

New Avenues for Organic Solar Cells Using Intrinsically Charge-Generating Materials

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Cite This: *JACS Au* 2024, 4, 1295–1302



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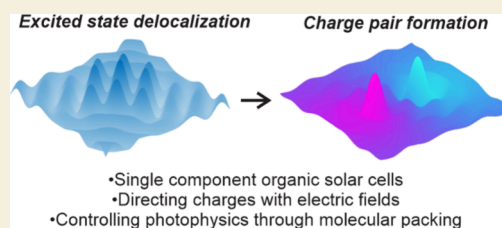
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ABSTRACT: The molecular electron acceptor material Y6 has been a key part of the most recent surge in organic solar cell sunlight-to-electricity power conversion efficiency, which is now approaching 20%. Numerous studies have sought to understand the fundamental photophysical reasons for the exceptional performance of Y6 and its growing family of structural derivatives. Though significant uncertainty about several details remains, many have concluded that initially photogenerated excited states rapidly convert into electron–hole charge pairs in the neat material. These charge pairs are characterized by location of the electron and hole on different Y6 molecules, in contrast to the Frenkel excitons that dominate the behavior of most organic semiconductor materials. Here, we summarize the current state of knowledge regarding Y6 photophysics and the key observations that have led to it. We then link this understanding to other advances, such as the role of quadrupolar fields in donor–acceptor blends, and the importance of molecular interactions and organization in providing the structural basis for Y6’s properties. Finally, we turn our attention to ways of making use of the new photophysics of Y6, and suggest molecular doping, crystal structure tuning, and electric field engineering as promising avenues for future exploration.

KEYWORDS: Solar Energy, Organic Photovoltaics, Non-Fullerene Electron Acceptors, Fused-Ring Electron Acceptors, Exciton Dissociation, Charge Transfer, Photophysics, Ultrafast Spectroscopy, Y6



INTRODUCTION

Increases in the efficiency of organic photovoltaics (OPVs/organic solar cells) are driven by the discovery of new materials with improved photophysics. This is particularly true of the molecular electron acceptor, Y6. First reported in 2019, OPVs containing Y6 broke the existing sunlight-to-electricity conversion record for OPVs by 3.5%, from 12.1% to 15.6% (Figure 1).^{1–3} All subsequent improvements have involved Y6-inspired electron acceptors, which have now propelled single junction OPV efficiency to 19.2%.^{2,4}

Y6-based materials have built on the success of fused-ring electron acceptors (FREAs) - the first materials to outperform fullerene acceptors in donor–acceptor blends.^{5,6} FREAs achieved this milestone in large part due to their intrinsic properties, such as their low reorganization energy, and low energetic disorder in film environments.^{7–10} In FREAs such as Y6, excitons and charges can rapidly transfer from molecule to molecule, relatively unimpeded by rearrangements of molecular geometry, or by immobilizing “trap” sites.^{7,8,11}

These observations lead to the following question: is the step-change in efficiency brought about by Y6 simply due to optimization of the nascent benefits of FREAs? Or is something new happening? The current consensus appears to be the latter, although there are differing views of precisely what this new behavior is.^{12–19} In the following perspective, we survey the unusual photophysics in Y6, attempt to integrate

