

Supporting Information

A new strategy for ratiometric fluorescence detection of transition metal ions

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Experimental Details

Materials and Methods. The solvents used in this study, tetrahydrofuran and acetonitrile were rigorously purified following standard procedure. All other reagents are commercially available and used as received. Column chromatography was performed using Brockman I activated neutral aluminium oxide (150 mesh). Thin-layer chromatography (TLC) analysis was performed using Merck F254 aluminium oxide-60 and viewed by UV light. IR spectra were recorded on a Jasco FT-IR/5300 spectrometer as KBr pellets. NMR spectra were recorded on a Bruker AVANCE 400 MHz spectrometer at ambient temperature and were referenced to the internal ^1H and ^{13}C solvent peaks. The absorption and fluorescence spectra were recorded on a Shimadzu spectrophotometer (UV-3101PC) and a Spex spectrofluorimeter (Fluoromax-3), respectively. All fluorescence spectra were corrected for instrumental response. The fluorescence decay profiles were recorded on a single photon-counting spectrofluorimeter (IBH-nanoLED).

Synthesis of N,N-dimethyl-N'-anthracen-9-ylmethylethylenediamine (2). 9-anthranaldehyde (1 g, 5 mmol) and N,N-dimethylethylenediamine (0.6 mL, 5.5 mmol) were taken in ethanol (50 mL) and the reaction mixture was stirred for 36 h at room temperature. The Schiff base formed was not isolated but immediately treated with an excess of solid NaBH₄ and the mixture was heated to reflux for 4 h. The pale yellow solid remained after complete removal of the solvent under reduced pressure was shaken with water (100 mL) and the desired product was extracted with CHCl₃ (3 × 50 mL). The organic layer, after drying over anhydrous Na₂SO₄, was filtered and completely evaporated to obtain **2** as a brown semisolid. Yield 92%. The product was characterized by the following analytical results.

CHN analysis calculated for C₁₉H₂₂N₂: C, 82.01; H, 7.91; N, 10.07. Found: C, 81.73; H, 8.07; N 9.91.

¹H NMR (CDCl₃, 400 MHz): δ (ppm) 2.17 (s, 6H), 2.47 (t, 2H), 2.93 (t, 2H), 4.73 (s, 2H), 5.23 (s, 1H), 7.44 (t, 2H), 7.52 (t, 2H), 7.88 (d, 2H), 8.3 (m, 3H).

Synthesis of N-Anthracen-9-ylmethyl-N-7-nitrobenzoxa[1,3]diazol-4-yl-N',N'-dimethylethylenediamine (1). **2** (0.1 g, 0.36 mmol) and K₂CO₃ (0.55 g, 0.4 mmol) were taken in ethylacetate (25 mL) and the mixture was stirred for 30 min. The solution was then cooled to 0°C and subsequently a solution of 4-chloro-7-nitrobenzoxa[1,3]diazole (0.07 g, 0.35 mmol) dissolved in ethylacetate (20 mL) was added drop-wise with continued stirring for 2 h maintaining the temperature at 0 – 5°C. The reaction mixture was then brought to room temperature and stirred for another 2 h to ensure the completion of the reaction. Subsequently, the solvent was evaporated under

vacuum and the residue was purified by column chromatography (neutral alumina, hexane/ethylacetate). Yield 70%. The desired product isolated as an orange-red coloured solid was characterized by the following analytical results.

CHN analysis calculated for C₂₅H₂₃N₅O₃: C, 68.03; H, 5.22; N, 15.87. Found: C, 67.72; H, 4.97; N, 16.05.

¹H NMR (CDCl₃, 400MHz): δ (ppm) 2.03 (s, 6H), 2.55 (t, 2H), 3.33 (t, 2H), 4.45 (s, 2H), 7.12(m, 3H), 7.79-7.81 (m, 6H), 8.24 (d, 1H), 8.56 (d, 1H).

Table S1. Absorption and fluorescence properties of **1**, **ANBD**, and **anthracene** in tetrahydrofuran (THF) and acetonitrile (AN).

Compound	THF			AN		
	λ (abs.)/nm	λ (flu.)/nm	Φ_f^a	λ (abs.)/nm	λ (flu.)/nm	Φ_f^a
1	351,369,389	397,420,444	0.0023 ^b	350,366,386	393,416,440	0.0019 ^b
	468	528	0.46 ^c	473	548	0.35 ^c
ANBD	445	525	0.90	447	532	0.70
Anthracene	339,358,377	382,403,427	0.297	338,357,376	378,399,423	0.29

^a \pm 10%; ^b Measured for the short wavelength anthracene-like emission; $\lambda_{exc.}$ = 350 nm. ^c Measured for the long wavelength **ANBD**-like emission; $\lambda_{exc.}$ = 440 nm.

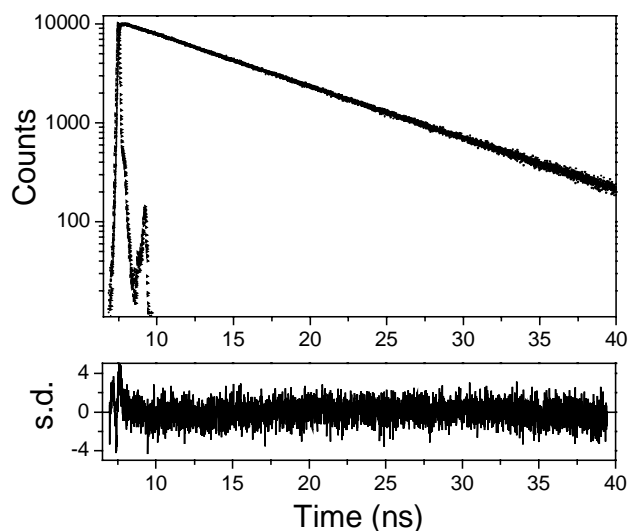


Figure S1. Fluorescence decay behaviour of **1** in THF. The solutions were excited at 439 nm and monitored at 550 nm: fit to a single-exponential decay function with $\tau = 8.1$ ns.

