Fluorescence quenching in aggregates of fucoxanthin-chlorophyll protein complexes: Interplay of fluorescing and dark states

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Diatoms, a major group of algae, account for about a quarter of the global primary production on Earth. These photosynthetic organisms face significant challenges due to light intensity variations in their underwater habitat. To avoid photodamage, they have developed very efficient non-photochemical quenching (NPQ) mechanisms. These mechanisms originate in their light-harvesting antenna – the fucoxanthin–chlorophyll protein (FCP) complexes. In 2019 the atomic resolution molecular structures of several FCP complexes were obtained: first, an FCP dimer from the pennate diatom *Phaeodactylum tricornutum* was resolved by crystallography[1], second, the structure of the PSII-FCP supercomplex from the centric diatom *Chaetoceros gracilis* was obtained by electron microscopy[2,3]. Recently, we evaluated if these available FCP structures are consistent with the previously obtained 2D spectroscopy results on FCP from another centric diatom *Cyclotella meneghiniana* and found that the published FCP structures are somewhat at odds with a few observations obtained from the ultrafast spectroscopy. We proposed a trimer-based FCP model for *Cyclotella meneghiniana*, that is consistent with experimental data[4].

Spectroscopic studies of NPQ *in vivo* are often hindered by strongly overlapping signals from the photosystems and their antennae. Fortunately, *in vitro* FCP aggregates constitute a useful model system to study fluorescence (FL) quenching in diatoms. In this work, we present streak-camera FL measurements on FCPa and FCPb complexes, isolated from a centric diatom *Cyclotella meneghiniana*, and their aggregates[5]. We find that spectra of non-aggregated FCP are dominated by a single fluorescing species, but the FL spectra of FCP aggregates additionally contain contributions from a redshifted emissive state. We relate this red state to a charge transfer state between chlorophyll *c* and chlorophyll *a* molecules. The FL quenching, on the other hand, is due to an additional dark state that involves incoherent energy transfer to the fucoxanthin carotenoids. Overall, the global picture of energy transfer and quenching in FCP aggregates is very similar to that of major light-harvesting complexes in higher plants (LHCII), but microscopic details between FCPs and LHCIIs differ significantly.

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