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Towards the Organic Double Heterojunction Solar Cell

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ABSTRACT

A perspective on the operating principles of organic bulk heterojunction solar cells is outlined and used to suggest an alternative device configuration, employing two type II semiconductor heterojunctions in series. Guiding principles to the implementation of this configuration, called a double heterojunction, are summarized. Assuming an exciton binding energy of 0.3 eV or less, results in a maximum achievable power conversion efficiency of well over 25%. Achieving a high efficiency organic double heterojunction requires a specific energy level alignment, charge separation in the absence of driving forces, high phase purity and excellent diode quality. Fully conjugated triblock polymers of the form $[D_1\text{-}A_1]\text{-}[D_1\text{-}A_2]\text{-}[D_2\text{-}A_2]$ appear to be a system that can fulfill these requirements. Going forward, the primary challenge is the identification and development of synthetically tractable materials which have the necessary properties.

MAIN

The nearly limitless variety of organic synthesis is a major part of the fundamental interest in organic electronics and organic solar cells in particular. This aspect cannot be overstated, the truly enormous parameter space that these materials occupy makes it difficult to accurately describe fundamental limitations and identify unexpected opportunities. More specifically, this space is not easily characterized by a few simple parameters because it exists in an incredibly high number of dimensions. Optimization in high dimensional space presents a challenge because the space is not simply connected in the way that common intuition suggests. One way to visualize high dimensional space is the Cayley tree, or Bethe lattice[1] pictured in figure 1. Overlaid on this figure is a false-color representation of a parameter one wishes to optimize. When the local maximum is placed at the center of the figure, it gives the misleading impression that this region of space is easily approached from any direction. Translating the center of the local maximum towards the edge provides a slightly more faithful representation. As the number of intermediate steps increases, the number of possible alternatives increases as 3^n (in this particular example of the simplest possible tree). In this example, most of these alternatives, including the points between *a* and the desirable region of parameter space are "dead," i.e., do not exhibit the desired property to a degree sufficient to guide an empirical optimization scheme. This description of the broader optimization problem puts into context an empirical fact which any materials chemist knows. Making highly novel materials with good performance is difficult, especially with the first few compounds of the series. This article will introduce an underexplored organic solar cell configuration, termed a double heterojunction, and will describe computational efforts to identify fertile regions of parameter space. The discussion will be developed from a brief review of bulk heterojunction solar cells as a means of highlighting the underlying assumptions and developing the necessary language to discuss the double heterojunction configuration.
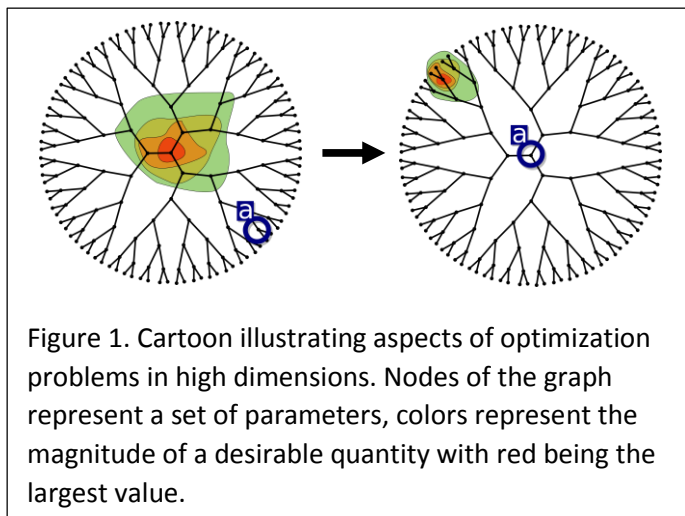
Despite the rather alarming challenges posed by the breadth of parameter space, the development of organic solar cell materials has been highly successful.[2] The first organic solar cell was constructed from a bilayer heterojunction.[3] The importance of a semiconductor heterojunction in organic photovoltaics results from the nature of the molecular excited states. In particular, the primary photoexcitations are most easily thought of as excitons, bound electron-hole pairs that are lower in energy than the charge separated state by an amount called the exciton binding energy (E_B).[4] This binding energy prevents all but a small fraction of excitons from being converted directly to charge carriers in a single component polymer or molecular film. Excitons are formed upon the absorption of solar radiation and must diffuse within the active layer of an organic photovoltaic until reaching an interface where charge separation can occur.[5]

The lifetime of the exciton and its diffusivity can be used to parameterize the relevant length scale for this process, called the exciton diffusion length. In disordered molecular and polymeric films, this length scale is ~20 nm,[6] which also appears to be the relevant length scale regardless of transient delocalization effects.[7] In highly ordered films, molecular excitons can become delocalized over much greater distances, with observed delocalization lengths reaching nearly 1 micron.[8] However, solar cell designs that take full advantage of this property have yet to be developed. In contrast, organic solar cell materials often employ the bulk heterojunction whereby nanoscale phase separation of creates an interpenetrating network of electron donating (p-type) and electron accepting (n-type) materials.[9] This nanoscale phase separation is aided by processing techniques including solvent additives.[10]

Providing excitons ample opportunity to reach the heterojunction interface is a necessary, but not sufficient condition for achieving high power conversion efficiency (η); efficient charge separation is also required. The key to efficient charge separation is defeating the charge-transfer exciton, a bound electron-hole pair across an organic semiconductor heterojunction.[11] Several groups have demonstrated the importance of ultrafast electron transfer in allowing charges to travel a sufficient distance from one another to circumvent the binding energy of this species.[12] This factor, not large energy offsets at the heterojunction interface appear to be the more fundamentally important aspect of efficient charge generation, an idea underscored by recent results with non-fullerene acceptors.[2c, 2e, 13]

In addition to the efficient separation of excitons, mobile electrons and holes must make their way to their respective electrodes in order to produce photocurrent. Several recombination mechanisms must be avoided, two of particular importance are associated with charge trapping. Trapped charges can recombining with the opposite charge[14] or causing the recombination of excitons through exciton-charge annihilation.[15] The latter mechanism is often overlooked because it does not affect solar cell fill factor, but instead manifests as a lower than expected solar cell current at short circuit conditions (J_{SC}). As a parenthetical aside, the term "free charges" should be avoided in the discussion of organic photovoltaic materials because it implies the Bloch waves typical of metals and crystalline inorganic semiconductors. The term "mobile charges" is preferable as it avoids this implication.

