Free Charge Photogeneration in a Single Component High Photovoltaic Efficiency Organic Semiconductor

Justin Hodgkiss (✉ justin.hodgkiss@vuw.ac.nz)

Victoria University of Wellington

Michael Price

Victoria University of Wellington

Paul Hume

Victoria University of Wellington

Aleksandra Ilin

Victoria University of Wellington

Isabella Wagner

Victoria University of Wellington <https://orcid.org/0000-0001-5009-2407>

Ronnie Tamming

Victoria University of Wellington

Karen Thorn

Victoria University of Wellington

Wanting Jiao

Victoria University of Wellington

Alison Campbell

The University of Sydney

Patrick Conaghan

The University of Sydney

Girish Lakhwani

The University of Sydney

Nathaniel Davis

Victoria University of Wellington

Yifan Wang

Qingdao University

Peiyao Xue

Peking University

Heng Lu

Peking University

Kai Chen

Victoria University of Wellington

Xiaowei Zhan

Peking University

Physical Sciences - Article

Keywords: photogeneration, solar energy

Posted Date: April 8th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-376343/v1>

License: This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Version of Record: A version of this preprint was published at Nature Communications on May 20th, 2022. See the published version at <https://doi.org/10.1038/s41467-022-30127-8>.

Free Charge Photogeneration in a Single Component High Photovoltaic Efficiency Organic Semiconductor

Michael B. Price^{a,b,1,*}, Paul A. Hume^{a,b,1,*}, Aleksandra Ilina^{a,b}, Isabella Wagner^{a,b}, Ronnie R. Tamming^{a,b}, Karen E. Thorn^{a,b}, Wanting Jiao^c, Alison Campbell^d, Patrick J. Conaghan^d, Girish Lakhwani^d, Nathaniel J.L.K. Davis^{a,b}, Yifan Wang^{e,f}, Peiyao Xue^e, Heng Lu^e, Kai Chen^{a,b}, Xiaowei Zhan^e, Justin M. Hodgkiss^{a,b,*}

^a School of Chemical and Physical Sciences, Victoria University of Wellington, Wellington, New Zealand

^b MacDiarmid Institute for Advanced Materials and Nanotechnology, New Zealand.

^c Ferrier Research Institute, Victoria University of Wellington, Wellington, New Zealand

^d ARC Centre of Excellence in Exciton Science, School of Chemistry, University of Sydney, NSW 2006, Australia

^e School of Materials Science and Engineering, Peking University, Beijing 100871, China.

^f College of Materials Science and Engineering, Qingdao University, Qingdao 266071, China

* Correspondence should be sent to J.M.H. (Justin.Hodgkiss@vuw.ac.nz), P.A.H. (Paul.Hume@vuw.ac.nz), and M.B.P. (Michael.price@vuw.ac.nz)

¹ Authors contributed equally to this work

ABSTRACT

Organic photovoltaic cells promise cheap, flexible and scalable solar energy.^{1,2} Whereas light directly generates free charges in silicon photovoltaic cells, bound electron and hole pairs known as excitons are understood to be the primary excitations in organic semiconductors due to their low dielectric constants.³ These excitons must then be split apart at molecular heterojunctions in order to extract current.⁴ Recent record efficiency organic photovoltaics utilise the small molecule, Y6,^{5–8} as a key component in the photon-absorbing blend layer. This molecule and its analogues – unlike previous organic semiconductors – have both low band-gaps and high dielectric constants.⁹ Here we show that, in a neat film of Y6, these factors lead to intrinsic free charge generation without the need for a molecular heterojunction to split the exciton. We use a suite of intensity-dependent optical spectroscopy measurements to show that a significant (20-90%) fraction of free charges exist in equilibrium with bound states at light intensity equivalent to 1 sun. Rapid bimolecular charge recombination constrains single

component Y6 organic photovoltaic devices to low efficiencies, but this recombination is reduced by the introduction of small quantities of donor polymer. Quantum-chemical calculations reveal charge generation pathways through strong coupling between exciton and CT states, and an intermolecular polarisation pattern that drives exciton dissociation. Our results challenge the understanding of how current record efficiency organic photovoltaics operate, and point towards new future possibilities – offering a molecular picture of intrinsic charge generation as a platform to improve charge yields, and renewing the possibility of efficient single-component organic photovoltaic devices.

INTRODUCTION

When light is absorbed by inorganic semiconductors, like silicon or gallium arsenide, a combination of free charges and excitons (bound electrons and holes) are created, and their ratio depends upon the material's dielectric constant. For organic semiconductors, the paradigm holds that only excitons are intrinsically photogenerated because the low dielectric constant^{10,11} of these materials ($\epsilon \sim 3 - 4$) means the electron and hole Coulombic interaction is not efficiently screened, leading to Frenkel excitons with high binding energies (E_B). For the last thirty years,^{4,12} this constraint has guided the development of organic photovoltaics (OPVs) - which promise a step-change in flexible, lightweight, non-toxic solution-processed solar energy production, but are yet to be widely commercialised. Splitting bound excitons into free charges has required sharp molecular heterojunctions between donor and acceptor materials (though some have recently shown field-assisted exciton dissociation, or CT-state/polaron-pair formation^{13–16}). Rather than purely optimising charge harvesting, OPV devices have been optimised for exciton splitting at interfaces, and demand complex interpenetrating networks of donor and acceptor materials. The molecular heterojunction approach limits device efficiencies,¹⁷ introduces inherent voltage losses and instabilities from interfaces,¹⁸ and complicates research progress.¹⁹

Recently, small molecule non-fullerene fused ring electron acceptors (FREAs)^{3,6,20–24} have driven a rapid uptick in the power conversion efficiency (PCE) of OPVs. Alongside this advance has arisen unexpected observations, namely: 1) Barrierless free charge generation in PM6:Y6 blends²⁵ (full chemical names and structures shown in Figure S1) 2) That charge generation efficiency in blends of PM6:Y6 increases with increasing incident light intensity.²⁶ 3) In Y6^{16,27} and IDIC,²⁸ excitons are delocalised, or form an 'intra-moiety' intermediate state

with likely charge-transfer (CT) like character. These observations have all been explained by invoking CT-states, however, with additional data, we show here that a more profound explanation is required.

FREAs have recently been measured to have very high refractive indices,^{29,30} and hence high complex dielectric constants. Of the FREAs, Y6 and its derivatives are present in both the binary and ternary OPVs that hold the highest PCEs.⁵⁻⁸

In inorganic semiconductors, the number of bound excitons versus free charges can be described by the Saha-Langmuir relation.

$$\frac{x^2}{1-x} = \frac{1}{n} \left(\frac{2\pi m^* k_B T}{h^2} \right)^{1.5} e^{-\frac{E_B}{k_B T}} \quad (1)$$

Where the free charge fraction, x , is dependent upon the temperature, T , excitation density, n , effective mass, m^* and the exciton binding energy, E_B (which is related to the inverse of the dielectric constant³¹). From comparison of the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap to the optical gap measured by Karuthedath *et al.*,¹⁸ the exciton binding energy of Y6 is $E_B = 100\text{-}250$ meV - much lower than for example, P3HT ($E_B \sim 700$ meV).³² Based on a midpoint, 175 meV binding energy, estimated for Y6 above, and assuming an effective mass between^{33,34} $m^* = 1.7 - 0.2 m_e$, this simple calculation would predict a high fraction (20-80%) of intrinsically generated free charges.

