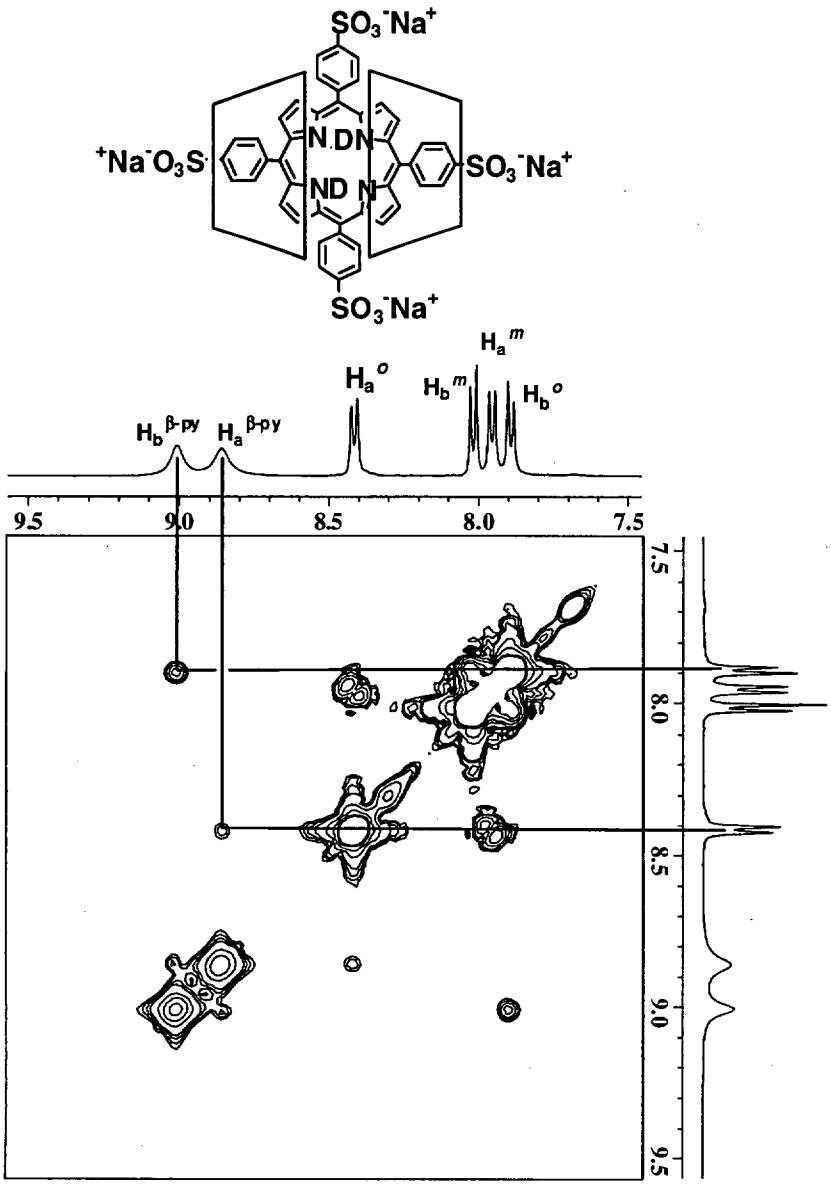
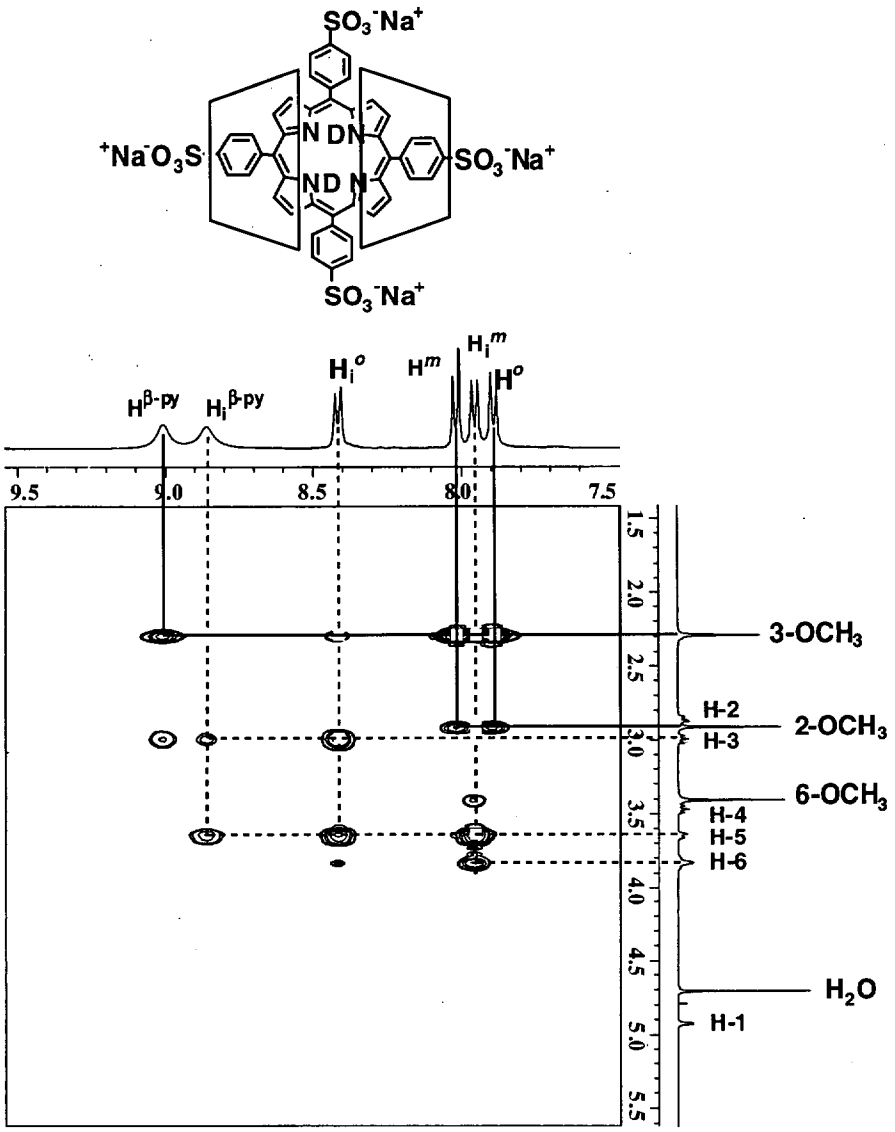