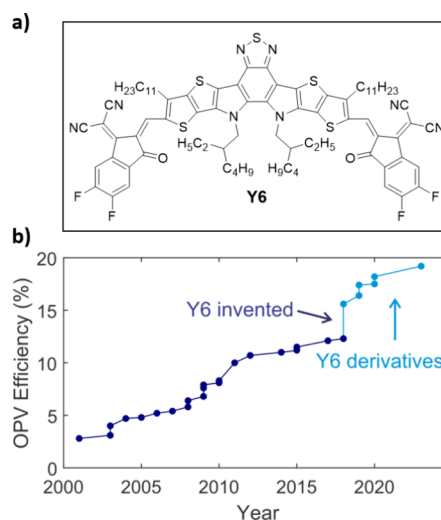


Figure 1. (a) Y6.¹ (b) Record OPV power conversion efficiency over time.²

Received: January 10, 2024

Revised: March 3, 2024

Accepted: March 4, 2024

Published: March 18, 2024



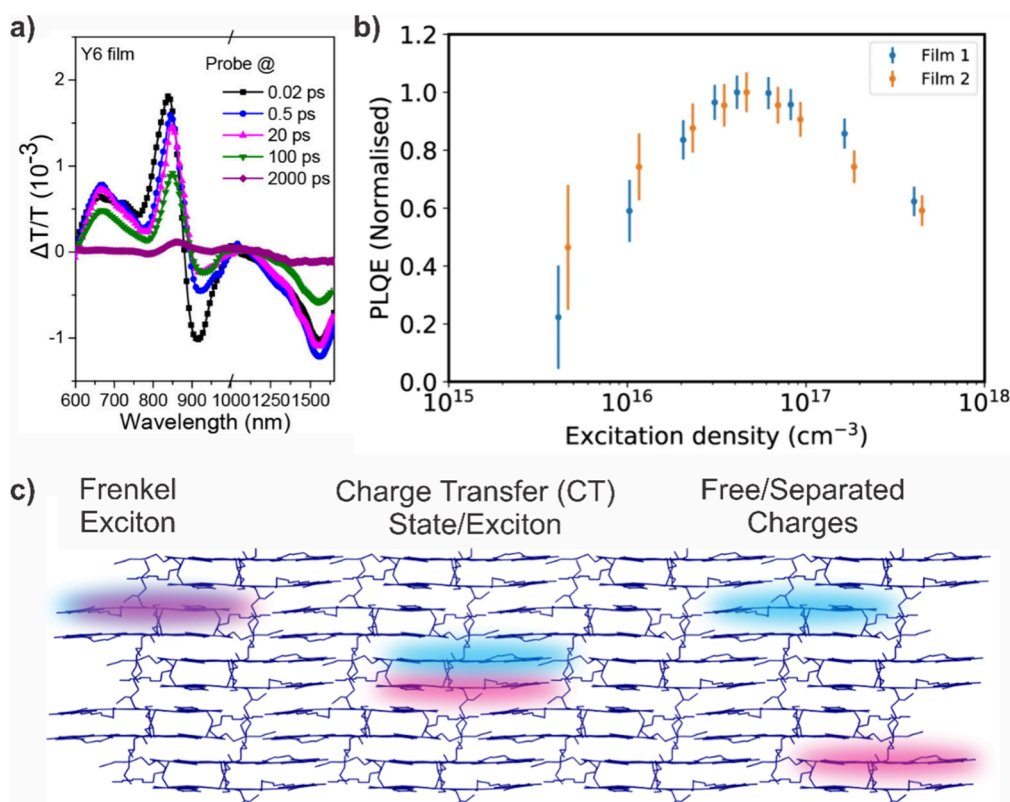


Figure 2. (a) Ultrafast transient absorption (TA) spectrum of a neat Y6 film, showing ultrafast conversion of the initially formed singlet exciton population (~ 920 nm) into charge transfer (CT) states/charges (~ 1550 nm). Reproduced with permission from ref 12. Copyright 2020 American Chemical Society. (b) Excitation intensity dependent relative photoluminescence quantum efficiency of Y6. Reproduced with permission from ref 13. Copyright 2022 The Authors. Published by Springer Nature. (c) Comparison between separated charges/polarons and CT states.

this understanding with other recent developments, and discuss ways to make use of it.

