

Optical and Magnetic Resonance Studies of the Interaction of Metallotetraphenylchlorin and Octaethylporphyrin with Trinitrofluorenone

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The interaction of metallo derivatives of tetraphenylchlorin (TPC) and octaethylporphyrin (OEP) with 2,4,7-trinitrofluorenone (TNF) is described in terms of 1:1 molecular complexes. The binding constants vary as $\text{CuOEP} > \text{ZnOEP} > \text{CuTPC} > \text{ZnTPC}$ and this variation is accounted in terms of the structure of the macrocycle and the substituents present on it. ESR studies of the complexes reveal that the π -complexation results in changes in the electronic structure of the central metal ion. The magnitude of different proton shifts of the acceptor in ^1H NMR spectra of the complexes are used to arrive at the possible solution structure of the complexes.

Molecular complexation of macrocyclic tetrapyrrole pigments with organic molecules has been the subject of numerous studies because of their presence and participation in many reactions of chemical and biochemical interest.^{1–3} It has been shown that the major source of stabilization in such complexes is π - π interaction between the donor and acceptor and charge transfer forces contribute to a small extent to the binding strength.^{4,5} The recent X-ray crystallographic work on the photosynthetic bacterial reaction center has revealed that the orientation of the donor and the acceptor relative to each other is crucial in such complexes to prevent back electron transfer.⁶ Thus a systematic study of the molecular complexes of porphyrins and related macrocycles with electron acceptors is important to get information about the factors and forces responsible for stability of such complexes in a particular orientation. We have been interested in the molecular complexation behavior of

tetrapyrrole pigments and our earlier studies have indicated that the stability of the complexes depends both on the metal ion present in the cavity of the macrocycle as well as on the compatibility in sizes of the donor and acceptor.^{7–9} In the present study the metal derivatives (Cu and Zn) of tetraphenylchlorin (TPC) and octaethylporphyrin (OEP) were employed as donors and 2,4,7-trinitro-9-fluorenone (TNF) as an acceptor (Fig. 1). Electronic absorption spectral method was used to evaluate the binding constants while the ^1H NMR and ESR measurements were recorded to ascertain the site of interaction in these complexes. The results of this study were used to derive information regarding the relative orientation of the donor and acceptor in the complexes in solution.

Experimental

TPC was prepared from tetraphenylporphyrin (TPP) following the literature procedure.¹⁰ OEP and TPP were obtained from Strem Chemicals, USA. TNF was procured from Aldrich Chemicals, USA. The metal derivatives of OEP and TPC were synthesized by refluxing the corresponding metal acetate with the macrocycle in DMF.¹¹ The purity was checked by NMR and optical spectra. All the solvents employed in the study were distilled before use. The preparation of the solutions and all the manipulations were carried out in dim light. The spectra of the solutions were recorded immediately after mixing.

The electronic absorption method employed for the evaluation of association constants involved the measurement of absorbance of the Q-bands of the porphyrins in the solvent CHCl_3 on increasing addition of TNF. The concentration of the donor was held constant (approx. 10^{-5} M; $1 \text{ M} = 1 \text{ mol dm}^{-3}$) and the range of concentration of TNF employed was 1.0×10^{-4} to 2.0×10^{-2} M.

The optical absorption spectra were recorded on Shimadzu double beam spectrophotometer. The ^1H NMR spectra of the complexes were recorded on a Bruker WH 400 FT NMR spectrometer using CDCl_3 as solvent and TMS as internal standard. The ESR spectra were recorded on a Varian E-109 ESR spectrometer using toluene as solvent. The spectra were recorded at about 100 K using liquid nitrogen. The IR spectra of the complexes were recorded on

