Luminescent 1*H*-1,3-benzazaphospholes

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Supporting Information

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D. Optical & Lifetime Measurements

A. NMR Characterization

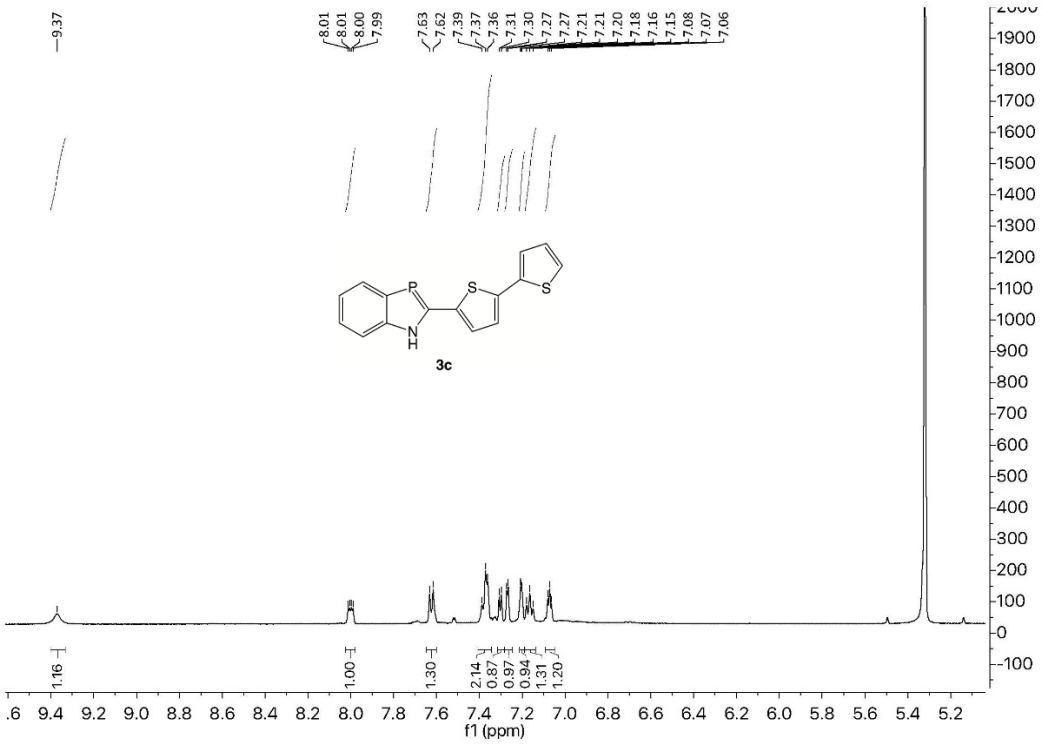


Figure S1. ^{1}H NMR spectrum of derivative **3c** in CD_2Cl_2, 500 MHz.

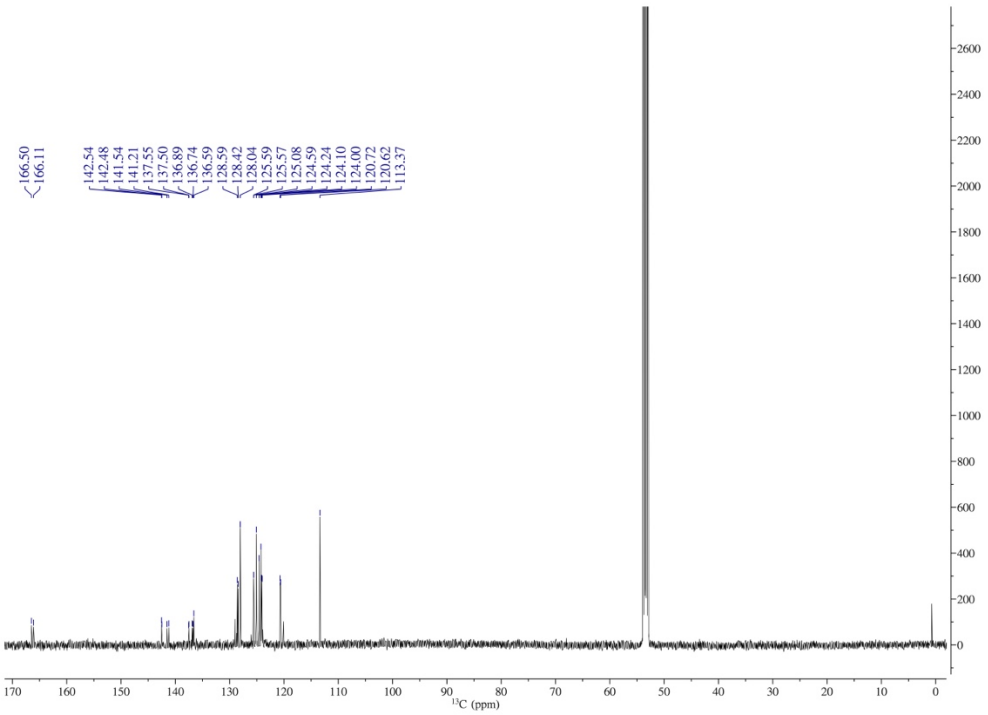


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of derivative **3c** in CD_2Cl_2, 126 MHz.

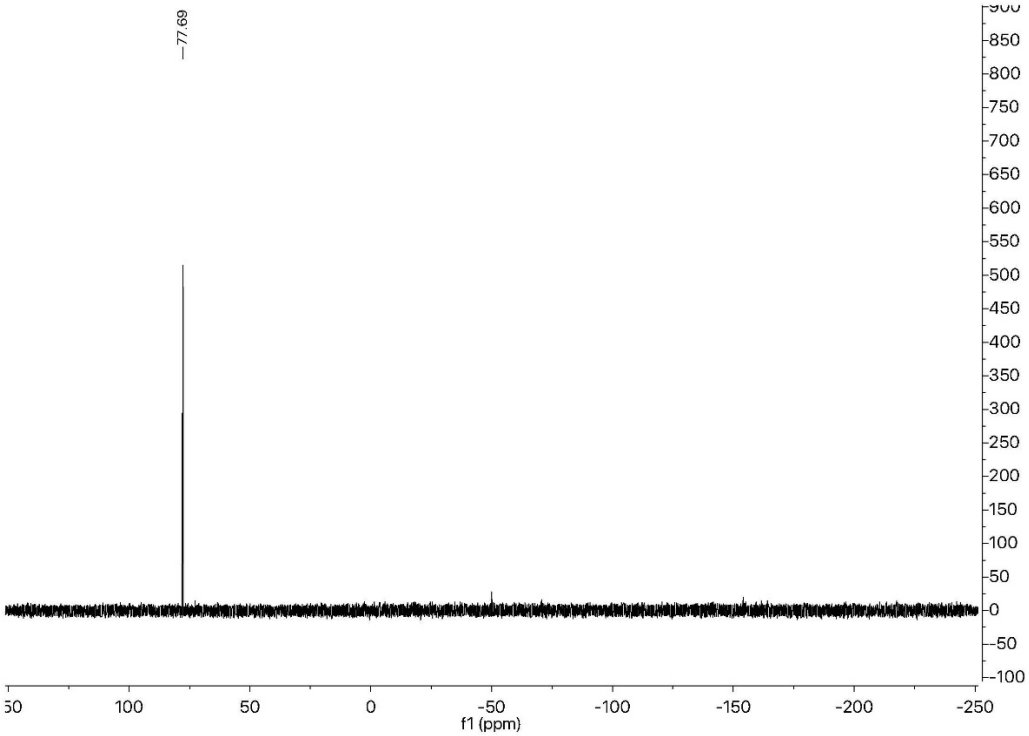


Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of derivative **3c** in CD_2Cl_2, 202 MHz.

