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

Photophysical properties of a boron analogue of coumarin

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Supplementary Information

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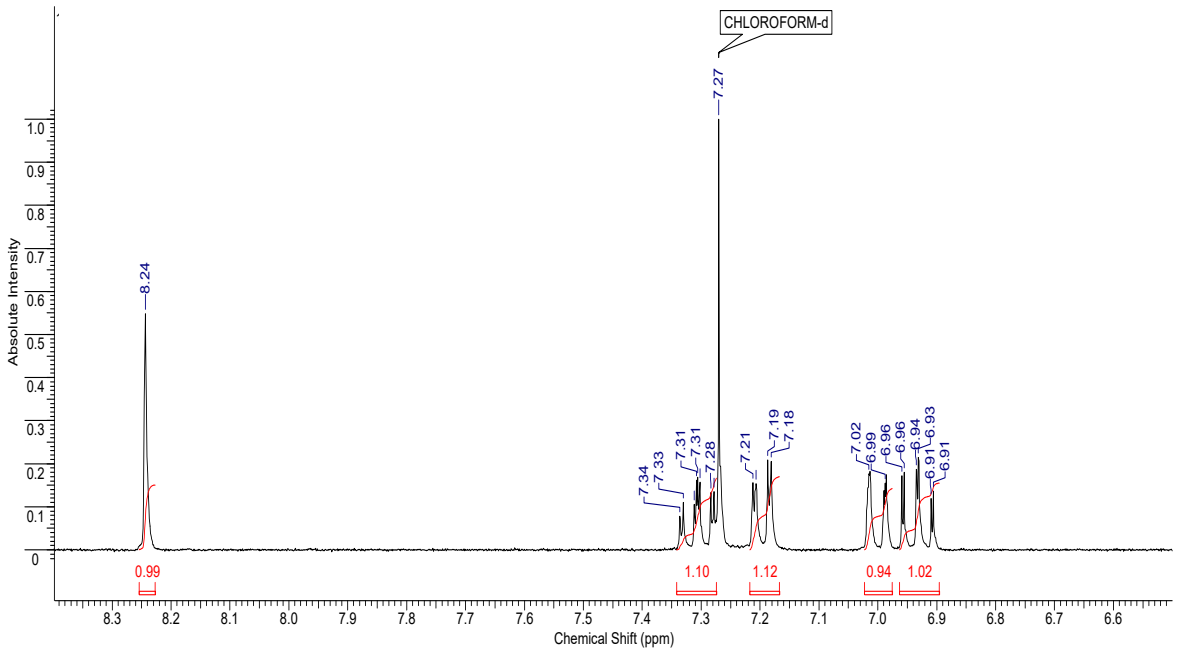

Figure S1: ^{1}H NMR of DFBS in $CDCl_3$, obtained from a 300 MHz instrument.

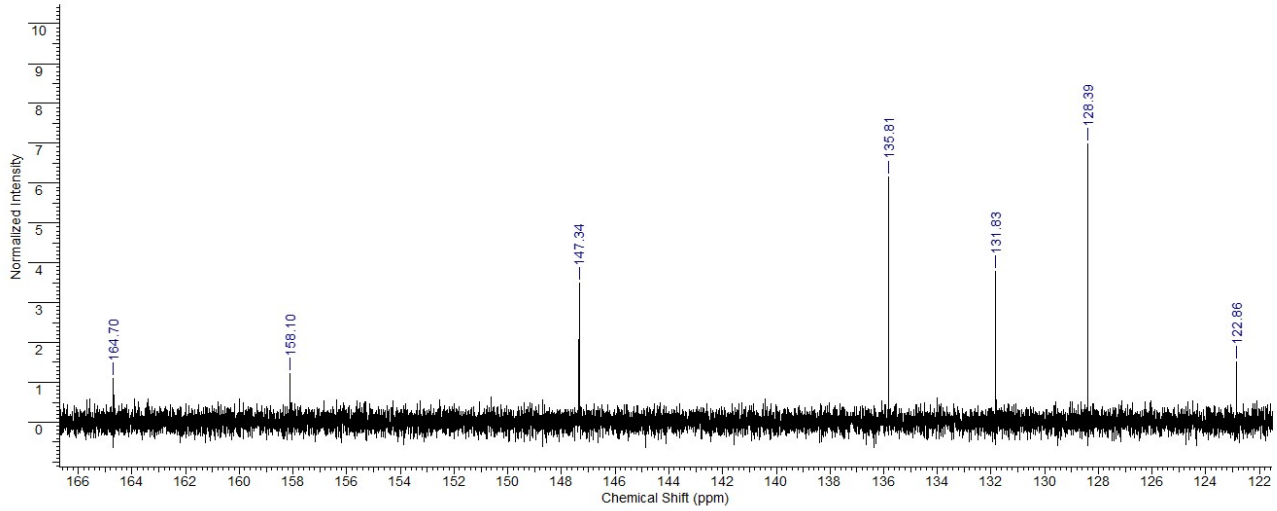

Figure S2: ^{13}C NMR of DFBS in $CDCl_3$, 400 MHz.

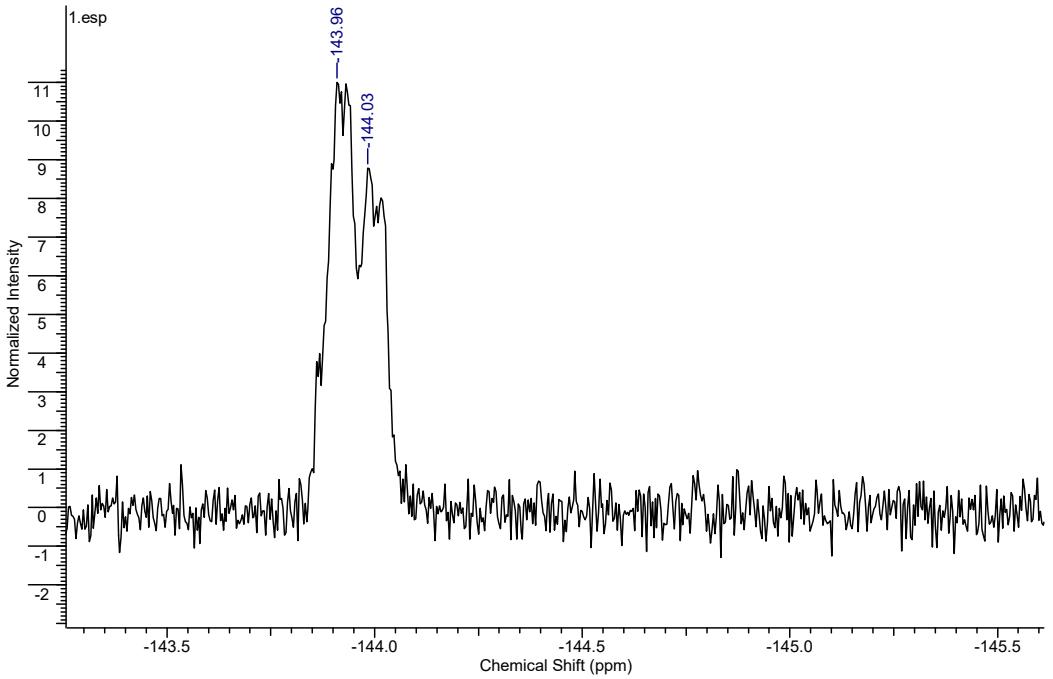

Figure S3: ^{19}F NMR of DFBS in $CDCl_3$, 300 MHz. Internal standard of CF_3OOH (sealed in glass capillary) response at 78.50 ppm.

