

Size Effect of α,ω -Diphenylpolyenes on the Formation of Nanotubes with γ -Cyclodextrin

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We have studied the size effect of the homologues of the α,ω -diphenylpolyenes series, with two, three and four double bonds, on the formation of nanotubes with γ -cyclodextrin. The data show that only the two longest polyenes facilitate the formation of tubular structures when mixed with the γ -cyclodextrin in the appropriate solvent, while the average length of these nanotubes increases with increasing size of the diphenylpolyenes. Using computer simulations, we have examined the processes by which nanotubes form, and from computer fits we have determined the various binding constants, some with extremely large values, involved in the formation of these supramolecular structures.

I. Introduction

Cyclodextrins, and in particular the so-called α , β , and γ homologues, have attracted considerable attention during the past decade.¹ In a recent publication² we discussed the formation of long, rodlike structures between α,ω -diphenylhexatriene (DPH) and γ -cyclodextrin (γ CD) (see structures in Scheme 1). These so-called nanotubes³ contain up to ca. 30 cyclodextrin units interconnected by means of DPH molecules. In these structures the γ CD units are understood^{2,3} to be lined up along their cylindrical axis so that H-bonding interactions between the rim OH groups of neighboring γ CDs are favored. The DPH molecules, on the other hand, penetrate the cavities of two neighboring γ CDs, thus stabilizing, by van der Waals interactions the superstructure. The crucial contribution of both γ CD- γ CD and DPH- γ CD interactions to the formation of nanotubes is demonstrated not only by the fact that these tubes do not form in the absence of DPH but also by the observation that when the rim hydroxyls of γ CD are replaced by the non-H-bonded OCH₃ groups, or when the pH of the solvent is high enough to render H-bonding ineffective, nanotubes do not form any more.² The rodlike structure of these DPH- γ CD aggregates has been established by several other physicochemical methods,^{2,3} including light scattering and scanning tunneling microscopy.³ Note that other rodlike structures involving cyclodextrins include catenanes,⁴ rotaxanes,^{4,5} polyrotaxanes,^{4,6–9} nanotubular structures,^{3,6} threaded cyclodextrins,⁶ etc.

The objective of the present work was to study the effect of the length of the α,ω -diphenylpolyenes, with the general formula Ph-(CH=CH-)_n-Ph, on nanotube formation. For this purpose we have examined the complexation of three such molecules, viz., $n = 2$ –4, with γ CD in a 60/40 v/v water/glycol solvent. Note that in this type of study diphenylpolyenes play a double role; one is that of a "shaft" that enhances the binding of two neighboring γ CD units, and the other is that of a fluorescent probe, which probes nanotube formation by the magnitude of its fluorescence anisotropy.^{2,3} **Another main point** of focus of this work was to extract numerical values for the equilibrium constants involved in the formation of these elongated superstructures, since so far the few publications on this subject^{2,3} deal exclusively with the qualitative aspects of nanotube formation. **To this** end, we have made extensive use of

computer fits and simulations to obtained values for the relevant kinetic parameters.

II. Experimental Section

γ -Cyclodextrin (γ CD) was purchased from Cyclolab. The Ph-(CH=CH-)_n-Ph diphenylpolyenes with $n = 2$ (DPB) and $n = 4$ (DPO) were obtained from Aldrich and the one with $n = 3$ (DPH) from Fluka. All chemicals were of the highest purity available, and therefore, they were used without further purification. Absorption spectra were recorded on a Perkin-Elmer Lambda-16 spectrophotometer, whereas for fluorescence, excitation, and fluorescence anisotropy measurements, we used the LS-50B Perkin-Elmer fluorometer. Fluorescence lifetimes (τ) were determined using the time-correlated single-photon counter FL900 of Edinburgh Instruments, which is capable of measuring lifetimes to 0.08 ns. The determinations of fluorescence quantum yields (Φ), and anisotropies (r), have been described elsewhere.¹⁰ It should be mentioned here that the excitation wavelengths for the measurements of the fluorescence quantum yields were chosen to be at isosbestic points, i.e., points at which the absorption coefficient of the polyene did not change upon addition of γ CD. Such points exist in all three polyene- γ CD systems:¹¹ DPB- γ CD at 331 nm, DPH- γ CD at 362 nm, and DPO- γ CD at 381 nm. The maximum possible r values for the three diphenylpolyenes, measured in vitrified solutions and polymer films, are $r_o = 0.38$ – 0.39 .^{12–14} All three Ph-(CH=CH-)_n-Ph are totally insoluble in pure water. For this reason we have used as solvent a mixture of water/ethylene glycol, 60/40 by volume, in which these molecules were found to form proper solutions with the following solubilities: DPB, 1.3×10^{-6} M; DPH, 8×10^{-8} M; DPO 4×10^{-8} M. Note that we have found nanotube formation to take place between our three polyenes and γ CD in pure water, but we will not elaborate on that. All computer fits and simulations were performed using the program "MicroMath Scientist for Windows", version 2.01, of MicroMath Inc.

