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HIGH BINDING AFFINITY OF DABCO WITH PORPHYRIN IN A PORPHYRIN-*CIS*-STILBENE-PORPHYRIN TRIAD

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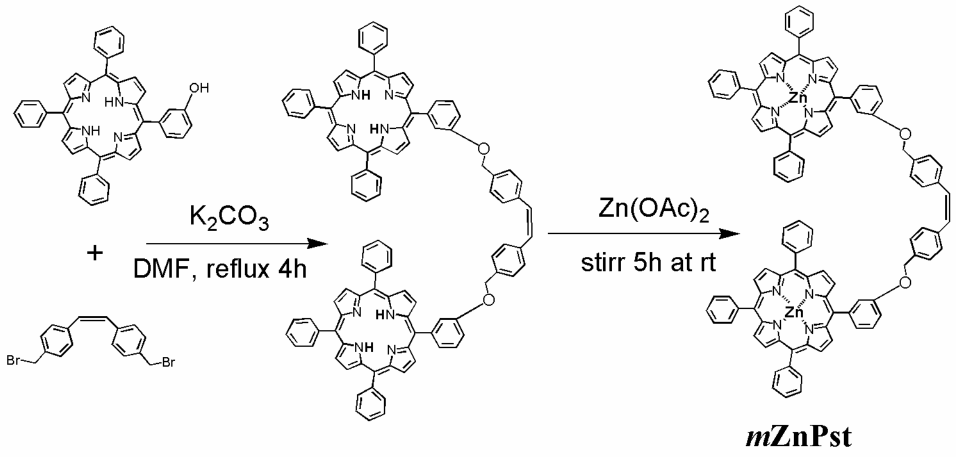
Abstract – Porphyrin-stilbene-porphyrin triad (***m*ZnPst**) where a central *cis*-stilbene unit is connected to zinc-tetraphenylporphyrin (**ZnTPP**) was synthesized and its binding ability with a selected guest ligand **DABCO** was investigated. The association constant was evaluated to be 2.47 x 10^8 M^{-1}, from the iterative least squares fitting to a 1:1 binding model, which is larger than that of monomer **ZnTPP**/**DABCO** complex (3.50 x 10^5 M^{-1}). In addition, when a toluene solution of ***m*ZnPst** is mixed with 1 equivalent of **DABCO**, the color of the solution was changed abruptly to light purple from bright reddish, providing further a visual evidence of forming strong complex. Such a high association constant suggests ***m*ZnPst/DABCO** to be a promising photoresponsive supramolecular system.

Nowadays, porphyrin appears to be a promising artificial host and/or receptor as its giant π surface to allow interacting efficiently with a suitable acceptor or ligand moiety give rise to a non-covalent complex. By taking the advantage of the ultimate rigidity of the porphyrin skeleton to which various functional groups can be attached at the periphery and the easier accessibility of incorporating various metals to the central part with varying Lews acidity, a variety of porphyrin based artificial receptors exhibiting strong binding affinity with ions,[1] organic molecules[2] and biological species,[3] have been reported in recent years. Besides, in the pursuit of superbly stable porphyrin based supramolecular complex potential for photovoltaic applications, a variety of porphyrin dimers using different linkers such as alkyl or ether chain,[4,5] 1,2-polyphenylene,[6] alkyne,[7,8] photoresponsive azobenzene[9] have also been developed and explored. The objective of inserting different spacer was nothing but to control as well as to optimize the electronic communication of host porphyrins with a guest acceptor or ligand.

Stilbene is well recognized photoresponsive material which, upon UV irradiation, undergoes reversible transformation between its two isomers (*cis* and *trans*) having completely different geometries (skewed and planer) as well as physical properties. We envisioned that, as like photoresponsive azobenzene,[9] if the *cis*-stilbene be utilized as the spacer for porphyrin dimer its skewed geometry may allow the two peripheral porphyrin units to orient in a face-to-face fashion which may provide a flexible molecular pocket to a selective ligand or acceptor to interact simultaneously with the both porphyrin units and thereby resulting in a strong ground state host-guest complex. Motivated by this anticipation, in this study, we have synthesized a porphyrin-stilbene-porphyrin triad (***m*ZnPst**) where a central *cis*-stilbene unit is connected to the meta position of zinc-tetraphenylporphyrin (**ZnTPP**) and investigated its binding ability with the selected guest ligand **DABCO**. We wish to report here the extraordinarily high binding affinity of **ZnTPP** with **DABCO** in ***m*ZnPst**.



Scheme 1. Preparation of porphyrin-*cis*-stilbene-porphyrin triad ***m*ZnPst**.

