Solid-state Fluorescence Changes of 2-(4-Cyanophenyl)-5-[4-(diethylamino)phenyl]-3*H*-imidazo[4,5-*a*]naphthalene upon Inclusion of Organic Solvent Molecules

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Novel imidazo[4,5-*a*]naphthalene-type fluorescent clathrate host, 2-(4-cyanophenyl)-5-[4-(diethylamino)phenyl]-3*H*-imidazo[4,5-*a*]naphthalene (**2**) with two tautomeric forms (**A** and **B**) that are possible for the imidazole ring, has been developed. The crystal of the fluorophore **2** exhibits sensitive colour change and fluorescence enhancement behaviour with a blue shift of the emission maximum upon enclathration of various kinds of organic solvent molecules.

The crystal structures of the guest-free and the clathrate compounds of **2** have been determined by X-ray analysis. On the bases of the spectral data and the crystal structures, the effects of the enclathrated guest on the solid-state photophysical properties of the clathrate compounds are discussed.

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Introduction

Solid-state fluorescence of organic fluorescent dyes has recently attracted increasing interest because of their many uses both in the fundamental research fields of solid state photochemistry and polymorphism and in the applied field of optoelectronic devices.^[1] To design of desirable solid-state fluorescent materials, it is very important to obtain information about the relationship between the photophysical properties and the chemical and crystal structures of fluorophores. During the last decade some studies demonstrated that the key point in designing new organic solid-state fluorescent dyes is to remove the intermolecular interactions between fluorophores causing fluorescence quenching in molecular aggregation states. For example, the introduction of bulky substituents to the original fluorophores^[2] and the construction of a non-planar structures with sterical hindered substituents^[3] are known to be very useful methods for solving the problem of fluorescence quenching by molecular aggregation. As other approach, Tohnai and Miyata *et al.* proposed the possibility of a tunable solid-state fluorescence system consisting organic salt with primary amine. In the system, the fluorescence intensity can be controlled by changing alkyl chain length of the amine.^[4]

On the other hand, organic fluorescent host which can exhibit sensitive colour and fluorescence changes upon formation of host-guest inclusion complexes are useful material for elucidation of the solid-state optical properties.^[5, 6] Recently, Imai *et al.* showed that a solid-state fluorescent host system was created by self-assembly of a 2₁-helical columnar organic fluorophore composed of (1*R*,2*S*)-2-amino-1,2-diphenylethanol and fluorescent 1-pyrenecarboxylic acid. The solid-state fluorescence of this host system can change depending to the induced guest molecules owing to the slight variation in molecular size and shape.^[7] Therefore, organic

fluorescent host can be the most promising material for the construction of desirable solid-state fluorescent system.

In our previous works, we have reported novel benzofuran[3,2-*b*]naphthoquinol-type^[5], imidazo[5,4-*a*]anthraquinol-type^[8], 5-hydroxy-5-substituent-benzo[*b*]naphtho[1,2-*d*]furan-6-one-type^[9] and phenanthro[9,10-*d*]imidazole-type^[10] fluorescent hosts whose crystals exhibit a dramatic fluorescence enhancement upon inclusion of various amines, organic solvents and carboxylic acids. In particular, imidazo[5,4-*a*]anthraquinol-type fluorophore in which two tautomeric forms (**A** and **B**) are possible for the imidazole ring that can include various kinds of organic solvent molecules in the crystalline state by changing the tautomeric form on the imidazole ring. A dramatic fluorescence enhancement and a blue-shift of the absorption and fluorescence wavelength maxima are observed depending on the enclathrated guest molecules. From the comparison of the X-ray crystal structures of the guest-free and several clathrate compounds, it was concluded that the destructions of the π - π interactions and the intermolecular hydrogen bonds binding fluorophores by the enclathrated guest molecules are the main reason for the guest-dependent fluorescence enhancement and the blue-shift of the absorption and fluorescence maxima of the crystals. Consequently, it is expected that the fluorescent hosts condensed with imidazole ring can include various kinds of organic solvent molecules and exhibit desirable solid-state fluorescent properties according to the change of the crystal structures, by changing the tautomeric form on the imidazole ring.

In connection with this research, we have further developed novel imidazo[4,5-*a*]naphthalene-type fluorescent clathrate host, 2-(4-cyanophenyl)-5-[4-(diethylamino)phenyl]-3*H*-imidazo[4,5-*a*]naphthalene (**2**) exhibiting tautomerism (**A** and **B**) on the imidazole ring. Here, we report sensitive colour and fluorescence changes of **2** upon enclathration of organic solvent molecules in the solid state. The X-ray crystal structures of **2** and its guest-inclusion compounds have been determined, on the basis of which the enclathrated guest effects on the solid-state fluorescence properties are discussed.

Results and Discussion

In molecular design of fluorescent clathrate hosts, it is required that specific structural units such as a rigid backbone (fluorophore skeleton), bulky substituents, and anchor groups are combined.^[11–13] In order to create new fluorescent clathrate hosts, we employed the imidazo[4,5-*a*]naphthalene-type fluorophore with an imidazole ring as anchor group. Due to two tautomeric forms (**A** and **B**) are possible for the imidazole ring, it is expected that the fluorescent hosts condensed with imidazole ring can include various kinds of organic solvent molecules and exhibit desirable solid-state fluorescent properties according to the change of the crystal structures, by changing the tautomeric form on the imidazole ring. Thus, we have designed and synthesized the imidazo[4,5-*a*]naphthalene-type fluorescent clathrate host, 2-(4-(diethylamino)phenyl)-5-[4-(diethylamino)phenyl]-3*H*-imidazo[4,5-*a*]naphthalene (**2**) (Scheme 1).

