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Spectroscopic studies on the intermolecular charge transfer interaction of Fe(II)- and Fe(III)-phthalocyanines with 2,3,5,6-tetrachloro-1,4-benzoquinone and its application in colorimetric sensing of amino acids and amines

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1. Introduction

Electron-transfer reactions play an important role in biological process such as photosynthesis and oxidative processes involved in the degradation of biological material in living cells [1]. Phthalocyanines (Pcs) and Phorphyrins (Por) have been used as electron donor building blocks in artificial photosynthetic system due to their strong absorption in solar spectrum for light harvesting, their redox potentials enabling photoelectron transfer and their structural tenability by chemical synthesis [2]. Metalophthalocyanines (MPcs) have also enjoy usage in printing inks, catalysis, display devices, data storage, chemical sensors, gas sensors, solar cells, organic light emitting devices, photovoltaic cells, semiconductive materials and photodynamic therapy [3–9].

Pcs are excellent candidates for electrocatalytic and photocatalytic processes because of its extensive redox chemistry coupled with their high thermal and chemical stability. It is also established that the redox characteristics of Pcs depend on metal ion, oxidation state, solvent, substituent, etc. The most colorful phthalocyanine solutions are obtained during redox chemistry that involves the ring or the central metal ion [10]. The most significant use of phthalocyanine complexes to date results directly from their

ABSTRACT

The interactions of Fe^{II}Pc and Fe^{III}Pc with π -acceptor 2,3,5,6-tetrachloro-1,4-benzoquinone (*p*-chloranil, *p*-CHL) have been investigated spectroscopically (UV/vis and FT-IR) and spectrofluorimetrically at three different temperatures. The stoichiometry of the complexes was found to be 1:1. The results of electronic spectral studies indicated that the formation constant for Fe^{II}Pc-*p*-CHL system is found to be higher than that for Fe^{III}Pc-*p*-CHL system. This observation is well supported by the results of fluorescence quenching studies and the association constants calculated for Fe^{II}Pc-*p*-CHL system is 4.2 × 10³ mol L⁻¹ and that for Fe^{III}Pc-*p*-CHL system is 2.2 × 10³ mol L⁻¹. The data are discussed in terms of physico-chemical parameters viz. molar extinction coefficient, oscillator strength, dipole moment, ionization potential, dissociation energy and thermodynamic parameters. The results indicated that the formation of π - π CT complex is spontaneous and endothermic. Preliminary studies indicated that the CT complex can effectively be used as a colorimetric agent for sensing amino acids and amines.

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spectral properties in the 600–750 nm region which is one of the two principal features in the electronic spectra of MPcs, i.e. the Q-band $[a_{1u}(\pi) \rightarrow e_g(\pi^*)]$ and the other being the B or Soret band $[a_{2u}(\pi) \rightarrow e_g(\pi^*)]$ near 325–425 nm [11,12].

Several reports have been published on the study of intramolecular charge transfer of MPcs [13,14] and only very few investigation have been reported on the intermolecular charge transfer of MPcs with electron acceptors [15,16]. Thus, a systematic investigation on the intermolecular charge transfer interaction of Fe(II) and Fe(III) PCs with a biologically significant quinone viz. *p*-chloranil (*p*-CHL) has been conceived and presented in this article with an aim to understand the mechanism and utility of such interaction. Electronic and fluorescence spectroscopic techniques were employed to evaluate various physico-chemical parameters of the charge transfer complexes and discussed. Preliminary attempts have also been made to test the applicability of the charge transfer adduct formed, in the present study, as a signal magnifier of chloranil for colorimetric sensing of amino acids and amines.

2. Experimental

2.1. Materials and measurements

The electron donors Fe^{II}Pc and Fe^{III}Pc were prepared and purified by reported procedure [17] and the electron acceptor *p*-chloranil (Aldrich, India) was used without further purification.

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Spectroscopy grade DMF (Merck, India) was used as received. The structures of the donors are shown below:



)
$$Fe^{II}Pc$$
 (M= Fe^{II} , X= Nil)

2)
$$Fe^{III}Pc$$
 (M= Fe^{III} , X= Cl)

Solutions for the spectroscopic measurements were prepared by dissolving accurately weighed amounts of donor (*D*) and acceptor (*A*) in the appropriate volume of solvent immediately before running the spectra. The electronic absorption spectra were recorded on a JASCO (V630, Japan) UV–vis double beam spectrophotometer using 1 cm matched quartz cells. The temperature of the cell holder was controlled with a water flow (± 0.1 °C). Fluorescence spectra were recorded in a JASCO (6200, Japan) spectrofluorimeter. The excitation emission slit width (10 nm) and scan rate (250 nm) were kept constant for all of the experiments. FT-IR spectra were recorded in a JASCO (FT-IR 460 Plus, Japan) spectrometer.

