Strikingly different luminescent properties arising from single crystals grown from solution or from the vapor phase in a diketopyrrolopyrrole analogue

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Abstract

The title compound (DCPP) is an analogue of diketopyrrolopyrrole known as a red pigment on the market. Brilliant orange photoluminescence has been observed in crystals of DCPP grown from solution (crystal I), although no luminescence was recognized in solution. Furthermore, the luminescence is found to be completely quenched above 300 °C ("thermal quenching"). On the other hand, the crystals grown from the vapor phase (crystal II) shows quite weak luminescence. To elucidate the difference in luminescent properties, a series of structure analysis have been carried out on crystals I and II at -180, RT, 150, and 200 °C. However, no crystallographic difference is recognized between crystals I and II. Nevertheless, a slight difference is observed in sublimation temperature (crystal I: 306.2°C; crystal II: 309.9°C). The present difference in cohesion is closely correlated to the lattice vibration and determines the "radiative/non-radiateive" fraction of the excited energy between crystals I and II.

INTRODUCTION

Electroluminescence (EL) has been the focus of considerable interest because of its high potential for compact and clear display devices [1]. Although a great number of compounds are known which fluoresce in solution, the fluorophores in the solid state are relatively limited.

In the course of our studies on the electronic structure of diketopyrrolopyrroles (DPP) [2-4] known as the red pigments on the market [5], we encountered a DPP derivative that emits intense orange photoluminescence in the solid state, although no luminescence was recognized in solution, as in tris(8-hydroxyquinolino)aluminum (Alq3) [6], α-pyrone [7], and oligopyridine [8]. This indicates evidently that the intermolecular interactions in the solid state are involved in the emission process. The present compound (*i.e. N,N'*-dimethyl-1,4-dicyanimino-3,6-diphenylpyrrolo-[3,4-c]-pyrrole: DCPP) has a conformation as shown in Fig. 1(a)) while Fig.1(b) shows the structure of DPP. The above brilliant luminescence is, however, found to disappear completely above 300 °C ("thermal quenching") and re-appears as the temperature is decreased. Furthermore, these outstanding phenomena were observed only in crystals recrystallized from solution, for example, in methylene chloride (crystal I). On the other hand, the crystal grown from the vapor phase (crystal II) shows extremely weak luminescence. In this connection, the present investigation has been undertaken in order to elucidate the difference in luminescent properties of DCPP on the basis of the crystal structure in combination with thermal analysis (TGA (thermogravimetric analysis) and DSC (differential scanning calorimetry)). A series of structure analysis have been therefore carried out on crystals I and II at of DCPP temperatures of -180, room temperature, 150, and 200 °C, in addition to our previous structure report on crystal II [9].

This paper describes the luminescent properties as viewed from the crystal structure and thermal analysis.

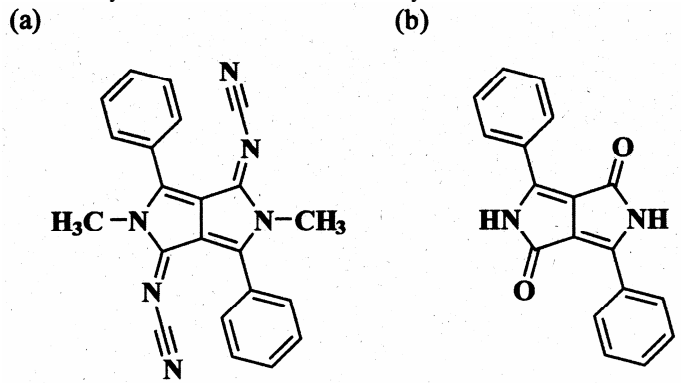

Fig. 1 Molecular conformation: (a) DCPP and (b) DPP.

Sample preparation and crystal growth

DCPP was prepared in two steps through 2,5-dimethyl DPP [10-11]. Single crystals of DCPP were grown by recrystallization from solution in methylene chloride. A number of single crystals of orange color (crystal I) were isolated in the form of platelets. Crystal I fluoresces intensely as recognized easily at room temperature. On the other hand, single crystals were also grown from the vapor phase in a closed system with a sublimation temperature of about 300 °C for 48 h. Prismatic crystals of dark red color (crystal II) were obtained in the low temperature region of about 200 °C. However, crystal II exhibits quite weak luminescence.

Results and discussion

Crystal structure

Table 1 details the crystallographic parameters at room temperature for crystals I grown from solution and crystal II grown from the vapor phase. Both crystals crystallize in the space group $P2_1/c$ with a molecular symmetry of C_i. No noticeable difference in crystallographic parameters is recognized between crystals I and II. Therefore, the structure is shown here only for crystal I at room temperature.

