

Accepted manuscript

Manuscript No.: BCSJ-2014-0409

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Received Date: 27-Dec-2014

Accepted Date: 8-Feb-2015

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Feb. 9, 2015

Optical properties of three differently colored crystal modifications of a 2,3-dicyanopyrazine dye

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Abstract

Optical properties of three crystal modifications of 5-*t*-butyl-2,3-dicyano-6-[4-(dimethylamino)styryl]-pyrazine having different color appearances were measured and interpreted on the basis of a crystal structure analysis. Two of the three modifications exhibited a bathochromic spectral shift both in absorption and fluorescence compared with those in a toluene solution of the dye. The crystal structure analysis revealed that a

two-dimensional brick-wall structure is formed in both modifications. In contrast, the third modification showed a hypsochromic absorption shift with a large bathochromic fluorescence shift. The crystal structure of this modification was characterized by a one-dimensional stacked molecular column. The optical characteristics of the three modifications were qualitatively interpreted in terms of excitonic intermolecular interaction on the basis of their crystal structures.

Solid-state optical properties of organic compounds are of great importance in their applications to solid materials and devices from a scientific as well as a technological perspective¹⁻⁴. Organic pigments are a typical application example of organic solids^{1,5}. Their color hue in a powdered form and/or in a mixed medium is an important material specification as colorants. Recently, organic light emitting technology has become very popular in the display industry for mobile devices; this technology is also expected to be used in large-sized displays for televisions as well as flexible planar light sources⁶⁻⁸. In such applications of solid-state organic compounds, it is very important to understand the structure–optical properties relationship, because a distinct difference between the optical properties of organic compounds in the solution and solid states has been observed¹⁻⁵. Further, crystal polymorphism is another important parameter to be considered in the applications of organic solids, because it results in two or more solid forms with (sometimes significantly) different solid properties^{9,10}. Polymorphic forms of a certain dye have been used to make different organic pigment products with different color hues and/or different pigment properties^{1,5}. It is also well known that polymorphism plays an important role in the technologies underlying organic photoconductors^{1,11} and organic semiconductors^{4,12}.

Organic dyes based on a pyrazine skeleton are known as good candidates for fluorescent materials¹³⁻¹⁶. Some of them have been reported to exhibit strong fluorescence even in the solid state^{13,17,18}. Their conformational polymorphs with different colors have also been reported¹⁹. 2,3-Dicyanopyrazine is a potential chromophore for a fluorescent dye emitting in the solid state^{13,18}. Dye **1**, 5-*t*-butyl-2,3-dicyano-6-[4-(dimethylamino)styryl]-pyrazine, shown in Scheme 1 was prepared for the investigation of thin solid film preparation of 2,3-dicyanopyrazine dyes²⁰. Crystallization experiments indicated that **1** forms three crystal modifications (**I**, **II**, and **III**) in a crystallization tube. Among the three modifications, one modification (**I**) with good solid-state fluorescence usually crystallized during the early stages of crystallization, and then transformed into the other two crystal modifications. This bright modification **I** was found to be a chloroform solvate of **1**, whose solid-state optical response and crystal structure bore a resemblance to those of

J-aggregates²¹. The color appearance of **1** in toluene and those of its three crystal modifications under room and UV light are shown in Fig. 1.

In this paper, the crystal structure and solid-state optical properties of the three crystal modifications of **1** are reported. Moreover, the spectral shifts of the three solid forms from that in solution in terms of excitonic intermolecular interaction are interpreted. Further, the crystal growth and phase transformation behaviors of the three modifications under crystallization conditions are also reported.

