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ORIGINAL ARTICLE

Study on inclusion complexes of meso-tetrakis(2-thienyl) porphyrin and Cu-meso-tetrakis(2-thienyl)porphyrin with cyclodextrins by spectroscopy method

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Abstract In phosphate buffer solution of pH5.4, the interaction of meso-tetrakis(2-thienyl)porphyrin(H_2TTP) and Cu-meso-tetrakis(2-thienyl)porphyrin(Cu-TTP) with α-cyclodextrin(α-CD), β-CD, γ-CD, heptakis(2,3,6-tri-O-methyl)-β-CD(TM-β-CD) has been studied by means of UV-vis, fluorescence and ^{1}HNMR spectroscopy, respectively. The H_2TTP and Cu-TTP can form 1:2 inclusion complexes with TM-β-CD and 1:1 inclusion complexes with the other three cyclodextrins. In this paper, the inclusion constants (K) of H_2TTP and Cu-TTP for the formation of the inclusion complexes have been estimated from the changes of absorbance and fluorescence intensity in phosphate buffer solution. The inclusive capabilities of different kinds of cyclodextrins are compared. The result shows that the inclusion ability of α-CD with H_2TTP and Cu-TTP is the strongest among the three native CDs. The inclusion ability of modified β-CD with H_2TTP and Cu-TTP is stronger, compared to the native β-CD, which indicates that the capacity matching plays a crucial role in the inclusion procedure except for the hydrophobic effect. In addition ^{1}HNMR spectra supports the inclusion conformation of the TM-β-CD-Cu-TTP inclusion complex, indicating the interaction mechanism of inclusion processes.

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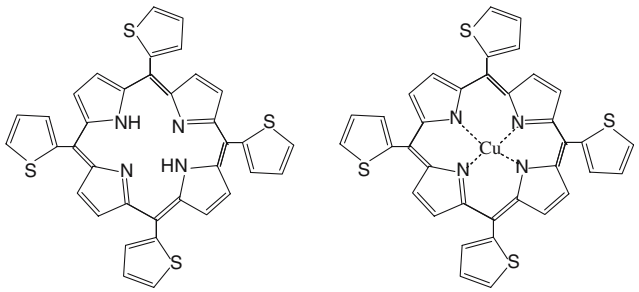
Keywords Meso-tetrakis(2-thienyl)porphyrin(H_2TTP) · Cu-meso-tetrakis(2-thienyl)porphyrin(Cu-TTP) · Cyclodextrins · Inclusion complexes · Spectroscopy

Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides. It is well known that, because of their unique cavity of hydrophobic interior and polar or hydrophilic exterior, many of organic or inorganic guest molecules can be fully or partly incorporated into the cavities of CDs to form inclusion complexes [1]. The capability of CDs and modified CDs to form inclusion complexes with various molecules is well known [2]. The formation of inclusion complex changes the physical and chemical properties of guest [3]. It can sustain the release rate of drugs [4], enhance the peak concentration of drugs in blood [5] and improve bioavailability [6] etc.

Porphyrins and metalloderivatives are requisite substances of cytochrome, hemachrome, and chlorophyll, which play significant roles in biological processes. They have been applied in artificial simulation [7, 8], suparmolecular assembly of the heme proteins and other molecular systems relevant to biology [9, 10], or employed as catalysts of oxidation processes [11, 12]. The formation of inclusion complexes of CDs with porphyrin derivatives modifies the photochemical and photophysical properties of porphyrin derivatives [13], and has been examined by many researchers. Consequently, it is very important to examine the formation of inclusion complexes of CDs with porphyrin derivatives. In our laboratory previous studies, several porphyrin-CD inclusion systems were investigated by different methods [14–18]. In recent years, many

meso-thienyl porphyrins were synthesized, and the photochemical characterization, redox, and axial ligation studies of meso-thienyl porphyrins were reported [19–24]. However, the paper about CDs interacting with H_2TTP and Cu-TTP (Scheme 1) has seldom found in literature.



Scheme 1 The chemical structure of H_2TTP and Cu-TTP

In this paper, the interaction of four cyclodextrins α-CD, β-CD, γ-CD and TM-β-CD with H_2TTP and Cu-TTP has been studied by UV-vis and fluorescence spectroscopy in 0.1 mol l^{-1} phosphate buffer (pH5.4, 20°C). The ^{1}HNMR spectra support the inclusion conformation of the TM-β-CD-Cu-TTP and TM-β-CD-H_2TTP inclusion complexes, indicating the interaction mechanism of inclusion processes. Their inclusion constants are calculated by the double-reciprocal method, and the inclusive capabilities of different kinds of cyclodextrins are compared too. The inclusion ability of α-CD with H_2TTP (Cu-TTP) is the strongest among the three native CDs. It indicates that the capacity matching between cyclodextrins and porphyrins plays an important role in the inclusion procedure except for hydrophobic effect.

