

Spectroscopic and Thermal Characterization of Charge-Transfer Complexes Formed In the Reaction of 2-Amino-6-Ethylpyridine with π -Electron Acceptors

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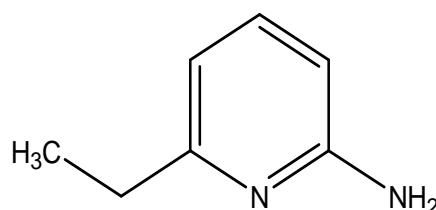
ABSTRACT: The spectrophotometric characteristics of the solid charge-transfer molecular complexes (CT) formed in the reaction of the electron donor 2-amino-6-ethylpyridine (2A6EPy) with the π -acceptors tetracyanoethylene (TCNE), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and 2,4,4,6-tetrabromo-2,5-cyclohexadienone (TBCHD) have been studied in chloroform at 25 °C. These were investigated through electronic, infrared, mass spectra and thermal studies as well as elemental analysis. The results show that the formed solid CT- complexes have the formulas [(2A6EPy)(TCNE)₂], [(2A6EPy)₂(DDQ)], [(2A6EPy)₄(TBCHD)] for 2-amino-6-ethylpyridine in full agreement with the known reaction stoichiometries in solution as well as the elemental measurements. The formation constant k_{CT} , molar extinction coefficient ϵ_{CT} , free energy change ΔG^0 and CT energy E_{CT} have been calculated for the CT- complexes [(2A6EPy)(TCNE)₂], [(2A6EPy)₂(DDQ)].

Keywords: DDQ, TCNE, TBCHD, Spectra, Thermal.

I. INTRODUCTION

The molecular interactions between electron donors and acceptors are generally associated in the formation of intensely colored charge-transfer (CT) complexes which absorb radiation in the visible region [1-8]. The photometric methods used to study these interactions are usually simple and convenient because of the rapid formation of the complexes. The chemical and physical properties of charge-transfer (CT) complexes formed by the reactions of π - and σ - electron acceptors with different donors like amines, crown ethers, polysulfur bases and oxygen-nitrogen mixed bases have been the subject of many studies both in solution and in the solid state [9-13]. It was found that the reaction stoichiometries as well as the structure of these CT-complexes depend strongly on the number of nitrogen donor atoms as well as on their terminal attached groups, hydrogen or donating groups like alkyl or withdrawing atoms like halogens. Electron donating alkyl groups were found to enhance the acceptor: donor stoichiometry. Interestingly, most of the CT- complexes have many applications in chemical analysis like quantitative drug estimation and some complexes have interesting physical properties like electrical conductivities [14-17].

In this paper, we report the formation of three new CT- complexes formed by the reaction of 2-amino-6-ethylpyridine with different types of π -electron acceptors. The π -acceptors are tetracyanoethylene (TCNE), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and 2,4,4,6-tetrabromo-2,5-cyclohexadienone (TBCHD). All reactions were carried out in CHCl₃ as a solvent. The obtained results enabled us to investigate the stoichiometries and structure of these new CT- complexes.



2-Amino-6-ethylpyridine
(2A6EPy)

III. RESULTS & DISCUSSION

3.1. Electronic spectra studies

The electronic absorption spectrum of the reaction of tetracyanoethylene (TCNE) with the donor 2A6EPy is shown in Fig.1. While none of the reactant's spectra display any measurable absorption in the region 400 – 650 nm, the resulting CT- complex shows strong absorptions centered on 597, 555 and 524 nm for 2A6EPy-TCNE reaction. These absorptions are associated with the strong change in color observed upon mixing of reactants (dark blue from colorless solution for 2A6EPy-TCNE), and reflect the electronic transitions in the formed CT- complex.

Photometric titration measurements based on these absorptions were performed in order to determine the reaction stoichiometry in CHCl_3 (Fig. 2). The results showed that the donor: TCNE molar ratio was found to be 1:2 for the donor. This is in good agreement with the obtained elemental analysis of the solid CT- complex. On the basis of these experimental data, the complex obtained can be formulated as $[(2A6EPy)(TCNE)_2]$.

Interestingly, the reaction stoichiometry using TCNE as a π -acceptor is 1:2 for the donor and the alkyl group (ethyl group at position 6) is enhancing the electron donation in comparison with the reaction stoichiometry of 2-aminopyridine with TCNE which was 1:1 in our previous study [19].

Fig.3 shows the electronic spectra recorded in the region 400 – 1100 nm of the reaction of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) with the donor (2A6EPy). Similar to the reaction with the previous acceptor, a strong change in color is observed upon mixing. A dark brown color indicated the formation of the 2A6EPy-DDQ charge-transfer complex and is associated with the electronic transitions at 716, 567, 501, and 460 nm. Photometric titration measurements were performed for 2A6EPy reaction in CHCl_3 as shown in Fig. 4. The results showed that the donor-DDQ molar ratio was 2:1. This is in good agreement with the obtained elemental analysis of the solid CT- complex which accordingly can be formulated as $[(2A6EPy)_2(DDQ)]$.

The reaction stoichiometry using DDQ as a π -acceptor is 2:1 because of the steric hindrance, the donation became less (2: 1) than that in case of 2-aminopyridine with DDQ which was 1:1 in our previous study [19] and the ethyl group in 2A6EPy isn't enhancing the donation as in the previous acceptor TCNE.

Fig.5 shows the electronic spectra recorded in the region 320-500 nm of the reaction of 2,4,4,6-tetrabromo-2,5-cyclohexadienone (TBCHD) with 2A6EPy. A strong change in color is observed upon mixing and a dark brown color indicated the formation of the 2A6EPy-TBCHD charge-transfer complex and is associated with an electronic transitions at 372 nm

The stoichiometry of the charge-transfer complex between 2A6EPy and TBCHD was obtained as 4:1. This was based on the elemental analysis of the isolated solid complex $[(2A6EPy)_4(TBCHD)]$. However, the use of photometric titration to determine the stoichiometry was unsuccessful and resulted in a straight line (Fig.6). Table 1 shows the spectroscopic data of the resulting CT- complexes.

These obtained UV/Vis spectra of the CT- complexes $[(2A6EPy)(TCNE)_2]$, $[(2A6EPy)_2(DDQ)]$ and $[(2A6EPy)_4(TBCHD)]$ have clarified that the variation of the CT-absorptions of TCNE, DDQ and TBCHD should be related to the electron affinity of each acceptor with the donor 2A6EPy. These pronounced variations of CT- interaction stoichiometries are relatively complicated and need to be evaluated. It is definitely connected to many factors such as the donor molecular symmetry, the type of electron withdrawing groups or atoms Cl, Br or $\text{C}\equiv\text{N}$ as well as the steric hinderance between reactants. All of these factors are expected to play an important role on the electron donation process from the nitrogen electron pairs of the donor 2A6EPy and the aromatic ring of DDQ and TBCHD acceptors. The aromatic ring in TBCHD has lower electron accepting ability compared with that in DDQ, related to the lower electron withdrawing process of the substituent Br in TBCHD compared with $\text{C}\equiv\text{N}$ in DDQ. This certainly, allows stronger electron donation from 2A6EPy base to DDQ compared with that with TBCHD.

3.2. Formation Constant and molar extinction coefficient

The formation constant (K_{CT}) and molar extinction coefficient (ϵ_{CT}) values for the formed CT-complexes of the donor 2-amino-6-ethylpyridine with the π -acceptors TCNE and DDQ in CHCl_3 at 25 °C were calculated.

