

## Electronic Supplementary Information (ESI)

# Azacrown-Oxabridged Macrocyclic: A Novel Hybrid Fluorogenic Chemosensor for Transition and Heavy Metal Ions

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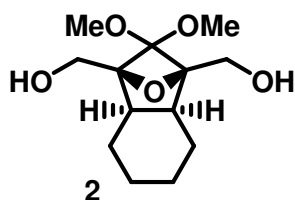
## General Methods:

Melting points were recorded on JSGW melting point apparatus and are uncorrected. IR spectra were recorded as KBr pellets (solids) or thin films (liquids).  $^1\text{H}$  NMR and proton-decoupled  $^{13}\text{C}$  NMR spectra were recorded at 400 and 100 MHz, respectively. Data are reported as follows: (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constant(s) in Hz.). TLC was performed on silica gel coated on microscopic slides. Visualization of spots was effected by exposure to iodine or spraying with 4% ethanolic  $\text{H}_2\text{SO}_4$  and charring. Samples for NMR were made in  $\text{CDCl}_3$ ; tetramethylsilane was used as the internal standard. X-ray data were collected on a Bruker SMART APEX diffractometer. The structures were solved using SIR-92<sup>1</sup> and refined using SHELXL-97<sup>2</sup>.

UV – Visible spectra were recorded on a JASCO V-570 spectrophotometer at 293 K and it was the average of three measurements. The deviation found for molar absorption coefficient in the last digit only. Steady-state Fluorescence spectra were obtained using a Perkin-Elmer LS 50B Luminescence spectrophotometer at 293 K with excitation and emission band-pass, 5 nm;  $\lambda_{\text{ex}} = 350$  nm. Steady-state Fluorescence anisotropy data were obtained using a Perkin-Elmer LS 55 Fluorometer at 293 K with slit width 5nm and integration time 40 sec. Quantum Yield of the all the compounds were determined by comparing the corrected  $\phi_{\text{FT}}$  spectrum with that of anthracene ( $\phi_{\text{F}} = 0.297$ ) in ethanol<sup>3</sup> taking the area under the total emission. The solid-state emission spectra were recorded using a Fluorolog3, model FL3-22, SPEX spectrometer excited at 350 nm with a 450 W Xenon lamp at a band pass of 2 nm and the integration time was kept at 0.2 sec.

## Experimental Procedures:

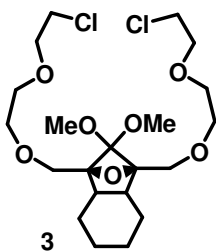
### Compound: 2



2

To a flame dried 50 mL round bottom flask charged with diester **1** (1.59 gm, 5.08 mmol) in 14 mL dry THF NaBH<sub>4</sub> (1.12 gm, 5.95 mmol) was added under argon atmosphere and refluxed for 21 h. Reaction mixture was cooled to room temperature and added ice pieces to quench excess NaBH<sub>4</sub> and diluted with water (20 mL), extracted with ethyl acetate (7 mL x 4) and organic layer washed with water (3 mL x 2), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated afforded the thick liquid which on drying under vacuum yields the colorless solid (1.259 gm). Yield: 96%; mp: 112–114 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.81 (q, *J* = 12.7 Hz, 4H), 3.44 (s, 3H), 3.26 (s, 3H), 2.3 (br, 2H), 2.24 (s, 2H), 1.63 (s, 2H), 1.3 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 108.4 94.5 (2C), 59.1 (2C), 52.2, 51.1, 39.5 (2C), 17.9 (2C), 17.4 (2C); IR (KBr): 3300, 2800, 1450, 1170 cm<sup>-1</sup>; Anal. Calcd. for C<sub>13</sub> H<sub>22</sub> O<sub>5</sub>: C 60.45, H 8.58; Found: C 60.43, H 8.55.

### Compound: 3

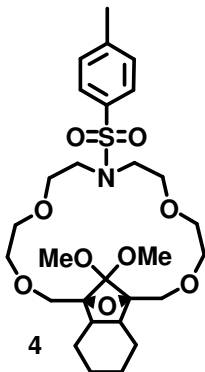


3

To a ice cold solution of diol **2** (500 mg, 1.94 mmol), bis(2-chloroethyl) ether (15 mL) and tetra-*n*-butylammonium hydrogen sulfate (1.32 gm, 3.88 mmol), 50% NaOH solution was added drop wise over 10 min. and the reaction mixture was stirred at room temperature for 48 h under argon atmosphere. 25 mL distilled water followed by 25 mL dichloromethane were added and stirred for 2 min. organic layer was separated and the aqueous layer was extracted by dichloromethane (5 mL x 4), combined organic layer was washed with water (3 mL), brine solution (3 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The product was purified by silica gel column chromatography using 20–30 % ethyl acetate / hexane as eluent afforded 772 mg thick liquid. Yield: 85%, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.79 – 3.51 (m, 20H), 3.46 (s, 3H), 3.27 (s, 3H), 2.39 – 2.33 (m, 2H), 1.69 – 1.67 (m, 2H), 1.47 – 1.32 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 105.7, 94.0 (2C), 71.2 (2C), 70.9 (2C), 70.3 (2C), 65.1 (2C), 51.8,

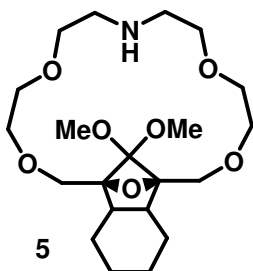
51.6, 42.6 (2C), 39.9 (2C), 18.1 (2C), 17.3 (2C); IR (Neat): 2940, 1454, 1120  $\text{cm}^{-1}$ ; Anal. Calcd. for  $\text{C}_{21} \text{H}_{36} \text{Cl}_2 \text{O}_7$ : C 53.50, H 7.70; Found: C 53.52, H 7.67.

#### Compound: 4



Compound **3** (1.24 gm, 2.63 mmol), anhydrous  $\text{K}_2\text{CO}_3$  (2.9 gm, 20.98 mmol) and p-toluenesulfonamide (540 mg, 3.15 mmol) were taken in dry acetonitrile (20 mL) and refluxed for 63 h under argon atmosphere. 25 mL water followed by 25 mL of dichloromethane was added, stirred for 2 min. Organic layer was separated and the aqueous layer was extracted with dichloromethane (4 mL x 5), washed with water (3 mL) and brine solution (3 mL), dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated. The product was purified by silica gel column chromatography using 40–50 % ethyl acetate / hexane as eluent afforded 802 mg of pale yellowish thick liquid. Yield: 57%,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.64 (d,  $J = 8\text{Hz}$ , 2H), 7.22 (d,  $J = 8.3\text{ Hz}$ , 2H), 3.94 – 3.16 (m, 23H), 3.12 (s, 3H), 2.35 (s, 3H), 2.1 – 2.08 (m, 2H), 1.6 – 1.58 (m, 2H), 1.29 – 1.28 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.2, 136.2, 129.6 (2C), 127.2 (2C), 107.6, 94.4 (2C), 71.2 (2C), 70.7 (2C), 70.1 (2C), 67 (2C), 52.5, 51, 49.9 (2C), 40.85 (2C), 21.5, 18.2 (2C), 18.02 (2C); IR (Neat): 2937, 1598, 1342, 1117  $\text{cm}^{-1}$ ; Anal. Calcd. for  $\text{C}_{28} \text{H}_{43} \text{N O}_9 \text{S}$ : C 59.03, H 7.61, N 2.46; Found: C 59.05, H 7.64, N 2.47.