2.2. Kinetic procedure

In both Fe^{II}Pc-*p*-CHL and Fe^{III}Pc-*p*-CHL cases, the kinetics of the interaction was followed at three different temperatures in DMF under pseudo-first-order conditions, keeping $[A] \gg [D]$ and with acceptor as the blank. In both the cases, the increasing absorbance at 682 nm (Fe^{II}Pc) and 678 nm (Fe^{III}Pc) was followed as a function of time. The pseudo-first-order rate constants (k_1) were calculated from the gradients of $\log(A_{\infty} - A_t)$ against time plots, where A_{∞} and A_t represent the absorbance at infinity and time *t*, respectively. The second order rate constants were calculated by dividing k_1 by [A].

3. Results and discussion

3.1. Electronic spectra of the donors

Most of the metallophthalocyanines belong to the point group D_{4h} [18]. The HOMO orbital is $a_{1u}(\pi)$ and next low-lying filled orbital is $a_{2u}(\pi)$. The LUMO is $e_g(\pi^*)$ (Scheme 1) from these concept to explain the electronic spectra of Fe^{II}Pc and Fe^{III}Pc [Fig. 1S (Supplemental information)]. The strong peak intensity of the Q-band $[a_{1u}(\pi) \rightarrow e_g(\pi^*)]$ is appeared at 659 nm (Fe^{II}Pc) and 662 nm (Fe^{III}Pc). The peak molar intensity of the Q-band does depend upon the oxidation state of the central metal ion, increasing and becoming narrower from Fe^{II}Pc to Fe^{III}Pc [12]. The peak molar intensity of the Q-band of Fe^{III}Pc is comparatively sharper than the Fe^{II}Pc. Transition from $a_{2u}(\pi)$ to $e_g(\pi^*)$ is responsible for the Soret band is appeared at 324 nm (Fe^{II}Pc) and 320 nm (Fe^{III}Pc). However, where empty metal d orbital lie inside the HOMO–LUMO gap, LMCT transitions of the general type Pc(π) \rightarrow d transition, LMCT of both Fe^{II}Pc and Fe^{III}Pc appeared at 424 nm and 426 nm, respectively.

3.2. Stoichiometry of the interaction

The stoichiometry of the CT complex, in both the cases, was determined by applying Job's continuous variation method [19,20]. In both the cases, the symmetrical curves with maximum at 0.5 mole fraction indicated the formation of a 1:1 (D:A) CT complex as evidenced from absorption [Fig. 2S (Supplemental Information)] and emission (Figs. 1 and 2) spectral methods. The photometric titration measurements were also performed for the determination of the stoichiometry in these interactions. The results of the photometric curves [Fig. 3S (Supplemental Information)] also indicated that the stoichiometry of the interaction, in both the cases, is 1:1 (D:A) [21].

3.3. Kinetics of the interaction

The electronic spectra of the mixture of the donors and the acceptor, under pseudo first order condition, i.e. [A]/[D] > 100, as a function of time were recorded. Representative spectra for Fe^{II}Pc-*p*-CHL and Fe^{III}Pc-*p*-CHL systems are given in Figs. 3 and 4, respectively. On mixing the donors with *p*-CHL, there was an instantaneous formation of CT complex with an absorption maximum at 682 nm for Fe^{II}Pc-*p*-CHL (Fig. 3) and at 678 nm for Fe^{III}Pc-*p*-CHL systems (Fig. 4). The intensity of these bands goes on increasing with time. The continuous increase in absorbance of these



Scheme 1. The energy levels in typical metallophthalocyanine, showing origin of the various LMCT, MLCT, Q and Soret bands.



Scheme 2. Interaction of Fe^{II}Pc and Fe^{III}Pc with *p*-CHL.



Fig. 1. Job's continuous variation plots Fe^{II}Pc-*p*-CHL system in DMF at 298 K.



Fig. 2. Job's continuous variation plots Fe^{III}Pc-*p*-CHL system in DMF at 298 K.



Fig. 3. Electronic spectra of Fe^{II}Pc with *p*-CHL in DMF at 298 K (curve A: *p*-CHL; D: Fe^{II}Pc; C: mixture of Fe^{II}Pc and *p*-CHL).



