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

Supporting Information

Interplay of conformational relaxation and hydrogen bond dynamics in the excited states of fluorescent Schiff base anions

Souradip Dasgupta, Arkaprava Chowdhury, Dipak Kumar Sahoo,

Anindya Datta

Department of Chemistry, Indian Institute of Technology Bombay,

Powai, Mumbai 400 076, India

e-mail: anindya@chem.iitb.ac.in (AD)
Phone: +91 22 2576 7149, Fax: +91 22 2576 7152

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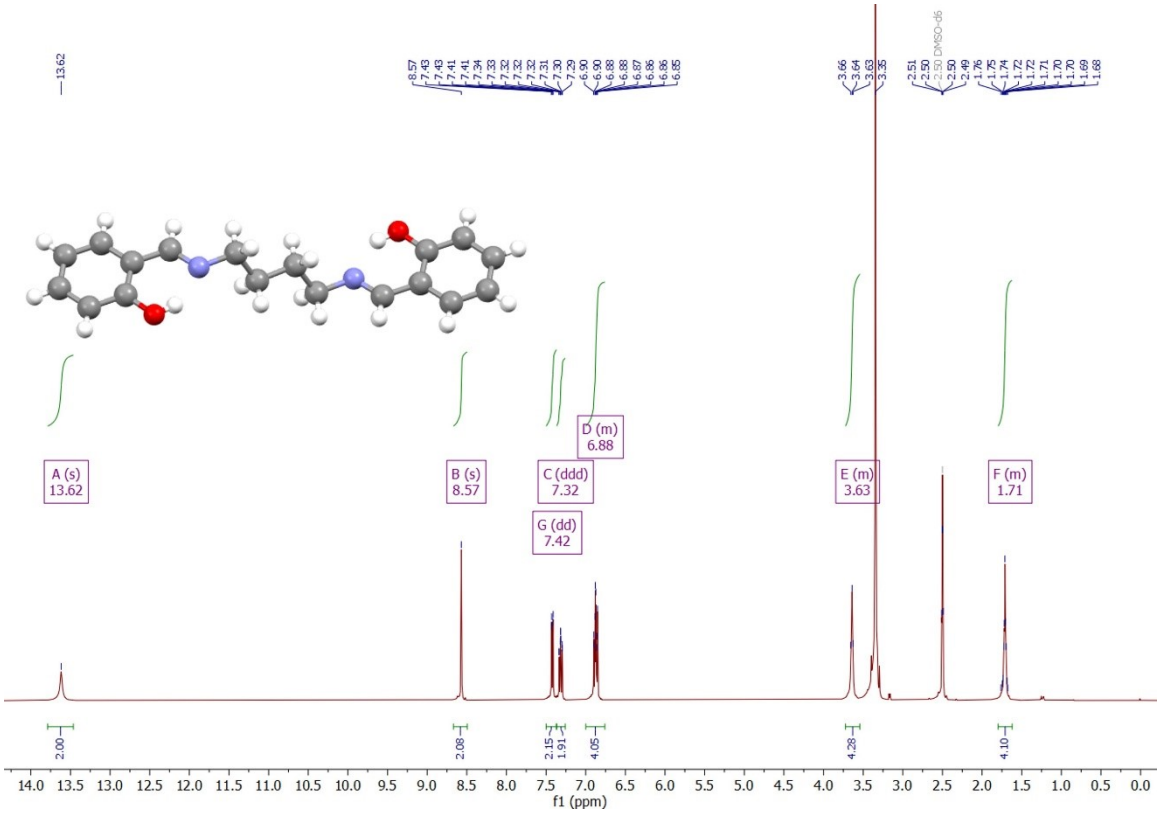

Figure S1. ^{1}NMR spectra of salbn in DMSO-d_6. Inset- crystal structure.

