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. $^1$H and $^{13}$C 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 H$_2$SO$_4$) and rhodamine B ($\Phi_f = 0.7$ in ethanol) as standard and the quantum yield is calculated using equation 1.

\[
\Phi_f = \Phi_r \left( \frac{A_r F_r}{A_s F_s} \right) \left( \frac{\eta_s^2}{\eta_r^2} \right) \quad (1)
\]

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 $\eta$ 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 $\chi^2 (< 1.2)$ 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-3-carbaldehyde (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 Na$_2$SO$_4$ 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)$\nu_{max}$ 2922, 2850, 1624, 1597, 1469, 1381, 1350, 1259, 1095, 960, 802, 744 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 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 -NCH$_2$, $J$ = 15 Hz), 1.90 (m, 4H, CH$_2$), 1.66 (s, 4H, CH$_2$), 1.40-1.37 (m, 24H, CH$_2$), 0.90-0.88 (t, 6H, -CH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 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 C$_{58}$H$_{67}$N$_4$, 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, λₑₓ = 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 (λₑₓ=430 nm), CHCl₃ (λₑₓ=476 nm), acetonitrile (λₑₓ=504 nm), DMSO (λₑₓ=514 nm) λₑₓ=335 nm.
**Figure S3.** a) Emission spectral response of 1 (6 × 10⁻⁶ M) in chloroform upon addition of Zn(NO₃)₂ (0–1 eqv.). Inset figure shows the Job’s plot showing the 1:1 binding of 1 to Zn(NO₃)₂. b) Plot of fluorescence intensity of 1 (6 μM) monitored at 596 nm with different metal ions.

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

**Figure S5.** Changes in the (a) absorption spectra of 1 (5.6 μM) 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 μM) upon addition of ZnCl$_2$ (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.
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 ($\pm 5 \%$ error) by exciting at 375 nm, emission monitored at the emission maximum.

<table>
<thead>
<tr>
<th>Salts</th>
<th>$\lambda_{em}$ /nm</th>
<th>$\Phi_f$</th>
<th>$\tau_b$ /ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(ClO$_4$)$_2$</td>
<td>597</td>
<td>0.30 ±.02</td>
<td>2.17</td>
</tr>
<tr>
<td>Zn(NO$_3$)$_2$</td>
<td>563</td>
<td>0.40 ±.01</td>
<td>1.89</td>
</tr>
<tr>
<td>ZnCl$_2$</td>
<td>554</td>
<td>0.50 ±.02</td>
<td>1.81</td>
</tr>
<tr>
<td>Zn(OAc)$_2$</td>
<td>548</td>
<td>0.50 ±.01</td>
<td>1.76</td>
</tr>
</tbody>
</table>

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 ($\pm 5 \%$ error) by exciting at 375 nm, emission monitored at the emission maximum.

<table>
<thead>
<tr>
<th>Salts</th>
<th>$\lambda_{em}$ /nm</th>
<th>$\Phi_f$</th>
<th>$\tau_b$ /ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(ClO$_4$)$_2$</td>
<td>574</td>
<td>0.33 ±.01</td>
<td>1.94</td>
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<tr>
<td>Cd(NO$_3$)$_2$</td>
<td>557</td>
<td>0.41 ±.01</td>
<td>1.81</td>
</tr>
<tr>
<td>CdCl$_2$</td>
<td>550</td>
<td>0.65 ±.02</td>
<td>1.65</td>
</tr>
<tr>
<td>Cd(OAc)$_2$</td>
<td>541</td>
<td>0.65 ±.01</td>
<td>1.51</td>
</tr>
</tbody>
</table>
Figure S9. $^1$H NMR of 1 in CDCl$_3$. 
Figure S10. $^{13}$C NMR of 1 in CDCl$_3$. 