

# Exocyclic coordination and translocation of metal ions in laterally non-symmetric aza cryptands

Bamaprasad Bag, Pritam Mukhopadhyay and Parimal K. Bharadwaj\*

Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India

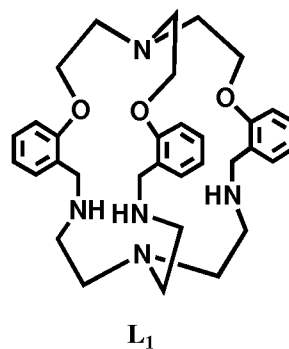
**Laterally non-symmetric aza cryptands incorporating N atoms in the three bridges, readily make inclusion complexes with a number of transition as well as main-group metal ions. The donor ability of the N atoms in the bridges can be modulated through attachment of electron-withdrawing groups. In this modified cryptand, a metal ion can be translocated from inside the cavity to the outside depending on the nature of the counter anion. Translocation of a metal ion between inside and outside a cryptand cavity is highly desirable as it can lead to the development of paradigms for a new class of molecular systems, adding a new dimension to the kinetic, thermodynamic and a multitude of other properties in these systems. This process of translocation of a metal ion can be studied in solution when a suitable group is attached and in some cases, the complexes can be characterized by X-ray crystallography.**

**Keywords:** Cryptand, exocyclic coordination, metal ion translocation, signal transduction, supramolecular chemistry.

MACROPOLYCYCLIC cryptands have found a wide range of applications<sup>1–5</sup> that cover most areas of chemistry and several fields of biological and material sciences as well. Since the early years of discovery<sup>6</sup> of cryptands, its use<sup>7–10</sup> for complexation of metal ions to tackle various problems has attracted considerable attention over the period. Cryptands can act as receptors for selective binding of substrates, as catalysts by assisting chemical transformation among bound substrates and as carriers for transport through membrane besides a host of other potential applications. These molecules provide a number and type of donor atoms in space, whose topology and binding site rigidity can be varied via ligand design to accommodate ions, neutral molecules or both forming inclusion complexes known as cryptates. The nature and selectivity of a cryptand can be modulated by placing appropriate donor atoms at strategic positions through ligand design. However, the desired selectivity of a cryptand towards a single metal ion in presence of several others remains an elusive goal. A number of books and review articles<sup>11–14</sup> are available in the literature devoted to the chemistry of N-

bridgehead polyether cryptands and their potential applications.

A laterally non-symmetric aza cryptand<sup>15</sup> such as **L<sub>1</sub>** is known to form complexes<sup>7,16,17</sup> with transition as well as main-group metal ions, many of which have been characterized by X-ray crystallography. Further, having three derivatizable bridging amino sites, functionalization with a group of interest leads this molecule to perform several functions<sup>18</sup> along with metal ion-assisted perturbation of these functional aspects upon its inclusion in the cavity of the cryptand, such as in fluorescence signalling<sup>19–21</sup> and molecular photonics<sup>22,23</sup>, nonlinear activity<sup>24,25</sup>, amphiphiles/vesicle formation<sup>26–29</sup>, etc. It is found that the metal ion always enters the cavity of the cryptand forming inclusion complexes<sup>30</sup> that originate from both thermodynamic and kinetic factors. Being a flexible covalent framework, this cryptand molecule gets pre-organized for effective binding with the metal ion prior to complexation and hence brings about selectivity towards a metal ion.



Translocation of a metal ion between inside and outside a cryptand cavity<sup>31</sup> is highly desirable as it can lead to the development of paradigms for a new class of molecular systems, adding a new dimension to the kinetic, thermodynamic and a multitude of other properties in these systems. A pertinent question, therefore, would be when can such a cryptand be forced to bind a metal ion from outside overcoming the *cryptate effect*? For the aza cryptands, the easiest way this can be achieved would be to alter the donor characteristics of the amino nitrogens in the three bridges. The donor ability can be tuned to effect translocation of a

\*For correspondence. (e-mail: pkb@iitk.ac.in)

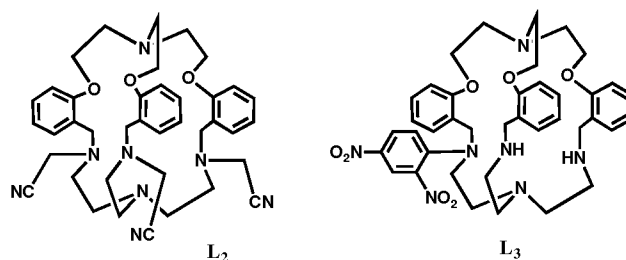
metal ion from inside the cavity to outside the cavity, depending on various factors such as nature of counter anions, dielectric constant of the solvent, temperature, and so on. Although reversible translocation of a metal centre between two unequivalent compartments in terms of nature and pattern of coordination sites of a diatopic ligand under the action of redox activity or pH variation have been reported<sup>32</sup>, no reports are available concerning translocation of metal ion 'in' and 'out' of the cavity of a macrocycle or a cryptand where the *macrocyclic* or *cryptate* effect comes into play to enforce the metal ion in forming inclusion complexes. Describing our effort in this direction with space limitation, the present review is restricted to probing the ways which allow translocation of a metal ion from inside the cavity to outside and vice versa.

The efficient and reversible metal ion translocation 'in and out' of the cryptand cavity comes into action through exploration of the coordination properties and the binding conditions of cryptand forming both inclusion and exocyclic complexes. Despite the *cryptate effect* that favours the metal ion entering the cavity, influential factors such as lower metal–ligand kinetics, larger size of the metal ion than the cavity, structural rigidity of the covalent architecture, availability of lesser number of donor atoms favouring inclusion complexes and reduction of their coordinating tendencies, etc. compels the metal ion to bind the cavity from outside. The easiest way for an exocyclic coordination with a non-symmetric cryptand **L**<sub>1</sub> is to attach rigid electron-withdrawing groups, which not only reduces the donor ability of the bridging amino atoms but also provides a steric rigidity to the cavity creating a thermodynamically unfavourable condition for the metal ion entering the cavity. This way, donor ability of the amino nitrogens for binding the metal ion inside the cavity will be modulated to encourage it to bind from outside. The perturbation of the donor ability of the bridging amino N atoms depends upon the electron-withdrawing nature of the substituents. A partial derivatization of the cryptand with moderate electron-withdrawing groups, preferably mono functionalization provides a better insight to the translocation process. In this situation, although the donating ability of functionalized amino group is modulated and depending upon its electron-withdrawing character, it may or may not participate in metal ion coordination, the other two unfunctionalized bridging amino groups are still available to form inclusion complexes that abide cryptate effect and also provides a basis for the metal ion to translocate under the influence of external agents.