The formation constant, K_{CT} (lmol^{-1}), and the molar extinction coefficient ϵ_T ($\text{lmol}^{-1}\text{cm}^{-1}$) have been calculated for the complexes $[(2A6EPy)(TCNE)_2]$ and $[(2A6EPy)_2(DDQ)]$ using the known [20] equation (1) of 1:2 complexes:

$$\frac{(A_0)^2 D_0 \ell}{A} = \frac{1}{k\epsilon} + \frac{A_0(A_0 + 4D_0)}{\epsilon} \quad (1)$$

Here A_0 and D_0 are the initial concentrations of the acceptors and donor, respectively, while A is the absorbance at the mentioned CT bands and ℓ is the light path length (1cm). The data obtained throughout this calculation

are given in Table 2. Plotting the values $(A_0)^2 D_0 \ell / A$ versus $A_0 (A_0 + 4D_0)$ values of equation (1), straight lines were obtained with a slope of $1/\epsilon_{CT}$ and intercept of $1/K_{CT} \epsilon_{CT}$ as shown in Figures 7 and 8.

These complexes show high values of both the formation constant (K_C) and the molar extinction coefficient (ϵ_{CT}). The obtained values of K_{CT} are 14.51×10^5 and $31.39 \times 10^5 \text{ l mol}^{-1}$ for $[(2A6EPy)(TCNE)_2]$ and $[(2A6EPy)_2(DDQ)]$ and their respective values of ϵ_{CT} are 0.564×10^3 and $0.225 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$. These values confirm the expected high stabilities of the formed CT- complexes as a result of the expected high donation of 2-amino-6-ethylpyridine. The formation constants are strongly dependent on the nature of the used acceptors including the type of electron withdrawing substituent on it such as cyanide group in DDQ and TCNE. For the system 4:1 we are not aware for the equation to calculate those parameters. Identification of charge transfer bands can be illustrated as follows:

The color of CT- complexes is reflective of the relative energy balance resulting from the transfer of electronic charge from donor to acceptor.

Solvatochromism: In solution, the transition energy and therefore the complex color varies with variation in solvent permittivity, indicating variation in shifts of electron density as a result of the transition. This distinguishes it from the $\pi\pi^*$ transitions on the ligand. Intensity: CT absorptions bands are intense and often lie in the ultraviolet and visible portion of the spectrum.

3.3. Measurement of ΔG^0 , E_{CT} and I_p

The free energy change ΔG^0 (cal mol^{-1}) values of the complexes $[(2A6EPy)(TCNE)_2]$, and $[(2A6EPy)_2(DDQ)]$ were calculated from Gibbs free energy of formation according to the equation (2) [21, 22]:

$$\Delta G^0 = -RT \ln K_{CT} \quad (2)$$

Where ΔG^0 is the free energy for the formation of the charge transfer complexes; R the gas constant ($1.987 \text{ cal mol}^{-1} \text{ }^\circ\text{C}$); T the temperature in Kelvin; K_{CT} the formation constant of donor-acceptor complexes (l mol^{-1}). The ΔG^0 values of the complexes $[(2A6EPy)(TCNE)_2]$, and $[(2A6EPy)_2(DDQ)]$ are -8.40×10^3 and $-8.86 \times 10^3 \text{ cal mol}^{-1}$ respectively.

The obtained results of ΔG^0 reveal that the CT- complexes formation process is spontaneous. The results of ΔG^0 are generally more negative as the formation constants of the CT- complexes increase. The more negative the value for ΔG^0 , the farther to the right the reaction will proceed in order to achieve equilibrium.

The charge - transfer energy E_{CT} of the formed solid CT- complexes is calculated using the following equation (3) [23, 24]:

$$E_{CT} (nm) = \frac{1243.667}{\lambda_{CT}} \quad (3)$$

Where λ_{CT} is the wavelength of the band of the studied CT-complexes $[(2A6EPy)(TCNE)_2]$ and $[(2A6EPy)_2(DDQ)]$, The E_{CT} values calculated from equation (3) for both complexes are 2.24 and 1.74 eV respectively.

The ionization potential of the free donor was determined from the CT energies of the CT band of its complexes. In case of the acceptors TCNE and DDQ the relationship becomes the following equation (4) [25]:

$$E_{CT} = I_p - 5.2 + \frac{1.5}{I_p - 5.2} \quad (4)$$

Where I_p is the ionization potential and E_{CT} is the charge transfer energy of the formed solid CT- complexes. The obtained values of I_p are 6.5 and 6.0 eV for the CT- complexes $[(2A6EPy)(TCNE)_2]$ and $[(2A6EPy)_2(DDQ)]$ respectively. It has been reported that the ionization potential of the electron donor may be correlated with the charge transfer transition energy of the complex [25].

These results in table 2 (K_{CT} , ϵ_{CT} , ΔG^0 and E_{CT}) suggest that the solid CT-complexes formed in the reaction of the donor 2A6EPy with the π -acceptors TCNE and DDQ have high CT energy and formation constants K_{CT} . These high values confirm the expected high stabilities of the formed CT- complexes as a result of the expected high donation of 2A6EPy.

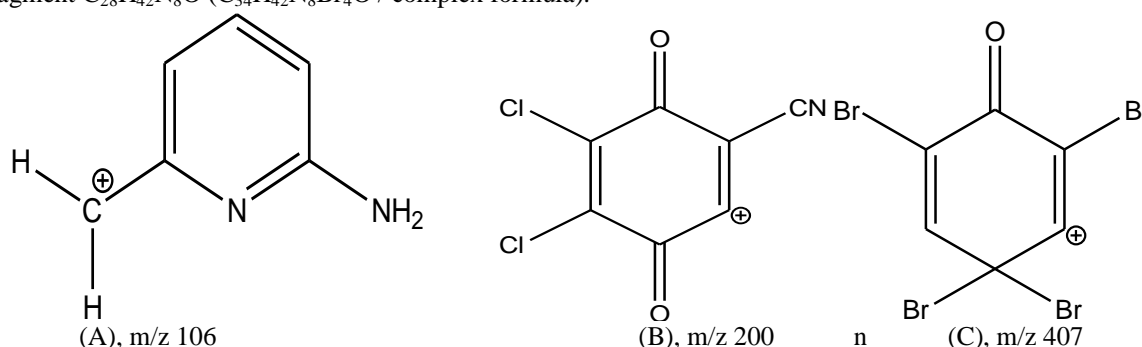
3.4. Mass Spectral studies

Mass spectral measurements were performed for the complexes $[(2A6EPy)(TCNE)_2]$, $[(2A6EPy)_2(DDQ)]$ and $[(2A6EPy)_4(TBCHD)]$. Fig.9 (A) shows the mass spectrum of $[(2A6EPy)(TCNE)_2]$ in the region $m/z = 100 - 380$. The molecular ion M^+ is observed as a short peak at $m/z = 377.2$ in good agreement

with the calculated value for the molecular weight of the CT- complex of 378.3 g. The found difference of about 1.1 between the observed and calculated molecular weight value is acceptable within the allowed experimental errors. The mass spectrum (Fig. 9 A) also shows a number of other peaks; the peak at $m/z = 106.1$ is for the donor 2A6EPy losing a methyl group (A), the peak at $m/z 123.1$ is for the mass of the donor (122.17 calculated) which is probably a protonated 2A6EPy. The peak at $m/z 187.2$ is for the fragment $C_{10}H_{10}N_4$ ($C_{19}H_{10}N_{10}$ / complex formula), the $m/z 224.2$ is the mass of fragment $C_{12}H_{12}N_5$ and the $m/z 256.2$ is the mass equivalent to two molecules of the acceptor TCNE ($m/z 256.18$ calculated) and $m/z 315.2$ is for the fragment $C_{16}H_{10}N_8$ ($C_{19}H_{10}N_{10}$ / complex formula).

