Arabian Journal of Chemistry (2011) 4, 83–97

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Spectroscopic characterizations on the N,N′-bis-alkyl derivatives of 1,4,6,8-naphthalenediimide charge-transfer complexes

Moamen S. Refat [a,b,*], Hamdy Al. Didamony [c], Khlood M. Abou El-Nour [d], Ivo Grabchev [e], Lamia El-Zayat [b], Abdel Majid A. Adam [a]

[a] *Department of Chemistry, Faculty of Science, Taif University, 888 Taif, Saudi Arabia*
[b] *Department of Chemistry, Faculty of Science, Port Said 42111, Port Said University, Egypt*
[c] *Department of Chemistry, Faculty of Science, Zagazig, Zagazig University, Egypt*
[d] *Department of Chemistry, Faculty of Science, Ismailia, Suez Canal University, Egypt*
[e] *Institute of Polymers, Bulgarian Academy of Science, 1113 Sofia, Bulgaria*

Received 17 June 2010; accepted 17 June 2010
Available online 25 June 2010

KEYWORDS

N,N′-bis-[2-hydroxyethyl)]-1,4,6,8-naphthalenediimide;
N,N′-bis-[2-N,N-dimethylaminoethyl)]-1,4,6,8-naphthalenediimide;
DDQ;
CHL;
TCNQ;
DCQ;
DBQ

Abstract Charge-transfer (CT) complexes formed from the reactions of two N,N′-bis-alkyl derivatives of 1,4,6,8-naphthalenediimide such as N,N′-bis-[2-hydroxyethyl]-1,4,6,8-naphthalenediimide (BHENDI) and N,N′-bis-[2-N,N-dimethylaminoethyl]-1,4,6,8-naphthalenediimide (BDMAE NDI) with DDQ, CHL, TCNQ, DCQ and DBQ as π-acceptors have been studied spectrophotometrically in chloroform and/or methanol at 25 °C. The photometric titration curves for the reactions indicated that the data obtained refer to 1:1 charge-transfer complexes of [(BHENDI)(DDQ)], [(BDMAENDI)(DDQ)], [(BHENDI)(CHL)], [(BDMAENDI)(CHL)], [(BHENDI)(TCNQ)], [(BDMAENDI)(TCNQ)], [(BHENDI)(DCQ)], [(BDMAENDI)(DCQ)], [(BHENDI)(DBQ)] and [(BDMAENDI)(DBQ)] were formed. Benesi–Hildebrand and its modification methods were applied to the determination of association constant (K), molar extinction coefficient (ε). The solid CT complexes have been synthesized and characterization by different spectral methods.

1. Introduction

In the recent few years N,N-bis-substituted-1,4,6,8-naphthalenediimides have been investigated intensively because of their promising applications. They can be used in solar energy collectors (Angadi et al., 1998), electronic and molecular devises (Lee et al., 1999; Andric et al., 2004), DNA sensors (Lee et al., 1999) or antibacterial agents (Gosztola et al., 2004; Takenaka et al., 2000) and photoactive materials (Yamashita

---

* Corresponding author at: Department of Chemistry, Faculty of Science, Taif University, 888 Taif, Saudi Arabia.
E-mail address: msrefat@yahoo.com (M.S. Refat).

1878-5352 Peer-review under responsibility of King Saud University.
doi:10.1016/j.arabjc.2010.06.024

Production and hosting by Elsevier

et al., 2002; Barros et al., 1997). The quenching effect on the fluorescence intensity of N,N-bis-substituted-1,4,6,8-naphthalendiimides have been investigated (Wiederrecht and Wasielievski, 1998; Alp et al., 2000). A systematic quantitative study of the solubility of various naphthalendiimides in organic solvents with different polarity has been investigated by means of UV–Vis spectroscopy (Usun et al., 2003).

