

Supporting Information

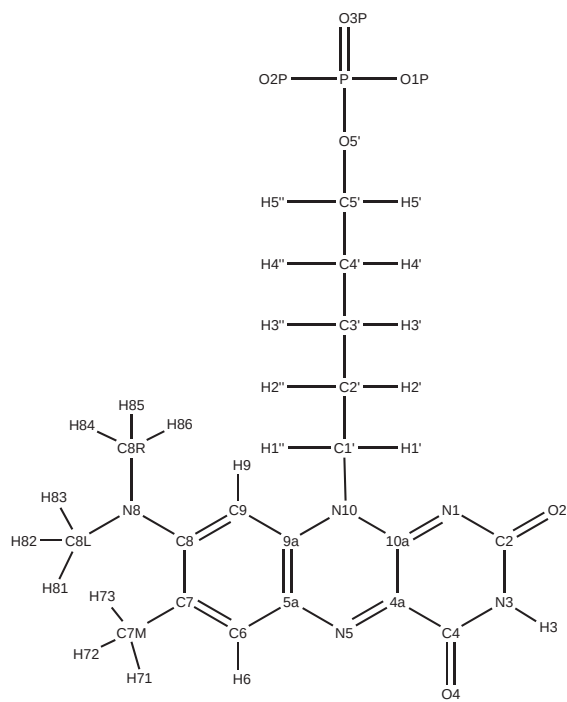


Figure SI1: Atomnames of roseoflavin.

atom	type	charge	atom	type	charge
N1	NN3	-0.660	9a	CN2	0.360
C2	CN1	0.520	N10	NN2	-0.050
O2	ON1	-0.490	10a	CN2	0.310
N3	NN2	-0.460	ribityl-chain		
H3	HN2	0.360	C1'	CN8	-0.180
C4	CN1	0.530	H1'	HN8	0.090
O4	ON1	-0.480	H1''	HN8	0.090
4a	CN2	0.360	C2'	CN7	0.140
N5	NN3	-0.660	H2'	HN7	0.090
5a	CN2	0.360	O2'	OH1	-0.660
C6	CN3	-0.115	HO2'	H	0.430
H6	HN3	0.115	C3'	CN7	0.140
C7	CN3	0.000	H3'	HN7	0.090
C7M	CN9	-0.270	O3'	OH1	-0.660
H71	HN9	0.090	HO3'	H	0.430
H72	HN9	0.090	C4'	CN7	0.140
H73	HN9	0.090	H4'	HN7	0.090
C8	CN9	0.050	O4'	OH1	-0.660
N8	NN2	-0.050	HO4'	H	0.430
C8L	CN9	-0.270	C5'	CN8	-0.080
H81	HN9	0.090	H5'	HN8	0.090
H82	HN9	0.090	H5''	HN8	0.090
H83	HN9	0.090	O5'	ON2	-0.620
C8R	CN9	-0.270	phosphate		
H84	HN9	0.090	P	P	1.500
H85	HN9	0.090	O1P	ON3	-0.680
H86	HN9	0.090	O2P	ON4	-0.820
C9	CN3	-0.115	O3P	ON3	-0.820
H9	HN3	0.115			

