

# Photovoltaic concepts inspired by coherence effects in photosynthetic systems

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The past decade has seen rapid advances in our understanding of how coherent and vibronic phenomena in biological photosynthetic systems aid in the efficient transport of energy from light-harvesting antennas to photosynthetic reaction centres. Such coherence effects suggest strategies to increase transport lengths even in the presence of structural disorder. Here we explore how these principles could be exploited in making improved solar cells. We investigate in depth the case of organic materials, systems in which energy and charge transport stand to be improved by overcoming challenges that arise from the effects of static and dynamic disorder — structural and energetic — and from inherently strong electron–vibration couplings. We discuss how solar-cell device architectures can evolve to use coherence-exploiting materials, and we speculate as to the prospects for a coherent energy conversion system. We conclude with a survey of the impacts of coherence and bioinspiration on diverse solar-energy harvesting solutions, including artificial photosynthetic systems.

Plants and algae are effective overall at converting solar energy to stored fuel<sup>1</sup> and, strikingly, operate successfully in an environment that includes oxygen and water, and can even include extreme physiological temperatures<sup>2</sup> and exceedingly low light flux<sup>3</sup>. The contrast with successful conventional materials for solar energy conversion — often characterized by long-range periodicity — could hardly be more stark. Still, the photosynthetic machinery<sup>4</sup> of biological systems, while strongly energetically disordered, functions incredibly well at solar energy conversion.

Different classes of energy-conversion systems use the fundamental processes of light absorption (or harvesting) and charge-carrier transport, although with varying emphasis. Inorganic photovoltaic materials photogenerate mobile charges essentially instantaneously, so their optimization depends to a large extent on effective charge-transport properties. On the other hand, photosynthesis generates solar fuels using eight photoexcitations per assimilation of CO<sub>2</sub>. The transduction of solar energy that powers this chemistry takes place in reaction-centre proteins that are surrounded by light-harvesting complexes whose role is to enhance the effective photoexcitation rate. Charge transport is a simple sequence of well-defined electron-transfer reactions that, importantly, are coupled to the translocation of protons. Materials for organic photovoltaics (OPV) fall somewhere between the limits of photosynthesis and crystalline solar-cell materials, with desirable properties often limited by energetic and structural disorder<sup>5</sup>. In such systems with intermediate properties, a key role in optimizing the light-conversion process may be played by coherent effects.

What is coherence and how might it help? Coherence refers to phase relations among the constituents of a superposition of waves. Broadly speaking, coherence means that correlations are significant between the waves<sup>6</sup>. Superposition states — quantum states comprising a superposition of wavefunctions — carry extra correlations beyond those predicted by classical probability theory<sup>7,8</sup>. For instance, they show quantum coherence when their quantum amplitudes are in phase. In the case of superpositions of electronic states — for example, the photoexcitations described above — the amplitudes of the states are locked together so that each wave flows synchronously with the others. Coherence involving molecular

excitons — quasiparticles formed by delocalization of electronic excitation among two or more molecules — involves a superposition of excitations of each molecule<sup>6</sup>. In this Review, we will imply electronic (or vibronic) excitation when we simply say excitation.

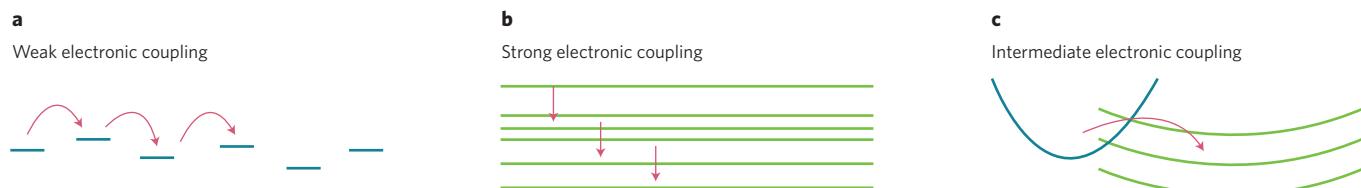
When dynamics are coherent, phase relationships among quantities are retained long enough to have a mechanistic and functional impact. That may be indicative of classical coherence (wave-like correlations) or it may arise from quantum-mechanical superpositions underlying or governing the dynamics of evolving states. In Fig. 1, we show a way of thinking about coherence in transport relevant to the kinds of systems we will discuss here. There are two limiting scenarios. Transport is incoherent when states (for instance, excitations or charges) are localized and hop randomly from site to site. Similarly, when states are delocalized over sites to form extended eigenstates, transport occurs stochastically in a disordered system by means of population relaxation. That is, population relaxes incoherently from state to state owing to small interactions with the environment. As noise and disorder increase, transport optimization becomes a more challenging problem<sup>9</sup>.

The intermediate case is most interesting — and is where coherence is found — because delocalization competes with localization. Transport emerges when free evolution — electronic coupling that drives delocalization — interplays with energy fluctuations that conspire to localize excitation (akin to scattering in solid-state physics). The resulting transport dynamics are complex: sometimes excitons tumble down a ladder of energy states, other times collective excitations (excitons) jump through space (Fig. 1c). Exciton or charge-carrier size can also change during dynamic evolution. For example, later in this Review we will describe an example in which an initial semi-localized state ‘jumps’ into a manifold of delocalized states (Fig. 1c) that subsequently localize to form a final localized state that is remote from the initial state. The characteristic of the intermediate regime is the competition of timescales, and often therefore coherent dynamics dominate at short times and convert to incoherent transport at longer times, as predicted recently for conjugated polymers<sup>10</sup>.

Overall, we associate coherence with transport that is not limited to be a random (incoherent) walk<sup>11–13</sup>. This, in turn, implies that

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**Figure 1 | Coherence as discussed in this work.** Model pictures for free energy (vertical axis) versus a schematic representation of position, or site (horizontal axis), comparing limiting model cases for transport. **a**, Weak electronic coupling: incoherent hopping transport among localized states. **b**, Strong electronic coupling: incoherent relaxation among delocalized states. **c**, Intermediate case: competition between timescales of localization and transport; (quasi-)localized states can transfer population to delocalized states. In each case, localized or pseudo-localized levels or free-energy curves are coloured blue, while delocalized levels are green.

on length scales relevant to transport, directionality is programmed into the system. Directed relationships between quasi-particles are endured by momentum conservation, a property characteristic of periodic solid-state systems. In these highly ordered systems, excitons and charge carriers are highly delocalized (Table 1).

In soft materials, such as  $\pi$ -conjugated molecules and polymers used in OPV, disorder arises because of the weak non-covalent (van der Waals-type) binding between the molecules or chains. This disorder has an immense impact on the optical and transport properties of organic semiconductors — in particular owing to wavefunction localization and spatially varying electronic properties that result from rough energetic landscapes. Examples include a reduced diffusion length for excitons and charge carriers, and the emergence of shallow and deep trap-states that can act as recombination centres.

