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A Spectroscopic Study of Charge Transfer Complexes of Tetraphenylporphyrin

Saleh A. Azim*, **Raafat M. Issa,** and **Eynas A. Saleh**

Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt

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Summary. The fluorescence quenching and complexation behaviour of tetraphenylporphyrin (*TPP*) with some organic acceptors such as chloranilic acid (*CHL*), 5,5′-dithiobis-2-nitrobenzoic acid (*DTNB*), or 3,4-dinitrobenzoic acid (*DNB*) and tetravalent metal ions such as Th^{4+} and Zr^{4+} have been studied in methanol. The second-order fluorescence quenching rate constant (k_q), the association constant (K), the molar absorption coefficient (ε), and the thermodynamic parameters of the complexation process (ΔG°, ΔH°, and ΔS°) have been evaluated using different organic solvents.

Keywords. Tetraphenylporphyrin complexes; Fluorescence quenching; Metals; Porphyrin.

Introduction

Porphyrin derivatives have attracted interest in recent years due to their potential use in the field of photodynamic therapy (PDT) [1, 2]. The interaction of porphyrin bases with metal ions has been extensively studied [3, 4]. They also have important applications in photocatalysis, photochemical conversion, and storage of solar energy as well as photosynthesis, photobiology, and photomedicine [5, 6]. We have described the fluorescence quenching and the complexation of *TPP* with some tetravalent metal ions in organic solvents at different temperatures. Less attention, however, has been devoted to interaction between porphyrin bases and electron-deficient organic compounds.

In this paper we report the dynamics of the interaction between a prototype porphyrin derivative, tetraphenylporphyrin (*TPP*), and some nitroaromatic acceptors, *e.g.* chloranilic acid (CHL), 3,4-dinitrobenzoic acid (*DNB*), and 5,5′-dithiobis-2-nitrobenzoic acid (*DTNB*).

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* Corresponding author. E-mail: saleh_abdelazim@yahoo.com

Results and Discussion

Reaction of TPP with Some Organic Acceptors

Fluorescence Quenching Studies

The fluorescence quenching of a 5×10^{-6} mol·dm^{-3} methanolic solution of *TPP* using some organic acceptors as *CHL*, *DTNB*, and DNB was studied by steady-state emission measurements. The fluorescence spectral pattern does not change indicating the absence of an exciplex emission under the experimental condition shown in Fig. 1. The second order rate constants k_q of the fluorescence quenching were determined from the *Stern-Volmer* (*SV*) plots using the method of linear regression according to Eq. (1) [8].

$$I_0/I = 1 + k_q\tau_0[Q] \tag{1}$$

where I_0 and I are the relative fluorescence intensities in the absence and presence of quencher of concentration $[Q]$, k_q is the second-order quenching rate constants, and τ_0 is the fluorescence lifetime of the fluorophore in the absence of the quencher. The measured lifetime values for *TPP* are 11.9 ± 0.02 and 7.88 ± 0.07 ns in methanol and chloroform, respectively [9].

Typical *Stern-Volmer* plots are linear in the investigated concentration range as shown in Fig. 2. At relatively high quencher concentrations, *Stern-Volmer* plots show positive deviations, especially with stronger quenchers, indicating the formation of ground-state complexes between donor and acceptor. The concentration of *TPP* used was 5×10^{-6} mol·dm^{-3}.

The second order quenching rate constants (k_q) of the fluorescence quenching was determined from the *Stern-Volmer* plots using the method of linear regression according to Eq. (1). The k_q values were found to be 5.3×10^{10}, 4.9×10^{10}, and

