Supplementary Information

Pyrene based fluorescent turn-on chemosensor: aggregation-induced emission enhancement and application towards Fe\textsuperscript{3+} and Fe\textsuperscript{2+} recognition

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**Experimental**

**Materials**

All chemicals for synthesis were purchased from Sigma Aldrich (Bengaluru, Karnataka, India) and are used without further purification, unless otherwise specified. Freshly prepared deionised water was used for sample preparation. The stock solutions of the metal ions were prepared from their perchlorate salts. \textsuperscript{1}H NMR spectra were recorded on AVANCE 400 as well as 500 MHz and \textsuperscript{13}C NMR 125 MHz NMR spectrometer, using TMS as internal standard and CDCl\textsubscript{3}-d as the solvent. Mass spectrometric data were obtained by positive electron spray ionization (ESI-MS) technique on an Agilent Technologies 1100 Series (Agilent Chemistation Software) mass spectrometer. High-resolution mass spectra (HRMS) were obtained by using ESIQTOF mass spectrometry. FT-IR spectra were recorded on a Perkin Elmer FT-IR 400 spectrometer. UV-vis absorption spectra were recorded by UV-vis-
1800 Schimadzu spectrophotometer. Fluorescence emission spectra were measured on RF-6000 (Schimadzu, Japan) Spectrofluorophotometer.

**Computational Study**

Gaussian 09 ab initio/DFT quantum chemical simulation package were employed to perform the ground state calculations in the frame of density functional theory and were optimized at DFT/B3LYP/6-31G** level of theory.

**Sample Preparation for UV-vis**

The probe Py-BTZ was dissolved in an acetonitrile: water (1:1; v/v) solvent mixture at a concentration ≈1.0 x 10⁻⁵ M corresponding to the maximum of absorbance in the range ≈ 0.1 to 0.4 for the UV experiments. The solution of the probe Py-BTZ was placed in a quartz cuvette (l= 1 cm, V₀ = 3 mL) followed by addition of various metal ion solutions (c ≈ 1 mM). The UV-vis spectrum was recorded for each at room temperature.

**Sample Preparation for Fluorescence Spectroscopic Measurements**

To a solution of Py-BTZ (1.0 × 10⁻⁵ M) in acetonitrile: water (1:1; v/v) the various metal ion solutions were added. Emission spectrum was recorded with an excitation wavelength of λ_ex = 400 nm, with each addition being at room temperature.

**Optical measurements**

The anion solutions were added to the solution of the Py-BTZ probe (25 μM) in acetonitrile: water (1:1; v/v). Addition of the anion solutions, at 3 equiv was performed at room temperature with the image being recorded using a well resolved camera.

**Reagents**

1-pyrenecarboxyaldehyde, 2-amino-6-methoxy-benzothiazole and all salts were purchased from Sigma (Bengaluru, Karnataka, India). All reagents were of analytical grade and were used without further purification. Milli-Q- water used in all experiments was doubly distilled and purified by a Milli-Q system (Millipore, USA).
Synthesis of Probe Py-BTZ

To a stirred solution of 1-pyrenecarboxyaldehyde and 2-amino-6-methoxy-benzothiazole in absolute ethanol a catalytic amount of H$_2$SO$_4$ was added. The solution was refluxed for 16 h. After completion of reaction solvent was removed under reduced pressure from reaction mixture and the crude solid was washed with child methanol to yield red solid as pyrene-benzothiazole conjugate (Py-BTZ). $^1$H NMR (CDCl$_3$, 400 MHz) δ: 3.91 (s, 3H), 7.12 (dd, 1H), 7.34 (d, J=2.4 Hz, 1H), 7.92 (d, J= 8.9 Hz, 1H), 7.81 (m, 2H), 8.20-8.31 (m, 5H, Ar-H), 8.8 (d, J=8.0, 1H), 9.15 (d, J= 9.2, 1H), 10.02 (s, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 55.8, 104.5, 105.3, 113.7, 115.6, 119.5, 122.5, 123, 123.7, 124, 125.1, 126.5, 127.2, 127.4, 128.1, 130, 130.8, 131.4, 131.8, 157.6, 163.3, 193; FT-IR (KBr, v cm$^{-1}$): 585, 737, 882, 1056, 1384, 1486, 1634, 2875, 2961 and 3417; ESI-MS (m/z %): 393 [M+H]$^+$, HRMS: calculated for C$_{25}$H$_{17}$ON$_2$S= 393.10561 Found [M+H]$^+$= 393.10400.

