Journal of Inclusion Phenomena and Macrocyclic Chemistry (2006) 56: 141–148
DOI 10.1007/s10847-006-9075-4

Selective Pseudo-Rotaxane Type Complex Formation of Zinc(II) (*t*-butylatedtetraphenyl) Porphyrin-Viologen Linked Compounds with Tri-*O*-methyl-*β*-Cyclodextrin

TATSUYA MOROZUMI, NAO SATO and HIROSHI NAKAMURA*
Division of Material Science, Graduate School of Environmental Earth ScienceHokkaido University, 060-0810, Sapporo, Japan

Key words: pseudo-rotaxane type complexation, supramolecular structure, tri-*O*-methyl-*β*-cyclodextrin, zinc(II) (*t*-butylatedtetraphenyl)porphyrin-viologen linked compounds

Abstract

Inclusion complexation behavior of 2,3,6−tri-*O*-methyl-*β*-cyclodextrin (TM-*β*-CD) with zinc(II) 5,10,15-tri-(4-*t*-butyl-phenyl)-20-(4-(*n*-alkyloxy)phenylporphyrin covalently linked with violgen by a polymethylene chain (Zn-*t*-bu-PC_nV^{2+}; $n=4$, 6, 8, 10 and 12) was investigated by means of ^{1}H NMR, UV/Vis absorption spectroscopies in acetonitrile-water (1:1, v/v). The ^{1}H NMR spectra indicated that Zn-*t*-bu-PC_nV^{2+} presumably existed as a mixture of a dimer and a monomer in high concentration ($> 1\times10^{-3}$ mol dm^{-3}), and the dimer was degraded by the complex formation with TM-*β*-CD. The ^{1}H NMR spectra of these compounds as a function of [TM-*β*-CD] showed the selective formation of 1:1 (= Zn-*t*-bu-PC_nV^{2+}: TM-*β*-CD) pseudo-rotaxane type complexes. The chemical modification by *t*-butyl groups on porphyrin showed a good protective effect on inclusion of benzene groups into the TM-*β*-CD cavity. These rotaxane formation constants (*K*) were determined by titration studies using UV/Vis absorption spectroscopy. These complex formation constants were somewhat affected by the spacer methylene chain between the porphyrin and viologen. The value of *K* for Zn-*t*-bu-PC_4V^{2+}·TM-*β*-CD is 1.0×10^3 M^{-1} which is the smallest whereas those for Zn-*t*-bu-PC_nV^{2+}·TM-*β*-CD ($n=8$, 10, 12) were similar (1.0×10^4 M^{-1}).

Introduction

Study on photoinduced electron transfer in electron donor–acceptor (D–A) linked compounds has been carried out as one of the most popular research subjects relevant to artificial photosynthesis [1–3]. Much effort has been paid to elucidate the role of the spacer between D and A in the long-range electron transfer processes for the construction of efficient photo energy conversion systems [1–5]. With the aid of several microenvironments and external stimulation such as electric fields or magnetic fields, the control of photoinduced electron transfer has succeeded in several D–A systems [6, 7]. The preparation of D–A linked compounds with a flexible polymethylene chain, $-(CH_2)_n-$, is easier than that of the molecules with a rigid bridge. However, the study on the dependence of distance on the electron transfer rates in the D–A linked compounds with a flexible bridge usually gave complicated results due to a distribution of different conformations in spite of the molecular assemblies.

It has been well known that cyclodextrins (CDs) have an ability to form supramolecular complexes with many organic compounds in aqueous solution [8]. Various photo-reactive groups, or electron acceptors, have been attached to the CDs, and efficient photoinduced electron transfers or energy transfers between the CD-appended moieties and guest molecules included in the cavity of the CDs have been demonstrated [9–11].

Recently, supramolecular chemistry concerning catenanes and rotaxanes with CDs has attracted considerable interest among many researchers. Especially, rotaxane-type cyclodextrin complexes have intensively been studied as one of the most important supramolecular assemblies in various fields [12, 13]. In these investigations, Matsuo *et al.* have reported the formation of stable rotaxane-type supramolecular complexes in several aromatic D–A linked compounds, such as phenothiazine- [14–17], carbazole- [18,19] and anthracence-viologen [20] linked system in water. The photoinduced electron transfer and its external magnetic field effects (MFEs) on the lifetimes of the photo-generated

* Author for Correspondence. E-mail: nakamura@ees.hokudai.ac.jp

triplet biradicals have appeared clearly in those complexes [15–17]. Other research groups have also reported the rotaxane-type complexes of ruthenium trisbipyridine- [21] or naphthalene derivartives-viologen [22] linked compounds with β-CD in aqueous medium.

Although photo-induced electron transfer and MFEs were investigated using porphyrin-viologen linked compounds [23–25], only a few investigations have been applied to rotaxane-type cyclodextrin complexes due to their solubility [26, 27].

On the other hand, the inclusion behaviors of the water-soluble tetraarylporphyrins with β-, γ-CD and 2,6-di-*O*-methyl-β-cyclodextrin (DM-β-CD) have been studied widely [28–32]. The *O*-methylated cyclodextrin is more suitable for many investigations due to the solubility in many organic solvents than native cyclodextrins [28]. With these facts in mind the present authors previously reported the complexation behavior of zinc porphyrin-viologen linked compound ($ZnPC_nV^{2+}$) with 2,3,6-tri-*O*-methyl-β-cyclodextrin (TM-β-CD) in acetonitrile-water (1:1, v/v) by means of ^1H NMR, UV/Vis absorption spectrometry [33]. Since $ZnPC_nV^{2+}$ compounds have four inclusion sites, their complexation acts were too complicated. To construct more simple and selective complex system, chemical modification by a *t*-butyl group was added on the porphyrin ring as a protective moiety for the inclusion complex into the TM-β-CD cavity. In this paper, the complexation behavior of *t*-butylated $ZnPC_nV^{2+}$ (Zn-*t*-bu-PC_nV^{2+}) with TM-β-CD was investigated in acetonitrile-water (1:1, v/v) by means of ^1H NMR, UV/Vis absorption spectrometry.