III. Results and Discussion

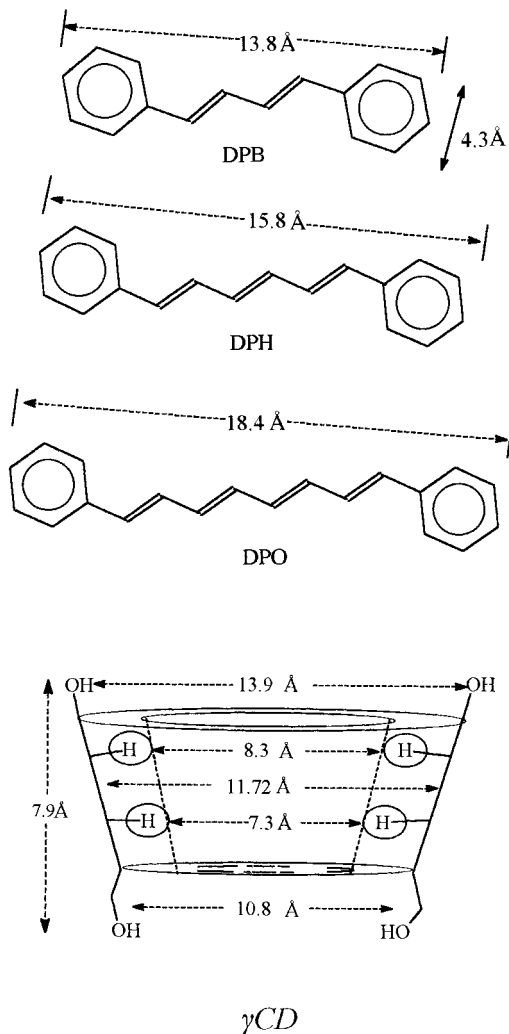
Some relevant spectroscopic data concerning the three polyenes of the present study are listed in Table 1. Although these molecules are consecutive homologues of the series Ph-

TABLE 1: Fluorescence Parameters, Lifetime (τ), Quantum Yield (Φ), and Anisotropy Polarization (r) of DPP, DPH, and DPO in Various Solvents

solvent	n_D	ϵ	η	DPP			DPH			DPO		
				τ (ns)	Φ	r	τ (ns)	Φ	r	τ	Φ	r
hexane	1.372	1.88	0.313	0.467	0.350	0.020	15.9	0.630	<i>b</i>	6.20	0.044	<i>b</i>
dodecane	1.400	2.00	1.508	0.668	0.490	0.030	13.2	0.660	<i>b</i>	6.43	0.052	<i>b</i>
ethanol	1.359	24.3	1.078	0.060 ^a	0.042 ^a	0.167	4.8	0.230	<i>b</i>	6.56	0.059	<i>b</i>
ethylene glycol	1.429	38.66	21	0.187	0.065	0.323	2.58	0.210	0.110	7.07	0.086	0.088
benzene	1.498	2.28	0.603	0.327	0.275	0.040	7.0	0.760	<i>b</i>	6.81	0.089	<i>b</i>
chloroform	1.444	4.64	0.542	0.156	0.069	0.110	6.2	0.570	<i>b</i>	6.73	0.085	<i>b</i>
60/40 w/ethylene glycol	1.375	68.40	3.00	0.08	0.011	0.295	0.355	0.031	0.152	5.0	0.038	0.045

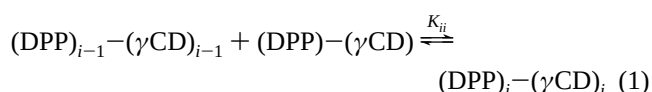
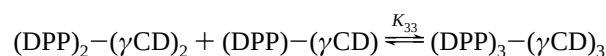
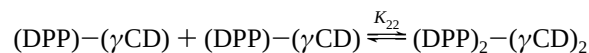
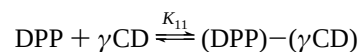
^a Taken from ref 19. ^b r values of DPH and DPO were below 0.01 because of their long fluorescence lifetimes.

SCHEME 1: Dimensions of α,ω -Diphenylpolyenes and γ CD



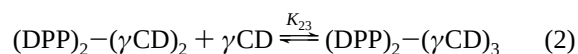
(CH=CH-)_n-Ph with $n = 2,3,4$, they demonstrate, nevertheless, some important differences in their fluorescence parameters, viz., quantum yields (Φ), anisotropies (r), and lifetimes (τ), as shown in Table 1. Thus, although τ and Φ of DPP and DPH depend on the solvent, in DPO they are nearly independent of it. Also, the very low lifetimes of DPP in all solvents make the fluorescence anisotropy of this molecule approximately constant in all media.

Nanotube Formation. The general assumption we have made concerning nanotube formation is that it proceeds as a self-association reaction of the initially formed (DPP)-(γ CD) unit. The steps therefore that lead to the formation of a nanotube are described by the following equations (1):

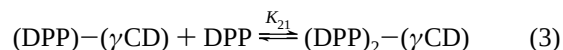


On the basis of previous theoretical¹⁵ and experimental¹⁶ studies of chain-association equilibria, we have further assumed that the equilibrium constant K_{ii} for all reactions with $i > 1$ is equal to K ; i.e., it is independent of i . Therefore, $K_{22} = K_{33} = \dots K_{ii} = K$.

