Cryo-electron microscopy extended into the quantum realms of photosynthetic energy transfer processes

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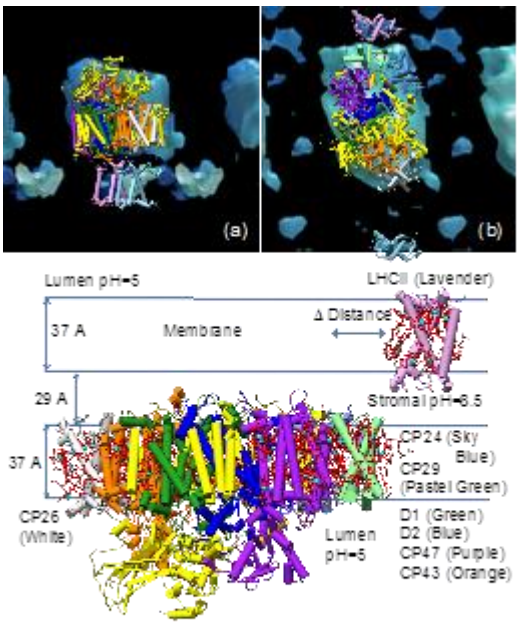

Figure 1. Crystal structures of PSII core (2AXT), LHCII (1RWT), and CP29 (3PL9) fitted into the *in situ* electron tomographic data viewed normal (a) and perpendicular (b) to the thylakoid membrane plane. Below, PSII atomistic model based on X-ray and cryo-EM data.

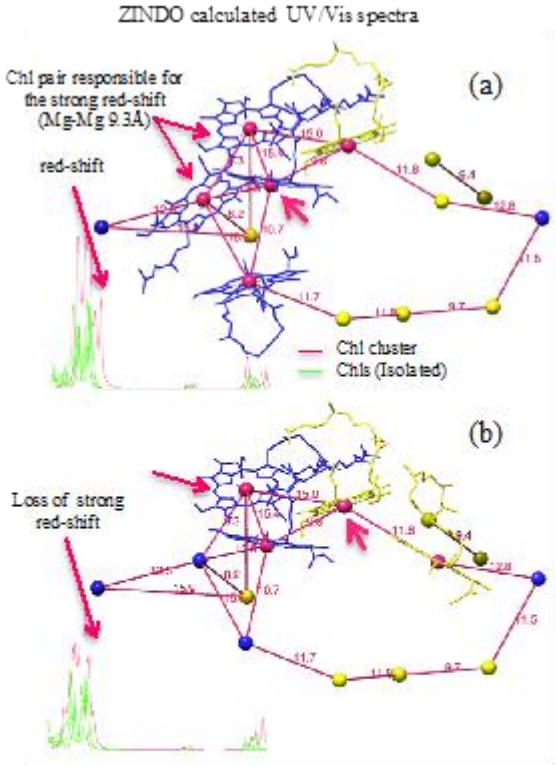

Figure 2. ZINDO calculated UV/Vis spectra for two possible Chl clusters in LHCII: (a) Chl cluster showing a red-shift. (b) Chl cluster without a red-shift. Blue-Chlb, Yellow-Chla, Magenta - Mg atoms of Chl included in the calculation.

Quantum phenomena are intrinsic to many phenomena in living systems such as birds and butterflies detecting the Earth's magnetic field, olfactory reception, ion channel-based concerted firing of action potentials culminating in conscious thoughts, quantum-tunneled electron travel in the respiratory chain, or the highly efficient quantum coherence-enabled energy-transfer processes employed by photosynthetic organisms[1]. With regards to the latter, checking the truth of the underlying principles is challenging as the experimental measurements employed may perturb a quantum system into a classical one[2]. This has, for instance, been a concern with 2DES experiments employing ultrashort broadband laser pulses when probing the quantum processes of photosynthesis[3]. Here we propose to uncover the foundations of photosynthetic energy transfer as a role model for other biological quantum systems using an approach that extends experimental data into those realms where the use of a non-perturbing approach is critically required. To this end, this project uses quantum chemical calculations to three-dimensionally map the patterns of quantum and non-quantum effects observed in the highly effective energy transfer process of photosynthesis. Atomistic details have been analyzed in the context of an *in situ* assembly as observed in higher plant thylakoid membranes in leaves of plants grown under controlled light regimes. There is a large body of structural data available for the individual components (X-ray crystallography) of the major photosynthetic complex photosystem II [PSII] and one data set for unperturbed, *in situ* PSII (electron tomography) that includes the 8 transmembrane subunits D1, D2, CP24, CP26, CP29, CP43, CP47, and LHCII. Combining X-ray and electron tomographic data into an atomistic model as a starting point (Fig. 1), this proposal uses both quantum and classical chemical calculations to unravel the energy transfer patterns within the confinement of a single PSII component (**intra-subunit**) and then across the subunit boundaries (**inter-subunit**) to cover the entire complex.

