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

Electronic Supplementary Information

Photoelectron spectroscopy of isolated luciferin and infraluciferin anions *in vacuo*: competing photodetachment, photofragmentation and internal conversion

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1 Photoelectron images

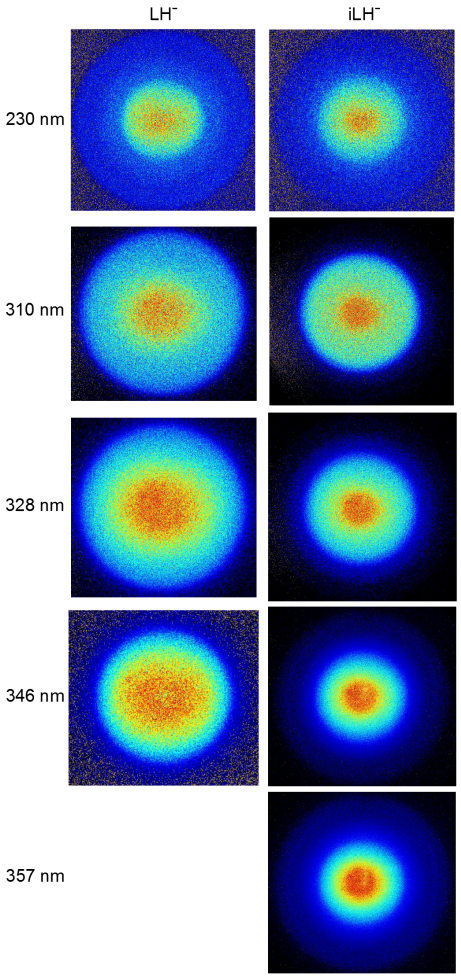


Figure S1: Photoelectron images recorded following photoexcitation of luciferin (LH^-) and infraluciferin (iLH^-) deprotonated anions.

2 LH^- D_0 detachment energy

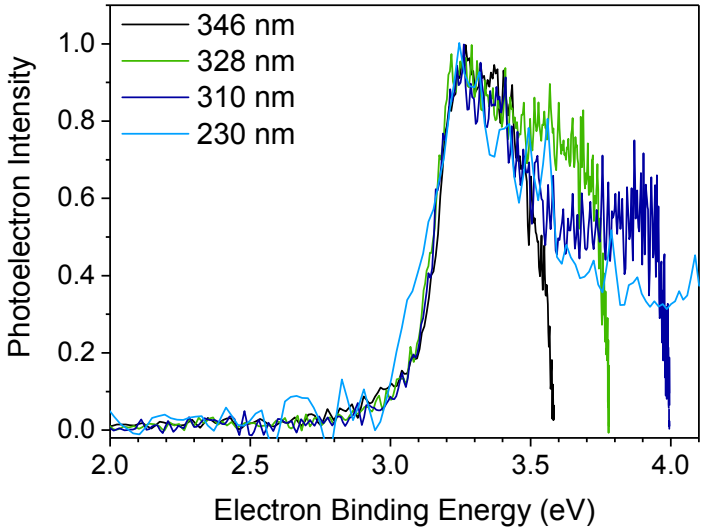


Figure S2: Plot of LH^- photoelectron spectra as a function of binding energy at the specified wavelengths.

3 iLH^- power dependence

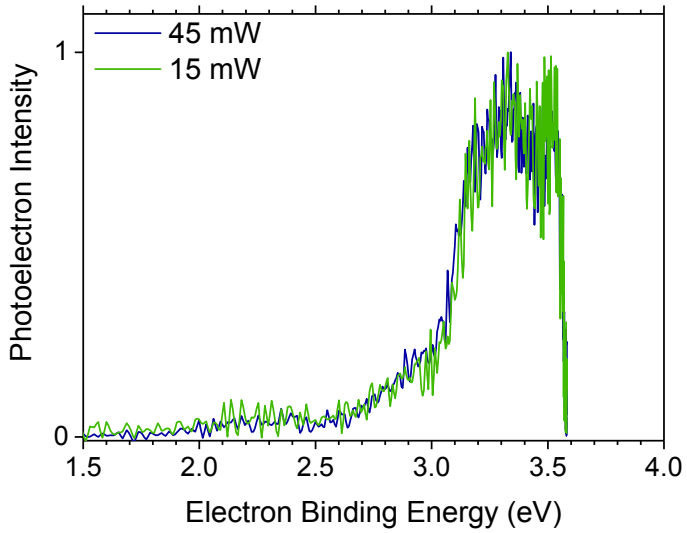


Figure S3: Plot of 346 nm iLH^- photoelectron spectrum as a function of binding at 15 mW and 45 mW.

4 iLH⁻ photofragmentation process

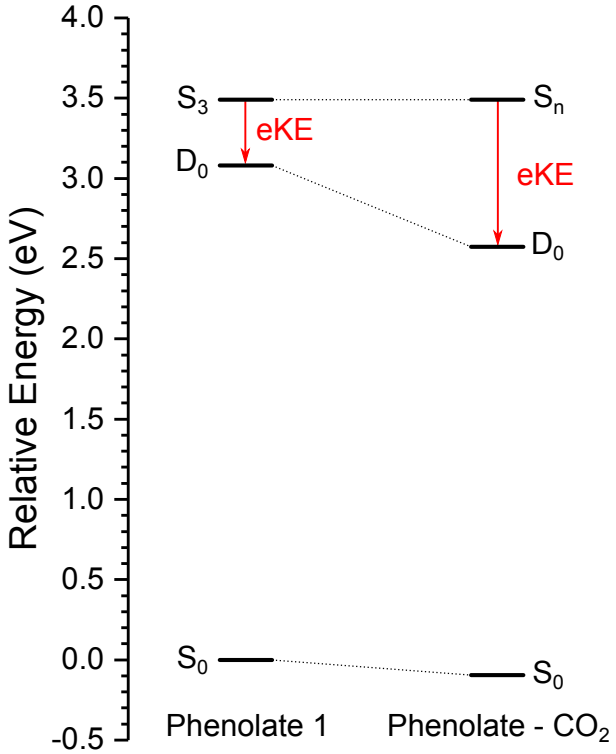


Figure S4: Energy level diagram of the loss of CO_2 from iLH⁻ phenolate 1 in the S_3 excited state. To illustrate the change in the upper limit of the kinetic energy of photoelectrons upon photofragmentation, it has been assumed that the electronic excited state (S_n) of the photofragmentation product anion lies at the same energy as the S_3 state of the parent anion. It is shown that if the electronic excition energy of the parent ion is retained during the photoframentation process the upper limit of the kinetic energy of detached electrons is higher after photofragmentation. The relative S_0 energies are determined from the DFT/B3LYP 6-311G++(3df,3pd) optimised geometries of the parent ion and fragmentation products. The S_3 vertical excitation energy was calculated with ADC(2)/aug-cc-pVDZ. The vertical detachment energies were calculated with EOM-IP-CCSD/aug-cc-pDVZ.

5 Mass spectra

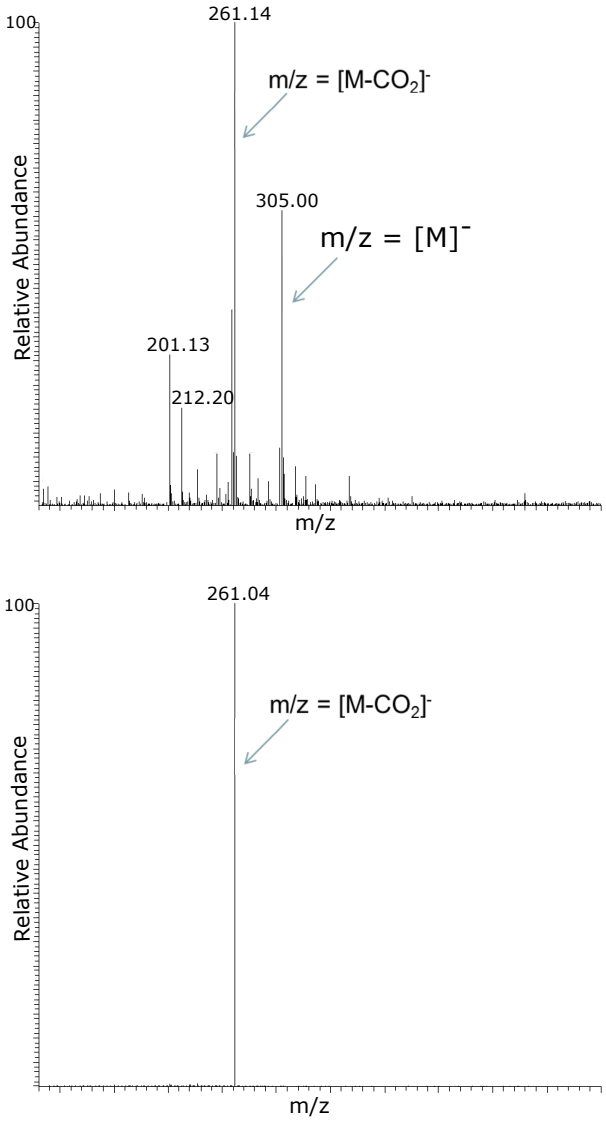


Figure S5: (a) Negative ion electrospray mass spectrum of infraluciferin anions. Solutions of 1ng/μL infraluciferin in dry methanol with ammonia base.
(b) CID MS-MS measurement of mass-selected infraluciferin deprotonated anions fragmented by collisions with He atoms. Deprotonated anions produced by negative ion electrospray in (a).