The host compound **mZnPst** was synthesized in two steps starting from 5-(3-Hydroxyphenyl)-10,15,25-triphenylporphyrin[10] and (*Z*)-4,4'-Bis(bromomethyl)stilbene[11] by following the Scheme 1. The desired compound was separated by column chromatography with silica gel and its structure was characterized by ^{1}H NMR and Maldi-Tof-Mass and UV-visible spectroscopies. The observed absorption spectrum of ***m*ZnPst** is fairly the superposition of its components spectra, suggesting that electronic interaction among the triad chromophores is feeble in the ground state.

Figure 1 represents the results of titration of ***m*ZnPst** with **DABCO** which demonstrates a blatant modification of the absorption spectrum of **ZnTPP** with increasing concentration of **DABCO**. As the proportion of **DABCO** in the mixture increases in succession, the absolute absorption intensity of both the Soret and Q bands reduces steadily and new absorption bands, the peaks of which are located at the wavelength region longer than those of the both bands, come up with the distinct signatures of isobestic points at 411, 421, 426.5, and 434.5 nm in the Soret band region and at 557.5, 582.5, and 590 nm in the Q bands region. The intensity of the newly formed absorption bands increases steadily with increasing

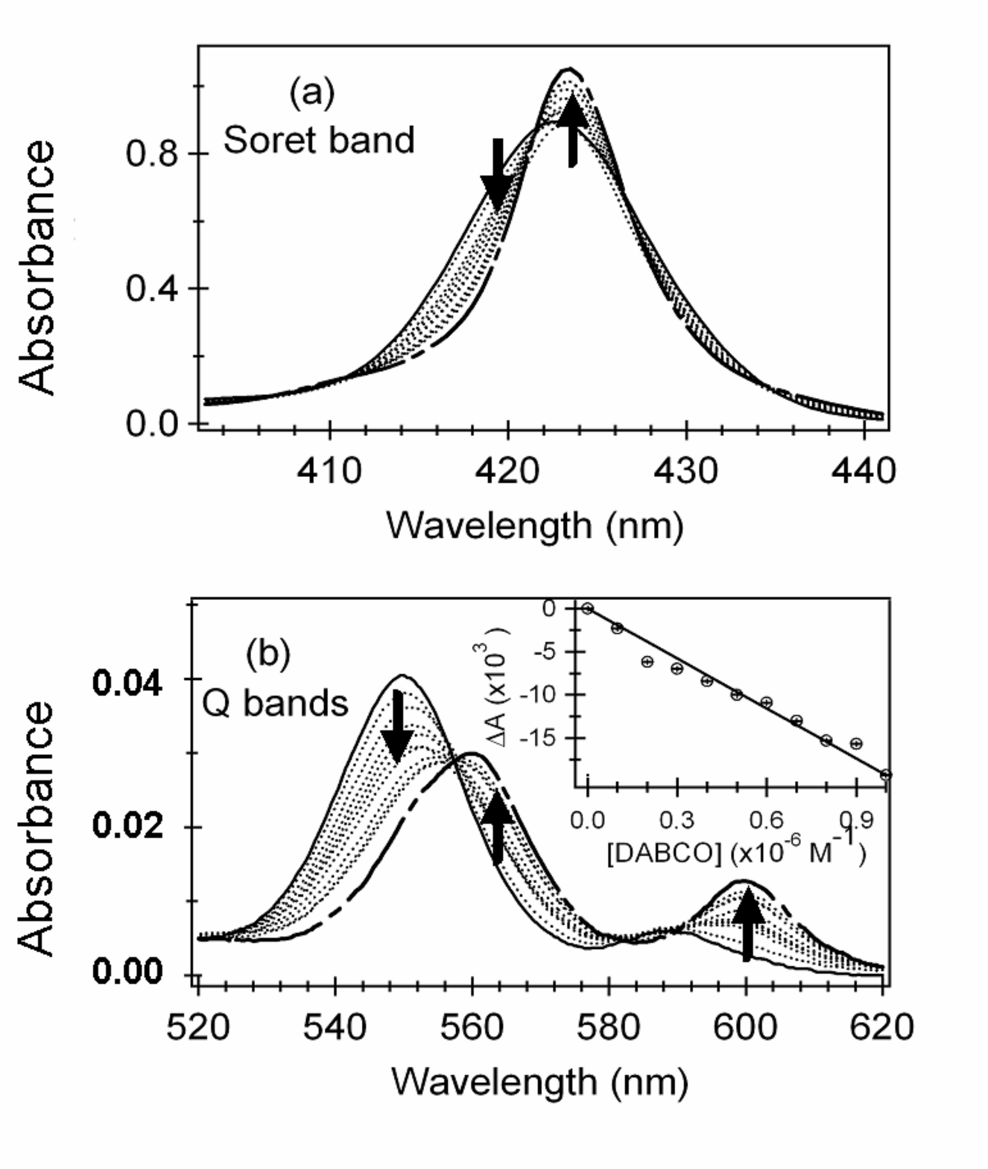


Figure 1. Change in the absorption spectrum of **mZnPst** around the Soret (a) and Q(b) bands upon addition of **DABCO** whose equivalent proportions (**mZnPst**/**DABCO**) are 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0. The inset of (b) illustrates the absorbance change at 550 nm and the non-linear least square fitting obtained on the basis of 1:1 binding model.

