A.1 Ternary Phase Calculations

In order to dilute a solution-processed semiconductor (low band gap polymer) by blending with an insulator (high band gap polymer) it is necessary that the polymers are at least partially miscible (i.e. weakly segregating). In case of full miscibility no (macro-)phase separation takes place during casting and the semiconductor will be suitably diluted throughout the film within a single phase. In case of weak segregation macro-phase separation results in mixed binodal phase compositions that contain semiconductor as well as insulator. Then the phase morphology will consist of domains in which the semiconductor is highly diluted and domains in which the semiconductor is the dominant species. Calculation of the phase diagram\(^1\) of the ternary blend MEH-PPV:PVK:chlorobenzene (CB) (see Figure A.1), while varying the molecular weight of PVK\(^2\), suggests that one should not significantly exceed \(M_{w,PVK} \sim 100\) kDa to either freeze the drying blend in the single phase region, or at least to stay within the limit of weak segregation and to make sure that the PVK-dominated branch of the binodal does not at large solvent content already coincide with the edge of the composition domain. For the purpose of this study we used \(M_{w,PVK} = 30\) kDa.
Figure A.1: Ternary phase diagrams calculated using Flory-Huggins theory for the blend MEH-PPV: PVK:CB with varying PVK molecular weight: M (kDa) = 20 (a), 30 (b), 60 (c), and 120 (d); the blue curve represents the binodal, the black curve represents the spinodal, and the thin blue solid lines represent tie-lines; the white area “above” the binodal represents the single phase region.
A.2 Morphology of MEH-PPV:PVK Blends

As a first step to reveal the blend morphology obtained upon solution casting, atomic force microscopy measurements were performed (AFM, Dimension 3100, Bruker), as shown in the left column of Figure A.2. The AFM images clearly reveal the blend to macro-phase separate into two morphological domains. The height difference between the domains typically amounts to a few tens of nanometers on a total film thickness of 200-300 nm. The domains with largest thickness increase in area with increasing PVK concentration, indicating that these are the PVK rich domains. Since AFM only scans the domain structure at the top surface, for a more in-depth study we performed transmission electron microscopy (TEM, Phillips EM-420) measurements on the MEH-PPV:PVK 1:3 and 1:9 blends, which are most interesting from dilution point of view. The TEM images (Figure A.2, middle column) confirm that the domain structure not only concerns the top surface, but extends throughout the bulk of the blend films.

To confirm the above given assignment of the PVK-rich and MEH-PPV-rich domains we performed confocal laser scanning fluorescence microscopy (CLSM, Carl Zeiss Axiovert 200 microscope with an LSM 510 module using an Xα-Plan-Fluar 100x oil immersion objective NA 1.46) measurements (Figure A.2, right column).

As CLSM directly resolves the spatial distribution of the MEH-PPV by means of probing its local fluorescence intensity (green color scale), comparison of the images corresponding to the 1:3 and 1:9 ratios unambiguously reveals that upon increasing the amount of PVK in the blend a phase inversion takes place during which the nature of the PVK-rich phase changes from dispersed (1:1 and 1:3 blends) to continuous (1:9 and beyond), the MEH-PPV-rich phase exhibiting the opposite trend. As a result, all representations of the phase morphology from AFM, TEM and CLSM are internally fully consistent.

An important question that still remains is whether the PVK-rich phase really contains a diluted fraction of MEH-PPV. For this also CLSM can be used; also from the dark PVK-rich regions of the morphology image residual fluorescence is observed once the intensity of the excitation light is increased (see Figure A.3). Bleaching part of the film (central black square in Figure A.4) confirms that the observed residual emission from the PVK-rich phase is not due to backscattered excitation light. In relation to the 1:1 and 1:3 blends we emphasize that the fact that the film thickness is much lower than the lateral dimensions of the dispersed PVK-rich domains, strongly suggests these to have a flattened “pancake-like” geometry.

For a more quantitative assessment of the composition of the individual phases in the studied blends we extracted fluorescent intensity profiles from the CLSM images shown in Figure A.2. These profiles (Figure A.5) allow a comparison between the fluorescent intensity originating from MEH-PPV chains distributed in the PVK-rich phase and in the MEH-PPV-rich phase respectively. We estimated that the fluorescent intensity originating from the PVK-rich phase is approximately 28% of that of the MEH-PPV-rich phase for the 1:3 blend and approximately 18% for the 1:9 blend. It should be stressed that there is not a straightforward linear dependence between the MEH-PPV concentration...
Figure A.2: Overview of the morphology characterization (AFM, TEM, and CLSM) of spin-coated MEH-PPV:PVK blends at various solids ratios; in the CLSM images the intensity of the fluorescent light emitted by the MEH-PPV is expressed by the green color scale, which is therefore a direct measure for the local concentration of semiconductor.
Figure A.3: CLSM image of the spin-coated MEH-PPV:PVK 1:9 blend film, (a) recorded under excitation with 488 nm laser light at normal (b) and elevated intensity; the intensity of the fluorescent light emitted by the MEH-PPV is expressed by the green color scale, which is therefore a direct measure for the local concentration of semiconductor.

Figure A.4: CLSM image of the spin-coated MEH-PPV:PVK 1:9 blend film at elevated intensity; the central dark square represent a deliberately bleached region of the film to show that the detected emission is not contaminated with backscattered excitation light.

and the fluorescent intensity of the respective phase. As the fluorescence quantum yield of the PPV-rich phase is likely to be suppressed by self-quenching, we consider the above mentioned values of $\sim$18% and $\sim$28% as upper limits of the actual MEH-PPV fraction in the PVK rich phase.