Intra-subunit: Preliminary theoretical investigations thus far have focused on UV-Vis spectra calculations to investigate the level of communication between chlorophyll chromophores in the LHCII subunit and the well-known strongly coupled special Chla/Chla pair (P680) in the D1/D2 subunit. The UV-Vis spectra of monomeric Chla and Chlb were calculated[4] using TD-DFT[5] with nine different functionals in ether (PCM) and compared to the experimental spectra of Chla and Chlb in ether. The dispersion corrected ωB97X-D functional produced the best spectra compared to experiment, therefore ωB97X-D was used to calculate the UV-Vis spectra for three Chl dimers: P680 Chla/Chla (D1/D2), 606/607 Chlb/Chlb (LHCII), and 605/606 (LHCII). As expected, the ωB97X-D results showed strong communication between the Chla/Chla (P680) pair that has a short Mg-Mg distance (8.15 Å) and are parallel to each other with respect to the porphyrin rings, as illustrated by a strong red-shift observed in the spectra of the dimer versus the monomers. The 606/607 Chlb/Chlb pair in LHCII a Mg-Mg distance of 9.33 Å and shows relatively strong communication but does not have the same level of communication as the P680 special pair. In contrast, the Chlb/Chlb pair at a Mg-Mg distance of 12.52 Å (605/606) and in a perpendicular configuration showed weak communication (no red-shift). To increase the number of Chl that could be reasonably investigated in a quantum level calculation, the less computationally intensive, semi-empirical ZINDO method was explored. ZINDO calculations on monomeric Chla and on the P680 were in qualitative agreement with the TD-DFT and experimental spectra. ZINDO calculations on clusters of up to 5 Chl in LHCII were calculated. Cluster composition was based on including Chl where the Mg atoms were within 16 Å of a single selected Chl. All possible combinations were calculated and a strong red-shift was only observed in clusters that contained two Chl's with a Mg-Mg distance of 9.3 Å and in a parallel orientation (Fig. 2). There were other Chl clusters in LHCII with Chls that had a shorter Mg-Mg distance, but showed little or no red-shift providing strong evidence of the angular dependence on the level of communication. In addition, it appears that in LHCII there is only one pair of strongly coupled Chl. While we have so far analyzed energy communication patters within LHCII and the reaction center residing within the D1/D2 heterodimer, the other major subunits of the PSII core [CP24, CP26, CP29, CP43, CP47] have still to be interrogated.

Inter-subunit: This work will start with a refined all atom model fitted to the *in situ* tomographic data set (Fig. 1). Based on the intra-subunit energy pathway peripheral chromophores delineating individual subunit-subunit contacts will be FRET-correlated to elucidate the most likely energy bridges between the two subunits in question. FRET uses the overlap integral of the orientation-dependent transition dipole-transition dipole interactions between two chromophores (or strongly coupled chromophore units) as determined from their UV-VIS spectra provided by the ZINDO calculations. Eventually the full dielectric patterns of the energy transfer pathway between all PSII core and antennae components will be determined inching through the entire complex from one chromophore couple to the next.

Basing the analysis of energy transfer on a biological macromolecular complex, means any conclusions drawn are *a priori* based on a system derived from earth-abundant elements thus making this approach particularly attractive for next generation technologies such as quantum computing, organic photovoltaics or artificial intelligence.

References

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