Another important charge recombination mechanism that is necessary to avoid is the formation of low energy triplet excitons. This can happen via a charge transfer exciton intermediate. If these species are lower in energy than the charge separated state, a significantly increased bimolecular recombination rate will be observed.[16] Although the triplet and singlet charge transfer excitons have a similar binding energy, the triplet charge transfer exciton serves as an intermediate to the formation of

Figure 1. Cartoon illustrating aspects of optimization problems in high dimensions. Nodes of the graph represent a set of parameters, colors represent the magnitude of a desirable quantity with red being the largest value.

a triplet exciton, presumably through a Dexter energy transfer mechanism. Because the triplet excited state is lower in energy than the singlet excited state that participates in charge transfer reactions, the triplet state is not likely to be converted back to mobile charges and recombines through radiative or non-radiative means. Fortunately, high performance organic photovoltaic devices frequently exhibit radically reduced bimolecular recombination rates,[17] indicating that some aspect of organic photovoltaic devices actively inhibit this pathway.

The fundamental challenge to the creation of organic photovoltaic devices with efficiencies approaching that of silicon is improving the open-circuit voltage (V_{OC}). This is accomplished by reducing voltage losses in the device.[13b, 18] The plain fact is that organic photovoltaic devices regularly achieve >90% quantum efficiency,[19] meaning that dramatic improvements to charge extraction are not possible and radical departures from conventional bulk heterojunction architectures in pursuit of higher J_{SC} appear misguided. Instead, approaches to increase photocurrent by increasing cell thickness,[17] or creating tandem cells,[2b, 20] are more fruitful approaches.

The Scharber equation[21] specifies an empirical relationship between the optical gap of an organic solar cell and the maximum Voc that can be achieved. This relationship places limits on the maximum efficiency of any solar cell that obeys it to around 15%.[22] Alternatively, recent analyses of solar cells based on non-fullerene acceptors indicate that efficiencies closer to 20% are possible.[18] A key aspect to understanding device efficiencies is quantifying energy levels and their alignment. From a fundamental/theoretical perspective, energy levels can be described in terms of ionization potentials and electron affinities, following the description of Zhu,[23] hereafter referred to as XYZ diagrams. This description is preferable to Jablonski diagrams because the latter obfuscates the importance of material specific energy levels and their relationship in the heterojunction. While XYZ diagrams appear similar to the "zero order" diagram describing the HOMO/LUMO energies of a heterojunction cell, they are superior because they rigorously describes excitonic energy levels in a way that makes it possible to predict the enthalpic favorability of a specific charge transfer reaction.

Figure 2 shows an XYZ diagram of a bulk hetrojunction material. The diagram is labeled in terms of ionization potentials (IP) and electron affinities (EA) which rigorously describe the energy required to remove or add an electron to a state, respectively. By convention, both energies are given as positive quantities. The states are also labeled according to whether they belong to the ground state (S_0) a singlet excited state (S_1) or a triplet excited state (T_3). Lastly, each state can be further labeled to differentiate which component of the cell it originates from, the electron donating (P) electron accepting (N) or the charge transfer state (CT) which arises at the heterojunction interface.

An unfortunate challenge with the conventional nomenclature exists. The term "donor" can refer to either the electron donating component of a solar cell (for example, P3HT or PCDTBT) or "donor" can refer to the electron rich subunit of a copolymer (for example, carbazole). To simplify the discussion, and maintain clarity in regards to the two different senses of "donor" and "acceptor," I will use the term "p-type" to refer to the electron donating, hole transporting component of the cell, and reserve "donor" for the electron rich subunit of the copolymer. Similarly, I will use "n-type" for the electron accepting and electron transporting component of the cell, and use "acceptor" for the electron poor subunit of the copolymer. It must be admitted that referring to "n-type" and "p-type" materials outside the context of doped inorganic semiconductors is a colloquial usage, put forward for the purpose of clarifying the discussion.
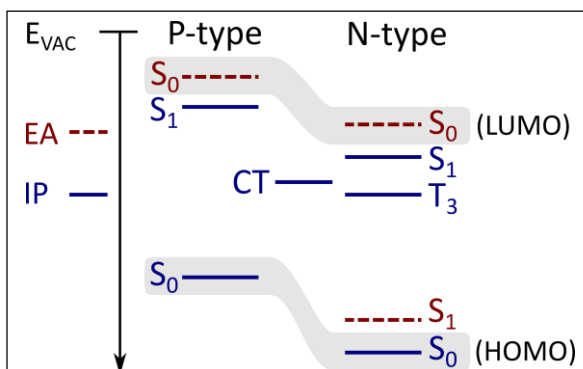

Figure 2. Diagram showing ionization potentials (IP) and electron affinities (EA) of key energy levels of an organic solar cell. Adapted from (28)

A few states and processes from fig. 2 deserve further comment. The ground state of the system is characterized by its HOMO (IP_{S0}) and LUMO (EA_{S0}) levels. The optical gap (E_{OPT}) can be represented either in terms of ionization energy or electron affinity. For the former, it is given by the difference between the ionization energy of the ground state and the deepest lying singlet exciton state ($E_{OPT} = IP_{S1} - IP_{S0}$). In terms of electron affinities, the optical gap is the difference between the unoccupied LUMO and the singlet state ($E_{OPT} = EA_{S0} - EA_{S1}$). The exciton binding energy is given in terms of the electron affinity of the lowest unoccupied state (LUMO) and the ionization potential of the lowest excitonic level ($E_B = EA_{S0} - IP_{S1}$). Alternatively, the exciton binding energy can be given in terms of the highest electron affinity of the exciton and the ionization potential of the ground state ($E_B = EA_{S1} - IP_{S0}$). Finally, the enthalpic favorability of an electron transfer reaction (often called the driving force) from the p-type to the n-type material can be assessed by the difference in energy between the ionization potential of the excitonic state and the electron affinity of the state into which the electron is transferred.

$$\Delta E_e(P - N) = IP_{S1}(P) - EA_{S0}(N) \tag{1}$$

In a similar manner, the enthalpic driving force for hole transfer is as follows:

$$\Delta E_h(P - N) = IP_{S0}(P) - EA_{S1}(N) \tag{2}$$

As in eq. 1, the parentheses indicate the cell component from which the state is primarily located. In short, XYZ diagrams provide a straightforward way to describe the energy of important processes in solar cell function, making it well worth the effort necessary to become comfortable with the symbols and terminology.

