Supporting Information

A Fluorescent Molecular Probe for the Identification of Zinc and Cadmium Salts by Excited State Charge Transfer Modulation

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Experimental Section

General

Solvents and the reagents used were purified and dried by usual methods. All starting materials were obtained from commercial suppliers and used as received. All melting points were determined with a Mel-Temp-II melting point apparatus. ¹H and ¹³C NMR were measured on a 500 MHz Bruker Avance DPX spectrometer or on a Varian Gemini 500 MHz spectrophotometer. IR spectra were recorded on a Nicolet Impact 400D infrared spectrophotometer. Fluorescence quantum yield was determined using optically matching solutions of quinine sulphate ($\Phi_f = 0.54$ in 1N H₂SO₄) and rhodamine B ($\Phi_f = 0.7$ in ethanol) as standard and the quantum yield is calculated using equation 1.

where, A_s and A_r are the absorbance of the sample and reference solutions, respectively at the same excitation wavelength, F_s and F_r are the corresponding relative integrated fluorescence intensities and η is the refractive index of the solvent.

Fluorescence lifetimes were measured using IBH (FluoroCube) time-correlated picosecond single photon counting (TCSPC) system. Solutions were excited with a pulsed diode laser (<100 ps pulse duration) at a wavelength of 375 nm (NanoLED-11) with a repetition rate of 1 MHz. The detection system consists of a microchannel plate photomultiplier (5000U-09B, Hamamatsu) with a 38.6 ps response time coupled to a monochromator (5000M) and TCSPC electronics (Data Station Hub including Hub-NL, NanoLED controller and preinstalled Fluorescence Measurement and Analysis Studio(FMAS) software). The fluorescence lifetime values were determined by deconvoluting the instrument response function with biexponential decay using DAS6

decay analysis software. The quality of the fit has been judged by the fitting parameters such as χ^2 (< 1.2) as well as the visual inspection of the residuals.

Synthesis and characterization

Method for the preparation of 1



A suspension of sodium hydride (0.288 g, 12 mmol) in dry THF was added slowly to a solution of the bisphosphonate (2) (0.912 g, 2 mmol) and the 9-decyl-9H-carbazole-3carbaldehyde (3) (1.35 g, 4 mmol) in THF. After refluxing for 12 h, the fluorescent reaction mixture obtained was cooled followed by the removal of THF under reduced pressure to give the residue. The residue was suspended in water and extracted with dichloromethane. The organic layer was washed with brine, dried over Na₂SO₄ and concentrated to give the crude product, which was further purified by column chromatography over basic alumina using petroleum ether/ethyl acetate (8:2) mixture as eluent. Yield = 45 %; mp: 169-172 °C; FT-IR (KBr)v_{max} 2922, 2850, 1624, 1597, 1469, 1381, 1350, 1259, 1095, 960, 802, 744 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ 8.82 (s, 2H, ArH), 8.44-8.42 (d, 2H, ArH), 8.28(s, 2H, ArH), 8.17-8.15(d, 2H, ArH), 8.03-8.01 (d, 2H, ArH), 7.72-7.70(d, 2H, ArH), 7.52-7.40 (m, 8H, ArH), 7.30-7.27 (d, 2H, vinylic, J =15 Hz), 7.19-7.16 (d, 2H, vinylic, J=15 Hz), 4.32-4.29 (t, 4H -NCH₂, J = 15 Hz), 1.90 (m, 4H, CH₂), 1.66 (s, 4H, CH₂), 1.40-1.37 (m, 24H, CH₂), 0.90-0.88 (t, 6H, -CH₃); ¹³C NMR (125 MHz, CDCl₃): δ 154.20, 147.92, 140.89, 140.57, 133.52, 132.93, 131.85, 127.91, 125.93, 124.56, 123.26, 122.84, 121.91, 120.85, 120.47, 119.15, 119.06, 109.00, 43.24, 31.86, 29.40, 22.67, 14.12; FAB-MS [M+H]+ :Calcd for C₅₈H₆₇N₄, 819.53; found, 820.59.



Figure S1. Absorption spectral changes of 1 (6×10^{-6} M) in hexane (-----), CHCl₃ (-----), acetonitrile (-----), DMSO (------).



Figure S2. a) Emission spectral changes of 1 [6×10^{-6} M, $\lambda_{ex} = 400$ nm] in hexane (____), CHCl₃ (____), acetonitrile (____), DMSO (____). The corresponding emission color changes under 365 nm uv light are shown in the inset. (b) Fluorescence decay profile of 1 in hexane (λ_{em} =430 nm), CHCl₃ (λ_{em} =476 nm), acetonitrile (λ_{em} =504 nm), DMSO (λ_{em} =514 nm) λ_{ex} = 335 nm.



Figure S3. a) Emission spectral response of 1 (6×10^{-6} M) in chloroform upon addition of $Zn(NO_3)_2$ (0-1 eqv.). Inset figure shows the Job's plot showing the 1:1 binding of 1 to $Zn(NO_3)_2$. b) Plot of fluorescence intensity of 1 (6μ M) monitored at 596 nm with different metal ions.



Figure S4. Changes in the (a) absorption and (b) emission spectra of **1** (5.6 μ M) upon addition of Zn(ClO₄)₂ (0 – 1 eqv.) in chloroform.



Figure S5. Changes in the (a) absorption spectra of **1** (5.6 μ M) upon addition of Zn(NO₃)₂ (0 – 1.3 eqv) in chloroform.



Figure S6. Changes in the (a) absorption and (b) emission spectra of **1** (8 μ M) upon addition of ZnCl₂ (0 – 2 eqv.) in chloroform.



Figure S7. a) Job's plot showing the 1:1 binding of 1 to $Zn(ClO_4)_2$ in chloroform. b) Benesi-Hildebrand plot for $1+Zn^{2+}$ system.



Figure S8. Plot showing the response of 1 (6×10^{-6} M) with various cations. The emission intensity monitored at 563 nm in chloroform. Black bars represent response of 1 with different cations. Gray bars shows the enhancement in emission of 1 with $Zn(NO_3)_2$ in the presence of different cations.

Salts	λ_{em}/nm	$\Phi_{\mathrm{f}}{}^{\mathrm{a}}$	τ^{b} /ns
$Zn(ClO_4)_2$	597	0.30 ±.02	2.17
$Zn(NO_3)_2$	563	0.40 ±.01	1.89
ZnCl ₂	554	0.50 ±.02	1.81
Zn(OAc) ₂	548	0.50 ±.01	1.76

Table S1. Photophysical properties of **1** with different zinc salts in chloroform.[a] Fluorescence quantum yield were measured using rhodamine B as standard ($\Phi_f = 0.7$ in ethanol) [b] Fluorescence decay profiles were recorded (±5 % error) by excitating at 375 nm, emission monitored at the emission maximum.

Salts	λ_{em}/nm	$\Phi_{\rm f}{}^{\rm a}$	τ^{b} /ns
$Cd(ClO_4)_2$	574	0.33 ±.01	1.94
Cd(NO ₃) ₂	557	0.41 ±.01	1.81
CdCl₂	550	0.65 ±.02	1.65
Cd(OAc) ₂	541	0.65 ±.01	1.51

Table S2. Photophysical properties of 1 with different cadmium salts in chloroform.[a] Fluorescence quantum yield were measured using rhodamine B as standard ($\Phi_f = 0.7$ in ethanol) [b] Fluorescence decay profiles were recorded (±5 % error) by excitating at 375 nm, emission monitored at the emission maximum.



Figure S9. ¹H NMR of 1 in CDCl₃.



Figure S10. ¹³C NMR of 1 in CDCl₃.