Here, we show that the high optical frequency dielectric constant of Y6 leads to free charge generation upon optical excitation within neat films. We use a combination of ultrafast transient absorption, photoluminescence up-conversion and time-resolved terahertz spectroscopy, and identify the spectral signatures and decay rates of singlet excitons and free charges (polarons). Intensity-dependent photoluminescence quantum efficiency (PLQE) measurements prove the existence of radiative bimolecular charge recombination, which not be the case if only CT states were formed. We present kinetic models that reproduce our experimental data, wherein a free charge fraction of between 0.2-0.9 exists in equilibrium with bound charges under steady-state illumination. Fast bimolecular charge recombination inhibits the efficiency of single-component devices, but this recombination can be slowed by doping our Y6 films with only a small amount of ‘p-type’ polymer electron donor. Using quantum-chemical calculations, we show that free charge generation is expected due to strong coupling between equienergetic exciton and CT states, and reveal that asymmetric polarisation of the different lattice positions results in a “donor/acceptor” system derived purely from intermolecular interactions. The

observation of intrinsic charge generation in a single organic material necessitates an expanded understanding of the photovoltaic process in organic materials. The implications for device design are far-reaching, showing that a new approach to reaching maximum efficiency may be to maximise intrinsic charge generation yield, whilst reducing rapid bimolecular charge recombination, rather than focus on exciton splitting in a donor-acceptor blend. Indeed, we suggest that the highest efficiency OPV blends (such as PM6:Y6) have in fact been optimised for the extraction of intrinsically formed charges.

MAIN

Radiative bimolecular recombination

Figure 1a shows the excitation density-dependent external photoluminescence quantum efficiency (PLQE) of a neat film of Y6 (BTP-4F). As the intensity of pulsed excitation is increased, the PLQE remains constant at 0.9% from 10^{14} to 10^{15} excitations per cubic cm, before rising to a peak of 1% at a density of $\sim 10^{16}$ cm⁻³. Figure 1 b illustrates the expected behaviour of excitation density-dependent PLQE for varying proportions of radiative monomolecular to bimolecular processes. The rise in efficiency observed in Fig 1a is not possible for a system undergoing monomolecular (geminate) radiative recombination, even from intra-moiety CT states, and proves that a significant fraction of photoexcited species are following a pathway that involves bimolecular recombination prior to, or concurrently with, a radiative transition. As exciton-exciton annihilation can only produce a non-radiative bimolecular contribution, we conclude that charges must be present in the neat film, and that these charges are formed ‘intrinsically’, rather than through exciton annihilation processes. Under steady-state illumination, this free charge (polaron) population will exist in equilibrium with a population of bound excitons, and potential ‘CT-like’ states, as illustrated by Figure 1c.

Figure 1. Intensity-dependent photoluminescence quantum efficiency of Y6.

a) Experimentally determined PLQE of a neat film of Y6 on glass substrate in an integrating sphere (normalised). The sample was excited by 600 ps pulses of 532 nm light. The PLQE peaks at 1% at $\sim 10^{16}$ excitations/ cm^3 . Figure S1 gives an indication of the error associated with the data. Intensity dependent PLQE of a film of P3HT is shown as orange circles, as comparison, to illustrate the expected response. **b)** Simulation of intensity-dependent PLQE values showing effect of increasing (orange) or decreasing (blue) radiative bimolecular recombination (from prompt free charge fraction, calculated using *Model 2* detailed in the SI). **c)** Graphic representation of exciton-CT state-free charge equilibrium in Y6.

Exciton - charge dynamics and equilibrium

To quantify the relative proportions of charges versus excitons, we perform ultrafast spectroscopic measurements on films of neat Y6. We identify spectral signatures of the singlet exciton, and free charge/CT-state species and their kinetics to estimate first and second order kinetic rates/lifetimes. Figure 2a shows the area-normalised transient absorption (TA) spectrum of a neat Y6 film pumped with a 150 fs, 700 nm laser pulse at a moderate excitation density of 10^{15} excitations/cm³. The spectrum evolves from one initial photoexcited species, a sharp negative peak at 915 nm, to another consisting of both positive and negative features, apparent after ~500 ps. Singular value decomposition, multivariate curve resolution analysis and application of a genetic algorithm (GA)³⁵ consistently resolve two major species present, shown as the blue and orange spectra in Figure 2b. We confirm that the orange species is that of the polaron – referred to as free charge (FC) for consistency in the rest of the manuscript – by comparing the spectra of TA measurements of Y6 blended with either hole or electron accepting species – PTB7-Th and poly-TPD respectively. We note that the charge is also likely to have a very similar spectrum to an intraspecies charge-transfer³⁶ state/excimer/weakly-bound exciton delocalised over 2 or more molecules in the Y6 crystal, and therefore designate the spectra here as representing the free charge plus CT state populations. We stress that we cannot explain all of our data unless there is a significant fraction of free charges, as detailed below.

Figure 2. Ultrafast transient absorption spectra and kinetics of singlets and free charges in neat Y6, and optical pump terahertz probe conductivity.

a) Transient absorption spectra, normalised to the absolute area integral, of a neat film of Y6 at different time delays. 700 nm, 200 fs pump pulse, excitation density = 10^{15} excitations/cm³. The spectrum evolves from the exciton, blue line, with a negative peak at 915 nm, to the red-shifted charge/CT state spectrum, orange line. **b)** Confirmation of charge and exciton transient absorption spectra by comparison of neat species (extracted using genetic algorithm) with species resolved from blends of Y6 with hole and electron accepting materials (PTB7-Th, polyTPD). The green dashed line shows the hole spectra of PTB7-Th blended with PCBM. **c)** Singlet component from GA of transient absorption (dark blue line), compared with up-converted PL signal (cyan), at an excitation density of 8×10^{14} cm⁻³. **d)** Initial kinetics of the exciton (blue) versus charge/CT (orange) TA kinetics in the first 2.5 ps after photoexcitation. The charge species shows a rise concomitant with the fast initial decay of the singlet species. **e)** Excited-state terahertz complex conductivity spectrum, excited with 150 fs, 800 nm light,

giving approximate excitation density 5×10^{15} excitations/cm³, with a THz probe delay of ~3 ps. The positive real (light blue) line is indicative that there are charge-like species present in addition to purely excitonic photoexcitations. The experimental data is fit to a modified Drude-Smith model (darker blue and darker red curves).

We confirm that the blue species is that of the singlet exciton in 2 ways: 1) through TA measurements of a ‘solid-solution’ of Y6 diluted in polystyrene (Figure S2), and 2) by comparing the TA spectra of the ‘blue’ species to the transient kinetics of upconverted PL signal from the same film at similar excitation density. As shown in Figure 2c, the singlet TA matches the transient PL signal, confirming our assignment of the ‘blue’ species as the emissive singlet. The singlet, and free charge/CT species show different kinetic decays to each other across multiple different excitation density regimes (see Figure 3b).

The singlet and charge species, as shown in Figure 2d, show a prompt, fluence independent (Fig. S3), interconversion within the first 2.5 picoseconds, which also has no clear excitation-energy dependence (Fig. S4). These observations are consistent with observations from Wang *et al.*,¹⁶ though our other measurements (Terahertz spectroscopy and fluence dependent PLQE) necessitate a model beyond pure CT generation. We quantify the initial prompt generation (within the first 2.5 ps) of charge/CT species in two ways - from the initial fast decay of the singlet, and from an estimation of the charge/CT visible TA bleach cross-section at 650 nm. These methods both estimate that by 2.5 ps after photoexcitation, ~30% of initially excited singlets are rapidly converted to the charge/CT species. As this effect appears not to be due to excess energy (based on TA measurements pumped with different excess energies), the rapid formation is likely an effect of increased exciton delocalisation at early times.^{37,38} In line with Gillet *et al.*,³⁹ we also observe a small 3rd spectral component in the TA which is consistent with a triplet signature (Fig. S5). As further evidence that there are significant free charges present, the triplet signal peak is significantly delayed compared to the charge/CT signal, which is consistent with a non-geminate triplet generation pathway rather than geminate triplet formation from inter-system crossing.

