Electronic Supplementary Material (ESI) for RSC Advances.

ESI

Imidazole-appended 9,10-anthracenedicarboxamide probe for sensing nitrophenols and selective determination of 2,4,6-trinitrophenol in an EtOH-water medium

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Materials and Methods

Nitro-containing explosives, including 2,4,6-trinitrophenol (TNP), 2,4-dinitrophenol (2,4-DNP), 3,4-dinitrophenol (3,4-DNP), 2-nitrophenol (2-NP), and 4-nitrophenol (4NP), 1,4-dinitrobenzene (1,4-DNB), 1,3-dinitrobenzene (1,3-DNB), 2-nitrobenzoic acid (2-NBA), 3,5-dinitrobenzoic acid (3,5-DNBA) were of analytical grade and were used directly without any purification. (Caution: all nitro-containing compounds used in the present study are highly explosive and should be handled only in small quantities). All other reagents were analytically pure. River and sea waters were collected from the Sincheon river, Daegu and seashore area of Busan, collected water samples were filtered through filter paper then used for UV-Vis and fluorescence experiments. Respective water samples quntitative analysis has done after caliberation during analysis.

Preparation of the buffer solution.

The solid standard buffer was used without purification. Respective solid buffers dissolved in EtOH-H_2O mixture (1:1 v/v) and the exact pH value was obtained by adjusting the using solution of 0.001 M NaOH. All pH value was measured in digital pH meter instrument.

pH dependent fluorescence studies

pH was maintained using the following solutions [all 0.01 M in EtOH-H_2O (1:1)] : trichloroacetate (pH 1); dichloroacetate (pH 2); chloroacetate (pH 3); acetate (pH 4 and 5); MES (pH 6); HEPES (pH 7 and 8); CHES (pH 9); CAPS (pH 10 and 11); TBAH (pH 12); NaOH (pH 13);

Abbreviations: Tetrabutylammoniumhydroxide (TBAH), 4-morpholineethanesulfonic acid sodium salt (MES), 4-(2-hydroxyethyl)piperazine-1-ethanesulfonicacid (HEPES), 2-(cyclohexylamino)ethanesulfonic acid (CHES), 3-cyclohexylamino-1-propanesulfonic acid (CAPS).

The fluorescence readings were obtained with maintaining constant pH using various standard buffer solutions*. Each fluorescence reading was taken and recorded after getting 3 concordant values.

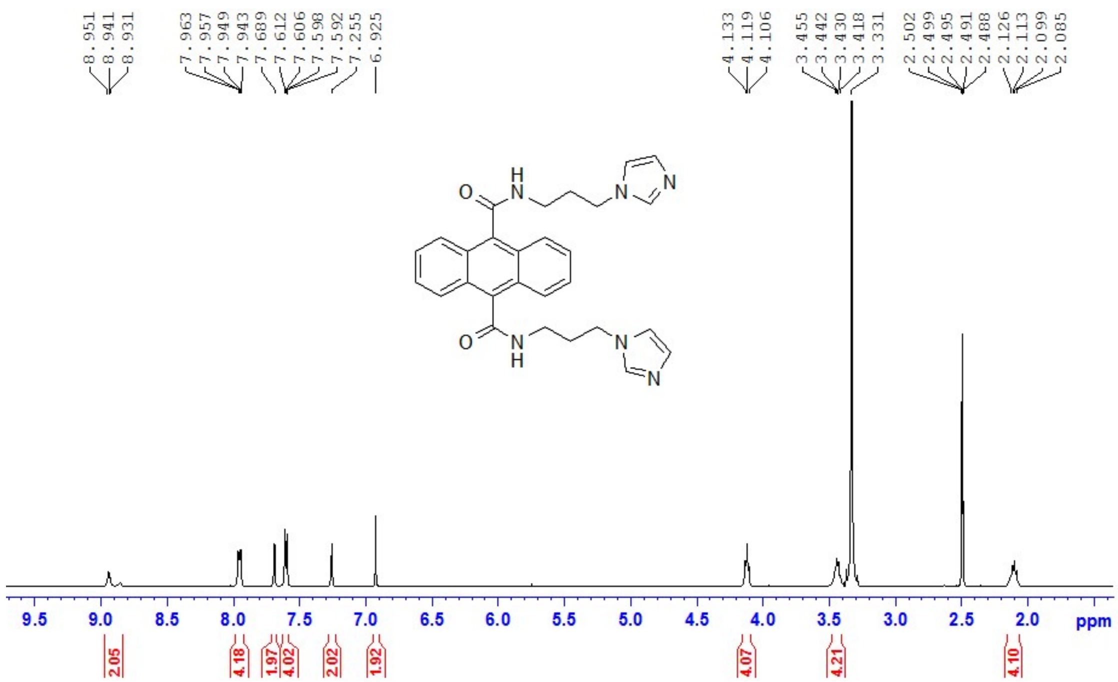

Fig. 1. ^{1}H NMR spectrum of probe **AIM-D** in DMSO-d6.

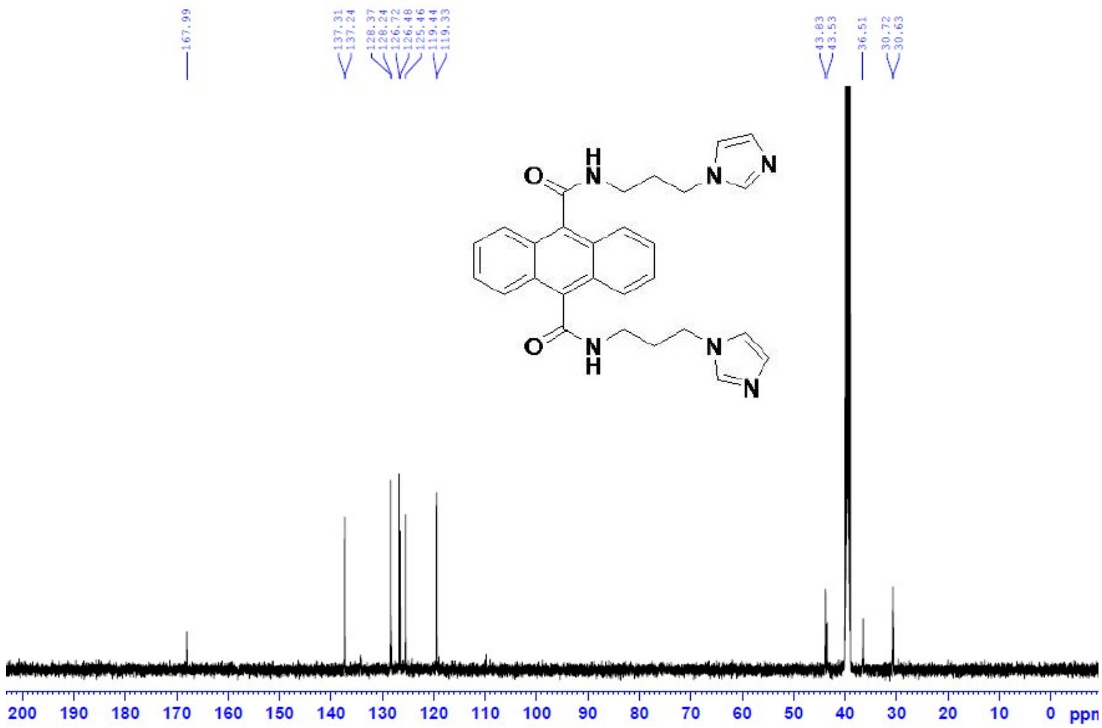

Fig. 2. ^{13}C NMR spectrum of probe **AIM-D** in DMSO-d_6.

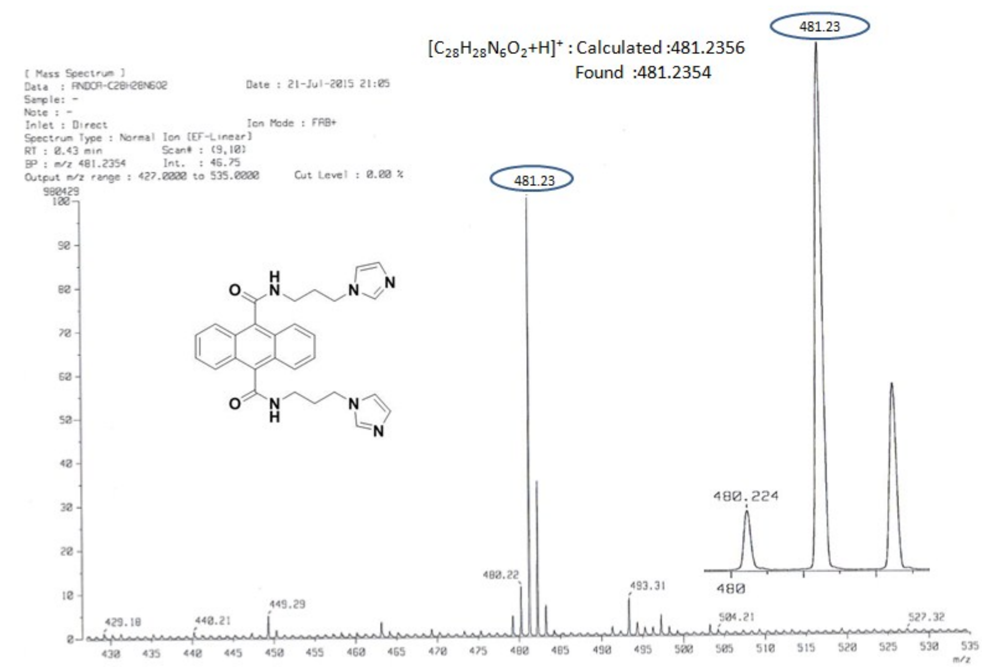

Fig. 3. HRMS spectrum of probe **AIM-D**.

