

Luminescence and Reversible Luminescence Thermochromism of Bulk and Microcrystals of Dibenzoylmethanoboron Difluoride

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Essential differences in the luminescence properties of dibenzoylmethanoboron difluoride (**1**) bulk and microcrystals were detected. Analysis of the spectral data showed that in every case the fluorescence spectrum of **1** consisted of three components: monomer fluorescence, excimer fluorescence, and fluorescence related with interdimer interaction. Evolution of luminescence spectra observed with decrease of the crystal size are bound with decrease of monomer fluorescence intensity and considerable growth of intensity of fluorescence related to interdimer interaction. The presence of reversible luminescence thermochromism was discovered for **1**: lowering the temperature from 300 to 77 K resulted in essential hypsochromic shift of the luminescence band maximum (~60 nm) connected with considerable decrease of the distances between the planes of the neighboring molecules (~0.1 Å) that lead to the weakening of interdimer interaction and intensification of monomer luminescence.

KEY WORDS: Dibenzoylmethanoboron difluoride; fluorescence; luminescence thermochromism; microcrystals.

INTRODUCTION

In recent years, the interest in optical properties of the nanostructures is growing [1]. The unique properties of such objects are conditioned in many respects by the electron processes both in the middle part and at the surface of the microcrystals [2]. The number of molecules at the surface and in the middle part become commensurable, therefore, the role of the surface as a more active component grows. It was found in several works [3–5] that luminescence properties of the molecular microcrystals such as perylene, pyrene, coronene, and anthracene were size-dependent and considerably differed from those of the bulk crystals. The dual emissions are explained by assum-

ing two emission centers, one in the middle and another on the periphery of microcrystals. The diffusion lengths of exciton were estimated for anthracene and perylene microcrystals from the intensity ratio of two emission bands [3]. One of the promising lines of search for new perspective luminescent materials is the study of molecular-organized organic systems, including dimers, trimers, and aggregates of conjugated molecules, whose supramolecular architecture produces different intermolecular interactions: dimeric (excimeric), interdimeric, and π -stacking interactions [6,7].

The present paper is the result of our study on the correlation of the structure and luminescence properties of β -diketonatoboron difluoride [8–10] and contains a comparative investigation of the fluorescence properties of bulk and microcrystals of dibenzoylmethanoboron difluoride (**1**); moreover, the essential dependence of the luminescence properties on the crystal size and temperature was detected.

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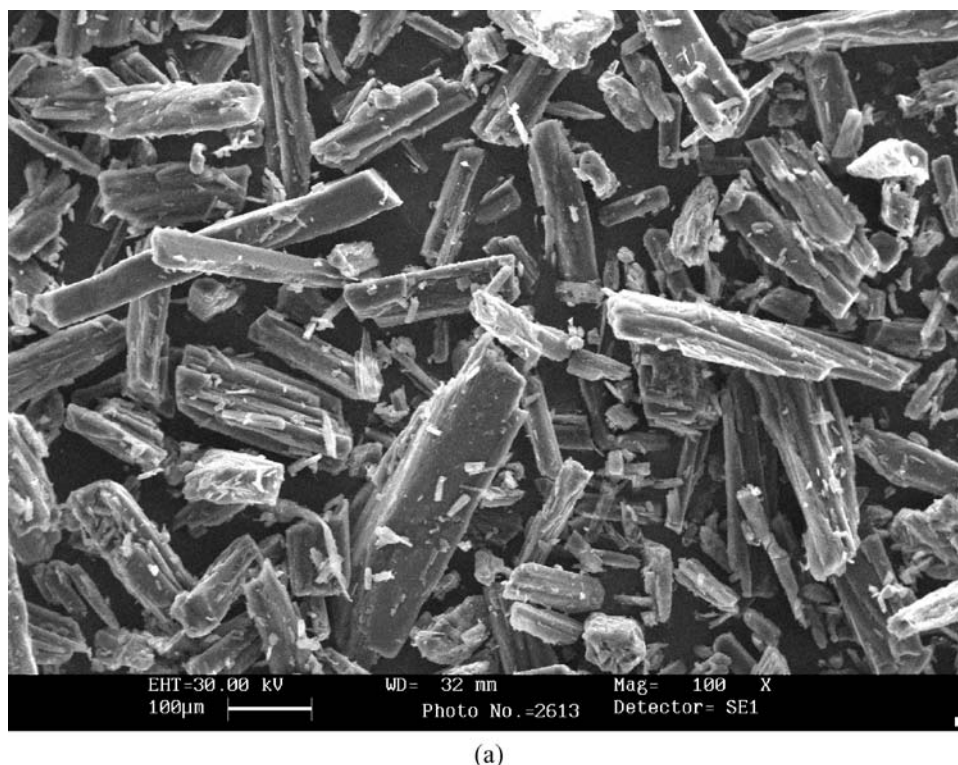


