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Letter

A new bridging ligand for the synthesis of luminescent polynuclear Ru(II) and Os(II) polypyridine complexes

Anna Börje, Oliver Köthe and Alberto Juris*

Dipartimento di Chimica "G. Ciamician", Università di Bologna, via Selmi 2, 40126 Bologna, Italy. E-mail: juris@ciam.unibo.it

Received (in Montpellier, France) 6th November 2000, Accepted 7th December 2000
First published as an Advance Article on the web 19th January 2001

A new bridging ligand has been synthesized by reacting 4-hydroxy-2,2′-bipyridine with a Ru(II)-coordinated 4-bromo-2,2′-bipyridine; this bridging ligand allowed the synthesis of polynuclear Ru(II) complexes that display the same luminescence properties as $[Ru(bpy)_3]^{2+}$.

Much attention is presently being devoted to the preparation of polynuclear metal complexes.[1] Each metal unit can impart to the resulting supramolecular structure specific properties such as the capability to absorb or emit visible light and to reversibly exchange electrons. These compounds could thus find application as components in molecular electronics and as photochemical molecular devices for solar energy conversion and information storage.[2] In the past few years we have used the "complexes-as-ligands and complexes-as-metals" synthetic strategy to build polynuclear complexes containing up to 22 metal centers.[3] The employed units were Ru(II) and Os(II) polypyridine complexes, connected by the bridging ligand 2,3-bis(2-pyridyl)pyrazine (2,3-dpp). Unfortunately, due to the electronic properties of the 2,3-dpp bridging ligand, the luminescence intensity and lifetime of these polynuclear species are strongly reduced compared to those exhibited by the mononuclear $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ prototype compounds. We now report on the synthesis of polynuclear Ru(II) and Os(II) polypyridine complexes that retain the well-known photophysical properties of the $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ species, due to the use of the new bridging ligand bpy-O-bpy {bpy-O-bpy = bis[4-(2,2′-bipyridinyl)] ether}.

The new bridging ligand is synthesized *in situ*, following a reaction scheme first proposed by Constable *et al.* for terpyridine-like ligands.[4] The procedure is based on the coupling of *coordinated* Br-bpy and free HO-bpy (Br-bpy = 4-bromo-2,2′-bipyridine,[5] HO-bpy = 4-hydroxy-2,2′-bipyridine[6]), two monosubstituted bipyridines that can be obtained *via* published procedures. As far as we know, this is the first time that such a coupling has been performed on monosubstituted bipyridines.

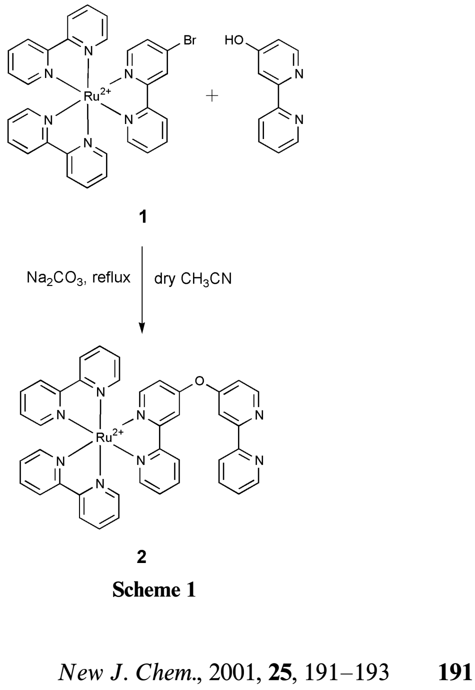
The mononuclear complex $[Ru(bpy)_2(Br\text{-}bpy)]^{2+}$, **1**, obtained by standard techniques, is "sterile" in the framework of the "complexes-as-ligands and complexes-as-metals" synthetic strategy, as it possesses neither free chelating sites nor labile ligands. However, as the electrophilic character of the *para* position in a pyridine ring is enhanced by metal coordination, the bromo function present can be exploited to transform **1** into a ligand complex, by connecting a HO-bpy unit (Scheme 1). Indeed, refluxing **1** with excess HO-bpy in anhydrous acetonitrile in the presence of Na_2CO_3 results in formation of $[Ru(bpy)_2(bpy\text{-}O\text{-}bpy)]^{2+}$, **2**. In this way a "sterile" complex (**1**) is transformed into a ligand complex (**2**), which now contains one free chelating site.