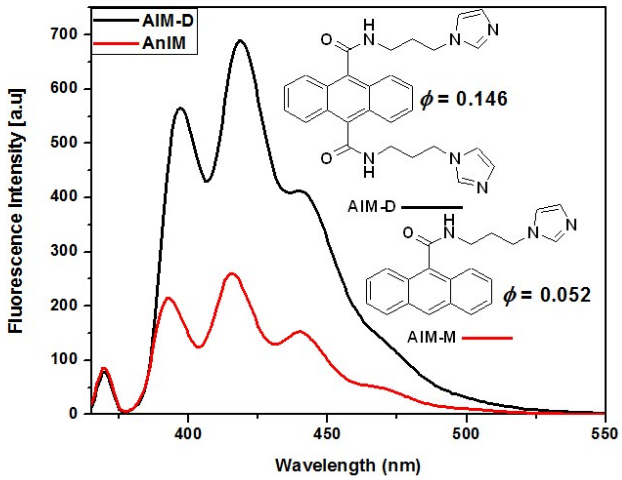

Fig. S1. Fluorescence emission behaviour of the probe **AIM-D** and **AIM-M** 0.2 μM in EtOH medium λ_{ex} = 366 nm.

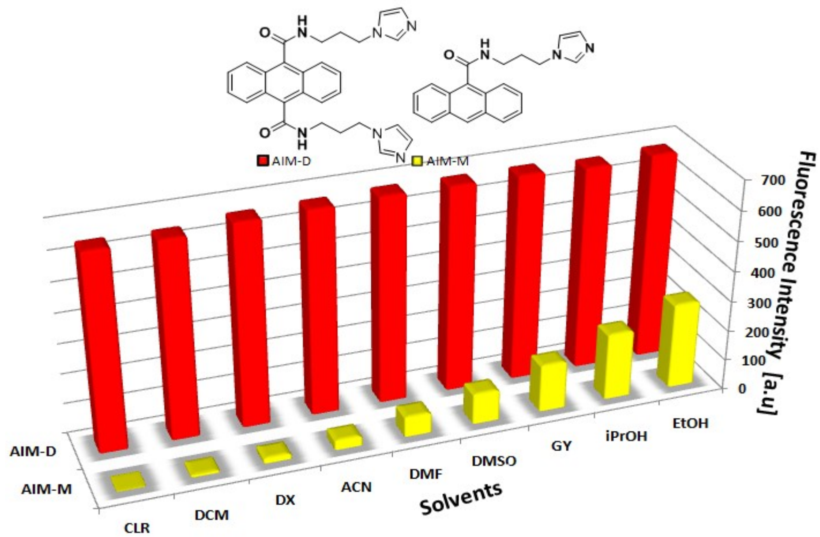

Fig. S2. Effect of solvents on the fluorescence emission behaviour of probe **AIM-D** and **AIM-M**, 0.2 μM in EtOH medium, λ_{ex} = 366 nm, λ_{em} = 417 nm.

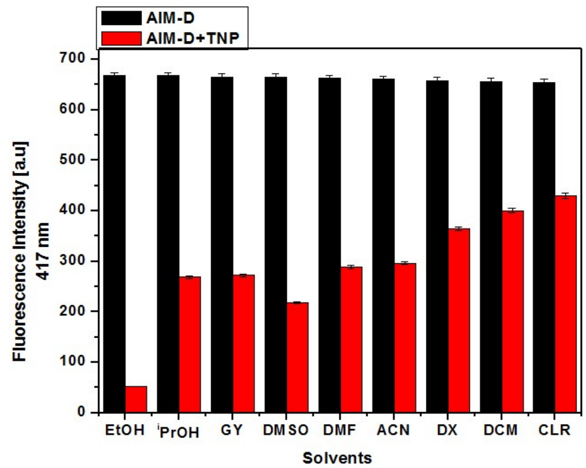

Fig. S3. Fluorescence quenching efficiency with probe **AIM-D** (0.2 μM) in EtOH medium, with TNP (0.2 μM) λ_{ex} = 366 nm, λ_{em} = 417 nm.

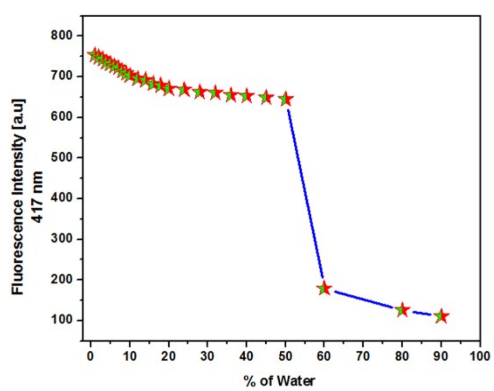

Fig. S4. Effect of water on the fluorescence emission behaviour of the probe **AIM-D** (0.2 μM) in EtOH medium, λ_{ex} = 366 nm, λ_{em} = 417 nm.

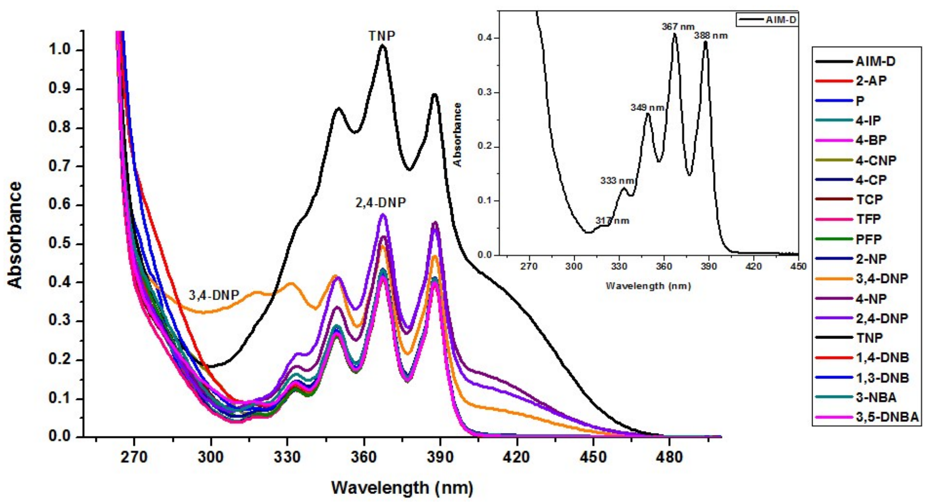

Fig. S5. UV-Vis, spectra of the probe **AIM-D** (0.2 μm) with various 5.0 eq. of phenol derivatives in EtOH-H_2O (1:1) system.

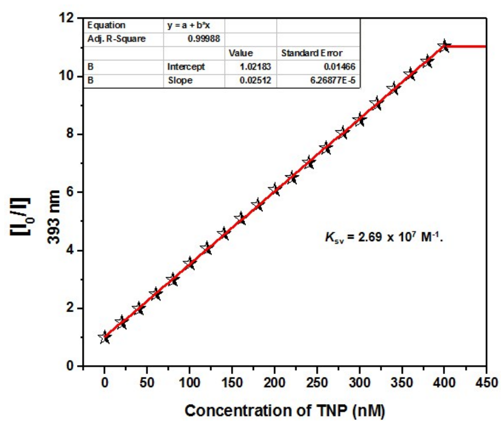

Fig. S6. Stern-Volmer plot of probe **AIM-D** with various concentration of TNP (0-400 nM) at λ_{ex} = 366 nm, λ_{em} = 393 nm.