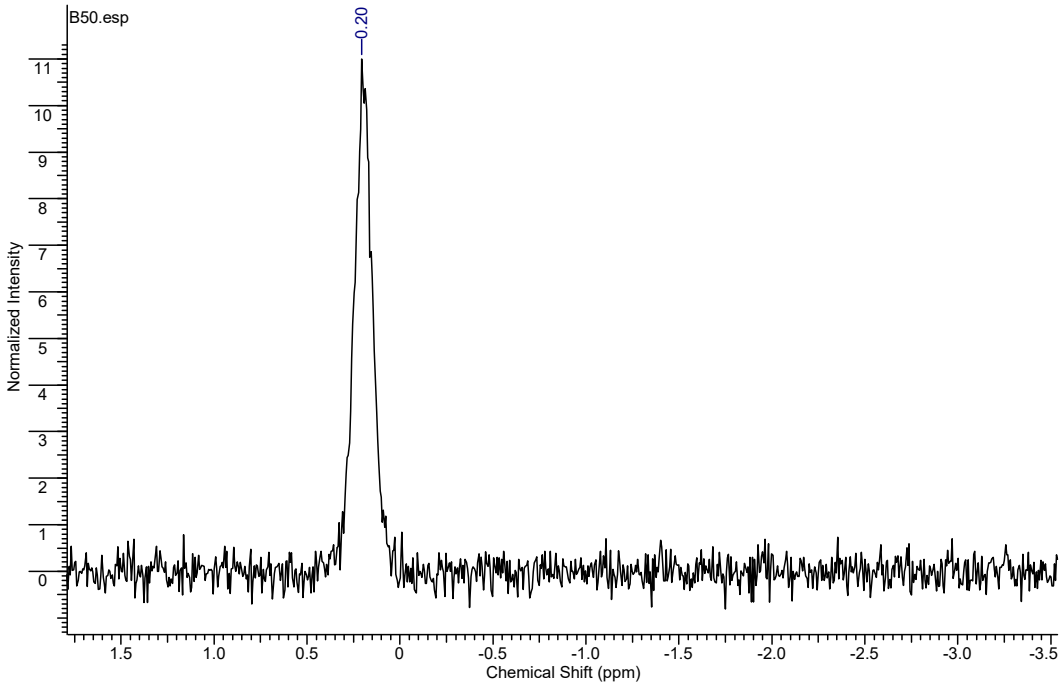

Figure S4: ^{11}B F-decoupled NMR of DFBS in $CDCl_3$, 50°C, 400 MHz.

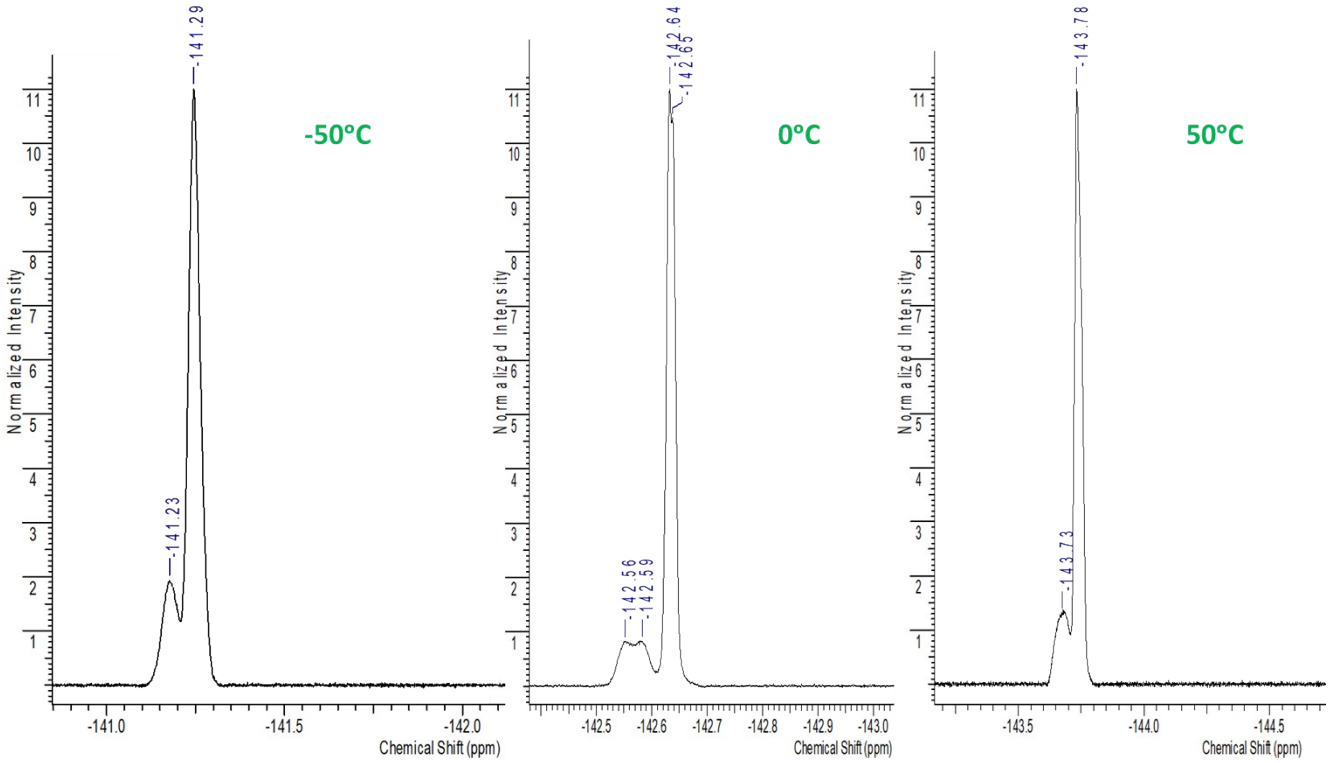

Figure S5: Variant temperature ^{19}F B-decoupled NMR of DFBS in $CDCl_3$, 400 MHz.

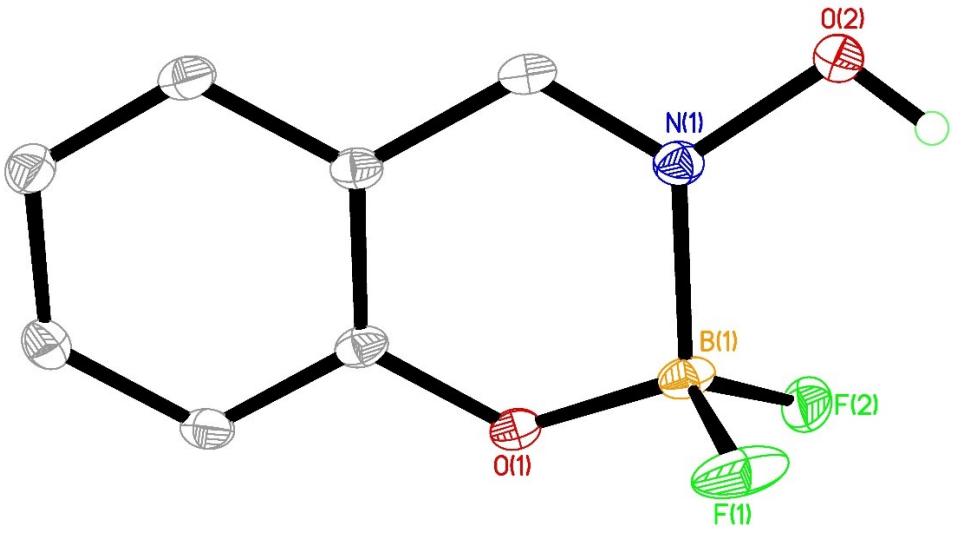

Figure S6: Structure of DFBS showing 35% probability ellipsoids.