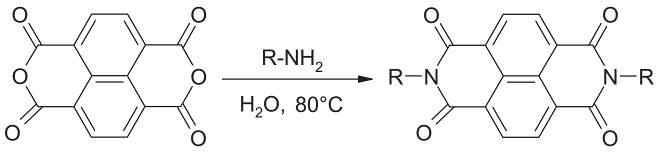
Charge-transfer complexes using organic species are intensively studied because of their special type of interaction, which is accompanied by transfer of an electron from the donor to the acceptor (Das et al., 2000; Jones and Jimenez, 1999). Also, protonation of the donor from acidic acceptors are generally rout for the formation of ion pair adducts (Smith et al., 2000, 1998, 1997).

Following our studies of charge-transfer complexes (Refat et al., 2006; Refat and El-Didamony, 2006; Refat et al., 2006a,b, 2007, 2008a,b; Refat et al., 2010-a, 2011), this work was undertaken to investigate spectrophotometrically the CT complexes formed between N,N′-bis-[2-hydroxyethyl)]-1,4,6,8-naphthalenediimide and N,N′-bis-[2-N,N-dimethylaminoethyl)]-1,4,6,8-naphthalenediimide as donor with DDQ, CHL, TCNQ, DCQ and DBQ as π-acceptors.

2. Materials and methods

2.1. Preparation of N,N′-bis-alkyl derivatives of 1,4,6,8-naphthalenediimide

All chemicals used throughout this work were Analar or extra pure grade. The synthesis of N,N′-bis-alkyl derivatives of 1,4,6,8-naphthalenediimide such as N,N′-bis-[2-hydroxyethyl)]-1,4,6,8-naphthalenediimide (BHENDI) and N,N′-bis-[2-N,N-dimethylaminoethyl)]-1,4,6,8-naphthalenediimide (BDMAENDI) was discussed (Lever, 1985) (Scheme 1). The synthesis route for obtaining 1,4,6,8-dicarboxnaphthalenes (BHENDI) and (BDMAENDI) were synthesized by condensation of 1,4,6,8-tetracarboxilic dianhydride (2.69 g, 0.01 mol) and 2-aminoethanol (1.9 ml, 0.04 mol) for (BHENDI) or 2-N,N-diethylethylamine (3.5 ml, 0.04 mol) for (BDMAENDI)



(Where R = CH_2CH_2OH for (BHENDI) and $CH_2CH_2N(CH_3)_2$ for (BDMAENDI))

Scheme 1 Synthesis of N,N′-bis-alkyl derivatives of 1,4,6,8-naphthalenediimide.

Table 1 CHN analysis and physical parameters data of N,N′-bis-alkyl-1,4,6,8-naphthalenediimide and their CT complexes.

Compounds (FW)	Mwt	Color	Mp (°C)	Elemental analysis[a]		
				%C	%H	%N
BHENDI	354.10	Light pink	321–323	(61.86)	(3.95)	(7.91)
$C_{18}H_{14}N_2O_6$				61.79	3.86	7.83
BDMAENDI	408.10	Yellow	279–281	(67.70)	(5.88)	(13.72)
$C_{22}H_{24}N_4O_4$				67.49	5.78	13.64
[(BHENDI)(DDQ)]	581.01	Dark violet	> 300	(53.70)	(2.41)	(9.63)
$C_{26}H_{14}N_4Cl_2O_8$				53.33	2.39	9.61
[(BDMAENDI)(DDQ)]	635.11	Red	301	(56.69)	(3.77)	(13.22)
$C_{30}H_{24}N_6Cl_2O_6$				56.57	3.65	12.98
[(BHENDI)(P-CHL)]	599.88	Brown	> 300	(48.01)	(2.33)	(4.66)
$C_{24}H_{14}N_2Cl_4O_8$				47.59	2.30	4.55
[(BDMAENDI)(P-CHL)]	653.98	Yellow	254	(51.37)	(3.67)	(8.56)
$C_{28}H_{24}N_4Cl_4O_6$				50.98	3.54	8.51
[(BHENDI)(TCNQ)]	558.19	Blue	> 300	(64.51)	(3.22)	(15.05)
$C_{30}H_{18}N_6O_6$				64.32	3.09	14.88
[(BDMAENDI)(TCNQ)]	612.29	Yellow	249	(66.66)	(4.57)	(18.30)
$C_{34}H_{28}N_8O_4$				66.31	4.50	18.11
[(BHENDI)(DCQ)]	654.45	Brown	245	(51.01)	(2.83)	(7.44)
$C_{24}H_{16}N_3Cl_3O_7$				50.42	2.80	7.35
[(BDMAENDI)(DCQ)]	618.55	Brown	229	(54.32)	(8.78)	(11.31)
$C_{28}H_{26}N_5Cl_3O_5$				54.09	8.74	10.98
[(BHENDI)(DBQ)]	653.37	Brown	239	(44.08)	(2.45)	(6.42)
$C_{24}H_{16}N_3Br_2O_7Cl$				43.55	2.35	6.34
[(BDMAENDI)(DBQ)]	707.47	Brown	228	(47.50)	(3.67)	(9.89)
$C_{28}H_{26}N_5Br_2O_5Cl$				47.36	3.56	9.77

