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Spectroscopic, Electrical Conductivity Measurements with Polystyrene Composites and Thermal Studies on Charge-Transfer Interactions Between bis(4-Amino-N-ethyl-1,8-Naphthalimide) Amine with Some Phenolic Acceptors

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Intermolecular charge-transfer (CT) complexes formed from the reaction of bis(4-amino-N-ethyl-1,8-naphthalimide) amine (BAENA) with some phenolic acceptors such as 4-aminophenol (4-AP), 4-methylphenol (4-MP) and 4-nitrophenol (4-NP) have been studied in methanol at room temperature. The isolated products have been discussed using (UV-Vis., mid infrared, and ^{1}H-NMR) spectra and thermal measurements (TGA/ DTG) as well as elemental analysis. The photometric titration curves for the reactions indicated that the data obtained refer to 1:2 charge transfer complexes [(BAENA)(4-AP)$_2$], [(BAENA)(4-MP)$_2$] and [(BAENA)(4-NP)$_2$] were associated. The infrared and ^{1}H-NMR spectra interpreted the mode of CT interaction formed with the hydrogen bonding exist between a proton (–OH) of phenolic acceptor and the two amine –NH$_2$ group of donor attached with 4-amino-N-ethyl-1,8-naphthalimide compound. The activation thermodynamic parameters ΔE, ΔH, ΔS and ΔG were obtained from the DTG diagrams by using Coats-Redfern method. The polymer composites of [(BAENA)(acceptor)$_2$] charge transfer complex with polystyrene have prepared by weight ratio (1(charge transfer complex):6(polystyrene)), respectively. The polymer composites exhibit semi conducting behavior having thermal activation energies in the range of 0.34 to 0.62 eV at different temperature.

Keywords: 1,8-naphthalimide; phenolic acceptors; CT complexes; Thermal studies; conductivity measurements.

1. INTRODUCTION

4-Substituted-1,8-naphthalimide derivatives have aroused scientific interest because of their potential use as polymerizable fluorophores for synthetic polymers. A series of fluorescent polymerizable 1,8-naphthalimides [1, 5] were synthesized and their ability to co-polymerize with styrene, methyl methacrylate or acrylonitrile, obtaining copolymers with intensive fluorescence [6-11] was studied. In literature survey, 1,8-naphthalimide dyes have been examined with regards their use in nematic liquid crystals for guest-host type electro-optical displays [12, 13]. Fluorescent 1,8-naphthalimide derivatives are very interesting in view of their usage as fluorescent dyes for solar energy collectors [14], organic light emitting diodes [15], markers in molecular biology [16], in laser active media [17]. In continuation of our work on the donor abilities “fluorescent dyes” and their tendency to form charge transfer (CTC) complexes with σ acceptor (iodine) [18-21], we considered it interesting to investigate the CT spectra, stabilities, conductivity and thermodynamic parameters of CT complexes of bis(4-amino-N-ethyl-1,8-naphthalimide) amine (BAENA) with *para* position of substituted phenols (4-AP, 4-MP and 4-NP) as acceptors. Further, we noticed from literature [22, 23] that the CT complexes can be stabilized for a long time in solvents of low polarity, at low temperatures and under low donor concentrations.

This paper showed the results obtained from the electronic, infrared, ^{1}HNMR, electrical conductivity and thermal gravimetric measurements as well as the kinetic thermodynamic parameters calculated on bis(4-amino-N-ethyl-1,8-naphthalimide) amine complexes formed in the reaction of substituted phenols (4-AP, 4-MP and 4-NP) with the important fluorescent compound (BAENA). This base contains, two terminals $–NH_2$ groups in both side of the donor that is expected to cause increasing in the stability of the resulted complexes. In this article enables us to make assessments of the stiochiometry, mode of the interaction resulted from these CT complexes along with the electrical conductivity behavior of the solid polymer composite of $[(BAENA)(acceptor)_2]$ CT complexes with polystyrene. The determination of association constant (K), molar extinction coefficients (ε) and oscillator strength (f) were carried out.

2. EXPERIMENTAL

The bis(4-amino-N-ethyl-1,8-naphthalimide) amine (BAENA) fluorescent donor compound Fig. 1, was prepared [24] and used without further purification. Pure 4-aminophenol (4-AP), 4-methylphenol (4-MP) and 4-nitrophenol (4-NP) were obtained from Merck Co. was further purified by re-crystallization from $CHCl_3$ prior to use. Reagent grade chloroform (Merck) and methanol (Fluka) were used without any further purification.

2.1. Synthesis of bis(4-amino-N-ethyl-1,8-naphthalimide) amine

The 4-nitro-1,8-naphthalic anhydride has been used as conventional starting material for the preparation of diimides. The synthetic route to obtaining bis(4-amino-N-ethyl-1,8-naphthalimide) amine is presented in Scheme 1. The bis(4-nitro-N-ethyl-1,8-naphthalimide) amine was synthesized by condensation of the 1,8-naphthalic anhydride and diethylenetriamine in boiling ethanol solution. The formation of bis(4-nitro-N-ethyl-1,8-naphthalimide) amine fluorophore followed by formed double acylation with the naphthalic anhydride. Scheme 1 shows the reduction of the nitro group's compound with an anhydrous stannous chloride in 35% aq hydrochloride acid solution [25].

