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Supporting Information

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Photophysics of Structurally Modified Flavin Derivatives in the Blue-Light Photoreceptor YtvA: A Combined Experimental and Theoretical Study

Mario R. Silva-Junior,[a] Madina Mansurova,[b] Wolfgang Gärtner,*[b] and Walter Thiel*[a]

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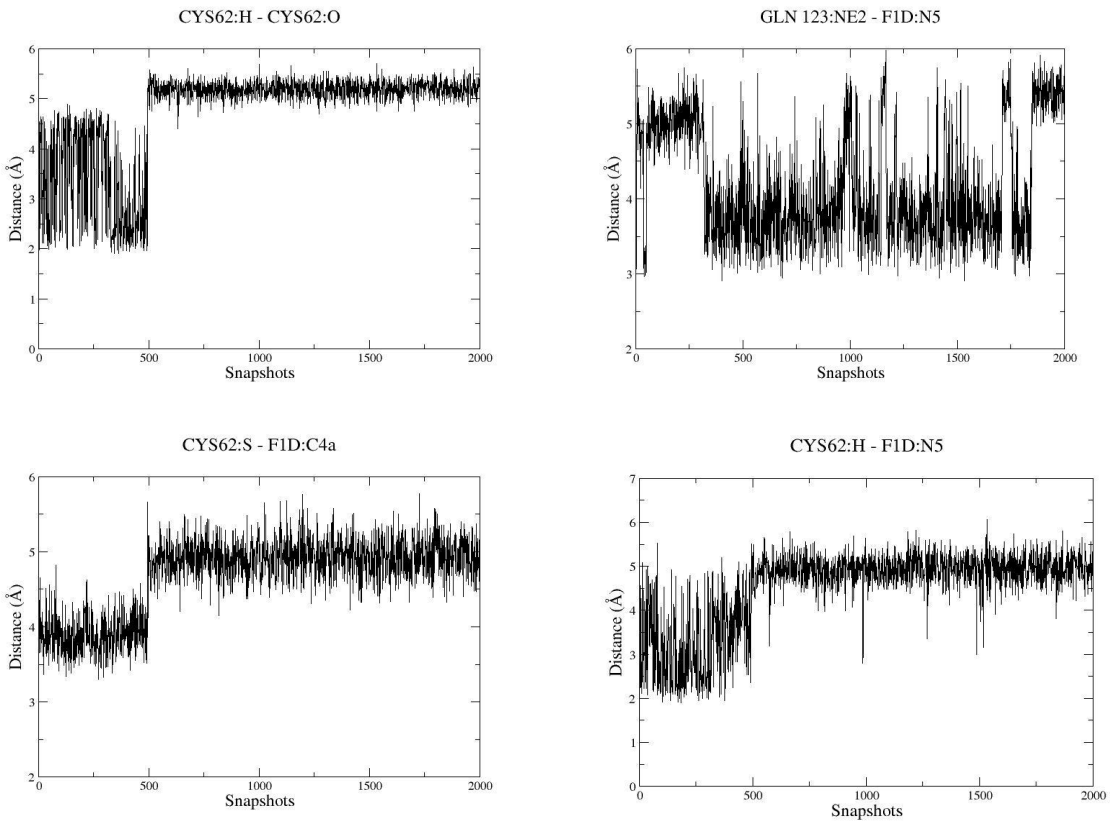
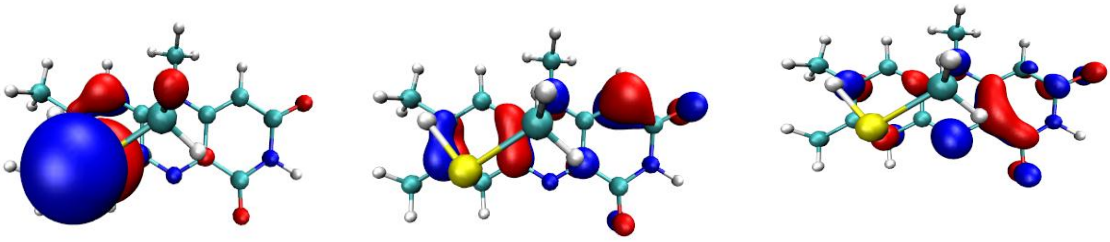


Figure S1: Selected distances from the production MD run for the 1DFMN-YtvA.