PHOTOPHYSICS

In typical OPVs, absorption of light results in the formation of Frenkel excitons (FEs).²⁰ A FE can be thought of as an electron–hole charge pair, with both charges located on the same molecule, i.e. the charge separation distance is small compared to the molecular length scale. To overcome this behavior, OPVs typically employ a bulk heterojunction (BHJ), a blend of two distinct organic materials that can separate the holes and electrons, which can flow as electricity.²⁰

The most direct evidence of unusual photophysics in Y6 comes from ultrafast transient absorption (TA) spectroscopy.¹² Unlike typical organic materials, the TA spectrum of Y6 shows conversion of the initially formed singlet exciton into a new species on a sub-to-early picosecond time scale (Figure 2a). This species is absent in molecularly dissolved Y6 solutions and likely reflects the formation of an intermolecular state.¹² In PM6/Y6 blends, the decay of the new state is coupled to the growth of the PM6 hole polaron.^{12,21}

The most likely candidate for this new species is an electron–hole pair, with the charges occupying different molecular sites. This assignment is supported by the optical dielectric constant on Y6 (~ 5.3) which is unusually large for an organic semiconductor,²² and the similarity of the TA spectrum to that of photogenerated charges in donor–Y6 blends and charge-doped films.¹³ These electron–hole charge pairs may be bound together in an intermolecular charge transfer (CT) state, or free charges separated from one

another, or a mixture of both (Figure 2c). The decay of the CT/charge population on a 10^{-10} – 10^{-9} s time scale is suggestive of an electrostatically bound charge transfer (CT) state. However, it is difficult to be certain of the electron–hole separation length scale from TA spectroscopy alone because free charge encounters with trap sites could also lead to pseudo-first order decay on this time scale. For example, a trap density of 10^{17} cm^{-3} (one trap site per several thousand molecules) combined with a bimolecular annihilation constant of 10^{-8} cm^3s^{-1} would yield an apparent first-order rate constant of $\sim 10^9$ s^{-1} . These values are consistent with experimentally determined hole trap densities for Y6 (8×10^{16} cm^{-3}).²³ Similarly, some studies have found charge carrier mobilities in the range of 0.01 – 0.1 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for as-cast Y6^{8,24} which would correspond to bimolecular recombination constants of $\sim 10^{-8}$ cm^3s^{-1} . The local mobilities probed in ultrafast spectroscopy measurements are also expected to be larger than the macroscopic mobilities from device measurements that include the effects of grain boundaries. This observation is qualitatively supported by the exceptionally high electron and hole mobilities (up to 2.4 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for electrons, and 0.84 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for holes) reported for single crystal Y6²⁵ and annealed Y6 phases.^{24,26}

This simple estimate of the trap-assisted charge recombination rate illustrates one of the difficulties in understanding the nature of Y6's photophysics: the wide range of values reported for key parameters, such as charge carrier mobilities, photoluminescence quantum efficiency (PLQE), excited state lifetime, and power conversion efficiency (PCE) of single component devices lacking a donor material. Charge carrier

mobilities for as-cast Y6 vary from 10^{-4} – 10^{-1} $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$,^{1,8,11,24,27} PLQEs from 0.02 to 7.5%,^{8,28,29} and excited state lifetimes from 100 to 1200 ps (note that this range of lifetimes combines studies that quote a single effective lifetime with those that distinguish biphasic lifetimes).^{8,12,17,30} In our view, this variability and the multiple crystal polymorphs that have been reported for Y6^{11,24,27,31} point to a key role of the underlying morphologies in determining the photophysical properties.

Beyond the short lifetimes observed through TA spectroscopy, several other pieces of evidence favor the assignment the charge pair-like species in Y6 as a CT state. Magnetic spectroscopy measurements show that triplet excitons and CT states dominate the excited state population after hundreds of nanoseconds following photoexcitation at 10 K.¹⁹ Time-resolved terahertz spectroscopy measurements show the formation of an electron–hole plasma with a similar photoconductivity spectrum to that of a PM6/Y6 blend at high excitation densities of 10^{22} cm^{-3} , but not at 10^{21} cm^{-3} . This was interpreted as evidence for the formation of CT states in Y6.³²

