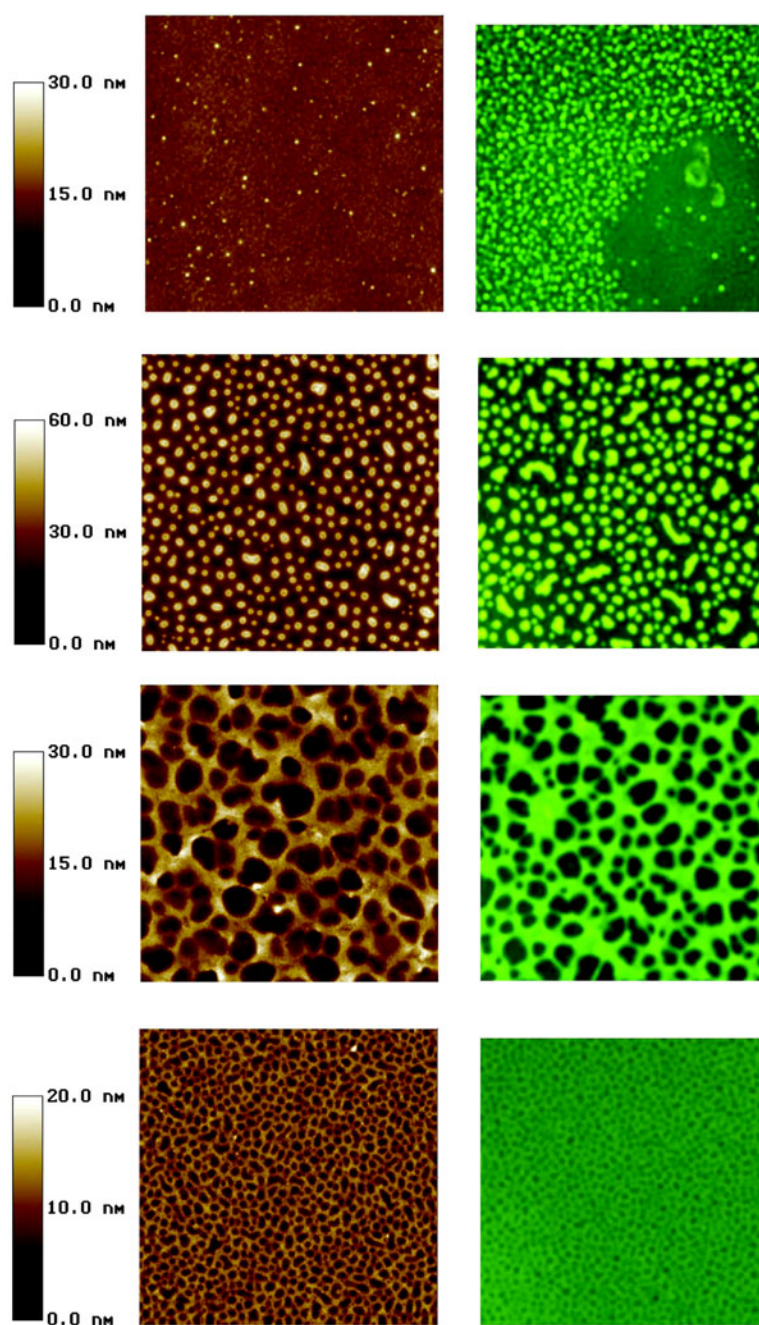


Figure 6. PL microscopy images (under blue excitation) (right) and Tapping-Mode AFM topographic images (left) of the blend F8BT:TFB spin-coated from a xylene solution, with varied blend ratio. From top to bottom the F8BT/TFB blend ratios are 1:10, 1:2, 1:1 and 2:1.

