Steady state fluorescence studies of the complexes between pyrene and per-6-*O*-*tert*-butyldimethylsilyl α-, β- and γ-cyclodextrins

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The complexation of pyrene by α-, β- and γ-cyclodextrins (CDs), persubstituted at the 6 position by *tert*-butyldimethylsilyl groups, has been investigated using steady state fluorescence spectroscopy. The α-CD derivative does not, as would be expected from steric considerations, form complexes. The β- and γ-CD derivatives form 1:1 host–guest complexes which show high association constants in 90:10 H_2O–DMF solution [*i.e.* β-CD(SiR)$_7$, 4.85 × 10^5 M^{-1}; γ-CD(SiR)$_8$, 4.91 × 10^5 M^{-1}]. Analysis of the polarity of the microenvironment by means of the I/III peak ratios shows a more polar cavity in the case of γ-CD(SiR)$_8$. The concentration dependence of I/III suggests that a weak supramolecular complex γ-CD(SiR)$_8$–pyrene–*n*·DMF, may exist.

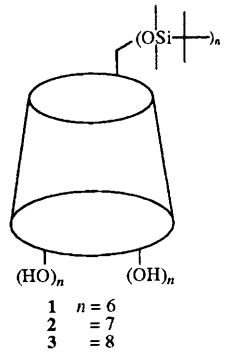
Introduction

Complete substitution of one face of the cyclodextrins leads to amphiphilic molecules capable of forming a wide variety of self assembling systems,[1] whilst still retaining their capacity to include guest molecules.[2] These amphiphilic derivatives have extremely low aqueous solubilities, and of the numerous techniques available for the study of the inclusion complexes,[3–20] fluorescence spectroscopy is particularly suited for providing information on the association constants and the molecular environments at such high dilutions.

Fluorescence spectroscopic techniques are highly sensitive, experimentally easy and sensitive to the local molecular environment. Of the readily fluorescent probes, pyrene has an extremely high quantum yield (φ = 0.7) and for the vibronic bands the intensity ratio I/III is strongly dependent on the local molecular polarity.[21] Pyrene has been used by Edwards[22] to study pyrene–β-cyclodextrin interactions, and more recently Munoz de la Pena used the variation in I/III band ratios to obtain both the stoichiometry and association constants for the β-CD; 2:1 complex, K_a = 8.53 × 10^5 M^{-2} and for γ-CD; 1:1 complex, K_a = 250 M^{-1} with pyrene.[17]

The high quantum yield of pyrene allows measurement of fluorescence emission at concentrations (10^{-7} M) necessary for the study of complexation by the amphiphilic cyclodextrin derivatives at the low aqueous solubilities of these molecules (10^{-6}–10^{-4} M).†,[22]

In this paper we have studied the formation of inclusion complexes between the α-(**1**), β-(**2**) and (per-6-*O*-*tert*-butyldimethylsilyl)-γ-cyclodextrin (**3**) complexes in aqueous DMF solutions. The interest in those compounds lies in their ability to form well organised monolayers at the air–water interface, which may complex calcium[23] and also show chiral discrimination with respect to terpene guests.[24] Interestingly there is no evidence of association in aqueous media† and so we may possibly use solution studies on association constants to extrapolate to monolayer behaviour. Even at the low concentrations required for this study, the minimal aqueous solubilities of **1**, **2** and **3** require the presence of a cosolvent. In view of this, the possible role of DMF in the complexation process was also investigated.



1 n = 6
2 = 7
3 = 8

Fig. 1 Per-6-*O*-(*tert*-butyldimethylsilyl) cyclodextrins

Experimental

Chemicals

Pyrene (P) and dimethylformamide (DMF) were of spectral grade and obtained from Aldrich, water was triply distilled in glass. The modified cyclodextrins (CDs) were prepared as previously described[25] and their purity confirmed by NMR and TLC. Absorption and fluorescence spectra confirmed the absence of any included impurities such as pyridine used in synthesis.

Solutions

Pyrene (40 mg, 0.2 mmol) was dissolved in DMF (20 ml) to yield a stock solution of concentration 10^{-2} M. Subsequent dilution was carried through to 10^{-3} (DMF), 10^{-5} (H_2O–DMF) and finally 10^{-7} M (90:10 or 95:5 H_2O–DMF). The stock solution was protected from air and light and renewed daily.