By comparing biological systems side-by-side with OPV materials, we learn that delocalization, coherence and quantum effects can, in fact, emerge even in such disordered systems. Recognizing this is a key step towards designing OPV devices with these concepts as design principles.

### Coherence effects in biology

Plants, algae and photosynthetic bacteria transform power from sunlight and perform energy-intensive chemical transformations, namely  $\text{CO}_2$  reduction and water splitting<sup>14</sup>. These systems have diversified and optimized over the past 3 billion years. They are particularly remarkable for their range of nimble, active responses to the Sun's irradiance and available spectrum<sup>15</sup>. For example, a variety of methods are deployed to dissipate excitation and adapt to the spectrum of available light<sup>4</sup>. While sophisticated, photosynthetic proteins are also disordered, so it is a surprise that experiments detect coherences involving the primary excitations of light-harvesting complexes.

Photosynthetic membranes capture sunlight using chromophores (for example various chlorophylls) and transfer the excitation to an interface between an electron donor and acceptor<sup>16</sup> (the reaction centre; Fig. 2). Core reaction-centre complexes such as

photosystem II (PSII) tend to be organized in arrays (such as the pair of PSII photosystems shown in the supercomplex illustrated in Fig. 2a) rather than randomly distributed throughout the membrane. The reaction centre is flanked by the primary light-harvesting complexes, LHCII, each trimer containing 45 chlorophylls. There are also a number of minor antenna complexes, not all structurally resolved in the figure (green shapes). Hence, the Sun's irradiance is concentrated by using many chromophores embedded in light-harvesting complexes to capture and then focus energy<sup>4</sup>. To achieve the level of excitation concentration required to reduce  $\text{CO}_2$  and split water, there are typically about 100–600 light-harvesting chromophores per reaction centre (Fig. 2a).

OPV active layers (Fig. 2b; ref. 17) similarly have light-absorbing units, represented by domains of conjugated polymers or molecules behaving as electron donors or acceptors. Excitons appearing at the donor–acceptor interface dissociate, and then carriers separate into the donor and acceptor domains. In contrast with their biological counterparts, where the molecules are arranged and optimized at the molecular level and embraced by a protein scaffold, here donors and acceptors are arranged as a disordered mixture of domains forming a thin film. The final target of an OPV material is to produce large numbers of charge carriers to be extracted as photocurrent, whereas in photosynthetic systems photogenerated electrons are transferred one at a time in the reaction centre and delivered to a site where they sequentially reduce a bound quinone.

In photosynthetic membranes, the excitation energy is conveyed efficiently among light-harvesting complexes, often with an internal quantum efficiency that can be up to 90%. To achieve that efficiency, given that chlorophyll has an excited-state lifetime of ~4 ns, ultrafast energy transfer on the timescale of 0.1–10 ps is required for the excitation transit among each of the many molecules in photosynthetic antenna complexes<sup>4</sup>. Photosynthetic proteins making up the light-harvesting complexes are specialized for the purpose of excitation transport, unlike OPV materials that must also transport charge carriers; hence, we expect photosynthetic proteins to be good models for optimal solar-energy capture and excitation transport.

**Table 1 | A collection of properties and materials organized into three distinct regimes of disorder.**

	Disorder dominates	Moderate to high order	Near-perfect order
Properties	Localization of excitons and charges Concentration quenching Wide distributions of observables Incoherent transport dominates	Potential for coherent transport on moderate length scales Long diffusion lengths Delocalization of excitons and charges Narrow distributions of observables Collective phenomena	Momentum is a good quantum number (physics in $k$ -space) Exotic electronic phases
Materials	Conjugated polymers Many molecular aggregates Discotic liquid crystals Biological light-harvesting complexes	Multicrystal perovskites Some molecular aggregates (J-aggregates, nanofibres, tubular aggregates) Carbon nanotubes Quantum-dot superlattices	Graphene and other 2D materials Polydiacetylene Layered oxide structures Single-crystal perovskites

Recent experimental studies of photosynthetic proteins have motivated reconsideration of the prospects for coherent phenomena in complex systems. For example, ultrashort ( $10^{-14}$  s) laser pulses were used to photoexcite superpositions of electronic absorption bands in photosynthetic light-harvesting complexes. These experiments revealed how the light-absorbing molecules (chromophores) interact<sup>18–21</sup>. These superpositions are excited by a short laser pulse (or pulse pair), the ‘pump’, that has a broad frequency bandwidth; thus, it impulsively drives all electronic transitions with which it overlaps. At a sequence of later times, another short laser pulse (the ‘probe’) detects the changes in signal amplitude as a consequence of the way the system evolves after the pump pulse. In broadband pump–probe spectroscopy, this information is laid out as a function of probe frequency. In two-dimensional (2D) electronic spectroscopy, an additional frequency axis is obtained, tagging the pump-induced excitations. The pump–probe signals can thus be correlated in a 2D pump-frequency/probe-frequency map.

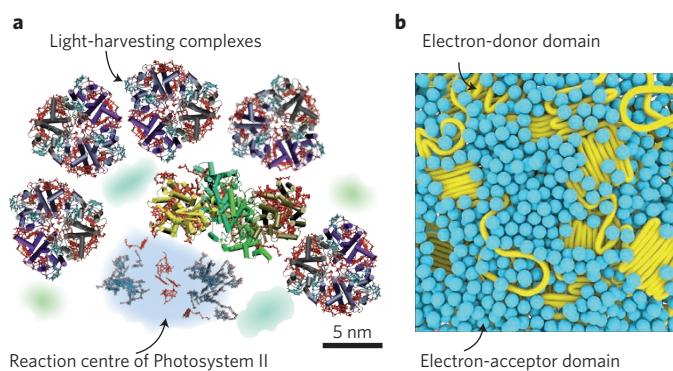
As an example, data for the PC645 light-harvesting protein from algae<sup>19,22,23</sup> are shown in Fig. 3. The 2D electronic spectrum has a clear cross-peak, coloured blue, which shows that two different coloured chromophores within the protein interact (when we pump one chromophore, the other can generate a signal detected by the probe). Oscillations in the cross-peak, seen also in broadband pump–probe data, show that the phase information in superpositions called wavepackets (electronic, vibrational and vibronic) prepared by the pump pulse is retained on the timescale of energy transfer. This is related to how we defined coherence.

