Supporting Information

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A New Thiophene-based Aggregation-induced Emission Chemosensor for Selective Detection of Zn²⁺ Ions and Its Turn Off

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Materials and Method

1.1. General Methods, Reagents and Measurements¹

All the reagents were purchased from Sigma-Aldrich (USA), SD-Fine chemicals (India), HI-MEDIA and used without further purification. Freshly prepared double distilled water was used in that experiment. Double distilled water obtained by smart2pure 6UV/UF water purifier (thermo-scientific). The solvents used were purified by standard methods. The aqueous solutions of different metal ions were prepared by dissolving KCl, NaCl, LiCl, CaCl₂, MgCl₂, FeCl₃, AgCl, AuCl₃, AlCl₃, BaCl₂, MnCl₂, CoCl₂, FeCl₂, NiCl₂, CdCl₂, PbCl₂, CuCl₂, ZnCl₂ and HgCl₂ in dd water. 2-aminophenol, thieno[2,3-b]thiophene-2,5-dicarbaldehyde were procured from Sigma-Aldrich (USA). A reported synthetic procedure was used to synthesize probe (**L**¹) with minor modification.

Solid-phase FT-IR spectra were recorded in Perkin-Elmer UATR TWO FT-IR Spectrometer, UV-Visible and emission spectra were recorded in Perkin-Elmer UV/VIS spectrometer and HITACHI F-7000 Fluorescence spectrophotometer respectively. Fluorescence lifetime measurement was carried out in Time-correlated single-photon-counting (TCSPC) spectrometer (Horiba Jobin Yvon) in which nanosecond laser of 375 nm was used as the excitation wavelength and the data were analyzed by bi-exponential fitting program using IBH DAS-6 decay analysis software. Molar conductivity measurements were done by using EUTECH INSTRUMENT CON 510 (India) conductivity meter. NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer, using CDCl₃ as solvent and tetramethylsilane (TMS) as the internal standard. Mass spectra (MS) were recorded with Bruker Esquire 3000 Plus spectro-photometer (Bruker-Franzen Analytic GmbH, Bremen, Germany). The DLS measurement for the hydrated particle size was done by the Malvern ZETASIZER nanoZS90 instrument. SEM measurement was done by using a Nova Nano SEM-450 model Scanning Electron Microscopy. All the theoretical calculations for ligand and complexes were carried out using Gaussian 09 rev. A.02. The input files to Gaussian 09 were prepared with Gauss view 5.0.8. The IUPAC names of all the compounds were determined by using ChemDraw professional 15.

1.2. Luminescence lifetime measurement²⁻³

The fluorescence lifetime of the ligand (**L**¹) and **Zn**²⁺ complex in MeOH at room temperature were determined by Time-correlated single-photon-counting (TCSPC) spectrometer (Horiba Jobin Yvon). Nanosecond laser of 375 nm was used as excitation source in following the decay kinetics. The data were analyzed by a bi-exponential fitting program using IBH DAS-6 decay analysis software considering reduced χ^2 -square value.

$$f(t) = a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2}$$

The average emission lifetime value (τ_{av}) of all the complexes have been determined using following from lifetime components (τ_1 and τ_2) and their corresponding pre-exponential contribution (a_1 and a_2).

$$\langle \tau \rangle = \frac{a_1 \tau_1^2 + a_2 \tau_2^2}{a_1 \tau_1 + a_2 \tau_2}$$

The Time resolved fluorescence spectroscopy measurements were carried out further to understand the mechanism of the turn-on sensor responses of **L**¹ toward **Zn**²⁺ ion. The fluorescence lifetime (τ) of **L**¹ (0.10 mM) in CH₃OH is 2 ns, when we added 1 equiv. of **Zn**²⁺, the fluorescence lifetimes almost ~4 times enhancement have been observed.

1.3. DLS and SEM Measurement⁴⁻⁵

The diffusion coefficients of molecules or particles undergoing Brownian motion can be measured by the DLS technique. Firstly, we have prepared one equivalent of ligand (**L**¹) and various equivalent concentrations of **Zn**²⁺ in CH₃CN. All the measurements were done at 25°C by using Malvern Zetasizer Nano S (Malvern Instruments Ltd., UK) with a detection angle of 173°. All the measurement were repeated three times for each sample to get a precise result. The Nano S uses a 4 mW He–Ne laser operating at a wavelength of 633 nm. The average particle size of the aggregated **L**¹ in CH₃CN is 68 nm. However, upon addition of 1 equivalent of **Zn**²⁺, the average size is found to be ~151 nm and the addition of 5 and 10 equivalents of **Zn**²⁺ resulted in a significant enhancement in the average size of aggregates, with average size is about ~396 nm and 1916 nm.

