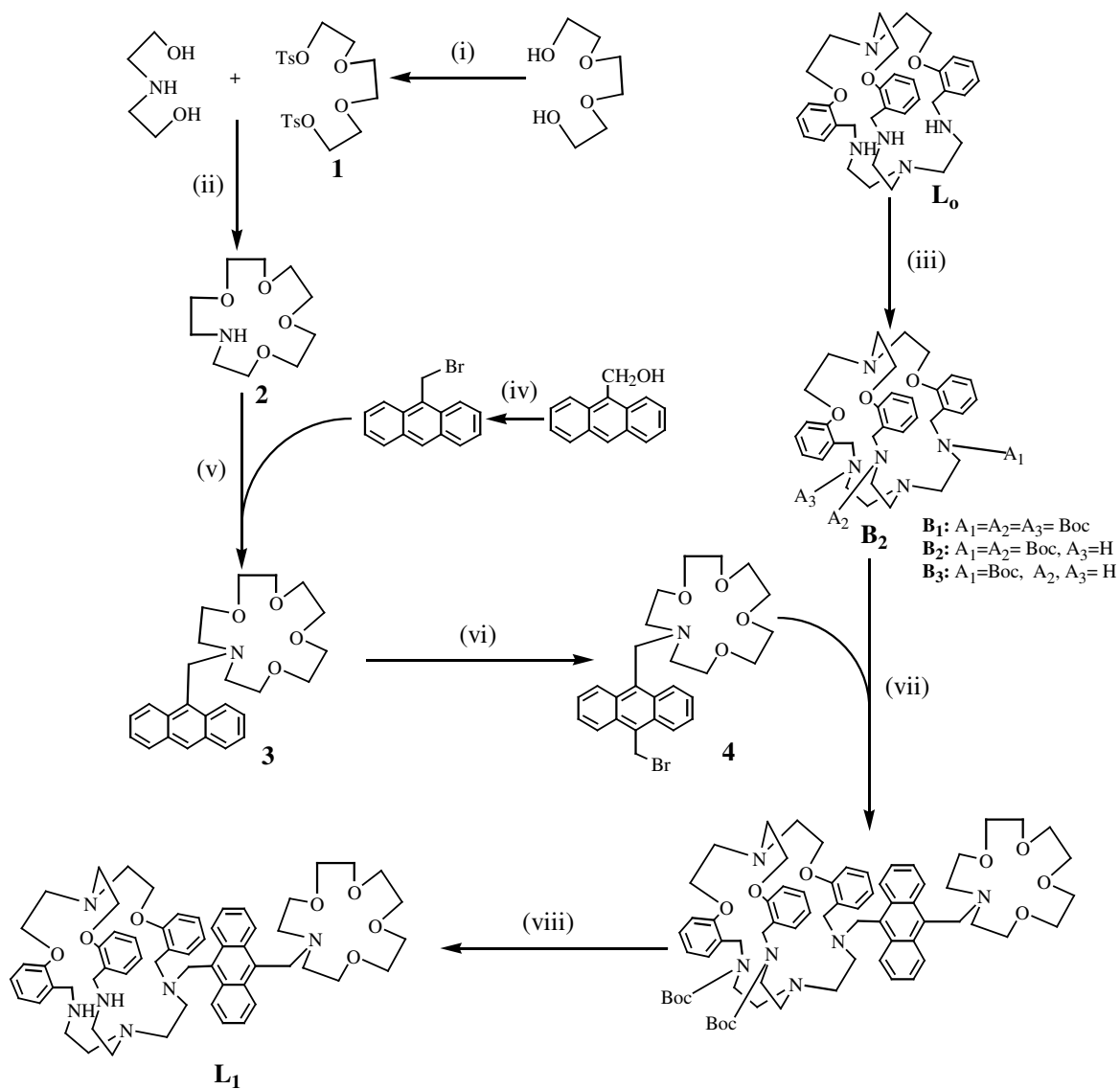Fluorescence enhancement of a signaling system in the simultaneous presence of a transition and an alkali metal ions: a potential AND logic gate

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Supplementary Information

Reagent and conditions: *(i)* NaOH, *p*-toluene sulfonyl chloride, THF: H$_2$O (2:1), 0°C *(ii)*
Na in *tert*-butanol, 40°C *(iii)* di-tert-butyl dicarbonate, DCM *(iv)* PPh$_3$, Br$_2$, MeCN, 25°C
(v) K$_2$CO$_3$, MeCN, KI *(vi)* paraformaldehyde, 30% HBr in AcOH, 45°C, 2h *(vii)* MeCN,
K$_2$CO$_3$, KI, reflux, 72h *(viii)* CF$_3$COOH, THF, RT, 48 h.

