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Inclusion complexes of naphthalimide derivatives with cyclodextrins

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Abstract

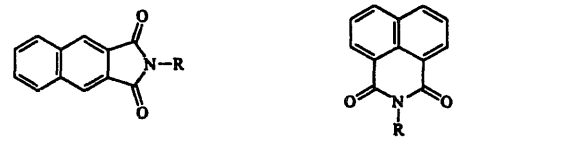
Complex formation between naphthalimide derivatives (2,3- and 1,8-naphthalimides and their respective *N*-butyl derivatives) and α-, β- and γ-cyclodextrins (CDs) was studied by UV and fluorescence spectroscopy. All the naphthalimides studied form 1 : 1 inclusion complexes with β- and γ-CDs, and the corresponding binding constants were determined. For β-CD complexes, the data obtained suggest a relatively tight axial inclusion of 2,3-naphthalimides and an equatorial inclusion of 1,8-naphthalimides. In contrast, for the γ-CD complexes, the data indicate a loose fit of the naphthalimides within the cavity. A remarkable exception is 2,3-*N*-butylnaphthalimide, which forms an unusually tight inclusion complex with γ-CD. In this complex, the quenching of the naphthalimide fluorescence by bromide ion is fully prevented.

Keywords: Cyclodextrins; Host–guest complexes; Inclusion complexes; Naphthalimides

1. Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides containing α-1–4-linked D-glucopyranosyl residues. α, β and γ-CDs contain six, seven and eight glucose units respectively. The linking of these glucose units gives rise to doughnut-shaped structures, with relatively hydrophobic cavities. Because the CD internal cavity is less polar than the surrounding aqueous solution, CDs have the ability to form inclusion complexes with a large variety of organic guests. The stability of a particular CD complex is determined mainly by geometric factors. Molecules having a size compatible with the dimensions of the cavity are likely to form stable complexes. Guests included within the CD cavity usually display changed photophysical properties, rendering these complexes interesting systems for the study of organic dyes [1].

2,3-Naphthalimides and 1,8-naphthalimides are fluorescent compounds for which a series of biological (local anaesthetics [2], DNA-cleaving agents [3], tumoricidals [4]) and non-biological (optical brighteners [5], Lucifer dyes [6]) applications have been found. Naphthalimide derivatives have yielded several interesting photophysical studies in both homogeneous solution [7–9] and micellar media [10]. Nevertheless, there are no reports, to our knowledge, of studies concerning CD complexes with naphthalimides.



2,3-naphthalimide (I, R=H) 1,8-naphthalimide (III, R=H)
2,3-N-butylnaphthalimide (II, R=Butyl) 1,8-N-butylnaphthalimide (IV, R=Butyl)

Scheme 1.

It is the goal of this study to clarify whether or not naphthalimides form inclusion complexes with the different CDs and, if so, to determine the complex stoichiometry and stability constants. The compounds employed in this study were 2,3-naphthalimide (**I**), 2,3-*N*-butylnaphthalimide (**II**), 1,8-naphthalimide (**III**) and 1,8-*N*-butylnaphthalimide (**IV**) (structures are shown in Scheme 1).

2. Experimental details

2.1. Materials

Compounds **I–IV** were prepared according to known procedures [11] and recrystallized (ethanol) prior to use. Product identification was confirmed by melting point, elemental analysis and ^{1}H NMR spectra. The α, β and γ-CDs (Aldrich)

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were used as received. Sodium bromide (Merck) was used without purification. Aqueous solutions were prepared with fresh doubly distilled water. Reagent-grade ethanol was distilled before use.

2.2. Equipment

UV–visible absorption spectra were recorded with a Hitachi U-2000 spectrophotometer using 5 cm path length quartz cuvettes. Fluorescence measurements were performed with air-equilibrated samples using a SPEX DM 3000F spectrometer (frontal face mode). Excitation and emission slits were fixed at 0.5 mm. The spectra were computer corrected (SPEX software). All measurements were carried out at 25 ± 1 °C.

2.3. Methods

All the CD-containing naphthalimide solutions were stirred for approximately 15 h (25 ± 1 °C) to attain thermodynamic equilibrium prior to measurement.

