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A New Chiral Probe for Sulfate Anion: UV, CD, Fluorescence, and NMR Spectral Studies of 1:1 and 2:1 Complex Formation and Structure of Chiral Guanidinium−*p*-Dimethylaminobenzoate Conjugate with Sulfate Anion

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Abstract: A new chiral chromophoric host **1**, possessing a 4-(*N*,*N*-dimethylamino)benzoate (DMAB) group tethered to a chiral bicyclic guanidinium subunit, was synthesized and applied to the probe for sulfate anion. Host **1** showed typical successive 1:1 and 2:1 host:guest complexation behavior toward the divalent sulfate anion, as revealed by UV−vis, CD, fluorescence, and ^{1}H NMR spectroscopic studies. The DMAB chromophore was shown to be a sensitive CD spectral probe for assessing not only the complexation behavior but also complex stoichiometry and structure. The stepwise 1:1 and 2:1 complexation constants (K_1 and K_2) were determined as 1.53×10^6 and 4.84×10^4 M^{-1}, respectively, by NMR titration in CD_3CN. The CD exciton chirality method allowed us to determine the chiral sense (spatial arrangement) of the two DMAB moieties in the 2:1 complex as negative (counterclockwise). The dual fluorescence behavior of DMAB was employed for elucidating the role of the countercation upon complexation of host **1** with sulfates possessing lipophilic countercation(s) such as tetrabutylammonium.

Introduction

The guanidinium group in the arginine side chain plays a crucial role in constructing the higher structures of proteins through hydrogen-bonding as well as electrostatic interactions with the carboxylate group. This biological supramolecular motif has led chemists to make use of the guanidinium group as an attractive anchor subunit in various artificial receptors.[1] For better performance upon complexation, the guanidinium group is incorporated into the bicyclo[4.4.0]decane framework, yielding a highly preorganized binding site particularly suitable for carboxylate, sulfonate, phosphate, and so on.[2] Indeed, the 1:1 complexation behavior of guanidinium hosts with anionic guests has been intensively investigated,[2] while the 2:1 guanidinium:anion complex formation is limited to ditopic bis-guanidinium hosts.[3]

The 4-(*N*,*N*-dimethylamino)benzoate (DMAB) chromophore, which can be readily introduced to organic compounds with hydroxyl group(s) and possesses a sizable absorption coefficient, is often employed in the exciton chirality method to establish the absolute configuration of chiral diols.[4] DMAB derivatives are also known to exhibit unique dual fluorescence behavior, originating from the simultaneous emission of the locally excited (LE) and twisted intramolecular charge transfer (TICT) states at different wavelengths.[5,6] The TICT dual fluorescence, by nature being highly susceptible to the solvent polarity, is a

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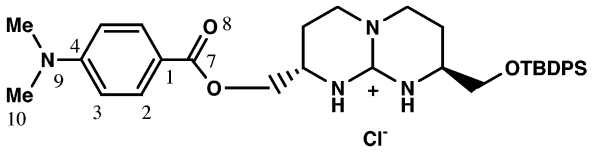
versatile tool for sensing microenvironmental polarity of heterogeneous media such as polymers[7] as well as homogeneous solutions.[8]

Combining the advantages of the guanidinium ion to efficiently bind anions and of the DMAB chromophore to sense chiral information, we designed a new class of anion host **1**, which contains a chiral bicyclic guanidinium subunit tethered to a DMAB chromophore. In this paper, we wish to report the synthesis of this novel chiral guanidinium host **1** and the unique 1:1 and 2:1 host:guest complexation behavior with the sulfate anion, investigated by using UV−vis, CD, fluorescence, and ^{1}H NMR spectroscopies.

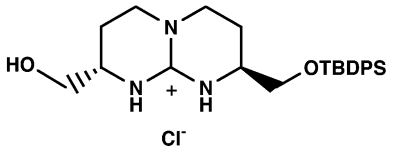


1

TBDPS ≡ —SiPh$_2$^{t}Bu

Results and Discussion

Synthesis of Guanidinium−DMAB Conjugate (1). The chiral bicyclic guanidinium subunit was prepared from L-methionine and L-asparagine, according to the literature procedure.[2h] The chiral host **1** was obtained as a monohydrate by condensation of the chiral alcohol **2**[2h] and 4-(*N*,*N*-dimethylamino)benzoyl chloride (**3**)[9] in the presence of triethylamine as a base. Subsequent purification by column chromatography over silica gel followed by preparative GPC gave a pure sample of **1** in 59% as a chloride salt.



2

UV−Vis Spectra and Intramolecular Hydrogen Bond Formation. In their work on the solvatochromic shift of methyl DMAB (**4**),[10] Revill et al. measured the electronic absorption spectra in hexane, acetonitrile, ethanol, and water to find that the absorption maximum (λ_{max}) shows substantial bathochromic shifts in polar and/or hydrogen-bonding solvents without any appreciable changes in extinction coefficient. We plotted the reported λ_{max} values as a function of the acceptor number (AN),[11] hydrogen bond donor ability (α),[12] and solvent polarity parameter $E_T(30)$[11] of the solvent used, as one or all of these solvent parameters would influence the λ_{max} value. As can be seen from Figure 1, the $E_T(30)$ value gives an excellent linear plot with a correlation coefficient (r) of 0.999, while the other solvent parameters lead to more scattered plots with appreciably smaller r values, such as 0.986 with AN and 0.927 with α, revealing the vital role of the solvent polarity in determining the λ_{max} of **4**.

