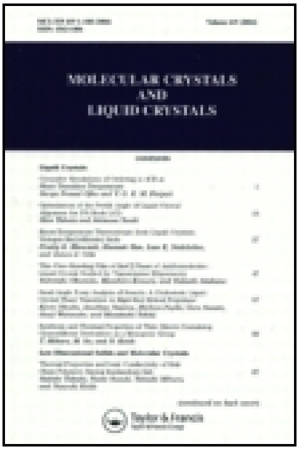

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Dinuclear Complexes of Ru and Os Containing A Rigid Bridging Ligand: Photophysical Properties and Photoinduced Energy Transfer

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Version of record first published: 04 Oct 2006.

To cite this article: Luisa De Cola , Francesco Barigelletti , Vincenzo Balzani , Peter Belser , Alex Von Zelewsky , Michael Frank & Fritz VöGtle (1993): Dinuclear Complexes of Ru and Os Containing A Rigid Bridging Ligand: Photophysical Properties and Photoinduced Energy Transfer, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 234:1, 115-120

To link to this article: http://dx.doi.org/10.1080/10587259308042905

Mol. Cryst. Liq. Cryst. 1993, Vol. 234, pp. 115–120
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Printed in the United States of America

DINUCLEAR COMPLEXES OF RU AND OS CONTAINING A RIGID BRIDGING LIGAND: PHOTOPHYSICAL PROPERTIES AND PHOTOINDUCED ENERGY TRANSFER

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Abstract

The homo- and hetero-nuclear complexes of Ru(II) and Os(II) containing a bis(bipyridine) rigid bridging ligand (**A**) have been prepared. Their absorption spectra, electrochemical behavior and luminescence properties have been investigated. Luminescence intensity and lifetime measurements indicate that in the mixed-metal complex $[(bpy)_2RuAOs(bpy)_2]^{4+}$ efficient energy transfer takes place from the Ru-based component to the Os-based one.

INTRODUCTION

In artificial photochemical molecular devices, light absorption and electronic energy transfer may be used to obtain important functions such as spectral sensitization, antenna effect, remote photosensitization, and light-energy up-conversion [1]. In an attempt to elucidate the role played by the various factors which control the occurrence of electronic energy transfer in multicomponent systems, much attention is currently devoted to the design and synthesis of supramolecular species [2,3] where energy transfer takes place between covalently-linked molecular building blocks [4-10]. Along this line, we have designed and synthesized the rigid bridging ligand A (Fig. 1) and prepared the $[(bpy)_2MA]^{2+}$ and $[(bpy)_2MAM(bpy)_2]^{4+}$ complexes (M = Ru(II) and /or Os(II)). In this paper we report the photophysical properties of these complexes and preliminary results on the occurence of electronic energy transfer in the mixed-metal dinuclear species.

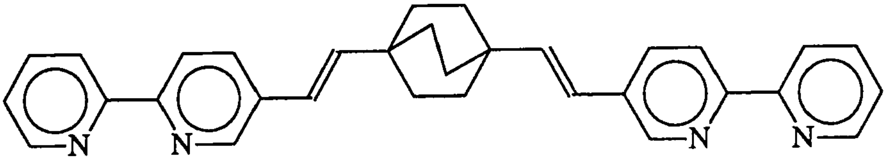

Figure 1. Schematic representation of the bis(bipyridine) bridging ligand A

EXPERIMENTAL

The $[Ru(bpy)_2A]^{2+}$, $[(bpy)_2RuARu(bpy)_2]^{4+}$ $[Os(bpy)_2A]^{2+}$ $[(bpy)_2OsAOs(bpy)_2]^{4+}$, and $[(bpy)_2RuAOs(bpy)_2]^{4+}$ complexes (bpy= 2,2'-bipyridine) will be hereafter indicated as RuA, RuARu, OsA, OsAOs, and RuAOs, respectively. The synthesis of A and of its metal complexes will be described elsewhere[11]. Absorption spectra were obtained with a Perkin Elmer Lambda 6 spectrophotometer and the luminescence spectra by a Perkin Elmer LS50 spectrofluorimeter. Luminescence lifetimes were obtained with an Edinburgh single-photon counting apparatus. Interference or cut-off filters were used to select appropriate spectral regions for lifetime measurements. In order to evaluate the quenching of the luminescence of the Ru-based component, solutions of RuAOs and of a 1:1 mixture of RuARu and OsAOs, having the same concentration, were prepared. They exhibited identical absorption spectra, as expected for non-interacting chromophores. The luminescence spectra of such solutions were then recorded (298 K) under identical instrumental conditions and the results obtained were elaborated to evaluate the difference in intensity at 620 nm, which corresponds to the maximum of the Ru-based component. In order to estimate the sensitization efficiency of the luminescence of the Os-based unit, a complex procedure had to be used because of the interference of the tail of the Ru-based luminescence on the weaker Os-based luminescence (λ_{max} = 730 nm). The luminescence of the Ru-based component was subtracted (using the RuA luminescence spectrum as a standard) from the luminescence spectrum of the RuAOs compound. The residual (Os-based) luminescence intensities of RuAOs and OsAOs were then compared and the amount of sensitized luminescence was estimated.

RESULTS AND DISCUSSION

The bridging ligand **A** is rigid since it contains a bicyclooctane unit linked to two bipyrydine moieties through two -CH=CH- groups. These last groups, in principle, could be in a trans-trans, cis-cis or cis-trans configuration. NMR analysis, however, shows that only the trans-trans form is present (Fig. 1). The absorption spectrum of **A** in dichloromethane at room temperature is slightly red shifted compared with that of bpy. In the complexes, ligand centered (LC) bands in the UV region are accompanied by the characteristic metal-to-ligand charge transfer (MLCT) bands in the visible (Fig. 2, Table I).