The effect of an increase in the CD concentration on the fluorescence intensity of the naphthalimides **I–IV** was used to measure the binding constants employing Benesi–Hildebrand plots (see Section 3). The solutions were prepared as follows. An aqueous solution of the naphthalimide (solution A, typically approximately 10^{-6} M) was prepared by dilution of a concentrated acetonitrile stock solution. A given amount of the CD was weighed and diluted with solution A to give a concentrated CD solution (solution B, typically 0.05, 0.01 and 0.1 M for α-, β and γ-CDs respectively). Aliquots from solutions A and B were mixed to give a range of solutions with different CD concentrations (note that solutions A and B are equimolar in naphthalimide, ensuring no dilution effects).

Solutions of **I–IV** in the presence of CDs, for absorption measurements, were prepared as above (solutions A and B, but with [naphthalimide] in the range $(1–5) \times 10^{-5}$ M).

The effect of the CDs on the fluorescence quenching of naphthalimides by bromide ion was studied by adding aliquots of bromide ion from a concentrated aqueous sodium bromide solution (approximately 1 M) to solutions A and B to give $[Br^-] \approx 0.1$ M.

3. Results

3.1. Absorption

The changes observed in the absorption spectra of naphthalimides **I–IV** in aqueous solution on addition of the CDs are very small. No changes at all are observed with α-CD, whereas slight blue shifts of 1–3 nm are observed for β- and γ-CDs. The maxima of **I–IV** in ethanol are also blue shifted relative to the water maxima [7], suggesting the inclusion of the naphthalimides in the relatively less polar CD cavities.

Although absorbance changes on inclusion of guest molecules in CDs have been employed to determine the corresponding binding constants [12,13], the observed changes of the naphthalimides are within experimental error, and therefore too small to allow measurements of the binding constants.

3.2. Fluorescence

The effect of CDs on the fluorescence spectra of naphthalimides **I–IV** is more pronounced than the corresponding effect on the absorption spectra. Two main effects can be observed, namely blue shifts in the maxima and decreases in the fluorescence quantum yields (Table 1). Fig. 1 illustrates the spectral blue shifts observed when α-, β- and γ-CDs are added to an aqueous solution of **II**. The maximum shifts from 417 nm in water to 412 nm and 403 nm in the presence of α- and β-CDs respectively; two maxima at 383 and 364 nm appear with γ-CD. Fig. 2(A) shows the concomitant blue shift and decrease in the quantum yield which occur when γ-CD is added to an aqueous solution of **I**. The relevant fluorescence data for compounds **I–IV** in the presence of α-, β- and γ-CDs are collected in Table 1, which shows the emission maxima and Φ/Φ_0 values (representing the fluorescence quantum yield ratio of complexed and free naphthalimide, see Section 3.3). The data in ethanol are also included in Table 1 for comparison. It should be noted that the maxima and Φ/Φ_0 values in the presence of CDs lie, in most cases, between those in water and ethanol, indicating that, in CD solution, the naphthalimides are located at a site intermediate

Table 1
Fluorescence emission data for naphthalimides **I–IV** in the absence and presence of CDs (data in ethanol included for comparison)

Naphthalimide	λ_{max}^{em} (Φ_{CD}/Φ_0) [a]				
	H_2O	EtOH [b]	α-CD	β-CD	γ-CD
2,3-Naphthalimide (**I**)	416	389 (0.34)	413 (0.97)	398 (0.61)	407 (0.56)
2,3-*N*-Butylnaphthalimide (**II**)	417	385 (0.61)	412 (0.88)	403 (0.72)	383, 364 (0.30)
1,8-Naphthalimide (**III**)	393	381 (0.07)	393 (1)	395 (0.41)	390 (0.50)
1,8-*N*-Butylnaphthalimide (**IV**)	396	381 (0.23)	393 (0.89)	395 (0.62)	389 (0.26)

[a] The Φ_{CD}/Φ_0 values represent the quantum yield ratio of complexed and free naphthalimide, calculated with either Eq. (1) or by the division of spectral areas (see text).
[b] The values in parentheses represent Φ_{EtOH}/Φ_0 in this case.

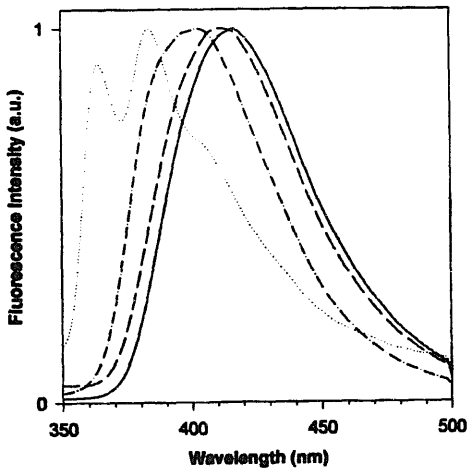


Fig. 1. Normalized fluorescence emission spectra of 2,3-*N*-butylnaphthalimide (II) ($C = 1.1 \times 10^{-6}$ M) in water (——) and in the presence of 0.05 M α-CD (– – –), 0.01 M β-CD (– · –) and 0.08 M γ-CD (· · ·). Excitation wavelength, 261 nm.