Table SI1: Chosen atomtypes and charges of roseoflavin for CHARMM27 force field

types	force constant k_{θ}	θ_0
CN7 NN2 HN2	30.0	118.5
NN3 CN1 ON1	130.0	123.8
NN2 CN1 ON1	130.0	121.5
NN2 CN2 NN3	70.0	122.2
CN3 CN3 CN3	40.0	120.0
CN7 CN8 NN2	110.0	111.0
CN7 CN7 OH1	75.7	110.1
CN7 CN7 CN7	53.3	111.0
CN3 CN2 NN2	100.0	125.7
CN7 CN8 ON2	70.0	108.4
HN7 CN7 OH1	45.9	108.8
CN7 OH1 H	57.5	106.0
CN8 CN7 OH1	75.7	110.1
CN2 NN2 CN2	90.0	122.0
CN2 NN2 CN8	70.0	125.9
CN2 NN3 CN2	90.0	119.4
CN2 CN2 CN3	60.0	121.0
CN2 CN1 ON1	50.0	124.7
CN2 CN2 NN2	100.0	116.0
CN2 CN2 NN3	60.0	123.0
CN1 CN2 CN2	70.0	119.6
CN1 NN2 CN1	50.0	125.0
CN1 CN2 NN3	125.0	129.0
CN2 CN1 NN2	70.0	116.0
CN3 CN3 CN9	45.8	122.3
CN3 CN9 NN2	85.0	122.9
CN9 NN2 CN9	70.0	125.9
HN3 CN3 CN9	38.0	122.1
CN9 CN3 CN9	45.8	122.3
CN3 CN9 CN3	40.0	120.0
CN9 CN3 CN2	85.0	117.8

Table SI2: Chosen angles of roseoflavin for CHARMM27 force field

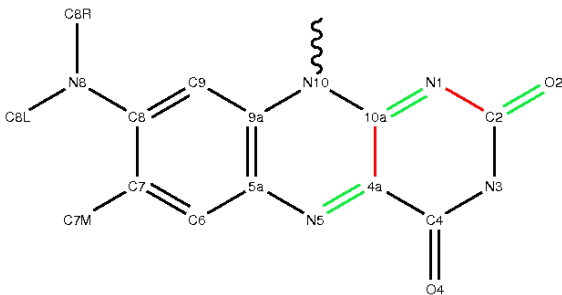


Figure SI2: Reaction coordinate Q_R . Elongation of bond is denoted in green, contraction in red.
 $Q_R = \alpha \times b(O2-C2) - \alpha \times d(C2-N1) + \alpha \times d(N1-10a) - \alpha \times d(10a-4a) + \alpha \times d(4a-N5)$, whereas $\alpha = 0.4472$.
 For simplicity no special weighting for the bond distances was chosen. A free geometry optimization has shown that the global minimum for the S_1 staet ($\rightarrow Q_R = 0.46$) and the minimum structure along the Q_R path ($Q_R = 0.45$) are energetically 0.0001 eV and geometrically 0.01 a.u. (RMSD) apart.

types	force constant k_ϕ	n	δ
X CN9 CN3 X	0.00	6	0.0
X CN7 CN7 X	0.20	3	0.0
X CN1 CN2 X	12.00	2	180.0
CN7 CN8 ON2 P	2.50	1	180.0
H OH1 CN7 CN8	1.33	1	0.0
X CN7 OH1 X	0.14	3	0.0
X CN2 NN2 X	5.00	2	180.0
X CN2 CN2 X	6.00	2	180.0
X CN8 CN7 X	0.15	3	0.0
CN2 NN2 CN8 HN8	0.40	3	0.0
CN2 NN2 CN8 CN7	0.60	3	0.0
CN9 CN3 CN3 CN2	4.00	2	180.0
NN3 CN2 CN7 CN1	2.00	2	151.7
CN9 NN2 CN9 HN9	0.00	3	0.0
CN3 CN9 NN2 CN9	5.00	2	180.0
CN3 CN3 CN9 NN2	9.00	2	180.0
CN2 CN3 CN9 NN2	9.00	2	180.0

Table SI3: Chosen diheadral angles of roseoflavin for CHARMM27 force field

bond	d_{GS} in Å	d_{S_1} in Å	$\Delta(d_{S_1}-d_{GS})$ in Å
O2-C2	1.22	1.23	0.01
C2-N1	1.39	1.40	0.01
N1-10a	1.31	1.37	0.06
10a-4a	1.46	1.40	-0.06
4a-N5	1.31	1.40	0.09

Table SI4: Significant changes of bond lengths from ground state (GS) to first excited state S_1

