Article type: Full Paper**Impact of Fullerene on the Photophysics of Ternary Small Molecule Organic Solar Cells**

Safakath Karuthedath, Yuliar Firdaus, Ru-Ze Liang, Julien Gorenflot, Pierre M. Beaujuge, Thomas D. Anthopoulos, Frédéric Laquai**

Dr. S. Karuthedath, Dr. Y. Firdaus, Dr. R. Liang, Dr. J. Gorenflot, Asst. Prof. P.M. Beaujuge,
Prof. T. D. Anthopoulos, Assoc. Prof. F. Laquai

King Abdullah University of Science and Technology (KAUST), KAUST Solar Center
(KSC), Physical Sciences and Engineering Division (PSE), Material Science and Engineering
Program (MSE), Thuwal 23955-6900, Kingdom of Saudi Arabia

Email: frederic.laquai@kaust.edu.sa; safakath.karuthedath@kaust.edu.sa

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Abstract

Ternary organic solar cells (OSC) are among the best-performing organic photovoltaic devices to date, largely due to the recent development of non-fullerene acceptors. However, fullerene molecules still play an important role in ternary OSC systems, since, for reasons not well understood, they often improve the device performance, despite their lack of absorption. Here, we study the photophysics of a prototypical ternary small molecule OSC blend composed of the donor DR3, the non-fullerene acceptor ICC6, and the fullerene derivative PC₇₁BM by ultrafast spectroscopy. Surprisingly, we find that after excitation of PC₇₁BM, ultrafast singlet energy transfer to ICC6 competes efficiently with charge transfer. Subsequently, singlets on ICC6 undergo hole transfer to DR3, resulting in free charge generation. Interestingly, PC₇₁BM improves indirectly the electron mobility of the ternary blend, while electrons reside predominantly in ICC6 domains as indicated by fast spectroscopy. The improved mobility

facilitates charge carrier extraction, in turn leading to higher device efficiencies of the ternary compared to binary solar cells. Using the (photo)physical parameters obtained from (transient) spectroscopy and charge transport measurements, we simulate the device's current-voltage characteristics and demonstrate that the parameters accurately reproduce the experimentally-measured device performance.

1. Introduction

Organic solar cells (OSCs) are one of the emerging PV technologies that are currently investigated as potentially low-cost renewable energy sources, combining appealing properties such as semi-transparency, high absorptivity, lightweight, flexibility, and color tunability using non-toxic organic molecules as photoactive materials.^[1] Ternary organic solar cells (TSCs), consisting of either two electron donors and one acceptor or two electron acceptors and one electron donor, are currently at the forefront of efficient OSCs and outperform binary systems in terms of power conversion efficiency (PCE), largely due to improved light absorption and morphology, especially if novel non-fullerene acceptors are employed.^[2] Ternary solar cells use a single (ternary blend) photoactive layer for photon harvesting and thus less challenging and costly to realize compared to tandem solar cells,^[3] which have the potential of even higher efficiencies.^[4] However, in TSCs, the third component of the blend not only improves light harvesting, but also plays an active role in the photo-physical processes including exciton and charge carrier dynamics and can, in fact, also influence the blend's morphology.^[5] This is of critical importance in small molecule based devices, where intermolecular charge transport dominates.^[6]

Often, the third component in ternary solar cells enhances the PCE by improving the short circuit current (J_{SC})^[5c] and open-circuit voltage (V_{OC}), which both can be tuned by the donor / acceptor composition.^[2d, 5b] The challenge here is, however, to improve all device parameters, while maintaining or increasing the fill factor (FF) of the ternary organic solar cell.^[7] Here, we

study the photophysics of such a high-performance all-small molecule ternary solar cell composed of DR3TBDTT (DR3)^[8] as electron donor in combination with a non-fullerene small molecule acceptor, namely IC-C6IDT-IC (or ICC6)^[9] and PC₇₁BM as third component, shown to enhance the device performance. The fully-optimized ternary devices (1:1:0.4 wt.%, DR3:ICC6: PC₇₁BM) yield an average PCE of 10.8 % with a *FF* of 72 %, *V_{OC}* of 0.87 V, and *J_{SC}* of 16.3 mA cm⁻². Using picosecond-nanosecond (ps-ns) transient absorption (TA) spectroscopy, we selectively excite each component of the blend and probe the processes following photoexcitation. We find that excitation of PC₇₁BM molecules results in fast singlet energy transfer to ICC6, subsequently followed by hole transfer to DR3. We confirm this observation by TA and time-resolved photoluminescence (TRPL) spectroscopy on binary blends of PC₇₁BM:ICC6, showing fast energy transfer from PC₇₁BM to ICC6. Our TA studies demonstrate that the increased EQE of the ternary blend is due to higher mobility of charge carriers in ICC6 observed in the presence of PC₇₁BM, leading to improved charge extraction, outcompeting faster non-geminate recombination. Nanosecond-microsecond (ns-μs) TA spectroscopy shows fluence-dependent charge carrier dynamics, which can be parametrized by a two-pool model of charge recombination.^[10] The obtained parameters determining the charge density decay, are used in steady-state device simulations to reconstruct the J-V curves of the DR3-based ternary devices.

2. Results and Discussions

2.1. Materials and Solar Cell Performance

Figure 1a shows the molecular structures of the small molecule donor DR3, fullerene derivative PC₇₁BM, and the non-fullerene acceptor ICC6. Figure 1b depicts their ionization energy (IE) and electron affinity (EA). The IEs were determined by photoelectron spectroscopy in air (PESA). EA values were estimated by adding the optical bandgap energy *E_{opt}* obtained from the intersection of the UV-vis absorption spectra and photoluminescence (PL) spectra to the IE.

For the PESA and UV-vis PL data we refer to Figures S1 and S2 in the Supporting Information. Figures 1c and 1d show the device architecture and the UV-vis absorption spectra of neat materials and of the ternary blends. Addition of PC₇₁BM to the blend increases its absorption in the 350-450 nm spectral region, where DR3 and ICC6 molecules absorb less.

Figure 1: Molecular structures of DR3, PC₇₁BM, and ICC6. b) Ionization energies (IE) and electron affinities (EA) for DR3, PC₇₁BM, and ICC6 estimated by photoemission spectroscopy in air (PESA). EA values inferred by adding the optical bandgap (E_{opt}) energy to the IE values, where E_{opt} was estimated from the intersection of the normalized UV-vis absorption and photoluminescence spectra. Panel (c) depicts the device structure used in this study and panel (d) shows UV-Vis absorption spectra of neat films and of the ternary blend. The vertical lines in panel (d) denote the excitation wavelength used for TA spectroscopy. Panel (e) shows the corresponding current density - voltage characteristics of devices at 1 sun illumination and panel (f-g) show the EQE and IQE spectra of the binary and ternary solar cell devices.