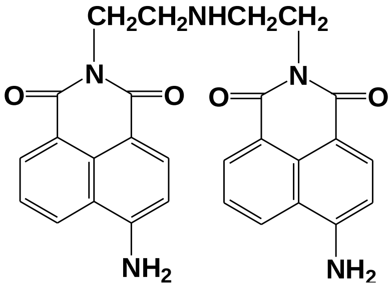
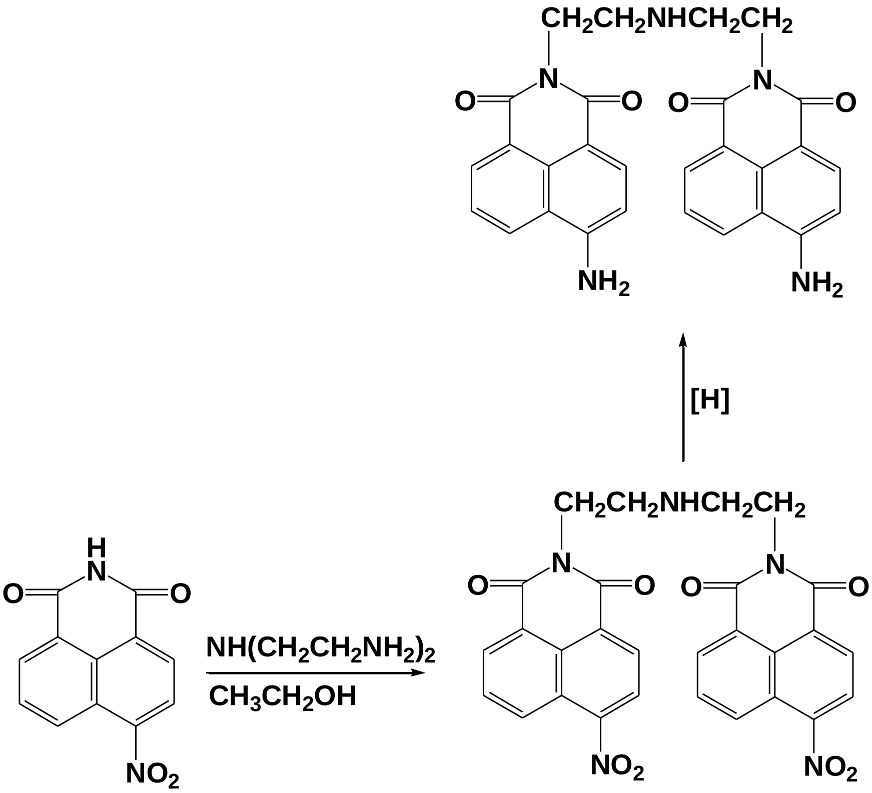


Figure 1. Bis(4-amino-N-ethyl-1,8-naphthalimide) amine



Scheme 1. The synthetic route of bis(4-amino-N-ethyl-1,8-naphthalimide) amine

2.2. Synthesis of charge transfer complexes

The isolated solid charge transfer complexes of bis(4-amino-N-ethyl-1,8-naphthalimide) amine with phenolic acceptors mentioned above were prepared by mixing 1mmol of the donor in chloroform/methanol (50/50%) mixture with 2 mmol of each 4AP, 4MP and 4NP of acceptors in the same solvent. The mixtures were stirred at room temperature for 2 hour, where the solid precipitated after reduced the volume of solvent by the evaporation of the 80% volume of respective solvent. The separated complexes were filtered off, washed several times with CCl_4, and then dried under vacuum.

2.3. Instruments

The electronic spectra of the donor (BAENA), acceptors and the resulted charge transfer complexes in methanol were recorded in the region of 800-200 nm using a Shimadzu UV-spectrophotometer model 1601 PC with a 1 cm quartz cell path length. Photometric titration were preformed [26] at 25 ^oC for the reactions of (BAENA) with 4AP, 4MP and 4NP in methanol as follow; the concentration of the donor in the reaction mixtures was kept fixed at $1.0X10^{-4}$ M, while the concentration of π-acceptors of para substituted phenols were changed over a wide range from $0.25X10^{-4}$ to $4.00X10^{-4}$ M. These produced solutions with donor: acceptor molar ratios varying from 1: 0.25 to 1: 4.00. The infrared spectra of the reactants and the resulted CT complexes were recorded from KBr discs using a Bruker FT-IR spectrometer. ^{1}H-NMR spectra were obtained on a Varian spectrophotometers Gemini 200 MHz using d_6–DMSO as a solvent. The thermal analysis (TGA/DTG) was carried under nitrogen atmosphere with a heating rate of 10 ^oC/min using Shimadzu TGA-50H thermal analyzers. The electrical conductivity measurements were made using Tesla 283 Megaohm-meter. For preparation of composites, the required amount of charge transfer complexes and polystyrene (weight ratio 1:6), respectively, were dissolved in excess of chloroform separately and then mixed together. The solvent was evaporated at room temperature with constant stirring. Then the solid CT polymer composites samples were pressed into discs of 12 mm diameter and 1-2 mm thickness at a pressure 8 tone/cm^{-2}. The temperatures were measured in air using a thermocouple type T (Copper /Constantan).

3. RESULTS AND DISCUSSION

Table 1. Physical parameters data of bis(4-amino-N-ethyl-1,8-naphthalimide) amine solid CT complexes

Acceptors	Formula (M.wt)	Mp/K	Elemental analysis[a]			λ_{CT} / (nm)	E_{CT} (eV)	color
			% C	% H	% N			
4-AP	$C_{42}H_{43}O_6N_7$ 741.834	>300	68.00 (67.78)	5.84 (5.77)	13.22 (13.10)	430	2.90	Yellowish Brown
4-MP	$C_{44}H_{45}O_6N_5$ 739.858	>300	71.43 (71.00)	6.13 (6.04)	9.47 (9.31)	390	3.20	Brown
4-NP	$C_{42}H_{39}O_{10}N_7$ 801.800	>300	62.91 (62.64)	4.90 (4.79)	12.23 (12.01)	480	2.60	brown

[a] calculated (found)

The elemental analysis and physical measurements data of the charge transfer complexes formed are listed in Table 1.