proportion of **DABCO** and finally reaches to the maximum when 1 equivalent of **DABCO** is added. The newly formed band is assigned to the absorption spectrum of the complex arising from the strong electronic interaction of ***m*ZnPst** with **DABCO** in the ground state. The stoichiometry of the complex was estimated on the basis of Job's plots to be 1:1 (Job plot is shown in the supporting information). The association constant was evaluated to be 2.47 x 10^8 M^{-1} from the iterative least squares fitting to a 1:1 binding model, which is certainly a large value exceeding apparently the upper limit of experimental determination for spectroscopic titration and found to be larger than that of monomer **ZnTPP**/**DABCO** complex (3.50 x 10^5 M^{-1}). In addition, when a toluene solution of ***m*ZnPst** is mixed with 1 equivalent of **DABCO**, the color of the solution was changed abruptly to light purple from bright reddish, providing further a visual evidence of forming strong complex. It seems that, due to strong binding between ***m*ZnPst** and **DABCO**, the resulting complex likely to be appeared as a stable and distinct species having a distinct fluorescence of its own.

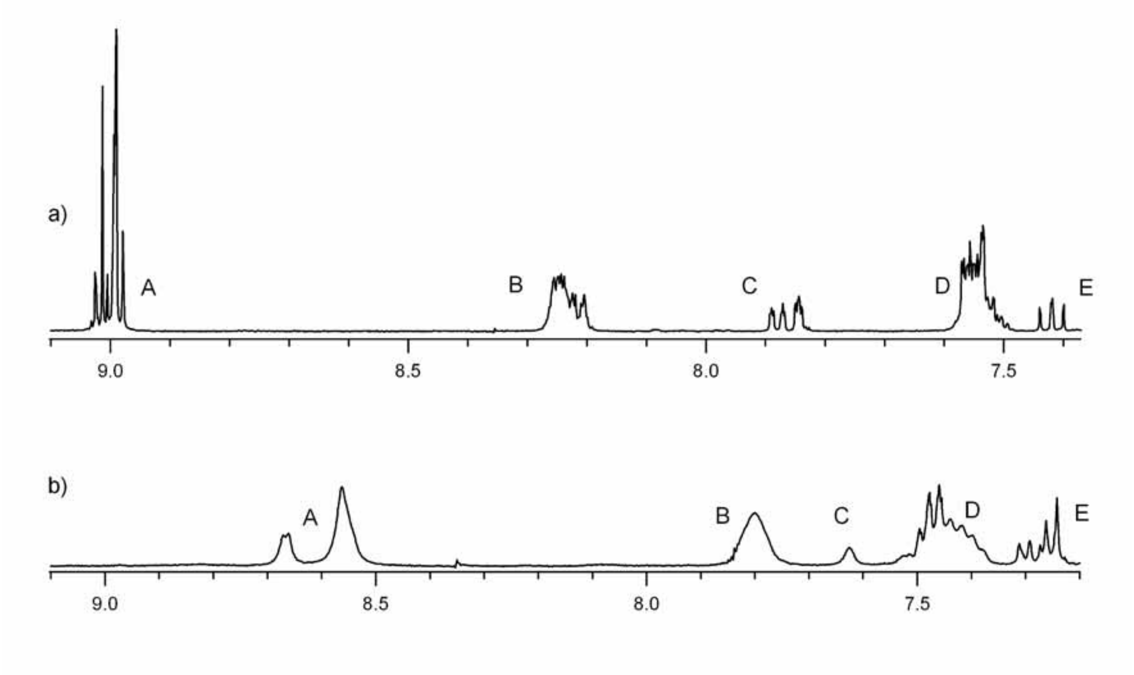


Figure 2. NMR spectra of ***m*ZnPst** taken in the absence (a) and in the presence (b) of 1 equivalent **DABCO**.

