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Lewis acidic stiborafluorenes for the fluorescence turn-on sensing of fluoride in drinking water at ppm concentrations

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SUPPORTING INFORMATION

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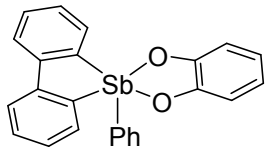
Table S6. XYZ coordinate of the optimized structure of **3**.

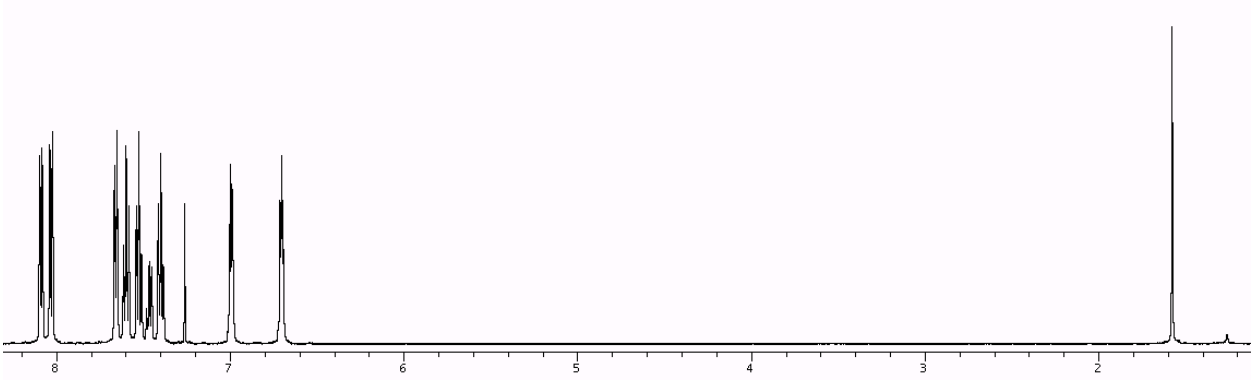
Table S7. XYZ coordinate of the optimized structure of [**3**-F]$^-$.

Table S8. TD-DFT calculation output showing the nature of the low energy excitation for **3** in CH_2Cl_2.

Table S9. TD-DFT calculation output showing the nature of the low energy excitation for [**3**-F]$^-$ in CH_2Cl_2.



^{1}H NMR



^{13}C{^{1}H} NMR

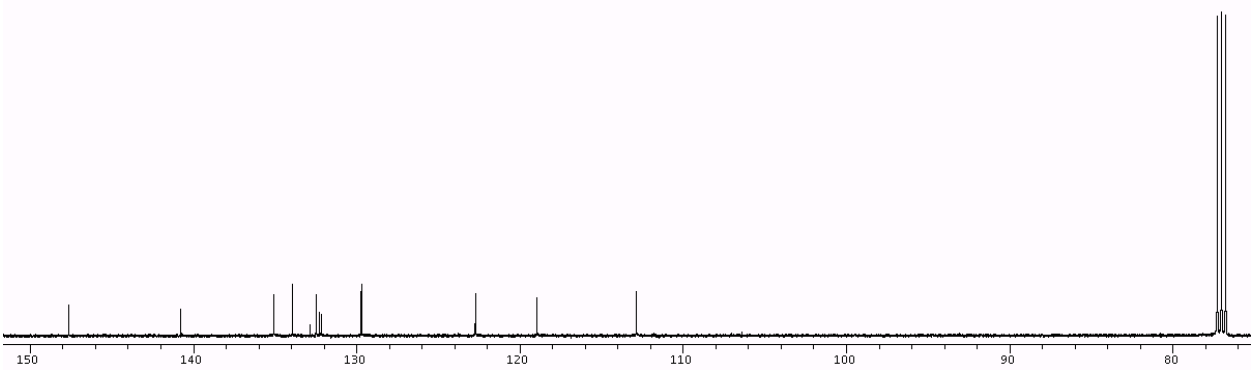
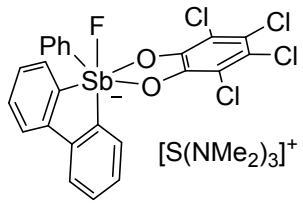
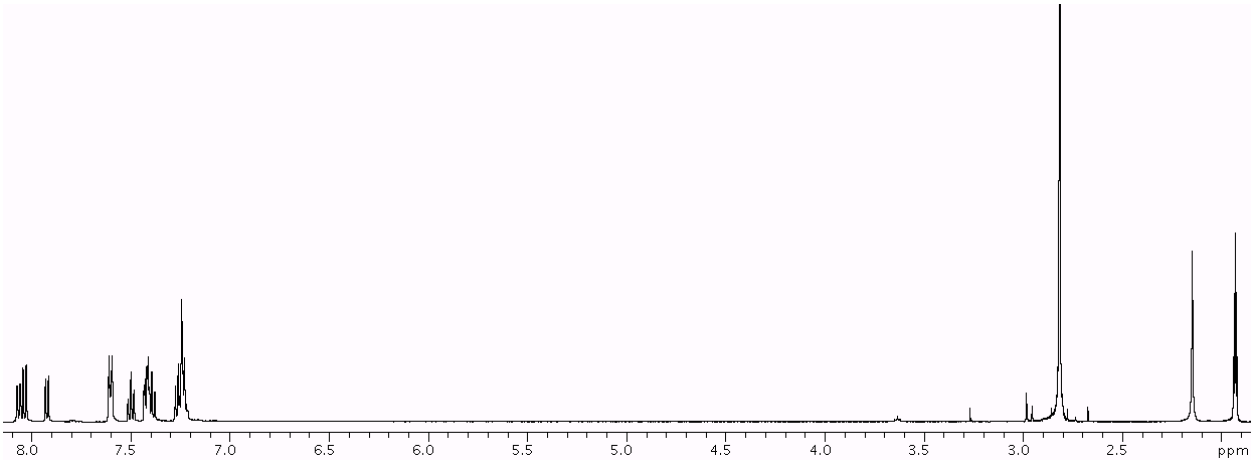


