SPECTRAL AND PHOTOPROTOTROPIC CHARACTERISTICS OF 4-AMINOBIPHENYL IN β-CYCLODEXTRIN

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The photophysical and photoprototropic behaviour of 4-aminobiphenyl (4ABP) in aqueous β-cyclodextrin (β-CDx) solution has been investigated using steady-state and time-resolved fluorescence spectroscopy. Fluorescence of the neutral form of 4ABP is enhanced due to the formation of a 1:1 complex with β-CDx. The formation of this complex has been confirmed by time-resolved spectroscopy. In the presence of β-CDx, no change was observed in the ground state pK_a value but the excited state pK_a value changed. Based on its photophysical and photoprototropic characteristics in β-CDx, the structure of the 1:1 inclusion complex is proposed.

Keywords: Inclusion complexes; Biaryls; Cyclodextrins; Photoprototropism; Excited-state acidity constant; Fluorescence spectroscopy.

Host–guest chemistry, i.e. the chemistry of two or more species assembled together without a covalent bond, is the basis for a new type of photoresponse where photochemistry and photophysics of the guest are modified and made unique[1–4]. Cyclodextrins (CDx) are cyclic oligosaccharides that have a central hydrophobic cavity capable of forming host–guest complexes in aqueous solution by accommodating the guest molecule. The size of the hydrophobic cavity depends on the number of glucopyranose units present in cyclodextrins. For example, α-, β- and γ-CDx are oligosaccharides containing six, seven and eight units of glucopyranose units, respectively[5,6]. Thus, CDx can accommodate a wide range of guest molecules, depending on their size, shape and hydrophobic character[7–9]. Further, given by the size of the guest molecules, different guest:CDx ratios (1:1 or 1:2) are observed that can change the photophysical and photochemical properties of hydrophobic organic molecules in aqueous solution. It is now well established that electronic absorption, fluorescence, phosphorescence and H^1 NMR spectra, acid-base characteristics and excited-state proton transfer of these guest molecules are varied upon the formation of the inclusion complex

with CDx [10–25]. Although some work was carried out on the ground-state acid-base characteristics[14,26–31], similar acid-base studies on the excited singlet state are very scarce.

In our laboratory, we have investigated the excited-state acid-base characteristics of amino- and hydroxy-substituted biphenyls[32–38], diphenyl sulfones[39,40], diphenylamines[41,42], diphenyl ethers[43,44] and diphenylmethane[45] in aqueous solution.

Recently we have reported an unusual fluorescence charateristics of aminobiphenyls in aqueous solution[46]. The present work deals with the spectral and photoprototropic characteristics of 4-aminobiphenyl in the presence of β-cyclodextrin.

EXPERIMENTAL

Materials and Methods

4-Aminobiphenyl was obtained from Aldrich and purified by recrystallisation from aqueous ethanol. The purity was checked by its sharp melting point and similar fluorescence spectra at different excitation wavelengths. β-Cyclodextrin was purchased from S.D. Fine Chemicals and used as received. Triply distilled water was used for the preparation of experimental solutions. A modified Hammett acidity scale (H_0)[47] was employed for the solutions below pH 1.5 (using a H_2SO_4–H_2O mixture). The concentration of the solutions was 2.7×10^{-4} mol dm^{-3}. To measure the fluorescence intensities for fluorimetric titration, the isosbestic wavelength was used for excitation.

Electronic absorption spectra were recorded with a JASCO UNIDEC-650 spectrophotometer, and the fluorescence with a JASCO FP-550 spectrofluorimeter. pH values in the range 1–12 were measured using an ELICO LI-1OT model pH-meter. Fluorescence lifetimes were determined with a time-correlated single-photon counting picosecond spectrofluorimeter (Tsunami, Spectra Physics).

RESULTS AND DISCUSSION

Spectral Characteristics

The UV absorption and fluorescence maxima of 4ABP at different concentrations of β-CDx are given in Table I.

There is no significant change in the absorption spectra of 4ABP. A small red shift with a decrease in the absorption intensity has been observed. This may be due to the formation of an inclusion complex between 4ABP and β-CDx. The change is too small to allow the determination of the binding constant.

