

## COMPARISON OF ACCEPTOR PROPERTIES FOR INTERACTION OF TCNE AND DDQ WITH SOME FREE BASE PORPHYRINS

Abedien Zabardasti\*, Leyla Shaebani, Ali Kakanejadifard and Fatemeh Faragi Morchegani

Chemistry Department, College of Sciences, Lorestan University, Khoramabad, Iran

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**ABSTRACT.** The interactions of free base porphyrins with tetracyanoethylene and 2,3-dichloro-5,6-dicyanobenzoquinone as acceptors result in charge-transfer adducts of composition 2:1 of acceptor to donor, [(acceptor)<sub>2</sub>(donor)]. Formation constants,  $K$ , as well as the thermodynamic parameters,  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  were determined by UV-Vis titration method for the adducts. Surprisingly, the values of  $\Delta S^\circ > 0$  and  $\Delta H^\circ > 0$  for TCNE are in contrast to  $\Delta H^\circ < 0$  and  $\Delta S^\circ < 0$  for DDQ. Negative values of  $\Delta G^\circ$  make these interactions favorable in the both cases.

**KEY WORDS:** DDQ, TCNE, Free base porphyrin, Thermodynamic properties

### INTRODUCTION

The existence of novel and unique physical properties of electron donor-acceptor complexes, such as magnetism [1], conductivity, and superconductivity [2], has generated considerable interest in recent years. It has been discovered that through control of external parameters such as temperature, pressure, and magnetic field strength, the magnitude of these properties can be tuned [3]. Although these materials are rapidly gaining extensive employment as integrated circuit components and sensors for mobile phones [4], widespread potential exists for other applications. These complexes have been experimentally characterized for many years, yet much of the chemistry and physics of these materials that result in such unusual properties only now is beginning to be discovered. For new applications to emerge, it is necessary to first gain a deeper understanding of the fundamental characteristics of these materials. Intermolecular charge-transfer (CT) complexes are formed when electron donors and electron acceptors interact, a general phenomenon in organic chemistry [5]. Mulliken [6] considered such complexes to arise from a Lewis acid-Lewis base type of interaction, the bonding between the components of the complex being postulated to arise from the partial transfer of a  $\pi$  electron from the base to an unoccupied orbital of the acid [7]. Tetracyanoethylene (TCNE) and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) readily exhibit CT complexes when mixed with molecules possessing  $\pi$ -electrons or groups having atoms with an unshared electron pair. Interaction of TCNE and DDQ as  $\pi$ -acceptors with hydrocarbon donors such as cycloalkanes, alkenes, alkynes, aromatic molecules, free base and metalloporphyrins have been of interest [7-20]. These interactions result in formation of CT complexes between the acceptor and donor molecules. Previous studies demonstrated that molecular adducts of free base porphyrins (FBPs), such as [H<sub>2</sub>T(4-X)PP]; (X= OCH<sub>3</sub>, CH<sub>3</sub>, H or Cl) with TCNE and DDQ have mole ratio 2:1 of acceptor to donor, [A<sub>2</sub>(FBP)] (Figure 1) [10, 11].

This work concerns thermodynamic studies of CT complexes of several free base tetraaryl- as well as tetraalkylporphyrins with TCNE and DDQ. It is instructive to compare their thermodynamic parameters to improve insight on their interactions and the efficiency of their applications. The free base porphyrins (*meso*-tetraphenylporphyrin) H<sub>2</sub>TPP, (*meso*-tetrakis-(4-chlorophenyl)porphyrin) H<sub>2</sub>T(4-Cl)PP, (*meso*-tetrakis-(4-methylphenyl)porphyrin) H<sub>2</sub>T(4-CH<sub>3</sub>)PP, (*meso*-tetrakis-(4-methoxyphenyl)porphyrin) H<sub>2</sub>T(4-OCH<sub>3</sub>)PP, (*meso*-tetra-*n*-butyl-

\*Corresponding author. E-mail: zabardasti.a@lu.ac.ir

porphyrin)  $H_2TnBP$ , and (*meso*-tetrakis-*tert*-butylporphyrin)  $H_2TtBP$  were considered for this study. To the best of the knowledge there exists few report in this context [21].