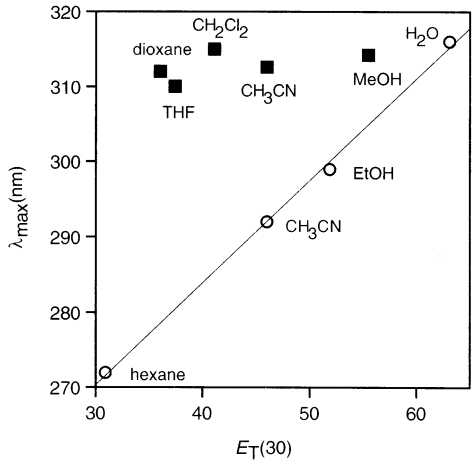
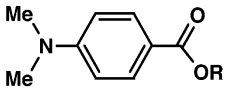


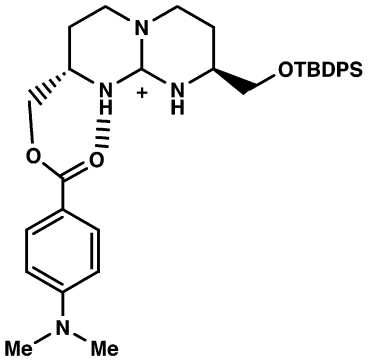
Figure 1. The absorption maxima of **1** (■) and **4** (○) in hexane, dioxane, THF, dichloromethane, acetonitrile, methanol, ethanol, and water as a function of solvent polarity parameter $E_T(30)$.



4 R = Me
5 R = Et

Unexpectedly, the guanidinium ester **1** gave almost constant λ_{max} values of around 310−315 nm in all of the solvents examined, which are very close to that of the reference compound **4** in water (316 nm); see Figure 1 (■). This result is in sharp contrast to the highly solvent-dependent λ_{max} observed for **4**, which ranges widely from 272 nm in hexane to 316 nm in water.

It is suspected that such large bathochromic shifts of **1** in nonpolar and moderately polar solvents, leading to the resemblance with the water λ_{max} value, are caused by the intramolecular hydrogen-bonding interaction of the guanidinium proton to the ester carbonyl oxygen. Indeed, strong hydrogen-bond donors, such as 4-fluorophenol, are known to interact intermo-



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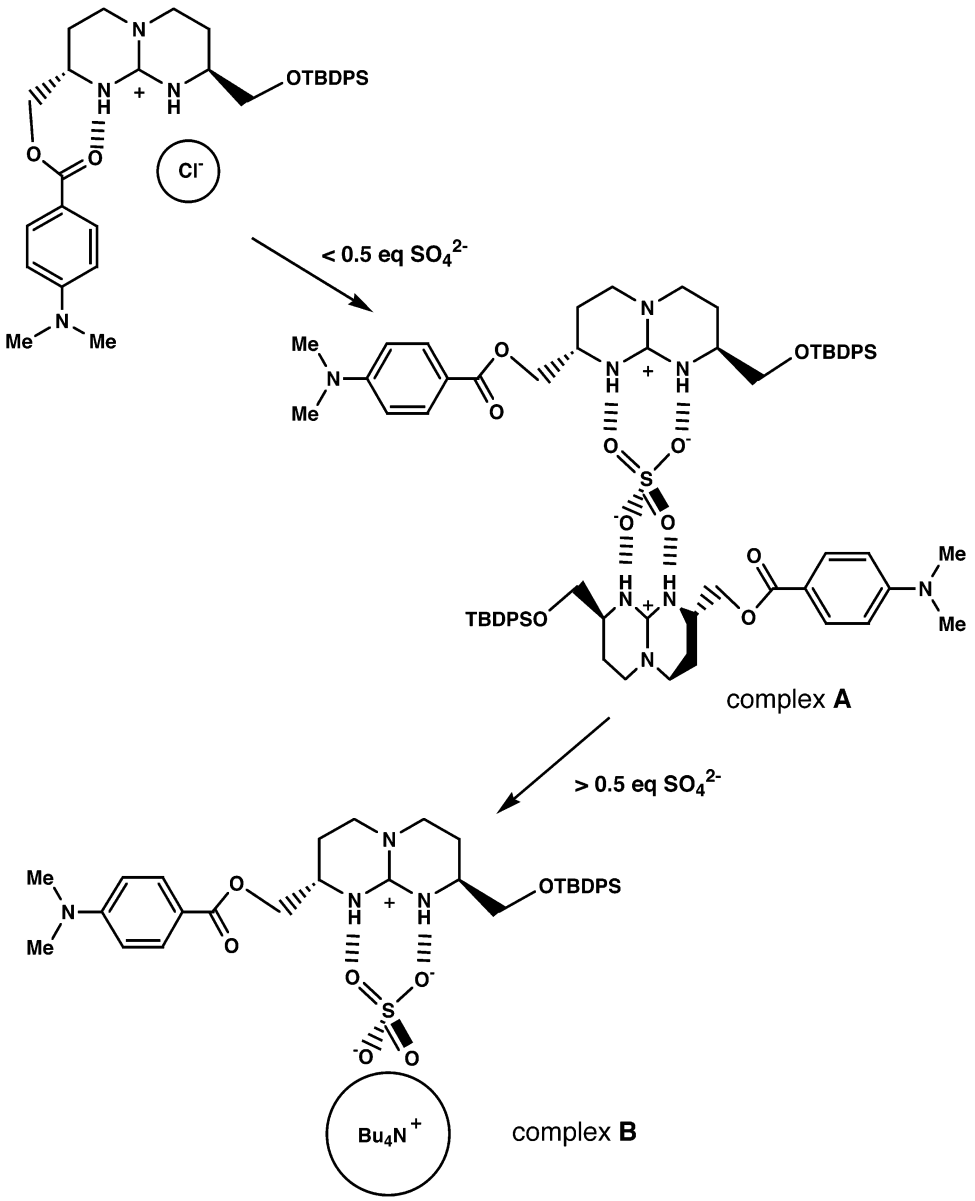
Scheme 1



