Pergamon

Tetrahedron Letters 39 (1998) 2993–2996

TETRAHEDRON
LETTERS

Self-organized Porphyrin Array

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Received 15 December 1997; revised 19 February 1998; accepted 20 February 1998

Key Words ; porphyrin, exciton coupling, array, self-organization

Abstract ; *New types of self-organized porphyrin arrays were constructed. The systems contain dimeric* ***TT*** *and trimeric tartrates* ***TTT*** *connected with 1,6-hexamethylendiol spacers and the trench porphyrin* ***P*** *bridged with 2,4-dinitro-isophthalic acid. The* ***TT - P*** *and* ***TTT - P*** *systems exhibit unique exciton splitting bands at 437 nm and 440 nm upon allowing the temperature of the samples to lower, of which splinting energies are 507 cm^{-1} and 691 cm^{-1} respectively. The observed splitting of the Soret bands strongly indicates the formation of porphyrin arrays on the tartarate templates.*

Large scale chemical structures containing multiporphyrin elements have been attracting special interest because of their characteristics as mimics of the photosynthetic light-harvesting pigment system.[1] Since such artificial systems are also expected to be important as so-called "molecular wire" which transmits energy and/or electron efficiently,[2] several synthetic methods have been developed to realize covalently-linked multiporphyrin systems.[3] Another attractive approach to this type of large scale molecular structures is to use self-organization processes where weak noncovalent interactions hold each molecular component at its proper position.[4] Combination of traditional syntheses and such self-organization is expected to provide powerful methodology for the construction of new types of large scale molecular systems and/or devices. We report herein self-organized porphyrin array systems showing characteristic exciton coupling between porphyrin components, which is suggested to play an important role in the energy transfer process of antenna systems of photosynthetic unit.[5]

The array systems are designed based on the trench porphyrin recognition system which we previously report to recognize dialkyl L-tartrates with simultaneous four hydrogen bonds.[6] In order to utilize this system as a porphyrin array, we employed dimeric **TT** and trimeric tartrates **TTT** connected with 1,6-hexamethylendiol spacers as templates and the trench porphyrin **P** bridged with 2,4-dinitro-isophthalic acid as a porphyrin component (Figure 1). We also prepared a reference monomer **T** as a standard non-array template. The complex formation between **P** and **T** in CH_2Cl_2 is easily confirmed by UV-visible spectrometry and, for example, the usual titration experiment gives the 1: 1 binding constant at 278 K to be $(1.8 \pm 0.4) \times 10^6$ M^{-1}. Van't Hoff type analyses of association constants collected at 273 - 303 K gave ΔH and ΔS for complexation

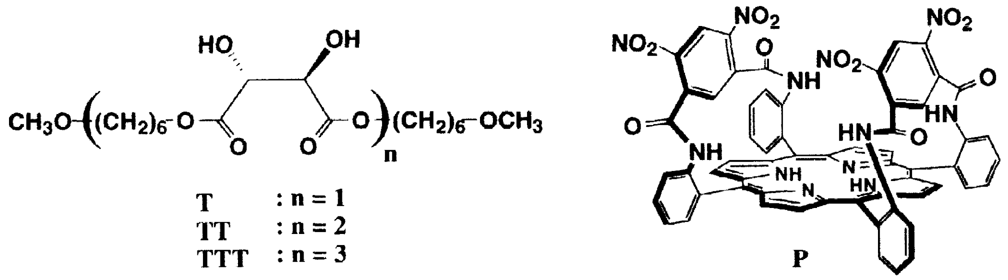


Figure 1. Structures of the trench porphyrin, **P**, and tartarate templates, and a schematic hydrogen bond network in the trench porphyrin-tatrate complex.

