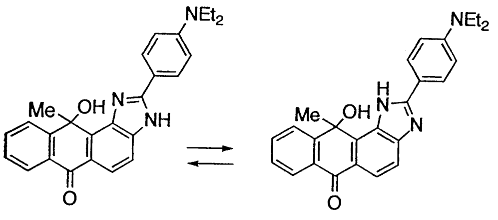
Solid-Surface Fluorescence Characteristics and X-Ray Crystal Structures of Inclusion Compounds of Imidazoanthraquinol-type Fluorescent Host with Ethanol and 1,4-Dioxane

Katsuhira Yoshida,* Tatsuya Tachikawa,*† Jun Yamasaki, Shigeru Watanabe, and Sumio Tokita†
Department of Chemistry, Faculty of Science, Kochi University, Akebono-cho, Kochi 780
†*Department of Applied Chemistry, Faculty of Engineering, Saitama University, 255 Shimo-Ohkubo, Urawa, Saitama 338*

(Received August 15, 1996)

The crystal structures of host-guest inclusion compounds of the title fluorescent host with ethanol and 1,4-dioxane were elucidated by X-ray crystal analysis. The solid-surface fluorescence spectra of the inclusion crystals were also measured. The fluorescence emission of the host was dramatically enhanced upon enclathration of the guest molecules.

The design of host molecules which can form crystalline inclusion compounds with organic guest molecules has actively been pursued and a variety of organic hosts have been developed.[1-4] However, few fluorescence hosts with enclathration properties have been reported. Recently, we have developed a new imidazoanthraquinol-type fluorescent host (**1**) which can form host-guest inclusion crystals in stoichiometric ratios with various kinds of solvent molecules.[5] This host undergoes dramatic changes in the fluorescence emission upon enclathration of guest molecules. The fluorescence emission characteristics of clathrate crystals are of our great interest in both basic and applied viewpoints. In this paper, we report the X-ray crystal structures and the solid-surface fluorescent emission behaviors of the two typical host-guest inclusion crystals with ethanol (host:guest=1:1)[6] (**2**) and 1,4-dioxane (host:guest=2:1)[6] (**3**) which are packing models for enclathration of protic and aprotic guest molecules, respectively.



1a **1b**

2: **1a** · Ethanol (1:1)

3: **1b** · 1,4-Dioxane (2:1)

In our previous paper,[5] we reported that two tautomeric forms (**1a** and **1b**) are possible for the imidazole ring of **1**. The crystal structures of **2** [7] and **3** [8] elucidated by X-ray crystal analysis suggest that the form of imidazole ring in **2** is **1a** and that in **3** is **1b**, which are shown in Figures 1 and 2, respectively. The positions of hydrogen atoms were determined by the difference Fourier synthesis. The bond alternation of the imidazol ring supports the propriety of imidazole amino proton's position in each of the inclusion crystals. The ratios of the host to guests are in good agreement with the values determined by ^{1}H NMR integration and thermogravimetry (TG) analysis. In the case of **2**, the crystals are built up by the hydrogen bonded cluster unit composed of a pair of enantiomers of the host (**1a**) and two ethanol molecules (Figure 1). An amino proton of an imidazole ring is directing toward a guest's oxygen and the hydroxy proton of the guest is directing toward a hydroxy

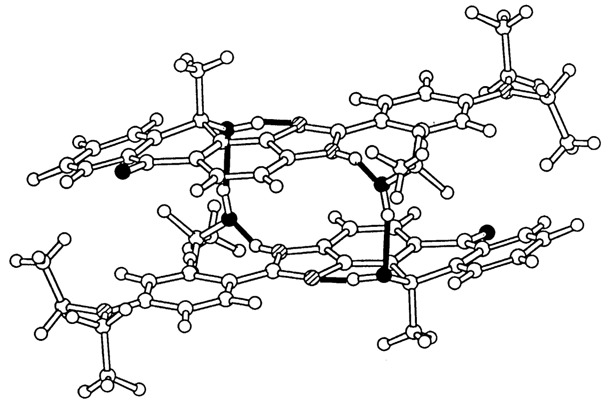


Figure 1. View of the hydrogen bonded cluster observed in **2** (=**1a**·Ethanol). The hydrogen bonds are indicated by bold lines.

