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Review Article

SPECTROSCOPIC STUDIES OF CHARGE-TRANSFER COMPLEXES OF 1,10-PHENANTHROLINE MONOHYDRATE WITH SOME π ACCEPTORS

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ABSTRACT

The charge-transfer complexes of 1,10-phenanthroline monohydrate with 1,3-dinitrobenzene and 4-hydroxybenzoic acid have been prepared and characterized by ^{1}H NMR, Melting point, TGA-DTA, Fluorescence, XRD and FT- IR. The Charge-transfer complexes of [(phMH) (MDNB)] and [(phMH) (PHB)] were proposed. In the ^{1}H NMR, FT-IR, melting point, TGA-DTA and Fluorescence of the complexes, the data indicate a charge-transfer interaction and as far as complexes are concerned, this interaction is associated with a hydrogen bonding and the transfer of proton from the acceptor to the donor.

Keywords: *1,10-Phenanthroline Monohydrate; FT-IR; ^{1}H NMR; XRD; Fluorescence.*

INTRODUCTION

Aromatic heterocyclic compounds represent a very important class of compounds in which the π and n-electrons, at least in principle, can form two types of charge-transfer complexes. The formation of CT complexes between π and n-donors with π acceptors has been investigated (Foster, 1969; Tong and Na, 1992; Mulliken and Person, 1969). On this basis, protonic charge-transfer complex was firstly introduced by Matsunaga and his coworkers. Pauling regarded the hydrogen bond as a special case of charge-transfer interaction (Saito and Matsunaga, 1974), while Atkins claims that a proton-transfer complex is a manifestation of dipole–dipole (or electrostatic) forces (Abdel-Khalik and Abdel-Hakim, 1998; Morukama, 1977; Kasha, 1991). Proton-transfer could sometimes be nothing more than a case of conventional hydrogen bonding, but in many cases, the concurrent transfer of an electron and a proton produces a new type of adducts and the complex formation may indeed be dramatic (Pauling, 1960; Atkins, 1990; Amett and Mitchell, 1971; Rice and Roth, 1972). Phenanthroline is a hetrocyclic organic compound, as a bidentate ligand in coordination chemistry; it forms strong complexes with most metal ions. In terms of its coordination properties, phenanthroline is similar to 2, 2'- bipyridine. The charge-transfer complexes of 2,9-dimethyl-1,10-phenanthroline with picric acid, chloranil and chloranilic acid was spectroscopically investigated (Gaballa *et al.,* 2008). 1,10-phenanthroline and its derivatives show high catalytic activity (Strohbusch *et al.*, 1978; Rhodes and Schimmel, 1974; Kruse and Brandt, 1952). In connection with such studies, 1,10-phenanthroline is an inhibitor of metallopeptidases, with one of the first observed instances reported in carboxypeptidase (Mo *et al.,* 2006). An inhibition of the enzyme occurs by removal and chelation of the metal ion required for catalytic activity, leaving an inactive apoenzyme. 1,10-phenanthroline targets mainly zinc, metallopeptidases with a much lower affinity for calcium (Felber *et al.,* 1962; Salvesen and Nagase 2001). This chapter, therefore, presents the investigation of molecular complexes formed during the reaction of 1,10-phenanthroline monohydrate as an electron donor with π-electron acceptors 1,3-dinitrobenzene and 4-hydroxybenzoic acid.

MATERIALS AND METHODS

Materials

All chemicals used were of high grade. 1,10-phenanthroline monohydrate was obtained from MERCK, 4-hydroxybenzoic acid from BDH England, 1, 3-dinitrobenzene from MERCK, acetone, methanol, ethanol and DMSO from MERCK were of the highest purity and used without further purification. Double distilled water was used throughout.

Synthesis of CT complexes

Synthesis of CT complex of 1,10-phenanthroline monohydrate with 4-hydroxybenzoic acid:

The solid CT complex was prepared by mixing a saturated solution of 1,10-phenanthroline monohydrate (0.59469 gm, 3 mmol) in 30 ml acetone with saturated solution of 4-hdroxybenzoic acid (0.41436 gm, 3 mmol) in 30 ml acetone, producing a white precipitate by stirring for around 2 hours. The precipitate was filtered off and washed several times with small amounts (6 ml) of hexane and dried under vacuum over $CaCl_2$. The melting point of CT complex was measured as 183-185 °C. The white powder was soluble in methanol, acetone, DMSO, partially soluble in $CHCl_3$, but insoluble in hexane and double distilled water.

Synthesis of CT complex of 1,10-phenanthroline monohydrate with 1,3-dinitrobenzene:

The solid CT complex was prepared by mixing a saturated solution of 1,10-phenanthroline monohydrate (0.59469 gm, 3 mmol) in 30 ml acetone with saturated solution of 1,3-dinitrobenzene (0.50436 gm, 3 mmol) in 30 ml acetone. A yellow to white coloured precipitate was formed by stirring for around 1 hour. The precipitate was filtered off and washed several times with small amounts (6 ml) of hexane and dried under vacuum over $CaCl_2$. The melting point of CT complex was measured as 123-125 °C. The yellow white crystal was soluble in methanol, acetone, DMSO, $CHCl_3$, but insoluble in hexane and double distilled water.

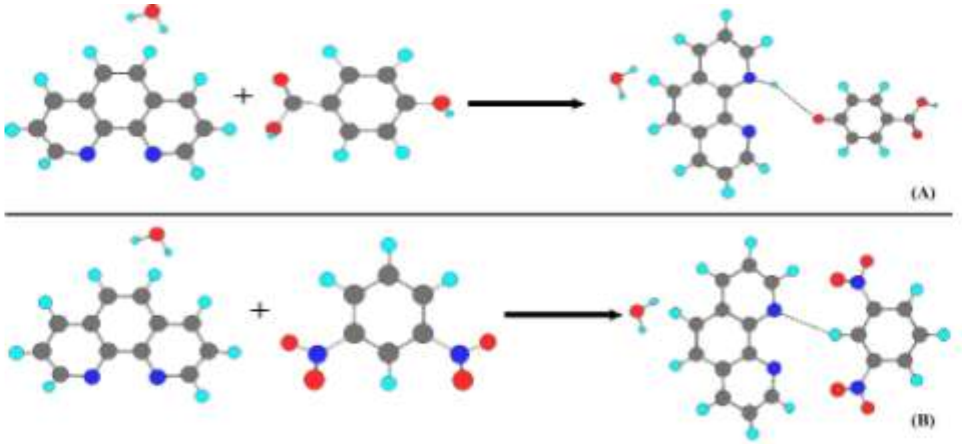
Methods

Reactions of 1,10-phenanthroline monohydrate (phMH) with 1,3-dinitrobenzene (MDNB) and 4-hydroxybenzoic acid (PHB) resulted in formation of stable charge-transfer complexes [(phMH) (MDNB)] and [(phMH) (PHB)] with a donor–acceptor molar ratio of 1:1. The infrared spectra of the reactants and complexes were recorded using KBr discs on Interspec 2020 FT- IR Spectrometer U.K. The X-ray diffraction measurements (Rigaku, Japan, Miniflex-II) were made using Cu-K_α radiation ($\lambda = 1.5418$ Å) in 2θ range from 5° to 80°. The proton NMR spectra of the reactants and the formed CT complexes were measured in DMSO using Bruker Advance 11 400 NMR spectrometer. Fluorescence spectra of the reactants and their complexes were measured by using F-2500 FL Spectrophotometer.