6 Ionisation potentials

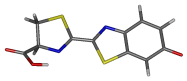
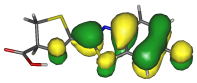
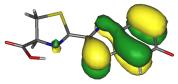
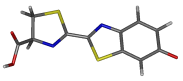
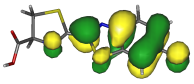
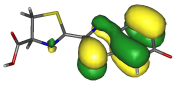
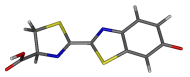
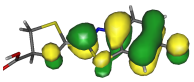
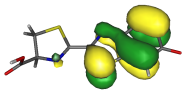
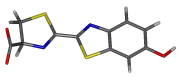
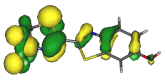
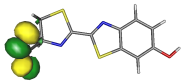
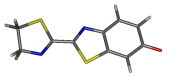
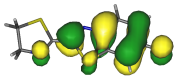
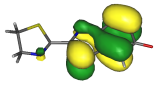
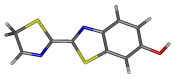
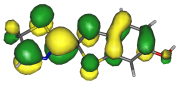
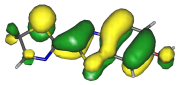
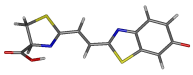
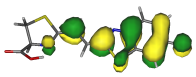
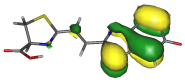
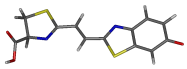
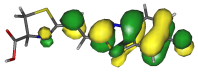
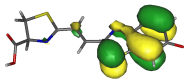
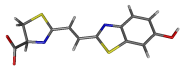
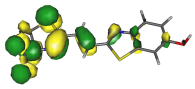
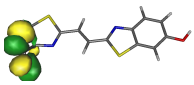
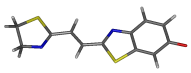
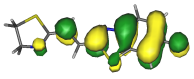
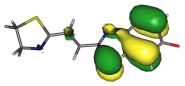
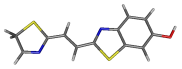
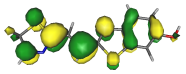
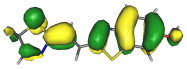
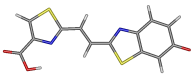
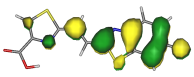
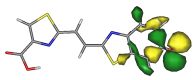
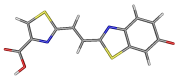
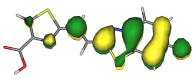
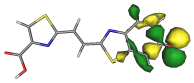
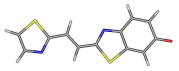
Anion + abs. E/a.u.		D_0 VDE	D_0 Orbital hole		D_1 VDE	D_1 Orbital hole	
Luciferin							
Phenolate 1 -1555.367885		3.13		92%	5.25		90%
Phenolate 2 -1555.356018		2.81		92%	4.91		91%
Phenolate 3 -1555.356005		2.85		92%	4.94		91%
Carboxylate -1555.350609		4.04		71%	4.42		80%
Phen minus CO_2 -1366.710127		2.66		92%	4.74		91%
Carb minus CO_2 -1366.680760		1.58		92%	4.20		87%
Infraluciferin							
Phenolate 1 -1632.801033		3.08		91%	5.33		88%
Phenolate 2 -1632.789877		2.80		91%	5.03		89%
Carboxylate -1632.780570		3.95		72%	4.39		85%
Phen minus CO_2 -1444.144144		2.67		91%	4.89		90%
Carb minus CO_2 -1444.121205		1.71		92%	4.19		89%
Phen1 minus H_2 -1631.601657		2.98		91%	4.88		88%
Phen2 minus H_2 -1631.593499		2.78		91%	4.63		88%
Phen minus H_2+CO_2 -1442.941333		2.63		91%	4.45		88%
Carb minus H_2 -1631.580480		4.28		48%	4.54		47%
				43%			44%
Carb minus H_2+CO_2 -1442.859803		2.37		90%	3.51		92%

Table S1: Absolute energies (B3LYP/6-311++G(3df,3pd) in a.u.) and geometries of the luciferin and infraluciferin anions and fragments after loss of CO_2, H_2 or H_2+CO_2 with EOM-IP-CCSD/aug-cc-pVDZ electron detachment energies in eV and the corresponding orbitals from which the electron is detached with the corresponding weights in %.

We have performed a linear interpolation of internal coordinates (LIIC) between the two phenolate isomers (Figure 1), where for each step we calculated the VDEs for D_0 and D_1 with electron propagator theory (EPT) using outer valence Green's function (OVGF) and the aug-cc-pVDZ basis set. The EPT VDEs are slightly lower than the EOM-IP-CCSD VDEs (by about the same amount for each isomer), but are faster calculations to run. The whole rotation from phenolate 1 to phenolate 2 requires a torsion around the NCCO dihedral angle (where the oxygen is the one to which the hydrogen is bound) of less then 90°.

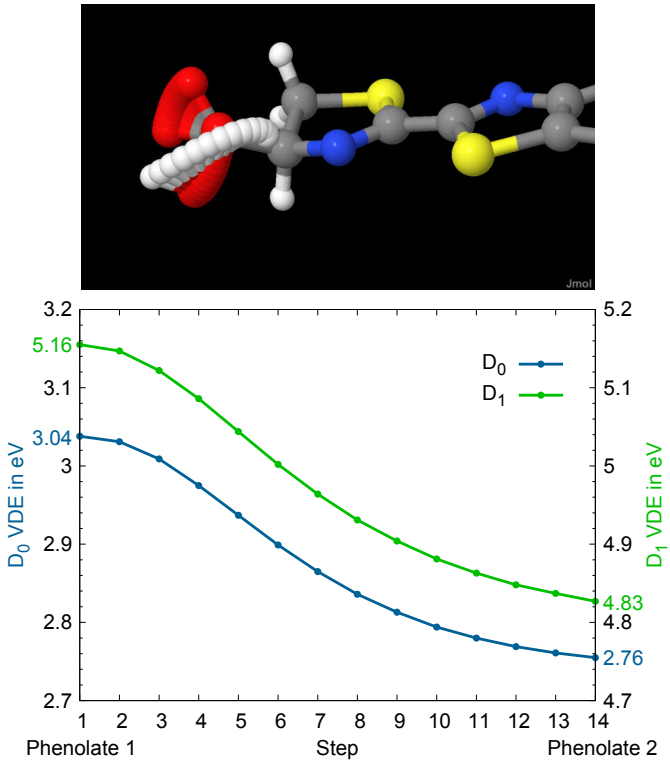


Figure S6: Top: Interpolated structures of luciferin phenolate between the geometries of phenolate 1 and 2 structures at which EPT/aug-cc-pVDZ D_0 and D_1 VDEs were calculated. Bottom: Plot of EPT/aug-cc-pVDZ VDEs for D_0 and D_1 as a function of steps along the geometry distortion coordinate connecting the geometries of phenolates 1 and 2.

7 ADC(2) excited states calculations

The following tables list the excited states calculated with ADC(2)/aug-cc-pVDZ for the luciferin and infraluciferin phenolates. The tables contain the state, VEE in eV, the excitations with weights c^2 and the oscillator strengths f. The excitations are given in terms of the involved orbital numbers. Where several excitations from the same orbital into different virtual orbitals occurs, the excitations are compressed to one line dividing the different virtual orbitals and weights by slashes. For the states with higher oscillator strengths (values >0.02) and for states that do not include diffuse virtual orbitals, excitations are also expressed by the orbital characters, where "diff" denotes that an excitation takes place into a diffuse orbital. The oscillator strengths of the brightest states ($f > 0.1$) are marked in bold. Selected orbitals involved in the transitions are shown in the figures next to the tables ordered by the number and where used in the table also with their unique discriptive name. Orbitals are involved in excitations but not shown are diffuse orbitals that do not provide any important information. In the ground state occupied and virtual orbitals are divided by a black line from each other.

