Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Hydrazine functionalized probes for chromogenic and fluorescent ratiometric sensing of pH and F^- : Experimental and DFT study

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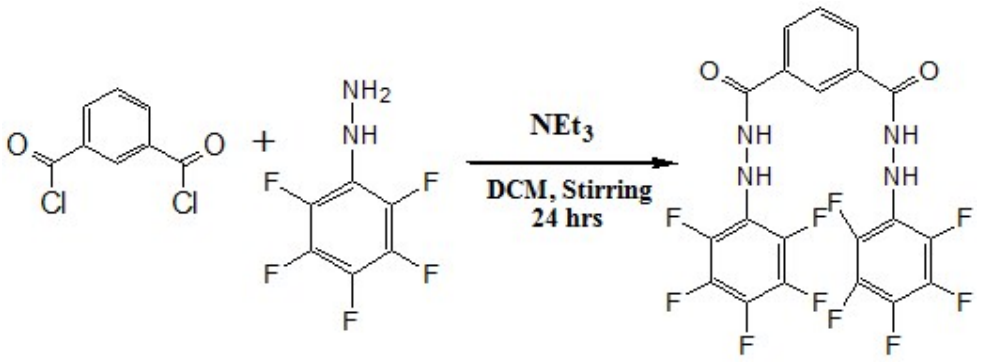
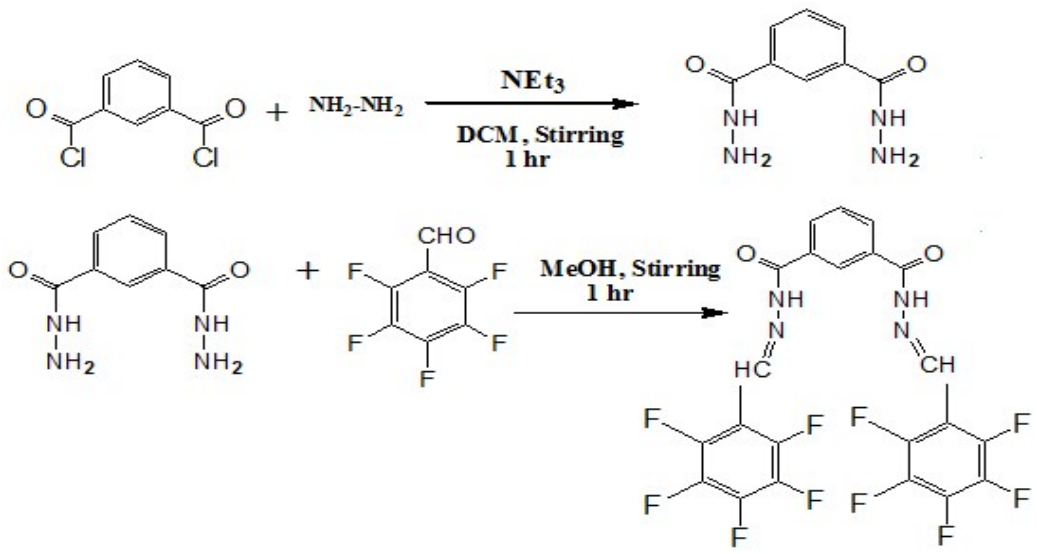


Scheme S1 Preparation of **BPPIH**.



Scheme S2 Preparation of **BPBIH**.

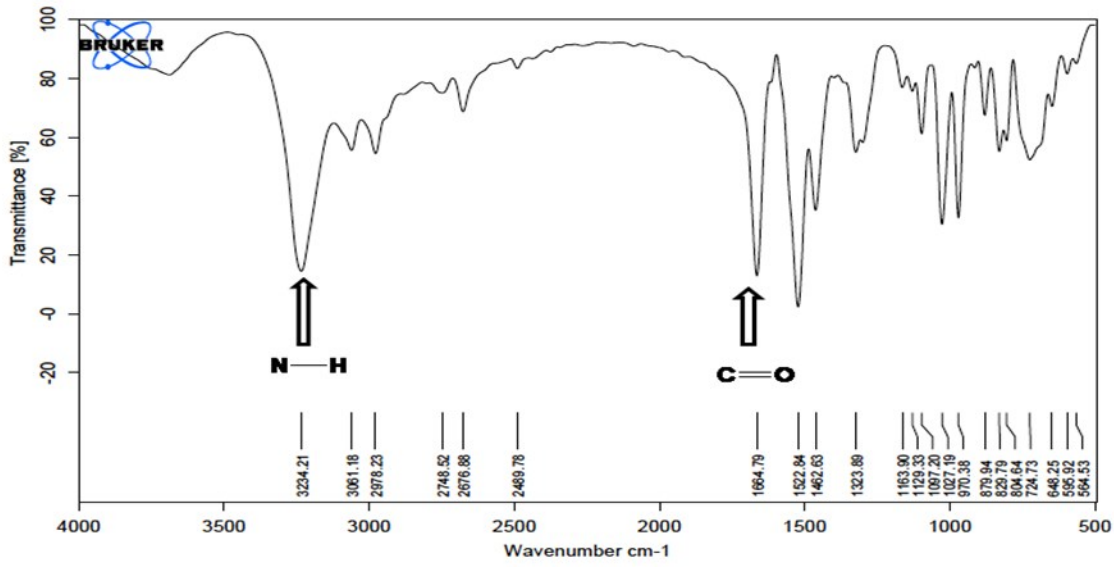


Fig. S1 IR data of **BPPIH**.

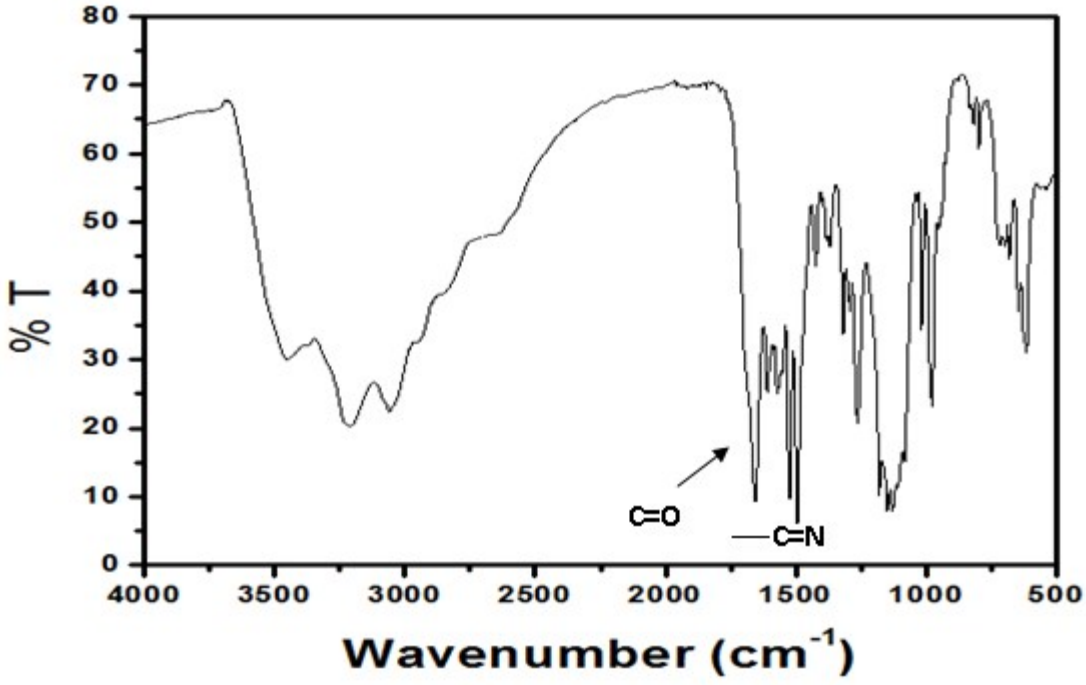


Fig. S2 IR data of **BPBIH**.

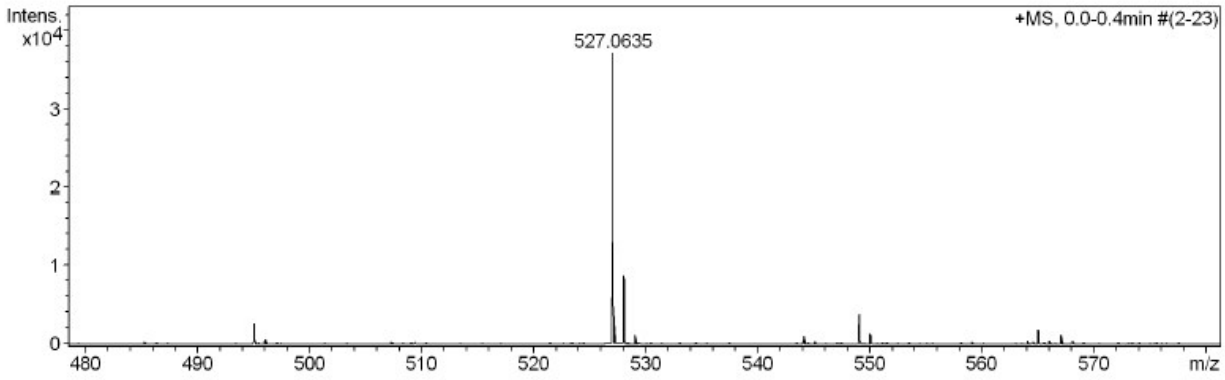


Fig. S3 ESI-Mass data of **BPPIH**.

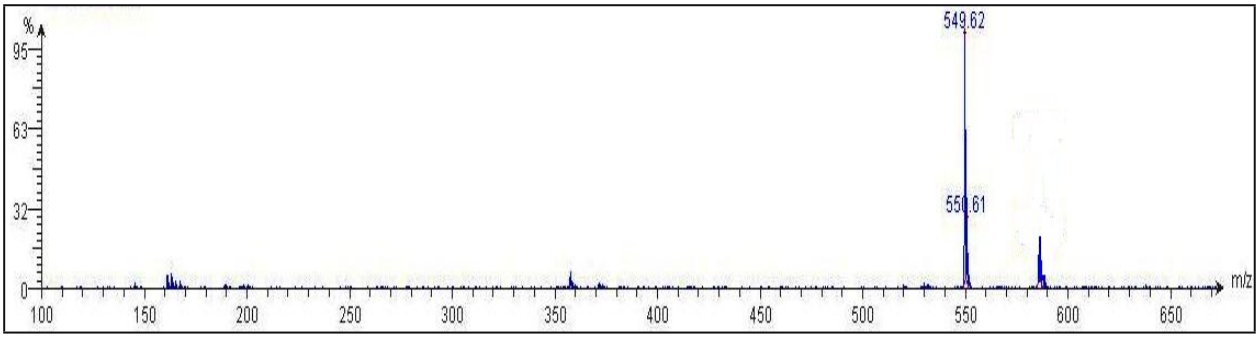


Fig. S4 ESI-Mass data of **BPBIH**.

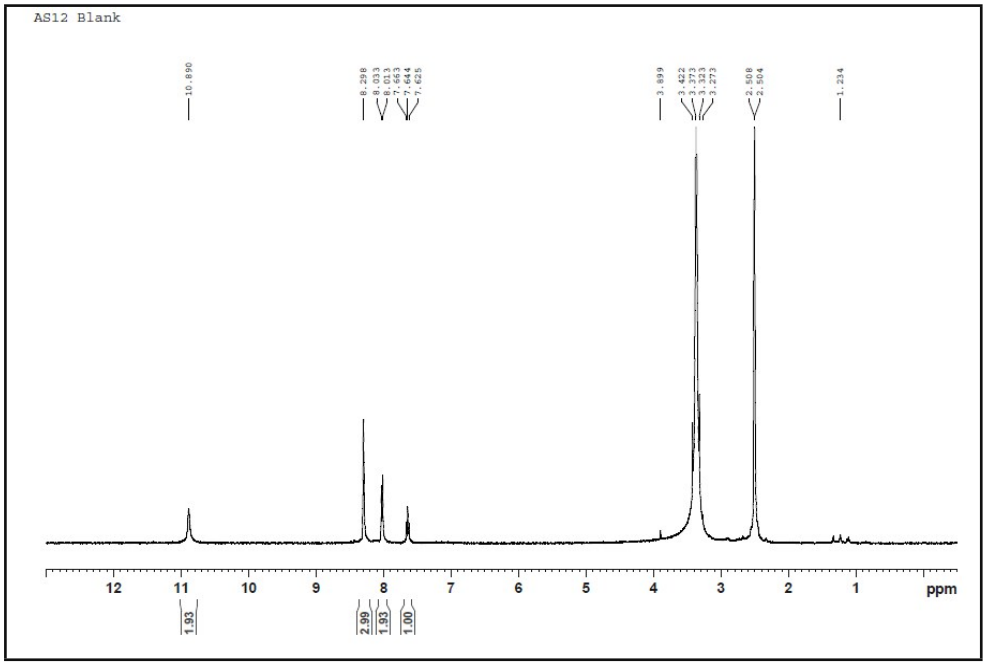


Fig. S5 ^{1}H NMR data of **BPPIH** in DMSO-d_6.