< Please insert Scheme 1 here >

The fluorophore **2** is conveniently synthesized as shown in Scheme 1. We first prepared 4-[4-(diethylamino)phenyl]-1,2-naphthoquinone **1** in 58% yield by the reaction of sodium 1,2-naphthoquinone-4-sulphonate with *N,N*-diethylaniline in acetic acid in the presence of nickel(II) chloride. Next, the fluorophore **2** was synthesized in 58% yield by the reaction of *p*-cyanobenzaldehyde with the 1,2-naphthoquinone **1** in the presence of an excess amount of ammonium acetate in acetic acid.

The absorption and fluorescence spectra of **2** in benzene are shown in Figure 1. The fluorophore **2** exhibits intense absorption bands at around 386 nm ($\epsilon_{\text{max}} = 27200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and a single intense fluorescence band at around 479 nm. The fluorescence quantum yield (Φ) is 0.91.

< Please insert Figure 1 here >

Inclusion Ability in Crystalline State

In order to investigate the inclusion ability of **2**, we recrystallized the fluorophore **2** from various organic solvents. We have found that the fluorophore **2** yields various host-guest inclusion compounds in stoichiometric ratios with organic solvent molecules such as ethanol, ethyl acetate, morpholine and 1,4-dioxane in the crystalline state. These results suggest that the imidazole ring is effective to fix guest molecules in the crystalline state. The guest-free crystal was obtained by recrystallization of **2** from acetonitrile. The characteristics of the guest free and various inclusion crystals obtained by recrystallization of **2** are summarized in Table 1. Compared to the guest-free crystal, the colour of the guest-inclusion crystals varied from yellowish orange to yellow and a dramatic fluorescence enhancement was observed.

The thermal analyses (TG and DTA) were performed to investigate the thermal stability of the clathrate crystals and the thermal analysis data are shown in Table 1. The guest release patterns were considerably different depending on the identity of enclathrated solvent molecules, and the guest release temperatures for the all guest-inclusion crystals were higher than their original boiling points of the guest. Interestingly, after releasing solvent molecules, only morpholine inclusion crystal showed the original melting point at around 245°C; the morpholine inclusion crystal shows two endothermic peaks associated with the guest release and melting points. The TG and DTA profiles of the morpholine and ethanol inclusion crystals are shown in Figure 2. From the visual observation of the thermal stability of the clathrate crystals, the morpholine inclusion crystal showed the melting at around 245°C.

On the other hand, the other guest inclusion crystals showed the melting at the temperature of guest release. It is known that some host-guest inclusion crystals show the melting with concomitant the guest release, which was considered that the degree of orientational disorder with concomitant the guest release are already close to that of the liquid.^[14] Actually, the comparison of the X-ray crystal structures of the guest-free and the guest-inclusion compounds demonstrated that the packing structures of the guest-free and the morpholine-inclusion compounds are quite similar to each other (See Figures 4 and 5). Thus, in the case of the morpholine-inclusion crystal, it was revealed that the crystal structure remained without destroying after the guest release was completed, which was well explained the appearance of the two endothermic peaks associated with the guest release and melting points. In the all guest-released guest-inclusion crystals, the fluorescence excitation and fluorescence maxima were red-shifted and their fluorescence intensities were decreased, so that the photophysical properties of the guest-released guest-inclusion crystals are close to that of the as-prepared guest-free crystal.

< Please insert Figure 2 here >

< Please insert Table 1 here >

Solid-state Fluorescence Enhancement Behaviour upon Formation of Guest-inclusion Crystals

In order to investigate the effect of clathrate formation on the solid-state photophysical properties, the fluorescence excitation and emission spectra of the guest-free and the guest-inclusion crystals were measured (Figure 3). Compared to the guest-free crystal, the excitation and emission maxima of the guest-inclusion crystals exhibit a blue shift and the fluorescence intensity is enhanced to various degrees depending on the identity of the enclathrated guest molecules. However, the fluorescence intensity of the morpholine inclusion crystal is almost same to the guest-free host crystal. The guest-free host crystal exhibits relatively weak fluorescence with emission maximum at 536 nm, while the guest-inclusion crystals exhibit much stronger fluorescence intensity with the emission maximum blue shifted to around 491–517 nm. In comparison with the guest-free crystal, the fluorescence intensities of the guest-inclusion crystals were *ca.* 1.6-fold in ethanol-, *ca.* 2.1-fold in ethyl acetate-, and *ca.* 4.8-fold in 1,4-dioxane-inclusion crystals, respectively. The solid-state fluorescence quantum yield (Φ) increases in the order of 2·1,4-dioxane ($\Phi = 0.26$) > 2·ethyl acetate ($\Phi = 0.10$) > 2·ethanol ($\Phi = 0.08$) > 2 (guest-free) ($\Phi = 0.06$) $\approx$ 2·morpholine ($\Phi = 0.05$).

< Please insert Figure 3 here >

Relation between Solid-state Fluorescence Properties and X-ray Crystal Structures of Various Clathrate Compounds of **2**

To understand the enclathrated guest effects on the fluorescence properties of the crystal, the crystal structures of the guest-free and the guest-inclusion compounds have been determined by X-ray diffraction analysis.

