Ground- and Excited-state Properties of some Ligand-bridged Ruthenium(II) Polypyridyl Complexes with Spectator-ligand-based Emission

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From an examination of the absorption, luminescence and redox properties, the lowest excited state of the ligand-bridged polypyridyl complexes $[\{Ru(biq)_2\}_2(dpp)]^{4+}$ and $[(bipy)_2Ru(dpp)Ru(biq)_2]^{4+}$ [dpp = 2,3-bis(2′-pyridyl)pyrazine, biq = 2,2′-biquinoline and bipy = 2,2′-bipyridine] is assigned to that of the charge-transfer type involving the spectator ligand biq.

There has been growing interest in the photophysics and photochemistry of polynuclear complexes with a view to designing systems for solar-energy conversion, photocatalysis, *etc.*[1,2] Polynuclear polypyridyl complexes of the type $[(L^S)_2M^1(dpp)M^2(L^S)_2]$, derived using polyimine bridging ligands such as 2,3-bis(2′-pyridyl)pyrazine (dpp), appear to be promising due to their rich visible-light absorption and long-lived excited states. Several homo- and hetero-dinuclear complexes of this type with identical or different non-bridging or spectator ligands (L^S) have been synthesised and their photophysical, photochemical properties determined.[3–6] In all reported cases, the lowest excited state of the dinuclear complex responsible for the emission and photochemistry is of the charge transfer (c.t.) type involving the bridging ligand dpp.

Recent studies on the dinuclear complexes of dpp have shown that their stability is rather limited, especially under photochemical conditions.[3d] Enhanced stability and better tuning of the excited state should be possible with dinuclear complexes that have lowest c.t. excited states associated with the spectator ligands, *i.e.* shifting the excited state and photochemistry to peripheral chromophore units without touching the crucial bridging ligands. Ligands with lower reduction potentials such as 2,2′-biquinoline(biq)[7–11] may be candidates to replace the usual spectator ligand 2,2′-bipyridine (bipy) so that the lowest excited state can be of the M→biq c.t. type. With this in mind, we recently synthesised a series of dinuclear ruthenium dpp complexes with biq and bipy as spectator ligands L^S.

We have examined two types of complexes, a symmetrical one with two biq ligands on each side, $[\{Ru(biq)_2\}_2(dpp)]^{4+}$ **1** and an asymmetrical one with two bipy on one side and two biq ligands on the other, $[(bipy)_2Ru(dpp)Ru(biq)_2]^{4+}$ **2**. Properties of the mononuclear precursor complex $[Ru(biq)_2(dpp)]^{2+}$ **3** are also described. Photophysical and redox properties of the complexes $[\{Ru(bipy)_2\}_n(dpp)]^{2n+}$, $n = 1$ or 2, have been reported earlier.[3] The asymmetric complex **2** also provides a direct comparison to the dinuclear ruthenium complex examined recently by Schmehl *et al.*,[12] $[(biq)_2Ru(L^b)Ru(bipy)_2]^{4+}$, where the bridging ligand L^b is the 4,4′-substituted bipy derivative 1,4-bis[2-(4′-methyl-2,2′-bipyrid-4-yl)ethyl]benzene. Owing to the specific design of the bridging ligand with a methylene group spacer between the two bipy units, the two chromophore units $Ru(biq)_2(L^b)$ and $Ru(bipy)_2(L^b)$ behave independently in this complex, with the possibility of intramolecular energy transfer from one to another. Studies on the asymmetric dpp complex may provide information on the extent of 'coupling' between the two chromophore units '$Ru(biq)_2(dpp)$' and '$Ru(bipy)_2(dpp)$'.

Experimental

Materials.—The polypyridyl ligands 2,2′-bipyridine (Fluka), 2,2′-biquinoline (Fluka) and 2,3-bis(2′-pyridyl)pyrazine (Aldrich) and $RuCl_3{\cdot}xH_2O$ (Fluka) were used as supplied. Solvents were p.a. grade chemicals also from Fluka.

