Electronic Supplementary Material (ESI) for ChemComm.

Reusable and Specific Proton Transfer Signalling by Inorganic Cyanide in Solution and Solid

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Supplementary information

1. General Information (S1)

All solvents and reagents were purchased from commercial sources and used without further purification. Anions in the form of Sodium salts were stored in a desiccator under vacuum containing silica. Mass spectra were recorded on a Bruker HR-MS spectrometer. The synthesis of receptor (**1**) was carried in the ambient conditions.^{13}C and ^{1}H NMR spectra were recorded using a Bruker instrument operating at 500 MHz in d_6-DMSO.

UV/Vis spectra were recorded on Shimadzu spectrophotometry UV-1800. Fluorescence emission spectra were recorded on a Horiba Jovin Vyon Fluoro log 3-111 spectrophotometer. Excitation slit and emission slit width is 5nm. Titrations were performed on 2.5mL volume of samples of receptor (**1)** in DMSO/HEPES and by addition of stock solutions of the appropriate anions in water. HEPES buffer used in this study possesses almost a neutral pH range (HEPES, 10 mM, **6.7-7.4**). All the graph plotting and curve fitting was done in Origin Pro 8.0. All the experiments are being carried out at 298K.

Needle shaped Single Crystals were obtained from slow evaporation method in DMSO/Hexane system after two months. Single crystal data was collected on a Bruker APEX II diffractometer equipped with a graphite monochromator and Mo-Kα (λ = 0.71073 Å) radiation. Data collection was performed using φ and ω scans. The structures was solved using direct method followed by full matrix least square refinements against F2 (all data HKLF 4 format) using SHELXTL. All calculations were carried out using SHELXL 97, PLATON 99, and WinGXsystemVer-1.6414.

2. Synthesis of Receptor (S2)

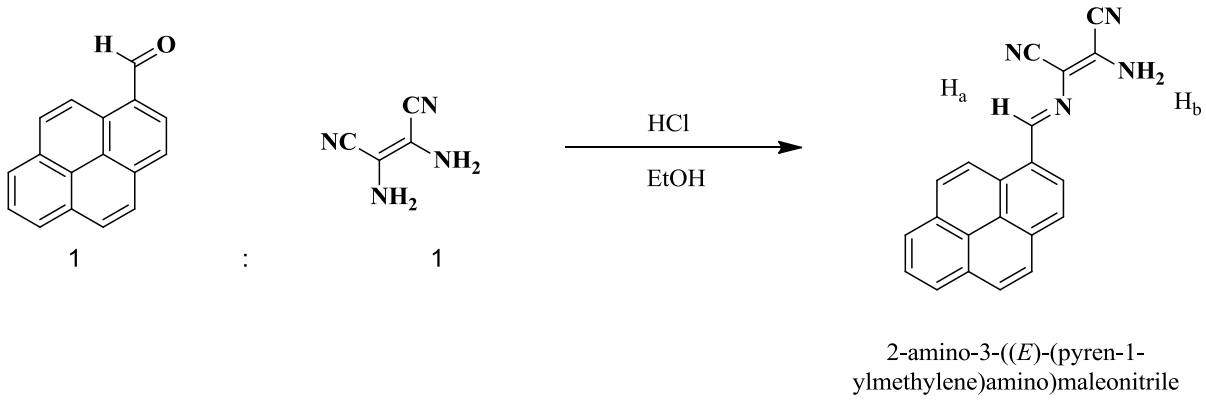

Fig. 1. Synthetic Scheme for Receptor **1**, with imine (H_a) and amine (H_b) protons assigned in the product.