172] and their application in LEDs appeared [75, 80, 165, 166, 173–178]. Blends of polyfluorene copolymers have been used extensively for application in photodiodes and

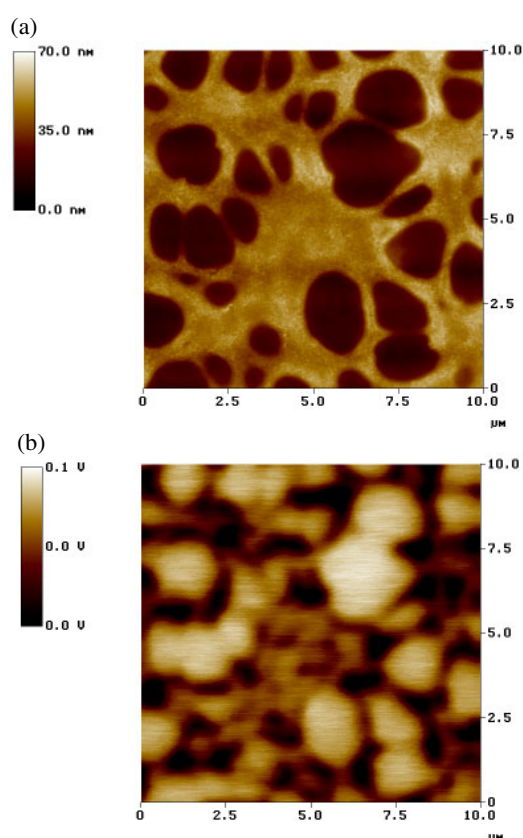


Figure 7. AFM topography and scanning surface potential microscopy images, taken in Lift Mode, of blend F8BT:TFB (1:1), spin-coated from a xylene solution.

LEDs [47, 76, 112, 113, 120, 141, 178–180]. The homopolymer F8, the green-emitting alternating copolymer poly(2, 7-(9, 9-di-n-octylfluorene-alt-benzothiadiazole) (F8BT) and the hole-transporting polymers poly((9, 9-dioctylfluorene)-alt-N-(4-butylphenyl)diphenylamine) (TFB) and poly((9, 9-dioctylfluorene)-alt-bis-N, N'-(4-butylphenyl)-bis-N, N'-phenyl-1, 4-phenylenediamine) (PFB) [75, 174] are the main components used in these devices. The chemical structures of these polymers are shown in figure 2 and energy levels in figure 3.

7.1. F8BT:PFB

An extended morphological and photovoltaic study of a blend of two polyfluorene copolymers, namely F8BT and PFB, was carried out by Arias [39]. In this work, the morphology of the F8BT:PFB (1:1) blend was imaged by optical microscopy, AFM, SNOM and environmental SEM (ESEM). A strong dependence on the solvent was found, with xylene solutions resulting in micron-sized phase domains and chloroform solutions yielding an intimately mixed blend. Strong PL quenching was observed in F8BT:PFB (1:1) spin-coated from chloroform, indicating efficient charge transfer from F8BT to PFB. A less strong quenching of PL was observed for the same blend spun from xylene [141]. By current–voltage measurements under illumination, higher conversion efficiencies were observed for photodiodes of an intimately

