

Spectroelectrochemically Determined Energy Levels of PM6:Y6 Blends and their Relevance to Solar Cell Performance

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Abstract:

Recent advances in organic solar cell performance have been mainly driven forward by combining high-performance p-type donor-acceptor copolymers (e.g. PM6) and non-fullerene small molecule acceptors (e.g. Y6) as bulk-heterojunction layers. A general observation in such devices is that the device performance, e.g. the open-circuit voltage, is strongly dependent on the processing solvent. While the morphology is typically named as key parameter, the energetics of donor-acceptor blends are equally important, but less straightforward to access. We propose to use spectral onsets during electrochemical cycling in a systematic spectroelectrochemical study of blend films to access the redox behavior and the frontier orbital energy levels of the individual compounds. Our study reveals that the highest occupied molecular orbital offset (ΔE_{HOMO}) in PM6:Y6 blends is ~ 0.3 eV, which is comparable to the binding energy of Y6 excitons and therefore implies a nearly zero driving force for the dissociation of Y6 excitons. Switching the PM6 orientation in the blend films from face-on to edge-on in bulk has only a minor influence on the positions of the energy levels, but shows significant differences in the open circuit voltage of the device. We explain this phenomenon by the different interfacial molecular orientations, which are known to affect the non-radiative decay rate of the charge-transfer state. We compare our results to ultraviolet photoelectron spectroscopy data, which show distinct differences in HOMO offsets in the PM6:Y6 blend compared to neat films. This highlights the necessity to measure energy levels of the individual compounds in device-relevant blend films.

Introduction

The material class of organic semiconductors has seen significant advances in recent years due to their wide range of applications in the field of organic electronics and optoelectronics^{1, 2} including organic solar cells (OSCs).³⁻⁵ The typically high extinction coefficients and the possibility to tune optical properties by the design of chemical structures strengthen the interest in developing and optimizing new materials for OSCs. Within the photoactive layer, bulk-heterojunction solar cells (BHJs) combine an electron donor material (D) and an electron acceptor material (A) to maximize the harvest of the solar spectrum and allow for an efficient charge generation and separation at the D/A-interface.^{6, 7} To improve the efficiency regarding light absorption and charge generation, both components need to be tuned in terms of energy level matching. Here, a balance between a reduction of the energy loss during charge transfer and a large enough highest occupied molecular orbital offset (ΔE_{HOMO}) to drive exciton dissociation needs to be found.⁸ This aspect demonstrates that it is crucial to have a profound knowledge of the energy levels to achieve efficient devices. There are multiple methods available to determine the energy levels including cyclic voltammetry (CV), ultraviolet photoelectron spectroscopy (UPS) or scanning tunneling spectroscopy. Serious discussions have unfolded about when it is reasonable to compare resulting energy levels from different experimental methods and when different data sources can be problematic. For example, it is quite common to combine the HOMO level derived from cyclic voltammetry or UPS with the optical bandgap to determine the lowest unoccupied molecular orbital (LUMO) level energy, which is, however, inappropriate because of the large exciton binding energy of organic materials.⁹⁻¹¹ Additionally, measurements on neat materials may not be suited to explain the energetic properties of material blends.^{12, 13} Microstructural order and morphology can be very unique in blends and therefore influence device-relevant parameters in a strong manner. Simply evaluating measurements on neat materials and translating them to material blends can therefore be a problematic approach. This work will deliver more insights into energy level determination in blend films and hence add more details to the prevailing discussions.

Due to its striking performance in solar cells, the present work is focused on thin films of the non-fullerene acceptor (NFA) molecule **Y6**¹⁴ (2,2'-((2Z,2'Z)-((12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4e]thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]-thieno[3,2-b]indole-2,10-diyl)bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))-dimalononitrile), the conjugated donor polymer **PM6** (Poly[(2,6-(4,8-bis(5-(2-ethylhexyl-3-fluoro)thiophen-2-yl)-benzo[1,2-

b:4,5b']dithiophene)))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']di-thiophene-4,8-dione)))] and their blends **PM6:Y6** (see Figure 1 for chemical structures).

One of the main achievements in the development of these high-performance materials was to tune the energy levels and shift the acceptor absorption into the region above 800 nm¹⁵⁻¹⁷ (see Figure 1 c) for the normalized absorbance spectrum). This way some of the limitations of previous state-of-the-art fullerene-based acceptor materials which had struggled for example with thermal and photochemical stability could be addressed.¹⁸ The blue shift of the absorption peak of Y6 in the blend compared to the neat film is a commonly observed phenomenon. The exact position of this peak is influenced by the degree of aggregation and by the intermolecular arrangements in the solid state of Y6.¹⁹ An exact decomposition of the absorption spectrum of Y6 in solution, neat film and blend and the contributions of different aggregates and non-aggregated molecules are currently subject of further investigations.

The acceptor Y6 is designed following the well-established internal electronic push-pull character with alternating electron donating and withdrawing groups,²⁰⁻²² leading to an internal A-DA'D-A structure. The electron deficient core in the center is realized by a benzothiadiazole moiety surrounded by two planar arms which are slightly tilted because of steric demands of the alkyl chains attached to the center.^{14,23} The exact attachment position and length of the alkyl chains were carefully adjusted and not only do not modify the solubility properties but also influence the packing structure and performance in the final devices.²⁴

PM6 belongs to the thriving family of D/A copolymers based on polythiophenes.²⁵⁻²⁷ Poly(3-hexylthiophene) (P3HT) being one of the most prominent polythiophenes is still considered to be a work horse in organic electronics applications.^{12, 28-30} Latest developments in the field of D/A copolymers present the introduction of halogen atoms, especially fluorine, to be one of the structural modifications that dramatically improves the properties of donor materials based on polythiophenes. The D/A copolymer PM6 carries a benzodithiophene donor unit which allows for the attachment of two fluorine atoms per unit. These groups shift down the HOMO level and are therefore an effective approach for increasing the transport gap (E_{tr}) which has a direct positive influence on the V_{OC} and increases the power conversion efficiency of the solar cell. Besides the energetic aspects, the fluorine atoms increase the tendency to aggregate and π - π stack by inducing a stronger dipole moment and improve the crystallinity favoring charge transport properties in general.^{26, 31} PM6's large bandgap leads to an absorption spectrum that perfectly complements the absorption spectrum of Y6. When processed in blends, the PM6:Y6 absorption spectrum covers a large part of the solar spectrum from around 350-1000 nm (see Figure 1 c)), making these two materials a promising match for BHJ solar cells.

