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COMMUNICATION

Gas-phase spectroscopy of singly reduced tris(bipyridine)ruthenium ions, Ru(bipy)$_3^+$

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Light absorption in the visible region by isolated Ru(bipy)$_3^+$ (bipy = 2,2′-bipyridine) monocations, prepared *in vacuo* by reduction of dications in collisional electron transfer from cesium atoms, was recorded using photodissociation mass spectroscopy and found to be broad and similar to that of acetonitrile-solvated ions (maximum at 520 nm).

Tris(bipyridine)ruthenium(II) is a prototype ruthenium complex whose distinct photophysics and photochemistry have been extensively studied for several decades.[1-4] This dication and its derivatives are strong light absorbers in the visible region via metal-to-ligand charge transfer (MLCT) transitions, making them strongly coloured. They have interesting luminescence properties as well and can undergo reversible redox processes in both the ground and excited states. These unique properties make the complexes relevant target systems for artificial light harvesting, water oxidation/CO$_2$ reduction catalysis and for supramolecular photochemistry.[1,4-11]

In this work, our focus is on the charge-reduced ion, Ru(bipy)$_3^+$ (Figure 1), whose absorption spectrum has previously been obtained from spectroelectrochemistry experiments.[12,13] While there has been much debate whether the MLCT transition of the dication involves only one bipyridine ligand (localised orbital, *i.e.*, dipolar excited state) or all three ligands (delocalised orbital, *i.e.*, no dipole moment), there is little doubt that upon reduction of the dication, the electron is attached to a single ligand keeping the low-spin 4d^6 configuration of the complex.[1,2,13] The negatively charged ligand interacts favourably with nearby polar solvent molecules (Figure 2). Hence a more descriptive formulation of the singly charged complex is [Ru(II)(bipy)$_2$(bipy$^-$)]$^+$. Earlier work has shown that the isolated dication *in vacuo*

absorbs maximally at 430 nm[14] whereas solvation by acetonitrile results in a redshift to 452 nm, in accordance with the localised orbital picture. The MLCT absorption by the acetonitrile- or dimethylsulfoxide (DMSO)- solvated monocation is further to the red,[12,13] which is easy to explain based on simple electrostatics as the photoactive electron in the singly charged ion moves away from the negative charge. The bipyridyl radical anion also accounts for the appearance of new bands in the visible region due to internal $\pi\pi^*$ transitions[12,13,15,16] (the MLCT band is actually a high-energy shoulder to these bands[12]). Indeed, the Li$^+$[bipy]$^-$ salt dissolved in diethyl ether shows a vibronic progression with the first three bands at 544 nm, 514 nm, and 484 nm; the average separation is 1140 cm^{-1}, corresponding to coupling to an interring stretching mode.[16] In the case of Ru(bipy)$_3^+$, the first two bands occur at 520 nm and 493 nm in acetonitrile (separation of 1050 cm^{-1})[13] and at 529 nm and 503 nm in DMSO (separation of 1000 cm^{-1})[12], that is, the bands are further to the red for the slightly more polar DMSO, and for both solvated complexes the absorption is blueshifted compared to that of the bipyridinium anion itself. These shifts are nontrivial to understand; both acetonitrile and DMSO are polar solvents and will influence both the ground and excited states in nonobvious ways. In addition to these solvent effects, the ruthenium 2+ center has an effect even though the transition is localised on the bipyridyl anion. A reduction in complexity is needed to disentangle different effects on the electronic absorption by Ru(bipy)$_3^+$.
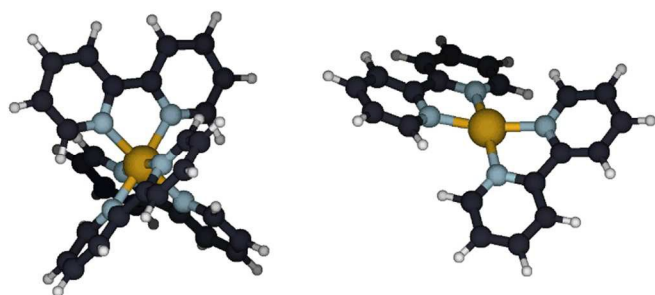
Figure 1. Structures of Ru(bipy)$_3^+$ (Left) and the Ru(bipy)$_2^+$ photofragment (Right), calculated using density functional theory (B3LYP functional, def2-TZVP basis sets for all atoms). The parent ion belongs to the D$_3$ point group. We note that the two bipy ligands are no longer planar in Ru(bipy)$_2^+$; the two rings are twisted by ca. 15 degrees about the central CC bond and tilted by ca. 8 degrees. Yellow: Ruthenium; Black: Carbon; White: Hydrogen; Blue: Nitrogen.
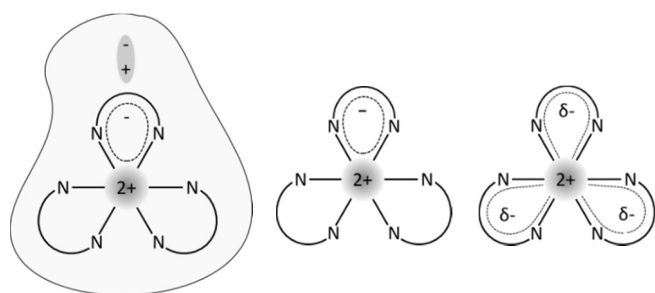

