Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information for: Insights into colour-tuning of chlorophyll optical response in green plants

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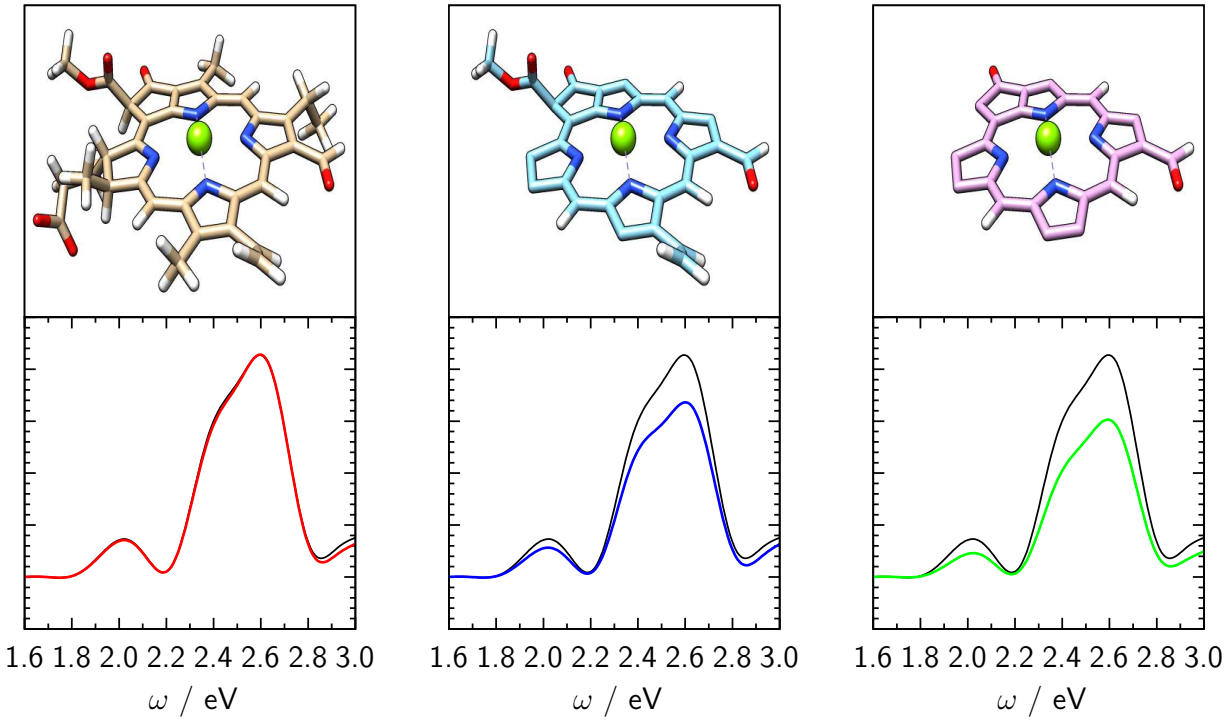

Figure S1: Comparison of the simulated spectra for a single chlorophyll molecule (607*b*) by decreasing the size of the ring used on the local dipole analysis. This study confirms that the phytyl chain does not play a significant role on the light absorption process. In addition, it reveals the need to take into account the complete chlorin ring for the correct prediction of the spectral intensities. The peak energies are, however, less sensitive to the modifications shown here.

