A variety of solid-state fluorescence properties of pyrazine dyes depending on terminal substituents

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Abstract

The optical properties of 2,5-diamino-3,6-dicyanopyrazine derivatives bearing singly methyl- or halogen-substituted benzyl groups were studied in both solution and crystalline phases. In solution, all derivatives showed similar absorption and fluorescence properties, since the electronic state of their fluorophore was not altered by substituents attached to the benzyl groups. In contrast, crystalline compounds exhibited a variety of fluorescence colours (yellow, orange, and red), since their solid-state absorption and fluorescence properties were correlated with a change in the electron-donating ability of amino groups due to crystallisation. The absolute fluorescence quantum yields of crystalline dyes (0.14–0.91) showed broad variability, depending on the nature and positions of terminal substituents.

1. Introduction

Organic fluorescent dyes have attracted increased attention due to their abundant applications in optoelectronics [1–8], biological imaging [9–12], and sensors [13–15]. In particular, the design of organic dyes with desirable solid-state fluorescence properties is very challenging, since these properties are changed upon aggregation due to molecular deformation and/or intermolecular interactions. Therefore, understanding the relationship between aggregated structures and fluorescence properties is essential for the successful molecular design of organic dyes exhibiting highly efficient solid-state fluorescence.

Introduction of bulky substituents such as alkyl and benzyl groups is one of the methods used to obtain compounds with intense solid-state fluorescence [16–18]. These substituents act as spacers between fluorophores, hindering intermolecular interactions that lead to fluorescence quenching in the solid state [19–22].

Introduction of small substituents such as halogen and methyl groups also significantly affects fluorescence properties by changing the electronic states of the fluorophore and creating new intermolecular interactions [23–26],

with the introduction of halogen atoms being especially effective, changing the optical properties of fluorescent dyes without modifying their conformational flexibility. Up to now, however, reports describing the solid-state optical properties of a complete series (F, Cl, Br, and I) of halogenated derivatives were scarce [27, 28]. Moreover, in past studies, halogen atoms were directly attached to the fluorophore π-system, i.e., their effects on solid-state fluorescence properties other than the above influence on the electronic states of the fluorophore are not yet clear.

2,5-Diamino-3,6-dicyanopyrazine exhibits intense yellowish-green fluorescence in solution, being non-emissive in the solid state [29]. When the amino groups of this compound are modified with bulky halogen- or methyl-substituted benzyl groups, the obtained derivatives exhibit intense orange fluorescence, both in solution and in the solid state (as films) [30]. In addition, derivatives with Cl/Br-substituted benzyl groups also exhibit polymorphism (existing as red, orange, and yellow forms) [31], with their crystal structures suggesting that the colour change is caused by molecular deformation. Moreover, the halogen substituents of benzyl groups significantly influence the above phenomenon by affecting intermolecular

interactions in the crystal structure [32, 33]. These results imply that halogen substituents that do not influence the fluorophore electronic states can contribute to the tuning of solid-state colour and fluorescence properties of pyrazine dyes.

Herein, we systematically investigated the structure-property relationships of a series of pyrazine derivatives (**1**–**3e**, Fig. 1) bearing benzyl groups mono-substituted with halogen (F, Cl, Br, or I) or methyl moieties and evaluated the effect of halogen substituents on the solid-state fluorescence properties of these dyes. In addition to **1**, **2b**, **2c**, **2e,** and **3a**–**3e**, which have been synthesised and identified previously [31–33], we newly prepared *para*-substituted F- (**2a**) and I-derivatives (**2d**) to systematically characterise the effect of terminal substituents on their solid-state fluorescence properties. The obtained results suggest that halogen atoms that are not a part of the chromophore tune the fluorescence colour of crystalline pyrazine derivatives. In addition, such indirect introduction of halogen atoms was found to weaken the heavy atom effect and achieve highly efficient solid-state fluorescence.

<Figure 1>

2. Experimental

2.1. Materials

Halogenobenzyl bromides (97%) were purchased from Tokyo Chemical Industry Co. (TCI). Sodium hydroxide (97%) was obtained from Wako Pure Chem. Ind., Ltd. Wako silica gel C-300 (45–75 μm) was used for column chromatography. **2a** and **2d** were synthesised using a previously reported general procedure [30]. Structural characterisation was performed using proton nuclear magnetic resonance (^{1}H NMR) spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, and high-resolution mass spectrometry (HRMS). ^{1}H NMR spectra were recorded on a DRX 300 MHz spectrometer (Bruker Co.) with tetramethylsilane as an internal standard. FT-IR spectra were collected using a Jasco FT/IR-6200 spectrometer. HRMS spectra were recorded on an Autoflex Speed spectrometer (Bruker Daltonics K. K.). Melting points (T_m) were measured by differential scanning calorimetry (DSC) on a Rigaku ThermoPlus DSC 8230 instrument at a heating rate of 10 °C/min and an air flow rate of 10 mL/min. Derivative **1** was

synthesised according to a previously described method [29] and characterised by ^{1}H NMR. Derivatives **2b**–**3e** were provided by Nippon Soda Co., Ltd. Syntheses of **2b**, **2c,** and **2e**–**3e** were described previously [29, 30, 33].