Fig. 4. Electronic spectra of Fe^{III}Pc with *p*-CHL in DMF at 298 K (curve A: *p*-CHL; D: Fe^{III}Pc; C: mixture of Fe^{III}Pc and *p*-CHL).

Table 1
Effect of concentration of donor and acceptor on the rate of the interaction at 298 K.

$[D](\times 10^{-5}\mathrm{M})$	$[A](\times 10^{-3}\mathrm{M})$	k_1 ($ imes 10^{-4}$), s $^{-1}$	k_2 , s ⁻¹ mol ⁻¹ dm ³		
Fe ^{II} Pc- <i>p</i> -CHL system (in DMF at 682 nm)					
5.5	0.2	2.5	1.1		
5.5	0.3	3.3	1.1		
5.5	0.4	4.1	1.0		
5.5	0.5	4.8	1.0		
5.5	0.6	5.6	0.9		
5.5	0.7	6.3	0.9		
5.5	0.8	7.1	0.9		
5.5	0.9	7.7	0.9		
5.5	1	8.3	0.8		
5.5	1	8.3			
4.4	1	8.2			
3.3	1	8.0			
2.2	1	8.1			
Fe ^{III} Pc-p-CHL syste	m (in DMF at 678 ni	m)			
5.5	0.2	1.9	0.8		
5.5	0.3	2.6	0.8		
5.5	0.4	3.1	0.7		
5.5	0.5	3.9	0.7		
5.5	0.6	4.6	0.8		
5.5	0.7	5.2	0.7		
5.5	0.8	5.8	0.7		
5.5	0.9	6.7	0.7		
5.5	1	7.3	0.7		
5.5	1	7.3			
4.4	1	7.2			
3.3	1	7.2			
2.2	1	7.1			

bands is indicative of the formation of the final interaction product (Scheme 2). This is also supported by the fact that the product isolated exhibited identical electronic spectra (Figs. 3 and 4).

The pseudo-first-order rate constant (k_1) values for the formation of the CT complex as a function of [D] and [A] are also collected in Table 1. It is evident from the results that the rate is independent of initial concentration of the donors indicating first order dependence on [D]. The k_1 increased with an increase in [A] suggesting the order with respect to [A] is also unity. The rate constant values increased with an increase in [A] and a plot of $\log k_1$ versus $\log [A]$ [Fig. 4S (Supplemental Information)], is linear in both Fe^{II}Pc-*p*-CHL (slope 0.94) and Fe^{III}Pc-*p*-CHL (slope 0.96) systems indicating first order dependence of rate on [A] and which was further supported by the constancy in k_2 values. These observations indicated that the interaction of the donors with *p*-CHL proceed via the following plausible mechanism.

The above mechanism (Scheme 2) leads to the following rate law:

Rate = $k_1[D][A]$

The rate constants as a function of temperature along with thermodynamic parameters for the Fe^{II}Pc-*p*-CHL and Fe^{III}Pc-*p*-CHL interactions are collected in Table 2. It is evident from the results that the enthalpy of activation, which is a measure of strength of the interaction between the donor and acceptor molecules in a molecular complex, is relatively higher for Fe^{II}Pc-*p*-CHL system than that of Fe^{III}Pc-*p*-CHL system indicating relatively stronger nature of the

Table 2

Kinetic and thermodynamic parameters for the interaction of *p*-CHL with Fe^{II}Pc and Fe^{III}Pc in DMF.

System	λ, nm	$k_1~(imes 10^{-4})$, s $^{-1}$			$\Delta H^{\#}$	$-\Delta S^{\#}$	$\Delta G^{\#}$
		298 K	305 K	313 K			
Fe ^{II} Pc-p-CHL	682	8.3	9.1	9.6	4.9	287	91
Fe ^{III} Pc-p-CHL	678	7.3	7.7	8.3	4.1	291	90

 $\Delta H^{\#}$, kJ mol⁻¹; $\Delta S^{\#}$, J K⁻¹ mol⁻¹; $\Delta G^{\#}$, kJ mol⁻¹.

Table 3

Spectral properties of the CT complexes formed between Fe^{II}Pc and Fe^{III}Pc with *p*-CHL in DMF at 298 K.