The surprising result is that these superpositions of states are much more resistant to dephasing than anticipated. Specifically, instead of relaxing rapidly to a statistical mixture of excitations associated locally with the chromophores, the excitation retains amplitude on both chromophores. This is a property indicative of coherence, familiar from waves and quantum states. While the details of these observations continue to be explored, the key advance is that despite structural and energetic disorder, transient coherent states can be prepared by making a superposition using a short laser ‘pump’ pulse and observed using a probe pulse. That, in turn, suggests that transport — at least on very fast timescales — is not limited to be an inefficient random walk. This is concluded because, although excitation is not strongly delocalized between these (different coloured) chromophores, weak superpositions are suggested by the presence of the cross-peak in the 2D spectrum. This is indicative of the intermediate coupling regime.

In sum, in biology, delocalized excitations are paramount for very long-range energy migration. Even moderate to weak exciton delocalization, probably mixed with intramolecular vibrations, helps to tune and thereby optimize energy transfer. Significantly, these coherence effects are present in quite disordered and noisy systems. These remarkable findings provoke the questions: can coherence help energy conversion in photovoltaic systems, for example OPV devices, and if so, how? Can similar effects aid charge separation and transport?

### Excitons and long-range energy migration

As described above, recent experiments and theory have highlighted the role of coherent transfer in femtosecond studies of light-harvesting proteins<sup>18–22,24–26</sup>, suggesting the need for accurate dynamical models to capture the subtle characteristics of energy-transfer mechanisms. The primary implication of coherence is that the donor fluorescence spectrum and acceptor absorption spectrum cannot be considered independently to construct the Förster spectral overlap for predicting energy transfer rates; instead the spectra are partially correlated by delocalization of the excitation<sup>6</sup>. Therefore, in light-harvesting systems, coherence means that the spectral line broadenings of donor and acceptor chromophores become linked owing to



**Figure 2 | Photosynthetic light harvesting compared with OPV.**

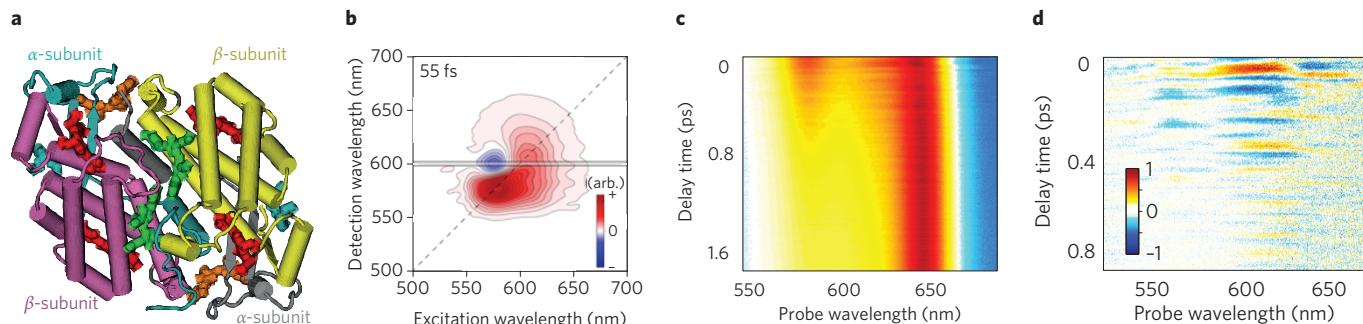
**a**, Plan view of the thylakoid membrane showing light-harvesting complexes surrounding a pair of PSII reaction centres — one of nature’s photosynthetic solar cells. Each LHCII trimer contains around 45 chlorophylls. The chlorophylls bound in the PSII protein are shown in the blue shaded region. Those coloured red (the reaction centre) mediate the electron-transfer process that starts the transduction of photoexcitation to fuel. The light-green shaded region indicates that the protein scaffold surrounding the chromophores of the PSII reaction has been removed from the drawing. The light-green shaded regions are minor antenna complexes whose structures were not resolved until recently. **b**, Schematic layout of an organic bulk heterojunction. In the electron-donor domain, conjugated polymers or molecules are often the primary light absorbers and also serve to transport holes. The electron-acceptor domain typically comprises fullerenes that mainly transport electrons. Reproduced from ref. 4, Nature Publishing Group (**a**) and ref. 17, ACS (**b**).

electronic delocalization. Thus, the Förster theory prediction is not accurate because it is founded on the independence of the donor emission spectrum and acceptor absorption.

Photosynthetic light-harvesting is found in an extreme range of environments, from bright sunlight to very weak photoexcitation conditions that are the equivalent of moonlight. Green sulfur bacteria tend to photosynthesize only under very low light conditions, and they have been documented to grow in microbial mats or in the deep sea where the solar irradiance is six orders of magnitude less than the sunlight impinging on plants. Green sulfur bacteria therefore must be very effective scavengers of sunlight. To that end, they use a unique, primitive light-harvesting complex comprising about 250,000 aggregated bacteriochlorophylls encased in a lipid–protein layer<sup>27</sup>. The characteristic of this antenna complex is that excitons are highly delocalized, quite unlike any other photosynthetic antenna complex. Highly delocalized excitations migrate rapidly through the aggregate<sup>28</sup>, which can be understood using a modified version of Förster theory, generalized Förster theory<sup>29</sup>, which explains how coherently delocalized states can jump rapidly and far.

What are the effects of coherence that we could realistically expect to influence excitation diffusion? Diffusion length is determined by the competition between a random walk of the excitation among the molecules of the material and the excited-state lifetime (energy migration is quenched once the molecules return to the ground state). Consider a 2D lattice of molecules where there is one trap and 1,000 donor sites. We equate these molecules to sites in the case where excitation is localized. Otherwise, the sites comprise the size of delocalized excitations. On average, trapping of the excitation will take  $(1/\pi)N \ln N = 2,200$  excitation transfers<sup>30</sup>. If we say the distance for an average energy-transfer jump is 1 nm and excited-state lifetime is 1 ns, then the total distance travelled by the excitation is 2.2  $\mu$ m.

If trapping is to be ensured on average, then the mean hopping time is 0.5 ps, and the average speed of the excitation is 2,200 m s<sup>-1</sup>,



**Figure 3 | Coherence in light harvesting.** **a**, Structure of a light-harvesting protein known as PC645, isolated from cryptophyte algae. Eight light-harvesting chromophores (bilins, coloured green, orange and red to distinguish the three slightly different chromophores) are arranged in a protein scaffold. The scaffold comprises four self-assembled proteins. **b**, A representative 2D electronic spectrum recorded at pump-probe time delay of 55 fs. **c**, Broadband pump-probe spectrum as a function of time delay. **d**, Coherent oscillations that modulate the amplitude of the broadband pump-probe spectra<sup>23</sup>. Those same oscillations are evident in the 2D electronic spectrum as a function of time delay<sup>19</sup>. The colour scale bar defines the signal amplitude, in arbitrary units. Reproduced from ref. 23, ACS.

which is approximately the speed of sound in organic media. This result is consistent with the assumptions of Förster theory. The excitation jumps from site to site, each time relaxing and thermalizing to the environment before the next jump, which can be viewed as a phonon cloud following the excitation. Moving the phonon cloud from site to site, indicated by the spectral overlap in Förster theory, introduces friction that limits the speed of excitation transport.

