Supporting Information

For

A BODIPY/pyrene-based chemodosimetric fluorescent chemosensor for selective sensing of hydrazine in the gas and aqueous solution state and its imaging in living cells

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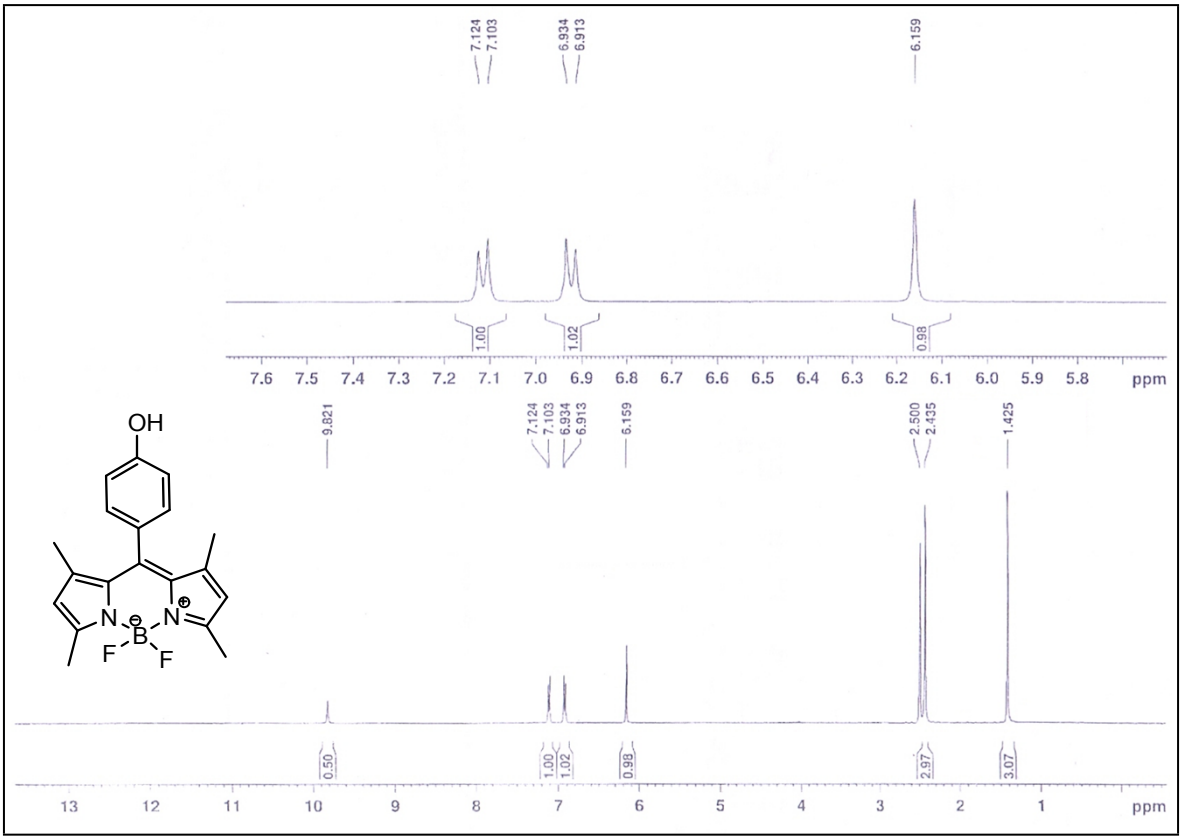


Figure S1. ^{1}H NMR of **Compound (2)** (d_6-DMSO, 400 MHz).

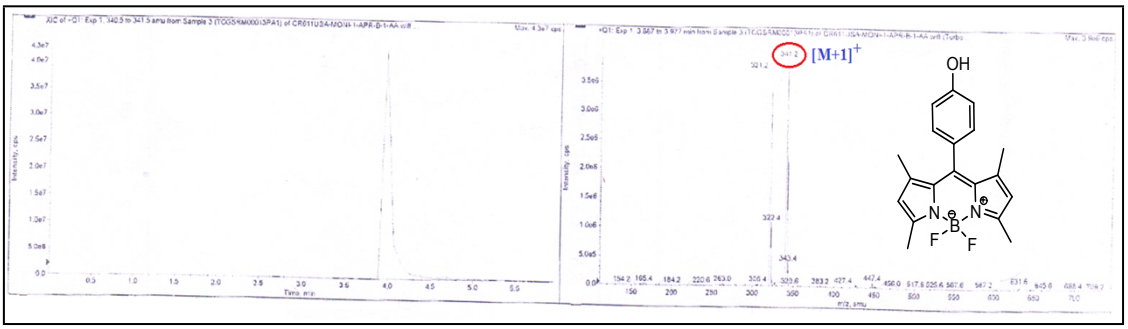


Figure S2. ESI LCMS $[M+1]^+$ spectrum of **Compound (2)**.