3.1. Electronic Spectra

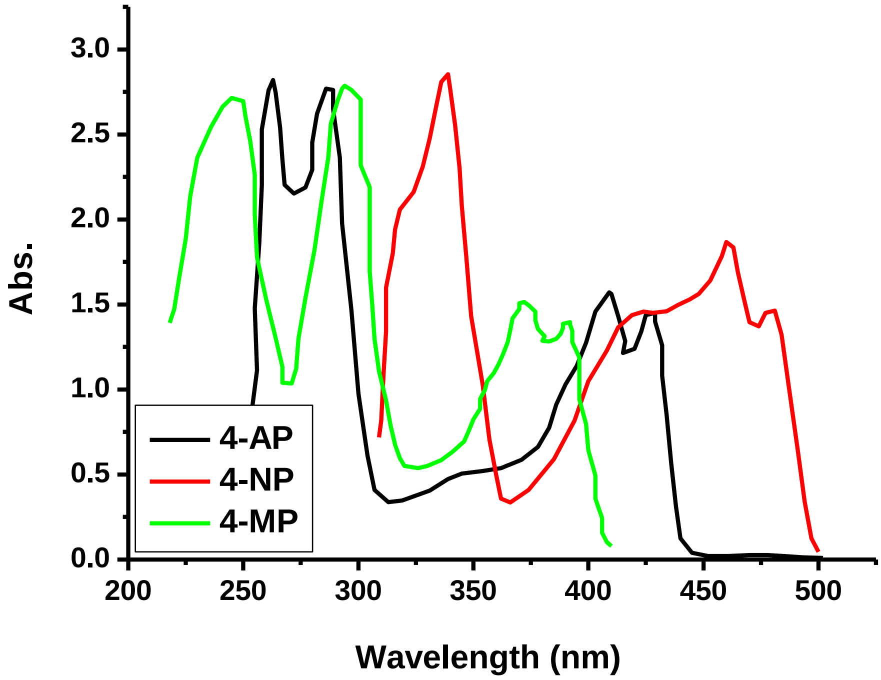
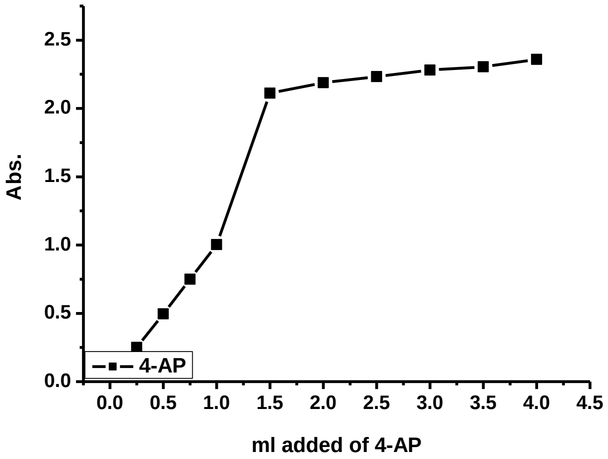


Figure 2. Electronic absorption spectra of [(BAENA)(4-AP)$_2$], [(BAENA)(4-MP)$_2$] and [(BAENA)(4-NP)$_2$] charge transfer complexes in methanol solvent

The electronic spectra of the bis(4-amino-N-ethyl-1,8-naphthalimide) amine as a donor, substituted phenols (acceptors; 4AP, 4MP and 4NP) and their 1:2 charge transfer complexes are shown in Fig. 2.



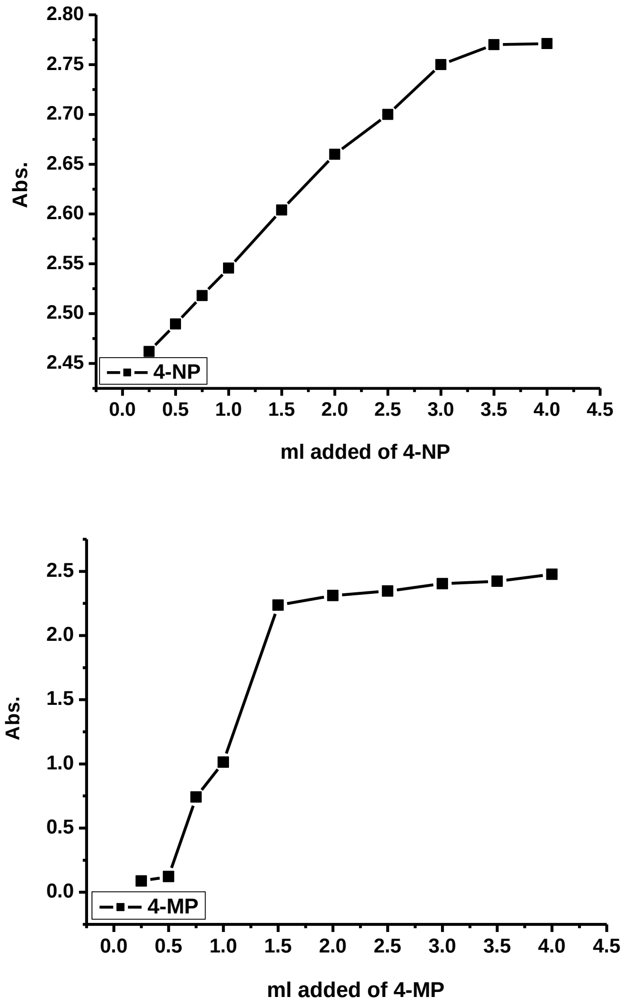


Figure 3. Photometric titration curves of [(BAENA)(4-AP)$_2$], [(BAENA)(4-MP)$_2$] and [(BAENA)(4-NP)$_2$] charge transfer complexes in methanol solvent

The spectra in each cases of the BAENA-acceptor systems have a definite bands at 440 nm for BAENA-4AP; 450 nm for BAENA-4MP and 445 nm for BAENA-4NP due to the formation of [(BAENA)(acceptor)$_2$] charge transfer complexes. The intensity of absorbance increased or decreased according to the kind of reaction and the type of acceptors once added the acceptors was investigated in Fig. 2. The stoichiometry of the charge transfer complexes was determined by applying photometric titration method [26]. These measurements were based on the charge transfer absorption bands exhibited by the spectra of the three systems mentioned above as shown in Fig. 3.

The association constant (*K*) and extinction coefficients (ε) values of the studied charge transfer complexes were calculated using the equation (1) of 1: 2 complexes [27];

$$(C^o_A)^2C^o_D/A=1/K\varepsilon+1/\varepsilon\ C^o_A(4C^o_D + C^o_A) \qquad (1)$$

Where, C^o_A and C^o_D are the initial concentrations of the various acceptors (Para-substituted phenol), and the donor (BAENA), respectively, while A is the absorbance at detected charge transfer bands. The data obtained throughout this calculation are given in Table 2.