Figures 4–8 show the X-ray crystal structures of the guest-free and the guest-inclusion compounds. The tautomeric forms (**A** and **B**) of imidazole ring of host **2** in the crystalline state were changed

depending on the enclathrated guest molecules. The tautomeric form of host **2** is A-form in the crystals of **2**·morpholine and **2**·ethanol and B-form in the crystals of the guest-free and **2**·1,4-dioxane. Interestingly, in the crystal of **2**·ethyl acetate, there are two crystallographically independent host molecules; the one is A-form, the other is B-form. These results indicate that the host **2** can include various guest molecules by changing the tautomeric form on the imidazole ring. The torsion angles between naphthoimidazole plane and *p*-cyanophenyl group are 0.5°–10° for the all compounds, which shows two rings are coplanar. On the other hand, *p*-diethylaminophenyl groups are twisted from naphthoimidazole plane by about 50°–70° for the all compounds.

Figures 4 and 5 show the molecular packing structure for the guest-free and **2**·morpholine (H : G = 1 : 1) crystals, respectively. The both crystals are built up by the π -stacking arrangements between the naphthoimidazole and the *p*-cyanophenyl moieties in the two hosts. There are 16 (= 8×2) and 14 (= 7×2) short interatomic π - π contacts of less than 3.6 Å in the pair of hosts for the guest-free and **2**·morpholine (H : G = 1 : 1) crystals, respectively. The average distance of the interatomic π - π contacts is ca. 3.51 Å for the guest-free compound and ca. 3.48 Å for **2**·morpholine, respectively, which suggest strong π - π interactions. In the crystal of **2**·morpholine, the intramolecular hydrogen bonds are observed between the host and the guest: the proton of imidazole ring of **2** is directing toward the oxygen of morpholine (N(2)H(1)···O(1) angle = 172(2)°, N(2)···O(1) distance = 2.881(6) Å).

< Please insert Figure 4 here >

< Please insert Figure 5 here >

On the other hand, the crystal of **2**·ethanol (H : G = 1 : 1) is made up by the stacking arrangements that avoid short contacts between the chromophores (Figure 6). There are 4 (= 2×2) short interatomic contacts of less than 3.6 Å between the host molecules (Figure 9-(c)). The average distance of the interatomic π - π contacts is ca. 3.52 Å, which is long distance in comparison with the cases of the guest-free and **2**·morpholine compounds. An one-dimensional chain ranging alternately host and guest (···H···G···H···) is formed through the intermolecular hydrogen bonding between the hydroxyl group of ethanol molecule and the imidazole ring of host molecule; the proton of an imidazole ring of the host is directing toward the oxygen of the guest (N(2)H(1)···O(1) angle = 159(4)°, N(2)···O(1) distance = 2.844(7) Å) and the hydroxyl proton of the guest is directing toward an imino nitrogen of another host molecules (O(1)H(25)···N(1) angle = 172(6)°, O(1)···N(1) distance = 2.952(6) Å) as shown in the Figure 6-(b).

< Please insert Figure 6 here >

Figure 7 shows the molecular packing structure for the crystal of **2**·ethyl acetate (H : G = 2 : 1). The crystal is made up by two-types of the stacking arrangements. The one is the π -stacking between the hosts with B-form (Figures 6(b) and (c): **I**) or A-form (Figures 6(b) and (d): **II**), and the other is the π -stacking between the host with A-form and the host with B-form (Figures 6(b) and (e): **III**): the former is the π -stacking between the naphthoimidazole π -planes containing the *p*-cyanophenyl moiety, and the latter is the π -stacking between the imidazole rings containing the *p*-cyanophenyl moiety. There are 18, 10 and 15 short interatomic contacts of less than 3.6 Å, respectively. The average distance of the interatomic π -

π contacts is ca. 3.53 Å, 3.52 Å and 3.52 Å, respectively, which is long distance in comparison with the cases of the guest-free and **2**·morpholine and is almost the same as that of **2**·ethanol. The enclathrated ethyl acetate molecule is bound to one host molecule by intermolecular hydrogen bond in which the proton of the imidazole ring of the host with B-form is directing toward the carbonyl oxygen of the guest molecule (N(1)H(1)···O(1) angle = 177(4)°, N(1)···O(1) distance = 2.908(5) Å). Furthermore, the neighbouring hosts with A-form and B-form are connected by the intermolecular hydrogen bond between the proton of the imidazole ring and cyano nitrogen (N(6)H(25)···N(3) angle = 161(4)°, N(6)···N(3) distance = 3.027(7) Å).

< Please insert Figure 7 here >

Figure 8 shows the molecular packing structure for the crystal of **2**·1,4-dioxane (H : G = 2 : 1). The crystal is made up by two-type of the stacking arrangements that avoid short contacts between the chromophores. There are 8 (Figure 6(c): **I**) and 4 (Figure 6(d): **II**) short interatomic contacts of less than 3.6 Å, and the average distance of the interatomic π - π contacts is ca. 3.54 Å and 3.57 Å, respectively, which is large distance in comparison with the cases of **2**·morpholine, **2**·ethanol and **2**·ethyl acetate. The enclathrated 1,4-dioxane molecule is tightly bound to two host molecules by two intermolecular hydrogen bonds in which the proton of the imidazole ring of host is directing toward the oxygen of the guest (N(1)H(1)···O(1) angle = 172(8)°, N(1)···O(1) distance = 2.91(1) Å), which may stabilize the crystal of **2**·1,4-dioxane: the guest release temperature of **2**·1,4-dioxane is considerably higher than those of the others guest-inclusion crystals (Table 1).

