

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

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Attachment of a laterally non-symmetric cryptand and a macrocycle at the 9- and 10-positions of anthracene leads to a fluorescent signaling system  $L_1$  which gives fluorescence enhancement in the simultaneous presence of alkali and transition metal ions.

Molecular systems combining binding ability with the initiation or inhibition of photoinduced electron transfer (PET) processes<sup>1</sup> as a mode of signal transduction are of great demand for developing molecular-scale information processors.<sup>2–4</sup> Depending upon the input/output functionality,<sup>5</sup> different types of molecular logic gates may be constructed with such systems. The modulation of the fluorescence signal by two simultaneous ionic inputs can emulate the behavior of an *AND* logic gate.<sup>6</sup> Presently available molecular systems with *AND* logic action uses a combination of proton and alkali/alkaline earth metal ion as ionic inputs. We present here, a fluorescent PET signaling system  $L_1$  which mimics the function of a molecular *AND* logic gate with a transition and an alkali metal as the ionic inputs. The use of transition metal ions in fabricating molecular photonic devices is potentially important due to the availability of various redox states of the metal ion.

In this modular design (Fig. 1), receptor<sub>1</sub> is an aza-oxa crown ether known for its binding tendency<sup>7</sup> toward alkali/alkaline earth metal ions whereas the receptor<sub>2</sub> is a cryptand having a strong affinity of forming inclusion complexes<sup>8</sup> with transition metal ions.

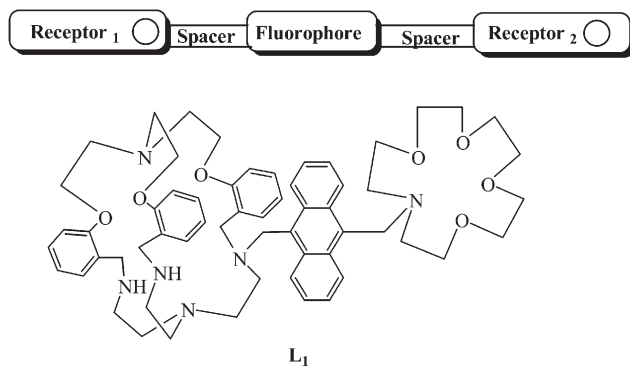


Fig. 1 Molecular structure of  $L_1$ .

Synthesis of the compound  $L_1$  is achieved in several steps. The macrocycle<sup>9</sup> 4,7,10,13-tetraoxa-1-azacyclopentadecane is derivatized with 9-bromomethylantracene followed by bromomethylation at the 10-position of anthracene in the presence of paraformaldehyde and 30% HBr in AcOH yielding 9'-methyl-(4,7,10,13-tetraoxa-1-azacyclopentadecanyl)-10'-bromomethylantracene. This compound is condensed with the di-BOC protected cryptand.<sup>10</sup> Removal of the BOC groups with trifluoroacetic acid in dry THF affords  $L_1$  in an overall 12% yield (see ESI†).

The photophysical properties of  $L_1$  have been determined in different solvents (see ESI†). The absorption spectra of  $L_1$  in dry THF exhibits the (0,0) band at 403 nm with vibrational structures at 382, 363 and 345 nm, characteristic of bis-9,10-alkyl substituted anthracene. This suggests the absence of any interaction between the N lone-pair of the receptors and the anthracene group in the ground state. These transitions do not exhibit any solvatochromic behavior. Upon complexation, a slight blue shift of these transition is observed along with a decrease in molar extinction coefficient ( $\epsilon$ ). When excited at 363 nm, anthracene  $\pi \rightarrow \pi^*$  emission is observed in all the solvents investigated and found to be slightly solvatochromic in nature. The fluorescence quantum yield ( $\phi_F$ ) of  $L_1$  is slightly higher<sup>11</sup> in solvents with low polarity compared to that in solvents of high polarity (e.g. 0.0206 in toluene *cf.* 0.0039 in DMF). In the absence of any input, the fluorescence quantum yield ( $\phi_F$ ) is extremely low (0.0037 in dry THF) due to efficient PET processes operative from both donor N atom lone pairs to the excited anthracene. When Na(I) or K(I) ion is added, the  $\phi_F$  is still low (Table 1) because receptor<sub>2</sub> still remains empty keeping the PET from its side operational. In presence of excess of alkali metal ion, the metal may bind to the upper deck of the receptor<sub>2</sub> that does not block the PET process, as observed earlier.<sup>12</sup> In a similar fashion, with only a transition metal ion input, PET from receptor<sub>1</sub> remains operative (Table 1).