Table 2. Charge transfer spectral data; stability constants (K), extinction coefficients (ε), ionization potentials (I_p), oscillator strength (f), and dipole moment (μ) of the BAENA -p-substituted phenol complexes

Acceptors	λ_{CT} / (nm)	K_{CT} (l mol^{-1})	ε (l mol^{-1}cm^{-1})	f x10^{-2}	I_p	μ
4-AP	430	$40x10^6$	$450x10^2$	86	7.14	79
4-NP	480	$45x10^6$	$550x10^2$	103	7.35	86
4-MP	390	$38x10^6$	$480x10^2$	91	6.93	80

Plotting the values of $(C^o_A)^2C^o_D/A$ versus $C^o_A(4C^o_D+C^o_A)$ values of equation (1), straight lines are obtained with a slope of 1/ε and the intercept of 1/Kε as shown in Fig. 4.

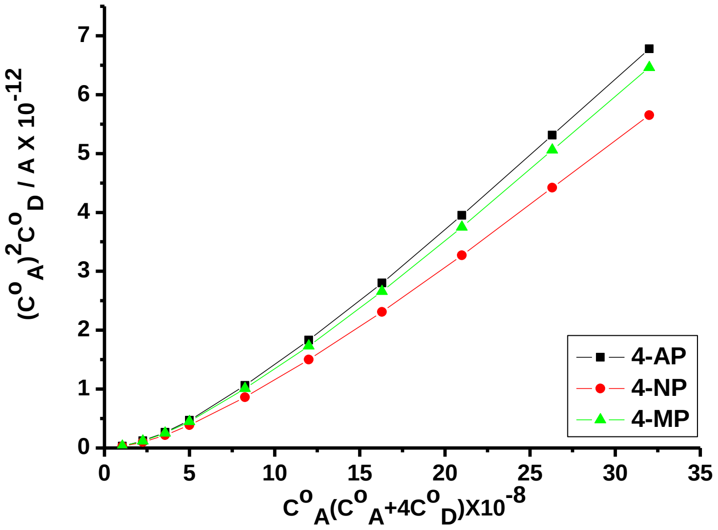


Figure 4. The plot of $C^o_A(4C^o_D+C^o_A)$ values against $(C^o_A)^2C^o_D/A$ of $[(BAENA)(4\text{-}AP)_2]$, $[(BAENA)(4\text{-}MP)_2]$ and $[(BAENA)(4\text{-}NP)_2]$ charge transfer complexes in methanol solvent

The values of both K and ε with the selected band from the CT complexes are given in Table 2. The (BAENA) charge transfer complexes show high values of both the formation constant and the extinction coefficients (ε). The high values of K in generally, reflects high stabilities of the formed charge transfer complexes as a result of the expected high donation of bis(4-amino-N-ethyl-1,8-

naphthalimide) amine as a fluorescence dye donor which contain a two terminal amino groups, two diethylamino groups and naphthalene aromatic ring. The oscillator strength (f) which has a dimensionless quantity used to express the transition probability of the charge transfer bands [28], and the transition dipole moment (μ) of the charge transfer complexes [29], Table 2, have been calculated from the following equations [30];

$$f = 4.32X10^{-9}(\varepsilon_{\max}\,\Delta\nu_{1/2}) \qquad (2)$$

$$\mu = 0.0958(\varepsilon_{max}\Delta\nu_{1/2}/\ \nu_{max})^{1/2} \qquad (3)$$

Where $\Delta\nu_{1/2}$ is the band width at half maximum of absorbance, $\varepsilon_{\max}$ and $\nu_{\max}$ the extinction coefficient and wavenumber at maximum absorption peak of the charge transfer complexes, respectively. The electronic absorption spectra of the solid charge transfer complexes resulted are characterized by detectable charge transfer bands within the wavelength range 440-450 nm which can be assigned to the n-π^* interactions. The existence of these charge transfer bands indicates that the n-π^* transition would have highly contribution to the bonding in the charge transfer complexes. The energy of the interaction between donor and acceptor E_{CT} is calculated using the following equation (4) [31];

$$E_{CT} = 1243.667\ /\lambda_{CT}\,\mathrm{nm} \qquad (4)$$

Where, λ_{CT} is the wavelength of the charge transfer band of the mentioned complexes. The values of E_{CT} were calculated from all charge transfer complexes and represented in Table 2. The position of the charge transfer bands of BAENA-acceptor in the range of (440-450 nm) are increasing or decreasing in the intensity of absorbance accordingly, the para substituted phenols attached to the phenol ring. The effect of substitutes on the position and intensity of the charge transfer bands is attributed to the interaction of substitutions with π-orbital of the benzene ring of phenol. The hyper conjugative effect of ethylene group and inductive effect of four carbonyl groups all perturb the resonance in the benzene ring and boost the energy of the donor level and bring it closer to the LUMO of BAENA and thus cause an increasing/decreasing in the intensity of charge transfer bands. The stabilities of the complexes increase with increasing electron withdrawing ability of the substitutions in benzene ring of phenol that the formation constant of [(BAENA)(4-NP)$_2$] and [(BAENA)(4-MP)$_2$] are greater than that of [(BAENA)(4-AP)$_2$] in the following sequence;

$$4NP \rangle\ 4MP \rangle\ 4AP$$

The higher stability of BAENA complexes may be due to the greater electron affinity of para substituted phenols and also for the greater polarity of phenols.

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

$$I_P = a + b\,(h\,\nu_{max}) \qquad (5)$$

Where $h\,\nu_{max}$ is the lowest transition energy in electron volts; *a*, and *b* are 5.11 and 0.701 [32]; 4.39 and 0.857 [33] or 5.156 and 0.778 [34], respectively. The average value of calculated (I_p) of donor by this method is 7.14 eV.

3.2. Infrared Spectra

The IR absorption spectra of the synthesized charge transfer complexes were recorded in the frequency range 4000-400 cm^{-1} with a Bruker FT-IR spectrometer.

