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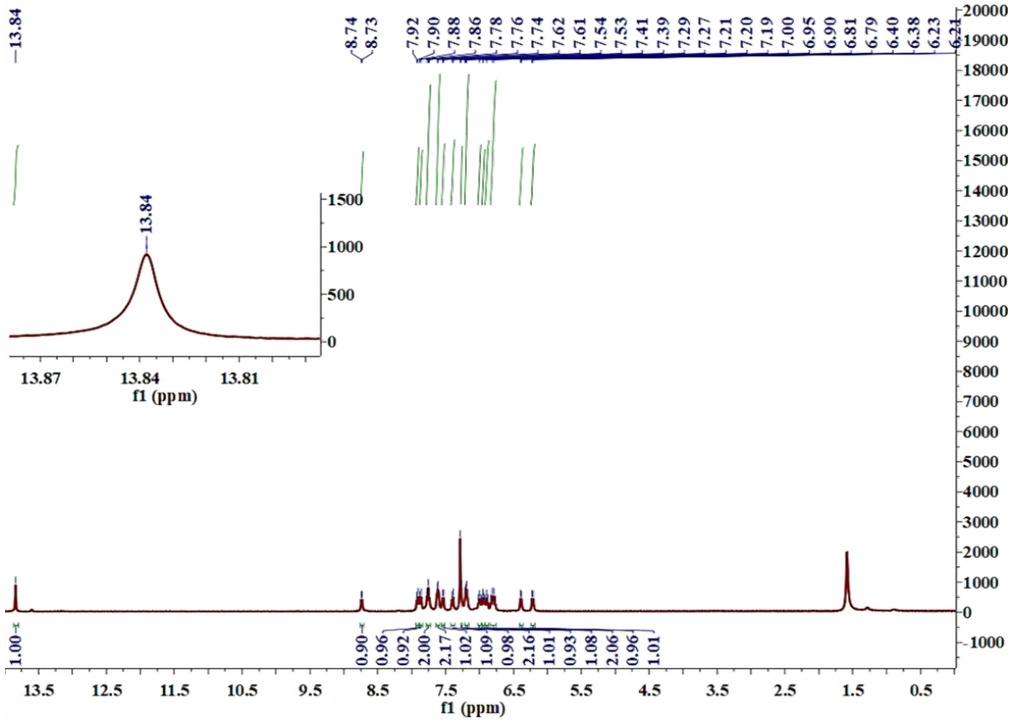
Multistimuli Responsive Heteroleptic Iridium (III) Complex: Role of Hydrogen Bonding in Probing Solvent, pH and Bovine Serum Albumin (BSA)

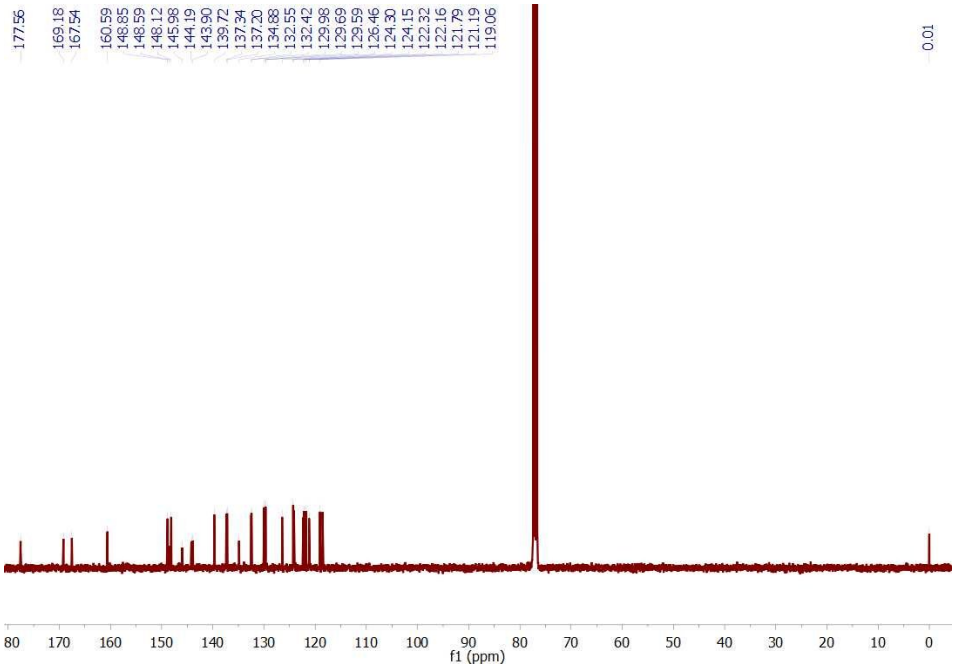
Vishal Kachwal[a], Parva Kumar Sharma[b], Amrit Sarmah[c,d], Shibasish Chowdhury[b]*, Inamur Rahaman Laskar[a]*

a) Department of Chemistry, BITS Pilani, Pilani campus Jhunjhunu Rajsthan 333031, India b) Department of Biological Science, BITS Pilani, Pilani campus Jhunjhunu Rajsthan 333031, India. c) Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, v.v.i., Flemingovo nám. 2, 16610 Prague 6, Czech Republic d) Regional Centre of Advanced Technologies and Materials, Palacký University, 77146 Olomouc, Czech Republic



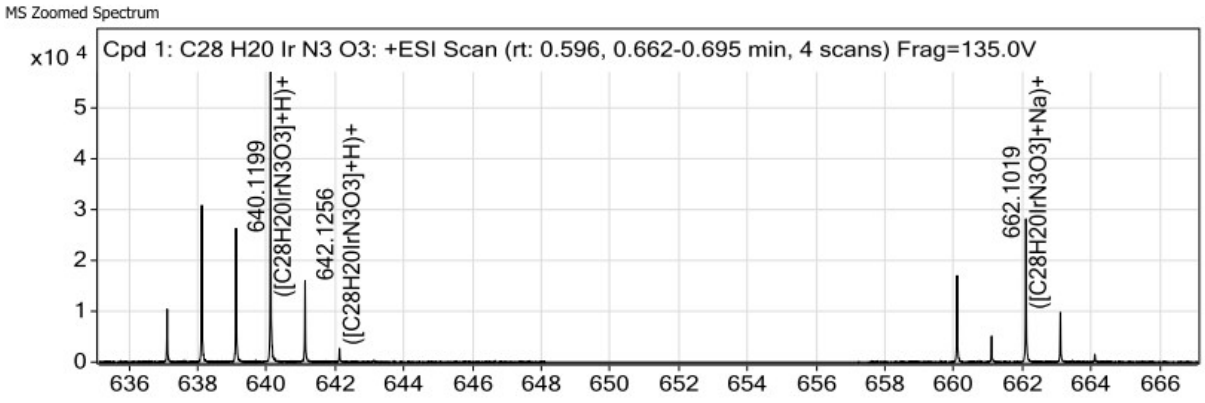
δ $_{H}$ (400 MHz, $CDCl_3$) 13.84 (1 H, s), 8.74 (1 H, d, *J* 5.2), 7.91 (1 H, d, *J* 7.8), 7.87 (1 H, d, *J* 8.1), 7.76 (1 H, t, *J* 7.5), 7.62 (1 H, d, *J* 3.4), 7.54 (1 H, d, *J* 5.4), 7.40 (1 H, d, *J* 8.1), 7.27 (1 H, s), 7.23 – 7.16 (1 H, m), 7.03 – 6.97 (1 H, m), 6.98 – 6.92 (1 H, m), 6.92 – 6.87 (1 H, m), 6.85 – 6.75 (1 H, m), 6.39 (1 H, d, *J* 7.4), 6.22 (1 H, d, *J* 7.5).

