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Supramolecular Chemistry; Dimerisation of Mono Zinc N,N'-bis[4'-(*meso*-triphenylporphyrinyl)benzyl]-4,13-diaza-18-crown-6.

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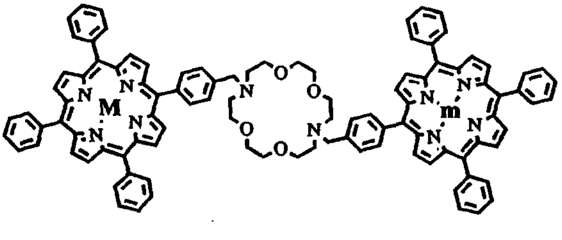
Abstract: *Observations of a well ordered ensemble of four porphyrins, two of which contain zinc, have been made. The ensemble is formed by dimerisation of mono zinc bisporphyrins and held together by twofold intermolecular nitrogen to zinc coordination. The enthalpy and entropy of formation of the dimer have been determined. A large entropy decrease was found consistent with the formation of a highly ordered dimer.*

Synthesis and studies of model compounds containing porphyrins held together by covalent bonds at different distances and orientations have and will contribute to the basic understanding of energy and electron transfer processes of fundamental biochemical importance. As an alternative to porphyrins linked together covalently, supramolecular chemistry can be used to form large structures kept together by complexation. A recent elegant example has been published by Harriman, Sauvage and coworkers[1].

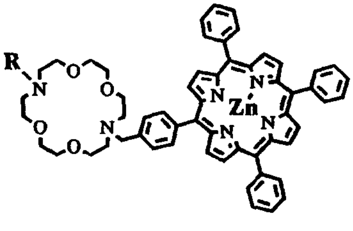
The central metal atom in metal porphyrins can coordinate a variety of ligands. If the ligand is covalently bound to the porphyrin a reversible intramolecular self-ordering[2] or alternatively formation of dimers, oligomers and polymers is possible under proper conditions[3]. During the course of our study of energy transfer between different porphyrins linked to each other *via* the nitrogen atoms in 4,13-diaza 18-crown-6, compound *1a*, we have observed the formation of an interesting dimer at relatively high concentrations at room temperature (NMR-samples) as well as in dilute solutions at low temperatures (UV-VIS-samples).

The dimer is held together by nitrogen to zinc coordination at two sites to form a complex with four porphyrin units, two of which contain zinc, dimer *2*. This type of reversible dimerisation is a simple method to form symmetric but complex structures in which porphyrins are held together in a defined way. By proper design of the bisporhyrins it should be possible to achive complexes with well defined three dimensional arrangements of four porphyrins, resembling parts of natural occuring pigment-protein complexes and mimicking their function in energy and electron transfer reactions.

The mono zinc N,N'-bis[4'-(*meso*-triphenylporphyrinyl)benzyl]-4,13-diaza-18-crown-6, *1a*, was pre-