7.1 ADC(2) excited states luciferin phenolate 1

State	VEE/eV	Excitation		c^2	f
S_1	2.31	72→80	$\pi_{HOMO} \rightarrow \pi^*_{LUMO}$	90	**0.6805**
S_2	2.80	70→80	$n_O \rightarrow \pi^*_{LUMO}$	90	0.0000
S_3	3.25	72→73		34	0.0010
		72→75/76		20/12	
S_4	3.45	72→73		38	0.0008
		72→74/77		19/13	
S_5	3.58	72→74		45	0.0000
		72→77/76		19/19	
S_6	3.74	72→75		15	0.0176
		72→84/76		13/12	
S_7	3.84	70→74		26	0.0030
		70→75		23	
		70→77		16	
S_8	3.89	71→80	$\pi_{HOMO-1} \rightarrow \pi^*_{LUMO}$	43	0.0499
		72→75	$\pi_{HOMO} \rightarrow$ diff	20	
S_9	3.93	71→80	$\pi_{HOMO-1} \rightarrow \pi^*_{LUMO}$	32	0.0473
		72→75	$\pi_{HOMO} \rightarrow$ diff	16	
S_{10}	3.96	72→76	$\pi_{HOMO} \rightarrow$ diff	19	0.0274
		72→77		13	
S_{11}	4.03	72→78		58	0.0039
S_{12}	4.12	70→74		29	0.0053
		70→77/76		26/22	
S_{13}	4.19	70→73		54	0.0036
		70→77		13	
S_{14}	4.21	70→92		12	0.0012
		70→97		10	
S_{15}	4.26	72→81		13	0.0007
		72→78/85		12/11	
S_{16}	4.33	72→79		42	0.0012
		72→83/85		18/11	
S_{17}	4.47	70→78		60	0.0075
S_{18}	4.53	72→79		16	0.0051
S_{19}	4.65	70→75		55	0.0006
		70→74		21	
S_{20}	4.72	70→76		38	0.0093
S_{21}	4.72	72→81		22	0.0009
S_{22}	4.73	69→80	$\pi_{S,N} \rightarrow \pi^*_{LUMO}$	61	0.0427
S_{23}	4.77	72→81		18	0.0122
		72→85		11	
S_{24}	4.84	72→84	$\pi_{HOMO} \rightarrow$ diff	17	0.0202
		72→97/83		13/11	
S_{25}	4.88	66→80	$n_{N,S} \rightarrow \pi_{LUMO}$	46	0.0120
		65→80	$n_N \rightarrow \pi_{LUMO}$	13	
S_{26}	4.92	72→82		17	0.0010
		66→80		11	
S_{27}	4.94	72→82		11	0.0150
S_{28}	5.05	69→73		13	0.0100

Table S2: Excited states calculated with ADC(2)/aug-cc-pVDZ for luciferin phenolate 1.

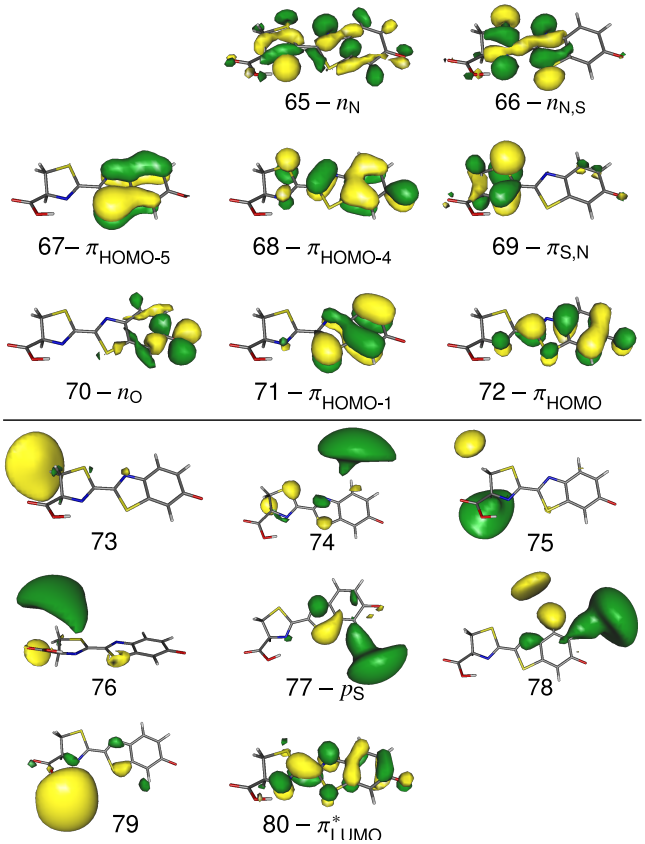


Figure S7: Hartree-Fock orbitals of luciferin phenolate 1 used in the ADC(2) calculation.

7.2 ADC(2) excited states luciferin phenolate 2

State	VEE/eV	Excitation		c^2	f
S_1	2.35	72→81	$\pi_{HOMO} \rightarrow \pi^*_{LUMO}$	85	**0.6206**
S_2	2.90	70→81	$n_O \rightarrow \pi^*_1$	85	0.0000
S_3	3.03	72→73		52	0.0024
		72→74/76		15/13	
S_4	3.20	72→76		43	0.0006
		72→78/73		17/15	
S_5	3.36	72→74		47	0.0000
		72→78/73		15/11	
S_6	3.48	72→74		22	0.0003
		72→78		20	
		72→76/73		13/12	
S_7	3.61	72→75		51	0.0061
S_8	3.67	70→76		51	0.0031
		70→78		22	
S_9	3.76	72→79		39	0.0021
		72→78/77		23/14	
S_{10}	3.80	72→75	$\pi_{HOMO} \rightarrow$ diff	12	0.0269
		72→92		11	
S_{11}	3.84	70→73		69	0.0017
S_{12}	3.95	72→79		25	0.0014
		72→77/80		19/15	
S_{13}	3.95	70→78		48	0.0095
		70→76		15	
S_{14}	4.00	71→81	$\pi_{HOMO-1} \rightarrow \pi^*_{LUMO}$	75	0.0935
S_{15}	4.12	72→79		12	0.0046
		72→77		10	
S_{16}	4.12	70→74		37	0.0002
		70→73		11	
S_{17}	4.15	70→74		17	0.0007
		70→88		10	
S_{18}	4.25	70→79		54	0.0053
S_{19}	4.26	72→77		13	0.0008
S_{20}	4.42	70→75		72	0.0004
S_{21}	4.42	72→84		30	0.0019
		72→82/80		20/12	
S_{22}	4.47	72→82		21	0.0015
		72→89/86		13/11	
S_{23}	4.56	72→80		29	0.0005
		72→82		11	
S_{24}	4.67	70→77		42	0.0041
		70→80		14	
S_{25}	4.71	72→85	$\pi_{HOMO} \rightarrow$ diff	24	0.0224
		72→98		13	
S_{26}	4.76	72→83	$\pi_{HOMO} \rightarrow$ diff	19	0.0240
		72→88		17	
S_{27}	4.83	69→81	$\pi_{S,N} \rightarrow \pi^*_{LUMO}$	23	0.0184
		69→74		13	
S_{28}	4.92	66→81	$n_{N,S} \rightarrow \pi^*_{LUMO}$	17	0.0135
		71→73	$\pi_{HOMO-1} \rightarrow$ diff	14	
		69→81	$\pi_{S,N} \rightarrow \pi_{HOMO}$	12	
S_{29}	4.96	66→81	$n_{N,S} \rightarrow \pi^*_{LUMO}$	13	0.0020
S_{30}	4.97	66→81	$n_{N,S} \rightarrow \pi^*_{LUMO}$	31	0.0197
		69→81	$\pi_{S,N} \rightarrow \pi^*_{LUMO}$	10	

Table S3: Excited states calculated with ADC(2)/aug-cc-pVDZ for luciferin phenolate 2.