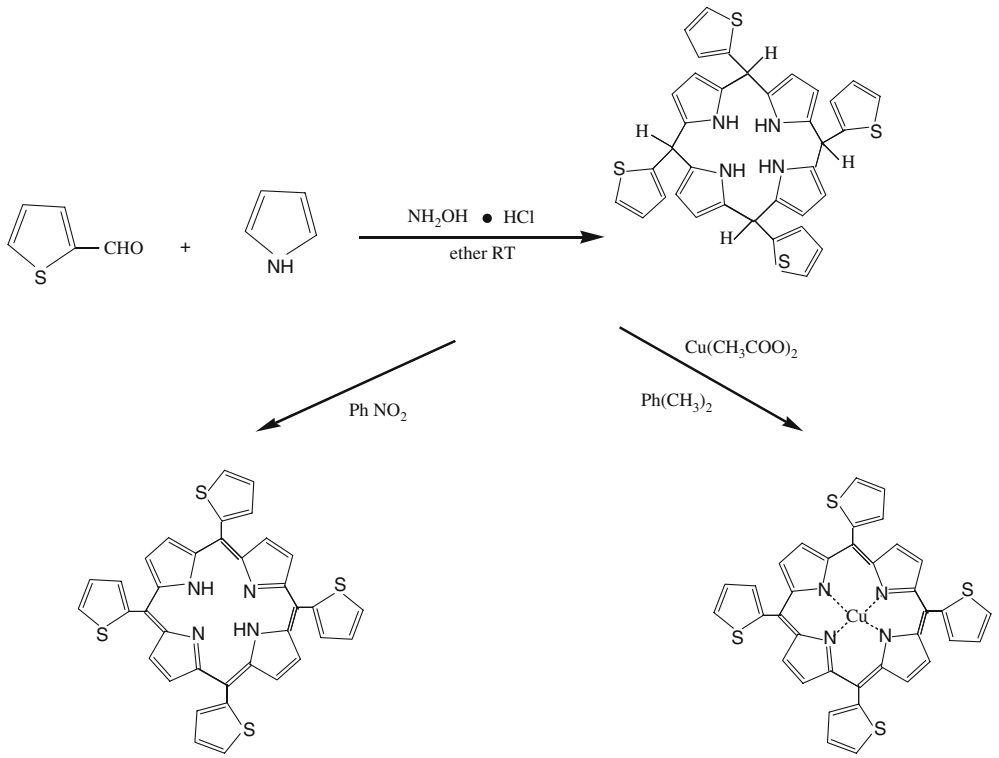
Experimental

Reagent and apparatus

β-CD (95% YuNan Gourment Factory) was purified by recrystallization in double distilled water. TM-β-CD, MW = 1427 was purchased from SIGMA. α-CD and γ-CD were purchased from Aldrich. All absorption and fluorescence measurements were performed with TU-1901 double beam UV-Vis spectrophotometer (Puxi instrument Co. Beijing, China) and Cary Eclipse Fluorescence Spectrophotometer (USA). Excitation and emission slits were set at 10 nm except for determining TM-β-CD which slits were set at 5 nm. The measurement of NMR was performed on DKX-300 MHz (Bruker, Switzerland). All experiments were carried out at 20 ± 1°C.

The synthesis of H_2TTP and Cu-TTP

5 mmol Pyrrole and 5 mmol thienanal were dissolved in 20–25 ml absolute ether at room temperature to



react for 2–4 h to give condensation product porphyrinogen using oxammonium hydrochloride as catalyst. The absolute ether was distilled after 20 ml nitrobenzene was added, and than the mixture was heating contraflow for 2 h. The reaction mixture was cooled to 50°C and 25 ml methyl alcohol was added, then it was allowed to stand overnight. Purple crystal was precipitated and was removed by vacuum filtration, and the filter cake was washed twice with methyl alcohol. The filtrate was diluted with 50 ml water after methyl alcohol being evaporated. Then the nitrobenzene and water were distilled to give crude product. The crude product was purified by chromatography column packed with 40–80 mesh silica gel and eluted by dichloromethane, the yield of meso-tetrakis(2-thienyl)porphyrin(H_2TTP) was 44%. At the step two, let xylene mixture substitute nitrobenzene and 3.3 g potassium ferricyanide was added at the same time. And the mixture was heating contraflow for 4 h after absolute ether being distilled. Then 2.0 g copper acetate was added and the mixture was heating contraflow for another 2 h. The crude product of Cu-meso-tetrakis(2-thienyl)porphyrin(Cu-TTP) was separated by chromatography column to 38% yield.

Elemental analyse: $C_{36}H_{22}N_4S_4$, Calcd: C67.71, H3.45, N8.78. Found: C67.31, H3.50, N8.34.

λmax(DMF:water = 1:9): 419, 526, 556, 596 nm. Fluorescence emission spectrum (ex = 421, DMF:water = 1:9): 847.02 nm. δ^1H(CD_3COCD_3): –2.63(2H,N–H, hydrogen in the porphyrin ring), 7.19~7.36(8H, hydrogen of the thienyl ring), 7.98(4H, hydrogen of the thienyl ring), 9.27(8H, hydrogen of the pyrrole ring)ppm.

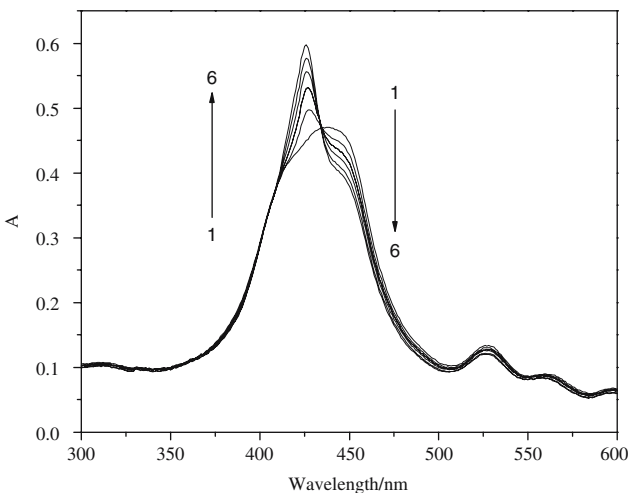


Fig. 1 Absorption spectra of H_2TTP (5.00×10^{-6} mol l^{-1}) in pH5.4 buffers containing various concentrations of TM-β-CD. Concentration of TM-β-CD: (1) 0, (2) 1.00×10^{-4}, (3) 2.00×10^{-4}, (4) 3.00×10^{-4}, (5) 4.00×10^{-4} and (6) 5.00×10^{-4} mol l^{-1}