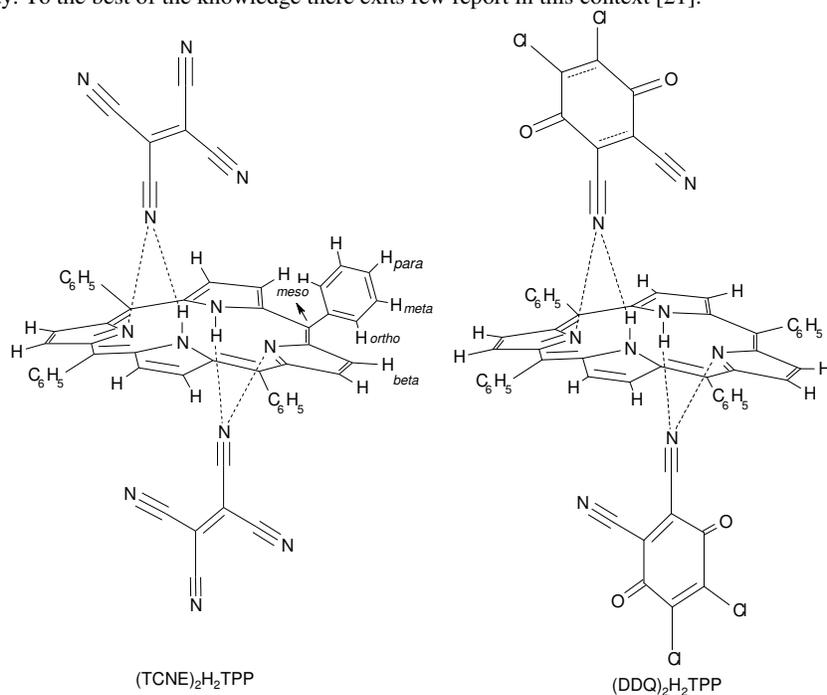


Figure 1. Schematic representation of  $[A_2(H_2TPP)]$  adduct [8, 15].

## EXPERIMENTAL

### Chemicals

Benzaldehyde and *para*-substituted benzaldehydes, pivaldehyde, and butyraldehyde (Merck and Fluka) were used as received. Pyrrole (Fluka) was distilled before use. Propionic acid and chloroform (Merck) employed for synthesis and purification of free base porphyrins were used as received. 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). TCNE recrystallized from chlorobenzene and twist sublimed before used.

### Instruments

UV-Vis measurements were carried out using a Scinco S-2100 UV-Vis spectrophotometer equipped with a Jeio Tech DTRC-620 DESK TOP REF.CIR.thermostat. The proton NMR spectra were run on a Bruker Avance DPX 250 MHz spectrophotometer. Mass data were obtained from a Shimadzu GC-MS model QP5050 instrument.

*Synthesis and characterizations*

*meso*-Tetraarylporphyrins [22], *meso*-tetra-*n*-butylporphyrin, and *meso*-tetrakis-*tert*-butylporphyrin were prepared by reported methods [23]. Adducts were prepared from mixing of DDQ and TCNE (2 mmol) with a solution of H<sub>2</sub>T(4-X)PP (1 mmol) in dry chloroform at room temperature. The <sup>1</sup>H NMR and UV-Vis data of the adducts as well as those of the free base porphyrins are given in Tables 1 and 2.

Table 1. UV-Vis peaks ( $\lambda_{\max}$ /nm in CHCl<sub>3</sub>) of FBPs and [(A)<sub>2</sub>FBP] adducts.