Improving device efficiency has provided an excellent impetus for fundamental mechanistic inquiry, however important practical challenges associated with organic bulk heterojunction solar cells are receiving much needed attention. For example, a push towards lower cost feedstocks and away from Stille coupling reactions is bringing material production costs into the range of industrial feasibility.[24] In addition, scale-up of organic solar cell production also requires a move away from chlorinated solvents during casting.[25] A related issue, and one whose importance cannot be overstated, is robustness to variations in film formation conditions. A process developed on a lab-scale blade coating machine is not straightforward to implement in to a roll to roll printing press. The challenge is caused by the morphological requirements of a high efficiency material, a difficult to obtain nanoscale morphology that also hinders long-timescale device stability.[26] While progress on this problem has been made, this is a particularly difficult challenge for the traditional solution cast two-component bulk heterojunction to address. As a result, a one-component active layer whose optimal morphology is thermodynamically favored is highly desirable. This point cannot be overstated. A one-component organic photovoltaic material which reliably adopts the optimum morphology to maximize solar cell efficiency is an enormously important goal.

To summarize the introductory review above, the primary factor limiting the efficiency of conventional organic solar cells is a low Voc. As a consequence of the binding energy of electrons and holes, organic heterojunctions require an energy offset between the HOMO and LUMO levels at the heterojunction interface to exhibit adequate diode behavior and separate excitons. Unfortunately, the energy offset reduces V_{OC} and limits single junction cell efficiency to far less than a comparable inorganic counterpart. This limitation appears innate to all variations of the standard two component organic bulk heterojunction. Although the bulk heterojunction is a highly successful configuration and is likely to see further improvements, it is likely not the best possible configuration given the enormous diversity of organic materials. In a pair of papers, my group has been developing an alternative configuration through a series of computational studies, hereafter referred to as a double heterojunction. A summary of the key findings of these studies comprises the remainder of the article.

The concept of the double heterojunction solar cell can be developed from two key observations. Charge transfer reactions can be efficient with a minimal driving force. Second, the open circuit voltage is limited by the electronic gap of the lowest energy state which serves as the precursor to voltage-driven charge carrier recombination. In

other words, detailed balance considerations determine V_{OC}.[27] In the bulk heterojunction, this precursor state is the charge transfer exciton, making the electronic gap of the charge transfer exciton the state which determines V_{OC}. While the electronic gap of the charge transfer exciton is a purely theoretical quantity, it can be used to specify an upper bound on the efficiency of the bulk heterojunction. Given a charge transfer exciton binding energy of 0.3 eV, an estimate of 16% is obtained.[28]
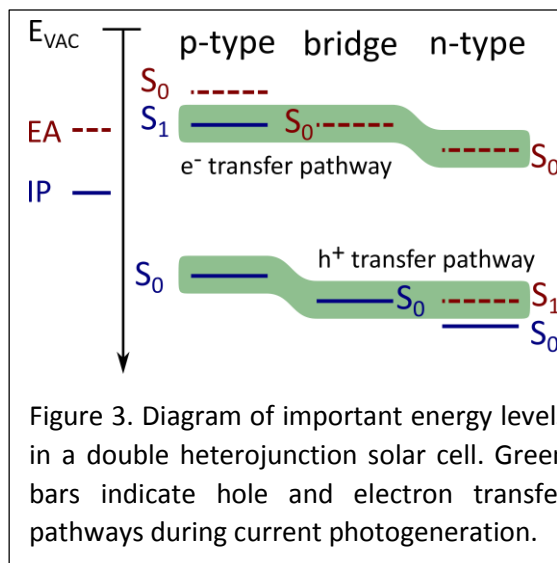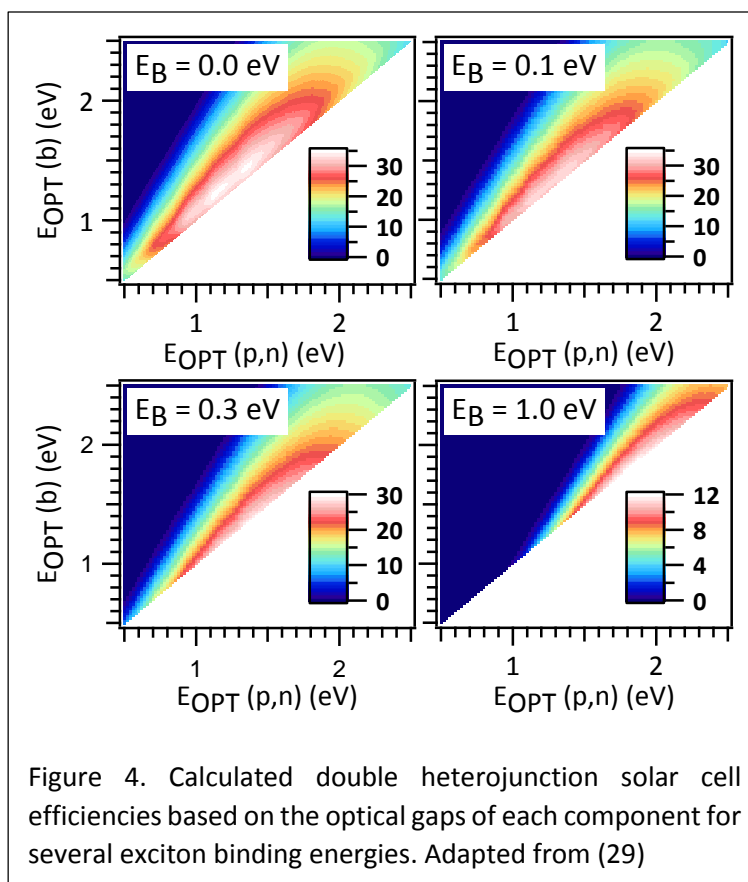

Figure 3. Diagram of important energy levels in a double heterojunction solar cell. Green bars indicate hole and electron transfer pathways during current photogeneration.

The key concept of the double heterojunction is to decrease the binding energy of the charge transfer exciton by spatially separating mobile electrons and holes with a subunit called the bridge. In this case, V_{OC} is determined by the electronic gap of the bridge. Because minimal driving force is required for charge transfer, this allows the open circuit voltage to be increased to the lowest optical gap. Thus, the Shockley-Quiessar limit[29] can be approached. The concept of a donor-bridge-acceptor material is not entirely new, charge transfer in covalently linked molecular dyads and triads is a well-established field of research.[30] However, leveraging the double heterojunction to its maximum utility requires a number of special considerations which heretofore have not been addressed. This also differentiates the double heterojunction from a structure referred to as an energy cascade or more generally, a ternary blend[2a, 31] which creates a bulk heterojunction from three intimately mixed components. This line of investigation, while interesting in its own right, does not directly address the issue of increasing cell V_{OC}. As we will see, improving cell voltage requires stringent conditions on the elimination of recombination pathways that do not include the bridge.