Fig. 1. SEM image of **1**: bulk crystal (a); microcrystal (b) and AFM image of surface of microcrystals (c).

EXPERIMENTAL

Compound **1** was prepared and purified according to [11], the microcrystals were obtained by grinding the bulk crystals in an agate mortar. The luminescence spectra of the crystal were registered at the temperatures 77 and 300 K on a SDL-1 (LOMO) spectrometer ($\lambda_{\text{ex}} = 365 \text{ nm}$).

The identity of the chemical composition and crystal structure of the bulk and microcrystals was proved by the ^{19}F and ^{11}B NMR spectroscopy and X-ray methods. The NMR spectra were registered on a Bruker Avance AV-300 spectrometer. The X-ray diffraction patterns of the samples were recorded on a D8 ADVANCE (CuK radiation).

The microscopic structure of the powders was studied on a scanning electron microscope (SEM) LEO-430 and on an atomic force microscope (AFM) (ZAO NT-MDT, Zelenograd, Russia).

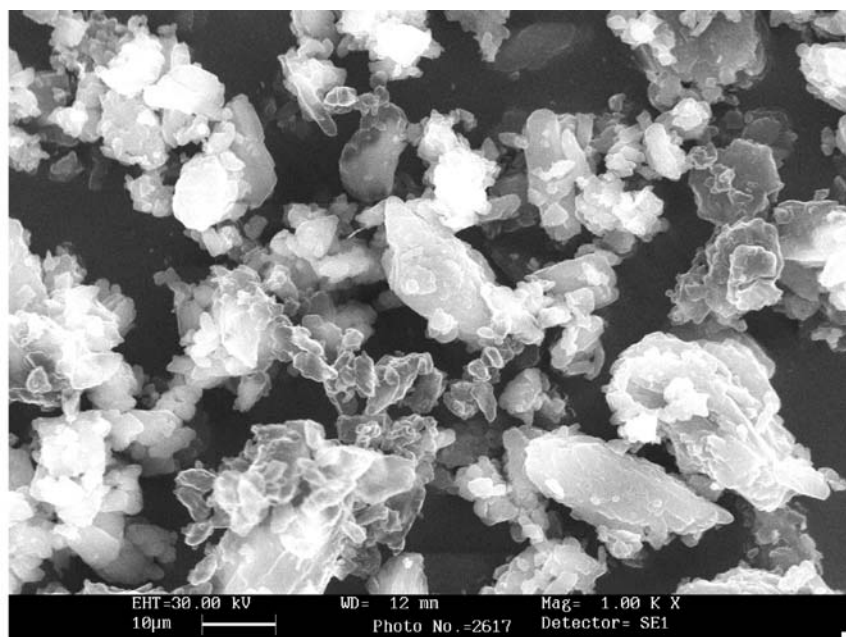
RESULTS AND DISCUSSION

The powder of the bulk crystals consists of the crystals of stretched form, size from 400–10 to 100–5 μm (Fig. 1a). The microcrystals powder consists of smaller

faceted microcrystals and particles of friable or oval form, size from 20–1 to 10–1 μm (Fig. 1b). There are the oval 100–10 nm size nanoparticles at the facets of the microcrystal (Fig. 1c).