However, when both transition and alkali metal ions are added, the PET is blocked from both ends leading to significant recovery of fluorescence. Addition of excess of  $H^+$  does not lead to significant recovery of fluorescence (Table 1) in comparison to the metal ions. The emission behavior on titration (see ESI†) with perchloric acid in dry THF shows that complete protonation of both the receptors yields only  $\sim 20$  fold enhancement of fluorescence. Also, in the situation when the Na(I) ion is bound to receptor<sub>1</sub>, addition of protons to the system exhibits  $\sim 29$  fold enhancement. Thus, the logic action in  $L_1$  is better expressed with metal ion inputs and not with the protons.

† Electronic supplementary information (ESI) available: Detailed synthetic procedure, characterization of  $L_1$  and optical spectroscopic data. See <http://www.rsc.org/suppdata/cc/b4/b413274b/>  
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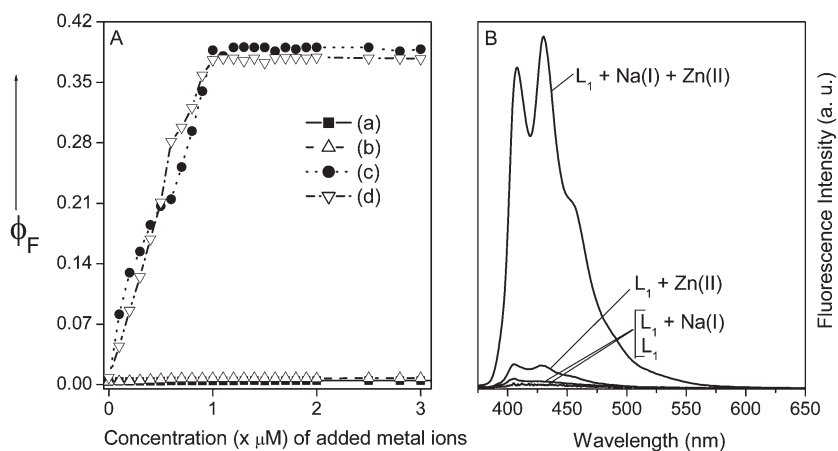
**Table 1** Fluorescence output with different cation input<sup>a</sup>

Chemical input		Fluorescence quantum yield <sup>d</sup> ( $\phi_F$ ), [FE, <sup>c</sup> output state <sup>d</sup> ]
Input 1 ( $I_1$ ), [state] <sup>b</sup>	Input 2 ( $I_2$ ), [state] <sup>b</sup>	
None [0]	None [0]	0.0037 [1, low, 0]
Na(I) [1]	None [0]	0.0047 [ $\sim 1$ , low, 0]
K(I) [1]	None [0]	0.0043 [ $\sim 1$ , low, 0]
Mn(II) [1]	None [0]	0.0084 [2, low, 0]
Fe(II) [1]	None [0]	0.0093 [ $<3$ , low, 0]
Co(II) [1]	None [0]	0.0066 [ $<2$ , low, 0]
Ni(II) [1]	None [0]	0.0051 [ $\sim 1$ , low, 0]
Cu(II) [1]	None [0]	0.0069 [ $<2$ , low, 0]
Zn(II) [1]	None [0]	0.0083 [2, low, 0]
H <sup>+</sup> [1]	H <sup>+</sup> [1]	0.074 [20, high, 1]
Na(I) [1]	Mn(II) [1]	0.339 [92, high, 1]
Na(I) [1]	Fe(II) [1]	0.375 [101, high, 1]
Na(I) [1]	Co(II) [1]	0.311 [84, high, 1]
Na(I) [1]	Ni(II) [1]	0.190 [51, high, 1]
Na(I) [1]	Cu(II) [1]	0.239 [65, high, 1]
Na(I) [1]	Zn(II) [1]	0.391 [106, high, 1]
Na(I) [1]	Cd(II) [1]	0.362 [98, high, 1]
Na(I) [1]	Pb(II) [1]	0.249 [67, high, 1]
Na(I) [1]	Tl(III) [1]	0.158 [43, high, 1]
Na(I) [1]	Ag(I) [1]	0.144 [39, high, 1]
Na(I) [1]	H <sup>+</sup> [1]	0.106 [29, high, 1]
K(I) [1]	Fe(II) [1]	0.372 [101, high, 1]
Mn(II) [1]	Na(I) [1]	0.327 [88, high, 1]
Fe(II) [1]	Na(I) [1]	0.375 [101, high, 1]
Co(II) [1]	Na(I) [1]	0.319 [86, high, 1]
Ni(II) [1]	Na(I) [1]	0.204 [55, high, 1]
Cu(II) [1]	Na(I) [1]	0.248 [67, high, 1]
Zn(II) [1]	Na(I) [1]	0.381 [103, high, 1]