The fluorescence spectra of 4ABP at different β-CDx concentrations are displayed in Fig. 1. The effect of β-CDx on the fluorescence spectra of 4ABP is more pronounced than the corresponding effect on the absorption spectra. Two main effects are observed, a blue shift and an increase in the fluorescence intensity on the addition of β-CDx up to a concentration of 2×10^{-3} mol dm^{-3}. Figure 2 shows the intensity increase at 381 nm accompanying the addition of β-CDx. The fluorescence intensity is 1.6 times larger in 2×10^{-3} mol dm^{-3} β-CDx than in the aqueous solution. The blue shift of

TABLE I
Absorption and fluorescence maxima[a] of 4ABP at different concentrations of β-CDx

c(β-CDx), mol dm^{-3}	λ_{abs}, nm (log ε)	λ_{em}, nm
0	273 (3.2425)	381
4×10^{-4}	273 (3.2342)	377
8×10^{-4}	273.4 (3.2285)	374
1.6×10^{-3}	273.4 (3.2208)	373
2×10^{-3}	273.8 (3.2179)	373
2.4×10^{-3}	273.8 (3.2120)	373

[a] λ_{exc} = 280 nm.

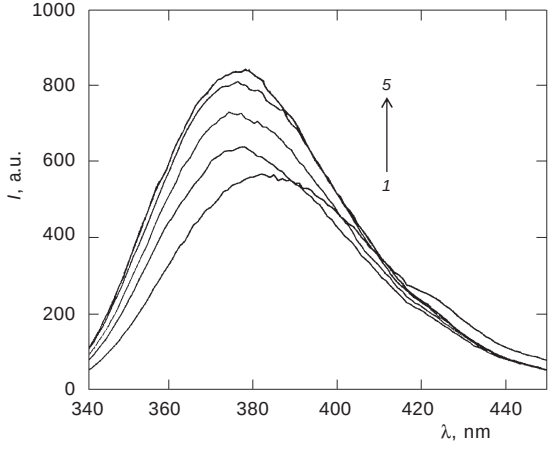

FIG. 1
Fluorescence spectra of 4ABP at various concentrations of β-CDx (in mol dm^{-3}): *1* 0, *2* 4×10^{-4}, *3* 8×10^{-4}, *4* 1.6×10^{-3}, *5* 2×10^{-3}

the fluorescence maximum and the enhancement of the fluorescence intensity suggest the formation of an inclusion complex between 4ABP and β-CDx. An increase in the fluorescence intensity for the formation of an inclusion complex was observed earlier[48–52]. The blue shift also reveals that 4ABP is included in the non-polar part of β-CDx. The complexation is complete at 2×10^{-3} mol dm^{-3} β-CDx and there is no change in the fluorescence by further addition of β-CDx. Although the fluorescence maximum is blue-shifted (8 nm), it is not close to the value in methanol (367.3 nm) or glycerol (365.5 nm)[46]. This comparison shows that there is no interaction of amino and OH groups of β-CDx in the inclusion complex formed. The formation of the inclusion complex is also confirmed by the fluorescence decay curves for 4ABP at different concentrations of β-CDx. The lifetimes and the amplitudes of the decay curves of 4ABP with and without β-CDx are given in Table II.

The fluorescence of 4ABP with added β-CDx shows a biexponential decay, indicating an equilibrium between the free and complexed forms. The lifetime of the complexed form is longer and its amplitude increases with increasing concentration of β-CDx up to 2×10^{-3} mol dm^{-3}. Above this concentration, no change in lifetimes and amplitudes of both forms is observed. The χ^2 values for the single and double exponential fittings were less than 1.2.

The β-CDx dependence of 4ABP fluorescence can be analysed by the Benesi–Hildebrand plot as given by Eq. (*1*)[53–55]