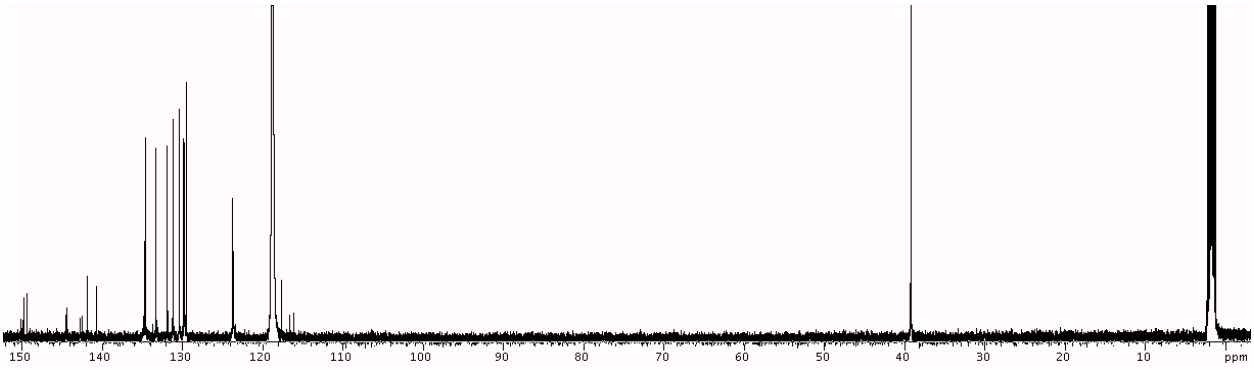
Figure S1. ^{1}H and ^{13}C NMR spectra of **1** in $CDCl_3$.



^{1}H NMR



^{13}C{^{1}H} NMR



^{19}F NMR

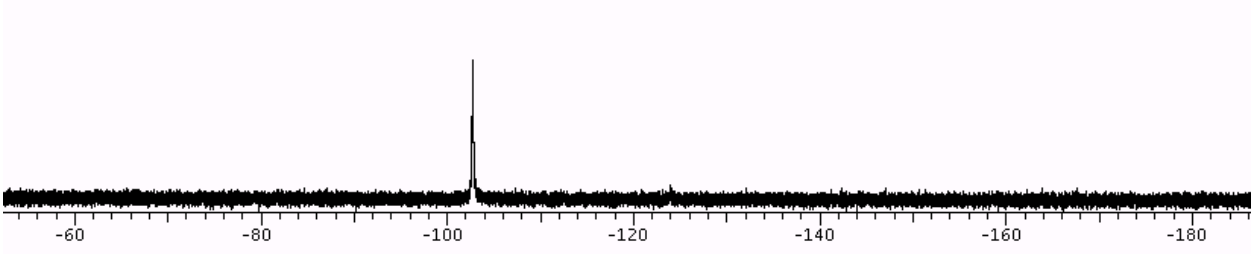
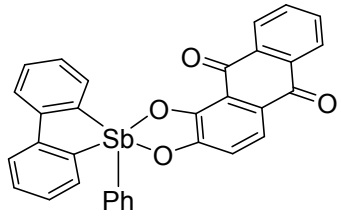
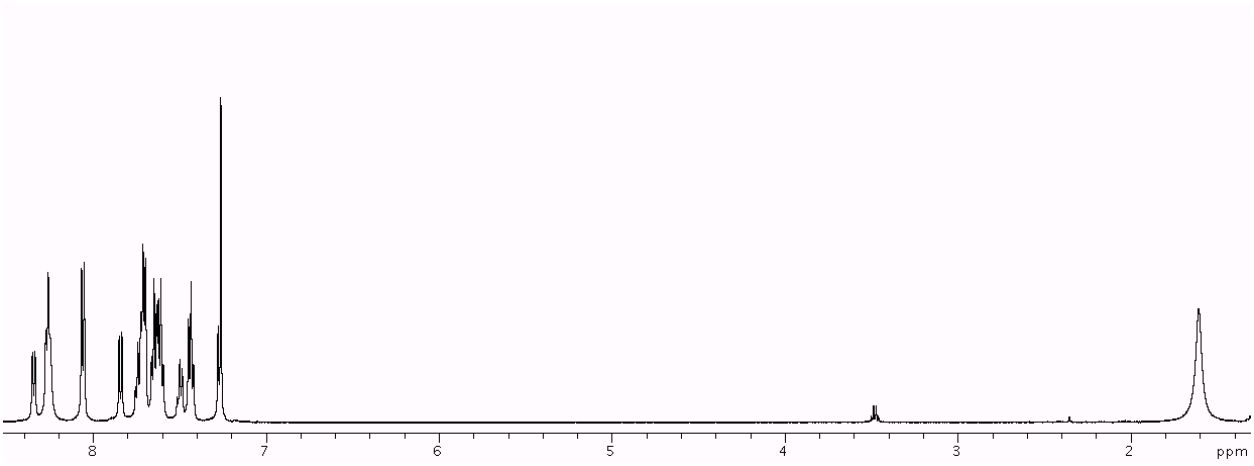


Figure S2. ^{1}H, ^{13}C, and ^{19}F NMR spectra of TAS[**2**-F] in CD_3CN.