2-amino-((E)-(pyren-1-ylmethylene) amino) maleonitrile (1):

(Yellow colour, 95% yield); ^{1}H NMR- (700MHz; d_6-DMSO): δ 9.31 (s, 1H, **H_a**), 9.05 (s, *J* = 14 Hz, 1H), 8.85 (d, *J*= 7 Hz, 1H), 8.41 (m, *J*= 14 Hz, 2H), 8.40 (d, *J* = 7 Hz, 1H), 8.37 (d, *J*= 14 Hz, 1H), 8.33 (d, *J* = 14 Hz, 1H), 8.27 (d, *J* = 7 Hz, 1H), 8.15 (t, *J*= 14 Hz, 1H), 8.12 (s, 2H, **H_b**).^{13}C NMR- (500 MHz; d_6-DMSO): δ 152.42, 133.48, 131.23, 130.50, 130.28, 129.73, 129.62, 127.97, 127.85, 127.28, 127.11, 126.92, 126.72, 126.65, 125.52, 124.42, 124.13, 122.15, 115.08, 114.42, 104.25. MS (HR-MS, negative mode) found 320.1049 for $C_{21}H_{12}N_4$ Calcd. 320.1062.

HR-MS, (negative mode) of receptor:

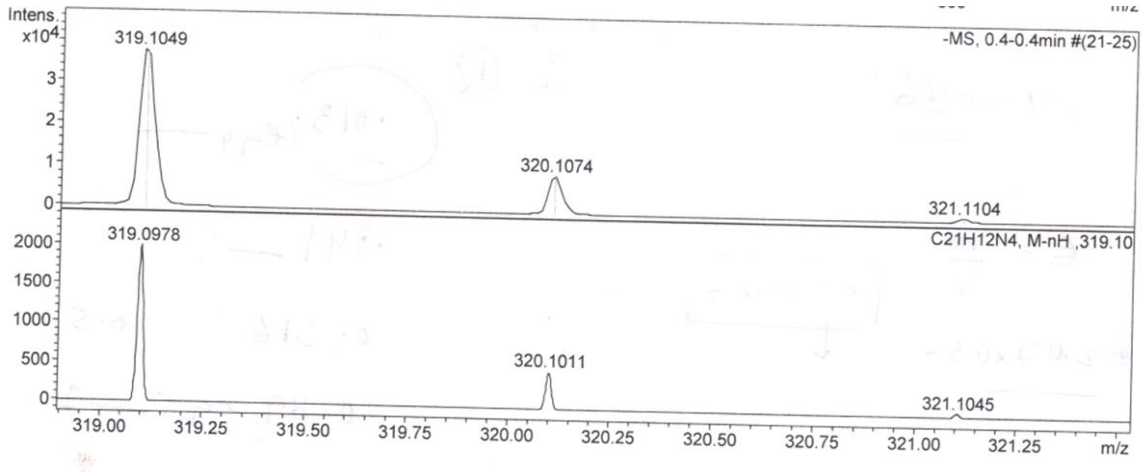

Fig. 1.1.HRMS spectra of Receptor **1** along with the calculated isotopic pattern

3. Jobs plot of 1 with CN^- (S3)

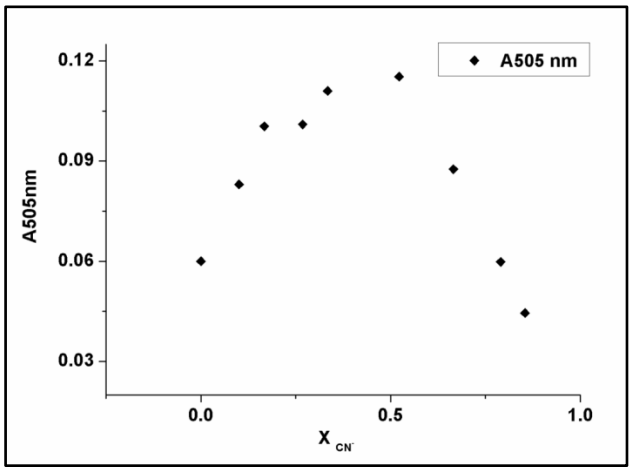

Fig. 2. Jobs plot for receptor **1** and CN^- confirming 1:1stoichiometry. X_{CN^-} = mole fraction of CN^-.