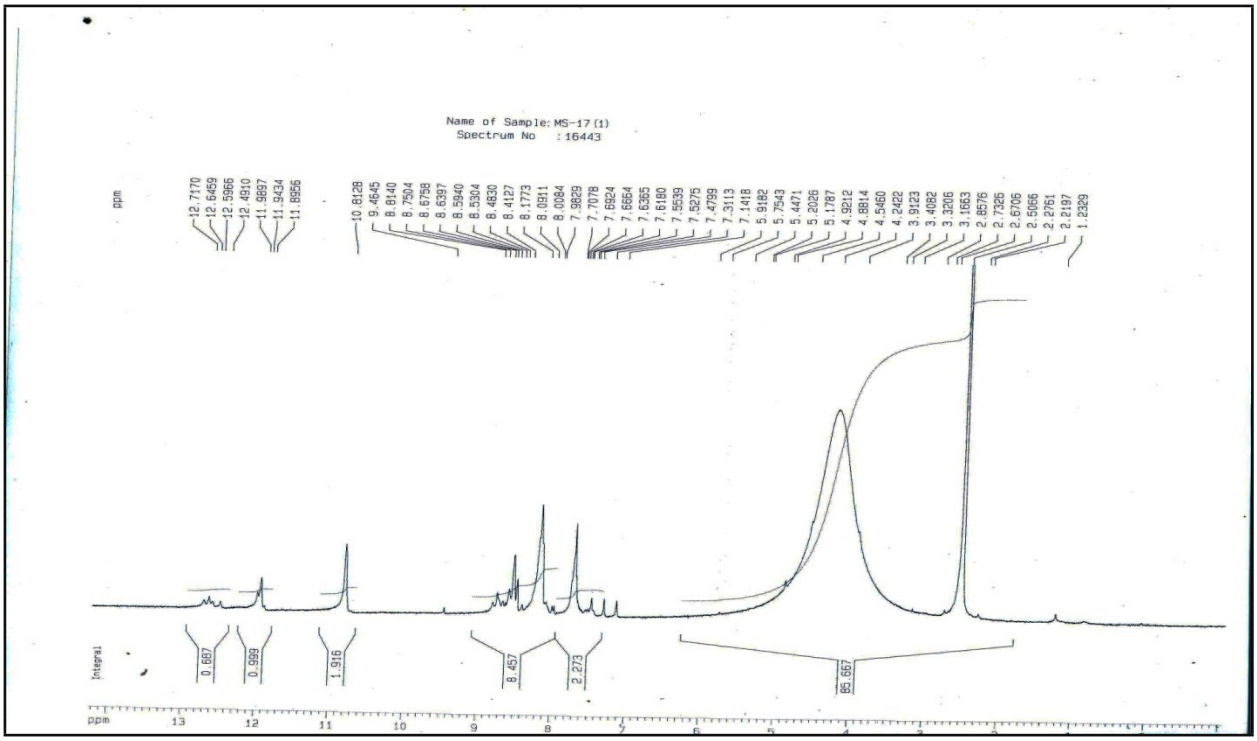


Fig. S6 ^{1}H NMR data of **BPBIH** in DMSO-d_6.

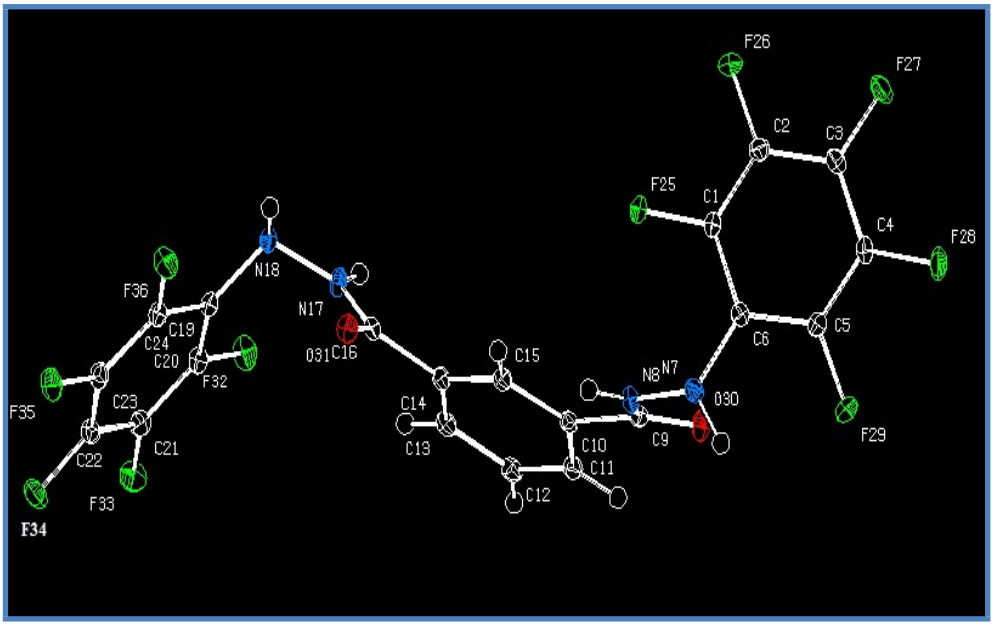


Fig. S7 ORTEP diagram of **BPPIH** crystal.

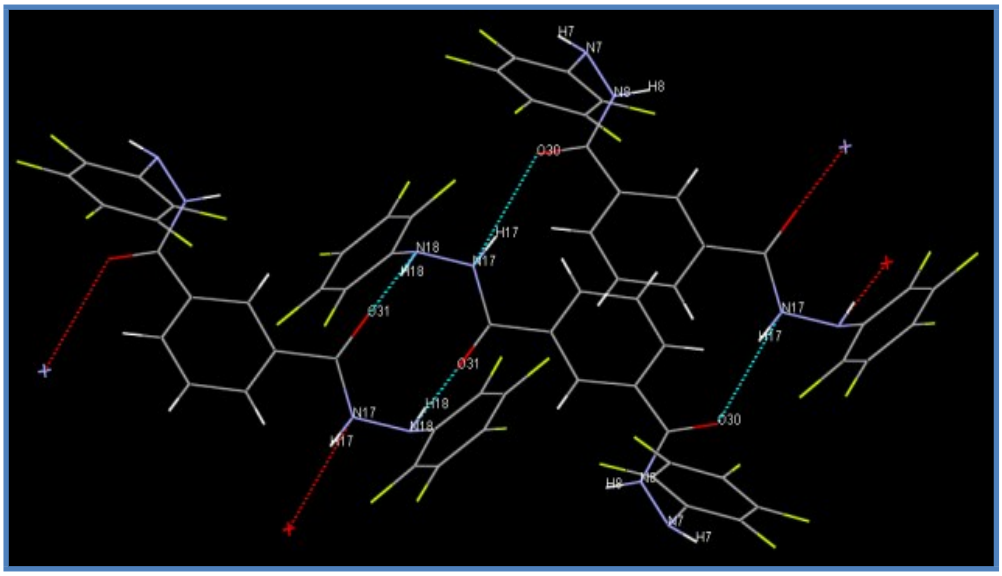


Fig. S8a Wireframe network showing intermolecular hydrogen bonding in **BPPIH**.

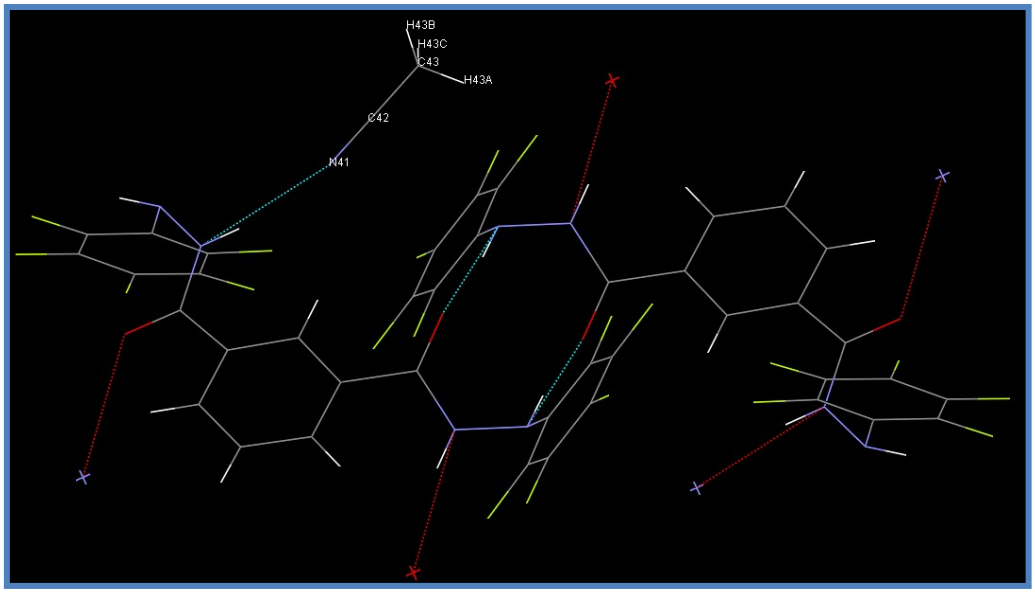


Fig. S8b Wireframe network showing intermolecular hydrogen bonding in **BPPIH** including bonding with ACN molecule.

Table S1 Crystallographic data of **BPPIH**.

Crystal Data	
Formula	C22 H11 F10 N5 O2
Formula Weight	567.36
Crystal System	triclinic
Space group	P-1 (No. 2)
a, b, c [Angstrom]	9.1588(9) 10.6738(11) 11.2243(11)
alpha, beta, gamma [deg]	96.254(2) 90.635(2) 93.181(2)
V [Ang**3]	1088.91(19)
Z	2
D(calc) [g/cm**3]	1.730
Mu(MoKa) [/mm]	0.172
F(000)	568
Crystal Size [mm]	0.08 x 0.12 x 0.32
Data Collection	
Temperature (K)	100
Radiation [Angstrom]	MoKa 0.71073
Theta Min-Max [Deg]	2.9, 32.0
Dataset	-13: 13 ; -15: 15 ; -16: 16
Tot., Uniq. Data, R(int)	34480, 7576, 0.022
Observed Data [I > 2.0 sigma(I)]	6636
Refinement	
Nref, Npar	7576, 365
R, wR2, S	0.0332, 0.0932, 1.03
w = S^2^(FO^2^)+(0.0469P)^2^+0.4439P] Where P=(FO^2^+2FC^2^)/3 '	
Max. and Av. Shift/Error	0.00, 0.00
Min. and Max. Resd. Dens. [e/Ang^3]	-0.23, 0.54

Table S2 Selected bond distances (angstrom) of **BPPIH**.