Property	Fe ^{II} Pc-p-CHL	Fe ^{III} Pc-p-CHL
λ_{max} (nm)	682	678
$h\nu_{\rm CT}$ (eV)	1.82	1.83
$10^{14} \nu_{\text{max}} (s^{-1})$	4.41	4.42
Formation constant, <i>K</i> (dm ³ mol ⁻¹)	7770	2221
Extinction coefficient, ε (dm ³ mol ⁻¹ cm ⁻¹)	20,861	20,958
Oscillator strength, f	0.063	0.054
Dipole moment, μ	3.03	2.79
Ionization potential (eV)	7.26	7.25
Dissociation energy (eV)	4.06	4.05

former CT complex. Negative entropies of activation indicated a greater degree of ordering during the interaction.

3.4. FT-IR studies of the CT complexes

In both Fe^{II}Pc-*p*-CHL and Fe^{III}Pc-*p*-CHL cases, the CT complexes were obtained by allowing the reactants to react for 24 h under equal molar conditions. The FT-IR spectra of the isolated products were recorded and the results indicated that the shifts in positions of some of the peaks could be attributed to the expected symmetry and electronic structure modification in both the donor and acceptor units in the formed CT complex relative to the free molecules. The stretching vibration of ν (C=O) of the free *p*-CHL is appeared at 1685 cm⁻¹ and the complexation with Fe^{II}Pc and Fe^{III}Pc which is shifted into 1662 cm⁻¹ and 1644 cm⁻¹, respectively. Such a bathochromic shift could be indicative of a higher charge density on the carbonyl group of the *p*-CHL molecule [22].

3.5. Characteristics of the CT complexes

In both Fe^{II}Pc-*p*-CHL and Fe^{III}Pc-*p*-CHL systems, an attempt was made to characterize the CT complexes formed. For that the absorbance of the new bands was measured using constant donor concentration and varying concentrations of the acceptor, but always $[A] \gg [D]$ [Fig. 5S and 6S (Supplemental Information)]. The formation constants (*K*) and molar extinction coefficients (ε) of the CT-complexes were determined spectrophotometrically in the temperature range 298–313 *K* using the Scott equation [23]. Representative Scott plots are shown in Fig. 7S (Supplemental Information) and the values of *K* and ε thus determined are given in Table 3. The observed high values of *K* suggested that the formed CT complexes are of strong type [24] and the linearity of the Scott plots further supports this result. The results indicated that the Fe^{II}Pc-*p*-CHL CT complex is relatively more stable than the other.

The values of oscillator strength (f) which is a measure of integrated intensity of the CT-band and transition dipole moment (μ), were calculated as described elsewhere [23] and the values thus obtained are also given in Table 3. The values of f are rather relatively large indicating a strong interaction between the donoracceptor pairs with relatively high probabilities of CT-transitions [25]. The magnitude of f is relatively greater for the Fe^{II}Pc-p-CHL complex, indicating relatively higher stability of the complex than the other. Out of the many applications of CT complex, one important application is to calculate the ionization potential of the donor. The ionization potential (I_p) of the highest filled molecular orbital of the donor was estimated from CT energies of its complexes with the acceptor making use of the empirical equations reported by Aloisi and Pignataro [26].

$$I_p(\text{eV}) = 5.00 + 1.53 \times 10^{-4} \bar{\nu}_{\text{p-CHL}}(\text{cm}^{-1})$$
(1)

The calculated I_p values for molecular orbital participating in CT interaction of the iron phthalocynines are also listed in Table 3.



Fig. 5. Fluorescence spectra for Fe^{II}Pc-*p*-CHL system in DMF at fixed concentrations of $[D] = \{1.4285 \times 10^{-5} \text{ M} \text{ (curve D)}\}$ and variable concentration of $[A] (\times 10^{-5} \text{ M}) = \{2.86 \text{ (curve a)}, 5.71 \text{ (curve b)}, 8.57 \text{ (curve c)}, 11.43 \text{ (curve d)}, 14.29 \text{ (curve e)}\}$ at 298 K.

These values support the interpretation that the new band can be regarded as the CT band. Further evidence for the nature of CT interaction in the present systems is the calculation of the dissociation energy (W) of the CT excited state of the complex. The dissociation energies of the complexes were calculated as described earlier [27] and the calculated values of W (Table 3) suggested that the investigated complexes are reasonably strong and stable under the studied conditions with higher resonance stabilization energy [28].