Experimental

Reagents and instruments

Dye **1** was prepared by a procedure reported earlier and was identified by several spectroscopic methods²¹. High-grade organic solvents were used as received without further treatment. UV-visible (UV-vis) absorption and fluorescence spectra of **1** in solution were recorded using a Perkin Elmer Lambda 750 spectrometer and a Perkin Elmer LS45 fluorescent spectrometer, respectively. A System Instruments SIS-50 surface and interface spectrometer based on optical waveguide spectroscopy²² was used to measure solid-state absorption spectra in the visible region. Fluorescence spectra and quantum efficiency in the solid state were determined using a home-made setup composed of a blue diode laser (CrystaLaser), an integrating sphere (Labsphere), and a photo-multichannel analyzer (Hamamatsu, PMA-11). We irradiated a laser beam on crystal samples placed on a quartz substrate, and evaluated the reflected and absorbed parts of the laser beam, as well as the fluorescence of the crystals. Then, we calculated photon numbers for the fluorescence and adsorbed laser beam. Fluorescence quantum efficiency was obtained as the ratio of the two photon numbers²³. Powder samples for fluorescence measurement were identified by powder X-ray diffraction before conducting measurement using a diffractometer (described in the next section). Differential scanning calorimetry (DSC) analysis was carried out using a Rigaku Thermoplus DSC8230 at a heating rate of 10 °C/min.

X-ray structural analysis

Single crystals of modifications **II** and **III** were obtained by a liquid–liquid diffusion method using tetrahydrofuran and cyclohexane in a thin glass tube. X-ray diffraction data for modifications **II** and **III** were collected on a Rigaku RAXIS RAPID imaging plate diffractometer using graphite-monochromated Cu-K α radiation ($\lambda = 1.54187 \text{ \AA}$) at 296 K and 93 K, respectively. Both structures were solved by a direct method (SIR 92²⁴) and then refined by full-matrix least-squares calculations. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located at calculated positions and refined using a riding model. All calculations were performed using the CrystalStructure 3.8 and 4.0 crystallographic software package^{25,26}. Crystal data for modification **II**: C₂₀H₂₁N₅, M = 331.42, triclinic, $a = 7.7125(2) \text{ \AA}$, $b = 9.6887(2) \text{ \AA}$, $c = 13.4815(3) \text{ \AA}$, $\alpha = 108.009(1)^\circ$, $\beta = 94.136(2)^\circ$, $\gamma = 98.974(2)^\circ$, $D_{\text{calcd}} = 1.173 \text{ g cm}^{-3}$, $V = 938.52(4) \text{ \AA}^3$, $T = 296 \text{ K}$, space group $P-1$, $Z = 2$, 10215 reflections measured, 3259 independent reflections ($R_{\text{int}} = 0.061$). The final R_1 value ($I > 2\sigma(I)$), final $wR(F^2)$ value (all data), and GOF were 0.0575, 0.1640, and 1.000, respectively. Crystal data for modification **III**: C₂₀H₂₁N₅, M = 331.42, orthorhombic, $a = 18.32(2) \text{ \AA}$, $b = 14.94(1) \text{ \AA}$, $c = 6.71(2) \text{ \AA}$, $D_{\text{calcd}} = 1.199 \text{ g cm}^{-3}$, $V = 1835.8(3) \text{ \AA}^3$, $T = 93.1 \text{ K}$, space group $Pna2_1$, $Z = 4$, 3251 reflections measured, 3251 independent reflections ($R_{\text{int}} = 0.120$). The final R_1 value ($I > 2\sigma(I)$), final $wR(F^2)$ value (all data), and GOF were 0.0782, 0.3335, and 0.863, respectively. The CCDC deposition numbers for **II** and **III** are CCDC1040960 and CCDC1040961, respectively.

Calculation of intermolecular interaction

Electronic spectra were calculated at a semi-empirical PM5 level²⁷ with a random phase approximation (RPA)^{28,29} by using the MO-S program in the SCIGRESS V2.0 program package³⁰. All calculations were performed on the basis of the molecular geometry of the crystal structure with H atoms at the calculated positions. In this study, 257 singly excited configuration state functions

were used for the RPA calculation. Exciton interactions³¹⁻³⁵ were estimated using an extended dipole model³³⁻³⁵ on the basis of the nearest neighbor approximation^{36,37}. For a dimer, exciton interaction energy (ΔE_{dimer}), which corresponds to a spectral shift, was calculated as follows:

$$\Delta E_{\text{dimer}} = |Q|^2 (1/r_1 + 1/r_2 - 1/r_3 - 1/r_4) / 4\pi\epsilon_0\epsilon \quad (1)$$

where Q is the charge, ϵ_0 is the vacuum permittivity, ϵ is the relative dielectric constant, and r is the distance between the charges. The relative dielectric constant of the organic compounds was considered as 2.5. The product of Q and the dipole length l was assumed to be the transition moment μ obtained from the molecular orbital calculation. The term $(1/r_1 + 1/r_2 - 1/r_3 - 1/r_4)$ depends on the geometrical relationship between the transition dipoles in the crystal structure. For an aggregate state, the total exciton interaction energy was approximated by the summation of all the exciton interaction energies between a reference molecule and all other molecules. In this study, 10 molecular pairs were taken into consideration.

