Electronic Supporting information

Rhodamine Appended Hexaphenylbenzene Derivative: Through Bond Energy Transfer for Sensing of Picric Acid

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Page No. **Contents**

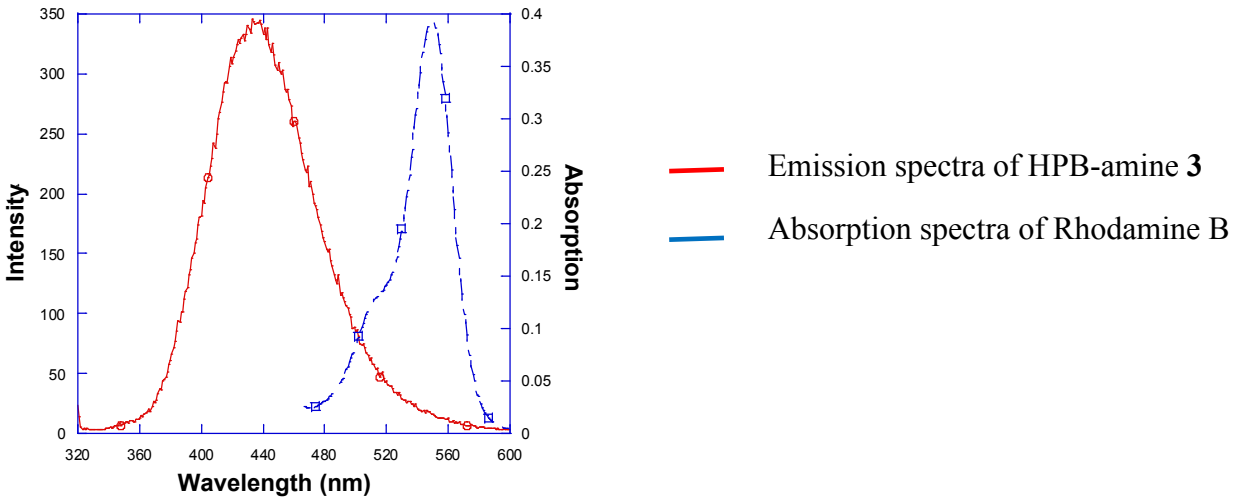


Fig. S1 Spectral overlap of absorption spectrum of rhodamine B and emission spectrum of HPB-amine **3** in methanol.

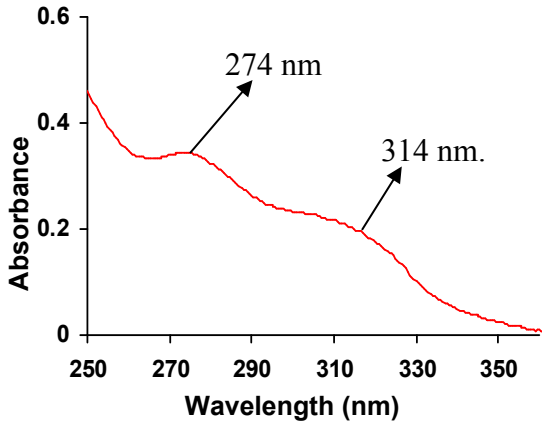


Fig. S2 UV-vis absorption spectra of derivative **5** (5 μM) in methanol.

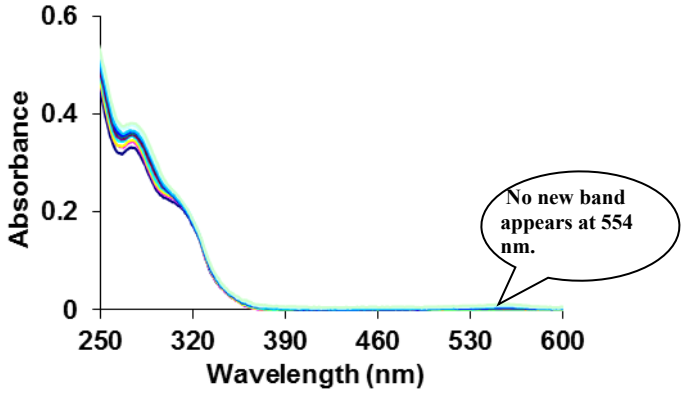


Fig. S3 UV-vis absorption spectra of derivative **5** (5 μM) in methanol with the addition of 60 equiv. of NP, DNP, NT, DNT, BQ, NM, DNB, BA and NBA.

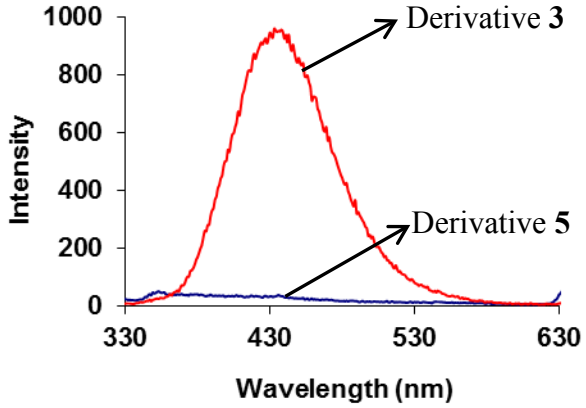


Fig. S4 Fluorescence emission spectra of derivative **3** (5 μM, red) and derivative **5** (5 μM, blue) in methanol; λ_{ex} =314nm.

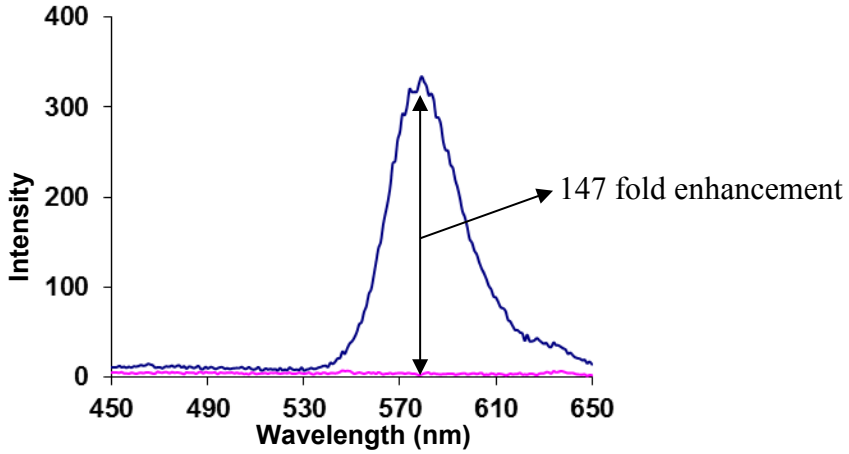


Fig. S5 Fluorescence emission spectra of derivative **5** (5 μM, blue) in presence of PA and rhodamine hydrazide (5 μM, pink) in methanol; λ_{ex} = 314 nm; equation used ($I-I_0/I_0$); I_0 = fluorescence intensity of rhodamine hydrazide at 578 nm; I = final fluorescence intensity at 578 nm of receptor **5** after the addition of picric acid.

