Unusual Temperature Dependence of Fluorescence caused by Aggregation

Low-Temperature Fluorescence of CP43 and CP47 Complexes from *Synechocystis* PCC 6803

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ABSTRACT

The absorption and fluorescence emission of His-tagged CP43 and CP47 antenna complexes isolated from *Synechocystis* PCC 6803 have been studied as a function of temperature between 4 K and RT, with the aim to detect differences with the corresponding spectra of these (non-His-tagged) complexes from spinach. When the complexes were diluted in glycerol solution with sufficient detergent (0.09% β–DM for His-tagged complexes) the 4 K emission spectrum of CP47 showed a blue-shifted main emission band compared to that of spinach (685.2 nm versus 690 nm), while that of CP43 showed a red-shifted main emission (684.9 nm versus 682.8 nm). The red shift of the latter is caused by a 2 nm red-shift of the narrow absorption band that is characteristic for CP43. The temperature dependence of the fluorescence quantum yield displayed a similar behaviour for all these complexes, i.e. an about two-fold increase of the yield upon cooling from RT to 4 K, which is typical for monomeric chlorophyll-protein complexes. Dilution in glycerol solution with smaller amounts of detergent (e.g., 0.03% for the His-tagged complexes) resulted in an unexpectedly strong temperature dependence of the fluorescence quantum yield, a very low yield at room temperature, red-shifts of the peaks at 4 K and even stronger red-shifts upon increasing the temperature (for CP47). We attribute all these characteristics to aggregation: if the excitations migrate among several complexes with inhomogeneously broadened red-most absorption bands, it will be easier to find a red form (explaining the red-shift at 4 K), and because uphill energy transfer will become more probable at higher temperatures, the effective domain size will increase (resulting in an even further shift to the red) as well as the possibility to meet a quencher (resulting in a lower fluorescence quantum yield). A similar behaviour was observed earlier for the main light harvesting complex LHCII.