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Cucurbit[8]uril/Cucurbit[7]uril Controlled Off/On Fluorescence of the Acridizinium and 9-Aminoacridizinium Cations in Aqueous Solution

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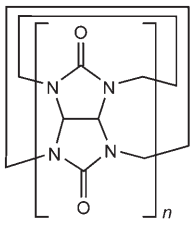
Abstract: The blue fluorescence of acridizinium bromide (ADZ^+) and the green fluorescence of 9-aminoacridizinium bromide ($AADZ^+$) in aqueous solutions can be almost entirely switched off upon the double inclusion of these guests in the cavity of cucurbit[8]uril (CB[8]) owing to the formation of a nonfluorescent, noncovalent dimer complex, and then fluorescence can be effectively restored by adding cucurbit[7]uril (CB[7]) to the complex because it competitively extracts the fluorophores out of the CB[8] cavity.

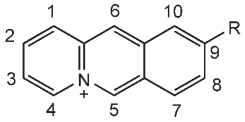
Keywords: acridizinium cations · cucurbiturils · fluorescence · host–guest systems · supramolecular chemistry

Introduction

The inclusion of fluorescent guest molecules in the cavities of nonfluorescent cyclic supramolecular hosts, such as cyclodextrins, calixarenes, and cucurbiturils, may have a pronounced effect on their emission spectra.[1] The changes observed in the energies and intensities of the fluorescence of the guest have been attributed to factors such as 1) a reduction in polarity around the guest upon going from the bulk medium (usually water) to a much less polar host cavity, 2) a reduction in the intramolecular rotational freedom of the guest within the cavity, 3) reduced exposure of the guest to adventitious or added fluorescence quenchers, and 4) regulation of excited-state acid–base reactions of fluorophores upon inclusion in host cavity.[1–4] Cucurbiturils (CB[*n*], in which *n* is most commonly 5–8), which are a family of cyclic host molecules that consist of methylene-bridged glycoluril units, have a fairly rigid hydrophobic cavity of low polarizability that may be accessed through portals that are lined with carbonyl groups.[5] Whereas CB[6] is the main product in the synthesis of CB[*n*],[6] improved methods for the preparations of CB[7] and CB[8][7] have led to extensive investigations into their host–guest behavior.[5]



n = 7 CB[7]
n = 8 CB[8]



R = H ADZ^+
R = NH_2 $AADZ^+$

CB[7] and CB[8] host molecules have the capacity to encapsulate larger molecules, such as aromatic compounds,[8] ferrocenes,[9] and platinum metal complexes,[10] or more than one guest molecule.[11–15] The confined cavities of CB[7] or CB[8] may catalyze stereoselective photodimerization reactions by orienting two aromatic molecules in close proximity.[11] CB[7] has also been shown to stabilize products and eliminate unwanted side products in photoisomerization processes.[12] Ternary 1:1:1 CB[8] complexes with π-acceptor/π-donor heteroguest pairs have been investigated as fluorescent sensors for biologically important molecules.[13–15] The fluorescence of CB[8] inclusion complexes of methylviologen,[13] 2,7-dimethyldiazapyrenium,[14] and 2,7-dimethyldiazaphenanthrenium[15] dications are suppressed upon addition

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. It includes additional UV-visible, ^1H NMR, and electrospray MS spectra; energy-minimization structural coordinates and calculations; and details on the binding constant calculations.

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of guests, such as indoles, tryptophans, catechols, or aromatic amino acids and peptides, upon the formation of the charge-transfer ternary complexes. In this paper, we report a substantial fluorescence quenching of the blue emission from the acridizinium cation (ADZ^+) and the green emission from the 9-aminoacridizinium cation ($AADZ^+$), upon their inclusion in the cavity of CB[8] as a homoguest pair.

