

# From Mononuclear Metal Complexes to Supramolecular Devices

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**Abstract:** One of the most important aims of photochemistry is the design and construction of artificial molecular devices for energy conversion and information processing. Assembling functionally integrated molecular components into an organised supramolecular structure can result in new functions and properties that are not available in each individual molecular component. Here artificial photonic devices are described, based on transition metal complexes, which can be used to study energy-transfer processes and can act as molecular switches.

**Keywords:** Data storage · Energy transfer · Metal complexes · Molecular devices · Molecular switches · Photochemistry · Photophysics · Polynuclear complexes · Supramolecular chemistry

## 1. Introduction

Supramolecular chemistry is a new and exciting area that has found widespread interest and has led to the exploration of new concepts and the design and preparation of new compounds [1]. Indeed supramolecular systems can carry out much more elaborate tasks than molecules: while molecules are involved in simple chemical acts, supramolecular systems are able to perform functions and therefore behave as molecular devices. A special class of molecular devices makes use of light to perform its functions. This class of devices includes converters of light energy into chemical or electrical energy, light-activated molecular switches (photonic devices), and light-harvesting systems (antenna systems) in the field of artificial photosynthesis.

The starting point of our activities in ruthenium and osmium chemistry was

the preparation and the study of the photophysical properties of mononuclear metal complexes (molecules) of the type  $[M(\text{diimine})_3]^{2+}$  with  $M = \text{Ru}^{\text{II}}$  and  $\text{Os}^{\text{II}}$  [2]. A deep understanding of the electrochemical and photophysical properties of these simpler compounds was essential for the conception and design of more complex polynuclear compounds (supramolecular systems).

Our investigations in the field of supramolecular chemistry started eight years ago. At that time we planned to synthesize dinuclear metal complexes of  $\text{Ru}^{\text{II}}$  and  $\text{Os}^{\text{II}}$ , connected by a spacer to study energy- and electron transfer reactions, which are the most important processes in natural phenomena such as photosynthesis in green plants. Very soon, we realised that we could attain interpretable results only if a linear and rigid bridging ligand connect the two metal centres [3]. In the present paper the synthesis and the photophysical properties of dinuclear metal complexes with two different spacer families are given and the results with respect to the energy- and electron-transfer processes are discussed. Recently we have also started the design and synthesis of molecular switches. Such compounds can be exploited in information processors to perform logic and arithmetic operations (YES, NOT, AND, OR...). Two examples of such supramolecular sys-

tems are discussed in the last part of the paper.

## 2. Model Compounds for the Study of Energy- and Electron Transfer Reactions

As mentioned above, photoinduced energy- and electron transfer processes are currently the object of much interest since they are often the active part in sensors, light-harvesting, and charge-separation devices. Progress in this field requires molecular components (building blocks) with well-defined structures and properties. Our model compounds are composed of at least three different molecular units (see Fig. 1).

- The first unit is a metal complex (donor part) that can act as a light sensitizer. For such a highly light absorbing unit, the excited state must be easily accessible and the metal centre must show reversible redox behaviour. In our model compound, we have chosen  $\text{Ru}(\text{diimine})_3^{2+}$  as active sensitizer.
- The second part of the molecule is a metal complex with acceptor properties. An  $\text{Os}(\text{diimine})_3^{2+}$  unit has the ideal photophysical properties to study electron- and energy-transfer reactions.

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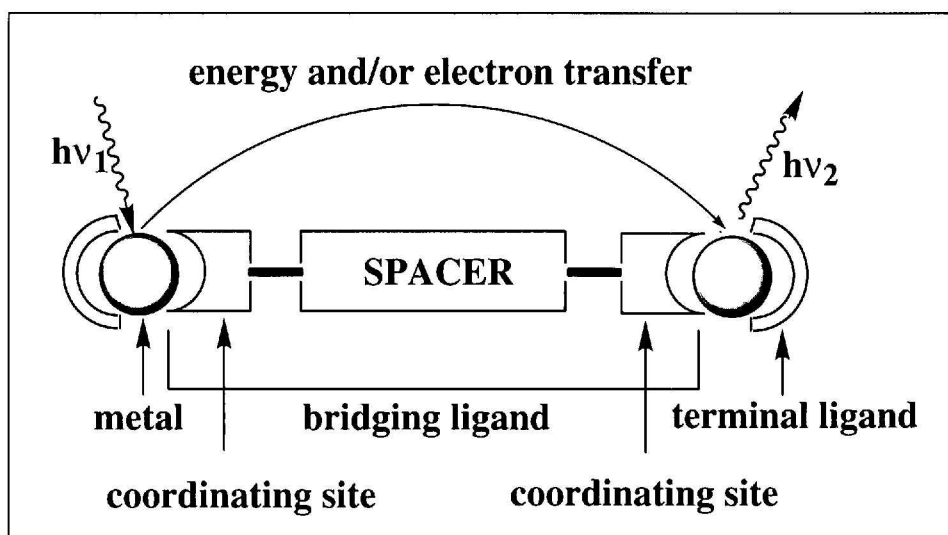


Fig. 1. Schematic representation of a model compound for the study of energy- and electron-transfer reactions.

