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Syntheses and Photophysical Studies of Cyclodextrin Derivatives with Two Proximate Anthracenyl Groups

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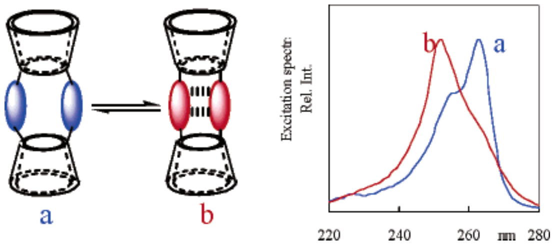

A series of permethylated cyclodextrin derivatives, cyclodextrin dimers doubly bridged with two anthracene moieties (**An_2CD_2**) and singly bridged with one (**$AnCD_2$**) and the monomer bearing two anthracene moieties (**An_2CD**), were newly synthesized. For **An_2CD_2**, the two isomeric forms are also identified. All compounds are soluble in both aqueous and various organic solvents. The bisanthracene systems, **An_2CD_2** and **An_2CD**, show the thermal equilibrium in an aqueous solution between the intramolecularly interacting (closed) and less-interacting (open) states of the anthracene moieties, which results in the temperature-dependent absorption changes. These systems also show the characteristic excimer emission that is enhanced in water and weakened in organic solvents. The excitation spectra for the monomer and excimer fluorescence are found to be quite different from each other and similar to the absorption spectra of the open and the closed forms, respectively. The observed unique parallelism between excitation and absorption spectra for the present excimer systems indicates the dual ground state−dual excitation scheme where the excitation state formed from the closed ground state mainly gives excimer. The fluorescence lifetime analyses reveal that the rates of the conversion from the excited state of the open form to that of the closed one ($6.0 \times 10^6\ s^{-1}$ for **An_2CD_2-2**) are largely retarded compared with that of the ethyleneoxy linked bisanthracene system ($8.8 \times 10^7\ s^{-1}$).

Introduction

Oligomeric cyclodextrins form an interesting category of host molecules having multiple binding sites soluble in an aqueous solution.[1] According to the connection mode of the cyclodextrin moieties, they may produce not only a variety of shapes of binding sites but also various types of chemical and thermodynamic properties due to the conformational changes of the linker moieties.[2] Recently we reported new types of oligomeric cyclodextrins of which all hydroxyl groups were methylated.[3] These types of cyclodextrin oligomers show interesting characteristics such as multi-host−guest complex formation through strong hydrophobic interaction in an aqueous solution.[4] Another characteristic property of these permethylated cyclodextrin oligomers is their amphiphilic solubility for organic and aqueous phases. Such characteristics provide the unique opportunity to explore the physical properties of various types of environmentally sensitive molecular interactions operating in these cyclodextrin oligomers. For example, the biphenyl-bridged permethylcyclodextrin shows a unique excimer formation in an aqueous solution, which is practically inhibited in organic solvents.[3] Since such environmentally sensitive photochemical properties are interesting in light of both their physical chemistry

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[1] (a) Breslow, R.; Greenspoon, N.; Guo, T.; Zarzycki, R. *J. Am. Chem. Soc.* **1989**, *111*, 8296−8297. (b) Breslow, R.; Chung, S. *J. Am. Chem. Soc.* **1990**, *112*, 9659−9660. (c) Breslow, R.; Dong, S. D. *Chem. Rev.* **1998**, *98*, 1997−2011.

[2] (a) Venema, F.; Rowan, A. E.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1996**, *118*, 257−258. (b) Baugh, S. D. P.; Yang, Z.; Leung, D. K.; Wilson, D. M.; Breslow, R. *J. Am. Chem. Soc.* **2001**, *123*, 12488−12494. (c) Nishiyabu, R.; Kano, K. *Eur. J. Org. Chem.* **2004**, 4985−4988.