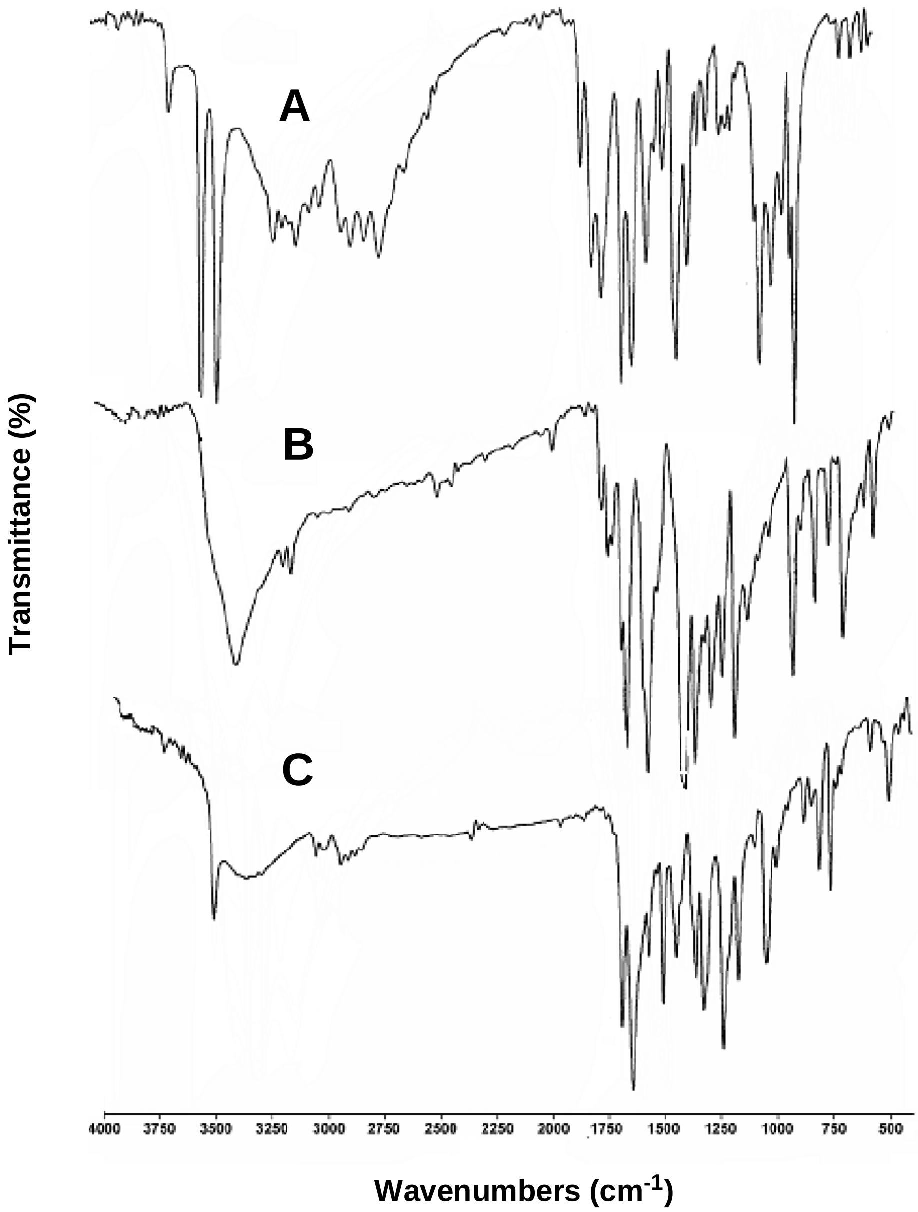


Figure 5. Infrared spectra of: (A) [(BAENA)(4-AP)$_2$], (B) [(BAENA)(4-NP)$_2$] and (C) [(BAENA)(4-MP)$_2$] charge transfer complexes.

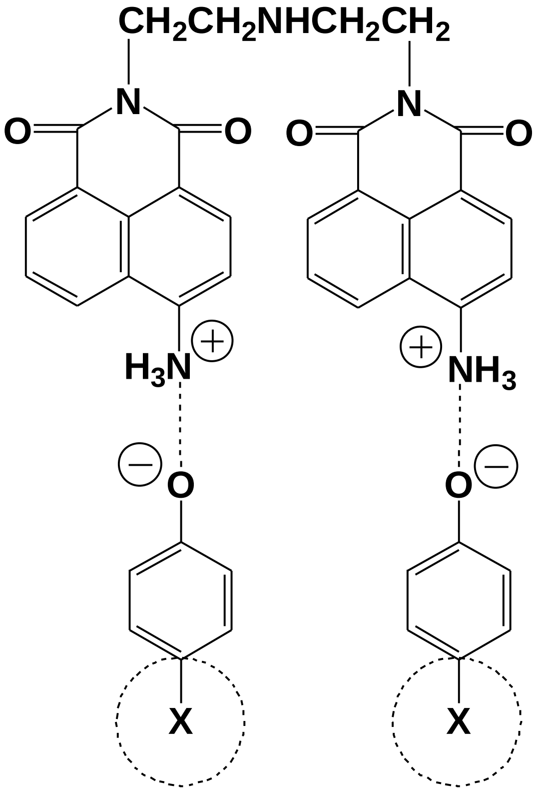
Table 3. Infrared frequencies[a] (cm^{-1}) and band assignments for (A): BAENA, (B): 4-AP, (C): 4-MP, (D): 4-NP, (E): [(BAENA)(4-AP)$_2$], (F): [(BAENA)(4-MP)$_2$], and (G): [(BAENA)(4-MP)$_2$] compounds