Ps π_H π_L

Figure S2: Frontier orbitals for QM region 1 of the 1DFMN chromophore.

Table S1: Selected bond distances (Å) of snapshot 1 for the dark state (S_0), the lowest singlet excited state (S_1) as well as two S_1/S_0 conical intersections of 1DFMN-Ytva, optimized at the (TD)-B3LYP / CHARMM level. The QM region 1 was used.

	S_0	S_1	CIn E_1[a]	CIn planar
N5C5a	1.364	1.335	1.365	1.365
N5C4a	1.294	1.360	1.321	1.345
C4aC10a	1.455	1.426	1.400	1.429
C10aN10	1.376	1.357	1.391	1.390
N10C9a	1.393	1.406	1.424	1.408
C4aC4	1.499	1.444	1.536	1.472
C4O	1.214	1.224	1.207	1.225
C4N3	1.382	1.426	1.416	1.392
N3H	1.013	1.013	1.018	1.013
N3C2	1.391	1.357	1.413	1.403
C2O	1.242	1.246	1.220	1.238
C2C1	1.427	1.445	1.474	1.426
C1C10a	1.374	1.413	1.488	1.383
$N5S_{cys}$	4.218	4.102	4.044	2.995
$N5H_{cys}$	4.959	4.874	4.799	1.123
C5aC6	1.409	1.414	1.393	1.401
C6C7	1.381	1.384	1.400	1.385
C7C8	1.419	1.424	1.411	1.419
C8C9	1.385	1.385	1.402	1.390
C9C9a	1.396	1.397	1.397	1.392

[a]Conical intersection illustrated on the left side of Figure 4 of the manuscript. The energy gap between S_1 and S_0 states is 0.14 eV.
[b]Conical intersection illustrated on the right side of Figure 4 of the manuscript. The energy gap between S_1 and S_0 states is 0.07 eV.

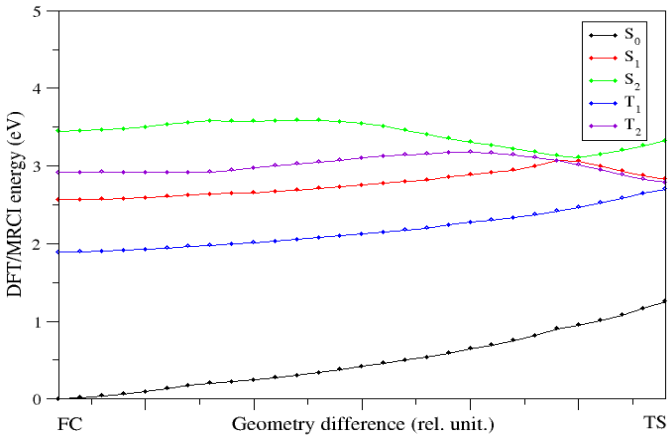


Figure S3: DFT/MRCI energy profiles for several excited states along a linearly interpolated path between the Frank-Condon point (FC) and the transition state for hydrogen transfer on the S_1 surface. Shown are the results for snapshot 1.

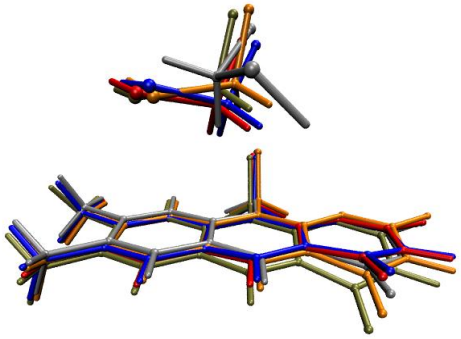


Figure S4: Overlay of QM/MM optimized geometries of the five snapshots of 5DFMN-LOV complex. For clarity, only atoms from the QM region are shown.

