

Thermodynamic Studies of the Molecular Interactions of 2,3-Dichloro-5,6-Dicyano-Benzoquinone with *meso*-Tetraarylporphyrins

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The interactions of 2,3-dichloro-5,6-dicyano-benzoquinone (DDQ) with free bases *para*-substituted *meso*-tetraphenylporphyrins (H₂T(4-X)PPs; X = OCH₃, CH₃, H and Cl) results adducts of composition 2:1 of DDQ to H₂T(4-X)PP, [(DDQ)₂(H₂T(4-X)PP)]. Formation constants, K, as well as other thermodynamic parameters, ΔH°, ΔS° and ΔG° of adducts were determined by UV-Vis titration method. Adducts have negative values of ΔH°, ΔS° and ΔG°. Adducts stabilities decrease in the order:
H₂T(4-OCH₃)PP > H₂T(4-CH₃)PP > H₂TPP > H₂T(4-Cl)PP.

Key Words: Charge transfer complexes, 2,3-Dichloro-5,6-dicyano-benzoquinone, Porphyrin.

INTRODUCTION

Studies of molecular interactions contribute to understanding of fundamental intermolecular forces, mimick biological functions and stimulate development of supramolecular devices¹. On the other hand, strong attractive interactions between π-systems leads to well known charge transfer adducts which has been subject of investigation²⁻⁷. Free base and metalloporphyrins are known to form charge transfer complexes with a variety of π-acceptors such as quinones^{5,8,9}. It has been demonstrated that 2,3-dichloro-5,6-dicyano-benzoquinone (DDQ) give charge transfer complexes of composition 2:1 of acceptor to donor when mixed with free base porphyrins⁵.

In this work, the thermodynamics of charge transfer complexes of DDQ with free base porphyrins H₂TPP (*meso*-tetraphenyl-porphyrin), H₂T(4-Cl)PP (*meso*-tetrakis-(4-chlorophenyl)porphyrin), H₂T(4-CH₃)PP (*meso*-tetrakis-(4-methylphenyl) porphyrin) and H₂T(4-OCH₃)PP (*meso*-tetrakis-(4-methoxyphenyl)porphyrin) are investigated.

EXPERIMENTAL

Benzaldehyde and *p*-substituted benzaldehydes (Merck and Fluka) were used as received. Pyrrole (Fluka) was distilled before use. Propionic acid and chloroform (Merck) employed. Chloroform solvent for UV-Vis measurements was distilled over K_2CO_3 before use. DDQ (Merck) was recrystallized twice from hot benzene-chloroform (2:3). UV-Vis measurements were carried out using a Scinco S-2100 UV-Vis spectrometer equipped with a Jeio Tech DTRC-620 DESK TOP REF. CIR. thermostat.

General procedure for the synthesis of *meso*-tetraarylporphyrins¹⁰: *meso*-Tetrakis(4-methoxyphenyl)porphyrin: 4-methoxybenzaldehyde (10 mmol) was mixed with propionic acid (35 mL) and nitrobenzene (15 mL). Pyrrole (10 mmol) was added and the mixture was kept at 120°C for 1 h. On cooling, the porphyrin precipitated directly from the reaction mixture and was isolated by filtration and purified by chromatography on a neutral alumina column.

Spectrophotometry measurements: UV-Vis measurements were carried out by titration method at 5, 10, 15, 20 and 25 ± 1°C. In a typical measurement, a solution of 2.5 mL of $H_2T(4-OCH_3)PP$ (2.5×10^{-6} M) in chloroform was titrated with DDQ (0.001 M). UV-Vis spectra were recorded in range 396-710 nm when reaction reached to equilibrium (Fig. 1). In this range of spectra about 20-25 wavelengths which had suitable variations of absorbance upon addition of DDQ were selected and the equilibrium constants and other thermodynamic parameters of adducts were calculated. Equilibrium constants were calculated by the SQUAD program¹¹.

