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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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 4.2×10^3 mol L^{-1} and that for $Fe^{III}Pc$-*p*-CHL system is 2.2×10^3 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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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 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:
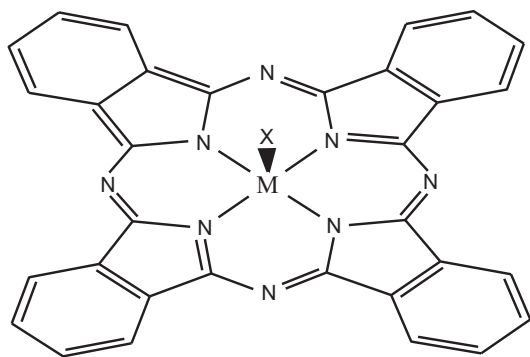
1) Fe^{II}Pc (M= Fe^{II}, X= Nil)

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 ($\pm$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) → 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
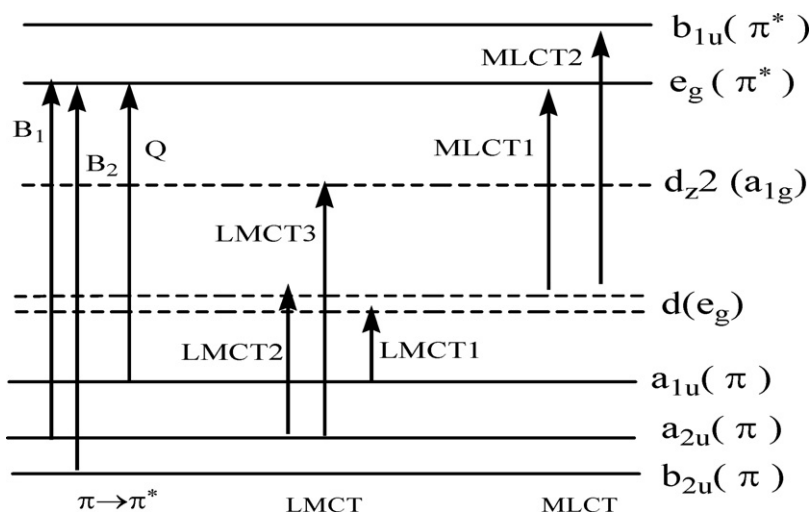
Scheme 1. The energy levels in typical metallophthalocyanine, showing origin of the various LMCT, MLCT, Q and Soret bands.