Compound	**DFBS**
CCDC	2051349
Empirical formula	$C_9H_{10}BF_2NO_3$
Formula weight	228.99
Crystal system	Monoclinic
Space group	$P2_1/c$
a/ Å	6.5253(16)
b/ Å	11.900(3)
c/ Å	13.029(3)
α(°)	90
β(°)	100.248(6)
γ(°)	90
Volume ($Å^3$)	995.6(4)
Z	4
Dc (Mg/m^3)	1.528
μ (mm^{-1})	0.135
F(000)	472
reflns collected	9395
indep. reflns	2478
GOF on F^2	1.054
R1 (on F_o^2, $I > 2\sigma(I)$)	0.0428
wR2 (on F_o^2, $I > 2\sigma(I)$)	0.0937
R1 (all data)	0.0661
wR2 (all data)	0.1042

Table S1: X-ray crystal data and structure parameters for DFBS.

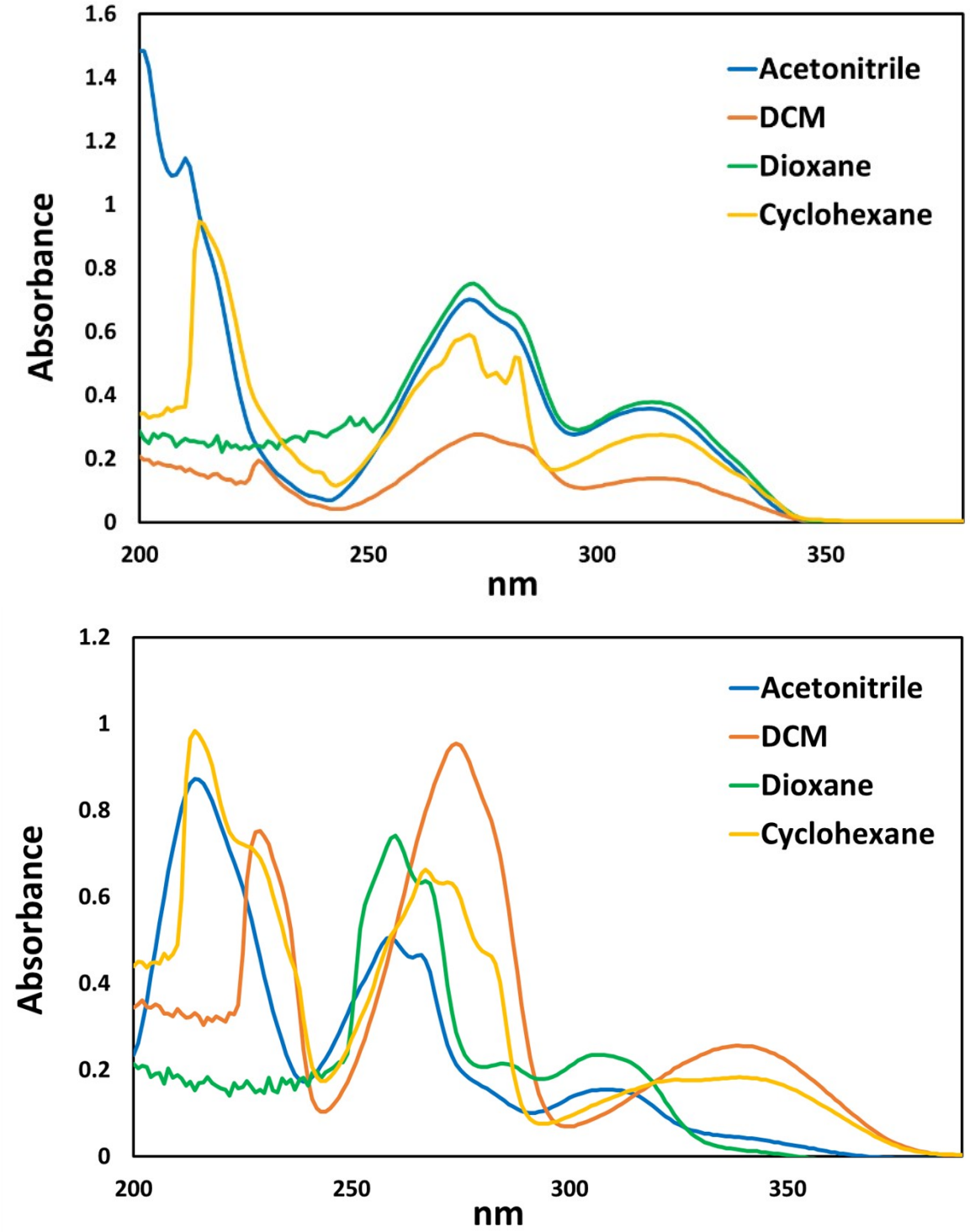

Figure S7: (Top) UV visible absorption spectra of unsubstituted coumarin in solvents with variable polarity. (Bottom) UV visible absorption spectra of DFBS in solvents with variable polarity. Solvents were dried with 3 angstrom molecular sieves but 1,4-dioxane could still be wet.

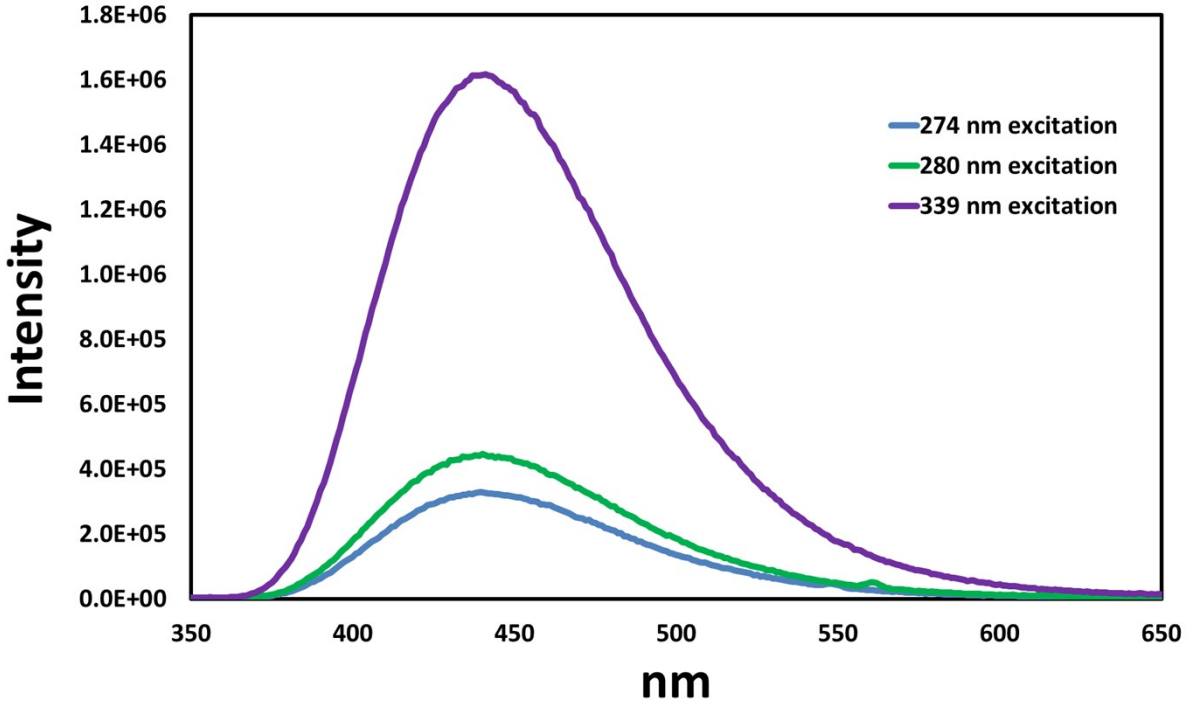

Figure S8: Emission spectra of DFBS in DCM obtained at different excitation wavelengths.