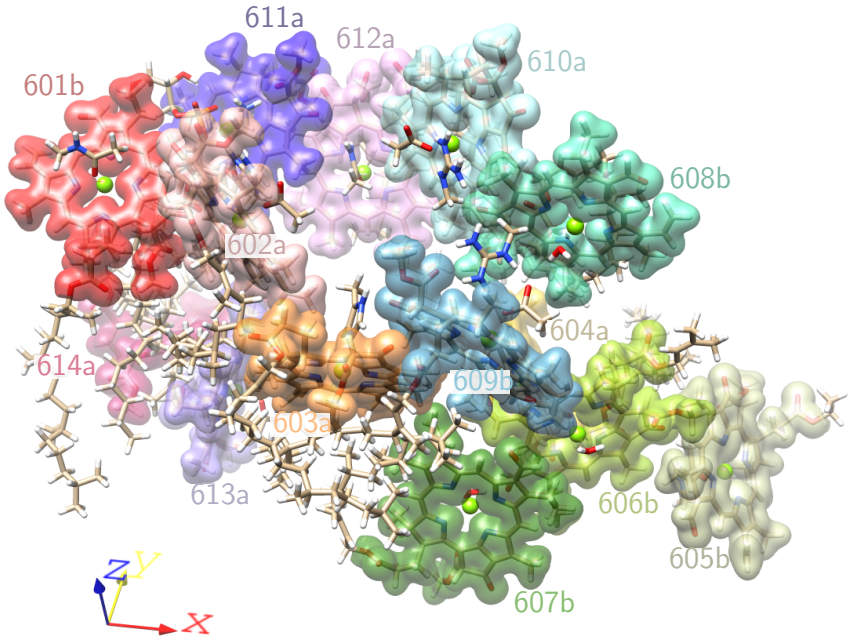

Figure S2: Chlorophyll network of a LHC–II monomer as used in this work. The systems consists of 14 chlorophyll molecules containing a total of 2025 atoms. Hydrogen atoms are excluded here to aid visualization. Bader volumes for each chlorophyll are represented as transparent surfaces. The local absorption spectrum decomposition has been performed over the densities enclosed in these surfaces.