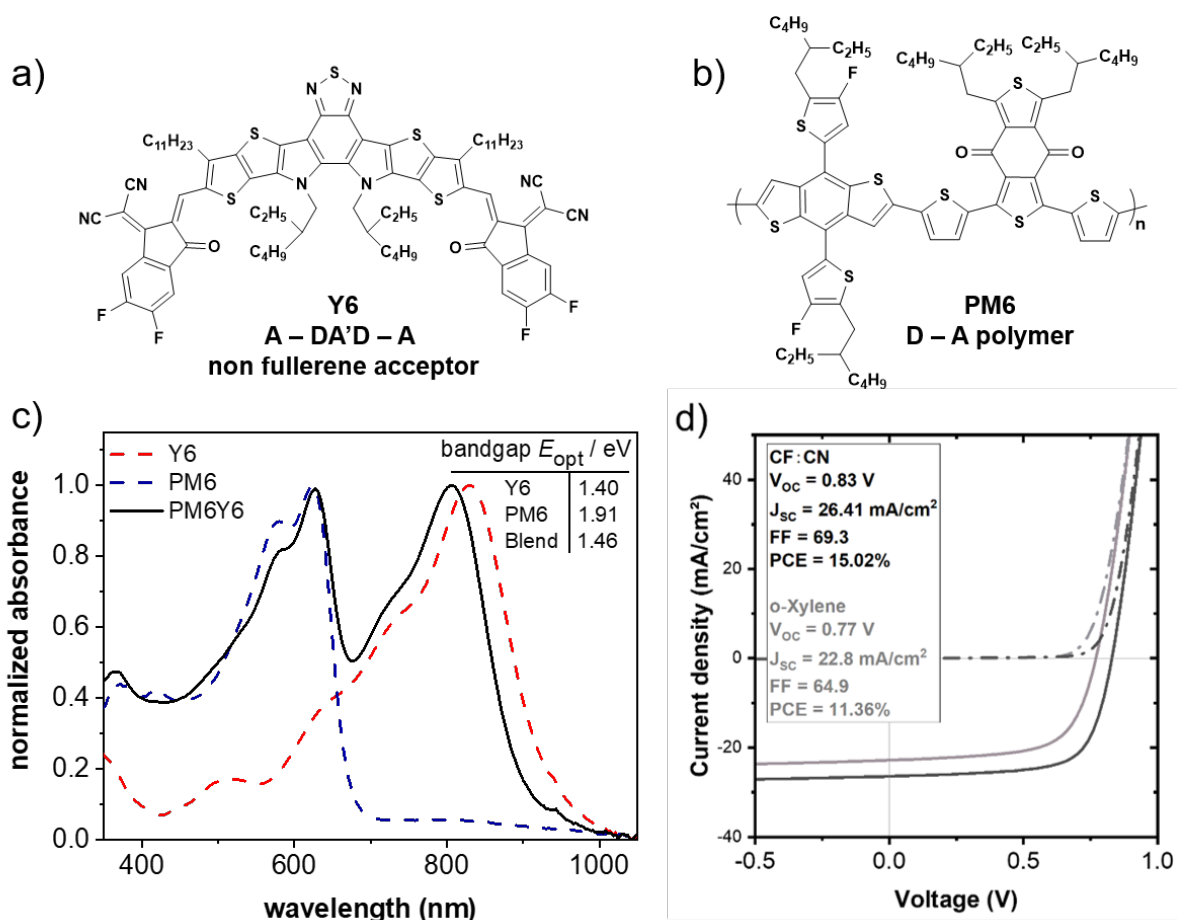


Figure 1: Chemical structures of a) Y6 and b) PM6. The corresponding UV-vis absorption spectra in thin films processed from CF:CN (chloroform + 0.5 v% chloronaphthalene) are given in c) showing Y6 in red, PM6 in blue and a blend of PM6:Y6 (1:1.2 wt%) in black. The device characteristics of PM6:Y6 BHJ solar cells processed from CF:CN (black line) and o-xylene (grey line) are presented in d).

When fabricated into BHJ solar cells, PM6:Y6 blends deliver an impressive power conversion efficiency of 15.7 %, which is among the highest achieved in BHJ devices.^{14, 32} This has been attributed to a negligible barrier for charge separation³³⁻³⁵ combined with a low density of traps.³⁶ Devices relying on PM6, Y6 or slightly modified versions of them currently reach efficiencies of up to 19 % and above^{37, 38} when fabricated in more complex layers, e. g. in ternary blends.³⁹⁻⁴⁴ The phase separation between the donor and acceptor plays a crucial role for efficient charge separation (exciton diffusion length is usually around 20 nm^{45, 46}) and is influenced by the miscibility between PM6 and Y6 on the one hand. On the other hand, the properties of the chosen processing solvent and the processing method itself significantly impact the drying kinetics during the film formation and therefore can influence the blend morphology. This D/A pairing shows suitable miscibility and interaction parameters for a favorable phase separation, which is beneficial for charge generation.³¹

Despite these advancements, there is an ongoing debate regarding the driving force of free charge generation in PM6:Y6. For fullerene-based OSCs, it is commonly accepted in the community that the HOMO energy offset of the frontier orbitals at the D/A heterojunction must be at least 300 meV to guarantee efficient exciton dissociation.^{47, 48} Several recent papers reported efficient charge generation in NFA-based devices with HOMO offsets as small as 50 to 100 meV.^{49, 50} The original paper on PM6:Y6 reported a HOMO offset of only 0.09 eV, based on CV scans on neat films of the two components.¹⁴ On the other hand, recent measurements of the ionization energy and electron affinity of neat layers with photoelectron spectroscopy suggested a HOMO offset as large as 0.7 eV.³⁵ Table S1 provides an overview over the reported HOMO and LUMO energy levels on neat films and on PM6:Y6 blends from literature. We notice a rather large variation of the energy values for the donor polymer PM6, while the scatter of data for Y6 is much smaller. This may indicate a large effect of the morphology but also of the chosen method on the polymer energetics. Only few studies concerned the HOMO and LUMO levels of the blend and reported slightly different values as for neat layers, however, none of the studies provided the HOMO offsets and transport in the actual blend.

In this study we prepared representative PM6:Y6 BHJ solar cells from two different solvent systems, namely CF:CN (chloroform + 0.5 v% chloronaphthalene) and o-xylene. The strong impact of the processing solvent on the active layer morphology is known in literature²⁵⁻²⁷ and by choosing CF:CN and o-xylene as different processing solvents we induce two opposing orientations in the bulk of the active layer. As Figure 1 d) demonstrates, the two orientations have significant influence on the device performance.

PM6:Y6 solar cells produced from CF:CN give an open circuit potential (V_{OC}) of 0.83 V (fill factor FF = 69.3) and an overall efficiency of 15.02 %, matching literature results.¹⁴ Switching the processing solvent to o-xylene, the measured V_{OC} decreases to 0.77 V (FF = 64.9) and the efficiency drops to 11.36 %.

Additionally, the J_{SC} of the PM6:Y6 blend cast from o-xylene is lower, reproduced by the EQE spectra (see Figure S1). Given that both blends yield fairly high FFs, we do not interpret this difference as a result of inefficient charge extraction (which is a field- dependent process). More likely, the lower J_{SC} come from less efficient exciton dissociation or the trapping of photogenerated charge on non-percolated domains. A central question to be answered in this work is whether this difference in device performance can be explained by changes of the energy levels of PM6 and Y6 induced by the opposing morphology in the blend or if other

aspects must be taken into consideration. Therefore, we utilize a spectroelectrochemical method to determine frontier orbital energies of the individual components in PM6:Y6 blend films with different morphologies. The morphology of the blend films will be discussed in detail at first to define the starting point of all following experiments. The results will be compared to experimental evidence from UPS measurements and discussed regarding device performance in the final section.

Results and Discussion

1. Morphology Characterization

In a first step we have studied the morphology of the blend films by a combination of grazing incidence wide-angle X-ray scattering (GIWAXS) and near-edge X-ray absorption fine-structure (NEXAFS) spectroscopy (see Figure 2).

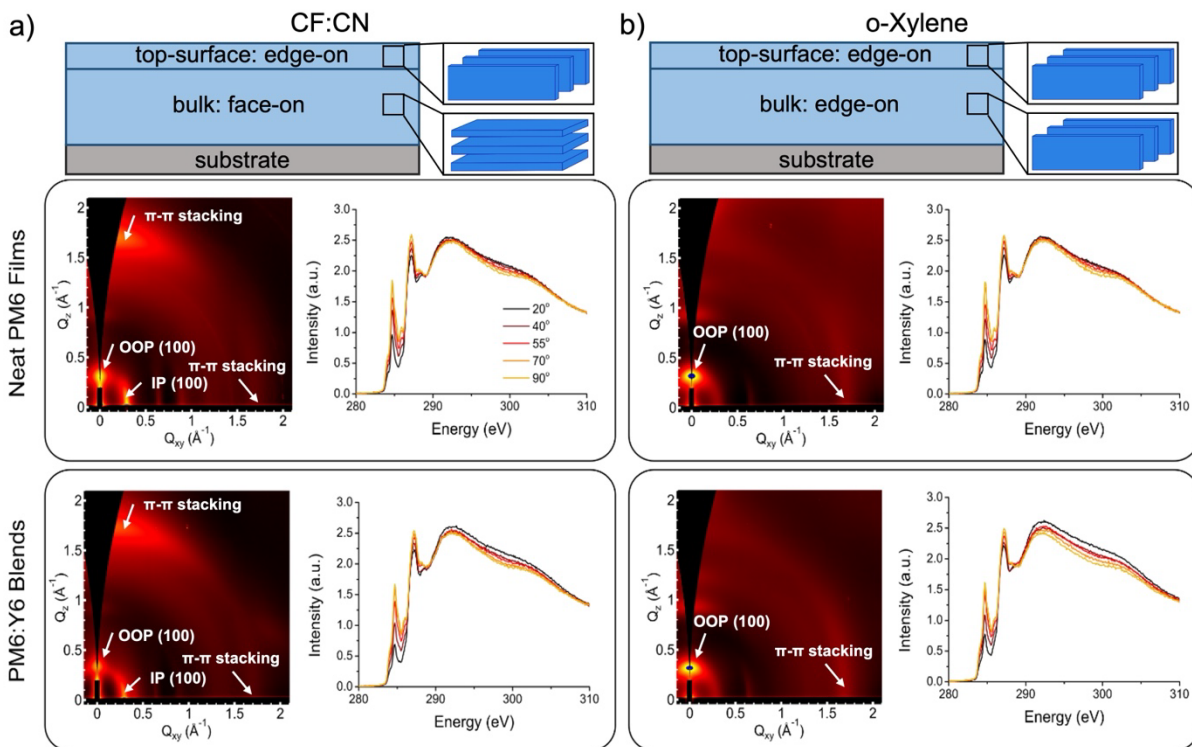


Figure 2: Morphology of neat PM6 films and PM6:Y6 blend films (1:1.2 wt%) spin coated from two different solvent systems: a) CF + 0.5 v% CN and b) o-xylene. Sketches of the top-surface and bulk morphologies as obtained from GIWAXS (bulk) and angle-resolved NEXAFS (top-surface). GIWAXS patterns were plotted on different color scales to properly illustrate all scattering features.