The term double heterojunction in this context means *two type II semiconductor junctions in series*. This could, in theory, be accomplished by a fully conjugated triblock polymer. Full conjugation is important because the inclusion of aliphatic chains between the blocks creates insulating layers between the type II heterojunctions. Thus, the material should no longer be expected to perform like a semiconductor heterojunction. A double heterojunction could, in theory, be created with small molecule or ternary blend. Obtaining the full benefit of the double heterojunction requires phase purity on ppm levels, which points toward a block polymer approach. This will discussed in the context of direct p-type to n-type contacts.

An XYZ diagram of a double heterojunction solar cell is shown in fig 3. The arrangement of type II semiconductor junctions proceeds from p-type to bridge then bridge to n-type. Ensuring enthalpic favorability for charge transfer reactions into the bridge requires exciton binding energies to be accounted for. In symbols this is represented as follows:

$$\Delta E_e(P - B) \geq 0 \qquad\qquad (3)$$

$$\Delta E_h(B - N) \geq 0 \qquad\qquad (4)$$

The next step in device function is charge transfer out of the bridge. The important fundamental question, yet to be answered, is whether the exciton binding energy plays an important role in the charge transfer reaction out of the bridge. I will focus on the best possible scenario, where the electron transfer reaction from the bridge into the n-type section proceeds when $EA_{S0}(B) - EA_{S0}(N) \geq 0$ and hole transfer from the bridge to the p-type section proceeds when $IP_{S0}(B) - IP_{S0}(P) \geq 0$. This likely requires that the fundamental charge transfer reactions are ultrafast, another rationale for the fully conjugated block polymer approach.

Provided that electron transfer reactions proceed across the bridge with unit efficiency, detailed balance considerations can be used in a straightforward manner to calculate the upper limits on device efficiency.[28] Maximum efficiencies are obtained when the lower bounds of eq. 3 and eq. 4 are saturated. That is, the case in which the enthalpic driving force for the charge transfer reactions are minimized. Every millielectron volt used for electron transfer from donor to bridge or hole transfer from acceptor to bridge is taken at the expense of V_{OC}. In order to reduce the optimization problem into 2D where it can be visualized, we set the optical gap of the donor and acceptor blocks equal to one another. This configuration was found to maximize efficiency when unit absorption above the optical gap is assumed. Fig. 4 shows the resulting 2D optimization surface relating the n-type and p-type optical gap to the optical gap of the bridge. The power conversion efficiency for a variety of exciton binding energies is shown.

Figure 4. Calculated double heterojunction solar cell efficiencies based on the optical gaps of each component for several exciton binding energies. Adapted from (29)

As fig. 4 demonstrates, the maximum power conversion efficiency of a double heterojunction cell is predicted to remain at or above 30% for exciton binding energies lower than or equal to 0.3 eV, nearly double that obtained from a similar bulk heterojunction. The reason for the improved efficiency relative to the bulk heterojunction is a direct result of improved V_{OC}. In turn, this requires that all recombination occur through the bridge with the V_{OC} being limited by the *electronic* gap of the bridge, that is $E_{ELEC}(B) = EA_{S0}(B) - IP_{S0}(B)$. Contrast this with the bulk heterojunction where the charge transfer states limit V_{OC}, which is inevitably lower in energy than the optical gap of either material.

The shape of the optimization surfaces in fig. 4 demonstrate a few design heuristics. The first is that the each step of the charge transfer reaction must be enthalpically favorable. This consideration limits the design space to the upper left half of the figure. The second heuristic is that lower exciton binding energies are favorable for higher solar cell efficiencies, suggesting that "push-pull" or "donor-acceptor" polymers are preferable to obtaining high efficiency cells. These materials tend to have lower exciton binding energies. The third, and more subtle aspect, is that the maximum efficiency is found when the electronic gap of the bridge is ~ 2 k_BT greater than the optical gaps of the p-type and n-type sections. A way to think of this result is that a slight energy offset between $EA_{S0}(B)$ and $EA_{S0}(N)$ helps to prevent electrons from entering the bridge from the acceptor side, improving the quality of the diode. Similarly, a slight offset between $IP_{S0}(B)$ and $IP_{S0}(P)$ helps to reduce hole recombination currents. Further increases in the offsets at the bridge may improve the diode characteristics, but would likely cause extremely large carrier densities to build in the p-type and n-type sections of the cell near V_{OC}. In this case, the absorption characteristics of the polymers would be dramatically altered due to polaron formation.[32] In this case p-type and n-type sections would no longer functions as a semiconductors, and the photocurrent is would drop precipitously. This consideration is necessary to obtain realistic predictions of cell efficiency.
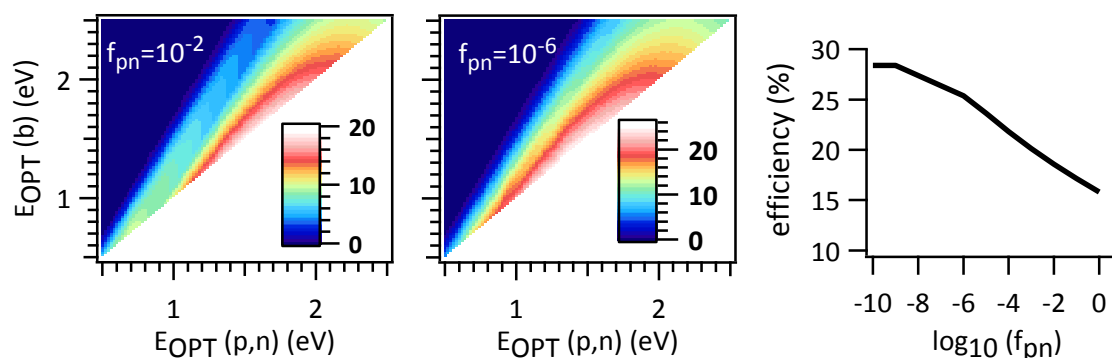
Figure 5. Effect of phase purity on solar cell efficiency. Left, center: power conversion efficiency versus the optical gaps of solar cell components for different levels of phase purity, expressed in terms of the probability of direct p-type to n-type contacts. Right, maximum achievable cell efficiency as a function of the probability of direct p-type to n-type contacts. Adapted from (29)

Morphology is likely to be an important consideration for the double heterojunction. With the most important considerations being more easily expressed in terms of structures and circumstances to avoid. Columnar stacks are a common morphology in the few examples of materials based on donor-bridge-acceptor small molecules.[30a, 30b] To aid in self-assembly, the molecules are surrounded by insulating aliphatic chains making the charge transport limited to one dimension (along the stack). Unfortunately, columnar stacks that rely on non-covalent interactions are an extremely poor morphology for charge transport. A single defect in the column destroys charge transport.[1] As a result, it is difficult to draw broad conclusions from poorly performing solar cells that rely on this motif. In contrast, the block polymer approach to a double heterojunction cell takes advantage of covalent interactions to enable 1-D charge transport and non-covalent interactions to move charges between chains. This increases the dimensionality of the transport, making the system tremendously more defect tolerant.