The building of dinuclear complexes can now be continued by reacting the ligand complex **2** with appropriate metal units. Thus, reaction of **2** with $[Ru(bpy)_2Cl_2]$ or $[Os(bpy)_2Cl_2]$ gives $[(bpy)_2Ru(\mu\text{-}bpy\text{-}O\text{-}bpy)Ru(bpy)_2]^{4+}$, **3**, or $[(bpy)_2Ru(\mu\text{-}bpy\text{-}O\text{-}bpy)Os(bpy)_2]^{4+}$, **4**, respectively.

The possibility of effecting efficient syntheses with multifunctional synthons was also tested. The tris-substituted sterile complex $[Ru(Br\text{-}bpy)_3]^{2+}$, **5**, was refluxed in acetonitrile in the presence of Na_2CO_3 with excess HO-bpy, leading to $[Ru(bpy\text{-}O\text{-}bpy)_3]^{2+}$, **6**. Complex **6** contains three free ligand sites, which were subsequently reacted with $[Ru(bpy)_2Cl_2]$, yielding the tetrametallic species $[Ru\{(\mu\text{-}bpy\text{-}O\text{-}bpy)Ru(bpy)_2\}_3]^{8+}$, **7**.

Polynuclear complexes like **3**, **4**, and **7** are usually formed as a mixture of diastereoisomers. The NMR data of **3** and **4** suggest that for each dimer two diastereoisomers exist, as expected. The NMR spectrum of **7**, on the other hand, is too complex to be thoroughly interpreted, suggesting the presence of several diastereoisomers. In any case, differences arising from the presence of isomeric species are not expected to be significant as far as photophysical and electrochemical properties are concerned.[7]

All the new complexes are stable in acetonitrile solution, as evidenced by the constancy of the absorption spectrum, for at least two days. Absorption and emission properties of the new compounds are collected in Table 1, where the data concerning $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ are also listed for comparison purposes. The absorption spectra of **3**, **4**, and **7** (Fig. 1) are essentially the sum of the absorption spectra of the mononuclear units present. The luminescence properties (emission wavelength, emission lifetime and quantum yield) of **3** and **7** are very similar to those of the parent $[Ru(bpy)_3]^{2+}$ species. Compound **4** features a single luminescence band that can be



Scheme 1

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Table 1 Spectroscopic properties of the Ru(II) and Os(II) complexes in acetonitrile solution at 20 °C.

	Absorption	Luminescence		
Compound	λ_{max}/nm (ε/M^{-1} cm^{-1})	λ_{max}/nm	τ/ns	Φ_{em}
1$[Ru(bpy)_2(Br\text{-}bpy)](PF_6)_2$	452(13 900)	634	920	0.058
2$[Ru(bpy)_2(bpy\text{-}O\text{-}bpy)](PF_6)_2$	454(10 300)	618	850	0.052
3$[(bpy)_2Ru(\mu\text{-}bpy\text{-}O\text{-}bpy)Ru(bpy)_2](PF_6)_4$	455(25 800)	630	670	0.046
4$[(bpy)_2Ru(\mu\text{-}bpy\text{-}O\text{-}bpy)Os(bpy)_2](PF_6)_4$	455(20 800) 573(2700)	753	23	0.002
5$[Ru(Br\text{-}bpy)_3](PF_6)_2$	458(15 000)	618	890	0.058
6$[Ru(bpy\text{-}O\text{-}bpy)_3](PF_6)_2$	458(13 300)	635	480	0.028
7$[Ru\{(\mu\text{-}bpy\text{-}O\text{-}bpy)Ru(bpy)_2\}_3](PF_6)_8$	456(51 500)	638	310	0.050
$[Ru(bpy)_3](PF_6)_2$[a]	450(13 000)	615	870	0.061
$[Os(bpy)_3](PF_6)_2$[b]	579(1860)[c]	743	60	0.005