Figure 2. Ru(bipy)$_3^+$ in a polar solvent (Left). *In vacuo*, the negative charge is either localised on one bipy (Center) or delocalised over all three (Right); there is no favourable interaction with a solvent dipole to facilitate the symmetry breaking. Here our focus is on the ππ* transitions involving negatively charged bipy(s).

As a simpler starting point, we decided to establish the intrinsic absorption by Ru(bipy)$_3^+$, free of solvent perturbations. It is in general difficult to measure the intrinsic absorption spectra of ions from solution-phase spectroscopy; one obvious problem is low solubility in nonpolar solvents but another is the effect from nearby counter ions. It is a valid question whether spectroscopy in solution really is done on individually solvated ions and not solvated ion-pairs. A resolution of these questions is gas-phase spectroscopy as here isolated ions *in vacuo* are present with no nearby solvent molecules or counter ions. These experiments are, however, difficult due to low ion-beam densities, preventing traditional absorbance measurements based on Lambert-Beer's law. Instead, absorption is monitored indirectly from ionic dissociation in the case of cations using specialised mass spectrometry setups. This is the approach taken here.

Gas-phase experiments were carried out using a home-built mass spectrometer that has been described in detail elsewhere.[17,18] Ru(bipy)$_3^{2+}$ dications were produced by electrospraying an

acetonitrile solution of the perchlorate salt. All ions were accumulated in an octopole ion trap for 25 ms before being accelerated to energies of $q{\times}50$ keV, where q denotes the charge state. The ions of interest (*i.e.*, Ru(bipy)$_3^{2+}$) were then selected by an electromagnet according to their mass-to-charge ratio. Monocations were produced by collisional electron transfer in a cell from cesium atoms to the fast-moving dications; this process occurs with a high cross section as demonstrated earlier.[19] Next the ions were irradiated with visible light from a pulsed laser. A 20-Hz Nd:YAG laser produces 1064-nm infrared light that is frequency tripled to 355-nm ultraviolet light. This light is sent into an optical parametric oscillator (OPO) to generate visible light and an idler beam. The laser pulse width is a few nanoseconds. The OPO was scanned from 420 nm to 640 nm. Notice that there is no mass selection before the irradiation so non-reduced Ru(bipy)$_3^{2+}$ dications were also present in the ion bunch. The product ions were separated in kinetic energy by a hemispherical electrostatic analyser and counted by a channeltron detector. Only every second ion bunch was irradiated by the laser pulse to obtain the true photodissociation signal as the difference between "laser on" and "laser off" signals. These signals were divided by the "laser off" signal in the case of absorption spectroscopy measurements to correct for ion-beam intensity fluctuations. The experiment was repeated nine times and on different days, and an average was taken of all the data.

