Supplementary Information for:

Quantum Chemical Evidence for the Origin of the Red/Blue Colors of Hydrangea macrophylla Sepals

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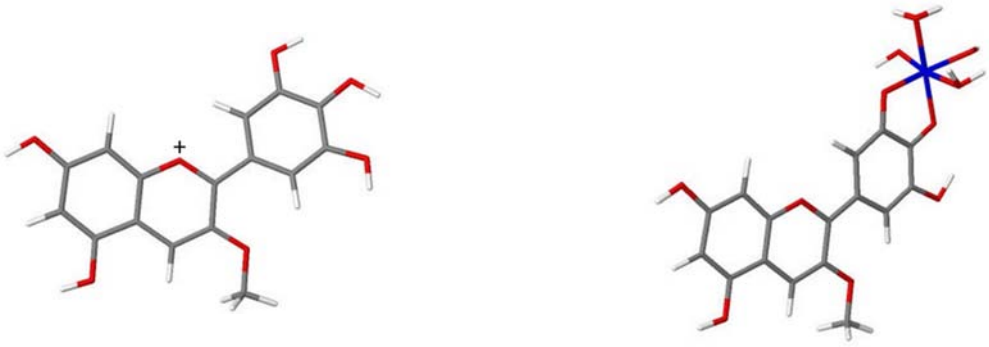
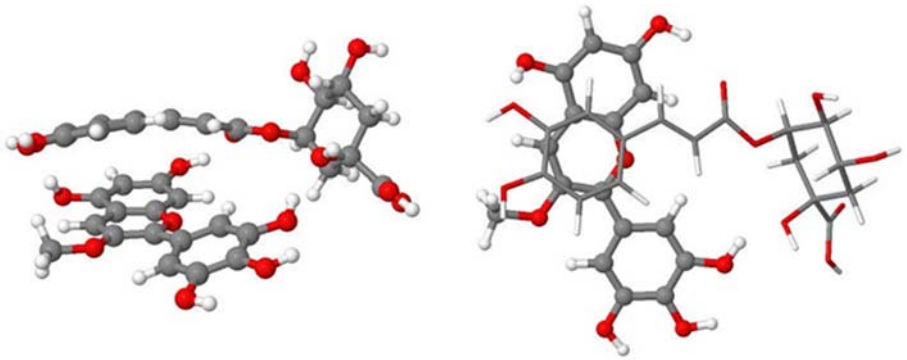


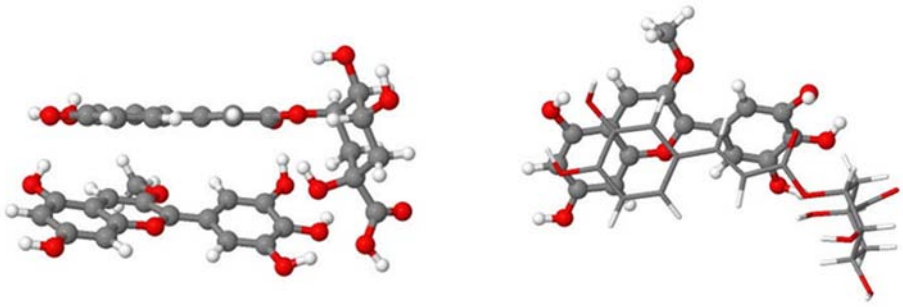
2 **2/Al**

Figure S1. MP2/def2-TZVP optimized geometries of the ground state of the methoxy analog (**2**), and the corresponding neutral binary complexes with Al(III) (**2/Al**). Atom color scheme: blue = Al, red = O, white = H, and gray = C.