We and others have proposed that a substantial population of free charges are generated upon photoexcitation of Y6.^{13–16,33,34} This interpretation does not exclude the formation of CT states as intermediates or products of charge recombination. A key additional observation supporting this claim is the intensity dependent relative photoluminescence quantum efficiency (PLQE), which rises to a peak as excitation density is increased, before decaying as nonradiative bi- and trimolecular annihilation processes begin to dominate (Figure 2b).¹³ The combined ultrafast spectroscopy and intensity dependent relative PLQE data are well described by ultrafast charge separation from a delocalized exciton state (S^*), which forms free charges (C) and thermalized/localized excitons (S). At low excitation densities, separated charges encounter traps and decay nonradiatively, leaving the emission dominated by the remaining undissociated singlet excitons. As the excitation density increases, bimolecular recombination of electrons and holes results in an increase in emission intensity due to the formation of excitons. Additional evidence advanced in support of charge formation in Y6 includes: efficient (relative to other pure materials) single component OPVs made with Y6 and its analogues, reaching up to 4.5% PCE^{13–15,35} surface photovoltage measurements,³⁰ field-independent photocurrent generation in time-delayed collection field experiments,¹⁴ and fast hydrogen evolution of single component Y6 nanoparticle photocatalysts.^{36,37} In another relevant study (albeit at high excitation densities) transient infrared spectroscopy measurements were interpreted as showing substantial charge yields in Y6.³⁴ From a theoretical perspective, delocalized kinetic Monte Carlo simulations^{38–40} support the feasibility of delocalization-mediated exciton dissociation to both CT states and free charges in neat materials.⁴¹

An additional layer of complexity is observed when considering the TA spectrum of Y6 triplet excitons (Figure 3). Sensitization experiments show that the Y6 triplet spectrum closely resembles that of the CT/charge, rather than the singlet exciton, with a blue shift of the photoinduced absorption at long wavelengths (from ~ 1550 nm to ~ 1450 nm).^{17,21} This suggests that the Y6 triplet possesses significant CT character. Different studies have demonstrated varying quantities of triplet excitons from photoexcitation of neat Y6, which may be

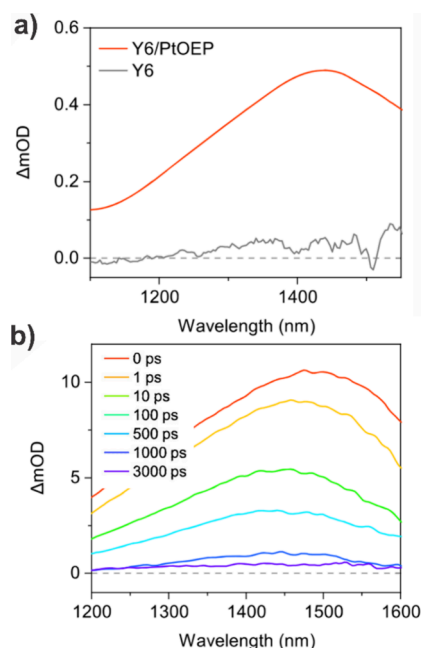


Figure 3. Transient absorption spectroscopy of Y6 triplet excitons. Note the units of ΔmOD for the y axis, as opposed to $\Delta T/T$ used in Figure 2. Adapted with permission from ref 17. Copyright 2020 American Chemical Society. (a) Y6 triplet spectrum from triplet sensitization with PtOEP. (b) Triplet formation in neat Y6 at high excitation density.

due to differences in excitation fluence, or differences in film morphology/crystal packing.^{16,17,21}