It is also conceivable that in addition to eq 1 more reactions of the types described by the equations in (2)



and eq 3



can also take place. Therefore, we have included them too in our computer simulations. The concentration of DPP in these simulations was taken to be equal to 5×10^{-8} M in accordance with our water solubility data for the three diphenylpolyenes used here. We should also mention that in our simulations the number of consequent associations in the equations of (1) has been restricted to $i = 10$ because beyond that number our computer program breaks down. Therefore, the longest complex in these simulations will be the (DPP)₁₀-(γ CD)₁₀. We have set as our criterion for nanotube formation that the magnitudes of the molar fractions f_{ii} , of the longest complexes (DPP)_i-(γ CD)_i are large compared with the magnitudes of f_{ii} and f_{ij} of the short complexes (DPP)_i-(γ CD)_i and (DPP)_i-(γ CD)_j. Furthermore, to avoid congestion of our figures we have included in Figures 1 and 2 only the [γ CD] dependence of the molar fractions, f_{11} , f_{22} , $f_{10,10}$ obtained from simulations according to the equations of (1) (Figure 1a), f_{12} , f_{23} , $f_{10,10}$ obtained from simulations according to the combined equations of (1) and (2) (Figure 1b), and f_{21} and $f_{10,10}$ from simulations according to the combined equations of (1) and (3) (Figure 2). Note finally that in our notation the first subscript i , in f_{ij} , K_{ij} , etc., corresponds to DPP while the second subscript j to γ -CD. In all computer simulations that follow, the value of the equilibrium constant K_{11} was always set equal to 100 M⁻¹, adopted as an ap-

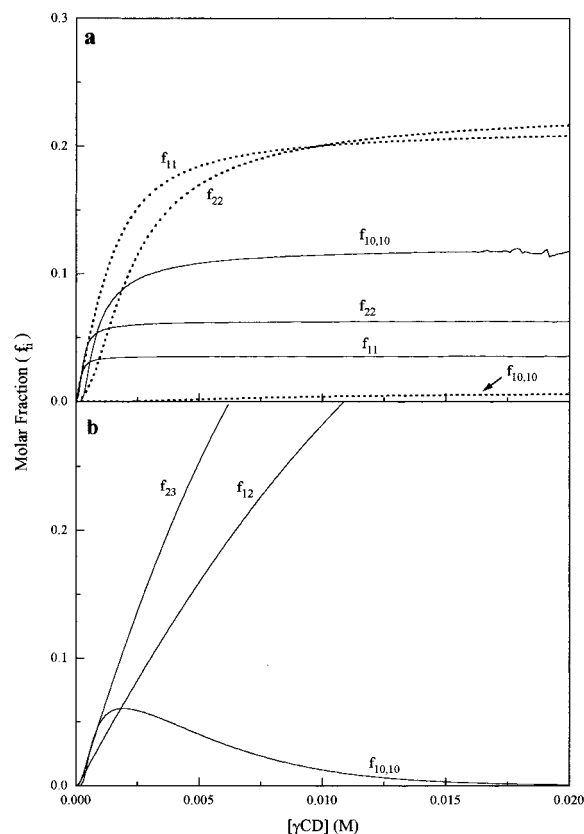


Figure 1. Computer simulations of the molar fraction (f_{ij}) vs cyclodextrin concentration ($[\gamma\text{CD}]$). (a) According to (1) for solid lines, $K_{11} = 100 \text{ M}^{-1}$, $K = 5 \times 10^8 \text{ M}^{-1}$; for dotted lines, $K_{11} = 100 \text{ M}^{-1}$, $K = 5 \times 10^7 \text{ M}^{-1}$. (b) According to (1) and (2) with $K_{11} = 100 \text{ M}^{-1}$, $K = 5 \times 10^8 \text{ M}^{-1}$, $K_{12} = K_{23} = 1000 \text{ M}^{-1}$. All simulations were performed for i up to 10 because beyond that point the program broke down.

proximately mean value between published data² and our unpublished results on the complexation of DPH with α - and β -cyclodextrins in the same medium, viz., 60/40 water/ethylene glycol.

In Figure 1a the solid lines correspond to the f_{11} , f_{22} , and $f_{10,10}$ obtained according to (1) and for binding constants $K_{11} = 100 \text{ M}^{-1}$ and $K = 5 \times 10^8 \text{ M}^{-1}$. These plots show that under these conditions nanotubes form, since above a small γCD concentration, ca. 10^{-3} M , $f_{10,10}$ stays larger than f_{11} and f_{22} . The dotted lines in Figure 1a, on the other hand, correspond to the same model of (1) with $K_{11} = 100 \text{ M}^{-1}$ but with $K = 5 \times 10^7 \text{ M}^{-1}$. These plots show that nanotubes do not form when K assumes some value lower than approximately 10^8 M^{-1} , since in this case the magnitude of $f_{10,10}$ is much smaller than those of f_{11} and f_{22} . The plots of Figure 1b correspond to the indicated molar fractions obtained from the combination of (1) and (2) with equilibrium constants $K_{11} = 100 \text{ M}^{-1}$, $K_{12} = K_{23} = 1000 \text{ M}^{-1}$, and $K = 5 \times 10^8 \text{ M}^{-1}$. It is quite clear from these plots that when the side reactions of (2) are included in the simulations, the molar fraction of the long structure, $f_{10,10}$, which accounts for the nanotubes, undergoes a dramatic decrease, while the molar fractions f_{12} and f_{23} , of the $(\text{DPP})_1-(\gamma\text{CD})_2$ and $(\text{DPP})_2-(\gamma\text{CD})_3$ complexes, which terminate nanotube formation, rise sharply. Therefore, nanotubes do not form.

