Advances in Contemporary Research

Tailored ruthenium polypyridyl complexes as molecular electronic materials

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In the present review, salient features of ruthenium polypyridyl complexes tailored for molecular electronic properties are presented. Attempts are also made to explore these newly synthesized materials in the construction of molecular wires, molecular rods, luminescence switches as well as sensors.

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Multidisciplinary scientific researches have provided technology for the fabrication of devices with the purpose of signal1 and information receiving2, storing3 and processing. Development of such devices on a molecular level falls under the purview of molecular electronics. However, the term electronics is more generic in nature and does not imply utilisation of motion of electrons for information processing. For example the concept of machine can be extended to the molecular level. A molecular level machine could be defined as an assembly of a discrete number of molecular components designed to perform mechanical movements (output) as a consequence of appropriate external stimuli (input). It is very young field of science initiated in late 1970.

The investigation of molecular machines and motors is an exciting area of contemporary research which lies at the interface of chemistry, biology, physics and material science.

Molecular level machines operate via electronic and molecular rearrangements i.e. bringing some kind of chemical reactions. Like macroscopic machines, they are characterized by (i) energy input to make them work, (ii) movement performed by their
components, (iii) the way in which their operation can be controlled and monitored, (iv) the possibility to repeat the operation at will, (v) time scale needed to complete a cycle of operation and (vi) the function performed.

Since a machine has to work by repeating cycles, an important requirement is that any chemical reaction in a molecular device has to be reversible. Currently there is an increasing interest in the development of photon- and electron/hole-powered molecular-level machines by taking advantage of the outstanding progress made in supramolecular photochemistry and electrochemistry. In the case of photoexcitation, the most suitable candidates are photoisomerisation and photoinduced redox reactions. Photochemical and electrochemical energy inputs offer other advantages compared to alternative chemical energy inputs. For example, they can be switched on and off easily and rapidly.

Thus, the development of concepts for the construction of the machines on the molecular level is very important not only from basic research point of view but also from the growth of nanoscience and nanotechnology. The idea of constructing artificial molecular-level machines was introduced by F.L. Carter, Naval Research Laboratory, USA and Richard P. Feynman, who got Nobel prize in Physics.

Microelectronics which is based on bulk properties of inorganic substances, has so far succeeded in producing cost effective, high speed, low energy consuming, small sized, low weight, long lasting and highly reliable devices. However, when the size of individual elements reaches less than tenth of a micron, thermal and quantum size effects will make the electronic components unreliable. Hence, the need to look for molecular devices. Molecular electronics should not be anticipated to emerge as a revolutionary technology, threatening to replace conventional solid state electronics but could be considered as a complementary technology. One may explore possibilities of novel applications which may be beyond present day electronics. A perfect marriage between man-made microelectronics and nature evolved systems is envisaged to produce more intelligent and high performance devices. Construction of molecular-based devices is expanding, especially, in the design and development of nanomachines. Bottom-up construction of miniaturized components capable of performing specific functions are important challenges before modern chemists. Progress in this field requires the availability of molecular components (building blocks) having well-defined structures and properties.

In this context, attention has been focussed on systems containing $M(N-N)_2^{2+}$ ($M = Ru^{II}$ or $Os^{II}$; $N-N = 2,2'$-bipyridine or 1,10-phenanthroline) units as building blocks. The choice of such blocks is justified by their favorable excited-state redox properties as well as chemical stability. The general behaviour of Ru(II) $L_3$ complexes used in the construction of molecular devices is depicted in Fig. 1.

**Synthetic Ru-based Materials**

The development of any device needs the corresponding materials synthesized by chemists. Therefore, it is of worth to look on the intelligent design and development of ruthenium-based materials, specially, from molecular electronic viewpoint.

In general, mononuclear and binuclear (homo/hetero) ruthenium complexes are synthesized following Scheme 1.

**Mononuclear**

- $\text{Ru}_2 \text{Cl}_2 + BL \rightarrow [\text{Ru}_2 \text{(BL)}]^{2+}$
- $[\text{RuCl}_3] + 2BL \rightarrow [\text{Ru} \text{(BL)}]^{2+}$
- $\text{RuCl}_3 + 3BL \rightarrow [\text{Ru} \text{(BL)}]^{3+}$

**Binuclear complexes**

- $\text{Ru}_2 \text{Cl}_2 + [\text{Ru}_2 \text{(BL)J}]^{2+} \rightarrow [\text{L}_2 \text{Ru} (\mu-\text{BL}) \text{Ru}_2]^{4+}$

**Scheme 1**

A detailed account of such synthesis and characterization techniques have been published previously.