The mass spectrum (Fig.9 B) for the complex $[(2A6EPy)_2(DDQ)]$ in the region $m/z = 100- 480$ is showing the molecular ion M^+ as a short peak at $m/z = 470.2.0$ very close to the calculated value for the molecular weight of that complex of 471.29 g. The peak at $m/z = 106.1$ is for the donor 2A6EPy losing a methyl group (A), the peak at $m/z 123.1$ is for one molecule of donor (122.17 calculated), the peak at $m/z 138.1$ is for fragment $C_8H_{13}N_2$ ($C_{22}H_{20}N_6Cl_2O_2$ / complex formula), at $m/z 200.1$ is for the cation of 2,3-dichloro-6-cyano-1,4-benzoquinone (200 calculated) (B) and the peak at $m/z 270.2$ is for the fragment ($C_{15}H_{20}N_5$).

The mass spectrum (Fig.9 C) for the complex $[(2A4EPy)_2(TBCHD)]$ in the region $m/z = 100 - 900$ is showing the molecular ion M^+ as a medium peak at $m/z = 897.1$ in a good agreement with the calculated value for the molecular weight of that complex of 898.26 g. The peak at $m/z 106.1$ is for the donor (2A4EPy) losing a methyl group (A), the peak at $m/z 123.1$ is for one molecule of donor (122.17 calculated) (A), $m/z 137.1$ is for fragment ($C_8H_{13}N_2$), the peak at $m/z 407.1$ is for the acceptor cation $[TBCHD]^+$ (C) and $m/z 506.9$ is for the fragment $C_{28}H_{42}N_8O$ ($C_{34}H_{42}N_8Br_4O$ / complex formula).



3.5. IR spectral studies

The infrared absorption spectra of the donor 2-amino-6-ethylpyridine and the formed CT-complexes $[(2A6EPy)(TCNE)_2]$, $[(2A6EPy)_2(DDQ)]$ and $[(2A6EPy)_4(TBCHD)]$ are shown in Fig.10. The infrared band assignments are given in Table 2. These assignments are based on the comparison of the spectra of the formed products with the spectra of the free reactants, the donor 2-amino-6-ethylpyridine and the acceptors TCNE, DDQ and TBCHD. Interestingly, the spectra of the reaction products contain the main infrared bands for both the reactants in each case.

This strongly supports the formation of the donor-acceptor CT- complexes. However, the absorptions of 2A6EPy and acceptors in the formed products show same changes in band intensities and in some cases small shifts in the frequency wavenumber values. These changes could be understood on the basis of the expected symmetry and electronic structure modifications in both donor and acceptor units in the formed products compared with those of the free molecules.

For example, the $\nu(N-H)$ vibrations of the free 2-amino-6-ethylpyridine in $[(2A6EPy)_2(DDQ)]$ has two strong absorptions at 3327 and 3181 cm^{-1} while in the $[(2A6EPy)(TCNE)_2]$, one weak absorption is observed at 3192 cm^{-1} and in $[(2A6EPy)_4(TBCHD)]$, two strong absorptions are observed at 3326 and 3181 cm^{-1} .

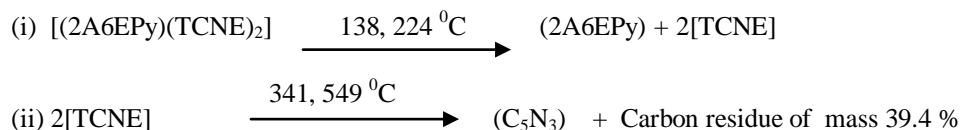
The outlined changes in $\nu(N-H)$ upon complexation clearly support the involvement of the nitrogen atoms of the donor 2A6EPy in the CT – interaction process.

It might also indicate here that $\nu(C\equiv N)$ vibrations of the acceptors TCNE and DDQ show some changes particularly in terms of band wavenumber values upon complexation. The $\nu(C\equiv N)$ vibrations for free TCNE are observed as a doublet at 2196 and 2182 cm^{-1} and for free DDQ at 2203 cm^{-1} . These vibrations occur at 2181 , 2148 and 2132 cm^{-1} in the spectrum of $[(2A6EPy)(TCNE)_2]$ and at 2202 cm^{-1} in the spectrum of $[(2A6EPy)_2(DDQ)]$ complexes.

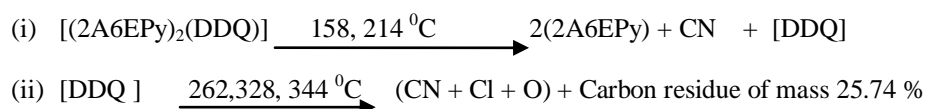
3.6. Thermal studies

Thermal analysis (TG and DTG) were carried out under a nitrogen gas flow (20 ml min^{-1}) within a temperature range $30 - 950\text{ }^\circ\text{C}$ and heating rate $10\text{ }^\circ\text{C min}^{-1}$ to confirm the proposed formula and structure for the obtained CT- complexes. Figs. 11 (A), (B) and (C) show the thermograms of $[(2A6EPy)(TCNE)_2]$,

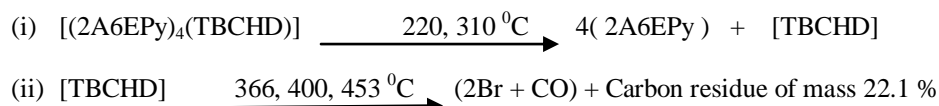
[(2A6EPy)₂(DDQ)] and [(2A6EPy)₄(TBCHD)] respectively. The thermogravimetric data for these complexes are shown in Table 3. The obtained data support the calculated formulas and structures of the formed CT-complexes. The degradation steps and their associated temperatures vary from one complex to another depending on the type of constituents as well as on the stoichiometry in each case. Obviously, these two factors have pronounced effects on the type of bonding, relative complex stabilities and geometries. For the CT-complex [(2A6EPy)(TCNE)₂] shown in Fig.11 (A) two degradation steps at temperatures 138 and 224 °C correspond to the decomposition of the donor [2A6EPy] with a mass loss of 31.8 % very close to the calculated value of 32.3 %. This step is followed by another two degradation steps at temperatures 341 and 549 °C correspond to the decomposition of (C₅N₃) of mass loss of 28.8 % very close to the calculated value of 27 % and carbon residue of mass 39.4 %, Table 4. Accordingly, a proposed mechanism for the thermal decomposition of [(2A6MPy)(TCNE)₂] as follows:



The second complex [(2A6EPy)₂(DDQ)] is shown in Fig.11 (B); at 158 and 262 °C correspond to the loss of [2(2A6EPy) + CN] with total mass loss of 57.9 % (57.36 % calculated), at 328 and 344 °C correspond to the loss of (CN + Cl + O) with mass of 16.36 % (16.44 % calculated) and carbon residue of mass 25.74 %; the following proposed mechanism clarifies the thermal decomposition steps:



The third complex [(2A6EPy)₄(TBCHD)] is shown in Figure 11 (C); at 220 and 310 °C correspond to the loss of the 4[2A6EPy] with a mass of 55.95 % very close to the calculated value of 54.4 %. The acceptor TBCHD decomposed at 366, 400 and 453 °C correspond to the loss of (2Br + CO) with mass loss of 21.96 % (20.91 % calculated) and remaining carbon residue with mass of 22.1 %; a proposed mechanism for the thermal decomposition of [(2A6EPy)₄(TBCHD)] as follows:



IV. CONCLUSION

Charge – transfer interactions between the donor 2-amino-6-ethylpyridine with the π-acceptors TCNE, DDQ and TBCHD were studied in CHCl₃ at 25 °C. We were able to show that the reaction stoichiometry is not the same for π-acceptors, TCNE, DDQ, TBCHD; the resulting CT – complexes were shown to have the formulas: [(2A6EPy)(TCNE)₂], [(2A6EPy)₂(DDQ)] and [(2A6EPy)₄(TBCHD)]. Our obtained results indicate that the nitrogen atom (>NH) of the donor is involved in the complexation with acceptors. Next studies will focus on using different donors with different substituent groups attached to the nitrogen atoms to further investigate the nature of such complexation.

