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Supplementary Supporting Information

Fluorescent chemodosimeter based on NHC complex for selective recognition of cyanide ions in aqueous medium

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1. EXPERIMENTAL SECTION

1.1. General Methods. The melting points were determined on a Mel-Temp II melting point apparatus and details of various equipments were published elsewhere.[14a] The IR spectra were recorded on a Perkin Elmer Model 882 infrared spectrometer. The electronic absorption spectra were recorded on a Shimadzu UV-3101 or 2401 PC UV-VIS-NIR scanning spectrophotometer. The fluorescence spectra were recorded on a SPEX-Fluorolog F112X spectrofluorimeter. ^{1}H and ^{13}C NMR were recorded on a 500 MHz Bruker advanced DPX spectrometer. MALDI-TOF MS analysis was performed with a Shimadzu Biotech Axima CFR plus instrument equipped with a nitrogen laser in the linear mode.[14b,c] All the solvents used were purified and distilled before use. Quantum yields of fluorescence were measured by the relative methods using optically dilute solutions. The quantum yields of fluorescence were calculated using quinine sulphate (Φ_f = 0.54; in 0.1 N H_2SO_4) as the standard and as per the equation 1,

$$\phi_u = \frac{A_s F_u n_u^2}{A_u F_s n_s^2} \phi_s \quad (1)$$

wherein, A_s and A_u are the absorbance of the standard and unknown, respectively. F_s and F_u are the areas of fluorescence peaks of the standard and unknown and n_s and n_u are the refractive indices of the solvents used for the standard and unknown, respectively. Φ_s and Φ_u are the fluorescence quantum yields of the standard and unknown. The fluorescence lifetimes were measured using IBH picoseconds time correlated single photon counting system. The fluorescence decay profiles were deconvoluted using IBH datastation software V2.1 and minimizing the χ^2 values of the fit to 1± 0.1.[14d] Doubly distilled water was used for all the studies and all experiments were carried out at room temperature (25 ± 1 °C), unless otherwise mentioned.

2. Materials. Anthracene, N-methylimidazole, HBr in acetic acid, paraformaldehyde, anthracenemethanol, phosphoroustribromide, silveroxide, tetrabutylammonium cyanide, tetrabutylammonium chloride, tetrabutylammonium iodide, sodium sulphide, ammonium thiocyanate, tetrabutylammonium bromide, tetrabutylammonium azide, tetrabutylammonium hydroxide, tetrabutylammonium hydrogensulphate, tetrabutylammonium benzoate, tetrabutylammonium perchlorate, and tetrabutylammonium fluoride were purchased from Aldrich and S. D. Fine Chemicals, India and used as received.

2.1. Synthesis of the NHC probe 2

*Synthesis of the imidazolium precursor **1***. To a mixture of N-methylimidazole (90 mg, 1.102 mmol) in dry acetonitrile (30 mL) was added 9-bromomethylanthracene (200 mg, 0.735 mmol) and the reaction mixture was then refluxed for 24 h at 80 ºC. The reaction mixture was then filtered and washed thoroughly with acetonitrile and dried. The product was further purified by recrystallization from acetonitrile to give 190 mg (61%) of the precursor **1**. Mp 245-269 °C; ^{1}H NMR (500 MHz, D_2O, TMS) δ 3.67 (s, 3H), 6.31 (s, 2H), 7.37 (s, 1H), 7.46 (s, 1H), 7.64-7.62 (t, 2H, J = 15 Hz), 7.69-7.67 (t, 2H, J = 15 Hz), 8.23-8.22 (d, 2H, J = 8.5 Hz), 8.28-8.26 (d, 2H, J = 9 Hz), 8.82 (s, 1H); ^{13}C NMR (125 MHz, CD_3CN) δ 35.5, 45.2, 120.4, 122.5, 123.4, 125.3, 128.1, 129.2, 130.6, 135.3; HRMS (FAB): Calcd for $C_{19}H_{17}N_2$, 273.139; Found, 273.138 (M^+).