To obtain dinuclear heterometallic complexes, the usual approach involves two steps. First, a mononuclear complex-ligand is prepared by reacting...
a metal precursor with an excess of the ligand. During this step, dinuclear homometallic by-products are unavoidably formed which may be separated from desired mononuclear complexes using column chromatography. In the following step, the second metal is added so that only the dinuclear homometallic species are obtained.

The complexes incorporating the Ru(bpy)_2²⁺ moiety are of interest since they construct efficient intramolecular electron or energy transfer systems. Several multicomponent systems (often called supramolecular species) have been designed and studied in terms of their photo and/or redox properties. In fact these properties have spurred the development of newer Ru(II) polypyridyl complexes either by incorporating the desired groups within the bipyridine or phenanthroline moiety, or by using other donor sites along with the [Ru(bpy/phenh)_2⁺]²⁺ core to form mixed ligand tris-chelate to modulate the photoredox activities of this class of complexes.

Complexes where bpy/phen-based photoactive centres are linked with the metal ions have shown problems in photoinduced processes due to the possible existence of different stereoisomers. To overcome such problems tridentate, terpyridine (tpy) type of ligands have emerged as a better choice. Such complexes are in fact achiral and the introduction of a single substituent in the 4′-position of each terpyridine ligand overcomes isomeric problems and offers the possibility of designing triads in which the two additional components are in opposite directions with respect to the photosensitizer.

However, such replacement of bpy to tpy-type ligand in the construction of Ru(II) complexes resulted into shorter excited-state lifetime and a much weaker luminescence intensity in solutions at room temperature. A systematic investigation of Ru(tpy)_2²⁺ type complexes has recently shown that this drawback can be overcome partially by appropriate substituents (e.g. MeSO₂) on the tpy ligand frame.

In the process of such development, Constable’s group in U.K. along with his collaborator in France successfully synthesized doubly cyclometallated diruthenium complex with strongly coupled metal centres. These complexes could easily be oxidized giving strongly coupled mixed Ru(III)-Ru(II) species. Thus, during the investigation of photoinduced energy and electron-transfer in geometrically well-defined polynuclear Ru-based systems, electronic and nuclear factors governing these processes could be studied. In this connection, the emission properties of a new Ru(tpy)_2²⁺ complex in which a 2,5-thiophenediy spacer connecting [Ru(tpy)_2]-chromophore modified the properties such that di- and tri-nuclear complexes luminesce like Ru(bpy)_2²⁺ have been reported. The excited states responsible for the luminescence were formally triplet Ru-tpy charge transfer. Luminescence maxima were found consistent with these sequential stabilization and passing from mono- to di- and tri-nuclear complexes. Barrigelleti _et al._ also prepared rigid rod-like dinuclear Ru(II)/Os(II) terpyridine complexes as shown in Fig. 2. These complexes were also studied for their luminescence and electronic energy transfer through phenylene bridges.

Thus, while assembling these units in the construction of supramolecular species, the selection of terminal as well as bringing ligand is very important and the distance between two metal centres bridging efficient bond coupling can be tuned by the bridging ligands. Supramolecular species consisting of oligo metal complexes having capability for use in photochemical molecular devices have been cited by Balzani _et al._

Keeping these points in view, Haga _et al._ developed novel bridging ligand based on benzimidazole unit. This unit has strong π-donor property and hence stabilizes Ru(III) state better than pyridine or pyrazing units. In the benzimidazole bridged dinuclear complexes (Fig. 3), when excited photochemically, negative charge on the bridging ligand enhanced hole-type super exchange interaction between the metal centres.

![Fig. 2—Heterotrinuclear complex having phenyl bridged extended conjugation](image-url)
Later, crown ether-bridged dinuclear Ru(II) polypyridyl complexes (Fig. 4) were synthesized by Beer et al.\textsuperscript{27} which show anion binding properties.

Recently our group has reported\textsuperscript{28-32} a series of homodinuclear Ru(II) polypyridyl complexes (Fig. 5) having extended conjugated bridging ligands. We have also studied their redox and luminescent properties. Extensive luminescence quenching observed from dinuclear Ru(II) complexes as compared to their mononuclear analogues suggested photoinduced intramolecular electron and/or energy transfer between the two metal centres.

Heterodinuclear complexes containing Ru(II) polypyridyl component as one of the core has been the subject of great importance\textsuperscript{33-34} for the intramolecular electron/energy transfer processes which have vital role in designing the photochemical molecular devices.