Scheme 1

Detailed Synthetic Procedure of L_1

Synthesis of the cryptand L_o

Cryptand L_o was synthesized as reported earlier from our laboratory. [K. G. Ragunathan and P. K. Bharadwaj, *Tetrahedron Lett*., 1992, **33**, 7581]

Synthesis of bis-protected cryptand B_1

The bis-protected cryptand was synthesized by partial derivatization of L_o with di-tert-butyl dicarbonate. To a stirring solution of L_o (1.68g, 1eq., 3 mmol) in dichloromethane, a solution of di-tert-butyl dicarbonate (1.3ml, 1.8eq., 5.4 mmol) in dichloromethane was added drop wise over a period of 30 min at 0°C after which it was allowed to react for 12h at RT. The solvent was removed under reduced pressure. The solid remained was washed with water, extracted with $CHCl_3$ finally, the organic layer after drying over anhydrous Na_2SO_4, evaporated to dryness to obtain a solid which was a mixture of *tris*-, *bis*- and *mono*-boc protected derivatives of L_o. The mixture was purified and separated through silica gel (100-200 mesh) column chromatography. The tri substituted (B_1) cryptand was obtained in low yields (<10%) with 15-20% ethyl acetate in hexane as eluent. The desired bis-protected cryptand (B_2) was obtained with 25% ethyl acetate in hexane as eluent as a brown crystalline solid.

Yield: 35%; mp. 96 °C; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ: (aliphatic) 1.4(s, 18H), 2.5 (m, 12H), 3.2 (br s, 2H), 3.8 (br s, 6H), 3.9 (br s, 4H), 4.1(br s, 2H), 4.4 (br s, 2H), (aromatic) 7.0 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ: 28.4, 29.7, 45.2, 46.3, 48.7, 53.4, 54.6, 54.8, 67.4, 67.7, 68.4, 79.7 (aliphatic), 111.1, 111.5, 111.8, 120.9, 121.5, 126.9, 128.6, 130.2, 130.6, 131.0, 132.1, 154(aromatic) 158.6 (C=O); ES-

MS, m/z (%): 760 (100) [$\mathbf{B_2}$]$^+$; Anal. Calcd. for $C_{43}H_{61}N_5O_7$: C, 67.96; H, 8.09; N, 9.22. Found: C, 67.87; H, 8.18; N 9.09 %.

Synthesis of triethylene glycol ditoluenesulfonate, 1:

Yield: 90%; M. pt. 81 °C; ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS) δ: 2.39(s, 6H), 3.54(t, 12H), 3.75 (t, 4H), 7.40(d, 4H), 7.82(d, 4H); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, TMS) δ: 144.2, 131.5, 130.9, 128.7, 71.2, 70.0, 62.5, 21.6; ES-MS, m/z (%): 458 (100) [M$^+$] Anal. Calcd. for $C_{20}H_{26}O_8S_2$: C, 52.39; H, 5.72. Found: C, 52.31; H, 5.79 %.

Synthesis of 4,7,10,13-tetraoxa-1-azacyclopentadecane, 2:

Yield: 35%, M. pt. 27 °C; ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS) δ: 2.74(t, J = 6 Hz, 4H, NCH$_2$), 3.03 (s, 1H, NH), 3.55-3.75 (m, 16H, 8 × OCH$_2$), ES-MS, m/z (%): 220 (100) [M+1]$^+$; Anal. Calcd. for $C_{10}H_{21}N_1O_4$: C, 54.78; H, 9.65; N, 6.39. Found: C, 54.69; H, 9.71; N 6.32 %.

Synthesis of 1-(9′-methyl anthracenyl) 4,7,10,13-tetraoxa-1-azacyclopentadecane, 3:

To a solution of monoaza 15-crown-5 (NO$_4$) macrocycle **2** (1.0 g; 4.6 mmol) in dry acetonitrile, anhydrous K$_2$CO$_3$ (0.63g; 4.6 mmol) was added and stirred for 15 min. To this, 9-bromomethyl anthracene (1.25 g, 4.6 mmol) was added along with a crystal of KI and the reaction mixture was stirred first at 60 °C under nitrogen atmosphere for 12 h and then refluxed for 36 h where the yellow solid precipitated out. After cooling to RT, the solvent was removed under vacuum. The solid remained was washed several times with water, extracted with CHCl$_3$ and the organic layer after drying over anhydrous

Na$_2$SO$_4$, evaporated to dryness to obtain a yellow solid. The product was purified and isolated by passing through a silica gel (100-200 mesh) column chromatography with 5% ethyl acetate in chloroform as eluent.