It was found that grinding the crystals of **1** changed the luminescence color from aquamarine to green (Fig. 2). Lowering the temperature from -300 to -77 K resulted essentially in a blue shift of the luminescence spectrum for both bulk and microcrystals (Fig. 2). For more detailed analysis of the spectral variations the luminescence spectra of the bulk and microcrystals at -300 and -77 K were deconvoluted into subcomponents according to Gauss function by means of MicroCal Origin (Version 7.0) program and the result is shown in Fig. 2. It was found that the luminescence spectrum of **1** in every case consisted of three components with the maxima at 470, 500, and 560 nm and only their relative intensity was changed.

To refine the nature of the components of the fluorescence spectra of compound **1**, we compared the spectra of the crystals and solutions at different concentrations. Boron difluoride β -diketonates are characterized by both the fluorescence of single molecules (in dilute solutions) and excimers (in concentrated solutions) [9]. As can be seen in Fig. 3, the band with a maximum at 500 nm is due



(b)



(c)

Fig. 1. Continued.

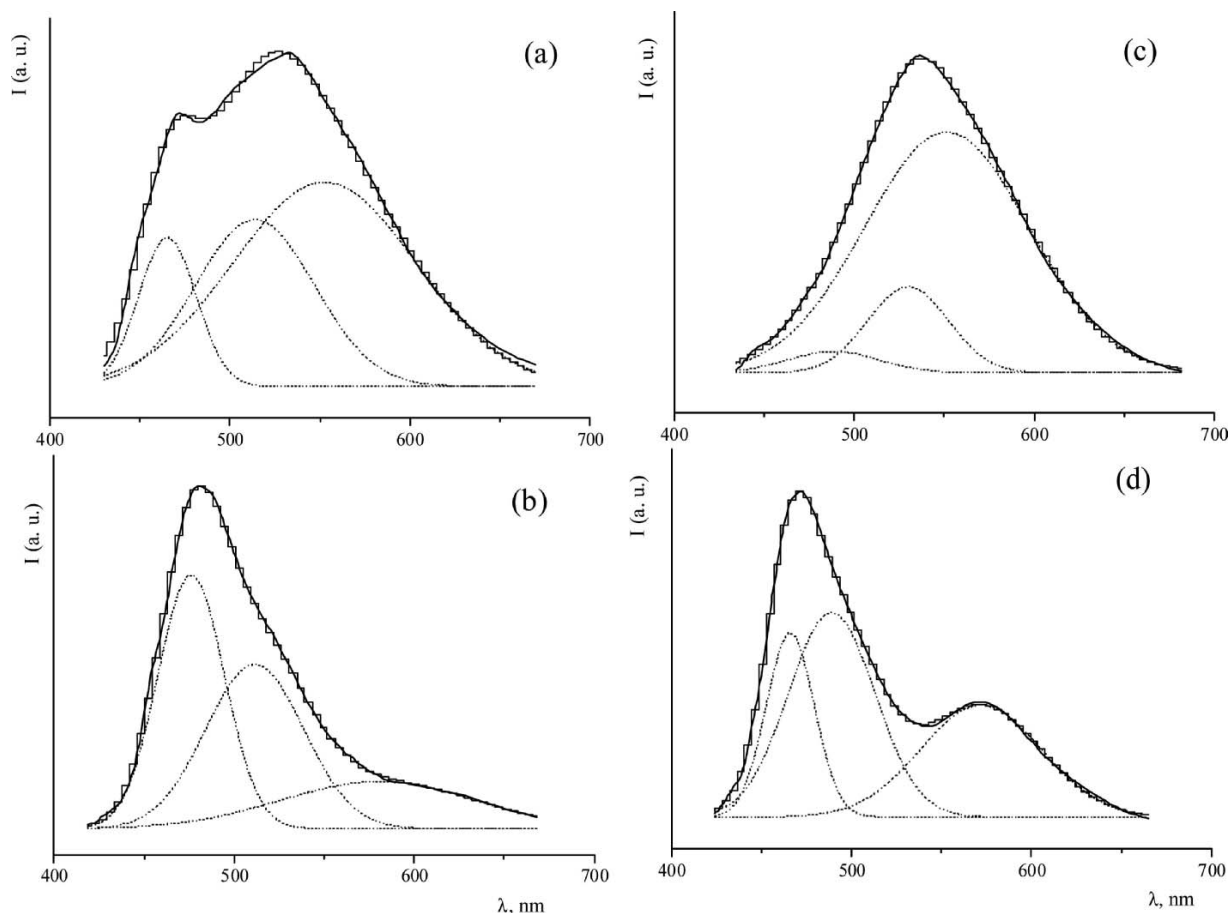
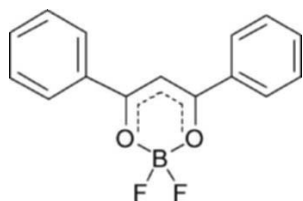