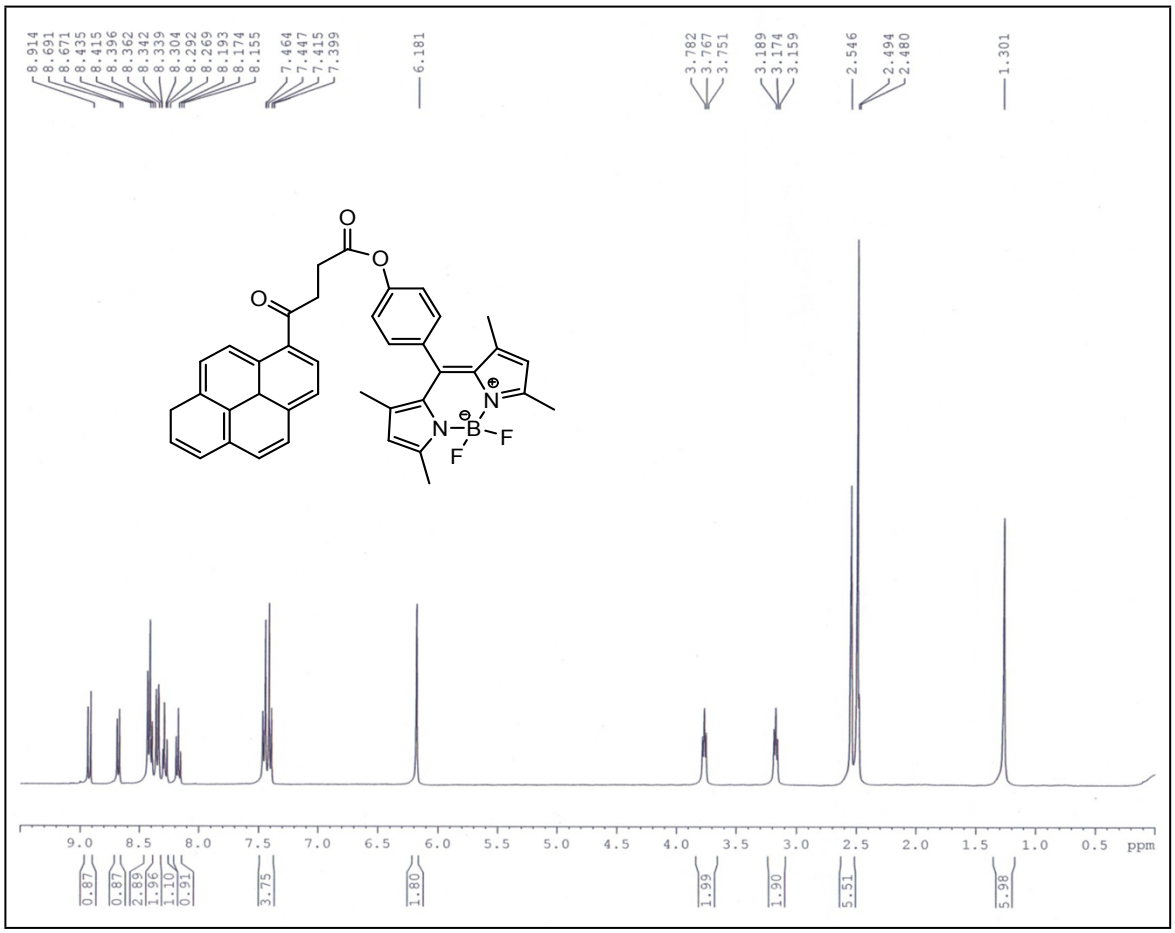


Figure S3. ^{1}H NMR of **Compound (BPB)** (d_6-DMSO, 400 MHz).

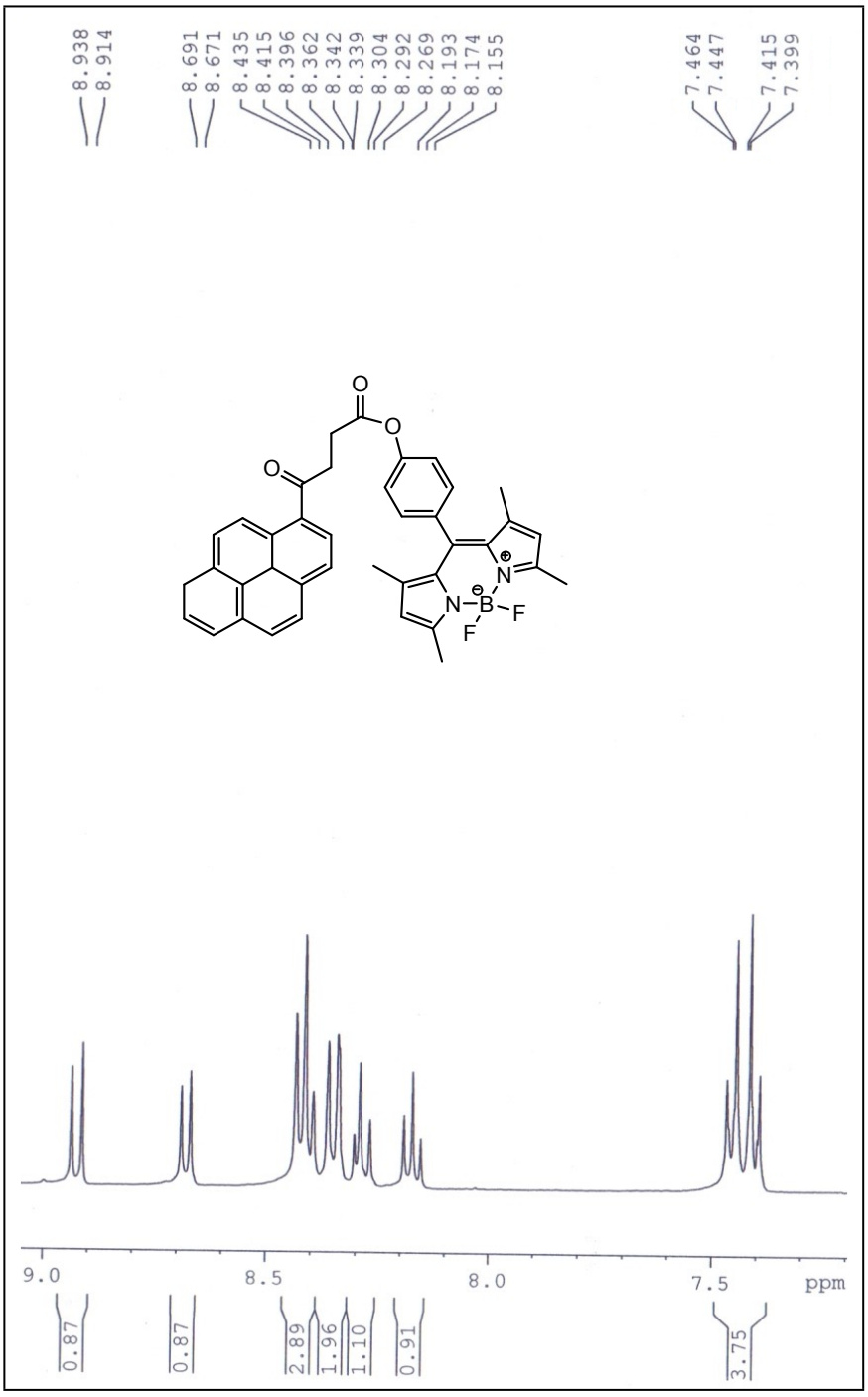


Figure S4. Expantion spectrum of ^{1}H NMR of **Compound (BPB)** (d_6-DMSO, 400 MHz).

