Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

for

An Integrated Urea and Halogen Bond Donor Based Receptor for Superior and Selective Sensing of Phosphates

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EXPERIMENTAL SECTION

Materials. All reactions were performed in either open atmosphere or in argon gas atmosphere followed by workup at ambient conditions. Acetonitrile and dichloromethane were refluxed over CaH_2 for reactions under dry condition and spectroscopic use. CH_3CN was purchased from Spectrochem Pvt. Ltd., India as HPLC grade and was used as it is for ITC and photophysical studies. $RuCl_3$. XH_2O, 1,10 phenanthroline, Deuterated solvents, tetrabutylammonium salts of anions (F^-, Cl^-, Br^-, I^-, $CH_3CO_2^-$, $PhCO_2^-$, ClO_4^-, NO_3^-, HCO_3^-, HO^-, HSO_4^-, $H_2PO_4^-$, and $HP_2O_7^{3-}$) were purchased from Sigma-Aldrich and were used as received. Distilled ethanol and millipore water were used for the synthesis of complex.

Methods. High-resolution ESI-MS experiments were performed with a Waters QtoF Model YA 263 mass spectrometer in ESI (+ve) mode. The sample for mass spectrometry was prepared for mass spectrometry by dissolving the ligand and complex in acetonitrile having a concentration ≈ 2 x 10^{-6}(M). C, H, N analysis for was performed on PerkinElmer 2500 series II elemental analyzer, PerkinElmer, USA. NMR experiments were carried out with FT-NMR Bruker DPX 500/400/300 MHz NMR spectrometer. The absorption and emission spectra were recorded in a PerkinElmer Lambda 900 UV−Vis−NIR spectrometer (NIR = near-infrared) (with a quartz cuvette of path length 1 cm) and FluoroMax-3 spectrophotometer, from Horiba Jobin Yvon, respectively. In case of time-correlated single photon counting (TCSPC) measurements, samples were excited at 400 nm using picoseconds diode laser (IBH Nanoled-07) in an IBH Fluoro-cube apparatus. The luminescence studies were performed on a Hamamatsu MCP photomultiplier (R3809) and were analyzed using IBH DAS6 software. All the chemical shifts values for ^1H and ^{13}C NMR were presented in parts per million (ppm) and calibrated to residual solvent peak set. The coupling constant values are reported in Hertz (Hz).

Isothermal Titration Calorimetric (ITC) Studies: The isothermal titration calorimetric (ITC) data were recorded in Micro-Cal VP-ITC instrument by using HPLC grade CH_3CN as solvent at 298K. **1[PF$_6$]$_2$** was dissolved in CH_3CN and kept in the measuring cell and this solution was titrated with 30 injections of the guest solution (10 µL per addition) in CH_3CN. An interval of 220 seconds was allowed between individual injection and the stirring speed was fixed at 329 rpm. All the titration data were processed by using Origin 7.0 software which was supplied with the ITC instrument. All the titration data were fitted to either one site or sequential site binding models as applicable. Reference titrations with only solvents were also performed and subtracted from the corresponding titration to remove any effect from the heats of dilution from the titrant.

Calculation of Binding Constant

Properties like emission intensity, chemical shifts were changed upon addition of anions into the solution of complex **1[PF$_6$]$_2$**, which was utilized for calculating the binding constants. Binding constant values of complex **1[PF$_6$]$_2$** with $H_2PO_4^-$ and $HP_2O_7^{3-}$ were calculated from ^{1}H-NMR and PL titration experiments. The binding constant values were calculated from ^{1}H-NMR titration data using Bindfit (http://supramolecular.org) for 1:2 (host: guest) binding stoichiometry. Following equation was used for calculating the binding constant from PL titration experiments *via* non-linear fitting method:

For 1:1 (host: guest) binding stoichiometry, following equation was used[1]

$$\Delta X = \left(\frac{X}{2 * H}\right) * \left\{\left(G_0 + H_0 + \frac{1}{K}\right) - \sqrt{\left(G_0 + H_0 + \frac{1}{K}\right)^2 + 4G_0H_0}\right\}$$

Where G_0 and H_0 are the initial concentrations of guest and host respectively, K is the binding constant and ΔX is the change in emission intensity for each addition of guest species.

For 1:2 (host: guest) binding stoichiometry, following equation was used[1]

$$\Delta X = \frac{X_{\Delta HG1} K_1 [H]_0 [G] + X_{\Delta HG2} K_1 K_2 [H]_0 [G]^2}{1 + K_1 [G] + K_1 K_2 [G]^2}$$

Where $[H]_0$ is the initial concentration of host, K_1 and K_2 are the stepwise association constants, and ΔX is the change in emission intensity.

Calculation of Detection Limit: Following equation was used for calculation of detection limit (DL),

$$\mathrm{DL} = \frac{(3 \times \text{standard deviation})}{\text{Slope}}$$

Slope was determined from the linear fit plot of the change in emission intensity *vs.* concentration of the anion. SD value was calculated form luminescence intensity the blank sample which was measured for 15 consecutive blank samples.

Calculation of Excited state lifetime: Following equation was used for analysis of experimental time-resolved luminescence decays:

$$\boldsymbol{P(t) = b + \sum_{i=1}^{i=n} a_i \; exp^{(-t/\tau_i)}}$$

Where ***P(t)*** is the decay, **n** is the number of discrete emissive species, **b** is a baseline correction factor, $\boldsymbol{\alpha_i}$ is a pre-exponential factor, and τ_i is the excited-state luminescence lifetimes associated with the i^{th} component.

Average lifetime $\langle\tau\rangle$ in case of multi-exponential decays were calculated from the following equation[2]

$$\boldsymbol{< \tau_i > = \sum a_i * \tau_i}$$

Where $\boldsymbol{\alpha_i}$ is the contribution from the i^{th} component.

Syntheses:

***Synthesis of tert-butyl (2-azidoethyl) carbamate, 1*:** The compound was prepared as reported previously.[3]

Synthesis of 2: Tert-butyl (2-azidoethyl) carbamate (**1**) (160 mg, 0.86 mmol) was dissolved in THF (1.0 mL) in a 10-mL round-bottom flask equipped with a magnetic stirrer bar. Into this solution, KI (572 mg, 3.44 mmol) and $Cu(ClO_4)_2 \cdot 6H_2O$ (640 mg, 1.73 mmol) were added, and the mixture was stirred for 3-5 min. DBU (130 mg, 0.86 mmol) was then added to this mixture and the mixture was stirred at r.t. for up to 6 hours. The mixture was then diluted with EtOAc (50 mL) and 28-30% aqueous NH_3 (25 mL) then transferred to a separating funnel. The organic layer was washed with saturated brine (2 × 25 mL), separated and dried over Na_2SO_4. The solvent was removed under reduced pressure to give a crude product. The crude product was purified by chromatography using 0-30% gradient of EtOAc-CH_2Cl_2 **(**57 mg; yield: 64%). ESI-MS $[\mathbf{2}+\mathbf{H}]^+$: calcd, m/z = 416.0505; found, m/z = 416.0658. ^{1}H-NMR (300 MHz, δ, ppm, DMSO-d_6): 8.68-8.66 (d, 1H); 8.02-8.00 (d, 1H); 7.93- 7.88 (m, 1H); 7.41-7.37 (m, 1H); 7.03-6.99 (m, 1H); 4.52-4.48 (t, 2H); 1.34 (s, 9H). ^{13}C-NMR (75 MHz, DMSO-d_6): δ= 156.1, 150.5, 149.5, 147.7, 137.6, 123.6, 121.7, 83.0, 78.5, 50.3, 40.4, 28.8 ppm.

Synthesis of 1-(Naphthynl)-3-(2-(4-(pyridin-2-yl)-1-Iodo-1,2,3-triazol-1-yl)ethyl)urea (L1): 160 mg (0.39 mmol) of tert-butyl (2-(4-(pyridin-2-yl)-1-Iodo-1,2,3-triazol-1-yl)ethyl) carbamate (**2**) was dissolved in 20 mL of DCM in a RB flux. An excess amount of CF_3COOH (1 mL) was dissolved in 10 mL of DCM and added drop wise via a pressure-equalizing funnel into the RB, kept at~0 °C. The reaction mixture was allowed to stir for 3-4 hours and then all the volatiles were removed under vacuum. After that, the reaction mixture was dissolved in dry DCM, and 514 μL dry Et_3N (3.9 mmol) was added to this mixture; this mixture was stirred for 10 min at room temperature. Finally, 56 μL naphthyl isocyanate (0.39 mmol) was dissolved in 10 mL dry

DCM and added drop wise to the reaction mixture kept at 0 °C *via* a pressure equalizing funnel. After 1 hour or so a precipitate appeared and the reaction mixture was stirred at RT for 6 hours. After that the solution was filtered and the precipitate was collected. The precipitate was washed several times with water and diethyl ether and dried overnight to yield the desired product **L1** as a light brown solid (170 mg, 89 % yield). Anal. calcd. for **L1**, $C_{20}H_{17}IN_6O$ (MW = 484.29) C, 49.60; H, 3.54; N, 17.35; found: C, 49.32; H, 3.47; N, 17.81%; ESI-MS [**L1+H**]+: calcd, m/z = 485.0587; found, m/z = 485.0308, [**L1+Na**]+: calcd, m/z = 507.0406; found, m/z = 507.0083. ^{1}H NMR (300 MHz, δ, ppm, DMSO-d_6): 8.67-8.66 (d, 1H); 8.56 (s, 1H); 8.04-8.00 (m, 2H); 7.92-7.85 (m, 3H); 7.57-7.36(m, 5H); 6.72-6.68(t, 1H), 4.62- 4.58(t, 2H), 3.70-3.69 (m, 2H). ^{13}C-NMR (75 MHz, DMSO-d_6): δ= 156.2, 150.5, 149.6, 147.9, 143.7, 137.6, 135.4, 134.2, 128.8, 126.4, 126.3, 126.0, 123.7, 123.0, 122.1, 121.8, 117.7, 83.3, 50.9, 39.7.