To diagnose the structural details as well as the dynamics of the complexation, NMR of spectrum of ***m*ZnPst** was taken in the absence and in the presence of 1 equivalent of **DABCO**. The NMR spectrum of ***m*ZnPst** devoid of **DABCO** (Figure 2a) exhibits multiplets at all the regions specified as **A** (β-pyrrole-H), **B** (orthophenyl-H), **C** (substituted orthophenyl-H), **D** (meta-, para-phenyl-H) and **E** (substituted meta-phenyl-H). The multiplet structure in the NMR spectrum probably results from the several conformational isomers of ***m*ZnPst** arising from the flexible spacer. Upon addition of 1 equivalent of **DABCO**, the bands **A** around 9.0 ppm were shifted and appeared around 8.50-8.70 ppm as two broadening peaks (Figure 2b). Simultaneously, peaks **B-E** (Figure 2a) were shifted to give broaden signals as in Figure 2b. Noteworthy modification of the NMR signals especially of **A** and **B** and the concomitant shifting upon adding **DABCO** provides another sheer evidence of a strong association of **DABCO** with **ZnTPP** in existing molecular framework of ***m*ZnPst**. In such a circumstance, it will not be an unusual consideration that **DABCO** is incorporated between the two **ZnTPP** units of ***m*ZnPst** and thereby resulting in a stable 1:1 sandwich type complex (Figure 3). The estimated extremely high association constant of ***m*ZnPst**/**DABCO** complex in comparison with monomer **ZnTPP**/ **DABCO** complex also provides a reasonable support for such a conclusion.

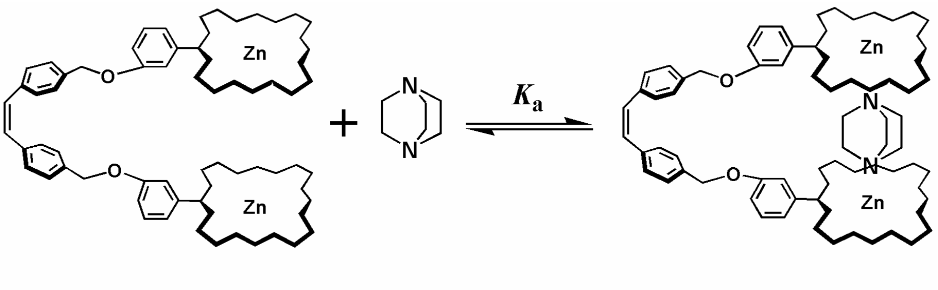


Figure 3. Expected structure of the complex.

