Design of a fluorescent host for monitoring multiple hydrogen-bonding interaction directly by intramolecular charge-transfer emission

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The hosts 2-dodecanamido-4-methyl-*N*-[4-(dimethylamino)phenyl]quinoline-7-carboxamide 1 and 2-dodecanamido-4-methyl-*N*-(4-methoxyphenyl)quinoline-7-carboxamide 2 bearing an aromatic amide unit exhibit an anomalous fluorescence with a large Stokes shift at around 500–600 nm (LW emission) due to an intramolecular charge-transfer (ICT) process. The guests 3-ethyl-3-methylglutarimide (bemegride) 4 and 1-methyluracil 5 are associated with the hosts by forming three hydrogen bonds, and LW emission of the hosts largely increase. On the other hand, the guest 3-methyluracil 6 does not affect the emission of the hosts at all, though formation of two hydrogen bonds with the hosts is confirmed by ^{1}H NMR measurement. It is concluded that the hosts 1 and 2 can selectively detect the guests 4 and 5 that form hydrogen bonds both at the quinoline ring nitrogen and the amide proton (H_α) of the hosts simultaneously to affect rotation of the amide bond.

Introduction

Design and development of artificial receptors have been the subject of intense studies, and various types of intermolecular interaction between host and guest molecules have been designed and tuned in order to attain high guest selectivity. High guest selectivity and sensitivity are the key properties required for artificial receptors. Though multiple hydrogen-bonding interaction plays a major role in molecular recognition,[1] limited tools are available for detecting the formation of hydrogen bonds. ^{1}H NMR spectroscopy has been most frequently used for this purpose, but it is not sensitive enough for detecting host–guest association at low ($<10^{-3}$ mol dm^{-3}) concentration. Recently, fluorescent spectrometry has increasingly been used for monitoring host–guest complexation due to its high sensitivity, and has been drawing considerable interest.[2] However, hydrogen-bonding interaction generally shows only a small effect on emission of fluorescent hosts.[3] Therefore, rational molecular design of the host is required in order to transduce guest-recognition by hydrogen bond formation to a specific and sensitive fluorescent response. A common host design is the introduction of environment-sensitive fluorophore(s) as a signaling auxiliary, and environmental change due to the host–guest association is converted to the fluorescent response.[4,5] Some other hosts utilize emission due to photo-induced electron[6] or energy[7] transfer, whose efficiency would be controlled by host–guest association. We recently reported[8] efficient guest recognition by the host and a large fluorescent response was achieved by hydrogen bond formation and simultaneous protonation of the fluorophore of the host.

In a previous letter,[9] we reported a novel fluorescent host that can directly monitor a specific mode of the multiple hydrogen-bonding interaction. The host molecule has an aromatic amide unit in its structure, and exhibits an anomalous fluorescence with a large Stokes shift.[10] In this paper, we have focused on the fluorescent response of this novel type of host, and wish to report the full details.

Experimental

Materials

Solvents used for spectroscopic measurements were all fluorometric grades from Dojin Chem. Co. and were used as received. Other chemicals were obtained commercially and purified according to standard procedures prior to use if necessary.