To rationalize the occurrence of macro-phase separation (seemingly via liquid phase demixing) during solution-casting for all used solids ratios of the MEH-PPV:PVK:CB blend, we reproduced the phase diagram (Figure A.1(b) in Figure A.6, while visualizing the change in blend composition upon solvent evaporation (red arrows). As shown by Figure A.6, all solids ratios plausibly allow for accessing at least the metastable region, if
not even the instable part of composition space, perhaps suggesting the observed structures (Figure A.2) to have formed via spinodal decomposition. In agreement with the conclusions drawn from the fluorescence intensity profiles, the phase diagram indeed suggests the PVK-rich phase to contain a significant fraction of MEH-PPV, as long as the drying film solidifies at a mean solvent volume fraction in excess of about $\varphi_{CB} = 0.2$. We note that the above mentioned uncertainty in the dependence of fluorescence intensity on MEH-PPV concentration, as well as the approximate nature of the calculated ternary phase diagram do not allow for full quantitative comparison.

The combined results of charge transport measurements, morphology study and phase diagram lead to the following representation for the transport in MEH-PPV:PVK blend films, as schematically shown in Figure A.7. During deposition of MEH-PPV:PVK blends from solution PVK-rich and MEH-PPV rich domains form upon phase separation due to their partial miscibility, with the PVK-rich domains having a slightly higher thickness. In the PVK-rich domains the energetic disorder of MEH-PPV is reduced, leading to an enhancement of the mobility. With increasing PVK fraction these domains grow in area, which results in an enhancement of the total current through the blend. The concentration of MEH-PPV in the PVK-rich domains is dependent on the initial blend ratio. As a result the desired dilution effect occurs in the PVK-rich domains that also provide the dominant current path. This dilution leads to a strong increase of the electron current with increasing PVK fraction. For the 1:9 MEH-PPV:PVK blend the dilution effect is the strongest, leading to nearly equal electron and hole currents. However, compared to the 1:3 MEH-PPV:PVK blend the amount of active semiconductor is so strongly reduced that the total amount of current drops, in spite of the reduced energetic disorder.
Figure A.6: Ternary phase diagram calculated for the blend MEH-PPV:PVK:CB; the dotted blue curve represents the binodal, the dotted yellow/black curve represents the spinodal, and the thin blue solid lines represent tie-lines; the white area “above” the binodal represents the single phase region; the dashed red arrows represent the change in composition during solvent evaporation for various solids ratios.

Figure A.7: Schematic representation of the blend morphology and dominant charge transport path in MEH-PPV:PVK blends. The high $M_w$ MEH-PPV is indicated in orange, the lower $M_w$ PVK in blue. The red arrow indicated the dominant current path.
A.3 Electroluminescence of PLEDs

Electroluminescence spectrum of PLEDs based on pristine (100%) MEH-PPV and 10:90% MEH-PPV PFO blends are shown in Figure A.8. In pristine MEH-PPV, where most of the light is generated at the cathode, the EL spectrum shifts in energy/wavelength with sample thickness due to differences in optical out-coupling. For the blend PLED, with the light generated more homogeneously in the active layer such a shift is absent. Furthermore, the emission peaks are sharper, in line with the reduced energetic disorder and the vibronic shoulder is more suppressed.

Figure A.8: Normalized electroluminescence of (a) MEH-PPV and (b) 10:90% MEH-PPV:PFO blend PLED for different thicknesses. The vibronic peak in the EL spectrum of the blend is suppressed, and there is no shift of the spectrum with PLED thickness.
References

[1] The ternary phase diagrams were calculated using Flory-Huggins theory assuming concentration-independent interaction parameters. Effective degrees of polymerization were obtained by normalizing the weight-average polymer molar volume by that of CB (i.e. 101 cm\(^3\)/mol): \(N_{\text{MEH--PPV}} = 2900\), \(N_{\text{PVK}} = 400\), \(N_{\text{CB}} = 1\). Binary Flory interaction parameters (\(\chi_{ij}\)) were estimated based on the Hildebrand solubility parameters (\(\delta\)) using: 

\[
\chi_{ij} = \frac{V_s}{RT} (\delta_i - \delta_j)^2,
\]

where \(V_s\) is the segmental molar volume, here taken to be the molar volume of CB. The solubility parameters \(\delta_{\text{MEH--PPV}} = 18.6 \text{ MPa}^{1/2}\), \(\delta_{\text{PVK}} = 19 \text{ MPa}^{1/2}\) (i.e. taken similar to that of chloroform), and \(\delta_{\text{CB}} = 19.6 \text{ MPa}^{1/2}\) were retrieved from Refs. 3 and 4 respectively. The resulting interaction parameters are: \(\chi_{\text{MEH--PPV:PVK}} = 4.0 \times 10^{-3}\), \(\chi_{\text{MEH--PPV:CB}} = 3.9 \times 10^{-2}\), and \(\chi_{\text{PVK:CB}} = 1.5 \times 10^{-2}\).

[2] The molecular weight of the MEH-PPV is not varied and kept high at \(M_{\text{w,MEH--PPV}} = 300.000\) in order to eliminate the detrimental effect end-groups have on optoelectronic performance.