RESULTS AND DISCUSSION

FT- IR Spectra: -

The infrared spectra of the characterized bands of phMH-PHB and phMH-MDNB are shown in Figures 1-2. The observations of the main infrared bands of donor {1,10-phenanthroline monohydrate (phMH)} and acceptors {1,3-dinitrobenzene (MDNB) and 4-hydroxybenzoic acid (PHB)} in the respective spectra of the complex strongly support the formation of CT Complexes by intermolecular hydrogen bonding. However, the analytical and spectroscopic data enable us to predict possible structures as shown in Scheme 1.



Scheme 1: Scheme 1 shows the reaction and the intermolecular hydrogen bonding between (A) phMH and PHB and (B) phMH and MDNB [Dim grey: Carbon atoms; Light cyan: Hydrogen atoms; Red: Oxygen atoms; Dark Blue: Nitrogen atom; Dotted Line: Hydrogen bonding].

The FT-IR absorption spectra of the donor and the acceptors and their CT Complexes are shown in Figures 1-2, and their band assignments are given in Table 1.

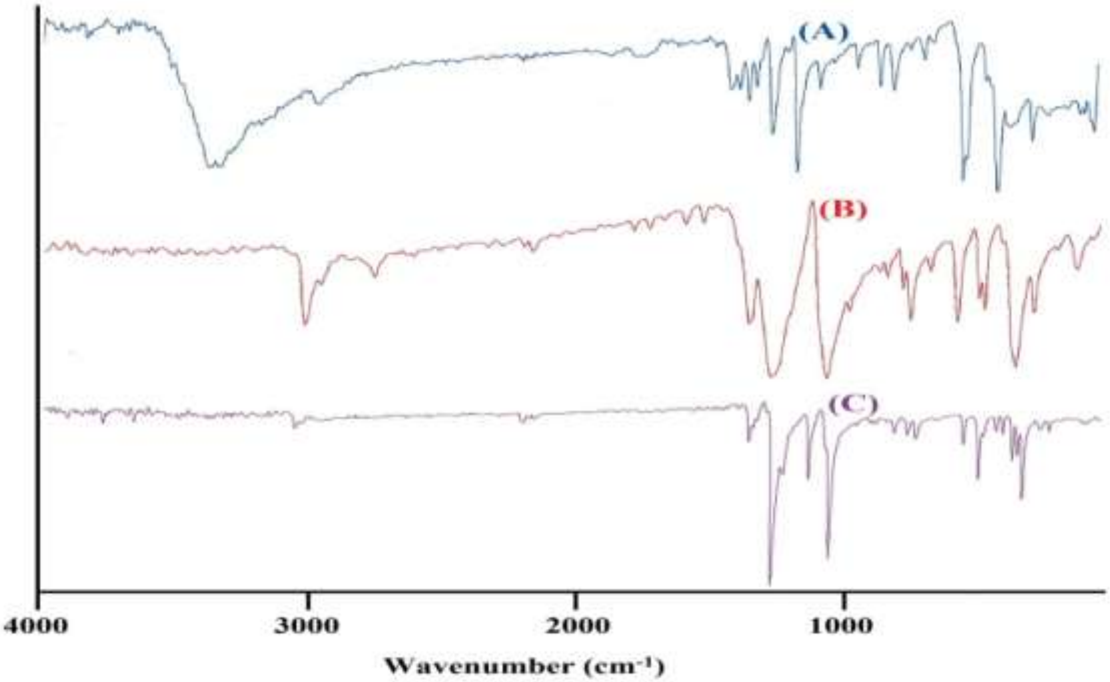


Figure 1: FT- IR spectrum of (A) phMH (B) MDNB (C) CTC of phMH and MDNB

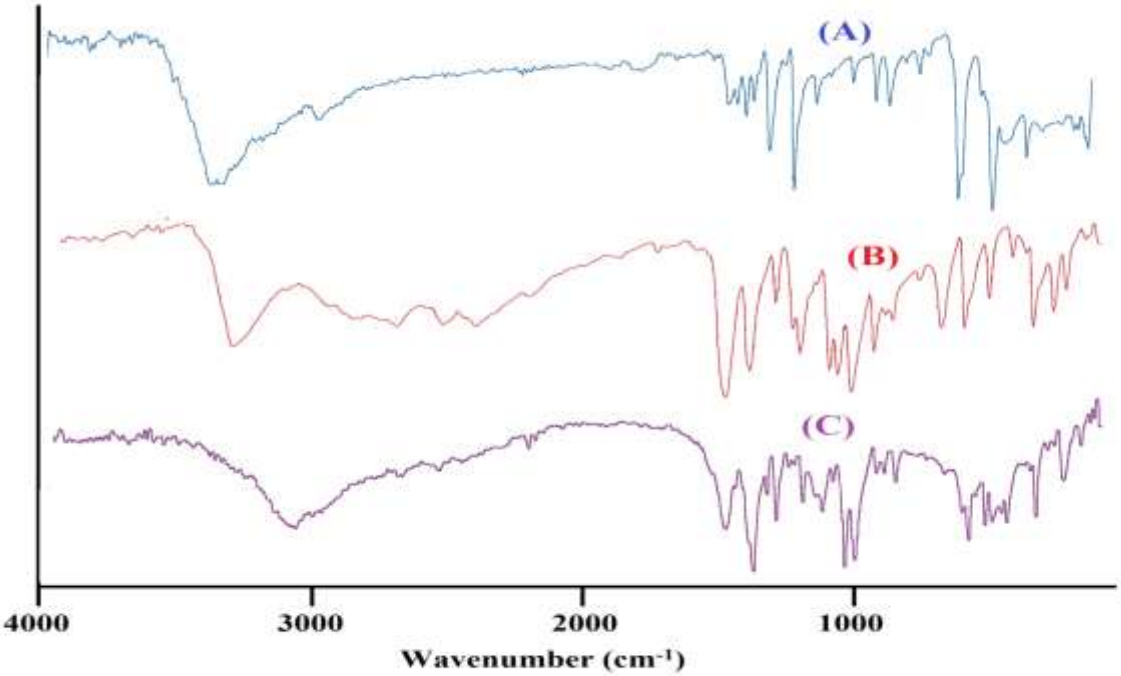


Figure 2: FT- IR spectrum of (A) phMH (B) PHB (C) CTC of phMH and PHB

Generally, the results of chemical analysis of the synthesized solid CT complexes (Table 1) indicate the formation of 1:1 CT complexes.