Komatsuzaki et al.\textsuperscript{35} reported a series of dinuclear heterometallic ruthenium-cobalt and ruthenium-nickel complexes which are shown in Fig. 6.

The lowest energy charge-transfer bands, attributable to the Ru$\rightarrow$bpy transition, were little affected by the intramolecularly attached Co(III) or Ni(II) moiety, and indicate that Ru(II) and Co(III) or Ni(II) have no electronic interaction. Their luminescence behaviour had also been studied. [Co(bpy)$_3$]$^{2+}$ and [Ni(bpy)$_3$]$^{2+}$ did not show emission since these compounds do not absorb light in this wavelength region. Other complexes containing the [Ru(bpy)$_3$]$^{2+}$ moiety emitted at $\sim$610 nm though the relative luminescence intensity from the dinuclear complexes was found to be 30-47% less than analogous mononuclear complexes.

Though the excited-state of [Ru(bpy)$_3$]$^{2+}$ moiety in 3 (Fig. 6) should have been quenched intramolecularly by the attachment of [Co(bpy)$_3$]$^{2+}$ and [Ni(bpy)$_3$]$^{2+}$ moieties as observed by several research groups, these dinuclear complexes did not
quench completely. Such incomplete quenching may be due to emission caused by Ru(II) species produced by the dissociation of \([\text{Co(bpy)}_2]^{2+}\) and \([\text{Ni(bpy)}_2]^{2+}\) from heterobimetallic complexes (Fig. 6) due to the instability of these complexes under irradiation condition.

Recently, the same group\(^\text{36}\) also studied the photochemical properties of some Ru-Ni and Ru-Cu heterodinuclear complexes (Fig. 7) and observed that the excited-state of \([\text{Ru(bpy)}_2]^{2+}\) moiety in the dinuclear complexes is quenched by intramolecularly attached metal Schiff base and their emission intensity also reduced drastically to 2% compared to that of \([\text{Ru(bpy)}_2]^{2+}\) itself. It is, therefore, inferred that quenching of the excited state occurs because of the attached Ni and Cu Schiff base moieties.

In this context, Kimura \textit{et al.}\(^\text{37}\) have also prepared heterodimetallic complexes of \([\text{Ru(II)} (\text{bpy})_2 (\text{bpy-cyclam}) \text{Ni (II)}]^{4+}\) (cyclam = 1, 4, 8, 11-tetrazacyclotetradecene) (Fig. 8). The distance between Ru and Ni has been found to be 6.4\(\text{Å}\). The most remarkable feature of this structure is the anomalously close distance of 2.41\(\text{Å}\) between H (5) of the pendent phenanthroline and [Ni(II)] bound in the cyclam cavity.

Recently, we have also developed\(^\text{38}\) trinuclear Ru-Ni-Ru systems (Fig. 9), which showed extensive luminescence quenching as compared to the standard complex \([\text{Ru(bpy)}_2]^{2+}\) upon excitation at 440 nm.

Prior to our report Balzani \textit{et al.}\(^\text{39}\) have also reported heterobimetallic Ru-Os complexes (Fig. 10) containing 3,5-bis (pyridin-1,2,4-triazol) (bpt) as bridging ligand.

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**Fig. 6**—Heterobimetallic (Ru-Co) complexes.

**Fig. 7**—Heterodinuclear (Ru-Cu and Ru-Zn) complexes.

**Fig. 8**—Structure of Ru(phen)$_2^{2+}$ covalently attached to Ni$^{3+}$-cyclam complex.

**Fig. 9**—Heterotrinuclear (Ru-Ni-Ru) complexes.

**Fig. 10**—Homo and heterobimetallic (Ru-Ru) and (Ru-Os) complexes.
Luminescence and redox properties of these Ru-Os complexes [(bpy)$_2$ (Ru) (bpt) Os (bpy)$_2$]$^{2+}$ and [(bpy)$_2$ Os (bpt) (Ru (tpy)$_2$]$^{3+}$ have been compared with those of the corresponding dinuclear homometallic Ru(II)-Ru(II) and Os(II)-Os(II) complexes. Excitation in the Ru-based component is followed by $100\%$ efficient energy transfer to Os-based component. One electron oxidation products (which makes Os in the +3 oxidation state) are not luminescent because of the presence of a low-energy intravalence charge transfer band which is likely to deactivate the luminescent level. It is observed that the bpt bridge is not involved in the lowest energy excited states, which allows energy transfer to occur very rapidly from Ru(bpy)$_2$$^{2+}$ component to Os(bpy)$_2$$^{2+}$ or Os(bpy)$_2$$^{3+}$ components in the dinuclear species. A schematic presentation of such processes is depicted in Fig. 11.