- The bridging ligand (BL), which links the two active metal units, is the third part. It is made of two coordinating sites and a spacer between them. The spacer determines the spatial arrangement of the whole molecule and the distance between the two metal centres. The bridging ligand plays an important role for the following reasons: a) the coordinating sites of the bridging ligand influence directly the spectroscopic and redox properties of the two metal-based units; b) the chemical nature of the spacer is responsible for the communication between the donor and acceptor part and c) the spacer influences the geometric topology of the supramolecular species.

Here we will focus our discussion mainly on energy-transfer processes. We have prepared a new interesting group of dinuclear metal complexes, containing spacers with variable lengths and spatial orientation (see Fig. 2). A short insight on the synthesis of the PP ligand is given in Scheme 1. The preparation of the other bridging ligands, PCP and PAP, as well as the synthesis of their metal complexes, was published elsewhere [4]. In this series, the bridging ligand length and consequently the metal to metal (M–M) distance in their dinuclear complexes, varies from 1.61 nm in PP, 1.97 nm in PCP, to 2.10 nm in PAP. We will see that the energy-transfer rate constant within the dinuclear complexes shows a linear dependence on the M–M distance. Moreover, in PP and PCP the two coordinating units are coplanar, while in PAP, an orthogonal arrangement of the two diimine units is fixed by the structure of the adamantane spacer. Therefore a study of the

influence of the spatial arrangement on the energy-transfer rate constant is possible.

### Electrochemical Behaviour, Absorption Spectra and Luminescence Properties

In all dinuclear compounds, each metal-based unit shows an oxidation potential very close to that of the corresponding  $M(\text{diimine})_3^{2+}$  mononuclear complex, as expected in the case of a very weak intercomponent coupling between the two metal units across the bridging ligand.

The absorption spectra of the three M-PP-M complexes (MeCN, RT) are displayed in Fig. 3. Two isosbestic points

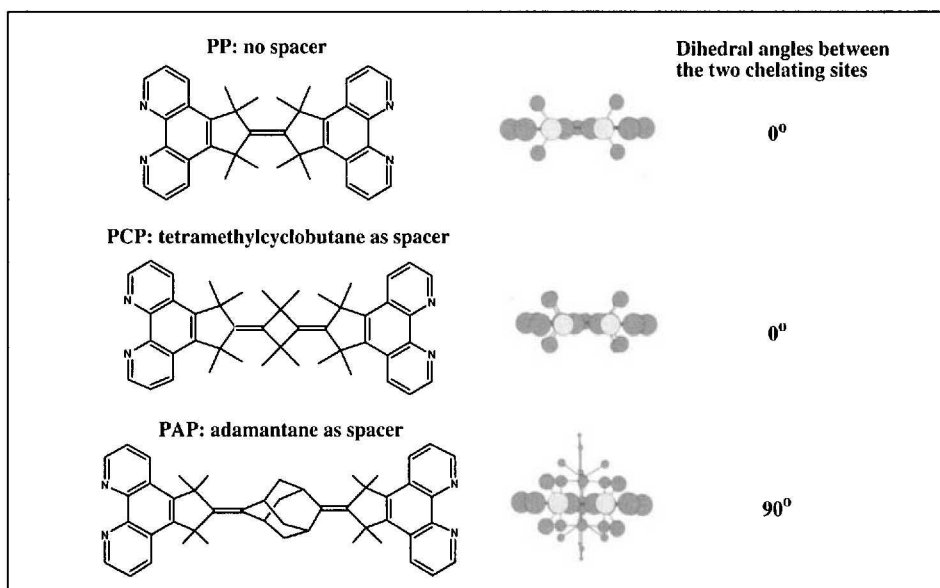
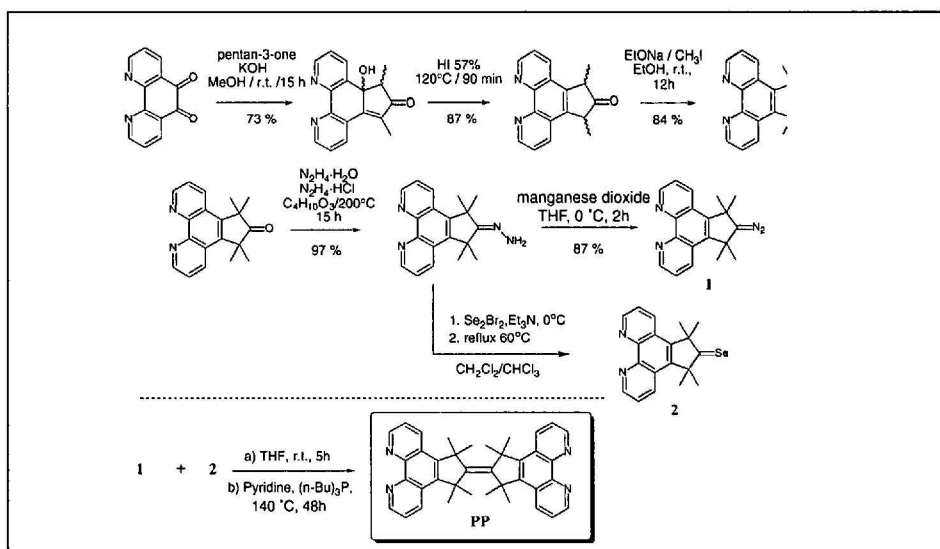


