Title	Quantasome Architecture as Biomimetic Solution for Efficient Charge Separation

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# months (min.3)	6

Project description (2 page max):

The quest for sustainable energy sources has led to a profound interest in understanding and replicating the remarkable efficiency of natural photosynthesis. In this context, this project outlines a comprehensive investigation into biomimetic photosynthesis, focusing on regulating exciton dynamics in supramolecular stacks mimicking chloroplast thylakoids. The project aims to unravel the intricacies of charge separation and energy transport processes critical for efficient solar energy conversion, thereby contributing to the development of next-generation photosynthetic technologies.

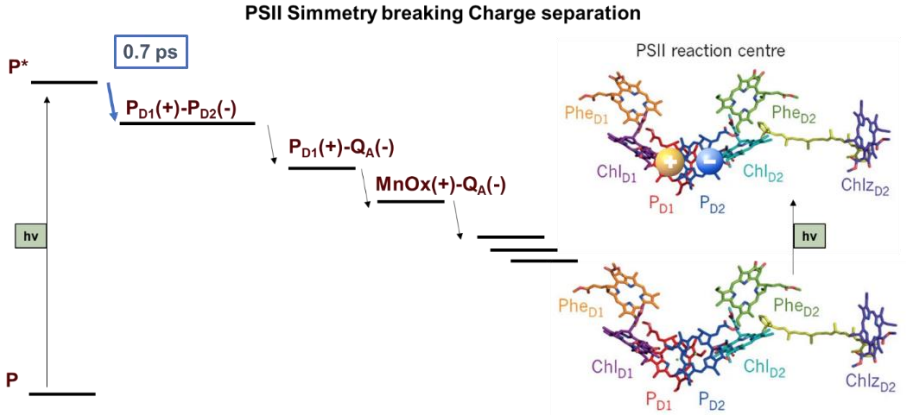

Figure 1. Decay pathway of photoexcited natural PSII, inset on SB-CS ultrafast event

Nature has perfected the art of solar energy conversion through billions of years of evolution, exemplified by the efficiency of photosynthesis in leaves. The hierarchical architecture of photosynthetic systems in natural leaves serves as an ideal template for biomimetic systems. Inspired by this, the proposed research aims to mimic nature's design principles to create artificial photosynthetic systems (APS) capable of performing ultrafast quantitative symmetry-breaking charge separation in femtoseconds regime and efficient solar energy conversion.

Adhering to nature's blueprint, the group has recently pioneered the creation of the first artificial "quantasome" (QS): a supramolecular photosynthetic material. This system involves a core–shell architecture, generated by the self-assembly of dicationic perylene bisimide derivatives (PBI^{2+}, the antennae) and a tetraruthenium polyoxometalate (Ru_4POM, the oxygen-evolving center). The so formed $[PBI]_5Ru_4POM$ complex, acts as photosynthetic QS exhibiting quantitative faradic efficiency and excellent performances on electrode. Moreover, in preliminary ultrafast spectroscopy experiments the QS reported quantitative charge separation and slow recombination, making this architecture a new starting point to further improve solar energy conversion in artificial PSII photosystems.

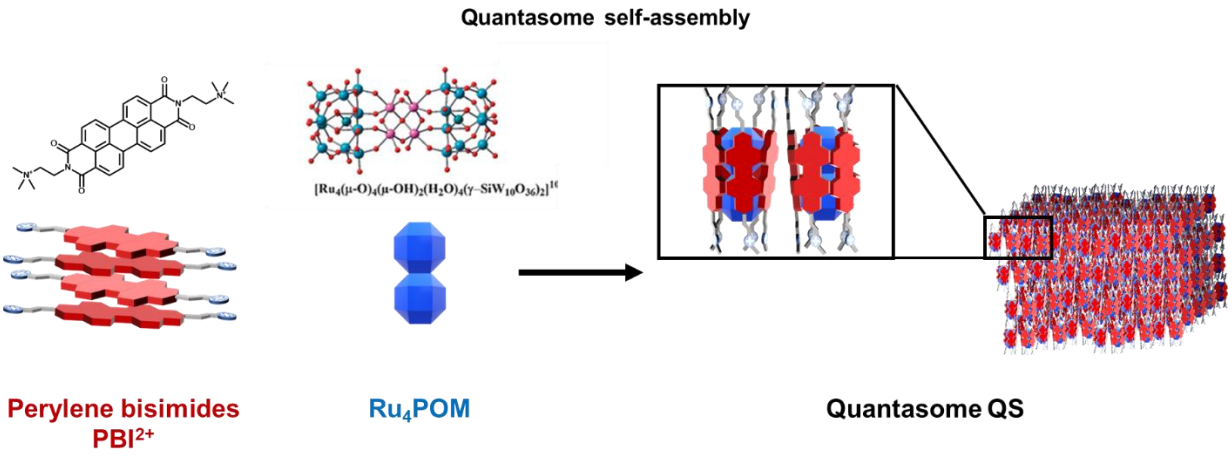

Figure 2. Self-assembly between PBIs and Ru_4POM to form the photosynthetic Quantasome (QS) complex.

Research Objectives:

i) Investigate the dynamics of exciton formation and decay in second-generation QS structures, advancing the understanding of artificial photosynthesis. ii) explore symmetry-breaking charge separation (SB-CS) mechanisms in supramolecular PBI stacks and QS to emulate natural photosynthetic processes and develop design principles to produce efficient energy conversion materials. iii) characterize the structural and functional properties of the charge separated state and prolong their lifetime to boost hole accumulation for efficient artificial photocatalytic processes.

Methodology:

The PhD candidate will join a multidisciplinary and enthusiastic group and the daily tasks will span from the organic synthesis of new chromophores and their supramolecular aggregates to their structural and photophysical characterization with state-of-the-art techniques such as NMR, FT-IR, Raman, DLS, PXRD, Absorption and Emission spectroscopy, Circular Dichroism, Cyclic Voltammetry. In parallel, Advanced Electron Paramagnetic Resonance (EPR) experiments on paramagnetic probes, populated in the photochemical process, will be performed in the EPR group, where a significant array of instrumental facilities, coupled to laser photoexcitation, is available. The international collaboration with C. Tait provides the access to the EPR facilities at the University of Oxford to perform experiments which require high field and specific set-ups. The PhD candidate will be hosted for a six-month period in the group of C. Tait where he/she will be trained by experts in the application of photo-induced EPR to Artificial Photosynthesis. Furthermore, the PhD candidate will have the possibility to collaborate with different groups on time-resolved spectroscopic techniques, including transient absorption and fluorescence anisotropy, and on computational simulations that will complement experimental findings to provide insights into the underlying mechanisms.

Publications: M. Bonchio et al., *Chemistry–A European Journal*, **2024**, e202303784; M. Bonchio et al*., Journal of the American Chemical Society*, **2022**, 144 (31), 14021-14025; M. Bonchio et al. *Nature Chemistry*, **2019**, 11 (2), 146-153; M. Di Valentin et al., *Journal of the American Chemical Society*, **2023**, 145 (42), 22859-22865; M. Di Valentin et al., *Journal of the American Chemical Society*, **2023**, 145 (1), 455-464; M. Di Valentin et al., *Physical Chemistry Chemical Physics* **2024**, 26, 3842-3856.