Phase purity is an important consideration in a double heterojunction cell. As discussed above, improvements in V_{OC} arise from the energy alignment between the bridge and the p-type or n-type sections. This improvement implicitly requires that all recombination currents flow across the bridge, which in turn requires that there are no direct contacts between the p-type and n-type sections. Lapses in phase purity act as short circuits, parallel circuit components with considerably worse diode performance characteristics owing to the presence of charge transfer excitons at the interface between p-type and n-type sections. Figure 5 shows the calculated effect of phase purity on the power conversion efficiency of a double heterojunction cell, demonstrating that high phase purities are required to obtain the full benefit of the double heterojunction configuration. The effect of phase purity also explains why a small increase in cell efficiency could be observed from an energy cascade or three component system. However, phase purity greater than parts per thousand levels is unlikely to be achieved in such systems, leaving much of the possible benefit out of reach for ternary blends.

The effect also suggests the importance of a block polymer approach. In the ideal case of long n-type and p-type sections, perfect phase purity is the thermodynamically favored state.[33] The importance of this cannot be overstated, as it represents a major advantage of the double heterojunction concept relative to the bulk heterojunction. Phase separation in rod-rod block copolymers has been reported by several groups.[34] One should therefore expect that a well-designed system would be highly stable and relatively insensitive to processing conditions. The self-assembly of fully conjugated block polymers is a topic of current interest.[35] This makes it difficult to comment more generally, except to say that a double heterojunction cell based on block polymers

represents a possibility for a solution processable, single-component material that is highly robust to processing conditions with a power conversion efficiency well over 20%.

The design considerations for a double heterojunction cell presented thus far are expressed abstractly in terms of energy alignments. However, designing a synthetic target requires considerably more specific information regarding useful structural motifs. One common motif in semiconducting molecules is the donor-acceptor system, with the general formula of (D-A) where in D represents an electron rich aromatic group, like carbazole or fluorene and A represents an electron poor aromatic group like benzothiodiazole or napthalene diimide. Because a large number of such groups are known, it would be useful to evaluate the entire class of donor-acceptor block polymers using a low level of theory rather than evaluating specific target molecules in order to provide a starting point for molecular design. Once a unique molecule has been identified, its properties could be evaluated at a higher level of theory. Therefore, we performed a series of self-consistent field calculations on a triblock system of the form $(D_1-A_1)-(D_1-A_2)-(D_2-A_2)$ where D_1 and D_2 are differing donor groups.[36]

When thinking of an appropriate synthetic target, the primary consideration must be the correct positioning of the energy levels. The first question to address is whether the energy levels of the n-type and p-type sections of the polymer can be tuned independently. In practice, this should be expected. In theory, this requires some degree of electron localization, necessitating a self-consistent field approach rather than a simple Huckel matrix diagonalization. Fig. 6 shows the calculated energy levels of the p-type,
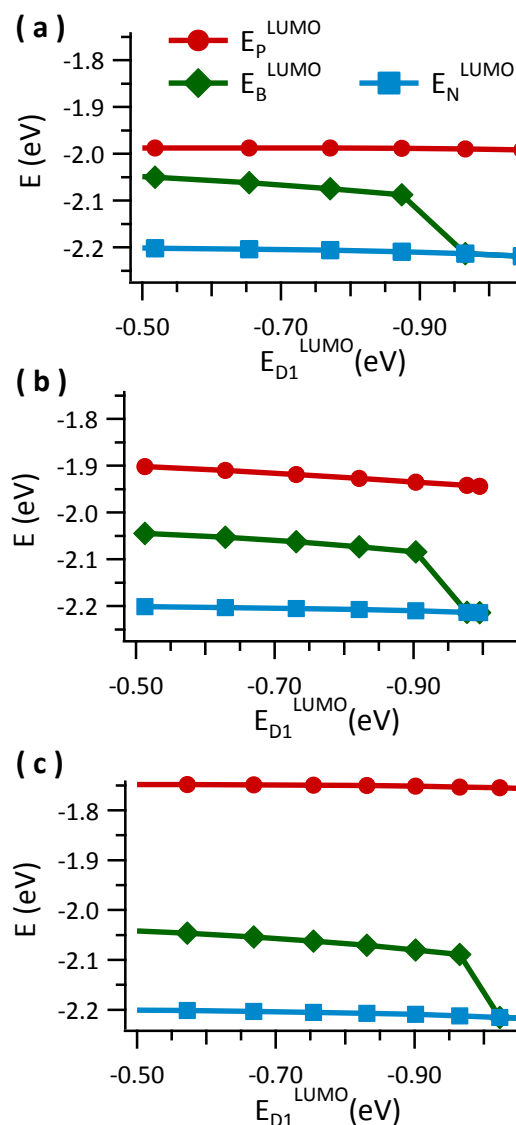

Figure 6. Energy levels of each component of a double heterojunction material with different compositions as described in the text. Panels a,b,c represent different energy offsets between p-type and n-type sections. Reproduced from (36)

bridge, and n-type sections of a model system of the form $(D_1-A_1)_4-(D_1-A_2)_2-(D_2-A_2)_4$. The p-type and n-type sections are represented as $(D_1-A_1)_4$ and $(D_2-A_2)_4$, respectively. A tetramer was found to sufficiently approximate the energy levels of arbitrarily long systems.

Fig. 6 shows how the energy of each component changes in response to a change in the energy of D_1. Changing this energy while leaving all other components unchanged will alter the energy of the p-type section. This effect was accounted for by altering A_1 such that the energy levels the tetramer would remain constant. This allows one to focus on the effect of coupling the different sections of the block polymer. As one would intuitively expect, the energy of the n-type and p-type sections are largely unchanged, meaning that in a block polymer, these sections can be tuned independently of one another.