Fig. 2. A new family of rod-like bridging ligands containing adamantane (PAP) and tetramethylcyclobutane (PCP) as spacer. PP represents the bridging ligand without a spacer. The CHEM3D representation is given (view along the bridge).



Scheme 1.

can be observed at 424 nm and 464 nm. According to the literature [2], absorption in the region of 450–500 nm is attributed to singlet-singlet MLCT transitions (Ru → diimine ligand). The broad bands occurring at 550–700 nm correspond to spin-forbidden singlet-triplet MLCT transitions (Os → diimine ligand).

The emission spectra of the three M-PP-M complexes in MeCN at 298 K are displayed in the inset of Fig. 3, while the photophysical data are collected in the Table. The most interesting dinuclear metal complex Ru<sup>II</sup>-PP-Os<sup>II</sup> shows two luminescence bands corresponding to the Ru<sup>II</sup> and Os<sup>II</sup> moieties. Compared to the compound Ru<sup>II</sup>-PP-Ru<sup>II</sup> the Ru-based luminescence is decreased by a factor of 95% in intensity and its lifetime is also strongly shortened. On the other hand, the Os<sup>II</sup>-based luminescence is highly sensitised and it shows the same intensity

as in Os<sup>II</sup>-PP-Os<sup>II</sup>. Since these measurements were carried out in highly diluted conditions (complex concentration = 2.10<sup>-5</sup> M) an intermolecular energy transfer cannot occur.

Therefore, we can conclude that in Ru<sup>II</sup>-PP-Os<sup>II</sup> an intramolecular energy-transfer process takes place. A simplified scheme of the excited-state energies involved in the energy-transfer process within Ru-PP-Os is depicted in Fig. 4. The rate constant of this energy-transfer process is given by the equation  $k = (1/\tau) - (1/\tau^0)$ , where  $\tau^0$  and  $\tau$  are the luminescence lifetimes of the Ru<sup>II</sup>-based moiety in Ru<sup>II</sup>-PP-Ru<sup>II</sup> and Ru<sup>II</sup>-PP-Os<sup>II</sup>, respectively. The calculated rate constants for the energy-transfer process is 2.6 × 10<sup>8</sup> s<sup>-1</sup> in Ru<sup>II</sup>-PP-Os<sup>II</sup>, 7.0 × 10<sup>7</sup> s<sup>-1</sup> in Ru<sup>II</sup>-PCP-Os<sup>II</sup> and 5.2 × 10<sup>7</sup> s<sup>-1</sup> in Ru<sup>II</sup>-PAP-Os<sup>II</sup>. A supplementary proof of the energy-transfer process is the observation of a so-

called risetime. An exponential increase of the induced emission signal from the Os<sup>II</sup>-based component in a pulsed-laser flash-photolysis experiment with a similar lifetime as in the remaining emission coming from the Ru<sup>II</sup>-based moiety indicates the existence of the mentioned risetime.