Supplementary figures

Fig. S1 Solution color and fluorescent changes of Py-BTZ (25 μM) upon the addition of Fe$^{2+}$ (1 x 10$^{-4}$) and Fe$^{3+}$ ions (1 x 10$^{-4}$) respectively in CH$_3$CN:H$_2$O (1:1, v/v) under (a) sunlight and (b) UV light, respectively.
Fig. S2 Frontier molecular orbitals (HOMO and LUMO) distributions of receptor Py-BTZ.

Fig. S3 UV-vis absorption titration of Py-BTZ with Fe$^{3+}$ ion (1× 10^{-4} M) in CH$_3$CN: phosphate buffer (pH = 7.4; 1:1, v/v) solvent mixes.
Fig. S4 UV-vis absorption titration of receptor Py-BTZ with Fe$^{2+}$ ion (1 × 10$^{-4}$ M) in CH$_3$CN: H$_2$O (1:1, v/v) solvent mixes.

Fig. S5 UV-vis absorption titration of receptor Py-BTZ with Fe$^{3+}$ ion (1 × 10$^{-4}$ M) in CH$_3$CN:H$_2$O (1:1, v/v) solvent mixes.
**Fig. S6** UV-vis absorption spectra of receptor Py-BTZ upon addition of (a) Fe$^{3+}$ ($c = 1 \times 10^{-4}$ M) and (b) Fe$^{2+}$ ($1 \times 10^{-4}$ M), in the presence of various other metal ions (Ni$^{2+}$, Co$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Ag$^+$, Pb$^{2+}$, Hg$^{2+}$, Li$^+$, Ba$^{2+}$, Mg$^{2+}$, Fe$^{2+}$ and Cr$^{3+}$ of their perchlorate salt) in CH$_3$CN:H$_2$O (1:1, v/v) solvent mixes, respectively.

**Fig. S7** Relative fluorescence emission at 456 nm ($\lambda_{ex} = 400$ nm) of Py-BTZ ($1 \times 10^{-5}$ M solution in CH$_3$CN:H$_2$O, 1:1,v/v) and upon addition of an equimolar amount of each perchlorate cations ($1 \times 10^{-4}$ M).
**Fig. S8** Change in the fluorescence emission intensity of receptor *Py-BTZ* monitored at 456 nm of Figure 2c (main manuscript).

**Fig. S9** Fluorescence titration of receptor *Py-BTZ* with Fe$^{2+}$ ion ($1 \times 10^{-4}$ M) in CH$_3$CN: H$_2$O (1:1, v/v) solvent mixes.
**Fig. S10** Fluorescence intensity ($\lambda_{ex} = 400$ nm) at 456 nm of Py-BTZ:Fe$^{3+}$ complex verses time in minutes.

**Fig. S11** Job’s plot for Py-BTZ with Fe$^{3+}$ ion.
Fig. S12 Job’s plot for Py-BTZ with Fe$^{2+}$ ion.

Fig. S13 Binding constant of probe Py-BTZ by Benesi-Hildebrand of Fe$^{3+}$ ion.
Fig. S14 ESI-MS of Py-BTZ:Fe$^{3+}$ complex
Fig. S15 Binding constant of probe Py-BTZ by Benesi-Hildebrand of Fe$^{2+}$ ion.

Limit of detection was calculated by using:

Equation \[ LD = \frac{3S}{\rho} \] \hspace{1cm} (I)

Where S is standard deviation of three blank readings and \( \rho \) is slope.
Fig. S16 Calibration plot for successive addition of Fe$^{3+}$ ion to Py-BTZ solution in CH$_3$CN:H$_2$O (1:1, v/v).

Fig. S17 Calibration plot for successive addition of Fe$^{2+}$ ion to Py-BTZ solution in CH$_3$CN:H$_2$O (1:1, v/v).
Fig. S18 FT-IR spectrum of Py-BTZ, Py-BTZ:Fe$^{2+}$and Py-BTZ:Fe$^{3+}$.

Fig. S19 Optical image for AIEE as the increment of H$_2$O% in CH$_3$CN.
Fig. S20 FT-IR spectra of compound Py-BTZ.

Fig. S21 $^1$H NMR spectra of compound Py-BTZ.
Fig. S22 $^{13}$C NMR spectra of compound Py-BTZ.

Fig. S23 ESI-MS spectra of compound Py-BTZ.
Fig. S24 HRMS spectra of compound Py-BTZ.