Experimental section

Apparatus

The ^1H NMR spectra (400 MHz) were measured with JEOL EX-400 ^1H NMR spectrometer, UV/Vis absorption spectra were recorded with a Shimadzu UV-2400PC spectrophotometer. All measurements were carried out in CD_3CN–D_2O (1:1,v/v) at 30 ± 0.2 °C for ^1H NMR and in CH_3CN–H_2O (1:1,v/v) at 25 ± 0.1 °C for UV/Visible spectra. The chemical shifts of ^1H NMR spectra of Zn-*t*-bu-PC_nV in $CDCl_3$–CD_3OD (9:1,v/v), which appeared in this section for identification of material, were quite sensitive to the composition of the solvent and also to the concentration of the compounds. So, the chemical shifts of these compounds in this section were not strict.

Materials

All organic compounds for the syntheses of ZnPCnV were commercially available and used without further purification. Acetonitrile (CH_3CN) was purchased from Dojindo (spectrophotometric grade) and used without further purification. Water was purified by distillation twice. 2,3,6-tri-*O*-methyl-β-cyclodextrin (TM-β-CD) was purchased from Nacalai Tesque, Inc. and used without further purification.

Synthesis of Reagents

Synthesis of $ZnPC_nV$

Zinc (II) tri-*t*-butyl-tetraphenylporphyrin-viologen linked compounds (Zn-*t*-bu-PC_nV, $n = 5$–9) were synthesized according to the usual methods. The synthetic pathway is summarized in Scheme 1 as described previously except for the synthesis of zinc 5-(4-hydroxyphenyl)-10,15,20-tri(4-*tert*-butylphenyl)porphyrin.

Zinc 5-(4-Hydroxyphenyl)-10,15,20-tri(4-tert-butylphenyl)porphyrin (Zn-t-bu-TPHOH)

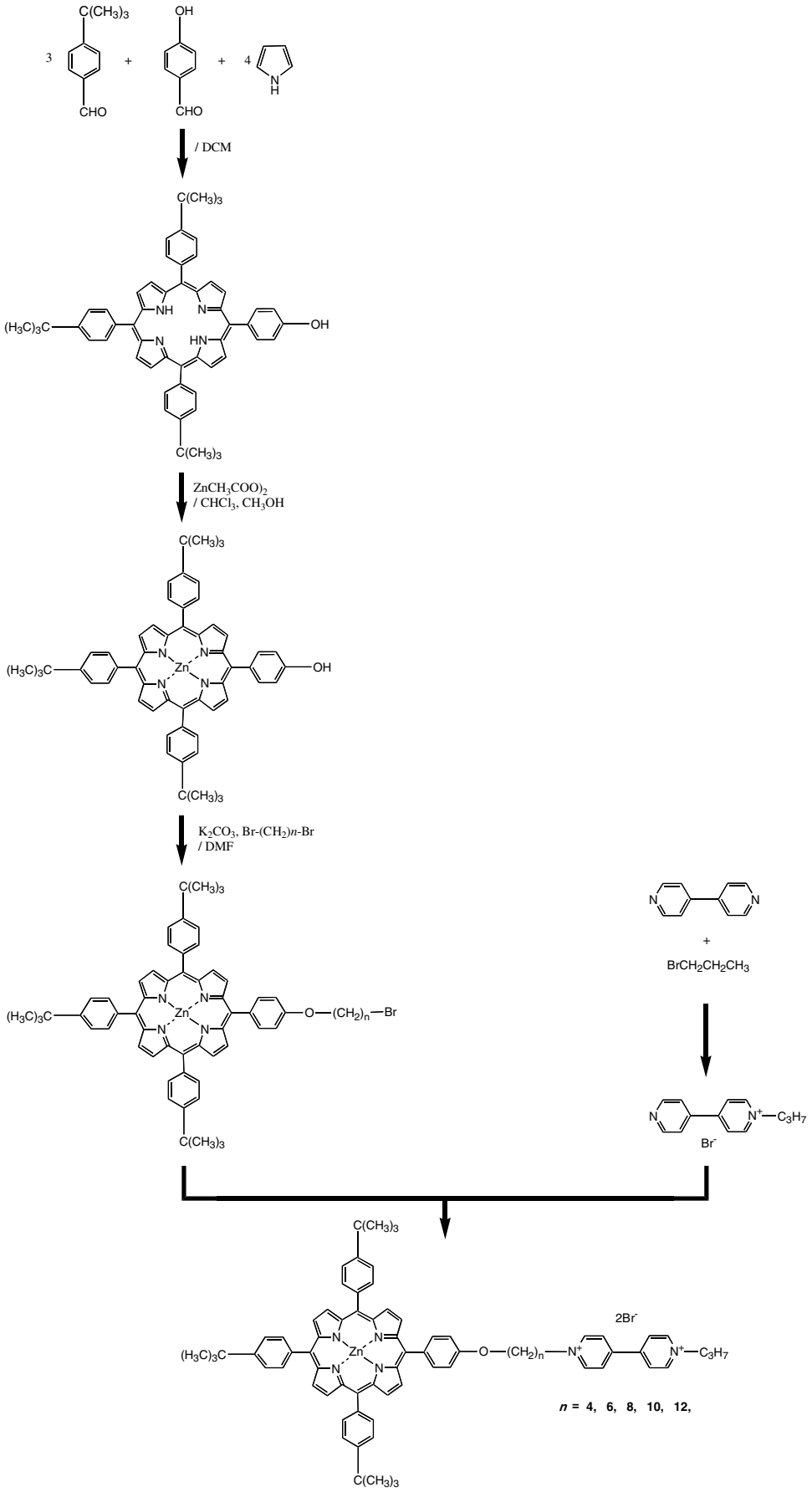
Pyrrole (0.82 g, 12 mmol) was added dropwise to a solution of 4-hydroxybenzaldehyde (0.38 g, 3 mmol), 4-*tert*-butylbenzaldehyde (1.5 g, 9.2 mmol) in the presence of trifluoroacetic acid (0.6 ml) in CH_2Cl_2 (600 ml), and the mixture was stirred at room temperature. After 24 hours DDQ (1.0 g, 4.8 mmol) was added, and the mixture was further stirred for 1 h. Continuously triethylamine (4.2 ml) was added, and the mixture was stirred 1 h more. The solvent was removed by distillation under reduced pressure, the resultant black solids were purified by chromatography on silica gel column (Wakogel C-200) (eluent: $CHCl_3$). To incorporate zinc ion into the porphyrin center, zinc acetate (6.68 g, 0.03 mol) in methanol (30 ml) was added to the solution of *t*-bu-TPHOH (0.4 g, 0.56 mmol) in chloroform – methanol (7:3, v/v, 30 ml), and was refluxed for 4 h. After evaporation of the solvent, the residue was dissolved in chloroform and excess zinc acetate was filtered off. The filtrate was concentrated and purified by chromatography on silica gel column (Wakogel C-200) (eluent: $CHCl_3$). The second fraction was collected and concentrated. This purification was repeated once more. Yield: 0.42 g (4.3%). ^1H NMR ($CDCl_3$) $\delta = 1.61$(27H, s; $-CH_3$), 5.20 (1H, s; –OH), 7.19 (6H, d; aromatic), 7.74 (6H, m; aromatic), 8.07(2H, d; aromatic), 8.13 (6H, m; aromatic), 8.94–8.98(8H, m; aromatic).

