# LUMINESCENT MATERIALS BASED ON LANTHANIDE IONS

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PhD

## **Declaration**

Except where specific reference has been made to other sources, the work presented in the thesis is the original work of the author. It has not been submitted, in whole or in part, for any other degree.

Seemas

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### Abstract

The inclusion of lanthanide (III) (Ln<sup>3+</sup>) ions into polymers by 'covalent' bonding has applications. Heteroleptic hydrotris(pyrazolyl)borate crotonate and cinnamate complexes were synthesised for reasons that, firstly, knowledge of the polymerisable double bond was helpful in establishing the conditions of any copolymerisation reaction; secondly, the chosen ligands are very good at receiving energy in the UV region; and thirdly, lanthanide complexes might undergo changes in properties, on moving between adjacent lanthanide ions, allowing potentially convenient isolations of pure materials at the monomer production stage, or even at the polymerisation stage. For both complexes, two classes of target complex were identified: the mononuclear (Er-Lu) and dinuclear (La-Ho). Mononuclear forms were identified by MS, <sup>1</sup>H NMR and elemental analysis and dinuclear forms were characterised by X-ray crystallography. For heteroleptic hydrotris(pyrazolyl)borate crotonate and cinnamate complexes, the ligands act as antennae for receiving and then transferring energy to metal ions and these complexes were studied in several homogeneous and heterogeneous copolymers as well as in rigid PMMA or polystyrene matrices. Luminescence decay of these complexes depends on the distance between the metal and C-H oscillators so the cinnamate complexes showed better luminescence life-times compared to crotonate complexes. The copolymer system helped to reduce the concentration guenching compared to corresponding metal complex / polymer blend systems. The thermal stabilities of the complex monomers were increased by incorporating them into polymer chains. Europium crotonate and cinnamate complexes in the poly(p-phenylenevinylene) (PPV) precursor blends showed the characteristic emission of europium, and the emission from PPV was guenched by increasing the europium content in the PPV precursor blends.

## List of publications

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## Abbreviations

A	Absorbance
acacH	Acetyl acetone
AAH	Acrylic acid
AI	Aluminium
Ar	Aryl
Alq <sub>3</sub>	Tris(8-hydroxyquinolinato)aluminium
AIBN	Azobisisobutyronitrile
<sup>13</sup> C NMR	Carbon NMR
Cin	Cinnamic acid
Crot	Crotonic acid
DCM	Dichloromethane
DBM	1,3-diphenyl-1,3-propanedione
DMSO	Dimethyl Sulphoxide
DNA	Dioxyribonucleic acid
DNM	Dinaphthyl methane
EDTA	Ethylenediaminetetraaceticacid
EL	Electroluminescence
GPC	Gel Permeation Chromatography
<sup>1</sup> H NMR	Proton NMR
ITO	Indium tin oxide
ICP-MS	Inductively Coupled Plasma Mass Spectrom
IR	Infra-red
In	Intensity
ISC	Inter-system crossing
IL	Intra-ligand
КТр	Potassium hydrotris(pyrazolyl)borate
Ln	Lanthanides
Ме	Methyl
m.p.	Melting point
MeOH	Methanol
MMA	Methyl methacrylate

M <sub>n</sub>	Number average molecular weight
Mw	Weight average molecular weight
Nn	Nanometre
NapT	Naphthoate
NaTp	Sodium hydrotris(pyrazolyl)borate
NMR	Nuclear Magnetic Resonance
OLEDs	Organic Light Emitting Diodes
OMe	Methoxy
Phen	Phenanthroline
PL	Photoluminescence
PEDOT	Poly(3,4-ethylenedioxythiophene)
PLEDs	Polymer Light Emitting Diodes
PMMA	Poly(methyl methacrylate)
PPP	Poly(phenylene)
PSS	Poly(styrenesulfonate)
PVK	Poly(vinyl carbazole)
PPV	Poly(phenylene vinylene)
PS	Polystyrene
pzH	Pyrazole
S <sub>0</sub>	Ground state
S <sub>1</sub>	Singlet state
TTFA	Thenoyltrifluoroacetyl
THF	Tetrahydrofuran
TGA	Thermo Gravimetric Analysis
т	Transmission
UV	Ultra-Violet
Vis	Visible

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# Chapter 1 Introduction

## 1. Introduction

### 1.1. Lanthanides

The history of the lanthanides<sup>1-3</sup> starts in 1787, with the discovery of an unknown mineral near the Swedish town of Ytterby. The first new element discovered (called "Ytterbit") was yttrium in 1794. Lanthanide cations have an extended 4f electronic configuration (n = 1-14) and unique optical properties due to the shielding of 4f orbitals by filled 5s and 5p outer shell electrons. In comparison to d-block elements, lanthanides are larger in size, and the small difference in ionic radii results in a regular variation in chemical properties. As the Ln<sup>3+</sup> radius decreases across the series, the salt become less ionic. This leads to small changes in their chemical properties. Most of the lanthanides are trivalent in nature but  $Ln^{2+}$  (Ln = Sm, Eu, Tm, Yb) and  $Ln^{4+}$  (Ln = Ce, Pr, Nd, Tb, Dy) species are also known. Ln<sup>2+</sup> species are strong reducing agents and Ln<sup>4+</sup> are oxidising agents, for example Ce<sup>4+</sup> is used as an oxidising agent in organic chemistry<sup>4</sup> and these oxidation states are more stable if an empty, half-filled or fully-filled 4f shell can be achieved. Lanthanides are hard Lewis acids, lanthanide-to-ligand bond is usually labile leading to rapid dissociation of product and thus the possibility of high catalytic turn over. Lanthanides interact preferentially with hard ligands and exhibit strong oxophilic character. Their acidity decreases with increasing ionic radius so among lanthanides La<sup>3+</sup> is the least acidic and Yb<sup>3+</sup> is the most acidic in nature. Due to the small difference in size, most of the lanthanide complexes are isomorphous to each other. The lanthanide complexes are vulnerable to hydrolysis and, in solution, exhibit fast ligand-exchange which can be limited by the use of chelating mostly determined ligands. These metal-ligand interactions are by electrostatic factors.

Coordination of lanthanides are with anionic or proton-ionizable ligands as they have the ability to displace more effectively the hydration sphere of the cation, providing more kinetically stable complexes. That is why the carboxylate group is the recurring function employed in many of the structures previously described.<sup>5</sup> Halide coordination is weak and Cl<sup>-</sup>, Br<sup>-</sup>, l<sup>-</sup> are thus easily excluded from the first coordination sphere. Oxygenated inorganic

anions such as nitrate, sulphate, carbonate and phosphate can form complexes with one or two oxygen atoms, although the complexes are only slightly stronger than those with chloride. Only carbonate forms strong complexes due to its double anionic charge and the much weaker acidity of its conjugated acid compared with nitric, sulphuric or phosphoric acids.<sup>6</sup> Similar to carbonate, carboxylates also strongly coordinate to lanthanides using the two oxygen atoms.

# 1.1.1.Lanthanides complexes using hydrotris(pyrazolyl)borate ligand (Tp)

As a result of the large size of the lanthanide ions and the predominantly ionic bonding, steric saturation is a critical factor in coordination number, the geometry and the structure of the lanthanide complexes. The isolation of well-defined complexes often requires the use of sterically demanding ligands. The poly(pyrazolyl)borate ligands, first introduced by Trofimenko,<sup>7</sup> represent an attractive, versatile and alternative ligand to cyclopentadienides and have been studied widely in coordination chemistry.<sup>8-12</sup> Poly(pyrazolyl)borates can be easily prepared from pyrazole and a borohydride salt (Equation 1). These ligands have been used as coordination-controlling environments for many transition metals. However, the coordination chemistry of the lanthanide series is more complex in comparison to the transition metals because of the larger size of the metal ions.<sup>13</sup> Coordination numbers in the lanthanides series can be up to 10 or 12 depending on the size of the metal and the size of the ligand. Based on the results with transition metals, poly(pyrazolyl)borates are good candidate ligands for the study of coordination on lanthanides.



Equation 1. Synthesis of KTp

Poly(pyrazolyl)borates are isoelectronic with cyclopentadienide because they are six electron donors with a single negative charge. Also they bind to three

coordination sites of a metal.<sup>8</sup> Figure 1.1 shows the bonding modes of coordinated hydrotris(pyrazolyl)borate and cyclopentadienyl ligands. The geometry of poly(pyrazolyl)borates can be monodentate, bidentate or tridentate depending on the metal, substituents on the pyrazole and anionic co-ligands.



Figure 1.1. Bonding modes of hydrotris(pyrazolyl)borate and cyclopentadienyl ligands

There are several reports of the synthesis of lanthanide complexes by the metathesis of a lanthanide halide with the sodium or potassium salt of a poly(pyrazolyl)borate. Reaction of anhydrous LnCl<sub>3</sub> or lanthanide chloride hydrate with KTp or NaTp in water affords a good yield of LnL<sub>2</sub>Cl.<sup>14</sup> Thus the  ${LnL_2}^+$  moiety would seem a suitable substrate for the preparation of more robust organo-lanthanide complexes. However, attempts to develop this synthetic strategy using LnL<sub>2</sub>Cl as a precursor have been hindered by disproportionation reactions leading to the air-stable homoleptic LnL<sub>3</sub> complexes; the molecular structures of these complexes were determined by the X-ray methods. In YbL<sub>3</sub> complexes the geometry about the eightcoordinate Yb<sup>3+</sup> ion was found to have one bidentate and two tridentate poly(pyrazolyl) borate ligands. Moss et al.<sup>15</sup> investigated whether a new series of heteroleptic complexes containing {LnL<sub>2</sub>}<sup>+</sup> could be prepared using other bidentate ligands such as β-diketonate, oxalates and carboxylates. Some of these lanthanide complexes are air and moisture sensitive; also  $\beta$ -diketonate complexes of metals have been used for the deposition of materials for electroluminescent devices (EL).<sup>16</sup> The common method to prepare the heteroleptic poly(pyrazolyl)borate complexes is shown in Equation 2.

 $2KTp + LnCl_3.nH_2O + X^- \longrightarrow [Tp_2LnX]$ 

Equation 2. Common method for the synthesis of heteroleptic poly(pyrazolyl)borate complexes

The stabilities and the structures of the lanthanide ion complexes are highly sensitive to the extent to which the ligand set around the ion can sterically saturate its coordination sphere. So it is of interest to assess the effect of variation in the size of the co-ligand X, on the steric saturation of the metal-coordination sphere<sup>17</sup> in [LnL<sub>2</sub>X]. For example, in the complexes [LnL<sub>2</sub>(acac)] (acac = acetyl acetone) the acac ligand forms a six-membered chelate ring with the Ln<sup>3+</sup> ion. The use of other bidentate uninegative ligands allows a study of the effects of reducing the size of the chelate ring formed between the lanthanide ion. The use of 2-hydroxycyclohepta-2,4,6-trien-1-one (Htrop) in place of Hacac, results in a five membered chelate ring, while the use of carboxylic acid ligands may result in the formation of four membered chelate rings.<sup>18</sup>

The mass spectra of the heteroleptic poly(pyrazolyl)borate complexes<sup>15</sup> show common fragments of the molecular ion, such as  ${LnL_2(x)}^+$ ,  $\{LnL_2\}^+$  ${LnL(pz)}^+$  and  ${Ln(pz)}^+$  (pz= C<sub>3</sub>N<sub>2</sub>H<sub>3</sub>). All these complexes show a common IR spectrum; the band at 2460 cm<sup>-1</sup> corresponds to the B-H vibrational stretch, the band at 1595-1620 cm<sup>-1</sup> corresponds to C=O vibrational stretch and the characteristic poly(pyrazolyl)borate bands in the region 1500-600 cm<sup>-1</sup> are also present. This work revealed that the repeated recrystallisation of these complexes from DCM-hexane gave different structural configurations for bigger lanthanides to smaller lanthanides. In the case of bigger lanthanides (La-Ho), the co-ligands (X) formed bridging bonds between the lanthanide ions, the molecular formulae of these complexes being  $[(TpLnX_2)_2]$ . For the smaller lanthanides (Er-Lu) the coligands are in bidentate mode and the resulting complexes are [(Tp(Ln)X)<sub>2</sub>]. Jones et al.<sup>15</sup>also suggested that in the IR spectra for bigger lanthanide complexes, the strong bands at 1600-1555 cm<sup>-1</sup> may be due to a bridging CO, this would be consistent with the reported value of 1600 cm<sup>-1</sup> for  $v(CO_2)$  in the acetate-bridged dimer [(YL(µ-O2CMe2))2]. All these complexes, including larger lanthanides and the smaller ones, are  $[(Tp(Ln)X)_2]$  complexes in powder form.

Heteroleptic poly(pyrazolyl)borate complexes of the lanthanides have been evaluated as possible high quantum yield, visible light emitters and the emission spectra of europium and terbium poly(pyrazolyl) borate complexes have been reported.<sup>19</sup> A ligand-to-metal charge transfer process present only in the complexes was thought to lead to the population of the lanthanide energy levels according to the Whan-Crosby mechanism.<sup>20</sup>

## **1.2. Luminescence properties of lanthanide complexes**

The optical properties of lanthanides are different from those of other ions and molecular species because they absorb and emit light over narrow wavelength ranges. Their unique optical properties are due to the shielding of 4f orbitals by filled 5s and 5p valence orbitals. The effective shielding of 4f orbitals minimizes interaction with the surrounding environment such as ligands and solvents. This results in weak transition intensities, long life-times, and transition energies that are relatively insensitive to the coordinating ligands.

Lanthanides are luminescent in the visible [Eu(III), Tb(III), Sm(III), Dy(III)] and near infrared [Yb(III), Nd(III), Er(III)] regions, this was first described by Dieke.<sup>21</sup> Figure 1.2 shows the energy states observed for lanthanide fluoride glasses.<sup>22</sup> Direct excitation of lanthanides is difficult due to the forbidden nature of the f-f transition and also the molar absorptivity of f-f transitions is typically 1-10 M<sup>-1</sup> cm<sup>-1</sup> compared with d-d transitions (10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>) of some transition metal complexes.<sup>23</sup> On the other hand, due to the forbidden nature of the involved electronic transitions, excited state life times are exceptionally generally in the hundreds of microseconds to several long and are milliseconds range.<sup>24</sup> The favourable luminescence properties of lanthanides development of chemosensors, applications in the have several supramolecular devices such as logic gates, electroluminescence devices and in optical telecommunication.<sup>25</sup>



Figure 1.2. Energy states observed for lanthanide fluoride glasses<sup>4</sup>

However the application of lanthanide based luminescence suffers from two serious drawbacks:<sup>26</sup> poor light absorption properties and the efficient non-radiative deactivation of their excited states by OH oscillators such as water. In order to avoid these disadvantages for the application of the lanthanides based luminescent devices, Weismann<sup>27</sup> found that when organic ligands were chelated to Eu<sup>3+</sup> and then excited at the  $\pi$ - $\pi$ \* transition energy of the ligand, a sensitized 4f-4f emission from Eu<sup>3+</sup> was obtained this is called the "antenna effect".

Sensitizers have been used to excite the lanthanide ion via energy transfer from the sensitizer (or antenna) to the lanthanide ion, this process is schematically represented in a Jablonski diagram (Figure 1.3). Upon absorption of light the sensitizer is excited to the singlet excited state ( $S_1$ ). The singlet state undergoes intersystem crossing (ISC) into the ligand based triplet state (T) or can decay to the ground state ( $S_0$ ) by fluorescence or nonradiatively. From the triplet state, energy is transferred to the lanthanide ion or the triplet state decays to the ground state. In general, energy is transferred

via the triplet state because the intersystem crossing is enhanced by the nearby, paramagnetic lanthanide ions and because energy transfer via the singlet state is not fast enough to compete with the sensitized fluorescence or the intersystem crossing.



Figure 1.3. Jablonski diagram for sensitized emission of lanthanide ions by a sensitizer

Energy transfer can proceed via dipolar or multipolar interactions between the sensitizer and the acceptor (lanthanide ion), a Forster mechanism of transfer,<sup>28</sup> or via an exchange mechanism - the Dexter mechanism of transfer.<sup>29</sup> The main difference between these two energy transfer processes is that in the Dexter mechanism, orbital overlap is needed whereas in the Forster mechanism the transfer is strongly dependent on the spectral overlap of the emission spectrum of the donor and the absorption spectrum of the acceptor. Energy transfer by the Dexter mechanism is only efficient at very small distances, whereas Forster energy transfer has been reported to occur over much longer distances.<sup>30</sup>

Lanthanides can only accept the energy from the sensitizer according to the following criteria:<sup>31,32</sup> (a) the energy gap between the donor (sensitizer singlet or triplet state) and acceptor (lanthanide ion levels) should not be too large, (b) significant matrix elements of the orbitals overlap. An important phenomenon in the sensitization of the lanthanide ion can be energy back-transfer from the excited lanthanide ion to the sensitizer. This will only happen when the donating sensitizer is very close to the lanthanide ion level. In the

cases of Eu<sup>3+</sup> and Tb<sup>3+</sup> this has been measured by Mukkala et al. <sup>33</sup> who showed that the triplet state of a sensitizer must be 1200 cm<sup>-1</sup> higher in energy than the accepting levels of Tb<sup>3+</sup> and Eu<sup>3+</sup>. The photophysical properties of Eu<sup>3+</sup> ions are the most studied of all the lanthanide ions. Only one emission line is observed at 580 nm when a single chemical species is present.<sup>34</sup> The energy transfer from  $\pi$ - $\pi$ \* states of aromatic ligands to the Eu<sup>3+</sup> emissive <sup>5</sup>D<sub>0</sub> state can also result in enhanced lanthanide emission. This type of sensitization is very common for Eu<sup>3+</sup> complexes, because many ligand triplet states lie just above the <sup>5</sup>D<sub>0</sub> emissive state. It has been reported for many different types of ligands including Schiff base ligands,<sup>35</sup> diketones,<sup>36</sup> tetracyclines,<sup>37</sup> derivatives,<sup>38</sup> crown-ether polyaminopolycarboylates,<sup>39</sup> multidentate polyheterocycles,<sup>40</sup> cryptands,<sup>41</sup> calixarenes<sup>42</sup> and cyclodextrins.<sup>43</sup>

When the  $\pi$ - $\pi^*$  state of the ligand lies just above the <sup>5</sup>D<sub>1</sub> state of the Eu<sup>3+</sup> ion, luminescence from both  ${}^{5}D_{1}$  and  ${}^{5}D_{0}$  states is observed upon excitation of the ligand.<sup>44</sup> Non-radiative deactivation from the <sup>5</sup>D<sub>1</sub> state tends to lower quantum yields for this type of sensitization compared to those when the energy transfer from the ligand is directly conducted to the <sup>5</sup>D<sub>0</sub> state. Thermal quenching of the Eu<sup>3+</sup> based emission is possible if the energy of the triplet state of the ligand is close enough to the emissive <sup>5</sup>D<sub>0</sub> state, because back energy transfer may take place. This phenomenon was reported for Eu<sup>3+</sup> complexes of the tridentate aromatic ligand bisbenzimidazolepyridine.<sup>45</sup> Biological applications of terbium emission have also been widely utilized. The luminescence from Tb<sup>3+</sup> ions is also quenched by the OH groups of coordinated water molecules, but to a much lower extent than in the case of Eu<sup>3+.</sup> This is due to the larger energy gap between the ground state and the emissive state of Tb<sup>3+</sup> (20500 cm<sup>-1</sup>) compared to that of Eu<sup>3+</sup>. Sensitized luminescence is common in Tb<sup>3+</sup> complexes, involving energy transfer from the lowest-lying ligand triplet excited state to the emissive <sup>5</sup>D<sub>4</sub> state. It was shown that for strong chelators the energy of the donor triplet state, which must lie above the <sup>5</sup>D<sub>4</sub> excited state of Tb<sup>3+</sup>, is the most important parameter for efficient energy transfer to take place.<sup>34</sup>

The ions Yb<sup>3+</sup>, Nd<sup>3+</sup>, Er<sup>3+</sup> display near-infrared emission centred at 880 nm, 1060 nm and 1330 nm respectively with life-times in the microsecond range. The smaller energy gap between the ground state and emissive state of these ions compared to Tb<sup>3+</sup> and Eu<sup>3+</sup>, results in more efficient non-radiative decay through solvent or ligand vibrations. However, sensitized emission is still possible in complexes of these ions. Emission from Pr<sup>3+</sup>, Ho<sup>3+</sup>, Er<sup>3+</sup>, Tm<sup>3+</sup>, and Yb<sup>3+</sup> ions is rather weak because the energy gap between the ground and emissive states is small in all cases,<sup>46</sup> thus making non-radiative decay an important factor in heavily decreasing the luminescence intensities of these ions. The f<sup>0</sup> and f<sup>14</sup> electronic configurations of La<sup>3+</sup>, Lu<sup>3+</sup> respectively, result in no f  $\rightarrow$  f transition for these ions. Complexes of Gd<sup>3+</sup> generally exhibit only ligand-centred emission, since the  $f \rightarrow f$  transition states of Gd have exceptionally high energies owing to the extreme stability of its half-filled f shell ( $f^7$ ). The lowest energy f  $\rightarrow$  f transition appears as an emission line at 312 nm. Owing to this behaviour, Gd<sup>3+</sup> complexes are frequently characterized by emissive intra-ligand (IL) states at lower energies. This IL fluorescence is largely quenched while the IL phosphorescence is facilitated. As a result, these complexes are often used to determine the energy of ligand triplet states.47

### 1.2.1. Visible emitting lanthanide complexes

The photoluminescence (PL is a process in which a substance absorbs photons and re-radiates photons) and electroluminescence (EL is an optical phenomenan and electrical phenomenan in which materials emits light in response to electric current passed through it) of the lanthanide complexes are affected by the structure of the ligand. Therefore ligand design is important in achieving ligand energy levels which give a high luminescent efficiency. Eu, Tb, Sm, Dy, Tm are the lanthanides that emit light in the visible range. The two most useful lanthanides, europium and terbium, have unusual spectroscopic characteristics, including millisecond life time and sharply spiked emission spectra. <sup>48</sup> Given the fact that in Eu<sup>3+</sup> the <sup>5</sup>D<sub>1</sub> level at 19000 cm<sup>-1</sup> is the receiving level and that the triplet state of the sensitizer should be 1000-2000 cm<sup>-1</sup> above this level, it follows that the singlet absorbing state of

the sensitizer for visible- emitting lanthanide complexes should be in the order of 25000 cm<sup>-1</sup>, which is in the UV region.

### $\beta$ -diketonate complexes.

The  $\beta$ -diketonate ligand is one of the important antennae from which the energy can be effectively transferred to Ln<sup>3+</sup> ions for high harvest emissions and these are negatively charged, bidentate ligands which may form 3:1 complexes, which are neutral overall. To complete the coordination sphere of the lanthanide, a phenanthroline or any other coligands could be used. Phenanthroline helps prevent water from directly binding to the lanthanide.<sup>49</sup> The structures of some of the visible emitting complexes are shown in Figure 1.4. B- diketonate complexes are of special interest in the fabrication of OLED with phenanthroline or because the ternary complexes devices bathophenenthroline co-ligands have a low sublimation point that allows easy sublimation of these materials on OLED devices. The lowered sublimation points are caused by distortion of the symmetry in the complexes and the vacuum deposition of the complexes is relatively easily achieved.



Figure 1.4. Some of the structures of  $\beta$ -diketonate ligand containing europium Complexes.<sup>49</sup>

Excitation of these  $\beta$ -diketonate complexes leads to sensitised emission from the europium at 590 nm ( ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ ) and 620 nm ( ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ ). These complexes are slightly red-shifted, depending on the substituent group present on the  $\beta$ -diketonate ligand. The energy absorption process of a lanthanide complex mostly depends on the anion ligand. The EL efficiency of a lanthanide complex is very sensitive to the singlet state energy as well as the triplet state energy of the anion ligand. The reason is that the triplet state energy, second vibrational state of anion ligand of lanthanide complex, has a large effect on energy transfer between anion ligand of lanthanide complex and central metal ion than singlet state energy. Bora *et al.*<sup>50</sup> synthesised a series of Eu and Tb complexes using TTA, acac, DBM as  $\beta$ -diketonate ligands; the ligands and metal energy levels are shown in Figure 1.5.



Figure 1.5. Singlet-triplet state energy level of the ligands and the metal ions

In case of Eu<sup>3+</sup> the anion ligand (TTA, DBM) absorbs energy and is excited to its singlet state, undergoes intersystem crossing to its triplet state, then intramolecular energy transfer to the emissive state of the Eu<sup>3+</sup> ion and the luminescence is emitted. In the case of Tb<sup>3+</sup>, efficient luminescence only obtained from the acac ligand. This is not an effective energy transfer ligand in the case of Eu<sup>3+</sup>, because the energy gap between the acac and Eu<sup>3+</sup> is too big. There is no luminescence from Tb<sup>3+</sup> ion with the TTA and DBM ligands because these ligands triplet levels are too low compared to the Tb<sup>3+</sup> absorption level.

### Poly(pyrazolyl)borate ligands

Lawrence *et al.*<sup>51</sup> prepared visible emitting hydrotris(pyrazolyl)borate lanthanide complexes using salicylaldehyde and methyl salicylaldehyde as coligands. Eu and Tb obtained their characteristic emission bands by exciting either in the poly(pyrazolyl)borate region or the coligand region.

### Other ligands

Bakier *et al.*<sup>52</sup> synthesised some samarium complexes using 7-acetoxy coumarin 3-carboxylic acid (ACCH) and 1-(4-methoxy phenyl) 3-(4-*t*-butyl phenyl) 1,3 propanedione (MBPKH) in different solvents, mixed solvents and the rigid medium of a polymethyl methacrylate matrix (PMMA). For these ligands, samarium complexes show the characteristic emission at 564, 599, 707 nm, but their studies revealed that the photophysical properties of the samarium ion in presence of ACC or MBPK antenna molecules are sensitive to the nature of the medium whether it is homogeneous, heterogeneous or rigid PMMA. Luminescence intensity is low in protic solvents and this is due to the vibronic coupling with O-H oscillators. Quantum efficiency is higher in Sm–ACC complexes than in Sm-MBPK complexes indicating more efficient ligand–metal energy transfer from the ACC ligand. The structures of both ligands are shown in Figure 1.6.





Figure 1.6. Structures of (a), ACCH (b), MBPKH ligands

### Using inorganic host materials

Numerous lanthanide-antenna conjugates operating via such an absorption. energy-transfer, and emission sequence have been generated, most of them in solution.<sup>53-57</sup> In order to obtain technological processing of lanthanidebased luminescence, it is necessary to implement this sensitization mechanism in solid state materials. Several efforts have been made to immobilize lanthanide antenna systems in zeolites and sol-gel materials.<sup>58,59</sup> Some recent reports show that layered materials based on zirconium organophosphonates are capable of binding lanthanides and providing antenna functionality. It is possible to obtain inorganic-organic hybrid structures which contain organic moieties in the galleries of these materials.<sup>60,61</sup> Pires *et al.*<sup>62</sup> introduced a new luminescent zirconium phosphonate (zirconium sulfophenyl phosphonate (ZrSPP) based on phenyl chromophores as antennae and several lanthanides [Eu(III), Tb(III), Sm(III), Dy(III)] as energy acceptors and luminescent centres. A host material capable of sensitizing lanthanide luminescence via energy transfer should fulfil two conditions: (1) present an antenna chromophore and (2) present a lanthanide binding site. ZrSPP possesses these two requirements by incorporating phenyl groups as antenna chromophores and sulfonic acid groups as potential ion exchange sites (Figure 1.7).

2).



Figure 1.7. Structural view of zirconium sulfophenyl phosphonate ligand

#### Possiblity of singlet energy transfer

Most of the studies showed that the emission in luminescent lanthanides occurs by transferring triplet energy of ligands to the lanthanide.<sup>45</sup> The probability of an energy transfer from the singlet state of the luminescent ligand is thought to be low because this process is usually too slow to compete with other processes such as luminescent ligand fluorescence and intersystem crossing. However several reports have mentioned the energy transfer from the excited singlet state to the lanthanide ion. Yang and co-workers<sup>63</sup> reported that the energy transfer in dipyrazolyl-triazine–functionalized Eu<sup>3+</sup> complexes occurred from the singlet state of the sensitizers to Eu<sup>3+</sup> centres. Kim *et al.* <sup>64</sup> reported two ligands that can

sensitize lanthanide emission through the singlet state. The two ligands are 4-naphthalen-1-yl-benzoic acid (NAH-1), 4-[4-(4-methoxyphenyl)-naphthalen-1- yl-benzoic acid (NAH-2), structures of these two ligands and their corresponding Eu complexes are shown in Figure 1.8.



Figure 1.8. NAH-1, NAH-2 ligands and the corresponding Eu complexes

To obtain an effective energy transfer between the singlet luminescent ligand and the lanthanide ion, the emission energy levels of the ligands should overlap well with the absorption energy level of the  $Eu^{3+}$ ion. The energy level of the  $Eu^{3+}$  ion for the highest oscillation strength of its absorption bands is estimated to be 25300 cm<sup>-1</sup> and this overlaps well with the singlet excited state of NA-1 and NA-2. Figure 1.9 shows the photophysical process leading to sensitized emission from the  $Eu^{3+}$  ion.



Figure 1.9. Schematic diagram of the photophysical processes leading to sensitized emission from Eu<sup>3+</sup> by NA-1 and NA-2 ligands

### 1.2.2. Near-Infrared emitting lanthanide complexes

Near infra-red emisson around 900-1600 nm is valuable for fluoroimmunoassay and optical communication, due to the high transparency through biological systems and fiber media. In the field of optoelectronics organic near-infrared electroluminescence devices have attracted attention as novel, semiconductor compatibile, light sources for optical fibre communications because their easy fabrication enables the integration of the signal source with the fibre media at the terminal of local area network.<sup>65</sup> The most important optical amplifier for telecommunication is the Er<sup>3+</sup>-doped fibre amplifier. Er<sup>3+</sup> has an optical transition in the 1.55 µm telecommunication window,<sup>66</sup> and the other lanthanide ions that are actually being used in optical amplifiers are Pr<sup>3+</sup> and Nd<sup>3+</sup>, which have optical transitions in the 1.33 µm window. Lanthanide complexes that are based on multidentate ligands<sup>67,68</sup> such asthose derived from calix[4]arenes<sup>69,70</sup> and the *m*-terphenyl moiety<sup>71,72</sup> can be used for this purpose. A typical ligand based on the *m*-terphenyl is shown in Figure 1.10. These multidentate ligands form strong and stable lanthanide ions, are water soluble and allow for complexes with functionalization with a variety of substituents and sensitizers.