F25	-C1	1.3458(10)	C3	-C4	1.3851(13)
F26	-C2	1.3372(11)	C4	-C5	1.3832(13)
F27	-C3	1.3355(11)	C5	-C6	1.3923(12)
F28	-C4	1.3390(12)	C9	-C10	1.4970(12)
F29	-C5	1.3449(11)	C10	-C15	1.3962(12)
F32	-C20	1.3437(11)	C10	-C11	1.4022(12)
F33	-C21	1.3401(11)	C11	-C12	1.3888(13)
F34	-C22	1.3382(11)	C12	-C13	1.3918(14)
F35	-C23	1.3393(11)	C13	-C14	1.4003(13)
F36	-C24	1.3451(11)	C14	-C15	1.3990(12)
O30	-C9	1.2333(11)	C14	-C16	1.4953(12)
O31	-C16	1.2316(11)	C19	-C24	1.3925(12)
N7	-N8	1.4058(11)	C19	-C20	1.3976(12)
N7	-C6	1.4063(11)	C20	-C21	1.3842(13)
N8	-C9	1.3563(11)	C21	-C22	1.3846(14)
N17	-N18	1.4116(11)	C22	-C23	1.3846(13)
N17	-C16	1.3563(11)	C23	-C24	1.3847(13)
N18	-C19	1.4121(12)	C11	-H11	0.9500

N7	-H7	0.901(14)	C12	-H12	0.9500
N8	-H8	0.857(12)	C13	-H13	0.9500
N17	-H17	0.839(14)	C15	-H15	0.9500
N18	-H18	0.865(13)	C42	-C43	1.4589(15)
N41	-C42	1.1437(14)	C43	-H43A	0.9800
C1	-C6	1.3941(12)	C43	-H43B	0.9800
C1	-C2	1.3861(13)	C43	-H43C	0.9800
C2	-C3	1.3861(13)			

Table S3 Selected bond angles (degrees) of **BPPIH**.

N8	-N7	-C6	115.82(7)	C1	-C6	-C5	116.50(8)
N7	-N8	-C9	119.87(7)	N7	-C6	-C1	122.55(8)
N18	-N17	-C16	120.23(7)	O30	-C9	-C10	121.87(8)
N17	-N18	-C19	112.09(7)	N8	-C9	-C10	116.67(7)
C6	-N7	-H7	110.6(9)	O30	-C9	-N8	121.46(8)
N8	-N7	-H7	110.4(9)	C11	-C10	-C15	119.93(8)
N7	-N8	-H8	115.7(9)	C9	-C10	-C11	117.08(8)
C9	-N8	-H8	124.3(9)	C9	-C10	-C15	122.88(7)
C16	-N17	-H17	122.0(10)	C10	-C11	-C12	120.29(8)
N18	-N17	-H17	117.5(10)	C11	-C12	-C13	119.96(8)
N17	-N18	-H18	109.1(9)	C12	-C13	-C14	120.01(8)
C19	-N18	-H18	113.4(8)	C15	-C14	-C16	118.96(8)
F25	-C1	-C6	119.67(8)	C13	-C14	-C15	120.17(8)
C2	-C1	-C6	121.80(8)	C13	-C14	-C16	120.87(8)
F25	-C1	-C2	118.48(8)	C10	-C15	-C14	119.53(8)
F26	-C2	-C3	120.10(8)	O31	-C16	-C14	122.94(8)
C1	-C2	-C3	120.40(8)	N17	-C16	-C14	114.41(7)
F26	-C2	-C1	119.43(8)	O31	-C16	-N17	122.66(8)
F27	-C3	-C2	120.88(8)	N18	-C19	-C24	123.14(8)
F27	-C3	-C4	120.24(8)	C20	-C19	-C24	116.38(8)
C2	-C3	-C4	118.88(8)	N18	-C19	-C20	120.44(8)
F28	-C4	-C3	120.22(8)	F32	-C20	-C19	119.52(8)
F28	-C4	-C5	119.75(8)	F32	-C20	-C21	118.22(8)
C3	-C4	-C5	120.02(9)	C19	-C20	-C21	122.26(8)
F29	-C5	-C4	118.77(8)	F33	-C21	-C20	120.09(8)
C4	-C5	-C6	122.40(8)	F33	-C21	-C22	120.01(8)
F29	-C5	-C6	118.83(8)	C20	-C21	-C22	119.89(8)
N7	-C6	-C5	120.66(8)	F34	-C22	-C21	120.54(8)
C21	-C22	-C23	119.20(8)	C12	-C13	-H13	120.00
F34	-C22	-C23	120.24(8)	C14	-C13	-H13	120.00
F35	-C23	-C24	120.40(8)	C10	-C15	-H15	120.00
C22	-C23	-C24	120.18(8)	C14	-C15	-H15	120.00
F35	-C23	-C22	119.39(8)	N41	-C42	-C43	179.62(12)
F36	-C24	-C23	118.54(8)	C42	-C43	-H43A	109.00
C19	-C24	-C23	122.07(8)	C42	-C43	-H43B	109.00
F36	-C24	-C19	119.39(8)	C42	-C43	-H43C	109.00
C10	-C11	-H11	120.00	H43A	-C43	-H43B	109.00
C12	-C11	-H11	120.00	H43A	-C43	-H43C	109.00
C11	-C12	-H12	120.00	H43B	-C43	-H43C	109.00
C13	-C12	-H12	120.00				

Table S4 Hydrogen bonding in **BPPIH**.

N7 -- H7 .. F29	0.901(14) -- 2.322(14).. 2.7618(11)
N8 -- H8 .. N41	0.857(12)-- 2.120(12).. 2.9582(13)
N17 -- H17 .. O30	0.839(14)-- 2.103(14).. 2.9302(10)
N18 -- H18 .. F36	0.865(13)-- 2.460(13).. 2.8252(10)
N18 -- H18 .. O31	0.865(13)-- 2.133(12).. 2.9774(11)
C12 -- H12 .. F35	0.9500-- 2.5100..3.4418(12)
C43 -- H43B .. O31	0.9800 -- 2.3600.. 3.3141(13)

Table S5 Cartesian coordinates (angstroms) of geometry optimized structure of **BPPIH**.

C	6.878891	14.131726	15.787299
C	6.574349	14.436661	17.115219
C	7.126686	15.566420	17.722106
C	7.977887	16.390966	16.984594
C	8.255141	16.084665	15.652638
C	7.717510	14.954152	15.017285
N	8.094094	14.624445	13.700038
N	7.056464	14.339911	12.807172
C	6.369751	15.357415	12.197699
C	5.378409	14.962167	11.140831
C	4.898427	15.972865	10.289453
C	3.987021	15.668214	9.277765
C	3.535324	14.355977	9.109615
C	3.995112	13.337163	9.961214
C	4.918713	13.649008	10.970483
C	3.570455	11.902424	9.838699
N	2.464920	11.653529	9.069359
N	1.954287	10.354594	8.968435
C	2.585645	9.515867	8.026107
C	2.724146	9.886643	6.678326
C	3.287315	9.025705	5.735274
C	3.707252	7.748756	6.113910
C	3.567122	7.349148	7.444008
C	3.020058	8.228650	8.378299
F	6.365445	13.007244	15.256825
F	5.770519	13.628327	17.821645
F	6.845916	15.852763	19.001793
F	8.512815	17.482102	17.551195
F	9.067568	16.903281	14.955804
O	6.565929	16.529952	12.512192
O	4.180684	10.984248	10.384154
F	2.287911	11.089321	6.263299
F	3.401785	9.414799	4.456924
F	4.236022	6.912960	5.208426
F	3.973875	6.129663	7.824463
F	2.906501	7.823191	9.657904
H	8.718531	15.334057	13.300717
H	7.089259	13.402307	12.406580
H	5.254848	16.996746	10.424005
H	3.628834	16.455778	8.609302

H	2.840745	14.142550	8.293352
H	5.246487	12.836544	11.621904
H	1.805416	12.391144	8.821082
H	1.919934	9.917951	9.896607

Table S6 Cartesian coordinates (angstroms) of geometry optimized structure of **BPBIH**

C	7.020307	14.436297	15.624988
C	6.046029	14.592850	16.612594
C	6.061710	15.725884	17.427640
C	7.053307	16.693934	17.249408
C	8.017814	16.510998	16.260292
C	8.019320	15.395648	15.409609
N	9.099715	14.862561	13.197464
N	7.910910	14.680246	12.521456
C	6.892259	15.615420	12.452292
C	5.823348	15.326486	11.436688
C	5.025759	16.403093	11.009504
C	4.008909	16.197757	10.077001
C	3.761727	14.916100	9.575167
C	4.538869	13.826571	10.005509
C	5.574438	14.043745	10.928904
C	4.352619	12.421641	9.502949
N	3.099648	12.137765	9.005759
N	2.610641	11.020116	8.403615
C	2.810652	8.804580	7.506998
C	1.491872	8.650336	7.033034
C	1.073146	7.495942	6.370007
C	1.965954	6.443223	6.158227
C	3.278503	6.555646	6.617767
C	3.676812	7.716724	7.277556
F	6.986818	13.313874	14.888945
F	5.107894	13.653369	16.792545
F	5.133580	15.883024	18.375988
F	7.069778	17.784494	18.027134
F	8.957128	17.459701	16.107587
O	6.865943	16.614321	13.163426
O	5.260841	11.592661	9.542374
F	0.576449	9.614595	7.197531
F	-0.189689	7.392860	5.931978
F	1.566367	5.339019	5.519821
F	4.147029	5.553898	6.423011
F	4.952920	7.778449	7.698849
C	3.349118	9.987551	8.191909
C	9.114717	15.233189	14.424691
H	8.061451	14.112249	11.684968
H	5.217611	17.401635	11.409129
H	3.405561	17.041697	9.731989
H	2.973066	14.790499	8.828667
H	6.155229	13.179354	11.257485

H	2.371530	12.845191	9.100643
H	4.396834	9.938629	8.492714
H	10.125118	15.417335	14.812551

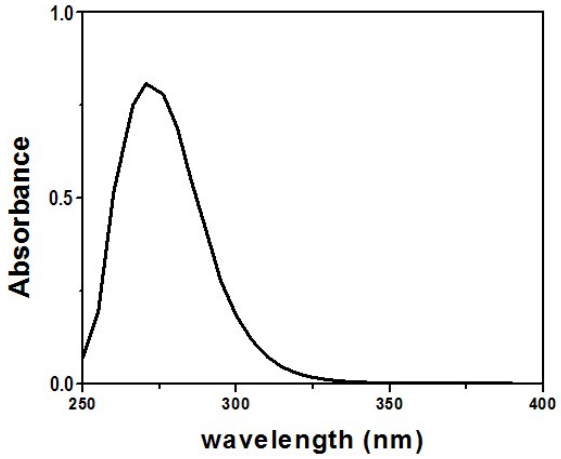


Fig. S9 UV-Spectra of **BPPIH** (1X 10^{-4}M) in DMSO.

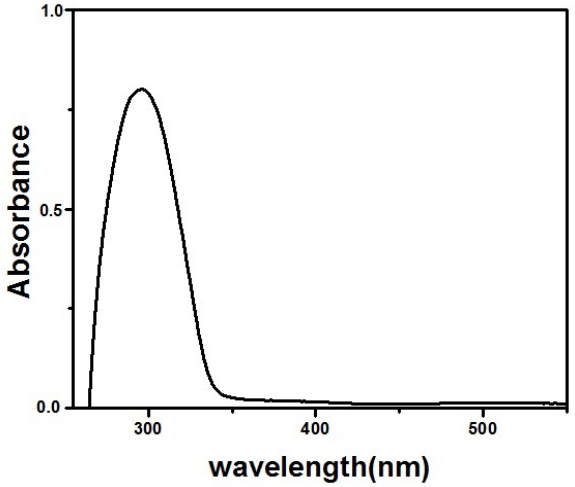


Fig. S10 UV-Spectra of **BPBIH** (1X 10^{-4}M) in DMSO.

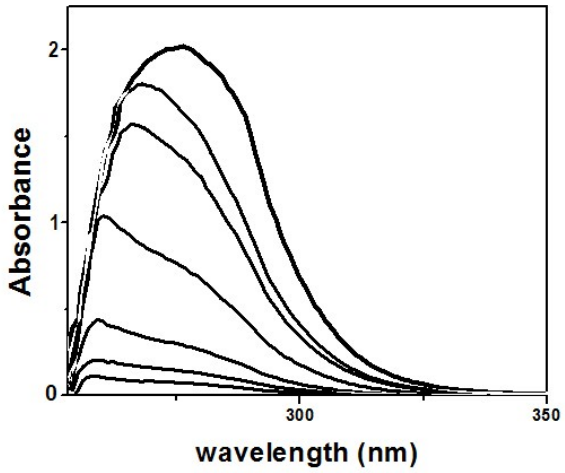


Fig. S11 UV-Spectra of **BPPIH** in DMSO in varying concentration from 10^{-5} M to 10^{-3}M.