Zn-t-bu-PC_4V

Yield: 0.042 g (50.8%). ^1H NMR ($CDCl_3$–CD_3OD(9:1, v/v))$\delta = 0.97$ (3H, t; $-CH_3$), 1.60 (27H, s; $-CH_3$), 1.95–2.46 (6H, m; $-CH_2-$), 4.30 (2H, t; $-CH_2-$), 4.45 (2H, t; $N-CH_2-$), 4.90 (2H, t; $N-CH_2-$), 7.22 (2H, d; aromatic), 7.72 (6H, m; aromatic), 8.07–8.12 (8H, m; aromatic), 8.72 (2H, d; aromatic), 8.80 (2H, d; aromatic), 8.83 – 8.90 (8H, m; aromatic), 8.99 (2H, d; aromatic), 9.27 (2H, d; aromatic).

Zn-t-bu-PC_6V

Yield: 0.051 g (50.1%). ^1H NMR ($CDCl_3$–CD_3OD(9:1, v/v))$\delta = 0.88$ (3H, t; $-CH_3$), 1.58 (27H, s; $-CH_3$), 1.65



Scheme 1. Synthetic Route of Zn-t-bu PC_nV^{2+} ($n = 4, 6, 8, 10, 12$).

(2H, m; $-CH_2-$), 1.70–2.25 (8H, m; $-CH_2-$), 4.20–4.28 (4H, m; $-CH_2-$ and $-N-CH_2-$), 4.74 (2H, t; $N-CH_2-$), 7.23 (2H, d; aromatic), 7.74 (6H, m; aromatic), 8.04–8.10 (8H, m; aromatic), 8.69 (2H, d; aromatic), 8.75–8.92 (12H, m; aromatic), 9.18 (2H, d; aromatic).

Zn-t-bu-PC$_8$V

Yield: 0.054 g (51.0%). ^{1}H NMR ($CDCl_3$–CD_3OD(9:1, v/v))$\delta = 1.02$ (3H, t; $-CH_3$), 1.30–1.60 (8H, m; $-CH_2-$), 1.61 (27H, s; $-CH_3$), 1.90–2.10 (6H, m; $-CH_2-$), 4.26 (2H, t; $-CH_2-$), 4.50–4.60 (4H, t; $N-CH_2-$), 7.25 (2H, d; aromatic), 7.73 (6H, m; aromatic), 8.07–8.14 (8H, m; aromatic), 8.55 (4H, d; aromatic), 8.88–8.97 (12H, m; aromatic).