Side view **Top view**

Binary **Complex VII** of **2** and **3**



Side view **Top view**

Binary **Complex VIII** of **2** and **3**

Figure S2. B3-LYP/def2-TZVP optimized geometries of the ground states of two possible relative orientations of the copigment 3 in binary complexes with the methoxy ether analog of 3-O-glucosyl delphinidin (2). Atom color scheme: red = O, white = H, and gray = C;

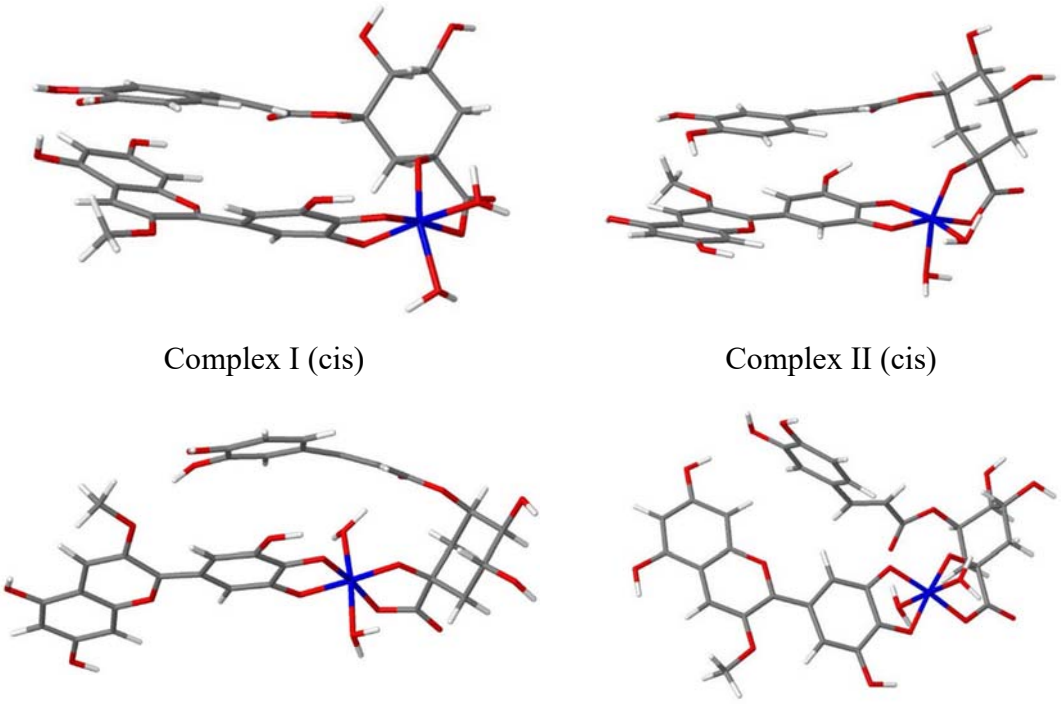


Figure S3. The four different optimized structures using B3-LYP/def2-TZVP in gas phase for the ternary anthocyanin-Al(III)-copigment complexes, varying the diaquo ligand coordination to aluminum(III) (denoted cis and trans) and the orientation of the anthocyanin (methoxy ether analog of 3-O-glucosyl delphinidin) relative to the copigment. Atom color scheme: blue = Al, red = O, white = H, and gray = C.

Table S1. Calculated TDDFT and ADC(2) (in vacuum and COSMO water) excitation energies ΔE(in eV), and maximum wavelength λ_{max} (in nm) and oscillator strength *f* of the delphindin cations **1** and **2**, of the corresponding neutral binary delphinidin-Al complexes(**1/Al** and **2/Al**) and of the copigment **3**.

