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Syn-Anti Conformational Changes in Zinc Porphyrin Dimers Induced by Temperature-Controlled Alcohol Ligation

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Unique temperature-dependent syn-anti conformational switching in bis- and monozinc ethane-bridged porphyrin dimers takes place in nonpolar solvents containing a small amount of alcohol (1–5%). These dimers adopt a syn conformation at any studied temperatures in the absence of alcohol added, while, in the presence of alcohol, a decrease in temperature from 310 to 183 K results in the gradual shift of the conformational equilibrium toward the anti conformer. Apparently the mechanism of this unprecedented phenomenon is based on the enhanced alcohol ligation to zinc porphyrins at low temperature which is capable of destroying the strong π – π interporphyrin interactions. This process is monitored by variable temperature (VT) UV–vis and VT ^1H NMR spectral methods and the corresponding thermodynamic parameters are evaluated using a van't Hoff type analysis. Strong exciton coupling between the B transitions of the anti dimers are observed at low temperatures.

Introduction

Environmentally induced conformational changes of natural enzymatic and photosynthetic systems that contain porphyrinoid prosthetic groups or chromophores play a crucial role in life processes. In addition, these conformational variations offer an attractive, simple mechanism for modulating a wide range of physical and chemical properties of porphyrin derivatives, both in vitro and in vivo.¹ Furthermore, porphyrin or porphyrin-driven conformational switching can also serve as a possible basis for various molecular electronic devices.² Such conformational effects can be induced by synthetic manipulations, axial ligation, hydrogen bonding, and through the variation of external physicochemical factors such as temperature, pH, concentration, etc.

Particularly, interporphyrin aggregation–disaggregation behavior upon axial coordination can be effectively employed to control chromophore spectral properties. Zinc porphyrins are acknowledged to be best suited to this purpose. Therefore, these processes were intensively studied using various systems of monomeric³ and dimeric⁴ zinc porphyrins with strong amino-containing ligands. However binding of relatively weak hydroxyl-containing ligands with zinc complexes have not been adequately investigated. There are a few reports⁵ on monomeric zinc porphyrin coordination with weak external ligands, but their binding with dimeric porphyrins and influence on conformational stability and interporphyrin interactions have not been studied so far. Herein, we report the first observation of alcohol ligand-induced syn-anti conformational switching of bis-zinc and zinc-free base ethane-bridged porphyrin dimers (**1** and **2**)^{6a,b} (Scheme 1) via temperature control.

Experimental Section

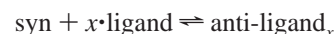
Materials. Dimers **1** and **2** were synthesized according to

the established procedure.^{6a,b} The solvents of an appropriate grade for spectroscopic measurements were purchased from either Wako Chemicals Co. or Aldrich Chemical Co. and were used as received.

Measurements. UV–vis spectra were recorded on a JASCO V-560 spectrophotometer using an Oxford cryostat connected to an Oxford ITC 4 temperature controller. The cryostat was vacuumed overnight using a rotary diffusion pump before measurements were made. The sample was kept at the measurement temperature for 20 min before recording the spectrum.

^1H NMR spectra were recorded at 400 MHz on a JEOL JNM-EX 400 spectrometer. Chemical shifts were referenced to the residual proton resonance in CDCl_3 (δ 7.25 ppm).

Definition of the Thermodynamic Parameters, ΔH° and ΔS° , Using a van't Hoff Type Analysis. The equilibrium constants for the ligation-induced conformational changes at each temperature



were obtained from the equation

$$K = [\text{anti-ligand}_x]/([\text{syn}] \cdot [\text{ligand}]^x)$$

where $x = 1$ for dimer **2**, and $x = 2$ for dimer **1**. ΔH° and ΔS° were then obtained from the following equation:

$$P_{\text{obs}} = (1 - \alpha)P_{\text{syn}} + \alpha P_{\text{anti-ligand}_x}$$

where P_{obs} , P_{syn} , and $P_{\text{anti-ligand}_x}$ are the chemical shifts or optical densities (monitored at the wavelength corresponding to the B_{\parallel} transitions of the anti species) of the observed syn and anti-

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SCHEME 1: Ligand- and Temperature-Induced Conformational Changes in Dimers 1 and 2

