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Temperature Dependence of the Photophysical Properties of Ruthenium Diphenylphenanthroline in Liquid and Solid Environments

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Temperature-dependent luminescence decay time measurements were performed on tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) perchlorate in liquid and solid environments. Analysis of the luminescence decay function in liquid solutions and in a solid, amorphous polymer showed that different nonfluorescent decay channels contribute to the emission in liquid and solid environments.

1. Introduction

The photophysical and photochemical properties of ruthenium compounds in solution have been subject to a large number of experimental studies[1−8] during the past decades. They can undergo energy- and electron-transfer processes with a broad range of organic and inorganic compounds, their absorption is situated in the visible range of the spectrum, and their luminescence lifetime is rather long even at room temperature, and thus these compounds have been suggested for various practical applications.

In particular, much attention has been devoted to the tris(2,2′-bipyridyl)ruthenium(II) complex ($Ru(bpy)_3^{2+}$). Many papers are related to the temperature dependence of the spectroscopic properties of the $Ru(bpy)_3^{2+}$ complex[9−12] showing the different spectroscopic behavior of the complex as a single crystal, in a solid polymer, or in solution.

In recent years, another ruthenium complex has gained much interest in the field of luminescence-based chemical sensors, namely tris(4,7-diphenyl-l,10-phenanthroline)ruthenium(II) ($Ru(dpp)_3^{2+}$).[13−16] Due to its high quantum efficiency and its rather long luminescence decay time $Ru(dpp)_3^{2+}$ proved to be a good indicator for sensing oxygen. However, the knowledge about its photophysical and photochemical behavior, especially when incorporated into a solid polymer, is rather poor.

The aim of this work is to investigate the photophysical properties of $Ru(dpp)_3^{2+}$ in different environments. It was shown in previous papers[16−18] that the shape of the luminescence decay changes dramatically by incorporating the dye in a solid polymer. While the decay can be fitted with a single exponential in solutions, it becomes nonexponential in polymers. This deviation from the exponential decay law has been attributed so far to a nonhomogeneous microenvironment of the luminophore in the solid phase. It is poorly understood, however, what physical or chemical parameters of the environment influence in which way the radiative or nonradiative rate constants.

In this work, the luminescence decay of $Ru(dpp)_3^{2+}$ in various liquid solutions is compared to that in a solid polymer. The solid polymer of choice was polystyrene of high molecular weight. As the most similar, but nonsolid environment, low-molecular-weight polystyrene was used, being a highly viscous liquid with the same chemical composition as the solid. A chemically very similar low-viscosity liquid is monomeric styrene. This compound, however, is more polar than the polymer because of the double bond in the vinyl group. The polarity of a solvent can alter the electron distribution at the ligands as well as shift the energy levels of the whole complex, and therefore may also modify the rate constants governing the luminescence decay. Therefore, toluene was chosen as a solvent of low polarity. In contrast, methanol was used as a highly polar solvent to investigate the influence of the solvent polarity.

Relaxation of excited ruthenium complexes includes temperature-independent and temperature-dependent processes. Measurements of the luminescence decay at various different temperatures therefore provide the possibility to discern between these processes and to get information on the relative positions of the energy levels in the metalloorganic complex and on the various rate constants.

2. Materials and Methods

Methanol (Merck), toluene (Merck), chloroform (Merck), styrene (Aldrich), and two different polystyrenes (average molecular weights 800 and 280 000; polystyrene standards, Aldrich) were used as purchased without further purification.

The transition metal complex ruthenium(II) tris(4,7-diphenyl-1,10-phenanthroline) ($Ru(dpp)_3^{2+}$) was prepared as described in ref 15 with perchlorate as the counterion. All liquid solutions were 10^{-4} mol/L.

Polymer membranes were produced by incorporating $Ru(dpp)_3^{2+}$ into polystyrene with different molecular weights. One gram of polystyrene and 13 mg of $[Ru(dpp)_3^{2+}](ClO_4)_2$ were dissolved in chloroform, spread on a substrate, and dried for 2 h at 90 °C. The thickness of the layer was of about 10 μm.

Luminescence decay time measurements were performed using a nitrogen laser (pulse width 300 ps) as the excitation source ($\lambda_{ex} = 337$ nm). The luminescence was monitored by a fast photomultiplier (Hamamatsu H5783, rise time 0.6 ns) and processed by a 1 GHz digital signal analyzer (Tektronix DAS 601A).

The decay functions were fitted using the commercially available mathematical software package Scientist (MicroMath Scientific Software, USA).