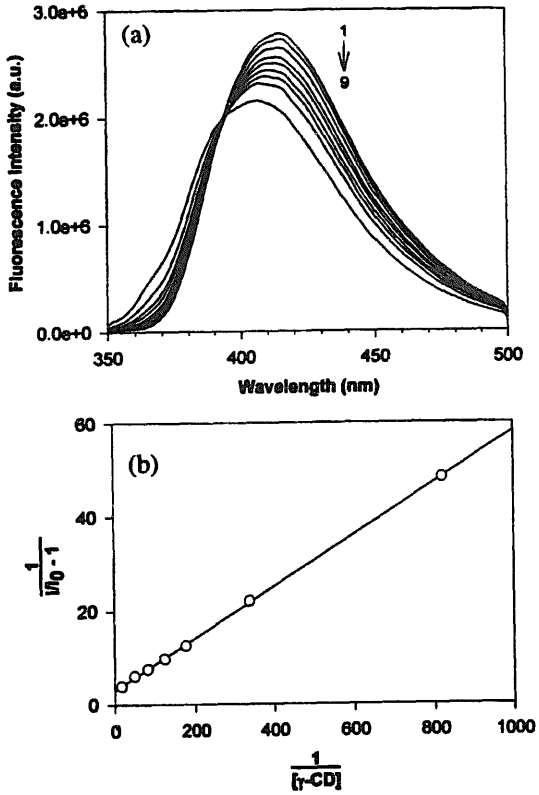


Fig. 2. (A) Effect of the addition of γ-CD on the fluorescence emission of 2,3-naphthalimide (I) ($C = 1.4 \times 10^{-6}$ M) in aqueous solution. [CD] (M) (from 1 to 9): 0; 1.2×10^{-3}; 3.0×10^{-3}; 6.0×10^{-3}; 8.1×10^{-3}; 1.2×10^{-2}; 1.7×10^{-2}; 2.6×10^{-2}; 6.2×10^{-2}. Excitation wavelength, 260 nm. (B) Benesi–Hildebrand plot (Eq. (1)) using the data from (A) ($\lambda = 415$ nm).

in polarity between these two solvents; this provides evidence for complex formation.

The effects observed with the three CDs on the naphthalimide fluorescence are generally more pronounced in the order γ-CD > β-CD > α-CD (Table 1). As for the absorption spectra, the addition of α-CD causes no significant changes to the fluorescence spectra of non-substituted naphthalimides I and III. For the butyl-substituted derivatives II and IV, however, spectral blue shifts of 3–5 nm and small quenching effects can be observed (Table 1, Fig. 1). Since the naphthalimide moieties in II and IV are too large for inclusion in α-CD, these results suggest that the butyl groups may be included in the cavity of α-CD (see Section 4).

In contrast with the effect of α-CD, large blue shifts (9–34 nm, Table 1) are observed when β- or γ-CD is added to solutions of I or II, suggesting that inclusion of the chromophoric portion of the molecules (the naphthalimide system) within the CD cavity occurs. Naphthalene can fit inside the cavities of β-CD (inside diameter (i.d.) = 7.8 Å) and γ-CD (i.d. = 9.5 Å) [1]. The most striking case is that of the II–γ-CD complex, where the broad band with a maximum at 417 nm observed in water is replaced by a structured band with two maxima at 383 and 364 nm. This is the only case where more than one maximum is observed (Fig. 1).

The effect of β- and γ-CDs on the fluorescence maxima of III and IV is smaller than that observed with I and II, reflecting the different sensitivities of 1,8- and 2,3-naphthalimides towards changes in the environment (see Section 4). Complex formation in the case of III and IV, however, is shown by the significant decrease in the fluorescence quantum yield in the presence of β- and γ-CDs (Table 1).

