Fluorescence Sensing Behavior of Crystals of an Imidazole-Type Clathrate Host upon Contact with Gaseous Carboxylic Acids

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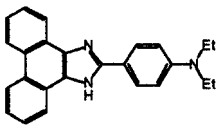
The crystals of the title fluorescent clathrand exhibit a drastic fluorescence enhancement behavior upon contact with carboxylic acid vapors. The magnitude of the fluorescence change is greatly dependent on the enclathrated carboxylic acid molecules and increase in the following order: formic acid < acetic acid < propionic acid. To elucidate the enclathrated guest effects on the fluorescence properties of the crystals, the X-ray crystal structures have been determined.

Chromogenic receptors which give fluorescence signals in response to recognition of ions or molecules are the subjects of current research interest because of their wide range of potential applications in analytical and material sciences.[1] Some trials that intend to apply clathrate formation to a fluorescence sensing system for detection of organic solvent molecules have been made.[2] However, there are still very few clathrate hosts that can exhibit sensitive fluorescence changes upon inclusion of organic guest molecules. We have recently developed a novel benzofuranoquinol-type fluorescent clathrand whose crystals or thin-films exhibit guest-dependent fluorescence enhancement with a blue shift of emission maximum upon contact with various gaseous amines.[3] Here, we report on a new fluorescent clathrand, 2-[4-(diethylamino)phenyl]-1*H*-phenanthro[9,10-*d*]imidazole (**1**), whose crystals exhibit guest-dependent fluorescence enhancement with a red shift of emission maximum upon contact with gaseous carboxylic acids. The X-ray crystal structures of **1** and its clathrate compounds have been determined, and the relationship between the solid-state fluorescence and the changes in crystal structure upon clathrate formation is discussed.



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The fluorescent host compound (**1**) was prepared according to a slightly modified procedure of the Davidson method[4] known for synthesis of imidazoles. Recrystallization of **1** from acetonitrile gave needle-shaped crystals that contain no solvent molecules. Interestingly, when the guest-free crystals were placed in a vessel saturated with carboxylic acid vapor at 30 °C, the color of the crystals turned from colorless to yellow. By solid-state fluorescence measurement we found that a bathochromic shift of the excitation and emission maxima and a guest-dependent fluorescence enhancement are induced upon inclusion of the guest molecules. Table 1 summarizes the time-dependent changes in the excitation and emission spectra of the guest-free crystals upon exposure to gaseous formic acid, acetic acid, and propionic acid, respectively. At the time intervals, a small portion of the exposed crystals was withdrawn and checked by ^{1}H NMR, which demonstrated that carboxylic acid molecules are gradually included into the crystals, clathrate formation via the solid–gas contact being suggested. The maximum fluorescence was obtained when the host-to-guest stoichiometric ratio was near 1:2 in every case. Continuous exposure of the crystals resulted in further inclusion of carboxylic acid molecules until the host-to-guest stoichiometric ratio became 1:3. The maximum fluorescence intensities of the inclusion crystals after exposure to gaseous formic acid, acetic acid, and propionic acid were about 5-, 33- and 50-fold stronger compared to the fluorescence intensity of the starting guest-free crystals, respectively. These results suggest that increasing molecular size of the enclathrated carboxylic acid tends to induce larger fluorescence enhancement but slow down the clathrate formation.

Table 1. Time-dependent changes in the excitation and emission wavelengths, fluorescence intensity, and host-to-guest ratios of the guest-free crystals of **1** upon contact with gaseous carboxylic acids at 30 ℃

Guest acid	Time /min	Excitation λ ex/nm	Emission λ em/nm	R.F.I[a]	Ratio[b] Host : Guest
Formic acid	0	377.5	467.5	1.00	1 : 0
	10	444.5	472.5	4.61	1 : 0.6
	20	446.0	473.5	5.05	1 : 1.2
	50	447.0	473.5	5.14	1 : 2.2
	150	447.5	473.5	4.42	1 : 2.9
Acetic acid	0	377.5	467.5	1.00	1 : 0
	50	436.0	467.5	17.9	1 : 0.5
	100	440.0	470.5	26.9	1 : 1.1
	200	442.0	473.5	32.8	1 : 1.9
	300	442.0	473.0	33.4	1 : 2.3
	500	441.5	467.5	31.1	1 : 2.8
	900	441.5	464.0	28.1	1 : 3.0
Propionic acid	0	377.5	467.5	1.00	1 : 0
	120	441.0	511.0	35.2	1 : 0.3
	300	443.0	511.0	43.4	1 : 1.1
	420	443.0	511.0	50.8	1 : 2.0
	1200	442.5	512.5	50.4	1 : 2.9
	2400	442.5	512.5	49.6	1 : 3.0

[a]Relative fluorescence intensity. [b]Determined by means of ^{1}H NMR integration.

To investigate the relationship between the observed photophysical properties and the changes in molecular packing structure upon inclusion of the guest molecules, the crystal structures of the guest-free[5] and the carboxylic acid inclusion compounds, **1**·$(CH_3CO_2H)_2$[6] and **1**·$(CH_3CH_2CO_2H)_2$,[7] have been determined by X-ray diffraction analysis. As shown in Figures 1 and 2, there are big differences in arrangement of host molecules between the guest-free and the guest-inclusion crystals. In the guest-free crystal, host molecules are linked by

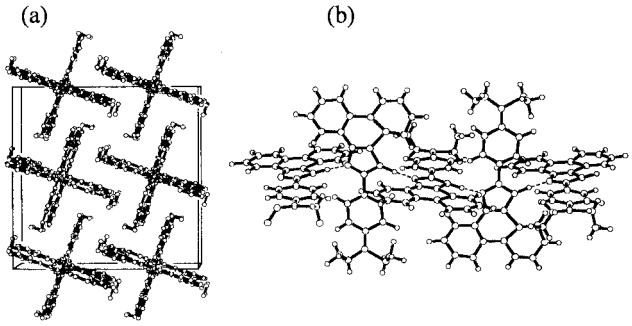

Figure 1. (a) Molecular packing structure (down *c* axis) and (b) perspective view of the guest-free of **1**; the dotted lines indicate hydrogen bonds.