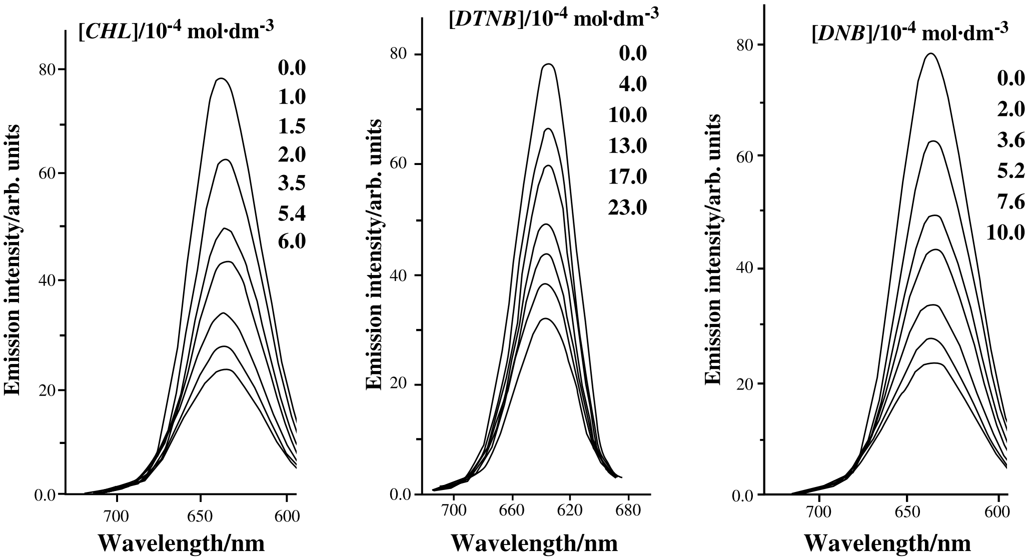


Fig. 1. Fluorescence quenching of 5×10^{-6} mol·dm^{-3} of *TPP* by *CHL*, *DTNB*, and *DNB* in methanol ($\lambda_{ex} = 400$ nm)

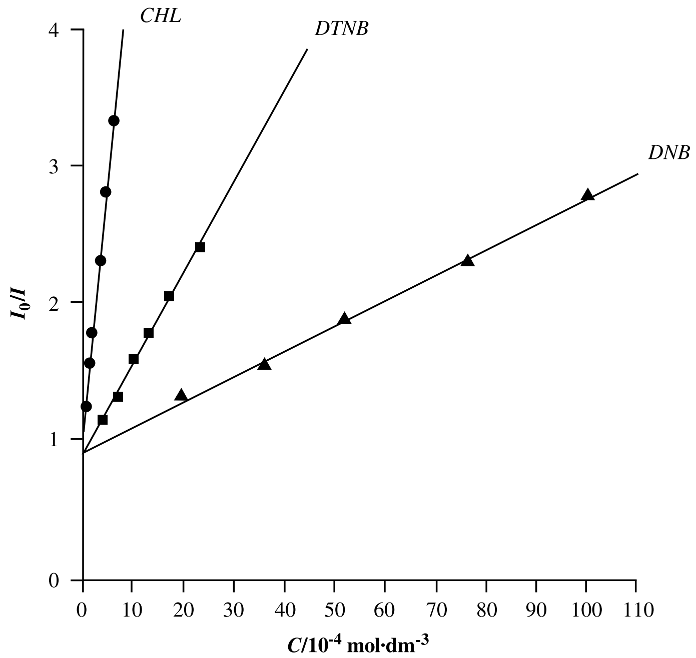


Fig. 2. *Stern-Volmer* plots of fluorescence quenching of 5×10^{-6} mol·dm^{-3} of *TPP* using different organic acceptors in methanol

3.4×10^{10} for *CHL* ($E_A = 0.577$ eV), *DTNB* ($E_A = 0.547$ eV), and 3,4-*DNB* ($E_A = 0.523$ eV), respectively. The magnitude of k_q increases with increasing electron affinity (E_A) of the quencher. This indicates the probable involvement of charge-transfer type quenching.

