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Evidence for Energy Transfer in the Luminescence of $Ru(bpy)_3(PF_6)_2$ Single Crystals

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Abstract

A number of recent papers have reported the luminescence of $Ru(bpy)_3^{2+}$ of both single crystal and powdered 'neat' salts. We report a polarized luminescence study of single crystals of the PF_6 salt, 'pure' and doped with a small (<1%) amount of $Os(bpy)_3^{2+}$. Evidence is presented for a temperature dependent energy transfer process. Conclusions made from the interpretation of recent data on these concentrated salts as due to intrinsic $Ru(bpy)_3^{2+}$ luminescence may be incorrect.

Introduction

Krol and Blasse [1] initially, and more recently Yersin, Gallhuber and a number of co-workers have presented a number of related studies [2–8] on the luminescence of $Ru(bpy)_3X_2 \cdot nH_2O$ materials with $X = PF_6$, ClO_4, Cl, Br, I etc. These luminescence spectra show, in some instances, remarkable polarization and temperature behaviour. Spectra are occasionally considerably more structured than the luminescence of the same chromophore ($Ru(bpy)_3^{2+}$) observed in dilute environments. It was claimed by Yersin *et al.* [8] that the large separation between chromophores (≈10 Å) led to intrinsic luminescence (see the appendix for a discussion of this point). The differences between luminescence profiles in different salts were attributed to counter-ion and second coordination sphere influences.

We report here a number of observations, made some years ago [9], that led us to concentrate on the luminescence properties of the $Ru(bpy)_3^{2+}$ chromophore in dilute environments only. The spectroscopy, in the PF_6 salt at least, seems dominated by temperature dependent and sample dependent energy transfer processes. Luminescence from a range of excitation trapping sites was indicated. The possibility of energy transfer was verified by doping the PF_6 salt with $Os(bpy)_3^{2+}$, the latter having a very characteristic luminescence at lower energy compared to the $Ru(bpy)_3^{2+}$ host luminophore. The recent observation of Yersin *et al.* [6] of a rise-time associated with luminescence of $Ru(bpy)_3(PF_6)_2$ is in itself suggestive of energy transfer process, though the authors prefer to interpret this data in terms of isolated luminophore properties. The original work of Krol and Blasse [1] on the ClO_4 salt noted the presence of energy transfer in their studies.

A great deal of effort has been put into the study of the luminescence of $Ru(bpy)_3^{2+}$ in dilute systems (~10^{-4} M), both as solid solutions [11–13] and doped in single crystals [11, 13]. Spectra in these environments have quite characteristic profiles and polarization behaviours, but do not show the intimate structure and some of the anomalous polarization behaviour reported for the 'neat' materials. We feel it is important to note that environmental studies on dilute glasses show weaker dependence on the solvent or counterion [12]. This seems inconsistent with the interpretation of the luminescence spectra of the powdered salts [4] in terms of effects not seen (of similar magnitude) in solid solution studies.

Experimental

$Ru(bpy)_3Cl_2$ was prepared by the method of Broomhead and Young [10] and twice recrystallized from water. The PF_6 salt was then prepared by metathesis with $NaPF_6$. Crystals were grown by slow evaporation from acetone and at a later stage from a mixture of acetonitrile and ethanol. Prismatic crystals up to 10 mm × 2 mm × 2 mm could be grown, but much smaller crystals were used for most luminescence studies and these were scrutinized under a polarizing microscope. Only cosmetically perfect crystals with good extinction behaviour were used for spectroscopic measurements. Doped crystals were grown from analogous solutions with ≈1% of the starting material being replaced with the corresponding osmium salt.

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Absorption spectra were measured either on a Cary 17 fitted with a cryogenic flow tube or measured photographically with a high resolution prism spectrograph with the sample immersed in (pumped) liquid helium in a quartz dewar. Polarized luminescence measurements were made using a Spex mini-mate fitted with a 1μ blaze grating and a Hamamatsu HTV-R374 photomultiplier. A photoelastic modulator (Morvue) was used to determine to polarization of the detected light. Excitation was with an Xe arc lamp mini-mate assembly fitted with a 300 nm blaze grating. It was established that neither the excitation wavelength nor polarization noticeably affected the results. Luminescence calibration was perfomed with a standard tungsten lamp. Data were digitized on a Tektronix plotter and processed on a VAX computer.