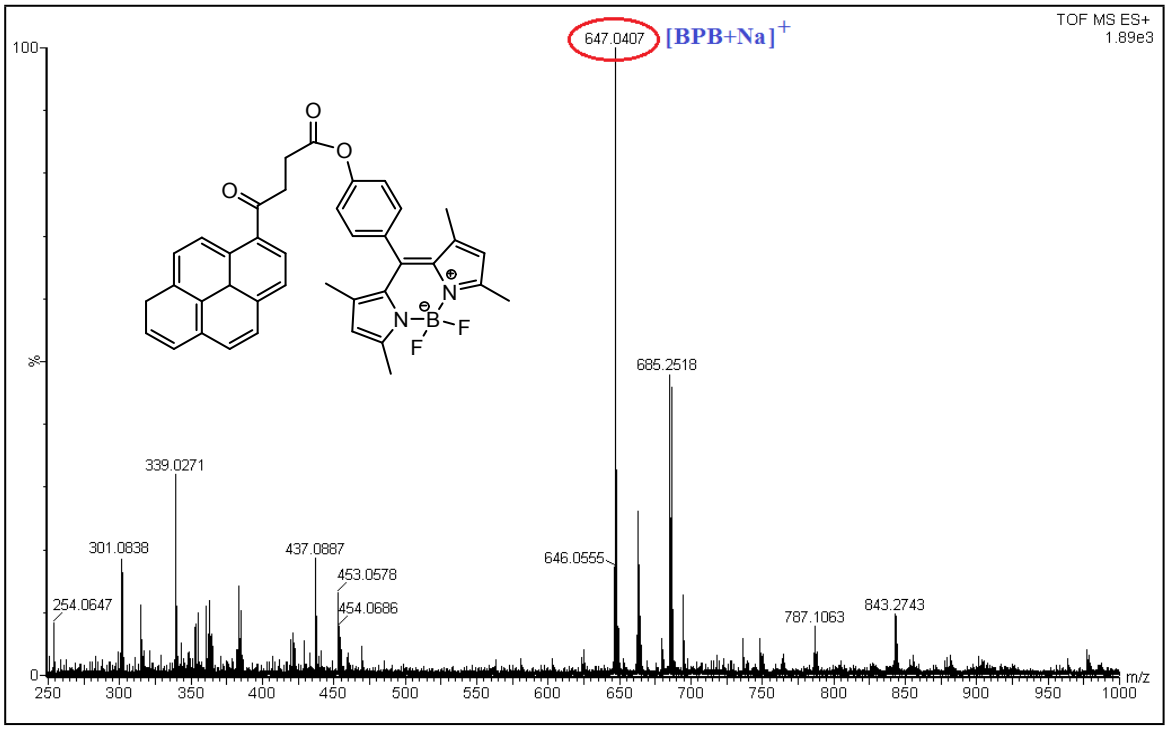


Figure S5. TOF MS ES+ mass spectrum of **Compound (BPB)**.

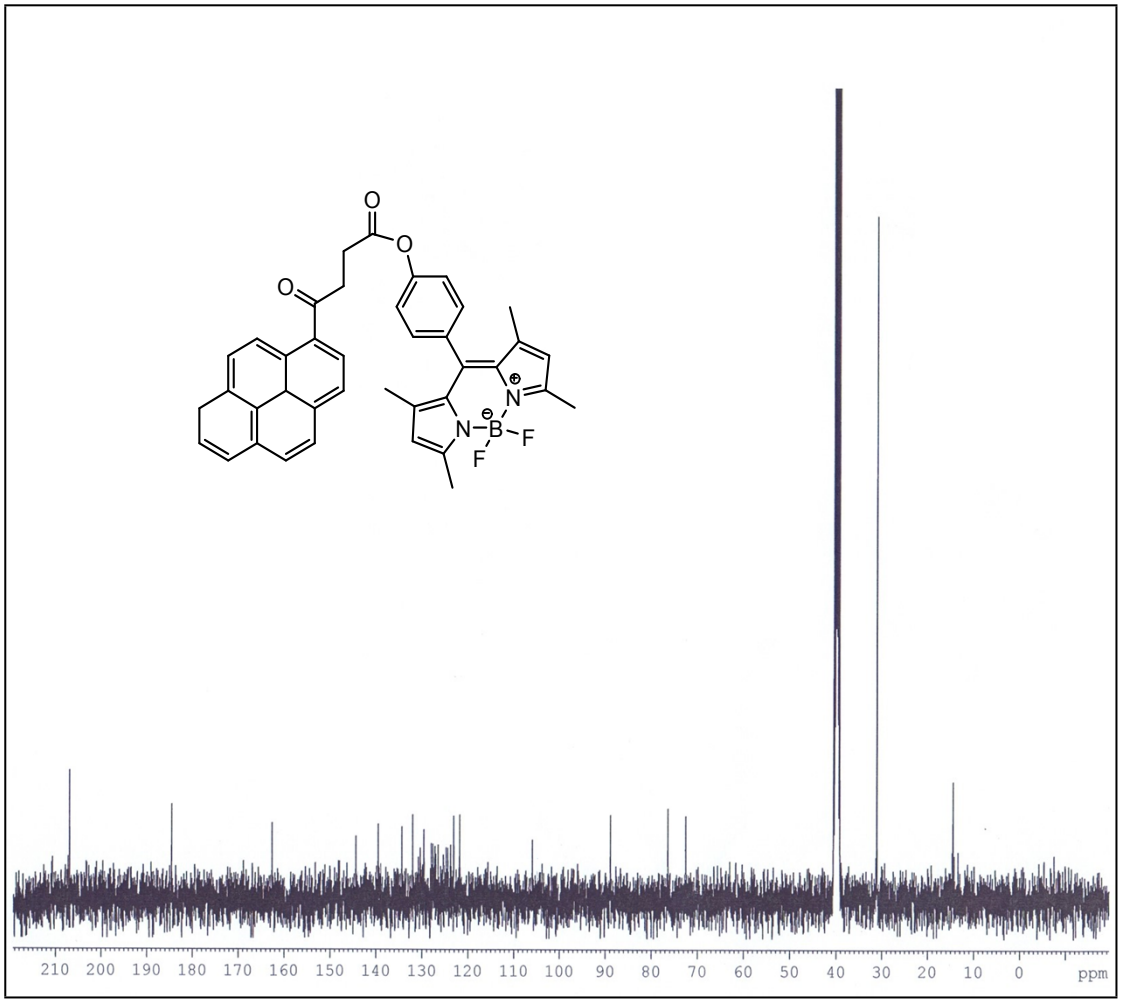


Figure S6. ^{13}C NMR spectrum of **Compound (BPB)** (d_6-DMSO, 100 MHz).