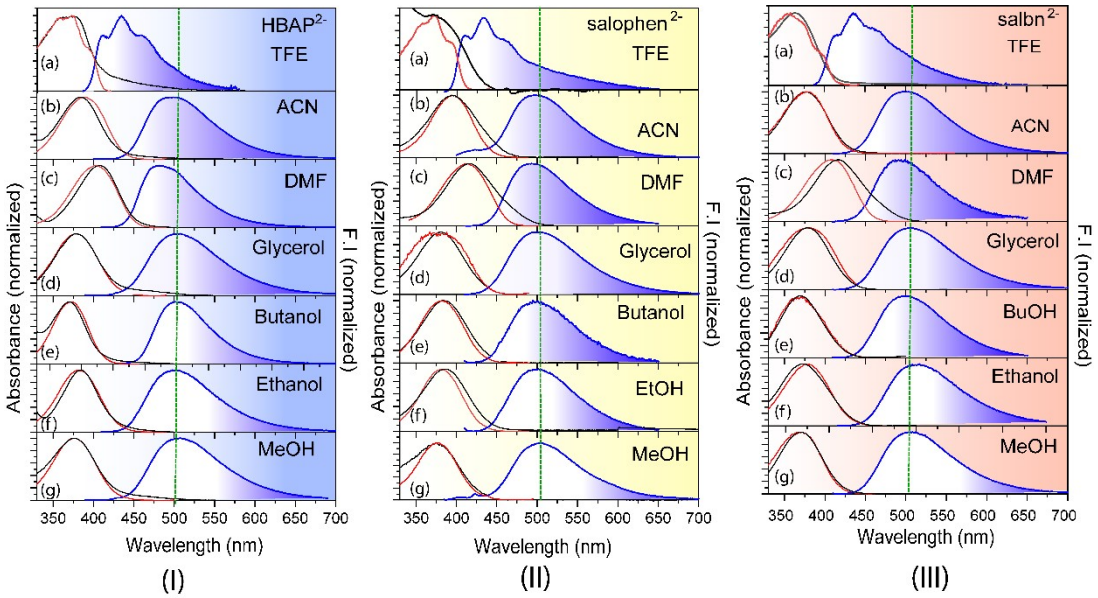

Figure S2. Absorption (black), Fluorescence Emission (blue) and excitation (red) of (I) $HBAP^{2-}$ (II) $salophen^{2-}$ (III) $salbn^{2-}$ in (a) TFE (b) ACN (c) DMF (d) Glycerol (e) BuOH (f) EtOH (g) MeOH. Steady state spectra of $salophen^{2-}$, $HBAP^{2-}$ in MeOH was found to be same as that reported in our earlier reports. (references 33-35 of the main manuscript)

Table ST1. Photophysical parameters of (a) $HBAP^{2-}$ (b)$salophen^{2-}$ (c) $salbn^{2-}$ in different solvents

Solvent	Δf	$\tilde{\nu}_{abs}$(cm^{-1})	$\tilde{\nu}_{em}$(cm^{-1})	$\Delta\tilde{\nu}$ (cm^{-1})	ϕ_f	τ_f (ns)
(a) $HBAP^{2-}$						
Glycerol	0.27	26316	19685	6631	0.13	1.5
ACN	0.31	25189	20619	4570	0.08	3.3
MeOH	0.31	26316	19685	6631	0.03	0.9
Acetone	0.28	24691	20619	4072	0.07	2.76
DMF	0.27	24570	20790	3780	0.07	4.2
EtOH	0.29	25974	20000	5974	0.03	1.2
IPA	0.27	25840	20080	5760	0.04	1.9
BuOH	0.24	26110	20040	6070	0.05	2.0
TFE	0.57	26667	23041	3626	0.005	-
(b) $salophen^{2-}$						
Glycerol	0.27	26042	19493	6549	0.15	1.4
ACN	0.31	25381	20833	4548	0.07	3.2
MeOH	0.31	25316	19493	5823	0.01	0.9
Acetone	0.28	24691	20534	4157	0.073	3.0
DMF	0.27	24631	20790	3841	0.077	4.1
EtOH	0.29	25381	19763	5618	0.02	1.4
IPA	0.27	25575	20040	5535	0.05	2.4
BuOH	0.24	26110	19881	6229	0.05	2.1
TFE	0.57	26738	22989	3749	0.003	-
(c) $salbn^{2-}$						
Glycerol	0.27	26247	19608	6639	0.15	2.1
ACN	0.31	25126	20704	4422	0.10	3.8
MeOH	0.31	25510	19569	5941	0.06	0.9
Acetone	0.28	24814	20492	4322	0.09	3.5
DMF	0.27	24691	20747	3944	0.09	3.9
EtOH	0.29	25840	20000	5840	0.06	1.8
IPA	0.27	25707	19920	5787	0.07	2.3
BuOH	0.24	26316	20202	6114	0.08	2.4
TFE	0.57	27778	23095	4683	0.001	-

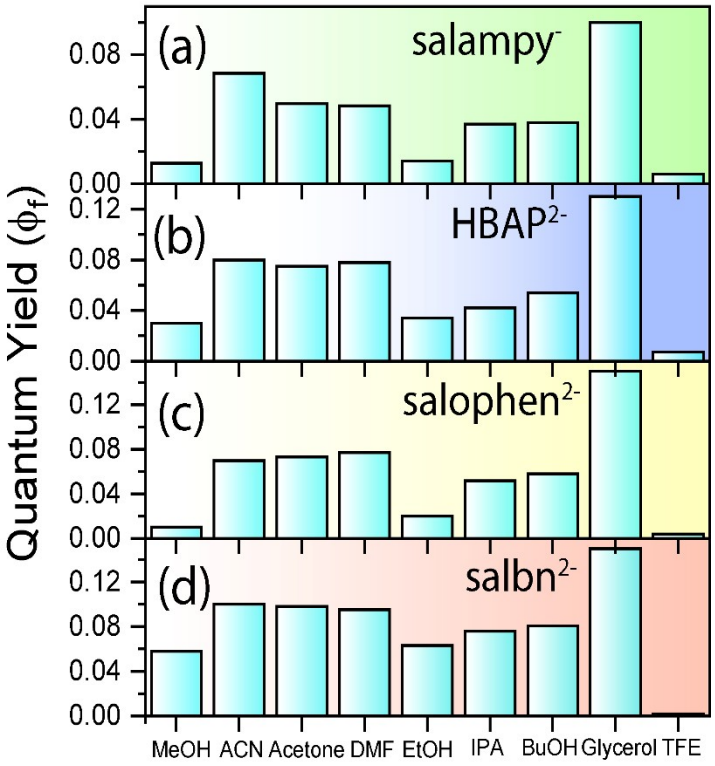

Figure S3. Quantum yields (ϕ_f) of (a) salampy$^-$ (b) HBAP^{2-} (c) salophen^{2-} (d) salbn^{2-} in different solvents.