REFERENCES

- [1] A.S.N. Murthy, A.P. Bhardwaj, Spectrochim. Acta, 39A, 1983, 415.
- [2] J. Casaszar, Acta Phys. Chim., 29, 1998, 34.
- [3] R. Foster, Organic Charge -Transfer Complexes, Academic Press, New York, 1969.
- [4] E.M. Abd-Alla, A.A.A. Boraie, M.R. Mahmoud, Can. J. Appl. Spectrosc., 39, 1994, 123.
- [5] A. Mostafa, H.S. Bazzi, J. Mol. Struct., 983, 2010, 153 – 161.
- [6] A. Mostafa, H.S. Bazzi, Spectrochim. Acta Part A, 79, 2011, 1613.
- [7] H.S. Bazzi, A. Mostafa, S.Y. AlQaradawi and E.M. Nour, J. Mol. Struct., 842, 2007, 1.
- [8] H.S. Bazzi, S.Y. AlQaradawi, A. Mostafa, and E.M. Nour, J. Mol. Struct., 879, 2008, 60.
- [9] S.Y. AlQaradawi, A. Mostafa, H.S. Bazzi, J. Mol. Struct., 1037, 2013, 209.
- [10] A. Mostafa, Nada El-Ghossein, S.Y. AlQaradawi, Spectrochim. Acta Part A, 118, 2014, 1012
- [11] S.Y. AlQaradawi, H. S. Bazzi, A. Mostafa and E. M. Nour, J. Mol. Struct., 998, 2011, 126.
- [12] A. Arslan, H. Duymus, Spectrochim. Acta Part A, 67, 2007, 573.
- [13] S.Y. AlQaradawi, E.M. Nour, J. Mol. Struct. 794, 2006, 251.
- [14] S.Y. AlQaradawi, E.M. Nour, Spectrochim. Acta Part A, 62, 2005, 578.
- [15] P.J. Trotter, P.A. White, Appl. Spectrosc. 32, 1978, 323.

- [16] H. Salem, J. Pharm. Biomed. Anal., 29, 2002, 527
 [17] S. Licht, Sol. Energy Mater. Sol. Cells, 35, 1995, 305
 [18] D.A. Skoog, F.J. Holler, T.A. Nieman, Principle of Instrumental Analysis, fifth ed., vol. 347, Saunders College Publishing, New York, 1992.
 [19] A. Mostafa, H.S. Bazzi, Spectrochim. Acta Part A, 74, 2009, 180.
 [20] A. El-Kourashy, Spectrochim. Acta Part A, 37, 1981, 399,
 [21] M. Arslan, H. Duymus, Spectrochim. Acta A, 67, 2007, 573.
 [22] A.A.A. Boraie, Spectrochim. Acta Part A, 58 (9), 2002, 1895.
 [23] G. Briegleb, Z. Angew. Chem., 72, 1960, 401.
 [24] G. Briegleb, Z. Angew. Chem., 76, 1964, 326.
 [25] M. Pandeewaran, K.P. Elango, Spectrochim. Acta Part A, 65, 2006, 1148.

Table 1

Spectroscopic data for the CHCl_3 solutions of solid CT- complexes of 2A6EPy with the acceptors TCNE, DDQ and TBCHD

Complex	Color	Absorption ^a (nm)	Stoichiometry (Donor: acceptor)
[(2A6EPy)(TCNE) ₂]	Dark green	597s, 555s, 524sh	1:2
[(2A6EPy) ₂ (DDQ)]	Dark brown	716m, 567sh, 501sh, 460sh	2:1
[(2A6EPy) ₄ (TBCHD)]	Dark brown	372m	4:1

^(a)The reactants 2A6EPy, TCNE, DDQ and TBCHD have no measurable absorptions in the region of study with used concentrations; m, medium; s, strong; sh, shoulder.

TABLE 2

Infrared wavenumbers (cm^{-1}) and tentative band assignments for 2-amino-6-ethylpyridine (2A6EPy), [(2A6EPy)(TCNE)₂], [(2A6EPy)₂(DDQ)] and [(2A6EPy)₄(TBCHD)]

2A4EPy	[(2A4EPy)(TCNE) ₂]	[(2A4EPy) ₂ (DDQ)]	[(2A4EPy) ₂ (TBCHD)]	Assignments
3460s	3439m	3429m	3412ms	ν (H ₂ O); KBr
3307ms,3153ms	3367ms	3328s	3296w	ν (NH); 2A4EPy
	3299ms, 3189ms	3180ms	3140m	ν (C-H); 2A4EPy
2967ms	2972m	2969ms	2967w	ν (C \equiv N); DDQ
	2214s	2201ms		and TCNE
	2191w			
		1638s	1668s	ν (C=O); DDQ, TBCHD
1613m	1567s	1624s	1628s	ν (C=C); DDQ,
1552s	1544w	1557ms	1563w	TBCHD, 2A4EPy
1393w	1377ms	1394w	1396w	Free and complexed 2A4EPy
1312m	1309ms	1355w	1372m	
1276m	1284ms	1233m	1276m	
1237m	1219s	1233m	1229m	ν (C-N); 2A4EPy
1181m	1153ms	1177m	1179m	
1132m	1153ms	1139w	1149w	ν (C-C); 2A4EPy
1054m	1056m	1069ms	1053m	
997m	985m	996ms	995m	δ (CH)deformation,

m,medium ; s,strong ; w,weak ; br,broad ; ν ,stretching ; δ ,bending

Table 3

Thermal decomposition data^a for the [(2A6EPy)(TCNE)₂], [(2A6EPy)₂(DDQ)] and [(2A6EPy)₄(TBCHD)] CT-complexes.

Complex	Reaction stoichiometry	DTG max. (°C)	TG% mass loss found / calc.	Residual species
[(2A6EPy)(TCNE) ₂]	1: 2	138, 224	31.8 / 32.3	[2A6EPy] { N ₂ 1.4 % Carbon Residue
		341, 549	28.8 / 27.0	
[(2A6EPy) ₂ (DDQ)]	2: 1	158, 262	57.9 / 57.36	{ Two [2A6EPy] CN (from DDQ) N + Cl + O 74 % Carbon Residue
		328, 344	16.36 / 16.44	
[(2A6EPy) ₄ (TBCHD)]	4: 1	220, 310	55.95 / 54.4	Four [2A6EPy] Br + CO 71 % Carbon Residue
		366, 400, 453	21.96 / 20.91	

^a Thermal measurements were carried out under N₂ flow rate at 20 ml.min⁻¹.