Synthesis of Complex 1[PF$_6$]$_2$: cis-[Ru(phen)$_2$Cl$_2$] was synthesized from reported procedure[4] and carried forward for the synthesis of the complex. **L1** (100 mg, 0.206 mmol) and cis-[Ru(phen)$_2$Cl$_2$] (108 mg, 0.206 mmol) were dissolved in 30mL of a well-degassed ethanol/water binary solvent mixture (2/1; v/v). The mixture was refluxed under argon atmosphere for 48 hours until the solution became dark red. After that the reaction mixture was cooled to room temperature and ethanol was evaporated. The solution of the crude complex in water was treated with excess KPF_6 salt dissolved in water. After addition, an orange-red precipitate was formed, which was filtered, washed with water, and dried under vacuum to give the desired complex 1[PF_6]$_2$ as an orange-red crystalline solid (196 mg, 78% yield). Anal calcd. for $C_{44}H_{33}F_{12}IN_{10}OP_2Ru$ (Mw = 1235.70) C, 42.77; H, 2.69; N, 11.34; Found: C, 42.42; H, 2.52; N, 11.07. FTIR in $CHCl_3$ (ν/cm^{-1}): 3311, 3055, 2925, 2961, 2857, 1544, 1505, 1411, 1258, 1229, 842, 779. ESI-MS $[C_{44}H_{33}F_6IN_{10}OPRu]^+$ calcd, m/z = 1091.0558; found. *m/z*= 1091.2587; ^{1}H NMR (300 MHz, δ, ppm, DMSO-d_6): δ= 8.76-8.59 (m, 7H), 8.32-8.27 (m, 5H), 8.17-8.11 (t,

1H), 7.97-7.82 (m, 5H), 7.72-7.67 (m, 1H), 7.61-7.57 (m,2H), 7.53-7.49 (m,2H), 7.41-7.17 (m, 5H), 6.87- 6.83 (t, 1H), 4.52-4.42 (m, 2H), 3.79-3.61 (m, 2H) ppm. ^{13}C-NMR (100 MHz, δ, ppm, DMSO-d_6): δ= 156.0, 152.7, 152.5, 152.4, 152.1, 150.5, 148.0, 147.5, 147.2, 147.0, 146.8, 138.0, 136.8, 136.7, 136.4, 136.2, 134.8, 133.7, 130.3, 130.2, 130.1, 128.1, 127.8, 127.7, 126.8, 126.1, 125.7, 125., 125.2, 118.4, 88.8, 52.6, 39.4 ppm.

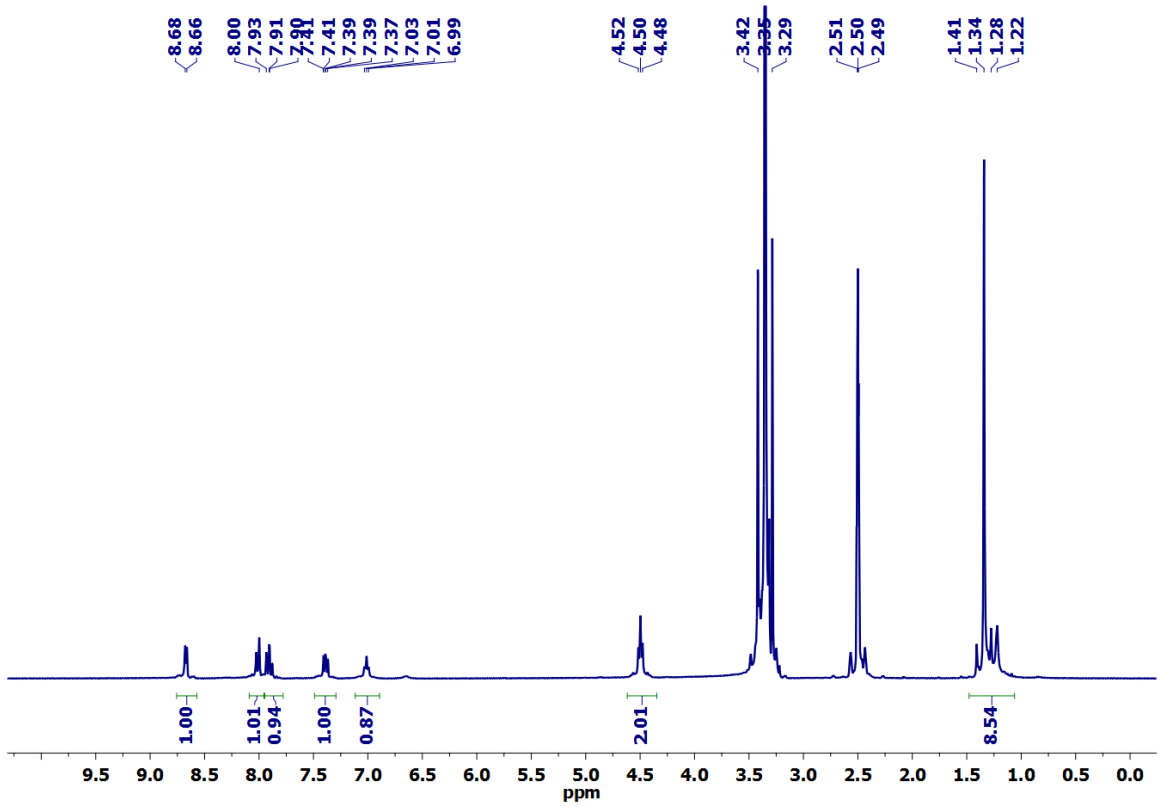

Fig. S1: ^{1}H-NMR spectrum of **2** in DMSO-d_6 at 298K in 300 MHz.

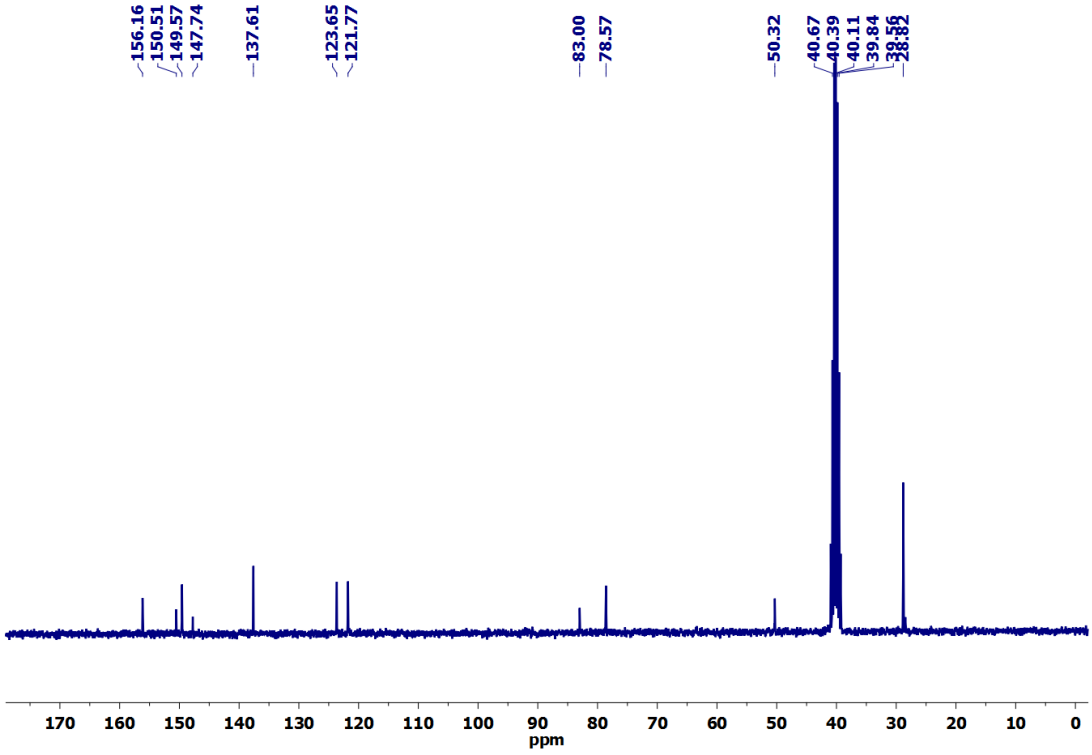

Fig. S2: ^{13}C-NMR spectrum of **2** in DMSO-d_6 at 298K in 75 MHz.

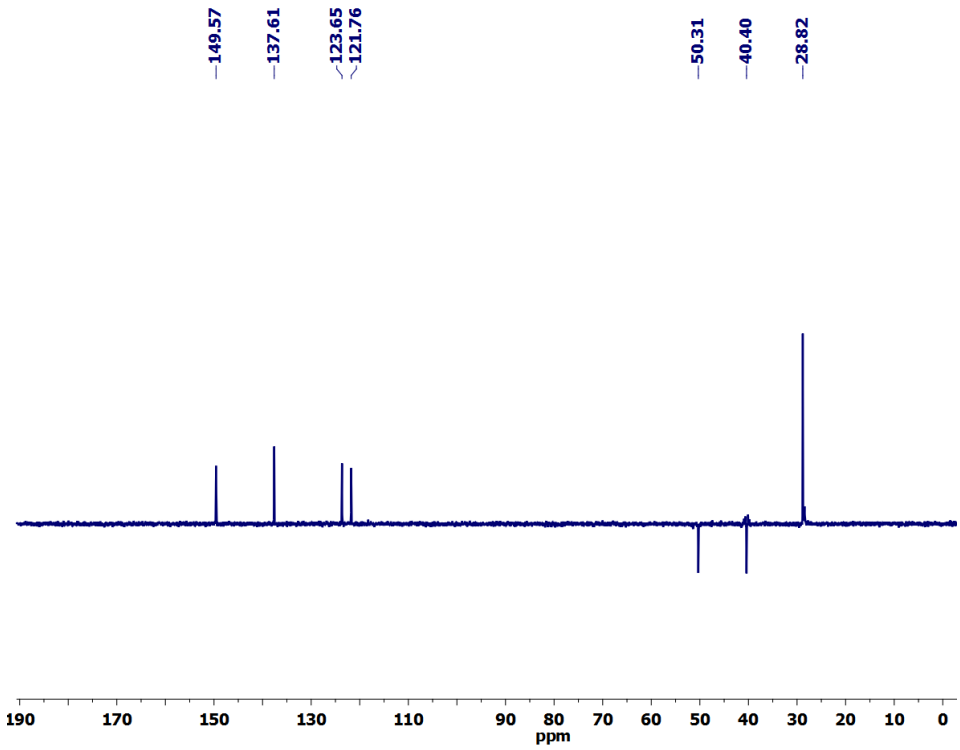

Fig. S3: ^{13}C-DEPT-135 spectrum of **2** in DMSO-d_6 at 298K in 75 MHz.