< Please insert Figure 8 here >

On the bases of the solid-state photophysical data and the crystal structures of the guest-free and the guest-inclusion compounds, we discuss the effects of the enclathrated guest on the solid-state photophysical properties of the clathrate compounds. A comparison of the above five crystal structures shows that the strength of the π - π interactions between the fluorophores decrease in the following order: **2** (guest-free) $\approx$ **2**·morpholine > **2**·ethyl acetate > **2**·ethanol > **2**·1,4-dioxane. Strong intermolecular π - π interactions between the fluorophores induce the large red-shift of the absorption and fluorescence maxima and an intense fluorescence quenching in the solid state.^[2, 3, 5, 9] However, the solid-state fluorescence intensity of **2**·ethanol is weaker than that of **2**·ethyl acetate. It is considered that the continuous intermolecular hydrogen bonding ranging alternately host and guest (···H···G···H···) was observed in only **2**·ethanol, which is a principal factor leading to fluorescence quenching in the solid state. Therefore, it is confirmed from these data that the crystal of **2**·1,4-dioxane exhibits comparatively strong fluorescent intensity because of the destructions of the π - π interactions and no continuous intermolecular hydrogen bonding between hosts in comparison with the cases of **2**·morpholine, **2**·ethanol and **2**·ethyl acetate.

Conclusions

It was found that the fluorophore **2** can include various guest molecules in the crystalline state by changing the tautomeric form on the imidazole ring. Solid-state fluorescence enhancement and a

blue-shift of the absorption and fluorescence wavelength maxima are observed depending on the enclathrated guest molecules. From the comparison of the X-ray crystal structures of the guest-free and several clathrate compounds, we have concluded that the differences in the destruction of the host-host π - π interactions by enclathration of the guest molecules are reflected on the solid-state fluorescence intensity and the fluorescence wavelength maxima of the crystals. Furthermore, it is found that an existence of the continuous intermolecular hydrogen bonds ranging alternately fluorescent host and guest ($\cdots\text{H}\cdots\text{G}\cdots\text{H}\cdots$) lead to a strong solid-state fluorescence quenching behaviour. Thus, new useful information concerning the solid-state fluorescence of fluorescent organic hosts has been obtained.

Experimental Section

General: Elemental analyses were measured with a Perkin Elmer 2400 II CHN analyzer. IR spectra were recorded on a JASCO FT/IR-5300 spectrophotometer for samples in KBr pellet form. Thermogravimetry (TG) and differential thermal analysis (DTA) spectra were performed on a Rigaku TG 8120. Single-crystal X-ray diffraction was performed on Rigaku AFC7S diffractometer. Absorption spectra were observed with a JASCO U-best30 spectrophotometer and fluorescence spectra were measured with a JASCO FP-777 spectrophotometer. The fluorescence quantum yields (Φ) in benzene were determined using 9,10-diphenylanthracene ($\Phi = 0.67$, $\lambda_{\text{ex}} = 357 \text{ nm}$)^[15] in benzene as the standard. The solid-fluorescence quantum yields (Φ) were determined by using a calibrated integrating sphere system ($\lambda_{\text{ex}} = 325 \text{ nm}$). For the measurement of the solid-state fluorescence excitation and emission spectra of the crystals, Jasco FP-1060 attachment was used. ^1H NMR spectra were recorded on a JNM-LA-400 (400 MHz) FT NMR spectrometer with tetramethylsilane (TMS) as an internal standard.

4-[4-(diethylamino)phenyl]-[1,2]naphthoquinone (1): A solution of sodium 1,2-naphthoquinone-4-sulphonate (10.0 g, 38.4 mmol), *N,N*-diethylaniline (8.6 g, 57.6 mmol), and $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$ (9.56 g, 38.4 mmol) in $\text{CH}_3\text{COOH} : \text{H}_2\text{O}$ [4 : 1 (v/v)] (200 ml) was stirred at room temperature for 7 days. The reaction mixture was poured into water. The solution was neutralized with aq. Na_2CO_3 and extracted with CH_2Cl_2 . The organic extract was washed with water and evaporated. The residue was chromatographed on silica gel (CH_2Cl_2 as eluent) to give **1** (6.78 g, yield 58 %); mp 116–118 °C; ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$, TMS) $\delta = 1.13$ (t, 6H), 3.42 (m, 4H), 6.29 (s, 1H), 6.79 (d, $J = 8.7 \text{ Hz}$, 2H), 6.39 (d, $J = 8.7 \text{ Hz}$, 2H), 7.61 (m, 1H), 7.72 (m, 1H), 7.72 (m, 2H), 8.03 (m, 1H); IR (KBr): $\tilde{\nu} = 1650, 1603 \text{ cm}^{-1}$; MS [m/z] %: 305 (100) [M^+].

2-(4-cyanophenyl)-5-[4-(diethylamino)phenyl]-3*H*-imidazo[4,5-*a*]naphthalene (2): A solution of **1** (5.63 g, 18.45 mmol), *p*-cyanobenzaldehyde (2.42 g, 18.5 mmol), and ammonium acetate (22.75 g, 0.3 mol) in acetic acid (170 ml) was stirred at 80 °C for 1 h. The reaction mixture was neutralized with aq. Na_2CO_3 and extracted with CH_2Cl_2 . The organic extract was washed with water and evaporated. The residue was chromatographed on silica gel (CH_2Cl_2 : ethyl acetate = 10 : 1 as eluent) to give **2** (5.75 g, yield 75 %); mp 244–247 °C; ^1H NMR (400 MHz, $[\text{D}_6]\text{SMSO}$, TMS) $\delta = 1.15$ (t, 6H), 3.34 (m, 4H), 6.80 (d, $J = 8.5 \text{ Hz}$, 2H), 7.31 (d, $J = 8.3 \text{ Hz}$, 2H), 7.46 (m, 1H), 7.54 (s, 1H), 7.65 (m, 1H), 7.96 (d, $J = 8.3 \text{ Hz}$, 1H), 8.04 (d, $J = 8.1 \text{ Hz}$, 2H), 8.41 (d, $J = 7.8 \text{ Hz}$, 2H), 8.58 (d, $J = 6.6 \text{ Hz}$, 1H); IR (KBr): $\tilde{\nu} = 2220 \text{ cm}^{-1}$; elemental analysis calcd (%) for $\text{C}_{28}\text{H}_{34}\text{N}_4$: C 80.74, H 5.81, N 13.45; found: C 80.88, H 5.61, N 13.68.