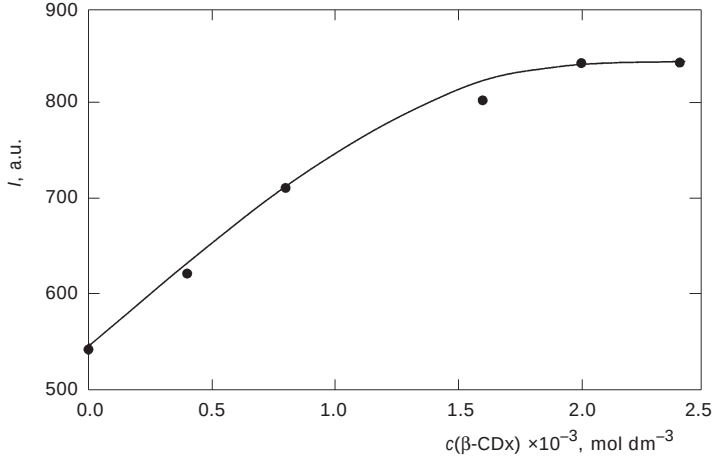

FIG. 2
Fluorescence of 4ABP at 381 nm: changes in intensity at different concentrations of β-CDx

$$\frac{1}{I - I_0} = \frac{1}{I' - I_0} + \frac{1}{K(I' - I_0)[\beta - \mathrm{CDx}]}, \qquad (1)$$

where K is the binding constant, I_0 is the intensity of fluorescence of 4ABP without β-CDx, I with a certain concentration of β-CDx, and I' is the fluorescence intensity of 4ABP with the highest concentration of β-CDx. Figure 3 shows the plot of $1/I - I_0$ vs 1/[β-CDx]. The linearity in the plot reflects the

TABLE II
Fluorescence lifetimes (τ) of the free and β-CDx-complexed forms of 4ABP and their amplitudes[a]

c(β-CDx), mol dm^{-3}	τ, s	Standard deviation, s	Relative amplitude
0	2.5×10^{-9}	5.3×10^{-12}	100
8×10^{-4}	2.2×10^{-9}	6.4×10^{-11}	33.43
	5.1×10^{-9}	3.7×10^{-11}	66.57
1.2×10^{-3}	2.3×10^{-9}	1.1×10^{-10}	19.87
	5.5×10^{-9}	3.0×10^{-11}	80.13
1.6×10^{-3}	2.1×10^{-9}	1.0×10^{-10}	16.01
	5.5×10^{-9}	2.4×10^{-11}	83.99
2×10^{-3}	2.1×10^{-9}	1.0×10^{-10}	14.22
	5.5×10^{-9}	2.4×10^{-11}	85.78
2.4×10^{-3}	2.1×10^{-9}	1.0×10^{-10}	14.22
	5.5×10^{-9}	2.4×10^{-11}	85.78

[a] λ = 280 nm; detection at 380 nm.

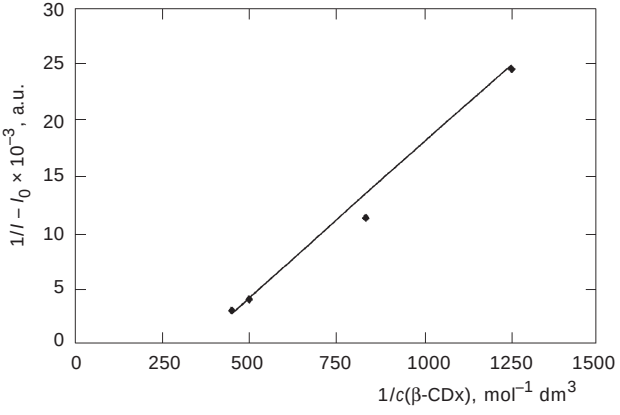

FIG. 3
Benesi–Hildebrand plot for the complexation of 4ABP with β-CDx

formation of a 1:1 complex between 4ABP and β-CDx. From the slope and intercept of the straight line, the binding constant K was calculated to be 2.97×10^2 dm^3 mol^{-1}. The double reciprocal Benesi–Hildebrand fit is obtained only when the complexation is complete. Although the binding constant K is obtained from fluorescence data, it only represents the ground-state equilibrium, as the lifetimes of both forms are shorter. Because of the shorter singlet lifetimes, the ground-state equilibrium remains unchanged in the excited state.

Photoprototropism

The absorption and fluorescence spectra of 4ABP with added 2.4×10^{-3} mol dm^{-3} β-CDx have been investigated in the H_0/pH range –5 to 12. UV-VIS absorption spectra at different pH are shown in Fig. 4. With decreasing pH from 7, the absorption maximum of 4ABP is blue-shifted. The blue-shifted maximum (248 nm) is close to that of biphenyl and, hence, this absorption spectrum corresponds to the formation of the monocation. No change in the absorption spectrum occurs below pH 1 and also in the pH range 7–12. A clear isosbestic point is observed at 260 nm. In the pH range 1–7, the absorption spectra of 4ABP in β-CDx are found to resemble those of the aqueous solution[46]. This again confirms that there is no interaction between the amino group of the 4ABP molecule and the OH groups of β-CDx in the complex.