We have also considered the combination of (1) with (3) as shown in the plots of Figure 2, but we found that the effect of this type of interaction is rather unimportant in these systems, as indicated by the low molar fraction f_{21} compared with $f_{10,10}$, for K_{21} values even as high as 10^8 M^{-1} . This is understood in terms of the aforementioned very low solubility of DPP in the

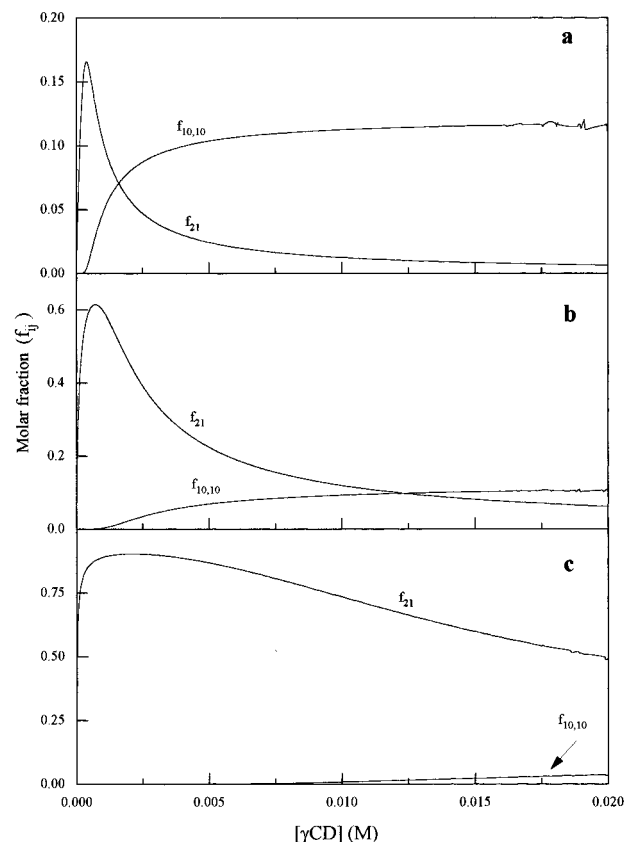


Figure 2. Computer simulations of the molar fraction (f_{ij}) vs cyclodextrin concentration ($[\gamma\text{CD}]$) according to (1) and (3): (a) $K_{11} = 100 \text{ M}^{-1}$, $K_{21} = 10^8 \text{ M}^{-1}$, $K = 5 \times 10^8 \text{ M}^{-1}$; (b) $K_{11} = 100 \text{ M}^{-1}$, $K_{21} = 10^9 \text{ M}^{-1}$, $K = 5 \times 10^8 \text{ M}^{-1}$; (c) $K_{11} = 100 \text{ M}^{-1}$, $K_{21} = 10^{10} \text{ M}^{-1}$, $K = 5 \times 10^8 \text{ M}^{-1}$. All simulations were performed for i up to 10 because beyond that point the program broke down.

solvent employed here, ca. $8 \times 10^{-8} \text{ M}$, which requires unreasonably large values of the equilibrium constant K_{21} in order for this reaction to assume a detectable role in the overall nanotube formation. Note that the effect of (3) is demonstrated in the case of the fluorescence quantum yield of the DPB- γCD system (see Figure 4). We conclude therefore that nanotube formation is adequately described by the self-association process of (1) whereas when (2) occurs, nanotubes do not form. Finally, processes of the type in (3) do not have any effect on nanotube formation unless they are assigned an unreasonably large equilibrium constant, viz., $K_{21} > 10^9 \text{ M}^{-1}$. All the findings of these simulations are confirmed by the experimental data discussed in the rest of this article. It should also be mentioned here that similar equations describing chain association equilibria in other systems have been reported before.¹⁶

Figure 3 shows the variation of the fluorescence quantum yield Φ and anisotropy r as the concentration of added γCD increases while keeping constant the concentration of the diphenylpolyenes, viz., $[\text{DPB}] = 1.3 \times 10^{-6} \text{ M}$, $[\text{DPH}] = 7 \times 10^{-8} \text{ M}$, $[\text{DPO}] = 4 \times 10^{-8} \text{ M}$. It becomes evident from these plots that each one of the homologues behaves differently from the others. Thus, in the case of DPB- γCD the quantum yield starts from a very low value, $\Phi = 0.011$, and then rises, slowly at the beginning and then more quickly, until it reaches the value of ca. 0.35 at about $5 \times 10^{-2} \text{ M}$ of added γCD . In DPH, Φ starts again from a low value of about 0.031 but then rises quickly to ca. $\Phi = 0.56$ at $[\gamma\text{CD}] = 1.2 \times 10^{-2} \text{ M}$ where it levels off. Finally, in a totally different fashion from the other two polyenes, DPO exhibits low fluorescence quantum yield,

