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Novel protection mechanisms against singlet oxygen formation by the Chl a molecule in the cytochrome b_6f complex of oxygenic photosynthesis SERGEI SAVIKHIN, Department of Physics, Purdue University, HANYOUP KIM, NARANBAATAR DASHDORJ, Department of Physics, Purdue University, HUAMIN ZHANG, JIUSHENG YAN, WILLIAM CRAMER, Department of Biological Sciences, Purdue University — A Chl molecule is known to produce highly toxic singlet oxygen under light illumination as a result of energy transfer from its triplet excited state to oxygen. To prevent that, a carotenoid is typically positioned close to a Chl molecule ($\sim$4 $\mathring{A}$) in Chl containing proteins to ensure rapid triplet-triplet energy transfer from Chl to carotenoid. Surprisingly, the X-ray structures of the cytochrome b_6f complex show that the β -carotene is much too far from the only Chl a found in this complex to provide effective protection by the usual triplet-triplet energy transfer mechanism. Our optical femtosecond time resolved experiments on diluted samples as well as on the single crystals of the b_6f complex suggest that the Chl a is protected by two novel mechanisms: (i) the yield of the Chl a triplet state formation is reduced through electron-transfer exchange with the nearby amino acid residues, and (ii) a long distance triplet energy transfer to carotenoid mediated by a third mobile molecule (NSF MCB- 0516939, NIH GM-38323).

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