ELECTRONIC SUPPLEMENTARY INFORMATION FOR

Mechanism of activated chemiluminescence of cyclic peroxides: 1,2-dioxetane and 1,2-dioxetanone

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Table S1. Cartesian coordinates (Å) of the optimized ACT-peroxide molecular complexes (Table 1) at MP2/6-31++g(d,p).

Naphthalene–1,2-dioxetane

C	-2.45795	-1.54215	-0.48188
C	-2.21994	-0.29609	-1.03221
C	-1.32322	0.61363	-0.40837
C	-0.70067	0.23580	0.82758
C	-0.95741	-1.05431	1.36377
C	-1.83368	-1.91775	0.73370
H	-1.55898	2.20392	-1.86017
H	-3.14198	-2.22673	-0.96953
H	-2.70285	-0.00560	-1.95975
C	-1.07056	1.90817	-0.93716
C	0.21170	1.13273	1.44293
H	-0.46201	-1.34592	2.28296
H	-2.02628	-2.89654	1.15678
C	0.44336	2.38336	0.90136
C	-0.19668	2.77145	-0.30124
H	0.71615	0.82500	2.35188
H	1.13889	3.05985	1.38335
H	-0.01061	3.75494	-0.71669
H	2.01382	-2.35251	-1.48021
C	1.53000	-1.53620	-0.94149
O	2.97206	-0.39131	0.03884
O	1.99883	-1.49483	0.44514
H	0.44535	-1.61541	-0.98449
C	2.16442	-0.18493	-1.16740
H	1.48293	0.65411	-1.03407
H	2.80226	-0.04830	-2.03942

Naphthalene–1,2-dioxetanone

C	-2.49961	1.00848	0.87676
C	-1.50972	0.30005	1.53394
C	-0.69910	-0.63576	0.83524
C	-0.95949	-0.87797	-0.55451
C	-1.97553	-0.12736	-1.20497
C	-2.74281	0.78425	-0.50157
H	0.49188	-1.22334	2.54501
H	-3.10946	1.71898	1.42234
H	-1.32108	0.47086	2.58874
C	0.30185	-1.40115	1.49198
C	-0.16205	-1.82461	-1.25021
H	-2.16158	-0.30195	-2.25972
H	-3.52460	1.33871	-1.00753
C	0.81593	-2.54154	-0.58892
C	1.05362	-2.32354	0.79011

H	-0.34093	-1.98497	-2.30815
H	1.41719	-3.26218	-1.13028
H	1.82373	-2.89089	1.29908
H	0.97233	3.13186	-0.89211
C	0.72325	2.09376	-0.67601
O	2.11790	0.53085	-0.60044
O	1.26296	1.18539	-1.68089
C	1.61234	1.42734	0.33680
H	-0.34342	1.94102	-0.52023
O	1.91214	1.50503	1.49770

Naphthalene–tetramethyl-1,2-dioxetane

C	-2.58584	-2.27224	-0.65347
C	-2.76446	-1.01583	-1.20291
C	-2.35794	0.14971	-0.49773
C	-1.73140	0.00123	0.78406
C	-1.55391	-1.30274	1.31894
C	-1.97901	-2.41618	0.61865
H	-3.02953	1.57042	-1.98889
H	-2.91136	-3.15129	-1.19760
H	-3.23604	-0.90463	-2.17428
C	-2.55483	1.45713	-1.01930
C	-1.32411	1.16240	1.49245
H	-1.07080	-1.40840	2.28396
H	-1.84843	-3.40495	1.04322
C	-1.54442	2.42171	0.96684
C	-2.16643	2.57065	-0.29691
H	-0.82230	1.04382	2.44613
H	-1.22875	3.29930	1.51855
H	-2.33221	3.56220	-0.70205
C	2.07135	-0.84282	-0.10971
O	2.12332	0.87078	1.09410
O	1.36881	-0.45656	1.13209
C	2.34771	0.65024	-0.35003
C	3.73618	1.10372	-0.74041
H	3.91971	0.87774	-1.79306
H	3.81103	2.18473	-0.61105
H	4.50315	0.62870	-0.13423
C	3.28920	-1.67143	0.25595
H	2.95866	-2.63901	0.63548
H	3.92252	-1.84150	-0.61768
H	3.86882	-1.17607	1.03252
C	1.14424	-1.58174	-1.04851
H	1.65562	-1.76885	-1.99628
H	0.87406	-2.54521	-0.61404
H	0.22967	-1.02528	-1.23803
C	1.26984	1.37072	-1.13716

