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Molecular architecture in the field of photonic devices

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Contents

Abstract

We report the synthesis and photophysical properties of two different photonic devices. The first system describes dinuclear metal complexes with a rigid and linear bridging ligand (PAP) that contains an adamantane spacer. We discuss the correlation between the nature of the bridging ligand and the electrochemical as well as photophysical properties of the metal

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complexes. Two interesting observations can already be pointed out: (i) the lifetime of the intermediate electron-transfer product Ru^{III}–PAP–Os^{II} is very long (130 μs); and (ii) for the first time in a dinuclear Ru/Os system, the rate constant of energy transfer from the Ru(II) to the Os(II) unit is faster than the rate of the electron transfer from the Ru(II) to the Os(III) unit. The second system represents a photonic switch which is built up by two subunits, a rhenium complex as the active switching part and an anthracene moiety as detector. We discuss the synthesis, the reversibility of the switch and the energy transfer properties of the new system.

Keywords: Molecular devices; Photonic devices; Energy transfer; Electron transfer; Photonic switch; Bridging ligand; Dinuclear complexes

1. Introduction

Photoinduced energy- and electron-transfer processes in molecular devices are currently the object of much interest since they can be the basic step in charge separation devices, in light-harvesting systems or sensors and switches [1–4]. Photochemical molecular devices (PMD's) or nanoscale materials can be prepared by the concept of controlled molecular architecture. That concept is mainly based on the use of different building blocks that are easily accessible to construct a more complicated molecule [5]. Building blocks for the PMD's are often complex organic molecules and fragments of coordination compounds. The construction of PMD's often requires special reaction conditions, such as high dilution, template reactions or differential solubility of reactants and products, in order to avoid potential side products. In this way PMD's can be designed and constructed to perform specific light-induced functions. Such functions are e.g. conversion of light energy to chemical or electrical energy, light-activated molecular switches (photonic devices) or light harvesting systems (antenna systems) in the field of artificial photosynthesis. 'Active components' and 'connectors' build up the Photochemical molecular devices [6]. The active components are molecular species that can perform the required photoinduced elementary act like light absorption, energy transfer, electron transfer or light emission. The connectors are molecular spacers, which are responsible for the correct spatial arrangement of the active components.

In the first part of the present paper the preparation of dinuclear, rigidly bridged metal complexes for the study of energy and/or electron transfer reactions is described. The second part gives some insights into the field of photonic switches.

2. Model compounds for the study of energy and/or electron transfer reactions

Model compounds that mimic energy or electron transfer processes in natural systems (e.g. photosynthesis) are of great interest. Our model compound is composed of at least three different molecular parts (see Fig. 1).

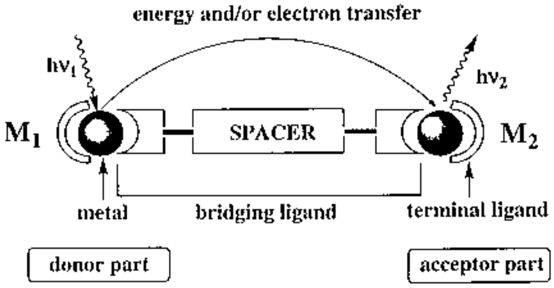


Fig. 1. Schematic representation of dinuclear metal complexes.

- First, a metal complex (donor part) is required which can act as an interface toward light. The excited state of such a light absorbing unit must be easily accessible and the metal center must show reversible redox behavior. Further requirements are: (a) high efficiency in light absorption; (b) high quantum yield for the population of the reactive excited state; (c) a long lifetime for the excited state; (d) stability towards thermal and photochemical decomposition reactions; and (e) appropriate kinetic factors for ground- and excited-state electron-transfer reactions. One of the most used metal complex for such a molecular component is $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine).
- The second unit (acceptor part) in our model compound is also a metal complex. In addition to the above mentioned conditions a good quenching ability for both transfer processes are necessary. We have used $[Os(bpy)_3]^{2+}$-type metal complexes as the acceptor part of the molecular devices.

