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Spectroscopic studies of charge transfer complexes of *meso*-tetra-*p*-tolylporphyrin and its zinc complex with some aromatic nitro acceptors in different organic solvents

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The charge transfer complex (CTC) formation of 5,10,15,20-tetra(*p*-tolyl)porphyrin (TTP) and zinc 5,10,15,20-tetra(*p*-tolyl)porphyrin with some aromatic nitro acceptors such as 2,4,6-trinitrophenol (picric acid), 3,5-dinitrosalicylic acid, 3,5-dinitrobenzoic acid (DNB) and 2,4-dinitrophenol (DNP) was studied spectrophotometrically in different organic solvents at different temperatures. The spectrophotometric titration, Job's and straight line methods indicated the formation of 1:1 CTCs. The values of the equilibrium constant (K_{CT}) and molar extinction coefficient (ε_{CT}) were calculated for each complex. The ionization potential of the donors and the dissociation energy of the charge transfer excited state for the CTC in different solvents was also determined and was found to be constant. The spectroscopic and thermodynamic properties were observed to be sensitive to the electron affinity of the acceptors and the nature of the solvent. No CT band was observed between Zn-TTP as donor and DNP or DNB as acceptors in various organic solvents at different temperature. Bimolecular reactions between singlet excited TTP (^{1}TTP*) and the acceptors were investigated in solvents with various polarities. A new emission band was observed. The fluorescence intensity of the donor band decreased with increasing the concentration of the acceptor accompanied by an increase in the intensity of the new emission. The new emission of the CTCs can be interpreted as a CT excited complex (exciplex). Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: charge transfer complexes; porphyrin; stoichiometry; UV-vis spectroscopy; fluorescence

INTRODUCTION

Porphyrins and metalloporphyrins have received much attention since their discovery. Porphyrins are very important compounds because of their wide use as photosensitizers in the model system of photosynthesis.[1] Furthermore, they have been found to be suitable candidates for use in the photodynamic and boron neutron capture therapies for cancer of internal organs.[2–5] Thus its optical properties and photophysical behaviors continue to attract much interest.

The composition, the interchromophore separation/angular relationship, the overall dynamic and stimulus-induced reorganization, and the electronic coupling are crucial factors in the development of charge transfer reaction centers. Electron donor acceptor (EDA) complexes are materials of current interest since they can be utilized as organic semiconductors[6] and photocatalysts[7] and in drug analysis.[8,9] Such complexes have also found application in the study of redox processes,[10] microemulsions,[11] nonlinear optical properties[12] and electrical conductivities.[13] The formation energy of charge-transfer complexes depends on the ionization potential of the donor and the electron affinity of the acceptor. The absorption spectrum of the formed molecular complex shows a characteristic absorption band either in the visible or in the UV region.[14] Such a band does not appear in the absorption spectra of either the donor or

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acceptor and can be used for identification of the charge transfer complex (CTC), particularly when the complex cannot be isolated.[15] Recently there has been a considerable interest in the study of CTCs between porphyrins and a variety of acceptor molecules.[16–18]

In connection with our previous studies carried out on the CTCs of porphyrins with TCNE acceptor,[18] here we report on results of UV–vis studies, equilibrium constant, molar extinction coefficient, stoichiometry, thermodynamic parameters, ionization potential and fluorescence quenching data concerning the interaction of 5,10,15,20-tetra(*p*-tolyl)porphyrin (TTP) and zinc 5,10,15,20-tetra(*p*-tolyl)porphyrin (Zn-TTP) with aromatic nitro acceptors such as 2,4,6-trinitrophenol (picric acid, PIC), 3,5-dinitrosalicylic acid (DNS), 3,5-dinitrobenzoic acid (DNB) and 2,4-dinitrophenol (DNP) in different organic solvents.

EXPERIMENTAL

The acceptors (PIC, DNS, DNB and DNP) were obtained commercially from Aldrich Co. and recrystallized from ethanol. TTP and Zn-TTP of the highest purity were prepared according to the literature method.[19] The purity of the donors and acceptors was proved by HPLC, NMR, UV–vis spectra, and elemental analysis. BDH solvents such as dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$) and carbontetrachloride (CCl_4) were redistilled before use. All UV–vis spectra were recorded on a Shimadzu 1601 PC spectrophotometer within the wavelength range 200–800 nm using the same solvent in the examined solution as a blank. Absorbance measurements as a function of time, at fixed wavelengths, were made with the same instrument. For thermodynamic studies, the apparatus was equipped with a temperature controlled cell holder. Both sample and blank compartments were kept at constant temperature using a Shimadzu TCC-240A thermostat, which allowed the temperature to be maintained constant to within $\pm 0.1\,^{\circ}C$. The fluorescence (excitation and emission) spectra were determined with Shimadzu RF-5301 PC spectrophotometer: excitation slit width = 5 nm, emission slit width = 5 nm. Fresh solutions of porphyrins and acceptors were prepared before each series of measurements by dissolving precisely weighed amounts of the component in the appropriate volume of solvent. All solutions were kept in the dark except during sampling. Acceptor and donor solutions were added using a Finnpipette.

Photometric titrations at 670 and 665 nm were performed for the reactions of TTP with acceptors (PIC, DNS, DNP and DNB) and Zn-TTP with PIC and DNS, respectively. The donor was dissolved in dichloromethane at room temperature and the titration was monitored using a Shimadzu 1601 PC spectrophotometer. The procedure was as follows: X mL of (1.5×10^{-4} mol l^{-1} acceptors = PIC, DNS and 0.2 mol l^{-1}, acceptors = DNP, DNB), where $X = 0.25$, 0.50, 0.75, 1.00, 1.50, 2.00, 2.50 and 3.00 mL, was added to 0.5 mL of 7.0×10^{-5} mol l^{-1} TTP and Zn-TTP. The concentration of TTP and Zn-TTP in the reaction mixture was kept fixed at 7.0×10^{-6} mol l^{-1} while the concentration of acceptors was varied. The stoichiometry of the molecular CTCs under investigation was determined by the application of the conventional spectrophotometric molar ratio according to the known methods.[20]

RESULTS AND DISCUSSION

Absorption spectra

The electronic absorption spectra of the CTC of the TTP/PIC, TTP/DNS, TTP/DNP and TTP/DNB systems were recorded using constant donor concentration, 7×10^{-6} mol l^{-1} (in a given solvent), while the concentrations of the acceptors were varied within the range from 8×10^{-5} to 0.06 mol l^{-1}, depending on the donor. The absorption spectra of mixed donor–acceptor solutions were characterized by the appearance of two new absorption bands at 455 and 670 nm, which were stable under the studied conditions. The representative charge transfer spectra formed between TTP and DNP in CH_2CL_2 at 25 °C is shown in Fig. 1. Furthermore, the absorption intensities of these two new bands increased as the concentration of the acceptor was increased (Fig. 1). Moreover, the absorbance increased as the temperature was decreased using the same solution (see for example Fig. 2). These new absorption bands, which are attributed to the formation of CTCs, are stable at constant temperature. The new and broad absorptions indicate the formation of EDA complexes.