Synthesis.—The mononuclear complex $[Ru(biq)_2(dpp)]^{2+}$ was prepared by refluxing $[Ru(biq)_2Cl_2]$ with a three-fold excess of the ligand dpp in ethylene glycol under N_2 for about 3 h.[3d] The reflux solution was then filtered and the complex precipitated as the PF_6^- salt using ammonium hexafluorophosphate. The symmetric dinuclear complex, $[\{Ru(biq)_2\}_2(dpp)]^{4+}$ was prepared[3d] in an analogous manner by refluxing $[Ru(biq)_2(dpp)]^{2+}$ with a three-fold excess of $[Ru(biq)_2Cl_2]$ also in ethylene glycol. The asymmetric dinuclear complex $[(bipy)_2Ru(dpp)Ru(biq)_2]^{4+}$ was prepared[3d] by cross-reaction of $[Ru(biq)_2(dpp)]^{2+}$ with a three-fold excess of $[Ru(bipy)_2Cl_2]$ under similar conditions. From a practical point of view, the synthesis of the asymmetric ruthenium complex by the reaction of $[Ru(bipy)_2(dpp)]^{2+}$ with $[Ru(biq)_2Cl_2]$ is of minor interest, due to the formation of trace amounts of the dinuclear complex even after *ca.* 36 h of reflux.

Methods.—Absorption spectra were recorded on a Hewlett-Packard diode-array spectrophotometer. Room-temperature emission spectra were recorded on a Spex Fluorolog spectrofluorimeter and are corrected for variation in the spectral response of the photomultiplier and detection optics. The low-temperature (77 K) spectra were recorded on a Perkin-Elmer MPF spectrofluorimeter equipped with a red-sensitive Hamamatsu R928 photomultiplier tube, but the reported emission maxima are uncorrected values. Emission lifetimes were determined using a neodymium (530 nm) laser flash-photolysis set-up. Electrochemical (redox potential) measurements were made using a three-electrode set-up with glassy carbon as working electrode and a Wenking potentiostat. Redox potential data quoted in this work were measured in dimethylformamide (dmf) and are in volts, referenced to the saturated calomel electrode (SCE).

Table 1 Absorption and emission properties of ligand-bridged ruthenium complexes and their monomeric precursors. Room-temperature (293 K) absorption and emission data are in dmf as the solvent and emission data at 77 K are in EtOH–MeOH glass (4:1 v/v)

Complex	Absorption, λ_{max}/nm (ε/dm^3 mmol^{-1} cm^{-1})	Emission, 77 K λ_{max}/nm	Emission, 77 K τ/μs	Emission, 293 K λ_{max}/nm	Emission, 293 K τ/ns	Ref.
$[Ru(biq)_2(bipy)]^{2+}$	547(8.55), 481(6.59)	728	1.4	742	270(N_2)	8
$[Ru(biq)_2(dmbipy)]^{2+}$ *	550(6.50), 480	739	2.2	750		12
$[Ru(biq)_2(dpp)]^{2+}$	526(10.4), 478(9.13)	712	2.36	720	330(N_2), 230(air)	This work
$[Ru(bipy)_2(dpp)]^{2+}$	468(11.0), 434(11.5)	624	5.36	686	382(N_2)	3*d*
$[(biq)_2Ru(dpp)Ru(biq)_2]^{4+}$	538(21.2), 478	714	2.24	746	232(N_2), 120(air)	This work
$[(bipy)_2Ru(dpp)Ru(biq)_2]^{4+}$	548(22.8), 478(sh)	710	3.17	760	175(N_2), 110(air)	This work
$[(dmbipy)_2Ru(L^b)Ru(biq)_2]^{4+}$	550(9.4), 456(17.0)	739	2.3	748		8
		586	0.298	620		8
$[(biq)_2Ru(dpp)Ru(bipy)(dpp)Ru(biq)_2]^{6+}$	546(28.7), 434(15.3)	702	2.18	742	142(air)	6
$[(bipy)_2Ru(dpp)Ru(bipy)_2]^{4+}$	526(24.8), 425(19.8)	702	2.38	790	140(N_2)	3*d*

