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## Making every photon count: Optical nanoscopy and single molecule spectroscopy applied to natural light-harvesting materials

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Artificial photosynthesis is envisioned by many to be an important component of mankind's long-term energy solution. Bio-inspired photosystems appear most promising, but the first constructs over the past few years have clearly pointed to the infancy of this field [1]. To make progress, a very detailed understanding of natural photosynthesis is required in order to wisely extract the most important design principles. Here, the primary steps of photosynthesis – light harvesting and charge separation – are the most crucial to ensure that the energy of an absorbed photon is stored with a sufficiently high probability, which is commonly 90-100% under conditions of low solar radiation! The latter of the two – charge separation – is understood sufficiently well for the purpose of designing artificial devices. However, the former – light harvesting – has proven to be a very complex process and further experimental and theoretical advances are being awaited. One such promising technique is known as single molecule spectroscopy (SMS), where the averaging effect of an ensemble is overcome by investigating dynamical processes of a single light-harvesting unit.

SMS, in fact, laid the foundation for optical nanoscopy, also known as superresolution microscopy, which has developed tremendously since the first experimental results appeared less than 10 years ago [2]. The new set of techniques enables optical imaging of structures down to the nanometer scale, a two orders of magnitude improvement over the diffraction limit. Application of the technique was found particularly useful in biology, because subcellular structures can now be unraveled using light. Optical nanoscopy is widely regarded as one of the most important developments in biophysical chemistry and chemical physics during the past two decades. It may therefore not be surprising that the founders were awarded the 2014 Nobel Prize in Chemistry.

The first part of the presentation will highlight the principles of optical nanoscopy, point out the limitations in applying the techniques to autofluorescent systems, such as photosynthetic light-harvesting complexes, and encourage application to other areas of materials science research where optical imaging on the mesoscopic scale will be instructive. The second part of the presentation will highlight three design principles of photosynthetic light harvesting that were revealed using SMS.

1. Results

In nature, proteins strongly bind a high density of chromophores to form extended, complex networks of light-harvesting antennae, operating at a remarkable speed and efficiency. Even more intriguing is the level of adaptability to environmental influences at the macromolecular scale to maintain a constant energy throughput at the photochemical reaction centre where charge separation occurs. One important part of this regulation involves very efficient absorption of solar energy and thermal dissipation of any excess excitation energy, leading to a finely tuned feedback self-protection mechanism. This should be done despite (or rather: with the help of) structural fluctuations of the protein on a wide range of timescales. By mimicking the natural conditions that would give rise to the self-protection state under levels of intense sunlight, we have shown that the main light-harvesting complex of plants - LHCII - uses intrinsically available thermal energy dissipation channels by finely controlling its structural disorder on timescales of ms to tens of seconds [3]. Furthermore, using a mutant of LHCII where the terminal emitter chromophore cluster is disrupted, it was demonstrated that the terminal emitter cluster in wild-type LHCII is responsible for energy transfer robustness due to the combination of the particular energy gaps of the lowest exciton states and the strong excitonic coupling of the chromophores in this cluster [4]. Finally, based on the spectral dynamics of light-harvesting complexes from plant photosystem I and II, we can conclude that the particular protein microenvironment of a chlorophyll dimer is responsible for considerable tuning of the extent of shade absorption of plants [5].

2. References

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## Are you currently a postgraduate student? (Yes/No)

No

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