Results and discussions

Crystallization of **1**

We first started the crystallization of **1** by a liquid–liquid diffusion method using chloroform and *n*-hexane. Under these solvent conditions, lustrous red platelets (modification **I**), which is a chloroform solvate of **1**²¹, was formed within one day after sample preparation. Afterward, modification **I** was gradually transformed to black block crystals (modification **II**) and/or reddish-purple flakes (modification **III**) in the same tube within the next several days. Modification **III** was infrequently found to change to modification **II**. We also observed several samples in which modification **II** was initially formed and no further change was recognized. The schematic growth outline for the three modifications in this solvent component is illustrated in Fig. 2. The quality of the obtained crystals of modifications **II** and **III** through the above-mentioned phase transition was usually not good for X-ray analysis. Therefore, the crystallization of **1** was again carried out using another solvent combination, as described in the Experimental section, for obtaining good-quality

single crystals for X-ray analysis.

Fig. 3 shows the DSC curves for the three crystal modifications. All modifications showed a sharp melting point at around 249 °C. For modification **I**, a large endothermic peak at around 68 °C was observed. This was characterized by a release of the included chloroform molecules, as revealed by thermogravimetric analysis²¹. Modification **II** showed a very small and broad endothermic peak at around 165 °C. On the basis of the observation of a thermal phase change in modification **II** by using a hot plate, it was suggested that modification **II** transformed into modification **III** around this temperature. This result indicates that modification **III** is more energetically stable than modification **II** in a high-temperature region. However, on the basis of the phase transition behavior in the preparation tubes, it was suggested that under room temperature conditions, modification **II** may be more stable than modification **III**.

Crystal structure of three modifications

The crystal structure of the three modifications is shown in Fig. 4; among these, the structure of modification **I** has already been reported earlier²¹. In all the three modifications, molecules had a planar π -conjugation system without any remarkable difference in their molecular geometry. This result suggests that no significant difference existed between the electronic states of a molecule in these modifications. However, the molecular arrangement of the three modifications was found to be completely different. In modifications **I** and **III**, molecules were stacked in a brick-wall fashion³² to form a J-aggregate-like two-dimensional (2D) molecular layer. The interplanar distance and slip angle between the stacking dye molecules were about 3.38 Å and 24.3°, respectively, in modification **I**, and about 3.28 Å and 24.0°, respectively, in modification **III**. These 2D layers aligned to form a three-dimensional (3D) structure in both modifications, although the molecular directions between neighboring 2D layers were same in modification **I** but opposite in modification **III**. Interestingly, modification **I** in which the 2D layers were oriented in the same direction was easily transformed into modification **III** in which the 2D layers were oriented in opposite directions.

Modification **II** had an independent molecular arrangement. In this modification, molecules were stacked in opposite directions along the *a*-axis to form a one-dimensional (1D) molecular column along with the formation of a complete overlap of the chromophore. The interplanar distance between the stacking dye molecules was about 3.42 Å and 3.48 Å in this modification. The corresponding slip angles were about 71.5° and 54.6°, respectively. These 1D molecular columns were aligned along the (101) direction and *b*-axis to form a 3D structure. The 2D stacking molecular layer shown in Fig. 4 can be regarded as a staircase molecular arrangement proposed for a potential 2D molecular arrangement of J-aggregates^{32,38,39}. The difference between the color appearances of these modifications can be correlated with this remarkable difference in their crystal structures.