We prepared neat and blend films from two different solvent systems resulting in two different orientations of PM6 in the bulk. GIWAXS data collected at critical angle shows that the films spin coated from CF:CN exhibit a dominant face-on orientation in the bulk for both neat PM6 films and blend films with Y6, marked by the intense in-plane (IP) lamellar (100) peak at around $0.3 \text{ \AA}^{-1}$ and the out-of-plane (OOP) π - π stacking peak around $1.7 \text{ \AA}^{-1}$. A minority edge-on

orientation is also observed in both neat and blend films as marked by the OOP lamellar (100) peak and IP π - π stacking peak. This matches works on GIWAXS analysis and peak assignment of neat and blend films of PM6:Y6 processed from different solvents currently present in literature.^{8, 14, 51} From surface-sensitive NEXAFS spectroscopy investigations, an edge-on orientation is found on the surface of the CF:CN-processed films (average tilt angle of conjugated backbone is $\langle\alpha\rangle = 64\pm1^\circ$). This observation is consistent with GIWAXS data collected at angle of incidence below the critical angle which probes surface microstructure, where the ratio of OOP to IP π - π stacking peak intensity decreases with shallower incident angle (see Figure S2). The existence of different orientations regarding bulk and surface and the strong dependence of morphology on the processing parameters have already been reported for other conjugated polymers like N2200.⁵²⁻⁵⁴ Processing of PM6 films and blends of PM6:Y6 from o-xylene solutions lead to edge-on orientation throughout the bulk, visible from the weak IP lamellar (100) peak and the corresponding strong OOP (100) signal, Figure 2 b). The surface shows an edge-on orientation as well, with an average tilt angle of the conjugated backbone of $\langle\alpha\rangle = 65\pm1^\circ$. In general, the choice of solvent in combination with the processing method has a strong impact on the resulting morphology in the blends. Alternative processing methods like slot-die coating offering different drying kinetics are presented in literature and prove to show how orientations can differ using similar solvents as we do.⁵⁵ Regarding Y6, it has a high tendency to pack with a face-on orientation when processed from different processing solvents.^{14, 24, 56-59} Here, literature also gives examples how small changes on the side groups of Y6 can impact the morphology although solution and processing parameters are kept constant.⁶⁰ These results underline the importance of the chosen solvent for film preparation since the influence on the morphology and orientation in the film is strong and decides whether there is face-on, edge-on or mixed orientations.^{25-27, 59, 61} This difference in morphological orientation of PM6 in PM6:Y6 films fabricated with CF:CN and o-xylene is reflected in the device performances (see Figure 1 d) for the corresponding current density-voltage (J - V) characteristics and the experimental section for the fabrication conditions). Compared to the device with the active layer prepared from CF:CN solution, the blend coated from o-xylene yields a considerably smaller power conversion efficiency, which is mainly due to a lower V_{OC} . Possible reasons for this will be discussed below.

In addition, the NEXAFS results show that the film surface in the blend is enriched in PM6 (~70-80 % PM6, see Figure S3). This result is important because HOMO levels of PM6 from UPS can differ compared to results from cyclic voltammetry. Since UPS is a surface sensitive method, surface morphology should definitely be considered. The impact of the different

morphological orientations on the resulting energy levels of the frontier orbitals of both PM6 and Y6 in the blend films is subject of the following experiments.

2. Energy Level Determination by *in situ* Spectroelectrochemistry

The next paragraph presents an in-depth electrochemical analysis by coupling cyclic voltammetry and *in situ* UV-vis spectroscopy to identify onsets of oxidation and reduction which will be the foundation for the energy level determination.⁶² An onset calculation purely based on cyclic voltammetry always suffers from a certain inaccuracy. In general, there is no thermodynamic foundation for an electrochemical onset potential which can vary due to kinetic effects (diffusion of ions into the film) and experimental aspects like background current and chosen electrolyte.¹² In particular, cyclic voltammetry of conjugated polythiophenes like PM6 with its inherent broad redox waves, offers much potential for errors when using the onset which is one of the reasons for the high deviations in the HOMO energies from CV in the literature (see Table S1). Additionally, a significant variation in overall CV quality can be found in the literature, regarding the electrochemical reversibility and the avoidance of charge trapping effects which unfortunately questions some of the published data.

Whilst it does not rule out the general problem of onsets (definition of the threshold value) entirely, our approach excludes errors arising from the electrochemical experiment by focusing on the spectroscopic response of the material to the applied electrochemical potential, from now on referred to as spectral onset.

Since most charged species have an individual spectral fingerprint (see Table 1), this elegant method allows for a more exact interpretation of the electrochemical processes. To discuss and disentangle multiple overlapping redox processes especially in context of possible second oxidation steps (creating double charged species) the data from the CV is completed with the *in situ* spectral information discussed in the next section. A transfer from neutral to charged form is usually accompanied by a significant change in the UV-vis spectrum, so the onset of spectral change can be used to determine HOMO/LUMO energies. *In situ* UV-vis techniques have already proven their worth in literature, describing film formation kinetics and analyzing the influence of the processing solvent and conditions on parameters like aggregation, phase separation and crystallinity in blends of PM6 and different NFAs. In this way morphology tuning of the BHJ active layers by annealing can be documented and modified towards increasing performance in the final device.^{63, 64}

Regarding the characterization of blend films our approach offers an additional advantage. The characteristic spectral response of each material allows us to discriminate between the two components in the blend and identify their individual contributions to the result. This means our technique helps us to differentiate between redox states of the individual components, e.g. whether a second redox wave in the CV scan corresponds a differently charged state of component A or if it is the actual onset of component B.

In order to avoid errors in the onset determination, the redox behavior of Y6 and PM6 and spectral characteristics of the charged species all need to be understood individually. Before moving on to the complex electrochemical behavior of PM6:Y6 blend films, it is fundamental to understand the redox properties of neat Y6 and PM6 films first. The knowledge on the spectral characteristics of the neat compounds and the blends can also be of great help for other spectroscopic methods like photo-induced absorption (PIA) or transient absorption spectroscopy (TAS). Cyclic voltammograms of the neat material and blend films are presented in Figure 3 and Figure 4, giving separate CVs for oxidation and reduction cycles to avoid charge trapping effects. The presented data in the following section are produced with films processed from CF:CN solutions. The corresponding results of films from o-xylene are found in the supporting information (see Figure S4 and S5).

2.1 HOMO Determination

Y6

The electrochemical behavior of the Y6 acceptor films show sharp and defined peaks in the CV for the oxidation in Figure 3 a). The oxidation displays an intense wave at 0.92 V with an additional subsignal at 1.04 V. The reduction half-waves are less pronounced showing a weak wave at around 0.8 V.

The spectral evolution during the charge half cycle of the oxidation (middle column) and the peak trends of significant absorption bands which are characteristic for the individual redox species (right column) is presented in Figure 3.

The characteristic UV-vis spectrum of a neutral Y6 film can be seen in Figure 1 c) and Figure 3 a) in purple color at -0.37 V. When increasing the electrochemical potential, the absorption intensity at 830 nm (neutral band) decreases and a new band develops at 750 nm (red spectrum in Figure 3 a)). The new band can be assigned to the first oxidized state (polaron). From the spectral evolution of the neutral species at 830 nm and the polaron species at 750 nm, the spectral onset can be determined via the tangent method (highlighted in Figure 3 a) right graph). In the case of Y6 this gives a value of 0.84 V. This onset value will be the basis for the

calculation of the HOMO energy of neat Y6 films and amounts to -5.64 eV. For the sharp and well-defined wave in the CV, the onset from CV at ~ 0.85 V (determined by the tangent method) is located quite close to our spectral onset.