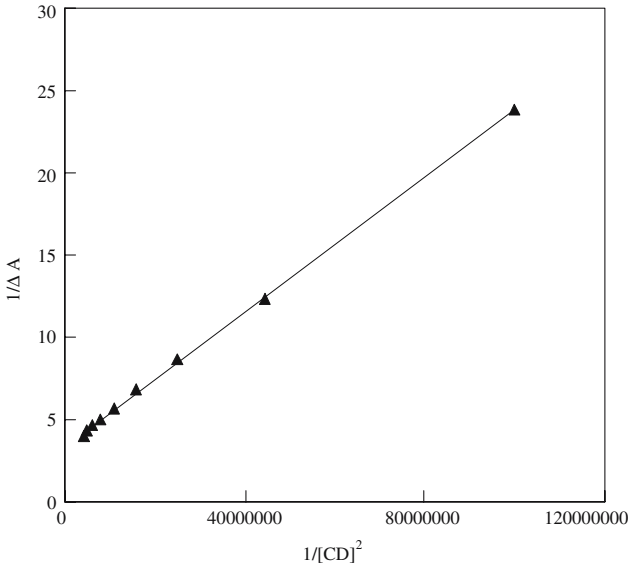


Fig. 2 Double reciprocal plots for H_2TTP complex to TM-β-CD

Elemental analyse: $C_{36}H_{20}N_4S_4Cu$, Calcd: C61.71, H2.86, N8.0. Found: C61.55, H3.01, N8.33. λmax(DMF:water = 1:9): 425, 551 nm. Fluorescence emission spectrum(ex = 423.03, DMF:water = 1:9): 849.05 nm.δ^1H(CD_3COCD_3): 7.37~7.63(8H, hydrogen of the thienyl ring), 8.12(4H, hydrogen of the thienyl ring), 9.10(8H, hydrogen of the pyrrole ring)ppm.

Method

5.00×10^{-5} mol l^{-1} stock solution of H_2TTP and 7.14×10^{-5} mol l^{-1} stock solution of Cu-TTP were prepared by N,N-Dimethylformamide(DMF). 5.00×10^{-6} mol l^{-1} working solution of H_2TTP and 7.14×10^{-6} mol l^{-1} working solution of Cu-TTP were obtained by transferring 1.0 ml stock solution and 1.0 ml 0.10 mol l^{-1} phosphate buffer (pH5.4, 20°C) into 10 ml volumetric flask. Different amount of cyclodextrins (α-CD, β-CD, γ-CD and TM-β-CD) were added to prepare a series of working solution. The mixed solution was diluted to final volume with distilled water and shaken thoroughly, following equilibrated for 15 min at 20 ± 1°C.

Table 1 The inclusion constants of H_2TTP with four CDs

	α-CD	β-CD	γ-CD	TM-β-CD
Absorption	2.8×10^{3a}	1.8×10^{3a}	5.0×10^{2a}	1.7×10^{7b}
Fluorescence	7.0×10^{3a}	2.7×10^{3a}	1.6×10^{3a}	3.0×10^{7b}

[a] The binding constant of 1:1 inclusion complex

[b] The binding constant of 2:1 inclusion complex

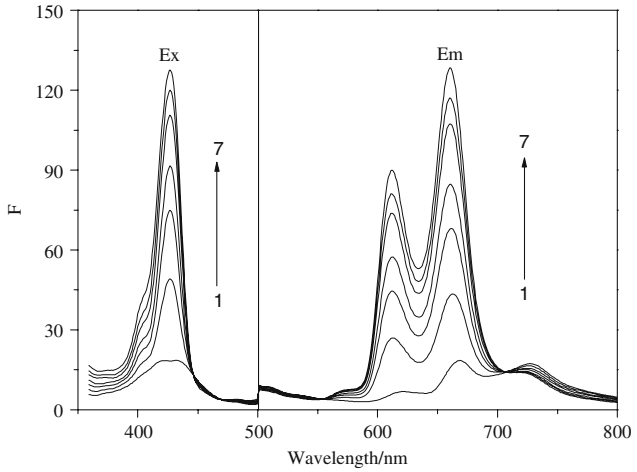


Fig. 3 Fluorescence spectra of H_2TTP (5.00×10^{-6} mol l^{-1}) in pH5.4 buffers containing various concentrations of TM-β-CD. Concentration of TM-β-CD: (1) 0, (2) 5.00×10^{-5}, (3) 1.00×10^{-4}, (4) 1.50×10^{-4}, (5) 2.50×10^{-4}, (6) 3.50×10^{-4} and (7) 5.00×10^{-4} mol l^{-1}

Results and discussion

Inclusion complexes of TM-β-CD with H_2TTP

To fix the concentration of H_2TTP at 5.00×10^{-6} mol l^{-1} and the concentration of cyclodextrin was varied from 1.00×10^{-4} to 5.00×10^{-4} mol l^{-1}. Figure 1 shows the Soret band in the absorption of H_2TTP (5.00×10^{-6} mol l^{-1}) in pH 5.4 buffers containing various concentrations of TM-β-CD. The absorption peak is shifted to shorter wavelengths with an increase in the TM-β-CD concentrations, accompanied by heighten of absorption peak. At 434 nm, there is an obvious isosbestic point. This finding indicates the formation of the single inclusion complex of TM-β-CD with H_2TTP.

