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Solid complexes between *N*-(*para*-alkylphenyl)-2,3-naphthalimides and β-cyclodextrin: characterization by diffuse reflectance infrared Fourier transform spectroscopy and laser induced luminescence studies

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Abstract

N-(*para*-alkylphenyl)-2,3-naphthalimides form complexes with β-cyclodextrin, which were characterized by diffuse reflectance infrared Fourier transform (DRIFT) and UV spectroscopy. DRIFT spectra of the complexes **1a**–**g**/β-CD revealed that the deformation band of crystallization water is largely reduced when compared to that observed for the mechanical mixture. Moreover, significant shift to either higher or lower wavenumbers for the out-of-phase carbonyl stretching mode of the naphthalimide confirmed the inclusion complex formation.

The fluorescence emission spectrum of the inclusion complex *N*-phenyl-2,3-naphthalimide/β-cyclodextrin (**1a**/β-CD) shows a strong band with maximum at 440 nm. *para*-Alkyl substitution on the *N*-phenyl ring of **1a** leads to a red shift of the fluorescence emission band from its solid complex with β-CD. This emission is strongly dependent on the alkyl chain length. Room temperature phosphorescence was observed for the complexes *N*-(*para*-*n*-butylphenyl)-, *N*-(*para*-*n*-hexylphenyl)- and *N*-(*para*-*n*-octylphenyl)-2,3-naphthalimide/β-CD.

The fluorescence results can be interpreted considering that a preferential complexation of a given ground state conformation of the 2,3-naphthalimide must occur, leading to complexes of different structures. This complexation is dependent on the *para*-alkyl substitution on the phenyl ring, with different degrees of extended conjugation between these two chromophores.

Keywords: β-cyclodextrin solid complexes; DRIFT spectra; Fluorescence; *N*-Aryl-2,3-naphthalimides

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1. Introduction

The spectroscopic properties of 2,3-naphthalimides have been extensively studied in the last few years. The parent compound, i.e. 2,3-naphthalimide, and its *N*-methyl derivative show vibrationally resolved fluorescence emission spectra in acetonitrile ($\lambda_{max}\approx380$ nm) that are mirror image of their long-wavelength absorption spectra, and with a lifetime of *ca*. 8 ns [1]. Similar behavior was reported for *N*-*n*-butyl-2,3-naphthalimide [2] and for other imides bearing longer chains such as *N*-*n*-hexyl-, *N*-*n*-dodecyl- and *N*-*n*-octadecyl-2,3-naphthalimides [3]. The fluorescence emission from these imides is clearly solvent dependent. Thus, the vibrationally resolved spectra observed in acetonitrile at 367 and 386 nm gives place to a broad emission in methanol with λ_{max}=393 nm [3,4].

N-phenyl-2,3-naphthalimide shows dual fluorescence at room temperature in acetonitrile, with emissions between 350 and 410 nm ($\tau\leq50$ ps) and at 490 nm (a broad and structureless emission, with $\tau=1.3$ ns). These emission bands were associated to two different excited singlet states. In one case, the phenyl group and the naphthalimide moiety are orthogonal to each other with this conformation leading to the short wavelength emission. In the other case, these two groups are in a fully conjugated coplanar conformation, which results in the long wavelength emission [1]. Time-resolved experiments indicate that the two emissive excited states are not kinetically connected and that the vibrationally relaxed Franck–Condon excited state populates both (the short and the long wave-

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length emitting) excited states [1]. Substitution by a bulky group in the 2′-position of the *N*-phenyl ring, as in *N*-(2′,5′-di-*tert*-butylphenyl)-2,3-naphthalimide, totally suppresses the long wavelength emission. This is due to a complete hindrance of the *N*-phenyl rotation. Similar effect was observed by varying the solvent viscosity [1].

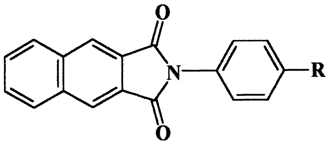
Fluorescence properties of *N*-phenyl-2,3-naphthalimides substituted on the *N*-phenyl ring by polar groups are dependent not only on the electron-donating or electron-withdrawing ability of the substituent, but also on its position [5,6]. Thus, a strong red shift and a decrease of the quantum yield for the long-wavelength fluorescence emission were observed on substitution by electron-donating groups such as the *para*-methoxy group. On the other hand, electron-withdrawing groups such as *para*-trifluoromethyl have the opposite effect.

Cyclodextrins are cyclic oligosaccharides that have the ability in forming inclusion complexes with a great variety of organic, inorganic, neutral and ionic molecules [7–9]. They consist of 6 (α), 7 (β) or 8 (γ) D-glucose units having a truncated cone shaped hydrophobic cavity with different inner diameters. It is well known that the restricted shape and size of the cyclodextrin cavity considerably affect spectral properties of included molecules, as well as their photochemical and photophysical behavior [10–14].

It has been shown that complexation of *N*-alkyl-2,3-naphthalimides with β-cyclodextrin (β-CD) results in a red shift of the fluorescence emission for short alkyl chains (methyl, *n*-butyl, *n*-hexyl) [3,15]. For longer chains, besides the red shift, a strong enhancement of the fluorescence emission, as well as the development of a clear vibrational progression, was observed. It was proposed that for the later case both the naphthalimide moiety and the alkyl group are included into the β-CD cavity [3].