B. Crystallographic Information & Results

Table S1. Crystal data and structure refinement at 100 K for derivative 3c.

Empirical formula	C15 H10 N P S2	
Formula weight	299.33	
Temperature	100.0 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	*a* = 8.1771(4) Å	α = 90°.
	b = 5.7977(3) Å	β = 90.684(4)°.
	c = 13.7003(7) Å	γ = 90°.
Volume	649.46(6) $Å^3$	
Z	2	
Density (calculated)	1.531 Mg/m^3	
Absorption coefficient	4.726 mm^{-1}	
F(000)	308	
Crystal size	0.28 x 0.05 x 0.03 mm^3	
Theta range for data collection	3.226 to 66.981°.	
Index ranges	-9<=h<=9, -6<=k<=6, -16<=l<=15	
Reflections collected	2535	
Independent reflections	1814 [R(int) = 0.0310]	
Completeness to theta = 66.981°	96.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.3207 and 0.1886	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1814 / 71 / 185	
Goodness-of-fit on F^2	1.058	
Final R indices [I>2sigma(I)]	R1 = 0.0407, wR2 = 0.1011	
R indices (all data)	R1 = 0.0442, wR2 = 0.1034	
Absolute structure parameter	0.16(2)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.379 and -0.310 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 3c. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	5319(4)	3628(3)	8644(1)	36(1)
S(2)	6332(2)	6423(2)	5758(1)	35(1)
P(1)	7906(2)	7455(2)	3515(1)	35(1)
N(1)	9111(5)	3345(8)	3733(3)	34(1)
C(1)	4086(10)	5513(16)	9273(6)	35(1)
C(2)	3713(15)	7397(18)	8727(8)	36(2)
C(3)	4340(30)	7310(30)	7780(13)	38(2)
C(4)	5291(6)	5347(9)	7618(3)	34(1)
C(5)	6164(6)	4612(9)	6755(4)	33(1)
C(6)	6982(6)	2598(10)	6608(4)	33(1)
C(7)	7759(6)	2495(10)	5697(4)	35(1)
C(8)	7551(5)	4435(9)	5153(4)	32(1)
C(9)	8189(6)	4937(9)	4194(4)	34(1)
C(10)	9640(6)	3995(9)	2820(3)	35(1)
C(11)	9100(6)	6194(9)	2557(4)	35(1)
C(12)	9515(6)	7043(9)	1624(4)	36(1)
C(13)	10486(7)	5737(10)	1028(4)	41(1)
C(14)	11025(6)	3551(10)	1317(4)	37(1)
C(15)	10610(6)	2656(10)	2219(4)	35(1)
C(3A)	5290(100)	4000(90)	8460(30)	36(1)
C(2A)	4430(70)	5160(100)	9190(40)	35(1)
C(1A)	3550(100)	7020(130)	8830(40)	36(2)
S(1A)	4360(50)	7720(40)	7693(17)	38(2)

Table S3. Bond lengths [Å] and angles [°] for 3c.

S(1)-C(1)	1.725(6)
S(1)-C(4)	1.723(5)
S(2)-C(5)	1.730(5)
S(2)-C(8)	1.740(5)
P(1)-C(9)	1.745(6)
P(1)-C(11)	1.800(5)
N(1)-H(1)	0.8800
N(1)-C(9)	1.353(7)
N(1)-C(10)	1.380(6)
C(1)-H(1A)	0.9500
C(1)-C(2)	1.357(10)
C(2)-H(2)	0.9500
C(2)-C(3)	1.402(14)
C(3)-H(3)	0.9500
C(3)-C(4)	1.394(13)
C(4)-C(5)	1.451(6)
C(4)-C(3A)	1.40(2)
C(4)-S(1A)	1.577(19)
C(5)-C(6)	1.362(8)
C(6)-H(6)	0.9500
C(6)-C(7)	1.409(6)
C(7)-H(7)	0.9500
C(7)-C(8)	1.359(8)
C(8)-C(9)	1.449(7)
C(10)-C(11)	1.395(8)
C(10)-C(15)	1.387(7)
C(11)-C(12)	1.415(7)
C(12)-H(12)	0.9500
C(12)-C(13)	1.374(8)
C(13)-H(13)	0.9500
C(13)-C(14)	1.397(9)
C(14)-H(14)	0.9500
C(14)-C(15)	1.387(7)
C(15)-H(15)	0.9500
C(3A)-H(3A)	0.9500
C(3A)-C(2A)	1.40(3)
C(2A)-H(2A)	0.9500
C(2A)-C(1A)	1.39(3)
C(1A)-H(1AA)	0.9500
C(1A)-S(1A)	1.75(2)
C(4)-S(1)-C(1)	92.2(3)
C(5)-S(2)-C(8)	91.5(2)
C(9)-P(1)-C(11)	88.8(2)
C(9)-N(1)-H(1)	122.6
C(9)-N(1)-C(10)	114.8(4)
C(10)-N(1)-H(1)	122.6
S(1)-C(1)-H(1A)	124.3
C(2)-C(1)-S(1)	111.3(6)
C(2)-C(1)-H(1A)	124.3
C(1)-C(2)-H(2)	123.3
C(1)-C(2)-C(3)	113.4(9)
C(3)-C(2)-H(2)	123.3