Although no reaction was found to occur between Zn-TTP/DNB or Zn-TTP/DNP systems under the same reaction conditions, a green color was obtained on interaction of the

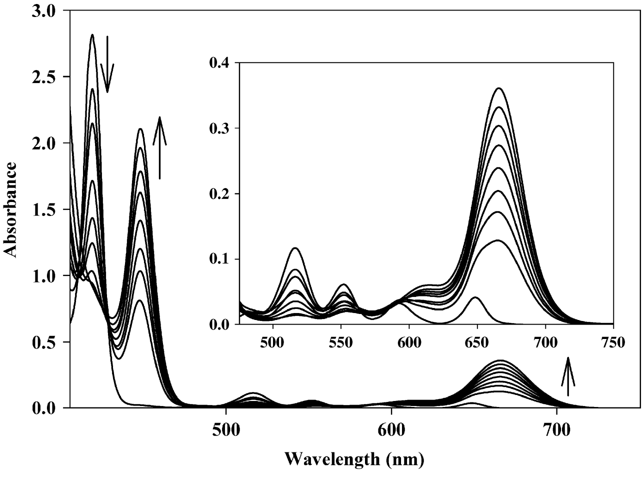


Figure 1. Electronic absorption spectra of the CTC solutions of TTP/DNP in CH_2Cl_2 at 25 °C. The concentration of TTP is 7×10^{-6} mol l^{-1}. The concentrations of DNP are 8.5×10^{-3} and (1.5, 2, 2.5, 3, 3.5, 4.0, 4.5) $\times 10^{-2}$ mol l^{-1}.

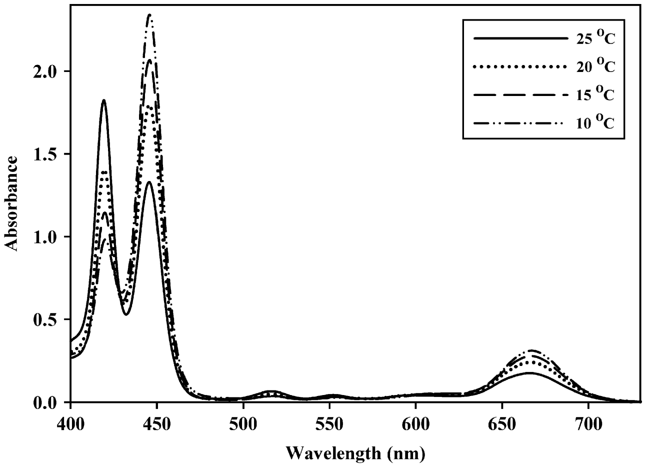


Figure 2. Variation of absorbance spectra of TTP/PIC system with temperature in $CHCl_3$. [TTP] = 7×10^{-6} mol l^{-1}, [PIC] = 2×10^{-5} mol l^{-1}.

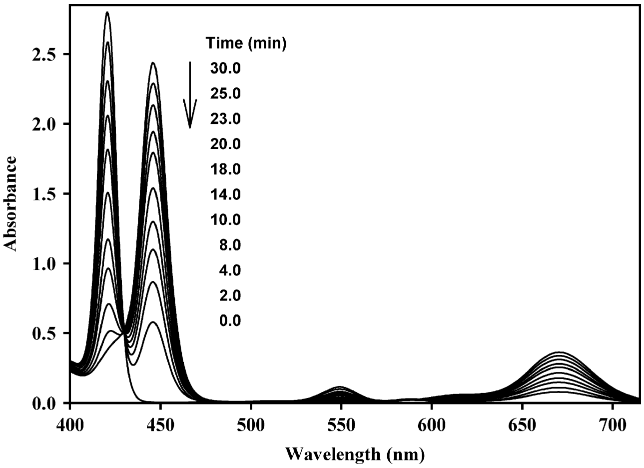


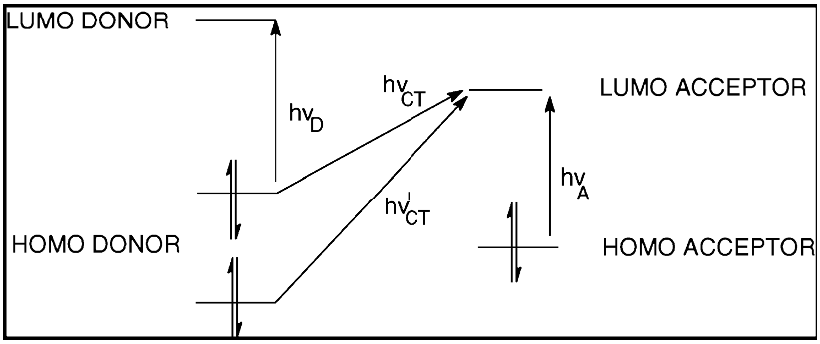
Figure 3. Effect of time on the CTC of Zn-TTP/DNS system in CH_2Cl_2 at 20 °C. [TTP] = 7×10^{-6} mol l^{-1}, [DNS] = 2.5×10^{-2} mol l^{-1}.

Zn-TTP with PIC and DNS acceptors. The reaction was time-dependent. The optimum reaction time was determined by following the color development spectrophotometrically at a temperature of 20 °C for PIC and DNS reagents. It was found that complete color development was attained after 30 min for PIC and DNS reagents, respectively (Fig. 3).

The porphyrin was relatively electron-rich, and PIC, DNS, DNP and DNB were relatively electron-poor compounds. When a solution contained both an electron-rich and an electron-poor compound, they tended to associate with one another in a loose interaction known as EDA complexes. The new, low-energy absorptions observed in solutions containing both a donor and an acceptor have been described by Mulliken[21] as charge transfer transitions involving the excitation of an electron on the donor to an empty orbital on the acceptor. This is shown in Scheme 1, in which $h\nu_{CT}$ depicts the energy of the CT transitions. The lowest energy CT transition involve promotion of an electron residing in the highest occupied molecular orbital (HOMO) of the donor to the acceptor, as shown for $h\nu_{CT}$. Charge transfer transitions involving electrons in lower energy orbitals also are possible and would result in higher energy CT transitions, as shown $h\nu_{1CT}$. The interaction between the TTP and DNB gave the reaction by the formation of radical ion pairs (Scheme 2). The transition involves promotion of an electron residing in the HOMO of TTP to the lowest occupied molecular orbital (LUMO) of the DNB, as shown in Scheme 2. Such a transition is more rapid in the non-polar solvent than in polar one, resulting in stabilization of the dative ($D^{\cdot+}$, $A^{\cdot-}$) structure in the non-polar solvent.