Energy transfer efficiency of derivative 5

Energy transfer efficiency = [(fluorescence of donor) - (fluorescence of donor in derivative **5**)/ (fluorescence of donor)] * 100

E = [946.96-34.191]/946.96*100

= 96.39 %

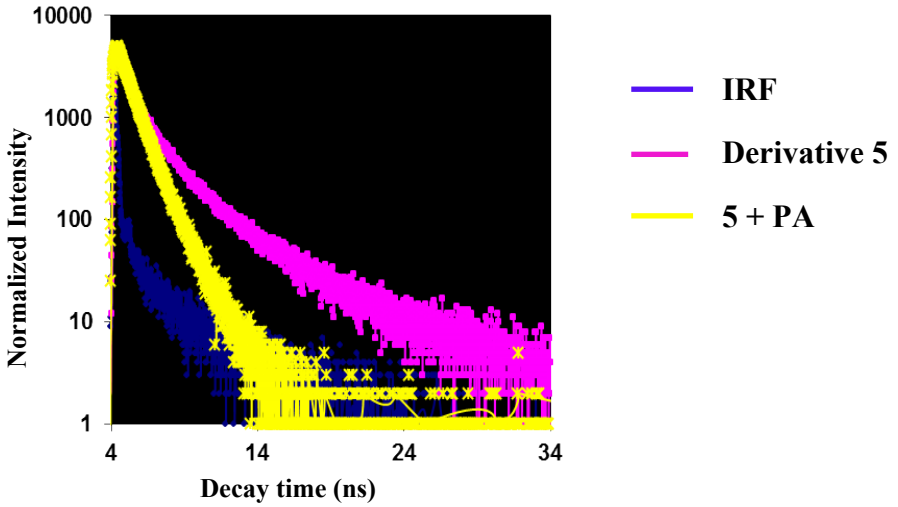


Fig. S6 Fluorescence life time decay profile of derivative **5** on addition of 30 equiv. of PA; λ_{ex} = 314nm.

Table S1 Comparative photophysical properties of derivative **5** monitored at corresponding emission spectra on addition of picric acid; [a]A_1, A_2, A_3; fractional amount of molecules in each environment; [b]τ_1, τ_2, τ_3 are decay time constants.

S.No.	Biexponential	Triexponential	τ_1[b]	τ_2[b]	τ_3[b]	Chi SQ Value
Derivative **5**	A_1/A_2[a]	------	0.82 ns	4.28 ns	-----	1.67034
	66.46/33.54					
5 +PA	-----	$A_1/A_2/A_3$[b]	0.11 ns	0.943 ns	3.3 ns	0.6754582
		-6.29/116.01 /-9.73				

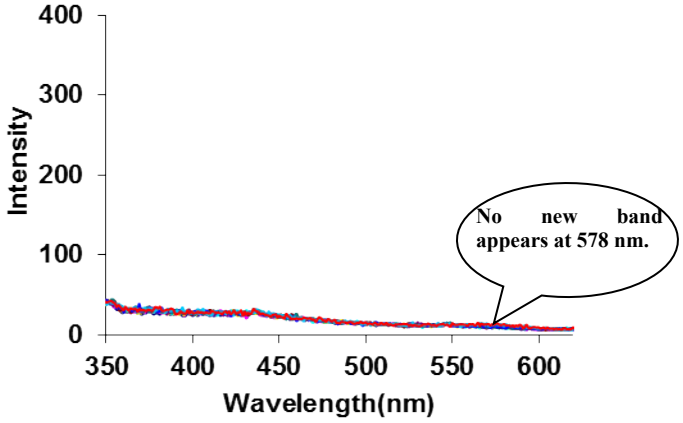


Fig. S7a Fluorescence emission spectra of derivative **5** (5 μM) in methanol with the addition of \50 equiv. of trifluoroacetic acid (TFA); λ_{ex} = 314 nm.

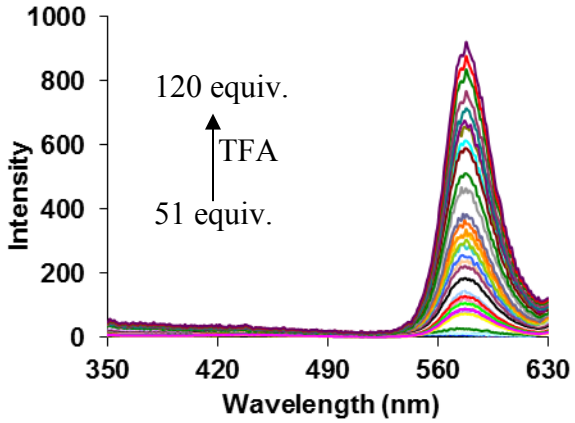


Fig. S7b Fluorescence emission spectra of derivative **5** (5 μM) in methanol with the addition of 51-120 equiv. of trifluoroacetic acid (TFA); λ_{ex} = 314 nm.

