

Formation of Cyclodextrin Nanotube Induced by POPOP Molecule

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Abstract: The interaction between 2,2'-*p*-phenylenebis (5-phenyloxazol) (POPOP) and cyclodextrins (CDs) was investigated using UV-Vis absorption, steady-state fluorescence, and dynamic light scattering (DLS). The results indicated that POPOP could form the 1:2 (guest:host) inclusion complex with β -CD at lower concentrations, which could further form the extended nanotube at higher concentrations. POPOP could also induce the formation of the nanotube of γ -CD. The fluorescence emission of POPOP in aqueous solution of γ -CD showed obvious red shift accompanied by the disappearance of fine structure compared with that in aqueous solution of β -CD, which could be attributed to the formation of the excimer of POPOP in the larger cavity of γ -CD. It was found that at pH greater than 12, the hydrogen bond between the neighboring CDs was destroyed, which led to the collapse of the nanotubular structure. The results also showed that the nanotube structure was not stable at temperatures above 331 K.

Key Words: Nanotube; Cyclodextrin; Fluorescence anisotropy; Dynamic light scattering

In 1994, Li and McGown^[1] reported on the formation of nanotubes of β - and γ - cyclodextrins (β -CD and γ -CD) through incorporation with the DPH molecule, i.e., all-*trans*-1,6-diphenyl-1,3,5-hexatriene, through supramolecular assembly. Pistolis *et al.*^[2] further studied the interaction between DPH and CDs using steady-state fluorescence and fluorescence anisotropy. It was found that DPH could also induce the formation of nanotubes of β -CD and γ -CD in a DMF/H₂O mixed solvent. However, when the two DPH derivatives, DPH-N(CH₃)₂ and DPH-NO₂, in which the substituents N(CH₃)₂ and NO₂ are attached at the *para* position of one of the benzene rings of DPH, replacing one hydrogen atom, were used, nanotube formation did not occur^[3]. Neither did nanotubes form when all the hydrogens of the OH groups in the γ -CD were replaced by CH₃ groups^[2]. Pistolis *et al.*^[4] also studied the interaction between CDs and two other homologues of DPH in the α - and ω - diphenylpolyenes series, i.e., DPB with two double bonds and DPO with four double bonds. The results indicated that the nanotube formation depended on the size of the guest molecules, i.e., DPB is of a smaller size

and can only form the inclusion complex with CD, whereas DPO is of comparatively larger size and can form the nanotube more easily. Agbaria *et al.*^[5–7] discovered that some oxazole molecules, such as 2,5-diphenyl-1,3,4-oxadiazole (PPD), 2,5-diphenyloxazole (PPO), 2-phenyl-5-(4-diphenyl)-1,3,4-oxadiazole (PBD), and 2,5-(4,4'-diphenyl)-1,3,4-oxadiazole (BBOD), could also induce the formation of γ -CD nanotube. During the course of the nanotube formation, the entry of the oxazole molecules into the cavity of γ -CD in pairs resulted in the formation of the excimer peak in their fluorescence spectra. In these types of structures, the conjugated fluorescent molecule is restrained and arranged linearly and its function is similar to that of a molecular wire or a photonic switch at the molecular level. Therefore, it can be developed as a molecular device. In addition, the nanotubular structure could also be formed between a drug molecule and cyclodextrin^[8].

In recent years, our research group has focused on the study of the formation of nanotubular structure of cyclodextrin induced by small organic molecules. Thus far, several such small molecules have been found^[9–14]. The formation of the

Received: May 19, 2006; Revised: July 11, 2006.

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The project was supported by the National Natural Science Foundation of China (90206020, 29901001).

cyclodextrin nanotube in the presence of small organic molecules does not seem to be an individual phenomenon.

The 2,2'-*p*-phenylenebis (5-phenyloxazol) (POPOP; see Fig.1) is a well-known oxazine dye characterized by intense fluorescence and has been widely used in the preparation of supramolecular films, plastic scintillators, liquid-phase thermometers, bacterial luciferase etc.^[15–21] In this article, using UV-Vis absorption, steady-state fluorescence, and dynamic light scattering measurements, it has been shown that POPOP could induce the formation of nanotubes of β - and γ -CDs.

