Chimia 43 (1989) 385–387
© Schweizerischer Chemiker-Verband; ISSN 0009–4293

Luminescence of Tris(2,2′-bipyridine)ruthenium(II) Incorporated at Moderate Temperature in Sol-Gel Glasses and Various Low-Melting Glasses**

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Abstract: The luminescent and higher excited states of $[Ru(bpy)_3]^{2\oplus}$ are critically discussed, and compared with new measurements in sol-gel glasses, a lead tin fluorophosphate glass (made at 280 °C), boric acid (230 °C), and polyvinylalcohol film (90 °C). The effects that decrease the luminescence yield to below 0.2 at 25 °C are considered.

Around 1930 (that is well before any extended rationalization of transitions within a partly filled d shell as grew up[1,2] after 1952) a great number of strong absorption bands were described[2-4] as *electron transfer bands* where one (or several) reducing ligands (collectively) lose an electron to an empty (say chromium(VI), manganese(VII), molybdenum(VI)...] or partly filled d shell. The wave-number of the first strong electron transfer band increases in the series iodide, bromide, chloride, and fluoride (bound to a definite central atom in a given oxidation state) as a linear function of the Pauling halogen electronegativity with the slope 30 000 cm^{-1} (3.7 eV) per unit.

Williams[5] pointed out in 1955 that conjugated, but colourless, organic ligands (such as 2,2′-bipyridine, 1,10-phenanthroline, and even pyridine[6]) may form strongly coloured complexes of fairly reducing central atoms having a partly filled [e.g. iron(II)] or full [copper(I)] d shell, and showing *inverted electron transfer* bands, one d-like electron jumping to an empty, delocalized orbital of the (usually heterocyclic) conjugated system. It is common to speak[7] about MLCT (metal to ligand charge transfer) excited states (the transfer from reducing ligands to M being LMCT in a desire for a symmetric notation). For whatever reason, the inverted electron transfer bands (i.e. MLCT) are only known for organic ligands (including cyanide) and are far closer related to the conventional organic colorants[8] than to the familiar orange to red or brown colours of most iron(III) compounds, here excepting practically colourless $[FeF_6]^{3\ominus}$ and very pale violet $[Fe(OH_2)_6]^{3\oplus}$. Some conjugated ligands, such as acetylacetonate[9] show both normal and inverted electron transfer bands, varying as one would expect with the oxidizing or the reducing character of M.

In this communication, we concentrate attention on the tomato-red, diamagnetic

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** *Acknowledgements:* The grant no. 2.5377.87 (previously 2.629–0.87) from the Swiss National Science Foundation made the collaboration possible between the universities in Jerusalem and Genève. The work in Israel was supported by the Volkswagen Foundation.

$4d^6$ ruthenium(II) complex of 2,2′-bipyridine (previously[6] also called 2,2′-dipyridyl; the abbreviations of this ligand bpy, bipy, dipy, and dip occur in literature). There is no doubt that the intense band observed very close to $\lambda = 452$ nm (molar extinction coefficient $\varepsilon = 14300$) in 28 different solvents[10] is due to a singlet MLCT state. However, the band does not vanish in any clear-cut way toward lower energy and allows one to suspect shoulders in the region 500 to 600 nm. One explanation might be internal $4d^6$ transitions well known from the isoelectronic rhodium(III) complexes[1,11]. The two weak bands ($\varepsilon = 11.5$ and 13.5) at 535 and 393 nm of $[Ru(OH_2)_6]^{2\oplus}$ indicate[12] the sub-shell energy difference $\Delta = 20050$ cm^{-1} when identified as transitions to $^1T_1$ and to $^1T_2$. A comparison with the nickel(II) aqua and bpy complexes[1,2] suggests Δ close to 26700 cm^{-1} in $[Ru(bpy)_3]^{2\oplus}$, providing $^1T_1$ not far from 400 nm. The regularities[1,13] in the distance from $^1T_1$ to the lowest $4d^6$ triplet $^3T_1$ should put it so close to the intense MLCT maximum at 452 nm as to be undetectable, and with certainty below 500 nm.

