Electronic Supporting Information

A pyrene-based optical probe capable of molecular computation using chemical input strings †

† A tribute to Late Dr. Tarkeshwar Gupta

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Material and Methods: 1-Pyrenecarboxaldehyde and 2-Acetylpyridine were purchased from Alfa Aesar and used as received for synthesis. Most of the salts for sensing experiments were purchased from BDH chemicals Ltd, Sigma Aldrich and used as received. Double distilled water was used for the experiment. Solvents (HPLC grade) were purchased from Merck and distilled using reported methods. Deuterated solvent was purchased from Sigma Aldrich and stored under freezer. UV-vis spectra were recorded by JASCO UV-Vis-NIR spectrometer (V670) using a quartz cuvette (path length = 1cm, volume = 3 ml). The $^1$H-NMR spectrum was recorded at room temperature using Jeol JNMECX 400P spectrometer in CDCl$_3$ All chemical shifts ($\delta$) were recorded in ppm with reference to tetramethylsilane and coupling constant ($J$) in Hz. Fluorescence spectra were recorded by Varian Cary eclipse instrument (slit width = 5 cm). Mass spectra were recorded on mass spectrometer by Agilent Technology, USIC, University of Delhi, India. Perkin-Elmer FT-IR spectrophotometer was used to record IR spectra in range 400-4000 cm$^{-1}$.

Synthesis of probe 1; (E)-3-(Pyren-1-yl)-1-(pyridin-2-yl)-prop-2-enone:

1-Pyrenecarboxaldehyde (0.26 g, 1.13 mmol) was dissolved in a mixture of ethanol (15 mL) and dichloromethane (8 mL) followed by the addition of 2-Acetylpyridine (0.14 g, 1.2 mmol). Sodium hydroxide (0.15 g in 3 mL water) was then added dropwise with stirring. After few minutes a bright orange compound started to precipitate out. The mixture was left for 18 h at room temperature with continuous stirring after which the resulting precipitate was filtered in a sintered crucible and washed several times with cold ethanol. The solid obtained was recrystallized form ethanol to get orange coloured needle shaped crystals of the desired compound. Yield: 0.26 g, (70%)

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 8.95 (d, $J$ = 16.1 Hz, 1H, vinylic hydrogen), 8.81 (d, $J$ = 5.2 Hz, 1H, H$_6$), 8.63 (d, $J$ = 8.8 Hz, 2H, two pyrenyl protons), 8.55 (d, $J$ = 15.8 Hz, 1H, vinylic hydrogen), 8.34–8.05 (m, 9H, H$_3$, seven pyrenyl protons, H$_4$), 7.70 (td, $J$ = 7.4, 1.5 Hz, 1H, H$_5$)

FT-IR: $\nu_{max}$ (cm$^{-1}$) (KBr): 3046 (w, arom C-H), 1664 (m, C=O), 1590, 1575 (s, C=C)

ESI-MS: (calculated for C$_{24}$H$_{15}$NO): 334.1221 [M + H]$^+$

UV-vis (10$^{-5}$M, CHCl$_3$): $\lambda$ (nm) ($\epsilon$, M$^{-1}$ cm$^{-1}$) = 270 (37,000), 312 (22,000), 340 (18,000), 392 (23,000), 430 (26,000). Emission: $\lambda_{em}$ (nm): 520 nm ($\lambda_{exc}$ = 270 nm)
Figure S1: $^1$H-NMR spectrum of probe 1 in CDCl$_3$