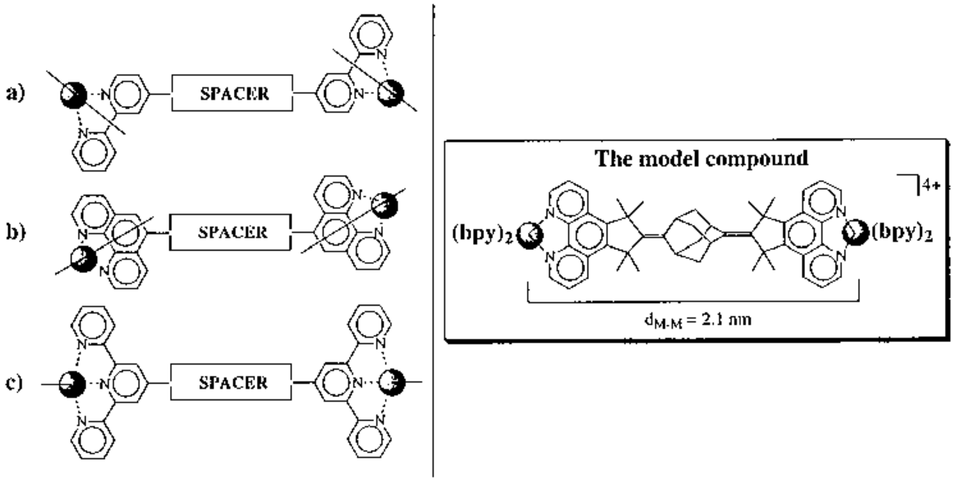
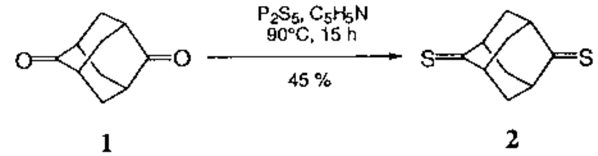


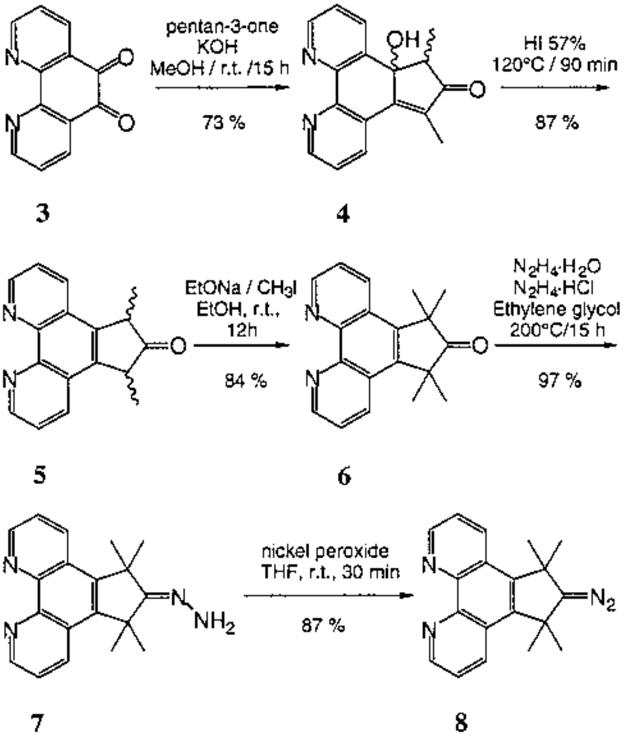
Fig. 2. Schematic representation of dinuclear complexes containing bpy (a), phen (b), and tpy (c) as coordinating unit. Inset: the model compound $[(bpy)_2M(PAP)M(bpy)_2]^{4+}$ (M = Ru and/or Os).



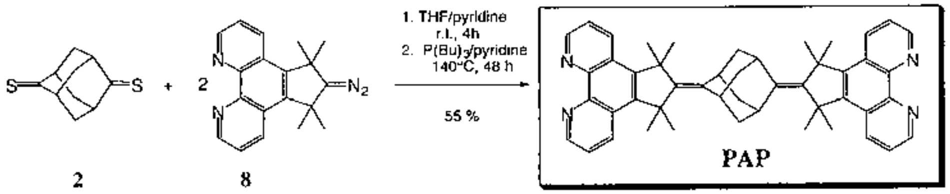
Scheme 1.

- The third part is a connecting component, which links the two active metal units. Such spacers determine the spatial arrangement of the whole molecule. The spacers play a very important role due to the following reasons: (a) the coordinating sites of the bridging ligand influences directly the spectroscopic and redox properties of the two metal-based units; (b) the chemical nature of the spacer determines the electronic communication between the donor and acceptor part of the molecule; and (c) the spacer influences the geometrical topology of the molecular device.

In the following section the importance of the geometrical arrangement of the three molecular units will be discussed.



Scheme 2.



Scheme 3.

