ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Uncovering the interactions driving carotenoid binding in light-harvesting complexes

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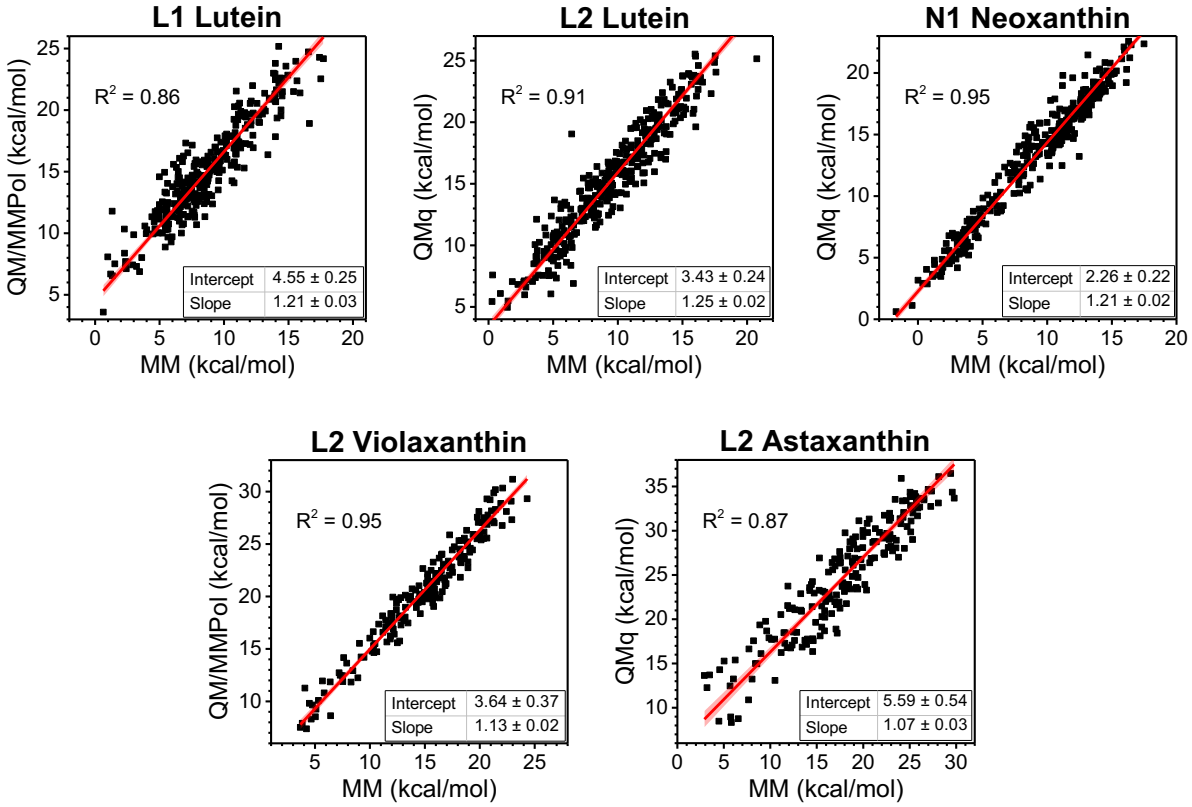

Figure S1. Correlation of electrostatic interaction energies calculated with MM (Amber) or QM/MMPol methodologies. Top: xanthophylls of native LHCII. Bottom: L2 with violaxanthin and astaxanthin. Fitted lines (with 95% confidence ranges) and R^2 are calculated by linear regression with error on both x- and y- axes. Fitted intercepts and slopes are accompanied by their standard errors.

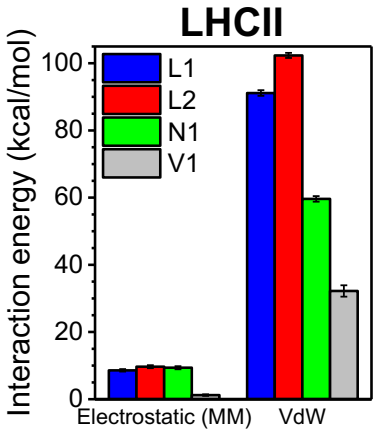

Figure S2. Driving forces in xanthophyll binding. Decomposition of interaction energy into electrostatic and VdW terms in different binding sites of LHCII. Note that both electrostatic and VdW energies shown here are calculated at MM level (Amber force field). The value of each bar represents the average over all cumulated MD snapshots, while the error bars represent 96% confidence intervals (i.e. 2 times the standard error, with N = 323).

