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Study on Supramolecular Systems of Mg-meso-Tetrakis(2-thienyl)Porphyrin with Cyclodextrins by Spectroscopy Method

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In phosphate buffer solution of pH 5.4, the formation of supramolecular systems of Mg-meso-tetrakis(2-thienyl)-porphyrin(Mg-TTP) with β-CD, carboxymethyl-β-CD (CM-β-CD), heptakis(2,6-di-O-methyl)-β-CD (DM-β-CD), heptakis(2,3,6-tri-O-methyl)-β-CD (TM-β-CD) and sulfurbutylether-β-CD (SBE-β-CD) has been studied by means of UV–vis, fluorescence and NMR spectroscopy, respectively. And the Mg-TTP can form 1:1 host-guest inclusion complexes with five cyclodextrins. In this paper, the inclusive capability of different kinds of cyclodextrins is compared. The inclusion ability of modified β-CD with Mg-TTP is stronger than the native β-CD. And the inclusion ability of TM-β-CD with Mg-TTP is the strongest among five CDs, which indicates that the hydrophobic effect plays a crucial role in the inclusion procedure except for the capacity matching. In addition, ^{1}H-NMR data and 2D-ROESY NMR spectra support the inclusion conformation of the TM-β-CD-Mg-TTP supramolecular system, indicating the interaction mechanism of inclusion processes.

Keywords: Mg-meso-tetrakis(2-thienyl)porphyrin(Mg-TTP); Cyclodextrins; Supramolecular systems; Spectroscopy

INTRODUCTION

The ability of cyclodextrins (CDs) and modified CDs to form supramolecular systems with various molecules is well known [1]. The formation of supramolecular system changes the physical and chemical properties of the guest. It can sustain the release rate of drugs [2], enhance the peak concentration of drugs in blood [3] and improve bioavailability [4], etc.

Porphyrins and their metalloderivatives are requisite substances of cytochrome, hemochrome, and chlorophyll, which play significant roles in biological processes. They have been applied in artificial simulation [5,6], supramolecular assembly of the heme proteins and other molecular systems relevant to biology [7,8], or employed as catalysts of oxidation processes [9,10]. In photosynthesis, chlorophylls, which are Mg complexes of porphyrin derivatives have critical roles [11]. So it is very meaningful to study Mg complexes of porphyrin derivatives. The formation of supramolecular systems of CDs with porphyrin derivatives modifies the photochemical and photophysical properties of porphyrin derivatives [12]. Consequently, it is very important to examine the formation of supramolecular systems of CDs with porphyrin derivatives. In our previous laboratory studies, several porphyrin-CD supramolecular systems were investigated by different methods [13–17]. In recent years, many meso-thienyl porphyrins were synthesized, and the photochemical characterization, redox, and axial ligation studies of meso-thienyl porphyrins were reported [18–22]. However, the papers about the synthesis of Mg-TTP and CDs (Scheme 1) interacting with Mg-TTP (Scheme 1) have not been found in literature.

In this paper, we have examined the formation of supramolecular systems of Mg-TTP with β-CD and four modified β-CDs by UV–vis, fluorescence and NMR spectroscopy in 0.1 mol L^{-1} phosphate buffer (pH 5.4, 20°C). The ^{1}H-NMR data and 2D-ROESY NMR spectra support the inclusion conformation

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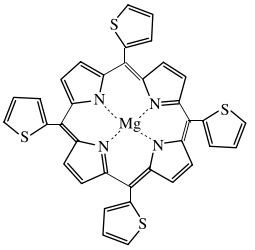
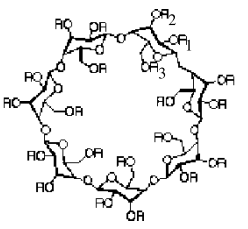




