Raman Characterization of Charge-transfer Transitions in Ligand-bridged Binuclear Polypyridyl Complexes of Ruthenium(II)

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In the ligand-bridged complexes $[(bipy)_2Ru(dpp)Ru(biq)_2]^{4+}$ and $[(biq)_2Ru(dpp)Ru(biq)_2]^{4+}$ [dpp = 2,3-bis(2′-pyridyl)pyrazine, bipy = 2,2′-bipyridine and biq = 2,2′-biquinoline], the photophysical and redox properties do not allow differentiation of the low-energy charge-transfer transitions Ru ⟶ biq and Ru ⟶ dpp. Based on the selective resonance enhancement of the intensities of the Raman bands of the ligand biq by excitation within the lowest-energy absorption band, the lowest excited states in the dinuclear complexes have been assigned unambiguously to Ru ⟶ biq charge transfer.

Currently there is extensive interest in polynuclear polypyridyl complexes composed of several chromophoric units linked together by suitable template ligands carrying a number of chelating centres.[1] Polyimine ligands such as 2,3-bis(2′-pyridyl)pyrazine (dpp) are used widely as templates. In order to develop possible applications as light-harvesting units, photophysical properties of the various chromophoric units and intramolecular interactions in the excited state have been examined for a number of dpp-based polynuclear complexes.[1] Characterization of the excited-state reactions first requires the establishment of the identity of the low-energy transitions. In ligand-bridged dinuclear complexes such as $[(L^s)_2Ru(L^b)Ru(L^{s'})_2]^{4+}$ (L^b = bridging ligand and L^s, $L^{s'}$ = non-bridging or spectator ligands), any one of the following charge-transfer (c.t.) transitions may form the lowest-energy excited state: $M \longrightarrow L^s$, $M \longrightarrow L^b$ or $M \longrightarrow L^{s'}$ and assignments are often based on the absorption spectral and electrochemical data of suitable model compounds. The formation of the metal-to-ligand c.t. excited state can be visualized as the transfer of an electron from the Ru^{II} centre to one of the polypyridine ligands [equation (1)].[2] The lowest-energy excited state reponsible

$$[Ru^{II}(L^s)_2(L^b)]^{2+} \xrightarrow{h\nu} [Ru^{III}(L^s)(L^{s-})(L^b)]^{2+*} \quad (1)$$

for the observed emission and photoreactions often involves that ligand which is most easily reduced. For example, in the mononuclear complexes $[RuL(bipy)_2]^{2+}$ (bipy = 2,2′-bipyridine) the ligand-based reduction occurs at −1.23 (L = bipy), − 1.0 (L = dpp) or −0.7 V[L = 2,2′-biquinoline (biq)], giving rise to the following order for the energies of the c.t. excited state: Ru ⟶ bipy > Ru ⟶ dpp > Ru ⟶ biq.

Recently we examined the excited-state properties of the mono- and di-nuclear complexes $[\{Ru(L)_2\}_n(dpp)]^{2n+}$ (n = 1 or 2, L = bipy or biq) and also the asymmetric dinuclear complex $[(bipy)_2Ru(dpp)Ru(biq)_2]^{4+}$.[3] In the mononuclear complex $[Ru(biq)_2(dpp)]^{2+}$ **1**, the first reduction occurs at −0.76 V *vs.* saturated calomel electrode (SCE). Based on the ordering of reduction potentials and excited-state energies in the model compounds referred to above, the lowest excited state in this complex is clearly assigned to Ru ⟶ biq c.t. In the dinuclear complexes $[(biq)_2Ru(dpp)Ru(biq)_2]^{4+}$ **2** and $[(bipy)_2Ru(dpp)Ru(biq)_2]^{4+}$ **3** the first reduction occurs at −0.7 V. In $[\{Ru(bipy)_2\}_2(dpp)]^{4+}$ the dpp-based reduction occurs at −0.70 V, a value lying in the range expected for the biq-based reductions.[3] Due to the similarity in the reduction potentials of the bridging (dpp) and spectator (biq) ligands in complexes **2** and **3**, the assignment of the low-energy c.t. absorption band observed in the 500–600 nm region is not straightforward. Employing a number of indirect arguments, we proposed that the lowest-energy excited state in these binuclear complexes is also based on the spectator ligand biq. However, an alternative assignment has been invoked[4] for the lowest-energy band in a number of oligonuclear complexes containing the above binuclear units, namely that it corresponds to Ru ⟶ dpp c.t. There is clearly an important issue to be resolved here.

