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

Supporting Information for

Determination of the protonation preferences of bilin pigments in cryptophyte antenna complexes

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Table S1. Electronic energies, free energy corrections and solvation free energies computed for pyridine, imidazole and their conjugated acids.

X	$E_{SCS-MP2/CBS}$ [a]	ΔE_{CCSD} [a]	G_{corr} [a]	$\Delta G_{sol,MST}$ [b]	$\Delta G_{sol,SMD}$ [b]
Pyridine					
X	-247.8279	-0.0568	0.0596	-4.3	-4.6
XH^+	-248.1942	-0.0579	0.0733	-58.0	-58.4
Imidazole					
X	-225.8370	-0.0461	0.0433	-10.0	-8.5
XH^+	-226.2080	-0.0482	0.0571	-64.9	-62.1

[a]Energies in hartree. [b]Solvation energies in kcal/mol.

Table S2. Electronic energies, free energy corrections and solvation free energies computed for deprotonated bilins on different pyrrole rings (A-D) as well as the fully protonated form (H^+).

	Ring	$E_{SCS-MP2/CBS}$ [a]	ΔE_{CCSD} [a]	G_{corr} [a]	$\Delta G_{sol,MST}$ [b]	$\Delta G_{sol,SMD}$ [b]
PEB						
	A	-1532.7499	-0.3571	0.5389	-17.1	-20.9
	B	-1532.7769	-0.3533	0.5397	-12.0	-15.6
	C	-1532.7802	-0.3535	0.5413	-11.7	-14.2
	D	-1532.6879	-0.3540	0.5391	-34.1	-40.3
	H^+	-1533.1724	-0.3557	0.5525	-49.8	-53.8
PEB'						
	A	-1572.7225	-0.3737	0.6034	-16.8	-20.5
	B	-1572.7477	-0.3700	0.6037	-10.7	-14.9
	C	-1572.7507	-0.3702	0.6046	-10.5	-13.5
	D	-1572.6558	-0.3710	0.6040	-34.4	-40.0
	H^+	-1573.1437	-0.3726	0.6179	-49.1	-53.7
DBV						
	A	-1531.5222	-0.3505	0.5150	-18.0	-21.9
	B	-1531.5608	-0.3456	0.5152	-11.8	-15.2
	C	-1531.5641	-0.3462	0.5171	-11.6	-14.2
	D	-1531.4713	-0.3469	0.5132	-33.0	-39.1
	H^+	-1531.9536	-0.3484	0.5274	-50.4	-54.4
DBV'						
	A	-1571.9913	-0.3672	0.5791	-17.0	-22.0
	B	-1572.0302	-0.3624	0.5791	-10.8	-15.2
	C	-1572.0335	-0.3630	0.5799	-10.5	-14.0
	D	-1571.9406	-0.3636	0.5798	-30.9	-38.4
	H^+	-1572.4240	-0.3653	0.5920	-49.2	-54.0
PCB						
	A	-1532.7702	-0.3533	0.5395	-16.4	-19.1
	B	-1532.7942	-0.3497	0.5412	-10.9	-14.0
	C	-1532.7940	-0.3494	0.5412	-10.8	-13.9
	D	-1532.7569	-0.3541	0.5396	-17.4	-19.9
	H^+	-1533.1937	-0.3525	0.5535	-45.7	-49.8
MBV						
	A	-1531.5408	-0.3463	0.5155	-16.5	-19.5
	B	-1531.5777	-0.3417	0.5163	-10.4	-13.5
	C	-1531.5776	-0.3417	0.5158	-10.3	-13.5
	D	-1531.5394	-0.3463	0.5137	-17.3	-20.0
	H^+	-1531.9740	-0.3449	0.5285	-46.6	-50.1

[a]Energies in hartree. [b]Solvation energies in kcal/mol.

Table S3. Acid dissociation constants computed using PROPKA for bilin pyrrole rings B and C in their specific protein environments based on the crystal structure.

