



LUMINESCENCE PROPERTIES OF DIFFERENT LANTHANIDE COMPLEXES

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ABSTRACT:

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 terpyridine ligands to improve complex stability. 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. 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.

KEYWORDS : Labeling, Luminescent, Ligands.

INTRODUCTION:

Quinone and its derivatives are known function as photo and electro chemically active molecules. They find extensive applications in the areas of fabrication of chemical transducers, molecular switch systems. Fluorescent heterocyclic compounds are widely used in the making of emitters in electroluminescence devices, probes in

biochemical research, photo-conductive materials . In this communication, we report the green synthesis of 1, 4- quinone derivatives by conventional heating methods using water and ethanol as solvents. The same compounds were also synthesized with the help of ultrasound. All the compounds were characterized. 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 Eu and Tb+3+ lanthanide ions with 2,2':6',2''-terpyridine exhibit excellent luminescent emission. The 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.

MATERIAL AND METHODS:

The synthesis was as follows,

Conventional heating method: A mixture of 2,3-dichloro-1,4-naphthaquinone (0.227 g, 0.01 mol.) and dapsone (0.248 g, 0.01 mol.) was added to ethanol (100 mL) and the solution was refluxed for 5 h at 60 °C. The resulting solution was cooled and the precipitate was filtered, dried at room temperature and purified.

Ultrasound assisted method: A mixture of 2,3-dichloro-1,4-naphthaquinone (0.227 g, 0.01 mol.) and dapsone (0.248 g, 0.01 mol.) was ground together and subjected to ultrasonication in water and acetone separately for 15 minutes. After the completion of the reaction, the product was set aside to cool and then ice cold water (100 mL) was added. The solid product was filtered, dried at room temperature and recrystallized from ethanol.

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 3-(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 x75 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%.

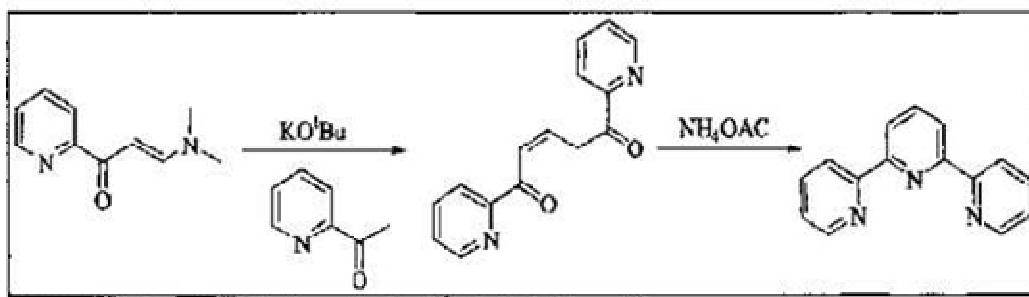


Fig.1 The reaction scheme for the synthesis of of unsubstituted terpyridine.

RESULTS & DISCUSSION:

The luminescence property exhibited by Eu⁺³ and Tb⁺³ metal ions as core complexed with ligands A, B, C, D in terms of intensity is tabulated in table 1 below :

Ligand	Luminescence intensity (□□)	
	Eu ⁺³	Tb ⁺³
A	1970	1900
B	3900	1500
C	580	32
D	220	53

Table 1. Luminescence intensity for metal ions, Eu⁺³ and Tb⁺³ with substituted terpyridine ligands.

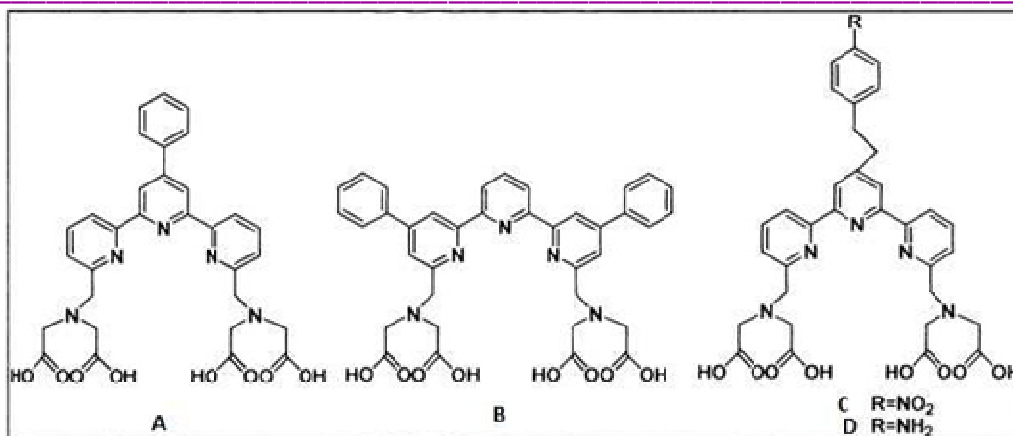


Fig.2 Structure of the of substituted terpyridine.

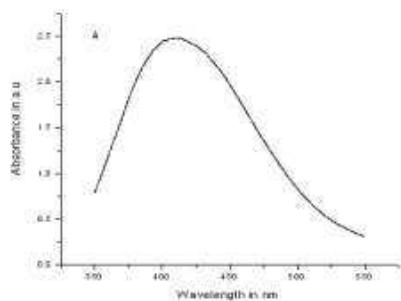


Fig.3: The fluorescence emission spectrum of compound (Conventional heating).

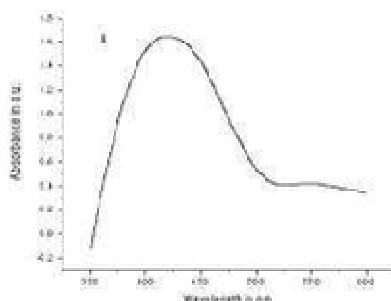


Fig.4: The fluorescence emission spectrum of compound (Ultrasound assisted)

CONCLUSION:

Quinones are known to exhibit photochemical properties⁴, the photochemical properties of the synthesized compounds were studied using UV-Vis and photoluminescence spectroscopy.

The presence of carboxylic groups had led to an enhancement of the overall stability of their complexes. The lanthanide ions like Eu^{+3} and Tb^{+3} ions form strong and thermodynamically stable complexes. It was found that these ligands are strong candidates for luminescent devices.

Careful consideration must be taken with ligand development as even small adjustments can give quite unpredictable results.

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