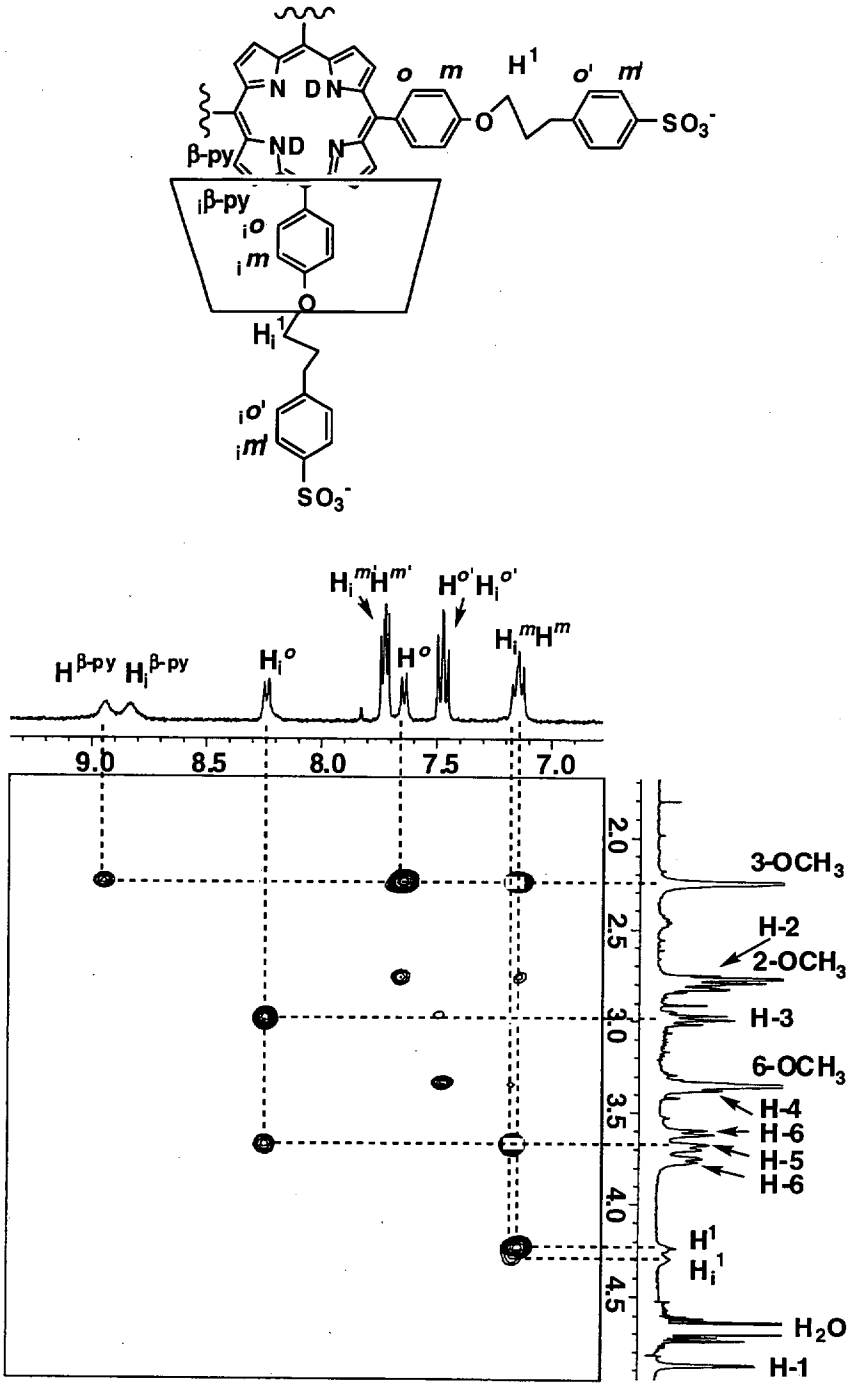


