

Functionalization of Macrobicyclic Amino Cryptands With Photoactive Fluorophoric Units for Metal Ion Sensing Application

Lakshminarayanan Piramuthu, Kumaresan Murugesan, Vanthana Jeyasingh, Sudha Lakshminarayanan, Selvapalam Narayanan

Abstract: In this report we discussed the photo physical properties of two hexaanthryl substituted cryptands, L^1 and L^2 respectively. Further, photophysical studies of L^1 and L^2 with different transition metal ions as an input are carried out to probe these molecules as metal ion sensors in solution.

Keywords : Cryptands, Metal Sensors, Anthracene, Photo Electron Transfer.

I. INTRODUCTION

In our earlier report, we reported the single-crystal X-ray structural feature of the chloroform-benzene-chloroform adduct which stabilized through different weak interactions inside the channel of a supramolecular assembly formed by van der Waals stacking of a highly symmetric hexaanthryl-substituted octaaminocryptand, L^1 . In the Functionalized cryptands L^1 and L^2 anthryl moieties are attached to nitrogen centers of cryptand architecture via methylene spacer, these molecules could be of interest for both anion and cation sensing applications. Detailed photophysical studies of L^1 and L^2 with different metal ions as solution state input was carried out to probe these molecules as chemical sensors of metals ions in solution state.

II. EXPERIMENTAL

The cryptands L^1 and L^2 are synthesized as per our reported

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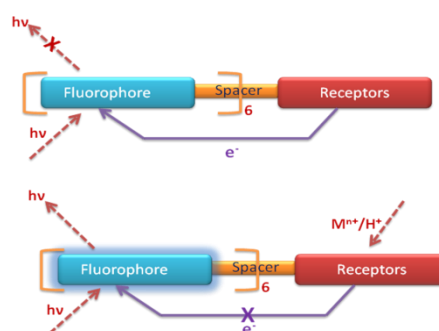
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literature procedure and isolated as the free bases[2]-[6].

III. RESULTS AND DISCUSSION

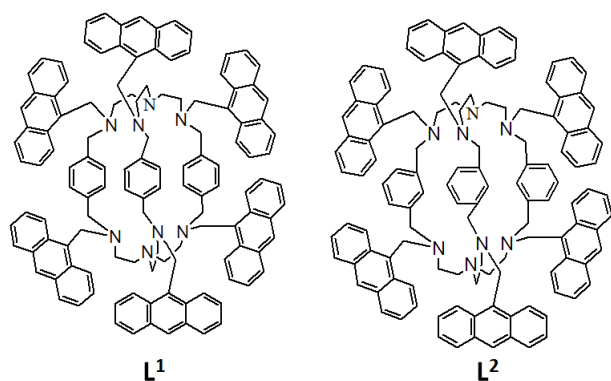
A. Photophysical studies on L^1 and L^2



Scheme 1. Schematic representation of Photo Electron Transfer (PET) system

The anthryl derivatized cryptands, L^1 and L^2 show the format of "fluorophore-spacer-receptor" configuration (Scheme 1), where fluorophore is anthryl group, spacer is methylene and receptor is the cryptand unit. The fluoroionophores show less fluorescence output due to nitrogen lone pairs active in excited state with efficient photo induced intramolecular electron transfer (PET). The mechanism of PET in case of "fluorophore-spacer-receptor" configuration is well established in the literature[7]. However, the fluorescence can be recovers to various aspects in the sight of various metal ions and protons as well. Cryptand unit and transition metal ion while complexation or protonation in a dry (THF) system, PET systems exhibits the nitrogen lone pairs are responsible for PET are engaged in bonding as shown in Scheme 1.

