Mixing of NFAs ionization energies: an additional tool to increase the quantum efficiency of ternary organic solar cells

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Abstract
Non-fullerene acceptor (NFA)-based ternary bulk heterojunction solar cells (TSC), represent the most efficient organic solar cells (OSCs) today due to their broader absorption, but also to quantum efficiencies (QE) often surpassing those of the corresponding binary blends. We study the relation between those QE and the energetics driving charge transfer at the electron donor:electron acceptor (D/A) interfaces in the blends of a donor (PBDB-T-2F) with several pairs of lower bandgap NFAs. Similar to binary blends, the QE increases with the ionization energy offset between donor and acceptor (ΔIE) due to the improved charge transfer efficiency, following an error function that maximizes and plateaus for ΔIE > 0.5 eV. Unexpectedly, photocurrent generation appears to proceed through a single channel, controlled by the difference between the IE of the donor and the weighted-average IE of both NFAs, rather than by individual D:NFA ΔIEs. As a proof of concept, we took a PBDB-T-2F:IEICO binary blend, having a ΔIE insufficient for charge generation, and significantly improved the photocurrent generation upon IEICO absorption by adding a deep IE third component: IT-4F. Those findings imply that combining two NFA can be used as an alternative to synthesizing new molecules, to optimize the D/A energy matching.
1. Introduction

The power conversion efficiency (PCE) of organic solar cells (OSC) has been booming in the latest year, now having reached 19% with 20% expected soon,\textsuperscript{1-3} driven by the development of novel non-fullerene acceptors (NFA) and improved device optimization.\textsuperscript{2,4} As of today, the most efficient single junction OSCs are ternary organic solar cells (TSC) combining one electron donor and two NFAs in the photo-active layer.\textsuperscript{5,6} TSC offer better performances\textsuperscript{6-9} and stability\textsuperscript{7-10} than the corresponding binary cells, and are easier to upscale than multi-junction solar cells.\textsuperscript{11,12} Looking into the near future and the development of tandem and multijunction OSC, this 3rd component offers an additional lever to adjust the photocurrent and open-circuit voltage in the subcells, as was recently demonstrated.\textsuperscript{10-12}

The primary reason for the higher performances of TSC is the improved photocurrent owing to their broader absorption, and often, to a larger quantum efficiency of the photocurrent generation.\textsuperscript{10,12,13} This larger quantum efficiency has been attributed to enhanced charge generation\textsuperscript{13} and charge carrier mobilities\textsuperscript{12,14} and reduced recombination.\textsuperscript{6,10} However, there is to our knowledge no detailed report of the effect of the three components energy levels on this quantum efficiency.

In the light of our recent finding on binary blends,\textsuperscript{18} we expect those energetics to play a major role also in ternaries. In binary blends, we found that energetics control not only the photovoltage, but also the photocurrent.\textsuperscript{15,16} Specifically an offset (ΔIE) of no less than 0.45 – 0.5 eV between the ionization energy of the donor and that of the NFA can drive a quantitative hole transfer from the exciton in the NFA to the donor.\textsuperscript{18} This offset is required to overcome the band bending at the interface between the donor and the acceptor that raises the energy of the interface charge transfer state (CT-state) compared to the singlet excitons.\textsuperscript{15,17} Note that singlet exciton is almost always located in the NFA even when the light is absorbed by the
donor. Indeed, by design, the NFA in modern cells has a lower bandgap than the donor, resulting in Förster resonance energy transfer (FRET) from the donor to the acceptor that outcompetes electron transfer.\textsuperscript{12,15,18} Note also that the interface band bending,\textsuperscript{15,17} while being a limit for the charge transfer, tends to push the charges away from the interface after the transfer has occurred, resulting in barrierless charge separation.\textsuperscript{19,20} Such an understanding determines the selection of the materials than can be combined for efficient charge generation, and is thus also very needed for TSC.

In TSC, the combination of the three components energy levels has mostly been studies in the frame of energy losses and cells open circuit voltage (V\textsubscript{OC}). Upon changing the blend ratio, V\textsubscript{OC} has been found to evolve linearly between the V\textsubscript{OC} of the binary cells corresponding to ratios 1:0:1 and 1:1:0.\textsuperscript{21-23} This has led to consider the existence of molecular organic alloys although it has since then been shown to be an inexact description.\textsuperscript{27} The exact nature of the interplay of the components energy levels thus remains to-date elusive, and their influence on the cells quantum efficiencies mostly unstudied.

We selected the common donor copolymer PBDB-T-2F (PM6) as a wide-bandgap electron donor in this work. We used as a primary/majority NFA (hereafter referred to as NFA-1) three fused-ring electron acceptors (FREA) offering different energetic landscapes: i- IEICO has a $\Delta$IE with PM6 lower than the average band bending $B = 0.39$ eV reported for PM6:NFA.\textsuperscript{18} ii- IEICO-4F has a $\Delta$IE with PM6 comparable to $B$ (slightly smaller). iii- finally IT-4F offers a $\Delta$IE with PM6 larger than $B$. As a third component / minority NFA, we used COiDFIC which offers a $\Delta$IE with PM6 slightly larger than the reported value of $B$. Previously, we reported that in binary PM6:IEICO and PM6:IEICO-4F solar cells, the photocurrent generation is low since the IE offset between the donor and acceptor is too small to drive efficient charge generation.
Here, COi8DFIC was chosen as the second acceptor due to its higher IE compared to IEICO and IEICO-4F.

