Heterocyclic Quinol-type Fluorophores: Solid-state Fluorescence Change of Crystals of Benzo[*b*]naphtho[1,2-*d*]furan-6-one-type Fluorophore upon Inclusion of Organic Solvent Molecules**

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Keywords: fluorescence / dyes / inclusion compounds / crystal structures / heterocycles

The crystals of novel benzo[*b*]naphtho[1,2-*d*]furan-6-one-type fluorophores (**1**) exhibit sensitive colour and fluorescence change upon enclathration of organic solvent molecules. The crystal of the fluorophore **1b** (R = Bu) exhibits fluorescence decrease upon inclusion of cyclohexane, however, the crystal of the fluorophore **1c** (R = Ph) exhibits a drastic fluorescence enhancement upon inclusion of chloroform. To elucidate the enclathrated guest effects on the photophysical properties of the crystals, the X-ray crystal

structures of the guest-free and guest-inclusion compounds have been determined. On the basis 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

The development of fluorescent molecular sensors is of importance because of the detection of cations, anions and biochemical analyses such as amino acids and applicable to a fluorescent switch.^[1] A number of fluorophores have been developed, and the relation between the chemical structure and their fluorescence properties in solution have been investigated in order to elucidate the mechanism of fluorescence changes upon formation of complexes with cations, anions, and neutral molecules.^[2] However, only several fluorescent hosts that exhibit fluorescence change upon enclathration of organic solvent molecules in the crystalline state have been reported.^[3]

We have recently developed novel benzofurano[3,2-*b*]naphthoquinol-type^[4], imidazo[5,4-*a*]anthraquinol-type^[5] and phenanthro[9,10-*d*]imidazole-type^[6] fluorescent hosts whose crystals exhibit a dramatic fluorescence enhancement upon inclusion of various gaseous amines, organic solvents and carboxylic acids, respectively. From the relation between the solid-state fluorescence properties and the crystal structures, it was confirmed that the destruction of π - π interactions between the fluorophores by guest enclathration is the main reason for the guest-dependent fluorescence enhancement behaviour. In the previous paper, we have reported the absorption and fluorescence properties in solution and in the solid state of novel heterocyclic quinol-type fluorophores, 5-hydroxy-5-substituent-benzo[*b*]naphtho[1,2-*d*]furan-6-one (**1**) and 3-hydroxy-3-substituent-benzo[*k*]xanthen-2-one (**2**) fluorophores (Scheme 1).^[7] Here, we report sensitive colour and fluorescence change of the

quinol **1** upon enclathration of organic solvent molecules in the solid state. The X-ray crystal structures of **1** 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

Inclusion Ability in the Crystalline State

In order to investigate their inclusion ability, we recrystallized the quinol compounds from various organic solvents such as ethanol, acetonitrile, cyclohexane, chloroform, benzene, 1,4-dioxane and morpholine. The quinols **1a** and **2a–2c** did not form any inclusion compounds. However, we have found that the quinols **1b** and **1c** yield inclusion compounds in stoichiometric ratios with cyclohexane and chloroform, respectively. Compared to the inclusion ability of the 1,4-quinol-type fluorescent hosts, benzofurano[3,2-*b*]naphthoquinol-type^[4] and imidazo[5,4-*a*]anthraquinol-type^[5] fluorophores, that of the 1,2-quinol-type fluorescent hosts, benzo[*b*]naphtho[1,2-*d*]furan-6-one (**1**) and benzo[*k*]xanthen-2-one (**2**) fluorophores was extremely poor. Crystal of **1b**·cyclohexane (Host : Guest = 2 : 1) was recrystallized from cyclohexane as greenish yellow prism. On the other hand, the crystal of **1c**·chloroform (H : G = 1 : 1) was recrystallized from chloroform as greenish yellow prism. Furthermore, a drastic fluorescence change upon inclusion of guest molecules was observed in both the crystals of **1b**·cyclohexane and **1c**·chloroform.