^{1}H NMR



^{13}C{^{1}H} NMR

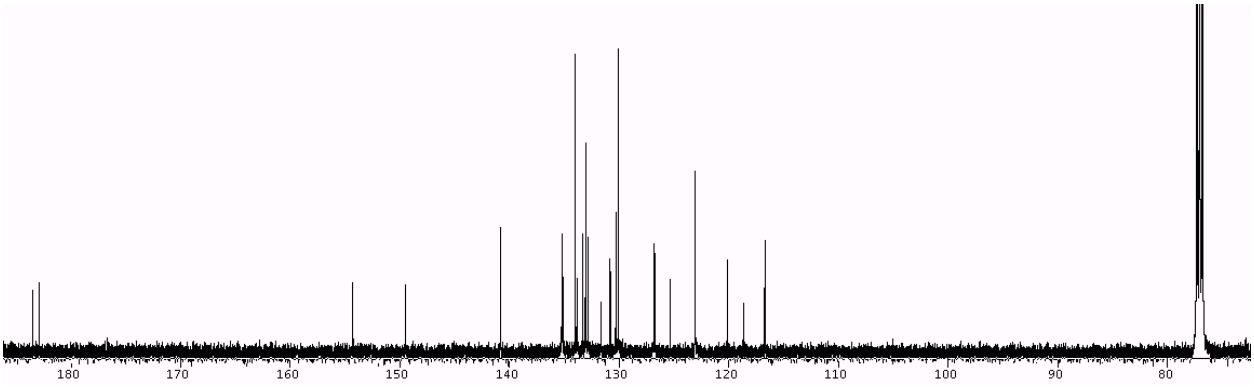
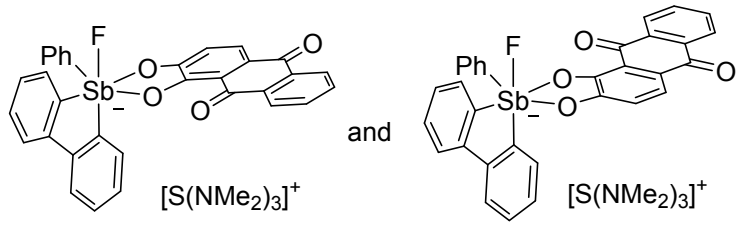
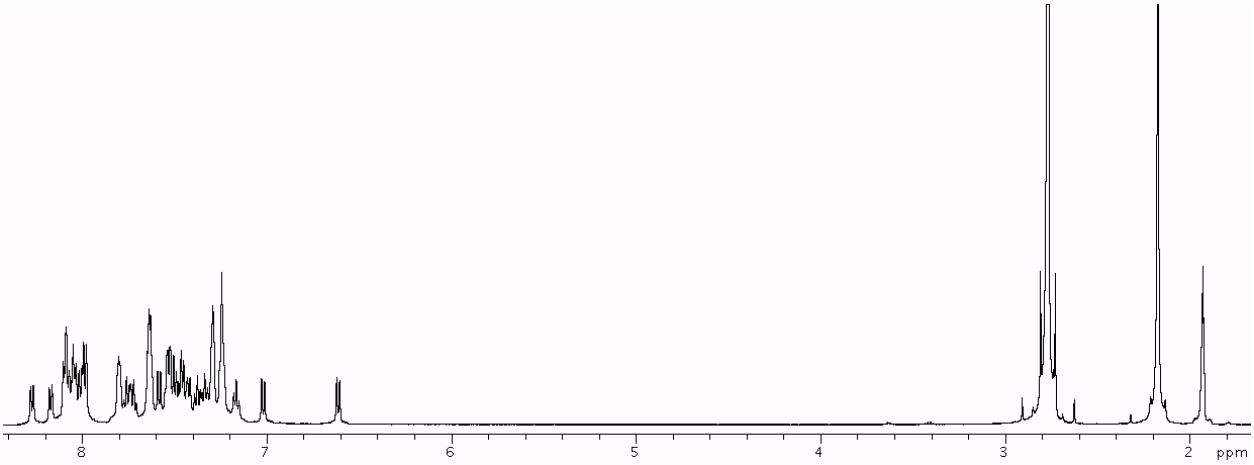
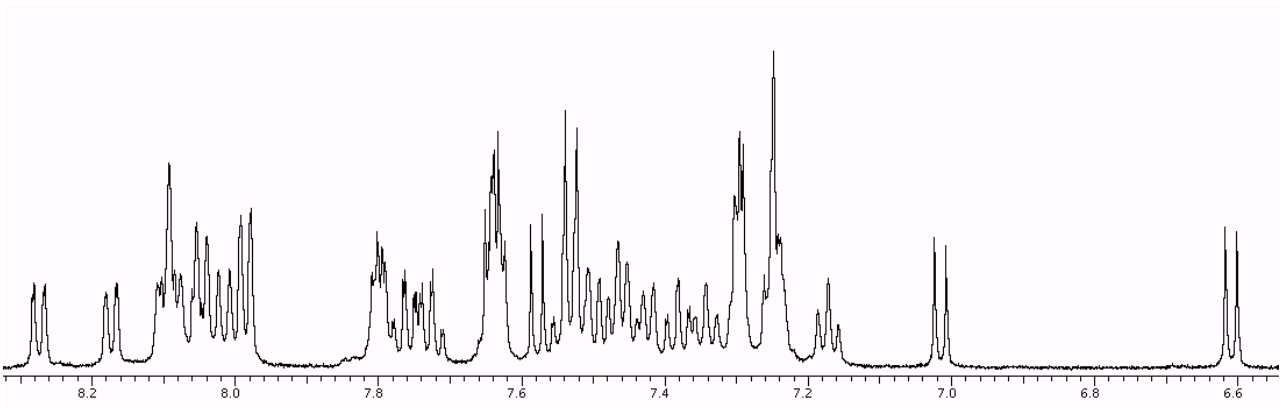


Figure S3. ^{1}H and ^{13}C NMR spectra of **3** in $CDCl_3$.