For our purpose, it is important that *Paris* and *Brandt*[14] detected a narrow emission band at $\nu = 17000$ cm^{-1} from a frozen 10^{-4} M solution of $[Ru(bpy)_3]^{2\oplus}$ kept at 77 K, ascribing it to the lowest MLCT state. It turned out[15] that the quantum yield is as high as $\eta = 0.4$ in ethanol-methanol glass (77 K) combined with a life-time of 5.2 microseconds (µs). The concomitant radiative life-time 14 µs corresponds to an oscillator strength P close to $4 \cdot 10^{-4}$ (some 0.3 percent of P observed for the 22100 cm^{-1} spin-allowed absorption). It is generally agreed[10] that the luminescent state is the lowest (essentially) triplet MLCT state. In aqueous solution, η decreases from 0.05 at 5°C to 0.01 at 82°C, and full deuteriation (eight D per bpy ligand) only increases the yield slightly[16], at most by a factor 2. It was pointed out that $^2T_2$ of $4d^5$ combined with the two e and one a_2 orbital (point-group D_3) among the lowest unoccupied MO of bpy ligands provide altogether 36 states, of which three out of four, 27, have essentially triplet character. The energies corresponding to these 36 wave-functions were calculated[17] to be situated between 18300 and 23300 cm^{-1} with a plausible choice of parameters. This is compatible with the three[18] distinct MLCT levels (A_1 lowest, E 8 cm^{-1} higher, and A_2 56 cm^{-1} above A_1) with the parametric life-times 208, 35, and 1 µs derived from the observed variation of the life-time with temperature (below 50 K). It is unexpected how little the replacement of one or two 2,2′-bipyridine ligands with substituted, similar heterocyclic ligands modify these life-time parameters[18]. It may also be noted that $[Ru(phen)_3]^{2\oplus}$ containing the much more rigidly planar ligand 1,10-phenanthroline has a slightly *smaller* quantum yield in aqueous solution[10].

Besides more common processes of non-radiative relaxation, the Ru^{II} complexes in many cases undergo various photochemical reactions. In principle, four molecules retaining an optical excitation energy even as low as 2.1 eV (the lowest triplet MLCT state of $[Ru(bpy)_3]^{2\oplus}$ would be able to split water[19] into 2 $H_2 + O_2$, and the standard oxidation potential $E^0 = +1.26$ V of the ground state is decreased (by the triplet excitation energy) to -0.80 V in the fluorescent state. By the same token, $E^0 = -1.3$ V of $[Ru(bpy)_3]^{\oplus}$ (known as a deep purple transient by flash illumination) *increases* by the same amount, to +0.8 V, meaning that the excited $[Ru(bpy)_3]^{2\oplus}$ is not only quite reducing (and would evolve H_2 if it had time) but at the *same moment also* oxidizing to a stronger extent that $[Fe(CN)_6]^{3\ominus}$.

It is well known that excited J-levels of $4f^q$ in glasses[20] and both $^4T_2$ and ^2E of $3d^3$ chromium(III) in glass-ceramics[21] show much higher propensity to luminescence than aqueous or other solutions of low viscosity. One way of circumventing this problem for organic compounds (or d-group metal complexes of organic ligands) is to soak solutions into porous glasses, separating each lumophore in a small, confining volume[22] or to synthesize sol-gel glasses[23–25] by hydrolysis of mixed alkoxides of boron, aluminium, silicon,... by quite moderate heating, originally having the luminescent compounds dissolved in the starting (usually methanolic) solution. A new laser[26] is a composite glass of polymethylmethacrylate containing a highly fluorescent molecule, dispersed in a silica sol-gel glass.

$[Ru(bpy)_3]^{2\oplus}$ does not show the dramatic decrease of fluorescence yield with mildly increasing temperature[16] so characteristic[21] for $^4T_2$ broad-band emission of Cr^{III}. Nevertheless, it is an obvious advantage to get η above 0.04 at 20°C. In 1983, the porous Vycor glass was studied[27,28] having the cation $[Ru(bpy)_3]^{2\oplus}$ bound to anionic silanol sites, without co-adsorbing the counter-ion (here $Cl^{\ominus}$). At 23°C, the life-time of «dry» (almost dehydrated) samples of $\lambda = 610$ nm emission is 0.74 µs, and when saturated with N_2-deaerated distilled water, 0.50 µs, values obtained for aqueous solutions too[10]. The main result of this study[28] was the quenching of fluorescence by low concentrations of quinones such as *p*-benzoquinone and 1,4-naphthoquinone. Since these molecules have their lowest triplet state above 19000 cm^{-1}, the quenching cannot be due to energy transfer from the MLCT triplet 2000 cm^{-1} below, but is rather due to electron transfer to the quinone and formation of $[Ru(bpy)_3]^{3\oplus}$.