Table ST2. Temporal parameters of salampy^{-}, HBAP^{2-}, salophen^{2-}, salbn^{2-} in different solvents at different wavelengths

(a) salampy^{-}		
Solvent	λ_{ex} / λ_{em} **(nm)**	τ **(ns)a**
EtOH	400/500	1.0 (1.0)
Glycerol	400/500	1.3 (1.0)
ACN	400/490	3.3 (1.0)
	λ_{ex} / λ_{em} **(nm)**	τ **(ns)a**
Glycerol	400/450	0.40 (0.33)
		1.23 (0.67)
	400/600	0.80 (-0.2)
		1.38 (1.2)
	λ_{ex} / λ_{em} **(nm)**	τ **(ps)a**
EtOH	400/450	11.33 (0.41)
		76.8 (0.34)
		1250 (0.235)
	400/600	27.96 (-0.69)
		1350 (1.69)
BuOH	400/450	8.18 (0.35)
		60.18(0.38)
		678.17 (0.27)
	400/600	128 (-2.03)
		270 (0.81)
		1800 (2.21)
ACN	400/450	5 (0.70)
		1200 (0.3)
	400/600	5.1 (0.67)
		1200 (0.33)
TFE	400/450	1.0(0.41)
		8.3(0.13)
		97.81(0.46)
	400/600	1.3(0.34)
		7.7(0.12)

		121.7(0.64)

(b) $HBAP^{2-}$

Solvent	λ_{ex} / λ_{em} **(nm)**	τ **(ns)a**
EtOH	400/500	1.2 (1.0)
Glycerol	400/500	1.5 (1.0)
ACN	400/490	3.3 (1.0)
	λ_{ex} / λ_{em} **(nm)**	τ **(ns)a**
Glycerol	400/450	0.60 (0.4)
		1.1 (0.6)
	400/600	0.70 (-0.18)
		1.4 (1.18)
	λ_{ex} / λ_{em} **(nm)**	τ **(ps)a**
EtOH	400/450	8.25 (0.33)
		50.75 (0.41)
		980 (0.36)
	400/600	50.51 (-0.35)
		1300 (1.35)
BuOH	400/450	5.04 (0.35)
		37.65 (0.46)
		971.46 (0.17)
	400/600	135 (-1.25)
		264.19 (1.17)
		1870 (1.07)
ACN	400/450	12.3 (0.2)
		1400 (0.8)
	400/600	12.3 (0.3)
		1400 (0.7)
TFE	400/450	1.0(0.42)
		12.2(0.36)
		212.7(0.22)
	400/600	3.24(0.25)
		20.50(0.59)
		159.24(0.16)

(c) salophen^{2-}

Solvent	λ_{ex} / λ_{em} (nm)	τ (ns)a
EtOH	400/500	1.4
Glycerol	400/500	1.4
ACN	400/490	3.2
	λ_{ex} / λ_{em} (nm)	τ (ns)a
Glycerol	400/450	0.3 (0.6) 800 (0.3)
	400/600	0.4(-0.2) 1450 (1.2)
	λ_{ex} / λ_{em} (nm)	τ (ps)a
EtOH	400/450	1.22 (0.63) 9.21 (0.10) 303.14 (0.27)
	400/600	23.61 (-0.94) 7.95 (0.01) 1200 (1.92)
BuOH	400/450	3.52 (0.35) 34.23 (0.43) 1118.1 (0.204)
	400/600	42 (-0.42) 1482.2 (1.42)
TFE	400/450	6.06(0.32) 87.19(0.38) 1200(0.28)
	400/600	12.8(0.12) 218.36(0.42) 333.93(0.46)

(d) salbn^{2-}

Solvent	λ_{ex} / λ_{em} (nm)	τ (ns)a
EtOH	400/500	1.8
Glycerol	400/500	2.1
ACN	400/490	3.8

	λ_{ex} / λ_{em} **(nm)**	τ **(ns)a**
Glycerol	400/450	0.4 (0.4)
		1.7 (0.6)
	400/600	0.6 (-0.3)
		2340 (1.3)
	λ_{ex} / λ_{em} **(nm)**	τ **(ps)a**
EtOH	400/450	3.5 (0.62)
		15.4 (0.23)
		730 (0.15)
	400/600	30.33 (-0.71)
		1200 (1.71)
BuOH	400/450	5.04 (0.35)
		37.65 (0.46)
		971.47 (0.17)
	400/600	135 (-1.25)
		264.19 (1.17)
		1870 (1.07)
ACN	400/450	50 (0.27)
		1100 (0.73)
	400/600	52 (0.30)
		1100 (0.70)
TFE	400/450	4.55(0.38)
		15.9(0.43)
		125.2(0.19)
	400/600	7.57(0.30)
		15.07(0.41)
		222.82(0.29)