1 Experimental section

1.1 Materials

α -CD (Acros, $\geq 98\%$), γ -CD (Aldrich, 99%), and POPOP (Acros, Laser Grade) were used as received. β -CD (Beijing Shuanghuan, China) was triply recrystallized from tridistilled water. All other chemical reagents used in this study were of analytical grade. All the experiments were carried out at room temperature unless stated otherwise.

1.2 Instruments

The dynamic light scattering (DLS) measurements were carried out using an ALV/DLS/SLS-5022F photon correlation spectrometer. The wavelength of laser was 632.8 nm, and the scattering angle was 90 °C. The experimental temperature was 25 °C, and the experimental error was about $\pm 5\%$. Absorption spectra were recorded on a U-3010 (Hitachi, Japan) spectrophotometer. The width of the slit was 2 nm. The steady-state fluorescence and polarization measurements were carried out using an FL-4500 spectrofluorimeter (Hitachi, Japan), and both the excitation and emission bandpasses were 10 nm. In the temperature experiments, the temperature was controlled by placing the sample in a cell compartment whose walls were accessible to water circulation. The final temperature of the sample was measured using a thermocouple (Checktemp, Hanna, Italy) (± 0.1 °C) immersed in the solution.

1.3 Methods

The stock solution of POPOP (2.5×10^{-4} mol·L⁻¹) was prepared in ethanol. For each sample, an aliquot of the stock solution was first injected into a 5-mL volumetric flask and then an appropriate amount of CD aqueous solution was added to make up the solution to the required volume. To study the effect of pH, the pH values of the solutions were adjusted by

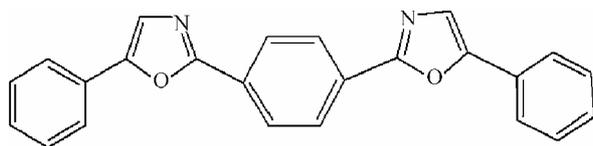


Fig.1 Molecular structure of POPOP
POPOP: 2,2'-*p*-phenylenebis(5-phenyloxazol)

adding hydrochloric acid (0.1 mol·L⁻¹) and sodium hydroxide. Before the DLS measurements, the samples were treated with 0.2- μ m filters (Membrana, micro PES).

2 Results and discussion

2.1 UV-Vis spectra of POPOP in different solvents

The UV-Vis spectra of POPOP in pure water, ethanol, *n*-heptane, and aqueous solutions of α -, β -, and γ -CDs, respectively, are shown in Fig.2. As can be seen clearly from Fig.2, POPOP showed a small red shift in ethanol and *n*-heptane, whereas no shift was observed in the solution of α -CD, as compared with pure water. However, an obvious red shift can be seen in β -CD and γ -CD solutions. It was also found that both POPOP- β -CD and POPOP- γ -CD systems exhibit a strong scattering from 420 to 600 nm. Actually, the POPOP- α -CD aqueous solution is clear, whereas the POPOP- β -CD and the POPOP- γ -CD aqueous solutions show some extent of turbidity, which leads to an error in the measurement of peak intensity.

2.2 Formation of 1:2 inclusion complexes in POPOP- β -CD solution

The fluorescence spectra of POPOP in the aqueous solution of β -CD at different concentrations are shown in Fig.3a. The fluorescence intensity of POPOP was found to increase with the increase of β -CD concentration and the system becomes transparent when its concentration is low (e.g., 4.0×10^{-8} mol·L⁻¹). Corresponding to the change in the microenvironment of POPOP from hydrophobic to relatively hydrophilic, the fluorescence spectra of POPOP exhibit an obvious blue shift in β -CD solutions compared with pure water. This can be attributed to the fact that an inclusion complex may be formed when POPOP enters into the hydrophobic cavity of β -CD. For the POPOP- β -CD systems at different concentrations, the stoichiometry and the association constant of the inclusion complex can also be obtained using the nonlinear regression analysis (NLR) method^[22]. The results showed that POPOP