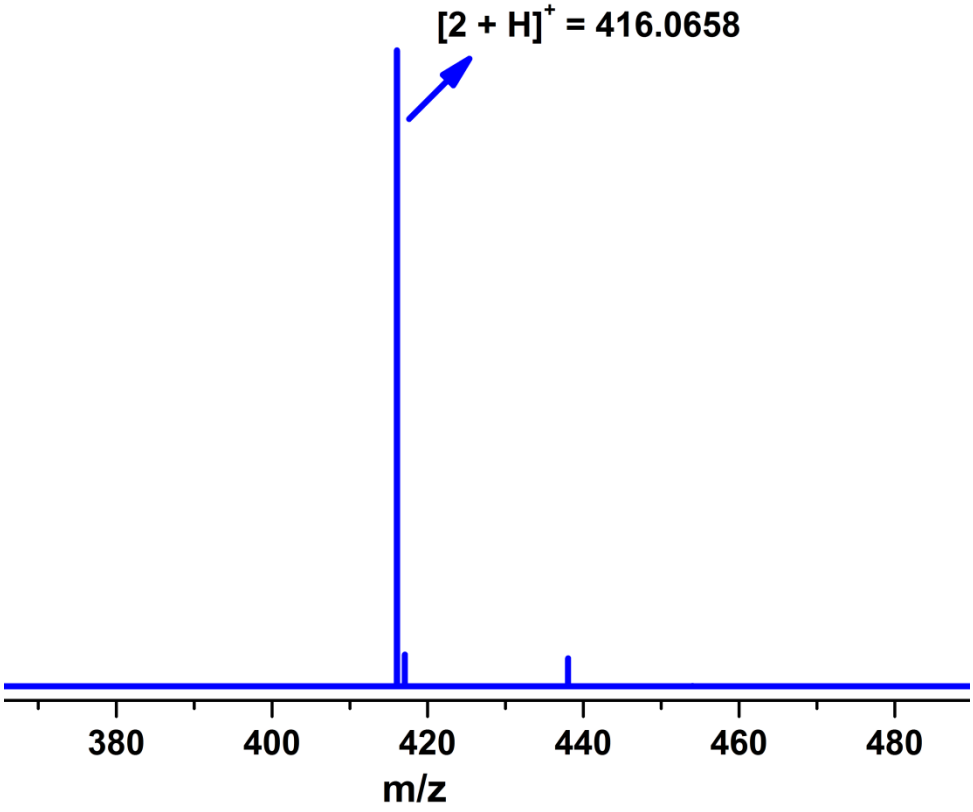

Fig. S3a: ESI-MS(+ve) spectrum of **2** at 298K.

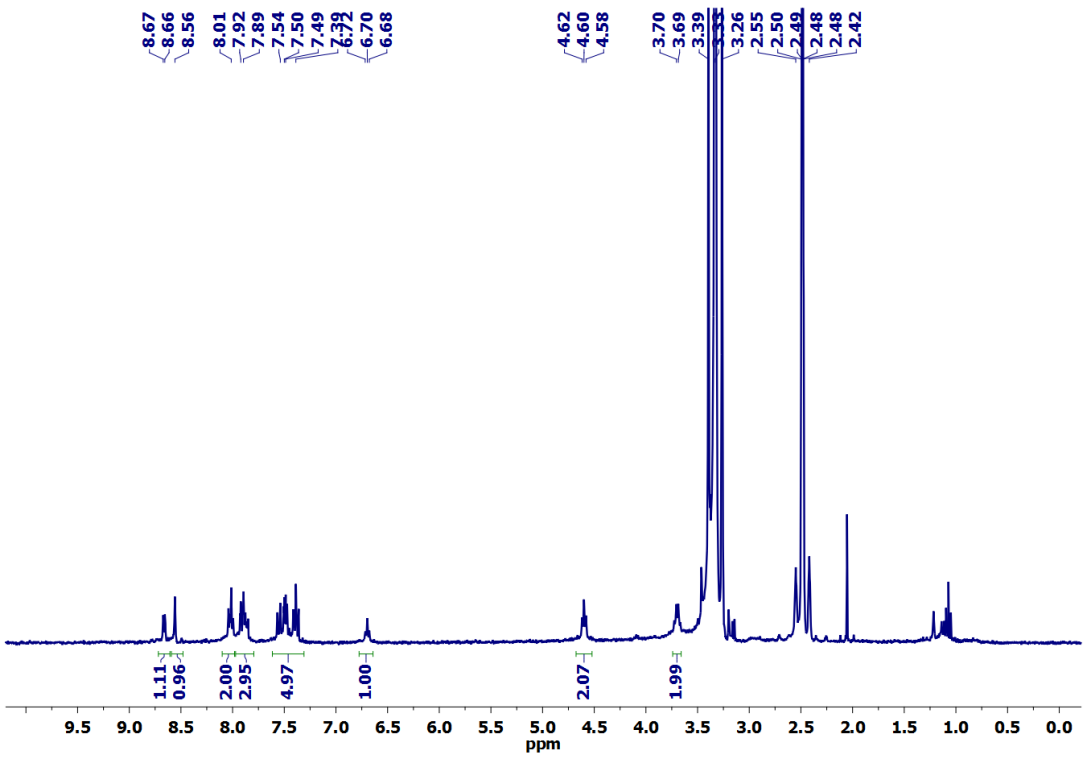

Fig. S4: ^{1}H-NMR spectrum of **L1** in DMSO-d_6 at 298K in 300 MHz.

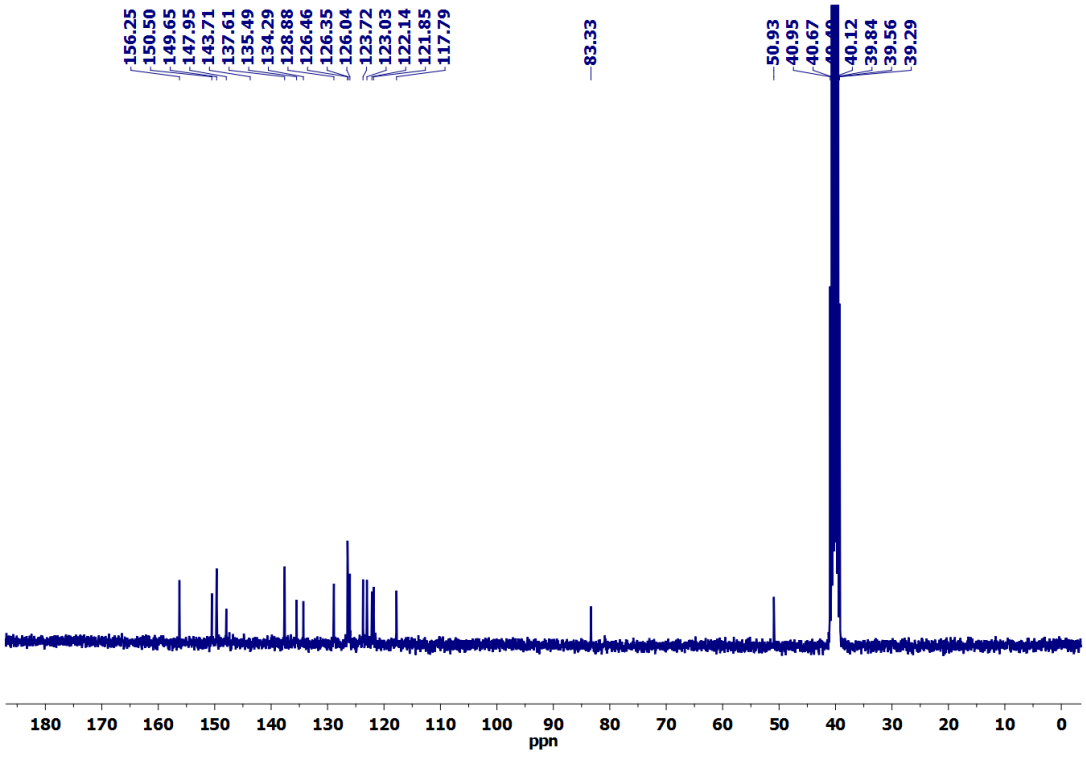

Fig. S5: ^{13}C-NMR spectrum of **L1** in DMSO-d_6 at 298K in 75 MHz.

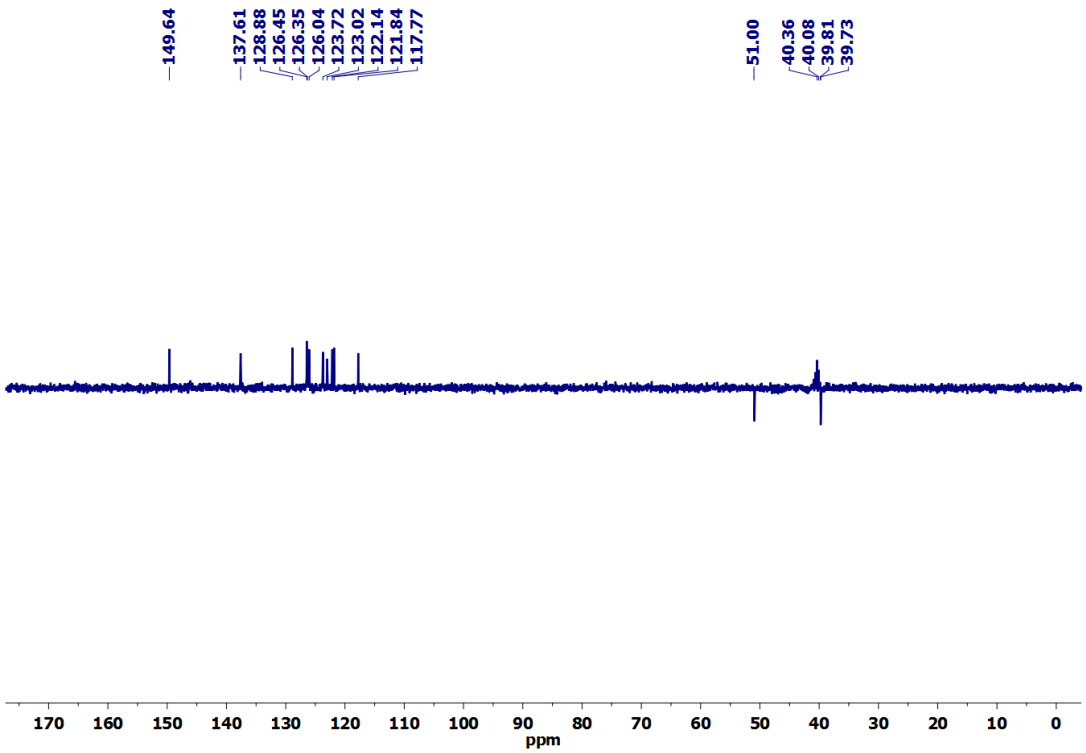

Fig. S6: ^{13}C-DEPT-135 spectrum of **L1** in DMSO-d_6 at 298K in 75 MHz.