		TDDFT				ADC(2)			
		Vacuum		Water		Vacuum		Water	
system	**state**	**ΔE (eV, nm)**	***f***	**ΔE (eV, nm)**	***f***	**ΔE (eV, nm)**	***f***	**ΔE (eV, nm)**	***f***
3-O-glucosyl delphindin (**1**)	S_1	2.39, 519	0.07	2.54, 488	0.52	2.27, 547	0.52	2.44, 509	0.58
	S_2	2.55, 485	0.41	2.62, 473	0.06	2.67, 464	0.03	2.89, 429	0.03
	S_3	2.69, 462	0.01	2.86, 433	0.06	2.85, 436	0.01	3.11, 398	0.02
	S_4	2.83, 439	0.03	3.55, 350	0.00	3.56, 348	0.08	3.75, 331	0.08
	S_5	2.91, 426	0.00	3.62, 343	0.08	3.61, 343	0.00	4.30, 288	0.00
	S_6	3.23, 384	0.00	3.85, 322	0.00	4.00, 310	0.01	4.62, 268	0.02
	S_7	3.35, 370	0.00	4.23, 293	0.00	4.40, 282	0.00	4.73, 262	0.32
	S_8	3.55, 349	0.08	4.28, 289	0.02	4.54, 273	0.05	4.92, 252	0.24
	S_9	3.92, 316	0.00	4.30, 288	0.11	4.60, 270	0.10	5.05, 246	0.02
	S_{10}	4.17, 297	0.12	4.47, 277	0.05	4.65, 267	0.00	5.26, 236	0.04
3-O-methyl delphindin (**2**)	S_1	2.49, 497	0.07	2.50, 497	0.53	2.30, 539	0.62	2.38, 521	0.58
	S_2	2.56, 484	0.43	2.75, 451	0.01	2.76, 450	0.01	3.04, 408	0.10
	S_3	2.91, 426	0.14	2.94, 422	0.24	2.92, 425	0.02	3.19, 388	0.02
	S_4	3.66, 339	0.04	3.66, 339	0.03	3.82, 324	0.03	3.86, 321	0.03
	S_5	4.29, 289	0.04	4.33, 286	0.01	4.55, 272	0.04	4.52, 274	0.01
	S_6	4.47, 277	0.04	4.52, 274	0.16	4.75, 261	0.25	4.74, 262	0.45
	S_7	4.55, 273	0.06	4.77, 260	0.01	4.98, 249	0.18	5.17, 240	0.10
	S_8	4.74, 262	0.13	4.78, 260	0.24	5.07, 245	0.02	5.22, 237	0.01
	S_9	5.11, 243	0.25	5.15, 241	0.22	5.32, 233	0.15	5.48, 226	0.11
	S_{10}	5.16, 240	0.06	5.19, 239	0.05	5.62, 221	0.27	5.63, 220	0.02
3-O-glucosyl Delphinidin – Aluminum (III) (**1/Al**)	S_1	2.04, 608	0.10	2.34, 529	0.51	1.92, 646	0.35	2.01, 616	0.77
	S_2	2.55, 486	0.65	2.59, 478	0.42	2.45, 506	0.51	2.68, 462	0.07
	S_3	3.22, 385	0.00	3.02, 411	0.01	3.58, 347	0.06	3.19, 389	0.02
	S_4	3.24, 383	0.07	3.64, 341	0.05	3.64, 341	0.03	3.94, 315	0.05
	S_5	3.34, 372	0.01	3.86, 322	0.06	3.67, 338	0.04	4.12, 301	0.05
	S_6	3.51, 353	0.00	3.88, 320	0.00	4.03, 308	0.00	4.38, 283	0.00
	S_7	3.60, 344	0.01	4.14, 300	0.00	4.15, 299	0.02	4.72, 263	0.05
	S_8	3.91, 317	0.08	4.22, 294	0.00	4.33, 286	0.00	4.73, 262	0.01
	S_9	3.97, 312	0.02	4.25, 292	0.00	4.46, 278	0.11	4.75, 261	0.10
	S_{10}	4.02, 308	0.05	4.29, 289	0.00	4.54, 273	0.01	4.97, 250	0.06
3-O-methyl Delphinidin-Aluminum(III) (**2/Al**)	S_1	2.10, 590	0.10	2.37, 523	0.59	1.94, 640	0.36	1.96, 632	0.76
	S_2	2.62, 473	0.75	2.59, 480	0.34	2.45, 507	0.56	2.63, 471	0.08
	S_3	3.23, 384	0.00	2.98, 417	0.07	3.56, 349	0.07	3.10, 400	0.01
	S_4	3.33, 373	0.00	3.68, 337	0.02	3.71, 334	0.00	3.92, 317	0.04
	S_5	3.44, 361	0.04	3.96, 313	0.05	3.77, 329	0.02	4.31, 288	0.05
	S_6	3.68, 337	0.01	4.16, 298	0.00	4.12, 301	0.00	4.40, 282	0.00
	S_7	3.82, 325	0.00	4.29, 289	0.00	4.19, 296	0.02	4.71, 263	0.09
	S_8	3.95, 314	0.02	4.40, 282	0.00	4.44, 279	0.01	4.80, 258	0.00
	S_9	4.05, 306	0.01	4.46, 278	0.01	4.53, 274	0.02	4.89, 254	0.09
	S_{10}	4.15, 299	0.06	4.55, 273	0.02	4.65, 267	0.07	5.07, 245	0.02
Copigment: 5-O-caffeoyl quinic acid (**3**)	S_1	3.31, 375	0.06	3.69, 336	0.47	4.31, 288	0.41	4.15, 299	0.60
	S_2	3.33, 372	0.13	4.27, 291	0.32	4.62, 268	0.21	4.56, 272	0.13
	S_3	3.80, 326	0.00	4.78, 259	0.00	4.72, 263	0.01	4.93, 251	0.00
	S_4	3.90, 318	0.00	4.92, 252	0.00	5.61, 221	0.79	5.52, 225	0.69
	S_5	3.92, 316	0.01	5.09, 244	0.40	5.89, 210	0.00	5.97, 208	0.00
	S_6	4.00, 310	0.36	5.17, 240	0.00	6.01, 206	0.00	6.23, 199	0.06
	S_7	4.18, 297	0.00	5.36, 231	0.00	6.22, 199	0.06	6.25, 198	0.10
	S_8	4.39, 282	0.01	5.63, 220	0.08	6.38, 194	0.11	6.53, 190	0.05
	S_9	4.46, 278	0.00	5.71, 217	0.01	6.55, 189	0.01	6.57, 189	0.00
	S_{10}	4.58, 271	0.02	5.79, 214	0.01	6.63, 187	0.01	6.87, 181	0.20