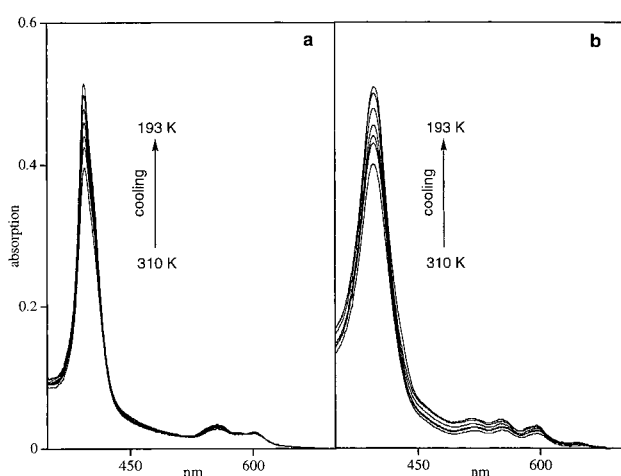
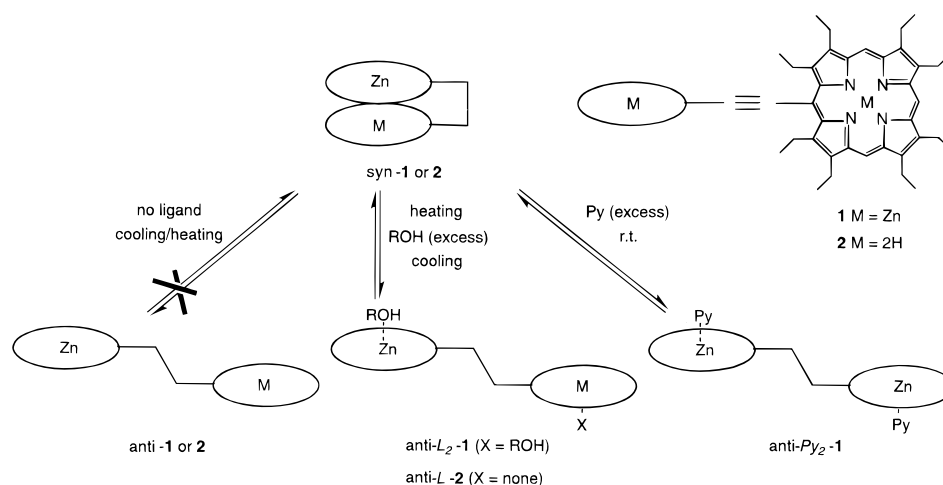


Figure 1. Absorption spectra of dimers **1** (a) and **2** (b) in dehydrated *n*-hexane upon cooling from 310 to 193 K.

ligand_x species, respectively, and α is the molar fraction of $P_{\text{anti-ligand}_x}$ species ($\alpha = [\text{anti-ligand}_x]/([\text{syn}] + [\text{anti-ligand}_x])$).

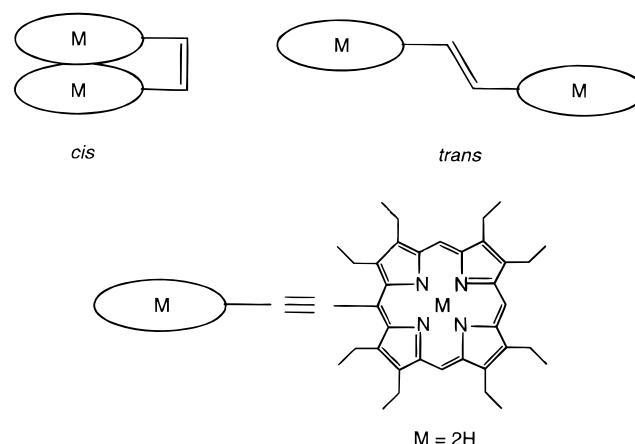
Since $K = e^{-\Delta H^\circ/RT} e^{\Delta S^\circ/R}$, $P_{\text{obs}} = \{1 - [Z/(Z + 1)]\}P_{\text{syn}} + [Z/(Z + 1)]P_{\text{anti-ligand}_x}$, where $Z = e^{-\Delta H^\circ/RT} e^{\Delta S^\circ/R} [\text{ligand}]^x$. P_{obs} is thus represented as a function which contains T as an independent variable and P_{syn} , $P_{\text{anti-ligand}_x}$, ΔH° , and ΔS° as optimized parameters.

