rounded by a polarizable continuum are in progress. For more details, see [4].

6. Modelling the Coordination Sphere of Lanthanides

Hydrated lanthanides(III) ions $Ln^{3+}(H_2O)_x$ ($x = 8, 9$) with $Ln^{3+} = Gd^{3+}$, Sm^{3+} and Dy^{3+} are currently studied using DFT and the results are in agreement with similar *Hartree-Fock* results [10]. The calculations are related to experimental results in order to elucidate the hydration behavior of lanthanide(III) ions. It has been established that the coordination number of the lanthanides changes in the middle of the serie: $Nd^{3+}, Sm^{3+}, Eu^{3+}$ [11].

The energies between different structures (*i.e.*, cube, square antiprism, and dodecahedron) of the first solvation sphere are compared. The bond energy as a function of ion-water distance obtained in the local density approximation (LDA) is pre-

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The charge polarization of the coordinated water molecules at different geometries is also being studied in order to design better interaction potentials to be used in molecular dynamics (MD) simulations of such systems. More results will be presented at the fall session 1994 of the *New Swiss Chemical Society*.

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Molecular Devices Based on Bridged Transition-Metal Complexes

Peter Belser*

Abstract. The article from *A. von Zelewsky*, in this issue gives a broad survey about some scientific activities at the Institute of Inorganic Chemistry of the University of Fribourg. The present contribution will be rather focused on a detailed study of the photophysical and photochemical behavior of a molecular device that is capable to undergo energy- and/or electron-transfer processes.

form functions and have, therefore, the potential to behave as *molecular devices*. Photochemical molecular devices are those that use light to achieve their functions.

The development of photochemical molecular devices for different applications (*e.g.*, artificial photosynthesis and information processing) [4] is based on the design of molecular species in which photoinduced energy- or electron-transfer processes can take place over a long distance with high efficiency.

To elucidate the role played by various factors in determining the occurrence of photoinduced energy- and electron-transfer processes, we have designed and synthesized different bridged polynuclear metal complexes [5][6]. The requirements for the construction of such a molecular device for charge separation are (*Fig. 1*):
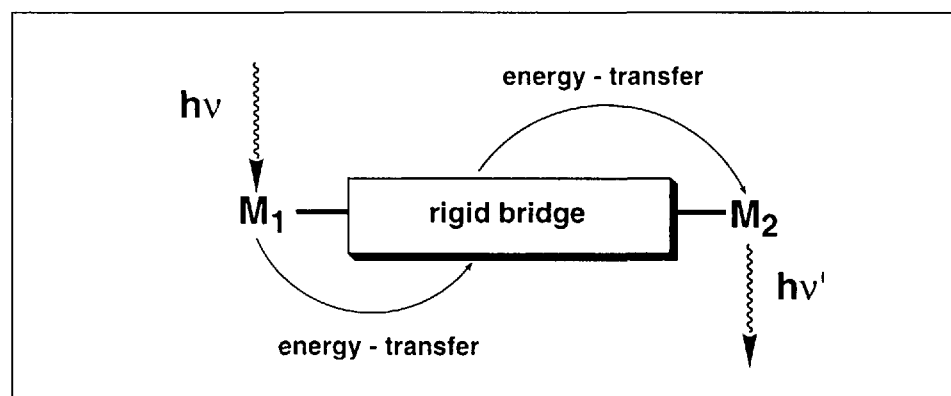
1. Introduction

The scientific field of supramolecular chemistry [1–3] means that such complicated systems have the potential to achieve much more capabilities than simple molecules. A simple molecule has only the possibility to participate in chemical reactions. Supramolecular systems can per-

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The development of photochemical molecular devices for different applications (*e.g.*, artificial photosynthesis and information processing) [4] is based on the design of molecular species in which photoinduced energy- or electron-transfer processes can take place over a long distance with high efficiency.

