Supporting Information

Fluorescent *Off-On* NBD Probe for Fluoride Sensing: Theoretical Validation and Experimental Studies

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I. Theoretical Calculations.

Geometry optimization of **4a**, **4**, **5a** and **5** were carried out at CAM-B3LYP/6-311G (d, p) level using Gaussian 09 software.[S1]

The Polarizable Continuum Model (PCM) calculations were performed to find excitation and emission energies. Procedure given in the Gaussian 09 documentation with an example of acetaldehyde molecule was followed.

Following steps were followed for excitation calculations in solvent:

1) Optimize ground state using keyword SCRF. This gives ground state optimized geometry with solvent equilibrated.

2) A TDDFT calculation is performed to find excited states at ground state equilibrium geometry. Solvent is not equilibrated with respect to excited states. This step assumes linear response of the solvent to excited state. Solvent effects are not accurately accounted in this step. State specific solvation method is followed after this step for describing solvent effects.
3) Self consistent calculation is done to consider interaction of solvent and excited state electron density of the molecule. These calculations are called as state specific calculation since; it assumes interaction of particular excited state with the solvent.

Emission calculations were done using following procedure:

1) Excited state is optimized, with linear response from solvent. This optimization is carried using TDDFT method, since, excited state calculation is done. Minimum energy geometry on the excited state (under consideration) is found.
2) State specific equilibrium solvation of excited state at corresponding equilibrium geometry is carried. Then solvation data at this step is written in PCM inputs for next step. This step is necessary to achieve equilibrium of solvent-molecule system for fast and slow degrees of freedom. Usually, electron density is treated as fast degree of freedom which adjusts instantaneously on excitation of molecule. Slow degree often refers to nuclear motion.
3) Ground state energy calculation at excited state geometry is done. Static solvation at excited state is read from PCM inputs written in last step.

Table S1. Atomic coordinates calculated for **4** from DFT/CAM-B3LYP/6-311G (d,p) ground state geometry optimization.

Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

Atom	Atom Type	x	y	z
1	C	-7.2547	-0.2743	0.6270
2	C	-6.1039	-1.1801	0.8425
3	C	-4.9199	-1.0198	0.0897
4	C	-4.8403	-0.0004	-0.8828

5	C	-5.9739	0.9072	-1.1195
6	N	-7.1235	0.6999	-0.3559
7	C	-3.6885	0.1433	-1.6150
8	C	-2.5846	-0.6884	-1.4087
9	C	-2.6263	-1.6855	-0.4549
10	C	-3.8217	-1.8869	0.3145
11	C	-6.2058	-2.1753	1.7820
12	C	-5.1321	-3.0501	1.9957
13	C	-3.9714	-2.9096	1.2802
14	N	-1.5372	-2.5103	-0.1917
15	C	-0.3748	-2.6289	-0.9124
16	O	-0.1019	-2.0506	-1.9359
17	O	-5.9361	1.8062	-1.9384
18	C	-8.2626	1.6000	-0.5789
19	C	-8.2109	2.8361	0.3106
20	C	-9.3980	3.7643	0.0726
21	C	-9.3584	5.0067	0.9558
22	O	-8.2807	-0.3664	1.2734
23	O	0.4185	-3.5144	-0.2963
24	C	1.7240	-3.7443	-0.8874
25	C	2.7293	-2.7273	-0.4347
26	C	3.0953	-1.6652	-1.2533
27	C	4.0141	-0.7150	-0.8297
28	C	4.5845	-0.8143	0.4380
29	C	4.2246	-1.8794	1.2652
30	C	3.3116	-2.8214	0.8290
31	O	5.4647	0.0874	0.9274
32	Si	6.5077	1.2308	0.2285

33	C	5.4587	2.6059	-0.5557
34	C	6.2196	3.9278	-0.7385
35	C	7.4640	1.8842	1.7278
36	C	7.6961	0.8348	2.8231
37	C	7.5229	0.2957	-1.0675
38	C	8.3386	1.1869	-2.0135
39	C	8.7921	2.5626	1.3570
40	C	8.4000	-0.8026	-0.4511
41	C	4.1664	2.8568	0.2350
42	H	-7.1247	-2.2748	2.3443
43	H	-5.2217	-3.8430	2.7265
44	H	-3.1772	-3.6200	1.4667
45	H	-1.6894	-0.5500	-1.9917
46	H	-3.6375	0.9267	-2.3599
47	H	-8.2431	1.8850	-1.6284
48	H	-9.1663	1.0271	-0.3824
49	H	-1.5654	-3.0877	0.6329
50	H	1.9864	-4.7430	-0.5457
51	H	1.6185	-3.7463	-1.9703
52	H	3.0473	-3.6466	1.4814
53	H	4.6776	-1.9518	2.2461
54	H	4.2761	0.1059	-1.4843
55	H	2.6457	-1.5701	-2.2342
56	H	6.7625	-0.2054	-1.6803
57	H	5.1772	2.2514	-1.5551
58	H	5.5894	4.6580	-1.2548
59	H	7.1342	3.8142	-1.3232
60	H	6.4929	4.3629	0.2264

61	H	6.8099	2.6570	2.1524
62	H	6.7628	0.3775	3.1519
63	H	8.3541	0.0336	2.4769
64	H	8.1746	1.2960	3.6927
65	H	9.2402	3.0248	2.2416
66	H	8.6760	3.3440	0.6040
67	H	9.5135	1.8373	0.9724
68	H	3.5683	3.6348	-0.2489
69	H	3.5477	1.9616	0.3143
70	H	4.3831	3.2000	1.2510
71	H	9.1086	1.7506	-1.4813
72	H	8.8461	0.5750	-2.7655
73	H	7.7098	1.9026	-2.5467
74	H	8.8597	-1.4113	-1.2357
75	H	7.8269	-1.4726	0.1938
76	H	9.2108	-0.3791	0.1468
77	H	-8.1937	2.5221	1.3586
78	H	-7.2780	3.3751	0.1195
79	H	-9.4178	4.0639	-0.9806
80	H	-10.3283	3.2156	0.2537
81	H	-10.2167	5.6554	0.7691
82	H	-9.3687	4.7353	2.0147
83	H	-8.4524	5.5900	0.7716

Table S2. Atomic coordinates calculated for **4a** from DFT/CAM-B3LYP/6-311G (d,p) ground state geometry optimization.

Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

Atom	Atom Type	x	y	z

1	C	0.7709	1.2580	-0.4450
2	C	-0.6796	1.3296	-0.1677
3	C	-1.4413	0.1446	-0.0650
4	C	-0.8131	-1.1115	-0.2016
5	C	0.6215	-1.2090	-0.4622
6	N	1.3265	-0.0056	-0.5945
7	C	-1.2731	2.5601	-0.0164
8	C	-2.6447	2.6534	0.2494
9	C	-3.4044	1.5144	0.3510
10	C	-2.8326	0.2349	0.1893
11	C	-1.5741	-2.2578	-0.0833
12	C	-2.9409	-2.2001	0.1519
13	C	-3.5983	-0.9799	0.2829
14	N	-4.9326	-0.9430	0.5349
15	O	1.2111	-2.2712	-0.5691
16	C	2.7653	-0.0855	-0.8733
17	C	3.6072	-0.1148	0.3966
18	C	5.0998	-0.2009	0.0936
19	C	5.9557	-0.2258	1.3554
20	O	1.4640	2.2552	-0.5413
21	H	-0.6615	3.4487	-0.1015
22	H	-3.1043	3.6246	0.3785
23	H	-4.4585	1.6175	0.5741
24	H	-3.5133	-3.1166	0.2266
25	H	-1.0840	-3.2176	-0.1870
26	H	2.9274	-0.9892	-1.4562

27	H	3.0231	0.7808	-1.4790
28	H	-5.4613	-0.1072	0.3535
29	H	-5.4549	-1.8004	0.4518
30	H	3.4021	0.7862	0.9823
31	H	3.3049	-0.9724	1.0054
32	H	5.2972	-1.0992	-0.5009
33	H	5.3920	0.6507	-0.5301
34	H	7.0191	-0.2862	1.1146
35	H	5.7992	0.6762	1.9528
36	H	5.7057	-1.0860	1.9820

Table S3. Atomic coordinates calculated for **5** from DFT/CAM-B3LYP/6-311G (d,p) ground state geometry optimization.

Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

Atom	Atom Type	x	y	z
1	C	-3.2811	-0.1147	-1.2845
2	C	-3.8961	0.4106	-0.1503
3	C	-3.2956	0.2438	1.0958
4	C	-2.1042	-0.4567	1.1990
5	C	-1.4864	-0.9937	0.0737
6	C	-2.0885	-0.8090	-1.1680
7	C	-0.1872	-1.7231	0.1906
8	O	0.8836	-0.7444	0.0786
9	C	2.1200	-1.2297	0.1313
10	N	3.0176	-0.1847	0.0213
11	C	4.3853	-0.2821	0.0286

12	C	5.1170	0.9495	-0.0954
13	C	6.5422	1.0125	-0.1072
14	C	7.2667	-0.2107	0.0117
15	C	6.5553	-1.3654	0.1291
16	C	5.1375	-1.4219	0.1396
17	N	4.6427	2.1580	-0.2140
18	O	5.7193	2.9539	-0.2971
19	N	6.8910	2.2682	-0.2331
20	N	8.7113	-0.2402	0.0078
21	O	9.2703	-1.3175	0.1211
22	O	-5.0444	1.1173	-0.3003
23	Si	-6.6105	0.9700	0.3255
24	C	-7.4297	2.5518	-0.2234
25	C	-7.4336	-0.5690	-0.4264
26	C	-8.8960	-0.6414	0.0437
27	C	-6.5669	0.8716	2.1930
28	O	9.2916	0.8243	-0.1100
29	O	2.4155	-2.3908	0.2546
30	C	-7.4055	-0.4871	-1.9597
31	C	-6.7048	-1.8457	0.0213
32	H	2.6156	0.7389	-0.0697
33	H	-0.0861	-2.2245	1.1527
34	H	-0.0597	-2.4572	-0.6041
35	H	-1.6473	-0.5854	2.1739
36	H	-3.7607	0.6662	1.9765
37	H	-7.8840	-1.3735	-2.3910

38	H	-6.3842	-0.4422	-2.3448
39	H	-7.9434	0.3888	-2.3313
40	H	-6.7180	-1.9651	1.1075
41	H	-5.6623	-1.8594	-0.3058
42	H	-7.1954	-2.7251	-0.4109
43	H	-6.0795	-0.0340	2.5584
44	H	-7.5855	0.8835	2.5891
45	H	-6.0425	1.7340	2.6114
46	H	-6.9120	3.4117	0.2079
47	H	-8.4706	2.5906	0.1060
48	H	-7.4143	2.6584	-1.3098
49	H	7.1087	-2.2903	0.2191
50	H	4.6526	-2.3787	0.2363
51	H	-1.6205	-1.2175	-2.0567
52	H	-3.7510	0.0279	-2.2494
53	H	-9.4722	0.2327	-0.2705
54	H	-8.9747	-0.7240	1.1309
55	H	-9.3808	-1.5247	-0.3866

Table S4. Atomic coordinates calculated for **5a** from DFT/CAM-B3LYP/6-311G (d,p) ground state geometry optimization.

Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

Atom	Atom Type	x	y	z
1	N	-0.1704	1.9759	0.0000
2	C	-0.0702	0.6698	-0.0001
3	C	1.3196	0.3368	0.0000

4	N	2.0176	1.4361	-0.0003
5	O	1.1177	2.4288	-0.0005
6	C	-1.0177	-0.3952	-0.0001
7	C	-0.5317	-1.6811	0.0003
8	C	0.8312	-2.0046	0.0003
9	C	1.8092	-1.0212	0.0002
10	N	3.1233	-1.2442	0.0001
11	N	-2.4262	-0.1520	0.0000
12	O	-3.1898	-1.1088	-0.0015
13	O	-2.8015	1.0116	0.0016
14	H	-1.2570	-2.4837	0.0005
15	H	1.1237	-3.0458	0.0005
16	H	3.7781	-0.4788	0.0000
17	H	3.4907	-2.1820	0.0002

Table S5. Atomic coordinates calculated for **4** from TDDFT/CAM-B3LYP/6-311G (d,p) excited state geometry optimization.

Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

Atom	Atom Type	x	y	z
1	C	3.2581	-2.7965	0.9086
2	C	2.7072	-2.7536	-0.3722
3	C	3.0872	-1.7206	-1.2215
4	C	3.9935	-0.7523	-0.8135
5	C	4.5372	-0.8033	0.4688
6	C	4.1591	-1.8363	1.3286
7	C	1.7186	-3.7916	-0.8087

8	O	0.3941	-3.5384	-0.2566
9	C	-0.3803	-2.6864	-0.9220
10	O	-0.1031	-2.1313	-1.9533
11	O	5.4088	0.1144	0.9408
12	Si	6.4601	1.2384	0.2213
13	C	7.4889	0.2701	-1.0393
14	C	8.3612	-0.8110	-0.3869
15	N	-1.5785	-2.5619	-0.2237
16	C	-2.6500	-1.7633	-0.4906
17	C	-2.5817	-0.7368	-1.4850
18	C	-3.6297	0.1058	-1.6765
19	C	-4.8105	-0.0283	-0.8890
20	C	-4.9233	-1.0405	0.0772
21	C	-3.8445	-1.9562	0.2871
22	C	-5.9054	0.9172	-1.1093
23	N	-7.0467	0.7439	-0.3493
24	C	-7.2074	-0.2407	0.6316
25	C	-6.1052	-1.1631	0.8311
26	C	-4.0115	-2.9780	1.2211
27	C	-5.2032	-3.0797	1.9759
28	C	-6.2295	-2.1950	1.7968
29	O	-8.2514	-0.2984	1.2780
30	O	-5.8169	1.8244	-1.9328
31	C	-8.1596	1.6744	-0.5689
32	C	-8.0735	2.9083	0.3212
33	C	-9.2352	3.8683	0.0842

34	C	-9.1656	5.1065	0.9714
35	C	5.4167	2.5900	-0.6096
36	C	4.1153	2.8576	0.1602
37	C	7.4024	1.9289	1.7125
38	C	8.7322	2.6015	1.3368
39	C	6.1763	3.9087	-0.8191
40	C	7.6275	0.9055	2.8336
41	C	8.3132	1.1388	-1.9988
42	H	-7.1449	-2.2613	2.3672
43	H	-5.2925	-3.8782	2.7016
44	H	-3.2535	-3.7328	1.3804
45	H	-1.6777	-0.6423	-2.0637
46	H	-3.5901	0.8948	-2.4130
47	H	-8.1348	1.9607	-1.6184
48	H	-9.0771	1.1256	-0.3676
49	H	-1.6235	-3.1472	0.5996
50	H	1.9687	-4.7751	-0.4188
51	H	1.6340	-3.8374	-1.8924
52	H	2.9803	-3.5967	1.5857
53	H	4.5899	-1.8701	2.3213
54	H	4.2679	0.0443	-1.4925
55	H	2.6612	-1.6643	-2.2158
56	H	6.7363	-0.2478	-1.6475
57	H	5.1469	2.2081	-1.6021
58	H	5.5501	4.6231	-1.3616
59	H	7.0978	3.7823	-1.3904

60	H	6.4378	4.3699	0.1369
61	H	6.7433	2.7099	2.1138
62	H	6.6923	0.4551	3.1663
63	H	8.2886	0.0973	2.5107
64	H	8.0992	1.3874	3.6956
65	H	9.1699	3.0886	2.2132
66	H	8.6213	3.3620	0.5620
67	H	9.4595	1.8685	0.9791
68	H	3.5216	3.6226	-0.3492
69	H	3.4972	1.9634	0.2537
70	H	4.3199	3.2254	1.1700
71	H	9.0768	1.7169	-1.4729
72	H	8.8294	0.5090	-2.7298
73	H	7.6889	1.8398	-2.5563
74	H	8.8295	-1.4383	-1.1515
75	H	7.7828	-1.4660	0.2687
76	H	9.1657	-0.3717	0.2084
77	H	-8.0649	2.5913	1.3683
78	H	-7.1263	3.4220	0.1306
79	H	-9.2453	4.1716	-0.9681
80	H	-10.1798	3.3433	0.2616
81	H	-10.0067	5.7776	0.7857
82	H	-9.1844	4.8320	2.0294
83	H	-8.2447	5.6672	0.7907

Table S6. Atomic coordinates calculated for **4a** from TDDFT/CAM-B3LYP/6-311G (d,p) excited state geometry optimization.

Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

Atom	Atom Type	x	y	z
1	C	0.7457	1.2790	-0.4393
2	C	-0.6689	1.3431	-0.1682
3	C	-1.4377	0.1643	-0.0669
4	C	-0.8166	-1.0907	-0.2170
5	C	0.6269	-1.1833	-0.4746
6	N	1.3167	0.0011	-0.5939
7	C	-1.3006	2.6073	-0.0092
8	C	-2.6455	2.6719	0.2394
9	C	-3.4309	1.5030	0.3443
10	C	-2.8350	0.2454	0.1940
11	C	-1.5586	-2.2986	-0.1181
12	C	-2.8945	-2.2451	0.1267
13	C	-3.5630	-0.9898	0.2903
14	N	-4.8755	-0.9963	0.5348
15	O	1.1876	-2.2706	-0.5815
16	C	2.7547	-0.0719	-0.8706
17	C	3.5931	-0.1224	0.4010
18	C	5.0867	-0.2058	0.1021
19	C	5.9388	-0.2448	1.3661
20	O	1.4647	2.2751	-0.5388
21	H	-0.6965	3.4997	-0.0915
22	H	-3.1262	3.6353	0.3595
23	H	-4.4885	1.6097	0.5422
24	H	-3.4815	-3.1517	0.2053

25	H	-1.0387	-3.2371	-0.2414
26	H	2.9216	-0.9645	-1.4703
27	H	3.0106	0.8084	-1.4561
28	H	-5.4029	-0.1474	0.6599
29	H	-5.3844	-1.8649	0.6048
30	H	3.3860	0.7713	0.9972
31	H	3.2881	-0.9879	0.9971
32	H	5.2858	-1.0976	-0.5018
33	H	5.3811	0.6524	-0.5114
34	H	7.0029	-0.3050	1.1281
35	H	5.7821	0.6516	1.9718
36	H	5.6853	-1.1107	1.9835

Table S7. Atomic coordinates calculated for **5** from TDDFT/CAM-B3LYP/6-311G (d,p) excited state geometry optimization.

Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

Atom	Atom Type	x	y	z
1	C	-2.0661	-0.8450	-1.1609
2	C	-1.4851	-0.9910	0.0959
3	C	-2.1161	-0.4134	1.1935
4	C	-3.3015	0.2896	1.0482
5	C	-3.8826	0.4159	-0.2122
6	C	-3.2526	-0.1495	-1.3189
7	C	-0.1962	-1.7273	0.2562
8	O	0.8910	-0.7593	0.1379
9	C	2.1146	-1.2588	0.1689

10	O	2.4186	-2.4171	0.2690
11	O	-5.0261	1.1180	-0.4062
12	Si	-6.5959	1.0177	0.2211
13	C	-7.3737	-0.6312	-0.3122
14	C	-7.2985	-0.7841	-1.8387
15	N	3.0224	-0.1971	0.0645
16	C	4.3707	-0.2552	0.0437
17	C	5.0841	0.9733	-0.0516
18	C	6.5108	1.0233	-0.0887
19	C	7.2263	-0.2084	-0.0233
20	C	6.5152	-1.4303	0.0721
21	C	5.1435	-1.4618	0.1049
22	N	4.6010	2.1826	-0.1198
23	O	5.7079	3.0021	-0.2000
24	N	6.8885	2.2704	-0.1799
25	N	8.6480	-0.2313	-0.0495
26	O	9.2089	-1.3267	0.0262
27	O	9.2419	0.8401	-0.1463
28	C	-6.5758	1.1887	2.0837
29	C	-7.4436	2.4866	-0.5523
30	C	-6.6476	-1.8151	0.3462
31	C	-8.8495	-0.6532	0.1207
32	H	2.6018	0.7257	0.0048
33	H	-0.1107	-2.2001	1.2342
34	H	-0.0557	-2.4819	-0.5164
35	H	-1.6752	-0.5120	2.1792

36	H	-3.7773	0.7439	1.9071
37	H	-7.7671	-1.7266	-2.1432
38	H	-6.2659	-0.7984	-2.1948
39	H	-7.8212	0.0238	-2.3572
40	H	-6.7008	-1.7718	1.4368
41	H	-5.5934	-1.8607	0.0625
42	H	-7.1123	-2.7567	0.0329
43	H	-6.0825	0.3529	2.5825
44	H	-7.6003	1.2412	2.4614
45	H	-6.0687	2.1104	2.3793
46	H	-6.9390	3.4093	-0.2562
47	H	-8.4835	2.5571	-0.2255
48	H	-7.4344	2.4316	-1.6425
49	H	7.0863	-2.3439	0.1197
50	H	4.6202	-2.4013	0.1785
51	H	-1.5870	-1.2858	-2.0280
52	H	-3.7075	-0.0372	-2.2949
53	H	-9.4255	0.1518	-0.3428
54	H	-8.9615	-0.5667	1.2048
55	H	-9.3101	-1.6006	-0.1805

Table S8. Atomic coordinates calculated for **5a** from TDDFT/CAM-B3LYP/6-311G (d,p) excited state geometry optimization.

Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

Atom	Atom Type	x	y	z
1	N	-0.1874	1.9740	0.0000

2	C	-0.0526	0.6749	-0.0001
3	C	1.3339	0.3456	0.0000
4	N	2.0524	1.4404	0.0001
5	O	1.1173	2.4678	0.0001
6	C	-1.0011	-0.3962	-0.0001
7	C	-0.5565	-1.7375	-0.0002
8	C	0.7851	-2.0312	-0.0002
9	C	1.7862	-1.0014	0.0000
10	N	3.0844	-1.2863	0.0001
11	N	-2.4031	-0.1327	0.0000
12	O	-3.1706	-1.0960	0.0005
13	O	-2.7713	1.0379	-0.0004
14	H	-1.2974	-2.5209	-0.0002
15	H	1.1105	-3.0633	-0.0002
16	H	3.7729	-0.5463	0.0001
17	H	3.4172	-2.2399	0.0000

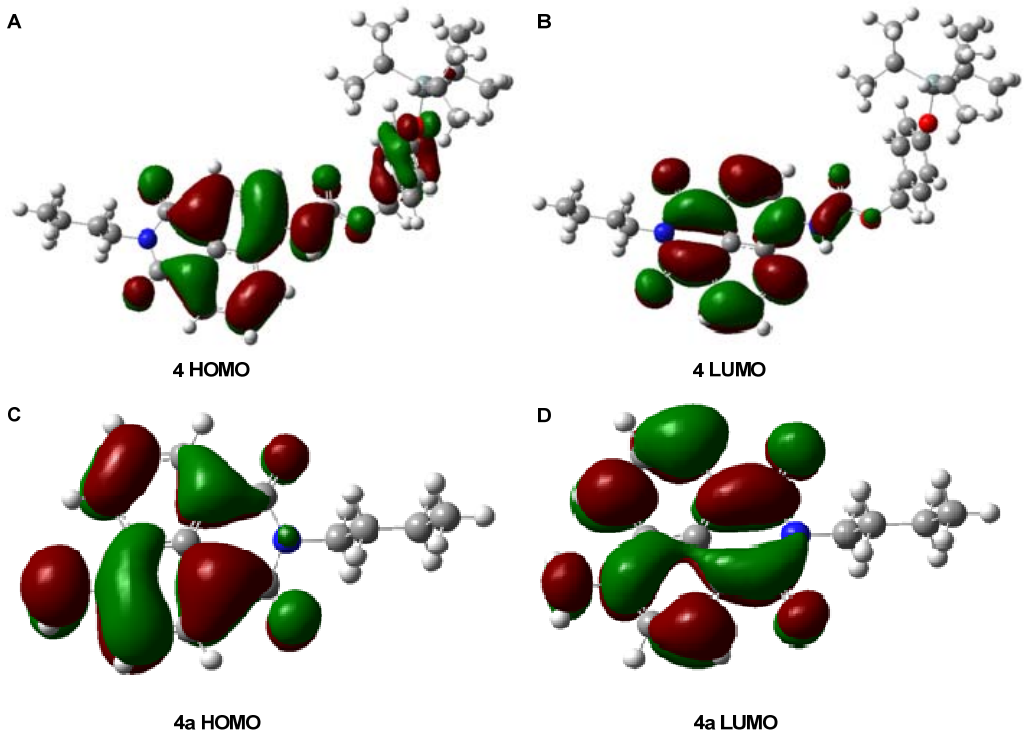


Fig. S1 View of the ground state frontier molecular orbitals (MOs), HOMO (**A**), LUMO (**B**) of **4** and HOMO (**C**), LUMO (**D**) of **4a** generated from TDDFT/CAM-B3LYP/6-311G (d,p) geometry optimization.

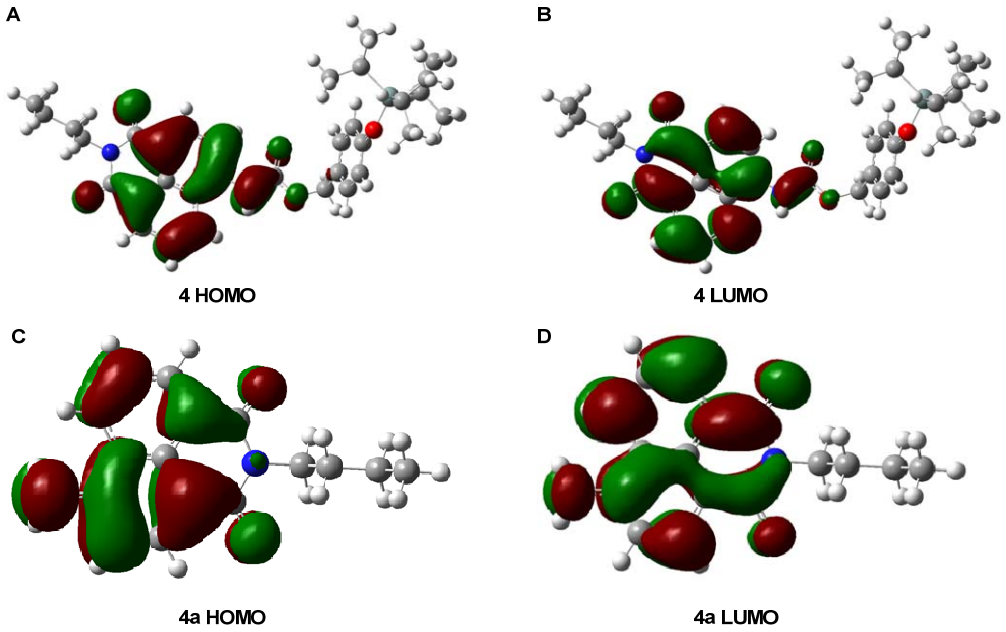


Fig. S2 View of the excited state frontier molecular orbitals (MOs), HOMO (**A**), LUMO (**B**) of **4** and HOMO (**C**), LUMO (**D**) of **4a** generated from TDDFT/CAM-B3LYP/6-311G (d,p) geometry optimization.