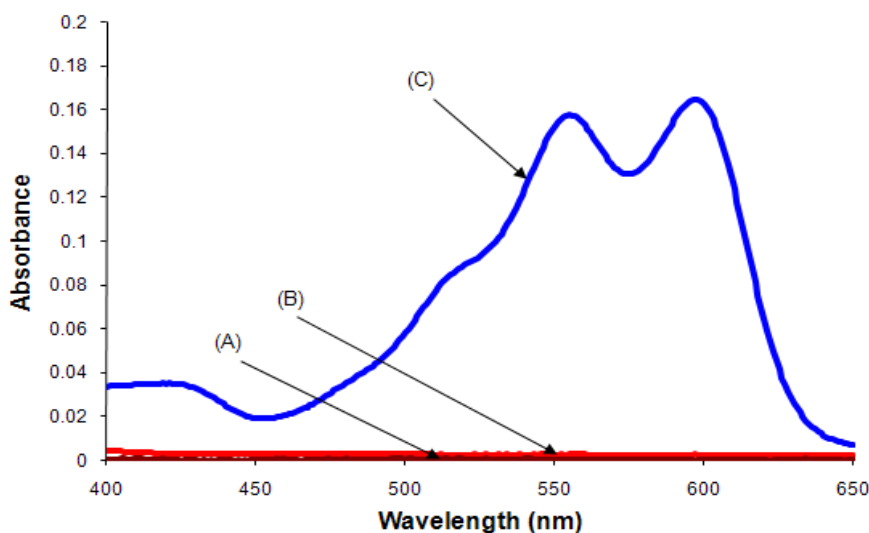


Figure 1. Electronic absorption spectra of 2-amino-6-ethylpyridine -TCNE reaction in CHCl₃. (A) [2A6EPy] = 1x10⁻³M; (B) [TCNE] = 1x10⁻³M; (C) 1:2 2A6EPy-TCNE mixture, [2A6EPy] = [TCNE] = 1x10⁻³ M.

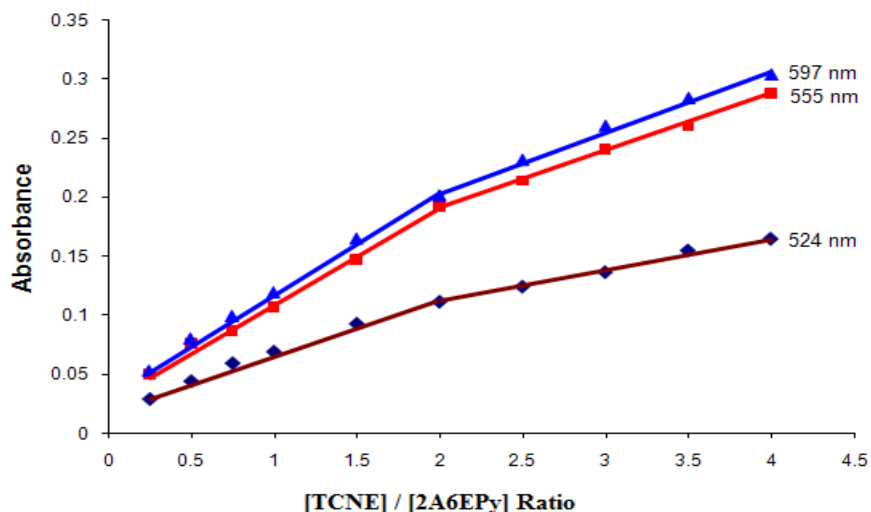


Figure 2. Photometric titration curves for 2A6EPy- TCNE reaction in CHCl_3 measured at the 597 nm, 555 nm and 524 nm absorptions.

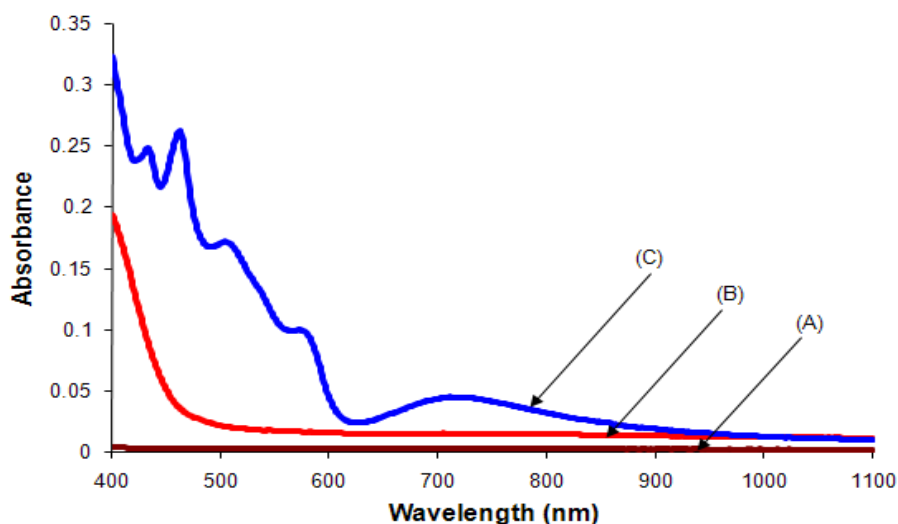


Figure 3. Electronic absorption spectra of 2-amino-6-ethylpyridine - DDQ reaction in CHCl_3 . (A) $[2\text{A6EPy}] = 1 \times 10^{-3}\text{M}$; (B) $[\text{DDQ}] = 5 \times 10^{-3}\text{M}$; 2:1 2A6EPy - DDQ mixture, $[2\text{A6EPy}] = 1 \times 10^{-3}\text{M}$ and $[\text{DDQ}] = 5 \times 10^{-3}\text{M}$.

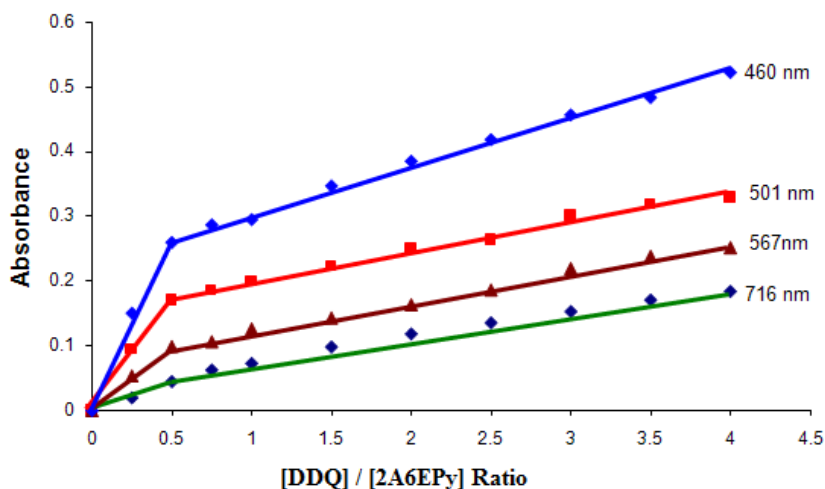


Figure 4. Photometric titration curves for 2A6EPy - DDQ reaction in CHCl_3 measured at the 716 nm, 567 nm, 501nm and 460 nm absorptions.