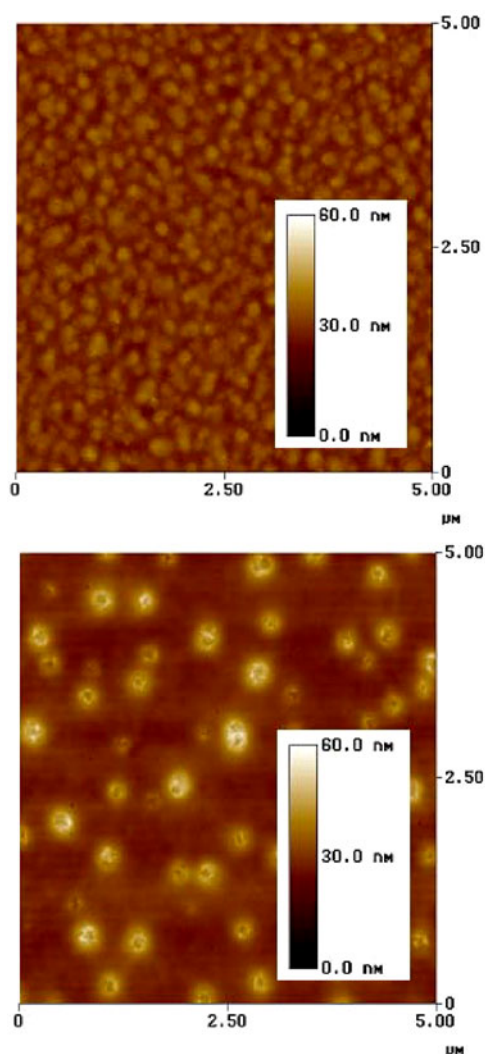


Figure 8. Tapping-Mode AFM topographic images of (a) a thin film of F8:F8BT:TFB (76:4:20) spin-coated from a xylene solution. (b) A thin film of F8BT:TFB (1:5) spin-coated a xylene solution.

blended mixture of F8BT and PFB, compared to rougher mixtures. However, in the case of large domain structures, the efficiency was only slightly lower. The latter was interpreted as an indication for the fact that the domains are not pure components, and that traces of minority components inside the domains are enough to obtain charge transfer [141]. However, the efficiency of the device improves when the polymers are intimately mixed in larger fractions of the film. Vertical and lateral phase separation in these F8BT:PFB blends were investigated by several techniques, such as AFM [179], SNOM [162] and Raman spectroscopy [98]. It was confirmed that the green-emitting F8BT-rich domain is the one forming the walls in the phase-separated structure, which are protruding from the surface. Control over the domain size was also achieved by heating the substrate [179], and drying time variation [141]. Morphologies of dip-coated and spin-coated films were compared.

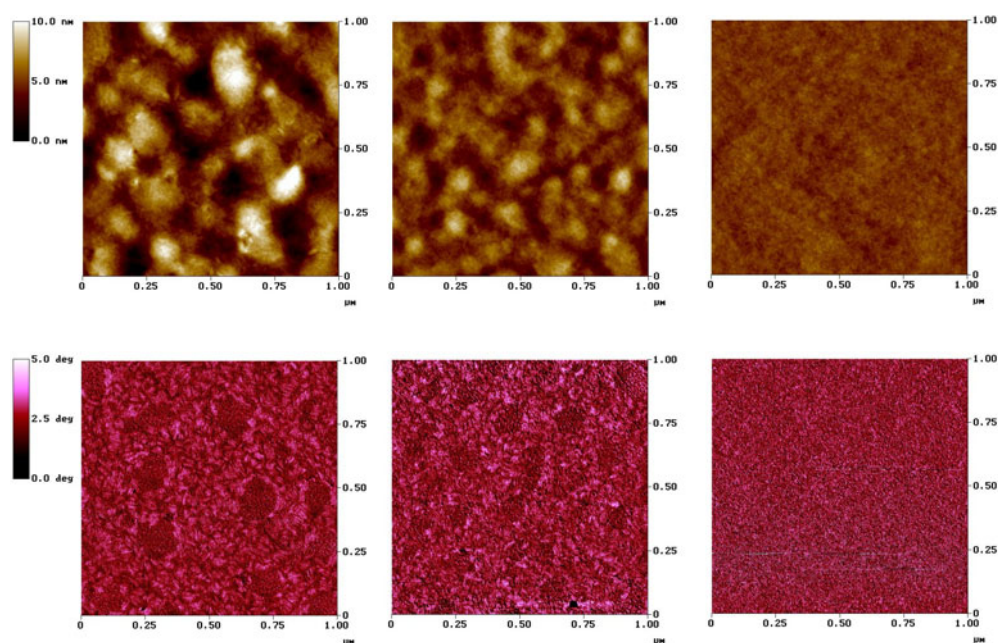


Figure 9. Tapping-Mode AFM topographic image of a thin film of the blend F8:F8BT:TFB (76:4:20), spin-coated from different solvents. From left to right: xylene, toluene and chloroform.

Furthermore, *in situ* fluorescence microscopy was used to picture the drying process of the film and the formation of phase-separated domains [141]. Finally, vertical segregation was promoted in polymer blend photodiodes by surface modifications, such as the adsorption of self-assembled alkyltrichlorosilane monolayers [39].