Cyclodextrins and derivatives were prepared as stock solutions in DMF (10^{-3} M) and working solutions were diluted either in H_2O–DMF 90:10 or 95:5 as needed.

† Even at the low concentrations under consideration 5 or 10% dimethylformamide is used as a cosolvent. From Electrospray Mass Spectrometry it has been shown that the compounds are not associated in picomolar concentrations in water–acetonitrile.

Measurements

Absorption spectra were measured using a Shimadzu 2100 UV–VIS spectrometer at ambient temperature (22 ± 2 °C) using a 10 mm quartz cell. Fluorescence spectra were measured on a Perkin-Elmer LS-50B spectrometer using a 10 mm quartz cell. In view of the importance of the slit width on measurement of vibrational bands,[16] the emission and excitation widths were set at 5 and 2.5 nm, respectively. The excitation wavelength was 335 nm. The intensities of bands I and III of pyrene were measured at 373.9 nm and 383 nm, respectively. Blanks at 373.9 and 383 nm were systematically recorded and subtracted, at each change in cyclodextrin concentration. In all cases, the blank signal never exceeds 3% in intensity at these two fixed wavelength. No smoothing was applied to the spectra.

Each measure was repeated three times on each of three different samples (9 measurements in total) and the results averaged. The average relative standard deviation (RSD) of the measurements was below 2%.

Calculation of association constants

The literature reports that the stoichiometry for cyclodextrin complexes in solution are generally 1:1 or 2:1 (cyclodextrin:guest). In the present study the occurrence of 1:1, 2:1 and 1:1 + 2:1 complexation was successively envisaged in order to determine the association constant between pyrene and the silyl derivatives. The equilibrium constant for a 1:1 complex between pyrene and the cyclodextrin may be given as:

$$K_1 = \frac{[PCD]}{[P][CD]} \quad (1)$$

with [PCD] = the concentration of the complex for a given CD concentration, [P] = concentration of free pyrene, [CD] = concentration of free cyclodextrin. Eqn. (1) may be solved by introducing the initial concentrations:

$$K_1 = \frac{[PCD]}{([P]_0 - [PCD])([CD]_0 - [PCD])} \quad (2)$$

with: $[P]_0$ = initial concentration of pyrene, $[CD]_0$ = initial concentration of cyclodextrin.

The initial concentration of cyclodextrin $[CD]_0$ being very much greater than the concentration of the complex [PCD] at equilibrium where:

$$K_1 = \frac{[PCD]}{([P]_0 - [PCD])([CD]_0)} \quad (3)$$

On the other hand, the expression of the quantum yield of the fluorescent PCD complex is:

$$\Phi_{PCD} = \frac{F_{PCD}}{G[PCD]} \quad (4)$$

with φ_{PCD} = the fluorescence quantum yield of the complex, F_{PCD} = the fluorescence signal of the complex (area of the emission spectrum), G = constant characteristic of the instrumental parameters with $G = KI_0\ 2.3\ \varepsilon lc$. Combining eqns. (3) and (4) gives eqn. (5):

$$\frac{[P]_0}{F_{PCD}} = \frac{1}{K_1 G\Phi_{PCD}[CD]_0} + \frac{1}{G\Phi_{PCD}} \quad (5)$$

To use this equation correctly, the concentration of pyrene must be constant and known for all solutions. As reported, this is extremely difficult to measure precisely due to the solubility and aggregation properties of pyrene in water and its tendency to adsorb onto the glass walls. Also, the quenching of pyrene emission by dissolved oxygen is well known in photochemistry.[26] Thus, degasing of the solution is mandatory, this is tedious and time consuming and frequently hampers the reproducibility of the measurements. For these reasons the measurement of the ratio of bands I and III offers an interesting possibility to overcome the difficulty of the need to use the exact concentration of pyrene as in eqn. (6).[22] Almgren has used the ratio I/III to determine the association constant between pyrene and tetraalkyl ammonium bromide micelles.[27] Under this approach, the ratio I/III represents a weighted average between free and complexed pyrene. If R is the weighting of the I/III ration signals of free pyrene and complexed pyrene at equilibrium:

$$R = R_0(1 - a) + R_1 a$$

thus:

$$R = R_0\left(1 - \frac{[PCD]}{[P]_0}\right) + R_1\left(\frac{[PCD]}{[P]_0}\right)$$

$$\frac{F_{PCD}}{F_P} = \frac{[PCD]_*}{[P]_0} = \frac{R_0 - R}{R_0 - R_1} \quad (6)$$

with R_0 = ratio I/III of pyrene in the absence of cyclodextrin = I_P/III_P, R_1 = ratio I/III of pyrene completely complexed = I_{PCD}/III_{PCD}, R = ratio I/III measured, a = molar fraction of complexed pyrene, F_P = fluorescence of the free pyrene, F_{PCD} = fluorescence of the pyrene totally complexed.