A scanning electron microscope (SEM) scans a focused electron beam over a surface to create an image. The electrons interact with atoms in the sample, producing various signals that contain information about the surface topography and composition of the sample. Scanning electron microscope (SEM) methods provide two-dimensional images of nanoparticles; these images can be used to produce number-based size distributions. The average particle size of the aggregated **L**¹+**Zn**²⁺ (5 equivalents) and **L**¹+**Zn**²⁺ (10 equivalents) are 300 nm and 750 nm by using scanning electron microscope (SEM) analysis.

1.4. Computational details⁶⁻⁷

Theoretical calculations of the ligand and complex were carried out using Gaussian 09 rev. A.02.

The input files to Gaussian 09 were prepared with Gauss view 5.0.8. The geometric structure of the complex, and ligand in the ground state were fully optimized at the B3LYP/GEN level by using 6-31G(d,p) basis set for H, C, N, O, S atoms and LANL2DZ basic set for Zn^{2+} atom in the gas phase using the DFT.

2. Synthesis and Characterization

2.1. Synthesis of the L^1

A reported synthetic procedure was used to synthesize thiophen-based Schiff base ligand (L^1) with minor modification and characterized by ^1H NMR, ^{13}C NMR, IR and Q-TOF ESI-MS Spectroscopy.⁸

The probe (L^1) was synthesized according to the published protocol (Berkési et al 2003) in which 2-aminophenol (0.50 g, 2.56 mmol) and thieno[2,3-b]thiophene-2,5-dicarbaldehyde (0.57 g, 5.20 mmol) in hot ethanol and 2 drop of liquor ammonia were mixed with continuous stirring at 80 °C for 4 hours.⁸ The reaction mixture was cooled to room temperature and the reaction was quenched in ice water. The yellow precipitate was filtered, dried and recrystallized from ethanol to give yellowish polycrystalline solid. The synthesized probe (L^1) was characterized analytically and spectroscopically. Yield, 0.67 g (78%, L^1).

L^1 : FT-IR (solid phase): ν (OH, C=N, C-S)/ cm^{-1} : 3390, 1592, 724; ^1H NMR (400 MHz, DMSO-d_6): 9.18 (2H, s), 8.92 (2H, s), 7.91 (2H, s), 7.16 (2H, d, $J = 8$ Hz), 7.09 (2H, m), 6.96 (2H, tri, m), 6.85 (2H, d, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, DMSO-d_6): 154.47, 151.60, 147.69, 147.00, 138.44, 128.14, 127.17, 121.75, 120.44, 117.15; Q-TOF ESI MS (m/z) in CH_3CN : 379.0576 (L^1H^+); $\lambda_{\text{max}} / \text{nm}$ ($\epsilon \times 10^{-4} / \text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 235(0.28), 298(1.012), 380(1.38); Fluorescence properties in CH_3CN , $\lambda_{\text{em}} / \text{nm}$ ($\lambda_{\text{ex}} = 360 \text{ nm}$): 428 nm; Luminescence lifetime (L^1)/ns in CH_3OH at 25 °C: 2 ns.

2.2. Synthesis of Zn^{2+} complex with L^1

Methanolic solution of the ZnCl_2 (0.500 g, 0.36 mmol) was added to CH_3CN solution of probe (L^1) (1.393 g, 0.36 mmol) in a round bottom flask with constant stirring at room temperature for 4 h. The precipitate was filtered, washed with cold methanol and dried over P_4O_{10} . Pure complex ($\text{L}^1 + \text{Zn}^{2+}$) was obtained after recrystallisation from methanol.

For ($\text{L} + \text{Zn}^{2+}$): FT-IR (solid phase): ν (C-S, C=N, M-O, M-N)/ cm^{-1} : 735, 1625, 456, 523; Q-TOF ESI MS (m/z) in CH_3CN : 440.9286 (MH^+); UV-visible spectra in CH_3CN , $\lambda_{\text{max}} / \text{nm}$ ($\epsilon \times 10^{-4} / \text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 460(0.018), 235(0.62), 300(1.69), 393(1.21) Luminescence lifetime, $\tau(\text{L} + \text{Zn}^{2+}) / \text{ns}$ at 25 °C: 7 ns; $\Lambda_{\text{M}} / \Omega^{-1} (\text{S m}^2 \text{ mol}^{-1})$: 65.