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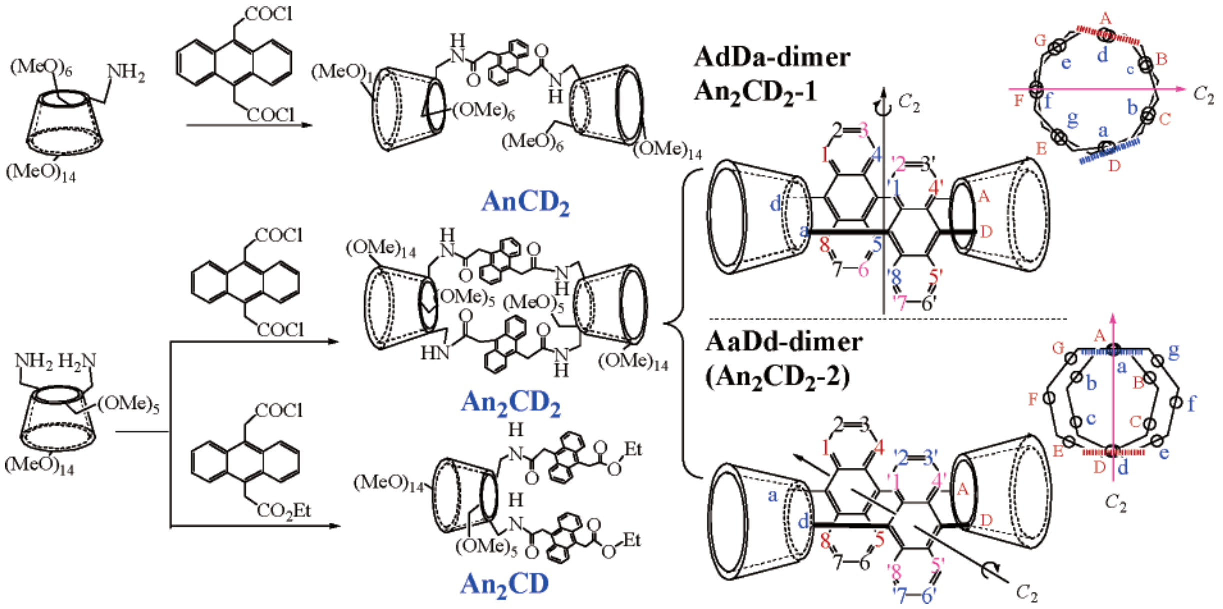
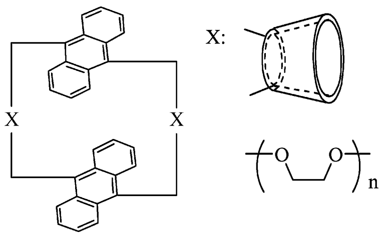
10.1021/jo060449w CCC: $33.50

SCHEME 1. Syntheses of Anthracene−Cyclodextrin Derivatives $AnCD_2$, An_2CD_2, and An_2CD, and Two Isomeric Structures of An_2CD_2 (AdDa-Dimer and AaDd-Dimer)



and application to practical use such as chemical sensors,[5] here we synthesized new cyclodextrin dimers doubly bridged with anthracene moieties. The anthracene molecule is well-known to form the relatively stable excimer or exciplex,[6] for example, the intramolecular anthracene dimer linked with ethyleneoxy units (bis(9,10-anthracenediyl)coronand) has been reported to form a unique metal sensitive intramolecular excimer.[7]



The comparison of present cyclodextrin linked systems with the ethyleneoxy linked one reveals that the hydrophobic interaction rather than the stacking interaction between two anthracenes plays an important role in the former system to stabilize the distinct excimer-like ground state as the thermally equilibrated species, which leads to the effective excimer emission even in an aqueous solution.

Results and Discussion

Syntheses. The new doubly bridge cyclodextrins were synthesized according to Scheme 1. The reaction of 6A,6D-diamino-2,3,6-trimethyl-*β*-cyclodextrin with 9,10-anthracene diethanoyl dichloride in THF gave two isomeric doubly bridged cyclodextrin dimers, **An_2CD_2-1** and **An_2CD_2-2**. The singly bridged cyclodextrin dimer (**$AnCD_2$**) and the doubly modified monomeric cyclodextrin (**An_2CD**) were also synthesized from the corresponding components as shown in Scheme 1. After the usual silica gel chromatography purification, the FAB-MS and ^{1}H NMR spectra of all compounds showed satisfactory agreement with the expected structures. The two structural isomers of doubly bridged cyclodextrin dimers, **An_2CD_2-1** and **An_2CD_2-2**, were separated by further purification with HPLC, using an ODS column. Both compounds show the identical molecular peak of the FAB-MS spectrum at 3313 daltons, which is expected for **An_2CD_2**. Interestingly, the structures of these isomers were definitely identified by analyses of ^{1}H NMR spectra shown in Figure 1 considering their molecular symmetry.

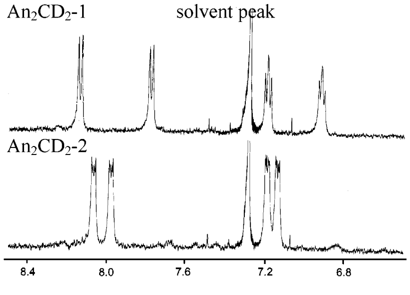


FIGURE 1. The 500-MHz ^{1}H NMR spectrum of the anthracene region of **An_2CD_2-1** and **An_2CD_2-2** in $CDCl_3$ at 298 K.

Because the 6A,6D-difunctionalized *β*-cyclodextrin is used as the starting material, the two expected isomers of **An_2CD_2** are the **AaDd**-dimer having **A−a** and **D−d** linkages of the anthracene bridges between two cyclodextrins, andthe **AdDa**-dimer having **A−d** and **D−a** linkages as shown in Scheme 1. The isomers have a different C_2 axis between two cyclodextrin moieties, i.e., the C_2 axis piercing through the two molecular centers of anthracenes for the **AaDd**-dimer and that going through the space between the two anthracenes for the **AdDa**-

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(5) (a) Ueno, A.; Fukushima, M.; Osa, T. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1067−1072. (b) Takakusa, H.; Kikuchi, K.; Urano, Y.; Higuchi, T.; Nagano, T. *Anal. Chem.* **2001**, *73*, 939−942. (c) Corradini, R.; Paganuzzi, C.; Marchelli, R.; Pagliari, S.; Sforza, S.; Dossena, A.; Galaverna, G.; Duchateau, A. *Chirality* **2003**, *15*, 30−39.