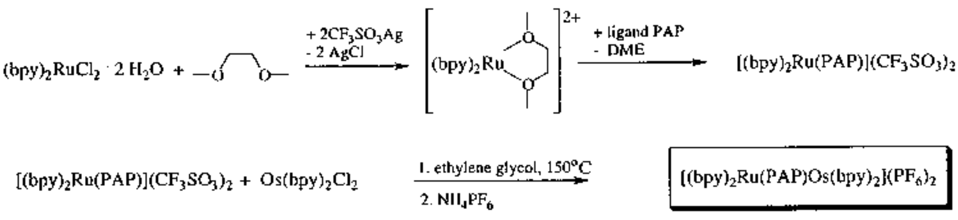
2.1. Geometrical aspects of the rigid, linear spacer

Often used chelating sites in bridging ligands are bpy, 1,10-phenanthroline (phen) or 2,2′:6′,2″-terpyridine (tpy). In contrast to metal complexes with tpy as ligand, the photophysical properties of the metal complexes (Ru or Os) with bpy or phen are much more interesting, exhibiting luminescent lifetimes which are ca. 1e3-fold longer. However, tpy based bridges are the ligands of choice for construction of rigid, rodlike dinuclear metal complexes (see Fig. 2).

To combine both desired features (excellent photophysical properties and ideal spatial arrangement) we have designed a new system of bridging ligands [7]. The bridging ligand with an adamantane spacer is called **PAP** (2.6-adamantane-bis(1,1,3,3-tetramethyl-1,3-dihydro-7,8-diaza)cyclopenta[1]phenanthrene-2-ylidene; see Fig. 2). Other members of the new family of bridging ligands contain a tetramethylcyclobutane and a stellane unit as spacers. PAP is a rigid ligand with C_2 symmetry and leads to dinuclear species where the two metals and the spacer are in linear arrangement. This allows the determination of the exact distance between the two metal centers. The metal–metal distance in the case of $[(bpy)_2M(PAP)M(bpy)_2]^{4+}$ (M = Ru and/or Os) is 2.1 nm as evaluated by molecular modelling using CHEM3D.

2.2. Synthesis of the bridging ligands and their metal complexes

The synthetic route for the preparation of PAP is depicted in Schemes 1–3. The precursor adamantane-2,6-dithione (**2**) was synthesized according to the method of Greidanus [8] by treatment of adamantane-2,6-dione (**1**) with P_2S_5/pyridine at 90°C (Scheme 1).



Scheme 4.

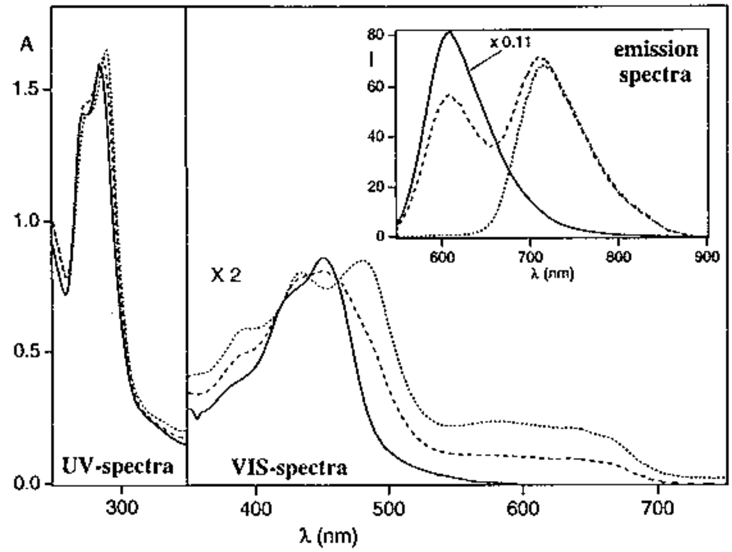


Fig. 3. Absorption and (inset) emission spectra in acetonitrile solution at room temperature of Ru^{II}–PAP–Ru^{II} (—), Ru^{II}–PAP–Os^{II} (- - -), and Os^{II}–PAP–Os^{II} (· · ·). The emission spectra were measured by exciting isoabsorptive solutions in the isosbestic point at 465 nm.