The inclusion constant (K) is an important parameter, which represents the inclusion interaction. The inclusion constants of complexes are estimated according to the double-reciprocal method. It can be obtained by the following equation [25].

$$\frac{1}{\Delta A} = \frac{1}{\alpha} + \frac{1}{\alpha K [CD]_0^n} \quad (1)$$

where ΔA denotes the difference of absorption of guest molecular in the presence and absence of CDs. α is a constant, and $[CD]_0$ denotes the concentration of CDs. K can be calculated from a plot of 1/A vs. $1/[CD]^n$. Figure 2 shows the double reciprocal plots of 1/ΔA versus $1/[CD]^2$ for H_2TTP with TM-β-CD at pH 5.4. The plot exhibits good linearity (the linear correlation coefficient $r = 0.9997$). This verifies the formation of inclusion complexes with a stoichiometry of 1:2 between H_2TTP and TM-β-CD. The inclusion constant value is calculated assuming the existence of complexes with 1:2 stoichiometry. The related inclusion constant for TM-β-CD with H_2TTP is 1.7×10^7 l mol^{-1} (see Table 1).

Figure 3 exhibits fluorescence spectra of H_2TTP (5.00×10^{-6} mol l^{-1}) in pH 5.4 buffers containing various concentration of TM-β-CD. The fluorescence intensity of H_2TTP increased with the stepwise addition of TM-β-CD. In addition, both the emission wavelength (668.98 nm) and the excitation wavelength (431.06 nm) shift towards shorter wavelength. There is an isosbestic point at 708 nm. The remarkable change

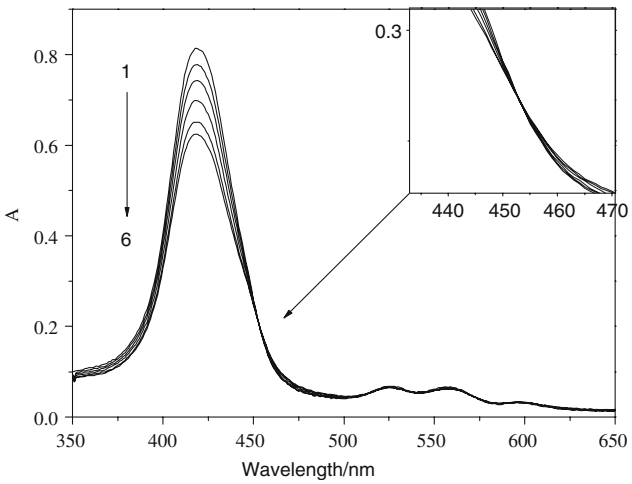


Fig. 4 Absorption spectra of H_2TTP (5.00×10^{-6} mol l^{-1}) in pH5.4 buffers containing various concentrations of α-CD. Concentration of α-CD: (1) 0, (2) 5.00×10^{-5}, (3) 1.00×10^{-4}, (4) 2.00×10^{-4}, (5) 3.00×10^{-4} and (6) 5.00×10^{-4} mol l^{-1}

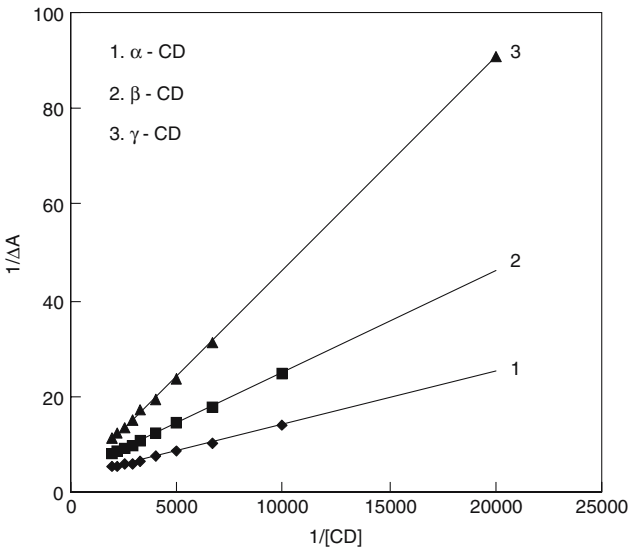


Fig. 5 Double reciprocal plots for H_2TTP complex to α-CD, β-CD and γ-CD(UV)

of the fluorescence spectra is due to the interaction between H_2TTP and TM-β-CD, implying the formation of H_2TTP-TM-β-CD inclusion complex. The reason for the enhancement of the fluorescence intensity is that the quantum efficiency of fluorescence will increase when fluorescence substance shifts from polar phase to non-polar phase [26]. Because the cyclodextrins cavity can offer hydrophobic environment for guest molecular, the fluorescence intensity would enhance when H_2TTP is included into the cyclodextrins cavity.