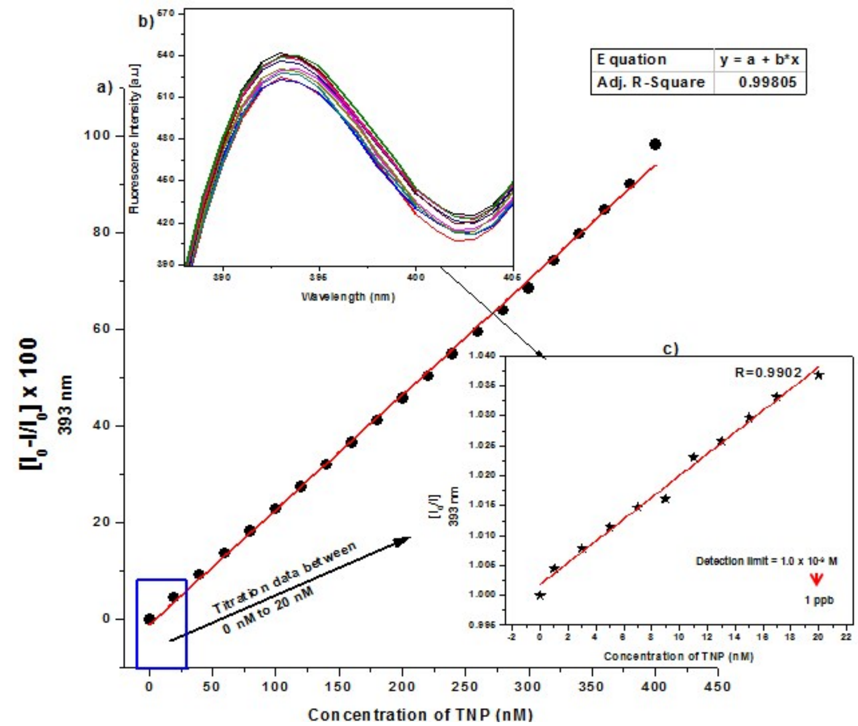

Fig. S7. a) Changes in the intial fluorescence intensity of **AIM-D**, upon gradual addition of TNP (0 - 400 nM) in EtOH-H_2O (1:1). Inset: b) The lowest possible quenching resposne of probe **AIM-D**, with PA (0 - 20 nM) showing the lowest detection limit of TNP, λ_{ex} = 366 nm : c) Plot of intensity quenching ratio vs concentration (0 - 20 nM) at λ_{ex} = 366 nm, λ_{em} = 393 nm.

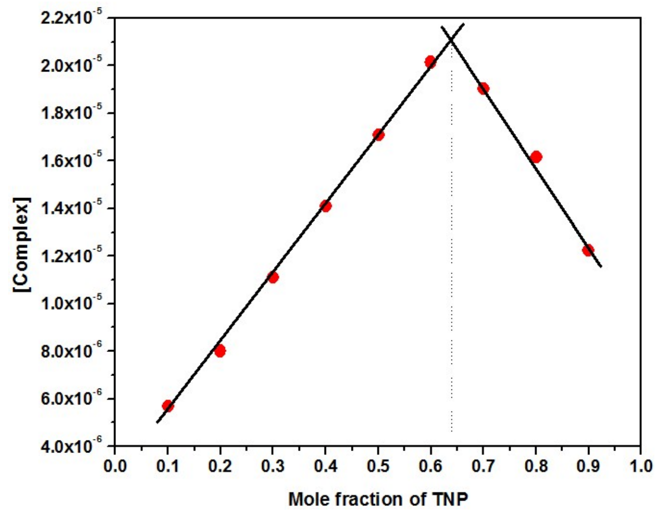

Fig. S8. Job's plot of **AIM-D** (0.2 μM) with TNP (0.2 μM) in EtOH:H_2O, 1:1 ratio: λ_{ex} = 366 nm, λ_{em} = 393 nm.

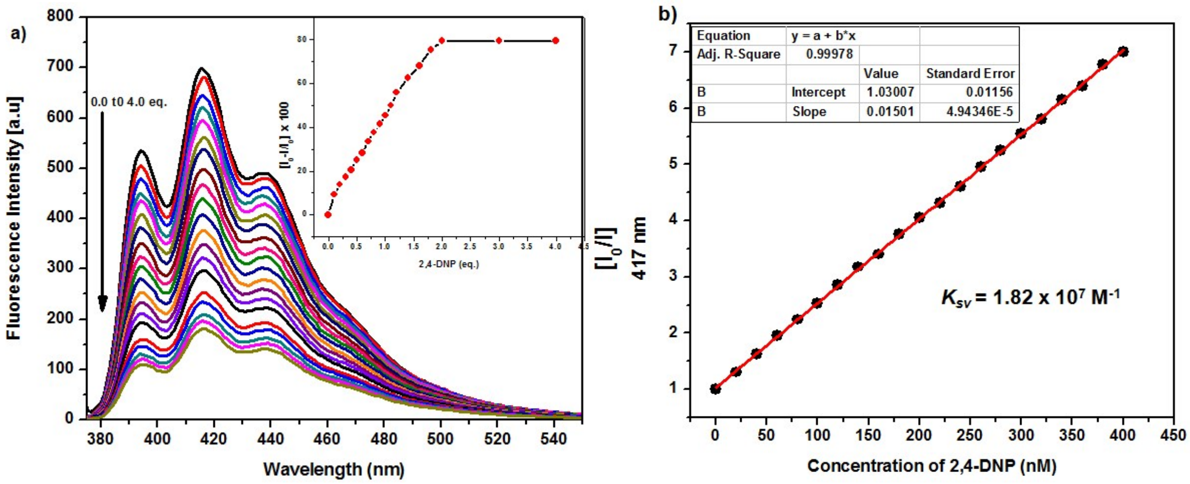

Fig. S9. Fluorescence titration spectra of probe **AIM-D** (0.2 μM) with 2,4-DNP (1 μM) in EtOH:H_2O (1:1) system, λ_{ex} = 366 nm; b) Stern-Volmer plot of probe **AIM-D** (0.2 μM) with 20 to 400 nM concentration of 2,4-DNP, λ_{ex} = 366 nm, λ_{em} = 417 nm.

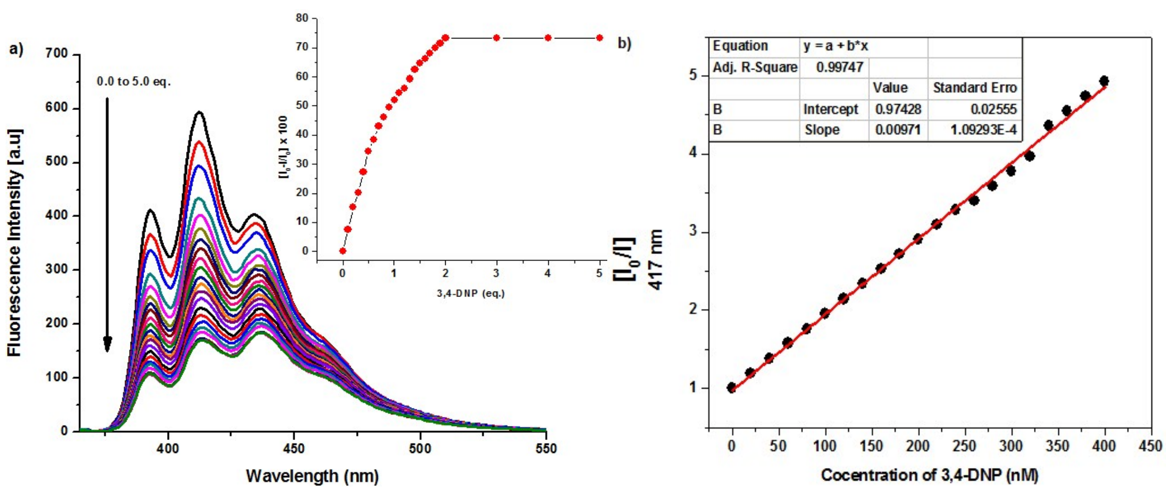

Fig. S10. Fluorescence titration spectra of probe **AIM-D** (0.2 μM) with 3,4-DNP (1 μM) in EtOH:H_2O (1:1) system, λ_{ex} = 366 nm; b) Stern-Volmer plot of probe **AIM-D** (0.2 μM) with 20 to 400 nM concentration of 3,4-DNP, λ_{ex} = 366 nm, λ_{em} = 417 nm.

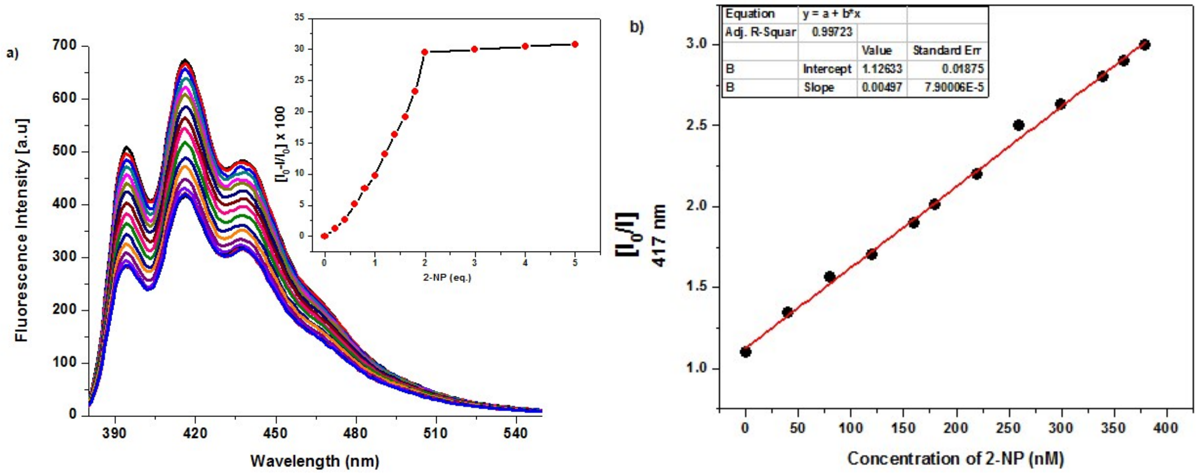

Fig. S11. Fluorescence titration spectra of probe **AIM-D** (0.2 μM) with 2-NP (1 μM) in EtOH:H_2O (1:1) system, λ_{ex} = 366 nm; b) Stern-Volmer plot of probe **AIM-D** (0.2 μM) with 20 to 400 nM concentration of 2-NP, λ_{ex} = 366 nm, λ_{em} = 417 nm.