Zn-t-bu-PC$_{10}$V

Yield: 0.05 g (50.8%). ^{1}H NMR ($CDCl_3$–CD_3OD(9:1, v/v))$\delta = 1.01$ (3H, t; $-CH_3$), 1.41–2.11 (45H, m; $-CH_2-$), 4.47 (2H, t; $-CH_2-$), 4.79–4.67 (4H, m; $N-CH_2-$), 7.31 (2H, d; aromatic), 8.01 (2H, d; aromatic), 8.02 (9H, m; aromatic), 8.21 (6H, m; aromatic), 8.54 (2H, d;

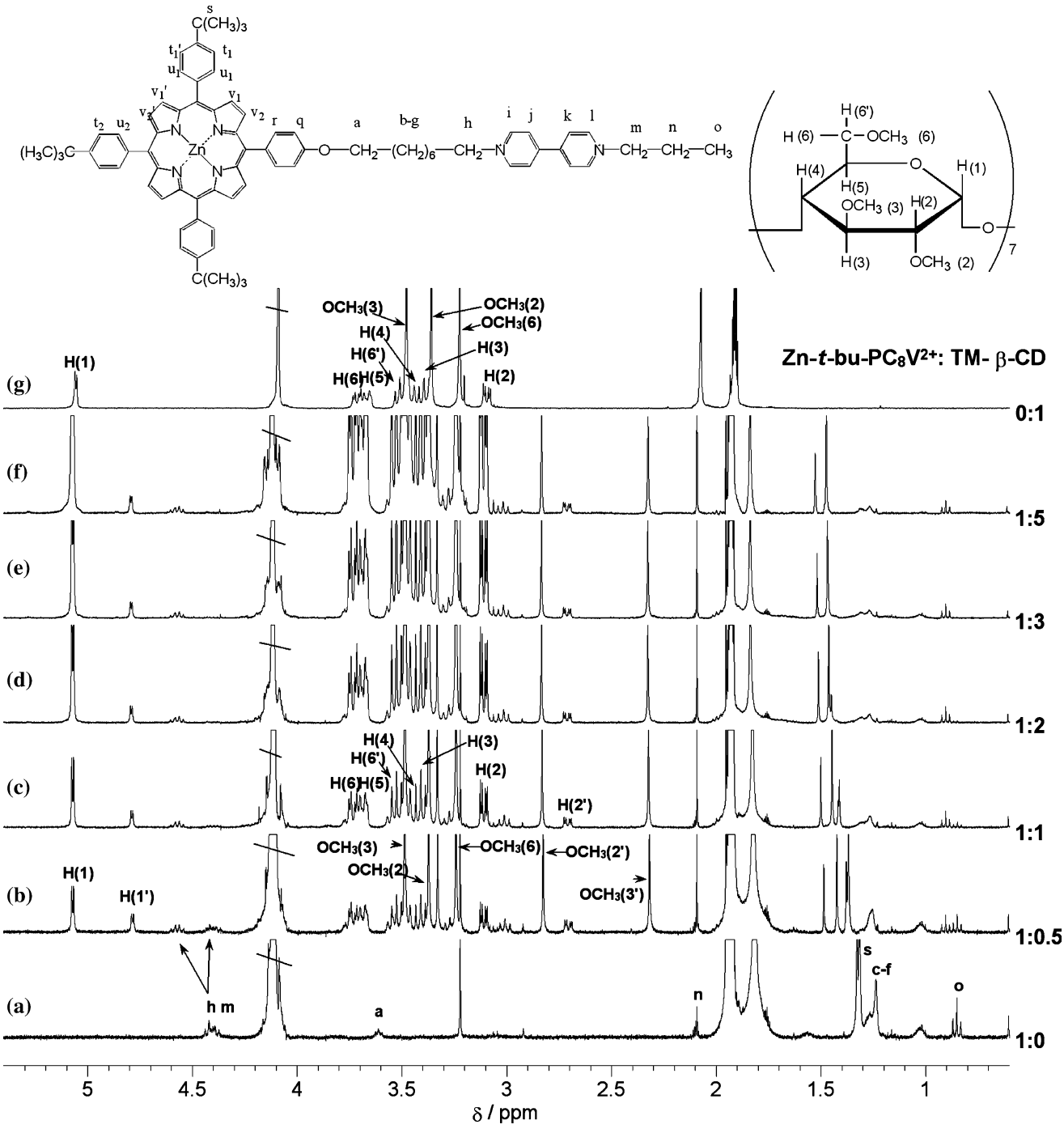


Figure 1. ^{1}H NMR spectra of Zn-*t*-bu-PC_8V^{2+} (1×10^{-3} mol dm^{-3}) in higher magnetic field with adding TM-*β*-CD ((a) 0 mol dm^{-3}, (b) 0.5×10^{-3} mol dm^{-3}, (c) 1×10^{-3} mol dm^{-3}, (d) 2×10^{-3} mol dm^{-3}, (e) 3×10^{-3} mol dm^{-3} (f) 5×10^{-3} mol dm^{-3} and (g) TM-*β*-CD only) in CD_3CN–D_2O (1:1, v/v) at 30 °C.

aromatic), 8.65 (2H, d; aromatic), 8.89 (8H, m; aromatic), 8.90 (2H, d; aromatic), 9.16 (2H, d; aromatic).

Zn-t-bu-PC$_{12}$V

Yield: 0.060 g (52.2%). ^{1}H NMR ($CDCl_3$–CD_3OD(9:1, v/v))$\delta = 1.04$ (3H, t; $-CH_3$), 1.51 (2H, m; $-CH_2-$), 1.65–2.13 (14H, m; $-CH_2-$), 4.27 (2H, t; $-CH_2-$), 4.58 (2H, t; $N-CH_2-$), 4.73 (2H, t; $N-CH_2-$), 7.27 (2H, d; aromatic), 7.74 (9H, m; aromatic), 8.10 (2H, d; aromatic), 8.21 (6H, m; aromatic), 8.60 (2H, d; aromatic), 8.66 (2H, d; aromatic), 8.87–8.91 (8H, m; aromatic), 9.03 (2H, d; aromatic), 9.16 (2H, d; aromatic).

