A green to blue fluorescence switch of protonated 2-aminoanthracene upon inclusion in cucurbit[7]uril†

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The inclusion of protonated 2-aminoanthracene in the cavity of cucurbit[7]uril increases its pK_a values in the ground and excited states, resulting in the disappearance of the green emission of the neutral excited state and the significant enhancement of the blue emissions from the protonated excited state guest.

The inclusion of fluorescent guest molecules in the cavities of nonfluorescent cyclic supramolecular hosts, such as cyclodextrins, calixarenes, and cucurbiturils, can have a pronounced effect on their emission spectra. The changes observed in the energies and intensities of the fluorescence of the guest have been attributed to factors such as (a) a reduction in the polarity around the guest upon going from the bulk medium (usually water) to a much less polar host cavity, (b) a reduction in the guest's intramolecular rotational mobility within the cavity, and/or (c) a reduced exposure of the guest to adventitious or added quenchers.[1] Wagner *et al.*[2] and others[3] have reported the effects on the emission spectra of several fluorescent dye molecules upon inclusion in cyclic cucurbituril (CB) hosts in aqueous solution. In the case of 2-anilinonaphthalene-6-sulfonic acid, for example, a 25-fold increase in emission was observed in a 1 : 1 guest–host complex with cucurbit[7]uril (CB[7]). These fluorescence enhancements of the emission bands were attributed to the inclusion of the molecules in the CB[7] cavity, and the resulting decrease in the intramolecular rotational freedom of the guest molecule and in the polarity of host cavity environment.

In this communication, we report the effects of the inclusion of protonated 2-aminoanthracene (2-AAH$^+$) in the cavity of cucurbit[7]uril on the guest's fluorescence spectrum in acidic aqueous solution (pH 1.5), and propose a different explanation for the observed simultaneous inclusion-induced fluorescence enhancements and reductions. With this particular guest–host system, inclusion of the guest significantly reduces its acidity in the ground and excited states and results in the observed changes in the absorption and emission spectra. While the bands in the absorption spectrum undergo modest bathochromic shifts as the result of solvatochromism, the fluorescence spectrum undergoes more profound emission changes from green to blue, arising from the stabilization of the protonated guest in the excited state (blue emission) with respect to the neutral form of the guest (green emission).

The cucurbiturils (CB[*n*], *n* is most commonly 5–8), a family of cyclic host molecules consisting of methylene bridged glycoluril units,[4] have a fairly rigid hydrophobic cavity of low polarizability[3] which may be accessed through carbonyl lined portals. The improved syntheses[5] and superior solubility of CB[7] in aqueous solution have prompted investigations into guest–host behaviour in this solvent with a variety of cationic hydrophobic guest molecules, such as viologens,[6] N-alkylated pyridines and bipyridines,[7] *cis*-diaminostilbenes,[8] metallocenium cations,[9,10] and polyaromatic cations such as 2,7-dimethyldiazapyrenium.[11] As with β-cyclodextrin, the cavity of CB[7] can accommodate aromatic molecules, with a portal diameter of 5.4 Å and an internal cavity diameter of 7.3 Å.[4]

The formation of a 1 : 1 guest–host complex between protonated 2-aminoanthracene and CB[7] has been confirmed by electrospray mass spectrometry, ^{1}H NMR spectroscopy, and UV-visible absorbance and emission spectroscopy (Job's plot). The ^{1}H NMR spectrum of the 1 : 1 guest–host complex of the 2-AAH$^+$ with CB[7] (Fig. 1) reveals complexation-induced upfield chemical shifts (0.2 to 1.1 ppm) for the majority of the aromatic guest resonances, consistent with their inclusion in the deshielding hydrophobic cavity. The H5 and H8 protons exhibit slight downfield shifts as they are located in line with the carbonyl groups of the portals, which have been observed to deshield guest protons.[4] The appearances of separate proton resonances for the