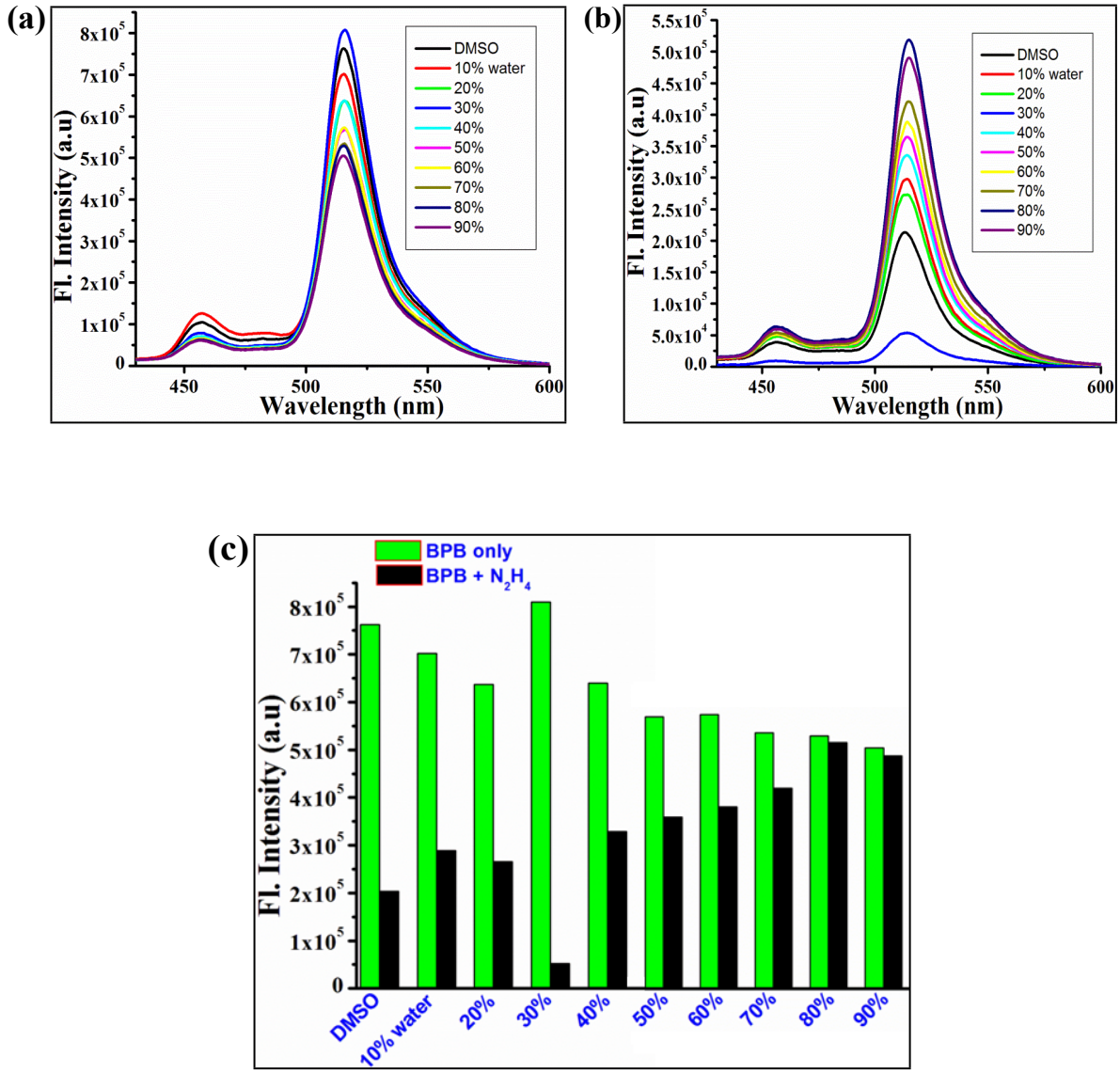


Figure S7. Effects of water composition on the fluorescence of (a) **BPB**, (b) **BPB** in the presence of hydrazine, and (c) their plot in aqueous DMSO.

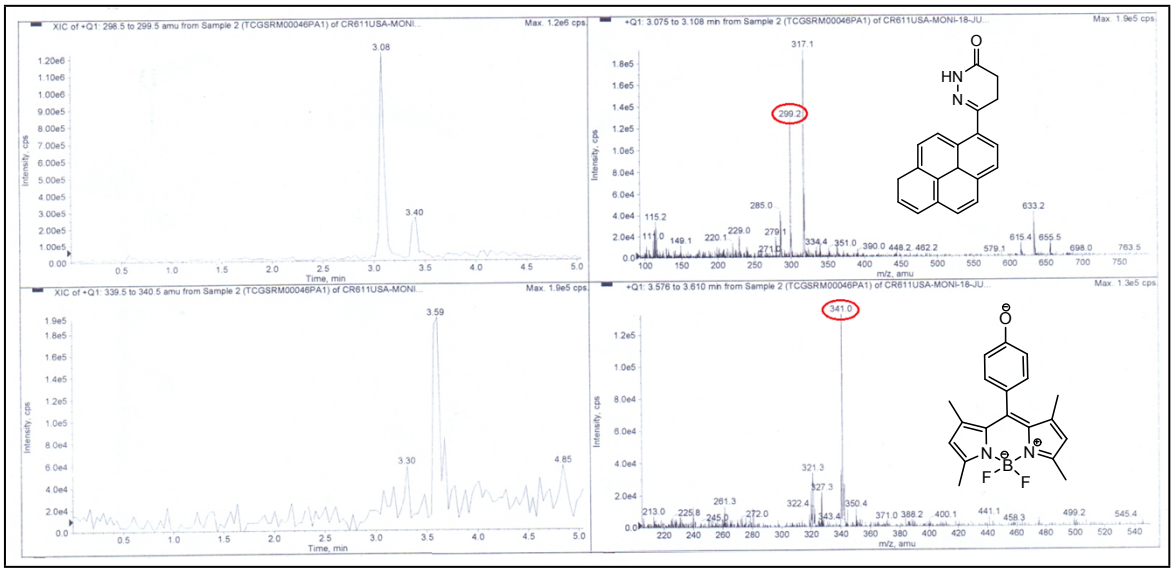


Figure S8. ESI LCMS spectra of **BPB**+ N_2H_4.

Calculations for detection limit

The detection limit (DL) of **BPB** for hydrazine was determined from the following equation:

DL = K* Sb1/S

Where K = 2 or 3 (we take 2 in this case); Sb1 is the standard deviation of the blank solution; S is the slope of the calibration curve.

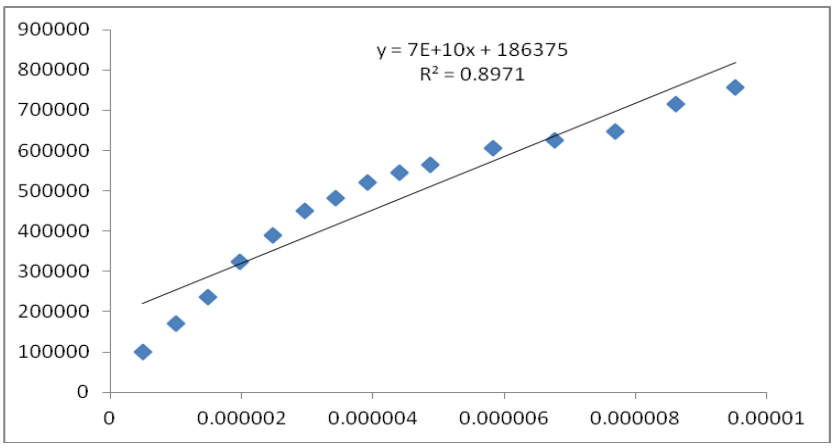


Figure S9. Calibration curve for fluorescence titration of **BPB** with hydrazine.

From the graph we get slope (S) = 7×10^{10}. Standard deviation (Sb1=65536.8123)

Thus using the formula we get the detection limit = 1.87 µM.