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Scheme 2. Structures of functionalized cryptands L^1 and L^2 used in these metal sensing studies

B. UV-Visible absorption spectroscopy of free L^1 and L^2 and in the presence of metal ion inputs

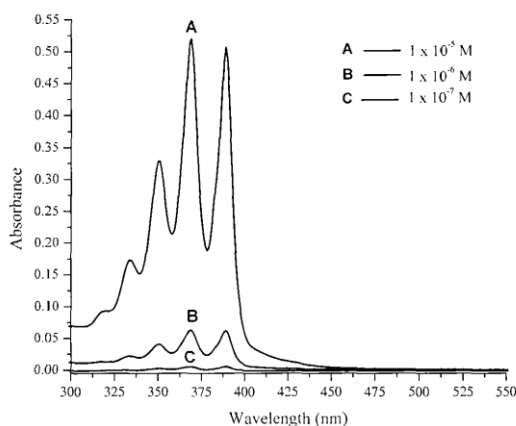


Fig. 1. UV-vis absorption spectra of free L^1 recorded at different concentrations in dry THF.

UV-Visible spectra of L^1 and L^2 were recorded in various concentrations such as 0.00001, 0.000001 and 0.0000001M in dry THF (Fig. 1). In case of L^1 optical density OD at λ_{max} , (368 nm) for the above three concentrations are 0.5124, 0.0559, and 0.0058 respectively whereas in L^2 corresponding OD are 0.5209, 0.0516, and 0.005 respectively (Fig. 1). The UV-Vis absorption band of the L^1 and L^2 were characteristic of 9-monoalkyl functionalized anthracene with well-resolved structures with the (0,0) band observed at 388.9 nm and vibrational structures at (368.8, 350.3 and 333.7 nm) for L^1 and the (0,0) band observed at 389.1 nm and vibrational structures at 368.7nm, 350.4nm and 333.1 nm for L^2 . These indicate where nitrogen lone pairs of the receptor part and the anthracene units has no interaction in the ground state. From these experiments 1×10^{-6} M concentration ($0.0 < 0.1$) is chosen for emission experiments to avoid the self-quenching from the concentrated fluoroionophores. In L^1 and L^2 a bathochromic shifts of the UV-peak positions 5 nm and 3 nm respectively were observed in addition of Cr(III) whereas all other competitive metal ions and including H^+ do not show any shift or shifts less than 3 nm in dry THF. Detailed UV-Vis absorption data are listed in the Table I.

Table-I : UV-vis spectral data of L^1 and L^2 with various

metal ion input at 298 K

Fluorophore	Cationic input	Band position, nm/O.D	
L^1	Nil	333.7(0.023),350.3(0.037),368.8(0.055),388.9(0.054)	
	Cr(III)	336.6(0.020),354.8(0.035),373.0(0.045),393.7(0.039)	
	Mn(II)	333.7(0.019),350.9(0.032),369.2(0.048),389.3(0.045)	
	Fe(II)	Broad band due to MLCT overlap	
	Co(II)	334.3(0.031),351.4(0.042),369.6(0.054),389.7(0.051)	
	Ni(II)	333.6(0.060),350.2(0.100),369.0(0.150),389.3(0.143)	
	Cu(II)	335.9(0.028),352.2(0.039),370.4(0.053),390.3(0.046)	
	Zn(II)	335.0(0.025),351.5(0.038),369.4(0.053),389.7(0.048)	
	H^+	334.2(0.017),351.2(0.026),369.5(0.040),389.8(0.037)	
	L^2	Nil	333.1(0.018),350.4(0.033),368.7(0.051),389.1(0.050)
		Cr(III)	337.7(0.020),353.5(0.033),371.8(0.045),391.6(0.039)
Mn(II)		333.9(0.025),350.3(0.038),368.9(0.054),388.9(0.050)	
Fe(II)		332.9(0.030),350.9(0.042),369.1(0.058),389.2(0.049)	
Co(II)		Broad band due to MLCT overlap	
Ni(II)		333.4(0.028),350.7(0.039),369.2(0.054),389.3(0.052)	
Cu(II)		333.4(0.013),350.6(0.027),368.7(0.044),389.0(0.044)	
Zn(II)		334.5(0.020),351.1(0.033),369.5(0.047),389.7(0.044)	
H^+		334.2(0.017),351.2(0.026),369.5(0.040),389.8(0.037)	