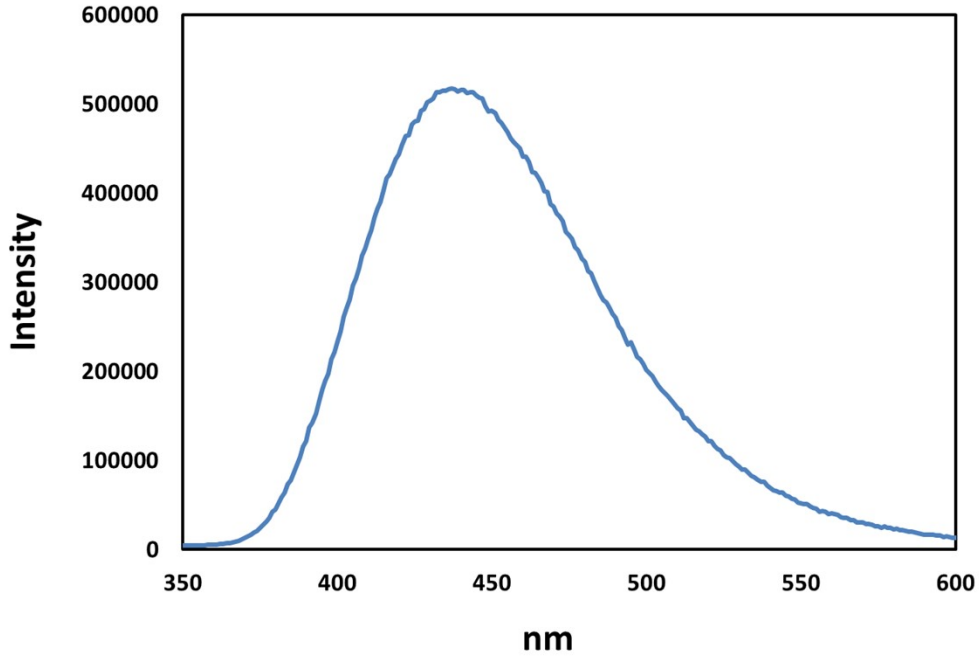

Figure S9: Emission spectra of DFBS in acetonitrile obtained at 313 nm excitation.

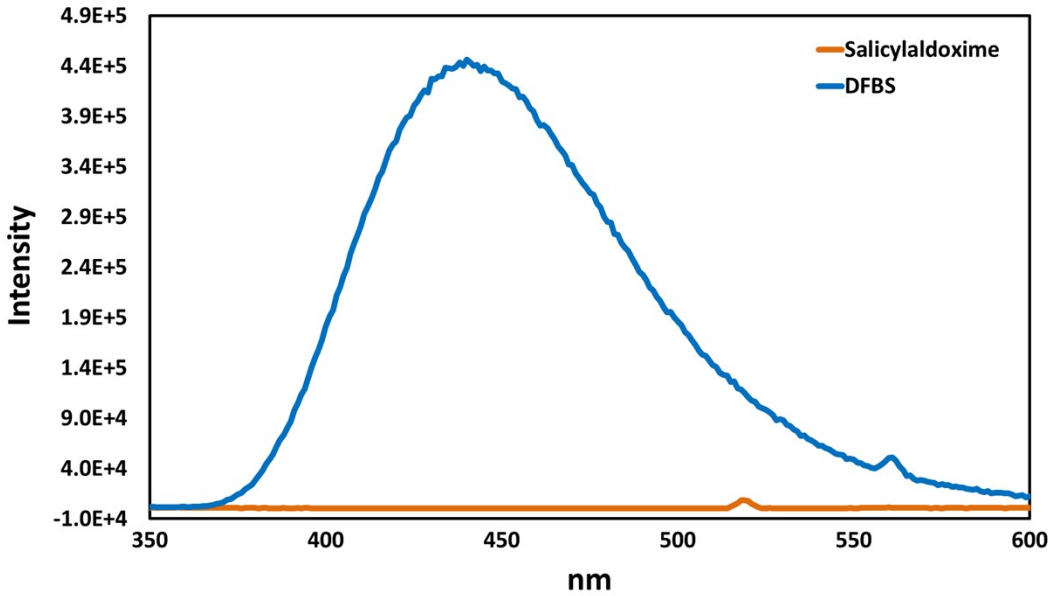

Figure S10: Emission spectra of DFBS and salicylaldoxime in DCM at 280 nm excitation wavelength. Salicylaldoxime is not emissive under the same aprotic solvent conditions as DFBS but low intensity emission is observed for the oxime in protic polar solvent such as methanol. Unsubstituted coumarin also has negligible emission.

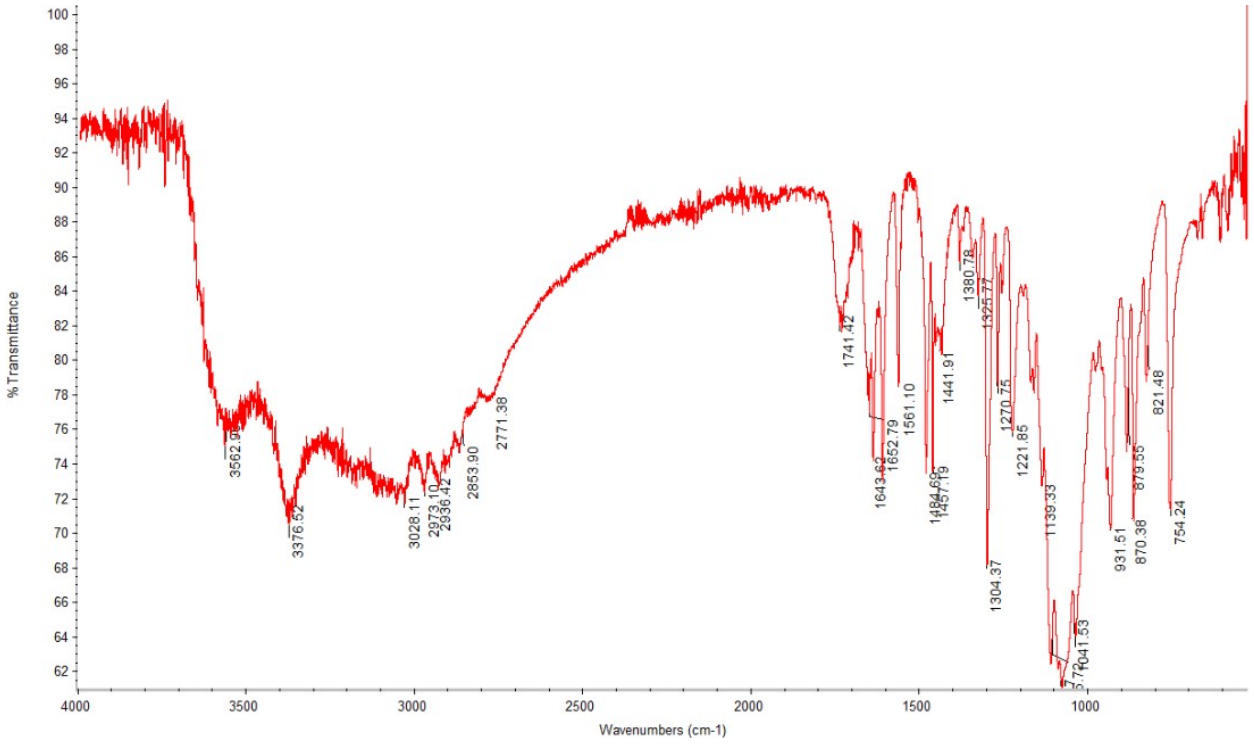

Figure S11: Solid-state FT-IR of DFBS.

