Pergamon

Tetrahedron Letters 40 (1999) 5051–5054

TETRAHEDRON
LETTERS

Temperature Controlled *Syn-Anti* Conformational Switching in Zinc Containing Porphyrin Dimers via Ligand Assistance

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Received 23 March 1999; revised 26 April 1999; accepted 30 April 1999

Abstract. Unique temperature dependent *syn-anti* conformational changes in bis- and monozinc ethane-bridged porphyrin dimers take place in alcohol containing solvents; these dimers adopt a *syn* conformation at room temperature, while a decrease in temperature results in the gradual shift of the conformational equilibrium towards the *anti* conformer. © 1999 Elsevier Science Ltd. All rights reserved.

Environmentally induced conformational changes of natural enzymatic and photosynthetic systems that contain porphyrinoid prosthetic groups or chromophores play a crucial role in natural 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 and/or by axial ligation, hydrogen binding, and through the application of external physico-chemical factors such as temperature, pH, concentration, etc. Herein, we report the first observation of temperature-induced and ligand assisted *syn-anti* conformational changes for bis-zinc and zinc-free base ethane-bridged porphyrin dimers (**1** and **2**).[3a,b]

Recently it was shown that dimers **1** and **2** adopt a *syn* conformation at room temperature in a variety of solvents,[3] and this conformation does not break apart, even upon heating up to 110 °C.[3d] The spectral characteristics of the *syn* isomer are typical of the porphyrin's face-to-face orientation.[3c,4] 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. Also the aggregation behavior of monomeric[5] and doubly strapped dimeric[6] zinc porphyrins via π-π interaction mechanism has been reported.

Variable temperature (VT) UV-vis and VT ^{1}H NMR experiments revealed dramatic changes in the initial spectral patterns of dimers **1** and **2** in alcohol containing solutions as the temperature decreased (see Figures 1 and 2), while no such changes were observed in alcohol free solutions (Figure 1, Inset, solid line). Thus, the Soret band at 397 nm which is assigned to the corresponding *syn* conformer[3] and observed for dimer **1** in a mixture of *n*-hexane:EtOH (24:1) at room temperature gradually decreases. Instead, a new, bathochromically shifted, split Soret band appeared at 420 nm, while the positions of the Q_{X00} and Q_{X01} bands remained

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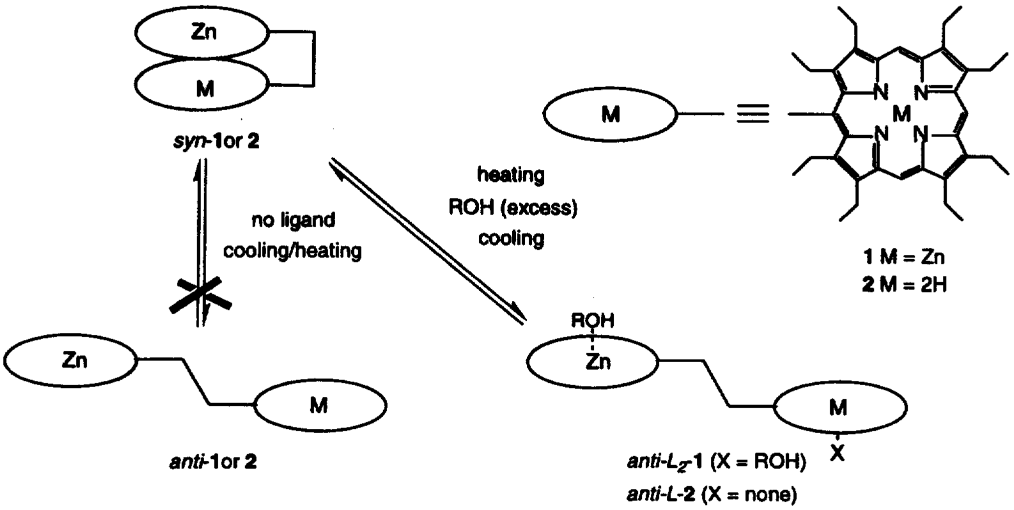
PII: S0040-4039(99)00931-4



Scheme 1. Ligand- and temperature-induced conformational changes in dimer **1** and **2**.