Table 1 Crystallographic parameters for crystals I and II at RT.

	Crystal I	Crystal II
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
Molecular symmetry	C_i	C_i
Z	2	2
a (Å)	6.522(1)	6.521(1)
b (Å)	6.518(1)	6.516(1)
c (Å)	21.714(4)	21.708(4)
β (°)	91.91(1)	91.98(1)
V (Å^3)	922.5(3)	921.9(10)
d (g/cm^3)	1.31	1.31

The ORTEP plot is shown in Fig. 2(a). The molecule possesses C_i. The phenyl rings are deviated, in the same direction, from the heterocyclic ring system by about 61°. The distance between N3 and C2 atoms corresponds approximately to that of the van der Waals radii. The angle of N2-C10-N3 atoms is not exactly 180° because of the repulsion between N3 and C3 atoms. All other bond parameters of the present analogue agree well with those of DPP [13-14].

Fig. 2(b) shows the overlap of two molecules: top view and side view. It should be noted that the molecules are stacked with overlap occurring only at the cyano group (top view). N3 of the lower molecule is directly under N1 of the upper molecule. Likewise, N1 of the lower one is nearly under N3 of the upper one. The distance between these atoms are shown in the side view.

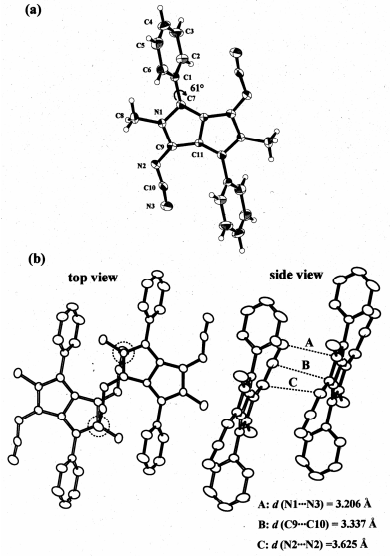

Fig. 2 (a) ORTEP plot of DCPP and (b) overlap of two molecules.

Figs. 3 shows the projection of the crystal structure onto the (*b, c*) planes. The molecules are stacked along the a-axis and arranged in a zigzag fashion along the *c*-axis.

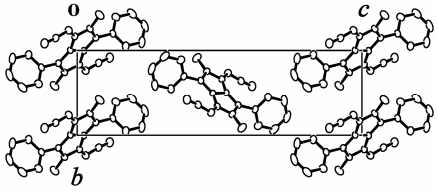

Fig. 3 Projection of the crystal structure of DCPP onto the (b,c) plane.

Temperature dependence of the lattice parameters for crystals I and II

Figs. 4(a) and 4(b) show the temperature dependence of the lattice parameters together with that of density as obtained by structure analysis for crystals I and II, respectively. The value of the parameters is expressed in percentage relative to the value at -180 °C. The lattice constants *a*, *b* and *c* increase with increasing temperature while the reverse is the case for the angle β and the density. The value of the lattice *c* coincides with that of lattice *b* at 200 °C. Exactly the same tendency is observed in crystal II.

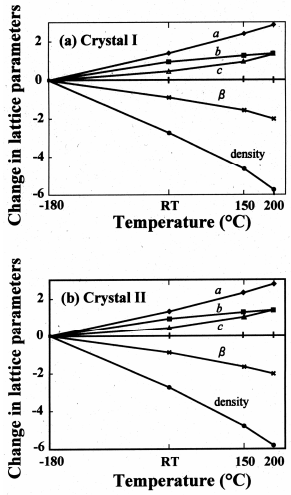

Fig. 4 Temperature dependence of the lattice parameters of DCPP at -180, RT, 150, and 200 °C: (a) crystal I and (b) crystal II.

Solution spectra

Fig. 5 shows the solution spectra of DCPP in methylene chloride and acetonitrile. In the former spectrum, a prominent absorption band appears around 518 nm together with two shoulders around 447 and 482 nm, forming a progression of absorption bands. It is to be noted that the longest-wavelength band is quite steep and the absorption bands are equally spaced (about 1400 cm^{-1}). Furthermore, our MO calculations (not presented here) predict only one electronic transition in the visible region. These facts suggest that the longest-absorption band is assigned to the pure electronic transition (*i.e.* 0–0) and the second-longest wavelength band to the 0–1 etc. as shown in Fig. 5, indicating that one single electronic transition is coupled with vibrational transitions.

The appearance of the progression of absorption bands is typical of the situation where the potential minima of the ground and excited states occur at the same position of the coordinate. The potential scheme will be discussed later.