Figure 1.10. A Nd<sup>3+</sup> complex of a multidentate ligand based on the *m*-terphenyl moiety.

For most of the NIR lanthanide complexes, two different types of pumping will bring the lanthanide ions into their excited state. One is optical pumping and the second is based on electrical pumping. Using optical pumping one can excite lanthanides directly (lanthanide absorption region) or indirectly (via antenna).<sup>73</sup> The luminescence of the NIR emitting ions is strongly quenched by O-H and C-H vibrations. Beeby and Faulkner reported luminescent life-times of Nd<sup>3+</sup> ions in solution, which were found to be in the microsecond region.<sup>74</sup> They determined quenching constants of O-H and C-H vibrations by measuring the luminescent life-time in a series of solvents such as water, D<sub>2</sub>O and methanol and deuterated methanol. Replacing O-H by O-D had a much stronger effect on the life-time than the replacement of C-H by C-D.<sup>75</sup>

Yanagida *et al.*<sup>76</sup>described the NIR luminescence of deuteriated and fluorinated  $\beta$ -diketonate complexes (Figure 1.11a) Their aim was to decrease the number of hydrogen atoms in the ligands as much as possible. They also reported a perfluorinated sulfonylaminate Nd<sup>3+</sup> complex which has no hydrogen or deuterium at all (Figure 1.11b). Its luminescence life-time in acetone is 12.0 µs and in deuterated acetone is 13.0 µs.<sup>77</sup>



Figure.1.11.(a), Deuteriated  $\beta$ -diketonate Nd complex, (b), Perfluorinated sulfonylaminate Nd complex.

#### Fluorescent dye as sensitizer of NIR emission.

For NIR luminescence, the great advantage is the possible use of VIS absorbing antennas for the sensitization of the lanthanides. Other advantages are that inexpensive excitation sources (lamps, diode lasers) and normal glass can be used for substrate handling instead of quartz. Xylenol orange was the first fluorescent dye used as a sensitizer for Nd<sup>3+</sup> and Yb<sup>3+</sup>(Figure1.12).<sup>78</sup>



Figure 1.12. Xylenol orange

The dyes lissamine and texas red are other Nd<sup>3+</sup> sensitizers. Upon complexation with Nd<sup>3+</sup> the fluorescence was quenched and the sensitization of the Nd<sup>3+</sup> was observed.<sup>79</sup> This emission is due to either intersystem crossing by the nearby heavy and paramagnetic lanthanide ions or singlet

energy transfer. Sensitization of Nd<sup>3+</sup> was also reported in dansyl or coumaryl based complexes that are excited by UV light.<sup>80</sup>

One of the most important dyes in biology is fluorescein, which is used as a green fluorescent probe in various applications. The maximum absorption of fluorescein is around 488 nm which makes it suitable for excitation with an argon laser. Eosin and erythrosine are structurally similar dyes. However, they possess heavy atoms (bromine in the case of eosin and iodine in the <sup>81</sup>case of erythrosine) which results in lower fluorescence quantum yields because of enhanced intersystem crossing to the triplet state of the dye. The sensitization of Nd<sup>3+</sup>, Er<sup>3+</sup> and Yb<sup>3+</sup> by fluorexon ( a dye similar to flurorescein)<sup>82</sup> has been reported (Figure1.13). This compound forms 1:1 complexes with lanthanide ions and the fluorescence is mainly due to the intersystem crossing and NIR emission from Nd<sup>3+</sup>, Er<sup>3+</sup>, Yb<sup>3+</sup>. Deoxygenation of the solutions did not enhance the sensitized luminescence, which shows that energy transfer to the lanthanide is fast.



Figure 1.13. Flurexon

A near-infrared luminescent label was made, based on the Yb<sup>3+</sup> ion and a fluorexon derivative (Figure 1.14).<sup>83</sup> The great advantage of using this complex as a label is that visible light can be used as an excitation source, and that the long-lived Yb<sup>3+</sup> luminescence can be distinguished from the auto-fluorescence of biological systems.



Figure 1.14. Flurexon derivative with a coupling moiety

Calix[4]arenes have been functionalized with fluorescein and NIR luminescence, sensitized by the fluorescein moiety was observed for Nd<sup>3+</sup> and Er<sup>3+</sup>.<sup>84</sup>

### Porphyrin based NIR emitters.

Porphyrins, phthalocyanines and texaphyrins are interesting lanthanide complexing compounds (Figure 1.15).<sup>85</sup> Yb<sup>3+</sup> luminescence in porphyrin complexes was first reported in 1976. It was found that the singlet emission is quenched due to enhanced intersystem crossing, intramolecular energy transfer from the singlet excited state to the lanthanide ion, or by intramolecular charge-transfer from the  $\pi$ -system of the porphyrin to the ion.<sup>86</sup>



Figure 1.15. Structures of (a) Porphyrin, (b), Phthalocyanine, (c), Texaphyrine

#### Inorganic sensitizers.

Inorganic antennae can sensitize the emission of lanthanides. Doping of inorganic materials has been achieved by ion implanting or wet chemical synthesis of powders. The sensitization of Nd<sup>3+</sup> by Cr<sup>3+</sup> in YAIO<sub>3</sub> crystals is reported, in which Cr<sup>3+</sup> ion pairs transfer energy to the Nd<sup>3+</sup> ion<sup>87</sup>. Laser action of Nd<sup>3+</sup> in YAG doped with Cr<sup>3+</sup> and Nd<sup>3+</sup> has been reported in which Cr<sup>3+</sup> ion centres are pumped. <sup>88</sup> Polman *et al.*<sup>89</sup> reported silicon nanocrystals as sensitizers for Er<sup>3+</sup> luminescence. Firstly silicon oxide is bombarded with silicon and after annealing at 1100 °C nanoparticles are formed with a

bandgap of about 1.1 eV.<sup>90</sup> Subsequently, Er<sup>3+</sup> ions are implanted and upon excitation of the silicon nanocrystals, Er<sup>3+</sup> luminescence is observed.

## Poly(pyrazolyl)borate ligands

Davies *et al.* <sup>91</sup>studied the near infrared emission of Yb, Nd and Er complexes containing poly(pyrazolyl)borate and 1,3 diketonate ligands. The structures of the ligands they used are shown in Figure 1.16.



Figure 1.16. NIR emitting poly(pyrazolyl)borate ligands

Subhan *et al.* <sup>92</sup> also synthesised chiral NIR-emitting lanthanide complexes using hydrotris(pyrazolyl)borate and pba as an axial ligand ( $pba^- = RS$ -and / orS-2-phenyl butyrate) and they obtained NIR emission from Yb and Er centres.

## 1.3. Luminescence properties of lanthanide complexes blended with conjugated polymers

Much work has been done to understand energy transfer processes in polymers such as saturated polymer backbones with pendant chromophores,<sup>93,94</sup> polymers with main-chain polychromophores<sup>95-97</sup> and fully conjugated polymers.<sup>98-104</sup> But there is an increasing interest in studying the energy transfer processes in conjugated polymers and in the blends of small molecules with conjugated polymers such as poly(phenylene vinylenes),<sup>105</sup> poly(phenylene ethynylenes)<sup>106</sup> and poly(p-phenylenes).<sup>107</sup> Small molecules have also been blended with conjugated polymers in order to tune the electroluminescent emission wavelengths and improve EL device efficiencies.

In these applications, the role of the conjugated polymer is to transport charge and funnel energy to the dopant. This idea has been used by

McGehee *et al.* <sup>108</sup> by blending europium tris- $\beta$ -diketonates in a cyano derivitized poly(p-phenylene) (PPP-CN) and PVK (Figure1.17). The processing of polymers in PLED devices is relatively easy, because thin films can be prepared from solution by spin coating. Using the concept of spectral overlap of the PPP-CN emission with the absorption of the europium complex, they showed that energy transfer from the polymer to the lanthanide occurs.



Europium complex

CN-PPP



Figure 1.17. Structures of the complex and the polymers were McGehee et al, used




Expanding on this idea Harrison *et al*,<sup>109</sup> prepared blends of several complexes of varying concentrations by using a series of visible and near infrared emitting lanthanide tris- $\beta$ -diketonates and monoporphyrinates with alkyl or alkoxy substituted poly(p-phenylenes). In these cases the energy transfer from the polymer to the lanthanide complex is monitored by the quenching of the PPP fluorescence and the resulting sensitization of the lanthanide luminescence by the polymer. The structures of the materials that Harrison *et al*, used are shown in Figure 1.18.

Harrison *et al*,<sup>109</sup> used tris- $\beta$ -diketonates because their absorption properties have some spectral overlap with the fluorescence of the PPP polymers, particularly PPP-R10 and PPP-OR11, the first atom of 10 and 11 atom-long side chain is carbon and oxygen respectively. Therefore energy transfer from polymer to lanthanide complex could occur. In addition,  $\beta$ -diketonates are known to sensitize the emitting states of europium, which emits in the visible region. When Eu(DNM)<sub>3</sub>Bath is blended into the film, the PPP-R10 fluorescence centered at 380 nm decreased and a series of peaks appeared in the 550-700 nm (Eu emission region ). Quenching of the polymer fluorescence and the emergence of the lanthanide emission upon increased lanthanide concentration indicate that the energy transfer from the polymer to the lanthanide is occurring in these polymer blends.

One report deals<sup>110</sup> with the Eu<sup>3+</sup> complex in PVK where the Eu<sup>3+</sup> complex is functionalized with a hole-conducting and an electron-conducting moiety (Figure 1.19). Charge recombination will take place in close proximity to the lanthanide ion, and should lead to efficient lanthanide luminescence.

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Figure 1.19. Hole and electron-transport moiety functionalized Eu<sup>3+</sup> complex Cimrova *et al.* <sup>111</sup>made a polymer and Tb complex blend by using poly(methylphenylsilanediyl) (PMPSi) as polymer and they observed the characteristic emission from the Tb (Figure 1.20).



Figure 1.20. PMPSi-Tb<sup>3+</sup> complex

The incorporation of lanthanide ions into polymeric matrices or sol-gel derived organic-inorganic nanostructured hybrids can improve their thermal stability and mechanical and light emission properties. The major interest in this approach is the possibility of preparing multifunctional nanoscale organic-inorganic frameworks with tunable designs and suitable features. Gatsouli *et* 

*al.*<sup>112</sup> synthesised a series of nanostuctured organic-inorganic hybrid materials based on functional diblock copolymers and Eu<sup>3+</sup> salts, and the polymers used are shown in Figure 1.21.



**Poly(styrene-b-ethylene oxide)** 



Poly(styrene-b-2-vinylpyridine)



Figure 1.21. Structures of functional diblock copolymers

They prepared block polymers by anionic polymerisation and europium nitrate is dispersed completely in a solution of the polymers resulting in a homogeneous solution. The incorporation of europium ions is monitored by the shifting of functional group peaks (eg the shifting of C-O-C stretching vibration peak in Poly(styrene-b-ethylene oxide) in the IR spectrum. These hybrid materials showed strong fluorescence of europium metal ions, suggesting that the copolymers used are suitable matrices for achieving the desired optical performance in the final materials, providing good mechanical stability accompanied by ease of processability.

# 1.3.1.Poly(p-phenylene vinylene) (PPV) and lanthanide complexes

Poly(p-phenylene vinylene) (PPV) and its derivatives are some of the most promising organic materials for LEDs due to the chemical tunability and good processability of the prepolymer<sup>113</sup>.



Figure 1.22. PPV

Upon excitation, PPVs generally fluoresce in the 500-700 nm region giving an orange to red coloured emission. The photoluminescence spectrum of PPV generally matches the electroluminescence spectrum, suggesting that the emitting excited state produced in PPV is the same regardless of the method of excitation. Since the discovery that PPV shows electroluminescence if sandwiched between a hole-injecting contact (In-Sn-oxide) and an electroninjecting contact (Al, Ca), a considerable amount of research has been done to improve the properties of these light-emitting diodes.<sup>114-117</sup> Without any substituents on its backbone, PPV is an insoluble and unprocessable polymer. So most researchers have tried to deposit PPV onto a substrate as a PPV precursor which is soluble in organic solvents and then is converted to PPV upon heating.<sup>118,119</sup> To overcome the need for a precursor some researchers have modified the PPV backbone. Figure 1.23 shows some PPV derivatives and these are soluble in polar organic solvents and used in PLEDs. Chemical modification can also affect the electronic properties of PPV, for example by attaching electron-withdrawing cyano groups to the vinylene bonds of a substituted PPV, a red-emitting polymer (CN-PPV) is obtained which can then be incorporated into an electroluminescent device showing internal quantum efficiency up to 4%.<sup>119</sup> Overall, the use of PPV polymers as active materials has a number of advantages, including versatility of fabrication, flexibility, low cost, low operating voltage and easy colour tuning of their light emission. The drawback of PPV is that the presence of singlet oxygen in the device can break down the linear nature of the polymer, so

these light emitting devices exihibit short life-times in an oxygen atmosphere. Therefore new techniques for improving PLEDs, long term stability against oxygen are needed. One of these techniques might be simply to incorporate the polymers into some inorganic-organic host materials, and the other technique is intercalation.



Figure 1.23. (a) MEH-PPV, (b) CN-PPV

Light emitting diodes based on organic and polymer materials are also interesting because of their extremely high quantum efficiencies in the visible region. Tang *et al.*<sup>120</sup> demonstrated that a diode based on poly(p-phenylene vinylene) PPV as the hole transport layer and with the electron transport layer formed from a solid state dispersion of 2-(4-biphenylenyl))-5-(4-t-butylphenyl)-1,3,4-oxadiazole (butyl PBD) in poly(methyl methacrylate) also has a high quantum efficiency. The luminescent spectra of organic dyes and polymers display broad peaks so they are not suited for actual display applications or the needs of recently-developed micro activity structures in LEDs. In order to obtain brighter and more efficient emissions from a diode with a narrow luminescent bandwidth, the lanthanide complexes might be incorporated into PPV. Chen Li *et al.*,<sup>121</sup> prepared electroluminescent devices

using Tb(acac)<sub>3</sub>Phen as an emitting layer and PPV as a hole-transport layer and Figure 1.24 shows the configuration of the diode.



Figure 1.24 Configuration of a diode

When a DC voltage of 16 V is applied, characteristic emission from Tb is obtained and there is no emission from the PPV. Harrison *et al.* <sup>109</sup> also prepared luminescent devices using MEH-PPV and lanthanide complexes. The main lanthanide complexes used were Yb(DNM)<sub>3</sub>Phen and Yb(TTFA)<sub>3</sub> Phen.

## 1.4. Copolymerisation of the lanthanide complexes

The previous section only described the blending of lanthanide complexes with polymers and this section will describe the copolymerisation of lanthanide complexes. Problems associated with the polymer complexes prepared by the direct reaction of the polymer ligand with the lanthanide ions are that the products usually have an ionic aggregation nature, resulting in weak fluorescence of the polymer luminophores.<sup>122,123</sup> The microscopic environment of rare earth ions is very complicated, which makes the elucidation of the fluorescent properties difficult.<sup>124</sup> For a practical approach it is desirable that the polymer complex yields a true solution and that ionic clusters be absent. The use of pre-functionalised ligands in lanthanide complexes leads to excellent homogeneous fluorescent polymer materials.<sup>125</sup> Ma et al,<sup>126</sup> naphthoate and containing europium-polymer complexes prepared They copolymerised of the prefunctionalised phenanthroline ligands. europium complexes (EuPhen(Nap)<sub>2</sub>AA) with styrene and methymethacrylate monomer and the copolymers obtained are shown in Figure 1.25. The ratio of the Eu complexes to the co-monomers are in the range 1.5-15 wt% and they used AIBN as initiator; the molecular weight of the resulting copolymer was determined by GPC and the europium content in the copolymer was determined by EDTA titration. These copolymers, IR spectra look exactly like polystyrene and PMMA polymers except for some small shifts in the CH vibrations because only very low contents of the Eu complexes are used for polymerisation. In their experiment the emission intensity of Eu<sup>3+</sup> was greatly enhanced upon copolymerisation. The emission intensity of copolymer 2 was about eight times that of the EuPhen(Nap)<sub>2</sub>AA complex under 365 nm excitation. The binding sites for both the copolymer and the Eu complexes are similar. The only difference between the copolymer and complex monomer lies in the fact that in the copolymer the complex molecules are linked to the polymer main chains and uniformly dispersed in the polymer matrices. Under these conditions the mean distance between two Eu<sup>3+</sup> ions may be larger than that of the complex. In copolymers the large distance between two means that all intermolecular energy transfer EuPhen(Nap)<sub>2</sub>AA moieties processes would be slow and, as a result, a much greater part of excitation energy is transferred to  $Eu^{3+}$ .



Copolymer 2

Figure 1.25. Europium containing copolymers

Ling *et al.* <sup>127</sup>synthesised light emitting copolymers of *N*-vinyl carbazole with Eu-4-vinylbenzoate complexes and, in this copolymer, the polyvinyl carbazole moiety will act as a hole transport layer in the electroluminescent devices (Figure 1.26).



Figure 1.26. Europium containing copolymer with hole transport group

Pan *et al.*<sup>128</sup>synthesised another series of copolymers using Eu complexes with styrene monomers and these copolymers showed better thermal stability than polystyrene; the corresponding Eu complex monomer and the characteristic emission from the Eu occurred and the emission intensity is again higher than that of the corresponding Eu complex (Figure 1.27).



Figure 1.27. Europium containing copolymers

### 1.5. Applications of lanthanide complexes

A traditional use of lanthanide complexes is as NMR shift reagents. Shift reagents are used in NMR spectroscopy to reduce the equivalence of nuclei by altering their magnetic moment either by bond formation or by magnetic effects of unpaired electrons. Paramagnetic transition metal complexes can be active with both mechanisms, but usually cause line broadening which affects the overall quality of the NMR spectrum.<sup>129</sup> Typical lanthanide complexes used as shift reagents are tris  $\beta$ -diketonates with bulky substituents to restrict mobility of the complex. The most active ligands are fluorinated, which increases the Lewis acidity of the central metal, improves the solubility of the complex, and hence allows for higher concentrations. A complex with higher shifting power is  $Eu(fod)_3$  (fod=1,1,1,2,2,2,3,3heptafluoro-7,7-dimethyloctane-4,6 dionato).<sup>130</sup> Lanthanide complexes can be used in magnetic resonance imaging (MRI). MRI produces two-dimensional images of internal organs of tissues, depending on a gradient of water concentration and relaxation time of H<sub>2</sub>O protons.<sup>131</sup> To alter the relaxation better sensitivity and resolution for tissue time. thus generating charecterisation, MRI contrast agents are used. They change either the longitudinal relaxation time  $T_1$  or the transverse relaxation time  $T_2$ . Positive contrast agents, such as  $Mn^{2+}$  or  $Gd^{3+}$  complexes, generate high T<sub>1</sub> values and negative contrast agents such as ion oxide nanoparticles shorten  $T_2$ . Most commonly used are Gd<sup>3+</sup> complexes.<sup>132</sup> They have to be soluble in aqueous solutions and kinetically stable to avoid poisoning. A widely used MRI contrast agent is [Gd DOTA] shown in Figure 1.28.



Figure 1.28. Widley used MRI agent Gd [DOTA]<sup>-</sup>

Asymmetric catalysis of organic reactions using lanthanide complexes started in the early 1990s. In contrast to transition metal complexes, lanthanide complexes are generally very labile in terms of stereochemical rigidity and the isolation of enantiomerically pure complexes, that retain their stereochemistry in solution, usually require the use of chiral ligands (Figure 1.29).<sup>133</sup> High coordination numbers are advantageous for organic catalysis. Lanthanide complexes with C<sub>2</sub> and C<sub>3</sub> symmetry are now widely used in industry and academia as low cost, low toxicity, Lewis acidic coordination reagents for catalysis.<sup>134,135</sup>



X= CI, OTf.

Figure 1.29. Chiral lanthanide complex

Complexes of Tb<sup>3+</sup> and Eu<sup>3+</sup> are highly luminescent and typically exhibit emission life times in the millisecond range. These long life times help to distinguish biomolecules labelled with lanthanides from the short-lived

background emission of biosystems.<sup>136</sup> This strategy is known as Time-Resolved Fluorescence and it has been commercially exploited in the field of Fluoroimmunoassay (TR-FIA).<sup>137</sup> Lanthanide complexes with appropriate functional groups in the ligand can be used as precursors of covalent linkers to biomolecules and have proven useful as highly luminescent probes in immunoassays. The binding of ligands to the lanthanide ion is evidenced by the strong emission displayed by the conjugated proteins in biological media. The sensitive detection of single-stranded regions of DNA, including mutations and mismatches, is critical in nucleic acid hybridization assays with applications including the determination of genetic diseases. Luminescence enhancement of a given probe in the presence of nucleic acids or other targeted biomolecules can in principle yield such detection, with marked safety and environmental advantages over radioactive labelling.<sup>138</sup>

### 1.6. Conclusion

The broad family of 4f elements shares quite remarkable physical and chemical properties. Enclosed in an organic molecular structure with a so called sensitizer or antenna, they may easily receive energy which is released as photons with quite characteristic spectra, comparatively independent of the co-ligands and the environment. The emission wavelengths range from the visible to the near-IR, depending on the lanthanide ion. The complex energy transfer process starting from the absorption by organic antenna and ending with the emissions for lanthanides are rather long, in the millisecond range. The luminescence intensities of the lanthanides are good in the polymer blends and in a copolymerisation matrix. Also these lanthanide complexes are widely used in LEDs.

For this introduction chapter the aim of the project could be outlined by the following synthetic route (Figure 1.30).The first step is the synthesis of lanthanide complexes using polyhydrotris(pyrazolyl) borate ligands and either cinnamic acid or crotonic acid as co-ligands followed by study of the luminescence properties of these lanthanide complexes. This mainly concentrates on their emission properties as well as luminescence life times. These lanthanide complexes have polymerisable double bonds and those bonds will help to achieve copolymerisation of these complexes with either

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styrene or methylmethacrylate monomers. Either these complexes or the copolymer might be blended with PPV precursor to check the energy transfer and luminescence properties between the PPV precursor and the lanthanide complexes, especially for Eu and Tb complexes because they are very good visible emitters. Polymerisation of PPV precursor into PPV can be achieved by heating. The aim could be extended to study the luminescence properties of lanthanide complexes using substituted poly(pyrazolyl)borate ligands and this is described in Chapter 2.





 $C_6H_5$ 





Tp.

C<sub>6</sub>H<sub>5</sub>

-R

 $C_6H_5$ 



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# **Chapter 2**

Synthesis of lanthanide complexes and their structural studies

This chapter describes the synthesis of lanthanide complexes mainly of sodium hydrotris(pyrazolyl)borate (NaTp) with crotonic acid or cinnamic acid. Some yttrium (Y) analogues were studied for comparison. Also some lanthanide complexes using substituted (pyrazolyl)borate ligands were synthesised

The lanthanide chlorides were synthesised by the digestion of lanthanide oxide with the minimum quantity of hot concentrated hydrochloric acid,  $LnCl_3.nH_2O$  crystals (Ln = La, Ce. n = 7: Ln = Pr, Nd, Sm-Lu, n = 6) being isolated from the solution by cooling and gentle vaccum desiccation (Scheme 2.1).

 $Ln_2O_3 + HCl \longrightarrow LnCl_3 \cdot nH_2O$ 



Sodium hydrotris(pyrazolyl)borate (NaTp) was prepared according to the literature.<sup>1</sup> Scheme 2.2 represents the synthetic method for NaTp. An IR band at 2440 cm<sup>-1</sup> confirmed the B-H peak in sodium hydrotris(pyazolyl)borate (Figure 2.1).



Scheme 2.2. Synthesis of NaTp



Figure. 2.1 IR spectrum of NaTp in its synthesis melt

### 2.1. Synthesis and discussion of lanthanide complexes

#### 2.1.1. Heteroleptic lanthanide hydrotris(pyrazolyl)borate crotonate complexes (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Tm, Lu, Y)

The ligand solution (A) is prepared as follows. Crotonic acid is neutralised completely with dilute KOH solution (pH meter) and NaTp added. The mixture is transferred quantitatively to a 250 ml volumetric flask and dissolved in water, by shaking and making the solution up to the mark. Solution A is used within 6 hours. In a typical procedure SmCl<sub>3</sub>.6H<sub>2</sub>O is dissolved in distilled water and the correct amount of solution A titrated directly into this solution from a micro-burette so as to afford a ratio of NaTp: Ln: Crotonic acid of 2:1:1 (Figure 2.2).



Figure 2.2. Synthesis of crotonate complexes

The solid obtained is dried and extracted with dichloromethane. A few drops of hexane are floated on this extract, and the solution allowed to evaporate slowly. Using this method the yield of dichloromethane soluble materials appeared to rise steadily as the lanthanide series is traversed. Yields for the early lanthanides were very low, and the IR spectrum for La-Ce was obtained by allowing some of the dichloromethane solution of the product, prior to crystallisation, to evaporate on NaCl plates. In the case of La, the yield was so low so that not even this method allowed a meaningful spectrum to be recorded. In the case of Ln = Pr-Dy increasing quantities of dichloromethane soluble materials were obtained as powdery or microcrystalline solids. IR spectra of all the new complexes were recorded as KBr discs. The IR spectra of the new complexes all exhibit bands consistent with the presence of the ligand HB(pz)<sub>3</sub> including the B-H peak in the range 2440- 2452 cm<sup>-1</sup>. A band in the range 1661-1655 cm<sup>-1</sup> is attributed to the carbonyl group of the crotonate ligand. This shows a bathochromic shift of 18 cm<sup>-1</sup> compared to the value found in free crotonic acid. A summary of the IR data is shown in Table 2.1. In the cases of Dy and Ho, the solid state spectra contain two bands in the region 2453-2454 cm<sup>-1</sup> and 2494 cm<sup>-1</sup> indicating the likely presence of two products.<sup>2</sup>



Figure 2.3. IR spectra of (a), crotonic acid, (b), [Tp<sub>2</sub>Er(crot)] (c), [Tp<sub>2</sub>Ho(crot)]

Indeed in the case of Ho, two visibly different morphological types resulted on evaporation of the dichloromethane extract. The first of these to form was crystalline, it being followed by a globular microcrystalline mass arising from a more concentrated solution. The crystalline form was analysed by single X-ray crystal diffraction techniques and was found to be  $[TpHo(crot)_2]_2$ , which indicated that the formulation of  $[TpLn(crot)_2]_2$  be assigned to the products of the bigger lanthanides. Subban *et al.*<sup>3</sup> prepared the mononuclear  $[Tp_2Ln(S-or RS-pba]$  (Ln = Er, Tm,Yb) using a molar ratio 1:2:1 (Ln:Tp:pba). The same ratio gave dimeric complexes  $[(Tp)_2Ln_2(S-orRS-pba)_4]$  for Nd-Dy instead of the monomer ones.

Ln	υ <sub>B-H (cm</sub> -1)	ບ <sub>C=O (cm</sub> -1)		
		(asym)	(sym)	
La	-	-	<u> </u>	
Се	2451	1661	1541	
Pr	2452	1660	1541	
Nd	2442	1660	1559	
Sm	2447	1657	1571	
Eu	2450	1657	1573	
Gd	2451	1658	1575	
Tb	2452	1659	1575	
Dy	2453/2494	1657	1573	
Но	2454/2494	1655	1574	
Er	2475	1656	1572	
Tm	2475	1665	1574	
Yb	2475	1655	1574	
Lu	2475	1655	1573	
Y	2475	1655	1572	
		·		

Table 2.1. IR data for lanthanide crotonate complexes [Tp2Ln(crot)]

In the case of the complexes, the larger lanthanides form dinuclear complexes according to equation 1 and the smaller lanthanides form mononuclear complexes according to equation 2.

 $[Ln(H_2O)_n]^{3+} + 2Tp^- + crot^- \longrightarrow [Ln_2(crot)_4(Tp_2)] + [Ln(Tp)_3] + nH_2O$ Equation 1. Formation of dinuclear complexes

 $[Ln(H_2O)_n]^{3+} + 2Tp^- + crot^- \longrightarrow [Tp_2Ln(crot)] + nH_2O$ Equation 2. Formation of mononuclear complexes

With erbium, the product possessed an identical IR spectrum to the globular product from the Ho synthesis, but is also crystalline. Its crystal structure was found to be mononuclear [Tp<sub>2</sub>Er(crot)] suggesting an analogous formulation to the later congeners. The IR spectra of these crotonate complexes fell into two corresponding categories. In keeping with this, electron impact MS spectra are almost fully assigned for [LnTp<sub>2</sub>(crot)] analogues Dy-Yb, showing predictable fragments in all cases. These typically arise from loss of {crot} or pyrazole {pz}, both sequences converging at  ${Ln(pz)_2}^+$ ; a summary is provided in Table 2.2. The spectra for Sm and Tb were consistent with the involatile [TpLn(crot)<sub>2</sub>]<sub>2</sub> being present in bulk, contaminated with traces of the more volatile product [Tp<sub>2</sub>Ln(crot)]; this situation has been seen before in the spectrum of [TpEu(μ-PhCOO)<sub>4</sub>EuTp], reported to contain peak а corresponding to  ${Tp_2Eu(H_2O)}^+$  4,5 which might arise from traces of [Tp2Eu(PhCOO)]. Earlier lanthanides failed to provide meaningful mass spectra.

ak in₀	M⁺	{M-pz}⁺	{Tp₂Ln}⁺	{TpLn(crot)}⁺	{TpLn(pz)}⁺	{TpLn}⁺	{Ln(pz)₃H} <sup>+</sup>	{Ln(pz)₂}⁺
	663(33)	-	574(87)	447(66)	434(100)	-	354(30)	286(94)
	749(34) <sub>d</sub>	603(32)	533(100) <sub>e</sub>	682(32) <sub>f</sub>	439(42)	618(30) <sub>g</sub>	228(38)	293(56)
	675(1)	608(1)	587(15)	459(9)	442(100)	375(18)	366(8)	298(25)
	676(3)	609(14)	591(100)	463(18)	445(66)	378(11)	367(14)	299(47)
	678(7)	610(12)	592(100)	464(19)	446(53)	378(10)	370(3)	300(26)
 I	680(2)	613(10)	595(78)	467(48)	449(97)	381(20)	371(9)	303(100)
	683(21)	616(27)	598(43)	471(52)	453(100)	385(59)	376(37)	306(50)

#### Table 2.2.Electron impact cation MS data<sup>a</sup> for [Tp<sub>2</sub>Ln(crot)].

<sup>a</sup>Data are quoted relative to the base peak and numbers in parentheses are the relative intensities of the ion. <sup>b</sup> Peaks were attributed as correct if they allowed for isotopic variation and proton loss/capture. All Ln-containing peaks bore their parent metals isotopic profiles. <sup>o</sup>Weak & noisy spectrum with some unassigned peaks. <sup>d</sup>[TpTb<sub>2</sub>(crot)(pz)<sub>2</sub>-H]<sup>+</sup>, <sup>e</sup>Tb(pz)<sub>3</sub>(crot)<sub>2</sub>H<sub>3</sub><sup>+</sup>, <sup>f</sup>[TpTb<sub>2</sub>(crot)pz-H]<sup>+</sup>, <sup>g</sup>Tb<sub>2</sub>Tp(crot)H<sub>2</sub><sup>+</sup>, <sup>h</sup>Tb(pz)<sup>+</sup>

The <sup>1</sup>H NMR data of new crotonate complexes [Tp<sub>2</sub>Ln(crot)] (Ln = Nd, Sm, Eu, Dy, Er, Ho, Yb, Lu, Y) are presented in Table 2.3. The spectra of complexes containing the diamagnetic ions yttrium and lutetium are essentially identical. The other lanthanide ions give rise to proton resonances which are subjected to paramagnetic shifts.<sup>6</sup> Coupling is unresolved in the spectra of the complexes containing the paramagnetic lanthanide ions. All of the spectra contain only three pyrazolyl proton resonances, each integrating for six protons; where coupling is resolved, these three resonances appear as two doublets and a triplet with coupling constant *J* (H-H) = 2 Hz. The crotonic acid protons appear as three signals of relative area 3:1:1 and three signals

	pz resonances (δ ppm)			crot resonances ( $\delta$ ppm)			
Intensity	6	6	6	3	1	1	
Sm	7.96(s)	4.25(s)	3.68(s)	10.1(s)	37.7(s)	76.4(s)	
Eu	10.26(s)	3.23(s)	2.64(s)	-18.0(s)	-21.5(s)	90.21(s)	
Dy	-18.5(br)	-2.35(br)	-42.15(br)	-8.2(s)	-7.33(s)	-21.4(s)	
Но	0.42(s)	0.53(s)	-28.28(br)	42.8(br)	-67.9(s)	-121.3(s)	
Er	33.23(br)	-10.87(s)	-47.18(br)	-1.12(s)	-27.3(s)	-57.9(s)	
Yb	10.0(s)	9.6(s)	5.6(s)	-47.9(br)	-32.9(br)	-18.1(s)	
Y	7.63(d)	7.05(d)	5.96(t)	1.86(d)	6.5(qd)	5.7(d)	
Lu	7.62(d)	6.99(d)	5.95(t)	1.87(d)	6.9(qd)	5.9(d)	
Nd	1.13(s)	3.25(br)	-5.76(s)	42.1(s)	10.2(br)	18.8(br)	

appear as doublet, quadruplet doublet and doublet respectively in the diamagnetic complexes.

Table 2.3.<sup>1</sup>H NMR spectra of [Tp<sub>2</sub>Ln(crot)] complexes<sup>a</sup>

<sup>a</sup> In CDCl<sub>3</sub> solution and run in a 400MHz instrument. s = singlet, d = doublet, t = triplet qd = quadruplet doublet

The elemental analyses of powder forms of these new crotonate complexes  $[Tp_2Ln(crot)]$  (Ln = Nd, Sm, Eu, Dy, Er, Ho, Tb, Lu) and crystal forms for  $[Tp_2Ho(crot)]$ ,  $[Tp_2Er(crot)]$  complexes are shown in Table 2.4. In general the powdery products seem to be  $[Tp_2Ln(crot)]$ , but in the crystal form, the Ho complex is dinuclear  $[TpHo(crot)_2]_2$  in nature and the Er complex is mononuclear,  $[Tp_2Er(crot)]$  and the division of IR spectra into two categories suggests that dinuclear  $[TpLn(crot)_2]_2$  are favoured for the early lanthanides Ce-Ho, but with increasing quantities of  $[Tp_2Ln(crot)]$  being formed. Thereafter, for Er-Lu, the monomeric  $[Tp_2Ln(crot)]$  complexes predominate.

Complex		Н	С	Ν
$C_{22}H_{25}B_2N_{12}O_2Er$	%Theory	3.68	38.93	24.71
powder	% observed	3.65	38.89	24.78
C <sub>22</sub> H <sub>25</sub> B <sub>2</sub> N <sub>12</sub> O <sub>2</sub> Er crystal	% Theory	3.68	38.93	24.71
	% observed	3.69	38.58	24.75
$C_{22}H_{25}B_2N_{12}O_2Ho$	% Theory	3.69	39.05	24.85
powder	% observed	3.62	38.87	24.69
C <sub>34</sub> H <sub>40</sub> B <sub>2</sub> N <sub>12</sub> O <sub>8</sub> Ho <sub>q</sub> crystal	% Theory	3.63	37.27	15.32
	% observed	3.66	37.16	15.17
$C_{22}H_{25}B_2N_{12}O_2Nd$	% Theory	3.81	40.29	25.63
powder	% observed	3.69	39.31	25.33
0.11.0.1.0.5		9 77	20.92	25.24
$C_{22}H_{25}B_2N_{12}O_2Eu$	% Theory	3.11	39.82 38.79	25.34 22.93
powder	% observed	3.59		-
$C_{22}H_{25}B_2N_{12}O_2Sm$	% Theory	3.78	39.91	25.40
powder	% observed	3.66	38.23	23.32
$C_{22}H_{25}B_2N_{12}O_2Tb$	% Theory	3.73	39.40	25.07
powder	% observed	3.59	38.87	24.23
$C_{22}H_{25}B_2N_{12}O_2Dy$	% Theory	3.71	39.19	24.90
powder	% observed	3.50	38.27	23.76
C <sub>22</sub> H <sub>25</sub> B <sub>2</sub> N <sub>12</sub> O <sub>2</sub> Lu	% Theory	3.64	38.48	24.49
powder	% observed	3.61	37.24	21.32

Table 2.4. Elemental analyses for [Tp2Ln(crot)] complexes

# 2.1.2. Heteroleptic lanthanide hydrotrispyrazolyl borate cinnamate complexes

Cinnamate complexes were prepared by the same method as the crotonate complexes.



Figure 2.4. Synthesis of cinnamate complexes

Yields of all these cinnamate complexes are very low. IR spectra of all the complexes were recorded as KBr discs. A band could be seen in the range 1646-1638 cm<sup>-1</sup> and is attributed to the carbonyl group of the cinnamic acid ligand. This shows a bathochromic shift of 52 cm<sup>-1</sup> compared to the value found in free cinnamic acid; The IR data summary is shown in Table 2.5.

Ln	<sup>-1</sup> <sup>-1</sup> <sup>-1</sup>	υ <sub>C=0 (cm</sub> <sup>-1</sup> )
		(asym) (sym)
La	-	-
Се	2467	1645 1572
Pr	2467	1645 1572
Nd	2468	1643 1574
Sm	2467	1642 1571
Eu	2462	1636 1573
Gd	2468	1644 1575
Tb	2465	1643 1575
Dy	2464	1644 1573
Но	2469	1646 1572
Er	2469	1646 1574
Tm	2463	1644 1572
Yb	2462	1638 1572
Lu	2463	1636 1571
Y	2462	1643 1573

Table 2.5. IR data for lanthanide cinnamate complexes [Tp2Ln(cin)]



Figure 2.5. IR spectra of (a), cinnamic acid, (b), [Tp<sub>2</sub>Eu(cin)], (c), NaTp

The IR spectra of the cinnamate series shows the same pattern of B-H peak absorption for bigger lanthanides as well as smaller lanthanides. Infact the IR spectra of the cinnamate series were very similar. The cinnamate complexes did not afford crystals when crystallisation was attempted from DCM-hexane mixtures. Complexes of larger lanthanides, La-Pr are poorly soluble in DCM. For the smaller lanthanides the crude complexes were dissolved in DCM (4 cm<sup>3</sup>) and the resulting solution filtered into a small tube, which was lowered into a large sample tube containing n-hexane (14 cm<sup>3</sup>) and a cap is placed on this tube.<sup>7</sup> After two weeks crystals of the Er and Ho cinnamate complexes (Figure 2.6) were obtained.







Figure 2.7. IR spectrum of (a), [TpHo(cin)<sub>2</sub>]<sub>2</sub>, (b), [Tp<sub>2</sub>Er(cin)]

The <sup>1</sup>H NMR spectra of the diamagnetic cinnamate complexes  $Y^{3+}$  or  $Lu^{3+}$  complexes contain three signals, each of relative area 6, attributable to the pyrazolyl protons of the Tp<sup>-</sup> ligands. These appear as two doublets and one triplet. The spectra also contain five signals which are attributable to the aryl protons and CH protons of the cinnamate ligand. The spectra of the remaining paramagnetic complexes contain three signals, each of relative area 6, attributable to the pyrazolyl protons of the Tp<sup>-</sup> ligand but these signals are paramagnetically shifted and the coupling is lost so that they appear as singlets. The spectra of the paramagnetic complexes also contain five signals attributable to the protons present in the aryl group and alkenyl protons of the cinnamate ligand, as shown in Table 2.6.

	pz resor	nances (δ	ppm)	cin resonances (δ ppm)		
Intensity	6	6	6	Ar 2 2 1	1	1
Dy	18.6(br)	-5.8(br)	3.71(br)	-10.15(s) -5.67(s)-1.15(s)	-44.4(s)	-11.2(s)
Eu	3.2(s)	3.08(s)	2.60(s)	-8.53(s) -4.15(s) -8.01(s)	-22.2(s)	-10.3(s)
Yb	2.84(br)	8.27(br)	8.53(s)	-4.89(s) -7.97(s)-5.8(s)	-18.65(s)	11.5(s)
Lu	7.62(d)	6.97(d)	5.95(t)	7.53(m) 7.94(m) 7.43(dd)	6.5(d)	7.71(d)
Y	7.62(d)	7.05(d)	5.97(t)	749(m) 7.89(m) 7.38(dd)	6.34(d)	7.69(d)

Table 2.6. <sup>1</sup>H NMR spectra of [Tp<sub>2</sub>Ln(cin)] complexes<sup>a</sup>

<sup>a</sup> In CDCl<sub>3</sub> solution and run in a 400MHz instrument. s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublets of doublet

Elemental analyses (C, H, N) of these cinnamate complexes in their initial powdery forms show that they correspond to the formulation  $[Tp_2Ln(cin)]$ , and these seem to be formed across the whole latter part of the lanthanide series. Interestingly, as is seen for the crotonate analogues, the crystalline material formed in the case of Ho corresponds to the dinuclear  $[TpHo(cin)_2]_2$ , whilst the crystals for Er are mononuclear  $[Tp_2Er(cin)]$  (Table 2.7).

Complex		Н	С	Ν
$C_{27}H_{27}B_2N_{12}O_2Er$	%Theory	3.64	43.78	22.71
powder	% Observed	3.65	42.17	21.87
$C_{27}H_{27}B_2N_{12}O_2Er$	% Theory	3.64	43.78	22.71
crystal	% Observed	3.57	43.07	21.35
$C_{27}H_{27}B_2N_{12}O_2HO$	% Theory	3.66	44.02	22.82
powder	% Observed	3.62	41.98	21.32
C <sub>54</sub> H <sub>48</sub> B <sub>2</sub> N <sub>12</sub> O <sub>8</sub> Ho	% Theory	3.57	48.21	12.46
crystal	% Observed	3.57	47.04	11.52
$C_{27}H_{27}B_2N_{12}O_2Sm$	% Theory	3.74	44.9	23.30
powder	% Observed	3.68	44.83	22.76
$C_{27}H_{27}B_2N_{12}O_2Eu$	% Theory	3.73	44.81	23.23
powder	% Observed	3.64	43.87	22.69
$C_{27}H_{27}B_2N_{12}O_2Tb$	% Theory	3.69	44.38	23.01
powder	% Observed	3.59	43.98	22.92
$C_{27}H_{27}B_2N_{12}O_2Yb$	% Theory	3.63	43.60	22.61
powder	% Observed	3.45	43.38	21.85

Toble 2.7	' Elomontal	analysis	of ITn. I r	o(cin)] (	romnlaves
Table 2.7	. Clemental	anaiyəiə			complexes

The mass spectra of these cinnamate complexes were obtained and are generally quite similar. The molecular ion [TpLn(cin)<sub>2</sub>]<sub>2</sub> is not seen in the mass spectra (which may be a result of its relative involatility) so it is not possible to distinguish the structural types of complex on the basis of MS data. Additionally similarities between the IR spectra of all cinnamate complexes mean that there are difficulties in distinguishing the structural types using any spectroscopic method other than single X-ray diffraction. Mass spectra data are shown in Table 2.8.
Peak orgin	M⁺	{M-pz}*	{Tp₂Ln}⁺	{TpLn(cin)}*	{TpLn(pz)}*	{TpLn}*	{Ln(pz) <sub>3</sub> H}*	{Ln(pz) <sub>2</sub> }*
Sm	723(33)	656(10)	578(87)	512(66)	434(90)	-	354(30)	286(90)
Eu	725(45)	658(18)	580(87)	514(53)	436(97)	365	356(51)	288(95)
Tb	732(10)	665(18)	587(75)	521(18)	443(90)	372(22)	363(10)	295(90)
Dy	735(6)	668(4)	587(75)	521(9)	442(85)	375(18)	366(8)	298(85)
Но	738(6)	671(10)	591(100)	525(18)	445(86)	378(11)	367(14)	299(87)
Er	740(7)	673(12)	592(94)	526(19)	446(73)	378(10)	370(3)	300(79)
Tm	742(7)	675(10)	595(90)	529(48)	449(87)	381(20)	371(9)	303(87)
Yb	745(21)	678(18)	598(84)	535(52)	453(80)	385(59)	376(37)	306(70)

Table 2.8. Electron impact cation MS data for [Tp2Ln(cin)]

### 2.2. Thermal properties of lanthanide crotonate [Tp<sub>2</sub>Ln(crot)] and cinnamate [Tp<sub>2</sub>Ln(cin)] complexes

All cinnamate and crotonate complexes show good thermal stability. These complexes exhibited no distinct melting points and started to decompose or charred at temperatures greater than 510 °C making vapour deposition of these complexes difficult. Thermal gravimetrical analysis (TGA) of europium and terbium cinnamate and crotonate complexes shows their thermal stability. Only 40% mass of these complexes were lost when the temperature reached 420 °C (Figure 2.8.)





Figure 2.8.TGA graph of[Tp<sub>2</sub>Ln(crot)] complexes Ln = Eu,Tb.

### 2.3. Synthesis of the lanthanide crotonate and cinnamate complexes using substituted poly(pyrazolyl)borate complexes

Eu and Tb crotonate and cinnamate complexes were synthesised using the substituted poly(pyrazolyl)borate ligands shown in Figure 2.9.

The general synthesis of these substituted complexes is as follows (Figure 2.10).<sup>1</sup>



Figure 2.9. Structures of substituted Tp ligands



Figure 2.10. Synthesis of lanthanide complexes using substituted Tp ligands

Due to limited quantities of these ligands, synthesis was limited to Eu and Tb complexes because these metals show good visible emission; Tb shows green emission and Eu shows red emission.

# 2.3.1.Synthesis of Eu and Tb crotonate complexes using substituted Tp ligands

The complex  $[(Tp-sub)_2Ln(crot)]$  (Ln = Eu, Tb) is prepared from methanol solution containing a 1:2:1 mixture of hydrated lanthanide chloride, the sodium salt of substituted Tp and crotonic acid. The crude precipitates were obtained in very low yield. After drying *in vacuo* the crude products are dissolved readily in dichloromethane and are slowly evaporate to get a powder of these complexes. Recrystalisation from DCM-hexane mixture failed to afford crystals. The synthetic scheme is shown in Figure 2.11.



Figure 2.11 Synthesis of crotonate complexes by Tp-sub

The solid state IR spectra of these complexes contain v(BH) at 2451 cm<sup>-1</sup>, v(C=O) at 1571 cm<sup>-1</sup> plus other bands characteristic of the substituted Tp ligand. Elemental analyses of these substituted Tp europium crotonate complexes suggested that the substituted complexes might be in the mononuclear form with molecular formulae [(Tp-sub)<sub>2</sub>Eu(crot)]. Mass spectra of the new substituted complexes generally contained a base peak attributable to pyrazolyl m/z=66 and the second most intense fragment correspond to {(Tp-sub)Ln}<sup>+</sup> formed by the loss of crotonate ligand. Further fragment ions listed in order of decreasing intensity are found to be {crot}<sup>+</sup>, {(pz-sub)Ln}<sup>+</sup> and {(pz-sub)<sub>2</sub>Ln}<sup>+</sup>. In case of [(Tp-Ar-OMe)<sub>2</sub>Eu(crot)] the base peak fragment M<sup>+</sup>=683 corresponds to {(Tp-Ar-OMe) Eu}<sup>+</sup>. The base

peak  $M^+= 611$  corresponds to {(Tp-thiophene)Eu}<sup>+</sup> and base peaks  $M^+= 635$ , 593 correspond to the molecular ions {(Tp-Ar-Me)Eu}<sup>+</sup>, {(Tp-Ar)Eu}<sup>+</sup> respectively. The Tb crotonate complexes with substituted Tp ligands also show similar sorts of ion fragments as do the europium complexes. Elemental analyses are included in the experimental section. Paramagnetic shift and broadening effects led to poorly resolved <sup>1</sup>H NMR spectra and it is difficult to interpret the spectra fully.

## 2.3.2. Synthesis of Eu and Tb cinnamate complexes using substituted Tp ligands

The complexes  $[(Tp-sub)_2Ln(cin)]$  (Ln = Eu, Tb) were prepared from a methanol solution containing a 1:2:1 mixture of hydrated lanthanide chloride, the sodium salt of substituted Tp and cinnamic acid (Figure 2.12). The crude products were obtained in essentially quantitative yield and, after drying in vacuum, the crude products dissolved readily in DCM and slow evaporation gave the complexes as powders.



Figure 2.12. Synthesis of cinnamate complexes with Tp-sub

The IR spectra of the new complexes all exhibit bands consistent with the presence of the substituted Tp ligand including  $v_{BH}$  at 2456 cm<sup>-1</sup>(Figure 2.13.) Elemental analysis of these europium and terbium cinnamate complexes suggested that the complexes are in mononuclear form with a molecular formula of [(Tp-sub)<sub>2</sub>Ln (cin)]. Elemental analyses are included in the experimental section. Paramagnetic shift and broadening effects led to poorly

resolved spectra and it is difficult to analyse the spectra so as to attribute each resonance unambiguously.



Figure 2.13. IR spectrum of [(Tp-thiophene)<sub>2</sub>Eu(cin)]

Mass spectra of all these substituted complexes show ions corresponding to  $\{(cin)\}^+$ ,  $\{(Tp-sub)Eu\}^+$ ,  $\{(Tp-sub)\}^+$  and a summary of the mass spectra data is shown in Table 2.9.

Complex	{(Tp-sub) -Ln-}* / M/Z	{(Tp-sub)}* / M/Z
[(Tp-Ar-OMe) <sub>2</sub> Eu (cin)]	683	531
[(Tp-Ar-OMe)2Tb (cin)]	690	531
[(Tp-thiophene)2Eu (cin)]	611	459
[(Tp-thiophene)2Tb (cin)]	619	459
[(Tp-Ar-Me) <sub>2</sub> Eu (cin)]	635	483
[(Tp-Ar-Me) <sub>2</sub> Tb (cin)]	652	483
[(Tp-Ar)₂Eu (cin)]	593	441
[(Tp-Ar) <sub>2</sub> Tb (cin)]	600	441

Table 2.9 Mass spectral data for [(Tp-sub)<sub>2</sub>Ln(cin)] (Ln = Eu, Tb)

### 2.4. Crystal structure studies of erbium and holmium hydrotris(pyrazolyl)borate crotonate complexes and holmium hydrotris(pyrazolyl)borate crotonate cinnamate complex

#### 2.4.1. Erbium and holmium crotonate complexes [Tp<sub>2</sub>Ln(crot)] (Ln = Er, Ho)

A crystalline sample of [Tp<sub>2</sub> Er(crot)] was analysed by single-crystal diffraction methods, as summarised in Table 2.10. The data quality is good and the discrepancy indices low, the structure being monomeric and 8-coordinate, with a ligand orientation analogous to some established precedents<sup>8-12</sup> such as [Tp<sub>2</sub>Tb(O=NC<sub>5</sub>H<sub>4</sub>-2-CO<sub>2</sub>)],<sup>13</sup> [Tp<sub>2</sub>Gd(1,2-O<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>-3,5-<sup>t</sup>Bu<sub>2</sub>)],<sup>14</sup> [Tp<sub>2</sub>Yb(µ- $C_2O_4)Co(acac)_2]$ ,<sup>15</sup> [{TpTb( $\mu$ -N<sub>3</sub>)}<sub>4</sub>],<sup>16</sup> [Tp<sub>2</sub>NdCl(H<sub>2</sub>O)],<sup>17</sup> or [Tp<sub>2</sub>Ln(O<sub>2</sub>C<sub>7</sub>H<sub>5</sub>)] (Ln = Ho, <sup>18</sup> Yb<sup>19</sup>). The structure is depicted in Figure 2.14 with numbering analogous to that in [Tp<sub>2</sub>Tb(O=NC<sub>5</sub>H<sub>4</sub>-2-CO<sub>2</sub>)].<sup>20</sup> The two Tp ligands are oriented so as to be related by an approximate C<sub>2</sub> molecular symmetry. This orientation can be seen as originating from a bicapped trigonal prismatic coordination geometry (pseudo-mirror-symmetry of coordination vertices), a further twisting of Tp ligands ultimately resulting in a dodecahedral coordination geometry - as can be derived from Figure 2.14 by envisaging two ensuing planes defined by N31-O1-O2-N51 and N11-N21-N41-N61. The geometry in [Tp2Er(crot)] is thus describable as being intermediate between bicapped trigonal prismatic and dodecahedral. The crotonate ligand distinctly twists somewhat towards one Tp ligand; there furthermore appears to be some slight disorder in the crotonate ligand, which may have a causal association with an exomolecular peak of high electron density, the disorder and the peak both occurring at about 22% occupancy when the peak is modelled as O (of water, for example).

	[Tp <sub>2</sub> Er(crot)]		[Tp <sub>2</sub> Er(crot)]
М	2731.28	Crystal habit	block
System	Monoclinic	T/K	120
Space group (no.)	P21/c (14)	µ/mm <sup>-1</sup>	3.10
Z	4	ρ/g cm <sup>-3</sup>	1.652
a/Å	12.8925(2)	Data measured	30360
b/Å	15.0406(2)	Unique data	6533
c/Å	14.2342(2)	R <sub>int</sub> (%)	3.08
βl°	95.9162(9)	<i>R</i> σ(%)	2.41
V/Å <sup>3</sup>	2745.46(7)	$R[l > 2\sigma(l)](\%)$	2.43
Crystal size/mm <sup>3</sup>	0.65×0.5×0.4	wR <sub>2</sub> (all data)(%)	5.59
the second se			

Table 2.10 Crystal data summary for [Tp<sub>2</sub>Er(crot)]



Figure 2.14. A view of  $[Tp_2Er(crot)]$ , showing only the major delocalisation site of the crotonate ligand and omitting the exomolecular O3 atom. For clarity all H atoms are omitted and not all remaining atoms are labelled, but the labelling system is consistent for each ligand. Thermal ellipsoids are at the 50% level.

### Chapter 2. Synthesis of lanthanide complexes and their structural studies

Single crystal X-ray diffraction of  $[TpHo(crot)_2]_2$  confirmed its dinuclear formulation. It crystallises in the centrosymmetric orthorhombic space group *Pccn* and its crystal details are shown in Table 2.11. The asymmetric unit comprises half a molecule of  $[TpHo(crot)_2]_2$  related to the complementary half by a centre of symmetry. The metal centre displays a 8-coordinated geometry and is coordinated to one Tp ligand and two crotonate ligands. The two crotonate ligands differ in their coordination modes; one is coordinated to the metal centre in a chelating fashion and the other one acts as a bridging ligand resulting in a dimeric complex (Figure 2.15). The metal-oxygen distances range from 2.249(2) – 2.876(4) Å. The metal-metal distance is 3.7861(3) Å and the metal–ligand bond lengths show considerable variation, the Ho–N lengths ranging from 2.433(3) - 2.502(3) Å.



Figure 2.15. A view of  $[TpHo(crot)_2]_2$  showing the pattern of dimerisation about an inversion centre. For clarity, H atoms are omitted and not all remaining atoms are labelled, but the labelling system is consistent for each ligand. Thermal ellipsoids are at the 50% level

	[TpHo(crot) <sub>2</sub> ] <sub>2</sub>		[TpHo(crot) <sub>2</sub> ] <sub>2</sub>
М	4385.04	Crystal habit	Tornote block
System	Monoclinic	T/K	120
Space group	P <sub>ccn</sub>	µ/mm⁻¹	3.91
Z	8	ρ <b>/g cm<sup>-3</sup></b>	1.785
a/Å	17.8986(3)	Data measured	34666
b/Å	14.7154(2)	Unique data	5174
c/Å	15.4874(3)	R <sub>int</sub> (%)	4.14
βl°	90	$R\sigma(\%)$	2.79
V/Å <sup>3</sup>	4079.15(12)	$R[l > 2\sigma(l)](\%)$	2.27
Crystal size/mm <sup>3</sup>	0.5×0.4×0.25	$wR_2$ (all data)(%)	7.12

Table 2.11 Crystal data summary for [TpHo(crot)<sub>2</sub>]

Selected bond lengths of the complexes  $[Tp_2Er(crot)]$ ,  $[TpHo(crot)_2]_2$  are shown in Table 2.12

Tp <sub>2</sub> Er(crot)			
Er(1)-O(1)	2.353 (3)	Er(1)-N(41)	2.475 (2)
Er(1)-O(2)	2.386 (3)	Er(1)-N(51)	2.411 (2)
Er(1)-N(11)	2.521 (2)	Er(1)-N(61)	2.472 (2)
Er(1)-N(21)	2.477 (2)	O(1)- C(71)	1.271 (9)
Er(1)-N(31)	2.405 (2)	O(2)- C(71)	1.259 (9)
[TpHo(crot) <sub>2</sub> ] <sub>2</sub>			
Ho(1)- O(3)	2.249 (2)	Ho(1)- N(11)	2.509 (3)
Ho(1)- O(1)	2.293 (2)	Ho(1)- N(31)	2.502 (3)
Ho(1)- O(2)	2.315 (2)	O(3) - O(4)	1.288 (4)
Ho(1)- Ho(1)	3.7861 (3)	O(1) - C(81)	1.263 (4)
Ho(1)- N(11)	2.433 (3)	O(4) - C(81)	1.271 (4)

Table 2.12 Selected bond lengths (Å) for Erbium and Holmium crotonate complexes

### 2.4.2. Holmium cinnamate complex [TpHo(cin)<sub>2</sub>]<sub>2</sub>

Single crystal X-ray diffraction studies of [TpHo(cin)<sub>2</sub>]<sub>2</sub> complex confirmed that the structure is dinuclear. It belongs to the centrosymmetric triclinic space group P-1 (Table 2.13). The asymmetric unit is composed of the halves of two independent molecules of [TpHo(cin)<sub>2</sub>]<sub>2</sub> each located on a centre of symmetry. The coordination geometry of the two metal centres is different; in one, the metal centre displays 8-coordinate geometry, the other one 7coordinate geometry (Figure 2.16). In one unit the cinnamate ligand acts as a bridging ligand between the two metal centres resulting in the 7-coordinate geometry of the metal centre. The metal-oxygen distances range from 2.250(3) - 2.293(3) Å. On the other hand, in the second unit, one of the cinnamate ligands is coordinated to the metal centre in a bridging and chelating fashion and the other one acts as a bridging ligand resulting in a 8coordinate geometry for the metal centre. The metal-oxygen distances for the second unit range from 2.261(3) - 2.364(3) Å and the bridging cinnamate ligands are twisted from the plane. In the crystal structure the 7-coordinate unit is surrounded by eight molecules with 8-coordinate geometry. The structure of this complex is interesting as the molecules display two distinct coordination geometries. Due to the mixed coordination centres the metalmetal distances are different. The Ho-Ho distance for the 7-coordinate unit is 4.1240(2) Å where that for the 8-coordainte is 3.8582(3) Å.

	[TpHo(cin) <sub>2</sub> ] <sub>2</sub>		[TpHo(cin) <sub>2</sub> ] <sub>2</sub>
Chemical formula weight	1342.51	Crystal habit	block
System	Triclinic	T/K	120
Space group	P-1	μ/mm <sup>-1</sup>	2.969
Z	2	ρ/g cm <sup>-3</sup>	1.648
a/Å	12.8141(2)	Relection numbers	55156
b/Å	13.9224(2)	Reflection numbers (total)	1067
c/Å	17.0478(3)	R <sub>int</sub> (%)	4.92
al°	78.89	<i>R</i> σ(%)	3.7
βl°	81.49	$R[l > 2\sigma(l)](\%)$	2.27
V/Å <sup>3</sup>	2705.30	wR <sub>2</sub> (all data)(%)	7.43

Table 2.13. Crystal data summary for [TpHo(cin)<sub>2</sub>]<sub>2</sub>



Figure 2.16. A view of [TpHo(cin)2]2 crystal



Figure 2.17. Crystal packing of [TpHo(cin)<sub>2</sub>]<sub>2</sub><sup>21-23</sup>

# 2.5. Steric angle sum of [Tp<sub>2</sub>Er(crot)], [TpHo(crot)<sub>2</sub>]<sub>2</sub> and [TpHo(cin)<sub>2</sub>]<sub>2</sub> crystals

In attempting to assess the relative steric demands of a notional lanthanide ion, as traversed from La to Lu, some authors <sup>24</sup> have attempted to visualise the steric demand as a "Steric Angle Sum" - a projection of the ligands onto a notional (1A°) radius sphere at the centre of the lanthanide ion and value used this as a direct indicator of crowding.

Our discussion of structural types must be limited to few examples, but the monomeric  $[Tp_2Er(crot)]$  example seems to appear sterically crowded, at a value of 0.799, as compared to its  $[TpHo(crot)_2]_2$  analogue, which had a value of 0.779. These values seem within one standard deviation of the mean found previously<sup>24</sup> in a survey of lanthanide structures in 1987, but it hard to say if this is a result of the lanthanide contraction, data being limited to two diverse examples in this study. In the case of the Ho cinnamate series, the crystalline  $[TpHo(cin)_2]_2$  isolated proved to be a remarkable, and unique in our studies also, example of a chemically homogeneous molecular tris(pyrazolyl)borate lanthanide species which displays heterogeneous

crystallographic metal sites. As a result, it has two metal SAS numbers, one corresponding to each coordination number. The 8-coordinate centre has an SAS value of 0.782 and the 7-coordinate site has an expectedly lower value of 0.730. The mean SAS value of 0.756 might be seen as an expression of the overall steric strain in the structure: the rather low value might be attributed to the presence of phenyl groups, which increasing crowding in the coordination sphere.

### 2.6. Conclusion

Lanthanide crotonate and cinnamate complexes with NaTp were synthesised and characterised. Structural studies show that both these series were mononuclear in powder form but in the crystal forms, holmium cinnamate and holmium crotonate complexes were dinuclear. Larger lanthanides (La-Ho) were in dimeric both in cinnamate and crotonate series. In the crystal form, the erbium crotonate complex shows a mononuclear structure, Er being one of the smaller lanthanides (Er-Lu). We can generalise that the smaller lanthanides were mononuclear as indicated by MS, <sup>1</sup>H NMR and elemental analysis. The cinnamate series, are formulated as [Tp<sub>2</sub>Ln(crot)] except in the case of [TpHo(cin)<sub>2</sub>]<sub>2</sub>. Europium and terbium crotonate and cinnamate complexes with substituted Tp were mononuclear in powder form; no crystals were obtained for substituted Tp, crotonate and cinnamate complexes.

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## **Chapter 3**

## Luminescence studies of lanthanide complexes

This chapter describes the luminescent properties of lanthanide complexes.

Sensitized lanthanide ion emission attracts a large interest,<sup>1</sup> because it is an efficient way to circumvent the low absorption coefficients of these ions.<sup>2</sup> Most of the research has been focused on the visible (VIS) emission of europium and terbium<sup>3,4</sup> which can be sensitized by UV absorbing sensitizers. In recent years the research has shifted to near-infrared (NIR) emissive ions, like neodymium, yetterbium and erbium.<sup>5-11</sup> NIR emitters have advantages over VIS emitters. For example the emission in the NIR is ideally applicable to biology,<sup>12</sup> because biological tissue is transparent to NIR light <sup>13</sup> and to telecommunications because in the optical amplifiers of the NIR signals the lanthanide ion acts as the active material. Sensitizers that absorb in the visible region can be used here to sensitize the NIR emitting lanthanide ions.<sup>14</sup> This gives the advantages of cheap excitation sources like diode lasers, glass instead of quartz for substrate handling in biological tests.

Studies are mainly focussed on visible-emitting cinnamate and crotonate lanthanide complexes, because hydrotris(pyrazolyl)borate and the co-ligands (cinnamate or crotonate) absorbing light in the high energy region (UV region) so it is easy to sensitize visible emitting lanthanides like Eu, Tb ,Sm and Dy complexes. Emission of these complexes in NIR was also studied by direct excitation of the Nd, Er and Yb metals and this is described later in this section.

# 3.1. Photoluminescent studies of lanthanide crotonate and cinnamate complexes [Tp<sub>2</sub>Ln(crot)] and [Tp<sub>2</sub>Ln(cin)]

Most of the work concentrated on photoluminescence studies rather than electroluminescence for crotonate and cinnamate lanthanide complexes.

## 3.1.1.Absorption properties of the lanthanide crotonate complexes [Tp2Ln(crot)]

All absorption measurements were made in  $CH_2Cl_2$ . Figure 3.1 shows the UVvisible absorption of crotonate complexes. The molar absorptivities were calculated using equation 1. *A* is the absorbance, *c* is the molar concentration (M) of the solution, and *I* is the cell path length,  $\varepsilon$  is the molar exctinction coefficient.

#### A=ɛcl

Equation 1. Formulae for molar absorptivity

The UV absorption spectra are dominated by the  $\pi$ - $\pi$ \* transitions of the ligands surrounding the lanthanide. The absorption corresponds very strongly with the Tp ligand, at 230-250 nm because the two Tp ligands surround the metal, as opposed by only one crotonate ligand and the weaker shoulder starting at 270 nm corresponds to the  $\pi$ - $\pi$ \* transition of crotonate ligand (Figure 3.8). Moreover, lanthanide ions do not contribute to the spectra of their complexes since f→f transitions are Laporte-forbidden, and consequently have a very low molar absorptivity (molar absorptivity coefficients of the order of only (0.5-3.0 M<sup>-1</sup> cm<sup>-1</sup>).<sup>15</sup> On the other hand, charge-transfer bands involving lanthanide orbitals are also typically not observed in the near-UV spectral regions.<sup>16</sup> Changing from one lanthanide to another has little influence on the  $\pi$ - $\pi$ \* transitions of the complexes. This indicates that the lanthanide metal centre has little or no orbital interaction with the ligand, other than electrostatic effects generated by the trivalent charge of each ion. This is due to the shielding of 4f orbitals by filled 5s and 5p orbitals.



Figure 3.1. Absorption spectra of crotonate complexes

**3.1.2.** Absorption properties of cinnamate complexes  $[Tp_2Ln(cin)]$ The absorption spectra of cinnamate complexes show a maximum absorption at 240-260 nm. This is due to the  $\pi$ - $\pi$ \* transition of the Tp ligands and the absorption of Tp is shifted to lower energy than in the crotonate complexes. This is due to the complexation of the lanthanide ion with the cinnamate coligand. The other peak at 320 nm corresponds to the absorption region of cinnamic acid. The Tp ligand region shows a higher absorption than the cinnamate co-ligand (Figure 3.2). For Ho and Er cinnamate complexes an extra small absorption in the low energy region 400 nm-800 nm. This is due to the f $\rightarrow$ f transition of the lanthanide metals (Figure 3.3).



Figure 3.2. Absorption spectra of [Tp<sub>2</sub>Ln(cin)] complexes





## 3.2. Metal centred Photophysical properties of lanthanide complexes

The luminescence of the lanthanides orginates from transitions within the partially filled 4f orbitals,<sup>16</sup> which are in principle spin-forbidden.<sup>17</sup> Lanthanide ions with completely filled (Lu<sup>3+</sup>) or unfilled (La<sup>3+</sup>) 4f orbitals do not possess any luminescence. The luminescence region of the other lanthanide ions ranges from the UV to the NIR. Line-like emission, low absorption coefficients and high luminescence life times (up to milliseconds) are the characteristics of lanthanide luminescence. The effect of the ligand field is very small because the energy levels of the emission are hardly affected by the environment of the metal ions.

A simplified Jablonski diagram for the sensitized emission is shown in Figure 3.4. After the excitation of the antenna and the intersystem crossing, the energy is transferred to the lanthanide ion. The sensitization occurs from the triplet state via a Dexter mechanism<sup>18,19</sup> although energy transfer from the singlet cannot be ruled out.



Figure 3.4. Simplified Jablonski diagram for sensitized emission,  $K_{fu}$ : rate of fluorescence,  $K_{ISC}$ : intersystem crossing rate,  $K_{phos}$ : phosphorescence rate,  $K_q$ : triplet quenching rate,  $K_{ET}$ : energy transfer rate,  $K_{Ln, rad}$ : radiative decay rate

In the sensitization of Eu complexes the sensitizer triplet state has to be about 1000-2000 cm<sup>-1</sup> higher than the Eu<sup>3+</sup> accepting level, to avoid any possible back energy transfer. <sup>20,21</sup> This limits the choice to ligands with a principal absorption in the UV or violet spectral region.<sup>22,23</sup> Whereas, for the NIR emitting lanthanide there is no limitation of sensitizer because most of the organic ligands accept energy in visible region. For better lanthanide emission, complexes should have high absorption coefficient, efficient

intersystem crossing and an efficient luminescence. The absorption coefficient is not a real problem as many organic ligands absorb strongly.

Homoleptic poly(pyrazolyl)borate complexes of the lanthanides have been evaluated as possible high-quantum yield, visible light emitters and the emission spectra of some partially characterised europium and terbium poly-(pyrazolyl)borate complexes have been reported. A ligand-to-metal charge transfer (I. m. c. t) process, present only in the complex, was thought to lead to population of the lanthanide excited state according to a Whan-Crosby mechanism.<sup>24</sup>

The heteroleptic poly(pyrazolyl)borates were the main area of interest and the europium, samarium, terbium and dysprosium crotonate complexes demonstrated good emission in the visible region, while Er, Nd, Yb crotonate complexes showed NIR emission by the direct excitation of the corresponding metals.

### 3.2.1. Photoluminescence studies of visible emitting lanthanides

The photoluminescence (PL) studies of lanthanide complexes which emit in the visible region was studied first. They are Sm, Dy, Tb and Eu complexes. All the photoluminescence studies were done in  $CH_2Cl_2$  (0.04 M) solution unless otherwise stated. The experimental set-up for visible emission is shown in Figure 3.5.



Figure 3.5. Experimental set up for visible emission

Source is a pulsed-xenon flash lamp .

**Monochromators** covers the excitation wavelength in the range between 200–800 nm with zero order selectable. Emission wavelength in the range between 200-650 nm with the R928 photomultiplier.

**Sample Holder** is a single position standard cell holder for 10-mm pathlength fluorescence cells, having windows on all four sides.

**Detector** is a gated photomultiplier with modified S5 response for operation to about 650 nm.

Read out is the FL WinLab<sup>™</sup> software loaded on the adjacent computer.

## 3.2.1.1. Lanthanide crotonate complexes $[Tp_2Ln(crot)]$ (Ln = Sm, Dy, Tb, Eu)

In these systems the crotonate coligand acted as an antenna (Figure 3.6) to absorb energy from the system and transfer the triplet energy to the metal via intersystem crossing. The excitation spectrum of the Tb crotonate complex (Figure 3.7) shows two absorption regions at 270 and 311 nm. Other metal complexes (Ln = Eu, Sm, Dy) also show similar excitation spectra. The intensity of absorption at 270 nm is higher than that of the 311nm absorption. 270 nm corresponds to crotonic acid absorption. The excitation spectrum of crotonic acid shows the same absorption at 270 nm (Figure 3.8). A higher intensity at 270 nm in the excitation spectrum would clarify whether energy transfer to the lanthanide ion is more efficient from the crotonate co-ligand than from the Tp ligand, although in the UV-VIS, molar absorption coefficient of the crotonate co-ligand is less than that associated with Tp.



Figure 3.6



Figure 3.7. Excitation spectrum of [Tp2Tb(crot)] complex



Figure 3.8. Excitation spectrum of crotonic acid

Excitation of samarium, europium, dysprosium and terbium crotonate complexes at a wavelength in the range 240-260 nm results in emission, and that from the Tb complex is more intense. In the case of samarium, which displays three main bands at 564, 599, 644 nm corresponding to the  ${}^{4}G_{5/2} \rightarrow {}^{6}H_{5/2}$  at,  ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$  and  ${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$  transitions respectively, the strongest emission is located at 599 nm. In the case of europium, two emission bands are resolved corresponding to the transition from the  ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$  (J = 1-2). The emission at 590 nm corresponds to  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  and 617nm corresponds to  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition, with the strongest emission located at 617 nm. The emission of Dy is composed of two intense lines at 482 and 574 nm, corresponding to  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$  and  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$  transitions. The most intense emission line is at 482 nm. The emission spectra of the terbium complex contains four bands corresponding to the transitions from the <sup>5</sup>D<sub>4</sub> excited state to the<sup>7</sup>F<sub>J</sub> (J = 3-6) levels. The emissions at 492 nm, 544 nm, 586 nm and 620 nm correspond to the transitions from  ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$ ,  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ ,  ${}^{5}D_{4} \rightarrow {}^{7}F_{4}$  and  ${}^{5}D_{4} \rightarrow {}^{7}F_{3}$  respectively, with the strongest emission located at 544 nm. Similar but more intense emission spectra are recorded for the crotonate complexes when excited at 270 nm, which is the crotonic acid absorption region, and it proved that energy transfer from co-ligand to the metal was more efficient compared to that from the Tp ligand. Excitation at 311-315 nm gave observable emission only for the Eu<sup>3+</sup> complex, in which the emissive  ${}^{5}D_{0}$  level lies at lower energy than the  ${}^{5}D_{4}$ ,  ${}^{4}G_{5/2}$   ${}^{4}F_{9/2}$  levels of Tb<sup>3+</sup>, Sm<sup>3+</sup>and Dy<sup>3+</sup> respectively. Emission spectra of these crotonate complexes, excited at 270 nm, are shown in Figure 3.9. The emission spectrum shows another peak at 300-500 nm. This is due to the  $\pi$ - $\pi$ \* emission of the co-ligand but the intensity of co-ligand emission was less in Sm, Dy and Tb complexes compared to the Eu complexes. This indicated that the intersystem crossing is faster and the energy transfer from crotonate ligand to metal was more efficient in Sm, Dy and Tb complexes compared to the Eu complex. Table 3.1 shows the emission spectral data for [Tp2Ln(crot)] complexes. For crotonate complexes we represent the general formulae as [Tp2Ln(crot)] because in powder form they exhibit the molecular configuration as discussed in chapter 2.

Complex	Excitation	Emission	Assignment	Measured	Relative		
	nm	nm		intensity <sup>a</sup>	intensity <sup>b</sup>		
[Tp <sub>2</sub> Eu(crot)]	240	590	${}^{5}D_{0} \rightarrow {}^{7}F_{1}$	1	30.3		
		615	${}^{5}D_{0} \rightarrow {}^{7}F_{2}$	1.5	100		
	270	590	${}^{5}D_{0} \rightarrow {}^{7}F_{1}$	2	60.6		
		615	$^{5}D_{0} \rightarrow ^{7}F_{2}$	3.3	100		
[Tp <sub>2</sub> Tb(crot)]	240	492	${}^{5}D_{4} \rightarrow {}^{7}F_{6}$	27.2	46.10		
		544	${}^{5}D_{4} \rightarrow {}^{7}F_{5}$	59	100		
		586	$^{5}D_{4}\rightarrow^{7}F_{4}$	11.2	18.9		
		620	$^{5}D_{4}\rightarrow^{7}F_{3}$	1	1.69		
	270	492	${}^{5}D_{4} \rightarrow {}^{7}F_{6}$	59	61.7		
		544	${}^{5}D_{4} \rightarrow {}^{7}F_{5}$	95.5	100		
		586	${}^{5}D_{4} \rightarrow {}^{7}F_{4}$	13.6	14.2		
		620	${}^{5}D_{4} \rightarrow {}^{7}F_{3}$	8.4	8.79		
[Tp <sub>2</sub> Sm(crot)]	240	564	${}^{4}\text{G}_{5/2} \rightarrow {}^{6}\text{H}_{5/2}$	2.2	34.9		
		599	${}^{4}\text{G}_{5/2} \rightarrow {}^{6}\text{H}_{7/2}$	6.3	100		
		644	${}^{4}\text{G}_{5/2} \rightarrow {}^{6}\text{H}_{9/2}$	1	15.8		
	270	564	4- 6.	64	41 5		
		599	$G_{5/2} \rightarrow H_{5/2}$	15.4	100		
		644	$^{\circ}\text{G}_{5/2} \rightarrow ^{\circ}\text{H}_{7/2}$	3.7	24		
· · · · · · · · · · · · · · · · · · ·			$^{*}G_{5/2} \rightarrow ^{\circ}H_{9/2}$				
[Tp₂Dy(crot)]	240	484	<sup>4</sup> F <sub>9/2</sub> → <sup>•</sup> H <sub>15/2</sub>	1.1	100		
		574	<sup>4</sup> F <sub>9/2</sub> → <sup>6</sup> H <sub>13/2</sub>	1	90.9		
	070	404	4- 6	2	100		
	270	674	$F_{9/2} \rightarrow H_{15/2}$	1	33		
		574	<sup>4</sup> F <sub>9/2</sub> →°H <sub>13/2</sub>	•			
Obtained from 0.04 M in DCM. "Reported in arbitary units in which the weakest emission of							
the series( <i>i.e.</i> for	the series( <i>i.e.</i> for [Tp <sub>2</sub> Eu(crot)], $D_0 \rightarrow F_1$ ) is set at unity. Relative to the strongest emission						
(set at 100%) for the complex at the specified excitation wavelength							

Table 3.1. Emission spectral data for  $[Tp_2Ln(crot)]$  complexes (Ln = Eu,Tb,Sm, Dy)



Figure 3.9. Emission spectra of (a),  $[Tp_2Tb(crot)]$ , (b)  $[Tp_2Sm(crot)]$ , (c),  $[Tp_2Eu(crot)]$ , (d),  $[Tp_2Dy(crot)]$  complexes when excited at 270 nm

### 3.2.1.2. Photoluminescence studies of cinnamate complexes [Tp<sub>2</sub>Ln(cin)] (Ln = Eu, Tb, Dy, Sm)

In photoluminescence studies of cinnamate complexes, only emission from Eu was observed. The excitation spectrum of the Eu cinnamate complex shows a maximum absorption intensity at 320-400 nm, and the absorption extends to 500 nm (Figure 3.10 **a**). This is due to the absorption by the cinnamate co-ligand (Figure 3.10 **b**). In these complexes, the cinnamate co-ligand acted as an antenna to receiving transfer the energy to the europium. Direct excitation of Eu at 390 nm did not lead to any observed emission



Figure 3.10. (a), Excitation spectrum of [Tp<sub>2</sub>Eu(cin)] (b), excitation spectrum of cinnamic acid

Excitation of the [Tp<sub>2</sub>Eu(cin)] complex at wavelengths of 240-260 nm or 320 nm showed the characteristic emission of Eu at 592 nm ( ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ ) and 617 nm ( ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ ), and the emission intensity was higher in the case of 320 nm excitation (Figure 3.11). Excitation of Tb, Dy and Sm cinnamate complexes at 320 nm, show no characteristic emission for these metals. This is because their emissive level lies slightly above the triplet energy level of the cinnamate ligand, back energy transfer from the metal to the coligand is possible. In order to check the triplet energy levels of these cinnamate complexes, gadolinium complexes were prepared. The excited state of the Gd<sup>3+</sup> ( ${}^{6}P_{7/2}$ ) lies at 32150 cm<sup>-1</sup> (~311 nm), <sup>25</sup> it is very difficult to populate it through organic excited ligand triplet states. When the Gd cinnamate complexes were excited at 320 nm, the phosphorescent ligand emission occurred at 470-550 nm, so

the triplet energy levels of these cinnamate complexes are too low to transfer energy to the Tb, Sm, and Dy emissive levels. Excitation at higher energy region (240 nm) there was a very low emission from Tb at 544 nm

 $({}^{5}D_{4} \rightarrow {}^{7}F_{5})$ . For Sm and Dy complexes there was no emission even at higher energy excitation. The emission intensity in the ligand region was weaker in [Tp<sub>2</sub>Eu(cin)] than that of the [Tp<sub>2</sub>Eu(crot)] complex. The delocalisation of electrons in the phenyl ring shifted the cinnamate co-ligand absorption to a lower energy compared to the crotonate co-ligand, so that triplet energy transfer from ligand to the europium ion was more efficient in the cinnamate complex. A comparison of the intensities is shown in Table 3.2.



Figure 3.11. Emission spectrum of [Tp2Eu(cin)] complex

Complex	Excitation	Emission	Assignment	Measured
	nm	nm		intensity (a.u.)
[Tp <sub>2</sub> Eu(crot)]	270	590	${}^{5}D_{0} \rightarrow {}^{7}F_{1}$	5.2
		615	${}^{5}D_{0} \rightarrow {}^{7}F_{2}$	9.8
[Tp <sub>2</sub> Eu(cin)]	320	590	${}^{5}D_{0} \rightarrow {}^{7}F_{1}$	11.2
		615	${}^{5}D_{0} \rightarrow {}^{7}F_{2}$	39.2

Chapter 3. Luminescence studies of lanthanide complexes

Table 3.2. Emission intensity comparison data for [Tp<sub>2</sub>Eu(crot)] and [Tp<sub>2</sub>Eu(cin)] complexes

### 3.2.2. Near-infrared emitting lanthanide complexes

Photoluminescence studies for the NIR crotonate and cinnamate complexes were done only in the solid state and were carried out at Queen Mary College, University of London. All the NIR emission and luminescent life-times were measured by direct excitation of the corresponding lanthanide ions rather than via the antenna effect, because in the crotonate and cinnamate complexes, the Tp ligands as well as cinnamic and crotonic acid coligands only absorb energy in the UV region. For NIR emission, the antenna should absorb excitation energy in the visible region so that there is an efficient ISC crossing to the lanthanides. The experimental set-up for NIR emission is shown in Figure 3.12.



for IR

\* Hamamatsu S20 photomultiplier for the visible range.

Figure 3.12. Experimental set up for NIR emission.

### 3.2.2.1 Crotonate complexes $[Tp_2Ln(crot)]$ (Ln = Yb, Er, Nd)

Direct excitation of the  $[Tp_2Ln(crot)]$  (Ln = Yb, Er, Nd) complexes gave the characteristic emission from the corresponding metals.



Figure 3.13. NIR emitting crotonate complexes

In the case of the [Tp<sub>2</sub>Er(crot)] complex, the direct excitation of erbium at 520 nm gave the characteristic emission of erbium with a maximum at 1540 nm corresponding to the  ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$  transition. Excitation of the [Tp<sub>2</sub>Yb(crot)] complex at 920 nm showed the maximum emission at 980 nm, corresponding to the  ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$  transition for yetterbium, and for the [Tp<sub>2</sub>Nd(crot)] complex excitation at 590 nm showed the characteristic emission of neodymium at 880 nm, 1060 nm and 1340 nm, corresponding to the  ${}^{4}F_{3/2} \rightarrow {}^{4}I_{13/2}$ ,

 ${}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}$  and  ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$  transitions respectively (Figure 3.14). Due to the direct excitation of these NIR emitters the emission intensity was weaker than that of the sensitized Eu and Tb complexes.





### 3.2.2.2 Cinnamate complexes [Tp<sub>2</sub>Ln(cin)] (Ln =Er, Nd, Yb)



Figure 3.15. NIR emitting cinnamate complexes

Er, Nd and Yb showed characteristic emissions after direct excitation of cinnamate derivatives. In the case of [Tp<sub>2</sub>Er(cin)] complex, the direct excitation of erbium at 520 nm produced the characteristic emission of erbium with a maximum at 1540 nm, corresponding to the  ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$  transition. Excitation of [Tp<sub>2</sub>Yb (cin)] complex at 920 nm shows a maximum emission at 980nm, corresponding to the  ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$  transition for Yetterbium and for the 590 nm showed the characteristic [Tp<sub>2</sub>Nd(cin)] complex, excitation at emissions from the neodymium at 880 nm, 1060 nm and 1340 nm corresponding to the  ${}^{4}F_{3/2} \rightarrow {}^{4}I_{13/2}$ ,  ${}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}$  and  ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$  transitions respectively (Figure 3.16). Due to the direct excitation of these NIR emitters the emission intensity was again weaker than that of the corresponding Eu<sup>3+</sup> and Tb<sup>3+</sup> complexes. The negative emission for Nd-cinnamate is due to the high that the the intensity is SO fact that detector becomes saturated and returns a negative value.



Figure 3.16.NIR emission spectra of (a), [Tp<sub>2</sub>Nd(cin)], (b), [Tp<sub>2</sub>Er(crot)]

### 3.3. Effect of solvent on the sensitized emission of [Tp<sub>2</sub>Eu(crot)] and [Tp<sub>2</sub>Eu(cin)] complexes

Solvents can play an important role in the emission properties of lanthanide complexes.<sup>26</sup> Therefore the emission studies of Eu crotonate and Eu cinnamate complexes were carried out in methanol, acetonitrile, DMSO and cyclohexane and compared with the results obtained from DCM solution; the intensities are summarised in Table 3.3. The table shows that Eu cinnamate showed higher intensity than the crotonate complex as expected. These two

complexes, showed higher intensity ratios in methanol but there was no emission observed for either complex in cyclohexane, a nonpolar solvent.

Solvent	Complex	Luminescence
		Intensity(a.u.)at 615 nm
DCM	[Tp <sub>2</sub> Eu(crot)]	9.8
	[Tp <sub>2</sub> Eu(cin)]	39.2
MeOH	[Tp <sub>2</sub> Eu(crot)]	11.3
	[Tp₂Eu(cin)]	43.1
Acetonitrile	[Tp <sub>2</sub> Eu(crot)]	8.7
	[Tp <sub>2</sub> Eu(cin)]	36.2
DMSO	[Tp <sub>2</sub> Eu(crot)]	9.7
	[Tp <sub>2</sub> Eu(cin)]	39.1
Cyclohexane	[Tp <sub>2</sub> Eu(crot)]	0
	[Tp <sub>2</sub> Eu(cin)]	0

Table 3.3. Luminescence intensity of cinnamate and crotonate complexes in various solvents

#### 3.3.1 Effect of mixed solvent

The sensitized luminescence spectrum of  $[Tp_2Eu(cin)]$  complex in DCM containing different concentrations of methanol is shown in Figure 3.17. The same behaviour was obtained in the case of crotonate complex. Addition of methanol to DCM solutions of Eu cinnamate and crotonate complexes, caused quenching of the Eu<sup>3+</sup> luminescence intensity. This is thought to be a consequence of the large non-radiative deactivation effects of the O-H oscillators of the methanol molecules, which interact with the coordination sphere of Eu<sup>3+</sup>. <sup>27,28</sup>


Figure 3.17. Luminescence spectra of Eu cinnamate complexes in DCM containing different concentrations of methanol

#### 3.4. Solid state PL studies of europium cinnamate complexes

Luminescent properties of the complexes were compared in the solid state as well as in solution; the solid state films were obtained by spin coating the [Tp<sub>2</sub>Eu(cin)] complex in DCM onto quartz substrates. Characteristic emission from the Eu was obtained at 590 and 619 nm with excitation at 320 nm and the emission intensity of the Eu<sup>3+</sup> in the solid substrate was than in solution. There was no obvious shift in the luminescent greater emission and excitation peaks. When the lanthanide complexes are in solution, the movement and the rotation of the complex molecules is relatively free. When the lanthanide complexes are introduced into the solid films, the molecular motion is restricted and the stretching and bending vibrations are weakened,<sup>29,30</sup> both of which decreased the non-radiative transitions. Thus the luminescent intensity of lanthanide complexes in the solid substrate was higher than that in solution. In solid state, emission from the ligand region was

weaker than that in the solution state, so energy transfer from the ligand to metal in the solid state was more efficient. Figure 3.18 shows the emission intensity in the solid state and solution states.



Figure 3.18. Emission spectra of (a), [Tp2Eu(cin)] in DCM, (b), on quartz substrate

Table 3.4 lists the emission intensity ratios between the solid and solution states for [Tp<sub>2</sub>Eu(cin)] complexes.

Complex	State	Emission nm	Observed intensity(a.u.)	Intensity ratio
	Solution	590	4.1	1
	Solution	619	13.2	1
[Tp <sub>2</sub> Eu(cin)]				1000
	Solid	590	17.2	4.19
	Solid	619	48.6	3.68

Table 3.4.Comparison of emission intensity of  $[Tp_2Eu(cin)]$  complex in solution state and solid state (0.04 M DCM)

# 3.5. Luminescence life-times of crotonate [Tp<sub>2</sub>Ln(crot)] and cinnamate [Tp<sub>2</sub>Ln(cin)] complexes

Luminescence life-times of the europium and terbium crotonate complexes  $[Tp_2Ln(crot)]$  (Ln = Eu, Tb) as well as the europium cinnamate complex  $[Tp_2Eu(cin)]$  were measured in DCM solution and the instrument was set up in phosphorescent mode and the gate time was 1 ms and the time delay in the range between 0.002 ms and 0.1 ms.<sup>31</sup> The emission of these complexes was observed with different time delays. When the time delay was increased the luminescence intensity decreased and the luminescence life-time was calculated according to equation 2<sup>32</sup> In the case of the crotonate complexes the life-time for Tb was 0.8 ms and for Eu was 1.6 ms. In the case of the cinnamate complexes, the luminescence life-time for Eu emission was 2.2 ms.

 $I_t = I_0 e^{-v/t}$   $I_t =$ Intensity at a particular time  $I_0 =$ Initial intensity  $\iota =$  luminescent decay t = time Equation 2. Formula for luminescence life time measurement

Luminescence life-time measurements for NIR emitters were done in the solid state and they showed that cinnamate complexes had longer luminescence life times than the crotonate complexes. The delocalisation of electrons in the phenyl ring in the cinnamate co-ligand helped to increase the distance between the metal and oxygen (Ho-O = 2.315 Å) and thereby increase the distance between the metal and the C-H oscillators compared to those in the crotonate complexes (Ho-O = 2.291 Å). The luminescence life-time values for these complexes are shown in Table 3.5.

Complex	Luminescence life time		
	μs		
[Tp <sub>2</sub> Er(crot)]	0.5		
[Tp <sub>2</sub> Er(cin)]	0.8		
[Tp <sub>2</sub> Yb(crot)]	0.9		
[Tp <sub>2</sub> Yb(cin)]	11.6		
[Tp <sub>2</sub> Nd(crot)]	0.87		
[Tp <sub>2</sub> Nd(cin)]	1.48		

Table 3.5. Luminescent life times for cinnamate and crotonate complexes



Figure 3.19. Luminescence decay of [Tp2Eu(crot)] at different time delays



Figure 3.20. Luminescence decay of [Tp2Tb(crot)] at different time delays.









Figure.3.22. Luminescence decay curves of (a), [Tp<sub>2</sub>Yb(crot)], (b), [Tp<sub>2</sub>Yb(cin)]



Figure.3.23. Luminescence decay curves of (a), [Tp<sub>2</sub>Nd(crot)], (b), [Tp<sub>2</sub>Nd(cin)]

# 3.6. Photoluminsecnce studies of substituted hydrotris (pyrazolyl)borate complexes

Studies of the luminescence properties of Eu and Tb complexes were extended to substituted Tp ligands. Luminescence studies of lanthanide complexes with these substituted Tp ligands were done in methanol solution. The synthesis of substituted Tp ligands and metal complexes of these ligands was described in chapter 2.

#### 3.6.1. Luminescence properties of [(Tp-Ar-OMe)2Eu(cin)] or [(Tp-Anis)2Eu(cin)]

The excitation spectra of these complex shows the maximum absorption at 326 nm. This absorption was red-shifted by 6 nm compared to the cinnamate absorption at 320 nm in [Tp<sub>2</sub>Eu(cin)]. In these complex, the cinnamic acid coligand played a vital role for transferring energy to the metal compared to the Tp-Ar-OMe ligand. The excitation spectrum of Tp-Ar-OMe showed a maximum absorption at 305 nm and was red-shifted by nearly 45 nm<sup>33-36</sup> compared to the Tp ligand. This is due to the substitution at the Tp ligand in the presence of the Ar-OMe group. Excitation of [(Tp-Ar-OMe)<sub>2</sub>Eu(cin)] at 326 nm showed emission from Eu in which the maximum intensity was located at 617 nm. The excitation spectra of [(Tp-Ar-OMe)<sub>2</sub>Eu(cin)] and Tp-Ar-OMe are shown in Figure 3.24 and the emission spectrum of [(Tp-Ar-OMe)<sub>2</sub>Eu(cin)] shown in Figure 3.25.



Figure 3.24. Excitation spectra of (a), [(Tp-Ar-OMe)<sub>2</sub>Eu(cin)] and (b), Tp-Ar-OMe



Figure 3.25. Emission spectrum of [(Tp-Ar-OMe)<sub>2</sub>Eu(cin)]

The emission intensities of these complex were weaker than those of [Tp<sub>2</sub>Eu(cin)].

#### 3.6.2. Luminescence properties of [(Tp-thiophene)<sub>2</sub>Eu(cin)]

Excitation of the [(Tp-thiophene)<sub>2</sub>Eu(cin)] complex at 326 nm also showed the characteristic emission from Eu<sup>3+</sup>, but the emission intensity was higher than that of the Ar-OMe derivative, because the presence of the sulphur group in the thiophene made the delocalisation stronger than the oxygen group in Ar-OMe derivative (Figure 3.26).





#### 3.6.3.Luminescence properties of [(Tp-Ar-Me)<sub>2</sub>Eu(cin)]

In these Ar-Me derivative complexes there was no strong delocalisation as seen in the Ar-OMe and thiazole derivatives. Excitation of these complexes at 326 nm showed the characteristic Eu emission, and the intensity was weaker than for the other two derivatives (Figure 3.27).



Figure 3.27.Emission spectrum of [(Tp-Ar-Me)<sub>2</sub>Eu(cin)]

## 3.6.4.Luminescence properties [(Tp-Ar)₂Eu(cin)]

The emission intensities of these complexes were higher compared to the

Ar-Me derivative when excited at 326 nm (Figure 3.28).



Figure 3.28.Emission spectrum of [(Tp-Ar)<sub>2</sub>Eu(cin)]

Emission spectral data for all these complexes are summarised in Table 3.6

Complex	Excitation	Emission	Assignment	Measured intensity	
	nm	nm		a.u.	
[(Tp-Ar-OMe) <sub>2</sub> Eu(cin]	326	619	${}^{5}D_{0} \rightarrow {}^{7}F_{2}$	5.6	
[(Tp-thiophene) <sub>2</sub> Eu(cin]	326	619	${}^{5}D_{0}\rightarrow {}^{7}F_{2}$	7.85	
[(Tp-Ar-Me) <sub>2</sub> Eu(cin)]	326	619	${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{2}$	2.56	
[(Tp-Ar) <sub>2</sub> Eu(cin)]	326	619	${}^{5}D_{0} \rightarrow {}^{7}F_{2}$	2.92	

Table. 3.6.

#### 3.6.5. Luminescence properties of [(Tp-Ar-OMe)<sub>2</sub>Eu(crot)], [(Tpthiophene)<sub>2</sub>Eu(crot)], [(Tp-Ar-Me)<sub>2</sub>Eu(crot)] and [(Tp-Ar)<sub>2</sub> Eu(crot)] complexes

Similar studies were done for the crotonate derivatives. In these complexes the excitation spectra showed the absorptions at 310-312 nm. This absorption corresponded to the crotonate ligand and was 40 nm red-shifted compared to  $[Tp_2Eu(crot)]$  complexes, due to the substituent present in the Tp ligand. All these complexes showed characteristic emission from europium and the maximum emission was located at 617 nm with a pattern similar to the substituted Tp cinnamate complexes described earlier. The emission intensities of these complexes were in the order thiophene > Ar-OMe > Ar > Ar-Me derivatives, for the reason discussed in the previous section. In these substituted Tp ligands, europium cinnamate complexes showed higher luminescence compared to the corresponding crotonate complexes. So cinnamate co-ligands are better energy transfer agents to the metal than crotonate co-ligands.



Figure 3.29. Excitation spectrum of [(Tp-Ar-OMe)<sub>2</sub>Eu(crot)]



Figure 3.30. Emission spectrum of [(Tp-Ar-OMe)<sub>2</sub>Eu(crot)]

Emission spectral data for all these complexes are summarised in Table 3.7.

Complex	Excitation	Emission	Assignment	Measured intensity	
	nm	nm	1.1.1.1.1.1.1	a.u.	
[(Tp-Ar-OMe) <sub>2</sub> Eu(crot)]	326	619	${}^{5}D_{0} \rightarrow {}^{7}F_{2}$	2.92	
[(Tp-thiophene) <sub>2</sub> Eu(crot)]	326	619	${}^{5}D_{0} \rightarrow {}^{7}F_{2}$	3.82	
[(Tp-Ar-Me) <sub>2</sub> Eu(crot)]	326	619	${}^{5}D_{0} \rightarrow {}^{7}F_{2}$	1.35	
[(Tp-Ar) <sub>2</sub> Eu(crot)]	326	619	$^{5}D_{0}\rightarrow ^{7}F_{2}$	1.83	

#### Table 3.7

#### 3.6.6. Luminescence properties of [(Tp-Ar-OMe)<sub>2</sub>Tb(crot)], [(Tpthiophene)<sub>2</sub>Tb(crot)], [(Tp-Ar-Me)<sub>2</sub>Tb(crot)] and [(Tp-Ar)<sub>2</sub> Tb(crot)] complexes

Similar studies were carried out for Tb compounds, and all these substituted Tp derivatives in crotonate complexes showed characteristic emission from Tb. There is no emission from Tb metal in substituted Tp cinnamate complexes, because the emissive level of Tb is above the triplet energy of the ligand compared to the  $[Tp_2Eu(cin)]$  complex. The

extra delocalisation of the substituted group in Tp ligand shifted the absorption of cinnamate ligands a lower wavelength region. Excitation of all these complexes at 306 nm showed the characteristic emission from Tb and the emission intensity was higher than that of  $[(Tp -R)_2 Eu(crot)]$ . (R= Ar-OMe, thiophene, Ar, Ar-Me). The luminescence intensities of these complexes were in the order thiophene > Ar-OMe > Ar > Ar-Me derivatives.





#### (pyrazolyl) borate complexes with other axial ligands R (R=malic acid, formic acid, *p*-toluic acid)

Synthesised and studied the emission properties of different series of hydrotris(pyrazolyl)borate lanthanide complexes using malic acid, formic acid and *p*-toluic acid. The synthetic method was similar to that used for previous hydrotris(pyrazolyl)borate complexes and the ratio Tp: Ln: R was 2:1:1. In these ligands, malic acid is a homochiral dicarboxlic acid, formic acid didn't have any antenna to absorb energy from the system so in the case of the formate complexes, the Tp ligand would play a major role in the energy transfer to the lanthanides. *p* - toluic acid showed a greater influence because of the delocalisation of electrons in the phenyl ring. In *p*- toluic acid the COOH group is a good electron withdrawing group and is attached directly to the phenyl ring. The ligand structures are shown in Figure 3.32. Luminescence studies of these complexes were carried out using 0.04 M solution in DCM.



Figure 3.32 Structures of formic acid, *p*-toluic acid, malic acid

## 3.7.1 Optical studies of [Tp2Ln(formate)] complexes (Ln =Tb, Eu)

The UV-visible spectra of these complexes showed the maximum absorption at 230-260 nm, which was due to the transitions of the Tp ligand. The UVvisible absorption spectrum of formic acid shows a maximum absorption at 225 nm. The excitation spectrum of both the Tb and Eu formate complexes showed a maximum absorption at 240 nm (Tp region). Excitation of formate complexes at 240 nm showed the characteristic emission from Tb and Eu metals. For Tb, the emissions at 492 nm, 544 nm, 586 nm and 620 nm correspond to the transitions from  ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$ ,  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ ,  ${}^{5}D_{4} \rightarrow {}^{7}F_{4}$  and

 ${}^{5}D_{4} \rightarrow {}^{7}F_{3}$  respectively, with the strongest emission located at 544 nm. For Eu, the emission at 590 nm corresponds to the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  and 617 nm corresponds to the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition with the strongest emission located at 617 nm. The luminescence from Tb and Eu occurred due to the energy transfer from Tp ligand rather than the formic acid axial ligand, because in formic acid there is no antenna present to absorb energy from the system. The  $\pi$ - $\pi$ \* emission in the ligand region was weak, and indicates that there was a good energy transfer from the ligand to the metal. Figure 3.33 shows the UV-visible spectra of the [Tp<sub>2</sub>Tb(formate)] complex and formic acid and Figure 3.34. shows the emission spectrum of the [Tp<sub>2</sub>Tb(formate)] complex.







Figure 3.34.Emission spectrum of [Tp<sub>2</sub>Tb(formate)]

**3.7.2. Optical studies of [Tp<sub>2</sub>Ln(malate)] complexes (Ln = Tb, Eu)** The UV-visible spectrum of malic acid showed a maximum absorption at 260 nm and the [Tp<sub>2</sub>Ln(malate)] complexes showed a maximum absorption at 230 nm. The excitation spectrum (Figure 3.35) shows a maximum intensity at 260 nm. So in these complexes the malic acid axial ligand played a greater role in transfer energy to the metal than the Tp ligand. The emission spectra (Figure 3.36) show characteristic emission of Tb and Eu when excited at 260 nm. The ligand region emission is stronger, so for in this complex system, intersystem crossing was not fast enough to transfer the energy to the metal efficiently.



Figure 3.35. Excitation spectra of [Tp2Eu(malate)]



Figure 3.36. Emission spectra of (a),[Tp<sub>2</sub>Tb(malate)], (b), [Tp<sub>2</sub>Eu(malate)]

3.7.3. Optical studies of [Tp<sub>2</sub>Ln(toluate)] complexes (Ln = Tb, Eu) In these toluate complexes, the maximum peak in the excitation spectrum was at 285 nm and corresponded to the  $\pi$ - $\pi$ \* transition of the *p*-toluate ligand. The UV-visible spectra of *p*-toluic acid showed an absorption in between 275-290 nm. The excitation spectra (Figure 3.37) of these toluate complexes were red shifted compared to malate and formate complexes. This was due to the delocalisation of the electrons on phenyl ring in *p*-toluic acid. Excitation at 285 nm led to the characteristic emission (Figure 3.37) from Tb and Eu metals. The emission from Tb was observable because the triplet level of the ligand was not lower than the Tb emissive level as in the cinnamate complexes [Tp<sub>2</sub>Ln(cin)] and [(Tp-R)<sub>2</sub>Ln(cin)]. In the toluate complexes the absorption was blue shifted (285 nm) compared to [Tp<sub>2</sub>Ln(cin)] (320 nm) and [(Tp-R)<sub>2</sub>Ln(cin)] (326 nm) complexes. So in the case of the toluate complexes, Tb emissive level is able to accept triplet level energy from the toluate ligand. The  $\pi$ - $\pi$ \* emission was weak, which indicated that the *p*-toluate ligand acted as a good antenna for these metal complexes.



Figure 3.37. (a) Excitation spectra of  $[Tp_2Tb(toluate)]$ , (b) Emission spectra of  $[Tp_2Tb(toluate)]$ 

## 3.7.4 NIR emission studies of [Tp<sub>2</sub>Ln(toluate)], [Tp<sub>2</sub>Ln(formate)] and [Tp<sub>2</sub>Ln(malate)] complexes

NIR studies were also carried out on [Tp2Er(toluate)], [Tp2Er(formate)] [Tp<sub>2</sub>Ln(malate)], [Tp<sub>2</sub>Yb(malate)], [Tp<sub>2</sub>Yb(toluate)] and [Tp<sub>2</sub>Yb(formate)] complexes. All these complexes showed the characteristic emission of the corresponding metals. For example, [Tp2Er(toluate)], [Tp2Er(formate)] and [Tp2Er(malate)] complexes showed the characteristic emission of Er at 1540 nm corresponding to the  ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$  transition when excited at 520 nm. Yb malate, formate and toluate complexes also showed the characteristic emission of Yb at 980 nm, corresponding to the  ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$  transition for Yb directly excited at 920 nm. The luminescence life-times of when [Tp<sub>2</sub>Yb(malate)], [Tp<sub>2</sub>Er(malate)], and [Tp<sub>2</sub>Er(toluate)], [Tp<sub>2</sub>Yb(toluate)]. complexes were in the microsecond region. Toluate complexes showed longer life-times compared to the malate complexes. This is due to the presence of electron- withdrawing group (COO<sup>-</sup>) on the phenyl ring which will increase the distance between the metal and C-H bonds in toluic acid. The microsecond life-times were due to the presence of CH oscillators which would increase the emission quenching. Measured luminescence life-times for these complexes are shown in Table 3.8.



Figure 3.37. Emission spectra of (a), [Tp<sub>2</sub>Yb(malate)], (b), [Tp<sub>2</sub>Yb(toluate)]

Luminescence life times
μs
0.5
0.98
1.7
6.3

Table 3.8. Luminescence life time for malate and toluate complexes



Figure 3.38.Luminescence decay curve of [Tp2Er(toluate)]



Figure 3.39.Luminescence decay curve of [Tp<sub>2</sub>Yb(toluate)]

#### 3.8. Conclusion

### a. [Tp2Ln(cin)] and [Tp2Ln (crot)]complexes

The studies of these complexes showed that both cinnamate and crotonate complexes showed the characteristic emission for Eu<sup>3+</sup> metal. But the emission properties for Sm<sup>3+</sup>, Dy<sup>3+</sup>and Tb<sup>3+</sup> were limited, and they showed emission only from the crotonate complexes. In both complexes the coligands

(crotonate, cinnamate) involved a more major role for absorbing energy from the system compared to Tp ligand. The emission intensities of cinnamate complexes were higher than those of crotonate complexes. Solvents played a key role in the luminescence properties of the metal complexes. Complexes showed higher luminescence intensity in solid substrate than in the solution. Also Yb, Nd and Er showed their characteristic emissions from their cinnamate and crotonate complexes, by direct excitation of the metal ions. Eu and Tb crotonates and cinnamates showed luminescence life-times in the millisecond region, compared to the microsecond region for the NIR emitters, because the NIR emitters were more sensitive to CH oscillator quenching than the visible emitters.

#### b. Substituted Tp complexes

The Europium cinnamate [(Tp-R)<sub>2</sub>Eu(cin)] and Europium crotonate [(Tp-R)<sub>2</sub>Eu(crot)] complexes showed the characteristic emission of Eu and their emission intensity depended on the the substituent present on the Tp ligand, which were in the order thiophene > Ar-OMe > Ar > Ar-Me. The relative intensity was higher in cinnamate complexes than in crotonate complexes. In the case of the Tb complexes, only the crotonate derivative showed the characteristic emission of Tb<sup>3+</sup> metal. The emission intensity of the Tb<sup>3+</sup> complexes was higher than that of the Eu<sup>3+</sup> complexes. For all these complexes, the  $\pi$ - $\pi$ \* emission intensity of the ligand was weak, which means that intersystem crossing from the ligand to the metal was fast. The cinnamate and crotonate absorption regions of all these complexes were red-shifted due to the presence of the substituent group in the Tp ligand. The relative emission intensity of the cinnamate complexes was higher than that of the presence of the substituent group in the Tp ligand. The relative emission intensity of the cinnamate complexes was higher than that of the presence of the substituent group in the Tp ligand. The relative emission intensity of the cinnamate complexes was higher than that of the presence of the cinnamate complexes was higher than that of the presence of the cinnamate complexes was higher than that of the presence of the cinnamate complexes was higher than that of the presence of the cinnamate complexes was higher than that of the presence of the cinnamate complexes was higher than that of the presence of the cinnamate complexes was higher than that of the presence of the cinnamate complexes was higher than that of the presence of the cinnamate complexes was higher than that of the presence of the cinnamate complexes was higher than that of the presence of the cinnamate complexes was higher than that of the presence of the cinnamate complexes was higher than that of the cinnamate complexes.

## c. $[Tp_2Ln(malate)], [Tp_2Ln(toluate)], [Tp_2Ln(formate)] complexes$

All these complexes showed the characteristic emission of Eu, Tb, Yb, Nd, Er metals. Emission intensities of the metal ions from the toluate complexes were higher than their corresponding malate and formate complexes. This was due

to the presence of the COO<sup>-</sup> group present on the phenyl ring. In the formate complexes, the Tp ligand acted as an antenna to transfer energy to the Eu and Tb ions. NIR emitters showed life-times in the microsecond region and the measured life time were higher in the toluate complexes.

#### 3.9. References

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# **Chapter 4**

# Copolymerisation of lanthanide complexes

This chapter describes the copolymerisation of the lanthanide complex monomers with styrene or MMA (Methyl methacrylate) monomer and also the luminescent properties of lanthanide complexes in copolymers and polymer blends.

Luminescent lanthanide metal complexes have been intensively studied due to their applications in luminescence devices and as laser materials. Due to their sharp emission bands and their potentially high internal quantum efficiencies lanthanide complexes have attracted considerable attention for organic electroluminescent (EL) devices as well as optical micro cavity emitters. There are three major problems in using lanthanide complexes. Firstly the lanthanide complexes are unstable in organic solution and tend to dissociate into other complex forms. Secondly most of the lanthanide complexes usually contain coordinated water molecules, leading to low luminescence quantum efficiency because the coordinated water molecules can effectively quench the luminescence by means of O-H oscillators. Thirdly it is often not possible to form vacuum-vapour deposited films due to the nonvolatile nature of lanthanide complexes.

Lanthanide metal-containing polymers have attracted considerable attention in the past decade due to the advantages of both the luminescence charecteristics of lanthanide ions and the material properties of plastics<sup>1</sup>. In polymer based lanthanide luminescent materials, any dissociation may be minimal.<sup>1-3</sup> Okamato<sup>4</sup> and co-workers have synthesised a series of lanthanide metal-containing polymers and studied their luminescence properties, even demonstrating the probability of laser action. However, most lanthanide metal containing polymers so far are prepared by the direct blending of polymers with lanthanide metal complexes.<sup>5</sup> This method, however, increases the complexity of synthesis and limits the choice of coordination ligands that can be attached to the polymer chain, this makes the use of polymer luminophores uneconomical. One of the approaches for addressing this problem is to prepare lanthanide complex monomers with conventional monomers like styrene or MMA. In this work we aimed to synthesise a lanthanide complex containing polymerisation activity and the luminescence property using hydrotris (pyrazolyl)borate, Tb<sup>3+</sup> or Eu<sup>3+</sup> ion in conjunction with the crotonic acid or cinnamic acid as co-ligands. In the following steps highly fluorescent lanthanide containing polymers are synthesised through the copolymerisation of the complex with either styrene or MMA (methyl methacrylate) monomers.

#### 4.1. Copolymerisation

The copolymerisation reactions of crotonate complexes  $[Tp_2Ln(crot)]$  (Ln = Eu, Tb) were performed with styrene and MMA monomers and cinnamate complexes  $[Tp_2Eu(cin)]$  with styrene or MMA monomers. For cinnamate complexes, copolymerisation was performed with Eu<sup>3+</sup> complexes only because, from the luminescence studies we knew that only the europium cinnamate complexes show emission.

#### 4.1.1. Copolymerisation reactions of crotonate complexes [Tp<sub>2</sub>Ln(crot)] (Ln = Eu, Tb) with styrene or MMA

synthesised through  $Tb^{3+}$ complexes first Eu<sup>3+</sup> copolymer and crotonate complexes with of corresponding metal copolymerisation methylmethacrylate or styrene. The synthetic route of crotonate complexes with styrene or MMA were shown in Scheme 4.1. Copolymer 1a and Copolymer 1b represent polymerisation with styrene and Copolymer 2a and Copolymer 2b with MMA.





Schemes 4.1. Copolymerisation reactions

The copolymers were prepared by the radical polymerisation of the corresponding complex monomers with styrene or MMA with AIBN as intiator

and DMSO as solvent. Under these conditions homo polymerisation will occur, the free-radical polymerisation mechanism of styrene with AIBN was shown in Figure 4.1. The ratio of the complex monomers to styrene or MMA monomers were in the range 5-20 wt%. The copolymers were fully soluble in THF and chloroform. The number-average molecular weight ( $M_n$ ) and the polydispersity indices of the resulting polymers were measured by gel permeation chromatography (GPC) using THF as eluent and polystyrene as standard and the data obtained were shown in Table 2.1. Europium and terbium metal contents were measured by ICP-MS analysis. Concentrated HCI and HNO<sub>3</sub> (1:1) were used, to decompose the polymer samples before performing the ICP analysis. The metal contents in the copolymers were in the range 0.09 - 2.51 wt%

Polymer	Monomer/ Metal complex-monomer (wt%)	Ln(%)	M <sub>n</sub>	PDI
Copolymer <b>1a</b>	Styrene / [Tp <sub>2</sub> Eu(crot)](15)	0.82	67500	4.31
Copolymer 1b	Styrene / [Tp <sub>2</sub> Tb(crot)] (15)	1.72	56300	5.62
Copolymer 2a	MMA / [Tp <sub>2</sub> Eu(crot)] (15)	1.72	62900	5.21
Copolymer 2b	MMA / [Tp <sub>2</sub> Tb(crot)] (15)	1.33	60100	4.79

#### Table 4.1.

It is possible for the metal complex monomer to homopolymerize, copolymerize, or not polymerize in the attempted copolymerization of this complex with styrene or MMA. Self polymerisation of metal-complex monomer is very low in this metal complex monomer/ styrene and metal complex / MMA system because, the ratio of the metal-complex monomers are much smaller than that of styrene and MMA monomer. If the complex had been simply mixed or blended in the PS matrix, the high amount of the complex should have been detectable by an analysis of the europium content in methanol after the purification or precipitation of the copolymer because the unbound metal complex dissolved well in methanol. This is not seen. Therefore the complex is indeed copolymerized with styrene or MMA monomer, leading to a stable copolymer that prevented the metal complex from being leached out.





Figure 4.1. Free radical polymerisation mechanism

Chapter 4. Copolymerisation of lanthanide complexes and their luminescence properties in copolymers, polymer blends

The structures of the copolymers with styrene monomers are confirmed by FT-IR and UV-visible. Figure 4.2 shows that the initial IR spectrum of the copolymer and is similar to that of polystyrene homopolymer (PS), except for several weak characteristic absorptions of the complex. This suggests that the IR spectrum of the copolymer mostly reflected the characteristic absorptions of the PS structure when the metal complex content is very low. The typical anti-symmetric and symmetric stretching vibrations of carboxylate at 1570 cm<sup>-1</sup> and 1430 cm<sup>-1</sup> could not be well identified. These bands are probably buried under the aromatic ring vibrations. C-H bending vibrations of

PS are shifted 1600, 1582, 1492, cm<sup>-1</sup> because of the low content of the complex monomer.



Figure 4.2. IR spectrum for (a), polystyrene (b), copolymer 1a

The above results suggested that, with one of the coordinated ligands linked to the polymer chains directly, the complex monomer moiety is fairly uniformly dispersed in PMMA or PS matrices, which is important in optical applications. Figure 4.3 shows the UV absorption spectra of copolymer **2b**, polystyrene and PMMA. The absorption spectra of different polymer complexes are very similar. Copolymer **2b** shows a maximum absorption at 245 nm, this is due to the absorption of PMMA. Another absorption at 285 nm is due to the

absorption of the crotonate ligand. In the case of copolymer **1a** and copolymer **1b**, the absorption due to crotonate ligand at 270 nm is buried under the phenyl  $\pi$ - $\pi$ \* absorption of PS at 265-276 nm.



Figure 4.3. UV-visible spectra of (a),Copolymer 2b (Tb content = 2.51 wt%), (b), PMMA, Polystyrene

#### 4.1.2. Luminescence properties of crotonate copolymers

Figure 4.4.shows the excitation spectrum of copolymer 2b and Figure 4.5 shows the emission spectra of copolymers 2a and 2b. The excitation spectra of copolymers 1a, 1b and 2a show absorptions similar to 2b. All the copolymers show maximum absorption at 270 nm, due to the absorption by

the crotonate ligand. The excitation spectra also contain the absorptions of PMMA and PS , and it suggests that the emission of Eu<sup>3+</sup> and Tb<sup>3+</sup> in the copolymer are sensitized not only by the crotonate ligand but also by the polymer absorptions at 240-260 nm. The emission spectra of copolymers obtained by the excitation at 270 nm do not show any significant differences and all exhibit ligand-sensitized emission typical of the corresponding metals in copolymer.



Figure 4.4. Excitation spectrum of copolymer 2a





Figure 4.5. Emission spectrum of (a), copolymer 2b, (b), copolymer 2a

When excited at 270 nm, the Tb copolymers (**1b** and **2b**) show characteristic emissions at 492 nm, 544 nm, 586 nm, 620 nm corresponding to  ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$ ,  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ ,  ${}^{5}D_{4} \rightarrow {}^{7}F_{4}$ ,  ${}^{5}D_{4} \rightarrow {}^{7}F_{3}$  transitions respectively with the strongest emission located at 544 nm. For the Eu containing copolymers, the emission at 590 nm corresponds to the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  and 617 nm corresponds to  ${}^{5}D_{0} \rightarrow$  ${}^{7}F_{2}$  transition with the strongest emission located at 617 nm. The emission intensities of the Tb<sup>3+</sup> and Eu<sup>3+</sup> ions are greatly enhanced upon copolymerisation. The emission intensity of copolymer **1a** at Eu content 5 wt% is about five times than that of the complex monomer at 270 nm excitation. The binding site of both complex monomer and the copolymer is similar. The only difference between the copolymers and complex monomer is that in
copolymers, the metal complex molecule links to the polymer main chains and is uniformly dispersed in the polymer matrices. Under this condition the mean distance between the two metal ions (Eu<sup>3+</sup>-Eu<sup>3+</sup>) may be larger than that of the complex. The large distance between metal complex moieties in the copolymer means that all intermolecular energy transfer processes would be slow, and as a result a greater part of the excitation is transferred to the metal ion under UV irradiation.

Figure 4.6a shows the excitation spectrum of the Tb copolymer (**1b**) at various concentrations and the excitation intensity is maximum when the concentration of the copolymer reaches 0.03 mol% and it shows the maximum absorption at 270 nm.The excitation spectra (Figure 4.6b) of Eu copolymer (**1a**) has a similar feature i.e, it also shows the maximum excitation intensity, at a concentration of 0.03 mol%. But the excitation spectrum is broadened compared to the Tb copolymer.







Figure 4.6 b . Excitation spectra of copolymer 1a with various concentrations

Figure 4.7.shows the emission spectra of the Tb copolymer (**1b**) at different concentrations when excited at 270 nm and it shows that the when concentration increases, the emission intensity increases and then the intensity starts to decline at higher concentration, and it shows that the metal emission quenched at higher concentration. The Eu copolymer (**1a**) also shows the same feature as Tb in higher concentration.







Figure 4.8. shows the emission intensity comparison of copolymer **2a** and copolymer **2b** at different metal concentrations. Copolymer **2b** shows a steady increase in intensity with concentration, reaching a maximum at 0.03 mol%. For Eu<sup>3+</sup>, there is very slow increase in intensity when the concentration is increased, and it reaches a maximum at 0.03 mol% then decreases. The

emission intensity of Tb copolymers in styrene or MMA is higher compared to Eu copolymers when excited at 270 nm. This is due to the fact that the triplet energy level of the ligand is higher compared to the Eu<sup>3+</sup> emissive level so a sufficient amount of triplet energy transfer only occurs in Tb metal.



Figure 4.8.Emission intensity comparison of coplolymer **2a** and **2b** at different concentrations

#### 4.2. Comparison of luminescence properties of copolymers and metal complex / polymer blends

The luminescence properties of the metal complex / polystyrene blends or metal complex / PMMA blends directly obtained by stirring complex monomer in polystyrene or complex monomer in PMMA in CHCl<sub>3</sub> were investigated. The excitation and emission spectra of all the samples in the solution and solid state were measured at room temperature. In the excitation spectra of the blends, the maximum absorption shows at 270 nm, same as the copolymers. When these blends are excited at 270 nm the characteristic emission of Tb and Eu obtained. The emission intensities of Eu copolymer (**2a**) and Eu crotonate complex / PMMA blend films with the different Eu content are shown in Figure 4.9. In the Eu crotonate complex / PMMA blends, the emission intensity increases with Eu content and reaches its maximum at 1.6 mol % and then exhibits emission quenching on further increase in Eu concentration. This quenching phenomenon may be caused by the deactivation of the  ${}^5D_0$  state through the electropolar multipolar interaction or by the exciton migration via the Forster dipole-dipole mechanism in solid

complexes.<sup>6,7</sup> When the content of Eu dopant in the PMMA matrix is small, the probability of energy migration via diffusional collision of Eu complexes will be small but at higher metal content, the aggregation of the complex often occurs. In the case of copolymers the emission intensity increases linearly with increasing Eu content up to 2.2 mol%. In the case of copolymers the Eu complexes units are uniformly dispersed in the polymer backbone and are surrounded by the polymer chain. This structure reduces the ligand interaction and decreases the excitation migration,<sup>8,9</sup> which results in the decreases of the emission concentration quenching.



Figure 4.9.Luminescence quenching of copolymer **2a** and Eu crotonate complex / PMMA blends in different concentrations

### 4.3. Copolymerisation reactions of europium cinnamate complexes [Tp<sub>2</sub>Eu(cin)] with styrene or MMA

The copolymerisation reaction of Eu cinnamate complexes with styrene or MMA is similar to that of crotonate complexes (Scheme 4.2). The reaction ratios of the complex monomers to styrene or MMA monomers are in the range 5-20 wt%. The resulting copolymer is fully soluble in THF and chloroform. The number-average molecular weight (M<sub>n</sub>) and the polydispersity indices of the resulting polymers were measured by gel permeation chromatography (GPC) using THF as eluent and polystyrene as standard. The data was summarised in Table 4.2.



Scheme 4.2 Copolymerisation reaction

Copolymer	Monomer / metal complex monomer(wt%)	Eu%	M <sub>n</sub>	PDI
Copolymer 3	Styrene / [Tp <sub>2</sub> Eu(cin)] (10%)	1.32	592000	4.92
Copolymer 4	MMA / [Tp <sub>2</sub> Eu(cin)] (10%)	1.53	524000	5.62

Table 4.2.