Syntheses

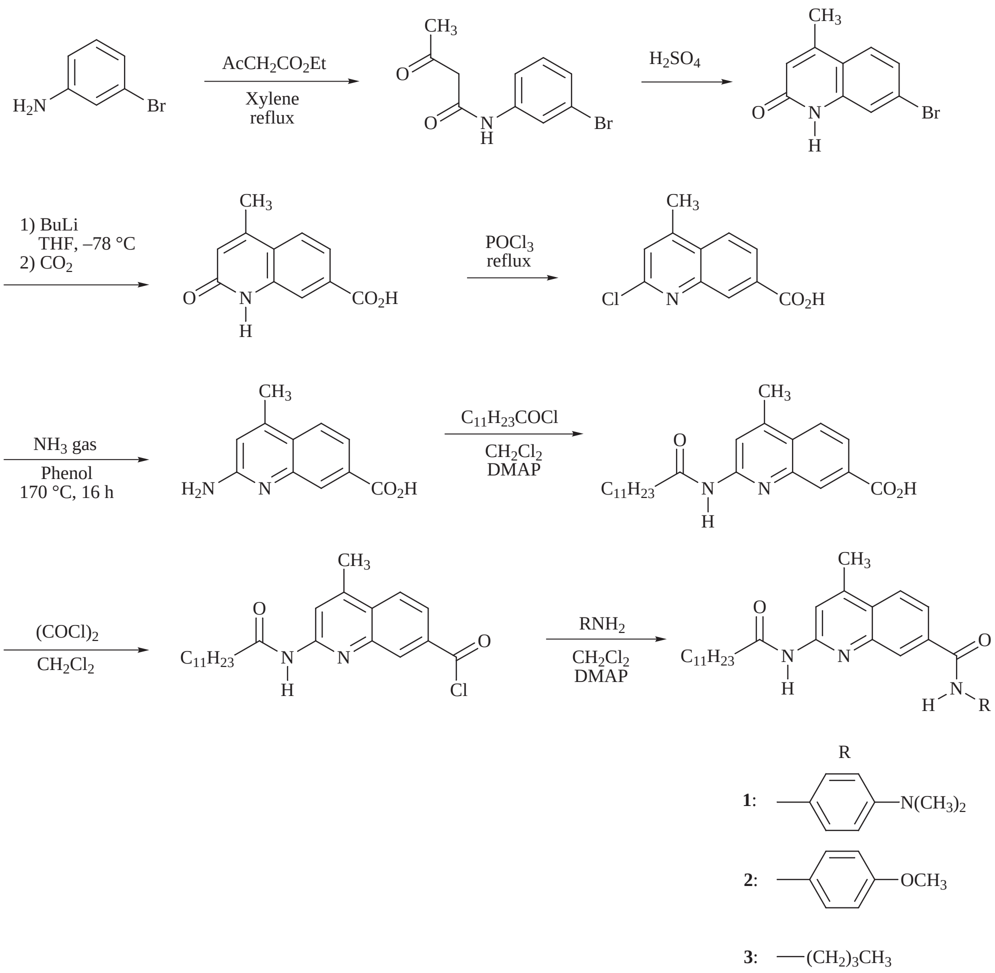
Amide host compounds were synthesized according to the method of Kelly *et al.*[11] as illustrated in Scheme 1. To 2-amino-4-methylquinoline-7-carboxylic acid[11] in dichloromethane, 4 equiv. of dodecanoyl chloride were added and stirred for 48 h at room temperature. Column separation (dichloromethane) gave 2-dodecanamido-4-methylquinoline-7-carboxylic acid (yield 65%), which was treated with 5 equiv. of oxalyl chloride in dichloromethane for 1 h at room temperature. After removal of excess oxalyl chloride, 1.2 equiv. of the corresponding amine compounds [4-(dimethylamino)aniline for **1**, 4-methoxyaniline for **2** and butylamine for **3**] and 1.1 equiv. of 4-(dimethylamino)pyridine were added and stirred for 24 h at room temperature. After evaporation the residue was purified by silica gel column separation (dichloromethane), and subsequent recrystallization gave the host compounds **1**, **2** and **3**.

1: Yield 34% by two steps. Mp 172.0–172.7 °C (Found: C, 74.05; H, 8.4; N, 11.55%; M$^+$, 507. $C_{31}H_{42}N_4O_2$ requires C, 74.1; H, 8.4; N, 11.15%; *M*, 507); δ(270 MHz; $CDCl_3$) 0.87 (3H, t), 1.26 (16H, m), 1.77 (2H, m), 2.46 (2H, t), 2.74 (3H, s), 2.96 (6H, s), 6.77 (2H, d), 7.54 (2H, d), 7.85 (1H, s), 7.95–8.04 (3H, m), 8.21 (1H, s), 8.39 (1H, s). **2**: Yield 55%. Mp 165.4–166.7 °C. δ(270 MHz; $CDCl_3$) 0.87 (3H, t), 1.27 (16H, m), 1.72 (2H, m), 2.43 (2H, t), 2.68 (3H, s), 3.79 (3H, s), 6.90 (2H, d), 7.31 (1H, d), 7.59 (2H, d), 7.91 (1H, br), 8.11–8.30 (3H, m), 8.43 (1H, s) (Found: M$^+$, 489.2993. Calc. for $C_{30}H_{39}N_3O_3$ *M*, 489.2993). **3**: Yield 43%. Mp 150 °C. δ(270 MHz; $CDCl_3$) 0.89 (3H, t), 0.97 (3H, t), 1.20–1.78 (22H, m), 2.46 (2H, t), 2.75 (3H, s), 3.52 (2H, q), 6.34 (1H, s), 7.85 (1H, d), 7.94 (1H, d), 8.08 (1H, br), 8.11 (1H, s), 8.38 (1H, s) (Found: C, 73.3; H, 9.7; N, 9.25%; M$^+$, 439.3205. $C_{30}H_{39}N_3O_2$ requires C, 73.75; H, 9.4; N, 9.55%; *M*, 439.3201).