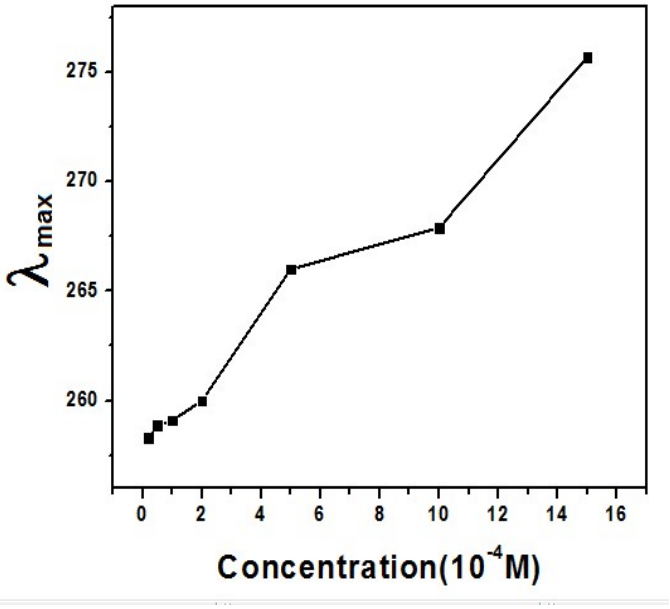


Fig. S12 Plot of λ max vs Concentration of **BPPIH**.

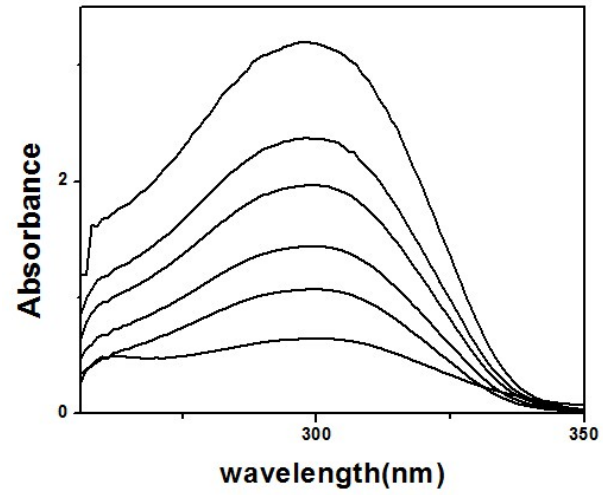
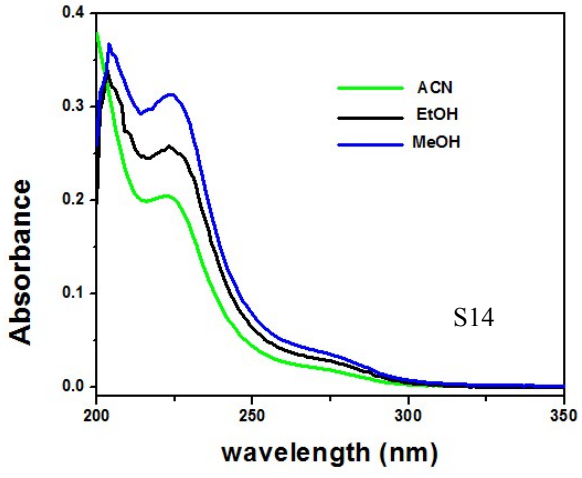


Fig. S13 UV-Spectra of **BPBIH** in DMSO from 10^{-5} M to 10^{-3}M in varying concentration.



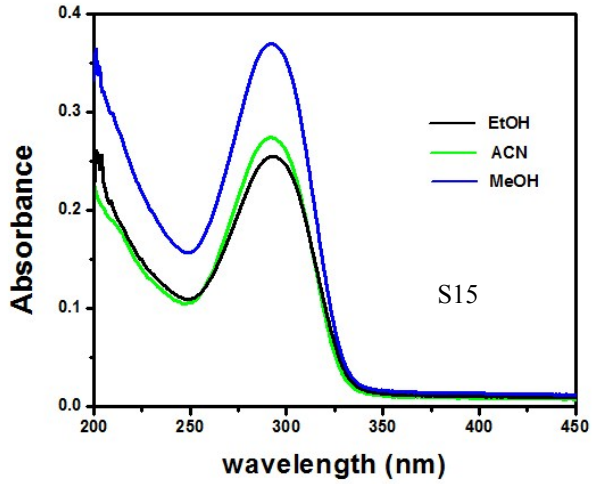


Fig. S14 UV-Spectra of **BPPIH** (1x 10^{-5} M) in methanol, ethanol and acetonitrile.

Fig. S15 UV-Spectra of **BPBIH** (1x 10^{-5} M) in methanol, ethanol and acetonitrile.

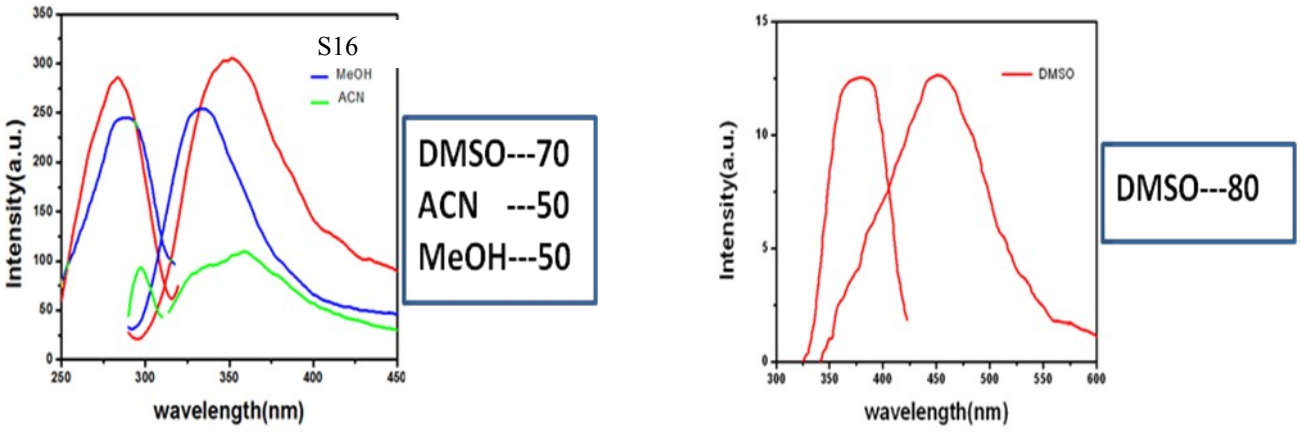


Fig. S16 Excitation-Emission Spectra of **BPPIH** (2x 10^{-6} M) showing stokes shifts in methanol, acetonitrile and DMSO.

Fig. S17 Excitation-Emission Spectra of **BPBIH** (2x 10^{-6} M) showing stokes shift in DMSO.

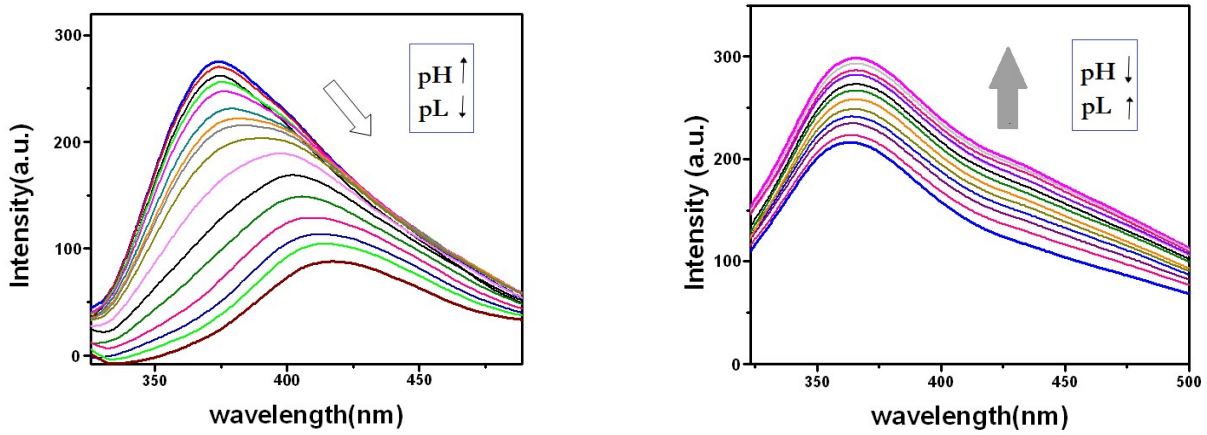


Fig. S18 Emission Spectra of **BPPIH** (2x 10^{-6} M) in DMSO-H_2O with NaOH solution (1 x10^{-3}M) pH changing from 5-10.

Fig. S19 Emission Spectra of **BPPIH** (2x 10^{-6} M) in DMSO-H_2O with HCl solution (pH 1) pH changing from 5-4.

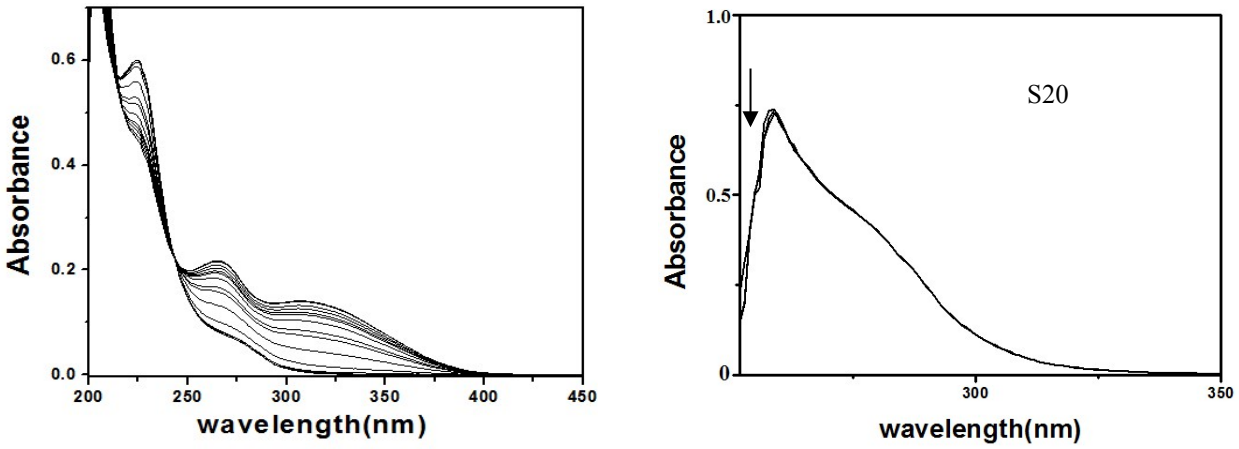


Fig. S20 Changes in UV-Vis Spectra of **BPPIH** (1x 10^{-5}M) in methanol-H_2O with NaOH solution (1 x10^{-3}M).

Fig. S21 Changes in UV-Vis Spectra of **BPPIH** (1x 10^{-5}M) in DMSO-H_2O with HCl solution (pH 1).

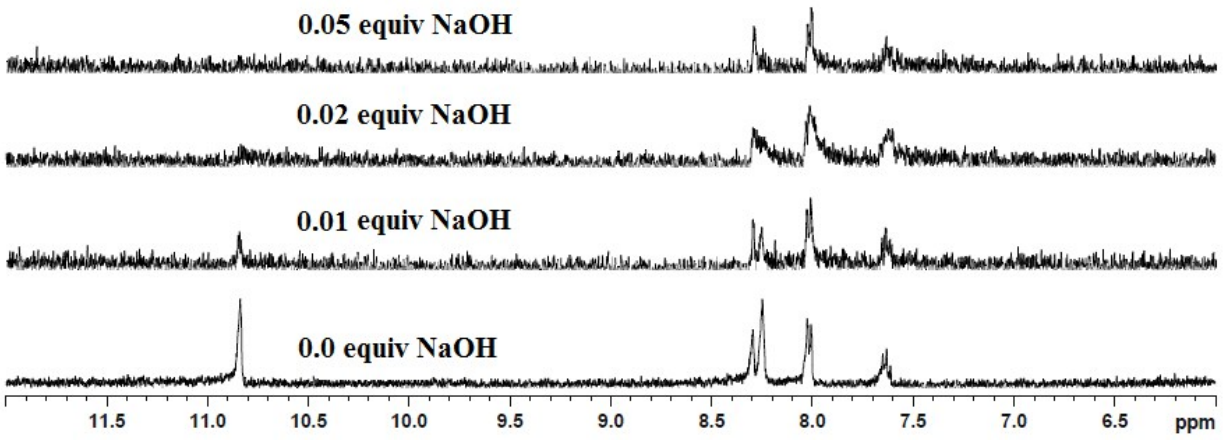


Fig. S22 ^{1}H-NMR titration of **BPPIH** ($1x10^{-3}$M) in DMSO-d^{6} with NaOH solution ($1x10^{-2}$M) in D_2O.