The quenched fluorescence is recovered upon the transference of guest molecules from the 2:1 CB[8] complex to the smaller CB[7] cavity with the formation of a 1:1 guest/host complex. This is the first example of using CB[*n*] host molecules of different sizes to control fluorescence intensity as a result of the binding stoichiometries between the cyclic hosts and the fluorophore guests. Both ADZ^+ and $AADZ^+$ are dyes,[16–20] which are intensely colored and have the propensity towards efficient emission properties, whose fluorescence may be used as a probe and as an intercalating DNA-damaging chromophore.[16–18] In addition, *N*-aryl-9-amino-substituted acridizinium derivatives have been reported to act as fluorescent "light-up" probes for DNA and protein detection.[18] Another phenomenon observed for ADZ^+ and $AADZ^+$ cations was that increasing the concentrations ($>10^{-2}$ M) of these fluorophores resulted in a decrease in their fluorescence intensity (quenching) and a redshift of the emission wavelength maxima.[16] This quenching is presumably a consequence of nonfluorescent (or weakly fluorescent) excimer formation (nonfluorescent ground-state complexes) at high concentrations of the fluorophores.

Results and Discussion

The formation of 2:1 guest/host complexes between ADZ^+ or $AADZ^+$ and CB[8], and 1:1 guest/host complexes between either ADZ^+ or $AADZ^+$ and CB[7] has been confirmed by electrospray mass spectrometry (see the Supporting Information), ^{1}H NMR spectroscopy, and UV-visible absorbance (titration spectra (Figure 1) and Job plots (Figure 2)) and emission spectroscopy in aqueous solution (pH 7). Titrations of $AADZ^+$ and ADZ^+ cations with CB[7] and CB[8] result in hypsochromic shifts in the peaks below $\lambda = 300$ nm and bathochromic shifts in the weaker bands above $\lambda = 300$ nm.

The Job plots (Figure 2) for the change in the UV-visible absorption spectrum reached a maximum at a ratio of 0.33 for CB[8]/[CB[8]]+[$AADZ^+$] and a maximum at a ratio of 0.50 for CB[7]/[CB[7]]+[$AADZ^+$] ([CB[*n*]]+[$AADZ^+$] = 50 μM). These results indicate that the major species in this concentration region is a 1:2 host/guest complex between CB[8] and $AADZ^+$, and a 1:1 complex between CB[7] and $AADZ^+$. The same results were obtained for the ADZ^+ guest. In addition, electrospray mass spectra for all four complexes confirmed their formation (see the Supporting Information).

The longest wavelength band (p band, S_0–S_1 transition)[16a] for ADZ^+ is shifted (Figure 1) from $\lambda = 385$ to 404 nm upon formation of the $[CB[8]\cdot(ADZ)_2]^{2+}$ complex. No shift in this band is observed for CB[7], which suggests that the bathochromic shift is associated with the presence of two ADZ^+ guests in close proximity within the CB[8] cavity. The absorbance spectrum of the $[CB[7]\cdot AADZ]^+$ complex was measured as a function of pH between 7.1 and 0.1 (see the Supporting Information). There is no change in the spectrum upon acidification until about pH 2, however, below this value the peak intensities decrease. The data indicate a pK_a value of about one for a protonated amine on the $AADZ^+$ guest inside the cavity. The long wavelength region ($\tilde{\nu} = 350$–400 nm) for the spectrum of the protonated $AADZ^+$ guest in the CB[7] host–guest complex (pH 0) is very similar to that of the $[CB[7]\cdot ADZ]^+$ complex, which is consistent with the fact that the lone pair of electrons on the

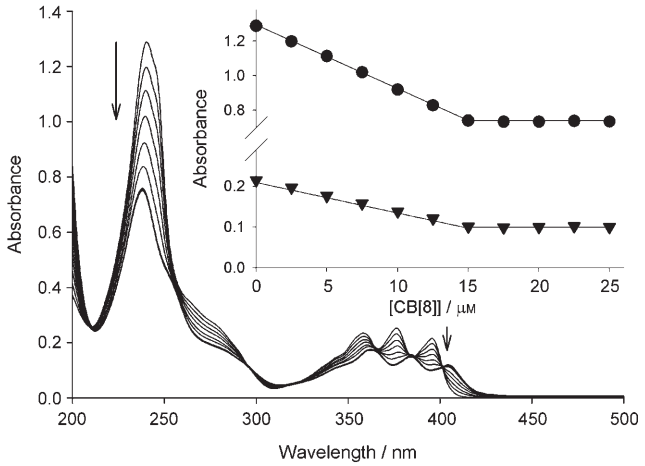

Figure 1. UV-visible titration of ADZ^+ (30 μM) with CB[8] (5 μM increments) in aqueous solution (pH 7). The inset contains plots of the absorbances at 240 nm (●) and 396 nm (▼) against the CB[8] concentration.