Fig. 2. Fluorescence spectra of bulk crystals of **1**: (a) 300 K, (b) 77 K; fluorescence spectra of microcrystals of **1**: (c) 300 K, (d) 77 K. Experimental spectrum (solid lines); calculate spectrum (step lines); the results of the deconvolution of the spectrum into the subcomponents (dotted lines).

to excimer fluorescence in concentrated solutions of **1** [9]. The band with a maximum at 470 nm coincides with the long-wave band in the fluorescence spectrum of a solution with a low concentration of compound **1**. According to published data [12], the absence of two other fluorescence bands of single molecules (420 and 444 nm) from the spectrum of the crystals can be due to the fact that solutions of **1** contain rotamers with different positions of the Ph rings relative to the plane of the diketonate cycle (Scheme 1).



Scheme 1

Rotamer formation becomes impossible on going to crystal **1**, because the fluorescence spectrum of the monomers is transformed into one band with a maximum at 470 nm, for which the contribution of torsional vibrations is insubstantial [12]. Thus, the first band in the fluorescence spectrum of crystals **1** (470 nm) can be assigned to fluorescence of the single molecules, the second band (500 nm) can be attributed to fluorescence of the excimers themselves, and the third band (560 nm), present only in crystals, is caused by fluorescence of interdimeric associates, which is characteristic of the compounds consisting of infinite stacks of mutually intersecting molecules [10].

According to these data, the change of the luminescence spectrum from aquamarine to green as a result of transition from bulk to microcrystals is related to a sharp decrease of intensity of the monomer fluorescence and considerable growth of intensity of fluorescence related to interdimer interaction (Fig. 2a, and c). Similar

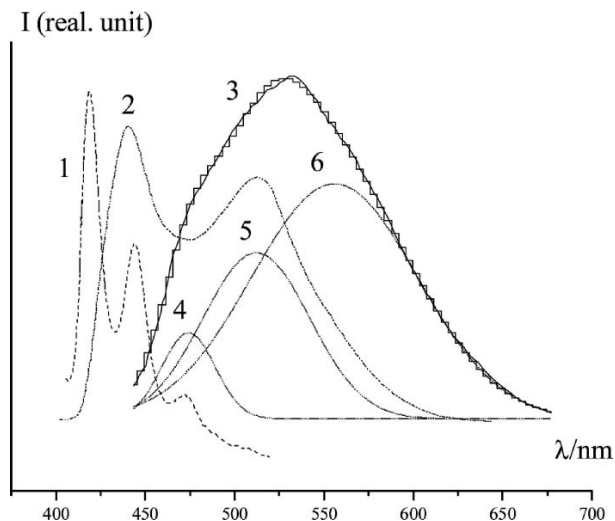


Fig. 3. Fluorescence spectra of compound **1**: (1)—solution in propanol-2 at 77 K, $C=10^{-4}$ mol L $^{-1}$; (2)—solution in chloroform at 300 K, $C=0.9$ mol L $^{-1}$; (3)—crystals at 300 K (Experimental spectrum (solid line); calculated spectrum (step line)); (4, 5, and 6)—result of deconvolution of the fluorescence spectrum to components