Photoexcitation led to depletion of the Ru(bipy)$_3^+$ monocations and concomitant production of Ru(bipy)$_2^+$ fragment ions (simple loss of bipy) (Figure 3). No other channels of importance were identified. A power dependence analysis at 520 nm reveals that dissociation is mainly the result of one-photon absorption and a minor contribution is from two-photon absorption. A power law fit to the ion yield *versus* laser power gave an exponent of 1.2 (see ESI). We calculated the energy needed to lose bipy from the complex based on density functional theory (B3LYP[20,21] and PBE0[22] functionals, def2-TZVP basis sets[23] for all atoms as implemented in the TURBOMOLE suite of programs[24]) and obtain dissociation energies of 2 eV (B3LYP) and 2.4 eV (PBE0). For comparison, experimental bond dissociation energies for other M(bipy)$_2^+$ complexes have been reported by Rodgers and co-workers to be 2.33 eV (M = Zn), 2.46 eV (M = Cu), and 2.81 eV (M = Ni); hence there is a weak dependence on the metal ion center.[25-27] The obtained geometries of Ru(bipy)$_3^+$ and Ru(bipy)$_2^+$ are shown in Figure 1, both verified to be stationary points and not transition states from calculations of vibrational frequencies determined using def2-SV(P) basis sets[23] (no imaginary frequencies). As our photon energies range from 2.95 eV to 1.94 eV, the ions have likely acquired some vibrational excitation energy during the collisional electron transfer process to account for dominant one-photon dissociation.
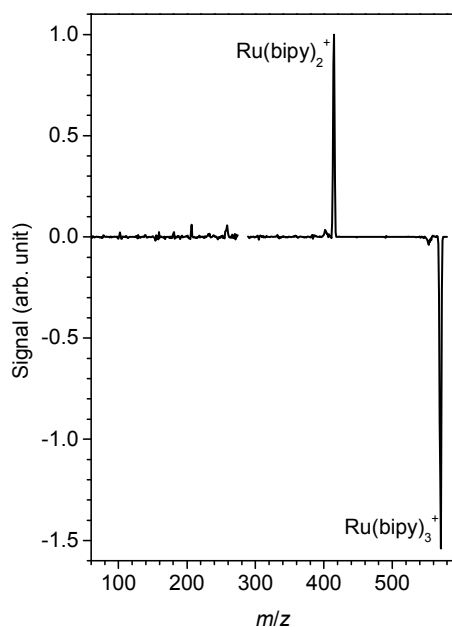
Figure 3. Photoinduced dissociation mass spectrum of $Ru(bipy)_3^+$ (525 nm). The signal of $Ru(bipy)_3^+$ is negative due to the dissociation into $Ru(bipy)_2^+$ and bipy after photon absorption. The region from m/z 275 to 288 was not recorded because of saturation of the detector from the intense beam of $Ru(bipy)_3^{2+}$ (m/z 285).

To obtain action spectra the signals for depletion of $Ru(bipy)_3^+$ and for formation of $Ru(bipy)_2^+$ were divided by the number of photons at each wavelength raised to the power of 1.2. It is evident from Figure 4 that these spectra are roughly mirror images of each other as expected when photodissociation only leads to one fragment ion (Figure 3). In other words, the depletion of $Ru(bipy)_3^+$ is accompanied by the formation of $Ru(bipy)_2^+$, and both ions therefore report on the absorption by $Ru(bipy)_3^+$ (Figure 4). Hence both action spectra are taken to represent the absorption by $Ru(bipy)_3^+$.

The $Ru(bipy)_3^+$ depletion signal is unaffected by the presence of the dications in the beam, as the $Ru(bipy)_3^+$ ion can only be produced by collisional electron transfer, and photoexcitation is first done after charge reduction. Photodissociation of residual $Ru(bipy)_3^{2+}$ dications in the ion bunch could potentially affect the signal of $Ru(bipy)_2^+$ fragment ions. However, the dominant fragment ion after photoexcitation of $Ru(bipy)_3^{2+}$ is $Ru(bipy)_2^{2+}$; at 430-nm photoexcitation, the ratio between $Ru(bipy)_2^+$ and $Ru(bipy)_2^{2+}$ is about 2 % (see ESI). The contribution of dication photodissociation to the $Ru(bipy)_2^+$ fragment peak in Figure 3 will therefore be negligible. Furthermore, at least two photons are needed for dissociation on the instrumental time scale, which implies – not surprisingly – that $Ru(bipy)_3^{2+}$ is a more strongly bound complex than $Ru(bipy)_3^+$. Finally, the fragmentation cross section of $Ru(bipy)_3^{2+}$ peaks between 430 nm and 440 nm, well below the region where $Ru(bipy)_3^+$ displays maximum absorption (see ESI).
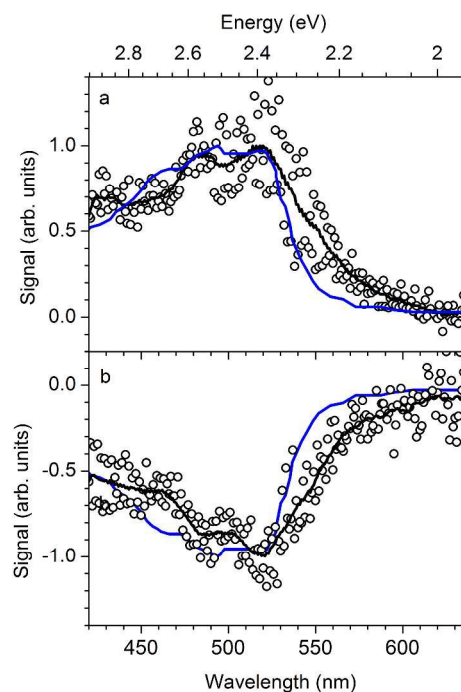