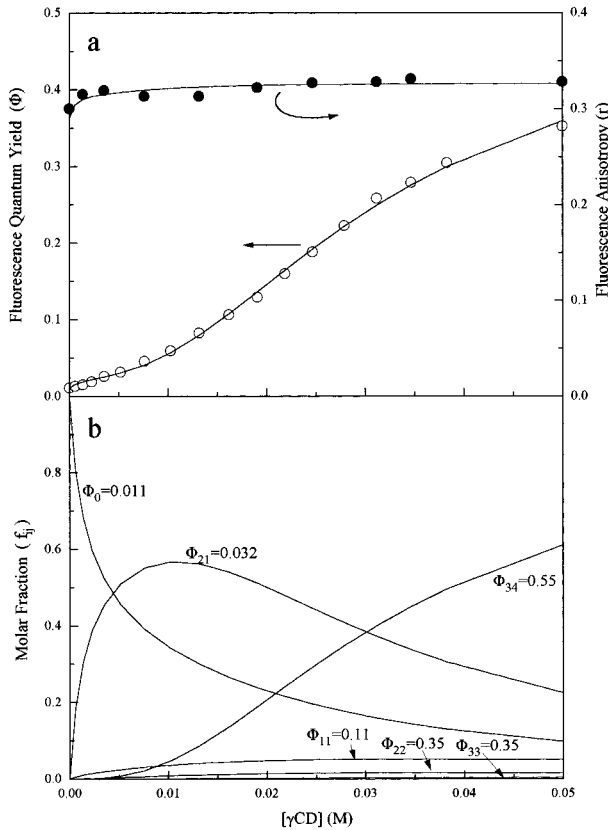


Figure 4. (a) Computer fits of (7) to the Φ vs $[\gamma\text{CD}]$ experimental data ($\square$) and of (10) to the r vs $[\gamma\text{CD}]$ experimental data ($\circ$) for DPB. (b) Plot of the molar fractions of the species involved in the fits of (a) vs $[\gamma\text{CD}]$. For fitting parameters see Table 3.

$$\begin{aligned}
 [(\text{DPB})_2-(\gamma\text{CD})_2] &= K_{22}[\text{DPB}-\gamma\text{CD}]^2 = \\
 &K_{22}K_{11}^2[\text{DPB}]^2[\gamma\text{CD}] \\
 [(\text{DPB})_3-(\gamma\text{CD})_3] &= K_{33}[(\text{DPB})_2-(\gamma\text{CD})_2][\text{DPB}-\gamma\text{CD}] = \\
 &K_{33}K_{22}K_{11}^3[\text{DPB}]^3[\gamma\text{CD}]^3 \\
 [(\text{DPB})_3-(\gamma\text{CD})_4] &= K_{34}[(\text{DPB})_3-(\gamma\text{CD})_3][\gamma\text{CD}] = \\
 &K_{34}K_{33}K_{22}K_{11}^3[\text{DPB}]^3[\gamma\text{CD}]^4 \quad (8)
 \end{aligned}$$

If the concentrations of the various species, from the above equations of (8), are introduced in (7a) the molar fractions f_{ij} can be expressed in terms of K_{ij} , $[\text{DPB}]$, and $[\gamma\text{CD}]$. In addition, the unknown $[\text{DPB}]$, i.e., the concentration of the free DPB at any instant during the titration, can also be expressed as a function of K_{ij} and $[\gamma\text{CD}]$. This is accomplished by replacing in (9) which expresses the balance of mass for DPB, the various $[(\text{DPB})_i-(\gamma\text{CD})_j]$ terms from (8):

$$\begin{aligned}
 [\text{DPB}]_T &= [\text{DPB}] + [\text{DPB}-\gamma\text{CD}] + 2[(\text{DPB})_2-\gamma\text{CD}] + \\
 &2[(\text{DPB})_2-(\gamma\text{CD})_2] + 3[(\text{DPB})_3-(\gamma\text{CD})_3] + \\
 &3[(\text{DPB})_3-(\gamma\text{CD})_4] \quad (9)
 \end{aligned}$$

Eventually the (7) assumes its final form in which the experimental parameter Φ is expressed in terms of the desired parameters K_{ij} , Φ_{ij} , and the known quantities $[\gamma\text{CD}]$, $[\text{DPB}]_T$, Φ , Φ_f , f_i , where $[\gamma\text{CD}]$ stands for the concentration of the free (uncomplexed) cyclodextrin after each addition of γCD during the titration. Note, however, that since throughout the titration we have used excess γCD relative to polyenes, viz. $[\gamma\text{CD}]/[\text{DPP}] \geq 10^2$, we can assume that at each moment $[\gamma\text{CD}]$ is

TABLE 3: Binding Constants and Quantum Yields of the Various Complexes Formed between Diphenylpolyenes and γCD in 60/40 v/v Water/Ethylene Glycol

complex	binding constants K_{ij} (M^{-1})	quantum yields Φ_{ij}	extracted from fits of	goodness of the fit R
DPB- γCD	$K_{11} = 11$	$\Phi_{11} = 0.11$	Φ vs $[\gamma\text{CD}]$ and r vs $[\gamma\text{CD}]$	0.9993
	$K_{21} = 1.7 \times 10^7$	$\Phi_{21} = 0.03$		
	$K_{22} = 2.6 \times 10^6$	$\Phi_{22} = 0.35$		0.9997
	$K_{33} = 1.0 \times 10^6$	$\Phi_{33} = 0.35$		
	$K_{34} = 5.8 \times 10^3$	$\Phi_{34} = 0.55$		
DPH- γCD	$K_{11} = 70^a$	$\Phi_{11} = 0.08^a$	Φ vs $[\gamma\text{CD}]$	0.999
	$K_{22} = 5 \times 10^8$	$\Phi_{22} = 0.46^a$		
	$K = 4 \times 10^8$	$\Phi = 0.75$		
DPO- γCD	$K_{11} = 313$	b	r vs $[\gamma\text{CD}]$	c
	$K = 4.2 \times 10^8$			

^a Values introduced in the program from the literature (see text).