C(2)-C(3)-H(3)	123.5
C(4)-C(3)-C(2)	112.9(10)
C(4)-C(3)-H(3)	123.5
C(3)-C(4)-S(1)	110.0(6)
C(3)-C(4)-C(5)	130.5(6)
C(5)-C(4)-S(1)	119.5(4)
C(5)-C(4)-S(1A)	123.4(7)
C(3A)-C(4)-C(5)	121(2)
C(3A)-C(4)-S(1A)	116(2)
C(4)-C(5)-S(2)	120.6(4)
C(6)-C(5)-S(2)	111.1(3)
C(6)-C(5)-C(4)	128.3(4)
C(5)-C(6)-H(6)	123.4
C(5)-C(6)-C(7)	113.2(5)
C(7)-C(6)-H(6)	123.4
C(6)-C(7)-H(7)	123.3
C(8)-C(7)-C(6)	113.3(5)
C(8)-C(7)-H(7)	123.3
C(7)-C(8)-S(2)	110.8(3)
C(7)-C(8)-C(9)	128.3(5)
C(9)-C(8)-S(2)	120.9(4)
N(1)-C(9)-P(1)	113.1(4)
N(1)-C(9)-C(8)	119.7(5)
C(8)-C(9)-P(1)	127.2(4)
N(1)-C(10)-C(11)	112.4(4)
N(1)-C(10)-C(15)	124.9(5)
C(15)-C(10)-C(11)	122.6(5)
C(10)-C(11)-P(1)	110.8(4)
C(10)-C(11)-C(12)	118.2(4)
C(12)-C(11)-P(1)	130.9(4)
C(11)-C(12)-H(12)	120.3
C(13)-C(12)-C(11)	119.5(5)
C(13)-C(12)-H(12)	120.3
C(12)-C(13)-H(13)	119.5
C(12)-C(13)-C(14)	121.0(4)
C(14)-C(13)-H(13)	119.5
C(13)-C(14)-H(14)	119.6
C(15)-C(14)-C(13)	120.8(5)
C(15)-C(14)-H(14)	119.6
C(10)-C(15)-H(15)	121.1
C(14)-C(15)-C(10)	117.9(5)
C(14)-C(15)-H(15)	121.1
C(4)-C(3A)-H(3A)	125.4
C(4)-C(3A)-C(2A)	109(4)
C(2A)-C(3A)-H(3A)	125.4
C(3A)-C(2A)-H(2A)	123.9
C(1A)-C(2A)-C(3A)	112(5)
C(1A)-C(2A)-H(2A)	123.9
C(2A)-C(1A)-H(1AA)	126.2
C(2A)-C(1A)-S(1A)	108(4)
S(1A)-C(1A)-H(1AA)	126.2
C(4)-S(1A)-C(1A)	92(2)

Symmetry transformations used to generate equivalent atoms:

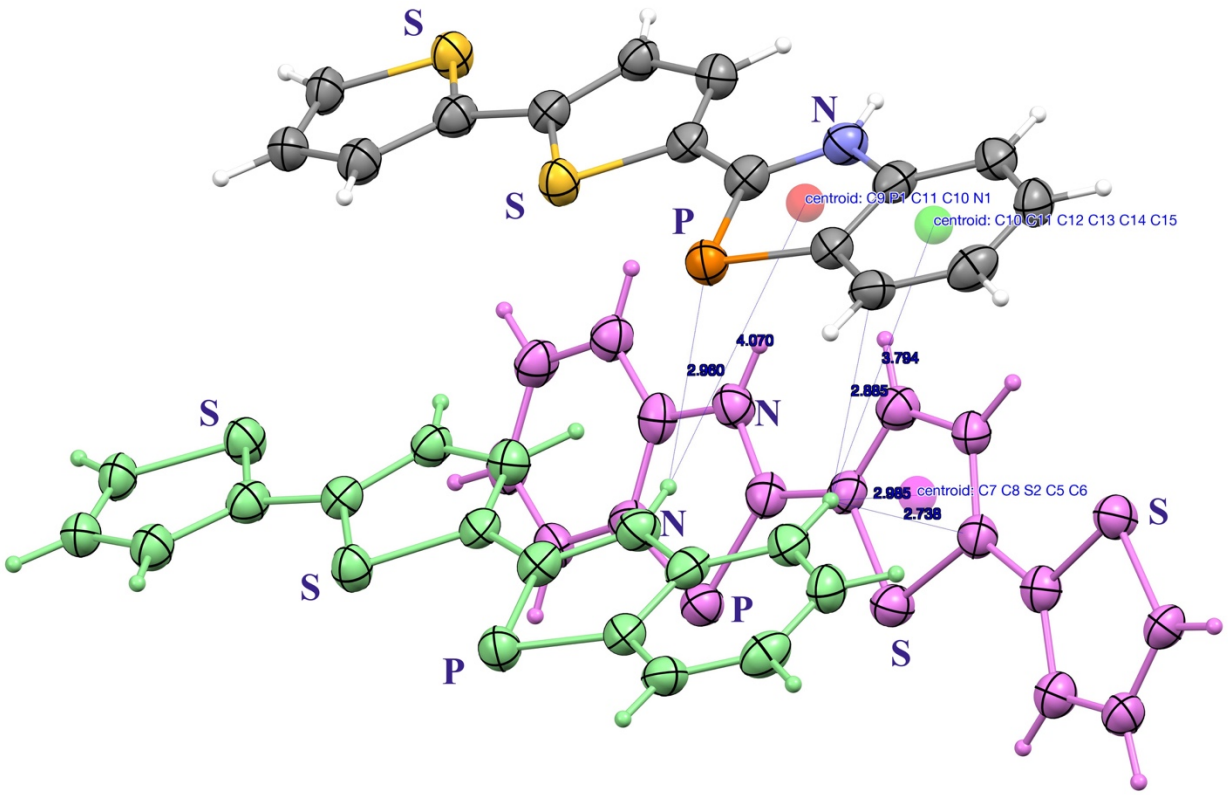
Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 3c. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	42(1)	35(1)	32(1)	3(1)	10(1)	3(1)
S(2)	38(1)	34(1)	33(1)	3(1)	7(1)	5(1)
P(1)	37(1)	32(1)	36(1)	1(1)	6(1)	3(1)
N(1)	38(2)	33(2)	32(2)	3(2)	5(2)	-2(2)
C(1)	32(5)	39(4)	35(2)	-2(2)	9(2)	3(2)
C(2)	35(4)	33(4)	41(3)	-3(2)	9(2)	0(4)
C(3)	37(2)	39(6)	38(3)	1(2)	7(2)	1(5)
C(4)	33(2)	37(2)	32(2)	1(2)	3(2)	-2(2)
C(5)	29(2)	34(2)	35(2)	0(2)	3(2)	-2(2)
C(6)	30(2)	34(2)	34(2)	4(2)	5(2)	-1(2)
C(7)	34(2)	36(2)	36(2)	-2(2)	4(2)	0(2)
C(8)	24(2)	35(2)	38(2)	-2(2)	1(2)	-2(2)
C(9)	30(2)	39(3)	35(2)	3(2)	1(2)	-2(2)
C(10)	30(2)	41(3)	33(2)	-2(2)	2(2)	-8(2)
C(11)	30(2)	33(2)	41(2)	-4(2)	3(2)	-2(2)
C(12)	34(2)	30(3)	45(3)	2(2)	1(2)	-5(2)
C(13)	38(3)	50(3)	34(2)	7(2)	3(2)	-8(2)
C(14)	36(2)	42(2)	35(2)	-6(2)	9(2)	1(2)
C(15)	33(2)	36(2)	37(2)	-5(2)	3(2)	-2(2)
C(3A)	42(1)	35(1)	32(1)	3(1)	10(1)	3(1)
C(2A)	32(5)	39(4)	35(2)	-2(2)	9(2)	3(2)
C(1A)	35(4)	33(4)	41(3)	-3(2)	9(2)	0(4)
S(1A)	37(2)	39(6)	38(3)	1(2)	7(2)	1(5)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for pro83_0m_a.

