Fluorescence of 1-Naphthol Induced by 2 : 1 Complexation with *N*(*N*′-formyl-L-phenylalanyl)-β-cyclodextrin

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The pH-dependent fluorescence of 1-naphthol was studied in the presence of β-cyclodextrin(β-CD) or *N*(*N*′-formyl-L-phenylalanyl)-β-cyclodextrin **1**. Compound **1** includes 1-naphthol to form a 2 : 1 complex, which completely restricts the H^+ dissociation in photoexcited 1-naphthol.

Molecular recognition by modified cyclodextrins (CD) is currently of great interest in host–guest chemistry. Recently, I prepared amino acid binding CDs and reported that *N*(*N*′-formyl-L-phenylalanyl)-β-cyclodextrin **1** includes the covalently bound phenyl moiety in its cavity to form an intramolecular host–guest complex.[1,2] Compound **1** exhibits enantioselectivity in the inclusion of optical isomers of dansylphenylalanine with guest-induced substituent movement.[3] I report here the recognition ability for naphthol forming 2 : 1 complexes with complete restriction of the H^+ dissociation in the photoexcited state.

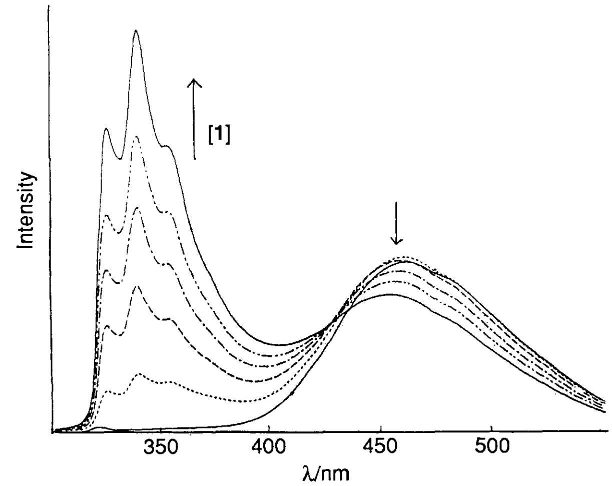


Fig. 1 Fluorescence spectra of 1-naphthol in the presence of **1** (0.0–1.0 × 10^{-3} mol dm^{-3}) at pH 7

Most of the molecules studied in the excited state are chemically new species with properties such as redox potential, acid–base strength and dipole moment very different from those in the ground state. The pK_a value of 1-naphthol (ROH) in the ground state is 9.26, but in the first excited singlet state, it behaves like a very strong acid (pK_a* is only 0.4).[4] Only the ionic form of 1-naphthol (RO^-) fluoresces with λ_{max} 470 nm in neutral aqueous solution, but in the

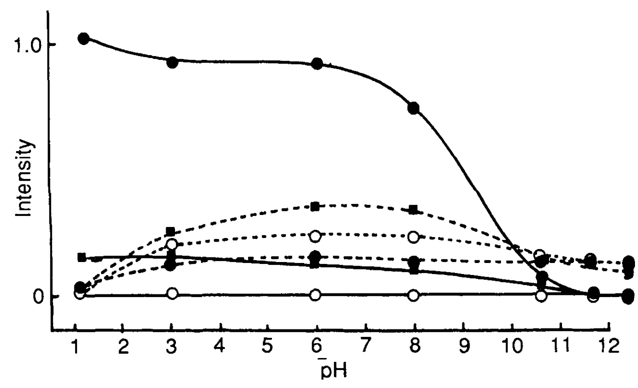


Fig. 2 Fluorescence intensity of 1-naphthol in the presence (●: **1**, ■: β-CD) or absence (○) of cyclodextrins as protonated ROH* (——) and deprotonated RO^{-*} (– – –) as a function of pH

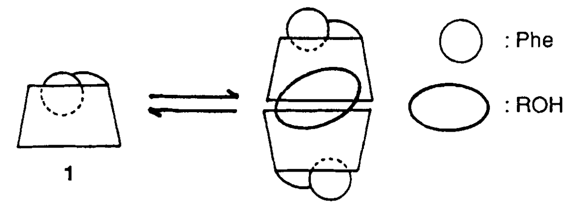
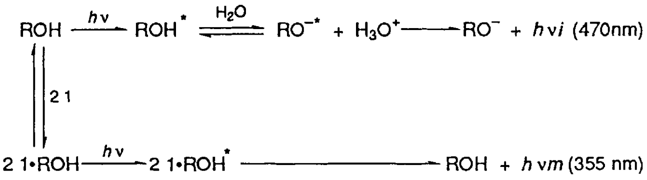


Fig. 3 Schematic representation of most likely averaged complex formation of ROH and **1**

presence of **1**, the fluorescence of the molecular form is observed at λ_{max} 355 nm; the intensity increases with an increase in the concentration of **1** (Fig. 1). This fluorescence behaviour in the ROH–**1** system could be analysed by the Beneshi–Hildebrand equation for the formation of the 2:1 complex of **1** and ROH [eqn. (1)].[5] A plot of ΔI^{-1} *vs.* $[\mathbf{1}]_0^{-2}$

$$\Delta I^{-1} = (aK_1K_2)^{-1}([\mathbf{1}]_0)^{-2} + a^{-1} \qquad (1)$$

gives K_1K_2 1.71 × 10^5 dm^6 mol^{-2}. In the presence of β-CD, the intensity of both forms increased. The ROH–β-CD system could not be analysed by eqn. (1). Fig. 2 shows the pH-dependent fluorescence of RO^- and ROH. In the presence of **1**, however, the pK_a* of ROH is 0.4, a strong fluorescence of the molecular form can be observed at pH < 9.5. At pH > 10.5, **1** had no ROH fluorescence. The threshold pH agrees with the pK_a of ROH in the ground state. These results suggest that **1** specifically includes only the molecular form of ROH and the included ROH is excited and then fluoresces without H^+ dissociation (Scheme 1). Proton dissociation from ROH was found to depend on a specific water structure: a cluster composed of a minimum of four water molecules. The formation of such a water cluster in these weak acid systems is determined by reorientational motions of the local solvent.[6,7,8] In the β-CD cavity, proton dissociation from ROH* is carried out, but in the **1** cavity, it is completely restricted, which means that **1** inhibits the formation of a water cluster around ROH*. The size and shape of the hydrophobic cavity consisted of two molecules of **1** attached to the ROH moiety with guest-induced movement of the phenyl moiety at **1** (Fig. 3). (*i*) Recognition of the moelcular form in the ground state, (*ii*) and inhibition of the formation of a specific water structure by **1** induced the specific fluorescence of the molecular form at pH < 9.5 as indicated here. Compound **1** can be practically used as a stabilizer for molecules that tend to undergo chemical change in the excited states.



Scheme 1

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