*Synthesis of the NHC probe **2***. To a solution of imidazolium precursor **1** (100 mg, 0.239 mmol) in dry acetonitrile (20 mL) was added Ag_2O (27.7 mg, 0.119 mmol). The reaction mixture was then refluxed under argon atmosphere at 80 ºC for 20 h yielded the NHC complex **2** in 70% yield. It was purified by recrystallization from a mixture (2:1) of acetonitrile and diethyl ether. Mp > 300 °C; ^{1}H NMR (500 MHz, D_2O, TMS) δ 3.71 (s, 3H), 6.45 (s, 2H), 7.40 (s, 1H), 7.49 (s, 1H), 7.67-7.64 (t, 2H, J = 8 Hz), 7.73-7.70 (t, 2H, J = 8.5 Hz), 8.27-8.15 (d, 2H, J = 7.5 Hz), 8.31-8.29 (d, 2H, J = 9 Hz), ^{13}C NMR (125 MHz, CD_3CN) δ 38.2, 45.9, 120.4, 122.5,123.4, 125.3, 128.1, 129.2, 130.6, 179.5; MALDI-TOF

MS: Calcd for $C_{38}H_{32}N_4AgBr$, 732.09; Found, 732.00 (M^+). Anal. Calcd for $C_{38}H_{32}AgBrN_4$: C, 62.14; H, 4.67; N, 7.63. Found: C, 62.04; H, 4.62; N, 7.59.

2.2. Synthesis of the NHC probe 4

*Synthesis of the imidazolium precursor **3***. To a mixture of N-methylimidazole (112 mg, 1.37 mmol) in dry acetonitrile (30 mL) was added 9,10-dibromomethylanthracene (200 mg, 0.549 mmol). The reaction mixture was refluxed for 24 h at 80ºC and then filtered and washed thoroughly with acetonitrile and dried. The product was further purified by recrystallization from acetonitrile to give 230 mg (63%) of the precursor **3**. Mp 255-282 °C; ^{1}H NMR (300 MHz, D_2O, TMS) δ 3.69 (s, 3H), 6.39 (s, 2H), 7.32 (s, 1H), 7.35 (s, 1H), 7.76-7.73 (m, 2H), 8.14 (s, 1H), 8.40-8.37 (m, 2H); ^{13}C NMR (125 MHz, CD_3CN) δ 35.9, 45.6, 122.3, 124, 126.1, 128.0, 131.0, 135.9; HRMS (FAB): Calcd for $C_{24}H_{24}N_4Br$, 447.118; Found, 447.117 (M^++Br).

*Synthesis of the NHC probe **4***. To a solution of the imidazolium precursor **3** (100 mg, 0.151 mmol) in dry acetonitrile (30 mL) was added Ag_2O (70.7 mg, 0.303 mmol). The reaction mixture was then refluxed under argon at 80 ºC for 20 h to give the NHC complex **4** in 69% yield. It was purified by recrystallization from a mixture (2:1) of acetonitrile and diethyl ether. Mp > 330 °C; ^{1}H NMR (500 MHz, D_2O, TMS) δ 3.69 (s, 3H), 6.32 (s, 2H), 7.37 (s, 1H), 7.42 (s, 1H), 7.75-7.73 (m, 2H), 8.34-8.32 (m, 2H); ^{13}C NMR (125 MHz, CD_3CN) δ 38.6, 45.6, 122.2, 124.6, 126.7, 127.5, 128.8, 130.8, 179.9; MALDI-TOF-MS: Calcd for $C_{48}H_{46}N_8Ag_2$, 950.19; Found, 951.53 (M^++1). Anal. Calcd for $C_{48}H_{44}Ag_2Br_2N_8$: C, 51.82; H, 4.35; N, 10.07. Found: C, 51.79; H, 4.33; N, 10.04.

3. Calculation of LOD. To determine the sensitivity of the detection, the fluorescence changes of the NHC complexes were recorded by the addition of various concentrations of the cyanide ions. The limit of detection (LOD) was calculated by plotting a graph between $(I-I_0)/(I_f-I_0)$ verses the log [CN^-], wherein 'I_0' represents the fluorescence intensity of the

complex alone, 'I' is the fluorescence intensity at each addition of cyanide ions and 'I_f' is the fluorescence intensity at the final addition of cyanide ions. By extrapolating, the straight line plot to the X-axis gave the logarithmic value of LOD, from which, the limit of detection (LOD) was determined.

4. References

1 (a) Kuruvilla, E.; Ramaiah, D. *J. Phys. Chem., B*, 2007, ***111***, 6549.(b) Neelakandan, P. P.; Ramaiah, D. *Angew. Chem., Int. Ed.*, 2008, ***47***, 8407. (c) Nair, A. K.; Neelakandan, P.P.; Ramaiah, D. *Chem. Commun*., 2009, 6352. (d) Neelakandan, P. P.; Nandajan, P.C.; Subymol, B.; Ramaiah, D. *Org. Biomol. Chem*., 2011, ***9***, 1021.