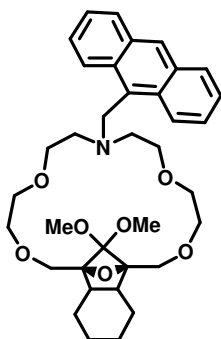
#### Compound: 5



In a flame dried 50 mL two neck round bottom flask charged with naphthalene (495 mg, 386 mmol), sodium metal (111 mg, 4.82 mmol) in dimethoxyethane (6 mL) was stirred at room temperature 1.5 h (until the deep greenish color develop), cooled to  $-55$  to  $-60$   $^\circ\text{C}$  and added compound **4** (275 mg, 0.483 mmol) dissolved in 2 mL of dimethoxyethane drop wise via septum over 5 min and allow to warm to  $-10$   $^\circ\text{C}$  and stirred for about 2 h (TLC). Reaction mixture was quenched with water at the same temperature and diluted with water (10 mL), extracted with dichloromethane (4 mL x 5). The organic layer washed with 1M HCl (4 mL x 5) and resultant aqueous layer was

basified (pH = 10) with NaOH pellet at 0 – 5 °C which upon extracted with dichloromethane (4 mL x 5). Organic layer washed with water (2 mL), brine solution (2 mL) dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The product was purified by neutral alumina column chromatography using 30–40 % ethyl acetate / hexane as eluent afforded 152 mg thick liquid. Yield: 76%, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.87 – 3.49 (m, 16H), 3.37 (s, 3H), 3.19 (s, 3H), 2.78 (t, *J* = 4.9 Hz, 4H), 2.15 (s, 2H), 1.61 (s, 2H), 1.29 – 1.27 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 107.3, 94.4 (2C), 71.3 (2C), 70.5 (2C), 69.9 (2C), 66.1 (2C), 52.5, 51.2, 49.7 (2C), 40.2 (2C), 18.1 (2C), 17.8 (2C); IR (Neat): 3421, 2934, 1634, 1456 cm<sup>-1</sup>; Anal. Calcd. for C<sub>21</sub> H<sub>37</sub> N O<sub>7</sub>: C 60.70, H 8.98, N 3.37; Found: C 60.67, H 8.98, N 3.35.

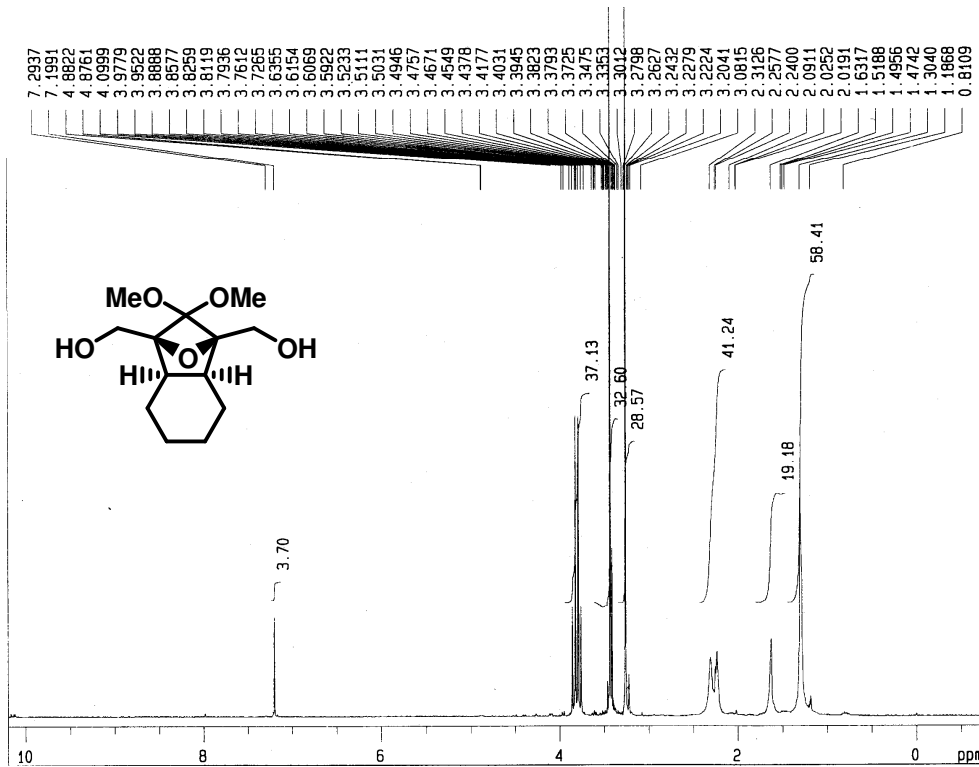
### Compound L1



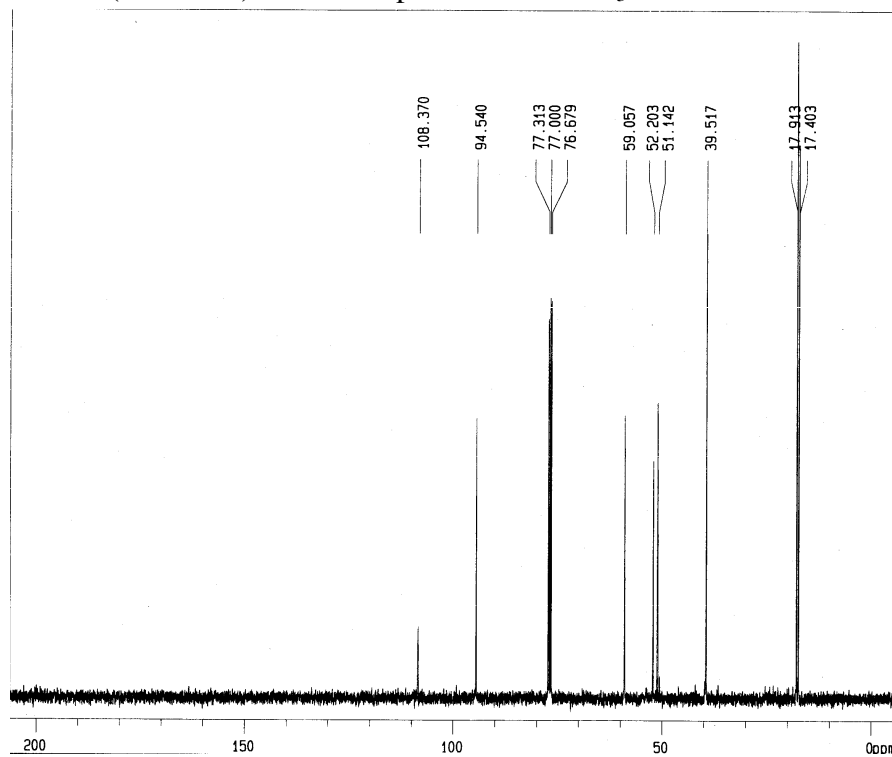
In a flame dried 50 mL round bottom flask compound **5** (100 mg, 0.24 mmol), 9-bromomethyl anthracene (98 mg, 0.361 mmol), K<sub>2</sub>CO<sub>3</sub> (83 mg, 0.6 mmol) and KI (30 mg, 0.18 mmol) were taken in N,N-dimethylformamide (10 mL) and heated to 80 °C for 8 h. Reaction mixture cooled to room temperature diluted with water (10 mL), extracted with ethyl acetate (4 mL x 3), washed with water (2 mL), brine solution (2 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated.

The product was purified by basic alumina column chromatography using 20 % ethyl acetate / hexane as eluent afforded 110 mg pale yellowish solid. Yield: 79%, mp: 120 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.53 (d, *J* = 8.8 Hz, 2H), 8.37 (s, 1H), 7.9 (d, *J* = 8.3 Hz, 2H), 7.49 – 7.4 (m, 4H), 4.59 (s, 2H), 3.91 – 3.46 (m, 16H), 3.36 (s, 3H), 3.19 (s, 3H), 2.9 – 2.82 (m, 4H), 2.19 – 2.17 (m, 2H), 1.74 – 1.67 (m, 2H), 1.36 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 131.3 (2C), 130.3 (2C), 128.8 (2C), 127.4 (2C), 125.5 (2C), 125.3 (2C), 124.7 (2C), 107.3, 94.5 (2C), 71.0 (2C), 70.4 (2C), 69 (2C), 66.3 (2C), 54.3 (2C), 52.4, 52.4, 51.1, 40.5 (2C), 18.2 (2C), 17.9 (2C); IR (KBr): 2800, 1440, 1330, 1080 cm<sup>-1</sup>; Anal. Calcd. for C<sub>36</sub> H<sub>47</sub> N O<sub>7</sub>: C 71.38, H 7.82, N 2.31; Found: C 71.41, H 7.85, N 2.32.