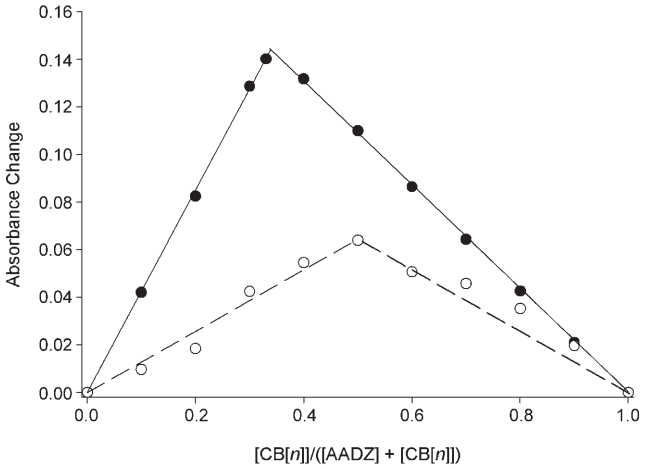

Figure 2. Job plots for the 1:1 $[CB[7]\cdot AADZ]^+$ (○) and 2:1 $[CB[8]\cdot(AADZ)_2]^{2+}$ (●) guest/host complexes from continuous variation titrations monitored at 386 nm. The absorbance change due to complex formation represents the difference between the observed absorbance (with a small correction for the CB[*n*] absorbance) and the absorbance with no CB[*n*] present (corrected for $AADZ^+$ concentration).

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amine nitrogen are no longer available for conjugation to the aromatic ring system.

The stability constants for the 1:1 $[CB[7]\cdot ADZ]^+$ and $[CB[7]\cdot AADZ]^+$ complexes were too large to be determined from UV-visible or ^1H NMR spectroscopic titrations, but could be determined from ^1H NMR competitive guest binding studies by using sodium 3-(trimethylsilyl)propionate-$[D_4]$-2,2,3,3 ($K_{CB[7]}=(1.82\pm0.22)\times10^7\,M^{-1}$) as the competing guest.[8] The values of $K_{CB[7]}$ were calculated to be $(7.11\pm0.86)\times10^8\,M^{-1}$ and $(4.24\pm0.51)\times10^8\,M^{-1}$ for the 1:1 $[CB[7]\cdot ADZ]^+$ and $[CB[7]\cdot AADZ]^+$ complexes, respectively. These stability constants are comparable to the values determined for other cationic aromatic guests,[8,21] such as 4,4′-bis(4,5-dihydro-1*H*-imidazol-2-yl)biphenyl ($K_{CB[7]}=(1.7\pm0.2)\times10^8\,M^{-1}$)[21] and 2,7-dimethyldiazapyrenium ($K_{CB[7]}=(3.81\pm0.61)\times10^7\,M^{-1}$),[8] which have been determined from competitive binding experiments. The lack of change in the absorption spectrum of $AADZ^+$ and ADZ^+ after the addition of CB[8] (0.5 equiv) indicates that the 2:1 guest/host complexes are much more stable than the 1:1 species. This stability arises from positive cooperativity in the formation of the ternary complexes.