Solutions were heated to temperatures some degrees below their boiling points, and polymers to 160 °C. Thereafter, the heating was reduced to allow cooling to a preset temperature that was stabilized by a thermostat to ±0.5 °C. Luminescence decay measurements were performed down to room temperature. Temperature was monitored by a digital thermometer (Cole

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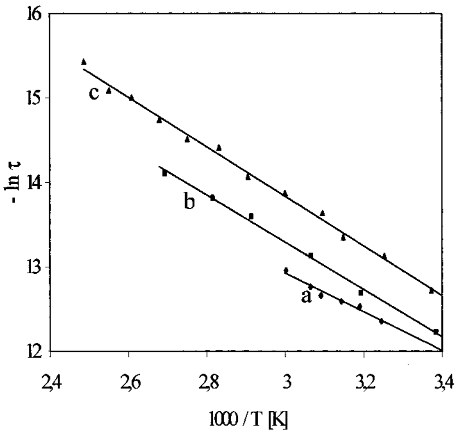

Figure 1. Arrhenius plot for the luminescence decay time of Ru(dpp)$_3^{2+}$ in (a) methanol, (b) toluene, and (c) styrene.

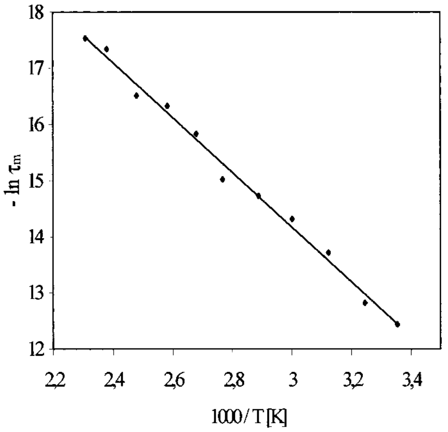

Figure 2. Arrhenius plot for the luminescence decay time of Ru(dpp)$_3^{2+}$ in low-molecular-weight polystyrene.

Parmer). The temperature probe was either dipped into the solution or the solid polymer was placed directly on the thermometer probe. The liquids as well as the polymer film were saturated with nitrogen before starting the measurement.

The luminescence decay of Ru(dpp)$_3^{2+}$ in liquid solutions usually is single exponential. The decay time decreases with increasing temperature due to a thermally activated population of nonluminescent states competing with the radiative decay. This can be described by an Arrhenius equation

$$\frac{1}{\tau} = k_0 + \sum_i k'_i \exp\left(-\frac{\Delta E_i}{k_B T}\right) \tag{1}$$

with τ being the observed luminescence decay time, k_0 the radiative and nonradiative rate constants for the relaxation of the MLCT excited state to the ground state, ΔE_i the energy differences, and k'_i the probability for transitions between MLCT and the nonluminescent states in the case of zero activation energy barrier, and k_B the Boltzmann constant.

If the luminescence decay is not exponential, as frequently reported for ruthenium complexes in a polymer environment,[17,18] the usual procedure is to apply a sum-of-exponentials fit, though it is clear that the components of the fit do not necessarily have a physical meaning. The decay time, that is, the average time an electron remains in the excited state, may be expressed as the "preexponential weighted mean lifetime" τ_m[16]

$$\tau_m = \sum_i a_i \tau_i \Big/ \sum_i a_i \tag{2}$$

where the index i denotes the respective exponential component of the fitting function.

3. Results and Discussion

In methanol, the decay of the Ru(dpp)$_3^{2+}$ luminescence is single exponential. The temperature range used for monitoring the decay was limited by the boiling point of methanol, that is 65.4 °C (only measurements under ambient pressure were performed). The luminescence decay time in dependence of temperature is given in Figure 1a.

From this Arrhenius plot a value of $\Delta E = 1597 \pm 143$ cm^{-1} for the energy difference between the emitting state and a nonluminescent, thermally populated higher state as well as a rate constant of $k' = (4.1 \pm 2.8) \times 10^8$ s^{-1} can be calculated.

Methanol is a rather polar solvent. It has been shown[19,20] that the polarity of the solvent has a considerable effect on the luminescence decay of ruthenium complexes. Hence toluene was chosen as a nonpolar solvent for comparison. The boiling point of toluene is 110.6 °C. The luminescence decay was single exponential over the whole temperature range between the boiling point and room temperature. Figure 1b shows the luminescence decay time of Ru(dpp)$_3^{2+}$ in toluene in dependence of the temperature. Values of $\Delta E = 1946 \pm 62$ cm^{-1} for the energy difference and $k' = (2.6 \pm 0.7) \times 10^9$ s^{-1} for the rate constant were obtained.