### Energy-Transfer Mechanism

The mechanism for the energy-transfer process can be described either by a dipole-dipole interaction (Förster mechanism) [5] between the donor and acceptor part of the molecule or a double electron exchange (Dexter mechanism) [6] between donor and acceptor. The rate constant according to the former mechanism can be calculated from spectroscopic and structural parameters by using the following equation:  $k_{en} = 1/\tau^0(R_0/r)^6$  in which  $R_0$  corresponds to the so-called critical radius [5] and  $r$  is the donor-acceptor distance. In the Dexter or superexchange mechanism the rate constant for the energy-transfer process decreases exponentially upon increasing of the donor-acceptor distance. Such a behaviour is described by the following equation:  $k_{en} \propto \exp(-\beta r)$  where  $\beta$  is the so-called attenuation coefficient.

Since the rate constant shows such a different length-dependence in the two mechanisms, it becomes easy to determine which mechanism is responsible for the observed energy-transfer process. A plot of  $\ln k_{en}$  vs. the metal-to-metal distance in the metal complex series Ru<sup>II</sup>-PP-Os<sup>II</sup>, Ru<sup>II</sup>-PCP-Os<sup>II</sup>, and Ru<sup>II</sup>-PAP-Os<sup>II</sup> is shown in Fig. 5. Fitting of the experimental data gives a straightline with  $R = 0.991$  and an attenuation coefficient of 0.32 per Å. The linearity of the plot indicates that a Dexter mechanism plays the most important role in the energy transfer within these complexes. The small  $\beta$ -value reflects an efficient electronic communication between the two metal centres. Recently we have published another series of dinuclear metal complexes with polyphenylene chains as connecting spacers [7]. In Fig. 6, the corresponding metal complexes are depicted.

The distance dependence of the energy-transfer rate constant is shown in Fig. 5. The same attenuation coefficient, as in the previous case, can be calculated, but the absolute rate is faster by a factor of 25. In conclusion, the absolute rate depends on the nature of the bridging ligand, which determines the electronic coupling between the two metal units. Fi-

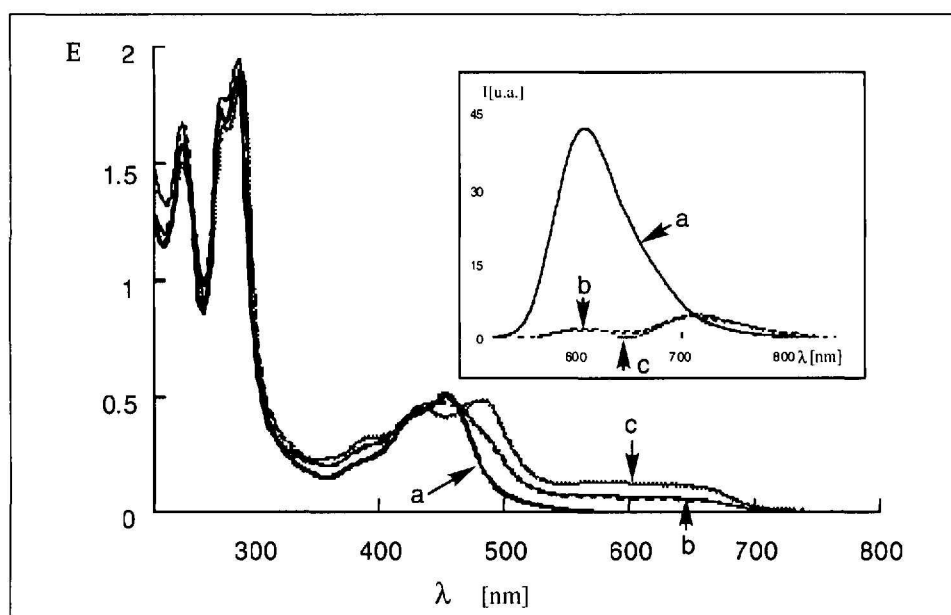


Fig. 3. Absorption and (inset) emission spectra in acetonitrile solution at room temperature of Ru<sup>II</sup>-PP-Ru<sup>II</sup> (a), Ru<sup>II</sup>-PP-Os<sup>II</sup> (b), and Os<sup>II</sup>-PP-Os<sup>II</sup> (c). The emission spectra were measured by exciting isoabsorptive solutions in the isosbestic point at 464 nm.

Table. Absorption and luminescence data.