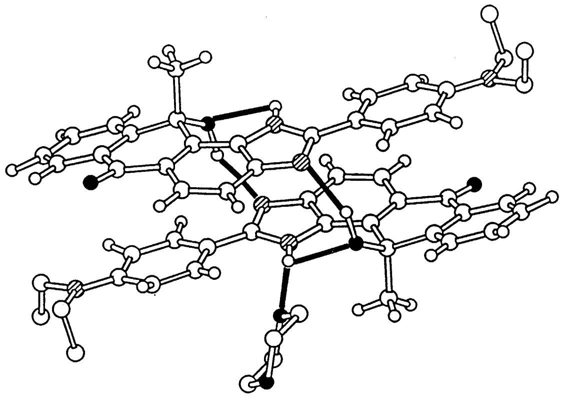


Figure 2. View of the hydrogen bonded cluster observed in **3** (=(**1b**)$_2$·Dioxane). The hydrogen bonds are indicated by bold lines. The positions of hydrogen atoms for the ethyl groups of **1b** and the ethylene groups of dioxane could not be determined by the difference Fourier synthesis presumably because of their large thermal motions.

oxygen of another host molecule. The intermolecular N···O and O···O distances are 2.785(3) and 2.765(5) Å, respectively. The hydrogen bonding relationship is realized on both sides of the host molecules, so the four-membered clusters are realized in the crystals. The intramolecular hydrogen bonding formations are also observed between the remaining hydroxy proton and imino nitrogen in each host molecule. Hydrogen bonding interactions between neighboring clusters are not observed in the clathrates and the clusters appear to be held together by van der Waals interactions. On the other hand, in the case of **3**, the crystals are built up by the hydrogen bonded unit of a pair of enantiomers of the host (**1b**) and dioxane guests are included into cavities formed among the pair of host molecules (Figure 2). The intermolecular hydrogen bonding between the hydroxy oxygen and imidazole nitrogen through the hydroxy proton is realized on both sides of the host molecules. The intermolecular N···O distances are 3.005(3)Å. The amino proton of imidazole ring have two proton acceptors, the intramolecular hydroxy oxygen and the oxygen atom of the dioxane guest, and become a bifurcated-donor hydrogen to construct the three-centered hydrogen bonding arrangements. These intra- and intermolecular N···O distances are 2.906(3) and 3.101(3)Å, respectively. The latter hydrogen bonding relationship is realized on both oxygen atoms of the dioxane.

In order to investigate the fluorescence characteristics of **1**, we measured the solid-surface fluorescence spectra of the guest-free crystals (**1**) and the guest inclusion crystals (**2** and **3**). Figure 3 shows the excitation and emission spectra of the three kinds of crystals. Very interestingly, the fluorescence emission of the host is dramatically enhanced upon enclathration of the guest molecules. The guest-free host crystals exhibit relatively weak fluorescence with emission maximum at 567 nm, whereas the clathrate crystals, **2** and **3**, exhibit ca. 46-fold and 23-fold stronger fluorescence intensities with the emission maxima blue shifted to 528 and 526 nm, respectively. It is considered that the differences in tautomeric form of the imidazole ring and packing pattern of the host in the crystals have significant influence on its fluorescence emission. The details of the effect of enclathration on fluorescence emission of the host have not been clarified yet, however, these results suggest that this host has potential applications in analytical and material sciences such as designing a new fluorescent molecular recognition sensor and an emitter layer in organic electroluminescent (EL) devices.