To elucidate the role played by various factors in determining the occurrence of photoinduced energy- and electron-transfer processes, we have designed and synthesized different bridged polynuclear metal complexes [5][6]. The requirements for the construction of such a molecular device for charge separation are (*Fig. 1*):
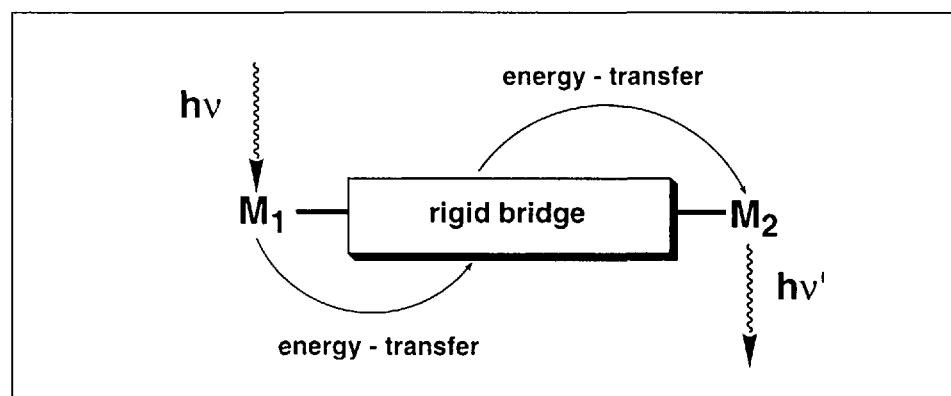
1. Introduction

The scientific field of supramolecular chemistry [1–3] means that such complicated systems have the potential to achieve much more capabilities than simple molecules. A simple molecule has only the possibility to participate in chemical reactions. Supramolecular systems can per-

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Fig. 1. *Block diagram of a molecular device that is capable for an energy-transfer process*

– A molecular component that can act as an interface toward light (M$_1$). This component can be easily transferred to the excited state and has fully reversible redox behavior. Further requirements in practical systems are: *a*) stability towards thermal and photochemical decomposition reactions; *b*) suitable ground- and excited-state redox potentials; *c*) high efficiency of population of the reactive excited state; *d*) sufficiently long lifetime of the reactive excited state, and *e*) appropriate kinetic factors for ground- and excit-

ed-state electron-transfer reactions. An excellent candidate for such a molecular component is [Ru(bpy)$_3$]$^{2+}$ (bpy = 2,2'-bipyridine) [7].

– The second molecular component (M$_2$) is a species capable of undergoing a one-electron reversible redox reaction. Other requirements are: *a*) suitable redox potentials; *b*) thermal and photochemical stability in both of the oxidation states; *c*) good quenching ability for electron transfer (or energy transfer), and *d*) suitable kinetic factors for electron-transfer reactions. In our study,

we have used [Os(bpy)$_3$]$^{2+}$-type metal complexes as the acceptor part of the molecular device.

– We need also a connecting component (rigid bridge), which can be used to link together the two above mentioned active components in the desired spatial arrangement. In the present article, some of such spacers, used in our laboratories, are depicted.

As mentioned before an important requirement for the usefulness of such supramolecular devices is their degree of spatial organization. Species in which the active components are linked by non-rigid spacers are of little practical interest, because practical devices require vectorial energy or electron transfer over long distances.

Ru^{II} and Os^{II} polypyridine-type complexes exhibit suitable excited-state and redox properties to play the role of building blocks for the construction of photoactive supramolecular systems [8]. For synthetic reasons, it is difficult to assemble these metal-containing building blocks with the appropriate bridges to build up *extended* and *rigid structures*.

We have now synthesized a series of binuclear metal complexes that are connected by the novel bridging ligand 1,4-bis[(2,2'-bipyridine-5-yl)ethynyl]bicyclo[2.2.2]octane (bpy-S-bpy and the corresponding metal complexes M$_1$-S-M$_2$; see *Fig. 2*). The ligand synthesis is depicted in the *Scheme*.

The two bpy units are separated by a 1.0 nm long spacer (S) which contains a rigid bicyclooctane component and two linear acetylene-type units. In the binuclear species, the distance between the two metal centers (*ca.* 1.7 nm; *Fig. 3*) changes only slightly on rotation around the single bonds connecting the bridge to the bpy units. These rod-like, nanoscale supramolecular metal complexes exhibit interesting excited-state and redox properties.

The novel ligand bpy-S-bpy has been synthesized [5][6] through the corresponding bis-alkene 3. The phosphonate 1 was obtained by an *Arbuzov* rearrangement from 5-(bromomethyl)-2,2'-bipyridine [9]. Bicyclo[2.2.2]octane-1,4-dicarboxaldehyde (2) [10] and 1 were coupled by a *Wadsworth-Emmons* reaction to give the (*E,E*)-diene 3. Bromination at room temperature gave 4 and subsequent dehydrobromination by refluxing with excess KOH yielded the diyne bpy-S-bpy 5, which was isolated as a colorless, crystalline solid. An X-ray structure of the bridging ligand bpy-S-bpy shows clearly the rod-like structure (*Fig. 4*).