	Absorption	Emission (298 K) <sup>a)</sup>					
		Ru			Os		
$\lambda_{max}$ [nm] (10 <sup>-3</sup> ε/dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup> )		$\lambda_{max}$ [nm]	τ [μs]	I <sub>rel</sub>	$\lambda_{max}$ [nm]	τ [μs]	I <sub>rel</sub>
[Ru <sup>II</sup> -PP-Ru <sup>II</sup> ] <sup>2+</sup>	452(3.1), 286(10.3), 242(8.9)	610	147	—	100	—	—
[Os <sup>II</sup> -PP-Os <sup>II</sup> ] <sup>2+</sup>	575(0.9), 482(2.60), 290(10.3), 243(8.3)	—	—	—	710	40	100
[Ru <sup>II</sup> -PP-Os <sup>II</sup> ] <sup>2+</sup>	575(0.5), 482(1.90), 451(2.80), 288(10.6), 243(9.5)	610	3.8	5	710	40 <sup>b)</sup>	100
[Ru(bpy) <sub>3</sub> ] <sup>2+</sup>	452(1.45), 285(8.71), 238(2.95)	615	170	—	—	—	—
[Os(bpy) <sub>3</sub> ] <sup>2+</sup>	579(0.33), 478(1.11)	—	—	—	743	49	—

<sup>a)</sup> Excitation was performed at 464 nm, which is an isosbestic point between the Ru-based and Os-based units.

<sup>b)</sup> Risetime is 4.5 ns.

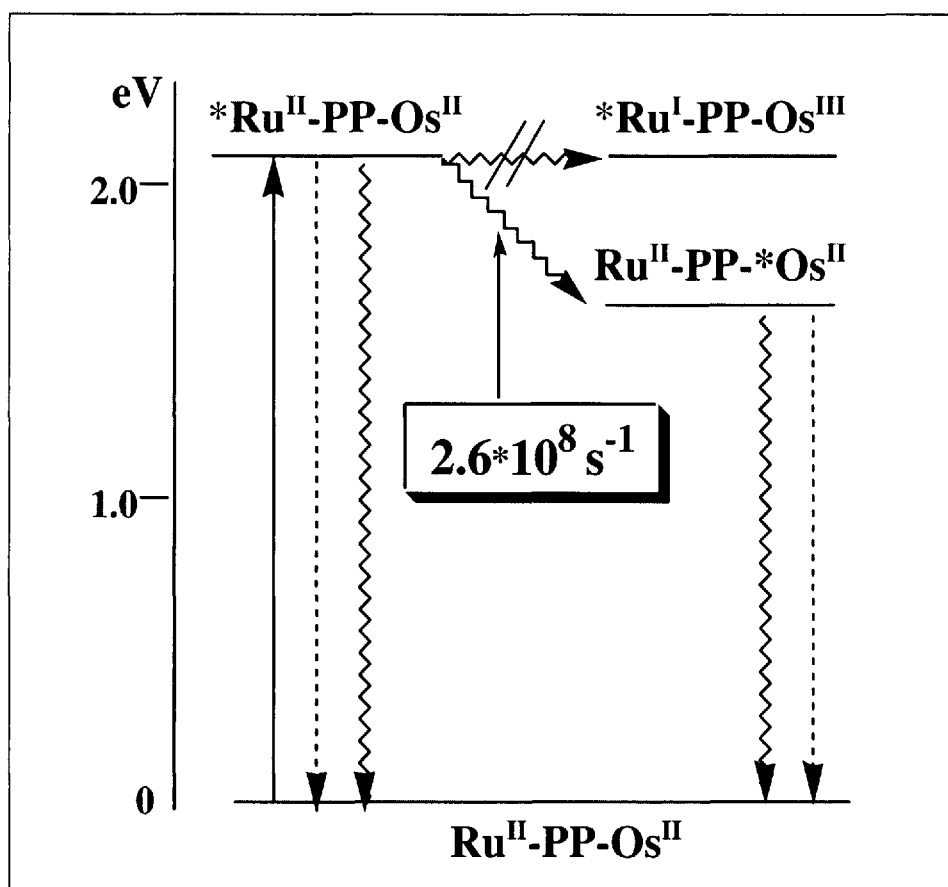


Fig. 4. Energy-level diagram showing the photoinduced energy-transfer process in the  $\text{Ru}^{\text{II}}\text{-PP-Os}^{\text{II}}$  complex. Full line, excitation; dotted line, luminescence; wavy line, radiationless decay.

nally, another interesting observation can be made. The spatial orientation of the co-ordinating phenanthroline units and the spacers has no influence on the rate of the energy-transfer process. This result is again in agreement with a Dexter mechanism, in which the rate of the energy transfer depends mainly on the overlap-integral between orbitals of the donor and acceptor units.