As another probe of free charge generation in Y6, we perform optical-pump-terahertz probe (OTTP) spectroscopy.^{40,41} Figure 2e shows the conductivity spectrum at 3 ps probe delay of a neat film of Y6, excited with an 800 nm pump beam, at an excitation density of $\sim 5 \times 10^{15}$ excitations/cm³. The non-zero real part of the terahertz (THz) spectrum (light blue line) is

indicative of a fraction of free polarons, rather purely bound excitons.^{40,42,43} The conductivity spectrum is well described by a fit to a modified Drude-Smith model (DSM) – an established description for charge carriers in pi-conjugated materials.^{40,42,43}

$$\tilde{\sigma}(\omega) = \frac{\varepsilon_0 \omega_p^2 \tau}{1 - i\omega\tau} \left[1 + \frac{c_1}{1 - i\omega\tau} \right] \quad (2)$$

Where ε_0 is the vacuum permittivity, ω_p the plasma frequency, τ the scattering time, and c_1 is the ‘localisation’ parameter. A best fit to our data is obtained with a scattering time of $\tau = 12$ fs, a plasma frequency of $\omega_p = 20$ THz, and $c_1 = -0.99$. The localisation parameter indicates carriers that are well-localised, consistent with other reports in small molecules and conjugated polymers, and with our computational results presented below. The fitted plasma frequency, $\omega_p^2 = \frac{nq^2}{\varepsilon_0 m_e}$, can be used to estimate an upper bound on the effective mass. Even assuming 100% charge yield, this gives a low effective mass of $m^* = 0.16 m_e$, a value below those estimated in various non-fullerene molecules from DFT models.³³ These results are again indicative of intrinsic charge generation, with rapid bimolecular recombination due to high local charge mobilities.⁴⁰

We can fit our transient absorption kinetics and intensity-dependent PLQE data based on a basic kinetic model of free charges, charge-transfer states, and singlet excitons present in a neat film of Y6 upon illumination. Figure 3a graphically presents this model, along with rate estimates from application of the model to our experimental TA and PLQE data (details in SI and in Figure 3 b and c). After the fast initial generation of CT/free charge states, the ratio of species present is governed by their interconversion rates: Singlet excitons can convert to CT states and vice versa, and CT states split easily into free charges, which can recombine bimolecularly back into CT states.

Figures 3b and 3c show the results of a global fit of this model to a multiple fluence series of transient absorption, and PLQE data. We calculate internal PLQE⁴⁴ (taking photon recycling into account – see below) as, $\eta_{int} = \frac{dS_{rad}}{dN_{total}}$, where dS_{rad} is the radiative rate of singlet decay, and dN_{total} is the total decay rate of all species in the film. The radiative and non-radiative singlet decay rates are obtained from comparison of the PLQE values of Y6 in a solid-state solution of polystyrene, and the intersystem CT crossing rate is estimated from literature.⁴⁵

This model simultaneously approximates the transient absorption data, and crucially, recreates the increase, or ‘hump’, in PLQE that is the signature of free charge generation. We thus view it as instructive for estimating free charge yields and transition rates in Y6. We note that we can also globally fit the data with an even simpler model, that does not explicitly include CT states, and which gives a higher (~75%) steady-state fraction of free charge population (Fig S8), and lower, likely more accurate estimate of bimolecular charge recombination rate – though the rate is still high ($6 \times 10^{-8} \text{ s}^{-1} \text{ cm}^3$). Error analysis of these models is shown in the supplementary information. Though there is significant interdependency between the fitted rates, and hence the individual error in each rate constant is high (and model dependent), we can use the models to put a lower and upper bound on steady-state free charge yield at a given excitation intensity. Setting the conservative criteria that there is a rise in PLQE with excitation intensity (of any magnitude), to match our experiments, the lower bound for steady-state free charge fraction, at an excitation density of 10^{16} cm^{-3} is 25% (our estimated solar excitation density is $5 \times 10^{16} \text{ cm}^{-3}$ under the AM1.5 spectrum). The upper bound for both models is 80-90%. A model that includes only singlet excitons and CT states cannot reproduce our PLQE data.

The red line in Figure 3d illustrates the fraction of free charges present at a steady state condition based on the model and rates described in Fig 3a, as a function of total excitation density. It mirrors the behaviour expected from using the Saha equation (blue line), with an effective mass of $1.7 m_e$ and exciton binding energy, $E_B = 175 \text{ meV}$. It shows that at low excitation densities, below $10^{15} \text{ excitations/cm}^3$, over 50% of excitations exist as free charges (~60% of which arise from prompt generation within the delocalised state), and this portion drops as the density is increased.

High photon reabsorption in thin films

As illustrated in Figure 4c, it is important to take into account photon reabsorption in PLQE measurements of Y6 thin films. This is a further consequence of their extremely high

refractive index. We use the same process as Richter *et al.*⁴⁴ to approximate photon reabsorption, and show that the true PLQE of Y6 is much higher (~6%) than what would be ascertained from a direct reading of the external PLQE (~1%). This has significant importance for solar cell material optimisation efforts, as maximising PLQE is a useful approach for assessing photovoltaic efficiency potential,⁴⁶ and ultimately, being able to harness radiative carrier recombination through photon recycling is key to approaching the Shockley-Queisser limit. Although we estimate photon recycling is small for these measurements (Fig S8), The high refractive index means that it will become significant if internal PLQE can be increased.

Fast bimolecular recombination in single component OPV devices

The results from the transient absorption, PLQE, and terahertz spectroscopy data explain why, even though charges are intrinsically generated, single component, monolayer devices are not efficient. High bimolecular charge recombination rates mean that free charges recombine before arriving at electrodes in a device. With our measured charge recombination rates, and assuming (for the sake of illustration), pure Langevin recombination, at 1 sun intensity the charge diffusion length would be less than 10 nm. We fabricated single component Y6 devices. The highest PCE based on a PEDOT:PSS/Y6/LiF/Al structure was 0.09%. By replacing PEDOT:PSS with PCP-Na, whose HOMO better aligns with that of Y6, the highest PCE obtained was 0.63% (Fig S12). This value is low (though there is no built-in voltage in the active layer). This loss of photocurrent and photovoltage is due in significant part to high bimolecular recombination, which we show by performing intensity dependent short-circuit current (J_{SC}) measurements. Previous reports have seen power law dependence of J_{SC} on illumination intensity (I) according to^{47,48}: $J_{SC} \propto I^\alpha$. Deviations of the fitting parameter, α , from unity signify bimolecular recombination or space-charge effects due to unbalanced charge mobilities.^{47–50} Electron and hole mobilities are relatively balanced in Y6 (being 1.8×10^{-4} and $5.6 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ respectively²⁷), and at intensities below 0.01 suns, the exponent, α , approaches 1 (Fig S13), indicating that space-charge losses could be limited. Figure 4a shows that for the region between 0.2 and 2 suns incident photo-intensity, the fitted exponent, $\alpha = 0.84$, indicating the device suffers from significant bimolecular recombination at 1 sun.

To further emphasise the importance of high bimolecular recombination, rather than exciton splitting, as a limiting factor in device efficiency, we investigated the effect of doping our Y6 material with very small amounts of donor polymer, PTB7-Th.⁵¹ We performed transient absorption spectroscopy on these blends, and measured the photovoltaic device

external quantum efficiencies of the corresponding devices. As shown in Figure 4b, when blended in a 1:50 ratio of PTB7-Th:Y6, the EQE is nearly twice as high as for the 1:100 parts blend. However, Figure 4c shows that this is not due to inefficient exciton splitting. The transient absorption kinetics show that for both blends the exciton species decay, and the charge species appear, with almost identical kinetics in the first 20 ps, but the charges recombine faster in the 1:100 blend, showing that the polymer donor's principal role is to decrease the rate of recombination, rather than split excitons for this system.

Figure 4. Single component short circuit current, and low donor active layer device EQEs, and corresponding exciton and charge kinetics. **a)** Intensity dependent J_{sc} of a monolayer Y6 device. The power exponent fitted to the data between 0.2 and 2 suns is 0.7, indicating a high number of bimolecular recombination events. **b)** External quantum efficiencies (EQEs) of devices with active layers consisting of small ratios of donor, PTB7-Th, to acceptor, Y6. For such low donor content, EQEs are unexpectedly high. **c)** Normalised transient absorption kinetics of exciton and charge species in blends of PTB7-Th:Y6 with ratios of 1:50 and 1:100. Pumped with 800 nm, 150 fs pulses at excitation density 1×10^{14} excitations/cm³. The exciton kinetics of both films, dashed lines, are matching, as are the rise times of the charge kinetics (orange and red lines), but the 1:50 blend shows slower charge recombination after 20 ps. The green-blue line shows the hole kinetics in the 1:50 blend, showing a gradual increase in hole population as excitons and charges in Y6 diffuse to the PTB7-Th.

