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Short communication

J-aggregate structure in a chloroform solvate of a 2,3-dicyanopyrazine dye – Separation of two-dimensional stacking dye layers by solvate formation

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ABSTRACT

Here, we report the J-aggregate structure of a chloroform solvate of 5-*t*-butyl-2,3-dicyano-6-[4-(dimethylamino)styryl]-pyrazine with a strong intramolecular charge transfer system. The dye was found to form a two-dimensional brick-wall structure separated by chloroform molecules in the solvated crystals, which exhibited intense red fluorescence. The absorption maximum of the solvate was also found to show a bathochromic spectral shift. These observed optical characteristics were interpreted in terms of excitonic intermolecular interaction based on two-dimensional brick-wall structure which is one of the proposed structures for J-aggregates.

1. Introduction

J-aggregates are one of the well-known supramolecular systems of organic dyes [1]. They exhibit an intense, sharp absorption band with resonance fluorescence in the longer wavelength region compared with those of a component dye monomer. These particular spectral features may be ascribed to a resonance quantum effect known as exciton interaction within the aggregates [2]. A representative example of their practical applications is as a photosensitizer for colour photographic films [1]. This industrial opportunity stimulated research into J-aggregates. One of the main research interests in J-aggregates is the structure. The structure of J-aggregates was first proposed with respect to the surface adsorption of J-aggregates on ionic substrates [3]. With much experimental evidence of the formation of J-aggregates on the surface of ionic substrates [1], the structure of J-aggregates was further considered on the basis of theoretical treatments [2]. There are also several reports on photographic images of J-aggregates using microscopic techniques [4]. Comprehensive analyses of the crystal structure of cyanine dyes showed that many cyanine dyes crystallize in a $\pi-\pi$ stacking structure and the proposed one- or two-dimensional molecular arrangement of J-aggregates is recognized as a part of their three-dimensional crystal structures [5]. However, the detailed structure and dimensionality of J-aggregates are still unknown except for the X-ray structure of a J-aggregate LB-film of a merocyanine dye reported by Kato et al. [6] The size of J-aggregates is also controversial: a range of some molecules to some thousands molecules have been reported as the number of component molecules within one J-aggregate [1e,7]. An alternate opinion is that J-aggregates are a macroscopic molecular assembly composed of meso-scale molecular assemblies [8]. The reported analysis of the J-aggregated LB-film [6] demonstrated that a two-dimensional infinite dye network is also a form of J-aggregates, whilst that film may possess structural defects like mosaicity in single crystals.

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In spite of the lack of clarity of the structure of J-aggregates, their spectral features have attracted much attention in state-of-the-art applications of organic dyes such as optical materials [7c,7d,9], organic solar cells [10], and organic light-emitting devices [4e,11]. Stable J-aggregates in solid films [12] or in powdered form are required for these applications. It is also very important that these bulk J-aggregates can be prepared through a conventional method. To achieve these demands, J-aggregate formation in a stable crystalline state [13] is a promising solution even though there is currently no design strategy for obtaining J-aggregate crystals. Here, we report the crystal structure and solid-state optical properties of a chloroform solvate of a 2,3-dicyanopyrazine dye as an example of a potential crystal structure towards the design of J-aggregate crystals.

2. Experimental section

2.1. Materials and equipments

4-(Dimethylamino)benzaldehyde was purchased from Hayashi Pure Chemical Industries Ltd. 5-*t*-Butyl-2,3-dicyano-6-methylpyrazine [14] was prepared as described in the literature.