The inclusion constants of complexes are estimated according to the double-reciprocal method. It can be obtained by the following equation [27].

$$\frac{[G]_0}{\Delta F} = \frac{1}{K \times k \times Q}\frac{1}{[CD]^n} + \frac{1}{k \times Q} \quad (2)$$

Where, $[G]_0$ is the initial concentration of guest molecular, [CD] is the equilibrium concentration of cyclodextrin. ΔF is the change of fluorescence intensity in the presence of cyclodextrin, k is an instrumental constant, n is the stoichiometry of inclusion complex, K is the inclusion constant and Q is the quantum yield for the complex. K can be calculated from a plot of 1/F vs. $1/[CD]^n$. Plot $1/\Delta F$ vs. $1/[CD]^2$, a good linearity of the plots verifies that 2:1 complex is formed between TM-β-CD and H_2TTP ($r = 0.9988$). From the double reciprocal plot of the fluorescence intensity changer, a K value of 3.0×10^7 l mol^{-1} is obtained for the (TM-β-CD)$_2$·H_2TTP. This K value obtained from the fluorescence intensity change is similar to that from the absorbance change. The agreement between the K values from both procedures supports the formation of (TM-β-CD)$_2$·H_2TTP inclusion complex.

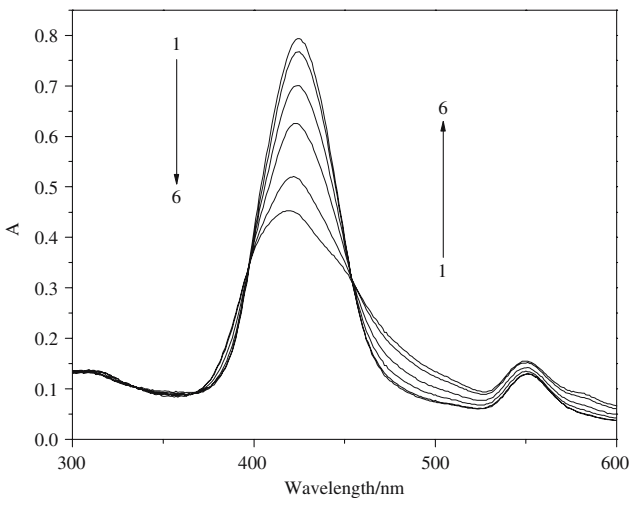


Fig. 6 Absorption spectra of Cu-TTP(7.14×10^{-6} mol l^{-1}) in pH5.4 buffers containing various concentrations of TM-β-CD. Concentration of TM-β-CD: (1) 0, (2) 6.67×10^{-6}, (3) 1.33×10^{-5}, (4) 2.00×10^{-5}, (5) 2.67×10^{-5} and (6) 5.33×10^{-5} mol l^{-1}

Inclusion complexes of α-CD, β-CD and γ-CD with H_2TTP

When α-CD was added to H_2TTP solution buffered at pH 5.4, the absorption peak of H_2TTP keep hardly changed, accompanied by a reduction of the absorption intensity (Fig. 4). There is an isosbestic point at 452 nm. The double reciprocal plots of $1/\Delta A$ vs. 1/[CD] for H_2TTP with α-CD exhibits good linearity (Fig. 5, $r = 0.9998$). This finding indicates the formation of a 1:1 α-CD- H_2TTP inclusion complex. From the fluorescence spectra of H_2TTP containing various concentrations of α-CD, it can be found that the fluorescence intensity is enhanced when the α-CD concentration is increased. This verifies that the moiety of H_2TTP shifts from the polar phase to the non-polar phase of α-CD and forms the inclusion complex between α-CD and H_2TTP. From the double reciprocal plot of $1/\Delta F$ vs. 1/[CD] for the fluorescence intensity change ($r = 0.9959$), a K value of 7.0×10^3 l mol^{-1} is obtained for the α-CD·H_2TTP.

When β-CD and γ-CD were added to H_2TTP solution buffered at pH 5.4 respectively, the absorption intensity was reduced and the fluorescence intensity was enhanced (not show). But no isosbestic point was observed. This finding indicates the formation of 2:1 CDs-H_2TTP inclusion complex and 1:1 inclusion complex. At low concentrations, the 1:1 CDs-H_2TTP inclusion complex is formed, while at high concentrations, 2:1 CDs-H_2TTP inclusion complex is formed

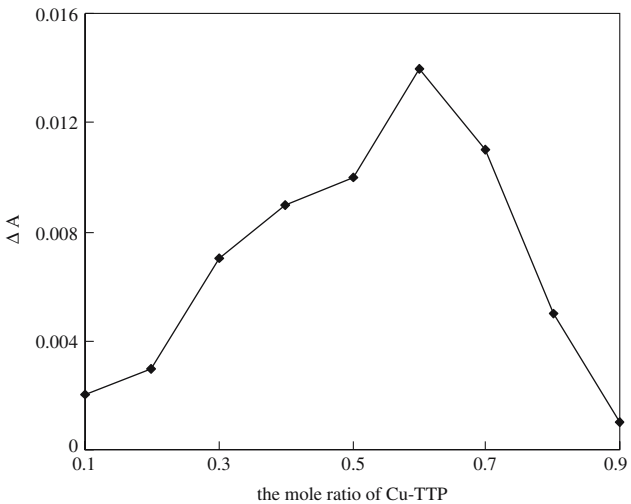


Fig. 7 The inclusion stoichiometry of Cu-TTP-TM-β-CD complexes (Job plot)

Table 2 The binding constants of Cu-TTP with four CDs

	α-CD	β-CD	γ-CD	TM-β-CD
Absorption	4.1×10^{3a}	3.7×10^{3a}	1.2×10^{3a}	9.0×10^{8b}

[a] The binding constant of 1:1 inclusion complex
[b] The binding constant of 2:1 inclusion complex

besides the 1:1 inclusion complex. The double reciprocal plots of 1/ΔA vs. 1/[CD] and 1/ΔF vs. 1/[CD] for H_2TTP with β-CD(γ-CD) exhibits good linearity, respectively (Fig. 5). This verifies the main formation of inclusion complexes with a stoichiometry of 1:1 between H_2TTP and β-CD(γ-CD). The inclusion constant values are calculated assuming the existence of complexes with 1:1 stoichiometry (see Table 1).

