Solid-Surface Fluorescence Enhancement Behavior of a Benzofuranoquinol-Type Fluorescent Host upon Enclathration of Alicyclic Amines

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A novel benzofuranoquinol-type fluorescent host which exhibits sensitive color change and fluorescence enhancement behavior upon enclathration of alicyclic amines has been developed. The X-ray crystal structures of the guest-free and morpholine inclusion compounds have been elucidated, on the basis of which the mechanism of the optical sensing is discussed.

The design of host molecules which form crystalline inclusion compouds has actively been pursued and various types of organic hosts have been developed.[1] However, crystalline hosts that can give optical signals response to the inclusion behavior are rare. A few inclusion hosts which exhibit sensitive color change upon enclathration of guest molecules are known,[2,3] but little is known about fluorescent hosts. Recently, we have developed novel imidazoanthraquinol-type fluorophores which form inclusion compounds with various kinds of solvent molecules, the solid-surface fluorescence intensity of which is dramatically enhanced upon enclathration of the solvent molecules.[4] Such fluorophores are expected to be available for designing novel fluorescent chemosensors or new emissive materials. Hence, we designed another quinol-type fluorophore, benzofurano[3,2-b]naphthoquinols (**2** and **3**), and have got a new fluorescent host which exhibits sensitive color and fluorescence changes upon enclathration of alicyclic amines in crystals.

The starting benzofurano[3,2-b]naphthoquinone dye (**1**) was prepared by the reaction of 1,4-naphthoquinone with *m*-(dibutylamino)phenol according to the procedure described in the previous paper.[5] In order to get quinols, we next examined the reaction of **1** with organolithium reagents (RLi: MeLi, BuLi, and PhLi) at -108 °C. As shown in Table 1, isomeric pairs of quinols (**2a**-**2c** and **3a**-**3c**)[6] were obtained. The ratio of the products was significantly influenced by steric factor of the counter anions (R^-) of organolithium reagents; **2a**/**3a**~**2c**/**3c** = 35/65~16/84. All the products exhibited fluorescence in solutions.

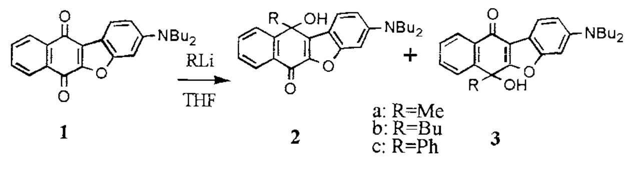

Table 1. The reaction of **1** with organolithium reagents at -108 °C

Run	RLi	Products	Yield/% 2 +3	Ratio 2 / 3
1	MeLi	**2a**, **3a**	50.8	35/65
2	BuLi	**2b**, **3b**	57.6	40/60
3	PhLi	**2c**, **3c**	50.6	16/84

In order to investigate the enclathration ability, we recrystallized the quinol products from various solvents such as ethanol, acetonitrile, benzene, 1,4-dioxane, morpholine and so on. The quinols (**2a**, **2b**, **3a**, and **3b**) did not give inclusion compounds, however, the quinol (**3c**)[7] yielded host-guest inclusion compounds with alicyclic amines such as piperidine (1:1), morpholine (1:1), and piperazine (2:1).[8] The corresponding inclusion compounds[9] were also formed when the guest-free crystals of **3c** were placed in a vessel saturated with piperidine or morpholine vapor at room temperature. Such specific clathration behavior between some other solid hosts and organic solvent vapors have been reported in previous papers.[2,3,10] In the case of **3c**, the color of crystals varied from orange to light yellow and a remarkable fluorescence enhancement was observed upon enclathration of the alicyclic amines. The excitation and emission spectra recorded at their corresponding emission or excitation maxima of the guest-free and the clathrate crystals are shown in Figure 1. The 504 nm band observed in the excitation spectrum of the guest-free crystals disappears in those of the piperidine, morpholine, and piperazine inclusion crystals. The three guest-inclusion crystals exhibit the longest excitation maximum at 444, 446 and 438 nm, respectively. The solid-surface fluorescence spectra are also dramatically changed depending on the enclathrated guest molecules. The guest-free crystals exhibit relatively weak fluorescence with emission maximum at 569 nm, whereas piperidine, morpholine, and piperazine inclusion crystals exhibit 7.0, 3.8 and 2.0-fold stronger fluorescence intensity with the emission maximum blue shifted to 501, 507 and 519 nm, respectively. Similar spectral changes were also obtained within a minute when thin-film layers (ca. 2000 nm thickness) of **3c** prepared on glass plates by a conventional vacuum-vapor deposition method were placed in the morpholine