redistribution of intensity of the luminescence spectrum components with decrease of size of pyrene and perylene crystals (decrease of monomer fluorescence) was observed in [3,13]. According to [3], the excimer emission centers might be formed on the edge of microcrystals, where the dislocations exist and the motion of molecules might be free to take a suitable orientation for the excimer formation. Unlike pyrene crystals where the distance be-

tween the molecule pairs is about three times as much as that between molecules within the pair [14], in crystals **1**, one can observe infinite stacks of the parallel molecules with the same intermolecular distance [9]. More efficient π -stacking interaction of **1** may promote the delocalization of bound excitonic states over the aggregate (increased interdimeric interaction). Indeed, morphology of microcrystals **1** surface (Fig. 1b, and c) promotes to the exciton trap. Excitons, which are generated in the middle part of the microcrystals **1**, may diffuse to the emission centers in the periphery during the lifetime of the exciton. The centers act as a trap for the exciton and the emission related with interdimeric interaction appeared. If the exciton diffusion length is not long enough to reach the periphery, the monomeric exciton emission will be observed, since the molecules in the center of the microcrystals might be tightly fixed.

It should be noted that the problem of the role of nanoparticles formed on the microcrystal facets (Fig. 1c) on dependence of fluorescence properties upon the crystal size and temperature requires further investigation.

Reversible luminescence thermochromism was detected for both bulk and microcrystals: considerable hypsochromic shift is observed with lowering of temperature (Fig. 2). It is known that for most organic molecules, the bathochromic shift of the luminescence maximum is observed when the temperature is lowered [15]. For bulk crystals of **1**, lowering of the temperature from room temperature to 77 K is accompanied by the change of luminescence color from aquamarine to blue. It is seen in

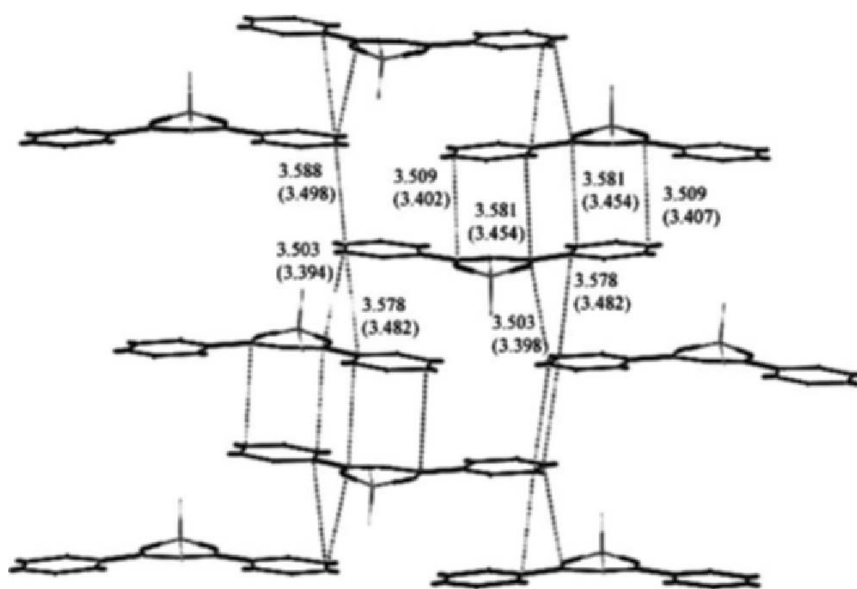


Fig. 4. Infinite stacks of molecule **1** [9]. Selected intermolecular distances in Å at 300 (123) K