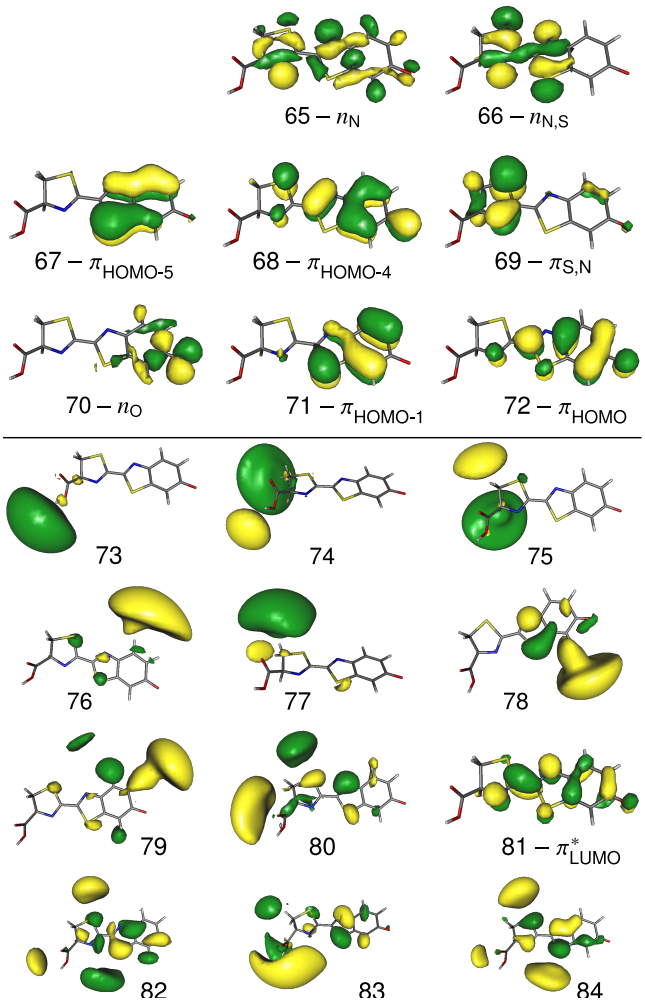


Figure S8: Hartree-Fock orbitals of luciferin phenolate 1 used in the ADC(2) calculation.

7.2.1 ADC(2) excited states luciferin carboxylate

State	VEE/eV	Excitation		c^2	f
S_1	2.67	72→79	$\pi_{HOMO} \rightarrow \pi^*_{LUMO}$	56	0.0955
		69→79	$\pi_{HOMO-3} \rightarrow \pi^*_{LUMO}$	17	
S_2	2.93	68→79	$n_{COO} \rightarrow \pi^*_{LUMO}$	70	0.0201
S_3	3.50	72→73		61	0.0005
		69→73		19	
S_4	3.57	71→79	$\pi_{COO} \rightarrow \pi^*_{LUMO}$	74	0.0038
S_5	3.66	72→77		40	0.0062
		69→77		16	
S_6	3.69	68→73		75	0.0001
S_7	3.81	68→77		55	0.0032
S_8	3.95	72→74		55	0.0001
		69→74		18	
S_9	3.99	72→75		45	0.0006
		69→75		15	
S_{10}	4.05	69→79	$\pi_{HOMO-3} \rightarrow \pi^*_{LUMO}$	32	0.0209
		72→79	$\pi_{HOMO} \rightarrow \pi^*_{LUMO}$	18	
S_{11}	4.09	72→81	$\pi_{HOMO} \rightarrow \pi^*_{LUMO+1}$	28	0.0017
		69→79	$\pi_{HOMO-3} \rightarrow \pi^*_{LUMO}$	27	
S_{12}	4.13	68→74		72	0.0001
S_{13}	4.18	68→75		62	0.0000
S_{14}	4.24	72→78		36	0.0060
		69→78		17	
S_{15}	4.33	66→79	$n_{N,S} \rightarrow \pi^*_{LUMO}$	68	0.0006
S_{16}	4.33	68→78		39	0.0020
		68→80		18	
S_{17}	4.37	71→73		84	0.0000
S_{18}	4.42	68→81		21	0.0040
		68→78		13	
S_{19}	4.50	71→77		60	0.0006
S_{20}	4.51	72→76		20	0.0064
S_{21}	4.53	67→79	$\pi_{HOMO-5} \rightarrow \pi^*_{LUMO}$	32	0.0486
		68→81	$n_{COO} \rightarrow \pi^*_{LUMO+1}$	12	
		70→79	$\pi_{HOMO-2} \rightarrow \pi^*_{LUMO}$	11	
S_{22}	4.55	72→80		30	0.0145
		69→80		14	
S_{23}	4.61	68→80		37	0.0097
		68→83		14	
S_{24}	4.67	70→73		55	0.0006
S_{25}	4.69	68→76		31	0.0004
		68→83		16	
S_{26}	4.74	70→79	$\pi_{HOMO-2} \rightarrow \pi^*_{LUMO}$	38	**0.2607**
S_{27}	4.78	72→76	$\pi_{HOMO} \rightarrow$ diff	14	0.0343
S_{28}	4.82	71→74		80	0.0001
S_{29}	4.86	71→75		68	0.0004

Table S4: Excited states calculated with ADC(2)/aug-cc-pVDZ for luciferin carboxylate.

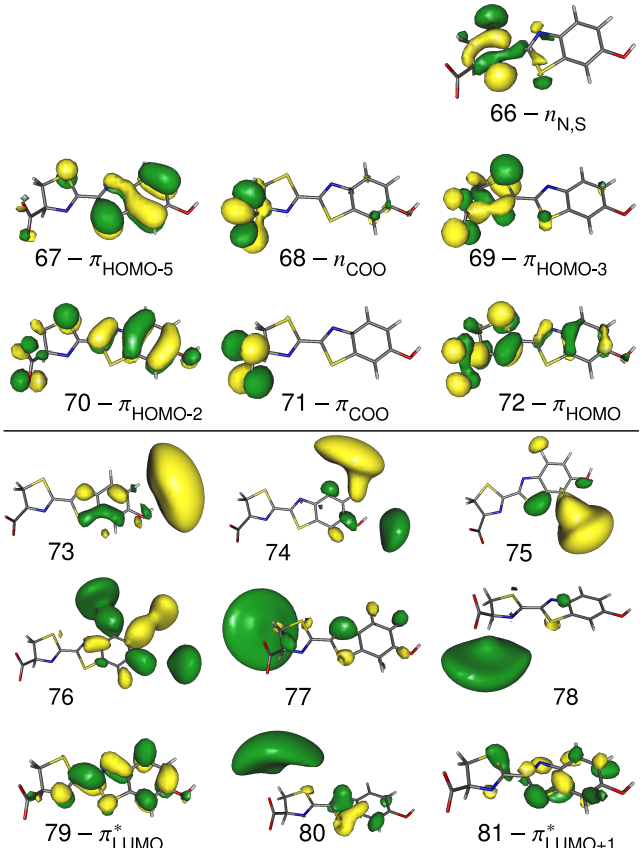


Figure S9: Hartree-Fock orbitals of luciferin carboxylate used in the ADC(2) calculation.

7.3 ADC(2) excited states infraluciferin phenolate 1

State	VEE/eV	Excitation		c^2	f
S_1	1.81	79→84	$\pi_{HOMO} \rightarrow \pi^*_{LUMO}$	92	**0.8615**
S_2	2.45	76→84	$n_O \rightarrow \pi^*_{LUMO}$	92	0.0000
S_3	3.22	79→82		45	0.0004
		79→80/86		19/13	
S_4	3.33	79→80		17	0.0011
		79→81/83		15/15	
S_5	3.49	78→84	$\pi_{HOMO-1} \rightarrow \pi^*_{LUMO}$	87	**0.2410**
S_6	3.55	79→85		33	0.0051
		79→80/81		19/12	
S_7	3.66	79→80		24	0.0001
		79→87/82		21/17	
S_8	3.71	79→81	$\pi_{HOMO} \rightarrow$ diff	13	0.0549
		79→92/96		11/10	
S_9	3.77	79→85		36	0.0030
		79→86/83		27/10	
S_{10}	3.86	79→81		29	0.0083
		79→83/107		12/12	
S_{12}	3.91	76→82		44	0.0103
		76→85		18	
S_{13}	4.09	79→81		15	0.0180
		79→113		11	
S_{14}	4.18	76→86		21	0.0109
		76/79→83		13/11	
S_{15}	4.20	79→83	$\pi_{HOMO} \rightarrow$ diff	14	0.0224
		76→86		12	
S_{16}	4.23	79→88		22	0.0025
		79→89/87		18/17	
S_{17}	4.24	76→107		21	0.0006
		76→96		13	
S_{18}	4.26	76→80		31	0.0048
		76→85/82		17/15	
S_{19}	4.32	77→84	$\pi_{HOMO-3} \rightarrow \pi^*_{LUMO}$	64	0.0596
S_{20}	4.35	72→84	$n_{N,S} \rightarrow \pi^*_{LUMO}$	82	0.0011
S_{21}	4.41	79→89		18	0.0088
		79→94/93		15/14	
S_{22}	4.44	76→86		29	0.0055
		76→85/86		23/15	
S_{23}	4.50	79→90		18	0.0082
		79→94/87		17/15	
S_{24}	4.56	79→88		41	0.0083
		79→93		13	
S_{25}	4.59	75→84	$\pi_S \rightarrow \pi^*_{LUMO}$	34	0.0680
		76→80	$n_O \rightarrow$ diff	19	
S_{26}	4.60	76→80	$n_O \rightarrow$ diff	29	0.0619
		75→84	$\pi_S \rightarrow \pi^*_{LUMO}$	21	
S_{27}	4.65	79→89		21	0.0103
S_{28}	4.71	76→81		20	0.0001
		76→83		15	
S_{29}	4.78	79→95		13	0.0053
S_{30}	4.86	76→81		16	0.0019
S_{31}	4.86	76→81		13	0.0021

Table S5: Excited states calculated with ADC(2)/aug-cc-pVDZ for infraluciferin phenolate 1.