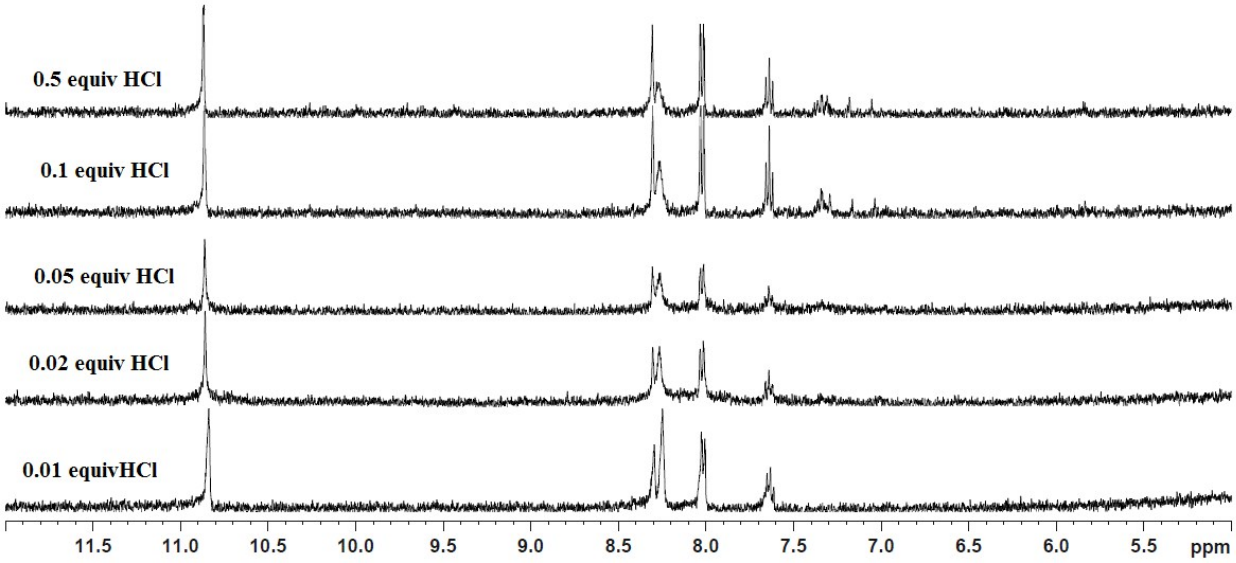
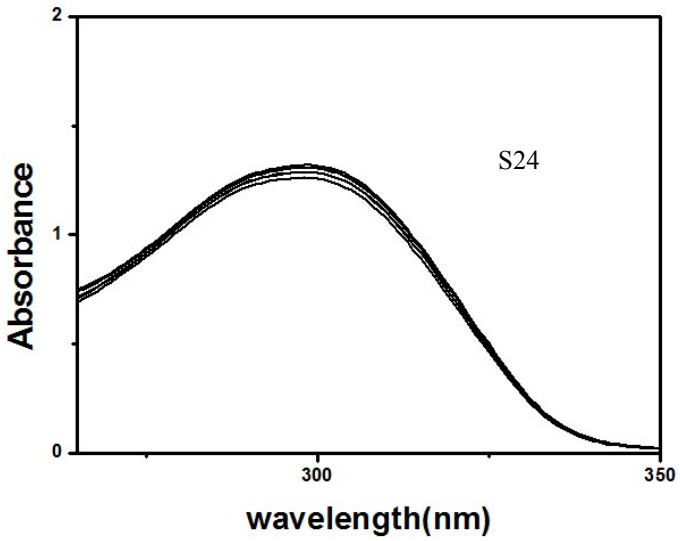


Fig. S23 ^{1}H-NMR titration of **BPPIH** ($1x10^{-3}$M) in DMSO-d^{6} with HCl solution in D_2O (pH 1).



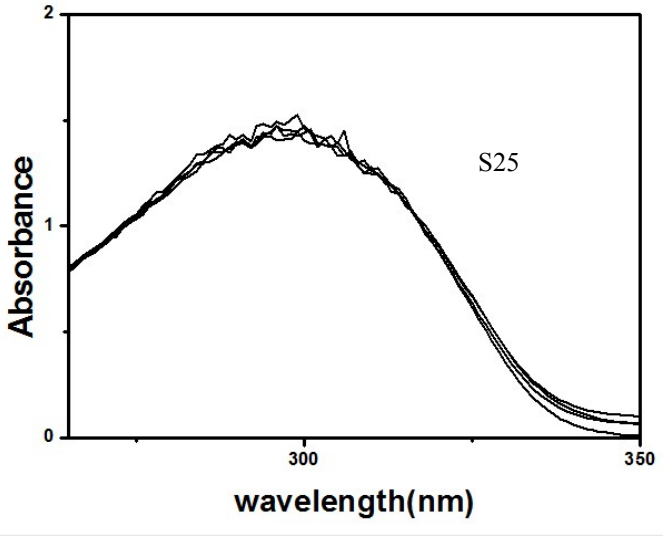
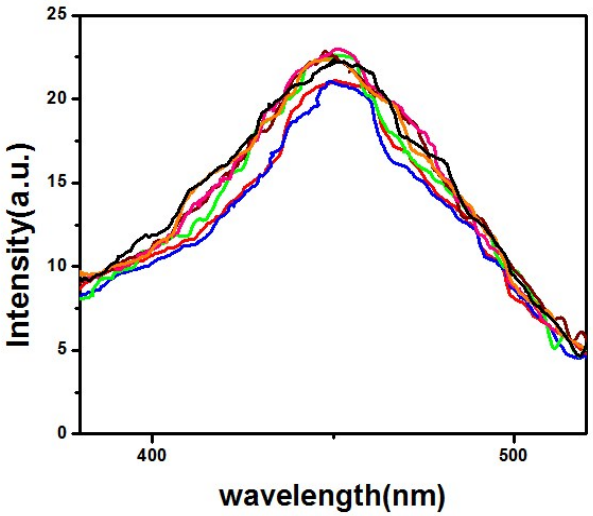
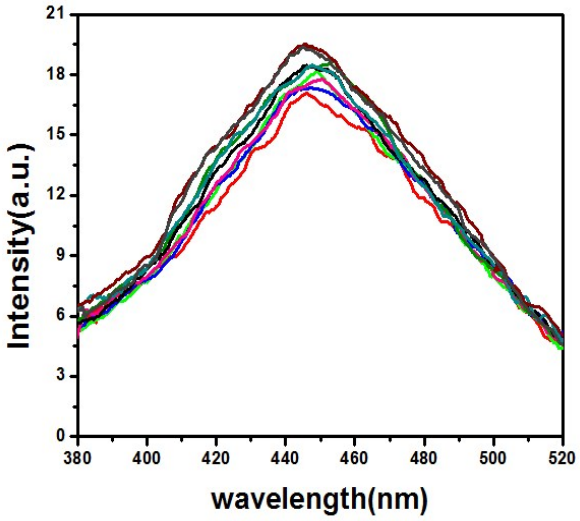


Fig. S24 Changes in UV-Vis Spectra of **BPBIH** (1x 10^{-5}M) in DMSO--H_2O with NaOH solution (1x 10^{-3}M).

Fig. S25 Changes in UV-Vis Spectra of **BPBIH** (1x 10^{-5}M) in DMSO-H_2O with HCl solution (pH 1).





S26

S27

Fig. S26 Changes in Emission-Spectra of **BPBIH** (2x 10^{-6}M) in DMSO-H_2O with NaOH solution (1x 10^{-3}M).

Fig. S27 Changes in Emission -Spectra of **BPBIH** (2x 10^{-6} M) in DMSO-H_2O with HCl solution (pH 1).

Table S7 Cartesian coordinates (angstroms) of geometry optimized structure of hydrazide part of **BPPIH**.

N	7.909004	15.654604	14.053598
N	7.225717	15.128858	12.943758
C	6.184803	15.791318	12.376031
C	5.546325	15.097268	11.198604
C	4.902171	15.894230	10.236155
C	4.286938	15.304149	9.131095
C	4.282794	13.912465	8.985888
C	4.904292	13.100551	9.949755
C	5.544326	13.703972	11.043992
C	4.949960	11.594802	9.865194
N	3.935219	11.023222	9.168064
N	3.858194	9.631105	8.991692
O	5.771033	16.882610	12.774292
O	5.856159	10.953444	10.402626
H	8.870495	15.888263	13.762977
H	7.612804	14.303547	12.479581
H	4.897158	16.980117	10.358435
H	3.808713	15.930314	8.372344
H	3.810412	13.475068	8.102047
H	6.012034	13.051463	11.784615
H	3.152096	11.599429	8.850095
H	3.739242	9.448906	7.984640
H	2.995057	9.297571	9.446026
H	7.992463	14.903860	14.753778

Table S8 Cartesian coordinates (angstroms) of geometry optimized structure of pentafluoro part of **BPPIH**.

C	3.092062	9.083219	7.867194
C	2.694433	9.725621	6.698531
C	2.053970	9.033802	5.667611
C	1.807715	7.666064	5.812996
C	2.199591	7.001830	6.978039
C	2.837816	7.720517	7.991889
F	2.921332	11.042180	6.539264
F	1.676304	9.665959	4.546785
F	1.194188	6.991428	4.832847
F	1.961865	5.688783	7.112431

F	3.205896	7.062504	9.106187
H	3.590128	9.634535	8.665978

Table S9 Cartesian coordinates (angstroms) of geometry optimized structure of singly protonated hydrazide part of **BPPIH**.

N	7.972310	15.490755	14.030048
N	7.231448	14.985546	12.945916
C	6.230944	15.685567	12.354283
C	5.555424	15.025363	11.180676
C	4.957639	15.851237	10.214267
C	4.295687	15.297222	9.115677
C	4.205014	13.912205	8.976481
C	4.784761	13.075035	9.948331
C	5.466795	13.634057	11.044407
C	4.676918	11.613383	9.840412
N	3.642361	11.040449	9.295127
N	3.449538	9.661407	9.225992
O	5.885401	16.800075	12.754809
O	5.602473	10.786746	10.295778
H	8.274157	16.448776	13.791455
H	7.624060	14.150309	12.511059
H	5.021736	16.935836	10.329128
H	3.852886	15.947931	8.357198
H	3.706687	13.489597	8.099982
H	5.873408	12.981203	11.821522
H	2.822977	11.605530	9.047333
H	4.370414	9.201161	9.164330
H	2.941225	9.468829	8.350422
H	7.329459	15.598591	14.829195
H	6.439367	11.249376	10.525760

Table S10 Cartesian coordinates (angstroms) of geometry optimized structure of doubly protonated hydrazide part of **BPPIH**.