Compound	$\lambda_{\max}$ /nm	Compound	$\lambda_{\max}$ /nm
H <sub>2</sub> TPP	417, 514, 549, 589, 646	H <sub>2</sub> T(4-OCH <sub>3</sub> )PP	421, 518, 555, 593, 650
<b>1</b>	441 - - - 653	<b>4</b>	454 - - - 653
<b>7</b>	445 - - - 663	<b>10</b>	453 - - - 688
H <sub>2</sub> T(4-Cl)PP	418, 514, 550, 589, 645	H <sub>2</sub> TnBP	417, 520, 555, 600, 659
<b>2</b>	443 - - - 652	<b>5</b>	425 - - - 636
<b>8</b>	448 - - - 665	<b>11</b>	433 - - - 643
H <sub>2</sub> T(4-CH <sub>3</sub> )PP	419, 516, 552, 591, 647	H <sub>2</sub> TtBP	448, 552, 596, 628, 691
<b>3</b>	445 - - - 653	<b>6</b>	451 - - - 690
<b>9</b>	447 - - - 677	<b>12</b>	455 - - - 692

Table 2. <sup>1</sup>H NMR of free base tetraarylporphyrins and their adducts with DDQ and TCNE.

Compound	$\delta$ N-H	$\delta$ H <sub><i>m,p</i></sub>	$\delta$ H <sub><i>o</i></sub>	$\delta$ H <sub><math>\beta</math></sub>	$\delta$ CH <sub>3</sub>
H <sub>2</sub> TPP					
<b>1</b>	-2.76	7.75	8.24	8.85	-
<b>7</b>	-1.26	8.04	8.64	8.81	-
H <sub>2</sub> T(4-Cl)PP	-0.40	7.98	8.67	8.59	-
<b>2</b>	-2.86	7.75	8.14	8.85	-
<b>8</b>	-1.16	8.05	8.57	8.81	-
H <sub>2</sub> T(4-CH <sub>3</sub> )PP	-0.29	8.00	8.56	8.56	-
<b>3</b>	-2.77	7.56	8.11	8.86	2.71
<b>9</b>	-1.20	7.83	8.52	8.76	2.80
H <sub>2</sub> T(4-CH <sub>3</sub> O)PP	-0.38	7.80	8.55	8.55	2.77
<b>4</b>	-2.82	7.27	8.11	8.86	3.95
<b>10</b>	-0.92	7.55	8.57	8.68	4.17
<b>12</b>	-0.11	7.50	8.59	8.48	4.11

Adducts of H<sub>2</sub>TnBP and H<sub>2</sub>TtBP, which have not been reported previously, were prepared in the same manner and investigated by means of <sup>1</sup>H NMR, FT-IR, UV-Vis, and mass spectroscopy methods (Tables 1, 3, and 4).

Table 3. <sup>1</sup>H NMR of free base tetraalkylporphyrins and their adducts with DDQ and TCNE.

Compound	δ N-H	δCH <sub>3</sub>	δCH <sub>2</sub>	δCH <sub>2</sub>	δCH <sub>2</sub>	δ H <sub>β</sub>
H <sub>2</sub> TnBP	-2.61	1.10	1.73-1.91	2.41-2.58	4.88	9.45
<b>5</b>	-3.45	1.22	1.93	2.54	4.83	9.03
<b>11</b>	-3.45	1.20	1.90	2.55	4.81	9.02
H <sub>2</sub> TtBP	1.52	2.01	-	-	-	9.08
<b>6</b>	-0.4	2.13	-	-	-	8.14
<b>12</b>	-0.6	2.10	-	-	-	8.16

Table 4. Some fragments from mass spectra of tetraalkylporphyrins adducts.

