Supporting Information

Novel pyrene- and anthracene-based Schiff base derivatives as Cu$^{2+}$ and Fe$^{3+}$ fluorescence turn-on sensors and for aggregation induced emissions

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Table of contents:

Experimental section (S1)
General information (S1)
Synthesis of F1 and F2 (S1-S2)
$^1$H NMR, $^{13}$C NMR and Mass (FAB) Scanned spectra of P1 and A1 (S3-S5)
Absorbance spectra and stoichiometries of sensor responses of P1 and A1 (S6-S7)
Detection limit (LOD) calculations and sensor reversibilities of P1 and A1 with Cu$^{2+}$ and Fe$^{3+}$ ions, respectively. (S8-S9)
P1+Cu$^{2+}$ and A1+Fe$^{3+}$ sensor responses as a function of pHs and PL spectra of P1 and A1 towards pH solutions (S10-S11)
Determination of association constants of sensor responses of P1 and A1 (S12)
Time dependent sensor responses of P1 and A1 (S13)
Counter ions effect on sensor responses (S14)
Absorbance spectra, quantum yield (Φ) changes of P1 and A1, upon increasing the concentrations of water (0-90%) as a function of time (S14-S16)
Time resolved fluorescence spectra (TRPL) of P1 in CH$_3$CN (0% and 80% of water) and A1 in THF (0% and 60% of water) measured after 18 hours (S17)
TRPL decay constants of P1 and A1 (Table S1) (S18)

Notes and References (S18)
Experimental Section

General Information

All anhydrous reactions were carried out by standard procedures under nitrogen atmosphere to avoid moisture. The solvents were dried by distillation over appropriate drying agents. Reactions were monitored by TLC plates and column chromatography was generally performed on silica gel. $^1$H and $^{13}$C NMR were recorded on a 300 MHz spectrometer. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz and relative to TMS (0.00) for $^1$H and $^{13}$C NMR, (s, d, t, q, m, and dd means single, double, ternary, quadruple, multiple, and doublet of doublet, respectively), and d-chloroform (7.26) & (77.0), d-THF (3.58) & (66.6) was used as references for $^1$H and $^{13}$C NMR, respectively. Mass spectra (FAB) were obtained on the respective mass spectrometer. Elemental analysis was carried out by Elemental Vario EL. Absorption and fluorescence spectra were measured on V-670 Spectrophotometer and F-4500 Fluorescence Spectrophotometer, respectively. Identification and purity of the compounds P1 and A1 were characterized by NMR ($^1$H & $^{13}$C), and Mass (FAB). Time-resolved photoluminescence (TRPL) spectra were measured using a home-built single photon counting system. Excitation was performed using a 450 and 500 nm diode laser (Picoquant PDL-200, 50 ps fwhm, 2 MHz). The signals collected at the excitonic emissions of solutions were connected to a time-correlated single photon counting card (TCSPC, Picoquant Timeharp 200). The emission decay data were analyzed with the biexponential kinetics in which two decay components were derived. The lifetime values ($\tau_1$ and $\tau_2$) and pre-exponential factors ($A_1$ and $A_2$) were determined and summarized. 0-14 pH buffers were freshly prepared as per the literature.1

Sensor titrations

Compounds P1 and A1 were dissolved in CH$_3$CN and THF at 1 x 10$^{-5}$ M concentration. Li$^+$, Ag$^+$, K$^+$, Na$^+$, Cs$^+$, Ni$^{2+}$, Fe$^{3+}$, Co$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, Pb$^{2+}$, Ca$^{2+}$, Mg$^{2+}$, Cu$^{2+}$, Mn$^{2+}$, Hg$^{2+}$, Fe$^{2+}$, and Ag$^{+}$ metal cations were dissolved in water medium at 1x10$^{-3}$ M concentration from their respective chloro compounds. 50% Pent methyl diethylene triamine (PMDTA) was dissolved in CH$_3$CN and THF, respectively for sensor reversibilities. For counter ion effect on Cu$^{2+}$ and Fe$^{3+}$ sensors responses Cu (OAc)$_2$, Cu(NO$_3$)$_2$, CuCl$_2$, CuBr$_2$, Cu (ClO$_4$)$_2$, Cu (IO$_3$)$_2$ and CuSO$_4$ and K$_2$ [Fe (CN)$_6$], Fe(NO$_3$)$_3$, FeCl$_3$, FeF$_3$, Fe (OH)$_3$, Fe (ClO$_4$)$_3$, Fe (IO$_3$)$_3$ and Fe$_2$ (SO$_4$)$_3$ were dissolved in water medium at 1x10$^{-3}$ M concentration. However, Cu (OH)$_2$ was dissolved in NH$_4$OH medium at 1x10$^{-3}$ M concentration.