### Exocyclic coordination

The three secondary amino groups in the un-substituted cryptand **L**<sub>1</sub> exhibit<sup>33</sup> different *pK<sub>a</sub>* values and can be functionalized with cyano-methyl groups to obtain **L**<sub>2</sub> and also can be selectively mono-derivatized<sup>34</sup> with 2,4-di-

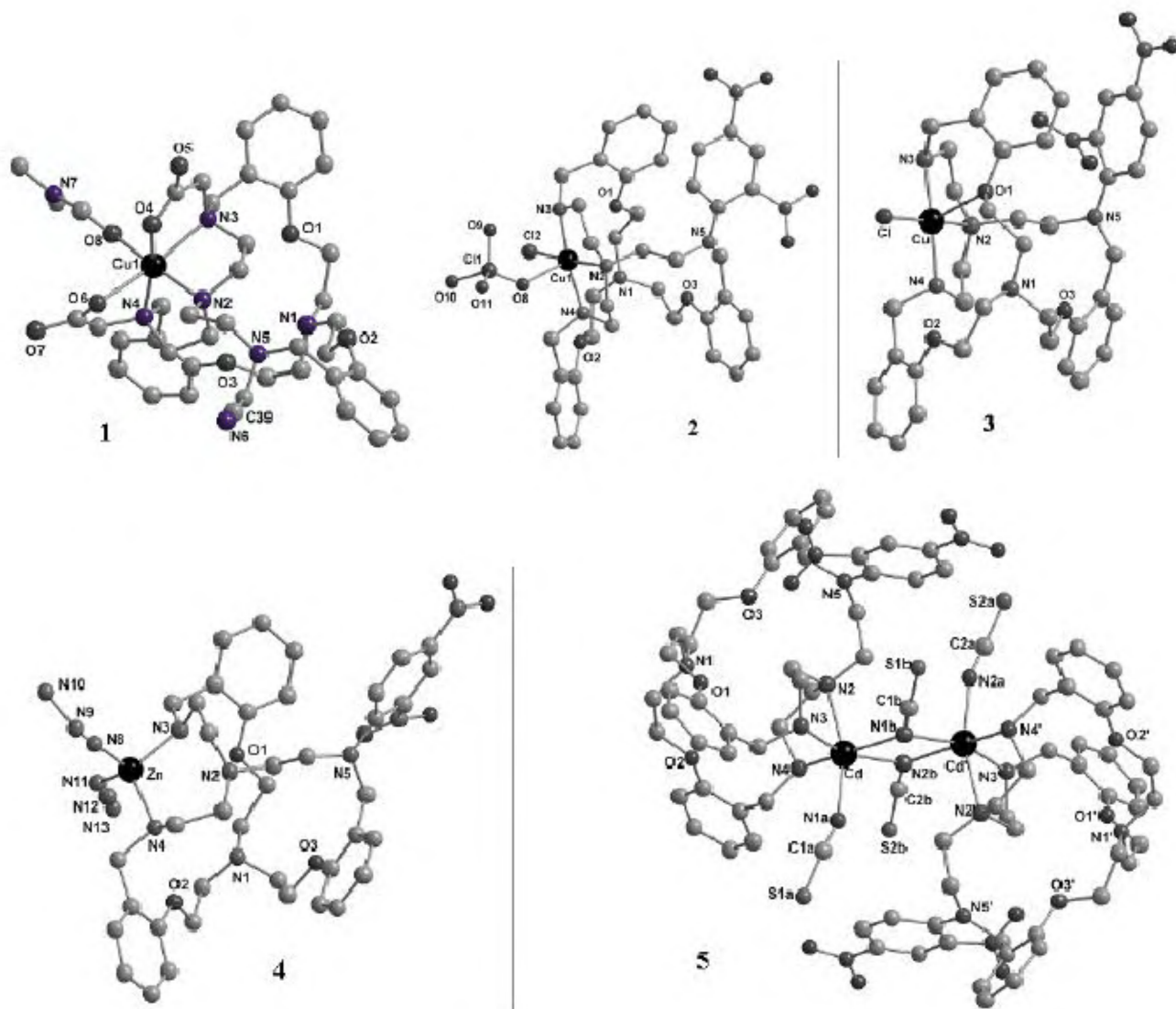
nitrobenzene via aromatic nucleophilic substitution to afford **L**<sub>3</sub>.



Single crystal X-ray structural analyses<sup>35,36</sup> of the various transition metal ion complexes of **L**<sub>2</sub> and **L**<sub>3</sub> such as [Cu(**L**<sub>2</sub>')(DMF)](BF<sub>4</sub>)<sub>2</sub> (**1**) (two of the cyanomethyl groups of **L**<sub>2</sub> are *in-situ* hydrolysed to carboxylic acids group to form **L**<sub>2</sub>'), [Cu(**L**<sub>3</sub>)Cl.ClO<sub>4</sub>].H<sub>2</sub>O (**2**), [Cu(**L**<sub>3</sub>)Cl].BF<sub>4</sub> (**3**), [Zn(**L**<sub>3</sub>')(N<sub>3</sub>)<sub>2</sub>] (**4**) and [Cd(**L**<sub>3</sub>')(NCS)<sub>2</sub>].1/2MeOH.1/2MeCN.2H<sub>2</sub>O (**5**) revealed that the metal ion in each case bind to the cryptand core from outside through three of the N atoms at the tren (tren = tris(2-aminoethylamine)) end. In all the cases, exocyclic coordination of metal ions results in the cryptand cavity to shrink from the bridgehead end. A perspective view of two of these complexes is shown in Figure 1.

The coordination geometry around the metal ion depends upon the nature of the electron withdrawing groups attached, the extent of rigidity induced of the covalent framework, counter anion, solvents in the coordination sphere, etc. In **1**, Cu(II) binds to the cryptand cavity in a distorted octahedral fashion where two bridging N atoms and two oxygen atoms of two caboxylates (generated as a part of metal ion activated *in-situ* hydrolysis of two of the cyanomethyl groups) occupy the basal plane while tren-end bridgehead N-atom and a DMF occupy the axial positions. The non-hydrolysed cyanomethyl groups remain farthest away from the metal ion.

Structural analysis of the complexes of **L**<sub>3</sub> explains the pattern of exocyclic coordination of the metal in different environment. The coordination geometry around the Cu(II) in complex **2** is square pyramidal with two free secondary bridging amino N atoms, the bridgehead nitrogen atom at N<sub>4</sub> end and a Cl<sup>−</sup> ion occupying the basal plane along with the oxygen atom of perchlorate at axial position. The binding mode of the same metal ion differs upon variation of counter anions. As in **3**, Cu(II) binds to the cavity from outside in a square pyramidal fashion where two bridging amino and the bridgehead nitrogen atoms along with a Cl<sup>−</sup> ion occupy the base and the axial position is occupied by an ethereal O atom of the cryptand architecture. This difference in the binding mode of Cu(II) with the derivatized cryptand **L**<sub>3</sub> in **2** and **3** is due to the less coordinating nature of BF<sub>4</sub><sup>−</sup> ion in comparison to that of ClO<sub>4</sub><sup>−</sup> ion. In complex **4**, Zn(II) is bound to **L**<sub>3</sub> from outside the cavity through two bridging amino N atoms,