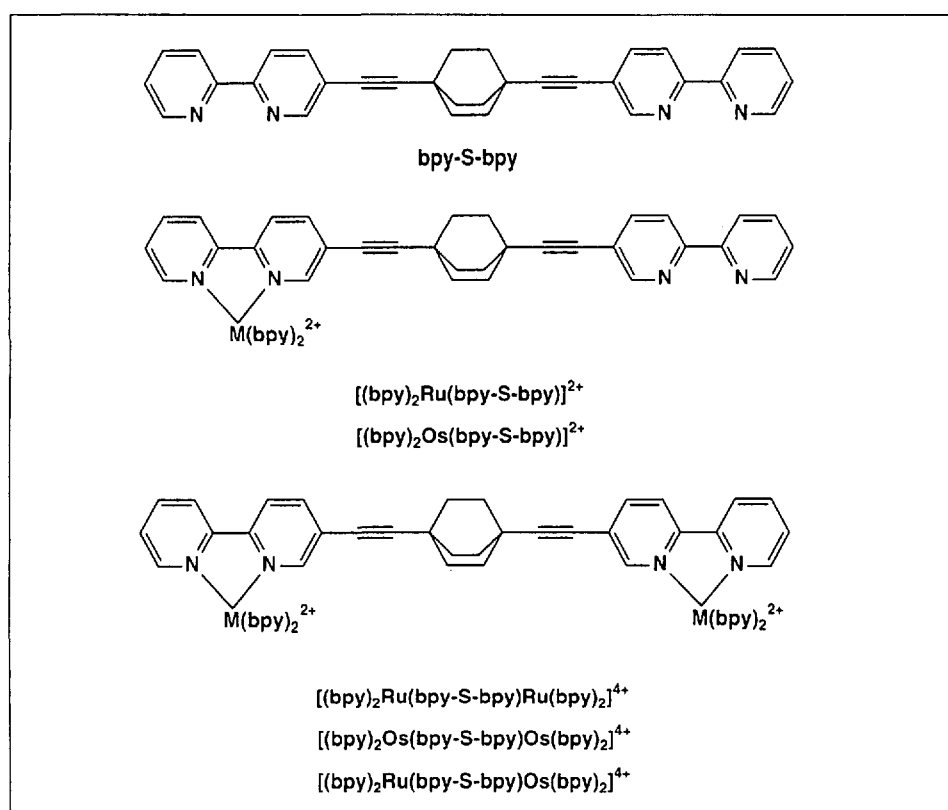bpy-S-bpy

M(bpy)$_2$$^{2+}$

[(bpy)$_2$Ru(bpy-S-bpy)]$^{2+}$

[(bpy)$_2$Os(bpy-S-bpy)]$^{2+}$

M(bpy)$_2$$^{2+}$ M(bpy)$_2$$^{2+}$

[(bpy)$_2$Ru(bpy-S-bpy)Ru(bpy)$_2$]$^{4+}$

[(bpy)$_2$Os(bpy-S-bpy)Os(bpy)$_2$]$^{4+}$

[(bpy)$_2$Ru(bpy-S-bpy)Os(bpy)$_2$]$^{4+}$

Fig. 2. *Schematic representation of the bridging ligand bpy-S-bpy and of its mononuclear and dinuclear complexes*