The precursor 1,10-phenanthroline-5,6-dione (**3**), prepared following the method of Yamada et al. [9], was condensed with pentan-3-one in a solution of KOH in methanol to give **4** as a white powder. The ketone 1,3-dihydro-1,3-dimethyl-7,8-diazacyclopenta[1]phenanthrene-2-one (**5**) was obtained after treatment of **4** with hydriodic acid at 120°C. A complete methylation of **5** led to the ketone **6**. The

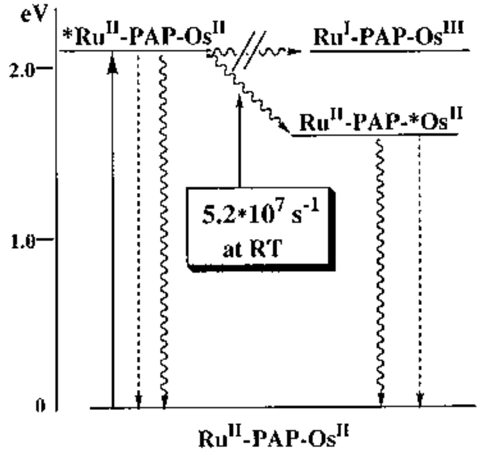


Fig. 4. Energy-level diagram showing the photoinduced energy-transfer process in Ru^{II}–PAP–Os^{II}. Key: full line, excitation; dashed line, luminescence; wavy line, radiation-less decay.

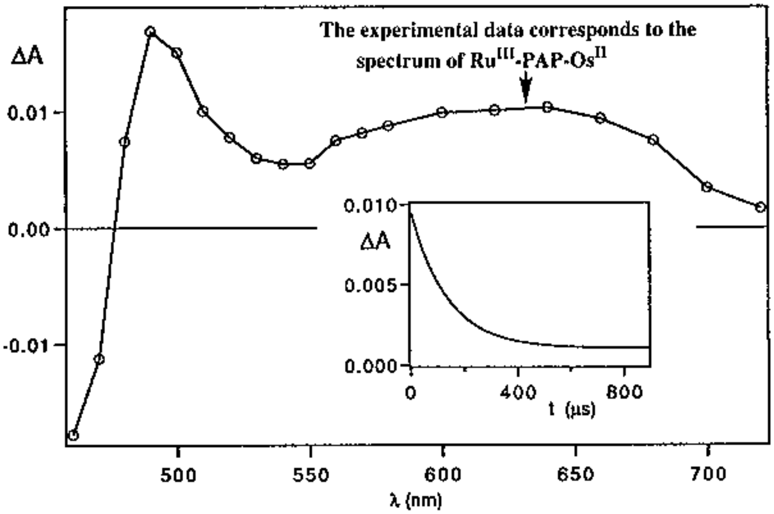


Fig. 5. Transient absorption spectrum of the product obtained upon excitation of the Ru-based unit of Ru^{II}–PAP–Os^{III}. The inset shows the absorbance decay at 650 nm.

ketone **6** was then transformed to the corresponding 1,3-dihydro-1,1,3,3-tetramethyl-7,8-diazacyclopenta[1]phenanthrene-2-hydrazone (**7**). A mild oxidation of the hydrazone with silver(I) oxide gave the final precursor **8** (Scheme 2).

Following the general method for the preparation of sterically hindered alkanes by Barton [10] and Guziec [11] the bridging ligand PAP was prepared by a 2-fold extrusion reaction. The precursors **2** and **8**, respectively, where condensed to the intermediate thiadiazoline which was then treated with triphenylphosphine to afford the desired bridging ligand PAP.

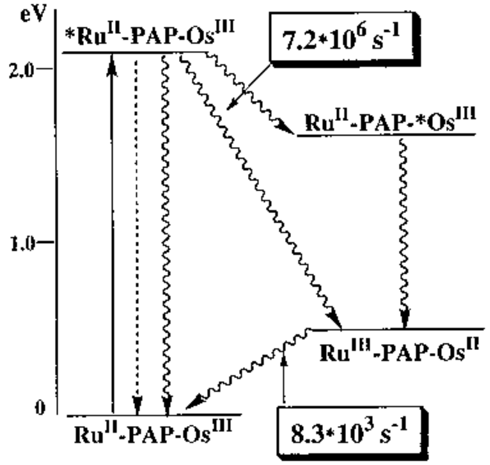


Fig. 6. Energy-level diagram showing the photoinduced electron-transfer process in Ru^{II}–PAP–Os^{III}.