THE ENERGETIC LANDSCAPE

Whether Y6 forms CT states, free charges, both species, or something in between (such as loosely bound charge pairs with a degree of bimolecular character), most interpretations agree that exciton dissociation is taking place. The next question is why? Our theoretical calculations showed that at least one of the Y6 crystal structures¹¹ polarizes inequivalent molecules differently, leading to a substantial ~ 0.1 – 0.2 eV disparity in ionization energies for molecules in different positions within the unit cell (Figure 4 a).¹³ Together with the large optical dielectric constant²² and strong electronic coupling from extensive orbital overlap between Y6 molecules,^{13,42} this effect promotes exciton dissociation. Related effects have since been experimentally observed in Y6 films, where crystallites with different molecular orientations relative to the substrate experience significant (~ 0.2 eV) energy level shifts.³⁰ Subsequent theoretical studies have also found that low energy CT states coupled to FE states are essential to simulate the steady-state absorption spectrum of Y6 films.^{19,43}

It is interesting to consider the degree of hybridization between Frenkel exciton (FE) and CT states in Y6. FE-CT hybridization is considered to be responsible for the low voltage losses observed in some high-performance blend systems, and depends on both the energy difference, and the electronic coupling strength between the FE and interfacial CT states.⁴⁴ The precise energetic offset between the Frenkel exciton (FE) and CT states of Y6 is difficult to quantify and likely to be sample/morphology-dependent, but temperature-dependent photoluminescence measurements have shown thermally activated Y6 emission, which means that $E_{CT} < E_{FE}$.¹⁵ The FE-CT coupling in Y6 is more challenging to probe

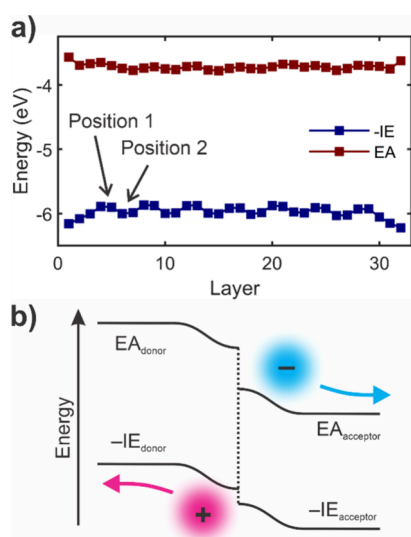


Figure 4. (a) Average ionization energy (IE) and electron affinity (EA) calculated as a function of layer position within a model 10 nm Y6 film, based on the crystal structure and equilibrated by molecular dynamics. Reproduced with permission from ref 13. Copyright 2022 The Authors. Published by Springer Nature. (b) Energy level bending at the interface in a donor–acceptor blend system.⁵²

experimentally, but calculations have estimated it at 10–75 meV, depending on the geometric configuration of the interacting molecules.¹³ The tendency for Y6 to form packing arrangements involving core–core terminal-terminal (CC-TT) stacking interactions appears to be a particularly key factor in determining its properties. Theoretical⁴⁵ and experimental⁴⁶ studies have found that these configurations are beneficial for exciton and charge transport in Y6 and these pairs also had the largest couplings for exciton-to-CT conversion.¹³ The design of structural derivatives that promote these types of interactions is an exciting avenue for exploration, with early studies revealing positive effects on device performance.^{46,47}

These observations speak to a broader recent trend in OPV photophysics: the importance of long-range electrostatic and polarization effects, particularly charge-quadrupole interactions. Even prior to the rise of nonfullerene acceptors, these effects were recognized as a potential explanation for how interfacial donor–acceptor CT states are able to separate into free charge pairs.^{48–50} In this framework, long-range interactions between charges and the quadrupole moments of the surrounding molecules perturb the ionization energies (IEs) and electron affinities (EAs) of molecules close to the donor–acceptor interface. These energy level shifts can compensate for the attraction between electron and hole in CT states, enabling them to separate. Such effects are accentuated for “A-D-A” and “A-D-A’-D-A” molecular electron acceptors (such as FREAs) because they are constructed from alternating electron-rich and deficient subunits, and therefore have large quadrupole moments. For example, in PM6/Y6 blends, quadrupolar band bending has been invoked as an explanation for barrierless (i.e., temperature independent) charge separation.⁵¹ Related work on a series of FREA-containing blends then showed that these energy level shifts also introduce a barrier to exciton dissociation (exciton → CT conversion) when the ionization energy level offset between the neat donor and acceptor materials is less than 0.4–0.5 eV.⁵² This finding is significant because it may impose a limit

on the maximum open circuit voltages that are achievable with excitonic FREA materials.

