PERKIN 2

Influence of cyclodextrins on the fluorescence of some short and long chain linked flexible bisbenzenes in aqueous solution

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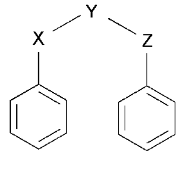
The UV absorption, induced circular dichroism (icd) spectra, steady state and time resolved fluorescence emission of the flexible bisbenzenes **1**–**4** were obtained in aqueous solution and in presence of α-, β-, and γ-cyclodextrin (CD). Bisbenzenes **1** and **2** in an aqueous environment exhibit a dual emission which is differently affected by the CDs. The long-wavelength emission is quenched by α- and β-CD and enhanced by γ-CD. This is due to the formation of inclusion complexes between the CDs and **1** (**2**) in the ground state, in agreement with the modifications of the UV spectrum and the appearance of icd signals. On the basis of these effects and of the influence of the CDs on the **1** and **2** lifetimes, the dual emission of these bisbenzenes is attributed to a set of different ground-state conformations.

Introduction

Multiple emission is a general phenomenon in non conjugated bichromophoric aromatic systems exhibiting conformational flexibility.[1–4] Bichromophoric systems have been used as references to study multichromophoric interactions in polymers and molecular assemblies[4–6] and have been found particularly efficient as signalling subunits in some photoresponsive systems for the detection of ions and molecules.[7,8] When the two chromophores are the same, an excimer-like emission can be observed. Combined steady-state and time-resolved measurements can give information about the nature of the interaction originating the excimer-like emission indicating, *inter alia*, whether the interaction occurs between the chromophores in an intramolecular ground state complex (denoted "*dimer*", as one refers to the chromophores and not to the molecule) leading to an excited "*dimer*", or takes place only in the excited state (true excimer).

Early studies of α,ω-diphenylalkanes by Hirayama[9] have shown that three-member alkane spacers favour excimer formation. Additional investigations on other short-chain-linked bisbenzenes, see Chart 1,[10] demonstrated that the flexibility of the chain or/and the inclusion of the compounds in micelles or cyclodextrins also induces the formation of excimer-like species.

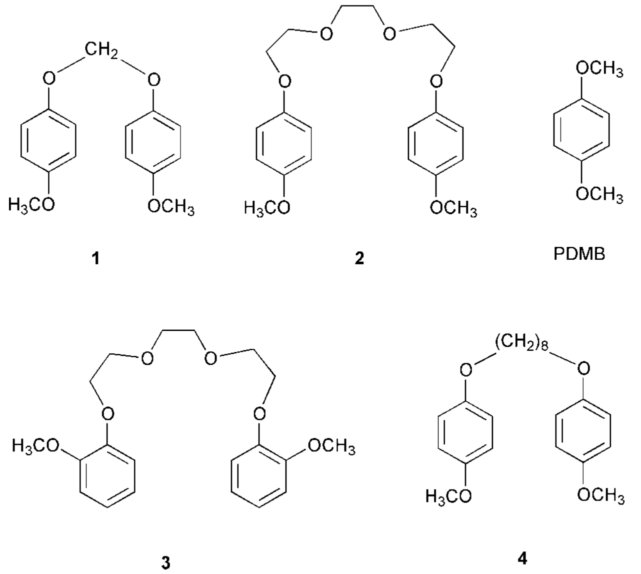


X	Y	Z	ref
CH_2	CH_2	CH_2	9
CH_2	O	CH_2	10
CH_2	NH_2^+	CH_2	10
O	CH_2	O	12
O	PO_2^-	O	21

Chart 1 Bisbenzenes with a three membered spacer previously studied by fluorescence.

Particularly flexible compounds such as diphenoxymethane and related derivatives have been thoroughly studied in solution (methylcyclohexane and methanol)[11] and in supersonic gas phase expansion by spectroscopy and theoretical calculations.[12,13] In solution, the fluorescence properties were found to be in agreement with the formation of intramolecular excimers: these latter were not detected in the gas phase, but the existence of two conformers was demonstrated.[13]

A striking feature of the examined compounds was that neither the UV absorption nor the fluorescence excitation spectra gave significant indications of the existence of ground-state bichromophoric ("*dimer*") interactions. It was anticipated that these interactions could be exhibited in aqueous solutions in the presence of cyclodextrins (CD) and evidenced by induced circular dichroism. Indeed, recent extensive studies have shown that *p*-dimethoxybenzene (PDMB in Chart 2) can form inclusion



1 **2** PDMB

3 **4**

Chart 2 Bisbenzenes examined in the present study; *p*-dimethoxybenzene (PDMB) is the reference monochromophoric compound for **1**, **2** and **4**; the reference for compound **3** is *o*-dimethoxybenzene.

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complexes with CDs.[14] We set out to extend this investigation to the bisbenzene **1** (Chart 2), and to the bichromophores **2**–**4**, having long chain spacers (10 atoms). Compound **2** has the potential to form a pseudo crown ether (see Scheme 1) with γ-CD if a 1 : 1 complex is favoured, owing to the helical conformation of polyoxyethylene chains.[15] In contrast **3**, for steric reasons, and **4**, due to chain rigidity, are not expected to have the same behaviour.