Increasing the potential above 1 V, another change in the spectrum becomes visible for Y6. The intensity at 750 nm decreases in favor of a new characteristic peak at 890 nm which we assign to a second oxidized state of Y6 (yellow spectrum at 1.22 V in Figure 3 a)). The potential of this spectral change fits to the previously observed signal in the CV at 1.04 V, which can now be assigned to the second oxidation step.

PM6

Moving from the small molecule Y6 to the conjugated donor polymer PM6 distinct differences in the electrochemical behavior become present. In particular the oxidation in Figure 3 b) shows the typical broad wave which is characteristic for polydisperse materials like polythiophenes and has been extensively studied for P3HT.^{12, 65} In contrast to Y6, the backwards half cycle of PM6 can be observed as well, transferring the created oxidized species upon charging back into the neutral form.

Regarding neat PM6 films the absorption spectrum of a neutral film can be seen in Figure 1 and Figure 3 b) in dark blue at -0.36 V. The rather well-defined peak at 625 nm (neutral band) decreases in intensity when extending the potential to positive values. The spectrum of the charged PM6 film now shows a broad absorption around 830 nm with a shoulder at 890 nm. The spectral evolution displays an isosbestic point at 660 nm, indicating a clear transition from the neutral species into the oxidized form. From earlier studies on P3HT we suspect a coexistence of both polaronic and bipolaronic forms at high potentials, since the spectral evolution upon electrochemical doping is similar to polythiophenes like P3HT.^{12, 30, 66} Although the absorption shoulder at 890 nm (marked by teal colored star) might be a feature of the polaron, an exact assignment remains difficult due to identical and overlapping bands from both charged species at 830 nm (marked by blue dot). The extracted spectral onset of the oxidation of neat PM6 is found at 0.50 V which amounts to a HOMO of -5.30 eV. Here, the onset of the CV is located at 0.55 V which is at least 0.05 V further into the direction of positive potentials, caused by the broadening of the obtained CV wave and increased difficulties in finding the correct onset. The same problem also occurs in the CVs from the blend films. This underlines the significant advantage of our method relying on a combination of CV and spectral onset determination.

Table 1: Characteristic absorption maxima of neutral and charged states of neat Y6 and PM6 films. The arrows indicate oxidation and reduction steps.

	$\text{Y6}^{\cdot-}$	←	Y6	→	$\text{Y6}^{+\cdot}$	→	Y6^{2+}
wavelength / nm	380		830		750		890

	$\text{PM6}^{\cdot-}$	←	PM6	→	$\text{PM6}^{+\cdot}$	→	PM6^{2+}
wavelength / nm	850, 1000		580, 625		830		890

PM6:Y6 Blend

Knowing the electrochemical characteristics of neat Y6 and PM6 films enables the experimental data on PM6:Y6 blends to be interpreted. In general, all the previously described waves and signals can be found in the CVs of the blend films as well. The oxidation in Figure 3 c) shows a broad underlying wave with a sharp signal at 0.92 V which can be attributed to the oxidation of Y6. The broad signal underneath can be assigned to the oxidation of PM6.

Following the neat material films, the spectral evolution of the PM6:Y6 blend film is considered. As already described in Figure 1, the absorption of the neutral state of the blend film in Figure 3 c) (black spectrum at -0.36 V) is almost a superposition of both neutral absorption bands of Y6 and PM6 with minor shifts occurring probably caused by different packing order in the blend. This superposition of bands basically applies for the entire doping process and is highlighted by the vertical lines connecting characteristic bands in the neat material and blend films. The spectral onsets of the individual compounds in the blend are found at 0.50 V for PM6 resulting in a HOMO of -5.30 eV (identical with the neat film) and at 0.83 V for Y6 with a HOMO of -5.63 eV.

For the presented films spin coated from CF:CN only a slight difference in the spectral onset of the oxidation between neat material and blend films can be found in the case of Y6, which can hardly be considered significant.

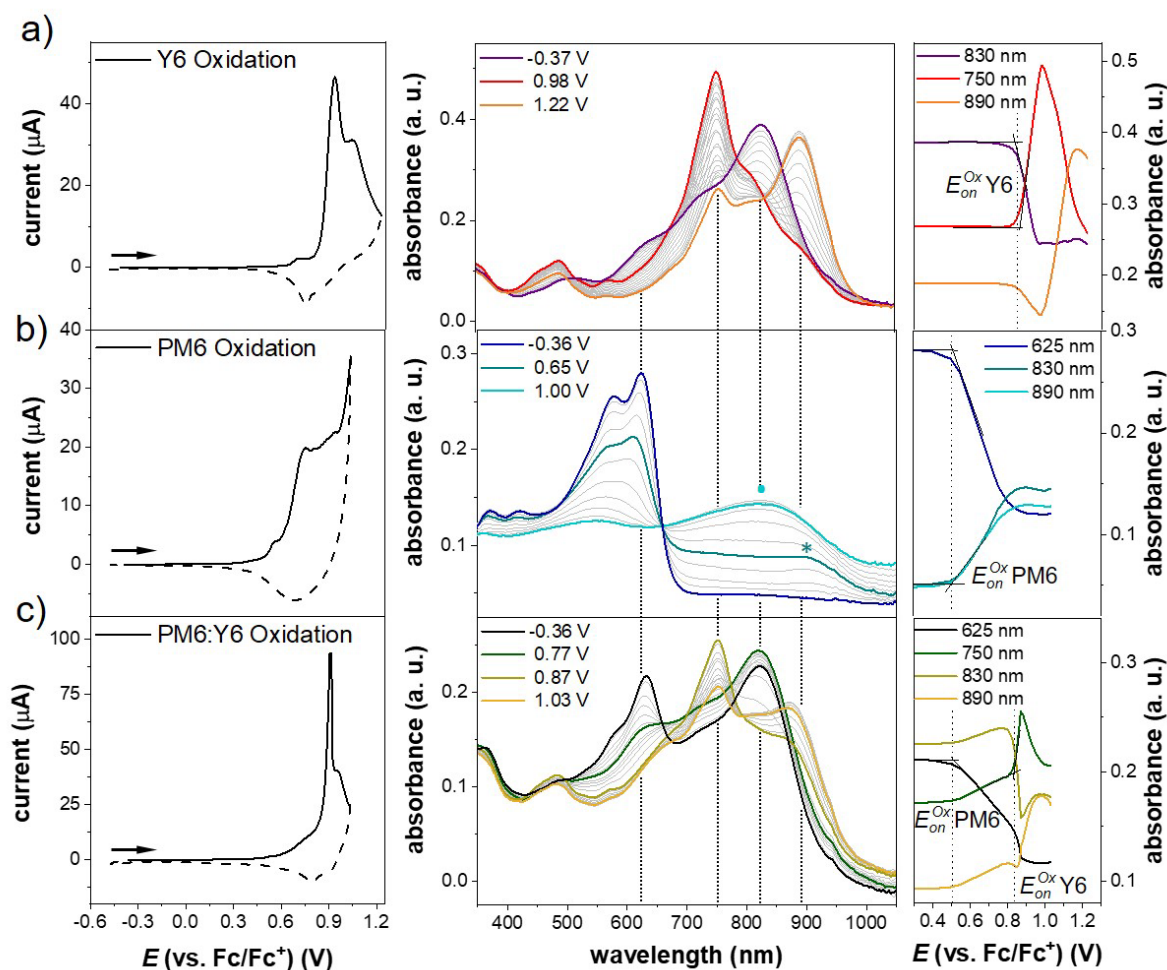


Figure 3: *In situ* CV measurements coupled with UV-vis spectroscopy of a) neat Y6, b) neat PM6 and c) a blend of PM6:Y6 (1:1.2 wt%) films, spin coated from CF:CN (0.5 wt%) solutions. CVs are given on the left (the forward half-cycle is highlighted as solid line), the spectra of the forward charge half-cycle of the oxidation are presented in the center, completed with peak trends of significant bands on the right side. The peak trends are used for the determination of the spectral onsets which are indicated by dotted lines and obtained via using tangents. Underlying CVs (1st cycles) are measured in 0.1 M TBAPF₆/MeCN at 20 mVs⁻¹ on ITO substrates.