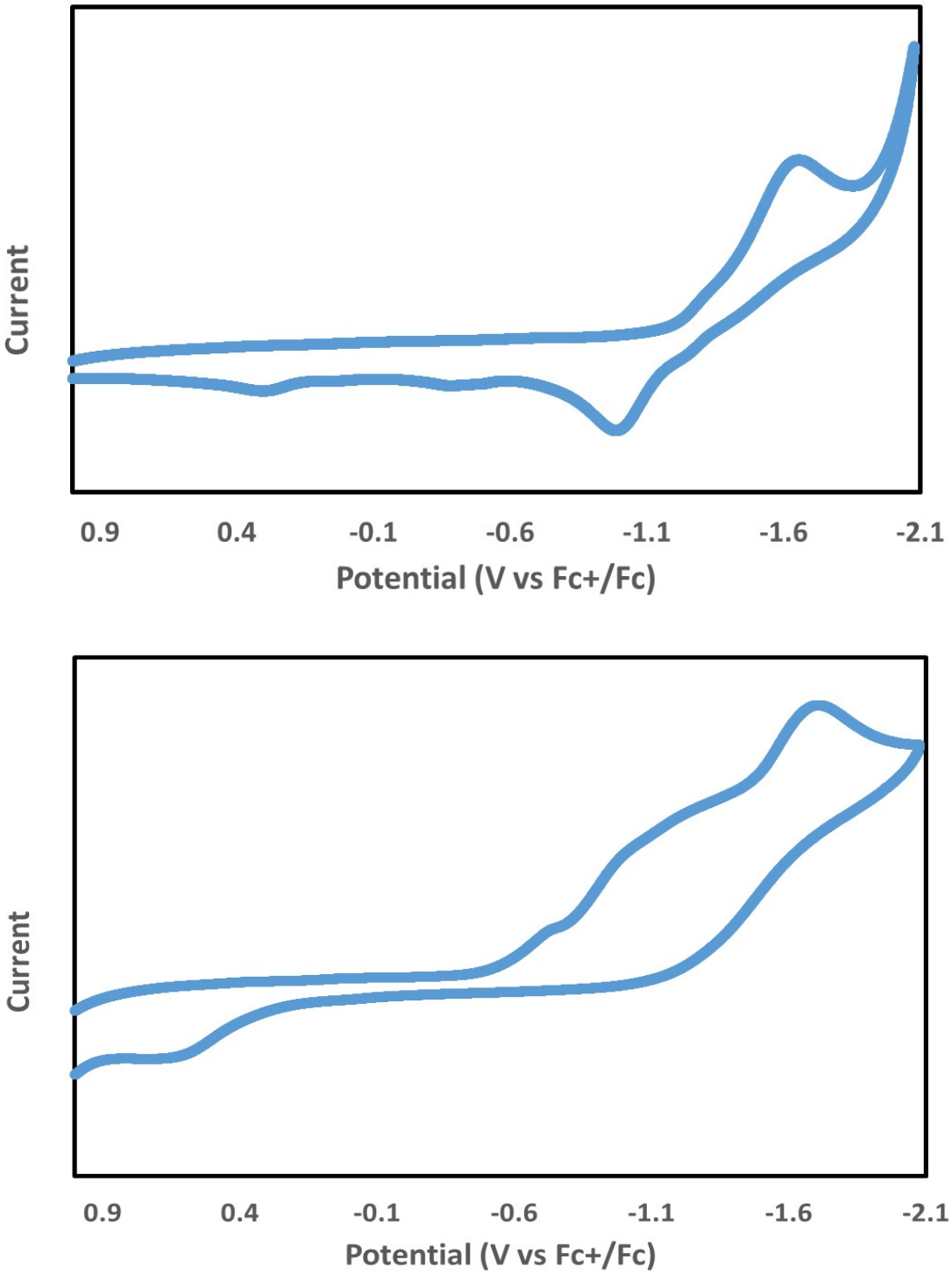

Figure S12: (Top) Cyclic voltammogram of coumarin in acetonitrile with 0.1M $TBAPF_6$. (Bottom) Cyclic voltammogram of DFBS in acetonitrile with 0.1M $TBAPF_6$.