Solution-processed thin film bulk heterojunction (BHJ) solar cells with conventional device structure ITO/PEDOT:PSS/blend/DPO/Al (device area: 0.1 cm²) were prepared and tested under simulated AM1.5G-equivalent illumination.^[11] Figure 1e compares the current density-voltage (J-V) curves for binary and ternary solar cells that were optimized by solvent vapor annealing (SVA). Details of the SVA optimization are reported elsewhere.^[12] The device figures-of-merit are shown in Table 1. Figure 1f shows the external quantum efficiency (EQE) spectra of the binary and ternary devices. The addition of PC₇₁BM not only enhances the EQE in the 350-450 nm region, but surprisingly also improves the EQE across the entire absorption range of the ternary blend. This improvement is a consequence of the improved charge carrier mobility in ICC6 due to increased crystallinity of ICC6 upon blending with PC₇₁BM, as has

recently been demonstrated by Liang et al.^[12a] However, excess of PC₇₁BM deteriorates the EQE due to morphological changes and decreased crystallinity.^[12a] In line with the higher EQE, the internal quantum efficiency (IQE) increases, reaching >90 % for the fully-optimized ternary devices.

Table 1: PV performance parameters of the SM binary and ternary solar cells (averaged over 10 devices for a device area of 0.1cm²).

DR3:ICC6:PC ₇₁ BM Blend Ratio (wt/wt)	DMDS SVA Time (s)	J _{sc} [mA cm ⁻²]	V _{oc} [V]	FF [%]	Avg IQE [%]	Avg EQE [%]	Avg. PCE [%]
1:1:0	60	15.2	0.87	64	83	60	8.4±0.3
1:1:0.4	60	16.3	0.87	72	90	69	10.4±0.4
1:1:2	60	14.1	0.81	60	85	62	6.9±0.5
1:0:1	20	13.2	0.88	72	91	65	8.2±0.3

2.2. Excited State Dynamics

The EQE of organic solar cells is determined by $EQE = \varphi_{abs} \times \varphi_{diss} \times \varphi_{sep} \times \varphi_{extr}$, where φ_{abs} describes the photon absorption, φ_{diss} the exciton dissociation efficiency, φ_{sep} the efficiency of charge pair separation, and φ_{extr} the efficiency of charge extraction.^[13] Concurrently, losses occur, for instance, exciton recombination,^[13a] incomplete exciton dissociation,^[14] geminate recombination,^[13] charge carrier trapping / trap-assisted recombination,^[13b] and non-geminate recombination of charge carriers competing with extraction, eventually populating the triplet manifold.^[15] Here, we monitored the presence of excited state and their dynamics in DR3:ICC6:PC₇₁BM ternary solar cells by time-resolved optical spectroscopy techniques, namely transient absorption (TA) spectroscopy and time-resolved photoluminescence (TRPL) experiments.

2.2.1. Exciton dissociation and energy transfer

Figure 2: (a) TRPL spectra of neat films integrated from 3-10 ps (dashed lines), of optimized ternary blends excited at 530 nm (green shades) and excited at 650 nm (red shades). (b) Decay kinetics obtained at PL peak position. Solid lines in (b) represent exponential fits to the data. All TRPL measurements were done in nitrogen atmosphere.

Exciton dynamics were investigated by photoluminescence (PL) measurements. **Figure 2** shows time-resolved photoluminescence (TRPL) spectra (panel (a)) and the corresponding dynamics (panel (b)) of optimized ternary blend films excited at different excitation wavelengths. Excitation of ICC6 at 650 nm results in ICC6 emission, peaking at 770 nm (solid red and dotted red lines). Interestingly, exciting DR3 and PC₇₁BM at 530 nm leads to exclusive emission from ICC6, indicating fast energy transfer (EnT) from PC₇₁BM to ICC6. After EnT, a PL lifetime of ICC6 of 75 ps was observed (Figure 2b), indicating diffusion-limited exciton quenching in a coarse D/A morphology in the ternary blend. Energy transfer from PC₇₁BM to ICC6 is ultrafast (sub-1 ps) and thus not resolved by our TRPL setup. All TRPL lifetimes are summarized in Table 2.

To reveal whether energy transfer occurs from DR3, PC₇₁BM or either ICC6, we performed TRPL measurements on binary blends of DR3:ICC6 and PC₇₁BM:ICC6 (Figure S3). No evidence of EnT is observed in the TRPL spectra and dynamics of DR3:ICC6 upon exciting DR3, whereas in PC₇₁BM:ICC6 blends energy transfer from PC₇₁BM to ICC6 molecules is dominant and ultrafast. Hence, we conclude that in the ternary blends DR3 excitons undergo fast charge transfer, while PC₇₁BM excitons undergo (ultra)fast EnT to ICC6. In line with the TRPL results, the photoluminescence quenching (PLQ) measurements support that energy transfer occurs from PC₇₁BM to ICC6 (see Figure S4), while again no evidence for EnT is observed from DR3 to ICC6 in the ternary blends. Precisely, the weak band at 770 nm in the steady-state PL of ternary blend (Figure S4a, red line) indicates energy transfer to ICC6, which could occur from DR3 or PC₇₁BM or either to ICC6. However, as the steady-state PL of the binary DR3:ICC6 blend (Figure S4a, dashed line) shows no indication of any ICC6 emission at 770 nm, energy transfer appears to occur exclusively from PC₇₁BM to ICC6.

To address whether energy transfer from PC₇₁BM to the smaller bandgap component of the ternary blend is a general phenomenon and not just specific to the system studied here, we measured the steady-state PL intensity of two other ternary OPV blends (see Figure S4b), namely PM6:Y6:PC₇₁BM (PCE 15.9%) and PBDB-T:ITIC:PC₇₁BM (PCE 10.2%), exciting primarily the PC₇₁BM. In fact, in both ternary blends, the PL intensity increases upon addition of PC₇₁BM, pointing to energy transfer from PC₇₁BM to the lower bandgap acceptor, very similar to the DR3:ICC6:PC₇₁BM ternary blend studied here.

Table 2: TRPL decay rates of neat compounds, binary, and ternary blends. Excitation wavelengths: DR3 @530 nm, ICC6 @650 nm, and neat PC₇₁BM @370 nm. The DR3:ICC6 blend film, the ICC6: PC₇₁BM blend film, and the ternary blend film were excited at 530 nm. All TRPL measurements were carried out in inert atmosphere.