Adduct	Fragment	<i>m/z</i>	Adduct	Fragment	<i>m/z</i>
<b>5</b>	M <sup>+</sup>	734	<b>11</b>	M <sup>+</sup>	932
	M – (3CN, 1H)	655		M – (CN)	906
	M – (3CN, 1H, 2CH <sub>3</sub> )	625		M – (nPr, Cl)	854
	M – (3CN, 3CH <sub>3</sub> , CH <sub>3</sub> CH <sub>2</sub> )	581		M – (2nPr)	846
	M – (3CN, 1H, 4CH <sub>3</sub> CH <sub>2</sub> )	539		M – (2nPr, CN)	820
	M – (2CN, 4CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> )	510		M – (3nPr, CN)	787
	M – (3CN, 1H, 4CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> )	481		M – (4nPr, CN)	734
			M – (4nPr, 2Cl)	689	
<b>6</b>	M <sup>+</sup>	790	<b>12</b>	M <sup>+</sup>	988
	M – (2CN)	738		M – (2Cl)	917
	M – (1H, CH <sub>3</sub> , C(CH <sub>3</sub> ) <sub>3</sub> )	717		M – (4CN)	884
	M – (CN, 2CH <sub>3</sub> , C(CH <sub>3</sub> ) <sub>3</sub> )	677		M – ( <i>t</i> -Bu, 2Cl)	860
	M – (CN, 2H, 2C(CH <sub>3</sub> ) <sub>3</sub> )	648		M – ( <i>t</i> -Bu, 2Cl, CN)	834
	M – (TCNE, 2CH <sub>3</sub> , C(CH <sub>3</sub> ) <sub>3</sub> )	575		M – (DDQ)	761
	M – (2TCNE)	535		M – (4 <i>t</i> -Bu)	760
	M – (2TCNE, 1H, 2C(CH <sub>3</sub> ) <sub>3</sub> )	419		M – (4 <i>t</i> -Bu, 2Cl)	689

#### Solution studies

UV-Vis measurements were carried out by titration method at 5, 10, 15, 20, and 25 ± 1 °C. In a typical experiment, a solution of 2.0 mL of H<sub>2</sub>TnBP (2.5 × 10<sup>-6</sup> M) in chloroform was titrated with DDQ (0.001 M). UV-Vis spectra were recorded until the reaction reached equilibrium (Figure 2). In this spectrum about 10-15 wavelengths had suitable variations of absorbance upon addition of DDQ and these were selected for the equilibrium constant measurements of the adducts and other thermodynamic parameter were subsequently calculated. Equilibrium constants were obtained by the SQUAD program [24].

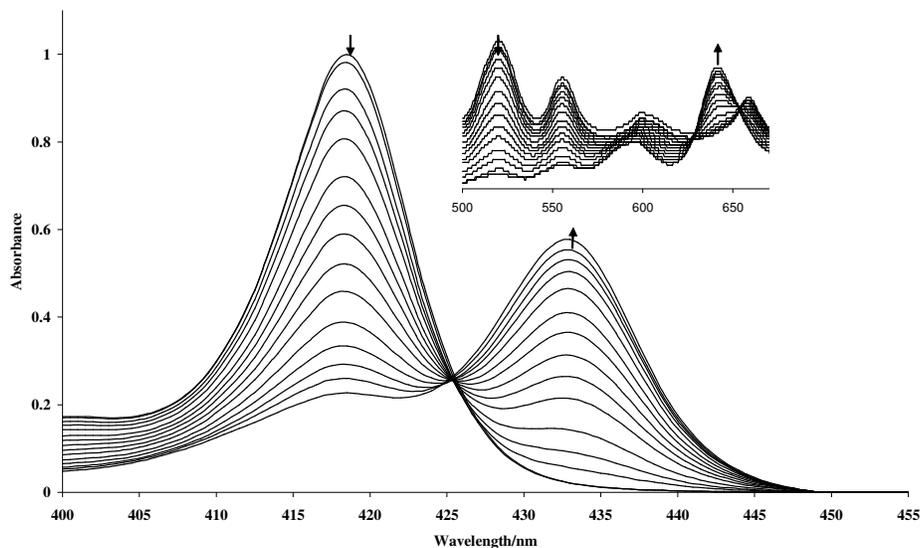


Figure 2. Titration spectra of  $H_2TnBP$  with DDQ. Peaks at 433 and 643 nm are related to the adduct, isosbestic point at 425 nm.