(a) ^{1}H NMR spectrum of Complex **1**



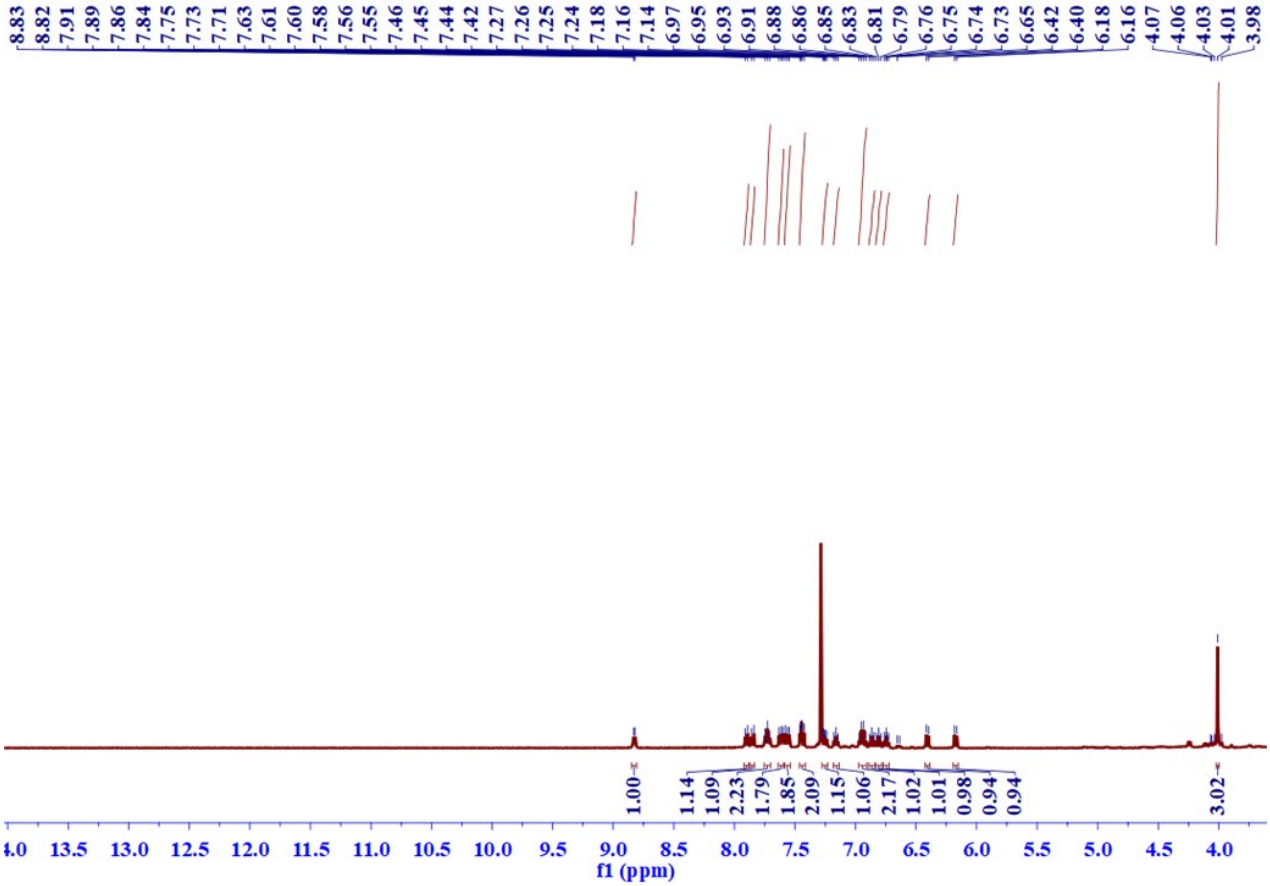
^{13}C NMR (101 MHz, $CDCl_3$) δ 177.56, 169.18, 167.54, 160.59, 148.85, 148.59, 148.12, 145.98, 144.19, 143.90, 139.72, 137.34, 137.20, 134.88, 132.55, 132.42, 129.98, 129.69, 129.59, 126.46, 124.30, 124.15, 122.32, 122.16, 121.79, 121.19, 119.06, 118.55.

(b) ^{13}C NMR spectrum of Complex **1**



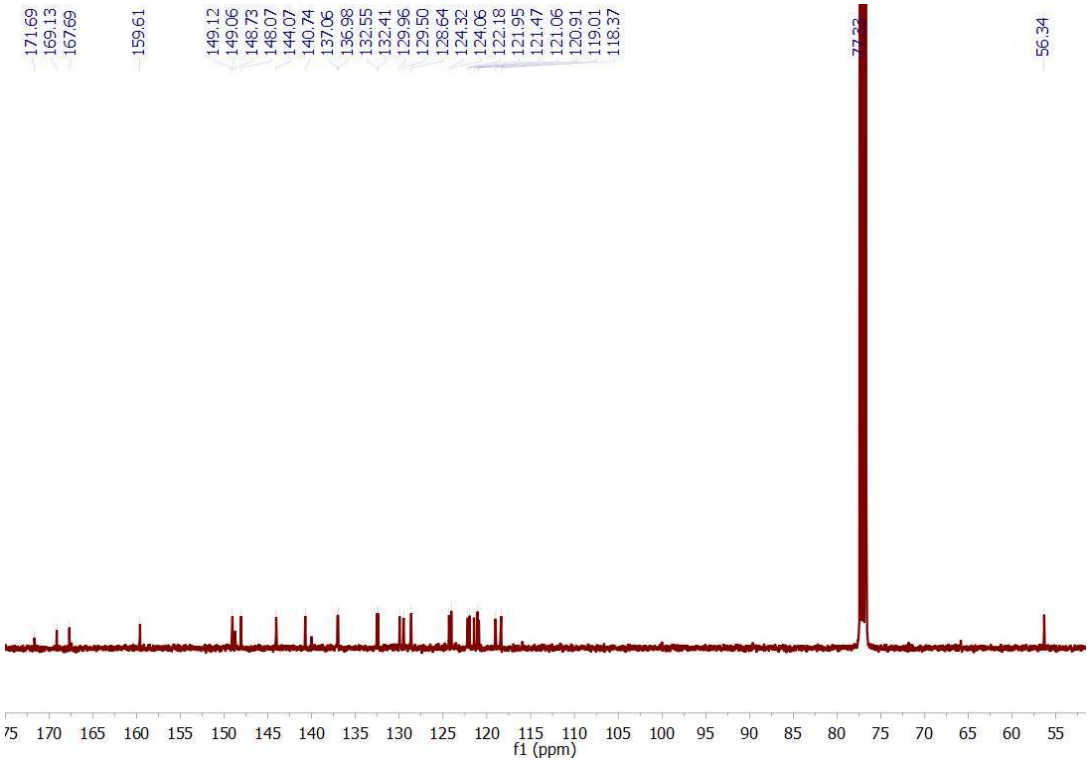
(c)

