

## Transition metal cryptate — enhanced fluorescence in a trianthroyl cryptand: effect of spacer on the photoinduced electron transfer process

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### Abstract

The three secondary nitrogens in a heteroditopic cryptand are derivatized with anthroyl groups to have a cryptand based system in the ‘(fluorophore)<sub>3</sub>-spacer-receptor’ format. This supramolecular system shows enhancement of fluorescence in presence of metal ions like Cu(II), Co(II), Zn(II). The quantum yields of fluorescence enhancement as well as the photophysical behavior of this system has been compared with those of a trianthryl cryptand where the spacer is a –CH<sub>2</sub> group. Such studies provide important clues in the development of photodriven molecular devices and sensors and also understanding of the PET process. © 2000 Elsevier Science S.A. All rights reserved.

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### 1. Introduction

Studies of photophysical behavior of supramolecular systems in the format, ‘fluorophore-spacer-receptor’ are currently being pursued in many laboratories in order to design efficient photodriven molecular switches and molecular sensors besides understanding the mechanism of photoinduced electron transfer (PET) process in detail [1]. A variety of acyclic/macrocyclic receptors with one or more nitrogen donors linked covalently to fluorophores have been reported [2]. These systems show fluorescence processes from the nitrogen lone pairs to the fluorophores [3]. In all studies, alkali/alkaline-earth/main group metal ions or molecular fragments have been used as the inputs [1]. It has been known for a long time that transition metal ions effectively quench fluorescence [4–6] and a number of mechanisms have been proposed to rationalise this behavior [7]. In the PET sensing process, fluorophore–receptor interaction leads to quenching while metal ion binding to the receptor leads to recovery of fluorescence. Hence, an effective PET sensor should have a stronger metal ion–receptor (M–R) interaction compared to the metal ion–fluorophore (M–F) communication [8]. We have shown that when the receptor is a cryptand, transition/inner-transition/heavy metal ions can be used as inputs to cause fluorescence enhancement [9,10].

The cryptand based systems were designed to have much weaker (M–F) communication while at the same time having much stronger (M–R) interaction due to the ‘cryptate’ effect [11]. In these systems, paramagnetic metal ions or inner transition metal ions were able to effectively block the PET from nitrogen lone pairs to the fluorophores without having significant M–F interactions leading to fluorescence enhancement [9,10]. Careful designing of such systems demand special overall molecular architecture, which must fulfil the following conditions: (i) PET should be fast in the free molecule, minimizing  $\phi_F$  of the fluorophore as much as possible; (ii) PET should be effectively stopped by metal ions, which recognize the cryptand cavity; (iii)  $S_1 \rightarrow T_1$  intersystem crossing efficiency in the fluorophore must be poor in the complexes [12] and (iv) the ligand when complexed must be photochemically very stable.

The photophysical behavior of the ligand L<sup>1</sup> (Fig. 1) where the cryptand is attached to the fluorophore anthracene through –CH<sub>2</sub> group as spacer has already been reported from this lab [9,10]. In the present compound L<sup>2</sup> (Fig. 1), the N atoms in the lower deck of the cryptand moiety are attached to the same fluorophore as in L<sup>1</sup> but through a different spacer (>C=O in L<sup>2</sup> in place of –CH<sub>2</sub> in L<sup>1</sup>). Introduction of >C=O group as spacer is expected to affect the interaction of the lone pairs on N atoms of the cryptand moiety with the anthracene  $\pi$  system and also the flexibility of the fluorophore units with respect to the cryptand moiety. Both the effects could influence the process of PET. The