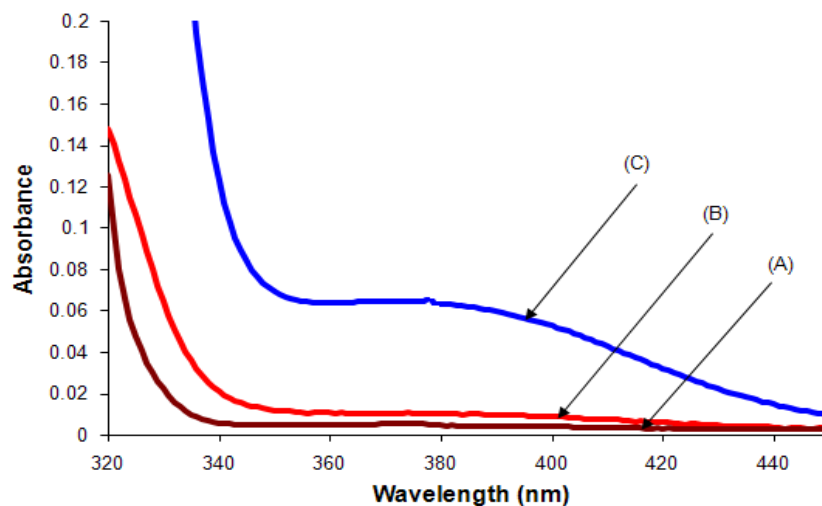


Figure 5. Electronic absorption spectra of 2-amino-6-ethylpyridine -TBCHD reaction in CHCl_3 . (A) $[2\text{A6EPy}] = 1 \times 10^{-3}\text{M}$; (B) $[\text{TBCHD}] = 5 \times 10^{-3}\text{M}$; 4:1 2A6EPy-TBCHD mixture, $[2\text{A6EPy}] = 1 \times 10^{-3}\text{M}$ and $[\text{TBCHD}] = 5 \times 10^{-3}\text{M}$.

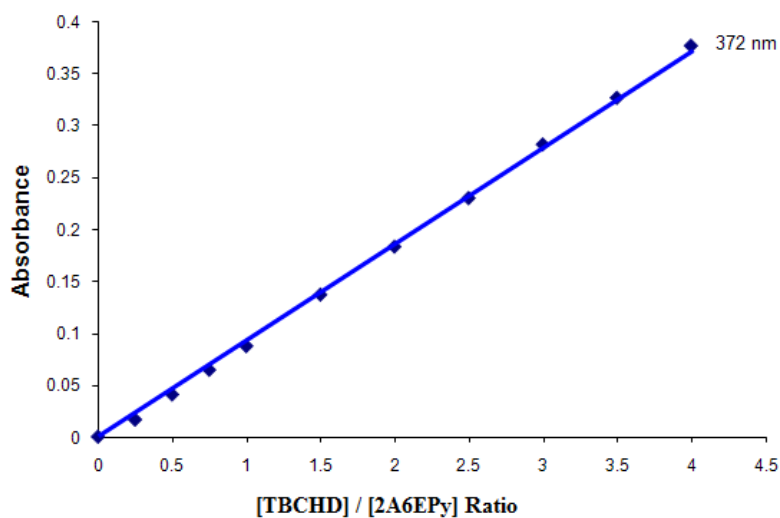


Figure 6. Photometric titration curve for 2A6EPy – TBCHD reaction in CHCl_3 measured at the 372 nm absorption.

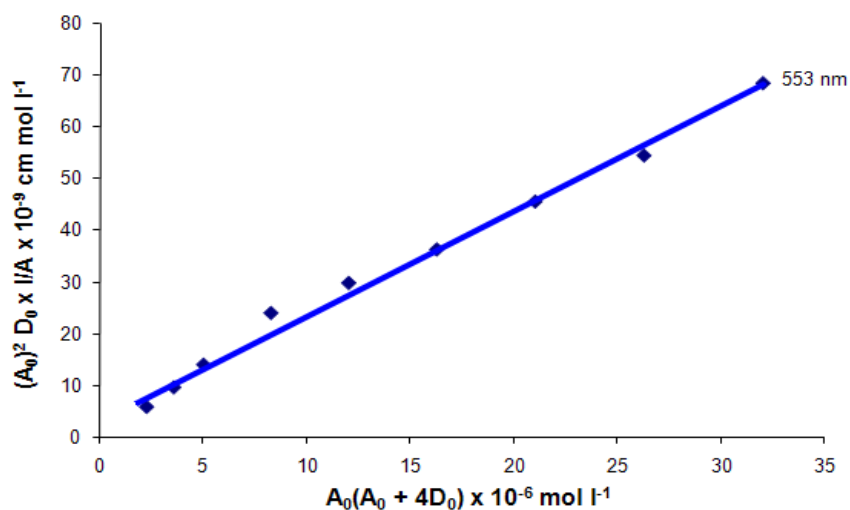


Figure 7. Spectral determination of formation constant and molar extinction coefficient of CT-complex $[(2\text{A6EPy})(\text{TCNE})_2]$ at 553 nm

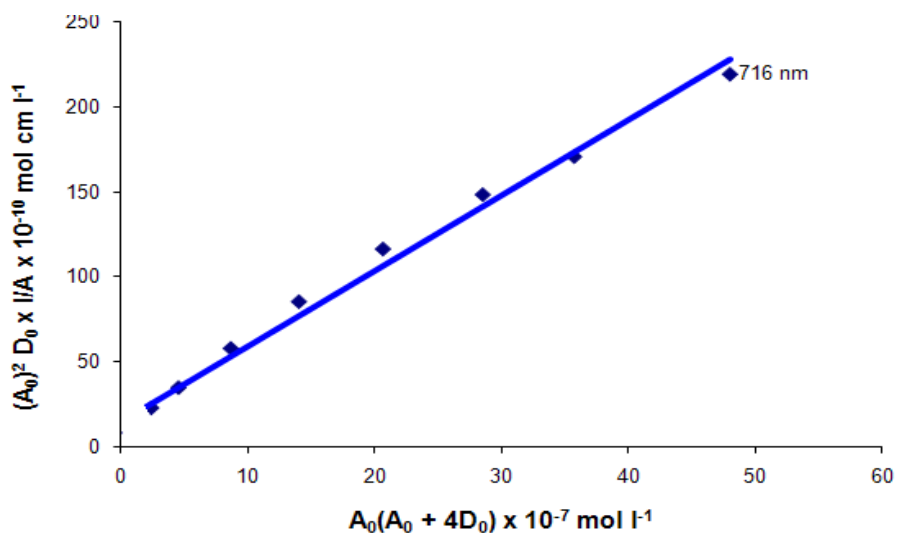
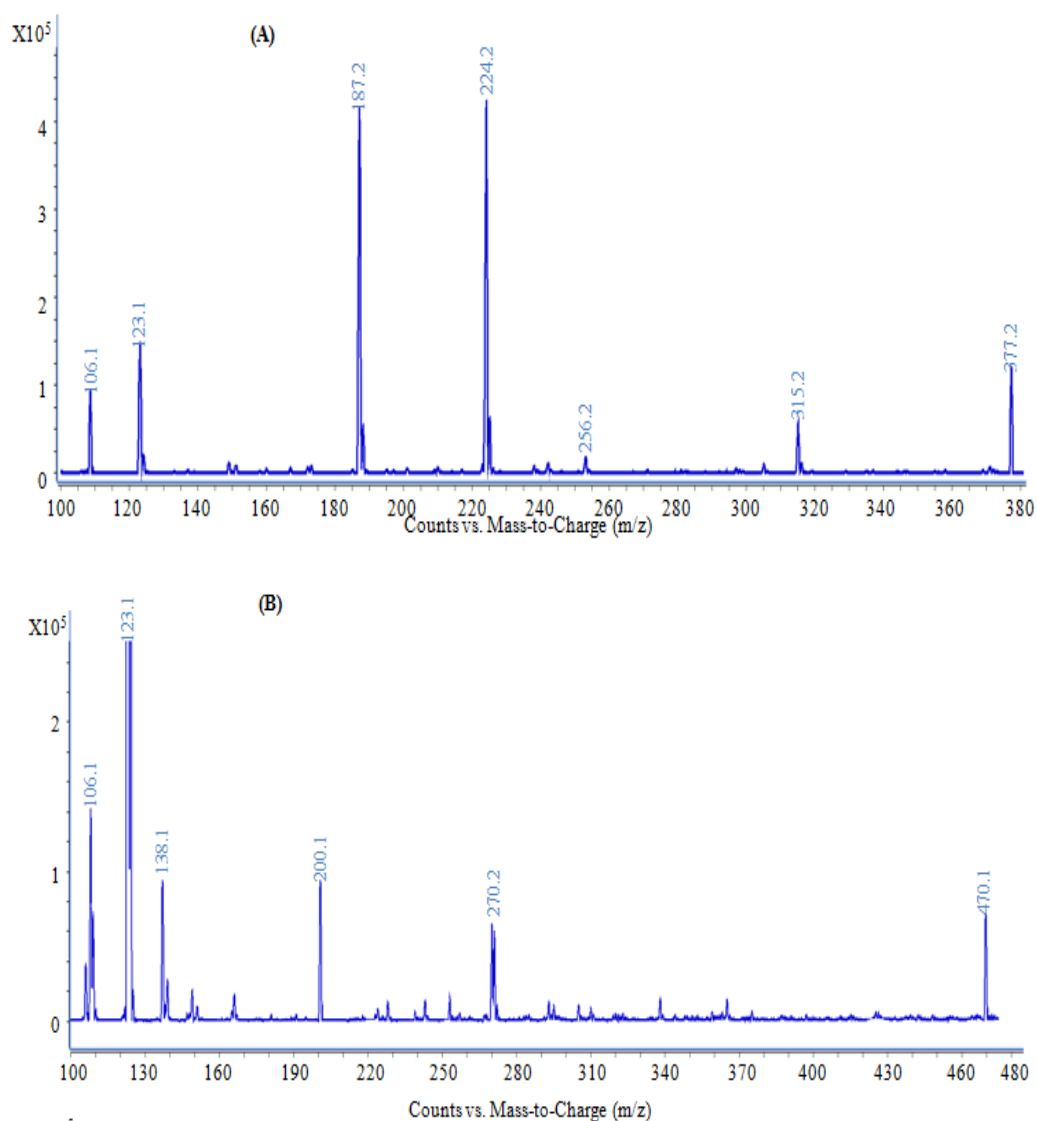