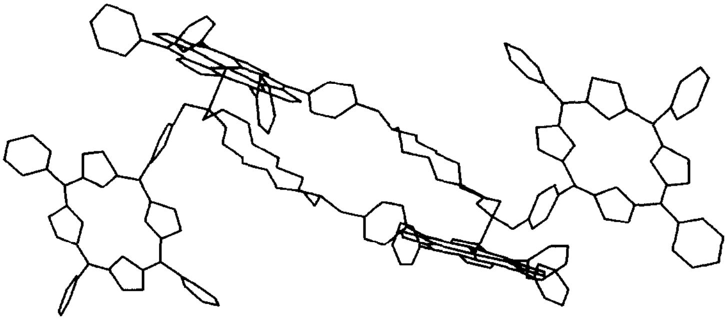


1a: **M = Zn, m = 2H,** *1b*: **M = m = 2H**
1c: **M = m = Zn.**



3a: **R = H,** *3b*: **R = $C_6H_5C(O)$.**

pared from 4,13-diaza-18-crown-6 and 5-(4'-bromomethylphenyl)-10,15,20-triphenylporphyrin to give the mono-N-substituted 4,13-diaza-18-crown-6. Further reaction with zinc 5-(4'-bromomethylphenyl)-10,15,20-triphenylporphyrin gave *1a* in an overall yield of 30%[4]. On excitation of the zinc porphyrin unit an energy transfer to the free base porphyrin unit occurs with a high efficiency, as observed by fluorescence spectroscopy[5]. The conformation of *1a* in solution is believed to be similar to its dibenzyl derivative[6] in agreement with NMR and UV-VIS data. Here, we report the dimerisation of *1a* in solution.



2: Dimer of 1a with a centre of inversion.

On cooling a UV-VIS-sample of *1a* (see Fig. 1), its absorption spectrum changed from that of the sum of the corresponding absorption spectra of zinc and free base porphyrin to that of the sum of nitrogen coordinated zinc porphyrin and unchanged free base porphyrin, indicative of dimerisation. The enthalpy and entropy of formation of the dimer was determined by assuming a fast and reversible reaction of *1a* to *2*. A large negative entropy was found (-54 cal $mol^{-1}K^{-1}$) and a reasonable enthalpy (-20 kcal mol^{-1}) compared to that of zinc *meso*-tetraphenylporphyrin-pyridin complex[7]. The large negative entropy of formation is consistent with the formation of a highly ordered dimer.

The dimerisation of *1a* causes broadening and chemical shift altering of the signals from the crown ether and benzyl protons and carbons in the NMR-spectra ($CDCl_3$-solution). In order to exclude π–π–interactions between the porphyrin rings as the driving force for dimerisation we studied complex formation between zinc *meso*-tetraphenylporphyrin and N,N'-dibenzyl-4,13-diaza-18-crown-6. The same broadening and upfield chemical shift of the proton signals from the crown ether was observed as for *1a* but now at much lower temperatures. Furthermore, the dimerisation is not observed if zinc is absent as in *1b* and clearly enhanced when both porphyrins contain zinc as in *1c*. However, according to UV-VIS-spectra only half of the zinc porphyrins are coordinated to nitrogen in the dimer of *1c*. On addition of pyridine to the samples the dimerisation is suppressed and replaced by coordination of pyridine to the zinc porphyrin.

On inspection of molecular models of *1a* it was found that coordination of the most distant nitrogen with respect to the zinc porphyrin would give good geometrical conditions for twofold coordination in the dimer. To make the nitrogen accessible to coordination geometrical restrictions would force the porphyrin unit attached to it to have the orientation shown in dimer 2. Having twofold coordination this orientation is only possible at the more distant nitrogen. Coordination to the nearest nitrogen would give not only a highly strained dimer, assuming twofold coordination, but would also lead to two strongly interacting zinc porphyrin units which is inconsistent with UV-VIS and NMR data. More probable, when coordination occurs to this nitrogen, is a dimer held together by only one nitrogen to zinc bond leaving the other zinc porphyrin in the dimer uncoordinated.

In order to confirm that coordination to the most distant nitrogen dominates we prepared and investigated the N-[4'-(zinc *meso*-triphenylporphyrinyl)benzyl]-4,13-diaza-18-crown-6, *3a* as well as the N-benzoyl-N'-

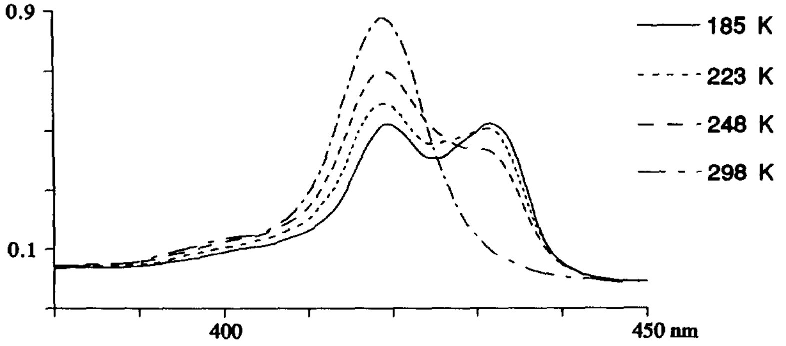


Fig. 1. UV-VIS spectra of compound 1a at different temperatures.