CD	R
β-CD	$R_1 = R_2 = R_3 = H$
CM-β-CD	$R_1 = R_2 = R_3 = -CH_2COONa$ (or H)
DM-β-CD	$R_1 = R_3 = -CH_3$, $R_2 = H$
TM-β-CD	$R_1 = R_2 = R_3 = -CH_3$
SBE-β-CD	$R_1 = R_2 = R_3 = -(CH_2)_4SO_3Na$ (or H)

SCHEME 1 The chemical structures of Mg-TTP, β-CD and its derivatives.

of the TM-β-CD-Mg-TTP supramolecular system, indicating the interaction mechanism of inclusion processes. Their inclusion constants are calculated by the double-reciprocal method, and the inclusive capability of different kinds of cyclodextrins is compared too. The result shows that the Mg-TTP can form 1:1 supramolecular systems with five cyclodextrins. The inclusion ability of modified β-CD is stronger than that of the native β-CD especially TM-β-CD. It indicates that the capacity matching and hydrophobic effect play important roles in the inclusion procedure.

RESULTS AND DISCUSSION

Formation of Inclusion Complexes of Mg-TTP With CDs

Figure 1 exhibits the Soret band in the absorption of Mg-TTP (5.0×10^{-6} mol L^{-1}) in pH 5.4 buffers containing various concentration of TM-β-CD. The absorption peak is shifted from 442 nm to 428 nm with an increase in the TM-β-CD concentration, accompanied by an isosbestic point at 436 nm. This finding indicates the formation of the supramolecular system of TM-β-CD with Mg-TTP. A double reciprocal plot [24–26] for the absorbance (A) of Mg-TTP solution containing various concentrations of TM-β-CD has afforded a good straight line (not shown), suggesting that the TM-β-CD-Mg-TTP supramolecular system has 1:1 stoichiometry.

From the variety of the UV–Vis spectrum of Mg-TTP in the absence and presence of CDs (Fig. 2), it can be found that the maximum absorption wavelength is red shift and the absorbance decreases. This finding indicates that the interaction of Mg-TTP with β-CD, CM-β-CD, DM-β-CD and

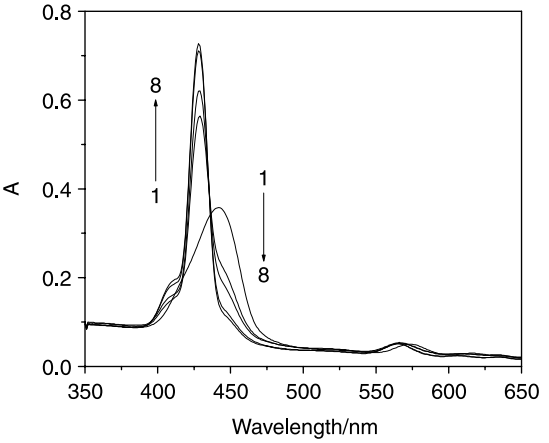


FIGURE 1 Absorption spectra of Mg-TTP (5.0×10^{-6} mol L^{-1}) in pH5.4 buffers containing various concentrations of TM-β-CD. Concentration of TM-β-CD: (1) 0, (2) 3.333×10^{-5}, (3) 6.667×10^{-5}, (4) 1.000×10^{-4}, (5) 1.333×10^{-4}, (6) 1.667×10^{-4}, (7) 2.000×10^{-4} and (8) 2.333×10^{-4} mol L^{-1}.

SBE-β-CD takes place in the ground state of Mg-TTP and demonstrates that Mg-TTP forms supramolecular systems with four cyclodextrins.

Figure 3 shows the effect of TM-β-CD on the fluorescence spectra of Mg-TTP in acidic media (pH 5.4). The maximum excitation wavelength was set at 442 nm. With the increasing concentration of TM-β-CD, the remarkable enhancement of the emission intensity was observed. The measured emission wavelength is 670 nm and shifts to shorter wavelengths with the addition of TM-β-CD, which implies the formation of supramolecular systems between Mg-TTP and TM-β-CD. It should be mentioned that the fluorescence intensity (F) of Mg-TTP in the presence of TM-β-CD increased nearly 10 times and an increasing factor of about 1.5 was detected for DM-β-CD. Figure 4 shows the dependence of fluorescence intensity of Mg-TTP on the concentration of TM-β-CD and DM-β-CD.