**Copies of <sup>1</sup>H and <sup>13</sup>C spectra:**



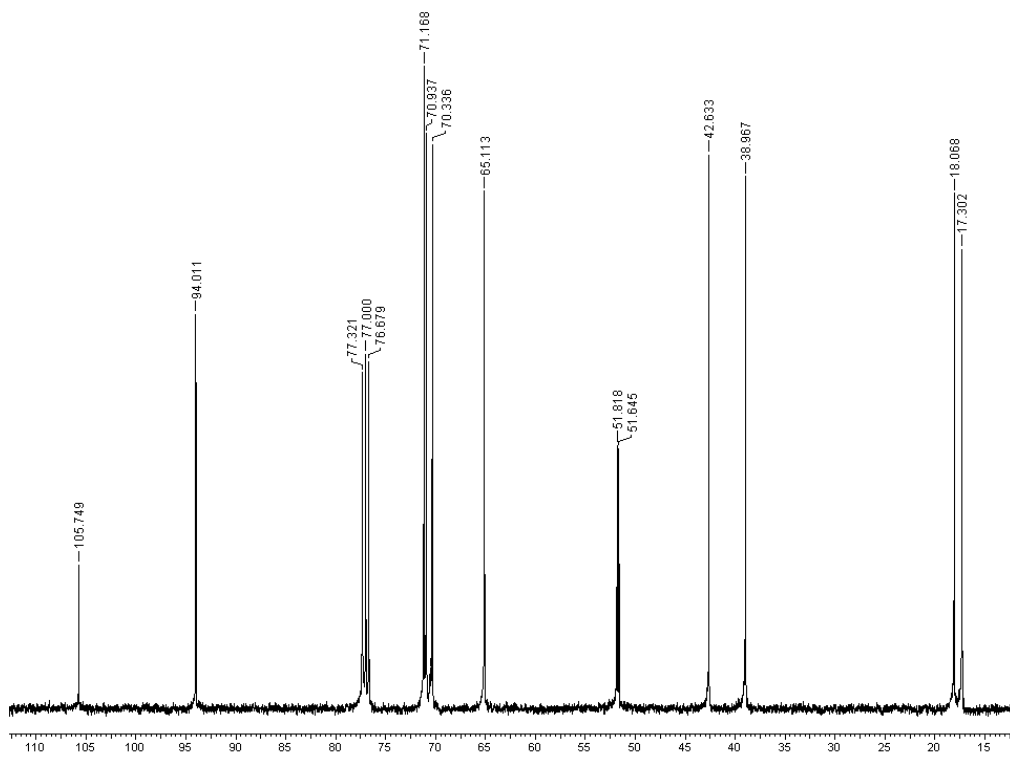
$^1\text{H NMR}$  (400 MHz) of the compound **2** in  $\text{CDCl}_3$