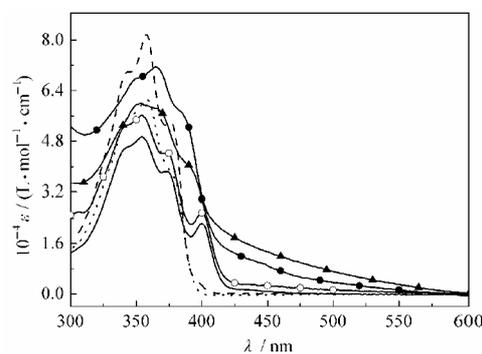


Fig.2 UV-Vis spectra of POPOP
 $c(\text{POPOP})=2.5 \times 10^{-6}$ mol·L⁻¹, $c(\text{CD})=15$ mmol·L⁻¹; (—) water, (---) ethanol,
(- · -) *n*-heptane, (○) α -CD, (▲) γ -CD, (●) β -CD

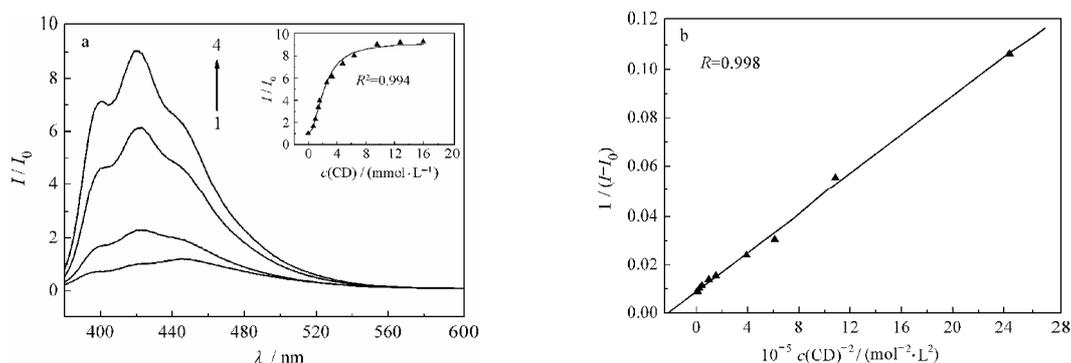


Fig.3 (a) Fluorescence emission spectra of POPOP in the aqueous solutions of β -CD at different concentrations; (b) Double-reciprocal plot of the 1:2 (POPOP/ β -CD) inclusion complex

$c(\text{POPOP})=4.0 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$; from 1 to 4, $c(\beta\text{-CD})=0, 1.0, 3.2, 9.6 \text{ mmol} \cdot \text{L}^{-1}$; the inset is the result of non-linear regression (NLR) analysis.

and β -CD formed 1:2 inclusion complex having the association constant $K=(1.9 \pm 0.1) \times 10^5 \text{ L}^2 \cdot \text{mol}^{-2}$ and correlation coefficient $R^2=0.994$ (see the inset of Fig.3). In addition, the rationality of the formation of the 1:2 POPOP- β -CD inclusion complex was validated using the double reciprocal plot (see Fig.3b).

2.3 Nanotube formation of POPOP with β -CD and γ -CD

Fig.4 shows the fluorescence spectra of POPOP ($2.5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$) in aqueous solutions of β -CD and γ -CD at various concentrations. According to simple inclusion patterns, no reasonable NLR results concerning the fluorescence intensity and the β -CD concentration can be obtained. This phenomenon suggests that the interaction of POPOP with β -CD and γ -CD does not result in simple inclusion complexes. Furthermore, the POPOP ($2.5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$)- β -CD ($0.015 \text{ mol} \cdot \text{L}^{-1}$) and POPOP ($2.5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$)- γ -CD ($0.015 \text{ mol} \cdot \text{L}^{-1}$) solutions are slightly turbid, whereas the individual solutions of β -CD ($0.015 \text{ mol} \cdot \text{L}^{-1}$), γ -CD ($0.015 \text{ mol} \cdot \text{L}^{-1}$), and POPOP ($2.5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$) are transparent. This implies that a certain complex of larger size might exist. Similar phenomena^[5,14]