Another photochemical deactivation of excited $[Ru(bpy)_3]^{2\oplus}$ was found in 1973, oxygen[29,30] being excited from its triplet ground state to the first singlet of O_2. This is a recognized problem for the triplet state of Bengal Rose and other luminescent colorants[31]. The superoxide anion $O_2^{\ominus}$ does not seem to form. Energy transfer from excited $[Ru(bpy)_3]^{2\oplus}$ is also known[10] to $^4A_2$ of $[Cr(CN)_6]^{3\ominus}$ forming ^2E at 12400 cm^{-1} higher energy.

Sol-gel glasses were made from a starting solution of 4.7 mL CH_3OH, 3.7 mL $Si(OCH_3)_4$, and 1.8 mL water (like in a previous study[32] of incorporated pyrene) being $7 \cdot 10^{-4}$ molar of $[Ru(bpy)_3]^{2\oplus}$, to which 0.1 mL strong hydrochloric acid was added as catalyst for the hydrolysis and silicate polycondensation. The gelation proceeded at room temperature; glass plates were covered with 1 mm thickness of gel and kept for two weeks. The fluorescent life-time is 1.34 µs (indicating a quantum yield close to 0.1 if the radiative life-time[10] remains unchanged). Thin sol-gel films[33] containing organic lumophores can show high yields of luminescence.

A 12 weight percent polyvinylalcohol (BDH) in water, containing 10^{-3} M

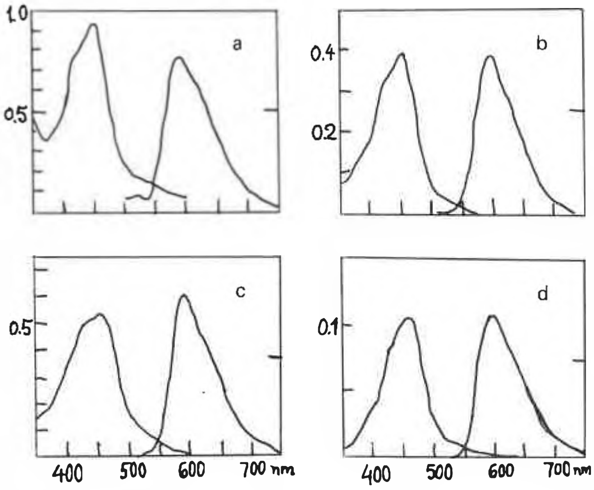

Fig. 1. Absorption and luminescence spectra of $[Ru(bpy)_3]^{2\oplus}$ *(***1***) at room temperature. The optical density* $lg_{10}(I_0/I)$ *is plotted on the left, and the normalized luminescence on the right. The samples (see the text) are* **1** *dissolved in (a) sol-gel glass; (b) polyvinylalcohol glass; (c) boric acid, after having being molten at 230°C; (d) tin(II) lead(II) fluorophosphate glass, having been molten at 400°C, cooled to 280°C, and* **1** *added.*

$[Ru(bpy)_3]^{2\oplus}$ was heated to 90°C and allowed to wet a microscope slide, which was subsequently cooled for 24 h. This system (which may have problems of photochemical degradation over a long time-scale) shows $\tau = 1.74$ µs. Even slightly longer life-times are observed in a tin lead fluorophosphate glass molten at 400°C, having the initial molar ratios 52.2 SnF_2:10.5 SnO:5.1 PbF_2:32.2 $PO_{2.5}$ [derived from $NH_4^{\oplus}$ $(HO)_2PO_2^{\ominus}$], cooled to 280°C, and then made 10^{-5} molar $[Ru(bpy)_3]^{2\oplus}$ chloride, showing $\tau = 1.98$ µs; 10^{-3} molar, $\tau = 1.89$ µs; and 0.003 molar, $\tau = 1.74$ µs, showing very little concentration quenching. The complex dication can hence be heated some minutes to 280°C without significant decomposition. This is, of course, less than the most heat-resistant organic compounds, such as the dark blue pigment copper(II) phthalocyanine, but still unexpected.