0040-4039/98/$19.00
PII: S0040-4039(98)00441-9

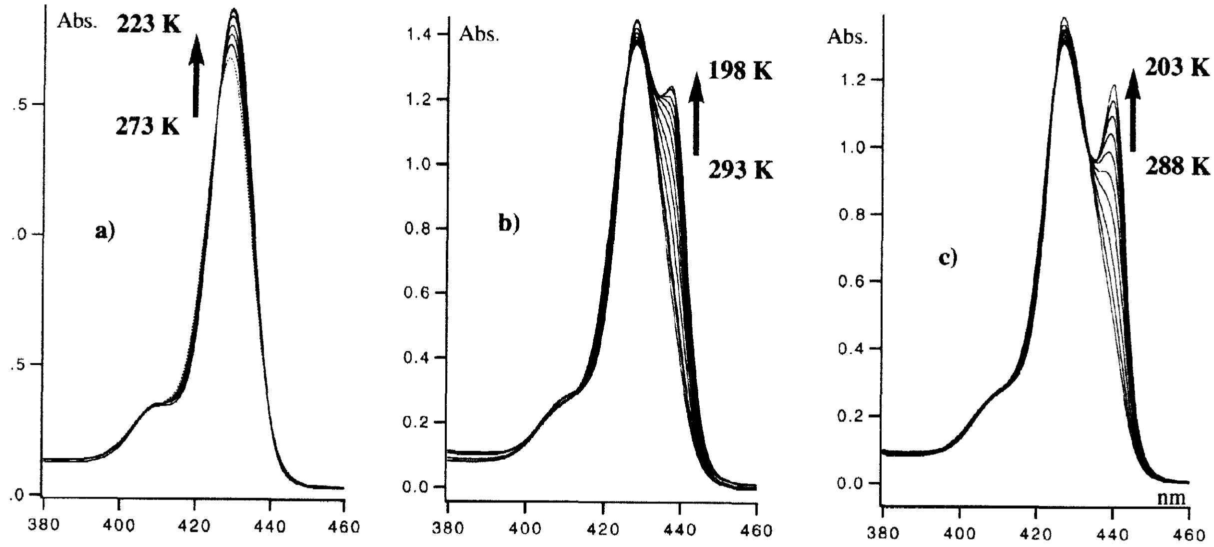
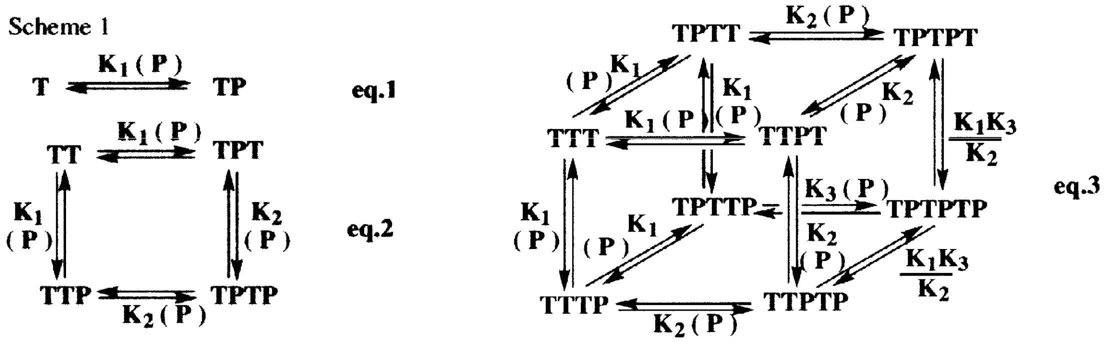


Figure 2. Variable-temperature electronic spectra of a) the **T** - **P** system ([T] = 5.85 mM, [P] = 5.18 mM) at 273, 263, 253, 243, 233 and 223 K, b) the **TT** - **P** system ([TT] = 2.62 mM, [P] = 4.81 mM) at 293, 288, 283, 273, 263, 253, 243, 233, 223, 213, 203 and 198 K, c) the **TTT** - **P** system ([TTT] = 1.77 mM, [P] = 4.81 mM) at 288, 283, 273, 263, 253, 243, 233, 223, 213, 203 and 198 K.