Measurements

UV/Vis absorption spectra were recorded with 10 mm standard quartz cell at 25 ± 0.1 °C. Typical concentrations of Zn-*t*-bu-PC$_n$V were 2×10^{-5} M in CH_3CN:H_2O (1:1, v/v). Complex formation constants (*K*) with TM-*β*-CD were obtained from the

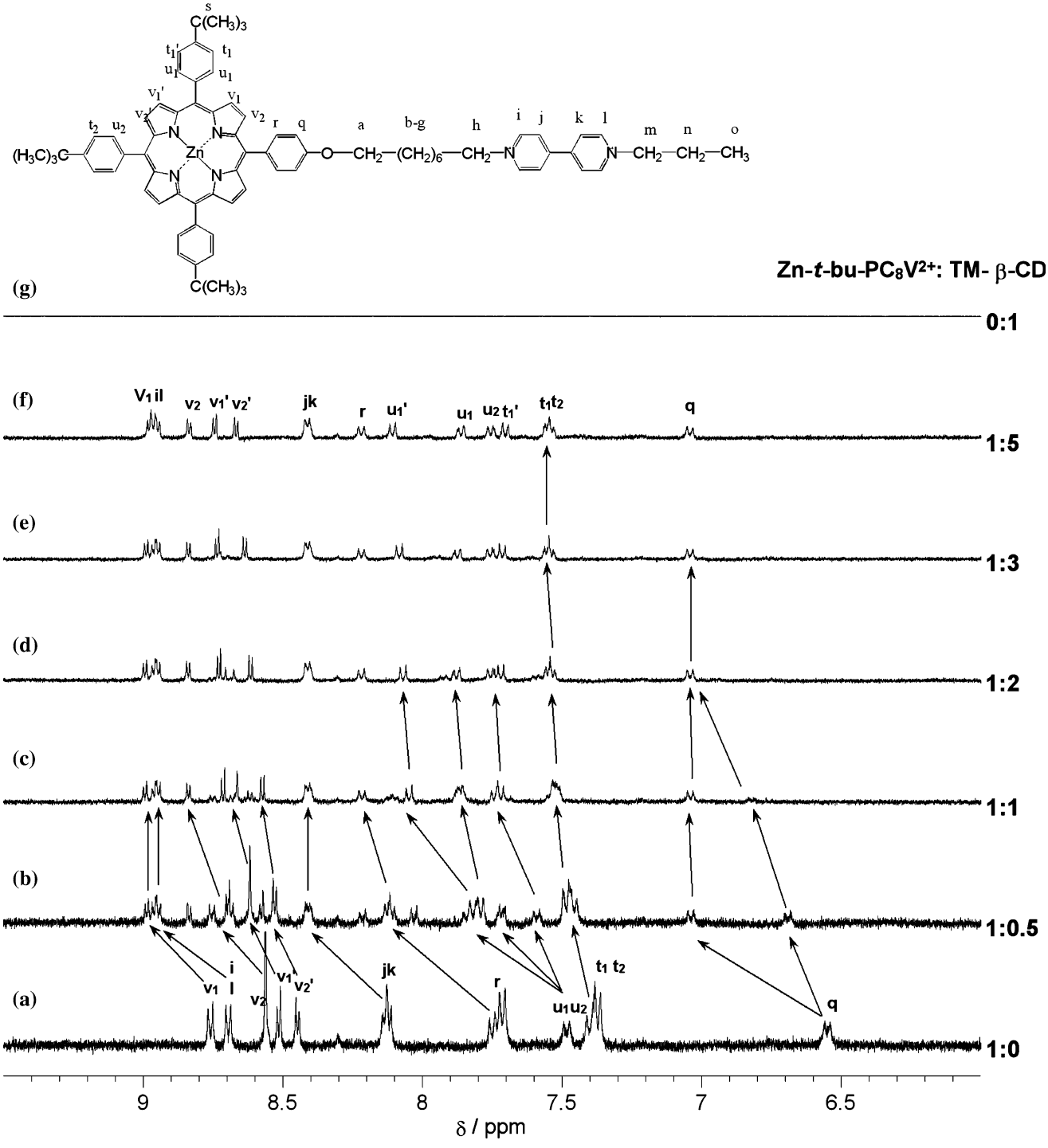


Figure 2. ^{1}H NMR spectra of Zn-*t*-bu-PC$_8$V^{2+} (1×10^{-3} mol dm^{-3}) in lower magnetic field with adding TM-*β*-CD ((a) 0 mol dm^{-3}, (b) 0.5×10^{-3} mol dm^{-3}, (c) 1×10^{-3} mol dm^{-3}, (d) 2×10^{-3} mol dm^{-3}, (e) 3×10^{-3} mol dm^{-3}, (f) 5×10^{-3} mol dm^{-3} and (g) TM-*β*-CD only) in CD_3CN–D_2O (1:1, v/v) at 30 °C.

absorbance change at 25 ± 0.1 °C by the use of non-linear least-square curve-fitting method (Marquardt's method) [34].

^{1}H NMR spectra for the complex formation of Zn-*t*-bu-PC_nV with TM-*β*-CD were measured at 30 °C. Concentration of Zn-*t*-bu-PC_nV was 2×10^{-3} M in CD_3CN–D_2O (1:1, v/v), unless otherwise mentioned. Chemical shifts were calculated from a solvent peak (CD_2HCN; $\delta = 1.913$ ppm). Peak assignments of ^{1}H NMR spectra were made by the use of 1D spectra, H-H COSY, NOESY and ROESY spectra.