Results and Discussion

Figure 1 displays the polarized luminescence spectra of three good quality crystals (**I**, **II** and **III**), grown at different times and rates by solvent evaporation. They display remarkable differences in both polarization properties and intensity profiles. The data on this system presented by Yersin *et al.* [2–8] is unfortunately not corrected for system response, and thus a quantitative comparison with our data is not possible. It is however clear from Fig. 1 of ref. 2, the single crystal 290 K spectrum, and Fig. 1 of ref. 4, the 300 K powder spectrum, that, even taking into account the polarization averaging expected in the powder, a significant sample dependence is evidenced in this work as well.

We note that the crystal of greatest degree of optical and cosmetic perfection used in our work has a luminescence spectrum with a distinctly stronger component at 620 nm (16 000 cm^{-1}), giving it a stronger resemblance to the powder spectrum (ref. 4), and the 'imperfect' crystal (**III** of Fig. 1) has a luminescence more resembling that presented in refs. 2 and 8. At 300 K our three crystals have σ polarization throughout the detected region although the absolute polarization value varies, with the so called 'imperfect' crystal (**I**) having the highest value. At 77 K the 'imperfect' crystal retains its overall σ polarization but the other two crystals show strong and even dominant π polarization of the luminescence. The spectrum of our 'imperfect' crystal at 77 K seems in rough qualitative agreement with the single crystal data reported previously. Again a more than qualitative comparison is not possible as the published spectra are not corrected.

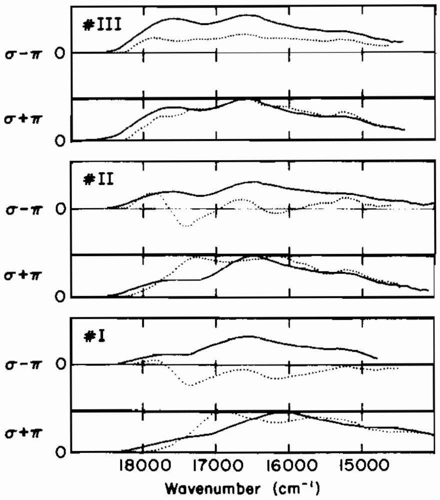

Fig. 1. Differential ($\sigma - \pi$) and total ($\sigma + \pi$) (corrected) luminescence spectra of three different Ru(bpy)$_3$(PF$_6$)$_2$ crystals observed at 300 K (solid lines) and 77 K (dotted lines). **I.** 'perfect' crystal, grown from acetonitrile/ethanol 1:1; **II.** 'less perfect' crystal, grown from same solvent; **III.** 'imperfect' crystal, grown from acetone. Spectra taken at different temperatures have been normalized but differential and total luminescence spectra (of a particular sample at a specific temperature) are on the same scale and can be directly compared, *i.e.* differential signal of the same intensity as the total signal would mean a completely polarized component.

We have also made measurements of the luminescence of a number of crystal samples at 4.2 K and 1.9 K. There were still significant differences amongst them, even though the complete range of crystals were not measured at these lowest temperatures. Our spectra, however, seem significantly different from one another though similar to those reported previously [8].

The Os(bpy)$_3$$^{2+}$ species is an ideal luminophore with which to specifically dope the pure crystalline host, as it is reasonably soluble in the host, having an analogous structure. It has a strong luminescence, well shifted to the red of that originating in the host material. Measurements of the luminescence, excited in a region where Ru(bpy)$_3$$^{2+}$ absorption dominates, lead to most of the luminescence appearing at low energies, attributable to the Os(bpy)$_3$$^{2+}$ system and centred around 710 nm (14 100 cm^{-1}). Some luminescence could be due to reabsorption of the host luminescence. This is minimized by using a thin crystal section and low dopant concentration.

Figure 2 shows the luminescence of a doped crystal at temperatures from 300 K to 1.9 K. At room temperature, it is immediately apparent that the bulk of the luminescence is due to the dopant. In fact, room temperature luminescence from the undoped material, easily seen as a red glow to the naked eye, could not be seen in the doped material, the bulk of the luminescence appearing outside the range of sensitivity of the eye. At 77 K the luminescence is even more dominated by the dopant. However, at 4.2 K and below, the luminescence of

