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

Electronic Supplementary Information

The role of CO_2 detachment in fungal bioluminescence: thermally vs. excited state induced pathways.

Cristina García-Iriepa,[a,b,c] Marco Marazzi[b,c] and Isabelle Navizet[a,d]*

[a] Université Paris-Est, Laboratoire Modélisation et Simulation Multi Echelle, MSME UMR 8208, CNRS, UPEC, UPEM, F-77454, Marne-la-Vallée, France

[b] Departamento de Química Analítica, Química Física e Ingeniería Química, Universidad de Alcalá, E-28871 Alcalá de Henares, Madrid, Spain.

[c] Chemical Research Institute Andrés M. del Río (IQAR), Universidad de Alcalá, E-28871 Alcalá de Henares (Madrid), Spain

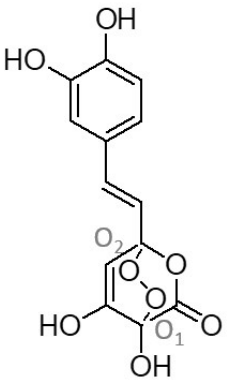
[d] MSME, Univ Gustave Eiffel, CNRS UMR 8208, Univ Paris Est Creteil, F-77454, Marne-la-Vallée, France

Content

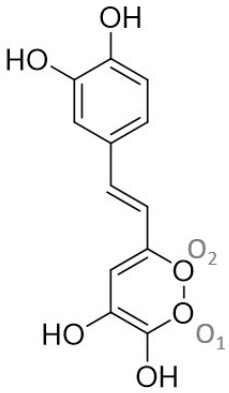
1. Charge distribution analysis.

Table S1. Mulliken charges computed at the CASSCF(14,12) level of theory in S_0 (S_1) for the two oxygen atoms of the endoperoxide moiety for the ES-BL mechanism and peroxide for the TH-BL mechanism.

Mec.	Atoms	HEI	CI	CI2
ES-BL	O_1	-0.2229 (-0.2201)	-0.2233 (-0.2328)	-0.2343 (-0.2369)
	O_2	-0.2292 (-0.2398)	-0.2305 (-0.2331)	-0.2447 (-0.2448)
		Peroxide	**HECI2**	**CI2**
TH-BL	O_1	-0.2394 (-0.2806)	-0.3572 (-0.2628)	-0.3824 (-0.3998)
	O_2	-0.245 (-0.2723)	-0.3479 (-0.303)	-0.3502 (-0.2809)



Endoperoxide HEI



Peroxide

2. SOC computed values.

Table S2. Computed spin orbit couplings (SOC) between the singlet and triplet states for selected geometries of the ES-BL mechanism.

State 1	State 2	HEI	CI	CI2	TS_{CO}
T1 (Ms=-1)	S0 (Ms=0)	<20.0		38.827	
T1 (Ms=1)	S0 (Ms=0)	<20.0		38.827	
T1 (Ms=0)	S0 (Ms=0)	<20.0	55.665	22.693	
T2 (Ms=-1)	S0 (Ms=0)	<20.0			
T2 (Ms=1)	S0 (Ms=0)	<20.0			
T2 (Ms=0)	S0 (Ms=0)	<20.0			66.297
T1 (Ms=0)	S1 (Ms=0)	<20.0	28.618		63.374
T2 (Ms=-1)	S1 (Ms=0)	<20.0	21.256	43.422	
T2 (Ms=1)	S1 (Ms=0)	<20.0	21.256	43.422	
T2 (Ms=0)	S1 (Ms=0)	<20.0	59.976	25.113	
T2 (Ms=-1)	T1 (Ms=-1)	<20.0	65.587	25.095	70.697
T2 (Ms=0)	T1 (Ms=-1)	<20.0	23.563	43.471	
T2 (Ms=-1)	T1 (Ms=0)	<20.0	23.563	43.471	
T2 (Ms=1)	T1 (Ms=0)	<20.0	23.563	43.471	
T2 (Ms=0)	T1 (Ms=1)	<20.0	23.563	43.471	
T2 (Ms=1)	T1 (Ms=1)	<20.0	65.587	25.095	70.697

Table S3. Computed spin orbit couplings (SOC) between the singlet and triplet states for selected geometries of the TH-BL mechanism.