The ideal case for the electron transfer pathway is described in terms of the energy levels of the bridge as follows: $IP_{S1}(P) = EA_{S0}(B)$ and $EA_{S0}(B) = EA_{S0}(N) + 0.05 \, eV$ at room temperature. Fig. 6 shows the energy levels of the bridge and their alignment with the n-type and p-type sections. Importantly, the energy of the bridge appears to pin to 0.15 eV above the n-type section. Identical results were obtained for the hole transfer pathway, with energy offsets varying from 0.10 to 0.15 eV at the p-type/bridge interface. Forming a double heterojunction as described above yields an energy offset compatible with favorable charge transfer pathways. Although a the bridge pins slightly above the ideal position from a device efficiency perspective, the extra 0.1 eV provides an additional tolerance factor which is highly desirable from the perspective of an initial synthesis. In summary, a bridge with appropriate energy level alignments for a double heterojunction can be formed with the electron donating portion of the p-type section and the electron accepting portion of the n-type section.

Block polymer systems without a bridge have been synthesized and tend to have poor fill factors, presumably because of large recombination currents and poor diode quality.[35d] Another important consideration in determining a synthetic target for a double heterojunction material is the length of the bridge necessary to obtain high quality diode behavior. There appears to be two main considerations. The first is to increase the separation of electron and hole to a degree sufficient to lower the binding energy of the charge transfer exciton to near or below thermal energy. The second is to hinder recombination via tunneling through the bridge. As a means of estimating both, the spatial overlap of electron and hole probability density as function of bridge length was calculated. Figure 7 shows the predictable result, that direct overlap is large for short bridge lengths and decreases as the bridge is made longer. In addition, the overlap also decreases with increasing offsets between p-type and n-type sections.

The results of self-consistent field calculations suggest that a triblock polymer of the type $(D_1\text{-}A_1)\text{-}(D_1\text{-}A_2)\text{-}(D_2\text{-}A_2)$ produces the energy level alignment necessary for a high performance double heterojunction material. In addition, the results of figure 7 show that a bridge of at least a few repeat units is necessary to inhibit recombination. However, the bridge should be considered the shortest section of the system. The cell should be much less sensitive to the length of the p-type and n-type sections as well as their relative ratios so long as the system shows good phase separation.
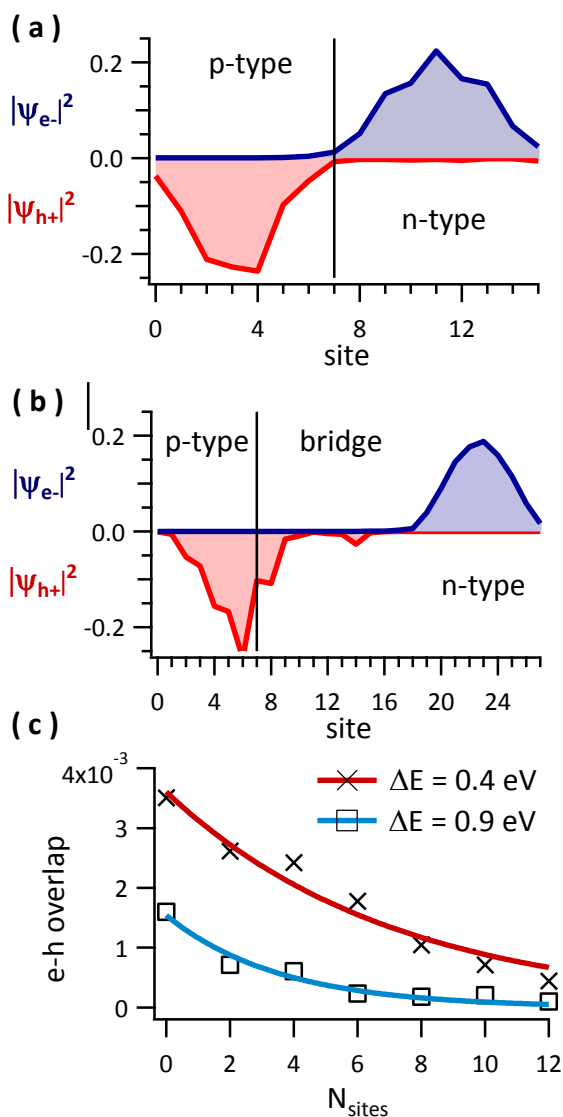

Figure 7. Lowest-energy excited states. (a) Offset of 0.4 eV without a bridge section. (b) Offset of 0.9 eV with bridge of 6 monomer units (12 sites). Red illustrates the hole density, and blue illustrates the electron density. (c) Spatial overlap between the electron and hole density for a series of double heterojunction systems. Reproduced from ref (36)

While these results point to a general class of materials, the complexity from a synthetic perspective remains high. With that in mind, it would be preferable to design a diblock system capable of functioning as a double heterojunction. One possibility is to synthesize the p-type and n-type polymers separately, forming the bridge from end groups that are bonded together in the final synthetic step. Such an approach would not allow for long bridge lengths, but direct electron-hole overlap across the bridge could be reduced through a variety of means including the induction of large dihedral angles in the bridge through steric effects. Computational studies to demonstrate the potential of this approach are ongoing.

The following are suggestions for researchers interested in identifying an exact synthetic target using the results presented here: (1) using figure 4 and an estimate of the exciton binding energy, determine the optical gap of the p-type polymer. This can be used to identify a target compound. (2) Determine a candidate n-type polymer with a very similar optical gap as the p-type polymer. The HOMO and LUMO levels of the n-type polymer should be offset by an amount slightly larger than the assumed exciton binding energy. (3) Use the structure of the p-type and n-type candidates to develop a bridge candidate using the donor unit of the p-type polymer and the acceptor unit of the n-type polymer as describe above. (4) The reasonableness of the target (i.e. each block should have close to the desired energy levels) should be assessed by DFT calculations and/or synthesizing the individual components. The development of synthetic methods for creating fully conjugated block polymers is a highly sought after research goal in this context.

SUMMARY

Based on the computational estimates which assume an exciton binding energy of 0.3 eV, conventional single-junction organic bulk heterojunction cells appear limited to a power conversion efficiency of close to 15%. However, this is not a fundamental limit of the materials, but rather the device configuration. Using the highly developed current mechanistic understanding, we suggested an alternative configuration, employing two type II semiconductor heterojunctions in series, called a double heterojunction. Detailed balance calculations suggest that this configuration could reach power conversion efficiencies just under 30%. However, a number of conditions must be met in order to achieve superior performance relative to the highly optimized bulk heterojunction configuration including proper energy alignment, phase purity, and an avoidance of 1-D columnar structures. According to a set of self-consistent field calculations, this can be accomplished using a triblock system of the general structure $[D_1-A_1]-[D_1-A_2]-[D_2-A_2]$. Limiting charge recombination through the central block is an important challenge, as is the development of more synthetically tractable structures.
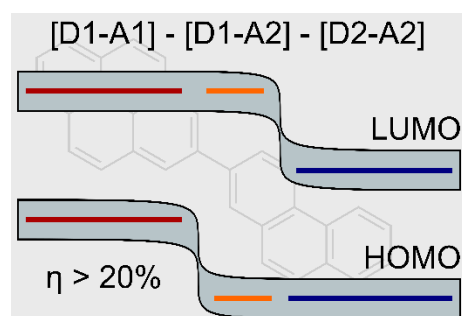
REFERENCES

[1]   D. Stauffer, A. Aharony, *Introduction To Percolation Theory*, Taylor & Francis, **1994**.

