Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Au Micro Particles Mediated Construction of Logic Based Dual Channel Molecular Keypad Lock

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General Information

Melamine, pyrene-1-carboxyldehyde and gold chloride were purchased from Sigma Aldrich and sodium borohydride, ascorbic acid and absolute alcohol were purchased from Merck and were used without further purification. All the fluorescence spectra were recorded on Agilent Technologies Cary Eclipse fluorescence spectrometer. UV-Vis spectra were recorded on Shimadzu UV-2450 spectrophotometer and FT-IR spectra were recorded on PerkinElmer FT-IR spectrometer (Spectrum Two, Serial No:88689). ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance II 400 NMR spectrometer using $CDCl_3$, DMSO and TMS as internal standards. Data are recorded as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d= doublet, br = broad singlet, m = multiplet), coupling constant, *J* (Hz) integration, and interpretation. High resolution transmission electron microscopy characterization has been done by SEI TECNAI F 20 HRTEM 200KV. The particle size (z-average diameter, d.nm) was measured using DLS (Dynamic Light Scattering) method (Zetasizer Nano ZS, Malvern Instrument Ltd., UK) at 25°C. All solution of compound **3** and reagents were prepared in Ethanol:H_2O (95:5) HEPES pH=7.0.

Preparation of HEPES Solution of pH = 7.

To prepare 1 L HEPES buffer of 7.0 pH add 11.92 g of HEPES, 11.0 ml of 1M NaOH and 89.0 ml of 1 M NaCl and dilute it to 1L by adding distilled water. [R1]

***R1- Buffers for pH and Metal Ion Control*, D. Perrin, B. Dernpsey, John Wiley and Sons, New York, 1974.**

Preparation of samples for TEM Samples Ligand **3** (0.003 g, 0.1 mmol) was dissolved in 5 ml of ethanol:H_2O. The solution was diluted 100 times to prepare solution of 0.001 mmol conc. To 3 ml of the prepared diluted solution of ligand **3**, 0.36 ml of 0.01 mmol solution of $AuCl_3$ in 1 ml of ethanol:H_2O was added. On addition of $AuCl_3$ solution, the colour changed from colourless to yellow. To the resultant solution, 0.14 ml of 0.1 mmol of ascorbic acid in ethanol:H_2O was added. Drops of all these solution of ligand **3**, **3**+ $AuCl_3$, **3**+ $AuCl_3$ + Ascorbic Acid and **3**+ Ascorbic Acid + $AuCl_3$ one by one were placed directly on the lacey carbon coated Cu grid using micropipette. The AuMPs present in the aqueous mixture were allowed to settle, and the extra solvent was subsequently removed by placing a TEM grid on a neat filter paper and dried at room temperature for half an hour. The morphology, size and shape distribution of AuMPs were recorded.

Experimental

Synthesis of N^2, N^4, N^6-tris((pyren-1-yl)methyl)-1,3,5-triazine-2,4,6-triamine ***(3)***

Melamine (0.03 g, 0.25 mmol) and pyrene-1-carboxaldehyde (0.20 g, 0.75 mmol) were refluxed in THF:MeOH for 6 h. The reaction mixture was cooled and sodium borohydride (0.27 g, 6.50 mmol) was added at 0^oC .The reaction mixture was again kept at constant stirring for 6 h at room temperature. After completion of reaction (*as monitored by TLC*), the solvent was removed under vacuum. The resulting crude was dissolved in minimum amount of water and pH was adjusted between 5-7 using dilute HCl. A yellow precipitates was formed which was filtered, dried under vacuum and was re-crystallized from ethanol: hexane (*1:2 v/v*) to give fine needle like yellow crystals of **3**. Yield (0.150 g, 82 %), m.p. 92 ^oC. IR (KBr) ν_{max} = 3302 cm^{-1} (-NH): ^1H NMR (400 MHz, $DMSO_{d6}$): δ = 3.37 (H_2O), 5.25 (d, 6H, *J* = 4.72, CH_2), 5.53 (t, 3H, *J* = 5.18, NH), 8.05-8.40 [(m, 27H, ArH (Pyrene)]; ^{13}C NMR (100 MHz, DMSO): 58.6 (NCH_2), 117.8 (ArC), 119.5 (ArC), 119.7 (ArC), 120.1 (ArC), 120.1 (ArC), 120.8 (ArC), 120.9 (ArC), 122.2 (ArC), 122.3 (ArC), 122.8 (ArC), 123.6 (ArC), 125.5 (ArC), 126.1 (ArC), 128.5 (ArC); MS-m/z 822 (**3**.3H_2O) $(M)^+$; Anal. Calcd for $C_{54}H_{42}N_6O_3$: C, 78.81; H, 5.14.; N, 10.21; Found: C, 78.53; H, 5.07; N, 10.03.