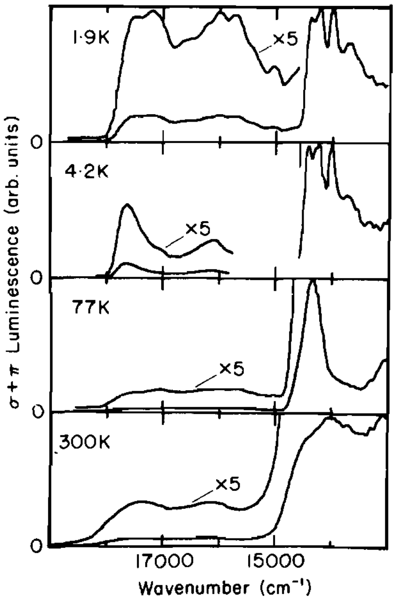

Fig. 2. Temperature dependence of the (corrected) total ($\sigma + \pi$) luminescence spectrum taken of a crystal of Ru(bpy)$_3$(PF$_6$)$_2$ doped with Os(bpy)$_3$(PF$_6$)$_2$ and grown from acetonitrile/ethanol 1:1. Spectra have been normalized to peak emission heights and do not reflect quantum efficiencies at different temperatures. Some noise is apparent at long wavelengths due to the large correction factors in this range. Substantial luminescence occurs beyond the range of the apparatus.

the host becomes relatively much stronger, though still dominated by the impurity.

The polarization of the low energy luminescence differs from that at higher energy and remains predominantly σ at both 300 K and 77 K. The high energy luminescence resembles the 'imperfect' crystal luminescence at 300 K but looks much more 'perfect' at 77 K in both its polarization and intensity dispersion. These data seem best interpreted as an energy transfer process from the host to the Os(bpy)$_3$$^{2+}$ impurity. The excitation transfer process, being perhaps phonon assisted, may depend strongly on temperature for a number of reasons (see appendix).

We discount the possibility that the phenomena observed in Fig. 2 are due solely to direct excitation of the dopant or reabsorption of the host luminescence on the following grounds:

(1) Excitation was made in a region completely dominated by host absorption.

(2) Reabsorption was minimised by using thin crystals.

(3) The Os(bpy)$_3$$^{2+}$ absorption process is not strongly temperature dependent and would not lead to the strong temperature dependence of the relative strengths of the host and dopant luminescences observed.

(4) Excitation with radiation around 600 nm did not lead to strong luminescence.

The beautiful, sharp, polarized structure observed only very recently in the luminescence (alleged zero-phonon origin region) of both the PF$_6$ and ClO$_4$ salts [5, 7] deserves particular comment. We would have to cast some doubt, based on the observations above, on whether these structured emissions are in fact intrinsic zero phonon lines or due to specific defect sites. We did not observe these sharp structures in Ru(bpy)$_3$(PF$_6$)$_2$ in our luminescence spectra*, due no doubt to the limited resolution of our minimate spectrometer. We have however made careful polarized single crystal absorption measurements at good resolution, at 1.9 K, of the absorption edge of a crystal approximately 1 mm thick. No sharp structure was seen but an optical density of unity was reached near 561.6 nm (17806 cm^{-1}) for σ polarization and 556.0 nm (17986 cm^{-1}) for π polarization. A shoulder is seen at 566.5 nm (17650 cm^{-1}) with a half width of several nm. The lowest energy sharp features observed by Yersin is reported at 561.2 nm and does not seem to appear in the σ absorption spectrum. There is definitely no sharp structure in the π spectrum in this region. Thus the assignment made of this structure as zero-phonon origins, intrinsic to the luminophore, must further be cast in doubt. In the absence of strong electron-phonon coupling, sharp zero phonon features should appear in absorption spectra taken under the same conditions. Gallhuber, Hensler and Yersin [5] do claim to have seen an absorption feature corresponding to zero phonon emission in the ClO$_4$ salt. The question of differing sites within the unit cell can not be established as yet, as the crystal structure has not been reported. However a racemic crystal would be expected to contain at least two sites in the unit cell.

In the presence of strong electron-phonon coupling, the lowest energy transitions eventually is not well described as 'zero-phonon' and an analysis of the energy spacings is questionable. A much broader shoulder is seen at lower energy in absorption than the assigned origins in luminescence. The 'origins' appear well into the absorption edge of the neat material. By comparison, the absorption and luminescence of Ru(bpy)$_3$$^{2+}$ doped in Zn(bpy)$_3$(PF$_6$)$_2$ shows a distinct gap (Stokes shift) [13].

What can be ascertained from a study of the single crystal absorption spectrum is a region of structured and polarized absorption between 16000 cm^{-1} and

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*One surviving crystal prepared by Nightingale (ref. 9) was examined at high resolution and low temperatures at A.N.U. Sharp structure was observed that was similar to, but not identical with that reported in ref. 6. The temperature dependence reported in ref. 6 was noticeably absent. Application of an external magnetic field, parallel to the c axis of the crystal, did not lead to the splitting of the sharp line but to the appearance of a second line approximately 2 nm lower in energy (561.8 nm).