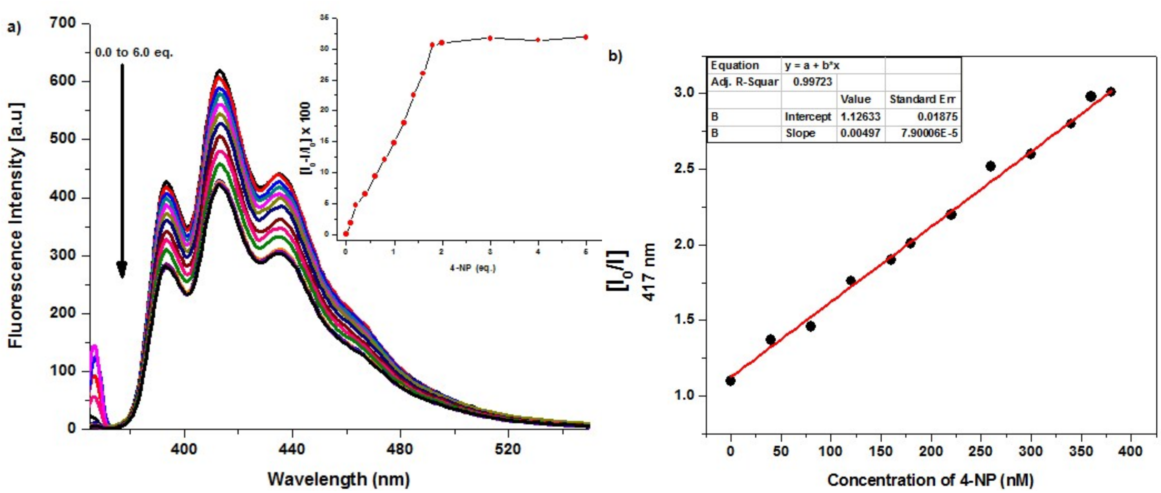

Fig. S12. Fluorescence titration spectra of probe **AIM-D** (0.2 μM) with 4-NP (1 μM) in EtOH:H_2O (1:1) system, λ_{ex} = 366 nm; b) Stern-Volmer plot of probe **AIM-D** (0.2 μM) with 20 to 400 nM concentration of 4-NP, λ_{ex} = 366 nm, λ_{em} = 417 nm.

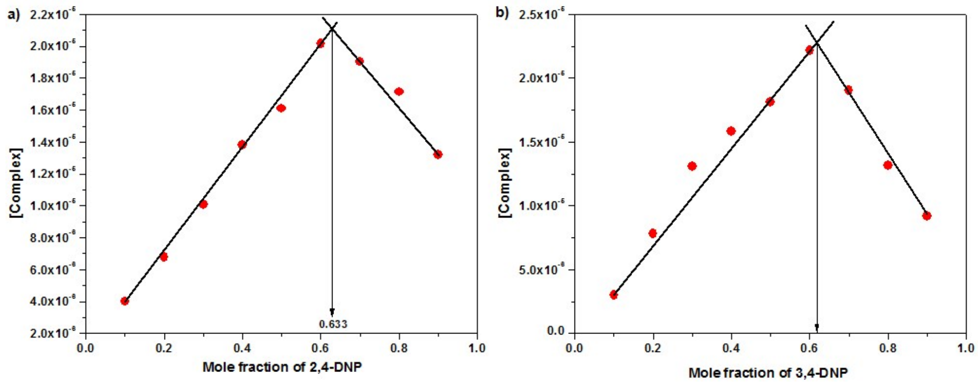

Fig. S13. Job's plot of probe **AIM-D** (0.2 μM) with a) 2,4-DNP (0.2 μM), b) 3,4-DNP in EtOH:H_2O (1:1) system, λ_{ex} = 366 nm, λ_{em} = 417 nm.

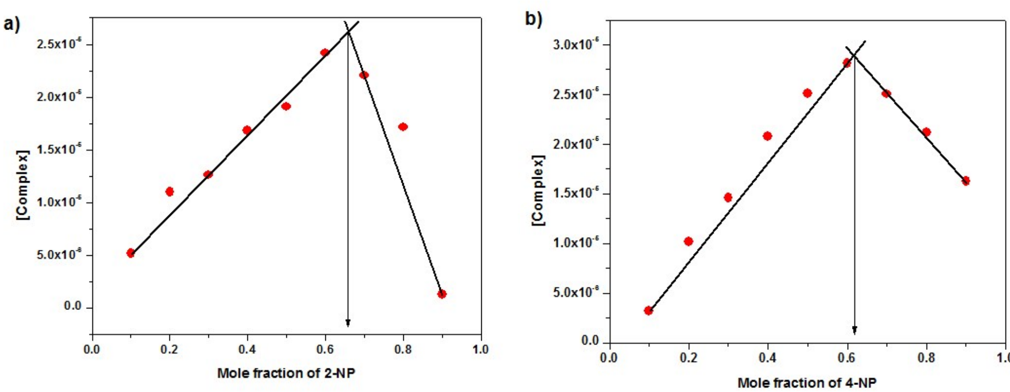

Fig. S14. Job's plot of probe **AIM-D** (0.2 μM) with a) 2-NP (0.2 μM), b) 4-NP in EtOH:H_2O (1:1) system, λ_{ex} = 366 nm, λ_{em} = 417 nm.

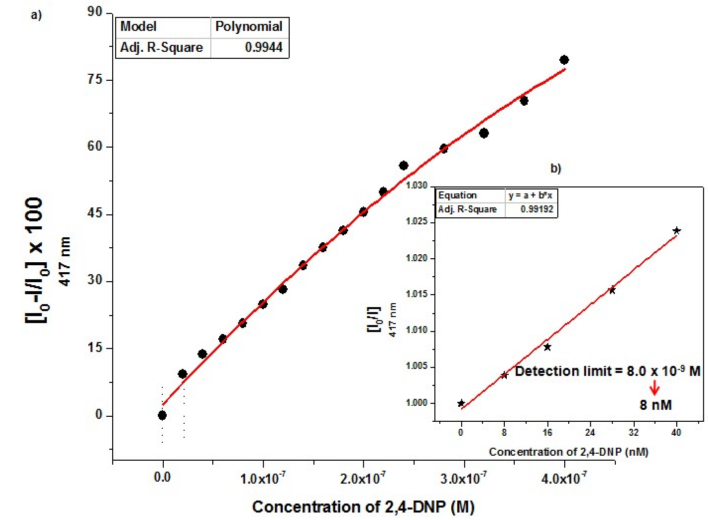

Fig. S15. a) Fluorogenic response of probe **AIM-D** (0.2 μM) with various concentration of 2,4-DNP (0-400 nm); b) shows fluorescence titration studies between probe **AIM-D** vs concentration of 2,4-DNP (0-40 nM) in EtOH:H_2O (1:1) system, λ_{ex} = 366 nm, λ_{em} = 417 nm.

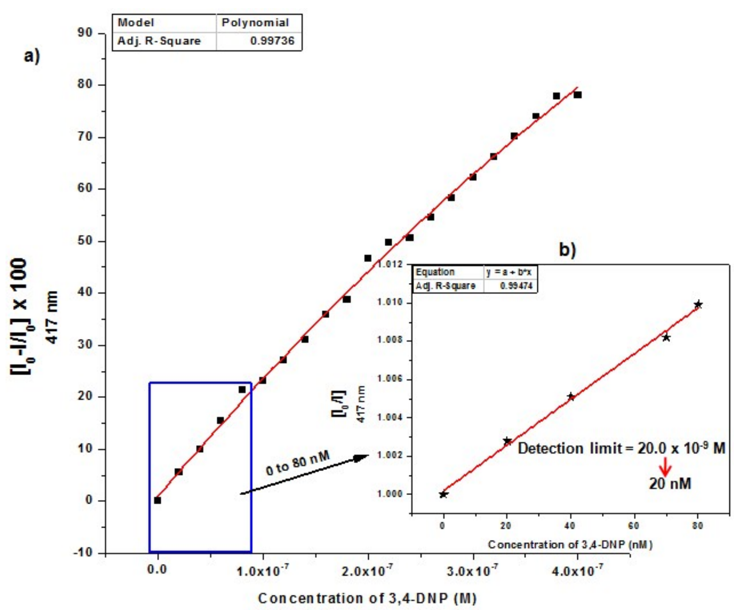

Fig. S16. a) Fluorogenic response of probe **AIM-D** (0.2 μM) with various concentration of 3,4-DNP (0-400 nm); b) shows fluorescence titration studies between probe **AIM-D** vs concentration of 3,4-DNP (0-80 nM) in EtOH:H_2O (1:1) system, λ_{ex} = 366 nm, λ_{em} = 417 nm.