In this paper we refer to the existence of multiple conformations in bisbenzenes **1**–**4** in aqueous solution as evidenced by their steady state and time-resolved fluorescence emission in the presence of cyclodextrins (CD). The most common cyclodextrins (α-, β-, and γ-CD) possess cavities of different size (inner diameter varying between ~5 Å for α-CD and ~8.5 Å for γ-CD), are able to confine a large variety of molecules and consequently can modify their ground- and excited-state behaviour.[16] In particular, the complexation of bichromophoric molecules by CD can favour or prevent the intramolecular interaction according to the CD dimensions. α- and β-CDs generally induce a reduction of the excimer-like fluorescence while the larger γ-CD causes an increase of such emission.[17–24] The formation of inclusion complexes was also evidenced by UV-absorption and induced circular dichroism (icd) spectroscopy.

Experimental

Synthesis

Bis(p-anisyloxy)methane (**1**) was reported in ref. 11. We describe below new and more convenient preparations of **2**, **3**, and **4**.

1,8-Bis(p-anisyloxy)-3,6-dioxaoctane (**2**). In a round bottomed flask fitted with a stirrer, a reflux condenser and isolated from moisture, 4.96 g (0.04 mol) of *p*-hydroxyanisole, 7.4 g (0.02 mol) of 1,8-diiodo-3,6-dioxaoctane, prepared according to reference,[25] and 27.6 g (0.2 mol) of dry K_2CO_3 were added to 300 mL of acetone (freshly distilled on P_2O_5) bubbled with nitrogen. The mixture was refluxed under vigorous stirring for 3 days and filtered; the filtrate was evaporated under reduced pressure and the oily residue was dissolved in CH_2Cl_2; the resulting solution was washed with aqueous $Na_2S_2O_3$ and dried over Na_2SO_4. After solvent evaporation, the brown residue was chromatographed on a silica column (eluent light petroleum ether–diethyl ether 1 : 3) and the white solid obtained recrystallized from a light petroleum ether–CH_2Cl_2 mixture (50 : 1) as pearly flakes mp 72 °C (yield 5.1 g, 70%).[‡] δ [$CDCl_3$] 3.9 (6H + 4H, s), 3.9–4.6 (8H, m), 7.05 (8H arom., app. s); ν_{max} (KBr)/cm^{-1} 3040, 3010, 2900, 1860, 1620, 1500, 1459, 1380, 1330, 1285, 1220, 1130, 1050, 1025, 925, 880, 820, 730, 525; *m*/*z* 362 ($M^{+\bullet}$ 62%), 195 (15), 151 (100) (Found C, 66.47; H, 7.12; O, 26.78. $C_{20}H_{26}O_6$ requires C, 66.3; H, 7.18; O, 26.52%).

1,8-Bis(o-anisyloxy)-3,6-dioxaoctane (**3**) was synthesized starting from 4.96 g (0.04 mol) of *o*-hydroxyanisole and 7.4 g (0.02 mol) of 1,8-diiodo-3,6-dioxaoctane, using the same procedure as for **2**. After chromatography on a silica column, 6.0 g, 83%, of a white solid, mp 84–86 °C (remelts 67 °C), were obtained; lit.,[§] 75–77°,[28] 67–83°.[29] δ [$CDCl_3$] 4.2 (4H, s), 4.3 (6H, s), 4.1–4.6 (8H, m), 7.1 (8H arom. app. s); ν_{max} (KBr)/cm^{-1} 3060, 2880, 1595, 1510, 1360, 1340, 1300, 1265, 1235, 1195, 1060, 1030, 995, 915, 830, 780, 755; *m*/*z* 362 ($M^{+\bullet}$, 18%), 151 (100) (Found C, 66.26; H, 7.24; O, 26.26. $C_{20}H_{26}O_6$ requires C, 66.3; H, 7.18; O, 26.52%).

1,8-Bis(p-anisyloxy)octane (**4**) was prepared starting from 4.96 g (0.04 mol) of *p*-hydroxyanisole, 5.44 g (0.02 mol) of 1,8-dibromooctane and using the same procedure as for compound **2** (white crystals mp 132–133 °C, 67% yield: lit. 131–132 °C[30]). δ [$CDCl_3$] 1.8–2.4 (12H, s), 4.2 (6H, s), 4.5 (4H, t), 7.2 (8H arom. app. s); ν_{max} (KBr)/cm^{-1} 2940, 2860, 1860, 1515, 1470, 1400, 1300, 1250, 1180, 1120, 1045, 1000, 950, 835, 770, 750, 550, 520; *m*/*z* 358 ($M^{+\bullet}$, 25%), 124 (100%) (Found C, 73.44; H, 8.17; O, 17.98. $C_{22}H_{30}O_4$ requires C, 73.74; H, 8.38; O, 17.88%).