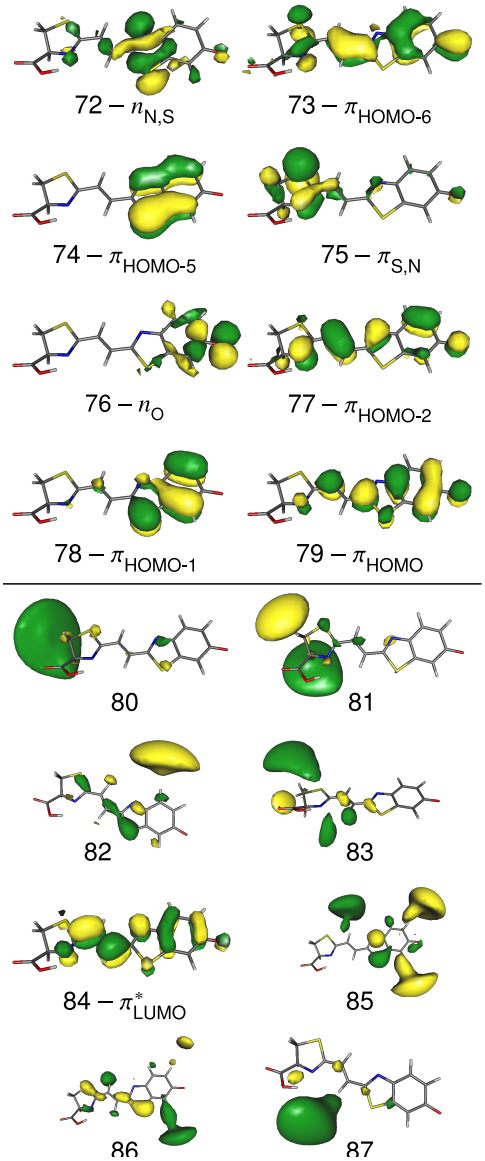


Figure S10: Hartree-Fock orbitals of infraluciferin phenolate 1 used in the ADC(2) calculation.

7.4 ADC(2) excited states infraluciferin phenolate 2

State	VEE/eV	Excitation		c^2	f
S_1	1.83	79→87	$\pi_{HOMO} \rightarrow \pi^*_{LUMO}$	60	**0.7687**
		79→86	$\pi_{HOMO} \rightarrow \pi^*_{LUMO+1}$	31	
S_2	2.52	76→87	$n_O \rightarrow \pi^*_{LUMO}$	60	0.0000
		76→86	$n_O \rightarrow \pi^*_{LUMO+1}$	31	
S_3	3.07	79→80		41	0.0004
		79→83/85		23/10	
S_4	3.15	79→83		37	0.0007
		79→80		27	
S_5	3.35	79→81		36	0.0008
		79→85/83		30	
S_6	3.46	79→81		29	0.0012
		79→85/88		19/18	
S_7	3.53	79→84		22	0.0012
		79→80/81		21	
S_8	3.55	78→87	$\pi_{HOMO-1} \rightarrow \pi^*_{LUMO}$	51	**0.1774**
		78→86	$\pi_{HOMO-1} \rightarrow \pi^*_{LUMO+1}$	27	
S_9	3.61	79→88		21	0.0027
		79→85		19	
S_{10}	3.66	79→82	$\pi_{HOMO} \rightarrow$ diff	44	0.0687
S_{11}	3.72	76→83		35	0.0080
		76→85		20	
		79→82		19	
S_{12}	3.77	79→82		20	0.0321
		76→83		18	
S_{13}	3.96	76→80		58	0.0009
		76→84		13	
S_{14}	4.00	76→85		13	0.0065
		76→80/83		12/11	
S_{15}	4.02	79→89		17	0.0047
		76→85		15	
S_{16}	4.11	79→89		36	0.0099
S_{17}	4.17	76→109		17	0.0008
S_{18}	4.20	79→84	$\pi_{HOMO} \rightarrow$ diff	20	0.0303
S_{19}	4.21	76→86	$n_O \rightarrow \pi^*_{LUMO+1}$	21	0.0006
		76→84	$n_O \rightarrow$ diff	13	
S_{20}	4.26	76→81		77	0.0009
S_{21}	4.30	79→95		17	0.0010
		79→92/94		15/13	
S_{22}	4.35	79→94		18	0.0029
		79→88		14	
S_{23}	4.38	79→89	$\pi_{HOMO} \rightarrow$ diff	13	0.0539
		79→88		10	
S_{24}	4.41	73→87	$n_{N,S} \rightarrow \pi^*_{LUMO}$	49	0.0008
		73→86	$n_{N,S} \rightarrow \pi^*_{LUMO+1}$	25	
S_{25}	4.43	76→88	$n_O \rightarrow$ diff	33	0.0282
S_{26}	4.43	77→87	$\pi_{HOMO-2} \rightarrow \pi^*_{LUMO}$	35	0.0848
		77→86	$\pi_{HOMO-2} \rightarrow \pi^*_{LUMO+1}$	18	
S_{27}	4.57	76→82		78	0.0005
S_{28}	4.59	79→90		33	0.0061
		79→93		15	
S_{29}	4.65	75→87	$\pi_{HOMO-1} \rightarrow \pi^*_{LUMO}$	12	0.0953

Table S6: Excited states calculated with ADC(2)/aug-cc-pVDZ for infraluciferin phenolate 2.

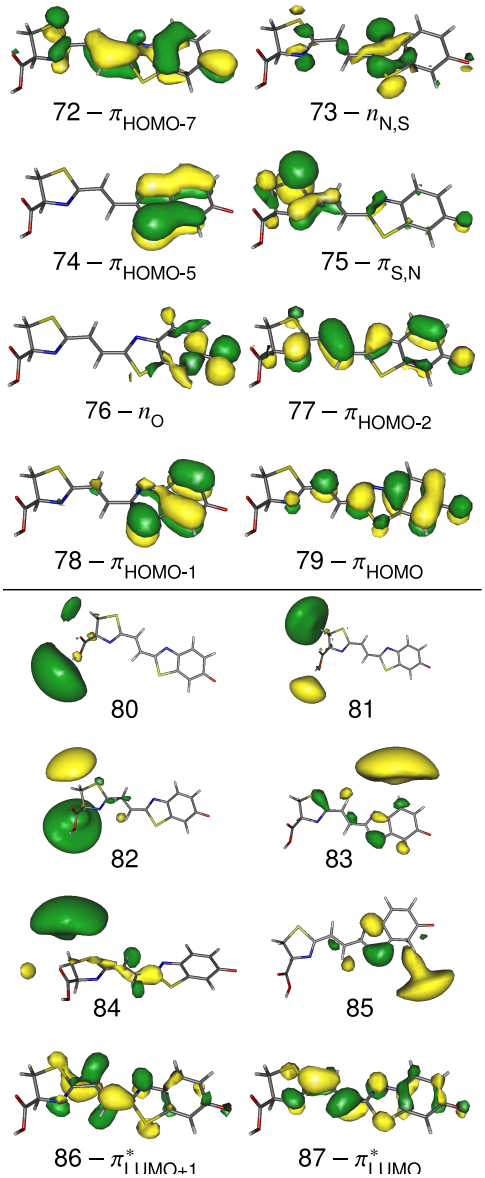


Figure S11: Hartree-Fock orbitals of luciferin phenolate 2 used in the ADC(2) calculation.