Film	DR3	ICC6	PC ₇₁ BM	DR3:ICC6	PC ₇₁ BM:ICC6	Ternary
τ_{PL} [ps]	258 ± 2	200 ± 3	159 ± 5	44 ± 1	63 ± 3	75 ± 2

2.2.2. Charge carrier generation

Figures 3a and **3b** show picosecond – nanosecond transient absorption (ps-ns TA) spectra and dynamics of optimized ternary blend films after selective excitation of PC₇₁BM. The photobleaching of ICC6 (PB_A) rises and peaks at ~5 ps, while the photobleaching of DR3 (PB_D) increases up to ~200 ps (panel (b)). The fast emergence of PB_A indicates fast energy transfer from PC₇₁BM to ICC6, as confirmed by time-resolved photoluminescence measurements (vide supra). The presence of energy transfer was also confirmed by TA experiments on ICC6:PC₇₁BM (1:0.4 wt%) blends (Figure S5a), which clearly revealed ultrafast EnT from PC₇₁BM to ICC6. However, no EnT was observed in DR3:ICC6 blends, instead, charge transfer occurred (Figure S5c). We assign the band centered at ~1.35 eV to DR3 cations (holes) and the band peaking at ~1.60 eV to ICC6 anions (electrons), as confirmed by TA on DR3:PC₇₁BM binary blends shown in Figure S6. We note that, signatures of PC₇₁BM anions are neither observed in the TA spectra of ternary blends nor in the spectra of DR3:PC₇₁BM binary blends, likely due to their smaller cross-section.^[16]

Figure 3: Picosecond-nanosecond TA spectra of optimized DR3:ICC6:PC₇₁BM ternary blends after excitation at (a) 365 nm (primarily excites PC₇₁BM molecules), (c) 475 nm (excites both DR3 and PC₇₁BM molecules), and (e) 720 nm (primarily excites ICC6 molecules). Lower panels (b,d, and f) represent the ps-ns kinetics of selected spectral regions as indicated by vertical colored bars in the corresponding upper panels.

Figure 3c-d show the ps-ns TA spectra and dynamics of optimized ternary blends after exciting both DR3 and PC₇₁BM. The PBA band of ICC6 exhibits a fast (1-5ps) increase due to EnT from PC₇₁BM. As can be seen from panels (c) and (d), charge carriers (PA1 band) are generated up to ~100 ps. Figure 3e and 3f show the ps-ns TA spectra and dynamics after exciting exclusively ICC6. Here, PBD rises due to hole transfer from ICC6 to DR3. We note, charge generation is slower than in the binary DR3:ICC6 blend due to larger ICC6 domains, as indicated by STEM (scanning tunneling electron microscopy) imaging coupled with EELS (electron energy-loss spectroscopy) reported earlier by Liang et.al.^[12a] This is also in line with the increased PL lifetime seen in ternary blends compared to binary blends (see Table 1).

The TA spectra in Figure 3 consist of convoluted contributions of excitons and charges. The individual exciton and charge carrier spectra and dynamics were obtained by multivariate curve resolution – alternating least squares (MCR-ALS) data analysis of the TA datasets.^[17] **Figure 4** shows the component (excited state) spectra and dynamics of ternary blend films. Component 1 (red solid line in panels a and b) represents the exciton-induced absorption spectrum of ICC6, while component 3 (dark blue line in panels a and b) corresponds to the exciton-induced spectrum of DR3. Here, we confirm ultrafast EnT from PC₇₁BM to ICC6 after excitation at 365 nm (see Figure 4a). We note that DR3 excitons are present as well, likely because DR3 weakly absorbs at 365 nm, however, the contribution from DR3 is significantly smaller as can be seen from the non-normalized data (Figure S15). Figure 4c shows the component spectra after exclusive excitation of ICC6. Here, component no DR3 exciton contribution is to be seen and component 1 is assigned to ICC6 excitons only, as it resembles the TA spectra obtained on neat ICC6 films (see Figure S8b in the SI). Component 2 (green line) is assigned to charge carriers, precisely a convolution of cation-induced absorption of DR3 and anion-induced absorption of ICC6. Figure 4g compares the charge-induced spectrum of DR3:ICC6 and DR3:PC₇₁BM binary blends to that of the ternary blend, clearly confirming that in the ternary blend, charges reside in DR3 and ICC6 domains. In fact, the shape and ratio of the charge-induced signatures are

very similar to those of the binary system DR3:ICC6, indicating that the same species are observed. We stress that this does indicate similar ICC6-anion and DR3-cation densities in the ternary and thus, if at all, only a minor fraction of the electrons could be residing in PC₇₁BM. Hence, it appears that the main role of PC₇₁BM is to contribute to the photocurrent generation via EnT, while charge transfer between DR3 and ICC6 dominates. We note, however, that the peaks are narrower in the ternary, potentially due to the increased crystallinity / lower energetic disorder.

Figure 4: MCR-ALS spectra and kinetics of components contributing to the ps-ns TA data for different excitation wavelength (a-f) and for the same fluence as shown in Figure 3. Panel (g) compares the charge-induced spectra (MCR) of ternary (green), DR3:ICC6 (blue), and DR3:PC₇₁BM (dotted black line) samples. The grey line in panel (b) corresponds to MCR-ALS spectra of charge carriers in the binary DR3:ICC6 blends and the grey line in panel (c) to the TA of neat ICC6.

Figures 4d-f represent the individual dynamics of singlet excitons and charge carriers obtained by MCR-ALS method. Clearly, the rise of the singlet exciton population in DR3 and ICC6

(component 1 and 3) depends on the excitation wavelength: at 365 nm (d) and 475 nm (e) the majority of singlets are generated ultrafast, while energy transfer from PC₇₁BM to ICC6 leads to an additional increase of the population in the first 2 ps. Contrarily, in the case of excitation of ICC6 (Figure 4f), no delayed increase of the singlet population is observed, as energy transfer is absent and all singlets are directly photogenerated on ICC6 by the excitation pulse. The results confirm energy transfer from PC₇₁BM to ICC6, which improves the device's external quantum efficiency in the 350-450 nm spectral region. We note that when DR3 is excited (Figure 4a and b) about 50 % of charges (component 2) are already present at 500 fs (panels (d) and (e) green line), followed by a further increase of the carrier population, whereas for ICC6 excitation, the charge generation appears to be entirely diffusion-limited. Irrespective of the excitation, the charge carrier density maximizes around ~200 ps. Details of the MCR-ALS analysis can be found in the SI.