Structure determination and characterization

Melting points were measured by projection using a Kofler block and are uncorrected. Infrared spectra were recorded with a Perkin-Elmer 412 apparatus. NMR spectra were taken with a 60 MHz Hitachi Perkin-Elmer R-24B in $CDCl_3$ (internal reference Me_4Si). Mass spectra were obtained by using a VG Micromass 70/72 type 16F instrument. Elemental analyses were performed at the Lyon CNRS Service Central d'Analyses.

Photophysical experiments

α- and β-CD (Serva), γ- and 2,6-di-*O*-methyl-β-cyclodextrin (Aldrich) were used as received. Water was purified by passage through a Millipore MilliQ system. Aqueous solutions of the compounds were obtained by direct dissolution of the probe under stirring and moderate heating for 48 hours. The obtained solution was filtered and stored in the dark. The concentration of the dissolved probe was estimated from the UV absorption by comparison with the spectra obtained by dissolving the compounds in methanol and then diluting with water to obtain a $CH_3OH–H_2O$ (1/9, v/v) solution.

All the spectroscopic measurements were carried out in cells thermostatted at 20 ± 1 °C. UV absorption spectra were recorded on a Perkin-Elmer λ5 spectrophotometer. Circular dichroism spectra (icd) were obtained by a Jasco J-715 dichrograph. Fluorescence emission and excitation spectra were obtained using a Spex Fluorolog 111–2 spectrofluorometer. The equilibrium constants (K_a) for the formation of the inclusion complexes were obtained from the fluorescence intensity variations by exciting the solutions at the isosbestic point of the absorption spectra, when present, or where the difference between the absorption spectra is the smallest.

Fluorescence lifetimes were determined on air-saturated solutions by a time-correlated single photon counting system (IBH Consultants Ltd). The nanosecond flash-lamp, filled with deuterium, was thyratron driven at 40 kHz: the instrumental response function had a full width at half maximum of *ca.* 2 ns. The excitation was at 280 nm and the emission was collected at 320 nm or 385 nm. Due to the low count rates (the absorbance of the solutions was low because of the poor solubility in water of these compounds), the emission time profiles were obtained with a number of counts at the maximum ~2000, in order to keep the accumulation time below 1–1.5 hours, which allows a good enough instrumental stability. Fluorescence decays, described by one or a sum of two exponential components, were extracted from the emission signals by deconvolution of the instrumental response *via* a non-linear fitting procedure which uses the least-squares method. The software package was provided by IBH Consultants Ltd. Distribution of residuals, the Durbin-Watson parameter, and χ^2 were used to evaluate the goodness of the fit.

Emission quantum yields were estimated by using 1,4-dimethoxybenzene in water ($\varphi_f = 0.135$) as standard.[14] The quantum yields for the complexes were estimated on the basis of the fluorescence enhancement ratios in the presence of cyclodextrins (*vide infra*).

Results and discussion

Absorption and induced circular dichroism spectra

The UV-absorption spectra of the compounds **1**, **2** and *p*-dimethoxybenzene in water–methanol (90 : 10 by volume) at

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[‡] Compound **2** was mentioned in ref. 26.

[§] This product has been already synthesized according to a different procedure.[27] These Authors noted the dimorphism of **3**, mp 67 °C by crystallization in water or methanol and 83 °C by crystallization from a 1 : 1 mixture of ethyl acetate–petroleum ether or from CCl_4.

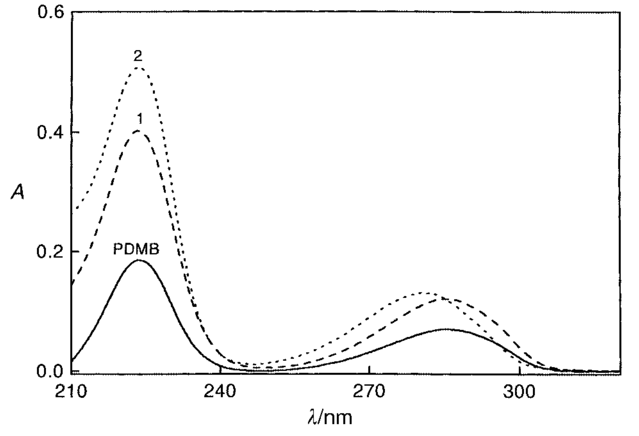


Fig. 1 Absorption spectra in CH_3OH–H_2O (10:90 v/v) of 2.7×10^{-5} mol dm^{-3} (——) 1,4-dimethoxybenzene; (······) compound **1**; (------) compound **2**; cells 1 cm thick.