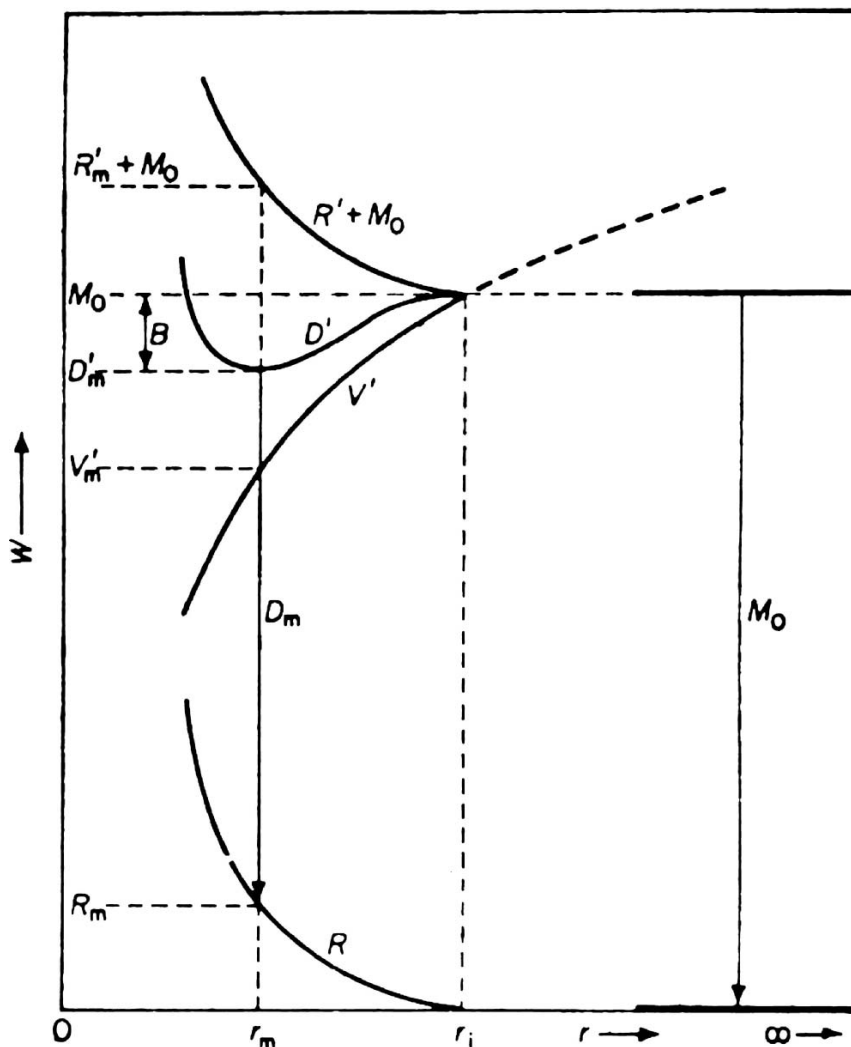


Fig. 5. Schematic potential energy (W) diagram of parallel molecules ${}^1M^*$ and 1M as a function of intermolecular separation (r). R , R' , repulsive potentials in ground (1M) and excited (${}^1M^*$) states; V' , excimer interaction potential; $D' = V' + R'$, resultant excimer energy; M_0 , molecular 0-0 transition; D_m , peak excimer transition; R_m , R'_m , V'_m , D'_m potentials at equilibrium excimer separation, r_m [16].

the luminescence spectra as considerable growth of intensity of the monomer and excimer fluorescence bands with simultaneous decrease of that related to interdimer interaction (Fig. 2b, and d). It should be noted that the decrease of intensity of fluorescence related to interdimer interaction in microcrystals with decreasing temperature is not so strong as for bulk crystals.