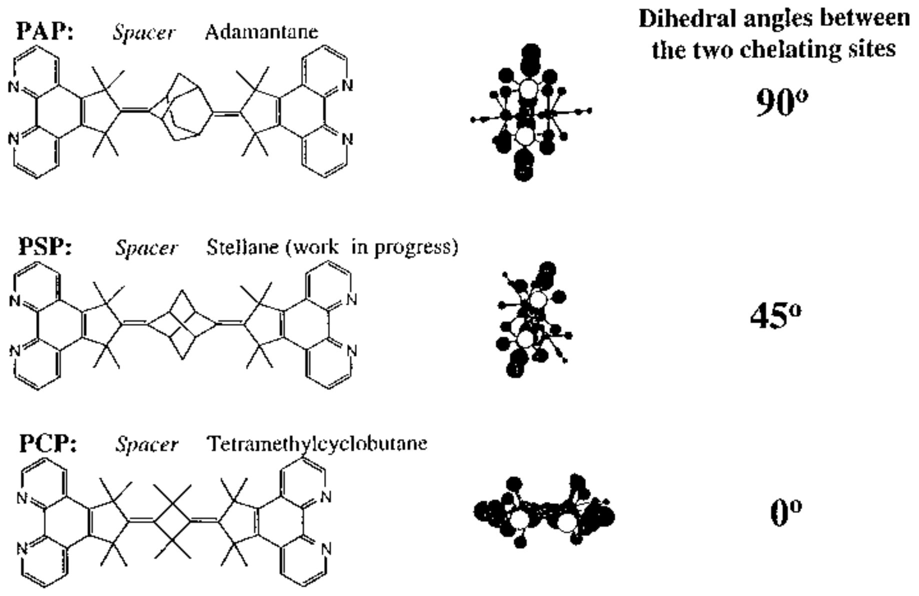


Fig. 7. Rigid rod-like bridging ligands with adamantane, stellane and tetramethylcyclobutane as spacers. The CHEM3D representation is given (view along the bridge). The preparation of the bridging ligand PSP is in progress.

The homonuclear metal complexes (Ru^{II}–PAP–Ru^{II} and Os^{II}–PAP–Os^{II}) were prepared by a conventional method using $[M(bpy)_2Cl_2]$ (M = Ru, Os) and the bridging ligand PAP in a refluxing mixture of ethylene glycol/10% water (microwave oven) [12].

The mixed-metal compound (Ru^{II}–PAP–Os^{II}) was prepared in a two step reaction. In the first step the mononuclear compound $[(bpy)_2Ru(PAP)]^{2+}$ was prepared via an intermediate $[(bpy)_2Ru(DME)]^{2+}$ complex (DME = dimethoxyethane) [13]. The DME-complex and the PAP ligand are both soluble in $CHCl_3$ and after its formation (boiling in hot $CHCl_3$) the metal complex $[(bpy)_2Ru(PAP)]^{2+}$ precipitates in pure form. The second step is similar to the

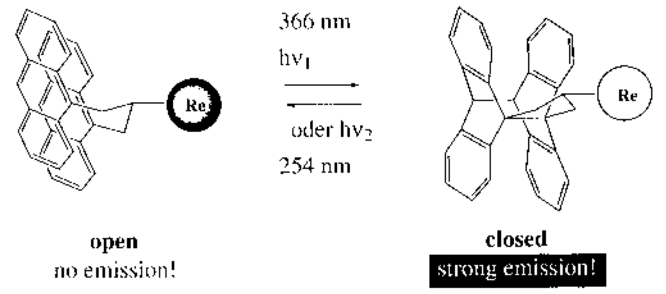
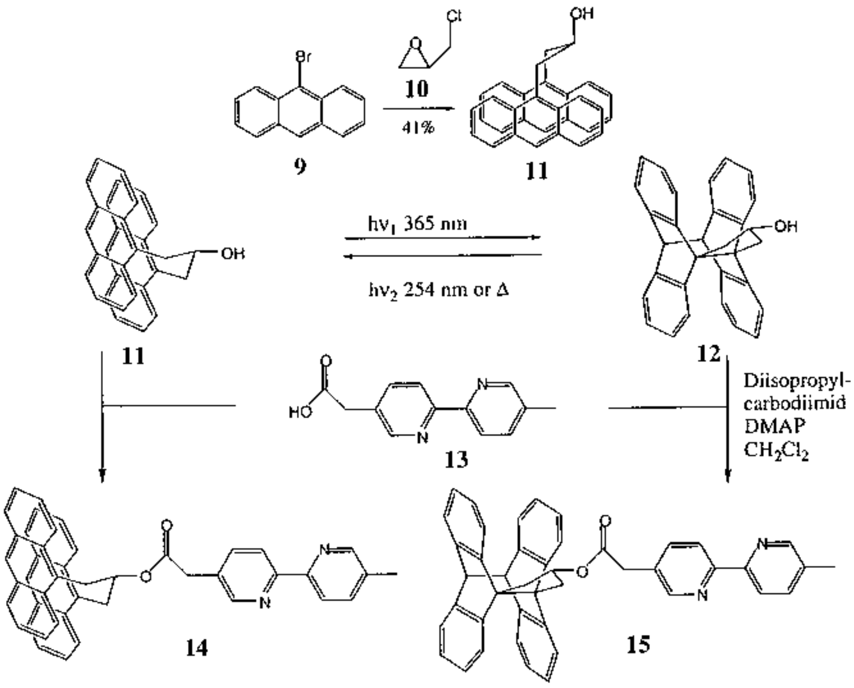


