Supplementary Information

Pyrrolidine constrained bipyridyl-dansyl click fluoroionophore as selective Al$^{3+}$ sensor

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1. General Experimental Procedure

All the solvents and reagents (analytical grade and spectroscopic grade) were obtained from Sigma-Aldrich and used as received unless otherwise mentioned. The solutions of metal ions were prepared from Al(ClO₄)₃·9H₂O, LiClO₄·3H₂O, NaClO₄, KClO₄, Mg(ClO₄)₂, Sr(NO₃)₂, Ba(ClO₄)₂, Mn(ClO₄)₂·6H₂O, Fe(ClO₄)₂, Co(ClO₄)₂·6H₂O, Ni(ClO₄)₂·6H₂O, Cu(ClO₄)₂·6H₂O, Zn(ClO₄)₂·6H₂O, Cd(ClO₄)₂·H₂O, Ag(ClO₄)₂, HgCl₂, Pb(ClO₄)₂, In(NO₃)₃ respectively in CH₃CN. 

¹H and ¹³C NMR were measured on a Bruker AV-400 spectrometer with chemical shifts reported as ppm (in CDCl₃/CD₃CN, TMS as internal standard). Mass spectra are measured on Shimadzu 2020 LC-MS and Bruker Ultraflex II MALDI/TOF spectrometers. Melting points were determined on hot oil-bath melting point apparatus in an open-mouth capillary and were uncorrected. IR spectra are recorded on a Bruker IFS 66/V spectrometer, using KBr discs. Thermalgravimetric analysis was carried out on a TGA 850 Mettler Toledo instrument. Elemental analysis was carried out on ThermoScientific FLASH 2000 Organic Element Analyzer and specific rotation [α]D²⁵ was recorded on a JASCO P-2000 polarimeter. UV spectra were recorded on a Perkin Elmer Model Lambda 900 spectrophotometer and fluorescence spectra were recorded on a Perkin Elmer model LS 55 spectrophotometer.

2. Synthesis of BD 1

Preparation of Boc-pyrrolidine methylene triazole bipyridine (4): To a solution of Boc-protected azido-pyrrolidine¹ (1g, 4.42 mmol) in toluene and tert-butanol (4:1), 6-Ethynyl-2,2'-bipyridine² (0.8g, 4.42 mmol), CuI (0.042g, 0.221 mmol) and N,N'-diisopropylethylamine (DIPEA) (1.54 mL, 8.84 mmol) were added. The reaction mixture was stirred at room temperature for overnight. After removal of the solvent under vacuo, the residue was diluted with 20 mL CH₂Cl₂
and washed with water (15 mL x 3). The organic phase was dried over Na$_2$SO$_4$ and solvent was evaporated to dryness. The crude product was purified by column chromatography on silica gel using chloroform-methanol (10:1) as an eluent to afford white product in good yield (1.72 g, 96%). M.P. 122-124°C. [α]$_D^{25}$ +79.5 (c 1.0, CH$_3$OH). $^1$H NMR (400 MHz, CDCl$_3$) δ 1.52 (9H, s), 1.72-1.75 (2H, m), 1.98-2.00 (2H, m), 3.18-3.43 (2H, m), 4.19 (1H, m), 4.50-4.78 (2H, m), 7.31-7.34 (1H, dd, J = 5.2 Hz, 1.6 Hz), 7.80-7.84 (1H, t, J = 7.4 Hz), 7.88-7.92 (1H, t, J = 7.6 Hz), 8.17-8.25 (2H, m), 8.35-8.37 (1H, d, J = 8 Hz), 8.48-8.50 (1H, d, J = 7.2 Hz), 8.685-8.6940 (1H, d, J = 3.6 Hz). $^{13}$C NMR (CDCl$_3$ 400MHz) δ 23.3, 28.2, 28.5, 47.1, 51.4, 57.2, 136.6, 137.7, 148.8, 149.1, 149.6, 154.7, 155.6, 155.9. GCMS : m/z = 406 [M$^+$] for C$_{22}$H$_{26}$N$_6$O$_2$. Elemental analysis: Found: C, 65.12; H, 6.38; N, 20.31, Calcd: C, 65.01; H, 6.45; N, 20.68 for C$_{22}$H$_{26}$N$_6$O$_2$.