This phenomenon was also supported by the decrease of absorption intensity on Q-bands at 525, 560 and 585 nm, as well as being slightly red-shifted to 529, 565 and 590 nm, respectively, as the concentration of the acceptor increased. Two isoesbestic points were observed at 425 and 595 nm, indicating a single equilibrium (Fig. 1). The interaction between TTP and π-acceptors gave $\pi-\pi^*$ transitions.

The small red shift (Tables 1 and 2) phenomenon of the CT band on going from CCl_4 to CH_2Cl_2 for such strong complexes ($K_{CT} = 7.5643–2.36681 \times 10^4$ l.mol^{-1} at 298 K, see below) can be explained by taking into account that the contribution of the dative structure relative to the ground



Scheme 1. Charge transfer transitions for HOMOs of the donor compounds and LUMOs of the acceptor compounds.

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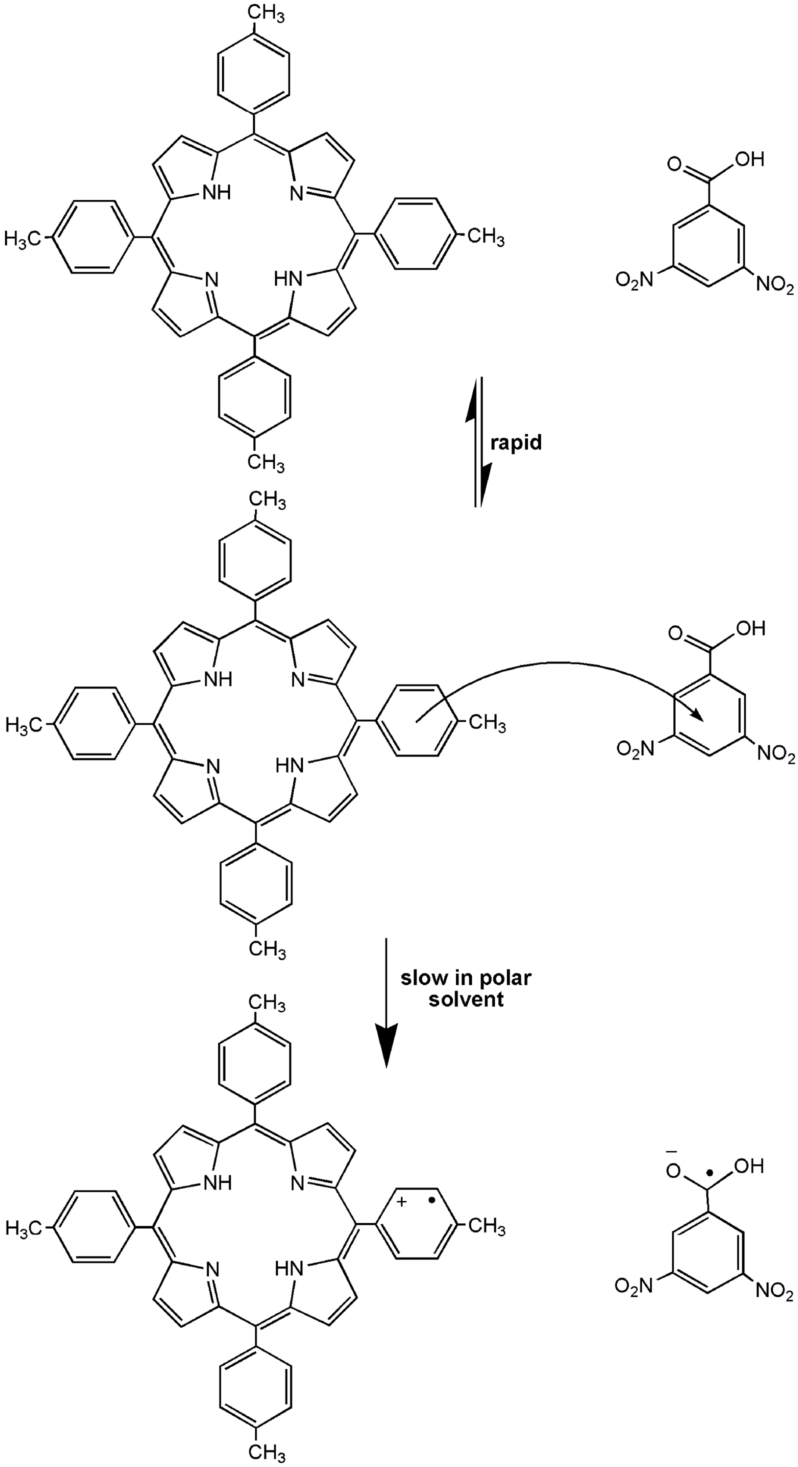

Scheme 2. The molecular structure of the compound and charge transfer transition between donor and acceptor.

state becomes larger.[16,22] Therefore, the difference of the dipole moment between ground and excited states is smaller for a stronger complex than for a weak one. The red shift of the CT band caused by polarity change on going from CCl_4 to CH_2Cl_2 is smaller in stronger complexes than in weak ones since the solvent stabilization energy difference at ground and CT excited is smaller for a strong complex than for a weak complex. A similar effect was observed for the relatively strong complex between diethyl sulfide–iodine.[23] The CT band of tetraphenylporphyrin (TPP) with similar acceptors appeared at 445 and 645 nm, respectively.[16] Compared with TTP, the red shift of the CT

Table 1. Spectral data of CTC of TTP with various acceptors at different temperatures

