Electronic Supplementary Information (ESI)

for

Mechanistic insights for the photoredox organocatalytic fluorination of aliphatic carbons by anthraquinone using time-resolved and DFT studies

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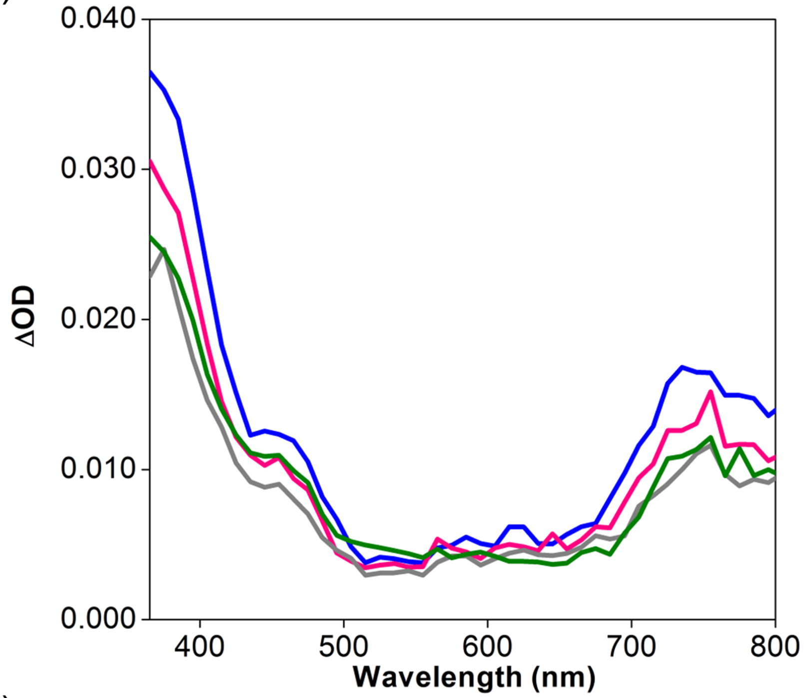
a)



b)

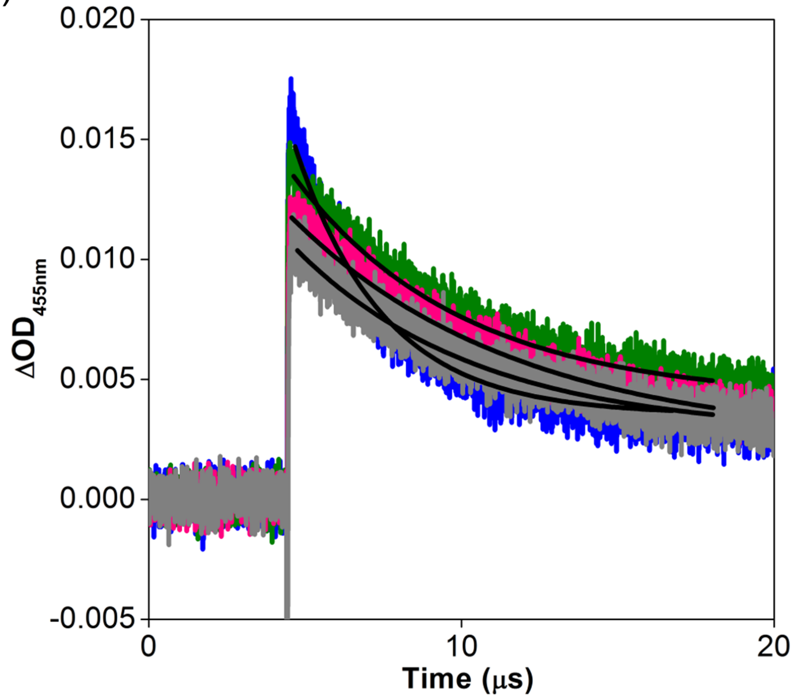


Fig. S1 (a) Transient absorption spectra of the AQN-Selectfluor® exciplex, and (b) transient absorption temporal decay profiles at 455 nm upon 355 nm pulsed irradiation of 165 μM AQN with different concentrations of Selectfluor® (green: 126 mM , blue: 63 mM, pink: 6.3 mM; gray: 0.63 mM). The black lines represent the mono-exponential fits for the respective decay signals.

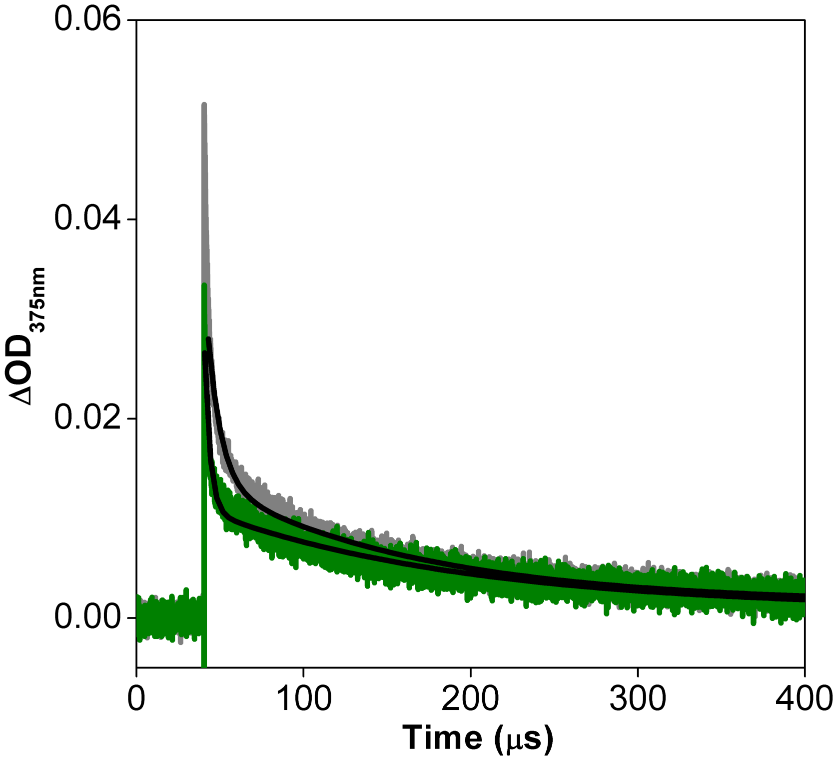


Fig. S2 Transient absorption signal at 375 nm upon 355 nm pulsed irradiation of AQN in the presence of Selectfluor® II (green) or 1-fluoro-2,4,6-trimethylpyridinium BF_4 (grey). The black lines represent the bi-exponential fits for the respective decay signals.

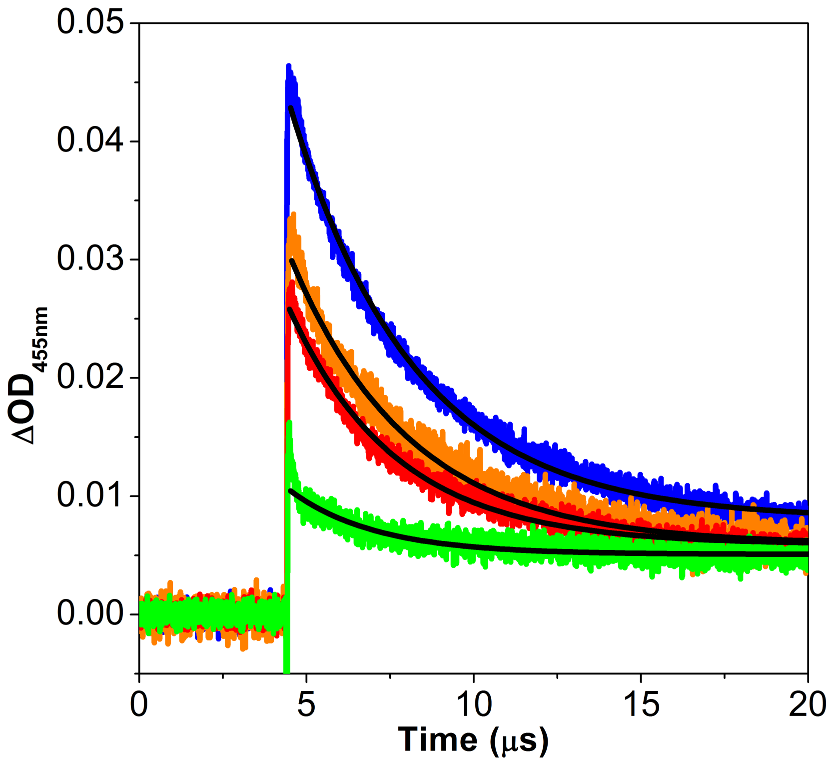


Fig. S3 Transient absorption signal of the AQN-Selecfluor® exciplex at 455 nm upon 355 nm pulsed irradiation of 165 µM AQN with 63 mM Selectfluor® with varying concentrations of dimethyl adipate (blue: 0 mM; orange: 94 mM; red: 376 mM; green: 752 mM)

General treatment for the error propagation of the decay lifetimes

The error propagation for the fits to the decay lifetimes are conducted by using the root-mean-square error from the sum of the square of the uncertainties of each measured value. In each time-resolved measurement, there are uncertainties associated with the laser pulse duration, spectrometer time-resolution, mass of samples, and volume of samples. For each fit, the error in the decay time $\delta\tau$ has been calculated with the following equation:

$$\delta\tau = \tau \bullet [(\delta\tau_a/\tau_a)^2 + (\delta\tau_b/\tau_b)^2 + (\delta m_1/m_1)^2 + ... + (\delta m_n/m_n)^2 + (\delta V_1/V_1)^2 + ... + (\delta V_l/V_l)^2]^{1/2}$$

Here, $\delta\tau_a$ = uncertainty of laser pulse duration; $\delta\tau_b$ = uncertainty of spectrometer time-resolution; δm_1 = uncertainty of first mass component, where 1 to n are the n different dissolved constituents such as AQN, dimethyl adipate, or other fluorinating agents; δV_1 = uncertainty of the first volume measurement, where 1 to l are the l different volume measurements used to prepare the sample.