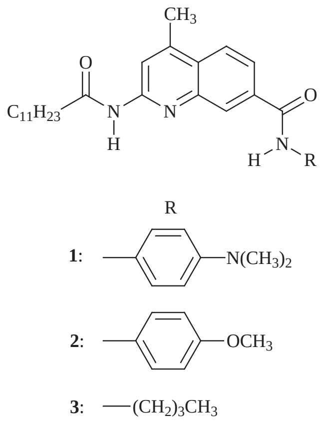
Spectroscopic measurement

Electronic absorption spectra were recorded on either a JASCO Ubest-50 or a SHIMADZU UV-2200 spectrophotometer at 20 °C, and emission spectra on a JASCO FP-770 spectrofluorometer under aerobic conditions at 20 °C. IR spectra were measured with a Perkin-Elmer FT-1600 and ^{1}H NMR spectra with a JEOL FX-100 or GX-270 spectrometer in [$^2H_2$]dichloromethane.

For the emission life-time measurement, a HAMAMATSU C4334 streak camera with a LN120C2: N_2 laser (337 nm) was used and the sample was deoxygenated by repeated freeze–thaw cycles before measurement.



Scheme 1 Synthesis of the hosts **1**–**3**



Results

Design and syntheses of the fluorescent hosts

Since Mulliken introduced the concept of charge-transfer (CT) transitions,[12] emission from the excited CT state has been the subject of intense studies. Recent topics studied in this field are the emission from the intramolecular CT (ICT) state, especially from the twisted intramolecular CT (TICT) state.[13] With some exceptions,[14] donor and acceptor units in the compounds showing TICT emission are connected by a rotatable single bond with or without aromatic systems in between. However, Azumaya *et al.*[15] reported a TICT emission exhibited from benzanilide derivatives, in which two aromatic units were connected by an amide bond.

In the host compounds **1** and **2**, the electron-deficient 4-methylquinoline-7-carboxyl unit is connected through the amide bond to the aniline unit having different electron-donating substituent at the *p*-position. The host **3** having the alkyl amine unit instead of aniline was also synthesized as a reference. The host compounds **1**–**3** have an additional amide bond at the other side of the quinoline unit. Kelly *et al.*[11] have reported that the host bearing two amide units at the 2- and 7-positions of quinoline can accommodate uracil derivatives by formation of three hydrogen bonds. The host compounds **1**–**3** were synthesized according to Scheme 1.

Electronic spectra of the hosts

Electronic absorption spectra of the hosts **1**, **2** and **3** in dichloromethane are shown in Fig. 1. The hosts showed an absorption maximum at around 345 nm, which is presumably due to the π–π^* transition of the quinoline unit. It is worth noting that the host **2** exhibited a red absorption tail and the tail became more profound for host **1** which had a stronger electron-donating *N*,*N*-dimethylamino group on the aniline unit. Since the absorbance at 400 nm of host **1** increased linearly with its concentration [Fig. 2(a)], it is unlikely that the red tail of the absorption was due to the dimer or higher molecular aggregates of the host. On the other hand, host **3** having the alkyl amine showed no absorption tail. These results suggest that the red tail of the absorption band of **1** and **2** originates from the ICT process.

Emission spectra of the hosts **1**–**3** (λ_{ex} = 265 nm) are included in Fig. 1, and emission and excitation spectra of host **1** in dichloromethane are shown in Fig. 3. Hosts **1**–**3** showed fluorescence at around 370–400 nm (SW emission), which is ascribed to the emission from the quinoline unit of hosts. In the case of the hosts **1** and **2**, a fluorescence with a large Stokes shift was

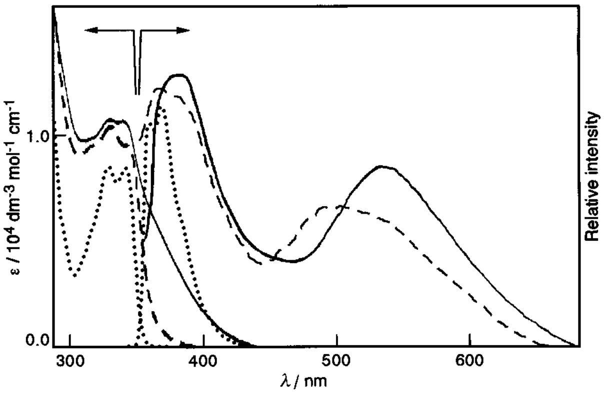


Fig. 1 Absorption and emission spectra of the host **1** (——), **2** (– – –), and **3** (•••••) in dichloromethane at 20 °C