Preparation of guest-inclusion crystals: The host compound **2** was dissolved with heating in respective guest-solvent. The solution was filtered and kept for a few days at room temperature. The crystals that formed were collected by filtration. The host (H) : guest (G) stoichiometric ratio of the

inclusion compounds was determined by means of ^1H NMR integration and CHN analysis.

2 (guest-free): The host **2** (500 mg) was dissolved by warming in nitromethane (26 ml), and the resulting solution was allowed to stand at room temperature. The crystals (orange-yellow, prism, 340 mg) were collected and dried on the filter paper.

2-morpholine (H : G = 1 : 1): The host **2** (200 mg) was dissolved by warming in morpholine (3 ml), and the resulting solution was allowed to stand at room temperature. The crystals (yellow, prism, 184 mg) were collected and dried on the filter paper. Elemental analysis calcd (%) for $\text{C}_{32}\text{H}_{33}\text{N}_5\text{O}$: C 76.31, H 6.60, N 13.91; found: C 76.02, H 6.97, N 14.23.

2-ethyl acetate (H : G = 2 : 1): The host **2** (100 mg) was dissolved by warming in ethyl acetate (2 ml), and the resulting solution was allowed to stand at room temperature. The crystals (yellow, needle, 70 mg) were collected and dried on the filter paper. Elemental analysis calcd (%) for $\text{C}_{60}\text{H}_{56}\text{N}_8\text{O}_2$: C 78.23, H 6.13, N 12.16; found: C 78.43, H 6.17, N 12.32.

2-ethanol (H : G = 1 : 1): The host **2** (420 mg) was dissolved by warming in ethanol (18 ml), and the resulting solution was allowed to stand at room temperature. The crystals (yellow, leaflet, 322 mg) were collected and dried on the filter paper. Elemental analysis calcd (%) for $\text{C}_{30}\text{H}_{30}\text{N}_4\text{O}$: C 77.89, H 6.54, N 12.11; found: C 77.60, H 6.24, N 11.92.

2,1,4-dioxane (H : G = 2 : 1): The host **2** (300 mg) was dissolved by warming in 1,4-dioxane (4 ml), and the resulting solution was allowed to stand at room temperature. The crystals (yellow, needle-like, 188 mg) were collected and dried on the filter paper. Elemental analysis calcd (%) for $\text{C}_{60}\text{H}_{56}\text{N}_8\text{O}_2$: C 78.23, H 6.13, N 12.16; found: C 78.39, H 6.05, N 12.26.

X-ray crystallographic studies: The reflection data were collected at $23 \pm 1^\circ\text{C}$ on a Rigaku AFC7S four-circle diffractometer by 2θ - ω scan technique, and using graphite-monochromated $\text{MoK}\alpha$ ($\lambda = 0.71069 \text{ \AA}$) radiation at 50 kV and 30 mA. In all case, the data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied. The reflection intensities were monitored by three standard reflections for every 150 reflections. An empirical absorption correction based on azimuthal scans of several reflections was applied. All calculations were performed using the teXsan^[16] crystallographic software package of Molecular Structure Corporation. CCDC-692724 (**2**), CCDC-692725 (**2-morpholine**), CCDC-692726 (**2-ethyl acetate**), CCDC-692727 (**2-ethanol**), and CCDC-692728 (**2,1,4-dioxane**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal of 2: The transmission factors ranged from 0.98 to 1.00. The crystal structure was solved by direct methods using SIR 92.^[17] The structures were expanded using Fourier techniques.^[18] The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, the rest were fixed geometrically and not refined. Crystallographic data: $\text{C}_{28}\text{H}_{34}\text{N}_4$, $M = 416.52$, monoclinic, $a = 11.665(2)$, $b = 12.531(2)$, $c = 15.743(2) \text{ \AA}$, $\beta = 107.38(1)^\circ$, $U = 2196.2(6) \text{ \AA}^3$, $\rho_{\text{calcd}} = 1.260 \text{ g cm}^{-3}$, $T = 296.2\text{K}$, space group $\text{P2}_1/\text{a}$ (no.14), $Z = 4$, $\mu(\text{Mo-K}\alpha) = 0.76 \text{ cm}^{-1}$, 4078 reflections measured, 3868 unique ($R_{\text{int}} = 0.023$) which were used in all calculations. The final R indices [$I > 2\sigma(I)$], $R1 = 0.053$, $wR(F^2) = 0.1185$.

