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Comparative Study on the Inclusion Interaction between *meso*-Tetrakis(4-N-ethylpyridiniurmyl) porphyrin and β-Cyclodextrin Derivatives

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Abstract: The interaction of β-cyclodextrin (β-CD) and the modified cyclodextrins, hydroxy propyl-β-cyclodextrin (HP-β-CD), sulfobutylether-β-cyclodextrin (SBE-β-CD) and synthesized *meso*-tetrakis(4-N-ethylpyridiniurmyl)porphyrin (TEPyP) in aqueous solution has been studied by spectroscopic methods systematically. A significant change in fluorescence and absorption properties has been observed in the presence of β-CD, HP-β-CD and SBE-β-CD. The stoichiometry and formation constants have been determined by the steady-state fluorescence technique. The results showed that the β-CD derivatives were *prior to* the native β-CD and the hydrogen bonding and static electric forces played important roles in the formation of the inclusion complexes. The conformation was further confirmed by NMR spectroscopy.

Keywords: *meso*-Tetrakis (4-N-ethylpyridiniurmyl) porphyrin (TEPyP), cyclodextrin, absorption, fluorescence, nuclear magnetic resonance (NMR).

Cationic porphyrin derivatives are valuable as probes for investigating the structure and dynamics of nucleic acid[1]. They are novel DNA binding agents and have been used as platform for application in photodynamic therapy and virus control[2,3], which has promoted much interest in their derivatives[4]. However, the study involving complexation of cationic porphyrins to CDs is rare. In this paper, a cationic porphyrin, TEPyP, was synthesized and its chemical structure was given in **Figure1**. The inclusion interaction of TEPyP with natural and modified β-cyclodextrin was investigated on the basis of change of spectroscopy.

Experimental

All absorption and fluorescence measurements were performed with UV-265 spectrophotometer (Shimadzu) and F-4500 spectrofluorimeter (Hitachi). ^{1}HNMR spectra were measured with DKX-300 MHz Bruker instrument. A 1 mL aliquot of the stock solution (5.0×10^{-5} mol·L^{-1}) of TEPyP was transferred into a 10 mL volumetric flask and an appropriate amount of 0.01 mol·L^{-1} β-CD and 0.001 mol·L^{-1} HP-β-CD (or SBE-β-CD) was added. The pH was fixed with a 0.5 mol·L^{-1} phosphate buffer solution.

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Results and Discussion

The aggregation of TEPyP above concentration of 2×10^{-6}mol·L^{-1} in aqueous solution was observed on the basis of the titration of UV-Vis absorption. The addition of CDs to the neutral buffered solution of TEPyP resulted in a good linear and Beer-law of TEPyP could be obeyed again, which suggested that β-CD, HP-β-CD and SBE-β-CD act as receptor to include TEPyP and inhibit the aggregation of guest molecular. In the presence of excess of β-CD, HP-β-CD and SBE-β-CD, the absorption spectrum of TEPyP was found to induce different red shift. The concentration of all three kinds of cyclodextrins was equal to 20-fold molar of TEPyP. In buffer solution (pH=3.0), the Soret band and the intensity of the Soret band kept unchanged in the case of three CDs. However, in neutral and basic solutions, the Soret band of TEPyP shifted markedly and the tendency of red-shifted was more than 5 nm and 9 nm, respectively. And, the absorbance of TEPyP in the Soret band was increased in the presence of three CDs. The assembly of TEPyP with CDs resulted in the changes in the fluorescence characteristics of guest molecular. The fluorescence excitation bands were fixed at 424 nm. With the addition of HP-β-CD and SBE-β-CD, the emission bands were red-shifted 5 nm and 3 nm, respectively. Whereas, the emission bands remained at 650 nm and were hardly affected in the presence of β-CD. The fluorescence intensity of TEPyP showed remarkable enhancement in the presence of β-CD, HP-β-CD and SBE-β-CD. The formation constants of TEPyP with CDs were determined from doubled reciprocal method. $1/(F-F_0)$ *versus* $1/[CD]$ was plotted and K was obtained from the ratio of the intercept to the slope. **Figure 2** showed the double reciprocal plots of $1/(F-F_0)$ *versus* $1/[CD]_0$ for TEPyP complexed with HP-β-CD at pH 10.00. The plot exhibited good linearity (the linear correlation coefficientR=0.9982). This implied the formation of inclusion complexes with a stoichiometry of 1:1. The same results were obtained for β-CD and SBE-β-CD. The K values for β-CD, HP-β-CD and SBE-β-CD with TEPyP were 550, 1.10×10^4 and 2.00×10^5 $(mol/L)^{-1}$ respectively. The remarkably

Figure1 The structure of TEPyP.