Results and Discussion

Syn Conformation. Recently it was shown⁶ that dimers **1** and **2** adopt a syn conformation at room temperature in a variety of solvents, and this conformation does not break apart, even upon heating to 110 °C.^{6d} The spectral characteristics of the syn isomer are typical of the porphyrin's face-to-face orientation.^{6c,7} These include a pronounced blue shift of the Soret band and small red shifts of the Q-bands (Figure 1a,b, see 310 K spectra) due to excitonic interactions between the porphyrin chromophores which have been brought into cofacial proximity. In the ¹H NMR spectrum, this state is characterized by a considerable upfield shift observed for the 10,20-*meso* protons (δ 8.32 ppm for **1** and δ 8.81, 8.86 ppm for **2** at 333 K), caused by the ring current effect of the neighboring porphyrin macrocycle. The appearance of eight nonequivalent signals of the CH₂CH₃ protons is observed (Figures 2 and 3, see 333 K spectra), which are, presumably, partially overlapped doublets of quartets derived from the nonequivalence of the two methylene protons due to the rigidity of the syn form. This

spectral pattern closely resembles that of the "face-to-face" cis-ethylene-bridged dimer^{6c,7a} (Chart 1), suggesting the existence

CHART 1



of strong intramolecular π - π interactions between the porphyrin macrocycles in dimers **1** and **2**. Indeed, a similar phenomenon was observed in a bis-zinc complex of doubly strapped dimer⁴ by Sanders. The energy of the zinc porphyrin π - π interaction in this system was estimated as high as -11.5 ± 2.4 kcal mol⁻¹.^{4a} The presence of zinc porphyrin is obviously an important factor in holding porphyrins together, since other ethane-bridged porphyrin dimers that do not contain zinc ions are found only in the anti form in various solvents.⁶ Also the early Abraham's and Smith's works clearly demonstrated that the monomeric zinc porphyrins tend to form face-to-face aggregates through π - π interactions.³

Absorption Spectral Changes. Variable temperature (VT) UV-vis experiments revealed dramatic changes in the initial spectral patterns of dimers **1** and **2** in alcohol-containing solutions as the temperature decreased (see Figures 4 and 5), while no such changes were observed in alcohol-free solutions, except for the overall intensity increase due to the solution's volume decrease at lower temperatures (Figure 1a,b). The Soret band of the syn conformer for dimer **1** is observed at 397 nm in a mixture of *n*-hexane:EtOH (24:1) at room temperature. The intensity of this band gradually decreases as the temperature is lowered, and a bathochromically shifted, split Soret band appears at 420 nm. The positions of the Q_{X00} and Q_{X01} bands remain essentially unchanged (small blue shifts of 30–65 cm⁻¹ and an increase of the Q_{X01} transition are observed) upon lowering

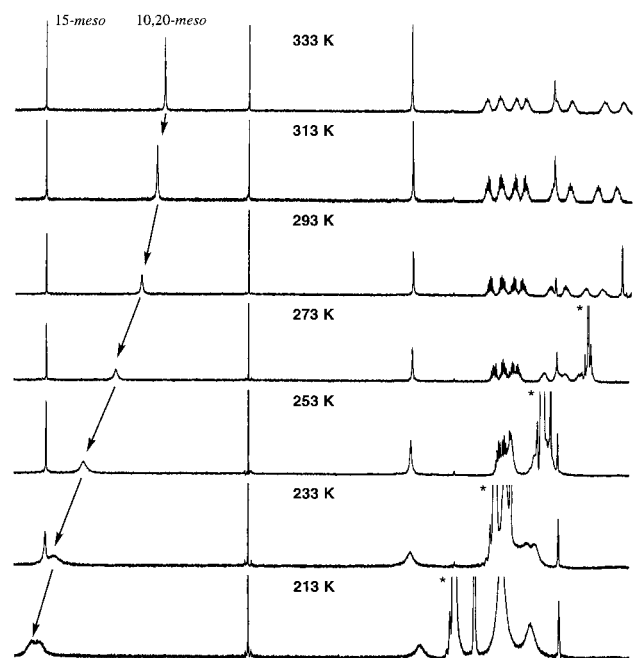


Figure 2. Temperature-induced changes in the ^1H NMR spectrum of dimer **1** in $\text{CDCl}_3:\text{CD}_3\text{OD}$ (24:1) upon cooling from 333 to 213 K. The residual MeOH and H_2O peaks are marked, *. At 213 K these residual peaks are splitted into two signals at ca. 4.4 (MeOH) and 4.7 ppm (H_2O) because of a slow exchange process.