Solid-state Fluorescence Change 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 (Figures 1 and 2). Compared to the guest-free crystal of **1b**, the excitation and emission maxima of the crystals of **1b**·cyclohexane are little affected: the guest-free host

crystal exhibits relatively strong fluorescence with emission maximum at 530 nm, while the crystals of **1b**-cyclohexane exhibit weak fluorescence intensity with the emission maximum at 527 nm, whose intensity is reduced to *ca.* 35 %. On the other hand, the excitation and emission maxima of the crystal of **1c**-chloroform exhibit a blue shift and the fluorescence intensity is greatly enhanced in comparison with the guest-free crystal of **1c**: the fluorescence intensity of **1c**-chloroform was *ca.* 3-fold.

Interestingly, when the guest-free crystals of **1c** were placed in a vessel saturated with chloroform vapour at 30 °C, the colour of the crystals turned from yellow to greenish yellow. The changes in the solid-state fluorescent excitation and emission spectra of **1c** upon exposure to chloroform vapour were investigated (Figure 3). We found that the hypsochromic shift of the excitation and emission maxima and a drastic fluorescence enhancement are induced upon formation of inclusion compound with chloroform. The initial excitation band at 519 nm shifted to 507 nm. The corresponding fluorescence spectra showed a increase of fluorescence intensity with the blue-shift of emission maximum from 558 nm to 530 nm. The formation of clathrate (**1c** : chlrorform = 1 : 1) was suggested from ¹H NMR integration. The host : guest ratio is 1 : 0.5, when the crystals were exposed to chloroform vapour for 30–40 min. It took about 150 min to reach the final saturated excitation and emission spectra which were in good agreement with the spectra of the clathrate compound (**1c** : chloroform = 1 : 1) obtained by recrystallization of compound **1c** from chlrorform.

Relation between the Solid-state Fluorescence Properties and X-ray Crystal Structures of the Guest-free and the Guest-inclusion Compounds

In order to investigate 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 4–6). The packing structures demonstrate that the quinol molecules of **1a**, **1b**, **1c** and **1b**-cyclohexane are arranged in a “tread on staircase” fashion. On the other hand, the packing structure of **1c**-chloroform demonstrates that the quinol molecules are arranged in a “bricks in a wall” fashion. All crystal structures are built up by a centrosymmetric dimer unit which is composed of a pair of quinol enantiomers. In the crystals of **1a**, **1b**-cyclohexane, **1c** and **1c**-chloroform, neighbouring enantiomers are connected by two intermolecular hydrogen bonds between the hydroxyl and carbonyl oxygens through the hydroxyl proton: O(1)···O(2)* distances for **1a**, **1b**-cyclohexane, **1c** and **1c**-chloroform are 2.844(3), 2.783(3), 2.812 (4), and 2.880(4) Å, respectively. On the other hand, in the crystal of **1b**, there are two crystallographically independent molecules: the intermolecular hydrogen bondings are also observed between the hydroxyl and carbonyl oxygens through the hydroxyl proton of each crystallographically independent molecule (O(1)···O(5) and O(2)···O(4) distance = 2.81(1) and 2.77(4) Å, respectively). Furthermore, the hydroxyl proton has two proton acceptors and become bifurcated-donor hydrogen to form the three-centered hydrogen bonding with above the inter- and intramolecular carbonyl oxygens. With respect to the intramolecular hydrogen bonding formation, O(1)···O(2) distances for **1a**, **1b**, **1c**, **1b**-cyclohexane and **1c**-chloroform are 2.767(2), 2.80(4), 2.740(2), 2.785(2), and 2.738(5) Å, and O(4)···O(5) distance for **1b**; 2.82(4) Å, respectively.