2.2 LUMO Determination

Y6

The analysis of the spectral evolution of the reduction and the following extraction of spectral onsets for determining the LUMO levels is carried out accordingly.

The CV upon reduction of Y6 shows a quite sharp wave at -0.92 V, which is more pronounced compared to the oxidation behavior. In both cases (oxidation and reduction) in Figure 3 a) and Figure 4 a) the backwards half cycles seem to be less pronounced which questions the

electrochemical reversibility at first sight. It is important to mention that these CVs were taken on thin films which are insoluble in the electrolyte in the pristine state. Experiments showed that the solubility properties of Y6 change when charged species of Y6 are being created. After completing the forward half cycle, the fully charged films start to dissolve into the electrolyte leading to a critical loss of electroactive material on the working electrode. As a result, the backwards half cycles are weakly pronounced in the case of the Y6 oxidation or not visible at all in the case of the reduction.

The displayed spectral evolution of the reduction of neat Y6 films in Figure 4 a) shows a decrease of the neutral band at 830 nm and a distinct increase at the low wavelength region of the spectrum around 380 nm. The isosbestic points clearly indicate a transition of the neutral state into a reduced form with a characteristic absorption band at 380 nm. The spectral onset of the reduction is located at -0.88 V which yields a LUMO of -3.92 eV.

PM6

The reduction of PM6 shows two separated waves in the CV at -1.65 V and -1.89 V. The exact interpretation of the signals purely from the CV is difficult.

The spectral evolution of neat PM6 films shows a unique behavior in the reduction. Upon decreasing the electrochemical potential, the absorption intensity of the neutral band (625 nm) seems to increase at first (spectra from dark blue at -0.35 V to teal color at -1.60 V). This increase of absorption intensity appears at the same potential as the first reduction peak observed in the CV. This is an indication that the PM6 film is slightly oxidized under ambient conditions prior to the experiment. The induced charges – probably originating from the exposure to oxygen - are re-extracted leading to a first reduction signal at around 1.65 V. This is accompanied by an increase of absorbance of the neutral band when the film reaches its fully neutral state. Only after the fully neutral state is reached and the potential is further decreased the typical bleaching of the neutral band is observed together with a broad increase of absorption above 800 nm. Additionally, a weak shoulder can be seen around 900 nm which might be a signature of the negative polaron. A supposed band overlap and a coexistence of different charged species at the same time, which is typical for polythiophenes, makes an exact interpretation of this feature difficult.^{30, 67} The characteristic absorption of the fully reduced state found at potentials around -1.9 V fits to the second, only relevant, reduction peak in the CV which now completes the description of two reduction peaks in the CV data. Using the spectral onset of this second reduction a value of -1.75 V can be extracted which leads to a LUMO of -3.05 eV for PM6.

PM6:Y6 Blend

The CV of the reduction of the blend films in Figure 4 c) displays three individual signals; one sharp wave (-1.02 V) which can be attributed to the reduction of Y6 and two broader signals (-1.45 V and -1.90 V) which can be seen at similar potentials in the reduction of the neat PM6 film. Evaluating the spectral onsets of the single compounds in the blend film results in a value of -1.74 V for PM6 which yields a LUMO of -3.06 eV and a value of -0.9 V for Y6 corresponding to a LUMO of -3.90 eV. Compared to the results of the neat films a shift of 0.02 V to lower potential was found for Y6 with respect to the blend. The observed shift of the spectral onset of PM6 is only 0.01 V and therefore not significant.

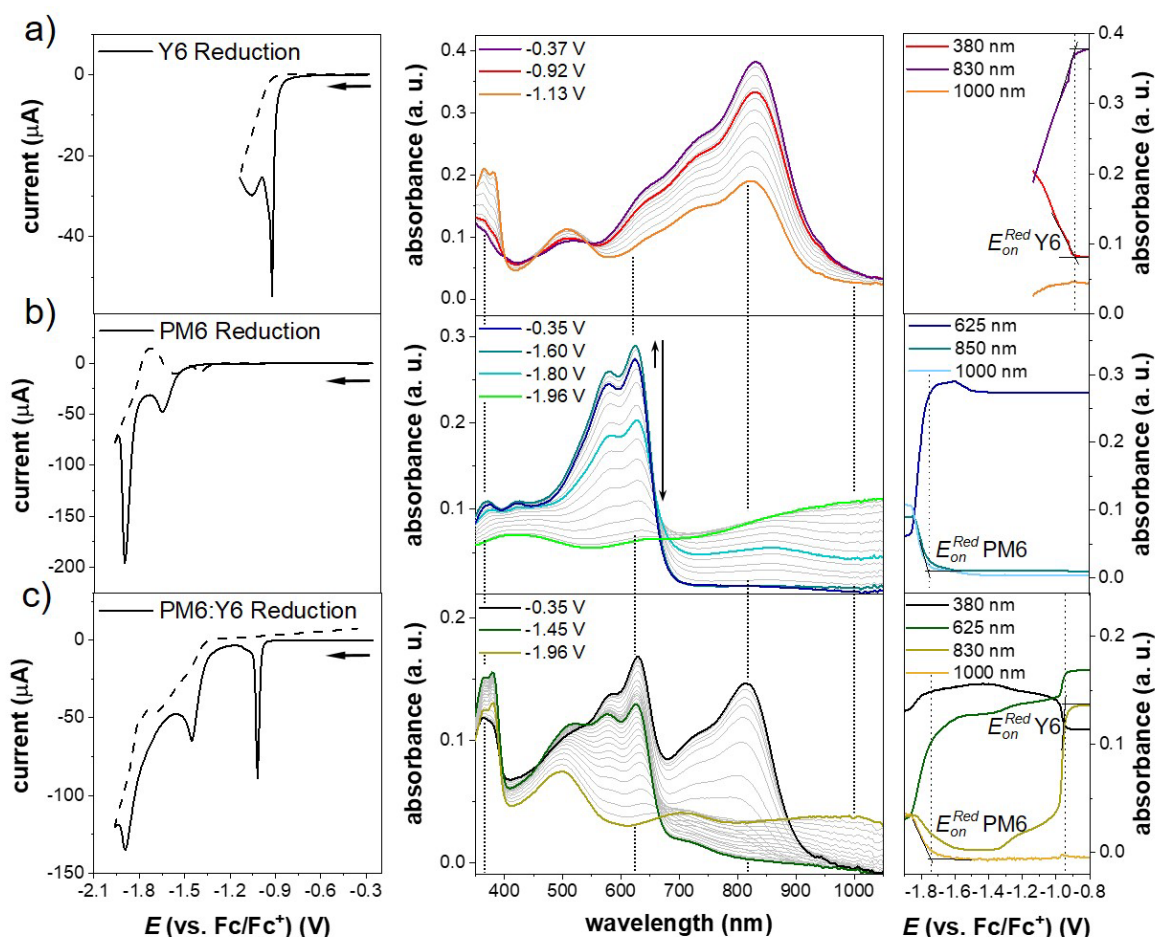


Figure 4: *In situ* CV measurements coupled with UV-vis spectroscopy of a) neat Y6, b) neat PM6 and c) a blend of PM6:Y6 (1:1.2 wt%) films, spin coated from CF:CN (0.5 wt%) solutions. CVs are given on the left (the forward half-cycle is highlighted as solid line), the spectra of the forward charge half-cycle of the reduction are presented in the center, completed with peak trends of significant bands on the right side. The peak trends are used for the determination of the spectral onsets which are indicated by dotted lines and obtained via using tangents. Underlying CVs (1st cycles) are measured in 0.1 M TBAPF₆/MeCN at 20 mVs⁻¹ on ITO substrates.

2.3 Comparison of Energy Levels, HOMO Offsets and Transport Gaps

All HOMO and LUMO levels of the neat material films and of the individual compounds inside the blend films (as obtained from the spectral onsets) are summarized in Figure 5.