<sup>a</sup> Experimental conditions: medium, dry THF; concentration of free ligand:  $1 \times 10^{-6}$  M; concentration of ionic input:  $\sim 1 \times 10^{-5}$  M;  $\lambda_{\text{ex}} = 363$  nm; excitation band-pass: 5 nm; emission band-pass: 5 nm; temperature: 298 K;  $\phi_F$  calculated by comparison of corrected spectrum with that of anthracene ( $\phi_F = 0.297$ ) taking the area under the total emission. The error in  $\phi_F$  is within 10%. <sup>b</sup> Chemical input state: absence [0] and presence [1],  $I_1$ ; first and  $I_2$ ; second ionic inputs, respectively. <sup>c</sup> FE: Fluorescence enhancement in comparison to the cation free ligand. <sup>d</sup> Fluorescence output state: low [0] and high [1].

The amount of fluorescence recovery depends upon the nature of metal ion inputs. Among all the metal ions investigated, fluorescence recovery is maximum ( $>100$  fold enhancement) with Na(I) and Zn(II)/Fe(II) as inputs. The nature of the graph of a fluorescence titration of  $L_1$  as a function of concentration of Na(I) and Zn(II) inputs (Fig. 2(A)) indicates a 1:1 complex formation with each of the ionic inputs. The overall fluorescence enhancement is found to be almost the same when Na(I) is added first and then Zn(II) or *vice-versa* (Table 1). The complexation binding constant ( $K_s$ ) determination<sup>13</sup> reveals that presence or absence of Zn(II) ions do not affect the  $K_{\text{Na(I)}}$  value and *vice-versa*, which indicates a significant inter-receptor separation<sup>6a</sup> independent of each other. As the fluorescence is significantly recovered only in presence of both the inputs,  $K_s$  for one input could only be determined in the presence of the other, which provides a basis for formation of inclusion complexes by the receptors. A similar emission behavior is observed in the fluorescence titration (see ESI†) of  $L_1$  with Na(I)/K(I) and Fe(II). This is found to be consistent for all the transition/heavy metal ions studied in combination with Na(I)/K(I) suggesting that alkali metals occupy the macrocyclic cavity while other metals are included in the cryptand cavity. Thus,  $L_1$  exhibits the function of a potential AND logic gate (Fig. 2(B)). However, restoring the logic levels is the essence of any logic operator where the operative gate is to be reset to its initial parameters. Structural modifications to the receptor cores and/or translocation of the metal ionic inputs 'in and out' of the receptor cavity by employing the coordinating tendencies of counter-anions can bring about the reversibility to the system, which further opens up a scope to improve its logic gate properties and efficiency.

In conclusion, we have shown here that with proper design, a molecular AND logic action can be observed with one of the ionic inputs as a transition metal ion. Efforts are under way to find out if any lanthanides can cause fluorescence enhancement in similar compounds as this would potentially mimic higher-order complex functions.



**Fig. 2** (A) Plot of fluorescence quantum yield of  $L_1$  at  $1 \times 10^{-6}$  M concentration as a function of amount of metal ion added: (a) Na(I), (b) Zn(II), (c) Zn(II) to a solution of  $L_1$  with 1 equivalent of Na(I) and (d) Na(I) to a solution of  $L_1$  with 1 equivalent of Zn(II). (B) Fluorescence emission spectra for  $L_1$  under different input conditions (details in Table 1). Pictorial representation of the function of a molecular AND logic gate.

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