Intrinsic exciton dissociation may offer a way to partially circumvent this barrier. If Y6 generates free charges, then quadrupolar fields (depending on their spatial extent) may be capable of pulling Y6 hole polarons across the interface into the donor material and repelling Y6 electrons. Even if Y6 predominantly forms CT states rather than free charges, the magnitude of the quadrupolar energy level shifts (0.3–0.4 eV) in typical blend systems are likely to be sufficient to drive CT state separation.⁵² Given that the open circuit voltage (which is closely linked to the difference between the donor IE and acceptor EA) is now the main target for OPV efficiency gains, we believe that understanding and engineering of quadrupolar fields will be key to efforts to improve performance.

Another question concerns the magnitude of the exciton and CT state binding energies in Y6. A simple estimate of 0.1–0.26 eV for the exciton binding energy can be obtained from experimental values for the optical gap (~1.45 eV from the intersection of the steady state absorption and emission spectra), the IE (5.81 eV from ultraviolet photoelectron spectroscopy, 5.65 eV from photoelectron spectroscopy in air), and the EA (4.1 eV from inverse photoelectron spectroscopy). If cyclic voltammetry values are used instead, the estimated value is 0.3 eV.^{14,53} Another value of 0.34 eV was also reported recently.⁵⁴ It is important to note that the branching model proposed for free charge generation does not imply a negative exciton binding energy.¹³ In this model, the fact that significant charge separation appears to be limited by the localization (i.e., $S^* \rightarrow S$) time scale suggests that the exciton binding energy is indeed positive.^{12,13}

MAKING USE OF INTRINSIC EXCITON DISSOCIATION

The most important question from a technological perspective is whether the unusual photophysics of Y6 can be leveraged to improve OPV performance. Having achieved parity with commercial silicon and perovskite solar cells in terms of short circuit current and fill factor, the open circuit voltage of OPVs is now the main target for improvement. As noted in the previous section, the quadrupolar fields of current nonfullerene electron acceptors may impose an intrinsic efficiency limitation when used in bulk heterojunction OPVs. The long-term stability of bulk heterojunction blend morphologies is also a longstanding area of concern.⁵⁵ In the remainder of this article, we therefore identify and discuss several nontraditional approaches to OPVs that would be interesting to explore.

The centrality of donor–acceptor blends in OPVs is often framed in terms of the excitonic nature of organic materials, i.e. blends are necessary to split Frenkel excitons into charges that can flow as electricity. Identifying a high-performance material that undergoes spontaneous exciton dissociation may therefore renew the prospect of single component OPVs. However, single component OPVs must face a fundamentally new challenge: the need to minimize charge recombination without using a BHJ to keep electrons and holes apart. Initial efforts to make single component OPVs based on Y6 have yielded functional, but inefficient devices.^{13–15,35} The efficiencies of single component Y6 devices are highly variable, ranging from 0.4 to 0.6%^{13,15} to 4.5%¹⁴ and appear strongly dependent on morphologies, packing modes, crystallite orientation, and choice of charge transport layers. The highest efficiency single component Y6 OPVs have employed a CuSCN hole transport

layer, which was attributed to improved charge extraction and exciton dissociation at the Y6-CuSCN interface.^{14,56–58} It should be noted that single component OPVs with CuSCN transport layers have also been used to quantify exciton diffusion lengths of FREAs via thickness dependent EQE measurements.⁸ The appreciable efficiencies at the EQE maxima (1–2.5%) highlight the role of interfacial charge generation in such devices. The comparatively low efficiencies of single component Y6 devices compared to BHJs have been attributed to the presence of hole traps because of intrinsic doping, and rapid charge recombination in the absence of distinct donor/acceptor phases to spatially segregate electrons and holes.