Yield: 68%; ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS) δ: 2.93 (t, J = 5.56 Hz, 4H, 2 × NCH$_2$), 3.48-3.56(m, 16H, 8 × OCH$_2$) 4.63(s, 2H, An-CH$_2$), 7.36(t, 2H, J = 7.55 Hz, An-H$_{3,6}$), 7.44(t, 2H, J = 7.55 Hz, An-H$_{2,7}$), 7.89(d, J = 7.79 Hz, 2H, An-H$_{4, 5}$), 8.31(s, 1H, An-H$_{10}$), 8.39(d, 2H, J = 8.75 Hz, An-H$_{1, 8}$); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, TMS) δ: 131.2, 128.9, 127.9, 126.0, 124.8, 71.4, 71.0, 70.4, 70.1, 69.5, 68.7, 60.9, 54.6, 49.8, 45.5, 27.3. FAB-MS, m/z (%): 410 (100) [M+1]$^+$; Anal. Calcd. for C$_{25}$H$_{31}$N$_1$O$_4$: C, 73.32; H, 7.63; N, 3.42. Found: C, 73.21; H, 7.68; N 3.34 %.

Synthesis of 9′-methyl(4,7,10,13-tetraoxa-1-azacyclopentadecanyl)-10′-bromomethyl anthracene, 4:

To a stirring solution of paraformaldehyde (0.190 g, 6.4mmol) in 30% HBr in AcOH solution (30mL), methyl-anthracene substituted NO$_4$ macrocycle **3** (2.6g, 6.4 mmol) was added and heated for 2h at 40 °C under nitrogen atmosphere. The reaction mixture was then poured into ice-water (150 mL). CHCl$_3$ (50 mL) was added to it and extracted. The organic layer, after drying over anhydrous Na$_2$SO$_4$, was evaporated to dryness under reduced pressure to obtain a deep yellow solid. Recrystallization from acetonitrile yields a yellow solid as the desired product.

Yield: 52%; ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS) δ: 2.45(t, J = 5.56 Hz, 2 × NCH$_2$, 4H), 3.41-3.54(m, 16H, 8 × OCH$_2$), 4.13(s, 2H, An-9-CH$_2$), 5.09 (s, 2H, An-10-CH$_2$), 7.41(t, J = 6.31 Hz, 2H, An-H$_{2, 7}$), 7.47 (t, J = 6.83 Hz, 2H, An-H$_{3, 6}$), 7.81 (d, J = 8.39 Hz, 2H, An-H$_{4, 5}$), 7.99(d, J = 8.55 Hz, 2H, An-H$_{1, 8}$); ^{13}C NMR (100 MHz, CDCl$_3$, 25

°C, TMS) δ: 135.9, 132.3, 129.2, 127.3, 126.3, 125.5, 125.4, 70.2, 69.8, 68.7, 55.4, 52.3, 33.4; FAB-MS, m/z (%): 503 (80) [M]$^+$; Anal. Calcd. for $C_{26}H_{32}N_1O_4$ Br: C, 62.15; H, 6.42; N, 2.79. Found: C, 62.01; H, 6.53; N 2.71 %.

Synthesis of L_1:

To the solution of bis-boc protected cryptand **B$_2$** (0.380 g; 0.5 mmol) in dry acetonitrile, anhydrous K_2CO_3 (0.084 g; 0.6 mmol) was added and stirred for 15 min under nitrogen atmosphere. **4** (0.255 g, 0.5mmol) was added to it along with a crystal of KI and the reaction mixture was stirred with heated to refluxed for 72 h where the yellow solid precipitated out. After cooling to RT, it was filtered off. The solid remained was washed several times with water, extracted with CHCl$_3$ and the organic layer after drying over anhydrous Na$_2$SO$_4$, evaporated to dryness to obtain a yellow solid. The product was purified and isolated by passing through a silica gel (100-200 mesh) column chromatography with 1% ethyl acetate in chloroform as eluent.

Yield: 69%; ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS) δ: 1.40(s, 18H, 6 × OCCH$_3$), 2.43(t, 2H), 2.59(t, 6H), 2.53(t, 4H), 2.73(t, 6H), 3.06(m, 4H), 3.44-3.57(m, 16H), 3.62(s, 2H), 4.09(m, 10H), 4.22(s, 4H), 6.76-7.04(m, 12H, Ph-H), 7.46(m, 4H, An-H$_{2, 3, 6, 7}$), 8.85(d, 2H, An-H$_{4, 5}$), 8.90(d, 2H, An-H$_{1, 8}$); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, TMS) δ: 163.7, 160.4, 158.0, 133.7, 131.4, 130.6, 129.7, 128.6, 127.4, 127.0, 126.1, 125.7, 125.2, 123.2, 122.8, 120.3, 119.0, 115.4, 114.2, 72.8, 71.3, 70.8, 70.4, 69.1, 56.5, 55.7, 54.9, 53.8, 53.2, 52.0, 49.9, 49.1, 43.6, 27.8; ES-MS, m/z (%): 1182 (55) [M]$^+$; Anal. Calcd. for $C_{69}H_{92}N_6O_{11}$: C, 70.14; H, 7.85; N, 7.11. Found: C, 69.99; H, 7.91; N 7.02 %.