N	7.822732	15.499929	14.133006
N	7.176588	15.012131	12.993017
C	6.248787	15.645488	12.312977
C	5.550904	15.026292	11.175540
C	4.923717	15.861174	10.231006
C	4.252631	15.302411	9.142888

C	4.188315	13.917345	8.994065
C	4.800788	13.076478	9.943852
C	5.488418	13.630873	11.032681
N	3.657361	11.035795	9.320618
N	3.478888	9.658980	9.241297
O	5.895532	16.863544	12.615582
O	5.673381	10.795129	10.209921
H	8.451662	16.279859	13.893077
H	7.490431	14.087688	12.680415
H	4.974969	16.945917	10.340050
H	3.783128	15.951477	8.400092
H	3.679025	13.494285	8.124322
H	5.916957	12.973194	11.793051
H	2.818698	11.594333	9.125525
H	4.395192	9.209200	9.093507
H	2.891475	9.471488	8.415853
H	7.139185	15.777522	14.850865
H	6.523492	11.260176	10.379308
H	6.443346	17.262575	13.336418

Cell Imaging studies inside cancer cells

Human cervical carcinoma cell lines (HeLa) were used for pH metric study. The Cells were allowed to grow on sterile cover glasses submerged in culture dish possessing 10 ml DMEM (Dulbecco's Modified Eagle's medium) (by Hi-Media) containing 10% FBS (Fetal Bovine Serum) (Hi-Media) with antibiotic concentration 1% of penicillin/streptomycin (50 IU/ml and 500 µg/ml), respectively in CO_2 incubator in a humidified atmosphere (95% air/5% CO_2) at 37°C for 1 day. Then fresh DMEM medium prepared with an adjusting different pH (6, 7 and 8) by adding 1N HCl and 1N NaOH. The given **BPPIH** compound solubilised in DMSO and adjusted its final concentration to 100µM in DMEM. The cells were allowed to grow in the above specified conditions until obtaining the expansion of cells around 75% - 80% confluence. Then these cells maintained in the same cultural conditions in addition of100 µM **BPPIH** with different pH. The negative controls were maintained without treating BPPIH. After 1 hrs continuous exposures to the compound at 37^{o}C these cells were washed with 1x PBS buffer and replaced with fresh medium and allowed to grow overnight. Next day these cultured cells on cover glasses fixed with fresh solution of 4% paraformaldehyde in PBS and ice cold methanol.

Multiple processing steps were allowed to culture cells for fluorescence microscopy. Fluorescence microscopy of live cells uses either genetically encoded fluorescent protein like GFP, mCherry, YFP, RFP, etc. or cell membrane-permeable, non-toxic fluorescent stains. Fluorescence microscopy of fixed cells uses a fixative agent that renders the cells dead, but maintains cellular structure, allowing the use of specific antibodies and dyes to investigate cell morphology and structure. Appropriate sample preparation is necessary to ensure high quality images are captured. Here we described a number of concepts and considerations regarding the sample preparation process that can assist with automated digital fluorescence microscopy of fixed cells. Cell fixation by using the cross linking agents does not reduce the cell membrane structure and rigidity. Therefore, formaldehyde fixation provides the cells to be permeabilized to allow **BPPIH** compound access into the interior of cells. The size and ionic nature of **BPPIH** compound prevent them from gaining access without membrane disruption. A mild detergent was used that generate large enough pores for the internalization of **BPPIH** compound to pass through without completely dissolving the plasma membrane. Triton X-100 is the most commonly used permeabilization agent for immunofluorescent staining. This detergent efficiently dissolves cellular membranes without disturbing protein-protein interactions. Triton is

usually used at of 0.1 % in PBS at room temperature for 10 minutes for permeabilization. Besides cell membrane permeabilization, this detergent will partially dissolve the nuclear membrane making them suitable for nuclear staining also and these fixed cells were analyzed for fluorescent emission by using standard filter sets. But with DAPI filter with the Excitation/Emission Wavelengths 358/400 nm in fluorescent microscope (Zeiss). The cells were showing decreased fluorescence lesser response in higher basic medium. Hence the **BPPIH** compound was internalized into the both cytoplasm and nucleus.

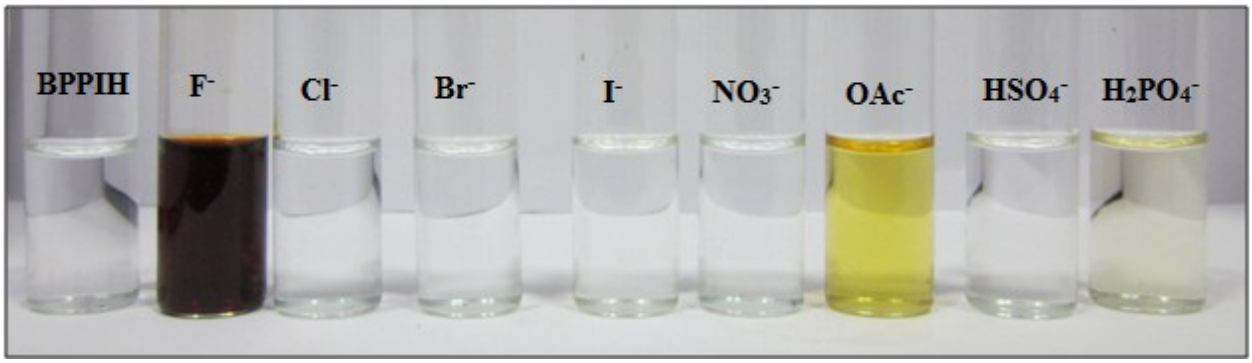


Fig. S28 Solutions of **BPPIH** in DMSO in presence of various anions.

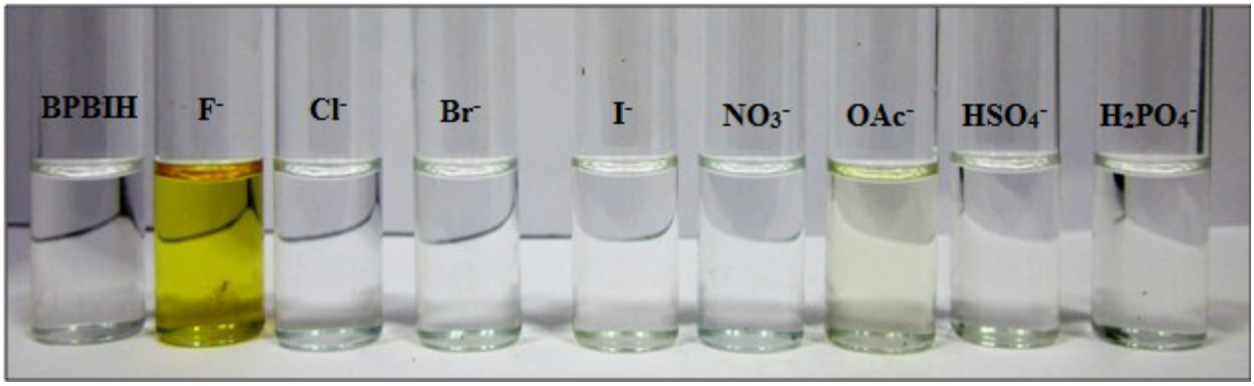


Fig. S29 Solutions of **BPBIH** in DMSO in presence of various anions.

S30

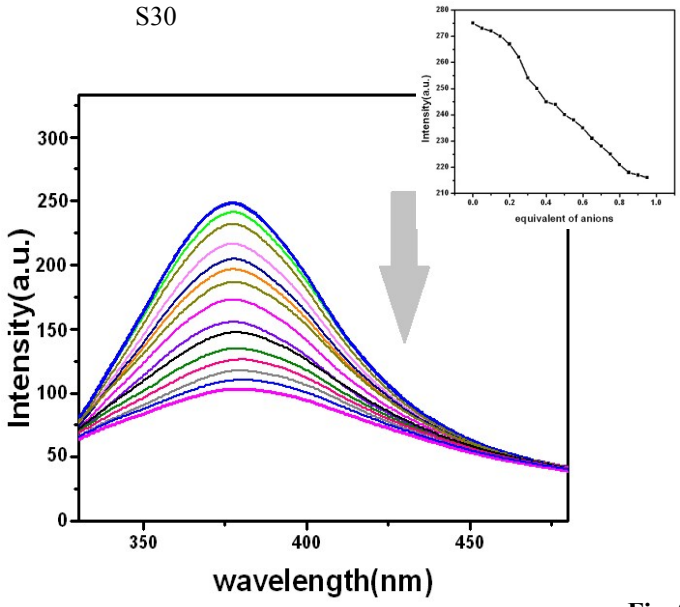


Fig. S31 Emission of **BPBIH** (2x10^{-6} M) with F$^-$ (0-2eq) in DMSO.

S31

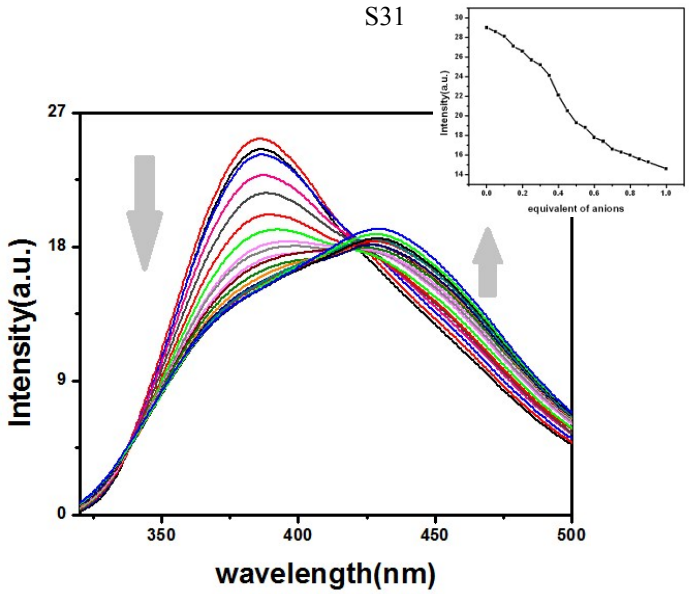
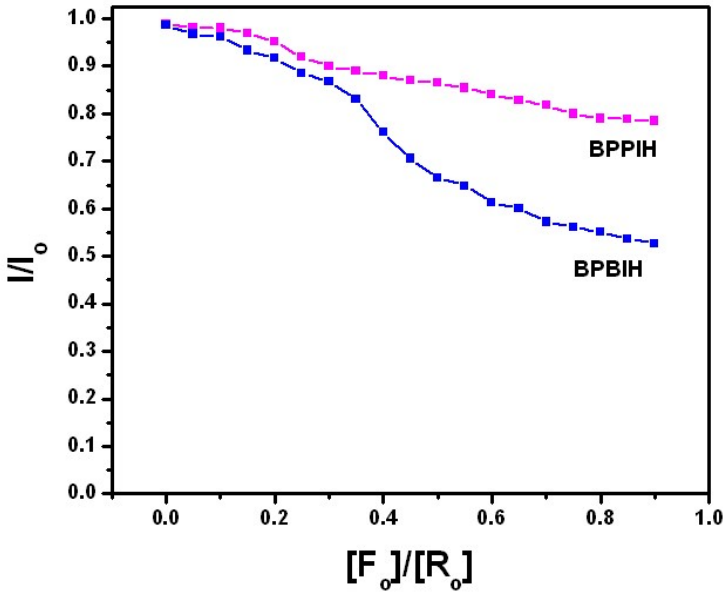


Fig. S30 Emission of **BPPIH** (2x10^{-6} M) with F$^-$ (0-2eq) in DMSO.

S33



S34

Fig. S32 Ratio of emission intensity of **BPBIH** with F$^-$.

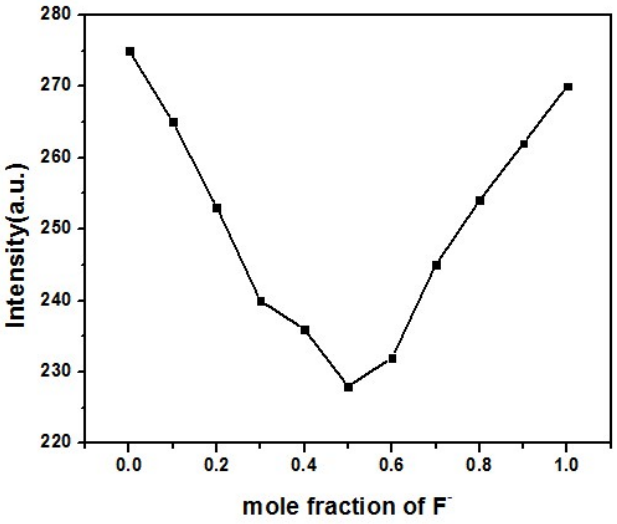


Fig. S33 Jobs Plot of **BPPIH** with F^-.