There has been great interest in chiral complexes. The report by Tzalis et al. about the synthesis of an interesting rod like arrangement (Fig. 12) could be probably the first example of controlled synthesis of stereochemically defined multinuclear complexes based on Ru(II) centres.

Adopting similar synthetic strategy, a mixed metal Ru(II)-Pd(II) trinuclear complex based on enantiomerically pure Ru-centres (Fig. 13) is made which is another interesting rod like structure (nm level).

As compared to Ru(II)-tpy systems, Ru(II)-bpy and phen complexes generally have a longer excited-state lifetime and are found suitable for the construction of photosensitizers and light harvesting devices.

However, the latter systems give rise to diastereoisomers when more than one octahedral metal tris-(bidentate ligand) centre is incorporated. Development of diastereomerically pure compounds is, therefore, important as diasteroisomers differ in their physical properties such as rates of energy or electron transfer. The use of inorganic enantiomerically pure building blocks allows the construction of diastereomerically pure polymeric architectures without subsequent separation of diasteroisomers which avoids complications due to its exponential increase $2^N$ (N = the number of incorporated metal centres) in the number of stereoisomers.

In this connection, the work of Warnmark et al. is worth mentioning as they have reported the synthesis of extended enantio and diastereomerically pure tris-ruthenium disks from pure building blocks (Fig. 14).

Multimetallic assemblies containing Ru(II) poly-pyridyl complexes are important due to their chemical stability, favourable redox properties as well as photophysical characteristics. These multinuclear...
Ru(II) complexes have been predominantly constructed by the stepwise synthesis of multitopic ligands followed by metal complexation. While the natural photobiological assemblies have no stereochemical ambiguity, the synthetic systems are formed as diastereomeric mixtures. The functions of such heterogeneous systems are not well-defined, and their characterization is limited. A control over the absolute stereochemistry at each metal center is of ultimate importance in the design and synthesis of functional supramolecular architectures.

Tor et al.\textsuperscript{49} have reported a novel and versatile approach for the efficient synthesis of diastereomerically pure multi-Ru(II) arrays using enantiomerically pure chiral coordination complexes as building blocks (Schemes 2a and 2b), which have been characterized by CD spectra. Similarly, Lehn and his group recently reported\textsuperscript{43} stereoselective synthesis of linear bipyridylphenylene based ruthenium rods from enantiopure building blocks with structure as shown in Fig. 15. The stereochemistry of these complexes has also been determined using CD studies.

Further investigations in this area have led to the development of hyper branched nano sized molecules called dendrimers which are also known as arborols, cauliflower or starburst polymers and are the subject...
of much interest because of their unique structure and properties. These aesthetically appealing synthetic macromolecules distinguish themselves from normal polymers in several ways. First, they are constructed from $AB_n$ monomers ($n$ usually 2 or 3) rather than the standard $AB$ monomers which produce linear polymers. Secondly, they are synthesized in an iterative fashion. The combination of these two features leads to a non-linear, stepwise synthetic growth wherein the number of monomer units incorporated in each successive iteration roughly doubles ($AB_2$) or triples ($AB_3$) to that in the previous cycle.

Strategies for synthesizing dendrimers which have emerged during the past decade can be classified into divergent and convergent approaches. In the divergent strategy, dendrimers are built from the central core out to the periphery whereas the convergent strategy builds the dendrimers from the periphery toward the central core. Metal based dendrimers\textsuperscript{50-52} have received significant attention in recent years because they contain multiple coordination sites or

![Fig. 15—Enantiomerically pure ruthenium based rod like structure](image)

![Fig. 16—A metallodendrimer reported by Newkome, Constable and co-workers\textsuperscript{53}](image)
multielectron transfer redox centres and hence have the potential for wider applications like catalysts, molecular electronics, photochemical devices for information storage and switching as well as energy transfer and conversion devices.

A variety of Ru-based dendrimers have recently been synthesized. A representative example is the ruthenodendrimer reported by Newkome and co-workers\textsuperscript{53} (Fig. 16).

Recently, much attention has been focussed on the incorporation of luminescent, redox-active transition metal complexes, such as ruthenium polypyridine species, into the dendrimer structure as the potential of such systems for applications in light harvesting and energy storage devices has been realized. Bodige \textit{et al.}\textsuperscript{54} reported stereoselective synthesis of rigid $D_3$-symmetric tetranuclear ruthenium complex (Scheme 3).