The use of the ratio I/III permits calculation of the association constant, two complete approaches have been derived from this equation. Warner and Munoz de la Pena have derived:

$$\frac{F_{PCD}}{F_P} = \frac{R_0 - R}{R_0 - R_1}$$

whilst Acree derived:[28]

$$\frac{F_{PCD}}{F_P} = \frac{R_0 - R}{R\left(\frac{III_{PCD}}{III_P}\right) - R_1\left(\frac{III_{PCD}}{III_P}\right)} \quad (7)$$

The approach of Acree differs in that it assumes R as the ratio of the average sum of the I band for complexed and uncomplexed pyrene on the III band for complexed and uncomplexed pyrene, *i.e.*:

$$R = I/III = \frac{[aI_{PCD} + (1 - a)I_P]}{[aIII_{PCD} + (1 - a)III_P]}$$

In reality III_{PCD} may not be isolated from III_P for inclusion complexes. This arises from III_{PCD} being the intensity of the pure pyrene–CD complex, as in solution this is always an equilibrium process, the intensity of the pure complex is obviously undeterminable.

Mechanistically the approach of Acree is more accurate as it takes into account local selective solvatation about a given fluorophore. Complexation within the cyclodextrin cavity may be considered as a total preferential solvatation of the probe molecule.

Unfortunately it is experimentally not possible to measure fluorescence of pyrene or any other fluorophore within the pure cyclodextrins only as a solid-state matrix, and in solution the equilibrium process intervenes. Thus we must accept that the K_a value derived from the I/III ratio is actually modulated by Acree's theory, which may, in some way, explain the differences between fluorescence derived K_a and those derived from the

other physical techniques. Given the above we have continued to use the I/III ratio derived equation of Warner. This leads for a complex of 1 : 1 stoichiometry to:

$$\frac{1}{R_0 - R} = \frac{1}{K_1(R_0 - R_1)[CD]_0} + \frac{1}{R_0 - R_1} \quad (8)$$

and for a complex of 2 : 1 stoichiometry to:

$$K_2 = \frac{[P(CD)_2]}{[P][CD]^2} \quad (9)$$

Hence:

$$\frac{1}{R_0 - R} = \frac{1}{K_2(R_0 - R_2)[CD]_0^2} + \frac{1}{R_0 - R_2} \quad (10)$$

If a complex is of 1 : 1 or 2 : 1 stoichiometry plotting eqns. (8) and (10) will yield straight lines only for the relevant stoichiometry.

In the case of stepwise complexation in which both 1 : 1 and 2 : 1 complexes will exist, it can be shown that

$$\frac{1}{R_0 - R} = \frac{1}{(R_0 - R_{1\text{-}2})(K_1[CD]_0 + K_2[CD]_0^2)} + \frac{1}{R_0 - R_{1\text{-}2}} \quad (11)$$

This equation is non-linear, in contrast to those equations for 1 : 1 and 2 : 1 stoichiometry, however it will tend to linearity when either of these constants can be neglected. Using eqn. (11) will allow evaluation of the proportion of 1 : 1 and 2 : 1 complexes present.

Results and discussion

[1] Polarity of the local microenvironment of the pyrene in the presence of 6-*O*-*tert*-butyldimethylsilyl-CDs

Fig. 2 shows the variation of the I/III pyrene band ratio as a function of increasing concentration of **1**, **2** and **3**. For **1** no significant variation in the I/III ratio is observed, and the local polarity of the pyrene molecule remains that of the H_2O–DMF (9 : 1) solvent system. The values between 1.53 and 1.51 obtained are typical of a dissociating aqueous microenvironment.[22] There is no formation of an inclusion complex between pyrene and **1**, this is in agreement with previous studies on unmodified α-cyclodextrin[14] or for the per-6-bromo- and azido-α-cyclodextrin derivatives.[29] Such a lack of inclusion may be anticipated from the size of the pyrene, 7.1 × 8.9 Å^2,[12] being significantly larger than the α-CD cavity which is 5.7 Å in diameter.