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) has been widely employed in the characterization of the structure of several finely divided powders such as silica [16], polystyrene [17], and cellulose [18,19], as well as in the study of their adsorbing properties [20,21]. In all cases the Kubelka–Munk treatment was employed [22].

In this work, we present an unambiguous characterization of the structure of solid complexes between *N*-(*para*-alkylphenyl)-2,3-naphthalimides **1a–g** and β-CD by DRIFTS technique, as well as a detailed study on their fluorescence and phosphorescence emission properties.



1 **a:** R = H; **b:** C_2H_5; **c:** *n*-C_4H_9; **d:** *n*-C_6H_{13}; **e:** *n*-C_8H_{17}; **f:** *n*-$C_{10}H_{21}$; **g:** *n*-$C_{12}H_{25}$

2. Experimental

2.1. Materials

The solvents methanol, benzene, acetonitrile (Aldrich, Spectroscopic grade) were used as received. Butyronitrile and *n*-butyl acetate (Aldrich) were purified by filtration over neutral alumina. β-Cyclodextrin (Sigma) was recrystallized from water. Aniline, *para*-ethyl-, *para*-*n*-butyl-, *para*-*n*-hexyl-, *para*-*n*-octyl-, *para*-*n*-decyl-, *para*-*n*-dodecylaniline, and 2,3-naphthalenedicarboxylic acid, employed in the synthesis of the different 2,3-naphthalimides used in this work, i.e. **1a–g**, were purchased from Aldrich. KBr for infrared experiments (from Aldrich, FTIR grade) was used as received.

2.2. General procedure for the synthesis of **1*a–g*** [23]

2,3-Naphthalene dicarboxylic acid (1.08 g, 0.005 mol) was mixed with a large excess of the corresponding amine and the resulting mixture was heated for 3 h at 180–200°C. After cooling, the crude solid was filtered, washed with hot aqueous HCl (1 M), filtered, and washed again with a 1 M hot solution of $NaHCO_3$. After drying, the product was purified by column chromatography (SiO_2; eluent: CH_2Cl_2) and then recrystallized from ethyl acetate. Spectroscopic data are fully in accord with the proposed structures for **1a–g**.

2.3. Preparation of solid complexes N-aryl-2,3-naphthalimides/β-CD

To a saturated solution of β-CD in water a saturated methanol solution of the 2,3-naphthalimide derivative was added. This mixture was magnetically stirred for 48 h and then lyophilized. The resulting complex was washed with 20 ml of diethyl ether (10 times 2 ml aliquots) to remove non-complexed imide, and dried under reduced pressure. In all cases solvent removal was performed overnight in an acrylic chamber with an electrically heated shelf (Heto, Model FD 1.0–110) with temperature control (25±1°C), at a pressure of ca. 10^{-3} Torr.

2.4. General techniques

UV–VIS spectra were recorded with a JASCO V-560 spectrophotometer. Typical solutions were 10^{-3} M of the imide in acetonitrile.

Ground state spectra for the solid complexes **1a–g**/β-CD were recorded using an OLIS 14 spectrophotometer with a diffuse reflectance attachment. Further details are given elsewhere [24–26].

Low temperature (77 K) fluorescence and phosphorescence emission spectra in solution (butyronitrile: *n*-butyl acetate 95:5), as well as their corresponding excitation spectra, were recorded with a SLM Aminco model 8100 spectrofluorimeter. Fluorescence quantum yields were determined in acetonitrile at room temperature using *N*-phenyl-2,3-naphthalimide (**1a**) (Φ_f=0.005) as in [1].

Laser flash photolysis experiments were carried out with a frequency-tripled YAG laser (354.7 nm, 8 ns FWHM) from B.M. Industries. The usual cross-beam alignment for the laser and monitoring beam was used (xenon lamp, Applied Photophysics). Intersystem crossing quantum yields were determined in oxygen-free solutions of acetonitrile from transient absorption measurements at the triplet absorption maximum (440 nm), using **1a** as a reference which shows a triplet yield of 0.24 in acetonitrile [5].

Fluorescence lifetime determinations were performed with a home-made single photon counting apparatus. Samples were excited at 337 nm employing a coaxial flash lamp, Edinburgh Instruments, model 199F, running in nitrogen. The reference decay curve employed in this work was from a dilute solution of 2,5-bis-(5-*tert*-butyl-2-benzoxazolyl)thiophene (BBOT) in 95% ethanol (τ=1.47 ns) [27]. Further details on this system are given elsewhere [28].

For laser induced luminescence measurements a Photon Technology Instruments PL 2300 nitrogen laser (337.1 nm, 600 ps, $\leq$1.6 mJ/pulse) was employed [29–31]. The light arising from the irradiation of solid samples by the laser pulses was detected by a gated intensified charged coupled device (ICCD, Oriel model Instaspec V) coupled to a monochromator (Oriel, model FICS 77440). The system can be used either by capturing all light emitted by the sample or in a time-resolved mode by using a delay box (Stanford Research Systems, model D6535).