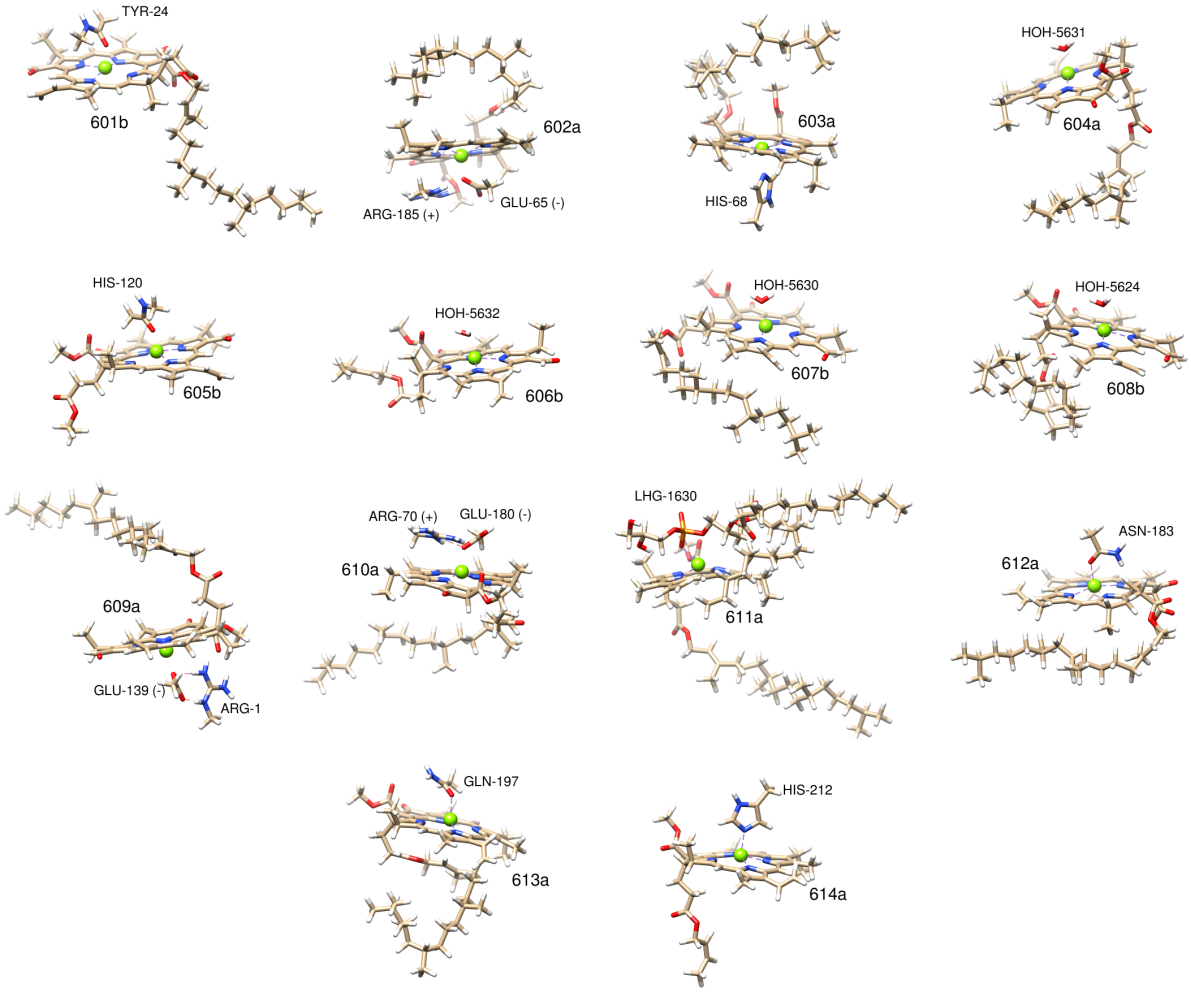

Figure S3: Spatial geometry of each of the 14 molecules that form the chlorophyll network of the one monomer of the LHC–II. Each chlorophyll presents a different conformation due to its specific axial coordination residue. As mentioned in the main text, the all atoms structure of the LHC–II ($\sim$ 17000 atoms) were optimized using the PM7 Hamiltonian implemented in the MOPAC semi-empirical electronic structure package.[S1] These individual structures have been used to compute the absorption spectra of each isolated chlorophyll.