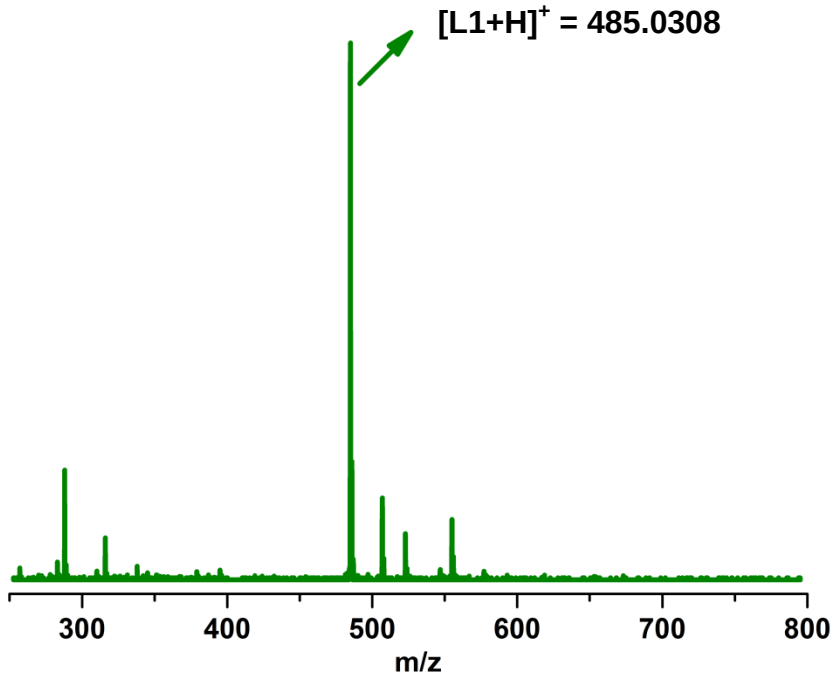

Fig. S7: ESI-MS(+ve) spectrum of **L1** at 298K.

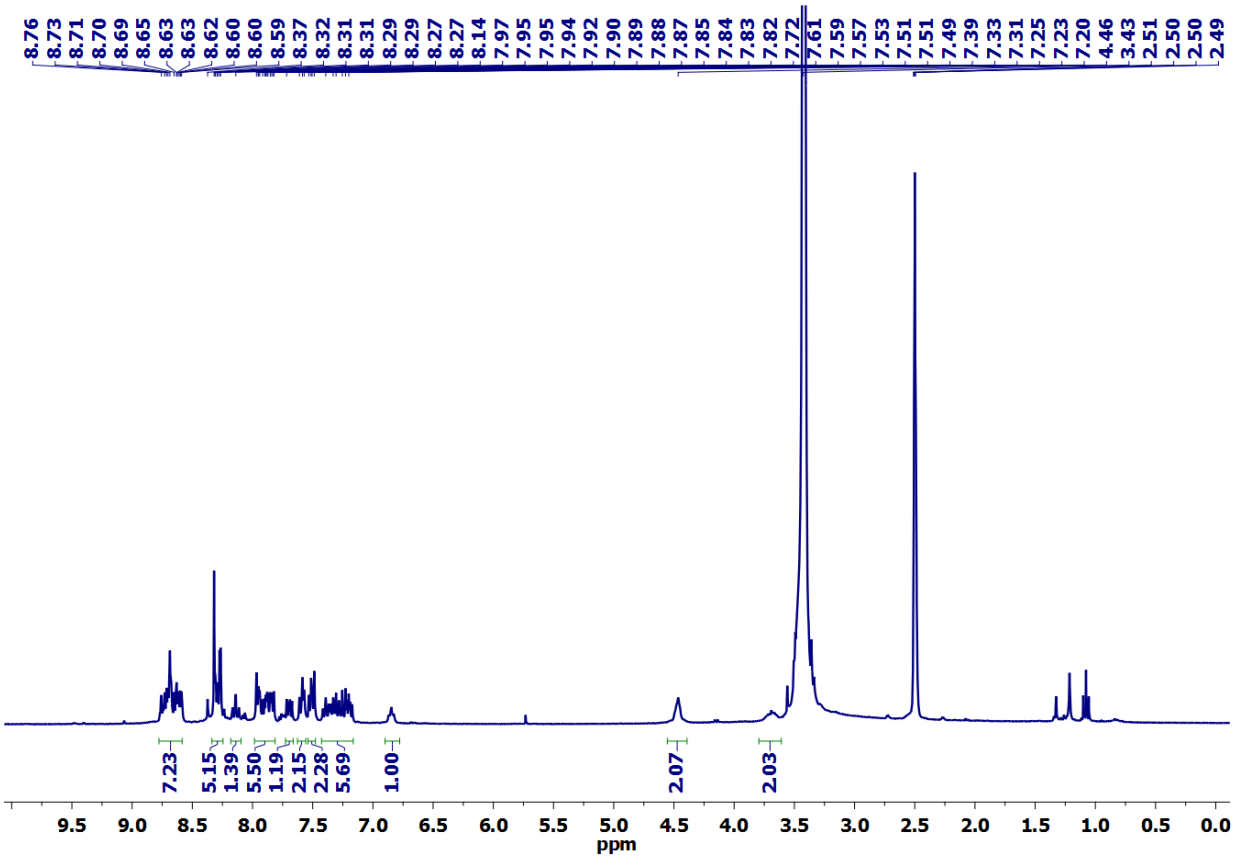

Fig. S8: ^{1}H-NMR spectrum of **1(PF$_6$)$_2$** in DMSO-d_6 at 298K in 300 MHz.

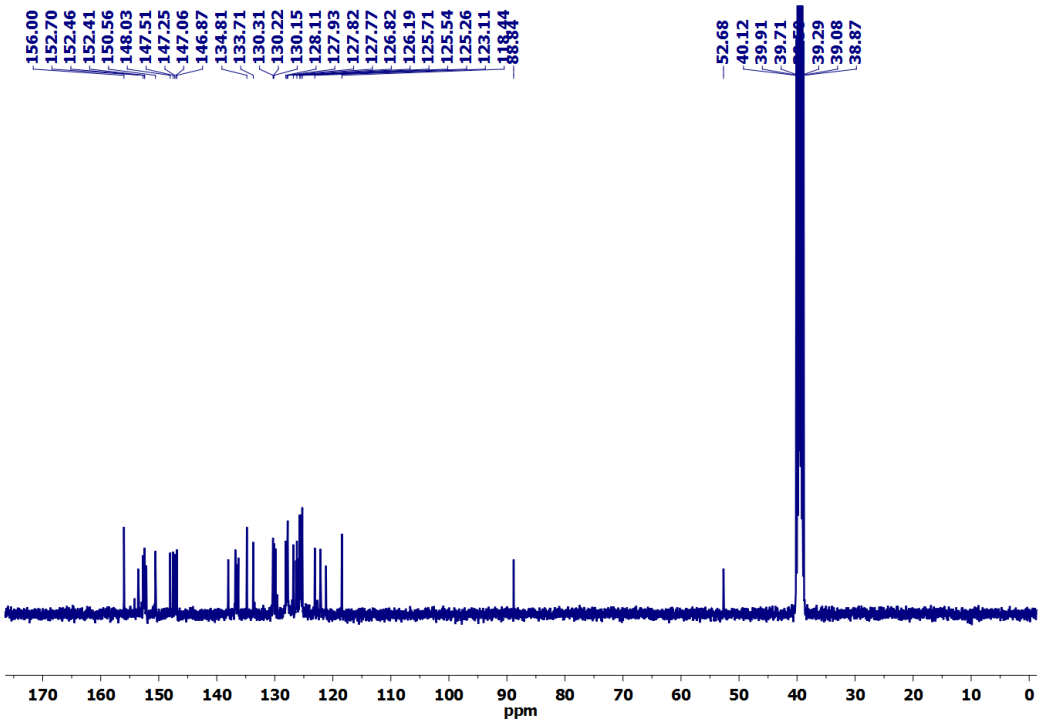

Fig. S9: ^{13}C-NMR spectrum of **1(PF$_6$)$_2$** in DMSO-d_6 at 298K in 100 MHz.