4. Benesi-Hilderbrand plot for Binding constant calculation (S4)

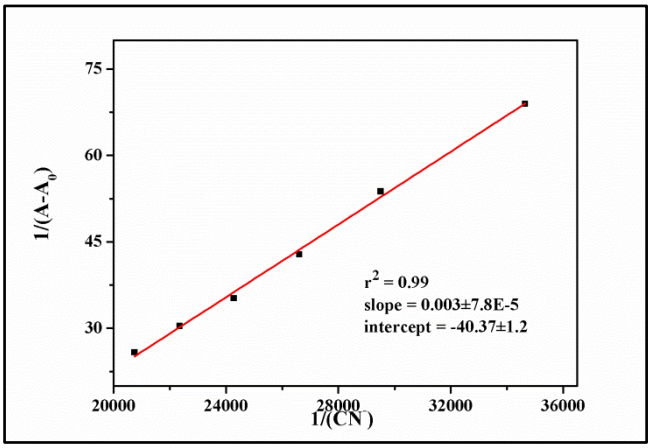

Fig. 3 Benesi-hilderbrand plot for the calculation of binding constant (K). Here A refers to the absorption of receptor at 505 nm at a given CN^- concentration and A_0 corresponds to the initial absorption of receptor at 505 nm in absence of CN^-.

5. Cross check of proposed mechanism (S5)

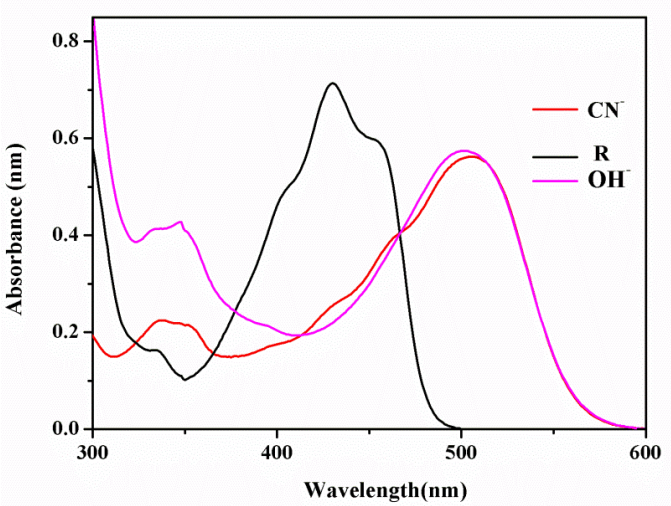

Fig. 4 UV/Vis Changes of **1** (50×10^{-6} M) in DMSO in presence of NaCN (0.15×10^{-6} M) and (0.38×10^{-6} M) of TBAOH in DMSO.

6. Absorption response of 1 with CN^- (S6)

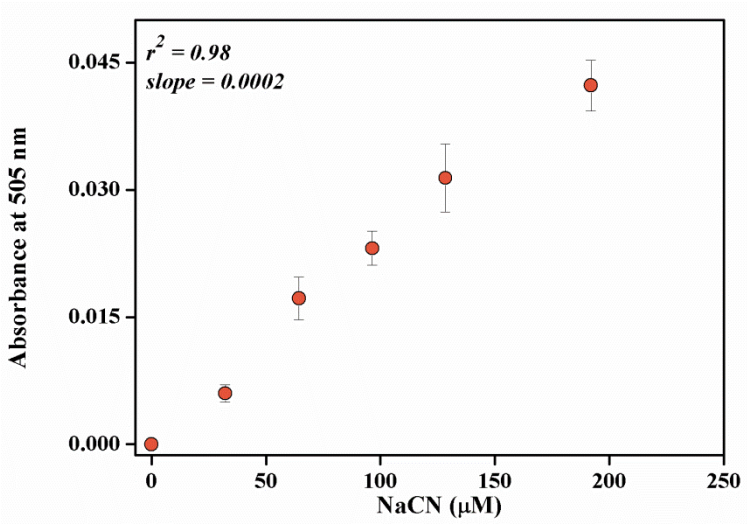

Fig. 5 Calibration curve from absorption studies for the estimation of CN^- with receptor concentration of 7.5×10^{-6} M in DMSO/HEPES (8:2, v/v) solvent system.