Both **2** and **3** cause a strong decrease in the I/III ratio with increasing concentration, this arises from the formation of inclusion complexes. In both the molecular cavity is capable of including pyrene, cavity diameters are 7.8 for **2**, 9.5 Å for **3**, respectively. The ratio reaches a limiting value of 1.32 at a concentration of 1 × 10^{-5} M for **2**, and a limiting value of 1.37 at a concentration of 1 × 10^{-5} M for **3**. Thus the observed apparent polarity of the cavity of **3** is higher than that of **2**.

Two possible explanations are: (*a*) the association constant for [**3**–pyrene] is smaller than that of [**2**–pyrene]; (*b*) if the association constants are similar, the solvent exposed surface of pyrene in **3** is larger than that in **2**.

For the corresponding per-6-bromo-, per-6-azido-β- and γ-cyclodextrin derivatives, the ratio I/III is much lower, typically 0.9–0.7. Thus the included pyrene in the current systems, which have much larger hydrophobic head groups, is in a more polar environment, than for complexes in which the hydrophobic groups are simply CH_2Br or CH_2N_3.

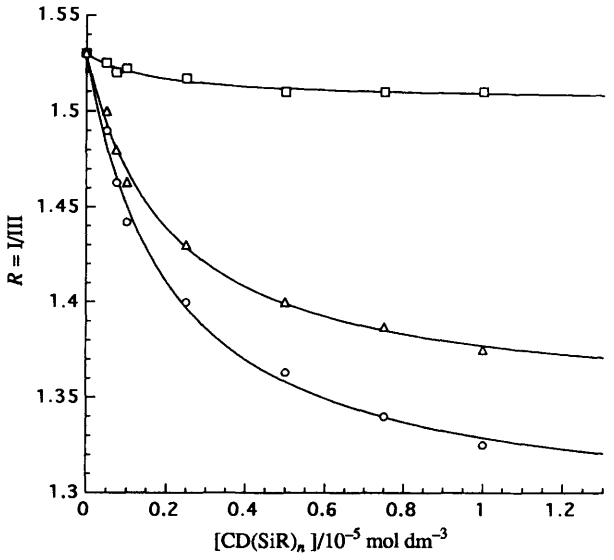


Fig. 2 Plot of the I/III vibronic intensity ratio for pyrene *vs.* cyclodextrin concentration with [Pyrene] = 10^{-7} M. (□) **1**, (△) **3**, (○) **2**

Table 1 Stoichiometry, association constants and the cavity polarity expressed as I/III ratio for the complex of **2** and **3** with pyrene according to 1 : 1 and 2 : 1 model. (*r* = coefficient of correlation). For experimental conditions see the text. K_1: The equilibrium constant for 1 : 1 complex between pyrene and the cyclodextrin. K_2: The equilibrium constant for 2 : 1 complex between pyrene and the cyclodextrin. I/III: Calculated ratio of pyrene completely complexed

Compounds	K_1 × 10^{-5} M^{-1}	K_2 × 10^{-10} M^{-2}	*r*	I/III
β-CD(SiR)$_7$	4.85 ± 0.45	—	0.998	1.29
	—	82.62	0.981	1.34
γ-CD(SiR)$_8$	4.91 ± 0.42	—	0.998	1.35
	—	82.00	0.982	1.39

[2] Inclusion complexes stoichiometry

The stoichiometry of the complexes formed is determined by the best fit of the data to eqns. (8, 10 or 11). However the mathematical treatment used gives slopes that will be overly influenced by the lowest concentrations of the CD-derivatives. It is more useful to use non-linear least squares regression directly on the values in Fig. 2, as has been previously applied.[14,27] Thus eqns. (8), (10), (11), respectively, are rewritten as follows:

$$R = \frac{R_0 + R_1K_1[CD]}{1 + K_1[CD]}$$

$$R = \frac{R_0 + R_2K_2[CD]^2}{1 + K_2[CD]^2}$$

$$R = \frac{R_0 + R_{1\text{-}2}(K_1[CD] + K_2[CD]^2)}{1 + K_1[CD] + K_2[CD]^2}$$

Table 1 shows the calculated association constants, K_1 and K_2, and the quality of fit calculated from the 1 : 1 and 2 : 1 models. The much higher quality of fit for the 1 : 1 complex is evident.