Optical properties

The absorption and fluorescence spectra of **1** in a toluene solution and those of the three modifications are depicted in Figs. 5 and 6, respectively. Their spectral characteristics are summarized in Table 1. The absorption spectrum of modification **I** was reported to shift toward the longer-wavelength region compared to that in toluene²¹. Modification **III** showed similar absorption characteristics as those of modification **I**. The bathochromic shift of modification **III** in solution was 91 nm. This relatively large bathochromic shift was estimated to be 3320 cm⁻¹ in energy units. The absorption of modification **II** was, in contrast, found to shift hypsochromically compared to that in toluene, where its absorption peak was observed at around 462 nm. Further, the shape of the absorption peak for modification **II** was more distinct than those for modifications **I** and **III**. The spectra for modifications **I** and **III** contained a long peak with a shoulder peak in the shorter-wavelength region. This spectral component was comparable to that of the solution spectrum, although there was no clear progression in the solution band. Modification **II** had a clearly different spectral shape. The absorption peak was in the shorter-wavelength region of the spectrum with a gentle and downward slope continuing toward the longer-wavelength region. This

spectral shape bore a resemblance of absorption spectra of dyes showing a hypsochromic spectral shift due to H-aggregate-type dimmer formation in solution^{40,41} and H-aggregate-type electronic interactions in a solid state^{20,42}. This result suggests that differences exist between the electronic states of these modifications, particularly between modifications **I** and **III**, and modification **II**. The color of crystals of modification **II** was recognized as black in crystal growth experiments. Its actual color was, however, reddish-orange as characterized from the observed absorption spectrum.

We also observed an interesting aspect of the electronic states of these modifications from the fluorescence measurement results. A characteristic sharp emission peak of modification **I** at around 619 nm was characterized by a J-aggregate-like electronic feature based on the specific brick-wall molecular arrangement in its crystal structure²¹. The shape of the fluorescence band of modification **III** can be characterized as being identical to that of the broad spectral component of modification **I** ranging from 600 nm to 750 nm. This assumption was supported by a corroborative experimental observation: the sharp emission peak of modification **I** gradually decreased with increasing emission intensity around the longer-wavelength broad component because of a gradual phase transition from **I** to **III**²¹. The fluorescence characteristics of modification **II** were different from those of the other two modifications. Its fluorescence maximum was observed around the near-infrared region, and its Stoke's shift was calculated to be about 272 nm. This Stoke's shift corresponds to a very large energy shift of 8021 cm⁻¹, thereby showing the formation of H-aggregate-like electronic states^{20,31,34,42}. The fluorescence quantum efficiencies of these modifications were not large and did not have any significant difference. The structure analysis showed that there was no significant difference between the molecular geometries of the three modifications. Therefore, the molecular arrangement of the modifications may affect their characteristic optical properties.

Interpretation of electronic states

Several intermolecular interactions are known to be responsible for spectral changes in organic

dyes from solution to crystalline states. Exciton interaction is a quantum mechanical resonance effect that is strongly dependent on absorption properties of a molecule and its arrangement in an aggregated state³¹⁻³⁵. This interaction is particularly important in case a dye molecule has a large molar extinction coefficient. Optical properties of dye aggregates and dye crystals have been successfully interpreted on the basis of this interaction^{21,32-37}. The electronic states of the three modifications in this study were considered in terms of this interaction. CT interactions⁴³ were not considered in this work for simplicity. The electronic states of a molecule in each modification were calculated using a fractional coordinate set of X-ray structure data, and it was confirmed that no remarkable difference existed among the modifications, as suggested by the structural analysis. Fig. 7 shows the HOMO, LUMO, and transition moment of the calculated visible absorption of a molecule in modification **II** as a representative. The major contribution of the calculated visible transition at around 430 nm was a HOMO–LUMO transition. Its oscillator strength was estimated to be about 0.8. As shown in Fig. 7(a), the HOMO and LUMO were distributed around the dimethylaminostyryl moiety and dicyanopirazine ring, respectively. This result clearly shows that **1** had an intramolecular charge transfer system along the direction shown in Fig. 7(c).