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Table S1. Selected Physicochemical data of the ligand (L¹) and Zn²⁺ complex.

Ligand and Complex	L ¹	L ¹ +Zn ²⁺
IR ^[a] : $\nu(\text{OH}, \text{C}=\text{N}, \text{C}-\text{S})/\text{cm}^{-1}$	3390, 1592, 724	1625, 735
$\Lambda_{\text{M}}^{[b]}$: $/\Omega^{-1} \text{ S m}^2 \text{ mol}^{-1}$	-	65
Q-TOF ESI MS (m/z) ^[c]	379.0576(L ¹ H) ⁺	440.9286(MH) ⁺
Electronic spectra ^[d] : $\lambda_{\text{max}} /$ nm ($\epsilon \times 10^{-4} / \text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)	235(0.28), 298(1.012), 380(1.38)	460(0.018), 235(0.62), 300(1.69), 393(1.21)
$\lambda_{\text{em}} / \text{nm}^{[e]}$ [$\epsilon_{\text{ex}}=380 \text{ nm}$]	428	455
Lumination lifetime ^[f] : $\tau_L / RT^j (\text{ns})$	2	7

[a] Infrared data for the ligand and Zn²⁺ complex; [b] Molar conductivity data of the complex in CH₃CN at 25 °C; [c] Q-TOF ESI Mass spectra of the complex recorded in CH₃CN; [d] UV-visible spectra of the complex in CH₃CN at 25 °C; [e] Luminescence spectra of the complex recorded in CH₃CN 25 °C; stoke shift of the complexes; [f] Luminescence lifetime of the complex in CH₃OH.

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Figure S5. UV-visible spectra of the Ligand (L¹) recorded in CH₃CN.

Figure S6. Emission spectra of the Ligand (L¹) (0.10 mM) recorded in CH₃CN [λ_{ex} , 380nm].

Figure S7. Fluorescence spectra of L^1+Zn^{2+} (0.02mM + 0.045 mM) in CH_3CN , upon increasing volume percentages of water from 0% to 90%.

Figure S8. The particle size analysis upon addition of various equivalents $ZnCl_2$ to L^1 in CH_3CN . (a) only L^1 (0 equivalent), (b) $L^1 + Zn^{2+}$ (1 equivalent), (c) $L^1 + Zn^{2+}$ (5 equivalent), (d) $L^1 + Zn^{2+}$ (10

equivalent) determined from DLS measurement.

Figure S9. SEM images of the aggregates obtained on addition of (d) 5 equivalent ZnCl_2 (scale bar: 300 nm) and (e) 10 equivalent ZnCl_2 (Scale Bar: 300 nm) to the L^1 in DMSO.

Figure S10. Time resolved emission spectra of L^1 (0.10 mM) and 1 equivalent of Zn^{2+} in CH_3OH .

Figure S11. Fluorescence spectra of the ligand (L^1), L^1+Zn^{2+} and $L^1+Zn^{2+}+EDTA$ in CH_3CN at $25^\circ C$.

Figure S12. Effect of the pH on luminescence spectra of L^1 (0.10 mM) at $25^\circ C$ [λ_{ex} , 380nm].

Figure S13. UV-Visible spectral traces of L¹(0.1 mM) on addition of different metal ions (0.1 mM) in CH₃CN at 25°C.

Figure S14. UV-visible spectral traces of L^1 (0.1 mM) on the gradual addition of increasing concentration of Zn^{2+} in CH_3CN 25°C.

Figure S15. Job's plot analysis of L¹ with Zn²⁺ in CH₃CN. The change of the absorbance of L¹ was determined from the UV-visible titration.

Figure S16. Q-TOF ESI Mass spectra of the Complex (L^1+Zn^{2+}) (M) recorded in CH_3CN . The peak at m/z 440.9286 corresponds to $[MH]^+$ species.

Figure S17. (a) Effect of the temperature on luminescence spectra of Zn^{2+} complex in 5-40°C. (b) Effect of the light on luminescence spectra of Zn^{2+} complex up to 40 min.

Figure S18. Optimized structure of the ligand (L^1), complex (L^1+Zn^{2+}), and the corresponding HOMO, LUMO energy gap, stereographs. Calculated at DFT/B3LYP/6-31G(d,p)/LanL2DZ level in gas phase with Gaussian 09W.

Figure S19. Combinational INHIBIT logic-gate circuits (a) logic scheme and truth table. (b) Molecular logic gate behaviour of L^1 with the chemical inputs of In A, Zn^{2+} ions; In B, EDTA by considering the emission changes at 447 nm.