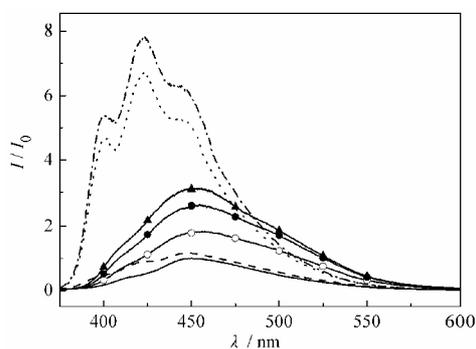


Fig.4 Fluorescence emission spectra of POPOP

$c(\text{POPOP})=2.5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$

—) water; - - -) $0.003 \text{ mol} \cdot \text{L}^{-1} \beta\text{-CD}$; ...) $0.009 \text{ mol} \cdot \text{L}^{-1} \beta\text{-CD}$;
 - · -) $0.015 \text{ mol} \cdot \text{L}^{-1} \beta\text{-CD}$; - ○ -) $0.003 \text{ mol} \cdot \text{L}^{-1} \gamma\text{-CD}$;
 - ● -) $0.009 \text{ mol} \cdot \text{L}^{-1} \gamma\text{-CD}$; - ▲ -) $0.015 \text{ mol} \cdot \text{L}^{-1} \gamma\text{-CD}$

observed both in the literature and in our previous study highlight the possible existence of cyclodextrin nanotube.

The steady-state fluorescence anisotropy (r) of POPOP against the concentrations of β - and γ -CDs are shown in Fig.5. At the maximum concentrations of β - and γ -CDs studied, i.e., $0.015 \text{ mol} \cdot \text{L}^{-1}$, r values of 0.28 and 0.29, respectively, are attained, whereas the r value is only 0.06 for POPOP in pure water. The large anisotropy values in the above-mentioned POPOP-CD systems indicate that POPOP molecules are limited to a great extent in a rigid microenvironment^[23]. This can be rationalized by the formation of nanotube. The fluorescence spectra of POPOP in solution of γ -CD show an obvious red shift and the small peak corresponding to the fine structure disappears and a broad peak appears instead, as compared with that in the solution of β -CD. This is because γ -CD has a larger cavity and can include a pair of POPOP molecules forming an excimer. Although POPOP can form nanotube with both β - and γ -CDs, the arrangement of POPOP molecules in the nanotube differs, i.e., single POPOP molecules are arranged linearly in the former but pairs of POPOP molecules are arranged linearly in the latter. For this reason, the UV-Vis absorption and fluorescence spectra exhibit considerable differences.

The artificial decrease in fluorescence anisotropy caused by

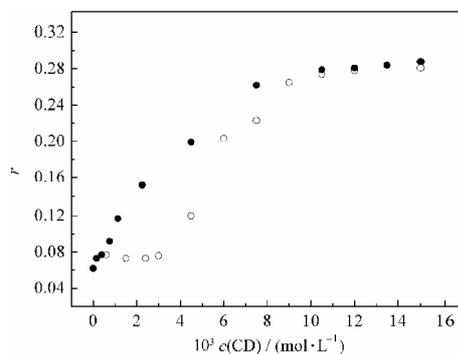


Fig.5 Steady-state fluorescence anisotropy (r) of POPOP

-○-) β -CD; -●-) γ -CD; $c(\text{POPOP})=2.5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$

light scattering has been described by Teale^[24]. The approximate expression for the fractional decrease in anisotropy is

$$(r' - r_{\text{obs}})/r' = (3 - 3T)/(3 + 7T) \quad (1)$$

where r' is the actual anisotropy that is not affected by the light scattering, r_{obs} is the observed anisotropy, and T is the total effective fractional transmission at the excitation and emission wavelengths.

Subsequently, Lentz *et al.*^[25] proved the general applicability of Teale's approach to the depolarization by membrane suspensions and suggested a more common equation as follows:

$$(r' - r_{\text{obs}})/r' = K \times A \quad (2)$$

where K is the observed proportionality constant and A is the absorbance.

The solutions of POPOP ($2.5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$)- β -CD ($0.015 \text{ mol} \cdot \text{L}^{-1}$) and POPOP ($2.5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$)- γ -CD ($0.015 \text{ mol} \cdot \text{L}^{-1}$) are slightly turbid because of the nanotube formation; therefore, it is necessary to correct the observed anisotropy value that may be affected by scattering of light by large particles in the solution. According to Eqs. (1) and (2), a series of absorbance values of POPOP in the aqueous solutions of β -CD at various concentrations were obtained. Fig.6 shows the dependence of $(r' - r_{\text{obs}})/r'$ of POPOP (calculated from $(3 - 3T)/(3 + 7T)$) and represents the difference between actual anisotropy values and the measured values) vs absorbance in aqueous solutions of β -CD at various concentrations. The linear correlation with the correlation coefficient of 0.999 agrees well with Teale's theory that in turbid solution the difference between actual anisotropy values and the measured values is proportional to the absorbance.