State 1	State 2	CI2	Min S_1
T1 (Ms=-1)	S0 (Ms=0)	38.827	45.948
T1 (Ms=1)	S0 (Ms=0)	38.827	45.948
T1 (Ms=0)	S0 (Ms=0)	22.693	<20.0
T2 (Ms=-1)	S0 (Ms=0)	<20.0	<20.0
T2 (Ms=1)	S0 (Ms=0)	<20.0	<20.0
T2 (Ms=0)	S0 (Ms=0)	<20.0	<20.0
T1 (Ms=0)	S1 (Ms=0)	<20.0	<20.0
T2 (Ms=-1)	S1 (Ms=0)	43.422	44.566
T2 (Ms=1)	S1 (Ms=0)	43.422	44.566
T2 (Ms=0)	S1 (Ms=0)	25.113	<20.0
T2 (Ms=-1)	T1 (Ms=-1)	25.095	<20.0
T2 (Ms=0)	T1 (Ms=-1)	43.471	43.849
T2 (Ms=-1)	T1 (Ms=0)	43.471	43.849
T2 (Ms=1)	T1 (Ms=0)	43.471	43.849
T2 (Ms=0)	T1 (Ms=1)	43.471	43.849
T2 (Ms=1)	T1 (Ms=1)	25.095	<20.0

3. Selected active spaces.

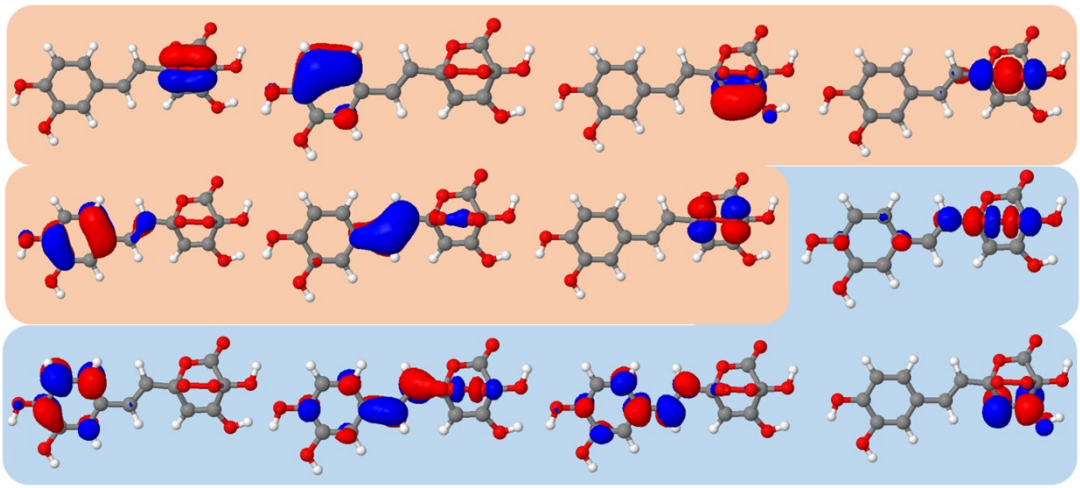


Figure S1. Active space selected for the Endoperoxide HEI for computing the ES-BL mechanism (bonding orbitals in red and antibonding in blue).

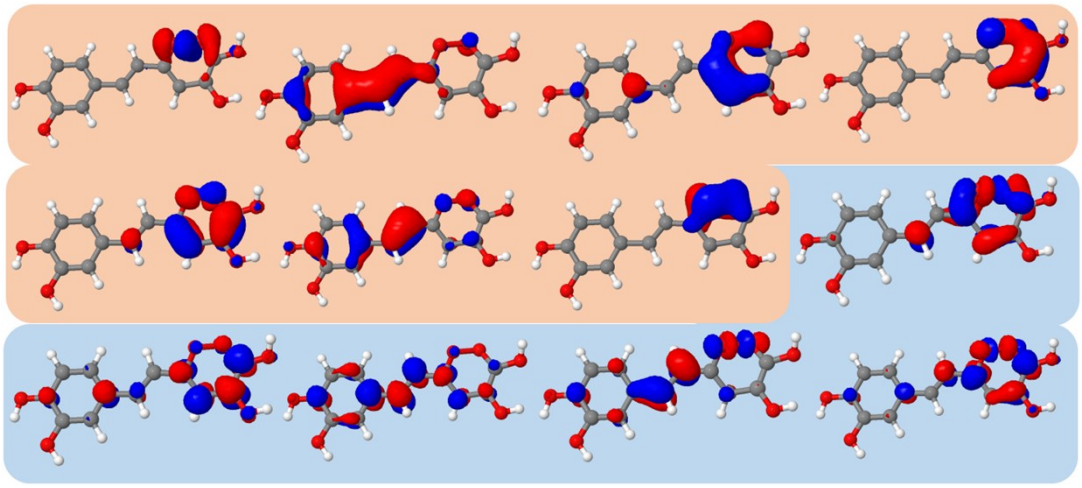


Figure S2. Active space selected for the peroxide intermediate computing the second step of the TH-BL mechanism (bonding orbitals in red and antibonding in blue).