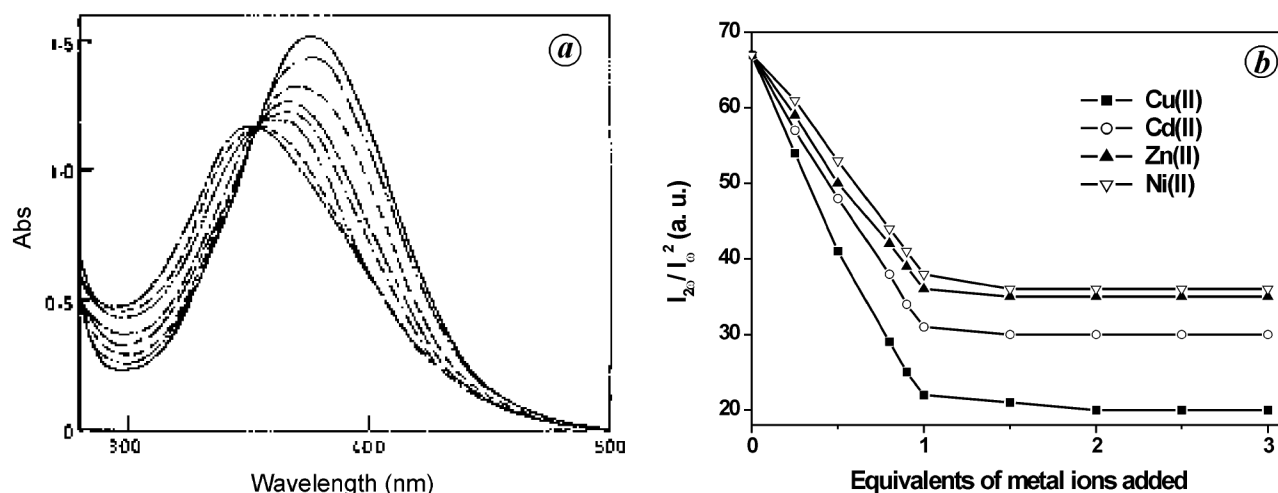


**Figure 1.** A perspective view of the crystal structures of  $[\text{Cu}(\text{L}_2')(\text{DMF})](\text{BF}_4)_2$  (**1**),  $[\text{Cu}(\text{L}_3)\cdot\text{Cl}(\text{ClO}_4)]\cdot\text{H}_2\text{O}$  (**2**),  $[\text{Cu}(\text{L}_3)\text{Cl}](\text{BF}_4)$  (**3**),  $[\text{Zn}(\text{L}_3)(\text{N}_3)_2]$  (**4**) and  $[\text{Cd}(\text{L}_3)(\text{NCS})_2]\cdot 1/2\text{MeOH}\cdot 1/2\text{MeCN}\cdot 2\text{H}_2\text{O}$  (**5**) showing the metal ion bound to the cryptand from outside as a result of structural modification to the cryptand architecture. The numbering pattern of the carbon atoms in all cases are omitted for clarity.

and along with two azide coordination, the geometry around Zn(II) is tetrahedral. Further, a dimeric structure of **5** reveals that each of the two Cd(II) is bonded<sup>36</sup> to the cryptand through its two bridging amino and the bridgehead nitrogen atoms, one terminal and two bridging thiocyanate anions with a distorted octahedral geometry. In these complexes, the N–C bond distance between the cryptand framework and the phenyl ring of the 2,4-dinitrobenzene group is significantly shorter (1.356–1.373 Å) compared to normal N–C bond length<sup>16,35</sup> of **L**<sub>1</sub>. This is due to delocalization of electron density from donor N atom of the cryptand to the attached electron-withdrawing aromatic  $\pi$  system, inducing a partial double bond character of N–C bond, which restricts the donor N atom for metal ion coordination. As the cryptand core is not very rigid, it distorts itself to different extent for optimum

binding metal ion outside the cavity at the *tren*-end while the electron withdrawing 2,4-dinitrobenzene group remains farthest away from the metal ion. The distance between the bridgehead nitrogens is reduced in all these complexes in comparison to that of cryptand **L**<sub>1</sub>. In each case, the metal ion has pulled the three N-donor atoms of the cryptand toward itself enforcing the lone pairs of these three N atoms directed towards the metal ions. Hence, upon metal binding, the derivatized cryptand gets modified to an *endo-exo* conformation.

Exploration of the favourable thermodynamic condition for both inclusion complexes and exocyclic coordination of the cryptand molecule provides a basis for operation of translocation process, which further performs many molecular functions upon covalent attachment of a group of interest to the cryptand architecture.



**Figure 2a, b.** a, Effect of **Cu(II)** addition on the UV spectra of **L3**: (—) metal free ( $5 \times 10^{-5}$  M); (---) **Cu(II)** ( $2.5 \times 10^{-5}$  M); (- -) **Cu(II)** ( $5 \times 10^{-5}$  M); (- · -) **Cu(II)** ( $1.6 \times 10^{-4}$  M); (- · · -) **Cu(II)** ( $5 \times 10^{-4}$  M); (- · · · -) **Cu(II)** ( $8 \times 10^{-4}$  M); (- - -) **Cu(II)** ( $1.6 \times 10^{-3}$  M); (· · ·) **Cu(II)** ( $5 \times 10^{-3}$  M). b, Titration curve of HRS signal ( $I_{20}/I_0^2$ ) of **L3** as a function of equivalents of metal ions added showing 1 : 1 stoichiometry.

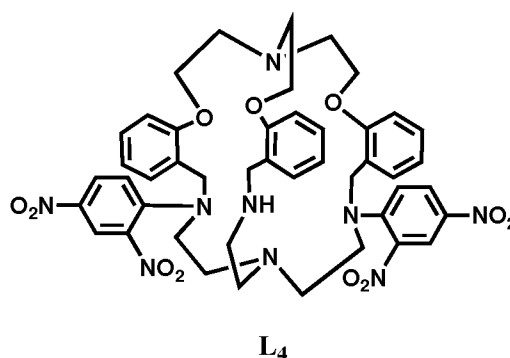
### Anion-driven translocation

Compound **L3** shows an intense absorption band centred at 380 nm due to an intramolecular charge transfer (ICT) transition from the donor N atom to the acceptor dinitrobenzene moiety which can accept electron density into its available  $\pi$ -symmetry orbital. The unsubstituted cryptand or its metal cryptate is almost transparent in the range 300–450 nm. Therefore, ICT can be used to monitor the inclusion of a metal ion inside the cavity as it can communicate with the D- $\pi$ -A chromophore modulating the position as well as intensity of the ICT band. Addition of a metal ion such as **Ni(II)**, **Cu(II)**, **Zn(II)** or **Cd(II)** as perchlorate or tetrafluoroborate salt to a THF solution of **L3** induces a blue-shift with concomitant lowering of intensity of the ICT band. Its complex with cupric perchlorate exhibits a maximum blue-shift (~21 nm with respect to free **L3**). Upon complexation, the N atom donates its electron density to the metal ion in the cavity and weakens the ICT operative in the D- $\pi$ -A unit, and hence, the higher degree of destabilization of the excited state dipole moment in comparison to that of the ground state results in a blue-shift of the transition. A well-defined isobestic point (Figure 2a) on absorption spectra of **L3** upon titration with metal perchlorate salts suggests a 1 : 1 stoichiometry. On adding NaCl, KSCN or  $\text{NaN}_3$  to the solution, the ICT band position and intensity slowly returns to the values of free **L3**. Also, when the chloride salts of these metal ions are used, no shift or change of intensity of the ICT band is observed, indicating that the metal ion preferably binds the cryptand from outside in presence of a coordinating anion.

### Modulation of quadratic optical nonlinearity

Cryptands having a three-fold symmetry axis passing through the two bridgeheads can act as perfect skeletons

for designing D(donor)- $\pi$ -A(acceptor) chromophores for nonlinear optical activity<sup>24,25</sup>. Besides, rigidity of the cryptand cavity can be varied by incorporating different groups in the three bridges. Some of the cryptand molecules can be selectively functionalized with different - $\pi$ -A units giving rise to molecules where metal ions can occupy the cavity and can bond the N atom attached to the - $\pi$ -A unit, thereby modulating the electrical polarizability of the system. This can, however, be further perturbed upon translocation of the metal ion from inside to outside of the cavity as a function of external agents. Compound **L3** consist of a D- $\pi$ -A unit in its architecture, hence it exhibits<sup>34</sup> quadratic optical nonlinearity ( $\beta$ ). Translocation of a metal ion in **L3** and the bis-2,4-dinitrobenzene functionalized cryptand, **L4** leads to switchability of this nonlinearity in solution as illustrated in Scheme 1.