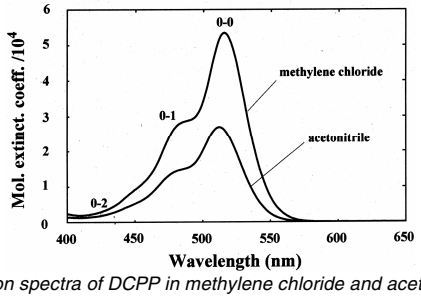

Fig. 5 Solution spectra of DCPP in methylene chloride and acetonitrile.

Temperature dependence of photoluminescence in crystals I and II

Figs. 6 (a) and 6 (b) show the temperature dependence of photoluminescence for crystals I and II, respectively, under the excitation of 365 nm measured at -50, RT, 150, and 250 °C. In crystal I, an intense band appears at -50 °C around 605 nm (band A) together with a shoulder around 564 nm (band B). The intensity of the present luminescence decreases remarkably with increasing temperature and is completely quenched above 300 °C ("thermal quenching"). The spectral shape changes also drastically in such a way that band A decreases in intensity while the band B remains nearly unaltered up to room temperature, accompanied by a slight spectral shift of both bands toward longer wavelengths. Then, band B is appreciably shifted to 571 nm at 150 °C whose intensity is now at the same level as that of band A. At 250 °C, the intensity of band B is larger than that of band A, although both intensities are quite weak. At 300 °C, the photoluminescence is completely quenched. However, the luminescence re-appears with decreasing temperature, indicating the reversibility of the appearance and disappearance of the photoluminescence.

On the other hand, as shown in Fig. 6(b), the temperature dependence in crystal II is quite similar to that of crystal I, although the intensity of crystal I is stronger than that of crystal II by a factor of 6-7. (The intensity scale in Figs. 6(a) and 6(b) is in common.) Crystal II is also found to exhibit thermal quenching at 300 °C. It should be however noted that the emission wavelength of band A in crystal II remains unchanged at all temperatures measured; whereas band A in crystal I is present at slightly shorter wavelength at -50 °C as compared with those at RT, 150, and 250 °C.

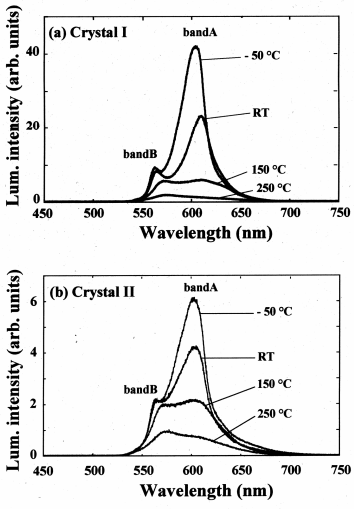

Fig. 6 Temperature dependence of the photoluminescence spectra of DCPP: (a) crystal I and (b) crystal II.

Figs. 7(a) and (b) show the Arrhenius plot of the temperature dependence of the integrated fluorescence intensity for crystals I and II, respectively. Both temperature dependences are quite similar and governed by double exponentials. This indicates that the thermal quenching occurs via two non-radiative paths. The activation energy of the high temperature region amounts to about 0.3 eV in crystals I and II.

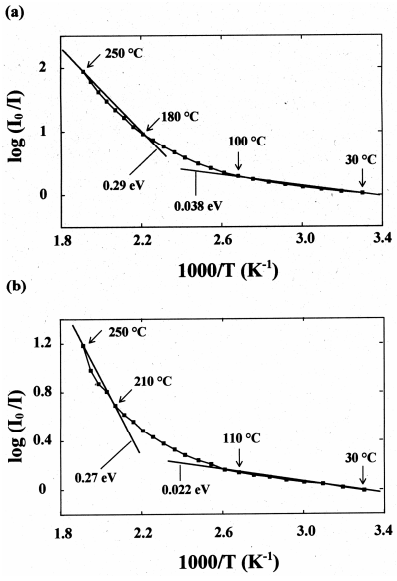

Fig. 7 Arrhenius plots of the integrated photoluminescence intensity of DCPP: (a) crystal I and (b) crystal II.

TGA/DTA measurements in air

A distinct difference in TGA/DTA (Thermogravimetric Analysis and Differential Thermal Analysis, respectively) diagram in air is observed between crystals I and II as shown in Fig. 8. The DTA peak which corresponds to the sublimation point appears at 369.4 in crystal I while at 373.5 °C in crystal II. This indicates that thte cohesion in the solid state (which directly correlated to the lattice energy) is higher in crystal II than in crystal I.