Figure 3 shows the *SV* plots for the fluorescence quenching of *TPP* at 650 nm by *CHL* in organic solvents of different polarities. It is apparent that k_q values decrease with increasing solvent polarity. The k_q values were found to be 2.2×10^{11} and 3.3×10^{12} in $CHCl_3$ and *Me*OH, respectively, indicating that the fluorescence quenching of *TPP* by *CHL* owing to the electron transfer processes leads to the disappearance of polar species [10]. In addition, k_q values of the *TPP–CHL* system in different solvents are much larger than the limiting diffusion rate constant k_{diff}. The k_{diff} values for chloroform and methanol are 1.12×10^{10} and 1.17×10^{10}, respectively, as calculated by the Eq. (2) [11].

$$k_{diff}/(\mathrm{dm}^3\cdot\mathrm{mol}^{-1}\cdot\mathrm{s}^{-1}) = \frac{8RT}{3000\eta} \tag{2}$$

where R is the gas constant, T is the temperature, and η is the viscosity in poise. This indicates that diffusion is not involved in the quenching mechanism [12]. Also, there is no spectral overlap between the emission of *TPP* and the absorption of the acceptor, and hence electronic energy transfer from $^1TPP^*$ to the acceptor can be ruled out.

Electronic Absorption Spectra

The interaction of *TPP* with some organic acceptors namely *CHL*, *DTNB*, and *DNB* has been investigated using spectrophotometric techniques. Figure 4 shows the

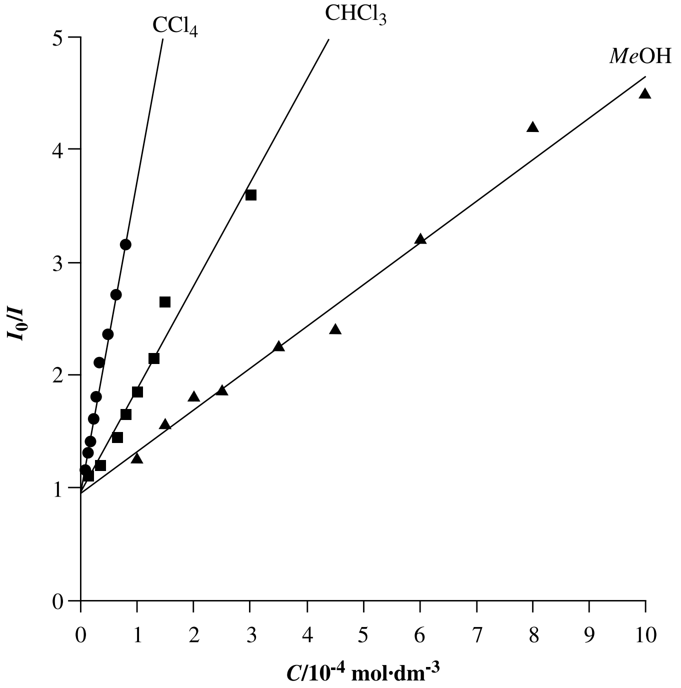


Fig. 3. *Stern-Volmer* plots of fluorescence quenching of *TPP* by *CHL* in different solvents

build-up of the *TPP*-acceptor complex absorbance in methanol as a result of an increasing acceptor concentration. It is apparent that, increasing the concentration of *CHL* (as an example) added to *TPP* (5×10^{-6} mol·dm^{-3}) leads to a consistent decrease of the *TPP* absorption band at 409.5 nm while a new absorption band develops at 432.6 nm. This new absorption band is characteristic of charge-transfer from the HOMO of *TPP* (donor) to the LUMO of *CHL* (acceptor). A clean isosbestic point is observed at 421 nm indicating a single equilibrium. Using the *Benesi-Hildebrand* method [13], the values of equilibrium constants (K) and molar absorption coefficients (ε) of the complexes were estimated under the concentration condition $C_{o3} > C_{o2}$, where C_{o2} and C_{o3} are the initial concentrations of the donor and acceptor, respectively (Table 1). At fixed concentration of *TPP* (5×10^{-6} mol·dm^{-3}) and variable concentrations of *CHL* ($C_{o3} = 1.5$–13.5×10^{-4} mol·dm^{-3}), the experimental data were measured in methanol in the temperature range 20–40°C at 432.5 nm. The temperature dependence of the equilibrium constant (K) was used for determination of the thermodynamic parameters ($\Delta G° = -19.3$ kJ mol^{-1}, $\Delta H° = -30.2$ kJ mol^{-1}, and $\Delta S° = -30$ J mol^{-1} K^{-1}) from linear-regression fits to the *van't Hoff* equation [14]. There is no evidence of a deviation from linearity of the plot of $\ln K$ *vs.* $1/T$ over the investigated temperature range up to 313°K for the *TPP–CHL* system indicating that a 1:1 complex is formed within the investigated temperature range for this system.