SI Figure 1. ROESY spectrum of the aromatic region of the TMe-β-CD-$TPPS_4$ complex in D_2O at 25 °C: $[TPPS_4]_0$ = 0.05 M; $[TMe\text{-}\beta\text{-}CD]_0$ = 0.1 M

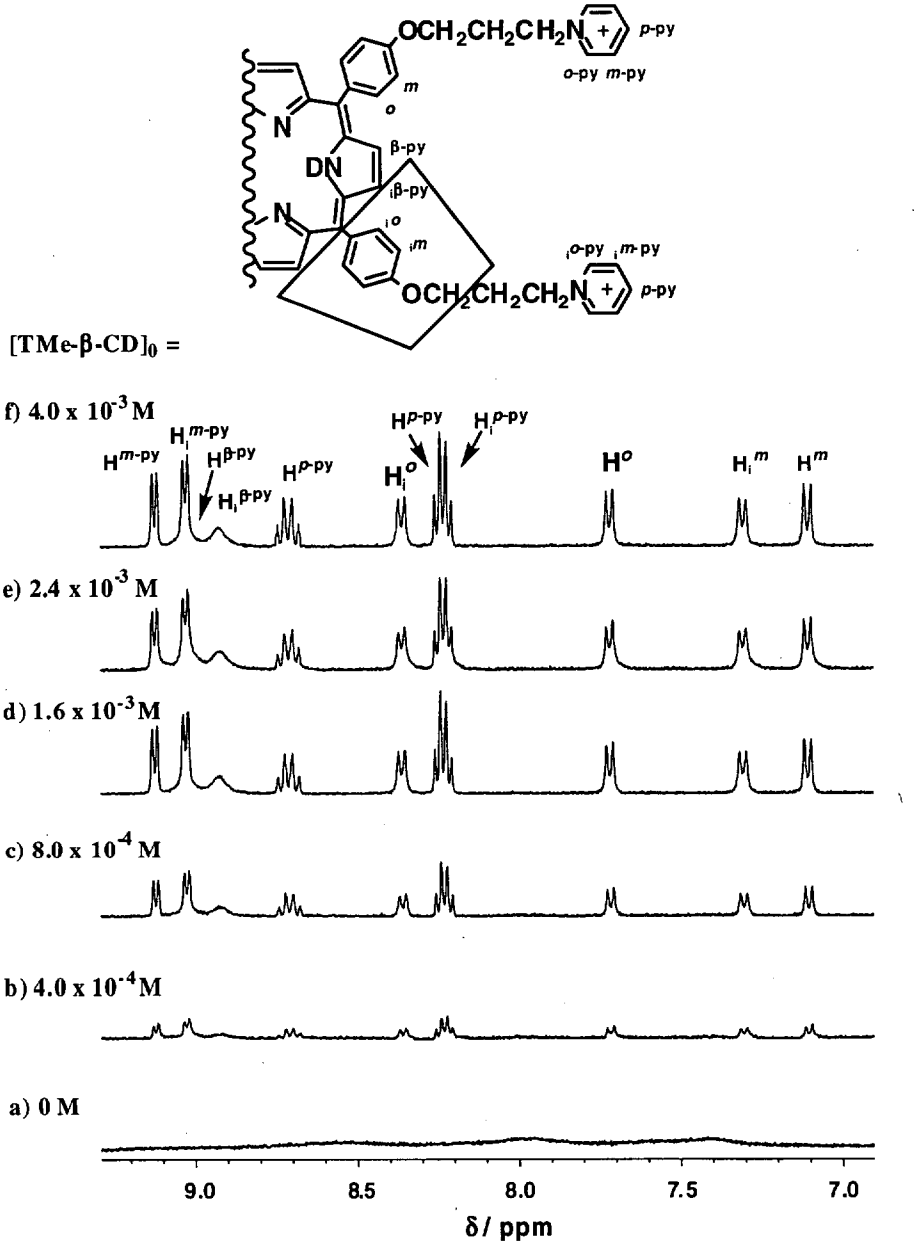


SI Figure 2. ROESY spectrum of the TMe-β-CD-$TPPS_4$ complex in D_2O at 25 °C: $[TPPS_4]_0 = 0.05$ M; $[TMe\text{-}\beta\text{-}CD]_0 = 0.1$ M