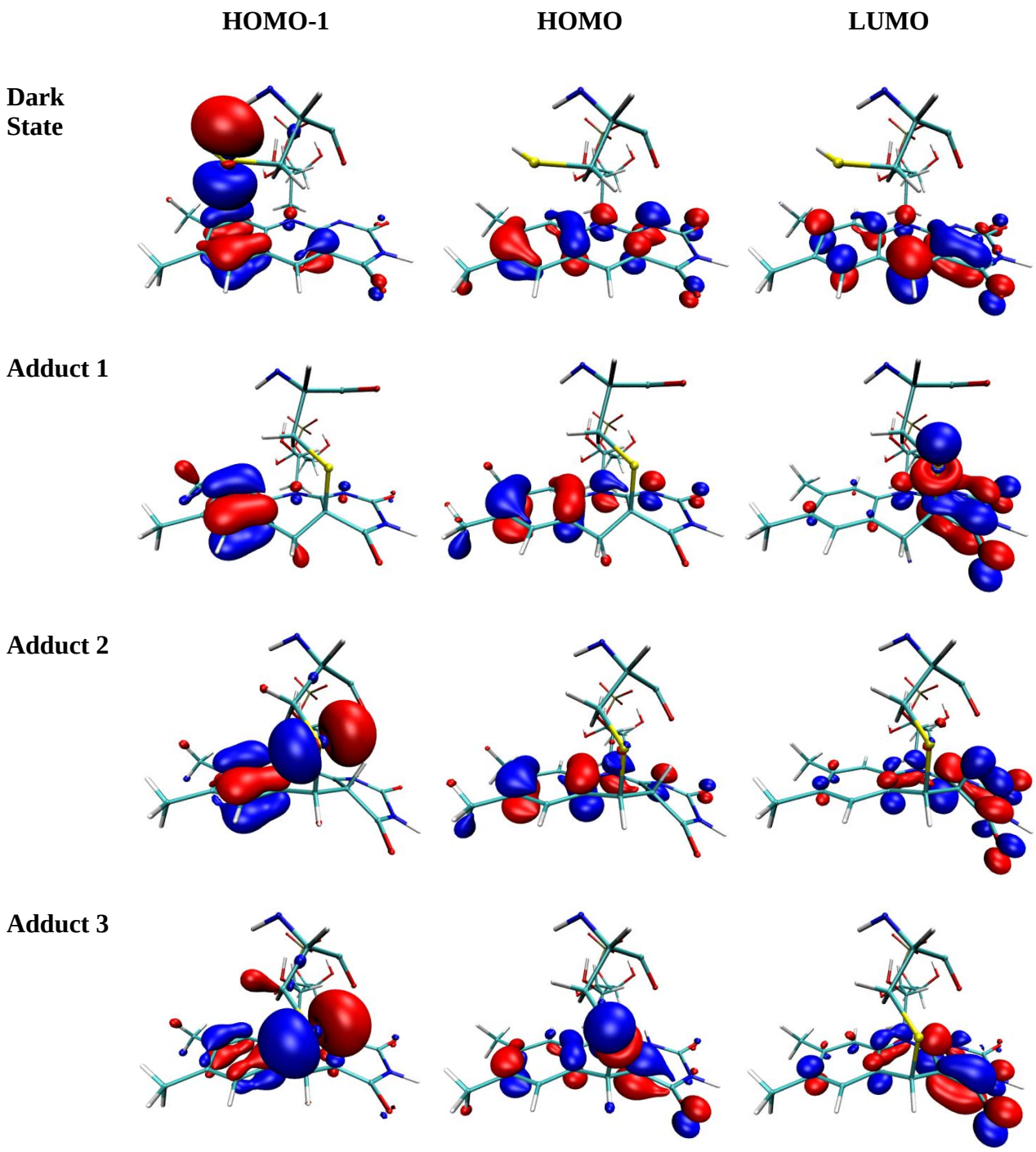


Figure S5: Frontier orbitals for QM region 1 of species involved in the photocycle of 5DFMN.