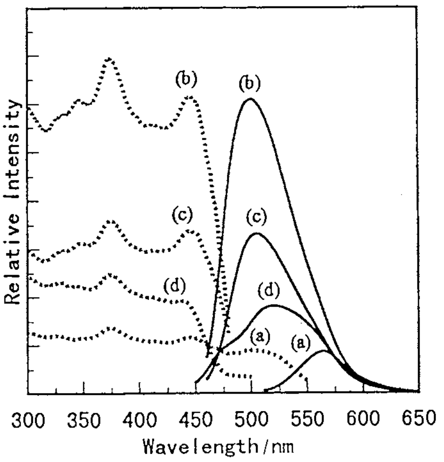

Figure 1. Excitation (···) and emission (—) spectra of (a) the guest-free crystals **3c**, and inclusion crystals; (b) **3c**·piperidine (1:1), (c) **3c**·morpholine (1:1), (d) **3c**·piperazine (2:1): (a) λex = 504, λem = 569 nm, (b) λex = 444, λem = 501 nm, (c) λex = 446, λem = 507 nm, (d) λex = 438, λem = 519 nm.

saturated vessel and the spectral changes of the films were measured at time intervals. This result suggest that the timescale of the phenomenon will allow practical applications.

The X-ray crystal structures of the guest-free host and its morpholine inclusion compound (1:1) are shown in Figures 2 (a) and (b),[11] respectively. In the crystal structure of the former, a pair of host enantiomers is cofacially bound by two intermolecular hydrogen bonds between the 6-hydroxy group of one and the 11-carbonyl group of the other enantiomer to form a centrosymmetric host-host dimer unit. The intermolecular O···O bond distance is 2.811(2) Å. The range of the interplanar distance between the aromatic planes of the electron-deficient naphthoquinol moiety and the furan ring is ca. 3.55 Å, which suggests a weak aromatic π–interaction. Hydrogen bonding interactions between neighboring host-host units are not observed. On the other hand, in the crystal structure of morpholine inclusion compound, there is no observed intermolecular hydrogen bond between the host molecules. Instead, the enclathrated morpholine molecule occupies a cavity formed between one of the butyl groups and the 6-phenyl ring that are situated vertically to the benzofurano[3,2-b]naphthoquinol plane. An intermolecular hydrogen bond between the 6-hydroxy group of the host and the morpholine nitrogen atom through the hydroxy proton is observed. The range of the intermolecular O···N bond distance is 2.778(7) Å. The enclathration of morpholine molecules results in cutting off the host-host hydrogen bonding and enlarging the host-host distance.

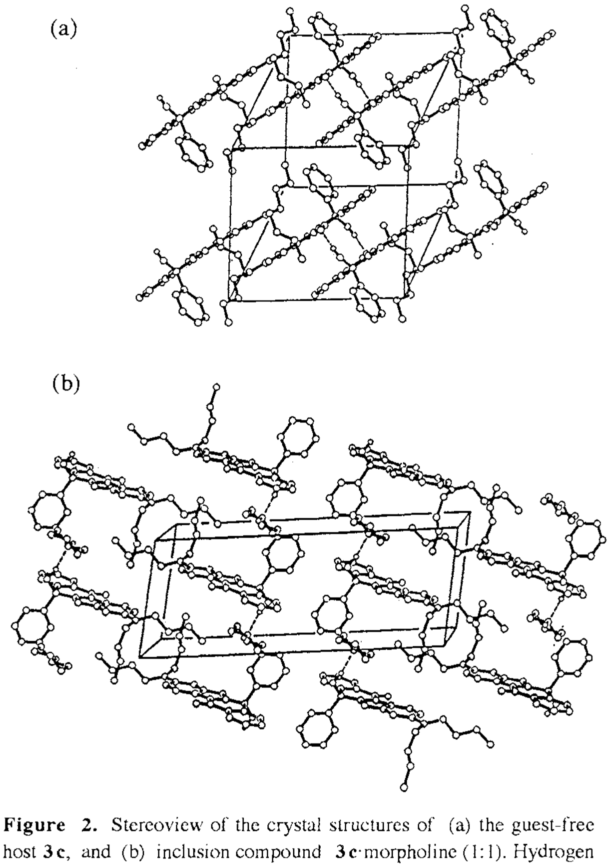

Figure 2. Stereoview of the crystal structures of (a) the guest-free host **3c**, and (b) inclusion compound **3c**·morpholine (1:1). Hydrogen bonds are shown as dotted lines.