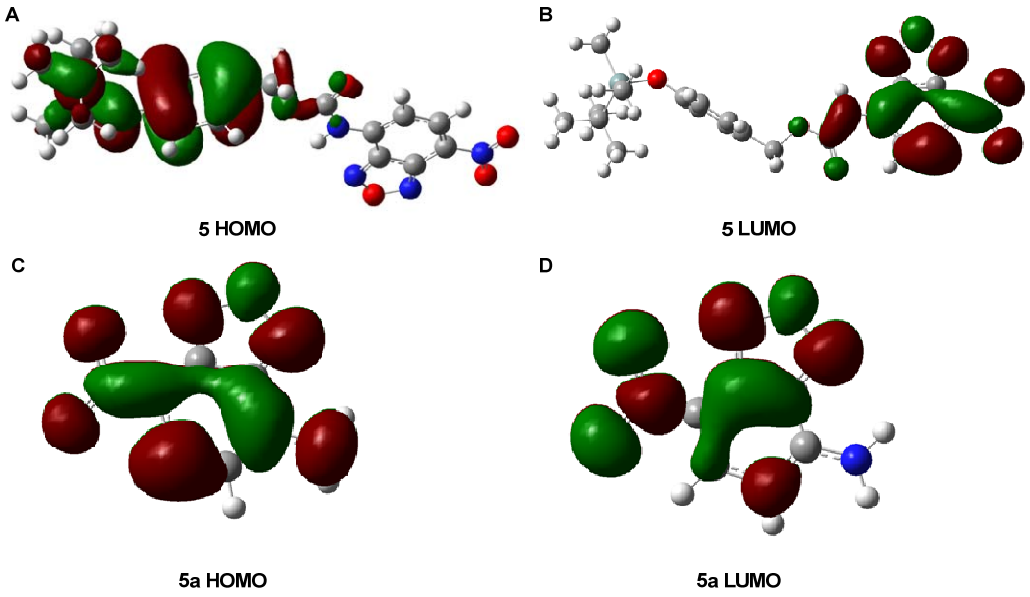


Fig. S3 View of the ground state frontier molecular orbitals (MOs), HOMO (**A**), LUMO (**B**) of **5** and HOMO (**C**), LUMO (**D**) of **5a** generated from TDDFT/CAM-B3LYP/6-311G (d,p) geometry optimization.

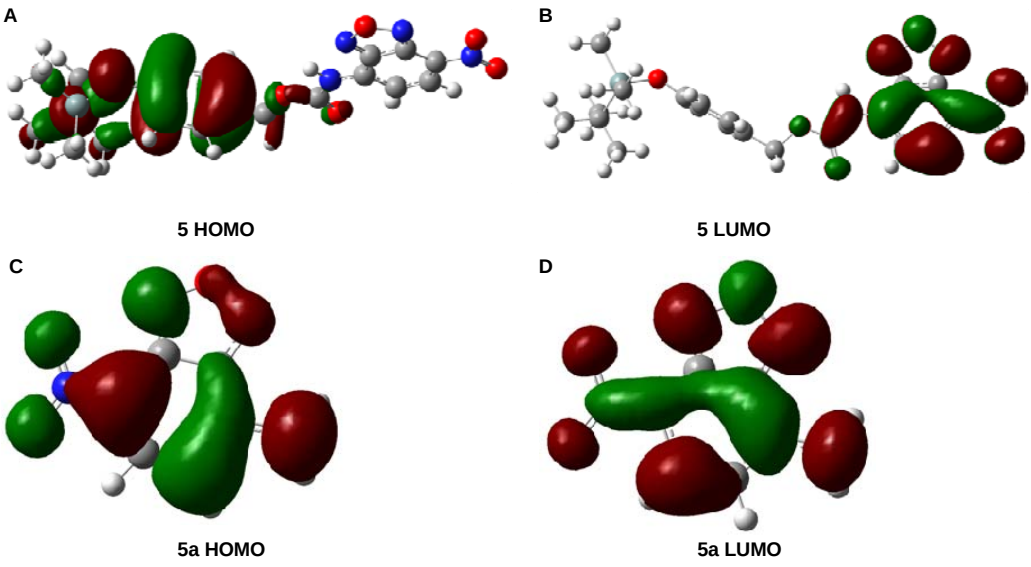
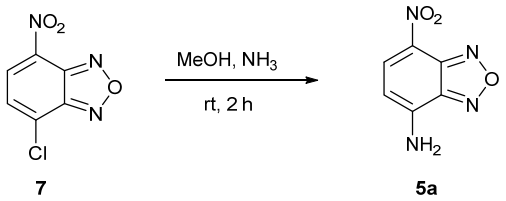


Fig. S4 View of the excited state frontier molecular orbitals (MOs), HOMO (**A**), LUMO (**B**) of **5** and HOMO (**C**), LUMO (**D**) of **5a** generated from TDDFT/CAM-B3LYP/6-311G (d,p) geometry optimization.

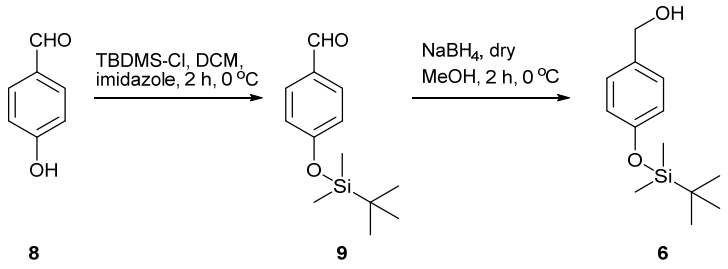
II. Synthetic Procedures.



7 5a

Scheme S1. Synthesis of NBD-amine **5a**.

Synthesis of NBD-amine 5a: Compound NBD-Cl **7** (1 g, 5.025 mmol) was dissolved in MeOH (100 mL). To this solution was added 25% aqueous ammonia solution (20 mL) was added dropwise and kept at room temperature for 12 hours. At the completion of the reaction, solvent was evaporated from the reaction mixture under reduced pressure and the residue was subjected to column chromatography to afford 60% **5a** as brown powder. **^{1}H NMR (400 MHz, 1:1 $CDCl_3$/CD_3OD)**: δ 8.23 (d, *J* = 8.6 Hz, 1H); 6.14 (d, *J* = 8.7 Hz, 1H). The obtained data were matched with the literature data.[S2]



8 9 6

Scheme S2. Synthesis of alcohol **6**.

Synthesis of 4-((*tert*-butyldimethylsilyl)oxy)benzaldehyde 9: 4-hydroxybenzaldehyde **8** (2 g, 16.39 mmol) was dissolved in DCM (30 mL) and subsequently imidazole (1.671 g, 24.58 mmol) was added to it. Then, *tert*-butyldimethylsilylchloride (TBDMS-Cl) (0.533 g, 32.7 mmol) solution in DCM was added dropwisely to the solution at 0 °C. This temperature was maintained for 2 h. After completion of reaction, organic layer was washed with water, brine (10mL) and dried over Na_2SO_4. The solvent was removed in reduced pressure and the obtained residue was purified by column chromatography (*Eluent:* 3% EtOAc in petroleum ether) to get pure product **9**. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.77 (d, *J* = 8.6 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 1H). Obtained data were matched with literature data.[S3]

Synthesis of (4-((tert-butyldimethylsilyl)oxy)phenyl)methanol 6: Compound **9** (1.25 g, 5.08 mmol) was dissolved in dry MeOH (20 mL) and stirred for 15 min at 0 ^{o}C. Then $NaBH_4$ (0.23 g, 6.1 mmol) was added to the reaction mixture and kept for 2 h at this temperature. The solvent was evaporated under reduced pressure and the crude was extracted with EtOAc (15 mL x 2), water (15 mL x 2), brine (20 mL) and dried over Na_2SO_4. The organic layer was evaporated under reduced pressure and the residue was purified through column chromatography over silica gel to get pure **6** (*Eluent:* 15% EtOAc in petroleum ether) as colorless liquid (1.1 g, 87%). **^{1}H NMR (400 MHz, $CDCl_3$)**: 7.21 (d, *J* = 8.4 Hz, 1H), 6.81 (d, *J* = 8.5 Hz, 1H). Obtained data were matched with literature data.[S3]

III. Crystal structure Parameters.[S4]

The compound was crystallized from THF at room temperature. Single-crystal X-ray data of compound **5** was collected at 200 K on a Bruker KAPPA APEX II CCD Duo diffractometer (operated at 1500 W power: 50 kV, 30 mA) using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data integration and reduction were processed with SAINT[S4a] software. A multi-scan absorption correction was applied to the collected reflections. The structures were solved by the direct method using SHELXTL[S4b] and were refined on F^2 by full-matrix least-squares technique using the SHELXL-97[S4c] program package within the WINGX programme.[S4d] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in successive difference Fourier maps and they were treated as riding atoms using SHELXL default parameters. The structures were examined using the *Adsym* subroutine of PLATON[S4e] to assure that no additional symmetry could be applied to the models.