3.3. Binding studies

The changes in the fluorescence of I on addition of increasing concentrations of γ-CD are shown in Fig. 2(A). As discussed above, an increasing CD concentration causes a blue shift in the maximum (416 nm to 407 nm in this case), together with a decrease in the fluorescence intensity ($\Phi/\Phi_0 = 0.56$). An isoemissive point can be seen at 392 nm. The data in Fig. 2(A) can be treated using the Benesi–Hildebrand equation for a 1 : 1 binding model (Eq. (1))

$$\frac{1}{(I/I_0 - 1)} = \frac{1}{(\Phi_{CD}/\Phi_0 - 1)} + \frac{1}{(\Phi_{CD}/\Phi_0 - 1)\gamma K} \frac{1}{[CD]} \quad (1)$$

where I/I_0 is the observed fluorescence intensity ratio for the naphthalimide in the presence (I) and absence (I_0) of CD, Φ_{CD}/Φ_0 represents the quantum yield ratio between complexed (Φ_{CD}) and free (Φ_0) naphthalimide, K is the stability constant for the association (M^{-1}) and [CD] is the CD concentration (M). The factor γ in Eq. (1) represents the ratio (ϵ_{CD}/ϵ_0) between the molar absorptivities (at the excitation wavelength) of naphthalimide for the complexed and free forms (γ in Eq. (1) has been assumed to be unity throughout this paper, since no significant effect of the CDs on the naphthalimide absorption was observed (see Section 3.1)). Eq. (1) has been employed by several workers to determine the binding constants to CDs by means of fluorescence measurements [14–16].

A plot of the data in Fig. 2(A) according to Eq. (1) is shown in Fig. 2(B). The good linearity obtained shows that complexation between I and γ-CD obeys a 1 : 1 process, with a stability constant of 60 M^{-1}. A good linear correlation with Eq. (1) was obtained for all the naphthalimides with β- and

Table 2
Binding constants for 1 : 1 complex formation between naphthalimide derivatives and CDs [a]

Naphthalimide	K (M^{-1}) [b]	
	β-CD	γ-CD
2,3-Naphthalimide (I)	780	60
2,3-*N*-Butylnaphthalimide (II)	2000	260
1,8-Naphthalimide (III)	140	60
1,8-*N*-Butylnaphthalimide (IV)	550	70

[a] The K values presented are the average of the values obtained by applying Eq. (1) for a number of different wavelengths in the fluorescence spectra.
[b] Estimated error of ± 10%.

γ-CDs, showing that 1 : 1 complexes are formed in our experimental conditions. The stability constants are given in Table 2.

It is interesting to compare the K values in Table 2 with those for 1 : 1 CD complexes with other naphthalene derivatives. The K value for the I–β-CD complex (780 M^{-1}) compares well with the values for β-CD complexes with naphthalene [17], 2-methoxynaphthalene [17], 2-naphthol [15] and 2-acetylnaphthalene [18] (all in the range 600–700 M^{-1}, determined by fluorometric methods). For the I–γ-CD complex, the binding constant (60 M^{-1}) is comparable with the value of $K = 53\ M^{-1}$ for the γ-CD–2-naphthol complex [15].

Finally, Eq. (1) allows the calculation of Φ_{CD}/Φ_0 (Table 1), the fluorescence quantum yield ratio of complexed and free naphthalimide. Another way of calculating the Φ_{CD}/Φ_0 ratio is by simply dividing the spectral area for the highest CD concentration employed by that in water. The values obtained by the two methods agree quite well (within 5% error), showing that the inclusion of the naphthalimides is almost complete at high [CD]. The Φ_{CD}/Φ_0 values given in Table 1 are those calculated by Eq. (1) (data for β- and γ-CDs) or by the ratios of the spectral areas (data for α-CD and ethanol).

3.4. Quenching studies

The effect of CDs on collisional quenching processes has been studied in detail. In most cases, the quenching is inhibited by inclusion in CDs [19,20], since the included molecule is less accessible to the quencher. Naphthalimide fluorescence is quenched by halide anions in water solution [21]. The quenching of naphthalimides I–IV by bromide ion is inhibited when the compound is included in the CD cavity, as shown in Table 3 and Fig. 3.

When 0.01 M Br^- is added to an aqueous solution of naphthalimide, a decrease in the fluorescence intensity is observed, as indicated by the I_{Br}/I_0 values in water (first column in Table 3) [21]. When β- or γ-CD is present, quenching by bromide is inhibited, as shown by the I_{Br}/I_0 ratios (second and third columns in Table 3), which are higher than those in the absence of CD. It is worth noting the unusually efficient protection offered by γ-CD against bromide quenching in the case of II. In the II–γ-CD complex, quenching of the naphthalimide fluorescence by bromide is completely prevented even at 0.1 M Br^- ($I_{Br}/I_0 = 1$), suggesting a rather tight fit in this complex (Fig. 3).