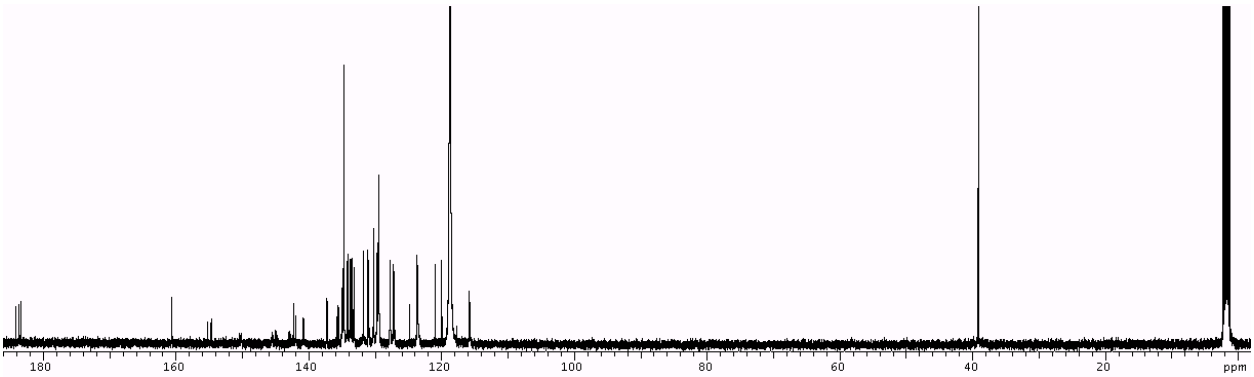


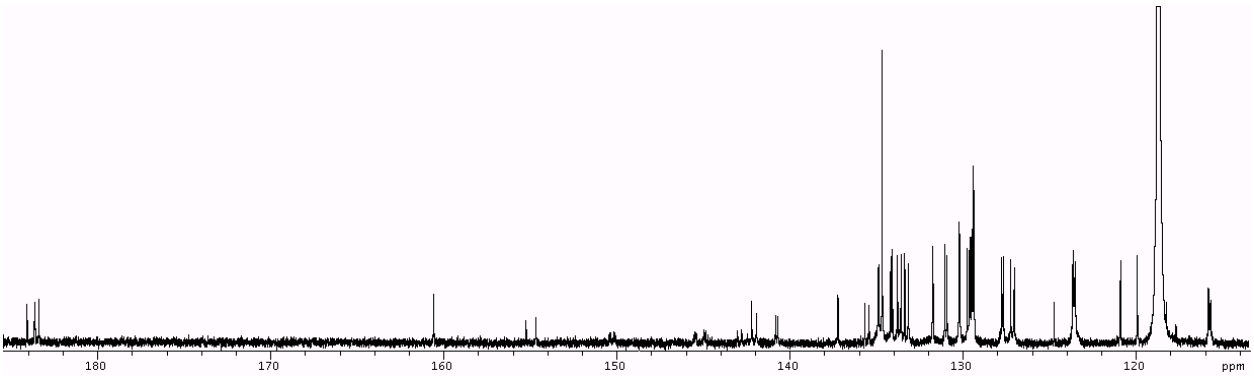
^{1}H NMR





^{13}C{^{1}H} NMR





^{19}F NMR

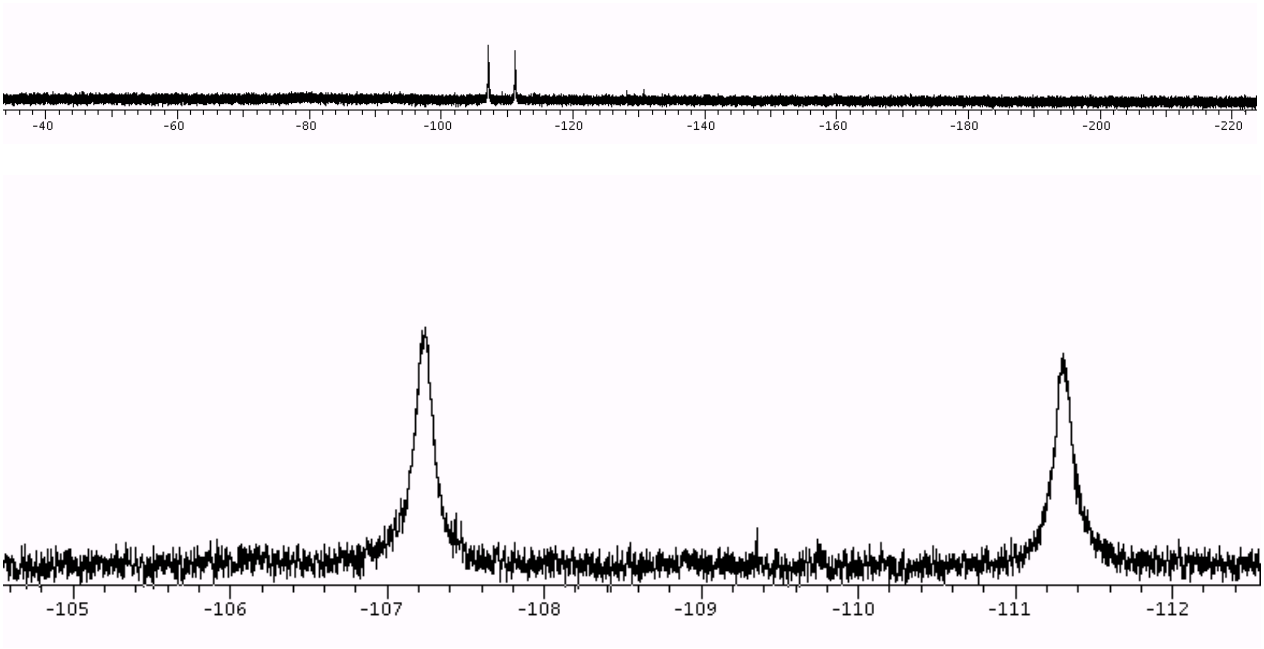


Figure S4. ^{1}H, ^{13}C, and ^{19}F NMR spectra of TAS[**3**-F] in CD_3CN.

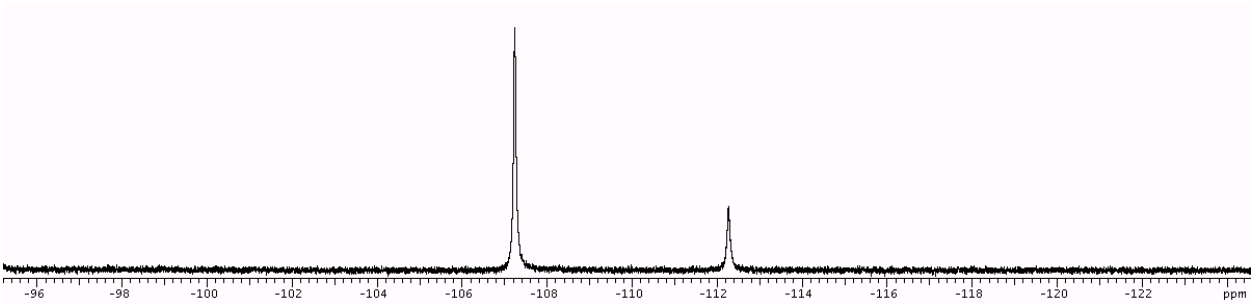


Figure S5. ^{19}F NMR of **3** in CH_2Cl_2 obtained after biphasic mixing with an aqueous fluoride solution (3.8 ppm) containing TPABr (20 mM) and a citrate buffer (10 mM, pH 4.68).