■ MOLECULAR DOPING

One strategy to improve the efficiency of single component organic solar cells is to quench charge traps using molecular doping. Doing so would potentially suppress trap-mediated charge recombination and extend charge lifetimes. Ideally, organic p–n junctions analogous to silicon PVs would bias the flow of photogenerated charges toward the electrodes. Although molecular doping methods for organic semiconductors are still in their infancy, doped single component OPVs would represent a fundamentally new approach. Importantly, this strategy could still succeed if Y6 forms CT states rather than free charges, if the electric field in the depletion region is sufficient to separate the charges. Asymmetric doping approaches would likely also yield improved charge extraction at electron or hole selective contacts.⁵⁹ Recent work on doping of bulk heterojunction blends have shown encouraging early results in molecular doping of Y6.⁶⁰ There is also opportunity in this area to borrow knowledge from the large body of work on organic molecular doping for thin film transistors.⁶¹

■ KINETIC SUPPRESSION OF CHARGE RECOMBINATION

The observation of intrinsic exciton dissociation in Y6 is significant because it is occurring in a crystalline material that we can study with atomic precision. In principle, this behavior is optimizable through crystal structure engineering. By modifying the molecular arrangement of a small number of unique intermolecular contacts, one can in principle control the orbital overlaps mediating exciton dissociation (exciton → CT conversion) and charge recombination (CT → ground state conversion). On a practical level, this would likely need to be achieved through side-chain engineering, annealing, or the use of morphological additives.

While acknowledging that this is an ambitious goal, extending CT/charge lifetimes is favorable regardless of whether a single component OPV or bulk heterojunction is considered. A key component of this strategy is that changes to molecular arrangement will affect the electronic couplings for charge formation and recombination independently. To a first approximation, the couplings for exciton dissociation are dominated by HOMO–HOMO and LUMO–LUMO interactions, while charge recombination involves electron transfer from the LUMO of one molecule to the HOMO of another. Tuning electronic couplings to maximize charge formation is therefore also expected to positively impact ground state charge transport properties, benefiting single component OPVs and BHJs alike.

Modifying molecular arrangements will no doubt affect the exciton/CT state/charge energies in addition to the couplings. At first glance, this would seem to complicate such a crystal structure engineering strategy. In practice, however, modifications to state energies may simplify the approach, because excitons/charges are more likely to occupy lower energy states/sites, which can then be the focus for tuning of electronic coupling. In our view, the opportunity to systematically optimize charge formation/recombination processes that were previously hidden within disordered donor–acceptor interfaces is an exciting development.

■ ELECTROSTATIC-POLARIZATION JUNCTION

As discussed, the large quadrupole moments and long-range molecular ordering of FREAs such as Y6 result in energy level “bending” in the vicinity of an interface. It is natural to picture these interfaces as donor/acceptor boundaries in a bulk heterojunction. However, there is no requirement for this to be the case, the only remaining ingredient needed for energy level bending is electrostatic contrast, i.e. a difference in the surrounding dielectric environment on either side of the interface.

We propose that it may be possible to use such energy level bending effects to create a junction between a single material in different environments (Figure 5). Consider a bilayer device,

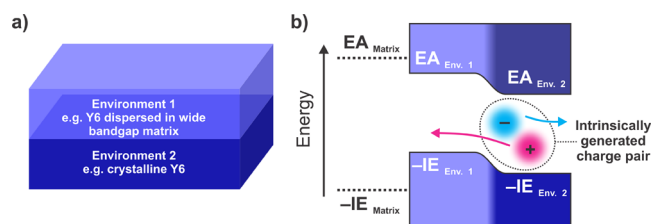


Figure 5. Electrostatic-polarization (EP) junction. (a) Device architecture. (b) Energy level diagram.

composed of a layer of neat Y6, and a second layer where Y6 is mixed with another material, such as an inert polymer matrix. It is important that the concentration of the second layer is high enough for charge percolation pathways via Y6 to both electrodes to exist.⁶² In this device, photogenerated CT states/charges are only transported by Y6 molecules, but the charges separate from one another due to the electric field, with the direction of charge flow defined by the energy level bending. For ease of reference, we refer to this device as an electrostatic-polarization (EP) junction.