Table 1: Infrared frequencies (cm^{-1}) and tentative assignments for phMH, PHB, MDNB, DNSA, DNBA and their HBCT complexes

phMH	PHB	MDNB	CTC of phMH-PHB	CTC of phMH-MDNB	Assignment
3436	3384		3169	3114	V(O-H), v(N-H)
3396	3197	3104			
3261	3062	3104	2910	2955	V(C-H), aromatic
3058	2955	3052	2800	2810	H-Bonding
2820	2832	2871	2673		
	2720	2363			
2333	2661	2420	2300	2367	-C=C-H
1958	2546	2002			
	2367				
	2053				
1827	1926	1950	1672	1680	-C=O
1700	1787	1890	1589	1616	-C-N
1648	1680	1827	1545	1525	V(NO_2)
1616	1596	1767	1505	1512	-(C=C)
1585	1509	1704	1469	1497	
1516	1449	1652	1422	1414	(C-H) monodef.
1509	1418	1612	1350	1342	-(C-C),-NO_2
1422	1366	1537	1318	1259	-(C-N)
1342	1318	1350	1271	1203	
1219	1283	1271	1239	1132	(C-H) in plane bending
1136	1235	1171	1168	1092	V(C-NO_2)
1092	1128	1180	1144	1064	
1037	1100	1096	1100	901	CH_2 rock skeletal vibration
989	1013	1068	937	845	C-H out of plane
957	929	1005	846	798	-NO_2 wag vibration
850	854	909	794	770	
753	770	838	762	707	
695	695	810	715	647	

Comparison of the infrared spectral bands of the free donor (phMH) and acceptors (PHB and MDNB) with the corresponding ones appearing in the IR spectra of the CT complexes show the following:

- The carbonyl C = O stretching vibration appearing at 1680 cm^{-1} in the IR spectrum of PHB is shifted to 1672, cm^{-1} in the IR of the CT complex of PHB with phMH.
- The IR Spectra of the formed CT complexes show NH bands at 2800, 2810 cm^{-1} for phMH- PHB and phMH-MDNB Complexes confirming the formation of hydrogen bonded proton transfer between OH of PHB, H at ortho position of two NO_2 of MDNB and the nitrogen ring of phMH.
- The phMH ring vibrations appearing at 1616, 1585, and 1516 cm^{-1} of the donor (phMH) shifted to 1589, 1545, 1515 cm^{-1} and 1525, 1512, 1497 cm^{-1} in the CT complexes of phMH with PHB and MDNB respectively (Bahat and Yrdakul, 2002; Jones II and Jimenez, 1999; Refat *et al*., 2006).

X- Ray Diffraction studies and determination of the particle size of complexes:-

In order to further confirm the crystalline structure of phMH-MDNB and phMH-PHB, Powder X-Ray Diffraction (XRD) measurements were performed by X-ray diffractometer (Rigaku, Japan, Miniflex-II) using Cu-K$_\alpha$ radiations (λ = 1.5418 Å) in 2θ range from 5.0º to 80º. The XRD spectra for all the reactants and products are obtained in Figures 3-4.

- The XRD spectrum of phMH (Figure 3 (A)) gave characteristic peaks at 2θ= 21.1°, 22.2°, 25.5°, 27.5°, 29.1°, 30.9°, 37.1°, 43.3°; PHB (Figure 3 (B)) gave 21.7°, 24.0°, 26.3°, 29.4°,37.°, 39.2°, 43.4°; and of CTC of phMH and PHB (Figure 3 (C)) gave 14.6°, 15.1°, 15.3°, 16.6°, 20.3°, 21.1°, 22.5°, 23.2°, 23.7°, 25.3°, 37.1°, 43.3° and new peak at 17.6° corresponding to the new compound formed and indicating the crystal structure of the phMH- PHB complex.
- The XRD spectrum of phMH (Figure 4 (A)) gave characteristic peaks at 2θ= 21.1°, 22.2°, 25.5°, 27.5°, 29.1°, 30.9°, 37.1°, 43.3°; MDNB (Figure 4 (B)) gave 23.5°, 26.0°, 37.1°, 43.3°and of the CTC of phMH and MDNB (Figure 4 (C)) gave 9.1°, 14.3°, 19.1°, 26.7° and a new peak at 39.9° corresponding to the new compound formed and indicating the crystal structure of the phMH-MDNB complex (Zhao *et al.*, 2003).

As evident from Figures 3-4, the main characteristic scattering pattern of CT complexes of 1,10-phenanthroline monohydrate—1,3-dinitrobenzene (phMH-MDNB) and 1,10-phenanthroline monohydrate—4-hydroxybenzoic acid (phMH-PHB) occurs at 9.1° and 37.1° respectively. The particle size of these three complexes was estimated from their XRD patterns based on the highest intensity values compared with other peaks using the well-known Deby-Scherrer formula given in equation below (Quazi *et al.*, 2009)

$$D = K \lambda / \beta \cos\theta$$

Where D is the apparent particle size of the grains, K is a constant (0.94 for Cu grid), λ is the X-ray wave length used (1.5418 Å), θ is half the scattering angle (the Bragg diffraction angle) and β is the full-width at half-maximum (FWHM) of the X-ray diffraction line (additional peak broading) in radians. Table 2 presents the XRD spectral data for the CT complexes. The particle size of these three complexes were estimated according to highest value of intensity compare with the other peaks and were found to be 6.299 and 5.909 nm for phMH-MDNB and phMH-PHB complexes respectively. These values confirmed that the particle sizes are located within the nanoscale range.

Table 2: XRD spectral data of phMH-DNSA, phMH-MDNB, phMH-DNBA and Tpy-phMH CT complexes

CT Complex	2θ°	θ°	d value (Å)	β (FWHM)	Height	Area	Particle size (D) (nm)
phMH-MDNB	9.1	4.55	9.70143	0.2308	24373.6	270115.2	6.299
phMH-PHB	37.1	18.55	2.418	0.2587	4632.3	56320.5	5.909