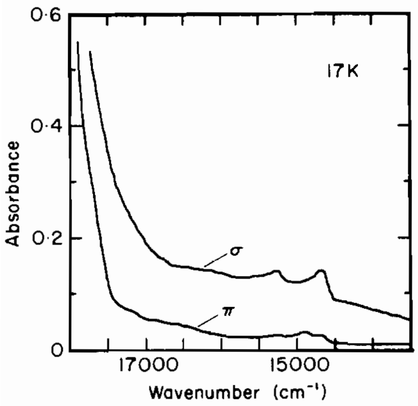

Fig. 3. Polarized absorption spectrum of a crystal, 1.5 mm thick, of 'pure' (see text) $Ru(bpy)_3PF_6$ crystal taken at 17 K.

14700 cm^{-1} (Fig. 3). This spectrum is most characteristic of triplet absorptions in $Os(bpy)_3^{2+}$ and is in very good agreement with spectra reported by Felix *et al.* [11] in the zinc host. Based on the published values of the molar extinction coefficient ϵ, the concentration of $Os(bpy)_3^{2+}$ can be estimated as $\approx 6 \times 10^{-5}$ M. This osmium impurity was not added to the crystals and is only traceable as an impurity in the original $RuCl_3 \cdot xH_2O$ sample (Johnson-Matthey) used in the preparation of the starting materials. This impurity has survived the purification procedures described in the experimental section. It could easily be speculated that even this level of impurity could influence the luminescence properties of the 'neat' crystalline salts.

Although the occurrence of energy transfer and impurity trapping in these systems deserves study in its own right, the use of concentrated materials to study intrinsic properties of a luminophore is contraindicated. Effort needs to be made to correlate with data taken on corresponding dilute systems. A preliminary study [14] of the luminescence of crystals of $Zn(bpy)_3PF_6$ doped with both $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$ establishes a complex energy transfer behaviour. However very little energy transfer is observed at the concentrations used in published work [13].

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Appendix

Estimation of Resonance Excitation Energy Transfer Rate

Excitation transfer has long been studied in aromatic crystals with which the names of Davydov, Forster and Dexter (DFD) are well known. Of importance to the $Ru(bpy)_3(PF_6)_2$ system as well is the dipole–dipole virtual photon exchange energy transfer process, used with considerable success for organic molecular crystals. Using the nomenclature of Di Bartolo [15] of the DFD theory as applied to inorganic solids, eqn. (18.78) p. 451 gives P_{SA}, the rate of excitation transfer from sensitiser S to the acceptor A as

$$P_{SA}(dd) = \frac{3e^4 f_{21}^{A} f_{12}^{S}}{8\epsilon^2\pi^2 m^2 c^3 (\bar{\nu})^2 R_{SA}^6} \int F_A(\bar{\nu}) f_S(\bar{\nu})\, d\bar{\nu}$$

Apart from the appropriate constants, the components of this expression are: R_{SA}, the separation of the two ions, f_{21}^{S} and f_{12}^{A} the sensitizer and acceptor oscillator strengths, the average energy $\bar{\nu}$ and the integral. The integral is related to the energy overlap between processes on the two ions and can be estimated using eqn. (18.93) p. 456.

We can estimate the upper limit for the resonant transfer rate in the $Ru(bpy)_3^{2+}$ systems by letting (from estimates of the triplet absorption spectra)

$f_{21}^{S} = f_{12}^{A} = 0.002$, $\bar{\nu} = 20\,000$ cm^{-1} and allowing for complete overlap between the processes with a width of 1000 cm^{-1} and allowing $\epsilon^2 = 6$. This leads to a transfer rate $P_{SA} \approx 2 \times 10^7$ s^{-1} for $R_{SA} = 10$ Å. The natural (radiative) lifetime of the excited triplet state is calculated, by the same formalism, as $\tau \approx 50 \times 10^{-6}$ s. This value is in reasonable accord with the experimentally determined radiative lifetimes [16]. We conclude that by the dipole–dipole process, two $Ru(bpy)_3{}^{2+}$ chromophores separated by 10 Å could transfer energy faster than the radiative rate. The formula used above is averaged for all dipole orientations, and the interaction between parallel dipoles in a crystalline system would be rather stronger.

$Ru(bpy)_3{}^{2+}$ system has a complex electronic manifold in the triplet state [16, 12, 13]. At low temperatures only a few sublevels will be populated and the effective value for f_{21} will be reduced, dropping the transfer rate. However, the radiative lifetime becomes longer and allows correspondingly more time for a weaker transfer process to occur. The competition between energy transfer and radiative emission then falls approximately as the reciprocal of the oscillator strength.