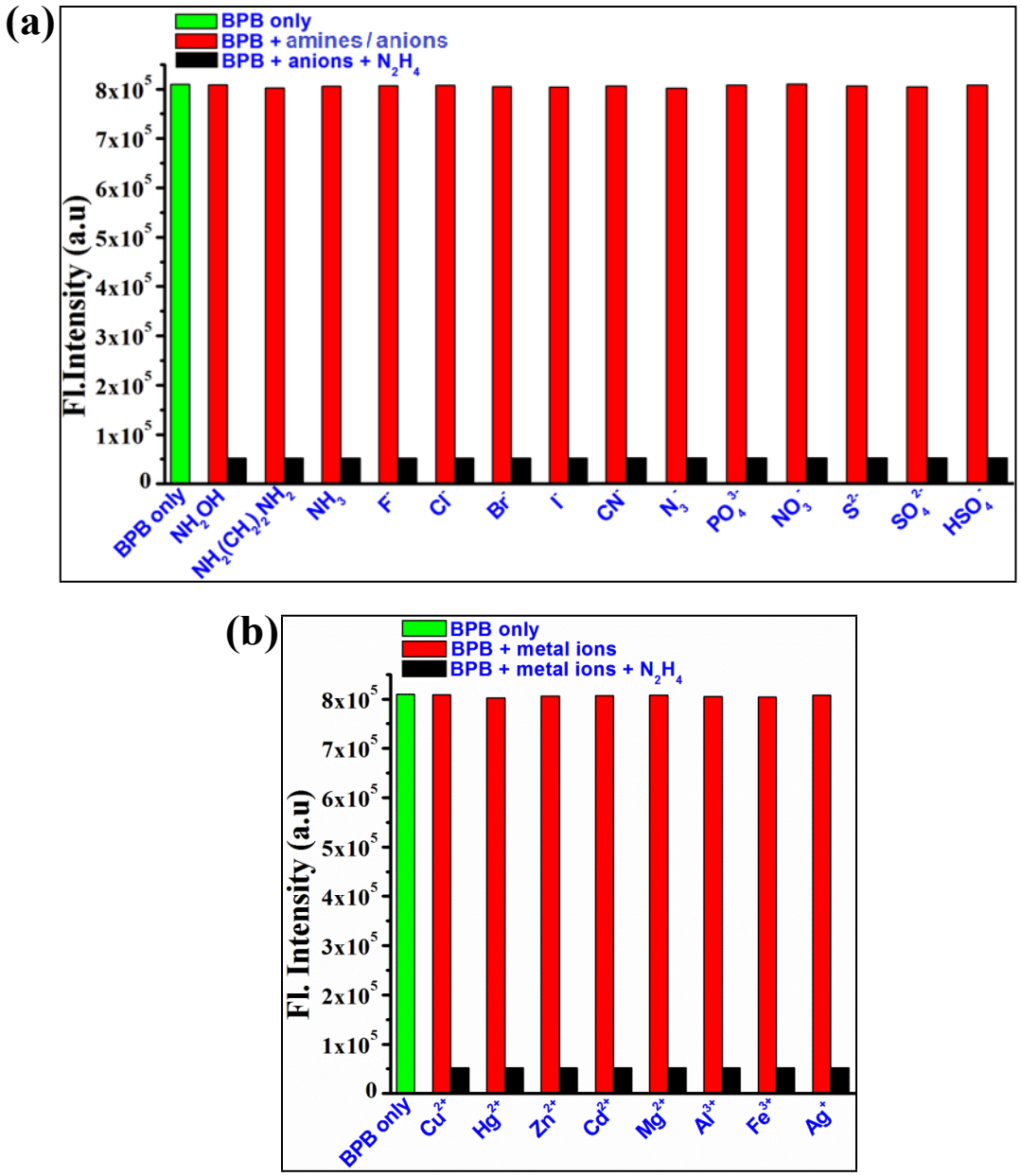


Figure S10. Competition Fluorescence experiments for a **BPB**-hydrazine system in the presence of coexisting (a) amines/anions and (b) cations. [**BPB**] = 1 x 10^{-5} M, 2.0 equiv. of hydrazine (c = 2 x 10^{-4} M) and 30 equiv of common anions and cations , redox anions and amines (c = 2 x 10^{-4} M) in H_2O–DMSO (3:7, v/v) solution (10 mM HEPES buffer, pH 7.4).

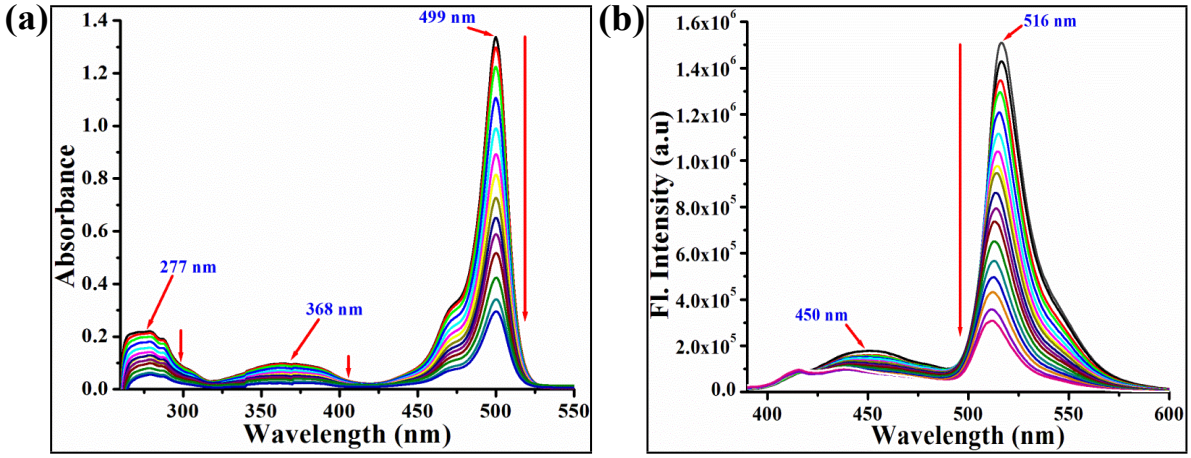


Figure S11. (a) Changes in the UV/vis absorption spectra of compound-**2** (c = 2 x 10^{-5} M) in H_2O–DMSO (3:7, v/v) solution (10 mM HEPES buffer, pH 7.4) in the presence of 0 – 10.0 equiv. of hydrazine and (b) Fluorescence spectra (excitation at 368 nm) of compound-**2** (c = 2 x 10^{-5} M) in H_2O–DMSO (3:7, v/v) solution (10 mM HEPES buffer, pH 7.4) in the presence of 0 – 10.0 equiv. of hydrazine.

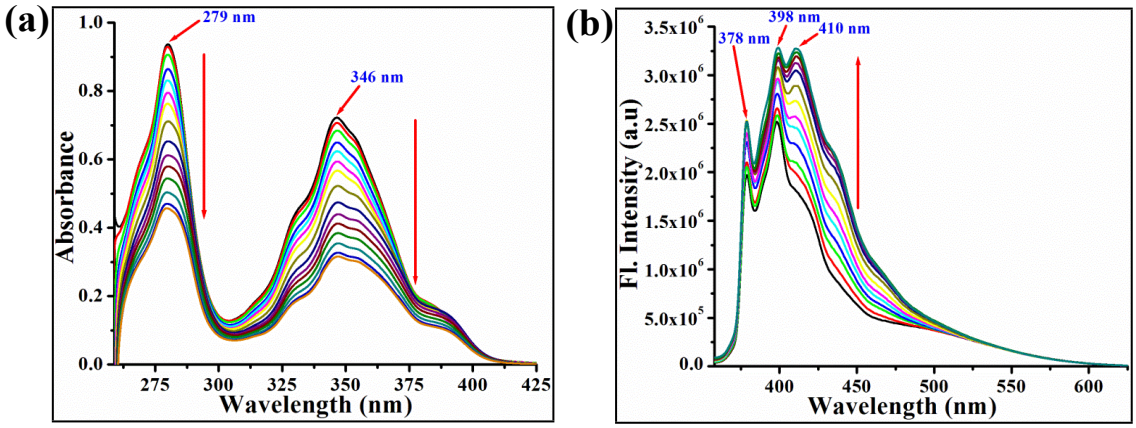


Figure S12. (a) Changes in the UV/vis absorption spectra of γ-oxo-1-pyrenebutyric acid (c = 2 x 10^{-5} M) in H_2O–DMSO (3:7, v/v) solution (10 mM HEPES buffer, pH 7.4) in the presence of 0 – 20.0 equiv. of hydrazine and (b) Fluorescence spectra (excitation at 346 nm) of γ-oxo-1-pyrenebutyric acid (c = 2 x 10^{-5} M) in H_2O–DMSO (3:7, v/v) solution (10 mM HEPES buffer, pH 7.4) in the presence of 0 – 20.0 equiv. of hydrazine.