^b Quantum yields do not appear in the fitting equation in this case (see text). ^c Data from simulation.

equal to the known analytical cyclodextrin concentration that has been added until then. The final fitting equation is not shown here because it forms an extremely long algebraic expression, while on the other hand, its derivation simply amounts to the above-mentioned straightforward substitutions. Note that similar procedures to express the corresponding fitting equations in terms of the known and of the desired parameters have been also used in the cases of DPH and DPO, and they will not be repeated here. In any case, there are 10 parameters in the modified (but not shown) fitting equation, viz., the binding constants K_{ij} and the quantum yields Φ_{ij} of the five different $(\text{DPB})_i-(\gamma\text{CD})_j$ species of (6). Of those 10 parameters only f_i and Φ_f of the free DPB are known (see Table 1). We have further reduced the number of the free-running parameters by 1, assuming that $\Phi_{22} = \Phi_{33}$. The justification for this simplification is that in both species, the $(\text{DPB})_2-(\gamma\text{CD})_2$ and the $(\text{DPB})_3-(\gamma\text{CD})_3$, the DPB molecules are equally protected from the environment, and therefore, they are expected to have similar quantum yields. The fitting gave the binding constants K_{ij} for each complex $(\text{DPB})_i-(\gamma\text{CD})_j$, along with the corresponding fluorescence quantum yields Φ_{ij} , listed in Table 3, and also, through (7a), the dependence of the various molar fractions f_{ij} on $[\gamma\text{CD}]$, as shown in Figure 4b.

At this point we may return to the r vs $[\gamma\text{CD}]$ plot of Figure 3b, and using the information obtained from the fitting of the quantum yields, viz., the complexes $(\text{DPB})_i-(\gamma\text{CD})_j$ formed and their molar fractions f_{ij} , we can try to fit the same model of (6) to the r vs $[\gamma\text{CD}]$ data. The fitting equation in this case is (10) where r is the total measured anisotropy at

$$r = I_f r_f + I_{11} r_{11} + I_{21} r_{21} + I_{22} r_{22} + I_{33} r_{33} + I_{34} r_{34} \quad (10)$$

any moment during the titration, I_f and I_{ij} refer to the fraction of the total fluorescence intensity due to the free molecule and each one of the $(\text{DPB})_i-(\gamma\text{CD})_j$ complexes respectively,¹⁸ $r_f = 0.295$ is the anisotropy of DPB in the mixed solvent before the addition of any γCD (see Table 1), and r_{ij} is the anisotropy of the $(\text{DPB})_i-(\gamma\text{CD})_j$ adduct. Note that r_{ij} is expressible in terms of (4) and (5), since $r_{ij} = \eta r_{0j} V / (\eta_j V + \tau RT)$ where all factors are known. When the intensity fractions are expressed as $I_{ij} = f_{ij} \Phi_{ij} / \Phi = f_{ij} \phi_{ij}$, where $\phi_{ij} = \Phi_{ij} / \Phi$ represents the ratio of the quantum yield of the particular $(\text{DPB})_i-(\gamma\text{CD})_j$ species to the total quantum yield Φ , (10) becomes (11):

$$r = f_f \phi_f r_f + f_{11} \phi_{11} r_{11} + f_{21} \phi_{21} r_{21} + f_{22} \phi_{22} r_{22} + f_{33} \phi_{33} r_{33} + f_{34} \phi_{34} r_{34} \quad (11)$$

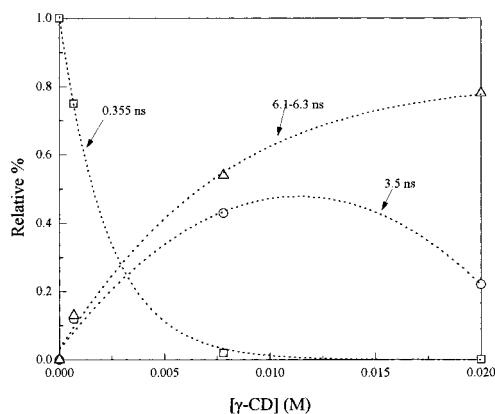


Figure 5. Plots of the relative percentages of the various species found in the DPH and γ CD solution in 60/40 water/ethylene glycol vs $[\gamma\text{CD}]$. The species were distinguished by their fluorescence lifetimes, indicated in the plots.

Using the variations of the molar fractions shown in Figure 3b, introducing $\tau = 0.08$ ns for the free DPB (see Table 1), and allowing two more free-running lifetimes, viz., a long one for the $(\text{DPB})_3-(\gamma\text{CD})_4$ complex and a short one for the $(\text{DPB})-(\gamma\text{CD})$ and $(\text{DPB})_2-(\gamma\text{CD})$ complexes, we have obtained for the r vs $[\gamma\text{CD}]$ curve the fit shown in Figure 4a, with a very satisfactory criterion for its goodness of fit (the parameters for the goodness of the fits are given in Table 3). The values obtained for the two free-running lifetimes were $\tau = 0.23$ and 0.9 ns, which are very close to the ones obtained from the independent fluorescence-decay measurements mentioned above ($\tau = 0.2$ ns, 75%; $\tau = 1.2$ ns, 25%). Of these two lifetimes, we have assigned the short one to those species that have the DPB more exposed to the solvent, viz. $(\text{DPB})-(\gamma\text{CD})$ and $(\text{DPB})_2-(\gamma\text{CD})$. The longer lifetime we have attributed to the species in which the DPB penetrates the dextrin cavities, and it is therefore protected from the solvent. This is the $(\text{DPB})_3-(\gamma\text{CD})_4$ complex. The above assignments were based on the observation that DPB has a much longer lifetime in hexane than in methanol (Table 1) and that although the solvent water/glycol resembles methanol, the interior of the dextrin cavities is expected to be less polar.