The product thus obtained was dissolved in THF (10 mL), CF$_3$COOH (excess) was added and stirred at RT for 48 h after which the solvent was removed in a rotary evaporator under reduced pressure. It was treated with saturated solution of NaHCO$_3$ and NaCl to neutralize the excess acid. Water (50 mL) was added to it and it was extracted with CHCl$_3$ (3 × 30 mL). The organic extracts after drying over anhydrous Na$_2$SO$_4$, evaporated to dryness to obtain a light brown solid as the desired product.

Yield: 73%; M. pt. 190° C; ESI-MS, m/z (%): 981 (36) [L$_1$]$^+$; Anal. Calcd. for C$_{59}$H$_{76}$N$_6$O$_7$: C, 72.21; H, 7.81; N, 8.56. Found: C, 72.14; H, 7.86; N 8.49 %.
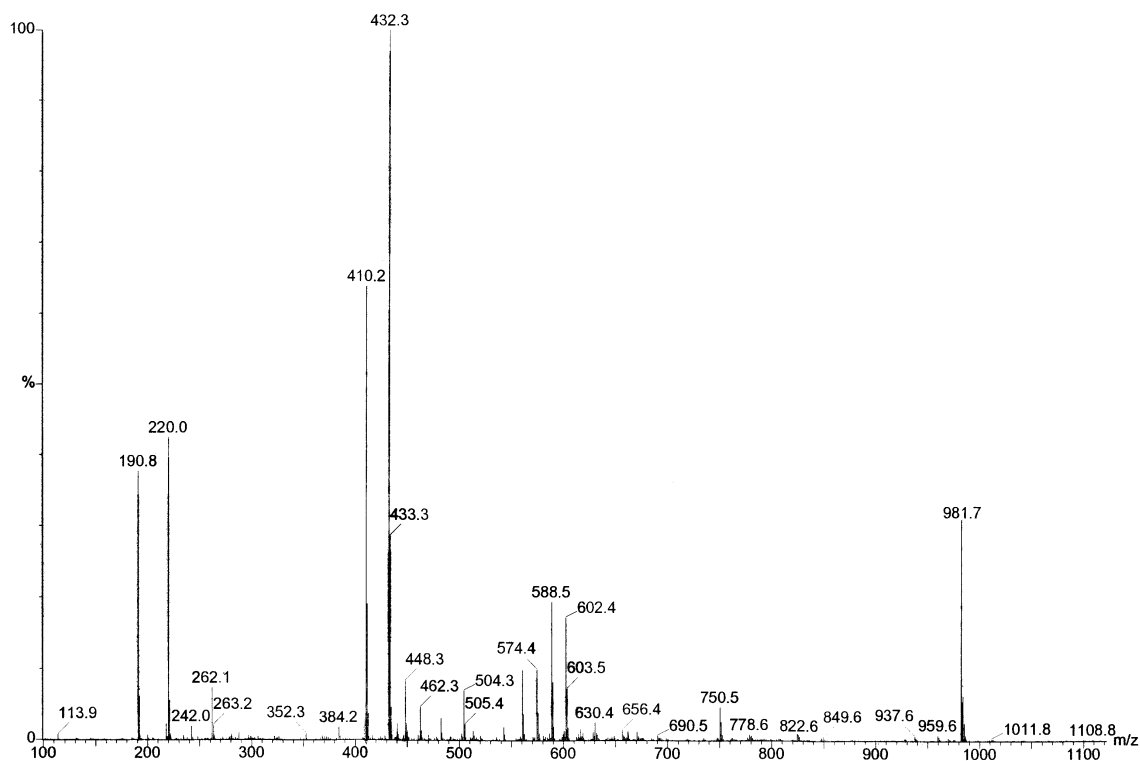

Figure 1: ESI-MS spectrum of L$_1$ (m/z = 981.7).