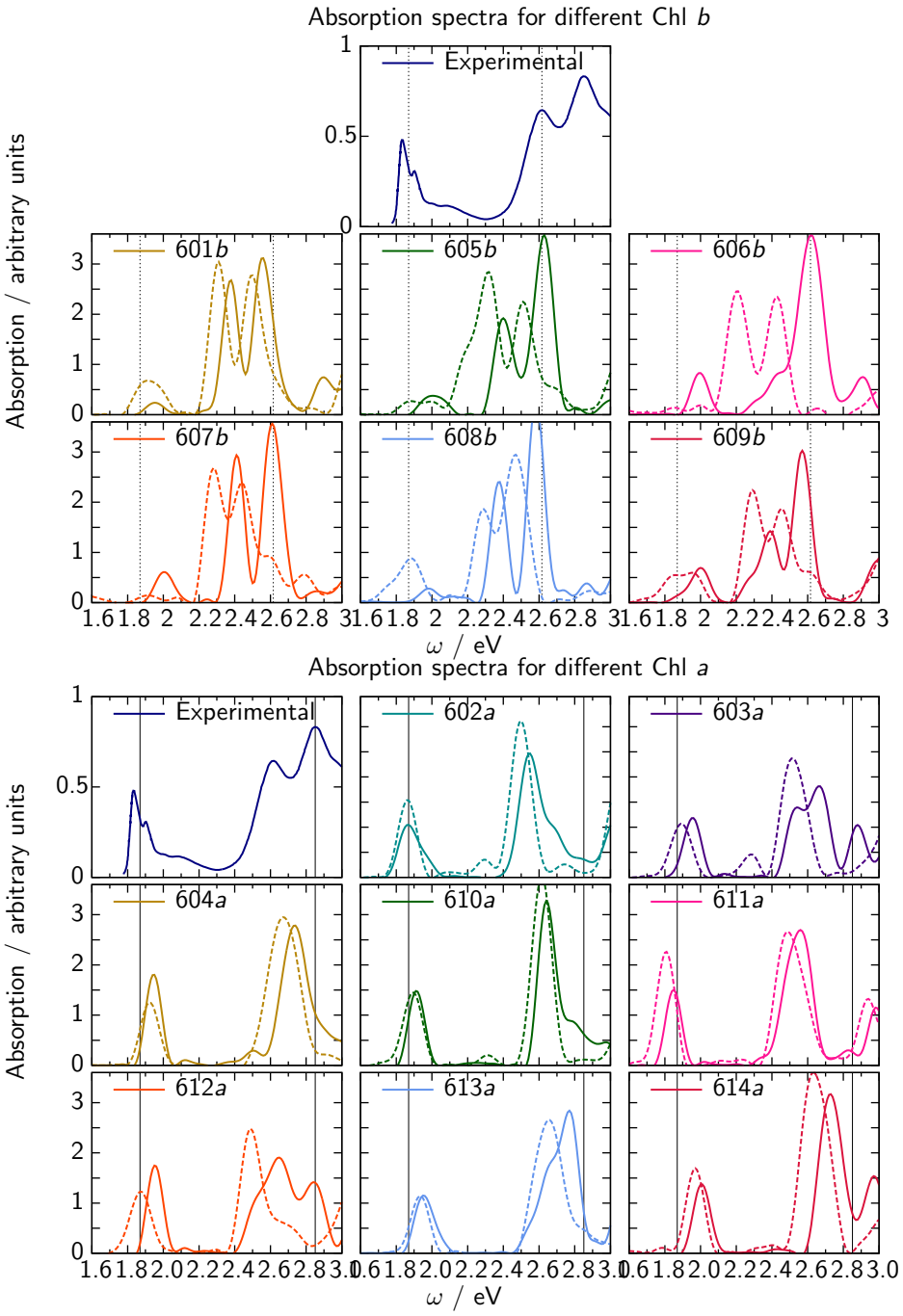

Figure S4: Absorption spectra of chlorophylls b and a of the chlorophyll network of the LHC–II monomer. Spectra obtained for the isolated chlorophylls (solid lines) are compared with those obtained from local dipole analysis (dotted lines). Direct observation on the simulated spectra shows a strong effect on the electronic transition of the chlorophyll b due to the environment effect while a small oscillator strength transfer effect is observed for cholorphylls a.