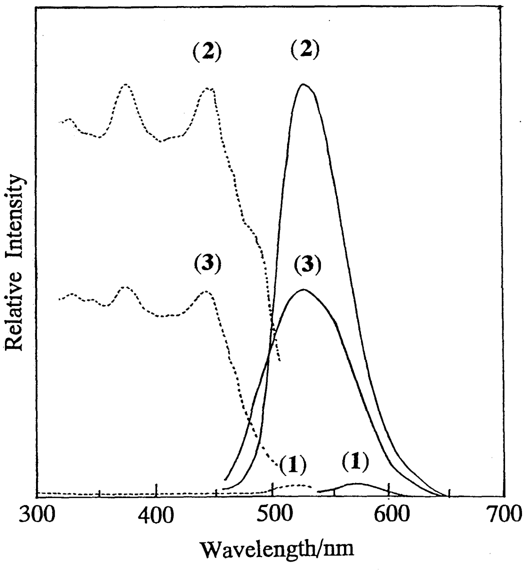


Figure 3. Excitation (·····) and emission (——) spectra of the guest-free host crystals (**1**) and the host-guest inclusion crystals (**2** and **3**) at 25 °C: (**1**) λ_{ex}=520 nm, λ_{em}=567 nm. (**2**) λ_{ex}= 451nm, λ_{em}=528 nm. (**3**) λ_{ex}=445 nm, λ_{em}=526 nm.

A part of the present work was supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

References and Notes

1 J. L. Atwood, J. E. Davies, and D. D. MacNicol, "Inclusion Compounds," Academic Press, London (1984), vol. 1-3; "Molecular Inclusion and Molecular Recognition-Clathrates I and II" (Topics in Current Chemistry), ed by E. Weber, Springer-Verlag, Berlin-Heidelberg (1987), vol. 140 and (1989), vol. 149.

2 E. Weber, N. Dorpinghaus, and I. Csoregh, *J. Chem. Soc., Perkin Trans. 2*, **1990**, 2167; L. Johnson, L. Nassimbeni, E. Weber, and K. Skobridis, *J. Chem. Soc., Perkin Trans. 2*, **1992**, 2131; I. Csoregh, O. Gallardo, E. Weber, and N. Dorpinghaus, *J. Chem. Soc., Perkin Trans. 2*, **1994**, 303; M. R. Caira, A. Coetzee, L. R. Nassimbeni, E. Weber, and A. Wierig, *J. Chem. Soc., Perkin Trans. 2*, **1995**, 281.

3 S. A. Bourne, M. R. Caira, L. R. Nassimbeni, M. Sakamoto, K. Tanaka, and F. Toda, *J. Chem. Soc., Perkin Trans. 2*, **1994**, 1899; M. R. Caira, A. Horne, L. R. Nassimbeni, K. Okuda, and F. Toda, *J. Chem. Soc., Perkin Trans. 2*, **1995**, 1063.

4 Y. Mazaki, K. Awaga, and K. Kobayashi, *J. Chem. Soc., Chem. Commun.*, **1992**, 1661; N. Hayashi, Y. Mazaki, and K. Kobayashi, *J. Chem. Soc., Chem. Commun.*, **1994**, 2351.

5 K. Yoshida, J. Yamasaki, Y.Tagashira, and S. Watanabe, *Chem. Lett.*, **1996**, 9.

6 The ratios of the host to guests were determined by means of ^{1}H NMR integration and thermogravimetry (TG) analysis.[5]

7 Crystal data for **2**: $C_{28}H_{31}N_3O_3$, M=457.50, *monoclinic*, space group P2$_1$/n, a=14.969(3)Å, b=20.742(4), c=7.960(2), β=96.84(2)°, V=2453.9(8)Å^3, Z=4, Dc=1.24 gcm^{-3}; Cu-Kα radiation (graphite monochromator, λ=1.54178) final conventional R=7.2%, R_W=7.6% for observed 3491 reflections [F>3σ(F)] and 422 parameters.

8 Crystal data for **3**: $C_{28}H_{29}N_3O_3$ M=455.55 *triclinic*, space group P$\bar{1}$, a=9.239(4)Å, b=16.596(4), c=8.096(2), α= 96.09(2)°, β=97.98(2)°, γ=96.18(2), V=1212.9(6)Å^3, Z=2, D_C=1.24 gcm^{-3}; Cu-Kα radiation (graphite mono-chromator, λ=1.54178) final conventional R=9.0%, R_W=10.9% for observed 3503 reflections [F>3σ(F)] and 367 parameters.