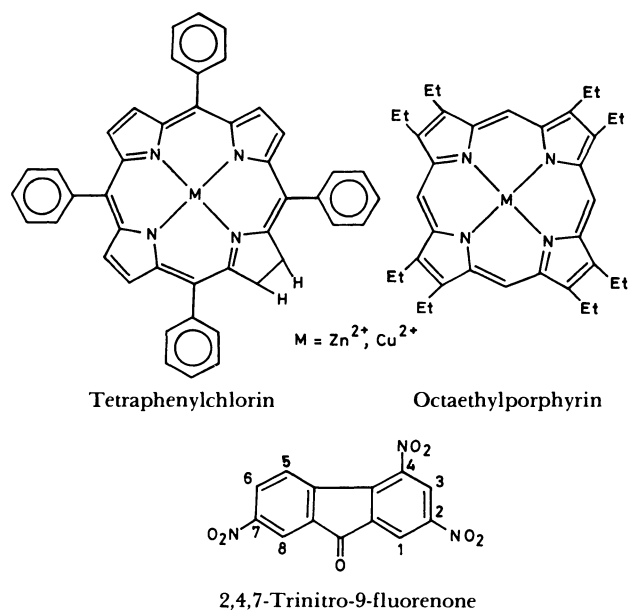


Fig. 1. Structure of metallomacrocycles and 2,4,7-trinitro-9-fluorenone.

a Perkin Elmer 580/7358 IR spectrometer. The 1:1 complexes for ^1H NMR, ESR, and IR studies were prepared as follows. To a solution of porphyrin [10^{-5} M] in CHCl_3 , TNF [10^{-3} M] was added and the mixture was stirred for an hour. Slow evaporation of solvent over a water bath gave the required complex. The air-dried complex was dissolved in appropriate solvents and used for spectral studies.

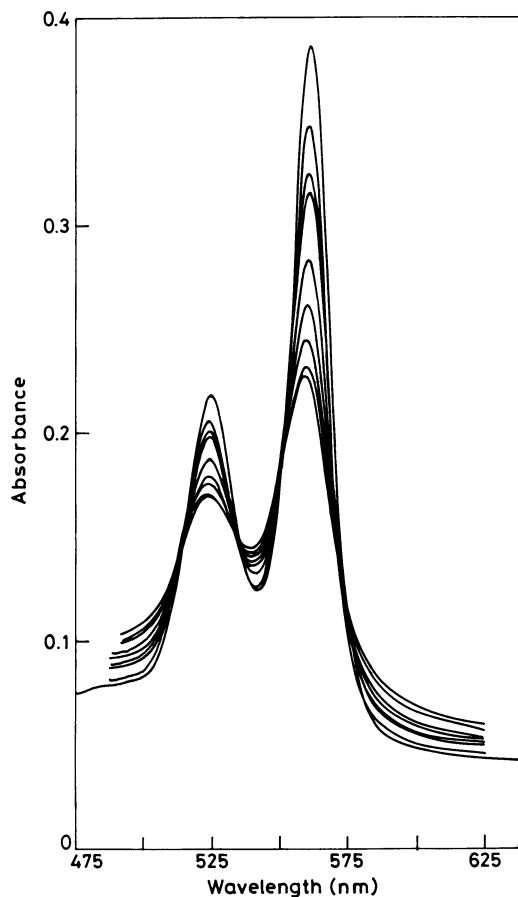


Fig. 2. Visible absorption spectra of CuOEP [1.06×10^{-5} M] containing increasing amounts of TNF [1.356×10^{-4} – 2.712×10^{-3} M].

Results and Discussion

The metal derivatives of TPC and OEP exhibited intense absorption bands (Q-bands) in the visible region (500–600 nm) in CHCl_3 . The acceptor, TNF, did not absorb in this region and showed intense absorption only in UV region. Addition of increasing amounts of TNF to CHCl_3 solutions of MTPC and MOEP derivatives progressively decreased the intensity of the Q-bands of the donors with the appearance of isosbestic points (Fig. 2). These observations are consistent with the formation of molecular complexes between TNF and the macrocycle.¹² The decrease in absorbance of donor upon increasing concentrations of the acceptor was analyzed for the calculation of association constant (K) using Nash equation.¹³ The linearity of the plots of $d^0/(d^0-d)$ versus $1/C_A$, where d^0 and d denote the absorbance values of donor in the absence and presence of TNF and C_A is the concentration of the acceptor, indicated that the predominant species that existed in solution is the 1:1 complex (Fig. 3). The possible existence of 1:2 (donor-acceptor) complexes in solution was then analyzed using the method of Bent and French.¹⁴ The slopes of the logarithmic plots yielded values in the range from 0.9–1.7 indicating the existence of higher order complexes.¹⁵ It was difficult to quantify the stability constants of these higher order complexes as they were present in only very low concentrations. However, the presence of these complexes did not alter the magnitudes of K -values calculated for 1:1 complexes appreciably. The association constants determined for 1:1 complexes are listed in Table 1.