7.4.1 ADC(2) excited states infraluciferin carboxylate

State	VEE/eV	Excitation		c^2	f
S_1	2.12	79→84	$\pi_{HOMO} \rightarrow \pi^*_{LUMO}$	65	**0.1018**
		76→84	$\pi_{HOMO-3} \rightarrow \pi^*_{LUMO}$	13	
S_2	2.44	75→84	$n_{COO} \rightarrow \pi^*_{LUMO}$	83	0.0167
S_3	3.07	78→84	$\pi_{HOMO-1} \rightarrow \pi^*_{LUMO}$	45	0.0045
		77→84	$\pi_{HOMO-2} \rightarrow \pi^*_{LUMO}$	41	
S_4	3.44	79→80		61	0.0002
		76→80		16	
S_5	3.56	76→84	$\pi_{HOMO-3} \rightarrow \pi^*_{LUMO}$	59	0.0315
		79→85	$\pi_{HOMO} \rightarrow$ diff	15	
S_6	3.58	79→85		33	0.0088
		76→85		15	
S_7	3.65	75→80		82	0.0000
S_8	3.69	73→84	$n_{N,S} \rightarrow \pi^*_{LUMO}$	77	0.0004
S_9	3.76	75→85		51	0.0051
S_{10}	3.77	75→85		14	0.0008
		79→82/81		13/12	
S_{11}	3.88	79→81		32	0.0001
		79→82/86		21/11	
S_{12}	4.00	75→81		27	0.0004
		75→82/83		26/13	
S_{13}	4.04	79→89	$\pi_{HOMO} \rightarrow$ diff	28	**0.1488**
		79→88		16	
S_{14}	4.08	75→81		25	0.0029
		75→86/82		17/16	
S_{15}	4.10	79→86		25	0.0145
		75→81/82		18/11	
S_{16}	4.13	77→84	$\pi_{HOMO-2} \rightarrow \pi^*_{LUMO}$	27	**0.5781**
		78→84	$\pi_{HOMO-1} \rightarrow \pi^*_{LUMO}$	24	
S_{17}	4.17	79→87/83		15/15	0.0143
		79→81/82		12/12	
S_{18}	4.19	79→88		18	0.0193
		79→89/90		14/10	
S_{19}	4.29	75→86		23	0.0015
		75→88/87		21/18	
S_{20}	4.33	75→86		20	0.0002
		75→88		19	
S_{21}	4.34	78→80		42	0.0001
		77→80		30	
S_{22}	4.40	75→89	$n_{COO} \rightarrow$ diff	17	0.0206
		75→83		11	
S_{23}	4.40	75→89		16	0.0114
		75→83/87		15/13	
S_{24}	4.42	79→91		9	0.0052
S_{25}	4.46	77→85		35	0.0010
		78→85		35	
S_{26}	4.48	74→84	$\pi_{HOMO-5} \rightarrow \pi^*_{LUMO}$	31	0.0251
		75→89	$n_{COO} \rightarrow$ diff	28	
S_{27}	4.57	77→80		39	0.0001
		78→80		23	
S_{28}	4.58	79→91		24	0.0124
S_{29}	4.61	75→91		34	0.0027

Table S7: Excited states calculated with ADC(2)/aug-cc-pVDZ for infraluciferin carboxylate.

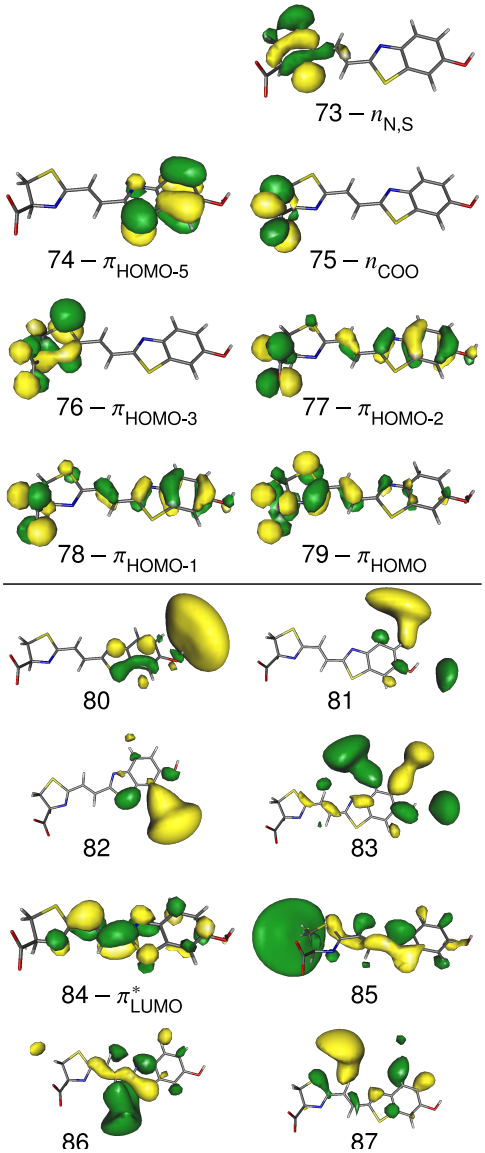


Figure S12: Hartree-Fock orbitals of infraluciferin carboxylate used in the ADC(2) calculation.

8 Optimised geometries

Luciferin Phenolate 1

C	-2.301203	0.743053	-0.082994
C	-2.481963	-0.671113	0.085445
C	-3.718455	-1.262113	0.090289
C	-4.910147	-0.459767	-0.076109
C	-4.691105	0.978731	-0.243708
C	-3.455410	1.550186	-0.247303
C	-0.165076	0.205100	0.098449
H	-3.848969	-2.328152	0.217332
H	-5.582629	1.580307	-0.368409
H	-3.324033	2.617860	-0.374463
C	3.555934	1.407722	-0.126794
C	3.469825	-0.008839	0.472366
H	3.810564	1.379014	-1.185581
C	1.239281	0.402710	0.168250
H	4.277069	2.031064	0.392554
H	3.711515	0.042442	1.542867
C	4.494729	-0.966935	-0.140285
O	5.674030	-0.730419	-0.200680
O	3.961202	-2.104320	-0.595978
H	2.993277	-2.020537	-0.433695
O	-6.060620	-0.947281	-0.078026
N	2.125370	-0.528615	0.308397
N	-1.031817	1.180199	-0.071717
S	-0.901324	-1.401880	0.269285
S	1.869636	2.081922	0.078494

Luciferin Phenolate 2

C	2.325357	0.724950	0.042760
C	2.489343	-0.696589	-0.029035
C	3.721128	-1.301516	0.000646
C	4.922689	-0.505736	0.104449
C	4.719161	0.941476	0.174878
C	3.487991	1.526504	0.145632
C	0.182228	0.199864	-0.090038
H	3.837007	-2.375678	-0.052717
H	5.617089	1.541688	0.253832
H	3.370703	2.602213	0.200235
C	-3.519236	1.464608	0.034990
C	-3.450921	0.014263	-0.469799
H	-3.796276	1.491097	1.086578
C	-1.226873	0.407956	-0.172766
H	-4.220825	2.067387	-0.537337
H	-3.685921	-0.029188	-1.541286
C	-4.448244	-0.892224	0.242874
O	-4.959341	-0.687636	1.313621
O	-4.714422	-2.002207	-0.479438
H	-5.296402	-2.553515	0.062456
O	6.069713	-1.006476	0.134981
N	-2.111884	-0.520632	-0.272893
N	1.055537	1.174209	0.007731
S	0.899487	-1.421969	-0.150816
S	-1.825380	2.106354	-0.178964

Luciferin Phenolate 3

C	2.325512	0.721785	0.077030
C	2.510767	-0.692237	-0.094422
C	3.754452	-1.283979	-0.099289
C	4.946168	-0.478443	0.069971
C	4.721797	0.960941	0.240099
C	3.478933	1.532677	0.244077
C	0.188394	0.172675	-0.106448
H	3.885716	-2.351411	-0.227912
H	5.612553	1.566354	0.366769
H	3.346481	2.601574	0.373366
C	-3.531232	1.399661	0.080002
C	-3.442856	-0.031977	-0.521550
H	-3.813184	1.369467	1.133722
C	-1.226206	0.367533	-0.177820
H	-4.234703	2.027237	-0.465056
H	-3.673574	0.010998	-1.592804
C	-4.517263	-0.924547	0.080118
O	-5.555006	-1.219943	-0.470145
O	-4.230385	-1.329410	1.336699
H	-4.978916	-1.871402	1.625831
O	6.103568	-0.965051	0.072764
N	-2.106744	-0.561204	-0.339351
N	1.047080	1.156664	0.065924
S	0.931330	-1.428791	-0.276128
S	-1.839015	2.061895	-0.071689