H	1.41396	2.44778	-1.03875
H	1.32335	1.10839	-2.19660
H	0.28494	1.12119	-0.75128

Naphthalene–dimethyl-1,2-dioxetanone

C	-1.45934	2.47840	0.91618
C	-1.43266	1.22477	1.50070
C	-1.59076	0.05302	0.71249
C	-1.69734	0.18321	-0.71262
C	-1.72739	1.48436	-1.28231
C	-1.60398	2.60940	-0.48674
H	-1.52506	-1.34229	2.36609
H	-1.35874	3.36461	1.53198
H	-1.32636	1.12229	2.57579
C	-1.62887	-1.24381	1.29085
C	-1.87883	-0.98572	-1.49890
H	-1.83631	1.58307	-2.35767
H	-1.63539	3.59573	-0.93508
C	-1.92769	-2.23280	-0.90603
C	-1.81083	-2.36175	0.49900
H	-1.96668	-0.88536	-2.57583
H	-2.06428	-3.11694	-1.51755
H	-1.84827	-3.34467	0.95393
C	2.42113	0.22352	-0.27782
O	1.08591	-1.41261	-0.24295
O	1.75141	-0.57048	-1.32732
C	1.69468	-0.62954	0.72912
O	1.58571	-0.73836	1.92366
C	3.91880	0.00049	-0.30721
H	4.33705	0.46155	-1.20216
H	4.37458	0.45878	0.57140
H	4.14515	-1.06447	-0.31470
C	1.99426	1.67195	-0.32767
H	2.37656	2.19317	0.55158
H	2.40646	2.14142	-1.22191
H	0.90999	1.75176	-0.34734

Anthracene–1,2-dioxetanone

C	-0.24575	0.49726	3.20006
C	-0.65394	-0.95346	3.20024
O	1.10721	0.19653	3.19992
O	-0.73866	1.58101	3.20003
O	0.71049	-1.32967	3.20010
H	-1.16611	-1.27803	2.30547
H	-1.16589	-1.27788	4.09518
C	-2.15475	-0.78542	-0.20788
C	-1.42859	-2.02559	-0.25783

C	-0.03521	-2.00632	-0.13514
C	0.66917	-0.80862	0.02551
C	-0.05573	0.43079	0.06759
C	-1.45047	0.41161	-0.04378
C	2.09436	-0.77802	0.16027
C	2.75385	0.40481	0.31853
C	2.03284	1.63825	0.35977
C	0.67450	1.65135	0.24016
C	-3.58302	-0.81962	-0.31689
C	-4.24529	-2.00315	-0.46654
C	-3.52330	-3.23609	-0.51727
C	-2.16262	-3.24600	-0.41605
H	0.51431	-2.94497	-0.16069
H	-1.99849	1.35002	0.00687
H	2.63621	-1.71950	0.14116
H	3.83371	0.41625	0.42601
H	2.57562	2.56771	0.49841
H	0.11933	2.58373	0.29077
H	-4.12693	0.12033	-0.27834
H	-5.32737	-2.01592	-0.54929
H	-4.06777	-4.16716	-0.63826
H	-1.60973	-4.18078	-0.45503

2-Naphtholate–1,2-dioxetanone

C	-2.43888	1.28989	0.72899
C	-1.50743	0.53223	1.41674
C	-0.79255	-0.51271	0.79472
C	-1.02478	-0.81986	-0.59372
C	-1.98552	-0.00378	-1.28056
C	-2.67199	1.00361	-0.64322
H	0.37538	-1.06987	2.53442
H	-2.98244	2.08885	1.22442
H	-1.30221	0.73952	2.46633
C	0.17308	-1.30480	1.48957
C	-0.33424	-1.86265	-1.21872
H	-2.16756	-0.20809	-2.33367
H	-3.39779	1.59517	-1.19747
C	0.62842	-2.67190	-0.54023
C	0.84314	-2.31514	0.86728
H	-0.51662	-2.07457	-2.26999
O	1.26166	-3.62271	-1.06786
H	1.58316	-2.90610	1.40258
C	1.60974	1.40942	0.34791
C	0.73543	2.08037	-0.68001
O	2.13497	0.51402	-0.57042
O	1.87080	1.48234	1.50723
O	1.23124	1.19634	-1.66787

H	-0.32621	1.95705	-0.51881
H	0.99240	3.10939	-0.88822

Table S2. Details on the active space used in the CASPT2//MP2 calculations of the VEAs (Table 2).