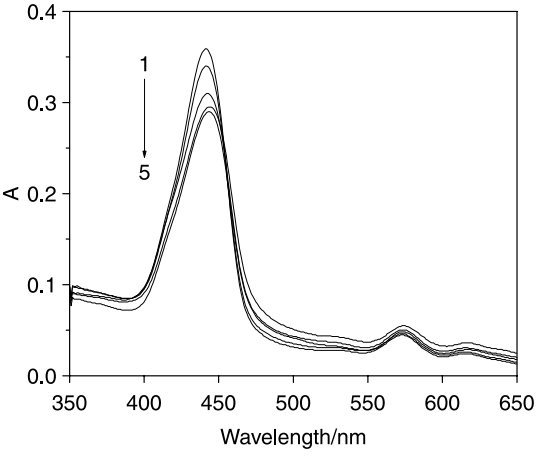


FIGURE 2 The absorption spectra of Mg-TTP in the absence and presence of different CDs: (1) Mg-TTP, (2) β-CD + Mg-TTP, (3) SBE-β-CD + Mg-TTP, (4) CM-β-CD + Mg-TTP, (5) DM-β-CD + Mg-TTP.

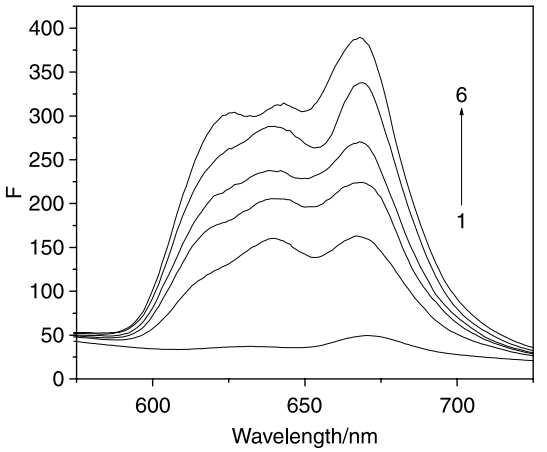


FIGURE 3 Fluorescence spectra of Mg-TTP (5.0×10^{-6} mol L^{-1}) in pH5.4 buffers containing various concentrations of TM-β-CD. Concentration of TM-β-CD: (1) 0, (2) 3.333×10^{-5}, (3) 6.667×10^{-5}, (4) 1.000×10^{-4}, (5) 1.667×10^{-4} and (6) 2.333×10^{-4} mol L^{-1}.

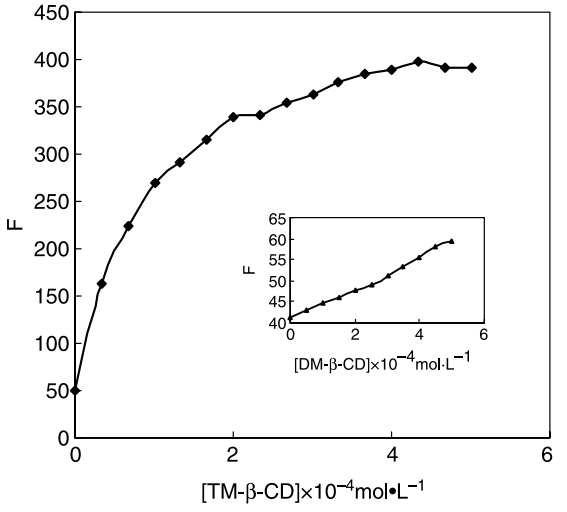


FIGURE 4 Dependence of fluorescence intensity of Mg-TTP (5.0×10^{-6} mol L^{-1}) on the concentration of TM-β-CD and DM-β-CD in pH5.4 buffer solution.