2.1.1. 2,5-Bis[*N*,*N*-di-(4-halogenophenyl)methylamino]-3,6-dicyanopyrazines (**2a** and **2d**)

A solution of 2,5-diamino-3,6-dicyanopyrazine (0.17 g, 1 mmol) and *p*-halogenobenzyl bromide (4.4 mmol) in dimethylacetamide (20 mL) was stirred at 0 °C for 30 min, followed by the addition of powdered sodium hydroxide (0.2 g). The mixture was further stirred at room temperature for 30 min and poured into brine (100 mL). The solid precipitate was filtered off, dissolved in $CHCl_3$, and concentrated in vacuo, and thus obtained crude product was purified by silica gel column chromatography using $CHCl_3$:*n*-hexane as an eluent (9:1 v/v for **2a** and 8:2 v/v for **2d**). **2a** was obtained as an orange oil (31 mg, 5%) with T_m = 134.7 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) = 4.67 (s, 8 H), 6.97–7.07 (m, 8 H), 7.16–7.25 (m, 8 H). IR (KBr): 2227 cm^{-1} (C≡N). MS found: $[M+Ag]^+$ 699.1039; molecular formula $C_{34}H_{24}N_6F_4$,

requires $[M+Ag]^+$ 699.1044. **2d** was obtained as a yellow solid (37 mg, 4%) with T_m = 248.9 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) = 4.64 (s, 8 H), 6.97 (d, J = 8.67 Hz, 8 H), 7.67 (d, J = 8.29 Hz, 8 H). IR (KBr): 2230 cm^{-1} (C≡N). MS found: $[M+Ag]^+$ 1130.7253; molecular formula $C_{34}H_{24}N_6I_4$, requires $[M+Ag]^+$ 1130.7287.

2.2. Crystallisation

Orange crystals of **1** (**1O**) were obtained by slowly evaporating a solution of **1** in *n*-hexane at 15 °C and exhibited a previously reported structure [32]. In addition, orange-red **1OR**, exhibiting a new crystal structure, was obtained by slowly evaporating a solution of **1** in petroleum ether at 5 °C. Other crystals were obtained by a solvent diffusion method using different solvent combinations (Table S1). **2a** and **2d** were crystallised in the form of orange platelets (**2aO**) and yellow crystals (**2dY**), respectively. Crystal forms of **2b**, **2c**, **2e**, and **3a**–**3e** were obtained in amounts sufficient for optical property measurements [32, 33].

2.3. X-ray diffraction analyses

Single-crystal X-ray diffraction analyses of **1OR** and **2aO** were performed at 296 K using a Rigaku RAXIS-RAPID imaging plate diffractometer with a graphite-monochromatic Cu K_α radiation source (λ = 1.54187 Å). The diffraction pattern of **2dY** was recorded at 93 K using a Rigaku XtaLAB P200 diffractometer with a graphite-monochromatic Cu K_α radiation source. Structures were solved using direct SIR2008 (**1OR**) [34] and SHELXT2014 (**2aO** and **2dY**) [35] methods and refined by full-matrix least-square calculations. Non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were placed in geometrically calculated positions and refined using a riding model. All calculations were performed using the Crystal Structure 4.2 crystallographic software package [36]. The CCDC deposition numbers for **1OR**, **2aO**, and **2dY** are 1540012, 1540581, and1540582, respectively.

Prior to spectroscopic measurements, the obtained crystals, except for **1OR**, **2aO** and **2dY**, were identified based on their powder X-ray diffraction patterns recorded using a Rigaku RAXIS-RAPID imaging plate diffractometer with a graphite-monochromatic Cu K_α radiation source.

2.4. Characterisation of photophysical properties

UV-Vis absorption spectra of **1**–**3e** in chloroform (2.0×10^{-4} M) were recorded on a Perkin-Elmer Lambda 750 spectrometer, and those of solids were recorded using an optical waveguide SIS-50 surface/interface spectrometer (SIS Co.). Fluorescence spectra of chloroform solutions (1.0×10^{-4} M) and solids were recorded using a Jasco FP-8500 spectrofluorometer. Absolute fluorescence quantum yields (Φ_F) were estimated using the above spectrofluorometer with an integrating sphere. UV-Vis absorption spectra, fluorescence spectra, and fluorescence quantum yields were measured in triplicate at room temperature. Photoluminescence lifetimes were determined using a FluoroCube fluorescence lifetime measurement system (HORIBA) at room temperature. Excitation was performed at 455 nm, and emission was monitored at the fluorescence maximum of each crystal.