Crystal of 2-morpholine: The transmission factors ranged from 0.00 to 1.00. The crystal structure was solved by direct methods using SIR 92.^[17] The structures were expanded using Fourier techniques.^[18] The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, the rest were fixed geometrically and not refined. Crystallographic data: $\text{C}_{32}\text{H}_{33}\text{N}_5\text{O}$, $M = 503.65$, triclinic, $a = 10.786(3)$, $b = 16.031(7)$, $c = 8.461(2) \text{ \AA}$, $\alpha = 98.18(3)^\circ$, $\beta = 90.26(2)^\circ$, $\gamma = 74.17(2)^\circ$, $U = 1392.3(8) \text{ \AA}^3$, $\rho_{\text{calcd}} = 1.201 \text{ g cm}^{-3}$, $T = 296.2\text{K}$, space group P1- (no.2), $Z =$

2, $\mu(\text{Mo-K}\alpha) = 0.75 \text{ cm}^{-1}$, 5081 reflections measured, 5078 unique ($R_{\text{int}} = 0.026$) which were used in all calculations. The final R indices [$I > 2\sigma(I)$], $R1 = 0.0638$, $wR(F^2) = 0.1406$.

Crystal of 2-ethyl acetate: The transmission factors ranged from 0.95 to 1.00. The crystal structure was solved by direct methods using SAPI 90.^[19] The structures were expanded using Fourier techniques.^[18] The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, the rest were fixed geometrically and not refined. Crystallographic data: $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_2$, $M = 212.27$, triclinic, $a = 13.153(2)$, $b = 18.937(2)$, $c = 11.983(2) \text{ \AA}$, $\alpha = 100.55(1)^\circ$, $\beta = 114.918(10)^\circ$, $\gamma = 101.35(1)^\circ$, $U = 2532.5(7) \text{ \AA}^3$, $\rho_{\text{calcd}} = 1.208 \text{ g cm}^{-3}$, $T = 296.2 \text{ K}$, space group $P1 - (\text{no.} 2)$, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 0.75 \text{ cm}^{-1}$, 9340 reflections measured, 9336 unique ($R_{\text{int}} = 0.018$) which were used in all calculations. The final R indices [$I > 2\sigma(I)$], $R1 = 0.0727$, $wR(F^2) = 0.1699$.

Crystal of 2-ethanol: The transmission factors ranged from 0.93 to 1.00. The crystal structure was solved by direct methods using SAPI 91.^[20] The structures were expanded using Fourier techniques.^[18] The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, the rest were fixed geometrically and not refined. Crystallographic data: $\text{C}_{10}\text{H}_{20}\text{N}_4\text{O}$, $M = 240.32$, triclinic, $a = 10.364(3)$, $b = 17.680(4)$, $c = 7.444(3) \text{ \AA}$, $\alpha = 98.23(3)^\circ$, $\beta = 107.68(3)^\circ$, $\gamma = 98.72(2)^\circ$, $U = 1258.2(8) \text{ \AA}^3$, $\rho_{\text{calcd}} = 1.221 \text{ g cm}^{-3}$, $T = 296.2 \text{ K}$, space group $P1 - (\text{no.} 2)$, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 0.75 \text{ cm}^{-1}$, 4801 reflections measured, 4431 unique ($R_{\text{int}} = 0.049$) which were used in all calculations. The final R indices [$I > 2\sigma(I)$], $R1 = 0.0716$, $wR(F^2) = 0.1760$.

Crystal of 2,1,4-dioxane: The transmission factors ranged from 0.88 to 1.00. The crystal structure was solved by direct methods using SIR 92.^[17] The structures were expanded using Fourier techniques.^[18] The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, the rest were fixed geometrically and not refined. Crystallographic data: $\text{C}_{10}\text{H}_{18}\text{N}_4\text{O}$, $M = 240.32$, triclinic, $a = 9.36(1)$, $b = 19.14(1)$, $c = 7.355(3) \text{ \AA}$, $\alpha = 91.70(5)^\circ$, $\beta = 107.67(6)^\circ$, $\gamma = 86.17(8)^\circ$, $U = 1253(1) \text{ \AA}^3$, $\rho_{\text{calcd}} = 1.221 \text{ g cm}^{-3}$, $T = 296.2 \text{ K}$, space group $P1 - (\text{no.} 2)$, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 0.75 \text{ cm}^{-1}$, 4705 reflections measured, 4699 unique ($R_{\text{int}} = 0.110$) which were used in all calculations. The final R indices [$I > 2\sigma(I)$], $R1 = 0.1533$, $wR(F^2) = 0.3070$.

