A Series of Polymorphs with Different Colors in Fluorescent 2,5-Diamino-3,6-dicyanopyrazine Dyes

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We found a series of polymorphs with different colors in 2,5-diamino-3,6-dicyanopyrazine dyes. Their color difference was found to be caused by conformational change in the crystals, not by exciton interactions.

Polymorphism is a phenomenon in which a substance exhibits two or more different arrangements of molecules in a crystalline state. The importance of polymorphism has long been recognized, because a single substance can yield solids having entirely different properties as a result of different molecular arrangements. Therefore, much scientific and technological work has been dedicated to the interpretation of polymorphic phenomena as well as to controlling the properties of solids exhibiting it.[1] Currently, polymorphism is playing an important role in a number of industrial fields such as pharmaceuticals, colorants, foods, and explosives. However, the structure–property relationships in polymorphs have still not been fully explained.

Recently, a form of polymorphism known as color polymorphism[2] involving color change has been intensively studied from the standpoint of structure–property relationships on the basis of intermolecular interactions. A very exciting example was given by Yu et al.[3] They reported six polymorphs of 5-methyl-2-[(2-nitrophenyl)amino]-3-thiophenecarbonitrile with different colors and habits. Previously, there had been no report of such a large number of polymorphs of a single substance in single crystals. Another famous example is phthalocyanine, one of the most important dyes for pigments as well as a functional dye.[4] In the case of phthalocyanines, many polymorphs are studied in polycrystalline powder or vacuum-deposited thin films. Therefore, the details are not well understood, despite many attempts to characterize the optical and electronic properties of their polymorphs.[5] The former example provides many polymorphs of a single substance in single crystals. This makes the interpretation of properties of polymorphs based on their structure, an attractive approach to studying structure–property relations. The latter example provides many polymorphs in a series of compounds, a situation which should be advantageous for efforts in R&D of functional organic materials. But, in order to follow the long-term goal of systematically improving and/or modifying solid-state properties via structure–property relationships, polymorphs in single crystal form are essential to obtain the structural details by single crystal analysis. Here, we report an important example of color polymorphism, a series of polymorphs of different colors in single crystals of fluorescent 2,5-diamino-3,6-dicyanopyrazine dyes.

2,5-Diamino-3,6-dicyanopyrazine derivatives have been developed as a functional dye for a wide variety of opto-electronic applications.[6] Their most important characteristic is intense fluorescence in solution and in the solid state. They are also found to have crystal polymorphs with different colors. The four dyes shown in Figure 1 have the same chromophoric system.[7] The substituent R is not conjugated with the chromophore, so that no significant difference is observed in the color and absorption spectra of their solutions. In the solid state, however, they exhibit a variety of colors from yellow to red (R, RO, YO, and Y are abbreviation for the color of crystals, red, reddish-orange, yellowish-orange, and yellow, respectively). Orange polymorphs for **1** and **3** were obtained by slow evaporation from a benzene solution. The other polymorphs were prepared by solvent diffusion method using an appropriate combination of good

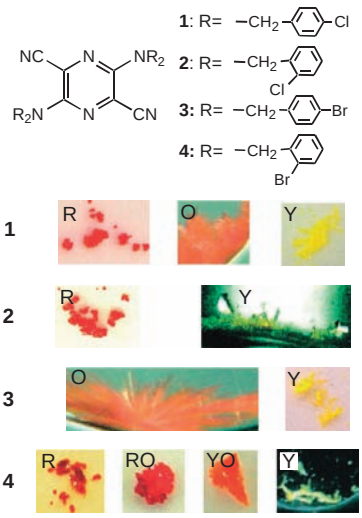

Figure 1. Chemical structure of pyrazine dyes and their polymorphs.

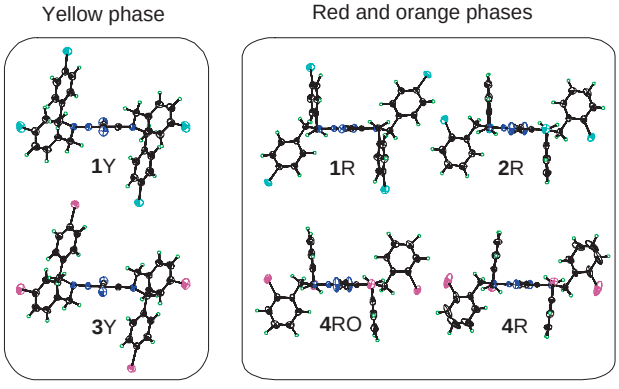

Figure 2. Conformational similarity of a molecule in the polymorphs.

