Structural and electronic properties of Z isomers of (4α→6´´,2α→O→1´´)-phenylflavans substituted with R=H, OH and OCH_3 calculated in aqueous solution with PCM solvation model.

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Table S1. Changes in relevant angles and dihedral angles in the presence of water, simulated by PCM model for the (4α→6′′,2α→*O*→1′′)-phenylflavans with R=OH and OCH_3[a]

	R=OH								R=OCH_3		
	$Z1_{CT}$	**$Z1_{CC}$**	**$Z1_{TC}$**	**$Z1_{TT}$**	**$Z2_{CT}$**	**$Z2_{CC}$**	**$Z2_{TC}$**	**$Z2_{TT}$**	**$Z1_{CT}$**	**$Z1_{CC}$**	**$Z2_{CC}$**
Dihedral angles (°)											
C-3—C-2—C-1′—C-6′	1.96	0.43	0.62	2.09	-0.98	0.41	-0.79	2.19	0.90	0.88	0.13
C-3—C-2—C-1′—C-2′	2.07	0.52	0.74	2.23	-1.05	0.31	-0.59	0.59	0.98	1.04	0.10
O1—C-2—C-1′—C-2′	2.18	0.74	0.85	2.23	-1.03	0.37	-1.42	2.19	1.21	1.41	0.43
H—O-5′′—C-5′′—C-4′′	0.47	0.44	19.81	20.54	0.25	0.36	47.77	50.02	—	—	—
H—O-3′′—C-3′′—C-4′′	0.30	-0.27	0.74	0.56	0.22	0.01	2.06	0.64	—	—	—
C-3a′′—O-3′′—C-3′′—C-4′′	—	—	—	—	—	—	—	—	-0.63	-0.57	-0.82
C-5a′′—O-5′′—C-5′′—C-4′′	—	—	—	—	—	—	—	—	0.55	-0.41	-0.19
Angles (°)											
C-3—C-2—C-1′	0.11	0.14	0.27	0.22	0.03	0.04	-0.02	-0.02	0.22	0.19	0.07
C-2—C-3—C-4	0.09	0.10	0.18	0.17	0.13	0.14	0.40	0.38	0.11	0.12	0.17
C-8a—O1—C-2	-0.05	-0.03	-0.61	-0.59	-0.05	-0.02	-0.86	-0.95	-0.02	-0.08	-0.01
C-4a—C-8a—C-8	0.12	0.14	0.19	0.16	0.15	0.17	0.29	0.27	0.13	0.15	0.17
O1—C-2—O	-0.66	-0.66	-0.73	-0.69	-0.37	-0.38	0.03	0.05	-0.76	-0.73	-0.49
C-4a—C-8a—O1	-0.12	-0.13	-0.10	-0.09	-0.10	-0.11	0.38	0.41	-0.13	-0.13	-0.24
C-4—C-4a—C-8[a]	0.06	0.05	0.59	0.58	0.05	0.03	1.32	1.45	-0.03	0.09	0.02
C-4a—C-4—C-3	-0.06	-0.09	0.37	0.40	-0.03	-0.01	1.13	1.37	-0.03	0.00	-0.01
C-4a—C-4—C-6′′	0.08	0.04	-0.77	-0.74	-0.04	-0.02	-0.91	-0.88	0.00	-0.05	-0.11
C-3—C-4—H-4	-0.21	-0.21	0.31	0.32	-0.22	-0.22	-0.86	-0.90	-0.23	-0.22	-0.22

Table S2. Topological properties at BCPs of the $Z1_{CT}$ conformer for R=OH calculated at the B3LYP/6-311++G** level of theory in the presence of water, simulated by PCM model.[a]