	x	y	z	U(eq)
H(1)	9354	2000	3995	41
H(1A)	3715	5264	9919	42
H(2)	3085	8654	8962	43
H(3)	4147	8459	7301	45
H(6)	7025	1384	7074	39
H(7)	8368	1198	5484	42
H(12)	9126	8506	1412	43
H(13)	10794	6327	410	49
H(14)	11685	2668	890	45
H(15)	10978	1174	2420	42
H(3A)	5800	2533	8530	43
H(2A)	4452	4716	9862	42
H(1AA)	2665	7767	9139	43

Figure S4. Detailed packing diagram for **3c**



C. Computational studies

Both the ground state and excited state geometry optimizations were performed at the ωB97X-D/6-311++G(d,p) level of theory.[1,2] The S1-optimizations of **3a**-**3c** were performed at the B3LYP/6-311++G(d,p) level. TDDFT calculations were performed with ωB97X-D/6-311++g(d,p) level of theory.[3,4] The 6-31G(d,p) basis set is used for SOC calculation. PCM with a dielectric 8.93 and refractive index 1.425 used to represent the DCM solvent. All calculations were performed using the Q- Chem 4.4 package.[5]

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2. (a) Chai, J.-D.; Head-Gordon, M. Systematic optimization of long- range corrected hybrid density functionals. J. Chem. Phys. 2008, 128, 084106. (b) Chai, J.-D.; Head-Gordon, M. Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections. Phys. Chem. Chem. Phys. 2008, 10, 6615−20. (c) Chai, J.-D.; Head-Gordon, M. Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections. Chem. Phys. Lett. 2008, 467, 176−178.
3. Closser, C. D.; Gessner, O.; Head-Gordon, M. Simulations of the dissociation of small helium clusters with ab initio molecular dynamics in electronically excited states. J. Chem. Phys. 2014, 140, 134306.
4. Ou, Q.; Subotnik, J. E. Electronic relaxation in benzaldehyde evaluated via TD-DFT and localized diabatization: intersystem crossings, conical intersections, and phosphorescence. J. Phys. Chem. C 2013, 117, 19839−19849.
5. Shao, Y.; et al. Advances in molecular quantum chemistry contained in the Q-Chem 4 program package. Mol. Phys. 2015, 113, 184−215.

Table S6. Optimized cartesian coordinates of **3a**

C	0.3855210296362960	0.2341745719594957	0.0438285590374763
N	-0.3869444278502195	-0.8639546851357215	-0.1368658901045878
C	-1.7455555018688815	-0.6376135297122917	-0.0664822727317680
C	-2.7553617092000637	-1.5909237818017543	-0.2132842334319362
C	-4.0680482041798554	-1.1689072122274402	-0.1170261590890490
C	-4.4010837309758806	0.1783452627515053	0.1275973050926884
C	-3.3815085633776163	1.1073032921083907	0.2722119192536871
C	-2.0369025107954073	0.7168245595984266	0.1805201005134812
P	-0.5235532661337633	1.6773172016936222	0.3205798997970258
H	-2.5120747315434144	-2.6308809602838923	-0.4034914294102077
H	-4.8642036786674332	-1.8968808234191041	-0.2364690291300946
H	-3.6289777710866424	2.1490621331534321	0.4578565392366876
H	0.0022007109499794	-1.7824925341146303	-0.2990452582147927
C	1.8723690245930507	0.0878323527172287	-0.0102072786592521
H	2.3594480985693451	1.0439351746297041	0.1816934900978714
H	2.2125950830790146	-0.6335719801728986	0.7387788177074414
H	2.1933873219564695	-0.2725757424231780	-0.9923223572963177
C	-5.8440057302682167	0.6098824632147849	0.2204161319098970
H	-6.0739105843758523	1.0102242452569317	1.2122823944019006
H	-6.0654931081031576	1.3944468328013049	-0.5082455452198049
H	-6.5222829103577160	-0.2244739405939334	0.0306964562396594

Table S7. Optimized cartesian coordinates of **3b**

C	4.1742508895624404	-1.0704723995286021	-0.1206933805569141
C	4.3821429106947560	0.3110924230849167	0.0536845068365042
C	3.3137879879302425	1.1778935831288690	0.1727919188855782
C	2.0006409312999369	0.6773851334405510	0.1159283267748042
P	0.4259887771191200	1.5238440595003322	0.2309069026626301
C	-0.3697186246034898	-0.0019353492698476	0.0145554989638813
C	-1.8034092007479656	-0.2578658681165137	-0.0194573277826236
C	-2.4702158544171402	-1.4131309754850241	0.2987175096517203
C	-3.8811754541456334	-1.2961647996292744	0.1675972396599526
C	-4.2695789613385697	-0.0581966407546132	-0.2490142707872009
S	-2.9219850527877487	0.9827816171739037	-0.4972328105308519
N	0.4892251560893004	-1.0481364842754577	-0.1105627447176494
H	0.1811823246494920	-1.9942861340161588	-0.2866498688645339
C	1.8197822929730221	-0.7076088609377732	-0.0594822633050331
C	2.8983352002074239	-1.5927661763881424	-0.1771968394855576
H	5.0259121950894965	-1.7346272135632734	-0.2162084735534479
H	5.3946504161265780	0.6971938699718897	0.0883828733093968
H	3.4821317115256170	2.2419977453072470	0.3031426075197473
H	-1.9778663872235855	-2.3125164158452955	0.6469912203332294
H	-4.5781033089690801	-2.0955048777755336	0.3815408701197917
H	-5.2694831276527383	0.3104456634111345	-0.4253555015797146
H	2.7299113323735225	-2.6561832836561514	-0.3096170423421686

Table S8. Optimized cartesian coordinates of **3c**

C	3.8827053185385534	0.0236380772950766	1.8589274715411219
C	4.2582899294537091	0.8717441661386001	0.7995560911340603
C	3.3320169510366244	1.2815789464127734	-0.1385566775278743
C	1.9952244350377777	0.8562064855750227	-0.0325149428231743
P	0.5712006704107708	1.2364787344043242	-1.0503524457723252
C	-0.3970074783647743	0.2642446108190047	0.0089307150160573