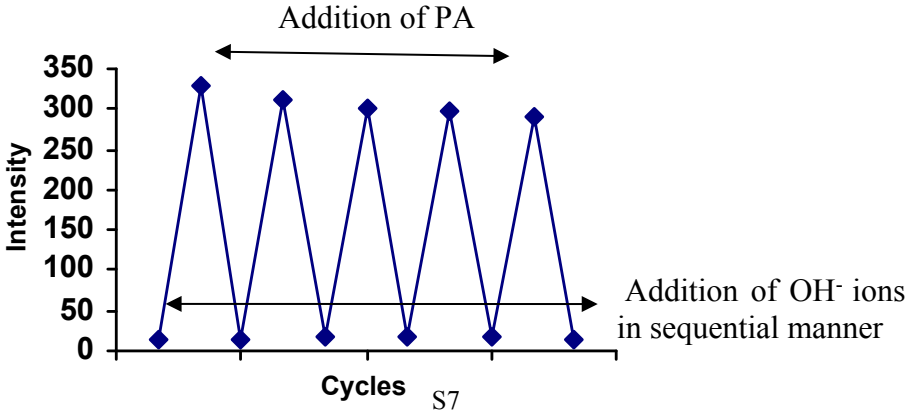


Fig. S8 Reversibility and reusability of the derivative **5** for the sensing of PA by adding sequentially PA and OH^- ions in methanol; λ_{ex} =314nm.

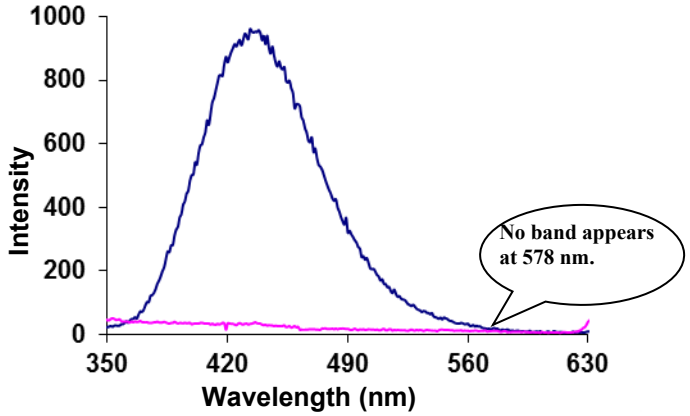


Fig. S9 Fluorescence emission spectra of equimolar mixture of derivative **3** (5 μM) and rhodamine hydrazide (5 μM) in methanol; λ_{ex} =314nm.

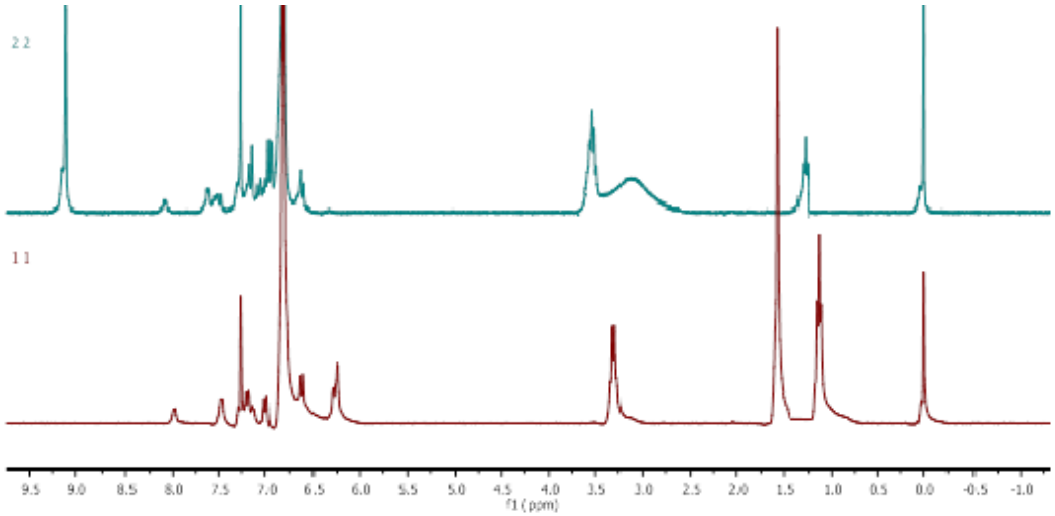


Fig. S10a Overlay ^{1}H NMR spectra ($CDCl_3$, 300 MHz, ppm) of derivative **5** with the addition of picric acid.

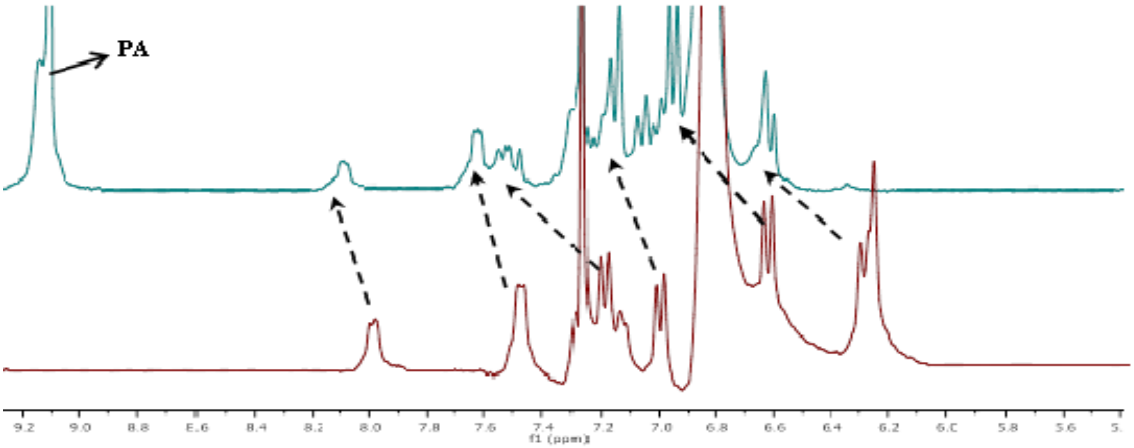


Fig. S10b Zoomed overlay ^{1}H NMR spectra of aromatic portion of derivative **5** with the addition of picric acid.