lecularly with ethyl DMAB (**5**).[13] In supersonic jet fluorescence experiments, the intramolecular hydrogen bond has also been demonstrated to exist between the ester and hydroxyl moieties of DMAB derivatives possessing a hydroxyl group.[14] Judging from these facts, we may conclude that the highly acidic guanidinium proton (p*K*a = 13.54 at 25 °C in water)[15] interacts with the DMAB's carbonyl oxygen to form a strong hydrogen bond in **1**.

^{1}H NMR Spectral Titration. The guanidinium ion is known to form a stable 1:1 complex with the carboxylate anion through dual-hydrogen-bonding and other electrostatic interactions. Possessing four equivalently negatively charged oxygens, divalent sulfate anion can interact with the guanidinium subunit of **1** to form not only the 1:1 complex (**B**) but also the 2:1 complex (**A**), as illustrated in Scheme 1. The stepwise binding constants (K_1 and K_2) for the 1:1 and 2:1 complexations are defined by eqs 1 and 2.

$$\mathbf{1}^+ + {SO_4}^{2-} \overset{K_1}{\rightleftharpoons} \mathbf{1}^+\cdot{SO_4}^{2-}$$

$$K_1 = [\mathbf{1}^+\cdot{SO_4}^{2-}]/([\mathbf{1}^+][{SO_4}^{2-}]) \quad (1)$$

$$\mathbf{1}^+\cdot{SO_4}^{2-} + \mathbf{1}^+ \overset{K_2}{\rightleftharpoons} (\mathbf{1}^+)_2\cdot{SO_4}^{2-}$$

$$K_2 = [(\mathbf{1}^+)_2\cdot{SO_4}^{2-}]/([\mathbf{1}^+\cdot{SO_4}^{2-}][\mathbf{1}^+]) \quad (2)$$

The complexation behavior of host **1** with the sulfate anion was studied by ^{1}H NMR titration in CD_3CN at 23 °C. The aromatic (H2 and H3) and *N*-methyl (H10) signals were monitored during the titration of **1** at a fixed concentration with bis(tetrabutylammonium) sulfate (TBA_2SO_4). Interestingly, all of the H2, H3, and H10 signals first shifted to high field almost proportionally to the amount of added sulfate until the sulfate/**1** ratio reached 0.5, and then they moved in the opposite direction until the ratio reached 1−1.2 and finally leveled off thereafter,

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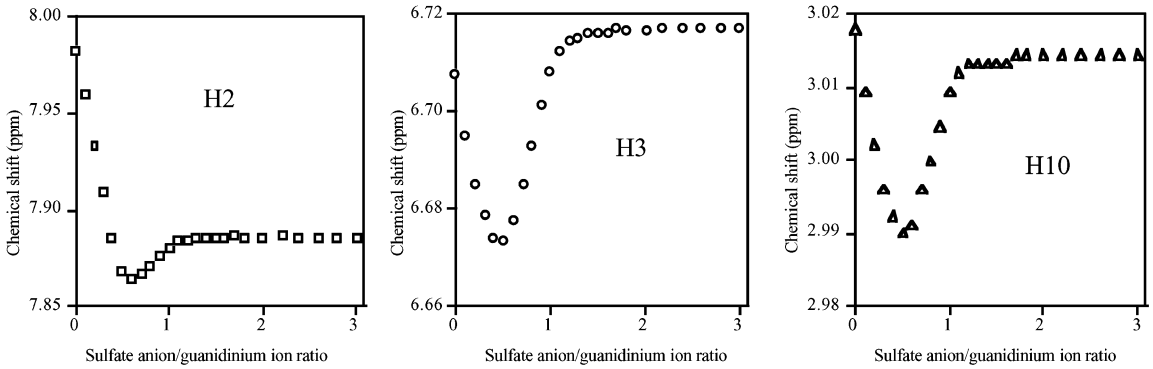


Figure 2. Chemical shift changes of aromatic (H2 and H3) and *N*-methyl (H10) protons of host **1** upon ^{1}H NMR titration with bis(tetrabutylammonium) sulfate in CD_3CN.