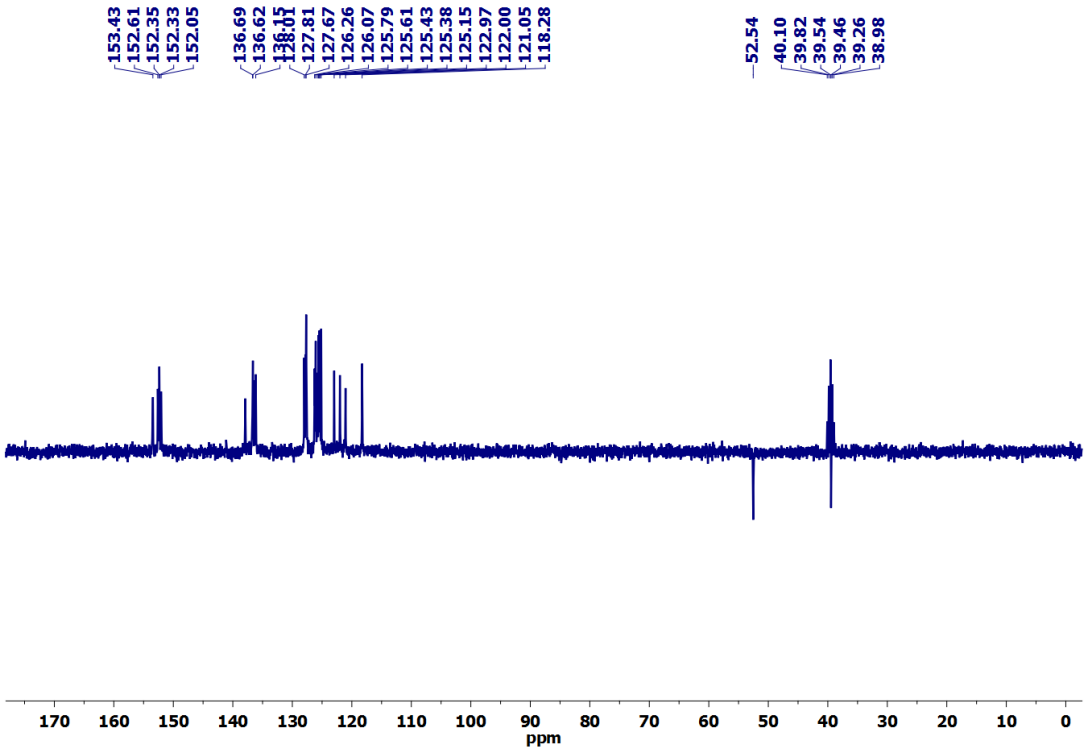

Fig. S10: ^{13}C-DEPT-135 spectrum of **1(PF$_6$)$_2$** in DMSO-d_6 at 298K in 75 MHz.

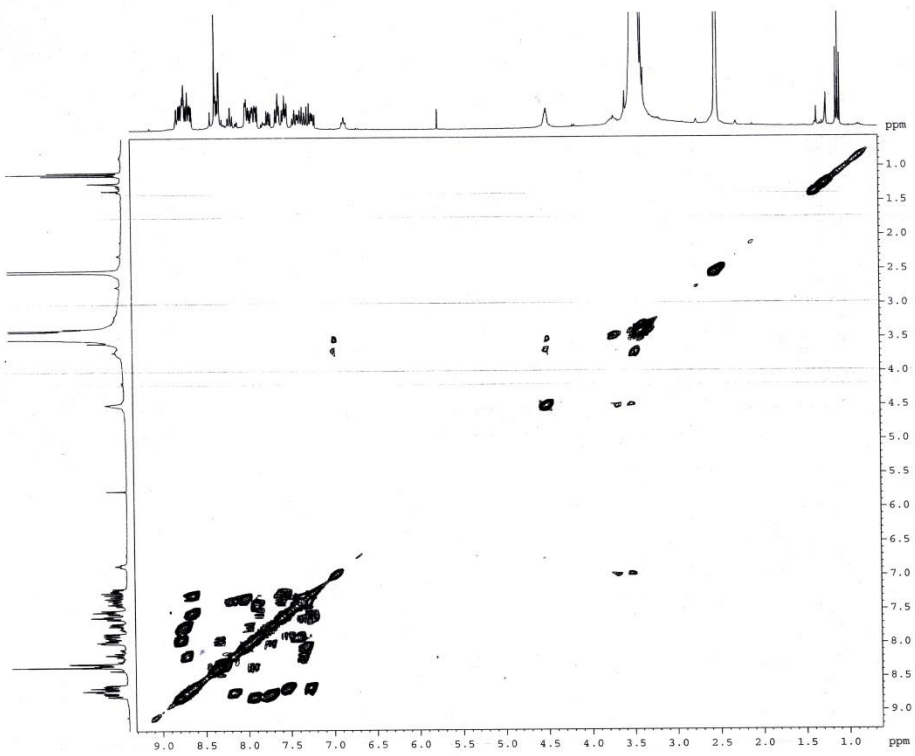

Fig. S11a: ^{1}H-^{1}H COSY-NMR spectrum of **1(PF$_6$)$_2$** in DMSO-d_6 at 298K in 75 MHz.

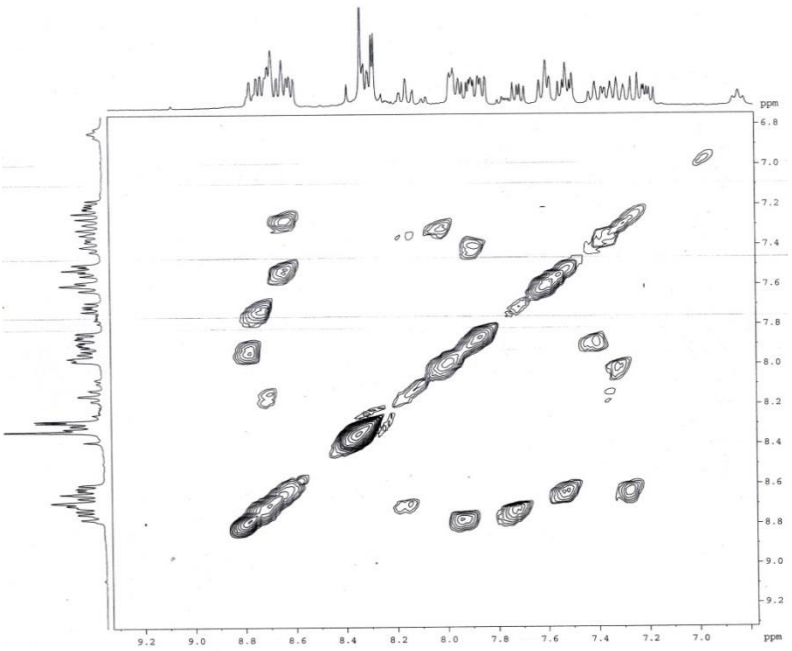

Fig. S11b: Expanded ^{1}H-^{1}H COSY-NMR spectrum of **1(PF$_6$)$_2$** in DMSO-d_6 at 298K in 75 MHz.

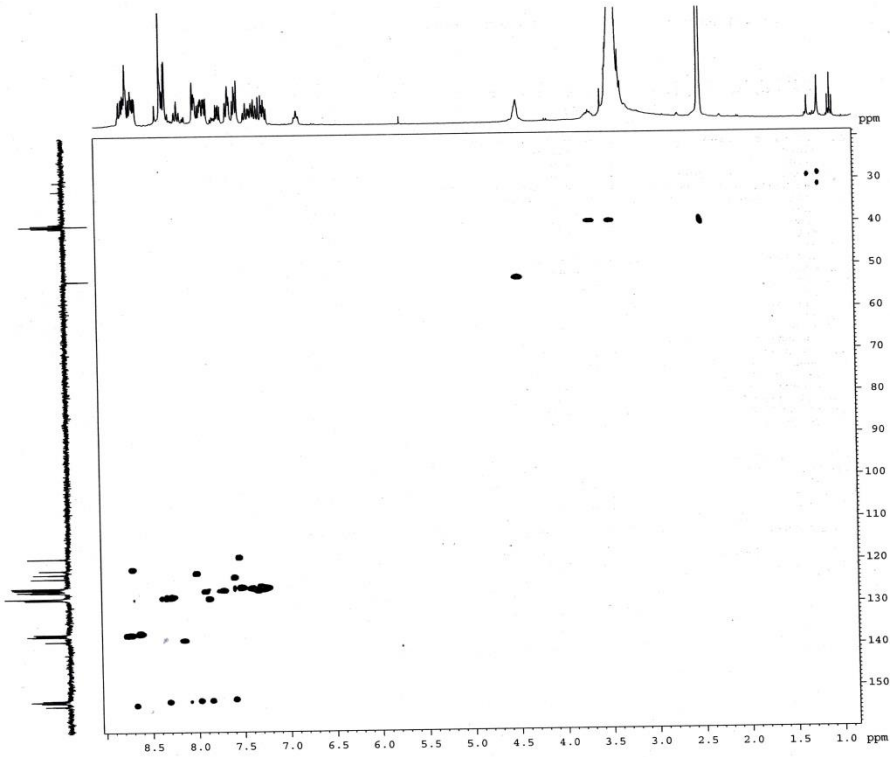

Fig. S12a: ^{1}H-^{13}C HSQC NMR spectrum of **1(PF$_6$)$_2$** in DMSO-d_6 at 298K in 75 MHz.

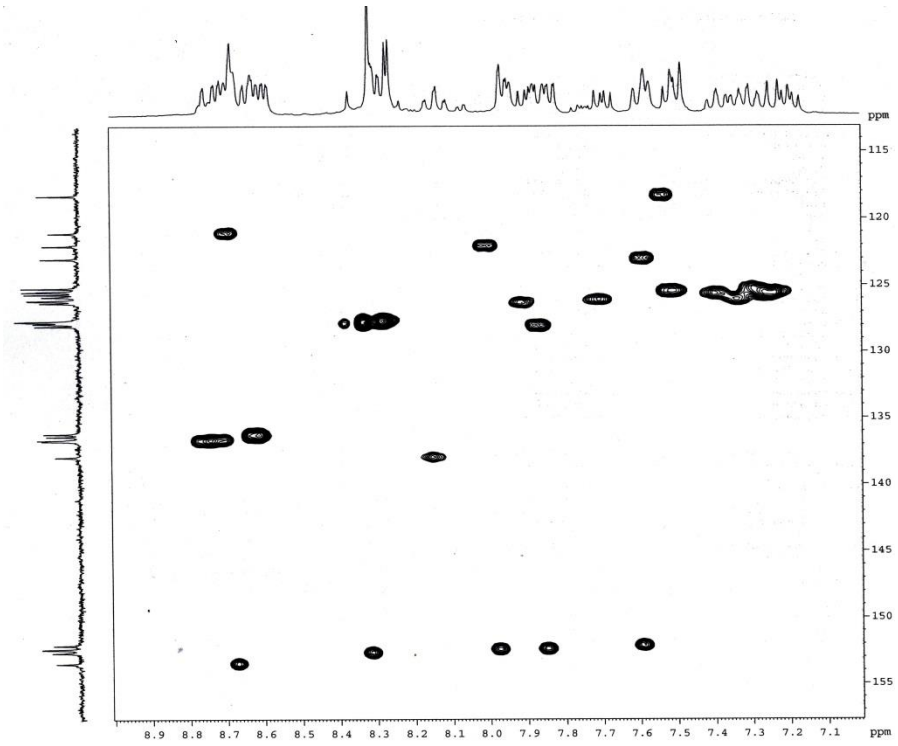

Fig. S12b: Expanded ^{1}H-^{13}C HSQC NMR spectrum of **1(PF$_6$)$_2$** in DMSO-d_6 at 298K in 75 MHz.