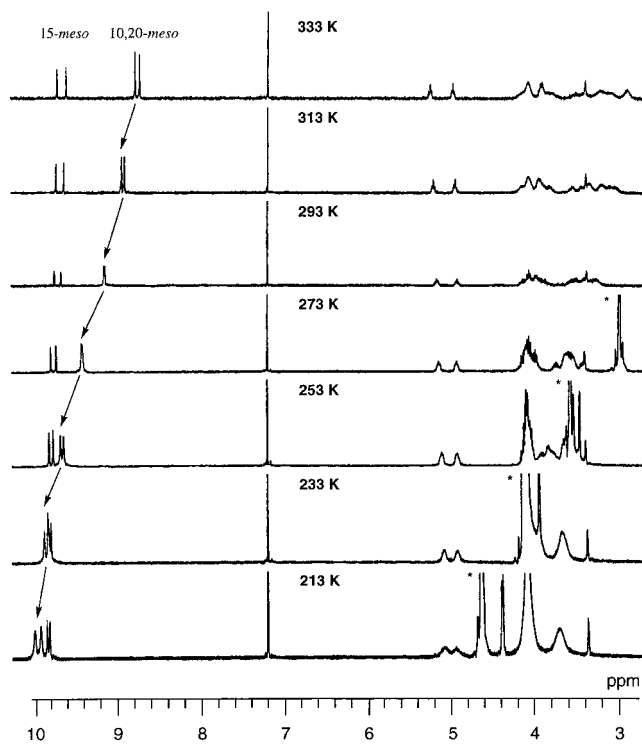


Figure 3. Temperature-induced changes in the ^1H NMR spectrum of dimer **2** in $\text{CDCl}_3:\text{CD}_3\text{OD}$ (24:1) upon cooling from 333 to 213 K. The residual MeOH and H_2O peaks are marked, *. At 213 K these residual peaks are splitted into two signals at ca. 4.4 (MeOH) and 4.7 ppm (H_2O) because of a slow exchange process.

the temperature from 310 to 183 K (Figure 4). The exciton splitting energy (ΔE) is evaluated as 821 cm^{-1} , and the final absorption spectrum of this system at 183 K is very similar to the spectrum of dimer **1** in the presence of pyridine (Py) added as an external ligand (Figure 6, see 310 K spectrum). This bis-Py adduct of dimer **1** is also characterized by a split and red-

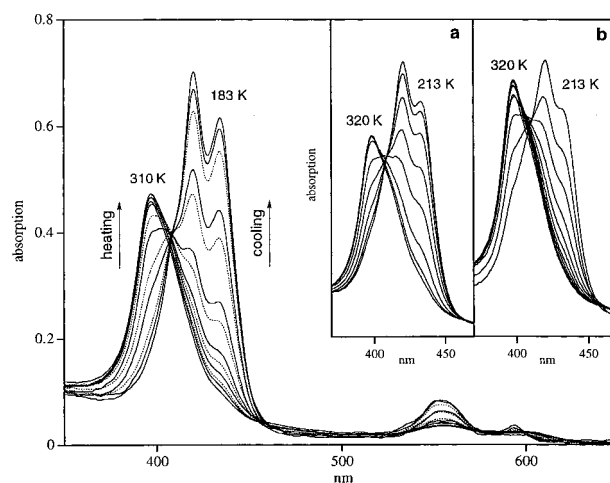


Figure 4. Temperature-induced changes in the UV-vis spectrum of dimer **1** in $n\text{-hexane}:\text{EtOH}$ (24:1) upon cooling from 310 to 183 K (solid lines), and upon heating from 183 to 283 K (dotted lines). Inset: Temperature-induced changes in the Soret region of UV-vis spectrum of dimer **1** in $\text{CHCl}_3:\text{EtOH}$ (24:1) (a) and (99:1) (b) upon cooling from 320 to 213 K.