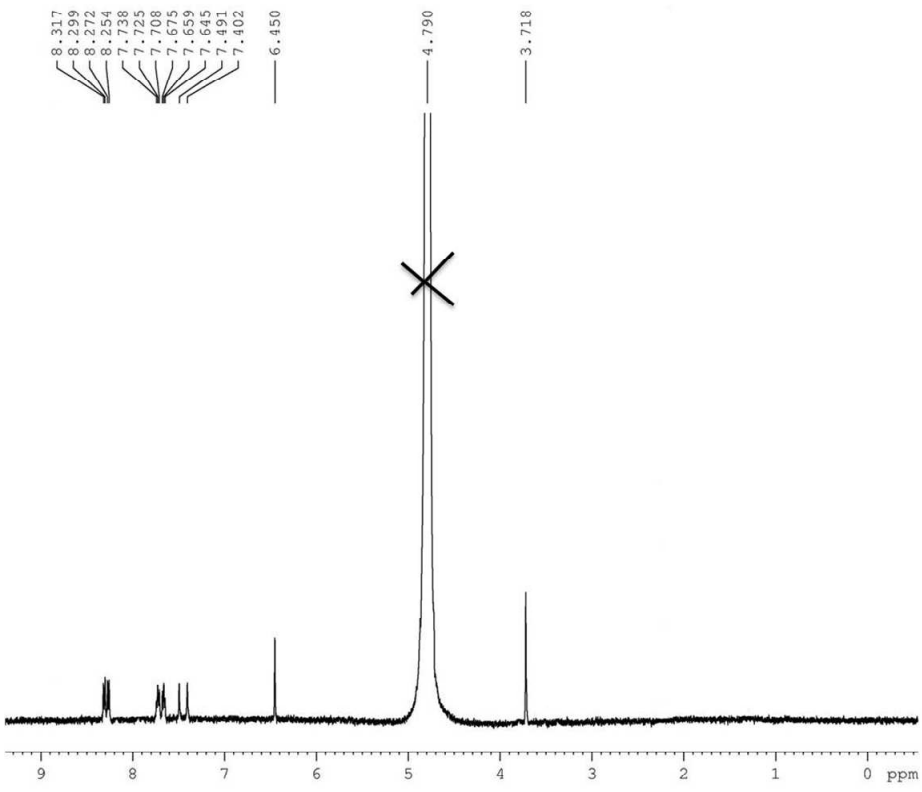

Figure S1. ^{1}H NMR spectrum of the probe **2** in D_2O.

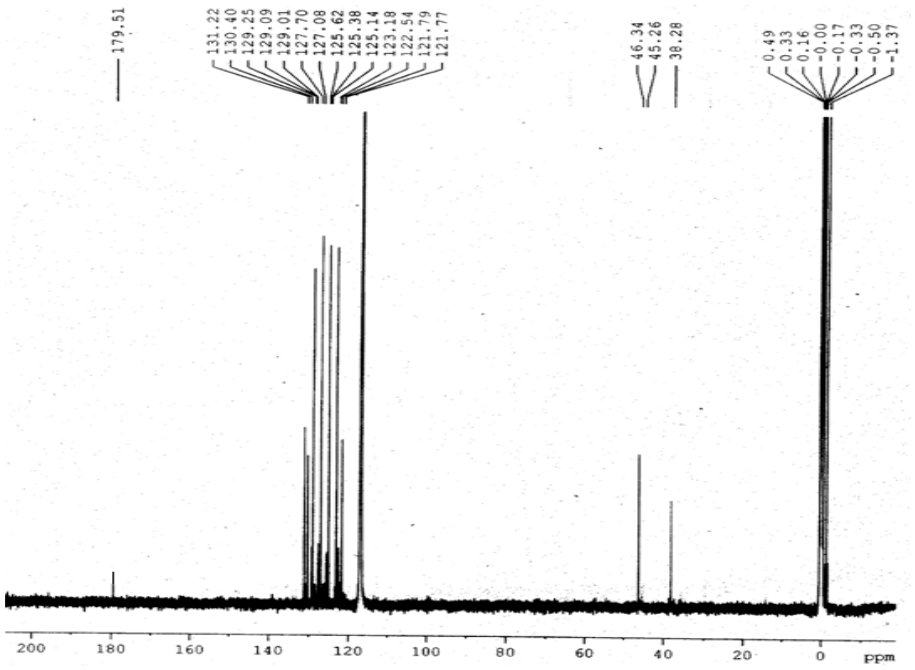

Figure S2. ^{13}C NMR spectrum of the probe **2**.