Table 1: Absorption and emission maximum, molar extinction coefficient (ε) and the fluorescence quantum yield (ϕ_F) of $\mathbf{L_1}$ in different solvents.

| Solvents	Absorption				Emission	
	λ, nm (ε, dm^3 mol^{-1} cm^{-1})				λ_{max}, nm	ϕ_F
Toluene	403(8517)	382(8448)	364(5927)	345(4050)	434	0.0206
Chloroform	403(9607)	383(9558)	363(6926)	346(5053)	434	0.00914
DCM	403(11554)	382(11463)	363(8211)		432	0.01111
1, 4-dioxane	402(6954)	382(6896)	363(4924)		436	0.01114
Acetone	401(6481)	380(6463)	362(4580)		436	0.00671
THF	403(13126)	382(13003)	363(9324)		438	0.00371
DMSO	405(10959)	383(10549)	364(7618)		439	0.00634
DMF	403(13179)	383(13120)	363(9365)	345(6578)	439	0.00393
Acetonitrile	401 (n.d.)	380(n.d.)	361(n.d.)	340(n.d.) 258(n.d.)	429	(n. d.)
Ethanol	399(n.d.)	379(n.d.)	361(n.d.)	344(n.d.) 258(n.d.)	423	(n. d.)
Methanol	400(n.d.)	380(n.d.)	361(n.d.)	343(n.d.) 259(n.d.)	423	(n. d.)
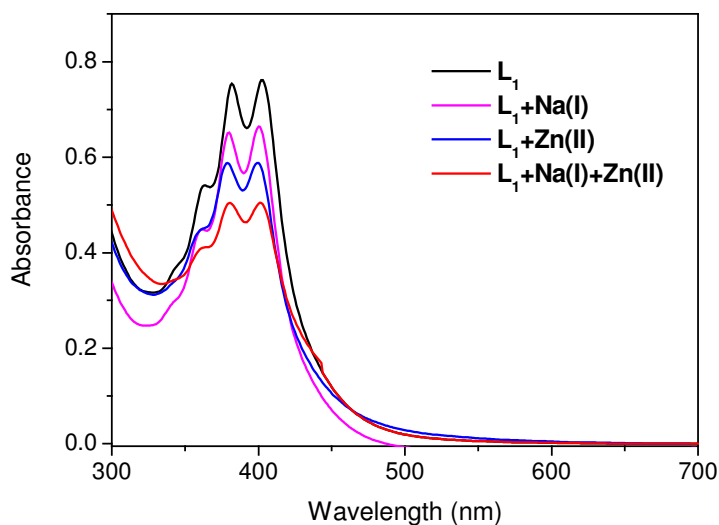
Figure 2: Absorption spectra of $\mathbf{L_1}$ alone, in presence of Na(I), Zn(II) and both Na(I) and Zn(II) in dry THF at 5.8×10^{-5} M concentration. A blue shift with decreased intensity of the transitions was observed upon complexation.
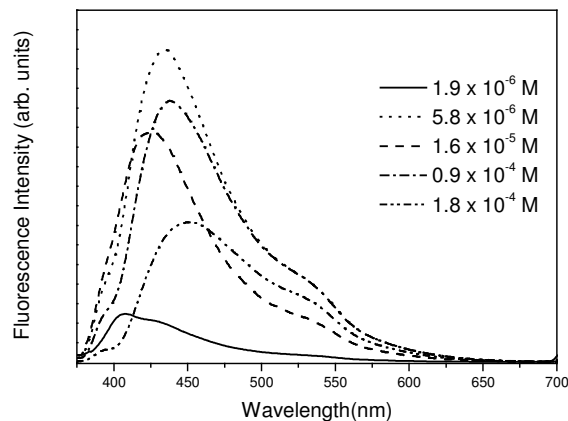
Figure 3: Fluorescence spectra of L_1 in dry 1,4-dioxane as a function of concentration. The shape of the spectra shows the non-resolved emission typical of antharacene π-π^* along with its vibrational bands, due to 9, 10-bismethyl substitutions and a strong PET from both ends. The similar kind of behavior is observed in all the solvents under investigation. However, the emission λ_{max} is red shifted with increase in concentration (inner-filter effect) as self-quenching of fluorescence occurs at higher concentrations. This red-shifted nature of the emission band can further be exploited through the solid-state properties of the system with stronger inter-molecular interactions.

