

## Synthesis of Complexes of Lanthanide ions with 2,2':6',2''-terpyridine Ligands for Luminescence Properties

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### Abstract

The design and development of lanthanide complexes with an encapsulating ligand is currently a key area of vital importance in the field of luminescence as it offers the possibility to obtain thermodynamically stable luminescent materials possessing better sensitivity and specificity vis-a-vis conventional methods like radioactive labelling. In this work, europium and terbium complexes of a series of ter-pyridine-N-oxide ligands have been synthesized and characterized for their luminescence properties. From the solid-state structures some interesting topologies of the ligands can be unraveled which are introduced due to the flexibility to the coordination sphere by the N-oxide donors. Luminescence studies of the N-oxide complexes in acetonitrile show typical europium and terbium emission spectra, dominated by some intense luminescence. Decomplexation of the non-oxidised ligand complexes was observed at low solution concentrations in the luminescence spectra and so strong lanthanide-binding groups were introduced to the external pyridine rings of the ter-pyridine ligands to improve complex stability.

Lanthanide-binding groups introduced were hard, anionic carboxylate groups and also, the more organic solvent soluble, tert-butyl amide groups being observed.

**Keywords :** Luminescent, Ligands, labeling, Decomplexation, ter-pyridine

## INTRODUCTION

Derivatives from 2,2':6',2''-terpyridine (TPy) have dragged much wider attention as they can work as functional templates or basic building blocks in the area like supramolecular and coordination chemistry as well as material science [1][2]. They find applications in light-harvesting devices, moreover due to their strong complexation tendency with many transition metal ions they form diverse metal-complexes and metallo-supramolecular architectures. The so synthesized organo-metallic complexes have amazing redox, photophysical and catalytic properties exhibited during many organic reactions. These properties have resulted into potential applications in the fields like light-to-electricity conversion, organic light-emitting diodes, sensors and non-linear optical devices[3][4]. They can also be very well used as building blocks in the development of well-defined two- or three-dimensional multilayers on the solid substrates of nanoscale materials and devices [5].

A silylated TPy derivative (SiTPy) based on an addition reaction of 4-(chloromethyl) phenyltrimethoxysilane with a polydentate ligand of 4'-(4-pyridyl)-2,2':6',2''-terpyridine (Pyterpy) that contains another pyridyl coordination site at the 4'-position of TPy was newly synthesized[6]. Further, after the addition reaction, the SiTPy was found to contain a substituent trimethoxysilane at the 4'-position of TPy, holding a potential to form organic-inorganic hybrid nanomaterials or composites [7], as well as holding a promise as a potential candidate to fabricate self-assembled monolayers (SAMs) on the hydrophilic solid supports [8].

In the present work, the luminescent properties of Lanthanide ions with 2,2':6',2''-terpyridine Ligands were investigated in the solutions[9]. Our results revealed that the resulting complexes of  $\text{Eu}^{+3}$  and  $\text{Tb}^{+3}$  lanthanide ions with 2,2':6',2''-terpyridine exhibit excellent luminescent emission. The  $\text{Eu}^{3+}$  chelates coupled to proteins gave luminescence intensities almost identical to the parent complexes, whereas  $\text{Tb}^{3+}$  chelates coupled to proteins behaved unpredictably with regard to decay times and luminescence intensities[10][11].

## MATERIALS & METHODS

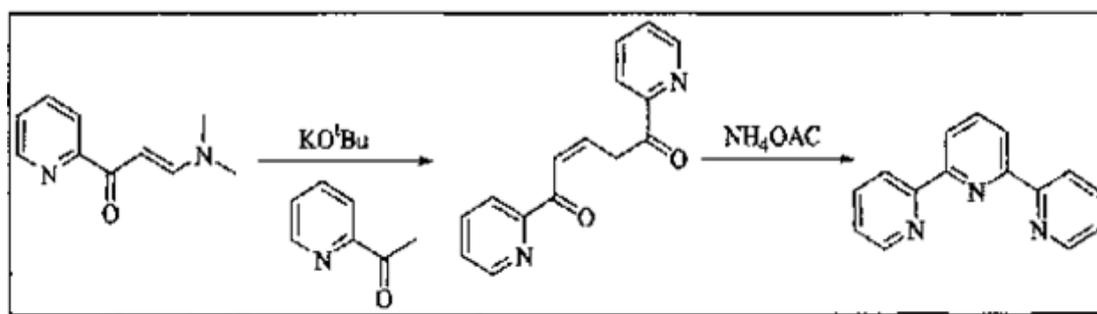
### Synthesis of 2,2':6',2''-terpyridine Ligands

The step wise procedure followed for the synthesis of ligands is as follows :

A flame dried 1L 2-neck flask was purged with Nitrogen to create inert environment in the reactor. Anhydrous Tetrahydrofuran, THF (400 ml) and potassium t-butoxide (20g, 0.179 mol) was added followed by 2-acetylpyridine (10.34 g, 85.4 mmol). The solution was subjected to stirring at room temperature for an hour followed by sonication for 15-20 minutes following which a white solid was found to be formed. The  $\beta$ -(dimethyl-amino)vinyl 2-pyridyl ketone (15.03 g, 85.4 mmol) was added and the solution colour intensity slowly turned to a very deep red, was further subjected to continuous stirring at room temperature for 48 hours on a magnetic stirrer . The reaction mixture was then cooled in ice and ammonium acetate solution (64.g, 0.833 mol) in acetic acid (200 ml) was added with stirring underway. Methanol (40 ml) was