![Scheme 3—Tetranuclear ruthenium(II) complex with $D_3$ symmetry](image)

**Applications**

**Molecular wires**

The origin of molecular wires can be traced to soliton theory\textsuperscript{55} of electronic conduction in DNA. The widespread interest in the studies of energy or electron transport schemes has resulted in the construction of molecular materials holding photoactive components usually at the termini of the system as well as in the storage and utilization of light-energy. As a consequence of specific interactions with light or after undergoing electrochemical process, such active units can be the initial and final sites for the temporary storage of energy. Other components, the linkers or bridge play a structural role and provide electronic connection between the active units.

A molecular wire thus possesses following criteria: (i) Contains an electron conducting chain; (ii) possesses terminal electroactive and planar groups for reversible electron exchange; and (iii) it should be long enough to span a typical molecular supporting element such a monolayer or bilayer membrane.

Molecular wires can be represented as $D - \sigma - A$ or $D^+ - \pi - A^-$ where $D =$ donor, $A =$ acceptor, and $\sigma$ and $\pi$ are bridging or spacer groups\textsuperscript{56} as shown in Fig. 17.

Examples of other Ru(II) complexes which may act as donor and electron acceptors are shown in Fig. 18.

A favourable factor which allows better performance includes a good energy matching between the donor and bridge components. The molecular wires incorporating ruthenium polypyridine complexes are amenable to studies of directional energy and electron transfer processes. The ruthenium based units usually exhibit luminescence and play as donor (D) or acceptor (A) units.

A bridging ligand provides both the structural and electronic connectivity between D and A and D-B-A unit could be either flexible or rigid depending upon the nature of spacer included within the bridge. The ruthenium polypyridyl complexes can frequently undergo well-defined oxidation and reduction process. In the presence of identical metal (homodimetallic), the conduction properties of the bridge can be evaluated via intervalence studies. There is a great interest\textsuperscript{57-58} in dinuclear Ru polypyridine complexes for understanding the electronic interaction between the metal ions and photoinduced intramolecular electron/energy transfer processes.

Energy-transfer process takes place either by coulombic (Forster) or exchange (Dexter) mechanism. In the former case, the main contribution to the rate
constant comes from the dipole-dipole interaction between donor and acceptor. The rate constant according to this mechanism can be calculated from spectroscopic and structural parameters using Eqs (1 and 2).

\[ k_{en} = \frac{1}{n^\circ} \left( \frac{R_0}{r} \right)^6 \]  

\[ R_0^6 = 5.87 \times 10^{-25} \eta_1^2 F(V) \chi(V) \nu d\nu \]  

where \( R_0 \) is critical radius i.e. the distance at which the energy transfer rate and the intrinsic deactivation of the donor are equal, \( \nu \) is the frequency (cm\(^{-1}\)) and \( \eta \), \( \phi \) and \( r \) are the refractive index of the solvent, the luminescence quantum yield of the donor and the donor-acceptor distance (\( \AA \)) respectively.

Dexter-type energy transfer mechanism is described as a double exchange of electrons between donor and acceptor and is related to direct or superexchange mediated electronic interaction between the two partners. The rate constant of energy transfer can be calculated using Eqs (3 - 5).

\[ k_{en} = v_{en} \exp \left( -\Delta G_e^*/RT \right) \]  

\[ v_{en} = \left[ 2 \left( H_{en} \right)^2 n / (\pi^2 / \lambda RT) \right]^{1/2} \]  

\[ \Delta G^* = \lambda / 4 \left( 1 + \Delta G^0 / \lambda \right)^2 \]  

\( H = \) intercomponent electronic interaction.

The free energy change \( \Delta G^0 \) can be expressed as the difference between the spectroscopic energies of the donor (D) and acceptor (A) and reorganisation energy (\( \lambda \)) can be estimated from the spectroscopic Stokes shift of the acceptor.

In context of ruthenium system, these reactions could be understood in terms of Scheme 4 proposed by Haga et al.\(^\text{26}\). In the electron type superexchange mechanism, the mixing between the LUMO \( \pi^* \) orbitals and Ru(II) \( \pi^* \) orbital is the major contribution for metal-metal interaction. On the other hand, the hole type superexchange mechanism is attributable to electronic interactions between the HOMO \( \pi \) orbitals of the bridged ligand and Ru(III) \( \pi^* \) orbitals.
In terms of distance, the rate constant for electron-transfer processes in bis-porphyrin donor/acceptor compounds with one, two and three phenylene spacers is expressed as:

\[ k_e = A_0 \exp(-B \delta r) \quad \ldots (6) \]

where \( \beta = 0.4 \, \text{Å} \) and \( r \) = donor-acceptor distance.