Synthesis of Au Micro particles.

To 3 ml solution of ligand **3** (1 X 10^{-3} mmol) in ethanol:H_2O, 0.36 ml solution of $AuCl_3$ (1 X 10^{-2} mmol) in ethanol:H_2O was added. After completion of addition, the colour of solution changed from colourless to yellow indicating the formation of **3.**Au^{3+} complex. To the resultant solution, we added 0.14 ml ascorbic acid ((1 X 10^{-2} mmol) in ethanol:H_2O. The colour of the solution turned black. This solution was analyzed for Au micro particles using TEM analysis.

Synthesis of 3. Au^{3+} complex.

Ligand **3** (0.08 g, 0.1 mmol) was dissolved in 5 ml of ethanol. To this solution, $AuCl_3$ (0.036 g, 0.12 mmol) in 2 ml ethanol was added drop wise. The yellow solution of ligand **3** changed to brownish colour on addition of $AuCl_3$ solution. After one hour brownish yellow precipitates were formed which were filtered and dried under vacuum to obtain **3.**Au^{3+} complex in 59 % Yield (0.09 g); m.p. 200 ^{o}C. MS-*m/z* 1015.7028 [ligand **3** (-3H of NH)**.** Au^{3+}**.** $3H_2O$]; ^{1}H NMR (400 MHz, $dmso_{d6}$): δ = 3.55 (H_2O), 5.25 (s, 6H, CH_2), 8.05-8.40 {(m, 27H, ArH (Pyrene)}; Anal. Calcd for $C_{54}H_{39}AuN_6O_3$: C, 63.78; H, 3.87.; N, 8.26; Found: C, 63.33; H, 3.57; N, 8.09.