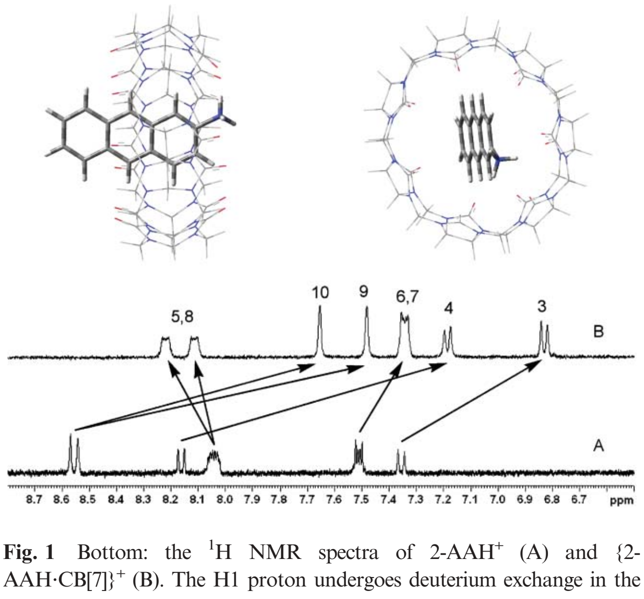

Fig. 1 Bottom: the ^{1}H NMR spectra of 2-AAH$^+$ (A) and {2-AAH·CB[7]}$^+$ (B). The H1 proton undergoes deuterium exchange in the D_2O solvent and is not observed. Top: two views of the energy-minimized structure of {2-AAH·CB[7]}$^+$.

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free and included guest and host molecules indicates that complexation–decomplexation processes between 2-AAH$^+$ and CB[7] occur at rates which are slow on the ^{1}H NMR timescale.

The effect of inclusion is also seen in the proton resonances for the methylene groups which bridge the glycoluril units in CB[7]. Upon complexation by an asymmetric 2-AAH$^+$ guest, the symmetry-related methylene doublet resonances at 5.64 (protons pointing towards the carbonyl oxygens) and 4.13 ppm are split into pairs of doublets (5.60/5.43 and 4.04/3.93 ppm). This inclusion induced asymmetry generated in the portals of the CB[7] cavity, reminiscent (in the opposite sense) of the splitting of the ^{1}H NMR resonances for symmetry-related protons of symmetrical guests included in the asymmetric cyclodextrin cavities,[12] was also recently reported for the inclusion of cationic substituted ferrocenes in the CB[7] cavity.[10] An energy-minimized structure[13] of the $\{$2-AAH·CB[7]$\}^{2+}$ complex from *ab initio* (HF/3-21G** basis set) calculations is consistent with the NMR results, with two of the three aromatic rings within the CB[7] cavity. The interaction of the ammonium group with the portal oxygens on CB[7] evidently stabilizes the protonated aromatic amine molecule, resulting in alterations in the energies of the excited states.

The UV-visible absorbance spectrum of 2-AAH$^+$ exhibits bathochromic shifts in the transitions in the presence of CB[7], as shown in Fig. 2, consistent with the solvatochromic behaviour reported previously.[14] A spectrophotometric titration of 2-AAH$^+$ with CB[7] provided a stability constant of $(8 \pm 2) \times 10^5$ dm^3 mol^{-1} (Fig. 3) which is similar to the values reported for the inclusion of other cationic aromatic molecules,[6–9,11] such as methylviologen ($K = 2 \times 10^5$ dm^3 mol^{-1})[6] in CB[7].

Protonated 2-aminoanthracene is well-known to exhibit dual fluorescent behaviour in aqueous solution when the pH is lower than its ground state pK_a and higher than its singlet excited state pK_a*,[14–16] with blue emission (422, 405, and 387 nm) from 2-AAH^{+}* and green emission (503 nm) from 2-AA*. The pK_a of the ground state 2-AAH$^+$ species has been determined to be 4.0 in water,[15] while the pK_a* values for the triplet and singlet excited states have been measured at 3.3 and −5.4, respectively in 1 : 1 water : alcohol.[14,16] As a result of the very low pK_a* of 2-AAH^{+*}, the major emission is always green in acidic aqueous solution because the 2-AAH^{+}* is instantaneously deprotonated to 2-AA* which returns to the ground state 2-AA species before reprotonation.[17,18]