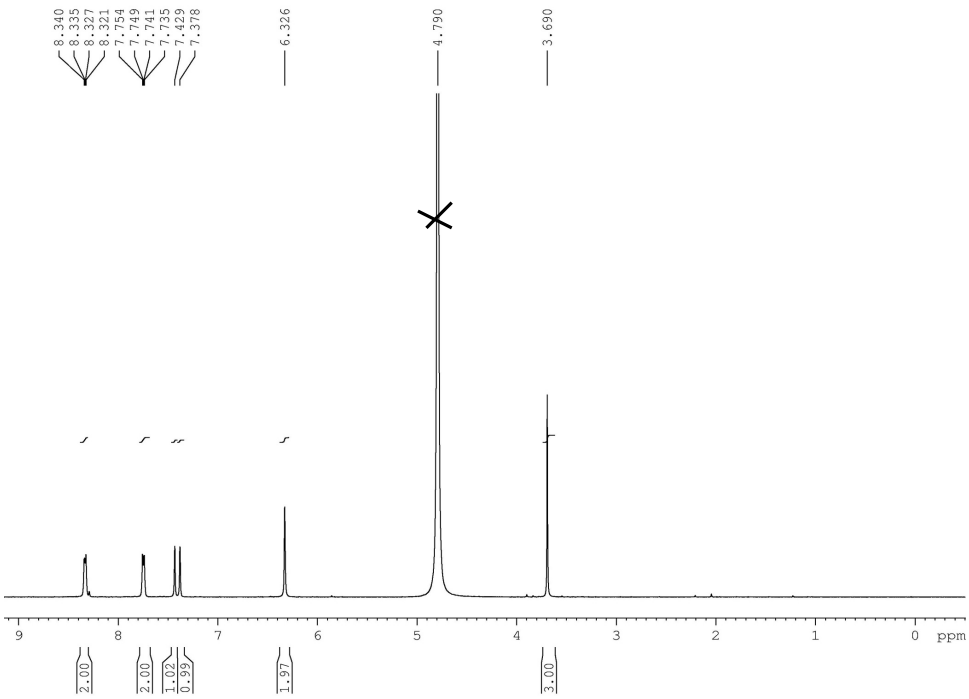

Figure S3. ^{1}H NMR spectrum of the probe **4** in D_2O.

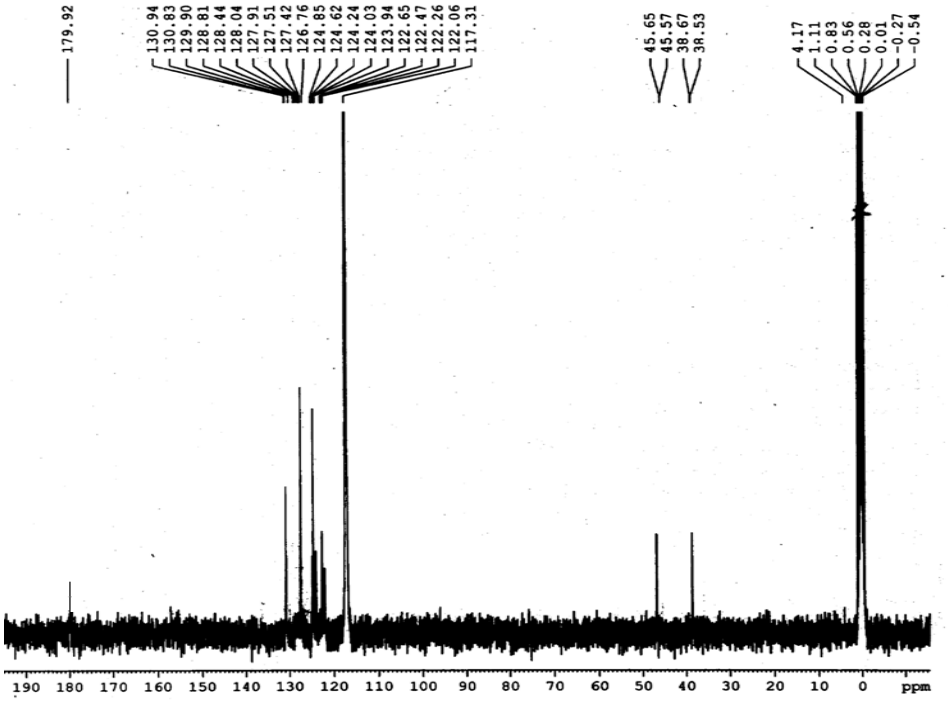

Figure S4. ^{13}C NMR spectrum of the probe **4**.