### 3. From Dinuclear Metal Complexes to Molecular Switches

Another interesting dinuclear metal complex ( $\text{Ru}/\text{Os}$ ) that we synthesized for the study of electron and energy transfer, contained an anthracene spacer within the bridging ligand (see Scheme 2) [8]. Irradiation with visible light under deaerated conditions led to an energy transfer from the excited  $\text{Ru}$ -based unit *via* the anthracene-based intermediate component, to the  $\text{Os}$ -based one. The transfer efficiency for the described process is nearly 100%. In air-equilibrated solution a 'self-poisoning' process was observed. The phosphorescence at 640 nm of the  $\text{Ru}$ -based unit increases strongly, and the sensitised  $\text{Os}$ -based emission at 770 nm decreases.  $^1\text{H}$  NMR and MS measurements of the irradiated supramolecular system indicate the formation of an anthracene endoperoxide spacer. In such a chemically modified system, the anthracene aromatic system is broken and therefore its lowest excited state becomes higher in energy with respect to the  $\text{Ru}$ -centred  $^3\text{MLCT}$  excited state. The self-poisoning process is only induced upon irradiation. The  $\text{Ru}^{\text{II}}\text{-An-}(^3\text{CT})\text{Os}^{\text{II}}$  excited state transfers energy to the oxygen molecules dissolved in solution, with formation of a very reactive singlet oxygen molecule.  $^1\text{O}_2$  reacts with the anthracene moiety to form the endoperoxide derivative  $\text{Ru}^{\text{II}}\text{-AnO}_2\text{-Os}^{\text{II}}$ . Because of this reaction, the  $\text{Ru}^{\text{II}}\text{-An-Os}^{\text{II}}$  system can be exploited as molecular switch for vectorial energy transfer. In such a device, information storage can be performed by writing with light under aerated conditions and reading under deaerated conditions.

After this experience, we decided to construct a new photonic switch capable of performing the logic operation YES/NO [9]. The switch is based on a photoinduced energy-transfer process. A molecular transformation, in the present case an intramolecular cyclisation, is induced by irradiation with visible light. It is well known that two anthracene molecules form a dimer by irradiation with light

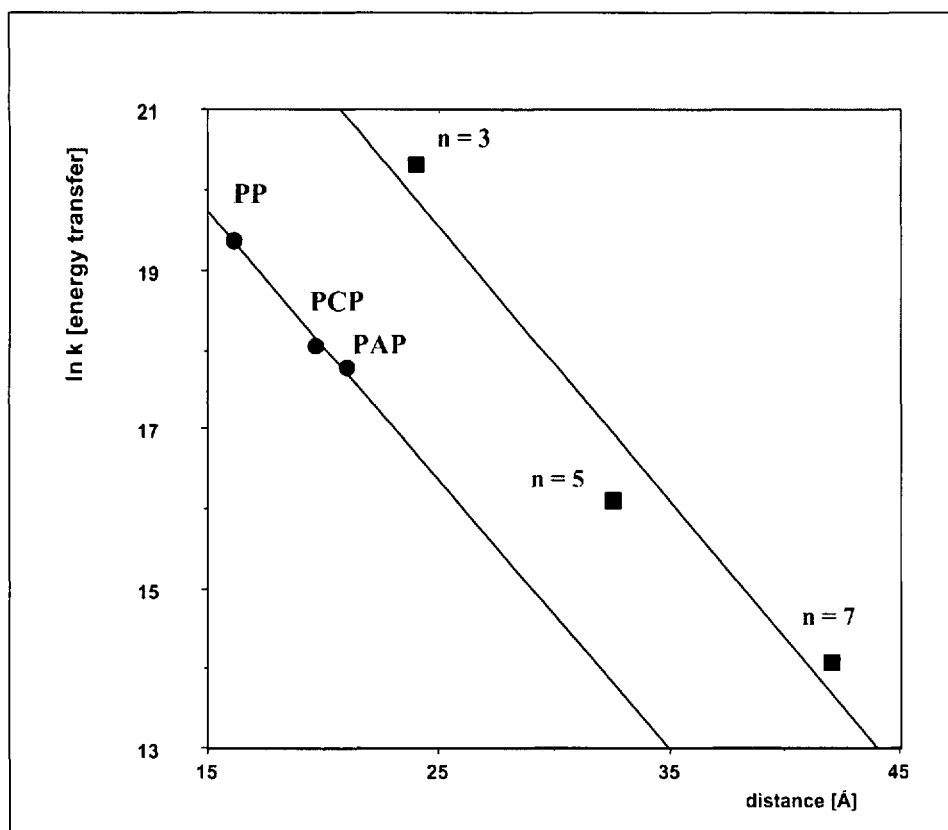


Fig. 5. Plot of  $\ln k_{\text{en}}$  versus metal-to-metal distance: (●)  $\text{Ru}^{\text{II}}\text{-spacer-Os}^{\text{II}}$  complexes with PP, PCP, and PAP as spacers, acetonitrile solution, 293K; (■)  $\text{Ru}^{\text{II}}\text{-spacer-Os}^{\text{II}}$  complexes with oligophenylene spacers, acetonitrile solution, 293K,  $n$  = number of phenylene units of the spacer.