Using a combination of steady-state and (ultrafast) transient spectroscopy techniques, we investigated the photophysical processes in TSCs with different IE offsets. Similar to the binaries situation, we find that FRET from the donor to the NFAs outcompetes electron transfer, leading to an IE offset controlled charge generation (hole transfer). We find that the hole transfer from NFA-1 and COI8DFIC to PM6 behaves as a single channel. As such, the hole transfer from COi8DFIC to PM6 can be efficient or inefficient depending on the associated NFA-1. We then investigated what offset controls this unique channel. By varying the NFA-1:COI8DFIC ratio, we observed that it is the offset $\Delta \text{IE}_{\text{weighted}}$ between the IE of the donor and the weighted-average of acceptors IEs that controls the charge generation process. This implies that even low IE offset acceptors D:A combinations can contribute to charge generation in ternary solar cells, unlike in binary devices, provided they are associated to a second NFA offering a larger offset.
2. Results and Discussion

2.1 Device performance and steady-state optical properties

Figure 1: a) Energy levels of the materials used in the study. Ionization energy (IE) and electron affinity (EA) were measured using ultraviolet photoelectron spectroscopy (UPS) and low energy inverse photoelectron spectroscopy (LE-IPES), see Figure S2. Comparative IE measured with photoelectron spectroscopy in air (PESA) are shown in Table S1. b) Normalized absorption spectra (continuous lines) of the neat films of the materials used and photoluminescence emission spectrum (shaded area) of PM6. c) J-V curves of the following binaries B0, PM6:Coi8DFIC (1:1); B1, PM6:IT-4F (1:1); B2, PM6:IEICO (1:1); B3, PM6:IEICO-4F (1:1) and ternaries T1, PM6:IT-4F:Coi8DFIC (1:0.9:0.1); T2, PM6:IEICO:Coi8DFIC (1:0.9:0.1); and T3, PM6:IEICO-4F:Coi8DFIC (1:0.9:0.1). d) External quantum efficiency (EQE) spectra of the corresponding devices. e) Normalized photoluminescence emission of the ternaries and corresponding neat films (not corrected for detectors sensitivity except for PM6 in 1b, the NIR part was smoothed here). All the ternary films were excited at 500 nm. The neat films of PM6, IT-4F, Coi8DFIC, IEICO, IEICO-4F were excited at 500 nm, 650 nm, 750 nm, 750 nm, and 800 nm, respectively.

Figure 1a shows the ionization energies and electron affinities of the materials measured by ultraviolet photoelectron spectroscopy (UPS) and low energy inverse photoelectron spectroscopy (LE-IPES), respectively. Details of UPS and LE-IPES are provided in the SI (Figure S2). PM6:IEICO has an IE offset of 0.32 eV, which is below the reported average band bending of 0.39 eV in PM6 based binaries, leading to poor charge generation. PM6:IEICO-4F and PM6:COi8DFIC have offsets of 0.35 and 0.42 eV, hence slightly below and slightly
above the average band bending, respectively, leading to expected hole transfer efficiencies below and above 50%, respectively. PM6:IT-4F, on the other hand, exhibits a large IE offset of 0.85 eV, leading to large QE.\textsuperscript{18} Furthermore, the overlap of the PM6 fluorescence spectrum and NFA absorption facilitates Förster Resonance Energy Transfer (FRET) from PM6 to the NFAs upon donor excitation (Figure 1b). The chemical structures of all materials are shown in Scheme S 1.

We fabricated binary and ternary OSCs using the inverted device architecture, precisely ITO/ZnO (sol-gel)/BHJ/MoO\textsubscript{x}/Ag.\textsuperscript{29} The photocurrent in the binaries increases with the IE offset, in line with our previous study,\textsuperscript{18} from: PM6:IEICO (B\textsubscript{2}), PM6:IEICO-4F (B\textsubscript{3}), PM6:COi8DFIC (B\textsubscript{0}) to finally PM6:IT-4F (B\textsubscript{1}), see Figure 1a and Error! Reference source not found.. This is also reflected by the external quantum efficiency (EQE) spectra. (Figure 1d). We prepared ternary BHJs by adding a small quantity of the acceptor COi8DFIC, that is, BHJs composed of D:NFA-1:COi8DFIC(COI8DFIC) with a ratio of 1:0.9:0.1. This corresponds to adding a lower IE NFA to IT-4F (B\textsubscript{1} to T\textsubscript{1}), a higher IE NFA to IEICO (B\textsubscript{2} to T\textsubscript{2}), and a slightly higher IE NFA to IEICO-4F, from B\textsubscript{3} to T\textsubscript{3}, respectively. The photocurrent in T\textsubscript{1}, T\textsubscript{2} and T\textsubscript{3}, follows the same trend as in the binaries.

Comparing the ternaries to the corresponding binaries, the addition of the third component COi8DFIC leads to an increase in the photocurrent in all three cases, but for different reasons. As shown by the EQE spectra (Figure 1d), in the large offset blend (T\textsubscript{1}, IT-4F), the photocurrent increase originates from the additional near-infrared absorption of COi8DFIC (Figure 1d). In contrast, in the case of the intermediate offset (T\textsubscript{3}, IEICO-4F) the EQE clearly increases across the entire spectrum. Finally, only a minor improvement was observed in the low offset case (T\textsubscript{2}, IEICO). Below we examine the reasons for the difference PCE improvements.
An improvement of the morphology and packing has often been reported to improve the charge transport\textsuperscript{30} and reduce the recombination\textsuperscript{6,25,26} in TSC. We thus conducted grazing incidence wide-angle X-ray scattering studies (GIWAXS) to track the evolution of the packing upon the addition of the third component.\textsuperscript{32} The GIWAXS patterns obtained for the binaries and the ternaries display solely diffraction features from PM6 aggregates (of similar intensity), indicating that the NFAs are mostly amorphous in all blends (Figure S7 of the supporting information). Hence, we concluded that the observed differences in charge generation do not result from differences in the solid-state microstructure.