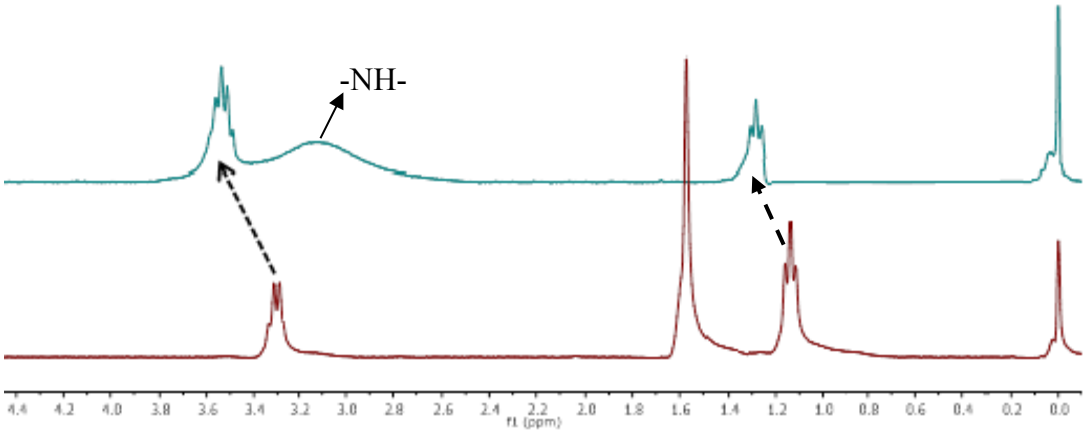


Fig. S10c Zoomed overlay ^{1}H NMR spectra of aliphatic portion of derivative **5** with the addition of picric acid.

Fig. S10d Change in chemical shift (δ) value of derivative **5** before and after addition of PA

Derivative **5** (δ_1 ppm)	**5** + PA (δ_2 ppm)	$\Delta\,\delta_1 = \delta_1 - \delta_2$
7.99 (d, aromatic)	8.08 (d)	0.09
7.47 (d, aromatic)	7.62 (d)	0.15
7.20 (s, aromatic)	7.55 (s)	0.35
7.18 (s, aromatic)	7.51 (d)	0.33
7.13 (d, aromatic)	7.47 (s)	0.34
6.99 (d, aromatic)	7.15 (d)	0.16
6.61-6.83 (m, aromatic)	6.61-6.83 (m)	No change

6.25-6.29 (m, aromatic)	6.60-6.66 (m)	0.36
3.30 (q, -N**CH$_2$**-)	3.55 (q)	0.25
1.14 (t, -NCH$_2$**CH$_3$**)	1.28 (t)	0.14
A new broad signal appears at 3.02 ppm (-NH-)		

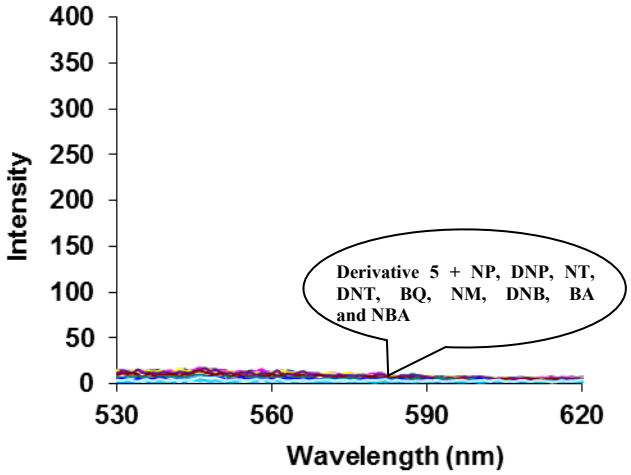


Fig. S11 Fluorescence emission spectra of derivative **5** (5 μM) in methanol with the addition of 60 equiv. of NP, DNP, NT, DNT, BQ, NM, DNB, BA and NBA; λ_{ex} = 314 nm.

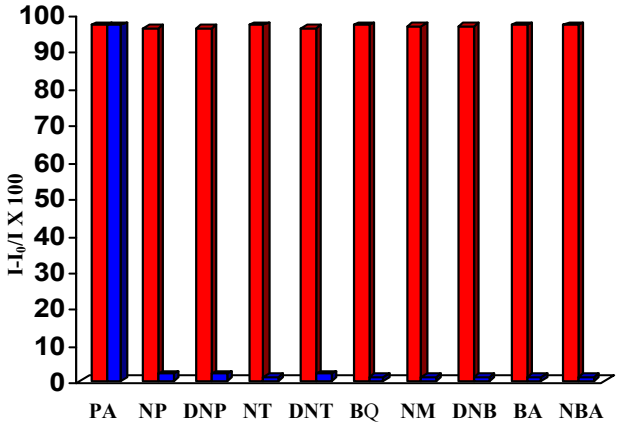
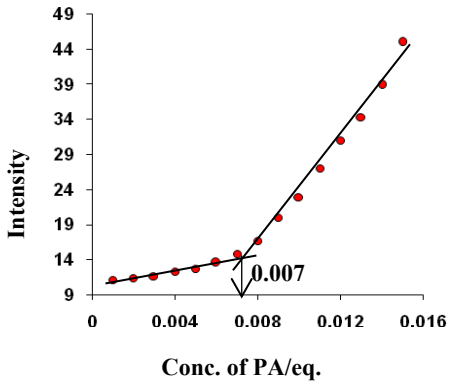


Fig. S12 Competitive selectivity of derivative **5** (5 μM) towards PA in presence of various nitroaromatics (30 equiv) in methanol; λ_{ex} = 314 nm. Bars represent the emission intensity ratio ($I-I_0/I$). I_0 is the initial fluorescence intensity at 578 nm and I is the final fluorescence intensity at 578 nm after the addition of nitroaromatics. The blue bars represent the addition of nitroaromatics, while the red bars represent the change in the emission that occurs upon the subsequent



Equation used for calculating detection limit (DL):

DL = CL× CT

CL = Conc. of Ligand; CT = Conc. of Titrant at which change observed.

Thus;

DL = 0.007× 5 × 10^{-6} = 35 nM.

Fig. S13 Fluorescence intensity at 314 nm as a function of picric acid in methanol.

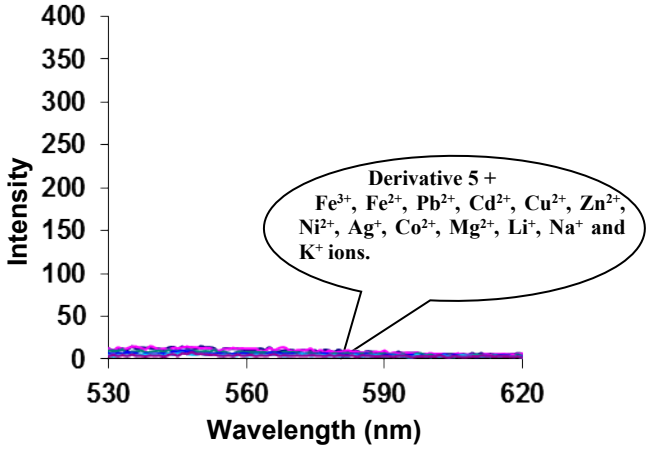


Fig. S14a Fluorescence emission spectra of derivative **5** (5 μM) in methanol with the addition of 30 equiv. of metal ions (Fe^{3+}, Fe^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Ag^{+}, Co^{2+}, Mg^{2+}, Li^{+}, Na^{+} and K^{+}); λ_{ex} = 314 nm.