Stern-Volmer plot for the quenching of the AQN-Selectfluor® exciplex by dimethyl adipate

As the concentration of dimethyl adipate increases, the lifetime τ of the signal owing to AQN-Selecfluor® exciplex decreases. The quenching rate constant, k_q, is related to the lifetime, τ, of the AQN-Selecfluor® exciplex in the presence of dimethyl adipate with a concentration of $[Q]$ by the Stern-Volmer equation:

$$\frac{\tau_0}{\tau} = 1 + k_q\tau_0[Q]$$

where τ_0 is the lifetime of AQN-Selecfluor® exciplex in the absence of dimethyl adipate

The transient absorption decay signal at 455 nm were fit to single exponential functions to obtain the time constants for the transient signals according to the following equation:

$$y = y_0 + A_1 e^{-(t-\tau_0)/\tau_1}$$

The parameters y_0, τ_0, A_n and τ_n were determined by a least-squares fitting procedure in Origin. The term y_0 corresponds to the vertical intercept at long lifetimes where the signal decays to a 'permanent' absorption (positive y_0). The variable τ_0 is the delay time of the excitation pulse from the start of the probe measurement during each photoexcitation cycle. A_1 is the change in optical density after irradiation and τ_1 is the corresponding time constant.

The quenching rate constant, k_q, of the AQN-Selecfluor® exciplex by dimethyl adipate can be obtained by plotting a graph of τ_0/τ against [Q] with a fixed vertical intercept of 1. The gradient ($k_q\tau_0$) was determined to be 0.54 ± 0.05 M^{-1} and τ_0 was determined to be 3.72 ± 0.04 µs. This gives a rate constant, k_q, of 1.5 ± 1 × 10^5 $M^{-1}s^{-1}$.

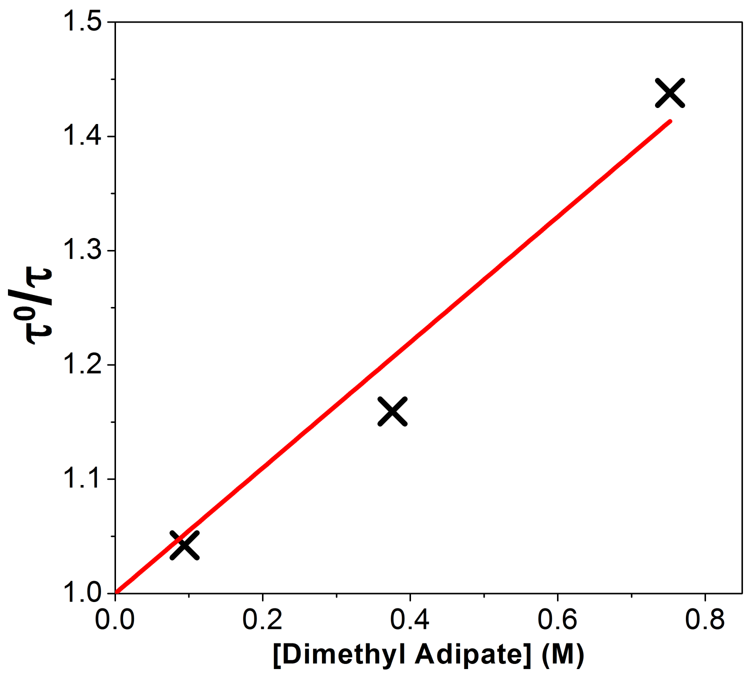


Fig. S4 Stern-Volmer plot for the quenching of the transient absorption signal of the AQN-Selectfluor® exciplex at 455 nm by varying concentrations of dimethyl adipate.

Fig. S5 Custom-made quartz cuvette fitted with high vacuum valves for use in the transient absorption experiments of AQN.

Table S1. Bi-exponential fits of the transient absorption decay signals at 375 nm, 455 nm, and 745 nm after pulsed 355 nm irradiation of anthraquinone (AQN) with varying concentrations of Selectfluor®.

Wavelength	**Decay lifetimes[a] (μs)**	
	126 mM Selectfluor®	**63 mM Selectfluor®**
375 nm	**3.31 ± 0.04 (84%)** [b] 159 ± 2 (16%)	**2.04 ± 0.02 (85%)**[b] 108 ± 1 (15%)
455 nm	**5.37 ± 0.06 (75%)** [b] 131 ± 1 (25%)	**3.72 ± 0.04 (86%)** [b] 65.9 ± 0.7 (14%)
745nm	3.82 ± 0.04 (82%) [b] 113 ± 1 (18%)	2.39 ± 0.03 (83%) [b] 123 ± 1 (17%)
Wavelength	**6.3 mM Selectfluor®**	**0.63 mM Selectfluor®**
375 nm	**5.40 ± 0.06 (85%)** [b] 169 ± 2 (15%)	**5.2 ± 0.1 (82%)** [b] 192 ± 4 (18%)
455 nm	**7.20 ± 0.08 (86%)** [b] 154 ± 2 (14%)	**5.8 ± 0.1 (80%)** [b] 119 ± 2 (20%)
745nm	5.47 ± 0.06 (82%) [b] 156 ± 2 (18%)	5.1 ± 0.1 (80%) [b] 152 ± 3 (20%)

[a] Relative contributions of the decay components are presented in parentheses. [b] Lifetimes shorter than 10 μs were fitted from transient absorption decay data within the first 15 μs.

Table S2. Bi-exponential fits of the transient absorption decay signals at 375 nm, 455 nm, and 745 nm after pulsed 355 nm irradiation of AQN with either 63 mM Selectfluor® II or 1-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate.

Wavelength	**Decay lifetimes[a] (μs)**	
	Selectfluor® II	**1-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate**
375 nm	3.65 ± 0.04 (72%)[b] 128 ± 1 (28%)	2.31 ± 0.03 (65%)[b] 157 ± 2 (35%)
455 nm	**4.67 ± 0.05 (74%)**[b] 86 ± 1 (26%)	**3.47 ± 0.04 (76%)**[b] 140 ± 2 (24%)
745nm	3.50 ± 0.04 (85%)[b] 111 ± 1 (15%)	2.56 ± 0.03 (70)[b] 139 ± 2 (30%)

[a] Relative contributions of the decay components are presented in parentheses. [b] Lifetimes shorter than 10 μs were fitted from transient absorption decay data within the first 15 μs.

Table S3. Bi-exponential fits of the transient absorption decay signals at 375 nm, 455 nm, and 745 nm after pulsed 355 nm irradiation of 165 μM AQN *and* dimethyl adipate with and without 63 mM Selectfluor®.

Wavelength	**Decay lifetimes[a] (μs)**	
	376 mM dimethyl adipate	**376 mM dimethyl adipate and 63 mM Selectfluor**
375 nm	**25.0 ± 0.3 (59%)** 156 ± 2 (41%)	2.74 ± 0.03 (76%)[b] 133 ± 2 (24%)
455 nm	3.17 ± 0.04 (31%)[b] 101 ± 1 (69%)	**3.28 ± 0.04 (81%)[b]** 106 ± 1 (19%)
745nm	3.63 ± 0.04 (63%)[b] 123 ± 1 (37%)	2.66 ± 0.03 (71%)[b] 106 ± 1 (29%)
Wavelength	**Decay lifetimes[a] (μs)**	
	752 mM dimethyl adipate	**752 mM dimethyl adipate and 63 mM Selectfluor**
375 nm	**20.5 ± 0.2 (66%)** 175.8 ± 2 (34%)	21.1 ± 0.2 (59%) 167 ± 2 (41%)
455 nm	5.20 ± 0.06 (53%)[b] 66.0 ± 0.7 (47%)	**2.62 ± 0.03 (54%)[b]** 58.0 ± 0.7 (46%)
745nm	13.0 ± 0.1 (49%)[b] 90 ± 1 (51%)	21.9 ± 0.2 (61%)[b] 177 ± 2 (39%)

[a] Relative contributions of the decay components are presented in parentheses. [b] Lifetimes shorter than 10 μs were fitted from transient absorption decay data within the first 15 μs.