Molecular picture of charge generation

Having shown the macroscopic properties necessary for intrinsic charge generation, density functional theory calculations were used to gain an understanding of the structural features responsible for charge generation in Y6. The first requirement is significant electronic coupling between S_1 and CT_1 . This parameter was calculated for the three molecular pairs in the Y6 crystal structure²⁷ exhibiting π - π stacking interactions using our previously described projective method,^{52,53} which enables us to simultaneously predict the energies of localised exciton/CT states, and the couplings between them (Figure 5 a).

328

Figure 5. Electronic couplings and energies for Y6 excitons, CT states, and charges. **a)** Exciton-CT energy offsets and electronic couplings (in meV) for π -stacked molecular pairs extracted from the Y6 crystal structure (Alkyl chains have been removed for clarity).²⁷ **b)** Density of states (DOS) for holes ($-IE$) in a 10 nm thick model thin film based on molecular dynamics equilibration of the Y6 crystal structure, normalized to unit area. Dashed line indicates the DOS onset determined by photoelectron spectroscopy in air.¹⁸ **c)** Average ionisation energy as a function of π -stacking layer showing differential hole stabilisation for the different lattice positions, which occur in an "...ABBA..." sequence.

The computed electronic couplings and energetics point to a kinetic pathway for exciton break-up (Figure 5, Figure S17). In all cases, the coupling between the lowest exciton and CT states is significant (25-75 meV), with the CT states either equal or lower in energy to the excitonic states (in the molecular geometry of the crystal). These two factors, combined with the low reorganisation energy (estimated as ~ 0.3 eV based on the reorganisation energies of the individual molecules) imply that exciton break-up is expected, even according to incoherent charge transfer theories. The same electronic coupling parameters/state energies are of course also consistent with the possibility of coherent, or "hot" CT). Indeed, as previously noted, the coupling between excitonic states suggests a high degree of exciton delocalisation,²⁷ which is expected to lower the reorganisation barrier for exciton-to-charge conversion.

The coupling of the CT states with the ground state is more variable (5-80 meV), increasing in the order of pair 3 < 2 < 1. This pattern does not simply follow the trend in intermolecular contact area, which is largest for pair 2. The large CT-GS couplings for pairs 1 and 2 are consistent with the rapid recombination observed experimentally. However, the

apparent independence of V_{Ex-CT} and V_{CT-GS} indicates that the recombination can, at least in principle, be overcome by crystal structure engineering to maximise the V_{Ex-CT}/V_{CT-GS} ratio.

Our calculations also offer a clue regarding the origin of charge formation in Y6. In pairs 1 and 2, there is a clear energetic preference (~ 0.15 - 0.3 eV) for which of the two possible CT states is formed, both of which place the positive and negative charges on the same lattice positions. In pair 3, the molecules occupy equivalent lattice positions, and the difference in CT state energy becomes negligible. It is also striking that pair 3 exhibits an end-on stacking arrangement common to indacenodithienothiophene (IDT) acceptors,^{27,54,55} whereas the remaining two possess extensive contact between the neighbouring chromophores - which is very different to standard FREAs. These observations indicate that although the two crystal positions in Y6 are chemically identical, the packing geometry results in two distinct polarisation environments, creating a donor-acceptor system through supramolecular, rather than synthetic means. This interpretation also explains the significant recombination observed experimentally: the alternation of “donor” and “acceptor” positions on the scale of the unit cell is akin to an extremely intermixed blend system – meaning that both charge formation and recombination are extremely rapid.

The energy levels calculated for free charges also reveal the presence of distinct polarisation environments. Figure 5b shows the ionisation energy (IE) distributions calculated for a Y6 thin film using the long-range embedding procedure available in VOTCA.⁵⁶⁻⁶² Electron affinity (EA) is also shown in Fig S13. The input structure for these calculations was taken from a molecular dynamics equilibration of the Y6 crystal structure.²⁷ The energetics of molecules occupying different crystal positions reveal an underlying bimodality in the density of states, particularly for holes. The presence of these distinct distributions confirm the presence of a driving force for charge formation inherent to the Y6 packing structure, on the order of the exciton binding energy.

Our calculations reveal equal energy exciton-CT manifolds (as a result from differential polarisation), strong exciton-CT coupling, and a flat energetic landscape for electron transport. Previous theoretical work on Y6 has demonstrated strong electronic coupling for electron and hole transfer in Y6. Taken together, these observations strongly suggest the existence of a kinetic pathway for exciton-to-free charge conversion in Y6.

Charge generation can aid high efficiency bulk heterojunction devices

We propose a mechanism for how recombination is suppressed in current Y6 blends, drawing on studies invoking energy level bending at the donor/acceptor interface as a result of long-range interactions of charges with molecular quadrupole moments.^{18,25,56,63–65} In an excitonic picture – where charges only form at the interface - these fields assist CT dissociation and suppress non-geminate recombination. However, these benefits come at the expense of exciton dissociation rates, resulting in an intrinsic limit for the ionisation energy offset between the neat materials.¹⁸ When free charges are intrinsically generated in Y6, not only is the interfacial exciton dissociation barrier bypassed, but the level bending defines an attractive potential for holes, which are pulled towards the interface before leaving the acceptor material, while electrons are repelled. Under this interpretation, champion efficiency systems, such as PM6/Y6, benefit from both exciton- and charge-funnelling effects: excitons in PM6 are funnelled to Y6 via resonant energy transfer,^{18,66} while level bending pulls holes from Y6 into the polymer domain, and suppresses recombination thereafter. We can test whether quadrupolar fields affect charge recombination in Y6 by comparing charge and exciton kinetics of neat Y6, to a film of Y6 blended with 20% weight ratio PCBM (a ratio present in highly efficient ternary devices⁵). The energy levels of PCBM mean that both electron and hole transfer from Y6 to PCBM are prohibited. Any reduction in charge recombination rate will therefore be due to interfacial level bending (one would expect the effect of increased crystallinity in Y6 due to the PCBM would increase recombination, rather than decrease). Figure S16 shows that, as predicted, there is a small reduction in charge recombination rate, and concurrent reduction of exciton population, when PCBM introduced.

Implications for Future OPV Systems

Efficient intrinsic charge generation, in the FREA small molecule Y6, has broad implications for OPV device design. Considering a population of excitons and free charges in neat Y6 necessitates a more nuanced understanding of the simplified four step process – exciton generation, exciton transport, charge separation at a heterojunction, charge transport – that has previously dominated OPV discussion. Exciton diffusion length is no longer a simple function of how fast a lone exciton travels and how long it lives - interconversion into free charges and the reverse process must also be considered. The ease of charge separation, but concurrent rapid bimolecular charge recombination, necessitate a renewed focus on reducing such recombination. This hints that for current devices the key purpose of the bulk heterojunction is

more to reduce bimolecular recombination, than to split excitons. Efforts focussed on simultaneously maximising intrinsic PLQE and charge generation should improve OPV device open circuit voltages – which have yet to achieve parity with inorganic photovoltaics. Specific directions of study include: improving crystal packing to further enhance dielectric constants and hence free charge fraction; tuning energy levels through packing structures and/or molecular orientation rather than different compounds; and crystal structure engineering to minimise CT-ground state coupling.

We have shown, through intensity-dependent PLQE measurements, that free charges exist in neat films of the molecular semiconductor Y6, at illumination intensities below 1 sun. We have corroborated this measurement with optically-pumped time-resolved terahertz, ultrafast photoluminescence up-conversion and transient absorption spectroscopy. Our data can be explained by simple kinetic models, along with a new quantum mechanical picture of exciton-CT state coupling and free charge energetics. We have outlined the implications of this finding for our understanding of the photovoltaic process, and the mechanism of action for current champion efficiency devices, and have suggested further avenues of study for enhancing efficiency in future devices. These findings open up the potential to think beyond the bulk heterojunction, and revisit the possibility of fabricating efficient doped organic p-n junctions.