Inclusion complexes of TM-β-CD with Cu-TTP

Figure 6 shows the Soret band in the absorption of Cu-TTP (7.14×10^{-6} mol l^{-1})in pH 5.4 buffers containing various concentrations of TM-β-CD. The absorption peak shifts to shorter wavelengths with an increase in the TM-β-CD concentration, accompanied by decrease of absorption peak. At 453 nm, there is an isosbestic point. This finding indicates the formation of an inclusion complex of TM-β-CD with Cu-TTP.

The double reciprocal plots of 1/ΔA vs. $1/[CD]^2$ for Cu-TTP with TM-β-CD exhibits good linearity ($r = 0.9995$). This verifies the formation of inclusion complex with a stoichiometry of 1:2 between Cu-TTP and TM-β-CD. A Job plot of absorbance changes vs. mole fraction of TM-β-CD is provided in Fig. 7. Under the equilibrium: porphyrin + *n*CD = porphyrin-(CD)*n*, the mole fraction of TM-β-CD ($f = 2/3$), inducing that a maximal absorbance change in Fig. 7 proves the formation of Cu-TTP-TM-β-CD complex with 1:2 stoichiometry. The inclusion constant of Cu-TTP with TM-β-CD can be calculated by the equation (1). The related inclusion constant for TM-β-CD with Cu-TTP is 9.0×10^8 l mol^{-1} (see Table 2). The formation of Cu-TTP with TM-β-CD is similar to that of H_2TTP with TM-β-CD. Cu-TTP and H_2TTP all form the inclusion complexes with a stoichiometry of 1:2 with TM-β-CD. But the inclusion complex of (TM-β-CD)$_2$·Cu-TTP is easier to form than the (TM-β-CD)$_2$·H_2TTP. It is because that the variety of absorption intensity of Cu-TTP is much larger than that of H_2TTP when the same concentration of TM-β-CD was added. The reason is that the ligand number of

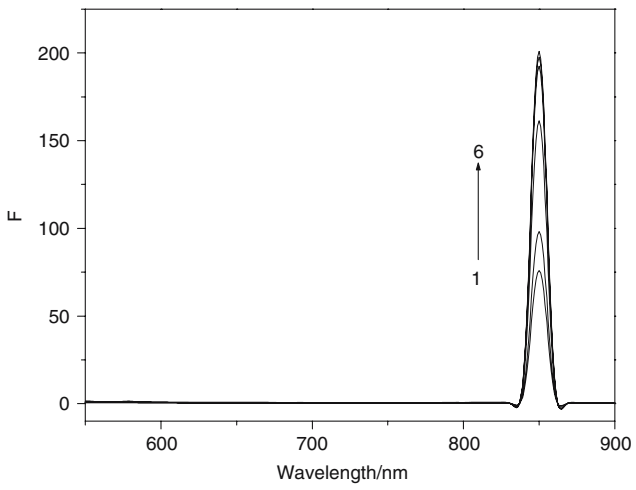


Fig. 8 Fluorescence spectra of Cu-TTP(7.14×10^{-6} mol l^{-1}) in pH5.4 buffers containing various concentrations of TM-β-CD. Concentration of TM-β-CD: (1) 0, (2) 2.00×10^{-5}, (3) 2.67×10^{-5}, (4) 3.33×10^{-5}, (5) 4.00×10^{-5} and (6) 5.33×10^{-5} mol l^{-1}

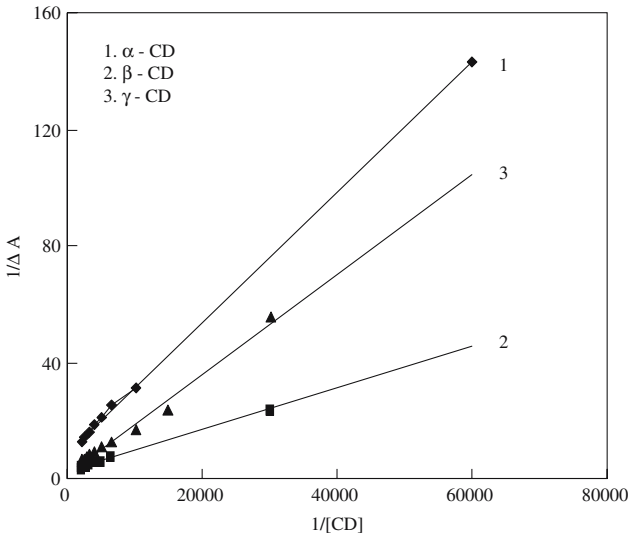


Fig. 9 Double reciprocal plots for Cu-TTP complex to α-CD, β-CD and γ-CD(UV)