Figure S2: FT-IR spectrum of probe 1
Figure S3: ESI-MS spectrum of probe 1
Preparation of ppm-level solutions: A stock solution of 1000 ppm of various salts, NiCl$_2$.6H$_2$O, MnCl$_2$.4H$_2$O, CuCl$_2$.2H$_2$O, CoCl$_2$.6H$_2$O, AgNO$_3$, Cd(NO$_3$)$_2$.4H$_2$O, Pb(NO$_3$)$_2$, Zn(NO$_3$)$_2$.6H$_2$O, FeSO$_4$.7H$_2$O, Hg(NO$_3$)$_2$.H$_2$O NaSO$_4$, MgSO$_4$.7H$_2$O, CaCl$_2$, FeCl$_3$, Al(NO$_3$)$_3$.9H$_2$O, CrCl$_3$.6H$_2$O, KCN, NH$_4$PF$_6$, NaClO$_4$, KSCN, [CH$_3$(CH$_2$)$_3$]$_4$NF, KCl, KBr and KI were made by dissolving 10 mg of each salt in 10 ml of appropriate solvent, mixture of dry solvents i.e., acetonitrile/ethanol/DMSO. Additionally, 1 ppm solutions of probe 1 were prepared by taking 5µl volume of stock solution and making it up to 5 ml of solvent.

Detection procedure of ppm-levels of Cu$^{2+}$ and Fe$^{3+}$: A 5 ml solution of 1 (10$^{-5}$ M, CHCl$_3$) was treated with 5 µl stock solution (1000 ppm, CH$_3$CN) of Cu$^{2+}$/ Fe$^{3+}$ and mixed thoroughly, to yield 1 ppm concentration of metal ion. The resulting solution was used for recording absorbance and emission spectra at room temperature. The same methodology was executed for higher concentrations of Cu$^{2+}$/ Fe$^{3+}$.

Selectivity and interference test for Cu$^{2+}$ and Fe$^{3+}$: The solution of probe 1 (10$^{-5}$ M, CHCl$_3$) was treated with 20 ppm and 5 ppm of all the test cations to test the selectivity of 1.
with Cu\(^{2+}\) and Fe\(^{3+}\), respectively. Furthermore, **1-Cu\(^{2+}\)** \((1 + 20 \text{ ppm} \text{ Cu}\(^{2+}\)) and **1-Fe\(^{3+}\)** \((1 + 5 \text{ ppm} \text{ Fe}\(^{3+}\)) solutions were checked for interference by addition of 20 ppm and 5 ppm of various test cations, respectively.

**Figure S5:** Visual colour changes in probe 1 (CHCl\(_3\)) upon addition of (a) 0 ppm (b) 2 ppm (c) 5 ppm (d) 10 ppm (e) 15 ppm and (f) 20 ppm of Cu\(^{2+}\) (CH\(_3\)CN).

**Figure S6:** Visual colour changes in probe 1 (CHCl\(_3\)) upon addition of (a) 0 ppm (b) 1 ppm (c) 2ppm (d) 3 ppm (e) 4 ppm and (f) 5 ppm of Fe\(^{3+}\) (CH\(_3\)CN).
**Figure S7:** Photographs depicting fluorescence quenching in 1 upon addition of Fe$^{3+}$ and Cu$^{2+}$.

**Figure S8:** Stern-Volmer plot for the fluorescence quenching of probe 1 ($10^{-5}$ M, CHCl$_3$) by (a) Cu$^{2+}$ and (b) Fe$^{3+}$.
Figure S9: Job’s plot for varying mole-fraction for probe 1 (10^{-5} M, CHCl₃) upon addition of (a) Cu^{2+} at \( \lambda = 567 \) nm and (b) Fe^{3+} at \( \lambda = 540 \) nm.

Figure S10: (a) ESI-MS spectrum of 1-Cu^{2+} in CH₃CN. (b) Zoomed in pattern for the peak at \( m/z = 729.79 \).
Figure S11: (a) ESI-MS spectrum of $1$-$\text{Fe}^{3+}$ in CH$_3$CN. (b) Zoomed in pattern for the peak at $m/z = 304.86$.

Figure S12: Benesi-Hildebrand plots for 2:1 molecular arrangement of (a) $1$-$\text{Cu}^{2+}$ and (b) $1$-$\text{Fe}^{3+}$. 
Figure S13: The sensing-recovery cycles for 1 (10^{-5} \text{ M, CHCl}_3) upon addition of Cu^{2+} (20 ppm, CH$_3$CN) (blue spheres) and Fe^{3+} (5 ppm, CH$_3$CN) (olive spheres) and subsequent regeneration by CN$^-$ (5 ppm, EtOH). Dotted lines serve guide to eyes.

References:
