CHAPTER - III

Study of Absorption Spectra, Luminescence Properties
And Inter- Component Energy Transfer Of
\[ [M(bpy)_3-(dph)_n-M'(bpy)_3]^{4+} \quad [M=M'=Os \text{ (II)}, Ru(II)] \]
Homo and Heterodinuclear Complexes
Introduction:

The reactivity of multinuclear compounds are generally photochemically activated, creating one or multiple co-ordinatively vacant sites of the metal\(^1\), Dinuclear metal complexes such as M, M' \((\text{CO})_{10}\) \([\text{M,M'}=\text{Mn, Re}]\) can be viewed as prototypical compounds\(^2\) resulting the primary photochemical reaction in solution to result in (i) homolytic fission of the metal-metal - s bond to form M(\text{CO})\(_3\) radicals, (ii) dissociation of CO ligand to form M, M'(\text{CO})\(_3\) and (iii) undissociative relaxation to the electronic ground state. Recently Hawyang et.al.\(^3\) investigated the ultrafast reaction dynamics and photo dissociation of Re(\text{CO})\(_{10}\) experimentaly and reported that the quantum yield of Re-Re bond dissociation is governed by germinate recombination, two time scale in \(\text{CCl}_4\); \(\approx 50\) and \(\approx 500\) ps. Polynuclear system with 3 or more metal ions bridged by oxo or acetato groups have recently attracted considerable attention due to existence of oxo-bridged tri and multinuclear metal constellation in metallo proteins and enzymes. Recently Sri Niwas, R. Korupoju\(^4\) et.al. reported the first tempalate free, trinucleating 3+3 shiff base macro-cycle \(\text{H}_2\text{L}-(\text{I})\) from the condensation of 2, 6-diformyl-4-Me-phenol (dpf) and trans-(1R, 2R) - cycle hexane diamine. The molecular structure of I have been deduced from crystal structure of its reduced analogue (II).

More recently the molecular level systems have attracted research workers where photoinduced energy and electro-transfer processes can be obtained over long distances and/or along predetertermined directions\(^5\). Light plays a major role in signal generation processes and storage so a molecular level system can be designed capable of elaborating light signals. In photoinduced energy and electron transfer processes, the spacer plays a fundamental role. When the spacer is not rigid (i.e. - \((\text{CH}_2)_n\) -) and geometry of the system is not well defined. Role played by spacer is not only structural,
its chemical nature controls the electronic communication between the selected terminal units. Another feature of spacer is its modular composition which allows changing distance without changing the electronic nature of the connection, Bridges like hydrocarbons $^6$ modified proteins and peptides$^8$, DNA$^9$ have been used. G. Mishra$^{10}$ et al. investigated and studied the spectroelectrochemical, electrochemical and crystallographic properties of Os-dioxolene. After spectroelectrochemical studies of complexes, the spectra were assigned with reference to the mononuclear model complex $[\text{Os}^{III} (\text{bpy})_2 (\text{CA})][\text{PF}_6] \{\text{H}_2(\text{CA})\} ((\text{A}=\text{catechol})$ which was examined spectro electrochemically and crystallographically.

In this paper we have synthesized the nanometric compounds of general formula $[\text{M(bpy)}_3-(\text{dph})_n - \text{M'(bpy)}_3]^{4+}$ ($\text{M}=\text{M'}=\text{Ru(II)}$, $\text{M}=\text{M'}=\text{Os(II)}$, $\text{M'}=\text{Os(II)}$; bpy = 2, 2'-bipyridine; dph = 1,2-diphenylene; $n=1,3$ and 5; the central diphenylene units bear 2 methyl groups). Further we discuss the absorption spectra luminescence properties and the occurrence of inter component electronic energy transfer process along with their rates and mechanism.

**Experimental Section:**

**Material:**

All the compounds have been purified and fully characterized by NMR, and mass spectra. Details of synthesis, purification methods and characterizations are given in literature.

**Instrumentation:**

Absorption and emission spectra were obtained on air-equilibrated solution using equipment$^{11}$. Luminescence decay measurements were performed with an Edinburgh single-photon-counting instrument. Hamamatsu C-5680 streak camera was equipped
with a M 5677 sweep unit used to get time-resolved emission spectra Excitation at 338 nm, achieved by a pulsed (fwhm 600 ps) nitrogen laser (LTB, MGS 405 TD) operating at a repetition rate of 20 Hz.

Synthesis :-

We first synthesized boronic acid derivatives of oligophenylene, \( (OH)_2 \) B-(dph), -B(OH), \( n=1,3,5; \) the central diphenylene unit bears two methyl groups) and then reacted them with 4'-Br-diphenyl - bipyridine to obtain the bis-bipyridine bridging ligands bpy - (dph) - bpy \( (n=1, 3, 5) \) as shown in scheme 1. The homo dinuclear \([Ru(bpy), -(dph) - Ru (bpy),]^2+\) and \([Os (bpy), -(dph) - Os (bpy),]^4+\) complexes were obtained by reacting the bridging ligands with 2 equiv. of the appropriate M(bpy), Cl, species, according to procedure used for homodinuclear Ru and Os compounds\(^{11, 12}\). Scheme (II), The heterodinuclear \([Ru(bpy), -(dph) - Os (bpy),]^4+\) complexes were prepared according to literature methods, reacting the bridging ligands with Os(bpy), Cl, to obtain mononuclear \([(bpy) - (dph) - Os (bpy),]^2+\) species followed by reaction with Ru(bpy), Cl, (Scheme 3). Molecular modeling shows that the metal-to-metal distance is 3.5, 4.2 and 5.2 for \( n = 1, 3 \) and 5 respectively.

Spacers and Bridging Ligands :-

Oligophenylene shows an intense absorption band and a strong short-lived fluorescence band in the near-UV spectral region\(^{13}\). The compounds TMS - (dph), Br (where TMS = trimethyl silyl, and two diphenylene units bear methyl group) shows an absorption maximum at 265 nm and a fluorescence band with maximum at 335 nm. The bpy - (dph), bpy bridging ligand (Scheme 1) shows an absorption band with
maximum at 315 nm and a fluorescence band with maximum at 390 nm. Both of the fluorescence bands are very intense (quantum yield around 0.4) and short lived (lifetime shorter than 1 ns). Even in rigid matrix at 77 K, the fluorescence bands are very strong.

Results:-

Metal Complexes :-

(i) Absorption Spectra :-

The absorption spectra of the homodinuclear \([\text{Ru(bpy)}_3-(\text{dph})_3-\text{Ru(bpy)}_3]^+\)
and \([\text{Os(bpy)}_3-(\text{dph})_3-\text{Os(bpy)}_3]^+\) and the heterodinuclear \([\text{Ru(bpy)}_3-(\text{dph})_5-\text{Os(bpy)}_3]^+\)
complexes in acetonitrile solution at 293 K. (Fig. 1) The spectra of the complexes with \(n=3\) or \(5\) are identical, within the experimental errors, The absorption spectra of the heterodinuclear \([\text{Ru(bpy)}_3-(\text{dph})_n-\text{Os(bpy)}_3]^+\) complexes are equal to the spectra of the 1: mixture of the corresponding homodinuclear \([\text{Ru(bpy)}_3-(\text{dph})_n-\text{Ru(bpy)}_3]^+\) and \([\text{Os(bpy)}_3-(\text{dph})_n-\text{Os(bpy)}_3]^+\) parent compounds, when excitation of the heterodinuclear \([\text{Ru(bpy)}_3-(\text{dph})_n-\text{Os(bpy)}_3]^+\) complexes is performed in correspondence with this isosbestic point, the Ru-based and Os-based units absorb the same fraction of incident light. This is a quite useful feature for the quantitative evaluation of the quenching and sensitization processes.

(ii) Luminescence Properties :-

The nine dinuclear complexes show emission bands only in the spectral region above 575 nm (Table 1). In particular, when excitation was performed with UV light, no emission was observed in the spectral region (1 <465 nm) where the free diphenylene spacers and the free diphenylene bridging ligands exhibits their fluorescence

(76)
bands. The steady-state luminescence spectra of the [Ru(bpy)$_3$ - (dph)$_5$ - Ru (bpy)$_3$]$^{4+}$ and [Os (bpy)$_3$ - (dph)$_5$ - Os (bpy)$_3$]$^{4+}$ complexes in acetonitrile solution at 293 K are shown in Fig. 2a. The spectra of the complexes with n = 3 or 5 are identical, with in the experiments error, to those with n = 5. Spectra of the heterodinuclear complexes [Ru(bpy)$_3$ - (dph)$_n$ - Os(bpy)$_3$]$^{4+}$ (n =1,3,5) is shown in Fig. 2b. The spectra have been obtained with diluted solutions and have been corrected for the fraction of absorbed light, their intensities are directly comparable. The maxima of the emission bands, the emission quantum yields, and the excited-state lifetimes are gathered in Table - 1 where the luminescence properties of the [Ru (bpy)$_3$]$^{2+}$ and [Os (bpy)$_3$]$^{2+}$ complexes taken as models of the metal-based chromophoric units are displayed for comparison. The luminescence intensity was found to show a monoexponential decay in all cases except for the emission at 735 nm of the [Ru(bpy)$_3$ - (dph)$_n$ - Os(bpy)$_3$]$^{4+}$ compounds where a rise time observed (Fig 3).

**Discussion :-**

**Absorption Spectra and Luminescence Properties :-**

The [M(bpy)$_3$ - (dph)$_n$ - M' (bpy)$_3$]$^{4+}$ compounds (chart 1) can be viewed as made of [M(bpy)$_3$]$^{2+}$ and [M' (bpy)$_3$]$^{2+}$ chromophoric groups (M = M' = Ru (II); M = M' = Os (II); M = Ru(II), M' = Os (II), separated by diphenylene-type spacers (n=1, 3 and 5). Each one of the three separated component units show characteristic absorption and emission bands (Fig- 1,3 Table 1) Investigations performed on [Ru (bpy)$_3$]$^{2+}$ and [Os (bpy)$_3$]$^{2+}$ and related complexes$^{14}$ have shown that (i) their high-intensity absorption bands in the 245-295 nm spectral region are due to spin-allowed ligand-centred (LC) transition; (ii) their absorption bands in the 450-600 nm region are due to spin-allowed
metal - to - ligand charge transfer (MLCT) transitions (iii) for the compounds of the heavier (Os) metal, spin- forbidden MLCT bands can also be seen in the 500-650 nm region; (iv) luminescence takes place from the lowest-energy triplet MLCT excited state; and (v) the luminescent excited state is very rapidly populated with unitary efficiency regardless of the excitation wavelength. As to the diphenylene units, their absorption and emission bands in the near -UV spectral region are due to spin-allowed p - p* transitions\textsuperscript{13}.

In dinuclear metal complexes, electronic interaction between the mononuclear components may range from very strong to very weak (with almost equal properties for separated and bridged units), depending on the type of bridge.\textsuperscript{15-17} The interaction between the two metal based units is weak and shows following results; (i) the absorption spectra in the visible region of the homodinuclear \([M(bpy)\textsubscript{3}(dph)\textsubscript{n} ]^{4+}\) species are identical to those of the corresponding \([M(bpy)\textsubscript{3}]^{2+}\) model compound; (ii) the absorption spectra in the visible region of the heteronuclear [Ru (bpy)\textsubscript{3}-(dph)\textsubscript{n} - Os(bpy)\textsubscript{3}]\textsuperscript{4+} complexes are practically identical to those of 1:1 mixtures of their corresponding homodinuclear [Ru(bpy)\textsubscript{3}-(dph)\textsubscript{n}-Os(bpy)\textsubscript{3}]\textsuperscript{4+} and [Os(bpy)\textsubscript{3}-(dph)\textsubscript{n} - Os(bpy)\textsubscript{3}]\textsuperscript{4+} parent compounds; (iii) the emission maximum, lifetime and quantum yield of the phosphorescence band of each \([M(bpy)\textsubscript{3}]^{2+}\) units are unaffected by the length of the diphenylene spacer by the nature of the metal contained in the \([M'(bpy)\textsubscript{3}]^{2+}\) unit.

**Intercomponent Energy Transfer :-**

The energy level diagram for the heterodinuclear Ru (bpy)\textsubscript{3}-(dph)\textsubscript{n} - Os (bpy)\textsubscript{3}\textsuperscript{4+} compounds are shown in Fig.4. For the metal-based components an approximate value of the energy of the lowest spin-allowed

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MLCT excited state is given by the energy of the maximum of the corresponding absorption band, where as the energy of the lowest spin-forbidden MLCT excited state can be obtained from the maximum of the emission band at 77K. The energy of the lowest triplet excited state is 22850 cm\(^{-1}\) for biphenyl and 20350 cm\(^{-1}\) for p-terphenyl\(^{19}\). If the energy of the lowest excited triplet decreases as 1/n as it is known to happen for the maximum of lowest energy absorption band\(^{18}\) and the singlet-triplet separation remains constant, it can be estimated that the energy of the lowest excited triplet is around 18500 cm\(^{-1}\) for hexaphenyl and 17000 cm\(^{-1}\) for decaphenyl. The lowest excited state of any of the oligophenylene spacers lies above the MLCT state of the Ru-based moiety is confirmed by the fact that the emission intensity and lifetime of the Ru-based units of the \([\text{Ru(bpy)}_3-(\text{dph})_n-\text{Ru(bpy)}_3]^{4+}\) compounds are not quenched by any spacer (Table 1). As far as the metal-based unit are concerned, the diagram shown in Fig. 4 can be used for each one of the three heteronuclear complexes. None of the dinuclear complexes shows any evidence of diphenylene fluorescence. This means that the potentially fluorescent diphenylene excited state is very efficiently quenched by the connected metal-based units. In the heterodinuclear \([\text{Ru(bpy)}_3-(\text{dph})_n-\text{Os(bpy)}_3]^{4+}\) compounds, the phosphorescence intensity and lifetime of the Ru-based units are quenched. Under experimental conditions used (complex concentration 3.0 \times 10^{-3} M) intermolecular quenching processes can be excluded so that the observed quenching has to be due to intercomponent interaction. By comparing the behaviour of the various complexes on excitation at 430 nm the amount of intensity quenching can be obtained, i.e. under conditions in which each metal-based units absorbs the same fraction of incident light- The emission quantum yield (Fig. 2 and Table 1) and life time of the Ru-based units are quenched in the heterodinuclear \([\text{Ru(bpy)}_3-(\text{dph})_n-\text{Os(bpy)}_3]^{4+}\)
compounds, and the quenching effect increases on decreasing the number of diphenylene units contained in the spacer. The quenching of the phosphorescence intensity of the Ru-based unit is accompanied by a corresponding sensitization of the Os-based unit. So the quenching process occurs via an energy-transfer mechanism. This is also confirmed by the fact that a rise time for the Os-based phosphorescence can be observed which is in good agreement with the lifetime of the decay of the Ru-based phosphorescence. The rate constant of the energy-transfer process can be obtained from the equation

\[ K = (1/\tau) - (1/\tau^0) \]  \hspace{1cm} (1)

Where \( \tau^0 \) and \( \tau \) are the phosphorescence life time of the Ru (II)-based component in the \([\text{Ru} \ (\text{bpy})_3 \cdots \text{(dph)}_n \cdots \text{Ru(bpy)}_3]^{4+} \) and \([\text{Ru(bpy)}_3 \cdots \text{(dph)}_n \cdots \text{Os(bpy)}_3]^{4+} \) compounds respectively. These values obtained in acetonitrile solution at 293 K and in butyronitrile rigid matrix at 77 K are shown in Table 2.

The energy-transfer rate constant can also be calculated from equation.

\[ K_{en} = (1/\tau^0) \left( I^0/I-1 \right) \]  \hspace{1cm} (2)

Where \( I^0 \) and \( I \) are the relative emission intensites, after appropriate normalization for absorption, of the Ru-based emission of \([\text{Ru} \ (\text{bpy})_3 \cdots \text{(dph)}_n \cdots \text{Ru(bpy)}_3]^{4+} \) and \([\text{Ru} \ (\text{bpy})_3 \cdots \text{(dph)}_n \cdots \text{Os(bpy)}_3]^{4+} \) compounds respectively. The values obtained in this way are equal, with in the experimental error, to those obtained from eq 1.

**Energy-Transfer Mechanism**

Energy transfer can take place by coulombic (Forster)\(^{19}\) and exchange (Dexter)\(^{20}\) mechanism. In Forster the main contribution to the rate constant comes from the dipole-dipole interaction between donor and acceptor.
and $D G^\circ$ can be obtained from eqs 6 and 7 respectively:

$$K_{en} = V_{en} \exp (-D G^\circ/RT) \quad (5)$$

$$V_{en} = [2(H_{en})^2/h \left( \frac{p^2}{\lambda RT} \right)]^{1/2} \quad (6)$$

$$D G^\circ = (\frac{\lambda}{4}) \left( 1 + D G^\circ / \lambda \right)^2 \quad (7)$$

Following the assumptions, the free energy change $D G^\circ$ can be expressed as the difference between the spectroscopic energies of the donor and acceptor (Ca. 2950 cm, $^{-1}$) as estimated from the energy of the Ru-based as Os-based emission maxima at 77 K), and the reorganization energy can be estimated to be Ca 1400 cm$^{-1}$. This yields a value of about 0.1 for the exponential term eq 5. This means that, for the compound with the shortest spacer ($n=3$), $V_{en}$ is less than $10^9$ S$^{-1}$, and, as a result (eq 6), the electronic interaction energy $H_{en}$ is less than 1 cm$^{-1}$, this justifies the nonadiabatic treatment. In the frame of the superexchange mechanism, $H_{en}$ follows an approximate exponential decay with increasing distance $r$, Viz,

$$H_{en} \propto \exp (-0.5 \beta r) \quad (8)$$

Since the other terms in eq 5-7 are not expected to be distance dependent, also the energy-transfer rate constant should fall off exponentially as

$$K_{en} \propto \exp (-0.5 \beta r) \quad (9)$$

The rate constant is also related to the number of diphenylene. units by the equation

$$K_{en} \propto \exp (-\gamma r) \quad (10)$$

Where $n$ is the number of diphenylene units. A plot of $K_{en}$ Vs the metal - to - metal distance or number of interposed diphenylone unit for the energy - transfer process in the $(Ru \ (bpy)_3-(dph)_n-Os(bpy)_3)_{1+}$ compounds.

For comparison, the attenuation co-efficient is 2.6 per $\sigma$ bond for triplet - triplet energy transfer from a benzophenonyl to a naphthyl unit connected by steroid -
type bridges, and 1.23 per $A^0$ and 1.49 per $\sigma$ bond for singlet-singlet energy transfer from 1,4- dimethoxynaphthalene to a cyclic ketone connected by rigid, elongated hydrocarbon bridges.

The results obtained are consistent with literature reports indicating that diphenylene spacer have a small effect in decreasing electronic coupling e.g. for photoinduced electron transfer in electron donor/electron acceptor bis-porphyrin compounds and singlet-singlet energy transfer between porphyrins. Efficient electronic communication through diphenylene bridges is also shown by the presence of intervalence bands in (Me dph -tpy) Ru II [tpy-(dph)$_2$ -tpy] Ru III (tpy - dph Me) $^{5+}$ (tpy = 2,2': 6, 2''-terpyridine: interaction energy Ca 170 cm$^{-1}$) and (NH$_3$)$_3$ Ru II [py - (dph)$_2$- py] Ru III (NH$_3$)$_5$ $^{5+}$ (py = Pyridine)
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<th>298K*</th>
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<th>77K^-</th>
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<td>Os</td>
<td>Ru</td>
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<td>$\tau(\text{ns})$</td>
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* Air-equilibrated acetonitrile solution
~ Butyronitrile rigid matrix
Table - 2

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<td>1.2 x 10$^6$</td>
</tr>
</tbody>
</table>

* Air-equilibrated acetonitrile solution

~ Butyronitrile rigid matrix
Scheme 1

$$\text{N} \quad \text{N} \quad \text{Br} + (\text{HO})_2 \text{B} \left( \text{O} \right)_m \text{B(OH)}_2$$

Pd(PPh3), Water/Toluene/Ba(OH)2

$$\downarrow$$

$$\text{N} \quad \text{N} \quad \text{CH}_3 \quad \text{CH}_3$$

bpy-(dph)$_m$-bpy

m = 0, 1, and 2
Scheme 2

\[ \text{[Os(bpy)]}_3-(\text{dph})_n-\text{Os(bpy)}_3]^{4+} \]

1) 2eq Os(bpy)$_2$Cl$_2$
2) NH$_4$PF$_6$

1) 2eq Ru(bpy)$_2$Cl$_2$
2) NH$_4$PF$_6$

\[ \text{[Ru(bpy)}_3-(\text{dph})_n-\text{Ru(bpy)}_3]^{4+} \]

Synthesis of Homodinuclear \([\text{Ru(bpy)}_3-(\text{dph})_n-\text{Ru(bpy)}_3]^{4+}\) and \([\text{Os(bpy)}_3-(\text{dph})_n-\text{Os(bpy)}_3]^{4+}\) complexes \((n = 3,5)\)
$M = M' = \text{Ru: } [\text{Ru(bpy)}_2\text{-(dph)}_n\text{-Ru(bpy)}_2]^+$
$M = M' = \text{Os: } [\text{Ru(bpy)}_2\text{-(dph)}_n\text{-Os(bpy)}_2]^+$
$M = \text{Ru: } M' = \text{Os: } [\text{Ru(bpy)}_2\text{-(dph)}_n\text{-Ru(bpy)}_2]^+$
n = 1, 3 and 5

Chart-1 Formulas of the compounds and abbreviations used
Figure-1

Figure-2

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Fig. 1 Absorption spectra of [Ru(bpy)$_2$-(dph)$_2$Ru(bpy)$_2$]" (full line), [Os(bpy)$_2$-(dph)$_2$Os(bpy)$_2$]" (dotted line) and [Ru(bpy)$_2$-(dph)$_2$Os(bpy)$_2$]" (dashed line) complexes in acetonitrile solution at 293K. The concentration of the solution was 3.0 x10-6M in all cases. The spectra of the complexes with n=1 or 3 are identical to those with n=5, except in the 250-350nm region, where the absorption of the oligophenylene spacers is not negligible compared with the spectra of the two metal-based units.
Fig. 2 (a) Luminescence spectra of the complexes [Ru(bpy)$_2$(dph)$_2$Ru(bpy)$_2$]$^{2+}$ (full line) and [Os(bpy)$_2$(dph)$_2$Os(bpy)$_2$]$^{2+}$ (dotted line). (b) Luminescence spectra of the complexes [Ru(bpy)$_2$(dph)$_2$Os(bpy)$_2$]$^{2+}$ (n=1, full line; n=3, dashed line; n=5, dotted line). The spectra were recorded in acetonitrile solution at 293K. In all cases, excitation was performed in the isosbestic point at 435nm.
Fig 3. Luminescence spectrum (a) and intensity decay (b and c) for the \([\text{Ru} (\text{bpy})_2 (\text{dph})_2 \cdot \text{Os} (\text{bpy})_2 ]^{1+}\) compound in rigid matrix at 77K. The emission of the Ru-based moiety occurs between 550 and 550 nm (b), and that of the Os-based moiety occurs between 680 and 750 nm (c). The decay of the Ru-based emission (93 ns) is the same as the rise time of the Os-based emission.
Fig. 4 Schematic energy-level diagram for the heterodinuclear Ru(bpy)$_3$-(dph)$_2$-Os(bpy)$_3$ complex. The energy of the $T_1$ level of the oligophenylene linker is estimated for the hexaphenylene.
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(93)


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