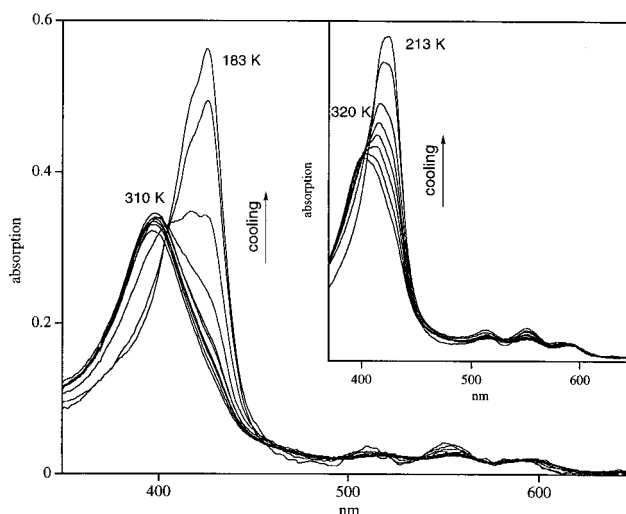


Figure 5. Temperature-induced changes in the UV-vis spectrum of dimer **2** in $n\text{-hexane}:\text{EtOH}$ (24:1) upon cooling from 310 to 183 K. Inset: Temperature-induced changes in the UV-vis spectrum of dimer **2** in $\text{CHCl}_3:\text{EtOH}$ (99:1) upon cooling from 320 to 213 K.

shifted Soret band at 424 nm, $\Delta E = 806\text{ cm}^{-1}$. Recently, it was reported that this adduct adopts an anti conformation.^{6c,8} Also it should be noted that the initial spectral pattern of the bis-Py adduct of dimer **1** is essentially invariant within the investigated temperature range from 310 to 183 K (Figure 6) with the only overall absorption intensity increase, as is the case of dimers **1** and **2** in $n\text{-hexane}$.

Similar spectral changes were observed for dimer **1** in other solvent mixtures—chloroform: EtOH (24:1) and (99:1)—upon lowering the temperature from 320 to 213 K (Figure 4, inset, a,b). The ΔE values were 715 and 661 cm^{-1} , respectively. In the case of dimer **2** in $n\text{-hexane}:\text{EtOH}$ (24:1) and in chloroform: EtOH (99:1) the bathochromic shift (1265 cm^{-1}) is almost the same as that of dimer **1**, whereas the excitonic splitting energy is reduced by a factor of approximately two to be 450 and 394 cm^{-1} , respectively, (Figure 5). Analogous but less pronounced effects of larger excitonic splittings for bis-zinc complexes in comparison to those for corresponding monozinc or/and bis-free bases have been found for different porphyrin dimers.⁹

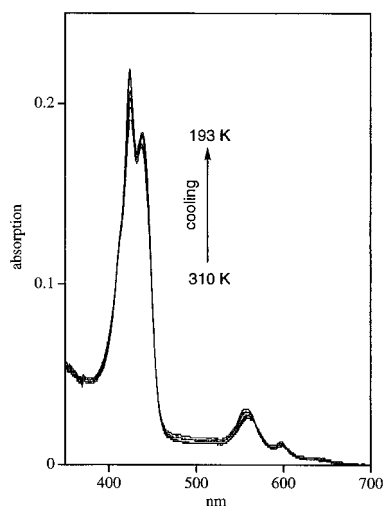


Figure 6. Absorption spectra of dimers **1** in *n*-hexane:Py (250:1) upon cooling from 310 to 193 K.

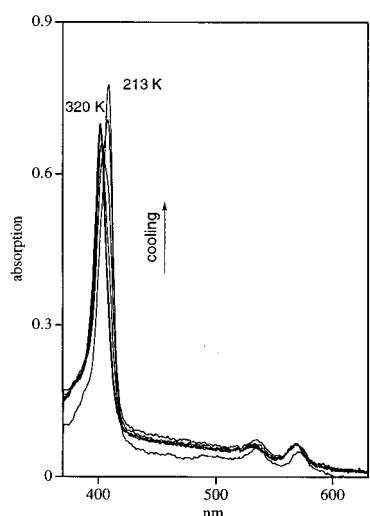


Figure 7. Temperature-induced changes in the UV-vis spectrum of zinc octaethylporphyrin in CHCl_3 :EtOH (99:1) upon cooling from 320 to 213 K.

An important point is that the spectral behavior of monomeric zinc octaethylporphyrin in a mixture of chloroform:EtOH (99:1) upon lowering the temperature from 320 to 213 K (Figure 7) differed drastically from that of dimers **1** and **2**. The bathochromic shift is substantially smaller (426 cm^{-1} only) and there is no Soret band split in the spectrum of this system at 213 K. This spectral pattern is the characteristic feature of axially ligated monomeric zinc porphyrins.¹⁰

