# Engineering Quantum Coherence in Bio-Inspired Systems for Efficient Solar-Energy Induced Charge Separation

Elisabet Romero

*ICIQ - The Institute of Chemical Research of Catalonia, Tarragona, Spain*

Photosynthesis is the fundamental biological process by which solar energy is converted into fuel in four basic steps: light harvesting, charge separation, water splitting and fuel generation. Photosynthesis therefore holds the key to the efficient use of solar energy by humans employing abundant and renewable materials. At the heart of Photosynthesis, the pigment-protein complex photosystem II reaction center (PSII RC), performs charge separation with near unity quantum efficiency despite its highly disordered energy landscape, and thus converts sunlight to electrochemical energy.

To achieve this amazing feat, the PSII RC exploits *The Quantum Design Principles of Photosynthetic Charge Separation*[1-2], complementary and interrelated solutions to ensure rapid forward and irreversible transfer of energy and electrons within a disordered and fluctuating environment. Therefore, these principles provide a guide for the rational design and construction of systems able to transfer energy and electrons with high efficiency and in the right direction.

In the first part of my talk I will describe these design principles (summarized below) in greater detail:

<u>collective excited states</u>[3] (<u>excitons</u>, that is, bound electron–hole pairs) increase the absorption cross-section, minimize the energy and/or electron transfer steps and are less sensitive to energetic disorder;

<u>multiple charge-separation pathways</u>[4] provide functional flexibility;

<u>coherent mixing between excitons and charge-transfer (CT) states promoted by resonant vibrations</u>[1] provides the optimal energetic configuration for ultrafast and irreversible electron transfer;

<u>the smart protein matrix controls the selection of the charge-separation pathways and the presence of coherence</u>[2].

Special attention will be paid to quantum coherence between the electronic states involved in energy or electron transfer which, in this context, introduces correlations between the wavefunctions of these states[5] enabling the excitation energy to move rapidly and to coherently sample multiple pathways in space[6] (Figure 1).

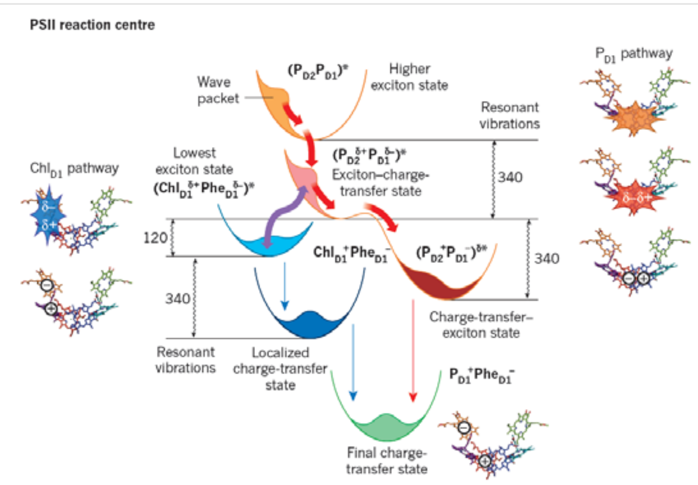


**Figure 1**. Coherent charge separation in the PSII RC[2].

In the second part of my talk, I will focus on the implementation of *The Quantum Design Principles of Photosynthesis*[2] in engineered light-harvesting and charge-separation units with the potential to perform efficient energy and electron transfer processes, respectively. These bio-inspired systems are composed by two elements:

<u>The chromophores</u> or light-absorbing molecules that participate in energy and/or electron transfer process, and

<u>The protein</u> folded in an α-helix structure and with two main functions: to provide a matrix to maintain the chromophores in a specific position via several kinds of interactions (e.g. dispersive interactions, covalent bonds, hydrogen bonds, etc), and to modulate the energy of the chromophores via these interactions.

These synthetic biological proteins (so-called maquettes[7]) equipped with chromophores have been shown to be able to reproduce light-activated energy and electron transfer without importing the complexity common to natural proteins[7-10]. Their design is founded on a structurally stable (even at temperatures up to 90°C) water-soluble 4-α-helix protein monomer that is able to accommodate various types of chromophores at different distances and relative orientations in its hydrophobic interior as well as other molecules at the exterior of the protein structure. For instance, catalysts could be coupled to the charge-separation units with the final goal of achieving the cost-effective conversion of solar energy to fuel.

*References*


1 Romero, E., Augulis, R., Novoderezhkin, V. I., Ferretti, M., Thieme, J., Zigmantas, D. & van Grondelle, R. Quantum coherence in photosynthesis for efficient solar-energy conversion. *Nat. Phys.* **10**, 676-682 (2014).

2 Romero, E., Novoderezhkin, V. I. & van Grondelle, R. Quantum design of photosynthesis for bio-inspired solar-energy conversion. *Nature* **543**, 355-365 (2017).

3 Romero, E., Diner, B. A., Nixon, P. J., Coleman, W. J., Dekker, J. P. & van Grondelle, R. Mixed exciton-charge-transfer states in photosystem II: Stark spectroscopy on site-directed mutants. *Biophys. J.* **103**, 185-194 (2012).

4 Romero, E., van Stokkum, I. H. M., Novoderezhkin, V. I., Dekker, J. P. & van Grondelle, R. Two different charge separation pathways in photosystem II. *Biochemistry* **49**, 4300-4307 (2010).

5 Scholes, G. D., Fleming, G. R., Olaya-Castro, A. & van Grondelle, R. Lessons from nature about solar light harvesting. *Nat. Chem.* **3**, 763-774 (2011).

6 Cheng, Y. C. & Fleming, G. R. Dynamics of light harvesting in photosynthesis. *Annu. Rev. Phys. Chem.* **60**, 241-262 (2009).

7 Moser, C. C., Sheehan, M. M., Ennist, N. M., Kodali, G., Bialas, C., Englander, M. T., Discher, B. M. & Dutton, P. L. in *Methods in Enzymology* Vol. 580 (ed L. Pecoraro Vincent) 365-388 (Academic Press, 2016).

8 Koder, R. L., Anderson, J. L. R., Solomon, L. A., Reddy, K. S., Moser, C. C. & Dutton, P. L. Design and engineering of an $O_2$ transport protein. *Nature* **458**, 305-309 (2009).

9 Farid, T. A., Kodali, G., Solomon, L. A., Lichtenstein, B. R., Sheehan, M. M., Fry, B. A., Bialas, C., Ennist, N. M., Siedlecki, J. A., Zhao, Z., Stetz, M. A., Valentine, K. G., Anderson, J. L. R., Wand, A. J., Discher, B. M., Moser, C. C. & Dutton, P. L. Elementary tetrahelical protein design for diverse oxidoreductase functions. *Nat. Chem. Biol.* **9**, 826-833 (2013).

10 Kodali, G., Mancini, J. A., Solomon, L. A., Episova, T. V., Roach, N., Hobbs, C. J., Wagner, P., Mass, O. A., Aravindu, K., Barnsley, J. E., Gordon, K. C., Officer, D. L., Dutton, P. L. & Moser, C. C. Design and engineering of water-soluble light-harvesting protein maquettes. *Chemical Science* **8**, 316-324, doi:10.1039/c6sc02417c (2017).