The FT-IR spectra of the copolymers are quite similar to that of PMMA or PS. For example, the IR spectrum of copolymer **4** looks similar to PMMA as the content of the Eu-complex moiety in the copolymer is low. The C=O and C=C stretching vibrations of cinnamic acid in the copolymer are observed at 1615 and 1543 cm<sup>-1</sup> respectively.

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Figure 4.10. shows the UV absorption spectra of polystyrene (PS) and copolymer **3** in THF solutions. The absorption spectrum of copolymer **3** is very similar to polystyrene and exhibited a superposition of absorption bands characteristic of the Eu cinnamate complex and PS. Copolymer 3 has an intense absorption band at 262 nm, due to the  $\pi$ -electron transition of the phenyl group in the styrene. The absorption edge starts at 320 nm and is due to the cinnamic acid absorption in the Eu cinnamate complex, but this absorption is small due to the low Eu content in the copolymer. All these experimental results confirmed that the complex monomer in copolymer 3 brought stable coordination and indeed copolymerized with styrene instead of being simply blended in PS. The UV-visible spectrum of copolymer 4 shows the maximum absorption at 242 nm which is due to the PMMA absorption and a small absorption at 320 nm corresponding to the cinnamic acid absorption region. The FT-IR and UV-visible absorption spectra revealed that the Eu cinnamate complex monomer moieties are directly bonded to the polymer backbone as an integrated unit and that the dissociation of cinnamic acid and Tp ligand is negligible during the copolymerisation and purification process.



Figure.4.10. UV-visible Spectra of (a), Polystrene, (b), Copolymer 3

## 4.3.1. Luminescence properties of Eu cinnamate containing copolymers

The excitation and emission spectra of copolymers 3 (Figure 4.11) and 4 (Figure 4.12) in THF solution and in the solid state were measured at room temperature. The solid state spectra of the copolymers were obtained by spin coating onto a quartz substrate. The excitation spectrum of the copolymers was obtained by monitoring the emission of Eu<sup>3+</sup> ions at 615 nm. The excitation spectrum of copolymer 3 shows the maximum intensity at 258 nm and this is due to the  $\pi$ -electron transition of the phenyl group of the styrene moiety and there is a small absorption at 298 nm which is due to the absorption of cinnamate ligand in the Eu cinnamate complex. When the Eu content is increased the absorption at 258 nm decreases and there is an increase in absorption at 298-315 nm. Similar features are present in the excitation spectrum of copolymer 4; when excited at 320 nm characteristic emission from the Eu occurred at 592 nm ( ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ ) and at 617 nm ( ${}^{5}D_{0} \rightarrow$ <sup>7</sup>F<sub>2</sub>) in both copolymers. The emission intensity increases steadily with increasing Eu content up to 0.04 mol% and then started to decrease due to the interaction between Eu<sup>3+</sup>ions.





Figure 4.11. Excitation spectra of (a), Polystyrene, (b), Copolymer 3



Figure 4.12. (a), Emission spectrum of copolymer 4, (b), Excitation spectrum of copolymer 4

The emission spectra of the Eu containing copolymers in both the solution and solid state are similar to the corresponding Eu-complex monomers. Emission at 617 nm ( ${}^5D_0 \rightarrow {}^7F_2$ ) is the strongest, suggesting low symmetry around the Eu ion in the Eu-copolymer and the complex monomer. It is more interesting to note that the emission intensities of the copolymers both in solution and soild state are much higher than that of the corresponding Eu cinnamate monomer with the same Eu content. The improvement of the luminescence properties of Eu ions in the Eu-copolymer may be due to the special chemical environment of the Eu-complex units in the polymers. In the polymerisation process the self polymerisation of the Eu-complex monomer is very unlikely to happen because the reaction ratio of the Eu-complex monomer to styrene or MMA is small. In this system the copolymer may be a block copolymer consisting of several successive styrene moieties and the Eu-complex moiety. These cinnamate containing copolymers show higher

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emission intensity than Eu crotonate containing copolymers. The reason is that the triplet energy level of the cinnamate ligand is at 480 nm and is slightly above the europium emissive level but for the crotonate ligand the triplet state energy level is 320 nm and it is at higher energy than the europium emissive state. Figure 4.13 shows the relationship between fluorescence intensity and Eu<sup>3+</sup> content in copolymers 3 and 4. Both copolymers show fluorescence quenching, with the former being more efficient. In copolymer 4 the emission intensity increases with increasing the Eu content and reaches a maximum at 5.3 mol%. Copolymer 3 showed the maximum fluorescence intensity at 4.2 mol%. This phenomenon suggests that ligand exciton migration is favoured when ligand coupling caused by coloumb electrostatic interactions is strong. An exciton migration process that competes with the ligand-to-metal energy transfer process is negligible in low Eu content polymer complexes, but becomes prevalent with increasing Eu content.<sup>10-13</sup> It is the energy migration process, along or across polymer chains, that enhances the probability that the excitation will encounter a quencher and consequently causes Eu emission quenching.



Figure 4.13. Emission quenching behaviour of copolymer 4 and copolymer 3

Blends of Eu cinnamate complex monomer with polystyrene or PMMA (Eu cinnamate / PS or Eu cinnamate / PMMA) show quick concentration quenching compared to their corresponding copolymers. It reveals that the copolymer system reduces the ligand interaction and decreases the exciton

migration, which results in a decrease of the emission concentration quenching.

#### 4.4. Thermal properties of the copolymers

The thermal stability of the copolymers was evaluated by TGA under a nitrogen atmosphere. Copolymers with different metal contents are expected to have similar thermal stability. Copolymers exhibited relatively good thermal stability compared with PS or PMMA. Figure 4.14 shows that the initial decomposition temperature of the copolymer **1b** is at 300 °C which is higher than that of PS. The slight increase in the decomposition temperature suggested that the complex structure improved the stability of the copolymers. This is possibly because Tb<sup>3+</sup> in copolymer **1b** created crosslinking due to the coordination effect and induced intramolecular or intermolecular association.<sup>14</sup> Copolymer **1b** decomposed sharply in the range 460-470 °C and decomposition possibly occured in the structure units of styrene. There is no weight loss at 300 °C, but in complex monomer, which began to lose weight at 300 °C and it suggests that the stability of the complex structure units is increased after it is incorporated into polymer chains. Copolymer **1a** also shows good thermal stability compared to polystyrene.



Figure 4.14. TGA of [Tp<sub>2</sub>Ln(crot)], polystyrene, copolymer **1b** (Tb content =1.72%).

Copolymers **2a** and **2b** also exhibited relatively good thermal stability compared with PMMA (Figure 4.15.). The glass transition temperatures  $T_g$  of the copolymers **2a** and **2b** are in the range 118-121 °C and 300-350 °C, both of which are higher than that of PMMA. This result indicates that the thermal stability of the copolymers can be enhanced through introducing metal complex moieties into the polymer chains. Since  $Ln^{3+}$  ions are quite large they might crosslink the chains through intra- and intermolecular coordination with the carbonyl oxygen of the MMA unit. This leads to the restriction of chain mobility of the polymers to enhance the  $T_g$  values.



Figure 4.15. TGA of [Tp<sub>2</sub>Ln(crot)], PMMA, copolymer **2b** (Tb content = 1.33%)

Copolymers 3 and 4 also exhibit good thermal stability (Figure 4.16).





Figure 4.16. TGA of [Tp<sub>2</sub>Eu(cin)], PMMA, Copolymer 4 (Eu content = 1.53%)

#### 4.5. Conclusion

The copolymers in our system exhibit intense fluorescence even at low metal content. These copolymers could be cast into thin films with good thermal and moisture stability which is important in optical applications. The copolymer system helped to reduce the concentration quenching compared to corresponding metal complex / polymer blend system. The thermal stability of the complex monomers were increased by incorporating them into polymer chains.

#### 4.6.References

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# **Chapter 5** Polyphenylene Vinylene (PPV)

This chapter describes the synthesis and emission properties of poly(p-phenylene vinylene) (PPV) and its emission properties when blended in lanthanide complexes.

#### 5.1. Poly(*p*-phenylene vinylene) (PPV)

Poly(*p*-phenylene vinylene) (PPV) is one of the most promising organic materials for opto-electronic devices due to the chemical tunability and good processability of the prepolymer. The conjugated  $\pi$ -electron system of PPV is responsible for its outstanding nonlinear optical and electrical properties. Since the discovery that PPV shows electroluminescence (EL)<sup>1</sup> if sandwiched between a hole injecting contact (ITO) and an electron-injecting contact (e.g. AI, Ca), considerable research has been done to improve the properties of these light emitting diodes (LEDs).<sup>2</sup>

This chapter describes work done to achieve high PL efficiencies by optimising the conversion of the prepolymer to the conjugated polymer PPV, in order to get the best conditions for the elimination process.

Synthesis of the monomer *p*-xylene-bis(diethyl-sulfonium chloride) was achieved by reacting  $\alpha, \alpha,$ '-dichloro-*p*-xylene at a concentration of 0.75 M with excess diethyl sulphide (2.25 M) at 50 ° C in a methanol / water (80:20) solution for 20 h.<sup>3</sup> This monomer (Figure 5.1) was purified by concentrating the reaction solution and precipitating the product in cold acetone (0 °C), followed by filtration and extensive vacuum drying. The monomer was characterised by <sup>1</sup>H NMR and <sup>13</sup>C NMR (Figure 5.2.).



Figure 5.1. p-Xylene-bis(diethyl sulfonium chloride) monomer

In the <sup>1</sup>H NMR spectrum<sup>4</sup> the peak at 1.34 ppm represents the methyl protons, the signal at 3.20 ppm represents the CH<sub>2</sub> protons in diethyl sulphide and the one at 7.53 ppm represents the aromatic-H nuclei. In the <sup>13</sup>C

NMR spectrum the CH<sub>3</sub> peaks are located at 15.77 ppm, CH<sub>2</sub> carbon peaks at 40.67 and 49.65 ppm and the aromatic carbons at 136.9 ppm and 139.19 ppm.The reaction to form the p-xylene-bis(diethyl sulfonium chloride) precursor polymer is effected in aqueous solution by the reaction of the monomer with an equi-molar quantity of sodium hydroxide (0.2 M) at 0 °C for 1 h under nitrogen. The reaction is quenched by addition of 1 M HCI to give a solution of pH 6 which yielded a highly viscous yellow solution. The polyelectrolyte is separated from residual monomer and NaOH by dialysis against deionized water for 3 days and the solution is tested against silver nitrate solution until there is no precipitate of AgCI. A small quantity of precursor polymer is wet cast into a free standing film by evaporation of water at or below room temperature and the precursor is kept in the refrigerator to avoid elimination of diethyl sulfide. Simple heating of the polyelectrolyte film resulted in an E1CB elimination of the diethyl sulfide yielding a yellow free standing film of PPV. The length of time and the temperature at which the film is annealed could be varied to control the extent of this elimination and hence the amount of unsaturation induced in the polymer. To obtain maximum elimination the films are annealed at temperatures greater than 300 °C. The synthetic scheme of the PPV is shown in Figure 5.3<sup>3</sup> and a possible mechanism of the reaction is shown in Figure 5.4.4





Figure 5.2.<sup>1</sup>H NMR and <sup>13</sup>C NMR of PPV monomer



Figure 5.3. Synthesis of PPV



Figure 5.4. Possible mechanism for the formation of PPV

The mechanism shows that the principal reaction involved in the formation of PPV is the elimination of diethyl sulphide and HCl, while an alternative undesirable reaction involves the nucleophilic attack of the halide counter- ion on the ethyl group to form ethyl chloride and diethyl sulphide.

There are several points concerning the quality of the polymer. For a 'good' polymer and consequently a stable device not only optimization of the conversion conditions is essential but also the purity of the prepolymer and the film formation process are crucial<sup>5</sup>. Other researchers have commented that oxygen might have a significant influence on the electrical and optical properties of PPV. One expects that oxygen might lead to carbonyl defects on the polymer chain, thus interrupting the conjugation. These defects can either be created *via* the synthesis of the prepolymer or during the conversion process. Several attempts have been made to reduce these problems. Hudson *et al.* <sup>6</sup> investigated the treatment of prepolymer films under different gases. The best results were obtained with gas 85% N<sub>2</sub>, 15% H<sub>2</sub>. However, even under these extremely pure conditions, they observed a carbonyl stretching band at 1690 cm<sup>-1</sup>. This carbonyl acts as a quenching site for PL and strongly affects the PL life time.

Figure 5.5 shows the AT-IR spectra of partially eliminated PPV film heated at 80 °C for 8 h and 180 °C for 8 h under vacuum respectively. All characteristic IR- active bands of fully converted PPV are clearly seen. The spectrum of a precursor polymer treated at 180 °C<sup>3</sup> shows the characteristic vinyl peak at 3016 cm<sup>-1</sup> and the absorbance value of this peak is higher compared to the sample heated at 80 °C, indicating that higher temperature increases the degree of elimination. However, both spectra show a sp<sup>3</sup> CH peak at

2924 cm<sup>-1</sup>, and this means that the elimination is not yet completed. The strong absorbance at 962 cm<sup>-1</sup> is consistent with the *trans*-CH out-of-plane bending mode, while no absorbance is observed near 630 cm<sup>-1</sup>, where the *cis* CH bending would be expected. Thus the elimination reaction yielded *trans*-PPV exclusively. The most noticeable point, however is that even under these vacuum conditions no carbonyl bands are detectable at 1690 cm<sup>-1</sup>. When temperature increases the elimination process is more favoured and, at

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200 ° C, the vinyl CH absorption is stronger compared to that of the  $CH_2$  peak at 2924 cm<sup>-1</sup>.



Figure 5.5. AT-IR spectra of partially- eliminated PPV. (a), 180 °C for 8 h, (b), 80 °C for 8 h

UV-visible spectra were obtained for the pure polyelectrolyte films and partially eliminated films prepared at different temperatures. The UV spectra for the clear, saturated film (Figure 5.6.) displayed three absorption bands with overlapping maxima associated with the phenyl group  $\lambda$ =198 and 229 nm and the sulfhonium group  $\lambda$  = 265, 270 and 276 nm.<sup>3</sup> As the sulphide was thermally eliminated, the absorption bands broadened and the new bands appeared at longer wavelengths at which point the UV spectrum showed a continuous absorption with an edge centred at 500 nm, indicative of a highly conjugated system (Figure 5.7). As the temperature and time of the elimination procedure increased, the energy gap decreased as shown in Table 5.1.



Figure 5.6. UV-Visible spectrum of free standing film of PPV



Figure 5.7. UV-visible spectra of PPV after heating of the precursor polymer at different temperatures

Energy gap	
3.46 eV	
3.1 eV	
2.75 eV	
2.43 eV	

Table 5.1. Energy gap obtained from UV-Visible absorption spectra of PPV at different elimination conditions

For the preparation of stable and efficient LEDs it is important to have a fully The with photoluminescence efficiency. converted material high photoluminescence properties of the precursor and of partially converted PPV on a quartz substrate were studied. When the PPV precursor is excited at 315 nm it shows the characteristic emission of PPV at 375-500 nm (Figure 5.8). For polymers heated at higher, the emission spectra are red-shifted to 500-600 nm. However, the PL efficiencies for the partially eliminated PPV are reduced, compared to pristine PPV on a quartz substrate (Figure 5.9.). This is taken to result from a more efficient non-radiative decay in the longer conjugated sequences.7



Figure 5.8. Emission of PPV precursor when excited at 315 nm



Figure 5.9. PL of partially eliminated PPV at various temperatures.

The thermalgravimetric analysis (TGA) of PPV (160 ° C, 8 h) showed three transitions at 263 °C, 388 ° C and 554 ° C. The first transition at 263 ° C is related to the thermal elimination of diethyl sulfhide and HCI and the second is due to the elimination of ethyl sulphide (see appendix C). The third thermal transition, seen at 554 ° C,<sup>5</sup> is the result of the degradation reaction of PPV.

#### 5.1.1. Photoluminescence studies of lanthanide complexes blended with PPV

The luminescence properties of europium and terbium crotonate complexes, [Tp<sub>2</sub>Ln(crot)] and europium cinnamate complexes, [Tp<sub>2</sub>Eu(cin)] in the PPV precursor blends were also studied. Europium crotonate and cinnamate complexes showed the characteristic emissions when blended with the PPV precursor.

Films for the luminescence studies were prepared as follows. Firstly the PPV precursor was dissolved in methanol then 0.2 mol % of  $[Tp_2Eu(crot)]$  or  $[Tp_2Eu(cin)]$  in methanol were added. The whole solution was stirred for 30 min after which the solution was coated onto the quartz substrate.

The excitation spectrum of the [Tp<sub>2</sub>Eu(cin)] complex shows (Figure 5.10) a maximum absorption at 316 nm which is the characteristic absorption of the PPV precursor polymer. Excitation at 316 nm<sup>8</sup> resulted in the characteristic emission from europium metal (Figure 5.11). The emission at 590 nm and 619 nm are  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ ,  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transitions respectively.











Figure 5.12. Emission spectrum of of  $[Tp_2Eu(cin)]$  / PPV precursor blends; emission in the PPV region

[Tp2Eu(cin)] / PPV precursor blends with various concentrations of the europium cinnamate complex show quenching of PPV emission and increasing emission from Eu<sup>3+</sup> metal (Figure 5.15 and Figure 5.13). Quenching of the polymer fluorescence and the emergence of the lanthanide emission upon increased lanthanide concentration indicates that energy transfer from the polymer to lanthanide occurs in these polymer blends. Excitation spectra (Figure 5.14) of these blends clearly indicate that PPV absorption is quenched when more europium complex is introduced and it proved that the energy is transferred from PPV to europium metal. Concentrations of the complex in these polymer blends are in the range 0.1-0.4 mol%. [Tp2Eu(crot)] complex in PPV precursor blends also show the similar behaviour as the [Tp2Eu(cin)] complex. When excited at 316 nm these europium crotonate blends show the characteristic emission from Eu. However, there is no characteristic emission from [Tp2Tb(crot)] complex / PPV precursor blends when excited at 316nm. This may be due to the triplet energy level of the PPV being too low compared to the terbium emissive state, so there is no intersystem energy transfer from the PPV to the terbium metal.



Figure 5.13. Emission spectra of the  $[Tp_2Eu(cin)]$  / PPV precursor blends with different concentration of the europium complex



Figure 5.14. Excitation spectra of the  $[Tp_2Eu(cin)] / PPV$  precursor blends in different concentrations of the europium complex



Figure 5.15. Flurosence quenching of PPV by different concentrations of the  $[Tp_2Eu(cin)] / PPV$  precursor blends

#### 5.2. Conclusion

The PPV precursor was successfully converted into PPV. The experiments showed that 180 °C was not sufficient for a complete conversion of our precursor polymer into PPV. Additionally, carbonyl defects were not detectable because the elimination process was carried out under vacuum. PL studies showed that when the temperature increased the emission spectra of partially eliminated PPV were shifted to longer wavelength and the emission intensity decreased with increasing temperature. of  $[Tp_2Eu(cin)]$  and  $[Tp_2Eu(crot)]$  complexes in the PPV precursor blends showed characteristic emission from europium and the emission from PPV was quenched by increasing europium content in these polymer blends. This suggested that energy transfer from polymer to metal occurred. There was no emission from  $[Tp_2Tb(crot)]$  complexes from similar polymer blends.

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# **Chapter 6** Summary and Future work

#### 6.1. Summary

Lanthanide complexes containing hydrotris(pyrazolyl)borate (Tp), crotonate ligand and complexes containing Tp and cinnamate ligand were synthesised in this work. These complexes were characterised by elemental analyses, FT-IR, UV spectroscopy and single crystal X-ray crystallography. For the crotonate and cinnamate complexes, the crystal structure and elemental analyses suggested that, the larger lanthanide complexes were dinuclear in nature [TpLn(crot)<sub>2</sub>]<sub>2</sub>, [TpLn(cin)<sub>2</sub>]<sub>2</sub> (Ln = Ln-Ho) and the smaller lanthanides were mononuclear [Tp<sub>2</sub>Ln(crot)], [Tp<sub>2</sub>Ln(cin)] (Ln = Er-Yb). Thermal analysis of these complexes suggested that they were thermally stable.

Luminescence studies of the crotonate complexes showed that the triplet energy level of the antenna was slightly above the Dy, Sm, Tb and Eu emissive states, so intersystem crossing was possible from the crotonate ligand to Dy, Sm, Eu, Tb and the metals showed their characteristic emission. For cinnamate complexes, the emission occurred only from the europium complex, because the triplet energy level of the antenna (cinnamate) was lower than the Dy, Sm and Tb emissive states and therefore ISC was not possible. The emission intensity of europium in the cinnamate complex was higher than those of the crotonate complexes. The absorption spectra of cinnamate complexes were red-shifted compared to the crotonate complexes. This was due to the delocalisation of electrons in the phenyl ring. NIR emission occurred from Nd, Er and Yb cinnamate and crotonate complexes, and the emission was obtained from the direct excitation of the metals. In our system the Tp, cinnamate, crotonate ligands were absorbing energy in the UV region. For NIR emitters the antenna should absorb energy in the visible region and only then should effective intersystem occur. Luminescence life times of the europium and terbium complexes were in the millisecond range but for the NIR emitters it was in the microsecond range. The luminescence decay time was longer in cinnamate complexes compared to crotonate complexes. In the cinnamate complexes the metal-oxygen bond length was longer than in the crotonate complexes, so luminescence quenching by C-H oscillators was less in the cinnamate complexes.

For the substituted Tp ligands, the cinnamate and crotonate derivatives of Eu complexes showed the characteristic emission of Eu, and their emission intensity depended on the strength of delocalisation of extra substituents present in the Tp ligand, and were in the order thiophene> Ar-OMe> Ar> Ar-Me. Also the relative intensity was higher in the cinnamate complexes than in the crotonate complexes. Both these complexes, cinnamic acid and crotonic acid played a vital role in transfer energy to europium metal. In case of the Tb complexes, only the crotonate derivative showed the characteristic emission from Tb not the cinnamate complexes suggested that the europium toluate and terbium toluate emission is higher than for their cinnamate anologues. This was due to the direct attachment of a COOH group to the phenyl ring so it helped the absorption of the toluate ligand more in the higher energy region compared to cinnamate ligand.

Copolymers containing lanthanide ions (Eu<sup>3+</sup>and Tb<sup>3+</sup>) were prepared via the copolymerisation of the cinnamate and crotonate complexes [Tp2Ln(crot), [Tp<sub>2</sub>Ln(cin)] with styrene and MMA monomer. Semitransparent, luminescent polymer materials with good fluorescence intensity were obtained. The assynthesized materials were further charecterised by means of IR and UV spectra, which indicated that they were copolymers instead of blends. The fluorescence spectra of the copolymers revealed the intense UV absorption characteristics of the lanthanide complex present in the materials. The large distance between two metal complex moieties in the copolymer means that all intermolecular energy transfer processes would be slow and, as a result a much greater part of the excitation was transferred to the metal ion under UV radiation. But when the metal content was increased, quenching of the fluorescence happened. The quenching phenomenon in the copolymer system was weaker compared to the complex/ polymer blends (Eu crotonate/ PMMA blends or Eu crotonate/ PS blends). In the copolymer system, the metal complex units were uniformly dispersed in the polymer backbone and were surrounded by the polymer chains. This special conformation reduced the ligand interaction and decreased the excitation migration, which resulted in a decrease of the probability of emission concentration quenching. The copolymers exhibited relatively good thermal stability compared with PS or

PMMA. This probably occurred because Ln<sup>3+</sup> in the copolymer system created crosslinking due to the coordination effect and induced intramolecular or intermolecular association.

In the PPV polymer, carbonyl defects were not detectable because the elimination process was carried out under vacuum. PL studies showed that when the temperature increased, the emission spectra of partially-eliminated PPV was shifted to longer wavelength and the emission intensity decreased with increasing temperature. Europium crotonate and cinnamate complexes [Tp<sub>2</sub>Ln(crot)], [Tp<sub>2</sub>Ln(cin)], in the PPV precursor blends showed the characteristic emission of europium and the emission from PPV was quenched by increasing the europium content in these polymer blends, suggesting that energy transfer from the polymer to the metal had occurred.

#### 6.2. Future work

Photoluminescence studies of our lanthanide complexes in all the system were successful so that our hydrotris(pyrazolyl)borate lanthanide complexes would be good candidates for LED applications. The copolymers can be cast into thin films with good thermal and moisture stabilities, which is important in optical applications. Photoluminescence studies of the europium complexes in a PPV precursor gave a promising result and this system could be used in polymer light emitting diodes. The construction of a possible EL device is shown in Figure 6.1.<sup>1</sup>





It would be possible to modify the axial ligands by replacing the C-H oscillators with some C-F bonds or C-D bonds in order to increase the

luminescence life-time for near-infrared emtters, there by reducing the emission quenching, and some promising co-ligands are shown in Figure.6.2.<sup>2,3</sup>



Figure 6.2. (a), Penta fluoro benzoic acid, (b), 2-thenoyltrifluoroacetone (TTA)

### 6.3. References

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## Chapter 7 Experimental

## 7. Experimental conditions and instruments used

All reagents were purchased from Aldrich, Lancaster Synthesis or Alfa Aesar and were used without any further purification. All reactions were carried out in air unless otherwise specified.

#### 7.1. Melting points

Melting points were obtained in glass capillaries, measured in GallenKamp apparatus; and are reported uncorrected.

#### 7.2. NMR

NMR spectra were recorded on a Jeol Eclipse 400 NMR spectrometer (400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C) with Jeol Delta version 4.3.6. control and processing software. Chemical shifts were reported in parts per million and referenced to residual solvent proton resonances calibrated against external TMS.

#### 7.3. Mass spectrometry

Mass spectra were run on a Varian 1200L Quadrapole Mass spectrometer by a direct insertion probe and probe PC-1 temperature controller

## 7.4. Infra- red spectroscopy

IR spectra were obtained using KBr discs or NaCl plates using on a PerkinElmer Paragon 1000 FT-IR instrument. The IR spectra of PPV films were obtained using a PerkinElmer Spectrum One FT-IR spectrometer with an ATR attachment.

## 7.5. UV-visible spectroscopy

UV-visible spectra were obtained in DCM,  $CHCl_3$  or MeOH solution unless otherwise stated on a 2x Varian Cary 100 UV-Visible spectrophotometer.

## 7.6. Fluoresence Measurement

Optical studies of lanthanide complexes were conducted using a Perkin -Elmer LS55 spectrometer. Luminescence spectra for lanthanide complexes in the solution state were measured in DCM,  $CHCl_3$  or MeOH unless otherwise specified. Luminescence spectra for lanthanide copolymers were obtained in THF or CHCl<sub>3</sub> solution. Solid state photoluminescence of visible-emitting lanthanide complexes and the lanthanide copolymers was obtained by the spin coating of the material from chloroform solution onto a quartz substrate; spin coating technique was also used for measuring the the photoluminescence of PPV. NIR emission studies of lanthanide complexes were obtained from Queen Mary College, University of London and the experimental set up for NIR studies was shown in Figure 3.12

## 7.7. Elemental analysis

Elemental analyses were determined commercially by MEDAC Ltd.

## 7.8. Gel Permeation Chromatography

Molecular weight and polydispersity indices of the polymers were determined on Perkin Elmer Model LC235 or LC135 instruments. The columns were eluted with THF and calibrated with polystyrene standards. All calibrations and analysis were performed at 25 °C and a flow rate of 1 ml / min.

## 7.9. Thermal Gravimetrical Analysis

The TGA was run on a Mettler TG 851 apparatus. Samples were weighed in aluminium pans and heated up to 600 °C under nitrogen.

## 7.10. X-ray Cystallography

Single-crystal X-ray crystallography data were obtained by sending crystals to University of Southampton, UK. Structure solution and refinement were carried out using the SHELX suite of programmes combined under the Wingx package.

## 7.11. ICP-MS Analysis

ICP-MS analyses of the copolymers were performed on a JY ultima ZC apparatus using 1kW plasma power and a flow of argon gas of 14 L / minute. Concentrated HCI and HNO<sub>3</sub> (1:1) are used, to decompose the polymer samples before performing the ICP analysis.

## 7.12. Experimental section for chapter 2

## 7.12.1. Synthesis of LnCl<sub>3</sub>.nH<sub>2</sub>O

 $Ln_2O_3 + 6$  HCl  $\longrightarrow$   $LnCl_3.nH_2O$ 

The lanthanide chlorides were synthesised by the digestion of lanthanide oxide (6 g) with the minimum quantity of hot concentrated hydrochloric acid solution (12 ml), LnCl<sub>3</sub>.nH<sub>2</sub>O being isolated from the solution on cooling and gentle vacuum desiccation.

## 7.12.2. Synthesis of sodiumhydrotris(pyrazolyl)borate (NaTp)



A mixture of pyrazole (4 mol) and sodium borohydride (1 mol) was heated at 210-220 °C. The reaction was monitored by IR spectroscopy until a single B-H peak was observed. The hot melt was poured into a hot toluene (600 ml), where upon a solid precipitate formed. The mixture was filtered, washed with toluene and hexane to get a white solid, which was then vacuum dried (yield = 65%);  $v_{max}$  (cm<sup>-1</sup>)(KBr) 2439 (B-H stretch); m.p. =188-189 °C.