General procedure$^{2,3}$ for the synthesis of compounds P1 and A1

To 1 equiv. of aromatic amine derivatives in 50 ml of methanol, 1 equiv. of aromatic aldehyde derivatives were added with constant stirring under nitrogen and then refluxed for 12 hrs. The reaction was monitored by TLC, after completion, the reaction mixture was cooled and the solvent was evaporated to give the crude product, which was recrystallized from ethanol to afford pure compounds (P1 and A1).

2-(pyren-1-ylmethyleneamino)phenol (P1): Bright yellow solid; 98% yield; $^1$H NMR (300 MHz, CDCl$_3$) δ: 6.95 – 6.99 (t, J = 6.0 Hz, 1H), 7.03 (d, J = 6.0, 1H), 7.07 – 7.13 (d, J = 9.0 Hz, 1H), 7.25 – 7.50 (m, 2H), 7.96 – 8.16 (m, 7H), 8.66 – 8.71 (dd, J = 7.5 Hz, 2H), 9.60 (s, 1H (-OH)); $^{13}$C NMR (300 MHz, CDCl$_3$) δ: 115.04, 115.98, 120.20, 121.63, 123.41, 125.77, 125.95, 126.03,
127.19, 128.53, 129.28, 133.41, 136.51, 152.38, 155.10; FAB: m/z = 321 (M⁺, 100%). Anal. Calcd for C₂₂H₁₃NO: C, 85.96; H, 4.70; N, 4.36. Found: C, 85.54; H, 4.68; N, 4.35.

2-((anthracen-2-ylimino)methyl)phenol (A1): Pale-yellow solids; 71% yield; ¹H NMR (300 MHz, d-THF) δ: 6.95 – 7.03 (t, J = 12 Hz, 2H), 7.07 (d, J = 9.0 Hz, 1H), 7.96 – 8.27 (m, 8H), 8.71 (s, 1H), 9.13 - 9.29 (m, 2H), 12.96 (s, 1H (-OH)); ¹³C NMR (300 MHz, CDCl₃) δ: 116.60, 118.35, 120.63, 123.41, 125.95, 126.03, 126.94, 127.19, 128.53, 129.28, 130.91, 131.60, 134.41, 138.91, 154.17, 156.59; FAB: m/z = 297 (M⁺, 100%). Anal. Calcd for C₂₁H₁₅NO: C, 84.82; H, 5.08; N, 4.71. Found: C, 84.50; H, 5.07; N, 4.73.
Fig. S1 $^1$H NMR spectrum of P1 in d-Chloroform.

Fig. S2 $^{13}$C NMR spectrum of P1 in d-Chloroform.
**Fig. S3** Mass (FAB) spectrum of P1.

**Fig. S4** $^1$H NMR spectrum of A1 in d-THF.
Fig. S5 $^{13}$C NMR spectrum of A1 in d-THF.

Fig. S6 Mass (FAB) spectrum of A1.
Fig. S7 Absorbance spectral changes of (a) P1 (1x10^-5 M) in CH3CN, titrated with 0-30 μM (with an equal span of 3 μM) of Cu²⁺ ions in H₂O and (b) stoichiometry calculations based on absorbance changes at 395 nm; Xₘ = [Cu²⁺] / [Cu²⁺] + [P1]; where Xₘ = mole fraction, [Cu²⁺] and [P1] are concentrations of Cu²⁺ and P1; P1+Cu²⁺ = 2:1 stoichiometry (ca. 0.412).
Fig. S8 Absorbance spectral changes of (a) A1 (1x10^{-5} M) in THF, titrated with 0-30 μM (with an equal span of 3 μM) of Cu^{2+} ions in H_2O and (b) stoichiometry calculations based on absorbance changes at 395 nm; X_M = [Fe^{3+}] / ([Fe^{3+}] + [A1]); where X_M = mole fraction, [Cu^{3+}] and [A1] are concentrations of Cu^{2+} and A1; A1+Fe^{3+} = 2:1 stoichiometry (ca. 0.370).
Fig. S9 Standard deviations and linear fitting for detection limit calculations of (a) P1 + Cu$^{2+}$ and (b) A1 + Fe$^{2+}$. [Note: Detection limit calculations were based on relative fluorescence intensity changes versus respective metal ion concentrations].
**Fig. S10** Sensor reversibilities and reversible cycles of (a, c) P1 + Cu$^{2+}$ and (b, d) A1 + Fe$^{3+}$. 
Fig. S11 Sensor responses of (a) P1 + Cu$^{2+}$ and (b) A1 + Fe$^{3+}$, as a function of pHs (0-14).
Fig. S12 PL spectral changes of (a) P1 (20 μM) in CH3CN and (b) A1 (20 μM) in THF upon the addition of 100 μM of pH (0-14) buffers in H2O.
Determination of Association Constant: Assuming a 2:1 complex formation, the association constant was calculated on the basis of the titration curves of the sensor P1 and A1 with Cu$^{2+}$ and Fe$^{3+}$. Association constants were determined by a linear least square fitting of data with the following equation as a referenced method.