(6) (a) Moore, G. F. *Nature* **1966**, *212*, 1452−1453. (b) Subudhi, P. C.; Kanamaru, N.; Lim, E. C. *Chem. Phys. Lett.* **1975**, *32*, 503−507. (c) Ferguson, J.; Morita, M.; Puza, M. *Chem. Phys. Lett.* **1976**, *42*, 288−292. (d) Weller, A. *Pure Appl. Chem.* **1968**, *16*, 115. (e). Fages, F.; Desvergne, J.-P.; Bouas-Laurent, H. *J. Am. Chem. Soc.* **1989**, *111*, 96−102.

(7) Marquis, D.; Desvergne, J.-P.; Bouas-Laurent, H. *J. Org. Chem.* **1995**, *60*, 7984−7996.

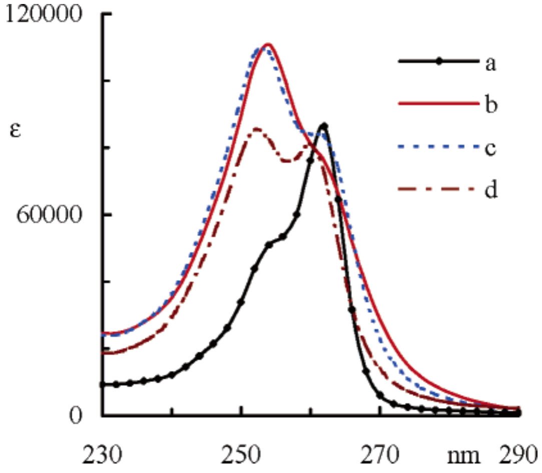

FIGURE 2. Electronic absorption spectra of **AnCD$_2$** (a), **An$_2$CD$_2$-1** (b), **An$_2$CD$_2$-2**, (c) and **An$_2$CD** (d) at 298 K in water.

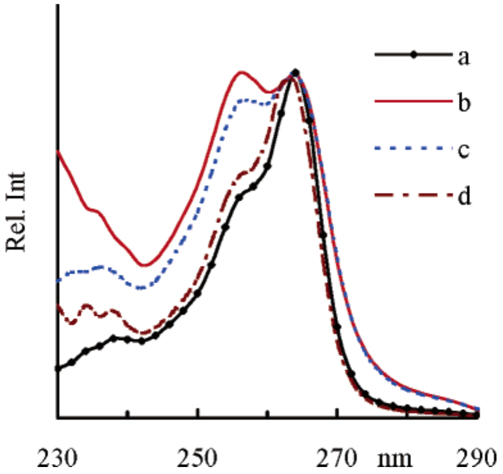

FIGURE 3. Electronic absorption spectra of **AnCD$_2$** (a), **An$_2$CD$_2$-1** (b), **An$_2$CD$_2$-2**, (c) and **An$_2$CD** (d) at 298 K in CHCl$_3$.

dimer. Assuming free rotation of the anthracene moieties along the C9−C10 axis, the aromatic protons of the anthracene moiety in the **AaDd**-dimer are classified into two groups containing four chemically equivalent protons at the positions 1•4•5•8 and 2•3•6•7, which give two double-doublet-like signals as observed for the usual 9,10-symmetrically substituted anthracenes. Since the environments of the two anthracenes in this isomer are different, four double-doublet-like signals are expected, which is true for the spectrum of **An$_2$CD$_2$-2**. On the other hand, the aromatic protons of the **AdDa**-dimer having two identical anthracene moieties are classified into four groups containing two chemically equivalent protons at the positions 1•8 (1′•8′), 2•7 (2′•7′), 3•6 (3′•6′), and 4•5 (4′•5′), which should give two double-doublet-like and two triplet-like signals as observed for the usual 9,10-unsymmetrically substituted anthracenes. The spectral feature of **An$_2$CD$_2$-1** shows good agreement with this prediction.

Absorption Spectrum. The electronic absorption spectrum of anthracene is known to present two transition bands at 300−420 and 240−270 nm. It has been shown that the shape of the latter transition band of the bisanthracene system is strongly dependent on the degree of intramolecular interaction between two anthracene chromophores,[7,8] i.e., the component at ca. 260 nm corresponds to the absorption of a nonperturbed aromatic ring and that at ca. 250 nm reflects that of the electronically interacting bisanthracene system. As shown in Figure 2, **AnCD$_2$** shows normal anthracene absorption ($\lambda_{max} = 262$ nm) in water. In contrast, the bisanthracene systems, **An$_2$CD**, **An$_2$CD$_2$-1**, and **An$_2$CD$_2$-2**, show a strong absorption band at ca. 250 nm in water, indicating a strong interaction between the two proximate anthracenes. Interestingly, the 250 nm band of **An$_2$CD** is greatly reduced in CHCl$_3$ to result in a similar shape to that of **AnCD$_2$**, while those of **An$_2$CD$_2$-1** and **An$_2$CD$_2$-2** remain even in CHCl$_3$ (Figure 3). Since the results suggest that the intramolecular interactions of the present bisanthracene systems involve reversible equilibrium processes, the thermal behavior of the spectral change in water was examined by the method of variable-temperature electronic spectrometry. All bisanthracene systems, **An$_2$CD$_2$-1**, **An$_2$CD$_2$-2**, and **An$_2$CD**, show enhancement of the 260 nm bands and decrease of the 250 nm bands with increasing temperature. The typical results for **An$_2$CD$_2$-2** are shown in Figure 4.

