Fluorescence Studies on Binary Aromatic Compounds by Utilizing the Intermolecular Quadruple Hydrogen Bonding

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Quadruple intermolecular hydrogen bonding of ureidopyrimidinone derivatives can be utilized to construct novel fluorescent excimer or exciplex system.

In recent years, the construction of the self-organized molecular system by intermolecular hydrogen bonding has received much attention. Hydrogen bonding is expected to be useful in construction of supramolecular structure because of its association character of directional and selective way. Practically, the molecular systems having multiple hydrogen bond can be used as building blocks for supramolecular structure. For example, the dimers with double or triple hydrogen bond are well known in DNA base pairs. Therefore, numerous triply hydrogen bonded molecules have been prepared and the association behavior has been investigated.[1] However, the association constant of usual hydrogen bonded system is small; for example, the association constant of adenine–thymine and guanine–cytosine dimer is in the range of 10^2 to 10^3 M^{-1} and 10^4 to 10^5 M^{-1}, respectively in chloroform.[2]

Recently, Meijer et al. have reported that 2-ureido-4[1H]-pyrimidinone (UPy) derivatives form dimers with considerably high dimerization constant with $>10^6$ M^{-1} by quadruple intermolecular hydrogen bonding.[3] Using this UPy derivatives, Meijer et al. also reported the formation of supramolecular polymers.[4] Because of its high dimerization constant, one can
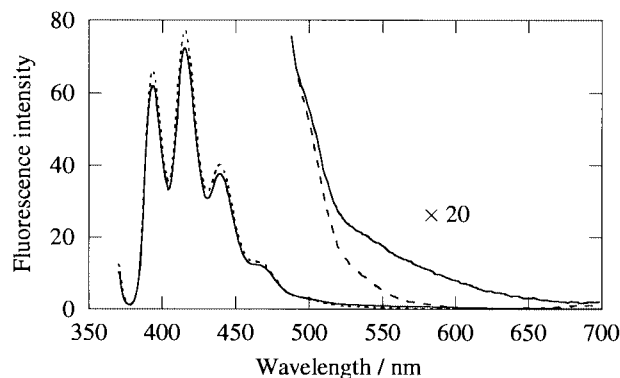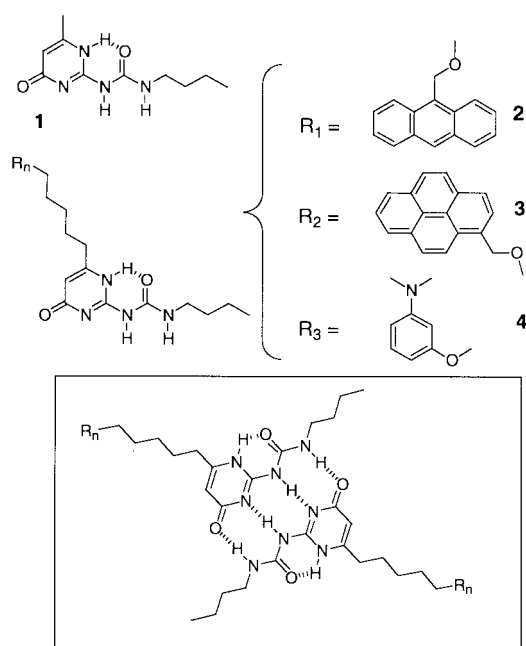
Scheme 1.

Figure 1. Fluorescence spectra of **2** (1×10^{-5} M) in the absence of **4** (dash line) and in the presence of **4** (1×10^{-5} M) (solid line).

use UPy group to construct supramolecular systems having varying photoresponsive chromophore.

When we have almost finished our work, the synthesis of the quadruple hydrogen bonding system with fullerene as a functional part was reported with the aim of construction of nano-scale materials.[5] However, the excited state properties of these hydrogen bonded compounds have not been reported.

We wish to report here the formation of excimer and/or exciplex by taking advantage of using UPy unit as a building block of the supramolecular photochemical system.

The synthetic procedure of 6-methyl-2-(3-butylureido)-4[1H]-pyrimidinone (UPy) (**1**) has already been reported.[3] The compounds having anthracene (**2**), pyrene (**3**), or N,N-dimethylaniline (DMA) (**4**) ring at the alkyl chain in UPy (Scheme 1) were prepared by the similar procedures.[6]

The absorption spectrum of **1** appeared at the wavelength shorter than 320 nm in chloroform. Fluorescence and transient absorption spectra were not observed on irradiation of **1** at room temperature.