System	T (K)	K_{CT} (l mol^{-1})	ε_{CT} (l mol^{-1} cm^{-1})	λ_{CT} (nm)	r
TTP/PIC-CH_2Cl_2	298	$2.3668 \times 10^4 \pm 1.23$	4.89611×10^5	670	0.996
	293	$3.2973 \times 10^4 \pm 0.94$	4.91926×10^5		0.972
	288	$4.1814 \times 10^4 \pm 1.17$	4.92337×10^5		0.975
	283	$4.6350 \times 10^4 \pm 1.42$	4.97582×10^5		0.979
TTP/DNS-CH_2Cl_2	298	$1.8772 \times 10^4 \pm 1.62$	5.67928×10^5	670	0.951
	293	$2.1918 \times 10^4 \pm 1.56$	5.75583×10^5		0.936
	288	$2.4986 \times 10^4 \pm 1.38$	5.90143×10^5		0.973
	283	$2.7818 \times 10^4 \pm 1.04$	6.01992×10^5		0.959
TTP/DNB-CH_2Cl_2	298	7.6075 ± 0.76	5.05888×10^5	667	0.965
	293	9.0321 ± 0.83	5.43817×10^5		0.949
	288	15.9360 ± 0.81	5.64030×10^5		0.962
	283	29.8689 ± 0.69	5.85015×10^5		0.954
TTP/DNP-CH_2Cl_2	298	24.3546 ± 1.12	4.56744×10^5	665	0.991
	293	33.5666 ± 1.08	4.79859×10^5		0.983
	288	43.7048 ± 0.98	4.80982×10^5		0.995
	283	56.7645 ± 1.24	4.85391×10^5		0.976
TTP/PIC-$CHCl_3$	298	$5.1345 \times 10^4 \pm 1.92$	5.56783×10^5	665	0.966
	293	$6.5684 \times 10^4 \pm 2.03$	5.63624×10^5		0.993
	288	$9.0985 \times 10^4 \pm 1.73$	5.73245×10^5		0.989
	283	$11.4327 \times 10^4 \pm 1.71$	5.74567×10^5		0.972
TTP/DNS-$CHCl_3$	298	$3.6285 \times 10^4 \pm 1.14$	4.71114×10^5	668	0.999
	293	$4.5473 \times 10^4 \pm 1.37$	4.71241×10^5		0.999
	288	$4.9636 \times 10^4 \pm 1.09$	4.713585×10^5		0.999
	283	$5.1516 \times 10^4 \pm 1.17$	4.788878×10^5		0.989
TTP/DNB-$CHCl_3$	298	12.5689 ± 1.45	5.124678×10^5	665	0.96
	293	19.7653 ± 1.49	5.23467×10^5		0.949
	288	45.1297 ± 1.19	5.25689×10^5		0.962
	283	65.7865 ± 1.32	5.43342×10^5		0.954
TTP/DNP-$CHCl_3$	298	33.1572 ± 0.56	5.65451×10^5	665	0.991
	293	43.5117 ± 0.53	5.56744×10^5		0.983
	288	58.8758 ± 0.78	5.87658×10^5		0.995
	283	73.7847 ± 0.63	5.99456×10^5		0.976
TTP/PIC-CCl_4	298	$7.5643 \times 10^4 \pm 1.86$	4.97582×10^5	662	0.996
	293	$8.4578 \times 10^4 \pm 1.57$	4.92337×10^5		0.999
	288	$13.6543 \times 10^4 \pm 1.74$	4.89611×10^5		0.978
	283	$16.345 \times 10^4 \pm 1.63$	4.91926×10^5		0.992
TTP/DNS-CCl_4	298	$5.7865 \times 10^4 \pm 1.09$	6.76383×10^5	667	0.951
	293	$7.7893 \times 10^4 \pm 1.11$	6.79425×10^5		0.936
	288	$9.9654 \times 10^4 \pm 1.29$	7.11433×10^5		0.973
	283	$13.6732 \times 10^4 \pm 1.13$	7.21455×10^5		0.959
TTP/DNB-CCl_4	298	16.1654 ± 1.18	5.18530×10^5	665	0.96
	293	23.1267 ± 1.37	5.19435×10^5		0.949
	288	49.6543 ± 1.31	5.87894×10^5		0.962
	283	71.321 ± 1.28	5.95553×10^5		0.954
TTP/DNP-CCl_4	298	39.1790 ± 1.22	5.04391×10^5	665	0.991
	293	48.4532 ± 1.03	5.36678×10^5		0.983
	288	67.8758 ± 1.17	5.46743×10^5		0.995
	283	82.7847 ± 1.05	5.87855×10^5		0.976

Table 2. Spectral data of CTC of Zn-TTP/PIC and Zn-TTP/DNS at different temperatures

System	T (K)	K_{CT} (l mol^{-1})	ε_{CT} (l mol^{-1} cm^{-1})	λ_{CT} (nm)	r
Zn-TTP/PIC-CH_2Cl_2	298	5.12 ± 1.45	4.23167×10^5	665	0.99
	293	6.43 ± 1.63	4.54876×10^5		0.99
	288	8.34 ± 1.59	4.78432×10^5		0.98
	283	10.32 ± 1.52	4.975823×10^5		0.99
Zn-TTP/DNS-CH_2Cl_2	298	3.94 ± 0.73	3.897654×10^5	665	0.97
	293	4.86 ± 0.62	3.956732×10^5		0.98
	288	6.56 ± 0.59	4.125674×10^5		0.99
	283	8.78 ± 0.63	4.23561×10^5		0.97
Zn-TTP/PIC-$CHCl_3$	298	7.54 ± 1.74	5.234567×10^5	663	0.99
	293	8.03 ± 1.83	5.45327×10^5		0.99
	288	11.78 ± 1.56	5.87654×10^5		0.99
	283	15.95 ± 1.61	5.976543×10^5		0.98
Zn-TTP/DNS-$CHCl_3$	298	5.67 ± 1.17	4.77443×10^5	665	0.99
	293	5.98 ± 1.32	4.79867×10^5		0.98
	288	7.56 ± 1.41	4.87432×10^5		0.99
	283	9.65 ± 1.28	4.98765×10^5		0.99
Zn-TTP/PIC-CCl_4	298	10.56 ± 1.13	6.12365×10^5	660	0.96
	293	12.87 ± 1.19	6.436243×10^5		0.99
	288	17.87 ± 1.06	6.732456×10^5		0.98
	283	25.67 ± 1.09	6.755688×10^5		0.97
Zn-TTP/DNS-CCl_4	298	8.86 ± 2.21	5.743218×10^5	665	0.99
	293	9.89 ± 1.94	5.876543×10^5		0.99
	288	14.56 ± 1.97	5.987654×10^5		0.99
	283	18.45 ± 1.77	6.125679×10^5		0.98

band gave an indication of the relative strength of the donors. Based upon this, we obtained the following trend of electron donor strength: TTP > TPP. This result is in accordance with the literature.[17]

Determination of the stoichiometry of the CTC by spectrophotometric titration and continuous variation methods