The energy contribution of the exciton interaction was estimated for 10 molecular pairs by using an extended dipole model on the basis of the nearest neighbor approximation. The total energy contribution for modifications **I**, **II**, and **III** was -845 cm^{-1} , $+14\text{ cm}^{-1}$, and -1019 cm^{-1} , respectively. The plus and minus signs in this energy contribution correspond to hypsochromic and bathochromic spectral shifts, respectively. The calculated values were qualitatively in good agreement with the observed spectral properties. The analogous absorption characteristics of modifications **I** and **III** showing a relatively large bathochromic spectral shift can be interpreted by this calculation result. In these modifications, molecular pairs in the 2D brick-wall molecular layer were found to give a large energy contribution. The sharp emission peak of modification **I** was assigned to correspond to a J-aggregate-like electronic state²¹. The difference between the molecular arrangements of modifications **I** and **III**, that is, the molecular direction between neighboring 2D stacking layers,

may have caused the difference in their fluorescent spectra. The hypsochromic energy shift calculated for modification **II** indicated that this modification formed H-aggregate-like electronic states^{31,34}, where a hypsochromic absorption shift may result with a bathochromic fluorescence shift and a large Stoke's shift. This is basically in agreement with the observed spectral characteristics of modification **II**. The different color appearances of the present three crystal modifications were thus characterized by considering intermolecular interactions dependent on the molecular arrangement in their crystal structures.

Conclusions

A 2,3-dicyanopyrazine dye, 5-*t*-butyl-2,3-dicyano-6-[4-(dimethylamino)styryl]-pyrazine, was found to form three crystal modifications having different color appearances. Their absorption and fluorescence properties were investigated on the basis of their crystal structures. Their crystal structures were categorized into two types: two modifications formed a two-dimensional brick-wall stacking structure and one modification formed a one-dimensional molecular column. These stacking structure types were successfully correlated with the absorption and fluorescence characteristics of the modifications in terms of excitonic intermolecular interactions. Thin film applications will be the next subject of research on this dye showing polymorphic forms with different optical properties.

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Figure captions

Scheme 1 Chemical structure of dye **1**.

Figure 1 Photographs of dye **1** in toluene and its three crystal modifications under (a) room light and (b) UV light.

Figure 2 Schematic outline of crystal growth and phase transition of dye **1** in chloroform and *c*-hexane.

Figure 3 DSC curves for three crystal modifications of dye **1**.

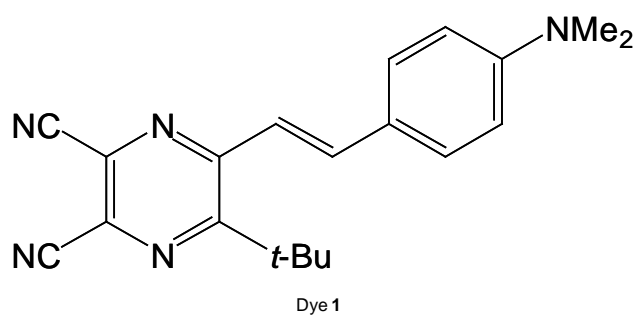
Figure 4 Crystal structure of three crystal modifications of dye **1**, focusing on two-dimensional molecular stacking structure.

Figure 5 UV-vis absorption spectra of dye **1** in toluene and its three crystal modifications.

Figure 6 Fluorescence spectra of dye **1** in toluene and its three crystal modifications.

Figure 7 Electronic properties of a molecule in modification **II** with respect to calculated visible absorption: (a) HOMO, (b) LUMO, and (c) corresponding transition dipole moment.

Table 1 Absorption and fluorescence characteristics of dye **1** in toluene and its three crystal modifications.