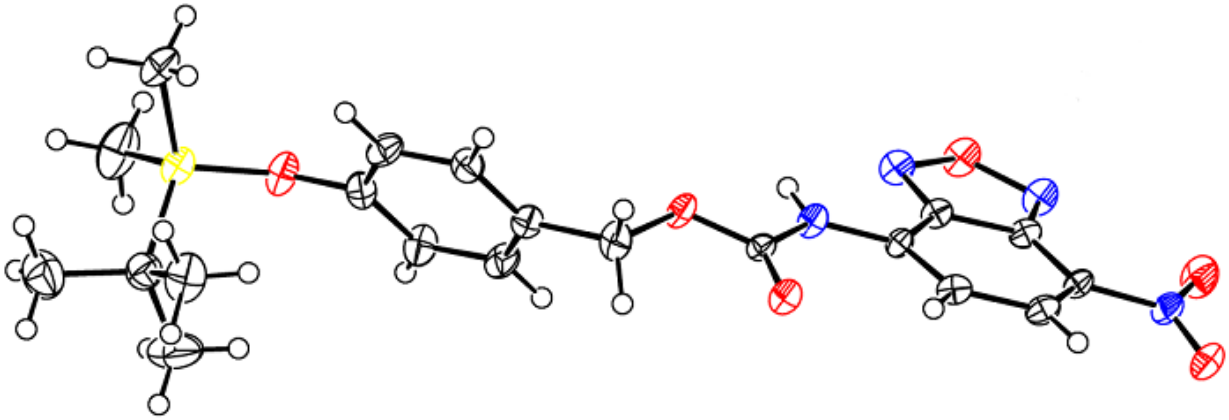


Fig. S5 ORTEP diagram of probe **5**.

IV. Photophysical Properties.

Absorption spectra, emission spectra and determination of molar extinction coefficient of species 5 and 5a.

Absorption spectra and fluorescence spectra of probe **5** (10 μM) were recorded in 9:1 EtOH/HEPES (10 mM, pH = 7.4) solution. Molar absorption coefficients were determined from absorption spectra using Lambert-Beer Law.

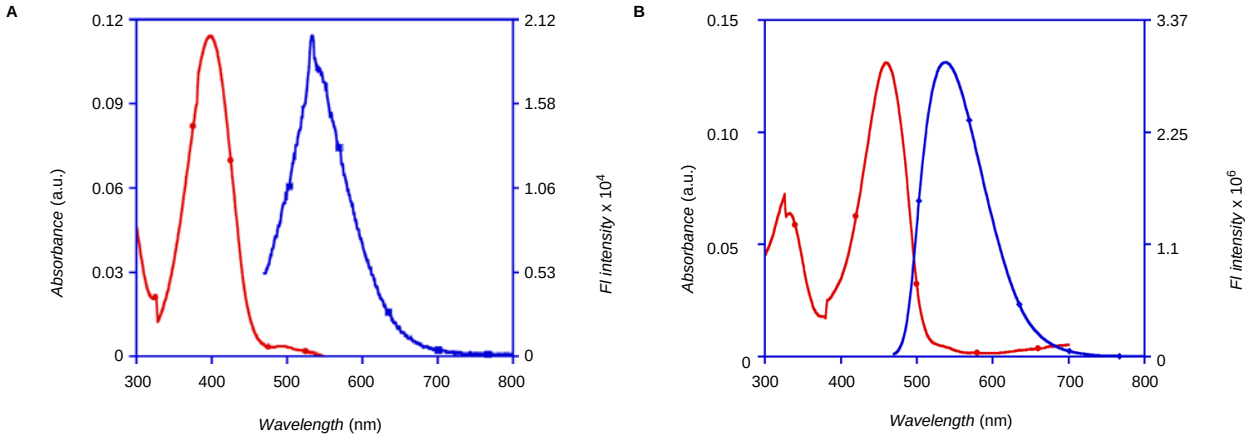


Fig. S6 UV-vis absorption and emission spectra of probe **5** (**A**) and **5a** (**B**) in 9:1 EtOH/HEPES buffer (10 mM, pH = 7.4) solution at room temperature. All data were recorded at 10 μM concentrations.

Table S6. Photophysical Properties of probe **5** and **5a**.

Compound	λ_{max} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Φ [a]
5	399	12190	535	0.0495
5a	459	13113	535	0.36

[a] Standard: NBD-NHMe in acetonitrile $\Phi_F = 0.38$.

Time Resolved Fluorescence data of 5 and 5a.

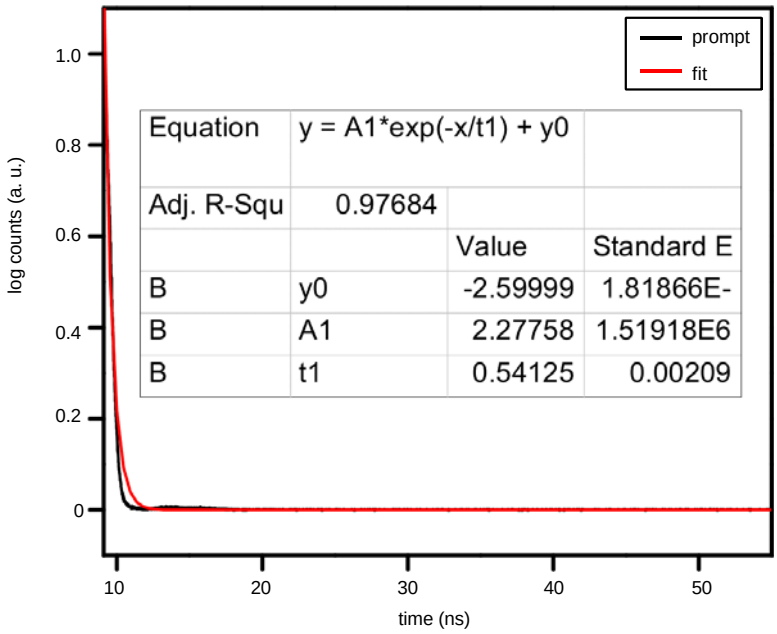


Fig. S7 Fluorescence lifetime decay profiles (λ_{ex} = 460 nm) of prompt (—) and fit (—) in 9:1 ethanol/HEPES buffer (10 mM, pH = 7.4) monitored at 535 nm.

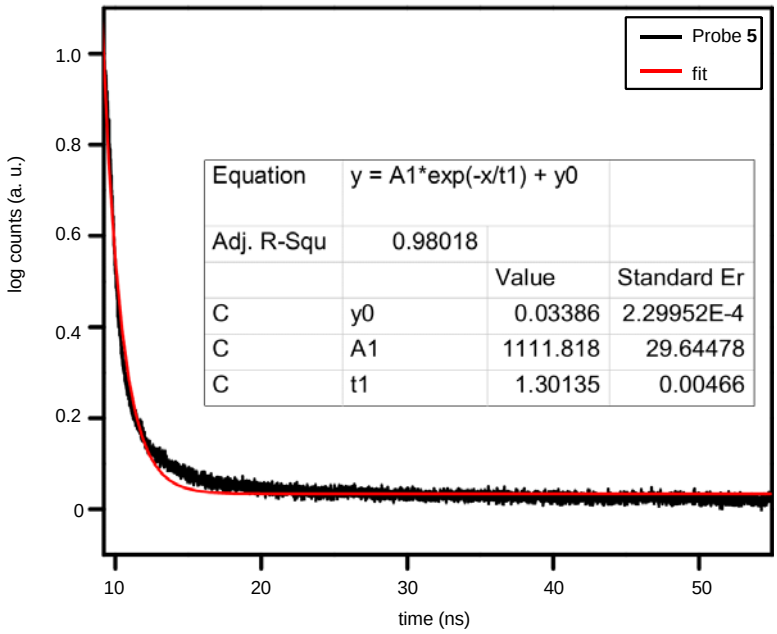


Fig. S8 Fluorescence lifetime decay profiles (λ_{ex} = 460 nm) of probe **5** (—) and fit (—) in 9:1 ethanol/HEPES buffer (10 mM, pH = 7.4) monitored at 535 nm.