Melting points were measured using a Yanaco MP-500P micro-melting-point apparatus. NMR spectra were obtained by a Jeol JNM-ECX-400 spectrometer. EIMS spectra were recorded on a Jeol JMS-GC mateII spectrometer. IR spectra were recorded on a Jasco FT-IR-4100 system for samples in a KBr pellet form. The elemental analysis was performed with an Elementar Vario EL III elemental analyzer. UV–vis absorption and fluorescence spectra in solution were taken on a Shimadzu UV3100PC UV/vis spectrometer and a Shimadzu RF5301PC fluorescence spectrometer, respectively. Solid-state absorption spectra were measured using a System Instruments SIS-50 surface and interface spectrometer based on optical waveguide spectrometry. Fluorescence quantum efficiency in the solid-state is determined using a blue diode laser (CrystaLaser), an integrating sphere (Labsphere), and photo-multichannel analyzer (Hamamatsu, PMA-11). After measured a reflected laser beam from a quarts substrate, we measured a reflected laser beam and fluorescence from the crystals placed on the substrate. Then, we calculated photon numbers of the fluorescence and the adsorbed laser beam. Fluorescence quantum efficiency was obtained as a ratio between the two-photon numbers [15]. Electronic states of this dye in the solvate were estimated by a semi-empirical molecular orbital calculation. The ground state dipole moment and the transition dipole moment were calculated by using the AM1 and the INDO/S Hamiltonians, respectively, on the basis of the crystal structure. These calculations were performed with a CAChe 5.2 program package [16].

2.2. Synthesis of 5-t-butyl-2,3-dicyano-6-[4-(dialkylamino)styryl] pyrazine

To a solution of 5-*t*-butyl-2,3-dicyano-6-methylpyrazine (2.00 g, 10 mmol) in benzene (50 mL) was added piperidine (0.3 mL, 3 mmol) and 4-(dimethylamino)benzaldehyde (1.49 g, 10 mmol). The mixture was refluxed for 37 h. The reaction mixture was cooled to room temperature and then poured into a 2% HCl solution. The precipitate was filtered off and the filtrate was extracted with EtOAc three times. The combined organic layers were washed with brine and dried over Na_2SO_4. After removing the solvent, the residue was isolated by silica gel column chromatography (benzene) to give a solid product. This solid and the precipitate obtained by filtration were mixed and further purified by recrystallization from chloroform to obtain the target compound (1.56 g, 31%) as reddish brown crystals. Yield 31%; mp 263–264 °C; Anal. Calcd. for $C_{20}H_{21}N_5$: C, 72.48; H, 6.39; N, 21.13%. Found: C, 71.92; H, 6.28; N, 20.97%; IR (KBr)/cm^{-1} 2225 (CN); ^{1}H NMR ($CDCl_3$) δ 1.54 (s, 9H), 3.10 (s, 6H), 6.74 (d, $J = 8.0$ Hz, 2H), 7.29 (d, $J = 16.0$ Hz, 1H), 7.55 (d, $J = 8.0$ Hz, 2H), 8.03 (d, $J = 16.0$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 29.4, 39.3, 40.2, 112.1, 113.8, 114.3, 116.3, 123.4, 126.0, 130.1, 130.3, 143.0, 152.1, 152.9, 162.8; MS (EI) m/z 331 (M^+).

2.3. X-ray structural analysis

Data collection of the solvate crystal was performed by a Rigaku RAXIS RAPID imaging plate diffractometer with graphite monochromated Cu–$K\alpha$ radiation. The structure was solved by direct method (SIR 2002 [17]) and refined by full-matrix least-squares calculations. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were simply located at the calculated positions and their parameters were constrained. All calculations were performed using the Crystal Structure 3.8 crystallographic software package [18]. Crystal data: $C_{20}H_{21}N_5 \bullet CHCl_3$, $M = 450.80$, orthorhombic, $a = 6.7574(5)$ Å, $b = 11.1520(6)$ Å, $c = 14.9279(9)$ Å, $V = 1124.9\ (1)$ Å^3, $T = 223.1$ K, space group $Pmn2_1$, $Z = 2$, 11891 reflections measured, 2202 independent reflections ($R_{\mathrm{int}} = 0.101$). The final R_1 value ($I > 2\sigma(I)$), the final $wR(F^2)$ value (all data), and the GOF was 0.075, 0.2163 and 0.900, respectively. The Flack parameter was $-0.05(4)$. The CCDC deposition number is CCDC834637.