An inspection of Table 1 reveals that the values of K vary as $\text{CuOEP} > \text{ZnOEP} > \text{CuTPC} > \text{ZnTPC}$. A comparison of these K values with other structurally similar macrocycles is also made in the table. The increase in K -values upon going from OEP to TPC derivatives can be attributed to the presence of eight strong electron-donating ethyl groups as the pyrrole

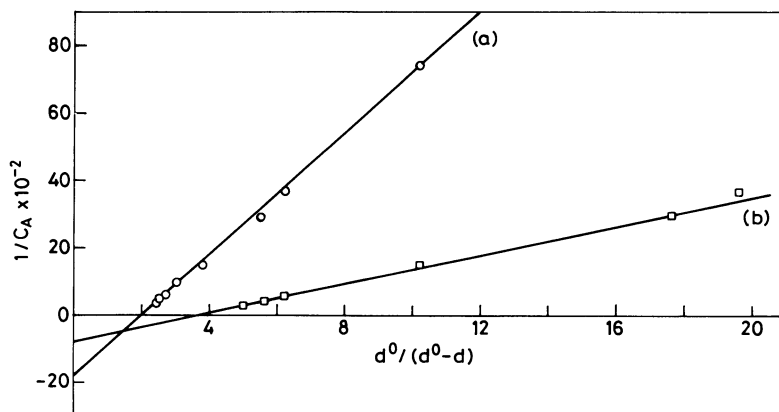


Fig. 3. Plot of $1/C_A$ versus $d^0/(d^0-d)$ for (a) CuOEP-TNF and (b) ZnOEP-TNF at 30°C .

substituents in OEP relative to TPC. Also, the presence of one reduced pyrrole ring in TPC decreases the conjugation thereby decreasing its donating ability. It should be mentioned here that the recent ESR study on the charge transfer complexation between OEP and TPP metal derivatives indicates that the effects of the interaction are generally much larger for OEP complexes than for TPP complexes, supporting our observation.¹⁶⁾ The higher values of K for pheophytin may arise due to the presence of an additional electron-rich cyclopentanone ring in pheophytin relative to chlorin. The limited study made here did not allow us to quantify the role of metal ions on the magnitude of K -values.

The ESR spectra of CuTPC and CuOEP and their 1:1 complexes in toluene at 100 K displayed characteristic features in parallel and perpendicular regions permitting evaluation of ESR parameter (Table 2).¹⁷⁾ The observed effects on ESR parameters upon complexation with TNF are (i) a small decrease in g_{\parallel} and g_{\perp} , and $A_{\parallel}^{\text{Cu}}$ values and (ii) a small increase in A_{\perp}^{Cu} , A_{\parallel}^{N} , and A_{\perp}^{N} values. These effects were consistent with the formation of molecular complex.¹⁸⁾ It was anticipated that the π -complexation would lead to a small change in the distribution of π -electrons over the macrocycle perturbing the electronic levels of central metal orbitals. Indeed, Iwaizumi et al.¹⁶⁾ in their recent EPR and ENDOR studies on OEP and TPP complexes of Co and Cu have shown that the charge transfer complex formation with π -acceptors perturbs the metal d-orbital states. If this is true, then one

Table 1. K Values for Complexation of TNF with Different Macrocycles at 30°C

Complex	$K/\text{dm}^{-3} \text{mol}^{-1}$	Reference
ZnTPC-TNF	47.0	This work
CuTPC-TNF	133.0	This work
ZnOEP-TNF	1083.0	This work
CuOEP-TNF	1863.0	This work
CuTPP-TNF	435.0±95	a)
ZnTPP-TNF	40.0±5.0	a)
ZnPheo-TNF	1030.0±8	b)

a) T. K. Chandrashekar and V. Krishnan, *Bull. Soc. Chim. Fr.*, Part I, 1-42, 1984. b) P.R. Droupadi and V. Krishnan, *J. Phys. Chem.*, **89**, 909 (1985).