* dmbipy = 4,4′-dimethyl-2,2′-bipyridine

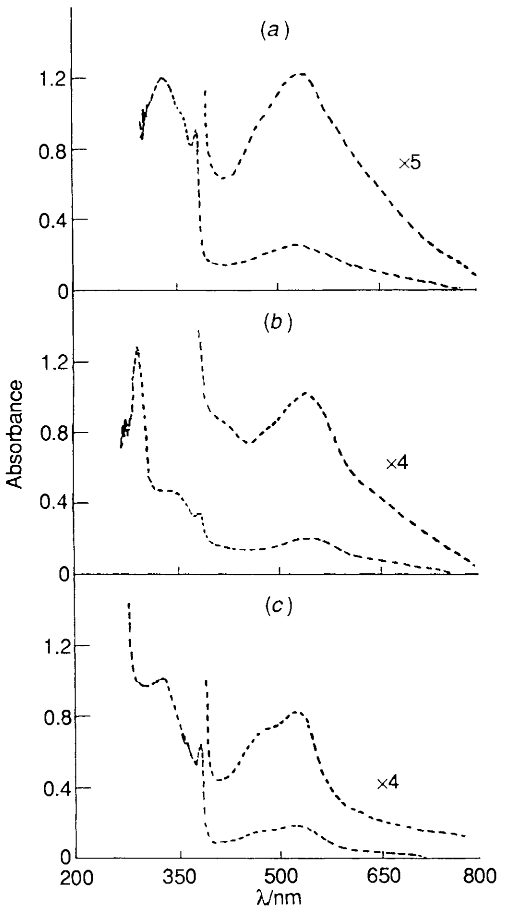

Fig. 1 Absorption spectra of the mono- and di-nuclear complexes: (*a*) $[(biq)_2Ru(dpp)Ru(biq)_2]^{4+}$, (*b*) $[(bipy)_2Ru(dpp)Ru(biq)_2]^{4+}$ and (*c*) $[Ru(biq)_2(dpp)]^{2+}$ in dmf at room temperature

Results and Discussion

During the course of our investigations it was found that the stability of ruthenium complexes containing biq was rather limited in solution at room temperature. Except for dmf, the stability is quite low in most solvents. For example, cleavage of the dinuclear complexes occurs rapidly in water so that no meaningful measurements can be made in this solvent. In organic solvents such as acetonitrile or ethanol the complexes have limited stability for a few hours, so allowing rapid measurements. We will return later to an analysis of the mode of cleavage and means of monitoring it. For stability reasons, most of the measurements reported below were made using dmf as a solvent.

Photophysical and Redox Properties of the Biquinoline Complexes.—(*a*) *Absorption spectral features*. Fig. 1 presents the absorption spectra of the three key biquinoline complexes examined. Data on the absorption maxima of the different polypyridyl complexes are listed in Table 1 along with molar absorption coefficients. The spectra are typical of ruthenium polypyridyl complexes with fairly intense metal-to-ligand charge-transfer (m.l.c.t.) bands in the visible region. In all cases the spectra in the 400–600 nm region are characterized by two well resolved bands, attributable to the M→L^b and M→L^t c.t. transitions. The lowest-energy c.t. band is located within a narrow range of 525–560 nm, considerably red-shifted as compared to analogous complexes with bipy as spectator ligands and is assigned as due to Ru→biq c.t. The Ru→dpp c.t. band is located at 468 and 526 nm for $[Ru(bipy)_2(dpp)]^{2+}$ and $[\{Ru(bipy)_2\}_2(dpp)]^{4+}$ respectively. The Ru→bipy c.t. band often occurs at 434 nm.

The shift in the longest-wavelength absorption band upon binucleation in the biq complex is rather small as compared to that observed for the analogous bipy complex $[\{Ru(bipy)_2\}_2(dpp)]^{4+}$.[3] During the course of this work, Campagna *et al.*[6] published a short communication on the properties of the trinuclear complexes $[(bipy)_2Ru(dpp)Ru(bipy)(dpp)Ru(bipy)_2]^{6+}$ and $[(biq)_2Ru(dpp)Ru(bipy)(dpp)Ru(biq)_2]^{6+}$. Interestingly, the longest-wavelength c.t. band maxima of the bi- and tri-nuclear complexes are nearly the same. Taken altogether, the results tend to suggest that in these dpp-bridged ruthenium complexes with biq as the spectator ligand the lowest-energy absorption band (hence the lowest excited state) is biq-based. Emission and redox potential data (*cf.* discussion below) also support such assignments.

(*b*) *Emission features*. Mono- and di-nuclear dpp complexes with biq, $[\{Ru(biq)_2\}_2(dpp)]^{4+}$ **1** $[(bipy)_2Ru(dpp)Ru(biq)_2]^{4+}$ **2** and $[Ru(biq)_2(dpp)]^{2+}$ **3** all emit in solution at room temperature. Fig. 2 presents the emission spectra of the complexes $[\{Ru(biq)_2\}_n(dpp)]^{2n+}$, n = 1 or 2. The mononuclear complex **3** has its emission maximum at 720 nm. The dinuclear complexes **1** and **2** show slightly red-shifted emission with maxima at around 746 and 760 nm respectively. Data on the emission maxima and lifetimes for various complexes at room temperature and also in EtOH–MeOH glass at 77 K are presented in Table 1. At ambient temperature the excited-state lifetime for the symmetric dinuclear complex is sufficiently long (232 ns), only slightly shorter than for the mononuclear complex (τ = 330 ns). At 77 K the emission lifetimes of all three complexes are nearly the same, 2.36 μs. For analogous dpp complexes with bipy as the spectator ligand, $[\{Ru(bipy)_2\}_n$-