Our observations are in good agreement with exciton coupling theory,¹¹ indicating the predominant formation of a “head-to-tail” oriented B transition at lower temperatures. Indeed, for porphyrin dimers or aggregates in a linear arrangement, the two degenerated $B_{||}$ and B_{\perp} transitions (which are in parallel or perpendicular orientation to the axis connecting two or more macrocycles) must couple differently to produce splitting in the excited state. Transitions are only allowed to the highest level of the two B_{\perp} states and to the lowest level of the two $B_{||}$ states. This results in a split of the Soret band into a blue-shifted B_{\perp} component and a red-shifted $B_{||}$ component, and such a phenomenon is often observed for linear porphyrin dimers and trimers linked through phenylene groups,^{8,9,12} triple,¹³ double,¹⁴ single,^{6c,8,15} hydrogen,¹⁶ or coordination¹⁷ bonds, as well as for porphyrin J-aggregates.¹⁸ The excitonic splitting for the above-mentioned systems range from 3812 to 449 cm^{-1} , with the

largest values (3800 – 2000 cm^{-1}) obtained for the systems with triple bonds and for J-aggregates, while the average splitting for the other systems varies from 1000 to 450 cm^{-1} . In the case of the bridged dimers in which triple bonds are directly attached at *meso*-carbons, an inter-porphyrin conjugation can contribute greatly to the large Soret band splitting.^{13b} The smaller splitting may be associated with reduced rotational freedom and more spatial ordering of the porphyrin moieties.

In general, the relative orientation of $B_{||}$ dipoles is unaffected by the torsional angle between the two porphyrin planes, while the B_{\perp} coupling is strongly dependent on mutual porphyrin orientation. In the ideal case, a coplanar and symmetrical porphyrin dimer with a linear orientation gives a well-resolved pair of peaks with nearly equal intensities. Conversely, the B_{\perp} component of a torsionally free linear dimer or unsymmetrical dimer may be considerably diminished, broadened, and/or multiply split. The former case can be seen clearly for fully metalated (Zn, Ni, Pd) porphyrin dimers,^{6c,8,9b,c,12b,c,14b,16,18a} connected by a phenyl group or by double or single bonds, while the latter case is observed for unsymmetrically metalated dimers and trimers,^{9b,12b} fully metalated dimers linked by triple bonds,^{13a,c,f,g} in partially overlapped multiporphyrin systems of J-aggregates,^{18b–e} as well as in Knapp’s self-assembled porphyrin hexamer.^{17a} Since the B_{\perp} and $B_{||}$ transitions of dimer **1** at 183 K are well-resolved and their intensities are nearly equal (the B_{\perp} : $B_{||}$ ratio is 1.14:1), it is reasonable to conclude that the two porphyrin planes in dimer **1** adopt a linear coplanar conformation. This is also true for dimer **2**, although the smaller ΔE values resulted in a poorer resolution of the B_{\perp} and $B_{||}$ transitions.

Thus, decreasing the temperature resulted in gradual conformational change of the dimers **1** and **2** in alcohol-containing solutions from the folded syn form at higher temperatures to the extended anti form at lower temperatures (Scheme 1). The driving force for this process must be an enhanced binding of the alcohol to the zinc porphyrin at lower temperature, since no conformational changes can be observed for dimers **1** and **2** in alcohol-free solutions, where the dimers adopt the syn conformation over the whole temperature range, or for Py-containing solutions, where the dimers adopt the anti conformation, even at higher temperatures (Figure 6). It is noteworthy that these changes are fully reversible, and the initial syn form is recovered upon heating from 183 to 310 K (Figure 4). To the best of our knowledge there is only one example of a temperature-dependent self-arrangement of porphyrins into a linear edge-to-edge array, but it operates through a different process based on intermolecular hydrogen bonding.¹⁶

¹H NMR Spectral Changes. The results of a VT ¹H NMR study of the conformational switching behavior phenomenon are in good agreement with VT UV-vis spectral data. Decreasing the temperature from 333 to 213 K leads to a significant downfield shift ($\Delta\delta$) of the 10,20-*meso* protons belonging to dimers **1** and **2** (CDCl_3 : CD_3OD ; 24:1), $\Delta\delta = -1.64$ and -1.22 ppm, correspondingly; while the position of the 15-*meso* protons is almost unchanged (Figures 2 and 3). These spectral features are reasonable, since the 10,20-*meso* protons are strongly shielded by a ring current effect arising from the neighboring porphyrin ring, and thus are most affected by syn-anti conformational changes in dimers **1** and **2**. Gradual changes of the spectral pattern in the region of CH_2CH_3 protons ($\delta = 4.26$ – 2.38 ppm at 333 K) are also observed. The eight well-resolved signals gradually transform into two broad multiplets that are located in a more downfield region ($\delta = 4.24$ – 3.44 ppm at 213 K). The spectra of the anti conformers of dimers **1** and **2**,