Table 2. ESR Parameters for the Interaction of CuTPC and CuOEP with TNF in Toluene at 100 K

Complex	g_{\parallel}	g_{\perp}	$10^4 A_{\parallel}^{\text{Cu}}$	$10^4 A_{\perp}^{\text{Cu}}$	$10^4 A_{\parallel}^{\text{N}}$	$10^4 A_{\perp}^{\text{N}}$	α^2
			cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	
CuTPC	2.185	2.047	208.10	31.55	14.70	15.70	0.7949
CuTPC-TNF (1:1)	2.180	2.031	206.64	32.24	15.27	16.15	0.7771
CuOEP	2.187	2.047	204.90	25.10	17.01	14.58	0.7878
CuOEP-TNF (1:1)	2.180	2.043	202.10	26.20	17.30	15.12	0.7693
CuOEP-TNF ^{a)} (diluted in NiOEP)	2.175	2.044	202.00	25.00	17.50	14.90	0.7645

a) Taken from Ref. 18.

would expect the covalency of the (Cu-N) σ -bond to get perturbed upon complexation. Therefore, bonding parameter α^2 of the (Cu-N) σ -bond was calculated using the $A_{\parallel}^{\text{Cu}}$ hyperfine tensor using the equation:¹⁹⁾

$$\alpha^2 = - \left(\frac{A_{\parallel}^{\text{Cu}}}{P} \right) + (g_{\parallel} - 2) + \frac{3}{7} (g_{\perp} - 2) + C$$

A value of $P=0.0354 \text{ cm}^{-1}$ was used for copper complexes. From Table 2 it can be seen that the α^2 value decreases slightly upon complexation with TNF for both CuTPC and CuOEP. This decrease in α^2

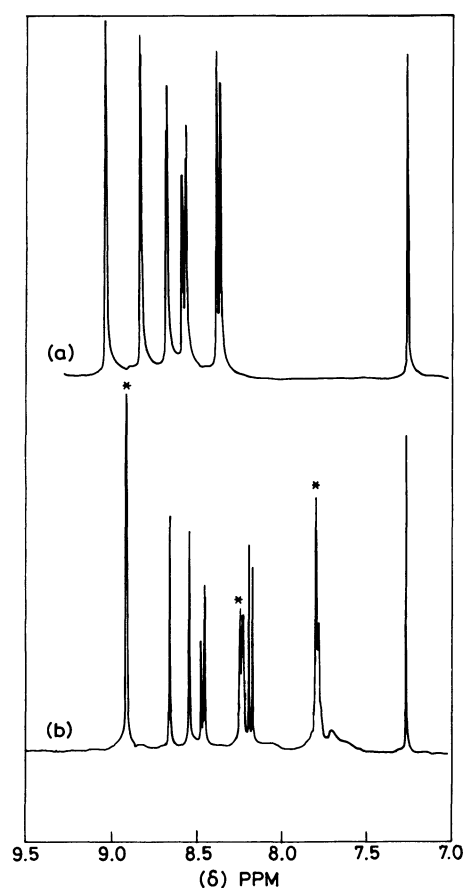


Fig. 4. ^1H NMR spectra of (a) TNF and (b) 1:1 complex of ZnTPC-TNF. The peaks marked * correspond to ZnTPC protons.

Table 3. ^1H NMR Data of TNF Protons and Their Shifts (ppm) in Molecular Complexes with ZnTPC and ZnOEP in CDCl_3

Complex	H_3	H_1	H_8	H_6	H_5
TNF	9.04	8.84	8.69	8.58	8.38
ZnTPC-TNF	-0.12	-0.18	-0.19	-0.37	-0.59
ZnOEP-TNF	-0.75	-1.16	-1.27	-1.33	-1.63

(-) Upfield shift.

value indicates an increase in the covalency of the (Cu-N) σ -bond. This was also supported by the experimental observation of a slight increase in both A_{\parallel}^{N} and A_{\perp}^{N} values upon interaction with TNF. These two observations qualitatively indicated that there is a slight rearrangement in the electronic environment of the central metal ion upon π -complexation.