Boric acid (Merck) mixed with $[Ru(bpy)_3]^{2\oplus}$ to make final concentrations in differing samples 10^{-6} to 10^{-3} M was molten at 230°C and allowed to cool in a glass test-tube. The viscous liquid can be poured on a microscope slide, and pressed with another, preheated, slide. At 25°C, $\tau = 2.00$ µs.

Contrary to non-radiative relaxation of many excited states of 4f- and d-group compounds, the presence of OH groups does not seem to be a main obstacle for luminescence (which is brilliant[15,18] at 77 K). It may be added that the quite high C-C and C-N vibrational frequencies cannot be avoided in the large heterocyclic ligands. Still, one gets the impression that much of the non-radiative rate may be due to mild (perhaps self-repairing) photochemistry. Conceptually, the quenching by oxygen[29] is intermediate between photochemistry and energy transfer, and it may be prevented in the tin lead fluorophosphate glass by the reducing Sn^{II}. We are now studying controlled argon or nitrogen atmospheres to find out whether O_2 intruding into sol-gel glass may decrease τ significantly.

The excellent review[7] by *Thomas J. Meyer* «Chemical Approaches to Artificial Photosynthesis» considers $[Ru(bpy)_3]^{2\oplus}$ and related complexes as (more or less remote) inorganic analogs to chlorophyll. In both cases, it may be easier to obtain photochemistry than luminescence. Another problem[16] may be the multi-dimensional $^3T_1$ potential surfaces of $4d^6$, distorting strongly[21] from the octahedral symmetry of the $^1A_1$ ground state, and contributing a rapid de-excitation of the triplet MLCT state at some 4000 cm^{-1} lower energy (by vertical projection up from the $^1A_1$ potential surface) via thermal equilibration at room temperature.

At the scale of resolution (and $T > 270$ K) used here, it is not too relevant what the time-scale is of change of localization of the promoted electron on *one* ligand (it should be remembered that both $(bpy)^{\ominus}$ and $M(bpy)_3$ with uncertain oxidation state[2] play a definite role in 2,2′-bipyridine chemistry) to a delocalized MO situation[10,34,35]. This dilemma has been probed with Raman spectra[36,37]. The related problem of the three first MLCT states[18] within 60 cm^{-1} has no real impact above 200 K[7,10] but fortunately, $[Ru(bpy)_3]^{2\oplus}$ can be diluted in the isotypic zinc salts $[Zn(bpy)_3]X_2$ for each choice of X being[38] $PF_6^{\ominus}$, $BF_4^{\ominus}$, and $ClO_4^{\ominus}$. The time-resolved luminescence and the magnetic circularly polarized luminescence has been measured in the transition range between a rigid glass and a fluid[39] and various techniques of magnetic circular dichroism have been applied[40] to $[Ru(bpy)_3]^{2\oplus}$ diluted in zinc salts, and[41] to the sharp zero-phonon lines at $\lambda = 561.4$ and 561.7 nm in the undiluted hexafluorophosphate. The Zeeman effect[42] of these two lines has been measured in luminescence and in absorption, and picosecond resonance Raman lines[43] investigated in view of the «one ligand $bpy^{\ominus}$ hypothesis». The detailed structure of the visible absorption spectrum of $[Ru(bpy)_3](PF_6)_2$ between the (non-luminescent) origin at 18770 cm^{-1} up to 28000 cm^{-1} is rationalized[44] by distorted bond lengths and angles in the excited ligand. *Ghosh* and *Chakravorty*[45] recently reviewed the redox properties and spectral band positions of a large number of ruthenium complexes of conjugated ligands.

Much of the argumentation[46] derived from high-resolution spectra at cryogenic conditions is based on energy differences from 10 to below 1 cm^{-1}. This may very well involve hyperfine effects from the ^{99}Ru and ^{101}Ru nuclei, isotope shifts enhanced by vibrational energy differences[47,48] and in a more general sense, perceptible deviations from the approximation of Born-Oppenheimer factorization of the wave-functions. Two further reviews[49,50] appeared late this month.

Received: October 2, 1989 [FC 182]

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