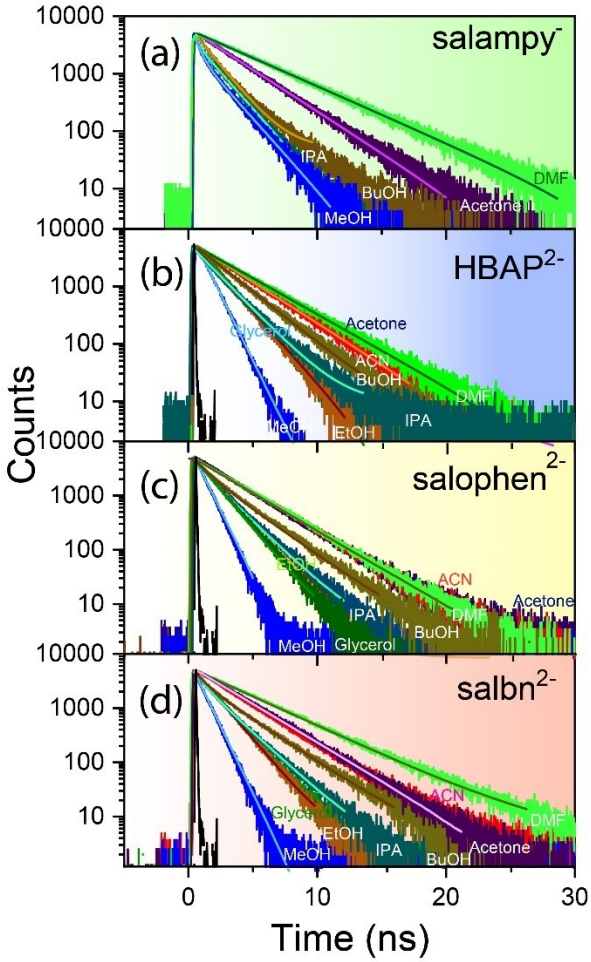

Figure S4. Fluorescence decays of (a) salampy^{-} (b) HBAP (c) salophen^{2-} (d) salbn^{2-} recorded at their corresponding emission maxima with $\lambda_{ex} = 400\ nm$.