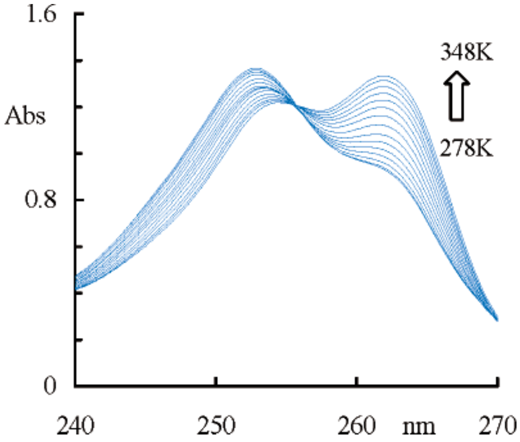

FIGURE 4. Absorption spectra of **An$_2$CD$_2$-2** (1.2×10^{-5} M) versus temperature (278 ∼348 K) in water.

These spectral changes with the clean isosbestic point indicate that the present bisanthracene systems exist in thermal equilibrium between two states, “open form” (**D$_o$**) having less overlapping between the two anthracenes and “closed form” (**D$_c$**) having strong interacting, as shown in Scheme 2.[9] The analyses of the observed temperature dependence gave the thermodynamic parameters for the interconversion of **D$_o$** and **D$_c$** as summarized in Table 1. In all cases, the transformation of **D$_o$** to **D$_c$** accompanies the negative enthalpy and entropy changes. As expected, **An$_2$CD** having the largest motional freedom of the anthracene moieties among the present series of compounds results in the most entropically unfavorable closed form and **An$_2$CD$_2$-1** and **An$_2$CD$_2$-2** show more favorable free Δ*G* gain

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[8] McSkimming, G.; Tucker, J. H. R.; Bouas-Laurent, H.; Desvergne, J.-P.; Coles, S. J.; Hursthouse, M. B.; Light, M. E. *Chem. Eur. J.* **2002**, *8*, 3331−3342.

[9] The most important factor affecting the variations of the two components of the 240−270 nm bands for the bisanthracene systems had been demonstrated to be the degree of parallelism along the long axis of the two anthracene units (see refs 7 and 11). In addition, the present compounds show the clear thermal equilibrium, which results in characteristic spectral changes common to all of the present bisanthracene systems. Since the spectra for the species at the high-temperature side in these equilibrium processes seem to resemble that of the monomeric anthracene compound, the distance variation accompanying the solvation change around the two anthracene moieties may be another additional factor affecting their spectral shapes in the present cases.

SCHEME 2. The Conversion between the Two Conformers (D_o and D_c)

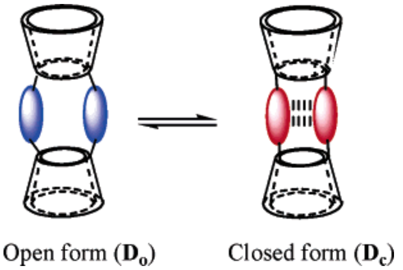

TABLE 1. Thermodynamics Parameters for the Conversion between the Two Conformers ($D_o \rightarrow D_c$) in the Ground State and in Water at 298 K

compds	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/(mol·K))	$\Delta G°$ (kJ/mol)
An$_2$CD$_2$-1	-44.5 ± 4.6	-147 ± 15	-4.8 ± 0.5
An$_2$CD$_2$-2	-44.3 ± 5.4	-138 ± 18	-3.1 ± 0.4
An$_2$CD	-52.7 ± 6.7	-175 ± 23	-0.6 ± 0.1

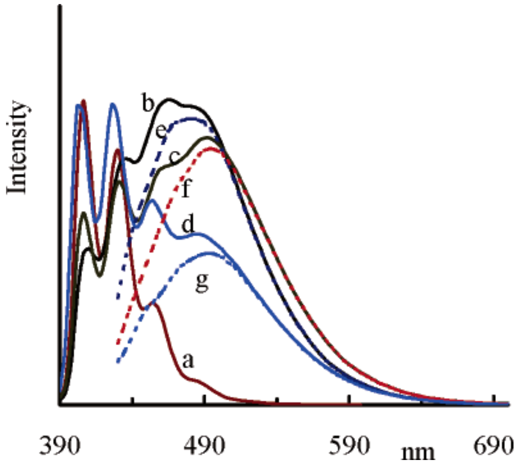

FIGURE 5. The fluorescence emission spectra of anthracene−cyclodextrin derivatives in water: (a) **AnCD$_2$**, (b) **An$_2$CD$_2$-1**, (c) **An$_2$CD$_2$-2**, and (d) **An$_2$CD** ($\lambda_{ex} = 380$ nm, at 298 K). The dotted curves are the excimer fluorescences estimated by subtracting the appropriately weighted spectra of AnCD$_2$ from those observed ones (e) **An$_2$CD$_2$-1**, (f) **An$_2$CD$_2$-2**, and (g) **An$_2$CD**, respectively.

in the formation of the closed forms due to their relatively smaller entropy loss compared with that of **An$_2$CD**. Furthermore, it should be noted that these observations are quite in contrast with those for the previously reported bis(9,10-anthracenediyl)coronand systems which show very weak temperature dependence of their electronic spectra suggesting the small enthalpy changes for the interacting process of the anthracenes in the organic solvents. The present results may indicate the equilibrium process of the present systems in water accompanies the more significant reorganization of the solvent during the anthracene rearrangement motion than that of the coronand system in the organic solvents.