2.2.3 Charge carrier recombination

Having analyzed the charge generation, we now discuss the charge recombination in the ternary blends. **Figure 5** shows the ns- μ s TA spectra and dynamics of optimized DR3:ICC6:PC₇₁BM ternary blends. The spectral shape of the ns- μ s TA spectra is virtually similar to that of the ps-ns TA at long time delays (~5 ns), indicating that other states (such as triplet states) have not been populated after charge generation is completed. The decay of the charge-induced absorption band is fluence dependent as shown in Figure 5b, indicating non-geminate recombination of spatially-separated charge carriers.^[13a, 18] We parametrized the decay dynamics using a two-pool recombination model, introduced earlier by Howard et al., and thereafter applied to several other fullerene and non-fullerene OSC blends.^[10, 13a, 18]

Figure 5: ns- μ s TA spectra (a) and kinetics (b) of optimized ternary films after exciting at 532 nm and under inert nitrogen atmosphere. (c) Bias dependent TDCF (symbols) compared with current-voltage characterization curve (line) for the same device pixel. (d) Decay dynamics of collected charges (symbols) and corresponding bi-molecular fit (line). (e) Comparison of TA and TDCF decay dynamics at $\sim 2.3 \mu\text{J}/\text{cm}^2$ excitation fluence.

As shown in Figure 5b, the two-pool model (black solid lines) fits the experimentally-measured carrier dynamics (green symbols) very well. We note that we fitted the dynamics globally, that is, across all measured fluences using a shared set of parameters. The model reveals that $\sim 89\%$ of the charge carriers are spatially separated and thus could be extracted as photocurrent. However, a small fraction of geminate (fluence independent) recombination is required for the best fit to the data, accounting for $\sim 11\%$ of the total charge carrier population.^[13a] The non-geminate recombination coefficient γ and apparent recombination order $\lambda+1$ can be recalculated to an effective bimolecular ($\lambda+1 = 2$) recombination coefficient β_{TA} of $1.5 \times 10^{-11} \text{ cm}^3/\text{s}$ at a carrier concentration of $1 \times 10^{16} \text{ cm}^{-3}$, corresponding to 1 sun illumination conditions (see SI for more details). The decay dynamics and fit for excitation at 355 nm are shown in Figure S9 of

the SI. For comparison, all parameters including those obtained for the DR3:ICC6 binary blend are shown in Table 3. We note that the bimolecular recombination coefficient of the ternary blend is larger than that of binary the binary DR3:ICC6 blends, implying that mobility is higher (see also below) and that charge trapping by PC₇₁BM is negligible.

Table 3: Fit parameters obtained from global fit to the ns- μ s charge carrier recombination dynamics in optimized ternary blends. Here f is the fraction of free charge carriers, k_{CT-GS} is the geminate recombination rate, $\lambda+1$ is the apparent non-geminate recombination order, γ is the non-geminate decay rate, and β is the effective bimolecular recombination coefficient for ternary and binary blends calculated for a carrier density of $1 \times 10^{16} \text{ cm}^{-3}$.

Parameter	Ternary ($\lambda_{\text{exc}} = 532 \text{ nm}$)	Ternary ($\lambda_{\text{exc}} = 355 \text{ nm}$)	DR3:ICC6 ($\lambda_{\text{exc}} = 532 \text{ nm}$)
f (%)	~ 89	~ 92	~ 90
$(1-f)$ (%)	~ 11	~ 8	~ 10
$k_{CT-GS} (\text{s}^{-1})$	4.0×10^8	4.0×10^8	3.5×10^8
$\lambda+1$	2.61 ± 0.002	2.63 ± 0.007	2.34 ± 0.009
$\gamma ([\text{cm}^3]^\lambda \text{s}^{-1})$	$1.79 \pm 0.1 \times 10^{-21}$	$8.9 \pm 0.1 \times 10^{-22}$	$4.01 \pm 0.2 \times 10^{-17}$
$\beta_{TA} (\text{cm}^3/\text{s})$	1.5×10^{-11}	1.07×10^{-11}	4.3×10^{-12}

2.2.4. Charge extraction dynamics

Time-delayed collection field (TDCF) experiments can provide information on the bias dependence of charge generation and non-geminate recombination, which both determine the fill factor of OSCs.^[19] Details of the TDCF measurements are shown in Figure S10 in the SI. The total extracted charge, Q_{tot} , as a function of the applied pre-bias is shown in Figure 5c. We deliberately chose a low excitation fluence, at which early-time non-geminate recombination losses are negligible. Under these conditions, Q_{tot} can be interpreted as a measure of the amount of free charges generated by the excitation laser pulse as a function of the applied pre-bias.^[20] We note that the applicability of TDCF to measure the true field dependence of charge generation has recently been questioned.^[21] However, here we do not observe any (apparent) field dependence of charge generation and use TDCF to study the charge recombination / extraction dynamics on a timescale faster than can typically be accessed by other charge extraction techniques. The TDCF results (Figure 5c) reflect the high device FF (see Table 1)

observed for optimized DR3:ICC6:PC₇₁BM ternary solar cells. From the carrier recombination dynamics, a strictly bimolecular recombination coefficient of $2 \times 10^{-11} \text{ cm}^3/\text{s}$ was calculated, which is very similar to that obtained by the two-pool model used to fit the charge recombination dynamics measured by TA experiments (Figure 5d). We note that the recombination coefficient falls into the range of values reported earlier for other polymer:fullerene and NFA blends.^[10, 13b, 22] Figure 5e compares the recombination dynamics of charge carriers obtained from TA measurements (open symbols, black) and TDCF measurements (closed symbols, red) at similar fluence. Interestingly, the recombination dynamics obtained by TDCF and TA are very similar in this system. We note that this similarity is not necessarily the case, as TA is measured on films and TDCF on devices and carrier recombination in devices can be affected by injection of dark carriers from the device electrodes. Furthermore, often it is challenging to use the same low excitation intensity in TA experiments due to the limited signal-to-noise ratio. We have recently discussed this issue for other all-polymer OPV systems.^[13a] The fast non-geminate recombination of free charge carriers indicates that the charge carrier mobility is high. In fact, SCLC (space charge-limited current) measurements reveal a mobility of $8.2 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and $3.5 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for electrons and holes, respectively.^[12a] We note that the hole mobility is similar in DR3:ICC6 binary solar cells: $2.7 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$; however, the electron mobility is lower in the binary system: $5 \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$.^[12a] The change in electron mobility observed for DR3:ICC6:PC₇₁BM ternary solar cells indicates that PC₇₁BM alters the blend morphology, as recently confirmed by GIWAXS (grazing incidence wide angle X-ray scattering) studies by Liang et al.^[12a]

2.2.5. Simulation of device J-V characteristics

In order to evaluate if the photophysical parameters determined by transient spectroscopy describe the experimentally-measured JV characteristics of devices, we simulated them for a device structure that closely resembled the experimentally-tested one (see Experimental part).

Here, the refractive index n and extinction coefficient k of the photoactive layer determined by ellipsometry (data shown in Figure S11), the charge carrier mobility obtained from space charge-limited current (SCLC) measurements, and the bimolecular recombination rate obtained from TA were used as input parameters. Details of the simulation tool Setfos 4.6 (Fluxim AG) and procedure can be found elsewhere.^[23] Figure 6 compares the simulated (black solid line) and experimentally-measured (red circles) J-V characteristics.

