

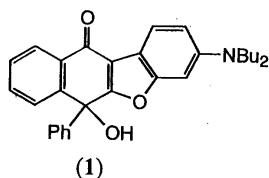
Fluorescence Sensing Behavior of Thin-films of Benzofuranoquinol Clathrate Host upon Exposure to Various Gaseous Amines

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The benzofuranoquinol clathrate host exhibits color and fluorescence changes upon exposure to various gaseous amines both in the crystalline state and in the thin-film state. The decrease of long-wavelength absorption and the dramatic fluorescence enhancement with blue-shift of emission maximum depending on the enclathrated amine molecules were observed. The response time for the optical sensing was greatly improved by using the host in the thin-film state.

The optical properties of organic chromogenic compounds in solid states have attracted increasing attention in material science due to their wide range of high-technology applications.¹⁻⁵ We have recently developed a novel benzofuranoquinol-type clathrate host (**1**) which exhibits sensitive color change and fluorescence enhancement behavior upon enclathration of alicyclic amines in the crystalline state.⁶ The clathrate host giving optical signals in response to host-guest complex formation is interesting from the viewpoint of developing novel chemosensors or new emissive materials. Conveniently, the quinol host crystals give clathrate compounds not only by being recrystallized from amine solvents but also by being exposed to amine vapor at room temperature. Such direct clathration via solid-gas contact has also been reported in previous papers.⁷⁻¹⁰ In general, the clathrate formation between host crystals and gaseous guest proceeds slowly, so the response time-scale would become a critical problem if the chromogenic clathrate host (**1**) is used as a solid chemosensor. However, we have found that this problem can be greatly improved by using thin-films instead of crystals; the thin-films of **1** undergo rapid absorption and fluorescence spectral changes upon contact with amine vapor. To the best of our knowledge, this is the first example of optical sensing behavior of a host compound based on clathrate formation in the thin-film state. Here, we report details of the optical sensing behavior of thin-films of **1** upon exposure to various gaseous amines.



The thin-films of **1** were prepared on glass plates by a conventional vacuum-vapor deposition method. Figure 1 shows the absorption spectra of **1** in 1,4-dioxane and in the thin-film state (ca. 2 μm thickness). The absorption peaks are located at 320 nm ($17,200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and 386 nm ($1,530 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) in 1,4-dioxane, while the absorption spectrum of the thin-film is considerably different; a peak at 376 nm with a broad shoulder at 400–500 nm is observed. The large red-shift of the film spectrum would be attributed to intermolecular host–host

π – π interactions with a charge-transfer character.^{1,6,11}

The absorption and fluorescence spectral changes of the thin-films of **1** upon exposure to various amine vapors were investigated. For example, as shown in Figures 2(a) and 2(b), the thin-film underwent rapid spectral changes when it was placed in a vessel saturated with piperidine vapor at 30 °C. A decrease of the absorbance of a shoulder around 420–500 nm

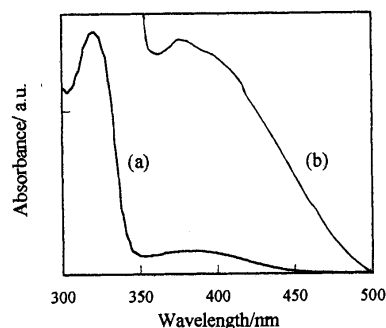


Figure 1. Absorption spectra of **1** (a) in 1,4-dioxane and (b) in the thin-film state.

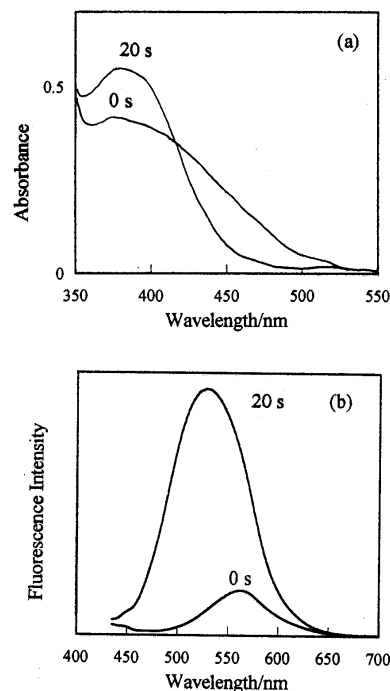


Figure 2. Absorption and fluorescence spectral changes of the thin-film of **1** upon exposure to piperidine vapor at 30 °C.