Steady-state photoluminescence (PL) spectroscopy confirms the expected energy transfer from the donor. PM6 photoexcitation leads to emission from the most abundant NFA-1 (Figure 1e-g) in all three ternaries, indicative of efficient singlet exciton energy transfer, while almost no PL from COi8DFIC (COI8DFIC) was observed. We note that this does not exclude energy transfer to COi8DFIC, but due to its low concentration in the blend (~10%), it is unlikely to have COi8DFIC-rich domains large enough for excitons to decay there via fluorescence.

Those preliminary measurements did not reveal any significant difference between the three ternary blends, we thus turned to transient absorption spectroscopy to investigate the differences in the charge generation and recombination processes.

2.2. Transient Absorption Spectroscopy
Ultrafast transient absorption spectroscopy (TAS) can reveal exciton and charge transfer dynamics in TSC’s photoactive layers. TAS allows to identify which of the blend’s component bears the photoexcited states by monitoring the components’ ground state bleach (GSB) caused by the depopulation of the ground state of the molecules. Moreover, excited states can be distinguished by their characteristics photoinduced absorption (PA) features.\textsuperscript{33} Finally, excited
state dynamics can be monitored across the entire sub-picosecond to microsecond timescale following photoexcitation.

Following PM6 excitation, ultrafast energy transfer is observed in the first few picoseconds in all three blends. More precisely, in T1, selective PM6 photoexcitation (~505 nm) causes distinct COi8DFIC and IT-4F exciton-induced absorption peaking at 1.2 and 1.3 eV, respectively, as early as 400 fs after photoexcitation, shown in Turning to charge generation, we observed a. Similarly, T2 and T3 exhibit NFA exciton-induced signatures such as the ground state photo-bleach at 1.5 and 1.42 eV, respectively, observed as early as 300 fs after PM6 photoexcitation, see Turning to charge generation, we observed b and c. In T1, the GSB of the NFAs is superimposed by the PM6 cation absorption (see Figure 3a), so it can not be directly observed. A detailed assignment of all spectral features, as well as their kinetics, can be found in the supporting information (Figure S9).
Notably, singlet excitons are observed in both NFAs upon PM6 photoexcitation, confirming that the lack of PL from COi8DFIC (Figure 1 e-g) is due to the absence or reduced size of pure COi8DFIC domains, while FRET takes place from PM6 to both NFAs. The COi8DFIC excitons are identified in T1 by their PA peaking at 1.2 eV, also seen as a shoulder in the TA spectra of T2. For T3, the COi8DFIC GSB peaking at 1.4 eV is observed in the first hundreds of femtoseconds following PM6 photoexcitation.
Turning to charge generation, we observed efficient and fast charge generation in T1 and a slower and less efficient charge generation in T2 and T3. PM6 cations are already present in T1 in the first hundreds of femtoseconds, as indicated by the presence of charge-induced absorption from 1.4 – 1.8 eV (+ symbols in Figure 3a). This charge-induced absorption is seen indirectly by their effect of masking the GSB of IT-4F and COi8DFIC (1.4 – 1.8 eV) that should be larger owing to the large PA signal of the NFAs excitons and anions between 1.1 – 1.4 eV. In contrast, PM6 charges are not seen at early times in T2 and T3 (Turning to charge generation, we observed b-c), here the PA and GSB signatures of NFA excitons are observed, similar to the spectra of neat samples, i.e., in the absence of charges and presence of excitons.

![Figure 3](image_url)

**Figure 3:** Evidence of efficient ultrafast charge generation in T1 contrasting with a slower and inefficient generation in T2 and T3. Evolution of the ps-ns TA spectra following the selective excitation of PM6 for (a) T1 ($I_{\text{pump}}$ = 505 nm), (b) T2 ($I_{\text{pump}}$ = 500 nm), and (c) T3 ($I_{\text{pump}}$ = 550 nm). The black open symbol plot in a) represents the PM6 cation spectra obtained by oxidation with FeCl3 and the horizontal breaks indicate the region affected by the probe scattering. (d,e,f) schematic representation of the blends excited state mechanism upon selective excitation of PM6.
The difference in charge generation efficiency remains or even increases over the time range monitored (Figure 3). In T1, the PM6 GSB seen from 1.9 – 2.3 eV remains important in the entire time range, indicating efficient formation of long-lived states. On the contrary, the GSB of PM6 decayed fast in T2 and T3, and only a limited excited states signal remains after 500 ps. In all three cases, the spectral signatures of the long-lived states (compare 50 - 100 ps spectrum of T1 and 500 – 800 ps spectrum of T2 and T3) differ from those of the excitons. We attribute this to PM6 cations and NFA anions generation. More precisely, in T1, the GSB of PM6 increased from 1 ps to 30 ps (Figure 3a and S8,S9d) due to diffusion-mediated hole transfer from the acceptor. We note that in T1, a new PA peak around 0.9 eV appears on the nanosecond time scale, which we attribute to COi8DFIC charge carrier formation since it corresponds to the charge-induced absorption of COi8DFIC seen in the binary systems, see Figure S 11 in the SI.

Charge generation appears to be the most critical step when comparing device performance. Its efficiency differs between the blends, while FRET from PM6 to both acceptors is observed in all three blends. Importantly, the two donor:acceptor interfaces present in each blend do not exhibit two distinct generation channels, but the charge generation is efficient in (T1) for both IT-4F and COi8DFIC, whereas in T2 and T3 it is less efficient for both NFA-1 and COi8DFIC. In other words, the presence of the primary / majority component NFA-1 controls the efficiency of the charge generation of the minority acceptor COI8DFIC, that is, at the PM6:COi8DFIC interface, which is present in all three blends, as summarized in Figure 3d-f.