## RESULTS AND DISCUSSION

On addition of A to a solution of FBP in chloroform a CT adduct was formed according to Equation 1:



These adducts with mole ratio 2:1 of A to FBP are denoted as: [(TCNE) $_2$ H $_2$ TPP] (**1**), [(TCNE) $_2$ H $_2$ T(4-Cl)PP] (**2**), [(TCNE) $_2$ H $_2$ T(4-CH $_3$ )PP] (**3**), [(TCNE) $_2$ H $_2$ T(4-OCH $_3$ )PP] (**4**), [(TCNE) $_2$ H $_2$ TnBP] (**5**), [(TCNE) $_2$ H $_2$ TiBP] (**6**), [(DDQ) $_2$ H $_2$ TPP] (**7**), [(DDQ) $_2$ H $_2$ T(4-Cl)PP] (**8**), [(DDQ) $_2$ H $_2$ T(4-CH $_3$ )PP] (**9**), [(DDQ) $_2$ H $_2$ T(4-OCH $_3$ )PP] (**10**), [(DDQ) $_2$ H $_2$ TnBP] (**11**), and [(DDQ) $_2$ H $_2$ TiBP] (**12**) [10, 11, 21]. The adducts **1-4** and **7-10** have been synthesized and characterized by IR, UV-Vis,  $^1H$  NMR, and  $^{13}C$  NMR spectroscopic methods, previously [10, 11]. Our IR, UV-Vis, and  $^1H$  NMR results for these adducts are in agreement with data previously reported (Tables 1 and 2) [10, 11].

Adducts **5**, **6**, **11**, and **12** have not been reported previously. They have been characterized by FT-IR, UV-Vis,  $^1H$  NMR, and mass spectroscopic methods.

### $^1H$ NMR analysis

The  $^1H$  NMR spectra of the porphyrin moiety of the adducts show clear differences with respect to corresponding FBP. Upon complexation the signals corresponding to N-H, H $_o$ , H $_{m,p}$ , and CH $_3$ - or -OCH $_3$  protons of tetraarylporphyrin are moved downfield, while H $_{\beta}$  has an upfield shift (Table 2). While the signals corresponding to H $_{\beta}$  have an upfield shift in the tetraalkylporphyrins, the N-H signal in **5**, and **11** is moved downfield whereas for **6** and **12** an upfield shift is observed upon adduct formation (Table 3).

*Infra-red spectra*

The most significant difference which emerges from a comparison of the vibrational spectra of FBPs and their complexes is the disappearance of the band  $\nu(\text{N-H})$  as a consequence of the complex formation. It seems that the N-H is hydrogen bonded to the N or O atoms of TCNE and DDQ, respectively, as acceptor. The IR-spectra of free TCNE shows CN stretching frequencies at 2225 and 2270  $\text{cm}^{-1}$ . The significant shift of these vibrations toward lower frequencies (2214  $\text{cm}^{-1}$ ) on complexation is indicative of charge transfer from FBPs to  $\pi^*$  of a CN group of TCNE which leads to a weakening of this bond. Similarly for DDQ, the CO and CN stretching frequencies that appeared at 1675 and 2245  $\text{cm}^{-1}$  were shifted to 1651 and 1696  $\text{cm}^{-1}$  and CN vibration shift to 2229  $\text{cm}^{-1}$  upon complex formation.

*UV-Vis analysis*

By interaction of FBP with A, the original peaks of FBP vanished and new peaks appeared (Table 1 and Figure 2). For example, by addition of DDQ to a solution of  $\text{H}_2\text{TnBP}$  the original peaks of the free base (417, 520, 555, 600, and 659 nm) disappeared and new peaks appeared at 433 and 643 nm (Figure 2). The presence of clear isosbestic points at 423 and 425 nm means that the CT complexes were formed through an equilibrium reaction (Figures 2-5) [25].