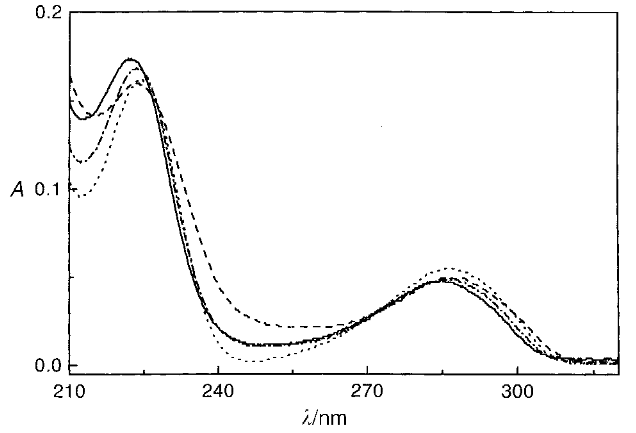


Fig. 2 Absorption spectra of **2**, $c = 4.65 \times 10^{-6}$ mol dm^{-3} in: (——) pure water; (— — — —) 10^{-2} mol dm^{-3} α-CD; (······) 10^{-2} mol dm^{-3} β-CD; and (------) 10^{-2} mol dm^{-3} γ-CD.

21 °C are shown in Fig. 1. The spectrum of **1** is characterized by a structureless band peaked at 281 nm, attributed to a S_0–S_1 (π,π*) transition, and an intense band with λ_{max} at 222 nm, attributed to the transition to the S_2 state. The position of the S_1 band is blue-shifted ($\Delta\nu \approx 620$ cm^{-1}) with respect to that of 1,4-dimethoxybenzene, $\lambda_{max} = 286$ nm, the model compound of **1**. The features of the absorption spectrum of **2** are more like those of 1,4-dimethoxybenzene: the S_1 band is blue-shifted only 1 nm ($\Delta\nu \approx 120$ cm^{-1}). For both **1** and **2**, the intensity of the integrated S_1 band is a little less than double that of 1,4-dimethoxybenzene. The blue shift of the **1** S_1 band with respect to that of 1,4-dimethoxybenzene indicates that the two *para*-dimethoxy-moieties linked by the methylene group do not behave as independent entities: an interaction between the aromatic rings and/or a decrease in conjugation between the oxygen lone-pairs and the aromatic π-clouds due to steric hindrance[13] could be responsible for the phenomenon.

For both **1** and **2**, the addition of cyclodextrins induces a 1–2 nm red-shift of the position of the S_1 and S_2 bands as shown in Fig. 2 for compound **2**. The red-shift of the UV spectrum induced by the cyclodextrins, similar to that observed for 1,4-dimethoxybenzene,[14] indicates that **1** and **2** experience an environment less H-bonding than water:[14] the formation of an inclusion complex between the CDs and the two probes accounts well for the observed effect. Induced circular dichroism provides a direct proof of the association between the two molecules and the CDs (*vide infra*).

The UV spectra of compound **3** and its model, 1,2-dimethoxybenzene, are practically superimposable ($\lambda_{max} = 272.5$ nm for the S_1 band and 222 nm for the S_2) and the intensity of the integrated band for **3**, double that of the model 1,2-dimethoxybenzene, indicates that the two aromatic groups in **3** behave as independent units. No appreciable effect of the CDs was observed on the UV spectrum of **3** and its model, 1,2-dimethoxybenzene. The extremely low solubility of **4** prevented our recording reliable spectra of this compound in water.

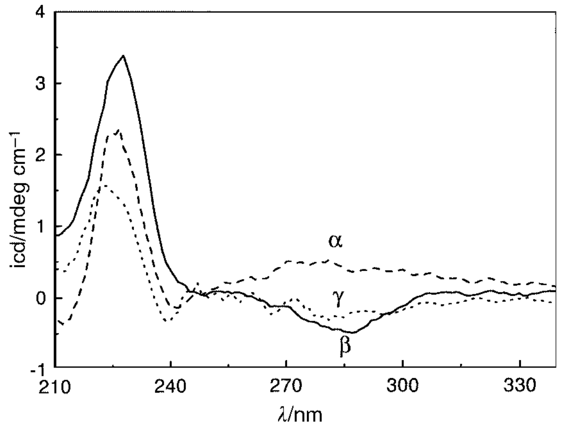


Fig. 3 Induced circular dichroism spectra of compound **1**, $c = 6.6 \times 10^{-6}$ mol dm^{-3} in presence of [α-CD] = 5×10^{-2} mol dm^{-3} (------); [β-CD] = 1×10^{-2} mol dm^{-3} (——); and [γ-CD] = 1×10^{-2} mol dm^{-3} (······). Cell path 5 cm.