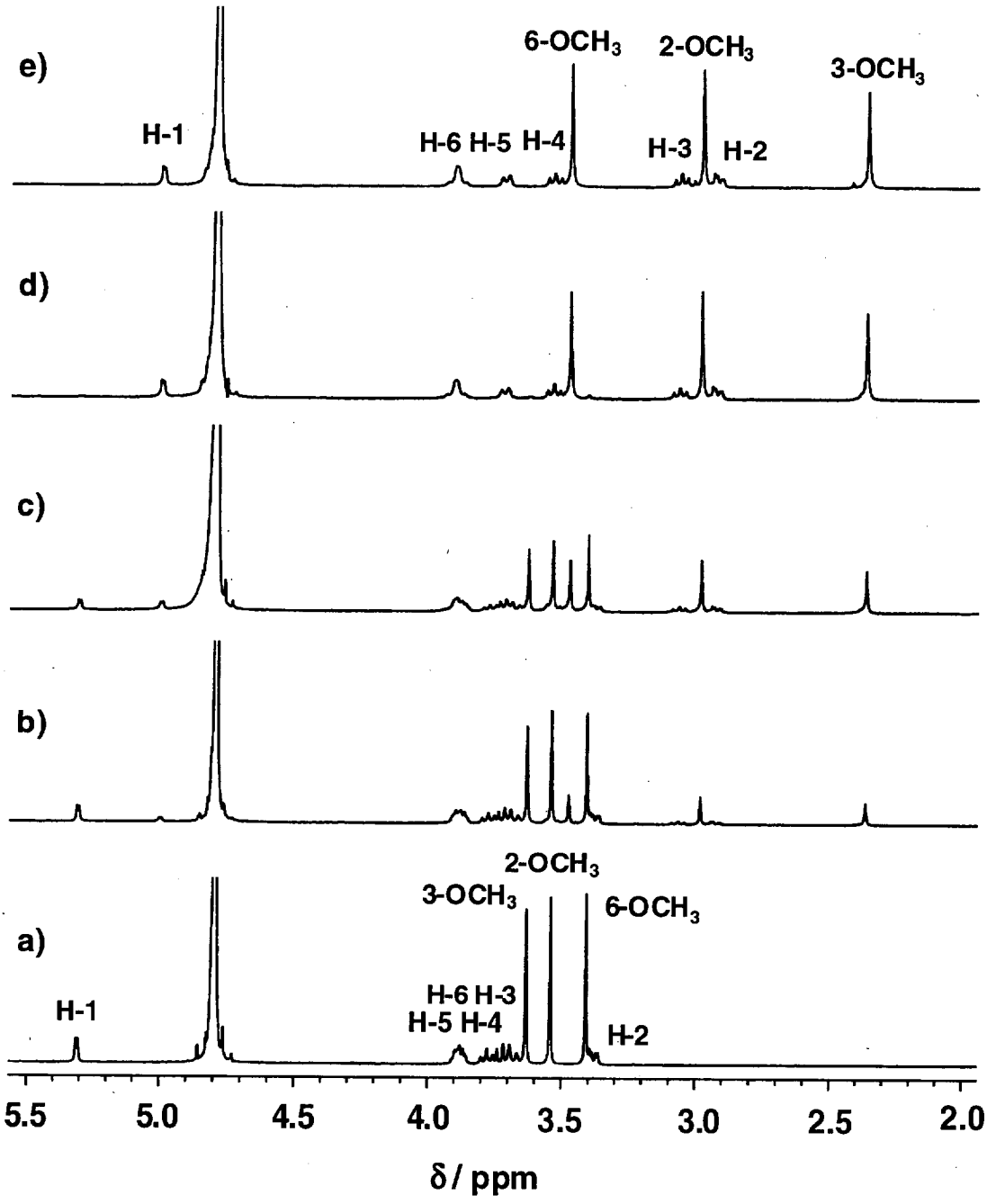
In SI Figure 1, $H_a^{\beta\text{-py}}$ and $H_b^{\beta\text{-py}}$ correlate with H_a^o and H_b^o, respectively, indicating H_a^o and H_b^o are the *ortho*-protons of the phenyl ring of $TPPS_4$. Hence H_a^m and H_b^m should be the *meta*-protons. From the ROESY spectrum in SI Figure 2, it becomes clear that H_a^o is the *ortho*-proton (H_i^o) of the phenyl ring included by TMe-β-CD because there are the cross peaks between H_a^o of $TPPS_4$ and H-3, H-5, and 3-OCH_3 of TMe-β-CD, while H_b^o does not correlate with H-3 and H-5 but correlates with 2-OCH_3 and 3-OCH_3. Therefore, H_b^o can be assigned to be the *ortho*-proton (H^o) of the phenyl ring that is free from inclusion by the CD. Since H_i^o correlates with $H_a^{\beta\text{-py}}$, $H_a^{\beta\text{-py}}$ is assigned to be the pyrrole proton ($H_i^{\beta\text{-py}}$) which is included by TMe-β-CD. All proton signals of $TPPS_4$ have been assigned by such a procedure.



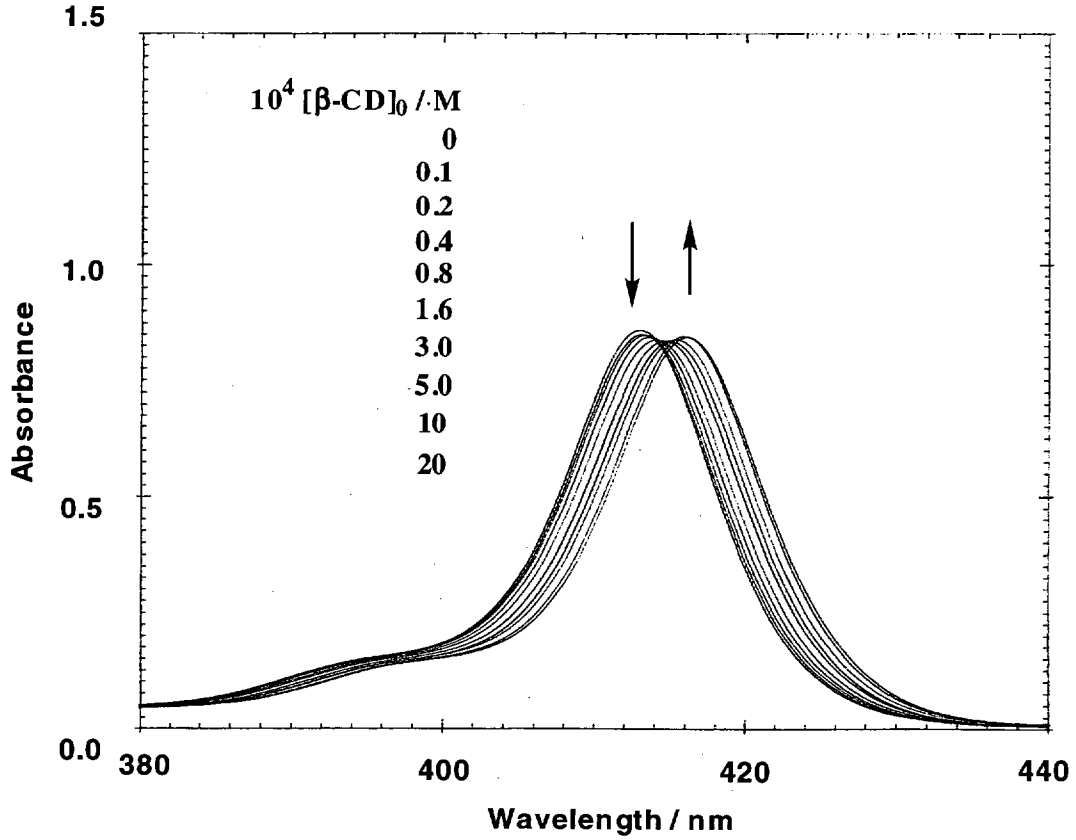
SI Figure 3. ROESY spectrum of the TMe-β-CD-TPPOCPS complex in D_2O at 25 °C: $[TPPOC3PS]_0$ = 1.0 x 10^{-3} M, $[TMe\text{-}\beta\text{-}CD]_0$ = 2.0 x 10^{-3} M. H-n denotes the proton of TMe-β-CD at the n-position