The main problem with the random walk is that despite travelling 2.2 μm in this example, the diffusion length of the excitation — the net change in position from the initial excitation — is estimated to be only 30 nm. Typical random walk trajectories are shown in Fig. 4a: without direction, the excitation is just as likely to go backwards as it is to go forwards. Since the lifetime of a singlet excited state is often of the order 1 ns, energy migration is a race against a fast clock. If the excited-state lifetime were extended to 10 ns, then this diffusion length could be increased to ~100 nm.

It is interesting to inquire whether it may be possible to achieve step-change increases in excitation diffusion lengths. Many materials, including conjugated polymer films and photosynthetic antenna complexes, show exciton diffusion lengths of only ~10–30 nm (refs 31–33). Nevertheless, extreme diffusion lengths (>1 μm) have been documented for certain molecular aggregates, along polydiacetylene chains, and in the rubrene crystal<sup>34–37</sup>. These extraordinary diffusion lengths have been found to go hand-in-hand with order and consequent long (wavefunction) delocalization lengths, which is likely to be significant. The observation in a recent report is compelling<sup>36</sup>, but a comprehensive explanation remains elusive in our opinion.

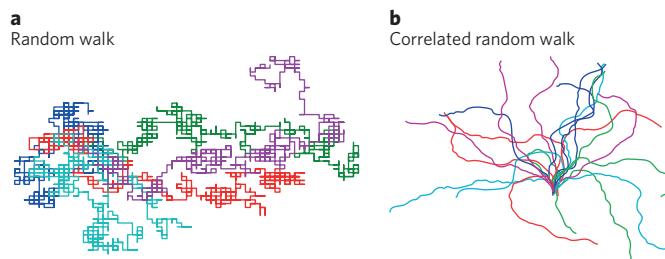
Coherence in itself does not provide a step-change solution to enhance excitation diffusion lengths, as was realized long ago in the context of photosynthetic light-harvesting<sup>38,39</sup>. The issue is that

as delocalization grows, the wavefunction amplitude at each site (decided by normalization) diminishes, concomitantly reducing the matrix element for trapping of excitation to an energy-acceptor state. Or, thought of in another way, in the dipole approximation the distance from the donor — measured from the centre of the delocalized wavefunction — to the localized acceptor increases. The electronic coupling diminishes concomitantly as  $1/R^3$ , making it negligibly small when the delocalization length is very large.

Simplifying the random walk with fewer, longer jumps may be a key improvement achieved by delocalization<sup>40</sup>. Noting that the distance the excitation can move for a fixed hopping rate depends on its size — that is, an exciton with larger area moves farther in one hop — we can estimate that the diffusion coefficient  $D$  depends on the square of the exciton size,  $a$  ( $D = ka^2/2$ , where  $k$  is the exciton hopping rate). The collective jump of excitation that is delocalized over many chromophores is sometimes referred to as ‘supertransfer’ and is explained in the context of generalized Förster theory<sup>29</sup>, as mentioned above. In supertransfer, excitons jump farther essentially because the scaling laws for the electronic coupling change when there are many molecules coherently coupled by delocalization, and the electronic coupling can no longer be understood with a simple point dipole model<sup>41</sup>.

But there is a compromise that needs to be considered in this model. The way the rate  $k$  diminishes with exciton delocalization depends on the geometry of the molecular aggregate<sup>42</sup>. We will take a best-case scenario where  $k$  scales with  $1/a$ , which implies that the diffusion coefficient might increase in proportion to exciton size. The design principle therefore is that delocalized excitons aid long-range energy transfer, but molecules must be arranged so that the lowest exciton state is not the bright state. The caveat to the design principle comes about because the net effect of this gain in diffusion length ( $L_D = \sqrt{D\tau}$ , where  $\tau$  is the excited-state lifetime) can be cancelled in the case of perfect J-aggregates, where the lowest exciton state is a bright state. That is because the radiative rate shortens with delocalization (a well-known phenomenon called superradiance)<sup>34,43</sup>, meaning a gain in  $D$  can be offset by a concomitant drop in  $\tau$ . If the lowest exciton state is not the bright (superradiant) state, however, then the diffusion length will be enhanced approximately proportionally to  $a^{1/2}$ .

The physical reason that delocalized excitons travel faster is adduced by first recalling that strong electronic coupling between molecules correlates the transition-energy fluctuations of those molecules, making the optical absorption bands significantly narrower. This is known as exchange narrowing, and is exemplified in the optical spectra of molecular J-aggregates. The exchange



**Figure 4 | Random walks and energy migration.** Examples of various trajectories from random walk simulations. **a**, A simple random walk; **b**, a biased (correlated) random walk. Reproduced from ref. 40, RSC.

narrowing, in turn, reduces the effective friction impeding transport of the exciton because friction in transition-state theory is proportional to the amplitude of energy-gap fluctuations. In the Förster theory model, the narrowing of donor fluorescence spectrum and acceptor absorption, and the decreased Stokes shift that necessarily accompanies line narrowing (according to a fluctuation-dissipation relation), conspire to increase the excitation hopping rate considerably. Synthetic systems in which excitons are highly delocalized include molecular nanotubes<sup>44</sup>, single-walled carbon nanotubes<sup>45</sup> and polydiacetylene<sup>46</sup>. These kinds of materials may well be useful exciton-transport systems.

Unravelling the random walk — that is, directing the excitation — seems the obvious substantive improvement that might maximize excitation transport lengths. A directed walk can be implemented in practice if the delocalized walker detects an energy sink at long range; or, alternatively, a partial solution can be attained with a biased walk. Notice how the trajectories of Fig. 4b appear unravelled and therefore extend remarkably farther than trajectories of the simple random walks shown in Fig. 4a (ref. 40). Biased random walks require memory about the previous step in the walk, which might be achieved using coherence to provide correlations from one step to the next.

Typical photosynthetic light-harvesting complexes contrast markedly with examples of strongly coupled molecular systems. They are disordered, and photosynthetic excitations tend to be quite localized. Rather than make electronic couplings very large, nature has taken the approach of engineering the environment (protein) so that the reorganization energy is comparable to the magnitude of moderate interchromophore electronic couplings. For example, the Stokes shift measures double the reorganization energy, which tells us how strongly the electronic transitions of the chromophores are coupled to the environment. For LHCII, the main light-harvesting complex from plants and green algae, the chlorophyll-*a* Stokes shift has been ascertained to be approximately 110 cm<sup>-1</sup>, which is small compared with chlorophyll-*a* in solution, measured to be 135–200 cm<sup>-1</sup>, depending on solvent polarity<sup>21</sup>. As will be discussed in the next section, this contrasts with reorganization energies in  $\pi$ -conjugated systems, which are in the  $\geq 1,000$  cm<sup>-1</sup> range.