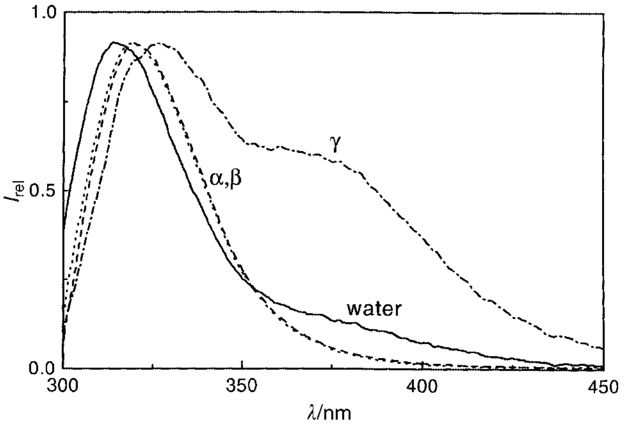


Fig. 4 Normalized fluorescence spectra of **2** in water (——); [α-CD] = 5×10^{-2} mol dm^{-3} (······); [β-CD] = 1×10^{-2} mol dm^{-3} (------); and [γ-CD] = 1×10^{-2} mol dm^{-3} (— — — —); [**2**] 1.09×10^{-5} mol dm^{-3}.

In the presence of all the CDs, compound **1** exhibits rather weak positive icd signals in the region of the S_2 absorption band. The icd signal is positive with α-CD and negative with the other cyclodextrins in the S_1 region (Fig. 3). Compound **2** shows qualitatively similar icd features, except for the intensity of the signal, which is slightly higher. The icd spectra of **1** and **2** in the presence of CDs are reminiscent of those observed in 1,4-DMB[14] and are therefore attributed to the formation of inclusion complexes. In the present case the weakness of the signals prevented any useful investigation of the dependence on the CD concentration.

Fluorescence emission

Study in the absence of cyclodextrins. The fluorescence spectrum of compounds **1** and **2** in water consists of a structureless band with a maximum at ≈315 nm and a low-intensity tail extending up to 450 nm (see Fig. 4). The intensity of the spectrum is not sensitive to the presence of oxygen. The fluorescence excitation spectra for the long- and the short-wavelength emission are identical to the absorption spectrum, pointing to a common origin of the two emission bands. The emission intensity is quenched and its spectral distribution modified by the addition of Ag^+ ions (not shown), the tail of the spectrum being much more efficiently quenched than the

Table 1 Emission quantum yields of the free molecules and the CD-complexes ($(CH_3)_2$-β-CD was investigated for the sake of comparison); time constants (τ) and integrated luminescence signals ($A\tau$) extracted by biexponential analysis of the emission time profiles; chi-square (χ^2); percentage of complexation in the time resolved experiments and association constants (K_a) of compounds **1** and **2** with the cyclodextrins

	φ_F[a]	τ_1/ns[b]	$A_1\tau_1$ (%)	τ_2/ns[b]	$A_2\tau_2$ (%)	χ^2	Complex (%)	K_a/dm^3 mol^{-1}[c]
1								
Water	0.05	0.65	97	6.0	3	1.5		
α-CD	0.21	2.6	73	0.5	27	1.4	67	40
β-CD	0.13	1.9[d,f]	95	118[f]	5	1.6	96	2600
$(CH_3)_2$-β-CD	0.14							7500
γ-CD	0.085	1.2	85	4.9	15	1.3	67	200
2								
Water	0.06	0.75	80	4.8	20	1.4		
α-CD	0.29	2.6	80	0.5	20	1.3	53	25
β-CD	0.13	2.1[e,f]	95	84[f]	5	1.6	81	430
$(CH_3)_2$-β-CD	0.155							680
γ-CD	0.02	0.65	74	4.4	26	1.1	88	900

[a] The values for the CD complexes are obtained from the ratios φ_b/φ_f (fluorescence quantum yields of bound and free molecules) extracted from best fittings based on eqn. (2). [b] Uncertainty ± 10%. [c] Uncertainty ± 20%. [d] If monoexponential analysis is applied $\tau = 2.0$ ns, $\chi^2 = 1.6$. [e] If monoexponential analysis is applied $\tau = 2.2$ ns, $\chi^2 = 1.2$. [f] Extracted by biexponential analysis. The extremely weak components of 118 ns (**1**) or 84 ns (**2**) should probably be considered as physically meaningless.

main band. At 77 K, in water–ethanol 50 : 50 by volume, the tail disappears and the emission of **1** and **2** consists of a band peaked at 311 and 314 nm, respectively, similar to that of 1,4-dimethoxybenzene ($\lambda_{max} = 315$ nm). These facts exclude the presence of impurities, pointing to the existence of only one chemical species in solution at room temperature.

The fluorescence decay of the two compounds was analyzed according to the scheme for the intramolecular excimer formation:[31]

$$1/\tau_o \leftarrow {}^1A^*\text{—}A \rightarrow {}^1(A^* \cup A) \rightarrow 1/\tau'_o$$