[a] (Calculated) found.

in aqueous solution. The suspension was heated at 80 °C for 8 h. The precipitate was filtered and washed with acetone.

2.2. Preparation of N,N′-bis-alkyl derivatives of 1,4,6,8-naphthalenediimide-acceptor charge-transfer complexes (acceptor = DDQ, DCQ, DBQ, CHL and TCNQ)

The charge-transfer (CT) complexes formed from the reactions of two N,N′-bis-alkyl derivatives of 1,4,6,8-naphthalenediimide such as N,N′-bis-[2-hydroxyethyl)]-1,4,6,8-naphthalenediimide (BHENDI) and N,N′-bis-[2-N,N-dimethylaminoethyl)]-1,4,6,8-naphthalenediimide (BDMAENDI) with DDQ, DCQ, DBQ, CHL and TCNQ as π-acceptors as following.

2.2.1. [N,N′-bis-[2-hydroxyethyl]-1,4,6,8-naphthalenediimide]–DDQ, DCQ, DBQ, CHL and TCNQ complexes

The (1:1) charge-transfer complexes [(BHENDI)(DDQ)] (dark violet(, [(BHENDI)(DCQ)] (dark brown), [(BHENDI)(DBQ)] (dark brown), [(BHENDI)(CHL)] (brown) and [(BHENDI)-(TCNQ)] (blue) were prepared by mixing 1 mmol of the donor in chloroform (10) ml with 1 mmol of the each acceptors DDQ, DCQ, DBQ, CHL and TCNQ in the same solvent with constant stirring for about 30 min. The solutions were allowed to evaporate slowly at room temperature, the solids filtered and washed several times with little amounts of solvent, and dried under vacuum over anhydrous calcium chloride.

2.2.2. [N,N′-bis-[2-N,N-dimethylaminoethyl]-1,4,6,8-naphthalenediimide]–DDQ, DCQ, DBQ, CHL and TCNQ complexes

The (1:1) charge-transfer complexes [(BDMAENDI)(DDQ)] (red), [(BDMAENDI)(DCQ)] (brown), [(BDMAENDI)(DBQ)] (brown), [(BDMAENDI)(CHL)] (yellow) and [(BDMAENDI)-(TCNQ)] (yellow) were prepared by mixing 1 mmol of the donor in chloroform (10) ml with 1 mmol of the each acceptors DDQ, DCQ, DBQ, CHL and TCNQ in the same solvent with constant stirring for about 30 min. The solutions were allowed to evaporate slowly at room temperature, the solids filtered and washed several times with little amounts of solvent, and dried under vacuum over anhydrous calcium chloride.

3. Instrumentation and physical measurements

3.1. Electronic spectra

The electronic spectra of the donors, acceptors and the resulted CT complexes were recorded in the region of (200–800 nm) by using a Jenway 6405 Spectrophotometer with quartz cells, 1.0 cm path in length.

3.2. Photometric titration

Photometric titration was performed at 25 °C for the reactions of donors with acceptors in chloroform, as follow: the concentration of the donors in the reaction mixtures was kept fixed at 5.0×10^{-4} M, while the concentration of acceptors were changed over a wide range from $X \times 10^{-4}$ to $Y \times 10^{-4}$ M. These produced solutions with donor: acceptor molar ratios varying from 1:0.25 to 1:4.00.