Particularly interesting was observed in the crystal of **1c**-chloroform (Figure 6c): the chloroform molecules were incorporated among two pairs of quinol enantiomers, and two types of the CH···O interactions were formed between the carbonyl of the host and proton of chloroform and between the furan oxygens of the host and proton of chloroform (C(31)···O(2) distance = 3.412

(7) and C(31)···O(3) distance = 3.489 (8) Å). In contrast, in the crystal of **1b**-cyclohexane (Figure 5c), the cyclohexane molecules were incorporated in the cavity which is constituted of butyl group and the 9-dibutylamino group are placed in the same side for the π -plane, that already have existed in the crystal of **1b** (Figure 4c).

Big differences in the π -stacking between a pair of quinol enantiomers among the three quinols were observed. In the crystal of **1a**, a pair of quinol enantiomers is overlapping over the whole molecule from the electron donor part of benzofurano moiety containing the 9-dibutylamino group to the electron acceptor part of naphthoquinol moiety, which is deeply related to the solid-state photophysical properties. A large red-shift of the absorption and fluorescence maxima and the solid-state fluorescence quenching by strong donor-acceptor type π - π interactions of fluorescent dyes are known.^[4–10] In fact, the fluorescence emission intensities of **1a–1c** are in the order of **1c**>**1b**>**1a** in the crystalline state. In the crystal of **1b**, a donor-acceptor type of π -stacking between a pair of quinol enantiomers is observed, however, the rang of the π -stacking is less than that of **1a**. The interplanar distances between the benzofuranonaphthoquinol planes are *ca.* 3.40, 3.38 and 3.58 Å for **1a**, **1b** and **1c**, respectively. There are 7, 4 and 5 short interatomic π - π contacts of less than 3.6 Å in a pair of enantiomers for **1a**, **1b** and **1c**, respectively.

On the other hand, in the crystals of **1b**-cyclohexane as shown in Figures 5c and d, a donor-acceptor type of π -stacking between a pair of quinol enantiomers is also formed and the interplanar distance between the benzofuranonaphthoquinol plates is *ca.* 3.43Å. There are 12 short interatomic contacts of less than 3.6 Å, which suggest stronger π - π interaction exists in the cyclohexane-inclusion crystal than in the guest-free crystal of **1b**. In contrast, such a π -stacking is not observed for **1c**-chloroform, the enclathrated chloroform disturbs the overlapping of the host aromatic planes. It was confirmed that the enclathrated chloroform molecules considerably weaken the host-host π - π interactions. Therefore, the solid-state fluorescence quenching in the crystal of **1b** are considered to be induced upon inclusion of cyclohexane molecules by the formation of donor-acceptor type π - π interactions. In the crystals of **1c**-chloroform, it is proved that the destructions of the π - π interactions between the fluorophores by the enclathrated chloroform molecules are the main reason for the fluorescence enhancement and the blue-shift of the absorption and fluorescence maxima of the crystals.

By comparing the crystal structures of the 1,2-quinols **1a–1c** with those of the 1,4-quinols, benzofurano[3,2-*b*]naphthoquinol-type^[4] and imidazo[5,4-*a*]anthraquinol-type^[5] fluorophores, we noticed the effects of geometric arrangement on the guest inclusion in the solid state (Figure 7). In the crystals of the 1,4-quinols, the packing structures demonstrate that the crystals are built up by a centrosymmetric dimer unit which is composed of a pair of quinol enantiomers bound cofacially by intermolecular hydrogen bonds between the hydroxyl and the carbonyl oxygen or imidazole nitrogen on both sides of the dimer unit through the hydroxyl proton. On the other hand, the crystals of 1,2-quinols **1a–1c** are built up by a centrosymmetric dimer unit which is composed of a pair of quinol enantiomers, and neighbouring enantiomers which exist on coplanar are connected by two strong intermolecular hydrogen bonds between the hydroxyl and carbonyl oxygens through the hydroxyl proton. These results show that the strong intra- and intermolecular hydrogen bonds between the fluorophores such as observed in the crystals of **1a–1c** make it difficult to enclathrate the guest molecules in the solid state. Consequently, it is difficult to construct flexible cavity upon enclathration of organic solvent molecules in the crystals of **1a–1c**. As the reason the inclusion ability of **1a** was extremely poor compared to that of **1b** and **1c**, it was considered that the difficulty of constructing the cavity among the host molecules because of small substituent

(methyl group) and the formation of strong donor-acceptor type π - π interactions between the fluorophores in the crystal of **1a** makes it also difficult to enclathrate the guest molecules.