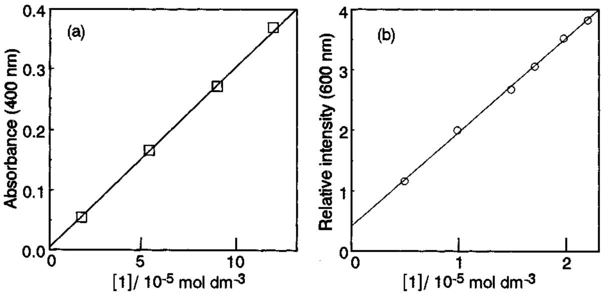


Fig. 2 Plot of absorbance at 400 nm (a) and emission intensity at 600 nm (b) *vs.* concentration of **1** in dichloromethane at 20 °C

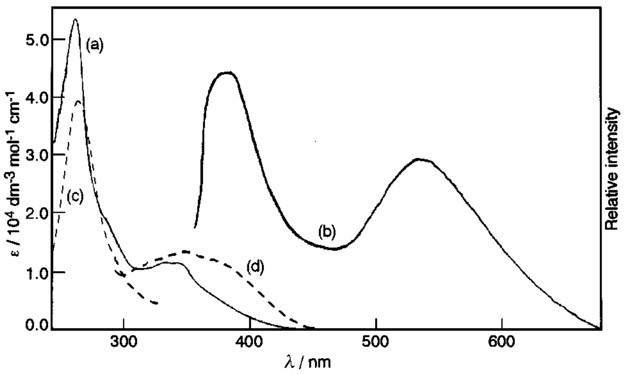


Fig. 3 Absorption (a), emission ($\lambda_{\mathrm{ex}} = 265$ nm) (b), and excitation (c, d) spectra of the host **1** in dichloromethane at 20 °C. Excitation spectra (c) and (d) were monitored at 373 and 532 nm, respectively.

observed at around 500–600 nm (LW emission) in addition to the SW emission. The LW emission of host **1**, having a stronger electron-donating group, appeared at a lower energy side compared to that of the host **2**. The LW emission of host **1** at 600 nm increased linearly as the concentration increased [Fig. 2(b)], and therefore the LW emission was not from the dimer or excimer formed by intermolecular association. However, host **3**, having an alkyl amine instead of the aromatic amine unit, exhibited only normal SW emission at 369 nm. Spectroscopic data of the hosts in dichloromethane at 20 °C are summarized in Table 1.

To clarify the nature of the LW emission, the solvent effect on the emission of host **1** was studied. The absorption and the LW emission maxima of host **1** in different solvents are collected in Table 2. The absorption and SW emission spectra were little affected by the solvent properties. In contrast, the LW emission became stronger in non-polar solvents such as methylcyclohexane, but was much weaker in methanol. Emission maxima also showed an appreciable red-shift as the polarity of the solvent increased. Similar solvent dependence was also observed for the LW emission of host **2**.

Table 1 Spectral data of the hosts in dichloromethane at 20 °C

Host	Absorption λ_{abs}/nm (log ε)	Emission λ_{em}/nm^{a}	
1	330.0 (4.08), 345.0 (4.10)	390	532
2	328.8 (4.03)	363	450
3	327.0 (3.74), 341.5 (3.74)	355, 368	—

^{a} Excitation at 265 nm.

Table 2 Absorption (λ_{abs}) and LW emission maxima (λ_{em}) of the host **1**

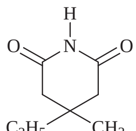
Solvent	λ_{abs}/nm	λ_{em}/nm^{a}	$\Delta\nu$/10^3 cm^{-1}
Methylcyclohexane	330	487	9.8
Benzene	330	534	11.6
Dichloromethane	330	532	11.5
Ethanol	331	556	12.2
Propan-2-ol	330	555	12.3
Methanol	330	569	12.7
Dimethylformamide	333	574	12.6
Acetonitrile	330	596	13.5

^{a} Excitation at 330 nm.

Flexible benzanilides are reported[15] to show a delayed rise in the TICT emission decay curve due to the transformation of the amide bond from planar into a twisted conformation by rotation. However, the LW emission of host **1** in methylcyclohexane fitted to a single exponential decay curve without showing initial delay of the emission rise, and the life-time was determined to be 1.2 ns. These results suggest that the LW emission of the hosts may not be interpreted as a TICT type emission.