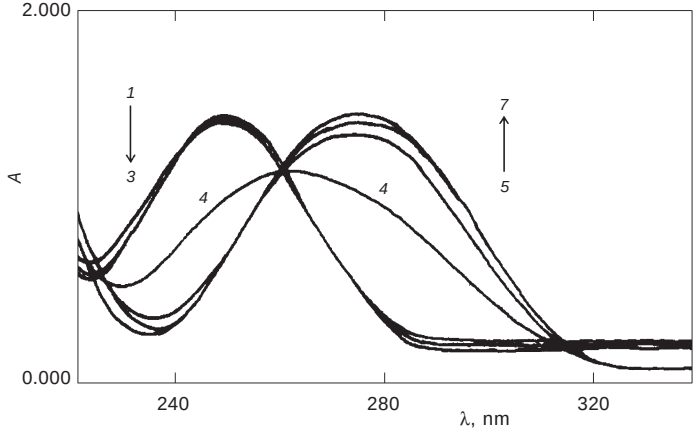

FIG. 4
Absorption spectra of the 4ABP–β-CDx complex at different pH values: *1* 2.0, *2* 2.4, *3* 2.8, *4* 3.2, *5* 3.6, *6* 4.0, *7* 4.6

The effect of pH on the fluorescence spectra of 4ABP in β-CDx (Fig. 5) is found to be different from that in the aqueous solution. When pH is decreased from 7, the intensity of fluorescence of 4ABP in β-CDx decreases down to pH 0.26 and then a new fluorescence band appears (λ_{exc} = 260 nm, the isosbestic wavelength in the absorption spectra of 4ABP at different pH values). The new fluorescence maximum (315 nm) is less intense and close to the fluorescence maximum of biphenyl, hence arising due to the formation of the monocation. The formation of the monocation is complete at H_0 = –4. The same fluorescence maximum starts to appear from pH 4 for 4ABP in aqueous solution[46]. There was no change in the fluorescence spectrum in the pH range 7–12.

The ground-state acidity constant (pK_a) value for the following prototropic equilibrium in 2.4 × 10^{-3} mol dm^{-3} β-CDx (Eq. (*2*)) was determined spectrophotometrically. For 2.4 × 10^{-3} mol dm^{-3} β-CDx, the complexation is almost complete. This pK_a value 3.42 is close to 3.6 reported for the aqueous solution[46]. There is no significant change in the pK_a value, as the amino group is not affected in the complex formation.

$$4ABPH^+ \rightleftharpoons 4ABP + H^+ \qquad (2)$$

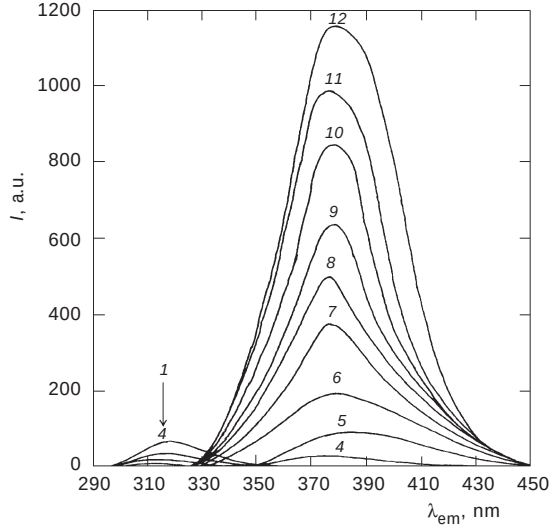

FIG. 5

Fluorescence spectra of the 4ABP–β-CDx complex at different H_0/pH values: *1* –3.87, *2* –2.76, *3* –1.85, *4* –0.26, *5* 1.2, *6* 1.6, *7* 2.0, *8* 2.4, *9* 3.0, *10* 4.0, *11* 5.0, *12* 6.0