C. Emission spectra of free L^1 and L^2 and in the sight of different metal ions inputs

1×10^{-6} M THF solution of compounds, L^1 and L^2 containing a Receptor-Spacer-Fluorophore configuration show a low intense well-resolved anthracene monomer emission at 390, 410.3, 439.4 nm and 390.2, 411.8, 436.7nm respectively (Fig. 3 and Table III). The details of emission data of both these fluoroionophores in presence of various metal inputs are also listed in Table II. The quantum yield Φ_F is calculated 0.012 and 0.013 or L^1 and L^2 respectively in THF at $5^\circ C$ (Table II), versus Φ_F of 0.297 for anthracene in ethanol medium with same exploratory conditions, i.e., a reduced by a factor of about 25, which was thought to be because of the PET from the lone pairs of nitrogen to the excited state of anthracene moiety.

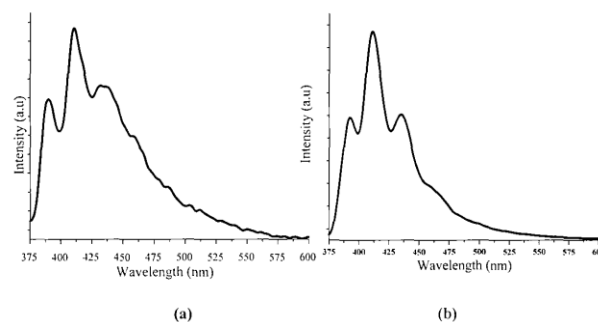


Fig. 3. Fluorescence emissions spectra of (a) L^1 and (b) L^2 in dry THF at 1×10^{-6} .

Table- II: Fluorescence spectral data of L^1 and L^2 with different metal ion input at 298 K.

Fluorophore	Cationic input	Band position, nm/intensity a.u	
L^1	Nil	390.0(73.6),410.3(113.2),439.4(78.3)	
	Cr(III)	398.2(715.3),421.7(817.9),442.0(482.3)	
	Mn(II)	390.8(244.4),413.4(302.4),439.7(232.5)	
	Fe(II)	397.4(484.7),420.4(582.5),44H(34.1.3)	
	Co(II)	395.1(6.17.5),418.7(758.4),442.0(504.6)	
	Ni(II)	391.5(276.7),414.1(400.9),438.4(316.6)	
	Cu(II)	397.4(833.1),420.2(954.5),444.4(573.6)	
	Zn(II)	395.3(666.9),416.9(813.1),440.5(574.5)	
	H^+	394.4(861.2),418.9(989.3),441.8(635.5)	
	L^2	Nil	390.2(86.8),411.8(115.2),436.7(93.41)
		Cr(III)	396.4(846.9),421.9(988.1),444.1(611.2)
Mn(II)		390.4(129.4),411.4(173.8),440.1(121.8)	
Fe(II)		390.6(412.2),413.9(506.6),439.5(370.5)	
Co(II)		391.5(300.5),414.1(366.1),440.7(274.9)	
Ni(II)		388.7(65.7),408.6(108.3),435.8(86.7)	
Cu(II)		396.1(589.8),416.8(678.8),442.8(413.6)	
Zn(II)		394.2(463.9),416.2(551.9),439.6(398.6)	
H^+		394.2(661.2),418.3(725.3),441.8(635.5)	

Table- III: Fluorescence output in terms of quantum yield (Φ_F) of L^1 and L^2 with different metal ion inputs^a

Fluorophore	Cationic input	(O,O) Band position (nm)	Fluorescence output (Φ_F)	FEF
L^1	Nil	390.0	0.012	1
	Cr(III)	398.2	0.108	9.0
	Mn(II)	390.8	0.036	3.0
	Fe(II)	397.4	0.019	1.6
	Co(II)	395.1	0.077	6.4
	Ni(II)	391.5	0.016	1.3
	Cu(II)	397.4	0.098	8.1
	Zn(II)	395.3	0.088	7.3
L^2	Nil	390.2	0.013	1
	Cr(III)	396.4	0.126	9.7
	Mn(II)	390.4	0.018	1.4
	Fe(II)	390.6	0.047	3.6
	Co(II)	391.5	0.039	3.0
	Ni(II)	388.7	0.011	0.8
	Cu(II)	396.1	0.077	5.9
	Zn(II)	394.2	0.068	5.2