Scheme 1

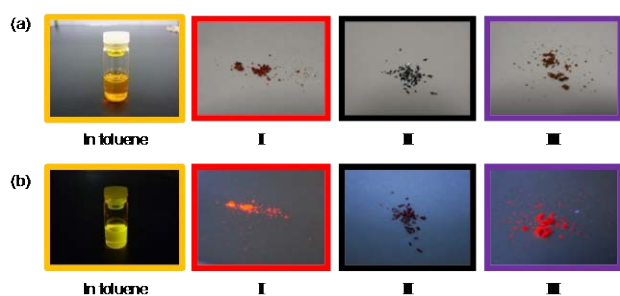


Figure 1

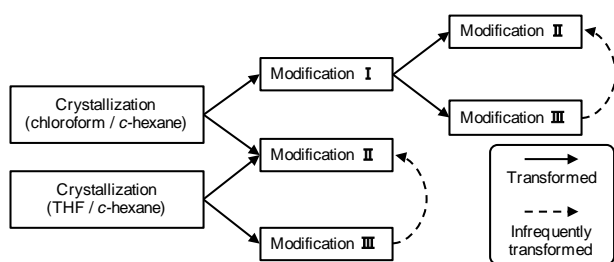


Figure 2

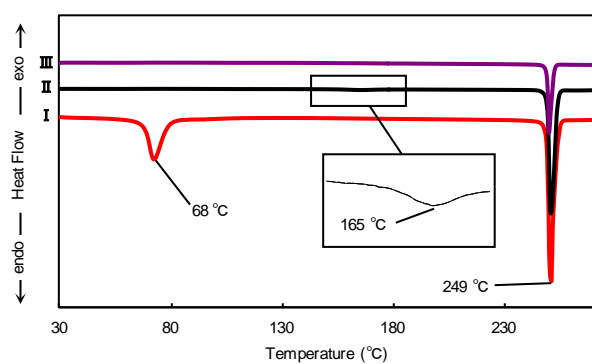


Figure 3

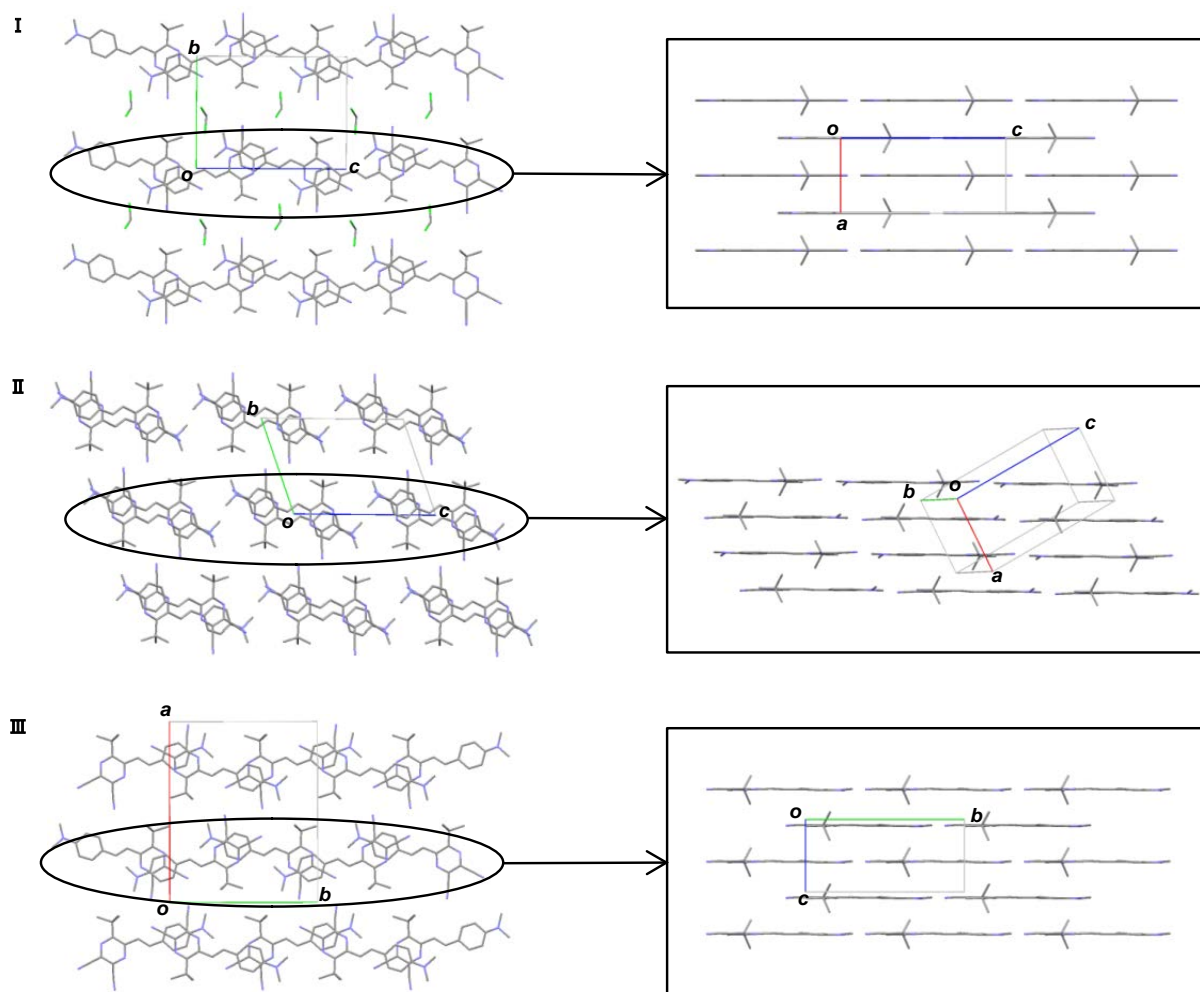


Figure 4

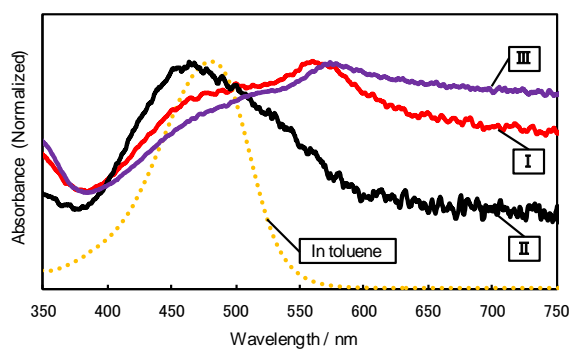


Figure 5

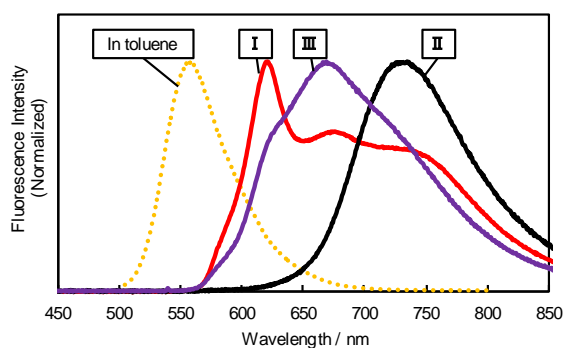


Figure 6

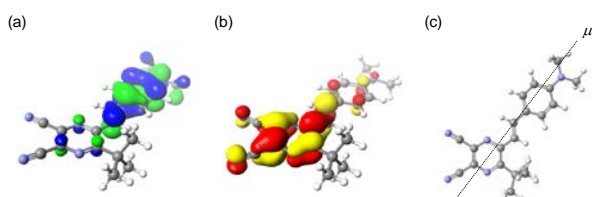


Figure 7

Table 1

	λ_{\max}/nm	$\Delta\lambda^a/\text{nm}$	$\Delta E^b/\text{cm}^{-1}$	F_{\max}/nm	Φ_f^e	SS^f/nm
In toluene	480			556 ^c	0.21	76
I	559	+79	-2944	619 ^d	0.11	60
II	462	-18	+812	734 ^d	0.07	272
III	571	+91	-3320	668 ^d	0.09	87

^a $\Delta\lambda = \lambda_{\max}(\text{Solid}) - \lambda_{\max}(\text{Solution})$. ^b $\Delta E = 1/\lambda_{\max}(\text{Solid}) - 1/\lambda_{\max}(\text{Solution})$. ^c F_{\max} (Solution) excited at 480 nm. ^d F_{\max} (Solid) excited at 375 nm. ^e Fluorescence quantum efficiency. ^f Stokes shift, $F_{\max} - \lambda_{\max}$.

Graphical abstract

Optical properties of three differently colored crystal modifications of a 2,3-dicyanopyrazine dye

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Absorption and fluorescence properties of differently colored three crystal modifications of a 2,3-dicyanopyrazine dye were interpreted by characteristic molecular arrangement in their crystal structures in terms of excitonic intermolecular interactions.