Photometric titration measurements of the characteristic absorption bands of the CTCs proved that the complex formation occurs in a 1 : 1 donor : acceptor ratio. These measurements were based on detected bands at 670 nm for TTP/PIC and TTP-DNS; and at 665 nm for TTP/DNP, TTP/DNB, Zn-TTP/PIC and Zn-TTP/DNS. In these measurements, the concentration of TTP and Zn-TTP was kept fixed, while the concentration of the acceptors (at the same) was varied, as illustrated in the Experimental section. Photometric titration curves based on these measurements are shown in Fig. 4. The base acceptors equivalence points indicate that the ratio in all cases was 1 : 1 and this result agrees quite well with Job's continuous variation method, as shown in Fig. 5.[24,25] Further support was observed in the straight line method, which can be used as a qualitative mean for the determination of the stoichiometry ratio of the donor and acceptor in the complex.[26] In this case the logarithmic plot of absorbance ($\log A$) vs volume ($\log V$) gave straight lines with slopes varying from 0.95 to 1.0, which also proves the formation of the 1 : 1 CTC.

Formation constant and molar extinction coefficients of the CTC

Estimation of the formation constant (K_{CT}) and the molar absorption coefficients (ε_{CT}) of the CTCs are calculated using the known equation (1).[27]

$$\frac{[D_o]}{\mathrm{A} - \mathrm{A_o}} = \frac{1}{\varepsilon_{CT} - \varepsilon_D} + \frac{1}{(\varepsilon_{CT} - \varepsilon_D)K_{CT}[A_o]} \qquad (1)$$

where A_o and A are the absorbance of the free donor solution and with acceptor complex at given wavelength, ε_D and ε_{CT} are the molar extinction coefficients of the donor and the complex, and $[D_o]$ is the initial concentration of the donor. For this purpose, the absorption spectra of solutions containing constant donor concentration and variable acceptor concentrations were recorded at four different temperatures within the range 10–25 °C. The values of K_{CT} and ε_{CT} obtained at different temperatures in all the solvents studied are listed in Table 1 and shown in Fig. 6. The observed decrease in formation constant values with rise in temperature indicates the exothermic nature of the interaction between the studied acceptor and donor molecules. However, the increase in K_{CT} value with decreasing solvent polarity can be attributed to the stability of the dative structure $D^+ - A^-$ in a non-polar solvent (Scheme 2). Moreover, the values of K_{CT} of the TTP or Zn-TTP increased as the electron affinity values of acceptors (E^A) were increased (Tables 1 and 2). The

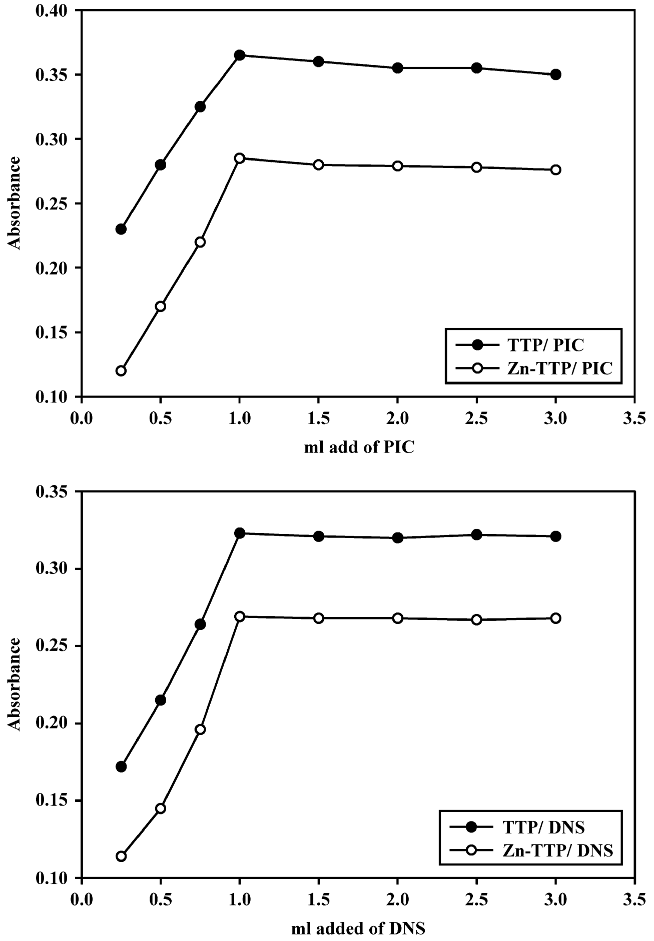

Figure 4. Photometric titration curves for the TTP/PIC, Zn-TTP/PIC, TTP/DNS and ZnTTP/DNS reactions in $CHCl_3$ at 670 nm.

relative magnitude of K_{CT} at the lowest temperature in each case gives an indication of the relative strengths of the electron acceptors. Based on this, we found the following trend of the electron acceptor strength: PIC > DNS > DNP > DNP. This is in agreement with their E^A.

To obtain information about the effect of the insertion of Zn into the porphyrin core on the K_{CT} values of TTP, it was found that K_{CT} decreased on going from TTP to Zn-TTP donors. The presence of Zn in the porphyrin core decreased the aromaticity and the ability of TTP as a donor resulted in decreasing values of K_{CT} (Table 2). As could be observed from the reported ε_{CT} values, there was a slight decrease with rising temperature in most cases. The decrease in ε_{CT} values with rising temperature was in agreement with Mulliken's theory[14] and can be attributed to broadening of the CT band with increasing temperature. The variation of ε_{CT} for the CTCs almost obeyed the following sequence: TTP > Zn-TTP.

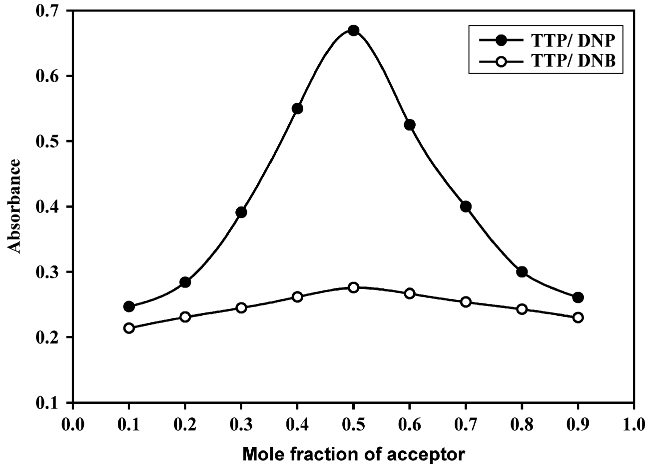

Figure 5. The plot of Job's method for TTP/DNP and TTP/DNB systems at 665 nm.