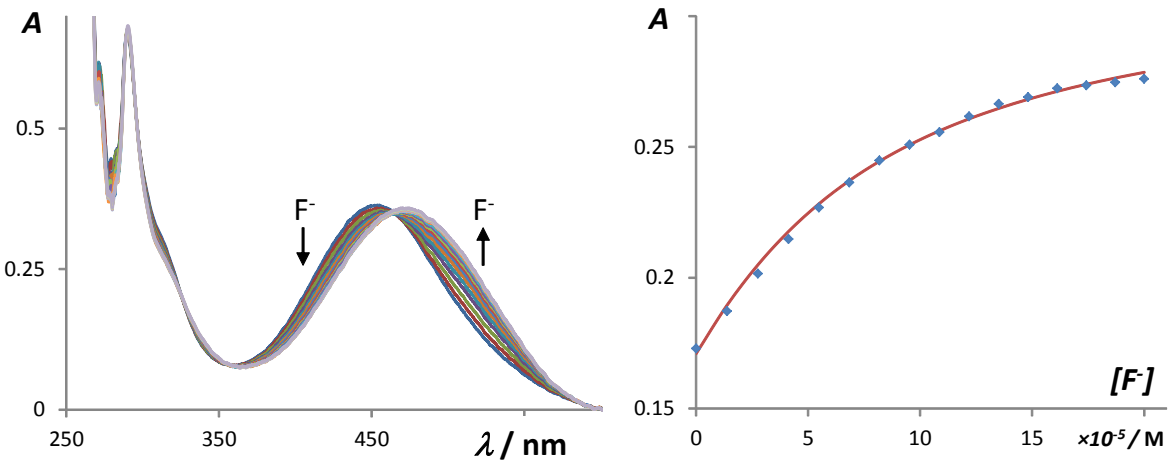


Figure S6. (left) Spectral changes in the UV-Vis absorption spectrum of **3** (3.8×10^{-5} M in 7/3 vol. THF/water) upon addition of fluoride. (right) The experimental and the calculated 1:1 fluoride binding isotherms for **3** at 510 nm. The data were fitted with K = 16100 M^{-1} (ε(**3**) = 4500 $M^{-1}cm^{-1}$ and ε([**3**-F]$^-$ = 8350 $M^{-1}cm^{-1}$)).

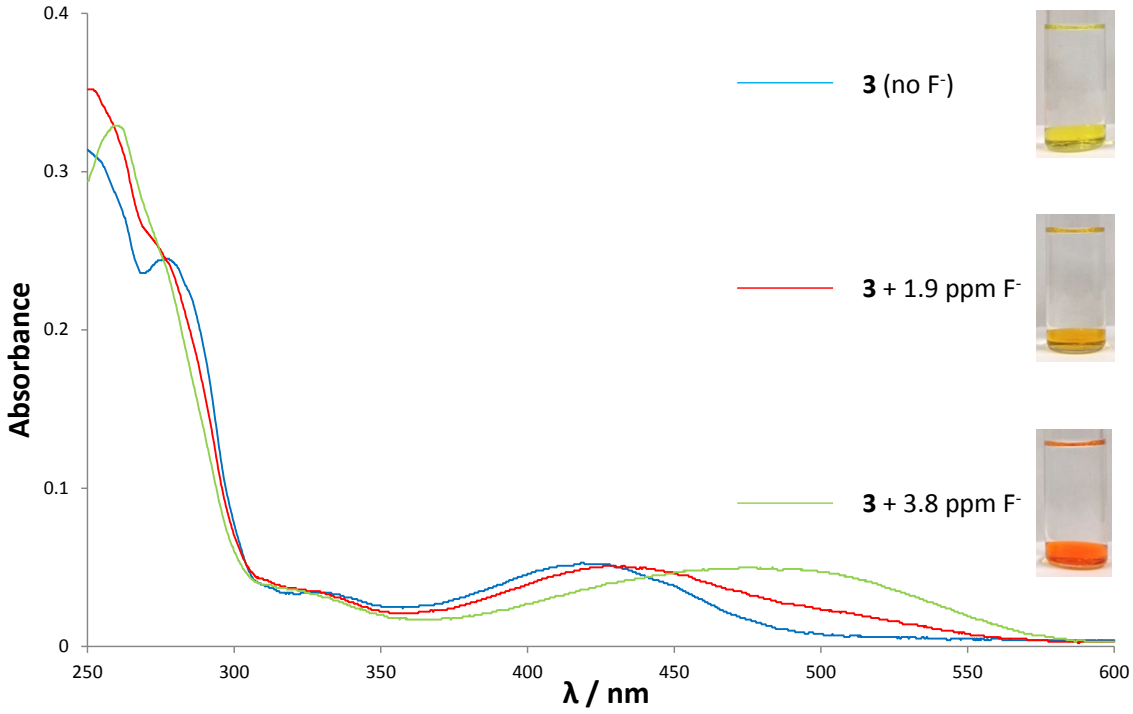


Figure S7. UV-Vis absorption spectra of solutions of **3** (5×10^{-6} M) in CH_2Cl_2. For each measurement, the solution was prepared by the 100-fold dilution of a 5×10^{-4} M solution of **3** which had been layered with an aqueous solution of KF (0, 1.9 and 3.8 ppm) containing TPABr (20 mM) and a citrate buffer (10 mM, pH 4.68).