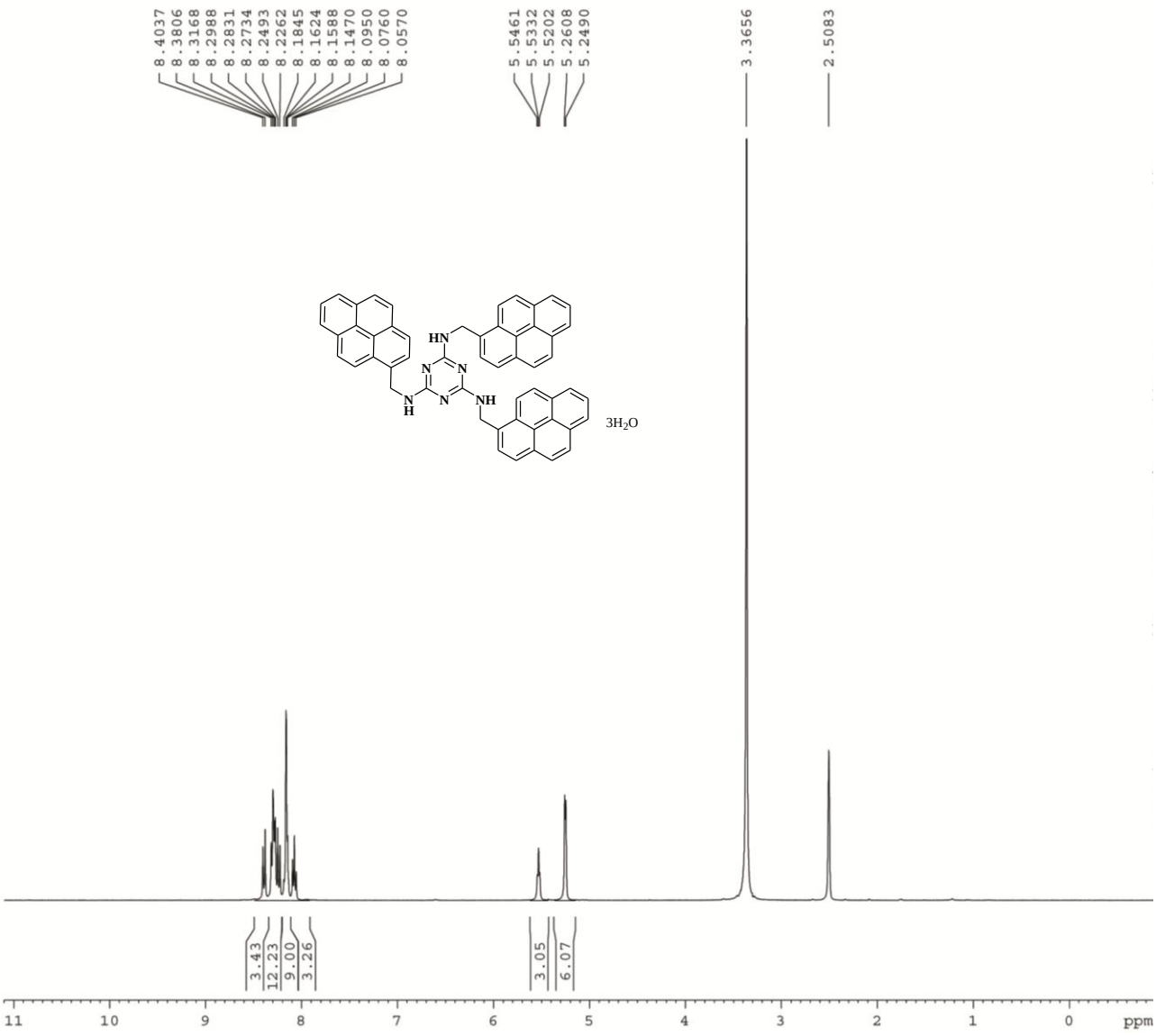
Fluorescence quantum yield

The fluorescence quantum yields for compounds **3** and **2** were determined at room temperature in analytical grade ethanol:HEPES (95:5) (pH= 7.0) using optically matching solution of pyrene (ϕ_R) = 0.65 in ethanol as a standard at an excitation wave length of 342 nm from xenon lamp of the spectrophotometer (Agilent Technologies Cary Eclipse fluorescence spectrometer). The quantum yield were calculate by using equation 1, in which (ϕ_S) is the radiative quantum yield of samples, (ϕ_R) is the radiative quantum yield of reference, $\mathbf{A_S}$ and $\mathbf{A_R}$ are the absorbance of the sample and the reference, respectively, $\mathbf{D_S}$ and $\mathbf{D_R}$ the areas of emission for the sample and reference, $\mathbf{N_S}$ and $\mathbf{N_R}$ are the refractive index of sample and reference solutions respectively, $\mathbf{L_S}$ and $\mathbf{L_R}$ are path length of sample and reference solutions (pure solvent were assumed).