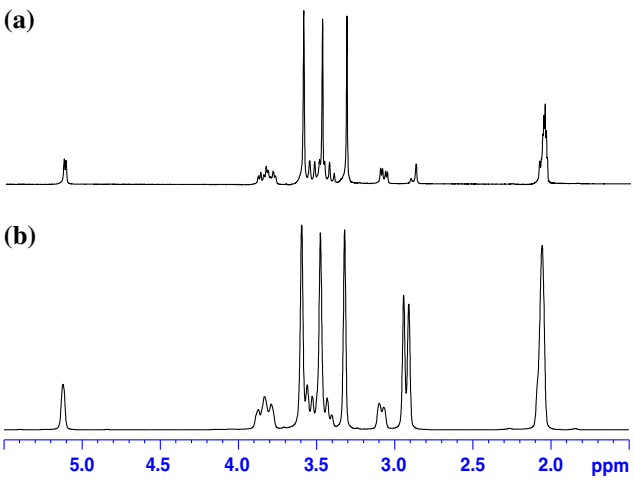


Fig. 10 ^{1}H-NMR spectra of TM-β-CD and Cu-TTP-TM-β-CD in CD_3COCD_3 at 25°C. (a) TM-β-CD, (b) Cu-TTP-TM-β-CD

Table 3 The chemical shifts (δ) of TM-β-CD, H_2TTP-TM-β-CD and Cu-TTP-TM-β-CD complexes

		δ(ppm)		
		TM-β-CD	H_2TTP-TM-β-CD complexes	Cu-TTP–TM-β-CD complexes
H-1	d	5.127	5.126	5.127
H-2	dd	3.093	3.093	3.094
H-3	t	3.527	3.526	3.527
H-4	d	3.558	3.560	3.559
H-5	m	3.836	3.836	3.835
H-6	dd	3.402	3.433	3.432
H-Me2	s	3.463	3.475	3.475
H-Me3	s	3.708	3.594	3.595
H-Me6	s	3.237	3.321	3.320

Cu^{2+} is six and the electron-deficient orbit of Cu^{2+} can form faint coordinate bond with CDs.

Figure 8 exhibits fluorescence spectra of Cu-TTP (7.14×10^{-6} mol l^{-1}) in pH 5.4 buffers containing various concentrations of TM-β-CD. There is a multi-frequency peak of Cu-TTP at 849.05 nm but no fluorescent peak. This is because that the fluorescent of Cu-TTP is quenched by the Cu^{2+} ion. Cu^{2+} is paramagnetic metal ion and transition metal ion, which has electron-deficient 3d-orbit. The mechanism of quenching is probably that the π-electron of H_2TTP and the orbit of Cu^{2+} interact to form a particular energy level. Another explanation is that the colored absorption of Cu^{2+} makes the energy of fluorescent substance convert to thermal energy, which increases the speed of intersystem crossing [28]. When TM-β-CD is added, the intensity of multi-frequency peak enhances. This spectral change also indicates the formation of the TM-β-CD-Cu-TTP inclusion complex.

Inclusion complexes of α-CD, β-CD and γ-CD with Cu-TTP

In the phosphate buffer (pH 5.4), the inclusion complexes of Cu-TTP with α-CD, β-CD and γ-CD were formed with a stoichiometry of 1:1. The double reciprocal plots of $1/\Delta A$ versus 1/[CD] for Cu-TTP with α-CD, β-CD and γ-CD exhibits good linearity, respectively (Fig. 9). The inclusion constants (K) of Cu-TTP with three CDs can be calculated by the Eq. 1. These *K* values evaluated for Cu-TTP are listed in Table 2.

^{1}H-NMR analysis

In order to explore the possible inclusion mode of H_2TTP-CDs and Cu-TTP-CDs complexes, we compare the ^{1}H-NMR spectra of H_2TTP and Cu-TTP in the presence of host CDs. The formation of H_2TTP-TM-β-CD and Cu-TTP-TM-β-CD complexes was confirmed by the changes of the chemical shifts of ^{1}HNMR spectra at 300 MHz in CD_3COCD_3 solution. The ^{1}HNMR spectrum of TM-β-CD and Cu-TTP-TM-β-CD are shown in Fig. 10. And the chemical shifts data for the inclusion complex are in Table 3. The TM-β-CD protons show different chemical shifts ($\Delta\delta$)after including Cu-TTP. By comparing these shifts, we can find the shifts of H-6 (0.030 ppm) protons are larger than those of H-3 protons (0.001 ppm), indicating that Cu-TTP may penetrate the cavity of TM-β-CD from the narrow side.

For a deeper insight into the investigation on the stereochemistry of supramolecular system, the