The absorption and fluorescence spectra of **2** at the concentration of 1.0×10^{-5} M were almost the same as the model compound 9-(methoxymethyl)anthracene (**5**). In addition, fluorescence lifetimes (τ_s) of **2** and **5** were almost the same (2.6 and 2.5 ns, respectively in chloroform under argon atmosphere at room temperature). These results showed that UPy unit did not affect the excited state behavior of anthracene ring.

The fluorescence intensity of **2** was decreased with increasing concentration of **4** and the weak fluorescence at 550 nm assigned to the exciplex emission between anthracene group and N,N-dimethylaniline group was observed as shown in Figure 1. The lifetime of the exciplex emission was determined to be 40 ns by nano-second laser photolysis under argon atmosphere at the concentration of 1.0×10^{-5} M for both **2** and **4**.
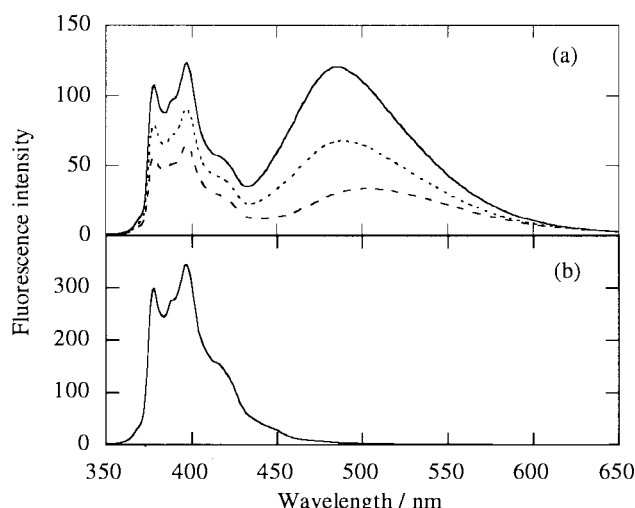
Figure 2. (a) Fluorescence spectra of **3** (1×10^{-5} M) in the absence of **4** (solid line) and in the presence of **4** with the concentration of 1×10^{-5} M (dotted line) and 1×10^{-4} M (dash line). (b) Fluorescence spectrum of **6** (1×10^{-5} M) in chloroform under argon at room temperature.

In order to clarify the effect of intermolecular hydrogen bonding for the photoinduced charge transfer interaction, we have studied the fluorescence quenching of the model compounds which cannot associate by hydrogen bonding but can interact by diffusion processes. The fluorescence intensity of anthracene ring decreased with the addition of DMA to the solution of **2** and **5** with concomitant increase of the intensity of the weak fluorescence emission of the exciplexes. The Stern–Volmer plot of the observed fluorescence intensity vs. the concentration of DMA gave the Stern–Volmer constant $k_q\tau_s$ to be 22.8 and 25.1 for **2** and **5**, respectively. By using the fluorescence lifetime of **2** and **5** in the absence of DMA, the quenching rate constants of the singlet excited states of **2** and **5** by DMA (k_q) were determined to be 9.1×10^9 M^{-1} s^{-1} and 1.0×10^{10} M^{-1} s^{-1}, respectively in chloroform. The above results suggest that exciplex formation between **2** and DMA could not be observed at the concentration of DMA lower than 10^{-4} M. Actually, the exciplex emission was not observed when the concentration of **2** and DMA was 1.0×10^{-5} M and 1.0×10^{-4} M, respectively. These results strongly indicate that UPy derivatives **2** and **4** would form dimer associated by intermolecular hydrogen bonding in chloroform even when the concentration of both compounds was as low as 1×10^{-5} M.

Compound **3** exhibited excimer emission with the maximum at 485 nm in addition to the normal emission around 400 nm even at very low concentration (1.0×10^{-5} M) as shown in Figure 2a. The lifetime of the excimer was determined to be 60 ns at 500 nm. Contrary to this observation, 1-(butoxymethyl)pyrene (**6**) (1.0×10^{-5} M) without UPy unit, exhibited only the monomer fluorescence (Figure 2b). These results clearly indicate the importance of quadruple intermolecular hydrogen bonding for the formation of pyrene excimer.