$^{13}\text{C NMR}$  (100 MHz) of the compound **2** in  $\text{CDCl}_3$

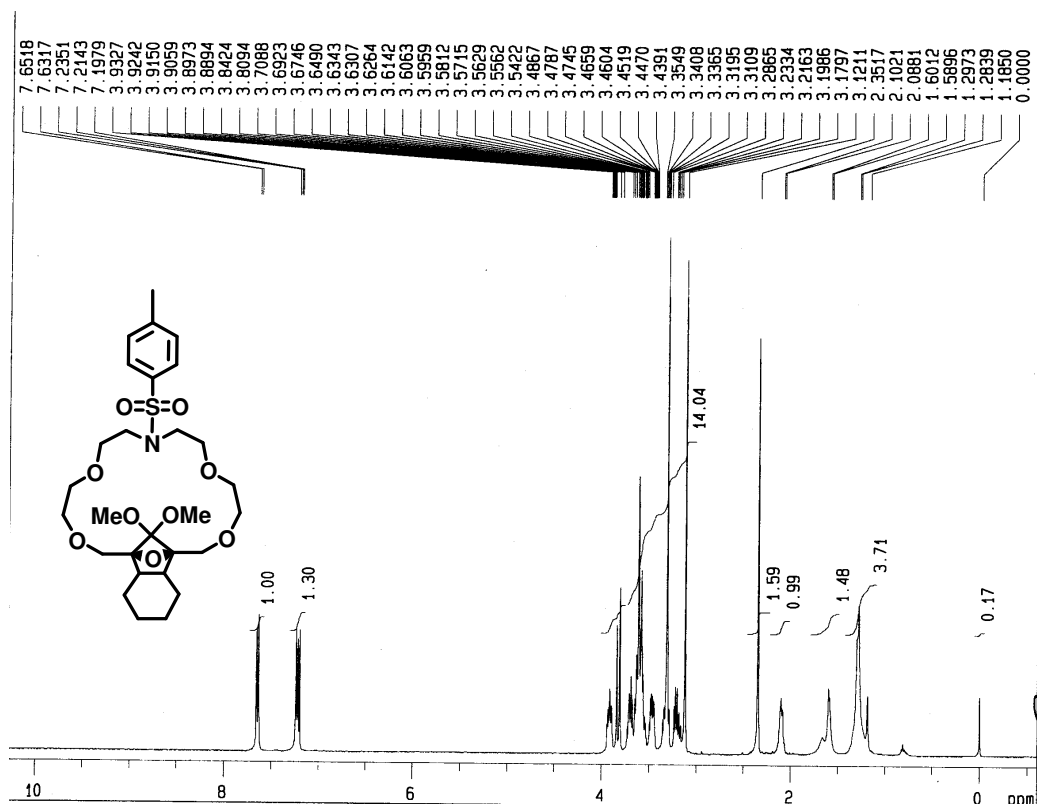


<sup>1</sup>H NMR (400 MHz) of the compound **3** in CDCl<sub>3</sub>

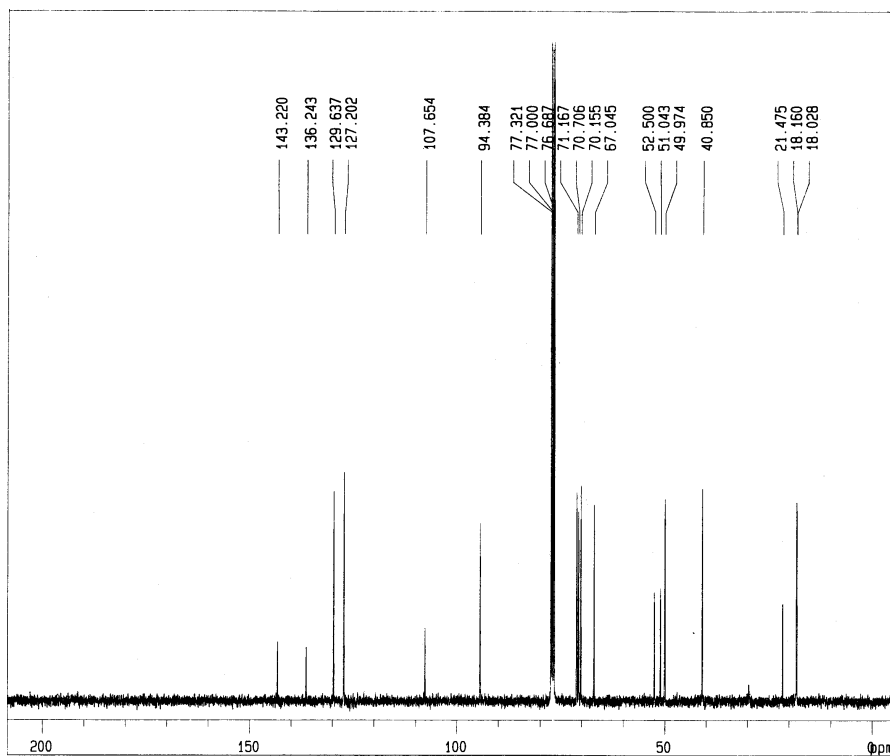


<sup>13</sup>C NMR (100 MHz) of the compound **3** in CDCl<sub>3</sub>

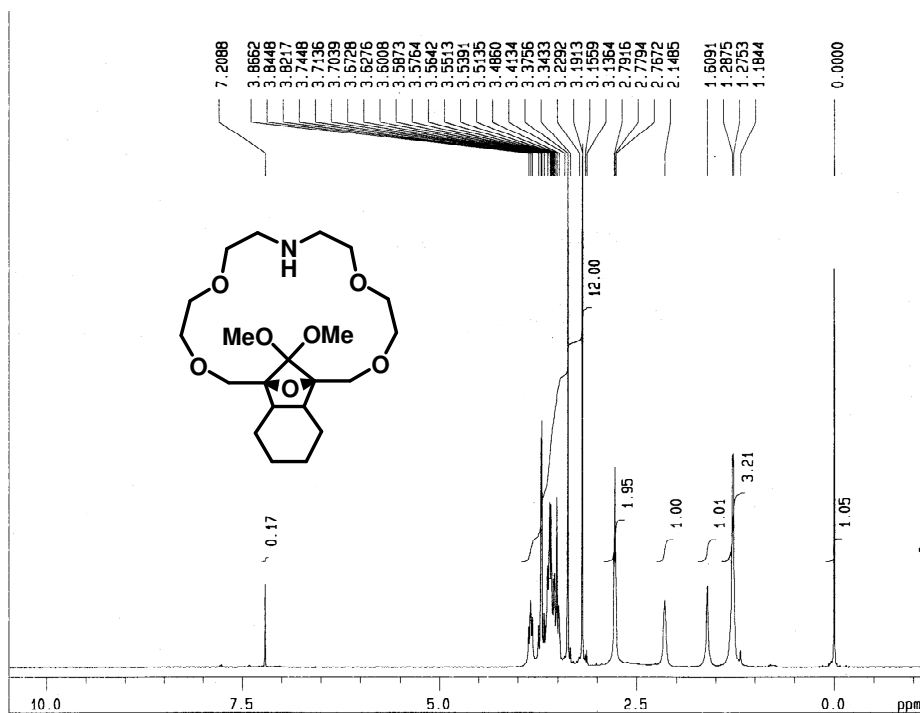




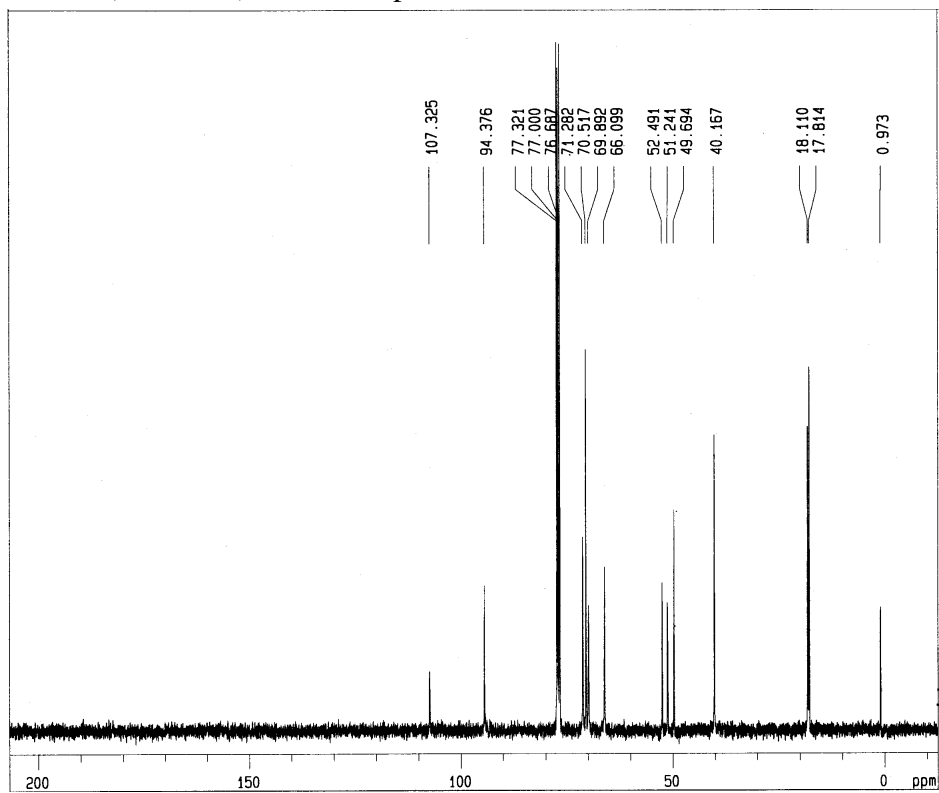
$^1\text{H NMR}$  (400 MHz) of the compound **4** in  $\text{CDCl}_3$



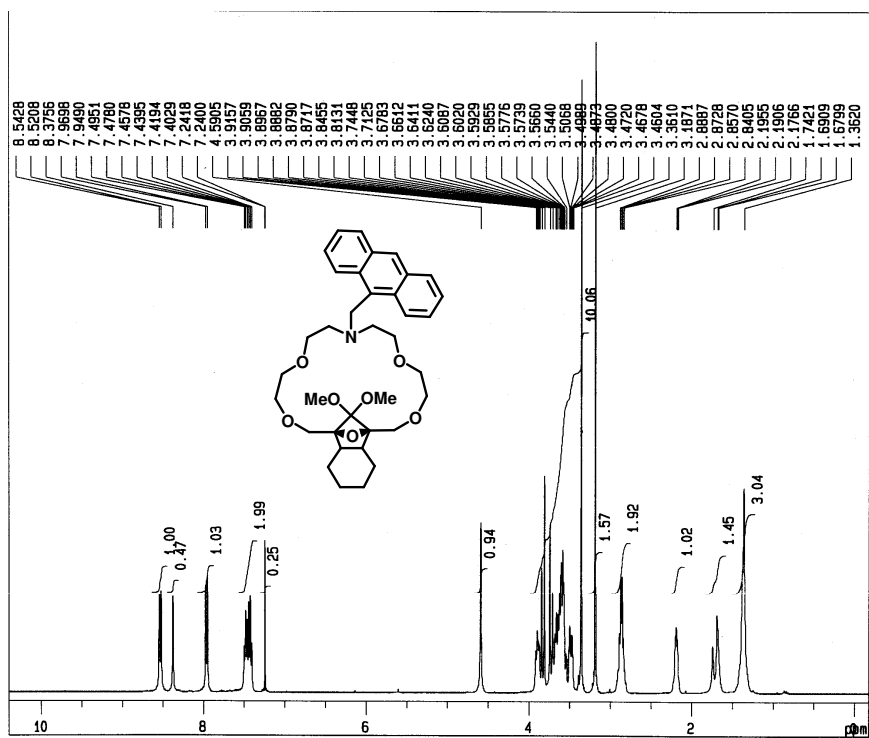
$^{13}\text{C NMR}$  (100 MHz) of the compound **4** in  $\text{CDCl}_3$



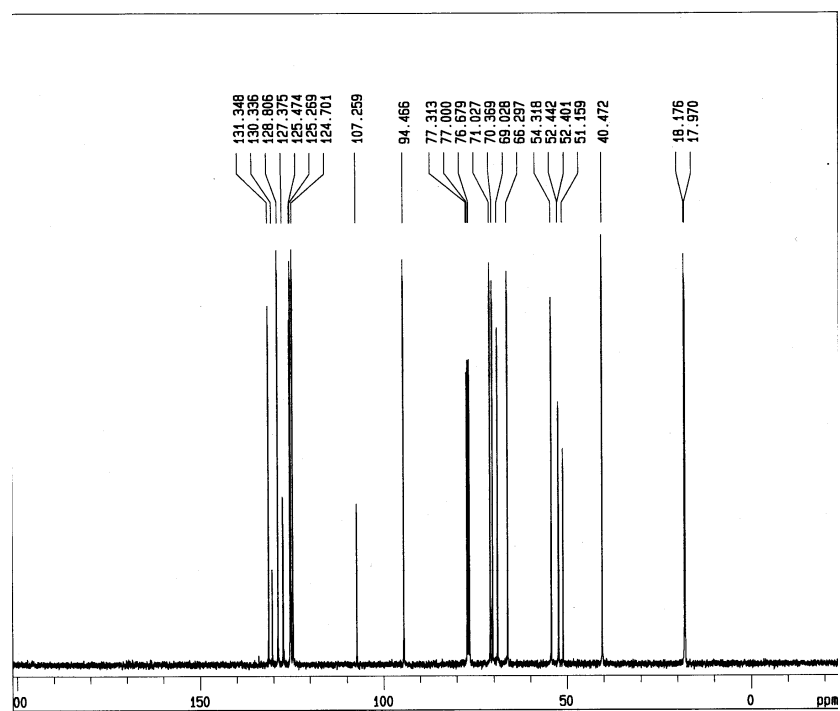
**<sup>1</sup>H NMR (400 MHz) of the compound 5 in CDCl<sub>3</sub>**