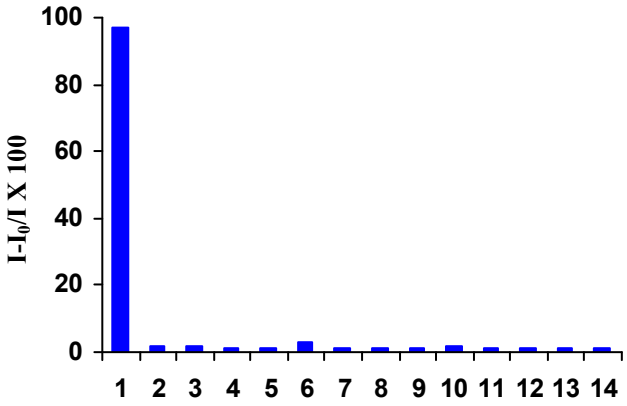


Fig. S14b Selectivity graph of derivative **5** (5 μM) towards Hg^{2+} amongst metal ions with respect to emission band at 314 nm.(1) Hg^{2+}, (2) Fe^{3+}, (3) Fe^{2+}, (4) Pb^{2+}, (5) Cd^{2+}, (6) Cu^{2+}, (7) Zn^{2+}, (8) Ni^{2+}, (9) Ag^{+}, (10) Co^{2+}, (11) Mg^{2+} , (12) Li^{+}, (13)

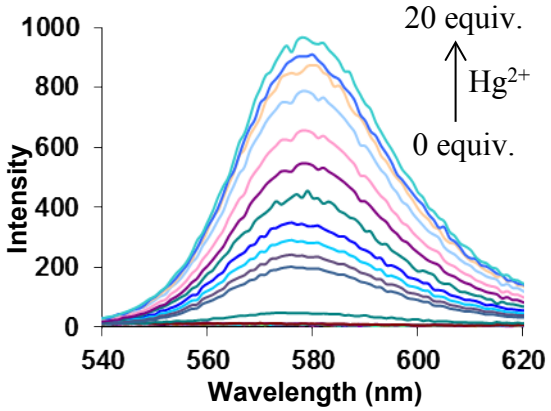


Fig. S15 Fluorescence emission spectra of derivative **5** (5 μM) in methanol with the addition of 20 equiv. of Hg^{2+}; λ_{ex} =314nm.

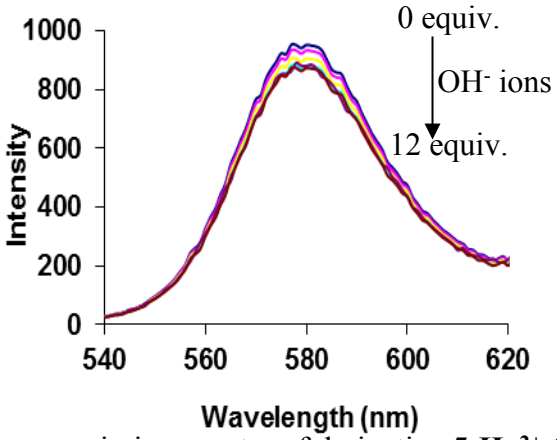


Fig. S16 Fluorescence emission spectra of derivative **5-Hg^{2+}** (5 μM) in methanol with the addition of 12 equiv. of OH^- ions; λ_{ex} = 314 nm.

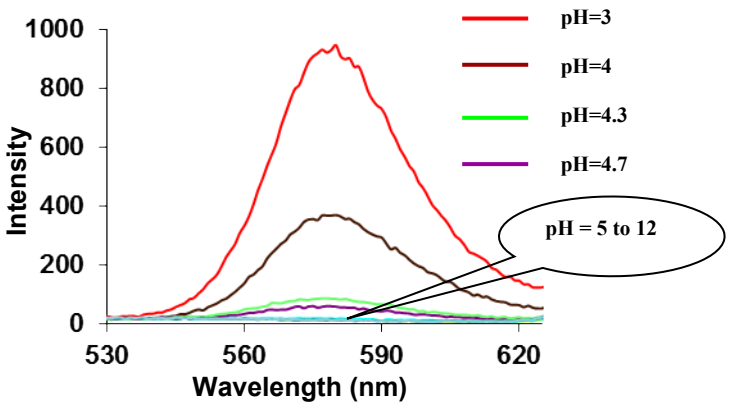


Fig. S17 Fluorescence emission spectra of derivative **5** (5 μM) at different pH scale in methanol; λ_{ex} = 314 nm.

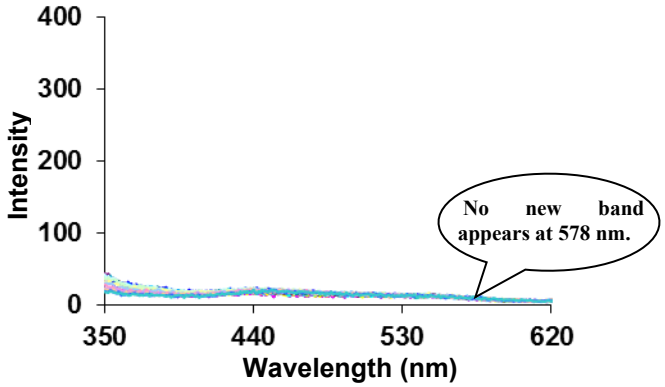


Fig. S18 Fluorescence emission spectra of derivative **6** (5 μM) in methanol with the addition of 30 equiv. of PA; λ_{ex} = 314 nm.