as shown in Figure 2. These results clearly indicate that the addition of sulfate to the solution of host **1** leads to the predominant formation of a 2:1 host:guest complex (**A** in Scheme 1) at the initial stages of titration up to the sulfate/**1** ratio of 0.5, which is then gradually replaced by the 1:1 complex (**B** in Scheme 1) with increasing sulfate/**1** ratio from 0.5 to 1 or 1.2, and ultimately the 1:1 complex prevails thereafter. We can also anticipate very large binding constants (K_1 and K_2) from the appearance of the sharp changes in curvature at the sulfate/**1** ratios of 0.5 and ca. 1. The titration curve obtained with the H2 signal, which exhibits the largest shifts upon complexation, was subjected to nonlinear least-squares curve fitting, assuming an equilibrium mixture of 1:1 and 2:1 complexes in the solution, to give the K_1 and K_2 values of 1.53×10^6 and 4.84×10^4 M^{-1}, respectively.[16]

CD Spectral Titration. As demonstrated above, the chiral guanidinium host **1** forms not only 1:1 but also 2:1 complexes with sulfate anion. In the 2:1 complex, the two guanidinium subunits are fixed in a perpendicular arrangement (as a statistical ensamble) to each other around the sulfate. A closer look at this structure immediately reveals that there exist two stereochemical possibilities in the complexation mode; one is complex **C** with negative chirality in which two DMABs are placed counterclockwise from the front-to-back, and the other is complex **D** with positive chirality in which two DMABs are placed clockwise. Complexes **C** and **D** are diastereomers.

CPK molecular model examinations indicate that the distance between the two methylenes adjacent to DMAB is ca. 8 Å in the 2:1 complex. Although the magnitude of CD couplets tends to decrease with increasing distance between the chromophores,[4] bis-DMAB esters of steroidal 3,15- and 3,17-diols, in which the chromophores are 13−16 Å apart, exhibit clear bisignated CD spectra. In this context, it is not unreasonable to expect an appreciable exciton coupling interaction to occur between the two DMAB chromophores in the 2:1 complex **C**/**D**. If the 2:1 complex exhibits negative first and positive second Cotton effect peaks, the two DMABs are judged to have negative chirality, indicating the formation of complex **C**. The oppositely signed CD couplet means the formation of complex **D** with positive chirality.

CD spectral titration of host **1** with sulfate anion was performed in acetonitrile. As can be seen from Figure 3, the CD spectrum of **1** displayed dramatic changes from the simple

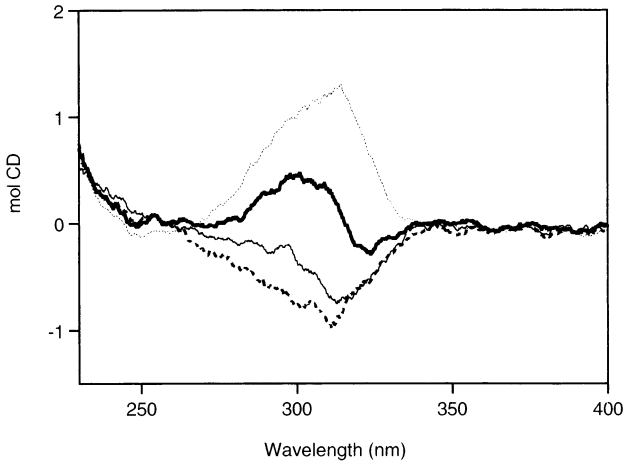
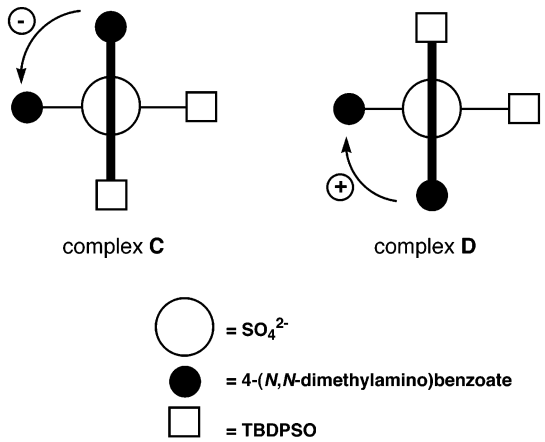


Figure 3. CD spectra of acetonitrile solutions of **1** (4.30×10^{-5} M) in the absence (thin dashed line) and in the presence of 0.5 (thick solid line), 1 (thin solid line), and 2 (thick dashed line) equiv of bis(tetrabutylammonium) sulfate.



positive Cotton effect peak in the absence of sulfate to bisignated and then to a negative Cotton effect peak, depending on the amount of sulfate added to the solution. Thus, the addition of a half-equivalent amount of sulfate led to weak, but clear, CD exciton coupling with negative first and positive second Cotton effect peaks. This directly and unambiguously indicates that the two DMABs are arranged counterclockwise and hence that complex **C** is more favored over **D** upon 2:1 complexation of chiral host **1** with sulfate. This preference seems reasonable because the DMAB substituent in each host of the 2:1 complex can avoid steric hindrance in complex **C** more than in **D**, where the two DMABs are protruding in the same direction.