For monomeric styrene the boiling point is 145.5 °C. The decay function could be fitted with a single exponential. Styrene contains 10−15 ppm of 4-*tert*-butylcatechol as stabilizer. Since this substance could be a possible quencher it cannot be excluded that a temperature-dependent bimolecular quenching occurs. The temperature dependence of the luminescence decay time in styrene is shown in Figure 1c. Values of $\Delta E = 2045 \pm 45$ cm^{-1} for the energy difference and $k' = (7.0 \pm 1.3) \times 10^9$ s^{-1} for the rate constant were calculated. The close similarity with the values obtained in toluene makes it very probable that bimolecular quenching is insignificant.

Polystyrene with low molecular weight (MW 800) is a highly viscous liquid. A solution of Ru(dpp)$_3^{2+}$ in this liquid was heated to about 160 °C. This case was exceptional among the liquid samples inasmuch as the decay was nonexponential. A two-component fit was satisfactory, but there are no reasons to attribute the two components any physical meaning. Hence the preexponential weighted lifetime was used to calculate the constants of the Arrhenius plot. The temperature dependence of the lifetime is shown in Figure 2. The Arrhenius plot is linear. Values of $\Delta E = 3398 \pm 164$ cm^{-1} and $k' = (3.4 \pm 1.5) \times 10^{12}$ s^{-1} were established. Both values are considerably higher compared to the measurements of Ru(dpp)$_3^{2+}$ in the low-viscosity solutions. If we use the two decay times and fit them separately to an Arrhenius equation, the results are comparable with those obtained from the preexponential weighted lifetime; i.e., the value of ΔE is increased by less than 10%, while that of k' is the same within the limits of deviation.

As a solid polymer, polystyrene of high molecular weight (MW 280 000) was used. The polymer film was placed directly on the thermometer probe to ensure an optimal contact between probe and thermometer. Again the sample was heated to about 160 °C, and the measurements were performed down to room temperature. The luminescence decay again was nonexponential and could be fitted satisfactorily with a sum of two exponentials. The average decay time in dependence on the temperature is shown in Figure 3 (experimental results).

In contrast to all other experiments the Arrhenius plot now is composed of two linear parts. The first one reaches from room

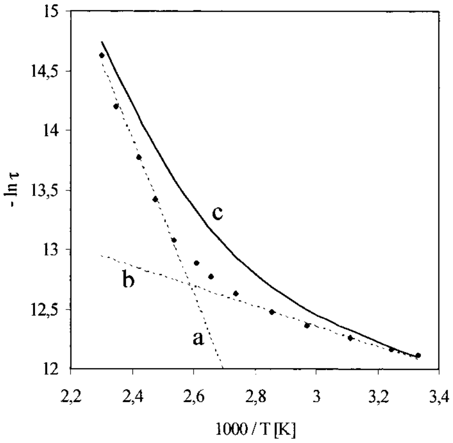

Figure 3. Arrhenius plot for the luminescence decay time of $Ru(dpp)_3^{2+}$ in high-molecular-weight polystyrene: dots, experimental results; lines, Arrhenius fits for (a) high-temperature branch only, (b) low-temperature branch only, and (c) both branches.

TABLE 1: Energy Differences between the Emitting State and the Higher-Lying Competing State, together with the Respective Rate Constants, for $Ru(dpp)_3^{2+}$ in Liquid and Solid Environment

environment	ΔE (cm^{-1})	k' (s^{-1})
methanol	1597 ± 143	$(4.1 \pm 2.8) \times 10^8$
toluene	1946 ± 62	$(2.6 \pm 0{,}7) \times 10^9$
styrene	2046 ± 45	$(7.0 \pm 1.3) \times 10^9$
polystyrene (MW 800)	3398 ± 164	$(3.4 \pm 1.5) \times 10^{12}$
polystyrene (MW 280 000), above T_g	4491 ± 235	$(6.0 \pm 5.5) \times 10^{12}$
polystyrene (MW 280 000), below T_g	583 ± 40	$(2.9 \pm 0.5) \times 10^6$

temperature to about 110 °C while the second part covers the temperature range from about 110 to 160 °C. This proves that thermally activated transitions to two different states come into play now. As the glass temperature of polystyrene is $T_g \approx 100$ °C, it is not immediately clear, however, whether these two states contribute to the relaxation both below and above T_g, or if one state is present above and the other one below the glass transition.

If the assumption is made that the states are different below and above T_g, then the two branches have to be fitted independently (Figure 3, a and b). The results are $\Delta E = 583 \pm 40$ cm^{-1} and $k' = (2.9 \pm 0.5) \times 10^6$ s^{-1} below and $\Delta E = 4491 \pm 235$ cm^{-1} and $k' = (6.0 \pm 5.5) \times 10^{12}$ s^{-1} above T_g. These values together with those from the other samples constants are summarized in Table 1.