Figure 6: Experimentally-measured (red dots) and simulated (black solid and green dotted line) current density-voltage (J-V) characteristics of DR3:ICC6:PC₇₁BM ternary solar cells.

Clearly, a bimolecular rate constant of $10^{-11} \text{ cm}^3/\text{s}$ (as obtained by both TA and TDCF) yields best fits of experimental and simulated JV data (Table 4). The large bimolecular recombination rate of $\beta \approx 10^{-11} \text{ cm}^3/\text{s}$ limits the device efficiency. In fact, as shown in Figure 6 and Table 4, reducing the bimolecular recombination rate used in the simulation to $\beta \approx 10^{-12} \text{ cm}^3/\text{s}$, improves the PCE to 12.7%, with FF and V_{OC} increasing to 80% and 0.93 V, respectively. Recent studies of charge recombination in BHJ solar cells have demonstrated that demixed blends exhibit lower bimolecular recombination rates.^[24] However, a trade-off exists between exciton harvesting, charge generation, and charge extraction, and therefore materials with improved molecular order (high carrier mobility) and increased exciton diffusion length are the way forward to reduce losses by bimolecular recombination and to improve performance further.

Table 4: Parameters used for the simulation of J - V curves of DR3:ICC6:PC₇₁BM ternary solar cells shown in Figure 6 and corresponding figures-of-merit of devices (V_{OC} , J_{SC} , FF, and PCE).

Simulation #	μ_h cm ² V ⁻¹ s ⁻¹	μ_e cm ² V ⁻¹ s ⁻¹	β_{sim} cm ³ /s	V_{OC} V	J_{SC} mAcm ⁻²	FF %	PCE %
1	4.0×10 ⁻⁴	1.1×10 ⁻³	10 ⁻¹¹	0.87	17.0	72	10.6
2	4.0×10 ⁻⁴	1.1×10 ⁻³	10 ⁻¹²	0.93	17.1	80	12.7

3. Conclusions

We unraveled for the first time the complex photophysics of the all-small molecule ternary blend DR3:ICC6:PC₇₁BM by transient spectroscopy and revealed how the presence of fullerene molecules improves the overall device performance. Specifically, we observed that photoexcitation of the donor molecule DR3 or acceptor ICC6 resulted in fast electron / hole transfer, while excitation of PC₇₁BM led to fast singlet energy transfer to the lower bandgap acceptor ICC6 followed by hole (back)transfer from ICC6 to DR3. The incorporation of PC₇₁BM into the blend improved the blend's electron mobility, surprisingly though, as electrons were found to reside primarily in the ICC6 acceptor. The improved mobility of electrons in the presence of PC₇₁BM explains the improved EQE across the entire photoactive spectral region of the ternary solar cells. Simulating the device JV characteristics by using the carrier mobility and non-geminate recombination rate constant determined by spectroscopy accurately reproduced the experimentally-measured device's JV characteristics under solar illumination. Finally, we demonstrated that energy transfer from PC₇₁BM is not only relevant for the ternary system studied here, but also for other ternary systems, including the high performance PM6:Y6:PC₇₁BM (PCE 15.9%) ternary BHJ system. Thus, we conclude that in ternary NFA systems energy transfer from PC₇₁BM to the lower bandgap acceptor is a ubiquitous phenomenon, which improves the quantum efficiency across the entire photoresponse spectrum of the blend and thereby increases the device performance.

4. Experimental Section

Sample preparation

The solar cells were prepared on glass substrates with tin-doped indium oxide (ITO, $15 \Omega \text{ sq}^{-1}$) patterned on the surface (device area: 0.1 cm^2). Substrates were first scrubbed with a dilute Extran 300 detergent solution to remove organic residues, and were then immersed in an ultrasonic bath of dilute Extran 300 for 15 min. Samples were rinsed in flowing deionized water for 5 min before being sonicated (Branson 5510) for 15 min each in successive baths of acetone and isopropanol. Next, the samples were dried with pressurized nitrogen before being exposed to a UV–ozone plasma for 20 min. A thin layer ($\sim 35 \text{ nm}$) of PEDOT:PSS (Clevios™ P VP AI 4083) was spin-coated onto the UV-treated samples, the samples were subsequently dried on a heating plate at 150°C for 15 minutes, and were then transferred into a dry nitrogen glovebox ($< 3 \text{ ppm O}_2$).

Optimized devices were obtained by dissolving DR3, ICC6 and PC₇₁BM in chloroform (CF), using a DR3:ICC6:PC₇₁BM ratio of 1:1:0.4 (wt/wt). Note: The as-prepared solutions were stirred for 3 hours at 50°C before being cast on the (room temperature) substrates. The active layers were spin-coated from the solutions at 50°C at an optimized speed of 4000 rpm over a time period of 45s, using a programmable spin-coater from Specialty Coating Systems (Model G3P-8), resulting in films of 205-220 nm in thickness. The active layers were then subjected to a solvent vapor annealing (SVA) treatment with dimethyl disulfide (DMDS) vapors for 60 s. Following SVA treatment, a $\sim 5 \text{ nm}$ -thin layer of Phen-NaDPO was spin-coated on top of the active layer. The samples were then dried at room temperature for 1 hour. Next, the samples were placed in a thermal evaporator for evaporation of a 120 nm-thick layer of aluminium (Al) evaporated at $5 \text{ \AA s}^{-1}$; pressure of less than $2 \times 10^{-6} \text{ Torr}$. Following electrode deposition, samples underwent J–V testing.

UV-Vis absorption spectroscopy

UV-vis absorption spectra were measured with a Perkin Elmer Lambda 900 UV-Vis-NIR absorption spectrometer.

Current-Voltage (J V), EQE and IQE measurements

J-V measurements of solar cells were performed in the glovebox with a Keithley 2400 source meter and an Oriel Sol3A Class AAA solar simulator calibrated to 1 sun, AM1.5 G, with a KG-5 silicon reference cell certified by Newport. The external quantum efficiency (EQE) measurements were performed at zero bias by illuminating the device with monochromatic light supplied from a Xenon arc lamp in combination with a dual-grating monochromator. The number of photons incident on the sample was calculated for each wavelength by using a silicon photodiode calibrated by NIST. The internal quantum efficiency (IQE) of optimized BHJ was calculated from Equation:

$$IQE = EQE / (1 - R\% - \text{Parasitic Absorption})$$

The reflectance (R%) spectra were collected with the integrating sphere using the same EQE system. The parasitic absorption was obtained from transfer matrix modeling.