Fig S1. Complex **1** (a) ^{1}H NMR (b) ^{13}C NMR & (c) HRMS



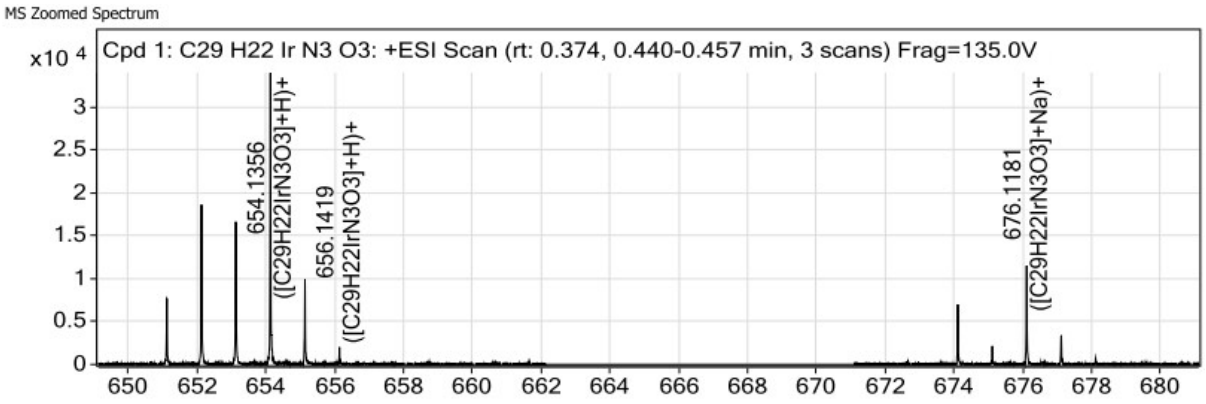
δ_H (400 MHz, $CDCl_3$) 8.83 (1 H, d, *J* 5.7), 7.87 (2 H, dd, *J* 20.4, 8.2), 7.73 (2 H, dd, *J* 10.7, 5.0), 7.64 – 7.59 (2 H, m), 7.59 – 7.53 (2 H, m), 7.44 (2 H, dd, *J* 7.3, 6.1), 7.25 (1 H, dd, *J* 8.7, 5.1), 7.16 (1 H, t, *J* 6.9), 6.98 – 6.91 (2 H, m), 6.86 (1 H, t, *J* 7.3), 6.81 (1 H, t, *J* 7.3), 6.74 (1 H, dd, *J* 8.1, 6.7), 6.41 (1 H, d, *J* 7.5), 6.17 (1 H, d, *J* 7.6), 4.02 (3 H, d, *J* 9.8).

(a) ^{1}H NMR spectrum of Complex **2**



^{13}C NMR (101 MHz, $CDCl_3$) δ 171.69, 169.13, 167.69, 159.61, 149.12, 149.06, 148.73, 148.07, 144.07, 140.74, 137.06, 136.98, 132.55, 132.41, 129.96, 129.50, 128.64, 124.32, 124.06, 122.18, 121.95, 121.47, 121.06, 120.91, 119.01, 118.37, 77.33, 56.34.

(b) ^{13}C NMR of Complex **2**



(c)

Fig S2. Complex **2** (a) ^{1}H NMR (b) ^{13}C NMR & (c) HRMS

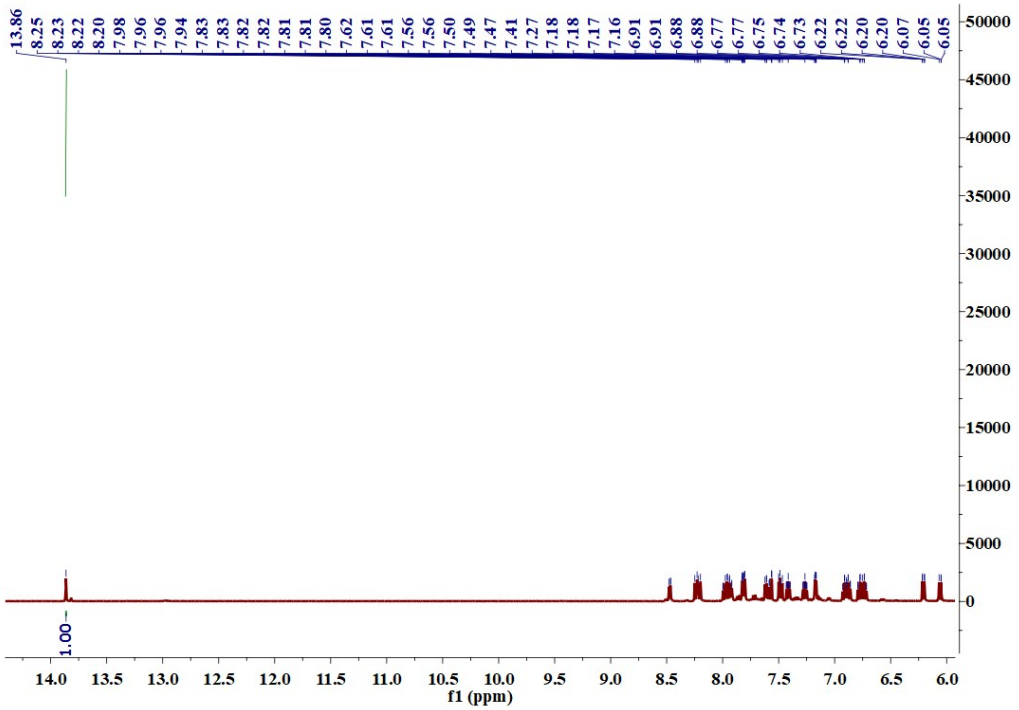
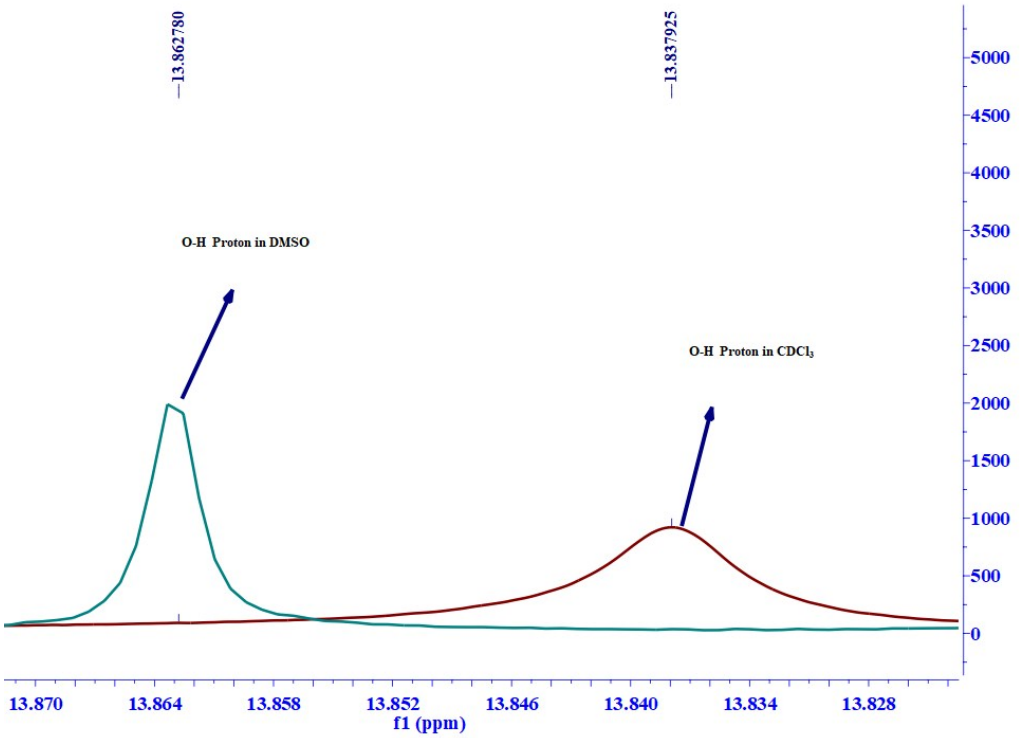


Fig S3 ^{1}H NMR of Compound **1** in DMSO



Δ (δΔ (O-H) DMSO - δΔ (O-H) $CDCl_3$) = 0.0098.