Table S2: Selected distances (Å) in 5DFMN-LOV (snapshot 5) for stationary points of the reaction mechanism (see manuscript):. Data are given for the dark state (S_0, S_1 and T_1), adducts 1 and 2 (S_0, S_1 and T_1), and adduct 3 (S_0, S_1/S_0). Ground states were optimized at the B3LYP/CHARMM level, S_1 states at the TD-B3LYP/CHARMM level, and T_1 states at the UB3lYP/CHARMM level. The QM region 1 was used.

	Dark state			**Adduct 1**			**Adduct 2**			**Adduct 3**	
	S_0	**S_1**	**T_1**	**S_0**	**S_1**	**T_1**	**S_0**	**S_1**	**T_1**	**S_0**	**S_1/S_0**
C4aC5	1.369	1.407	1.406	1.520	1.504	1.467	1.369	1.407	1.406	1.520	1.504
C5C5a	1.408	1.414	1.409	1.493	1.499	1.487	1.408	1.414	1.409	1.493	1.499
C4aC10a	1.438	1.423	1.412	1.515	1.463	1.422	1.438	1.423	1.412	1.515	1.463
C10a N10	1.378	1.392	1.423	1.354	1.395	1.384	1.378	1.392	1.423	1.354	1.395
N10C9a	1.396	1.395	1.384	1.441	1.406	1.420	1.396	1.395	1.384	1.441	1.406
C4C4a	1.459	1.424	1.435	1.532	1.446	1.454	1.459	1.424	1.435	1.532	1.446
C4O	1.240	1.251	1.247	1.220	1.233	1.230	1.240	1.251	1.247	1.220	1.233
C4 N3	1.356	1.393	1.380	1.358	1.392	1.370	1.356	1.393	1.380	1.358	1.392
N3 C2	1.417	1.376	1.383	1.411	1.374	1.404	1.417	1.376	1.383	1.411	1.374
C2O	1.225	1.227	1.229	1.222	1.221	1.229	1.225	1.227	1.229	1.222	1.221
C2 N1	1.359	1.390	1.382	1.365	1.403	1.362	1.359	1.390	1.382	1.365	1.403
N1C10a	1.319	1.324	1.316	1.311	1.296	1.326	1.319	1.324	1.316	1.311	1.296
$C4aS_{cys}$	4.765	4.782	4.795	1.898	2.395	4.231	4.765	4.782	4.795	1.898	2.395
$C5H_{cys}$	3.393	3.326	3.334	1.095	1.095	1.100	3.393	3.326	3.334	1.095	1.095
C5aC6	1.415	1.396	1.398	1.389	1.376	1.395	1.415	1.396	1.398	1.389	1.376
C6C7	1.376	1.410	1.402	1.393	1.407	1.391	1.376	1.410	1.402	1.393	1.407
C7C8	1.423	1.409	1.423	1.405	1.420	1.410	1.423	1.409	1.423	1.405	1.420
C8C9	1.384	1.392	1.384	1.393	1.382	1.389	1.384	1.392	1.384	1.393	1.382
C9C9a	1.402	1.409	1.408	1.394	1.411	1.402	1.402	1.409	1.408	1.394	1.411
C9aC5a	1.421	1.432	1.453	1.398	1.421	1.406	1.421	1.432	1.453	1.398	1.421

Table S3: Relative energies of 5DFMN-YtvA for QM region 2 calculated at the B3LYP/CHARMM level for some selected snapshots. Values in kcal mol^{-1}.

		snap 3	snap 4	snap 5	average
Dark state (S_0)[a]	QM	0.0	0.0	0.0	0.0
	QM/MM	0.0	0.0	0.0	0.0
Adduct 1 (S_0)	QM	26.8	25.4	5.1	19.1
	QM/MM	32.2	35.7	23.4	30.4
Adduct 2 (S_0)	QM	25.0	19.9	6.9	17.3
	QM/MM	43.6	31.6	21.1	32.1
Adduct 3 (S_0)	QM	19.8	26.9	-2.6	14.7
	QM/MM	38.1	29.5	0.0	22.5

[a]Absolute QM (QM/MM) energies in a.u.: Snap 3, -2853.212279 (-2966.954472); snap 4: -2853.209447 (-2966.965865); snap 5: -2853.138276 (-2967.068763).