We have earlier [9] determined the crystal structure of compound **1**. The molecules in the crystal are arranged as infinite stacks parallel to the c -axis (Fig. 4). The two types of intersecting molecules alternate within the stacks of crystals **1**. For the first type, the Ph rings of the two adjacent molecules overlap, and the second case is the

overlap of the β -diketonate and phenyl rings of the adjacent molecules [9]. As a whole, the architecture of the molecular crystal **1** favors the appearance of stacking interaction.

The unit cell parameters of crystal **1** were measured at different temperatures. As the temperature decreases, the a and b parameters reflect their natural decrease in directions close to the plane of molecules **1**, whereas a considerable decrease in the parameter toward the c -axis (0.386 Å) reflects a substantial decrease in the distances between the planes of adjacent molecules in the stacks. The details of the temperature changes of the intermolecular distances in **1** are shown in Fig. 4. The figure shows that

the average decrease of the distance between the planes of the neighboring molecules is about $\sim 0.1 \text{ \AA}$ [8].

The optimum conditions for excimer formation depending on the intermolecular distance r are given in [16]. Figure 5 is a schematic potential energy diagram of a pair of parallel singlet-excited ($^1M^*$) and unexcited (1M) molecules of the same species as a function of intermolecular separation (r). $V'(r)$ is the excimer interaction potential of the lowest singlet excimer states $^1D^*$. $R(r)$ and $R'(r)$ are the intermolecular repulsive potentials in ground and excited states, respectively, and it is normally assumed that $R(r) = R'(r)$. The resultant singlet excimer energy is

$$D' = V' + R'$$

$M_0 = S_1^0$ is the $^1M^*$ energy corresponding to the 0–0 S_1-S_0 fluorescence transition, and D_m is the energy of the $^1D^*$ fluorescence maximum. For excimer formation to occur the parameter

$$\begin{aligned} B(r) &= M_0 - D'(r) = M_0 - V'(r) - R'(r) \\ &= \Delta E_{DM}(r) - R'(r) \end{aligned}$$

must have a positive maximum of B , the $^1D^*$ binding energy, at $r = r_m$, the equilibrium D separation. R_m , $R'_m = R_m$, $V_m = D_m$ and D_m are the potentials at $r = r_m$, so that

$$B = M_0 - D_m - R_m$$

$\Delta E_{DM}(r) = M_0 - V'(r)$ is the excimer associative potential, which must exceed the repulsive potential $R'(r)$ for excimer formation to occur. At $r = r_m$, $\Delta E_{DM}(r)$ becomes

$$\Delta E_{DM} = M_0 - D_m$$

the $^1M^*-^1D^*$ spectroscopic energy gap.

As seen from the scheme presented, a decrease of intermolecular separation (r) results in a breach of the optimum conditions of excimer formation. Decrease of r in a certain point of the potential curve D' may result in isoenergetic transition of excimer state into monomer one. Thus, the decrease of the intermolecular distance in stack of **1** with decrease in temperature (Fig. 4) promotes an increase in the repulsion potential R' and thereby results in the growth of monomer fluorescence intensity.

CONCLUSION

The essential differences in the luminescence properties of the bulk and microcrystals of **1** were found. An analysis of spectral data showed that the fluorescence spectrum of **1** in every case consisted of three components: monomer fluorescence, excimer fluorescence, and that related to interdimer interaction. The spectral changes

observed with the decrease of the crystal size are connected with the decrease of intensity of monomer fluorescence and considerable growth of fluorescence related to interdimer interaction.

The presence of reversible luminescence thermochromism was also observed for **1**: the temperature decrease from 300 to 77 K resulted essentially in a hypsochromic shift of the luminescence band maximum. This shift is due to considerable decrease of the distances between the planes of the neighboring molecules and results in weakening of interdimer interaction and strengthening of the monomer fluorescence.