3. Results and discussion

Dye **1**, 5-*t*-butyl-2,3-dicyano-6-[4-(dimethylamino)styryl]-pyrazine, shown in Fig. 1 was synthesized as one of a series of compounds to study the effect of the amino substituent on thin film growth by vacuum deposition [19]. This dye system is also known to exhibit good fluorescence properties in the crystalline state [14,20]. We carried out single crystal growth of **1** using liquid–liquid diffusion from chloroform and *c*-hexane. Lustrous red

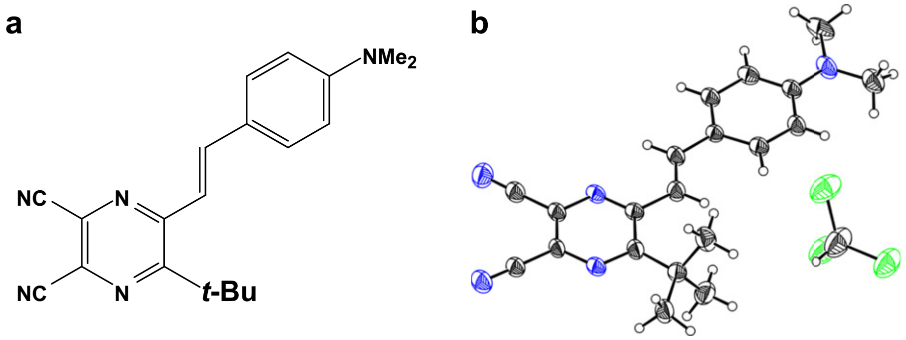

Fig. 1. (a) Chemical structure of **1** and (b) molecular structure of its chloroform solvate (30% probability level ellipsoids).

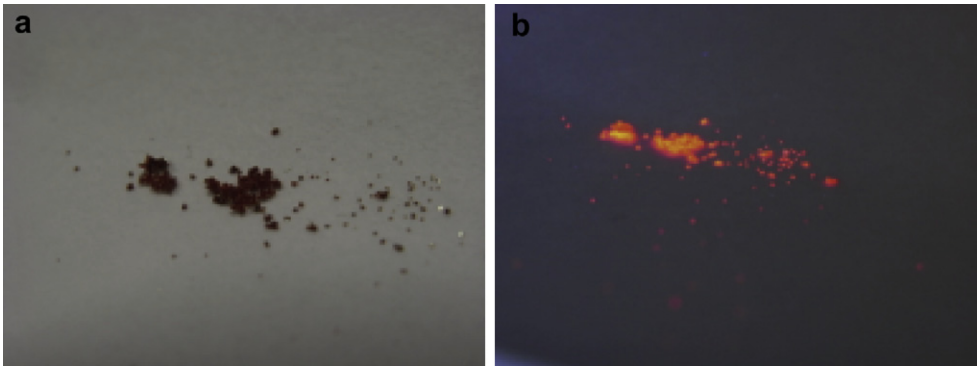

Fig. 2. Photographs of dye **1** under (a) a room light and (b) a UV light.

platelets were observed in the glass tube within a few days, and, after that, the red crystals transitioned into black block crystals and/or reddish-purple flakes in the next several days. The red crystals were found to emit brightly under a UV lamp (Fig. 2). They are stable at about 263 K without any colour change.

We initially thought that **1** had three crystal polymorphs; however, the red one was proved to be a chloroform solvate. Thermogravimetric (TG) analysis revealed that the red crystals include one chloroform molecule per dye (Fig. 3). The other two crystals were identified as polymorphic forms without any solvent molecules and their structures and optical properties will be reported elsewhere.