DFT and TD-DFT calculations for the AQN-Selectfluor® exciplex

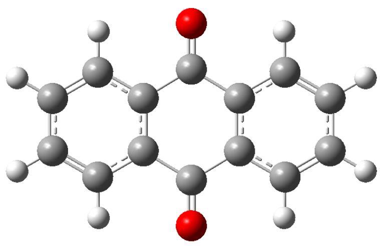
All calculations in this work were performed using the Gaussian 09 D01 package.[1] The WB97XD DFT functional was used in both DFT and TD-DFT calculations, and the 6-311+G(2d) basis set was used.[2-5] The default convergence criteria and ultrafine integration grids were used for the numerical integration in the DFT and TD-DFT calculations. Unrestricted spin DFT calculations were conducted and we found that the spin contamination was negligible in total spin of the compounds during the optimizations. Many reviews in computational chemistry have concluded that WB97XD is the most up-to-date functional to calculate thermochemistry, excited state properties, and UV-Vis spectra.[6,7] We have thus adopted this functional in all our calculations.

Frequency calculations were performed on the optimized geometries in the gas phase to obtain the thermodynamic data. To study the solvent effect, the default solvent model was used in the calculation of energies and frequencies in acetonitrile solutions based on the optimized geometries in the gas phase.

To arrive at the predicted structure of the AQN-Selectfluor® exciplex, we first assessed the polarity and frontier orbital properties of both AQN and Selectfluor® independently. Based on the expectation that Selectfluor® will be most electrophilic at the F atom, whereas AQN is most nucleophilic at the carbonyl motifs, we initially constructed models with bare F atoms, and subsequently Selectfluor® in close proximity with the O and C atoms in AQN. We found that the direct transfer of a F atom from Selectfluor® to AQN with complete N-F bond cleavage has thermally inaccessible kinetic barriers. On the other hand, regardless of the initial geometry, the Selectfluor® would rearrange and converge on a most stable structure with the F atom interacting with only one benzene ring in AQN, with elongated N-F bonds. This structure is illustrated in Figure 8c of the main manuscript.

Table S4. Geometry-optimized XYZ coordinates of AQN (singlet ground state).

AQN (singlet ground state)

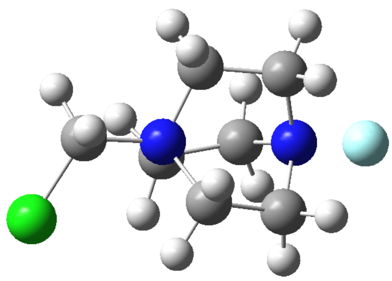


	X	Y	Z
C	-3.67995	0.69539	0.00013
C	-2.48349	1.39043	0.00005
C	-1.27744	0.6983	-0.00003
C	-1.2774	-0.69832	-0.00006
C	-2.48348	-1.3904	-0.00008

C	-3.67994	-0.69536	0.00006
C	0	1.47179	-0.00008
C	0	-1.47182	-0.00006
C	1.2774	-0.69832	-0.00009
C	1.27744	0.69831	0
C	2.48349	1.39043	0.00012
H	2.45924	2.47442	0.00016
C	3.67995	0.69539	0.00018
C	3.67994	-0.69536	0.00002
C	2.48348	-1.3904	-0.00015
H	-4.6199	1.2372	0.00033
H	-2.45924	2.47441	0.00004
H	-2.45927	-2.47439	-0.00016
H	-4.61988	-1.2372	0.00016
H	4.6199	1.23721	0.00042
H	4.61988	-1.2372	0.00006
H	2.45927	-2.47439	-0.00027
O	0	-2.68357	0.00011
O	0	2.68353	-0.00021

Table S5. Geometry-optimized XYZ coordinates of Selectfluor®.

Selectfluor®

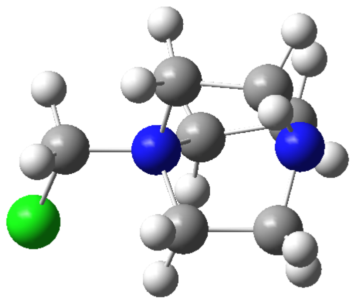


	X	Y	Z
F	-3.18047	-0.54851	-0.00214
C	-1.25832	-0.6585	1.29408
C	-1.19384	-0.89899	-1.15149
C	-1.7514	1.27291	-0.14213
C	0.26716	-0.50129	1.16467
H	-1.55362	-1.69537	1.44921
H	-1.69707	-0.04613	2.08097

C	0.21681	-0.30069	-1.28163
H	-1.80265	-0.71824	-2.03638
H	-1.19649	-1.96619	-0.93336
H	-2.09377	1.52782	-1.14424
H	-2.42662	1.72066	0.58579
C	-0.2814	1.64431	0.1198
H	0.76325	-1.45231	0.98378
H	0.69121	-0.06421	2.06815
H	0.27994	0.42982	-2.08822
H	0.95301	-1.08118	-1.4651
H	0.06299	2.38102	-0.60522
H	-0.1347	2.05256	1.11954
N	-1.85564	-0.21087	-0.00076
N	0.57549	0.40823	0.00026
C	2.03475	0.83945	-0.00068
H	2.19196	1.44022	-0.89496
H	2.19233	1.44211	0.8924
Cl	3.12664	-0.51758	-0.00032

Table S6. Geometry-optimized XYZ coordinates of Selectfluor® •N-radical.

Selectfluor® •*N*-radical

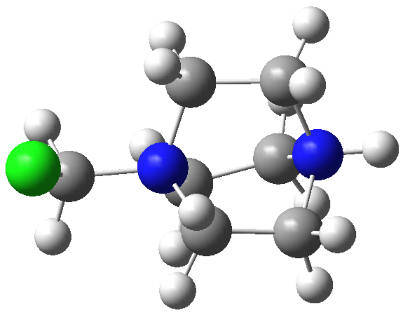


	X	Y	Z
C	-4.11277	7.61995	1.31211
C	-4.03708	5.15498	1.26695
C	-6.19224	6.31267	1.5107
C	-4.19411	7.59955	-0.21559
H	-3.06919	7.60844	1.6392
H	-4.659	8.44248	1.77908
C	-4.28838	5.13295	-0.24152

H	-4.44949	4.2897	1.78944
H	-2.97026	5.28075	1.47661
H	-6.56931	5.36465	1.90005
H	-6.66254	7.13023	2.06078
C	-6.34602	6.45135	-0.00777
H	-3.18614	7.50018	-0.6273
H	-4.69053	8.48788	-0.61332
H	-4.92267	4.29807	-0.55108
H	-3.33054	5.09645	-0.76586
H	-6.95625	5.64322	-0.41819
H	-6.8082	7.4027	-0.28254
N	-4.73385	6.35721	1.81511
N	-4.99252	6.39972	-0.6624
C	-5.20783	6.42092	-2.16657
H	-5.78513	5.52866	-2.41939
H	-5.78332	7.32122	-2.39389
Cl	-3.71053	6.43153	-3.0592

Table S7. Geometry-optimized XYZ coordinates of Selectfluor®-H.

Selectfluor®-H

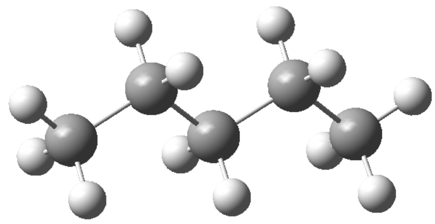


	X	Y	Z
C	-4.11277	7.61995	1.31211
C	-4.03708	5.15498	1.26695
C	-6.19224	6.31267	1.5107
C	-4.19411	7.59955	-0.21559
H	-3.06919	7.60844	1.6392
H	-4.659	8.44248	1.77908
C	-4.28838	5.13295	-0.24152

H	-4.44949	4.2897	1.78944
H	-2.97026	5.28075	1.47661
H	-6.56931	5.36465	1.90005
H	-6.66254	7.13023	2.06078
C	-6.34602	6.45135	-0.00777
H	-3.18614	7.50018	-0.6273
H	-4.69053	8.48788	-0.61332
H	-4.92267	4.29807	-0.55108
H	-3.33054	5.09645	-0.76586
H	-6.95625	5.64322	-0.41819
H	-6.8082	7.4027	-0.28254
N	-4.73385	6.35721	1.81511
N	-4.99252	6.39972	-0.6624
C	-5.20783	6.42092	-2.16657
H	-5.78513	5.52866	-2.41939
H	-5.78332	7.32122	-2.39389
Cl	-3.71053	6.43153	-3.0592
H	-4.62898	6.34432	2.80952

Table S8. Geometry-optimized XYZ coordinates of pentane.

pentane

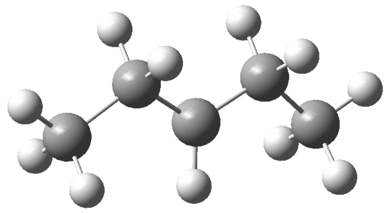


	X	Y	Z
C	-0.23399	1.78824	-0.34365
C	1.27316	1.78824	-0.34365
H	-0.6238	2.8346	-0.34365
H	-0.62752	1.26505	-1.24856
H	-0.62762	1.26494	0.56114
H	1.64723	2.34096	-1.24602
H	1.6473	2.3409	0.55871

C	1.84511	0.35839	-0.34373
H	1.4598	-0.17131	-1.24869
H	1.4597	-0.17147	0.5611
C	3.38484	0.38767	-0.34369
C	3.94203	-1.00528	-0.34376
H	3.72297	0.94867	0.56127
H	3.72303	0.94885	-1.24852
H	5.05887	-0.98449	-0.3438
H	3.60355	-1.56617	0.56117
H	3.60352	-1.56611	-1.24873

Table S9. Geometry-optimized XYZ coordinates of 3-pentyl radical.