Results and discussion

Formation of rotaxane complexes of $ZnPC_nV^{2+}$ with TM-β-CD

Figure 1 shows the typical ^{1}H NMR spectra of Zn-*t*-bu-PC_8V^{2+} in the absence and presence of TM-*β*-CD in higher field region. On the addition of a small amount of TM-*β*-CD to Zn-*t*-bu-PC_8V^{2+} ([TM-*β*-CD]/[Zn-*t*-bu-PC_8V^{2+}] = 0.5), methyl protons of $-OCH_3$ (2 and 3) in TM-*β*-CD split free and two new peaks appeared (2.83 and 2.34 ppm, respectively) Figure 1.

The peak positions did not change under the condition of the addition of TM-*β*-CD until [TM-*β*-CD] / [Zn-*t*-bu-PC_8V^{2+}] = 1.0. This result means that only one type of complex formed and it was quite stable. The same behavior was also observed for $-CH_3$(2). The chemical shifts of $-OCH_3$(3) and $-OCH_3$(2) of the complexes were unusually shifted to higher field by the complexation. Especially, the amount of high field shift of $-OCH_3$(3) was *ca.* 1.2 ppm for slow exchanging complexes. On the other hand, the chemical shift of $-OCH_3$(6) was little affected by the complexation. Since this high field shift should be due to the ring current effect of the porphyrin ring of Zn-*t*-bu-PC_8V^{2+}, the large rim of TM-*β*-CD where $-OCH_3$(3) and $-OCH_3$(2) are positioned faced the porphyrin center. This TM-*β*-CD could be of the through-ring (Rotaxane) type complex as shown in Figure 2, whose type was also reported for the carbazole-viologen linked compound [18] and our previous work [33]. These results were also observed for other protons in TM-*β*-CD (e.g. H(1) and H(2)).

Two NMR peaks of *t*-butyl groups observed in around 1.5 ppm were gradually shifted to lower chemical shift region with increase of TM-*β*-CD concentration. In our previous work, an ionic species $ZnPC_9V^{2+}$ assumed a dimer formation in this medium, and the association constants were determined ($K_a = 80$ M^{-1}). It is known that porphyrin derivatives sometimes existed as a dimer in several solvents at high concentration [35, 36]. Although the association constants for Zn-*t*-bu-PC_nV^{2+} dimer were not determined in the present study, the value of K_a would be bigger than that of Zn PC_nV^{2+} because of an increase of hydrophobicity by the *t*-butyl group. This lower chemical shift change can be considered to be due to the fact that Zn-*t*-bu-PC_nV^{2+} dimer separated to a monomer accompaning the rotaxane complex formation, and showed normal *t*-butyl chemical shift value.

The NMR observation of Zn-*t*-bu-PC_8V with TM-*β*-CD in the low field region ($\delta > 6$ ppm) is shown in

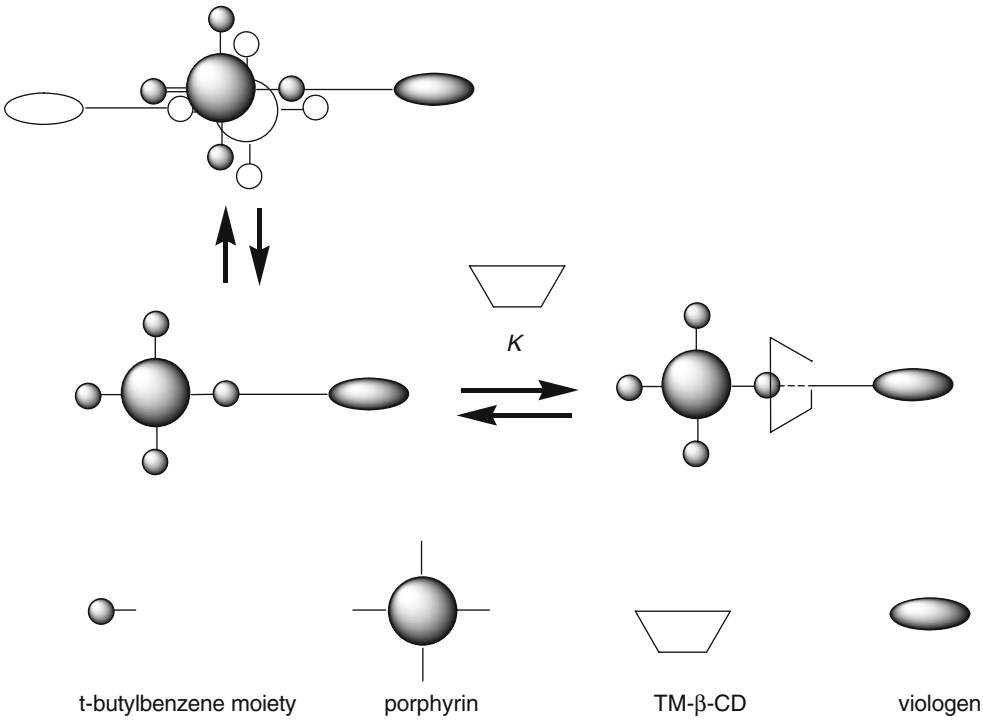


Figure 3. Schematic representation of the kinetics of the supramolecular complex formation of Zn-*t*-bu-PC_nV^{2+} with TM-*β*-CD. *K* is apparent complex formation constants with TM-*β*-CD for 1:1.