Table 3
Quenching of naphthalimide fluorescence by 0.01 M bromide ion in the absence and presence of CDs

Naphthalimide	I_{Br}/I_0 [a]		
	H_2O	β-CD (0.01 M)	γ-CD (0.1 M)
2,3-Naphthalimide (I)	0.62	0.86	0.88
2,3-*N*-Butylnaphthalimide (II)	0.66	0.87	1
1,8-Naphthalimide (III)	0.73	0.80	0.91
1,8-*N*-Butylnaphthalimide (IV)	0.80	0.92	0.86

[a] Ratio between the fluorescence intensities in the presence (I_{Br}) and absence (I_0) of bromide.

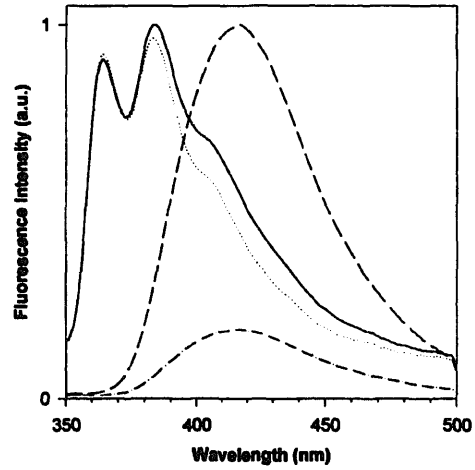


Fig. 3. Effect of bromide ion on the fluorescence emission of 2,3-*N*-butylnaphthalimide (II) ($C = 1.1 \times 10^{-6}$ M) in water and included within the γ-CD cavity. Spectra: water (– – –); water + 0.1 M NaBr (– · –); 0.08 M γ-CD (——); 0.08 M γ-CD + 0.1 M NaBr (· · ·). For clarity, the spectra in the absence of bromide were normalized, and the corresponding spectra in the presence of bromide were rescaled by the same factor. Excitation wavelength, 261 nm.

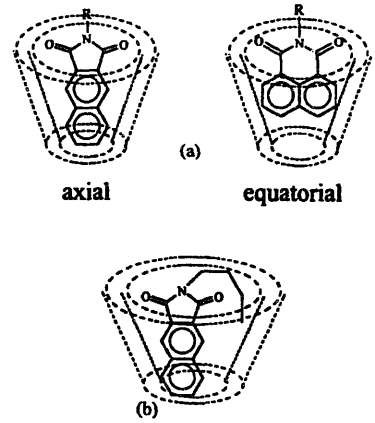
4. Discussion

4.1. Naphthalimide photophysics

In order to interpret the effects of CD addition on the spectroscopic properties of naphthalimides, some considerations about their photophysical behaviour should be made. Remarkable differences have been found between the behaviour of 2,3- and 1,8-naphthalimides [7], arising from the different contributions of the (mixed) close-lying n,π* and π,π* states to the lowest unoccupied molecular orbital (LUMO) energy [22]. It has been shown that the n,π*

contribution is more important in the case of II, whereas in IV the LUMO displays nearly pure π,π^* character. The differences arise from the fact that, in II, a more strained five-membered imide ring occurs, which is somewhat twisted out of the plane of the naphthalene ring, in contrast with the six-membered imide ring in IV, where all the rings are coplanar and conjugation is favoured [7].

These differences are reflected in the spectroscopic properties of compounds I–IV (Table 1). Solvent effects on the spectral maxima are rather more pronounced with 2,3-naphthalimides (compare the data in water and ethanol), and the absorption coefficients (ϵ) for 1,8-naphthalimides are approximately threefold higher than those for 2,3-naphthalimides [7]. The different environmental sensitivities of 2,3- and 1,8-naphthalimides should therefore be taken into account when interpreting the effects of CDs on the spectra of I–IV.



Scheme 2. A: Proposed structure for the naphthalimide: β-cyclodextrin complexes, showing axial inclusion of 2.3-naphthalimides and equatorial inclusion of 1,8-naphthalimides. B: Proposed structure for the II:γ-CD complex, showing the foldback of the butyl group.

4.2. *Structures of the complexes*

It can be seen as a general trend that the spectroscopic properties of the naphthalimides studied in the presence of β- and γ-CDs (and α-CD as well in the case of butyl-substituted derivatives) lie between those in water and ethanol, indicating that, in CD solution, the naphthalimides are located at a site intermediate in polarity between these two solvents. Since CD cavities have a polarity similar to water–alcohol mixtures [1], these results indicate complex formation with inclusion of the naphthalimides within the CD cavities. Although the low water solubility of naphthalimides I–IV precludes the use of techniques such as ^{1}H NMR, which could reveal structural details, the present results, together with current knowledge about CD complexes, allow some speculation regarding the structures of the complexes.