As shown in Figure 5, **AnCD$_2$** exhibits a typical mirror-symmetry relationship between fluorescence and absorption spectra, while the present bisanthracene systems show the excimer fluorescence overlapping with the monomeric anthracene emission. The net excimer fluorescence spectra of **An$_2$CD$_2$-1**, **An$_2$CD$_2$-2**, and **An$_2$CD** which are estimated by subtracting the appropriately weighted spectrum of the monomeric anthracene emission of **AnCD$_2$** show the typical broad and structureless excimer spectra with $\lambda_{max} = 482$, 493, and 495 nm, respectively (see Figure 5). Interestingly, the observed excimer emissions are significantly blue-shifted compared with the usual anthracene excimer emission with $\lambda_{max} > 530$ nm.[10] The higher energy emission of the present bisanthracene systems indicates more partially and/or distantly overlapping excimers,[11] suggesting the significant contribution of the hydrophobic effect for the favorable excimer formation in addition to that of the stacking effect between the two anthracenes. Thus, the excimer emission of the present bisanthracene systems is strongly diminished in CHCl$_3$, and especially, the fluorescence spectrum of **An$_2$CD** having high conformational freedom becomes practically the same as that of **AnCD$_2$** as shown in Figure 6. The interesting feature of the present excimer systems is the distinct existence of the closed form in the ground state, which seems to be closely related to the excimer conformation. The situation is clarified by measurements of the excitation spectra of these compounds. As shown in Figure 7, for example, the excitation spectra of **An$_2$CD$_2$-2** monitored at 415 and 500 nm are quite different to provide the spectra with $\lambda_{max} = 263$ and 252 nm, respectively. The observed excitation spectra are evidently related to the absorption band of the open and closed forms of **An$_2$CD$_2$-2** (see Figure 2), suggesting that the present excimer is formed via the excited state of the closed form and the monomeric anthracene emission mainly comes from that of the open form. Since a similar behavior is also observed for **An$_2$CD$_2$-1** and **An$_2$CD**, all present bisanthracene systems are concluded to have the dual ground state−dual excitation scheme shown later. Finally, the total fluorescence quantum yields are evaluated in water at 25 °C to be 0.30 ($\phi_{mono} = 0.03$, $\phi_{ex} = 0.27$), 0.24 ($\phi_{mono} = 0.04$, $\phi_{ex} = 0.2$), and 0.27 ($\phi_{mono} = 0.12$, $\phi_{ex} = 0.15$) for **An$_2$CD$_2$-1**, **An$_2$CD$_2$-2**, and **An$_2$CD**, respectively.[12] The observation that the present systems retain considerable emission yield in water is in contrast to that for the coronand systems which show significant fluorescence

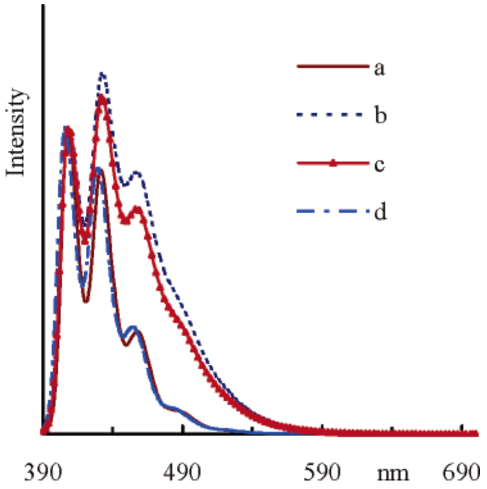

FIGURE 6. The fluorescence emission spectra of anthracene−cyclodextrin derivatives in CHCl$_3$: (a) **AnCD$_2$**, (b) **An$_2$CD$_2$-1**, (c) **An$_2$CD$_2$-2**, and (d) **An$_2$CD** ($\lambda_{ex} = 380$ nm, at 298 K).

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[10] Desvergne, J.-P.; Fages, F.; Bouas-Laurent, H.; Marsau, P. *Pure Appl. Chem.* **1992**, *64*, 1231−1238.

[11] (a) Vala, M.; Haebig, J.; Rice, S. A. *J. Chem. Phys.* **1965**, *43*, 886−897. (b) Sakata, Y.; Toyoda, T.; Misumi, S.; Yamazaki, T.; Yamazaki, I. *Tetrahedron Lett.* **1992**, *33*, 5077−5080. (c) Gonzalez, C.; Lim, E. C. *Chem. Phys. Lett.* **2000**, *322*, 382−388. (d) Bouas-Laurent, H.; Castellan, A.; Daney, M.; Desvergne, J.-P.; Guinand, G.; Marsau, P.; Riffaud, M.-H. *J. Am. Chem. Soc.* **1986**, *108*, 315−317. (e) Becker, H.-D.; Sandros, K.; Skelton, B. W.; White, A. H. *J. Phys. Chem.* **1981**, *85*, 2930−2933.