IR measurements (KBr discs) of the solid donors, acceptor and CT complexes were carried out on a Bruker FT-IR

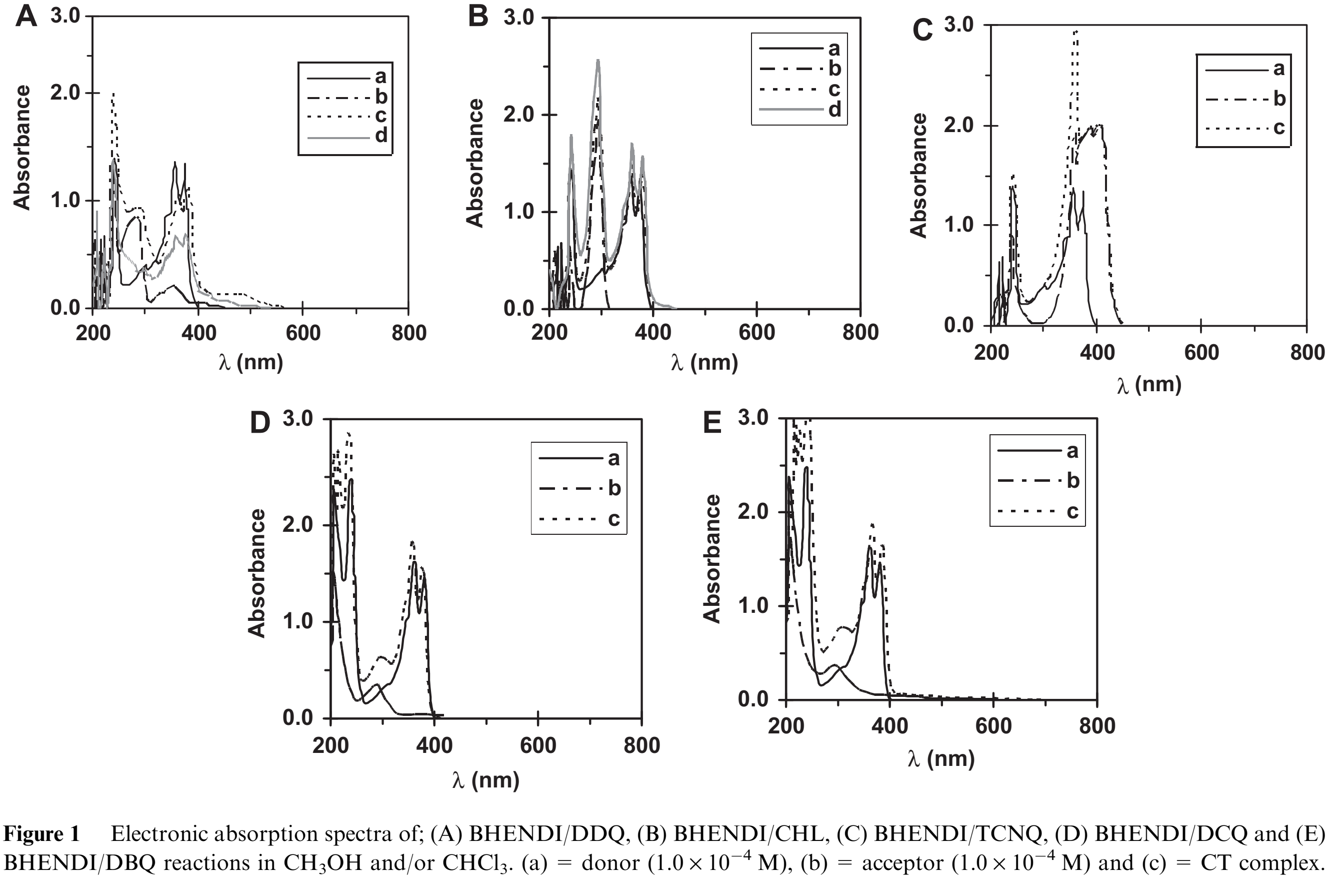


Figure 1 Electronic absorption spectra of; (A) BHENDI/DDQ, (B) BHENDI/CHL, (C) BHENDI/TCNQ, (D) BHENDI/DCQ and (E) BHENDI/DBQ reactions in CH_3OH and/or $CHCl_3$. (a) = donor (1.0×10^{-4} M), (b) = acceptor (1.0×10^{-4} M) and (c) = CT complex.