The ^1H NMR spectra of the 2:1 guest/host complex of ADZ^+ with CB[8] and the 1:1 guest/host complex of ADZ^+ with CB[7] revealed complexation-induced upfield chemical shifts for the majority of the aromatic guest resonances that are consistent with their inclusion in the shielding hydrophobic cavity. The remainder of the resonances exhibit downfield shifts that result from the deshielding effect of the carbonyl groups of CB[*n*] on the portion of guest that is located in the portal. The complexation–decomplexation processes between ADZ^+ and both CB[7] and CB[8] occur at rates that are fast on the ^1H NMR spectroscopy timescale because there are no separate peaks for free and bound guests observed. The ^1H NMR spectra of $AADZ^+$ complexes with CB[7] and CB[8] also support the formation of 1:1 and 2:1 guest/host complexes, respectively, with guest exchange rates that are slow on the NMR timescale. For $[CB[8]\cdot(AADZ)_2]^{2+}$, the guests exhibit two sets of proton resonances owing to the presence of two isomers, anti-*trans* and anti-*cis*, in a 5:4 ratio (Figure 3). Both orientations would presumably also be present in the $[CB[8]\cdot(ADZ)_2]^{2+}$ complex, however, owing to fast exchange of the guests, only an average chemical shift for each orientation is observed for each proton resonance. The relative energies of the gas-phase structures of the two $[CB[8]\cdot(Guest)_2]^{2+}$ isomers determined from ab initio calculations[22] (Figure 3) support the preference (by 6.3 kJ mol^{-1} for $AADZ^+$ and 0.4 kJ mol^{-1} for ADZ^+) for the anti-*trans* configuration.

The 2:1 complex in CB[8] is facilitated by π–π stacking of the acridizinium rings (Figure 3). The slower exchange and the greater 1:1 stability constant for the $AADZ^+$ guest compared with ADZ^+ may be related to the amino group in the 9-position. Hydrogen-bonding interactions between the amine hydrogen atoms of $AADZ^+$ and the carbonyl oxygen atoms in the CB[*n*] portals would enhance binding of this guest to the cavity. Whereas transitions in the absorption

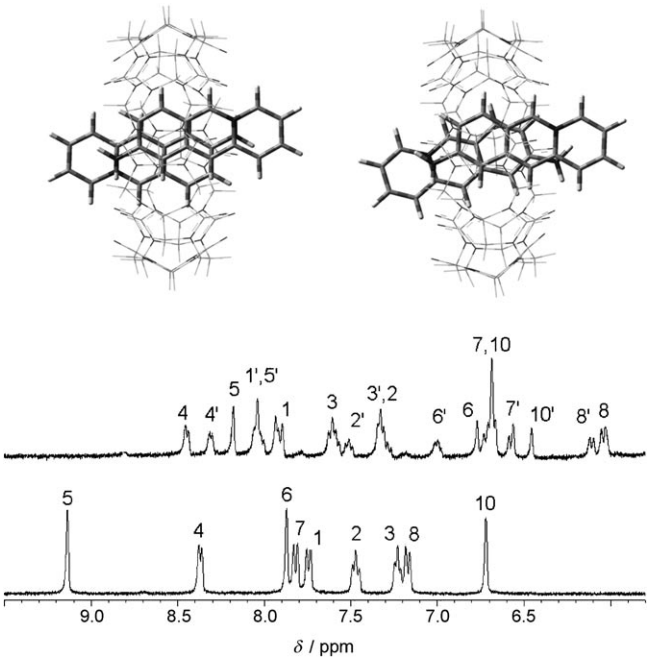

Figure 3. The energy-minimized calculated structures (HF/3-21G**)[22] of $[CB[8]\cdot(AADZ)_2]^{2+}$ and the ^1H NMR spectra (400 MHz) of $AADZ^+$ in the absence (lower) and presence (upper) of CB[8] (0.5 equiv). The upper spectrum contains a 5:4 mixture of the anti-*trans* (left structure) and anti-*cis* (right structure, primed labels) orientations of the two guests in the $[CB[8]\cdot(AADZ)_2]^{2+}$ complex.

spectra undergo modest bathochromic shifts as a result of solvatochromism[16] and modest absorbance decreases owing to inclusion (Figure 2), fluorescence quenching of the blue and green fluorophores by CB[8] and its subsequent restoration by CB[7] (Figure 4) can be readily observed by the naked eye and are clearly illustrated in the emission spectra.