TABLE 1: Thermodynamic Parameters for the Syn-Anti Conformational Changes in Ethane-Bridged Dimers

| parameter | dimer 1 | | | | dimer 2 | | |
|---|---|--|--|--|--|--|--|
| | <i>n</i> -hexane: EtOH 24:1 ^a | CHCl ₃ :EtOH 24:1 ^a | CHCl ₃ :EtOH 99:1 ^a | CDCl ₃ :CD ₃ OD 24:1 ^b | <i>n</i> -hexane:EtOH 24:1 ^a | CHCl ₃ :EtOH 99:1 ^a | CDCl ₃ :CD ₃ OD 24:1 ^b |
| $\epsilon_{\text{anti}}/10^5$ (M ⁻¹ cm ⁻¹) or (435) | 2.51 (435) | 2.21 (433) | 2.28 (432) | | 2.91 (426) | 3.44 (425) | |
| δ_{anti}^d (ppm) | | | | 10.08 | | | 10.11 |
| ΔH° (kcal mol ⁻¹) | -6.4 ± 0.4 | -9.0 ± 0.7 | -7.3 ± 0.3 | -5.7 ± 0.2 | -4.7 ± 0.2 | -6.1 ± 0.4 | -4.9 ± 0.1 |
| ΔS° (cal mol ⁻¹ K ⁻¹) | -27.7 ± 1.7 | -34.9 ± 2.8 | -25.2 ± 1.2 | -21.4 ± 0.7 | -22.1 ± 0.8 | -20.3 ± 1.6 | -16.6 ± 0.4 |
| ΔG° at 303 K (kcal mol ⁻¹) | 2.0 | 1.6 | 0.3 | 0.8 | 2.0 | 0.1 | 0.1 |
| ΔG° at 213 K (kcal mol ⁻¹) | -0.5 | -1.6 | -1.9 | -1.1 | 0.0 | -1.7 | -1.4 |

^a Monitored by UV-vis. ^b Monitored by ¹H NMR. ^c Calculated molar absorption coefficient of the anti isomer at the corresponding B_{II} transition wavelength (in nm) shown in parentheses (see Experimental Section). ^d Calculated chemical shift for the 10,20-*meso* protons of the anti isomer (see text and Experimental Section). ^e Obtained from a van't Hoff type analysis (see Experimental Section). Quoted uncertainties represent two standard deviations, as given by the fitting program.

recorded at 213 K (Figures 2 and 3), are very similar to those of the previously reported *trans*-ethylene-bridged dimer^{6c,7a} (Chart 1) and the anti-conformer of the nonmetalated ethane-bridged dimer.^{6a,c,d} These results indicate that the syn-anti conformational changes in dimers 1 and 2 take place at concentrations ranging from 10⁻⁶ M (UV-vis) to 10⁻³ M (¹H NMR).

Theoretical Fitting. The gradual changes in the UV-vis and ¹H NMR spectra with respect to a change in temperature fit well to a set of theoretical equations for the syn-anti conformational equilibrium (see Experimental Section and Figure 8, parts a and b) using the nonlinear least-squares optimization. We have used these equations to estimate the molar absorption coefficients (ϵ_{anti}) of the anti conformer in various solutions as well as the chemical shift (δ_{anti}) of the 10,20-*meso* protons (Table 1). Interestingly, the $\epsilon_{\text{anti}}(\text{B}_{\text{II}}):\epsilon_{\text{syn}}$ ^{6a} ratio of corresponding Soret bands (1.43:1) was observed to be almost the same as the $\epsilon_{\text{trans}}/\epsilon_{\text{cis}}$ ^{7a} ratio (1.46:1). Furthermore, the calculated δ_{anti} values for the 10,20-*meso* protons (10.08 ppm for 1 and 10.11 ppm for the free base part²⁰ of 2) of the anti forms (Table 1) are equal to the corresponding δ_{trans} value (10.12 ppm).^{19a} This is additional evidence for the spatial similarity between the folded and linear dimer pairs; these being the syn conformer/cis isomer pair, and the anti conformer/trans isomer pair.