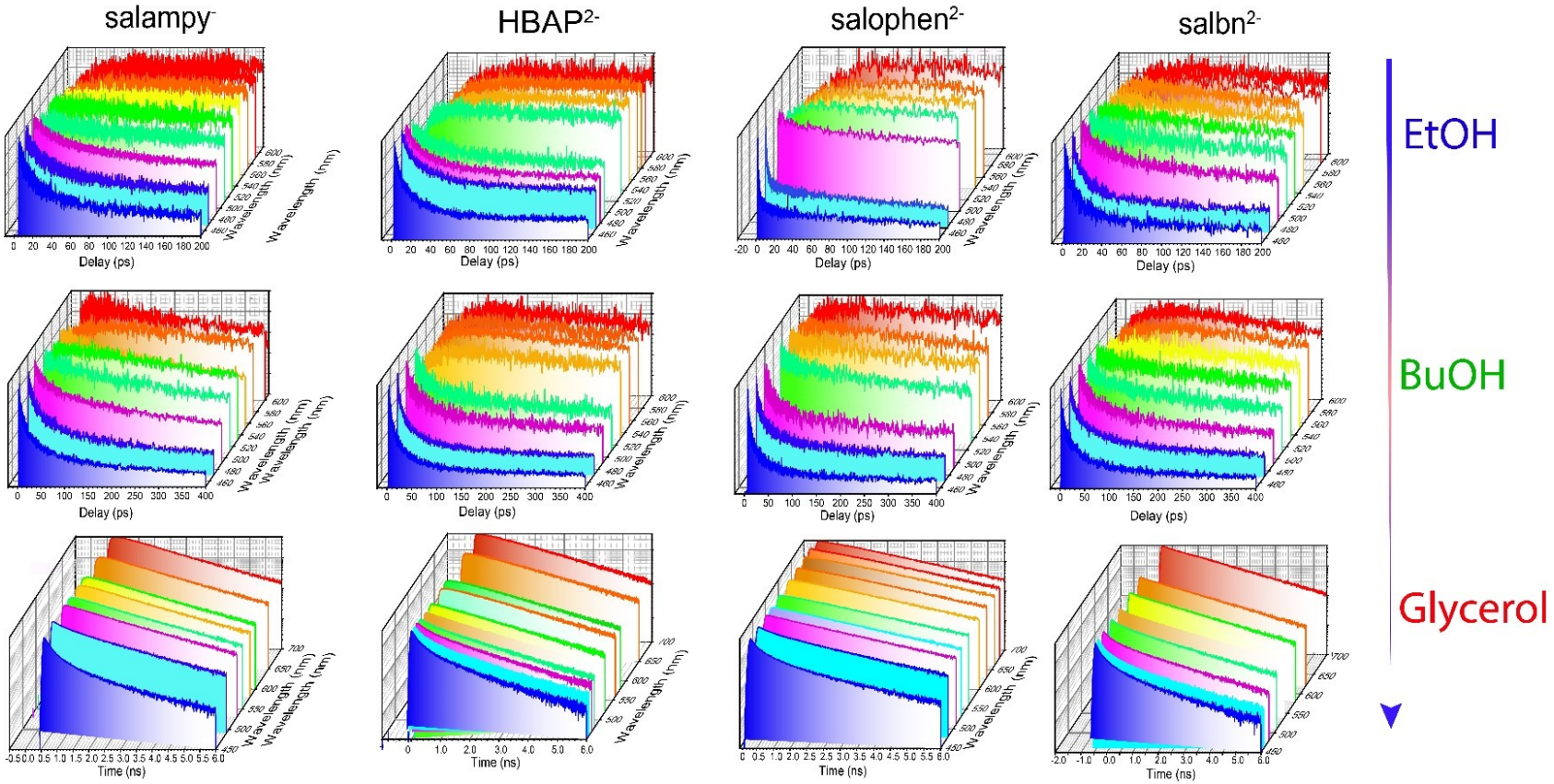

Figure S5. Wavelength dependent fluorescence decays of salampy^{-}, HBAP, salophen^{2-}, and salbn^{2-} recorded at their corresponding emission maxima with $\lambda_{ex} = 400\ nm$.

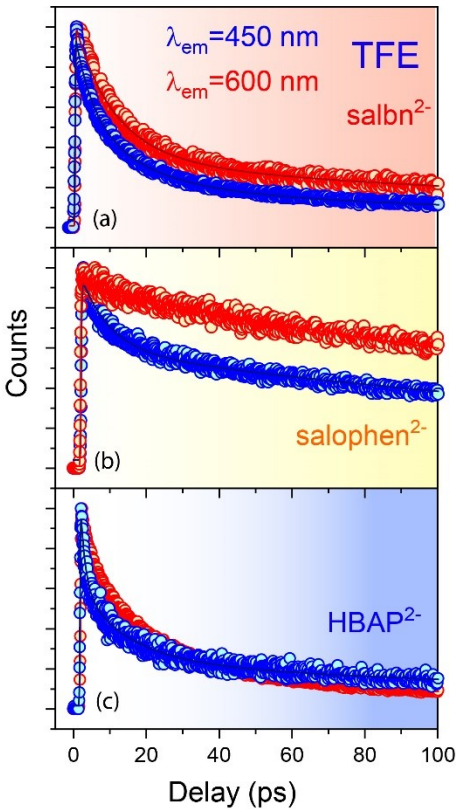

Figure S6. Fluorescence decays of (a) salbn^{2-} (b) salophen^{2-} (c) HBAP^{2-} in TFE

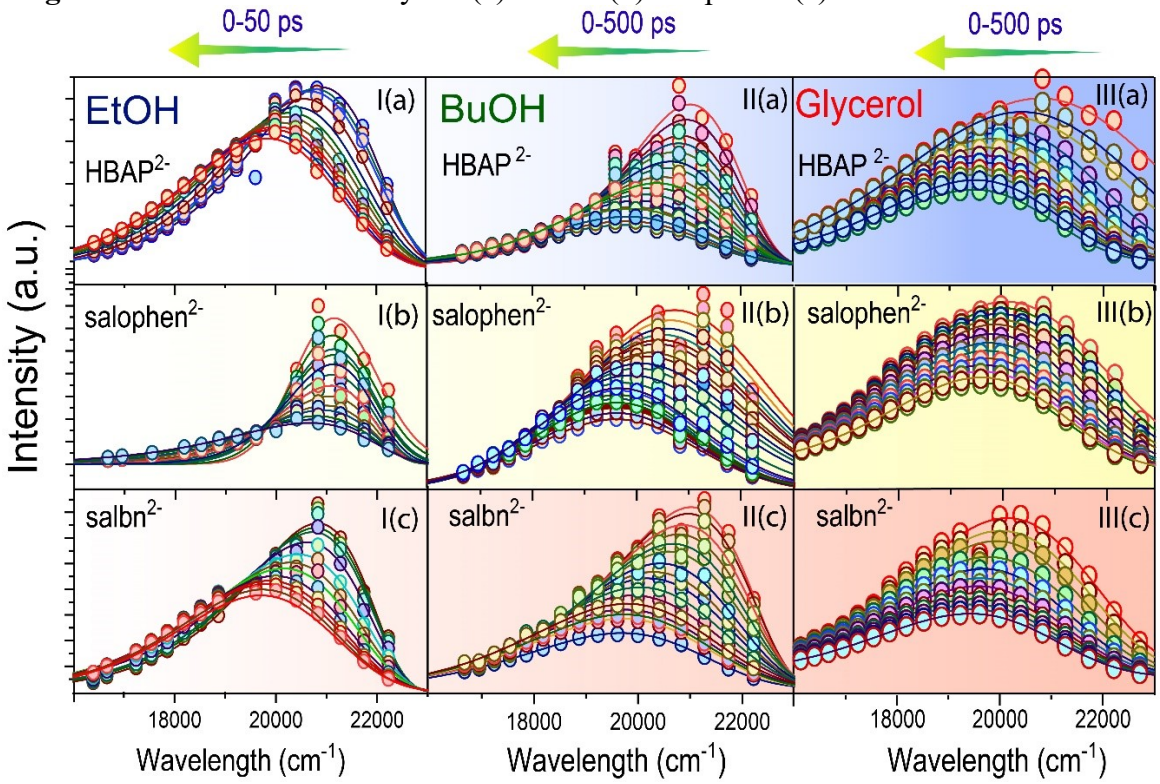

Figure S7. Time Resolved Emission Spectra of (a) HBAP^{2-} (b) salophen^{2-} (c) salbn^{2-} in (I) EtOH (II) BuOH and (III) Glycerol