Diffuse reflectance infrared Fourier transform (DRIFT) spectra were recorded with a Mattson RS1 FTIR spectrometer, using a wide band MCT detector, and a Graseby/Specac Selector (the diffuse reflectance accessory). The spectra were recorded in the 4000–500 cm^{-1} range, at 4 cm^{-1} resolution, and a ratio of 1000 single-beam scans of the sample to the same number of scans for pure KBr was used as background. The spectra thus obtained were transformed to Kubelka–Munk units using the FIRST software. The samples of pure imide crystals, pure β-CD, imide/β-CD mechanical mixtures and imide/β-CD solid complexes were diluted in KBr (~4% w/w) and ground. The fine powders thus obtained were placed in a sampling cup with 11 mm diameter and manually pressed, in order to obtain a smooth surface, before recording the DRIFT spectra.

3. Results and discussion

3.1. *Absorption and emission properties for* ***1a–g*** *in solution*

The UV spectra in acetonitrile for *N*-phenyl-2,3-naphthalimide (**1a**) and its derivatives **1b–g** show structured absorption in the 330–370 nm region, with maxima at 342 and 358 nm in all cases. The constancy of these absorption spectra indicates that the introduction of the *para*-alkyl group on the *N*-phenyl ring of **1a** does not have any influence on the absorption properties of these compounds, independently of its chain length.

Similar fluorescence behavior as observed for **1a** (see above) was found for all *para*-alkyl substituted naphthalimides **1b–g**, either at room temperature or at 77 K. In all cases the emission maximum is independent of the alkyl chain length. Again, the excitation spectrum obtained for the fluorescence emission perfectly matches the ground state absorption spectrum. Fig. 1A shows representative spectra for the room- and low-temperature fluorescence emission of *N*-(*para*-*n*-dodecylphenyl)-2,3-naphthalimide (**1g**). It is worth noting that the maximum emission for **1b–g** at room temperature is slightly red shifted when compared to the parent compound **1a**. This shift can be associated to the presence of the electron-donating alkyl group at the *para* position of the *N*-phenyl group in the former.

The phosphorescence emission spectrum of **1a–g** in butyronitrile: *n*-butyl acetate, 95:5 v/v, at 77 K, shows vibrational resolution with maxima at 496, 518 and 558 nm. As for the fluorescence emission case, the excitation spectrum in all cases is similar to the corresponding absorption spectrum (Fig. 1B). As expected, no room temperature phosphorescence (RTP) emission was observed in solution.

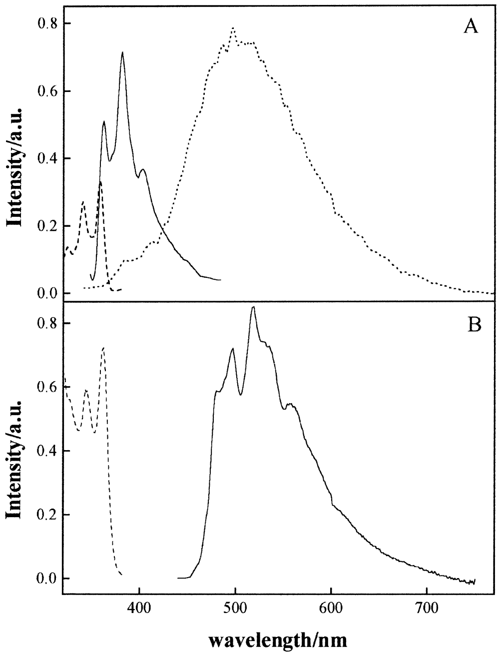


Fig. 1. (A) Fluorescence emission spectra for *N*-(*para*-*n*-dodecylphenyl)-2,3-naphthalimide (**1g**) in butyronitrile:*n*-butyl acetate (95:5) at room temperature (···) and at 77 K (—), and excitation spectrum (- - -) at 77 K of the fluorescence emission. (B) Phosphorescence emission (—) and excitation (···) spectra for **1g** in butyronitrile:*n*-butyl acetate (95:5) at 77 K.

Table 1
Fluorescence and phosphorescence emission data for **1a**–**g** in acetonitrile solution and for solid complexes with β-CD at room temperature

Imide	Φ_{fluo} in ACN	Φ_{isc} in ACN	Fluorescence (room temperature)		Phosphorescence (room temperature)	τ_{fluo}[a] in β-CD (ns)
			λ_{max} (ACN) (nm)	λ_{max} (β-CD) (nm)	λ_{max} (β-CD) (nm)	
1a	0.005	0.24	480	440	–	3.0
1b	0.0029	0.092	510	446	–	2.0
1c	0.0027	0.101	510	476	490, 562	2.3
1d	–	0.096	510	476	492, 530	2.2
1e	0.0031	0.096	510	452	495, 543	2.0
1f	0.0029	0.088	510	476	–	1.9
1g	0.0027	0.096	510	490	–	1.6

[a] Errors: ±10%.

3.2. Solution quantum yields

Despite the absence of any effect on the shape of the emission spectra of **1a** upon *para*-alkyl substitution (see above), quantum yield determination for the long-wavelength fluorescence emission show a slight decrease for **1b**–**g** ($\Phi_{fluo}\approx0.003$) when compared to **1a** ($\Phi_{fluo}\approx0.005$). A more substantial decrease was observed for the intersystem crossing quantum yield (Φ_{isc}). Thus, for the substituted imides a value close to 0.1 was measured in all cases, whereas for **1a** a $\Phi_{isc}=0.24$ was obtained (Table 1).