Transient absorption spectroscopy

TA spectroscopy was carried out on blend films using a homebuilt pump–probe setup. Two different configurations of the setup were used for either short delay, namely 100 fs to 8 ns experiments, or long delay, namely 1 ns to 300 μs delays, as described below:^[17c, 25]

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). Two of them were used to separately pump two optical parametric amplifiers (OPA) (Light Conversion TOPAS Prime). TOPAS 1 generates tunable pump pulses, subsequently frequency doubled to 350 nm with a 2 mm thick barium metaborate (BBO) crystal, 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 is 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 pump pathway length was varied between 5.12 and 2.6 m with a broadband retroreflector mounted on an automated mechanical delay stage (Newport linear stage IMS600CCHA controlled by a Newport XPS motion controller), thereby generating delays between pump and probe from -400 ps to 8 ns.

For the 1 ns to 300 μ s delay (long delay) TA measurement, the same probe white-light supercontinuum was used as for the 100 fs to 8 ns delays. Here the excitation light (pump pulse) was provided by an actively Q-switched Nd:YVO₄ laser (InnoLas piccolo AOT) frequency-doubled to provide pulses at 532 nm and 355 nm. The pump laser was triggered by an electronic delay generator (Stanford Research Systems DG535) itself triggered by the transistor–transistor logic (TTL) sync from the Legend DUO, allowing control of the delay between pump and probe with a jitter of roughly 100 ps. Pump and probe beams were focused on the sample which was kept under a dynamic vacuum of $<10^{-5}$ mbar. 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 mechanically chopped to 1.5 kHz (100 fs to 8 ns delays) or directly generated at 1.5 kHz frequency (1 ns to 300 μ s delays), 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 $\Delta T/T$. 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 homebuilt Matlab code. 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.

Time delayed collection field (TDCF)

The home-built TDCF setup uses the second harmonic (532 nm) of an actively Q-switched sub-ns Nd:YVO₄ laser (INNOVAS piccolo AOT) operating at 5 kHz as excitation. To minimize the RC response time, a small device area of 1 mm² is used. The samples were measured under dynamic vacuum conditions to avoid any degradation. A Keysight S1160A functional generator was used to provide the pre-bias and extraction bias, while a Keysight four channel digital oscilloscope was used to measure the current response of the device. Detailed TDCF description can be found elsewhere.^[13a]

Numerical device simulator

The 1D numerical drift-diffusion device simulator (Setfos 4.6 from FLUXiM AG) was used to simulate the ternary blend single-junction OPV device J-V characteristics. Optical constants (refractive index n and extinction coefficient k) of all layers were determined by variable angle spectroscopic ellipsometry (VASE) with an M-2000 ellipsometer (J.A. Woolam Co., Inc).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Energy and charge transfer in ternary organic solar cells were investigated by transient spectroscopy. Depending on the excitation wavelength, either exclusive charge transfer or a competition between energy and charge transfer was observed. The presence of PC₇₁BM in the ternary increases the absorption in the UV spectral region and indirectly enhances the electron mobility of ICC6 in the blend. (59 words, max 60 words)

Keyword: Ternary organic solar cells

Safakath Karuthedath,* Yuliar Firdaus, Ru-Ze Liang, Julien Gorenflot, Pierre M. Beaujuge,

Thomas D. Anthopoulos, Frédéric Laquai*

Impact of Fullerene on the Photophysics of Ternary Small Molecule Organic Solar Cells

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Supporting Information

Impact of Fullerene on the Photophysics of Ternary Small Molecule Organic Solar Cells

Safakath Karuthedath, Yuliar Firdaus, Ru-Ze Liang, Julien Gorenflot, Pierre M. Beaujuge,*

*Thomas D. Anthopoulos, Frédéric Laquai**

King Abdullah University of Science and Technology (KAUST), KAUST Solar Center (KSC), Physical Sciences and Engineering Division (PSE), Material Science and Engineering Program (MSE), Thuwal 23955-6900, Kingdom of Saudi Arabia

Emails: frederic.laquai@kaust.edu.sa; safakath.karuthedath@kaust.edu.sa

Supporting Figures

Figure S2: The optical band gap of neat films estimated from the intersection of absorption spectra (red) and photoluminescence spectra (black) of a) DR3, b) ICC6, and c) PC₇₁BM.

Figure S3: PESA measurements for (a) DR3, (b) ICC6, (c) IEICO (neat films); PESA-inferred ionization potentials (IPs) are depicted in the plots (red values).

Figure S3: Time-resolved photoluminescence (TRPL) spectra of a) binary DR3:ICC6 blends and b) binary PC₇₁BM:ICC6 blends and corresponding PL decay dynamics and fits to the data (c and d).

Figure S4a: Photoluminescence quenching (PLQ) spectra of ternary and binary blends upon exciting a) the donor (DR3) and b) the acceptor (ICC6) separately.

Figure S4 shows PL quenching spectra of ternary blends compared to DR3:ICC6 binary blends.

The ternary blends exhibit PL quenching efficiencies of ~93 % and ~86 % upon DR3/PC₇₁BM and ICC6 excitation respectively, lower than those of DR3:ICC6 binary blends. Compared to

the PLQ of binary DR3:ICC6 blends upon ICC6 excitation (dashed lines in panel (b) of Figure S4), the PLQ of ternary blends is lower, indicating that the addition of PC₇₁BM molecules reduced the PLQ. Likewise, the PLQ of ternary blends upon DR3 excitation is lower than that of the binary DR3:ICC6. Interestingly, as observed from the TRPL spectra shown above, the steady-state PL of ternary blends shows an emission peaking at 770 nm upon DR3/PC₇₁BM excitation. This further supports that EnT occurs from PC₇₁BM to ICC6 and not from DR3 to ICC6 in the ternary blend.

Figure S4b. (a) Absorption spectra of PM6, Y6, and PC₇₁BM, (b) PL spectra of Y6 and Y6:PC₇₁BM for excitation at 550 nm (normalized to the absorption at 550 nm) (c) PL spectra of PM6:Y6 and PM6:Y6:PC₇₁BM. (d) Absorption spectra of PBDB-T, ITIC, and PC₇₁BM, (e) PL spectra of ITIC and ITIC:PC₇₁BM for excitation at 500 nm (normalized to the absorption at 500 nm). (f) PL spectra of ITIC:PC₇₁BM and PBDB-T:ITIC:PC₇₁BM

Figure S5: Picosecond-nanosecond TA spectra of ICC6:PC₇₁BM blends after excitation at (a) 510 nm (primarily exciting PC₇₁BM molecules). Panel (b) represents the ps-ns kinetics of selected spectral regions as indicated by vertical coloured bars in panel (a). Panel (c) and (d) represent the ps-ns TA spectra and kinetics of selected spectral regions.

Figure S6: Picosecond-nanosecond TA spectra of DR3:PC₇₁BM blends.