When we added **4** as an electron donor to the solution of **3** (1×10^{-5} M), the fluorescence intensities of both excimer and monomer were decreased to give the red shift of the fluorescence maximum with λ_{max} = 488 nm at the concentration of both **3** and **4** to be 1×10^{-5} M. At this experimental condition, **3**

and **4** should exist as hetero dimers **3·4** in addition to homo dimers **3·3** and **4·4** with the ratio of **3·4** : **3·3** : **4·4** = 2 : 1 : 1. Further addition of **4** shifted emission peak to give λ_{max}=505 nm in the presence of **4** to be 1×10^{-4} M as shown in Figure 2a. The change of fluorescence spectra can be explained by the formation of the hetero dimers between **3** and **4** instead of the homo dimer of **3**, since the final concentration of **4** (1.0×10^{-4} M) is 10 times higher than that of **3**; in this case at least 95% of **3** forms the dimer with **4**. In this case, the lifetime of the exciplex emission determined at 500 nm was 50 ns. Thus, by utilizing the quadruple intermolecular hydrogen bonding, one can observe an efficient charge transfer interaction between pyrene group and N,N-dimethylaniline group, where charge transfer should take place from the N,N-dimethylaniline to the excited state pyrene group.

Finally, we should mention here that by taking advantage of quadruple intermolecular hydrogen bonding, we can construct molecular assemblies exhibiting efficient charge transfer interaction or excimer formation. Further studies on this line by connecting appropriate donor and acceptor molecules may open the way to construct macromolecules formed by weak interaction capable to induce efficient electron transfer reaction.

References and Notes
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6   Compound **2**: ^{1}H NMR (CDCl$_3$, 400 MHz), δ 0.91 (3H, t, J = 7.2 Hz; –CH$_3$), 1.2–1.7 (10H), 2.34 (2H, t, J = 7.6 Hz; CH$_2$CH_2–Ar), 3.21 (2H, m; NHCH_2), 3.63 (2H, t, J = 6.4 Hz; ArCH$_2$OCH_2), 5.45 (2H, s; ArCH_2O), 5.73 (1H, s; Ar-H), 7.45 (2H, m; Ar-H), 7.53 (2H, m; Ar-H) 7.98 (2H, m; Ar-H), 8.36 (2H, d, J = 9.2 Hz; Ar-H), 8.43 (1H, s; Ar-H) 10.1 (1H, s; NH), 11.8 (1H, s; NH), 13.1 (1H, s; NH) ppm. mp 144–145 °C. ESI-MS calcld for C$_{29}$H$_{34}$N$_4$O$_3$ [M+H]$^+$ = 487.2704 found: 487.2714. Compound **3**: ^{1}H NMR (CDCl$_3$, 400 MHz), δ 0.91 (3H, t, J = 7.2 Hz; –CH$_3$), 1.2–1.8 (10H), 2.36 (2H, t, J = 7.6 Hz; CH$_2$CH_2-Ar), 3.24 (2H, m; NHCH_2), 3.59 (2H, t, J = 6.2 Hz; ArCH$_2$OCH_2), 5.19 (2H, s; ArCH_2O), 5.69 (1H, s; Ar-H), 7.98 (4H, m; Ar-H), 8.15 (4H, m; Ar-H), 8.34 (1H, d, J = 9.2 Hz; Ar-H), 10.1 (1H, s; NH), 11.7 (1H, s; NH), 13.1 (1H, s; NH). mp 174–175 °C. ESI-MS calcld for C$_{31}$H$_{34}$N$_4$O$_3$ [M+H]$^+$ = 511.2704 found: 511.2760. Compound **4**: ^{1}H NMR (CDCl$_3$, 400 MHz), δ 0.92 (3H, t, J = 7.2 Hz; –CH$_3$), 1.2–2.0 (10H), 2.48 (2H, t, J = 7.6 Hz; CH$_2$CH_2-Ar), 2.91 (6H, s; NCH_3), 3.24 (2H, m; CONHCH_2CH$_2$), 3.94 (2H, t, J = 6.2 Hz; ArO–CH$_2$), 5.81 (1H, s; Ar-H), 6.25 (2H, m; Ar-H), 6.34 (1H, m; Ar-H), 7.10 (1H, m; Ar-H), 10.2 (1H, s; NH), 11.8 (1H, s; NH), 13.2 (1H, s; NH) ppm. mp 121–122 °C. ESI-MS calcld for C$_{22}$H$_{33}$N$_5$O$_3$ [M+H]$^+$ = 416.2656 found: 416.2641.