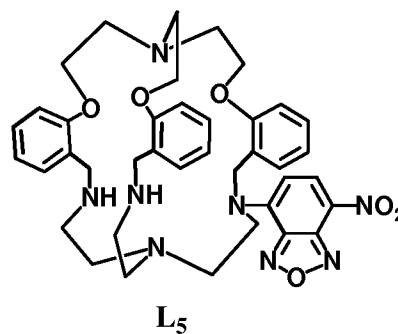
In agreement with the UV-vis studies, addition of an alkali or alkaline earth metal ion does not change the HRS signal intensity for **L3** and **L4** as these metal ions occupy the upper deck of the cavity. However, addition of a transition metal perchlorate salt causes substantial decrease in the  $\beta$  values. In conformity with the absorption spectral

studies, Cu(II) modulates  $\beta$  to the maximum extent of 47% and 60% for **L**<sub>3</sub> and **L**<sub>4</sub> respectively as this metal ion can tune its geometry according to the pre-organized binding sites in these molecules, compared to the other metal ions like Ni(II), Zn(II) and Cd(II) that prefer higher coordination numbers. Titration experiments with **L**<sub>3</sub> to explore NLO modulation show a 1:1 stoichiometry of complex formation (Figure 2*b*). Addition of NaCl or NaN<sub>3</sub> to the Cu(II) complex of **L**<sub>3</sub> leads to gradual increase of SHG intensity until it almost reaches the value shown by the metal-free cryptand due to complete removal of the Cu(II) ion from the cavity. Removal of the Cl<sup>−</sup> ion by adding an equivalent amount of AgBF<sub>4</sub> coax the Cu(II) ion to enter the cavity leading to decrease in the  $\beta$  value once again.

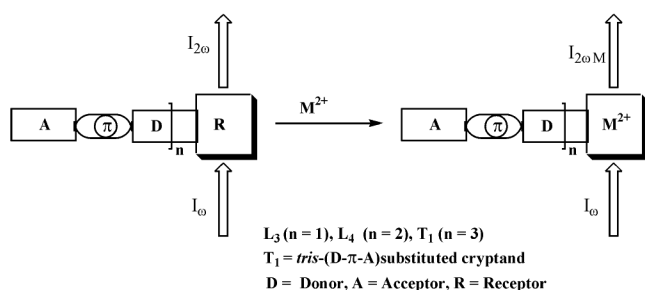
### Reversibility of fluorescence signalling and chemical logics

Many fluorescent signalling systems exploiting photo-induced intramolecular electron transfer (PET) mechanism with metal ions as input are known<sup>37–42</sup>. These systems are designed to covalently link fluorophores to nitrogen atoms present in the receptor. In the metal-free state, the nitrogen lone-pair is donated to the excited fluorophore via PET and the excited fluorophore comes to the ground state through a non-radiative pathway causing quenching of fluorescence. When a metal ion engages this lone-pair through bonding, the PET is blocked leading to recovery of fluorescence. A system with fluorescent ON/OFF capability can potentially act as a molecular photonic switch<sup>43,44</sup>, which is the most important component of any true photonic device. Many problems remain with crafting and operating such a device. A cryptand-based receptor is ideal for efficient fluorescence signalling because, once a metal ion enters the cavity of this receptor, it is isolated from the surroundings, enabling it to nullify most, if not all, of the quenching pathways. The immediately realizable objective is, however, to build molecular systems exhibiting useful photonic properties that can be modulated. A

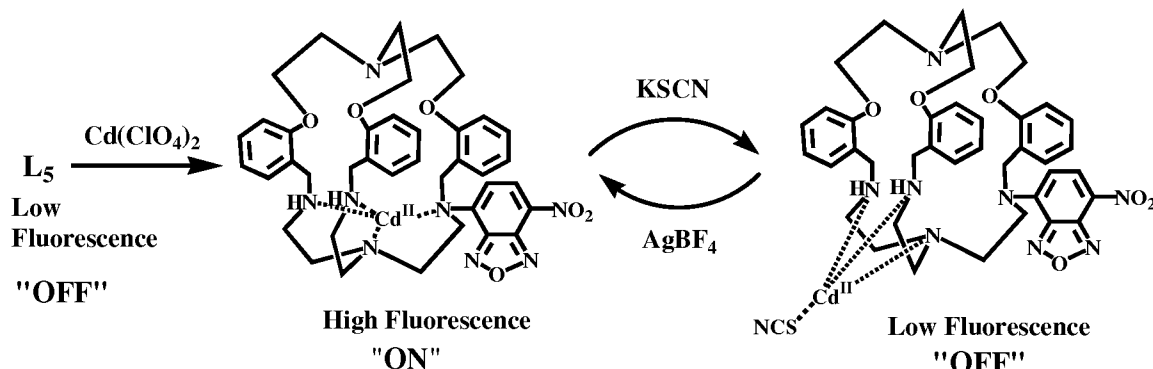
fluorophore with electron-withdrawing ability such as 7-nitrobenzo-2-oxa-1,3-diazole is when directly attached<sup>45</sup> to the secondary N atom in one of the bridges of **L**<sub>1</sub> to obtain **L**<sub>5</sub> forming a 'PET reagent' with fluorescent ON-OFF capability, responds efficiently towards signal transduction upon translocation of the metal ion in and out of the cavity.



With Cd(II) ion, it works well as a reversible signal transducer<sup>46</sup>. The translocation of the Cd(II) ion can be studied in solution by monitoring both the ICT as well as the emission characteristics. Metal-free **L**<sub>5</sub> exhibits the ICT band at 479 nm in dry THF that undergoes a small blue-shift in presence of Cd(II) due to stabilization of the N donor orbital. It exhibits a very weak fluorescence ( $\phi_F = 0.0019$ , THF) in the metal-free state due to an efficient PET. The fluorescence can be recovered by adding a perchlorate/tetrafluoroborate salt of a transition/heavy metal ion in dry THF due to disruption of the PET process. Among the metal ions studied, Cd(II) exhibits a maximum of ~240 fold enhancement ( $\phi_F = 0.457$ , THF) with respect to the metal-free **L**<sub>5</sub>. Fluorescence titration with Cd(II) indicates that it forms a very stable 1:1 inclusion complex, is consistent with the solution and solid state studies of the parent cryptand **L**<sub>1</sub> with the same metal ion. Modulation of the fluorescence signal is effected through translocation of the Cd(II) ion. When coordinating anions such as Cl<sup>−</sup>, SCN<sup>−</sup> or N<sub>3</sub><sup>−</sup> are added, the metal comes out of the cavity and prefers to bind the receptor from outside away from the fluorophore causing restoration of PET and quenching of the fluorescence. The extent of quenching depends upon the coordinating ability of the counter anion toward Cd(II). Addition of SCN<sup>−</sup> exhibits lowest fluorescence quantum yield ( $\phi_F = 0.006$ , THF); lowering the emission almost to the level of **L**<sub>5</sub> alone. The metal ion can be put back into the cavity upon addition of AgBF<sub>4</sub> with the fluorescence mostly recovered ( $\phi_F = 0.333$ , THF). Of course, the quantum yield is much higher compared to the situation when AgBF<sub>4</sub> is added to **L**<sub>5</sub>, confirming the enhancement due to Cd(II) and not due to Ag(I). The excess Ag(I) present in the solution can be removed by adding NaCl in aqueous THF. However, the enhancement is still lower compared to the original situation which could be due to protons generated in the system. This is further supported by the experiment that when AgBF<sub>4</sub> is added to the solution of **L**<sub>5</sub> containing Cd(II)



**Scheme 1.** A schematic representation for NLO switching responses in D- $\pi$ -A functionalized cryptand molecules. R = receptor, D = donor,  $\pi$  = aromatic ring, A = acceptor,  $n$  = number of D- $\pi$ -A units,  $I_0$  = fundamental light,  $I_{2\omega}$  = second harmonic light,  $I_{2\omega M}$  = modulated second harmonic light as an impact of  $M^{2+}$ -R interaction.