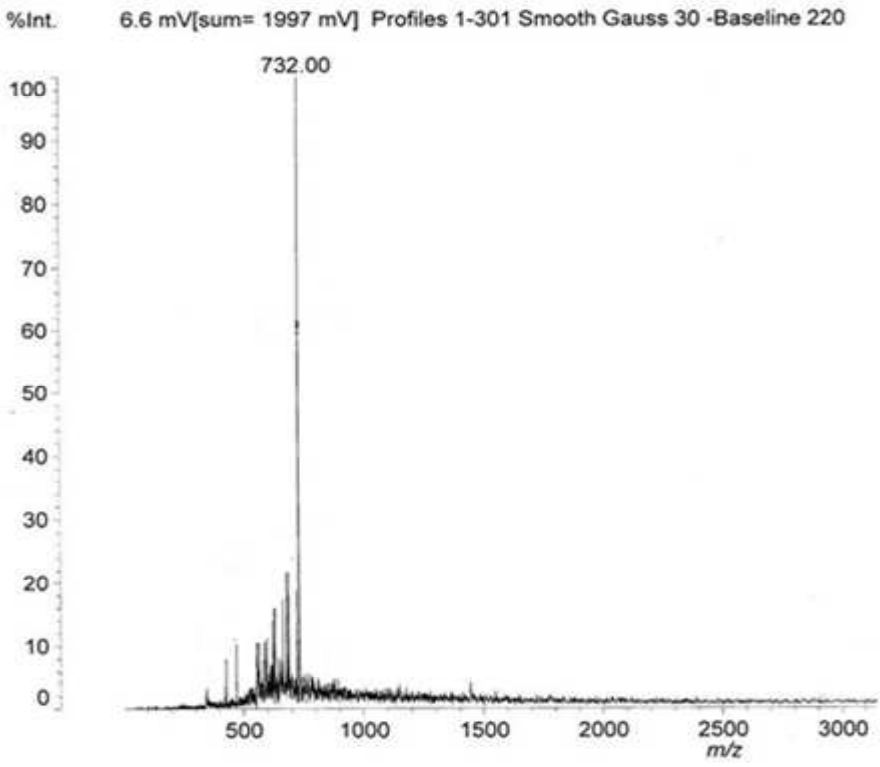

Figure S5. MALDI-TOF MS of the probe **2**.

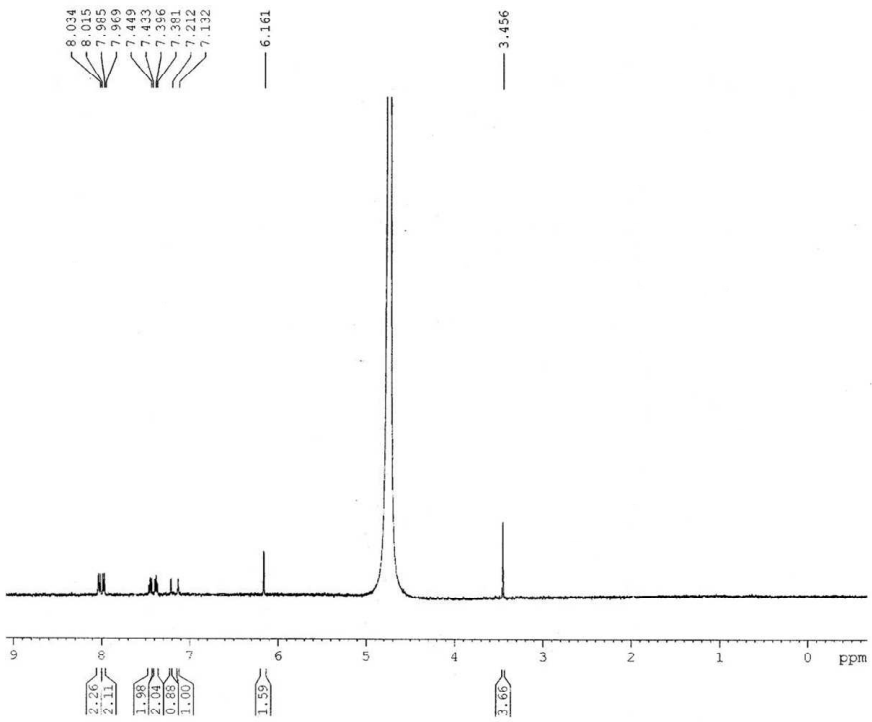

Figure S6. ^{1}H NMR spectrum of the probe **2** after the addition of TFA in D_2O.