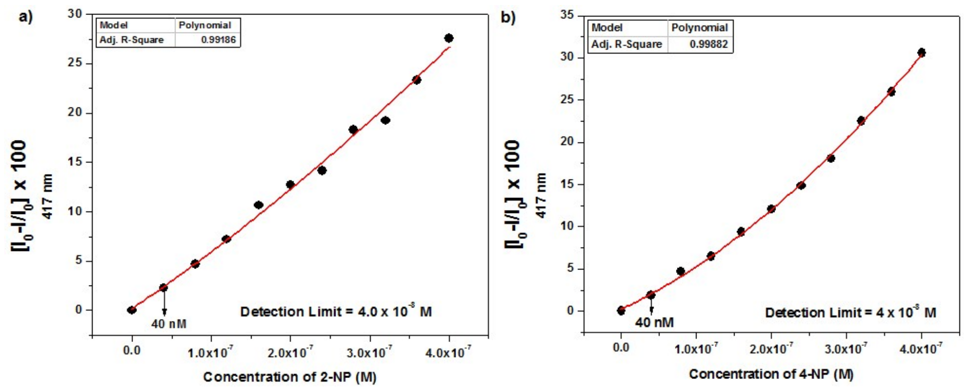

Fig. S17. Fluorogenic response of probe **AIM-D** (0.2 μM) with various concentration of a) 2-NP and b) 4-NP (0-400 nM) in EtOH:H_2O (1:1) system, λ_{ex} = 366 nm, λ_{em} = 417 nm.

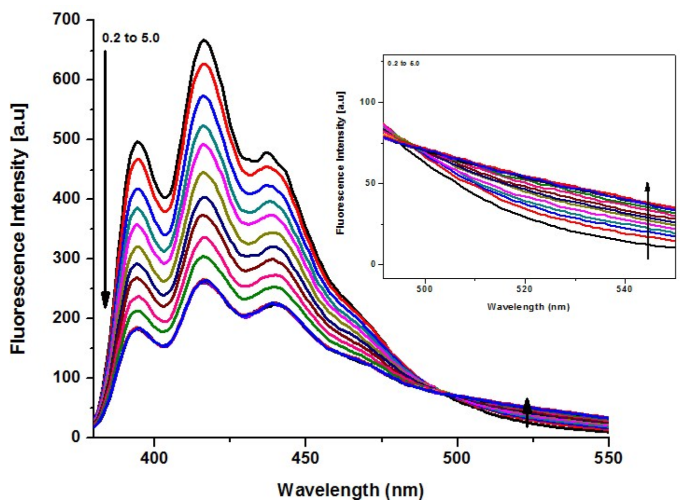

Fig. S18. Fluorescence titration spectra of probe **AIM-D** (0.2 μM) with TNP (1 μM) in DMSO:H_2O (1:1) system, λ_{ex} = 366 nm.

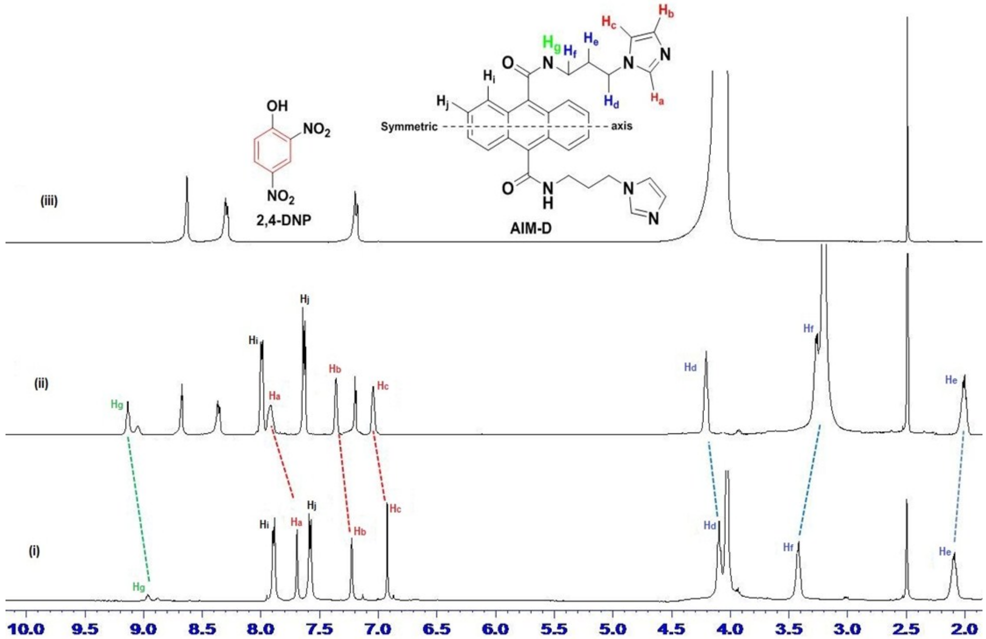

Fig. S19. Partial ^{1}H-NMR studies of probe (i) **AIM-D** (5.0×10^{-3} M) (ii) 2,4-DNP (2.0 eq) and (iii) 2,4-DNP in DMSO-d_6-D_2O (2:1).

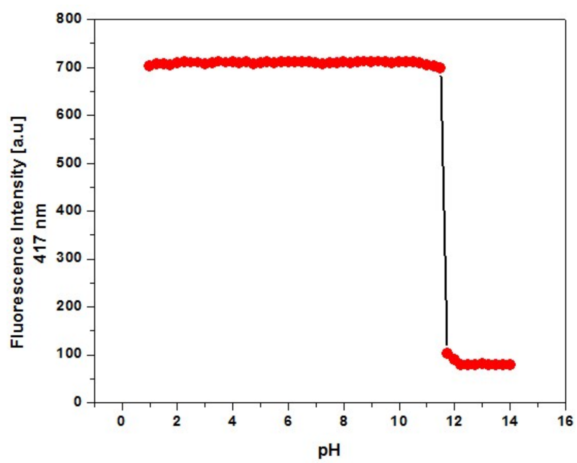

Fig. S20. pH dependent fluorescence studies of the probe **AIM-D** (0.2 μM) in EtOH-H_2O (1:1) system, λ_{ex} = 366 nm, λ_{em} = 417 nm.

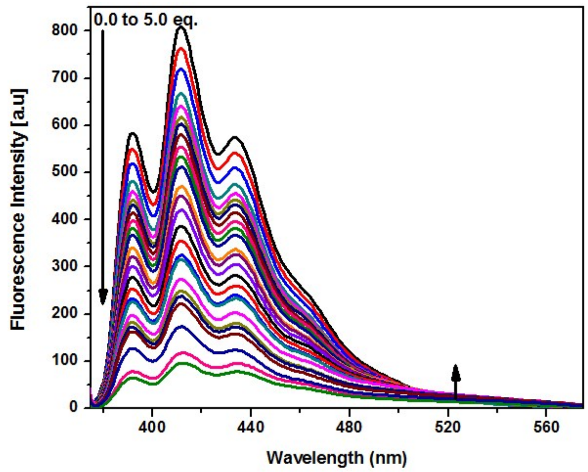

Fig. S21. Fluorescence titration spectra of probe **AIM-D** (0.2 μM) with TNP (1 μM) in EtOH:H_2O (1:1) system, at pH 1.5 (Trichloroacetate buffer) λ_{ex} = 366 nm.

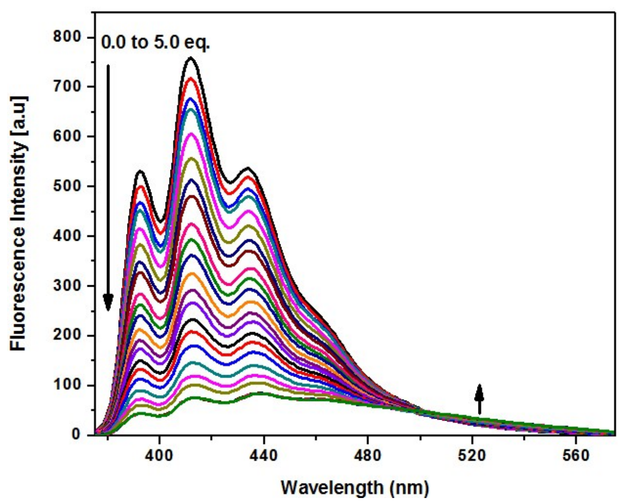

Fig. S22. Fluorescence titration spectra of probe **AIM-D** (0.2 μM) with TNP (1 μM) in EtOH:H_2O (1:1) system, at pH 3.5 (Chloroacetate buffer) λ_{ex} = 366 nm.