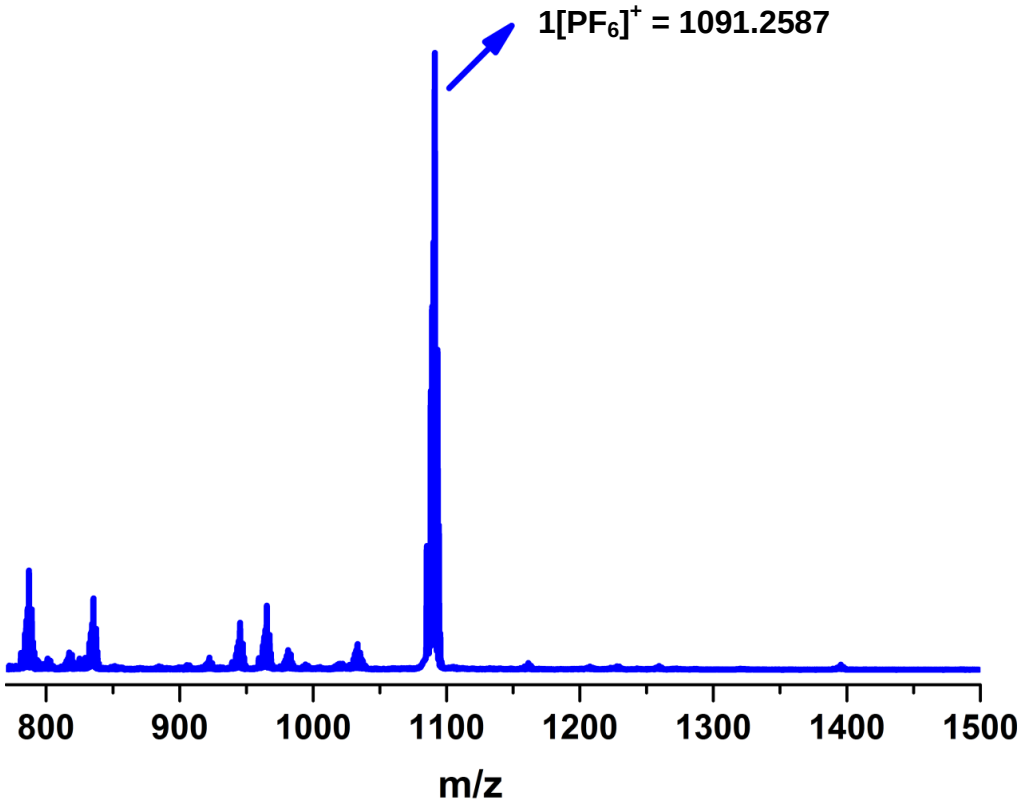

Fig. S13a: ESI-MS(+ve) spectrum of **1(PF$_6$)$_2$** at 298K.

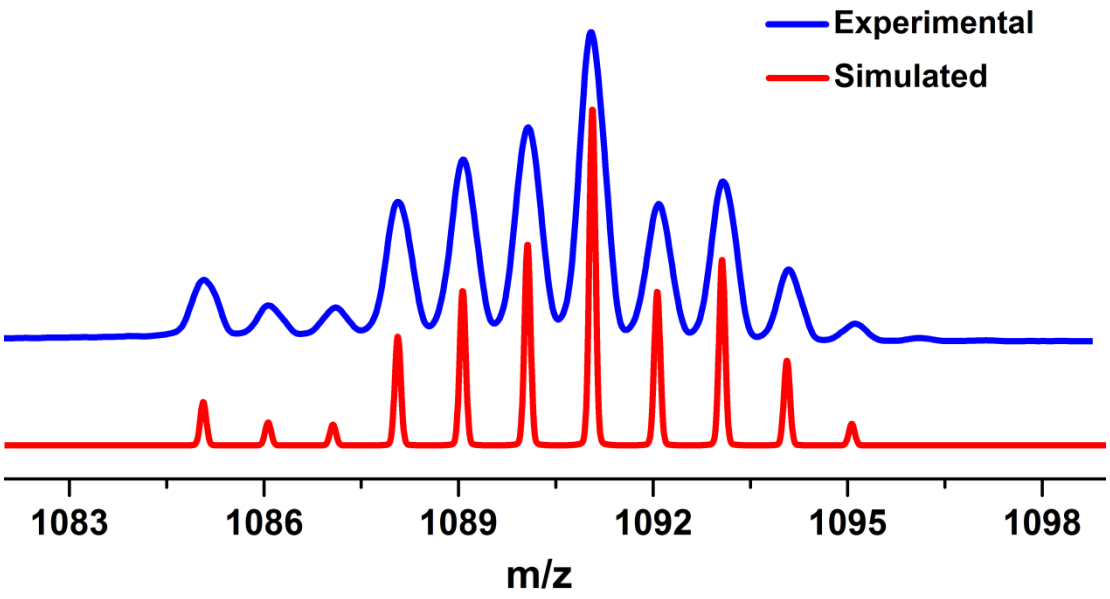

Fig. S13b: Isotopic distribution of mass spectrum of **1(PF$_6$)$_2$** at 298K.

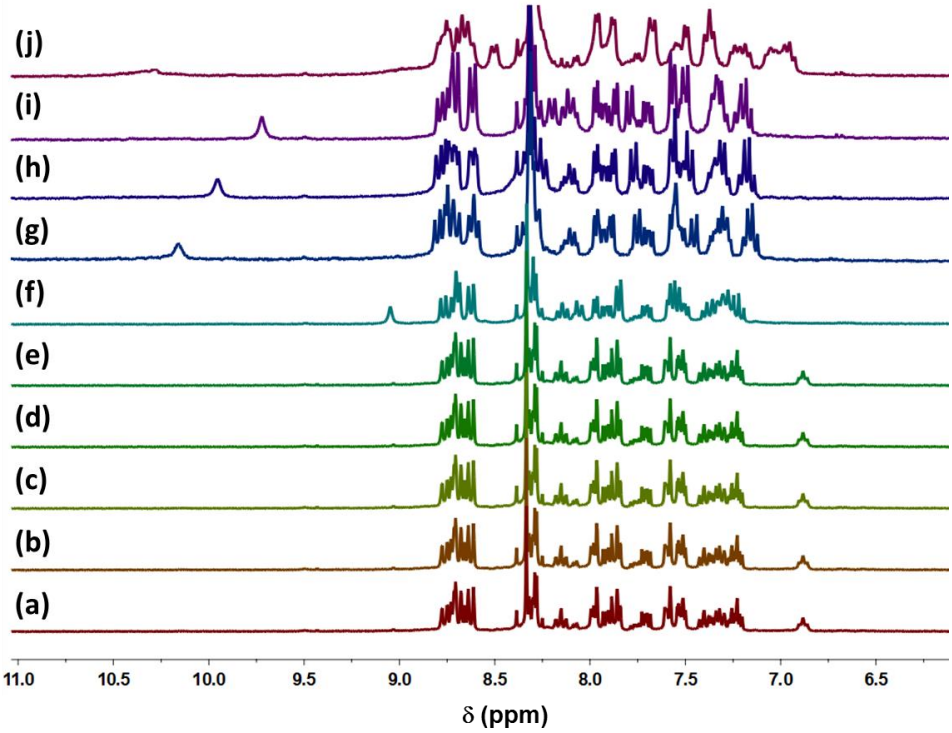

Fig. S14: Partial ^{1}H-NMR spectra of (a) complex **1(PF$_6$)$_2$** (6 x 10^{-3} M) and complex **1(PF$_6$)$_2$** with three equivalents of (b) $TBAClO_4$, (c) $TBANO_3$, (d) $TBAHSO_4$, (e) TBABr, (f) TBACl, (g) $TBAO_2CCH_3$ (h) $TBAH_2PO_4$, (i) $TBAO_2CPh$, (j) $(TBA)_3HP_2O_7$.

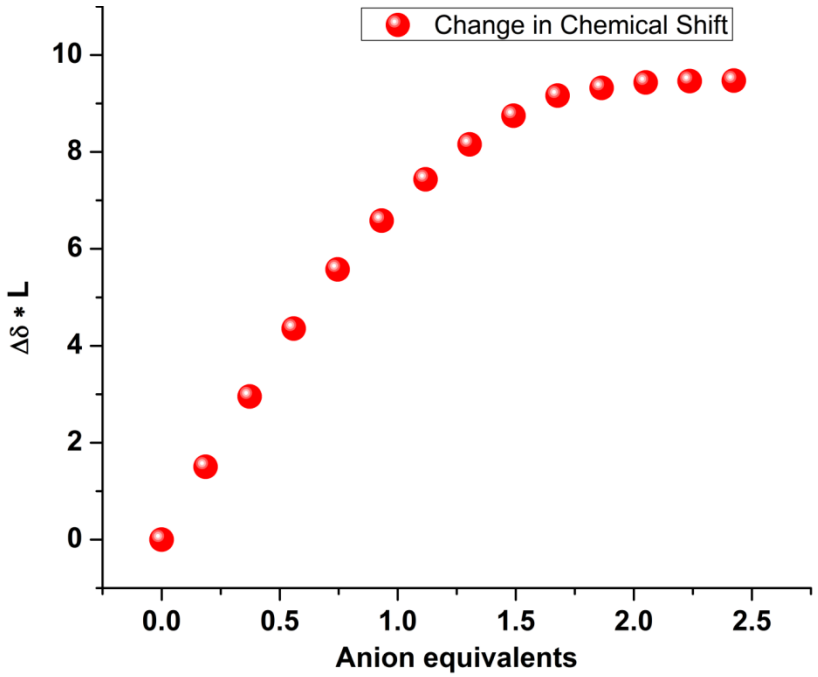

Fig. S15a: Plot of change in the chemical shift of the urea–NHa groups of complex **1(PF$_6$)$_2$** (4 x 10^{-3} M) with increasing amounts of **TBAH$_2$PO$_4$** (6.2 x 10^{-2} M) in DMSO- d_6 at 298K.