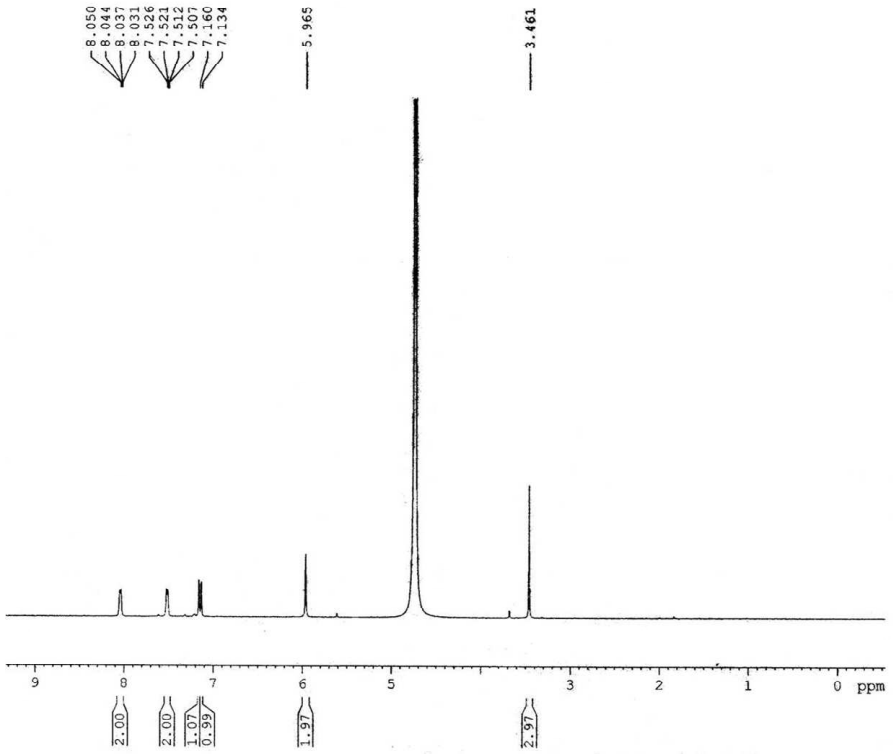

Figure S7. ^{1}H NMR spectrum of the probe **4** after the addition of TFA in D_2O.

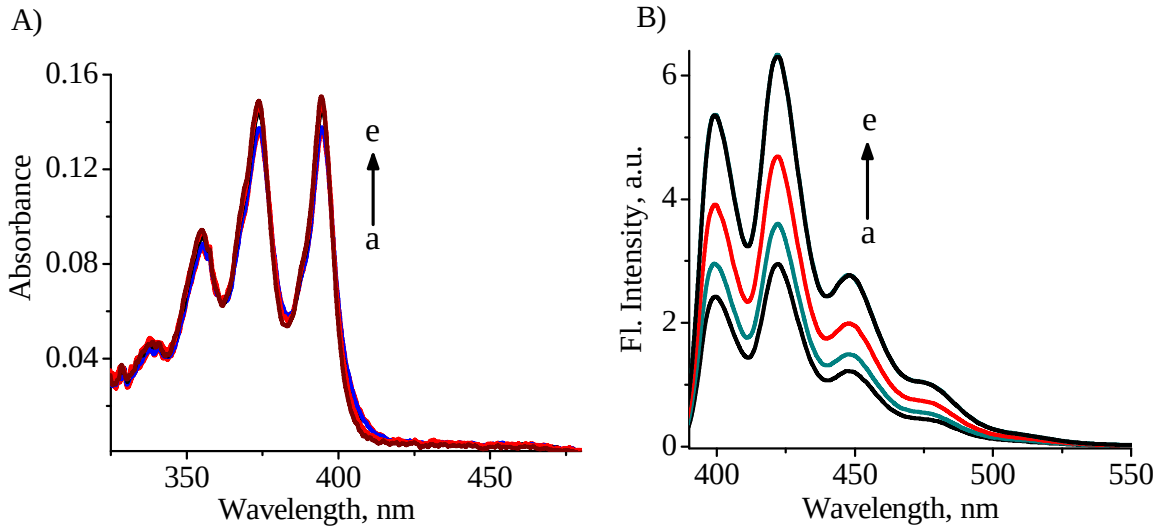

Figure S8. Changes in the A) absorption and B)emission spectra of the probe **4** (5 μM) with the addition of CN^- ions in aqueous medium. [CN^-] a) 0, and e) 20 μM. λ_{ex} 365 nm.