**Preparation of Pyrrolidine methylene triazole bipyridine (5):** To Boc-protected product 4 (406 mg, 1.0 mmol), CH$_2$Cl$_2$-TFA (30 mL, 50:50) was added slowly at ice temperature. The mixture was warmed to room temperature and stirred for 2 hrs. After evaporating reaction mixture to dryness under vacuo, the residue was dissolved in CH$_2$Cl$_2$ (15 mL) and then treated with a saturated NaHCO$_3$ solution (30 mL) for 1h at room temperature. The aqueous layer was extracted with CH$_2$Cl$_2$ (10 mL x 3) and combined extracts were dried over anhydrous Na$_2$SO$_4$. After filtration the CH$_2$Cl$_2$ was evaporated to obtain light yellowish solid of free amine 5 (300 mg, Yield 98 %). $^1$H NMR (400 MHz, CDCl$_3$) δ 1.54-1.61 (1H, m), 1.74-1.86 (2H, m), 1.97-2.05 (2H, m), 2.97-3.03 (2H, m), 3.68-3.75 (1H, m), 4.30-4.54 (2H, m), 7.31-7.34 (1H, ddd, J = 1.2 Hz, 3.6 Hz, 1.2 Hz), 7.81-7.85 (1H, td, J = 6 Hz, 1.6 Hz), 7.88-7.93 (1H, t, J = 7.6 Hz), 8.17-8.19 (1H, dd, J = 7.2 Hz, 0.8 Hz), 8.33-8.35 (1H, dd, J = 7.2 Hz, 0.8 Hz), 8.39 (1H, s), 8.48-8.50 (1H, d, J = 8 Hz), 8.69-8.70 (1H, dd, J = 4 Hz, 0.8 Hz). $^{13}$C NMR (CDCl$_3$ 400MHz) δ 25.3, 28.9, 46.4, 55.4, 57.8, 119.8,
Preparation of Dansylated pyrrolidine methylene triazole bipyridine (BD 1): To a solution of free amine 5 (300 mg, 0.98 mmol) and dansyl chloride (264 mg, 0.98 mmol) in dry DMF (15 mL) triethylamine (TEA) (0.27 mL, 1.96 mmol) was added drop wise over 30 min. The reaction mixture was stirred for 3 hrs at room temperature. After removal of solvent in vacuo, the residue was dissolved in CH$_2$Cl$_2$ (15 mL) and was washed with water (10 mL x 3). The organic phase was dried over Na$_2$SO$_4$ and solvent was evaporated on rotavap. The crude product was purified by column chromatography on silica gel using chloroform-methanol (10:1) as an eluent to afford green fluorescent solid 1 in good yield (520 mg, 98 %). M.P. 76-78 °C. [α]$_D$$^{25}$ +71.25 (c 1.0, CH$_3$OH). $^1$H NMR (400 MHz, CDCl$_3$) δ 1.35-1.46 (1H, m), 1.54-1.63 (1H, m), 1.73-1.82 (1H, m), 1.98-2.04 (1H, m), 2.78 (1H, s), 3.24-3.33 (2H, m), 4.26-4.31 (1H, m), 4.64-4.77 (2H, m), 7.17-7.19 (1H, d, J = 7.6 Hz), 7.33-7.36 (1H, m), 7.54-7.62 (1H, m), 7.89-7.93 (2H, m), 8.14-8.17 (1H, dd, J = 6.8 Hz, 0.8 Hz), 8.27-8.29 (1H, dd, J = 6.4 Hz, 0.8 Hz), 8.36-8.38 (1H, dd, J = 6.8 Hz, 0.8 Hz), 8.41 (1H, s), 8.53-8.60 (3H, m), 8.69-8.71 (1H, ddd, J = 2.4 Hz, 0.8 Hz, 0.8 Hz, 0.8 Hz). $^{13}$C NMR (CDCl$_3$ 400MHz) δ 23.8, 29.1, 45.3, 49.2, 54.0, 58.9, 115.4, 119.2, 120.0,120.1, 121.2, 123.2, 123.4, 123.8, 128.4, 130.1, 130.2, 130.6, 131.0, 133.1, 136.9, 137.7, 148.8, 149.1, 149.5, 151.8, 155.7, 155.9. LCMS: m/z = 540.28 [M$^+$ + H] for C$_{29}$H$_{29}$N$_7$O$_2$S. Elemental analysis: Found: C, 64.43; H, 5.52; N, 17.88; S, 5.42; Calcd: C, 64.54; H, 5.42; N, 18.17; S, 5.94. for C$_{29}$H$_{29}$N$_7$O$_2$S. Elemental analysis for BD 1•Al(ClO$_4$)$_2$•2H$_2$O: Found, C, 38.74; H, 3.95; N, 10.43; S, 3.36; Calcd, C, 38.66; H, 3.69; N, 10.88; S, 3.56. for C$_{29}$H$_{33}$AlCl$_3$N$_7$O$_{16}$S.
3. General method of UV-Vis and fluorescence titration

UV-vis spectra were recorded on a Perkin Elmer Model Lambda 900 spectrophotometer and fluorescence spectra were recorded on a Perkin Elmer model LS 55 spectrophotometer. 1mm cell was used for both types titration. For UV-vis and fluorescence titrations, stock solution of BD 1 was prepared (c = 500 µM) in acetonitrile. The solution of guest cations was prepared in acetonitrile in the order of 10^{-3}. Working solutions of BD 1 and metal ions were prepared from the stock solutions. Excitation was carried out at 350 nm with all excitation and emission slit widths at 10 and 10 nm, respectively.