Table 2 Redox potentials of ligand-bridged ruthenium complexes and their monomeric precursors in dmf at ambient temperature (in V *vs.* SCE)

Complex	$E_{\frac{1}{2}}^{red}(1)$	$E_{\frac{1}{2}}^{red}(2)$	$E_{\frac{1}{2}}^{red}(3)$	Ref.
$[Ru(biq)_2(bipy)]^{2+}$	−0.84			8
$[Ru(biq)_2(dmbipy)]^{2+}$	−0.84	−1.08(biq)	−1.67(dmbipy)	12
$[Ru(biq)_2(dpp)]^{2+}$	−0.76(biq)	−0.95(biq)	−1.37(dpp)	This work
$[(biq)_2Ru(dpp)Ru(biq)_2]$	−0.71(biq)	−0.87(biq)	−1.07(dpp)	This work
$[(bipy)_2Ru(dpp)Ru(biq)_2]$	−0.75(biq)	−0.93(biq)	−1.10(dpp)	This work
$[(dmbipy)_2Ru(L^b)Ru(biq)_2]$	−0.85	−1.08	−1.38	12

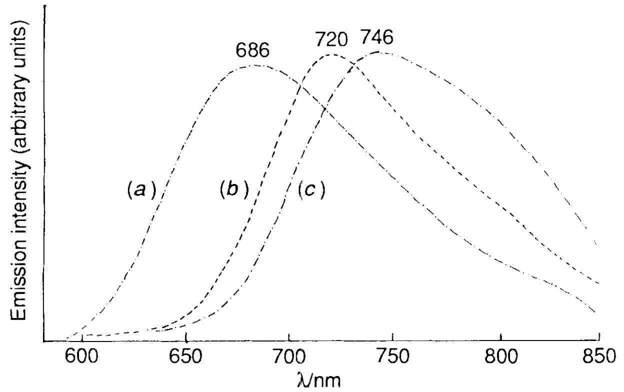

Fig. 2 Emission spectra of the mono- and di-nuclear complexes in dmf at room temperature: (*a*) $[Ru(bipy)_2(dpp)]^{2+}$, (*b*) $[Ru(biq)_2(dpp)]^{2+}$ and (*c*) $[\{Ru(biq)_2\}_2(dpp)]^{4+}$

$(dpp)]^{2n+}$, $n = 1$ or 2, there is substantial shortening of the lifetime (nearly a factor of 3) upon binucleation. Near constancy of the emission maxima and lifetimes for the polynuclear complexes again support the assignment that the emission is Ru→biq based. In terms of relative (c.t.) energy ordering in ruthenium polypyridyl complexes,[13] the following is noted: Ru→bipy > Ru→dpp > Ru→biq. The assignment of Ru→biq as the lowest-energy band in absorption and emission is thus consistent with such deductions.

(*c*) *Redox potentials.* Redox potentials were determined in dmf. Within the working anodic potential limit available for this solvent (*ca.* +1.60 V), no authentic oxidation wave was detected. Within the range of 0 to −2.0 V, several reversible reduction waves are observed and the first reduction potentials ($E_{\frac{1}{2}}$ values, *vs.* SCE) are listed in Table 2 along with their tentative assignments.

Examination of the compilation[13] of redox potentials for various mononuclear ruthenium polypyridyl complexes containing biq, bipy or dpp shows that the first reduction wave $Ru^{2+/1+}$ (actually corresponding to the ligand reduction) occurs at −0.84(biq), −1.00(dpp) and −1.26 V(bipy) respectively. In the new biq/dpp complexes examined in this work (complexes **1**–**3**) the first reduction occurs invariably at −0.75 ± 0.05 V, corresponding to biq-based reduction. It is reasonable that replacement of bipy by the better electron-withdrawing ligand dpp {as in $[Ru(biq)_2(bipy)]^{2+}$ to give $[Ru(biq)_2(dpp)]^{2+}$} anodically shifts the first reduction wave by *ca.* 100 mV.