The fluorescence of ADZ^+ and $AADZ^+$ is significantly quenched ($F_0/F_{complex}=20$ and 40 for ADZ^+ and $AADZ^+$,

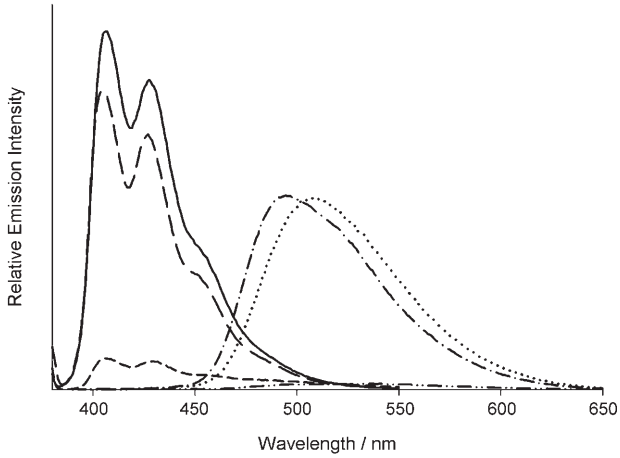

Figure 4. Fluorescence spectra in aqueous solution (pH 7) for free ADZ^+ (——) and $AADZ^+$ (•••••), $[CB[8]\cdot(ADZ)_2]^{2+}$ (-----) and $[CB[8]\cdot(AADZ)_2]^{2+}$ (••–••) after addition of CB[8] (1.0 equiv) and $[CB[7]\cdot ADZ]^+$ (1.0 equiv; – – –), and $[CB[7]\cdot AADZ]^+$ (–•–•) after subsequent addition of CB[7] (1.2 equiv).

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respectively), which arises from the formation of a nonfluorescent ground-state dimer upon complexation with CB[8], as seen in Figure 5 for $AADZ^+$ encapsulation. The quenched fluorescence can be effectively restored upon the

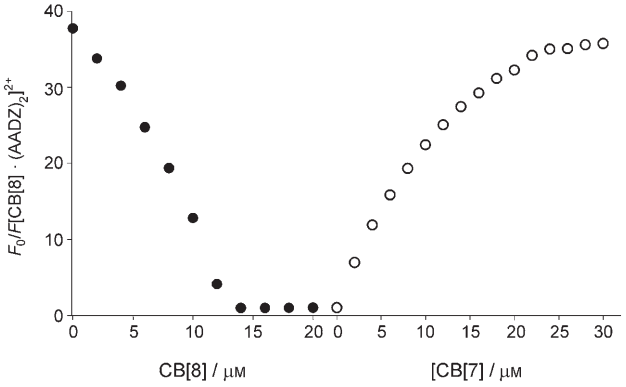

Figure 5. Fluorescence titration of $AADZ^+$ (25 μM) with CB[8] (●) followed by the addition of CB[7] (○), which was monitored at 508 nm (pH 7).

addition of CB[7] (1.0 equiv) to the solution because the dissociated dimer is extracted into the cavity of CB[7] as a fluorescent monomer when it is released from the cavity of CB[8].

The emission band of the $[CB[7]\cdot AADZ]^+$ species (Figure 4) exhibits a hypsochromic shift to $\lambda = 495$ nm from that of free $AADZ^+$ at $\lambda = 507$ nm. Whereas bathochromic shifts have previously been observed for $AADZ^+$ emission in most organic solvents ($\tilde{\nu} = 508$–516 nm),[16] the emission maximum for $AADZ^+$ in CH_3CN and CH_3COOH were at $\tilde{\nu} = 501$ and 497 nm, respectively. For ADZ^+, there is no change in the emission maxima between the free guest and $[CB[7]\cdot ADZ]^+$. This suggests that the hypsochromic shift observed for $[CB[7]\cdot AADZ]^+$ is related to an interaction between the amino group and the carbonyl portal on CB[7] or the binding pocket of the host. The polarity of the CB[7] cavity resembles that of acetic acid ($E_T(30) = 51.7$ kcal mol^{-1}[23]), and is comparable to that of ethanol[2e] ($E_T(30) = 51.9$ kcal mol^{-1}[23]) or 1-octanol[4c] ($E_T(30) = 48.3$ kcal mol^{-1}[23]); these three solvents have similar $E_T(30)$ values and are consistent with the nature of CB[7]. CB[7] has both a hydrophobic cavity and polar portals, which result in several specific and nonspecific noncovalent interactions that contribute to the shift in the emission spectrum. The emission spectrum of $[CB[7]\cdot ADZ]^+$ was also measured as a function of pH (see the Supporting Information), and no change was observed upon acidification from pH 7 to below pH 1, which indicated that the observed emission was not from the excited state of the protonated ammonium, but rather from the amine monocation bound in the cavity.