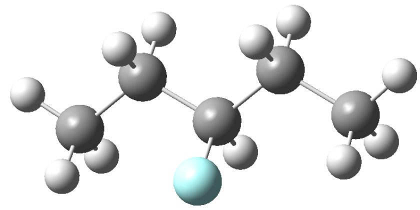
3-pentyl radical



	X	Y	Z
C	-0.23399	1.78824	-0.34365
C	1.27316	1.78824	-0.34365
H	-0.6238	2.8346	-0.34365
H	-0.62752	1.26505	-1.24856
H	-0.62762	1.26494	0.56114
H	1.64723	2.34096	-1.24602
H	1.6473	2.3409	0.55871
C	1.84511	0.35839	-0.34373
H	1.4598	-0.17131	-1.24869
C	3.38484	0.38767	-0.34369
C	3.94203	-1.00528	-0.34376
H	3.72297	0.94867	0.56127
H	3.72303	0.94885	-1.24852
H	5.05887	-0.98449	-0.3438
H	3.60355	-1.56617	0.56117
H	3.60352	-1.56611	-1.24873

Table S10. Geometry-optimized XYZ coordinates of 3-fluoropentane.

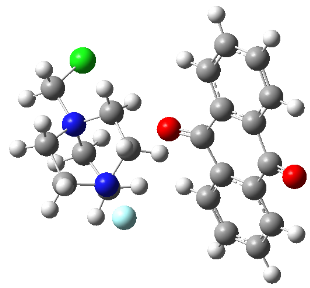
3-fluoropentane



	X	Y	Z
C	-0.23399	1.78824	-0.34365
C	1.27316	1.78824	-0.34365
H	-0.6238	2.8346	-0.34365
H	-0.62752	1.26505	-1.24856
H	-0.62762	1.26494	0.56114
H	1.64723	2.34096	-1.24602
H	1.6473	2.3409	0.55871
C	1.84511	0.35839	-0.34373
H	1.4598	-0.17131	-1.24869
C	3.38484	0.38767	-0.34369
C	3.94203	-1.00528	-0.34376
H	3.72297	0.94867	0.56127
H	3.72303	0.94885	-1.24852
H	5.05887	-0.98449	-0.3438
H	3.60355	-1.56617	0.56117
H	3.60352	-1.56611	-1.24873
F	1.37937	-0.28191	0.7497

Table S11. Geometry-optimized XYZ coordinates of **RC1**.

RC1



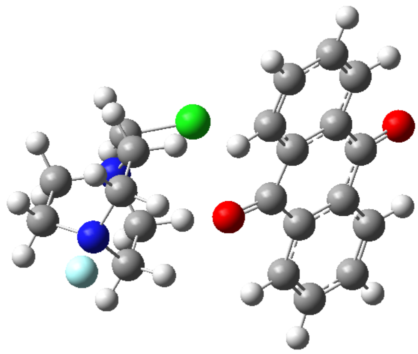
	X	Y	Z
C	-1.40306	3.8216	-0.92742
C	-1.24168	2.55351	-1.46299

C	-1.80594	1.45669	-0.82286
C	-2.53078	1.63949	0.36438
C	-2.66354	2.9094	0.91063
C	-2.10738	3.99832	0.25822
C	-1.60077	0.10398	-1.383
C	-3.14564	0.48784	1.05465
C	-3.28364	-0.78987	0.27433
C	-2.57615	-0.95157	-0.95897
C	-2.82794	-2.04126	-1.73798
H	-2.32947	-2.1599	-2.69225
C	-3.73854	-3.01451	-1.27692
C	-4.39162	-2.88976	-0.02401
C	-4.14606	-1.80234	0.76051
H	-0.98667	4.68023	-1.44026
H	-0.69769	2.4066	-2.38864
H	-3.21587	3.03568	1.83406
H	-2.23379	4.99277	0.66857
H	-3.93369	-3.88921	-1.88755
H	-5.08875	-3.65641	0.29053
H	-4.62497	-1.65892	1.72113
O	-3.54218	0.50393	2.19272
O	-0.71203	-0.16774	-2.15882
F	-0.73277	-0.90849	1.01591
C	1.64346	-1.60918	-0.28847
C	1.47235	0.71634	0.29835
C	1.76502	-0.94052	2.02014
C	3.13575	-1.32074	-0.5765
H	1.04148	-1.48549	-1.1863
H	1.48822	-2.61275	0.101
C	2.9991	0.93657	0.39903
H	0.93057	1.40113	0.94723
H	1.11196	0.84588	-0.71982
H	1.46473	-0.15569	2.71036
H	1.35975	-1.88164	2.3828
C	3.30022	-1.01535	1.85423
H	3.28083	-0.80565	-1.52211

H	3.73981	-2.22632	-0.58139
H	3.28292	1.50402	1.28438
H	3.39868	1.43749	-0.47869
H	3.82276	-0.4584	2.62982
H	3.66879	-2.03995	1.85541
N	1.21083	-0.65077	0.71173
N	3.66678	-0.41457	0.51339
C	5.16558	-0.29341	0.45865
H	5.4696	0.40581	1.23346
H	5.58413	-1.27776	0.65295
Cl	5.75527	0.28303	-1.09229

Table S12. Geometry-optimized XYZ coordinates of **S_1**.

S_1

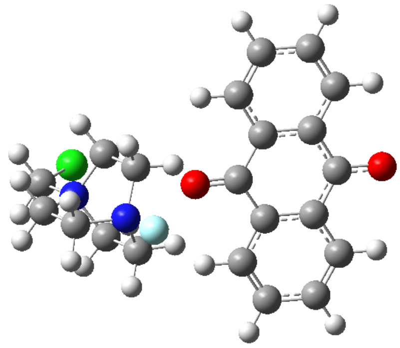


	X	Y	Z
C	2.63299	3.39975	-1.15251
C	1.79869	2.40402	-1.63233
C	1.83499	1.13524	-1.05824
C	2.6992	0.87602	0.01488
C	3.51062	1.88834	0.50669
C	3.48424	3.14261	-0.08429
C	0.93759	0.07652	-1.55479
C	2.7297	-0.46866	0.65547
C	2.05495	-1.58605	-0.07094
C	1.21582	-1.3221	-1.15956
C	0.60466	-2.37579	-1.83761
H	-0.00007	-2.16812	-2.71336
C	0.82769	-3.68036	-1.42904
C	1.64276	-3.93811	-0.33194

C	2.25157	-2.89516	0.34874
H	2.63126	4.37753	-1.61873
H	1.14524	2.58878	-2.47675
H	4.16816	1.67783	1.34144
H	4.13793	3.92391	0.28424
H	0.3845	-4.50281	-1.97778
H	1.81954	-4.96034	-0.01969
H	2.89863	-3.08294	1.19719
O	3.25502	-0.64863	1.72894
O	-0.06152	0.34817	-2.21803
F	-3.84406	0.47601	-2.12658
C	-2.45226	-0.87617	-0.8572
C	-2.35607	1.58289	-0.73485
C	-4.31519	0.37873	0.1342
C	-1.94306	-1.04708	0.58386
H	-1.64018	-0.76049	-1.57726
H	-3.1202	-1.68056	-1.15616
C	-1.55351	1.37974	0.56085
H	-3.00178	2.4582	-0.71205
H	-1.69254	1.61345	-1.59899
H	-4.97359	1.22257	-0.05982
H	-4.87517	-0.5453	0.00847
C	-3.62358	0.48574	1.50424
H	-0.88032	-1.28444	0.58207
H	-2.47788	-1.82903	1.12077
H	-1.58218	2.27124	1.18446
H	-0.51445	1.14023	0.35102
H	-3.746	1.47521	1.94092
H	-4.02802	-0.24947	2.19706
N	-3.24215	0.39119	-0.8979
N	-2.14544	0.23782	1.34791
C	-1.54472	0.14894	2.73996
H	-1.81073	1.0646	3.26347
H	-1.99471	-0.71207	3.22897
Cl	0.19363	-0.03387	2.71993

Table S13. Geometry-optimized XYZ coordinates of $\mathbf{T_1}$.