\[
[Cu^{2+}] = \frac{1}{2K_a[L]_T} \cdot \frac{x}{(1-x^2)} + \frac{[L]_T}{2} \cdot x \quad \text{and} \quad [Fe^{3+}] = \frac{1}{3K_a[L]_T} \cdot \frac{x}{(1-x^3)} + \frac{[L]_T}{3} \cdot x
\]

Where $K_a$ is complex association constant; $[Cu^{2+}]$ and $[Fe^{3+}]$ are the concentrations of Cu$^{2+}$ and Fe$^{3+}$ ions; $[L]_T$ is the initial concentration of sample; $x = I-I_0/I_{\text{max}}-I_0$; I, I$_0$ and I is the absorption intensity at 455 nm (P1) or 495 nm (A1) of respective species, free ligand and the absorption intensity at 455 nm (P1) or 495 nm (A1) upon the addition of Cu$^{2+}$ and Fe$^{3+}$, respectively.

**Fig. S13** Determination of association constants of (a) P1+Cu$^{2+}$ and (b) A1+Fe$^{3+}$ based on linear least square fitting.
Fig. S14 Time dependent fluorescence spectral changes of (a) P1 (20 μM) in CH3CN (λex = 395 nm) with 10 μM Cu2+ in H2O and (b) A1 (20 μM) in THF (λex = 395 nm) with 10 μM Fe3+ in H2O (each measurement carried out at equal span of 20 seconds). (c and d) relative fluorescence intensity changes of P1 and A1, respectively, as a function of time (0-10 min.).
**Fig. S15** Sensor responses of (a) P1 and (b) A1 towards Cu$^{2+}$ and Fe$^{3+}$ in presence of different counter ions (for Cu$^{2+}$ sensors CH$_3$COO$^-$, NO$_3^-$, Cl$,^-$, Br$,^-$, OH$,^-$, ClO$_4^-$, IO$_3^-$ and SO$_4^{2-}$ and for Fe$^{3+}$ sensors CN$,^-$, NO$_3^-$, Cl$,^-$, F$,^-$, OH$,^-$, ClO$_4^-$, IO$_3^-$ and SO$_4^{2-}$ were taken as counter ions)
Fig. S16 Absorbance spectral changes of (a) P1 and (b) A1, upon increasing the concentration of water (0-90%) (Note: the spectra were taken after 18 hours).
Fig. S17 Quantum yield (Φ) changes of (a) P1 and (b) A1, upon increasing the concentration of water (0-90%) as a function of time (0-18 hours).
Fig. S18 Time resolved fluorescence spectra (TRPL) of (a) P1 in CH$_3$CN (0% and 80% of water) and (b) A1 in THF (0% and 60% of water) measured after 18 hours.
Table S1. Time-resolved fluorescence decay constants of P1 and A1, sensor complexes and their aggregation induced emissions concentrations.

<table>
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<th>Compound</th>
<th>τ₁(ns)</th>
<th>τ₂(ns)</th>
<th>A₁(%)</th>
<th>A₂(%)</th>
<th>τₐavg(ns)</th>
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<td>P1</td>
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<td>6.9600</td>
<td>96.16</td>
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<td>P1 (80%)</td>
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<td>85.69</td>
<td>10.60</td>
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<tr>
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<td>A1 (60%)</td>
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<td>24.17</td>
<td>8.40</td>
<td>91.60</td>
<td>22.30</td>
</tr>
</tbody>
</table>

Notes and References