^a Experimental conditions: In dry THF concentration of L^1 and L^2 0.000001 M and concentration of metal ionic input was 0.0001 M. Excitation were fixed at 368 nm with band pass 5.0 nm and emission band pass was 5.0 nm; temperature, 5°C, Φ_F calculated by comparison of emission spectrum with that of anthracene ($\Phi_F = 0.297$) taking area under the total emission.

The tertiary nitrogen atoms of fluoroionophores would be promoting coordination between L^1 and L^2 added transition metal ions. The effect of different metal ions along with H^+ as inputs in the fluorescence emission spectra of L^1 and L^2 are shown in Figures 4 & 5 and Table 4. Further quantum yields of were calculated for both these fluoroionophores in presence of various metal ionic inputs. The quantum yield increased maximum (9 to 10 times) in both the cases when Cr(III) ion is used as input (Fig. 4, Fig. 5 and Table IV) in dry THF medium.

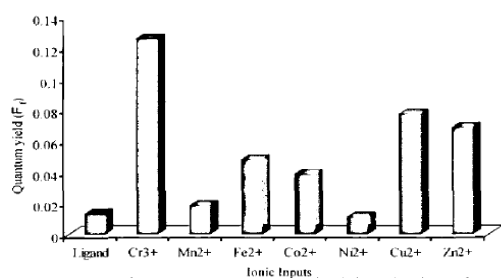


Fig. 4. Bar chart view of comparative fluorescence quantum yield for fluoroionophore L^1 along with the metal ion inputs.

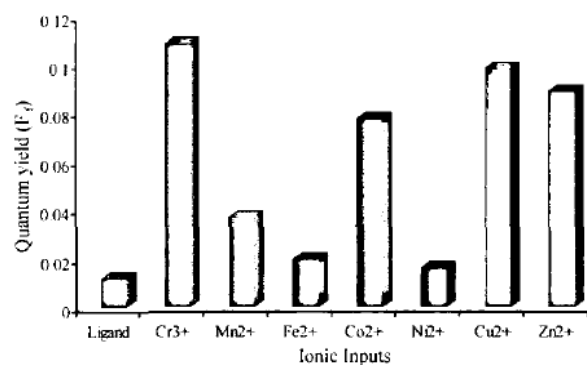


Fig. 5. Bar chart view of comparative fluorescence quantum yield for fluoroionophore L^2 along with the metal ion inputs.

In cases of Cu(II) fluorescence enhancement factor (FEF) are 8 and 6 for L^1 and L^2 respectively whereas FEF are 7 and 5 with the Zn(II). The Co(II) also showed about 6 and 3 times fluorescence enhancement in L^1 and L^2 respectively in similar experimental conditions. No effect or slight quenching was observed in case of Ni(II). The poor performance with respect to fluorescence recovery of these systems with transition metal ions compared to the similar cryptand based system reported in the literature [6], [7] could be due to huge steric hindrance of six attached anthryl moieties. Steric hindrance does not allow encapsulation of metal ion inside the cryptand's cavity and therefore, efficient recovery of the fluorescence output does not take place.

IV. CONCLUSION

Solution state studies on this derivative along with another hexa anthryl functionalized cryptand of different cavity show 6-10 times fluorescence intensity enhanced upon the addition of transition metal ions. These systems as well as new cryptand based systems should be attempted in sensing applications in solution as well as in solid surface and molecular self-assembly studies to encapsulate different guests of biological and environmental relevant. If successful, these studies should provide important results both in fundamental and applied research. Solution state fluorescence studies on these fluoroionophores show only 6-10 times enhancement of fluorescence in cases of Cr(III), Cu(II), Zn(II), and Co(II).

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Water Cluster")

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