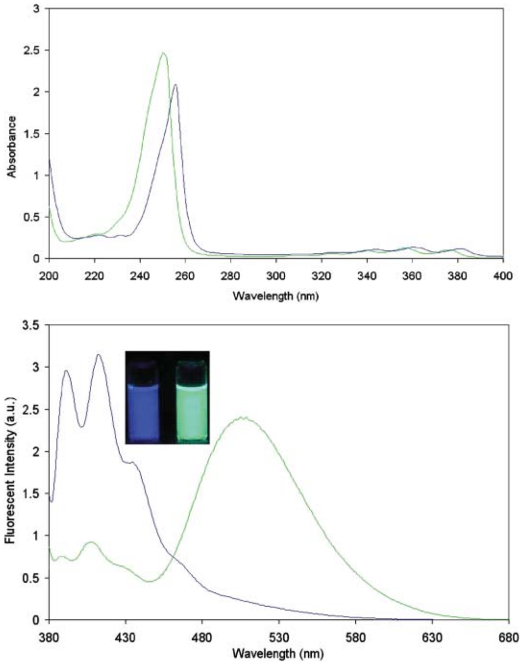

Fig. 2 The UV-visible absorption (top) and emission (bottom, excitation at 342 nm) spectra of 2-AAH$^+$ (5.0×10^{-5} mol dm^{-3}) in the absence (green lines) and presence (blue lines) of CB[7] (1.0×10^{-4} mol dm^{-3}) in acidic aqueous solution (pH 1.5).

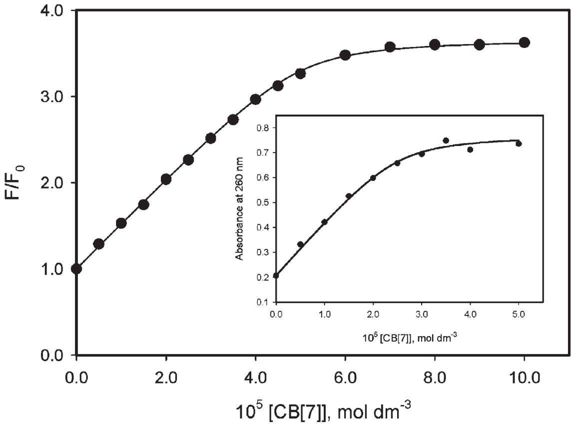

Fig. 3 The dependence of the fluorescence intensity [(F/F_0) (2-AAH$^+$) = 5.0×10^{-5} mol dm^{-3}] at 412 nm and (inset) the absorbance (2-AAH$^+$ = 2.5×10^{-5} mol dm^{-3}) at 260 nm of 2-AAH$^+$ on the concentration of CB[7] in acidic aqueous solution. The solid lines are fit with a stability constant for $\{$2-AAH·CB[7]$\}^{2+}$ of 8×10^5 dm^3 mol^{-1}.

In the presence of CB[7] we observe a switch in the fluorescence of 2-AAH$^+$ from green to blue (Fig. 2), which we attribute to a dramatic decrease in the acidity of the excited state of 2-AAH^{+*} once encapsulated in the cavity of CB[7]. Fig. 2 shows the changes in the emission spectrum of 2-aminoanthracene upon inclusion in CB[7]. Both the disappearance of the green emission band (to about 10% of its original intensity at 512 nm) and a significant enhancement (about four-fold increase in the band at 406 nm) of the second, higher energy blue emission band are observed for the $\{$2-AAH·CB[7]$\}^+$ complex. No change in the fluorescence is observed in the same experiment with up to a 10-fold excess of β-cyclodextrin. The change in the fluorescence intensity at 412 nm was used to determine the stability constant of the 1 : 1 $\{$2-AAH·CB[7]$\}^+$ complex. The stability constant was determined to be $(8 \pm 1) \times 10^5$ dm^3 mol^{-1}, with a fluorescence enhancement of $F_\infty/F_0 = 3.68 \pm 0.02$ (Fig. 3).