This clear effect on both the fluorescence and the triplet quantum yields with the *para*-alkyl substitution on the *N*-phenyl group can be explained by assuming that the presence of the alkyl group leads to an increase of the internal conversion rate constant at the expenses of both fluorescence and intersystem crossing efficiency. Since fluorescence and intersystem crossing quantum yields do not decrease in the same ratio, and the long-wavelength fluorescence emission arises only from one of the singlet excited states [1], this indicates that the triplet excited state of **1a**–**g** is not exclusively populated from the long-wavelength emitting excited state.

3.3. Characterization of the solid complexes **1*a*–*g***/*β-CD*

3.3.1. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

The DRIFT spectra of pure β-CD and **1a**/β-CD solid complex (molar ratio 1:10) are compared in the region 1550–1800 cm^{-1}, in Fig. 2A. The spectra were normalized to the most intense band of β-CD, at ~1032 cm^{-1} (not shown in the figure). In the β-CD spectrum, the only band observed in this region is broad, with maximum absorption at ~1653 cm^{-1} and is assigned to the deformation mode ($\delta_{H\text{–}O\text{–}H}$) of crystallization water present in the cyclodextrin cavity. In the spectrum of the complex, this band is largely reduced, indicating that the naphthalimide has occupied part of the β-CD cavity, displacing water molecules. This is a clear indication that an inclusion complex has been formed. A similar effect was observed for all the complexes between *N*-(*para*-alkylphenyl)-2,3-naphthalimides and β-CD studied in this work.

The naphthalimide/β-CD interactions, responsible for the formation of the inclusion complex, can be inferred from the modifications of the infrared spectra of the naphthalimide when the complex is formed. More specifically the band for the carbonyl group was monitored. For this purpose, the DRIFT spectra of the mechanical mixtures of **1a**, **1d** and **1g** with β-CD were compared with those of the respective solid complexes which is shown in Figs. 2B and 3, respectively. These spectra were normalized to the maximum of the carbonyl band.

The spectrum of the mechanical mixture between **1a** and β-CD is a superposition of those of the two compounds [20]. The bands at 1777 and 1717 cm^{-1} are assigned to the strongly coupled carbonyl stretching modes of **1a**, in-phase (symmetric) and out-of-phase (anti-symmetric) [32],

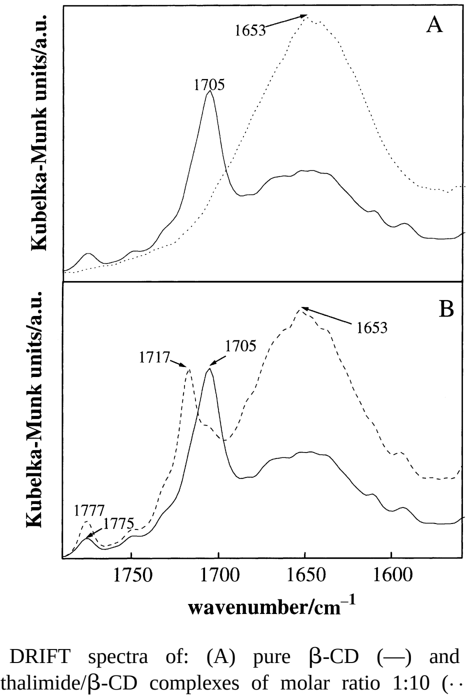


Fig. 2. DRIFT spectra of: (A) pure β-CD (—) and *N*-phenyl-2,3-naphthalimide/β-CD complexes of molar ratio 1:10 (···) normalized to the more intense band of β-CD (1032 cm^{-1}, not shown); (B) *N*-phenyl-2,3-naphthalimide (**1a**) and β-CD mechanical mixture (- - -) and **1a**/β-CD complex (molar ratio 1:10) (—), normalized to 1 in the carbonyl stretching band.

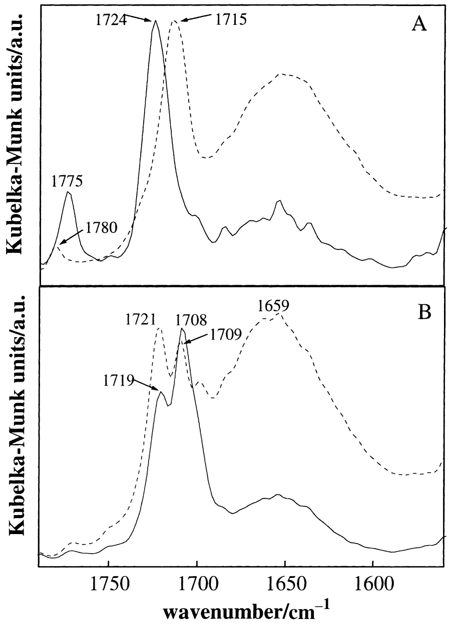


Fig. 3. DRIFT spectra of: (A) *N*-(*para*-*n*-hexylphenyl)-2,3-naphthalimide (**1d**) and β-CD mechanical mixture (- - -) and **1a**/β-CD complex (molar ratio 1:10) (—), normalized to 1 in the carbonyl stretching band; (B) *N*-(*para*-*n*-dodecylphenyl)-2,3-naphthalimide (**1a**) and β-CD mechanical mixture (- - -) and **1a**/β-CD complex (molar ratio 1:10) (—), normalized to 1 in the carbonyl stretching band.