**<sup>13</sup>C NMR (100 MHz) of the compound 5 in CDCl<sub>3</sub>**



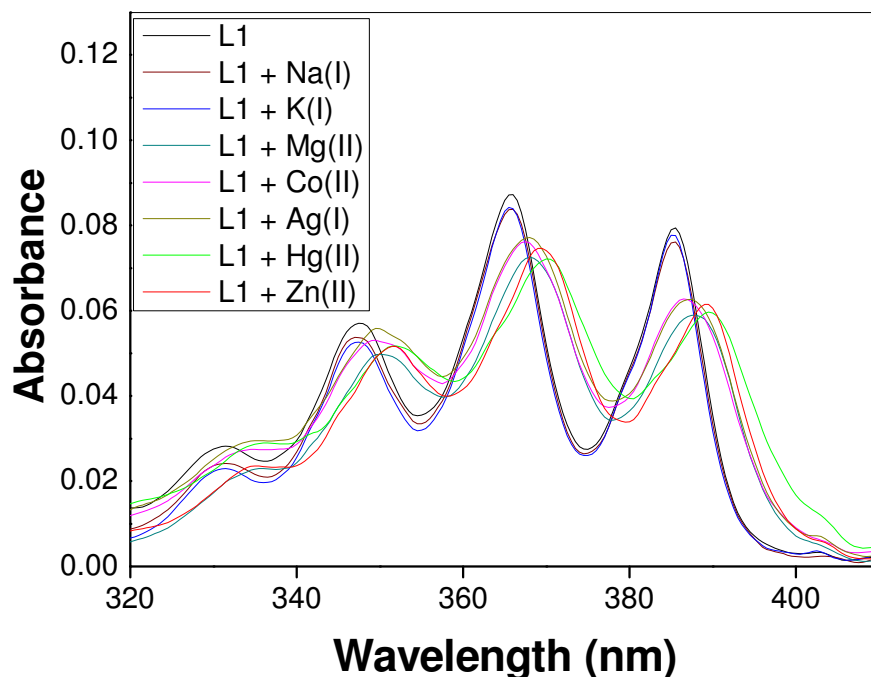
<sup>1</sup>H NMR (400 MHz) of the compound **L1** in CDCl<sub>3</sub>



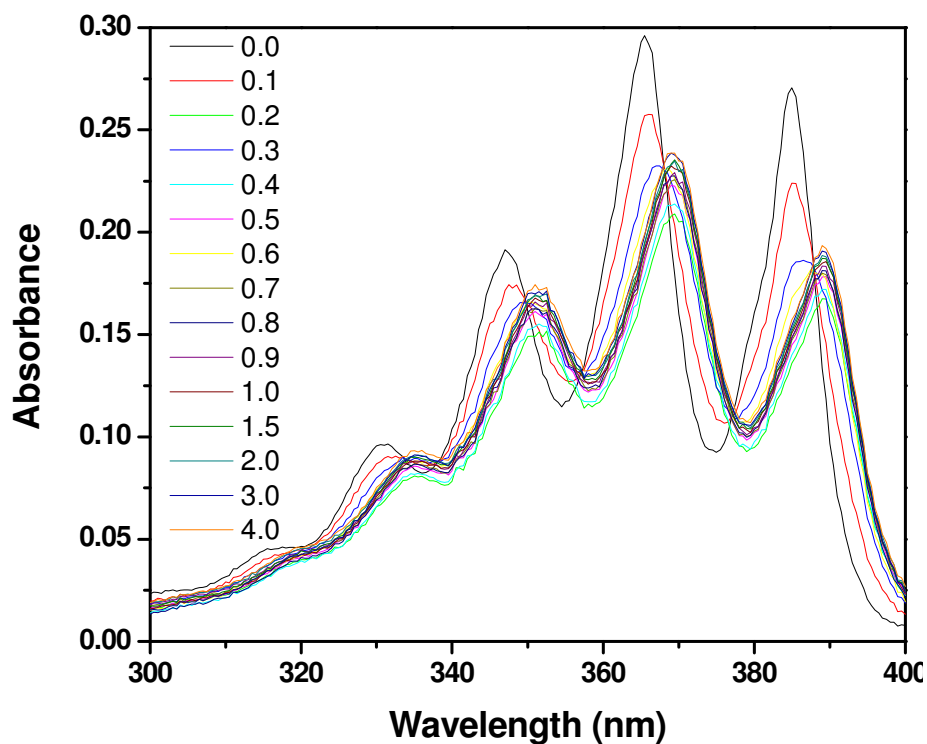
<sup>13</sup>C NMR (100 MHz) of the compound **L1** in CDCl<sub>3</sub>

**Table S1:** Absorption maxima and corresponding molar extinction coefficients ( $\epsilon$ ), total fluorescence quantum yields ( $\phi_F$ ) and corresponding enhancement factor in MeCN in presence of various ionic input for **L1**.  $[L1] = 1 \times 10^{-5}$  M,  $[M^{n+}] = 1 \times 10^{-3}$  M.

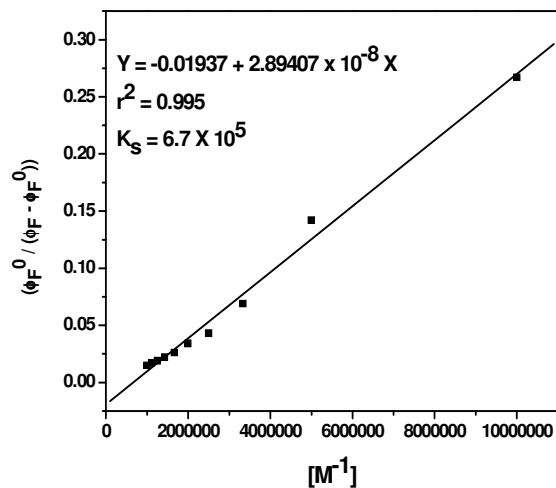
S.No.	Ionic Input	Band position, nm ( $\epsilon$ , dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup> )	Quantum Yield ( $\phi_F$ )	FE
1	<b>L1</b>	386 (8159) 366 (8956) 348 (5788) 332 (2939)	0.004	1
2	Li(I)	386 (7852) 365 (8521) 349 (5367) 331 (2295)	0.007	2
3	Na(I)	386 (7787) 367 (8509) 347 (5567) 332 (2468)	0.006	2
4	K(I)	385 (7873) 365 (8503) 347 (5332) 331 (2327)	0.022	6
5	Mg(II)	388 (5944) 369 (7410) 350 (5109) 336 (2377)	0.094	24
6	H <sup>+</sup>	389 (5249) 369 (6825) 351 (5215) 336 (2752)	0.029	7
7	TEA	385 (7901) 365 (8510) 347 (5329) 332 (2369)	0.007	2
8	Mn(II)	389 (6146) 369 (7595) 353 (5365) 336 (2680)	0.102	26
9	Co(II)	387 (6365) 367 (7722) 350 (5483) 335 (2844)	0.110	28
10	Ni(II)	387 (6129) 369 (7516) 350 (5231) 333 (2401)	0.078	20
11	Cu(II)	389 (5746) 369 (7042) 352.5 (5194) 335 (3085)	0.104	26
12	Zn(II)	390 (6317) 369 (7560) 352 (5512) 336 (2439)	0.393	98
13	Ag(I)	388 (6328) 369 (7777) 350 (5699) 335 (3038)	0.228	57
14	Cd(II)	389 (7283) 369 (8614) 353 (5816) 336 (2721)	0.075	19
15	Hg(II)	389 (6107) 371 (7322) 352 (5355) 336 (2941)	0.277	69
16	Pb(II)	391 (6215) 370 (6931) 353 (4871) 338 (2189)	0.005	1