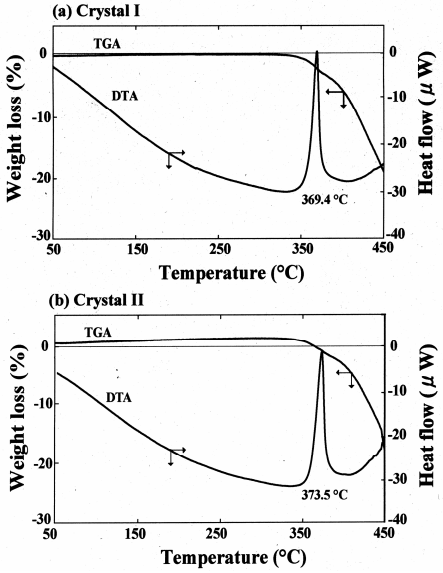

Fig. 8 TGADTA diagrams measured in air: (a) crystal I and (b) crystal II.

Crystals grown from solution in different solvents

Crystals were also recrystallized from acetonitrile, acetone and dimethylsulfoxide. All these crystals were colored orange just as in crystal I and gave strong luminescence. The crystal structure of these single crystals was also in accord with that of crystal I.

Franck-Condon diagrams in solution and in the solid state

No luminescence of DCPP was recognized in solution. On the other hand, intense luminescence appears in crystal I while crystal II exhibits weak luminescence. These observations evidently indicate that the luminescence appears as a result of intermolecular interactions in the solid state.

As previously preseted, the solution spectrum is typically characterized by a progression of absorption bands: 0-0, 0-1 and 0-2 transitions. This indicates that the potential minima of both the ground and excited states are present at the same position of the coordinate. On the basis of this consideration, the Franck-Condon Configuration Coordinate (FC CC) for the solution state can be drawn as shown in Fig. 9(a).

Thermal quenching is not unique for crystal I and also observed in crystal II. Thermal quenching of fluorescence is usually explained by means of the energy dissipation through the cross point of the ground state and of the excited state potentials.18 This is an activation process governed by Boltzmann's distribution. The potential barrier which the electrons must surmount is about 0.3 eV as deduced from temperature dependence of the photoluminescence (see section III E). On the basis of the above consideration, we propose a FC CC diagram for crystals I and II as shown in Fig. 9 (b), where the activation energy ΔE is equal for both crystals. The difference between crystals I and II consists in the ratio of the radiative to the non-radiative process. In other words, crystal I is 6-7 times more efficient for photoluminescence than crystal II.

As discussed above, the luminescence of DCPP arises from intermolecular interactions in the solid state. Furthermore, a slight difference in sublimation temperature is observed between crystals I and II, indicating that the cohesion in crystal I is slightly weaker than that of crystal II. The cohesion in the solid state is, in turn, closely correlated to the lattice vibration. The non-radiative decay of the excited energy means the excitation of the lattice vibrations (i.e. formation of phonons). In other words, the emission process is sensitively linked to the lattice vibration. Although no difference is crystallographically recognized between crystals grown from solution or from the vapor phase, a subtle difference in cohesion exists between them and this determines the fraction of the radiative and non-radiative process.

Conclusions

The luminescent properties of crystals I and II of DCPP have been investigated from the standpoint of the crystal structure and thermal analysis. The following conclusions can be drawn from the present study.

1. DCPP exhibits no luminescence in solution while it fluoreses in the solid state. This indicates that the luminescence is due to intermolecular interactions in the solid state.
2. Crystal I (recrystallized from solution) exhibits intense orange emission, but it disappears completely above 300 °C ("thermal quenching").
3. The luminescence in crystal II (grown from the vapor phase) is much weaker than in crystal I by a factor of 6-7. However, the spectral shape of the photoluminescence and the behavior of thermal quenching are exactly the same as those of crystal I.
4. No structural difference was crstallographically recognized between crystals I and II at -180, RT, 150, and 200 °C.
5. A slight difference in sublimation temperature is observed between crystals I and II, indicating that the cohesion is slightly weaker in crystal I than in crystal II. This is closely related to the difference in lattice vibration. As a result, this may affect the fraction between the radiative and non-radiative process in crystals I and II.

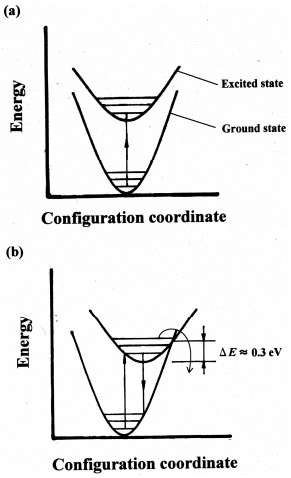

Fig. 9 Proposed Franck-Condon CC Diagrams for DCPP: (a) solution and (b) crystals I and II.

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