METHODS

General. UV-Vis absorption spectra were obtained using Carry 5000 (Agilent) and a Cary 50 Bio UV-vis spectrometer in the range 190 – 1100 nm. Photoluminescence spectra were obtained using a Cary Eclipse (Varian). Photoluminescence quantum efficiency measurements were obtained in an integrating sphere using the method of de Mello et al.⁶⁷ A Q-switched frequency doubled ND:YAg laser with output wavelength 532 nm, pulse-length 600 ps, and rep-rate set to 25kHz was used to excite the sample for the intensity dependent PLQE measurements. Sample film thicknesses were performed using a Dektak profilometer. Thin films of Y6, and Y6 blends were spin-coated onto quartz spectroil substrates in a glovebox from 11 mg/ml chloroform solutions, at a spin-speed of 3000 rpm. Solid solutions of Y6:polystyrene were prepared in a 1:50 weight ratio, and spincoated in a glovebox at 800 rpm.

Device fabrication. Indium tin oxide-patterned glass substrates were cleaned by sequential sonication in acetone and propan-2-ol and subjected to ozone treatment. A 35 nm film of PEDOT:PSS was spin coated in air from aqueous solution and baked on a hotplate at 110°C

for 15 minutes. A 30 nm layer of Y6 was spin coated from a chlorobenzene solution in a nitrogen-filled glovebox (0.1ppm O₂, 0.0ppm H₂O). The cathode of 1 nm LiF and 90 nm Al was deposited by vacuum thermal evaporation at pressure $\sim 10^{-6}$ mbar through a shadow mask to define 6 mm² pixels. The devices based on PTB7-Th:Y6 were fabricated with a normal structure as ITO glass/PEDOT:PSS/PTB7-Th:Y6/PNDIT-F3N/Ag. Patterned ITO glass was precleaned in an ultrasonic bath with deionized water, acetone and isopropanol, and treated in an ultraviolet–ozone chamber (Jelight Company, USA) for 20 min. PEDOT:PSS was spin-coated on the pre-cleaned ITO at 5000 rpm, followed by baking at 150 °C for 15 min. Then, the active layers were spin-coated on PEDOT:PSS (PTB7-Th:Y6, X:12 mg mL⁻¹ in chloroform, 2500 rpm). Afterwards, the PNDIT-F3N solution (0.5 mg mL⁻¹ in methanol) was spin-coated on the active layer at 2000 rpm. Finally, Ag electrode (ca. 80 nm) was slowly evaporated onto the surface of the underneath layer under vacuum (ca. 10⁻⁵ Pa). The devices were not masked and the active area of devices were 4 mm².

Device characterisation. Photovoltaic device JV characteristics were measured using a solar simulator and source-measure unit. Light intensity was determined using a calibrated silicon diode. Light intensity was varied by adjusting the distance between source and device under test and also by use of neutral density filters. EQE spectra of PTB7-Th:Y6 devices were obtained using a Solar Cell Spectral Response Measurement System QE-R3011 (Enlitech Co.).

Transient absorption spectroscopy measurements were performed using a homebuilt experimental setup illuminated by an amplified Ti:sapphire laser, with pulse durations of 100-150 fs, centred around 800 nm and at a repetition rate of 3 kHz. The excitation pulses are generated either using this fundamental, or by using an optical parametric amplifier (TOPAS) with the 800 nm fundamental input and then chopped at $f/2$ (1.5 kHz). Photoexcitations in the materials were probed via a broadband white light continuum generated by focusing a portion of the fundamental to an undoped YAG (Yttrium Aluminium Garnet) crystal. Pump-probe polarizations were kept under magic angle (54.7°) configuration to avoid orientational dynamics. After passing through the photoexcited sample, the probe pulses were spectrally dispersed using a prism spectrometer and are then collected using a CMOS camera (visible components) or an InGaAs photodiode array (IR components). The time resolution is obtained via introducing time delays in the pump path which is achieved using a retroreflector connected to a motorized translational stage. The differential transmission signals at various time delays are calculated from the sequential probe shots corresponding to the pump on versus off. For typical measurements, 8000 shots were averaged at each time point and were repeated at least four times. To avoid degradation, all the samples were measured under a vacuum, or inert nitrogen environment.

Time-resolved terahertz spectroscopy was performed using a dual lock-in technique, similar to that described by Tiwana *et al.*⁶⁸ THz pulses are generated by an amplified Ti:sapphire laser, with pulse durations of 100-150 fs, centred around 800 nm, generated at a repetition rate of 3 kHz chopped to 1.5 kHz, incident onto a 1 mm thick ZnTe crystal. THz pulses are measured by balanced photodetectors using electrooptic sampling in a separate ZnTe crystal. The 800 nm ‘optical’ pump is chopped at 750 Hz, and incident on the sample with a spot-size diameter of 4-5 mm. The THz probe diameter was measured as ~ 1 -2 mm. The entire THz beam path is enclosed in a cavity pumped with dry air, with humidity monitored to ensure % water remains

below 2%. The sample is enclosed in a nitrogen environment to avoid laser degradation and is excited from the glass substrate side. THz conductivity was calculated⁶⁸ as:

$$\Delta\sigma = -\frac{\varepsilon_0 c (n_A + n_B)}{L} \frac{\Delta T}{T}$$

Where ε_0 is the vacuum permittivity, c is the speed of light, n_A and n_B are the refractive indices of the media on both sides of the sample in the THz region – quartz, and air, L is the sample thickness, and $\frac{\Delta T}{T}$ the measured change in THz transmittance.

Ultrafast transient photoluminescence dynamics were measured using a photoluminescence up-conversion technique. The setup's light source is a Ytterbium fiber laser (Tangerine SP, Amplitude Systemes) operating at 44 kHz and generating 150 fs pulses. The laser output was split into pump and gate parts. The pump was frequency-doubled to 515 nm using a BBO crystal and focused to a 50 μm^2 spot to excite the sample. The sample fluorescence was collimated and refocused on a nonlinear mixing crystal (1 mm BBO, $\theta=32^\circ$) by a pair of aluminium-coated off-axis parabolic mirrors. The crystal angle is set for the phase-matching condition (type I) to produce sum frequency signals at 480 nm from mixing the 1030 nm gate and 900 nm photoluminescence. Two achromatic lenses collimated and focussed the upconverted signals onto the spectrometer (Princeton Instruments SP 2150). Signals were detected by an intensified CCD camera (Princeton Instruments, PIMAX3). A combination of 550 nm long- and 800 nm short-pass filters were used to remove residual excitation and 1030 nm gate light, respectively. The time delay between pump and gate beams was controlled via a motorized optical delay line on the excitation beam path. For each delay time, 240 000 shots were accumulated. Samples were measured under a vacuum environment.

Density functional theory calculations were performed using Gaussian 09⁶⁹ with an ultrafine integration grid, and the accuracy of two-electron integrals increased to 10^{11} . Optimized geometries were confirmed by calculation of the associated vibrational modes, which revealed no imaginary frequencies in all cases.

Electronic Coupling calculations were conducted on pairs of molecules extracted from the X-ray crystal structure, with alkyl chains truncated to ethyl. These calculations used the long-range corrected CAM-B3LYP⁷⁰ exchange–correlation functional in combination with the 6-31+G(d,p) basis set. Linear response TD-DFT calculations for excited states were performed within the Tamm–Dankoff approximation (TDA). Dielectric stabilisation was treated using a polarisable continuum model with $\epsilon = 5.0$, based on the experimentally-determined value.^{29,71–74} To treat CT states, the exchange–correlation functional was range-tuned according to the established non-empirical procedure,^{71–74} resulting in an optimal range-separation parameter of 0.0120 Bohr⁻¹. Electronic couplings and exciton/CT energetics were accessed from the DFT output using our previously described projective coupling method.^{52,53}

Density of States calculations for electrons and holes were performed using the long-range embedding procedure available in VOTCA-CTP.^{56–62} Molecular charge densities and polarizabilities for the ground state, cation, and anion were calculated using B3LYP/6-311G(d,p). The charge densities were used to fit distributed atomic multipoles (specifically, atomic charges, dipoles, and quadrupoles) using GDMA (version 2.3)⁷⁵. Polarizabilities for atoms in alkyl chains were taken directly from the set of Thole polarizabilities.⁷⁶ Atomic polarizabilities for atoms in the Y6 chromophore were obtained by scaling Thole

polarizabilities to match the DFT-calculated polarisable volume of the core.⁵⁶ Solid state corrections to the gas-phase IE/EA were calculated using the long-range Ewald summation scheme in VOTCA-CTP. These calculations employed a molecular dynamics equilibrated $8 \times 8 \times 6$ supercell constructed from the Y6 crystal structure,²⁷ with the π - π stacking direction aligned with the z -axis, to match the experimentally observed face-on packing preference relative to the substrate. This simulation cell was used to mimic a ~ 10 nm thin film by including a ~ 20 nm vacuum buffer in the z direction and applying the shape term for a periodically repeated supercell in the xy plane. The interaction cut-offs for electrostatic and polarization interactions were 8 and 6 nm, respectively.