[a] K. Kalyanasundaram, *Photochemistry of Polypyridine and Porphyrin Complexes*, Academic Press, London, 1992. [b] E. M. Kober, J. V. Caspar, R. S. Lumpkin and T. J. Meyer, *J. Phys. Chem.*, 1986, **90**, 3722. [c] In methanol: R. H. Fabian, D. M. Klassen and R. W. Sonntag, *Inorg. Chem.*, 1980, **19**, 1977.

unambiguously attributed to the $[Os(bpy)_3]^{2+}$ unit, indicating that the expected energy transfer from the ^{3}MLCT state centered on the $[Ru(bpy)_3]^{2+}$ unit is at least 98% complete.

The photophysical results indicate that the electronic communication through the new bridging ligand is small enough to not modify substantially the properties of the metal units, which are those of the corresponding isolated $[M(bpy)_3]^{2+}$ units, but large enough to allow efficient energy transfer through the bridge, a necessary condition for the build-up of multimetallic antenna systems.

Preliminary electrochemical investigations showed that oxidation of the $[Ru(bpy)_3]^{2+}$ units in compounds **3** and **7** occurs in a single process at +1.290 V *vs.* SCE in acetonitrile solution, the number of electrons exchanged being equal to the number of metal units present. Compound **4** features two monoelectronic oxidation waves at +0.855 and +1.310 V, corresponding to the $[Os(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ units, respectively. These results further indicate that the electronic structure of the $[M(bpy)_3]^{2+}$ units is essentially unaffected by the new bridging ligand and that the electronic communication between the connected metal units is small.

The present results indicate that using the new bridging ligand bpy-O-bpy it is possible to obtain in high yield polynuclear species in which the basic properties of the $[M(bpy)_3]^{2+}$ units are maintained. Work is now in progress to extend the basic scheme presented to the synthesis of other high-nuclearity complexes.

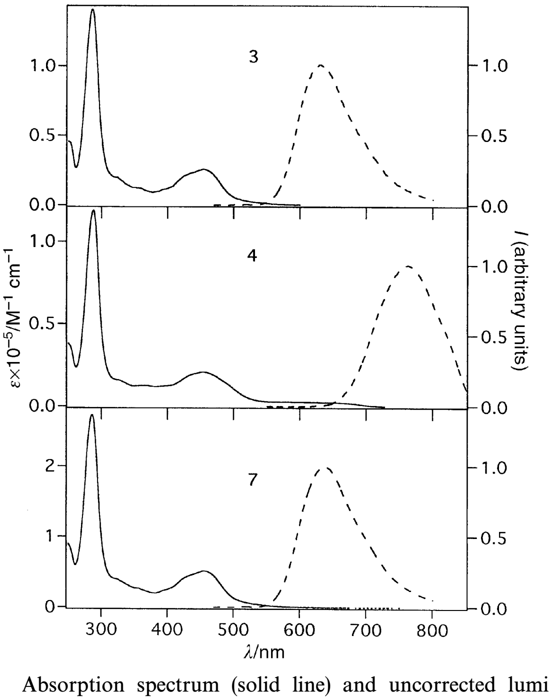

Fig. 1 Absorption spectrum (solid line) and uncorrected luminescence spectrum (dashed line) in acetonitrile at room temperature for compounds **3**, **4**, and **7**.

Experimental

^{1}H NMR (400 MHz) measurements were acquired on a Bruker ARX400 spectrometer. MALDI-TOF spectra were run on a Bruker Biflex III using α-cyano-4-hydroxycinnamic acid as matrix. Photophysical and electrochemical measurements were performed as described elsewhere.[8]

Syntheses

$[Ru(bpy)_2(bpy\text{-}O\text{-}bpy)](PF_6)_2$, 2. Complex **1** (0.027 mmol), HO-bpy (0.060 mmol), and dried K_2CO_3 (0.17 mmol) were refluxed in anhydrous acetonitrile under argon for 20 h. After cooling the solution was filtered and the solvent removed. The crude product was dissolved in acetone and recrystallized from water containing a few milligrams of NH_4PF_6. The product was washed with ether and dried. Yield, 70%. Complex **6** was obtained with the same procedure from **5** in 85% yield (reflux time, 36 h).