In view of the observation that the interactions are essentially localized in the π -system of macrocycles, the ^1H NMR spectral studies were undertaken to arrive at the relative orientations of the molecules in solution. We examined the effect of complexation from proton resonance shifts experienced by acceptor and donors (ZnOEP and ZnTPC). Figure 4 shows the ^1H NMR of TNF and ZnTPC-TNF (1:1) complex. The assignment of TNF proton resonance was made according to the literature.²⁰ It is seen from the spectra that all the protons of TNF are upfield shifted in the complexes relative to pure TNF indicating that the TNF is positioned in the diamagnetic shielding zone of the macrocycle. A similar shielding of the acceptor proton resonances have been observed in the charge-transfer complexes with aromatic donors.²¹ The proton resonance of donor [β -pyrrole, *o*-, *m*-, and *p*-hydrogens of aryl groups in TPC and ethyl substituents in OEP] also showed both upfield and downfield shifts. The magnitude of shifts were very small (0.15–0.2 ppm). The shifts observed for different proton resonances of TNF upon complexation are listed in Table 3. Examination of Table 3 clearly reveals that the magnitude of shifts observed for TNF protons is much higher for ZnOEP complex than those observed for ZnTPC complex. This may be due to the stronger donating capacity of OEP relative to TPC. This was also reflected in the magnitude of *K*-values. Moreover, the table also illustrates that among the different protons of TNF, the upfield shift experienced by H_5 and H_6 are relatively large compared to other protons [H_3 , H_1 , and H_8] consistent with the observation made by Hill et al. for the interaction of Co(II) and Ni(II) mesoporphyrin dimethyl ester with TNF.²⁰ These results indicate that the protons H_5 and H_6 are closer to the π -system of the macrocycle relative to other protons of TNF.

The spectral data obtained in the present study provides some insight into the proposition of possible overlap structures of donor and the acceptor in solution. The observation that the strong IR vibrations of

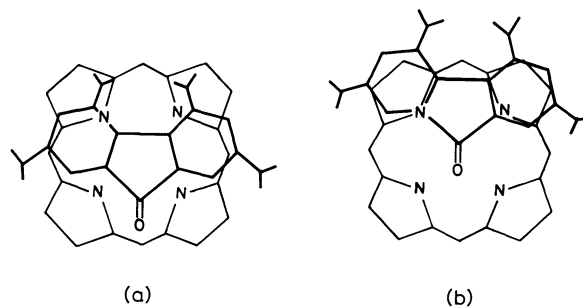


Fig. 5. Possible overlap pictures of the donor and the acceptor in solution. (a) The C_4 axis of the porphyrin is coincident with the C_5 axis of the fluorenone skeleton and (b) the carbonyl group of the fluorenone is tilted away from the metal ion (see text). For clarity the double bonds and the substituents on porphyrin are omitted.

the acceptor [$\nu(\text{CO})$ and $\nu(\text{NO}_2)$] were not perturbed upon complexation clearly rules out any possibility of coordinative type of interaction of the acceptor with the metal. Thus the major stabilization for the complexes arises from the π - π interaction of the donor and acceptor. Several structures could be perceived by juxtapositioning the acceptor over the macrocycle keeping the intermolecular distance at van der Waals interaction level. CPK models indicate that one can visualize two structures in terms of plane to plane overlap.

In structure (a), the acceptor can be placed over the porphyrin plane such that the axis passing through the five membered ring of the fluorenone is coincident with the C_4 axis of the porphyrin. This would dispose TNF protons over the porphyrin core. In this case all the protons of TNF would experience a uniform shielding since both the planes are exactly parallel. In the alternate structure, (b), the acceptor can be displaced over the porphyrin plane such that the carbonyl group of TNF is tilted away from the metal center (Fig. 5). This will bring H_5 and H_6 protons of TNF near to the porphyrin core. In this case the protons H_5 and H_6 of TNF are expected to shield more relative to other protons. ^1H NMR shift data seems to support the structure (b).^{5,18,20} These proposed overlap structures are in general agreement with the only reported X-ray crystallographic structure for the 1:2 [porphyrin-acceptor] charge transfer complex²³ of a nickel porphyrin with tetranitrofluorenone. In this structure the porphyrin and the fluorenone rings are both approximately planar and the angle between the porphyrin and the fluorenone ring is 11.4° . The only difference between the proposed structure in the present study and the X-ray study lies in the fact that the carbonyl oxygen is tilted towards the metal ion while in the present case it is tilted away from the metal ion. This difference might arise from the fact that the X-ray structure reported is for a 1:2 complex while our data is for a 1:1 complex. Secondly, the choice of the

porphyrin is different from the reported structural study. In conclusion, the solution structure described here is strongly supported by experimental data presented. Further confirmation of the structure must come from X-ray crystallographic studies.

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