If a stepwise model is used, the experimental data for **2** and **3** leads to values of $K_1 = 4.85 \times 10^5$ M^{-1}, $K_2 = 1.30 \times 10^6$ M^{-2} and $K_1 = 4.91 \times 10^5$ M^{-1}, $K_2 = 7.40 \times 10^5$ M^{-2}, respectively.

Applying eqns. (1) and (9) for a given concentration of the pyrene $K_2 \times [CD]^2$ will be negligible compared to $K_1 \times [CD]$ and hence $K_2 \times [CD]^2 \ll K_1 \times [CD]$. Therefore the stepwise 1 : 1 + 2 : 1 complex may be ignored and again the 1 : 1 complex is the preferred model. There is absence of a broad

Table 2 Association constants of compounds **2** and **3** compared with the other CD compounds (native CD, ref. 17), bromo and azido derivatives (ref. 29)

Compounds	K_1 M^{-1}	K_2 M^{-2}
β-CD(SiR)$_7$	4.85 (±0.45) × 10^5	—
γ-CD(SiR)$_8$	4.91 (±0.42) × 10^5	—
β-CD	—	8.53 × 10^5
γ-CD	250	—
β-CD(Br)$_7$	—	1.64 × 10^{10}
γ-CD(Br)$_8$	—	4.30 × 10^{10}
β-CD(N$_3$)$_7$	—	1.11 × 10^{10}
γ-CD(N$_3$)$_8$	—	2.63 × 10^{10}

band centred at 480 nm, thus ruling out the formation of excimers of pyrene, this rules out either 1:2 and more importantly 2:2 inclusion complexes.[30-32]

The 1:1 model being established, the association constants (*i.e.* 4.91 × 10^5 and 4.85 × 10^5 M^{-1} for γ- and β-silyl cyclodextrin, respectively) are much higher than that observed using the same fluorescence technique methodology for complexes of the same stoichiometry (*i.e.* γ-CD–pyrene 250 M^{-1}).[17] For comparison with other CD–pyrene complexes various association constants are assembled in Table 2.

Direct comparison is difficult between the 1:1 and 2:1 complexes. The stoichiometry of the obtained complex is strongly dependent on the nature of the substituent at the primary face.

Whilst the obtained association constants are high, the I/III ratios are much higher than observed for the bromo- and azido-derivatives, this is due to 1:1 stoichiometry. Comparison with the native cyclodextrins is informative, for β-CD, which forms a 2:1 complex the limiting I/III in 90:10 H_2O–DMF is 1.04, whereas for γ-CD which forms a 1:1 complex the limiting value is 1.3. For the 1:1 complexes a large surface of the included pyrene is available to solvent molecules, and hence the microenviroment must be more polar.

[3] Role of dimethylformamide in the inclusion process

As stated above the limiting value for I/III ratios in 90:10 H_2O–DMF are 1.32 and 1.37, respectively, for β-CD and γ-CD; in 5% the values are 1.25 and 1.32, respectively. This decrease in polarity for both compounds for a lower concentration DMF points to formation of a ternary inclusion complex with pyrene as has been widely seen for alcohols with the native compounds. To probe this role, the relationship between I/III and the concentration of the CD derivatives was studied at fixed concentrations, 5% and 10%, of DMF, the results are given in Fig. 3. In both cases the observed I/III ratios are higher at 10%, suggesting that DMF is displacing the pyrene from the cavity.

The association constants are given in Table 3, at 10% values of 4.85 × 10^5 M^{-1} and 4.91 × 10^5 M^{-1} are observed for **2** and **3**, respectively, at 5% the values are 7.76 × 10^5 M^{-1} and 6.12 × 10^5 M^{-1}. There is an increase at 5% for both molecules but in the case of the β-CD derivative **2** this increase is significantly higher.