2.5. Theoretical calculations

Electronic spectra were simulated at a semi-empirical PM5 level [37] with a random phase approximation (RPA) [38] using the MO-S program of the SCIGRESS V2.1 program package [39]. We carried out these calculations

using a single-molecule geometry of crystal structures with H atoms at the calculated positions.

3. Results and discussion

Eleven pyrazine derivatives (**1**–**3e**) bearing various substituents were investigated in terms of their optical properties, with crystallographic data of their fifteen crystal forms listed in Table S2.

*3.1. Optical properties of **1**–**3e** in solution*

Chloroform solutions of **1**–**3e** exhibited orange colour and strong orange fluorescence, showing no significant absorption/fluorescence property differences, despite some slight spectral shifts (Fig. S1). In addition, their relatively high fluorescence quantum yields (0.61–0.81) also showed no significant variation, indicating that substituents attached to the benzyl groups did not significantly affect the optical properties of pyrazine derivatives in solution.

<Table 1>

*3.2. Absorption properties of solid **1–3e***

Crystals of **1–3e** showed colours from red to yellow, regardless of terminal substituents (Fig. 2). Red and orange crystals (**2bR**, **2eR**, **3aO**, **3bR**, **3cRO**, **3cR,** and **3eR**) exhibited two absorption peaks (Fig. 3), whereas only one intense absorption peak was observed in solution. The longer-wavelength absorption components were observed at 540–588 nm as small broad peaks (Fig. 3). In contrast, yellow and orange crystals (**1O**, **1OR**, **2aO**, **2bY**, **2cY**, **2dY**, and **2eY**), and **3dR** exhibited only one large broad absorption band, with peaks located between 477 and 504 nm.

<Figure 2>

<Figure 3>

Exciton interactions [40, 41] and molecular deformations [42, 43] play an important role in the colour change of organic dyes observed upon crystallisation. In this case, the effect of exciton interaction, which is inversely proportional to the cube of the distance between two dipoles in a

dipole approximation [44], was expected to be small due to the relatively large distance between neighbouring chromophores (Table S3). It is also worth noting that the studied pyrazine dyes showed relatively small molar absorption coefficients corresponding to the first absorption band, which are proportional parameters for estimating exciton interactions based on the dipole approximation. In fact, the exciton interaction energies calculated for this series of compounds were an order of magnitude smaller than the corresponding molecular deformation energies [31].

A previous study [31] suggested that the colour of these crystals can be rationalised based on the geometry of amino groups. For example, the amino group in **2eR** adopted an sp^2-like planar conformation, while that in **2eY** was sp^3-like pyramidal. The amino groups of **1OR**, **2aO,** and **2dY**, newly obtained in this study, also exhibited sp^3-like geometries. Thus, crystal colour changes were correlated with the deformation of amino group geometry in single molecules.

MO calculations focused on the electronic states of isolated molecules in the crystalline state, utilising molecular structures obtained by X-ray diffraction analyses. The major contribution to the visible absorption band was assigned

to the HOMO–LUMO transition in all crystals (Table S4). Figure 4 shows the HOMOs and LUMOs of **2eY** and **2eR**, together with their energies, revealing that the HOMO of **2eR** was destabilised compared to that of **2eY**, whereas their LUMOs had almost similar energies. Introduction of strong donor substituents is generally known to destabilise the HOMO of intramolecular charge-transfer dye systems [45], in good agreement with the results of the above calculations, where differences in the geometry of amino groups, indicating their electron-donating ability, were related to the calculated absorption maxima of **2eY** and **2eR**.

<Figure 4>

Figure 5 shows the longer-wavelength absorption maxima of crystal forms plotted as functions of the deviation of aminic nitrogen from the least-squares plane defined by three neighbouring carbon atoms calculated for each crystal structure, with small and large deviations corresponding to sp^2- and sp^3-like configurations, respectively (Table S5). The average deviation of two amino groups was used as the "mean deviation" for **1O**,

which has an unsymmetrical molecular shape, exhibiting both sp^2- and sp^3-like amino geometries. **2dY** was excluded in Fig. 5 due to its disordered molecular conformations.

<Figure 5>

As shown in Fig. 5, the amino group geometry and absorption maxima of crystal forms were well correlated. Red crystal forms exhibited red-shifted absorption peaks and almost planar amino group geometries. In contrast, the amino group geometries of yellow crystal forms were sp^3-like, and the corresponding absorption maxima were blue-shifted. For orange crystal forms, amino group planarity and absorption maxima positions were located between the extremes of red and yellow forms, clearly indicating that the colour difference between these crystal forms originated from the different electron-donating ability of amino groups in the intramolecular charge-transfer chromophoric system, which could be roughly estimated from their geometry.