[4'-(zinc *meso*-triphenylporphyrinyl)benzyl]-4,13-diaza-18-crown-6, ***3b***. In NMR-samples (≈ 10^{-2} M) of ***3a*** dimerisation is almost complete at a temperature as high as 323 K, in ***3b*** complexation is much weaker and induce smaller proton and carbons chemical shifts in the crown ether units. Moreover, at higher temperatures the chemical shift of the benzylic protons in ***3a*** and ***3b*** is consistent with coordination of zinc to different nitrogens of the diaza crown ether in the two compounds. In ***3a*** the zinc preferably coordinates to the most distant nitrogen which also is the least hindered one. In ***3b*** this is suppressed because amide nitrogens are poorer ligands than amine nitrogens. Thus, coordination between the nitrogen, nearest to the zinc porphyrin unit, or the carbonyl oxygen, next to the distant nitrogen, and zinc occurs. Carbonyl oxygen to zinc coordination gives the possibility to twofold coordination similar to that in ***3a*** but with lower complex constant. In a UV-VIS-sample (≈ 10^{-5} M) compound ***3a*** forms a dimer at room temperature whereas the dimer of ***3b*** is formed only on cooling to 173 K. However, at this temperature both zinc atoms are coordinated, indicative of zinc to oxygen coordination.

We have chosen to illustrate the dimer as formed from two enantiomers of ***1a*** resulting in a dimer with a centre of inversion. A similar dimer with a C_2-axis of symmetry formed from two homotopic monomers is equally probable. The intramolecular distance between the centra of the porphyrin rings is 24 Å and the intermolecular distances in dimer ***2*** are: Zn to Zn′ 16.5 Å; Zn to center of free base porphyrin 12 Å; free base to free base porphyrin 29 Å.

The result of an analysis of the ^{1}H and ^{13}C NMR spectra of ***1a-c*** (≈ 10^{-2} M) recorded at different temperatures is consistent with the structure presented here. The ^{1}H NMR spectra of ***1a*** (at 293 and 323 K), of ***1b*** (293 K) and of ***1c*** (293 K) are shown in Fig 2. Compound ***1b*** is shown as a reference compound in which no coordination occurs. From the two spectra of ***1a*** shown, it is clear that the dimerisation is detectable at 323 K and is significant at 293 K where the rate of exchange between different dimers is still fast on the NMR time scale. The signals from the protons of the *para*-substituted benzene rings in the uncoordinated porphyrin are shifted more upfield than the corresponding protons in the coordinated zinc porphyrin. In the dimers two protons undergo a large upfield shift at low temperatures and give a broad peak at -0.5 to -1.5 ppm. These are assigned as two of the protons adjacent to nitrogen in the crown ether ring. However, because of the number of possible complexes and dynamic processes a complete analysis of the observed chemical shifts in the crown ether units is not possible. Except for the reversible monomer to dimer dynamic process, inversion at nitrogen occurs as well as conformational changes within the crown ether. In ***1c*** a dynamic shift of nitrogen to zinc coordination also occurs. All these processes guarantee broad peaks for most of the ^{1}H NMR signals observed even at low temperatures.

