

Fluorescence Line Narrowing and Δ -FLN Spectra in the Presence of Excitation Energy Transfer between Weakly Coupled Chromophores

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Supplemental Materials: FLN and Δ -FLN spectra calculated for a dimer of pigments with non-identical but overlapping SDF. Calculated FLN spectra for non-identical dimer (two 200 cm^{-1} wide SDF peaked at 15,000 and 14,900 cm^{-1} ; $S_{\text{phonon}} = 0.8$) are presented in Figure S1. Frames A, B and C depict spectra obtained for $V = 0$, $V = 1 \text{ cm}^{-1}$ and $V = 5 \text{ cm}^{-1}$. Black, blue, red, green, magenta and orange curves correspond to excitation frequencies of 14750-15250 cm^{-1} , with 100 cm^{-1} step. The grey curves in the background represent full SDF (solid curves) and partial SDF of the two pigments. Dashed curves are partial SDF of the pigments which are the lower-energy ones in their dimers; dotted curves represent the partial SDF of the higher-energy pigments. In both figures below the magenta arrows indicate the location of the weak ZPL at 15150 cm^{-1} , the orange arrows indicate the location of the weak ZPL at 15250 cm^{-1} . As can be seen, at the red edge of the combined band of the two pigments the FLN spectra do not depend on the inter-pigment coupling. Indeed, almost no higher-energy pigments of the pair can be found at these frequencies.

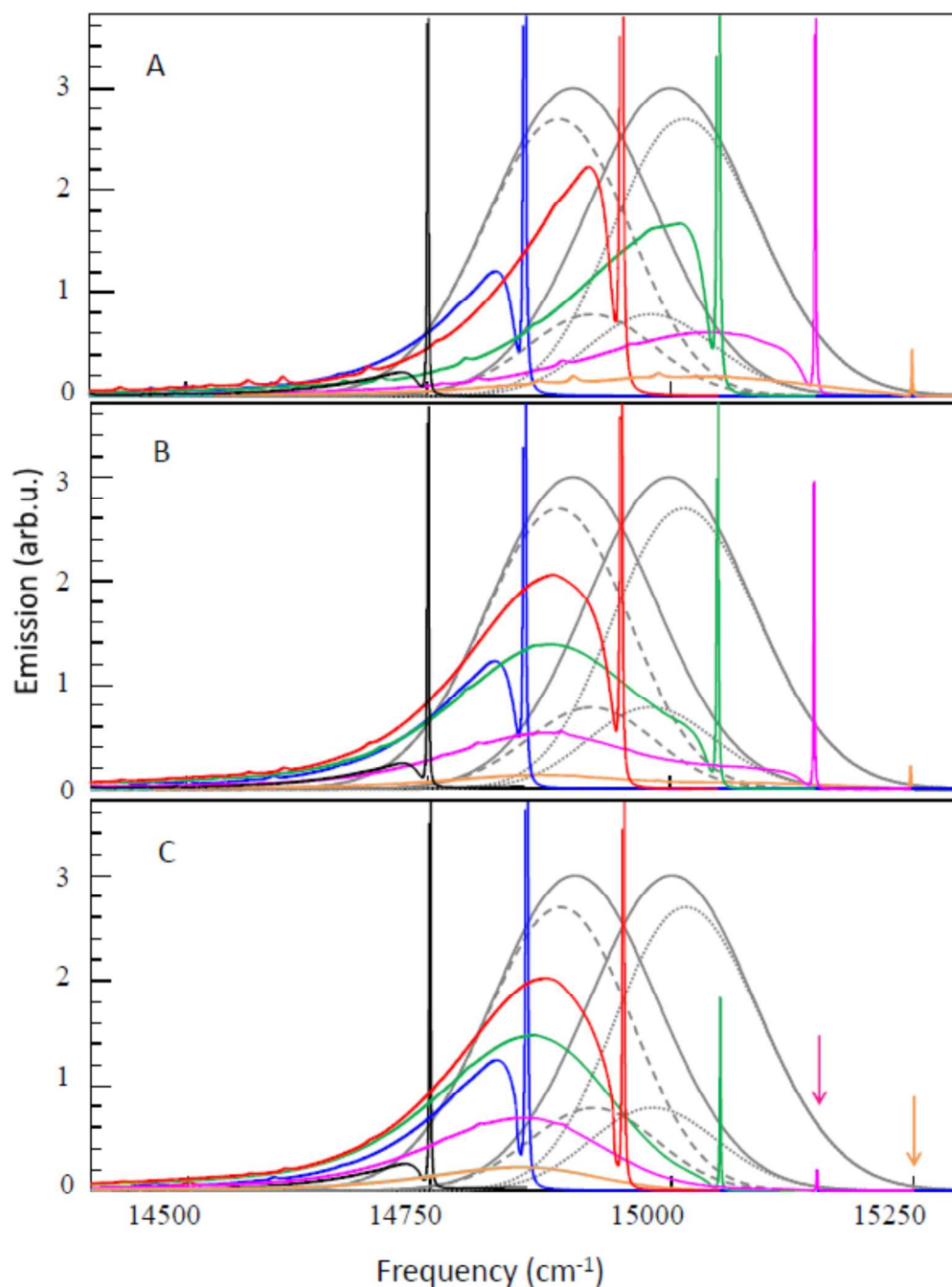


Figure S1. Frames A, B and C depict FLN spectra calculated for $V = 0.0$, 1.0 and 5.0 cm^{-1} , respectively in the case of non-identical dimer. Black, blue, red, green, magenta and orange curves correspond to excitation frequencies of 14750 , 14850 , 14950 , 15050 , 15150 and 15250 cm^{-1} , respectively. Solid grey curves are full SDF of the two pigments. Dashed grey curves are partial SDF of the lower-energy pigments, while dotted grey curves are partial SDF of the higher-energy pigments. Arrows (see text) indicate the locations of the ZPL that are too weak.