The bridging ligand **A** shows fluorescence in fluid solution at room temperature and both fluorescence and phosphorescence in rigid matrix at 77 K. These bands can no longer be observed in the metal

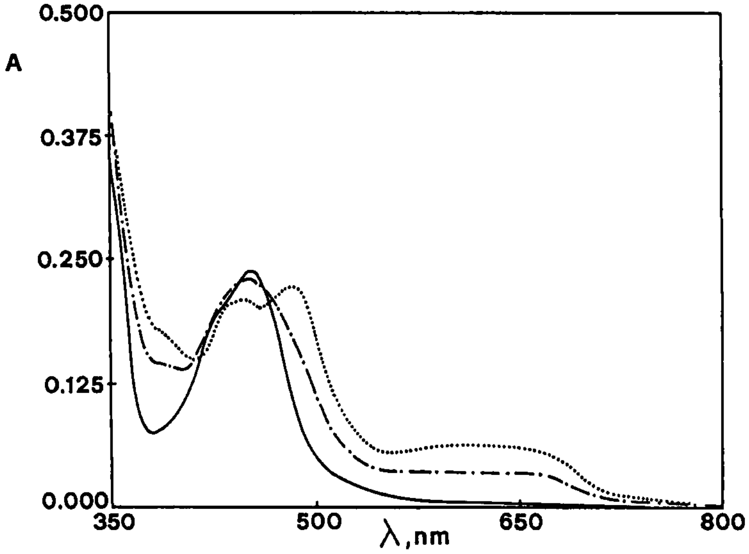

Figure 2 . Absorption spectra in CH_3CN of :
——— RuARu ; —·—·— RuAOs; ······· OsAOs.

complexes, suggesting that efficient energy transfer from LC to the lower lying MLCT excited states occurs. The complexes examined exhibit the characteristic ^{3}MLCT luminescence both in rigid matrix at 77 K and in fluid solution at room temperature. The luminescence spectra of the dimers and the mixed metal complex are displayed in Fig. 3. Some data concerning absorption and luminescence are collected in Table I. Some electrochemical data are shown in Table II.

Table I. Spectroscopic data

Complex	Absorption	Emission (298 K)		Emission (77 K)	
	λ, nm (ε)	λ, nm	τ, ns	λ, nm	τ, μs
RuA	450 (11000)	625	205	599	4.54
RuARu	450 (25000)	628	209	604	4.46
RuAOs	450 (26000)	625, 730	18, 39	601, 723	0.031, 1.28
OsA	483 (13600)	736	40	723	0.97
OsAOs	483 (22600)	740	40	727	0.89

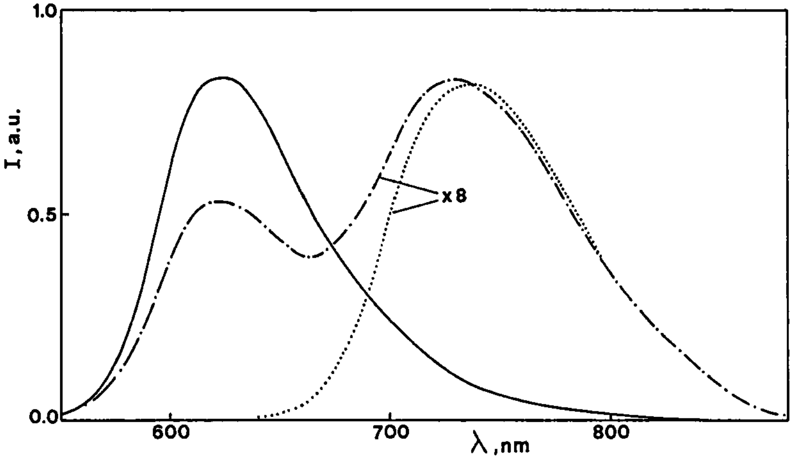

Figure 3. Emission spectra in CH_3CN of :
——— *RuA Ru;* —·—·— *RuAOs;* ······· *OsAOs.*

The photophysical and electrochemical properties of the Ru and Os monomers are very similar to those of the $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$, respectively[8]. The photophysical and electrochemical properties of the dinuclear homometallic species are almost the same as those of the corresponding mononuclear species (Table I and II), indicating that interactions between the two metal-containing units is, at most, weak.

Table II. Electrochemical data[a]

	Ox (V)	Red (V)
RuA	+1.255	-1.305
RuARu	+1.245[b]	-1.310[b]
OsA	+0.810	-1.245
OsAOs	+0.810[b]	-1.245[b]
RuAOs	+0.810, +1.240	-1.290[b]

[a] Room temperature acetonitrile solution; potential values vs SCE. [b] Two-electron peak.

Comparison between the luminescence behavior of the RuAOs species and that of the RuARu/OsAOs mixture (see experimental) shows that in the RuAOs species the luminescence intensity of the Ru-based chromophoric group is quenched to less than 10% and that the efficiency of energy transfer from the Ru-based components to the Os-based one is close to 100%. Evidence for intercomponent energy transfer is also obtained from excited state lifetime experiments. The lifetime of the Ru-based luminescence in RuAOs is 10 times shorter than that of the dinuclear RuARu complex. This result is in quantitative agreement with the luminescence intensity data and indicates that the rate constant for energy transfer in the mixed-metal complex is 5.0×10^{-7} s^{-1}.

Acknowledgments. We wish to thank V. Cacciari and G. Gubellini for technical assistance. This work was supported by CNR and MURST (Italy), Swiss National Science Foundation, and Bundesministerium für Forschung und Technologie (Project N. 0329120 A)

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