**Scheme 2.** Translocation of Cd(II) ion 'in and out' of the cryptand cavity leading towards a reversible ON-OFF signaling response.

**Table 1.** Truth table for the three inputs molecular switch exhibited by  $L_5$

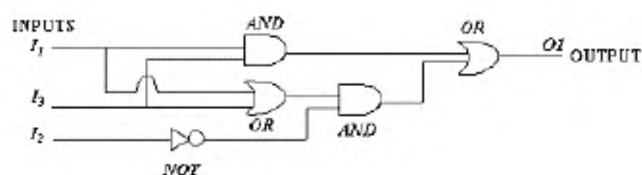
$I_1$ ( $Cd^{II}$ )	Ionic inputs <sup>a</sup> $I_2$ ( $SCN^-$ )	$I_3$ ( $Ag^I$ )	Fluorescence output state <sup>b</sup> (quantum yield)
0	0	0	0 [0.0019, Low]
1	0	0	1 [0.4567, High]
0	1	0	0 [0.002, Low]
0	0	1	1 [0.1503, High]
1	1	0	0 [0.0058, Low]
1	0	1	1 [0.4532, High]
0	1	1	0 [0.0021, Low]
1	1	1	1 [0.442, High]

<sup>a</sup>Chemical input state: Absence, 0; Presence, 1.

<sup>b</sup>Fluorescence output state: Low, 0; High, 1.

and  $SCN^-$  followed by NaCl in aqueous THF in presence of a non-coordinating base like di-*tert*-butyl pyridine, the fluorescence recovery is almost same ( $\Phi_F = 0.442$ , THF :  $H_2O :: 95 : 5$ ). A schematic representation of this ON-OFF switchability through metal ion translocation is shown in Scheme 2.

This system acts like a complex molecular logic<sup>47,48</sup>. The perturbation of photo-physical process by the translocation of metal ion 'in' and 'out' of the cryptand cavity as a function of counter anion results in integrated circuitry. Here, the chemical input signals are  $I_1(Cd^{2+})$ ,  $I_2(SCN^-)$  and  $I_3(Ag^+)$  whereas the output signal  $O_1$  is represented by the fluorescence. When three inputs are absent, the input module is 000; the fluorescence of  $L_5$  is OFF, results a binary output '0'. When  $Cd(II)$  ion is added, the input string reads 100 which produce an output digit '1' as the fluorescence is ON. When  $SCN^-$  is added to the solution containing  $Cd(II)$ , the input string reads 110, the fluorescence of  $L_5$  is quenched, leading to the output state '0'. All possible eight combinations of input data with these three inputs and the corresponding output are given in Table 1. The combinational logic circuit equivalent to the truth table of the communicating ensemble is given in Figure 3.

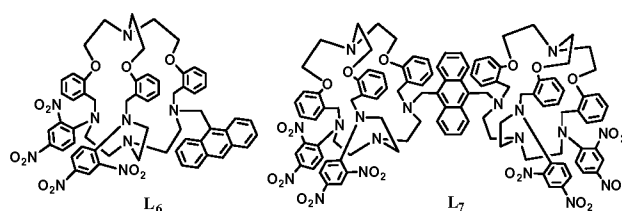


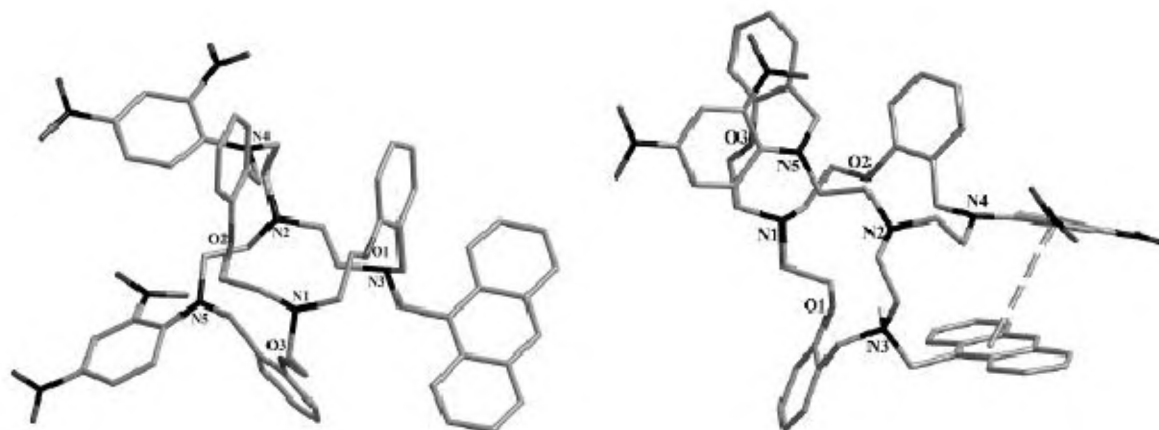
**Figure 3.** Equivalent circuit diagram for the output (fluorescence) of  $L_5$  in combination with three inputs (ionic).

In this circuit, the three inputs  $I_1$ – $I_3$  are processed through an integration of two AND, two OR and a NOT logic operation to produce the output data. Thus, five interconnecting logic gates are required to reproduce the operation executed by  $L_5$  which has the output of eight arrays. In other words, this single molecule can perform the function of an eight array combinational integrated circuit consisting of five logic gates with three inputs.

## Movements of side groups

Binding of a metal ion to a cryptand from outside the cavity affords one to design a molecule showing reversible controlled movements of its parts. Such controlled movement due to an external stimuli enables the system to act as a machine<sup>49–51</sup> working at the molecular level. With a cryptand such as  $L_1$ , exploiting its flexible nature and taking its ability to bind the metal ion within and outside the cavity in consideration, few such molecules, for example  $L_6$  and  $L_7$  were designed which are synthesized<sup>52,53</sup> by derivatization of  $L_1$  with anthryl groups and electron withdrawing 2,4-dinitrobenzene groups at different proportions.





**Figure 4.** A perspective view of  $L_6$  and  $[L_6.H].ClO_4.2MeCN$  showing the movements of one of the 2,4-dinitrobenzene group aligning parallel to the anthracene group which results in exciplex formation.