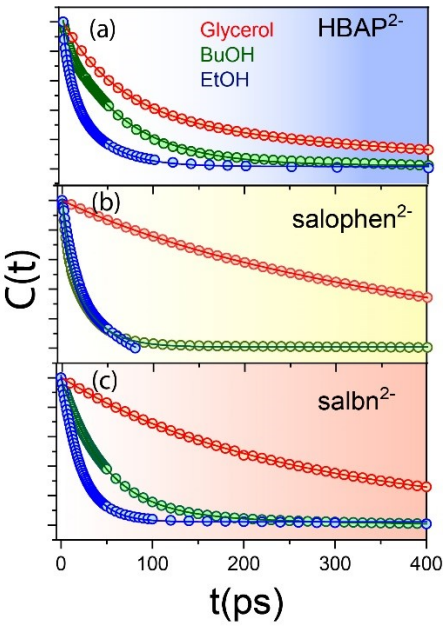

Figure S8. Apparent solvent correlation function $[\tilde{\nu}(t) - \tilde{\nu}(\infty)]$ of (a) $HBAP^{2-}$ (b) $salophen^{2-}$ (c) $salbn^{2-}$

Table ST3. Decay parameters of $[\tilde{\nu}(t) - \tilde{\nu}(\infty)]$ vs t(ps)					
	Solvent	τ_1(ps)	a_1	τ_2(ps)	a_2
salampy$^-$	EtOH	14.8	0.4	79.8	0.6
	BuOH	15.3	0.4	137.2	0.6
	Glycerol	103	0.3	680	0.7
$HBAP^{2-}$	EtOH	7.5	0.3	36.1	0.7
	BuOH	16.8	0.1	66.5	0.8
	Glycerol	62	0.5	510.0	0.4
$salophen^{2-}$	EtOH	5	0.3	28.0	0.7
	BuOH	4.8	0.3	37.6	0.7
	Glycerol	148.6	0.2	639.6	0.8
$salbn^{2-}$	EtOH	22.3	0.5	55.3	0.5
	BuOH	31.6	0.3	70.3	0.7
	Glycerol	165	0.2	650.1	0.8

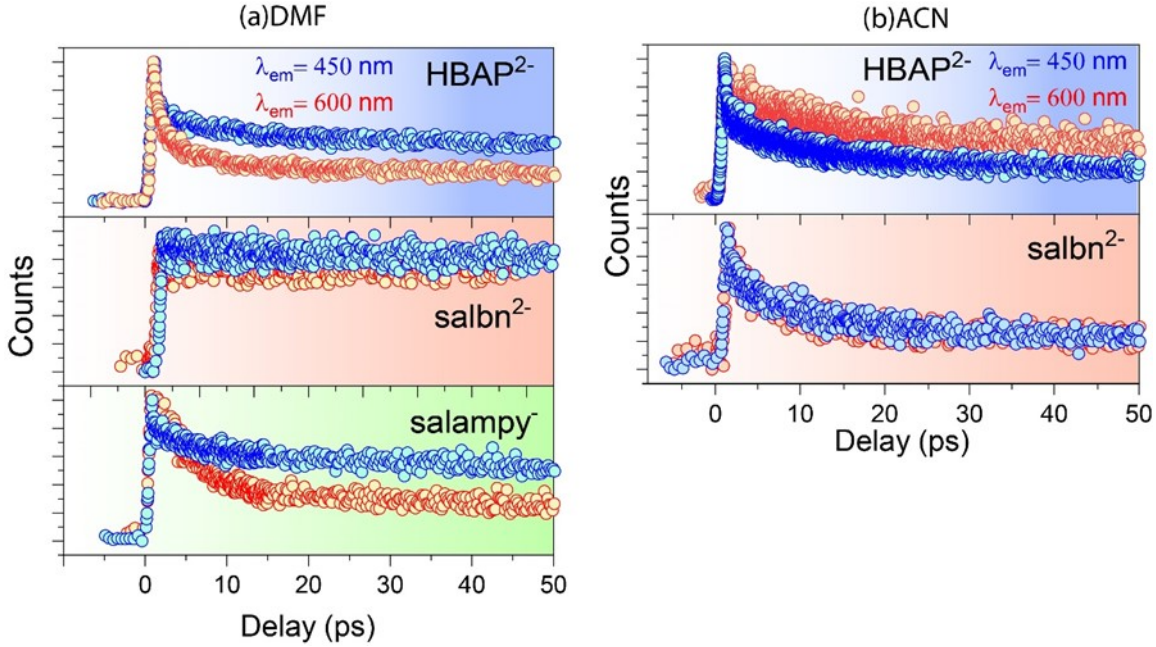

Figure S9. Wavelength dependent fluorescence decays of salampy^{-}, salbn^{2-}, HBAP^{2-} in (a) DMF and (b) ACN