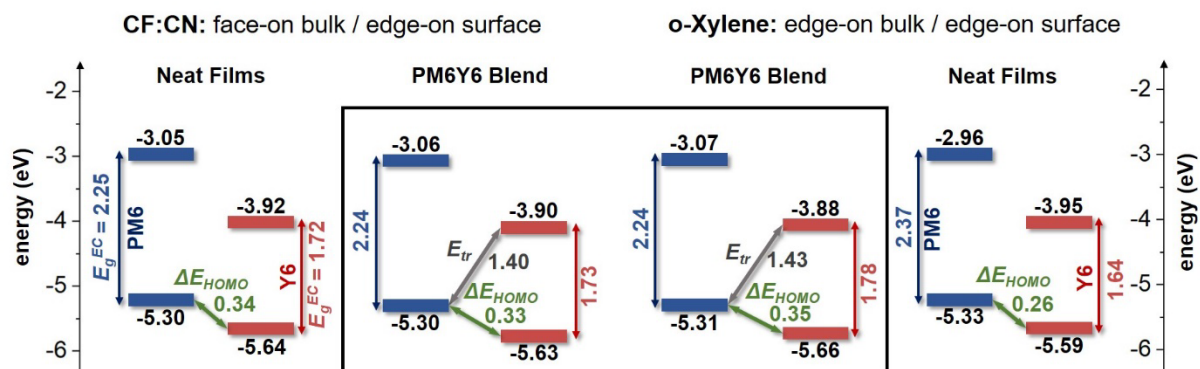


Figure 5: Calculated HOMO/LUMO energy levels from the spectral onsets (Figure 2 and 3) for films of neat PM6, neat Y6 and the individual compounds in the blend films of PM6:Y6 (1:1.2 wt%) processed from the two solvent systems CF:CN and o-xylene. The potentials were transformed to the Fermi scale using the correction factor of -4.8 eV. Electrochemical band gaps E_g^{EC} of the individual compounds are given as well as HOMO offsets ΔE_{HOMO} and transport gaps E_{tr} .

The determined frontier orbital energies of PM6 and Y6 neat films processed from CF:CN are positioned at -5.30 eV/-3.05 eV (HOMO/LUMO PM6) and at -5.64 eV/-3.92 eV (HOMO/LUMO Y6). The resulting electrochemical band gap for PM6 is found to be 2.25 eV and 1.72 eV for Y6. The HOMO offset of the two components calculated from the neat films is obtained at 0.34 eV. Compared to the results for the blend prepared from CF:CN, the energy levels of PM6 (-5.30 eV/-3.06 eV) and Y6 (-5.63 eV/-3.90 eV) are located at rather identical values. The blend shows a HOMO offset of 0.33 eV and a transport gap of 1.40 eV. The results for the neat films processed from o-xylene show slight changes in energy levels. Our experiments yield energy levels of -5.33 eV/-2.96 eV (HOMO/LUMO PM6) and -5.59 eV/-3.95 eV (HOMO/LUMO Y6). This has a direct influence on the HOMO offset which shrinks to 0.26 eV. In the blend processed from o-xylene the HOMO/LUMO levels slightly differ from the neat films and are located at -5.31 eV/-3.07 eV (HOMO/LUMO PM6) and at -5.66 eV/-3.88 eV (HOMO/LUMO Y6). This correlates to a HOMO offset of 0.35 eV and a transport gap of 1.43 eV. The calculated energy levels from the spectral onsets for the blend films show a HOMO offset (ΔE_{HOMO}) which is consistently positioned between 0.33 and 0.35 eV.

Comparing textures, in the blend prepared from CF:CN solution (face-on orientation in bulk) the offset is 0.33 eV whereas the offset slightly increases to 0.35 eV in the case of blends from o-xylene solutions (in edge-on orientation in bulk). The calculated effective transport gap of 1.4 eV for blend films processed from CF:CN (face-on orientation) is also slightly smaller than for blends from o-xylene solution (edge-on orientation) with an effective transport gap of 1.43 eV.

When comparing the HOMO offset in the neat films with the results of the blend films, differences regarding the solvent systems become visible. While the HOMO offsets remain rather constant for CF:CN films, an increase in HOMO offset for films prepared from o-xylene solutions is registered. Our study therefore clearly shows that the impact of morphology and molecular orientation on device relevant parameters like HOMO offset and effective transport gaps is small but measurable. Especially for the investigated materials Y6 and PM6 the results from the spectroelectrochemical experiments lead to the conclusion that blending both components give measurable differences in the energy levels.

The occupied energy levels of the films (HOMO) prepared from different processing solvents (CF:CN and o-xylene) were further measured using ultraviolet photoelectron spectroscopy (UPS). Being a highly surface sensitive technique, UPS results are only influenced by the properties of the top surface of the films and cannot take differing bulk morphologies into account. Since films from CF:CN and o-xylene show identical surface orientations with edge-on orientation (see Figure 2) no difference within the experimental error was measurable, as expected. The UPS spectra of neat PM6 and Y6 films as well as a PM6:Y6 blend processed from CF:CN are shown in Figure 6, the spectra of blends from other processing solvents are shown in the SI (see Figure S6).

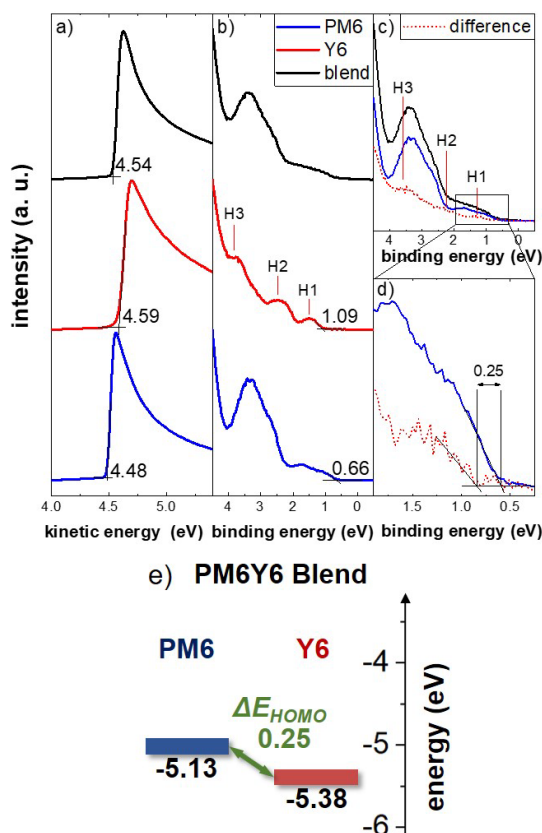


Figure 6: a) Secondary electron cut-off (SECO) and b) valence band spectra of neat PM6, neat Y6 and PM6:Y6 (1:1.2 wt%) blend films prepared from CF:CN (0.5 wt%). c) Subtraction of the PM6 valence band spectrum (scaled) from the PM6:Y6 blend spectrum. The residual intensity resembles a broadened Y6 valence band spectrum, as indicated by the HOMO features labeled H1, H2 and H3. d) Zoom into the valence band onset region marked in c), yielding a HOMO offset between PM6 and Y6 in the blend of 0.25 eV, significantly smaller than the HOMO offset of the neat films (0.54 eV). Extracted energy levels and HOMO offset (ΔE_{HOMO}) for the blend film are displayed below in e).

The secondary electron cut-off (SECO) spectra in Figure 6 a) are used to calculate the work function of the material and give energies of -4.48 eV for PM6, -4.59 eV for Y6 and 4.54 eV for the PM6:Y6 blend. Adding the work function to the HOMO onsets extracted from the valence band spectra in Figure 6 b) yields the ionization energy of the respective components. The onset used to calculate the binding energy of neat PM6 is rather broad (blue line in Figure 6 b)), while the HOMO of Y6 has a more distinct onset. For binding energies, we extract 0.66 eV for PM6 and 1.09 eV for Y6. This results in ionization energies of the neat films (HOMO levels) of PM6 of -5.14 eV and of Y6 of -5.68 eV (HOMO offset 0.54 eV), in good agreement with other values reported in the literature from photoelectron spectroscopy on neat layers (see Table S1 in the SI).