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- [1] a) C. W. Tang, S. A. Vanslyke, *Appl. Phys. Lett.* **1987**, *51*, 913–915; b) L. S. Sapochak, F. E. Benincasa, R. S. Schofield, J. L. Baker, K. K. C. Riccio, D. Fogarty, H. Kohlmann, K. F. Ferris, P. E. Burrows, *J. Am. Chem. Soc.* **2002**, *124*, 6119–6125; c) C. J. Tonzola, M. M. Alam, W. K. Kaminsky, S. A. Jenekhe, *J. Am. Chem. Soc.* **2003**, *125*, 13548–13558; d) Y. Sonoda, Y. Kawanishi, T. Ikeda, M. Goto, S. Hayashi, N. Tanigaki, K. Yase, *J. Phys. Chem. B* **2003**, *107*, 3376–3383; e) Y. Kim, J. Bouffard, S. E. Kooi, T. M. Swager, *J. Am. Chem. Soc.* **2005**, *127*, 13726–13731; f) H. Zhang, Z. Zhang, K. Ye, J. Zhang, Y. Wang, *Adv. Mater.* **2006**, *18*, 2369–2372; g) E. Sakuda, K. Tsuge, Y. Sasaki, N. Kitamura, *J. Phys. Chem. B* **2005**, *109*, 22326–22331; h) C.-H. Zhao, A. Wakamiya, Y. Inukai, S. Yamaguchi, *J. Am. Chem. Soc.* **2006**, *128*, 15934–15935; i) Z. Ning, Z. Chen, Q. Zhang, Y. Yan, S. Qian, Y. Cao, H. Tian, *Adv. Funct. Mater.* **2007**, *17*, 3799–3807; j) R. Davis, N. S. S. Kumar, S. Abraham, C. H. Suresh, N. P. Rath, N. Tamaoki, S. Das, *J. Phys. Chem. C* **2008**, *112*, 2137–2146; k) N. S. S. Kumar, S. Varghese, N. P. Rath, S. Das, *J. Phys. Chem. C* **2008**, *112*, 8429–8437.
- [2] a) H. Langhals, T. Potrawa, H. Nöth, G. Linti, *Angew. Chem. Int. Ed.* **1989**, *28*, 478–480; b) H. Langhals, R. Ismael, O. Yürük, *Tetrahedron* **2001**, *56*, 5435–5441; c) K. Yoshida, Y. Ooyama, H. Miyazaki and S. Watanabe, *J. Chem. Soc. Perkin Trans. 2* **2002**, 700–707; d) Y. Ooyama, T. Nakamura, K. Yoshida, *New J. Chem.* **2005**, *29*, 447–456; e) Y. Ooyama, T. Okamoto, T. Yamaguchi, T. Suzuki, A. Hayashi, K. Yoshida, *Chem.-Eur. J.* **2006**, 7827–7838; f) Y. Ooyama, Y. Harima, *Chem. Lett.* **2006**, 902–903; g) Y. Ooyama, Y. Kagawa, Y. Harima, *Eur. J. Org. Chem.* **2007**, *22*, 3613–3621; h) Y. Ooyama, T. Mamura, K. Yoshida, *Eur. J. Org. Chem.* **2007**, *30*, 5010–5019; i) Y. Ooyama, T. Mamura, K. Yoshida, *Tetrahedron Lett.* **2007**, *48*, 5791–5793.
- [3] a) H.-C. Yeh, W.-C. Wu, Y.-S. Wen, D.-C. Dai, J.-K. Wang, C.-T. Chen, *J. Org. Chem.* **2004**, *69*, 6455–6462; b) Y. Ooyama, S. Yoshikawa, S. Watanabe, K. Yoshida, *Org. Biomol. Chem.* **2006**, *4*, 3406–3409; c) Y. Ooyama, S. Yoshikawa, S. Watanabe, K. Yoshida, *Org. Biomol. Chem.* **2007**, *5*, 1260–1269.
- [4] Y. Mizobe, N. Tohnai, M. Miyata, Y. Hasegawa, *Chem. Commun.* **2005**, 1839–1841.
- [5] a) K. Yoshida, H. Miyazaki, Y. Miura, Y. Ooyama, S. Watanabe, *Chem. Lett.* **1999**, 837–838; b) K. Yoshida, Y. Ooyama, S. Tanikawa, S. Watanabe, *Chem. Lett.* **2000**, 714–715; c) K. Yoshida, Y. Ooyama, S. Tanikawa, S. Watanabe, *J. Chem. Soc. Perkin Trans. 2* **2002**, 708–714.
- [6] a) Z. Fei, N. Kocher, C. J. Mohrschlatt, H. Ihmels, D. Stalke, *Angew. Chem. Int. Ed.* **2003**, *42*, 783–787; b) J. L. Scott, T. Yamada, K. Tanaka, *New J. Chem.* **2004**, *28*, 447–450.
- [7] Y. Imai, K. Murata, K. Kawaguchi, T. Sato, N. Tajima, R. Kuroda, Y. Matsubara, *Chem. Asian, J.* **2008**, *3*, 625–629.
- [8] a) K. Yoshida, J. Yamazaki, Y. Tagashira, S. Watanabe, *Chem. Lett.* **1996**, 9–10; b) K. Yoshida, T. Tachikawa, J. Yamasaki, S. Watanabe, S. Tokita, *Chem. Lett.* **1996**, 1027–1028; c) Y. Ooyama, K. Yoshida, *New J. Chem.* **2005**, *29*, 1204–1212.
- [9] Y. Ooyama, K. Yoshida, *Eur. J. Org. Chem.* **2008**, *15*, 2564–2570.
- [10] K. Yoshida, K. Uwada, H. Kumaoka, L. Bu, S. Watanabe, *S. Chem. Lett.* **2001**, 808–809.
- [11] a) E. Weber, M. Czugler, in *Molecular and Molecular Recognition-Clathrates I and II*, ed. E. Weber, in *Top. Curr. Chem.*, Springer-Verlag Berlin, **1988**, vol. 149, p. 45; b) E. Weber, in *Inclusion Phenomena and Molecular Recognition*, ed. J. L. Atwood, Plenum Press, New York, **1990**, vol. 4, p. 188.
- [12] F. Toda, *Acc. Chem. Res.* **1995**, *28*, 480–486.
- [13] K. Ochiai, Y. Mazaki, S.-I. Nishikiori, K. Kobayashi, S. Hayashi, *J. Chem. Soc. Perkin Trans. 2* **1996**, 1139–1145.
- [14] a) S. A. Bourne, L. Hohnson, C. Marais, L. R. Nassimbeni, E. Weber, K. Skobridis, F. Toda, *J. Chem. Soc. Perkin Trans. 2* **1991**, 1707–1713; b) I. Csöreg, E. Weber, L. R. Nassimbeni, O. Gallardo, N. Dörpinghaus, A. Ertan, A. A. Bourne, *J. Chem. Soc. Perkin Trans. 2* **1993**, 1775–1782; c) J. D. Wright, *Molecular crystals*, 2 ed. Cambridge University Press, New York, **1995**, p.32.
- [15] C. A. Heller, R. A. Henry, B. A. McLaughlin, D. E. Bills, *J. Chem. Eng. Data* **1974**, *19*, 214–219.
- [16] teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation **1985** and **1992**.
- [17] A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidori, *J. Appl. Cryst.* **1994**, *27*, 435.
- [18] DIRDIF94. P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, J. M. M. Smits, The DIRDIF94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, **1994**.
- [19] Fan Hai-Fu (1990). Structure Analysis Programs with Intelligent Control, Rigaku Corporation, Tokyo, Japan.
- [20] Fan Hai-Fu (1991). Structure Analysis Programs with Intelligent Control, Rigaku Corporation, Tokyo, Japan.