(a)   (b)
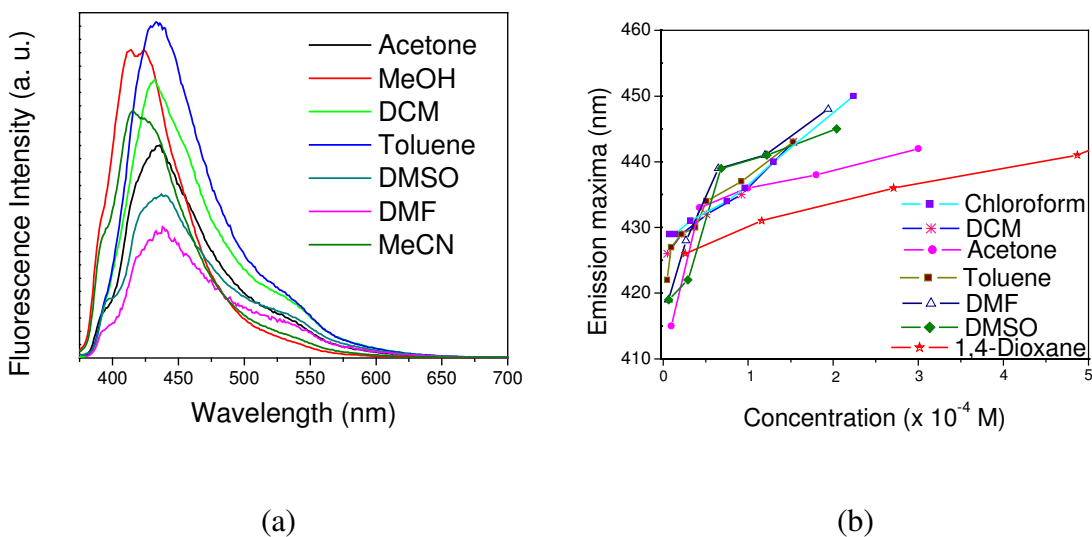
Figure 4: (a) Fluorescence spectra of L_1 in various solvents. The emission maxima (λ_{max}) is found to be slightly solvatochromic in nature. For comparison, all the samples were excited at 363nm at concentration = ~2×10^{-6} M, 298K. (b) Plot of emission maxima vs. concentration of L_1 in different solvents under investigation. λ_{max} is red-shifted upon increase in concentration although ϕ_F decreases at higher concentrations.

Table 2: Absorption and molar extinction coefficients of L_1 in presence of different cation inputs in dry THF measured at 5.8×10^{-5} M concentration.