DPH- γ CD. The complex formation between DPH and γ CD in 60/40 water/glycol leads to a rapid increase of both Φ and r with increasing γ CD concentration in the fashion shown in Figure 3. The analysis of the fluorescence decay at various added γ CD concentrations gave three different lifetimes. The shortest one, $\tau = 0.36$ ns, corresponds to the free DPH (see Table 1), while the others, $\tau = 3.5$ ns and $\tau = 6.1$ ns, we have assigned to complexes in which the exposure of the DPH to the medium is decreased because of its enclosure in the nanotubes formed by the cyclodextrin cavities. As shown in Figure 5, the fraction of the free DPH, with $\tau = 0.36$ ns, sharply declines with increasing $[\gamma\text{CD}]$, the population of the species with $\tau = 3.5$ ns rises and then decreases, while the concentration of the third species with $\tau = 6.1$ ns, which presumably corresponds to the nanotubes, increases continuously. The average length of the DPH- γ CD structures formed at $[\gamma\text{CD}] = 2 \times 10^{-2}$ M, calculated from (4) and (5) and the data of Table 2, was found to correspond to $\langle j \rangle = 37$ cyclodextrin units, which is a genuine nanotube superstructure. Computer fitting of a model, consistent with the above results, to the r vs $[\gamma\text{CD}]$ data for DPH shown in Figure 3b is not feasible because of the very large size of these nanotubes and the fact that as the length of the tube increases, with increasing $[\gamma\text{CD}]$, its rotational correlation time τ_c increases too.

In the case of Φ vs $[\gamma\text{CD}]$ the overall fitting equation is

$$\Phi = f_i \Phi_i + \sum_{i=1}^{37} f_{ii} \phi_{ii} \quad (12)$$

where f_{ii} is given by (7a). The derivation from (12) of the final fitting equation, which is expressed in terms of the known and the unknown parameters, is the same as the derivation for the case of the DPB- γ CD complex, which was described in terms of (7–9), and therefore, it need not be repeated again. The situation with the fittings here is equally complicated as in the r vs $[\gamma\text{CD}]$ case, since there are approximately 37 steps in the nanotube formation, with a different binding constant K_{ii} and a different fluorescence quantum yield Φ_{ii} corresponding to each step. It is possible, however, by making some reasonable simplifications to obtain estimates for the magnitudes of the binding constants involved in this DPH- γ CD nanotube formation. Thus, we first take into account the fact that nanotube formation proceeds in the self-association fashion of (1) and that for $i \geq 2$ all the binding constants K_{ii} are equal to K . We have also assumed that for $i \geq 2$ all the fluorescence quantum yields are also equal, i.e., $\Phi_{ii} = \Phi$. For the reaction of the first step we have taken the equilibrium constant K_{11} equal to that known from the similar complex $(\text{DPH})-(\alpha\text{CD})$, where $K_{11} = 70 \text{ M}^{-1}$,¹¹ whereas the value of Φ_{11} for the quantum yield of the 1:1 complex, was set equal to the known quantum yield of the DPH- βCD ¹¹ complex, viz., $\Phi_{11} = 0.08$. The fits obtained in this way, however, were not very good. For this reason we introduced two more parameters, the binding constant K_{22} , as free-running, and the corresponding quantum yield Φ_{22} to which we assigned the value 0.45 known from the similarly structured complex $(\text{DPH})_1-(\alpha\text{CD})_2$.¹¹ The new fitting was acceptable and the parameters obtained very reasonable, viz., $K_{22} = 5 \times 10^8$, $K = 4 \times 10^8 \text{ M}^{-1}$ and $\Phi = 0.75$. The fact that K_{22} turned out to be of the same order of magnitude as K confirms that the assumption made in discussing (1) namely, that all binding constants K_{ii} for $i \geq 2$ are set approximately equal to K , is correct. On the other hand the value 0.75 found for the quantum yield Φ is the same as the quantum yield of DPH in benzene. This is very reasonable, since, from absorption and fluorescence spectra, we have found¹¹ that the environment in the interior of the nanotubes resembles very much that of pure benzene. Finally, it is worth mentioning that our attempts to make the above fittings $\langle i \rangle = \langle j \rangle = 37$ caused a breakdown of the program. For this reason we made several fits, one example of which is shown in Figure 6, increasing the number of steps from three up to the point where the program starts breaking down. We found that the program can work up to 18 steps and that for steps more than 6, the parameters extracted turn out to have the same values. All the parameters obtained from these fittings are listed in Table 3.

DPO- γ CD. Obviously, there is little information provided by the flat Φ vs $[\gamma\text{CD}]$ plot for the case of DPO- γ CD in Figure 3a. In fact, there is no evidence even that complexation between this polyene and γ CD takes place. It is only because of the r vs $[\gamma\text{CD}]$ plot of Figure 3b that we know of the complex formation between DPO and γ CD. Here, we have again adopted the self-association scheme of (1) and following the same derivation as for (11), we have obtained (13) as the fitting equation for the fluorescence anisotropy r vs $[\gamma\text{CD}]$ of DPO- γ CD nanotubes.