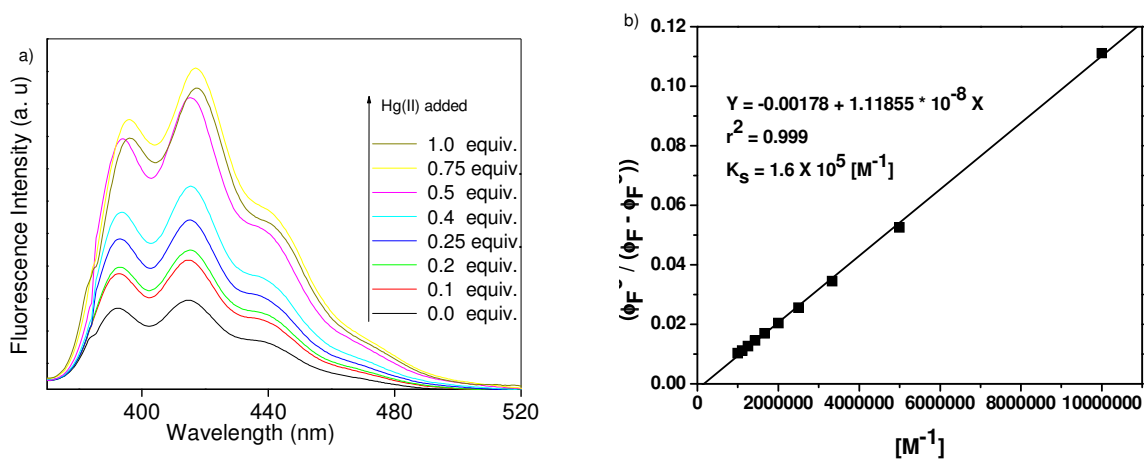
**Figure S1:** The absorption spectral changes of **L1** in the presence of alkali, alkaline earth metal and the transition metal ions in dry acetonitrile.  $[L1] = 1 \times 10^{-5} \text{ M}$ ,  $[M^{n+}] = 1 \times 10^{-3} \text{ M}$ .



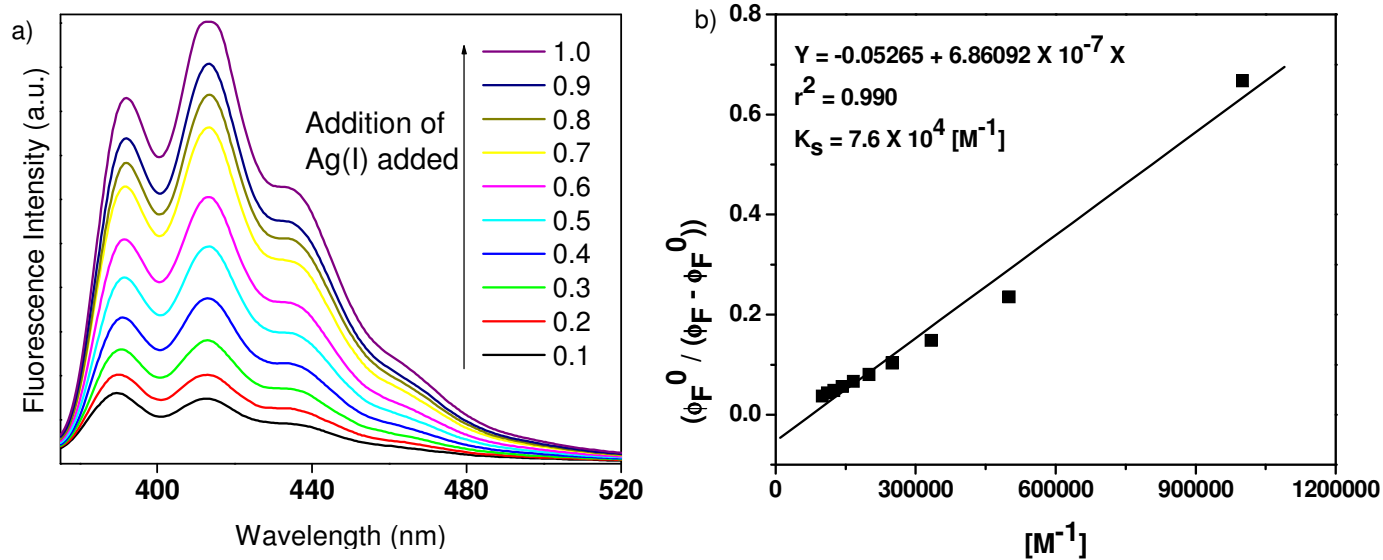
**Figure S2.** The absorption spectral changes of **L1** in dry acetonitrile ( $1 \times 10^{-5} \text{ M}$ ) upon addition of increasing equivalent of  $Zn^{2+}$



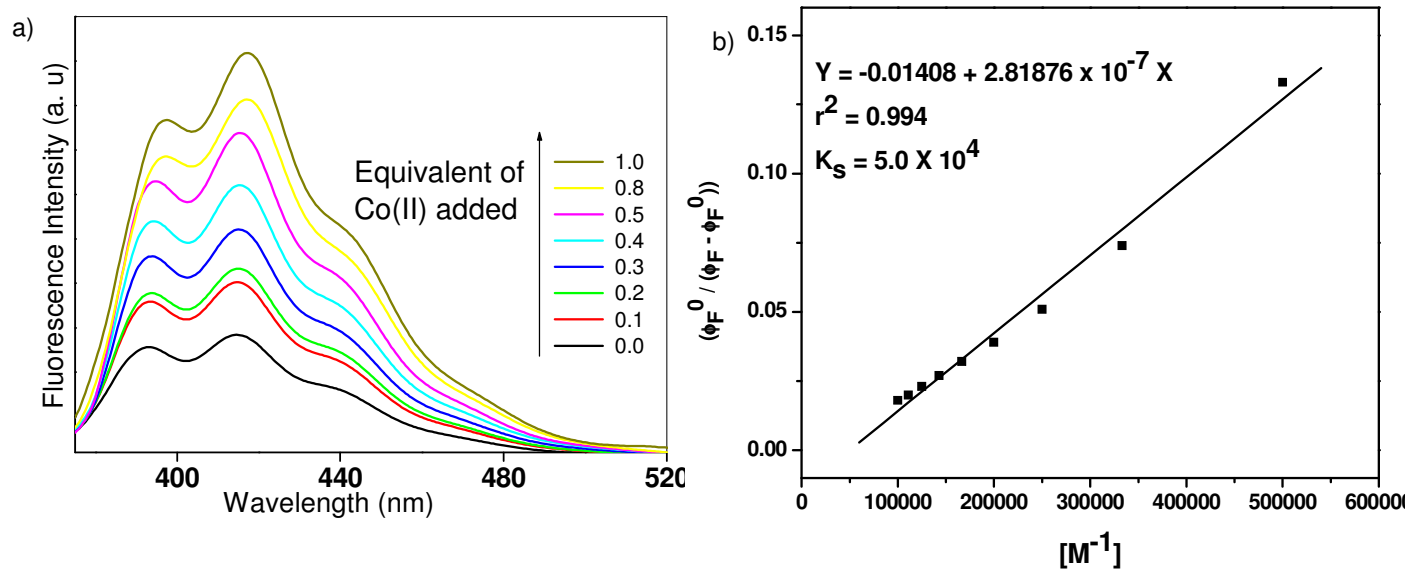
**Figure S3.** Plot for association constant determination of 1: 1 **L1**:  $Zn^{2+}$  complex.  $\lambda_{ex} = 350$  nm.