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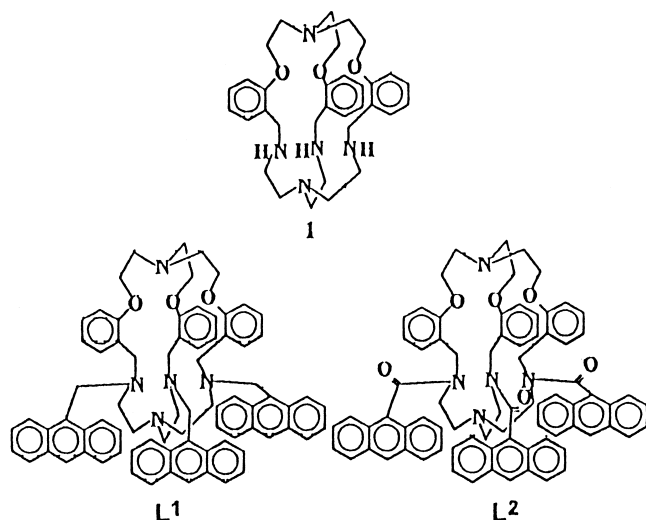


Fig. 1. Chemical structures of the compounds.

photophysical behavior of  $L^2$  has been explained on the basis of the published results of  $L^1$  [9,10] as well as those of the carbonyl substituted anthracene derivatives 9-anthramide and *N,N*-diethyl-9-anthramide [13,14]. A comparison of the results obtained for  $L^2$  with that of  $L^1$  will therefore help us to explore further our understanding of PET process in cryptand based systems and thus, provide important information to design higher generation molecular switch based on '(fluorophore)<sub>n</sub>-spacer-receptor' format.

## 2. Experimental

### 2.1. Analysis and measurements

$^1\text{H}$  NMR spectra were recorded on a Bruker WP-80 FT (80 MHz) instrument. Elemental analyses (C, H, N) were carried out at CDRI, Lucknow. Melting points were obtained using an electrical melting point apparatus by Perfit (India) and were not corrected. UV–VIS absorption spectra were recorded on a Hitachi model 3021 spectrophotometer at 298 K. Fluorescence spectra were obtained with a Hitachi model F-4010 spectrofluorimeter and corrected for emission. Fluorescence quantum yield was determined in each case by comparing the corrected spectrum with that of anthracene in ethanol, taking the area under the total emission. Quantum yields of the samples were measured with respect to the purified anthracene. The quantum yield of anthracene was measured using quinine sulfate in 1 M  $\text{H}_2\text{SO}_4$  as reference at  $\lambda_{\text{exc}}$  of 350 nm. The standard quantum yield value thus obtained was used for the calculation of the quantum yields of the samples.

### 2.2. Materials

All chemicals were of reagent grade, which were used without further purification unless otherwise noted. Tri-

ethanolamine, salicylaldehyde, tris(2-aminoethyl)amine, sodium borohydride, 9-anthracic acid and the metal salts were obtained from Aldrich (US). Sodium hydroxide, anhydrous sodium sulfate, triethylamine, perchloric acid, and thionyl chloride were received from S.D. Fine Chemicals (India). Thionyl chloride and all solvents (from S.D. Fine Chemicals) were purified prior to use following standard methods. Tetrahydrofuran (THF) was dried under a dinitrogen blanket from potassium benzophenone ketyl.

### 2.3. Synthesis of the cryptand 1

Synthesis of the cryptand 1 was achieved following our method reported earlier [15].

#### 2.3.1. 9-Anthroyl chloride

The acid (0.05 mol) was heated under reflux for 2 h with thionyl chloride (20 ml), the excess of thionyl chloride removed under reduced pressure. The product obtained was used without further purification.

#### 2.3.2. Synthesis of $L^2$

The cryptand 1 (1 mmol) is dissolved with constant stirring at room temperature in 50 ml of dry THF containing triethylamine (3 mmol). The solution is cooled at  $\sim 5^\circ\text{C}$ . A solution of the acid chloride (3 mmol) taken in 50 ml of dry THF is added dropwise to the cold cryptand solution over a period of 6 h dinitrogen atmosphere with constant stirring and maintaining the reaction temperature at  $\sim 5^\circ\text{C}$ . After the addition is complete, the reaction mixture is allowed to warm up to room temperature and then refluxed for 1 h. The solid hydrochloride is removed by filtration and the filtrate is completely evaporated to obtain a reddish-brown oily liquid. This is shaken with 100 ml of water and  $L^2$  is extracted with chloroform ( $4 \times 25$  ml). The organic layer after drying over anhydrous sodium sulfate was completely evaporated to obtain the product as a pale yellow/white product. Further purification is achieved by repeated crystallization from chloroform.