X-ray structural analysis of the solvated crystals was carried out at 223 K. The analytical data indicated that the structural unit is composed of one dye molecule and one chloroform molecule, which confirms the results of the TG analysis. The molecules are oriented on a mirror plane parallel to the *bc* plane. This indicates that the molecules have a planar conformation. Fig. 4 illustrates the crystal structure of the solvate. The crystal structure is characterized by a two-dimensional stacking dye layer and a layer composed of chloroform molecules. These two layers alternate along the *b*-axis to form the three-dimensional crystal structure. Fig. 4 also shows a portion of the two-dimensional dye layer viewed from both the *a*-axis and the *b*-axis. The dye molecules are stacked along the *a*-axis in a brick-wall fashion [2c] with a slip angle of *ca.* 24°. This dye chromophore has an unsymmetrical intramolecular charge transfer (CT) system. Therefore, **1** has a large dipole moment in the ground state along the CT direction of the molecular plane. It should be noted that the polar molecules are aligned in the same direction in all the stacking layers. This is intriguing because molecules with a large ground state dipole moment generally align themselves to minimize electrostatic repulsion resulting in a non-polar or less-polar crystal structure [21]. The transition dipole moment of the visible absorption was estimated to be aligned in the same direction as the ground state dipole moment. Therefore, this two-dimensional layer can be regarded as a model structure for J-aggregates, specifically the two-dimensional brick-wall structure.

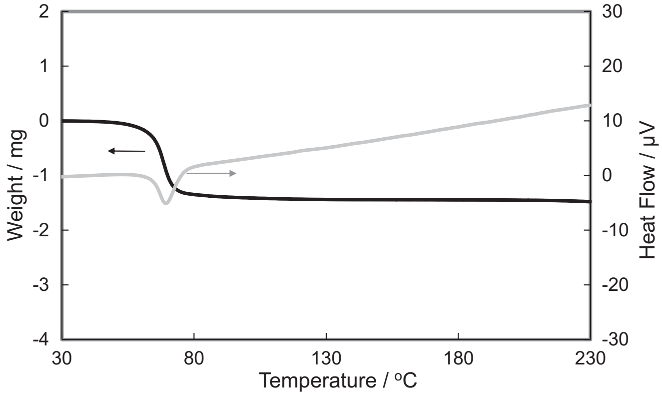

Fig. 3. The TG/DTA data for the solvate.

The effect of the exciton interactions in this J-aggregate structure was estimated by using the extended dipole model [1d,2d,6] on the basis of a nearest neighbour approximation. The interaction from six neighbouring dye molecules in the same layer induced a bathochromic energy shift of 991 cm^{-1}. The contribution from two neighbouring dye molecules in the neighbouring layers was a hypsochromic energy shift of 155 cm^{-1}. Therefore, the total from eight neighbouring molecules resulted in a bathochromic energy shift of 836 cm^{-1}. This suggests that this solvate has an excitonic electronic nature resembling that of J-aggregates and this was imparted by the two-dimensional brick-wall structure, even though the transition dipole moments in the stacking layer are aligned with a small declination, which may result in negligible breaking of the symmetry limitation for light absorption based on exciton interactions [2].

We then measured the optical properties of this solvate. The powder samples were characterized by the crystal structure of the solvate using powder X-ray diffraction. The absorption and fluorescence spectra of **1** (in toluene) and the solvate are illustrated in Fig. 5. Generally it is not easy to obtain an absorption spectrum of dye crystals because dye solids have a strong extinction over the visible region. The measurements were then performed using optical waveguide spectroscopy [22]. Dye **1** exhibits an absorption maximum around 480 nm in toluene with a molar extinction coefficient of *ca.* 2.5×10^4. Its fluorescence in toluene was recognized around 556 nm with 21% quantum efficiency, which was measured using quinine sulphate as a reference. The Stoke's shift is 2848 cm^{-1}. The absorption spectrum of the solvate was found to shift drastically towards the bathochromic region. Its λ max was around 559 nm with a broad shoulder around 460 nm. The bathochromic shift of the absorption maximum from a toluene solution to the solvate was estimated to be 2944 cm^{-1}. This spectral shift is qualitatively in agreement with the calculated bathochromic shift (836 cm^{-1}) based on exciton interactions. Fluorescence of the solvate was measured by using a homemade set-up with excitation at 375 nm. Its quantum efficiency was estimated in comparison with purified anthracene crystals. The fluorescence spectrum comprised a sharp fluorescence band around 619 nm and a broad component in the longer wavelength region. Its quantum efficiency is *ca.* 10%. This sharp peak was found to decrease gradually during the measurements with a simultaneous increase of the longer wavelength component. The longer fluorescence component was