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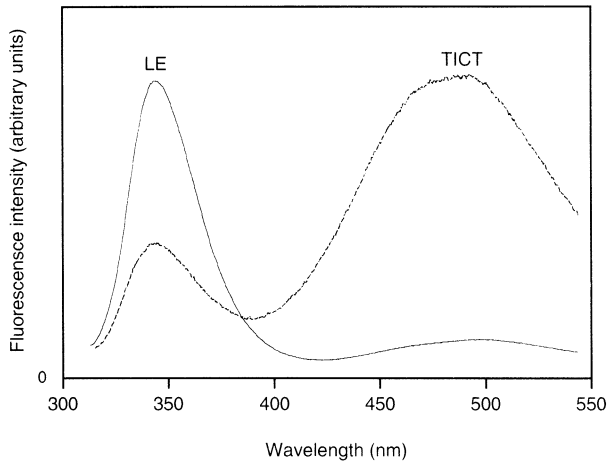


Figure 4. Fluorescence spectra of acetonitrile solutions (4.00×10^{-6} M) of guanidinium ester **1** (solid line) and ethyl ester **5** (dashed line) excited at 280 nm.

Table 1. Selected Results of PM3 Calculations on **4**, **6a**, and **6b**

compound	ΔH_f / kcal mol^{-1}	bond order		
		C(1)–C(7)	N(9)–C(4)	NH- - -O(8)
4	−62.2	0.963	1.064	
6a	89.7	0.974	1.095	
6b	81.9	1.007	1.122	0.046

By further adding sulfate up to the equimolar amount or more, the 2:1 complex interacts with another sulfate anion to give two 1:1 complexes with an accompanying CD spectral change from the couplet pattern to a simple negative peak, which is almost a mirror image of the original shape. The 1:1 ligation of sulfate to **1** appears to drive the DMAB chromophore from the original position into a different sector of the chiral field created by the chiral guanidinium skeleton.

LE versus TICT Fluorescence. The fluorescence spectra of the guanidinium ester **1** and the ethyl ester **5** were measured in acetonitrile. As can be seen from Figure 4, both compounds exhibited two fluorescence peaks at 344 and 497 nm, which are attributable to the locally excited (LE) and twisted intramolecular charge transfer (TICT) states, respectively. However, the relative intensity of TICT and LE bands, Φ^{TICT}/Φ^{LE}, differs greatly between the guanidinium ester **1** and ethyl ester **5**, affording a significantly smaller Φ^{TICT}/Φ^{LE} value for **1**. It is likely that the greatly reduced relative TICT fluorescence intensity observed for **1** originates from the intramolecular hydrogen-bonding interaction between the guanidinium proton and the ester carbonyl, which decelerates the relaxation of the DMAB moiety to the TICT state even in polar acetonitrile.

Semiempirical PM3 calculations on compound **6**, a simplified model for **1**, support the retarded rotational relaxation of the dimethylamino group in the presence of the intramolecular hydrogen-bonding interaction, at least in the ground state. As shown in Table 1, the intramolecularly hydrogen-bonded, lowest energy, conformer **6b** gives a N(9)−C(4) bond order of 1.122, which is appreciably greater than that of reference compound **4** (1.064) or non-hydrogen-bonded conformer **6a** (1.095). This result can be rationalized by the increased barrier of **1** upon rotational relaxation from the LE to TICT state, leading to the decreased Φ^{TICT}/Φ^{LE} ratio. These experimental and theoretical results indicate that the intramolecular hydrogen bond not only

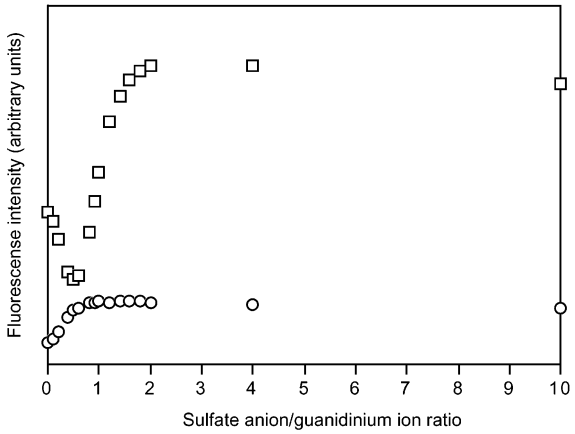
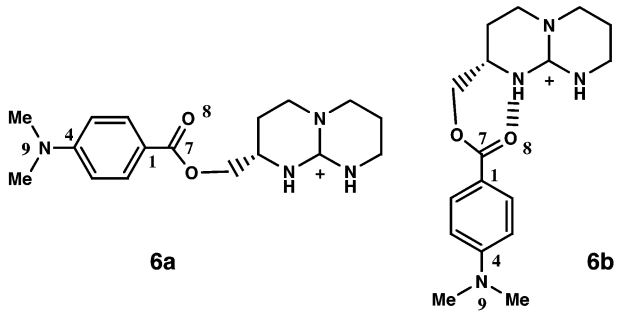


Figure 5. Fluorescence intensity changes of the LE band at 346 nm (□) and of the TICT band at 491 nm (○) upon titration of host **1** with bis(tetrabutylammonium) sulfate in acetonitrile; excitation wavelength: 280 nm.

reduces the conformational freedom of the ester moiety but also hinders the rotational motion of the dimethylamino group at the opposite side of the chromophore, which is essential for the TICT relaxation.