This idea is closely related to single component solar cells composed of crystallites with different molecular packing orientations relative to the substrate. Such OPVs have been shown to exhibit impressive performance for excitonic materials because excitons can dissociate at interfaces between differently oriented domains which have different energy levels.⁶³ Charge generation in these excitonic systems requires that either the exciton diffusion length, or the donor–acceptor FRET radius be large enough for excitons to reach the interfacial region. This means that the layer thicknesses are typically limited to tens of nanometers, since exciton diffusion lengths are <50 nm for most materials, including FREAs.^{7,8} By contrast, exciton dissociation is intrinsic in an EP junction, and the field is used to sweep the resulting charges across the interface between two environments. The required energy level shifts can be induced via environmental changes (as suggested

above), by differences in molecular orientation between the two layers, or by other mechanisms. An EP junction is therefore limited by the diffusion length of the CT state or charge and the strength/extent of the electric field, rather than the (Frenkel) exciton diffusion length.

A key advantage of the EP junction is the bilayer architecture, and simplified role of the second active layer component (i.e., the matrix material in Figure 5), if present, which does not need to be involved in charge transfer for either electrons or holes. This means that a wide range of materials are potentially suitable, and potentially that the energy levels of the two layers can be more finely tuned. It is still preferable that the second component absorbs light, so that high energy photons can be absorbed, followed by energy transfer to Y6 and subsequent charge generation. An exciting variant of this idea would be to employ a wide bandgap material capable of singlet fission, followed by triplet injection into Y6, to provide triplet excitons that might dissociate under the influence of the interfacial field. Finally, we also note that EP junctions may be particularly suitable for organic photodetectors, where the energy level differences and bilayer architecture would be expected to lead to low dark current—a key figure of merit for photodetectors.⁶⁴

CONCLUSION

Y6 is an exceptional material with intriguing fundamental photophysics at the heart of its technological significance. A growing body of evidence shows that Y6 forms electron–hole charge pairs intrinsically, without the need for a second material. This development is important because movement of charges can be engineered much more easily than that of Frenkel excitons. We suggest molecular doping, kinetic tuning of charge formation/recombination, and electrostatic-polarization junctions as interesting avenues for exploration. With intrinsic exciton dissociation, the most important step toward moving past the bulk heterojunction has been taken, because electric fields and doping techniques can now be used as tools of persuasion for photoexcitations in single component organic materials.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

P.A.H., M.B.P., and J.M.H. acknowledge the support of the MacDiarmid Institute and the Marsden Fund. M.B.P. acknowledges the support of Royal Society Te Apārangi of New Zealand, and the Royal Society (UK) for funding.

ABBREVIATIONS

ADA, acceptor–donor–acceptor; ADA'DA, acceptor 1–donor–acceptor 2–donor–acceptor 1; BHJ, bulk heterojunction; CC-TT, core–core terminal-terminal; CT, charge transfer; EA, electron affinity; EP junction, electrostatic-polarization junction; FE, Frenkel exciton; FREA, fused-ring electron acceptor; HOMO, highest occupied molecular orbital; IE, ionization energy; lowest unoccupied molecular orbital; OPV, organic photovoltaic; PCE, power conversion efficiency; PL, photoluminescence; PLQE, photoluminescence quantum efficiency; TA spectroscopy, transient absorption spectroscopy

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