$\mathbf{T_1}$

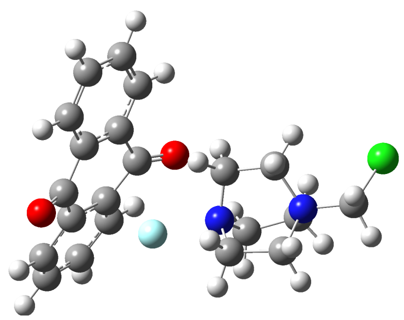


	X	Y	Z
C	0.25484	2.72823	0.3213
C	-0.4498	3.90625	0.35762
C	0.19714	5.14737	0.35525
C	1.61095	5.15117	0.3096
C	2.32432	3.94069	0.27426
C	1.65261	2.74654	0.28089
C	-0.56141	6.38066	0.39869
C	2.2972	6.40077	0.3006
C	1.5944	7.64085	0.32883
C	0.18071	7.6246	0.37504
C	-0.48238	8.85698	0.39794
H	-1.56854	8.85894	0.42698
C	0.20602	10.04484	0.37946
C	1.60384	10.04609	0.33754
C	2.29141	8.86127	0.31197
H	-0.2695	1.77728	0.32287
H	-1.53599	3.89002	0.3847
H	3.41049	3.95966	0.24097
H	2.20707	1.81362	0.25319
H	-0.33112	10.98848	0.39657
H	2.14575	10.98667	0.324
H	3.37772	8.85733	0.27784
O	3.58732	6.40965	0.26482
O	-1.82185	6.37185	0.45859
F	-4.59866	6.33729	3.17515
C	-4.11277	7.61995	1.31211

C	-4.03708	5.15498	1.26695
C	-6.19224	6.31267	1.5107
C	-4.19411	7.59955	-0.21559
H	-3.06919	7.60844	1.6392
H	-4.659	8.44248	1.77908
C	-4.28838	5.13295	-0.24152
H	-4.44949	4.2897	1.78944
H	-2.97026	5.28075	1.47661
H	-6.56931	5.36465	1.90005
H	-6.66254	7.13023	2.06078
C	-6.34602	6.45135	-0.00777
H	-3.18614	7.50018	-0.6273
H	-4.69053	8.48788	-0.61332
H	-4.92267	4.29807	-0.55108
H	-3.33054	5.09645	-0.76586
H	-6.95625	5.64322	-0.41819
H	-6.8082	7.4027	-0.28254
N	-4.73385	6.35721	1.81511
N	-4.99252	6.39972	-0.6624
C	-5.20783	6.42092	-2.16657
H	-5.78513	5.52866	-2.41939
H	-5.78332	7.32122	-2.39389
Cl	-3.71053	6.43153	-3.0592

Table S14. Geometry-optimized XYZ coordinates of AQN-Selectfluor® exciplex (**Int1**).

AQN-Selectfluor® exciplex (Int1).



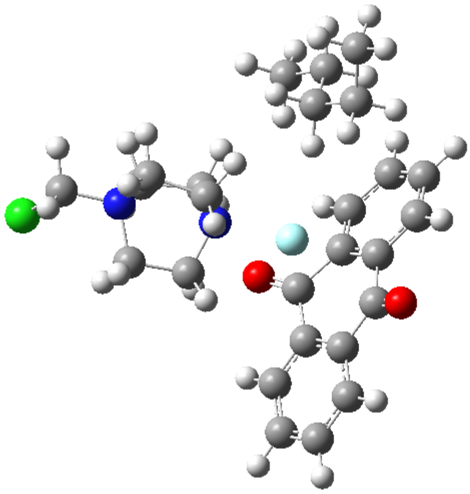
	X	Y	Z
C	-1.60077	0.10398	-1.38300
C	-3.14564	0.48784	1.05465

C	-3.28364	-0.78987	0.27433
C	-2.57615	-0.95157	-0.95897
C	-2.82793	-2.04126	-1.73798
H	-2.32947	-2.15990	-2.69225
C	-3.73854	-3.01451	-1.27692
C	-4.39162	-2.88976	-0.02401
C	-4.14606	-1.80234	0.76051
H	-0.98667	4.68023	-1.44026
H	-0.69769	2.40660	-2.38864
H	-3.21587	3.03568	1.83406
H	-2.23379	4.99277	0.66857
H	-3.93369	-3.99921	-1.88755
H	-5.08875	-3.65641	0.29053
H	-4.62497	-1.65892	1.72113
O	-3.54218	0.50393	2.19272
F	-0.73277	-0.90849	1.01591
C	1.64346	-1.60918	-0.28847
C	1.47235	0.71634	0.29835
C	1.76502	-0.94052	2.02013
C	3.13575	-1.32074	-0.57650
H	1.04148	-1.48549	-1.18630
H	1.48822	-2.61275	0.10100
C	2.99910	0.93657	0.39903
H	0.93057	1.40113	0.94723
H	1.11196	0.84588	-0.71982
H	1.46473	-0.15569	2.71036
H	1.35975	-1.88164	2.38280
C	3.30022	-1.01535	1.85423
H	3.28083	-0.80565	-1.52211
H	3.73981	-2.22632	-0.58139
H	3.28292	1.50402	1.28438
H	3.39868	1.43749	-0.47869
H	3.82276	-0.45840	2.62982
H	3.66879	-2.03995	1.85541
N	1.21083	-0.65077	0.71173
N	3.66678	-0.41457	0.51339

C	5.16558	-0.29341	0.45865
H	5.46960	0.40581	1.23346
H	5.58413	-1.27776	0.65295
Cl	5.75527	0.28303	-1.09229

Table S15. Geometry-optimized XYZ coordinates of **Int2**.

Int2



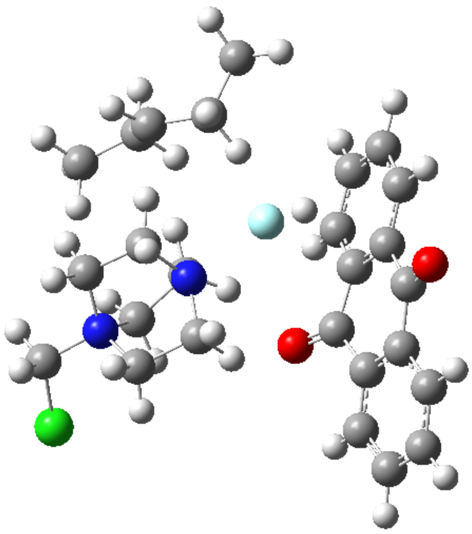
	X	Y	Z
C	-1.40306	3.8216	-0.92742
C	-1.24168	2.55351	-1.46299
C	-1.80594	1.45669	-0.82286
C	-2.53078	1.63949	0.36438
C	-2.66354	2.9094	0.91063
C	-2.10738	3.99832	0.25822
C	-1.60077	0.10398	-1.383
C	-3.14564	0.48784	1.05465
C	-3.28364	-0.78987	0.27433
C	-2.57615	-0.95157	-0.95897
C	-2.82794	-2.04126	-1.73798
H	-2.32947	-2.1599	-2.69225
C	-3.73854	-3.01451	-1.27692
C	-4.39162	-2.88976	-0.02401
C	-4.14606	-1.80234	0.76051
H	-0.98667	4.68023	-1.44026
H	-0.69769	2.4066	-2.38864

H	-3.21587	3.03568	1.83406
H	-2.23379	4.99277	0.66857
H	-3.93369	-3.88921	-1.88755
H	-5.08875	-3.65641	0.29053
H	-4.62497	-1.65892	1.72113
O	-3.54218	0.50393	2.19272
O	-0.71203	-0.16774	-2.15882
F	-0.73277	-0.90849	1.01591
C	1.64346	-1.60918	-0.28847
C	1.47235	0.71634	0.29835
C	1.76502	-0.94052	2.02014
C	3.13575	-1.32074	-0.5765
H	1.04148	-1.48549	-1.1863
H	1.48822	-2.61275	0.101
C	2.9991	0.93657	0.39903
H	0.93057	1.40113	0.94723
H	1.11196	0.84588	-0.71982
H	1.46473	-0.15569	2.71036
H	1.35975	-1.88164	2.3828
C	3.30022	-1.01535	1.85423
H	3.28083	-0.80565	-1.52211
H	3.73981	-2.22632	-0.58139
H	3.28292	1.50402	1.28438
H	3.39868	1.43749	-0.47869
H	3.82276	-0.4584	2.62982
H	3.66879	-2.03995	1.85541
N	1.21083	-0.65077	0.71173
N	3.66678	-0.41457	0.51339
C	5.16558	-0.29341	0.45865
H	5.4696	0.40581	1.23346
H	5.58413	-1.27776	0.65295
Cl	5.75527	0.28303	-1.09229
C	-0.55197	-3.85574	1.54605
C	-0.55197	-3.85574	3.08605
H	-1.48832	-4.23115	3.44272
H	-0.40891	-2.85713	3.44272

C	-0.75787	-5.29299	1.03272
H	0.03542	-5.91619	1.38938
C	-0.75788	-5.29299	-0.50728
H	-0.84753	-6.2978	-0.86395
H	-1.58325	-4.71294	-0.86395
H	0.15714	-4.86822	-0.86395
C	0.58977	-4.75268	3.59938
H	0.86086	-4.45296	4.59013
H	0.26462	-5.77201	3.61152
H	1.43713	-4.65627	2.95317
H	-1.69422	-5.6684	1.38938
H	0.38438	-3.48033	1.18938
H	-1.34526	-3.23254	1.18938

Table S16. Geometry-optimized XYZ coordinates of **Int3**.

