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

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$\delta_H$ (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

$\delta_C$ (101 MHz, CDCl$_3$) 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
Fig S1. Complex 1 (a) $^1$H NMR (b) $^{13}$C NMR & (c) HRMS

$\delta$ (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, $J$ 5.0), 7.04 – 6.91 (2 H, m), 6.86 (1 H, t, $J$ 7.3), 6.81 (1 H, t, 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
Fig S3  $^1$H NMR of Compound 1 in DMSO

$\Delta (\delta_{\text{O-H}}} \text{DMSO} - \delta_{\text{O-H}}} \text{CDCl}_3 = 0.0098.$

$A = 0.0065 + 0.133(\delta_{\text{O-H}}} = 0.0098$

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 ($1 \times 10^{-5}$ M)

**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) ($1 \times 10^{-5}$ 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 = Tetrahydrofuran, Ben = Benzene, Ethylace = Ethyl acetate, Diox = Dioxane, CH_2Cl_2 = Dichloro methane, CHCl_3 = chloroform, ACN = Acetonitrile, DMSO = Dimethyl sulphoxide).

(a) (b)

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 acceptors (HBA) solvents (DMSO = dimethyl sulfoxide, ACE = acetone, Acetamide, P=O = hexamethyl phosphoramid, NMP = N-methyl pyrrolidine) (d) Hydrogen bond donating (HBD) solvents (Met = methanol, ET = ethanol, PRP = propanol, BUT = butanol, TBUT = terytiary butanol, CYCHXOH = cyclohexanol).
Fig S10. (a) Lippert Mataga plot of 1 in alcohols between stokes shift vs $f(\varepsilon, \eta)$ (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$_2$Cl$_2$ = Di chloro methane, CHCl$_3$ = chloroform, ACN = Acetonitrile, DMSO = Dimethyl sulphoxide)

Fig S11. Emission spectra of 1 in THF ($1 \times 10^{-5}$ M) by gradually increasing the methanol concentration
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 (\lambda_{ex}, 365 nm) c) Comparative 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,
Fig S14. (a) PL emission image of 1 in different methanol/ water mixture under UV-lamp ($\lambda_{ex}, \text{365 nm}$); (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.

Fig S19. (a) PL spectra of 1 in presence of BSA, Protein and 90% methanol/water fraction. (b) Image of 1 in presence of BSA, Protein and 90% methanol/water fraction under UV-Lamp 365 nm.
Fig. S20 (a) Binding of the complex within the hydrophobic pocket of pepsin; (b) It shows the absence of hydrogen bond with hydroxyl 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)

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References