When two molecules are encapsulated in the cavity of CB[8], the concentration of the fluorophore is increased to >1 M in the microenvironment (based on two guests confined within the CB[8] cavity (479 $Å^3$)[5d]). The nonfluorescent complex (a noncovalent dimer in the cavity), which was previously observed in solution at high concentrations ($>10^{-2}$ M)[16a] is therefore assisted by CB[8] to form at low concentrations of the fluorophores in aqueous solutions. The sigmoidal shape of the plot showing the change in $AADZ^+$ emission with increasing CB[8] concentration is consistent with positive cooperativity[24] for the formation of the 1:2 host/guest complex, which proceeds via the 1:1 species that has a greatly reduced binding constant, both of which can affect the emission intensity compared with the free $AADZ^+$ (as seen with the 1:1 complex with CB[7]). Assuming that these two features occur, the ternary binding constant for the 1:2 host/guest complex is calculated to be $(4\pm 2)\times 10^9\,M^{-2}$ from emission data recorded at low CB[8] concentrations.[23] Urbach has reported values in the range of 10^9–$10^{11}\,M^{-2}$ for binding two tripeptides in CB with positive cooperativity.[8,13] Kuz'mina et al.[12b] have reported overall ternary binding constants of $4\times 10^7\,M^{-2}$ for the binding of two guests with CB[8]; however, the binding constant for the 1:1 host/guest complex is larger ($4\times 10^4\,M^{-1}$) than that for the 1:2 host/guest complex ($1\times 10^3\,M^{-1}$).

The possibility that fluorescence quenching in the CB[8] cavity could be a result of permanent damage to the fluorophore, for example, a photoreaction, such as photodimerization,[16,19] may be excluded owing to the almost complete and instantaneous restoration of fluorescence upon addition of CB[7] (1.0 equiv) to solutions of the 1:2 host/guest complexes (Figures 4 and 5) because such a photoreaction would be expected to take much longer in both solution and the solid state.[16,19] In addition to restoring the fluorescence of the guest dye cations by adding CB[7] to the 2:1 dye/CB[8] complex, it should be possible to add a competing guest molecule(s) to displace ADZ^+ or $AADZ^+$. This hypothesis may tested by adding a guest that has a high and selective affinity for CB[8]. We have recently found that the dication of 1,3-bis(4,5-dihydro-1*H*-imidazol-2-yl)adamantane dihydrochloride ($BIAD^{2+}$) binds strongly to CB[8], but much more weakly and through external binding to CB[7].[21] Other dicationic 1,3-disubstituted adamantanes are also reported to have considerably higher stability constants when complexed with CB[8] ($K_{CB[8]} \approx 10^{11}\,M^{-1}$) compared with CB[7] complexes ($K_{CB[8]} \approx 10^4\,M^{-1}$).[8] The addition of $BIAD^{2+}$ to $[CB[8]\cdot(ADZ)_2]^{2+}$ (Figure 6) or $[CB[8]\cdot(AADZ)_2]^{2+}$ results in the restoration of the fluorescence of the liberated dye molecules. Therefore, $[CB[8]\cdot(AADZ)_2]^{2+}$-type guest/host complexes may act as fluorescence "light-up" probes.[18] Studies with biologically relevant competing guests are in progress.