Int3



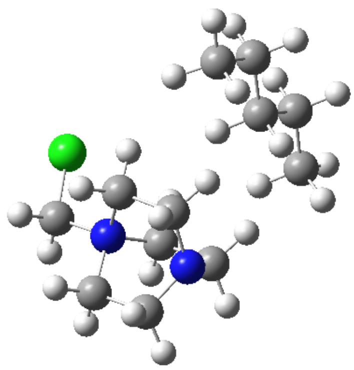
	X	Y	Z
C	-1.45777	-5.02294	0.22667
C	-1.13383	-3.89643	0.96528
C	-1.65302	-2.6592	0.60118
C	-2.49367	-2.55625	-0.51918
C	-2.79112	-3.68582	-1.26887
C	-2.28142	-4.91727	-0.88824
C	-1.28724	-1.46407	1.38327
C	-3.05138	-1.25129	-0.93271

C	-2.96729	-0.12167	0.06013
C	-2.18111	-0.26995	1.25098
C	-2.26666	0.6675	2.24044
H	-1.70281	0.54876	3.15733
C	-3.09015	1.78538	2.04314
C	-3.81455	1.97071	0.83474
C	-3.7308	1.04291	-0.16105
H	-1.07353	-5.99116	0.52377
H	-0.4963	-3.96919	1.83824
H	-3.4304	-3.592	-2.13833
H	-2.53397	-5.80271	-1.45876
H	-3.1673	2.53455	2.82294
H	-4.44305	2.84595	0.72493
H	-4.27578	1.13865	-1.09165
O	-3.57579	-1.04099	-1.9963
O	-0.32193	-1.41079	2.11568
F	-0.74175	-0.06567	-0.93101
C	1.66413	0.66139	0.64655
C	1.72272	-1.4115	-0.58059
C	1.7515	0.68915	-1.75866
C	3.18867	0.47258	0.82465
H	1.11918	0.2234	1.48039
H	1.39009	1.70923	0.55751
C	3.25828	-1.40923	-0.76001
H	1.22995	-1.93769	-1.39469
H	1.42312	-1.86728	0.36087
H	1.51252	0.09861	-2.63965
H	1.2232	1.63664	-1.83021
C	3.2733	0.90151	-1.59087
H	3.42752	-0.27455	1.57654
H	3.6905	1.40164	1.08929
H	3.56086	-1.66221	-1.77528
H	3.75149	-2.08837	-0.06976
H	3.82133	0.6619	-2.50027
H	3.52019	1.9199	-1.29466
N	1.29793	-0.02326	-0.58057

N	3.76627	-0.01146	-0.48735
C	5.27006	0.03621	-0.48879
H	5.61336	-0.37452	-1.43491
H	5.56771	1.07798	-0.39912
Cl	5.9902	-0.87987	0.82533
C	-0.64302	3.35499	-0.34882
C	-1.52301	3.73385	-1.53742
H	-2.575	3.67872	-1.23462
H	-1.40373	2.97823	-2.32031
C	-0.86191	4.18633	0.909
H	-0.66047	5.24014	0.70526
C	-0.00623	3.73122	2.08217
H	-0.20467	4.31236	2.9832
H	-0.17874	2.67659	2.32429
H	1.059	3.8484	1.86101
C	-1.23858	5.1144	-2.11339
H	-1.85063	5.30566	-2.99483
H	-1.44776	5.91042	-1.39751
H	-0.1922	5.21036	-2.41493
H	-1.92358	4.14842	1.18451
H	0.41247	3.4567	-0.64734
H	-1.61552	0.0389	-0.93101

Table S17. Geometry-optimized XYZ coordinates of **Int4**.

Int4



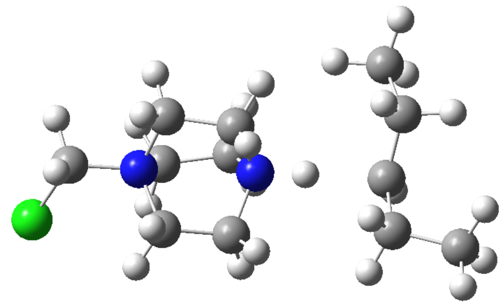
	X	Y	Z
C	1.25575	0.99436	-1.87949
C	1.33144	-1.47062	-1.92466

C	-0.82372	-0.31293	-1.6809
C	1.17441	0.97395	-3.40719
H	2.29932	0.98284	-1.5524
H	0.70952	1.81689	-1.41252
C	1.08014	-1.49265	-3.43312
H	0.91903	-2.33589	-1.40216
H	2.39826	-1.34485	-1.715
H	-1.20079	-1.26094	-1.29156
H	-1.29403	0.50463	-1.13082
C	-0.9775	-0.17424	-3.19938
H	2.18238	0.87459	-3.81891
H	0.67799	1.86228	-3.80493
H	0.44584	-2.32752	-3.74269
H	2.03797	-1.52914	-3.95747
H	-1.58773	-0.98237	-3.6098
H	-1.43968	0.77711	-3.47415
N	0.63466	-0.26839	-1.37649
N	0.376	-0.22588	-3.854
C	0.16069	-0.20468	-5.35817
H	-0.41661	-1.09693	-5.611
H	-0.41481	0.69563	-5.5855
Cl	1.65799	-0.19406	-6.2508
C	5.08225	-0.62435	-3.4896
H	5.43892	-0.11995	-2.61594
C	5.59559	0.10161	-4.747
H	6.66559	0.10329	-4.74602
H	5.24052	-0.40392	-5.62065
C	5.59557	-2.07628	-3.4896
H	6.66557	-2.07629	-3.48997
H	5.23859	-2.58079	-4.36306
C	5.08267	-2.80208	-2.23192
H	5.43741	-3.81156	-2.23308
H	5.44155	-2.29892	-1.35846
H	4.01267	-2.80004	-2.23037
C	5.07998	1.55273	-4.74841
H	5.50034	2.08141	-3.91853

H	5.3683	2.0328	-5.66016
H	4.01304	1.55221	-4.66751
H	4.01225	-0.62433	-3.4896

Table S18. Geometry-optimized XYZ coordinates of **Int5**.

Int5

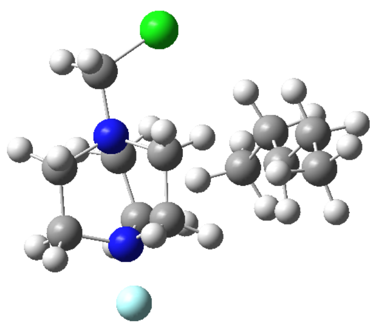


	X	Y	Z
C	-0.77903	1.21477	-0.4512
C	-2.28647	1.21178	-0.23443
H	-0.3125	2.08244	0.08125
H	-0.54424	1.32327	-1.54074
H	-2.58756	2.0785	0.40756
H	-2.81918	1.31777	-1.21371
C	-0.4862	-0.21567	1.5609
H	-0.03649	-1.16258	1.95476
H	-0.01555	0.63595	2.11517
C	-1.99353	-0.21757	1.77843
H	-2.31112	-1.16494	2.28401
H	-2.29045	0.63373	2.44261
C	-2.31372	-1.26444	-0.45365
H	-2.63397	-2.22372	0.02723
H	-2.84756	-1.18575	-1.43488
C	-0.80646	-1.26139	-0.67166
H	-0.35937	-2.21947	-0.30259
H	-0.57285	-1.1803	-1.76383
N	-0.17704	-0.08653	0.07189
N	-2.71143	-0.091	0.43754
C	-4.16637	-0.0936	0.64742

H	-4.45715	-1.0093	1.11842
H	-4.438	0.73107	1.27275
Cl	-4.98326	0.05302	-0.90461
C	3.35637	-0.08023	-0.43792
H	3.56573	0.01033	-1.48332
C	3.95399	-1.39645	0.09315
H	3.73954	-1.48983	1.13727
H	3.52388	-2.22195	-0.43453
C	5.47928	-1.39014	-0.11908
H	5.89441	-2.30497	0.24922
H	5.69373	-1.29598	-1.16313
H	5.90948	-0.56508	0.40923
C	3.98163	1.10835	0.31569
H	3.94857	0.92032	1.36852
H	4.99878	1.23106	0.00706
C	3.19055	2.39092	-0.00181
H	2.74772	2.30583	-0.97215
H	2.42209	2.52642	0.73031
H	3.85221	3.23163	0.01581
H	2.29734	-0.08212	-0.28512

Table S19. Geometry-optimized XYZ coordinates of **Int7**.