Since intramolecular electron and energy transfer rates in donor-acceptor (D-A) linked by spacer are dependent on several molecular and environmental parameters, it is often difficult to design D-A systems where a single parameter can be studied independently. In view of this, Larson et al.\(^{60} \) have studied the rates of intra-molecular energy transfer from the MLCT excited state of a tris (bipyridine) Ru(II) donor to a ground state tris (bipyridine) iron (II) acceptor within a series of heterodinuclear (Ru-Fe) complexes (Fig. 19).

Due to identical metal-metal separation as well as relative ligand orientations, these complexes provide a unique opportunity to investigate the role of D-A connectivity in an energy transfer process while maintaining other parameters virtually constant.

<table>
<thead>
<tr>
<th>Complex</th>
<th>( d_{MM} ) (Å)</th>
<th>( k_q ) (ns(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>7.61</td>
<td>2.440</td>
</tr>
<tr>
<td>II</td>
<td>7.57</td>
<td>2.870</td>
</tr>
<tr>
<td>III</td>
<td>7.50</td>
<td>2.710</td>
</tr>
<tr>
<td>IV</td>
<td>7.50</td>
<td>2.940</td>
</tr>
<tr>
<td>V</td>
<td>8.70</td>
<td>0.370</td>
</tr>
<tr>
<td>VI</td>
<td>9.23</td>
<td>0.075</td>
</tr>
<tr>
<td>VII</td>
<td>9.89</td>
<td>0.029</td>
</tr>
</tbody>
</table>

\( d_{MM} \) = metal-metal separation; \( k_q \) = energy transfer rate constant.

The data shown above indicate that for I-VII, the quenching rate falls exponentially as metal-metal separation increases. After many supporting experiments, they concluded that the MLCT state of the RuL\(_3\) is quenched by an exchange energy-transfer mechanism. It is remarkable that the rate is independent of the nature of the bridges and appears to depend only on the donor-acceptor separation.

For the design of an efficient molecular wire, the role of the spacer is significant which could be easily understood with the following examples (Fig. 20).

Thus, the above rate constant data indicate that the alkane chain does not provide a good electronic interaction between D and A and D-A interaction is of dipole-dipole interaction type. On comparing the above three cases, we find that in complex C, the energetic and spatial parameters are similar to those of A and B. However, Ru \( \rightarrow \) Os energy step is faster by several orders of magnitude, and the alkyne bridge provides an efficient electronic interaction between D and A centres.

An unique case of energy trapping has been identified by looking at the homodimetallic complex (Fig. 21) reported by Mishra et al.\(^{63} \). In this case the anthraquinone unit collects the excitation energy from either of the two identical Ru centres.
As mentioned earlier in the Ru-bipyridine system, there is always a possibility of co-existence of different stereoisomers which may cause specific difficulties in the study of photoinduced processes. In this regard, a better alternative for the ligand coordination is ensured by the use of 2,2':6,2''-terpyridine building block via the possible use of 4'-position of tpy for developing wires (Fig. 22).

In view of above, a series of Ru(II)-Rh(III) dyads of the general formula\[ \text{[tpy Ru(phen)(Rh)(tpy)]}^{2+} \] with n = 0, 1, 2 (tpy = 4'-p-tolyl-2,2':6,2''-terpyridine; phen = bridging ligand where two 2,2':6,2''-terpyridine units are connected at the 4'-position through a variable number of p-phenylene spacers) have been studied for their photoinduced electron-transfer processes. When n = 1, excitation of the Ru(II)-based molecular component is followed by efficient intramolecular quenching by electron transfer to the Rh(III) centre (Fig. 23). The rate constant $k \geq 3 \times 10^9$ s$^{-1}$ is high despite the relatively small driving force of the process (ca. 0.1 eV). When n = 2, with the same driving force as above, no intramolecular electron transfer quenching is observed ($k < 5 \times 10^9$ s$^{-1}$). The decrease in electron transfer rate is going from n = 1 to n = 2 is in line with the behaviour of other systems containing poly-p-phenylene spacers.