Yield 48% mp  $180\text{--}183^\circ\text{C}$ .  $^1\text{H}$  NMR (80 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ , TMS)  $\delta$  ppm: 2.53 (m, 6H), 2.84 (m, 6H), 3.94 (m, 6H), 4.87 (br s, 6H), 6.78–8.47 (br m, 39H); Anal. Calcd for  $\text{C}_{78}\text{H}_{60}\text{N}_5\text{O}_6$ : C, 79.93, H, 5.89, N, 5.98. Found C, 80.15, H, 6.05, N, 6.26. IR  $\nu_{\text{max}}$  (neat)  $\text{cm}^{-1}$ : 1645 (C=O).

## 3. Results and discussion

### 3.1. Absorption spectra

The absorption spectra of the free trianthroyl cryptand,  $L^2$  in THF at 300 K have well resolved structures having (0,0) band at 398.4 nm and vibrational structures at 377.2, 357.6, 340.8 nm (Fig. 2A) similar to that of anthracene in THF. The spectra also resemble those of 9-anthramide

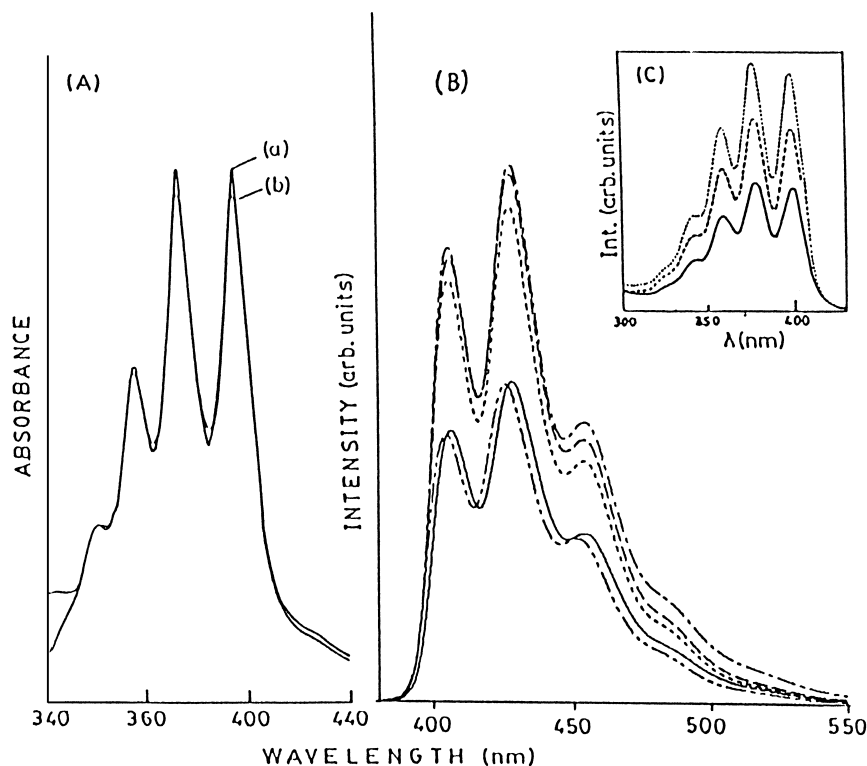


Fig. 2. (A) UV-VIS absorption spectra of (a) free L<sup>2</sup> (10<sup>-5</sup> M); (b) L<sup>2</sup> in presence of Cu(II) ion (10<sup>-4</sup> M) in dry THF at 298 K. (B) Corrected fluorescence emission spectra of (—) free L<sup>2</sup>, (- · - ·) L<sup>2</sup> in EtOH, (- · - ·) L<sup>2</sup> in presence of H<sup>+</sup>, (.....) Cu(II)-complexed L<sup>2</sup>, (----) Zn(II)-complexed L<sup>2</sup> in dry THF at 298 K. (C) Excitation spectra of L<sup>2</sup> monitored at (—) 455 nm, (---) 410 nm and (- · - ·) 430 nm.

and *N,N*-diethyl-9-anthramide observed in THF at 300 K [14]. Earlier studies reveal that in the ground state ( $S_0$ ) of 9-substituted carbonyl anthracenes like 9-anthramide and *N,N*-diethyl-9-anthramide, steric hindrance between the carbonyl group and the ring hydrogen keep the carbonyl group twisted almost 90° out of plane of the anthracene ring which precludes extensive conjugation of the carbonyl group and the anthracene  $\pi$  electrons. These compounds thus exhibit structured absorption spectra similar to that of anthracene [14,16,17]. The (0,0) band of the  $\pi$ - $\pi^*$  transition in L<sup>2</sup> is however, somewhat red shifted (398.4 nm) compared to that in L<sup>1</sup> where the (0,0) band appeared at 388 nm [9,10] (Fig. 2A). This small shift of the (0,0) band position may be attributed to some conjugative effect between the lone pairs of the N atoms of the cryptand unit and the anthracene