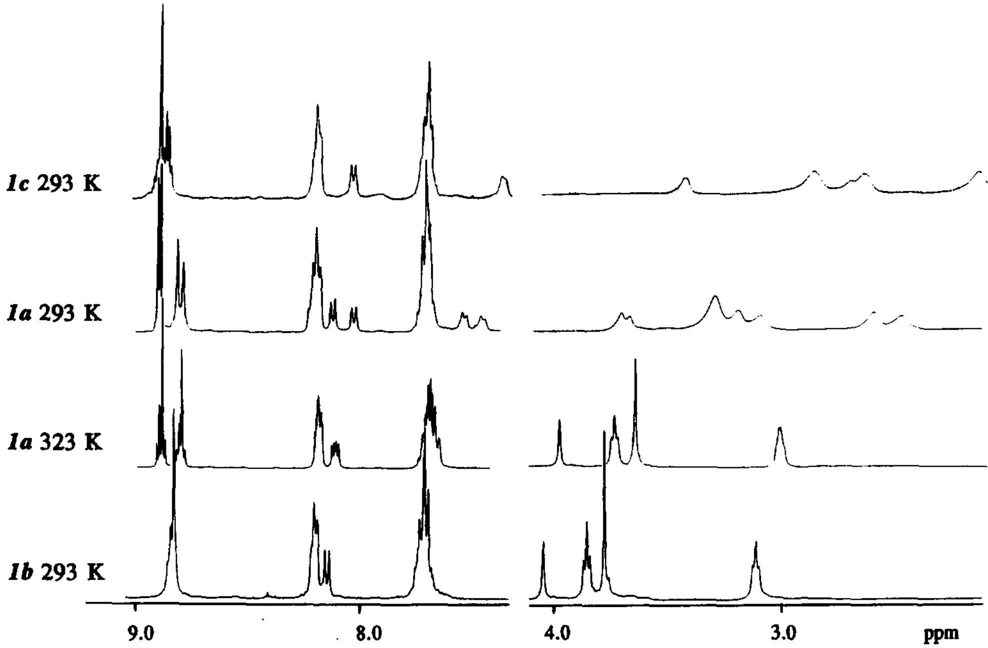


Fig. 2 ^{1}H NMR spectra (400 MHz, $CDCl_3$) of *1a, 1b* and*1c*.

Conclusions. We have found that the dimerisation of zinc porphyrins covalently bonded to nitrogens in proper positions leads to well defined supramolecular structures as exemplified by the dimerisation of the bisporphyrin *1a*. The dimerisation is reversible and occurs on cooling within a narrow temperature range and we think that this method might allow us to build complex structures of interest for the modelling of important bioreactions such as energy and electron transfer.

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References and notes

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4. ^{1}H-NMR(400 MHz, $CDCl_3$, $1\cdot10^{-2}$ M, 323 K): $\delta = 8.87$-8.92 (8H, m, pyrrole-**H**[Zn]), 8.78-8.83 (8H, m, pyrrole-**H**), 8.15-8.22 (12H, m, 2-**H**-Ar, 2-**H**-Ar[Zn]), 8.12 (2H, d, J = 8 Hz, 2-**H**-Ar'[Zn]), 8.11 (2H, d, J = 8 Hz, 2-**H**-Ar'), 7.63-7.77 (22H, m, 3,4-**H**-Ar, 3,4-**H**-Ar[Zn], 3-**H**-Ar', 3-**H**-Ar'[Zn]), 3.98 (4H, br s, Ar'CH_2N, Ar'[Zn]CH_2N), 3.73 (8H,br t, J = 5 Hz, NCH_2CH_2O), 3.64 (16H, s, OCH_2CH_2O), 2.96-3.04 (8H, br m, NCH_2CH_2O), -2.72 (2H, br s, pyrrole-N**H**). UV-VIS(CH_2Cl_2): λ_{max} = 418, 515, 548, 587, 646 nm. MS(FAB): m/z ($M+H^+$) 1577.5 (calcd for $C_{102}H_{84}N_{10}O_4Zn+H^+$: 1577.60).
5. Synthesis and photophysical properties of *1a-c* will be presented elsewhere.
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