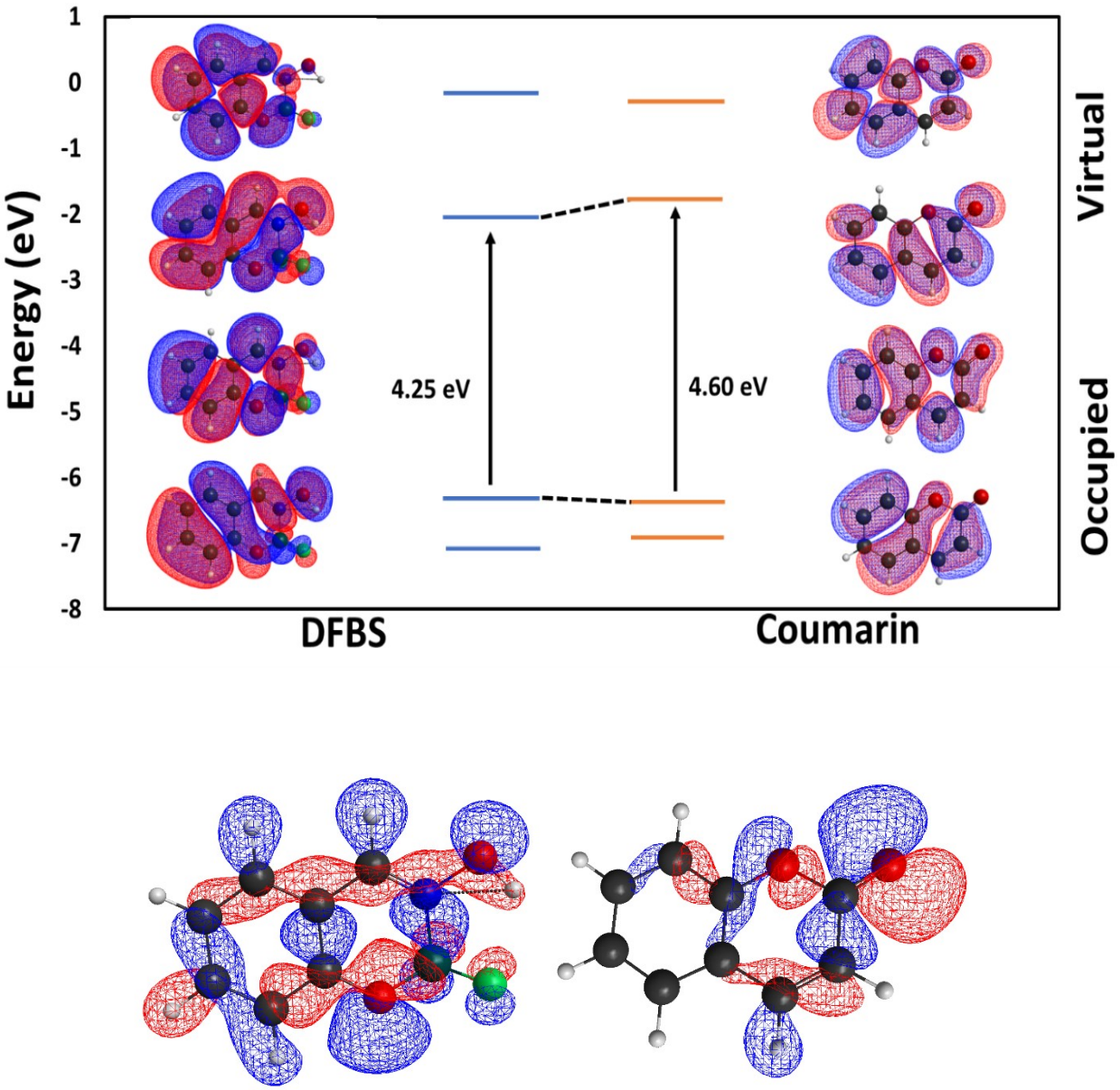

Figure S13: (Top) TDDFT calculated relative energies of the frontier orbitals for DFBS and UC along with modelled TDDFT natural orbitals. (Bottom) Left: n-HOMO orbital of DFBS. Right: n-HOMO orbital of unsubstituted coumarin.

Table S2: Gas phase TDDFT results for unsubstituted coumarin. Only excited states with f > 0.05 are shown.

State 1	Energy	Oscillator strength	Symmetry of state	OCC I	VIR A	Excitation Amp	De-excitation Amp
	4.1772 eV	0.111667	A	37	39	0.354408	0.004618
	296.8 nm			38	39	-0.910556	0.065626
				35	40	0.05161	0.013919
				37	40	0.178439	0.033579
				38	40	0.068477	0.013547
				33	41	-0.037418	-0.019955
				33	43	0.033475	0.017477
				36	48	0.032347	0.013916
State 3	Energy	Oscillator strength	Symmetry of state	OCC I	VIR A	Excitation Amp	De-excitation Amp
	4.6751 eV	0.152607	A	33	39	0.059764	0.013372
	265.2 nm			37	39	0.866344	-0.045717
				38	39	0.35762	-0.052224
				33	40	0.051281	0.015383
				38	40	0.31527	0.015745
				37	41	-0.113472	-0.019982
State 5	Energy	Oscillator strength	Symmetry of state	OCC I	VIR A	Excitation Amp	De-excitation Amp
	5.882664 eV	0.083778	A	30	39	0.067829	0.008396
	210.7 nm			33	39	0.032325	0.000274
				35	39	0.501329	0.008791
				37	39	0.091899	-0.018156
				35	40	0.073208	0.010799
				37	40	0.077004	-0.004198
				38	40	-0.423353	0.03225
				37	41	-0.226993	-0.009112
				38	41	-0.698371	0.017743

Table S3: Gas phase TDDFT results for DFBS. Only excited states with f > 0.05 are shown.

State 1	Energy	Oscillator strength	Symmetry of state	OCC I	VIR A	Excitation Amp	De-excitation Amp
	3.736489 eV	0.06977	A	46	48	0.211256	0.014231
	331.80 nm			47	48	-0.965896	0.066795
				44	49	0.038122	0.013032
				46	49	0.130202	0.038774
				47	49	0.045874	0.010349
				47	50	0.048843	0.017276
State 2	Energy	Oscillator strength	Symmetry of state	OCC I	VIR A	Excitation Amp	De-excitation Amp
	4.713108 eV	0.273923	A	43	48	-0.049723	-0.00273
	263.10 nm			44	48	-0.035847	-0.011441
				45	48	-0.035405	-0.003531
				46	48	-0.930859	0.078746
				47	48	-0.227883	0.050798
				46	49	-0.073251	-0.00657
				47	49	-0.24427	-0.011715
				46	50	0.045796	0.008309
				47	50	-0.0793	-0.017287
State 4	Energy	Oscillator strength	Symmetry of state	OCC I	VIR A	Excitation Amp	De-excitation Amp
	5.67612 eV	0.082521	A	44	48	0.129915	0.004676
	218.40 nm			46	48	-0.188191	0.031459
				44	49	0.043942	-0.002502
				46	49	0.326462	0.010416
				47	49	0.758623	-0.04214
				46	50	0.222201	0.020779
				47	50	-0.458612	-0.011453
State 5	Energy	Oscillator strength	Symmetry of state	OCC I	VIR A	Excitation Amp	De-excitation Amp
	6.102842 eV	0.08378	A	39	48	0.032554	0.002705
	203.20 nm			41	48	0.084388	0.004518
				43	48	0.484619	0.007492
				44	48	-0.563212	0.0193
				45	48	-0.078696	0.001997
				46	48	0.052148	-0.020234
				47	48	0.042539	-0.019744
				45	49	0.033543	0.001727
				46	49	0.496549	-0.014303

				47	49	-0.30084	0.027004
				46	50	0.121254	0.010544
				47	50	-0.262814	0.009134

Table S4: TDDFT calculated results for unsubstituted coumarin in dichloromethane. Only excited states with f > 0.05 and energy > 200 nm are shown.

State 1	Energy	Oscillator strength	Symmetry of state	OCC I	VIR A	Excitation Amp	De-excitation Amp
	4.094564 eV	0.287024	A	35	39	-0.03021	-0.01099
	302.80 nm			37	39	-0.23592	-0.00496
				38	39	0.958331	-0.05774
				35	40	-0.03513	-0.00986
				37	40	0.122156	0.02721
				38	40	0.058278	0.012644
State 2	Energy	Oscillator strength	Symmetry of state	OCC I	VIR A	Excitation Amp	De-excitation Amp
	4.48237 eV	0.249067	A	33	39	0.041058	0.01072
	276.60 nm			37	39	-0.93782	0.03717
				38	39	-0.24698	0.031707
				33	40	-0.03388	-0.01096
				35	40	-0.03546	-0.01042
				37	40	0.040418	0.000806
				38	40	0.210603	0.019379
				37	41	-0.07876	-0.01828
				38	41	-0.0367	0.000706
State 5	Energy	Oscillator strength	Symmetry of state	OCC I	VIR A	Excitation Amp	De-excitation Amp
	5.825154 eV	0.206623	A	30	39	0.064164	0.009333
	212.84 nm			33	39	-0.04269	-0.00055
				35	39	-0.36973	-0.00839
				37	39	0.058296	-0.01498
				35	40	0.065404	0.010496
				37	40	-0.25137	0.008336
				38	40	0.541971	-0.03585
				37	41	0.097327	0.006123
				38	41	0.691661	-0.01318
State 6	Energy	Oscillator strength	Symmetry of state	OCC I	VIR A	Excitation Amp	De-excitation Amp
	6.081462 eV	0.47002	A	33	39	-0.11447	-0.00932
	203.87 nm			35	39	0.591119	-0.00705
				37	39	0.064006	-0.01868
				38	39	0.09226	-0.03142
				37	40	-0.63416	0.033645
				38	40	0.376952	-0.03584

				35	41	-0.06478	-0.01158
				37	41	-0.1646	-0.00143
				38	41	-0.2094	0.004545

Table S5: TDDFT calculated results for DFBS in dichloromethane. Only excited states with f > 0.05 and energy > 200 nm are shown.