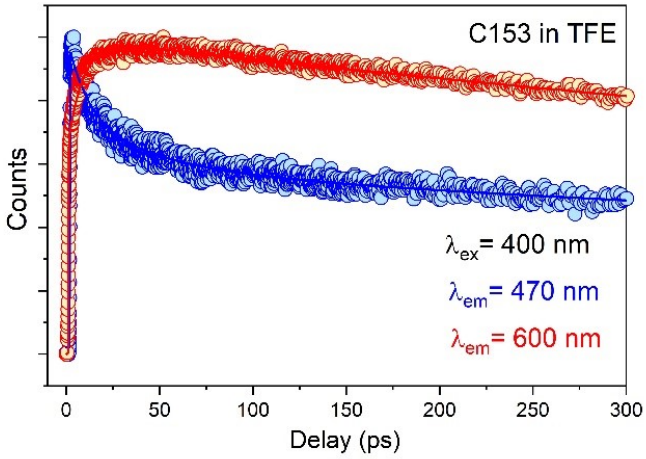

Figure S10. Fluorescence decays of C153 in TFE recorded at $\lambda_{em} = 470\ nm$ and 600 nm with $\lambda_{ex} = 400\ nm$

Table ST4. Temporal parameters of C153 in 2,2,2-Trifluoroethanol (TFE)

Wavelength (ex/em) nm	τ_1**(ps)**	$\mathbf{a_1}$	τ_2**(ps)**	$\mathbf{a_2}$	τ_3**(ps)**	$\mathbf{a_3}$
400/470	10.84	0.21	44.7	0.18	1594.3	0.61
400/600	10.0	-0.82	13.5	0.36	1610.7	1.45

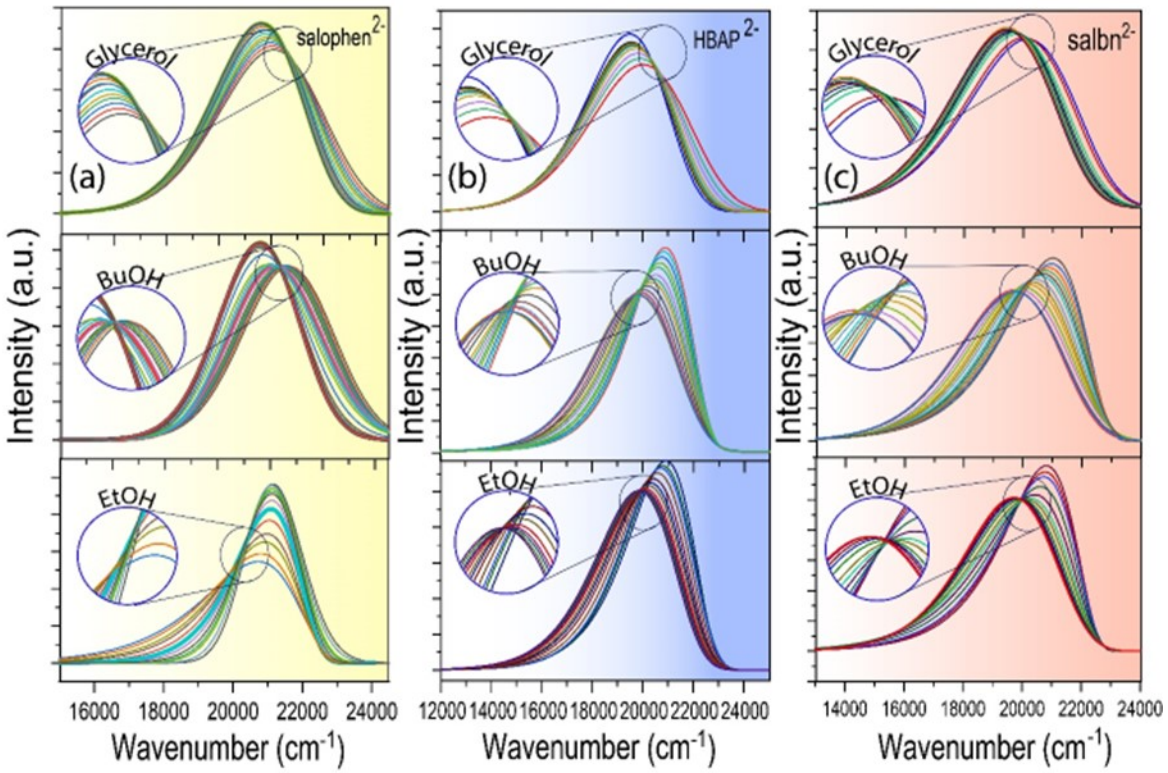

Figure S11. Time Resolved Area Normalized Emission Spectrum (TRANES) of (a) salophen^{2-} (b) HBAP^{2-} (c) salbn^{2-} in EtOH, BuOH and Glycerol (inset shows zoomed in view of the diffused isoemissive point)

Table ST5. Parameters of different solvents

Solvent	**Δf**	$E_T(30)$	**Viscosity (η) cP**	**Hydrogen bond donating ability (α)**
Glycerol	0.265	57	934	1.13
ACN	0.305	45.6	0.37	0.19
MeOH	0.308	55.5	0.54	0.98
Acetone	0.284	42.2	0.31	0.08
DMF	0.272	43.8	0.79	0.00
EtOH	0.288	51.9	1.07	0.86
IPA	0.272	48.6	2.04	0.76
BuOH	0.239	50.2	2.54	0.84
TFE	0.57	59.8	0.90	1.51