L2 partners	LHCII Lutein (%)	LHCII Violaxanthin (%)	LHCII Astaxanthin (%)
ASP 47	38 ± 17	66 ± 27	5 ± 4
THR 48	35 ± 15	37 ± 11	51 ± 23
Water (lumen)	41 ± 9	52 ± 24	90 ± 18

Table S1. HB partners of L2 xanthophyll in different LHCII variants. Occurrence of HB contacts between the L2 xanthophyll and selected amino acids/cofactors in native LHCII (lutein), LHCII with violaxanthin in L2, and LHCII with astaxanthin in all binding sites, expressed as the percentage of MD snapshots with an electrostatic attraction > 3 kcal/mol between the residues of interest. The values shown in the table are the averages of the percentages obtained for each independent MD trajectory plus/minus the standard error (N = 6 for native LHCII, 3 for LHCII violaxanthin and 4 for LHCII astaxanthin). In the case of astaxanthin, whose lumenal ring has two potential HB sites, MD frames with *n* water molecules interacting in the same frame are counted *n* times in the average.

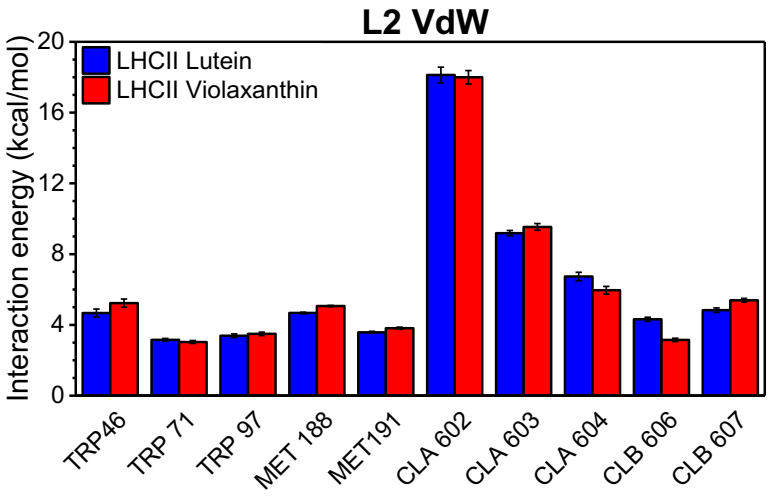

Figure S3. L2 interaction energy in different LHC variants. Average VdW interaction energies of the L2 xanthophyll of native LHCII (lutein), and LHCII with violaxanthin in L2. The value of each bar represents the average over all cumulated MD snapshots, while the error bars represent 96% confidence intervals (i.e. 2 times the standard error, with N = 323 for native LHCII, and 188 for LHCII with violaxanthin). Only the interactions with an average > 3.0 kcal/mol in at least one of the complexes are shown. The specific interactions shown here are relatively similar independent of the xanthophyll content (lutein or violaxanthin).