If, on the other hand, it is assumed that both states are present simultaneously, below as well above T_g, the Arrhenius plot has to be fitted with two terms contributing to the sum in eq 1. The result is shown in Figure 3c. The calculated values fit very well to the measured points at high and low temperatures, but level off considerably near the glass transition. Therefore, the measured results are not compatible with the assumption of both energy levels contributing simultaneously to the relaxation.

Comparing the high-temperature branch of the Arrhenius plot with the results from the low-molecular-weight polystyrene, the values agree rather well. The values for the lower branch, on the other hand, disagree strongly with all other measurements. Not only ΔE but also k' is largely different, which suggests a substantially different thermally populated level. This is in agreement with other observations for $Ru(bpy)_3^{2+}$ in cellulose acetate films[23] or in single-crystal measurements,[10] where it was shown that an additional state in the energy region around 700 cm^{-1} comes into effect and replaces the previous state as the main thermally activated relaxation channel. It was suggested that below the glass transition a low-lying MLCT state is in effect, while in liquid environments the decay is dominated by a dd state. Unfortunately, from the present measurements no hints on the character of the state can be deduced.

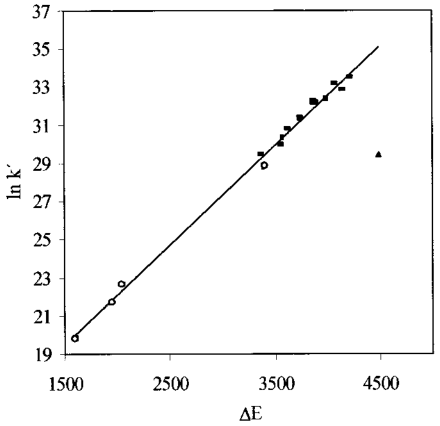

Figure 4. Barclay–Butler plot: (○) $Ru(dpp)_3^{2+}$ in liquid solutions, this work; (■) $Ru(bpy)_3^{2+}$ in liquid solutions, from ref 20; (▲) $Ru(dpp)_3^{2+}$ in solid polymer, this work.

Figure 4 shows a Barclay–Butler plot,[21,22] that is, a semi-logarithmic plot of the dependence of k' on ΔE. In this plot the results of $Ru(dpp)_3^{2+}$ in different environments from this work are shown, together with results obtained from the $Ru(bpy)_3^{2+}$ complex some years ago in our working group.[20] For all liquid samples, the Barclay–Butler plot gives (within the experimental error) the same straight line, irrespective of the kind of ruthenium complex. The only difference between the two complexes is the magnitude of the ΔE and k' values. The results of the $Ru(bpy)_3^{2+}$ complex show much higher values compared to $Ru(dpp)_3^{2+}$. Similar results have been found for the ruthenium phenanthroline complex.[22] Since the radiative rate constant (determined from the actual decay time and the quantum yield) is fairly the same for all these complexes, but the luminescence decay times strongly vary, the main difference must be in the radiationless processes. Due to the fact that the energy barrier for transition to the dd state is smaller in $Ru(dpp)_3^{2+}$, the process should be much faster than in the $Ru(bpy)_3^{2+}$. However, this is more than compensated by a lower value of k'. As a result, the observed luminescence decay time in $Ru(dpp)_3^{2+}$ is much longer than in the $Ru(bpy)_3^{2+}$ complex. Despite these differences, all complexes follow the same linear Barclay–Butler relation.

There is only one point in Figure 4 that shows a strong deviation from that line, namely $Ru(dpp)_3^{2+}$ in polystyrene at temperatures below the glass transition.

Comparing these results with that of polystyrene of low molecular weight, it can be concluded that it is not the molecular weight that is responsible for the different behavior in the two polymers, but the state of matter, namely solid or liquid. The comparison with the other solvents also proves that the emission properties of the complex are more influenced by the state of the microenvironment than by the chemical composition, molecular weight, or polarity.

4. Conclusion

From these results it can be concluded that in a liquid environment for $Ru(dpp)_3^{2+}$, as for $Ru(bpy)_3^{2+}$, a thermally activated MLCT → dd transition with subsequent nonradiative decay from the dd state takes place. The magnitudes of ΔE and k' depend on the solvent. In solid environments, however, an additional state is present that is populated thermally. This new transition replaces the original MLCT → dd transition.

This investigation therefore shows that the emission properties of ruthenium complexes depend strongly on the state of matter of the microenvironment, but are much less dependent on its chemical and molecular properties. In amorphous solids even new energy levels play an important role in the relaxation that are not effective in a liquid environment.

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