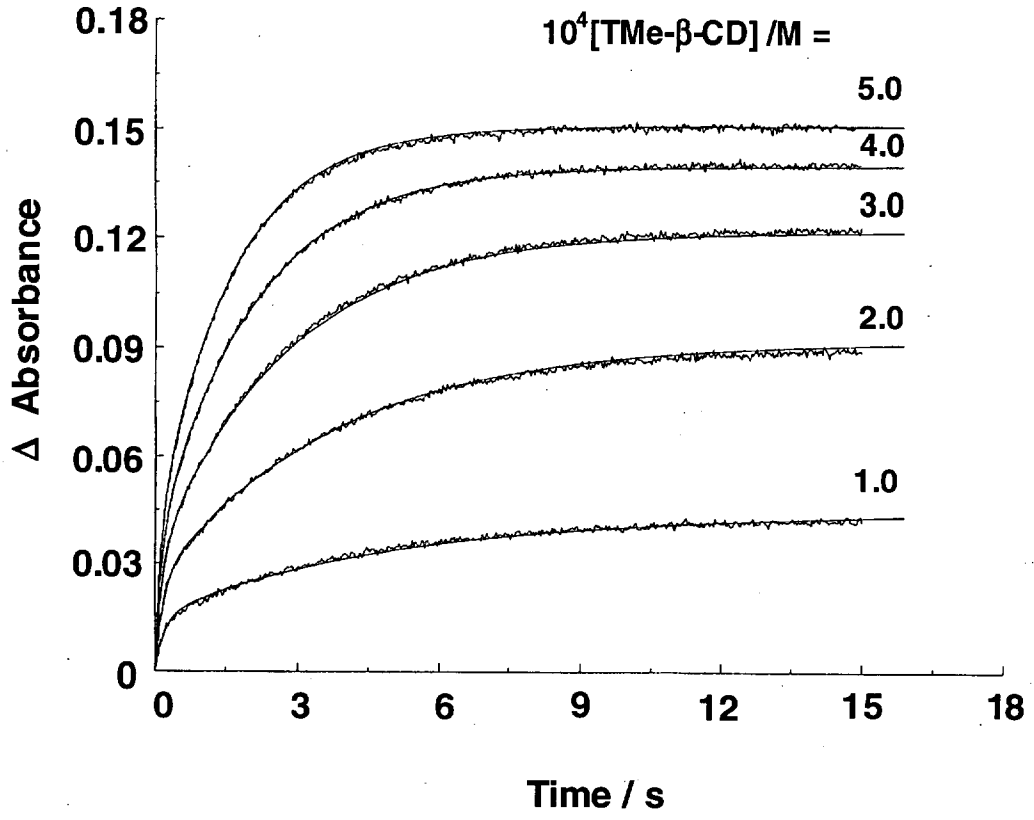
SI Figure 4. ^{1}H NMR spectra of TPPOC3Py (8.0×10^{-4} M) in D_2O at 25 °C in the absence and the presence of various amounts of TMe-β-CD.



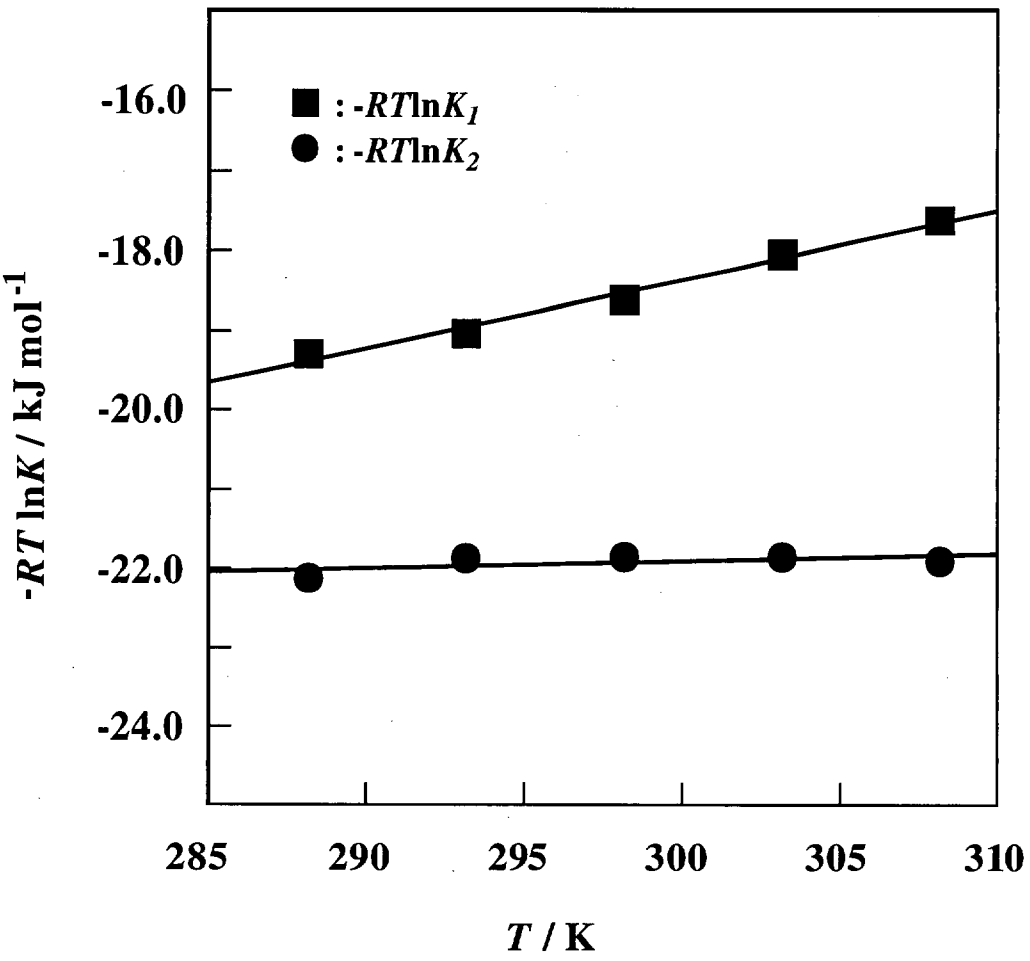
SI Figure 5. ^{1}H NMR spectra of TMe-β-CD (1.0×10^{-3} M) in D_2O at 25 °C in the absence and the presence of various amounts of $TPPS_4$: a) 0, b) 0.125×10^{-3}, c) 0.25×10^{-3}, d) 0.5×10^{-3}, and e) 1.0×10^{-3}.