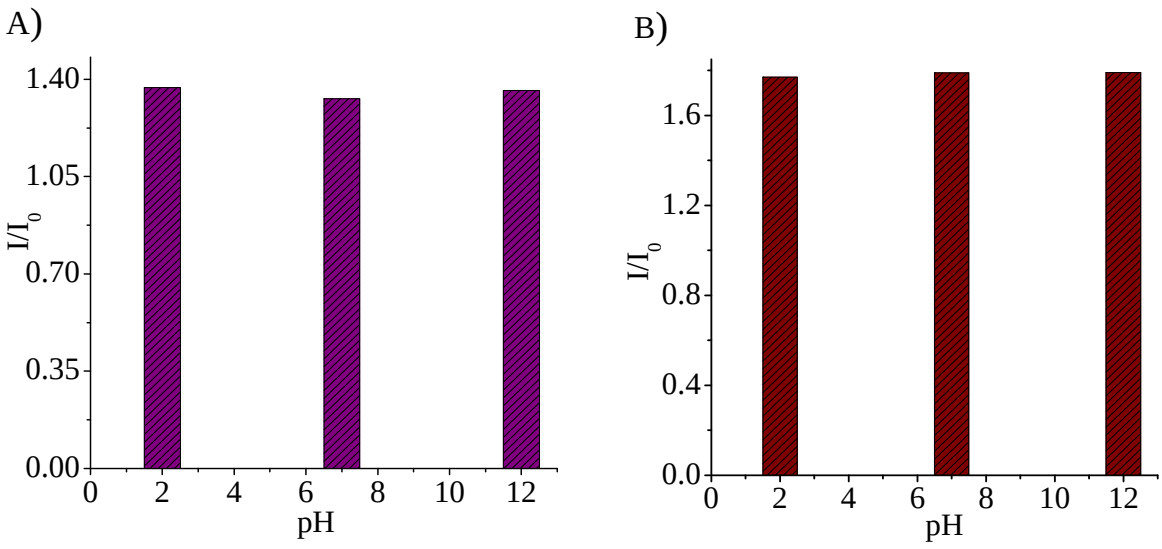

Figure S9. Changes in the fluorescence spectra of A) the probe **2** and B) the probe **4** with the addition of cyanide ions at differnt pH conditions.

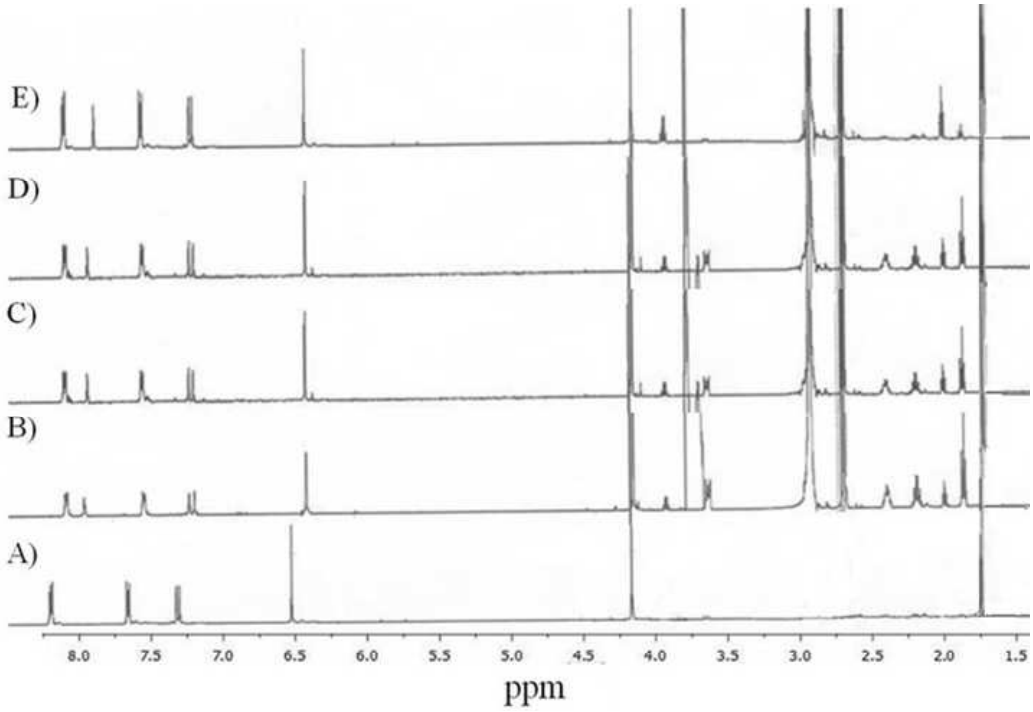

Figure S10. ^{1}H NMR spectra of A) the probe **4** alone and (B-E) with the addition of differnt concentrations of tetrabutylammoniumcyanide solution in CD_3CN.