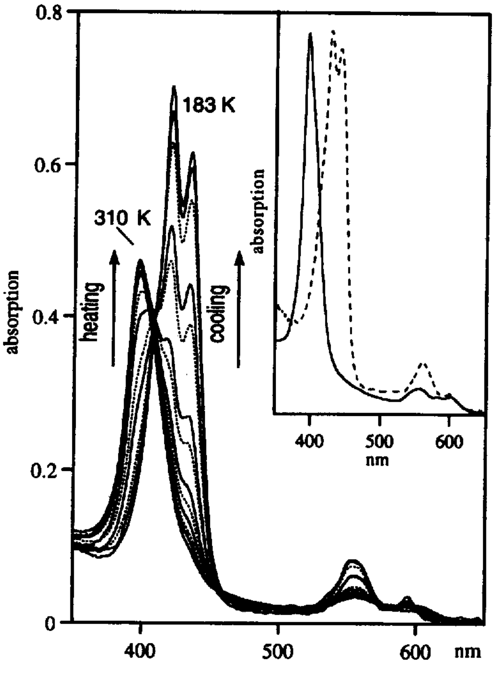


Fig. 1. Temperature-induced changes in the UV-vis spectrum of dimer **1** in n-hexane:EtOH (24:1) upon cooling from 310 K to 183 K (solid lines), and upon heating from 183 K to 283 K (dotted lines). Inset: The UV-vis spectra of dimer **1** in n-hexane at 183 K (solid line) and in n-hexane:Py (250:1) at 310 K (dashed line).

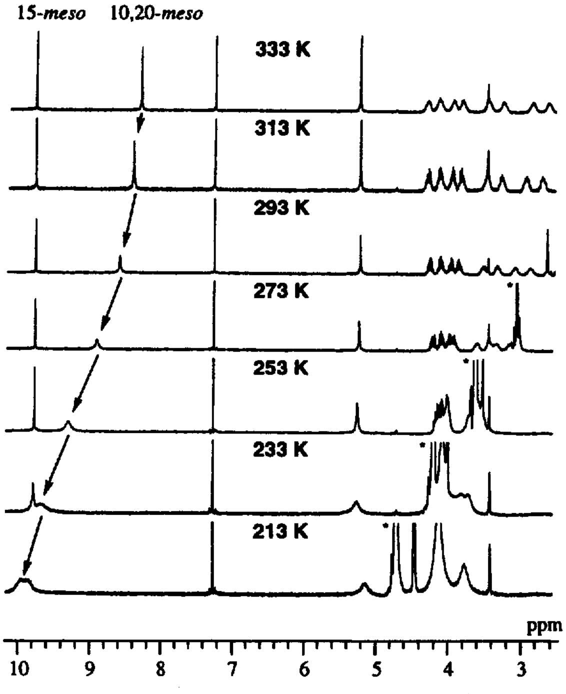


Fig. 2. Temperature-induced changes in the ^{1}H NMR spectrum of dimer **1** in $CDCl_3$:CD_3OD (24:1). The residual MeOH peak is marked, *.

essentially unchanged (small blue shifts of 1 – 2 nm and an increase of the Q_{X01} transition were observed) upon lowering the temperature from 310 K to 183 K (Figure 1). The exciton splitting energy (ΔE) was 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 1, Inset, dashed line). This bis-Py adduct of dimer **1** is also characterized by a split and red-shifted Soret band at 424 nm, ΔE = 806 cm^{-1}. Recently, it was reported that this adduct adopts an *anti* conformation.[3c,7]

Our observations are in good agreement with exciton coupling theory,[8] indicating the predominant formation of a "head-to-tail" oriented B transition at lower temperatures. Since the $B_\perp$ and $B_\parallel$ transitions of dimer **1** at 183 K are well-resolved, and their intensities are nearly equal (the $B_\perp$:$B_\parallel$ ratio is 1.14:1) it is reasonable to conclude that the two porphyrin planes in dimer **1** adopt a linear coplanar conformation. This phenomenon is often observed for linear porphyrin dimers and trimers linked through phenyl groups,[7,9] triple,[10] double,[11] single,[3c,7,12] hydrogen[13] or coordination[14] bonds as well as for porphyrin J-aggregates.[15]