Systems	MOs							# e^- (neutral)	# e^- (anion)	TOTAL MOs
	σ_{CO}	$\pi_{C=O}$	σ_{OO}	n_O	σ^*_{CO}	$\pi^*_{C=O}$	σ^*_{OO}			
Tetramethyl-1,2-dioxetane, 1,2-dioxetane	2	-	1	2	2	-	1	10	11	8
Dimethyl-1,2-dioxetanone, 1,2-dioxetanone	2	1	1	3	2	1	1	14	15	11

Table S3. Cartesian coordinates (Å) of highlighted structures for the dissociation of a CT complex formed between 1,2-dioxetanone and anthracene (Figure 3).

Reactant – Reaction coordinate –0.7 a. u.

C	-0.24575	0.49726	3.20006
C	-0.65394	-0.95346	3.20024
O	1.10721	0.19653	3.19992
O	-0.73866	1.58101	3.20003
O	0.71049	-1.32967	3.20010
H	-1.16611	-1.27803	2.30547
H	-1.16589	-1.27788	4.09518
C	-2.15475	-0.78542	-0.20788
C	-1.42859	-2.02559	-0.25783
C	-0.03521	-2.00632	-0.13514
C	0.66917	-0.80862	0.02551
C	-0.05573	0.43079	0.06759
C	-1.45047	0.41161	-0.04378
C	2.09436	-0.77802	0.16027
C	2.75385	0.40481	0.31853
C	2.03284	1.63825	0.35977
C	0.67450	1.65135	0.24016
C	-3.58302	-0.81962	-0.31689
C	-4.24529	-2.00315	-0.46654
C	-3.52330	-3.23609	-0.51727
C	-2.16262	-3.24600	-0.41605
H	0.51431	-2.94497	-0.16069
H	-1.99849	1.35002	0.00687
H	2.63621	-1.71950	0.14116
H	3.83371	0.41625	0.42601

H	2.57562	2.56771	0.49841
H	0.11933	2.58373	0.29077
H	-4.12693	0.12033	-0.27834
H	-5.32737	-2.01592	-0.54929
H	-4.06777	-4.16716	-0.63826
H	-1.60973	-4.18078	-0.45503

Transition state – Reaction coordinate 0.0 a. u.

C	-0.13888	0.45308	3.20283
C	-0.58298	-0.98629	3.18962
O	1.18408	0.62417	3.21814
O	-0.83009	1.45147	3.18309
O	0.57021	-1.75295	3.20422
H	-1.19827	-1.16600	2.31566
H	-1.15673	-1.18771	4.08745
C	-2.15475	-0.78542	-0.20788
C	-1.42859	-2.02559	-0.25783
C	-0.03521	-2.00632	-0.13514
C	0.66917	-0.80862	0.02551
C	-0.05573	0.43079	0.06759
C	-1.45047	0.41161	-0.04378
C	2.09436	-0.77802	0.16027
C	2.75385	0.40481	0.31853
C	2.03284	1.63825	0.35977
C	0.67450	1.65136	0.24016
C	-3.58302	-0.81962	-0.31689
C	-4.24529	-2.00315	-0.46654
C	-3.52330	-3.23609	-0.51727
C	-2.16262	-3.24600	-0.41605
H	0.51431	-2.94497	-0.16069
H	-1.99849	1.35002	0.00687
H	2.63621	-1.71950	0.14116
H	3.83371	0.41625	0.42601
H	2.57562	2.56771	0.49841
H	0.11933	2.58373	0.29077
H	-4.12693	0.12033	-0.27834
H	-5.32737	-2.01592	-0.54929
H	-4.06777	-4.16716	-0.63826
H	-1.60973	-4.18078	-0.45503

After the transition state – Reaction coordinate 0.1 a. u.

C	-0.02921	0.67305	3.19836
C	-0.52058	-1.10513	3.20183
O	1.17731	0.61724	3.17620
O	-0.99804	1.36674	3.21647
O	0.44108	-1.94690	3.21649
H	-1.10263	-1.08927	2.28613

H	-1.12061	-1.07997	4.10551
C	-2.15475	-0.78542	-0.20788
C	-1.42859	-2.02559	-0.25783
C	-0.03521	-2.00632	-0.13514
C	0.66917	-0.80862	0.02551
C	-0.05573	0.43079	0.06759
C	-1.45047	0.41161	-0.04378
C	2.09436	-0.77802	0.16027
C	2.75385	0.40481	0.31853
C	2.03284	1.63825	0.35977
C	0.67450	1.65135	0.24016
C	-3.58302	-0.81962	-0.31689
C	-4.24529	-2.00315	-0.46654
C	-3.52330	-3.23609	-0.51727
C	-2.16262	-3.24600	-0.41605
H	0.51431	-2.94497	-0.16069
H	-1.99849	1.35002	0.00687
H	2.63621	-1.71950	0.14116
H	3.83371	0.41625	0.42601
H	2.57562	2.56771	0.49841
H	0.11933	2.58373	0.29077
H	-4.12693	0.12033	-0.27834
H	-5.32737	-2.01592	-0.54929
H	-4.06777	-4.16716	-0.63826
H	-1.60973	-4.18078	-0.45503

Population of the excited state – Reaction coordinate 0.3 a. u.