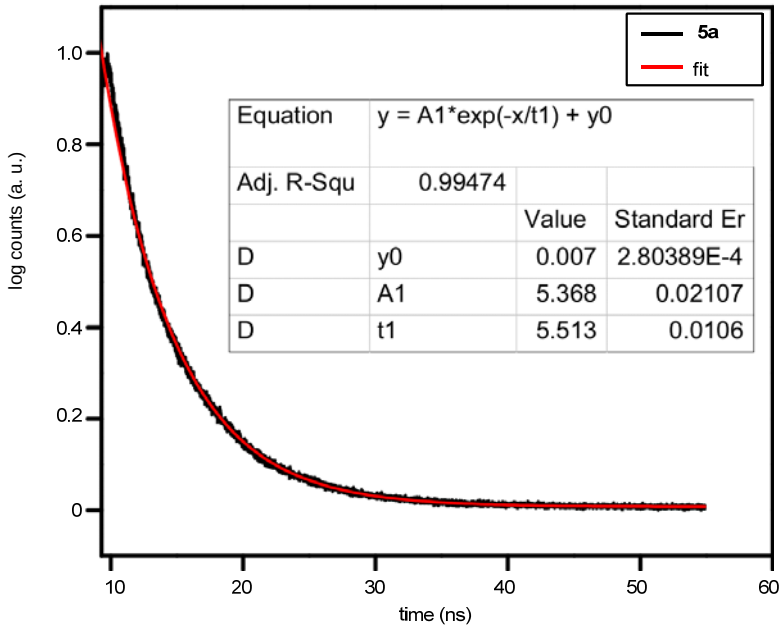


Fig. S9 Fluorescence lifetime decay profiles (λ_{ex} = 460 nm) of NBD-amine **5a** (—) and fit (—) in 9:1 ethanol/HEPES buffer (10 mM, pH = 7.4) monitored at 535 nm.

V. Fluoride Sensing.

Procedures:

Preparation of Solvent System: HEPES (10 mM, pH = 7.4) buffer was prepared by using deionized water. Solvent system was prepared by mixing 90% EtOH and 10% HEPES buffer (10 mM, pH = 7.4).

Preparation of the sample Solutions: A stock solution of probe (3777 μM) was prepared in THF. The final concentration during assay is 10 μM. Stock solution of TBAF was prepared by diluting 1 M TBAF in THF.

General Methods for UV-vis and Fluorescence titration:

For absorbance and emission studies 1 cm path length was used for cells. All UV and Fluorescence measurements were performed with 10 μM of probe. Fluorescence measurements were done using 2 nm x 5 nm slit. Fluorescence titrations were performed after 1 hour of mixing of probe and TBAF.

Determination of quantum yields:

The quantum yield of probe was determined according to the following equation:

$$\Phi_1 = \Phi_B \times \frac{I_1 \times A_B \times \lambda_{exB} \times (\eta_1)^2}{I_B \times A_1 \times \lambda_{ex1} \times (\eta_B)^2} \qquad \textbf{Equation S1}$$

where, Φ is quantum yield; I is integrated area under the corrected emission spectra; A is absorbance at the excitation wavelength; λ_{ex} is the excitation wavelength; η is the refractive index of the solution; the subscripts 1 and B refer to the unknown and the standard, respectively.

N-methyl NBD was used as standard (Φ = 0.38) in acetonitrile.[S5]

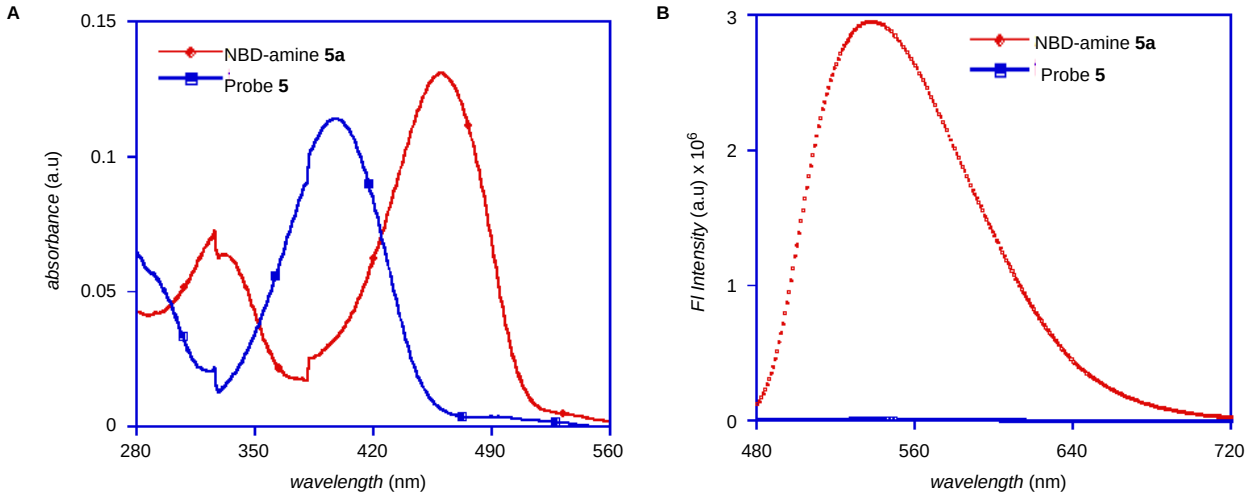


Fig. S10 UV-vis absorption spectra (left) and emission spectra (right) of **5a** (10 μM) and probe **5** (10 μM) in 9:1 EtOH/HEPES buffer (10 mM, pH = 7.4) solution at room temperature.

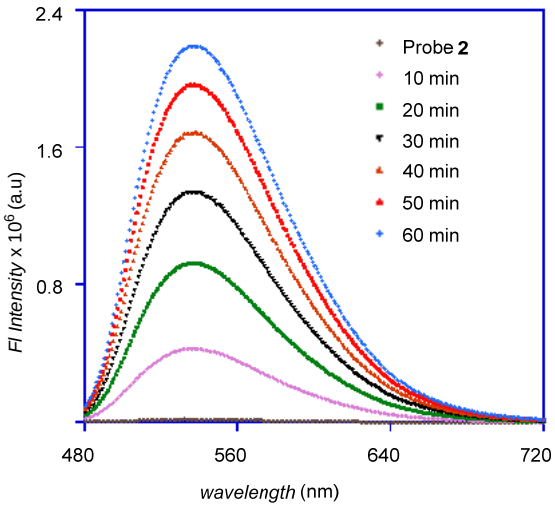


Fig. S11 Reaction time profile of probe **5** (10 μM) in 9:1 EtOH/HEPES buffer (10 mM, pH = 7.4) solution upon addition of TBAF (2 mM) at rt.

VI. Live Cell Imaging.

The A549 cells were purchased from National Centre for Cell Science, Pune (India). A549 cells were grown in DMEM supplemented with 10% heat inactivated fetal bovine serum (FBS), 100 IU/mL penicillin, 100 mg/mL streptomycin and 2 mM L-glutamine. Cultures were maintained in a humidified atmosphere with 5% CO_2 at 37 ^oC. The cultured cells were subcultured twice in each week, seeding at a density of about 15 × 10^4 cells/mL. Typan blue dye exclusion method was used to determine Cell viability. The fluorescence images were taken using Olympus Inverted IX81 equipped with Hamamatsu Orca R2 microscope by exciting at λ_{ex} = 460-480 nm (by using GFP filter). The A549 cells were incubated with solution of the probe (50 μM in 1:100 DMSO-DMEM v/v, pH = 7.4) at 37 ^oC for 7 h. After washing with PBS the fluorescence images were acquired. In this case no significant fluorescence was observed. Another set of A549 cells were treated with NaF (50 mM in 1:100 DMSO-DMEM v/v, pH = 7.4) at 37 ^oC for 3 h and then the cells were washed thoroughly by PBS and incubated with solution of the probe (50 μM in 1:100 DMSO-DMEM v/v, pH = 7.4) at 37 ^oC for 7 h. After washing with PBS the fluorescence images showed strong green fluorescence.