	Bond	Bond length	ρ_b	$\nabla^2\rho$	ε
Ring A	**C-4a—C-5**	1.399	0.305	-0.829	0.214
	C-5—C-6	1.396	0.307	-0.848	0.207
	C-6—C-7	1.398	0.306	-0.845	0.201
	C-7—C-8	1.395	0.307	-0.846	0.211
	C-8—C-8a	1.398	0.309	-0.864	0.241
	C-8a—C-4a	1.402	0.307	-0.838	0.246
	C-5—H	1.088	0.280	-0.961	0.020
	C-6—H	1.088	0.280	-0.955	0.024
	C-7—H	1.089	0.280	-0.961	0.019
	C-8—H	1.088	0.279	-0.953	0.024
Ring B	**C-1′—C-2′**	1.401	0.304	-0.829	0.205
	C-2′—C-3′	1.396	0.307	-0.852	0.198
	C-3′—C-4′	1.397	0.307	-0.855	0.194
	C-4′—C-5′	1.397	0.308	-0.855	0.195
	C-5′—C-6′	1.397	0.307	-0.851	0.197
	C-6′—C-1′	1.400	0.304	-0.829	0.206
	C-2′—H	1.086	0.282	-0.973	0.019
	C-3′—H	1.089	0.280	-0.961	0.019
	C-4′—H	1.089	0.280	-0.962	0.018
	C-5′—H	1.089	0.280	-0.961	0.019
	C-6′—H	1.086	0.283	-0.975	0.019
	C-1′—C-2	1.523	0.255	-0.622	0.066
Ring C	**O1—C-2**	1.435	0.250	-0.510	0.111
	C-2—C-3	1.530	0.250	-0.580	0.015
	C-3—C-4	1.533	0.241	-0.536	0.013
	C-4—C-4a	1.519	0.247	-0.567	0.026
	C-8a—C-4a	1.402	0.307	-0.838	0.246
	C-8a—O1	1.382	0.271	-0.358	0.003
	C-3—H	1.094	0.276	-0.924	0.004
	C-3—H′	1.094	0.276	-0.923	0.004
	C-4—H	1.094	0.279	-0.941	0.002
Ring E	**C-2—O**	1.433	0.250	-0.508	0.115
	O—C-1′′	1.380	0.273	-0.372	0.006
	C-2—C-3	1.530	0.250	-0.580	0.015
	C-3—C-4	1.533	0.241	-0.536	0.013
	C-1′′—C-6′′	1.397	0.307	-0.835	0.284
	C-6′′—C-4	1.517	0.245	-0.554	0.038
Ring D	**C-1′′—C-2′′**	1.398	0.307	-0.846	0.266

	C-2′′—C-3′′	1.397	0.307	-0.843	0.270
	C-3′′—C-4′′	1.401	0.306	-0.844	0.262
	C-4′′—C-5′′	1.396	0.308	-0.844	0.272
	C-5′′—C-6′′	1.407	0.303	-0.821	0.267
	C-1′′—C-6′′	1.397	0.307	-0.835	0.284
	C-2′′—H	1.088	0.276	-0.930	0.038
	C-4′′—H	1.088	0.276	-0.928	0.038
Substituents	**O-5′′—H**	0.984	0.341	-2.399	0.020
	O-3′′—H	0.985	0.340	-2.395	0.020
	C-3′′—O-3′′	1.363	0.287	-0.399	0.008
	C-5′′—O-5′′	1.363	0.286	-0.396	0.003

[a] ρ_b and $\nabla^2\rho_b$ are expressed in a.u. and bond lengths in Å.

Table S3. Topological properties at BCPs of the $Z1_{CT}$ conformer for R=OCH_3 calculated at the B3LYP/6-311++G** level of theory in the presence of water, simulated by PCM model.[a]