3.6. Fluorescence study

One of the most important binding forces that produce favorable interaction between the donors and acceptor is the CT interaction. The nature and magnitude of donor interaction significantly influences the biological activity of the donor. In the present study, a preliminary attempt has been made to employ fluorimetric method to investigate the mode of CT interaction of Fe^{II}Pc and Fe^{III}Pc with *p*-CHL. The fluorescence spectra of both donors were recorded at room temperature (298 K) in the range of 230–730 nm upon excitation at 320 nm. It is observed that *p*-CHL quenched the fluorescence of both Fe^{II}Pc and Fe^{III}Pc through CT complexation. The experimental results indicated that the quenching efficiency increased with an increase in the concentration of *p*-CHL at a fixed concentration of the donors [Figs. 5 and 8S (Supplemental Information)].

The fraction of *p*-CHL bound to the FePcs (θ) was determined using the following equation [29].

$$\theta = \frac{F_0 - F}{F_0},\tag{2}$$

where *F* and *F*₀ denote the fluorescence intensities of the donors in a solution with a given concentration of *p*-CHL and without *p*-CHL, respectively. From the values of θ the association constant, *K*_f, for the interaction of FePcs with *p*-CHL was computed using the method described by Ward [30]. It has been shown that for equivalent and independent binding sites:

$$\frac{1}{(1-\theta)K_f} = \frac{[A_t]}{\theta} - n[D_T],\tag{3}$$

where *n* is the number of binding sites, $[A_t]$ is the total *p*-CHL concentration and $[D_T]$ is the total donor concentration. The plot



Fig. 6. Stern–Volmer plots for the fluorescence quenching of $Fe^{II}Pc$ and $Fe^{III}Pc$ with *p*-CHL in DMF at 298 K.

of $1/(1 - \theta)$ versus $[A_t]/\theta$ was linear (r 0.96 for Fe^{II}Pc-p-CHL system; r 0.98 for Fe^{III}Pc-p-CHL system) indicating that under the experimental conditions all the binding sites are equivalent and independent. The value of K_f obtained from the plots for Fe^{II}Pc-p-CHL and Fe^{III}Pc-p-CHL systems were found to be 4.2×10^3 mol L⁻¹ and 2.2×10^3 mol L⁻¹, respectively. Parallel to the observation made in the electronic spectral studies, as enumerated earlier, the Fe^{II}Pc-p-CHL complex. The standard Gibbs energy change ΔG° was calculated from the K_f using the relation $\Delta G^{\circ} = -2.303 RT \log_{10} K_f$. The ΔG° values for Fe^{II}Pc-p-CHL and Fe^{III}Pc-p-CHL systems were found to be -20 kJ and -19 kJ, respectively, which indicated that the interactions between the Pcs and p-CHL are spontaneous [31].

Fluorescence intensity data was also analyzed according to the Stern–Volmer law:

$$\frac{F_0}{F} = 1 + K_{\rm SV}[Q],$$
 (4)

where F_0 is emission intensity in the absence of quencher (*Q*), *F* emission intensity at quencher concentration [*Q*] and K_{SV} is the Stern–Volmer constant. In both the Fe^{II}Pc-*p*-CHL and Fe^{III}Pc-*p*-CHL systems the linear Stern–Volmer relationship observed (Fig. 6) suggested that either static or dynamic quenching is dominant [32–34].

The relationship between the fluorescence quenching intensity and the concentration of quencher can be described by the following equation.

$$\log_{10} \frac{F_0 - F}{F} = \log K_A + n \log_{10}[Q],$$
(5)

where K_A is the binding constant and n is the number of binding sites per Fe^{II}Pc or Fe^{III}Pc [32]. In the present study, a plot of $\log_{10}(F_0 - F)/F$ versus $\log_{10}[Q]$ is linear in both cases [Fig. 9S (Supplemental Information)]. The binding constant values of Fe^{II}Pc-p-CHL system are $9.9 \times 10^3 \text{ mol}^{-1} \text{ L}$ (n = 1.1) and $1.3 \times 10^3 \text{ mol}^{-1} \text{ L}$ (n = 0.9) for Fe^{III}Pc-p-CHL system. The results showed that the binding constant in Fe^{II}Pc-p-CHL system is higher than that in Fe^{III}Pc-p-CHL system indicating higher stability of the former than the later. These observations are in corroboration with the results of absorption spectral, kinetics and thermodynamic studies as enumerated earlier in this paper. The values of n, for both the Pcs are nearly constant indicating the presence of equivalent binding sites.