By rationalizing this observation in terms of the energetic landscape, it appears that charge generation follows the same trend as we previously reported for binary BHJs. The charge (hole) transfer is driven by the IE offset between the donor and acceptor, compensating the energy level bending (bias potential B) at the donor:acceptor interface caused by the acceptors’
quadrupole moment\textsuperscript{15,17,29,30} as illustrated in Figure 4 in the framework of the energy level bending model\textsuperscript{20}.

![Figure 4: Schematic of the interplay of energy level bending at the donor-acceptor heterojunction and ionization energy offset for the three different situations corresponding to the blends studied here: the charge transfer efficiency corresponds to the fraction of the interfaces where the local energy bending is lower than $\Delta IE$.](image)

Qualitatively, it appears that charge transfer is controlled by the IE offset between the donor and the majority acceptor, as the hole transfer efficiency from COi8DFIC to PM6 follows the one of the majority NFA. The EQE spectra are in good agreement with the difference between the IE of PM6 and the IE of the majority NFA: considering a typical bias potential $B$ of 0.4 eV. The PM6:IEICO interface does not provide sufficient driving force (0.32 eV) to overcome the bias potential, the PM6:IEICO-4F interface provides an offset of 0.4 eV that is comparable to $B$, for which a hole transfer efficiency of $\sim50\%$ can be expected. And the PM6:IT-4F interface exhibits an IE offset of $\sim0.85$ eV, which is sufficient to obtain hole transfer efficiencies close to 100%. Consequently, at this stage, it appears that the hole transfer efficiency of the PM6:COi8DFIC interface follows the majority NFA.

2.3 The role of the third component in the charge generation

The TAS studies suggest that the IE of the majority NFA dictates the EQE of the TSC. However, the EQE spectra (see Figure 1) do show that in some cases the third component has some effect other than just the additional absorption: the EQE of PM6:IEICO-4F:COi8DFIC (T3) is increased compared to PM6:IEICO-4F across the entire spectral region, rather than only in the COi8DFIC absorption region. On the other hand, this effect appears to be minimal in the case 13
of the other two blends, which showed only a minor improvement (T2), or no change at all (T1).

To clarify the role of the minority NFA, we enhanced its impact by increasing the weight fraction of COi8DFIC in the ternary blends.

As shown in Figure 5 a-c, the EQE spectra evolve continuously with the NFA-1:COi8DFIC ratio from the EQE of the PM6:NFA-1 binary to that of the PM6:COi8DFIC binary. Noticeably, the spectra appear relatively flat as long as the absorption is not limited by the too low weight fraction of one of the components, the waviness of the spectra being most likely related to

\[ \text{IQE} = \frac{\Delta E \text{sat}}{2} \left(1 + \text{erf} \left(\frac{\Delta E - B}{\sigma}\right)\right). \]

The fits to this function yield \( B = 0.40 \pm 0.01 \text{ eV}, \sigma = 0.07 \pm 0.01 \text{ eV} \) and IQE\text{sat} = 62 +/- 6%.
optical interference features caused by the multilayer structure of the solar cell. This flateness is also consistent with our observation of a single channel for charge generation.

This flateness of the EQE spectrum have two important consequences. First, we can safely use its maximum value \( EQE_{\text{max}} \) as representative of the efficiency of internal processes: as the spectral variations are due mostly to the absorption spectrum of the active layer in the device structure, using \( EQE_{\text{max}} \) enables to minimize the influence of absorption losses and focus on other photophysics. Second, if we want to evaluate the influence of energetics on the efficiency of those processes, we need to find a variable that accounts for the three blend components. In the frame of our previous findings for charge generation in binary blends, we chose \( \Delta I_{E_{\text{weighted}}} \): the difference between the ionization energy of the donor, and the average of the acceptors ionization energies, weighted for their weight ratio in the ternary blend. The result is shown in Figure 5d.

Figure 5d clearly shows that a relation exist between \( EQE_{\text{max}} \) and \( \Delta I_{E_{\text{weighted}}} \). We fitted a relation derived from that observed for binary blends,\(^{18}\) and obtained an excellent agreement (solid line):

\[
EQE_{\text{max}} = \frac{EQE_{\text{sat}}}{2}\left(1 + erf\left(\frac{\Delta I_{E_{\text{weighted}}} - B}{\sigma}\right)\right)
\]  

(1)

As a reminder, this relation considers a Gaussian distribution of band bendings at the D/A interface, with an average \( B \) and a variance \( \sigma \). The internal quantum efficiency is equal the integration of this distribution from a bending of 0 eV to a bending equal to \( \Delta I_{E} \), multiplied by a prefactor \( IQE_{\text{sat}} \). This correspond to the fraction of the band bending distribution for which the hole in the valence band of the donor at the interface is higher in energy than in the valence band of the acceptorat the interface, making the hole transfer favorable (see also Figure 4).

For the ternary blends represented here, the fit yielded an average bending \( B = 400 \pm 10 \text{ meV} \) with a variance of \( \sigma = 70 \pm 10 \text{ meV} \) similar to what has been reported for the binaries,\(^{18}\) and an
upper EQE_{sat} limit of 62 ± 6 %. The variance is however a little bit larger (around 40 - 50 meV in binaries), possibly because the NFA-1:COi8DFIC ratio may not be perfectly homogeneous through the film. We note that the fit applied here describes the evolution of the quantum efficiency of the hole transfer process. Other losses, such as incomplete photon absorption, exciton decay to the ground state - note that the films exhibit some remaining PL (see Figure 1e) – are not accounted for, thus explaining that the EQE_{sat} is limited to about ~62%.