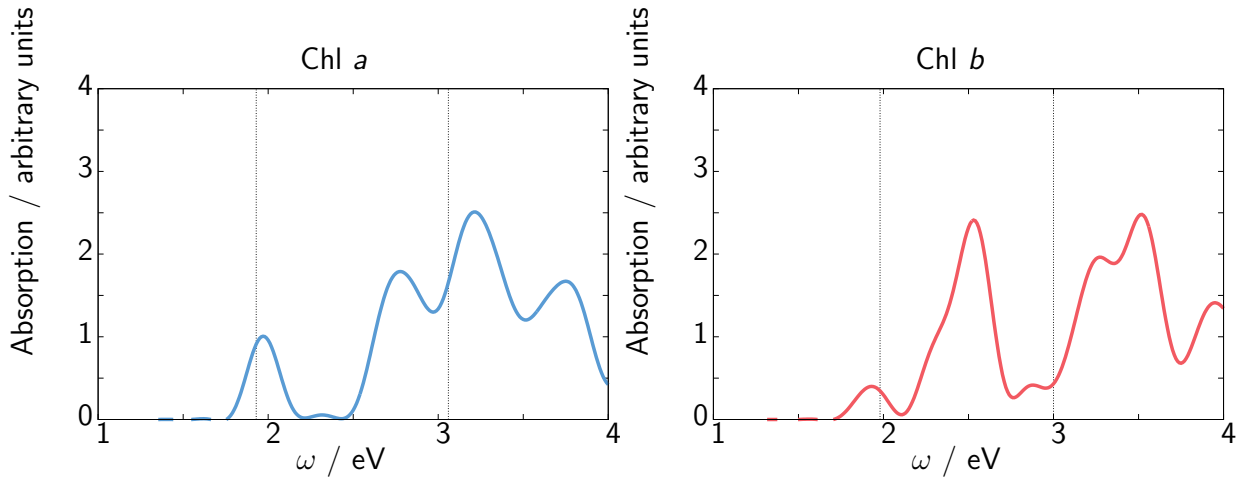

Figure S5: Simulated absorption spectra of chlorophylls *a* (left) and *b* (right) *in vacuo* using the TD-PBE-ADSIC method. The molecular structures used in these spectra were those used in previous studies[S2,S3] and were optimized at the PBE/Def2-SVP level with the ORCA electronic structure package.[S4] Dotted lines shows the Q– and Soret–band location for experimental absorption spectra.[S2,S3]

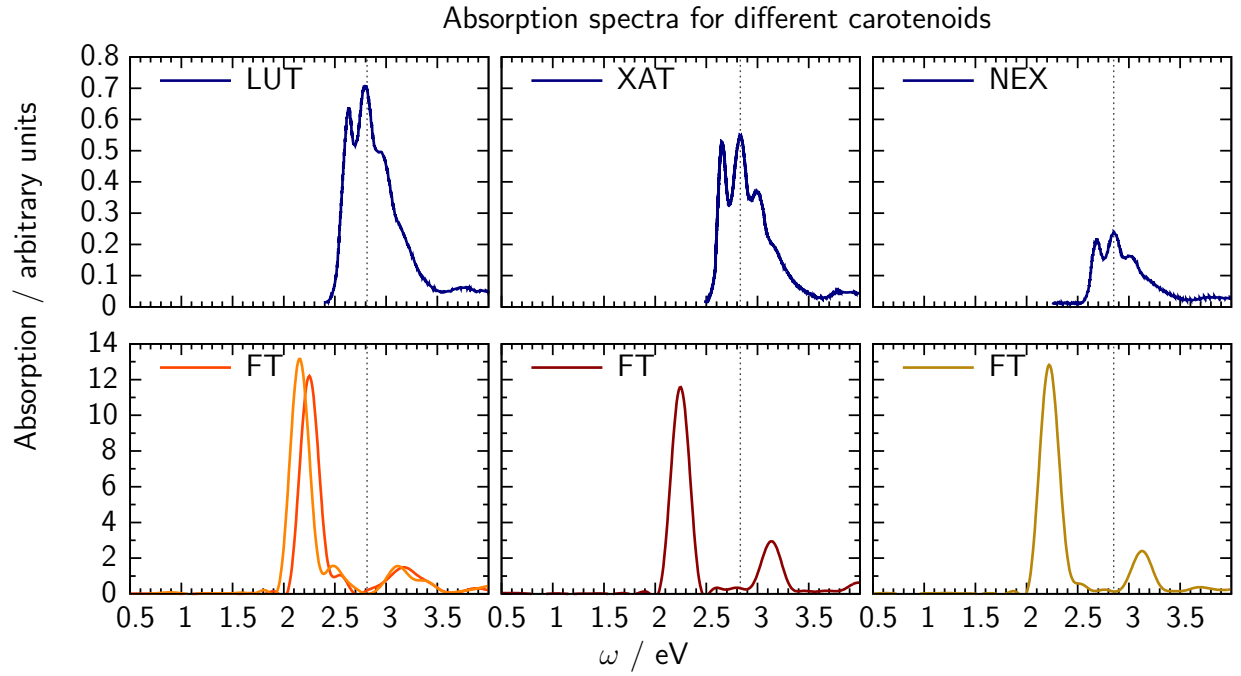

Figure S6: Comparison between experimental[S5] (top) and simulated (bottom) absorption spectra of the 3 types of carotenoid molecules: lutein (LUT), violoxanthin (XAT) and neoxanthin (NEX). Given the inherent difficulties for TDDFT in simulating multi-electron excitations, an unexpectedly good agreement between experimental and simulated ($\Delta \sim 0.5$ eV) was obtained. This is attributed to the non-planar conformation of the polyene chains due to the geometry optimization within the LHC–II complex environment.