Figure 4. (a) Photo-yield of $Ru(bipy)_2^+$ fragment ions and (b) depletion signal of $Ru(bipy)_3^+$ as a function of excitation wavelength. The black curves are 20-point sliding averages. The solid blue curve is the absorption spectrum in acetonitrile solution (inverted in panel b), taken from reference 13. All spectra are normalised.

The monocations display broad absorption from 420 nm and up to about 620 nm. The spectrum is clearly redshifted compared to that of $Ru(bipy)_3^{2+}$ (maximum at 430 nm). We cannot establish the position of the MLCT band from the spectrum, since there is overlap with the $\pi\pi^*$ transitions, but as the Coulomb repulsion between the two electrons on the bipy ligands after a MLCT transition is less than that in the ground state between an electron on ruthenium and the one on the ligand(s), a redshift is expected. The spectrum reveals two bands with maxima at 520 nm and 485 nm (uncertainty of ±5nm or ±0.03 eV) that we assign to $\pi\pi^*$ transitions, the latter likely being a vibronically allowed transition (*vide supra*). The energy spacing is about 1388 cm^{-1} which is higher than that for the solvated complex ions and the solvated bipyridinium anion (about 1000-1100 cm^{-1}). This difference may reflect a delocalisation of the excess electron over all three ligands in the gas-phase complex (Figure 2, Right) and that the transition involves all three. Our density functional theory calculations together with natural population analysis show that the charge density on the three bipy ligands is the same, consistent with this idea.

In the figure, the absorption spectrum of $Ru(bipy)_3^+$ in acetonitrile solution is included. The gas-phase and the solution-phase spectra are surprisingly similar. The tail to higher wavelengths is a bit more pronounced for the gas-phase spectrum, which may be due to hot band absorption by vibrationally excited ions.

It should be noted that the photon energies are close to the calculated dissociation energy of the complex at long wavelengths. However, the internal energy prior to photoexcitation is 0.8 eV (assuming room temperature), which brings the internal energy after photoabsorption at 520 nm up to 3.2 eV, that is, the excess energy is more than 1 eV. If this is not enough to cause dissociation with near unit probability within the time window for sampling dissociation (1 μs), a potential kinetic shift would skew our spectrum towards the blue. Hence if solvation causes any shift, it would be a minor blueshift.

Still, the almost identical band origin in the gas-phase and in acetonitrile shows that the interaction energy between [bipy]$^-$ and the solvent in the ground state is similar to that in the excited state, which implies minimal changes in the charge density distribution after photoexcitation. The redshift to 529 nm observed for the slightly more polar DMSO on the other hand indicates a small movement of negative charge density towards the oriented solvent dipoles. The even higher redshift for [bipy]$^-$ in apolar diethyl ether to 544 nm can be accounted for by a nearby lithium ion (*i.e.*, ion-pair formation) as the negative charge density will move towards the cation upon photoexcitation, owing in general to a larger polarisability of an excited state than of the ground state. When [bipy]$^-$ is formed electrochemically in THF, TBAPF$_6$ (THF = tetrahydrofuran, TBA = tetrabutylammonium), the absorption maximum is at an even higher wavelength (585 nm).[28] Clearly, a gas-phase absorption spectrum of the bipyridinium anion would be highly useful to pinpoint exactly the effect of a microenvironment in this case.

Conclusions

We have recorded action spectra of Ru(bipy)$_3$$^+$, isolated *in vacuo*, and found that the gaseous monocations absorb much further to the red than the dications do, which is mainly ascribed to the promotion of an electron from a π orbital to a π* orbital centred on the bipyridine(s). Importantly, the absorption by isolated Ru(bipy)$_3$$^+$ is very similar to that by ions solvated by acetonitrile molecules. In both cases the absorption band maximum is at about 520 nm. In this work, we provide a reference spectrum of the bare ion that can be used to benchmark future theoretical descriptions of this complex ion.

Acknowledgements

Notes and references

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