RESULTS AND DISCUSSION

On addition of DDQ to a $H_2T(4-X)PP$ solution in chloroform, the solution turns to green because DDQ forms a charge transfer adduct with free base porphyrin. This adduct has mole ratio 2:1 of DDQ to $H_2T(4-X)PP$ and can be separated as a solid product by mixing of free base porphyrin with an excess of DDQ in $CHCl_3$ or CH_2Cl_2 followed by evaporation of the solvent at room temperature⁵.

Stability of these charge transfer adducts decrease in elevated temperature, so that a green solution of adduct at 5°C turns to a purple solution of free base porphyrin by heating of adduct solution to 40°C. It shows that by increasing of temperature the corresponding equilibrium is shifted to the left, eqn. 1.



UV-Vis analysis: By interaction of $H_2T(4-X)PP$ with DDQ, the original peaks of free base porphyrin vanished and two new peaks were appeared (Fig. 1, Table-1). For example, by addition of DDQ to a solution

of H₂T(4-Cl)PP the original peaks of free base (418, 514, 550, 589, 645 nm) were disappeared and new peaks were observed at 448 and 666 nm with a clear isosbestic point at 430 nm.

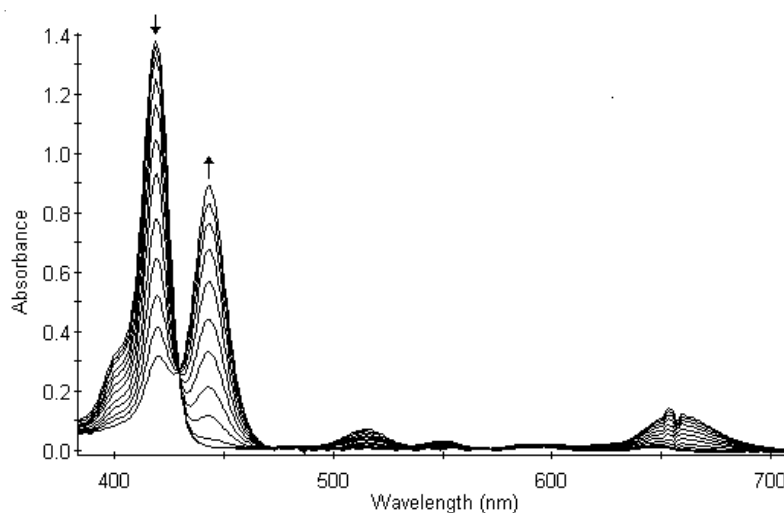


Fig. 1. Titration spectra of [DDQ₂H₂T(4-OCH₃)PP] adduct: by addition of DDQ (0.001 M) to a solution of H₂T(4-OCH₃)PP (2.5 × 10⁻⁶ M, 2.5 mL) in chloroform in an UV/Vis cell at 5°C, the [DDQ₂H₂T(4-OCH₃)PP] adducts were formed, the isosbestic point at 433 nm

TABLE-1
UV-VIS PEAKS [λ (nm) IN CHCl₃] OF FREE BASE H₂T(4-X)PPS
AND [DDQ₂H₂T(4-X)PP] ADDUCTS

Compound	λ (nm)				
H ₂ TPP	417	514	549	589	646
[DDQ ₂ H ₂ TPP]	445				663
H ₂ T(4-Cl)PP	418	514	550	589	645
[DDQ ₂ H ₂ T(4-Cl)PP]	448				665
H ₂ T(4-CH ₃)PP	419	516	552	591	647
[DDQ ₂ H ₂ T(4-CH ₃)PP]	447				677
H ₂ T(4-OCH ₃)PP	421	518	555	593	650
[DDQ ₂ H ₂ T(4-OCH ₃)PP]	453				688

Thermodynamic studies: The thermodynamic parameters were investigated for these interactions. The equilibrium constants, K, were determined at several temperatures by analyzing the concentration and temperature dependence of UV-Vis absorptions by the SQUAD program (Table-2). These absorptions were analyzed for 1:1, 2:1 and simultaneous

formation of the 1:1 and 2:1 adducts in solution, respectively. For the proposed models, the formation of adducts with mole ratio 2:1 of acceptor to donor had the best fitting. Van't Hoff plots of these formation constants, K , led to the other thermodynamic parameters ΔH° , ΔS° and ΔG° (Table-3).