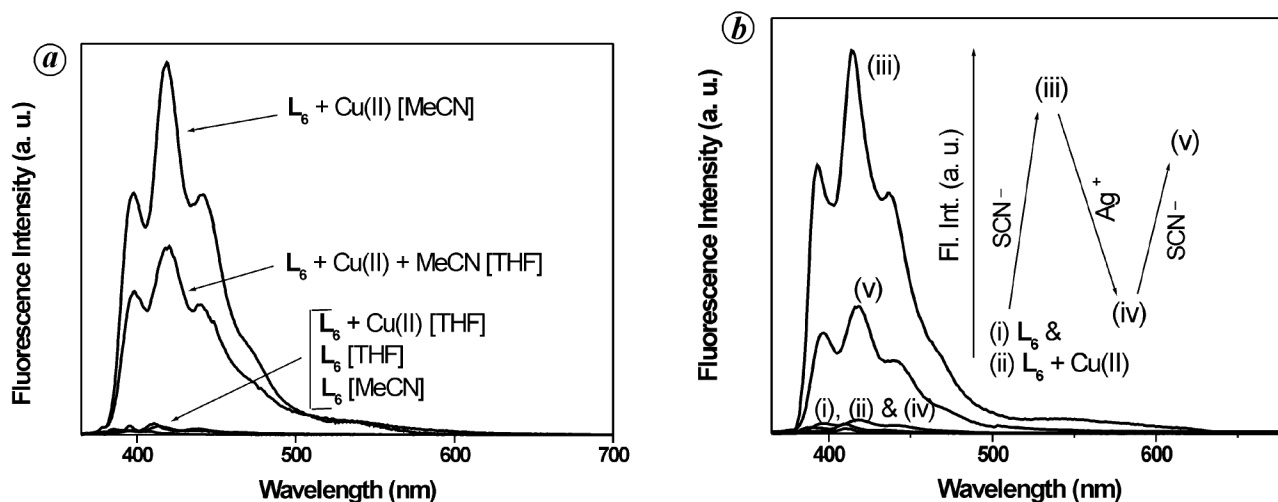
Absorptions observed in 340–400 nm region in metal-free ligands are due to two operative processes – (i) anthracene  $S_0 \rightarrow S_1$  transition with  $\pi-\pi^*$  nature and (ii) the ICT as before. The ICT overlaps with the anthracene transitions and both are non-solvatochromic in nature. Complexation with a transition metal ion in MeCN results in a small shift of the (0, 0) band retaining the spectral pattern, except in presence of Cu(II) where the Frank–Condon vibrational structures of ligand absorption transitions are modulated with decrease in molar extinction coefficient. This is indicative of a different binding mode of these signaling systems with Cu(II) in the ground state in contrast to other metal ions.

The LE behaviour of  $L_6$  and  $L_7$  is typical of 9-substituted anthracene as the ICT operative is non-emissive. These compounds do not show any exciplex in metal-free state, particularly in polar solvents. However, in presence of Cu(II) perchlorate in MeCN, depending upon the nature of the architecture of the system, the monomer emission (with emission maxima at ~420 nm) selectively exhibits 80–180 fold increase due to blockade of the PET along with a red-shifted emission centering at ~540 nm. With other transition metals, the fluorescence enhancement is not pronounced, hardly reaches ~20 fold while no enhancement resulted with Cu(I). However, with protons, the fluorescence enhancement varies from 22 to 156 fold. The efficiency of fluorescence recovery to a lesser extent in presence of other transition metal ions except Cu(II) is due to lack of proper interaction in terms of thermodynamic affinity. The attachment of electron-withdrawing groups reduces the donating tendency of the cryptand receptor and thus may only form a stable complex with the metal ion higher in Irving–Williams order of stability. The compounds  $L_6$  form 1:1 and  $L_7$  forms 1:2 complexes with Cu(II) in MeCN. The lower stability constant values<sup>52,53</sup> obtained compared to that<sup>33</sup> of the parent cryptand  $L_1$  suggests that Cu(II) binds to these systems from outside

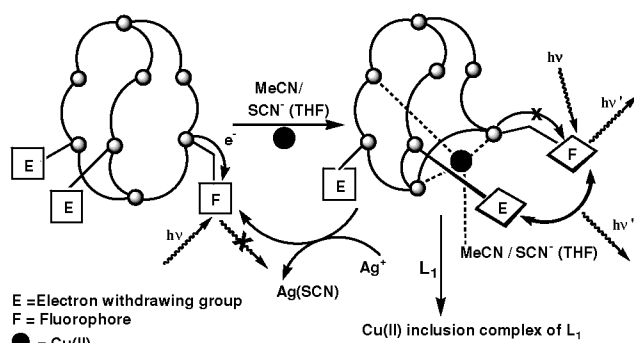
the cavity staying farthest away from the electron-withdrawing groups attached to these systems.

Complexation with Cu(II) also results in the appearance of a broad, red-shifted charge transfer emission band at ~540 nm (excitation at 368 nm) attributable to an exciplex emission originating from the intramolecular interaction between the anthracene and one of the aromatic sidearms. This exciplex is specifically resulted in a coordinating solvent like acetonitrile which usually quenches exciplex emission, and is not observed in other less coordinating solvents like THF,  $CH_2Cl_2$ , etc. From the correlation of the photoluminescence spectra and the X-ray crystal structures (Figure 4) of  $[L_6.H].ClO_4.2MeCN$ , it is evident that one of the 2,4-dinitrobenzene groups moves on protonation and aligns parallel to the anthracene plane showing  $\pi-\pi$  stacking interactions leading to exciplex formation. The intensity of exciplex emission in presence of Cu(II) in MeCN is higher compared to the corresponding protonated species, indicating a stronger  $\pi-\pi$  stacking interaction in the former.

Induction of reversibility can be achieved, in this case, by simply varying the solvent. With  $Cu(H_2O)_6.2ClO_4$ , no significant fluorescence enhancement of these systems is observed in a less coordinating solvent such as THF or  $CH_2Cl_2$ . However, on adding MeCN, monomer emission of  $L_6$  increases ~130 fold along with the exciplex at ~540 nm suggesting participation of MeCN in binding Cu(II) to these systems. Alternatively, when a coordinating counter anion like  $SCN^-$  is added in THF medium, the fluorescence is enhanced (~160 fold) to a similar extent (Figure 5). When  $AgBF_4$  is added to the solution of  $L_6$  containing Cu(II) and  $SCN^-$ , the fluorescence is quenched, almost to the level of metal-free compound due to preferential binding of Ag(I) to  $SCN^-$ , leaving the Cu(II) with  $BF_4^-$  anion when Cu(II) does not bind to  $L_6$  and allows PET to restore. Thus, a reversibility in Cu(II) binding to the systems can be induced with the coordinating tenden-



**Figure 5 a, b.** Cu(II)-induced monomer fluorescence enhancement and exciplex emission of  $L_6$  (a) in THF and/or MeCN shows that MeCN plays the crucial role in Cu(II) binding/detachment to the cryptand cavity, (b) Fluorescence spectra (in THF) of (i)  $L_6$  (ii)  $L_6$  in presence of Cu(II), (iii) after addition of  $SCN^-$ , (iv) further addition of  $AgBF_4$  and (v) addition of  $SCN^-$  again to the same solution for Cu(II)-induced reversible OFF-ON switching driven by counter anions.



**Scheme 3.** Metal-ion induced controlled movements of side arms of the derivatized cryptand results in signalling by both monomer enhancement as well as exciplex emission.

cies of the counter anions. However, further addition of  $SCN^-$  to the solution results in fluorescence enhancement up to ~40 fold, a much lesser extent in comparison with the earlier  $SCN^-$  to the  $Cu(II) \subset L_6$  (~160 fold, MeCN), possibly due to the change in the ionic strength of the solution. When the Cu(II) chloride salt is used as the input, the dual emission with comparable enhancement is observed in THF as well.

The detachment of Cu(II) bonded to the derivatized cryptand cavity irreversibly achieved by addition of unsubstituted cryptand  $L_6$  in MeCN to the solution containing Cu(II) and **5** in MeCN. The quenching of both monomer and the exciplex emissions thus indicates that Cu(II) which was bound to  $L_6$  from outside of the cavity promptly forms an 1:1 stable inclusion complex with  $L_1$ . As supplemented by the binding constant values, the unsubstituted cryptand has higher affinity towards Cu(II) than the derivatized core. As discussed earlier, the exci-

plex emission which was observed due to  $\pi$ - $\pi$  stacking interactions of the side groups upon complexation with Cu(II), when disappears in presence of  $L_1$  indicates the backward movements of the side groups to their original positions, i.e. that in the metal-free state. Although the movements of the side arms take place here in an irreversible manner, it could be reversible in association with the Cu(II)-binding/detachment depending upon the counter anion and the solvent. A schematic sketch of controlled movements of the side arms of the derivatized cryptand and its detection by dual emissions is illustrated in Scheme 3.