where τ_o and τ'_o are the decay times of the monomer and excimer, respectively. This scheme leads to the observation of double-exponential response functions for the monomer and the excimer emission, as in the classic case of the intermolecular excimer formation described by Birks.[32] Time resolved experiments confirmed the presence of two main components in the emission (Table 1) with $\tau_1 \sim 0.6$ ns and $\tau_2 \sim 6$ ns for **1** and $\tau_1 \sim 0.75$ ns and $\tau_2 \sim 5$ ns for **2**. Similar results were found in ethanol and *n*-hexane. In all the solvents inspected the short-lived component predominates as regards the integrated relative amplitude. In ethanol, due to better solubility, it was possible to obtain a reliable decay profile at 385 nm. Global analysis at 320 and 385 nm confirmed the applicability of a two exponential model with positive pre-exponential factors at both wavelengths, which excludes excimeric kinetics based on the Birks model.[32] Rather high χ^2 values (1.1–1.6) were obtained with the biexponential model, but the introduction of one more exponential component in the fitting function did not significantly improve the goodness of the fit. This led us to conclude that a distribution of emitting species with slightly different equilibrium geometries is most likely present in homogeneous solvents. Two main conformations, corresponding to a short-wavelength emitting monomer, and a long-wavelength emitting, dimer-like species, in which the two chromophores weakly interact, can be hypothesized. The statement that the Birks kinetics cannot be applied, in general, to intramolecular excimers,[33–36] because assemblies of different conformers are generally present, is in agreement with the present findings.

No double emission was detected for compound **3** whose fluorescence superimposes that of the model compound 1,2-DMB ($\lambda_{max} = 305$ nm). Similar results were obtained for **4**, but its fluorescence decay was determined only in *n*-hexane and ethanol owing to the inadequate solubility of the compound in water. A pure mono-exponential describes the fluorescence decays of **3** and **4**.

It is noteworthy that the two methoxybenzene units in **2**, **3** and **4** are linked together by a ten atom chain *i.e.* by a bridge which allows the easy formation of intramolecular excimers in α,ω-di-(pyren-1-yl)alkanes[35] without any detection of ground-state dimers.[36] However, within the series **1**–**4** the fluorescence decay of **1** and **2** is biexponential in the examined solvents: this suggests that the flexibility of the chain linking the *p*-methoxybenzene units in **1** and **2** is greater than that of the polymethylene sequence linking the two aromatics in **4**. Such a flexibility would favour conformations leading to the excimer-like emission. The single exponential decay of **3** could be attributed to steric interactions of the two *o*-methoxy groups, which should hamper an appreciable coupling of the aromatic rings.

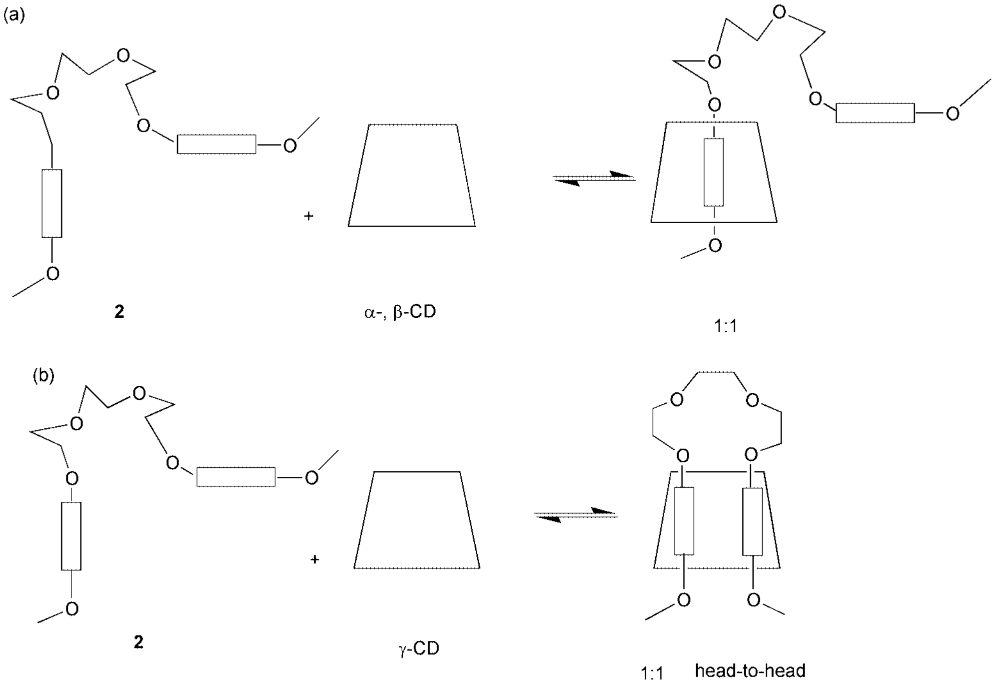
Study in the presence of cyclodextrins. A strictly similar effect on the fluorescence emission was observed for **1** and **2** in aqueous solutions by addition of cyclodextrins: a bathochromic shift of the emission maximum, shown in Fig. 4 for **2**, and a significant enhancement of the overall emission yield were observed in the presence of α-, β-, and dimethyl-β CD (investigated for the sake of comparison), shown in Fig. 5 for the couple **1**–β-CD. No effect of the CD addition was observed on the emission of **3**. The fluorescence variations, attributed to the formation of an inclusion complex between the CD and the probes, were well described by a model involving a 1 : 1 stoichiometry. In Table 1 are collected the association constants K_a, calculated by assuming that the ground-state equilibrium remains unchanged in the excited state. This hypothesis is reasonable because the singlet lifetime of the two molecules is a few nanoseconds and the dissociation of this type of complex is known to occur on the microsecond scale.[37–40] The integrated fluorescence emission, F, of a mixture of free (f) and bound (b) molecules is expressed by eqn. (1), where C is an instrumental