State 1	Energy	Oscillator strength	Symmetry of state	OCC I	VIR A	Excitation Amp	De-excitation Amp
	3.591382 eV	0.116144	A	46	48	0.112375	0.012728
	345.23 nm			47	48	-0.98708	0.056741
				46	49	0.100593	0.036432
				47	49	0.043676	0.009664
				47	50	-0.03093	-0.01489
State 2	Energy	Oscillator strength	Symmetry of state	OCC I	VIR A	Excitation Amp	De-excitation Amp
	4.563929 eV	0.480295	A	42	48	0.041489	0.008235
	271.66 nm			45	48	0.060251	0.000853
				46	48	0.975104	-0.06516
				47	48	0.123279	-0.02936
				46	49	0.072624	0.009003
				47	49	0.126535	0.011774
				46	50	0.034008	0.008914
				47	50	-0.04659	-0.01504
State 4	Energy	Oscillator strength	Symmetry of state	OCC I	VIR A	Excitation Amp	De-excitation Amp
	5.722493 eV	0.186849	A	41	48	0.032215	0.004261
	216.66 nm			44	48	0.186537	0.005727
				46	48	0.113759	-0.02187
				47	48	-0.04545	0.012534
				46	49	-0.23922	-0.01036
				47	49	-0.86832	0.046992
				46	50	0.173655	0.019779
				47	50	-0.31883	-0.01093
State 6	Energy	Oscillator strength	Symmetry of state	OCC I	VIR A	Excitation Amp	De-excitation Amp
	6.097662 eV	0.111128	A	41	48	-0.03902	0.001506
	203.33 nm			43	48	0.610951	-0.00033
				44	48	-0.16733	0.000534
				44	49	0.034787	0.003524
				46	49	-0.53761	0.005461
				47	49	0.281488	-0.02433
				46	50	0.06795	0.004842
				47	50	-0.46551	0.005166

Table S6: TDDFT calculated results for unsubstituted coumarin in dioxane. Only excited states with f > 0.05 and energy > 200 nm are shown.

State 1	Energy	Oscillator strength	Symmetry of state	OCC I	VIR A	Excitation Amp	De-excitation Amp
	4.14497 eV	0.186901	A	36	39	-0.03572	-0.00017
	299.12 nm			37	39	-0.30591	-0.00477
				38	39	0.933035	-0.06219
				35	40	-0.04344	-0.01194
				37	40	-0.14981	-0.03026
				38	40	-0.06283	-0.01312
				33	41	0.031472	0.01775
				38	41	-0.03077	-0.00455
				33	42	-0.03034	-0.01626
State 3	Energy	Oscillator strength	Symmetry of state	OCC I	VIR A	Excitation Amp	De-excitation Amp
	4.579997 eV	0.20811	A	33	39	-0.0493	-0.01194
	270.71 nm			36	39	-0.07372	0.00115
				37	39	0.901424	-0.04085
				38	39	0.311258	-0.04223
				33	40	-0.04115	-0.01286
				35	40	0.034762	0.009391
				38	40	0.260885	0.01805
				37	41	0.093113	0.019022
State 5	Energy	Oscillator strength	Symmetry of state	OCC I	VIR A	Excitation Amp	De-excitation Amp
	5.852769 eV	0.134049	A	30	39	0.066208	0.008856
	211.84 nm			33	39	0.035665	0.000295
				35	39	-0.44103	-0.00907
				37	39	-0.07235	0.016046
				35	40	-0.07014	-0.01057
				37	40	-0.16474	0.006277
				38	40	0.468607	-0.03342
				37	41	-0.15251	-0.00747
				38	41	-0.71729	0.015906
State 6	Energy	Oscillator strength	Symmetry of state	OCC I	VIR A	Excitation Amp	De-excitation Amp
	6.142483 eV	0.331482	A	33	39	-0.10952	-0.0088
	201.85 nm			34	39	-0.19349	-4.5E-05
				35	39	-0.50511	0.008745
				36	39	0.068977	0.001844

				37	39	0.074991	-0.0195
				38	39	0.108257	-0.03523
				35	40	0.032859	0.006864
				36	40	0.335455	-0.00059
				37	40	0.580228	-0.03332
				38	40	-0.37426	0.037452
				35	41	0.064706	0.010599
				36	41	-0.22496	0.002346
				37	41	-0.10046	-0.00072
				38	41	-0.07781	-0.00102
				36	42	0.080153	-0.00235
State 7	Energy	Oscillator strength	Symmetry of state	OCC I	VIR A	Excitation Amp	De-excitation Amp
	6.158439 eV	0.084608	A	31	39	0.036124	-0.00136
	201.32 nm			33	39	-0.11552	-0.00482
				34	39	0.296278	-0.00369
				35	39	-0.27178	0.005508
				36	39	-0.12863	-0.00428
				37	39	0.033511	-0.01002
				38	39	0.053828	-0.01733
				34	40	0.034083	0.000527
				36	40	-0.66834	0.003135
				37	40	0.286977	-0.01699
				38	40	-0.19397	0.019705
				35	41	0.033099	0.005338
				36	41	0.450935	-0.00452
				36	42	-0.15836	0.003847

Table S7: TDDFT calculated results for DFBS in dioxane. Only excited states with f > 0.05 and energy > 200 nm are shown.

State 1	Energy	Oscillator strength	Symmetry of state	OCC I	VIR A	Excitation Amp	De-excitation Amp
	3.643339 eV	0.095428	A	46	48	-0.15508	-0.01387
	340.30 nm			47	48	0.979489	-0.06201
				46	49	0.111594	0.037229
				47	49	0.043485	0.009982
				47	50	-0.03926	-0.01596
State 2	Energy	Oscillator strength	Symmetry of state	OCC I	VIR A	Excitation Amp	De-excitation Amp
	4.61006 eV	0.386304	A	36	48	0.03087	0.01024
	268.94 nm			41	48	-0.03881	-0.00759
				43	48	0.034671	0.00135
				45	48	0.042129	-0.00125
				46	48	0.959492	-0.07228
				47	48	0.168926	-0.03877
				46	49	-0.07759	-0.00849
				47	49	-0.17758	-0.01222
				46	50	-0.03704	-0.00785
				47	50	0.062294	0.016976
State 4	Energy	Oscillator strength	Symmetry of state	OCC I	VIR A	Excitation Amp	De-excitation Amp
	5.68917 eV	0.139249	A	44	48	-0.16748	-0.00445
	217.93 nm			46	48	0.153517	-0.02736
				47	48	-0.03564	0.010082
				44	49	0.039734	-0.0021
				46	49	0.278522	0.010875
				47	49	0.827266	-0.04524
				46	50	-0.19303	-0.02014
				47	50	0.376275	0.011799
State 6	Energy	Oscillator strength	Symmetry of state	OCC I	VIR A	Excitation Amp	De-excitation Amp
	6.157454 eV	0.108838	A	36	48	-0.03612	-0.00117
	201.36 nm			40	48	-0.0554	-0.00014
				41	48	0.144268	0.002603
				42	48	0.066343	-6.9E-05
				43	48	0.564492	-0.00329
				44	48	0.428162	-0.0186
				45	48	-0.1243	0.010335

				46	48	0.038292	-0.01323
				44	49	-0.03045	-0.00171
				45	49	0.038603	0.002488
				46	49	-0.39414	0.008398
				47	49	0.349765	-0.03634
				46	50	-0.12064	-0.01361
				47	50	-0.38193	0.00523

	Dipole moment (Debye)	
	Unsubstituted Coumarin	DFBS
Gas Phase	4.795488	4.573199
Dioxane	5.553159	6.058899
DCM	6.239841	7.898987

Figure S14: TDDFT calculated dipole moment comparison of UC and DFBS in gas phase, dichloromethane, and 1,4-dioxane.