Table S4: DFT/MRCI vertical singlet and triplet excitation wavelengths λ (nm) at the QM/MM B3LYP/CHARMM ground-state equilibrium geometry for three snapshots of adduct 2 of 5DFMN-YtvA. The average values are also listed together with the available experimental data. The dominant excitations are specified, and oscillator strengths are given in parentheses.

State	**excitation**	**snap 3**	**snap 4**	**snap 5**	**average**	**exp.[a]**
S_1	$\pi_H \rightarrow \pi_L$	323 (0.348)	322 (0.374)	330 (0.364)	327 (0.362)	340
S_2	$\pi_{H-1} \rightarrow \pi_L$	297 (0.012)	295 (0.016)	310 (0.013)	301 (0.014)	
S_3	$\pi_{H-2} \rightarrow \pi_L$ + $\pi_H \rightarrow \pi_{L+1}$	278 (0.029)	275 (0.039)	284 (0.026)	279 (0.031)	
S_4	$n_O \rightarrow \pi_L$	270 (0.066)	267 (0.039)	268 (0.005)	266 (0.037)	
T_1	$\pi_H \rightarrow \pi_L$	399	399	411	404	
T_2	$\pi_{H-1} \rightarrow \pi_L$ + $\pi_H \rightarrow \pi_{L+1}$ + $\pi_{H-1} \rightarrow \pi_{L+1}$	337	335	345	340	
T_3	$\pi_{H-1} \rightarrow \pi_L$ + $\pi_{H-2} \rightarrow \pi_{L+1}$	310	309	314	312	
T_4	$\pi_{H-1} \rightarrow \pi_{L+1}$	301	299	307	303	

[a] Maxima of UV/Vis experimental absorption spectra of photoproduct. This work.

Table S5: DFT/MRCI vertical singlet and triplet excitation wavelengths λ (nm) at the QM/MM B3LYP/CHARMM ground-state equilibrium geometry for three snapshots of adduct 3 of 5DFMN-YtvA. The average values are also listed together with the available experimental data. The dominant excitations are specified, and oscillator strengths are given in parentheses.

State	**excitation**	**snap 3**	**snap 4**	**snap 5**	**average**	**exp.**[a]
S_1	$\pi_H \rightarrow \pi_L$	293 (0.143)	298 (0.227)	311 (0.274)	301 (0.215)	340
S_2	mixed $\pi \rightarrow \pi^*$ contributions	290 (0.132)	291 (0.048)	297 (0.006)	293 (0.062)	
S_3	mixed $\pi \rightarrow \pi^*$ contributions	263 (0.083)	267 (0.081)	275 (0.048)	268 (0.071)	
S_4	$n_O \rightarrow \pi_L$	257 (0.005)	254 (0.001)	271 (0.026)	260 (0.011)	
T_1	$\pi_H \rightarrow \pi_L$	370	376	385	377	
T_2	mixed $\pi \rightarrow \pi^*$ contributions	338	340	343	340	
T_3	mixed $\pi \rightarrow \pi^*$ contributions	316	316	313	315	
T_4	$n_O \rightarrow \pi_L$	302	304	310	305	

[a] Maxima of UV/Vis experimental absorption spectra of photoproduct. This work.

Emission and excitation spectra of 5DFMN-LOV at various wavelengths

The fluorescence spectra shown below yield evidence for the fluorescence of the photoproduct: *top left*, excitation at photoproduct maximum, mostly giving the fluorescence emission maximum of the dark state ($\lambda_{em} \approx 450$ nm) with a shoulder around 400 nm; *bottom left*, excitation at shorter wavelength (325 nm) causes an increase of the 400 nm-component. *Top right*, detection at 450 nm yields emission spectrum of the dark state; *bottom right*, detection at 400 nm provides emission spectrum unlike dark state, similar to the photoproduct absorbance spectrum (note low emission intensity).