C	-1.8340187842128846	0.0319104870752937	-0.0493993634147226
C	-2.7091117313492488	-0.0884390233446153	0.9976023488673390
C	-4.0476747222094538	-0.3061289530034249	0.5849183919292492
C	-4.1916305744685483	-0.3517870910977945	-0.7761640431437650
S	-2.6624847761976440	-0.1166584284806132	-1.5674416360496612
N	0.3040518602108033	-0.2863477415727287	1.0359026139095187
H	-0.1175182544443614	-0.9087020012362541	1.7115301197742945
C	1.6421803147904697	0.0230856398691283	1.0456934543593712
C	2.5795862860855476	-0.4083506620122673	1.9928285417080565
H	4.6266642298731853	-0.2848704784709423	2.5848493285876870
H	5.2854905476749261	1.2113938900370331	0.7289037680225209
H	3.6272919806272714	1.9389318280905794	-0.9497346752823909
H	-2.4008233959777616	-0.0145029477553393	2.0329602544659875
H	-4.8711411596972019	-0.4436021641088093	1.2739461060113326
H	2.2824926053345735	-1.0613654305655966	2.8060648267233619
C	-5.4014012102574256	-0.5781682407901498	-1.5551816990027081
C	-5.5292068622664416	-1.2125959551847321	-2.7617906188057977
S	-6.9484079480753618	-0.0209477782694347	-0.9875888113187494
C	-6.8724932029578678	-1.2604299219187538	-3.2286891906376232
H	-4.6896686363839972	-1.6531004353376753	-3.2853155782608345
C	-7.7475874401929072	-0.6662388914375699	-2.3709416345019649
H	-7.1755850017667955	-1.7254724651746882	-4.1573737595497740
H	-8.8198936602514806	-0.5710630559554366	-2.4615341059586000

Table S9. Optimized cartesian coordinates of **3a** (S1 state)

C	0.4548263286232766	0.1780124249956259	-0.0039001193591396
N	-0.3706959352767319	-0.8578171888903392	-0.0737484534036312
C	-1.7570384816785627	-0.6204069556937674	-0.0219754512839401
C	-2.7510041926340145	-1.6200719453935917	-0.0916861634293967
C	-4.1048859310785337	-1.1741439392493420	-0.0193298307628055
C	-4.4403745159563011	0.1593862162996952	0.1085601363098407

C	-3.4071475455157763	1.1576270479076833	0.1725940458957831
C	-2.0601616721111182	0.7433651519383399	0.1068794847813218
P	-0.5488122682441465	1.7260330817074683	0.1631259100972554
H	-2.4981314637988423	-2.6648061148687008	-0.1945688223473842
H	-4.8948189835976521	-1.9129277042645163	-0.0661383095975571
H	-3.6616843898619069	2.2042034994613608	0.2732869725170949
H	-0.0167677914042238	-1.8095713962970268	-0.1609028482223482
C	1.9322329345264260	0.0660980098522095	-0.0420071551761225
H	2.3805378099340158	0.4935592440436720	0.8681874356237150
H	2.2534665121944468	-0.9761551049226133	-0.1323527807061546
H	2.3466075053893638	0.6363095395560223	-0.8876628775539465
C	-5.8785567727690617	0.6000648557024452	0.1851767212911082
H	-6.0830126430351239	1.1205676308449748	1.1271635019970132
H	-6.1191235472606547	1.3049060623312398	-0.6179978464046501
H	-6.5598401164448159	-0.2471595150608435	0.1103186097339627

Table S10. Optimized cartesian coordinates of **3b** (S1 state)

C	4.2083065692163970	-1.0270994269788931	-0.0031844366682554
C	4.3814534864653192	0.3617307469990644	-0.0026056344715105
C	3.2831486852382121	1.2111538553454688	-0.0033011532815040
C	1.9810052974574051	0.6772075921260370	-0.0041652438863120
P	0.4118023510972105	1.5147492407420065	-0.0066073362714013
C	-0.4066887397541911	-0.1401915166668960	-0.0043202995923764
C	-1.7745014886307742	-0.3367785823816693	-0.0005580982223314
C	-2.5402099089696422	-1.5291308242135924	0.0078472434201733
C	-3.9098419864125287	-1.2762526104296619	0.0116579929644079
C	-4.2372210315738634	0.0713170479784151	0.0062982049865780
S	-2.8461790778396368	1.0810490793664411	-0.0038842604972415
N	0.5127808206658225	-1.1408765940653731	-0.0049452041429378
H	0.2606199086047513	-2.1191829524728210	-0.0056809629115012
C	1.8375541494229102	-0.7336305688136143	-0.0042579870074657

C	2.9320856829683000	-1.5889834731314676	-0.0040082949658494
H	5.0750340791360413	-1.6806517346908523	-0.0029809818473473
H	5.3843182500415834	0.7756678302896851	-0.0017965146255034
H	3.4212435443042080	2.2881025689944665	-0.0029653670042511
H	-2.1048601432858720	-2.5181719544262036	0.0106996895592957
H	-4.6657065081977773	-2.0505467367766301	0.0184424305749839
H	-5.2237017906610745	0.5092946273721372	0.0074869466029474
H	2.7959640044622147	-2.6655369983888511	-0.0044017815010628

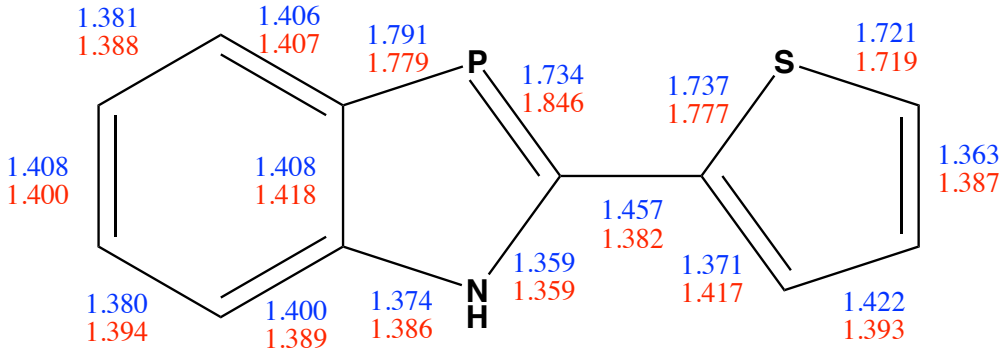
Table S11. Optimized cartesian coordinates of **3c** (S1 state)

C	3.8635167078227473	0.4353559508879213	1.9111685445140709
C	4.2610623626492243	0.7503583349643175	0.6006070584224743
C	3.3350457926186658	0.7747926147500799	-0.4265466776092118
C	1.9825635286266394	0.4857882639964865	-0.1613007666707854
P	0.5993328105171866	0.4325897030295581	-1.2740721717961465
C	-0.4565905274941039	0.0043105784191315	0.1287101527361812
C	-1.8247119275864383	-0.2140163563229729	0.0621447721569997
C	-2.7568909758621380	-0.5126067404403191	1.0926827350253880
C	-4.0404269847316021	-0.6717702840285258	0.6310815082789563
C	-4.1774177946051090	-0.5130643851631793	-0.7689868978069030
S	-2.6396069537817199	-0.1363698020783276	-1.5076293656702273
N	0.2589206883351521	-0.0742839097259638	1.2947881543933393
H	-0.1559322605034936	-0.3004851891375433	2.1869395598727657
C	1.6064484730093709	0.1797460882730928	1.1703888105736051
C	2.5387050746976971	0.1504039810376159	2.2087317463449199
H	4.6044224031230847	0.4148472276546977	2.7039761492288261
H	5.3030468596313085	0.9732078748162041	0.3958805835741313
H	3.6484993964479320	1.0193406475994138	-1.4369221789432201
H	-2.4736315475707125	-0.5931216852197293	2.1333983765276994
H	-4.8822025972052128	-0.9017970239531766	1.2721379775977042
H	2.2263413985025822	-0.0950981528242549	3.2185285189964028