The above results suggest that the fluorescence enhancement and the blue shift are related to packing pattern of the crystal structures. The close host-host distance in the guest-free crystals may lead an excimer formation in the excited state, which appears to explain the red shift of emission band and weak fluorescence of the crystals. The excimer formation should be suppressed in the guest-inclusion crystals, because the enclathrated guest molecules enlarge the host-host distance. Hence, the changes in the emission mode is considered to be concerned with the fluorescence enhancement behavior.

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References and Notes

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6 All the products gave satisfactory CHN analytical data. ^{1}H NMR spectra (90 MHz) were recorded in $CDCl_3$ with TMS as the internal standard. Selected physical data for the products (**2a**-**2c** and **3a**-**3c**): **2a**: mp 156-157 °C. ^{1}H NMR δ = 0.99 (6H, t), 1.3-1.7 (8H, m), 1.86 (3H, s), 2.85 (1H, s), 3.37 (4H, t), 6.64 (1H, d), 6.74 (1H, dd), 7.3-7.9 (4H, m), 8.06 (1H, dd); **2b**: mp 160-161 °C. ^{1}H NMR δ = 0.60 (3H, t), 0.99 (6H, t), 0.3-1.9 (12H, m), 2.0-2.6 (2H, m), 2.84 (1H, s), 3.37 (4H, t), 6.68 (1H, d), 6.72 (1H, dd), 7.2-7.9 (4H, m), 8.12 (1H, dd); **2c**: mp 242-243 °C. ^{1}H NMR δ = 0.94 (6H, t), 1.1-1.6 (8H, m), 3.10 (1H, s), 3.29 (4H, t), 6.55 (1H, dd), 6.60 (1H, d), 7.1-7.6 (9H, m), 8.08 (1H, dd); **3a**: mp 120-121 °C. ^{1}H NMR δ = 0.99 (6H, t), 1.2-1.7 (8H, m), 1.89 (3H, s), 3.09 (1H, s), 3.32 (4H, t), 6.67 (1H, d), 6.72 (1H, d), 7.2-7.9 (4H, m), 8.06 (1H, dd); **3b**: mp 133-134 °C. ^{1}H NMR δ = 0.65 (3H, t), 0.99 (6H, t), 0.3-1.9 (12H, m), 2.0-2.7 (2H, m), 2.99 (1H, s), 3.34 (4H, t), 6.69 (1H, dd), 6.75 (1H, d), 7.2-7.9 (4H, m), 8.09 (1H, dd); **3c**: mp 158-159 °C. ^{1}H NMR δ = 0.95 (6H, t), 1.1-1.6 (8H, m), 3.27 (4H, t), 3.71 (1H, s), 6.60 (1H, d), 6.65 (1H, dd). 7.1-7.6 (8H, m), 7.79 (1H, d), 8.04 (1H, dd).

7 The isomeric fluorophore (**2c**) , a minor product of run 3 in Table 1, also exhibited enclathration ability.

8 The piperazine clathrate was obtained by recrystallization of an equimolar mixture of **3c** and piperazine from chlorofrom.

9 The host : guest ratios of the inclusion compounds were determined by means of ^{1}H NMR integration.

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11 Crystal data for (a) the guest-free **3c** and (b) **3c**·morpholine (1:1): (a) $C_{30}H_{31}NO_3$, M=453.58, triclinic, space group $P\bar{1}$, a = 11.738(2), b = 12.244(2), c = 10.879(2) Å, α = 90.69(2), β = 116.39(1), γ = 64.73(1)°, V = 1235.8(5) Å^3, Z = 2, Dc = 1.219 gcm^{-3}; Mo-Kα radiation (graphite monochromator, λ = 0.7107 Å) final conventional R = 0.040, Rw = 0.050 for observed 2573 reflections [$I > 3\sigma(I)$] and 360 parameters; (b) $C_{34}H_{40}N_2O_4$, M = 540.70, triclinic, space group $P\bar{1}$, a = 8.759(3), b = 21.675(3), c = 8.388(2) Å, α= 99.77(1), β = 109.72(2), γ = 81.88(2)°, V = 1471.2(6) Å^3, Z = 2, Dc = 1.220 gcm^{-3}; Mo-Kα radiation (graphite mono-chromator, λ = 0.7107 Å) final conventional R = 0.070, Rw = 0.098 for observed 2718 reflections [$I > 3\sigma(I)$] and 418 parameters. The structure was solved by direct method (SAPI91) and expanded using Fourier techniques.