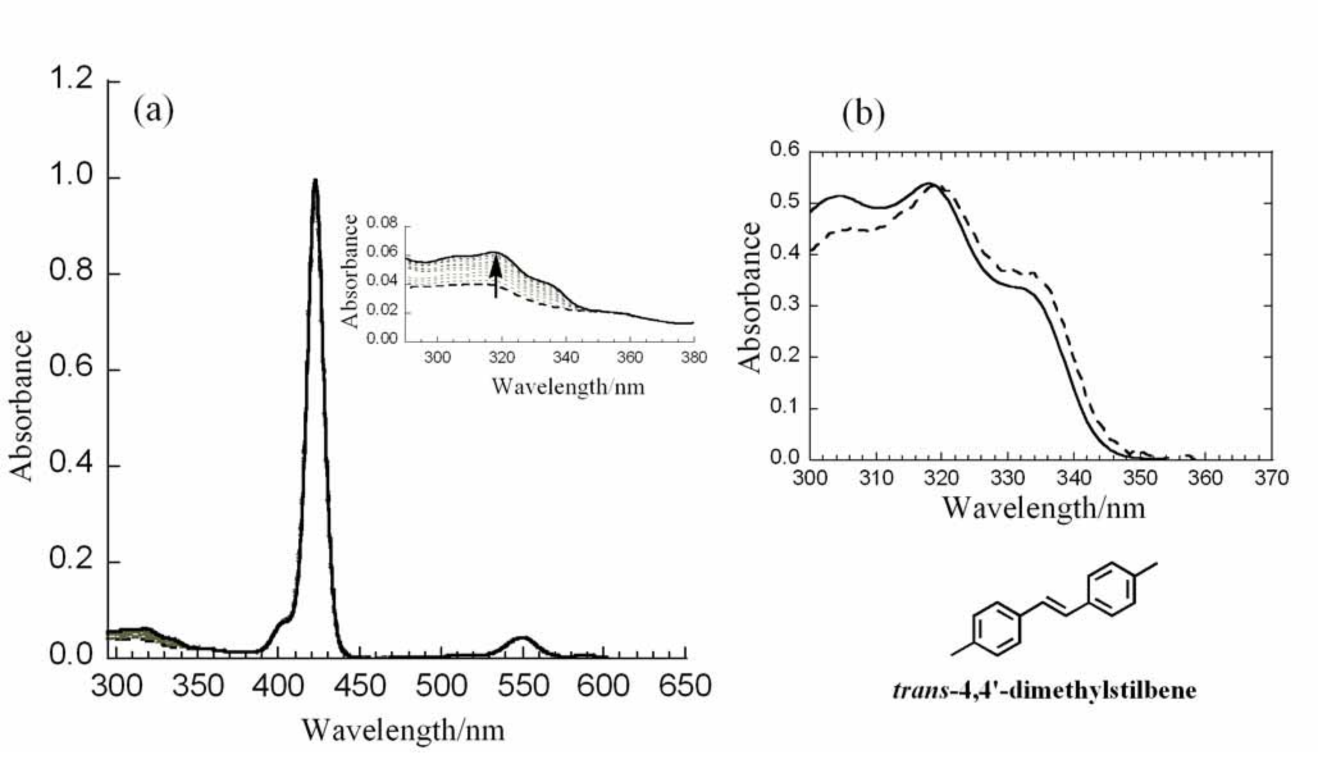


Figure 4. Change of absorption spectra of ***m*ZnPst** (0 min: dash line, 180 min: solid line) on irradiation with 308 nm light in toluene (a). Inset of (a) shows the expanded spectra around the absorption band of the stilbene moiety (290-350 nm). Difference spectrum between the samples before and after irradiation (dash line) and the absorption spectrum of ***trans*-4,4'-dimethylstilbene** (solid line) in toluene (b).

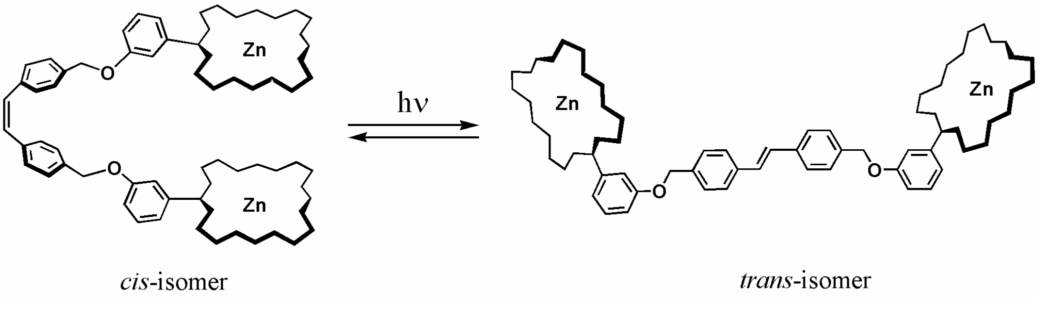


Figure 5. Photoisomerization between *cis*- and *trans*-***m*ZnPst**.

On UV irradiation at room temperature in toluene, ***m*****ZnPst** underwent photoisomerization to *trans*-***m*****ZnPst**, which was revealed by the change in the absorption spectra. The absorption changes for irradiation of ***m*****ZnPst** are shown in Figure 4a. The initial absorbance of the *cis*-stilbene moiety around 320 nm increased with irradiation time to give a new band. Figure 4b shows the differential spectrum between the samples before and after irradiation of ***m*****ZnPst,** which is similar to the absorption spectra of model compound, ***trans*****-4,4'-dimethylstilbene**. The result indicates that the new band shown in Figure 4a is due to the *trans*-stilbene chromophore (Figure 5). During the photoirradiation, the absorption spectrum of porphyrin moiety did not change, probably because the electronic structure of *trans*-***m*****ZnPst** is similar to that of original *cis*-isomer except stilbene moiety.

In conclusion, we have synthesized a porphyrin-stilbene triad (***m*****ZnPst**) and explored its binding affinity with **DABCO**. **DABCO** is found to interact strongly with both **ZnTPP** units in ***m*****ZnPst** yielding a superbly stable 1:1 complex. The association constant of the complex is estimated to be 2.47 x 10^8 M^{-1}. Such an extremely high association constant suggests ***m*****ZnPst/DABCO** to be a promising supramolecular system and thus a full investigation of its photophysics is warranted indeed Finally, we demonstrated the photochemical isomerization to give *trans*-isomer of ***m*****ZnPst**.

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