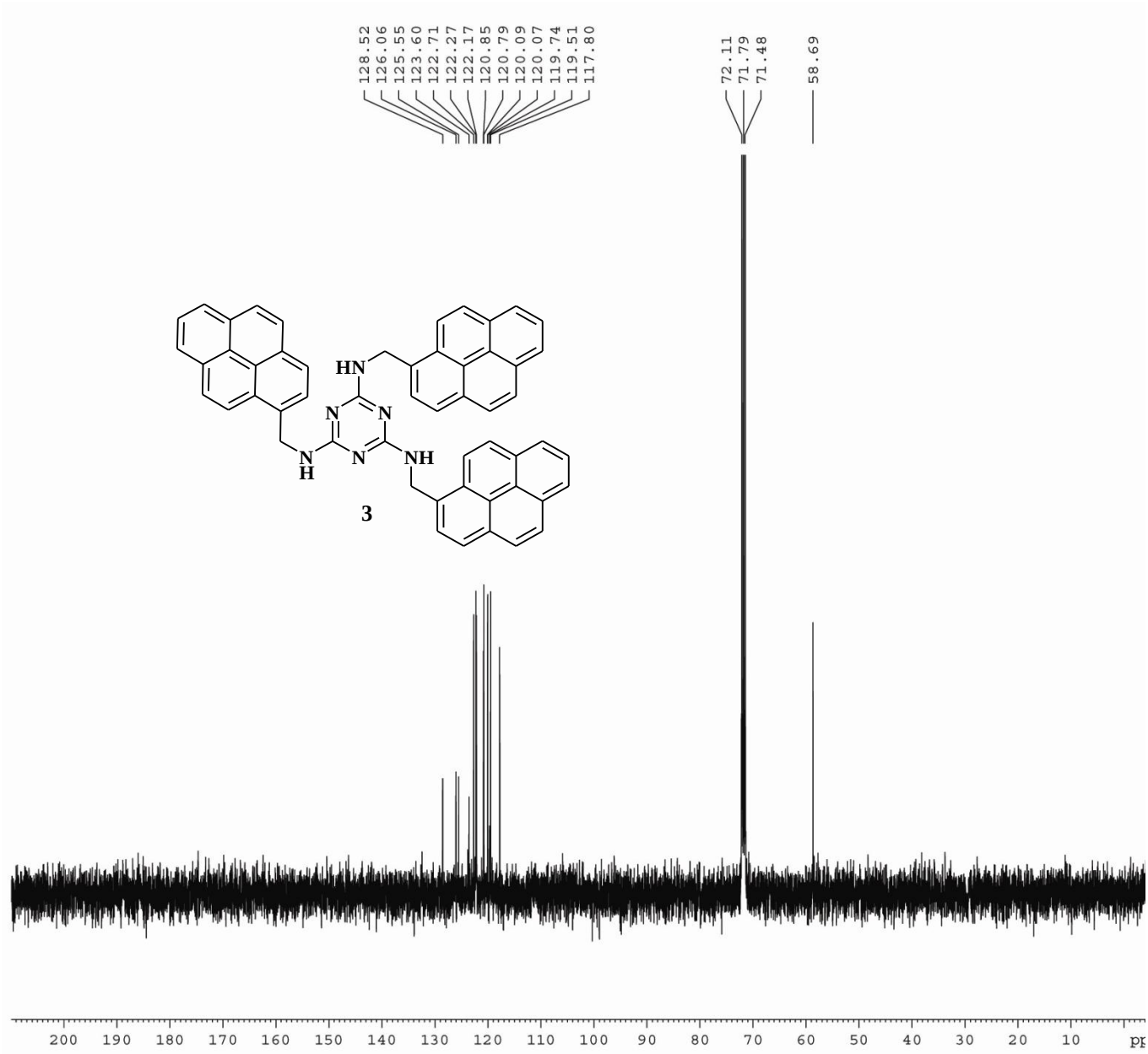
Equation

$$\emptyset_s = \emptyset R \times \frac{1-10^{A_R.L_R}}{1-10^{A_S.L_S}} \times \left(\frac{N_S}{N_R}\right)^2 \times \frac{D_S}{D_R}$$