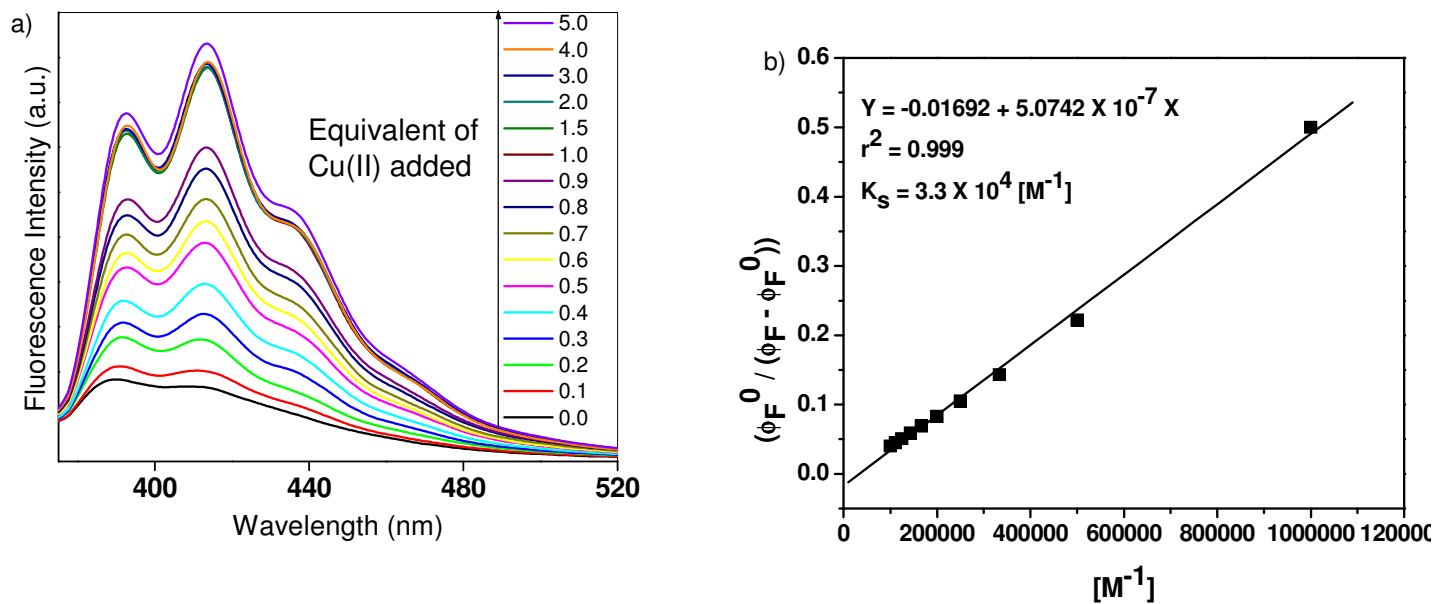
**Figure S4.** (a) Fluorescence spectral changes of **L1** ( $1 \times 10^{-7}$ ) with the addition of  $Hg^{2+}$  in dry acetonitrile solution. (b) Plot for association constant determination.



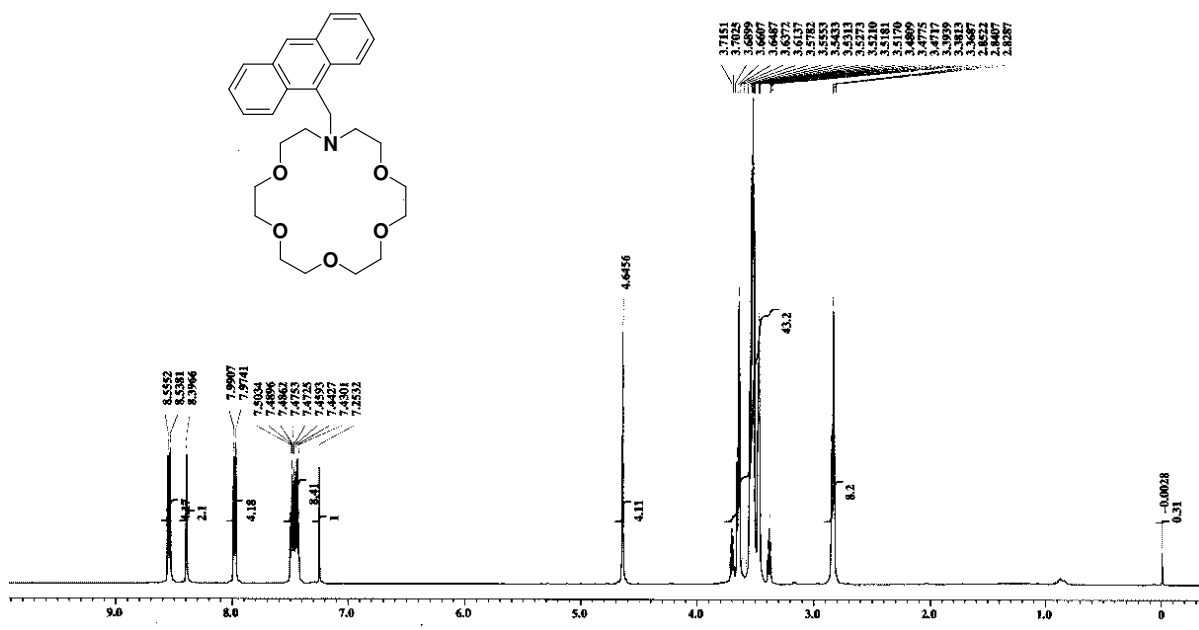
**Figure S5.** (a) Fluorescence spectral changes of **L1** ( $1 \times 10^{-7}$ ) with the addition of  $Ag^+$  in dry acetonitrile solution. (b) Plot for association constant determination



**Figure S6.** (a) Fluorescence spectral changes of **L1** ( $1 \times 10^{-7}$ ) with the addition of  $Co^{2+}$  in dry acetonitrile solution. (b) Plot for association constant determination



**Figure S7.** (a) Fluorescence spectral changes of **L1** ( $1 \times 10^{-7}$ ) with the addition of  $\text{Cu}^{2+}$  in dry acetonitrile solution. (b) Plot for association constant determination

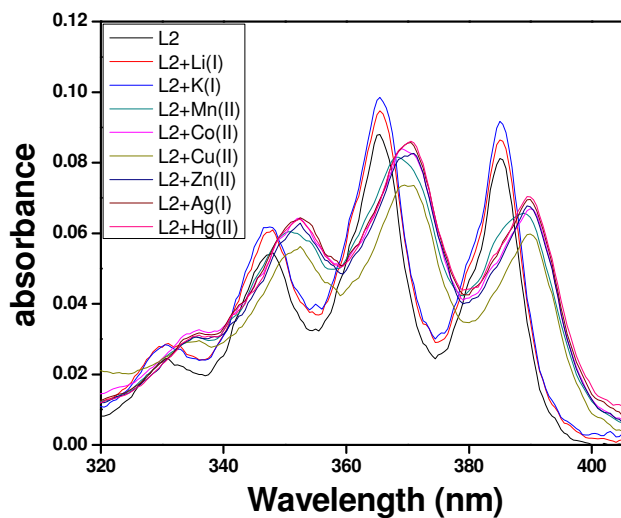


**Figure S8.** <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) of the compound **L24**

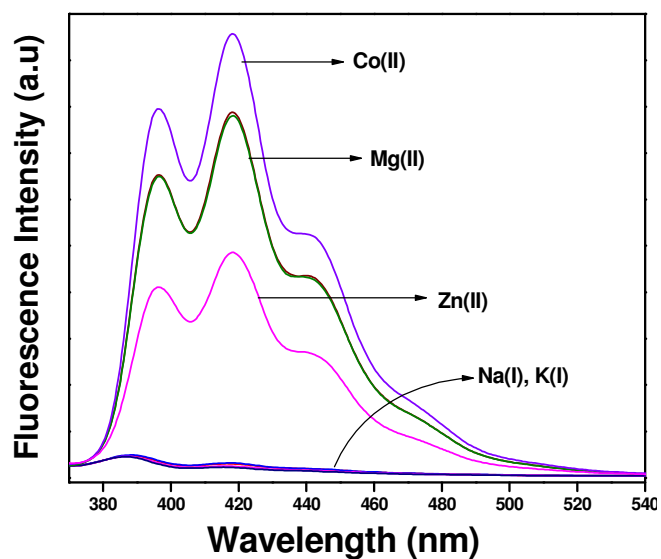


**Table S2:** Absorption maxima and corresponding molar extinction coefficients ( $\epsilon$ ), total fluorescence quantum yields ( $\phi_F$ ) and corresponding enhancement factor in MeCN in presence of various ionic input for **L2**.  $[L2] = 1 \times 10^{-5}$  M,  $[M^{n+}] = 1 \times 10^{-3}$  M.