## 7.12.3. Synthesis of Lanthanide crotonate complexes using NaTp



Crotonic acid (Hcrot, 1.29 g for 15 lanthanides, 0.015 mol)) was neutralised with dilute KOH solution (pH meter) and NaTp (7.98 g for 15 lanthanides, 0.03 mol) added. The whole was transferred quantitatively to a 250 ml volumetric flask made up to the mark with water. This solution (A) was used within 6 h. In a typical procedure, ErCl<sub>3</sub>.6H<sub>2</sub>O (0.3817 g, 0.001 mol) was dissolved in distilled water (5 ml) and solution A (14.98 ml, 0.001mol) titrated directly into this solution from a micro-burette. The resulting solution was stirred for a few minutes and the solid collected by suction filtration. The solid was dried overnight in a vacuum oven at 50 °C, and extracted into dichloromethane (5 ml). A few drops of hexane were floated on this extract, which was covered and set aside to evaporate slowly to obtain crystals.

$$\begin{split} & [\mathsf{Tp}_2\mathsf{Nd}(\mathsf{crot})]: \text{ lilac powder (0.092 g, 14\%), m.p. > 300 °C (Found C, 39.31; H, 3.69; N, 25.33; C_{22}H_{25}B_2N_{12}O_2Nd requires C, 40.29; H, 3.81; N, 25.63; \\ & \upsilon_{max} \, (\mathsf{cm}^{-1})(\mathsf{KBr}) \,\, 2442 \,\, (\mathsf{B}\text{-H stretch}), \, 1660 \,\, (\mathsf{C=O stretch}); \, \delta_{\mathsf{H}} \, (400 \,\, \mathsf{MHz}, \mathsf{CDCl}_3) \\ & 42.1[3 \,\,\mathsf{H}, \,\,\mathsf{s}, \, \mathsf{CH}_3], \, 18.8 \,\, [\mathsf{1H}, \,\,\mathsf{br}, \,\, \mathsf{CH}], \,\, 10.2 \,\, [\,\,\mathsf{1H}, \,\,\mathsf{br}, \,\, \mathsf{CH}], \,\, 3.2 \,\, [\,\,\mathsf{6H}, \,\,\mathsf{br}, \\ & \mathsf{HB}(\mathsf{C}_3\mathsf{N}_2\mathsf{H}_3)_3] \,, \, 1.1 \,\, [\mathsf{6H}, \,\,\mathsf{s}, \,\, \mathsf{HB}(\mathsf{C}_3\mathsf{N}_2\mathsf{H}_3)_3], \,\, -5.7 \,\, [\,\,\mathsf{6H}, \,\,\mathsf{s}, \,\, \mathsf{HB}(\mathsf{C}_3\mathsf{N}_2\mathsf{H}_3)_3]. \end{split}$$

 $[Tp_2Sm(crot)]: yellow powder (0.056 g, 9\%), m.p. > 325 °C (Found C, 38.23; H, 3.66; N, 23.32; C_{22}H_{25}B_2N_{12}O_2Sm requires C, 39.91; H, 3.78; N, 25.40;$  $<math>\upsilon_{max} (cm^{-1})(KBr) 2447 (B-H stretch), 1657 (C=O stretch); \delta_H (400 MHz,CDCI_3) 10.1 [3 H, s, CH_3], 76.4[1H,s, CH] , 37.7 [ 1H, s, CH], 7.9 [6H, s, HB(C_3N_2H_3)_3] , 4.2 [6H, s, HB(C_3N_2H_3)_3] , 3.6 [ 6 H, s, HB(C_3N_2H_3)_3]; m/z 663 (M^+), 574 ({Tp_2Sm}^+), 447 ({TpSm(crot)}^+), 434 ({TpSm(pz)}^+).$  [Tp<sub>2</sub>Eu(crot)]: white powder (0.012 g, 8%), m.p. > 340 °C (Found C, 38.79; H, 3.59; N, 22.93;  $C_{22}H_{25}B_2N_{12}O_2Eu$  requires C, 39.82; H, 3.77; N, 25.34;  $\upsilon_{max}$  (cm<sup>-1</sup>)(KBr) 2450 (B-H stretch), 1657 (C=O stretch);  $\delta_{H}$  (400MHz,CDCl<sub>3</sub>) -18.0 [3 H, s, CH<sub>3</sub>], 90.2 [1H, s, CH], -21.5 [ 1H, s, CH], 10.2 [6H,s, HB(C<sub>3</sub>N<sub>2</sub>H<sub>3</sub>)<sub>3</sub>] 3.2[6H, s, HB(C<sub>3</sub>N<sub>2</sub>H<sub>3</sub>)<sub>3</sub>], 2.6 [6 H, s, HB(C<sub>3</sub>N<sub>2</sub>H<sub>3</sub>)<sub>3</sub>]

 $[Tp_{2}Ho(crot)]: off pink powder (0.023 g, 3\%), m.p. > 300 °C (Found C, 38.87; H, 3.62; N, 24.69; C_{22}H_{25}B_{2}N_{12}O_{2}Ho requires C, 39.05; H, 3.69; N, 24.85;$  $<math>v_{max} (cm^{-1})(KBr) 2454 (B-H stretch), 1655 (C=O stretch); \delta_{H} (400 MHz, CDCI_{3})$   $42.8 [3 H, br, CH_{3}], -67.9 [1H,s, CH], -121.3 [1 H, s, CH], 0.5 [6H, s, br$   $HB(C_{3}N_{2}H_{3})_{3}], 0.4[6H, s, HB(C_{3}N_{2}H_{3})_{3}], -28.2 [6 H, br, HB(C_{3}N_{2}H_{3})_{3}]; m/z 676$   $(M^{+}), 609 (\{M-pz\}^{+}), 591 (\{Tp_{2}Ho\}^{+}), 463 (\{TpHo(crot)\}^{+}), 445(\{TpHo(pz)\}^{+}).$ 

 $[Tp_{2}Er(crot)]: pink powder (0.08 g, 12\%), m.p. > 360 °C (Found C, 38.89; H, 3.65; N, 24.78; C_{22}H_{25}B_{2}N_{12}O_{2}Er requires C, 38.93; H, 3.68; N, 24.71;$  $<math>\upsilon_{max} (cm^{-1})(KBr) 2475 (B-H stretch), 1656 (C=O stretch); \delta_{H} (400 MHz, CDCl_{3}) -1.1 [3 H, s, CH_{3}], -27.3 [1H, br, CH], -57.9 [1 H, br, CH], 33.2 [6H, br, HB(C_{3}N_{2}H_{3})_{3}], -10.8 [6H, br, HB(C_{3}N_{2}H_{3})_{3}], -47.1 [6 H, br, HB(C_{3}N_{2}H_{3})_{3}]; m/z 678 (M^{+}), 610 ({M-pz}^{+}), 592 ({Tp_{2}Er}^{+}), 464 ({TpEr(crot)}^{+}), 446 ({TpEr(pz)}^{+}).$ 

 $[Tp_{2}Lu(crot)]: white powder (0.03 g, 4\%), m.p. > 350 °C (Found C, 37.24; H, 3.61; N, 21.32; C_{22}H_{25}B_2N_{12}O_2Lu requires C, 38.48; H, 3.64; N, 24.49;$  $<math>v_{max} (cm^{-1})(KBr) 2475 (B-H stretch), 1655 (C=O stretch); \delta_{H} (400 MHz, CDCl_3)$   $1.8 [3 H, d, J = 6.8 Hz, CH_3], 6.9 [1H, dq, J = 6.8, 15.7 Hz, CH], 5.9 [1 H, d, J$  $= 15.7 Hz, CH], 7.6 [6 H, d, J = 1.9 Hz, HB(C_3N_2H_3)_3], 6.9 [6 H, d, J = 1.9 Hz , HB(C_3N_2H_3)_3], 5.9 [6 H, t, J = 2 Hz, HB(C_3N_2H_3)_3].$ 

 $\label{eq:started_st$ 

m/z 675 (M<sup>+</sup>), 608 ({M-pz}<sup>+</sup>), 587 ({Tp<sub>2</sub>Dy}<sup>+</sup>), 459 ({TpDy(crot)}<sup>+</sup>), 442 ({TpDy(pz)}<sup>+</sup>).

[Tp<sub>2</sub>Y(crot)]: white powder (0.042 g, 7%), m.p. > 320 °C  $\upsilon_{max}$  (cm<sup>-1</sup>)(KBr) 2475 (B-H stretch), 1655 (C=O stretch);  $\delta_{H}$  (400 MHz,CDCl<sub>3</sub>) 1.8 [3 H, d, *J* = 6.8 Hz, CH<sub>3</sub>], 6.5 [1H, dq, *J* = 6.8, 15.7 Hz, CH], 5.7 [1 H, d, *J* = 15.72 Hz, CH], 7.6 [6 H, d, *J* = 1.94 Hz, HB(C<sub>3</sub>N<sub>2</sub>H<sub>3</sub>)<sub>3</sub>], 7.0 [6 H, d, *J* = 2 Hz, HB(C<sub>3</sub>N<sub>2</sub>H<sub>3</sub>)<sub>3</sub>], 5.9 [ 6 H, t, *J* = 2 Hz, HB(C<sub>3</sub>N<sub>2</sub>H<sub>3</sub>)<sub>3</sub>].

## 7.12.4. Synthesis of Lanthanide cinnamate complexes using NaTp



Cinnamic acid (Hcin, 2.22 g for 15 lanthanides, 0.015 mol) was neutralised with dilute KOH solution (pH meter) and NaTp (7.98 g for 15 lanthanides, 0.03 mol) added. The whole was transferred quantitatively to a 250 ml volumetric flask and made up to the mark with water. The solution (B) was used within 6 h. In a typical procedure, SmCl<sub>3</sub>.6H<sub>2</sub>O (0.3648 g, 0.001 mol) was dissolved in distilled water (5 ml) and solution B (22.77 ml, 0.001) titrated directly into this solution from a micro-burette. The resulting solution was stirred for a few minutes and the solid collected by suction filtration. The solid was dried overnight in a vacuum oven at 50  $^{\circ}$ C, and extracted into dichloromethane (5 ml). A few drops of hexane were floated on this extract, which was covered and set aside to evaporate slowly to obtain crystals.

[Tp<sub>2</sub>Dy(cin)]: white powder (0.072 g, 10%), m.p. >  $360 \,^{\circ}$ C;  $\upsilon_{max} \, (cm^{-1})(KBr)$ 2464 (B-H stretch), 1644 (C=O stretch);  $\delta_{H} (400 \, \text{MHz}, \text{CDCl}_3) \, -1.1 \, [1H$ , s, C<sub>6</sub>H<sub>5</sub>], -5.6 [2 H, s, C<sub>6</sub>H<sub>5</sub>], -10.1 [2 H, s, C<sub>6</sub>H<sub>5</sub>], -11.2 [1H, s, CH], -44.4 [ 1 H, s, CH], 18.6 [6 H, br, HB(C<sub>3</sub>N<sub>2</sub>H<sub>3</sub>)<sub>3</sub>], 3.7 [6 H, br, HB(C<sub>3</sub>N<sub>2</sub>H<sub>3</sub>)<sub>3</sub>], -5.8 [ 6 H, br, HB(C<sub>3</sub>N<sub>2</sub>H<sub>3</sub>)<sub>3</sub>]; m/z 735 (M<sup>+</sup>), 668 ({M-pz}<sup>+</sup>), 587 ({Tp<sub>2</sub>Dy}<sup>+</sup>), 521 ({TpDy (cin)}<sup>+</sup>), 442 ({TpDy(pz)}<sup>+</sup>).

 $[Tp_{2}Eu(cin)]: white powder (0.082 g, 11\%), m.p. > 375 °C (Found C, 43.87; H, 3.64; N, 22.69; C_{27}H_{27}B_{2}N_{12}O_{2}Eu requires C, 44.81; H, 3.73; N, 23.23;$  $<math>v_{max} (cm^{-1})(KBr) 2462 (B-H stretch), 1636 (C=O stretch); \delta_{H} (400 MHz, CDCI_{3})$  $-4.1 [1 H, s, C_{6}H_{5}], -8.0 [2 H, s, C_{6}H_{5}], 8.5 [2 H, s, C_{6}H_{5}], -10.3 [1H, s, CH],$  $22.2 [1 H, s, CH], 3.2 [6 H, s, HB(C_{3}N_{2}H_{3})_{3}], 3.08 [6 H, s, HB(C_{3}N_{2}H_{3})_{3}], 2.6 [$  $6 H, s, HB(C_{3}N_{2}H_{3})_{3}]; m/z 725 (M<sup>+</sup>), 658 ({M-pz}<sup>+</sup>), 580 ({Tp_{2}Eu}<sup>+</sup>), 514$  $({TpEu (cin)}<sup>+</sup>), 436 ({TpEu(pz)}<sup>+</sup>).$ 

[Tp<sub>2</sub>Lu(cin)]: white powder (0.063 g, 8%), m.p. > 350 °C  $\upsilon_{max}$  (cm<sup>-1</sup>)(KBr) 2463 (B-H stretch), 1636 (C=O stretch);  $\delta_{H}$  (400 MHz, CDCl<sub>3</sub>), 7.9 [2 H m, C<sub>6</sub>H<sub>5</sub>], 7.5 [2 H, m, C<sub>6</sub>H<sub>5</sub>], 7.4 [1 H, dd, *J* = 7.9 Hz, 7.1 Hz, C<sub>6</sub>H<sub>5</sub>], 7.7 [1 H, d, *J* = 15.5 Hz, CH], 6.5 [1H, d, *J* = 15.5 Hz, CH], 7.6 [6 H, d, *J* = 1.9 Hz, HB(C<sub>3</sub>N<sub>2</sub>H<sub>3</sub>)<sub>3</sub>], 6.9 [6 H, d, *J* = 1.9 Hz, HB(C<sub>3</sub>N<sub>2</sub>H<sub>3</sub>)<sub>3</sub>], 5.9 [6 H, t, *J* = 1.9 Hz, HB(C<sub>3</sub>N<sub>2</sub>H<sub>3</sub>)<sub>3</sub>].

[Tp<sub>2</sub>Y(cin)]: white powder (0.032 g, 5%), m.p. > 370 °C  $\upsilon_{max}$  (cm<sup>-1</sup>)(KBr) 2462 (B-H stretch), 1643 (C=O stretch);  $\delta_{H}$  (400 MHz, CDCl<sub>3</sub>) 7.3 [1 H ,dd, *J* = 7.93 Hz, 7.13 Hz, C<sub>6</sub>H<sub>5</sub>], 7.4 [2 H, m, C<sub>6</sub>H<sub>5</sub>], 7.8 [2 H m, C<sub>6</sub>H<sub>5</sub>], 7.6 [1 H, d, *J* = 15.53 Hz, CH], 6.3 [1H, d, *J* = 15.53Hz, CH], 6.9 [6 H, t, *J* = 1.9 Hz, HB(C<sub>3</sub>N<sub>2</sub>H<sub>3</sub>)<sub>3</sub>], 7.0 [6 H, d, *J* = 1.9 Hz, HB(C<sub>3</sub>N<sub>2</sub>H<sub>3</sub>)<sub>3</sub>], 7.0 [6 H, d, *J* = 1.9 Hz, HB(C<sub>3</sub>N<sub>2</sub>H<sub>3</sub>)<sub>3</sub>], 7.6 [6 H, d, *J* = 1.9 Hz, HB(C<sub>3</sub>N<sub>2</sub>H<sub>3</sub>)<sub>3</sub>]

 $\label{eq:2.1} \begin{array}{l} [Tp_{2}Ho(cin)]: \mbox{ off pink powder (0.073 g, 10\%), m.p. > 370 °C (Found C, 41.98; H, 3.62; N, 21.32; C_{27}H_{27}B_2N_{12}O_2Ho requires C, 44.02; H, 3.66; N, 22.82; \\ \upsilon_{max} \mbox{ (cm}^{-1})(KBr) \ 2469 \ (B-H \ stretch), 1646 \ (C=O \ stretch); \ m/z \ 738 \ (M^{+}), \ 671 \ (\{M-pz\}^{+}), \ 591 \ (\{Tp_{2}Ho\}^{+}), \ 525 \ (\{TpHo(cin)\}^{+}), \ 445(\{TpHo(pz)\}^{+}). \end{array}$ 

[Tp<sub>2</sub>Er(cin)]: pink powder (0.08 g, 11%), m.p. > 360 °C (Found C, 42.17; H, 3.65; N, 21.87;  $C_{27}H_{27}B_2N_{12}O_2Er$  requires C, 43.78; H, 3.64; N, 22.71;

 $\upsilon_{max}$  (cm<sup>-1</sup>)(KBr) 2469 (B-H stretch), 1646 (C=O stretch); m/z 740(M<sup>+</sup>), 673 ({M-pz}<sup>+</sup>), 592 ({Tp<sub>2</sub>Er}<sup>+</sup>), 526 ({TpEr(cin)}<sup>+</sup>), 446 ({TpEr(pz)}<sup>+</sup>).

 $[Tp_2Yb(cin)]: white powder (0.069 g, 9\%), m.p. > 375 °C (Found C, 43.38; H, 3.45; N, 21.85; C_{27}H_{27}B_2N_{12}O_2Yb requires C, 43.60; H, 3.63; N, 22.61;$  $v_{max} (cm^{-1})(KBr) 2462 (B-H stretch), 1638 (C=O stretch); <math>\delta_{Hr}(400MHz,CDCI_3) - 4.8 [2 H, s, C_6H_5], -5.8 [1 H, s, C_6H_5], -7.9 [2 H, s, C_6H_5], 11.5 [1H, s, CH] - 18.6, [1H, s, CH], 8.5 [6 H, br, HB(C_3N_2H_3)_3], 8.2 [6 H, s, HB(C_3N_2H_3)_3], 2.8 [6 H, br, HB(C_3N_2H_3)_3]; m/z 745 (M^+), 678 ({M-pz}^+), 598 ({Tp_2Yb}^+), 535 ({TpYb} (cin)}^+), 453 ({TpYb}(pz))^+).$ 

## 7.12.5.Synthesis of europium and terbium crotonate complexes using substituted Tp

Substituted Tp ligands were obtained from Prof. S. Trofimenko, Du Pont Corporation.



The typical synthetic method for lanthanide crotonate complexes with substituted Tp was as follows.

The substituted Tp ligand (0.002 mol) was dissolved in methanol (5 ml) and crotonic acid (0.001 mol) was dissolved in water (2 ml) and then neutralised with 2 M NaOH solution. After mixing the two ligands by stirring, the pH was adjusted to 8 using a pH meter. To this solution,  $EuCl_3.6H_2O$  or  $TbCl_3.6H_2O$  (0.001 mol) in water (5 ml) were added and the resulting solution was stirred for a few minutes and the solid collected by suction filtration. The solid was dried overnight in a vacuum oven at 50 °C, then extracted into dichloromethane (5 ml). A few drops of hexane were floated on this extract, which was covered and set aside to evaporate.

$$\label{eq:constraint} \begin{split} & [(Tp-Ar-OMe)_2Eu(crot)]: \mbox{ white powder (0.012 g, 0.9\%), m.p. > 375 °C (Found C, 56.7; H, 4.59; N, 11.12; C_{64}H_{61}B_2N_{12}O_8Eu \mbox{ requires C, 59.12; H, 4.69; N, 12.93; } & \upsilon_{max} \ (cm^{-1})(KBr) \ 2451 \ (B-H \ stretch), \ 1571 \ (C=O \ stretch); \ m/z \ 683 \ (\{(Tp-Ar-OMe)Eu\})^+, \ 531 \ (\{Tp-Ar-OMe\})^+. \end{split}$$

 $[(Tp-Ar-Me)_2Eu(crot)]$ : white powder (0.010 g, 0.8%), m.p. > 375 °C;  $v_{max}$  (cm<sup>-1</sup>)(KBr) 2454 (B-H stretch), 1573 (C=O stretch); m/z 635 ({(Tp-Ar-Me)Eu})<sup>+</sup>, 483 ({Tp-Ar-Me})<sup>+</sup>.

 $[(Tp-Ar)_{2}Eu(crot)]$ : white powder (0.032 g, 3%), m.p. > 375 °C (Found C, 62.45; H, 4.31; N, 14.21; C<sub>58</sub>H<sub>49</sub>B<sub>2</sub>N<sub>12</sub>O<sub>2</sub>Eu requires C, 62.19; H, 4.37; N, 15.01;  $\upsilon_{max}$  (cm<sup>-1</sup>)(KBr) 2460 (B-H stretch), 1572 (C=O stretch); m/z 593 ({(Tp-Ar)Eu})<sup>+</sup>, 441 ({Tp-Ar})<sup>+</sup>.

[(Tp-thiophene)<sub>2</sub>Eu (crot)]: white powder (0.033 g, 3%), m.p. > 375 °C ; υ<sub>max</sub> (cm<sup>-1</sup>)(KBr) 2451 (B-H stretch), 1571 (C=O stretch); m/z 611, ({(Tp-thiophene)Eu})<sup>+</sup>, 459 ({Tp-thiophene})<sup>+</sup>.

 $[(Tp-Ar-OMe)_2Tb(crot)]$ : white powder (0.013 g, 1%), m.p. > 375 °C;  $v_{max}$  (cm<sup>-1</sup>)(KBr) 2451 (B-H stretch), 1573 (C=O stretch); m/z 690 ({(Tp-Ar-OMe)Tb})<sup>+</sup>, 531 ({Tp-Ar-OMe})<sup>+</sup>.

 $[(Tp-Ar)_2Tb(crot)]$ : white powder (0.023 g, 2%), m.p. > 375 °C;  $v_{max}$  (cm<sup>-1</sup>)(KBr) 2453 (B-H stretch), 1571 (C=O stretch); m/z 600 ({(Tp-Ar)Tb})<sup>+</sup>, 441 ({Tp-Ar})<sup>+</sup>.

[(Tp-thiophene)<sub>2</sub>Tb(crot)]: white powder (0.019 g, 3%), m.p. > 375 °C (Found C, 43.37; H, 3.97; N, 14.68;  $C_{46}H_{43}B_2N_{12}O_2S_6Tb$  requires C, 47.20; H, 3.68;

N, 14.30; υ<sub>max</sub> (cm<sup>-1</sup>)(KBr) 2451 (B-H stretch), 1571 (C=O stretch); m/z 618, ({(Tp-thiophene)Tb})<sup>+</sup>, 459 ({Tp-thiophene})<sup>+</sup>.

## 7.12.6. Synthesis of europium and terbium cinnamate complexes using substituted Tp



The substituted Tp ligand (0.002 mol) was dissolved in methanol (5 ml) and cinnamic acid (0.001 mol) was dissolved in water (2 ml) and then neutralised with 2 M NaOH solution. After mixing the two ligands by stirring and the pH was adjusted to 8 using a pH meter. To this solution,  $EuCl_3.nH_2O$  or  $TbCl_3.nH_2O$  (0.001 mol) in water (5 ml) were added and the resulting solution was stirred for a few minutes and the solid collected by suction filtration. The solid was dried overnight in a vacuum oven at 50 °C, then extracted into dichloromethane (5 ml). A few drops of hexane were floated on this extract, which was covered and set aside to evaporate.

 $[(Tp-Ar-OMe)_2Eu(cin)]$ : white powder (0.08 g, 6%), m.p. > 360 °C;  $v_{max}$  (cm<sup>-1</sup>)(KBr) 2456 (B-H stretch), 1572 (C=O stretch); m/z 683 ({(Tp-Ar-OMe)Eu})<sup>+</sup>, 531 ({Tp-Ar-OMe})<sup>+</sup>.

 $[(Tp-Ar-Me)_2Eu(cin)]$ : white powder (0.011 g, 1%), m.p. > 360 °C (Found C, 60.32; H, 3.83; N, 12.79;  $C_{69}H_{63}B_2N_{12}O_2Eu$  requires C, 60.81; H, 4.62; N, 12.34;  $\upsilon_{max}$  (cm<sup>-1</sup>)(KBr) 2452 (B-H stretch), 1571 (C=O stretch); m/z 635 ({(Tp-Ar-Me)Eu})<sup>+</sup>, 483 ({Tp-Ar-Me})<sup>+</sup>.

 $[(Tp-Ar)_2Eu(cin)]$ : white powder (0.023 g, 2%), m.p. > 360 °C;  $v_{max}$  (cm<sup>-1</sup>)(KBr) 2456 (B-H stretch), 1575 (C=O stretch); m/z 593 ({(Tp-Ar)Eu})<sup>+</sup>, 441 ({Tp-Ar})<sup>+</sup>. [(Tp-thiophene)<sub>2</sub>Eu (cin)]: white powder (0.045 g, 4%), m.p. > 360 °C (Found C, 49.38; H, 4.09; N, 13.78;  $C_{51}H_{45}B_2N_{12}O_2S_6Eu$  requires C, 50.43; H, 3.67; N, 13.71;  $\upsilon_{max}$  (cm<sup>-1</sup>)(KBr) 2451 (B-H stretch), 1571 (C=O stretch); m/z 611, ({(Tp-thiophene)Eu})<sup>+</sup>, 459 ({Tp-thiophene})<sup>+</sup>.

$$\begin{split} & [(\text{Tp-Ar-OMe})_2\text{Tb}(\text{cin})]: \text{ white powder (0.013 g, 1\%), m.p. > 360 °C (Found C, 60.39; H, 4.47; N, 11.64; C_{69}H_{63}B_2N_{12}O_2\text{Tb requires C, 60.52; H, 4.60; N, 12.28; } \upsilon_{\text{max}} (\text{cm}^{-1})(\text{KBr}) 2456 (B-H \text{ stretch}), 1573 (C=O \text{ stretch}); m/z 690 ({(Tp-Ar-OMe)Tb})^+, 531 ({Tp-Ar-OMe})^+. \end{split}$$

 $[(Tp-Ar-Me)_2Tb(cin)]$ : white powder (0.039 g, 3%), m.p. > 360 °C;  $v_{max}$  (cm<sup>-1</sup>)(KBr) 2453 (B-H stretch), 1575 (C=O stretch); m/z 652 ({(Tp-Ar-Me)Tb})<sup>+</sup>, 483 ({Tp-Ar-Me})<sup>+</sup>.

$$\begin{split} & [(Tp-Ar)_2 Tb(cin)]: \text{ white powder (0.023 g, 2\%), m.p. > 360 °C °C (Found C, 62.65; H, 4.09; N, 13.41; C_{63}H_{51}B_2N_{12}O_2Tb requires C, 63.9; H, 4.31; N, 14.21; <math>\upsilon_{max}$$
 (cm<sup>-1</sup>)(KBr) 2453 (B-H stretch), 1572 (C=O stretch); m/z 600 ({(Tp-Ar)Tb)}<sup>+</sup>, 441 ({Tp-Ar})<sup>+</sup>.

 $[(Tp-thiophene)_2Tb(cin)]$ : white powder (0.027 g, 2%), m.p. > 360 °C  $v_{max}$  (cm<sup>-1</sup>)(KBr) 2456 (B-H stretch), 1572 (C=O stretch); m/z 618, ({(Tp-thiophene)Tb})<sup>+</sup>, 459 ({Tp-thiophene})<sup>+</sup>.

## 7.13. Experimental section for chapter 4

## 7.13.1. Copolymerisation of lanthanide crotonate complexes [Tp<sub>2</sub>Ln(crot)] using styrene monomer (Ln = Tb, Eu)

For the polymerisation reaction, the  $[Tp_2Ln(crot)]$  (Ln = Tb, Eu) complexes were used in 5-20 wt% relation to monomers (MMA, styrene).



The europium or terbium crotonate complex (0.3 g, 15 wt%) was dissolved in DMSO (15 ml), mixed with styrene (0.7 g) and AIBN (0.006 g) added, the resulting and the homogeneous solution was heated in a oil bath at 70 °C for 15 minutes. The styrene (1.3 g) and AIBN (0.006 g) were injected into this mixture and the whole mixture was heated at 70 °C for 8 h. The viscous mixture was dissolved in THF, the polymer precipitated by addition of methanol and dried *in vacuo* at room temperature for 1 day to give a white solid (62% yield), (Eu% = 0.82;  $M_n = 67500$ ).

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The europium or terbium crotonate complex (0.3 g, 15 wt%) was dissolved in DMSO (15 ml), mixed with MMA (2 g) and AIBN (0.012 g) added and the resulting homogeneous solution was heated in a oil bath at 70 °C for 24 h. The viscous mixture was dissolved in THF, the polymer precipitated by addition of methanol and dried *in vacuo* at room temperature for 1 day to give a white solid (65% yield), (Tb% =1.33;  $M_n = 60100$ ).

## 7.13.3. Copolymerisation of europium cinnamate complexes [Tp<sub>2</sub>Eu(cin)] using MMA monomer



The europium cinnamate complex (0.2 g, 10 wt%) was dissolved in DMSO (15 ml), mixed with MMA (2 g) and AIBN (0.012 g) added and the resulting homogeneous solution was heated in a oil bath at 70 °C for 24 h. The viscous mixture was dissolved in THF, the polymer precipitated by addition of methanol and dried *in vacuo* at room temperature for 1 day to give a white solid (76% yield), (Eu% = 1.53;  $M_n = 52400$ ).

## 7.13.4. Copolymerisation of europium cinnamate complexes [Tp₂Eu(cin)] using styrene monomer



The europium cinnamate complex (0.2 g, 10 wt%) was dissolved in DMSO (15 ml), mixed with styrene (0.7 g) and AIBN (0.006 g) added and the resulting homogeneous solution was heated in a oil bath at 70 °C for 15 minutes. The styrene (1.3 g) and AIBN (0.006 g) were injected into this mixture and the whole mixture was heated at 70 °C for 8 h. The viscous mixture was dissolved in THF, the polymer precipitated by addition of methanol and dried *in vacuo* at room temperature for 1 day to give a white solid (63% yield), (Eu% = 1.32; M<sub>n</sub>= 59200).

## 7.14. Experimental section for chapter 5

## 7.14.1 Synthesis of PPV monomer



p-Xylene-bis(diethyl sulfonium chloride) monomer

 $\alpha, \alpha$ '-dichloro- *p*-xylene (0.05 mol) was treated with diethyl sulphide (0.14 mol) in a methanol : water solution (80:20) for 20 h. The monomer was purified by concentrating the solution and precipitating the product in cold acetone. The monomer was collected by filtration and vacuum dried to give the product as

50% yield.  $\delta_{H}$  (400 MHz, D<sub>2</sub>O) 7.5 [4 H, s], 4.5 [4 H, s], 3.2 [8 H, q, J = 7.5 Hz], 1.3 [12 H, t, J = 11.2 Hz];  $\delta_{C}$  (100 MHz, D<sub>2</sub>O) 15.7 (CH<sub>3</sub>); 40.6 (CH<sub>2</sub>); 49.6 (CH<sub>2</sub>); 136.9 (C); 139.1 (CH).

The PPV precursor and PPV were prepared by the following methods.



A 0.2 M aqueous solution of monomer and a 0.2 M solution of sodium hydroxide were stirred together at 0 °C for 1 h under nitrogen. The reaction was quenched by neutralization with HCI (1M) to a slightly acidic pH 6.8 which yielded a highly viscous solution. This precursor solution was separated from monomer and NaOH by dialysis against distilled water for 3 days. This PPV precursor was converted to PPV by coating a thin film on glass and heating in a vacuum at 200 °C for 8 h.  $v_{max}$  (cm<sup>-1</sup>)(KBr) 3016, (C-H stretch), 956, (trans C-H stretch).