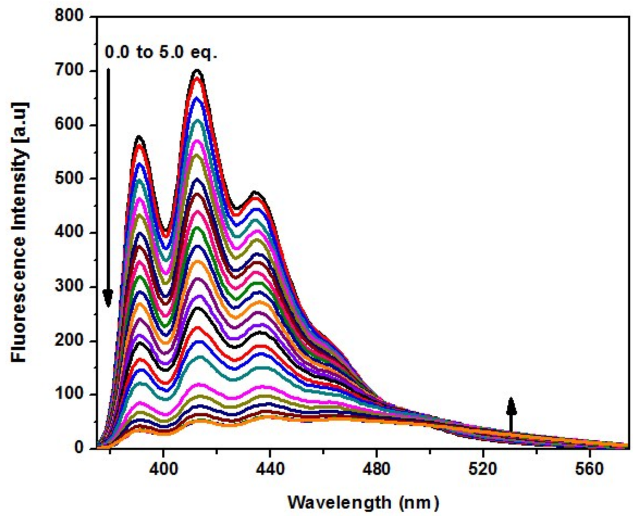

Fig. S23. Fluorescence titration spectra of probe **AIM-D** (0.2 μM) with TNP (1 μM) in EtOH:H_2O (1:1) system, at pH 9.5 (CHES buffer) λ_{ex} = 366 nm.

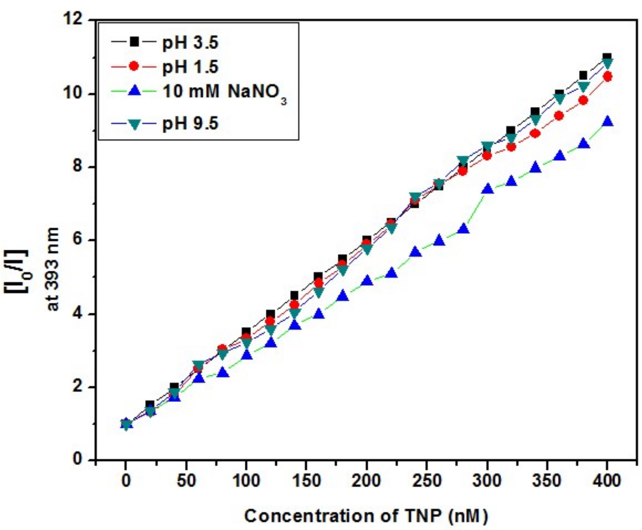

Fig. S24. Stern-Volmer plot of the probe **AIM-D** (0.2 μM) with TNP (0.4 μM) in at various pH values (1.5-black, 3.5-red and 9.5-green) and in the presence of 10 mM $NaNO_3$ (blue) in EtOH-H_2O (1:1), λ_{ex} = 366 nm, λ_{em} = 417 nm.

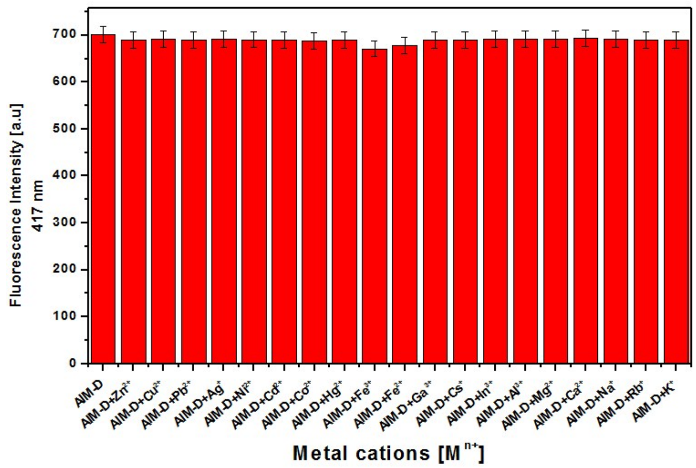

Fig. S25. Fluorescence studies of the probe **AIM-D** (0.2 μM) with various metal ions (2.0 μM) in EtOH-H_2O (1:1) system, λ_{ex} = 366 nm, λ_{em} = 417 nm.

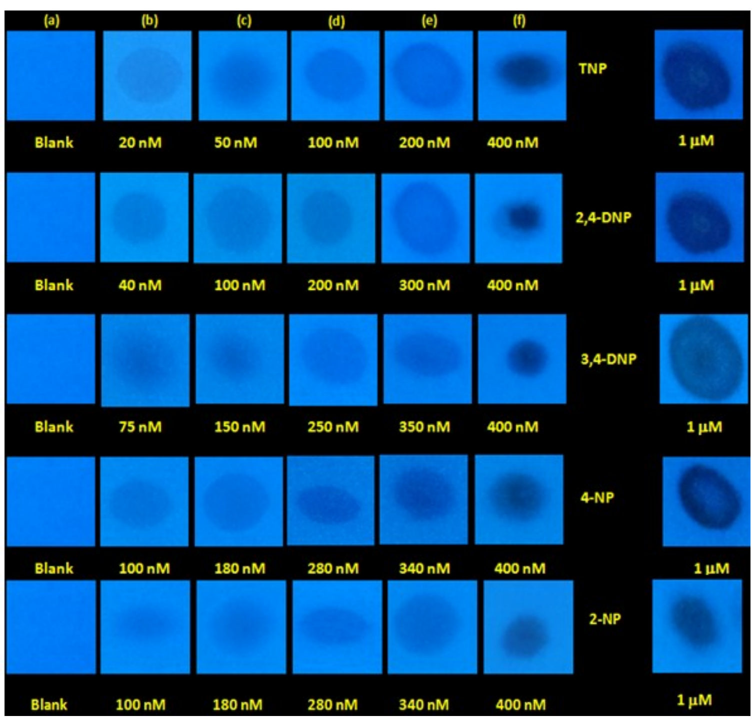

Fig. S26. Photographs of **AIM-D** coated Whatman filter paper strips spotted with very small amount of different concentration of nitrophenols, blank has taken with a drop of water, upon illumination at 365 nm in UV lamp.

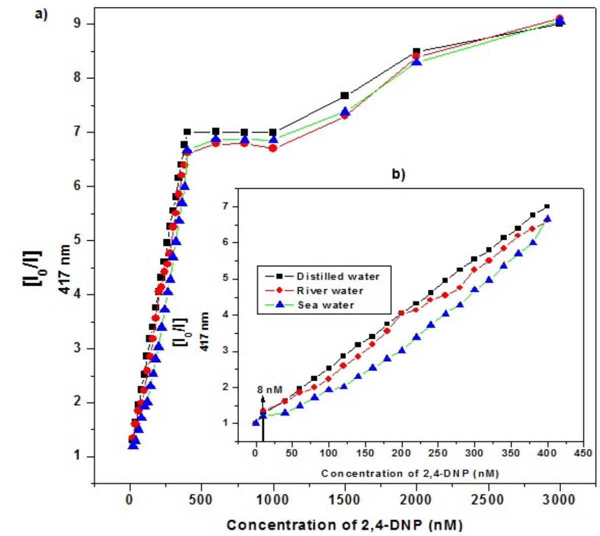

Fig. S27. Stern-Volmer plot of the probe **AIM-D** (0.2 μM) with 2,4-DNP (3.0 μM) in EtOH-H_2O (1:1), λ_{ex} = 366 nm, λ_{em} = 417 nm; b) shows enlarged portion from 0-400 nM. Water ratio's was chosen from respective water samples such as distilled water (black), river (red) and sea water (blue).

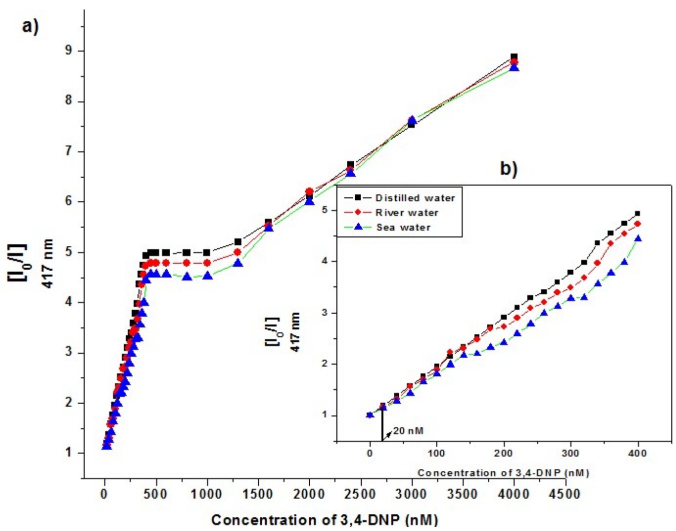

Fig. S28. Stern-Volmer plot of the probe **AIM-D** (0.2 μM) with 3,4-DNP (4.0 μM) in EtOH-H_2O (1:1), λ_{ex} = 366 nm, λ_{em} = 417 nm; b) shows enlarged portion from 0 - 400 nM. Water ratio's was chosen from respective water samples such as distilled water (black), river (red) and sea water (blue).