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REFERENCES

1. M. Wu, J. R. Lakowicz, and C. D. Geddes (2005). Enhanced lanthanide luminescence using silver nanostructures: Opportunities for a new class of probes with exceptional spectral characteristics. *J. Fluoresc.* **15**(1), 53–58.
2. S. C. Tjong and H. Chen (2004). Nanocrystalline materials and coatings. *Mater. Sci. Eng.: R: Reports* **45**(1–2), 1–88.
3. T. Seko, K. Ogura, Y. Kawakami, H. Sugino, H. Toyotama, and J. Tanaka (1998). Excimer emission of anthracene, perylene, coronene and pyrene microcrystals dispersed in water. *Chem. Phys. Lett.* **291**(17), 438–444.
4. R. Weinberger and L. J. Cline Love (1984). Luminescence properties of polycyclic aromatic hydrocarbons in colloidal or microcrystalline suspensions. *Spectrochim. Acta. Part A* **40**(1), 49–55.
5. N. Ikeda, M. Koshioka, H. Masuhara, and K. Yoshihara (1988). Picosecond dynamics of excited singlet states in organic microcrystals: Diffuse reflectance laser photolysis study. *Chem. Phys. Lett.* **150**(6), 452–456.
6. M. L. Glowka, D. Martynowski, and K. Koztowska (1999). Stacking of six-membered aromatic rings in crystals. *J. Mol. Struct.* **474**, 81–89.
7. P. W. Carter, S. G. DiMugno, J. D. Porter, and A. Streitwieser (1993). (-) Stacking and aggregation of pyridinium-substituted indolizines. *J. Phys. Chem.* **97**(5), 1085–1096.
8. A. G. Mirochnik, E. V. Fedorenko, B. V. Bukvetskii, and V. E. Karasev (2005). Reversible luminescence thermochromism of dibenzoylmethanaboron difluoride. *Russ. Chem. Bull.* **54**(4), 17–19.
9. A. G. Mirochnik, B. V. Bukvetskii, E. V. Gukhman, and V. E. Karasev (2001). Crystal structure and excimer fluorescence of dibenzoylmethanaboron difluoride. *Russ. Chem. Bull.* **50**(9), 1612–1615.
10. A. G. Mirochnik, B. V. Bukvetskii, E. V. Gukhman, and V. E. Karasev (2003). Crystal structure and excimer fluorescence of some benzoylacetonaboron difluorides: stacking factor. *J. Fluoresc.* **13**(2), 157–162.
11. V. E. Karasev and O. A. Korotkich (1986). Spectral-luminescence properties of F₂B(-diketonates). *Russ. J. Inorg. Chem.* **31**(4), 869–872.
12. Y. L. Chow, X. Cheng, and C. I. Johansson (1991). Molecular interactions of dibenzoylmethanaboron difluoride (DBMBF₂) in the excited and ground states in solution. *J. Photochem. Photobiol. A: Chem.* **57**, 247–255.

13. J.-I. Nitsuma, T. Fujimura, T. Itoh, H. Kasai, H. Oikawa, and H. Naknishi (2001). Scanning near-field optical microscopy of single perylene microcrystals. *Int J. Modern Phys. B* **15**(28–30), 3901–3903.
14. S. C. Ganguly and N. K. Choudhury (1953). Polarized fluorescence of molecules of some single organic crystals. *J. Chem. Phys.* **21**(3), 554–557.
15. M. D. Cohen, Z. Ludmer, and V. Yakhot (1975). The fluorescence properties of crystalline anthracenes and their dependence on the crystal structures. *Phys. Stat. Sol. (b)* **67**, 51–61.
16. J. B. Birks (1975). The photophysics of aromatic excimers. In M. Gordon and W. R. Ware (eds.), *The Exciples*, Academic Press, Inc., New York, pp. 39–73.