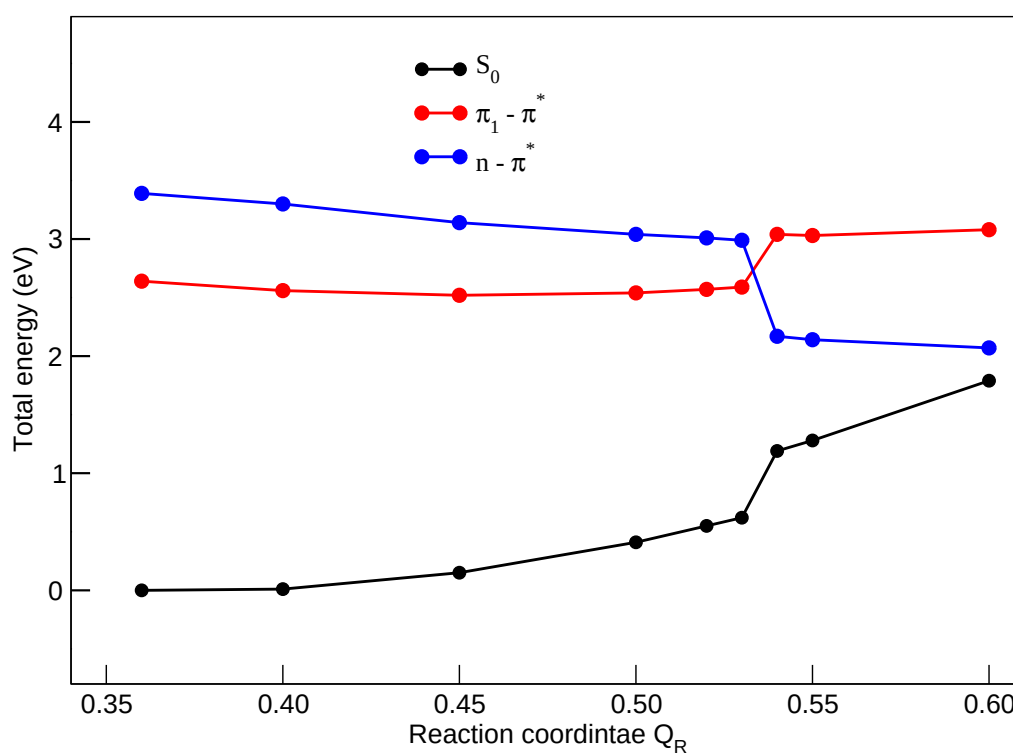


Figure SI3: Geometry optimization at TD-CC2 level with def-SVP basis set of roseoflavin in gasphase on the lowest excited state ($\pi_1 - \pi^*$ or $n - \pi^*$) along the reaction coordinate Q_R . At $Q_R = 0.45$ one can find a minimum with this constraint, that is almost the global one.

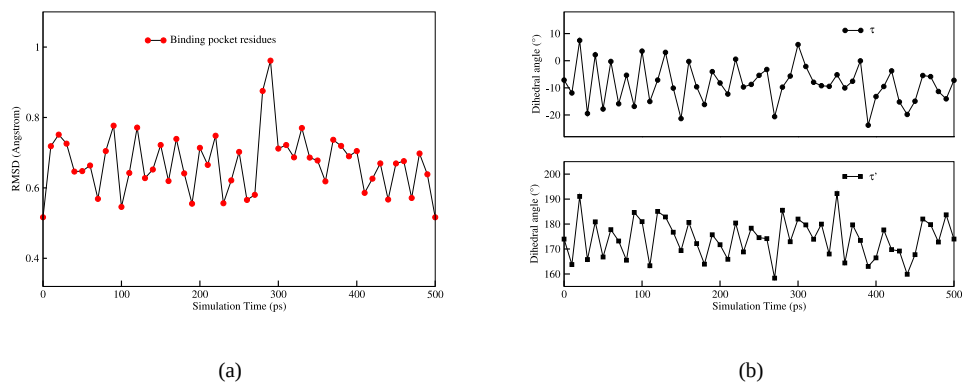


Figure SI4: Analysis of the MD-trajectory (a) RMSD of RoF and adjacent residues. (b) Values of dihedral angles τ (top) and τ' (bottom) along the MD trajectory.