moiety through C=O linkages. In the presence of metal ions, there is no appreciable change in the absorption spectrum (Fig. 2A). Since the metal ions attach to the N atoms which is separated from the anthracene moiety by several bonds, it is normally difficult to observe the effect of complexation in the absorption bands of anthracene. In our earlier study in anthracene cryptand systems with -CH<sub>2</sub> spacer, in some cases only slight bathochromic shifts (2–5 nm) could be observed while in some other cases there was no detectable change in the absorption spectrum [9,10]. Although NMR spectroscopy may be a useful tool, it is difficult to obtain precise NMR spectra when paramagnetic chemical

species such as transition metal ion or a fast exchange process between complex and free molecules are present in solution. However, the binding of metal ion in the cryptand cavity is clearly revealed by the observed effect on the emission spectra in Section 3.2. Several control experiments were carried out [9,10] to establish that the observed effect in the emission is due to the binding of metal ions (see Section 3.2).

### 3.2. Emission spectra

The free ligand L<sup>2</sup> shows a well resolved anthracene monomer emission from locally excited lowest <sup>1</sup>( $\pi$ ,  $\pi^*$ ) state in THF at 298 K (Fig. 2B). The excitation spectra monitoring the different bands of the structured luminescence of L<sup>2</sup> in THF are identical and match well with the absorption spectra of the free ligand L<sup>2</sup> in THF at 298 K (Fig. 2). In comparison, free L<sup>1</sup> shows dual emission consisting of a well resolved anthracene monomer emission from locally excited lowest <sup>1</sup>( $\pi$ ,  $\pi^*$ ) state along with a broad structureless emission centred ~550 nm [9,10].

With increasing concentration of the ligand, the total intensity of fluorescence emission decreases significantly without the appearance of any broad band in the higher wavelength region. This suggests that self quenching takes place without formation of any excimer at higher concentration [13,21]. The concentration of the ligand was

maintained at  $10^{-5}$  M throughout the study as the emission intensity is found to be maximum at this concentration.

