

Conformation Analysis and Thermodynamics of Binding Behavior of DABCO to *p/p* type Dimeric Porphyrin Hosts

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Abstract: The binding conformations of bidentate ligand DABCO(1,4-diazobicyclo [2,2,2]octane) to a series of *p/p* type zinc porphyrin dimers covalently linked with flexible alkoxy chain -O(CH₂)_nO- (n=2~10) are described by ¹H NMR and UV-vis spectroscopy. DABCO can bind inside the cavities of porphyrin dimers and form a ternary sandwich complex as the alkoxy chain length is long enough. The thermodynamic parameters which control the binding behavior are investigated.

Keywords: Zinc porphyrin dimer, DABCO, thermodynamic parameters, binding conformation.

Covalently linked metalloporphyrin dimers have attracted considerably interest among chemists as models for metalloenzymes, which derive from their remarkable electron, energy transfer and special conformation properties^{1,2}. Metalloporphyrins with large cavities have been designed and assembled with the idea of creating multisite complexing hosts incorporating functionalized subunits for binding organic substrates and transition metals so as to mimic metalloenzymes, as well as supermolecular photochemical devices³.

The structural flexibility of covalently linked porphyrin dimers, the size of the cavity and the interplanar distance between the two porphyrin cores are determined by the nature of the linked chains⁴. We had reported covalently linked iron porphyrin dimers as biomimetic model of Cytochrome P450, their catalytic activities have been proved to be related to the steric hindrance, electron transfer and energy transfer caused by their different conformation equilibrium⁵. We now report a series of covalently linked zinc porphyrin dimers (**Figure 1**), their structural flexibility was proved by accommodating axial bidentate ligand DABCO within their cavities. The corresponding binding behavior and thermodynamic parameters were obtained by ¹H NMR and UV-vis methods.

Experimental

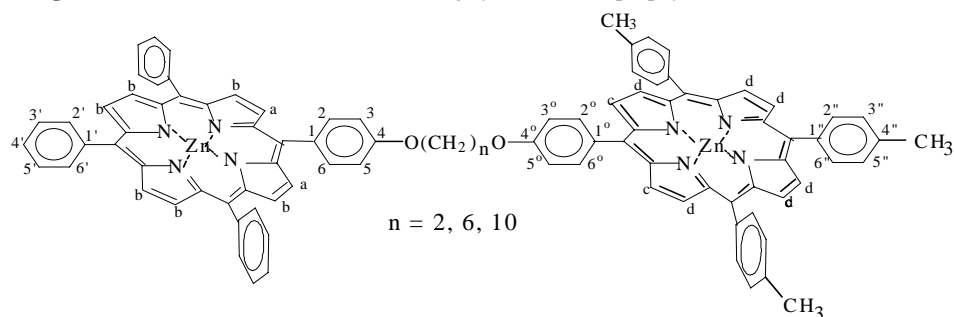
The porphyrins were synthesized as described previously⁶.

UV-vis absorption spectra were recorded on Shimadzu UV-2401PC Spectro-photometer with variable temperature facility. Accurately determined DABCO solutions were titrated into *ca.* 10⁻⁶mol/L porphyrins in CH₂Cl₂. The absorbance of the

mixtures was recorded according to the shift of Soret band.

^1H NMR spectra were recorded on UNITY INOVA 500NB (Varian) spectrometer and typically acquired by using 32K data points over 5000Hz spectral width, double precision was used, number of increments was 512, transient power was 53. For ^1H - ^1H COSY spectra, typically 2K data points were used in f_1 and f_2 , with a spectral width 5000Hz in each dimension. Zero-filling was used in f_1 but not used in f_2 . Suitable apodization was applied in processing spectra. DABCO in CDCl_3 solution was accurately added to *ca.* 10^{-3} mol/L porphyrin solutions *via* a 25- μL syringe.