# Appendix

## Appendix

## A. Recation mechanism for the formation of Na-Tp

Na<sup>+</sup> BH<sub>4</sub>



## B. TGA graph of PPV



## C. Crystallographic data for

## a, Tp<sub>2</sub>Er(crot)

Table 1 Bond distances (Angstroms)  $Tp_2Er(crot)$ 

Er1	02A	2 347(6)
5 51	01	2.347(0)
	01	2.333(3)
ET T	02	2.386(3)
Erl	N7	2.405(2)
Er1	01A	2.412(6)
Er1	N1	2.411(2)
Er1	N12	2.472(2)
Er1	N10	2.475(2)
Er1	N6	$2 \ 477(2)$
5-1 5-1	NΛ	2.177(2)
		2.321(2)
ELT	C4A	2.712(4)
Erl	C4B	2.733(9)
N11	C12	1.352(4)
N11	N12	1.364(3)
N11	В2	1.535(4)
N3	C11	1.348(4)
N3	N4	1.367(3)
N3	B1	1 540(4)
NO		1, 340(4)
NO	C9 N7	1.342(4)
N8	N/	1.368(3)
N8	B2	1.551(4)
N6	C5	1.331(4)
N6	N5	1.368(3)
N1	C3	1.338(4)
N1	N2	1.365(3)
N2	C13	1.341(3)
N2	B1	1546(4)
N5	C6	1 348(4)
N5	בט 1	1.540(4) 1.5/1(/)
		1 - 241(4)
N4		1.341(4)
N9	08	1.351(4)
N9	N10	1.363(3)
N9	В2	1.537(4)
C1	C6	1.371(4)
C1	C5	1.388(4)
N7	C4	1.343(4)
N10	C7	1.337(4)
C3	C17	1.386(4)
C4	C14	1.381(4)
C7	C16	$1 \ 377(4)$
C8	C16	1,375(5)
C0 C0		1,373(3)
		1.375(4)
	CII	1.3/5(5)
C10	C18	1.390(5)
N12	C19	1.342(4)
C12	C15	1.368(5)
C13	C17	1.377(4)
C15	C19	1.381(5)
C1A	C2A	1.490(6)
C2A	C3A	1.314(7)
C3A	C4A	1.495(6)
C4A	02	1.259(9)
C43	01	1,271(9)
	C2P	1 485(14)
CTD	C2D	

C2B	C3B	1.310(15)	)	
C3B	C4B	1.476(13)	)	
C4B	01A	1.267(16)	)	
C4B	02A	1.293(18)	)	
Table	2. в	ond angle	es (degrees)	for
		2	(=========;	-01
02A	Er1	01	43.3(3)	
02A	Er1	02	13.9(2)	
01	Er1	02	55.58(19)	
02A	Er1	N7	84.3(3)	
01	Er1	N7	126.17(12)	
02	Er1	N7	74.67(13)	
02A	Er1	01A	55.5(4)	
01	Er1	O1A	14.61(17)	
02	Er1	O1A	68.6(3)	
N7	Er1	01A	133.44(18)	
02A	Er1	N1	124.3(2)	
01	Er1	N1	82.72(13)	
02	Er1	N1	132.47(11)	
N7	Er1	N1	151.05(8)	
01A	Er1	N1	74.2(2)	
02A	Er1	N12	74.2(2)	
01	Er1	N12	77.46(11)	
02	Er1	N12	82.06(11)	
N7	Er1	N12	76.59(8)	
01A	Er1	N12	71.01(17)	
N1	Er1	N12	112.65(8)	
02A	Er1	N10	144.47(18)	
01	Er1	N10	133.61(15)	
02	Er1	N10	146.18(9)	
N7	Erl	N10	78.88(8)	
		NIU NIO	119.3(3)	
N1 N12	Erl Eml	NIU NIO	78.00(8) 71 50(9)	
NIZ OZZ	ELI Em1	NIU	12.52(0)	
02A 01	Ef 1 Er 1	NO	133.9(3) 143.47(10)	
02	БГТ Б∽1	NO	143.47(10) 122 9/(15)	
02 N7	⊡⊥⊥ ⊽∽1	NG NG	122.94(13)	
01 2	Er1	NG NG	145 61(15)	
N1	Er1	N6	76 49 (8)	
N12	Er1	N6	138.39(8)	
N10	Er1	N6	70.95(7)	
02A	Er1	NG N4	76.83(19)	
01	Er1	N4	75.99(12)	
02	Er1	N4	71.42(10)	
N7	Er1	N4	108.57(7)	
01A	Er1	N4	86.0(2)	
N1	Er1	N4	77.64(8)	
N12	Er1	N4	149.94(8)	
N10	Er1	N4	138.27(7)	
N6	Er1	N4	70.45(7)	
02A	Er1	C4A	16.3(3)	
01	Er1	C4A	27.9(2)	
02	Er1	C4A	27.7(2)	
N7	Er1	C4A	100.63(13)	
01A	Er1	C4A	41.3(3)	
N1	Er1	C4A	108.01(13)	
N12	Er1	C4A	78.85(11)	
N10	Er1	C4A	149.69(12)	

Tp<sub>2</sub>Er(crot)

N6	Er1	C4A	139.16(12)
N4	Er1	C4A	71.09(11)
02A	Er1	C4B	28.2(4)
01	Er1	C4B	15.3(3)
02	Er1	C4B	41.0(3)
N7	Er1	C4B	111.1(2)
01A	Er1	C4B	27.6(4)
N1	Er1	C4B	97.8(2)
N12	Er1	C4B	73.57(19)
N10	Er1	C4B	$140 \ 1(2)$
N6	Er1	C4B	147 6(2)
N4	Er1	C4B	77.1(2)
C4A	Er1	C4B	13 90(19)
C12	N11	N12	109.5(3)
C12	N11	B2	128.1(3)
N12	N11	B2	122.3(2)
C11	N3	N4	109 8(2)
C11	N3	B1	$128 \ 1(3)$
N4	N3	B1	120.1(3) 122 0(2)
C 9	N8	N7	109 1(2)
C9	N8	B2	$128 \ 9(2)$
N7	N8	B2	120.9(2) 121 $1(2)$
C5	N6	N5	$105 \ 8(2)$
C5	N6	Er1	129.4(2)
N5	NG	Er1	123.4(2)
C3	N1	N2	105 8(2)
C3	N1	Er1	129.3(2)
N2	N1	Er1	123.3(2) 124 36(16)
C13	N2	N1	1097(2)
C13	N2	R1	109.7(2) 128 $1(2)$
N1	N2	B1	120.4(2) 121 9(2)
CG	N5	N6	109.9(2)
C6	N5	B1	129.4(2)
N6	N5	B1	120.4(2)
C18	NA	N3	105.6(2)
C18	N4 NA	אס די1	132.6(2)
N3	N4 NA	Er1	121, 71(16)
N3	R1	N5	107 7(2)
N3	B1	N2	109.8(2)
N5	B1	N2	110.1(2)
C8	N9	N10	110.1(2)
C8	N9	B2	128.7(2)
N10	N9	B2	121.2(2)
C6	C1	C5	105.1(3)
C4	N7	N8	105.7(2)
C4	N7	Er1	130.33(19)
N8	N7	Er1	123.79(16)
N11	B2	N9	108.5(2)
N11	B2	N8	109.4(2)
N9	B2	N8	109.8(2)
C7	N10	N9	105.4(2)
C7	N10	Er1	130.62(19)
N9	N10	Er1	121.85(17)
N1	C3	C17	111.2(3)
N7	C4	C14	111.3(3)
N6	C5	C1	111.0(3)
N5	C6	C1	108.2(3)
N10	C7	C16	111.6(3)
N9	C8	C16	108.0(3)
N8	C9	C14	109.2(3)
C11	C10	C18	104.4(3)

C19	N12	N11	105.9(3)
C19	N12	Er1	132.3(2)
N11	N12	Er1	121.75(16)
N3	C11	C10	108.8(3)
N11	C12	C15	108.5(3)
N2	C13	C17	109.0(3)
С9	C14	C4	104.4(2)
C12	C15	C19	105.2(3)
C8	C16	C7	104.9(3)
C13	C17	C3	104.3(3)
N4	C18	C10	111.3(3)
N12	C19	C15	110.8(3)
C3A	C2A	C1A	125.5(5)
C2A	C3A	C4A	123.6(4)
02	C4A	01	121.7(4)
02	C4A	C3A	118.9(5)
01	C4A	C3A	119.3(5)
02	C4A	Er1	61.6(2)
01	C4A	Er1	60.1(2)
C3A	C4A	Er1	175.7(3)
C4A	01	Er1	92.0(3)
C4A	02	Er1	90.7(3)
C3B	C2B	C1B	125.4(10)
C2B	C3B	C4B	124.8(9)
01A	C4B	02A	119.9(8)
01A	C4B	C3B	116.4(10)
02A	C4B	C3B	123.7(10)
01A	C4B	Er1	61.9(5)
02A	C4B	Er1	59.1(4)
СЗВ	C4B	Er1	169.5(6)
C4B	01A	Er1	90.4(7)
C4B	02A	Er1	92.7(6)

## b, [TpHo(crot)<sub>2</sub>]<sub>2</sub>

Table 3. Bond distances (Angstroms) for [TpHo(crot)2]2

Ho1	03	2.249(2)
Ho1	01	2.293(2)
Ho1	02	2.315(2)
Ho1	011	2.367(3)
Ho1	N11	2.433(3)
Ho1	N31	2.502(3)
Ho1	N22	2.509(3)
Ho1	03	2.639(2)
Ho1	04	2.876(4)
Ho1	Ho1	3.7861(3)
N11	C11	1.341(4)
N11	N12	1.367(4)
N12	C13	1.347(4)
N12	B11	1.533(5)
C11	C12	1.387(5)
C12	C13	1.381(5)
B11	N21	1.545(5)
B11	N32	1.552(5)
N21	C21	1.350(5)
N21	N22	1.369(4)
N22	C23	1.344(5)

C21	C22	1.38	4(6)			
C22	C23	1.39	1(5)			
N31	C31	1.34	5(5)			
N31	N32	1.37	0(4)			
N32	C33	1 34	0(5)			
C31	C32	1 3 9	9(5)			
C37	C32	1 20	9(5)			
$C_{32}$	C33	1.30	1 (5)			
011	04	1.25	1(5)			
01	CIA	1.26	3(4)			
02	C1A	1.27	1(4)			
03	04	1.28	8(4)			
03	Ho1	2.24	9(2)			
04	C8A	1.47	6(5)			
C8A	C6A	1.32	5(5)			
C3A	C2A	1.32	(3(5))			
C3A	C5A	1 50	5(6)			
C67	C71	1 / 9	9(5)			
		1 26				
		1.20	3 (4) X (5)			
CIA	CZA	1.48	6 (5)			
Tabl	le 4.	Bond	angles	(degrees)	for	[TpHo(crot) <sub>2</sub> ] <sub>2</sub>
03	Ho1	01	78.66(9)			
03	Ho1	02	81.50(9)			
01	Ho1	02	136.45(9	))		
03	Ho1	011	130.51(8	3)		
01	Ho1	011	80,41(9)	,		
02	но1	011	83 82 (9)			
03	пот чо1	N11	15/ 37/0	• •		
03			110 01(0	· )		
01	HOI		10.81(9	· )		
02	HOT	NII	103.77(9	")		
011	Hol	N11	75.11(9)			
03	Ho1	N31	81.98(9)			
01	Ho1	N31	141.09(1	.0)		
02	Ho1	N31	72.02(9	))		
011	Ho1	N31	136.33(	(9)		
N11	Ho1	N31	76.09(9	))		
03	Ho1	N22	86.62(9	))		
01	Ho1	N22	72.03(9	$\mathbf{\hat{)}}$		
02	но1	N22	144.67	(9)		
011	ਸ਼ਹੂ ਧੂਨੀ	N22	127 720	(9)		
NT1 1		N22	74 61 / 0			
	HOL Hol			/ ) ) )		
1CM	HOL	NZZ	73.44(3	· )		
03	HO⊥	03	/8./8(8	5) 		
01	Hol	03	69.40(8	3)		
02	Hol	03	68.92(8	3)		
011	Ho1	03	51.88(7	7)		
N11	Hol	03	126.70(	(8)		
N31	Ho1	03	138.42	(8)		
N22	Ho1	03	140.69(	(8)		
03	Ho1	04	105.30	(10)		
01	Ho1	04	73.51(1	0)		
02	но <u>1</u>	04	75.01(9	)		
011	нот но1	04	25 30(1	0)		
		04	100 274	(10)		
		04	1 1 1 7 7 4	(10)		
1122	HOT	04	110 01 4	(10)		
NZZ	ної	04		(TO)		
03	Hol	04	20.58(5	7 J - \		
03	Ho1	H01	43.14(6	)		
01	Ho1	Ho1	68.77(6	))		
02	Ho1	Ho1	70.21(6	5)		

011	Ho1	Ho1	87.45(6)
N11	Ho1	Ho1	162.21(6)
N31	Ho1	Ho1	116.01(6)
N22	Ho1	Ho1	120.29(7)
03	Ho1	Ho1	35,64(5)
04	Ho1	Ho1	62, 18(8)
C11	N11	N12	106 2(3)
C11	N1 1	H_1	130.2(3)
N12	N11		130.0(2)
012	NTT O	NUL 1	123.2(2)
C13	N12	NII D11	109.3(3)
CI3	NIZ	BII	126.7(3)
NII	NIZ	B11	123.9(3)
N11	C11	C12	111.1(3)
C13	C12	C11	104.4(3)
N12	C13	C12	109.0(3)
N12	B11	N21	109.5(3)
N12	B11	N32	110.3(3)
N21	B11	N32	107.0(3)
C21	N21	N22	110.5(3)
C21	N21	B11	127.8(3)
N22	N21	B11	121.4(3)
C23	N22	N21	105.5(3)
C23	N22	Ho1	1309(2)
N21	N22	Ho1	123 3(2)
N21	C21	C22	107 0(3)
C21	$C_{21}$	C22	107.9(3)
	C22	$C_{2,2}$	103.0(3)
NZZ			$1 \downarrow \downarrow$
		N3Z	105.8(3)
C31	N31	HOL	130.4(2)
N32	N31	HOL	123.4(2)
C33	N32	N31	110.0(3)
C33	N32	B11	128.5(3)
N31	N32	B11	121.3(3)
N31	C31	C32	111.1(3)
C33	C32	C31	104.4(3)
N32	C33	C32	108.7(3)
04	011	Ho1	100.7(2)
C1A	01	Ho1	136.5(2)
C1A	02	Ho1	133.1(2)
04	03	Ho1	171.0(2)
04	03	Ho1	87.0(2)
Ho1	03	Ho1	101.22(8)
011	04	03	120.4(3)
011	04	C8A	120.5(4)
03	04	C8A	119.1(4)
011	04	Ho1	53 99(18)
03	04	нот чо1	$66 \ 13 \ (19)$
03	04		1745(3)
COA	04		172.0(3)
COA	COA		106 7(4)
CZA	C3A	C5A	120.7(4)
C8A	C6A	C/A	$\perp 20.1(4)$
01	CIA	02	124.6(3)
01	C1A	C2A	118.4(3)
02	C1A	C2A	117.0(3)
C3A	C2A	C1A	122.3(4)

## C, [TpHo(cin)]<sub>2</sub>

Table 5. Bond distances (Angstroms) for  $[TpHo(cin)_2]_2$ 

Ho1 O1 2.261(3)

•

Ho1	04	2.264(3)
Ho1	03	2.287(3)
Ho1	02	2.364(3)
Ho1	N2	2.449(3)
Ho1	N3	2.498(3)
Ho1	N1	2.510(3)
Ho1	01	2.678(3)
Ho1	C10	2.892(4)
Ho1	Ho1	3.8582(3)
Ho2	07	2.250(3)
Ho2	05	2.275(3)
Ho2	06	2.292(3)
Ho2	08	2.293(3)
Ho2	NG	2.460(3)
Ho2	N7	2.477(3)
Но2	N8	2,480(3)
B1	N22	1,537(6)
B1	N4	1,542(6)
B1	N5	1.542(0) 1.547(6)
B2	N11	1,541(6)
B2	N9	1.541(6)
B2	N10	1.544(0) 1.546(6)
N1	C1	1,339(5)
N1	N22	1.368(5)
N2	C4	1.300(5) 1.342(5)
N2	N/	1.342(5) 1.376(5)
M2	C7	1.3/6(5)
N3	N5	1.340(5)
NΔ	C6	1.306(5)
NG NG		1.330(0)
MC	C28	1.343(5)
NG		1.354(5)
NO N7	C21	1,309(5)
IN 7 NT'7	N10	1.332(3) 1.370(5)
N /		1.370(3)
NO	СJ4 м11	1.339(3) 1.367(5)
NQ	C30	1.307(5)
M10	C33	1.342(5)
N11	C32	1.340(3)
MOO	C30	1.330(3)
01	C1 0	1.347(0) 1.283(5)
01		2.261(3)
02	C10	2.201(5)
02	C10	1.202(5)
01	C19	1.263(5)
05	C37	$1.20 \pm (5)$ 1.270(5)
05	C37	1.270(5)
07	C16	$1.25 \pm (5)$
08	C46	1.265(5)
C1	C2	1,200(5) 1,381(6)
C1	С2 H1	0 9500
C2	C3	1,377(7)
C2	ч2	0 9500
C2 C2	н2 Н2	0.9500
CJ C1	05 05	1 380(6)
C1	нЛ	0 9500
C5	<u>-</u> C6	1,369(7)
С5 С5	со 45	0 9500
C5 C6	нс	0.9500
C7	C8	1,380(6)
C7	со н7	0.9500
$\sim$ $i$		

C8	С9	1.375(7)
C8	Н8	0.9500
С9	Н9	0.9500
C10	C11	1.468(6)
C11	C12	1.326(6)
C11	H11	0.9500
C12	C13	1.463(6)
C12	H12	0.9500
C13	C14	1.395(6)
C13	C18	1.399(6)
C14	C15	1.379(6)
C14	H14	0.9500
C15		1.386(7)
C15	H15 C17	0.9500
C10		1.304(7)
C17	C18	1 374(7)
C17	С10 H17	0 9500
C18	н18	0.9500
C19	03	1.265(5)
C19	C20	1,481(6)
C20	C21	1.329(6)
C20	н20	0.9500
C21	C22	1.464(6)
C21	H21	0.9500
C22	C23	1.380(6)
C22	C27	1.395(6)
C23	C24	1.387(7)
C23	H23	0.9500
C24	C25	1.388(8)
C24	H24	0.9500
C25	C26	1.353(8)
C25	H25	0.9500
C26	C27	1.387(7)
C26	H26	0.9500
C27	H27	0.9500
C28	C29	1.399(6)
C28	HZ8	0.9500
C29	U20	1.3/3(0)
C29	п29 ЦЗО	0.9500
C30		1 389(6)
C31	С32 H31	0 9500
C32	C33	1.375(7)
C32	H32	0.9500
C33	H33	0.9500
C34	C35	1.388(6)
C34	Н34	0.9500
C35	C36	1.373(6)
C35	H35	0.9500
C36	H36	0.9500
C37	06	1.254(5)
C37	C38	1.478(5)
C38	C39	1.328(5)
C38	Н38	0.9500
C39	C40	1.466(5)
C39	H39	0.9500
C40	C41	1.395(6)
C40	C45	1.396(6)
C41		T.3/2(0)
C41	H41	0.3000

C42	C43	1.397(7)
C42	H42	0.9500
C43	C44	1.367(7)
C43	H43	0.9500
C44	C45	1.394(6)
C44	H44	0.9500
C45	H45	0.9500
C46	07	1.263(5)
C46	C47	1.476(5)
C47	C48	1.327(6)
C47	H47	0.9500
C48	C49	1.471(6)
C48	H48	0.9500
C49	C54	1.389(6)
C49	C50	1.395(6)
C50	C51	1.371(6)
C50	Н50	0.9500
C51	C52	1.392(6)
C51	H51	0.9500
C52	C53	1.370(6)
C52	H52	0.9500
C53	C54	1.385(6)
C53	Н53	0.9500
C54	H54	0.9500

Table 6. Bond angles (degrees) for  $[TpHo(cin)_2]_2$ 

01	Ho1	04	79.00(10)
01	Ho1	03	77.98(10)
04	Ho1	03	135.20(10)
01	Ho1	02	128.86(10)
04	Ho1	02	84.02(11)
03	Ho1	02	81.35(10)
01	Ho1	N2	154.85(11)
04	Ho1	N2	119.00(11)
03	Ho1	N2	96.80(10)
02	Ho1	N2	73.42(11)
01	Ho1	N3	96.57(11)
04	Hol	N3	72.76(11)
03	Ho1	N3	147.72(11)
02	Ho1	N3	123.60(11)
N2	Ho1	N3	74.60(11)
01	Ho1	Nl	79.85(10)
04	Ho1	N1	137.09(11)
03	Ho1	N1	74.59(10)
02	Ho1	N1	137.33(10)
N2	Ho1	N1	75.06(11)
N3	Ho1	N1	73.13(11)
01	Ho1	01	77.58(10)
04	Ho1	01	69.01(9)
03	Ho1	01	68.79(9)
02	Ho1	01	51.32(9)
N2	Ho1	01	123.87(10)
N3	Hol	01	141.76(10)
N1	Ho1	01	140.09(10)
01	Ho1	C10	103.58(11)
04	Ho1	C10	77.90(11)
03	Ho1	C10	70.97(11)
02	Ho1	C10	25.32(10)
N2	Ho1	C10	97.71(11)
04 03 02 N2	Hol Hol Hol Hol	C10 C10 C10 C10	77.90(12 70.97(12 25.32(10 97.71(12

N3	Ho1	C10	140 25(12)
N1	Ho1	C10	143 68(11)
01	Ho1	C10	26 28(10)
01	но1	Ho1	42 68(7)
04	нот Но1	Ho1	42.00(7)
03	Ho1	Ho1	68.09(7)
02	Ho1	пот чо1	96.09(7)
N2	Ho1		156 = 2/0
M2			100.52(8)
NJ N1			127.75(8)
N1 01		HO1	115.41(8)
01 010			54.90(6)
07	HOT No2	HOI	51.00(8)
07		05	79.86(10)
	HOZ	06	80.21(10)
05	HOZ	06	128.76(9)
07	HOZ	80	128.44(10)
05	Ho2	08	81.07(10)
06	Ho2	08	75.57(10)
07	Ho2	N6	93.45(11)
05	Ho2	N6	151.97(10)
06	Ho2	N6	75.74(10)
08	Ho2	N6	122.62(10)
07	Ho2	N7	156.44(11)
05	Ho2	N7	99.71(10)
06	Но2	N7	116.18(10)
08	Ho2	N7	74.11(10)
N6	Ho2	N7	75.79(11)
07	Ho2	N8	82.65(11)
05	Ho2	N8	77.25(10)
06	Ho2	N8	144.83(10)
80	Но2	N8	137.72(11)
N6	Но2	N8	74.90(11)
N7	Ho2	N8	74.37(11)
N22	в1	N4	109.1(4)
N22	В1	N5	108.7(4)
N4	B1	N5	109.2(4)
<b>N1</b> 1	B2	N9	108.2(4)
N11	в2	N10	109.6(3)
N9	в2	N10	109.5(3)
C1	N1	N22	105.5(3)
C1	N1	Ho1	130.5(3)
N22	N1	Ho1	123.9(3)
C4	N2	N4	105.4(3)
C4	N2	Ho1	131.0(3)
N4	N2	Ho1	123.5(3)
C7	N3	N5	105.5(3)
C7	N3	Ho1	130.4(3)
N5	N3	Ho1	124.1(3)
C6	N4	N2	109.3(4)
C6	N4	в1	127.7(4)
N2	N4	в1	123.0(3)
C9	N5	N3	110.0(4)
C9	N5	в1	128.8(4)
N3	N5	в1	121.2(3)
C28	N6	N9	105.9(3)
C28	N6	Но2	129.8(3)
N9	N6	Но2	123.9(2)
C31	N7	N10	106.6(3)
C31	N7	Ho2	131.1(3)
N10	N7	Но2	122.3(2)
C34	N8	N11	105.5(3)

## Appendix

C34	N8	Ho2	130 6(3)
N11	N8	Ho2	$123 \ 4(2)$
C30	N9	N6	110 2(3)
C30	N9	B2	128 0(3)
N6	NQ	22 B)	120.0(3)
C33	N10	DZ N7	121.5(3)
C22	N10	N /	109.2(3)
C33	N10	BZ	128.0(4)
	NIU	BZ	122.8(3)
036	NII	N8	109.9(3)
C36	NII	B2	128.4(4)
N8	N11	B2	121.5(3)
C3	N22	N1	109.8(4)
C3	N22	B1	128.9(4)
N1	N22	B1	121.3(3)
C10	01	Ho1	168.0(3)
C10	01	Ho1	86.2(2)
Ho1	01	Ho1	102.42(10)
C10	02	Ho1	101.4(3)
C19	03	Ho1	133.2(3)
C19	04	Ho1	137.0(3)
C37	05	Ho2	139.4(3)
C37	06	Ho2	141.8(2)
C46	07	Ho2	162.0(3)
C46	08	Ho2	123 9(3)
N1	C1	C2	111 5(4)
N1	C1	н1	124 2
C2	C1	н1	124.2
C2	$C^2$	C1	104.7(4)
C3	C2	U Ц	104.7(4)
CJ C1	C2 C2	11Z 112	107 7
		п <u>∠</u> СЭ	109 E(4)
NZZ			106.5(4)
NZZ	C3	H3	125.7
CZ NO	03	H3	125.7
NZ	C4	C5	111.2(4)
NZ	C4	H4	124.4
C5	C4	H4	124.4
C6	C5	C4	104.6(4)
C6	C5	H5	127.7
C4	C5	H5	127.7
N4	C6	C5	109.5(4)
N4	C6	Н6	125.3
C5	C6	Н6	125.3
N3	C7	C8	110.9(4)
N3	C7	H7	124.5
C8	C7	Н7	124.5
C9	C8	C7	105.1(4)
C9	C8	H8	127.4
C7	C8	Н8	127.4
N5	C9	C8	108.4(4)
N5	C9	Н9	125.8
C8	C9	н9	125.8
02	C10	01	119.8(4)
02	C10	C11	120.2(4)
01	C10	C11	120.0(4)
02	C10	Ho1	53.2(2)
01	C10	Ho1	67.5(2)
C11	C10	Ho1	166.4(3)
C12	C11	C10	121.6(4)
C12	C11	H11	119.2
C10	C11	н11	119.2
	C12	C13	129.5(4)
	U I 2		

C11	C12	H12	115.3
C13	C12	H12	115.3
C14	C13	C18	118.4(4)
C14	C13	C12	118.1(4)
C18	C13	C12	123.5(4)
C15	C14	C13	121.2(4)
C15	C14	H14	119.4
C13	C14	H14	119.4
C14	C15	C16	119.3(4)
C14	C15	Н15	120.4
C16	C15	H15	120.4
C17	C16	C15	120.2(4)
C17	C16	H16	119.9
C15	C16	H16	119.9
C16	C17	C18	121.3(4)
C16	C17	H17	119.4
C18	C17	H17	119.4
C17	C18	C13	119.8(4)
C17	C18	H18	120.1
C13	C18	H18	120.1
04	C19	03	124.6(4)
04	C19	C20	118.1(4)
03	C19	C20	117.3(4)
C21	C20	C19	121.4(4)
C21	C20	H20	119.3
C19	C20	H20	119.3
C20	C21	C22	127.2(4)
C20	C21	H21	116.4
C22	C21	H21	116.4
C23	C22	C27	118.9(4)
C23	C22	C21	122.8(4)
C27	C22	C21	118.3(4)
C22	C23	C24	119.7(5)
C22	C23	H23	120.1
C24	C23	H23	120.1
C23	C24	C25	120.6(5)
C23	C24	H24	119.7
C25	C24	H24	119.7
C26	C25	C24	120.0(5)
C26	C25	H25	120.0
C24	C25	H25	120.0
C25	C26	C27	120.1(5)
C25	C26	H26	120.0
C27	C26	HZ6	120.0
C26	C27		120.7(5)
C26	CZI		119.0
	C27	HZ/	119.0
N6	C28	C29	110.6(4)
N6	C28	HZ8	124.7
C29	C28	H28	124.7
C30	C29		105.0(4)
C30	C29	H29	127.5
C28	C29	H29	127.5
N9 NO	C30	029	100.3(4)
N9 GDD	C30	H3U	125.0
C29		020	110 E(A)
IN /		し34 1121	107 7
		רכד רכים	エムせ・/ 1 つ Λ - ワ
032	C31	пэт СЗ1	105 1 <i>(1</i> )
033	(34 (32)	U20	107 /
633	C34	1172	14/.4

C31	C32	Н32	127.4
N10	C33	C32	108.5(4)
N10	C33	Н33	125.7
C32	C33	H33	125.7
N8	C34	C35	111.2(4)
N8	C34	H34	124.4
C35	C34	H34	124.4
C36	C35	C34	104.4(4)
C36	C35	Н35	127.8
C34	C35	H35	127.8
N11	C36	C35	108.9(4)
N11	C36	Н36	125.5
C35	C36	H36	125.5
06	C37	05	124.4(3)
06	C37	C38	119.3(3)
05	C37	C38	116.3(3)
C39	C38	C37	123.1(4)
C39	C38	Н38	118.5
C37	C38	H38	118.5
C38	C39	C40	127.1(4)
C38	C39	Н39	116.4
C40	C39	H39	116.4
C41	C40	C45	118.4(4)
C41	C40	C39	122.8(4)
C45	C40	C39	118.7(4)
C42	C41	C40	121.1(4)
C42	C41	H41	119.4
C40	C41	H41	119.4
C41	C42	C43	119.7(4)
C41	C42	н42	120.1
C43	C42	н42	120.1
C44	C43	C42	120.1(4)
C44	C43	H43	120.0
C42	C43	Н43	120.0
C43	C44	C45	120.3(4)
C43	C44	H44	119.8
C45	C44	H44	119.8
C44	C45	C40	120.3(4)
C44	C45	H45	119.8
C40	C45	H45	119.8
07	C46	08	122.9(4)
07	C46	C47	121.1(4)
08	C46	C47	116.0(3)
C48	C47	C46	124.4(4)
C48	C47	H47	117.8
C46	C47	H47	117.8
C47	C48	C49	125.8(4)
C47	C48	H48	117.1
C49	C48	H48	117.1
C54	C49	C50	118.1(4)
C54	C49	C48	119.5(4)
C50	C49	C48	122.4(4)
C51	C50	C49	121.5(4)
C51	C50	H50	110.3
C49	C50	H50	119.3
C50	C51	C52	120 1
C50	C51		120.1
C52	CSI		110 ///
C53	052	UD1 UE2	エエブ・4(4) 1つへ つ
C53	C52	по <u>и</u> псо	120.3
C51	C52	п <i>э</i> 2	120.3

## Appendix

C52	C53	C54	121.0(4)
C52	C53	Н53	119.5
C54	C53	H53	119.5
C53	C54	C49	120.2(4)
C53	C54	н54	119.9
C49	C54	H54	119.9