A = 0.0065 + 0.133(δΔ) = 0.0098

Fig S4 The chemical shift of -OH proton of **1** in d^6-DMSO & $CDCl_3$ and calculation of Hydrogen Bond Acidity (A).

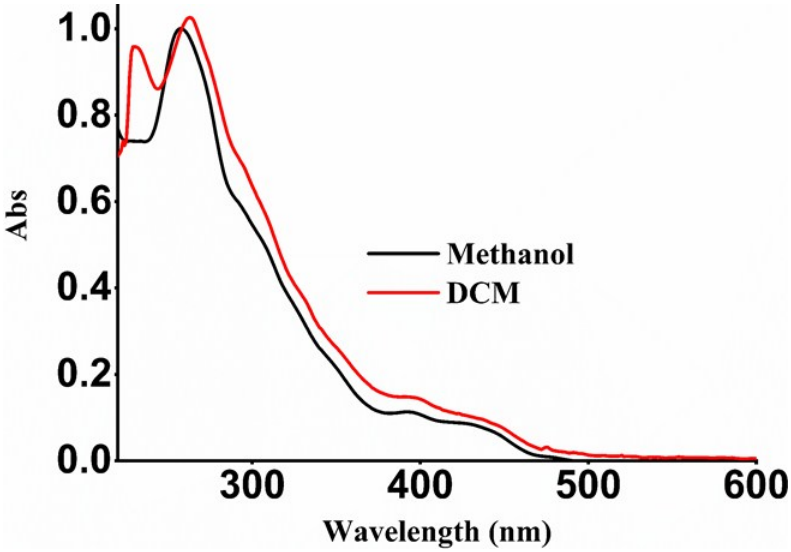
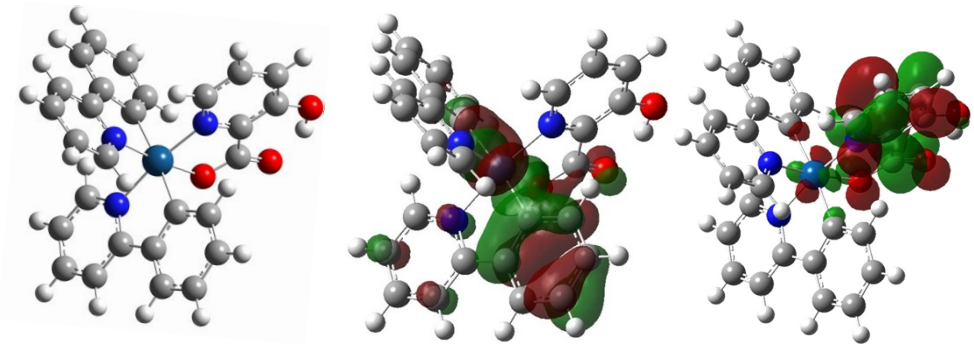


Fig S5. Absorbance spectra of Complex **1** in methanol and DCM ($1*10^{-5}$ M)



(a) (b) (c)

Fig S6. Frontier molecular orbital diagram of **1** a) optimized geometry b)HOMO and c) LUMO, calculated by using B3LYP/6-31G+ (d,p)* and LANL2DZ as implemented on Gaussian 09.

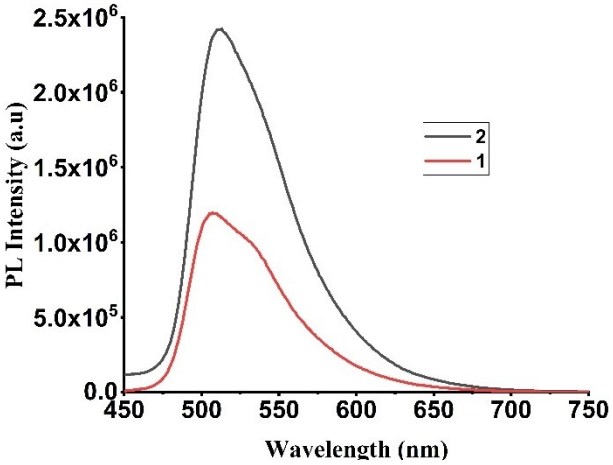


Fig S7. PL spectra of the compound **1** and **2** in THF (tetrahydrofuran) ($1*10^{-5}$ M) solutions.

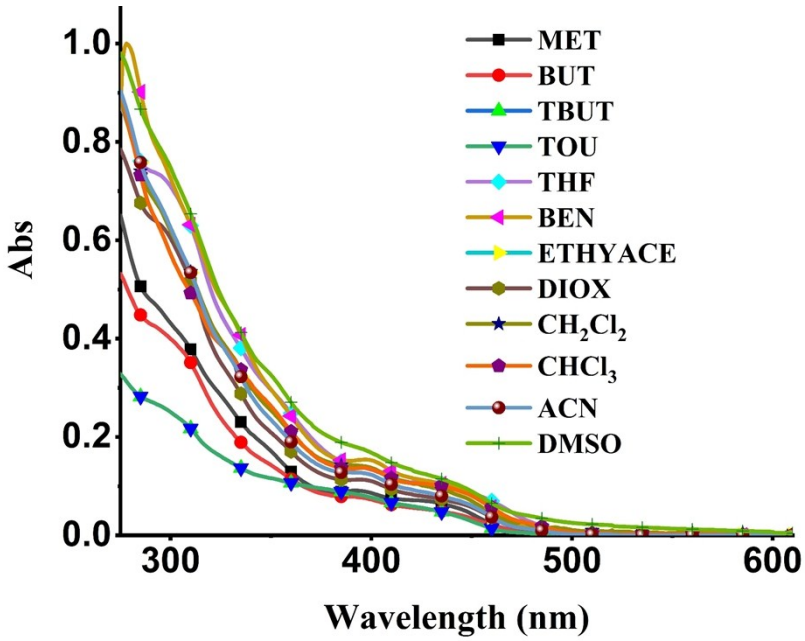


Fig S8. Absorption Spectra of complex **1** in different solvents ($1*10^{-6}$ M) (Met = Methanol, But = Butanol, TBUT = Tertiary butanol, Tou= Toluene, THF = Tetra hydrofuran , Ben = Benzene, Ethylace = Ethyl acetate, .Diox = Dioxane, CH_2Cl_2 = Di chloro methane, $CHCl_3$= chloroform,.ACN = Acetonitrile.DMSO = Dimethyl sulphoxide) .