Table ST6. Time Dependent Fluorescent Stokes Shift of the anions in polar protic solvents

Sample	Solvent	$\tilde{\nu}(t)$ (cm^{-1})	$\tilde{\nu}(\infty)$ (cm^{-1})	$[\tilde{\nu}(t) - \tilde{\nu}(\infty)]$ (cm^{-1})
salampy^{-}	EtOH	20850	19850	1000
	BuOH	21600	20050	1550
	Glycerol	20760	19600	1160
HBAP^{2-}	EtOH	20900	20000	900
	BuOH	21000	19900	1100
	Glycerol	20850	19600	1250
salophen^{2-}	EtOH	21200	20500	700
	BuOH	20801	19700	1100
	Glycerol	20200	19600	600
salbn^{2-}	EtOH	20850	19800	1050
	BuOH	21100	19900	1200
	Glycerol	20300	19550	750

Table ST7. Optimized coordinates of Ground State and excited states of salampy$^-$

Ground State			
Atom	**x**	**y**	**z**
N	-0.2018	0.86143	0.19426
N	-3.78807	0.5568	-0.49995
C	2.7883	0.60937	-0.36864
C	2.00622	1.82467	-0.27968
C	-2.45414	0.37257	-0.44797
C	-1.57817	1.18618	0.45357
H	-1.8431	2.25247	0.33867
H	-1.84107	0.91821	1.48897
C	4.74972	2.04039	-0.81091
H	5.81594	2.12068	-1.01782
C	4.19299	0.79988	-0.64403
H	4.79071	-0.10376	-0.71722
C	-2.04996	-0.6309	-1.30029
C	-4.10475	-1.19392	-2.15923
H	-4.78648	-1.75458	-2.78947
C	3.97301	3.21316	-0.72143
H	4.42132	4.19261	-0.8544
C	0.58929	1.84982	-0.0055
H	0.17431	2.8762	0.03097
C	-2.72889	-1.34388	-2.0662
C	-4.56301	-0.17874	-1.30497
H	-5.62424	0.05573	-1.27145
C	2.6287	3.07517	-0.45941
H	2.00496	3.96592	-0.38401
O	2.29635	-0.54675	-0.2194
C	4.34497	-2.54975	1.1904
H	3.49215	-2.97032	1.75307
H	4.54231	-1.55865	1.63201
O	4.07355	-2.46006	-0.17688
H	3.35391	-1.76603	-0.27894
C	-4.73334	2.43131	2.32989
H	-3.86389	1.85291	2.68101
H	-5.61197	1.77224	2.4371
O	-4.56697	2.85973	1.00213
H	-4.37471	2.07369	0.4507
C	-4.91207	3.65454	3.20815
H	-5.78192	4.23005	2.87986
H	-5.05352	3.37229	4.25576
H	-4.03333	4.3002	3.13492
C	5.55903	-3.44063	1.39395
H	5.80284	-3.55325	2.456
H	5.37202	-4.43259	0.97174
H	6.42625	-3.01739	0.87867
Excited State			
N	-0.8403	-0.59463	-0.27617
N	-3.37919	1.12486	-0.74681

C	2.21376	0.03532	0.14914
C	1.00632	0.83528	0.26776
C	-3.18284	-0.27604	-0.88999
C	-2.22902	-0.97543	0.00264
H	-2.45793	-0.78289	1.07047
H	-2.3147	-2.05249	-0.16577
C	3.47683	2.07664	-0.32836
H	4.40852	2.58039	-0.56454
C	3.44827	0.71779	-0.17568
H	4.33369	0.09824	-0.2676
C	-3.95852	-0.75133	-1.95338
C	-4.98392	1.25303	-2.60872
H	-5.63788	1.8657	-3.21258
C	2.29773	2.82791	-0.17254
H	2.32946	3.90515	-0.28968
C	-0.31348	0.20416	0.54299
H	-0.82512	0.54545	1.45318
C	-4.74741	-0.15686	-2.70059
C	-4.20803	1.77284	-1.55758
H	-4.27603	2.84425	-1.3639
C	1.08175	2.20385	0.12834
H	0.17051	2.78273	0.2485
O	2.203	-1.20591	0.35245
C	5.09361	-2.27702	1.65079
H	4.54918	-3.09031	2.15634
H	4.81802	-1.34511	2.16961
O	4.76921	-2.21789	0.28315
H	3.81721	-1.99867	0.21836
C	-2.6674	2.91591	1.9986
H	-2.03077	3.48036	2.69363
H	-2.75537	1.89673	2.4111
O	-2.03656	2.91113	0.74814
H	-2.49069	2.2092	0.18009
C	-4.05362	3.54819	1.94893
H	-4.70088	2.9711	1.28442
H	-4.51541	3.58189	2.94258
H	-3.98782	4.56873	1.56005
C	6.58643	-2.5095	1.78017
H	6.88701	-2.57318	2.83022
H	6.86696	-3.43959	1.27887
H	7.13887	-1.69294	1.30732