between **P** and **T** to be -15.2 ± 0.8 kcal/mole and -27 ± 3 e.u. The spectroscopic behavior of the **T** - **P** system is similar to that for simple dialkyl tartrates reported previously.[6] The 1 : 1 complex formation behavior of the **T** - **P** system is also detected by variable-temperature electronic spectrometry shown in Figure 2a, which shows monotonic increase of the 1 : 1 complex **TP** upon lowering temperature from 273 K to 223 K. In contrast to this normal behavior of the **T** - **P** system, the **TT** - **P** and the **TTT** - **P** systems exhibit unique spectroscopic response to the change of temperature, i.e., the CH_2Cl_2 solution containing 2.6 μM of **TT** and 4.8 μM of **P** shows a new split Soret band at 437 nm upon allowing the temperature of the samples to lower (Figure 2b). For the solution of **TTT** (1.8 μM) and **P** (4.8 μM), a similar but much clearer split Soret band is observed at 440 nm as shown in Figure 2c. These spectroscopic changes are completely reversible and no irregular process such as a precipitation phenomenon is found during mesurements. The characteristic splitting of the Soret bands found for the **TT** - **P** and the **TTT** - **P** systems strongly indicates that the present trench porphyrins are arranged in an array mode and approach each other within the range of exciton coupling interactions at low temperature.[8] Similar split Soret bands are sometimes observed for the covalently linked porphyrin arrays and the splitting has been illustrated by the theory of exciton coupling between multi-chromophors, where the exciton splitting energies for these arrays increase with increasing number of chromophor constructing the systems.[3a,7] In the present cases, the exciton splitting energies are evaluated to be 507 cm^{-1} and 691 cm^{-1} for the **TT** - **P** and the **TTT** - **P** systems respectively.[9] These values are somewhat smaller than those for phenylene-linked linear porphyrin arrays but much larger than those for face-to-face type porphyrin oligomers.[3d]

The most rational processes to form present porphyrin arrays are expressed by the stepwise equlibria (Scheme 1), which shows all possible complex formation processes to generate final array forms, **TPTP** for the **TT** - **P** system (eq. 2) and **TPTPTP** for the **TTT** - **P** system (eq. 3). To analyze these multi-equilibrium processes, we collected the data of absorbance dependencies on temperature at different concentrations of the components. The results are summarized in Figure 3. Since, though clear saturation behavior is observed in the low temperature region, the dependencies observed for these systems are very similar each other and

Scheme 1



basically monophasic, it is difficult to separate each equilibrium and determine corresponding equilibrium constants by using these data. Therefore, we simplify the systems by assuming following working hypotheses and try to carry out successive analyses. First, for the **TT** - **P** system, the binding constant of the **TPTP** array, K_2, is determined based on the assumption that the binding constant for **TPT** or **TTP** is the same as that for monomeric **TP**, K_1 (eq.2). Actual fitting calculation is performed by nonlinear least square computation using above mentioned thermodynamic parameters for K_1 as constants and optimizing ΔH and ΔS for K_2 to fit the calculated absorbance changes to the observed ones. Optimization gave the values of ΔH and ΔS to be -10.4 ± 0.8 kcal/mol and -10 ± 3 e.u. and the simulated curves show fairly good agreement with the observed ones as shown in Figure 3a. These thermodynamic parameters correspond to the binding constant K_2 of ca. 1×10^6 M^{-1} at 278 K. For analyses of the **TTT** - **P** system, which needs six independent binding constants for full description, the system was simplified as follows ; a) all binding constants for 1 : 1 complex formation between **TTT** and **P** are equal to K_1, b) the binding constant of **TPTTP** having an open binding site between two occupied ones is also equal to K_1, c) the binding constants of **TPTPT** and **TTPTP** having two adjacent occupied binding sites are equal to K_2. Under these conditions, the unknown independent binding constant in the system is only K_3 which describes the formation of **TPTPTP** from **TPTTP** (eq. 3) and data analyses may be performed using this binding constant as an optimized variable. Similar optimization of thermodynamic parameters for K_3 gave the values of ΔH and ΔS to be -9.6 ± 0.9 kcal/mol and -8 ± 4 e.u., which correspond to the binding constant K_3 of ca. 7×10^5 M^{-1} at 278 K. It should be noted that all binding constants, K_1, K_2 and K_3, are large enough to generate the array type