Figure 1. Structure and ^1H NMR numbering system of zinc porphyrin dimers $\text{C}_n\text{Zn}_2\text{D}$

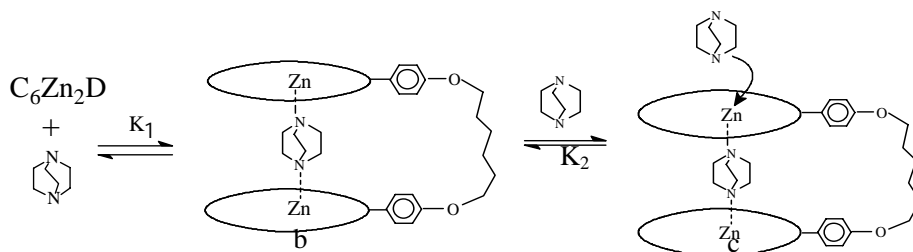


Results and Discussion

Binding conformations for zinc porphyrin dimers to DABCO

When $[\text{DABCO}]/[\text{C}_6\text{Zn}_2\text{D}]$ molar ratio is 1:1, chemical shifts of protons of both $\text{C}_6\text{Zn}_2\text{D}$ and DABCO move to upfield: for $\text{C}_6\text{Zn}_2\text{D}$, protons pyrrole-H, phenyl 2',6',2,6, 2°,6° and tolyl 2'',6'' move about 0.4 ppm, phenyl 3'-5' and tolyl 3'',5'' move about 0.1ppm(**Figure 2**), while the chemical shifts of DABCO protons move upfield 7.256 ppm. As the molar ratio is increased continuously, all protons of dimer and DABCO move to downfield.

Scheme 1 Binding behavior of $\text{C}_6\text{Zn}_2\text{D}$ and DABCO



When molar ratio is 1:1, DABCO may bind inside the cavity of two porphyrin rings of $\text{C}_6\text{Zn}_2\text{D}$ and form a ternary sandwich complex, two porphyrin rings exist in cofacial

conformation (**Scheme 1b**), in this case, the strong ring current effect of two porphyrin π systems causes upfield shift of porphyrin protons within two π systems; DABCO is inside the cavity of two porphyrin rings, its signals have large upfield shift due to the strong shielding effect⁷. When more than 1 equiv. of DABCO has been added, a second molecule of DABCO is competitively bound to the outside of the dimer, which assists the first Zn-N bond cleavage in dissociation of complex (**Scheme 1c**), the closed conformation is opened at the same time. The decreased ring current effect of two porphyrin rings causes the downfield shifts of protons of both DABCO and dimers. For $C_{10}Zn_2D$, similar behavior is observed.

Different behavior is observed for C_2Zn_2D dimer, when $[DABCO]/[C_2Zn_2D]$ is 1:1, shift values of pyrrole-H move about 0.08 ppm to upfield, $\Delta\delta$ value ($\Delta\delta = \delta_{\text{binding}} - \delta_{C_nZn_2D}$) of phenyl and tolyl protons change about 0.02ppm, $\Delta\delta$ of DABCO is -1.271ppm, much smaller than that of C_6Zn_2D and $C_{10}Zn_2D$. When more DABCO is increased, $\Delta\delta$ of all protons still change slightly. $\Delta\delta$ value vs. protons of zinc porphyrin dimers with molar ratio 1:1 are shown in **Figure 2**. It is obvious that the $\Delta\delta$ curves of C_6Zn_2D and $C_{10}Zn_2D$ are quite similar but larger than that of C_2Zn_2D , indicating that the flexibility of alkoxy chain can adjust the optimum conformation for the binding of DABCO and form ternary sandwich complex as the chain length is long enough. For C_2Zn_2D , DABCO can hardly bind inside the cavity of two porphyrin rings and form closed conformation, since the strong tension of the short alkoxy chain.