$[(bpy)_2Ru(\mu\text{-}bpy\text{-}O\text{-}bpy)Ru(bpy)_2](PF_6)_4$, 3. $Ru(bpy)_2Cl_2$ (0.068 mmol) and $AgNO_3$ (0.134 mmol) were stirred in 20 ml of H_2O–EtOH (1 : 2) under argon for 2 h at room temperature. Complex **2** (0.056 mmol) was added and the solution refluxed for 24 h. After cooling, the solution was filtered to remove AgCl, and the solvent evaporated. The crude product was recrystallized three times following the procedure described for **2**. Yield 56%. ^{1}H NMR (acetone-d_6, 25 °C): δ 7.35 (2 dd, $J = 6.4$, 2.6, 2H$_{5'}$ bridging ligand), 7.53–7.63 (m, 10H$_5$), 7.95 (2 d, $J = 6.4$, 2H$_{6'}$ bridging ligand), 8.00–8.08 (m, 8H$_6$), 8.14–8.25 (m, 10H$_4$), 8.61 (2 d, $J = 2.4$, 2H$_{3'}$ bridging ligand), 8.71 (d, $J = 8.2$ Hz, 2H$_3$), 8.77–8.83 (m, 8H$_3$). MALDI-TOF *m*/*z*: 1154 $[M - 4PF_6]^+$.

$[(bpy)_2Ru(\mu\text{-}bpy\text{-}O\text{-}bpy)Os(bpy)_2](PF_6)_4$, 4. **4** was synthesized analogously to **3** using $Os(bpy)_2Cl_2$ instead of $Ru(bpy)_2Cl_2$. Yield 40%. ^{1}H NMR (acetone-d_6, 25 °C): δ 7.30 (2 dd, $J = 6.5$, 2.7, 1H$_{5'}$ bridging ligand-Os), 7.34 (2 dd, $J = 6.4$, 2.6, 1H$_{5'}$ bridging ligand-Ru), 7.44–7.52 (m, 5H$_5$ Os), 7.53–7.61 (m, 5H$_5$ Ru), 7.89 (2 d, $J = 6.5$ Hz, 1H$_6$ bridging ligand-Os), 7.90–8.08 (m, 6H$_4$, 8H$_6$, 1H$_{6'}$ Ru), 8.16–8.25 (m, 6H$_4$), 8.61 (m, 2H), 8.71 (m, 2H), 8.77–8.83 (m, 8H$_3$). MALDI-TOF *m*/*z*: 1242 $[M - 4PF_6]^+$.

$[Ru\{(\mu\text{-}bpy\text{-}O\text{-}bpy)Ru(bpy)_2\}_3](PF_6)_8$, 7. $Ru(bpy)_2Cl_2$ (0.134 mmol) and $AgNO_3$ (0.285 mmol) were stirred in 25 ml of H_2O–EtOH (1 : 2) under argon for 2 h at room temperature. After addition of **6** (0.056 mmol) the solution was refluxed for 36 h. The crude product was recrystallized three times following the procedure described for **2**. Yield 37%. ^{1}H NMR (acetone-d_6, 25 °C) δ 7.37–7.46 (m, 6H$_{5'}$ bridging ligand), 7.62–7.75 (m, $18H_5$), 7.94–8.01 (m, $6H_{6'}$ bridging ligand), 8.03–8.18 (m, $18H_6$), 8.20–8.30 (m, $18H_4$), 8.61–8.67 (m, 6H), 8.74–8.82 (m, 6H), 8.82–8.89 (m, $12H_3$).

Acknowledgements

This work has been supported by MURST (Artificial Photosynthesis Project), Università di Bologna (Funds for Selected Research Topics) and EC (TMR grant FMRX-CT96-0031).

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