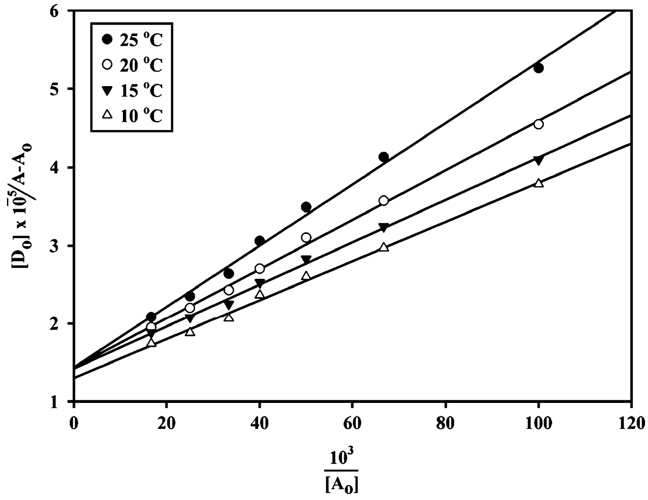

Figure 6. Relation between $[D_o]/A - A_o$ and $1/[A_o]$ for CTC of TTP/TCNE system in CH_2Cl_2 at different temperature.

Thermodynamic parameters of the CTC

The thermodynamic parameters, viz. Gibb's free energy, enthalpy and entropy changes, were evaluated from the temperature dependence of the formation constant using the Van't Hoff plots, and a representative plot is shown in Fig. 7. As can be seen, there is no evidence of deviation from the linearity over the investigated temperature range, indicating that a 1 : 1 complex formed over all investigated temperatures for all systems. The parameters thus obtained are represented in Table 3, and these values show that complexation is thermodynamically favored. The enthalpy change of the complexation also reveals that the CTC formation between the used donors and the acceptors is exothermic in nature. The values of $\Delta H°$ and $\Delta S°$ generally become more negative as the stability constant for molecular complexes increases. As the bond between the components becomes stronger and thus the components are subjected to more physical strain or loss of freedom, the $\Delta H°$ and $\Delta S°$ values should be more negative. Additionally, there are parallel increases in the values of $\Delta H°$

Table 3. Thermodynamic standard reaction quantities of TPP/PIC and Zn-TTP/PIC complexes in different organic solvents

System	$-\Delta H^\circ$ (kJ mol^{-1})	$-\Delta S^\circ$ (J mol^{-1} K^{-1})	$-\Delta G^\circ$ (298 K) (kJ mol^{-1})	r
TTP/PIC-CH_2Cl_2	448.28 ± 0.55	14.20 ± 1.9	24.95 ± 0.24	0.99
TTP/PIC-$CHCl_3$	551.35 ± 0.23	16.66 ± 0.8	26.87 ± 0.34	0.96
TTP/PIC-CCl_4	524.53 ± 0.41	17.60 ± 1.4	27.83 ± 0.15	0.98
Zn-TTP/PIC-CH_2Cl_2	478.59 ± 0.12	15.92 ± 0.42	4.04 ± 0.12	0.99
Zn-TTP/PIC-$CHCl_3$	512.62 ± 0.31	17.03 ± 1.22	5.00 ± 0.21	0.97
Zn-TTP/PIC-CCl_4	599.109 ± 0.32	19.90 ± 1.07	5.83 ± 0.11	0.98

and ΔS° as the polarity of the solvent decreases (Table 3). This behavior indicates the solvent dependent stability of the CTC. Finally, the enthalpy of formation ΔH° for both TTP and Zn-TTP complexes increases with increasing E^A of the acceptors, accompanied by parallel increases in ΔG° and ΔS°.

Spectral properties of the CTC

The experimental oscillator strength (f) and the transition dipole moment (μ) were calculated using the following approximate formulas:[28]

$$f = 4.32 \times 10^{-9}[\varepsilon_{\max}\Delta\nu_{1/2}] \tag{2}$$

$$\mu = 0.0958\left[\frac{\varepsilon_{\max}\Delta\nu_{1/2}}{\nu_{\max}}\right]^{1/2} \tag{3}$$

where $\Delta\nu_{1/2}$ is the band with at half intensity, and $\varepsilon_{\max}$ and $\nu_{\max}$ are the molar extinction coefficient and wavenumber at the absorption maximum of the complex, respectively. The $\Delta\nu_{1/2}$, f and μ values are reported in Table 4. The values of the calculated oscillator strength are rather relatively large, indicating a strong interaction between the donor–acceptor pairs with relative high probabilities of CT transitions.

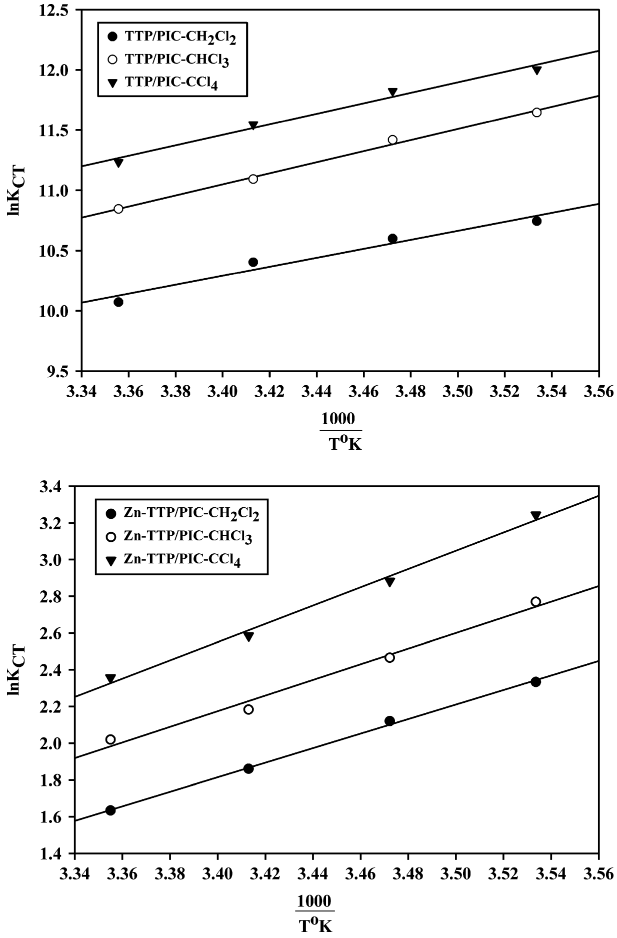

Figure 7. Relation between lnK_{CT} and 1000/TK for CTC of TTP/PIC and Zn-TTP/PIC systems in CH_2Cl_2, $CHCl_3$ and CCl_4.