[2]   aZ. Xiao, X. Jia, L. Ding, *Science Bulletin* **2017**, *62*, 1562-1564; bL. Meng, Y. Zhang, X. Wan, C. Li, X. Zhang, Y. Wang, X. Ke, Z. Xiao, L. Ding, R. Xia, H.-L. Yip, Y. Cao, Y. Chen, *Science* **2018**; cS. S. Chen, Y. H. Liu, L. Zhang, P. C. Y. Chow, Z. Wang, G. Y. Zhang, W. Ma, H. Yan, *J. Am. Chem. Soc.* **2017**, *139*, 6298-6301; dW. C. Zhao, S. S. Li, H. F. Yao, S. Q. Zhang, Y. Zhang, B. Yang, J. H. Hou, *J. Am. Chem. Soc.* **2017**, *139*, 7148-7151; eP. Cheng, M. Y. Zhang, T. K. Lau, Y. Wu, B. Y. Jia, J. Y. Wang, C. Q. Yan, M. Qin, X. H. Lu, X. W. Zhan, *Adv. Mater.* **2017**, *29*.

[3]   C. W. Tang, *Applied Physics Letters* **1986**, *48*, 183-185.

[4]   J.-L. Bredas, *Materials Horizons* **2014**, *1*, 17-19.

[5]   O. V. Mikhnenko, P. W. M. Blom, T. Q. Nguyen, *Energy Environ. Sci.* **2015**, *8*, 1867-1888.

[6]   aP. E. Shaw, A. Ruseckas, I. D. W. Samuel, *Adv. Mater.* **2008**, *20*, 3516-3520; bA. Haugeneder, M. Neges, C. Kallinger, W. Spirkl, U. Lemmer, J. Feldmann, U. Scherf, E. Harth, A. Gugel, K. Mullen, *Physical Review B* **1999**, *59*, 15346-15351.

[7]   aL. G. Kaake, D. Moses, A. J. Heeger, *Physical Review B* **2015**, *91*, 075436; bL. G. Kaake, C. Zhong, J. A. Love, I. Nagao, G. C. Bazan, T.-Q. Nguyen, F. Huang, Y. Cao, D. Moses, A. J. Heeger, *The Journal of Physical*

Chemistry Letters **2014**, *5*, 2000-2006; cL. G. Kaake, J. J. Jasieniak, R. C. Bakus, G. C. Welch, D. Moses, G. C. Bazan, A. J. Heeger, *J. Am. Chem. Soc.* **2012**, *134*, 19828-19838.

[8]   F. Dubin, R. Melet, T. Barisien, R. Grousson, L. Legrand, M. Schott, V. Voliotis, *Nat. Phys.* **2006**, *2*, 32-35.

[9]   G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, *Science* **1995**, *270*, 1789-1791.

[10]   J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger, G. C. Bazan, *Nat. Mater.* **2007**, *6*, 497-500.

[11]   aM. A. Loi, S. Toffanin, M. Muccini, M. Forster, U. Scherf, M. Scharber, *Advanced Functional Materials* **2007**, *17*, 2111-2116; bA. C. Morteani, P. Sreearunothai, L. M. Herz, R. H. Friend, C. Silva, *Phys Rev Lett* **2004**, *92*, 247402.

[12]   aQ. X. Yang, M. Muntwiler, X. Y. Zhu, *Physical Review B* **2009**, *80*, 115214; bA. E. Jailaubekov, A. P. Willard, J. R. Tritsch, W. L. Chan, N. Sai, R. Gearba, L. G. Kaake, K. J. Williams, K. Leung, P. J. Rossky, X. Y. Zhu, *Nat. Mater.* **2013**, *12*, 66-73; cY. Song, S. N. Clafton, R. D. Pensack, T. W. Kee, G. D. Scholes, *Nat Commun* **2014**, *5*, 4933; dS. Gélinas, A. Rao, A. Kumar, S. L. Smith, A. W. Chin, J. Clark, T. S. van der Poll, G. C. Bazan, R. H. Friend, *Science* **2014**, *343*, 512-516; eA. C. Jakowetz, M. L. Bohm, A. Sadhanala, S. Huettner, A. Rao, R. H. Friend, *Nat Mater* **2017**, *16*, 551-557.

[13]   aY. X. Li, X. D. Liu, F. P. Wu, Y. Zhou, Z. Q. Jiang, B. Song, Y. X. Xia, Z. G. Zhang, F. Gao, O. Inganas, Y. F. Li, L. S. Liao, *Journal of Materials Chemistry A* **2016**, *4*, 5890-5897; bJ. Liu, S. S. Chen, D. P. Qian, B. Gautam, G. F. Yang, J. B. Zhao, J. Bergqvist, F. L. Zhang, W. Ma, H. Ade, O. Inganas, K. Gundogdu, F. Gao, H. Yan, *Nature Energy* **2016**, *1*.

[14]   aM. Kuik, L. J. A. Koster, G. A. H. Wetzelaer, P. W. M. Blom, *Phys. Rev. Lett.* **2011**, *107*, 256805; bS. R. Cowan, W. L. Leong, N. Banerji, G. Dennler, A. J. Heeger, *Advanced Functional Materials* **2011**, *21*, 3083-3092.

[15]   L. Kaake, X. D. Dang, W. L. Leong, Y. Zhang, A. Heeger, T. Q. Nguyen, *Adv. Mater.* **2013**, *25*, 1706-1712.

[16]   A. Rao, P. C. Y. Chow, S. Gelinas, C. W. Schlenker, C.-Z. Li, H.-L. Yip, A. K. Y. Jen, D. S. Ginger, R. H. Friend, *Nature* **2013**, *500*, 435-439.

[17]   Q. Burlingame, C. Coburn, X. Che, A. Panda, Y. Qu, S. R. Forrest, *Nature* **2018**, *554*, 77.

[18]   J. Hou, O. Inganäs, R. H. Friend, F. Gao, *Nat. Mater.* **2018**, *17*, 119.