Recent studies on dinuclear dpp complexes have shown that the ligand dpp when it is binucleating undergoes reduction at significantly more positive potentials of *ca.* −0.70 V. Hence, *a priori*, it is difficult to assign the first reduction as due to biq- or due to dpp-based reduction. Based on the above empirical correlations, Campagna *et al.*[6] recently assigned the first reduction (and hence the lowest excited state) in the trinuclear ruthenium biq/dpp complex as dpp-based. In view of our electrochemical data on the mononuclear biq complexes and the similarities in the absorption and emission behaviour of the mono-, bi- and tri-nuclear complexes, we feel that in all these cases one is dealing with biq-based reductions and the lowest excited state is consequently of the Ru→biq c.t. type.*

Dynamics of Cleavage of Dinuclear biq/dpp Complexes.—It was mentioned earlier that the stability of dinuclear biq complexes is rather limited in solution, with cleavage occurring with time. For example, the initial purple-violet solution of the dinuclear complex turns darker (bluish) with time. The absorption spectra change with new bands appearing at *ca.* 490 and 590 nm. Though the changes are indicative of cleavage of the dinuclear complex, the spectra are too broad to support inferences on the nature of the fragments formed. Due to decomposition of the ruthenium biq complexes in most chromatographic columns, such separation of the products also yields ambiguous results. However, monitoring of the emission from the cleaved products provides interesting clues as to the mode of cleavage in these dinuclear complexes.

A freshly prepared solution of the asymmetric dimer **2** shows the typical Ru→biq c.t. emission at 760 nm. Upon standing in the dark there is a slow decrease in the emission intensity of the band at 760 nm with concomitant growth of a new emission with a maximum at 686 nm. In acetonitrile, the mononuclear complexes $[Ru(bipy)_2(dpp)]^{2+}$ and $[Ru(biq)_2(dpp)]^{2+}$ have distinct emission maxima at 686 and 720 nm respectively. The results suggest that the cleavage of the dinuclear complex occurs *via* pathway (1) rather than (2).

$$[(bipy)_2Ru\text{–}dpp\text{–}Ru(biq)_2]^{4+} \xrightarrow{X^-}$$
$$\lambda_{em}\ 760\ \text{nm}$$
$$\underset{686\ \text{nm}}{[Ru(bipy)_2(dpp)]^{2+}} + [Ru(biq)_2X_2] \qquad (1)$$

$$[(bipy)_2Ru\text{–}dpp\text{–}Ru(biq)_2]^{4+} \xrightarrow{X^-}$$
$$\underset{720\ \text{nm}}{[Ru(biq)_2(dpp)]^{2+}} + [Ru(bipy)_2X_2] \qquad (2)$$

It should be pointed out that, in our experiments, by selective synthetic procedures we have avoided introduction of the $[Ru(bipy)_2(dpp)]^{2+}$ complex during the synthesis. The loss of the bridging ligand dpp with the $Ru(bipy)_2$ fragment in the cleavage process is consistent with steric constraints imposed on the dinuclear complex. Such constraints may also account for the very inefficient formation of the asymmetric dinuclear complex in the reaction of $[Ru(bipy)_2(dpp)]^{2+}$ with $[Ru(biq)_2Cl_2]$.

In the dinuclear complex $[(bipy)_2Ru(L^b)Ru(biq)_2]^{4+}$ of Schmehl *et al.*[12] referred to earlier the chelating centres on the bipy fragment are so well separated that two chromophore units

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* A referee has pointed out that, in this situation, in which the first reduction, the lowest c.t. absorption and emission could be predicted to involve either the spectator or bridging ligand, it is entirely possible that: (*a*) the nature of the lowest-energy orbital may be different in the mononuclear complex and its dinuclear (or trinuclear) analogues; (*b*) the ligand involved in the reduction and in the emission may not be the same. Resonance-Raman and/or spectroelectrochemical studies may provide additional information on this point.

exist as independent species with their own unique emission. The resulting intramolecular energy transfer from one to the other can be monitored directly. In the dpp complexes examined here, owing to the absence of distinct ligand fragments that can be associated with each of the two possible chromophore units, any discussion of discrete emission from the individual chromophores is questionable. In heterodinuclear dpp complexes of the type $[(bipy)_2Ru(dpp)M(bipy)_2]^{n+}$, M = Re^I ($n = 3$)[5] or Rh^{III} ($n = 5$),[14] for example, the emission from the $Ru(bipy)_2(dpp)$ unit always occurred at wavelengths considerably red-shifted as compared to that of the corresponding mononuclear complex $[Ru(bipy)_2(dpp)]^{2+}$.

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