![UV-Vis absorption spectra of BD1](image)

**Fig. S1** UV-Vis absorption spectra of BD1 [100 µM] in the presence of different metal ions [100 µM] in acetonitrile.
A series of solutions containing BD 1 and Al(ClO$_4$)$_3$ were prepared such that the sum of the total metal ion and BD 1 concentration remained constant (100 µM). The mole fraction (X) of Al$^{3+}$ was varied from 0.1 to 1.0. The corrected absorbance (OD$_{332}$X$_{Al^{3+}}$x10$^3$) at 332 nm was plotted against the molar fraction of the Al$^{3+}$ solution.

**Fig. S2** UV-Vis absorption spectra of BD 1 [100 µM] upon addition of different equivalents of Al$^{3+}$ in acetonitrile.

**Job Plot by UV-vis method**
4. Determination of Binding Constant

Tsein et al. proposed a calibration equation for 1:1 complexation of a fluoroionophore and Ca$^{2+}$.

Li et al. derived the Tsein equation\(^3\) to the following equations that can be used in any stoichiometric ratio between the ligand and analyte.

\[
[M^{n+}]_m = \frac{1}{n \cdot K} \cdot \frac{1}{[L]_1^{m-1}} \cdot \frac{1-\alpha}{\alpha^n}
\]

Where K is complex equilibrium constant, \(M_nL_m\) is metal-ligand, L is ligand, [L], [M\(^{n+}\)], and [M\(_nL_m\)] are the concentrations of respective species. \(\alpha\) is the ratio between free ligand concentration,
[L], and the initial concentration of ligand, [L]_T. In our case, the stoichiometric ratio of the Al^{3+}: fluoroionophore is 1:1. So, this equation can be written as

\[ [\text{Al}^{3+}] = \frac{1}{K} \cdot \frac{1 - \alpha}{\alpha} \]

The curve fitting experimental data points were calculated from this equation with log K = 3.94.

**Fig. S4** Response parameter values (\(\alpha\)) as a function of the logarithm of Al^{3+} concentration. \(\alpha\) is defined as the ratio between the free ligand (BD 1) concentration and the initial concentration of the ligand.
Fig. S5 Control experiment. UV-Vis absorption spectra of various concentrations of Al(ClO$_4$)$_3$ (0, 1.25, 2.5, 5, 12.5, 25, 62.5, 125, 187.5, 250, 500, 750 and 1000 mM). Inset: absorption intensity in the range 400-600 nm as a function of [Al$^{3+}$].
5. NMR Spectra

$^1$H NMR Spectrum of Boc-pyrrolidine methylene triazole bipyridine (4)
$^{13}$C NMR Spectrum of Boc-pyrrolidine methylene triazole bipyridine (4)
$^1$H NMR Spectrum of Pyrolidine methylene triazole bipyridine (5)
$^{13}$C NMR Spectrum of Pyrolidine methylene triazole bipyridine (5)
$^1$H NMR Spectrum of Dansylated pyrrolidine methylene triazole bipyridine (BD 1)
$^{13}$C NMR Spectrum of Dansylated pyrrolidine methylene triazole bipyridine (BD 1)
6. Mass spectral analysis of BD 1•Al$^{3+}$•2H$_2$O complex

MALDI-MS spectrum of complex BD 1•Al$^{3+}$•2H$_2$O in acetonitrile.
7. Thermogravimetric Analysis

Fig. S6 Thermogravimetric analysis of BD 1·Al^{3+} Complex. Experimentally 3.98% water loss is corresponding to two water molecules.
8. IR Spectra

Fig. S7 IR spectra of BD 1 and complex BD 1·Al\(^{3+}\)·2H\(_2\)O.
9. Observed Colour Changes during UV and visible sensing of $\text{Al}^{3+}$ using BD 1

**Fig. S8** Colour changes on addition of $\text{Al}^{3+}$ to **BD 1** solution. Visible color change shown corresponding to addition of excess of $\text{Al}^{3+}$ salt.
10. References