$$F = C(\varphi_f[f] + \varphi_b[b]) \qquad (1)$$

constant and φ_f and φ_b are the fluorescence quantum yields of the free and the bound molecules, respectively. When the cyclodextrin concentration is in large excess with respect to the emitting molecule eqn. (2) is obtained:[40]

$$F/F_o = \{1 + K_a(\varphi_b/\varphi_f)[CD]\}/1 + K_a[CD] \qquad (2)$$

which allows us to obtain K_a by a nonlinear least-squares fitting procedure (F_o is the emission in the absence of CD): in Fig. 5, the experimental points and the calculated curve are shown for the complex **1**–βCD.



Scheme 1

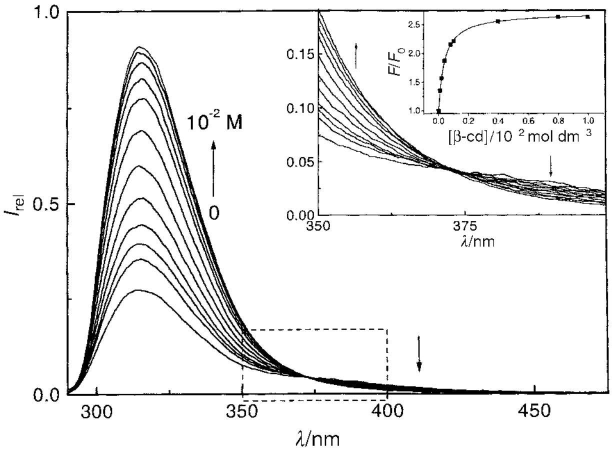


Fig. 5 Fluorescence variations of **1**, 6.6×10^{-6} M in water, following β-CD addition up to 10^{-2} mol dm^{-3}. The insert shows an expansion of the 350–400 nm region and a non-linear fitting of the experimental values of F/F_0 according to eqn. (2). Extracted parameters: $K_a = 2600$ mol^{-1} dm^3, $\varphi_b/\varphi_f = 2.7$.

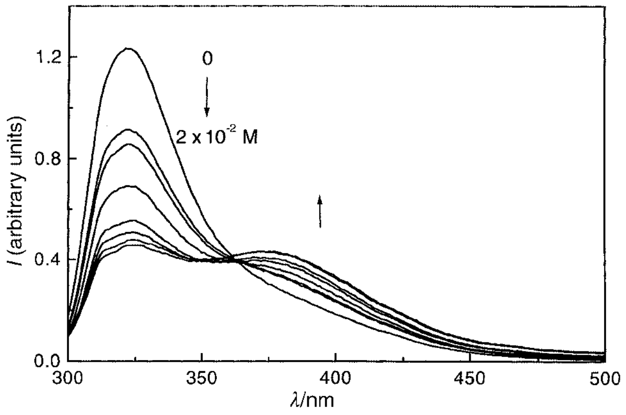


Fig. 6 Fluorescence variations of compound **2** following γ-CD addition up to 2×10^{-2} mol dm^{-3}.

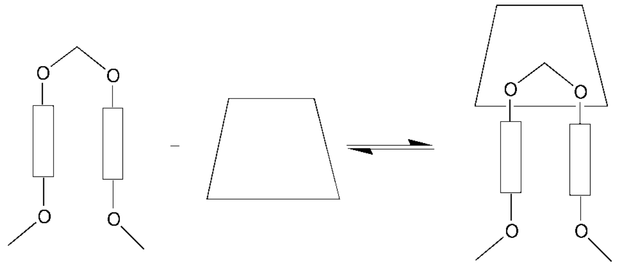
An enlargement of the fluorescence variations in the 350–400 nm range is reported in the inset of Fig. 5: it clearly shows that the long-wavelength emission is quenched by the addition of β-CD with the maintenance of an isolampsic¶ point at ~372 nm. This indicates that the inclusion in the cyclodextrin cavity inhibits the formation of the excimer-like species. The same behaviour was displayed by both **1** and **2**, both in the presence of α-CD and dimethyl-β-CD: a sketch of the structure proposed for these complexes is shown in Scheme 1a.