Similarly, rod like dinuclear ruthenium terpyridyl complexes have been developed$^{65,66}$ by coupling at 4'-position of the terpyridine ring.

Sauvage et al.$^{67}$ synthesized a series of rod like Ru-B-Os heterodinuclear complexes (Fig. 24) for the study of electronic energy transfer and observed that the temperature independent Ru $\rightarrow$ Os electronic energy transfer process occurs over the 200-900 K interval and energy transfer is neither affected by temperature changes nor by the state of the solvent, which is fluid at $T > 110$ K and frozen below that temperature.

The study of the excited state properties of chiral transition metal complexes appears to be very promising. At present, however, extension to cases of mixed metal enantiomERICally pure complexes does not seem to be easy. Of course, these complexes would be suitable for energy/electron transfer studies of the type treated above and seem to be appropriate for further development. Some ruthenium polypyridyl based rod like structures$^{68,70}$ are shown in Scheme 5.

**Molecular redox switches**

Last few years have seen a great interest$^{71-72}$ in the field of molecular switches in the development of molecular electronics and photonics. Several examples of the latter are based on supramolecular devices whose optical properties (photochromism, luminescence, optical non-linearity) can be switched by external stimuli such as chemical, electrochemical and light inputs. Attention has been paid to molecular switches whose emission properties are influenced by redox potential data as they could find application in conjunction with imaging techniques$^{73}$, in biology$^{74}$ and biochemistry, to detect synaptic activity and in general to perform membrane potential measurements in organelles (e.g. mitochondria) and cells.

**Design of fluorescence redox switches** consists of assembling a redox active subunit (control unit), which can exist in two different oxidation states of comparable stability (i.e. bistable system) and a
luminescent fragment (the active unit) whose emission depends on the oxidation state of the control unit. It is the different extent of interaction between the control subunit and the active subunit that generates the function which can be turned on/off through the external parameter. Thus the control subunit behaves as a switch.

Transition metal complexes are found to be good candidates for molecular switches due to following properties.

1. They can form couples of consecutive oxidation states which are easily interconvertible through a fast and reversible one electron redox change. The relative stability of the two states can also be modulated by the variation of co-ordination environment around the metal centre.

2. In most cases the one electron change significantly modifies the properties of the metal centre.

A pictorial presentation of such behaviour is shown as depicted in Fig. 25.

An organic fluorophore F is linked covalently to a multidentate receptor which hosts a metal centre M. The metal complex part is redox active through the two oxidation states M^{n+}/M^{n-} which are connected in a fast and reversible manner. Each state may or may not interact with proximate photoexcited fluorosphere through either an electron transfer or on energy transfer process. Interaction results in the quenching of light emission by the fluorosphere. Favourable
condition for switching behaviour are those in which one oxidation state quenches the fluorescence and the other does not. In such situations, the emission by the fluorophore can be switched on/off through $M^{n+1}/M^{n\text{+}}$ couple chemically (by adding consecutively an oxidising and reducing agent) or electrochemically (by adjusting the potential values). Several photoredox switches based on this principle have been developed.

Based on the above concept, the organic redox couple quinone/hydroquinone has been found ideal as a control unit with the luminescent molecular switch containing $[\text{Ru(N-N)}]^{2+}$ (N-N = 2,2'-bipyridine or 1,10-phenanthroline) group as an active unit. The quinone/hydroquinone redox couple is found better by virtue of its reversible electrochemical interconversion in protic media by the exchange of two protons (Scheme 6a and 6b).

The electrochemical cycle was initiated by the complete reduction at -0.60V of non-luminescent solution of the quinone to form strongly emitting hydroquinone. Same electrolytic solution in a quantitative oxidation at +1.10V afforded the non-luminescent starting solution and the cycle is repeated successfully upon consecutive reduction and oxidation.

Using the same principle Maiya et al. prepared a photoredox switch having $[\text{Ru(phen)}]^{2+}$ as active unit and quinone/hydroquinone as control unit.

The quinone form was found to be almost non-luminescent but electrochemically generated hydroquinone form of the ruthenium complex showed luminescence at 601 nm ($\Phi = 0.02$). Thus $2e/2H^+$ couple Ru(phen)$_2$ (qdppe)$^{2+}$/Ru(phen)$_2$(Hqdppz)$^{2+}$ represents a redox activated luminescent on/off switch device (Fig. 26).

Another interesting example of proton-controlled on/off luminescence switching compound has been reported by Haga et al. using molecule shown in Fig. 27.