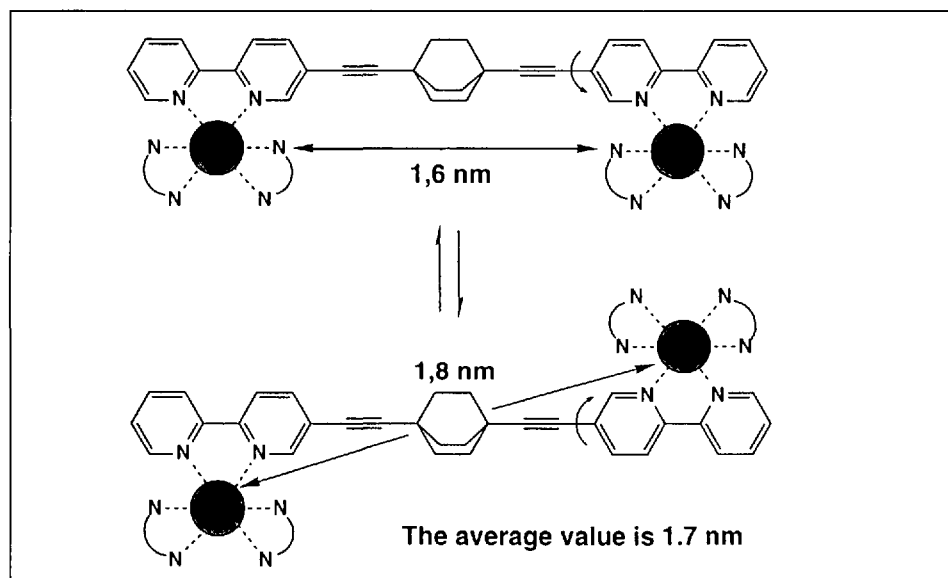1,6 nm

1,8 nm

The average value is 1.7 nm

Fig. 3. *Conformational arrangement of the dinuclear metal complexes*

Using this bridging ligand, we have synthesized the mononuclear metal complexes [(bpy)$_2$Ru(bpy-S-bpy)]$^{2+}$ (**Ru-S**); [(bpy)$_2$Os(bpy-S-bpy)]$^{2+}$ (**Os-S**) and the dinuclear complexes [(bpy)$_2$Ru(bpy-S-bpy)Ru(bpy)$_2$]$^{4+}$ (**Ru-S-Ru**); [(bpy)$_2$Os-(bpy-S-bpy)Os(bpy)$_2$]$^{4+}$ (**Os-S-Os**), and [(bpy)$_2$Ru(bpy-S-bpy)Os(bpy)$_2$]$^{4+}$ (**Ru-S-Os**) as PF$_6^-$-salts [8]. We have characterized the compounds by elemental analysis, FAB mass spectrometry, ^{1}H-NMR, UV/VIS spectroscopy and determined their spectroscopic, luminescence, and electrochemical properties. We have also investigated the quenching of the luminescence of the Ru-based unit by the Os-based unit in the heterometallic species [(bpy)$_2$Ru(bpy-S-bpy)Os(bpy)$_2$]$^{4+}$. The rate constant for the photoinduced energy-transfer process was measured and compared with the current theories.

2. Discussion and Results

The absorption spectra in the visible region and the luminescence spectra of the binuclear compounds are displayed in *Fig 5*. Two isosbestic points are present at 416 and 466 nm. Excitation at one of these wavelengths on the **Ru-S-Os** compound (as was the case for the luminescence experiments), each metal-based unit absorbs 50% of the incident light.

In oligonuclear 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 of the nature of the bridge. In the case of the novel bridge bpy-S-bpy, we can notice (*Table*) that the first oxidation potential, the first reduction potential, the absorption maxima, and all the luminescence properties are almost identical for **Ru-S, Os-S, Ru-S-Ru**, and **Os-S-Os**. This suggests little or a very weak electronic interaction between the metal-containing units in the dinuclear compounds.

In the dinuclear heterometallic species **Ru-S-Os**, the quantum yield of the Ru-based luminescence is *ca*. ten times smaller than those of the reference compounds **Ru-S** and **Ru-S-Ru**, whereas the quantum yield of the Os-based luminescence is about the same as that observed for the reference compounds **Os-S** and **Os-S-Os**.