The electronic absorption spectra of the *TPP–CHL* system were studied in different solvents. The K and ε values were calculated and collected in Table 2. It should be noted that these data illustrate the solvation effects on the spectra and thermodynamic properties of the charge transfer complexes. The CT band displays

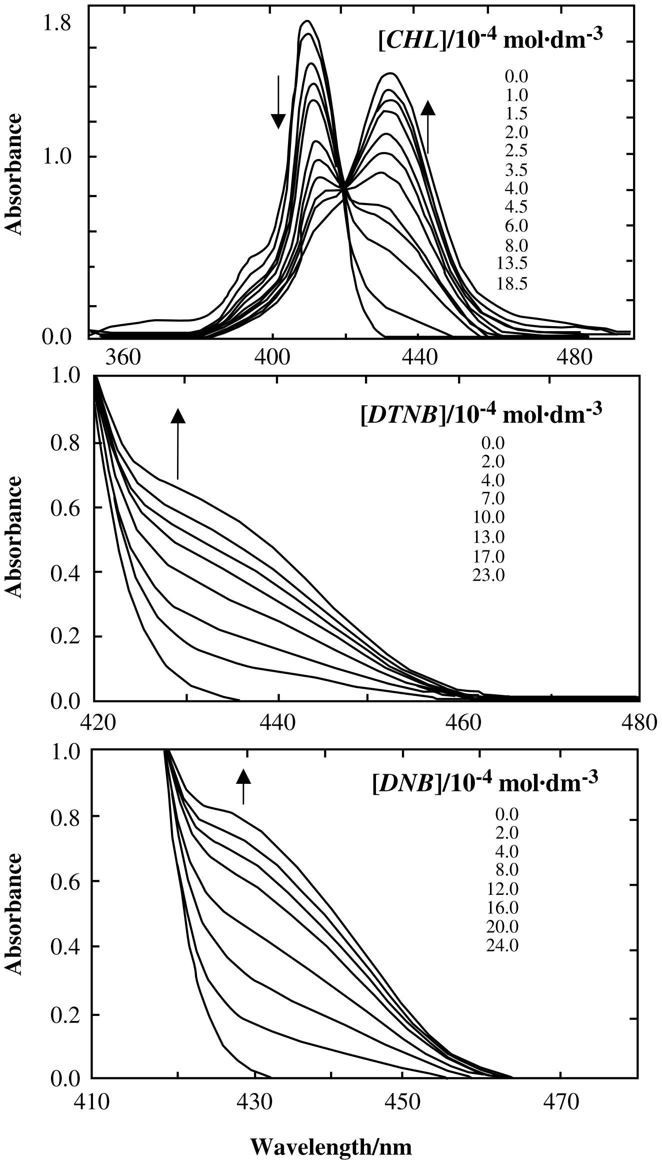


Fig. 4. Change in the *TPP* absorption spectrum as a result of complexation with *CHL*, *DTNB*, and *DNB* in methanol, $C_{o2} = 5\times10^{-6}$ mol·dm^{-3}

a blue shift on increasing solvent polarity, *e.g.* on going from CCl_4 to *Me*OH. However, the equilibrium constant *K* increases with decreasing solvent polarity since the CT complex is stabilized in non-polar solvents.