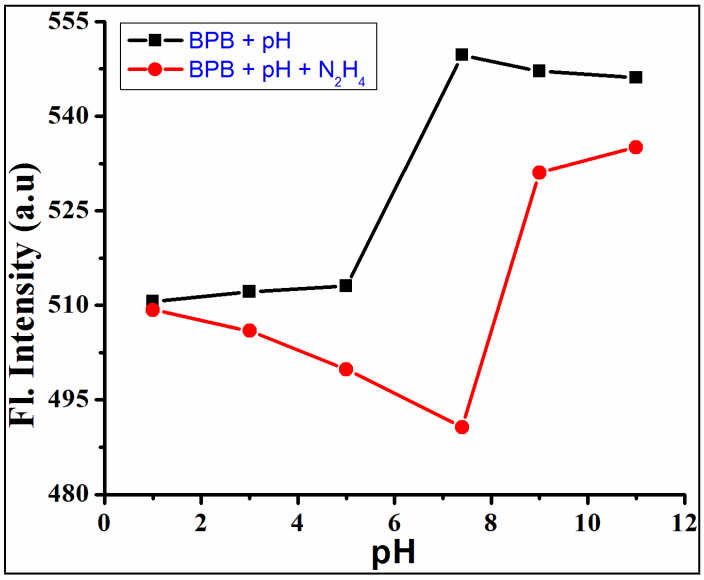


Figure S13. Fluorescence pH titration of **BPB** (1.0 x10^{-5} M) in presence (red) and absence (black) of 2.0 equiv. of hydrazine (c = 2 x 10^{-4} M) at 516 nm in H_2O–DMSO (3:7, v/v) solution.

Computational Method

All the geometries have been optimized at the B3LYP density functional method with 6-31G(d,p) basis set for all atom. A polarizable continuum model (PCM) has been employed to take into account the influence of water as a solvent during optimization. The geometries are verified as proper minima by frequency calculations. To further refine the energy and optical properties single point population analysis and time-dependent density functional theory (TDDFT) calculations have also been performed using triple ς quality 6-311G(d,p) basis set . All calculations have been performed using Gaussian03 program. All the data presented here are calculated in solvent phase.

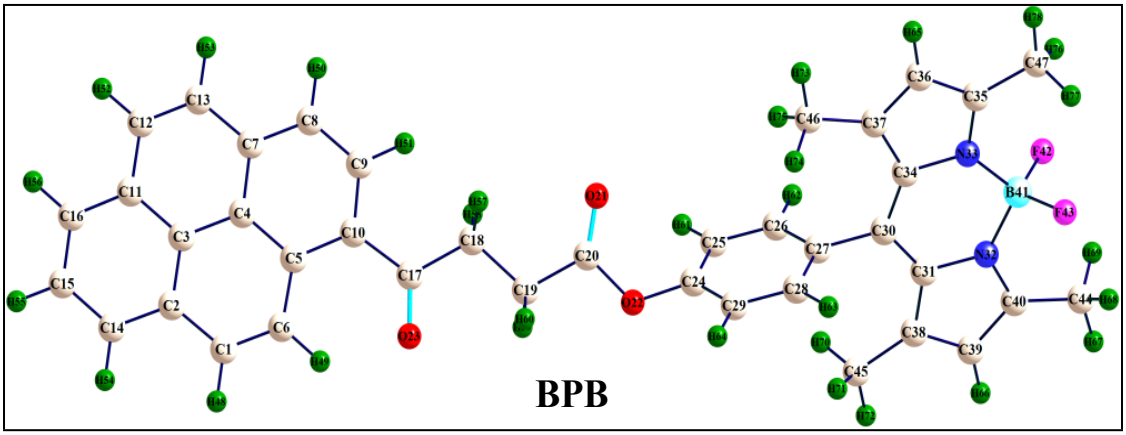
Table S1. Selected electronic excitation energies (eV), oscillator strengths (f), main configurations, and CI Coefficients of the low-lying excited states of sensor **BPB, 3** and **4**. The data were calculated at the TDB3LYP/6-311G(*d,p*)//B3LYP/6-31G(d,p) level of theory.

Molecules	Electronic Transition	Excitation Energy[a]	f[b]	Composition[c]	(composition) %
BPB	$S_0 \rightarrow S_1$	2.9040 eV 426.94 nm	0.5740	H → L	98.0
	$S_0 \rightarrow S_4$	3.1580 eV 392.60 nm	0.5401	H-1 → L+1	94.6
	$S_0 \rightarrow S_{18}$	4.2964 eV 288.57 nm	0.2634	H-1 → L+3 H-2 → L+2	71.2
	$S_0 \rightarrow S_{28}$	4.8553 eV 255.36 nm	0.4601	H-9 → L	86.2
	$S_0 \rightarrow S_{47}$	5.5001 eV 225.42 nm	0.3664	H-2 → L+5 H-12 → L+1	61.9
4	$S_0 \rightarrow S_1$	3.2138 eV 385.79 nm	0.6140	H → L	95.6
	$S_0 \rightarrow S_4$	4.1665 eV 297.57 nm	0.2843	H-1 → L	34.8
	$S_0 \rightarrow S_{14}$	5.2876 eV 234.48 nm	0.7580	H-2→ L+1 H-1→ L+1 H-1→ L+2	75.4
	$S_0 \rightarrow S_{32}$	6.3831 eV 194.24 nm	0.3278	H-4→ L+3 H-4→ L+4	53.4
	$S_0 \rightarrow S_{46}$	6.9420 eV 178.60 nm	0.5644	H-5→ L+3 H-3→ L+4 H-3→ L+5	59.1
3	$S_0 \rightarrow S_1$	2.1496 eV 576.79 nm	0.3563	H → L	100.0
	$S_0 \rightarrow S_3$	2.9351 eV 422.42 nm	0.4862	H-1 → L	98.6
	$S_0 \rightarrow S_{42}$	6.6929 eV 185.25 nm	0.3313	H-4 → L+1	50.0