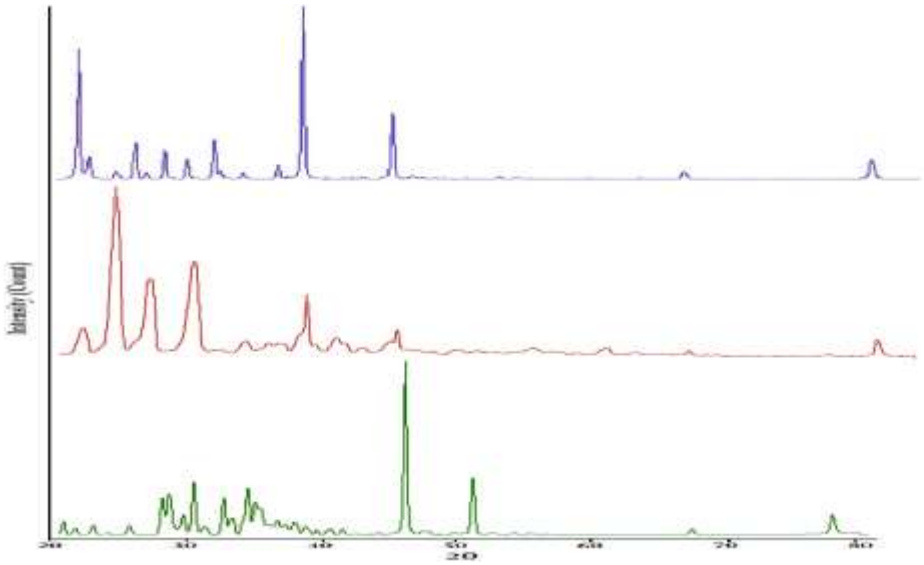


Figure 3: XRD spectrum of (A) phMH; (B) PHB; (C) CTC of phMH and PHB

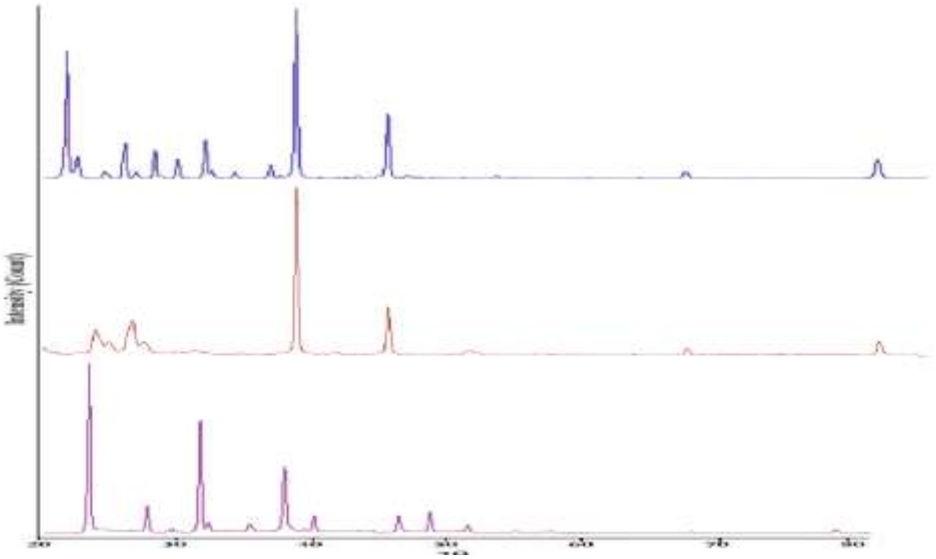


Figure 4: XRD spectrum of (A) phMH; (B) MDNB; (C) CTC of phMH and MDNB

Thermogravimetric analysis (TGA-DTA): -

The thermal analysis (TGA and DTA) of samples were performed using instrument at constant heating rate of 10 °C/min over temperature range of 20-850 °C using α-alumina powder (10mg) as reference material. The sample of about (1-10 mg) was uniformly spread over the balance pan. The degradation of samples was carried out under oxidizing atmosphere (flowing dry air) at a flow rate of 30 ml/minute. The thermogravimetric analysis curves (TGA and DTA) of phMH, MDNB and PHB and their complexes are shown in Figures 5-6. The thermal analysis data of phMH, MDNB, PHB and their complexes are given in Table 3.

Table 3: Thermal analysis data of phMH, DNBA, DNSA, MDNB, PHB and their complexes

Compound	**Range of temperature (°C)**	**Stage**	**TGA**			**DTA**
			Mid point (°C)	**Weight loss (mg)**	**% Weight loss**	**Peak (°C)**
phMH	94.82-130.12	First	97.06	-0.703	-10.079	106.77
	245.00-323.28	Second	286.04	-5.892	-84.473	307.19
PHB	215-232	First	254.14	-6.07	-91.628	221.69
	243.06-291.48	Second	375.24	-0.539	-8.131	268.76
MDNB	88.97-107.57	First	206.2	-6.715	-99.075	95.25
	172.18-239.27	Second				222.93
CTC of phMH and MDNB	130.79-147.50	First	237.03	-4.569	-96.555	135.69
	264.81-298.55	Second	-	-	-	285.96
CTC of phMH and PHB	180.11-215.12	First	251	-4.194	-99.29	195
	260.21-318.23	Second	-	-	-	294

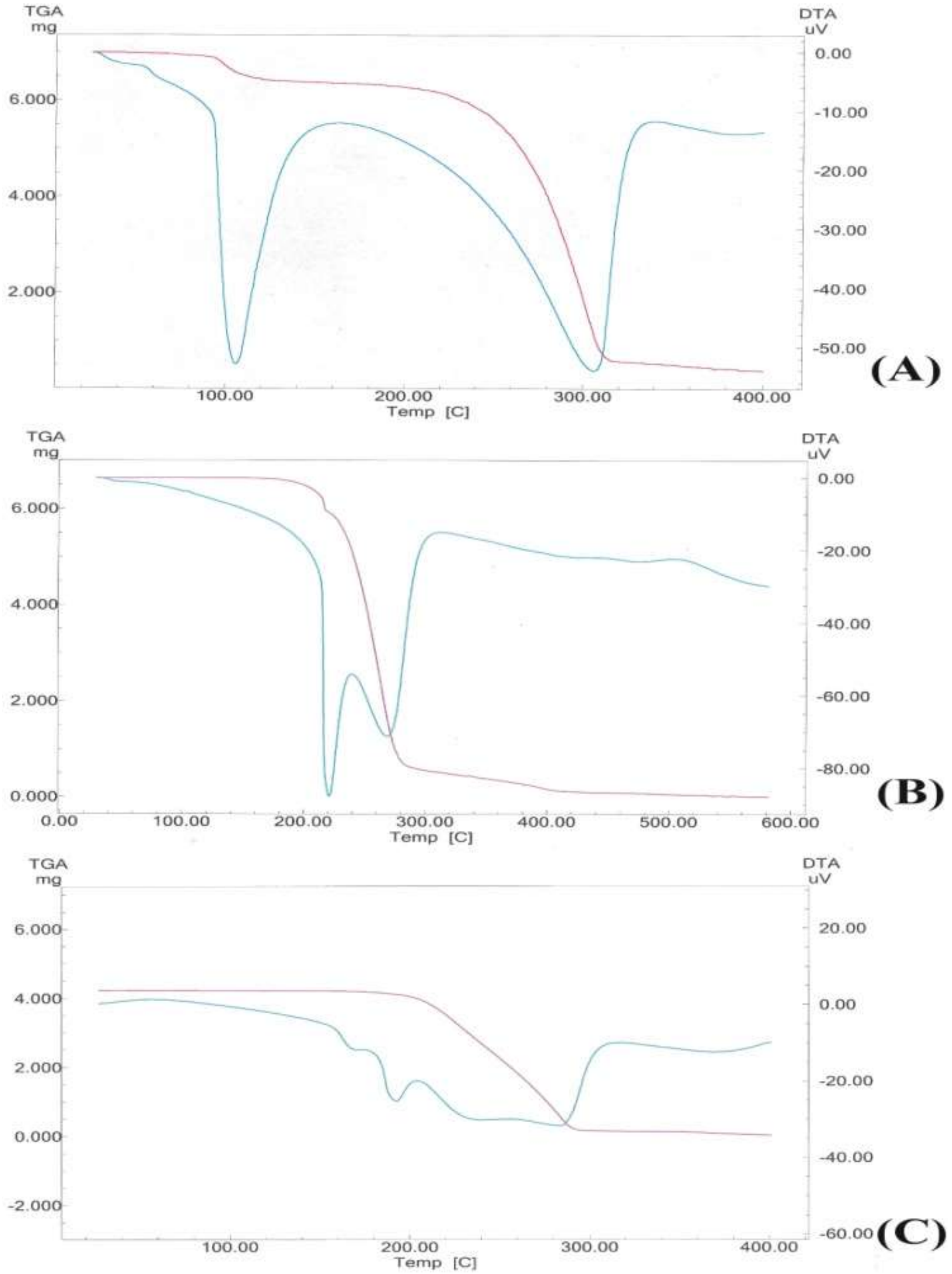


Figure 5: TGA- DTA curves of (A) phMH; (B) PHB; (C) CTC of phMH and PHB

The decomposition of the CTC of phMH and PHB as well as of phMH occurs in two stages (Refat *et al.*, 2007; Laidler, 1972; Mo *et al.*, 2007). The decomposition of CTC of phMH- PHB is shown in Figure 5 (C). In the first stage, the range of temperature is 180.11- 215.12 °C with weight loss of about -4.194 mg, -99.290 %, whereas in the second stage, the temperature range was found to be 260.21 - 318.23 °C with loss of the remaining weight. The decomposition of the CTC of phMH-MDNB, shown in Figure 6 (C), occurs in two stages. In the first stage, the range of temperature is 130.79-147.50 °C with weight loss of about -4.569 mg, -96.555 %; and in the second stage, the range of temperature is 264.81 - 298.55 °C with loss of the remaining weight (Ng *et al.*, 2002; Majchrzak-Kucêba and Nowak, 2004).