TABLE-2
log K FOR DDQ-H₂T(4-X)PP ADDUCTS IN CHCl₃

Adduct	log K				
	5°C	10°C	15°C	20°C	25°C
[DDQ ₂ H ₂ T(4-Cl)PP]	9.50 ± 0.01	9.24 ± 0.02	9.09 ± 0.03	8.92 ± 0.01	8.70 ± 0.02
[DDQ ₂ H ₂ TPP]	9.66 ± 0.02	9.41 ± 0.01	9.24 ± 0.01	9.06 ± 0.03	8.83 ± 0.01
[DDQ ₂ H ₂ T(4-CH ₃)PP]	10.11 ± 0.01	9.85 ± 0.01	9.64 ± 0.03	9.45 ± 0.01	9.24 ± 0.02
[DDQ ₂ H ₂ T(4-OCH ₃)PP]	10.34 ± 0.02	10.12 ± 0.02	9.93 ± 0.04	9.69 ± 0.01	9.42 ± 0.03

The data of Table-3 show that adducts stabilities undergo a regular increase from H₂T(4-Cl)PP to H₂TPP, H₂T(4-CH₃)PP and H₂T(4-OCH₃)PP. For example, at 10°C the following order of formation constants has been observed:



Table-3 gives the thermodynamic parameters for the charge transfer complexes of DDQ with H₂T(4-X)PPs in chloroform.

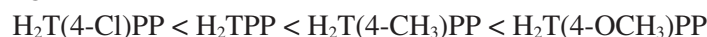
TABLE-3
THERMODYNAMIC PARAMETERS FOR INTERACTION OF DDQ
WITH H₂T(4-X)PPs IN CHLOROFORM

Adduct	$-\Delta H^\circ$	$-\Delta S^\circ$	$-\Delta G^\circ$
[DDQ ₂ H ₂ T(4-Cl)PP]	61 (±3)	38 (±10)	49 (±3)
[DDQ ₂ H ₂ TPP]	64 (±3)	45 (±10)	50 (±3)
[DDQ ₂ H ₂ T(4-CH ₃)PP]	68 (±2)	52 (±7)	52 (±3)
[DDQ ₂ H ₂ T(4-OCH ₃)PP]	72 (±4)	61 (±12)	54 (±4)

The results show that strength of interactions, between H₂T(4-X)PPs and DDQ, significantly depends on the X-substitute of H₂T(4-X)PPs. The further electron releasing property of X-substitute makes this interactions more favourable while the electron withdrawing X-substitute has an unfavourable effect on this interaction.

The adducts, [DDQ₂H₂T(4-X)PP], have negative values of ΔH° , ΔS° and ΔG° . On the basis of ΔH° values, reactions that carried out between DDQ and different H₂T(4-X)PPs are exothermic and negative values of ΔG° make these reactions favourable under present experimental conditions. Both the free energy and the enthalpies of adducts become more negative through the series H₂T(4-Cl)PP, H₂TPP, H₂T(4-CH₃)PP and to H₂T(4-OCH₃)PP, considerably, which indicates stronger interaction along this sequence.

In addition, the negative values of ΔS° refer to an associative reaction which occurs between donor and acceptor molecules. The [DDQ₂H₂T(4-OCH₃)PP] adducts have the most negative values of ΔG° among these systems which it return to a stronger interaction in this adduct relative to the other members of the series. The present results show that the interactions of various H₂T(4-X)PPs with DDQ alter with porphyrin basicity according to this order:



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