C	0.03467	0.84144	3.19680
C	-0.57452	-1.27931	3.20302
O	1.17425	0.60251	3.17539
O	-1.02297	1.33811	3.21648
O	0.42765	-1.94773	3.21657
H	-1.08554	-1.06238	2.26934
H	-1.10620	-1.05687	4.12341
C	-2.15475	-0.78542	-0.20788
C	-1.42859	-2.02559	-0.25783
C	-0.03521	-2.00632	-0.13514
C	0.66917	-0.80862	0.02551
C	-0.05573	0.43079	0.06759
C	-1.45047	0.41161	-0.04378
C	2.09436	-0.77802	0.16027
C	2.75385	0.40481	0.31853
C	2.03284	1.63825	0.35977
C	0.67450	1.65135	0.24016
C	-3.58302	-0.81962	-0.31689
C	-4.24529	-2.00315	-0.46654
C	-3.52330	-3.23609	-0.51727

C	-2.16262	-3.24600	-0.41605
H	0.51431	-2.94497	-0.16069
H	-1.99849	1.35002	0.00687
H	2.63621	-1.71950	0.14116
H	3.83371	0.41625	0.42601
H	2.57562	2.56771	0.49841
H	0.11933	2.58373	0.29077
H	-4.12693	0.12033	-0.27834
H	-5.32737	-2.01592	-0.54929
H	-4.06777	-4.16716	-0.63826
H	-1.60973	-4.18078	-0.45503

Anthracene excited state populated – Reaction coordinate 0.4 a. u.

C	0.06937	0.93756	3.19589
C	-0.60731	-1.35083	3.20336
O	1.18636	0.61413	3.17482
O	-1.02763	1.33897	3.21654
O	0.42719	-1.96020	3.21677
H	-1.08917	-1.07352	2.26922
H	-1.11146	-1.07034	4.12440
C	-2.15475	-0.78542	-0.20788
C	-1.42859	-2.02559	-0.25783
C	-0.03521	-2.00632	-0.13514
C	0.66917	-0.80862	0.02551
C	-0.05573	0.43079	0.06759
C	-1.45047	0.41161	-0.04378
C	2.09436	-0.77802	0.16027
C	2.75385	0.40481	0.31853
C	2.03284	1.63825	0.35977
C	0.67450	1.65135	0.24016
C	-3.58302	-0.81962	-0.31689
C	-4.24529	-2.00315	-0.46654
C	-3.52330	-3.23609	-0.51727
C	-2.16262	-3.24600	-0.41605
H	0.51431	-2.94497	-0.16069
H	-1.99849	1.35002	0.00687
H	2.63621	-1.71950	0.14116
H	3.83371	0.41625	0.42601
H	2.57562	2.56771	0.49841
H	0.11933	2.58373	0.29077
H	-4.12693	0.12033	-0.27834
H	-5.32737	-2.01592	-0.54929
H	-4.06777	-4.16716	-0.63826
H	-1.60973	-4.18078	-0.45503

Products – Reaction coordinate 0.9 a. u.

C	0.19152	1.18880	3.19484

C	-0.69826	-1.52463	3.20403
O	1.30809	0.85560	3.17271
O	-0.94033	1.48584	3.21661
O	0.39444	-2.02982	3.21818
H	-1.19152	-1.26927	2.26857
H	-1.21659	-1.27075	4.12606
C	-2.15475	-0.78542	-0.20788
C	-1.42859	-2.02559	-0.25783
C	-0.03521	-2.00632	-0.13514
C	0.66917	-0.80862	0.02551
C	-0.05573	0.43079	0.06759
C	-1.45047	0.41161	-0.04378
C	2.09436	-0.77802	0.16027
C	2.75385	0.40481	0.31853
C	2.03284	1.63825	0.35977
C	0.67450	1.65135	0.24016
C	-3.58302	-0.81962	-0.31689
C	-4.24529	-2.00315	-0.46654
C	-3.52330	-3.23609	-0.51727
C	-2.16262	-3.24600	-0.41605
H	0.51431	-2.94497	-0.16069
H	-1.99849	1.35002	0.00687
H	2.63621	-1.71950	0.14116
H	3.83371	0.41625	0.42601
H	2.57562	2.56771	0.49841
H	0.11933	2.58373	0.29077
H	-4.12693	0.12033	-0.27834
H	-5.32737	-2.01592	-0.54929
H	-4.06777	-4.16716	-0.63826
H	-1.60973	-4.18078	-0.45503