## Conclusion

In conclusion, it is known that cryptands tend to form higher order stable inclusion complexes with many transition as well as heavy metal ions due to their cryptate effect. However, overall tuning of the cryptand architecture and the donor ability of binding sites with a variation of the coordination environment, we find that when the aza cryptand is functionalized with an electron-withdrawing group, it allows translocation of a metal ion from inside to outside the cavity. Depending upon the nature of the substituting group, the system can be made useful as ON/OFF fluorescence signalling, modulation of optical quadratic nonlinearity, and so on. The translocation can be engineered by varying the coordinating tendencies of the counter anions offering possibilities of both cation and anion sensing. Coordination of a metal ion from outside the cavity can also trigger controlled movements of one of the side groups of the cryptand reversibly. It will be of great interest to probe if a cryptand which is much more rigid compared to the present one can translocate a metal



ion in a similar fashion. Our present efforts are directed toward designing complex systems of higher order based on metal ion translocation in aza cryptands.

- Lehn, J.-M., *Supramolecular Chemistry – Concepts and Perspectives*, VCH, Weinheim, 1995; Lehn, J.-M., From molecular recognition towards information and signal processing at supramolecular level. *Front. Supramol. Org. Chem. Photochem.*, 1991, 1–28; Lehn, J.-M., Design to organic complexing agents: strategies towards properties. *Structure Bonding*, 1973, **16**, 1–69.
- Lehn, J.-M. and Ball, P., Supramolecular chemistry. In *New Chemistry* (ed. Hall, N.), Cambridge University Press, Cambridge, 2000, pp. 300–351.
- Lindoy, L. F., *The Chemistry of Macrocyclic Ligands*, Cambridge University Press, Cambridge, 1989.
- Schneider, H.-J. and Yatsimirsky, A. K., *Principles and Methods in Supramolecular Chemistry*, John Wiley & Sons, Chichester, 2000.
- Hossain, A., Kang, S. and Bowman-James, K., Structural aspects of halide with cryptands. *Macrocyclic Chem.*, 2005, 173–188.
- Park, C. H. and Simmons, H. E., Macrobicyclic amines. II. out-out in-in prototropy in 1, (k + 2)-diazabicyclo [k.l.m] alkaneammonium ions. *J. Am. Chem. Soc.*, 1968, **90**, 2429–2431; Dietrich, B., Lehn, J.-M. and Sauvage, J.-P., Diaza-polyoxa-macrocyclic and macrobicyclic compounds. *Tetrahedron Lett.*, 1969, 2885–2888.
- Sarkar, B., Mukhopadhyay, P. and Bharadwaj, P. K., Laterally non-symmetric aza-cryptands: synthesis, catalysis and derivatization to new receptors. *Coord. Chem. Rev.*, 2003, **236**, 1–13; Nelson, J., McKee, V. and Morgan, G., Coordination chemistry of azacryptands. *Prog. Inorg. Chem.*, 1998, **47**, 167–316.
- Dietrich, B., Cryptands. In *Comprehensive Supramolecular Chemistry* (eds Atwood, J. L. et al.), Pergamon Press, Exeter, UK, 1996, vol. 1; Graf, E. and Hosseini, M. W., Cryptands revisited: design, synthesis, complexation behaviour and structural analysis of borocryptands. *Coord. Chem. Rev.*, 1998, **178**, 1193–1209.
- Weber, E. and Vögtle, F., Crown type compounds – an introductory overview. *Top. Curr. Chem.*, 1981, **98**, 1–41; Izatt, R. M., Pawlak, K., Bradshaw, J. S. and Bruening, R. L., Thermodynamic and kinetic data for macrocycle interaction with cations, anions and neutral molecules. *Chem. Rev.*, 1995, **95**, 2529–2586; Izatt, R. M., Pawlak, K., Bradshaw, J. S. and Bruening, R. L., Thermodynamic and kinetic data for macrocycle interaction with cations and anions. *Chem. Rev.*, 1991, **91**, 1721–1785; Sargeson, A. M., Stereo- and regio-specificity in organic synthesis prompted by metal ion. *Pure Appl. Chem.*, 1978, **50**, 905–913.
- Busch, D. H., The complete coordination chemistry – one practitioner's perspective. *Chem. Rev.*, 1993, **93**, 847–860.
- Lehn, J.-M., Cryptates: macropolycyclic inclusion complexes. *Pure Appl. Chem.*, 1977, **49**, 857–870.
- Alexander, V., Design and synthesis of macrocyclic ligands and their complexes of lanthanides and actinides. *Chem. Rev.*, 1995, **95**, 273–342.
- Martell, A. E., Hancock, R. D. and Motekaitis, R. J., Factors affecting stabilities of chelate, macrocyclic and macrobicyclic complexes in solution. *Coord. Chem. Rev.*, 1994, **133**, 39–65.
- Marcus, Y., Metal ion complexing by cryptand 222 in solution: a thermodynamic approach. *Rev. Anal. Chem.*, 2004, **23**, 269–302.
- Raghunathan, K. G. and Bharadwaj, P. K., Template synthesis of a cryptand with hetero-ditopic receptor sites. *Tetrahedron Lett.*, 1992, **33**, 7581–7584.
- Ghosh, P., Sengupta, S. and Bharadwaj, P. K., Complexation properties of a heteroditopic cryptand towards Cu(II) and Ni(II) ions: X-ray crystal structures of the cryptand L and its Ni(II) cascade complex, [Ni(L)(H<sub>2</sub>O)(MeCN)(ClO<sub>4</sub>)<sub>2</sub> · H<sub>2</sub>O · 2MeCN. *J. Chem. Soc. Dalton Trans.*, 1997, 935–938; Ghosh, P. and Bharadwaj, P. K., Synthesis, characterization and complexation properties of a heteroditopic cryptand L towards Cu(II) and Zn(II): crystal structures of L · 3H<sub>2</sub>O and [Zn(L)](ClO<sub>4</sub>)<sub>2</sub> · 2H<sub>2</sub>O. *J. Chem. Soc. Dalton Trans.*, 1997, 2673–2676.
- Chand, D. K., Ghosh, P., Shukla, R., Sengupta, S., Das, G., Bandyopadhyay, P. and Bharadwaj, P. K., Synthesis and uses of macrobicyclic cryptands: from complexation of transition metal ions to molecular devices. *Proc. Indian Acad. Sci. (Chem. Sci.)*, 1996, **108**, 229–233.
- Bharadwaj, P. K., Laterally non-symmetric aza cryptands. *Prog. Inorg. Chem.*, 2003, **51**, 251–331.
- Ghosh, P., Bharadwaj, P. K., Roy, J. and Ghosh, S., Transition metal(II)/(III), Eu(III), and Tb(III) ions induce molecular photonic or gates using trianthryl cryptands of varying cavity dimension. *J. Am. Chem. Soc.*, 1997, **119**, 11903–11909.
- Bag, B. and Bharadwaj, P. K., Cryptand-based fluorescent signaling systems: high enhancement with transition, inner-transition as well as heavy main-group metal ions. *J. Lumin.*, 2004, **110**, 85–94.
- Bag, B. and Bharadwaj, P. K., Fluorescence-enhancement with different ionic inputs in a cryptand-based multi-receptor signalling system. *J. Chem. Sci.*, 2005, **117**, 145–151.
- Ghosh, P., Bharadwaj, P. K., Mandal, S. and Ghosh, S., Ni(II), Cu(II), and Zn(II) cryptate-enhanced fluorescence of a trianthryl-cryptand: a potential molecular photonic OR operator. *J. Am. Chem. Soc.*, 1996, **118**, 1553–1554.
- Bag, B. and Bharadwaj, P. K., Fluorescence enhancement of a signaling system in the simultaneous presence of transition and alkali metal ions: a potential AND logic gate. *Chem. Commun.*, 2005, 513–515.
- Mukhopadhyay, P., Bharadwaj, P. K., Savitha, G., Krishnan, A. and Das, P. K., The first D–π–A octupolar cryptand molecule to exhibit bulk non-linearity. *Chem. Commun.*, 2000, 1815–1816.
- Mukhopadhyay, P., Bharadwaj, P. K., Savitha, G., Krishnan, A. and Das, P. K., A new class of three dimensional D–π–A trigonal cryptand derivatives for second-order nonlinear optics. *J. Mater. Chem.*, 2002, **12**, 2237–2244.
- Das, G., Ghosh, P., Bharadwaj, P. K., Singh, U. and Singh, R. A., Langmuir films of a cryptand-based amphiphile at the air-water interface. *Langmuir*, 1997, **13**, 3582–3583.
- Ghosh, P. and Bharadwaj, P. K., Derivatization of heteroditopic cryptands: a new generation of amphiphiles. *Curr. Sci.*, 1997, **72**, 797–801.
- Bandyopadhyay, P. and Bharadwaj, P. K., Spontaneous formation of vesicles by a cryptand-based bola-amphiphile. *Langmuir*, 1998, **14**, 7537–7538.
- Ghosh, P., Khan, T. K. and Bharadwaj, P. K., Cryptand-based metal-free or complexed amphiphiles which readily form vesicles. *Chem. Commun.*, 1996, 189–190.
- Lehn, J.-M., Cryptates: the chemistry of macropolycyclic inclusion complexes. *Acc. Chem. Res.*, 1978, **11**, 49–57.
- Shestakova, A. K., Chertkov, V. A. and Schneider, H.-J., Structures and equilibria involving the [222] cryptand and europium ion. *Tetrahedron Lett.*, 2000, **41**, 6753–6756.
- Amendola, V., Fabbri, L., Mangano, C. and Pallavicini, P., Molecular machines based on metal ion translocation. *Acc. Chem. Res.*, 2001, **34**, 488–493.
- Bazzicalupi, C. et al., Complexation properties of heteroditopic cryptands towards Cu(II), Zn(II), Cd(II) and Pb(II) in aqueous solution: crystal structures of [H<sub>3</sub>L<sub>1</sub>] (ClO<sub>4</sub>)<sub>5</sub> · 4H<sub>2</sub>O and [NiL<sub>2</sub>(Cl)]Cl<sub>5</sub> · 5H<sub>2</sub>O · MeOH. *Eur. J. Inorg. Chem.*, 2000, 2111–2116.
- Mukhopadhyay, P., Bharadwaj, P. K., Savitha, G., Krishnan, A. and Das, P. K., Synthesis and characterization of mono- and bis-D–π–A cryptand derivatives for second order nonlinear optics and its modulation with different metal ions. *J. Mater. Chem.*, 2002, **12**, 2786–2791.
- Roy, D. and Bharadwaj, P. K., Alteration in the binding property of laterally non-symmetric aza cryptand toward Cu(II), Ag(I) and