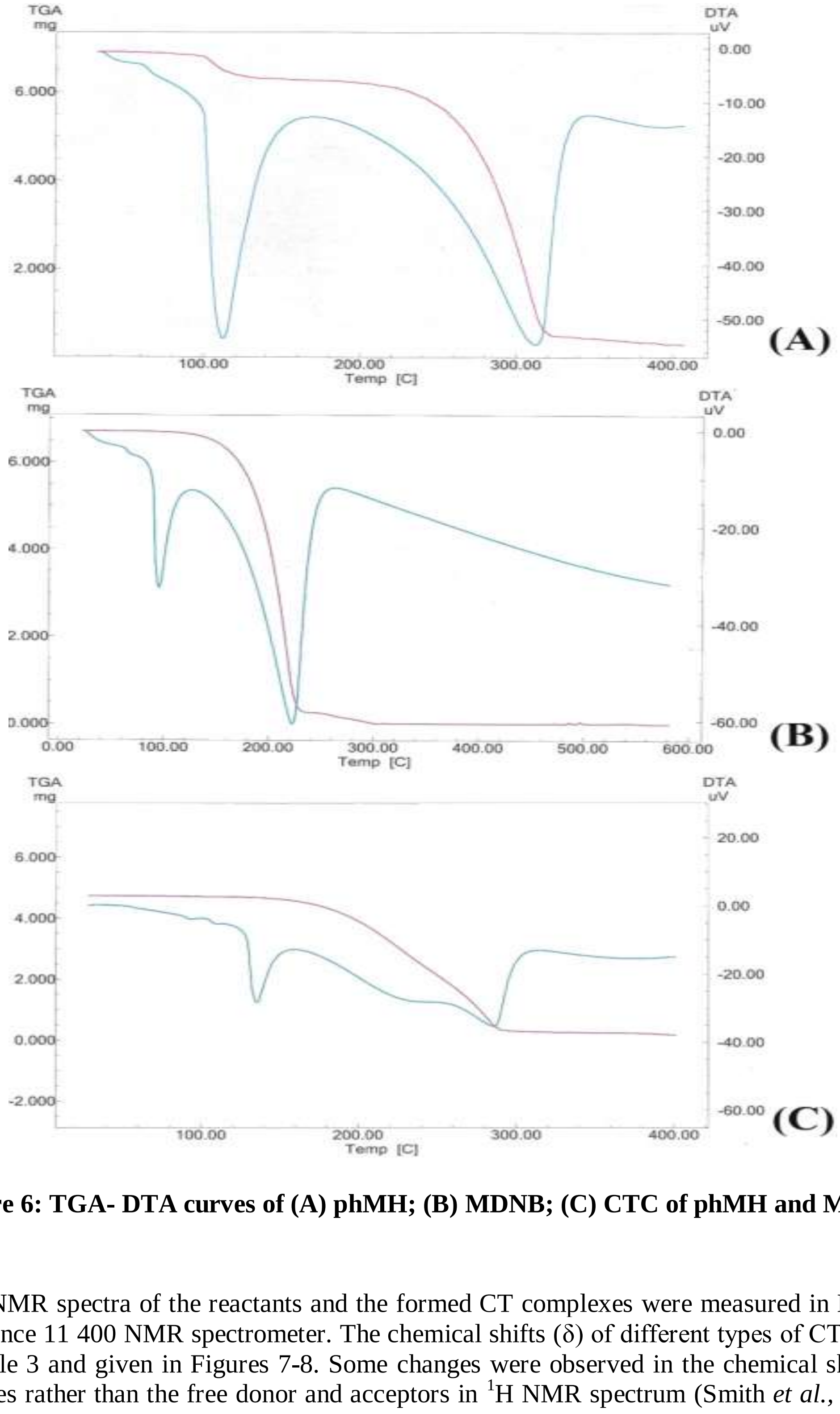


Figure 6: TGA- DTA curves of (A) phMH; (B) MDNB; (C) CTC of phMH and MDNB

^{1}H NMR

The proton NMR spectra of the reactants and the formed CT complexes were measured in DMSO using Bruker Advance 11 400 NMR spectrometer. The chemical shifts (δ) of different types of CT complex are listed in Table 3 and given in Figures 7-8. Some changes were observed in the chemical shift values of CT complexes rather than the free donor and acceptors in ^{1}H NMR spectrum (Smith *et al.*, 2000). In the ^{1}H NMR spectrum of the complexes formed by the interactions between phMH as an electron donor with π acceptors (PHB and MDNB), one or two of the nitrogen atoms from the donor interact to make intermolecular hydrogen bonding with the hydrogen atom at ortho position related to two nitro electron withdrawing group (EWD) in MDNB which makes that hydrogen more liberate, and in PHB with the proton of OH group and may be with proton of COOH group.

- The ^{1}H NMR of phMH- MDNB (Figure 7 (C)) shows a signal at 2.2 ppm attributing to NH$^+$ and confirming the hydrogen bonding interaction between protons between the two nitro groups of MDNB and the nitrogen of phMH.
- The ^{1}H NMR of phMH- PHB CT Complex (Figure 8 (C)) shows a signal at 2.1 ppm attributing to NH$^+$ and confirming the hydrogen bonding interaction between the OH of PHB and the nitrogen of phMH.