7.2. F8:F8BT

F8:F8BT blends are used for green-emitting LEDs, particularly the (95:5) w/w blend, also called 5BTF8 [176, 177, 180]. The morphology and optical properties of this blend, with 5, 15 and 25% F8BT, have been studied by AFM and PL and EL spectroscopy [112, 113]. The efficient charge transfer from F8 to F8BT is expressed in the green PL and EL emission from the F8BT. Nevertheless, the surface structure of F8:F8BT (75:25), observed by AFM, shows domains of 200–300 nm in diameter protruding out of the surface (figure 4(a)). It was concluded that these domains cannot be pure homopolymer, and that at least the F8-rich domain should contain a trace of F8BT, which is responsible for the absence of blue emission from F8. However, when the blend film was treated with acetone, a very poor solvent for the polyfluorene components, and when a film of 2-(4-biphenyl)-5-butylphenyl-1,3,4-oxadiazole, PBD, (75 wt%) in PMMA was spin-coated on top from an acetone solution, the blue emission appeared in the PL and EL spectra while no change in the morphology could be detected by AFM. This was interpreted as a promotion of the mobility of the components in the blend induced by contact with a poor solvent, leading to completion of component separation [113]. A SEM image of the (75:25) polymer blend film, without metal coating, was collected by a field emission SEM (LEO 1530), using an acceleration voltage of 2 kV and the In-Lens detector (figure 4(b)). The contrast in this image does not only confirm the

topographic structure of the blend, but is also partly due to a difference in electron density in the blend. SNOM was used to identify the components in the blend and it was found that the F8-rich phase is the one protruding from the surface [163].

7.3. F8BT:TFB

The green–yellow blend F8BT:TFB (1:1) w/w consists of F8BT and the hole-transporting polymer TFB. LEDs produced with this blend have an exceptionally high brightness and high efficiency at low operation voltages [181, 186]. The emission switches on at operation voltages of 1.9 V and has a typical peak efficiency of 16 lm W^{-1} at 2.2 V and 100 cd m^{-2} . The luminance level of 1000 cd m^{-2} is achieved at 2.4 V and $30\,000 \text{ cd m}^{-2}$ at 5 V [99, 181]. Systematic investigations of the F8BT:TFB (1:1) morphology by Tapping-Mode AFM have shown that the thin film surface is rough [120, 181, 186] and consists of well-like micrometre-size domains (dark wells) in a homogeneous phase (bright areas) (see figure 5(a)). The corresponding phase images show a clear difference in roughness between the two domains (figure 5(b)). Furthermore, the morphology changes drastically with the blend ratio when thin films are spin-coated to the same film thickness. It changes from isolated spikes, sticking out of the surface for low F8BT fractions (1:10) w/w, to the above described wells of $1 \mu\text{m}$ diameter for (1:1) w/w. For even higher F8BT fractions the morphology evolves to a less rough structure with smaller wells of 200–300 nm diameter for (2:1) w/w (figure 6). The (1:1) ratio is the one that produced the roughest surface topography. Changing the molecular weight of the components will also modify the morphology [181, 182]. By optical fluorescence microscopy under blue illumination the domains can be distinguished, since F8BT absorbs the blue light and emits green, while TFB does not and remains non-emitting (figure 6). The wells in the (1:1) blend were thus identified as dominantly consisting of TFB and the homogeneous phase as rich in F8BT.

Figure 7 shows the map of the relative work function, as measured by scanning surface potential microscopy. In the work function image bright areas indicate lower work function and darker areas correspond to higher work function. The scale has been determined by a calibration using a sample with Au and Al stripes. This result indicates that TFB-rich regions have a higher work function (by about 150 meV) than F8BT-rich domains. Though this is qualitatively in agreement with our expectations based on the p-type character of TFB and n-type character of F8BT, the measured quantitative difference in work function is likely to be smaller than the difference between pure TFB and F8BT work functions. The reasons for this are firstly that the domains are not pure homopolymer due to incomplete separation of the components, and secondly that the electrical field at the interface may not be completely developed due to the small lateral size of the domains and the small number of charge carriers. By micro Raman spectroscopy it was indeed shown that the phases are not pure components [99]. This explains how the energy transfer from TFB to F8BT, leading to light emission by the F8BT, can happen efficiently within the domains, as well as at the domain interface. This is similar to what was concluded by Morgado *et al* for the F8:F8BT blend [112, 113], and shown for the blend F8BT:PFB by Arias *et al* [98].