In the case of the bromo- and azido- derivatives, for γ-CD-Br$_8$ it was shown that there exists a cooperative binding effect with formation of a ternary complex [2 γ-CDBr$_8$:1 pyrene:*n*DMF].[29]

To examine whether such an effect might occur here, the variation of I/III at fixed concentration of **2** and **3** (7.5 × 10^{-6} M) against DMF concentration was measured. The results are given in Fig. 4, above 10% DMF there is simply displacement of pyrene by the DMF, and at 35% *v/v* the value of I/III is the same as that observed in the absence of the cyclodextrin derivatives. For **3**, below 10% the value of I/III decreases with decreasing DMF concentrations but there is a slight variation in the slope, however for **2**, at 7.5 and 5% the I/III ratios are identical.

Table 3 Association constants of compounds **2** and **3** calculated in H_2O–DMF 90:10 and 95:5 (*v/v*) respectively. (*r* = coefficient of correlation; I/III ratio expressing the polarity of the cavity)

Compounds	DMF (%)	K_1 × 10^{-5} M^{-1}	*r*	I/III
β-CD(SiR)$_7$	10	4.85 ± 0.45	0.998	1.29
	5	7.76 ± 0.57	0.998	1.20
γ-CD(SiR)$_8$	10	4.91 ± 0.42	0.998	1.35
	5	6.12 ± 0.40	0.999	1.25

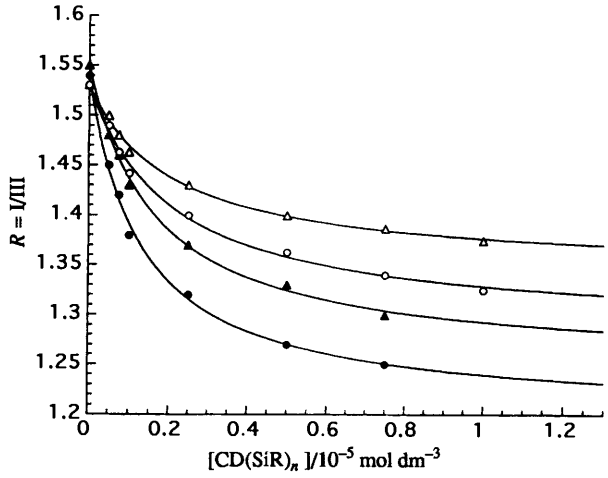


Fig. 3 Plots of the I/III vibronic intensity ratio for pyrene *vs.* the cyclodextrin concentration with [pyrene] = 10^{-7} M in a mixture DMF–H_2O 10:90 *v/v*: ○ (**2**), △ (**3**), in a mixture DMF–H_2O 5:95 *v/v*: ● (**2**), ▲ (**3**)

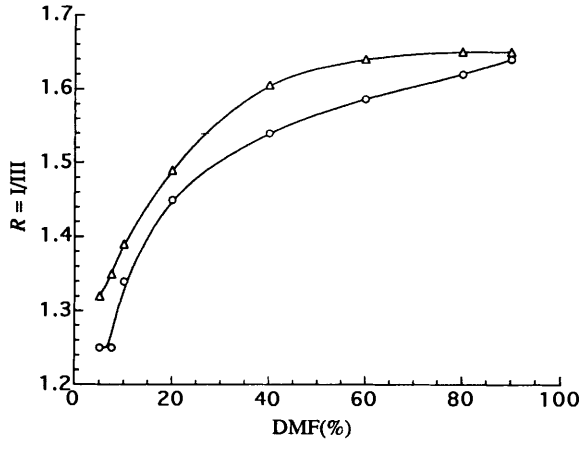


Fig. 4 Plots of the I/III vibronic band intensity ratio for pyrene *vs.* the DMF percentage (in volume) with **2** = 7.5 × 10^{-6} M (○), **3** = 7.5 × 10^{-6} M (△) and [pyrene] = 10^{-7} M

This is not as dramatic as the increase in I/III observed for γ-CDBr$_8$ but is significant, probably a weak supramolecular complex [**2**:1 pyrene:*n* DMF] forms at low DMF concentrations.

Unfortunately the extremely low solubility of the amphiphilic cyclodextrins prevents the use of NMR to obtain the stoichiometry of the ternary complex, or probe the exact role of DMF in inclusion process.

Conclusions

We have shown that the amphiphilic cyclodextrin derivatives, carrying *tert*-butyldimethyl groups at the primary face form strong 1:1 inclusion complexes with pyrene in aqueous dimethylformamide solutions.

The polarity of the microenvironment of the pyrene in these complexes is high, and there is probably participation of DMF molecules in the formation of the ternary complexes.

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