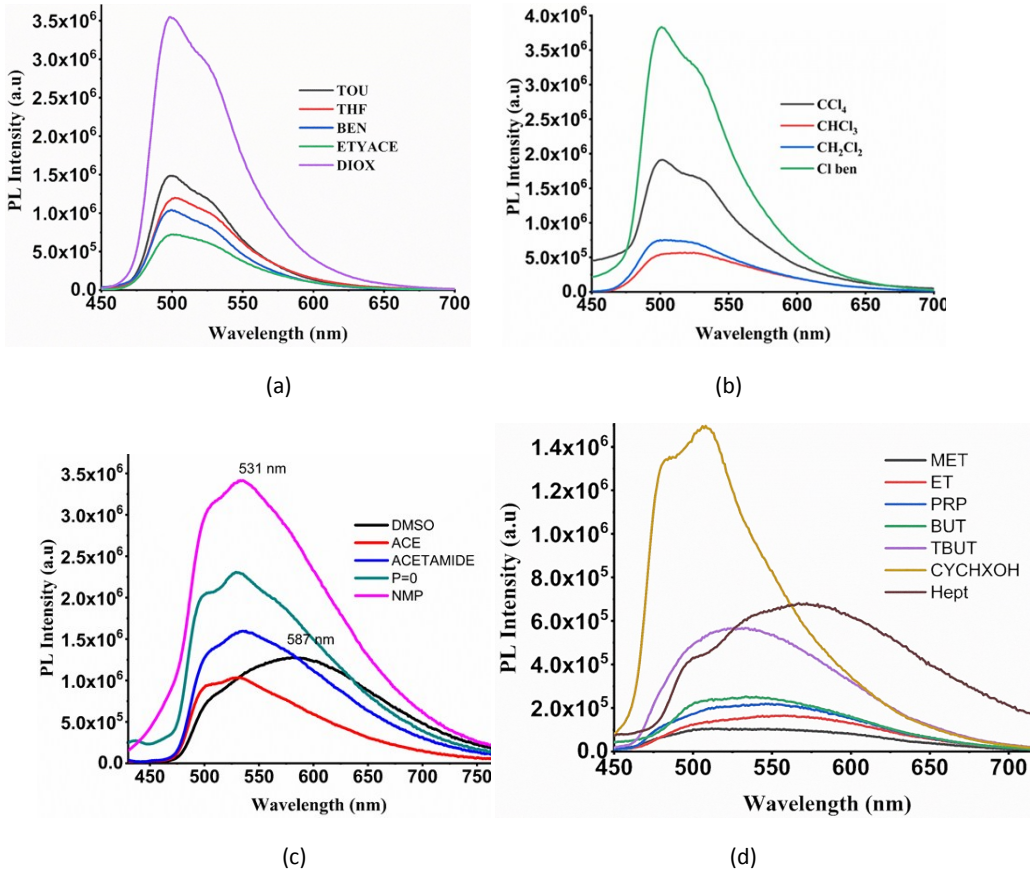
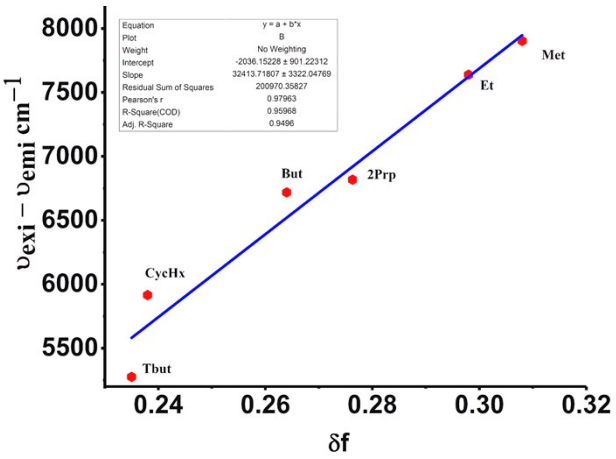
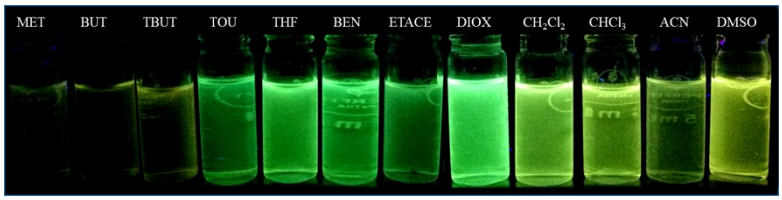


Fig S9. PL spectra of the **1** in the presence of (a) Nonhydrogen bonding (NHB) or weak hydrogen bonding acceptors solvents (WHB) (TOU= Toulene, THF = tetrahydrofuran, BEN = benzene, ETHYACE = ethylacetate, DIOX = dioxane) (b) Chlorinated solvent (c) Hydrogen bonding aceptors (HBA) solvents (DMSO = dimethyl sulfoxide, ACE = acetone, Acetamide , P=O = hexamethyl phosphoramide, NMP = N-methyl pyrrolidine) (d) Hydrogen bond donating (HBD) solvents (Met = methanol, ET = ethanol, PRP = propanol, BUT = butanol, TBUT = terytiary butanol, CYCHXOH = cyclohexanol).



(a)



(b)

Fig S10. (a)Lippert Mataga plot of **1** in alcohols between stokes shift vs f(ε,η) (orientational polarizibility) (b) Photoluminiscence image of compound **1** in different solvents (Met = Methanol, But = Butanol, TBUT = Tertiary butanol, Tou= Toluene, THF = Tetra hydrofuran , Ben = Benzene, Ethylace = Ethyl acetate, .Diox = Dioxane, CH_2Cl_2 = Di chloro methane, 9.$CHCl_3$= chloroform,.ACN = Acetonitrile.DMSO = Dimethyl sulphoxide)

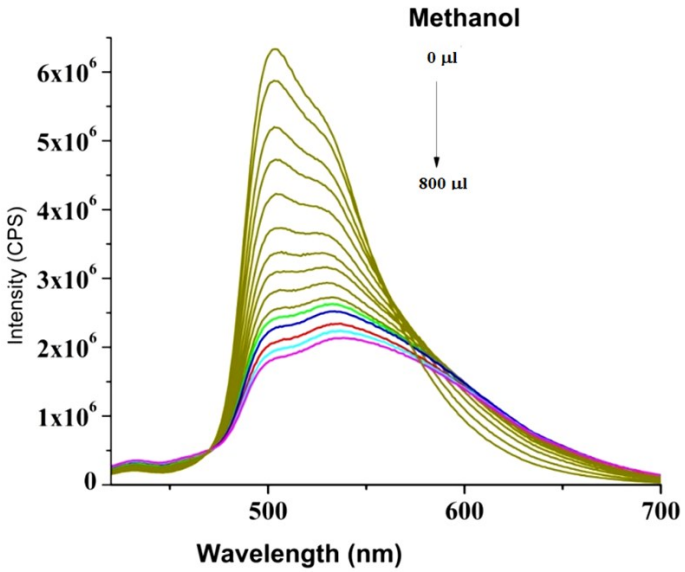
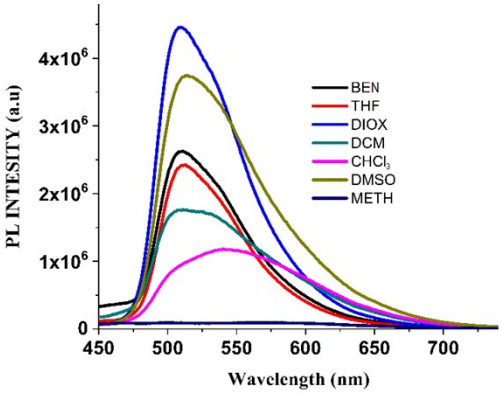
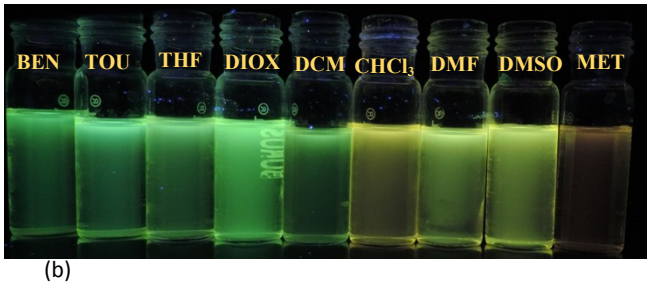