The lowest concentrations of TM-β-CD and DM-β-CD which caused the variety of fluorescence intensity are 5×10^{-7} and 2.5×10^{-5}, respectively. Comparative to supramolecular systems, the low yield of free molecules may be due to the easy formation of non-emitting oligomers of porphyrins. However, the inclusion provides a more rigid microenvironment and brings some protection for molecules quenched by water or metal ions. Furthermore, the cyclodextrins cavity can offer a hydrophobic environment for guest molecules. When fluorescence substance shifts from polar phase to non-polar phase, the quantum efficiency of fluorescence will increase [27]. Consequently, the fluorescence intensity would enhance when Mg-TTP is included into the cyclodextrin cavity. ΔF of Mg-TTP with the addition of TM-β-CD is greater than that of Mg-TTP with the addition of DM-β-CD. This is due probably to the fact that there are three methoxyl groups in TM-β-CD molecule, while only two in the DM-β-CD molecule.

With the addition of β-CD, CM-β-CD and SBE-β-CD, the fluorescence intensity of Mg-TTP decreases and the emission wavelength shifts to shorter wavelengths. The changes of the fluorescence spectra are due to the interaction between Mg-TTP and above-mentioned three CDs respectively, implying the formation of Mg-TTP-CDs supramolecular systems. Because hydrophobic methoxyl groups existed in TM-β-CD and DM-β-CD molecules, the interaction mechanism of Mg-TTP with TM-β-CD and DM-β-CD is different from that of Mg-TTP with β-CD, CM-β-CD and SBE-β-CD. Compared to native β-CD, the modified β-CD has stronger inclusive capability with Mg-TTP. The reason is that the bigger opening of the native CDs is enlarged, the small opening of the native CDs is shrunk, and the strong hydrogen bond network of the native CDs is destroyed after the native CDs being substituted [28], which makes it easier for guest molecules to gain access to the cavity of cyclodextrins and to have a bigger inclusion constant.

Inclusion Constants of Inclusion Complexes

The inclusion constant (K) is an important parameter, which represents the inclusion interaction. The inclusion constant can be obtained from fluorescence data by the following equation [29].

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

Where, $[G]_0$ is the initial concentration of Mg-TTP, [CD] is the equilibrium concentration of cyclodextrin. ΔF is the change of fluorescence intensity in the absence and 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 $1/\Delta F$ vs. $1/[CD]^n$. Figure 5 shows the double reciprocal plots of $1/\Delta F$ versus $1/[CD]$ for Mg-TTP included with β-CD, CM-β-CD, DM-β-CD, TM-β-CD and SBE-β-CD at pH 5.4. The plot exhibits good linearity, and the linear correlations are listed in Table I. This implies the formation of supramolecular systems with a stoichiometry of 1:1 between Mg-TTP and five CDs. A Job Plot of fluorescence changes vs. mole fraction of TM-β-CD (x) is provided in Fig. 6 (Job Plot). It shows a maximum at $x = 0.5$, indicating that the Mg-TTP-TM-β-CD complex has 1:1 stoichiometry.

The inclusion constant values were calculated assuming the existence of complexes with 1:1 stoichiometry. The related inclusion constants for β-CD, CM-β-CD, DM-β-CD, TM-β-CD and SBE-β-CD

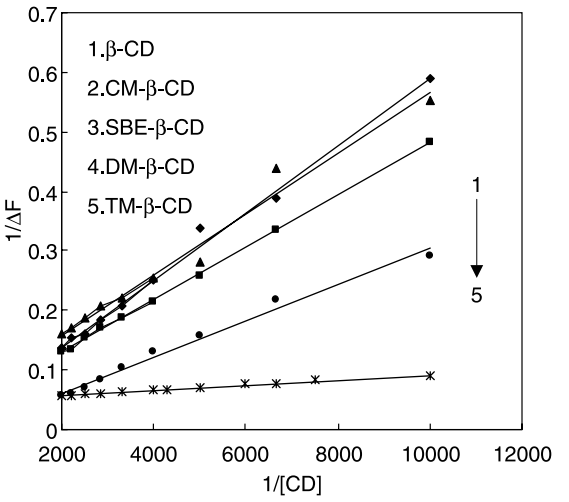


FIGURE 5 Double reciprocal plots for Mg-TTP complex to β-CD, CM-β-CD, DM-β-CD, TM-β-CD and SBE-β-CD.