Figure S7: STEM and EELS images of non-optimized (upper panel) and optimized (lower panel) ternary blends. Scale bar: 500 nm

Figure S8: Picosecond-nanosecond TA spectra of neat DR3 film (a) and neat ICC6 film (b) measured in vacuum.

Figure S9: ns- μ s TA kinetics of optimized ternary blend films after exciting at 355 nm in inert nitrogen atmosphere.

Figure S10: Schematics of the TDCF experiment: photocurrent transients, delay times, applied voltages. In the TDCF measurement, the sample is excited by a laser pulse, while being kept at a constant pre-bias (V_{pre} , as shown in the scheme). After a delay time t_{delay} , a rectangular voltage pulse (V_{col}) is applied to extract all remaining carriers, resulting in two photocurrent peaks, one observed after the laser excitation and the other after application of V_{col} , respectively. The integration of the area under the two curves yields the quantity of charges generated during the laser excitation and extracted before (Q_{pre}) (with V_{pre} applied) and during (Q_{col}), that is, the application of the collection field, respectively. The sum of Q_{pre} and Q_{col} reveals the total number of generated charges Q_{tot} .

Figure S11: Optical constant profiles (extinction coefficient k and refractive index n) of the ternary blend films obtained by ellipsometry measurements.

Parametrization of the charge carrier dynamics by a two-pool model:

Here, we briefly outline the boundary condition and assumptions used to fit the charge carrier dynamics on the ns- μ s timescale using the previously introduced two-pool model.^[79] For each fluence i we determined an initial density $n_{0,i}$ of charges from the TA signal amplitude divided by the coefficient determined from TDCF results (see above). We assume that the charges occupy two different populations, namely a density $f \times n_{0,i}$ of spatially-separated charges and a density $(1-f) \times n_{0,i}$ of coulombically bound charges, namely geminate pairs. For these two populations the following rate equations apply.

Coulombically bound charges recombine geminately with an inverse rate constant of τ :

$$\frac{dn_{CT,i}}{dt} = - \frac{n_{CT,i}}{\tau} \quad (1)$$

while spatially-separated charges recombine non-geminately with an apparent recombination order of $\lambda+1$ and a prefactor k_λ :

$$\frac{dn_{SSC,i}}{dt} = - k_\lambda n_{SSC,i}^{\lambda+1} \quad (2)$$

Those equations and initial conditions yield the following analytical solution used to fit the charge-induced absorption decay at each fluence i :

$$n_i(t) = (1 - f)n_{0i}e^{-t/\tau} + (\lambda k_\lambda t + (fn_{0i})^{-\lambda})^{-1/\lambda} \quad (3)$$

All fluences are fit simultaneously in a global fit using the shared parameters f , τ , λ and k_λ across all fluences. Note that at low fluence the onset of non-geminate recombination is delayed, so that geminate and non-geminate recombination are sequential instead of parallel and are clearly separated by a plateau observed at early times in the charge carrier density dynamics. In that case, each of the parameters can be assigned to a specific feature of the decay:

- n_0 is the initial signal amplitude (carrier concentration);
- τ determines the first part of the carrier concentration decay (geminate recombination);
- f corresponds to the y value of the plateau of the carrier concentration (equivalent to the fraction of charges left after geminate recombination is completed);
- k_λ determines the position of the end of the plateau of the carrier concentration (non-geminate recombination actually sets in around $t = (fn_{0i})^{-\lambda} / \lambda k_\lambda$, but the values of f , λ and n_0 are already determined by other factors);
- λ is the asymptotic slope of the decay at long times on a log-log representation.

At low fluences the limited signal-to-noise ratio makes the fit ambiguous, whereas at high fluences, geminate and nongeminate recombination are occurring in parallel.^[80] Consequently, employing a global fit that across several fluences mitigates these problems. Note that the non-geminate recombination prefactors k_λ extracted for different materials cannot be directly compared as they are a function of the recombination order λ – see Equation (2). To allow a comparison, we reduced the recombination to an entirely bimolecular process and determined its prefactor k_2 by:

$$k_2 n^2 = k_\lambda n^{\lambda+1} \quad (4)$$

Using this approach, the value of k_2 now depends on the density of charges. To get a value relevant for solar illumination conditions, we use a density of charges of $n = n_{1sun} = 1 \times 10^{16} \text{ cm}^{-3}$, corresponding to the steady-state density of charges obtained at a photon flux equivalent to 1 sun illumination. Thus

$$k_2 = k_\lambda n_{1sun}^{\lambda-1} \quad (5)$$

Table S4. N_0 obtained from the two-pool model fits to the carrier recombination dynamics when initializing the fit with the initial carrier concentration determined by TDCF measurements.

Fluence (Binary)	Charge density (N_0)	Fluence (Ternary)	Charge density (N_0)
25 $\mu\text{J}/\text{cm}^2$	$1.3 \times 10^{18} \text{ cm}^{-3}$	25 $\mu\text{J}/\text{cm}^2$	$9 \times 10^{17} \text{ cm}^{-3}$
12 $\mu\text{J}/\text{cm}^2$	$8.7 \times 10^{17} \text{ cm}^{-3}$	12 $\mu\text{J}/\text{cm}^2$	$7 \times 10^{17} \text{ cm}^{-3}$
9 $\mu\text{J}/\text{cm}^2$	$6 \times 10^{17} \text{ cm}^{-3}$	8.7 $\mu\text{J}/\text{cm}^2$	$4 \times 10^{17} \text{ cm}^{-3}$
6 $\mu\text{J}/\text{cm}^2$	$3.3 \times 10^{17} \text{ cm}^{-3}$	6 $\mu\text{J}/\text{cm}^2$	$2.3 \times 10^{17} \text{ cm}^{-3}$
2.3 $\mu\text{J}/\text{cm}^2$	$2.5 \times 10^{17} \text{ cm}^{-3}$	2.3 $\mu\text{J}/\text{cm}^2$	$1.7 \times 10^{17} \text{ cm}^{-3}$

MCR-ALS analysis

As explained in ref. ^[1], any MCR decomposition is not a unique solution. Mathematically, the MCR-ALS algorithm decomposes the data matrix (D) into the product of a concentration matrix (C) (here densities) multiplied with a spectral matrix (S): $D = C \times S + E$ (here, E is the error matrix). Thus, for any invertible matrix T: $D = C \times T \times T^{-1} \times S + E$.

This implies that $C \times T$ and $T^{-1} \times S$ are mathematically valid decompositions of the data. Setting constraints, for example keeping the densities of excited species positive at all times, limits the parameter space of possible decompositions. However, a certain range of possible solutions might still remain, depending on how many constraints can be applied and how strict they are: for example, the spectrum of one species can be obtained from independent reference experiments (such as triplet sensitization, chemical oxidation / reduction), but the reference spectrum can be different from the one obtained by MCR due to the different chemical environment and measurement conditions.