Fig. 8. Schematic representation of the switch in the open and closed form.



Scheme 5.

synthesis of the homonuclear metal complexes (see Scheme 4). We have prepared the following metal complexes:

$[(bpy)_2Ru(PAP)Ru(bpy)_2]^{4+}$	**Ru^{II}–PAP–Ru^{II}**
$[(bpy)_2Os(PAP)Os(bpy)_2]^{4+}$	**Os^{II}–PAP–Os^{II}**
$[(bpy)_2Ru(PAP)Os(bpy)_2]^{4+}$	**Ru^{II}–PAP–Os^{II}**
$[(bpy)_2Ru(PAP)Os(bpy)_2]^{5+}$	**Ru^{II}–PAP–Os^{III}**

The anion PF_6^- was used as counter-ion.

2.3. Photophysical properties in the ground and excited state

The electrochemical potential for the oxidation ($M^{II} \Rightarrow M^{III}$) and the first ligand centered reduction ($L \Rightarrow L^-$) are collected in Table 1. A summary of the photophysical data is given in Table 2. The data for the parent compounds $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ are also reported in both tables for comparison.

The metal centered oxidation of the homonuclear compounds Ru^{II}–PAP–Ru^{II} and Os^{II}–PAP–Os^{II} can be observed at $+1.235$ and $+0.800$ V (vs. SCE), respectively, and corresponds closely to the potentials measured for the parent compounds $[Ru(bpy)_3]^{2+}$ ($+1.260$ V) and $[Os(bpy)_3]^{2+}$ ($+0.83$ V). The heteronu-

Table 1
Absorption and electrochemical data[a]

Complex	Absorption maxima (λ, nm (ε, M^{-1} cm^{-1}))				Electrochemical data		
					Redox potentials, Ru (oxidn)	[Relative current intensity] Os (oxidn) (V)	($E_a - E_c$) (mV vs.NHE) (redn)
$[Ru^{II}(bpy)_3]^{2+}$			452 (14 600)	288 (76 600)	+1.25 [1] (90)		−1.35 [1] (90)
$[Os^{II}(bpy)_3]^{2+}$	579 (3270)	479 (11 100)	436 (10 700)	290 (78 000)		+0.83 [1] (80)	−1.28 [1] (90)
$[Ru^{II}–PAP–Ru^{II}]^{4+}$			450 (28 100)	285 (103 200)	+1.24 [2] (105)		−1.38 [2] (70)
$[Os^{II}–PAP–Os^{II}]^{4+}$	600 (7500)	480 (27 800)	433 (26 800)	288 (107 900)		+0.80 [2] (85)	−1.31 [2] (70)
$[Ru^{II}–PAP–Os^{II}]_4$	600 (3800)		449 (27 800)	288 (110 500)	+1.24 [1] (105)	+0.80 [1] (85)	−1.35 [2] (135)

[a] For experimental details see [6].

Table 2
Luminescence data[a]

Complex	298 K						77 K			
	Ru			Os			Ru		Os	
	λ_{max} (nm)	τ (ns)	I_{rel}[b]	λ_{max} (nm)	τ (ns)	I_{rel}[b]	λ_{max}	τ (ms)	λ_{max}	τ (ms)
$[RuIIPAPRuII]^{4+}$	610	150	100	–	–	–	583	5.5	–	–
$[OsIIPAPOsII]^{4+}$	–	–	–	717	41	100	–	–	709	1.0
$[RuIIPAPOsII]^{4+}$	609	17	8	712	41[c]	95	581	0.041	705	1.2

[a] For experimental details see [6].

[b] Excitation was performed at 465 nm, which is an isobestic point of the Ru- and Os-based units.

[c] Rise time is 15 ns.

clear metal complex Ru^{II}–PAP–Os^{II} shows two monoelectronic waves at + 1.240 and + 0.795 V. The absorption spectra are depicted in Fig. 3. The spectrum of the mixed metal complex is the superposition of the spectra of both homonuclear species.