From an energetic perspective, the NFA-1 and COi8DFIC appear to behave as a single material whose IE can be described by the linear combination of their IEs. Such behavior has previously been predicted theoretically and observed experimentally on co-evaporated acceptor molecules.\textsuperscript{30} However, to the best of our knowledge, it is described for the first time in solution-processed blends.\textsuperscript{24}

This description readily explains why a difference was observed between the QE of the binary blend PM6:IEICO-4F and that of the ternary PM6:IEICO-4F:COi8DFIC but not in the two other cases (see Figure 1). Indeed the ΔIE between PM6 and IEICO-4F as well as between PM6 and COi8DFIC are very close to B, which means to the maximum of the Gaussian distribution of band bendings. As such, even the slight increase of ΔIE_{weighed} caused by adding 10% of COi8DFIC to the blend is making a significant fraction of the band bendings become smaller than ΔIE_{weighed} thus making those interfaces able to generate charges. On the other hand the ΔIE of the PM6:IEICO and PM6:IT-4F are on the lower, resp. higher, plateaus of the error function, and are thus relatively immune to small changes in ΔIE_{weighed}. 
We confirmed that the evolution of the blends’ EQE originated from the hole transfer efficiency by monitoring charge generation in PM6:IT-4F:COi8DFIC ternary films with different NFA ratios using TAS (Figure 6). For both the 1:1:1 and 1:0.1:0.9 blends, fast FRET occurs following PM6 excitation, leading to the immediate presence of NFA exciton-induced absorption signals. However, the intense PM6 cation absorption signal (1.4 – 1.8 eV) previously seen in the 1:0.9:0.1 blend at early delay times (Figure 2a and Figure 3a) was not observed here. Moreover, in contrast to the 1:0.9:0.1 ternary blend, that converts almost all initial PM6 photoexcitations into long-lived states, in the 1:1:1 blend film, a small decrease of the PM6 GSB (1.9 – 2.2 eV) signal was observed within the formation time of long live species, finally on the 1:01:0.9 blend, more than 50% of the signal had decayed before forming long lived
species (subnanosecond timescale). This indicates that an equivalent fraction of the initial photoexcitations were not converted into charges in these blends.

Finally, we investigated whether the charge transfer channel can be activated in a low IE offset system by adding a second acceptor with deeper IE. We selected PM6:IEICO with an IE offset ~0.3 eV and thus EQE below 5% (See Figure 1) and added a third component, IT-4F, with a higher IE, with an offset of 0.8 eV with PM6. Interestingly, as shown in Figure 7a, the EQE in the spectral region of IEICO absorption increases from close-to zero to more than 25% upon adding 40 wt.% IT-4F. Any further increase is impeded since with decreasing the IEICO fraction in the blend, the limited absorption in this spectral region becomes the bottleneck.

![Figure 7: a) EQE spectra of PM6:IEICO:IT-4F blends for different PM6:IEICO ratios. b) EQE maximum vs weighted average IE offset for PM6:IEICO:IT-4F solar cells (black) and the evolution Voc with weighted average electron affinity (EA) offset (red). c) The error function fit to the evolution of EQE maximum vs weighted average IE offset yield B = 0.39 eV and a = 0.08 eV. Schematic of the energy level bending at the donor–acceptor heterojunction due to the electrostatic interaction of charges with quadrupole moments of surrounding molecules.](image-url)
We observe (Figure 7c) that $\text{EQE}_{\text{max}}$ obeys the same trend found previously for binary donor:NFA blends\textsuperscript{18} as well as reported here for the other ternary systems. The insets in Figure 7c schematically represent the proposed interfacial energetics for a selection of different blending ratios. The corresponding device J-V curves can be found in the S.I (Figure S11).

Those results demonstrate that the mixing of two acceptors ionization energies can effectively be used to continuously adjust the $\Delta\text{IE}$ between the donor(s) and the acceptor(s) to satisfy the previously identified criteria of $\Delta\text{IE} > B + 2\sigma$ that enables to maximize charge separation. This is a very interesting alternative to the use of molecular engineering to modify existing molecules or synthesizing new ones. We stress the fact, that using this approach, IE of the pair of NFA can be adjusted continuously between the two NFAs IEs, which is not possible through molecular engineering. Finally those findings paves the way to the easier use of low bandgap acceptors, which would otherwise suffer of either low $\Delta\text{IE}$ with the donors impeding efficient charge generation, or low difference between their electron affinity and the IE of the donor, thus negatively affecting the open circuit voltage of resulting cells.

As an opening to future studies, we note that while $\text{V}_{\text{OC}}$ also changes continuously between the two extreme ratios (Figure 7b), suggesting that the EA may also be mix similarly to what the IE do, the change is only of 40 meV upon changing the average EA of more than 0.3 eV. This stresses that a lot is still to learn about how exactly those energy levels mix, as well as about the energy losses in organic solar cells in general.

3. Conclusion

We have investigated the energetics driving the quantum efficiency of ternary solar cells composed of one donor and two NFAs. The JVs showed a clear improvement of the current
upon adding the third component in all three cases; the EQE spectra further showed that in PM6:IT-4F:COi8DFIC this improvement was primarily due to the additional absorption feature while for PM6:IEICO:COi8DFIC and PM6:IEICO-4F:COi8DFIC a QE improvement was observed over the whole spectral range. Photoluminescence and transient absorption measurement revealed efficient energy transfer from the donor to the acceptors in all three cases, implying that charge transfer mostly occurs from the acceptor, hence being a hole transfer controlled by ionization energies.