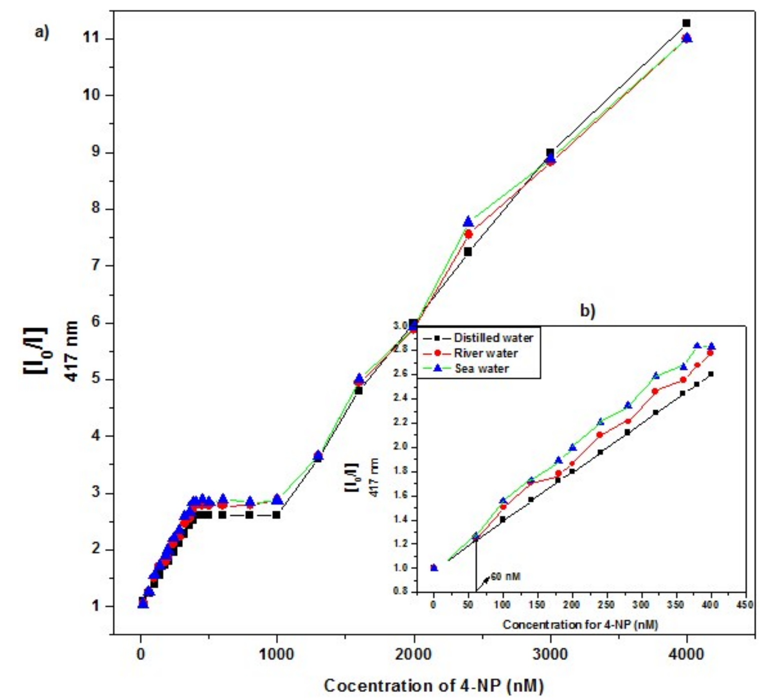

Fig. S29. Stern-Volmer plot of the probe **AIM-D** (0.2 μM) with 4-NP (4.0 μM) in EtOH-H_2O (1:1), λ_{ex} = 366 nm, λ_{em} = 417 nm; b) shows enlarged portion from 0 - 400 nM. Water ratio's was chosen from respective water samples such as distilled water (black), river (red) and sea water (blue).

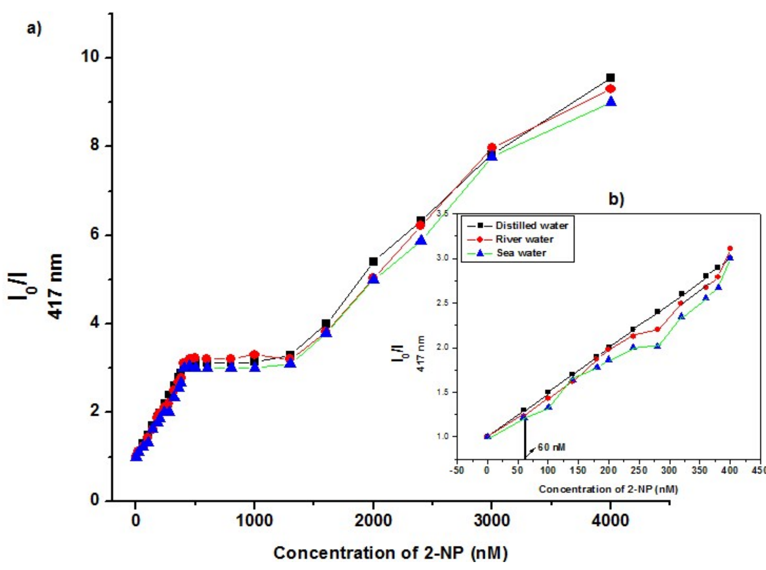

Fig. S30. Stern-Volmer plot of the probe **AIM-D** (0.2 μM) with 2-NP (4.0 μM) in EtOH-H_2O (1:1), λ_{ex} = 366 nm, λ_{em} = 417 nm; b) shows enlarged portion from 0-400 nM. Water ratio's was chosen from respective water samples such as distilled water (black), river (red) and sea water (blue).

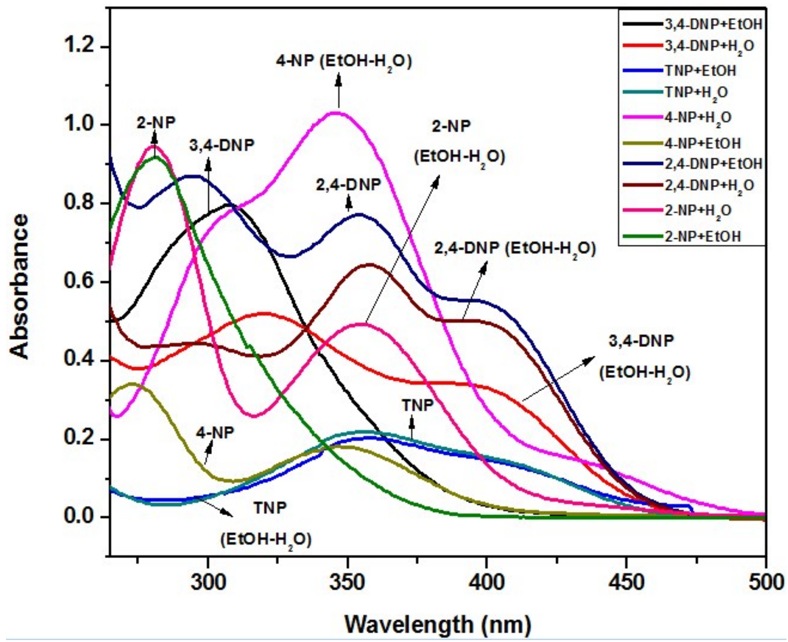

Fig. S31. UV-Vis spectra of nitrophenols (2.0 μM) **AIM-D** in absolute EtOH and aqueous EtOH (EtOH:H_2O, 1:1).

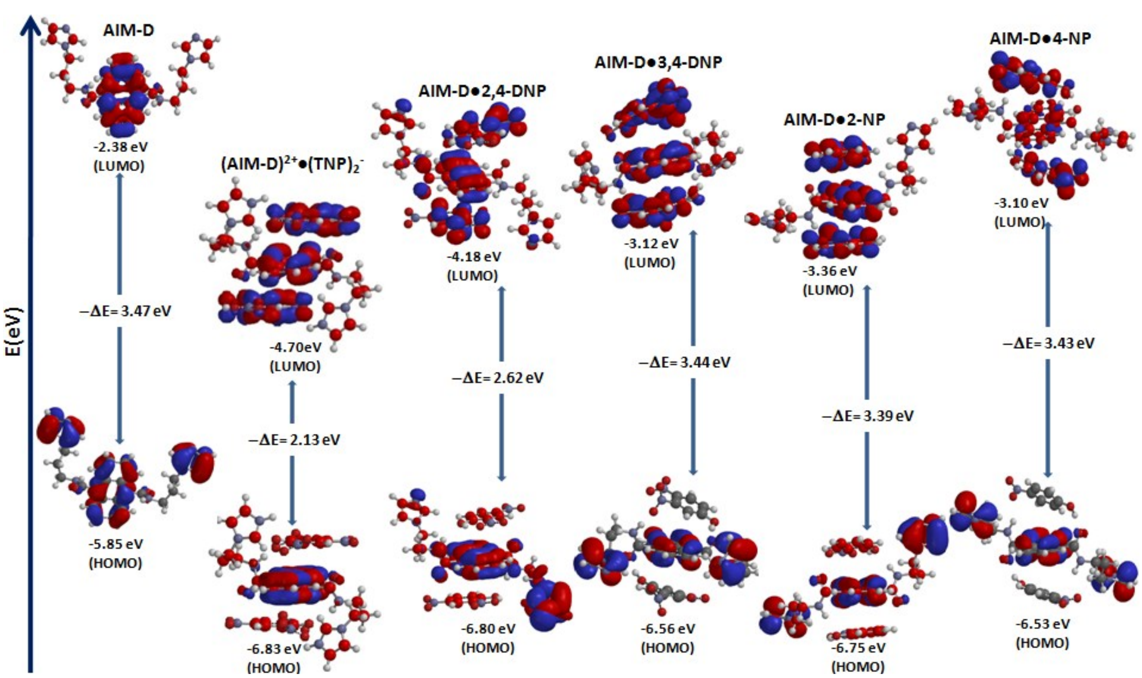

Fig. S32. DFT based computational studies of probe **AIM-D** and its complexes with nitrophenols in EtOH medium using B3LYP/6-31G* set and SM8 solvent model.