Fluorescence Titration. The complexation behavior of **1** toward the sulfate anion was assessed also by fluorescence titration in acetonitrile by using the DMAB group as a fluorescence probe. Fluorescence intensities of both LE (346 nm) and TICT (491 nm) bands of **1** were recorded during the titration to give the results shown in Figure 5. The titration curve profile of the LE band is very similar to those observed in ^{1}H NMR titration. The LE intensity first drops sharply to one-half of the original value on addition of up to 0.5 equiv of sulfate, then rapidly increases to exceed the original value until 2 equiv of sulfate is added, finally forming a plateau thereafter. In sharp contrast, the TICT fluorescence affords a completely different profile, which shows an initial rapid increase (up to 0.5 equiv) but no appreciable changes thereafter (even up to 10 equiv).

The first step, accompanying the compensatory intensity changes of the LE and TICT fluorescence, is readily understandable, because the intramolecular hydrogen bond of **1** is broken upon complexation of sulfate anion with the guanidinium moiety, allowing the rotational relaxation from the LE to TICT state. Hence, the TICT intensity increases with the loss of the LE intensity on increasing concentration of the 2:1 complex in solution.

However, the second step is more complicated. In the 0.5−2 equiv region of Figure 5, the LE and TICT fluorescence no longer behave synchronously; the LE intensity rapidly increases, while the TICT intensity is practically constant in this and the

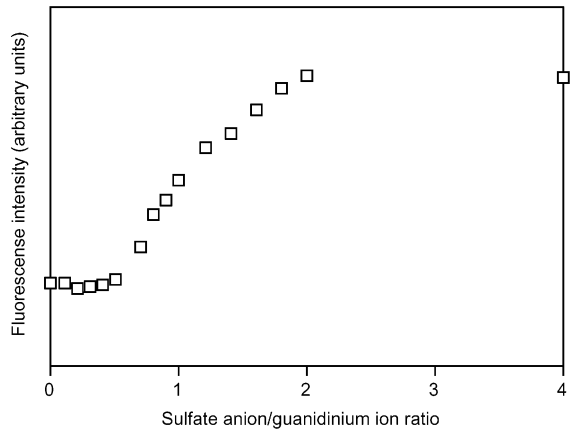


Figure 6. Fluorescence intensity change at 329 nm of **2** upon titration with bis(tetrabutylammonium) sulfate in acetonitrile; excitation wavelength: 280 nm.

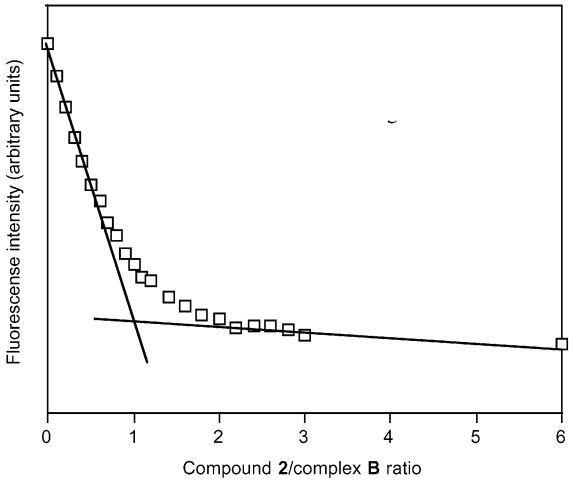
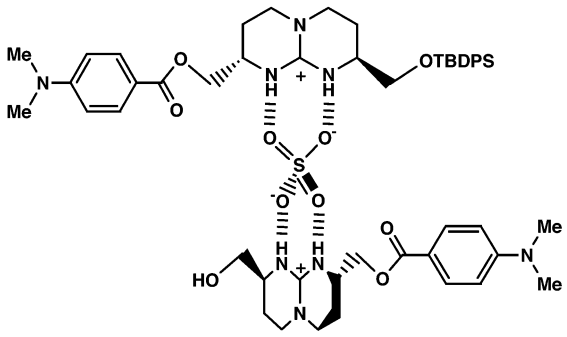


Figure 7. Fluorescence intensity change at 491 nm of the $(TBA^+)(\mathbf{1}^+\cdot SO_4^{2-})$ complex upon titration with **2** in acetonitrile; excitation wavelength: 280 nm.