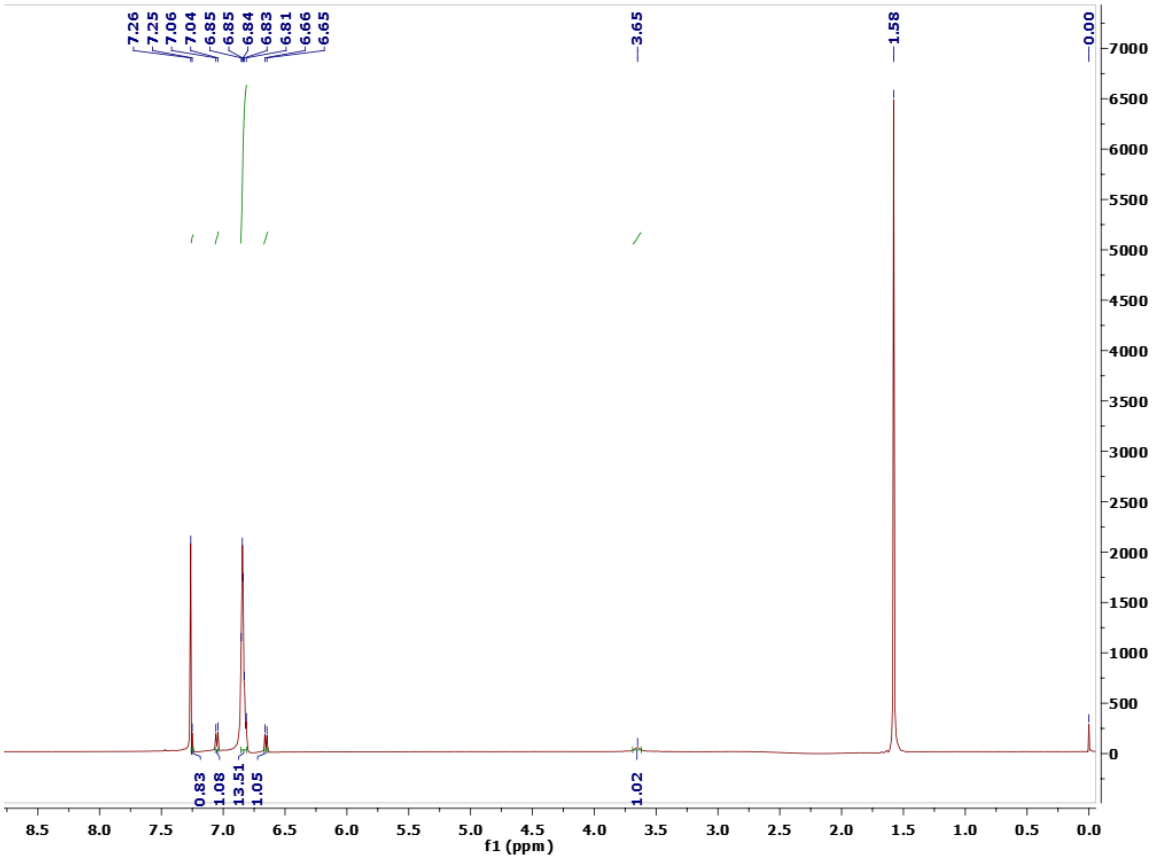


Fig. S19 ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) of derivative **3**

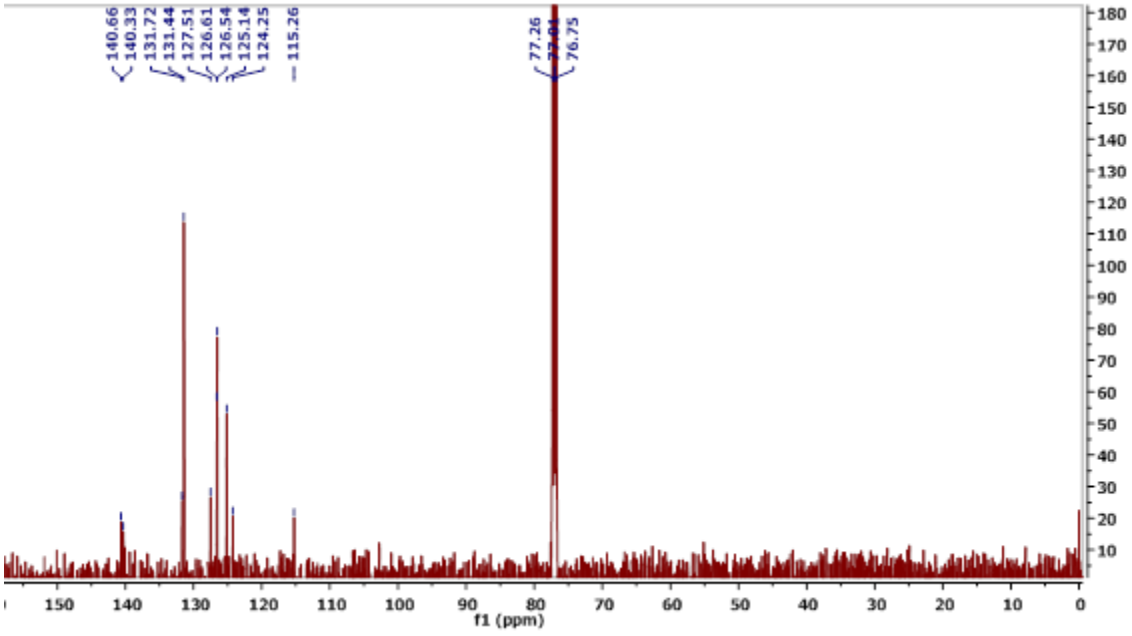


Fig. S20 ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) of derivative **3**