respectively. Since the two C=O groups are coplanar and form a wide angle, the symmetric stretch originates smaller dipole variations than the anti-symmetric and consequently is weaker. The two wavenumbers are characteristic of carbonyl groups subject to the strain of a five member ring and involved in a resonant system [33]. Since the two moieties of this naphthalimide are not coplanar, the resonance is not extended to the phenyl group. In the spectrum of the solid complex, the out-of-phase band is shifted to a lower wavenumber (~12 cm^{-1}), which is a good indication that the carbonyl groups are involved in hydrogen bonds with the β-CD hydroxyl groups. The symmetric mode, although less sensitive to these bonds, is also informative on the molecular geometry. Its intensity decreases in the complex, indicating that the C=O groups vibrate in more opposite directions than in the crystals (this mode becomes more forbidden). This geometrical adjustment is induced by the short range repulsions between the carbonyl groups and the phenyl substituent, which arise from a more planar conformation of the whole molecule extending the resonant system to the phenyl group. In fact, when the resonant system is reduced, a large blue shift of the carbonyl stretching band occurs, which offsets the hydrogen bond effect. This is clearly not the case. Therefore, the DRIFT data point to the naphthalimide **1a** undergoing some conformational change towards a more planar conformation when the inclusion complex with β-CD is formed. Similar effects were observed for the naphthalimide **1b**.

Comparing the DRIFT spectra of the mechanical mixtures of the naphthalimides **1a** and **1d** with β-CD (Figs. 2B and 3A, respectively), we observe that the *para*-alkyl substitution on the *N*-phenyl group does not have a significant influence on the frequency of the carbonyl stretching modes. Indeed, the out-of-phase mode appears at 1717 cm^{-1} for **1a** and at 1715 cm^{-1} for **1d**. A similar effect, or rather, absence of effect, was observed for the diffuse reflectance ground state spectra of these compounds in solution (see below).

The DRIFT spectrum of the **1d**/β-CD complex (Fig. 3A) shows that the out-of-phase carbonyl stretching mode of **1d** is strongly affected by the inclusion into β-CD, being shifted to higher wavenumbers (from 1715 to 1724 cm^{-1}). Since it was shown above that the naphthalimide moiety is included in the β-CD cavities, this shift probably occurs because the vibrational mode in the complex is influenced by the two opposite effects already referred to above: hydrogen bonding formation with the β-CD hydroxyl groups, resulting in a shift to lower wavenumbers, superimposed by an increase of the C=O bond force constant due to the reduction of the resonant system. This is a clear indication that the phenyl group rotates towards a more orthogonal position relatively to the naphthalimide moiety of the molecule upon inclusion. Other simultaneous effects reinforce this conclusion, such as the relative intensity increase of the in-phase C=O mode, which occurs when the angle C–N–C in the naphthalimide is reduced. In other words, the phenyl group seems to assume a more orthogonal position, reducing the short range repulsion with the carbonyls. The smaller value of $\Delta\nu$ between the maxima of the two bands corresponding to the carbonyl also indicates that the C=O modes are less coupled, i.e., the two carbonyl groups are less coplanar in the complex, possibly due to the proximity of a second β-CD molecule. This behavior was also observed for the complex **1e**/β-CD.

In the case of naphthalimide **1g**, there is the possibility of the long alkyl chain to bend over, even in the crystalline phase, leading to different dipolar interactions with the two carbonyl groups. As a result, the coupling between the two C=O stretching modes is lost. In fact, the DRIFT spectrum of the mechanical mixture of **1g** and β-CD shows a doublet of similar intensities (at 1709 and 1721 cm^{-1}, Fig. 3B), assigned to the stretching modes of two carbonyl groups in different environments.

The DRIFT spectrum of **1f**/ and **1g**/β-CD complex do not show significant band shifts compared to their mechanical mixtures. Apparently, in these two cases, there are no important conformational changes in the naphthalimide upon inclusion in the β-CD cavities, neither the formation of hydrogen bonds with the β-CD hydroxyl groups. However, the relative intensities of the two bands in **1g** change drastically. This led to the conclusion that the alkyl chain is also included in the same cavity as the naphthalimide group, causing a steric hindrance to the stretching of the closest carbonyl group and preventing the formation of the highly directional hydrogen bonds. Nevertheless, since the two

C=O modes are not coupled, no information on the coplanarity of the molecule can be drawn from these spectra.

It is clear from the changes in the DRIFT spectra that the inclusion complexes between **1a–g** and β-CD were formed, with significant reduction in the amount of water in β-CD cavities. The three cases analyzed here are examples of three different behaviors: hydrogen bond formation with increase in planarity (**1a** and **1b**), hydrogen bond formation with the complex imide acquiring a more orthogonal conformation (**1c**, **1d** and **1e**) and inclusion of the long alkyl substituent in the cavity without evidence of hydrogen bond formation (**1f** and **1g**).

A more detailed, quantitative analysis of the DRIFT spectra of the *N*-(*para*-alkylphenyl)-2,3-naphthalimides **1a–g** and involving the deconvolution of their main bands, which is beyond the scope of this work, will be described elsewhere [34].