Interestingly, the donor molecules that are among the best performers in OPVs include subphthalocyanines at the heart of certain multilayer organic cells<sup>47</sup>. Porphyrins and phthalocyanines, like chlorophyll, have small geometry relaxations in the excited state because of their cyanine-like nature<sup>48</sup> (for which the degrees of wavefunction polarizations are equivalent in the S<sub>0</sub> ground state and S<sub>1</sub> excited state); squaraines share similar properties. This suggests an alternative design principle that will particularly aid long-range energy migration among a single material system — that is, to minimize the coupling to the environment (line broadening) and therefore the Stokes shift. The result is better Förster spectral overlap and fast energy migration.

### Coherent versus hopping charge transport

Charge-carrier mobilities in organic  $\pi$ -conjugated systems have been extensively studied, and detailed descriptions of the charge-transport mechanisms are emerging<sup>49–53</sup>. Models for electron and hole mobilities can be qualitatively related by the conceptual interpretation that coherence in the case of electron transfer is associated with low-friction transport, and incoherent electron (or hole) hopping happens in the high-friction limit. An important aspect is that charge transport in conjugated materials can happen in various regimes depending on morphology and structural disorder, such as chain twists. The kinds of intermolecular interactions that are most important depend on whether transport is predominantly intra-chain — which probes covalent bonding — or interchain and thus decided by weak van der Waals interactions between molecules.

That organic semiconductors are based on  $\pi$ -conjugated systems implies that the relevant transport levels (highest occupied orbitals for holes; lowest unoccupied orbitals for electrons) are related to the (de)localization of  $\pi$ -electron wavefunctions. An essential characteristic of these  $\pi$ -conjugated systems is the strong connection between electronic structure and geometric structure: that is, the presence of strong electron–vibration couplings. This comes from the fact that the lengths of the bonds between  $\pi$ -electron-carrying atoms along the molecular backbones or polymer chains directly depend on the  $\pi$ -electron densities on these bonds. Thus, any charge injection (ionization) process (or optical excitation) usually results in modifications of the  $\pi$ -bond densities and therefore of the bond lengths. The corresponding intramolecular geometry relaxation energies (and reorganization energies) easily reach a few tenths of an electronvolt (thousands of cm<sup>-1</sup>)<sup>54</sup> and are mainly driven by C–C stretching and/or ring breathing modes, with typical periods of vibrations of the order of 20 fs.

Whether the material can assume coherent transport in the band regime or incoherent transport in the hopping regime depends strongly on the relative strengths of electronic couplings and electron–vibration couplings. Along a highly ordered, structurally perfect  $\pi$ -conjugated chain, such as a polydiacetylene or ladder polyparaphenylene chain, the intrachain electronic couplings reach 2.5 eV, which is far larger than the geometry relaxation energies. Coherent transport is then achievable, and remarkable mobilities up to 600 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> have been reported along ladder polyparaphenylene chains<sup>55</sup>. In contrast, in the polymer materials used in practice (which have a significant degree of disorder) or in molecular semiconductor thin films, the charge carriers have to jump from one chain or one molecule to another. Thus, charge transport depends on inter-chain electronic couplings. These interchain couplings, because of the much weaker wavefunction overlap, are at least one order of magnitude lower than the intrachain couplings; they are generally of the order of a few hundredths of an electronvolt at best. In such instances, it quickly becomes energetically favourable to localize the charge carriers and benefit from geometry relaxations. In addition, structural disorder and the presence of species such as water and/or oxygen can produce traps, which further limit transport<sup>56</sup>; deep traps can be removed through the action of strong n-type or p-type dopants<sup>57</sup>.

High-mobility molecular crystals offer an interesting intermediate picture since they are highly ordered but transport is exclusively intermolecular (that is, interchain). Models have been developed<sup>53</sup> that suggest the coexistence of localized, incoherent states with delocalized, coherent Bloch states, as depicted in Fig. 1c. This kind of transport reveals the potential importance of coherence — specifically electronic couplings that are at least comparable to energetic disorder — for high mobilities in conjugated materials. Indeed, systematic studies of organic field-effect transistors have shown that conjugation length of the molecules, and control of morphology and disorder, are crucial parameters<sup>58</sup>. A very recent report points to short-range hole mobilities up to 170 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in the molecular crystal of a benzothiophene derivative; there, the alkyl side-chains appended to the conjugated core appear to strongly reduce some of the intermolecular vibrations (typically, in the 10<sup>-13</sup> s regime) that would otherwise cause large fluctuations in the electronic couplings between adjacent molecules<sup>59</sup>.

An important result comes from the study of electrical resistance of conjugated oligomers as a function of their length<sup>60</sup>, which demonstrates that charges tunnel quantum mechanically through chains that are up to about five repeat units long; beyond this length, charges diffuse by a hopping-type process. Thus, it can be expected that in thin films of  $\pi$ -conjugated systems, when some degree of local order is present and electronic couplings are large, a combination of transport regimes can be operational, adding coherent processes to incoherent processes.

### Coherence at donor-acceptor interfaces

Coherence effects in electron-transfer reactions can come in various guises. In the reaction centre of purple bacteria, coherent electronic coupling through an intermediate chromophore (bacteriochlorophyll-*a*) provides an electronic coupling bridge. The electron skips over this bridge from the special pair *en route* to the acceptor molecule (bacteriopheophytin-*a*) via a superexchange process<sup>61,62</sup>. In such a way, delocalized states (from the donor and acceptor to the bridge) can help to separate electrons and holes expediently.

The free-energy differences among the states in PSII from plants and algae are different than those in purple bacteria, leading to mixed exciton/charge-transfer states. Molecular vibrations appear to contribute little to the function of purple bacteria<sup>63</sup>, yet recent studies of plant PSII using two-dimensional electronic spectroscopy suggest that vibronic coherences help to decide the pathways for charge separation<sup>64,65</sup>. Here the wavefunctions of reactant and

product states form a sparse ladder and are connected not only by electronic coupling, but also by the vibrational motions (they are vibronic states; Fig. 5a). There has been a large amount of work recently that examines how such vibronic effects aid electron or energy transfer<sup>66</sup>, but we will not delve into that topic here.