C	-5.3516735546199836	-0.6316970952054763	-1.5432853958805002
C	-5.4916820641441495	-0.5425054643168997	-2.9277172172713364
S	-6.9169521917064953	-0.9223160341711052	-0.7992849919680376
C	-6.8220127389345198	-0.7056961556700817	-3.3610122851161366
H	-4.6590910478881309	-0.3703974551699770	-3.5974703514602595
C	-7.7035875130974629	-0.9168499407727978	-2.3334931006270718
H	-7.1312897440399690	-0.6735638120043069	-4.3976788145361372
H	-8.7726647822103168	-1.0646605792238681	-2.3857295828875063

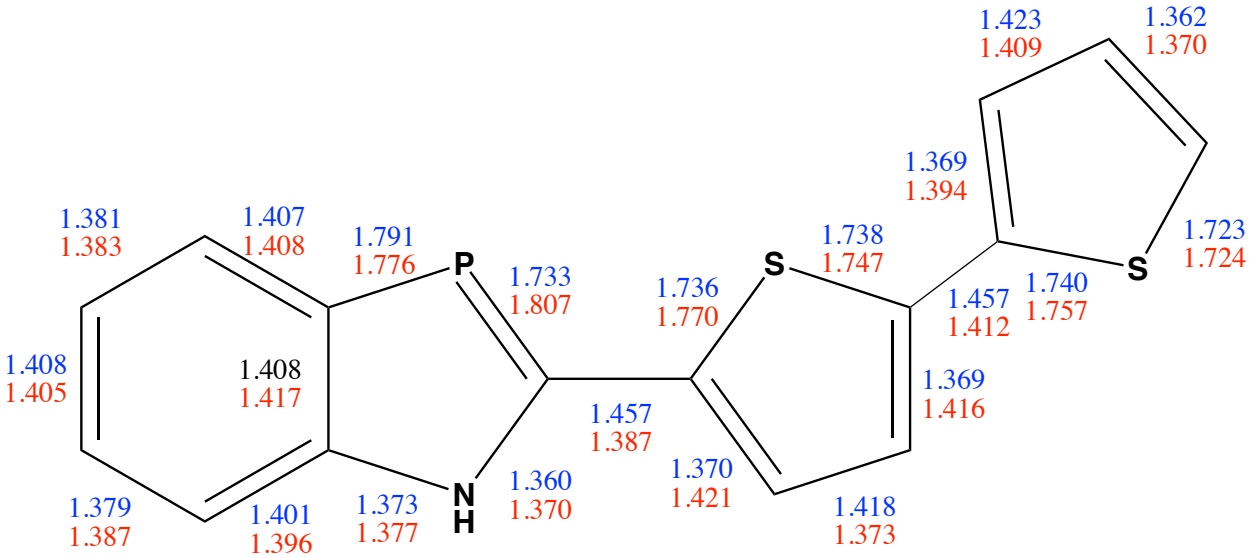
Figure S5. Comparison of key calculated bond distances in ground state and first excited states of **3b** and **3c**

BLUE = Ground State Results
RED = Excited State Results



CPC angles = 88.8°/88.2°

3b

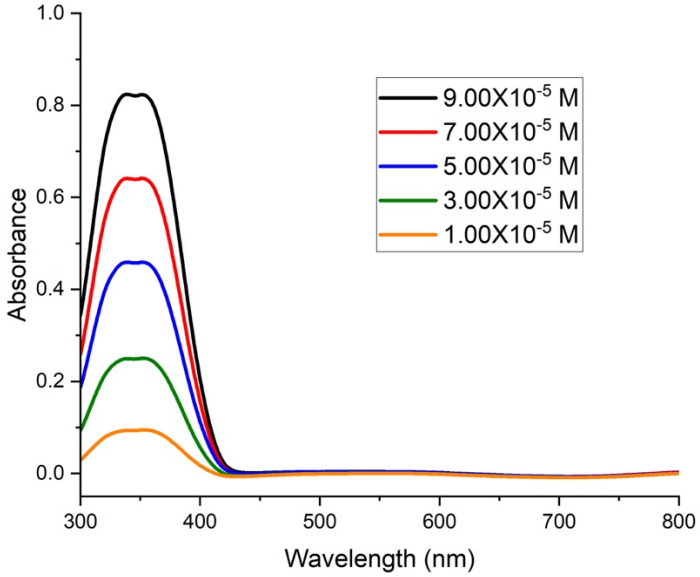


3c

CPC angles = 88.7°/88.6°

Figure S6. (a) UV-vis spectra as a function of concentration (b) plot of Abs vs concentration for **3b** in CH_2Cl_2

(a)



(b)

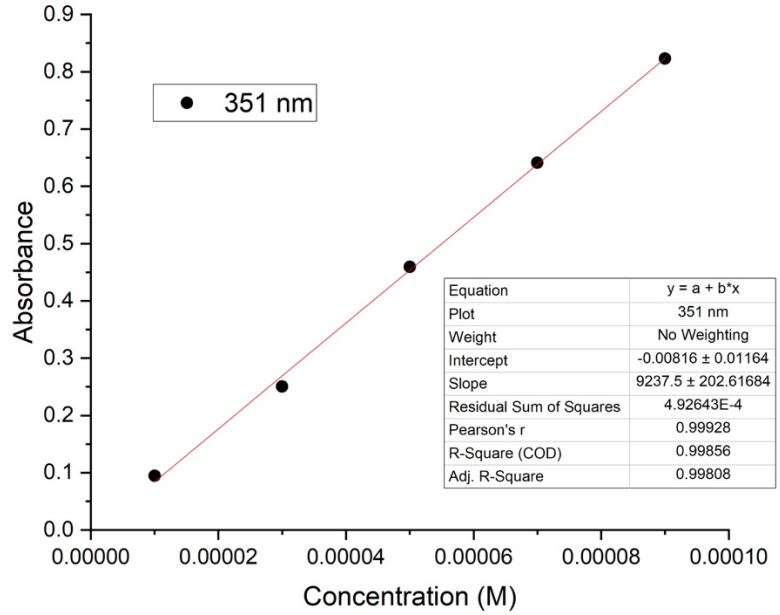
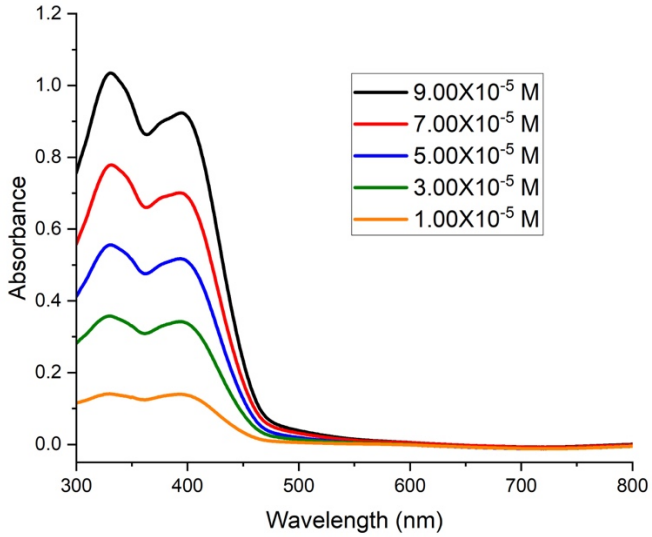