The emission spectra of carbonyl substituted anthracenes have been found to be greatly influenced by the nature of the carbonyl substituent [14,18]. Thus, although 9-substituted anthryl ketones are virtually non-fluorescent at room temperature in aprotic solvents due to suitably placed ( $n, \pi^*$ ) triplet level which enhances inter system crossing, the anthracene amide carbonyls have the ( $n, \pi^*$ ) too high in energy to affect  $S_1$  decay and are fluorescent in nature [14]. The shape and the position of the emission spectra of 9-anthramide has been found to be quite solvent dependent, the spectra being most structured in solvents of intermediate polarity as THF and dioxane [13,18]. Upon excitation of these derivatives to the first excited singlet state ( $S_1$ ) the conjugative interaction becomes more competitive as a result of the magnitude and direction of the transition moment that accompanies excitation [19,20] so that the excited state becomes more planar and polar than  $S_0$  [14]. Thus, the fluorescence spectra of 9-anthramide becomes quite diffuse and red shifted in solvents of low or high polarity where there is extensive conjugation, while in THF or dioxane the same compound exhibits anthracene like emission due to restricted rotation of the carbonyl group in the excited state [13,14]. In contrast, in *N,N*-diethyl-9-anthramide, the carbonyl rotation in  $S_1$  is completely inhibited in all solvents due to strong steric hindrance as a result of which the emission spectra of this derivative is highly structured similar to that of free anthracene in all solvents [14]. The behavior of the present ligand  $L^2$  is similar to that of *N,N*-diethyl-9-anthramide as  $L^2$  also exhibits structured anthracene like emission in THF as well as in polar solvents like ethanol (Fig. 2) which indicates restricted rotation of the carbonyl group in the excited state of  $L^2$ .

The broad band around 550 nm in the emission spectrum of  $L^1$  in THF at 298 K is due to an exciplex formed between the lone pair on the nitrogen and the fluorophore [9,10]. The absence of an exciplex emission in the present system  $L^2$  implies that the presence of the carbonyl group as spacer makes the system somewhat rigid and delocalizes the lone pair on the nitrogen atoms onto the carbonyl group (Fig. 1).

Table 1 shows the quantum yield of monomer emission ( $\varphi_{FM}$ ) in the absence and presence of different inputs. The value of  $\varphi_{FM}$  for free  $L^2$  in THF (0.128) is much higher compared to that for free  $L^1$  (0.0005) [9,10], although the value is considerably lower compared to that of anthracene in THF (0.297) [9,10] or 9-anthramide in THF (0.353) [13]. The very low  $\varphi_{FM}$  value in case of  $L^1$  is due to very efficient PET from the HOMO of the tertiary N atoms to the anthracene  $\pi$  system [9,10]. As has been pointed out earlier, the rotation of the carbonyl group to a planar configuration in the excited state ( $S_1$ ) is inhibited in 9-anthramide in THF as well as in *N,N*-diethyl-9-anthramide in any solvent so that there is no aromatic ring-carbonyl group conjugation in these systems in the  $S_1$  state and their fluorescence spectra and quantum yields are comparable to that of anthracene

Table 1  
Fluorescence output of  $L^1$  and  $L^2$  with different cationic inputs<sup>a</sup>

Fluorophore	Ionic input	Fluorescence output quantum yield ( $\varphi_{FM}$ )
$L^1$	Nil	0.0005
	Cu(II)	0.28
	Co(II)	0.215
	Zn(II)	0.31
	H <sup>+</sup>	0.21
$L^2$	Nil	0.128
	Cu(II)	0.18
	Co(II)	0.26
	Zn(II)	0.19
	H <sup>+</sup>	0.21

<sup>a</sup> For  $L^1$  see [9] and for  $L^2$  this work. Experimental conditions: medium-dry THF; concentration of  $L^2$ ,  $10^{-5}$  M; concentration of input,  $10^{-4}$  M. Excitation at 370 nm with excitation band-pass 5 nm and emission band-pass 5 nm; temperature 298 K.  $\varphi_{FM}$  calculated by comparison of corrected spectrum with that of anthracene ( $\varphi_F=0.297$ ) taking the area under the total emission. The error in  $\varphi_F$  is within 10% in each case, except free ligands where error in  $\varphi_F$  is within 15%.