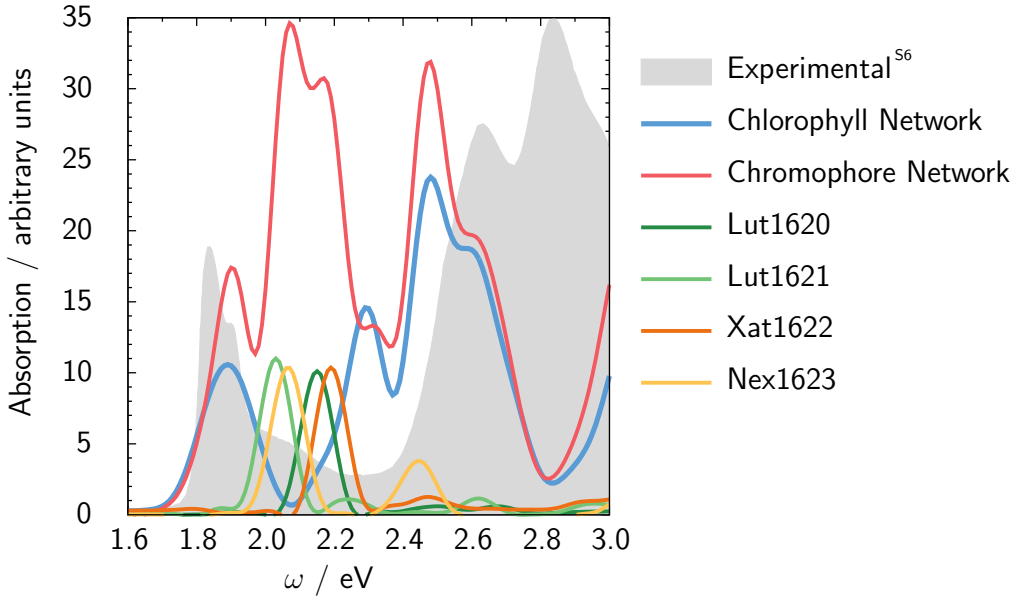

Figure S7: Study of the effect of the inclusion of carotenoid molecules on the simulated absorption spectrum. The observed strong band around 2.1 eV on the spectrum of the chromophore network (upper red line) is assigned to the carotenoids effect by direct comparison with the spectra obtained for the chlorophyll network (blue line). The spectral decomposition for the carotenoid contributions confirm that the absorption peaks do not significantly overlap with the chlorophyll bands. The grey shaded curve shows the experimental spectrum of LHC–II.[S6]