VII. NMR and Mass Data.

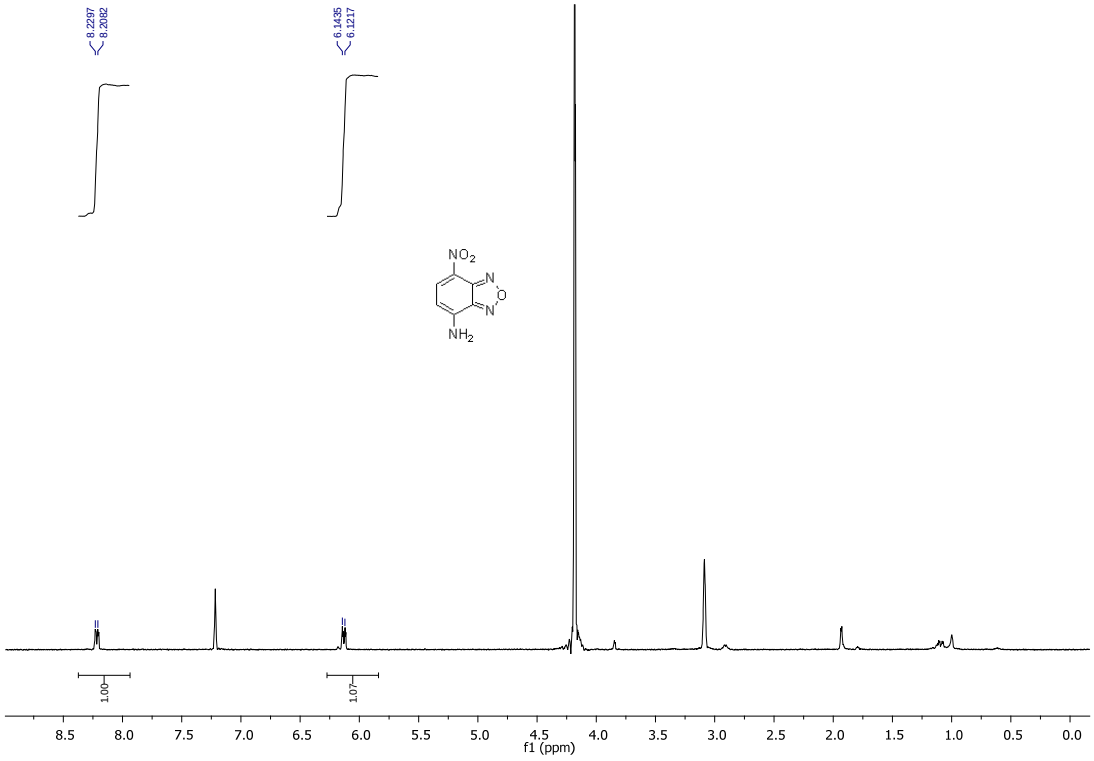


Fig. S12 ^{1}H NMR data of **5a** in $CDCl_3$.

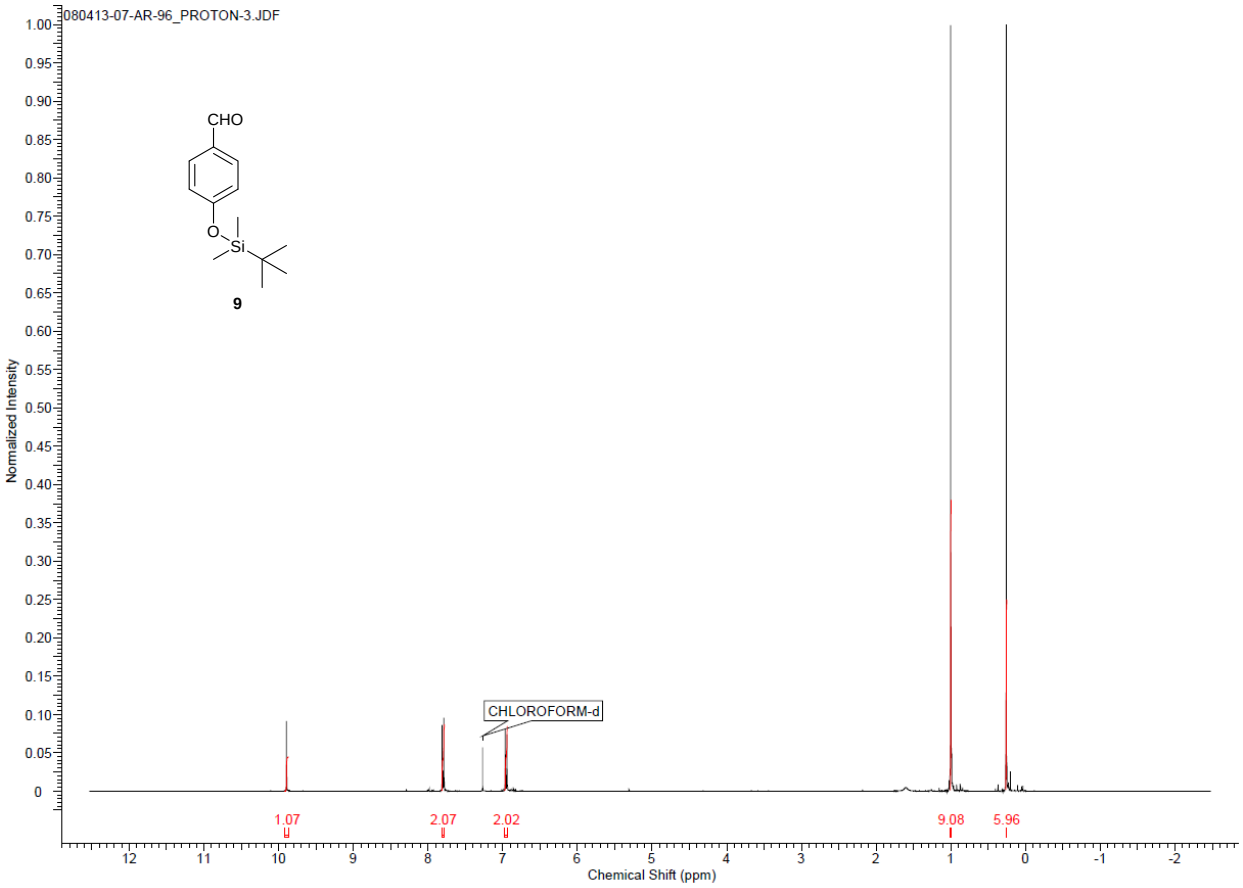


Fig. S13 ^{1}H NMR data of **9** in $CDCl_3$.

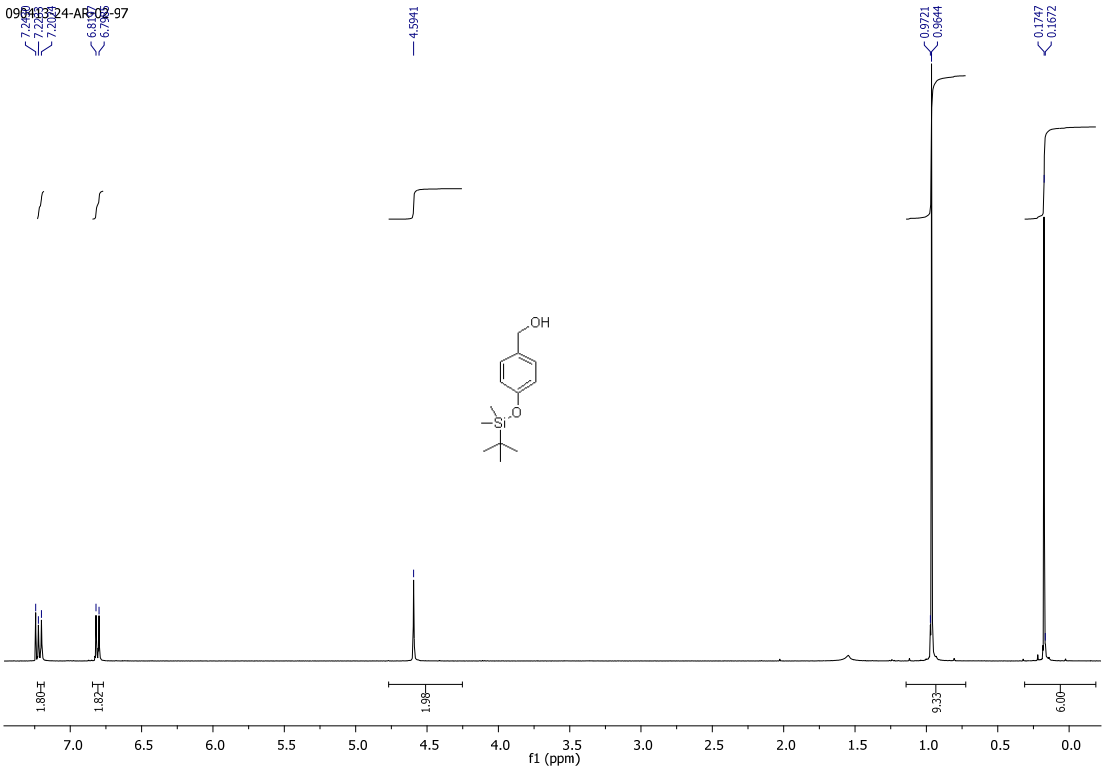


Fig. S14 ^{1}H NMR data of **6** in $CDCl_3$.