| Ionic input	Absorption λ, nm (ε, dm^3 mol^{-1} cm^{-1})			
-	403(13126)	382(13003)	363(9324)	273(28941)
Na(I)	402(10997)	382(10791)	363(7425)	258(60145)
K(I)	402(11298)	382(11118)	363(7857)	259(61620)
Li(I)	402(13012)	382(12878)	363(9396)	258(62152)
Mn(II)	404(9214)	384(9481)	363(7164)	259(71662)
Fe(II)	404(10829)	384(11143)	363(8338)	259(84210)
Co(II)	402(6452)	383(6817)	365(5645)	259(55931)
Ni(II)	405(11691)	384(11557)	364(8576)	258(68936)
Cu(II)	405(10085)	384(10031)	364(7498)	259(60644)
Zn(II)	406(10141)	385(10136)	364(7567)	259(62369)
Na(I) + Mn(II)	405(8301)	384(8559)	366(7388)	260(49316)
Na(I) + Fe(II)	408(7426)	386(7817)	367(7484)	259(54751)
Na(I) + Co(II)	408(9207)	383(9595)	365(8376)	260(64441)
Na(I) + Ni(II)	404(11060)	384(11010)	365(8555)	256(57831)
Na(I) + Cu(II)	406(9423)	385(9527)	368(7958)	257(59983)
Na(I) + Zn(II)	406(9972)	385(9998)	369(8092)	257(55648)
Na(I) + Cd(II)	404(9646)	383(9583)	367(7561)	257(50410)
Na(I) + Pb(II)	406(10236)	385(10233)	367(8324)	257(56135)
Na(I) + Ag(I)	404(10576)	383(10485)	365(8531)	257(54001)
Na(I) + Tl(III)	403(11168)	382(11154)	364(8470)	257(57084)
Na(I) + H$^+$	408(7207)	386(7586)	367(7263)	262(61389)
K(I) + Fe(II)	405(9948)	384(9973)	365(8068)	260(58099)
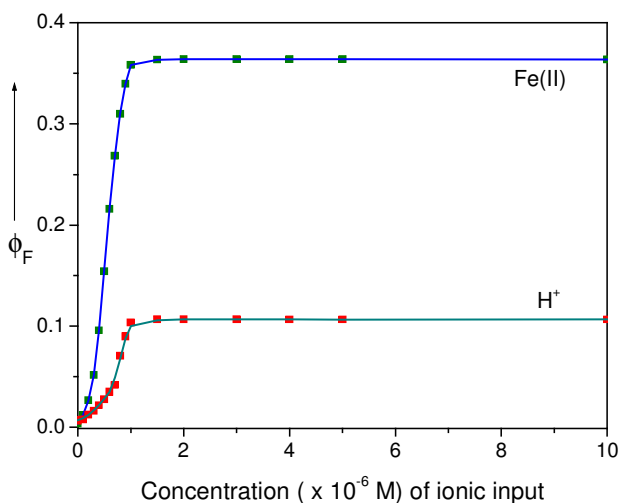
Figure 5: Plot of fluorescence quantum yield of L_1 as a function of added Fe(II) and H$^+$ at 1×10^{-6} M concentration in presence of Na(I) input ($\sim 1 \times 10^{-6}$ M concentration) at 298 K in dry THF. λ_{ex} = 363nm.
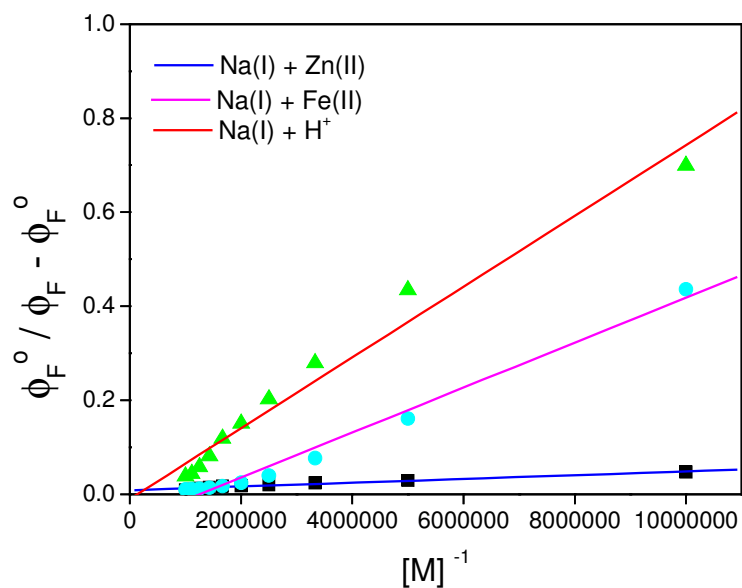
Figure 6: Linear regression plots of $\phi^0_F / (\phi_F - \phi^0_F)$ *vs.* $[M]^{-1}$ of the added ionic inputs (a) Zn(II), (b) Fe(II), (c) H^+ in presence of Na(I). The binding constants (log K_s) for Zn(II), Fe(II) and H^+ determined from the intercept / slope of the plot are found to be 6.4, 6.1 and 5.1 respectively in presence Na(I). These values are in consistent with those reported in literature for core L_o cryptand [P. K. Bharadwaj, *Prog. Inorg. Chem.* 2003, **51**, 251].
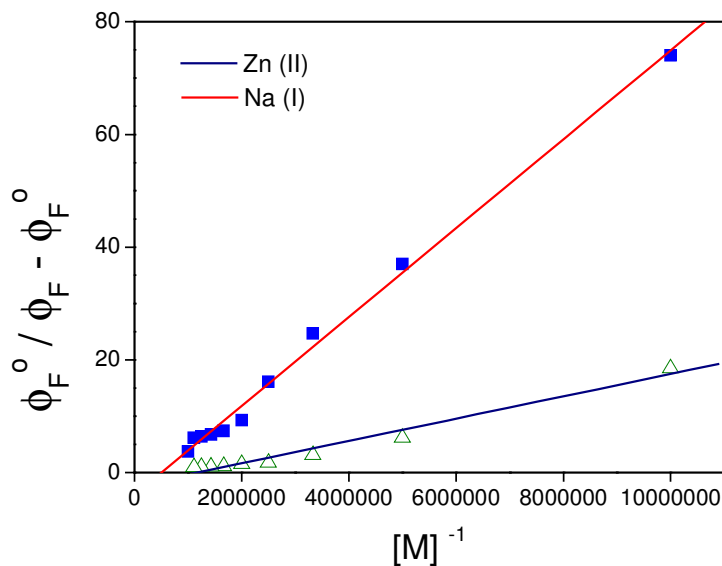
Figure 7: Linear regression plots of $\phi^0_F / (\phi_F - \phi^0_F)$ *vs.* $[M]^{-1}$ of the added ionic inputs (a) Na(I), (b) Zn(II) to L_1. The binding constants (log K_s) for Na(I) and Zn(II) thus determined from the intercept / slope of the plot are found to be 5.7 and 6.1 respectively.
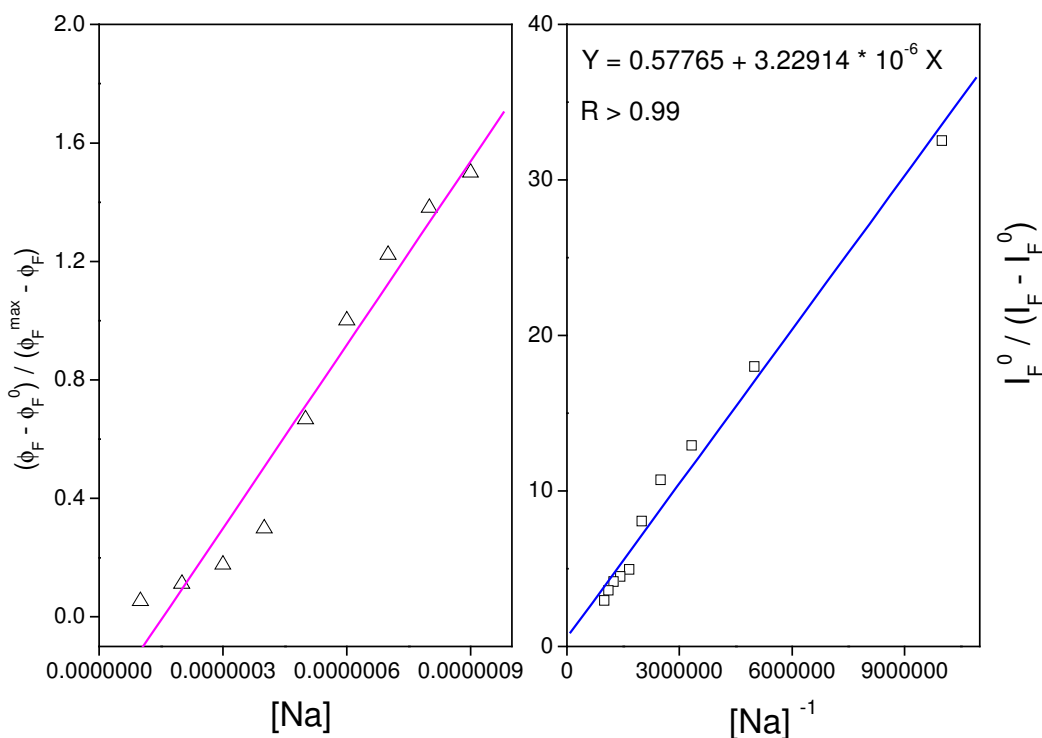
Figure 8: Plot of Fluorescence output of L_1 as a function of added Na(I) concentration. The binding constants thus obtained for Na(I) with L_1 (log K_{Na} ~5.2) is found to be higher than that in NO_4 macrocycle as Na(I) binds to the macrocycle as well as the upper deck of the cryptand cavity.