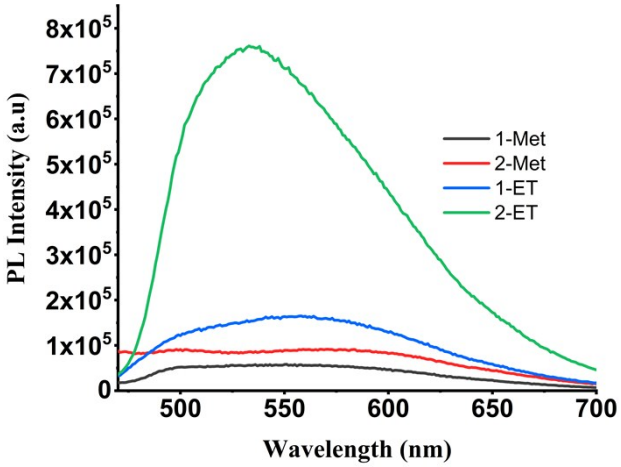
Fig S11. Emission spectra of **1** in THF ($1*10^{-5}$ **M)** by gradually increasing the methanol concentration



(a)



(b)



(c)

Fig S12. a) PL spectra of **2** in different solvents ($1*10^{-5}$ M), b) Emission color of **2** indifferent solvents excited under UV-lamp (λ_{ex}, 365 nm) c) Comparitive emission spectra of **1** and **2** in solvents (methanol and ethanol)

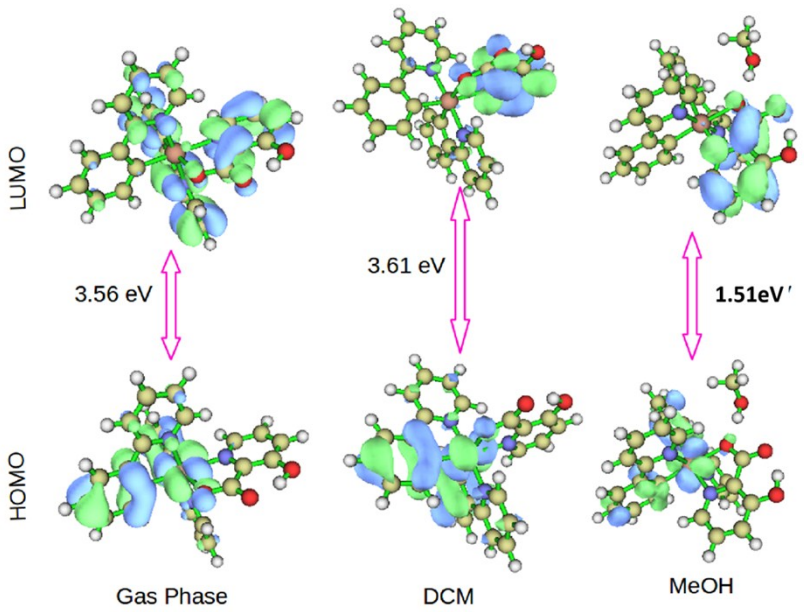
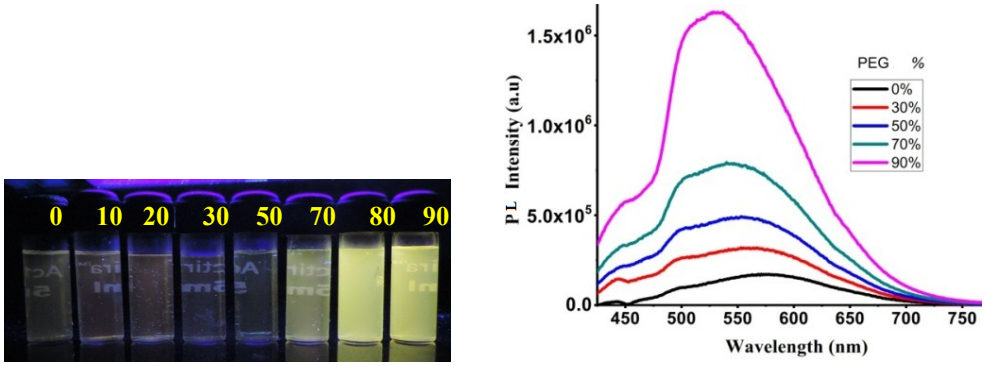


Fig S13. Frontier orbital diagram energy level from DFT of **1** in DCM and Methanol,



(a) (b)

Fig S14. (a) PL emission image of **1** in different methanol/ water mixture under UV-lamp (λ_{ex}, 365 nm); (b) Emission spectra of **1** in methanol/PEG mixtures.