Conclusions

We have showed that the crystals of novel benzo[*b*]naphtho[1,2-*d*]furan-6-one-type fluorophore (**1**) exhibit sensitive colour and fluorescence change upon enclathration of organic solvent molecules. From the comparison of the X-ray crystal structures of the guest-free and its guest inclusion compounds, it is concluded that the destruction or increase of the π - π interactions between the fluorophores by the enclathrated guest molecules are the main reason for the fluorescence properties change of the crystals. These results also show that the quinol-type fluorescent hosts can be utilized as a selective chemical-sensor for recognition of gaseous organic solvent molecules.

Experimental Section

General: Elemental analyses were measured with a Perkin Elmer 2400 II CHN analyzer. Single-crystal X-ray diffraction was performed on Rigaku AFC7S diffractometer. Fluorescence emission and excitation spectra were measured with a JASCO FP-777 spectrometer. 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.

Preparation of Guest-inclusion Crystals of **1b and **1c**:** The host compound **1b** or **1c** 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 : guest stoichiometric ratio of the inclusion compounds was determined by means of ^1H NMR integration and CHN analysis.

Measurement of the time-dependent spectral changes of **1c upon exposure to chloroform vapour:** The guest-free crystal of the host quinol **1c** was placed in a vessel saturated with chloroform vapour at 30 °C. The exposed sample was taken out at different time intervals, and the measurement of the absorption and fluorescence spectra was carried out. For the measurement of the solid-state fluorescence excitation and emission spectra of the crystals, a JASCO FP-1060 attachment was used. The host : guest stoichiometric ratio of the inclusion compound was determined by means of ^1H NMR integration.

X-ray Crystallographic Studies: The reflection data were collected at 23 $\pm$ 1 °C on a Rigaku AFC7S four-circle diffractometer by 2θ - ω scan technique, and using graphite-monochromated $\text{MoK}\alpha$ (λ = 0.71069 Å) 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^[11] crystallographic software package of Molecular Structure Corporation. CCDC-294660 (**1a**), CCDC-294661 (**1b**), CCDC-294662 (**1c**), CCDC-635414 (**1b-cyclohexane**), and CCDC-635415 (**1c-chloroform**) 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.

Inclusion Compound **1b-cyclohexane:** Crystals of **1b-cyclohexane** were recrystallized from cyclohexane as greenish yellow prism, air stable. The

one selected had approximate dimensions 0.87 $\times$ 0.40 $\times$ 0.20 mm. The transmission factors ranged from 0.98 to 1.00. The crystal structure was solved by direct methods using SIR 92.^[12] The structures were expanded using Fourier techniques.^[13] The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, the rest were fixed geometrically and not refined. **Crystal data.** $\text{C}_{31}\text{H}_{41}\text{NO}_3$, M = 475.67, triclinic, a = 12.870(2), b = 13.638(2), c = 9.514(2) Å, α = 109.59(1)°, β = 96.89(2)°, γ = 63.57(1)°, U = 1408.0(4) Å³, T = 296.2K, space group P1- (no.2), Z = 2, $\mu(\text{Mo-K}\alpha)$ = 0.71 cm⁻¹, 6738 reflections measured, 6467 unique (R_{int} = 0.029) which were used in all calculations. The final R indices [$I > 2\sigma(I)$], $R1$ = 0.0611, $wR(F^2)$ = 0.1447.