Electronic spectra of the hosts in the presence of guest 4

The hosts **1**–**3** have two amide units at both sides of quinoline and have an ability to accommodate uracil derivatives by triple hydrogen bonding interactions.[11] To examine the effects of guest association on the spectroscopic properties of the hosts, 3-ethyl-3-methylglutarimide (bemegride) **4** was selected as a guest



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because it has the same hydrogen bonding ability as uracil but shows no fluorescence and no absorption above 300 nm. Addition of the guest **4** caused only a small change in the absorption spectra of the hosts, though an isosbestic point was observed at around 320 nm. Excitation at the isosbestic point caused an appreciable increase in the LW emission of hosts **1** and **2**, whereas the SW emission of hosts **1**–**3** essentially showed no changes. Fig. 4 shows the typical spectral change of host **1** on addition of guest **4** in dichloromethane at 20 °C. A small increase in the absorbance of the host at 310 nm on addition of the guest followed the 1 : 1 association mechanism, and the association constant (K_a) for **1** and **4** was determined to be 1.4×10^2 dm^3 mol^{-1}. An increase in the LW emission also agreed with the 1 : 1 association mechanism, and the association constant determined at 589 nm was 1.3×10^2 dm^3 mol^{-1}, which is in good agreement with that obtained from the absorption spectral change.

Use of host **2** instead of host **1** gave essentially the same results with guest **4**. A small absorption spectral change on addition of **4** gave a K_a value of 0.97×10^2 dm^3 mol^{-1} in dichloromethane at 20 °C, and a noticeable increase in the LW

Table 3 Proton chemical shifts (δ) and 100% complexation-induced shifts ($\Delta\delta$) of the host in [$^2H_2$]dichloromethane

		δ or $\Delta\delta$							
Host	Guest	H_a	H_b	H_c	H_d	H_e	H_f	$H_{g,g'}$	$H_{h,h'}$
2	None	8.01	8.11	8.25	8.41	8.08	7.97	7.63	6.97
	4	1.37	2.50	0.78	0.12	0	0.20	0.29	0
	5	1.35	2.64	0.81	0.13	0	0.21	0.25	0
	6	0.07	0.36	0.09	0.01	0	0	0.09	0
	7	0	0	0	0	0	0	0	0
3	None	6.34	8.09	8.12	8.38	8.04	7.85	—	—
	4	0.51	0.74	0.13	0.05	0	0.05		

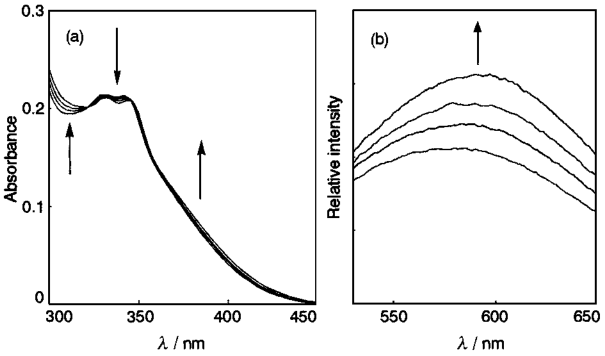


Fig. 4 Absorption (a) and emission (b) spectra of **1** (1.81 × 10^{-5} mol dm^{-3}) in the presence of **4** (0, 1.51, 3.92, 9.05 × 10^{-3} mol dm^{-3}) in dichloromethane at 20 °C. Excitation at 324 nm.

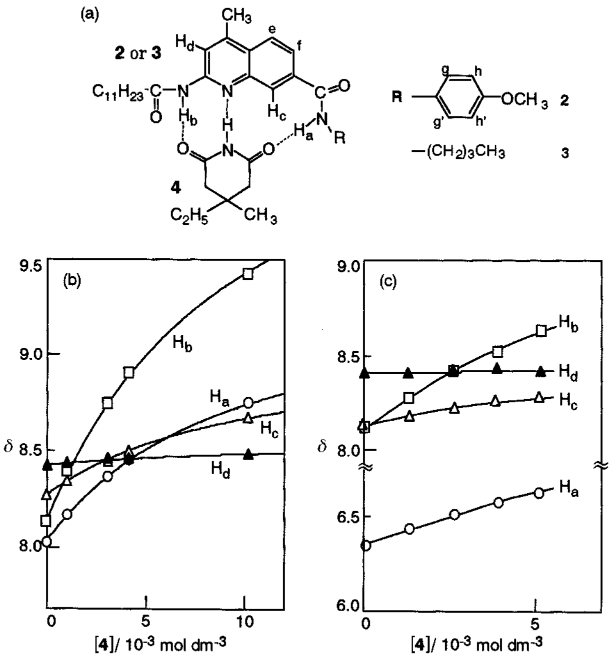


Fig. 5 Proposed structure of the host–guest complex (a), and complexation induced shifts of ^1H NMR chemical shift (δ) of **2** (b) and **3** (c) (1.4 × 10^{-3} mol dm^{-3}) by addition of **4** in [$^2H_2$]dichloromethane