3.4. Ground state diffuse reflectance spectra

Ground state diffuse reflectance spectra for the complexes **1a–g**/β-CD show that the spectral properties of these complexed imides depend on the chain length of the alkyl group substituted in the *para* position of the *N*-phenyl ring. Thus, the complexes **1a**/, **1b**/, **1f**/, and **1g**/β-CD display a broad and slightly red-shifted absorption band (Fig. 4) when compared to the vibrationally resolved absorption spectrum for **1a** in acetonitrile. This shift is much more significant for the complexes **1f**/ and **1g**/β-CD, and is a clear indication that the ground state conformation of these naphthalimides complexed with β-CD is more planar than in solution. These results are fully in accord with the inclusion of the naphthalimide moiety inside the cyclodextrin cavity.

The complexes formed between **1c–e** and β-CD show a significantly different behavior (Fig. 4). The two band progression in the visible region of the diffuse reflectance ground state spectrum of these imides perfectly matches those observed in solution. The absorption results clearly indicate that in these complexes the naphthalimide chromophore and the phenyl group are still in an orthogonal geometry even after inclusion into the β-CD cavity.

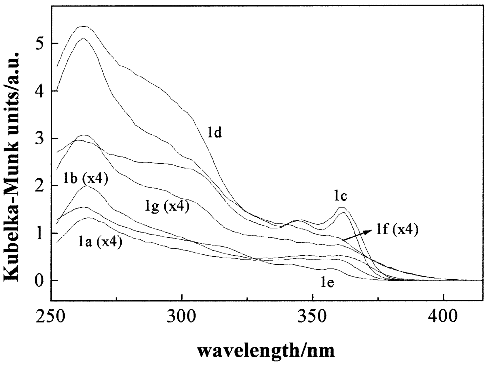


Fig. 4. Ground state diffuse reflectance spectra for the complexes **1a–g**/β-CD. *Inset*: absorption spectrum for **1a** in acetonitrile.

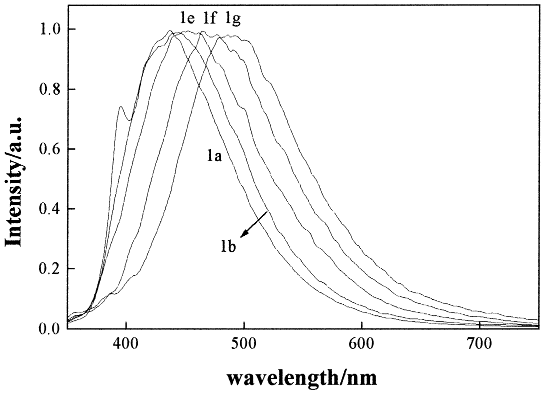


Fig. 5. Normalized fluorescence emission spectra for solid complexes between **1a**, **1b**, **1e–g** and β-CD.

3.5. Laser induced luminescence spectroscopy

The emission spectrum of the inclusion complex of *N*-phenyl-2,3-naphthalimide (**1a**: R=H) with β-CD, induced by nitrogen laser excitation in a nanosecond time-scale, shows a strong band with maximum at 440 nm (Fig. 5). *para*-Alkyl substitution on the *N*-phenyl ring of **1**, i.e. **1b–g**, leads to a red shift fluorescence of the β-CD solid complex, which is dependent on the alkyl chain length (Table 1). Thus, the introduction of an ethyl group in **1a** results in a fluorescence emission at 446 nm, whereas a much more pronounced effect could be observed for n-$C_{12}H_{25}$ (λ_{max}=490 nm) (**1g**). However, it is important to note that the fluorescence emission maximum for these complexes, in all cases, shows a significant blue shift when compared to the fluorescence emission of the corresponding imide in solution.

Previous work in the literature for *N*-phenyl-2,3-naphthalimide reported lifetimes of $\leq$50 ps for the short (weak emission, $\Phi_{fluo}\leq 0.0002$, λ_{max}=370, 385 nm) and 1.3 ns for the long-wavelength emission (broad and structureless emission, $\Phi_{fluo}=0.005$, λ_{max}=480 nm) [1]. From these data, the origin of the fluorescence emission from these complexes can be explained by two alternatives: either the β-CD cavity imposes some restriction to nitrogen–phenyl bond rotation, and the emission is not coming from a fully coplanar phenyl-2,3-naphthalimide conformation, or there is a strong effect on the short wavelength emission caused by cyclodextrin complexation, resulting in an extremely large red shift. To differentiate between these alternatives, fluorescence lifetime (τ_{fluo}) measurements were performed for the solid complexes between the naphthalimides and β-CD. Single photon-counting experiments show values for τ_{fluo} in the range 1.6 ns (**1g**/β-CD) to 3.0 ns (**1a**/β-CD) (Table 1), close to those reported for the long-wavelength state of *N*-phenyl-2,3-naphthalimide in acetonitrile [1].

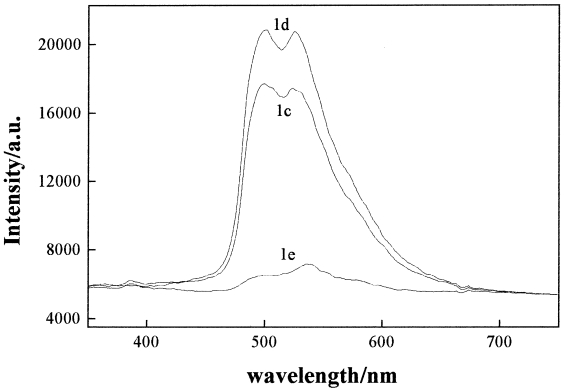


Fig. 6. Room temperature phosphorescence emission spectra for the solid complexes between **1c**–**e** and β-CD (λ_{exc}=337 nm), recorded 1 μs after the laser pulse.