These results indicate that the metal-based units in the dinuclear complexes are independent of each other. Therefore we can expect a very weak intercomponent interaction between the active centers.

The steady state luminescence spectra of the three dinuclear compounds are displayed in the inset of Fig. 3. Ru^{II}–PAP–Ru^{II} and Os^{II}–PAP–Os^{II} show emission spectra similar to $[Ru(bpy)_2(phen)]^{2+}$ and $[Os(bpy)_2(phen)]^{2+}$, respectively [14]. The mixed-metal compound Ru^{II}–PAP–Os^{II} has two emission bands, corresponding to the Ru(II) and Os(II) metal centers, respectively. A strongly quenched emission from the Ru(II)-based moiety (see inset of Fig. 3) together with a sensitized Os(II)-based luminescense is observed. Excluding an intermolecular energy-transfer process (high dilution technique) an intramolecular (intercomponent) energy-transfer process can explain the observed data. The rate constant for such a process can be calculated and the corresponding values are 5.2×10^7 and 2.4×10^7 s^{-1} at 298 and 77 K, respectively. In Fig. 4 the energy level diagram for the photoinduced energy-transfer process in Ru^{II}–PAP–Os^{II} is shown.

Selective oxidation of Ru^{II}–PAP–Os^{II} leads to the mixed-valence species Ru^{II}–PAP–Os^{III}. The non-emissive Os(III)-based unit quenches the emissive

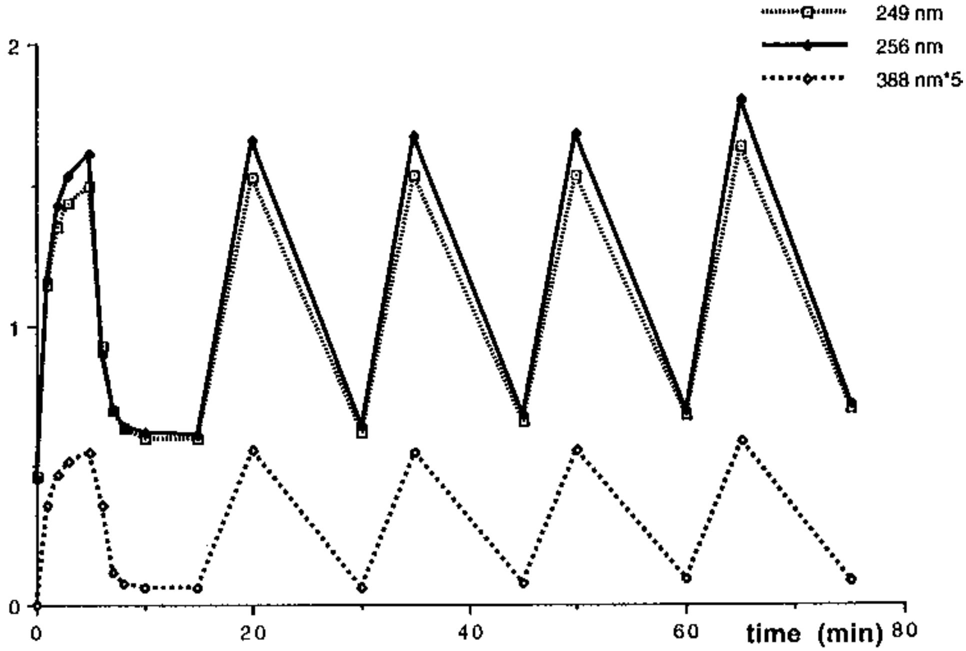


Fig. 9. Reversible on/off response by irradiation at 249, 256, and 388 nm, respectively, into the photo-switch.

Ru(II)-based unit proportional to the amount of oxidant added. In the oxidized Ru^{II}–PAP–Os^{III} complex the measured lifetime of the Ru(II)-based unit is 72 ns. Therefore the rate constant for the quenching process of the Ru(II)-based unit by the Os(III)-based unit is 7.2×10^6 s^{-1}.

Laser flash photolysis experiments showed that an electron transfer quenching process does take place (see Fig. 5). The quenching process leads to the formation of the Ru^{III}–PAP–Os^{II} intervalence-transfer product by a direct way or first via an energy-transfer step (see Fig. 6).