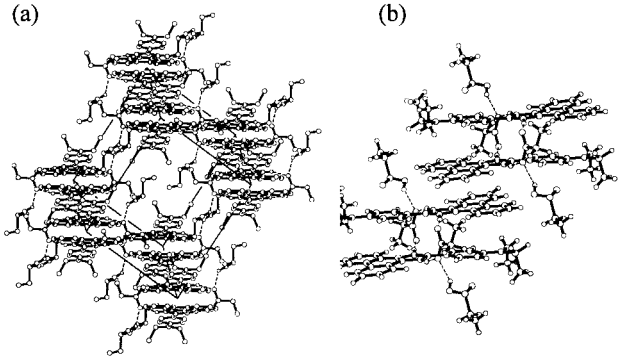

Figure 2. (a) Molecular packing structure and (b) perspective view of **1**·$(CH_3CH_2CO_2H)_2$; the dotted lines indicate hydrogen bonds.

intermolecular NH···N hydrogen bonds between the imidazole nitrogen atoms to form a linear molecular chain along the *c*-axis (Figure 1(b)). The host molecules along the chain are related by 4^1 (fourfold screw axis) symmetry. Between the adjacent chains there are two short molecular contacts between host molecules; one is the overlapping of *p*-(diethyamino)phenyl parts and the other is the π–π overlapping (3.49–3.58 Å) of phenanthrene parts. These long-range host–host interactions based on the intermolecular hydrogen bond and the π–π interaction would cause a strong fluorescence quenching in the guest-free crystal. On the other hand, in the case of the guest-inclusion crystals, such direct intermolecular hydrogen bonding between host molecules is not found. Instead, the crystal is made up by a hydrogen bonded cluster unit composed of two imidazole hosts and four carboxylic acid guests (Figure 2(b)). The two hosts and two of the four guests are alternately linked by four NH···O hydrogen bonds to form a centrosymmetric ring, in which the imidazole ring is protonated by the propionic acid proton. The protonation of the imidazole ring would contribute to a red-shift of the absorption and emission spectra of the crystals because of an increase of intramolecular charge-transfer character of the host fluorophore. The rest two guests are linked by a hydrogen bond to each of the two ring-forming guests to form a hexamer cluster unit. There are two styles of π–π stacking overlap between host molecules in the guest-inclusion crystal. One is the π–π overlapping (3.24–3.58 Å) between the phenanthroimidazole and *p*-(diethylamino)phenyl parts in the cluster unit. The other is observed between the neighboring cluster units, where the phenanthrene ring parts are overlapping (3.40–3.60 Å). The X-ray crystal structure of **1**·$(CH_3CO_2H)_2$ was quite similar to that of **1**·$(CH_3CH_2CO_2H)_2$, however, a detailed comparison of the crystal structures of the guest-inclusion compounds clarified that the π–π interactions between the host molecules decreased with the increase in the size of the enclathrated guest molecules. These results indicate that the fluorescent clathrand (**1**) can be utilized as a chemical solid-sensor for recognition of gaseous carboxylic acids. A more detailed relationship between the crystal structure and the photophysical properties of some carboxylic acid inclusion crystals of **1** will be reported in due course.

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References and Notes

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5 The guest-free crystals were obtained by recrystallization of **1** from acetonitrile. Crystal data: $C_{25}H_{23}N_3$, MW = 365.48, tetragonal, space group $I4_1/a$, a = 20.675(2), b = 20.675(2), c = 19.151(6) Å, α = β = γ = 90°, V = 8186(2) Å^3, Z = 16, D_c = 1.186 g cm^{-3}; Mo Kα radiation (graphite monochromator, λ = 0.7107 Å) final conventional R = 9.2%, R_w = 11.1% for observed 760 reflections [$I > 3\sigma(I)$] and 258 parameters.

6 Inclusion compound of **1**·$(CH_3CO_2H)_2$ was obtained by recrystallization of **1** from a mixture solvent of acetic acid and acetonitrile (1:3); Crystal data: $C_{29}H_{31}N_3O_4$, MW = 485.58, triclinic, space group $P\bar{1}$, a = 11.423(1), b = 14.126(2), c = 8.770(2) Å, α= 105.92(1), β = 105.44(1), γ = 83.68(1)°, V = 1310.7(4) Å^3, Z = 2, D_c = 1.230 g cm^{-3}; Mo Kα radiation (graphite monochromator, λ = 0.7107 Å) final conventional R = 7.4%, R_w = 8.7% for observed 2265 reflections [$I > 3\sigma(I)$] and 401 parameters.

7 Inclusion compound of **1**·$(CH_3CH_2CO_2H)_2$ was obtained by recrystallization of **1** from a mixture solvent of propionic acid and acetonitrile (1:1); Crystal data:$C_{31}H_{35}N_3O_4$, MW = 513.64, triclinic, space group $P\bar{1}$, a = 11.712(2), b = 13.955(2), c = 9.611(2) Å, α= 107.03(1), β = 108.59(2), γ = 84.76(1)°, V = 1423.6(5) Å^3, Z = 2, D_c = 1.198 g cm^{-3}; Mo Kα radiation (graphite monochromator, λ = 0.7107 Å) final conventional R = 6.8%, R_w = 9.1% for observed 2583 reflections [$I > 3\sigma(I)$] and 438 parameters.