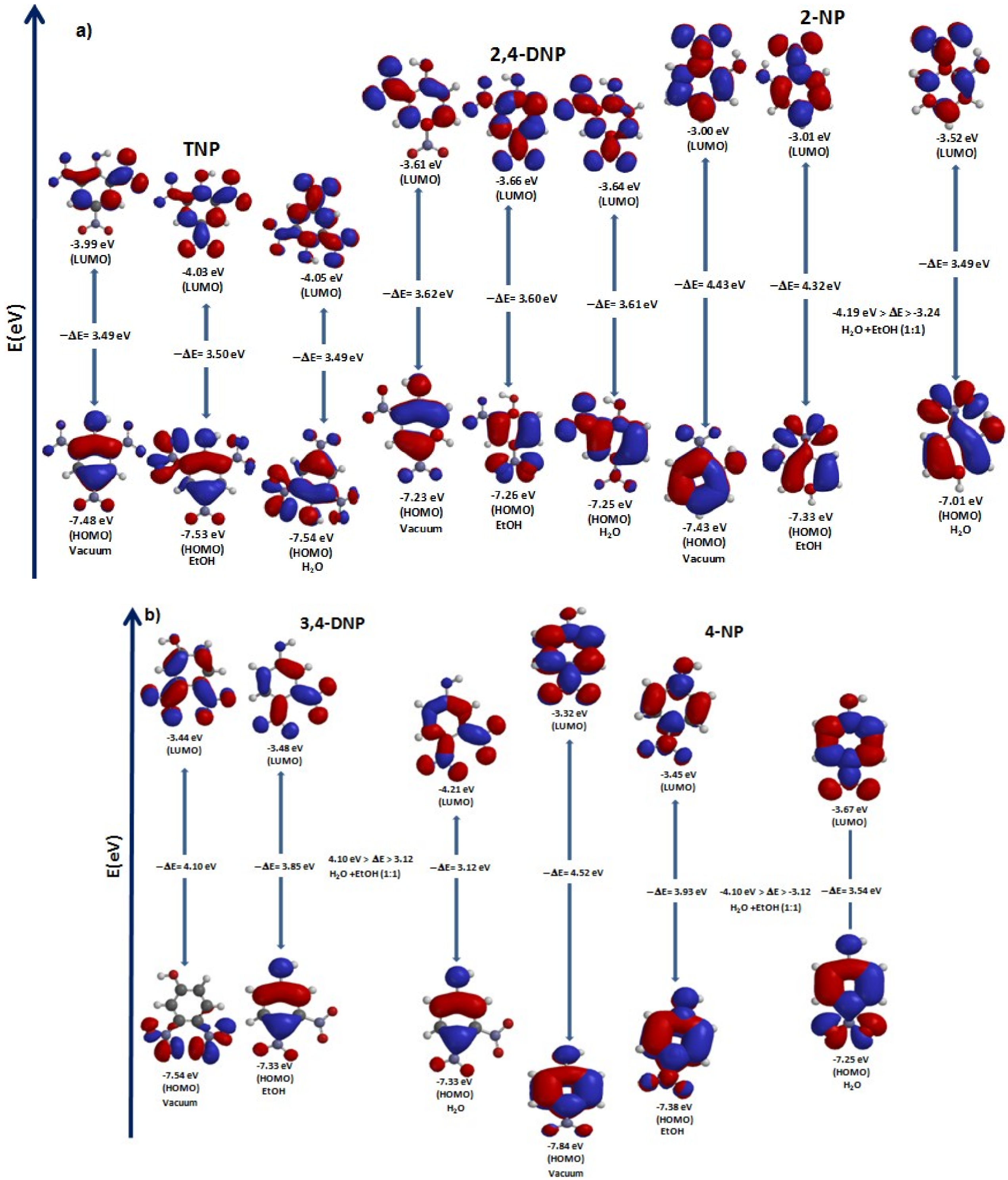
a)
E(eV)
TNP
-3.99 eV (LUMO)
−ΔE= 3.49 eV
-7.48 eV (HOMO) Vacuum
-4.03 eV (LUMO)
−ΔE= 3.50 eV
-7.53 eV (HOMO) EtOH
-4.05 eV (LUMO)
−ΔE= 3.49 eV
-7.54 eV (HOMO) H2O
2,4-DNP
-3.61 eV (LUMO)
−ΔE= 3.62 eV
-7.23 eV (HOMO) Vacuum
-3.66 eV (LUMO)
−ΔE= 3.60 eV
-7.26 eV (HOMO) EtOH
-3.64 eV (LUMO)
−ΔE= 3.61 eV
-7.25 eV (HOMO) H2O
2-NP
-3.00 eV (LUMO)
−ΔE= 4.43 eV
-7.43 eV (HOMO) Vacuum
-3.01 eV (LUMO)
−ΔE= 4.32 eV
-7.33 eV (HOMO) EtOH
-4.19 eV > ΔE > -3.24
H2O +EtOH (1:1)
-3.52 eV (LUMO)
−ΔE= 3.49 eV
-7.01 eV (HOMO) H2O
b)
E(eV)
3,4-DNP
-3.44 eV (LUMO)
−ΔE= 4.10 eV
-7.54 eV (HOMO) Vacuum
-3.48 eV (LUMO)
−ΔE= 3.85 eV
-7.33 eV (HOMO) EtOH
4.10 eV > ΔE > 3.12
H2O +EtOH (1:1)
-4.21 eV (LUMO)
−ΔE= 3.12 eV
-7.33 eV (HOMO) H2O
4-NP
-3.32 eV (LUMO)
−ΔE= 4.52 eV
-7.84 eV (HOMO) Vacuum
-3.45 eV (LUMO)
−ΔE= 3.93 eV
-7.38 eV (HOMO) EtOH
-4.10 eV > ΔE > -3.12
H2O +EtOH (1:1)
-3.67 eV (LUMO)
−ΔE= 3.54 eV
-7.25 eV (HOMO) H2O

Fig. S33. DFT based computational studies of nitrophenols in vacuum and in solvents such as EtOH and H_2O using B3LYP/6-31G* set and SM8 solvent model was used to calculate in respective solvent medium.

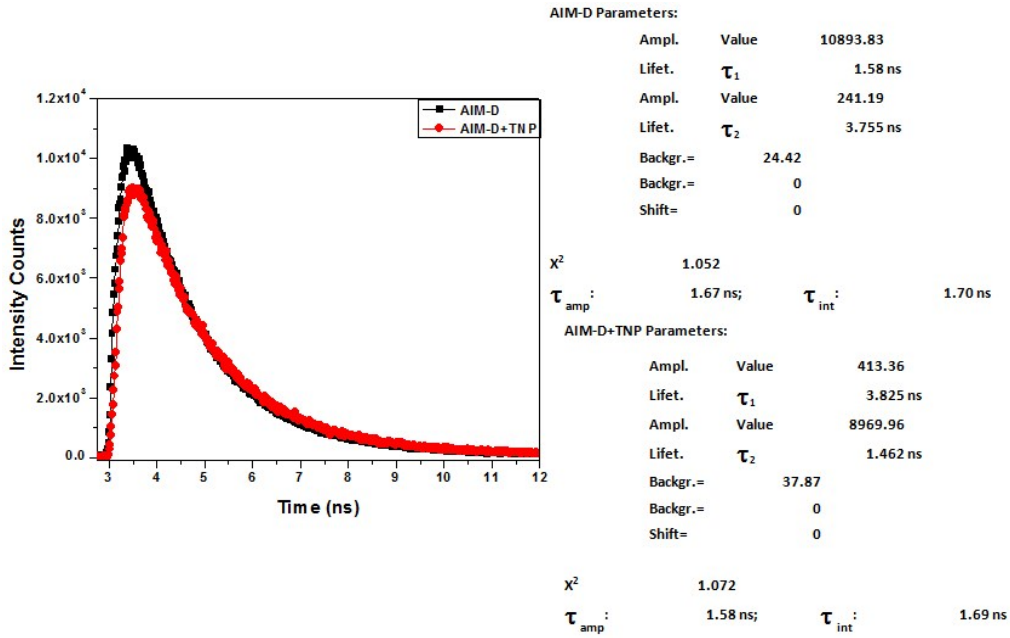

Fig. S34. Fluorescence decay time measurement (fitted) of probe **AIM-D** (black) and **AIM-D●**TNP (1:2 mole ratio) complex in EtOH-H_2O (1:1) medium.

Table S1. DFT based calculations of band gap energies (eV), interaction energies (kcal/mol) in vacuum, EtOH, DMSO and H_2O solvents using B3LYP/6-31G* basis set and SM8 solvent model.

AIM-D/AIM-D●Nitrophenol complexes	**$-\Delta E_{(HOMO-LUMO)}$ (eV)**				**$-\Delta E_{(Interaction\ energy)}$ (kcal/mol)**			
	$-\Delta E_{(vac)}$	**$-\Delta E_{(DMSO)}$**	**$-\Delta E_{(EtOH)}$**	**$-\Delta E_{(H2O)}$**	**$-\Delta E_{(vac)}$**	**$-\Delta E_{(DMSO)}$**	**$-\Delta E_{(EtOH)}$**	**$-\Delta E_{(H2O)}$**
AIM-D	3.69	3.60	3.47	3.68	----	----	----	----
$(AIM\text{-}D)^{2+}$●$(TNP)_2^-$	2.78	2.40	2.13	2.69	25.72	10.97	16.31	5.23
AIM-D●$(2,4\text{-}DNP)_2$	2.70	2.58	2.62	2.70	16.16	5.02	8.27	1.67
AIM-D●$(3,4\text{-}DNP)_2$	3.62	3.59	3.44	3.61	10.98	3.20	5.32	1.02
AIM-D●$(2\text{-}NP)_2$	3.59	3.47	3.39	3.56	7.29	3.45	4.65	0.67

AIM-D●(4-NP)$_2$	3.63	3.60	3.43	3.63	3.43	1.09	2.03	0.19

*All calculations has been done according to the most stable stationary points were verified as minima through full calculations of the Hessian and Harmonic frequency analysis.