Molecular dynamics simulations were conducted using the Y6 crystal structure with the missing atoms of the alkyl side chains built in. The system containing $8 \times 8 \times 6$ unit cells was generated using Maestro⁷⁷ in the Schrödinger Material Science Suite, and then prepared for molecular dynamics simulation with the OPLS3e force field using the System Builder in Desmond.^{78,79} The prepared system first underwent 100 ps of Brownian minimization, followed by 1 ns of equilibration using *NPT* molecular dynamics simulation at 1 fs timestep, 300 K and 1.01325 bar. A further 10 ps molecular dynamics simulation was conducted to collect 200 frames of trajectories at 50 fs time interval for analysis.

Acknowledgements

M.B.P., P.A.H., A.I., I.W., R.R.T., K.E.T., N.J.L.K.D, K.C and J.M.H. acknowledge support from the MacDiarmid Institute of New Zealand. P.A.H., A.I., I.W., R.R.T., K.E.T., N.J.L.K.D, K.C and J.M.H. acknowledge funding from the Marsden Fund of NZ. M.B.P and N.J.L.K.D. acknowledge support from the Royal Society of New Zealand. P.A.H. would like to acknowledge the support of Professor Denis Andrienko, Dr Anastasia Markina and Dr. Carl Poelking for support in utilising VOTCA software.

References

1. Riede, M., Spoltore, D. & Leo, K. Organic Solar Cells—The Path to Commercial Success. *Adv. Energy Mater.* **11**, 1–10 (2021).
2. Burlingame, Q. *et al.* Intrinsically stable organic solar cells under high-intensity illumination. *Nature* **573**, (2019).
3. Hou, J., Inganas, O., Friend, R. H. & Gao, F. Organic solar cells based on non-fullerene acceptors. *Nature Materials* 119–128 (2018) doi:10.1038/NMAT5063.
4. Halls, J. J. M. *et al.* Efficient photodiodes from interpenetrating polymer networks. *Nature* vol. 376 498–500 (1995).
5. Wen, Z. C., Yin, H. & Hao, X. T. Recent progress of PM6:Y6-based high efficiency organic solar cells. *Surfaces and Interfaces* **23**, 100921 (2021).
6. Cui, Y. *et al.* Single-Junction Organic Photovoltaic Cells with Approaching 18%

- 570 Efficiency. *Adv. Mater.* **32**, 1–7 (2020).
- 571 7. Lin, Y. *et al.* 17.1% Efficient Single-Junction Organic Solar Cells Enabled by n-Type
572 Doping of the Bulk-Heterojunction. *Adv. Sci.* **1903419**, 1–9 (2020).
- 573 8. Wang, Y. *et al.* High-Efficiency Perovskite Quantum Dot Hybrid Nonfullerene
574 Organic Solar Cells with Near-Zero Driving Force. *Adv. Mater.* **32**, (2020).
- 575 9. Kerremans, R. *et al.* The Optical Constants of Solution-Processed Semiconductors—
576 New Challenges with Perovskites and Non-Fullerene Acceptors. *Adv. Opt. Mater.* **8**,
577 (2020).
- 578 10. Few, S., Frost, J. M. & Nelson, J. Models of charge pair generation in organic solar
579 cells. *Phys. Chem. Chem. Phys.* **17**, 2311–2325 (2015).
- 580 11. Chen, S., Tsang, S. W., Lai, T. H., Reynolds, J. R. & So, F. Dielectric effect on the
581 photovoltage loss in organic photovoltaic cells. *Adv. Mater.* **26**, 6125–6131 (2014).
- 582 12. Tang, C. W. Two-layer organic photovoltaic cell. *Appl. Phys. Lett.* **48**, (1986).
- 583 13. Kozlov, O. V. *et al.* Ultrafast Exciton-to-Polaron Conversion in Densely Packed Small
584 Organic Semiconducting Molecules. *Adv. Opt. Mater.* **5**, 1–7 (2017).
- 585 14. Chandran, H. T. *et al.* Direct Free Carrier Photogeneration in Single Layer and Stacked
586 Organic Photovoltaic Devices. *Adv. Mater.* **29**, (2017).
- 587 15. Nikolis, V. C. *et al.* Field Effect versus Driving Force: Charge Generation in Small-
588 Molecule Organic Solar Cells. *Adv. Energy Mater.* **10**, (2020).
- 589 16. Wang, R. *et al.* Charge Separation from an Intra-Moiety Intermediate State in the
590 High-Performance PM6:Y6 Organic Photovoltaic Blend. *J. Am. Chem. Soc.* **142**,
591 12751–12759 (2020).
- 592 17. Benduhn, J. *et al.* Intrinsic non-radiative voltage losses in fullerene-based organic solar
593 cells. *Nat. Energy* **2**, (2017).
- 594 18. Karuthedath, S. *et al.* Intrinsic efficiency limits in low-bandgap non-fullerene acceptor
595 organic solar cells. *Nat. Mater.* (2020) doi:10.1038/s41563-020-00835-x.
- 596 19. Xiao, F., Li, C., Sun, J. & Zhang, L. Knowledge domain and emerging trends in
597 organic photovoltaic technology: A scientometric review based on citespace analysis.
598 *Front. Chem.* **5**, 1–12 (2017).

- 599 20. Yuan, J. *et al.* Single-Junction Organic Solar Cell with over 15% Efficiency Using
600 Fused-Ring Acceptor with Electron-Deficient Core. *Joule* (2019)
601 doi:10.1016/j.joule.2019.01.004.
- 602 21. Lin, Y. *et al.* An electron acceptor challenging fullerenes for efficient polymer solar
603 cells. *Adv. Mater.* (2015) doi:10.1002/adma.201404317.
- 604 22. Yan, C. *et al.* Non-fullerene acceptors for organic solar cells. *Nat. Rev. Mater.* **3**,
605 (2018).
- 606 23. Wang, J. & Zhan, X. Fused-Ring Electron Acceptors for Photovoltaics and beyond.
607 *Acc. Chem. Res.* **54**, (2021).
- 608 24. Cheng, P., Li, G., Zhan, X. & Yang, Y. Next-generation organic photovoltaics based
609 on non-fullerene acceptors. *Nat. Photonics* **12**, (2018).
- 610 25. Perdígón-Toro, L. *et al.* Barrierless Free Charge Generation in the High-Performance
611 PM6:Y6 Bulk Heterojunction Non-Fullerene Solar Cell. *Adv. Mater.* **32**, (2020).
- 612 26. Zhu, X. *et al.* Self-Stimulated Dissociation in Non-Fullerene Organic Bulk-
613 Heterojunction Solar Cells Self-Stimulated Dissociation in Non-Fullerene Organic
614 Bulk-Heterojunction Solar Cells. *Joule* **4**, 1–15 (2020).
- 615 27. Zhang, G. *et al.* Delocalization of exciton and electron wavefunction in non-fullerene
616 acceptor molecules enables efficient organic solar cells. *Nat. Commun.* **11**, 1–10
617 (2020).
- 618 28. Liu, J. *et al.* Charge separation boosts exciton diffusion in fused ring electron
619 acceptors. *J. Mater. Chem. A* **8**, (2020).
- 620 29. Kerremans, R. *et al.* The Optical Constants of Solution-Processed Semiconductors—
621 New Challenges with Perovskites and Non-Fullerene Acceptors. *Adv. Opt. Mater.*
622 **2000319**, (2020).
- 623 30. Park, S. Y. *et al.* Photophysical pathways in efficient bilayer organic solar cells: The
624 importance of interlayer energy transfer. *Nano Energy* **84**, (2021).
- 625 31. Lin, Q. *et al.* Electro-optics of perovskite solar cells. *Nat. Photonics* **9**, 106–112
626 (2014).
- 627 32. Li, H. *et al.* On the Study of Exciton Binding Energy with Direct Charge Generation in

628 Photovoltaic Polymers. *Adv. Electron. Mater.* **2**, (2016).

629 33. Mondelli, P. *et al.* Meta-analysis: The molecular organization of non-fullerene
630 acceptors. *Mater. Horizons* **7**, 1062–1072 (2020).

