Photosynthetic systems harness sunlight to power most life on Earth. In the initial steps of photosynthetic light harvesting, absorbed energy is converted to chemical energy with near-unity quantum efficiency. This is achieved by an efficient, directional and regulated flow of energy through a network of proteins. Here, we discuss the following three key principles of this flow and of photosynthetic light harvesting: thermal fluctuations of the protein structure; intrinsic conformational switches with defined functional consequences; and environmentally triggered conformational switches. Through these principles, photosynthetic systems balance two types of operational costs: metabolic costs, or the cost of maintaining and running the molecular machinery, and opportunity costs, or the cost of losing any operational time. Understanding how the molecular machinery and dynamics are designed to balance these costs may provide a blueprint for improved artificial light-harvesting devices. With a multi-disciplinary approach combining knowledge of biology, this blueprint could lead to low-cost and more effective solar energy conversion. Photosynthetic systems achieve widespread light harvesting across the Earth’s surface; in the face of our growing energy needs, this is functionality we need to replicate, and perhaps emulate.

1. Introduction

Sunlight is a ubiquitous and abundant energy source. In just 1 h, enough energy hits the Earth’s surface (approx. 4.320 J) to provide for human consumption over an entire year (approx. 4.120 J) [1]. The challenge lies in efficiently capturing and storing this energy. Photosynthetic organisms have met this challenge, and are able to use sunlight to fuel almost all life on Earth [2]. The molecular machinery behind this large-scale power conversion process can serve as a guide for the development of solar energy sources [3–6]. The efforts towards artificial photosynthesis can be considered in three categories: (i) create elements inspired by photosynthetic systems [7–11]; (ii) incorporate components from photosynthetic organisms [12–15]; and (iii) use living organisms, either wild-type or genetically modified [16–19]. Recent work upregulating light harvesting through downstream processes has been particularly promising. The workflow behind all of these efforts is summarized in figure 1. Essentially, realization of a sustainable solar energy device requires that we understand the mechanisms of photosynthesis, use these mechanisms to develop smarter designs and with these designs build optimized devices. Finally, advocating for the widespread usage of these devices is an equally critical component. We focus on the first step of this process: understanding natural photosynthesis. To allow this understanding to be useful for later steps, we highlight general principles observed in photosynthetic light harvesting, which may be implemented in artificial systems dramatically different from the natural systems.

Several aspects of photosynthesis exhibit functionality that far exceeds what we can currently replicate in devices. Although overall power conversion efficiency is, at best, only 7% [20], in the early events in photosynthesis, absorbed sunlight is converted to electricity with near-unity quantum efficiency [2,20]. This electricity is part of generating the transmembrane electrochemical potential that drives photosynthesis. This remarkable efficiency is achieved by a series of energy transfer steps through a network of pigment–protein complexes (PPCs),

as shown in figure 2. PPCs are carotenoids and chlorophylls surrounded by a protein matrix. Energy migrates hundreds of nanometres through this network to reach the reaction centre (RC), where the energy drives an electron transfer chain, which, in turn, drives downstream biochemistry [2,21]. How photosynthetic systems achieve an efficient and directional energy flow remains incompletely understood.

In most systems, the majority of PPCs are the antenna complexes, which absorb sunlight and perform the initial energy transfer steps. While the antenna complexes differ in structural motif across organisms, the RC structures are conserved [4]. The RCs are metabolically expensive to construct, as they must complete a complex electron transfer chain [2]. The antenna complexes lack electron transfer functionality, but ensure the electron flux is optimal. That is, water-splitting requires four electrons, and all four electrons must arrive before the intermediates relax. At the same time, electrons arriving faster than the speed of the water-splitting reaction cannot be used, and may generate deleterious products. These two limits mean that the rate of charge generation must be regulated. The antenna complexes are responsible for this regulation, and implement multiple multi-time-scale processes that prevent the build-up of excess energy. These processes can obfuscate the intrinsic characteristics of the antenna complexes as well as the mechanisms of the individual processes.