4. ES-BL: Relaxed scan along the d_{O-O} coordinate

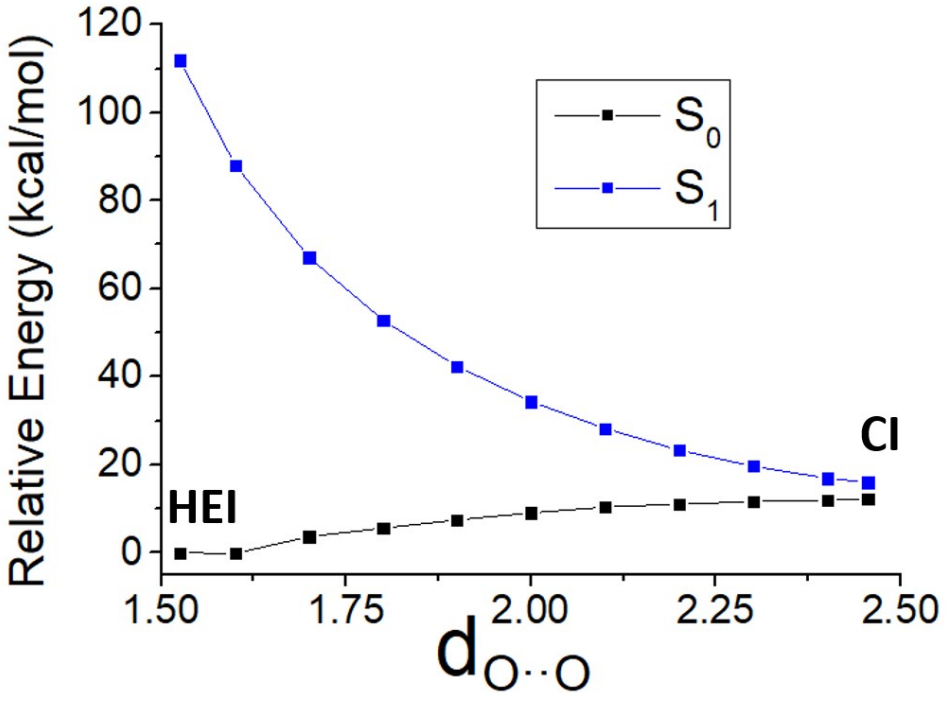


Figure S3. Relaxed scan along the peroxide O-O bond in the ES-BL path from Endoperoxide HEI to Open Endoperoxide at the CASSCF (14,12) level of theory.