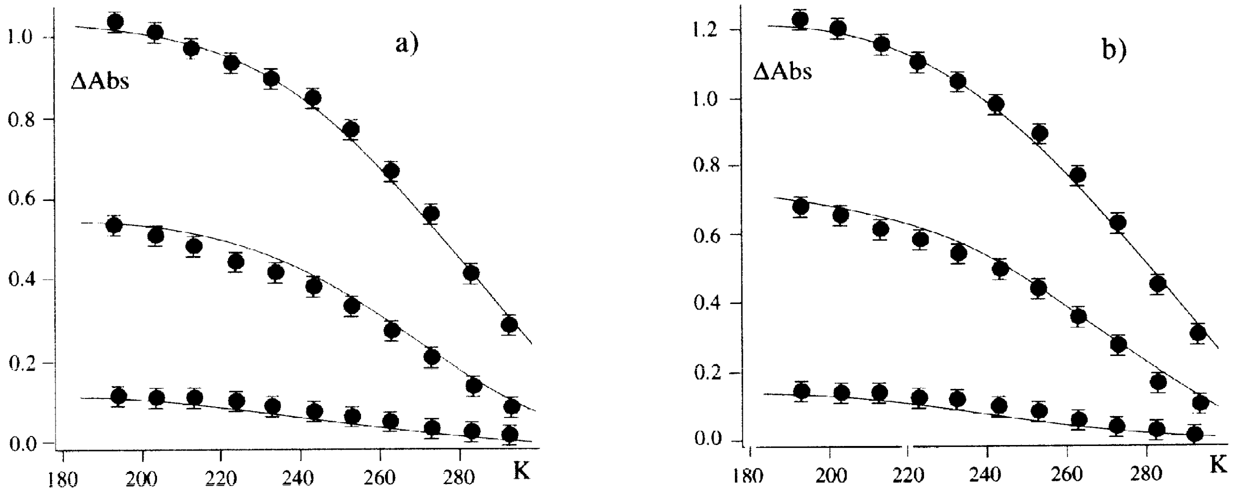


Figure 3. Plots of absorbance change vs. temperature, where Δabs is the absorbance difference between those of the sample and free **P**. The solid curves are theoretical ones calculated using parameters shown in the text. a) {[**P**],[**TT**]} = {6.10 mM, 3.03 mM}, {3.27 mM, 1.62 mM},{0.673 mM, 0.333 mM}, ΔAbs at 437 nm. b) {[**P**],[**TTT**]} = {6.19 mM, 2.10 mM}, {3.56 mM, 1.18 mM},{0.715 mM, 0.240 mM}, ΔAbs at 440 nm.

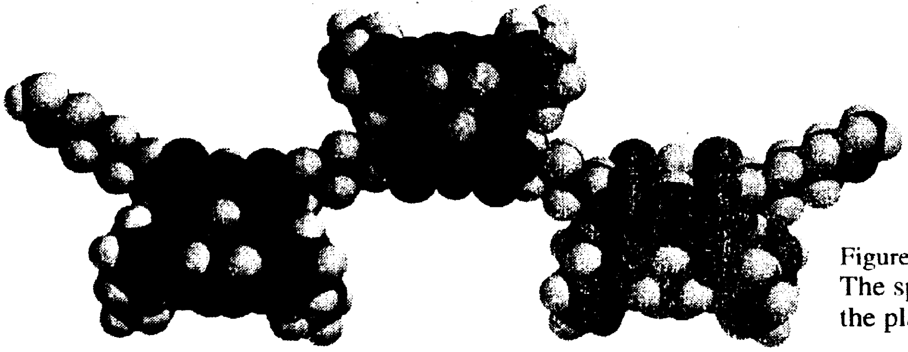


Figure 4
The space-filling model of one of the plausible **TPTPTP** complexes.

complexes and rather insensitive to occupancies of adjacent binding sites. Since present analyses contain evident over-simplifications, especially that for **TPTTP** formation, there are some ambiguities remaining for quantitative discussions. The observations, however, strongly support the present schematic conclusion shown above and consideration of molecular models indicates that hexamethylene spacer of the templates in an extended conformation allows trench porphyrins to occupy all binding sites without serious steric repulsion between adjacent porphyrins as shown in Figure 4.

Further extensions of the present porphyrin array to larger scale systems are now under investigation in our laboratory.

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(8) The ESI masss spectrum of 1 : 3 mixture of **TTT** and **P** shows the mass peak at *m/e* 4249, which is possibly assigned as **TTT•P**$_3$+K$^+$+Na$^+$-1.

(9) Although available examples are limited to three, **TP**, **TPTP** and **TPTPTP**, there is a clear linear relationship between these exciton splitting energies and the term of 2cos[π / (N+1)], where N is the number of porphyrins. For this relationship, see ref. 3a and b.