Figure 2. $\Delta\delta$ Value of C_nZn_2D after addition of 1 equiv. of DABCO

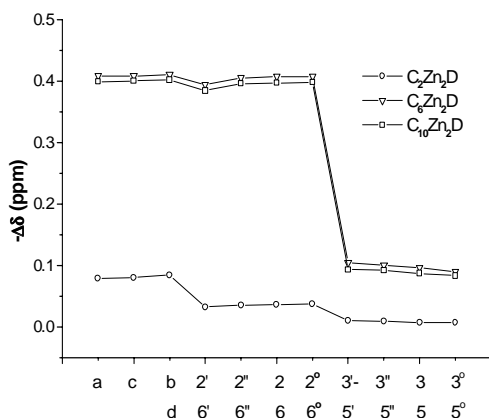
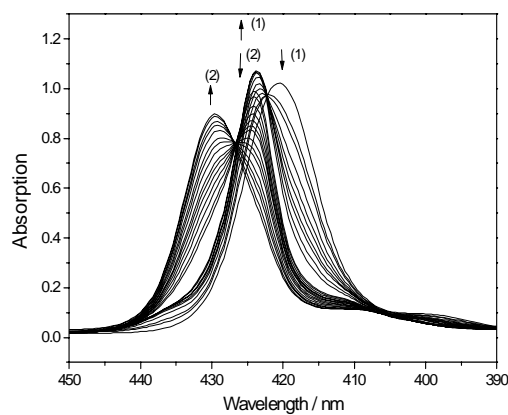


Figure 3. UV-vis spectra of binding processes of DABCO and C_6Zn_2D



Thermodynamic study of binding behavior of DABCO to zinc porphyrin dimers

Axial ligation of DABCO to both dimer C_nZn_2D and monomer ZnTPP results in red shift of the Soret band. The equilibrium constants (K) and the stoichiometric number (n) of DABCO from 15~30°C, the enthalpies (Δ_rH_m) and the entropies (Δ_rS_m) for the reactions are listed in **Table 1**.

On addition of DABCO to C_6Zn_2D , Soret band 420.4nm decreases in intensity and is red shifted to 423.6nm at first, then shifts to 429.6nm at last, two good isosbestic points are observed (**Figure 3**), indicating the formation of two binding equilibriums.

The stoichiometric numbers n_1 and n_2 are about 1, coinciding with the binding conformations shown in **Scheme 1b** and **1c**. Equilibrium constant K_1 is larger than K_2 suggesting the sandwich complex exists in a very stable conformation. For $C_{10}Zn_2D$, similar results are obtained, proving again that the flexibility of alkoxy chain can adjust the optimum conformation for the binding of DABCO.

Table 1. UV-vis changes and thermodynamic parameters of the binding reaction*

	ZnTPP	C_2Zn_2D	C_6Zn_2D	$C_{10}Zn_2D$
porphyrin λ_{max}	418.3	420.8	420.4	420.4
Porphyrin+DABCO λ_{max}	425.0	427.0	423.6 429.6	423.6 429.6
$\ln K / \text{mol}^{-1} \cdot \text{L} (n)$	11.5 (1.10)	10.1(1.23)		
$\ln K_1 / \text{mol}^{-1} \cdot \text{L} (n_1)$			12.7(1.15)	12.5(1.11)
$\ln K_2 / \text{mol}^{-1} \cdot \text{L} (n_2)$			8.51 (1.12)	8.43(1.02)
$\Delta_r H_m / \text{kJ} \cdot \text{mol}^{-1}$	-59.2	-49.9		
$\Delta_r H_{m1} / \text{kJ} \cdot \text{mol}^{-1}$			-80.5	-82.0
$\Delta_r H_{m2} / \text{kJ} \cdot \text{mol}^{-1}$			-48.9	-62.1
$\Delta_r S_m / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	-106	-86.2		
$\Delta_r S_{m1} / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$			-164	-167
$\Delta_r S_{m2} / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$			-93.6	-138

* $K (n)$, $K_1 (n_1)$ and $K_2 (n_2)$ value listed above are measured at 298K

The binding process of DABCO to C_2Zn_2D is similar to that of ZnTPP, but different from that of C_6Zn_2D and $C_{10}Zn_2D$: Soret band red-shifted 7nm, only one equilibrium is observed, K value is lower than K_1 of C_6Zn_2D and $C_{10}Zn_2D$, the total stoichiometric number is only 1.23, may be caused by the steric hindrance between two porphyrin rings of C_2Zn_2D . Obviously, the UV-vis results coincide with the above ^1H NMR study.

In conclusion, covalently linked zinc porphyrin dimers can be used to bind with DABCO and generate a new series of supermolecular porphyrin complexes, the difference of the chain length of the dimers show diverse binding properties, allowing us to probe subtly both the size of the binding pockets and the binding processes of multicomponent enzymes.

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