Figure 8. Spectral determination of formation constant and molar extinction coefficient of CT- complex [(2A6EPy)₂(DDQ)] at 716 nm.



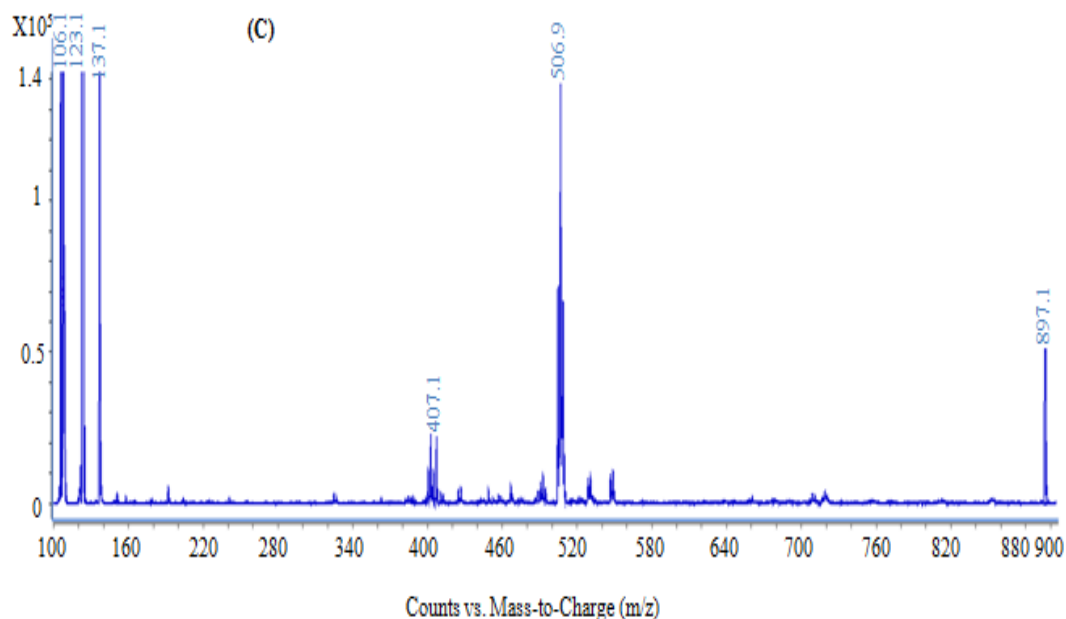


Figure 9. Mass spectra of CT- complexes: (A) [(2A6EPy)(TCNE)₂], (B) [(2A6EPy)₂(DDQ)] And (C) [(2A6EPy)₄(TBCHD)].