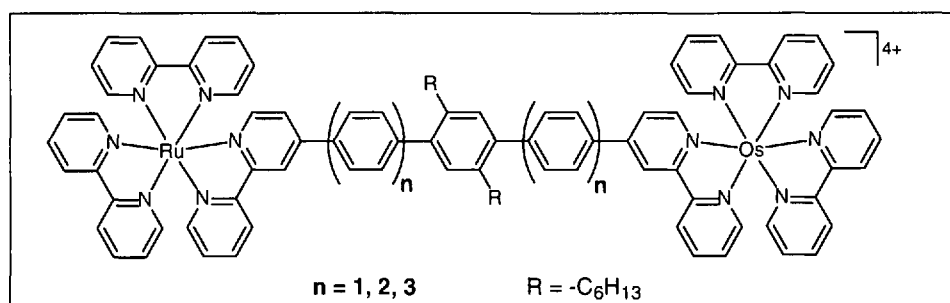
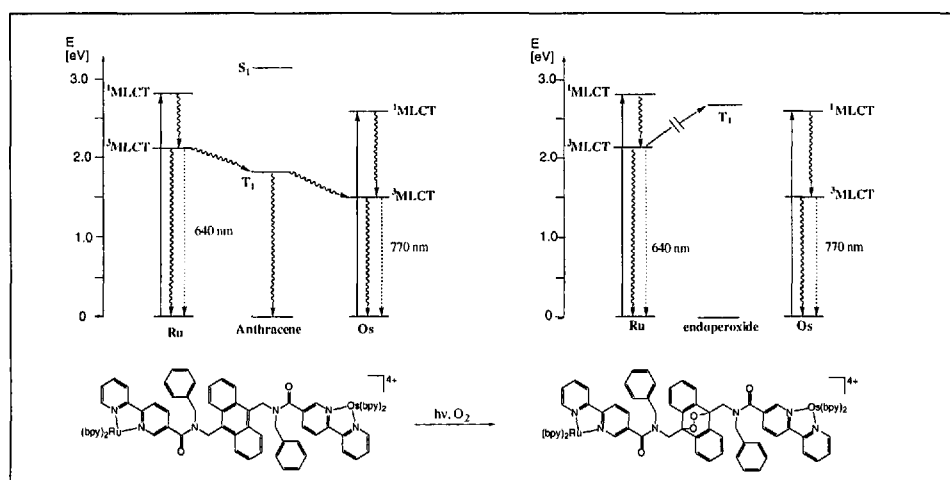


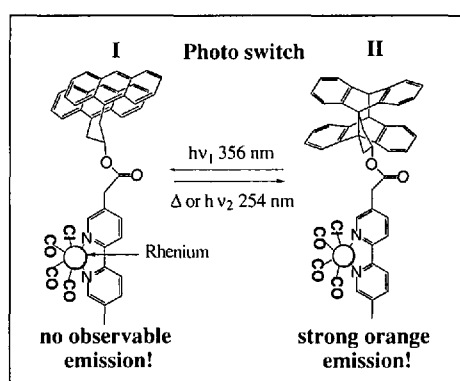
Fig. 6. Dinuclear metal complexes with oligophenylene spacers. The metal-to-metal distance increases from 2.4 nm ( $n = 3$ ), 3.25 nm ( $n = 5$ ), to 4.2 nm ( $n = 7$ ).



Scheme 2. a) A 'self-poisoning', anthracene-bridged, dinuclear metal complex. b) Energy-level diagram showing the photoinduced energy-transfer processes in  $\text{Ru}^{\text{II}}\text{-An-Os}^{\text{II}}$  and  $\text{Ru}^{\text{II}}\text{-AnO}_2\text{-Os}^{\text{II}}$ .

[10]. The inverse process (bond breaking) occurs upon irradiation with UV light. Linking the anthracene moieties to a bipyridine ligand introduced a chelating site, which was coordinated to a  $\text{Re}^{\text{I}}$  metal centre. This rhenium complex was able to act as a sensor for the opening and closing reaction of the two anthracene units (Scheme 3).