631 34. Northrup, J. E. Mobility enhancement in polymer organic semiconductors arising from
632 increased interconnectivity at the level of polymer segments. *Appl. Phys. Lett.* **106**,
633 (2015).

634 35. Gélinas, S. *et al.* Ultrafast Long-Range Charge Separation in Organic Semiconductor
635 Photovoltaic Diodes. *Science (80-.)*. **343**, 512–517 (2014).

636 36. Westenhoff, S. *et al.* Charge recombination in organic photovoltaic devices with high
637 open-circuit voltages. *J. Am. Chem. Soc.* **130**, 13653–13658 (2008).

638 37. Bakulin, A. A. *et al.* The role of driving energy and delocalized states for charge
639 separation in organic semiconductors. *Science (80-.)*. **335**, (2012).

640 38. Gélinas, S. *et al.* Ultrafast long-range charge separation in organic semiconductor
641 photovoltaic diodes. *Science (80-.)*. **343**, 512–516 (2014).

642 39. Gillett, A. J. *et al.* The role of charge recombination to spin-triplet excitons in non-
643 fullerene acceptor organic solar cells. *ArXiv* (2020).

644 40. Krauspe, P. *et al.* Terahertz short-range mobilities in neat and intermixed regions of
645 polymer:fullerene blends with controlled phase morphology. *J. Mater. Chem. A* **6**,
646 22301–22309 (2018).

647 41. Hendry, E., Schins, J. M., Candeias, L. P., Siebbeles, L. D. A. & Bonn, M. Efficiency
648 of exciton and charge carrier photogeneration in a semiconducting polymer. *Phys. Rev.*
649 *Lett.* **92**, 1–4 (2004).

650 42. Cooke, D. G., Krebs, F. C. & Jepsen, P. U. Multi-THz spectroscopy of mobile charge
651 carriers in P3HT:PCBM on a sub-100 fs time scale. *Phys. Chem. Interfaces*
652 *Nanomater. XII* **8811**, 88111H (2013).

653 43. Sun, Y. *et al.* Electronic processes investigation from ultrafast terahertz in photovoltaic
654 DPPDTT-PCBM films. *Sol. Energy Mater. Sol. Cells* **215**, 110684 (2020).

655 44. Richter, J. M. *et al.* Enhancing photoluminescence yields in lead halide perovskites by
656 photon recycling and light out-coupling. *Nat. Commun.* (2016)

doi:10.1038/ncomms13941.

45. Hou, Y. *et al.* Charge separation, charge recombination, long-lived charge transfer state formation and intersystem crossing in organic electron donor/acceptor dyads. *J. Mater. Chem. C* **7**, 12048–12074 (2019).
46. Yablonovitch, E., Miller, O. D. & Kurtz, S. R. A great solar cell also needs to be a great LED: External fluorescence leads to new efficiency record. in *AIP Conference Proceedings* vol. 1519 (2013).
47. Kyaw, A. K. K. *et al.* Intensity dependence of current-voltage characteristics and recombination in high-efficiency solution-processed small-molecule solar cells. *ACS Nano* **7**, (2013).
48. Koster, L. J. A., Kemerink, M., Wienk, M. M., Maturová, K. & Janssen, R. A. J. Quantifying bimolecular recombination losses in organic bulk heterojunction solar cells. *Adv. Mater.* **23**, (2011).
49. Koster, L. J. A., Mihailetschi, V. D., Xie, H. & Blom, P. W. M. Origin of the light intensity dependence of the short-circuit current of polymer/fullerene solar cells. *Appl. Phys. Lett.* **87**, (2005).
50. Mihailetschi, V. D., Wildeman, J. & Blom, P. W. M. Space-charge limited photocurrent. *Phys. Rev. Lett.* **94**, (2005).
51. Liao, S. H., Jhuo, H. J., Cheng, Y. S. & Chen, S. A. Fullerene derivative-doped zinc oxide nanofilm as the cathode of inverted polymer solar cells with low-bandgap polymer (PTB7-Th) for high performance. *Adv. Mater.* **25**, (2013).
52. Hume, P. A. & Hodgkiss, J. M. A Projective Method for the Calculation of Excited-State Electronic Coupling: Isolating Charge Transfer/Recombination Processes in Organic Photovoltaics. *J. Phys. Chem. A* **124**, 591–600 (2020).
53. Hume, P. A., Jiao, W. & Hodgkiss, J. M. Long-range exciton diffusion in a non-fullerene acceptor: approaching the incoherent limit. *J. Mater. Chem. C* 1419–1428 (2021) doi:10.1039/d0tc05697a.
54. Aldrich, T. J. *et al.* Fluorination Effects on Indacenodithienothiophene Acceptor Packing and Electronic Structure, End-Group Redistribution, and Solar Cell Photovoltaic Response. *J. Am. Chem. Soc.* (2019) doi:10.1021/jacs.8b13653.

- 687 55. Lai, H. *et al.* Isomer-free: Precise Positioning of Chlorine-Induced Interpenetrating
688 Charge Transfer for Elevated Solar Conversion. *iScience* **17**, 302–314 (2019).
- 689 56. Poelking, C. & Andrienko, D. Long-Range Embedding of Molecular Ions and
690 Excitations in a Polarizable Molecular Environment. *J. Chem. Theory Comput.* **12**,
691 4516–4523 (2016).
- 692 57. Kirkpatrick, J. An approximate method for calculating transfer integrals based on the
693 ZINDO Hamiltonian. *Int. J. Quantum Chem.* **108**, (2008).
- 694 58. Rühle, V., Junghans, C., Lukyanov, A., Kremer, K. & Andrienko, D. Versatile object-
695 oriented toolkit for coarse-graining applications. *J. Chem. Theory Comput.* **5**, (2009).
- 696 59. Baumeier, B., Kirkpatrick, J. & Andrienko, D. Density-functional based determination
697 of intermolecular charge transfer properties for large-scale morphologies. *Phys. Chem.*
698 *Chem. Phys.* **12**, (2010).
- 699 60. Lukyanov, A. & Andrienko, D. Extracting nondispersive charge carrier mobilities of
700 organic semiconductors from simulations of small systems. *Phys. Rev. B - Condens.*
701 *Matter Mater. Phys.* **82**, (2010).
- 702 61. Rühle, V. *et al.* Microscopic simulations of charge transport in disordered organic
703 semiconductors. *Journal of Chemical Theory and Computation* vol. 7 (2011).
- 704 62. Kordt, P. & Andrienko, D. Modeling of Spatially Correlated Energetic Disorder in
705 Organic Semiconductors. *J. Chem. Theory Comput.* **12**, (2016).
- 706 63. Poelking, C. & Andrienko, D. Design rules for organic donor-acceptor heterojunctions:
707 Pathway for charge splitting and detrapping. *J. Am. Chem. Soc.* **137**, 6320–6326
708 (2015).
- 709 64. Schwarze, M. *et al.* Impact of molecular quadrupole moments on the energy levels at
710 organic heterojunctions. *Nat. Commun.* **10**, 1–9 (2019).
- 711 65. Poelking, C. *et al.* Impact of mesoscale order on open-circuit voltage in organic solar
712 cells. *Nat. Mater.* **14**, 434–439 (2015).
- 713 66. Park, S. Y., Chandrabose, S. & Price, M. B. Photophysical pathways in efficient
714 bilayer organic solar cells: the importance of interlayer energy transfer. *Nano Energy*
715 (2021).