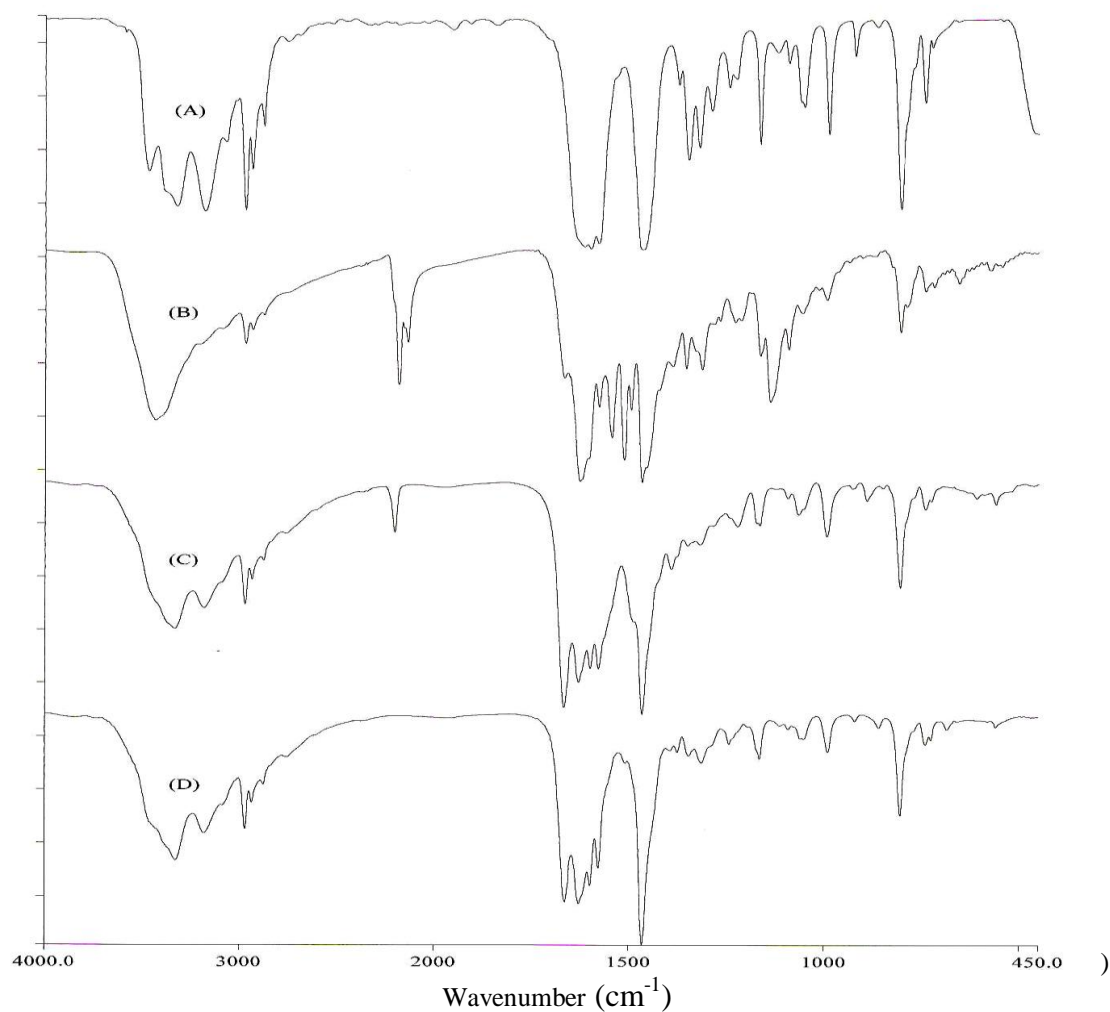


Figure 10. Infrared absorption spectra of: (A) 2-amino-6-ethylpyridine (2A6EPy); (B) [(2A6EPy)(TCNE)₂]; (C) [(2A6EPy)₂(DDQ)] and (D) [(2A6EPy)₄(TBCHD)].

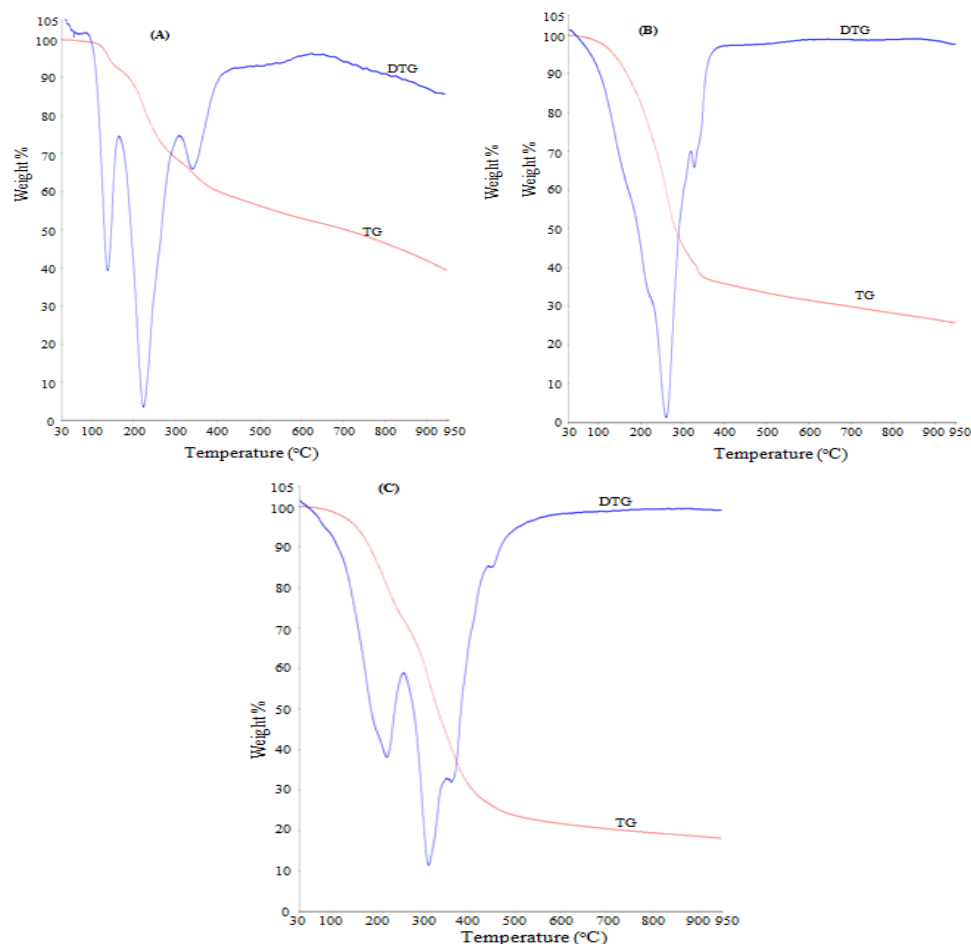
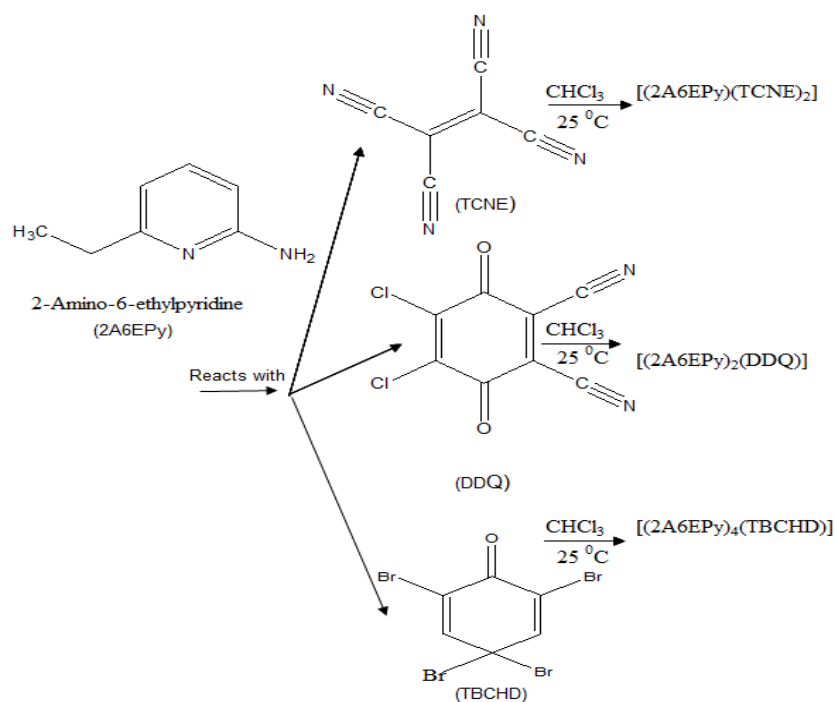


Figure 11: Thermograms of: (A) [(2A6EPy)(TCNE)₂]; (B) [(2A6EPy)₂(DDQ)] and (C) [(2A6EPy)₄(TBCHD)].

Graphical abstract



- TCNE : Tetracyanoethylene
- DDQ : 2,3-Dicchloro-5,6-dicyano-4-benzoquinone
- TBCHD: 2,4,4,6-Tetrabromo-2,5-cyclohexadienone

Highlights

- Three CT- complexes of donor 2A6EPy with the acceptors TCNE, DDQ and TBCHD are obtained.
- The CT- complexes are characterized through FTIR, UV- Vis, TGA, elemental analysis and LC MS/MS.
- The values of K_{CT} , ϵ_{CT} , E_{CT} , ΔG^0 and I_p are calculated