emission at 550 nm yielded a K_a value of 1.1 × 10^2 dm^3 mol^{-1}. The K_a values obtained were in agreement with each other. In the less polar methylcyclohexane solvent, where the LW emission of **2** is stronger than in dichloromethane, addition of **4** caused a large increase in the LW emission intensity with a concomitant shift of the emission peak from 550 to 520 nm. By plotting of the intensities at several wavelengths, the association constant was roughly estimated to be 9 × 10^3 dm^3 mol^{-1}, which is nearly two orders of magnitude larger than that in dichloromethane.

^1H NMR Study of the host–guest association

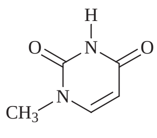
To study the mode of host–guest association, the ^1H NMR spectral change of the host **2** on addition of guest **4** was measured in [$^2H_2$]dichloromethane at 20 °C. As shown in Fig. 5, the amide N–H protons H_a and H_b of the host showed considerable down-field shift, indicating formation of the hydrogen bonds with the guest. Since the hosts bearing two amide units at both sides of quinoline can accommodate uracil derivatives by triple hydrogen bonding interactions,[11] it is quite likely that the host **2** binds with guest **4** through the triple hydrogen bonds as illustrated in Fig. 5(a). Complexation-induced chemical shifts of the protons H_a, H_b and H_c fitted with the 1 : 1 association stoichiometry [Fig. 5(b)], and all three curves gave the same association constant of 1.2 × 10^2 dm^3 mol^{-1}. This value agreed with those obtained from the electronic spectral changes, and therefore, changes in the absorption, LW emission and ^1H NMR spectra of host **2** are concluded to be the results of the host–guest association shown in Fig. 5(a). Complexation-induced chemical shifts of protons at 100% complexation (CIS) of **2** with **4** ($\Delta\delta$ in ppm) are calculated from the obtained association constants, and are summarized in Table 3. The protons at or close to the guest binding site showed large CIS values, but H_d and other protons located at the opposite side were little shifted by complexation, further supporting the mode of association of **2** with **4** by the three hydrogen-bonds shown in Fig. 5(a).

In the case of host **3**, the presence of guest **4** also caused down-field shifts of the amide protons (H_a and H_b) and the quinoline H_c proton of the host [Fig. 5(c)], indicating the formation of the same type of the host–guest complex. The association constant was determined to be 6.6 × 10 dm^3 mol^{-1} and CIS values are also included in Table 3.

Effect of the guest structure

Instead of guest **4**, *N*-methyl substituted uracil derivatives **5**–**7** were used as guest molecules, and association with host **2** was studied. The structure of the host–guest complex with 1-methyluracil **5** as guest is identical to that with guest **4**. Complexation-induced spectral changes of host **2** on addition of **5** were essentially the same as those observed for **4**, *i.e.* very small changes in the absorption and SW emission spectra, a noticeable increase in the LW emission and down-field shifts of the ^1H NMR signals. The association constants obtained from emission and ^1H NMR spectral changes were not much different from each other, and were several times larger than with guest **4** (Table 4).

In the case of 3-methyluracil **6** as guest, absorption, and both SW and LW emission spectra of the host **2**, were little affected. However, chemical shifts of the amide H_b proton of **2** showed a down-field shift, indicating complex formation with **6**. Since



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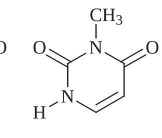

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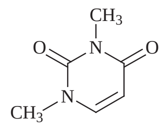

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Table 4 Association constants for the 1 : 1 host–guest complexes in dichloromethane at 20 °C

Host	Guest	$K_{a\,\mathrm{LW}}$ [a]/10^2 dm^3 mol^{-1}	$K_{a\,\mathrm{NMR}}$ [b]/10^2 dm^3 mol^{-1}
1	**4**	1.3	
2		1.1, (90[c])	1.2
3		*d*	0.66
2	**5**	6.7	9
	6	*d*	1.6
	7	*d*	0

[a] Determined from LW emission change. [b] Determined from the chemical shift change of ^{1}H NMR resonances. [c] Determined in methylcyclohexane. [d] No change in the emission spectrum was observed.

the amide H$_a$ signal was only slightly affected, the mode of association of **2** with **6** is suggested to be the formation of two hydrogen bonds shown in Fig. 6(a). The complex shown in Fig. 6(b) cannot be formed because of steric repulsion between the 3-methyl group of the guest and the aniline unit of the host.