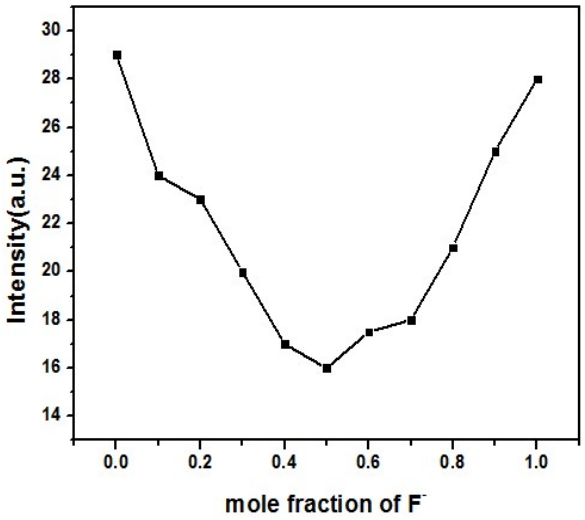


Fig. S34 Jobs Plot of **BPBIH** with F^-.

Benesi-Hildebrand Equation and Plot:

The association constant of a complex formed in between the receptors and the incoming anions has been determined from the following complex equilibrium.

$$L + mX^{n-} \longleftrightarrow (X_mL)^{mn-}$$

$$K = \frac{[(XmL)]^{mn-}}{[L][X^{n-}]^m}$$

For 1:1 type complex formation with m=1 following the Benesi-Hildebrand relation, can be expressed in terms of optical density (A) as follows:

$$A = \frac{A_o + A_1K[X^{n-}]}{1 + K[X^{n-}]}$$

Or,

$$\frac{1}{A - A_0} = \frac{1}{(A_1 - A_0)} + \frac{1}{(A_1 - A_0)K[X^{n-}]}$$

Where $[X^{n-}]$, [L] and $[(X_mL)^{mn-}]$ are the concentration of the added anions, receptors and the complexation between anions and receptors, respectively. A_o, A and A_1 indicates the optical density or absorbance at a particular wavelength of receptor **1** or receptor **2** without adding any anion, absorbance after adding anion at every successive step and excess amount of added anion, respectively. The binding constant or association constant K (M^{-1} or M^{-2}) is determined from the ratio of intercept and slope of Benesi-Hildebrand plot of optical density.

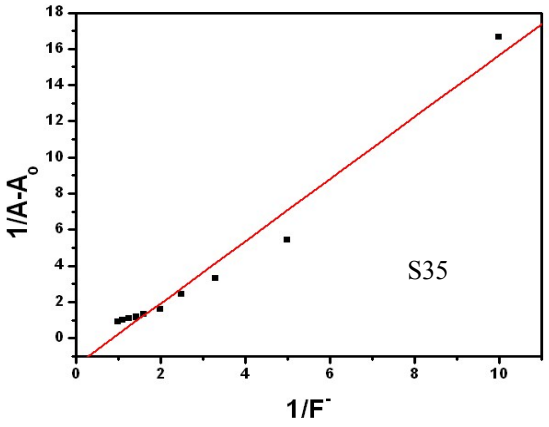


Fig. S35 B-H Plot of **BPPIH** with F^-.

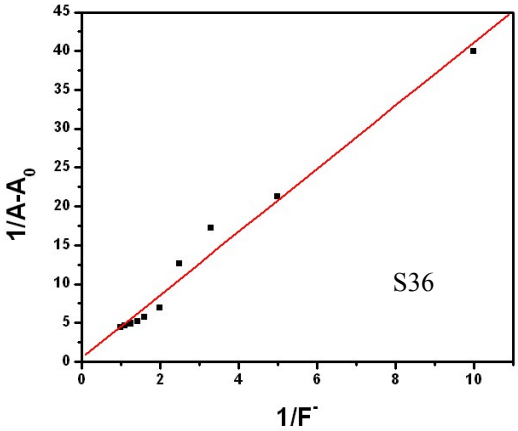


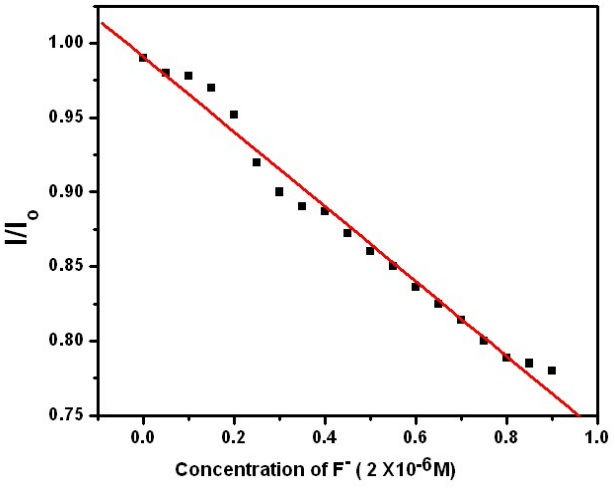
Fig. S36 B-H Plot of **BPBIH** with F^-.

Detection limit calculation

The detection limit (DL) has been calculated following fluorescence titration [ref]. The fluorescence emission spectrum of **BPPIH** and **BPBIH** is repeated 10 times, and its standard deviation is measured. The limit of detection (LOD) is calculated from the following formula:

$$DL = 3\sigma/k$$

σ is the standard deviation of the blank solution of BPPIH and BPBIH. Gradual quenching of BPPIH and **BPBIH** emission intensity at 365 nm and 380 nm respectively during fluorimetric titration with TBAF is plotted against its concentration. The slope (k) is derived from these plots.



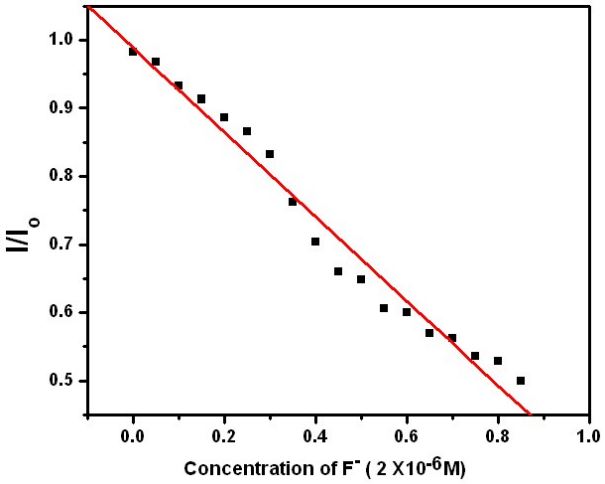
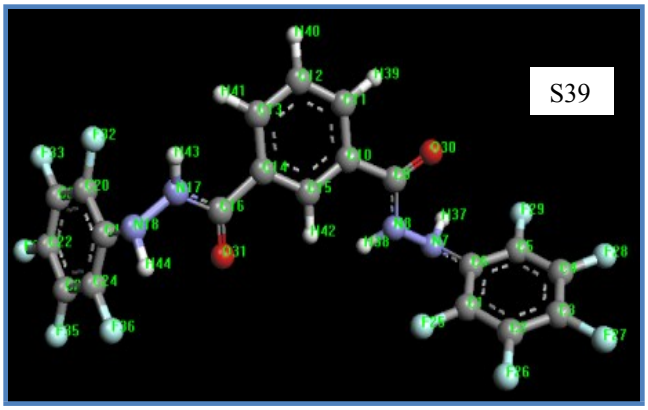


Fig. S37 Ratio of emission intensity of **BPPIH** with F^-.

Fig. S38 Ratio of emission intensity of **BPBIH** with F^-



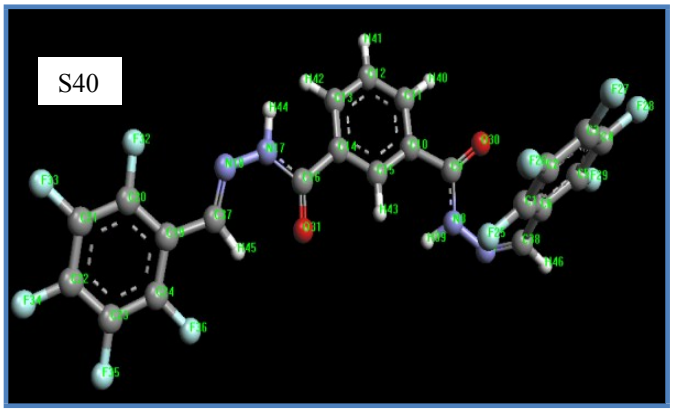


Fig. S39 Geometry optimized structure of **BPPIH** with the atoms labeled.

Fig. S40 Geometry optimized structure of **BPBIH** with the atoms labeled.

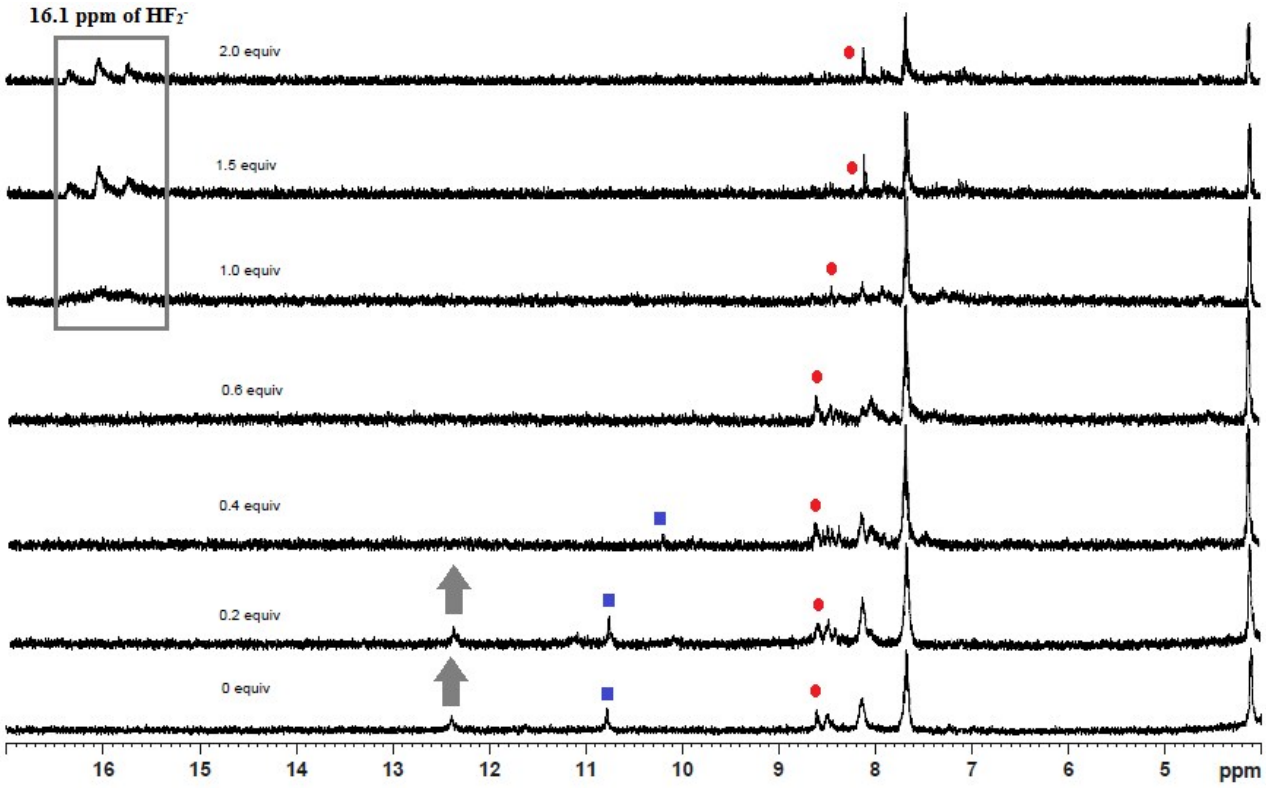


Fig. S41 ^{1}H-NMR titration of **BPBIH** (1x10^{-3} M) with TBAF (0-2eq) in DMSO-d^6.