Still, it is very surprising that precisely this blend ratio (1:1), which has the largest phase domains, is the one that yields the highest EL efficiency for the F8BT:TFB blend. The reason for this unexpected relation between film morphology and device efficiency in this blend, which is opposite to the relation in photodiodes, is still not understood. One possible explanation might be the confinement of one phase (TFB) to a very thin area, creating locally a very high electric field that helps the charges of one type (holes) to overcome the barrier at the polymer–polymer interface and recombine, thus resulting in F8BT emission [181].

In order to understand the difference in performance of F8BT:TFB with F8BT:PFB devices, we compare the energy levels of the F8BT:PFB and F8BT:TFB blends, and the consequences this has on the energy transfer (figure 3). F8BT has a bandgap of 2.4 eV, while TFB and PFB have bandgaps of 3.0 and 2.8 eV, respectively. The band offsets in the F8BT:TFB blend are 0.6 eV for the HOMO and 1.2 eV for the LUMO, while in F8BT:PFB they are 0.8 and 1.2 eV, respectively. In both cases the band offsets are sufficient for charge transfer. The bandgap difference in F8BT:TFB is 0.6 eV, while in F8BT:PFB it is only 0.4 eV. Based on the bandgap difference, we can conclude that excitons in F8BT:PFB are more likely to undergo charge transfer than in F8BT:TFB, where energy transfer will be favourable [123]. This is confirmed by the absence of PL quenching in F8BT:TFB [39].

7.4. F8:F8BT:TFB

Another efficient blend for LEDs is the green-emitting three-component blend F8:F8BT:TFB (76:4:20), which contains the host polymer, F8, the green-emitting copolymer, F8BT, and the hole-transporting polymer, TFB. The EL efficiency of this blend is considerably higher than for F8:F8BT, with the same F8/F8BT ratio, while the emission colour is the same. The presence of the hole-transporting component, TFB, improves the hole-injection from the electrode and the transport of the holes through the layer. Because of its role in the device as hole-transporting layer, it is interesting to find out where the TFB component is located in the blend device structure. Ideally, a layer of TFB should be located near the hole-injecting electrode. The Tapping-Mode AFM images of the topography of a thin film of this tri-blend, spun from a xylene solution, show quasi-circular islands with a diameter ranging from 100 to 400 nm, surrounded by a lower background. The height of the peaks varies between 10 and 25 nm (figure 8(a)). The thin film morphology of this green-emitting blend F8BT:F8:TFB is less rough than the binary blend without the F8 component but with the same F8BT:TFB ratio (1:5) (figure 8(b)). We interpret this tentatively as an indication that the homopolymer F8 lowers the enthalpic interactions in the ternary blend as compared to the binary one. Furthermore we found a strong dependence of the morphology on the solvent. Thin films were spin-coated to the same film thickness from polymer solutions in a series of solvents with different boiling points and solubility parameters. Substitution of the xylene by solvents toluene and chloroform decreases the size of the phase-separated domains. Figure 9 shows AFM height and phase images for films spun from xylene, toluene and chloroform solutions, respectively. The constant film thickness of 80 nm was obtained by adjusting the spin speed and acceleration for each of the solvents. For chloroform solutions, phase separation domains were not detectable in AFM, and thus smaller than about 50 nm. In parallel, a clear difference in the initial device efficiency (lm W^{-1}) versus voltage is observed for the different solvents. The peak efficiency at 3 V was 50% larger for toluene than for xylene, and more than double the maximum efficiency (at 4.5 V) for devices made from polymers dissolved in chloroform. The highest initial efficiency was hence observed for toluene, which produced the second-largest domain size (figure 10). This indicates that there appears to be an optimal domain size that produces the highest luminescence efficiency for the blend. More investigations of this morphology–efficiency relation are needed in order to be able to draw conclusions about this optimal morphology. Furthermore, we observed that the F8:F8BT:TFB devices made from toluene solution had a longer lifetime. The EL half-life time for devices operating at 100 cd m^{-2} at 70°C was 28 h for xylene, while over 900 h was reached for toluene (results not shown). Better understanding of the decay mechanisms of these devices is required to be able to understand this difference in life times. Though morphology of the film is important, it cannot at this moment be excluded that other factors play a crucial role in the lifetime of LEP devices.