The plots of fluorescence intensities of 4ABP at different H_0/pH values, with 2.4×10^{-3} mol dm^{-3} β-CDx and without β-CDx, are shown in Fig. 6. The fluorimetric titration curves in β-CDx are stretched, lying in the H_0/pH range –4 to 6. This reveals that the prototropic behaviour of 4ABP in β-CDx is not the same as in the aqueous solution. The fluorimetric titration curves of 4ABP in the absence of β-CDx meet at the middle of their inflection and the pK_a* value 2.2 is closer to the ground-state p*K*a value 3.42. However, in the presence of β-CDx, the fluorescence intensity of the neutral form of 4ABP decreases with pH decreasing from 6 to 0.26 and the fluorescence of the monocation appears at pH 0.26. There is no correspondence between the decrease of the fluorescence of the neutral form and the appearance of the fluorescence of the monocation. This indicates that there is no direct equilibrium between the complexed neutral form and the monocation. Initially, the fluorescence of the neutral form is quenched by an increase in the acidity. This may be due to the proton-induced fluorescence quenching that occurs from pH 6.3 to 0.26. When the acidity is further increased, the formation of the monocation starts. In this case, the middle of inflection of the monocation formation curve at –2.2 may be taken as the pK_a* value.

In the absence of β-CDx there is no proton-induced fluorescence quenching. However, the fluorimetric titration gives the pK_a* value close to the ground-state pK_a value. As reported earlier[46], in the aqueous solution the equilibrium is not established during the lifetime of the excited state, i.e., the excited neutral species loses its energy before undergoing protonation

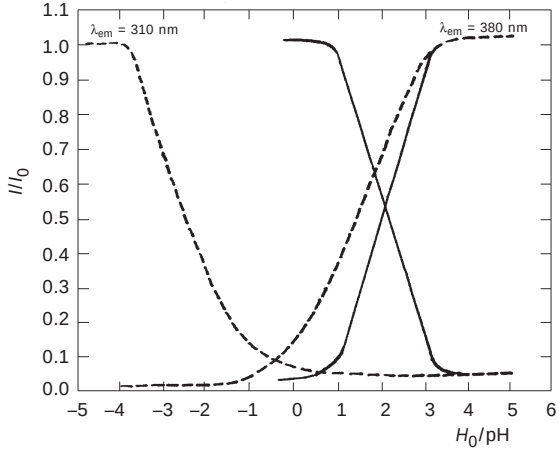

FIG. 6

Plot of relative fluorescence intensities I/I_0 vs H_0/pH of the prototropic species of 4ABP, with 2.4×10^{-3} mol dm^{-3} β-CDx (– – –) and without β-CDx (——) in the aqueous solution

due to its short lifetime. In the presence of β-CDx, the lifetime of the molecule inside the cavity is longer than that of the free species. The protonation of the 4ABP–β-CDx complex in the excited state therefore occurs within the lifetime of the excited species. This leads to the establishment of excited-state equilibrium; the pK_a^* value determined by the fluorimetric titration method is close to reported pK_a^* –3.7 obtained by the Förster cycle method[56]. In the latter method, the pK_a^* value is calculated by using Eq. (*3*)

$$pK_a - pK_a^* = 2.1 \times 10^{-3} \left[\nu_{BH^+} - \nu_B \right], \qquad (3)$$

where ν_{BH^+} is the absorption or fluorescence maximum of the protonated form and ν_B is the absorption or fluorescence maximum of the neutral form.

From the Benesi–Hildebrand plot it has been found that the stoichiometry of the complex is 1:1. The spectral and photoprototropic studies show that there is no interaction between the NH_2 group of 4ABP and the OH groups of β-CDx. This indicates that the NH_2 group of 4ABP lies outside the cavity of β-CDx and is in an aqueous environment. Further, there is no possibility of complete accommodation of the linear 4ABP molecule in the cavity of β-CDx having a length of 7.8 Å. Therefore, the complex formed is an axial inclusion complex with the benzene ring inside the β-CDx cavity, as shown in Fig. 7.

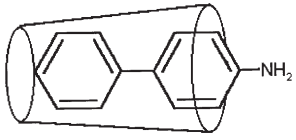

FIG. 7
Schematic representation of the inclusion complex of 4ABP in β-CDx

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