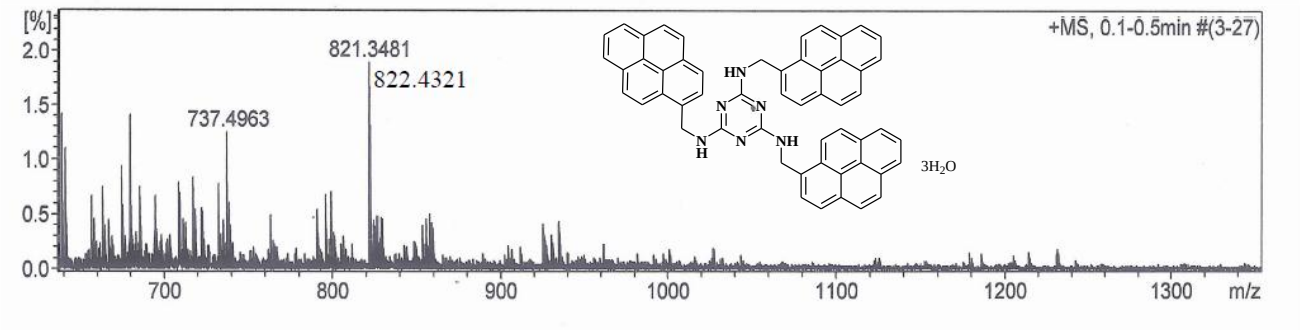
^{1}H NMR Spectrum of 3 in DMSO



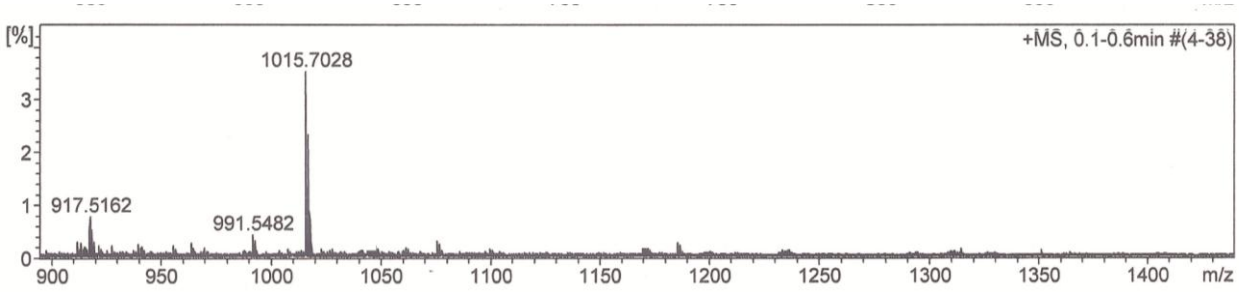
^{13}C NMR Spectrum of 3 in DMSO



Mass Spectrum of Compound 3



Mass spectrum of 3 + Au^{3+} ions



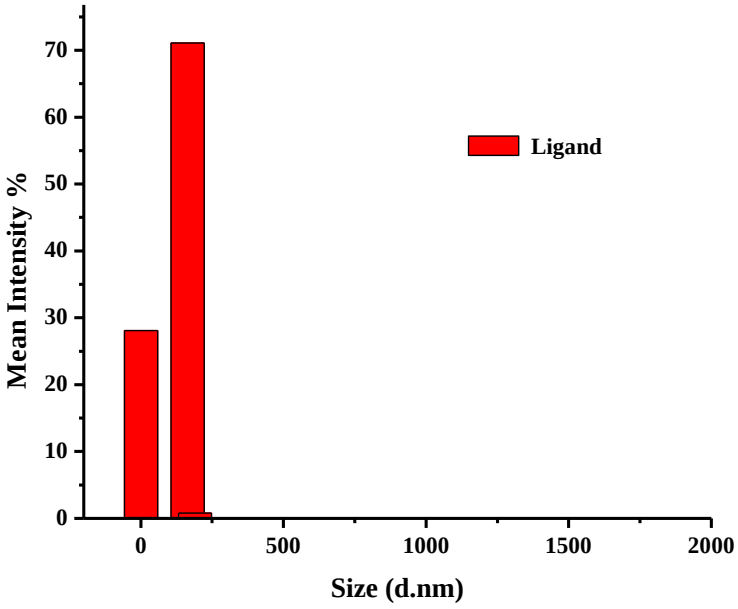


Figure S6. DLS data of ligand **3**.