Only through understanding the behaviour and dynamics of PPCs, however, can we understand how photosynthetic systems achieve high quantum efficiency in conversion of absorbed sunlight to electricity, and how this efficiency responds to the orders of magnitude changes in solar flux seen in nature. In studying the response to these changes in solar flux, one constraint that emerges is the balance of two types of costs: metabolic cost and opportunity cost. Metabolic cost is the energy spent to construct and repair and insert the molecular machinery. Opportunity cost is not capturing energy owing to inoperability or non-optimal functioning of the molecular machinery [22]. Optimizing these two costs guides the principles behind light harvesting under natural conditions.

Here, we describe three key principles by which natural photosynthesis achieves efficient and effective light-harvesting functionality. The identification of these principles can aid the development of solar energy devices. We focus on phenomena observed by studying single antenna complexes. For the first principle, we explore how these systems are robust to fluctuations in the protein structure owing to thermal motion. We characterize the resultant energetic disorder by experimentally characterizing the distribution of behaviours. For the second principle, we discuss how discrete conformational switches allow one protein to perform multiple functions. For the third principle, we examine how the cellular environment can be a trigger for such conformational changes, and how this enables the protein to participate in a system-wide feedback loop. We conclude this perspective with a discussion of how these principles can be applied to the design of an artificial photosynthetic device.
whereas another widely studied photosynthetic complex, the Fenna–Matthews–Olson complex, has an inhomogeneous broadening of just 35 cm$^{-1}$ [35]. To investigate the intrinsic inhomogeneity, we apply the ABEL trap to study single LH2 complexes.

By simultaneously recording fluorescence intensity, lifetime and spectra, changes in the excited state manifold can be explored. Intensity and lifetime traces of two representative complexes are shown in figure 3b,c. The corresponding fluorescence spectra for the shaded intensity levels in figure 3b are displayed in figure 3d. As illustrated here, occasionally (approx. 5%) the intensity changes were accompanied by a spectral change, in this case a 5 nm red shift. By examining thousands of individual complexes, the intensity/lifetime changes and spectral changes were found to be uncorrelated. Furthermore, the spectral changes were small; the spectra shifted 5 nm or less. At these wavelengths, a 5 nm shift corresponds to a small amount of energy, only approximately $1/2kT$ [32]. Thus, the shifts induced by thermal fluctuations are not large enough to create either a barrier (shift to higher energy) or a trap (shift to lower energy), and so the spectral dynamics observed will not interfere with the energy transfer dynamics.

Overall, to be robust to the disorder from thermal fluctuations, the protein functions so that the fluctuations produce energy shifts $<kT$. With this constraint, photosynthetic systems balance both metabolic and opportunity costs: they do not pay the metabolic cost to construct a rigid system without fluctuations, e.g. by inserting multiple bonds or strong electrostatic interactions into the protein, nor do they pay the opportunity cost of lost light harvesting from fluctuations interrupting the energy transport chain.

### 3. Multi-functionality through conformational switches

As shown in the traces in figure 3b,c, intensity and lifetime primarily exhibit correlated changes. Similar intensities occasionally will have very different concomitant lifetimes, however, indicated with an asterisk in figure 3c. To investigate the correlations between intensity and lifetime, each period of constant intensity with its concomitant lifetime is represented by the direct proportionality between states A and B, state B exhibits an increased rate of quenching, or non-radiative decay off the emissive state. Non-radiative decay occurs through the electronic excitation dissipating into the vibrations on the pigment, which, in turn, transfer to the vibrations in the protein. A conformational change could produce a conformation that facilitates this process through increased coupling between the electronically excited state and the pigment vibrations or between the vibrations on the pigment and the vibrations on the protein. Thus, state B is most likely to be formed through a conformational change [32].