Reaction of TPP with Th^{4+} and Zr^{4+} Ions

Fluorescence Quenching Studies

Fluorescence quenching of 5×10^{-6} mol·dm^{-3} methanolic solution of *TPP* has been studied using Zr^{4+} and Th^{4+} at room temperature (Fig. 5). It is clear that the

Table 1. Maximum absorption wavelength λ_{CT}, molar absorption coefficient ε_{CT}, and equilibrium constant K for *TPP–DNB*, *TPP–CHL*, and *TPP–DTNB* complexes

$\frac{T}{K}$	$\frac{K}{dm^3 \cdot mol^{-1}}$	$\frac{\varepsilon_{CT}}{dm^3 \cdot mol^{-1} \cdot cm^{-1}}$	$\frac{\lambda_{CT}}{nm}$
DNB			
293	1.034×10^4	2.200×10^5	430.0
CHL			
293	2.510×10^5	3.636×10^5	
303	2.080×10^5	3.200×10^5	432.6
313	1.920×10^5	2.857×10^5	
DTNB			
293	1.604×10^4	1.800×10^5	434.5

Table 2. Maximum absorption wavelength λ_{CT}, molar absorption coefficient ε, and equilibrium constant K for *TPP–CHL* in different solvents

Solvent	D	$\frac{K \times 10^{-3}}{dm^3 \cdot mol^{-1}}$	$\frac{\varepsilon \times 10^{-5}}{dm^3 \cdot mol^{-1} \cdot cm^{-1}}$	λ_{CT}/nm
CCl_3	2.238	25.4	6.06	440.5
$CHCl_3$	4.806	7.8	6.45	439.5
*Me*OH	32.70	2.9	3.51	432.6

D is the dielectric constant of the solvent

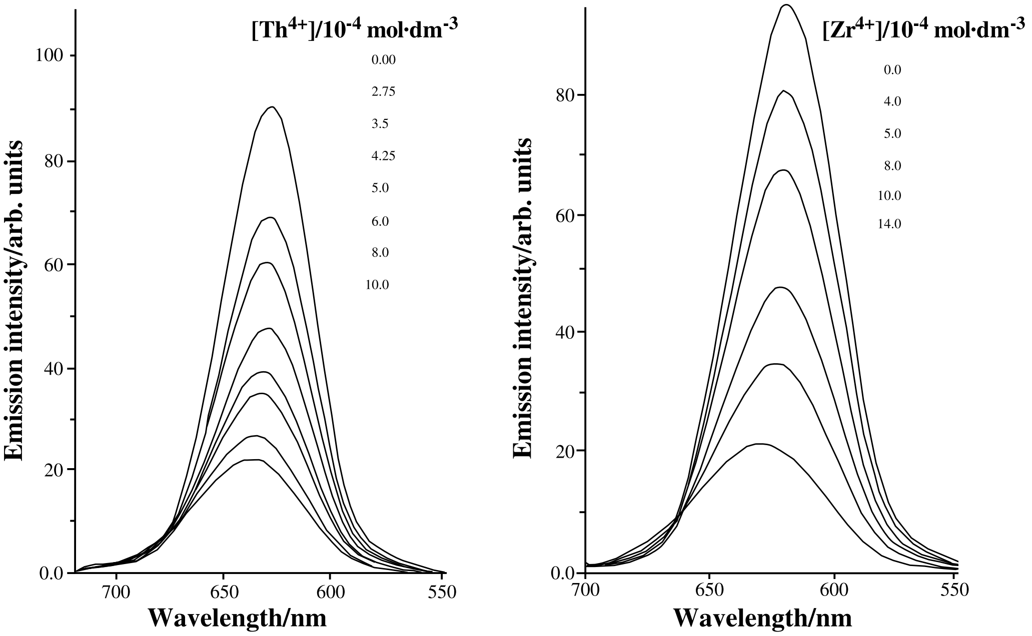


Fig. 5. Fluorescence quenching of 5×10^{-6} mol·dm^{-3} of *TPP* using Th^{4+} and Zr^{4+} in methanol ($\lambda_{ex} = 400$ nm)