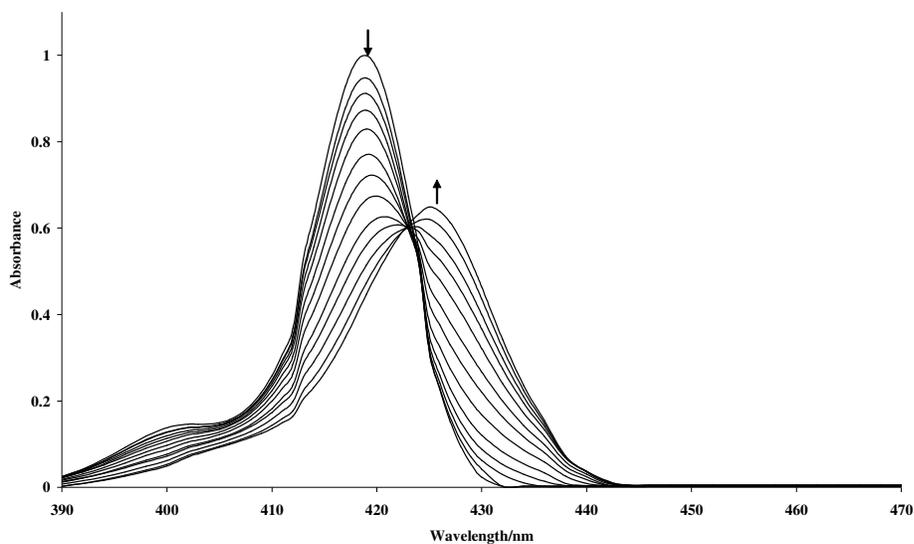


Figure 3. Titration spectra of  $\text{H}_2\text{TnBP}$  with TCNE, Peak at 425 nm is related to the adduct, isosbestic point at 423 nm.

Temperature has opposite effects on the stability of adducts of DDQ and TCNE with FBPs. For DDQ, the interactions were weakened at elevated temperatures, so that a solution of adduct at 5 °C dissociates to FBP and DDQ on raising the temperature to 35 °C (Figure 4). It shows that by increasing temperature the equilibrium in equation 1 is shifted to the left. On the other hand, the interaction of TCNE with FBP is increased at elevated temperatures, so that a purple solution of reactant at 5 °C turns to a green solution of adduct at 35 °C (Figure 5). It shows that for TCNE the equilibrium in Equation 1 is moved to the right at higher temperatures.

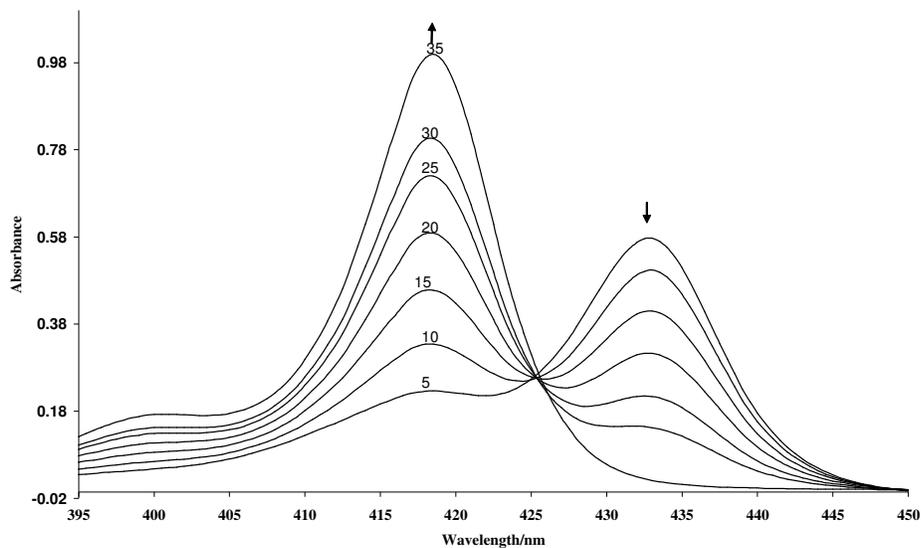


Figure 4. Temperature dependent spectra of the  $(\text{DDQ})_2\text{H}_2\text{TnBP}$  adduct. Peak at 433 nm is related to adduct, isosbestic point: 425 nm. At evaluated temperatures intensity of adduct (433 nm) decreased in contrast intensity of FBP (417 nm) increased.

#### Thermodynamic studies

Thermodynamic parameters were investigated for these interactions by the UV-Vis spectrometry method. The formation constants,  $K$ , were determined at several temperatures by analyzing the concentration and temperature dependence of the UV-Vis absorptions using the SQUAD program, Table 5. Van't Hoff plots of these formation constants,  $K$ , led to the thermodynamic parameters  $\Delta H^\circ$ ,  $\Delta S^\circ$  (Table 6). Then  $\Delta G^\circ$  was calculated using equation 2.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (2)$$

Table 5. The log  $K$  for  $[(A)_2\text{FBP}]$  adducts in  $\text{CHCl}_3$ .