	Bond	Bond length	ρ_b	$\nabla^2\rho_b$	ε
Ring A	**C-4a—C-5**	1.398	0.305	-0.829	0.215
	C-5—C-6	1.396	0.307	-0.848	0.206
	C-6—C-7	1.398	0.306	-0.845	0.201
	C-7—C-8	1.395	0.307	-0.846	0.211
	C-8—C-8a	1.397	0.309	-0.865	0.241
	C-8a—C-4a	1.402	0.307	-0.839	0.246
	C-5—H	1.088	0.281	-0.963	0.020
	C-6—H	1.088	0.280	-0.955	0.024
	C-7—H	1.089	0.280	-0.961	0.019
	C-8—H	1.088	0.279	-0.953	0.024
Ring B	**C-1′—C-2′**	1.401	0.304	-0.829	0.206
	C-2′—C-3′	1.396	0.307	-0.852	0.197
	C-3′—C-4′	1.397	0.308	-0.855	0.195
	C-4′—C-5′	1.397	0.308	-0.855	0.195
	C-5′—C-6′	1.396	0.307	-0.852	0.197
	C-6′—C-1′	1.401	0.304	-0.828	0.205
	C-2′—H	1.086	0.282	-0.974	0.019
	C-3′—H	1.089	0.280	-0.961	0.019
	C-4′—H	1.089	0.280	-0.962	0.018
	C-5′—H	1.089	0.280	-0.961	0.019
	C-6′—H	1.086	0.282	-0.974	0.019
	C-1′—C-2	1.523	0.255	-0.622	0.066
Ring C	**O1—C-2**	1.434	0.250	-0.510	0.111
	C-2—C-3	1.529	0.250	-0.581	0.015
	C-3—C-4	1.533	0.241	-0.536	0.013
	C-4—C-4a	1.519	0.247	-0.566	0.026
	C-8a—C-4a	1.402	0.307	-0.839	0.246
	C-8a—O1	1.383	0.270	-0.356	0.005
	C-3—H	1.094	0.276	-0.924	0.004
	C-3—H′	1.094	0.276	-0.924	0.004
	C-4—H	1.094	0.279	-0.942	0.002
Ring E	**C-2—O**	1.433	0.250	-0.508	0.116
	O—C-1′′	1.379	0.273	-0.376	0.004
	C-2—C-3	1.529	0.250	-0.581	0.015
	C-3—C-4	1.533	0.241	-0.536	0.013
	C-1′′—C-6′′	1.393	0.310	-0.845	0.292
	C-6′′—C-4	1.518	0.245	-0.553	0.038
Ring D	**C-1′′—C-2′′**	1.402	0.305	-0.838	0.250
	C-2′′—C-3′′	1.393	0.308	-0.845	0.274

	C-3′′—C-4′′	1.406	0.303	-0.832	0.247
	C-4′′—C-5′′	1.393	0.308	-0.842	0.276
	C-5′′—C-6′′	1.412	0.300	-0.810	0.256
	C-1′′—C-6′′	1.393	0.310	-0.845	0.292
	C-2′′—H	1.084	0.280	-0.949	0.037
	C-4′′—H	1.084	0.280	-0.948	0.037
Substituents	**C-5′′—O-5′′**	1.366	0.284	-0.385	0.013
	O-5′′—C-5a′′	1.426	0.243	-0.317	0.006
	C-5a′′—H	1.096	0.279	-0.947	0.042
	C-5a′′—H	1.096	0.279	-0.948	0.042
	C-5a′′—H	1.091	0.283	-0.982	0.042
	C-3′′—O-3′′	1.366	0.284	-0.387	0.008
	O-3′′—C-3a′′	1.426	0.244	-0.323	0.007
	C-3a′′—H	1.091	0.283	-0.981	0.042
	C-3a′′—H	1.097	0.279	-0.946	0.042
	C-3a′′—H	1.097	0.279	-0.946	0.042

[a] ρ_b and $\nabla^2\rho_b$ are expressed in a.u. and bond lengths in Å.

Table S4. Natural bond orbital (NBO) second-order stabilization energies, $E^{(2)}$, calculated at B3LYP/6-311++G** level of theory, for $\sigma_{(C3—H)}$ donors in the presence of water, simulated by PCM model.[a]

		R=OH									R=OCH$_3$			
Donor	**Acceptor**	**Z1$_{CT}$**	**Z1$_{CC}$**	**Z1$_{TC}$**	**Z1$_{TT}$**	**Z2$_{CT}$**	**Z2$_{CC}$**	**Z2$_{TC}$**	**Z2$_{TT}$**	**Average**	**Z1$_{CT}$**	**Z1$_{CC}$**	**Z2$_{CC}$**	**Average**
σ C-3—H	**σ C-4—C-6´´**	2.67	2.67	2.65	2.65	2.63	2.63	2.73	2.7	2.67	2.61	2.67	2.65	2.64
σ C-3—H	**σ C-4—C-4a**	2.66	2.66	2.71	2.71	2.70	2.69	2.71	2.74	2.70	2.65	2.65	2.70	2.67
σ C-3—H	**σ C-2—O**	5.41	5.41	5.43	5.42	5.48	5.48	5.41	5.48	5.44	5.34	5.29	5.50	5.38
σ C-3—H	**σ C-2—O1**	5.44	5.43	5.38	5.38	5.58	5.58	5.58	5.54	5.49	5.48	5.33	5.58	5.46

[a]All values are expressed in kcal mol^{-1}.