Resonance Raman spectroscopy is a powerful structural technique and can, in principle, provide direct information on this question. Excitation into an allowed Ru ⟶ π* transition of one of the ligands gives rise to enhancement of the symmetrical stretching modes of that ligand. The presence of different electronic transitions underneath one absorption band can be detected and identified by studying the wavelength dependence of the resonance-Raman spectra. There have been a number of studies of the c.t. excited states of mononuclear polypyridyl complexes.[5] Herein we report our results on the examination of the lowest-energy absorption band using resonance Raman spectroscopy. The Raman spectral data provide unambiguous support for our earlier tentative assignments.

Experimental

The mono- and di-nuclear ruthenium complexes **1**, **2** and **3** were synthesised as described previously.[3] Raman spectra were obtained from methylene chloride solutions which were typically 0.1–0.5 mmol dm^{-3} in the metal complex. Spectra were obtained from solutions contained in spinning cells, using krypton-ion laser excitation (Spectra Physics model 171) and a Spex Raman spectrometer. A detailed description of this apparatus has been given earlier.[5c]

Results and Discussion

Identification of the lowest-energy c.t. transition is based on the selective resonance enhancement of the marker Raman bands of the biq or dpp ligands during the excitation of the ruthenium complex within the absorption envelope of the lowest-energy

Table 1 Wavenumbers (cm^{-1}) and relative Raman band intensities* at two excitation wavelengths of complexes **1**–**3** in methylene chloride at ambient temperature

1		**2**		**3**		
530.9 nm	568.2 nm	530.9 nm	568.2 nm	530.9 nm	568.2 nm	Ligand assignment
—	—	1070 (1.1)	1071 (2.1)	—	1078	biq
—	—	1171 (3.8)	1176 (4.5)	1163	1173 (2.0)	biq
1181 (3.2)	1189	—	—	1186 (2.7)	1189 (1.1)	dpp
—	—	—	—	1243 (2.7)	1239 (2.8)	dpp
1252 (4.6)	1254 (4.7)	1250 (4.5)	1253 (12.8)	—	1253	biq
—	1263	1261	1263	1261	1264	biq
—	1304	1306 (2.0)	1307 (2.5)	1314 (5.0)	1314 (1.5)	dpp
1346 (3.5)	1339 (6.2)	1340 (11.9)	1344 (12.1)	1339 (2.7)	1345 (4.5)	biq
1374 (4.3)	1373 (3.6)	1373 (7.3)	1376 (5.6)	1365 (1.6)	1370 (4.9)	biq
—	—	—	—	1395 (2.5)	1399 (2.5)	dpp
1457 (4.0)	1460 (5.3)	1459 (13.1)	1463 (14.2)	1465	1458 (6.7)	biq
—	—	—	1474 (10.0)	1480 (8.8)	1475 (3.1)	dpp
1550 (3.7)	1550 (28)	1548 (5.9)	—	1551 (7.9)	—	dpp
—	—	—	1559 (14.6)	—	1558 (2.4)	biq
1591 (5.2)	1592 (1.4)	1594 (3.0)	1601 (4.2)	—	1598 (1.6)	biq
1605 (5.8)	—	—	—	1600 (6.9)	—	dpp

* Intensities normalized with respect to the intensity of the solvent band at 1422 cm^{-1}, taken as 10.0.

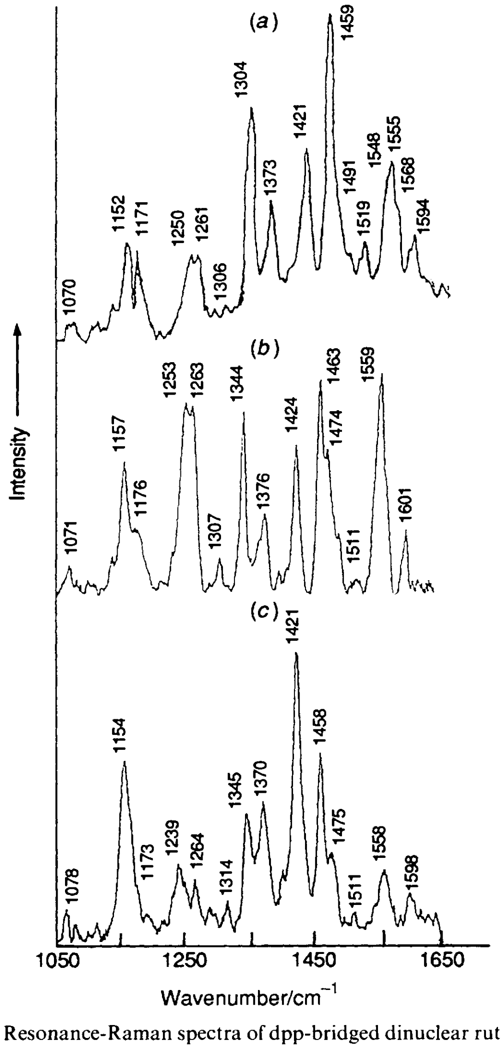

Fig. 1 Resonance-Raman spectra of dpp-bridged dinuclear ruthenium complexes: $[(biq)_2Ru(dpp)Ru(biq)_2]^{4+}$ **2** with excitation at 530.9 nm (*a*), complex **2** with excitation at 568.2 nm (*b*) and $[(bipy)_2Ru(dpp)Ru(biq)_2]^{4+}$ **3** with excitation at 568.2 nm (*c*)