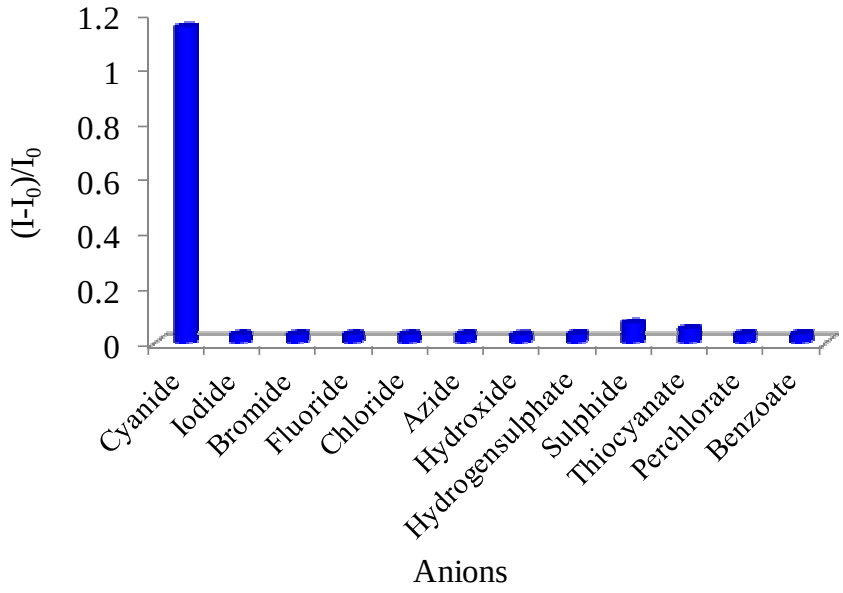

Figure S11. Selectivity plot showing the changes in the fluorescence intensity $(I-I_0)/I_0$ of the complex **4** with the addition of different anions.

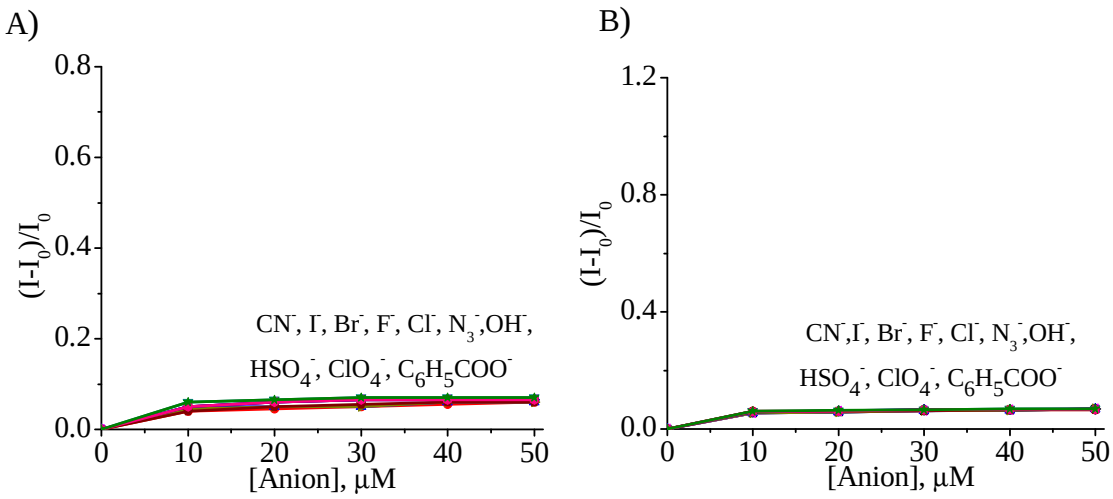

Figure 12. Selectivity plot showing the changes in the fluorescence intensity $(I-I_0)/I_0$ of the complexes A) **1** and B) **3** with the addition of different anions.

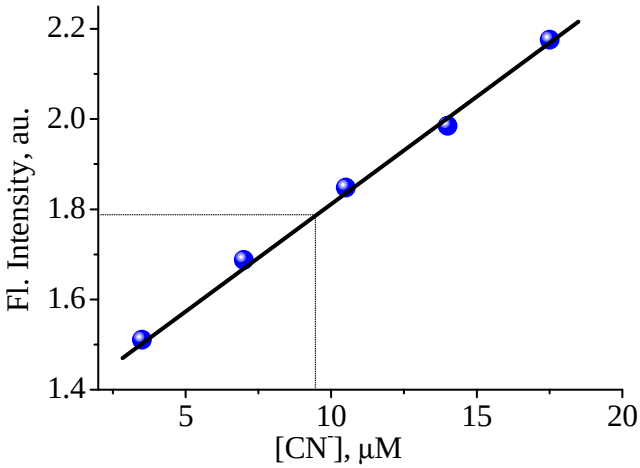

Figure S13. Linear plot between the changes in the fluorescence emission of the probe **2** at 416 nm vs cyanide ions for the quantitative estimation of cyanide ions in water.