Inclusion Compound **1c-chloroform:** Crystals of **1c-chloroform** were recrystallized from chloroform as greenish yellow prism, air stable. The one selected had approximate dimensions 0.50 $\times$ 0.40 $\times$ 0.65 mm. The transmission factors ranged from 0.98 to 1.00. The crystal structure was solved by direct methods using SIR 92.^[12] The structures were expanded using Fourier techniques.^[13] The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, the rest were fixed geometrically and not refined. **Crystal data.** $\text{C}_{31}\text{H}_{32}\text{NO}_3\text{Cl}_3$, M = 572.96, triclinic, a = 11.463(2), b = 13.591(3), c = 10.556(2) Å, α = 97.01(2)°, β = 113.75(1)°, γ = 98.15(2)°, U = 1460.6(6) Å³, T = 296.2K, space group P1- (no.2), Z = 2, $\mu(\text{Mo-K}\alpha)$ = 3.5 cm⁻¹, 5426 reflections measured, 5147 unique (R_{int} = 0.029) which were used in all calculations. The final R indices [$I > 2\sigma(I)$], $R1$ = 0.0782, $wR(F^2)$ = 0.1883.

Acknowledgments

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

Layout 1:

The crystals of novel benzo[*b*]naphtho[1,2-*d*]furan-6-one-type fluorophore (**1**) exhibit sensitive colour and fluorescence changes upon enclathration of organic solvent molecules.

(Solid-state fluorescence)

Yousuke Ooyama* and **Katsuhira Yoshida*** Page No. – Page No.

Heterocyclic Quinol-type Fluorophores:
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Inclusion of Organic Solvent Molecules

Keywords: fluorescence / dyes /
inclusion compounds / crystal structures
/ heterocycles

Figure and Scheme captions

Scheme 1. Heterocyclic quinol-type fluorophores **1a–1c** and **2a–2c**.

Figure 1. Excitation (···) and emission (–) spectra of the crystals of **1b** and **1b**·cyclohexane: **1b**: $\lambda_{\text{ex}} = 503$ nm, $\lambda_{\text{em}} = 530$ nm; **1b**·cyclohexane: $\lambda_{\text{ex}} = 505$ nm, $\lambda_{\text{em}} = 527$ nm.

Figure 2. Excitation (···) and emission (–) spectra of the crystals of **1c** and **1c**·chloroform: **1c**: $\lambda_{\text{ex}} = 519$ nm, $\lambda_{\text{em}} = 558$ nm; **1c**·chloroform: $\lambda_{\text{ex}} = 509$ nm, $\lambda_{\text{em}} = 533$ nm.

Figure 3. Time-dependent spectral changes of the guest-free crystals of **1c** upon exposure to chloroform vapour at 30 °C; the excitation (···) and emission (–) spectra were recorded at their corresponding emission and excitation maxima.

Figure 4. Crystal packing and hydrogen bonding pattern of **1a–1c** (a) a stereoview of the molecular packing structure, (b) a schematic structure, (c) a side view, and (d) a top view of the pairs of fluorophores.

Figure 5. Crystal packing and hydrogen bonding pattern of **1b**·cyclohexane (2 : 1): (a) a stereoview of the molecular packing structure, and (b) a schematic structure, (c) a side view, and (d) a top view of a cluster unit.

Figure 6. Crystal packing and hydrogen bonding pattern of **1c**·chloroform (1 : 1): (a) a stereoview of the molecular packing structure, and (b) a schematic structure, (c) a side view, and (d) a top view of a cluster unit.

Figure 7. Schematic structure of a pair of quinol enantiomers for (a) benzofurano[3,2-*b*]naphthoquinol-type^[4] and (b) imidazo[5,4-*a*]anthraquinol-type^[5] fluorophores. Hydrogen bonds are shown as dotted lines.

1a: R=Me
1b: R=Bu
1c: R=Ph

2a: R=Me
2b: R=Bu
2c: R=Ph

Scheme 1

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7