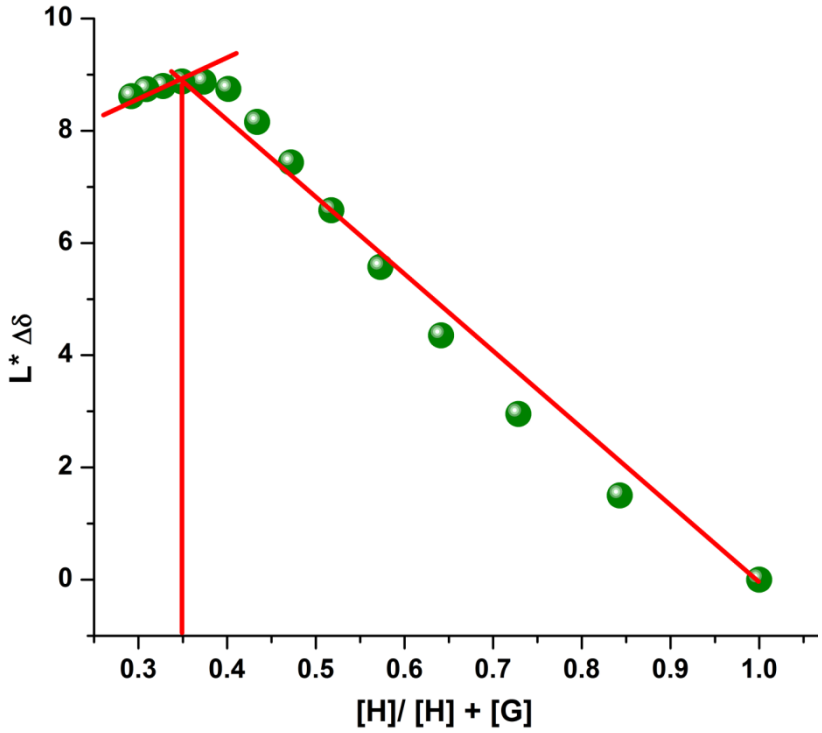

Fig. S15b: Molar ratio plot of titration between complex **1(PF$_6$)$_2$** with **TBAH$_2$PO$_4$** obtained by monitoring the shift in resonance position of urea–NHa proton in DMSO- d_6 at 298K.

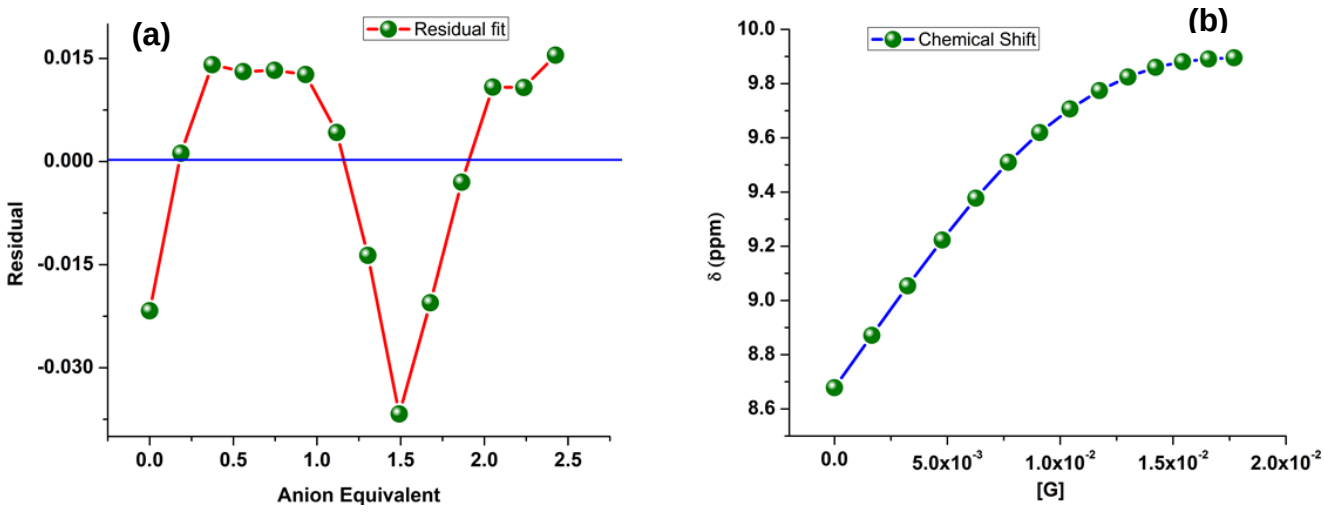

Fig. S16: (a) Residual fit plot and (b) non-linear curve fitting for titration of **$1(PF_6)_2$** with **$TBAH_2PO_4$** in DMSO- d_6 at 298K.

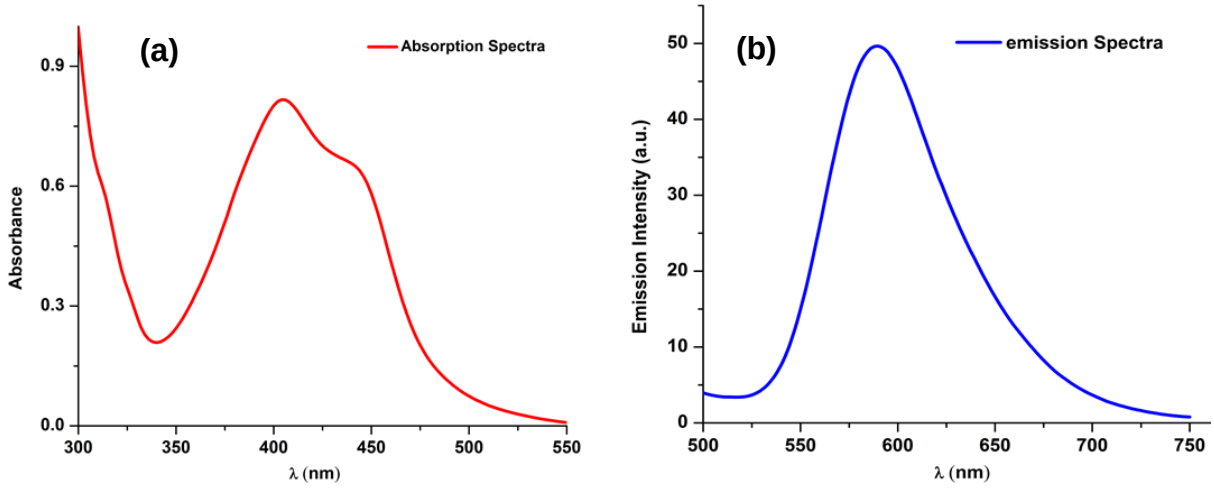

Fig. S17: (a) UV-Vis and (b) PL spectra of **$1(PF_6)_2$** in acetonitrile.

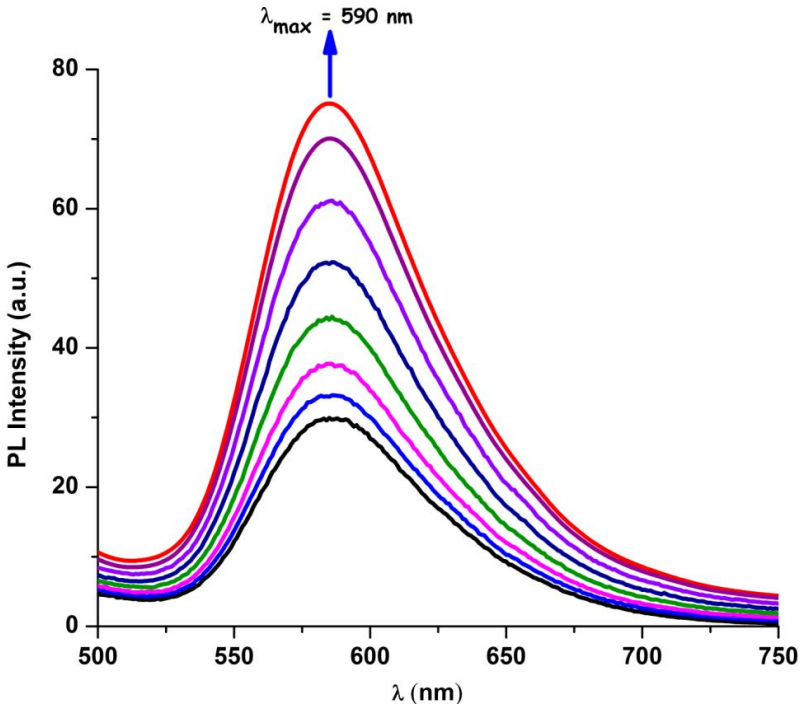

Fig. S18: PL titration profile of **1(PF$_6$)$_2$** (2 x 10^{-5} M) upon addition of **HP$_2$O$_7$** $^{3-}$ (7.5 x 10^{-4} M) in CH_3CN.

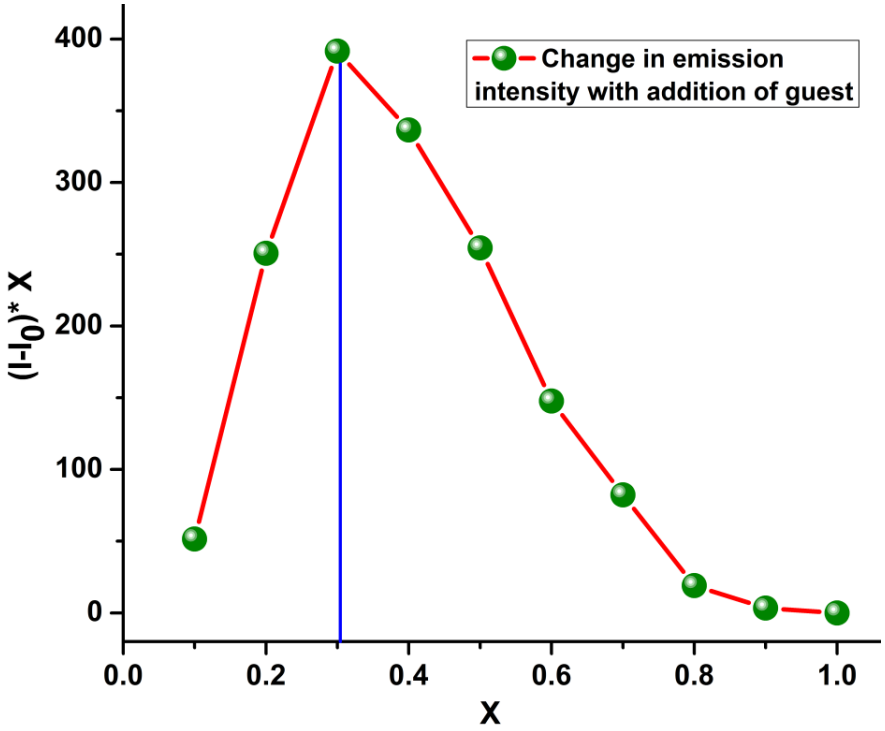

Fig. S19: Molar ratio plot from PL titration in CH_3CN between **1(PF$_6$)$_2$** and **H$_2$PO$_4$** $^{-}$.