The previous results coincide with results of the FT- IR Spectra. Consequently, one concludes that the molecule complexes between phMH and the studied acceptors are formed through electron and proton transfer that can be formulated as:

Table 3: ^{1}H NMR spectral data of phMH, MDNB, PHB and their CT complexes

Compound	^{1}H NMR chemical shift δ ppm	Assignments
PHB	6.9	D, 2H; Ar- H
	7.9	D, 2H; Ar- H
	10.2	Br, 1H; Ar- OH
	12.1	Br, 1H; Ar- COOH
MDNB	7.7	D, 1H; Ar- H
	8.5	D, 1H; Ar- H
	8.6	D, 1H; Ar- H
	8.9	S, 1H; Ar- H (between two NO_2 groups)
CTC of phMH and PHB	2.1	S; NH-ph-O-Ar
	2.7	Q; 1H-OH
	3.5	Br; OH-ph
	6.9	M; 4H-Ar, 2H-ph (3,8)
	7.8	M; 4H-Ar, 2H-ph (5,6)
	8.0	S; 2H-ph (4,7)
	8.3	S; 2H-ph (2,9)
	11.8	Br; 1H-COOH-Ar
CTC of phMH and MDNB	2.2	S; NH-ph-Ar
	2.5	T; 1H-ph
	3.5	S; OH-ph
	7.7	Q; 3H-ph(3,8), 1H-Ar-H
	7.9	Q; 2H-ph(5,6)
	8.3	Q; 3H-ph(4,7), 1H-Ar
	8.5	Q; 2H-ph (2,9)
	9.1	Q; 1H-Ar

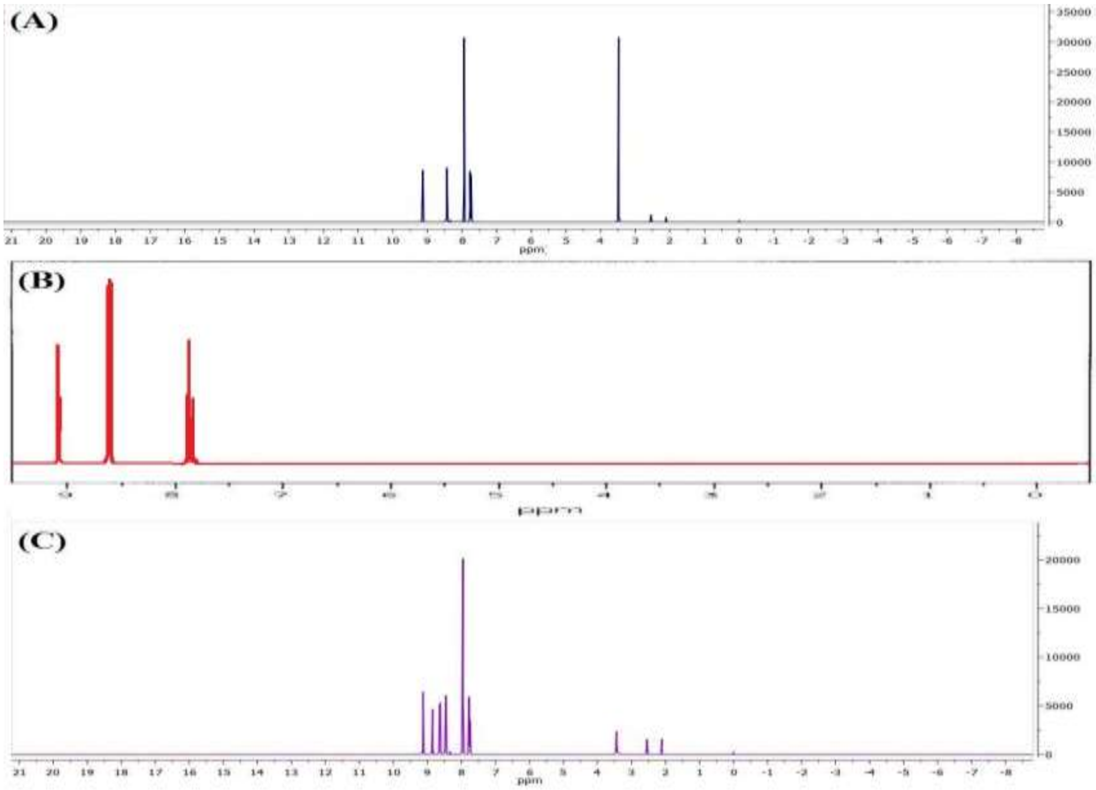


Figure 7: ^{1}H NMR of (A) phMH; (B) MDNB; (C) CTC of phMH and MDNB

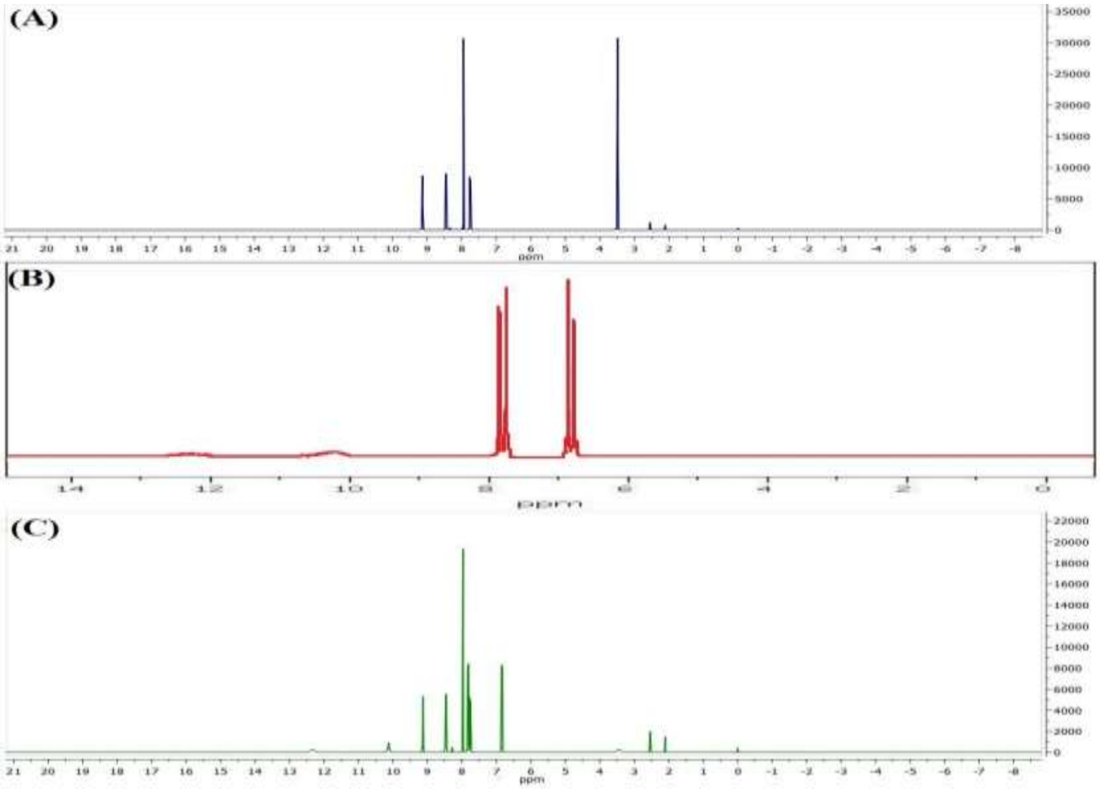
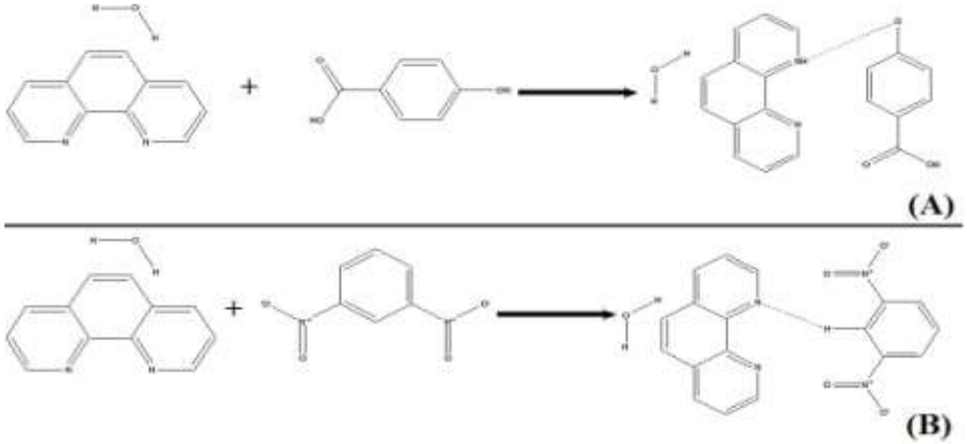