- Tl(I) ions upon derivatization with methylinitile group. *Eur. J. Inorg. Chem.*, 2006, 1771–1775.
36. Mukhopadhyay, P., Sarkar, B., Bharadwaj, P. K., Nattinen, K. and Rissanen, K., Metal binding characteristics of a laterally nonsymmetric aza cryptand upon functionalization with a  $\pi$ -acceptor group. *Inorg. Chem.*, 2003, **42**, 4955–4960.
37. Czarnik, A. W. (ed.), *Fluorescent Chemosensors of Ion and Molecule Recognition*, ACS Symposium Series 538, Washington DC, 1993.
38. Valeur, B., Principles for fluorescent probe design for ion recognition. In *Topics in Fluorescence Spectroscopy* (ed. Lakowicz, J. R.), Plenum Press, New York, 1994, vol. 4, pp. 21–48.
39. Bag, B. and Bharadwaj, P. K., Transition metals-based nanomaterials for signal transduction. In *Encyclopedia of Nanoscience and Nanotechnology* (ed. Nalwa, H. S.), American Scientific Publishers, 2004, vol. 10, pp. 519–536.
40. Valeur, B. and Leray, I., Design principles of fluorescent molecular sensors for cation recognition. *Coord. Chem. Rev.*, 2000, **205**, 3–40.
41. de Silva, A. P., Gunaratne, H. Q. N., Gunnlaugsson, T., Huxley, A. J. M., McCoy, C. P., Rademacher, J. T. and Rice, T. E., Signaling recognition events with fluorescent sensors and switches. *Chem. Rev.*, 1997, **97**, 1515–1566.
42. Fabbrizzi, L. and Poggi, A., Sensors and switches from supramolecular chemistry. *Chem. Soc. Rev.*, 1995, **25**, 197–202.
43. Feringa, B. L. (ed.), *Molecular Switches*, Wiley-VCH, Weinheim, Germany, 2001.
44. Ramamurthy, V. and Schanze, K. S. (eds), *Optical Sensors and Switches*, Marcel Dekker, New York, 2001.
45. Bag, B. and Bharadwaj, P. K., Attachment of an electron-withdrawing fluorophore to a cryptand for modulation of fluorescence signaling. *Inorg. Chem.*, 2004, **43**, 4626–4630.
46. Desvergne, J.-P., Lahrahar, N., Gotta, M., Zimmermann, Y. and Bouas-Laurent, H., 2,3-Anthraceno[2.2.2]cryptand. Mutual interactions between the receptor and the signal transducing subunit. *J. Mater. Chem.*, 2005, **15**, 2873–2880.
47. de Silva, A. P., McClenaghan, N. D. and McCoy, C. P., Logic gates. In *Electron Transfer in Chemistry* (ed. Balzani, V.), Wiley-VCH, Weinheim, 2000, vol. V, p. 156.
48. de Silva, A. P. and McClenaghan, N. D., Molecular state logic gates. *Chem. Eur. J.*, 2004, **10**, 574–586.
49. Special issue: Molecular Machines. *Acc. Chem. Res.*, 2001, **34**, Issue 6, 409.
50. Badjic, J. D., Balzani, V., Credi, A. and Stoddart, J. F., A molecular elevator. *Science*, 2004, **303**, 1845–1849.
51. Balzani, V., Credi, A., Raymo, F. M. and Stoddart, J. F., Artificial molecular machines. *Angew. Chem. Int. Ed. Engl.*, 2000, **39**, 3348–3391.
52. Bag, B. and Bharadwaj, P. K., Attachment of electron-withdrawing 2,4-dinitrobenzene groups to a cryptand-based receptor for Cu(II)/H<sup>+</sup>-specific exciplex and monomer emissions. *Org. Lett.*, 2005, **7**, 1573–1576.
53. Bag, B., Mukhopadhyay, P. and Bharadwaj, P. K., Fluorescence signaling systems with a cryptand receptor incorporating electron-withdrawing groups: metal ion specificity and solvent dependence. *J. Photochem. Photobiol. A*, 2006, **181**, 215–220.

ACKNOWLEDGEMENT. We thank DST, New Delhi for financial support.

Received 10 April 2006; revised accepted 28 September 2006