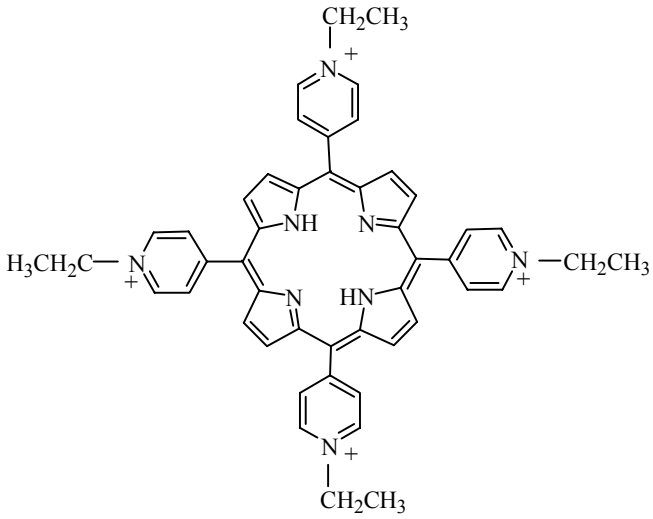
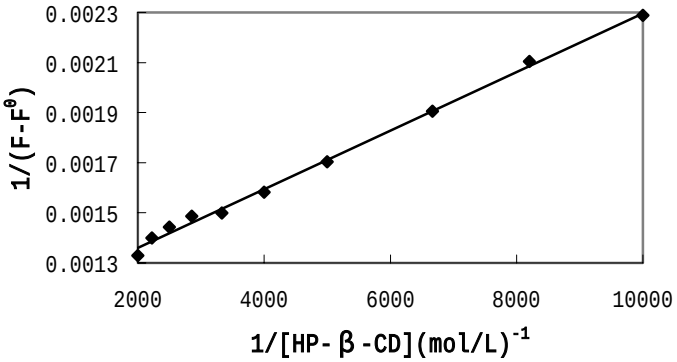


Figure 2 Double reciprocal plots for TEPyP complex to HP-β-CD in pH=10.00 buffer solution:



large inclusion constants for HP-β-CD, SBE-β-CD than that for β-CD may be explained by the fact that the chemically modified cyclodextrins are endowed with specially functional groups. Then, the solubility and flexibility of cyclodextrins have been improved in the great degree comparing with native β-CD. Moreover, the strongest inclusion capacity of SBE-β-CD was caused by its negative charge, while TEPyP was positively charged. And electrostatic forces play important roles in the process of weak inclusion interaction. The conformation of complexed TEPyP-CDs was further confirmed by the NMR analysis. The chemical shifts for the inclusion complex were different from these for the free compounds (**Table 1**). As the guest molecule, the more shielded protons of β-pyrrole, pyridyl and methyl moiety showed apparently downfield shift in the presence of β-CD and HP-β-CD. In addition, the protons of CDs, located within or near the cavity (H3, H5, H6) shifted remarkably upfield. The results confirmed the desired fashion that ethyl and pyridyl groups of porphyrin entered into the cavity of β-CD and HP-β-CD through primary face.

Table 1 The chemical shifts (δppm) data (20°C,D_2O) of β-CD and HP-β-CD in ^{1}H NMR

	β-CD			HP-β-CD		
Proton	δ_{free}	δ_{com}	△δ	δ_{free}	δ_{com}	△δ
H3 of CDs	3.778	3.693	-0.085	3.831	3.673	-0.158
H5 of CDs	3.687	3.601	-0.087	3.675	3.513	-0.162
$H6_{a,b}$ of CDs	3.687	3.635	-0.052	3.675	3.620	-0.055
*m*H of pyridyl	9.202	9.218	0.016	9.202	9.214	0.012
*o*H of pyridyl	8.803	8.823	0.020	8.803	8.823	0.020
H of methyl	1.784	1.798	0.015	1.784	1.791	0.007

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