Van't Hoff type analyses of the ligand-assisted syn-anti equilibrium constants at various temperatures (see Experimental Section) gave an excellent fit (Figure 8, parts a and b) that allowed us to determine the corresponding thermodynamic parameters for these processes (Table 1). Both the ΔH° and ΔS° values became less negative as the solvent polarity decreases (from UV-vis data) and as the dimer concentration increases (from ¹H NMR data). Although a direct comparison of the dimeric systems 1 and 2 is not completely correct since the interactions between two porphyrin rings in these dimers are apparently different, the ΔH° values for dimer 1 are more exothermic than those for dimer 2. This difference arises because the equilibrium process for dimer 1 includes an additional ligation step. Conversely, ΔS° changes are always less favorable for dimer 1 than for dimer 2 in the same media. The calculated ΔG° values are positive for all the systems at 303 K (Table 1) making the syn-anti conformational transformations thermodynamically unfavorable. On the other hand, decreasing the temperature to 213 K leads to a significant decrease of a total free energy change resulting in the negative ΔG° values and shifting the equilibrium to the anti form.

Conclusion

In conclusion, the importance of temperature was clearly demonstrated for the first time in the ligand assisted syn-anti

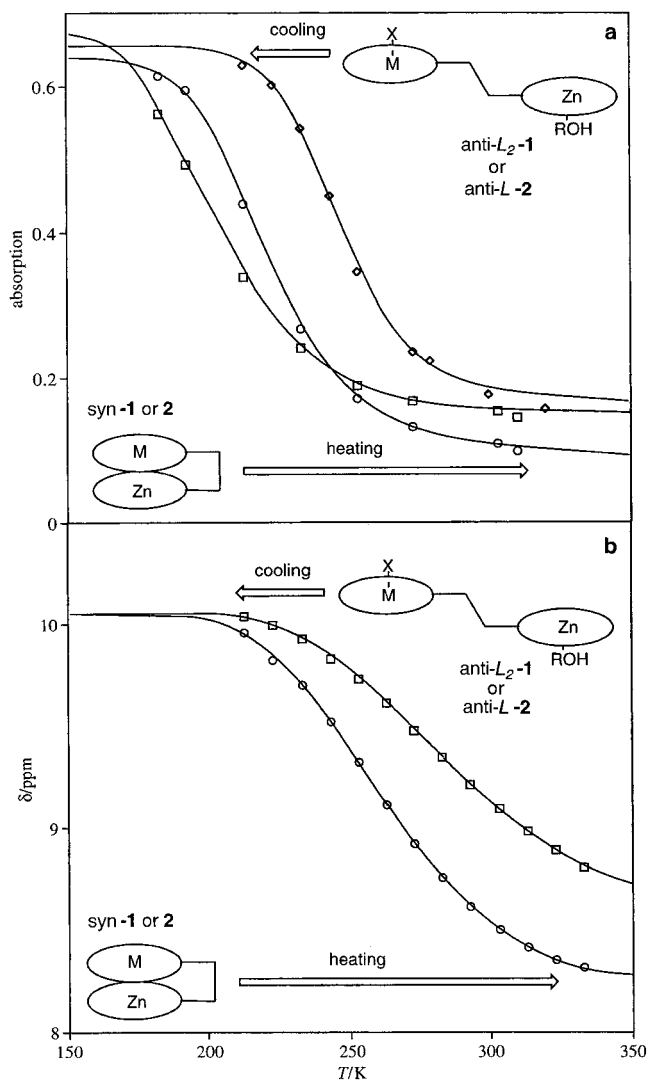


Figure 8. Temperature dependence of (a) B_{II} absorption intensity upon cooling for dimer 1 in *n*-hexane:EtOH (24:1) (circles) and in CHCl₃:EtOH (24:1) (rhombus) and for dimer 2 in *n*-hexane:EtOH (24:1) (squares), (b) 10,20-*meso* proton's position upon cooling for dimers 1 (circles) and 2 (squares) in CDCl₃:CD₃OD (24:1). The solid lines represent the best theoretical fit of the thermodynamic syn-anti equilibrium for this system (see Experimental Section).

conformational switching of Zn-containing porphyrin dimers. Since temperature-induced syn-anti switching can be detected easily at 435 nm by monitoring formation of the anti species it may serve as a concept for a temperature-controlled reversible optically readable molecular device. Further steady-state and

time-resolved spectroscopic measurements that consider the photophysical and energy-transfer properties of the syn and anti conformations of dimers **1** and **2** are currently in progress, and these will be the subject of future reports from our group.

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