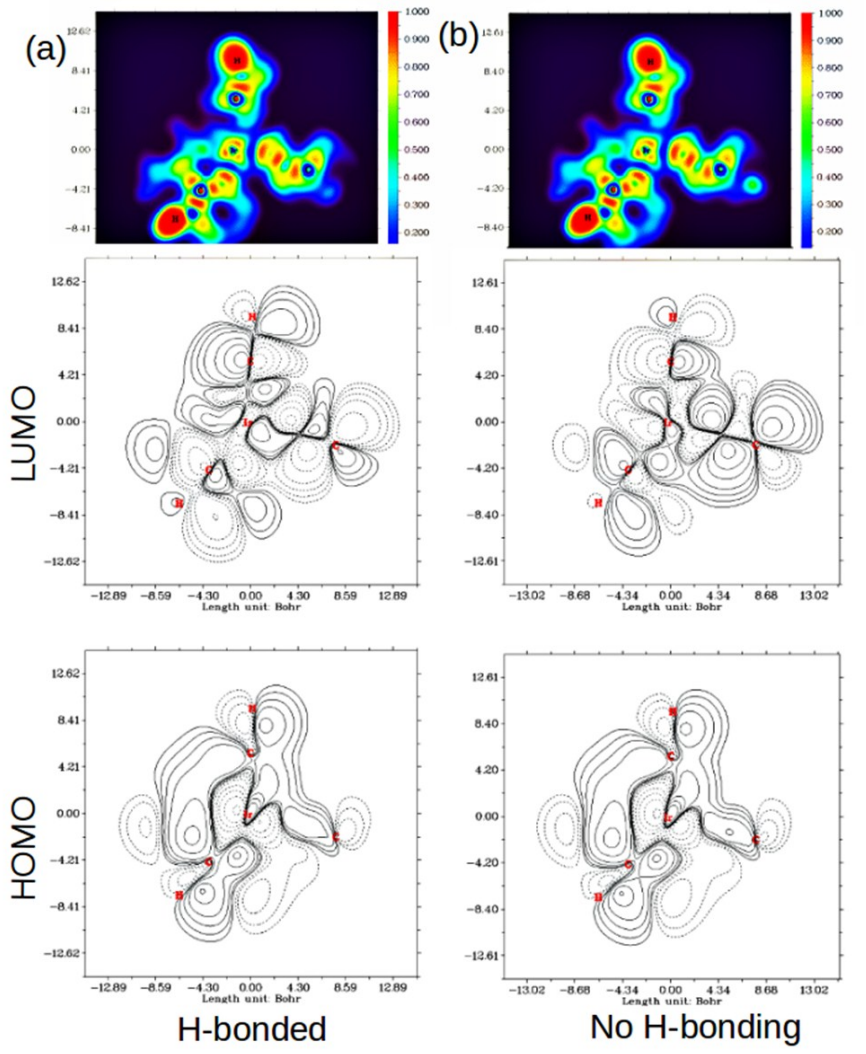


Fig S15. Electron localization function (ELF) and FMO contour maps for the H-bonded (left panel) and without H-bonded (right panel) forms of the complex **1**

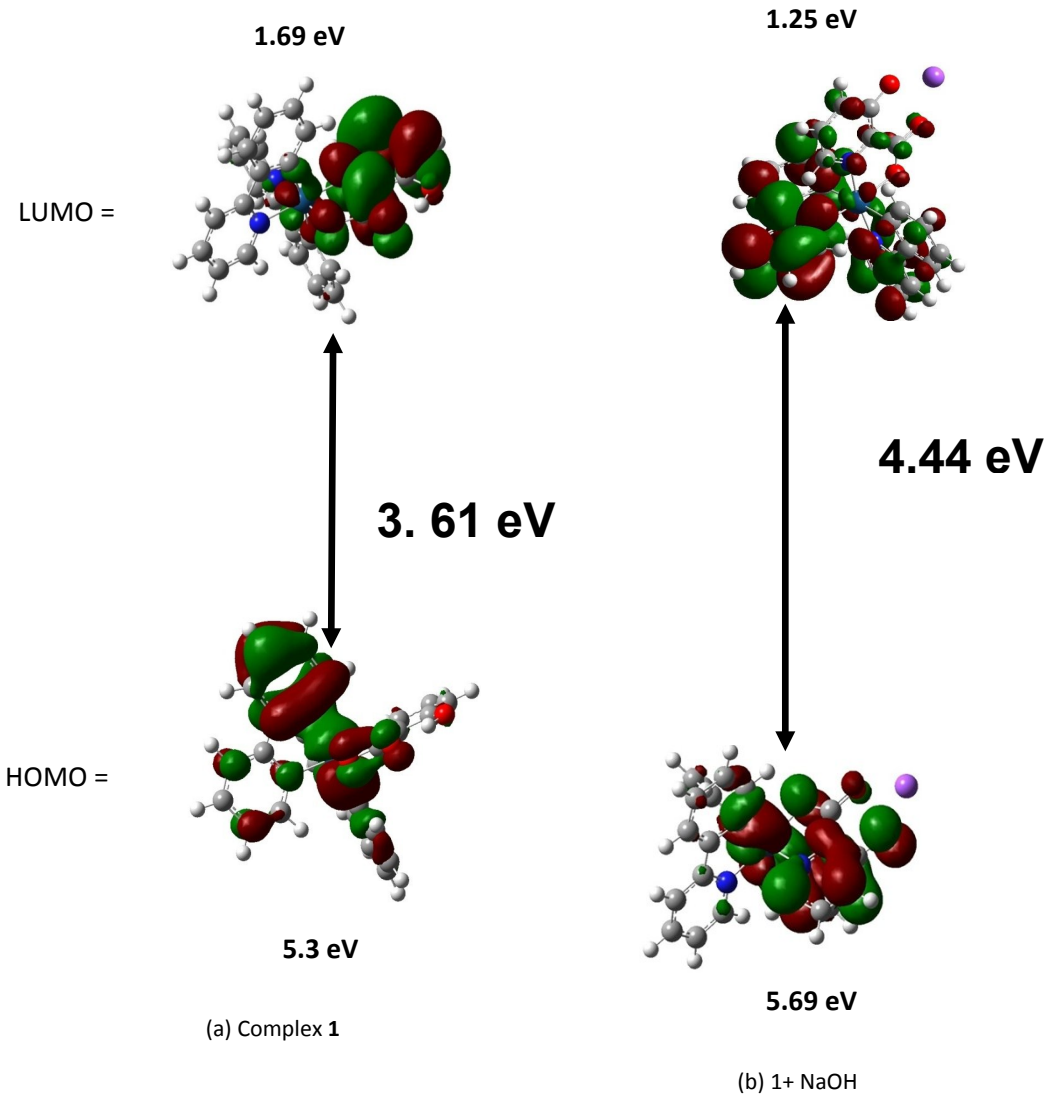


Fig S16. Frontier molecular orbital images of HOMO and LUMO energy levels of **1** and **1**+ base (NaOH), it indicates that the HOMO is getting stabilized while the LUMO is getting destabilized in the presence of a base.

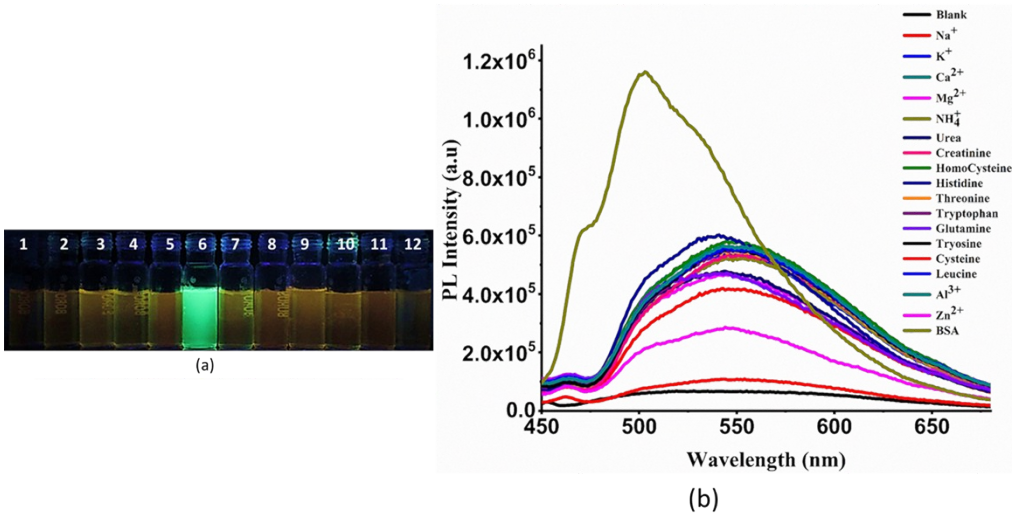


Fig S17. (a) PL emission image of 1 (c = 10^{-5}M) with 1 equivalent of different metals and proteins, respectively, from left to right (1-Na_2SO_4, 2- $MgSO_4$, 3- $ZnSO_4$, 4-$Al_2(SO_4)_3$, 5- Urea, 6-BSA, 7- Histidine, 8- Creatinine, 9- Cystine, 10- Tyrosine, 11-Lysine, 12-Tryptophan) (under exciting at 365nm with a UV lamp). (b) Emission spectra of 1 (c = 10^{-5}M) with 1 equivalent of different metal salts[Na_2SO_4, K_2SO_4, $CaSO_4$, $MgSO_4$, $(NH_4)_2SO_4$, Na_3PO_4, $ZnSO_4$, $Al_2(SO_4)_3$] , creatinine and BSA. (BSA results in green emission and remaining species produces weak yellow emission)