Figure S7. (a) UV-vis spectra as a function of concentration (b) plot of Abs vs concentration for **3c** in CH_2Cl_2

(a)



(b)

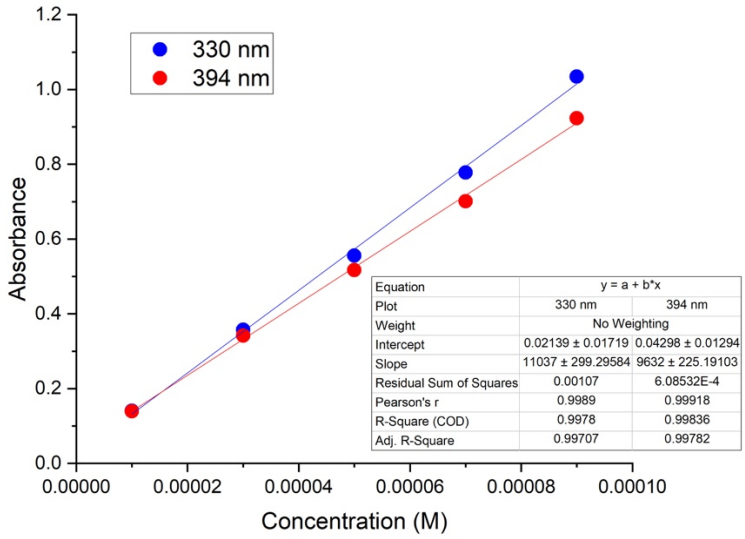
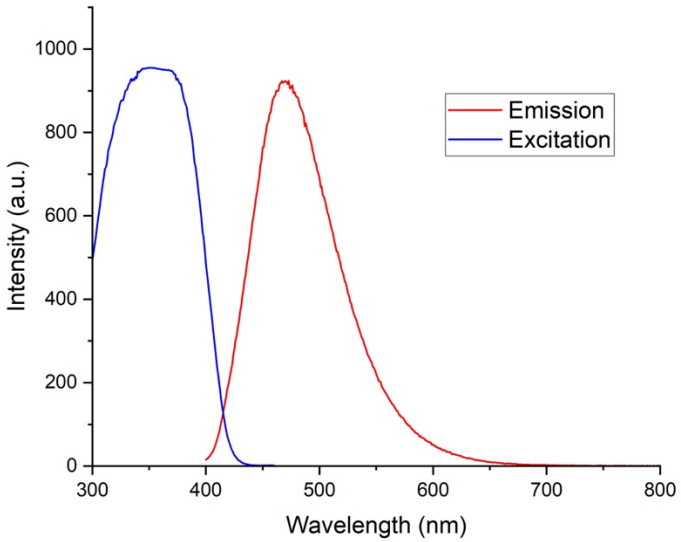


Figure S8. (a) Excitation and emission spectra for **3b** (b) Excitation and emission spectra for **3c** in CH_2Cl_2

(a)



(b)

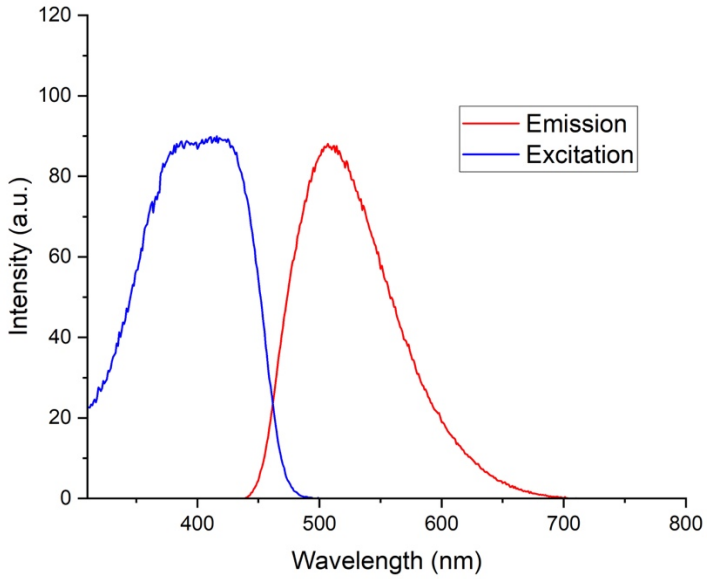
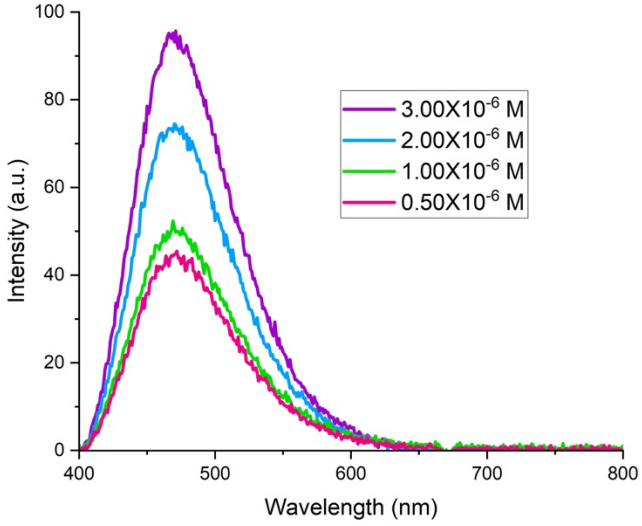


Figure S9. (a) Fluorescence spectra as a function of concentration for **3b** (b) plot of Fluorescence intensity vs concentration for **3b** in CH_2Cl_2

(a)



(b)