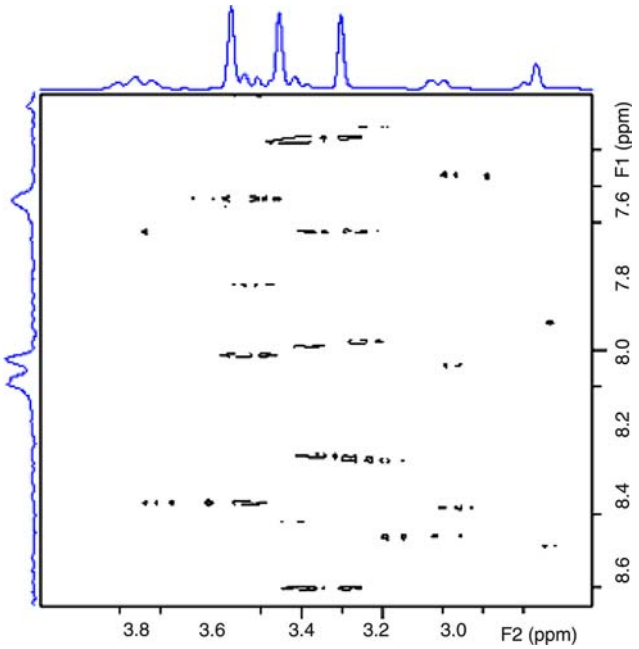


Fig. 11 The 2D-ROESY NMR (300 MHz, 20°C, CD_3COCD_3) of Cu-TTP-TM-β-CD

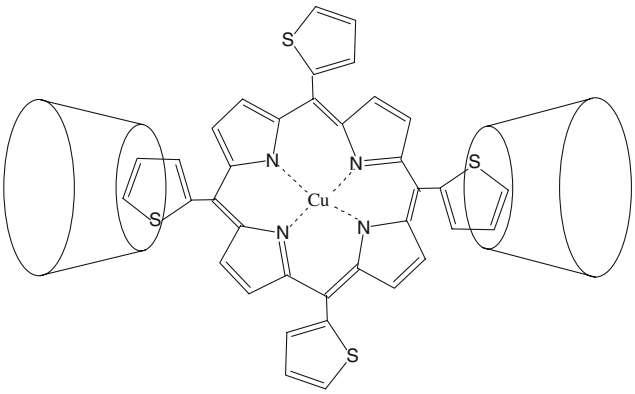


Fig. 12 The proposed structure of the Cu-TTP-TM-β-CD inclusion complex

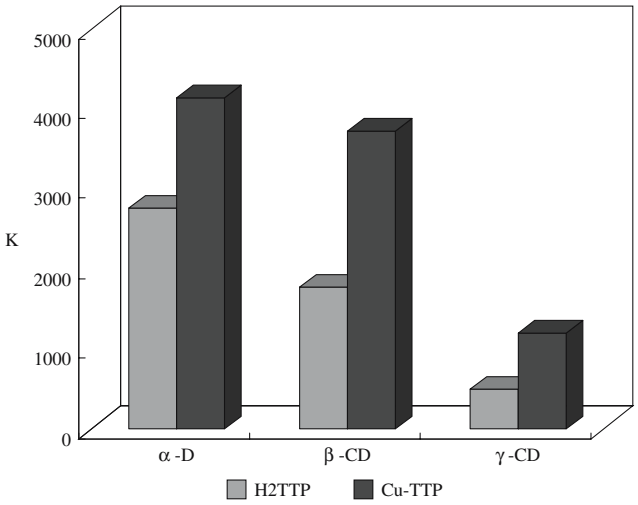


Fig. 13 The K of different CDs with H_2TTP and Cu-TTP

ROESY spectrum is more powerful. The inclusion interaction will be assumed from the NOE correlation between a proton of the guest molecule and a proton of CDs. The 2D-ROESY spectra of Cu-TTP with TM-β-CD are given in Fig. 11, which also reveals the interaction between Cu-TTP and TM-β-CD. The weaker NOE effect of the host H-5, H-6 and guest thienyl moiety protons proves the insertion of Cu-TTP. It is illustrated that Cu-TTP enters the cavity of TM-β-CD from the narrow side. This is in accord with ^{1}H-NMR. Based on the information provided by ^{1}H-NMR and 2D-ROESY NMR, we propose the spacial configuration about the Cu-TTP-TM-β-CD supramolecular system as shown in Fig. 12.

Discussion of interaction mechanism

According to the results of experiments above, H_2TTP and Cu-TTP can form inclusion complexes with four CDs, respectively. The inclusive capability of Cu-TTP is stronger than that of H_2TTP (Fig. 13). One reason is that the electron-deficient orbit of Cu^{2+} can form faint coordinate bond with CDs so that Cu-TTP can form stable inclusion complexes easily.

In three native CDs, the magnitude of the *K* value for both H_2TTP and Cu-TTP decreases in the order α-CD > β-CD > γ-CD (Fig. 13). This trend reflects the degree of the capacity matching between the CD cavity and H_2TTP (Cu-TTP). It shows that the inclusive capability of α-CD with H_2TTP and Cu-TTP is the strongest among the three native CDs, which is because the cavity of α-CD has the best size to match to the thienyl moiety. The K values for γ-CD-porphyrins are smallest because of the wider cavity of γ-CD. This finding indicates the major factors affecting inclusive capability are size matching and the hydrophobicity of the guest molecular.

The inclusion complexes between TM-β-CD and H_2TTP(Cu-TTP) were formed with a stoichiometry of 2:1 but the inclusion complexes between β-CD and H_2TTP(Cu-TTP) were formed with a stoichiometry of 1:1, which also shows that TM-β-CD exhibits stronger inclusive capability than its native β-CD, implying that the cavity of TM-β-CD provides a better protective microenvironment. Strong inclusive capability can be understood that β-CD modified by tri-o-methyl groups leads to the enlargement of the bigger opening, shrinks the small opening, and destroys the strong hydrogen bond network, which makes it easier for guest molecules to gain access to TM-β-CD cavity and to have bigger inclusion constant.

Conclusion

In the phosphate buffer (pH 5.4), TM-β-CD forms 2:1 host-guest inclusion complexe with H_2TTP and Cu-TTP, α-CD forms 1:1 inclusion complexe, and β-CD/γ-CD all form both 1:1 and 2:1 inclusion complexes, respectively. Compared the native β-CD with the modified β-CD, the latter forms the inclusion complex with H_2TTP and Cu-TTP more easily. The inclusive capability of α-CD with H_2TTP and Cu-TTP is the strongest among the three native CDs, and the K values for H_2TTP and Cu-TTP decrease in the order, α-CD > β-CD > γ-CD. Compared to H_2TTP, Cu-TTP is easier to form host-guest inclusion complexes with TM-β-CD.

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