Figure 8: ^{1}H NMR of (A) phMH; (B) PHB; (C) CTC of phMH and PHB

The aromatic protons in phMH were assigned following the previously known in the literature (Gaballa *et al.*, 2003) in the regions 8-9.1 ppm, while the phenolic protons of PHB were assigned at 10.2 and 12.1 ppm and at 8.9 ppm in MDNB. The ^{1}H NMR spectra of the complexes reveal several observations. All the observed peaks in the spectra of the individual components are also present in the complexes spectra suggesting their formation. The proton signals of the donor phMH are downfield shifted to higher ppm values indicating a charge migration from the donor towards the acceptor. The ^{1}H NMR signal due to the phenolic protons in PHB disappeared in the spectra of the complexes indicating deprotonation while in the phMH-MDNB complex spectra, a new peak was observed in the region 2.0–3.0 ppm and assigned to N+–H protons indicating protonation of the donor phMH. Finally, it is suggested that the interaction of phMH as a donor with PHB and MDNB occur in a molar ratio of 1:1 according to the following equations in Scheme 2.



Scheme 2: Shows the reaction and the intermolecular hydrogen bonding between (A) phMH and PHB and (B) phMH and MDNB.

Fluorescence

Fluorescence spectra were recorded at room temperature (35 °C) in acetone in the range of 300-750 nm, using an excitation 250 nm. It was observed that the acceptors (MDNB and PHB) quenched the emission of fluorescence of phMH through the formation of charge-transfer complexes.

The fluorescence changing is usually classified as dynamic and static quenching (Liu *et al.*, 2005).

Dynamic quenching results from collision between flurophore and quencher whereas static quenching is due to ground state complex formation between flurophore and quencher. The binding of phMH with some acceptors where studies in the intrinsic fluorescence of CTC at different concentration of donor in Figures 9-10. The experimental results indicate that the quenching efficiency depends on the type of the acceptor and the concentration of the donor.

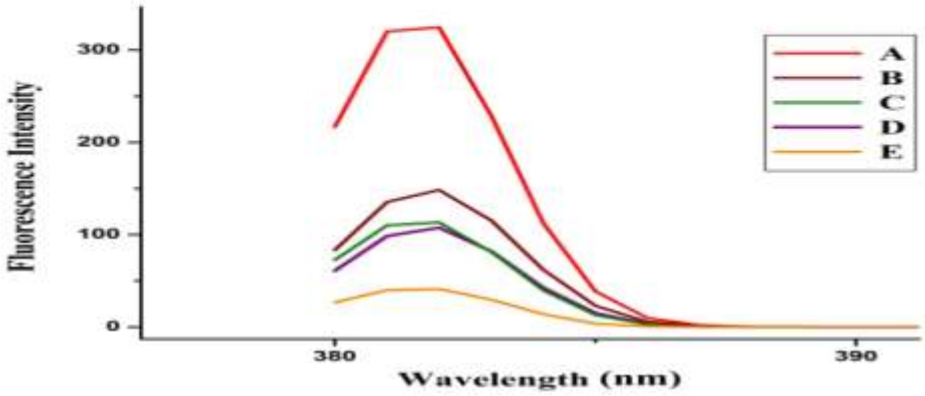


Figure 9: Fluorescence Spectra of 0.01 to 0.05 Mol/L phMH with 0.01 Mol/L MDNB from top to bottom.

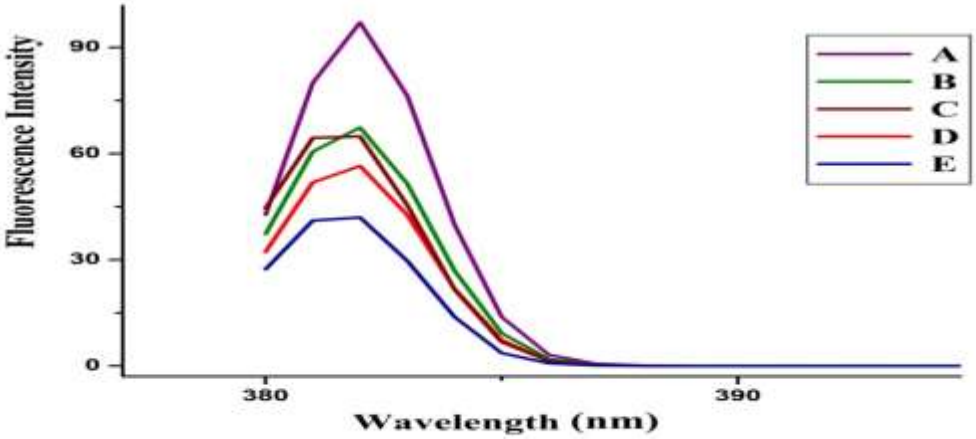


Figure 10: Fluorescence Spectra of 0.01 to 0.05 Mol/L phMH with 0.01 Mol/L PHB from top to bottom.

From Figure 9, we obtained that the intensity of emission of CTC of 0.01 Mol/L phMH (3ml) with 0.01 Mol/L PHB (3ml) is 330 but it became 45 at 0.05 Mol/L phMH with a fixed concentration of PHB (0.01 Mol/L) (Ratio 1:5).

From Figure 10, we obtained that the intensity of CTC of 0.01 Mol/L phMH (3ml) with 0.01 Mol/L MDNB (3ml) equals to 100 and it decreased to 47 at 0.05 Mol/L phMH with 0.01 Mol/L MDNB in the ratio of 1:5.

Conclusions

The electron donor 1,10-phenanthroline monohydrate (phMH) reacts with the π-accepters {4-hydroxybenzoic acid (PHB) and 1,3-dinitrobenzene (MDNB)} in acetone and methanol at room temperature to form charge-transfer complexes. The foregoing discussion has shown that 1,10-phenanthroline monohydrate formed with PHB and MDNB, formed 1:1 molecular complexes in which phMH was found to act as hydrogen acceptor. The FT-IR data provides evidence for the existence of new bands of CTC complexes with some changes and indicate the formation NH^+. From the ^1H NMR, we obtained new signals and shifts while others disappeared, which indicate that new complexes are formed. The fluorescence spectrum of the CT Complexes shows that the intensity of emission decreases with increase in the concentration of the donor.

Further, the TGA-DTA thermograms of solid state of the donor and acceptors and their complexes supports the fact that the interactions occur between the donor and the acceptors by some change in the in the position of peaks and weight loss for donor and acceptors and their complexes. Furthermore, the XRD spectrum shows that in the CT complexes, new bands are obtained corresponding to the new compounds formed and indicating the crystal structures of phMH-MDNB and phMH-PHB. The paricle size determination using Deby-Sherrer equation confirms that the particles of the CT complexes are located in nanoscale range.