The diprotonated form of the above heterodinuclear complex $[(\text{bpy})_2\text{Ru(H}_2\text{L})\text{Rh(bpy)}_2]^{2+}$ is non-emissive due to the intramolecular electron transfer from excited Ru to Rh; however, emission was observed in the monoprotonated form and such switching behaviour was rationalised by the preferential deprotonation at the rhodium (III) site, accompanying the negative potential shift in the reduction potential at this site. One can see from this example as to how
the introduction of asymmetry can provide not only a potential difference but a preferential protonation site in dinuclear complexes.

With the above examples in view, a schematic representation of such behaviour is shown in Fig. 28.

Fluorescent PET "on/off" switches are the opposite of the "off/on" switches with regard to the nature of the phenomenon and their popularity.

Metal based redox systems has also been found amenable to signalling schemes. In the heterodinuclear complex, no luminescence was detected when the two metal centres (Ru, Os) are bridged with azo groups which act as a trap for the excitation based on the two terminal chromophores. However, reduction of azo group allows the occurrence of Ru → Os energy transfer. Thus, the complex (Fig. 29) acts as a redox responsive molecular switch.

Sensor

The assembly of a specific receptor with a subunit capable of signalling a receptor-substrate interaction constitutes a sensor. It involves basically three units (i) receptor, (ii) signalling, and (iii) spacer as depicted in Fig. 30.

The receptor unit plays the role of recognizing and reversibly binding a given target substrate. The signalling unit must be capable of either producing a signal or significantly altering its intensity following the binding of the substrate, preferably without changing other chemical properties. Finally, the spacer links binding and signalling unit controlling their mutual separation and geometric arrangements.
The efficiency of a sensor is related to a comparable extent (i) to the selectivity of the binding and (ii) to the simplicity of detecting and measuring the displaying system.

A number of fluorescent sensors for metal ions developed by several groups during the past decades contain anthracene as a fluorescent subunit because of its strong and well-characterized emission and chemical stability. The anthracene fluorescence is quenched via an electron-transfer process from the fairly reducing tertiary amine group of macrocyclic ring to the photo-excited fluorophore. Lowering in oxidation potential of the amine group occurs as a result of metal coordination and consequently the electron transfer is prevented on thermodynamic grounds. As a consequence, fluorescence is restored. Therefore, the interaction between the receptor and K⁺ ion is communicated to the outside by the appearance of the intensive emission spectrum of anthracene.

Sensors which work through a photo-induced electron transfer mechanism (PET) contain besides the receptor and the fluorophore, an internal device providing the electron release (Fig. 31).

Ruthenium based species have been frequently used in the construction at various sensors due to unique combination of their luminescence characteristics, chemical stability and redox properties.

Recently a new class of chemosensor containing a polyamine unit connected to a Ru(II) metal centre has been synthesized (Fig. 32) and studied for its cation [Cu(II) and Zn(II)] and anion binding properties.

In a similar way a ruthenium based complex (Fig. 33) containing free bipyridine site has been synthesized and used for the study of cation bindings.

The luminescence properties undergo changes in the presence of the guest and this may be an useful approach towards molecular based devices for chemical sensing.

The molecular recognition of anionic guest species of biochemical and environmental importance by positively charged or neutral electron-deficient abiotic receptor molecules is an area of ever increasing research activity. Anions play various fundamental roles in biological and chemical processes. In this context, Beer et al. synthesized different ruthenium based azacrown ether type macrocyclic system (Fig. 34) having amide linkages for the study of group I metal cation and halide anion complexing properties.
Chloride anion coordination studies indicate that receptors containing secondary amide can complex and electrochemically sense the halide anions through mutual electrostatic attraction and favourable amide CONH anion hydrogen binding interaction. Ru(II) polypyridal complexes also provide sensitive luminescent probes for double helical DNA. The mixed ligand complexes (Fig. 35) Ru(phen)$_2$(DPPN)$_2^+$ (phen = 1,10-phenanthroline and Ru(bpy)$_2$(DPPN)$_2^+$ (bpy = 2,2'-bipyridine) causes molecular light switching for DNA. No detected emission was observed in aqueous solution due to quenching by hydrogen bonding between water and the phenazine nitrogens of the dppz ligand. Binding to DNA, however, protects the phenazine nitrogens from water through preferential intercalation of the dppz ligand and leads to intense photoluminescence.

Conclusion
Ruthenium polypyridyl based systems serve as promising candidates in the field of molecular electronics due to their unique combination of photophysical, photochemical and redox properties. It is expected that these systems have bright future in development of molecular devices.

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References