		$pK_a\ (B)$	$pK_a(C)$
PE545 ($\alpha_1\beta\alpha_2\beta$)			
	DBV_{19A}	5.6	5.1
	DBV_{19B}	5.5	5.0
	$PEB_{50/61C}$	8.1	6.8
	PEB_{158C}	7.4	6.9
	PEB_{82C}	6.8	6.5
	$PEB_{50/61D}$	7.6	7.2
	PEB_{158D}	5.7	5.2
	PEB_{82D}	6.9	6.6
PC577 ($\alpha\beta\alpha\beta$)			
	PCB_{20A}	7.9	7.8
	$DBV_{50/61B}$	7.6	6.7
	PCB_{158B}	7.9	8.1
	PCB_{82B}	7.1	7.4
	PCB_{20C}	7.9	7.8
	$DBV_{50/61D}$	7.7	6.7
	PCB_{158D}	7.8	8.1
	PCB_{82D}	7.1	7.3
PC612 ($\alpha\beta\alpha\beta$)			
	PCB_{20A}	8.0	8.0
	$DBV_{50/61B}$	7.5	6.5
	PCB_{158B}	7.8	8.1
	PCB_{82B}	7.0	7.4
	PCB_{20C}	8.0	8.1
	$DBV_{50/61D}$	7.7	6.6
	PCB_{158D}	7.9	8.2
	PCB_{82D}	7.2	7.4
PC630 ($\alpha_1\beta\alpha_2\beta$)			
	MBV_{19A}	5.7	4.9
	$DBV_{50/61B}$	7.3	6.7
	PCB_{158B}	7.8	7.9
	PCB_{82B}	7.1	7.3
	MBV_{19C}	5.1	4.7
	$DBV_{50/61D}$	7.1	6.4
	PCB_{158D}	7.7	8.1
	PCB_{82D}	7.0	7.3
PC645 ($\alpha_1\beta\alpha_2\beta$)			
	MBV_{19A}	5.9	5.2
	$DBV_{50/61B}$	7.3	6.7
	PCB_{158B}	7.8	8.1
	PCB_{82B}	7.2	7.4
	MBV_{19C}	5.2	4.7
	$DBV_{50/61D}$	6.9	6.1
	PCB_{158D}	7.7	8.2
	PCB_{82D}	6.9	7.4

Table S4. MD-averaged acid dissociation constants computed using PROPKA for the propionic groups linked to pyrrole rings B and C of the bilins in their specific protein environments.

		$pK_a\ (B)$[a]	$pK_a(C)$[a]
PE545 ($\alpha_1\beta\alpha_2\beta$)			
	DBV_{19A}	3.7	5.0
	DBV_{19B}	3.6	4.3
	$PEB_{50/61C}$	4.9	4.6
	PEB_{158C}	4.3	2.7
	PEB_{82C}	2.7	3.6
	$PEB_{50/61D}$	4.8	4.2
	PEB_{158D}	4.5	4.1
	PEB_{82D}	3.5	3.4
PC577 ($\alpha\beta\alpha\beta$)			
	PCB_{20A}	3.0	2.7
	$DBV_{50/61B}$	3.7	4.3
	PCB_{158B}	4.3	3.7
	PCB_{82B}	3.8	3.2
	PCB_{20C}	3.5	2.7
	$DBV_{50/61D}$	3.6	4.0
	PCB_{158D}	4.3	3.8
	PCB_{82D}	3.8	3.4
PC612 ($\alpha\beta\alpha\beta$)			
	PCB_{20A}	4.8	2.5
	$DBV_{50/61B}$	4.2	4.5
	PCB_{158B}	4.4	4.1
	PCB_{82B}	3.4	3.5
	PCB_{20C}	4.9	2.8
	$DBV_{50/61D}$	4.3	4.6
	PCB_{158D}	4.4	3.8
	PCB_{82D}	3.6	3.5
PC630 ($\alpha_1\beta\alpha_2\beta$)			
	MBV_{19A}	3.6	2.7
	$DBV_{50/61B}$	4.5	4.6
	PCB_{158B}	4.4	3.6
	PCB_{82B}	3.7	3.3
	MBV_{19C}	3.8	3.0
	$DBV_{50/61D}$	4.0	4.4
	PCB_{158D}	4.3	3.6
	PCB_{82D}	2.9	3.4
PC645 ($\alpha_1\beta\alpha_2\beta$)			
	MBV_{19A}	4.7	3.0
	$DBV_{50/61B}$	4.7	4.7
	PCB_{158B}	4.3	3.9
	PCB_{82B}	3.9	3.4
	MBV_{19C}	3.9	2.9
	$DBV_{50/61D}$	4.7	4.3
	PCB_{158D}	4.4	3.7
	PCB_{82D}	3.7	3.2

[a]Values are averaged over PROPKA calculations where the central pyrrole ring is assumed to deprotonate either on ring B or C, which present minor differences below 0.2 pK_a units in all cases.