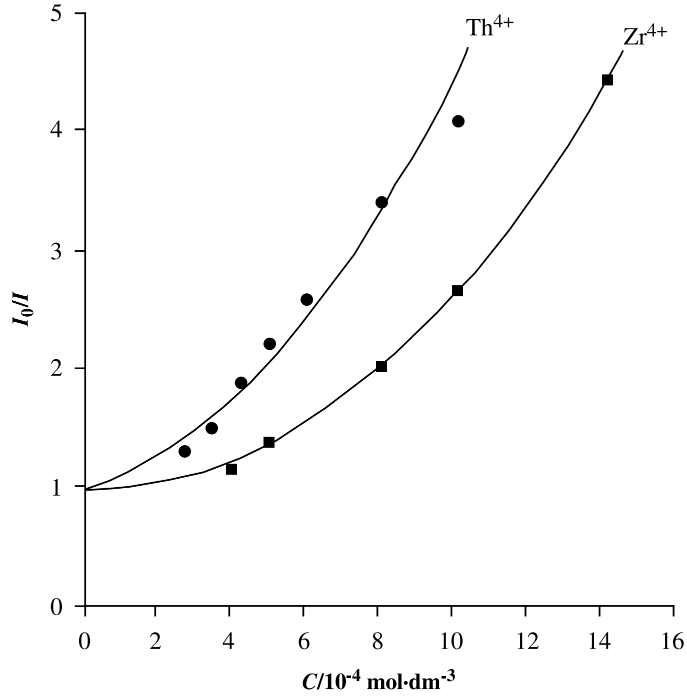


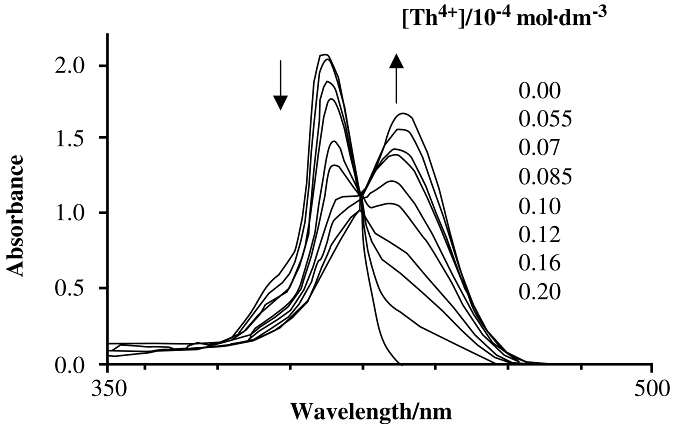
Fig. 6. *Stern-Volmer* plots of fluorescence quenching of 5×10^{-6} mol·dm^{-3} *TPP* solution in *Me*OH using Th^{4+} and Zr^{4+} ions

fluorescence spectral pattern does not change, indicating the absence of an emitting excited-state complex under these experimental conditions.

As shown in Fig. 6, the *Stern-Volmer* plots are not linear. This indicates that the quenching is enhanced *via* ground-state complexation. The fluorescence quenching of *TPP* using Zr^{4+} ions in organic solvents of different polarity has also been studied. The *Stern-Volmer* relation showed, that the quenching efficiency decreases in the order $CCl_4 > CHCl_3 >$ *Me*OH with increasing solvent polarity indicating complexation between *TPP* and Zr^{4+} ions *via* electron transfer in the ground state.