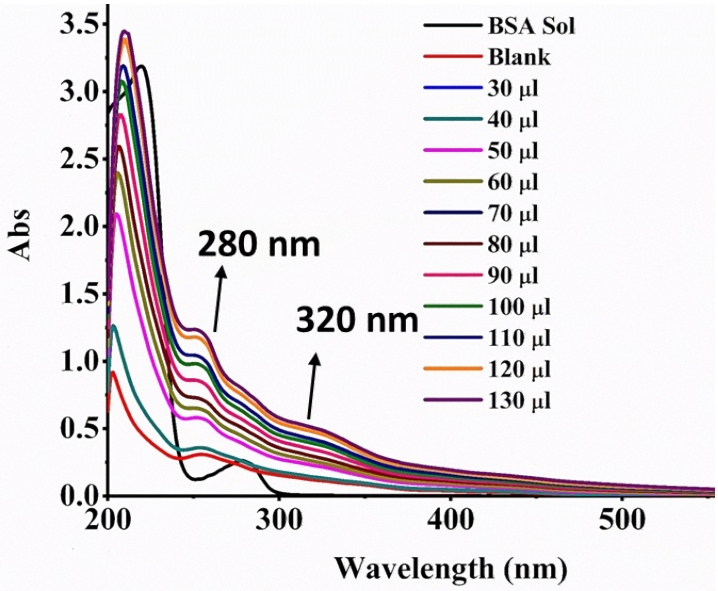
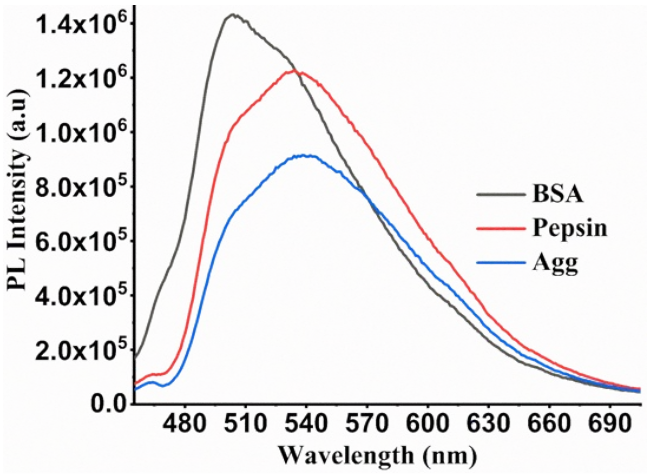
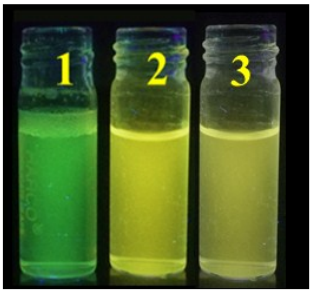


Fig S18. UV-Visible spectra of **1** by gradually increasing the BSA concentration

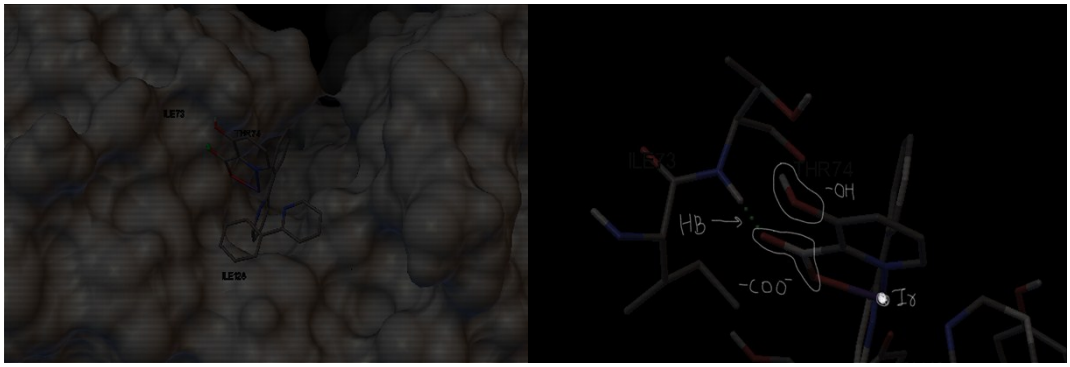


(a)



(b)

Fig. S19. (a) PL spectra of **1** in pressence of BSA, Protien and 90% methanol/water fraction. (b) Image of **1** in pressence of BSA, Protien and 90% methanol/water fraction under UV-Lamp 365 nm.



(a) (b)

Fig. S20 (a) Binding of the complex within the hydrophobic pocket of pepsin; (b) It shows the absence of hydrogen bond with hydroyl group of **1** and presence of hydrogen bond with the carbonyl of **1** in pepsin (used software for docking, AutoDock 4.2) [1,2]

Table S1 : It shows the binding energy for the complex 1 with BSA (Binding pockets of top 10 conformations of the complex **1)**

S. No.	**Chain identifier of the binding pocket**	**Binding Energy (kcal/mole)**	**Close Residues**
1	B	-6.4	Gln416, Ser418, Thr419, Thr466, Val468, Lys499, Lys533
2	B	-6.06	Arg194, Trp213, Arg217, Lys221, Lys294, Val342, Asp450, Cys447
3	B	-6.04	Pro415, Gln416, Ser418, Thr419, Thr466,Val468, Lys499, Lys533
4	A	-6.03	Arg194, Trp213, Arg217, Glu291, Val292, Lys294, Pro338, Val342
5	A	-5.9	Asp111, Pro420, Ile522
6	B	-5.52	Asp111, Lys114, Arg144
7	B	-5.26	Pro415, Gln416, Val468, Lys499, Tyr496, Ala500, Lys533
8	B	-5.16	Tyr155, Asn158, Gly162, Pro281, Leu283, Glu284
9	A	-4.86	Glu17, His18, Pro281, Leu282, Leu283
10	B	-4.69	Glu48, Phe49, Thr52, Glu73, Lys76

References

1) Morris, G. M., Huey, R., Lindstrom, W., Sanner, M. F., Belew, R. K., Goodsell, D. S. and Olson, A. J. (2009) Autodock4 and AutoDockTools4: automated docking with selective receptor flexibility. *J. Computational Chemistry* 2009, **16**: 2785-91.

2) Majorek, K.A., Porebski, P.J., Dayal, A., Zimmerman, M.D., Jablonska, K., Stewart, A.J., Chruszcz, M., Minor, W. (2012) Structural and immunologic characterization of the bovine, horse, and rabbit serum albumins. Mol.Immunol. 52: 174-182