[19]   S. H. Park, A. Roy, S. Beaupre, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee, A. J. Heeger, *Nat. Photonics* **2009**, *3*, 297-302.

[20]   aA. Hadipour, B. de Boer, J. Wildeman, F. B. Kooistra, J. C. Hummelen, M. G. R. Turbiez, M. M. Wienk, R. A. J. Janssen, P. W. M. Blom, *Advanced Functional Materials* **2006**, *16*, 1897-1903; bJ. Y. Kim, K. Lee, N. E. Coates, D. Moses, T. Q. Nguyen, M. Dante, A. J. Heeger, *Science* **2007**, *317*, 222-225.

[21]   M. C. Scharber, N. S. Sariciftci, *Prog. Polym. Sci.* **2013**, *38*, 1929-1940.

[22]   aM. C. Scharber, *Adv. Mater.* **2016**, *28*, 1994-2001; bR. A. J. Janssen, J. Nelson, *Adv. Mater.* **2013**, *25*, 1847-1858.

[23]   X. Y. Zhu, *J. Phys. Chem. Lett.* **2014**, *5*, 2283-2288.

[24]   J. R. Pouliot, F. Grenier, J. T. Blaskovits, S. Beaupre, M. Leclerc, *Chemical Reviews* **2016**, *116*, 14225-14274.

[25]   aX. Chen, X. Liu, M. A. Burgers, Y. Huang, G. C. Bazan, *Angewandte Chemie* **2014**, *126*, 14606-14609; bA. D. Hendsbee, J.-P. Sun, W. K. Law, H. Yan, I. G. Hill, D. M. Spasyuk, G. C. Welch, *Chemistry of Materials* **2016**, *28*, 7098-7109.

[26]   aC. H. Peters, I. T. Sachs-Quintana, J. P. Kastrop, S. Beaupre, M. Leclerc, M. D. McGehee, *Adv. Energy Mater.* **2011**, *1*, 491-494; bS. Bertho, I. Haeldermans, A. Swinnen, W. Moons, T. Martens, L. Lutsen, D. Vanderzande, J. Manca, A. Senes, A. Bonfiglio, *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 385-389; cC. J. Brabec, S. Gowrisanker, J. J. M. Halls, D. Laird, S. J. Jia, S. P. Williams, *Adv. Mater.* **2010**, *22*, 3839-3856; dM. Jorgensen, K. Norrman, F. C. Krebs, *Sol. Energy Mater. Sol. Cells* **2008**, *92*, 686-714; eJ. A. Hauch, P. Schilinsky, S. A. Choulis, R. Childers, M. Biele, C. J. Brabec, *Sol. Energy Mater. Sol. Cells* **2008**, *92*, 727-731.

[27]   J. Nelson, *The Physics of Solar Cells*, Imperial College Press, **2003**.

[28]   M. P. J. Hutnan, L. G. Kaake, *Materials Horizons* **2016**, *3*, 575-580.

[29]   W. Shockley, H. J. Queisser, *Journal of Applied Physics* **1961**, *32*, 510-519.

[30]   aP. E. Hartnett, S. M. Dyar, E. A. Margulies, L. E. Shoer, A. W. Cook, S. W. Eaton, T. J. Marks, M. R. Wasielewski, *Chem. Sci.* **2015**, *6*, 402-411; bJ. L. Logsdon, P. E. Hartnett, J. N. Nelson, M. A. Harris, T. J.

Marks, M. R. Wasielewski, *ACS Appl. Mater. Interfaces* **2017**, *9*, 33493-33503; cM. R. Wasielewski, *Chemical Reviews* **1992**, *92*, 435-461; dN. V. Tkachenko, L. Rantala, A. Y. Tauber, J. Helaja, P. H. Hynninen, H. Lemmetyinen, *J. Am. Chem. Soc.* **1999**, *121*, 9378-9387; eF. D. Lewis, R. L. Letsinger, M. R. Wasielewski, *Accounts Chem. Res.* **2001**, *34*, 159-170; fA. Harriman, J. P. Sauvage, *Chemical Society Reviews* **1996**, *25*, 41-&; gM. Kuss-Petermann, O. S. Wenger, *J. Am. Chem. Soc.* **2016**, *138*, 1349-1358.

[31]   P. Cheng, X. Zhan, *Materials Horizons* **2015**, *2*, 462-485.

[32]   A. J. Heeger, N. S. Sariciftci, E. B. Namdas, *Semiconducting and Metallic Polymers*, Oxford University Press, **2010**.

[33]   aF. S. Bates, *Science* **1991**, *251*, 898-905; bP. C. Hiemenz, T. P. Lodge, *Polymer Chemistry, Second Edition*, Taylor & Francis, **2007**.

[34]   aJ. Hollinger, D. S. Seferos, *Macromolecules* **2014**, *47*, 5002-5009; bE. L. Kynaston, Y. Fang, J. G. Manion, N. K. Obhi, J. Y. Howe, D. F. Perepichka, D. S. Seferos, *Angewandte Chemie International Edition* **2017**, *56*, 6152-6156; cJ. Hollinger, A. A. Jahnke, N. Coombs, D. S. Seferos, *J. Am. Chem. Soc.* **2010**; dF. Lombeck, H. Komber, A. Sepe, R. H. Friend, M. Sommer, *Macromolecules* **2015**, *48*, 7851-7860.

[35]   aY.-H. Lin, K. A. Smith, C. N. Kempf, R. Verduzco, *Polym. Chem.* **2013**, *4*, 229-232; bC. R. Bridges, H. Yan, A. A. Pollit, D. S. Seferos, *ACS Macro Letters* **2014**, *3*, 671-674; cG. L. Tu, H. B. Li, M. Forster, R. Heiderhoff, L. J. Balk, U. Scherf, *Macromolecules* **2006**, *39*, 4327-4331; dV. D. Mitchell, D. J. Jones, *Polym. Chem.* **2018**, *9*, 795-814; eK. Johnson, Y.-S. Huang, S. Huettner, M. Sommer, M. Brinkmann, R. Mulherin, D. Niedzialek, D. Beljonne, J. Clark, W. T. S. Huck, R. H. Friend, *J. Am. Chem. Soc.* **2013**; fY. M. Lee, E. D. Gomez, *Macromolecules* **2015**, *48*, 7385-7395.

[36]   L. G. Kaake, *ACS Energy Letters* **2017**, 1677-1682.

TOC FIGURE

Keywords

Organic Solar Cells, Organic Photovoltaics, Conjugated Block Polymers