Thus, decreasing the temperature resulted in gradual conformational change of the dimer **1** 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 dimer **1** in alcohol free solutions, where the dimer adopts the *syn* conformation over the whole temperature range, or for Py containing solutions, where the dimer adopts the *anti* conformation, even at higher temperatures (Figure 1, Inset). It is noteworthy that these changes are fully reversible, and the initial *syn* form is recovered upon heating from 183 K to 310 K (Figure 1). 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.[13]

The results of a VT ^{1}H NMR study of the conformational switching behavior phenomenon are in good agreement with VT UV-vis spectral data. Decreasing the temperature from 333 K to 213 K leads to a significant downfield shift of the 10,20-*meso* protons ($\Delta\delta$: -1.64 ppm) belonging to dimer **1** ($CDCl_3$:CD_3OD; 24:1), while the position of the 15-*meso* protons is almost unchanged (Figure 2). 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 dimer **1**. Gradual changes of the spectral pattern in the region of CH_2CH_3 protons (δ = 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 (δ = 4.24 – 3.44 ppm at 213 K). The spectrum of the *anti* conformer of dimer **1**, recorded at 213 K (Figure 2), is very similar to that of the previously reported *trans*-ethylene bridged dimer[3c,4a] and the *anti*-conformer of the non metallated ethane bridged dimer.[3a,c,d] These results indicate that the *syn-anti* conformational changes in dimer **1** take place at concentrations ranging from 10^{-6} M (UV-vis) to 10^{-3} M (^{1}H NMR).

This unique phenomenon was found to be general for dimers **1** and **2**, which were studied in the different alcohol containing solutions. The gradual changes in the UV-vis and ^{1}H NMR spectra with respect to a change in temperature were analyzed by Van't Hoff type method for the *syn-anti* conformational equilibrium 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.[16] Interestingly, the $\varepsilon_{anti}(B_\perp)$:$\varepsilon_{syn}$[3a] ratio of corresponding Soret bands (1.43:1) was observed to be almost the same as the ε_{trans}[17]/ε_{cis}[4a] ratio (1.46:1). Furthermore, the δ_{anti} values for the 10,20-*meso* protons (10.08 ppm for **1** and 10.11 ppm for **2**) of the *anti* forms are equal to the corresponding δ_{trans} value (10.12 ppm).[16] 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.

In conclusion, the importance of temperature was clearly demonstrated for the first time in the ligand assisted *syn-anti* conformational changes of Zn-contained porphyrin dimers. Since temperature-induced *syn-anti* switching can be detected easily at 435 nm by monitoring formation of the *anti* specie 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.

We would like to thank Dr. S. Everitt for assistance in the preparation of this manuscript.

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16. Calculated data: for dimer **1**: $\varepsilon_{anti}\cdot 10^5/M^{-1}cm^{-1}$ at the corresponding B_{II} transition wavelength/nm shown in parentheses 2.51 (435) in *n*-hexane:EtOH (24:1), 2.21 (433) in $CHCl_3$:EtOH (24:1), 2.28 (432) in $CHCl_3$:EtOH (99:1); δ_{anti} 10.08 (10,20-*meso* H) in $CDCl_3$:CD_3OD (24:1) and for dimer **2**: $\varepsilon_{anti}\cdot 10^5/M^{-1}cm^{-1}$ 2.91 (426) in *n*-hexane:EtOH (24:1), 3.44 (425) in $CHCl_3$:EtOH (99:1); δ_{anti} 10.11 (10,20-*meso* H) in $CDCl_3$:CD_3OD (24:1). The thermodynamic parameters (ΔH, ΔS and ΔG of this equilibrium will be reported in the forthcoming article, Borovkov, V. V.; Lintuluoto, J. M.; Inoue, Y. *J. Phys. Chem.*, **1999**, in press.
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