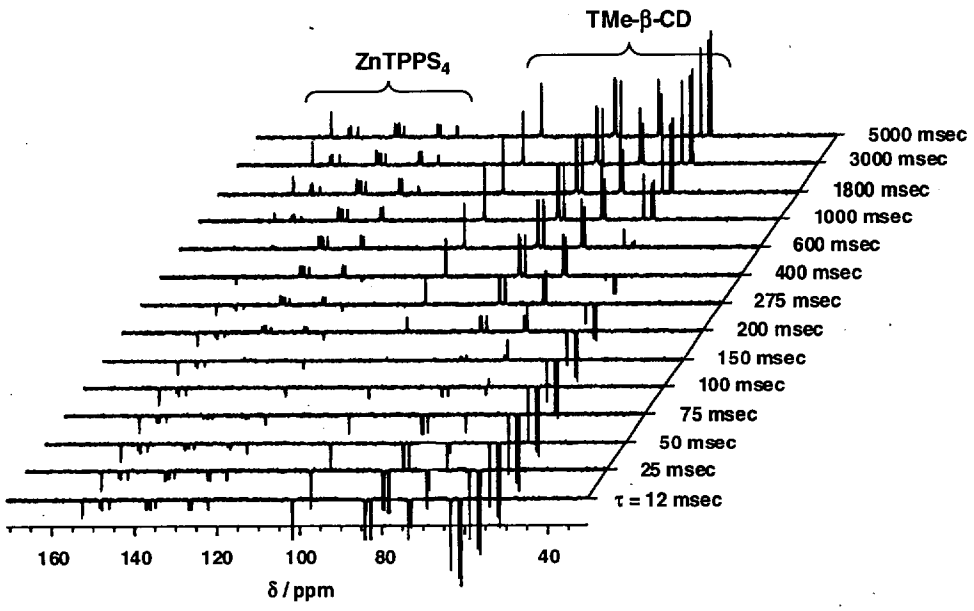
SI Figure 6. Absorption spectra of $TPPS_4$ (2.0×10^{-6} M) in water containing various amounts of β-CD at 25 °C.



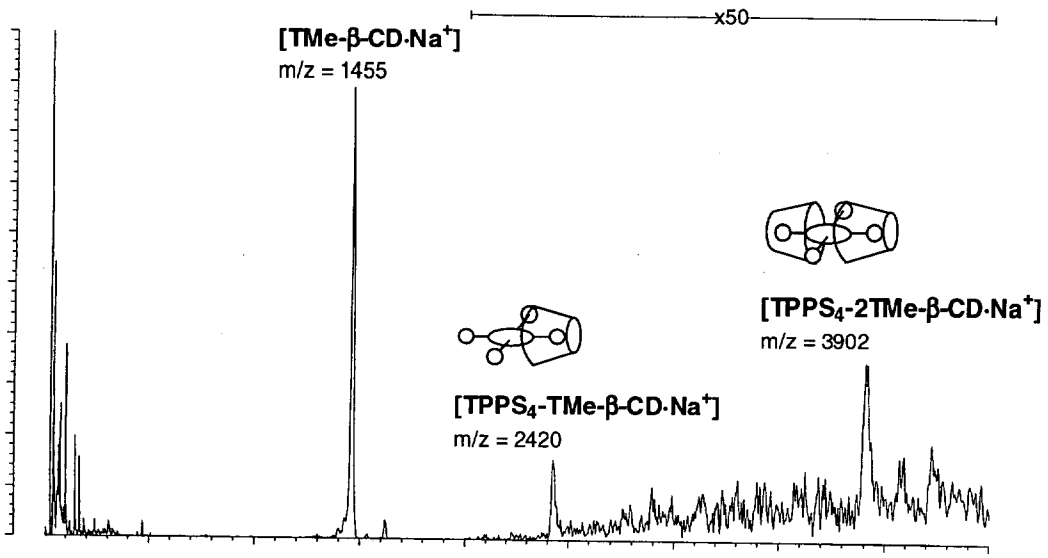
SI Figure 7. Time-courses of the absorbances of TPPOC3Py (5.0×10^{-6} M) at 411.2 nm after addition of various amounts of TMe-β-CD in ethylene EG-H_2O (3:1) at 25 °C. The solid lines are theoretical curves.