and an increase of the absorbance of a band at around 376 nm are observed with an isosbestic point at 415 nm. The corresponding fluorescence spectra show a dramatic increase of fluorescence intensity with the blue-shift of emission maximum from 560 nm to 533 nm. When other various amines were used instead of piperidine, similar absorption and fluorescence spectral changes were also observed and almost saturated within 10–20 sec. This result suggests that the time-scale of the phenomenon will allow practical applications. Figure 3 summarizes the results of the fluorescence spectral changes obtained by using various amines. The degrees of the fluorescence enhancement and the blue-shift of fluorescence wavelength are dependent on the enclathrated amine molecules and increase in the following order: ethylamine < diethylamine < morpholine < *N*-methylmorpholine < piperidine < *N*-methylpiperazine. The formation of clathrates (1 : guest = 1:1) was suggested for all the above amines from NMR integrations of the dissolved samples prepared from the exposed thin-films. Furthermore, when the guest-free crystals of **1** instead of the thin-films were exposed to various gaseous amines, the same amine order and similar spectral changes were also obtained. However, as shown in Figure 4, the crystals need 18–20 h to reach the final saturated spectra that are in good agreement with the spectra of crystals of the clathrate compound (1 : piperidine = 1:1). In the case of crystals, the initial fluorescence band at 569 nm shifts to 501 nm with 7.0-fold increase of fluorescence intensity. Both the fluorescence enhancement and blue-shift of the crystals in the spectral changes are larger than those of the thin-film, which was always observed when other gaseous amines were used.

Though there are some differences in the spectral changes between the two states, the above results suggest that the mechanism of the optical sensing of the thin-films is substantially the same as that of the guest-free crystals. The X-ray crystal

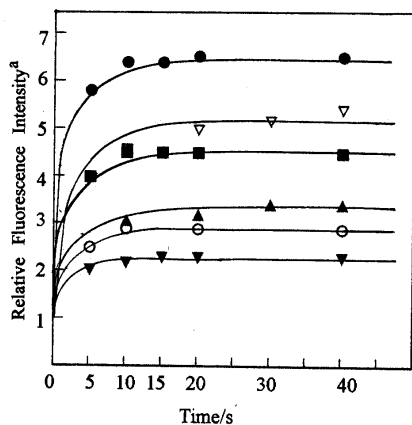


Figure 3. Time-dependent fluorescence spectral changes of the thin-films of **1** upon exposure to various amine vapors at 30 °C; ^a RFI = FI (after exposure)/FI (before exposure), ^b $\lambda_{\text{ex}} = 376$ nm, ^c $\Delta \lambda_{\text{em}} = [560 \text{ (before exposure)} - \lambda_{\text{em}} \text{ (after exposure)}]$ nm.

	$\lambda_{\text{em}}/\text{nm}^b$	$\Delta \lambda_{\text{em}}/\text{nm}^c$
●—●— <i>N</i> -methylpiperazine	504	29
▽—▽— piperidine	533	27
■—■— <i>N</i> -methylmorpholine	540	20
▲—▲— morpholine	542	18
○—○— diethylamine	553	7
▼—▼— ethylamine	555	5

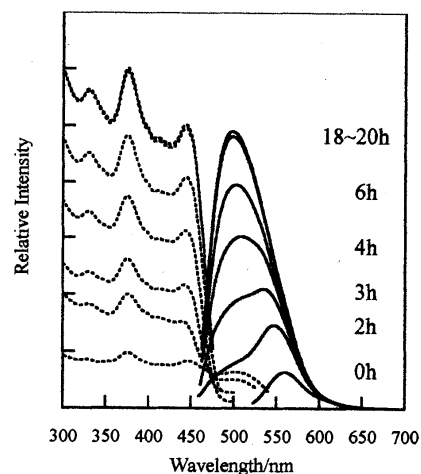


Figure 4. Time-dependent spectral changes of the guest-free crystals of **1** upon exposure to piperidine vapor at 30 °C; the excitation (···) and emission (—) spectra were recorded at their corresponding emission and excitation maxima.

structures of the guest-free host of **1** and its morpholine inclusion compound have been elucidated and reported in our previous paper.⁶ In the guest-free host crystals, a pair of host enantiomers is cofacially bound by two intermolecular hydrogen bonds to form a centrosymmetric host–host dimer unit with close interplanar distance. On the other hand, in the guest-inclusion crystals, the enclathrated guest molecules cut off the intermolecular hydrogen bonds binding the host pairs and enlarge the distance of host–host aromatic planes, suggesting a reduction of π – π interactions of the host molecules. Hence, the destruction of the host–host π – π interactions by the enclathrated amine molecules is considered to be a main reason for the guest-dependent optical sensing behavior. The fact that the rapid fluorescence spectral changes of the thin-films are not so large as those of the guest-free crystals may result from the existence of amorphous structure in the thin-film state.

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