A	B	C	D	E	F	G	Assignments[b]
3378 3351	3375 3305	3386	3323	3372 3301	3375 3313	3325	ν(O-H); 4AP, 4MP, 4NP ν(N-H); NH_2
3077 3065	3018	3024	3118 3084	3051 3013	3064 3032	3122 3081	ν_{as}(C-H); CH_2+CH_3 ν(C-H); aromatic ν ($^+$NH)
2957 2892 2821 2770	2900 2851	2920 2861 2730	2980 2947	2952 2853	2955 2927 2893	2962 2814	ν(C=C); CH aromatic ν_s(C-H); CH_2+CH_3
---	---	---	---	2753 2716 2653 2582 2472 2371 2342	2762 2655 2667 2373 2348 2272 1975	2716 2567 2434 2371 2219 1974 1922	Hydrogen bonding
1685 1645	---	---	---	1691 1652	1699 1643	1700 1672	ν(C=O); BAENA
1610 1580	1603 1512	1875 1759 1560 1514	1612 1589	1605 1512	1573 1516	1612 1599	ν(C=C); aromatic $\nu_{as}(NO_2)$; 4NP
1455	1468 1403	1438 1362	1495	1462 1401	1452 1362	1490	δ(CH); CH def. δ(CH); aromatic $\delta(NH_2)$
1385 1340 1245 1178	1337 1268 1220 1142	1293 1236 1173 1106 1041	1325 1284 1216 1164 1109	1332 1262 1226 1177 1144	1333 1242 1173 1102	1322 1284 1212 1161	ν_{as}(CN) ν(C-O); C-OH $\nu_s(NO_2)$; 4NP
1052	1080 1030	---	1004	1084 1035	1052 1015	1112 1052	ν_s(CN)
1009 960 886 856	898 847 803	1017 982 954 926 814	960 851 819	931 892 842 800	963 883 852 812	961 855 819	δ(CH); in-plan bend
780 722	743	740 705 642	751 693 623	761 741	765 728	759 691 623	δ(CH); CH-def δ(NH); NH def.
591 501 4462	548 497 449 420	509 465	536 495	542 491 441 413	592 501 448	539 491	δ(CH); out-of-plan

[a] br, broad; m, medium; s, strong; sh, shoulder; w, weak; [b] ν, stretching; δ, bending.

The infrared spectrum of bis(4-amino-N-ethyl-1,8-naphthalimide) amine as a donor, showed absorption bands in the 3378-3513 cm^{-1} region which assigned to –NH group. The bands at 3065-3077 cm^{-1} can be assigned to stretching C-H vibrations and bands at 1610 and 1580 cm^{-1}, assigned to stretching C-C vibrations. These are characteristic of the aromatic system in the naphthalene ring of the naphthalimide structure. The band at 780cm^{-1} is characteristic of aromatic ring deformation vibration. It is well known that imides give rise to both frequency bands of the C=O absorption [35]. The IR spectrum of free donor show intensive absorption bands at 1685 and 1645 cm^{-1}, respectively, which are characteristic of symmetrical and asymmetrical carbonyl group vibrations. The absorption bands in the 1340-1385 cm^{-1} region are characteristic for the imide C-N-C bonds. The stretching vibrations of the primary amino groups appear in the range 3240-3351 cm^{-1}. Figure 5 is show the infrared spectra of the reaction products of 1:2 (donor:acceptor) with the molecular formula, $[(BAENA)(acceptor)_2]$. Their band assignments are given in Table 3.

The spectra of the resulted interaction between donor and acceptors contain main bands distinguish for both reactants. In comparison between the infrared spectral data of the free donor and the various acceptors, these deduced that some changes in band intensities and some shift in the band wavenumber values. For instance, in all spectra of the CT complexes of 4AP, 4MP and 4NP are characterized by an absent or decreasing in the intensities of the band specialized to phenolic group which present in all acceptors, this fact supported the involvement of –OH group of acceptors in the CT complexation. The IR spectra of the three charge transfer products are characterized by a group of bands around 2550 cm^{-1} which are not present in the spectra of the free reactants. This kind of bands is due to the stretching mode of $^{+}NH_3$ proton upon the nitrogen atom of terminal primary $–NH_2$ group [35]. These results from the protonation of two nitrogen atoms of both primary amino groups for the donor, BAENA, through proton transfer from the acidic hydrogen proton (phenolic group) of acceptor to the basic nitrogen atoms of two primary terminal amino groups of the donor, the presence of two terminal amino groups in both sides of donor give the nitrogen atom the priority to occurs the complexation through it. Generally, phenols are one million to one billion times more acidic than alcohols and this is the characteristic property that distinguishes them. Phenols will react with the base sodium hydroxide but alcohols will not. The acidic of phenols is explained by the resonance stabilization of the phenoxide ion; the negative charge is dispersed throughout the benzene ring as opposed to being concentrated on the oxygen as it is the alkoxide ion. Electron-withdrawing groups on the benzene ring increase the acidic of phenol, accordingly, this fact that phenols play role of the acceptors. The proposed mechanism of the interaction between acid and base, meaning that acidic proton of the acceptor has a tendency to transfer to the donor (base). This fact can be applied herein in our study between para substituted phenols (acceptors) and BAENA as donor. Such assumption is strongly supported by the existence of a new bands of medium weak intensity in the spectra of each complexes prepared. This band is observed at a range of 3050-3100 cm^{-1} for the three CT complexes, and indicated that the formation of $^{+}NH_3$ species i.e, from which a labile proton is expected. These results revealed that the CT complexes were just some changes in their band intensities and shifts of some band frequency values and chemical interactions were present in the constituents as shown in Scheme 2.



Scheme 2. Mode of the interaction between BAENA and p-substituted phenols (where; X = NH_2, CH_3 and NO_2)

3.3. ^{1}H-NMR Spectra

The ^{1}HNMR spectra of the BAENA donor (2.58(s, 6H, CH_3 of DMSO); 2.90(t, 4H, 2x($NCH_2\underline{CH_2}NH$); 3.89(t, 4H, 2x($N\underline{CH_2}CH_2NH$); 5.26(br, s, 2H, $ArNH_2$); 6.76(br, s, 1H, NH) and 6.94-8.22 (m, 5H, ArH)) and their charge transfer complexes were measured in (DMSO-d6) solvent using tetramethylsilane (TMS) as internal standard. The chemical shifts (δ) of the different types of protons of the donor and charge transfer complexes prepared are listed in Table 4. The spectra of all three charge transfer complexes were compared with the reactants. It was clearly that found –OH signal for all acceptors at the range of 9.50-10.80 ppm was disappeared.