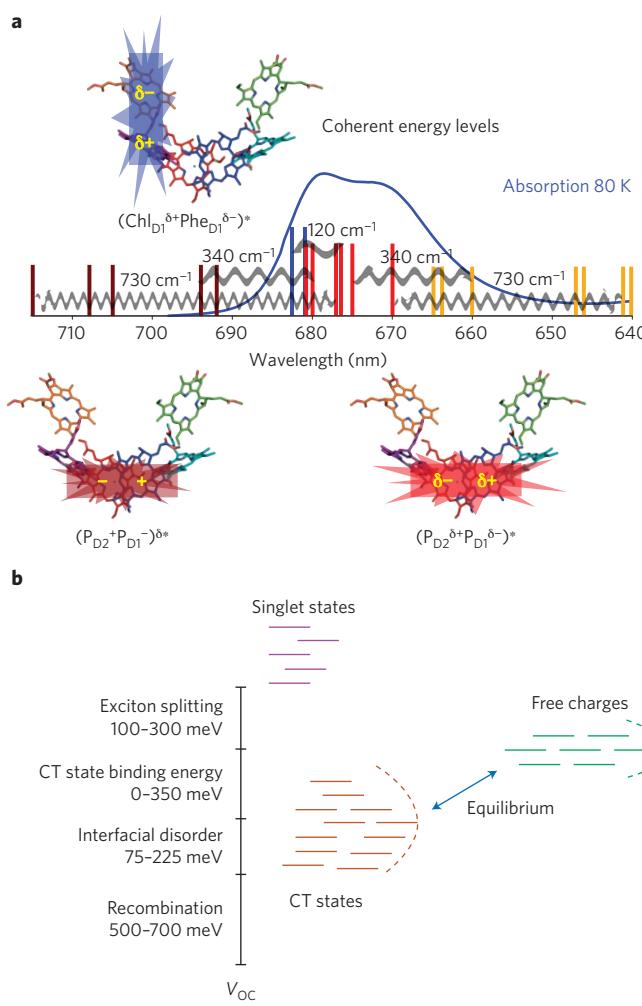
In some ways similar to those examples from biology, delocalization effects in organic solar cells are especially interesting at interfaces, where charge-transfer electronic states — corresponding to a hole on a donor chain or aggregate interacting with an electron on an adjacent acceptor molecule or aggregate — appear at the nexus of electron-donor and electron-acceptor components (Fig. 5b; ref. 67). In polymer-fullerene organic solar cells, the first step to produce mobile carriers is the evolution from an exciton state formed on the polymer phase to a dissociated electron–hole pair at the interface between polymer and fullerene<sup>52</sup>. This sounds simple, but precisely how it happens on an ultrafast timescale, and what drives the separation of the charges — which should be coulombically bound at the interface — while retarding recombination<sup>68</sup>, are some of the most vexing questions in the field.

Figure 5b depicts an insightful model<sup>67</sup> that has emerged from the interplay of innovative experiments on polymer–fullerene systems and theory over the past years. The key elements are that, first, there is a large density of states, and, second, there is an equilibrium between free-carrier states and interfacial charge-transfer states. The usually higher-lying (from an enthalpic standpoint) charge-separated states comprise widely separated electron–hole pairs. Importantly, there is an immense density of states, and the electronic coupling that promotes electron and hole hopping between subunits overwhelms the electron–hole attraction in the band of charge-separated states, meaning the electron and hole are independently mobile<sup>69</sup>. The charge-separated states are therefore important for generating photocurrent despite possibly not being the lowest-lying states.

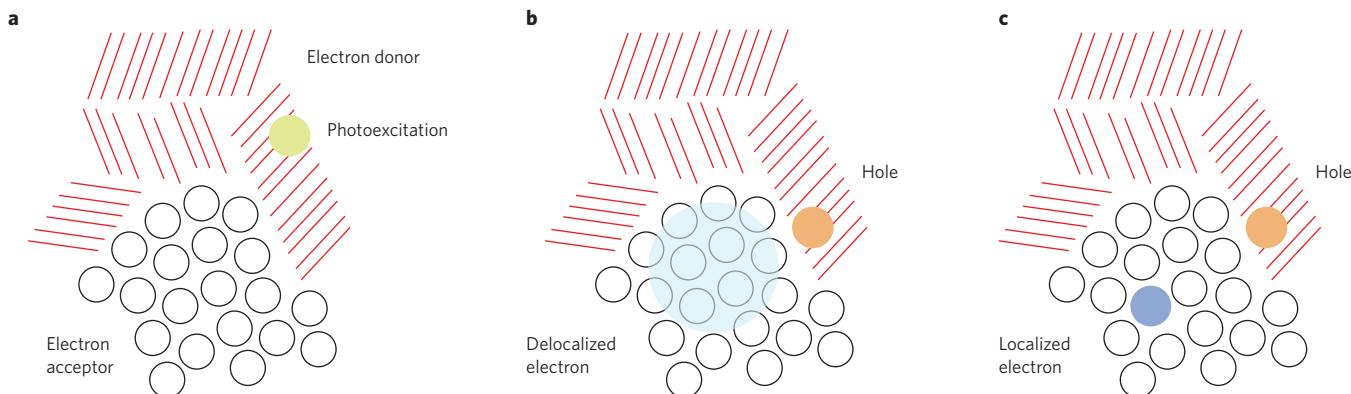
The thermal fluctuations of the frontier molecular orbitals can lead to coherent processes, through equalization of the energies of the exciton and charge-transfer states and therefore mixing of the exciton and product electron–hole pair. For instance, it has been reported that the fluctuations at room temperature of the lowest unoccupied molecular orbital energies of C<sub>60</sub> molecules follow a Gaussian distribution with a full width at half-maximum of about 0.15 eV (ref. 70), meaning there is ample opportunity for resonances and delocalization. This perhaps partly explains the surprisingly weak correlation between energy-level alignment and power conversion efficiency of OPV devices<sup>71</sup>. Consistent with this complexity, recent work has revealed that ultrafast photoinduced electron–transfer dynamics in systems relevant to organic photovoltaics are much more complicated than imagined, as we discuss below.

An instructive example of how charge separation across a donor–acceptor interface might be aided by coherence — and most importantly, how the associated recombination can be suppressed, has been proposed recently<sup>72</sup>. The charge separation in conjugated-molecule/fullerene blends is extraordinarily fast and probably involves delocalized acceptor and/or donor states. The ultrafast time-development of a Stark shift accompanying electron transfer at the donor–acceptor interface of a model OPV active layer was measured to be several tens of femtoseconds, leading to the question of how the electron and hole could possibly separate so fast. The observation was explained in that instance by the electron transiting deep into the fullerene acceptor domain coherently — preceding the phonon cloud (Fig. 6). In other words, the relaxation of molecular structure lags behind the change of electronic state.