In MCR-ALS, when considering only two (2) species, the algorithm will naturally tend to find the mathematical solution in which the initial spectrum (here the one right after excitation) corresponds to a single species, while the last spectrum corresponds to the second species only. This is indeed sufficient in many cases, specifically when on the timescale of the experiment the reaction is completed, that is, the reactant has been converted entirely to the product. However, this may cover the fact that the final state (here charges) can be created ultrafast below the time resolution of the experiment. In our example, the MCR analysis originally returns the following spectra and kinetics for 365 nm excitation:

Figure S12: Initial result of the MCR-ALS decomposition of the TAS data of the ternary blend when excited at 365 nm. (a) Normalized (in surface area) spectra, (b) normalized kinetics.

However, the decomposition shown in Figure 12 is not satisfactory, because the singlet states do not exhibit any negative contribution in the 2.5 eV region, in contrast to the charges. This is thus a clear indication that component 1 as extracted by MCR contains some contributions from charges. On the contrary, the charge-induced spectrum is meaningful as excitons are neither expected to remain until 8 ns in the neat material nor in the blend. Furthermore, the spectral evolution does not show any indication of the existence of a 2nd long-lived species such as triplets (no spectral evolution on the nanosecond time scale is observed).

In such a case where one of the components can be clearly identified, it is possible to remove its contribution from the other component 1. We simply replaced the spectrum S_I of component

1 by a spectrum S_I' , where the contribution of component 2 (S_2) had been subtracted $S_I' = S_I - rS_2$, where r is the amplitude of component's 2 contribution to S_I .

Mathematically, this corresponds to multiplication of an invertible matrix T^{-1} with a matrix S containing the MCR extracted spectra of the 2 components:

$$\begin{pmatrix} S_1' \\ S_2' \end{pmatrix} = \begin{pmatrix} S_1 + rS_2 \\ S_2 \end{pmatrix} = \begin{pmatrix} 1 & r \\ 0 & 1 \end{pmatrix} \times \begin{pmatrix} S_1 \\ S_2 \end{pmatrix} = T^{-1} \times S$$

A normalization term (multiplication by a matrix $\begin{pmatrix} 1/\|S_1'\| & 0 \\ 0 & 1 \end{pmatrix}$, to respect the condition that the spectra are normalized in surface area) has to be added. The resulting transformation (subtracting the S_2 contribution $\times$ renormalization) is a rotation and is invertible. Physically, applying the inverse transformation to the concentration matrix corresponds to adding the charge contribution that has been taken from component 1 back to component 2, to where it belongs. Specifically, this will add a density contribution to component 2 that corresponds to the charges generated ultrafast within the experiment's time resolution.

In our case r values between -0.6 and -0.4 give physically meaningful results. Using lower values of r does not remove entirely the charge contribution, as evidenced by the negative signal at 2.5 eV. On the contrary, subtracting a larger charge contribution results again in a new negative feature at 2 eV.

As can be seen from the density figures, this rotation reveals the presence of ultrafast charge generation, accounting for a fraction between 58% ($r = -0.4$) and 84% ($r = 0.6$) of the overall charge generation. This is a substantial difference compared to the initial result from MCR, which showed component 1 as the only species initially contributing to the spectra. Spectrally, those two cases also exhibit very notable differences as component 1 in the case of $r = -0.6$ matches the ICC6 exciton-induced spectrum, without any DR3 contribution, while component 1 in the case of $r = -0.4$ contains both ICC6 exciton and DR3 exciton spectral contributions. The presence of two excitonic contributions in component 1 comes here from the fact that those two – a priori distinct – species exhibit dynamics too similar to be actually distinguished by the

MCR algorithm. Due to the 365 nm excitation exciting some of the DR3 molecules as well, we consider the presence of both excitonic contribution to be more likely.

Figure S13: 365 nm excitation (mostly PC₇₁BM): Original and rotated MCR spectra (left graph of each subset) and dynamics (right graph of each subset, the 3 lines per color represent the following fluences: 8.8 $\mu\text{J}/\text{cm}^2$, 5.6 $\mu\text{J}/\text{cm}^2$, 3.7 $\mu\text{J}/\text{cm}^2$), for different weights (labels as 'rot') of component 2 removed from component 1. The red lines represent component 2 (charges), and the blue ones the component 1 (excitons or excitons + charges depending on the rotation). The circles on subfigure (a), (b) and (e) stress the non-physical aspects of component 1 spectra.

A similar procedure performed on the data obtained by DR3 excitation (475 nm) leads to the spectra shown in Figure S14 and to a re-evaluation of the fraction of ultrafast charge generation to 33% instead of zero. As expected, the excitonic spectrum exhibits a much larger contribution from DR3 excitons.

Figure S14: 475 nm (mostly DR3) excitation: Original MCR decomposition of the ternary's TA response and selected rotation for the ternary blend. The red lines represent component 2 (charges), and the blue ones the component 1 (excitons or excitons + charges depending on the rotation). (for $3.7 \mu\text{J}/\text{cm}^2$)

The MCR decomposition of the data obtained after ICC6 excitation (720 nm) immediately provides the exciton spectrum and an almost perfect match with the spectrum obtained from pristine ICC6, so that it does not require any further correction.

For the excitation at 475 nm and 365 nm, the single value decomposition (SVD) carried out prior to the MCR-ALS analysis showed the presence of two components only. However, the MCR-ALS also showed that component 1 is actually a composition of both DR3 and ICC6 signals, thus indicating the presence of excitons in both materials. Hence, we decomposed the data further by using 3 components: ICC6 excitons (TA spectra taken from neat ICC6 films @ 1 ps after photoexcitation), DR3 excitons (TA spectra from neat DR3 films @ 1 ps after photoexcitation), and the charge-induced spectrum equivalent to the component 2 of the previous MCR-ALS analysis. The results are shown in Figure S15.

Figure S15: Three-component decomposition of the TA signal upon 475 nm (upper panel) and 365 nm (lower panel) excitation: The red lines represent component 1 (ICC6 excitons), the yellow spectrum component 2 (charges), and the blue lines component 3 (DR3 excitons) for excitation fluences of $3.7 \mu\text{J}/\text{cm}^2$ for the 475 nm excitation (upper panel) and $8.8 \mu\text{J}/\text{cm}^2$, $5.6 \mu\text{J}/\text{cm}^2$, $3.7 \mu\text{J}/\text{cm}^2$ for the 365 nm excitation (lower panel).

Reference

[1] Howard, I. A.; Mangold, H.; Etzold, F.; Gehrig, D.; Laquai, F. in: *Ultrafast Dynamics in Molecules, Nanostructures and Interfaces* (World scientific, 2013).