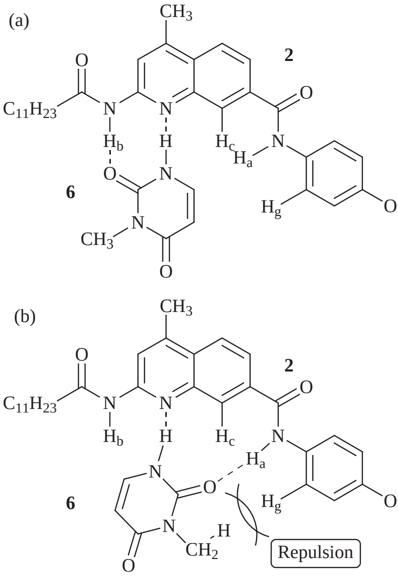


Fig. 6 Association of **2** + **6**. (a) Supposed structure of **2** + **6** complex. (b) A mode of **2** + **6** association in which certain steric repulsion is predicted.

1,3-Dimethyluracil **7** as guest induced no absorption, emission and ^{1}H NMR spectral changes, showing that **7** has no ability to form hydrogen bonds with the host because of steric hindrance by the *N*-methyl groups.

Discussion

Emitting state of the LW emission

The red absorption tail was observed for hosts **1** and **2**, which was more profound for **1**, bearing a stronger electron-donating substituent, than **2**. However, host **3** having no electron-donating unit showed no red absorption tail. Therefore, this absorption tail is attributed to the intramolecular charge-transfer (ICT) process. Hosts **1** and **2** exhibited dual fluorescence; *i.e.* the SW emission at 360 nm and the LW emission at 500–600 nm, but host **3** showed only the SW emission. The LW emission of **1** was observed in a much longer wavelength region than that of **2**, and the excitation spectra of the LW emission corresponded to the CT absorption band (Fig. 3). Furthermore, while no substantial solvent effect on the absorption maxima was observed, a noticeable red-shift of the LW emission was observed in polar solvents. These results strongly suggest that the emitting level of the LW emission is the excited ICT state of hosts **1** and **2**, and the excited ICT state has much more polar structure than the ground state.

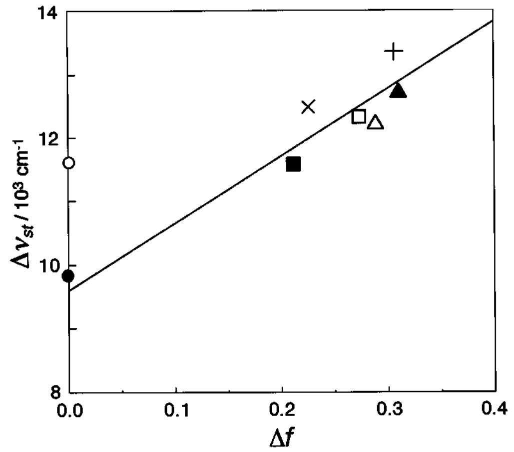


Fig. 7 Plot of difference between absorption and emission wavenumber ($\Delta\nu_{st}$) *vs.* solvent polarity parameter (Δf) of host **1** in methylcyclohexane (●), benzene (○), dichloromethane (■), propan-2-ol (□), ethanol (△), methanol (▲), acetonitrile (+) and dimethylformamide (×)

The results were further analyzed by the Lippert–Mataga equation [eqn. (1)],[16] where Δf is Lippert's solvent polarity

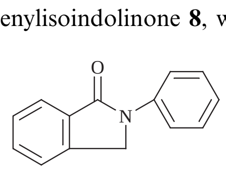
$$\Delta\nu_{st} = \nu_{abs} - \nu_{fluo} = \frac{2\Delta\mu}{hca^3}\Delta f + \text{Const.}$$

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \qquad (1)$$

parameter, ε and n are the relative permittivity and the optical refractive index of solvents, respectively, and a is an effective radius of the Onsager cavity[17] of a compound. As shown in Fig. 7, Stokes shifts ($\Delta\nu_{st}$) of the host **1** in various solvents were linearly dependent on Δf. The difference in the dipole moment between the excited and ground states, $\Delta\mu$, is estimated to be 14.6 D by assuming the effective radius of the Onsager cavity of **1** as 5.72 Å.[18] The $\Delta\mu$ values reported for some donor–acceptor molecular systems are as follows; 14.8 D for 4-(dimethylamino)stilbene,[19] 14.6 D for 4-(dimethylamino)-4′-cyanostilbene,[20] and 14 D for 1-(4-cyanophenyl)-3-[4-(dimethylamino)-phenyl]propane-1,3-dione.[21] These compounds are known to have TICT excited states, and substantial charge-transfer from the donor unit to the acceptor unit is suggested. Therefore, the emitting level of host **1** is concluded to be the highly polar ICT excited state.