7. Emission response of 1 with CN^- (S7)

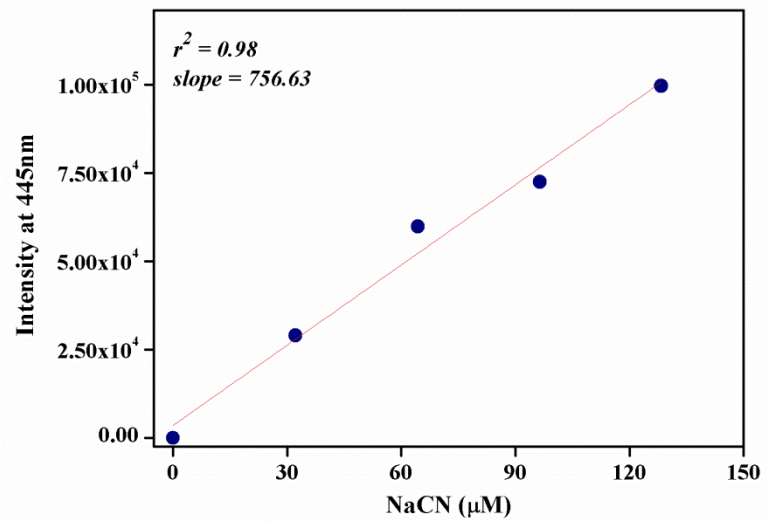

Fig. 6 Calibration curve from emission studies for the estimation of CN^- with receptor concentration of 7.5×10^{-6} M in DMSO/HEPES (8:2, v/v) solvent system.

8. Effect of pH (S8)

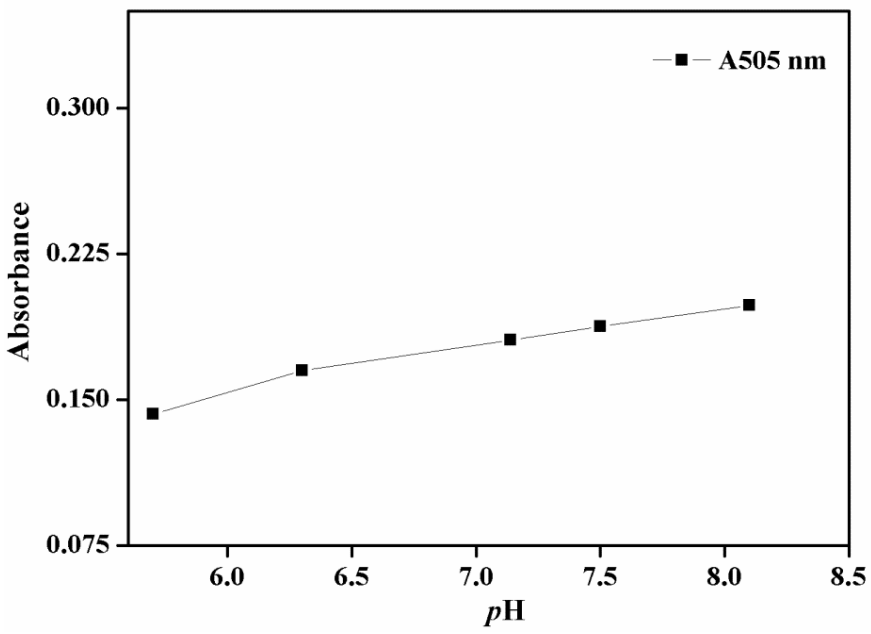

Fig. 7 Effect of pH on the receptor and CN^- interaction in DMSO/HEPES (8:2, v/v) solvent system. The concentration of receptor used was 13 μM in presence of 0.5 mM NaCN.