Adduct	log K				
	5 °C	10 °C	15 °C	20 °C	25 °C
<b>1</b>	5.72±0.02	6.47±0.02	6.79±0.01	7.33±0.03	8.03±0.02
<b>2</b>	4.40±0.01	5.01±0.02	5.42±0.01	6.20±0.03	6.45±0.02
<b>3</b>	6.10±0.02	6.65±0.03	7.06±0.01	7.88±0.02	8.36±0.01
<b>4</b>	6.30±0.02	6.87±0.03	7.30±0.01	8.00±0.03	8.62±0.01
<b>5</b>	6.03±0.02	6.33±0.03	6.82±0.01	7.06±0.03	7.30±0.01
<b>6</b>	7.51±0.02	7.86±0.03	8.29±0.01	8.59±0.02	8.80±0.01
<b>7</b>	9.66±0.02	9.41±0.01	9.24±0.01	9.06±0.03	8.83±0.01
<b>8</b>	9.50±0.01	9.24±0.02	9.09±0.03	8.92±0.01	8.70±0.02
<b>9</b>	10.11±0.01	9.85±0.01	9.64±0.03	9.45±0.01	9.24±0.02
<b>10</b>	10.34±0.02	10.12±0.02	9.93±0.04	9.69±0.01	9.42±0.03
<b>11</b>	9.45±0.02	9.30±0.02	9.13±0.04	8.95±0.01	8.81±0.03
<b>12</b>	10.17±0.02	10.01±0.02	9.81±0.04	9.62±0.01	9.48±0.03

The data in Table 5 shows that stability of adducts for both DDQ and TCNE undergo a regular increase from H<sub>2</sub>T(4-Cl)PP to H<sub>2</sub>TPP, H<sub>2</sub>T(4-CH<sub>3</sub>)PP, and H<sub>2</sub>T(4-OCH<sub>3</sub>)PP; also adducts of H<sub>2</sub>TtBP are more stable than H<sub>2</sub>TnBP. These sequences are in agreement with the electron releasing property of FBPs.

Table 5 shows that formation constants of [(DDQ)<sub>2</sub>FBP] adducts **7-12** decreased at higher temperatures. In contrast, for [(TCNE)<sub>2</sub>FBP] adducts **1-6**, formation constants increased at higher temperatures. This indicates that the weakest interaction for TCNE occurs at 5 °C whereas for DDQ an inverse correlation with the stronger interaction occurring at 5 °C (Figures 4 and 5). This discrepancy might be due to presence of different mechanisms for CT between FBPs and these acceptors. Although DDQ and TCNE are both strong  $\pi$ -acceptors and oxidizing agents in organic chemistry, this dual influence of temperatures on their interactions with FBPs is an interesting point that has been considered only rarely previously. Also our results show that DDQ is a stronger acceptor than TCNE.

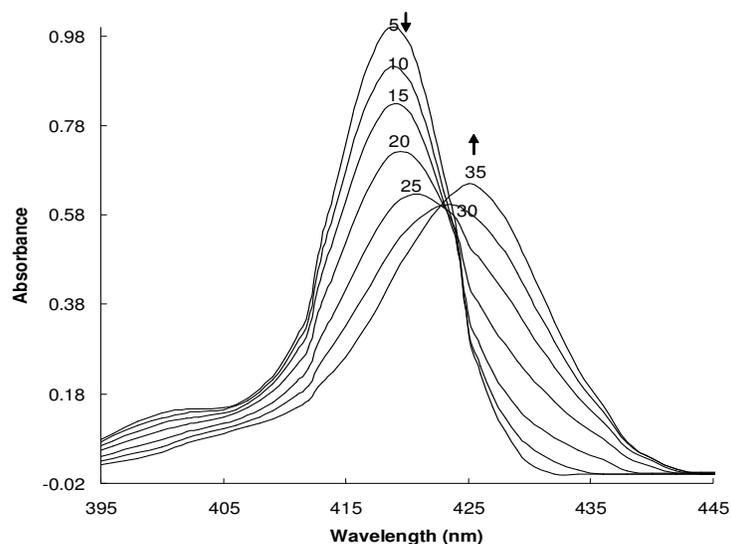


Figure 5. Temperature dependent spectra for the (TCNE)<sub>2</sub>H<sub>2</sub>TnBP adduct. Peak at 425 nm is related to adduct, isosbestic point: 423 nm. At evaluated temperatures intensity of adduct (433 nm) increased and intensity of FBP (417 nm) decreased, in contrast to Figure 4.