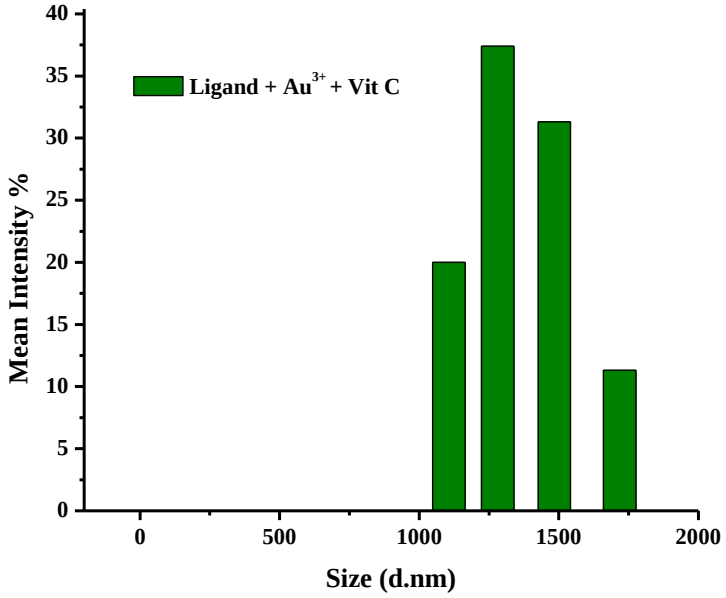


Figure S7. DLS data of **3** +Au^{3+} + Ascorbic Acid**.**

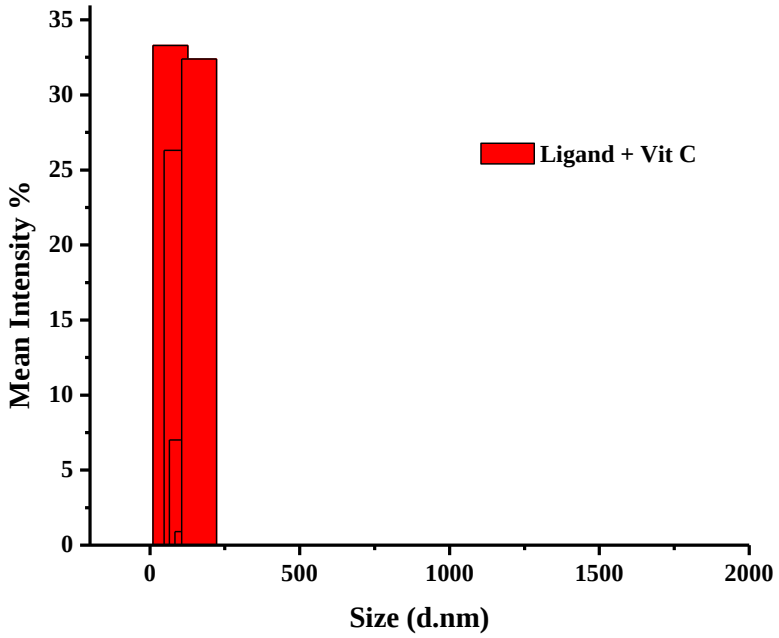


Figure S8. DLS data of **3** + Ascorbic Acid