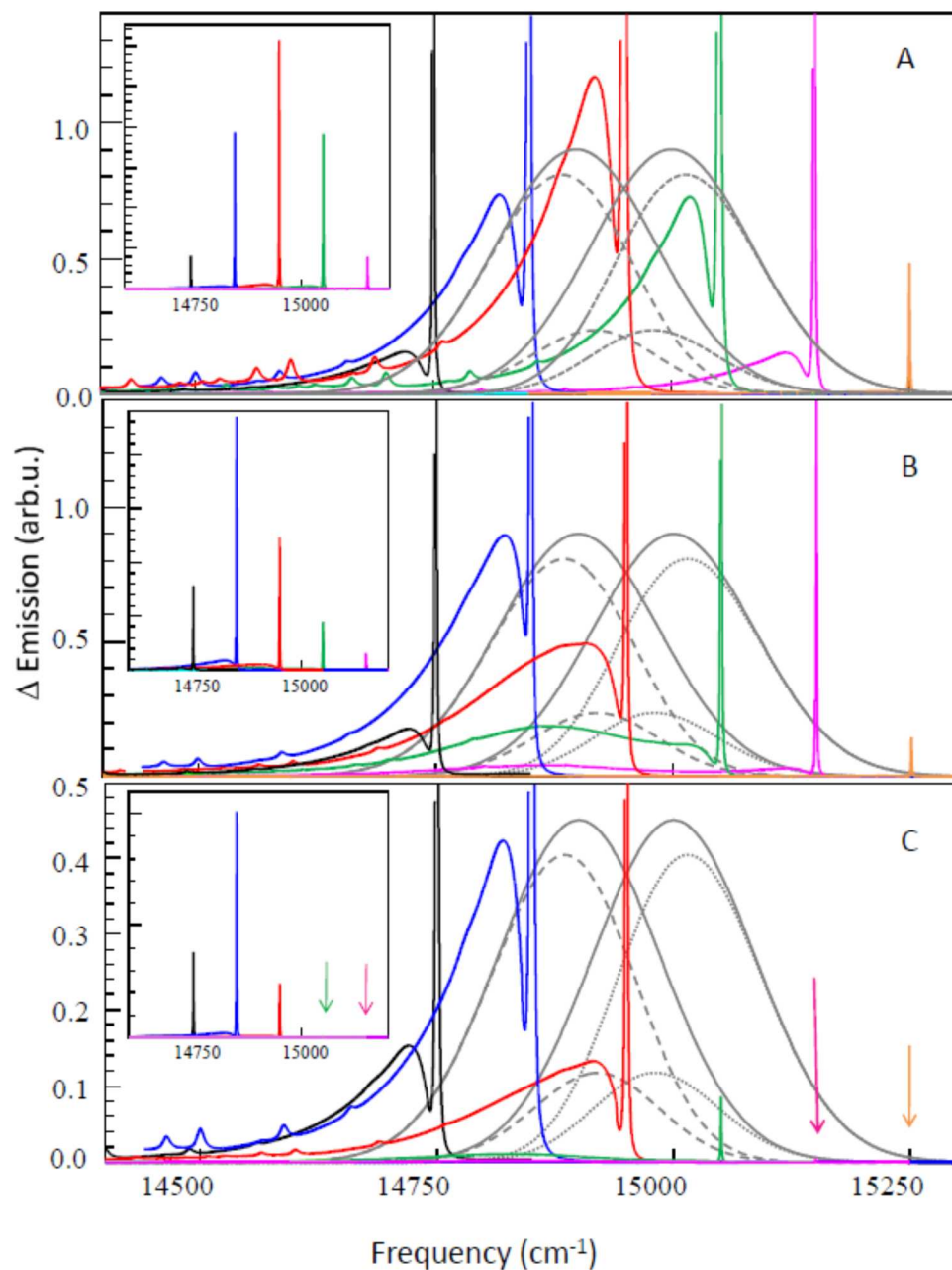


Figure S2. Frames A, B and C depict Δ -FLN spectra calculated for $V = 0.0, 1.0$ and 5.0 cm^{-1} , respectively. Black, blue, red, green, magenta and orange curves correspond to excitation frequencies of $14750, 14850, 14950, 15050, 15150$ and 15250 cm^{-1} , respectively. Solid grey curves are full SDF of two pigments. Dashed grey curves are partial SDF of the lower-energy pigments, while dotted grey curves are partial SDF of the higher-energy pigments. Inserts depict the full Δ -emission range and allow judging relative intensities of ZPL contributions. Color-coded arrows indicate the locations of the ZPL that are too weak.

Figure S2 depicts matching Δ -FLN spectra, obtained for shallow, several percent deep, burns. The longest-wavelength spectra do not depend on inter-pigment coupling. For larger inter-pigment coupling V the shorter-wavelength Δ -FLN spectra are suppressed, note that vertical scale in Frame C is different from that in Frames A and B. The inserts depict full vertical range, allowing the reader to assess relative intensities of the ZPL contributions to the Δ -FLN spectra. As can be seen, and in agreement with the results for identical dimer and trimer, for high excitation frequencies increase of inter-pigment-coupling results not only in suppression of the ZPL contribution to the Δ -FLN spectra, but also in suppression of the apparent non-resonant contribution. As discussed in the main text, this can be explained by the total number of lower-energy pigments to the red of the excitation frequency remaining practically unchanged (since the hole burning is non-photochemical).