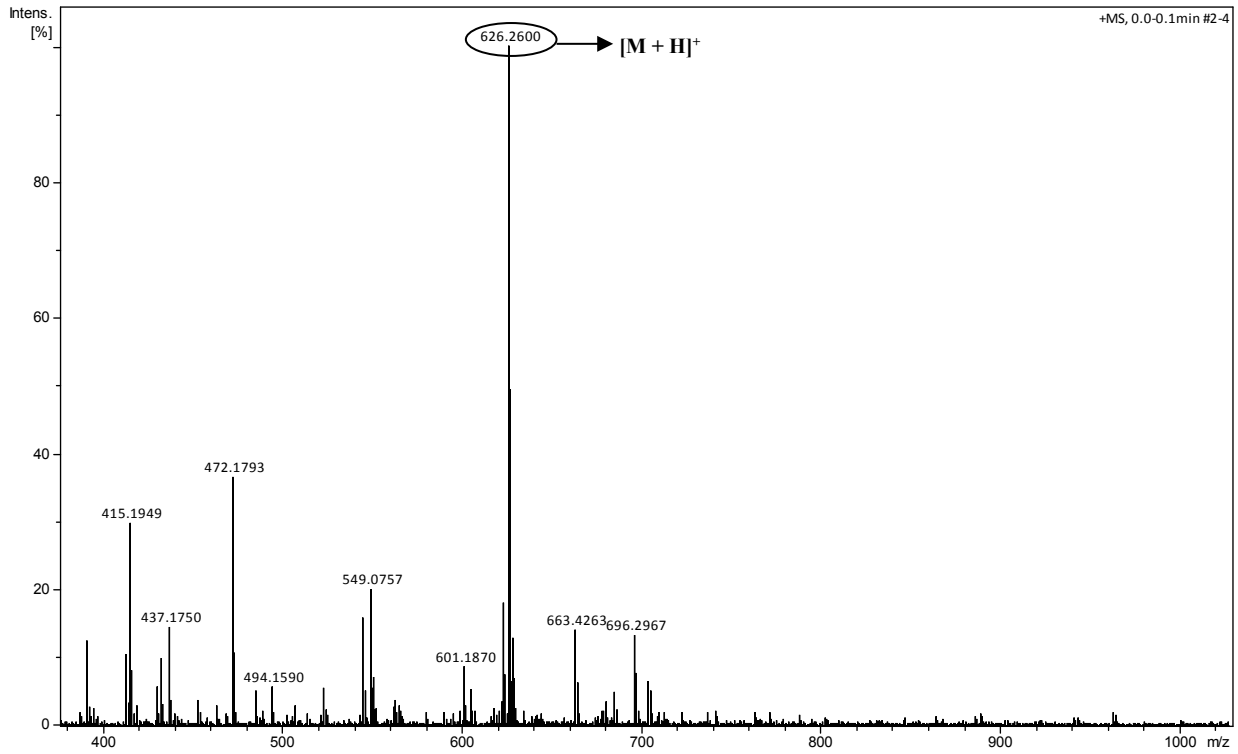


Fig. S21 Mass spectrum of derivative **3**

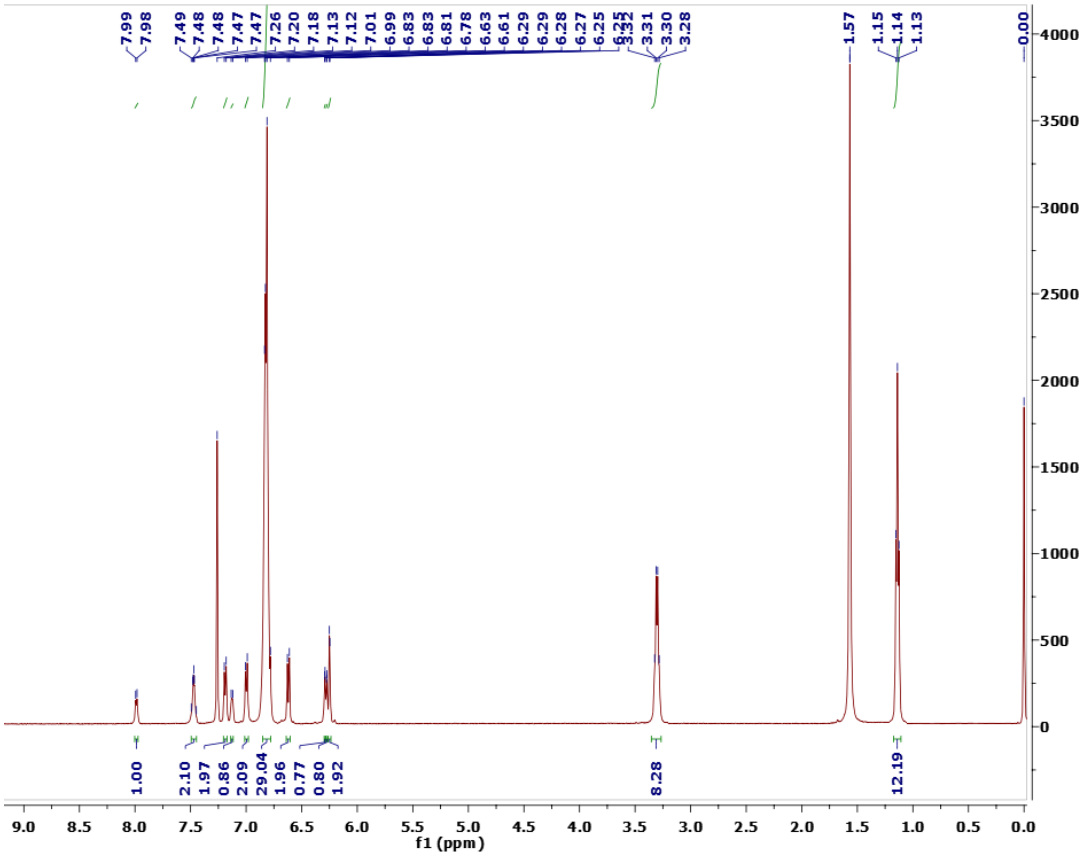


Fig. S22 ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) of derivative **5**