Table S2. Calculated TDDFT (in vacuum) and ADC(2) (in vacuum and in water) excitation energies ΔE(in eV), and maximum wavelength λ_{max} (in nm) and oscillator strength *f* of the binary complexes of the delphinidin cations **1** and **2** with the copigment **3** without aluminum and of the neutral ternary complexes **1/Al/3** and **2/Al(III)/3.**

		TDDFT				ADC(2)			
		Vacuum		Water		Vacuum		Water	
system	state	ΔE (eV, nm)	*f*	ΔE (eV, nm)	*f*	ΔE (eV, nm)	*f*	ΔE (eV, nm)	*f*
Binary Copigment Complex **V** of **1** and **3** without Al	S_1	2.29, 542	0.03	2.19, 566	0.02	2.30, 540	0.41	2.35, 528	0.47
	S_2	2.55, 487	0.06	2.55, 486	0.39	2.71, 457	0.01	2.82, 439	0.02
	S_3	2.59, 479	0.26	2.59, 478	0.06	2.79, 444	0.00	2.85, 435	0.01
	S_4	2.82, 439	0.06	2.83, 438	0.05	2.91, 427	0.01	2.91, 427	0.00
	S_5	3.05, 407	0.00	3.10, 399	0.00	3.55, 349	0.05	3.65, 340	0.03
	S_6	3.15, 394	0.00	3.31, 375	0.00	3.81, 325	0.00	3.80, 327	0.00
	S_7	3.38, 367	0.02	3.40, 365	0.05	3.94, 315	0.00	3.87, 320	0.44
	S_8	3.46, 358	0.00	3.59, 346	0.19	4.03, 308	0.33	4.03, 308	0.02
	S_9	3.51, 354	0.00	3.65, 339	0.05	4.31, 288	0.02	4.33, 286	0.01
	S_{10}	3.60, 344	0.01	3.72, 333	0.08	4.33, 286	0.02	4.48, 277	0.17
Binary Copigment Complex **VI** of **1** and **3** without Al	S_1	2.30, 538	0.01	2.26, 550	0.02	2.02, 615	0.50	2.27, 547	0.52
	S_2	2.46, 505	0.12	2.50, 496	0.52	2.45, 506	0.01	2.73, 454	0.03
	S_3	2.48, 499	0.34	2.61, 475	0.00	2.79, 445	0.01	2.84, 437	0.01
	S_4	2.88, 430	0.00	2.85, 435	0.04	3.07, 404	0.01	2.94, 422	0.01
	S_5	3.18, 390	0.01	3.20, 388	0.04	3.64, 341	0.07	3.68, 337	0.08
	S_6	3.20, 388	0.00	3.39, 366	0.02	4.19, 296	0.27	3.68, 337	0.06
	S_7	3.29, 377	0.00	3.46, 358	0.00	4.22, 294	0.02	3.93, 316	0.62
	S_8	3.46, 358	0.04	3.62, 343	0.01	4.23, 293	0.08	4.01, 309	0.00
	S_9	3.52, 352	0.01	3.70, 335	0.53	4.27, 290	0.33	4.45, 279	0.03
	S_{10}	3.61, 343	0.04	3.77, 329	0.00	4.29, 289	0.01	4.50, 276	0.01
Binary Copigment **Complex VII** of **2** and **3** without Al	S_1	2.36, 526	0.05	2.27, 545	0.03	2.38, 521	0.39	2.41, 515	0.44