Electronic Absorption Spectra

The change of the *TPP* absorption spectrum indicates the presence of a ground state complexation between donor and acceptor as shown in Fig. 7. There is no significant overlap between *TPP* emission and absorption of the acceptors indicating the absence of energy transfer. When *TPP* ($C_{o2} = 5\times10^{-6}$ mol·dm^{-3}) is mixed with Th^{4+} (as an example) with different concentrations of Th^{4+} ($C_{o3} = 2.75$–10×10^{-5} mol·dm^{-3}) in methanol, a consistent decrease of the *TPP* absorbance at $\lambda = 409.5$ nm occurs and a new absorption band appears at $\lambda = 432$ nm. A clear isosbestic point is observed at $\lambda = 419$ nm, indicating a single equilibrium. Using the *Benesi-Hildebrand* method, values of equilibrium constants (*K*) and molar absorption coefficients (ε) of the complexes formed were estimated (Table 3). The *TPP*–Zr^{4+} and *TPP*–Th^{4+} complex absorbances have been studied at different temperatures. The temperature dependence of the equilibrium constants (*K*) was



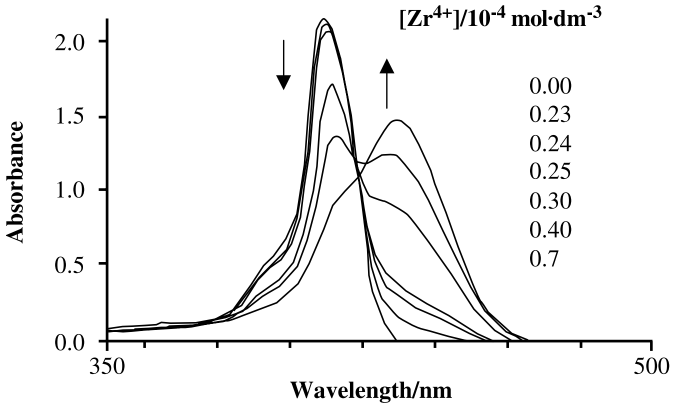


Fig. 7. The change in absorption spectrum of 5×10^{-6} mol·dm^{-3} of *TPP* in methanol with increasing the concentration of Th^{4+} and Zr^{4+}

Table 3. Maximum absorption wavelength λ_{CT}, molar absorption coefficient ε, and equilibrium constant *K* for *TPP*–Th^{4+} and *TPP*–Zr^{4+} at different temperatures in *Me*OH

T/K	$\frac{K}{dm^3 \cdot mol^{-1}}$	$\frac{\varepsilon}{dm^3 \cdot mol^{-1} \cdot cm^{-1}}$	$\frac{\lambda_{CT}}{nm}$
TPP–Th^{4+}			
293	1.30×10^{-5}	3.30×10^{-6}	432
TPP–Zr^{4+}			
293	2.50×10^{-4}	4.160×10^{-5}	430
303	1.26×10^{-4}	4.70×10^{-5}	
313	0.75×10^{-4}	5.60×10^{-5}	

used to determine the thermodynamic parameters ($\Delta G^\circ = -23.89\,\text{kJ mol}^{-1}$, $\Delta H^\circ = 45.98\,\text{kJ mol}^{-1}$, and $\Delta S^\circ = 72.30\,\text{J mol}^{-1}\text{K}^{-1}$). It is obvious that *K* decreases as the temperature increases indicating the thermal instability of the *TPP*–Zr^{4+} complex. However, the values of ε show a slight decrease with increasing temperature, which is due to a temperature band broadening.

Experimental

Tetraphenylporphyrin (*TPP*) was obtained from Aldrich and used without further purification. Metal salts (Merck) were also used without further purification. Organic acceptors used for the fluorescence quenching studies have been recrystallized several times from ethanol. UV-visible absorption spectra were recorded on a Shimadzu UV-160A spectrophotometer with a band pass of 5 nm. The electronic absorption spectra at different temperatures were recorded on a Shimadzu UV-3101 PC UV-VIS-NIR scanning double beam spectrophotometer. Steady state emission spectra were measured with a Shimadzu RF 510 spectrofluorophotometer with a band pass of 10 nm using right-angle arrangement. The fluorescence spectra were corrected for the machine response using a 10^{-3} mol·dm^{-3} anthracene solution in benzene as reported earlier [7]. The temperature was controlled using an ultrathermostated Julabo F 10 of temperature precision ±0.1°C.

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