TABLE I The inclusion constants of Mg-TTP with different CDs

	β-CD	CM-β-CD	DM-β-CD	TM-β-CD	SBE-β-CD
K	433	1144	1769	19600	1025
R	0.9966	0.9987	0.9950	0.9996	0.9996
RSD($n = 5$)	4.29%	4.87%	3.94%	3.62%	4.58%

with Mg-TTP are 433, 1144, 1769, 19600 and 1025, respectively (see Table I). And the relation standard deviations (RSD) are listed in the Table I. The difference of inclusion constants for CM-β-CD, DM-β-CD, TM-β-CD, SBE-β-CD and β-CD may be explained that comparing with native β-CD, the chemically modified β-CD are endowed with specially functional groups and the flexibility of CDs have been improved to a great degree. Moreover, the strongest inclusion capacity of TM-β-CD is caused by the strong hydrophobic effect between Mg-TTP and TM-β-CD.

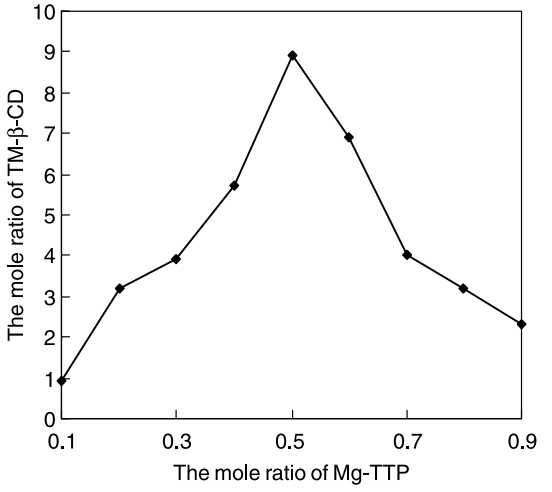


FIGURE 6 The inclusion stoichiometry of Mg-TTP-TM-β-CD complexes (Job plot).

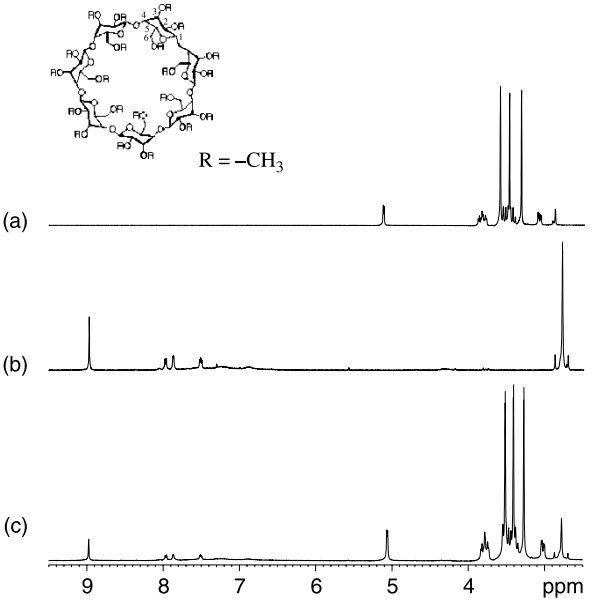


FIGURE 7 ^{1}H-NMR spectra of Mg-TTP in the absence and presence of TM-β-CD in CD_3COCD_3 at 25°C. (a) TM-β-CD, (b) Mg-TTP and (c) Mg-TTP-TM-β-CD.