The interaction of the ammonium group with the portal oxygens on CB[7] evidently changes its acidity in both the ground and excited states. For the $\{$2-AAH·CB[7]$\}^+$ complex, the ground state pK_a value increases to 7.1 ± 0.2, as determined from the pH titration measurements. Marquez and Nau had previously reported that CB[6] inclusion of cycloalkylmethylamines increases the pK_a of the protonated ammonium guests by over one pK_a unit.[19] The singlet excited state pK_a* value increases substantially in the $\{$2-AAH·CB[7]$\}^+$ guest–host complex. A value of 2.0 has been estimated from the use of Förster's cycle calculations,[20] while a value of 5.2 ± 0.2 was determined from the fluorescence titration. The discrepancy between the two values is in the range commonly observed for aromatic amines, and has been attributed

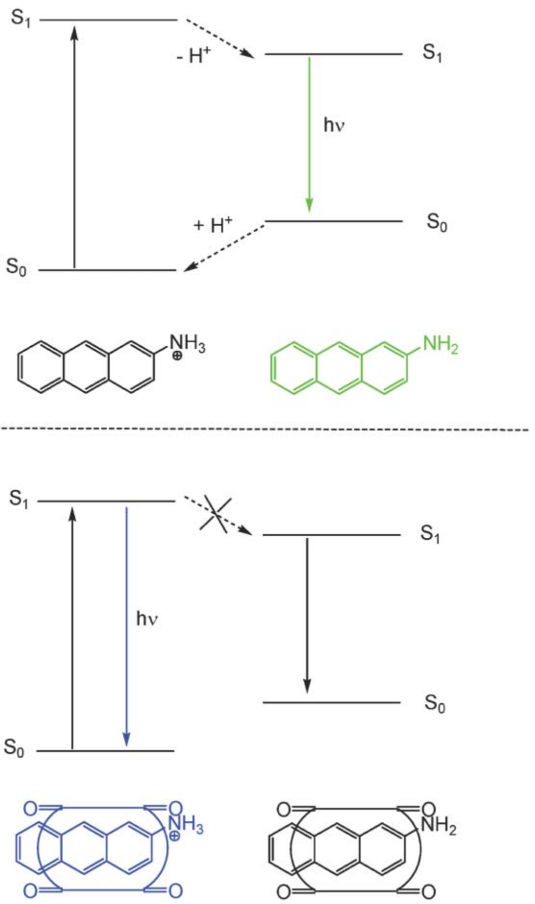

Fig. 4 Schematic representation of the excitation and emission of 2-AAH$^+$ with and without CB[7] in acidic aqueous solution. The acidity of the excited state of 2-AAH$^+$ (pK_a* = -3.5 ± 1) decreases considerably within the {2-AAH·CB[7]}$^+$ complex (pK_a* = 5.2 ± 0.2) such that the blue emission dominates (pH < 5.0).

to a number of factors, including assumptions made in the use of the Förster's cycle.[20] Applying a method reported for correcting the Förster pK_a* value for aromatic amines gives a pK_a* value of about 4.7,[21,22] in good agreement with the fluorescence titration value.

As a result of the increased basicity of the included 2-aminoanthracene in the excited state, emission from the S_1 state of the 2-AAH^{+}* now occurs prior to deprotonation to 2-AA* in acidic solution. This shuts off the pathway for the green emission, and enhances the blue emission from the included 2-AAH^{+}* species (Fig. 4).

The phenomenon reported here could have applications in photonic devices, ratiometric fluorescent pH probes, and sensors for polyaromatic amines and other cationic aromatic molecules. We are currently extending this study to other polyaromatic amines, such as 1-aminoanthracene, 1- and 2-aminonaphthalenes, and 1-aminopyrene, all of which bind to the cucurbit[7]uril host molecule in acidic aqueous solution and show similar, but less dramatic, changes in fluorescence behaviour.

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