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

Novel imidazo[4,5-*a*]naphthalene-type fluorescent clathrate host (**2**) with two tautomeric forms (**A** and **B**) that are possible for the imidazole ring, exhibits sensitive colour change and drastic fluorescence enhancement behaviour with a blue shift of the emission maximum upon enclathration of various kinds of organic solvent molecules.

Fluorescent Clathrate Host

Yousuke Ooyama,* Shinobu Nagano, Miyako Okamura, and Katsuhira Yoshida* Page No. – Page No.

Solid-state Fluorescence Changes of 2-(4-Cyanophenyl)-5-[4-(diethylamino)phenyl]-3*H*-imidazo[4,5-*a*]naphthalene upon Inclusion of Organic Solvent Molecules

Keywords: (Dyes / Clathrate / Imidazole / Crystal structures / Solid-state fluorescence)

Table 1. Host-guest molar ratio, crystal form, crystal color, and thermal analysis of the guest-free and the guest-inclusion crystals of **2**

Guest	Host : Guest (molar ratio)	Crystal form	Crystal colour	TG weight loss [%]		Guest loss peak point [°C]	endotherm peak point [°C]	Host 2 melt peak point [°C]
				Calculation	Observation			
None	1 : 0	Prism	Yellowish orange	0	0	–	245	
Morpholine	1 : 1	Prism	Yellowish orange	17.29	17.23	146	245	
Ethanol	1 : 1	Leaflet	Yellowish orange	9.96	9.63	138	–	
Ethyl acetate	2 : 1	Needle	Yellow	9.56	9.85	159	–	
1,4-Dioxane	2 : 1	Needle	Yellow	9.56	9.63	176	–	

Figure and Scheme captions

Scheme 1. (i) *N,N*-diethylaniline, $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CH}_3\text{COOH} : \text{H}_2\text{O}$ [4 : 1 (v/v)], 7 days, RT, 58%; (ii) *p*-cyanobenzaldehyde, $\text{CH}_3\text{COONH}_4$, CH_3COOH , 1 h, 80 °C, 75%.

Figure 1. Normalized absorption ($\cdots$) (2.5×10^{-5} M) and fluorescence ($-$) (2.5×10^{-6} M, $\lambda_{\text{ex}} = 386$ nm) spectra of **2** in benzene. Measured under oxygen-free condition.

Figure 2. TG and DTA traces for the guest inclusion compounds; a) **2**·morpholine and b) **2**·ethanol.

Figure 3. Solid-state excitation ($\cdots$) and fluorescence ($-$) spectra of the guest-free and guest inclusion crystals of **2**; (a) **2** (guest-free): $\lambda_{\text{ex}} = 451$ nm, $\lambda_{\text{em}} = 536$ nm, $\Phi = 0.06$; (b) **2**·morpholine: $\lambda_{\text{ex}} = 452$ nm, $\lambda_{\text{em}} = 517$ nm, $\Phi = 0.05$; (c) **2**·ethanol: $\lambda_{\text{ex}} = 451$ nm, $\lambda_{\text{em}} = 515$ nm, $\Phi = 0.08$; (d) **2**·ethyl acetate: $\lambda_{\text{ex}} = 446$ nm, $\lambda_{\text{em}} = 491$ nm, $\Phi = 0.10$; (e) **2**·1,4-dioxane: $\lambda_{\text{ex}} = 440$ nm, $\lambda_{\text{em}} = 495$ nm, $\Phi = 0.26$.

Figure 4. Crystal structure of **2** : (a) a stereoview of the molecular packing structure, and (b) schematic structure, and (c) top view of the pairs of fluorophores.

Figure 5. Crystal structure of **2**·morpholine : (a) a stereoview of the molecular packing structure, and (b) schematic structure, and (c) top view of the pairs of fluorophores.

Figure 6. Crystal structure of **2**·ethanol : (a) a stereoview of the molecular packing structure, and (b) schematic structure, and (c) top view of the pairs of fluorophores.

Figure 7. Crystal structure of **2**·ethyl acetate : (a) a stereoview of the molecular packing structure, and (b) schematic structure, (c) top view of the pairs of fluorophores with B-form (stacking **I**), and (d) with A-form (stacking **II**), and (e) the π -stacking between the host with A-form and the host with B-form (stacking **III**).

Figure 8. Crystal structure of **2**·1,4-dioxane : (a) a stereoview of the molecular packing structure, and (b) schematic structure, and (c) (stacking **I**) and (d) (stacking **II**) top view of the π -stacking between the fluorophores.

Scheme 1

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8