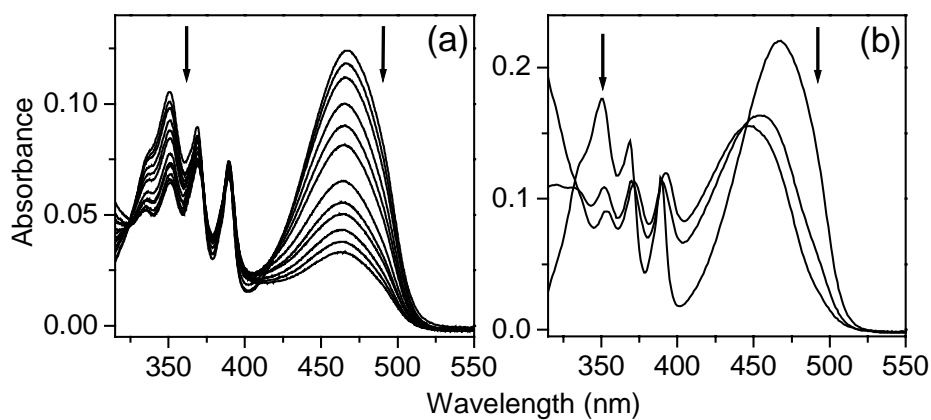


Figure S2. Effect of (a) Zn^{2+} and (b) Cu^{2+} ions on the absorption spectrum of **1** (10^{-5} M) in THF. The various amounts of Zn^{2+} ions in decreasing order of absorbance at 475 nm are 0 – 1.1 equivalents with increments of 0.1 equivalent. The amounts of Cu^{2+} ions are 0, 0.8 and 1.1 equivalents.

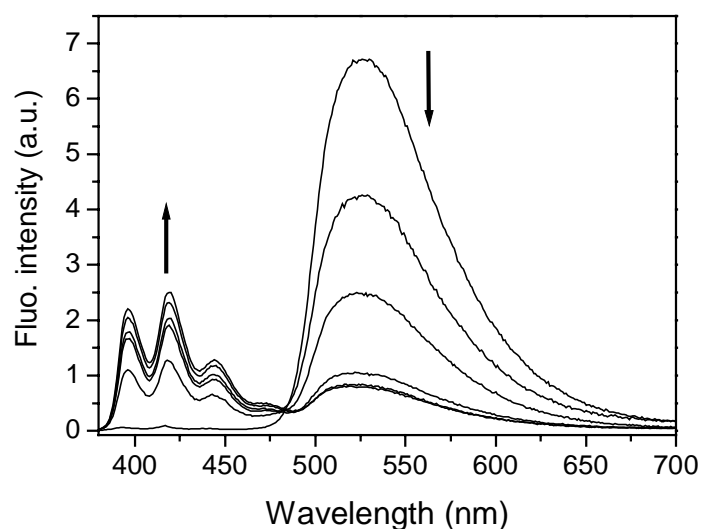


Figure S3. Fluorescence spectra of **1** (10^{-5} M) in THF in the presence of Cu^{2+} ions. The various amounts of Cu^{2+} ions in increasing order of the fluorescence intensity at 425 nm and decreasing order of fluorescence intensity at 550 nm are 0, 0.4, 0.8, 1.1, 1.2 and 1.3 equivalents. $\lambda_{\text{exc.}} = 370$ nm.

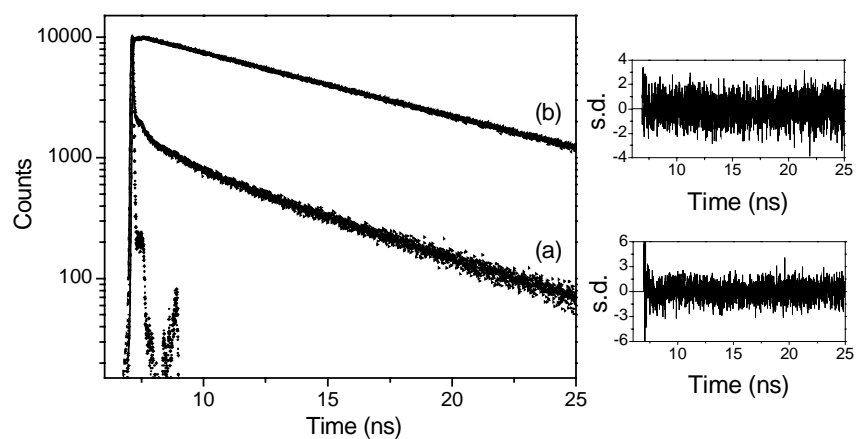


Figure S4. Fluorescence decay curves of **1** (10^{-5} M) in THF as measured at 425 nm (a) in the absence and (b) in the presence of one equivalent of Zn^{2+} ions. The excitation wavelength was 374 nm. The excitation prompt profiles, best exponential fit to the measured decay curves and the corresponding weighted residuals are also shown.