The colour of the above crystals was not directly dependent on the nature

and position of substituents, suggesting that the attachment of a mono-substituted benzyl group to amino groups in certain intramolecular charge-transfer chromophoric systems can tune the colour of crystals by inducing an indirect electronic state change.

*3.3 Fluorescence properties of solid **1**–**3e***

The fluorescence colours of solid **1**–**3e** were also independent of terminal substituents (Fig. S2). As shown in Fig. 6, the red forms (**2bR**, **2eR**, **3cR,** and **3eR**) showed red fluorescence with maxima (F_{max}) above 610 nm. In contrast, **2bY** and **2eY**, colour polymorphs of **2b** and **2e**, respectively, exhibited strong yellow fluorescence (F_{max} = 557 and 561 nm, respectively). Other crystal forms also showed single fluorescence bands with different maxima (Table 1, Fig. S2).

<Figure 6>

The fluorescence maxima of solid **1**–**3e** exhibited a dependence on amino group geometry similar to that of absorption maxima (Fig. 7), with larger

mean deviations from planarity resulting in blue-shifted fluorescence maxima.

<Figure 7>

This result clearly indicated that the fluorescence colours of these crystal forms were also correlated with the electron-donating ability of amino groups, which could be roughly estimated from their geometries.

The fluorescence quantum yields of all crystal forms lied in the range of 0.14–0.91, being lower for bromine and iodine derivatives (**2cY**, **2dY**, **3cRO**, **3cR,** and **3dR**) due to the heavy atom effect of these substituents [46]. However, the indirect conjugation of these heavy atoms to π-conjugated systems seemed to help avoid strong fluorescence quenching and maintain moderate quantum yields of 0.23–0.39, whereas other derivatives with Br or I atoms directly connected to the chromophore exhibited no fluorescence [27, 28]. This result suggests the effect of the indirect introduction of heavy atoms can avoid strong fluorescence quenching caused by the heavy atom effect.

The lowest Φ_F of 0.14 was observed for the *ortho*-substituted fluorine derivative **3aO**, although this compound was highly emissive in solution (Φ_F = 0.79), similarly to other derivatives. To elucidate this large difference in Φ_F, the excited-state dynamics of **3aO**, **3bR** (Φ_F = 0.91), and **3eR** (Φ_F = 0.42) were investigated by fluorescence lifetime measurements that determined the time constants (τ) of their fluorescence decay. **3bR** and **3eR** were chosen as compounds exhibiting the highest and average Φ_F among the present crystals and exhibited monoexponential decay curves with τ = 58.9 and 29.8 ns, respectively. Considering Φ_F and τ, we calculated radiative and non-radiative decay rate constant (k_r) and (k_{nr}) as 1.54×10^{-7} and 0.15×10^{-7} s^{-1} for **3bR** and 1.41×10^{-7} and 1.95×10^{-7} s^{-1} for **3eR**, respectively. These results indicate that the high Φ_F of **3bR** is due to the suppression of its k_{nr}, since its k_r is almost similar to that of **3eR**. Thus, chlorine atoms introduced into the *ortho*-position of benzyl groups were suggested to suppress non-radiative decay, achieving a high fluorescence quantum yield.

On the other hand, the fluorescence decay curve of **3aO** was fitted by a biexponential model. The τ value of the faster component was determined as 2.81 ns, while that of the slower one equalled 23.7 ns, which was of the same

order of magnitude as the τ values of **3bR** and **3eR**. Since the increase of τ was correlated with the suppression of k_{nr} and the increase of Φ_F for **3bR** and **3eR**, it was suggested that the faster decay observed for **3aO** corresponds to an efficient non-radiative pathway, resulting in a very low Φ_F of 0.14.

4. Conclusions

The optical properties of crystalline 2,5-diamino-3,6-dicyanopyrazine derivatives bearing *para-*/*ortho-* halogen- or methyl-substituted benzyl groups were investigated, with all derivatives showing similar properties in chloroform solution. However, in the solid state, the colour of crystals, related to their absorption and fluorescence characteristics, was found to be strongly dependent on the geometries of amino groups. In red crystal forms, the amino groups adopted sp^2-like planar configurations, whereas those of yellow crystal forms were sp^3-like. All halogenated derivatives exhibited moderate to very good fluorescence quantum yields ranging from 0.14 to 0.91. Strong fluorescence quenching due to the heavy atom effect was avoided by the indirect introduction of heavy atoms into the chromophoric system. In

addition, it was suggested that chlorine atoms introduced into the *ortho*-position of the benzyl groups contribute to the realisation of highly efficient fluorescence by suppressing non-radiative decay in crystals.

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