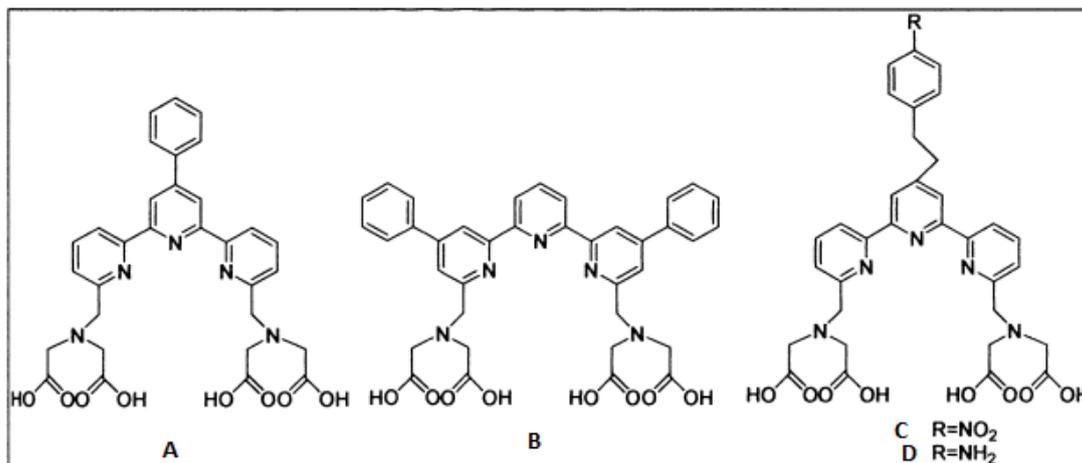
added, the flask fitted with a distillation column, the mixture heated to reflux and the THF gradually removed by distillation over a three hour period. The distillation continued until the temperature attained 115°C. The mixture was poured into water (400 ml) and the excess acetic acid was neutralized with sodium carbonate (~300 g). Toluene (120 ml) and celite (20 g) was added and the mixture was stirred and heated at 80°C. The mixture was cooled to room temperature and filtered through whatmann filter paper no. 41. The solid was powdered and washed with toluene (3 x 75 ml). The organic layer of the filtrate was separated and the aqueous layer extracted with (2 x 100 ml) of toluene. The organic layers was agitated with 25 g of alumina and then filtered. The powder was evaporated till we get a brown coloured oil which was dissolved in 80 ml of chloroform and 40 g of alumina. The powder was then poured onto the top of alumina column and eluted with 20:1 cyclohexane/ethyl acetate as a eluent composition for separation of the product as a light yellow fraction which was further washed and dried to get the pure product. Yield: 63%.

The reaction scheme for the synthesis of of unsubstituted terpyridine is as shown in fig. 1.



**Fig.1.** Reaction scheme for the synthesis of unsubstituted terpyridine

In a similar fashion Mukkala and co-workers went on to report the synthesis of 20 different 2,2',6',2''-terpyridine derivatives with (methylenenitrilo)bis(acetic acid) groups as the stable complex forming moieties and applied them to protein labelling. The different ligands synthesised included the ligands A,B,C and D as shown in fig.2 which is meant for the structure of the substituted terpyridine.



**Fig. 2.** Structure of the of substituted terpyridine

## RESULTS & DISCUSSION

All the chemicals used are AR grade including Lanthanide salts and solvents used are of high purity. The luminescence property exhibited by  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  metal ions as core complexed with ligands A, B, C, D in terms of intensity is tabulated in table 1 below :

**Table 1.** Luminescence intensity for metal ions,  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  with substituted terpyridine ligands

Ligand	Luminescence intensity ( $\epsilon\phi$ )	
	$\text{Eu}^{3+}$	$\text{Tb}^{3+}$
A	1970	1900
B	3900	1500
C	580	32
D	220	53

These ligands were shown to be excellent shielders of the metal ion core from decay time experiments and it was estimated that water molecules were coordinated to the metal ions. The parent compound A showed relatively high luminescence intensities for both  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ( $\text{Eu}^{3+}$ :  $\epsilon\phi=1970$ ,  $\text{Tb}^{3+}$ :  $\epsilon\phi=1900$ ) and ligand B nearly doubled the relative luminescence of the  $\text{Eu}^{3+}$  complex ( $\epsilon\phi=3900$ ). Conversely, it decreased the relative luminescence of the  $\text{Tb}^{3+}$  complex ( $\epsilon\phi=1500$ ). Ligands C and D gave even worse relative luminescence intensities for both  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  (C  $\text{Eu}^{3+}$ :  $\epsilon\phi=580$ ,  $\text{Tb}^{3+}$ :  $\epsilon\phi=32$ ; D  $\text{Eu}^{3+}$ :  $\epsilon\phi=220$ ,  $\text{Tb}^{3+}$ :  $\epsilon\phi=53$ ) seeming to indicate that the substituents in the aromatic part caused lowering of the ligand triplet state causing an energy leakage back to the ligand triplet state.

Further coupling of these ligands to proteins gave varied results. The  $\text{Eu}^{3+}$  chelates coupled to proteins gave luminescence intensities almost identical to the parent complexes, whereas Tb chelates coupled to proteins behaved unpredictably with regard to decay times and luminescence intensities.

## CONCLUSION

The lanthanide ions like  $\text{Eu}^{+3}$  and  $\text{Tb}^{+3}$  ions form strong and thermodynamically stable complexes[11][12]. It was found that these ligands are strong candidates for luminescent devices and with this study proven that it is quite possible to develop acyclic ligands that could be applied as luminescent labels. The presence of carboxylic groups had led to an enhancement of the overall stability of their complexes and they had also shown that careful consideration must be taken with ligand development as even small adjustments can give quite unpredictable results.

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