

THE LUMINESCENCE OF SOLID BIS(2,9-DIPHENYL-1,10-PHENANTHROLINE) COPPER(I)

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The luminescence of the title complex $[\text{Cu}(\text{dpp})_2]^+$ in the solid state is reported. The results are compared with those of related Cu^+ complexes and with those for $[\text{Cu}(\text{dpp})_2]^+$ in solution.

1. Introduction

The luminescence of Cu(I) complexes has been the subject of investigation for some time. Isolated complexes have been investigated in glasses or in solution [1–4], but the luminescence of solid complexes has also been reported [5,6]. The emission originates from low-lying metal-to-ligand charge-transfer (MLCT) excited states. These complexes can also be used as sensitizers of wide-band-gap semiconductors [7,8].

In $[\text{Cu}(\text{dpp})_2]^+$ the bulky ligands protect the metal center from its environment, i.e. the molecules of the solvent. This leads to a marked increase of the luminescence intensity in comparison with, e.g. $[\text{Cu}(\text{dmp})_2]^+$ [4]. Such an effect should play no role in the solid state. The luminescence of solid $[\text{Cu}(\text{dpp})_2]^+$ is expected to be in line with the other Cu^+ complexes. This hypothesis initiated the present investigation.

2. Experimental

The preparation of $[\text{Cu}(\text{dpp})_2]^+ \cdot \text{BF}_4^-$ was carried out as described in ref. [4]. The way in which the op-

tical measurements were performed has been reported in ref. [6].

3. Results

The complex $[\text{Cu}(\text{dpp})_2]^+ \cdot \text{BF}_4^-$ in the solid state shows only a very weak, deep-red emission. The quantum efficiency at room temperature is lower than 0.01. The emission consists of a broad band with a maximum at about 710 nm. An emission spectrum is given in fig. 1.

At 4.2 K the position of the emission maximum is at about the same wavelength. The emission intensity at 4.2 K is only slightly higher than at room temperature, but there is a shallow minimum at about 200 K. This is very similar to what has been reported for the other Cu^+ complexes [6].

In table 1 the luminescence properties of the different Cu^+ complexes in the solid state are compared (data from refs. [1–6]). For this purpose we measured the decay time of the luminescence of $[\text{Cu}(\text{dmp})_2]^+ \cdot \text{BF}_4^-$ at 4.2 K. The decay curve is exponential and yields a decay time of 3.2 μs . At 300 K the emission is too weak to allow decay-time measurements with the apparatus at our disposal. The same is true for $[\text{Cu}(\text{dpp})_2]^+ \cdot \text{BF}_4^-$ at all temperatures.

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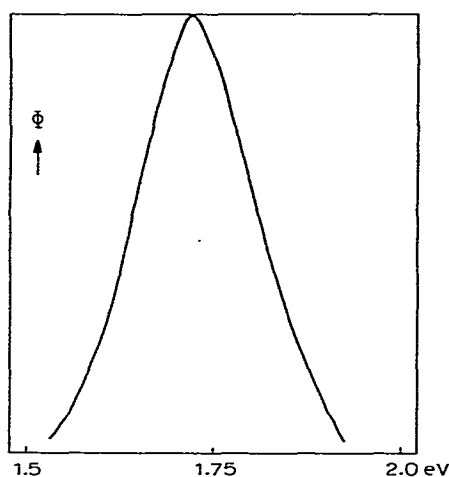


Fig. 1. Emission spectrum of solid $[\text{Cu}(\text{dpp})_2]^+ \cdot [\text{BF}_4]^-$ at 300 K. Φ gives the spectral radiant power per constant energy interval in arbitrary units.

4. Discussion

In table 1 the Cu^+ complexes are arranged in sequence of increasing emission wavelength maximum, i.e. from top to bottom the MLCT transition energy decreases. Simultaneously the quantum efficiency at 300 K decreases. This is due to the fact that the probability for non-radiative transitions increases if the (broad-band) MLCT transition shifts to lower energy

[9]. The decrease of the decay times is related to the increase of the non-radiative transition probability [6]. No luminescence was observed for the $[\text{Cu}(\text{biq})_2]^+$ complex. This is in line with the outspoken long-wavelength position of the absorption band, i.e. the MLCT transition. From these data we conclude that the luminescence properties of the $[\text{Cu}(\text{dpp})_2]^+$ complex in the solid state are well in line with those of the other complexes in the solid state.

For the complexes in solution the situation is different, because $[\text{Cu}(\text{dpp})_2]^+$ in solution luminesces more efficiently than $[\text{Cu}(\text{dmp})_2]^+$ in solution [4]. The present results confirm the hypothesis put forward elsewhere [4], viz. the four phenyl rings around the copper centre protect the complex from external molecules. In this way they reduce the non-radiative transition probability. In the solid state this effect has no influence on the non-radiative transitions.

These complexes can be applied as sensitizers of wide-band-gap semiconductors [7]. We have found the highest quantum efficiencies for photocurrent generation for the Cu^+ complexes with the highest MLCT transition energy. It was found, however, that $[\text{Cu}(\text{dpp})_2]^+$ sensitizes more efficiently than $[\text{Cu}(\text{dmp})_2]^+$ in spite of the longer-wavelength emission of the former [8]. This result may suggest that other factors are important in addition to the excited-state lifetime.

Table 1
Luminescence properties of Cu^+ complexes

Complex ion ^{a)}	Color of the solid complex	Absorption maximum (nm) in solution	Emission maximum (nm)		Quantum efficiency at 300 K	Decay time (μs)	
			4.2 K	300 K		4.2 K	300 K
$\text{Cu}(\text{PPh}_3)_2\text{phen}^+$	yellow	365	535	515	0.75	250	30
$\text{Cu}(\text{PPh}_3)_2\text{dmp}^+$	yellow	365	530	515	0.75	250	30
$\text{Cu}(\text{PPh}_2\text{CH}_3)_2\text{dmp}^+$	yellow	365	560	525	0.75	250	30
$\text{Cu}(\text{PPh}_3)_2\text{bpy}^+$	yellow	356	585	560	0.15	30	7
$\text{Cu}(\text{PPh}_3)_2\text{biq}^+$	orange	415	630	605	0.17	30	7
$\text{Cu}(\text{dmp})_2^+$	red	454	680	650	≈ 0.01	3	—
$\text{Cu}(\text{dpp})_2^+$	deepred	439	≈ 710	≈ 710	< 0.01	—	—
$\text{Cu}(\text{biq})_2^+$	black	545	—	—	"0"	—	—

a) PPh_3 : triphenylphosphine; phen: 1,10-phenanthroline; dmp: 2,9-dimethyl-1,10-phenanthroline; PPh_2CH_3 : methyldiphenylphosphine; bpy: 2,2'-bipyridine; biq: 2,2'-biquinoline; dpp: 2,9-diphenyl-1,10-phenanthroline.

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