Conclusion

The fluorescence of acridizinium and 9-aminoacridizinium cations may be turned off and on by the sequential additions of CB[8] and CB[7], respectively, in aqueous solutions. The formation of fluorescent 1:1 CB[7]/acridizinium and nonfluorescent 1:2 CB[8]/acridizinium host–guest complexes are supported by ^1H NMR and UV-visible absorbance and emis-

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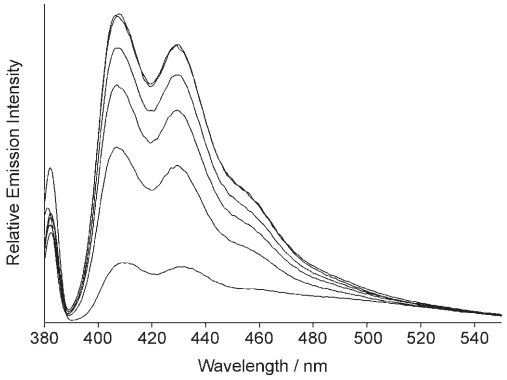

Figure 6. Fluorescence titration of $[CB[8]\cdot(ADZ)_2]^{2+}$ (12.5 μM) with, from bottom to top, 1.0, 2.0, 4.0, 6.0, and 8.0 equivalents of $BIAD^{2+}$ in aqueous solution (pH 7).

sion spectroscopies, and electrospray mass spectrometry measurements. The fluorescence behavior of the CB[*n*] complexes reported herein could have applications as supramolecular fluorescent switches and sensors, such as light-up probes and other photonic devices.

Experimental Section

Materials: CB[7] was prepared and characterized as reported by Day et al.[7b] CB[8] was used as received (Aldrich). ADZ^+ and $AADZ^+$ were prepared and characterized as described previously.[16a,25] Sodium 3-(trimethylsilyl)propionate-[D_4]-2,2,3,3 and D_2O (Aldrich) were used as received. 1,3-Bis(4,5-dihydro-1*H*-imidazol-2-yl)adamantane dihydrochloride $BIAD^{2+}$ was prepared as described previously.[21]

Methods: NMR spectra were recorded by using Bruker Avance 400 and 500 MHz instruments by using D_2O as the solvent. UV-visible spectra were recorded by using a Hewlett Packard HP8452A diode array spectrometer. Fluorescence spectra were recorded by using a Proton Technologies International QuantaMaster C-60 spectrometer. Electrospray mass spectra were recorded by using an Applied Biosystems/MDS Sciex QSTAR XL instrument. The ternary $K_{CB[8]}$ binding constant for the 2:1 guest/host complex $[CB[8]\cdot(AADZ)_2]^{2+}$ was determined from the results of a fluorescence spectrophotometric titration experiment, as shown in Figure 5, which assumes that binding of the first $AADZ^+$ guest is much weaker than binding of the second $AADZ^+$ guest and that the fluorescence emission spectra of unbound $AADZ^+$ ($AADZ^+_{free}$ and that of the $[CB[8]\cdot AADZ]^+$ complex are similar (as observed with CB[7]). The value of $K_{CB[8]}$ was calculated from $K_{CB[8]}=\frac{[[CB[8]\cdot(AADZ)_2]^{2+}]}{[CB[8]]_{free}[AADZ^+]^2_{free}}$ (in which $[CB[8]]_{free}=[CB[8]]_{total}-[[CB[8]\cdot(AADZ)_2]^{2+}]$ and $[AADZ^+]_{free}=[AADZ^+]_{total}-2[[CB[8]\cdot(AADZ)_2]^{2+}]$) by using the emission intensities at $\tilde{\nu}=508$ nm at low CB[8] concentrations ($<5\times10^{-6}$ M). The $K_{CB[7]}$ binding constants for $[CB[7]\cdot AADZ]^+$ and $[CB[7]\cdot ADZ]^+$ were determined from ^1H NMR competitive binding experiments in neutral D_2O by using sodium 3-(trimethylsilyl)propionate-[D_4]-2,2,3,3 as the competitor for both ADZ^+ and $AADZ^+$ with a limiting amount of CB[7]. The binding constants were calculated by using the method described previously.[8] The structures of the host–guest complexes in this study were calculated by energy minimizations by using Gausssian 03,[22] and run on the computing facilities of the High Performance Virtual Computing Laboratory (HPVCL) at Queen's University. The structures of the complexes were originally constructed by using ChemDraw and Chem3D (ChemOffice 7.0, CambridgeSoft) programs and imported into Gaussian 03. The basis set used for the calculations was HF/3-21G**.

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