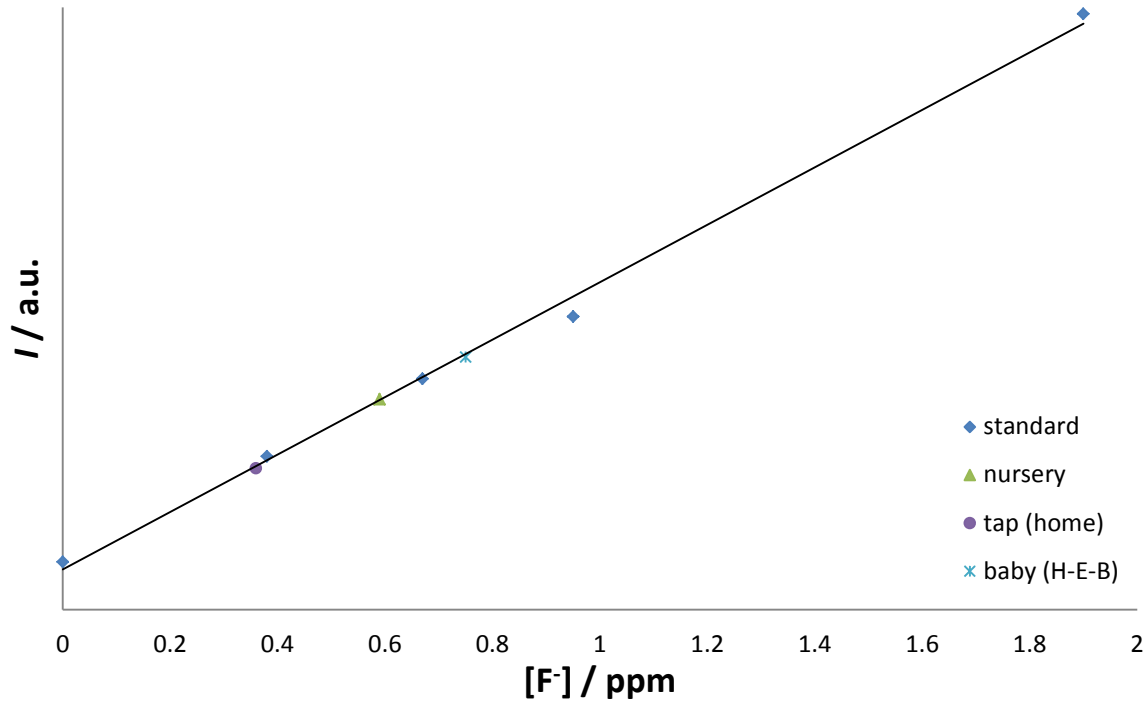


Figure S8. Drinking water analysis. Fluorescence intensity of a solution of **3** in CH_2Cl_2 (1 mL, 5.0×10^{-5} M) measured at 610 nm ($\lambda_{excitation}$ = 482 nm). For each measurement, a 5 mm NMR tube was filled with a solution of **3** in CH_2Cl_2 (1.0 mL, 5.0×10^{-5} M) and layered with an aqueous solution containing TPABr (20 mM) and a citrate buffer (10 mM, pH 4.6). To obtain a calibration curve, the aqueous layer was doped with different amounts of fluoride (0, 0.4, 0.7, 1.0, 1.9 ppm). After vigorous shaking (1 min), the tube was inserted into the cavity of the fluorometer such that only the CH_2Cl_2 layer was position in the optical path. The plot shows that the fluorescence intensity increases linearly with the fluoride concentration in the 0 – 1.9 ppm range. Drinking water samples (Nursery® Water, H-E-B® Baby Purified Water, and tap water of College Station) where combined with TPABr (20 mM) and buffered with citrate (10 mM, pH 4.6). The resulting solutions were transferred into a 5 mm NMR tube filled with a solution of **3** in CH_2Cl_2 (1.0 mL, 5.0×10^{-5} M). The fluorescence intensity was measured as described above for the standard.

Table S1. Crystal data, data collection, and structure refinement for **1**.

Empirical formula	C24 H17 O2 Sb
Formula weight	459.14
Temperature	110(2) K
Wavelength	0.71073
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 9.8268(8) Å α = 90.00 b = 14.9773(12) Å β = 111.2550(10) c = 13.5372(11) Å γ = 90.00
Volume	1856.9(3) $Å^3$
Z	4
Density (calculated)	1.642 Mg/m^3
Absorption coefficient	1.502
F(000)	912
Crystal size	0.55 × 0.38 × 0.34 mm^3
Theta range from data collection	2.61 to 29.63°
Index ranges	-13<=h<=13 -20<=k<=20 -18<=l<=18
Reflections collected	23397
Independent reflections	4996 [R(int) = 0.0265]
Completeness to theta = 29.67°	95.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.3617 and 0.6292
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4996 / 0 / 244
Goodness-of-fit on F^2	1.128
Final R indices [I>2sigma(I)]	R1 = 0.0200, wR2 = 0.0482
R indices (all data)	R1 = 0.0223, wR2 = 0.0490
Largest diff. peak and hole	0.453 and -0.638 e. $Å^{-3}$

Table S2. Crystal data, data collection, and structure refinement for TAS[**2**-F].

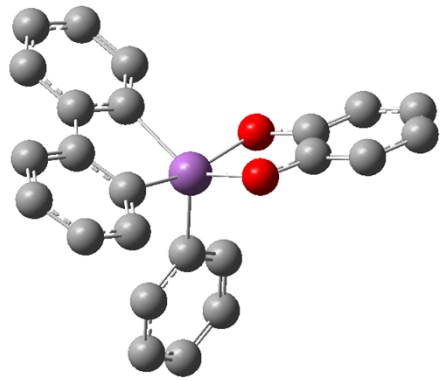
Empirical formula	C30 H31 Cl4 F N3 O2 S Sb
Formula weight	780.19
Temperature	110(2) K
Wavelength	0.71073
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 10.011(8) Å α = 90.00°
	b = 21.4018(18) Å β = 122.404(3)°
	c = 16.9437(11) Å γ = 90.00°
Volume	3061.9(4) Å^3
Z	4
Density (calculated)	1.692 Mg/m^3
Absorption coefficient	1.359
F(000)	1568
Crystal size	0.28 × 0.22 × 0.22 mm^3
Theta range from data collection	1.71 to 28.36°
Index ranges	-13<=h<=13 -28<=k<=28 -22<=l<=22
Reflections collected	38078
Independent reflections	7649
Completeness to theta = 28.36°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7542 and 0.7021
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7649 / 0 / 385
Goodness-of-fit on F^2	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0693, wR2 = 0.1890
R indices (all data)	R1 = 0.0800, wR2 = 0.1988
Largest diff. peak and hole	3.313 and -3.658 e. Å^{-3}

Table S3. Crystal data, data collection, and structure refinement for TAS[**3**-F].