NMR Analysis

NMR spectroscopy is the most powerful tool for the study of formation of supramolecular systems between CDs and a variety of guest molecules, it has been successfully used to confirm the formation of supramolecular systems [30,31]. The formation of Mg-TTP-TM-β-CD complex 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, Mg-TTP and Mg-TTP-TM-β-CD are shown in Fig. 7. And the chemical shift data for the supramolecular system are listed in Table II. As can be seen from Fig. 7 and Table II, the chemical shifts data for the supramolecular systems were different from those for the free compounds. As far as the guest molecule, the more shield protons of thienyl showed an apparent downfield shift in the presence of TM-β-CD, which provided further analytical results that the supramolecular system was formed between Mg-TTP and TM-β-CD. The TM-β-CD protons shows different chemical shifts (Δδ) after forming supramolecular system with Mg-TTP.

TABLE II The chemical shifts (δ) of TM-β-CD and Mg-TTP-TM-β-CD supramolecular system

Proton	δ_{free}(ppm)	δ_{com}(ppm)	Δδ
H-1 of CD	5.127	5.127	0
H-2 of CD	3.105	3.101	0.004
H-3 of CD	3.836	3.843	0.007
H-4 of CD	3.073	3.070	0.003
H-5 of CD	3.463	3.439	0.024
H-6 of CD	3.558	3.529	0.029
3-H of thienyl	7.873	7.871	0.002
4-H of thienyl	7.515	7.508	0.007
5-H of thienyl	7.962	7.956	0.006

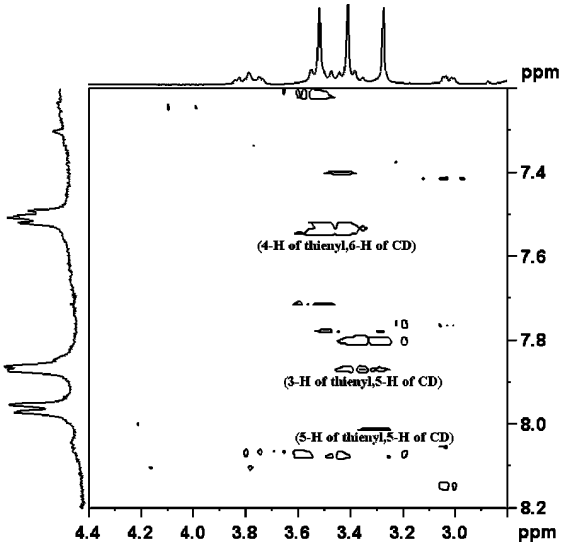


FIGURE 8 The 2D-ROESY NMR (300 MHz, 20°C, CD_3COCD_3) of Mg-TTP-TM-β-CD.

By comparing these shifts, it can be found that the shifts of H-5 (0.024 ppm) and H-6 (0.029 ppm) protons are larger than those of H-3 protons (0.007 ppm), indicating that Mg-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 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 Mg-TTP with TM-β-CD are given in Fig. 8, which also reveals the interaction between Mg-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 Mg-TTP. It is illustrated that Mg-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 Mg-TTP-TM-β-CD supramolecular system as shown in Fig. 9.

EXPERIMENTAL

Reagent and Apparatus

β-CD, CM-β-CD, DM-β-CD and TM-β-CD were purchased from FLUKA. SBE-β-CD was synthesized employing the paper written by Luna *et al.* [23]. The degrees of substitution of CM-β-CD and SBE-β-CD are 4.8 and 0.7, respectively.

All absorption and fluorescence measurements were performed with TU-1901 double beam UV spectrophotometer (Puxi instrument Co. Beijing, China) and Cary Eclipse Fluorescence Spectrophotometer (USA). Excitation and emission bandwidths were set at 20 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 Mg-TTP

Pyrrole and thienanal were dissolved in absolute ether at room temperature to react for 4 h to give condensation product porphyrinogen using oxammonium hydrochloride as catalyst. Then dimethyl benzene and magnesium acetate were added, and absolute ether was evaporated out of the mixture. The reaction was allowed to heating contraflow for 2 h. The product Mg-meso-tetrakis(2-thienyl)porphyrin(Mg-TTP) was isolated with chromatography column to 12% yield (Scheme 2).