The Y6 HOMO from UPS at -5.68 eV agrees quite well with the value from the spectral onsets, while the UPS HOMO of PM6 is shifted by about 0.15 eV to -5.14 eV. This is in line with previously reported data.³⁶ The reason for this is not clear yet, but we emphasize here that the ionization energy from UPS is very sensitive to the electrostatics at the surface, which will most likely be different in neat and blend films. Therefore, we point out that experiments on neat films have to be taken with caution when they are used to explain the energetics of blend films. To actually access the HOMO energies of the individual components in the blend films, we subtract the (scaled) reference valence band spectrum of neat PM6 from the blend spectrum (see Figure 6 c)). The residual intensity resembles the spectral shape of neat Y6, as indicated by the three features labeled H1, H2 and H3. A broadening is observed, which can be caused by the intermixing of the two molecules and the concomitant disorder.^{68, 69} A zoom into the HOMO onset region is shown in Figure 6 d) and yields HOMO energies of -5.13 eV and -5.38 eV for PM6 and Y6, respectively. This corresponds to a HOMO offset of 0.25 eV between the two materials, significantly smaller than the HOMO offset determined from the pristine films and in good agreement with CV and UV-vis results. The difference in the absolute values compared to the CV/UV-vis results, could be caused by different electrostatic interactions, e.g. dipole, quadrupole or higher order moments, polarization and screening effects etc., as has been demonstrated before.⁷⁰⁻⁷²

3. Discussion of Solar Cell Performance

With the transport gaps of the neat components and the blends at hand, we now turn to the performance of our PM6:Y6 blend in solar cells. As pointed out earlier, it was proposed that the PM6:Y6 blend exhibits a small barrier for free charge generation. Other groups argued that Y6-based solar devices function efficiently because of a very low or even vanishing exciton binding energy, E_b of the Y6 singlet exciton. For example, a recent self-consistent quantum mechanics/embedded charge study predicted the energy of the Y6 S_1 (ca. 2 eV) to lie 0.1 eV above that of the charge separated state (1.9 eV). There is, indeed, experimental evidence for direct free charge generation in Y6 solid films.^{73, 74} Our spectroelectrochemistry data put the electrochemical band gap of Y6 in neat films at 1.72 eV (CF:CN) and 1.64 eV (o-xylene, see Figure 5). This is up to 0.17 eV larger than the mean HOMO-LUMO gap from conventional CV (see Table S1), but compares very well with the gap of 1.7 V determined by photoelectron spectroscopy in literature.³⁵ The Y6 band gap is slightly higher in the blend with 1.73 eV from CF:CN and 1.78 eV from o-xylene and consistent with a slight blue shift in absorption, indicating a slightly more distorted structure. On the other hand, we determined the energy of

the Y6 singlet energy by the intersection between the normalized absorption and PL of the blend to of 1.42 ± 0.02 eV (see Figure S7). This yields an Y6 exciton binding energy at 0.33 ± 0.05 eV. This is in the same range as the HOMO offset in the blend, suggesting that the driving force for free charge formation by exciton dissociation is nearly zero. This contrasts the efficient free charge generation of the blend. A similar scenario has been reported by Wu *et al.* where it was suggested that the formation of free charges is driven by entropy.³⁶ This is because an electron-hole pair in the charge separated state has many more options to distribute in the blend volume than when its bound in an exciton or in a charge transfer state.⁷⁵ However, our own recent studies showed a pronounced decrease of the free carrier density with temperature,⁷⁶ which questions a strong contribution by entropy-driven processes. An alternative approach is to consider the presence of sub-bandgap states not accessibly by our spectroscopy.⁷⁷⁻⁷⁹ Such states will be able to situate the free electron hole pair at energies well below the singlet exciton of Y6.

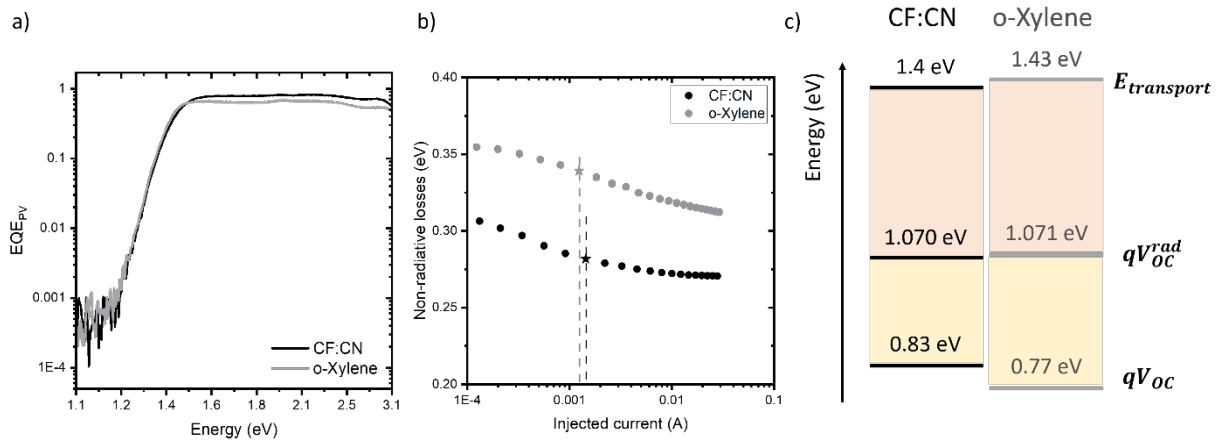


Figure 7: EQEPV (a), non-radiative voltage loss as a function of injected current (b), and schematic of relevant energy losses (c) of PM6:Y6 devices fabricated in CF:CN (black) and o-Xylene (grey). The dash lines in b) indicate when the injected current equals short-circuit current at 1 sun.

We finally address the reason for the significantly lower V_{OC} of the device prepared from o-xylene (0.77 V vs. 0.83 V for the CF:CN). According to Figure 5, the fundamental transport gaps are 1.43 eV and 1.40 eV for the blend prepared from o-xylene and CF:CN, respectively, showing the inverse trend. However, the relation between V_{OC} and the fundamental gap is not straight forward. In general, the V_{OC} of a device is given by the radiative voltage limit reduced by the non-radiative voltage loss: $V_{OC} = V_{OC}^{rad} - \Delta V_{OC}^{nr}$. The radiative V_{OC} limit is mainly determined by the ratio of the short circuit current, J_{SC} , and the radiative dark current, $J_{0,rad}$, the latter being proportional to the convolution of the external photovoltaic quantum efficiency

(EQE_{PV}) of the device and the blackbody photon flux (ϕ_{BB}) over photon energy:⁸⁰ $qV_{OC}^{rad} = \ln(J_{SC}/J_{0,rad})$ where $J_{0,rad} = q \int EQE_{PV}(E)\phi_{BB}(E)dE$.

Here, the transport gap may enter indirectly via the onset of the EQE_{PV} spectrum. However, it has been shown before that the low energy tail of the PM6:Y6 EQE_{PV} is entirely determined by the Y6 singlet exciton, which has a very similar energy for the two blends.⁸¹ As a consequence, the band-edge of the EQE spectra in Figure 7 a) overlaps almost completely, yielding nearly the same V_{OC}^{rad} for the two devices (Table S2). Therefore, the difference in V_{OC} of the two devices must be entirely caused by the non-radiative losses (ΔV_{OC}^{nrad}). To confirm this, we measured the external electroluminescence quantum yield ($ELQY$), which is related to ΔV_{OC}^{nrad} via $q\Delta V_{OC}^{nrad} = -k_B T \ln(ELQY)$ (see Figure S8 in the SI for the emission spectra). This measurement revealed an almost 10 times lower $ELQY$ for the device prepared from o-xylene (see Figure 6 b) and Table S2 for the values). It has been shown that the $ELQY$ of PM6:Y6 blend is limited by the non-radiative decay properties of the CT state.⁸¹ In organic solar cells, the predominant non-radiative decay pathway of the CT state is through vibronic coupling to the ground state.^{82, 83} There is experimental and theoretical evidence that this process is significantly affected by the interfacial molecular orientation.^{84, 85} Our results suggest that this is the determining factor also in our PM6:Y6 devices.

Conclusion

In summary, this work presented an absorption spectroscopy assisted, spectroelectrochemical approach to determine the frontier orbital energies of PM6 and Y6 in blend films. A central advantage of our technique is the detection of the energy levels of the individual compounds inside the blend films and therefore examines influences arising from blending both materials. By preparing solar cells from two solvent systems resulting in two opposing bulk morphologies we investigated the influence of morphology on the energetics in blend films of the model system PM6:Y6.