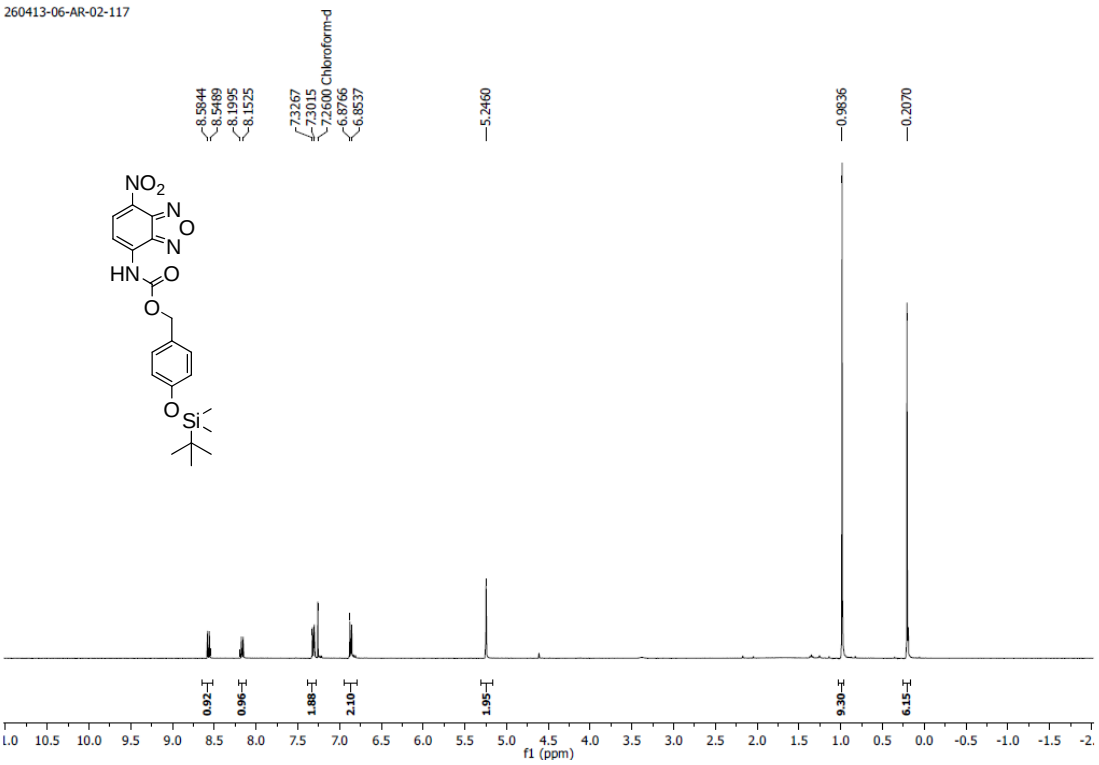


Fig. S15 ^{1}H NMR data of probe **5** in $CDCl_3$.

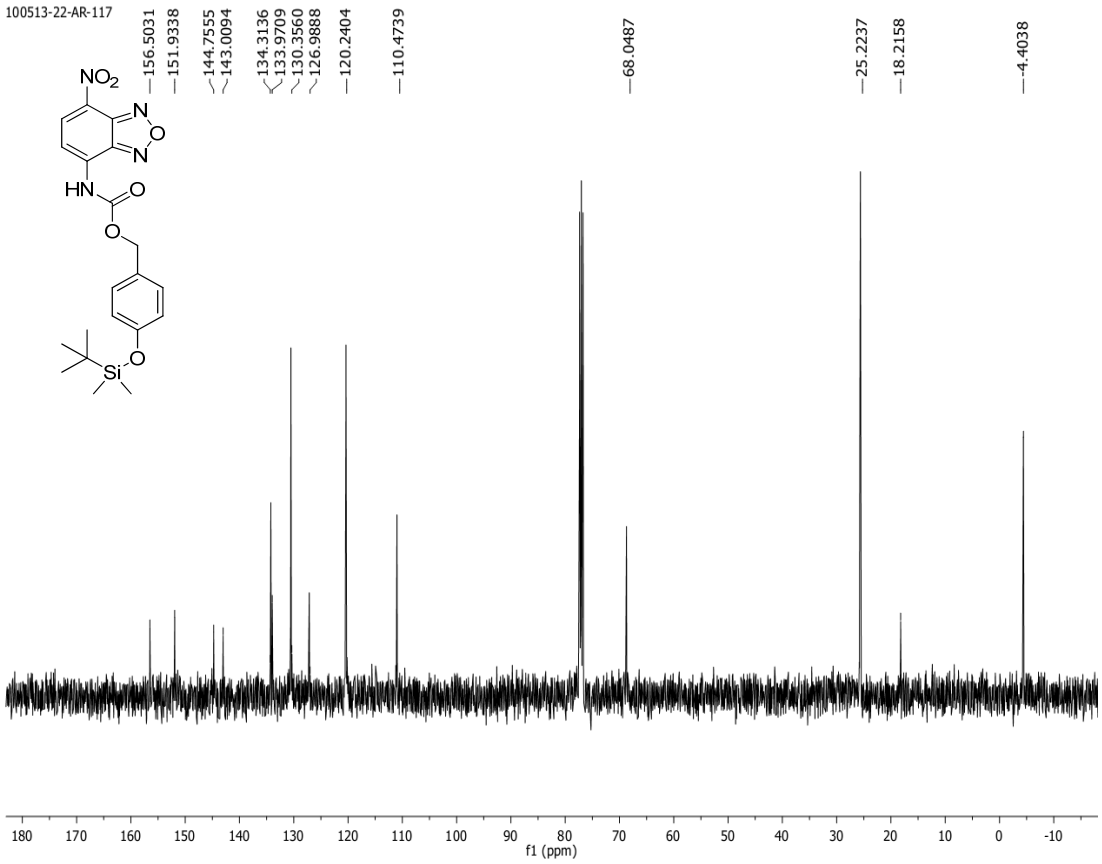


Fig. S16 ^{13}C NMR data of probe **5** in $CDCl_3$.

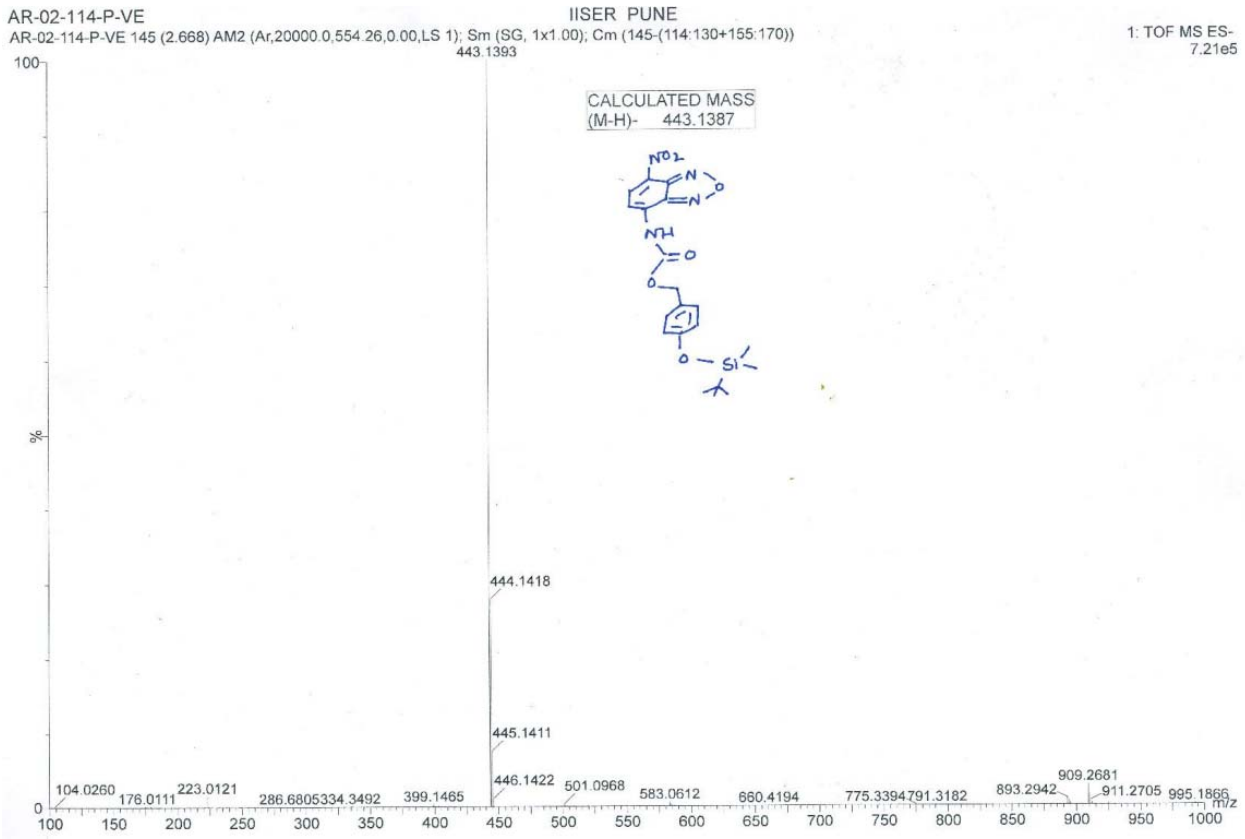


Fig. S17 HRMS data of probe **5**.

VIII. References.

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