REFERENCES

Abdel-Khalik S and Abdel-Hakim S (1998). Spectroscopic and Conductive Properties of some charge transfer complexes of Iodine. *Spectroscopy Letters* **31** (2) 459.

Adam AMA, Refat MS, Sharshar T and Heiba ZK (2012). Synthesis and charactization of highly conductive charge-transfer complexes using positron annihilation spectroscopy. *Spectrochimica Acta part A* **95** 458-477

Amett EM and Mitchell EJ (1971). Hydrogen bonding. VI. Dramatic difference between proton transfer and hydrogen bonding. *Journal of American Chemical Society* **93** (9) 4052-4053.

Atkins PW (1990). *Physical Chemistry* 4th Edition (Oxford University Press, England).

Bahat M and Yrdakul S (2002). Vibrational spectroscopic study on pyrimidine metal (II) tetracyanometalate complexes. *Spectrochimica Acta part A* **58** (5) 933-939.

Dwivedi PC, Banga AK and Agarwal R (1982). Interaction of aliphatic amines with substituted quinines- a conductimetric study. *Electrochimica Acta* **27** 1697-1699.

El-Zaria ME (2008). Spectrophotometric study of the charge transfer complexation of some prophyrin derivatives as electron donors with tetracyanoethylene. *Spectrochimica Acta part A* **69** (1) 216-221.

Felber JP, Coombs TL and Vallee BL (1962). The mechanism of inhibition of carboxypeptidase A by 1,10-phenanthroline. *Biochemistry* **1** (2) 231-238.

Foster R (1969). *Organic Charge-Transfer Complexes* (Academic press, London, New York).

Gaballa A, Wagner C, Schmidt H and Steinborn D (2003). Ligand substitution reactions on aquapentachloro- and hexachloroplatinic acid- synthesis and characterization of tetrachloroplatinum (IV) complexes with Heterocyclic N,N Donors. *Zeitschrift für Anorganische und Allgemeine Chemie* **629** 703-710.

Gaballa AS, Wanger C, Teleb SM, Nour E, Elmosallamy MAF, Kaluderovic GN, Schmidt H and Stembom D (2008). Preparation, spectroscopic and structural studies on charge-transfer complexes of 2,9-dimethyl-1,10-phenanthroline with some acceptors. *Journal of Molecular Structure* **876** 301-307.

Hasani M and Shamsipur M (1998). Interaction of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone with aza-18-crown-6 and aza-12-crown-4, Kinetic and Spectrophotometric studies in chloroform and acetonitrile solutions. *Journal of Chemical Society Perkin Transactions* **2** (5) 1277-1282.

Hu. Liu YZ, Shen XS, Fang XY and Qu SS (2005). Host channel framework determined by C-H·····π interaction in the inclusion crystal of 2,5-bis(diphenylmethyl)hydroquinone and benzaldehyde. *Journal of Molecular Structure* **738** 143-149.

Jones II G and Jimenez JAC (1999). Intramolecular photoinduced electron transfer for cations derived from azole-substituted coumarin dyes. *Tetrahedron Letters* **40** (49) 8551-8555.

Kasha M (1991). Energy transfer, charge transfer and proton transfer in molecular composite systems. *Basic Life Sciences* **58** 231-251.

Kruse JM and Brandt WW (1952). Investigation and application of zinc-1,10-phenanthroline complexes. *Analytical Chemistry* **24** (8) 1306-1308.

Laidler KJ (1972). *Chemical Kinetics* 2nd edition (Tata McGraw, Hill) 1.

M.S. Refat, S.A. Sadik and H.M. Khater (2006). Electronic, infrared, and ^{1}H NMR spectral studies of the novel charge- transfer complexes of o-tolidine and p-toluidine with alternation π acceptoes (3,5-dinitro benzoic acid and 2,6-dichloroquinone-4-chloroimide) in $CHCl_3$ solvent. *Spectrochimica Acta part A* **64** (3) 778-788.

Majchrzak-Kucêba I and Nowak W (2004). Thermal analysis of fly ashes-based zeolites. *Journal of Thermal Analysis and Calorimetry* **77** 125-131.

Mo W, Li G, Xiong H and Liu H (2007). Preparation of CuCl/1,10-phenanthroline immobilized on polystyrene and catalytic performance in oxidative carbonylation of methanol. *Applied catalysis A: General* **333** 172-176.

Mo WL, Xiong H, Li T, Guo XC and Li GX (2006). The catalytic performance and corrosion inhibition of CuCl/Schiff base system in homogeneous oxidative carbonylation of methanol. *Journal of Molecular Catalysis A: Chemical* **247** (1-2) 227-232.

Morukama K (1977). Why do molecules interact? The origin of electron donor-acceptor complexes, hydrogen bonding and proton affinity. *Accounts of Chemical Research* **70** (8) 294-300.

Mulliken RS and Person WB (1969). *Molecular Complexes* (Wiley Interscience, New York).

Ng JCY, Cheung WH and McKay G (2002). Equilibrium studies of the sorption of Cu (II) ions onto Chitosan. *Journal of Colloid Interface Science* **255** 64-74.

Pauling L (1960). *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York).

Qazi SJS, Rennie AR, Cockcroft JK and Vickers M (2009). Use of wide- angle X-ray diffraction to measure shape and size of dispersed colloidal particles. *Journal of Colloid Interface Science* **338** 105-110.

Refat MS, Killa HMA and Grabeher I (2007). Synthesis and characterization of N,N'bis[2-hydroxyethyl]-1,4,6,8-naphthalenediimide with para substituted of phenols based on charge-transfer complexes. *Spectrochimica Acta part A* **68** (1) 123-133.

Rhodes LM and Schimmel PR (1974). Intermolecular proton transfer reaction between base and phosphate moieties of mononucleotides in solution. *Journal of American Chemical Society* **96** 2609-2611.

Rice MJ and Roth WL (1972). Ionic transport in super ionic conductors. *Journal of Solid State Chemistry* **4** (2) 294-310.

Saito G and Matsunaga Y (1974). Charge-Transfer and Proton-Transfer in the Formation of Molecular Complexes VIII. Benzidine-2,4-Dinitrophenol Complexes. *Bulletin of Chemical Society of Japan* **47** 1020-1021.

Salvesen GS and Nagase H (2001). *Proteolytic enzymes: A practical approach*, 2nd edition105–130.

Smith G, Bott RC, Rae AD and Willis AC (2000). The modulated crystal structure of the molecular adduct of 2,4,6-trinitrobenzoic acid with 2,6-diaminopyridine. *Australian Journal of Chemistry* **53** 531-534

Strohbusch F, Marshall D and Eyring EM (1978). Kinetics of proton transfer between picric acid and two azo indicators in acetonitrile. *Journal of Physical Chemistry* **82** 2447.

Tong S and Na L (1992). *Chinese Chemical Letters* **3** (3) 201.

Zhao Y, Zhang Z and Dang H (2003). Preparation of Tin nanoparticles by solution dispersion. *Journal of Material Science and Engineering A* **59** 405-407.