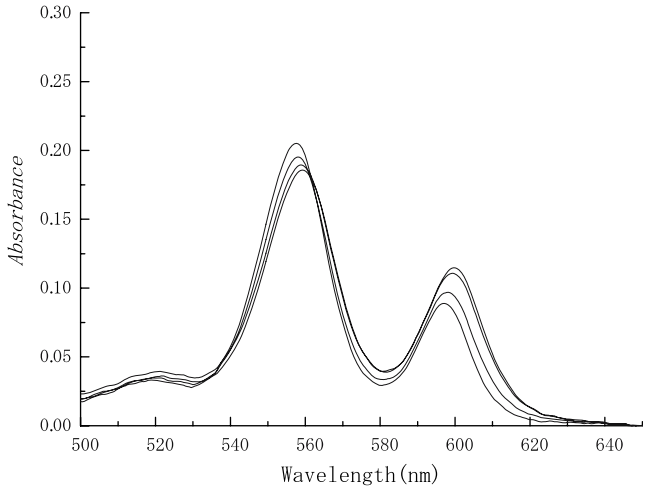


Figure 4. Absorption spectra of $ZnPC_8V^{2+}$ in CH_3CN–H_2O (1:1, v/v) in the presence of various concentration of TM-β-CD. [Zn-*t*-bu-PC_8V^{2+}] = 2×10^{-5} mol dm^{-3}.

Figure 2. The proton *q*, which is on the benzene ring attached to the oxyalkyl chain, showed a characteristic change in its chemical shift. The chemical shift of *q* shifted to lower magnetic field by the addition of TM-β-CD. At the same time, a new peak (*q*′) appeared at 7.04 ppm. With the increase of TM-β-CD, the position did not change, but the intensity increased. The high field shift was mainly caused by the decrease of uncomplexed monomer Zn-*t*-bu-PC_8V^{2+} as shown in the previous section. The peak height of the new peak *q*′ at 7.04 ppm increased on the addition of TM-β-CD. This peak intensity was clearly proportional to [TM-β-CD], and no other new peaks were observed. This shows that the new lower field *q* peak (7.04 ppm) was assigned to the peak of the rotaxane complex. The existence of only one *q* peak in Zn-*t*-bu-PC_8V^{2+}·TM-β-CD is also supported strongly by the fact that a rotaxane complex structure was formed selectively in this system.

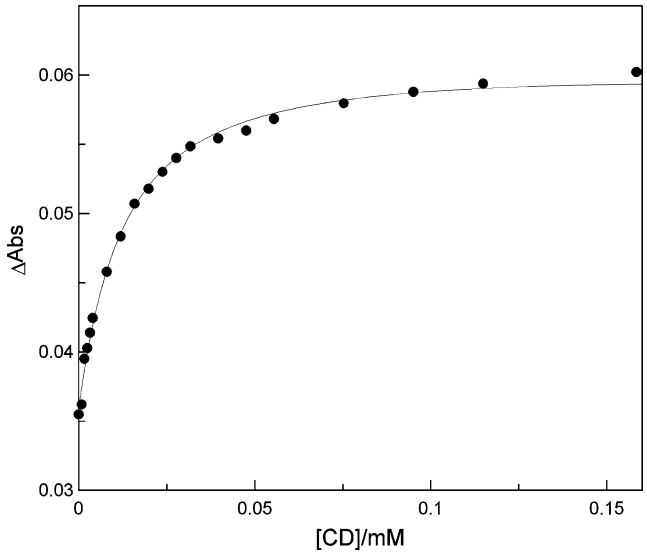


Figure 5. Titration curve of the absorbance of Zn-*t*-bu-PC_8V^{2+} at 598.5 nm by the addition of TM-β-CD. [$ZnPC_8V^{2+}$] = 2×10^{-5} mol dm^{-3}.

Table 1. Complex formation constants of Zn-t-bu-PC_nV with TM-β-CD

Zn-*t*-bu-PC_nV (*n*)	*K* [M^{-1}]
4	1.0×10^3
6	3.6×10^3
8	1.4×10^4
10	1.4×10^4
12	1.1×10^4
$ZnPC_nV$	$>10^5$

Relatively small changes of other aromatic protons in lower field were also observed. Two couples of protons (t_1 with t_1' and u_1 with u_1') can be recognized individually after the formation of Zn-*t*-bu-PC_8V^{2+}·TM-β-CD. The NMR observation indicated an inhibition of free rotation along the porphyrin-phenyl axis. It can be explained that the inhibition of free rotation was induced by steric hindrance after the rotaxne formation.

These quite similar results of NMR observation for other Zn-*t*-bu-PC_nV^{2+}·TM-β-CD were obtained, and the rotaxane-type complex formations were supported.

Complexation constants of $ZnPC_nV^{2+}$ with TM-β-CD

The typical absorption spectral change of Zn-*t*-bu-PC_nV^{2+} ($n=8$) on the addition of TM-β-CD are shown in Figure 4. In both cases, two main absorption peaks of the Q-band around 560 and 598 nm shifted to shorter wavelength by the addition of TM-β-CD. Coincidently, the peak height at shorter wavelength increased and that at longer wavelength decreased. However, the peak at the Soret band around 422.5 nm did not shift by the addition of TM-β-CD. The same trends were observed for other Zn-*t*-bu-PC_nV^{2+}·TM-β-CD. In consideration of the results by the NMR spectra, these spectral changes indicated the formation of 1:1 rotaxane complexes of Zn-*t*-bu-PC_8V^{2+} with TM-β-CD showing a hypochromicity of porpyrin. The formation constants *K* can be evaluated from the absorbance change of the solution by the use of non-linear least square curve-fitting method (Marquardt method) [34] (Figure 5), and the data are listed in Table 1. These values are 10 times smaller than that of no *t*-butylated $ZnPC_nV^{2+}$ ($>10^{-5}$ M). Although the decrease of *K* clearly was induced by the introduction of a *t*-butyl moiety for $ZnPC_nV^{2+}$, the *t*-butyl group contributed to selective formation of 1:1 rotaxane Zn-*t*-bu-PC_nV^{2+}·TM-β-CD. Study on photoinduced electron transfer using the rotaxane Zn-*t*-bu-PC_nV^{2+}·TM-β-CD will be published elsewhere.