Based on Eq.(1), the $(r' - r_{\text{obs}})/r'$ value was obtained, from which the actual anisotropy (r') was also calculated. As shown in Fig.7, when the concentration of β -CD is low, the difference between r' and r_{obs} is not obvious. The maximum difference is less than 4% at relatively high concentration of β -CD. Thus, in the solution of POPOP ($2.5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$)- β -CD ($0.015 \text{ mol} \cdot \text{L}^{-1}$), the influence of the turbidity, which originated from

the nanotube formation, on the anisotropy value of POPOP can be ignored. However, in the solution of PBD ($1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$)- β -CD ($0.010 \text{ mol} \cdot \text{L}^{-1}$), wherein the secondary assembly of the cyclodextrin nanotube results in significant turbidity, the maximum difference between r' and r_{obs} could attain a value of 24%, which cannot be ignored^[14].

The measurement of steady-state fluorescence anisotropy provides a method for estimating the relative size of the POPOP-CD nanotube and the average number of the CD per nanotube (n_{CD}). According to the Perrin-Weber formula^[23]:

$$r_0/r = 1 + \tau RT/\eta V \quad (3)$$

where r_0 is the maximum value of anisotropy for a certain probe that is usually measured in a pure solution of glycerol at 273 K. The r_0 value of POPOP molecule is 0.33 in this study. τ is the fluorescence lifetime and η is the viscosity of the medium. If the τ and η values remain constant^[13], the anisotropy change is related to the change in the size of the complex. In this case, the relative size of the POPOP-CD complexes can be estimated according to the following equation^[21]:

$$[r_2(r_0 - r_1)]/[r_1(r_0 - r_2)] = V_2/V_1 \quad (4)$$

where r_1 and r_2 are the fluorescence anisotropy values measured in two different systems, whereas V_1 and V_2 represent the effective volumes of the two systems.

To estimate the n_{CD} value, the r_2 value must be investigated at varying concentrations of CD. By introducing the value of 1:2 (POPOP: β -CD) inclusion complex ($c(\text{POPOP}) = 4 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$, $c(\beta\text{-CD}) = 0.007 \text{ mol} \cdot \text{L}^{-1}$, $r_1 = 0.13$), the value of $2 \times (V_2/V_1)$ is approximated to the number of β -CD molecules in a nanotube. Therefore, Eq.(4) can be used to calculate the value of V_2/V_1 and the number of β -CD per nanotube (Fig.7). It is estimated that the maximum number of β -CD in the POPOP- β -CD nanotube is 19.

2.4 DLS analysis

Using the DLS analysis, Gonzalez-Gaitano *et al.*^[26] investigated the size distributions of α -, β -, and γ -CDs, respectively, in aqueous solutions. The results indicated that most CDs in

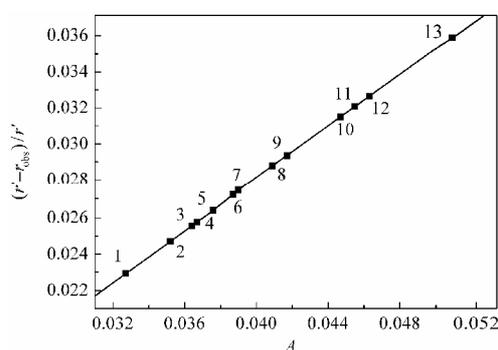


Fig.6 Dependence of $(r' - r_{\text{obs}})/r'$ of POPOP vs absorbance in aqueous solutions of β -CD at various concentrations from 1 to 13, $c(\beta\text{-CD}) = 0, 0.6, 1.2, 1.8, 2.4, 3.0, 4.5, 6.0, 7.5, 9.0, 10.5, 12.0, 13.5 \text{ mmol} \cdot \text{L}^{-1}$