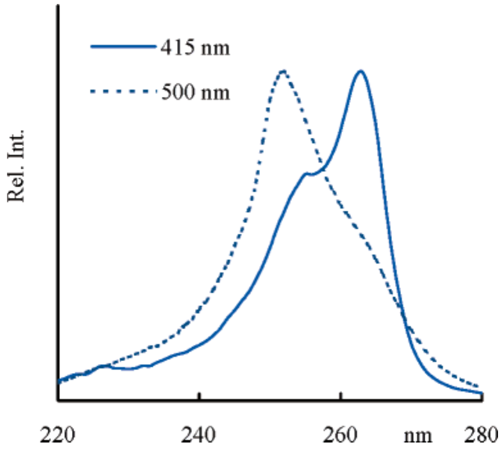


FIGURE 7. Normalized fluorescence excitation spectra of **An$_2$CD$_2$-2** in water at 298 K, λ_{em} = 415 and 500 nm.

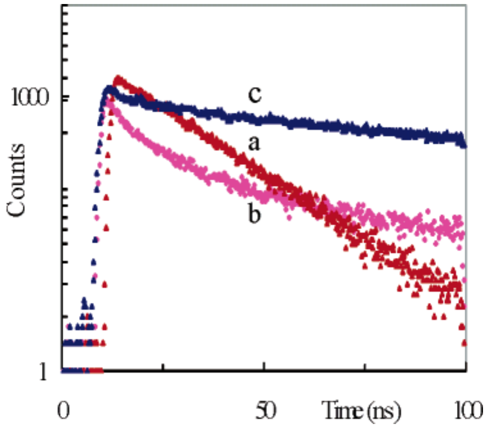


FIGURE 8. Fluorescence decay profiles of **AnCD$_2$** (a) and **An$_2$CD$_2$-2** (b, c), observed for (b) 390−415 and (c) 450−520 nm.

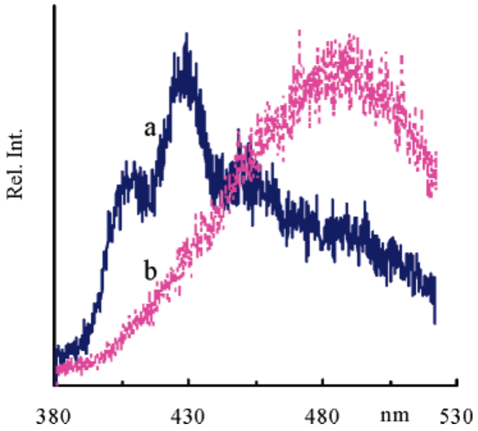
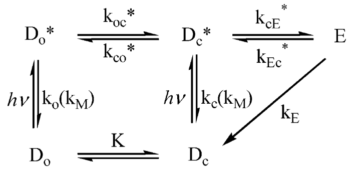


FIGURE 9. Time-resolved fluorescence spectra of **An$_2$CD$_2$-2** in water: (a) 0−10 and (b) 52−91 ns.

SCHEME 3. Proposed Kinetic Scheme Describing the Interconversion among Conformers and Excimers



quenching in polar solvents such as methanol. Since the strong hydrogen bonding medium is known to make nonradiative pathways favorable,[13] the results suggest the relatively strong hydrophobic environment around the anthracene moieties of these compounds, which prevents the direct solvent interaction between the chromophore and water-containing H bonds.

Transient Kinetics. The photophysical dynamic aspects of the present anthracene−cyclodextrin derivatives in water were examined by the method of fluorescence lifetime analyses. The fluorescence decay of **AnCD$_2$** is well fitted to the single exponential profile with the lifetime of 15.4 ns in the all fluorescence region. In contrast, the present bisanthracene systems show the wavelength-dependent decay profiles as shown in Figure 8. The time-resolved fluorescence spectra (Figure 9) clearly show that the faster decay component (0−10 ns) mainly consists of the monomeric fluorescence and the slower one (52−91 ns) practically consists of pure excimer emission. These observations, together with the results of analyses of the static electronic and emission spectra discussed above, indicate that the present fluorescence emission decay process is not compatible with the classical Birks's excimer scheme[14] but with the scheme containing dual ground, dual excited states and one excimer as shown in Scheme 3, which was originally proposed for the intramolecular exciplex and later applied for the bis(9,-10-anthracenediyl)coronand systems by Desvergne et al.[7] Assuming $k_o = k_c = k_M$, $k_{Ec}^* \ll k_E$, and $k_{co}^* \ll k_{cE}^* + k_M$, the theoretical decay profiles for the monomeric ($\mathbf{I}_{monomeric}$) and excimer emissions ($\mathbf{I}_{excimeric}$) are described with the following equations.

