

Tuning mixing of electronic and vibrational states to steer excitonic dynamics

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Photosynthetic species evolved to protect their light-harvesting apparatus from photooxidative damage driven by intracellular redox conditions or environmental conditions. The Fenna-Matthews-Olson (FMO) pigment-protein complex from green sulfur bacteria exhibits redox-dependent quenching behavior partially due to two internal cysteine residues. We find that the redox chemistry of these two residues controls the degree of vibronic mixing thereby changing the excitonic dynamics and effectively activating an oxidative photoprotective mechanism. This readily switchable biological mechanisms suggests that fine tuning of vibronic coupling can dramatically change energy transfer as well as coherent dynamics. We use a simple (incoherent) Redfield model to show that the complex achieves this effect by tuning the site III energy via the redox state of its internal cysteine residues. Further efforts are underway to more accurately model this dynamics and to extend the ideas to inorganic systems.

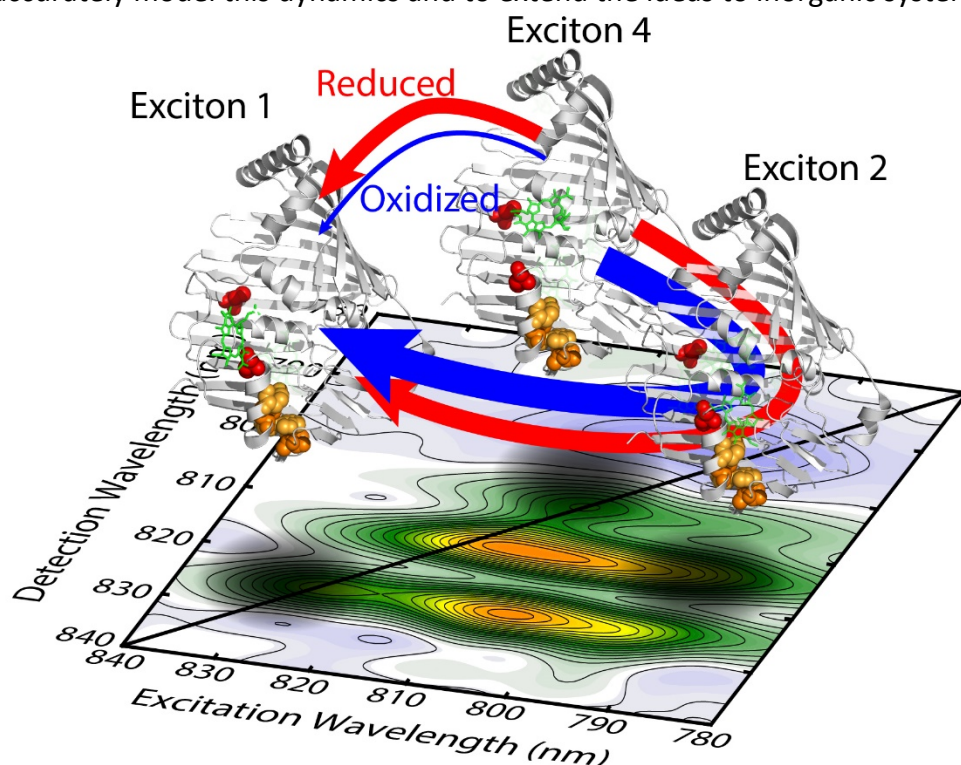


Figure 1: Energy transfer pathways under reduced (red) and oxidized (blue) conditions reroute energy flow through the FMO complex (gray) based on the oxidation of the cysteine residues (maroon). This shift causes the energy to pass through exciton 2 putting the energy near the tyrosine-tryptophan chain that can help to quench the excitation and protect the reaction center from oxidative damage.

Reference:

J.S. Higgins, L.T. Lloyd, S.H. Sohail, M.A. Allodi, J.P. Otto, R.G. Saer, R.E. Wood, S.C. Massey, P.-C. Ting, R.E. Blankenship, and G.S. Engel, "Photosynthesis tunes quantum mechanical mixing of electronic and vibrational states to steer exciton energy transfer", PNAS 118 e2018240118 (2021)