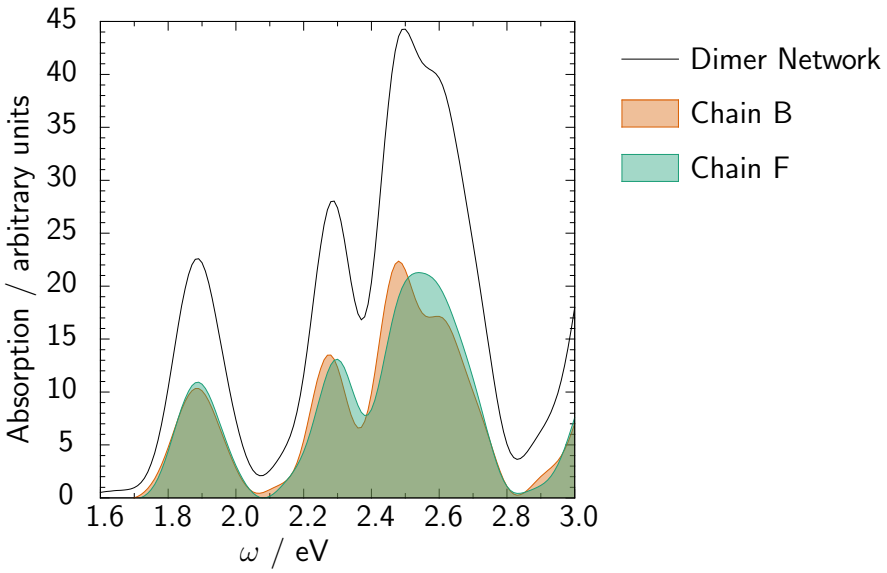

Figure S8: Absorption spectra decomposition of the chlorophylls network of the LHC–II dimer into its component monomers: chain B (orange) and F (green) according to the PDB file 1RWT nomenclature. The total absorption spectra for the chlorophyll network of the dimer is also represented (solid black line). The small difference in the shape of the Soret–band can be attributed to small structural differences between monomers, since no symmetry has been applied during the structural optimization.