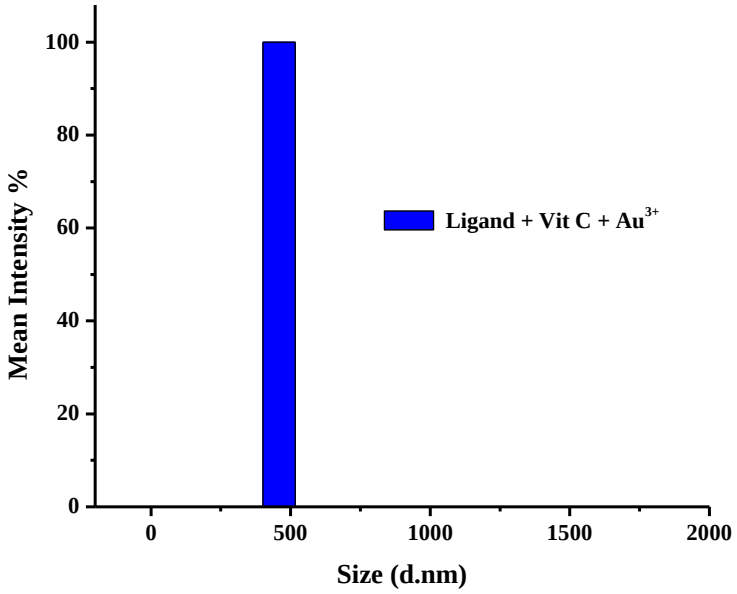


Figure S9. DLS data of **3 +** Ascorbic Acid + Au^{3+}

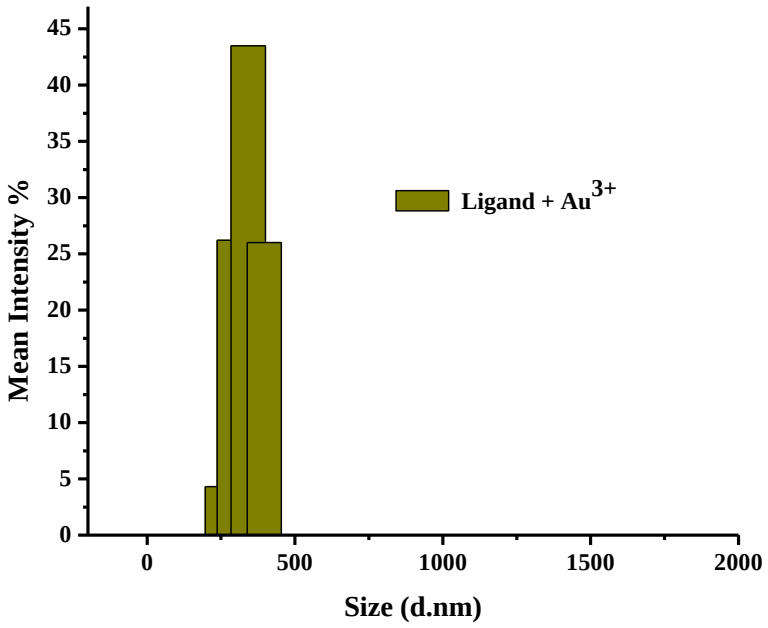
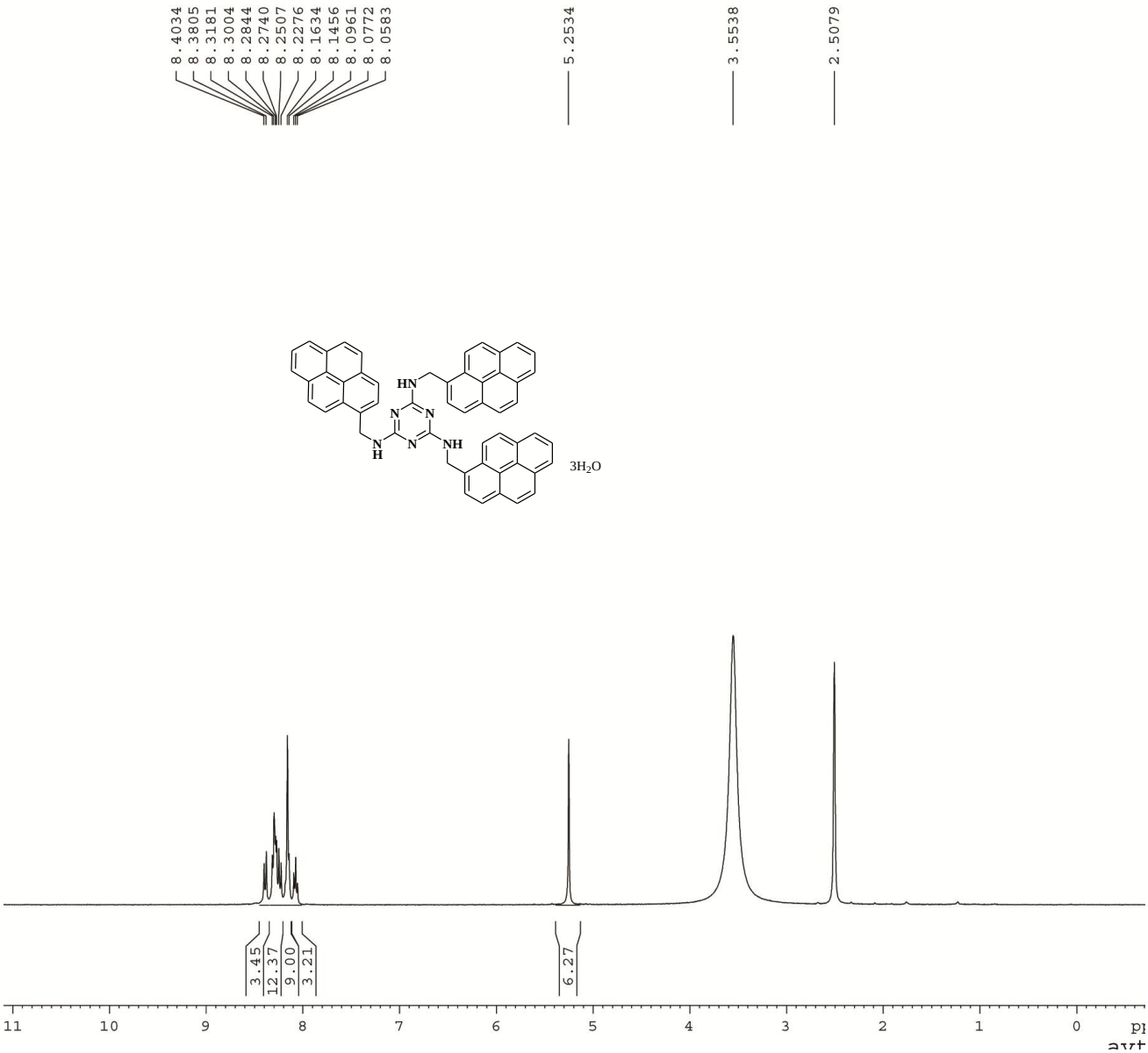