Additionally, transient absorption showed that in the 1:0.9:0.1 blends, the two D:NFA interfaces behave identically as a single channel through which the hole transfer efficiency seems to be controlled by the offset between the donor and the acceptor present in the largest proportion. However, varying the blend ratios revealed that the EQE and the charge transfer efficiency are following the offset between the IE of the donor and the average IE of the acceptors, weighted for their blending ratio. We found that the evolution of the EQE with the D:A IE offset can be described by the same equation as previously reported for binary solar cells, provided the acceptor’s IE is replace by the average of the acceptors IEs.

This as important implications: it enables to use the mixing of two acceptors to continuously adjust the energetics of a D/A heterojunction to maximize the quantum efficiency while minimizing the energy losses. This also paves the way to the use on NFAs that would otherwise suffer from their too limited IE (weak current generation) or EA (low V_{oc}) offsets with the donors. This is especially relevant for low bandgap materials for which the proximity of the IE and EA would otherwise offer very limited freedom for adjustment.
4. Experimental Section

**OPV Device Fabrication and Measurements:**
Pre-patterned Indium Tin Oxide (ITO) glass substrates were cleaned in an ultrasonic bath with acetone and isopropyl alcohol for 8 min. each, and treated with oxygen plasma. A ZnO sol-gel interlayer was deposited by spin coating at 4000 rpm for 40 s, followed by annealing for 10 min at 200 °C in air. The recipe can be found elsewhere. The PM6, ITIC-4F, and IEICO, Coi8DFIC, IEICO-4F and IEICO were dissolved (20 mg/ml) in chlorobenzene overnight at 80 °C. The appropriate ratios of each were stirred for a couple of hours before spin-coating the active layer. Active layers were spin-coated at 2000 rpm inside a glove box. The thickness of the active layers is approximately 100 nm. Finally, 10 nm MoO\textsubscript{x} followed by 100 nm silver were thermally evaporated at 1*10\textsuperscript{-6} bar. J–V curves were measured using Keithley 2400 source meter and a WaveLabs sinus-70 solar simulator calibrated to 1 sun, AM1.5 G. The EQE was measured using an integrated system from Enlitech, Taiwan.

**UV-Vis-NIR absorption spectroscopy:**
Films:

The UV-Vis-NIR absorption spectra were measured with a Cary 5000 UV-Vis-NIR spectrophotometer. The PM6 film for cation spectrum measurement was obtained by oxidizing the PM6 layer with FeCl\textsubscript{3} inside a glove box. Thin layer of PM6 was spin-coated onto a UV treated quartz substrate with spin speed of 2500 rpm for 60 s, followed by annealing on a hot plate at 100 °C for 10 min. After cooling down to room temperature, the FeCl\textsubscript{3} was spin casted over it with the same speed. The active layers were obtained by dissolving the PM6 in chlorobenzene and FeCl\textsubscript{3} in isopropyl alcohol, yielding solutions with concentrations of 10mg/ml and 5mg/ml, respectively.
The transmittance spectra of both neat \((T_n)\) and oxidized \((T_{ox})\) films were measured in a nitrogen-filled custom-made sample chamber and the TA spectra simulated \((sTA)\) by calculating the transmission change:

\[
sTA = \frac{T_{ox} - T_n}{T_n}
\]

where, \(T_{ox}\) and \(T_n\) are the transmittance of the oxidized and the neat film, respectively.

**Steady state PL spectroscopy:**

The steady state PL emission spectra were measured with a Fluoromax-4 spectrofluorometer from Horiba scientific. The respective films were spin-coated inside glove box on a cleaned quartz substrate. The monochromatic beam was incident at an angle of 60° to the film and emission was collected at the same angle. The films were excited using Xe lamp source and detected using PMT-Si detector and/or InGaAs detector subjected to the emission range of NFA. To verify the energy transfer from PM6 to acceptors, PM6 was excited at 500 nm in all blend films (binary and ternary). The neat films were excited at different wavelengths as mentioned in the different parts of text.

We note that the PL-spectra presented on Figure 1e-g were not corrected for the detectors, spectral sensitivity, due to the lack of information for one the the used detectors, but where realized in the same conditions to ensure comparability. As such the emission’s spectral shape is inexact, but the evidence of energy transfer is still valid (the blends still have the emission of the acceptors, even upon donor excitation, although we do not know how this emission should exactly look like after sensitivity correction).
**Grazing incident wide-angle X-ray scattering (GIWAXS):**

The active layer films were spin coated on Si substrate under similar spin speeds as device. Si substrates were cleaned by ultra-sonicating in IPA and acetone consecutively for 8 minutes each. Further cleaned in oxygen-plasma for 5 minutes to remove any possible organic dust. GIWAXS measurements were performed at the BL11 NCD-SWEET beamline at ALBA Synchrotron Radiation Facility (Spain). The incident X-ray beam energy was set to 12.4 eV using a channel cut Si (1 1 1) monochromator. The angle of incidence $\alpha_i$ was set between 0.1-0.15° to ensure surface sensitivity. The scattering patterns were recorded using a Rayonix® LX255-HS area detector, which consists of a pixel array of $1920 \times 5760$ pixels (H x V) with a pixel size of $44 \times 44 \mu m^2$.

Data are expressed as a function of the scattering vector ($q$), which was calibrated using $Cr_2O_3$ as standard sample, obtaining a sample to detector distance of 201.17 mm. The exposure times of the samples were 5s. 2D GIWAXS patterns were corrected as a function of the components of the scattering vector. Edges of the samples were removed to eliminate edge effects in the GIWAXS pattern.