References

1. G.L. Closs and J.R. Miller: *Science* **240**, 440 (1998).
2. M.R. Wasielewski: *Chem. Rev*. **92**, 435 (1992).

3. D. Gust, T.A. Moore, and A.L. Moore: *Acc. Chem. Res.* **26**, 198 (1993).
4. N.J. Turro: In Benjamin Cummings (ed.), *Modern Molecular Photochemistry*, Menlo Park, (1978).
5. G.J. Kavarnos and N.J. Turro: *Chem. Rev.* **86**, 401 (1986).
6. U.E. Steiner and T. Ulrich: *Chem. Rev.* **89**, 51 (1989).
7. H. Hayashi: In J.F. Rabek (ed.), *Photochemistry and Photophysics*, CRC Press, Boca Raion, Vol. I, 59 (1990).
8. M.C.T. Fyfe and J.F. Stoddart: *Acc. Chem. Res.* **30**, 393 (1997).
9. M.L. Bender and M. Komiyama: *Cyclodextrin Chemistry*, Springer–Verlag, New York (1978).
10. G. Wenz: *Angew. Chem. Int. Ed. Engl.* **33**, 803 (1994).
11. A. Harada, J. Li, and M. Kamachi: *Nature* **356**, 325 (1992).
12. H. Ogino: *New. J. Chem.* **17**, 683 (1993).
13. S.A. Nepogodiev and J.F. Stoddart: *Chem. Rev.* **98**, 1959 (1998).
14. H. Yonemura, H. Saito, S. Matsushita, H. Nakamura, and T. Matsuo: *Tetrahedron Lett.* **30**, 3143 (1989).
15. H. Yonemura, H. Nakamura, and T. Matsuo: *Chem. Phys. Lett.* **155**, 157 (1989).
16. H. Yonemura, H. Nakamura, and T. Matsuo: *Chem. Phys. Lett.* **162**, 69 (1992).
17. Y. Fujiwara, T. Aoki, K. Yoda, H. Cao, H. Mukai, T. Haino, Y. Fukazawa, Y. Tanimoto, H. Yonemura, T. Matsuo, and M. Okazaki: *Chem. Phys. Lett.* **259**, 361 (1996).
18. H. Yonemura, M. Kasahara, H. Saito, H. Nakamura, and T. Matsuo: *J. Phys. Chem.* **96**, 5765 (1992).
19. H. Yonemura, T. Nojiri, and T. Matsuo: *Chem. Lett.* **1994**, 2097.
20. A. Toki, H. Yonemura, and T. Matsuo: *Bull. Chem. Soc. Jpn.* **66**, 3382 (1993).
21. E.H. Yonemoto, G.B. Saupe, R.H. Schmehl, S.M. Hubig, R.L. Riley, B.L. Iverson, and T.E. Mallouk: *J. Am. Chem. Soc.* **116**, 4786 (1994).
22. J.W. Park, B.A. Lee, and S.Y. Lee: *J. Phys. Chem. B* **102**, 8209 (1998).
23. H. Nakamura, A. Uehata, A. Motonaga, T. Ogata, and T. Matsuo: *Chem. Lett.* **1987**, 543.
24. A. Uehata, H. Nakamura, S. Usui, and T. Matsuo: *J. Phys. Chem.* **93**, 8197 (1989).
25. T. Ito, M. Naka, A. Miura, T. Ujiie, H. Nakamura, and T. Matsuo: *Bull. Chem. Soc. Jpn.* **74**, 657 (2001).
26. V.Ya. Shafirovich, E.E. Batova, and P.P. Levin: *Chem. Phys. Lett.* **210**, 101 (1993).
27. T. Ito, T. Ujiie, M. Naka, and H. Nakamura: *Chem. Phys. Lett.* **340**, 308 (2001).
28. J.S. Manka and D.S. Lawrence: *Tetrahedron Lett.* **30**, 7341 (1989).
29. D.L. Dick, T.V.S. Rao, D. Sukumaran, and D.S. Lawrence: *J. Am. Chem. Soc.* **114**, 2664 (1992).
30. J.M. Ribo, J.-A. Farrera, M. L. Valero, and A. Virgili: *Tetrahedron* **51**, 3705 (1995).
31. F. Venema, A.E. Rowan, and R.J. Nolte: *J. Am. Chem. Soc.* **118**, 257 (1996).
32. K. Kano, N. Tanaka, H. Minamizono, and Y. Kawakita: *Chem. Lett.* **1996**, 925.
33. T. Ujiie, T. Morozumi, T. Kimura, T. Ito, and H Nakamura: *J. Inclusion Phenom.* **42**, 301 (2002).
34. D.W. Marquardt: *J. Soc. Ind. Appl. Math.* **11**, 431 (1963).
35. K. Kano, H. Minamizono, T. Kitae, and S. Negi: *J. Phys. Chem. A* **101**, 6118 (1997).
36. K. Kano, K. Fukuda, H. Wakami, R. Nishiyabu, and R.F. Pasternack: *J. Am. Chem. Soc.* **122**, 7494 (2000).