Empirical formula	C38 H37 F N3 O4 S Sb
Formula weight	772.52
Temperature	110(2) K
Wavelength	0.71073
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 14.7131(16) Å α = 90.00°
	b = 16.7493(18) Å β = 90.00°
	c = 27.433(3) Å γ = 90.00°
Volume	6760.4(13) Å^3
Z	8
Density (calculated)	1.518 Mg/m^3
Absorption coefficient	0.929
F(000)	3152
Crystal size	0.28 × 0.20 × 0.08 mm^3
Theta range from data collection	1.57 to 28.33°
Index ranges	-19<=h<=19 -22<=k<=22 -36<=l<=36
Reflections collected	84322
Independent reflections	16829
Completeness to theta = 28.33°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9294 and 0.7809
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	16829 / 0 / 886
Goodness-of-fit on F^2	1.060
Final R indices [I>2sigma(I)]	R1 = 0.0391. wR2 = 0.0908
R indices (all data)	R1 = 0.490, wR2 = 0.0957
Largest diff. peak and hole	3.399 and -0.909 e. Å^{-3}

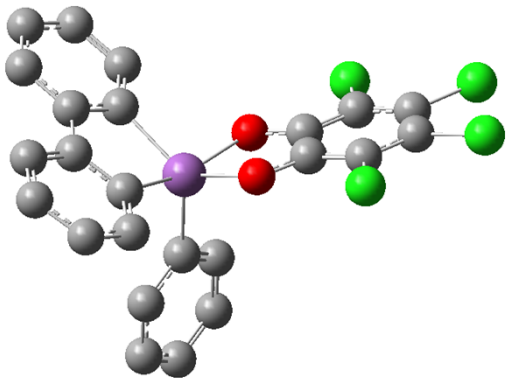
DFT optimized structural coordinates

Table S4. XYZ coordinate of the optimized structure of **1**.



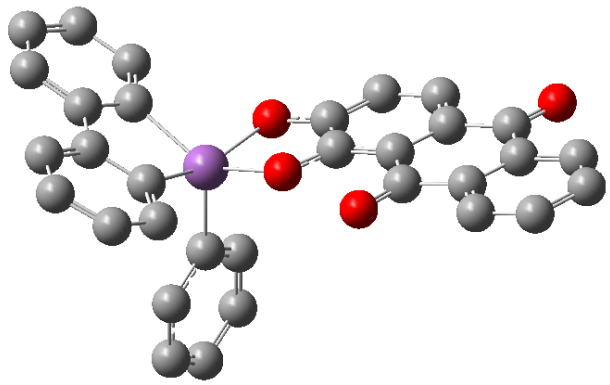
Sb	0.000000	0.000000	0.000000	C	-2.935466	-0.311216	0.904942
O	0.000000	0.000000	2.080837	H	-2.584820	-1.000115	1.419831
O	2.053098	0.000000	0.407561	C	0.449626	0.627297	-4.370390
C	-0.086743	-2.114962	-0.167592	H	0.527530	1.317516	-4.990034
C	2.307856	0.248979	1.677809	C	-0.294723	-4.419229	0.522353
C	0.289598	-0.119843	-2.098981	H	-0.423441	-5.047321	1.197201
C	0.013795	-2.520934	-1.508900	C	-4.016670	1.712365	-0.619120
C	0.180650	-1.444571	-2.543225	H	-4.390812	2.393366	-1.132360
C	0.364889	-0.693049	-4.793208	C	-2.616404	1.481235	-0.648594
H	0.391366	-0.884549	-5.703579	H	-2.060133	2.011629	-1.173872
C	1.219399	0.228296	2.575411	C	-4.825810	0.914943	0.180934
C	-0.157465	-4.818917	-0.801823	H	-5.743326	1.059041	0.193642
H	-0.162100	-5.725198	-1.011304	C	-4.297351	-0.059507	0.934885
C	-0.012060	-3.875130	-1.821145	H	-4.848269	-0.570877	1.480954
H	0.066837	-4.151127	-2.705476	C	1.439392	0.424604	3.928183
C	-2.089423	0.448562	0.119552	H	0.614594	0.368088	4.607457
C	0.419059	0.904261	-3.002960	C	2.720942	0.693650	4.406692
H	0.484945	1.782798	-2.703970	H	2.895636	0.837072	5.452547
C	-0.237481	-3.067881	0.818607	C	3.775462	0.776307	3.526035
H	-0.300399	-2.795801	1.705619	H	4.753049	1.019058	3.886999
C	0.241458	-1.716189	-3.898814	C	3.558123	0.543139	2.175754
H	0.199790	-2.594077	-4.199041	H	4.382572	0.591821	1.495449

Table S5. XYZ coordinate of the optimized structure of **2**.



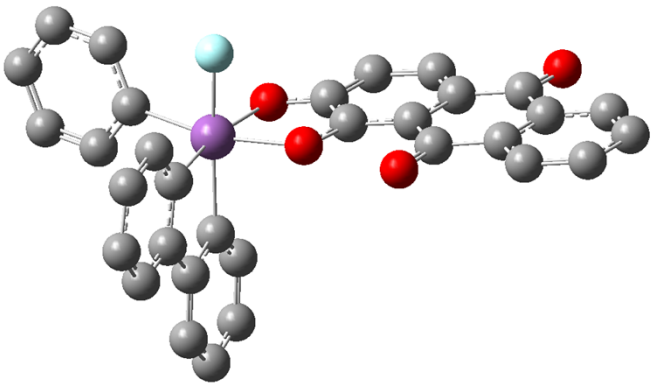
Sb	0.016262	0.578290	-0.159407	C	0.714909	-0.592895	-1.791777
Cl	0.279066	-2.200095	4.003057	C	-2.916175	-0.694289	0.064806
Cl	4.728595	1.468841	1.487388	H	-2.462721	-1.639917	0.348652
Cl	3.143065	-2.040787	5.394037	C	3.805510	-0.300231	3.391766
Cl	5.381226	-0.193908	4.128290	C	0.541477	3.657519	-0.697945
O	1.937235	1.040763	0.520911	H	1.598926	3.466324	-0.545041
O	0.079464	-0.493308	1.574212	C	-4.082656	1.756216	-0.625086
C	-0.382311	2.623163	-0.568278	H	-4.558724	2.696595	-0.884777
C	1.545399	-1.199089	3.347297	C	2.087653	-0.681098	-2.058494
C	1.277481	-0.465948	2.193559	H	2.800044	-0.154888	-1.431835
C	-2.119346	0.421595	-0.186456	C	-4.306913	-0.586933	-0.034019
C	-1.767242	2.829217	-0.728238	H	-4.935811	-1.449918	0.165642
C	2.814876	-1.118991	3.952566	C	0.086251	4.941181	-1.011966
C	-2.686627	1.667208	-0.524416	H	0.792860	5.759798	-1.113825
C	3.530146	0.439279	2.225729	C	0.241758	-2.033604	-3.675175
C	-4.881100	0.637156	-0.383802	H	-0.474289	-2.559077	-4.300986
H	-5.961205	0.725880	-0.462415	C	-0.210665	-1.268462	-2.598186
C	2.272372	0.361580	1.626098	H	-1.275288	-1.204197	-2.392077
C	-1.281364	5.164358	-1.188412	C	1.609324	-2.124226	-3.943378
H	-1.639267	6.160977	-1.432128	H	1.958598	-2.721828	-4.780951
C	-2.201486	4.123841	-1.047380	C	2.529229	-1.449713	-3.137096
H	-3.257953	4.333870	-1.182179	H	3.593129	-1.520654	-3.345491

Table S6. XYZ coordinate of the optimized structure of **3**.