Int7

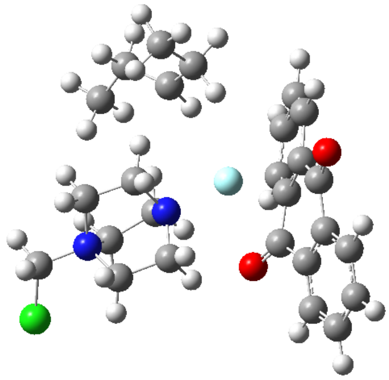


	X	Y	Z
C	1.25575	0.99436	-1.87949
C	1.33144	-1.47062	-1.92466
C	-0.82372	-0.31293	-1.6809
C	1.17441	0.97395	-3.40719
H	2.29932	0.98284	-1.5524

H	0.70952	1.81689	-1.41252
C	1.08014	-1.49265	-3.43312
H	0.91903	-2.33589	-1.40216
H	2.39826	-1.34485	-1.715
H	-1.20079	-1.26094	-1.29156
H	-1.29403	0.50463	-1.13082
C	-0.9775	-0.17424	-3.19938
H	2.18238	0.87459	-3.81891
H	0.67799	1.86228	-3.80493
H	0.44584	-2.32752	-3.74269
H	2.03797	-1.52914	-3.95747
H	-1.58773	-0.98237	-3.6098
H	-1.43968	0.77711	-3.47415
N	0.63466	-0.26839	-1.37649
N	0.376	-0.22588	-3.854
C	0.16069	-0.20468	-5.35817
H	-0.41661	-1.09693	-5.611
H	-0.41481	0.69563	-5.5855
Cl	1.65799	-0.19406	-6.2508
C	3.76209	-0.48522	-2.66367
H	4.11876	0.01918	-1.79002
C	4.27543	0.24074	-3.92107
H	5.34543	0.24242	-3.9201
H	3.92036	-0.26479	-4.79472
C	4.2754	-1.93715	-2.66367
H	5.3454	-1.93717	-2.66405
H	3.91842	-2.44166	-3.53713
C	3.76251	-2.66295	-1.40599
H	4.11725	-3.67243	-1.40716
H	4.12139	-2.15979	-0.53253
H	2.69251	-2.66092	-1.40445
C	3.75982	1.69185	-3.92248
H	4.18018	2.22053	-3.09261
H	4.04814	2.17193	-4.83424
H	2.69288	1.69134	-3.84158
F	0.76986	-0.2883	-0.01645

Table S20. Geometry-optimized XYZ coordinates of **Int9**.

Int9

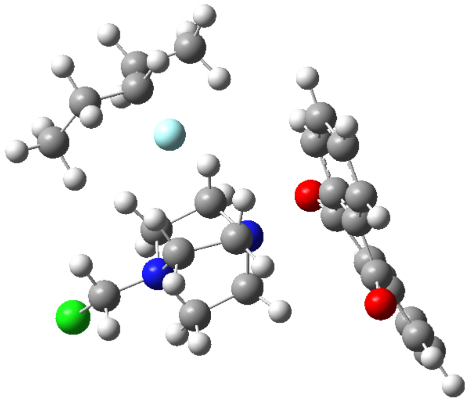


	X	Y	Z
C	-1.40306	3.8216	-0.92742
C	-1.24168	2.55351	-1.46299
C	-1.80594	1.45669	-0.82286
C	-2.53078	1.63949	0.36438
C	-2.66354	2.9094	0.91063
C	-2.10738	3.99832	0.25822
C	-1.60077	0.10398	-1.383
C	-3.14564	0.48784	1.05465
C	-3.28364	-0.78987	0.27433
C	-2.57615	-0.95157	-0.95897
C	-2.82794	-2.04126	-1.73798
H	-2.32947	-2.1599	-2.69225
C	-3.73854	-3.01451	-1.27692
C	-4.39162	-2.88976	-0.02401
C	-4.14606	-1.80234	0.76051
H	-0.98667	4.68023	-1.44026
H	-0.69769	2.4066	-2.38864
H	-3.21587	3.03568	1.83406
H	-2.23379	4.99277	0.66857
H	-3.93369	-3.88921	-1.88755
H	-5.08875	-3.65641	0.29053
H	-4.62497	-1.65892	1.72113
O	-3.54218	0.50393	2.19272
O	-0.71203	-0.16774	-2.15882
F	-0.73277	-0.90849	1.01591
C	1.64346	-1.60918	-0.28847

C	1.47235	0.71634	0.29835
C	1.76502	-0.94052	2.02014
C	3.13575	-1.32074	-0.5765
H	1.04148	-1.48549	-1.1863
H	1.48822	-2.61275	0.101
C	2.9991	0.93657	0.39903
H	0.93057	1.40113	0.94723
H	1.11196	0.84588	-0.71982
H	1.46473	-0.15569	2.71036
H	1.35975	-1.88164	2.3828
C	3.30022	-1.01535	1.85423
H	3.28083	-0.80565	-1.52211
H	3.73981	-2.22632	-0.58139
H	3.28292	1.50402	1.28438
H	3.39868	1.43749	-0.47869
H	3.82276	-0.4584	2.62982
H	3.66879	-2.03995	1.85541
N	1.21083	-0.65077	0.71173
N	3.66678	-0.41457	0.51339
C	5.16558	-0.29341	0.45865
H	5.4696	0.40581	1.23346
H	5.58413	-1.27776	0.65295
Cl	5.75527	0.28303	-1.09229
C	-0.55197	-3.85574	1.54605
H	-1.55844	-4.0215	1.86922
C	-0.55197	-3.85574	3.08605
H	-1.48832	-4.23115	3.44272
H	-0.40891	-2.85713	3.44272
C	-0.75787	-5.29299	1.03272
H	0.03542	-5.91619	1.38938
C	-0.75788	-5.29299	-0.50728
H	-0.84753	-6.2978	-0.86395
H	-1.58325	-4.71294	-0.86395
H	0.15714	-4.86822	-0.86395
C	0.58977	-4.75268	3.59938
H	0.86086	-4.45296	4.59013

H	0.26462	-5.77201	3.61152
H	1.43713	-4.65627	2.95317
H	-1.69422	-5.6684	1.38938

Table S21. Geometry-optimized XYZ coordinates of **Int10**.

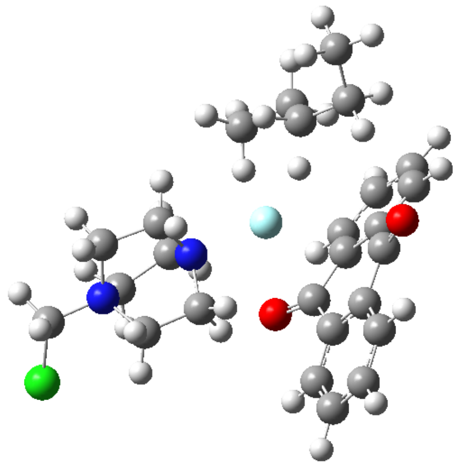
Int10			
	X	Y	Z
C	0.98684	-4.94512	0.03806
C	0.92542	-3.8481	-0.80676
C	1.58244	-2.6732	-0.46164
C	2.29923	-2.6034	0.74238
C	2.33208	-3.69711	1.5976
C	1.68368	-4.86821	1.23871
C	1.4841	-1.49744	-1.35248
C	3.01157	-1.36692	1.12258
C	3.24737	-0.34768	0.04275
C	2.54578	-0.45102	-1.20015
C	2.87963	0.37825	-2.229
H	2.38503	0.28808	-3.18838
C	3.87032	1.36014	-2.02064
C	4.52086	1.50852	-0.76898
C	4.19345	0.68234	0.26468
H	0.49766	-5.86993	-0.24309
H	0.38799	-3.90001	-1.74633
H	2.87948	-3.62658	2.52986
H	1.73162	-5.73096	1.89189
H	4.13148	2.03014	-2.8324

H	5.28076	2.27112	-0.65215
H	4.66657	0.75185	1.2363
O	3.41441	-1.12258	2.23195
O	0.61446	-1.36278	-2.18385
C	-1.60058	0.69613	-0.77715
C	-1.61546	-1.40698	0.38837
C	-1.7582	0.65422	1.62389
C	-3.11366	0.4653	-1.00157
H	-1.0178	0.29791	-1.60513
H	-1.36079	1.75004	-0.65587
C	-3.15426	-1.46959	0.52169
H	-1.12636	-1.94394	1.19828
H	-1.27489	-1.82213	-0.55767
H	-1.51762	0.05106	2.49617
H	-1.27454	1.62085	1.7386
C	-3.28341	0.80807	1.42381
H	-3.30779	-0.26164	-1.78542
H	-3.64172	1.38516	-1.24649
H	-3.47653	-1.76602	1.51902
H	-3.60033	-2.14485	-0.20359
H	-3.84359	0.51294	2.30917
H	-3.56699	1.82505	1.1574
N	-1.23986	-0.0054	0.441
N	-3.70838	-0.08485	0.27697
C	-5.21245	-0.09419	0.23505
H	-5.56649	-0.54423	1.15905
H	-5.54761	0.93762	0.16494
Cl	-5.85946	-0.99949	-1.12408
C	0.78546	3.15267	0.44949
C	0.79758	3.54774	1.9379
H	1.76426	3.92496	2.19893
H	0.57621	2.68903	2.53666
C	1.10408	4.38856	-0.41228
H	0.3672	5.14454	-0.23791
C	1.09197	3.99349	-1.90069
H	1.26062	4.8625	-2.50175

H	1.86434	3.27648	-2.08568
H	0.14252	3.567	-2.14878
C	-0.26298	4.63578	2.18886
H	-0.54984	4.62324	3.21961
H	0.14447	5.59431	1.94368
H	-1.12043	4.44578	1.57766
H	2.07076	4.76579	-0.15124
H	1.52234	2.39669	0.27512
F	-0.43417	2.67672	0.12015

Table S22. Geometry-optimized XYZ coordinates of **TS1**.