Luciferin Carboxylate

C	2.244042	0.787450	0.077315
C	2.356884	-0.613969	-0.082011
C	3.594709	-1.250098	-0.062034
C	4.727455	-0.471150	0.118726
C	4.633981	0.918117	0.277699
C	3.400597	1.546979	0.257879
C	0.098586	0.330948	-0.140622
H	3.694504	-2.319476	-0.180111
H	5.537632	1.500118	0.417940
H	3.317998	2.617844	0.380568
C	-3.727816	1.315766	-0.175321
C	-3.504405	-0.166428	-0.566815
H	-4.177337	1.342145	0.814555
C	-1.342412	0.497462	-0.249929
H	-4.353378	1.847137	-0.889008
H	-3.833439	-0.384847	-1.584674
C	-4.366050	-1.183934	0.358846
O	-4.710052	-0.717933	1.458520
O	-4.568721	-2.282834	-0.172235
O	5.941696	-1.115488	0.135838
H	6.639444	-0.469763	0.275261
N	-2.103200	-0.492977	-0.487690
N	0.958995	1.280048	0.039494
S	0.775608	-1.301080	-0.284500
S	-2.076407	2.114864	-0.112784

Luciferin Phenolate minus CO_2

C	1.357247	0.732068	0.002171
C	1.759358	-0.641106	0.009060
C	3.078134	-1.026268	0.011109
C	4.128747	-0.035476	0.003057
C	3.682560	1.356543	-0.005872
C	2.367659	1.722067	-0.006040
C	-0.669298	-0.153078	0.014477
H	3.373719	-2.066901	0.017274
H	4.465741	2.104562	-0.012083
H	2.070434	2.764072	-0.011899
C	-4.532359	0.469145	0.254546
C	-4.230869	-0.985813	-0.152744
H	-4.764104	0.544782	1.317376
C	-2.099296	-0.198816	-0.003707
H	-5.350551	0.901731	-0.317642
H	-4.501307	-1.146584	-1.204820
O	5.346280	-0.333360	0.003541
N	-2.816220	-1.260534	0.010463
N	0.025380	0.957176	0.007007
S	0.313462	-1.630874	0.015862
S	-2.985841	1.377167	-0.086833
H	-4.821536	-1.687543	0.440359

Luciferin Carboxylate minus CO_2

C	0.706147	-1.348013	0.000000
C	-0.690559	-1.628491	0.000000
C	-1.183246	-2.923709	0.000000
C	-0.278008	-3.983566	0.000000
C	1.091415	-3.742515	0.000000
C	1.585079	-2.437717	0.000000
C	0.000000	0.769166	0.000000
H	-2.244587	-3.131855	0.000000
H	1.782686	-4.579542	0.000000
H	2.650970	-2.253461	0.000000
C	0.556295	4.677510	0.000000
C	-0.883979	4.200176	0.000000
H	0.798780	5.281556	0.880441
C	-0.001666	2.149426	0.000000
H	0.798780	5.281556	-0.880441
H	-1.710266	4.900847	0.000000
O	-0.800800	-5.272266	0.000000
H	-0.066898	-5.891518	0.000000
N	-1.101102	2.924891	0.000000
N	1.059400	-0.032154	0.000000
S	-1.578988	-0.124969	0.000000
S	1.533987	3.120455	0.000000

Infraluciferin Phenolate 1

C	3.279403	0.647503	0.137160
C	3.676507	-0.713078	-0.116511
C	4.988352	-1.106770	-0.135994
C	6.040873	-0.145168	0.103487
C	5.604867	1.230920	0.359674
C	4.298234	1.607587	0.375646
C	1.238965	-0.179588	-0.120122
H	5.282274	-2.129592	-0.327271
H	6.394426	1.949436	0.539520
H	4.003620	2.631857	0.567473
O	7.251613	-0.449148	0.096459
N	1.964447	0.896152	0.127638
S	2.226986	-1.649806	-0.368172
C	-0.167200	-0.233155	-0.203032
H	-0.603912	-1.203611	-0.406683
C	-1.020484	0.827870	-0.057351
H	-0.614794	1.812550	0.123627
C	-2.435985	0.700544	-0.145347
C	-4.927408	1.251093	0.081919
C	-4.547517	-0.149537	-0.441995
H	-5.751738	1.687713	-0.472696
N	-3.133250	-0.386428	-0.229823
S	-3.405070	2.222095	-0.162238
H	-4.773303	-0.197243	-1.516136
C	-5.383268	-1.253618	0.211412
O	-4.649490	-2.229871	0.753450
H	-3.713684	-1.960996	0.600556
O	-6.587269	-1.252369	0.232487
H	-5.182780	1.228689	1.140625

Infraluciferin Phenolate 2

S	-3.387919	2.258893	-0.208386
C	-2.429966	0.724457	-0.165816
N	-3.116936	-0.361176	-0.237706
C	-4.535025	-0.120748	-0.443467
C	-4.910016	1.294052	0.035512
C	-1.005998	0.849891	-0.084122
C	-0.163507	-0.220992	-0.160701
C	1.248552	-0.171672	-0.088110
N	1.985272	0.909625	0.065381
C	3.301587	0.646696	0.090347
C	3.680455	-0.732663	-0.049543
S	2.217828	-1.669275	-0.216341
C	4.988845	-1.144260	-0.041508
C	6.055082	-0.181754	0.110760
C	5.636670	1.214572	0.250813
C	4.333006	1.608249	0.241244
O	7.263849	-0.502135	0.124004
C	-5.324952	-1.198813	0.290454
O	-5.866826	-1.081086	1.359126
O	-5.356557	-2.353635	-0.408619
H	5.267164	-2.183876	-0.147647
H	6.434959	1.937116	0.365143
H	4.053675	2.649375	0.347084
H	-0.610245	-1.199624	-0.289636
H	-0.596046	1.841786	0.039911
H	-5.723849	1.722996	-0.544213
H	-4.757657	-0.230126	-1.513076
H	-5.815185	-3.001853	0.144448
H	-5.181835	1.283905	1.088615

Infraluciferin Phenolate 3

S	-3.386598	2.226004	-0.129392
C	-2.419915	0.689707	-0.163817
N	-3.106688	-0.389841	-0.283247
C	-4.515008	-0.153108	-0.487972
C	-4.903257	1.244665	0.071202
C	-0.997579	0.821451	-0.080510
C	-0.148130	-0.239624	-0.207693
C	1.262889	-0.185233	-0.127233
N	1.991555	0.891765	0.086049
C	3.309050	0.636350	0.106359
C	3.698135	-0.731785	-0.101316
S	2.243005	-1.667943	-0.325861
C	5.008999	-1.135061	-0.104595
C	6.067591	-0.174909	0.105604
C	5.638916	1.209897	0.314042
C	4.332971	1.595459	0.314482
O	7.278162	-0.487893	0.112378
C	-5.392582	-1.226335	0.135689
O	-6.339778	-1.737421	-0.409655
O	-5.043813	-1.528716	1.402116
H	5.295038	-2.166085	-0.261594
H	6.431641	1.930388	0.471726
H	4.045919	2.627972	0.471529
H	-0.588570	-1.213547	-0.384804
H	-0.593626	1.808422	0.092463
H	-5.724167	1.690463	-0.484020
H	-4.741728	-0.184844	-1.558937
H	-5.667233	-2.202929	1.706338
H	-5.162891	1.191119	1.127578

Infraluciferin Carboxylate

S	-3.531980	2.209490	-0.011552
C	-2.555994	0.722293	-0.248473
N	-3.186337	-0.346650	-0.530322
C	-4.616637	-0.221579	-0.561933
C	-5.050918	1.191139	-0.088637
C	-1.109258	0.820465	-0.148138
C	-0.284558	-0.241281	-0.206058
C	1.150751	-0.138720	-0.122696
N	1.858521	0.943091	0.003348
C	3.203288	0.675626	0.053043
C	3.560270	-0.691796	-0.040713
S	2.116035	-1.637400	-0.194481
C	4.886608	-1.108227	-0.004527
C	5.871055	-0.140203	0.127436
C	5.539965	1.217925	0.221490
C	4.217984	1.626773	0.185236
O	7.176329	-0.567862	0.161350
C	-5.295903	-1.399627	0.333224
O	-5.689491	-1.034376	1.453702
O	-5.333029	-2.494152	-0.240648
H	5.166692	-2.149234	-0.074833
H	6.330626	1.952211	0.324090
H	3.956243	2.672931	0.258223
H	7.756538	0.191889	0.258797
H	-0.713699	-1.228236	-0.319129
H	-0.686695	1.808516	-0.018427
H	-5.764567	1.658444	-0.763396
H	-4.948846	-0.441282	-1.578691
H	-5.476858	1.100618	0.907952