**Transient absorption spectroscopy (TA):**

TA spectroscopy was carried out using a previously described custom pump–probe setup. The output of a titanium:sapphire amplifier (Coherent LEGEND DUO, 4.5 mJ, 3 kHz, 100 fs) was split into three beams (2, 1, and 1.5 mJ). One of them was used to produce a white-light super continuum from 550 to 1700 nm by sending the 800 nm pulses through a sapphire (3 mm thick) crystal which is mounted on a stage. The other two beams were used to separately pump two optical parametric amplifiers (OPA) (Light Conversion TOPAS Prime). TOPAS 1 generates tunable pump pulses, while TOPAS 2 generates signal (1300 nm) and idler (2000 nm) only. TOPAS 2 was used to produce a white-light super continuum from
350 to 1100 nm by sending the 1300 nm pulses through a calcium fluoride (CaF2) crystal which was mounted on continuously moving stage. For short delay TA measurements, TOPAS 1 was used to generate pump pulses, while the probe pathway length to the sample was kept constant at ≈5 m between the output of TOPAS 1 and the sample.

The samples (films on quartz substrates) were kept under vacuum (10⁻⁶ mbar) during the entire measurements. The excitation wavelength used was 550 nm for all ternary blend films and the neat NFA and neat PM6 were excited at their absorption maxima. The transmitted fraction of the white light was guided to a custom-made prism spectrograph (Entwicklungsbüro Stresing) where it was dispersed by a prism onto a 512 pixel complementary metal-oxide semiconductor (CMOS) linear image sensor (Hamamatsu G11608-512DA). The probe pulse repetition rate was 3 kHz, while the excitation pulses were directly generated at 1.5 kHz frequency, while the detector array was read out at 3 kHz. Adjacent diode readings corresponding to the transmission of the sample after excitation and in the absence of an excitation pulse were used to calculate ΔT/T. Measurements were averaged over several thousand shots to obtain a good signal-to-noise ratio. The chirp induced by the transmissive optics was corrected with a custom Matlab script. The delay at which pump and probe arrive simultaneously on the sample (i.e., zero time) was determined from the point of maximum positive slope of the TA signal rise for each wavelength.

Ultraviolet photoelectron spectroscopy (UPS) and low energy inverse photoelectron spectroscopy (LE-IPES):

UPS measurements on thin films of organic semiconductor were performed in ultrahigh vacuum chamber (base pressure of 10⁻¹⁰ mbar) equipped with a Sphera II EAC 125 7-channeltron electron analyzer, calibrated with the Fermi edge of clean polycrystalline silver. The measurements were performed using the He I line (excitation energy of 21.22 eV) at pass energy
of 10 eV, with -10 eV of an external bias. The experimental uncertainty in the measurements is ± 0.05eV.

LE-IPES measurements were performed in isochromatic mode using an ultra-high vacuum (base pressure 10⁻⁹ mbar) set-up build in-house. The emitted photons were detected using a solid-state PMT detector (Hamamatsu R585) mounted outside of vacuum and equipped with a band pass filter of 280 nm (Semrock) with a narrow wavelength window of 10 nm. Samples were measured immediately after the UPS measurements by transferring to the LE-IPES manipulator without air-exposure.

The ionization energy and the electron affinity of materials was determined from the UPS and LE-IPES spectra as described previously. Samples for UPS/LE-IPES were prepared by spin coating a thin film of the organic semiconductor (polymer/NFAs) on a clean silicon substrate sequentially coated with a 10 nm Ti and 100 nm of sputtered gold. The onset energies of the occupied and unoccupied frontal molecular orbitals were derived by de-convoluting the spectra using Gaussian functions and a Taugard background. The peaks fits are only used as a guide for precisely calculating the onset energies, and the attribution of deconvoluted peaks to specific orbitals need complimentary calculations.

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Supporting Information

Mixing of NFAs ionization energies: an additional tool to tune the quantum efficiency of ternary solar cells

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Scheme S1: Chemical structures of the studied molecules
Figure S1: Absorption spectra of pristine and respective films of binary (1:1 ratio) and ternary (1:0.9:0.1 ratio) blends.
Figure S2: UPS and LE-IPES spectra obtained on thin films of the pristine molecules, demonstrating the onset energies of occupied (UPS) and unoccupied (LE-IPES) frontal molecular orbitals.

Table S1: Summary of the Ionization energy (IE) and electron affinity (EA) values measured using UPS and LE-IPES.

| Material    | Ionization Potential (eV) (±0.05 eV) | Electron Affinity (eV) |
|-------------|-------------------------------------|------------------------|
| PM6         | 5.1                                 | 3                      |
| COi8DFIC    | 5.52                                | 3.87                   |
| ITIC-4F     | 5.95                                | 4.05                   |
| IEICO       | 5.42                                | 3.68                   |
| IEICO-4F    | 5.45                                | 3.84                   |

UPS and LE-IPES

UPS measurements on thin polymer and NFA films were performed in an ultrahigh vacuum chamber (base pressure of 10^{-10} mbar) equipped with a Sphera II EAC 125 7-channeltron electron analyzer calibrated with the Fermi edge of clean polycrystalline silver. The spectra were recorded using the He I line (excitation energy of 21.22 eV) at pass energy of 10 eV, with -10 eV of an external bias. The experimental uncertainty in the measurements is ± 0.05eV. The work function of the samples was determined from the secondary electron cut-off of the UPS spectra, as described elsewhere.1, 2

LE-IPES measurements were performed in isochromatic mode using an ultra-high vacuum (base pressure 10^{-9} mbar) set-up build in-house, as described elsewhere.3 The emitted photons were detected using a solid-state PMT detector (Hamamatsu R585) mounted outside of vacuum.
and equipped with a band pass filter of 280 nm (Semrock) with a narrow wavelength window of 10 nm. Samples were measured immediately after the UPS measurements by transferring to the LE-IPES manipulator within an ultra-high vacuum atmosphere without air-exposure.