These results demonstrate that states A and B arise from a photoactivated, reversible quenching process [32]. As illustrated by the direct proportionality between states A and B, state B exhibits an increased rate of quenching, or non-radiative decay off the emissive state. Non-radiative decay occurs through the electronic excitation dissipating into the vibrations on the pigment, which, in turn, transfer to the vibrations in the protein. A conformational change could produce a conformation that facilitates this process through increased coupling between the electronically excited state and the pigment vibrations or between the vibrations on the pigment and the vibrations on the protein. Thus, state B is most likely to be formed through a conformational change [32].

A conformational change is also supported by the changes in the relative populations of states A and B with excitation fluence. The rate of transition from state A to state B increases roughly linearly with excitation fluence, indicating a photoactivated process [32]. Each photon deposits enough energy
into the protein to enable a conformational change, which causes the probability of the transition to increase with the number of photons [36]. In contrast, the rate of transition from state B to state A is independent of excitation fluence, indicating a thermal process [32]. State C, however, most likely arises from an irreversible photodegradation process [32].

The two conformations of states A and B, and their dynamics allow a single protein to have both light-harvesting and photoprotective functionality. Under high light intensities, many LH2 complexes switch into a quenched state via a conformational switch, where they can safely dissipate excess energy. Under low light intensities, most LH2 complexes revert into the unquenched state via thermal fluctuations. Instead of assigning a single function to a single protein, here, we observe that photosynthetic organisms embed multifunctionality into LH2. In this way, they control the metabolic cost associated with protein synthesis.

4. Environmentally controlled functionality

In addition to the intrinsic conformational heterogeneity and photo-induced conformational dynamics discussed in §3, photosynthetic proteins can also exhibit conformational dynamics in response to changes in the cellular environment caused by fluctuations in light intensity [22]. In particular, these environmentally induced conformational dynamics have been observed and explored in higher plants, and so, in this section, we focus on these type of dynamics in green plants. Under low light conditions, such as a cloudy day, all absorbed sunlight is converted to electricity for photosynthesis [20]. Under high light conditions, such as direct sunlight, the capacity of the antenna complexes to absorb and transfer energy exceeds the capacity of downstream photosynthesis. To prevent a build-up of excess energy, plants and algae dissipate this energy through a series of multi-time-scale processes. These processes are collectively known as non-photochemical quenching (NPQ) [37]. The short-time, energy-dependent component of NPQ is qE, and is triggered by a pH drop in the lumen and the resulting electrochemical gradient across the membrane [37,38]. While many of the time scales of NPQ have been identified, the mechanism and specific PPC responsible for quenching remains under debate. Specifically, which PPC, which carotenoid, and whether or not charge transfer states play a role have all been discussed [37–39].

One known effect of the drop in lumen pH is to cause PsbS, a non-pigment binding photosynthetic protein, to activate quenching [40]. In this way, the environmental conditions control whether PsbS is inactive or active. Thus, the change here is not isolated to a single protein, as discussed in §3, but rather is part of a larger feedback loop within the organism [22]. An area of active investigation is the impact of the environmental conditions associated with high light on the primary antenna complex from green plants, light-harvesting complex II (LHCCI). LHCCI is trimeric, and each monomer contains 14 chlorophyll (Chl), six Chl-b and eight Chl-a, and four carotenoids surrounded by a protein matrix [24]. Energy rapidly transfers to the Chl-a, and fluorescence occurs out of the Chl-a band [41–47]. On-going efforts are focused on characterizing the changes in the excited state manifold of LHCCI under conditions that mimic high light. The questions are whether LHCCI is the site of dissipation, and, if so, what the photophysical mechanism of dissipation is.