The Ru-based luminescence intensity of a 1:1 mixture of **Ru-S-Ru** and **Os-S-Os** in MeCN solutions is 50% of an isoabsorptive (at the 466 nm isosbestic point) **Ru-S-Ru** solution, indicating that *intermolecular quenching* does not occur un-
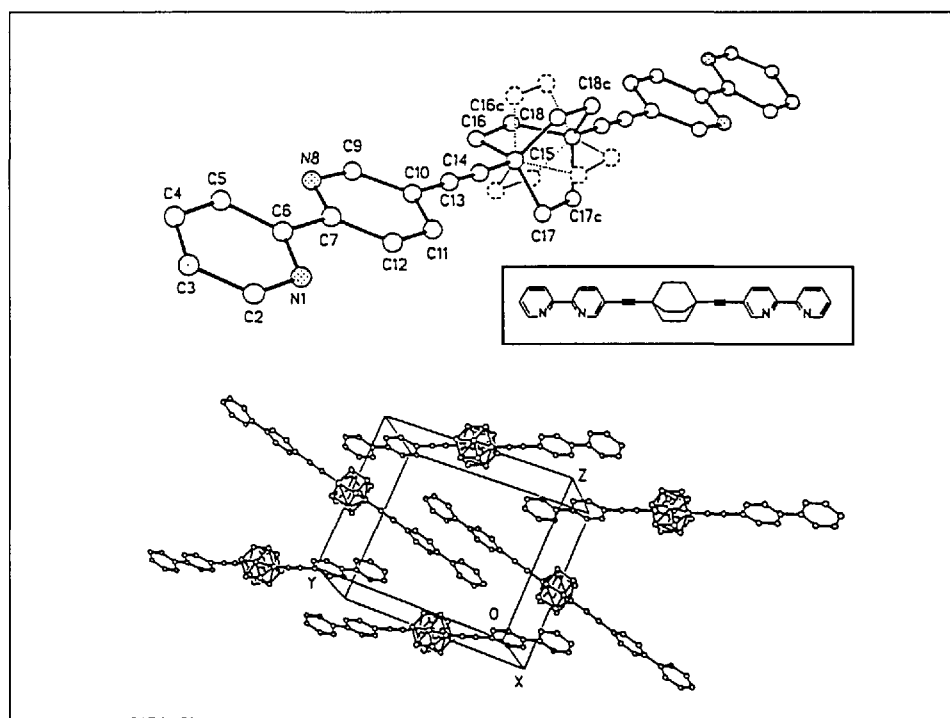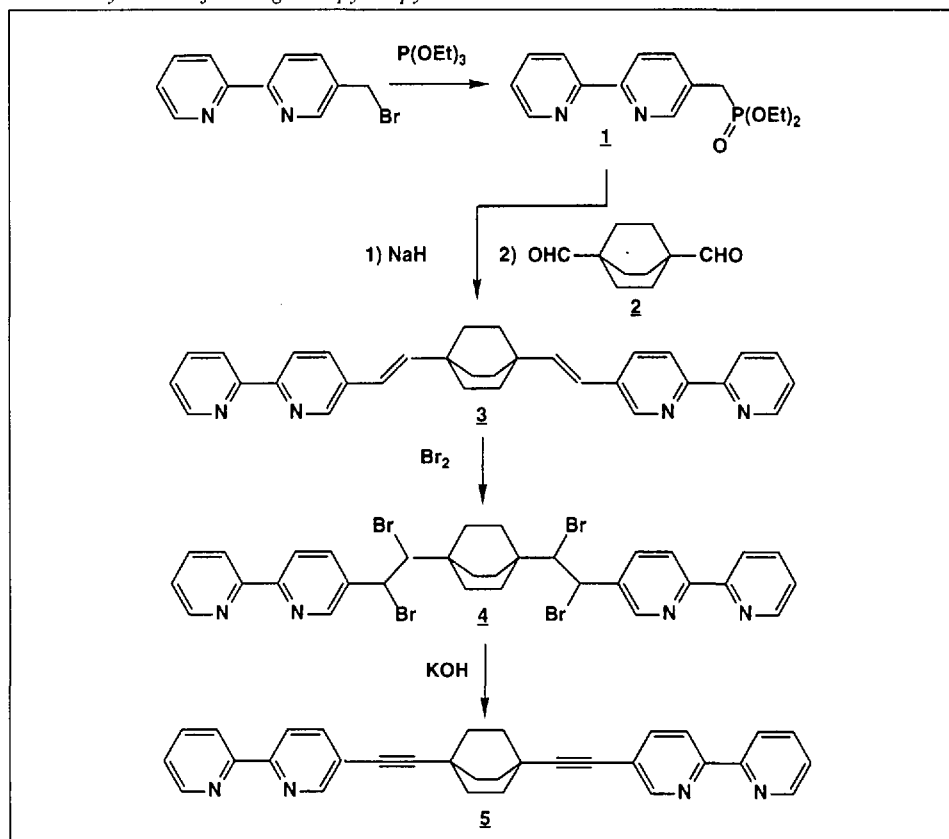
Scheme. *Synthesis of the Ligand bpy-S-bpy*

Fig. 4. *Crystal structure and unit cell of the bridging ligand bpy-S-bpy.* The bicyclooctane unit is disordered.

der the experimental conditions used. Therefore, the results demonstrate that in **Ru-S-Os** an *intramolecular energy-transfer process* takes place, which quenches the luminescent excited state of the Ru-based unit and sensitizes the luminescent excited state of the Os-based

unite one. This is confirmed by the decrease in the excited state lifetime of the Ru-based unit (from 231 ns in **Ru-S-Ru** to 22 ns in **Ru-S-Os**) and by the *rise time* (21 ns) observed for the development of the luminescence of the Os-based unit.