Ionization potential of the donor

The ionization potential (I_p) of the free donor of the highest filled molecular orbital on the donor was determined using the following relation:

$$I_p = a + b(h\nu_{\max}) \tag{4}$$

where $h\nu_{\max}$ is the lowest transition energy in electron volts; a and b are 5.11 and 0.701,[29] 4.39 and 0.857,[30] or 5.156 and 0.778[31], respectively. The average values of calculated I_p of TTP and Zn-TTP by this method were 6.42 and 6.49 eV, respectively. The determined I_p values are given in Table 5. It has been reported that the ionization potential of the electron donor may be correlated with the charge transfer transition energy of the complex.[32] Comparison of the transition energies of the CTC in different solvents with the I_p values of the electron donors in the corresponding solvents forming the complex reveals a regular relationship, which is in accord with the results obtained by McConnel *et al.*[33]

Further evidence for the nature of CT-interaction in the present systems is the calculation of the dissociation energy (W) of the charge transfer excited state of the complex in different solvents. Hence the dissociation energies of the complex were calculated from their CT-energy ($h\nu_{CT}$), I_p and E^A of the acceptor using the empirical relation given in eqn (5).[33]

$$h\nu_{CT} = I_p - E^A - W \tag{5}$$

The calculated values of W are reported in Table 5. The plot of W vs I_p shown in Fig. 8 is linear as was expected

Table 4. Bandwidth $^{-}\nu_{\max}$, half-bandwidth $\Delta^{-}\nu$ 1/2, oscillator strength f and transition dipole moment μ of TPP/DNS and Zn-TTP/DNS complexes at various temperatures

System	$\Delta^{-}\nu$ 1/2 (cm^{-1})	f	μ (debyes)	r
TPP/DNS-CH_2Cl_2	$^{-}\nu_{\max} = 14925.37$			
298	1462.31	3.63	22.59	0.99
293	1475.27	3.66	22.85	0.99
288	1497.25	3.81	23.30	0.99
283	1512.47	3.93	23.66	0.99
TTP/DNS-$CHCl_3$	$^{-}\nu_{\max} = 14970.05$			
298	1484.21	3.08	20.70	0.99
293	1524.41	3.1	20.98	0.98
288	1556.59	3.16	21.2	0.97
283	1587.12	3.28	21.58	0.99
TPP/DNS-CCl_4	$^{-}\nu_{\max} = 14992.5$			
298	1595.64	4.64	25.65	0.99
293	1614.23	4.71	25.85	0.99
288	1645.47	5.05	26.76	0.99
283	1678.51	5.23	27.66	0.99
Zn-TTP/DNS-CH_2Cl_2	$^{-}\nu_{\max} = 14970.05$			
298	1510.14	2.54	18.99	0.99
293	1552.16	2.65	27.15	0.98
288	1573.25	2.80	19.94	0.99
283	1595.34	2.91	20.35	0.98
Zn-TTP/DNS-$CHCl_3$	$^{-}\nu_{\max} = 15037.59$			
298	1615.42	3.33	21.69	0.99
293	1658.1	3.43	22.03	0.97
288	1672.25	3.52	22.3	0.98
283	1686.25	3.63	22.65	0.99
Zn-TTP/DNS-CCl_4	$^{-}\nu_{\max} = 15037.59$			
298	1635.74	4.05	23.94	0.97
293	1675.68	4.25	24.51	0.96
288	1692.36	4.37	24.86	0.99
298	1716.92	4.54	26.32	0.99

from eqn (5). Thus, the acquired values of W of charge transfer excited states of the complex in different solvents were constant, which suggests that the investigated complex is reasonably strong and stable under the studied conditions with higher resonance stabilization energy.[34]

FLUORESCENCE SPECTRA

The fluorescence quenching of TTP by PIC, DNS, DNP and DNB was studied by steady-state emission measurements in dichloromethane, chloroform and carbontetrachloride (Fig. 9, Table 6). The second-order Stern–Volmer (SV) quenching constants ($K_{SV} = K_q\tau_o$) of the fluorescence quenching were determined from the SV plots using the method of linear regression according to the relation:[35]

Table 5. Charge transfer energy, ionization potential and dissociation energy of CTCs of TTP and Zn-TTP with different acceptors

Acceptor	TTP, E_{CT} (eV)	TTP, I_p (eV)	Zn-TTP, I_p (eV)	W (eV)
PIC	1.85	6.42	6.46	3.95
DNS	1.85	6.42	6.48	4.01
DNP	1.86	6.43	6.50	4.11
DNB	1.87	6.43	6.51	4.18

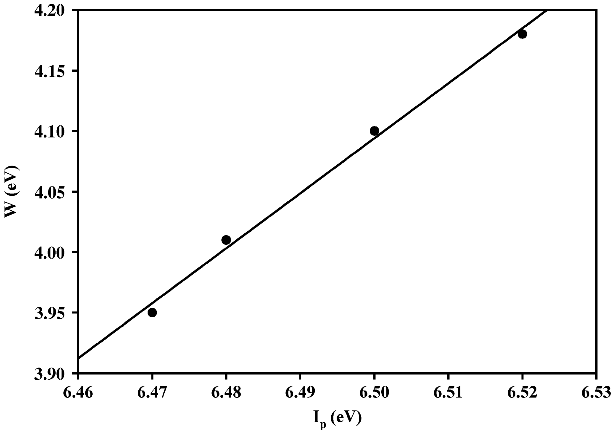

Figure 8. The plot of dissociation energy (W) vs the ionization potential (I_p) of TTP/PIC system in CH_2Cl_2, $CHCl_3$ and CCl_4.

$$I_o/I = 1 + K_q\tau_o[Q] \tag{6}$$

where I_o and I are the relative fluorescence intensities in the absence and presence of quencher of concentration $[Q]$, and K_q and τ_o are the quenching rate constant of the fluorescence quenching and the fluorescence lifetime of the fluorophore in the absence of quencher, respectively. Typical SV plots were linear in the investigated concentration range, as shown in Fig. 10. At relatively high quencher concentrations, SV plots showed positive deviations, especially with stronger quenchers, indicating the formation of ground state complexes. Hence, all studies were performed at low $[Q]$. It is readily seen that the quenching efficiency (magnitude of K_{SV}) increased with increasing E^A of the quencher. There was a good linear dependence of $\ln K_{SV}$ on E^A of the quencher, as shown in Fig. 11. This indicated the probable involvement of charge transfer type quenching. Also, Table 6 shows that the K_{SV} values decreased with increasing solvent polarity. It was observed that all systems exhibited a new emission fluorescence band in all solvents under investigation (Fig. 9).