Figure 4 shows the behaviours of single LHCCI complexes. Two intensity traces of single LHCCI complexes are shown in figure 4a. These traces exhibit representative dynamics. The intensity changes from the higher (dominant) level to a lower level, and vice versa (figure 4e, right). The individual complexes also transiently enter into and recover from a dark state in a process known as blinking, observed in the brief disappearance of fluorescence (e.g. event at 35 s in figure 4e, left). Assuming a constant absorbance, the fluorescence decrease indicates a quenching process is occurring in both the low-intensity complexes and the ones in a dark state. To investigate the distribution of intensity levels, we construct a histogram from all periods of constant intensity as determined by a change-point-finding algorithm (figure 4b). The histogram shows a significant population in both the higher intensity and lower intensity levels, revealing a significant population of LHCCI in a quenched conformation. The correlation of this quenched conformation with conditions that mimic high light is currently under investigation. Previous experiments have extensively studied the correlation between the dark states and conditions that mimic high light. In this work, blinking was shown to correlate with these conditions, leading to the hypothesis that blinking underlies qE [48]. Additionally, experiments suggest the underlying mechanism may be dissipation on the carotenoids by increased coupling between the Chl and the carotenoids [49,50] or charge transfer [51,52].

While the detailed molecular mechanisms require further experimentation, it can be argued that NPQ serves as a feedback loop to optimize between metabolic cost and opportunity cost. In this way, systems are able to protect their expensive molecular machinery, while keeping the input, the photon energy, as close to the capacity of downstream photosynthesis as possible. One process by which this feedback loop is implemented is...
through protein conformational changes in response to changes in the local environment, illustrating the ability of biological systems to design feedback loops that extend throughout the organism.

5. Application to artificial devices

Photosynthesis generates enough energy from sunlight to power most life on Earth. Thus, it provides a natural source of inspiration for improving the design of artificial solar energy devices. There are several principles of the biological circuitry that could improve these devices. Here, we have highlighted three of these principles: we have discussed how photosynthetic proteins are robust to disorder; exhibit multi-functionality through conformational switches; and have environmentally controlled functionality.

One overarching tenet that emerges from studying biological systems is that biological structures are dynamic. They are constantly fluctuating and responding to the organism’s changing needs. Often, artificial devices are designed as static structures that are either operational or broken. However, biological systems exploit their intrinsic lack of rigidity to embed additional functionality in thermal fluctuations and multiple conformations. In this way, they are able to balance metabolic cost and opportunity cost under the varying environmental conditions found in nature. Current research focusing on building bioinspired devices has achieved impressive initial results. Photosynthetic systems have evolved over billions of years to balance metabolic and opportunity costs by dynamically adapting to the local environment heterogeneity and dynamic structures. This behaviour could be replicated in artificial systems by switching the device from one mode to another, such as through a chemical transition [10], or selectively using concentrators to control the amount of incident sunlight. Additionally, the observation of dynamic and static heterogeneity suggests that natural systems do not require perfect structural and functional precision, and this type of flexibility could be advantageous in the design and manufacture of cost-effective devices.

By incorporating the dynamic behaviours observed in nature, the performance of artificial devices could be improved to meet our increasingly critical energy needs. With these steps, we move down the steps illustrated in figure 1. However, this is a fundamentally interdisciplinary effort, requiring expertise in biology, material science and engineering. As a result, success requires greater interdisciplinary communication and cooperation. This could be initiated through efforts such as an exchange between natural and artificial photosynthetic researchers, and sustained through funding projects requiring multi-disciplinary teams. The studies of biological dynamics described here are one piece of the process of understanding and developing new approaches to solar energy conversion.

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References

9. Moore GF, Brudvig GW. 2011 Energy conversion in photosynthetic systems by switching the device from one mode to another, adapting to the local environment heterogeneity and dynamic structures. This behaviour could be replicated in artificial systems by switching the device from one mode to another, such as through a chemical transition [10], or selectively using concentrators to control the amount of incident sunlight. Additionally, the observation of dynamic and static heterogeneity suggests that natural systems do not require perfect structural and functional precision, and this type of flexibility could be advantageous in the design and manufacture of cost-effective devices.

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