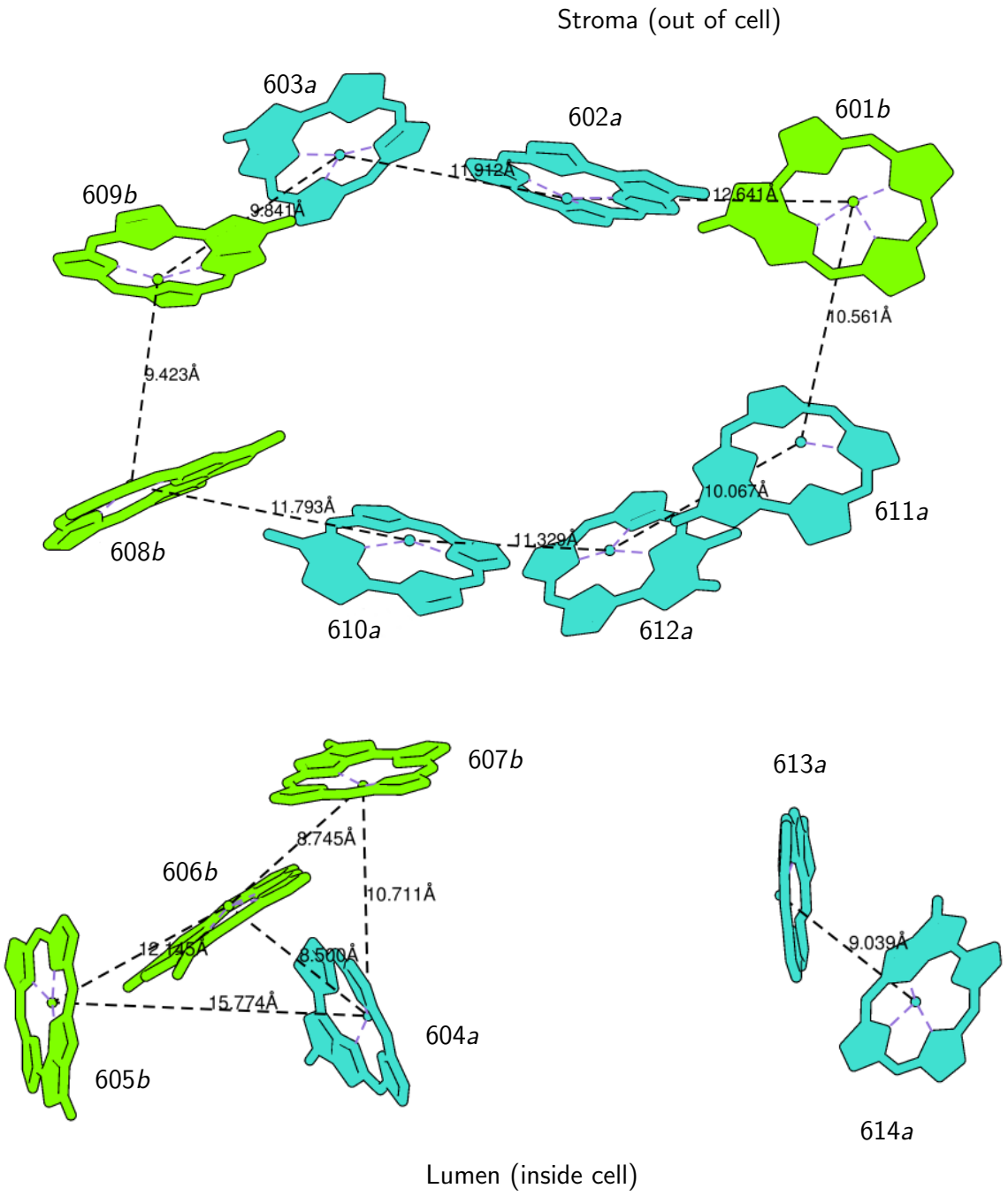

Figure S9: Relative distribution of the different chlorophyll molecules of the stroma (top) and lumen (bottom). Distances between the Mg centres of the chlorophyll molecules are highlighted in order to indicate the proximity of neighbouring molecules. Chlorophyll molecules are displayed only as chlorin rings to improve clarity. Chlorophyll *a* are represented in blue and chlorophyll *b* in green.

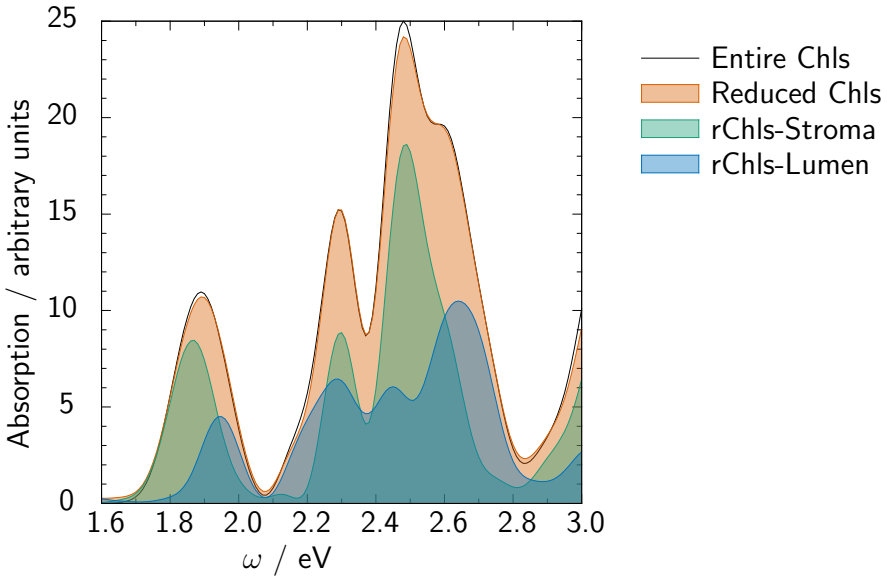

Figure S10: Contribution on the absorption spectra of chlorophyll networks (solid line) from stromal (green shade) and lumenal (blue shade) halves of LHC–II. This decomposition indicates that the chlorophylls located on the stroma have higher probability of light absorption than the chlorophylls located on the lumenal part. Orange shade are obtained as a superposition of all chlorophylls contribution, and confirms the validity of the model used to select the Bader volumes.

References

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(S2) Milne, B. F.; Rubio, A.; Brøndsted Nielsen, S. *Angew. Chem. Int. Ed. Eng.* **2015**, *54*, 2170–2173.

(S3) Stockett, M. H.; Musbat, L.; Kjær, C.; Houmøller, J.; Toker, Y.; Rubio, A.; Milne, B. F.; Brønsted Nielsen, S. *Phys. Chem. Chem. Phys.* **2015**, *DOI: 10.1039/C5CP01513H*.

(S4) Neese, F. *WIREs Comput. Mol. Sci.* **2012**, *2*, 73–78.

(S5) Lichtenthaler, H. K.; Buschmann, C. *Current Protocols in Food Analytical Chemistry*; John Wiley & Sons, Inc., 2001.

(S6) Siefermann-Harms, D. *Biochim. Biophys. Acta - Reviews on Bioenergetics* **1985**, *811*, 325–355.