Samples for UPS/LE-IPES were prepared by spin coating a thin film of the organic semiconductor (polymer/NFAs) on a clean silicon substrate sequentially coated with a 10 nm Ti and 100 nm of thermally evaporated gold. The onset energies of the occupied and unoccupied frontal molecular orbitals were derived by de-convoluting the spectra using Gaussian functions and a Taugaard background.

**PESA (photoelectron spectroscopy in air)**

PESA measurements were performed using a Riken Keiki PESA spectrometer (Model AC-2) with a power setting of 10 nW and a power number of 0.33. Thin film samples for PESA were prepared on glass substrates. HOMO values are derived by fitting the PESA curves and LUMO is calculated by using the absorption onset.

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**Table S1: Ionization energy and electron affinity values obtained from PESA and absorption onset measurements. Details of the data analysis can be found in Nature Materials 2021, 20, 378**

| Material     | HOMO (eV) | LUMO (eV) |
|--------------|-----------|-----------|
| PM6          | 5.15      | 3.23      |
| IEICO        | 5.35      | 3.88      |
| IEICO-4F     | 5.50      | 4.13      |
| ITIC-4F      | 5.80      | 4.16      |
| COi8DFIC     | 5.60      | 4.28      |
Table S2: Device figures-of-merit obtained from JV-curves. Values are averaged over five solar cells.

| Device | Jsc (mA/cm²) | Voc (V) | FF (%) | PCE (%) |
|--------|--------------|---------|--------|---------|
| PM6:COi8DFIC (1:1, B0) | 14.5±0.4 | 0.79±0.05 | 61.6±1 | 7.1±0.3 |
| PM6:IT-4F (1:1, B1) | 20.6±0.2 | 0.84±0.02 | 70.3±1.1 | 12.0±0.2 |
| PM6:IT-4F:COi8DFIC (1:0.1:0.9) | 12.9±0.5 | 0.81±0.04 | 45.7±0.2 | 4.8±0.5 |
| PM6:IT-4F:COi8DFIC (1:1:1) | 13.1±0.2 | 0.83±0.0 | 58.0±0.4 | 6.3±0.4 |
| PM6:IT-4F:COi8DFIC (1:0.9:0.1, T1) | 21.7±0.2 | 0.83±0.02 | 74.0±0.8 | 13.3±0.2 |
| PM6:IEICO (1:1, B2) | 1.3±0.03 | 0.90±0.03 | 32±2 | 0.51±0.03 |
| PM6:IEICO:COi8DFIC (1:0.1:0.9) | 10.2±0.4 | 0.79±0.04 | 40.8±0.0 | 3.3±0.4 |
| PM6:IEICO:COi8DFIC (1:1:1) | 5.5±0.1 | 0.83±0.02 | 35.1±0.0 | 1.6±0.1 |
| PM6:IEICO:COi8DFIC (1:0.9:0.1, T2) | 1.9±0.08 | 0.94±0.01 | 31.3±1 | 0.54±0.03 |
| PM6:IEICO-4F (1:1, B3) | 7±0.01 | 0.84±0.01 | 49.0±1 | 2.8±0.02 |
| PM6:IEICO-4F:COi8DFIC (1:0.1:0.9) | 11.6±0.39 | 0.80±0.0 | 42.3±0.0 | 3.9±0.18 |
| PM6:IEICO-4F:COi8DFIC (1:1:1) | 5.2±0.25 | 0.72±0.05 | 40.9±3 | 1.6±0.29 |
| PM6:IEICO-4F:COi8DFIC (1:0.9:0.1, T3) | 8.5±0.23 | 0.84±0.01 | 49.0±1 | 3.45±0.07 |
Figure S 3: Current – Voltage characteristics of the ternary blends in 1:0.1:0.9 PM6:NFA1:COi8DFIC blending ratios.
Figure S 4: Parameters deduced from J-V curves for different weight ratio of 1:0.1:0.9 [PM6:NFA1:COi8DFIC]
Figure S 5 Current – Voltage characteristics of the ternary blends in 1:1:1 PM6:NFA1:COi8DFIC blending ratios.

Figure S 6: Parameters deducted from J-V curves for equal weight ratio of PM6, NFA1 and NFA2.
Figure S 7: The diffractograms of the three ternaries with similar D:A1:A2 (1:0.9:0.1) ratio and respective binaries.

Figure S 8. Normalized photoluminescence spectra for ternaries ($\lambda_{ex} = 550$ nm) a) T1, b) T2, and c) T3, and neat d) IT-4F ($\lambda_{ex} = 700$ nm), Co8DFIC ($\lambda_{ex} = 750$ nm), IEICO ($\lambda_{ex} = 750$ nm), and IEICO-4F ($\lambda_{ex} = 790$ nm). NIR spectra were smoothed (77 points Savitzky-Golay).
**Figure S9:** Evolution of the TA spectra in the ps-ns timescale following the selective excitation at 505 nm of T1. The break between 1.35-1.4 eV is because we used two spectrographs to measure the whole TA spectral range plotted here, as indicated in the figure.

**Figure S10:** ps-ns TA spectra and kinetics after exciting at 505 nm of T1(a and d), T2(b and e) and T3(c and f).
Figure S11: TA spectra of neat COi8DFIC after the excitation at 750 nm (red and black lines). Pink symbols show the triplet sensitized TA spectrum with PtOEP. Green open symbols represent the charge spectrum at 500 ns for PM6:COi8DFIC blend films.
Figure S 12: JV curves and EQE spectra of the PM6:IT-4F:IEICO ternary blends with different blending ratios.

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