Fig. 7. Electronic spectra of complex $Fe^{III}Pc-p$ -CHL (2.5 × 10⁻⁵ M) (blank) and in the presence of 4.0×10^{-4} M of various amines in 80% (v/v) aq. DMF at 298 K. Inset: solution (a) $Fe^{III}Pc-p$ -CHL, (b) amine, (c) ($Fe^{III}Pc-p$ -CHL) + amine in 80% (v/v) aq. DMF.

3.7. Colorimetric application of the π – π CT complex

Recently, Liu et al. [35] have reported the interaction and colorimetric sensing properties of calix[4]pyrrole-chloranil charge transfer complex with amino acids and amines in chloroform/ethanol/water medium using UV-vis spectroscopic technique. The results indicated that the CT complex behaves like a signal magnifier in sensing basic amino acids and aliphatic amines. Also no CT complex formation was noticed in more polar solvents like acetonitrile and DMSO. Hence they have used chloroform/ethanol/water mixture to sense amino acids.

A preliminary attempt was made, in the present study, to utilize the Fe^{III}Pc-*p*-CHL CT complex to sense amino acids and amines. As this supramolecular assembly is investigated in more polar DMF, this can very well be used to sense amino acids in DMF/water mixtures. On adding 20% water to the CT complex in DMF, as shown in Fig. 7, the CT absorption at 669 nm exhibited only slight perturbation and retains the blue color indicating the stability of the complex in DMF/water mixture. (For interpretation of the references to color in text, the reader is referred to the web version of this article.)

The colorimetric properties of the Fe^{III}Pc-p-CHL CT complex in DMF/water (80:20%, v/v) for amines and amino acids were investigated and the results are shown in Figs. 7 and 8, respectively. FellPc-p-CHL CT complex also exhibited similar behavior but only the results of Fe^{III}Pc-p-CHL CT complex are presented here. Upon addition of aliphatic amines (ethylene diamine, triethyl amine), aromatic amines (pyridine, aniline, p-bromoaniline, p-toluidine, o-phenylene diamine), basic amino acids (arginine) and neutral amino acids (alanine, leucine, proline), the blue solution instantly turned to green with new absorption band(s) in the region of 390-490 nm along with a band at 658 nm corresponds to Fe^{III}Pc. (For interpretation of the references to color in text, the reader is referred to the web version of this article.) This dramatic color change may be due to the formation of $n-\pi$ CT complex between chloranil and the *n*-donor amines and amino acids. The new absorption peaks around 425 and 450 nm is due to chloranil anion radical [35,36]. Such peaks have not occurred during the formation of $\pi - \pi$ Fe^{III}Pc-*p*-CHL



Fig. 8. Electronic spectra of complex Fe^{III}Pc-*p*-CHL (2.5×10^{-5} M) (blank) and in the presence of 8.0×10^{-4} M of various amino acids in 80% (v/v) aq. DMF at 298 K. Inset: solution (a) Fe^{III}Pc-*p*-CHL, (b) amino acids, (c) (Fe^{III}Pc-*p*-CHL)+ amino acids in 80% (v/v) aq. DMF.

CT complex even in more polar DMF (Fig. 4). The present study indicated that the Fe^{III}Pc-*p*-CHL CT complex is a better candidate for colorimetric sensing of amino acids and amines. The advantages of the present sensor are (i) the CT complex can be formed in more polar solvent like DMF and hence aqueous solutions of amino acids or amines can easily be mixed with it, (ii) aromatic amines and neutral amino acids can be sensed and (iii) the Fe^{III}Pc-*p*-CHL CT complex can also be prepared in solid state by grinding the reactants in 1:1 ratio and which can be dissolved in DMF (This CT complex also exhibited identical spectral behavior with that prepared in solution). As a detailed study on the colorimetric application of the CT complexes is out of the scope of the present study, only this preliminary report has been presented here.

4. Conclusion

The stoichiometry of the molecular complexes of $Fe^{II}Pc$ and $Fe^{III}Pc$ with *p*-CHL was found to be 1:1. The association constants of both the systems were evaluated by the Scott and spectrofluorimetric methods. The results indicated that $Fe^{II}Pc$ -*p*-CHL complex is relatively stronger than $Fe^{III}Pc$ -*p*-CHL complex. This observation is well supported by the kinetic and thermodynamic studies. The results showed that the investigated complexes were found to be stable, endothermic and spontaneous. The results obtained in the present study would definitely help to understand the mechanism of interaction of Pc like molecules with quinones in real situations. The electronic spectral changes of the CT complex solution observed in the presence of amino acids and amines indicated that it can be used as a colorimetric sensor.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2011.09.054.

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