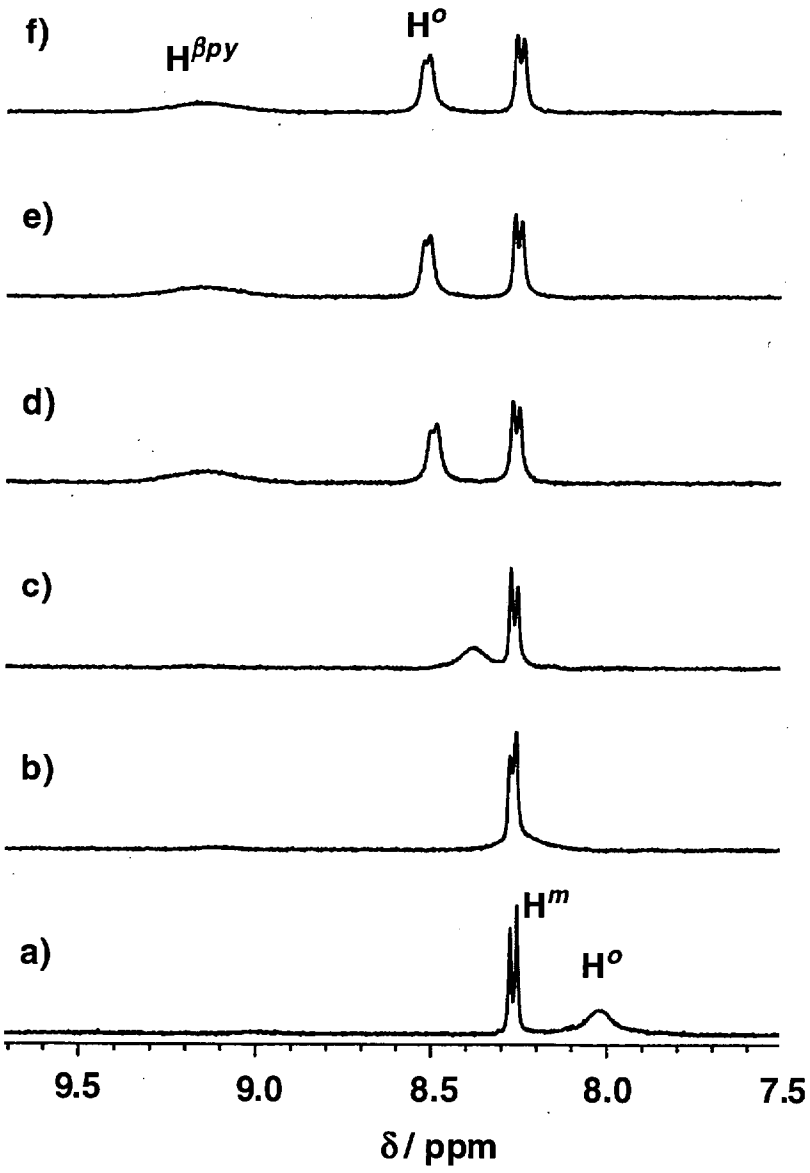
SI Figure 8. van't Hoff plots for complexation of TPPOC3Py with TMe-β-CD in ethylene glycol-water (1:1).



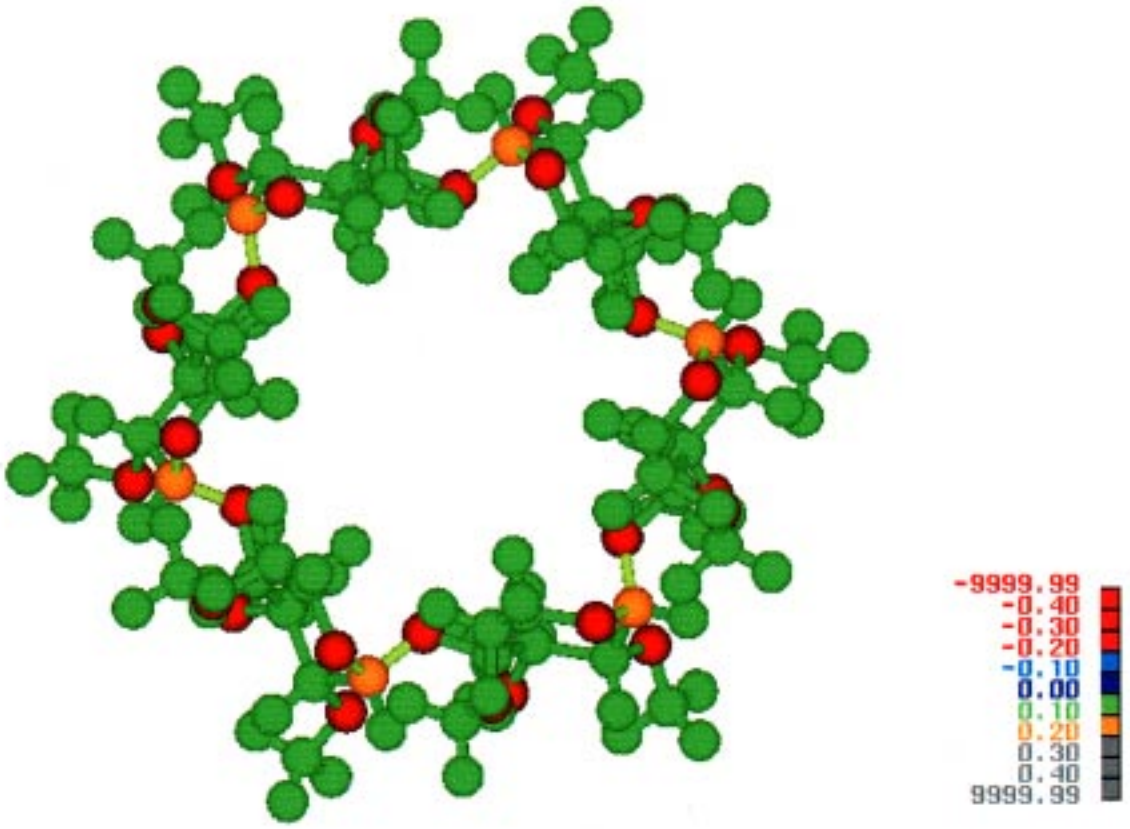
SI Figure 9. Measurements of ^{13}C-T_1 for TMe-β-CD-$ZnTPPS_4$ complex in D_2O by the inversion-recovery method (180°-τ-90°-T)$_N$: Conditions, T (> $5T_1$); 11.0 s, [$ZnTPPS_4$] = 0.05 M, [TMe-β-CD] = 0.1 M.