method	basis set	structure	GS minimum				LE-state minimum			
			$\omega(\text{LE})$	$\omega(\text{LE2})$	$\omega(\text{CT})$	$\Delta\omega$	$\omega(\text{LE})$	$\omega(\text{LE2})$	$\omega(\text{CT})$	$\Delta\omega$
BH-LYP	def-TZVP	$\text{Ros}_p^{(np)}$	3.11	3.62	3.44	0.33	3.05	3.60	3.55	0.50
		$\text{Ros}_p^{(pl)}$	3.13	3.66	3.52	0.39	3.08	3.67	3.64	0.56
CC2	cc-pVDZ	$\text{Ros}_p^{(np)}$	2.68	3.22	3.78	1.10	2.60	3.24	3.95	1.35
		$\text{Ros}_p^{(pl)}$	2.75	3.31	3.85	1.10	2.69	3.31	4.03	1.34
	aug-cc-pVDZ	$\text{Ros}_p^{(np)}$	2.57	3.14	3.57	1.00	2.49	3.11	3.73	1.24
		$\text{Ros}_p^{(pl)}$	2.65	3.20	3.64	0.99	2.59	3.19	3.82	1.23

Table SI5: QM/MM excitation energies (in eV) for the optimized ground state (GS) structure and LE-state structure of the $\text{Ros}_p^{(pl)}$ and $\text{Ros}_p^{(np)}$ conformations.

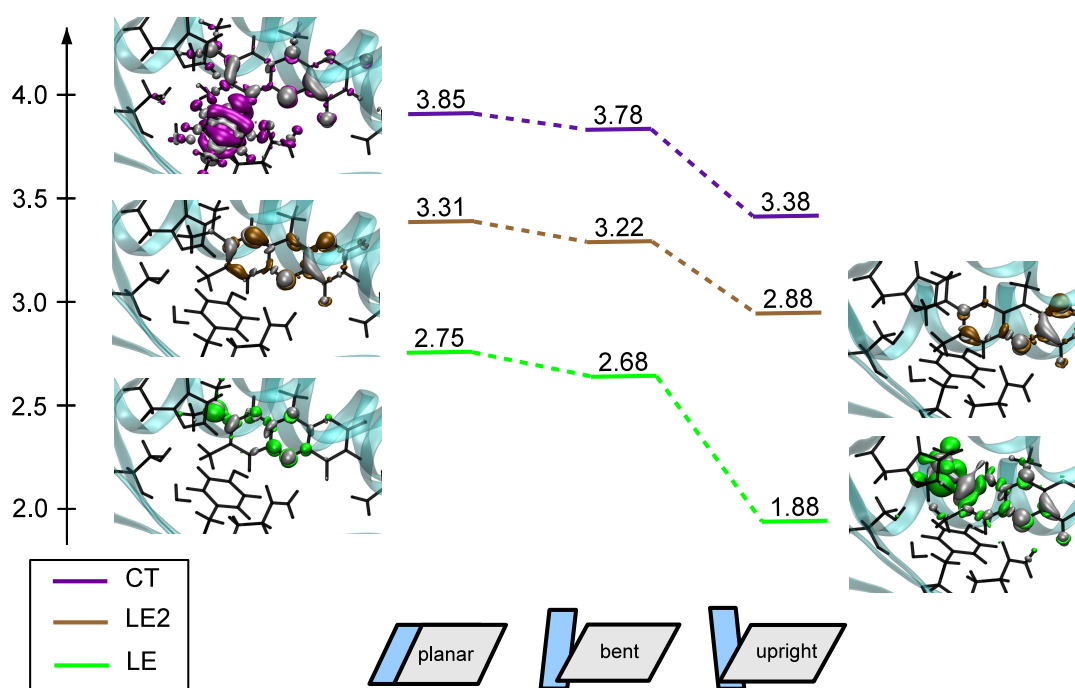


Figure S15: QM/MM excitation energies of planar, non-planar (both optimized with BP/Charmm at the Frank-Condon point), and upright (not optimized) RoF conformations calculated with TD-CC2/Charmm and the cc-pVDZ basis.