5. CO_2 detachment in the excited state.

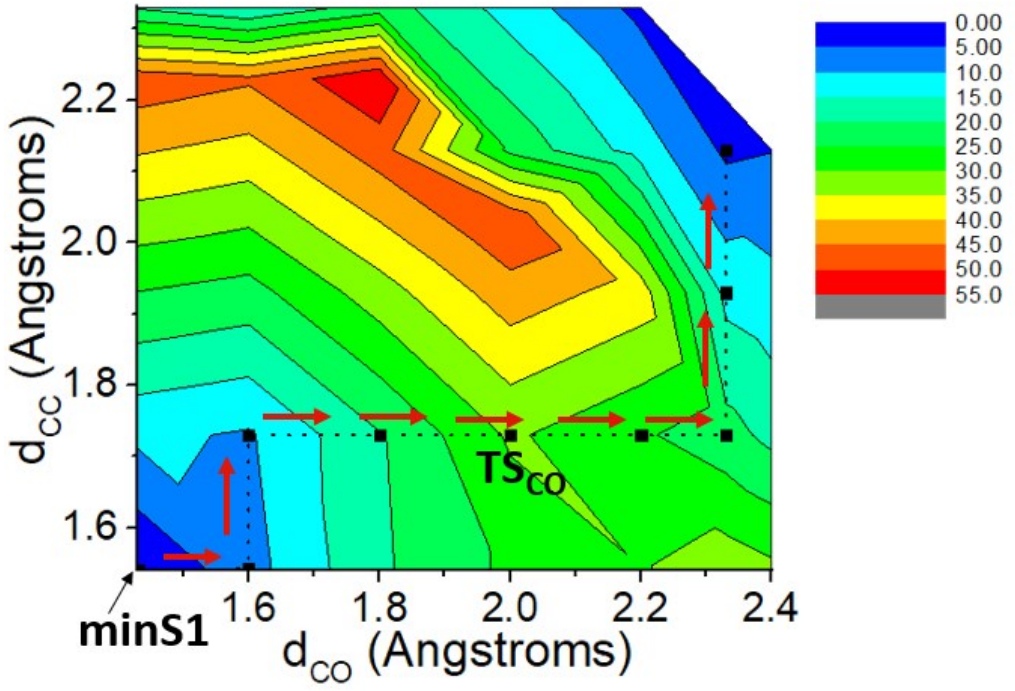


Figure S4. Graph of the double scan performed along the dissociation of the CO bond (dCO) and dissociation of the CC bond (dCC) coordinates to evaluate the energy barriers of the CO_2 release in S_1. The data were computed at the CASSCF(14,12) level of theory.

6. Relaxed scan along the rotation coordinates.

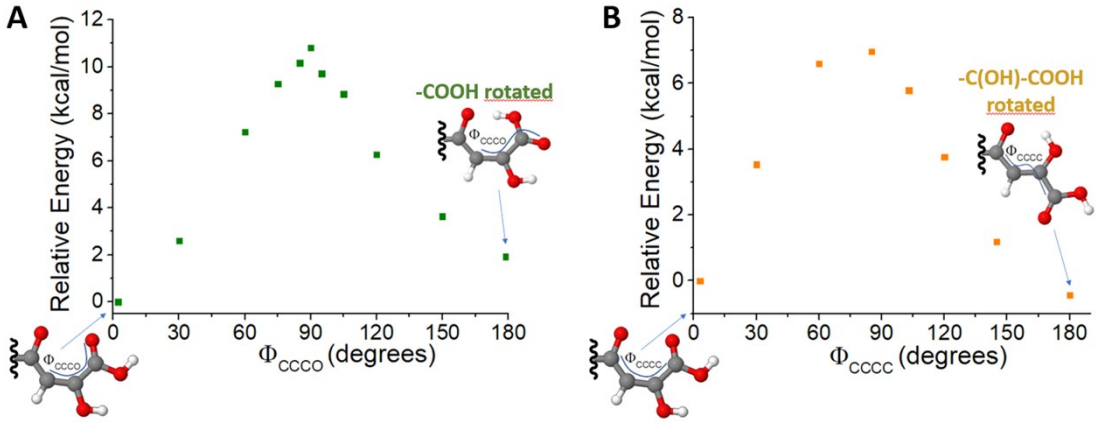


Figure S5. Relaxed scans performed along the torsion coordinate to evaluate the energy barriers for the rotations of Excited Oxyluciferin in its minimum in S1 at the CASPT2//CASSCF level.

7. CI search for TH-BL computed path.

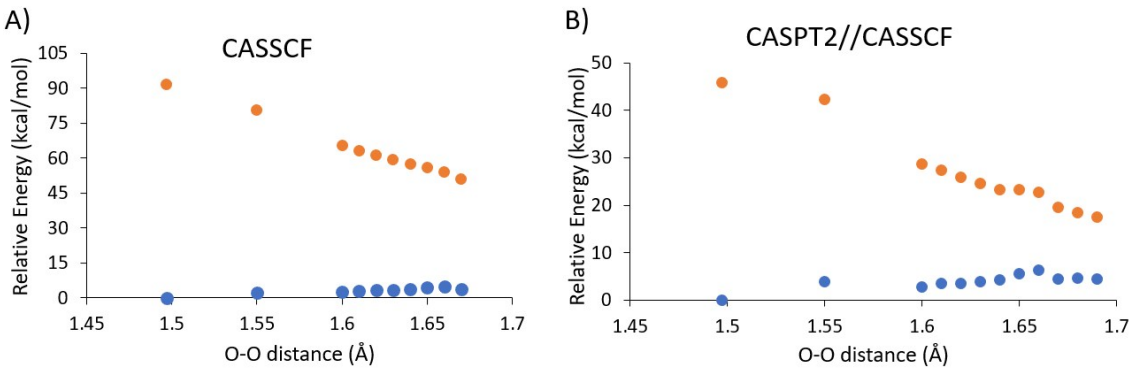


Figure S6. A) Scan performed along the peroxide O-O bond elongation at the CASSCF level. B) CASPT2 single point energy calculations on top of the CASSCF geometries.