Table. *Spectroscopic and Electrochemical Data of the Ru and Os Complexes.* The data are measured in acetonitrile solutions. For comparison purposes the 'parent' $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ are also shown. Further informations about the experimental conditions are given in [3].

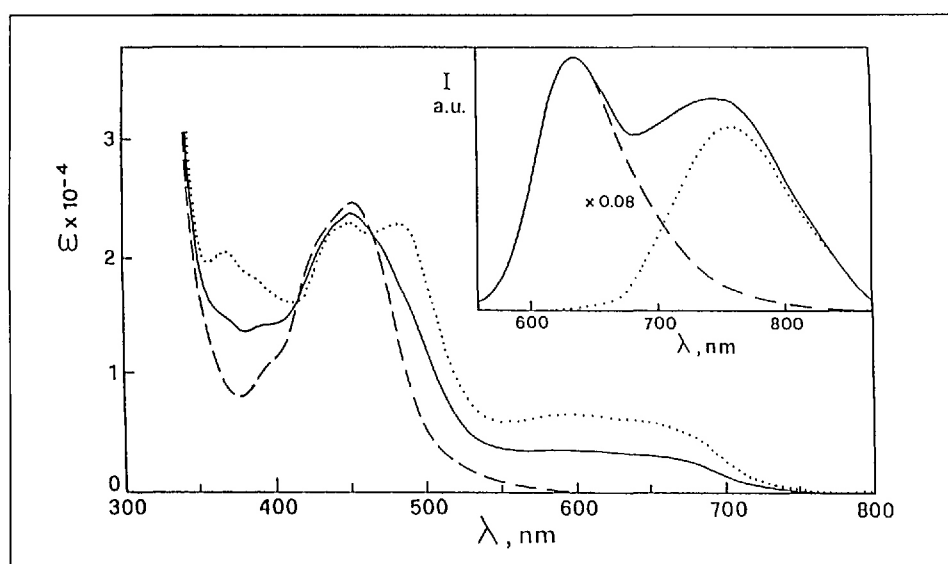|	Absorption λ_{max} [nm]		Luminescence [ns]						Electrochemistry $E_{1/2}$ [V]	
			λ_{max}	τ	$\Phi \times 10^2$	λ_{max}	τ	$\Phi \times 10^2$		
	Ru	Os	Ru			Os			Ru	Os
Ru-S	453	–	635	226	1.5	–	–	–	+1.25(1)	–
Os-S	–	484	–	–	–	787	28	0.18	–	+0.84(1)
Ru-S-Ru	452	–	635	231	1.5	–	–	–	+1.28(2)	–
Os-S-Os	–	484	–	–	–	787	29	0.18	–	+0.84(2)
Ru-S-Os	452	484 sh	638	22	0.13	787	29	0.18	+1.27(1)	+0.84(1)
$[Ru(bpy)_3]^{2+}$	452	–	615	170	1.5	–	–	–	+1.26(1)	–
$[Os(bpy)_3]^{2+}$	–	478	–	–	–	743	49	0.32	–	+0.83(1)

Fig. 5. *Absorption and (inset) uncorrected luminescence spectra of [(bpy)$_2$Ru(bpy-S-bpy)Ru(bpy)$_2$]$^{4+}$ (---), [(bpy)$_2$Os(bpy-S-bpy)Os(bpy)$_2$]$^{4+}$ (···), and [(bpy)$_2$Ru(bpy-S-bpy)Os(bpy)$_2$]$^{4+}$ (—)*

3. The Rate Constant of the Energy-Transfer Process

The rate constant for energy transfer of (**Ru-S-Os**) can be calculated from *Eqn. 1*,

$$k_{en} = \frac{1}{\tau} - \frac{1}{\tau^0} = 4.1 \times 10^7 \, s^{-1} \quad (1)$$

where τ and τ^0 are the luminescence lifetime of the Ru-based component in **Ru-S-Os** and in the **Ru-S-Ru** species, respectively. Energy-transfer processes can take place by *Förster*-type (dipole-dipole resonance) [11] and/or *Dexter*-type (electron exchange) [12] mechanisms (*Fig. 6*).