Table S5. MD-averaged acid dissociation constants computed using PROPKA for residues interacting with bilin central pyrrole rings in their specific protein environments.

			$pK_a\ (B)$[a]	$pK_a(C)$[b]
PE545 ($\alpha_1\beta\alpha_2\beta$)				
	DBV_{19A}	His16A[c]	4.6	4.5
	DBV_{19B}	His16B[c]	3.8	3.7
	$PEB_{50/61C}$	Asp54C	4.6	4.8
	PEB_{158C}	Asp39C	5.1	5.0
	PEB_{82C}	Asp85C	5.0	5.1
	$PEB_{50/61D}$	Asp54D	3.8	3.9
	PEB_{158D}	Asp39D	6.9	6.8
	PEB_{82D}	Asp85D	5.1	5.2
PC577 ($\alpha\beta\alpha\beta$)				
	PCB_{20A}	Glu16A	4.3	4.3
	$DBV_{50/61B}$	Asp54B	4.6	4.6
	PCB_{158B}	Asp39B	5.3	5.2
	PCB_{82B}	Asp85B	4.9	5.0
	PCB_{20C}	Glu16C	4.6	4.5
	$DBV_{50/61D}$	Asp54D	4.7	4.7
	PCB_{158D}	Asp39D	5.3	5.3
	PCB_{82D}	Asp85D	4.8	5.0
PC612 ($\alpha\beta\alpha\beta$)				
	PCB_{20A}	Glu16A	4.0	4.0
	$DBV_{50/61B}$	Asp54B	4.8	4.8
	PCB_{158B}	Asp39B	5.3	5.2
	PCB_{82B}	Asp85B	4.9	5.0
	PCB_{20C}	Glu16C	4.6	4.6
	$DBV_{50/61D}$	Asp54D	4.8	4.9
	PCB_{158D}	Asp39D	5.6	5.5
	PCB_{82D}	Asp85D	4.9	5.0
PC630 ($\alpha_1\beta\alpha_2\beta$)				
	MBV_{19A}	-	-	-
	$DBV_{50/61B}$	Asp54B	4.6	5.0
	PCB_{158B}	Asp39B	6.8	6.7
	PCB_{82B}	Asp85B	4.8	4.9
	MBV_{19C}	His22A[d]	7.4	7.4
	$DBV_{50/61D}$	Asp54D	3.3	3.7
	PCB_{158D}	Asp39D	4.6	4.5
	PCB_{82D}	Asp85D	4.9	5.0
PC645 ($\alpha_1\beta\alpha_2\beta$)				
	MBV_{19A}	-	-	-
	$DBV_{50/61B}$	Asp54B	4.8	5.3
	PCB_{158B}	Asp39B	5.6	5.5
	PCB_{82B}	Asp85B	4.8	5.0
	MBV_{19C}	His21A[d]	7.6	7.6
	$DBV_{50/61D}$	Asp54D	4.0	4.3
	PCB_{158D}	Asp39D	4.4	4.3
	PCB_{82D}	Asp85D	4.9	5.0

[a]Values computed assuming deprotonation on bilin pyrrole ring B. [b]Values computed assuming deprotonation on bilin pyrrole ring C. [c]Histidines in PE545 interacting with DBV central pyrrole rings through a water molecule as shown in Fig. S1a.[d] Histidines in PC630 and PC645 interacting with a propionic group of MBV in chain C and Glu26A/Glu25A, respectively, as represented in Fig. S1b.