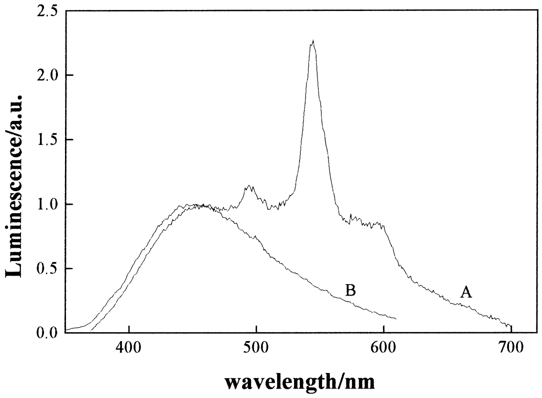


Fig. 7. Luminescence spectra of *N*-(*para*-*n*-octylphenyl)-2,3-naphthalimide (**1e**) complexed with β-CD in different conditions. (A) Total luminescence at 77 K; (B) laser induced fluorescence at room temperature.

Assuming that fluorescence lifetimes are not affected by cyclodextrin complexation, as previously observed for *N*-alkyl-2,3-naphthalimides [3], these data confirm the involvement of the coplanar conformation of the naphthalimides **1a**–**g** as the fluorescence emitting species. Fluorescence lifetimes and fluorescence quantum yields (Table 1) for the solid complexes **1a**–**g**/β-CD exhibit slightly increased values when compared to those observed in solution. This is in accordance with previous results for solid samples where the non-radiative mechanisms of excited state deactivation are reduced relative to the case of solution samples.

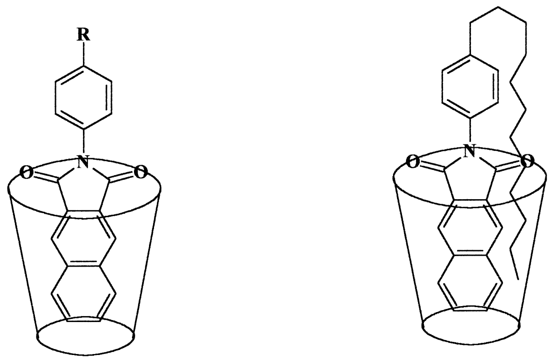
RTP spectra for the complexes **1c**,**d**/β-CD in non-degassed samples show some vibrational resolution with maxima at 492 and 526 nm (Fig. 6). These spectra are similar to those recorded in rigid glass at 77 K. Phosphorescence spectrum for the complex between **1e**/β-CD showed only a weak band at 535 nm (Fig. 6). For the other complexes, an extremely low intensity emission was detected under these conditions.

Total luminescence spectra recorded under steady state conditions at 77 K for complexes **1c**–**e**/β-CD show, besides the above cited phosphorescence emission, a new broad band with maximum around 480 nm for **1c/** and **1d**/β-CD, and 455 nm for **1e**/β-CD. This emission perfectly matches the fluorescence emission displayed by these complexes at room temperature and arising from the planar conformation of the naphthalimide. Furthermore, the expected structured fluorescence emission in the short-wavelength part of the spectrum, and due to the fully orthogonal conformation for the imide, was not observed for these complexes at 77 K. Representative low temperature total luminescence and phosphorescence spectra are shown in Fig. 7, taking the complex *N*-(*para*-*n*-octylphenyl)-2,3-naphthalimide (**1e**)/β-CD as an example.

The ground state absorption and emission spectra together with the infrared data described above allow us to propose possible structures for the complexes between **1a**–**g** and β-CD. From the above data, it is clear that in all cases the fluorescence emission is blue shifted when compared to those observed in acetonitrile solution. The fluorescence emission at 480 nm for **1a** and at 510 nm for **1b**–**g** in this solvent arise from a fully coplanar conformation of these compounds. The blue shift observed for the cyclodextrin complexed naphthalimides indicates that a completely planar conformation is not achieved for any of these guests. This suggests that the inclusion process leads to a restriction on the conformational mobility of the naphthalimides. Thus, the β-CD is imposing a decrease in the degree of freedom of the nitrogen–phenyl bond rotation.

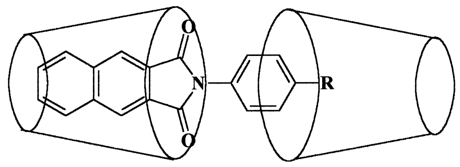
These results can be interpreted in terms of a preferential complexation of a given conformer of the 2,3-naphthalimides in the ground state, with the structure of the complex being dependent on *para*-alkyl substitution on the *N*-phenyl ring of these compounds. Different dihedral angles between the *N*-aryl group and the 2,3-naphthalimide moiety must lead to different degrees of extended conjugation between these two chromophores. Thus, for **1a**/β-CD and **1b**/β-CD one can suggest a geometry for their inclusion complexes in which the naphthalimide moiety is deeply included into the cyclodextrin cavity (Fig. 8A). It is very well known that naphthalenes substituted in the 2′-position are axially and deeply included into the β-CD cavity [35–37]. The fluorescence emission from those complexes is probably arising from a preferential conformation of the 2,3-naphthalimides and having some coplanarity degree in the ground state. This conformation could be stabilized by some sort of interaction between the hydroxyl groups located at the entrance of the cyclodextrin cavity and the *N*-phenyl group [38].