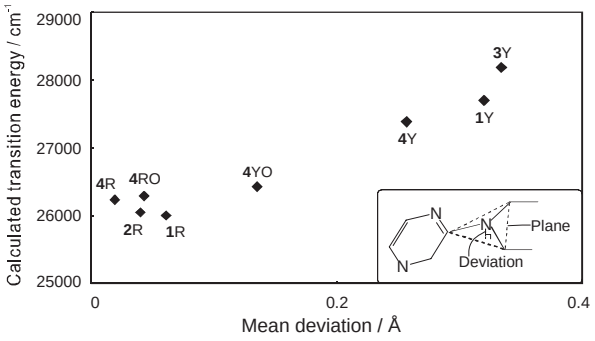

Figure 3. The relationship between the calculated absorption band and the geometry of the amino nitrogen.

and poor solvents. Their color difference must be characterized by considering intermolecular interactions in a crystalline state. Thus, crystal structure analysis was carried out for some polymorphs[8] and their molecular and crystal structures were correlated with the color differences.

The color of these polymorphs was found to reflect different molecular conformations in the crystals (Figure 2). Detailed examination of the molecular geometry revealed that the present conformational similarity can be mainly attributed to the geometry of the amino nitrogen atoms. The amino nitrogens in the red and orange phases have a trigonal planar geometry; whereas a tetrahedral conformation of the amino groups was found in the yellow phase. Thus, an attempt to correlate this geometrical feature with the electronic states of a molecule in a crystal was made by means of molecular orbital calculations. The INDO/S Hamiltonian was used for calculations of absorption spectra using the X-ray fractional coordinates set. In Figure 3 the calculated absorption bands corresponding to those in the visible region are plotted against the deviation of the amino nitrogen from the least-squares plane calculated by the three bonded carbon atoms. The small and large deviations can be correlated to sp^2 and sp^3 electronic states of a nitrogen atom, respectively. It clearly shows that the calculated absorption bands are well related to the electronic state of the amino groups. As shown in Figure 2, in the red and reddish-orange phases the methylene moieties of the benzyl substituents are almost coplanar to the pyrazine ring. The sp^2 hybridization of the amino groups leads the π-orbital of the nitrogen atoms to sufficient conjugation with the π-electron system of the pyrazine ring. In contrast, the methylene moieties of the benzyl substituents are significantly deviated from the pyrazine ring in the yellow phase. The tetrahedral conformation of the amino groups reflects little conjugation between the amino groups and the π-electron system of the pyrazine ring. The present color difference can thus be ascribed to the degree of the conjugation of the amino groups with the π-electron system. This can be also regarded as the example of conformational polymorphism.[1]

Exciton interaction was also estimated by calculating dipole–dipole interactions using the nearest neighbor approximation. This is also a well-known interaction in which an aggregation of molecules gives rise to a change in the electronic energy levels depending on their molecular arrangement.[9] The electronic states of some molecular crystals[10] and dye-aggregates[11] were successfully characterized on this basis. The change in energy levels for a dimer, which corresponds to the spectral shift, is given by $\Delta E = |\mu|^2 \ (1 - 3\cos^2\theta)/r^3$, where the transition dipole moment is denoted by μ, and the distance and angle between two transition dipoles by r and θ, respectively. In this study, the transition dipole moment was obtained by molecular orbital calculations and the geometrical term was determined from the crystal structure. The calculated result was found in the range of -408 to $210\,cm^{-1}$. This indicates that the exciton interaction is about one order of magnitude smaller than the effect of the conformational change. The effect of the conformational change is thus considered to dominate the electronic states of these polymorphs. This property indicates the potential of these dyes for imaging and recording materials. From this point of view, their phase relationship is also an important subject. The yellow and red phases of **1** were found to be stable and meta-stable phases, respectively, by DSC measurement. But phase relationships for the others are not yet clear, and will be the subject of future investigations.

In conclusion, we have found a series of color polymorphs of 2,5-diamino-3,6-dicyanopyrazine dyes. Their color differences can be mainly attributed to conformational changes of the molecule within its crystal. We consider that this result points to a possible design strategy for creating molecules of controlled color polymorphism. According to the results obtained so far, this involves a small chromophoric system with bulky substituents. Our group is currently engaged in attempts to discover polymorphs of the related pyrazine dyes. The results including further experiments will be reported elsewhere.

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8 Crystal data for eight polymorphs are summarized in Table S1 as Supporting Information. These data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers for **1**R (CCDC-600794), **1**Y (CCDC-600795), **2**R (CCDC-600796), **3**Y (CCDC-600797), **4**R (CCDC-600798), **4**RO (CCDC-600799), **4**Y (CCDC-600800), and **4**YO (CCDC-600801), respectively.
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