Elemental analysis: $C_{36}H_{20}N_4S_4Mg$, Calcd: C, 65.40; H, 3.05; N, 8.33. Found: C, 65.55; H, 3.01; N, 8.53. λ_{max} (DMF:water = 1:9): 442,565 nm. Fluorescence emission spectrum (ex = 442, DMF:water = 1:9): 670.00 nm δ^1H (CD_3COCD_3): 7.866–7.977 (8H, hydrogen of the thienyl ring), 7.509–7.526 (4H, hydrogen of the thienyl ring), 8.97 (8H, hydrogen of the pyrrole ring) ppm.

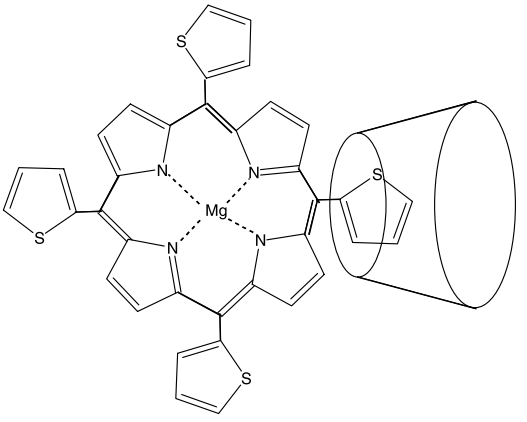
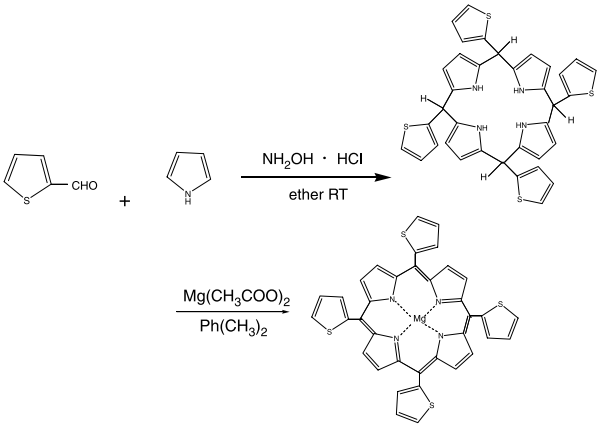


FIGURE 9 The proposed structure of the Mg-TTP-TM-β-CD inclusion supramolecular.



SCHEME 2 Synthetic mechanism of Mg-meso-tetrakis(2-thienyl)porphyrin.

Method

A 5.0×10^{-5} mol L^{-1} stock solution of Mg-TTP was prepared by N, N-Dimethylformamide(DMF). A 5.0×10^{-6} mol L^{-1} working solution of Mg-TTP was obtained by transferring 1.0 ml stock solution and 1.0 ml 0.1 mol L^{-1} phosphate buffer (pH 5.4, 20°C) into 10 ml volumetric flask. An appropriate amount of cyclodextrin (β-CD, CM-β-CD, DM-β-CD, TM-β-CD and SBE-β-CD) was added. The mixed solution was diluted to final volume with distilled water and shaken thoroughly, following equilibrated for 15 min at 20 ± 1°C.

CONCLUSION

In the phosphate buffer (pH 5.4), Mg-TTP formed 1:1 supramolecular systems with β-CD, CM-β-CD, DM-β-CD, TM-β-CD and SBE-β-CD, respectively. The fluorescence intensity of Mg-TTP increases with the addition of TM-β-CD and DM-β-CD, while decreases with the addition of β-CD, CM-β-CD and SBE-β-CD. The inclusion capability of TM-β-CD with Mg-TTP is stronger than that of DM-β-CD with Mg-TTP. Comparing the native β-CD with the modified β-CD, the latter forms a supramolecular system with Mg-TTP more easily.

Acknowledgements

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