higher equivalents region. In a TICT dual fluorescence system, the LE fluorescence is enhanced by increasing the solvent lipophilicity or by hindering the relaxation to the TICT state. Apparently, there is no such factor for enhancing the LE fluorescence intensity in the present system, except for the active participation of the lipophilic countercation, that is, tetrabutylammonium (TBA), in the complex species. In the ground electronic state, the interaction of DMAB's carbonyl oxygen with TBA cation may be very weak or almost negligible. However, upon excitation, the DMAB moiety udergoes the TICT transformation, developing a negative charge on the former carbonyl oxygen, which should attract positively charged TBA, and then the microenvironmental hydrophobicity around the DMAB is increased greatly, and therefore the fluorescence intensity is enhanced. Thus, we examined the possible effect of the TBA cation on the fluorescence behavior of the guanidinium host **2**, which shows only regular fluorescence from the phenyl group as it lacks the DMAB. Under comparable conditions, host **2** emitted weak fluorescence at 329 nm, the intensity of which showed small, but appreciable (ca. 12%), enhancement upon addition of TBA sulfate of 0.5−4 equiv. As can be seen from Figure 6, the titration profile obtained with **2** is completely different from those of the LE and TICT fluorescence of host **1**. The fluorescence intensity of **2** does not show any appreciable change in the 0−0.5 equiv region, but starts to deviate from the original value at 0.5 equiv and gradually increases in the 0.5−2 equiv region to reach a plateau at >2 equiv. The absence of any intensity change at the initial stage is reasonable, because there is no intramolecular hydrogen bond to be broken in host **2** or countercation to be involved in the neutral 2:1 complex ($\mathbf{2}^+\cdot SO_4^{2-}\cdot\mathbf{2}^+$). Further addition of TBA sulfate leads to an increase of the 1:1 complex at the expense of the 2:1 complex, the former of which eventually becomes dominant at high TBA sulfate concentrations. Thus, the gradual fluorescence intensity enhancement in the 0.5−2 equiv region can be reasonably accounted for in terms of the association of a TBA cation with the anionic 1:1 complex to form a contact ion pair $(TBA^+)(\mathbf{2}^+\cdot SO_4^{2-})$, in which the lipophilic TBA enhances the microenvironmental hydrophobicity around the fluorophore.

To further elucidate the role of TBA in the fluorescence intensity change, we performed a fluorescence titration experiment using the 1:1 complex of **1** with TBA. In this titration experiment, the fluorescence intensity of the 1:1 complex was monitored upon gradual addition of host **2** (Figure 7). If TBA is not involved in the 1:1 complex, no appreciable change is expected to occur in the TICT fluorescence. On the other hand, if the TBA ion is incorporated into the 1:1 complex $(TBA^+)(\mathbf{1}^+\cdot SO_4^{2-})$, the second ligation by host **2** will drive out the lipophilic TBA to form a mixed 2:1 complex ($\mathbf{1}^+\cdot SO_4^{2-}\cdot\mathbf{2}^+$) (**E**), which leads to a substantial decrease of microenvironmental hydrophobicity around the fluorophore and therefore an appreciable decrease in TICT intensity. In fact, the TICT intensity was monotonically decreased upon addition of host **2** to the 1:1 complex, most probably due to the loss of the lipophilic TBA ion, giving the hetero bis-guanidinium 2:1 complex **E**, that is, ($\mathbf{1}^+\cdot SO_4^{2-}\cdot\mathbf{2}^+$). The 1:1 stoichiometry between host **2** and the 1:1: complex was obtained from the crossing point of the extrapolation of the titration curve.



complex **E**

It is therefore concluded that the contrasting behavior of the LE and TICT fluorescence, observed upon titration of host **1** with TBA sulfate (in the 0.5−2 equiv region of Figure 5), originates from the occurrence of TBA in the 1:1 complex. The presence of lipophilic TBA as a countercation raises the microenvironmental hydrophobicity around the DMAB fluorophore, which plays dual roles of enhancing the fluorescence efficiencies of both the LE and the TICT states and of decelerating the LE-to-TICT relaxation rate. Eventually, the LE fluorescence intensity is greatly increased, while the TICT intensity does not show appreciable changes in this region as a

result of cancellation of the enhanced fluorescence efficiency by the retarded relaxation rate.

The unique complexation behavior demonstrated in this work for conjugate host **1**, which possesses a chiral bicyclic guanidinium subunit as sulfate binder and a DMAB chromophore as dual-fluorescing probe, allows us to use this chiral host not only as a versatile probe for sulfate anion by means of UV, CD, fluorescence, and NMR spectra but also as a convenient tool for elucidating the detailed complex structure, such as chiral sense, stoichiometry, and counterion participation.

Experimental Section

^{1}H and ^{13}C NMR spectra were obtained on a JEOL EX400 NMR spectrometer operating at 399.65 and 100.40 MHz, respectively. IR spectra were measured on a JEOL JIR-6000 spectrometer. Mass spectra were recorded on a JEOL D-300 spectrometer. Electronic absorption and fluorescence spectra were taken on JASCO V-560 and Hitachi F-4500 spectrophotometers, respectively. CD spectra were obtained on a JASCO J-725WI spectrometer.

Spectroscopic grade solvents from Dojindo Laboratories were used without further purification for all spectrophotometric measurements. Ethyl 4-(*N*,*N*-dimethylamino)benzoate (**5**) from Wako Pure Chemicals was purified by sublimation before use. Tetrabutylammonium sulfate from Aldrich was used as received.