These indicating that involvement the proton of –OH phenolic group in chelating through the deprotonation process from the acceptor to donor migration. The new peaks formed in the location at around 4.55 ppm in the three complexes assigned to $^+NH_3$ protons confirm the protonation of the donor. All the observed proton signals in the spectra of the starting reactants are also exist in the formed charge transfer complexes spectra with small shifted (ppm). These changes in the δ(ppm) values of the donor and reaction products are strongly supported the charge migration from the acceptor acid towards the donor base.

Table 4. ^{1}H-NMR spectral data of BAENA and its charge transfer complexes

Compound	Chemical shift, δ (ppm)	Assignment
BAENA	2.90	(t, 4H, 2x($NCH_2\underline{CH_2}NH$)
	3.89	(t, 4H, 2x($N\underline{CH_2}CH_2NH$)
	5.26	(br, s, 2H, $ArNH_2$)
	6.76	(br, s, 1H, NH)
	6.94-8.22	(m, 5H, ArH)
$[(BAENA)(4\text{-}AP)_2]$	2.88	(t, 4H, 2x($NCH_2\underline{CH_2}NH$)
	3.85	(t, 4H, 2x($N\underline{CH_2}CH_2NH$)
	4.55	(br, s, H, $^+NH_3$)
	5.11	(br, s, 2H, $ArNH_2$)
	6.74	(br, s, 1H, NH)
	6.90-8.20	(m, 5H, ArH)
$[(BAENA)(4\text{-}MP)_2]$	2.87	(t, 4H, 2x($NCH_2\underline{CH_2}NH$)
	3.86	(t, 4H, 2x($N\underline{CH_2}CH_2NH$)
	4.62	(br, s, H, $^+NH_3$)
	5.09	(br, s, 2H, $ArNH_2$)
	6.73	(br, s, 1H, NH)
	6.91-8.26	(m, 5H, ArH)
$[(BAENA)(4\text{-}NP)_2]$	2.79	(t, 4H, 2x($NCH_2\underline{CH_2}NH$)
	3.83	(t, 4H, 2x($N\underline{CH_2}CH_2NH$)
	4.48	(br, s, H, $^+NH_3$)
	5.04	(br, s, 2H, $ArNH_2$)
	6.71	(br, s, 1H, NH)
	6.88-8.31	(m, 5H, ArH)

3.4. Electrical conductivity

The electrical conductivity was determined for the temperature range 298-373 K on the solid charge transfer composite samples. The measurements were measured firstly, at 373 K and then the sample was cooled to 298 K. The values of the activation energy were calculated [36] and are presented in Table 5.

Table 5. The values of the electrical conductivity (ohm^{-1}cm^{-1}) and of the activation energy (eV) for the CT polymer composite at the temperatures, 298, 323, 348 and 373 K

Charge transfer complexes/polymer composite	K_{298}	K_{323}	K_{348}	K_{373}	E
$[(BAENA)(4\text{-}AP)_2]$	4.1×10^{-5}	5.2×10^{-5}	6.43×10^{-5}	7.79×10^{-4}	0.34
$[(BAENA)(4\text{-}MP)_2]$	3.5×10^{-6}	4.9×10^{-6}	6.5×10^{-5}	5.34×10^{-4}	0.62
$[(BAENA)(4\text{-}NP)_2]$	2.11×10^{-7}	3.9×10^{-6}	5.48×10^{-6}	4.69×10^{-5}	0.57

Hydrogen bonding has an effect on the activation energy and conduction mechanism. In literature, the high electrical conductivity obtained was due to hydrogen bonding [37]. The three new charge transfer complexes composites give a semi conductive properties and high thermal stability properties that are very rarely exhibited in the same compounds. It is known that the increase in conductivity with temperature is related to the increase in the population of electrons in the conduction band. The effect of temperature can be estimated by calculating the activation energy. The activation energy most likely belongs to the energy gap between valence and conduction band. This means that there is a positive relation between the electrical conductivity and the activation energy. The values of activation energy vary between 0.34 to 0.62 eV at different temperature where decreased with increasing double bond conjugation in the charge transfer complexes studied. These results for activation energy are expected for organic semiconductors.

3.5. Thermal analysis

The characteristic temperatures for the thermal decomposition of the studied complexes, [(BAENA)(4-AP)$_2$], [(BAENA)(4-MP)$_2$] and [(BAENA)(4-NP)$_2$] are presented in Fig. 6. The following steps discussed the decomposition stages occur in the three types of complexes;

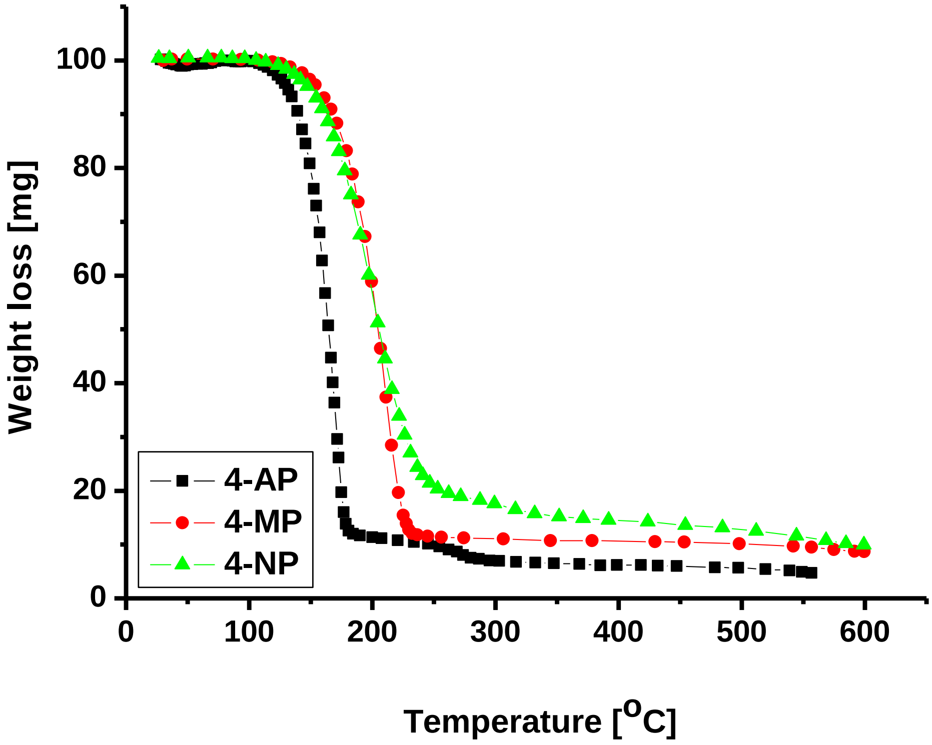


Figure 6. TGA diagrams [(BAENA)(4-AP)$_2$], [(BAENA)(4-MP)$_2$] and [(BAENA)(4-NP)$_2$] charge transfer complexes