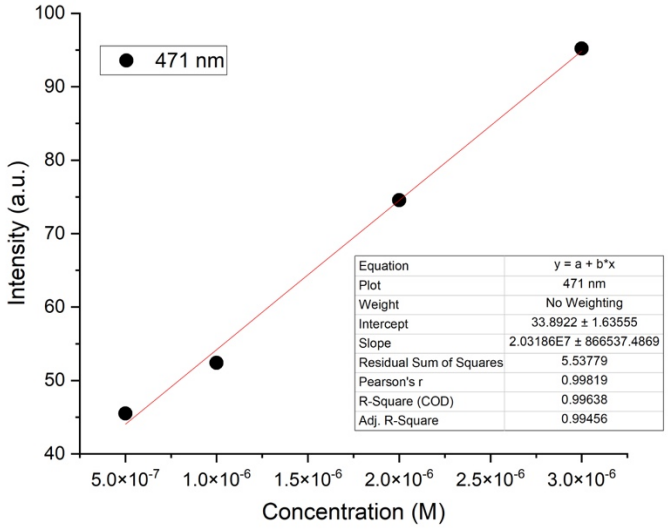
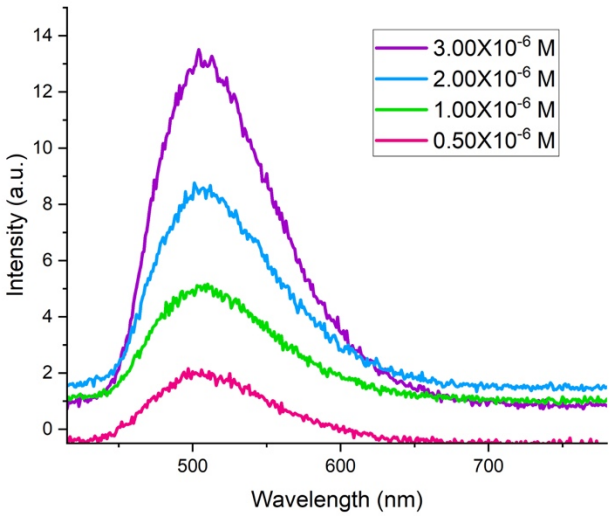


Figure S10. (a) Fluorescence spectra as a function of concentration for **3c** (b) plot of Fluorescence intensity vs concentration for **3c** in CH_2Cl_2

(a)



(b)

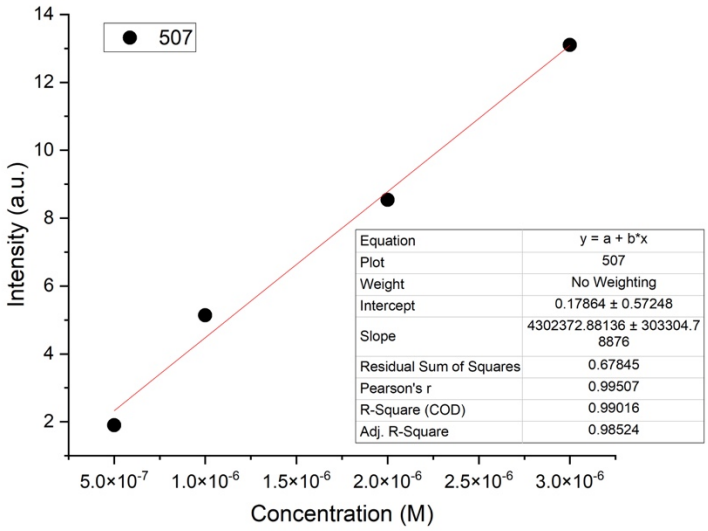
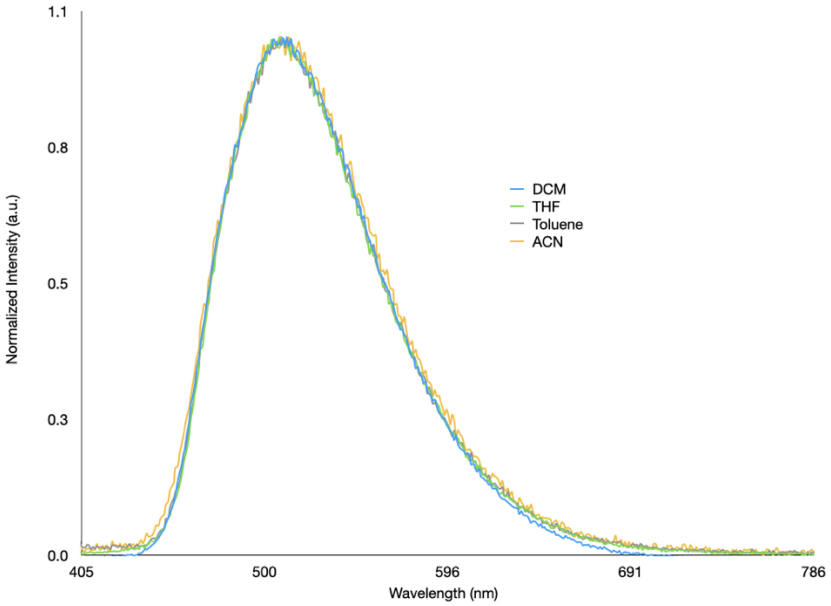


Figure S11. Fluorescence spectra for **3c** in different solvents (normalized).



Lifetime Measurements

Physical Methods. To exclude air, all samples were prepared in a nitrogen-filled glovebox, and kept under nitrogen until immediately before measurement. Fluorescence lifetimes were recorded in deoxygenated dichloromethane in screw-capped 1 cm quartz cuvettes using a Horiba DeltaFlex Lifetime System, using 330 nm pulsed diode excitation sources.

Figure S12 (a). Compound 3b Lifetime (τ): 7.4 ns

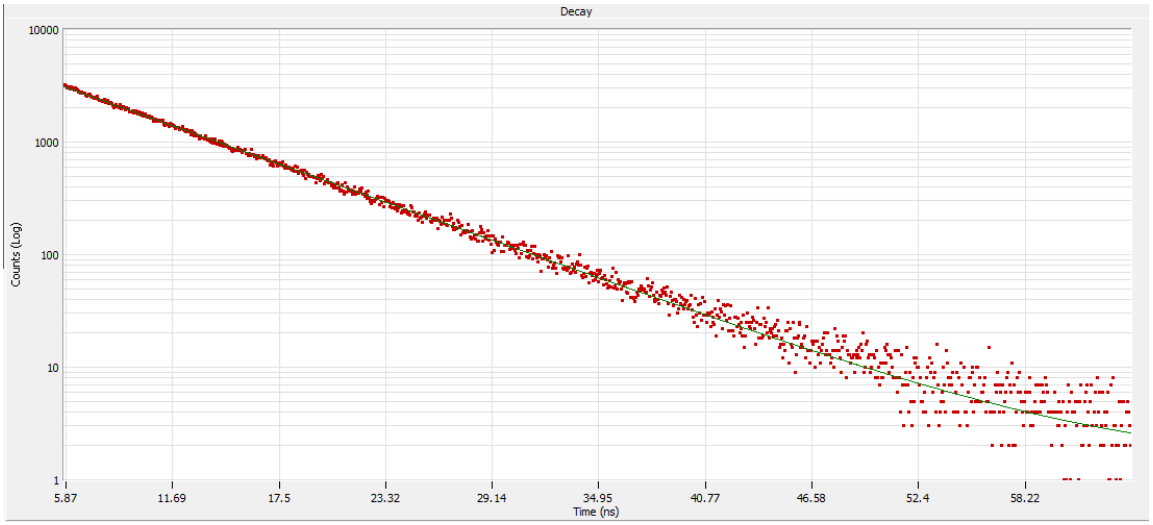


Figure S12 (b). Compound 3c Lifetime (τ): 1.7 ns (bi-exp; 9.0×10^{-10} s (83.58%) & 3.0×10^{-9} s (16.42%))