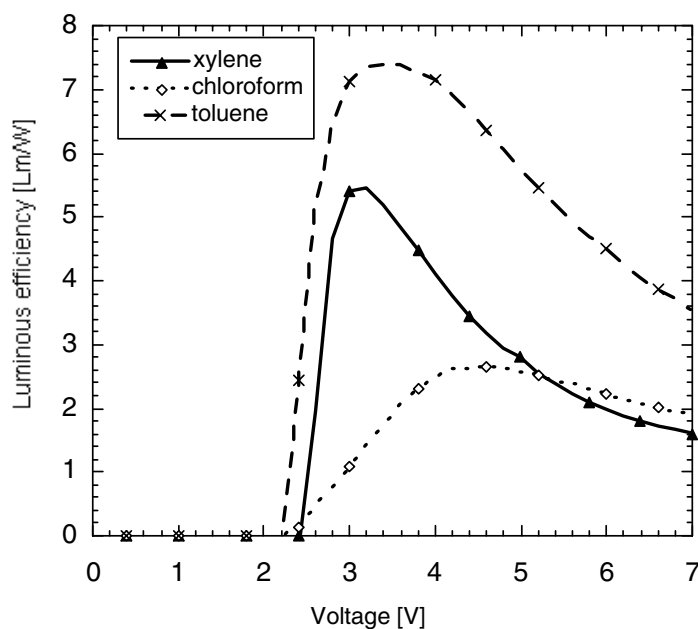


Figure 10. EL efficiency (1 m W^{-1}) versus voltage characteristics of F8:F8BT:TFB (76:4:20) LEDs, spin-coated from different solvents: xylene, toluene and chloroform. The devices were made by thermal evaporation of a Ca layer and an Al overlayer (50 nm Ca, 300–600 nm Al) on top of the polymer film, and by encapsulating the device to protect it from moisture and oxygen.

8. Summary and future prospects

We have shown that the investigation of conjugated polymer blends is an active field of research, where progress has been made in terms of characterization and understanding of phase domain formation, and its implementation in device structures. Nevertheless, major challenges remain. First of all, despite recent progress, it is at present not straightforward to predict and to achieve control over the blend morphology for given polymer structures and film formation conditions. The manifold parameters involved in the spin-coating process, such as spin speed, concentration, blend ratio, molecular weight of the components and solvent volatility, offer a handle to optimize the film thickness, and morphology, but further systematic studies are needed.

The blend morphology, in its turn, has implications on the PL efficiency, and on the brightness and EL efficiency of polymer blend LEDs, as well as on the conversion efficiency in solar cells. Control over the morphology is therefore one of the crucial factors in device optimization. Some fundamental results were obtained, when similar PPV- and polyfluorene-based blends were compared in LED and photodiode device structures. From these studies it was concluded that, apart from the blend morphology, also the relative positions of the energy strongly affect the exciton dynamics at the interface between two polymers. These results give some guidelines, in terms of bandgaps and the relative positions of the HOMO and LUMO, for the selection of polymers for specific devices. It is obvious that charge transfer and energy transfer between the conjugated polymers are of critical importance for the optimization of the efficiencies of photodiodes, photovoltaic devices and LEDs made of polymer blends. It is, however, still not entirely clear what the desired morphologies are for photovoltaic and light-emitting devices, that yield an optimal electronic performance and long lifetime.

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