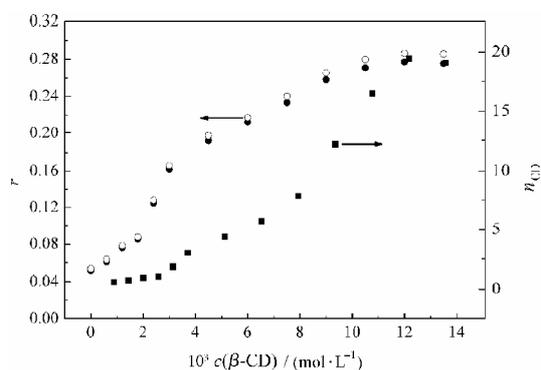


Fig.7 Corrected (\circ) and observed (\bullet) fluorescence anisotropies of POPOP ($2.5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$) in aqueous solutions of β -CD at various concentrations and the estimation of CD unit in a single POPOP- β -CD nanotube (\blacksquare)

the solution existed in the monomeric form and few existed in the aggregated form. In our recent work^[13], it was also reported that the CDs existed in two forms in the aqueous solutions, one was the monomeric form with a hydrodynamic radius between 0.6 and 0.8 nm and the other was the aggregated form with a hydrodynamic radius between 60 and 100 nm, which were in accordance with the results obtained by Gonzalez-Gaitano *et al.*^[26].

Fig.8 shows the DLS results of the size distributions of CDs (0.015 mol·L⁻¹) in the aqueous solution in the presence of POPOP (2.5×10⁻⁶ mol·L⁻¹), which have also been summarized in Table 1. It can be seen from Fig.8 and Table 1 that the presence of POPOP has little influence on the size distributions of α -CD in the aqueous solution, indicating that POPOP molecule and α -CD may form simple inclusion complexes whose size approximates to that of monomeric α -CD, leading to the similarity between the DLS results in the presence and absence of POPOP. In contrast, in the presence of POPOP, the aqueous solutions of β -CD and γ -CD exhibit an additional peak at around 15 nm besides the peaks of monomeric and aggregated forms as observed in α -CD solutions. These results are also in agreement with those of our recent investigation on the interaction between *N,N'*-diphenyl-benzidine and CDs^[13]. It is noteworthy that the additional peak in the β -CD and γ -CD aqueous solutions can be observed only in the presence of POPOP. This clearly suggests that a new structure that is different from the monomeric and aggregated forms may have formed in the system. In this study, this new structure is addressed with regard to the formation of CD nanotube induced by POPOP molecule, and this coincides very well with the results of previous UV-Vis, fluorescence, and fluorescence anisotropy analyses.

With the availability of data on the scattering intensity and the mole fraction of each component, the approximate calculation of mass contribution of the nanotube in the POPOP-CDs systems has been carried out using the method suggested by Gonzalez-Gaitano *et al.*^[26]. The estimated values are 0.0002% for POPOP- β -CD and 0.0061% for POPOP- γ -CD (see Table 1).

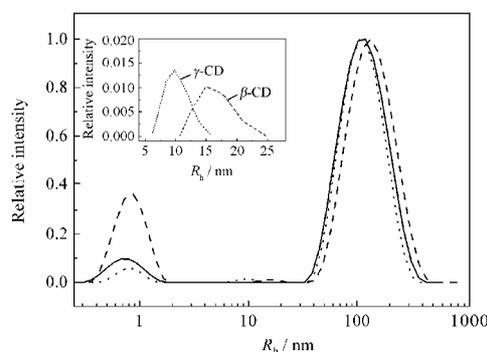


Fig.8 DLS results of POPOP in the aqueous solutions filtered with the 0.2- μ m filter

The inset is the enlargement of R_h ranging from 5 to 25 nm.

$c(\text{POPOP})=2.5\times 10^{-6}$ mol·L⁻¹, $c(\text{CD})=0.015$ mol·L⁻¹;

—) α -CD, ---) β -CD, ...) γ -CD

2.5 The effects of pH value and temperature on the POPOP- β -CD nanotube

As hydrogen bonding is always regarded as the main driving force for the formation of cyclodextrin nanotube^[1-14], the effects of pH on the anisotropy of POPOP molecule are investigated and the results are shown in Fig.9a. It can be seen that the r value of POPOP showed slight change in weak acidic and basic, and neutral environments. However, as the pH value exceeds 12, the r value exhibits a sharp decrease, suggesting that the nanotube can only exist stably below pH 12. As the pK_a value of β -CD is 12.20^[27], the hydroxyl groups of β -CD will undergo a deprotonated process to become negative oxygenic ions when pH values are higher than the pK_a value, 12.20, leading to ineffective hydrogen bonding between neighboring CDs and thus the collapse of the nanotube structure. These results are in good agreement with those of the previous studies^[2,8,9,13].