The implications of this mechanism for the reverse reaction (geminate recombination) are, perhaps, even more important. Once the phonon cloud catches up with the electron (that is, molecular relaxation that stabilizes the charge), the electron will be localized



**Figure 5 | Coherence in charge separation.** **a**, Excitons and charge-transfer excitons mix into a ladder of states in the PSII reaction centre. Vibrations, indicated by wiggly lines, help to direct relaxation and charge separation among these states. The vertical lines indicate the positions of various electronic states. Chl, chlorophyll; P, special pair; Phe, pheophytin. D1 and D2 refer to protein subunits in the PSII core complex. **b**, In the case of OPVs, there is an enormous density of excited states. There are two key kinds of states where the electron and hole are separated, as well as states where they are bound. The energy losses from various processes are indicated on the left. CT, charge transfer. Reproduced from ref. 64, Nature Publishing Group (**a**) and ref. 67, Wiley (**b**).



**Figure 6 | Coherent charge separation across an interface.** **a**, Example of a photoexcitation (yellow circle) in the donor domain of an OPV bulk heterojunction migrating to the interface with the electron-acceptor (fullerene). **b**, Electron transfer to an initial delocalized electron state in the fullerene domain, leaving a (probably localized) hole in the donor. **c**, Rapid localization of the electron away from the interface, which suppresses recombination.

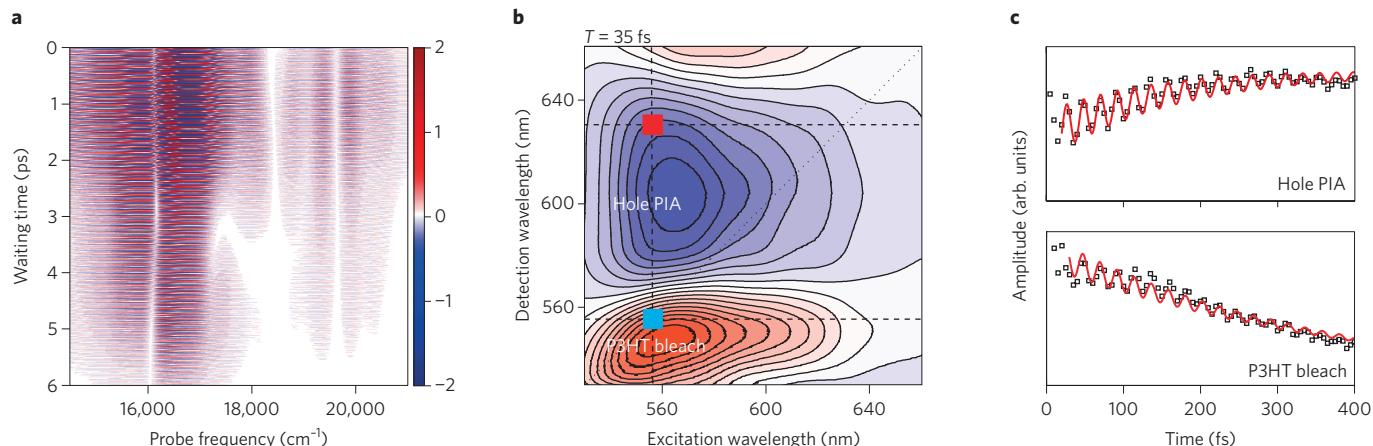
some distance from the interface. The electron–hole attraction is now reduced by the electron's average remoteness from the interface. Moreover, the back electron-transfer process is greatly suppressed because the electron must now be transported with the phonon cloud, requiring hopping transport. Classically, this is like having ballistic forward transport, and backwards transport subject to high friction. However, the explanation is quantum mechanical; the electron wavefunction can be strongly delocalized on very short timescales, aided by coherence effects, then become localized, trapping the electron quite far from the interface. A later theoretical study shows that coupling to intramolecular vibrations probably plays a key role in ensuring the conversion of delocalized states to separated electron–hole pairs<sup>73</sup>.

As introduced above, vibrations are now known to be more than passive observers of ultrafast dynamics. Indeed, it is another consequence of the strong coupling between geometric structure and electronic structure in  $\pi$ -conjugated systems that vibrational carbon–carbon bond stretches (occurring in the 1,400–1,600 cm<sup>−1</sup> range, thus with periodicities of about 20–25 fs as mentioned above) modulate the energies of the frontier molecular orbitals and are therefore notable in the spectroscopy of conjugated molecules. Advanced quantum dynamics calculations to study ultrafast charge transfer in conjugated-oligomer/fullerene complexes predict that these high-frequency vibrations enhance electronic coherence effects during charge-separation dynamics<sup>74</sup>. Similarly, a report of an

experimental study of ultrafast charge transfer in a polythiophene–fullerene photovoltaic blend concludes that the charge-transfer process is associated with coherence related to the vibrational motions of the polymer backbones and fullerene cages<sup>75</sup>.

Ultrafast electron-transfer reactions can involve intramolecular degrees of freedom in the reaction coordinate, which is a potential avenue where coherence can play a role through intramolecular geometrical reorganizations that drive charge separation. It has been documented that high-frequency intramolecular vibrations can reduce the activation barrier for electron transfer or recombination, greatly accelerating it relative to predictions based on models that ignore vibrations<sup>76,77</sup>.

Ultrafast spectroscopic experiments can reveal vibrations in molecules by preparing and probing ‘vibrational wavepackets’ in reactant and product spectroscopic signals<sup>78</sup>. These wavepackets are the superpositions of states produced a femtosecond laser ‘pump’ pulse. An example of coherent oscillations in the amplitude of the (broadband) pump–probe signal as a function of time delay is seen in Fig. 7a. Here, the population dynamics have been subtracted to expose the oscillations, which otherwise are ripples on top of multiexponential decaying signal amplitude. It is likely to be the damping or loss of certain coherent oscillations that will signal reactive modes in ultrafast electron transfer, whereas oscillations will either report on spectator modes or expose mixing between reactant and product states.



**Figure 7 | Coherent vibrational wavepackets.** **a**, Vibrational wavepackets from a vibration detected by broadband pump–probe studies of the laser dye cresyl violet dissolved in methanol (ambient temperature)<sup>80</sup>. **b**, Two-dimensional electron spectrum of a P3HT/PCBM (20%) blend. **c**, Time dependence of the amplitudes in **b** at the hole PIA cross-peak and P3HT bleach<sup>79</sup>. Reproduced from ref. 80, ACS (**a**) and ref. 79, Nature Publishing Group (**b,c**).

As an example of these kinds of coherent oscillations relevant to an OPV active layer, in Fig. 7b,c representative ultrafast (broad-band) data are shown — in this case for an advanced pump–probe type experiment called two-dimensional electronic spectroscopy (2DES). Excitation of regio-regular poly-3-hexylthiophene (P3HT) when blended with a fullerene acceptor, the C<sub>60</sub> derivative PCBM, results in rapid electron transfer from the polymer to the fullerene domain. This is seen as a rise of the P3HT hole signal, indicated by a photoinduced absorption (PIA) that is clearly resolved as a cross-peak in 2DES<sup>79</sup> (Fig. 7b).