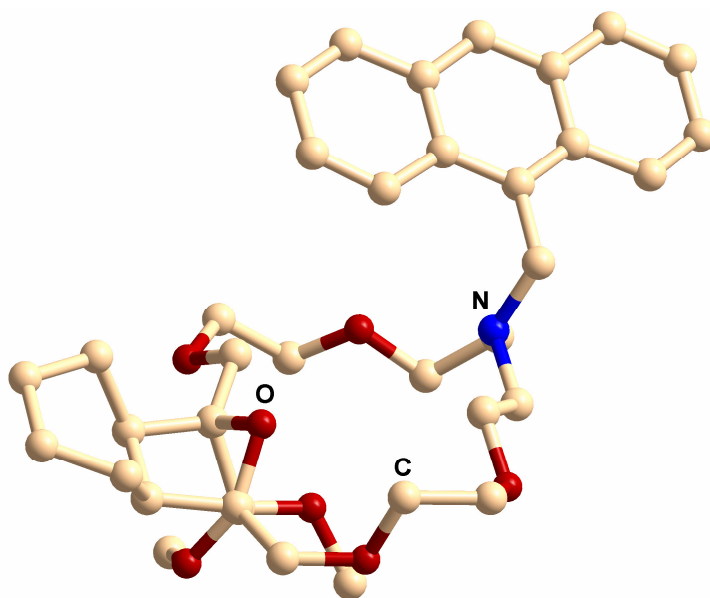
S.No.	Ionic Input	Band position, nm ( $\epsilon$ , $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ )	Quantum Yield ( $\phi_F$ )	FE
1	<b>L2</b>	385 (9191) 365 (9901) 347 (6224) 331 (2847)	0.006	1
2	Li(I)	385 (9092) 365 (9808) 348 (6491) 331 (2870)	0.006	1
3	Na(I)	385 (8702) 366(9472) 348 (6059) 331 (2937)	0.007	1.2
4	K(I)	386(8131) 365 (8841) 348 (5494) 331 (2483)	0.008	1.3
5	Mg(II)	390 (6780) 370 (8349) 352 (6287) 335 (3147)	0.09	15
6	H <sup>+</sup>	390 (6793) 371 (8470) 352 (6329) 337 (3015)	0.14	23
7	Mn(II)	390 (6631) 368 (8223) 352 (6173) 336 (3086)	0.08	13
8	Co(II)	391 (6743) 369 (8479) 352 (6488) 336 (3283)	0.12	20
9	Ni(II)	390 (6372) 370 (7953) 353 (5958) 335 (2896)	0.11	18
10	Cu(II)	390 (6008) 369 (7522) 353 (5611) 337 (2967)	0.12	20
11	Zn(II)	390 (6823) 372 (8345) 352 (6322) 335 (3086)	0.06	10
12	Ag(I)	390 (6954) 370 (8591) 354 (6441) 336 (3186)	0.12	20
13	Cd(II)	390 (7145) 372 (8598) 353 (6434) 337 (3215)	0.12	20
14	Hg(II)	390 (7119) 371 (8708) 353 (6450) 336 (3161)	0.13	22
15	Pb(II)	390 (6940) 371 (8356) 352 (6398) 336 (3069)	0.05	8



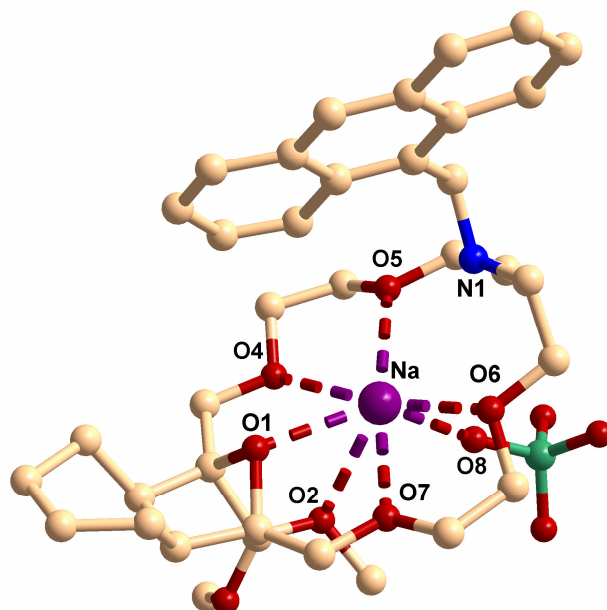
**Figure S9.** The absorption spectral changes of **L2** in the presence of alkali, alkaline earth metal and the transition metal ions in dry acetonitrile.  $[L2] = 1 \times 10^{-5} M$ ,  $[M^{n+}] = 1 \times 10^{-3} M$ .



**Figure S10. (a)** Fluorescence spectra of the **L2** alone and in the presence of different ionic inputs in acetonitrile.  $[L2] = 1.9 \times 10^{-7} M$ ,  $[M^{n+}] = 1.9 \times 10^{-5} M$ .  $\lambda_{ex} = 350 nm$ .



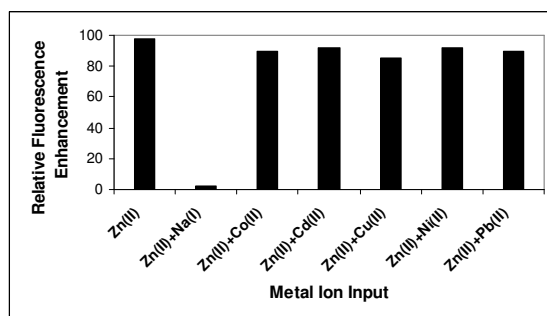
**Figure S11:** X-ray crystal structure of the **L1**. Hydrogen atoms are omitted for clarity.



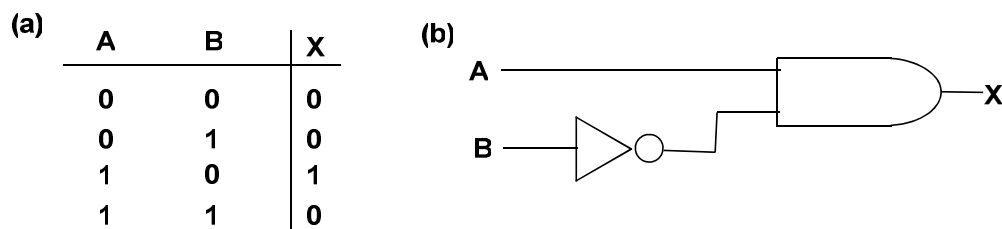
**Figure S12:** X-ray crystal structure of the **L1+Na<sup>+</sup>**. Hydrogen atoms are omitted for clarity.

### Experimental for data collection and structure solution:

All data were collected on a Bruker SMART APEX diffractometer. The structure was solved using SIR-92 and refined using SHELXL-97. Single crystal of **L1** was recrystallised from the acetonitrile solution and data was collected at 100 k; **L1+Na<sup>+</sup>** was recrystallised from acetonitrile-diethyl ether solution and data was collected at 100 k.



**Figure S13.** Fluorescence response of **L1** in the presence  $\text{Zn}^{2+}$  and other metal ion mixtures in acetonitrile.  $[\text{L1}] = 1.9 \times 10^{-7} \text{ M}$ ,  $[\text{M}^{n+}] = 1.9 \times 10^{-5} \text{ M}$ .  $\lambda_{\text{ex}} = 350 \text{ nm}$ .



**Figure S14**

- (a) A truth table for the inhibit (INH) logic gate; inputs A and B correspond to the  $\text{Zn}^{2+}$  and  $\text{Na}^+$  respectively; X [fluorescence emission], is the output signal.
- (b) The INH gate represented using a conventional gate notation; an active output signal (fluorescence emission) is obtained when  $A = 1$  and  $B = 0$ .

**Table S3.** Selected bond length (Å) and angles (°) for the Na<sup>+</sup> coordination environment in L1+Na<sup>+</sup> complex.

**Bond distances (Å)**

O5...Na = 2.537(3)

O7...Na = 2.550(3)

O6...Na = 2.703(3)

O2...Na = 2.702(3)

O1...Na = 2.534(2)

O4...Na = 2.571(3)

O8...Na = 2.433(3)

**Bond angles (°)**

O8..Na..O1 = 139.84(10)

O8..Na..O5 = 81.93(9)

O1..Na..O5 = 120.17(9)

O8..Na..O7 = 96.83(10)

O1..Na..O7 = 65.30(7)

O5..Na..O7 = 172.41(9)

O8..Na..O4 = 103.33(10)

O1..Na..O4 = 65.59(8)

O5..Na..O4 = 63.72(8)

O7..Na..O4 = 123.74(9)

O8..Na..O2 = 78.06(8)

O1..Na..O2 = 62.06(7)

O5..Na..O2 = 118.53(8)

O7..Na..O2 = 68.26(8)

O4..Na..O2 = 65.64(8)

O8..Na..O6 = 83.72(9)

O1..Na..O6 = 113.56(8)

O5..Na..O6 = 110.89(8)

O7..Na..O6 = 61.53(7)

O4..Na..O6 = 169.89(9)

O2..Na..O6 = 123.54(9)

**References:**

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