The intervalence-transfer product then decays to the ground-state isomer Ru^{II}–PAP–Os^{III} with a rate constant of 8.3×10^3 s^{-1}. Such a very long lived intermediate (130 μs) is exceptional. A possible explanation can be given by the orthogonal arrangement of the two chelating phenanthroline units of the bridging ligand (induced by the adamantane spacer). The spatial orientation of the phenanthroline units in the excited state of the Ru(II)-based unit must not be exactly orthogonal. Therefore the electron transfer process to the Os(III)-based unit is much faster.

Two interesting observations can already be pointed out: (i) the lifetime of the intermediate electron-transfer product Ru^{III}–PAP–Os^{II} is very long (130 μs); and (ii) for the first time in a dinuclear Ru/Os system, the rate constant of energy transfer from the Ru(II)- to the Os(II) unit is faster than the rate of the electron transfer from the Ru(II)- to the Os(III) unit.

2.4. New spacers

On the basis of the results discussed above, we have started to investigate two different aspects of energy- and electron-transfer. First we have changed the spacer of the bridging ligand. In the PAP ligand the two phenanthroline-units are arranged perpendicular (90°). Exchange of the adamantane spacer for a stellane spacer (see Fig. 7) reduces the dihedral angle between the two chelating sites to 45°. The incorporation of the spacer tetramethylcyclobutane leads to a planar ligand system (0°). Such changes in the spatial orientation of the coordinating sites must by reflected in the rate constant of the transfer processes.

The second project is based on the idea that complicated bridging ligands and the corresponding metal complexes can be prepared by a building block system from appropriate spacers and metal complex fragments. The reaction (e.g. Suzuki cross-coupling reaction) [15] that connects the spacer and a metal fragment must be executed in strong polar solvents like dimethylformamide. Under such reaction conditions the spacer and the metal complex fragment are soluble. That strategy opens then the possibility to synthesize dinuclear metal complexes step by step in high yield.

3. A mononuclear photoswitch

The understanding of energy- and electron-transfer processes in extended molecular systems has given us the opportunity to search for some applications in the field of photonic devices. Recently we have developed a molecular photonic switch that is capable of performing the logic operation YES/NO [16]. The switch works on the basis of a photoinduced energy-transfer process (PET). Irradiation triggers a molecular transformation, in this case an intramolecular cyclisation.

3.1. Principle of the switch

The photonic switch consists of two separate subunits: the switch and the detector. The detector will indicate the state of the switch (YES or NO). As photoactive subunit we have chosen two anthracenes linked by a C_3 bridge that are stacked in a parallel way. On irradiation with visible light under strict exclusion of oxygen, intramolecular dimerization takes place (**11** ⇒ **12**). The back reaction (bond breaking process) is triggered by irradiation with UV light (254 nm). A linkage of the anthracene unit to a bpy ligand introduces a chelating site. The corresponding rhenium complex (see Fig. 8) indicates then the state of the switch. Its emission can only be observed in the closed form of the anthracene unit. In the open form anthracene is an efficient quencher.

The emission properties of the two rhenium complexes (**16**; open form) and (**17**; closed form) are remarkable. While the emission of the switch in the closed form was as expected, that of the open form was almost completely quenched. The anthracene moieties quench the emission of the excited rhenium complex very effectively. In this case a fast energy transfer from the metal complex to the anthracene unit can be observed.

3.2. Synthesis of the switch

The anthracene unit (**11**) was prepared by linkage of two molecule 9-bromoanthracene (**9**) with epichlorhydrin (**10**) in moderate yield (see Scheme 5). The closed form of the anthracene unit (**12**) was synthesized photochemical. For steric reasons an esterification was the only reaction to connect the anthracene unit and the bpy ligand. Therefore **11** or **12** were condensed with the acid (**13**) to get the open (**14**) or closed form (**15**) of the switch.

Diisopropylcarbodiimide was used for the esterification instead of the usual dicyclohexylcarbodimide (DCC) [17], since the later gives a very stable 1:1 adduct with the resulting ester.

The rhenium complexes (**16**) and (**17**) were prepared following methods in the literature [18].

3.3. Reversibility of the photoswitch

The reversibility of the new switch **16** ⇒ **17** was tested by irradiation with visible light (365 nm; dimerization reaction) followed by UV light (**17** ⇒ **16**) (254 nm; back reaction). The switching process can be easily monitored by the absorption spectra. Fig. 9 shows the changes at different wavelengths (249, 256 and 388 nm (× 5)).

For both the forward and backward reactions, the changes in the signals observed were constant. This new system provides an efficient photoswitch, which permits a reversible change in absorption and emission of a spatially separated subunit of the switching molecule.

Acknowledgements

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