$$r = f_i \phi_i r_i + \sum_{i=1}^{50} f_{ii} \phi_{ii} r_{ii} \quad (13)$$

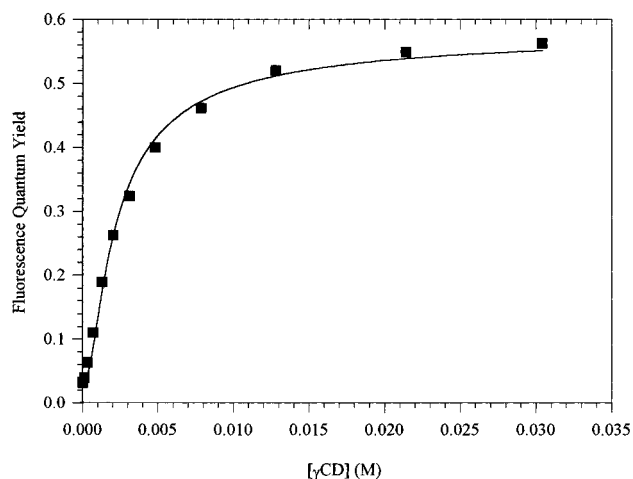


Figure 6. Computer fit of (12) to the fluorescence quantum yield data of DPH vs $[\gamma\text{CD}]$. Solvent is 60/40 water/ethylene glycol. For fitting parameters see Table 3.

All the parameters in (13) have the same meaning as those in (11) viz., r_{ii} is the fluorescence anisotropy of the complex $(\text{DPO})_i-(\gamma\text{CD})_i$, $\phi_{ii} = \Phi_{ii}/\Phi$ is the ratio of the fluorescence quantum yield Φ_{ii} of the species $(\text{DPO})_i-(\gamma\text{CD})_i$ to the total quantum yield Φ , and f_i and ϕ_f refer to the free DPO molecule. Moreover, since the quantum yield of DPO is independent of complex formation with γCD (compare the flat Φ vs $[\gamma\text{CD}]$ curve for DPO in Figure 3a), ϕ_f and ϕ_{ii} can be set equal to unity. Therefore, (13) takes the form of (14), which is a simplified expression of the fitting equation. This was further manipulated, in the same way as for (7)–(11), to produce the final fitting equation (not shown) in terms of known parameters and the unknown binding constants.

$$r = f_f r_f + \sum_{i=1}^{30} f_{ii} r_{ii} \quad (14)$$

From the fluorescence lifetimes of $(\text{DPO})_i-(\gamma\text{CD})_i$ during the titration, we have calculated, by means of (4) and (5), the contribution to the overall value of r of the fluorescence anisotropy r_{ii} of each one of the $(\text{DPO})_i-(\gamma\text{CD})_i$ adducts, for $i = 1-30$. The values of i did not extend to 50, the mean number of the γCD unit per nanotube, because we found that for i above ca. 30 the program was consistently breaking down. Figure 7 shows computer fittings of the data r vs $[\gamma\text{CD}]$ for the DPO- γCD nanotubes. The program soon breaks down, as also indicated in Figure 7, but still the fitting is very good in the small γCD concentration range, before the failure of the program, where even the initial slight upward curvature of the experimental points is reproduced (see insert in Figure 7). The parameters obtained in this case from the computer fits do not involve the fluorescence quantum yields, since the Φ s were eliminated from the fitting equation of (14).

IV. Conclusions

The main conclusions of the present study may be summarized as follows. (1). The effect of the length of the diphenylpolyene turns out to be very important for nanotube

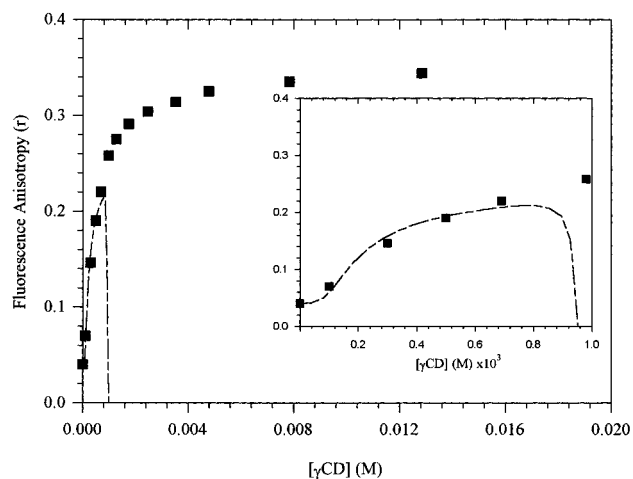


Figure 7. Computer fit of (14) to the fluorescence anisotropy vs $[\gamma\text{CD}]$ data. The fitting was performed with $i = 30$, but the calculations broke down as shown. The inset shows the details of the fit at very low $[\gamma\text{CD}]$.

formation. Thus, DPB, the shortest homologue, does not induce formation of long tubes, DPH facilitates the formation of tubes consisting of up to ca. 37 γCD units, whereas DPO produces the largest structures with ca. 50 cyclodextrin units. (2) Nanotube formation between γCD and α,ω -diphenylpolyenes proceeds as a self-associative chain reaction, each step of which consists of the attachment of one DPP- γCD unit to the growing nanotube. (3) The binding constant K_{11} of the very first step, viz., the formation of the DPP- γCD unit, increases from ca. 10 to 300 M^{-1} as the length of the polyene increases from $n = 2$ to $n = 4$. (4) The binding constants K for the rest of the interactions turn out to be independent of the length of the polyene (at least for $n = 3$ and $n = 4$), and to be consistently above ca. $1 \times 10^8 \text{ M}^{-1}$, while for lower K values nanotubes do not form. (5) Attachment of one dextrin molecule to the $(\text{DPP})_i-(\gamma\text{CD})_i$ growing complex has detrimental effects on nanotube formation, whereas attachment of one DPP to the chain of the growing nanotube does not seem to have any effect.

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