Table 6 gives the thermodynamic parameters ( $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$ ) for CT interactions of TCNE and DDQ with FBPs in chloroform. The results show that the *meso*-group of FBPs significantly affected their interactions with acceptor species. While the electron releasing property of a *meso*-substituent is along with a stronger interaction, in contrast its electron withdrawing character leads to weaker interactions.

Table 6. The thermodynamic parameters for [(A)<sub>2</sub>FBP] adducts in CHCl<sub>3</sub><sup>a</sup>.

TCNE Adduct	$\Delta H^\circ$	$\Delta S^\circ$	$\Delta G^\circ$	DDQ Adduct	$\Delta H^\circ$	$\Delta S^\circ$	$\Delta G^\circ$
<b>1</b>	174(±12)	734(±43)	-45(±12)	<b>7</b>	-64(±3)	-45(±10)	-50(±3)
<b>2</b>	168(±12)	688(±43)	-37(±12)	<b>8</b>	-61(±3)	-38(±10)	-49(±3)
<b>3</b>	179(±10)	761(±35)	-47(±10)	<b>9</b>	-68(±2)	-52(±7)	-52(±3)
<b>4</b>	183(±10)	784(±33)	-51(±10)	<b>10</b>	-72(±4)	-61(±12)	-54(±4)
<b>5</b>	107(±7)	495(±26)	-40(±7)	<b>11</b>	-53(±1)	-8(±4)?	-51(±1)
<b>6</b>	109(±6)	529(±22)	-49(±6)	<b>12</b>	-63(±3)	-26(±11)	-70(±3)

<sup>a</sup> $\Delta H^\circ$ (kJ mol<sup>-1</sup>) and  $\Delta S^\circ$  (J K<sup>-1</sup> mol<sup>-1</sup>);  $\Delta G^\circ$  at 25 °C (kJ mol<sup>-1</sup>).

For [(TCNE)<sub>2</sub>FBP] adducts,  $\Delta H^\circ$  and  $\Delta S^\circ$  are positive but in the case of [(DDQ)<sub>2</sub>FBP] they are negative. Since interactions of FBPs with various acceptors are exothermic [26-31], these endothermic interactions for a strong  $\pi$ -acceptor such as TCNE are quite interesting. It seems that the presence of a strong self  $\pi$ -stacking between initial TCNE molecules make its dissolution endothermic or enthalpically unfavorable, on the other hand dissolving of such  $\pi$ -stacks will be entropically a favorable phenomena.

The standard Gibbs free energies,  $\Delta G^\circ$ , of interactions are negative in both series of CT complexes. It seems that for TCNE, contribution of an  $\Delta S^\circ$  value greater than zero is more effective than the positive  $\Delta H^\circ$  term in the equation 2. Thus, the negative values of  $\Delta S^\circ$  gives a negative value for  $\Delta G^\circ$ . Negative values of  $\Delta G^\circ$  show that interactions of both TCNE and DDQ with FBPs are favorable with the same ordering as electron releasing property of FBPs.

The main outcome in this work is "a positive  $\Delta H^\circ$  for [(TCNE)<sub>2</sub>FBP] adducts". Our results show that interactions of DDQ and TCNE with free base porphyrins are exothermic and endothermic, respectively. In view of this discrepancy for enthalpies of interactions, further studies are certainly necessary to clarify this essential issue. Also the electron acceptor properties of DDQ and TCNE depend on temperature and this might be important to consider for facilitating their subsequent applications. We plan to investigate these effects for other donors in future studies.

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