Synthesis of Bicyclic Guanidinium 4-(*N*,*N*-Dimethylamino)-benzoate Chloride Monohydrate (1·H$_2$O). To a mixture of 300 mg (0.633 mmol) of monohydroxyguanidinium salt **2**,[2h] 1 mL of triethylamine, and 25 mL of dry tetrahydrofuran (THF) was added 140 mg (0.762 mmol) of 4-(*N*,*N*-dimethylamino)benzoyl chloride (**3**)[9] in one portion at room temperature under argon atmosphere. The mixture was stirred for 15 h at room temperature before another 50 mg (0.27 mmol) of **3** was added. The resulting mixture was then heated to 65 °C and stirred for 3 h at that temperature. After the mixture was cooled to room temperature, the solvent was evaporated in vacuo. The residue was diluted by chloroform and washed with water. The organic phase was separated, and the solvent was evaporated in vacuo to give 0.477 g of an oily product, which was chromatographed on silica gel (Merck #109385) with 2-propanol/chloroform (3/7) eluent and further purified by recycling GPC (JAI LC-908 equipped with JAI gel 1H and 2H, chloroform eluent) to give an oily product. The product was finally solidified by adding hexane to give 0.238 g (59%) of pure product (**1**·H$_2$O): mp 89−90.5 °C. α_D^{20} +74.5° (*c* 0.0510, dioxane). λ_{max} (CH_3CN): 313 nm (ϵ 2.88 × 10^4 M^{-1} cm^{-1}). IR (KBr): ν 1700 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.28 (s, 1H, N*H*), 9.09 (s, 1H, N*H*), 8.01 (d, 2H, J = 9.3 Hz, aminobenzoate), 7.66−7.58 (m, 4H, Ar), 7.47−7.36 (m, 6H, Ar), 6.66 (d, 2H, J = 9.3 Hz, aminobenzoate), 4.49 (dd, 1H, J = 5.9, 11.2 Hz, OCH_2), 3.86 (dd, 1H, J = 3.9, 9.8 Hz, OCH_2), 3.83−3.75 (m, 1H, OCH_2), 3.66−3.52 (m, 2H, OCH_2 + NCH), 3.39−3.30 (m, 1H, NCH_2), 3.25−3.12 (m, 3H, NCH_2), 3.03 (s, 6H, CH_3), 2.1−1.8 (m, 4H, CH_2), 1.06 (s, 9H, ^{t}Bu). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5 (s), 153.6 (s), 151.3 (s), 135.6 (d), 135.5 (d), 132.7 (s), 131.8 (d), 129.9 (d), 127.9 (d), 115.7 (s), 110.8 (d), 65.1 (t), 64.3 (t), 49.1 (d), 47.4 (d), 44.8 (t), 44.6 (t), 40.0 (q), 26.9 (q), 22.7 (t), 19.2 (s). HRMS (FAB, 3-NBA + PEG600) calcd for $C_{34}H_{45}N_4O_3Si$ [M^+ − Cl]: 585.3268. Found: 585.3275. Anal. Calcd for $C_{34}H_{45}ClN_4O_3Si$·H_2O: C, 63.88; H, 7.41; N, 8.76. Found: C, 64.26; H, 7.28; N, 9.12.

^{1}H NMR Titration of 1 by Bis(tetrabutylammonium) Sulfate. A host solution of 2.00 × 10^{-3} M concentration of **1** in CD_3CN and a guest solution of 1.20 × 10^{-2} M bis(tetrabutylammonium) sulfate in CD_3CN were prepared. Next, 0.600 mL of host solution was transferred into an NMR tube. After the NMR spectrum of host itself was measured, an aliquot of the guest solution was added to the NMR tube, and the chemical shift changes of host molecule were monitored; this procedure was repeated for each aliquot addition.

Spectral Titrations of 1 by Bis(tetrabutylammonium) Sulfate. CD and fluorescence spectral titrations were performed by the method similar to that described above for ^{1}H NMR titration, except for the concentration used. In CD titration in CH_3CN, a 4.30 × 10^{-5} M solution of **1** (3.00 mL) and a 1.29 × 10^{-3} M solution of bis(tetrabutylammonium) sulfate were used. In the fluorescence titration of **1**, a 4.07 × 10^{-5} M solution of **1** (3.00 mL) and a 2.44 × 10^{-3} M solution of bis-(tetrabutylammonium) sulfate in CH_3CN were used. The excitation wavelength was fixed at 280 nm, and fluorescence intensities of the 346 and 491 nm bands were monitored. In the fluorescence titration of **2**, a 4.07 × 10^{-5} M solution of **2** in CH_3CN (3.00 mL) and a 2.44 × 10^{-3} M solution of bis(tetrabutylammonium) sulfate in CH_3CN were used. The excitation wavelength was 280 nm, and the fluorescence intensity of the 329 nm band was monitored. In fluorescence, titration of the 1:1 complex of compound **1** and bis(tetrabutylammonium) sulfate by compound **2** was performed as follows: to a solution of **1** in CH_3CN (4.00 × 10^{-6} M, 3.00 mL) was added an equimolar amount of bis(tetrabutylammonium) sulfate (2.40 × 10^{-3} M, 5.00 μL, in CH_3CN). The mixed solution was titrated with a 2.40 × 10^{-3} M solution of **2** in CH_3CN. The excitation wavelength was 280 nm. The fluorescence intensity of the 491 nm band was monitored.

Semiempirical Molecular Orbital Calculation. PM3 semiempirical calculations were performed using CAChe MOPAC 94 (MOPAC version 94.10) software on a Power Macintosh 7300/180.[17]

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