The expected rate of energy transfer according to the *Förster* mechanism can

be calculated on the basis of spectroscopic quantities by *Eqn. 2*.

$$k_{en} = 5.9 \times 10^{-25} \left(\Phi_D / n^4 \tau_D r^6 \right) \int_0^\infty F_D(\tilde{v}) d\tilde{v} / \tilde{v}^4 \quad (2)$$

For Ru-S-Os, $\Phi_D = 0.015$, $\tau_D = 226$ ns, $r = 1.7$ nm (n = refractive index of the used solvent, $\tilde{v}$ = wavenumber, ε_A = molar extinction coefficient), and the value obtained for the overlap integral is 4.7×10^{-14} $M^{-1}cm^{-3}$. The calculated value obtained for k_{en} (*Eqn. 2*; 2.4×10^7 s^{-1}) is of the same order of magnitude of the experimental value (4.1×10^7 s^{-1}). In view of the approximations involved, it could well be that the *Förster* mechanism counts for the observed energy-transfer process. The pos-

sibility cannot be excluded, however, that a *Dexter*-type energy-transfer mechanism (*Fig. 6*) is also involved and plays a major role.

For an exchange energy-transfer mechanism, the rate constant in the nonadiabatic limit can be expressed as in *Eqn. 3* [13] [14] v_{en} and $\Delta G^{\ddagger}$ can be obtained from *Eqns. 4* and *5*, respectively. In an absolute

$$k_{en} = v_{en} \exp(-\Delta G^{\ddagger}/RT) \quad (3)$$

rate formalism v_{en} can be expressed with the following factors: $v_N * \kappa$, as where v_N is the average nuclear frequency factor, κ is the electronic transmission coefficient, and $\Delta G^{\ddagger}$ is the free activation energy. This last term can be expressed by the *Marcus* quadratic relationship (*Eqn. 5*), where λ_{en} is the intrinsic barrier and ΔG^0

$$v_{en} = \frac{2(H_{en})^2}{h} \left(\frac{\pi^3}{\lambda_{en} RT} \right)^{1/2} \quad (4)$$

$$\Delta G^{\ddagger} = \left(\frac{\lambda}{4} \right) \left(1 + \frac{\Delta G^0}{\lambda} \right)^2 \quad (5)$$

the standard free-energy change of the energy-transfer process.

Using the reasonable assumptions [15][16] that *i*) the free energy change can be understood as the difference between the zero-zero spectroscopic energies of the donor and acceptor excited state (–0.33 eV), and *ii*) the reorganizational

energy λ_{en} is equal to the spectroscopic *Stokes* shift [15][16] (*i.e.*, *ca.* 0.2 eV) between absorption and emission of donor, the process falls in the *Marcus* inverted region with a value of 0.4 for the exponential term of *Eqn. 3* at room temperature. Assuming $v_N = 1 \times 10^{13}$ s^{-1}, the experimental value $k_{en} = 4.1 \times 10^7$ s^{-1} yields (*Eqn. 1*) a value of *ca.* 1×10^{-5} for the electronic factor κ. This shows that the process is strongly nonadiabatic. From *Eqn. 4*, a value of 0.4 cm^{-1} can thus be obtained for the through-bond electronic interaction energy H_{en} between the two metal-containing units, under the assumption that the observed energy-transfer process takes place only by an exchange mechanism.

5. Conclusion and Further Developments

In conclusion, we have synthesized a rigid bis(bipyridine) bridging ligand, bpy-S-bpy, which has been used to construct rod-like dinuclear metal complexes on nanometric dimension. In spite of the long metal-metal distance (1.7 nm), in the dinuclear, heterometallic Ru-S-Os compound light excitation of the Ru-based unit is followed by a very efficient (>90%) energy-transfer process ($k_{en} = 4.1 \times 10^7$ s^{-1}), which causes the sensitized emission of the Os-based unit.