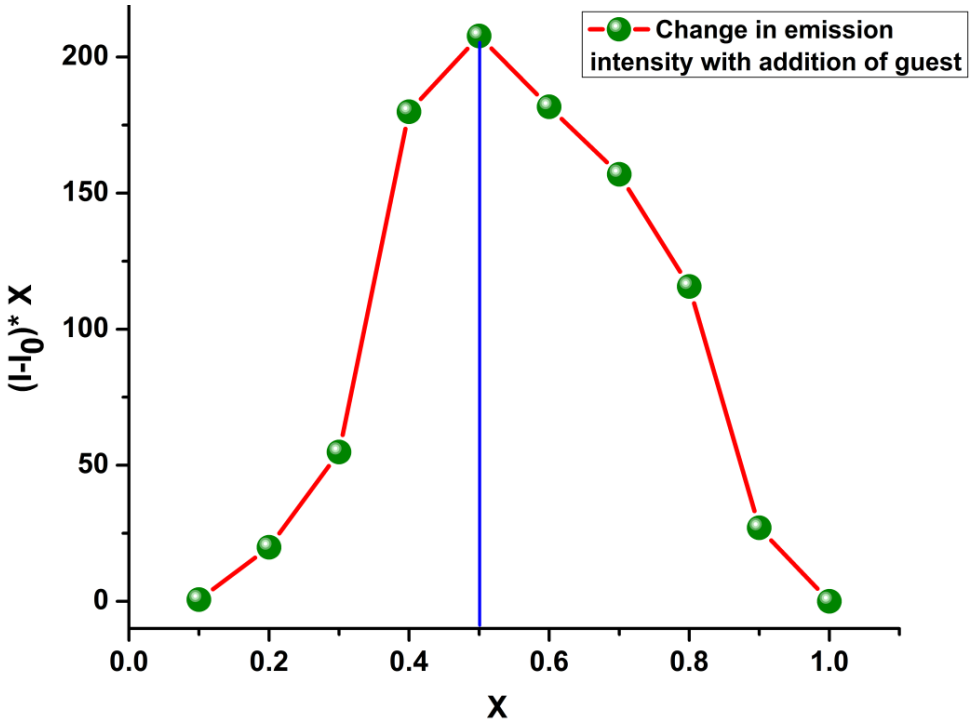

Fig. S20: Molar ratio plot from PL titration in CH_3CN between **1(PF$_6$)$_2$** and **HP$_2$O$_7$ $^{3-}$.**

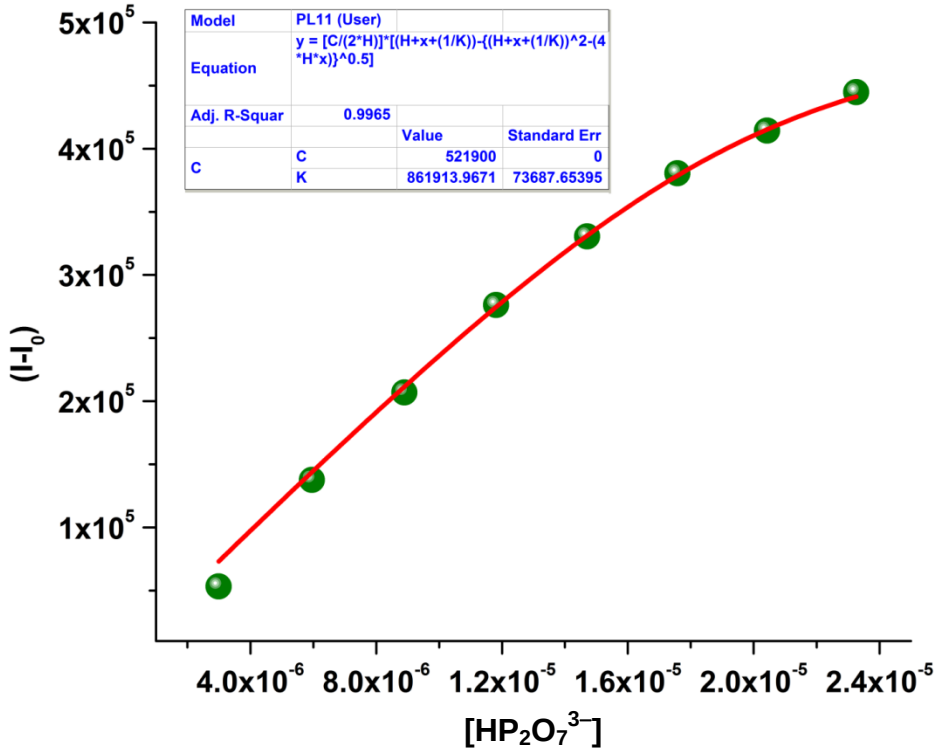

Fig. S21: Non-linear 1:1 curve fitting of PL titration data in CH_3CN at 298K to calculate association constant of **1(PF$_6$)$_2$** with **(TBA)$_3$HP$_2$O$_7$**.

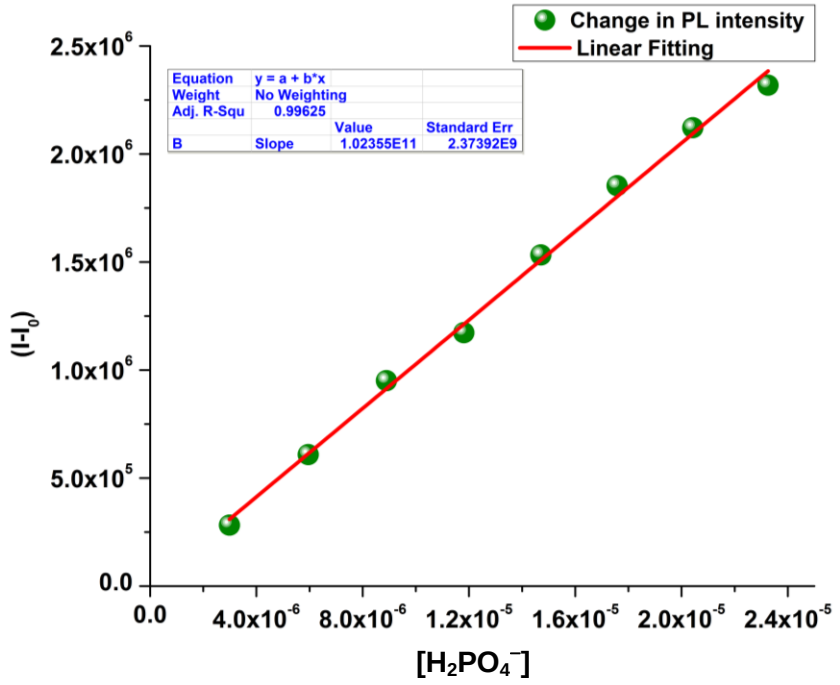

Fig. S22: Calibration curve from PL titration for **1(PF$_6$)$_2$** (10.0 μM) with **H$_2$PO$_4^-$** over the concentration range between 2.0 and 24.0 μM.

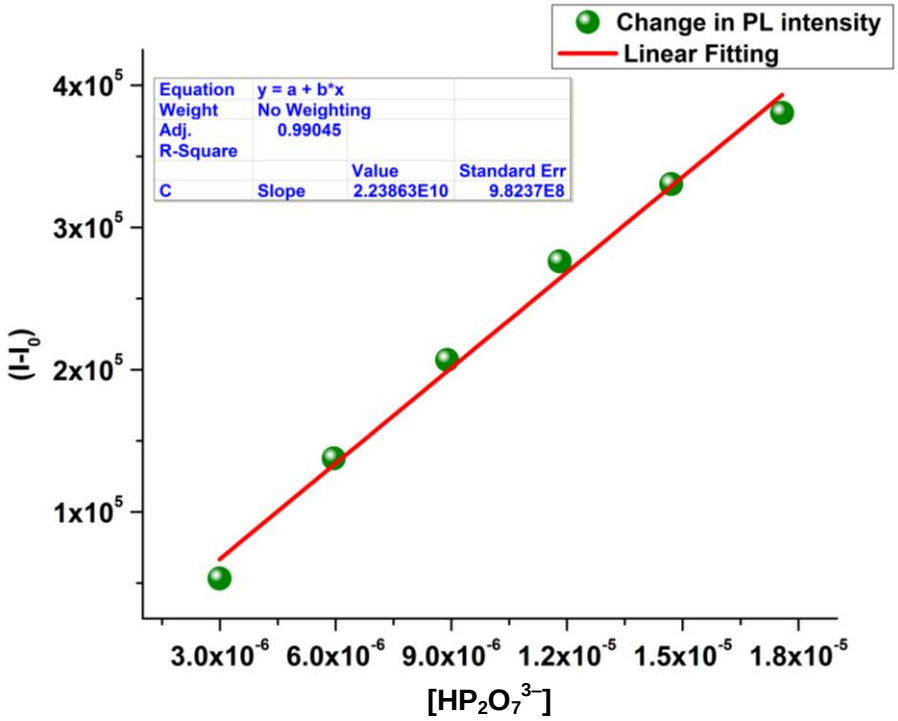

Fig. S23: Calibration curve from PL titration for **1(PF$_6$)$_2$** (10.0 μM) with **HP$_2$O$_7^{3-}$** over the concentration range between 3.0 and 18.0 μM.

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