If the two anthracene units are not dimerised (open form), after irradiation of  $\text{Re}^{\text{I}}$ , an efficient energy-transfer process to the anthracene units takes place, which quenches the luminescence of the rhenium centre. Upon UV irradiation, the anthracene units yield the dimer (closed form) and lose the capability to act as an intramolecular quencher. In this case, a bright emission from the rhenium complex is observed. Moreover, the observed quenching and the restored emission were constant over a long period of closing and opening cycles respectively. This new system is an efficient photoswitch for observation of cyclisation and bond breaking processes.



Scheme 3. Schematic representation of the anthracene/rhenium-complex switch in the open and closed form.

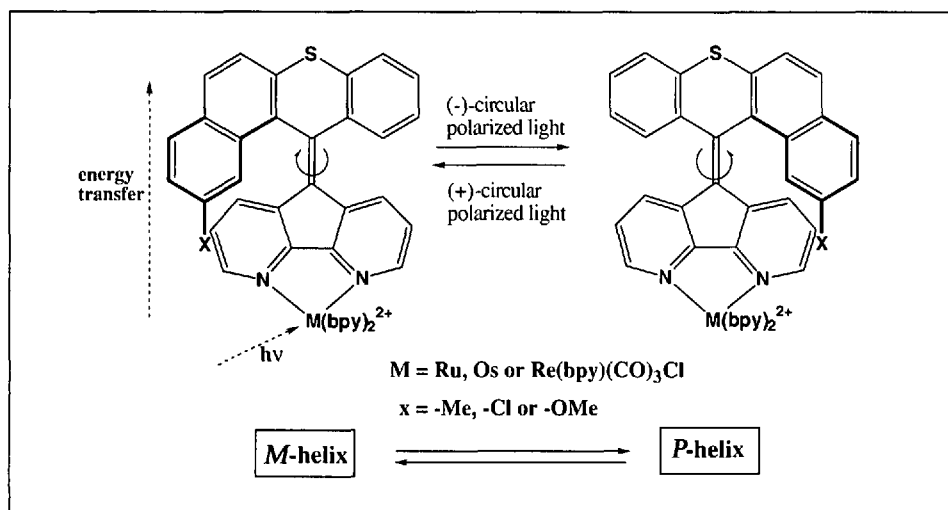
Within the context of the 'Supramolecular Functional Materials' program promoted by the Swiss National Science Foundation, we have started the design and preparation of several other molecular switches. The general principle of the molecular device is based on an energy-transfer process from a ruthenium-*tris*-

diimine sensitizer to a switchable organic function like a bond breaking/bond making process, cyclisation reaction or induction of a conformational change in the switching molecule. As an example, we will discuss a molecular switch that can be used for information storage [11]. The system is depicted in Scheme 4.

The above-mentioned device contains a chiral element, namely the helical arrangement of two aromatic moieties connected by a central double bond. The two chiral forms of the 'helical-shaped' device are denoted *P* and *M*, for the right- and left-handed helical structures, respectively. The compound is prepared as a racemic mixture with a *P*:*M*-ratio of 1:1. In the excited state, formed by energy transfer from the sensitizer, the central double bond changes into a single bond and for a short time free rotation around it is enabled. One of the two chiral forms can then be slightly enriched when irradiation is performed with circular polarised light. Indeed, circular polarised light induces a diastereomeric interaction between the two helical molecules. Therefore one of the two helical forms is thermodynamically favoured and the initial equilibrium is disturbed. We can write and store information by irradiation with circular polarised light and read the information with linear polarised light (CD measurement). The information is easily erased by nonpolarised light through a photochemical racemisation process in which the ratio of the two helical forms becomes 1:1. Incorporated in a solid, transparent matrix, the photonic device can be applied to data storage systems [12]. A supplementary chiral information is contained in the octahedral metal centre, which can exist in either a  $\Delta$ - or  $\Lambda$ -conformation. Therefore, when a pure enantiomeric form of the metal complex is incorporated into this molecular device, the influence of a further chiral element on the 'deracemisation' process with circular polarised light can be studied.

#### 4. Outlook

Our long-standing experience in the design and construction of organic ligand systems (e.g. rodlike, rigid, bridging ligands) and their metal complexes has given us the opportunity to expand our understanding from energy- and electron-transfer processes in dinuclear metal complexes to similar processes in molecular switches. We will now focus our interest on molecular systems in which the



Scheme 4. A molecular switch that changes by irradiation with circular polarised light between two helical arrangements (M- and P-helix).

switching part of the device is chemically bonded to a metal complex. Our final aim is to apply such devices as components of optical data storage systems [13], molecular-level logic gates [14], solar energy converters, [15], and electronically conducting organic wires with switchable conductivity [16].

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