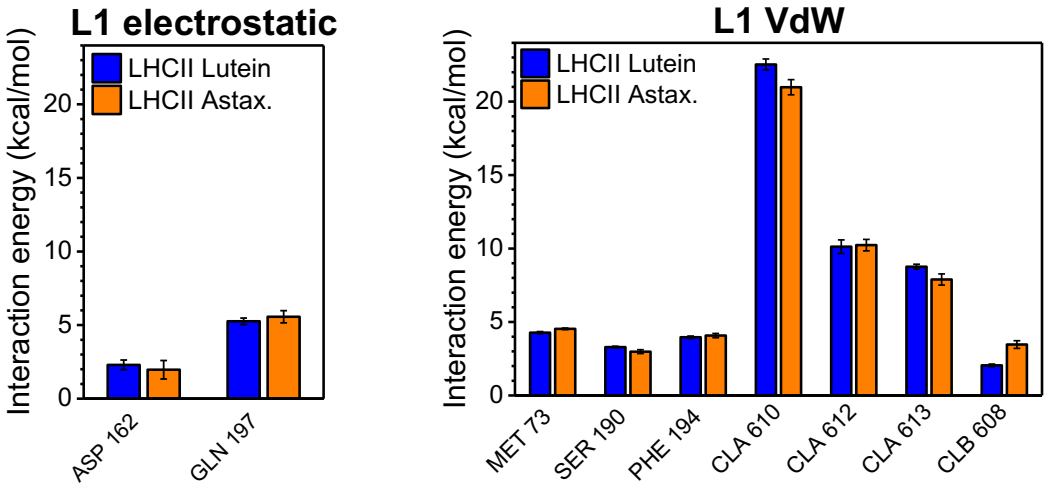

Figure S4. L1 interaction energy of different xanthophylls. A) HB interaction energy between the L1 xanthophyll and selected residues in native LHCII (lutein, blue) and LHCII with astaxanthin (orange). The only residue giving rise to an average electrostatic interaction > 3.0 kcal/mol is GLN 197. The interaction with ASP 162 is also indicated, as it is predicted to be relatively strong in the static structure of LHCII (see also Figure 3 in the main text). B) Main VdW interaction partners of the L1 xanthophyll in native LHCII (lutein) and LHCII with astaxanthin. All fragments with an average interaction > 3.0 kcal/mol in at least one of the samples are shown in the bar chart. Despite some small differences, the replacement of lutein with astaxanthin in L1 does not change the VdW interaction patterns substantially. In both (A) and (B), the value of each bar represents the average over all cumulated MD snapshots, while the error bars represent 96% confidence intervals (i.e. 2 times the standard error, with N = 323 for native LHCII and 198 for LHCII with astaxanthin).

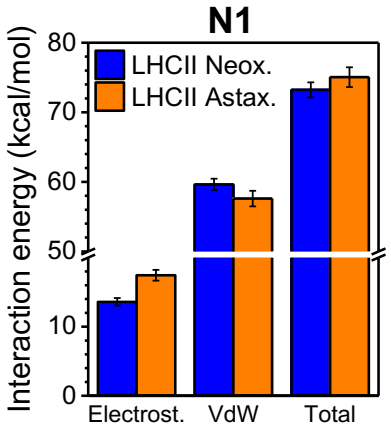

Figure S5. N1 interaction energy of different xanthophylls. Decomposition of interaction energy into electrostatic and VdW terms for the N1 xanthophyll of native LHCII (neoxanthin) and LHCII with astaxanthin. The value of each bar represents the average over all cumulated MD snapshots, while the error bars represent 96% confidence intervals (i.e. 2 times the standard error, with N = 323 for native LHCII and 198 for LHCII with astaxanthin).

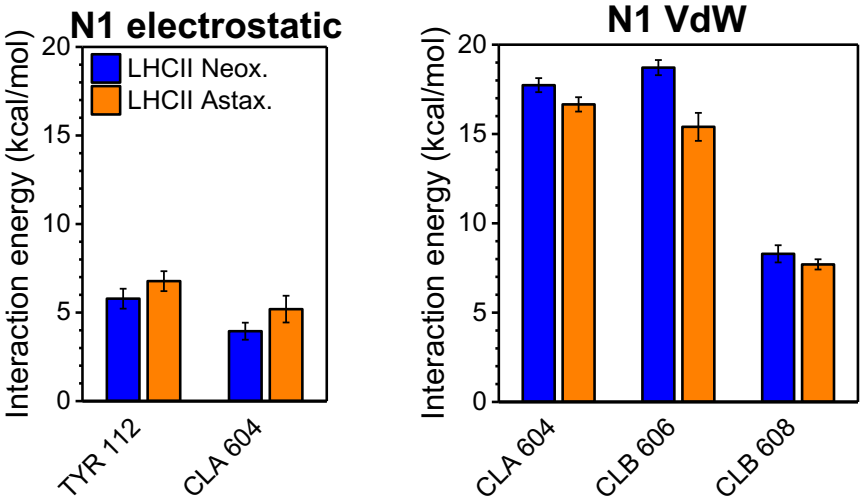

Figure S6. N1 interaction energy of different xanthophylls. Average electrostatic (A) and VdW (B) interaction energies of the N1 xanthophyll of native LHCII (neoxanthin) and LHCII with astaxanthin with selected residues. The value of each bar represents the average over all cumulated MD snapshots, while the error bars represent 96% confidence intervals (i.e. 2 times the standard error, with N = 323 for native LHCII and 198 for LHCII with astaxanthin). Only the interactions with an average > 3.0 kcal/mol in at least one of the complexes are shown.