The metal salts $Zn(ClO_4)_2(H_2O)_6$, $Cu(ClO_4)_2(H_2O)_6$, $Ni(ClO_4)_2(H_2O)_6$, $Co(ClO_4)_2(H_2O)_6$, $Fe(ClO_4)_2(MeCN)_4$, $Mn(ClO_4)_2(H_2O)_6$, $Cd(ClO_4)_2$ xH_2O and $HClO_4$, $Pb(NO_3)_2$, $AgBF_4$, $Tl(ClO_4)_3.xH_2O$ were used as ionic input for the photophysical studies. The hydrated metal perchlorate and nitrate salts can generate protons in organic solvents. These protons can engage the lone pair of nitrogens causing fluorescence enhancement by effectively blocking the PET. It is expected that like metal ion complexation, protonation will result in a significant fluorescence recovery of L_1. But, Fluorescence enhancement (20 fold) due to protonation is found to be much lower in comparison to the metal ions. This indicates that PET is not completely blocked upon protonation even in

the presence of excess H^+. The complex binding constant for H^+ in presence of Na(I) is found to be one order lower than that for transition metal ions. This is in consistent with our earlier observation that all the N atoms in the cryptand cannot be protonated.

[For further details, one can see: (a) D. K. Chand and P. K. Bharadwaj, *Inorg. Chem.*, 1998, **37**, 5050; (b) M. B. Roy, S. Ghosh, P. Bandyopadhyay and P. K. Bharadwaj, *J. Lumin.*, 2001, **92**, 115].

Hence, in order to verify that the fluorescence enhancement is due to the metal ion input not because of protonation, control experiments have been carried out with acid in dry as well as aqueous THF medium.

[For details, one can see (a) P. Ghosh, P. K. Bharadwaj, J. Roy and S. Ghosh, *J. Am. Chem. Soc.*, 1997, **119**, 11903; (b) B. Ramachandram, G. Saroja, N. B. Sankaran and A. Samanta, *J. Phys. Chem. B*, 2000, **104**, 11824].