Strong vibrational wavepackets in both the ground and excited electron states are seen in the P3HT exciton spectral region. Those same wavepackets are later detected in the product (P3HT hole) PIA (Fig. 7c)<sup>80</sup>. These experiments indicate that this vibration is likely to be a spectator mode, not involved in the reaction coordinate — or if it is, then its role is obscured. The example shows how excited states can be labelled with vibrational wavepackets and the time evolution of the amplitude (and phase) can be probed in reactant and product states during the electron-transfer reaction.

Advanced spectroscopic methods, including broadband pump–probe<sup>74</sup>, 2DES with optical detection<sup>79,81</sup>, pump–push–probe<sup>82</sup>, or 2DES detected by photocurrent<sup>83</sup>, are playing an important part in elucidating the mechanism of electron–hole separation in OPV materials. These kinds of techniques, particularly 2DES, will help to identify new kinds of materials systems in which coherence is robust and plays a decisive role in tuning or enabling function.

### Impact of coherence on photovoltaic performance

In this Review, we have aimed to investigate how researchers can take inspiration from nature in using coherence to advance materials for energy. In particular, we asked which biological precedents offer strategies worth emulating, and how such strategies can most effectively be practised in artificial materials and devices for energy harvesting. We conclude that a principal lesson learned from biological systems is that disorder and complexity do not always extinguish functional coherence. In fact, it can be that the interplay of coherence and decoherence — when there is a reasonable separation among their respective timescales — suggests powerful design principles: not only can we make use of the desirable properties of delocalized states, but we can also capitalize on their decoherence. Combining delocalization and electron–vibration coupling in complex disordered materials may have the potential to drive photoinduced dynamics vectorially by certain vibrational motions and quantum-mechanical overlaps along the reaction coordinate. Ultimately, however, the engineering of functional quantum effects is simplest in disorder-free systems.

A broad conclusion from bioinspired research is that, given the delicate balance usually needed for optimal coherence and resonantly enhanced processes, a modular design approach will probably be required to separate function and optimization spatially. What we still lack at this point are the clear instructions for design, and what we hope to achieve here is to set the scene for the next stage of research that will develop relevant design elements.

Organic solar cells may offer specific, shorter-term, avenues for improvement via coherence-related strategies. It might seem at first blush that, with their impressive external quantum efficiencies, OPVs have little to gain from inspirations obtained from biological systems. But the near-unity external quantum efficiency of an OPV device is achieved using bulk heterojunction architectures, which overcome an exciton diffusion length considerably shorter than the absorption length of the donor material by providing a charge-separating heterojunction lying well within the diffusion length of each photogenerated charge-carrier pair. However, the increased interfacial area produces opportunities for recombination; and the expected increase in disorder (and wavefunction localization) due

to mixing can hinder the coherent processes that help charge separation<sup>67</sup>. Both these effects contribute to the open-circuit voltage deficit in organic photovoltaics.

In this context, it is interesting to note that the lower degree of order in the mixed polymer–fullerene phase compared with the pure polymer and fullerene phases has been suggested to help prevent charge recombination<sup>84</sup>. Since disorder is expected to reduce conjugation, it acts to increase the ionization potentials and decrease the electron affinities of the species present in the mixed phase. As a result, a hole on a chain in the polymer pure phase (with low ionization potential) would have an energetic barrier to jump back into a chain (with higher ionization potential) in the mixed phase. Thus, a compelling bulk heterojunction architecture could be one where the mixed phase is designed to remain reasonably ordered to exploit coherence effects, but has higher donor ionization potential and acceptor electron affinity than in the pure domains (for instance, as a consequence of polarization effects<sup>85</sup>) to prevent recombination. Recent work has shown the importance of order for open-circuit voltage, even on the mesoscale, in OPV active layers<sup>86</sup>.

Planar OPV devices will also become a possibility once vastly expanded exciton diffusion lengths are realized. One can envisage moving towards this goal by making use of the coherence phenomena discussed in this work. The gain in voltage available is of the order of  $kT \times \ln[\text{roughness factor}]$ , with the roughness factor corresponding to the ratio between interfacial area and geometric area. Thus, for example, if the roughness factor of a present-day bulk heterojunction device is in the vicinity of 40, then fully 100 mV of additional voltage are available. This offers the potential to provide a more than 10% further increase in power conversion efficiency, as long as current and fill factor, crucially, are both retained. This, once again, would demand diffusion lengths well in excess of 100 nm, corresponding to directed/linear excursions of order at least 100 molecules, and random walks over thousands of molecular chromophores. A gain in 100 mV in voltage will represent a significant step forward for OPV, although it should be pointed out that the remaining open-circuit voltage deficit will require additional parallel efforts such as on the efficient separation of excitons at more modest energetic cost than implemented in today's heterojunctions (Fig. 5b; ref. 67).

### Outlook and predictions

Organic photovoltaics have a number of interesting advantages over some of their inorganic counterparts: they are free of heavy metals and free of mobile halide anions, and they can be successfully stabilized as a result of decades' worth of important work. These materials operate in the distinct transport regime we have discussed that is more akin to biological systems than inorganic materials. The success of biological systems in pervasive and 'efficient enough' energy harvesting provides a contrasting and intellectually stimulating precedent for continued advances in this parallel domain. The power of the biological precedent of coherence in energy transport is its enablement of the ultimate paradigm in efficient photocarrier transport: one that achieves long-range transport. This could obviate reliance on excess interfacial area, which leads to a loss in open-circuit voltage. To combine excellent exciton or charge diffusion with selective contacts (electron and hole filters) — without reliance on a built-in field within the active layer — provides the needed net-current-flow directionality without undue cost to voltage. A coherence-driven solar cell does not require any appreciable electric field to separate charges; clearly, the conditions at play in natural systems illustrate proof of possibility of these simultaneous qualities.

Looking more widely, biological energy-harvesting systems offer a number of other qualities desired, and not yet achieved, in artificial systems. The low cost and carbon footprint of self-organized, self-sustained and self-repairing growth of photosynthetic systems is the

envy of those working on high-temperature solar materials, such as crystalline silicon with its time to pay back the energy consumed — with CO<sub>2</sub> emitted — in solar module fabrication. Additionally, fully integrated photon-to-chemical conversion, which obviates the need for highly conductive and highly transparent layers, is the dream of the artificial photosynthesis community, a vision already implemented in natural photosynthetic systems. Finally, perhaps the largest qualitative difference between photosynthesis and artificial photosynthesis today resides in the nature of the chemical products synthesized: the heterogeneous catalysis community in particular stands to learn from the compelling precedent of multistep CO<sub>2</sub>-to-multicarbon molecules that ultimately provide the cost-effective, energy-dense liquid-carbon-based fuels on which industrialized society relies.

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## Competing financial interests

The authors declare no competing financial interests.