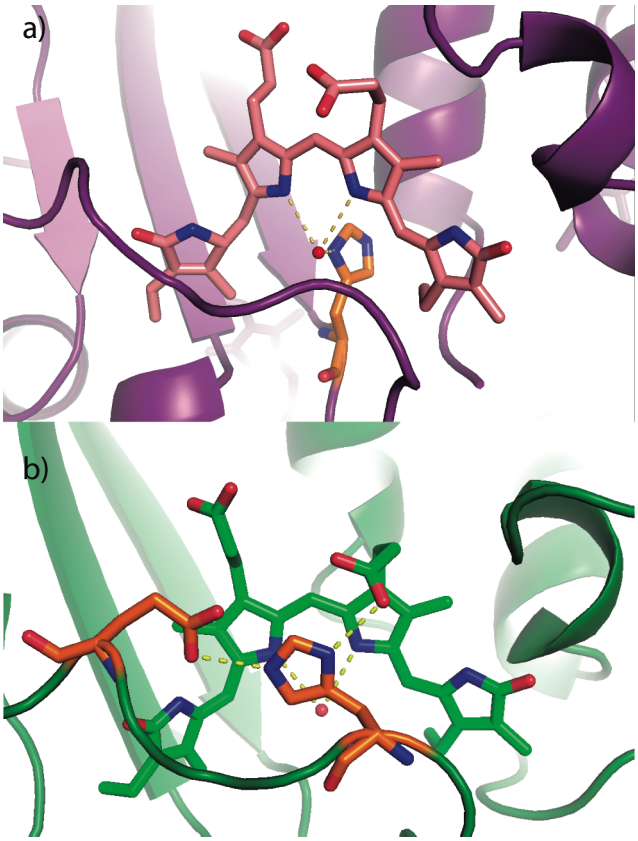

Figure S1. Representation of the environment surrounding bilin pigments. a) DBV_{19A} pigment in the PE545 complex with central pyrrole rings interacting with His16A through a water molecule. b) MBV_{19C} pigment in the PC645 complex with a propionic group and Glu25A interacting with His21A and central pyrrole rings interacting with a crystallographic water.

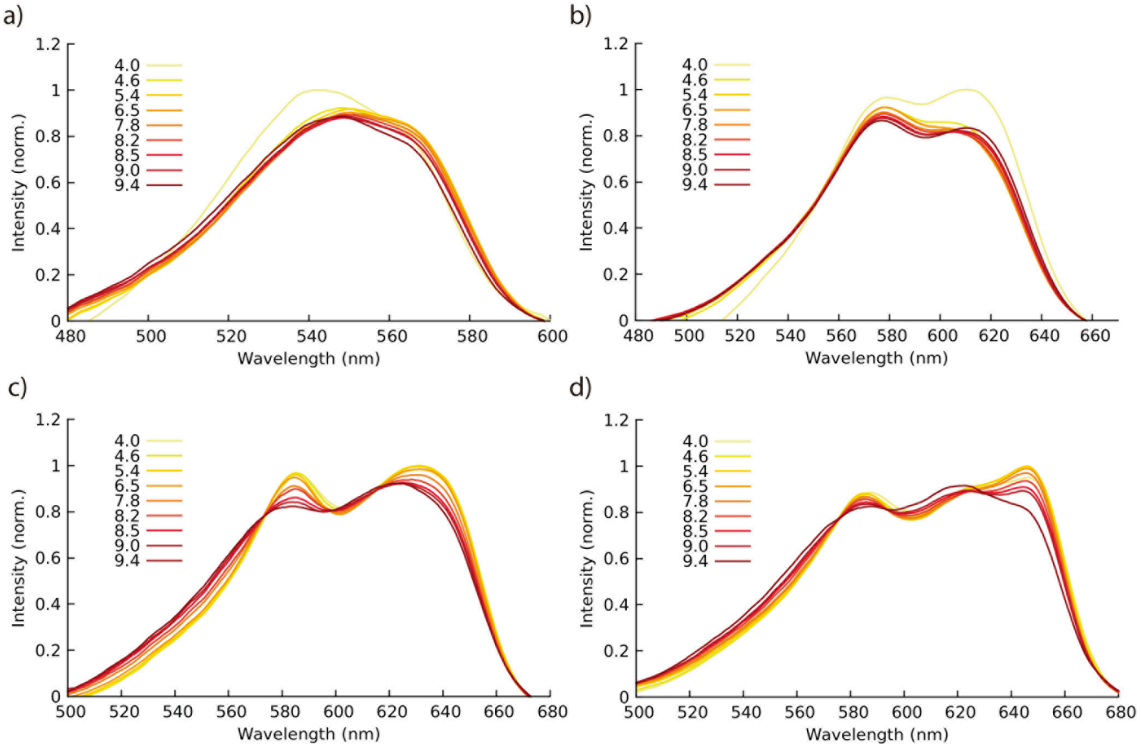

Figure S2. Normalized absorption spectra of cryptophyte antenna complexes at different pH values. a) PE545, b) PC577, c) PC630 and d) PC645.