	S_2	2.48, 501	0.25	2.48, 501	0.44	2.75, 451	0.05	2.81, 442	0.06
	S_3	2.57, 483	0.04	2.66, 466	0.01	2.85, 436	0.03	2.99, 415	0.02
	S_4	2.86, 434	0.16	2.88, 430	0.14	3.17, 391	0.05	3.31, 374	0.06
	S_5	3.19, 388	0.00	3.13, 396	0.00	3.52, 353	0.01	3.53, 352	0.01
	S_6	3.46, 359	0.01	3.46, 359	0.01	3.76, 330	0.02	3.89, 319	0.02
	S_7	3.46, 358	0.00	3.63, 341	0.02	4.13, 300	0.00	4.15, 299	0.36
	S_8	3.56, 349	0.02	3.77, 329	0.35	4.34, 286	0.20	4.45, 279	0.05
	S_9	3.81, 325	0.00	3.81, 326	0.00	4.50, 275	0.03	4.51, 275	0.05
	S_{10}	3.92, 317	0.00	4.00, 310	0.04	4.54, 273	0.01	4.54, 273	0.05
Binary Copigment Complex **VIII** of **2** and **3** without Al	S_1	2.26, 549	0.09	2.20, 564	0.05	2.11, 588	0.33	2.26, 550	0.41
	S_2	2.45, 507	0.07	2.51, 493	0.35	2.59, 478	0.01	2.88, 430	0.08
	S_3	2.58, 480	0.22	2.79, 444	0.02	2.70, 459	0.09	2.92, 425	0.08
	S_4	2.87, 433	0.08	2.93, 424	0.11	2.85, 435	0.07	3.16, 393	0.01
	S_5	3.01, 411	0.00	3.17, 391	0.03	3.51, 354	0.04	3.73, 333	0.04
	S_6	3.24, 383	0.04	3.36, 370	0.11	3.69, 336	0.01	3.87, 320	0.53
	S_7	3.36, 369	0.01	3.64, 341	0.02	3.70, 335	0.01	3.89, 319	0.18
	S_8	3.52, 352	0.00	3.72, 333	0.63	4.00, 310	0.00	4.40, 282	0.01
	S_9	3.58, 346	0.02	3.78, 328	0.00	4.13, 300	0.53	4.47, 278	0.00
	S_{10}	3.68, 337	0.02	3.94, 315	0.00	4.31, 288	0.00	4.55, 272	0.08
Ternary **1/Al/3** *trans*-diaquo Aluminum Complex **IV**	S_1	2.06, 603	0.06	2.30, 539	0.37	1.99, 623	0.36	1.97, 631	0.64
	S_2	2.43, 511	0.00	2.56, 484	0.35	2.40, 516	0.39	2.60, 477	0.11
	S_3	2.47, 499	0.04	2.59, 478	0.07	3.49, 355	0.00	3.18, 390	0.02
	S_4	2.51, 493	0.52	3.03, 410	0.00	3.56, 348	0.02	3.64, 340	0.00
	S_5	3.12, 398	0.00	3.05, 407	0.00	3.59, 345	0.08	3.92, 317	0.05
	S_6	3.18, 390	0.00	3.30, 375	0.00	3.65, 340	0.02	4.04, 307	0.05
	S_7	3.19, 389	0.00	3.35, 370	0.00	3.84, 323	0.00	4.17, 297	0.00
	S_8	3.27, 379	0.07	3.61, 343	0.01	4.03, 307	0.00	4.23, 293	0.26
	S_9	3.36, 369	0.02	3.63, 342	0.02	4.13, 300	0.02	4.26, 291	0.19
	S_{10}	3.69, 336	0.00	3.73, 333	0.40	4.24, 292	0.00	4.33, 287	0.00