The new ligand might be used to build up more complicated molecular devices, which contains donor and acceptor ligands. Such types of supramolecules are capable to held the charge separated state for a long time and open the field for chemical applications. An interesting question is the dependence of the length of the bridge on the effectiveness of the energy- or electron-transfer process. To answer this question, we are preparing new bridging systems with different length of the spacer unit (*Fig. 7*).
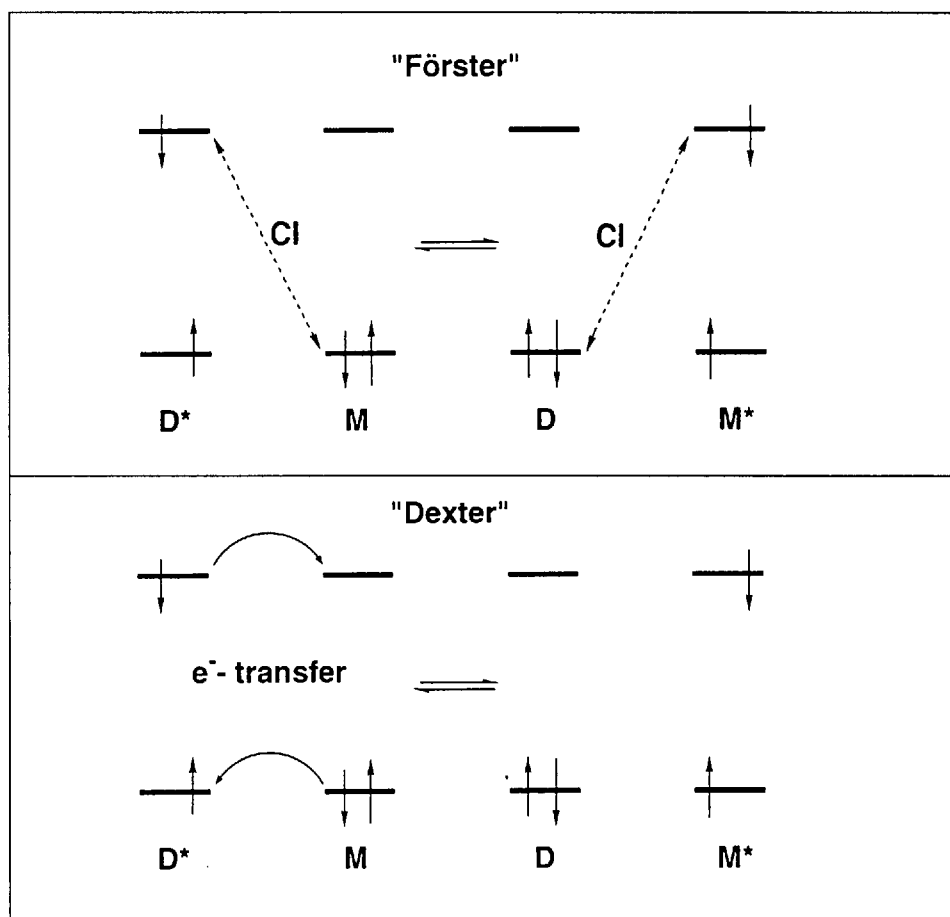
Fig. 6. *Schematic representation of the* 'Förster' *and* 'Dexter' *mechanism for energy transfer.* Cl corresponds to the *Coulomb* interaction.
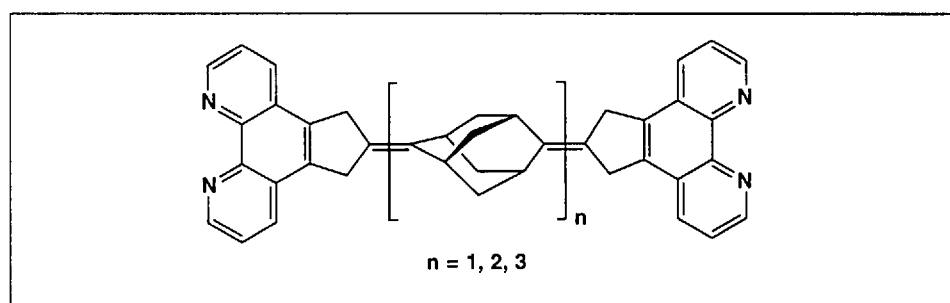

Fig. 7. *A new series of dridging ligands for dinuclear complex formation*

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