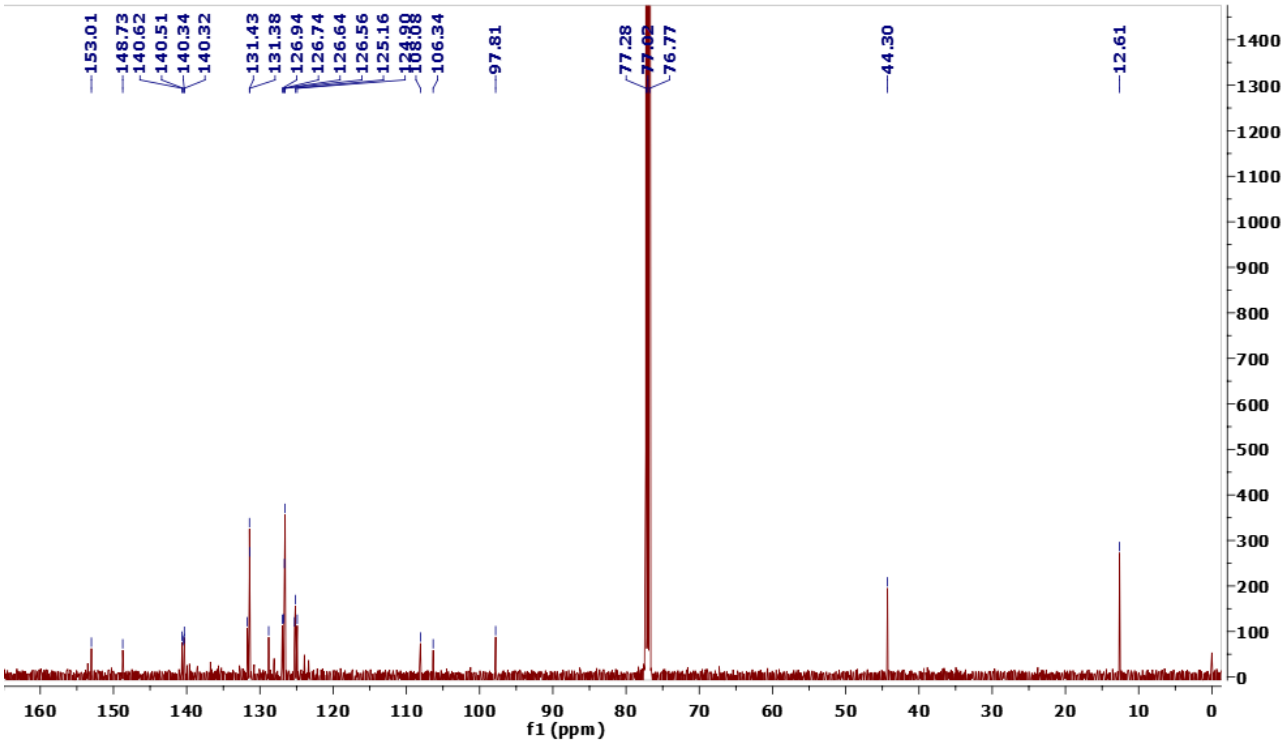


Fig. S23 C^{13} NMR ($CDCl_3$, 125 MHz, ppm) of derivative **5**

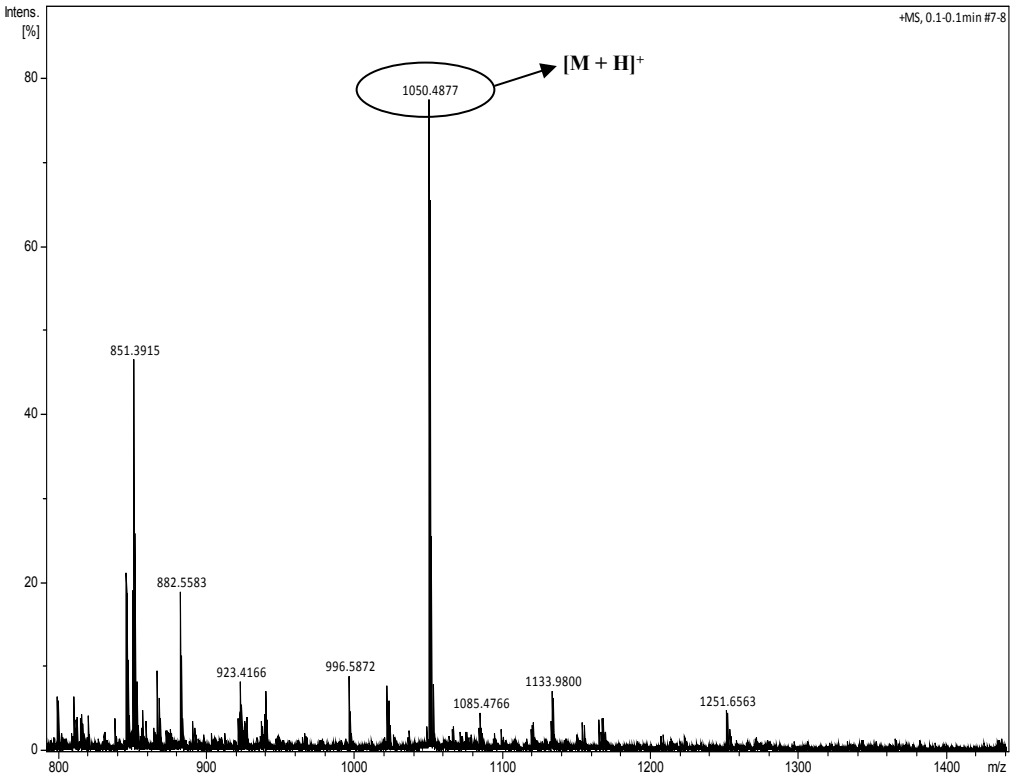


Fig. S24 Mass spectrum of derivative **5**

Publication	**Selectivity Towards PA**	**Detection limit**	**Response with PA**	**Sensing Mechanism**	**Stokes Shift**	**Solvent**	**Reversibility with probe**
Present manuscript	high	104.9 pg	Turn on	Through bond energy transfer	264 nm	MeOH	Yes
J. Mater. Chem. 2008, **18**, 3143	Low	100 pg	Turn on	Excited state electron transfer	148 nm	Toluene	Not mentioned
Chem. Commun. 2013, **49**, 4764	high	70 nM	Turn on	Intramolecular charge transfer	64 nm	$CH_3CN:H_2O$ (9 : 1, v/v)	Not mentioned
RSC Advances, 2014, **4**, 7120	high	162 ppb	Turn on	Inhibition of photo-induced electron transfer process	46 nm	$CH_3CN:H_2O$ (9 : 1; v/v)	Not mentioned
RSC Advances, 2014, **4**, 30828	high	45 nM	Turn on	Intermolecular hydrogen bonding	77 nm	H_2O	Not mentioned
J. Mater. Chem.	high	26 nM	Turn on	photoinduced	187 nm	H_2O:EtOH	Not

2014, **2**, 3936				intermolecular excited state proton transfer		(6:4)	mentioned

Table S2 Comparison of selectivity, detection limit, sensing mechanism, stokes shift, solvent and reversibility of derivative **5** towards PA with literature reports.