The thermogram for the [(BAENA)(4-AP)$_2$], show two degradation steps at 430 and 600 k with a weight losses of 94%, dealing with a good agreement to the loss of two 4-AP and donor

(BAENA), respectively. The proposed degradation mechanism is as follows:

$[(BAENA)(4AP)_2] \rightarrow BAENA + 2(4\text{-}AP)$

The thermogram for $[(BAENA)(4\text{-}MP)_2]$, shows two decomposition steps at 390 and 560 k, with a weight losses of about 93%, respectively, correspond to the loss of two 4-MP and BAENA molecules, respectively, in a good agreement with the theoretical losses of 92%, respectively, the decomposition equation as follows:

$[(BAENA)(4\text{-}MP)_2] \rightarrow BAENA + 2(4\text{-}MP)$

The $[(BAENA)(4\text{-}NP)_2]$ CT complex show a two decomposition steps at 480 and 592 k which accompanied by a weight loss of 90% corresponds the loss of two molecules of 4-NP and BAENA, respectively . The following mechanism deduced the decomposition feature as follows:

$[(BAENA)(4\text{-}NP)_2] \rightarrow BAENA + 2(4\text{-}NP)$

The physical results (melting points of reactants and products are difference) clearly indicating that the reaction products seem newly compounds that have a chemical and physical behavior than reactants.

3.6. Kinetic study

The effective of the variety of para substituted position of phenolic acceptors on the stability of the resulted charge transfer complexes can be investigated kinetically using the Coats-Redfern method equation (6) [38].

Table 6. Kinetic thermodynamic data of $[(BAENA)(4\text{-}AP)_2]$, $[(BAENA)(4\text{-}MP)_2]$ and $[(BAENA)(4\text{-}NP)_2]$ charge transfer complexes

Complexes	T_{max}/K	ΔE $kJmol^{-1}$	ΔH $kJmol^{-1}$	ΔS $Jmol^{-1}K^{-1}$	ΔG $kJmol^{-1}$	r
$[(BAENA)(4\text{-}AP)_2]$	430	61	-36	-194	83	0.9876
$[(BAENA)(4\text{-}MP)_2]$	390	54	-33	-215	80	0.9989
$[(BAENA)(4\text{-}NP)_2]$	480	65	-40	-155	72	0.9972

The data are listed in Table 6 and Fig. 7. The thermodynamic data was applied on the first decomposition peak (430, 390 and 480 k for $[(BAENA)(4\text{-}AP)_2]$, $[(BAENA)(4\text{-}MP)_2]$ and $[(BAENA)(4\text{-}NP)_2]$ charge transfer complexes, respectively in each three charge transfer complexes.

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]=\ln\left(\frac{ZR}{\varphi E}\right)-\frac{E}{RT} \qquad (6)$$

Where α, and φ are the fraction of the sample decomposed at time t and the linear heating rate, respectively. R is the gas constant and E is the activation energy in kJ mol^{-1}.

A plot of $\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]$ against $1/T$ was found to be linear (Fig. 7) from the slope of which E, was calculated and Z (Arrhenius constant) can be deduced from the intercept.

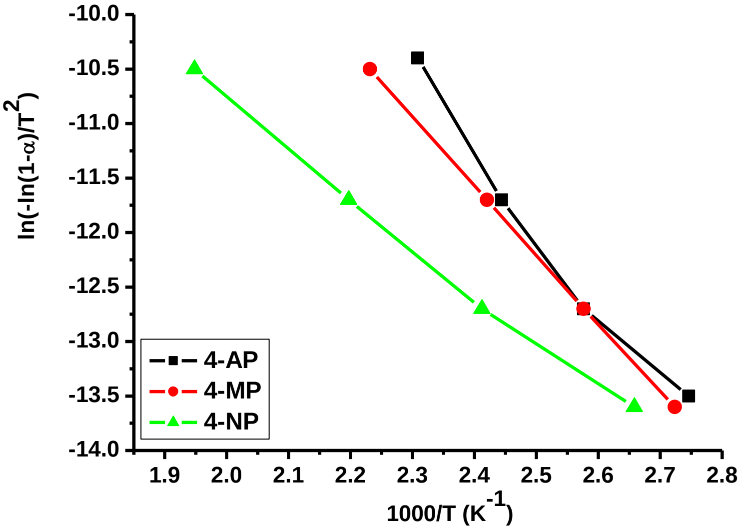


Figure 7. The kinetic thermodynamic diagrams of [(BAENA)(4-AP)$_2$], [(BAENA)(4-MP)$_2$] and [(BAENA)(4-NP)$_2$] charge transfer complexes using Coats-Redfern equation.

The enthalpy of activation, ΔH, and the free enthalpy of activation, ΔG, can be calculated (Table 6) via the equation 7;

$$\Delta H = E - RT_m \ ; \Delta G = \Delta H - T_m \Delta S \qquad (7)$$

Accordingly, the kinetic data in Table 6, all of the charge transfer complexes have −ve entropy, which indicates that activated complexes have more ordered systems than reactants. In Table 6, we found that the [(BAENA)(4-NP)$_2$] complex has a higher thermal stability than other two complexes, because of the 4-NP has an electron withdrawing group (nitro group) make more facility to liberated the proton of phenolic group to make strongly migrated to donor to forming hydrogen bond.

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