absorption band. In the present case, complexes **1**, **2** and **3** have respective c.t. absorption maxima (in *N,N'*-dimethylformamide) at 526 (ε = 10 400), 538 (21 200) and 548 nm (22 800 dm^3 mol^{-1} cm^{-1}). Raman spectra of the three complexes were recorded in methylene chloride solutions at room temperature for two excitation wavelengths [530.9 nm (in the region of the absorption maxima) and 568.2 nm (in low-energy tail region)]. The Raman bands of the solvent appear at 1155, 1265, 1422 and 1464 cm^{-1}. Table 1 presents the various Raman bands observed together with their relative intensities (normalized to the intense solvent band at 1422 cm^{-1}, taken as 10.0) and assignments. There have been some Raman spectral studies on the mono- and di-nuclear complexes of dpp, $[\{Ru(bipy)_2\}_n(dpp)]^{2n+}$ (n = 1 or 2),[6] and on the homo tris-chelate complex $[Ru(biq)_3]^{2+}$.[7] In the binuclear complexes Raman bands due to dpp have been reported[6b] at 1248, 1314, 1401, 1473 and 1600 cm^{-1}. In polypyridyl complexes incorporating biq, 2-pyridylquinoxaline or 2,3-bis(2-pyridyl)quinoxaline (dpq), the dominant Raman bands are due to the quinoline/quinoxaline part of the ligand and they appear at *ca.* 1257, 1333, 1371, 1461 and 1560 cm^{-1}.

Fig. 1 presents the resonance Raman spectra of complex **2** upon excitation at 530.9 and 568.2 nm and of complex **3** upon excitation at 568.9 nm. Taking the marker Raman bands of dpp and biq as the reference, it can be noted that spectra for **2** and **3** with excitation near the c.t. absorption have moderately intense bands from both the spectator and bridging ligands. However, shifting the excitation line into the lower-energy tail (568 nm for example) leads to substantial weakening of the marker bands of dpp with concomitant increase in intensity of the biq bands. Based on the present study the following Raman bands can be labelled as marker bands of biq: 1559, 1458, 1376, 1345 and 1171 cm^{-1}.

The relative intensities of the various Raman bands of complexes **2** and **3** and their dependence on the excitation wavelength suggest that in the region of the visible light absorption maximum (530 ± 20 nm) there are substantial contributions by both the Ru ⟶ biq and Ru ⟶ dpp c.t. transitions but the former is at a lower energy than the latter. The Raman data are also in agreement with the trends expected for variations in the nature of the spectator ligands. The Raman spectrum of **2** obtained at 568 nm consists essentially of resonance-enhanced biq bands. The replacement of the spectator ligands biq on one of the two ruthenium centres of complex **2** by the better electron-donor ligand bipy (complex **3**) leads to a red-shift of the c.t. band of nearly 10 nm. For this reason the spectrum of **3** upon excitation at 530 nm (not shown) is dominated by marker bands of dpp; however, these bands become weak (but still distinct) upon excitation at 568 nm (*e.g.* the bands at 1189, 1239, 1314 and 1399 cm^{-1}).

In all the dinuclear complexes $[\{Ru(bipy)_2\}_2(L^b)]^{4+}$ (L^b = dpp,[6a,b] dpq[6b] or benzo[1,2-*b*:3,4-*b*′:5,6-*b*″] tripyrazine[6c] examined previously, the electrochemical data were quite unambiguous in indicating the assignment of the lowest-energy transitions to Ru ⟶ L^b c.t. The resonance Raman results merely confirmed the deductions based on redox potentials. For complexes **2** and **3** the electrochemical data were not unambiguous however, but the Raman spectral data provide clear evidence for assignment of the lowest-energy absorption (hence the excited state) to Ru ⟶ biq c.t.

Unambiguous assignments of the low-energy electronic transitions in polynuclear complexes are by no means trivial and the present studies show how resonance Raman spectroscopy can be used to advantage. The results presented here have important implications in the working of light-harvesting devices based on these units. The efficient unidirectional flow of energy requires the presence of a graded series of excited states in a supramolecular assembly, and this study shows that by appropriate changes in the nature of the spectator ligands (*e.g.* from bipy to biq) it is possible to achieve such a series of chromophores.

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Received 29*th May* 1992; *Paper* 2/02825E