Complexes **1f**/β-CD and **1g**/β-CD probably have similar inclusion modes to **1a** and **1b**. However, in the former cases, both the naphthalimide chromophore and part of the alkyl chain must be included into the β-CD cavity (Fig. 8B). As already reported for *N*-alkyl-2,3-naphthalimides [3], the strong hydrophobicity of the alkyl chain favors such conformation. For these two cases the blue shift observed when comparing the fluorescence emission from the complexes



(A) 1a, b
(R=H; n-C_2H_5)

(B) 1f, g
(alkyl: n-$C_{10}H_{21}$; n-$C_{12}H_{25}$)



(C) 1c-e
(R=n-C_4H_9; n-C_6H_{13}; n-C_8H_{17})

Fig. 8. Possible structures for the complexes between **1a**,**b**/β-CD (A); **1f**,**g**/β-CD (B) and **1c**–**e**/β-CD (C).

with those in acetonitrile solution could be due to the rigidity imposed to the probe by the alkyl chain in the complex. This would be more important for **1f** than for **1g**, due to the shorter alkyl chain length of the former. That is why the observed blue shift is larger for **1g**.

The solid complexes **1c**/β-CD and **1d**/β-CD show fluorescence emission at 476 nm, whereas for **1e**/β-CD the maximum for this emission is at 452 nm. It is important to note that for the imides *N*-(*para*-*n*-butylphenyl)- (**1c**), *N*-(*para*-*n*-hexylphenyl)- (**1d**) and *N*-(*para*-*n*-octylphenyl)-2,3-naphthalimide (**1e**) the *para*-*n*-alkylphenyl end is as strongly hydrophobic as the longer chains *n*-decyl or *n*-dodecyl in **1f** and **1g**, respectively. This suggests that this part of the molecule is also able to perform a preferential complexation with the cyclodextrin. In accord with these, molecular models clearly show that unlike **1f** and **1g** the alkyl chain in **1c**–**e** is too short to fold over and co-include into the cavity containing the naphthalimide moiety. Therefore, a complex 1:2 between **1c**–**e** and β-CD, in which the stretched alkyl chain is included in one cyclodextrin cavity and the naphthalimide group into the other, better explains their spectroscopic behavior (Fig. 8C).

It was recently shown that the space between two cyclodextrins forming a head-to-head dimer, and stabilized by hydrogen bonds, provides a specially hydrophobic environment for an included probe [39]. Thus, in the present case, 1:2 complexes between **1c**–**e** and β-CD would allow a special protection of the naphthalimide moiety against quenching by oxygen and other species, at the same time providing a hydrophobic site for the imide location. This protection would explain the observation of RTP for the complexes between each of these three imides and β-CD.

Furthermore, it seems that in these 1:2 complexes there is a chance of free rotation for the *N*-aryl group bound to the naphthalimide chromophore in the Franck–Condon excited state, even at 77 K. This can be seen by inspecting the low-temperature total luminescence spectrum of **1c**–**e**/β-CD, in which only the long-wavelength fluorescence emission is observed. Such intramolecular mobility was already reported for probes adsorbed on silica at 77 K [40].

For **1e**/β-CD an alternative inclusion mode, similar to that described for the complexes **1f**/ and **1g**/β-CD (Fig. 8B) can be proposed. Molecular models show that for **1e** at least the methyl group located at the end of the alkyl chain is able to be included in the CD cavity. The existence of two different inclusion modes for this imide would explain the reason why the ground state absorption spectrum for the solid complex **1e**/β-CD does not show a vibrational progression similar to that of **1c**/ and **1d**/β-CD. It would also explain the very weak RTP observed for the former complex.

4. Conclusion

In conclusion, this work presents combined IR and UV diffuse reflectance results that show that *N*-(*para*-alkylphenyl)-2,3-naphthalimides **1a**–**g** readily form inclusion complexes with β-CD. From these results it was suggested that three types of inclusion complexes may be formed: (i) those where the phenyl substituent is a H atom (**1a**) or an ethyl group (**1b**), in which the inclusion complex is stabilized by hydrogen bonds involving the carbonyl groups of the imide and the hydroxyl groups of β-CD, with the phenyl moiety coplanar to the naphthalimide chromophore; (ii) those where the alkyl group is *n*-butyl (**1c**), *n*-hexyl (**1d**), or *n*-octyl (**1e**), in which hydrogen bonds are involved in the formation of the inclusion complex, but showing an orthogonal conformation between phenyl and naphthalimide groups, with these two moieties possibly included in two neighbor β-CD molecules, and (iii) those where the alkyl group is *n*-decyl (**1e**) or *n*-dodecyl (**1f**), in which the inclusion complex is formed with the long alkyl chain in the same cavity as the naphthalimide moiety. The fluorescence emission spectra for these complexes are dependent on the *n*-alkyl substitution on the *para* position of the *N*-phenyl ring and were associated to a coplanar conformation of the 2,3-naphthalimides in the β-CD complex. The observation of RTP for some of these complexes, namely **1c**/, **1d**/ and **1e**/β-CD, strongly suggests the formation of inclusion complexes of the type 1 guest: 2 hosts in these three cases.

Acknowledgements

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