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Table 6. Fluorescence quenching data of TTP (7×10^{-6} mol l^{-1}) with PIC, DNS ($1-3 \times 10^{-5}$ mol l^{-1}), DNP ($1-4 \times 10^{-2}$ mol l^{-1}) and DNB ($1-8 \times 10^{-2}$ mol l^{-1}) in different organic solvents with λ_{max} excitation = 420 nm and λ_{max} emission = 650 nm at room temperature

	$K_{SV}/10^3$ (l mol^{-1})				
Solvents	PIC	DNS	DNP	DNB	*r*
CH_2Cl_2	101.49 ± 0.05	77.43 ± 0.03	0.53 ± 0.03	0.46 ± 0.21	0.999
$CHCl_3$	127.03 ± 0.02	92.62 ± 0.05	0.69 ± 0.07	0.51 ± 0.32	0.999
CCl_4	143.12 ± 0.08	119.76 ± 0.03	0.87 ± 0.04	0.63 ± 0.15	0.999

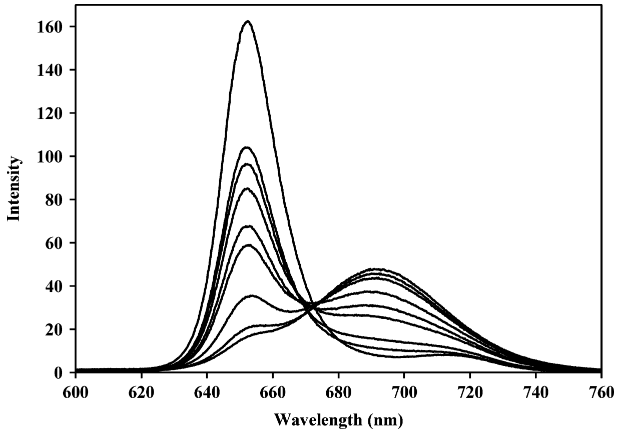

Figure 9. The emission spectra of free TTP (7×10^{-6} mol l^{-1}) and TTP/DNP solution at different DNP (1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0 and 6.0×10^{-2} mol l^{-1}) in CH_2Cl_2 at room temperature.

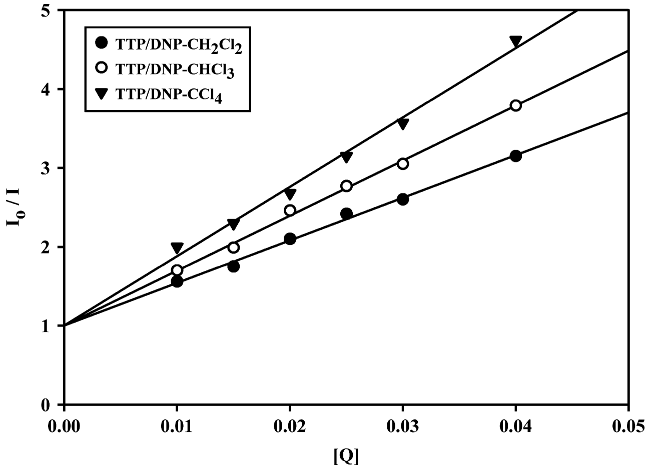

Figure 10. Stern–Volmer plots for the TTP/DNP system in CH_2Cl_2, $CHCl_3$, and CCl_4.

This band was not due to either the individual components or impurities. The new emission of the CTCs was characteristic of a CT excited state. The resulting new band was red-shifted on increasing the solvent polarity. The emitting excited state was obtained via an exciplex formed between singlet-excited TTP (^{1}TTP*) and the acceptors in its ground state.[16] It could also obtained by absorption of a photon by the ground state of the complex. Also, there was no spectral overlap between the emission of the TTP and the absorption of the nitro aromatic acceptor, and hence electronic energy transfer from ^{1}TTP* to the acceptor can be ruled out. According to these considerations, it is possible to say that charge transfer is the major pathway for quenching of ^{1}TTP*. The quenching efficiency decreased as the temperature was increased from 10 to 25 °C.

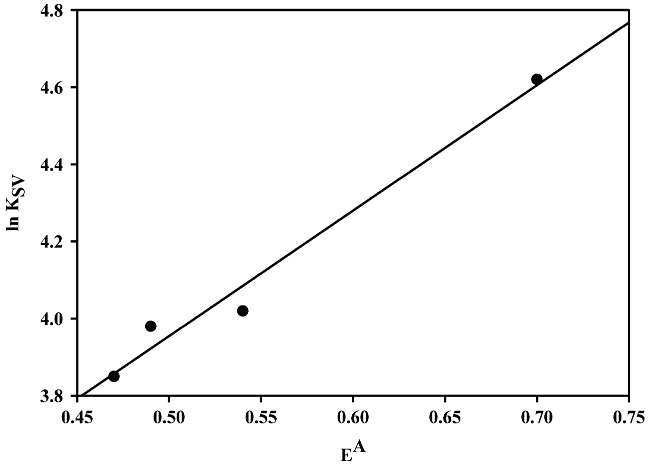

Figure 11. Relation between lnK_{SV} and E^A at 25 °C.

CONCLUSIONS

It may be concluded that the TTP donors form strong CTC of 1 : 1 stoichiometry with the nitro aromatic acceptors in all the solvents studied. However, Zn-TTP do not display any detectable CT band with DNP and DNB, even at higher donor and acceptor concentrations at different temperatures in various organic solvents. Strong CTC was only formed from the reaction of Zn-TTP with acceptors of high E^A such as PIC and DNS. The equilibrium constant (K_{CT}) values decreased with increasing temperature and solvent polarity. The spectroscopic and thermodynamic parameters of the complex were found to be highly solvent-dependent. From the trends in the CT-absorption bands, the ionization potential of the donor molecules was estimated. The oscillator strength and transition dipole moment of the CTCs were also determined. The investigated complexes were stable and exothermic in nature. A detectable emission band was formed between TTP and all studied acceptors in non-polar and moderately polar solvents. The fluorescence emission observed was not due to either of the individual components. The fluorescence quenching increased with increasing electron affinity of the acceptors.

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