However, no delay of the emission rise was observed in the LW emission decay curve of host **1**, and an emission life-time of 1.2 ns is within the range of common organic fluorophores. These results indicate that the ICT excited state of the hosts is not necessarily the TICT excited state.

While Azumaya *et al.*[15] assigned the lower energy emission of the benzanilide to be from the TICT excited state, they also reported that *N*-phenylisoindolinone **8**, whose amide nitrogen and *ortho*-position of the benzoyl unit was linked by a methylene unit in order to freeze the rotation of the amide bond, also showed dual emission. The lower energy emission appeared in the same region as the TICT emission of other benzanilide derivatives, but no initial delay of emission rise was observed at all in the emission decay curve of **8**. Based on these observations, they suggested that the observed lower energy emission



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of **8** was not from the TICT excited state, though detailed analysis of this emission was not presented.

Mode of the guest recognition

The hosts **1**–**3** bind with guest **4** in dichloromethane. As evidenced from ^{1}H NMR spectroscopy, recognition of the guest was due to the formation of three hydrogen bonds between the host and the guest (Fig. 7). Association constants obtained in this study were in the order of 10^2 dm^3 mol^{-1} in dichloromethane (Table 4). Similar values are reported for the hosts that can associate with guest compounds by triple hydrogen bonding interactions in dichloromethane or chloroform.[10,22] Because of the polar nature of the hydrogen bonding interaction, association constants were two orders of magnitude larger in non-polar methylcyclohexane solution.

Larger association constants for guest **5** compared to that of guest **4** may be because **5** has a planar structure, which might be suitable to form multiple hydrogen bonds with the hosts. The *N*-methylated guests **6** and **7** offer further insight into host–guest association. Due to the steric effect of the methyl group(s), association of the dimethylated guest **7** with host **2** did not take place and that of the monomethylated guest **6** was limited to the mode shown in Fig. 6(a). In the case of the host–guest pair, simultaneous hydrogen bonding interactions of the anilide proton (H_a) and the quinoline ring nitrogen of the host with the guest forces the quinoline ring and the amide of the anilide into a co-planar arrangement, but association of guest **6** with the hosts does not affect the conformation of the quinoline ring and the anilide as shown in Fig. 6(a).

Fluorescent response of the host upon recognition of the guest

Association of the guests **4** and **5** induced an appreciable increase in the LW emission of the hosts **1** and **2**. Since no increase in the LW emission was observed on addition of excessive amounts of methanol or dimethylformamide which have hydrogen bonding ability, to the host in dichloromethane solution, hydrogen bond formation with the amide units or the quinoline unit alone cannot induce the increase in the LW emission. The guest **6** formed the complex with the hosts in the mode shown in Fig. 6(a), but no increase in the LW emission was observed at all. Only for guests **4** and **5**, which formed three hydrogen bonds, was an increase in LW emission observed. Therefore, simultaneous hydrogen bonding interaction at H_a and the quinoline ring nitrogen of the hosts is suggested to be responsible for the appreciable increase in LW emission.

The rotation of the amide bond between the donor and acceptor units is limited, which might increase the emission from the ICT state by enhancement of the ICT process from the S_1 state and/or suppression of the non-radiative process from the ICT excited state.

This gives special advantage to the hosts **1** and **2** as fluorescent hosts. Though many organic molecules have hydrogen bonding ability, formation of a single hydrogen bond with the hosts **1** and **2** does not affect their emission property. Only the guest that can fix both the anilide unit and the quinoline unit of the host induces an increase in the LW emission.

There is another advantage of hosts **1** and **2** in terms of utilizing the emission increase. Vibrational modes of hydrogen bonds are known to act as accepting modes for the energy from excited species,[23] and many of the reported fluorescent hosts[3,7,24] show emission quenching by formation of hydrogen bond(s) with their guest. However, the emission is often quenched by various impurities in the solution such as transition metals, oxygen, or residual organics, which would unfavorably reduce the emission of the fluorescent hosts.

Conclusions

In this report, the origin of the dual emission of **1** and **2**, and their ability as a photo-responsive host were studied. The longer wavelength (LW) emission of the hosts **1** and **2** were confirmed to emit from the intramolecular charge-transfer (ICT) excited state.

The specific photo-response of the host is observed only for the guests that can fix the rotation of the connecting bond between the electron-donor and -acceptor unit, but not for other hydrogen bonding molecules.

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