- 716 67. de Mello, J. C., Wittmann, H. F. & Friend, R. H. An improved experimental
717 determination of external photoluminescence quantum efficiency. *Adv. Mater.* **9**, 230–
718 232 (1997).
- 719 68. Tiwana, P., Parkinson, P., Johnston, M. B., Snaith, H. J. & Herz, L. M. Ultrafast
720 terahertz conductivity dynamics in mesoporous TiO₂: Influence of dye sensitization
721 and surface treatment in solid-state dye-sensitized solar cells. *J. Phys. Chem. C* **114**,
722 1365–1371 (2010).
- 723 69. Frisch, M. J. *et al.* Gaussian09 Revision D.01, Gaussian Inc. Wallingford CT.
724 *Gaussian 09 Revision C.01* (2010).
- 725 70. Yanai, T., Tew, D. P. & Handy, N. C. A new hybrid exchange-correlation functional
726 using the Coulomb-attenuating method (CAM-B3LYP). *Chem. Phys. Lett.* **393**,
727 (2004).
- 728 71. Kronik, L., Stein, T., Refaely-Abramson, S. & Baer, R. Excitation gaps of finite-sized
729 systems from optimally tuned range-separated hybrid functionals. *Journal of Chemical*
730 *Theory and Computation* vol. 8 (2012).
- 731 72. Sun, H. *et al.* Ionization Energies, Electron Affinities, and Polarization Energies of
732 Organic Molecular Crystals: Quantitative Estimations from a Polarizable Continuum
733 Model (PCM)-Tuned Range-Separated Density Functional Approach. *J. Chem. Theory*
734 *Comput.* **12**, (2016).
- 735 73. Refaely-Abramson, S. *et al.* Gap renormalization of molecular crystals from density-
736 functional theory. *Phys. Rev. B - Condens. Matter Mater. Phys.* **88**, (2013).
- 737 74. Chen, X. K. & Brédas, J. L. Voltage Losses in Organic Solar Cells: Understanding the
738 Contributions of Intramolecular Vibrations to Nonradiative Recombinations. *Adv.*
739 *Energy Mater.* **8**, (2018).
- 740 75. Stone, A. J. Distributed multipole analysis: Stability for large basis sets. *J. Chem.*
741 *Theory Comput.* **1**, (2005).
- 742 76. Van Duijnen, P. T. & Swart, M. Molecular and atomic polarizabilities: Thole's model
743 revisited. *J. Phys. Chem. A* **102**, (1998).
- 744 77. Schrödinger Release 2020-2: Maestro. (2020).

- 745 78. Shaw, D. E. *et al.* Millisecond-scale molecular dynamics simulations on Anton. in
746 *Proceedings of the Conference on High Performance Computing Networking, Storage*
747 *and Analysis, SC '09* (2009). doi:10.1145/1654059.1654099.
- 748 79. Schrödinger Release 2020-2: Desmond Molecular Dynamics System. (2020).

749

Figures

Figure 1

Intensity-dependent photoluminescence quantum efficiency of Y6. a) Experimentally determined PLQE of a neat film of Y6 on glass substrate in an integrating sphere (normalised). The sample was excited by 600 ps pulses of 532 nm light. The PLQE peaks at 1% at $\sim 10^{16}$ excitations/ cm^3 . Figure S1 gives an

indication of the error associated with the data. Intensity dependent PLQE of a film of P3HT is shown as orange circles, as comparison, to illustrate the expected response. b) Simulation of intensity-dependent PLQE values showing effect of increasing (orange) or decreasing (blue) radiative bimolecular recombination (from prompt free charge fraction, calculated using Model 2 detailed in the SI). c) Graphic representation of exciton-CT state-free charge equilibrium in Y6.

Figure 2

Ultrafast transient absorption spectra and kinetics of singlets and free charges in neat Y6, and optical pump terahertz probe conductivity. a) Transient absorption spectra, normalised to the absolute area integral, of a neat film of Y6 at different time delays. 700 nm, 200 fs pump pulse, excitation density = 10^{15} excitations/cm³. The spectrum evolves from the exciton, blue line, with a negative peak at 915 nm, to the red-shifted charge/CT state spectrum, orange line. b) Confirmation of charge and exciton transient absorption spectra by comparison of neat species (extracted using genetic algorithm) with species resolved from blends of Y6 with hole and electron accepting materials (PTB7-Th, polyTPD). The green dashed line shows the hole spectra of PTB7-Th blended with PCBM. c) Singlet component from GA of transient absorption (dark blue line), compared with up-converted PL signal (cyan), at an excitation density of 8×10^{14} cm⁻³. d) Initial kinetics of the exciton (blue) versus charge/CT (orange) TA kinetics in the first 2.5 ps after photoexcitation. The charge species shows a rise concomitant with the fast initial decay of the singlet species. e) Excited-state terahertz complex conductivity spectrum, excited with 150 fs, 800 nm light, giving approximate excitation density 5×10^{15} excitations/cm³, with a THz probe delay of ~ 3 ps. The positive real (light blue) line is indicative that there are charge-like species present in addition to purely excitonic photoexcitations. The experimental data is fit to a modified Drude-Smith model (darker blue and darker red curves).

Figure 3

Kinetic model of charge generation in Y6 with transient absorption, PLQE and predicted steady-state free charge fractions. a) Jablonski diagram highlighting key excited-state pathways, with associated rate constants. Monomolecular, k_1 , values are given in units s^{-1} , and bimolecular, β , values given in $cm^3 s^{-1}$. b) Normalised transient absorption kinetics of excitons (blue circles) and charges+CT states (orange circles) at different excitation densities, fitted with a global fit to the kinetic model described in the text and SI

(solid blue and orange lines). c) Internal (blue) and external (red) PLQE values of Y6 as a function of excitation density, with corresponding simulated values from fits to the transient absorption and intensity dependent PLQE. Internal PLQE is calculated from external PLQE as per Richter et al.⁴⁴ d) Steady-state free charge fraction as a function of total excitation density calculated from the rate constants gathered from the kinetic model (red line), and from an estimate from the Saha equation (blue line).

Figure 4

Single component short circuit current, and low donor active layer device EQEs, and corresponding exciton and charge kinetics. a) Intensity dependent J_{sc} of a monolayer Y6 device. The power exponent fitted to the data between 0.2 and 2 suns is 0.7, indicating a high number of bimolecular recombination events. b) External quantum efficiencies (EQEs) of devices with active layers consisting of small ratios of donor, PTB7-Th, to acceptor, Y6. For such low donor content, EQEs are unexpectedly high. c) Normalised transient absorption kinetics of exciton and charge species in blends of PTB7-Th:Y6 with ratios of 1:50 and 1:100. Pumped with 800 nm, 150 fs pulses at excitation density 1×10^{14} excitations/ cm^3 . The exciton kinetics of both films, dashed lines, are matching, as are the rise times of the charge kinetics (orange and red lines), but the 1:50 blend shows slower charge recombination after 20 ps. The green-blue line shows the hole kinetics in the 1:50 blend, showing a gradual increase in hole population as excitons and charges in Y6 diffuse to the PTB7-Th.

Figure 5

Electronic couplings and energies for Y6 excitons, CT states, and charges. a) Exciton-CT energy offsets and electronic couplings (in meV) for π -stacked molecular pairs extracted from the Y6 crystal structure (Alkyl chains have been removed for clarity).²⁷ b) Density of states (DOS) for holes (-IE) in a 10 nm thick model thin film based on molecular dynamics equilibration of the Y6 crystal structure, normalized to unit area. Dashed line indicates the DOS onset determined by photoelectron spectroscopy in air.¹⁸ c) Average ionisation energy as a function of π -stacking layer showing differential hole stabilisation for the different lattice positions, which occur in an "...ABBA..." sequence.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SupplementaryinformationFreechargegenerationinY6300321.pdf](#)