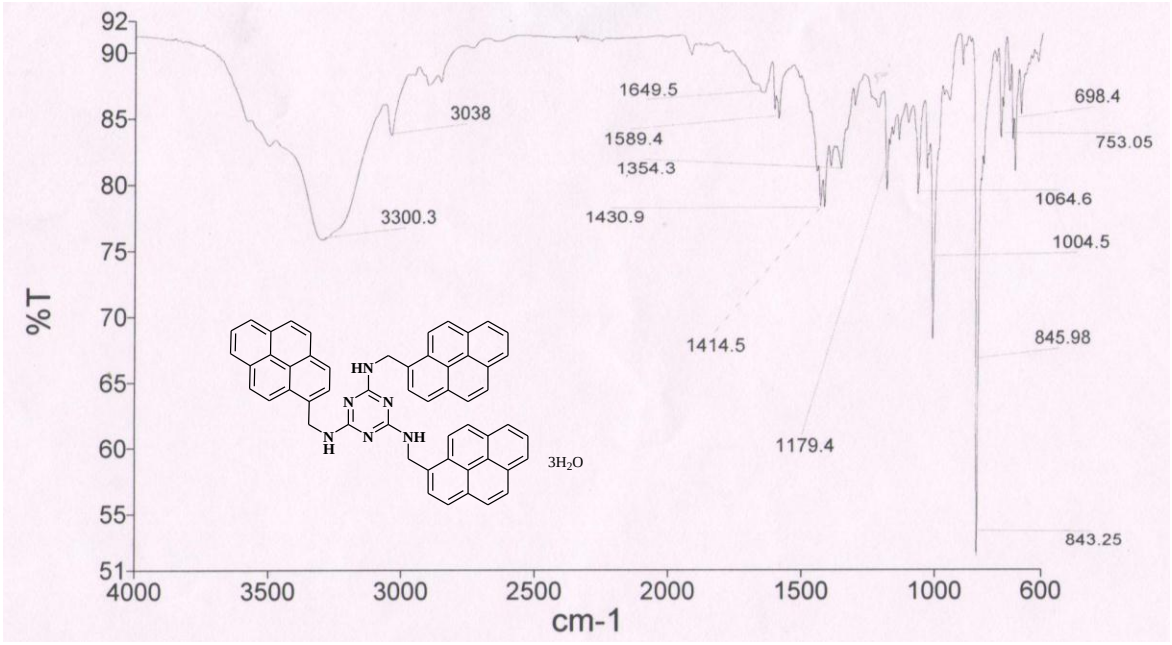


Figure S10. DLS data of **3** + Au^{3+} ions.

^{1}H NMR spectrum of 3 + Au^{3+} ions in DMSO



IR spectrum of **3**.



IR spectrum of **3** + Au^{3+} ions.