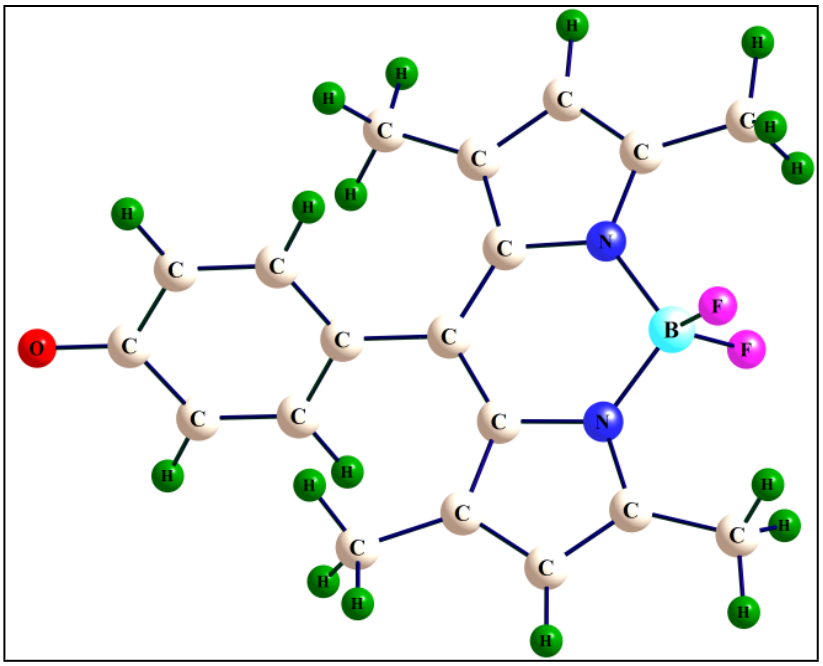
[a] Only selected excited states were considered. The numbers in parentheses are the excitation energy in wavelength. [b] Oscillator strength. [c] H stands for HOMO and L stands for LUMO.

Table S2. Energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) calculated at the B3LYP/6-311G(d,p)//B3LYP/6-31G(d,p) level of theory

Species	E_{HOMO} (a.u)	E_{LUMO}(a.u)	ΔE(a.u)	ΔE(eV)	ΔE(kcal/mol)
BPB	-0.21298	-0.1024	0.11058	3.0089596	69.4
4	-0.20831	-0.08043	0.12788	3.4797043	80.2
3	-0.17653	-0.08759	0.08894	2.4201196	55.8



BPB



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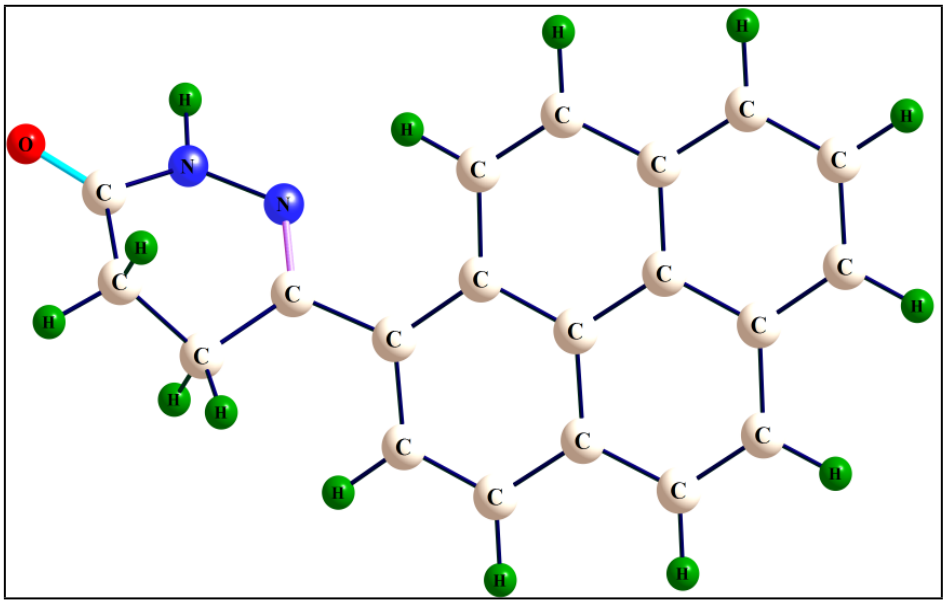

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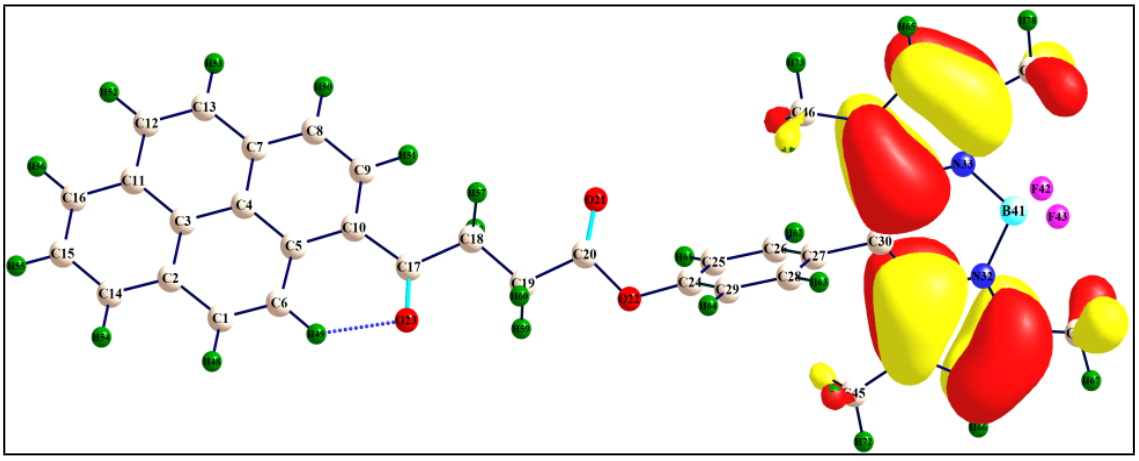
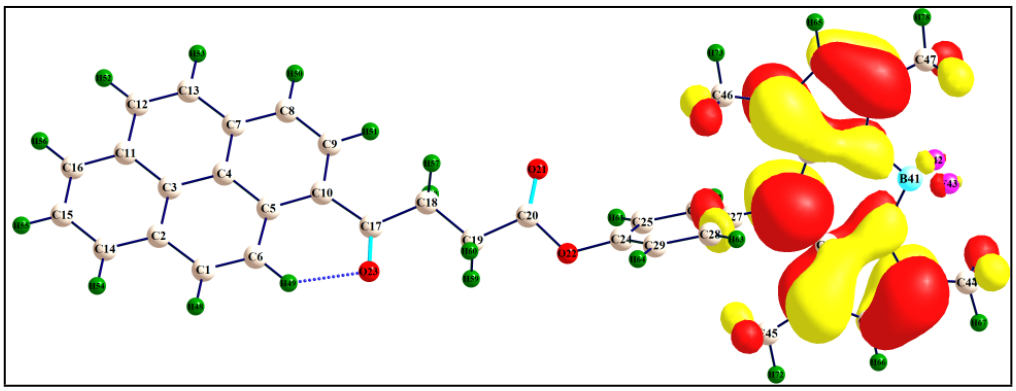
Figure S14. Optimized ground-state geometries of Compound **(BPB), 3** and **4**.