$$\mathbf{I}_{monomeric} = A_{m1}\exp(-(k_M + k_{oc}^*)t) + A_{m2}\exp(-(k_M + k_{cE}^*)t) \quad (1)$$

$$\mathbf{I}_{excimeric} = A_{e1}\exp(-(k_M + k_{oc}^*)t) + A_{e2}\exp(-(k_M + k_{cE}^*)t) + A_{e3}\exp(-k_Et) \quad (2)$$

According to these equations, the decay data for the monomer fluorescence of **An$_2$CD$_2$-2** monitored at the 390−412 nm range is analyzed as the double exponential profile to give two lifetimes of 2.4 and 14 ns with satisfactory statistical fitting. Then, the excimer decay profile collected at the 450−520 nm range is analyzed by using three exponential functions of which two lifetime parameters are fixed as the same values obtained from the monomeric emission analysis. These procedures were successfully applied for all the present bisanthracene systems to give the lifetime of the excimers, $\tau_E = 1/k_E$. Assuming the same intact monomeric fluorescence decay rate constant of k_M = 1/15.2 ns for all compounds, other rate constants, k_{oc}* and k_{cE}*, are evaluated as shown in Table 2.

The comparison of the resulting parameters with those of the coronand systems reveal that the kinetic processes of the excimer formation (k_{cE}*) and excimer emissions (k_E) are very similar but the interconversion processes (k_{oc}*) between **D$_o$*** and **D$_c$***

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[12] The detailed data of the quantum yields for **An$_2$CD$_2$-1**, **An$_2$CD$_2$-2**, and **AnCD$_2$** in water and methanol are shown in the Supporting Information.

[13] (a) Werner, T. C.; Hoffman, R. M. *J. Phys. Chem.* **1973**, *77*, 1611−1615. (b) Werner, T. C.; Matthews, T.; Soller, B. *J. Phys. Chem.* **1976**, *80*, 533−541. (c) Biczók, L.; Bérces, T.; Inoue, H. *J. Phys. Chem. A* **1990**, *103*, 3837−3842.

[14] Briks, J. B. *Photophysics of Aromatic Molecules*; Wiley Interscience: New York, 1970.

TABLE 2. Kinetic Parameters for the Interconversion Processes of the Bisanthracene Systemsin Water at 298 K

	k_{oc}* (s^{-1})	k_{cE}* (s^{-1})	k_E (s^{-1})
An$_2$CD$_2$-1	2.5×10^6	3.4×10^8	1.0×10^7
An$_2$CD$_2$-2	6.0×10^6	3.5×10^8	1.0×10^7
An$_2$CD	2.2×10^7	3.4×10^8	1.1×10^7
coronand[a]	8.8×10^7	5.2×10^8	1.4×10^7

[a] The data for the coronand compound in methanol are reported by Desvergne et al., see ref 7.

are sensitive for the molecular structure connecting two anthracene moieties, i.e., the k_{oc}* values for **An$_2$CD$_2$-1** and **An$_2$CD$_2$-2** are over 10 times smaller than that of the coronand system in methanol (8.8×10^7 s^{-1}),[7] though **An$_2$CD** having the largest motional freedom in the present bisanthracene systems shows significantly larger k_{oc}*. The results indicate that the bridging structure between the two anthracenes with the bulky cyclodextrin moiety results in the higher thermal barrier for the interconversion of **D$_o$*** and **D$_c$***, which at the same time brings the relative stability of the **D$_c$*** state, thereby leading to effective excimer formation despite its less favorable overlapping of two anthracene groups.

Conclusion

Several new anthracene−cyclodextrin derivatives have been synthesized. The doubly anthracene bridged cyclodextrin dimers show strong high-energy eximer emission. As shown by the solvent-dependent properties, the present excimers in the aqueous solution seem to be significantly stabilized by the hydrophobic effect. This strong effect in water makes it possible to form the excimer even for the single bridged bisanthracene derivative, **An$_2$CD**, which shows very weak excimer fluorescence in the organic solvents. The large negative entropies estimated for the equilibrium between **D$_o$** and **D$_c$** in the ground states suggest that the driving force for the formation of **D$_c$** is somewhat different from so-called hydrophobic interaction, which sometimes shows the positive entropy change due to the liberation of the solvating water molecules. Although the exact origin of this driving force is not clear at this stage, one of the most plausible explanations is that the interconversion between **D$_o$** and **D$_c$** also accompanies the large negative entropy change due to conformational changes of the highly bulky cyclodextrin. To our knowledge, it is a rare example where the anthracene excimer shows the two distinct excitation spectra which correspond to the monomeric and excimeric fluorescence emission. The observation that the excitation spectra for the excimer fluorescence show the distinct spectral characteristic resembling the absorption spectra of **D$_c$** indicates that the present excimer formation in the excited state is also more strongly controlled by the hydrophobic effect rather than by the stacking interaction of the anthracene moieties. Thus, these bisanthracene cyclodextrin systems provide one of the interesting examples which indicate the environmental control of the excited state of the aromatic molecules.