The fluorescence anisotropy of POPOP as a function of temperature was measured to discuss the thermostabilization of this cyclodextrin nanotube. As shown in Fig.9b, the r value remains almost invariable until the temperature is increased to 331 K. However, when the temperature becomes much higher,

Table 1 Mean hydrodynamic radius (R_h), correlative intensity (I), and mass fraction (w) contributions of various components in the aqueous solutions of CDs and POPOP-CDs

Sample	R_{h1}/nm	I_1 (%)	w_1 (%)	R_{h2}/nm	I_2 (%)	w_2 (%)	R_{h3}/nm	I_3 (%)	w_3 (%)
α -CD*	0.6±0.1	6.68	99.9989	—	—	—	64.4±0.5	93.32	0.0011
POPOP- α -CD	0.7±0.2	6.56	99.9989	—	—	—	114.2±0.5	93.44	0.0011
β -CD*	0.8±0.1	14.02	99.9998	—	—	—	114.7±0.4	85.98	0.0002
POPOP- β -CD	0.8±0.2	19.93	99.9997	15.8±0.2	0.31	0.0002	133.3±0.5	79.76	0.0001
γ -CD*	0.7±0.2	3.19	99.9977	—	—	—	76.7±0.5	96.81	0.0023
POPOP- γ -CD	0.8±0.1	3.24	99.9928	11.4±0.4	0.57	0.0061	111.4±0.4	96.19	0.0011

The aqueous solutions of CDs and POPOP-CDs were filtered with the 0.2- μ m filter; $c(\text{POPOP})=2.5\times 10^{-6}$ mol·L⁻¹,

$c(\text{CD})=0.015$ mol·L⁻¹; *taken from Ref[13], $c(\text{CD})=0.01$ mol·L⁻¹

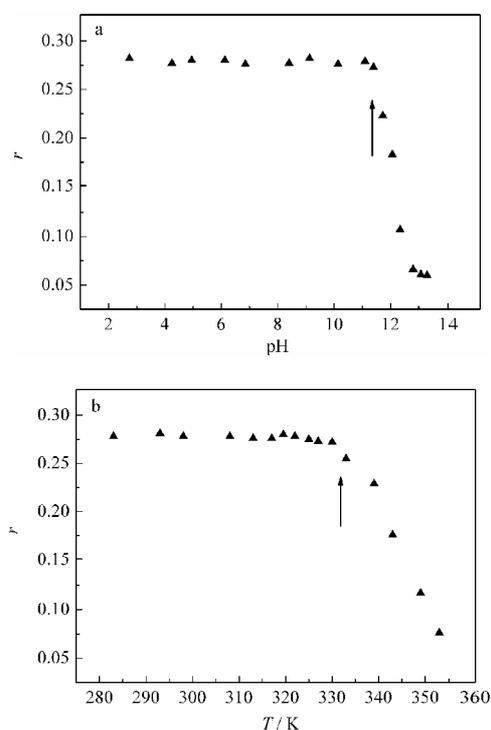


Fig.9 Steady-state fluorescence anisotropy (r) of POPOP in the aqueous solution of β -CD (0.015 mol·L⁻¹) as a function of pH (a) and temperature (b)

the r value decreases significantly. This indicated that the POPOP- β -CD nanotube could exist stably below 331 K and would collapse when the temperature became higher. This character of the POPOP- β -CD nanotube implies its potential applications in the fields of temperature controlling molecular wires or switches.

3 Conclusions

The UV-Vis spectra and DLS measurement clearly suggest that the formation of β -CD and γ -CD nanotube can be induced by POPOP molecule. In the combination of steady-state fluorescence and fluorescence anisotropy experiments, it was found that the POPOP formed 1:2 (guest:host) inclusion complex with β -CD at low concentrations, whereas POPOP induced the formation of nanotube with β -CD or γ -CD at high concentrations. The broad peak that appeared in the fluorescence spectra of the POPOP- γ -CD system was assigned to the formation of POPOP excimer, which is caused by the inclusion of POPOP molecule pair in the relatively larger cavity of γ -CD. The studies regarding the effects of pH and temperature indicated that the β -CD nanotube induced by POPOP was not stable at pH higher than 12 and temperature above 331 K.

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