Sb	-1.505197	-0.241495	-0.022492	H	-5.033138	-2.187002	-3.523974
O	-0.548741	-1.820743	-0.973227	C	-2.622586	-1.207740	4.110659
O	0.425081	0.406788	0.008246	H	-3.031055	-0.660962	4.956111
C	-3.160205	-0.360452	-1.358886	C	-2.387540	-0.543906	2.904687
C	1.325034	-0.486671	-0.437831	H	-2.612105	0.515693	2.819009
C	-2.175164	1.773148	0.214235	C	-2.330012	-2.568166	4.228916
C	-3.893543	0.843165	-1.331879	H	-2.512415	-3.081928	5.168881
C	3.559695	-1.294019	-0.933327	C	-1.801216	-3.269462	3.142652
C	-3.368609	1.975818	-0.507225	H	-1.571620	-4.327405	3.235988
C	-3.390187	4.263632	0.303816	C	2.713778	-0.278310	-0.401225
H	-3.870444	5.237899	0.337968	C	3.286508	0.959215	0.187999
C	0.789832	-1.691033	-0.980181	C	5.035908	-1.150243	-0.941346
C	-5.464598	-0.170983	-2.882671	C	5.610250	0.102225	-0.371369
H	-6.369964	-0.092336	-3.478522	O	2.596728	1.845008	0.685756
C	-5.060847	0.916427	-2.105997	O	5.769527	-2.024675	-1.400327
H	-5.660401	1.821377	-2.114665	C	4.778532	1.101601	0.164180
C	-1.858541	-1.249762	1.816592	C	5.349589	2.265080	0.694891
C	-1.576451	2.799537	0.943164	C	6.731623	2.433150	0.691026
H	-0.627543	2.632780	1.445051	H	4.686496	3.020460	1.103288
C	-3.553520	-1.445886	-2.137941	C	6.999827	0.277043	-0.371042
H	-2.953991	-2.350727	-2.152905	C	7.559060	1.437235	0.156817
C	-3.973943	3.239346	-0.443912	H	7.168411	3.338895	1.103407
H	-4.894816	3.439562	-0.983101	H	7.615331	-0.512077	-0.790344
C	-1.563239	-2.614261	1.932958	H	8.637727	1.569697	0.154644
H	-1.150182	-3.156559	1.088293	C	3.016022	-2.462256	-1.468879
C	-2.191283	4.054735	0.989784	H	3.699063	-3.206719	-1.863215
H	-1.732853	4.864991	1.549736	C	1.636989	-2.668766	-1.494592
C	-4.716131	-1.350217	-2.907945	H	1.207587	-3.575780	-1.908897

Table S7. XYZ coordinate of the optimized structure of [**3**-F]$^-$.



Sb	-1.391528	-0.251838	-0.284405	H	-3.961065	3.086645	2.379243
F	-0.610105	-0.738999	-2.029900	C	-3.389099	1.693062	3.752344
O	-0.436855	-1.893438	0.538153	H	-3.857718	2.073017	4.486198
O	0.553584	0.467629	0.014553	C	-2.621427	0.545122	3.933041
O	5.828210	-2.440814	0.572868	H	-2.529982	0.165451	4.798963
O	2.851050	1.982420	-0.165674	C	-1.994473	-0.043828	2.856744
C	-2.997378	-1.578567	-0.704149	H	-1.490022	-0.839491	2.980909
C	-4.312968	-1.220748	-0.382694	C	-2.092392	0.516782	1.585844
H	-4.490921	-0.379573	0.020399	C	0.886084	-1.796448	0.566010
C	-5.352999	-2.083722	-0.650475	C	1.707229	-2.869422	0.842967
H	-6.244001	-1.829870	-0.440656	H	1.329076	-3.707600	1.081717
C	-5.107246	-3.321521	-1.220924	C	3.080302	-2.732379	0.775496
H	-5.828449	-3.920140	-1.379927	H	3.637171	-3.484826	0.937101
C	-3.809301	-3.690446	-1.564294	C	3.658935	-1.499944	0.473010
H	-3.643407	-4.533976	-1.967929	C	5.130470	-1.457722	0.369291
C	-2.750364	-2.808854	-1.311770	C	5.764261	-0.152342	-0.024238
H	-1.864684	-3.048690	-1.556670	C	7.143728	-0.089583	-0.184590
C	-2.171180	1.590359	-1.003702	H	7.675523	-0.867679	-0.074781
C	-2.153531	2.106584	-2.293613	C	7.738802	1.131737	-0.510279
H	-1.764051	1.601870	-2.996666	H	8.677259	1.181279	-0.635074
C	-2.701562	3.346483	-2.563595	C	6.958242	2.271483	-0.650115
H	-2.647509	3.707799	-3.442514	H	7.374763	3.101643	-0.854219
C	-3.337697	4.072903	-1.553498	C	5.596716	2.212206	-0.496126
H	-3.698196	4.931535	-1.742375	H	5.070492	2.999447	-0.591211
C	-3.439960	3.538441	-0.263764	C	4.980808	0.978639	-0.196602
H	-3.913118	4.009288	0.412326	C	3.475127	0.944777	-0.055685
C	-2.844279	2.305292	0.021840	C	2.849060	-0.345997	0.231365
C	-2.826953	1.712743	1.409636	C	1.443116	-0.506636	0.266067
C	-3.466770	2.285248	2.493077				

Table S8. TD-DFT calculation output showing the nature of the low energy excitation for **3** in CH_2Cl_2.

Excitations	Energy	Oscillator strength	MO→MO transition	Contributions
E_a	2.8526 eV (434.63 nm)	0.2598	133→134	0.69855

Table S9. TD-DFT calculation output showing the nature of the low energy excitation for [**3**-F]$^-$ in CH_2Cl_2.

Excitations	Energy	Oscillator strength	MO→MO transition	Contributions
E_a	2.5633 eV (483.69 nm)	0.2824	138→139	0.70012