Experimental Section

General. The solvents and reagents were obtained from commercial supplies and used without further purification. Anhydrous solvents were dried by the usual procedures and used directly. All aqueous solutions were prepared in a sodium carbonate−sodium bicarbonate buffer (pH 9.0). The sample concentration was less then 4×10^{-6} M for fluorescence measurement. The fluorescence quantum yields were determined by comparison with anthracene in ethanol ($\phi_F = 0.27$),[15] and all the solutions were used after bubbling with nitrogen. Fluorescence decay measurements were performed by the single-photon counting technique, using nitrogen laser. The experimental decay profiles were treated with the least-squares method, and the reduced chi squared χ_r^2 values were in the acceptable 0.8−1.3 range.

Syntheses. 6-Amino-2,3,6-trimethyl-β-cyclodextrin,[16] 6A,6D-diamino-2,3,6-trimethyl- β-cyclodextrin,[17] anthracene-9,10-diacetic acids,[18] and 9,10-anthracene diethanoyl dichloride[19] were prepared as described in previously reported articles.

AnCD$_2$. 6-Amino-2,3,6-trimethyl-β-cyclodextrin (224 mg, 0.158 mmol) was added to a THF solution (2 mL) of 9,10-anthracene diethanoyl dichloride (26 mg, 0.079 mmol) at room temperature. After the addition of triethylamine (0.1 mL), the reaction mixture was stirred for 3 h. The solvent was evaporated in a vacuum, and the residue was dissolved in $CHCl_3$. The solution was washed with water. The crude material was purified with silica gel chromatography with methanol/chloroform elution and subsequent HPLC, using an ODS column, to give **AnCD$_2$**. Yield: 43%. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 3.08−3.90 (m, 211H), 4.66 (s, 4H, An-CH$_2$), 4.23−5.14 (m, 14H, C$_1$−H), 5.78 (t, 2H, NH), 7.62−7.64 (q, $J = 6.8$, 3.0 Hz, 4H, An), 8.32−8.34 (q, $J = 6.7$, 2.9 Hz, 4H, An). HRMS (FAB) (m/z) calcd for $C_{142}H_{232}N_2O_{70}$ 3085.4658 ([M]$^+$), found 3085.4688.

An$_2$CD$_2$. A similar procedure with 6A,6D-diamino-2,3,6-trimethyl-β-cyclodextrin and other corresponding reagents provided crude **An$_2$CD$_2$**. The crude material was purified by silica gel chromatography with methanol/chloroform and subsequent HPLC, using an ODS column, to give **An$_2$CD$_2$-1** (7% yield) and **An$_2$CD$_2$-2** (8% yield). **An$_2$CD$_2$-1**: ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 2.98−4.12 (m, 206H), 4.26−4.51 (m, 8H, An-CH$_2$), 4.90−5.52 (m, 14H, C$_1$−H), 5.72 (t, 2H, NH), 6.19 (t, 2H, NH), 6.91−6.94 (t, $J = 6.7$, 8.6 Hz, 4H, An), 7.18−7.21 (t, $J = 6.8$, 8.6 Hz, 4H, An), 7.77−7.79 (d, $J = 8.8$ Hz, 4H, An), 8.14−8.16 (d, $J = 8.8$ Hz, 4H, An). HRMS (FAB) (m/z) calcd for $C_{158}H_{240}N_4O_{70}$ 3313.5346 ([M]$^+$), found 3313.5343. **An$_2$CD$_2$-2**: ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 2.87−4.07 (m, 206H), 4.31−4.49 (m, 8H, An-CH$_2$), 4.84−5.36 (m, 14H, C$_1$−H), 5.81 (t, 2H, NH), 6.11 (t, 2H, NH), 7.13−7.15 (q, $J = 6.7$, 2.9 Hz, 4H, An), 7.18−7.20 (q, $J = 7.1$, 2.8 Hz, 4H, An), 7.97−7.99 (q, $J = 6.8$, 3.0 Hz, 4H, An), 8.05−8.07 (q, $J = 6.7$, 3.0 Hz, 4H, An). HRMS (FAB) (m/z) calcd for $C_{158}H_{241}N_4O_{70}$ 3314.5424 ([M + H]$^+$), found 3314.5361.

An$_2$CD. The similar procedure gave **An$_2$CD** (80% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 1.25−1.30 (t, 6H, CH$_3$), 2.80−3.85 (m, 103H), 4.15−4.23 (q, 4H, CH$_2$), 4.56−4.70 (m, 8H, An-CH$_2$), 4.36−5.08 (m, 7H, C$_1$−H), 5.70−5.76 (m, 2H, NH), 7.54−7.62 (m, 8H, An), 8.23−8.31 (dd, $J = 8.8$ Hz, 4H, An), 8.38−8.34 (d, $J = 7.2$ Hz, 4H, An). HRMS (FAB) (m/z) calcd for $C_{101}H_{142}N_2O_{39}$ 2006.9190 ([M]$^+$), found 2006.9144.

Supporting Information Available: The HPLC chart of **An$_2$CD$_2$-1** and **An$_2$CD$_2$-2**, the fluorescence excitation spectra for **An$_2$CD$_2$-1** and **An$_2$CD**, the absorption spectral change versus temperature for **An$_2$CD$_2$-1** and **An$_2$CD**, and the fluorescence quantum yields of **An$_2$CD$_2$-1**, **An$_2$CD$_2$-2**, **An$_2$CD**, and **AnCD$_2$** in water and CH_3OH. This material is available free of charge via the Internet at http://pubs.acs.org.

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