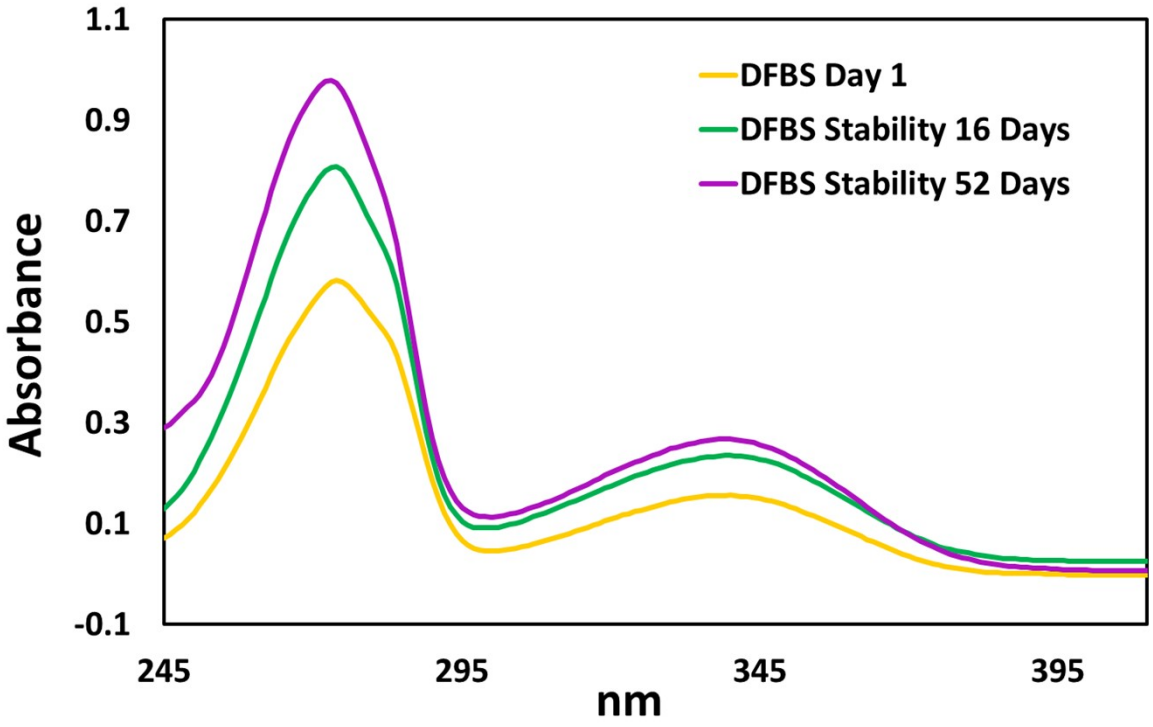

Figure S15: Stability results of DFBS dissolved in DCM. A control solution of DFBS dissolved in DCM was kept in a capped volumetric flask at room temperature and ambient conditions without extra precautions from light or moisture. Solution was tested periodically via UV-vis absorption for any degradation of DFBS.

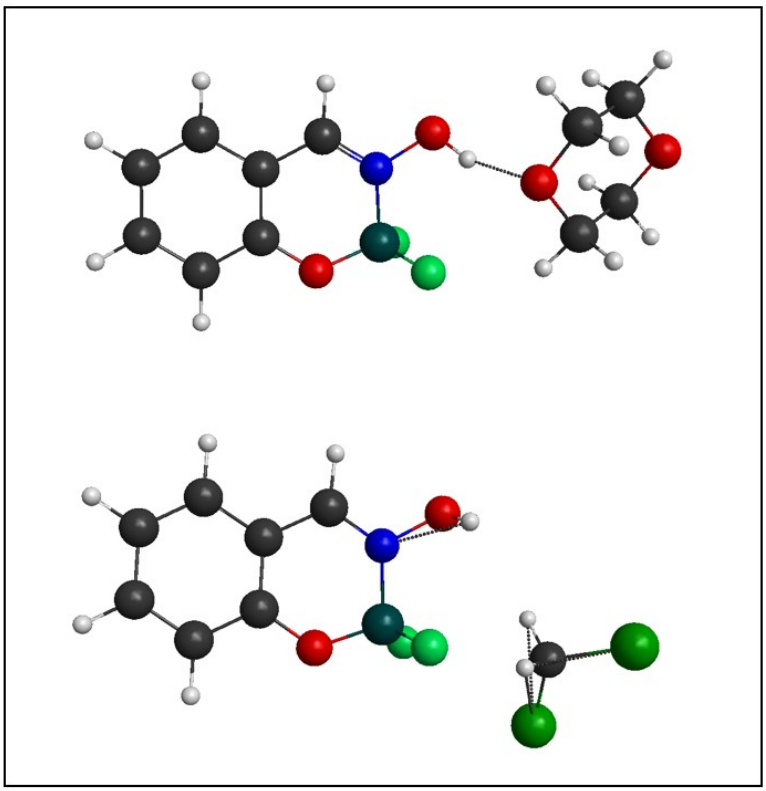

Figure S16: DFT geometry optimization results for DFBS using the PCM solvation model and one explicit solvent molecule to better visualize any intermolecular interactions in solution. (Top) DFBS with an explicit dioxane molecule. (Bottom) DFBS with an explicit DCM molecule.

B3LYP		**CAM-B3LYP**		**WB97XD**	
Absorption (nm)	f	Absorption (nm)	f	Absorption (nm)	f
262.98	0.2740	243.74	0.2404	244.11	0.2412
331.38	0.0695	299.34	0.1109	300.33	0.1116
Emission (nm)		Emission (nm)		Emission (nm)	
419.97		352.76		358.90	

Figure S17: Gas phase TDDFT results for DFBS utilizing three different exchange functionals. Only the two lowest absorption transition energies are shown. All calculations are performed using Gaussian and the 6-31G(d,p) basis set.

Experimental Results		**B3LYP**		**CAM-B3LYP**		**WB97XD**	
Absorption (nm)	ε ($M^{-1}cm^{-1}$)	Absorption (nm) Solvent corrected	f	Absorption (nm) Solvent corrected	f	Absorption (nm) Solvent corrected	f
274	$1.1x\ 10^4$	265.14	0.3757	247.35	0.3381	247.60	0.3383
339	$3.0x10^3$	332.02	0.0861	296.37	0.1380	297.08	0.1393
Emission (nm)		Emission (nm) Solvent corrected		Emission (nm) Solvent corrected		Emission (nm) Solvent corrected	
440		458.73		372.80		374.20	

Figure S18: TDDFT results for DFBS in DCM utilizing three different exchange functionals. Only the two lowest absorption transition energies are shown. Only solvent corrected results are shown. All calculations are performed using Gaussian and the 6-31G(d,p) basis set. Results using B3LYP are shown to correlate best with experimental data.