

Tuning vibronic coupling to affect energy transfer within a photosynthetic complex.

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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. Here, we will show evidence that a photosynthetic complex exploits the quantum mechanics of vibronic mixing to activate an oxidative photoprotective mechanism. We use two-dimensional electronic spectroscopy (2DES) to capture energy transfer dynamics in wild-type and cysteine-deficient FMO mutant proteins under both reducing and oxidizing conditions. Under reducing conditions, we find equal energy transfer through the exciton 4-1 and 4-2-1 pathways because the exciton 4-1 energy gap is vibronically coupled with a bacteriochlorophyll-*a* vibrational mode. Under oxidizing conditions, however, the resonance of the exciton 4-1 energy gap is detuned from the vibrational mode, causing excitons to preferentially steer through the indirect 4-2-1 pathway to increase the likelihood of exciton quenching. We use a 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. This result shows how pigment-protein complexes exploit the quantum mechanics of vibronic coupling to steer energy transfer.