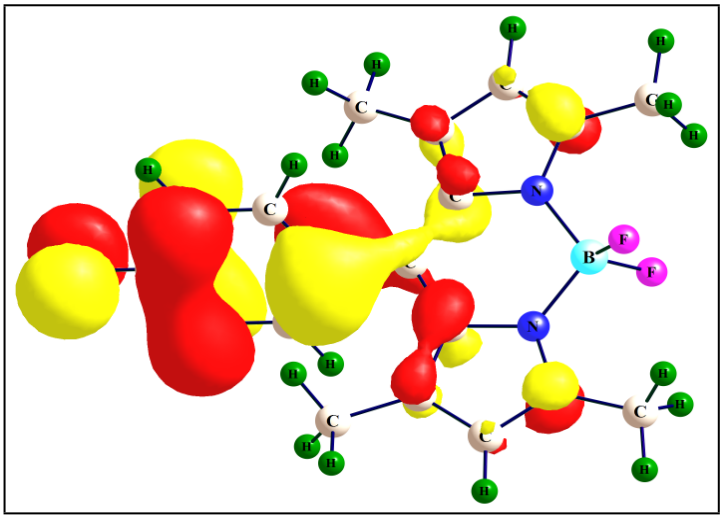


HOMO

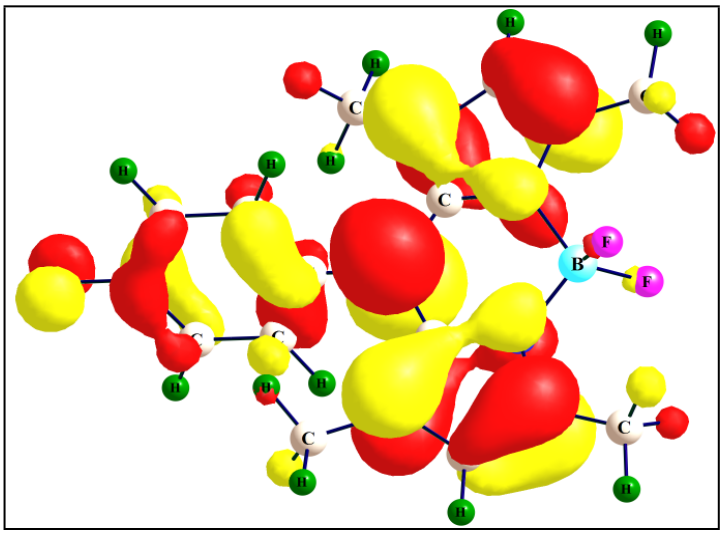


LUMO

Figure S15. Plots of the frontier orbitals of Compound **(BPB)**.

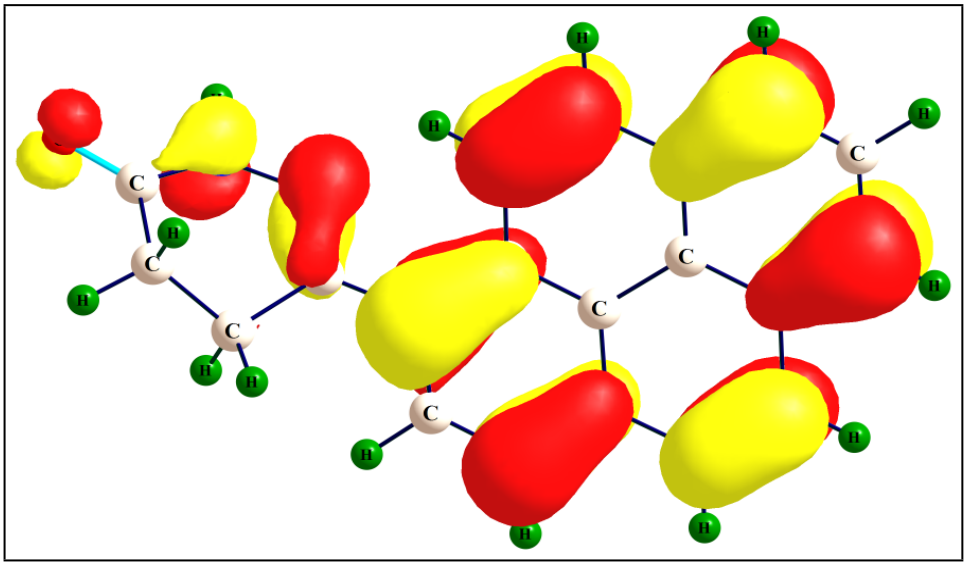


HOMO



LUMO

Figure S16. Plots of the frontier orbitals of Compound **(3)**.



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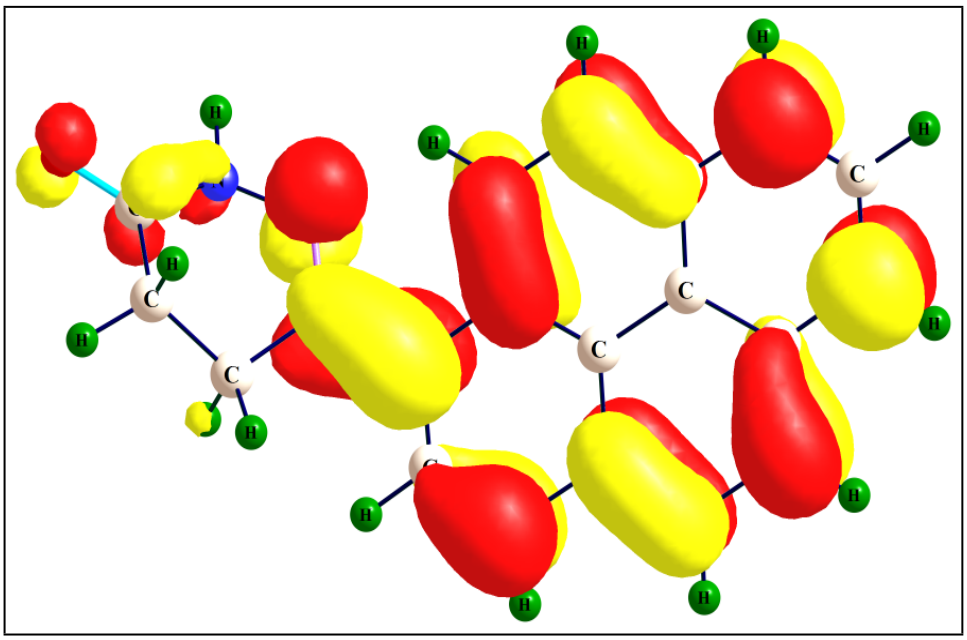

LUMO

Figure S17. Plots of the frontier orbitals of Compound **(4).**