Table S5. Bond polarizations of C-2—C-3 and C-3—C-4 (electron density percentage on C-2, C-3 and C-4).

Substituent	Conformer	C-2—C-3		C-3—C-4	
		%C-2	%C-3	%C-3	%C-4
R=OH	$Z1_{CT}$	51.07	48.93	49.46	50.54
	$Z1_{CC}$	51.06	48.94	49.45	50.55
	$Z1_{TC}$	50.98	49.02	49.14	50.86
	$Z1_{TT}$	50.99	49.01	49.14	50.86
	$Z2_{CT}$	51.07	48.93	49.73	50.27
	$Z2_{CC}$	51.06	48.94	49.72	50.28
	$Z2_{TC}$	50.99	49.01	49.41	50.59
	$Z2_{TT}$	50.99	49.01	49.42	50.58
$R=OCH_3$	$Z1_{CT}$	51.06	48.94	49.43	50.57
	$Z1_{CC}$	51.08	48.92	49.41	50.59
	$Z2_{CC}$	51.07	48.93	49.7	50.30

Figure S1. Optimized geometry of the conformers of Z1-isomer of (4α→6′′,2α→*O*→1′′)-phenylflavans substituted with R′=H, R=OH at the B3LYP/6-31G** level of theory in the presence of water, simulated by PCM model.

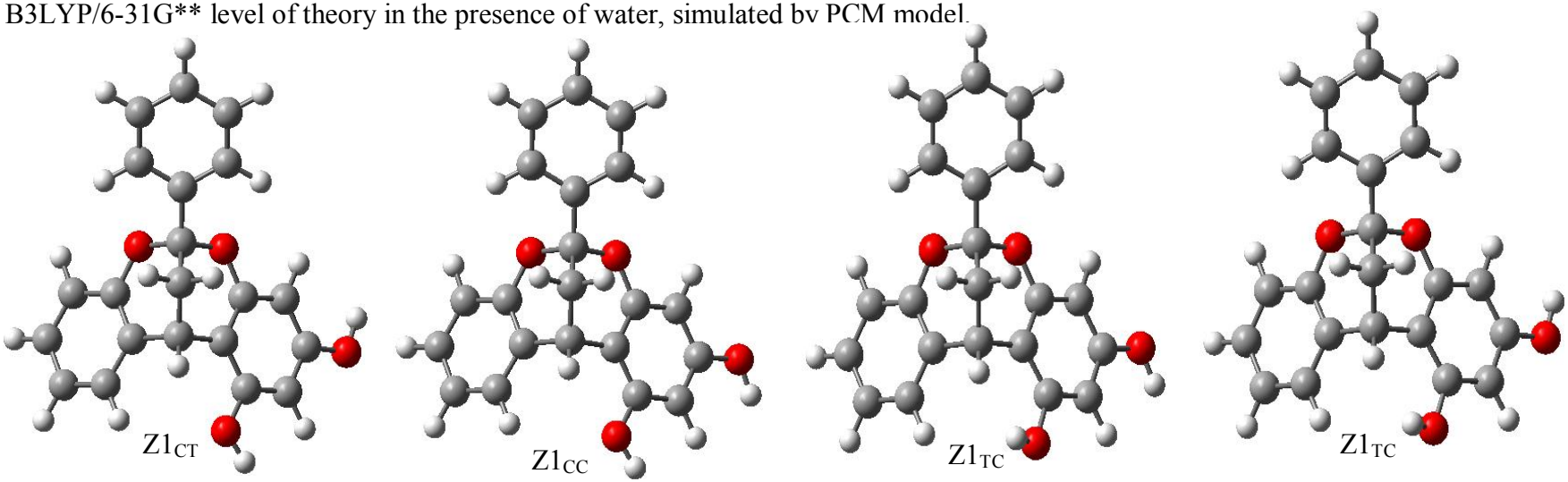

Figure S2. Optimized geometry of the conformers of Z-isomer of (4α→6′′,2α→*O*→1′′)-phenylflavans substituted with R′=H and R=OCH_3 at the B3LYP/6-31G** level of theory in the presence of water, simulated by PCM model.