Our results provided HOMO/LUMO levels for PM6 of -5.30 eV/-3.06 eV and for Y6 of -5.63 eV/-3.90 eV in blend films processed from CF:CN (face-on morphology in bulk). Respective results for blend films processed from o-xylene (edge-on in bulk) delivered HOMO/LUMO levels for PM6 of -5.31 eV/-3.07 eV and for Y6 of -5.66 eV/-3.88 eV. Interestingly, these values differ only slightly from the corresponding energies of the neat layers. Our data show that the effect of the different morphologies in the two blends on the energy levels is measurable but too small to explain the distinct difference in device performance. From our spectroelectrochemical measurements, we could determine the HOMO

offsets and the transport gaps to be 0.33 eV and 1.4 eV for films from CF:CN and 0.35 eV and 1.43 eV for films from o-xylene, respectively. The HOMO offset was confirmed by UPS measurements on the blend, which yielded a value of 0.25 eV. Notably, the UPS measurements on the neat layers would suggest a HOMO offset of 0.54 eV, meaning that a comparison with neat material films must be taken with care. Finally, we determined the S_1 binding energy of the CF:CN coated Y6 to be 0.33 eV, very similar to the HOMO offset. This suggests that an additional driving force exists for free charge generation. This study exemplifies the importance of precisely determining energy levels in blend films to generate device relevant information.

Experimental

Materials.

PM6 ($M_n \sim 100$ kg/mol, PDI ~ 2.3) and Y6 (1451.94 g/mol) were both purchased from 1-Material and used without further purification. All used solvents were purchased from Sigma-Aldrich and used as received.

Film preparation and treatment.

Thin films of neat PM6, neat Y6 and a blend of PM6:Y6 (1:1.2 wt%) were spin-coated from CF:CN (0.5 wt%) and o-xylene to obtain ~ 30 nm thick films on ITO substrates. The solutions were stirred at elevated temperatures (40 °C for CF:CN and 70 °C for o-xylene) to guarantee good solution quality before spin coating under dry nitrogen atmosphere. All ITO substrates were previously cleaned by ultrasonication in isopropanol and acetone. The samples fabricated with CF:CN were annealed for 10 min at 110 °C under dry nitrogen atmosphere right after the deposition of the active layer. For the samples fabricated with o-xylene, the active layer solution and substrate were heated up to 100 °C and 110 °C, respectively, prior to the spin coating. The deposition of active layer was conducted with hot solution and hot substrate.

Device geometry:

All PM6:Y6 devices were prepared in the same conventional structure (ITO/PEDOT:PSS/PM6:Y6/PDINO/Ag). Patterned ITO substrates (Psiotec, UK) were sonicated in Hellmanex, deionized water, acetone, and isopropanol for 20 min, 20 min, 10 min and 10 min, respectively. The cleaned ITO substrates were then treated with O₂ plasma (200 W, 4 min). Filtered (through 0.2 μ m PA filter) PEDOT:PSS (Clevios, AL4083) was spin coated on the plasma treated ITO substrates at 5000 rpm for 30 s in ambient condition to form the hole transport layer. The PEDOT:PSS layer was then thermal annealed at 150 °C for 25 min. The rest of the fabrication was conducted in the glovebox. The PM6:Y6 active layers made with CF:CN (0.5 wt%) and o-xylene were prepared, deposited, and treated on the top of PEDOT:PSS layer exactly as described in the film preparation and treatment section. After the deposition and treatment of the active layer, a thin layer of PDINO (~ 10 nm) was spin coated on the top of the active layer to form the electron transport layer. Silver was then thermally evaporated through a patterned mask on the top of PDINO layer to complete the devices with a pixel area of 0.06 cm².

Electrochemical measurements.

Cyclic voltammograms were recorded in an electrochemical three-electrode setup under inert conditions. ITO substrates were used as working electrode against a Pt counter electrode. An AgCl covered Ag wire was used as pseudo reference electrode in 0.1 M TBAPF₆ (electrochemical grade) in MeCN as standard electrolyte. All potentials were referenced against the Fc/Fc⁺ redox couple (added after the measurements) as internal standard. The experiments were carried out on a PGSTAT204 potentiostat from Metrohm. The working electrodes were positioned in the beam path of a UV-vis spectrometer to collect *in situ* spectral data. The modular diode array spectrometer system from Zeiss was provided with a MCS621 vis II detector and CLH600 F halogen lamp.

Grazing-incidence wide-angle x-ray scattering (GIWAXS).

GIWAXS measurements were performed at the SAXS/WAXS beamline at the Australian Synchrotron.⁸⁶ A photon energy of 15 keV was used with 2D scattering patterns recorded using a Pilatus 2M detector. The sample-to-detector-distance was 742 mm calibrated using a silver behenate reference standard. The sample and detector were enclosed in a vacuum chamber to suppress air scatter. Scattering patterns were measured as a function of angle of incidence, with the bulk-sensitive data acquired with an angle of incidence near the critical angle that maximized scattering intensity from the sample, and the surface-sensitive data acquired below the critical angle. The experimentally determined critical angles range from 0.105° to 0.13°. The difference in these apparent critical angles is within the acceptable range of error, which is defined by the resolution of incident angle alignment with a value of 0.02°. Data reduction and analysis was performed using a modified version of NIKA,⁸⁷ implemented in Igor Pro.

Near-edge X-ray absorption fine-structure (NEXAFS) spectroscopy

NEXAFS measurements were performed under high vacuum conditions at the Soft X-ray beamline at the Australian Synchrotron.⁸⁸ Data was acquired in partial electron yield (PEY) mode whereby X-ray absorption was detected via the measurement of energetic photons that were ejected from the sample that were detected by a channeltron detector. Data was calibrated and normalized using the so-called “stable monitor method” that uses an upstream gold mesh to monitor the beam intensity whose response is calibrated by measuring the signal at the sample position with a photodiode. Data analysis was performed in QANT,⁸⁹ with further details of data analysis procedures provided elsewhere.⁹⁰

Ultraviolet photoelectron spectroscopy (UPS).

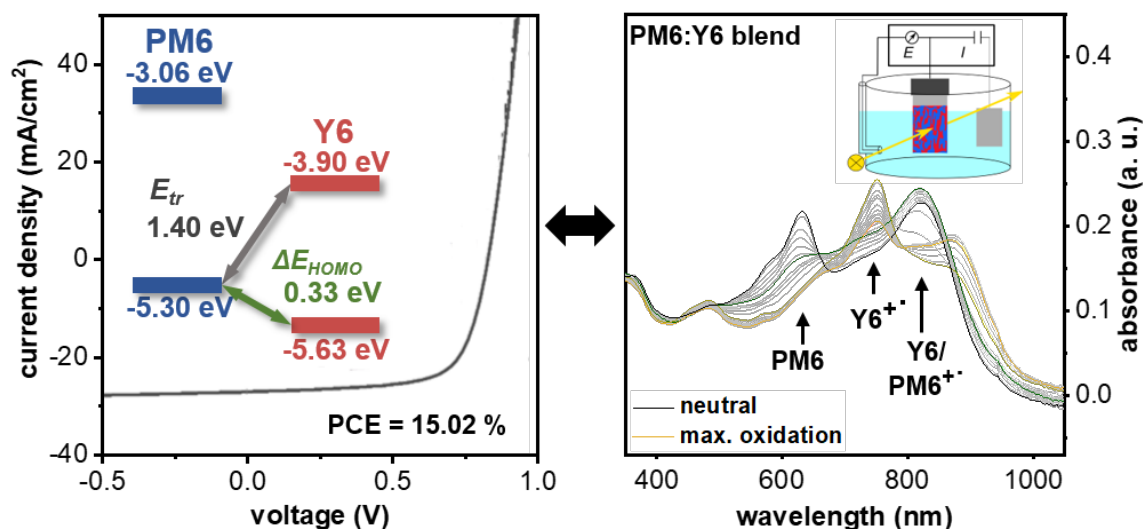
All samples were transferred to an UHV system with a base pressure of 10^{-10} mbar without air exposure. A *HIS 13* helium discharge lamp from *ScientaOmicron* equipped with a monochromator was used for excitation, yielding a reduced UV flux and therefore minimum degradation of the samples. The kinetic energy of the emitted photoelectrons was measured using a *Specs Phoibos 100* hemispherical analyzer and pass energies of 5 eV or 2 eV for the valence band or the secondary electron cut-off (SECO) spectra, respectively. A bias of -10 V was applied between sample and analyzer during the SECO measurements. The binding energy axis was calibrated by measuring the Fermi-edge of a polycrystalline gold sample and setting its center to 0 eV. The resolution of the setup in this configuration was 0.15 eV as determined from the width of the Fermi-edge.

Conflicts of interest

There are no conflicts to declare.

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A systematic spectroelectrochemical approach is presented to determine frontier orbital energies of PM6:Y6 blends in controlled morphologies. The new insights are discussed regarding their impact on solar cell performance and stress the importance to measure energy levels of the individual compounds in device-relevant blend films.

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