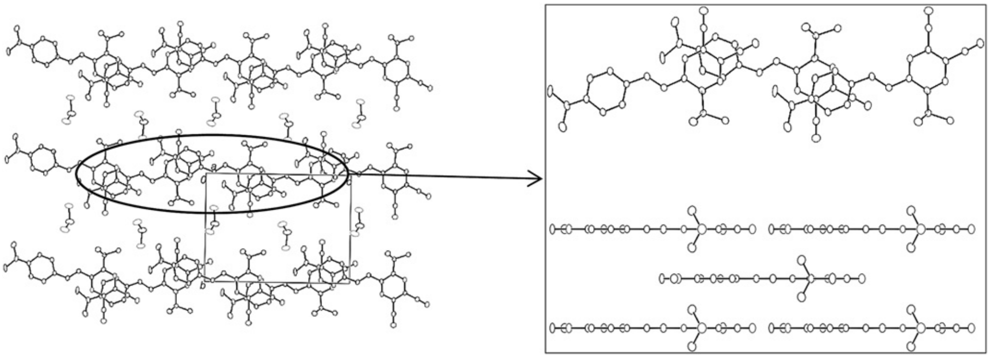

Fig. 4. Crystal structure of the solvate.

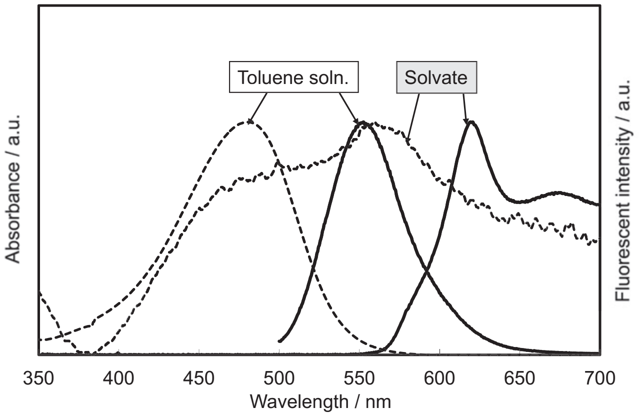

Fig. 5. UV–vis absorption (the dotted line) and fluorescence (the solid line) spectra of **1** (in toluene) and the solvate measured in an ambient condition.

also observed from the black and reddish-purple phases and thus this spectral change should be caused by the local phase transition from the solvate to these phases. This sharp fluorescence peak can be considered to reflect the excitonic band formation.

These separated two-dimensional stacking dye layers by solvent molecules are regarded as a possible structure for realizing quasi-low dimensional electronic states in a three-dimensional crystalline state, i.e. crystals exhibit the aggregate properties. To make the distance between the adjacent brick-wall layers being larger than an effective exciton coherent length may adjust the optical properties of the solvate to those of typical J-aggregates such as sharp line-like absorption and resonance fluorescence. The stability of the solvates is also an important parameter in their practical applications.

4. Conclusions

A 2,3-dicyanopyrazine dye, 5-*t*-butyl-2,3-dicyano-6-[4-(dimethylamino)styryl]-pyrazine, was found to form a chloroform solvate which emit intense red fluorescence. Its optical property was interpreted in terms of intermolecular interactions based on two-dimensional brick-wall structure, one of the proposed structure for J-aggregates, in the crystal. The present result suggests an interesting idea for achieving J-aggregates in a three-dimensional crystalline state based on a solvate structure, although crystal engineering of such a small organic molecule is still a tough task.

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