SI Figure 10. MALDI-TOF MS of $TPPS_4$-TMe-β-CD complex prepared in H_2O and cationized with α-cyano-4-hydroxycinnamic acid (CHCA) matrix. A Shimadzu/Kratos KOMPACT MALDI IV spectrometer was used for measurement.



SI Figure 11. ^{1}H NMR spectra of $TPPS_4$ (1×10^{-3} M) in D_2O at 25 °C in the absence and the presence of various amounts of β-CD: a) 0, b) 0.5×10^{-3}, c) 1×10^{-3}, d) 2×10^{-3}, e) 4×10^{-3}, and f) 8×10^{-3} M.



SI Figure 12. Mulliken's population of hekakis(2,3,6-tri-O-methyl)-α-cyclodextrin evaluated from MOPAC.

Reliability of the method for determining rate constants

The reliability of the present method for determining the k_1, k_{-1}, k_2, and k_{-2} values was checked. Professor Pasternack at Swarthmore College, who was a distinguished visiting professor of Doshisha University, kindly offered his own program to determine k_1, k_{-1}, and k_2 where unknown parameters are reduced to three. Detail of this analytical method is omitted in this Supporting Information because we need large space to explain. Professor Pasternack's method is theoretically understandable when the condition of [Por] << [TMe-β-CD] is held. Comparison of these two analytical methods can be possible from the data shown in SI Table 1.

SI Table 1. Comparison of rate constants obtained using independent two analytical methods for complexation of TPPOC3Py and TPPOC2Py with TMe-β-CD in EG-water (1:1) at 25 °C

method	porphyrin	$10^{-3}k_1/M^{-1}s^{-1}$	k_{-1}/s^{-1}	$10^{-3}k_2/M^{-1}s^{-1}$	$10^{2}k_{-2}/s^{-1}$
this work	TPPOC3Py	13±0.2	0.41±0.01	3.6±0.1	2.6±0.1
this work	TPPOC2Py	11±0.3	0.35±0.01	3.7±0.4	3.2±0.5
Pasternack	TPPOC3Py	13	0.28	3.4	nd
Pasternack	TPPOC2Py	10	0.21	3.4	nd

The k_1 and k_2 values obtained from the present method are in excellent agreement with those from the Prof. Pasternack's method. The rate constants for the backward reactions from the present method are somewhat larger than those from the Prof. Pasternack's method, because Prof. Pasternack's method involves presumption to victimize reaction rates of backward processes. However, we can confirm that our method applied in this study is reliable.

Analytical Data of TPPOC3PS and Its Precursors.

Phenyl 4-(3-bromopropyl)benzenesulfonate. ^{1}H NMR ($CDCl_3$, TMS): δ 7.75 (d, 2H, arom), 7.35 (d, 2H, arom), 7.24-7.27 (m, 3H, arom), 6.98 (d, 2H, arom), 3.38 (t, 2H, $BrCH_2$), 2.88 (t, 2H, CH_2Ph), 2.15-2.22 (m, 2H, CH_2). FAB$^+$MS (*m/z*): 335 M + H$^+$.

5,10,15,20-Tetrakis{4-[3-(4-phenoxysulfonylphenyl)propoxy]phenyl}porphyrin. ^{1}H NMR ($CDCl_3$, TMS): δ 8.87 (s, 8H, pyrrole), 8.12 (d, 8H, arom), 7.83 (d, 8H, arom), 7.50 (d, 8H, arom), 7.26-7.34 (m, 12H, arom), 7.03 (d, 8H, arom), 4.27 (t, 8H, OCH_2), 3.11 (t, 8H, CH_2Ph), 2.32-2.35 (m, 8H CH_2), -1.19 (s, 2H, NH). FAB$^+$MS (*m/z*): 1777 M + H$^+$.

TPPOC3PS. ^{1}H NMR (DMSO-d_6, TMS): δ 8.87 (s, 8H, pyrrole), 8.11 (d, 8H, arom), 7.60 (d, 8H, arom), 7.39 (d, 8H, arom), 7.32 (d, 8H, arom), 4.29 (t, 8H, OCH_2), 2.92 (t, 8H, CH_2Ph), 2.22 (m, 8H, CH_2), -2.89 (s, 2H, NH). Anal. Calcd for $C_{80}H_{66}N_4O_{16}S_4Na_4$: C, 57.62; H, 4.71; N, 3.36. Found: C, 57.98; H, 4.43; N, 3.41.