Table S11 Cartesian coordinates (angstroms) of geometry optimized structure of **BPPIH…F**$^-$ adduct

C	7.7850532	14.1409618	14.9557795
C	7.6951813	13.7212548	16.2924087
C	7.9261555	14.6235975	17.3428895
C	7.9261555	14.6235975	17.3428895
C	7.9261555	14.6235975	17.3428895
C	7.9261555	14.6235975	17.3428895
C	7.9261555	14.6235975	17.3428895
C	7.9261555	14.6235975	17.3428895
C	8.1826978	15.9729314	17.0372812
C	8.2503441	16.3839320	15.6983202

C	8.0196829	15.4938300	14.6247241
N	8.1516814	15.9544281	13.3006394
N	7.2537109	15.4399254	12.3667938
C	6.1420380	16.1965105	12.0047065
C	5.2516693	15.5434696	10.9888012
C	4.3768394	16.3459134	10.2240497
C	3.5174688	15.7465611	9.2918785
C	3.4959440	14.3472850	9.1371151
C	4.3415438	13.5340757	9.9203190
C	5.2257604	14.1467312	10.8269607
C	4.3925932	12.0236326	9.8695432
N	3.2132820	11.4084953	9.5261414
N	3.0512053	10.0342838	9.6404017
C	3.5621089	9.2377972	8.6252627
C	3.5999121	9.6101730	7.2551730
C	4.0961334	8.7495757	6.2623389
C	4.5219715	7.4515266	6.5877890
C	4.4746001	7.0458697	7.9320961
C	4.0027253	7.9206184	8.9204017
F	7.6031409	13.2118850	13.9915662
F	7.4363763	12.4301620	16.5625649
F	7.8676415	14.2148093	18.6143854
F	8.3777687	16.8555726	18.0202037
F	8.4925251	17.6763194	15.4177116
O	5.9334149	17.2993637	12.5069230
O	5.4255271	11.4097469	10.1478998
F	3.1574748	10.8243543	6.8637521

F	4.1209370	9.1565116	4.9836192
F	4.9797380	6.6200566	5.6378996
F	4.8918972	5.8160337	8.2746137
F	3.9980136	7.4945603	10.1982121
N	5.7130743	9.2697685	13.9422872
C	4.8594447	8.0231510	13.8722970
C	6.8546781	9.0995010	14.8923642
C	4.8245349	10.4191251	14.3697377
C	6.2086070	9.5685692	12.5435445
F	3.3550935	9.6233205	12.1013283
H	8.1415658	16.9855499	13.2600688
H	7.6380038	14.7405153	11.7252964
H	4.3899308	17.4373283	10.3726152
H	2.8545521	16.3737896	8.6735657
H	2.8326282	13.8947971	8.3810333
H	5.8675155	13.4842805	11.4274795
H	2.3528147	11.9605970	9.4581753
H	3.1587860	9.7202410	10.6999697
H	5.2851482	9.6887776	11.9299868
H	4.0403968	8.2862407	13.1498657
H	4.4751512	7.8018542	14.8890169
H	6.4581377	8.8498098	15.8973795
H	7.5082935	8.2794213	14.5321733
H	4.0147224	10.4525803	13.5925150
H	4.4281822	10.1966832	15.3816529
H	5.4395525	11.3407056	14.3949342
H	6.8316800	8.7180732	12.2008384

H	7.4254872	10.0482282	14.9445975
H	5.4882994	7.1857920	13.5080807
H	6.8021061	10.5023855	12.5679491

Table S12 Cartesian coordinates (angstroms) of geometry optimized structure of **BPPIH…2F**$^-$ adduct

C	5.083418659	16.450703631	14.644443688
C	4.169232639	17.132544549	449499171
C	4.468195033	18.412309895	15.917538311
C	5.664774752	19.020286879	15.523585659
C	6.542163831	18.341368245	14.679529171
C	6.291092361	17.035059131	14.222269444
N	7.183909766	16.365006016	13.391217290
N	6.631199595	15.883501689	12.207931941
C	5.958010120	16.702372547	11.355059913
C	5.446883390	16.051188974	10.115883081
C	4.222030145	16.487762625	9.587676920
C	3.718929210	15.907211538	8.423879173
C	4.437195288	14.900201053	7.774033307
C	5.677202183	14.484812714	8.280661079
C	6.179546315	15.060182012	9.454946483
C	6.505732309	13.456703343	7.582957278
N	5.780507057	12.541062289	6.917433141
N	6.508405186	11.505003284	6.330935412
C	5.897864473	10.754488526	5.357200857
C	5.090650449	11.281041348	4.326416044
C	4.580676121	10.460838234	3.318594045
C	4.859602884	9.095789458	3.290599347

C	5.644336011	8.540216639	4.311651891
C	6.116074644	9.359091213	5.331251228
F	4.760590582	15.199638313	14.244788271
F	3.011392802	16.550838915	15.800518037
F	3.609137091	19.048509187	16.736394573
F	5.949576776	20.273994788	15.934504247
F	7.633207644	18.990734049	14.244560525
O	5.786701807	17.902033529	11.579139725
O	7.748323511	13.464492633	7.649692829
F	4.814530008	12.600656152	4.267879906
F	3.828818573	10.980178281	2.329867942
F	4.405498848	8.356387716	2.265259175
F	5.921279017	7.225617682	4.315035955
F	6.832149413	8.815531552	6.346071037
F	3.609059535	11.663167437	7.616813514
N	1.153795659	10.197572861	6.171762199
C	0.762521862	10.620985649	7.564888903
C	-0.006590364	9.517148261	5.519741783
C	2.334229878	9.266281927	6.250297984
C	1.552701812	11.417489656	5.388160918
F	9.647082808	16.902535728	13.111414511
N	10.242498931	15.594953005	16.171671401
C	11.506177581	15.787595921	15.380717549
C	10.558898311	15.097825575	17.548295272
C	9.530423875	16.916830419	16.245853944
C	9.370963357	14.603921551	15.459418949
H	8.197900656	16.723458062	13.272441860

H	6.607042207	14.876939378	12.082132668
H	3.669448873	17.275978845	10.100792504
H	2.768159838	16.251879955	8.010534240
H	4.040380659	14.446958878	6.863143960
H	7.154315039	14.734298360	9.824016488
H	4.757448644	12.226427169	7.251886051
H	7.053446565	10.970413941	7.006847397
H	1.628568559	11.131489547	8.003507059
H	0.487940473	9.725345381	8.136770620
H	-0.097528129	11.298475166	7.489719204
H	-0.843885328	10.222074637	5.466813892
H	0.287301051	9.198005919	4.512063745
H	-0.284693027	8.646003713	6.124875981
H	2.633619659	8.978669177	5.235675778
H	3.129909073	9.828580150	6.754817197
H	2.042942542	8.379669256	6.824796705
H	2.391006257	11.881556455	5.922534177
H	1.848956204	11.104778153	4.377468428
H	0.693332441	12.096410218	5.331586713
H	9.907908056	13.649607497	15.406664467
H	9.164733840	14.999562486	14.459672751
H	8.440266520	14.482091094	16.026570144
H	9.391469332	17.254143712	15.211928914
H	8.572772881	16.779702882	16.762758299
H	10.159919685	17.618190149	16.806054293
H	11.179867181	15.845014235	18.056664810
H	9.618158112	14.951077258	18.091669542

H	11.098701897	14.146787774	17.465072456
H	12.149481368	16.489132990	15.925289588
H	12.005530835	14.816632358	15.278556351
H	11.212654788	16.194188569	14.401979461

Table S13 Cartesian coordinates (angstroms) of geometry optimized structure of **BPBIH…F**$^-$ adduct

C	5.780913301	15.843196302	16.023630002
C	5.408396401	17.004377802	16.718049502
C	6.376310401	17.728685602	17.435339202
C	7.714035401	17.294710102	17.439883802
C	5.780913301	15.843196302	16.023630002
C	8.059101101	16.130404802	16.740422002
C	7.117600901	15.387893902	15.990989002
N	7.179249401	13.434486202	14.334029502
N	6.317979401	13.847728602	13.373564802
C	6.178663401	15.144752602	12.867983902
C	5.344652701	15.212985302	11.615841101
C	4.656306901	16.397843902	11.279430201
C	3.825472600	16.423953702	10.144713301
C	3.652017400	15.275113002	9.353039201
C	4.346011001	14.090160302	9.678357401
C	5.224777401	14.096908902	10.773304101
C	4.097839700	12.836648502	8.882665301
N	4.509695101	11.659888401	9.526580801
N	4.432966901	10.386929501	9.086752601
C	3.857595300	8.688884501	7.474794701
C	4.244482401	7.544936301	8.217552201

C	4.106659800	6.242062001	7.714850701
C	3.570144200	6.032464101	6.432337001
C	3.176466800	7.139513601	5.661962701
C	3.323756700	8.433565701	6.183984701
F	4.814823601	15.145590902	15.412967002
F	4.131579000	17.405927602	16.730513902
F	6.027810101	18.826865502	18.111907202
F	8.640226301	17.986546502	18.114748902
F	4.814823601	15.145590902	15.412967002
F	9.342976001	15.732981702	16.770309302
O	6.693745701	16.137537402	13.385910202
O	3.542755800	12.850262802	7.780698201
F	4.769781601	7.653687101	9.454422001
F	4.482954501	5.191441801	8.457571801
F	3.438253300	4.793431601	5.951782001
F	2.664124500	6.955299101	4.441587201
F	2.935248600	9.458891401	5.413167701
C	3.938821700	10.084302301	7.917030201
C	7.558270001	14.126901002	15.368513902
N	6.807630001	8.751108601	12.674404102
C	7.219993001	9.204180401	11.289732401
C	5.299400601	8.842594301	12.774027402
C	7.267238801	7.348225401	12.925832402
C	7.410779601	9.699910701	13.683696102
F	5.720398101	11.579360701	11.973712201
H	5.984394701	13.017981702	12.808224202
H	4.771779701	17.285010602	11.922585601

H	3.285963400	17.350163502	9.885847201
H	2.975664800	15.272845902	8.483249101
H	5.808649301	13.196816102	11.003472101
H	4.918105201	11.692100401	10.503002101
H	3.556588400	10.850070101	7.223378701
H	8.357629601	13.615264302	15.938241702
H	8.515267601	9.641913101	13.610941702
H	7.078857401	9.399550501	14.697720502
H	7.048939801	10.720222101	13.432102302
H	6.960953301	7.040706601	13.945947102
H	8.371627301	7.304609701	12.835820902
H	6.802044501	6.679268601	12.174612801
H	4.992629901	8.500957501	13.783224302
H	4.856456401	8.201965501	11.986832701
H	5.058386001	9.917418701	12.591059102
H	8.326487101	9.176554701	11.226540001
H	6.759056201	8.528183201	10.544931901
H	6.810553301	10.236658201	11.191205101

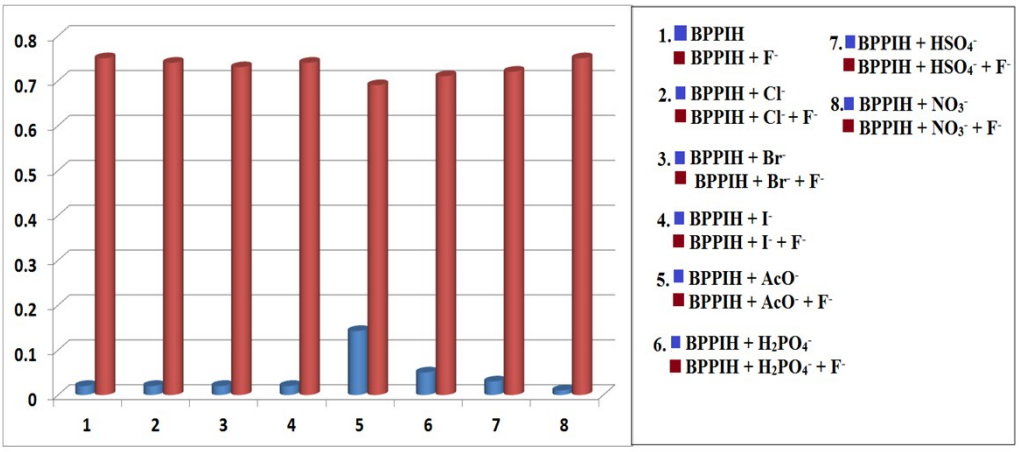


Fig. S42 Interference study in F^- detection with **BPPIH** in presence of various other anions.