A different behaviour is displayed by the two molecules when γ-CD is added to the solution. The emission of **1** is slightly enhanced in both the short- and long-wavelength component, while for **2** the short-wavelength emission is quenched and the long-wavelength enhanced, as shown in Fig. 6. This could be indicative of a different mode of complexation of γ-CD with **1** and **2**. In the complex **2**–γ-CD the two aromatic rings are forced to attain a sandwich conformation thus explaining the increase of the excimer-like emission and the concomitant decrease of the monomeric one: the structure proposed for this complex is shown in Scheme 1b.|| A similar behaviour has been reported for bis(biphenyl-4-ylmethyl)ammonium chloride,[17] 2,2-bis(α-naphthylmethyl)-1,3-dithiane,[42] diphenyl phosphate[21] and the isomeric 1,11-bis(1-naphthyloxy)- and 1,11-bis(2-naphthyloxy)-3,6,9-trioxaundecane.[43] All the above compounds have a double emission in water whose long-wavelength component is enhanced in the presence of γ-CD. In the complex **1**–γ-CD, the cyclodextrin could cap the –O–CH$_2$–O– bridge without substantially reducing the rotational mobility of the aromatic rings (Scheme 2). In agreement with the suggested structures are the substantial invariability of the UV spectrum of **1** after γ-CD addition and, conversely, the red-shift of the **2** spectrum which ensues on CD complexation.

Lifetime analysis of the **1** and **2** fluorescence in presence of CD was performed at $\lambda_{em} = 320$ nm and the data are collected in Table 1. In presence of α- and β-CD the behaviour of **1** and **2**

¶ Generally called "isoemissive". However, "isolampsic" should be preferred, see ref. 41.

|| The absence of a well defined isolampsic point in Fig. 6 could indicate the occurrence of multiple complexation in the ground state: for example, structures like those in Scheme 1a could also be present. However, molecular modelling strongly suggests that a head-to-tail 1 : 1 complex is unlikely.



Scheme 2

looks closely similar, and thus in the following paragraph only the results relevant for the analysis of the fluorescence decay of **1** are described. Based on the equilibrium constant value, ~70% of compound **1** is complexed when [α-CD] = 5×10^{-2} mol dm^{-3}. Two main components, with time constants of *ca.* 2.5 ns (relative amplitude ~73%) and *ca.* 0.5 ns (relative amplitude ~ 27%), resulted from the analysis by using either a two- or a three-exponential function. We propose that the long-lived component is due to the monomer included in the cavity, which experiences a less polar environment. On the basis of the quantum yield values (obtained from best fitting using eqn. (2)) the radiative and non-radiative rates can be calculated. The inclusion slows down the non-radiative component, leaving unchanged the radiative one, as found in 1,4-DMB.[14] The short lived component is due to the monomer in water while the dimer, which is not associated with the CD, is assumed to be present in a negligible concentration. Similar results were obtained with β-CD. Due to the much higher association constant, *ca.* 96% of **1** is complexed when [β] = 0.01 mol dm^{-3}. The analysis of the decay by a biexponential function exhibits only one significant component of $\tau \approx 2$ ns with relative amplitude 95%, attributable to the included monomer.

With [γ-CD] = 2×10^{-2} mol dm^{-3} both the short- and the long-wavelength emission of **1** are slightly enhanced. This is consistent with the larger cavity size, allowing the inclusion of both monomeric and "*dimeric*" structures. On the basis of K_a, *ca.* 70% of **1** is complexed and an enrichment of the "*dimeric*" structure seems favoured by the inclusion. In fact, the longer lifetime (*ca.* 5 ns) is similar to the value found in pure water, while its relative amplitude increases from 3 to 15%. The monomer emission appears more sensitive to the environment and in the CD cavity is longer-lived than in water. The interaction of **2** with γ-CD causes a quenching of the monomeric emission and a concomitant enhancement of the excimer-like one, as shown in Fig. 6. Again the analysis gives a biexponential decay with lifetimes and relative amplitudes very similar in water and in presence of γ-CD in spite of the fact that ~90% of **2** is complexed, as shown in Table 1.

We underline that the picture obtained on the basis of a two-exponential analysis is to be considered as qualitative only. In fact, an analysis of the system **1**–γ-CD, in which ~70% complexation occurs, would require time resolved analysis on the basis of four different species, *i.e.* free and complexed monomer and "*dimer*". However the goodness of the fits did not improve significantly on passing from two to three exponential terms and the quality of the data was not good enough for a four-exponential analysis.

Conclusions

In the light of the results obtained with the cyclodextrins we conclude that our hypothesis, based on the kinetics of the fluorescence decay (*vide supra*), about the existence of two main sets of conformations for the compounds **1** and **2**, is substantially confirmed. By keeping in mind that in our system complex formation occurs only between the CDs and the probes in the ground state, α-, β-, and dimethyl-β-CD enhance the monomeric emission and quench the excimer-like one because their cavity can accommodate only one of the two aromatic groups and therefore the conformational equilibrium is shifted towards the form emitting the short-wavelength fluorescence. γ-CD has a larger cavity which can accommodate simultaneously both the aromatic groups of **2**. This shifts the conformational equilibrium towards the "*dimeric*" form and, consequently, increases the excimer-like emission. In addition, these results are consistent with the formation of a pseudo-crown ether through encapsulation of **2** in γ-CD, but the concentration of **2** in water was too low to check the cation binding ability of the new complex.

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