[13,14]. Moreover, as the ( $n, \pi^*$ ) states of the anthramides are too high in energy [14,22], they are not likely to affect the  $S_1$  decay. Thus, contribution of  $S_1 \rightsquigarrow T_1$  intersystem crossing to the fluorescence quenching of the ligand might be excluded. PET has been reported even in donor-acceptor systems in which donor and acceptor are separated by several bonds as well as in systems where donor-acceptor are not directly connected [23–26]. Thus, the considerably lower value of  $\varphi_{FM}$  in  $L^2$  as compared to that of anthracene or the anthramide derivatives suggest that PET occurs in this system. The key role in any PET process is played by the orbital overlap factor [27] which necessarily means that both donor and acceptor must be properly mutually oriented. Our results indicate that in the excited state of  $L^2$  there is a favorable ‘in-line’ approach of the lone pair electrons of the amide N and the  $\pi$  orbital of anthracene. It is well known that the electron migration in such systems upon the induction of light may either take place through space or through bond [23,24]. As our results point towards an ‘out of plane’ orientation of the carbonyl group, it is most likely that a through space type of interaction is operative in this system.

However, the efficiency of PET in  $L^2$  is much less compared to that in  $L^1$  as is evident from the  $\varphi_{FM}$  values. The carbonyl group in the ligand  $L^2$  makes the system somewhat more rigid and probably has the donor and the acceptor in an orientation which is not as favorable for PET as in  $L^1$ .

In  $L^2$ , the three anthracene units are attached to three N atoms of the cryptand moiety (Fig. 1) through a spacer C=O. Since each anthracene unit may be differently oriented with respect to the lone pairs of the N atom to which anthracene unit is connected, all the N atoms may not be equally efficient donor for the PET process. Besides, one N atom in the cryptand moiety is free (Fig. 1). To unravel the competition of the involvement of each N atom in the PET process one needs photophysical studies of the system with one and two

fluorophore units. However, an attempt to synthesize such compounds in pure state has not yet been successful.

The quantum yield of monomer emission  $\phi_{FM}$  increases noticeably for  $L^2$  upon the addition of a transition metal ion or proton as input (Table 1). The extent of fluorescence enhancement observed was different in the presence of different metal ions and protons which indicates that the effect is certainly due to the binding of the metal ions in the cryptand cavity. The metal perchlorate salts are hydrated and can generate protons in organic solvents like THF. To prove that the fluorescence enhancement are indeed due to metal ion(s) entering the cryptand cavity and not due to the protons generated, several control experiments were carried out as described earlier [9,10]. All these control experiments definitely suggest that fluorescence enhancement observed is due to the binding of the metal ions in the cryptand cavity and not due to the protons generated in the medium. The fact that the quantum yield of fluorescence emission of  $L^2$  increases considerably in presence of metal ions also proves that PET is operative in this system too. Metal ions in the cavity block the lone pair on the N atom and prevent PET in the metal complexes.

The addition of alkali metal ions like  $Na^+$  had no effect on the  $\phi_{FM}$  values of either  $L^1$  or  $L^2$ . This is because these metal ions are known to occupy the upper deck of the cryptand cavity and will thus, not affect the process of PET.

#### 4. Conclusion

Although cryptand based fluorophores in the format ‘fluorophore-spacer-receptor’ are excellent systems showing enhancement of fluorescence by transition metal ions, the extent of enhancement depends critically upon the nature of the spacer. In the present system  $L^2$ , the introduction of  $>C=O$  group as spacer in place of  $-CH_2$  group ( $L^1$ ) induces rigidity in the system as a result of which the donor and the acceptor are not properly mutually oriented leading to inefficient PET. The presence of  $C=O$  group also prevents exciplex emission as observed in case of  $L^1$ . This study thus aims at proper designing of efficient molecular switches (OR logic gate).

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