TS1



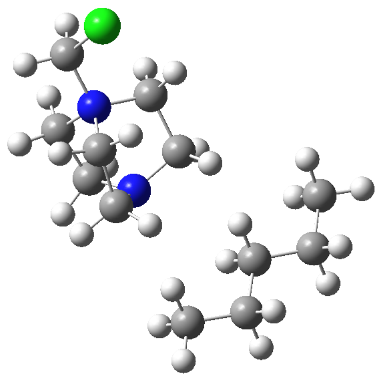
	X	Y	Z
C	-0.7567	4.50922	-0.14605
C	-0.46727	3.51545	0.77432
C	0.52493	2.58203	0.49499
C	1.23066	2.65423	-0.71373
C	0.91245	3.63391	-1.64587
C	-0.07648	4.56113	-1.3582
C	0.79106	1.49054	1.4586
C	2.33548	1.7103	-1.00041
C	2.90777	0.96932	0.17527
C	2.1424	0.84666	1.38311
C	2.67216	0.20054	2.47126
H	2.09426	0.10626	3.38193
C	3.96857	-0.30362	2.38583
C	4.73802	-0.16109	1.19449

C	4.20126	0.45572	0.09477
H	-1.50768	5.25564	0.08351
H	-0.99129	3.46537	1.72182
H	1.46029	3.67335	-2.57975
H	-0.30585	5.3419	-2.07328
H	4.41391	-0.79726	3.24196
H	5.7492	-0.54941	1.17281
H	4.75497	0.56563	-0.82882
O	2.81538	1.5459	-2.09305
O	-0.01317	1.13598	2.29116
F	0.62981	-0.55897	-0.36972
C	-1.74671	-1.301	0.82084
C	-2.14183	0.73504	-0.38253
C	-1.71511	-1.30424	-1.5782
C	-3.2847	-1.41679	0.92576
H	-1.33524	-0.78623	1.68701
H	-1.26802	-2.27461	0.74252
C	-3.63871	0.44766	-0.64136
H	-1.73002	1.38051	-1.15667
H	-1.99065	1.21586	0.58092
H	-1.55177	-0.66993	-2.44698
H	-1.02195	-2.13978	-1.63607
C	-3.17668	-1.80119	-1.49553
H	-3.70092	-0.74772	1.67396
H	-3.61142	-2.43041	1.15181
H	-3.9344	0.65708	-1.66864
H	-4.28467	1.00912	0.02842
H	-3.71645	-1.64602	-2.42806
H	-3.24341	-2.85465	-1.22804
N	-1.444	-0.53818	-0.377
N	-3.88438	-1.02383	-0.40706
C	-5.34885	-1.35616	-0.48213
H	-5.72035	-1.00328	-1.44082
H	-5.44704	-2.43665	-0.41358
Cl	-6.29214	-0.61452	0.80122
C	2.32083	-2.38158	-0.6748

C	3.46066	-2.25803	-1.66943
H	4.35103	-1.86937	-1.16634
H	3.20054	-1.52675	-2.44009
C	2.67824	-2.92972	0.68123
H	3.23666	-3.86773	0.5688
C	1.49181	-3.12569	1.60876
H	1.79718	-3.51084	2.5822
H	0.96225	-2.18262	1.76934
H	0.78225	-3.84269	1.187
C	3.81156	-3.58654	-2.33799
H	4.63558	-3.46088	-3.04043
H	4.11305	-4.34081	-1.60875
H	2.96199	-3.98578	-2.89578
H	3.41506	-2.26198	1.16562
H	1.50378	-2.97631	-1.11081
H	1.74716	-1.38646	-0.53335

Table S23. Geometry-optimized XYZ coordinates of **TS2**.

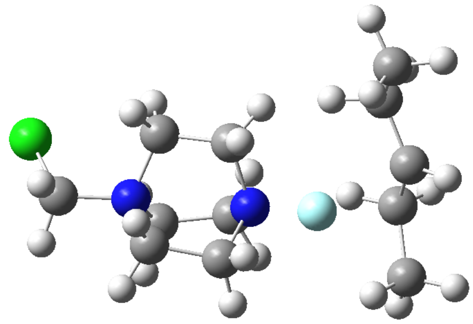
TS2



	X	Y	Z
C	0.02549	-1.4198	0.42843
C	-0.01042	0.13113	-1.44069
C	-1.13602	-2.01279	-1.61491
C	-1.15576	-0.56671	0.99905
H	0.98247	-1.04001	0.78779
H	-0.06981	-2.47447	0.67584
C	-1.42065	0.71082	-1.08681
H	0.1665	0.17562	-2.51445

H	0.79262	0.64436	-0.9168
H	-1.16898	-1.80822	-2.68237
H	-0.97789	-3.0774	-1.44896
C	-2.42778	-1.52136	-0.87804
H	-0.80389	0.37146	1.41916
H	-1.69741	-1.11973	1.76413
H	-2.05244	0.80959	-1.9678
H	-1.32374	1.67964	-0.60314
H	-3.2232	-1.32274	-1.59381
H	-2.77689	-2.25119	-0.15004
N	-0.08624	-1.23874	-0.99642
N	-2.1037	-0.24429	-0.13574
C	-3.4107	0.34005	0.38128
H	-4.01502	0.59784	-0.48549
H	-3.89972	-0.4333	0.96948
Cl	-3.16534	1.76293	1.36894
C	3.20101	0.29069	0.19544
H	2.85047	-0.47969	-0.51389
C	4.04741	-0.37854	1.27061
H	4.93679	-0.81069	0.80505
H	4.41242	0.3828	1.96446
C	3.9154	1.38804	-0.5827
H	4.80748	0.96677	-1.05306
H	4.27555	2.1463	0.11701
C	3.04336	2.04383	-1.64262
H	3.58198	2.82273	-2.18124
H	2.70785	1.31813	-2.39206
H	2.16345	2.52554	-1.19831
C	3.30161	-1.45709	2.04151
H	2.96261	-2.26345	1.38108
H	3.93259	-1.92057	2.79918
H	2.4342	-1.04521	2.57251
H	2.3046	0.72764	0.67557

Table S24. Geometry-optimized XYZ coordinates of **TS3**.

TS3			
	X	Y	Z
C	-0.22021	1.04897	1.02801
C	0.07326	-0.78983	-0.56444
C	-0.4918	-1.27094	1.77458
C	-1.62951	1.13967	0.41893
H	0.49447	1.68968	0.51244
H	-0.19166	1.27166	2.09279
C	-1.43178	-0.97885	-0.80469
H	0.63605	-1.71234	-0.69691
H	0.52159	-0.01693	-1.18602
H	-0.20696	-2.28965	1.51961
H	-0.1647	-1.05453	2.78945
C	-1.99214	-0.98785	1.57903
H	-1.61994	1.59529	-0.56765
H	-2.29382	1.71932	1.05713
H	-1.7278	-2.02614	-0.7654
H	-1.72449	-0.57162	-1.76945
H	-2.55739	-1.91746	1.54855
H	-2.39677	-0.36384	2.37418
N	0.23752	-0.35804	0.8536
N	-2.1956	-0.25345	0.27543
C	-3.68513	-0.22669	-0.02498
H	-4.00209	-1.2563	-0.17588
H	-4.18138	0.20113	0.84351
Cl	-4.06614	0.71854	-1.44615
C	3.74831	0.2976	-0.37985
H	4.45131	0.15523	0.43612
C	3.19339	1.65696	-0.60481

H	3.73195	2.14884	-1.42859
H	2.16312	1.57695	-1.00635
C	3.65678	-0.75677	-1.42272
H	4.45138	-0.60111	-2.16799
H	2.73075	-0.63194	-2.00508
C	3.76741	-2.18182	-0.88958
H	3.72219	-2.91398	-1.69598
H	4.71252	-2.33192	-0.36652
H	2.97274	-2.41629	-0.17269
C	3.22349	2.56481	0.6184
H	4.24949	2.74305	0.94109
H	2.77994	3.53961	0.41042
H	2.70432	2.12136	1.47435
F	1.58929	-0.40939	1.14653

Table S25. Oscillator strengths for the TD-DFT-calculated absorption spectra of the AQN-Selectfluor® exciplex.

Wavelength (nm)	Oscillator strength
492.61	0.0282
479.36	0.0078
432.67	0.083
422.59	0.0075
416.22	0.0012
413.25	0.0062
396.37	0.0031
382.93	0.0246
379.75	0.0032
361.27	0.0037
342.08	0.0022
332.59	0.0013
320.65	0.0017
311.51	0.0026
299.58	0.0362
298.82	0.021
296.1	0.0493

292.86	0.0049
286.12	0.056
282.8	0.0014
280.67	0.0855
276.46	0.04
273.18	0.0585
267.92	0.1016
263.53	0.0125
261.21	0.0223
257.32	0.0382
255.53	0.0011
253.47	0.0033
243.9	0.0654
239.97	0.0582
234.89	0.0451
233.71	0.0048
232.07	0.005
229.97	0.0197
227.77	0.1167
225.07	0.009
221.76	0.0172
221.27	0.0064
220.08	0.1802
217.22	0.0076
214.87	0.0093
214.6	0.0694
212.97	0.0117
212.18	0.0311
211.14	0.003
208.61	0.0652
207.58	0.0126
206.88	0.0204
205.3	6.00E-04
204.75	3.00E-04
203.69	0.0025
203.06	0.0109

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