Infraluciferin Phenolate minus CO_2

S	-4.530866	1.412587	-0.146067
C	-3.373890	0.015811	0.005208
N	-3.918443	-1.140997	0.081823
C	-5.357077	-1.113355	-0.084956
C	-5.901243	0.286763	0.265160
C	-1.973171	0.334258	0.005023
C	-1.000807	-0.619579	-0.005891
C	0.397818	-0.385815	0.000441
N	0.996934	0.784818	0.021236
C	2.338749	0.687233	0.017772
C	2.881558	-0.641619	-0.007098
S	1.542013	-1.760487	-0.025716
C	4.231308	-0.891042	-0.013126
C	5.174962	0.201709	0.005426
C	4.590388	1.543117	0.030424
C	3.247174	1.774539	0.036466
O	6.415041	0.031218	0.000673
H	4.631305	-1.895718	-0.031701
H	5.295260	2.365082	0.044305
H	2.845740	2.780481	0.055162
H	-1.318598	-1.655454	-0.019025
H	-1.695693	1.378540	0.014167
H	-6.786324	0.546909	-0.311217
H	-5.599713	-1.358522	-1.127677
H	-6.129526	0.372815	1.327743
H	-5.825185	-1.876335	0.540901

Infraluciferin Carboxylate minus CO_2

S	-3.014839	-3.798688	0.000000
C	-2.810265	-1.980127	0.000000
N	-4.014041	-1.353663	0.000000
C	-5.045504	-2.123011	0.000000
C	-4.834952	-3.624998	0.000000
C	-1.576621	-1.377013	0.000000
C	-1.299233	-0.003170	0.000000
C	0.000000	0.508533	0.000000
N	1.155255	-0.136232	0.000000
C	2.228947	0.702408	0.000000
C	1.944471	2.098000	0.000000
S	0.217029	2.315461	0.000000
C	2.944868	3.057675	0.000000
C	4.272083	2.636007	0.000000
C	4.582798	1.279397	0.000000
C	3.574710	0.317100	0.000000
O	5.254968	3.616656	0.000000
H	2.722893	4.115938	0.000000
H	5.622762	0.968746	0.000000
H	3.819948	-0.736257	0.000000
H	6.111794	3.183034	0.000000
H	-2.121729	0.697691	0.000000
H	-0.714951	-2.034946	0.000000
H	-5.273120	-4.103577	0.881546
H	-6.045584	-1.704204	0.000000
H	-5.273120	-4.103577	-0.881546

Infraluciferin Phenolate 1 minus H_2

C	1.921894	-2.692692	0.000000
C	3.147696	-1.939935	0.000000
C	4.380991	-2.537188	0.000000
C	4.492362	-3.978286	0.000000
C	3.226797	-4.716564	0.000000
C	2.009010	-4.108954	0.000000
C	0.994669	-0.678722	0.000000
H	5.299362	-1.966390	0.000000
H	3.310378	-5.795944	0.000000
H	1.088979	-4.680352	0.000000
O	5.590302	-4.573892	0.000000
N	0.785319	-1.981403	0.000000
S	2.729062	-0.245759	0.000000
C	0.000000	0.323497	0.000000
H	0.344934	1.350268	0.000000
C	-1.349494	0.100778	0.000000
H	-1.709806	-0.918512	0.000000
C	-2.318418	1.139815	0.000000
C	-4.441219	2.414658	0.000000
C	-3.291108	3.145412	0.000000
N	-2.118044	2.444520	0.000000
S	-4.047753	0.741782	0.000000
C	-3.222901	4.629965	0.000000
O	-1.960459	5.098843	0.000000
H	-1.375787	4.316764	0.000000
O	-4.177361	5.365412	0.000000
H	-5.451457	2.782379	0.000000

Infraluciferin Phenolate 2 minus H_2

S	-4.064523	0.559381	0.000000
C	-2.345890	1.032290	0.000000
N	-2.190450	2.336472	0.000000
C	-3.386298	2.991022	0.000000
C	-4.512587	2.211275	0.000000
C	-1.336315	0.026964	0.000000
C	0.000000	0.306610	0.000000
C	1.039004	-0.654109	0.000000
N	0.889818	-1.962985	0.000000
C	2.060198	-2.622623	0.000000
C	3.248314	-1.814718	0.000000
S	2.751468	-0.141582	0.000000
C	4.509548	-2.353740	0.000000
C	4.689927	-3.786984	0.000000
C	3.460615	-4.582291	0.000000
C	2.214530	-4.031934	0.000000
O	5.816147	-4.330778	0.000000
C	-3.477909	4.463995	0.000000
O	-4.516489	5.089167	0.000000
O	-2.276780	5.080783	0.000000
H	5.399216	-1.738955	0.000000
H	3.593364	-5.656878	0.000000
H	1.322940	-4.647047	0.000000
H	0.296944	1.348366	0.000000
H	-1.656974	-1.005679	0.000000
H	-2.469261	6.028469	0.000000
H	-5.534776	2.544617	0.000000

Infraluciferin Phenolate minus H_2+CO_2

C	2.193636	0.830887	0.000000
C	1.815888	2.215161	0.000000
C	2.735321	3.234586	0.000000
C	4.149334	2.941831	0.000000
C	4.501514	1.521946	0.000000
C	3.575757	0.520874	0.000000
C	0.000000	0.501259	0.000000
H	2.440895	4.275267	0.000000
H	5.560947	1.297817	0.000000
H	3.869614	-0.521821	0.000000
O	5.029577	3.832322	0.000000
N	1.187247	-0.063669	0.000000
S	0.071131	2.287933	0.000000
C	-1.251258	-0.166888	0.000000
H	-2.137194	0.456335	0.000000
C	-1.426247	-1.518460	0.000000
H	-0.555523	-2.159791	0.000000
C	-2.709035	-2.145957	0.000000
C	-4.552383	-3.784153	0.000000
C	-4.903686	-2.466842	0.000000
N	-3.889799	-1.560488	0.000000
S	-2.830803	-3.911721	0.000000
H	-5.190733	-4.650269	0.000000
H	-5.925048	-2.111873	0.000000

Infraluciferin Carboxylate minus H_2

S	-4.004623	1.050035	0.000000
C	-2.272519	1.344200	0.000000
N	-1.968272	2.616359	0.000000
C	-3.065081	3.422010	0.000000
C	-4.261665	2.736998	0.000000
C	-1.342258	0.249858	0.000000
C	0.000000	0.398169	0.000000
C	0.913413	-0.712622	0.000000
N	0.617414	-1.978726	0.000000
C	1.738683	-2.769798	0.000000
C	2.975984	-2.080374	0.000000
S	2.665763	-0.374424	0.000000
C	4.192298	-2.753735	0.000000
C	4.170799	-4.140795	0.000000
C	2.958798	-4.842802	0.000000
C	1.750314	-4.166691	0.000000
O	5.381387	-4.790997	0.000000
C	-3.011894	4.974608	0.000000
O	-4.147411	5.501263	0.000000
O	-1.881654	5.482724	0.000000
H	5.139389	-2.233905	0.000000
H	2.971698	-5.926656	0.000000
H	0.812349	-4.703904	0.000000
H	0.416054	1.396720	0.000000
H	-1.754836	-0.751277	0.000000
H	-5.238120	3.187843	0.000000
H	5.231428	-5.740127	0.000000

Infraluciferin Carboxylate minus H_2+CO_2

C	2.222327	0.418429	0.000000
C	2.058729	1.826845	0.000000
C	3.145064	2.693388	0.000000
C	4.421058	2.146302	0.000000
C	4.607700	0.760829	0.000000
C	3.519598	-0.099858	0.000000
C	0.000000	0.432722	0.000000
H	3.024641	3.767247	0.000000
H	5.614552	0.358502	0.000000
H	3.660025	-1.171753	0.000000
O	5.486342	3.021525	0.000000
N	1.066366	-0.318226	0.000000
S	0.362280	2.191725	0.000000
C	-1.369426	0.026384	0.000000
H	-2.126715	0.798101	0.000000
C	-1.761747	-1.275807	0.000000
H	-0.993651	-2.038654	0.000000
C	-3.119931	-1.716166	0.000000
C	-5.192982	-2.965918	0.000000
C	-5.406187	-1.590943	0.000000
N	-4.189112	-0.941094	0.000000
S	-3.507680	-3.427486	0.000000
H	-5.933056	-3.752451	0.000000
H	6.303881	2.516991	0.000000