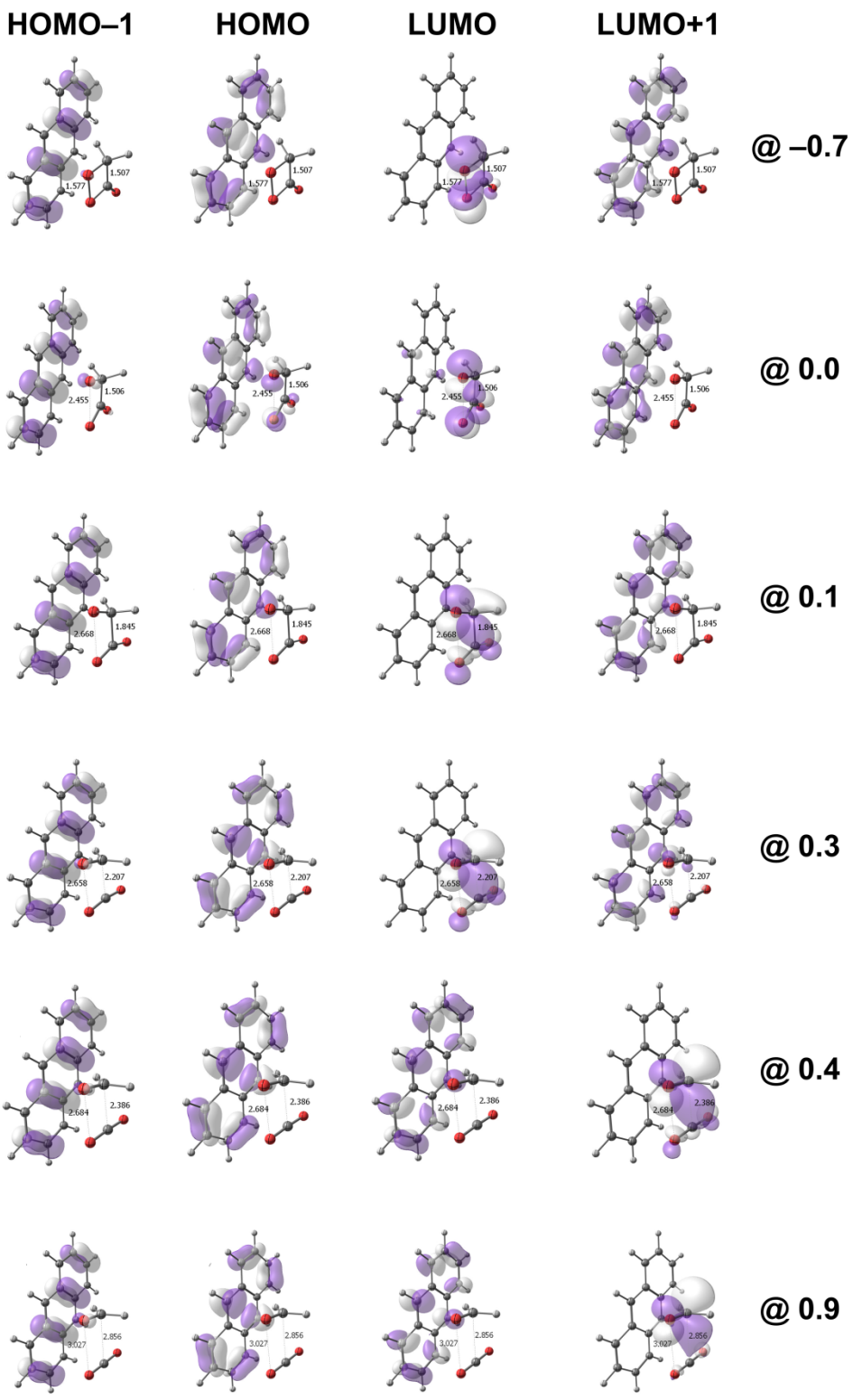

Figure S1. Nature of some molecular orbitals in the highlighted coordinates for the dissociation of a CT complex formed between 1,2-dioxetanone and anthracene (Figure 3).