Ternary **1/Al/3** *cis*-diaquo Aluminum Complex **II**	S_1	2.17, 572	0.23	2.22, 559	0.33	1.95, 638	0.48	1.93, 644	0.55
	S_2	2.20, 563	0.02	2.49, 498	0.06	2.48, 500	0.09	2.72, 456	0.05
	S_3	2.39, 519	0.02	2.73, 454	0.24	2.94, 421	0.00	3.12, 397	0.09
	S_4	2.69, 461	0.24	3.04, 407	0.04	3.29, 377	0.10	3.24, 383	0.03
	S_5	2.99, 415	0.02	3.08, 402	0.10	3.48, 357	0.07	3.80, 327	0.06
	S_6	3.10, 400	0.04	3.13, 396	0.01	3.52, 352	0.02	3.88, 319	0.02
	S_7	3.17, 391	0.00	3.21, 387	0.01	3.59, 346	0.01	3.89, 319	0.01
	S_8	3.30, 376	0.06	3.59, 346	0.05	3.93, 316	0.00	3.98, 312	0.00
	S_9	3.39, 365	0.07	3.64, 341	0.00	3.96, 314	0.02	4.03, 308	0.21
	S_{10}	3.40, 364	0.00	3.70, 335	0.02	4.01, 309	0.02	4.13, 300	0.00
Ternary **2/Al/3** *trans*-diaquo Aluminum Complex **IV**	S_1	2.18, 568	0.10	2.32, 535	0.46	2.02, 613	0.49	1.97, 631	0.67
	S_2	2.51, 494	0.37	2.55, 486	0.33	2.43, 511	0.29	2.60, 477	0.10
	S_3	2.53, 490	0.20	2.75, 451	0.00	3.26, 380	0.02	3.10, 400	0.01
	S_4	2.86, 433	0.00	2.98, 416	0.03	3.54, 350	0.00	3.82, 325	0.01
	S_5	3.04, 408	0.00	3.08, 403	0.00	3.85, 322	0.02	3.85, 322	0.03
	S_6	3.09, 401	0.00	3.35, 370	0.00	3.89, 319	0.01	4.16, 298	0.00
	S_7	3.21, 387	0.00	3.53, 352	0.00	3.94, 314	0.05	4.21, 295	0.05
	S_8	3.54, 351	0.03	3.62, 342	0.02	3.96, 314	0.01	4.31, 288	0.01
	S_9	3.65, 340	0.01	3.68, 337	0.00	4.09, 303	0.00	4.37, 284	0.00
	S_{10}	3.66, 339	0.00	3.77, 329	0.00	4.30, 288	0.00	4.45, 279	0.43
Ternary **2/Al/3** *cis*-diaquo Aluminum Complex **II**	S_1	2.20, 563	0.01	2.31, 538	0.45	2.16, 575	0.61	2.01, 617	0.68
	S_2	2.26, 550	0.02	2.45, 507	0.04	2.42, 512	0.09	2.65, 469	0.02
	S_3	2.27, 547	0.23	2.67, 465	0.20	3.02, 411	0.00	3.09, 401	0.00
	S_4	2.57, 482	0.33	2.95, 420	0.03	3.20, 388	0.04	3.23, 384	0.05
	S_5	2.97, 417	0.02	3.00, 413	0.05	3.44, 361	0.05	3.80, 326	0.02
	S_6	3.15, 394	0.04	3.21, 387	0.01	3.62, 343	0.00	3.87, 320	0.10
	S_7	3.19, 389	0.02	3.25, 382	0.02	3.80, 327	0.02	4.00, 310	0.00
	S_8	3.25, 381	0.00	3.62, 343	0.05	4.00, 310	0.02	4.14, 300	0.00
	S_9	3.39, 366	0.00	3.64, 340	0.01	4.10, 303	0.00	4.19, 296	0.05
	S_{10}	3.47, 357	0.04	3.76, 330	0.00	4.11, 302	0.08	4.23, 293	0.34