4.2.1. *α-CD*

Geometric considerations show that naphthalene is too large to be included in the small α-CD cavity (i.d. = 5.7 Å) [1]. Accordingly, the lack of any significant effect of α-CD on the absorption and fluorescence spectra of naphthalimides I and III indicates that no association occurs between these compounds and α-CD. This also ensures that any spectroscopic changes observed with the other CD–naphthalimide combinations are due to host–guest association, rather than to changes in the bulk properties (viscosity, dielectric constant, etc.).

For the butyl-substituted naphthalimides II and IV, inclusion of the alkyl chain in the cavity of α-CD may possibly account for the small effects observed on the emission spectra. Inclusion of the side chains of large molecules within CD cavities is a well-known phenomenon [1]. This type of inclusion would minimize unfavoured interactions between the alkyl chain and bulky water molecules (hydrophobic effect), and extra stabilization could be achieved by hydrogen bonding between the imide carbonyls and the CD hydroxyls at the rim of the cavity.

4.2.2. *β-CD*

All the studied naphthalimides form 1 : 1 inclusion complexes with β-CD, but the binding constants show that the affinity of the 2,3-naphthalimides for β-CD is approximately four to five times higher than that of the corresponding 1,8-derivatives (Table 2). This finding suggests a tighter fit of I and II within the β-CD cavity, which is consistent with the axial inclusion of 2,3-derivatives and equatorial inclusion of 1,8-derivatives (Scheme 2(A)). In the structures shown in Scheme 2, the hydrophobic naphthalene ring is located within the low polarity environment of the CD cavity, with the polar imide group exposed to the bulk water. Additional stabilization could be acquired by hydrogen bonding between the naphthalimide carbonyls and the CD hydroxyl groups. The proposed structures are supported by previous results which show that 2-substituted naphthalenes form axial inclusion complexes with β-CD, whereas equatorial inclusion occurs with 1-substituted naphthalenes [23]. In our case, this trend should be even more pronounced due to the disubstitution pattern, since 1,8-substituted naphthalimides are too bulky for axial inclusion.

For the *N*-butyl-substituted naphthalimides II and IV, it is reasonable to suppose that "inverted complexes", with inclusion of the butyl groups, are also formed in addition to the "normal" complexes shown in Scheme 2(A). The formation of "normal" and "inverted" complexes has been observed with coumarin derivatives [24]. The increase in the number of possible inclusion modes increases the probability that collision will result in complex formation, which may account for the fact that the binding constants for β-CD complexes with the *N*-butyl naphthalimides II and IV are three to four times higher than with the corresponding *N*-H derivatives (Table 2) (the binding constants experimentally obtained are the sum of the so-called microscopic constants for the formation of individual complexes of "normal" and "inverted" type should they exist [12]).

4.2.3. γ-CD

As for β-CD, γ-CD forms 1 : 1 complexes with all the naphthalimides investigated, but the binding constants are lower than those of the corresponding β-CD complexes. Furthermore, the K values are hardly affected by the molecular structure (K=60–70 M^{-1}), with the exception of 2,3-*N*-butylnaphthalimide (see below). These results are a clear indication of the loose fit of compounds **I**, **III** and **IV** within the cavity of γ-CD, which is large enough to include the guests together with low-ordered water molecules.

A distinctive behaviour can be observed for the γ-CD complex with **II**. In this case, the binding constant (K=260 M^{-1}), which is four times larger than those for the complexes with **I**, **III** and **IV**, the splitting of the emission band into two maxima (Fig. 1) and the highly efficient protection against quenching by bromide (Fig. 3) reveal an unusually tight interaction of **II** with the γ-CD cavity. The structured emission band can be attributed to the decreased vibrational freedom of included **II**, whereas the quenching inhibition can be explained by the absence of low-ordered water molecules sharing the cavity with **II**, thus preventing diffusion of bromide into the cavity interior.

A possible explanation for such a tight arrangement involves the folding back of the alkyl chain towards the cavity, dislodging low-ordered water molecules, which are then expelled from the cavity, increasing its apolar character (Scheme 2(B)). Such structures have been proposed for a series of alkyl-substituted 4-bromo-1-naphthoyl probes included in γ-CD [25].

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