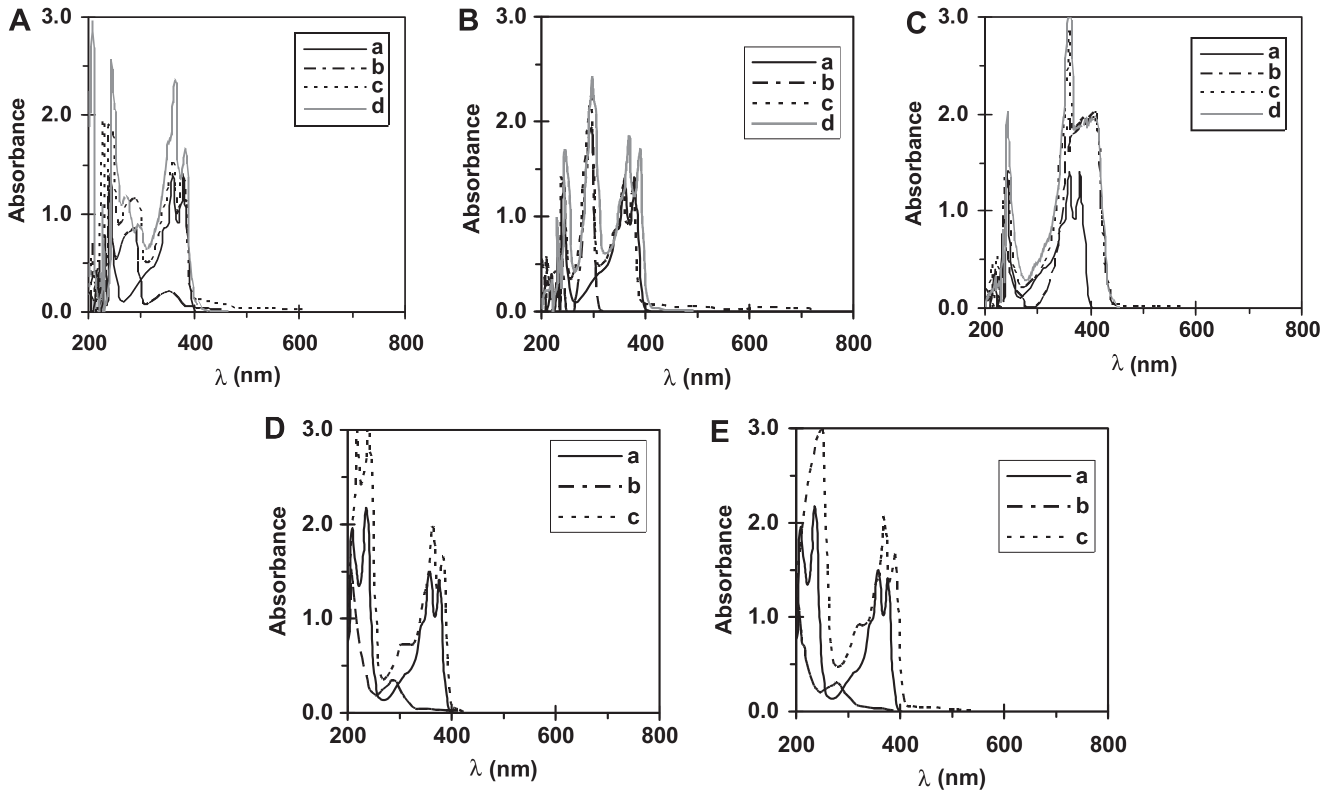


Figure 2 Electronic absorption spectra of: (A) BDMAENDI/DDQ, (B) BDMAENDI/CHL, (C) BDMAENDI/TCNQ, (D) BDMAENDI/DCQ and (E) BDMAENDI/DBQ reactions in CH_3OH and/or $CHCl_3$. (a) = donor (1.0×10^{-4} M), (b) = acceptor (1.0×10^{-4} M) and (c) = CT complex.

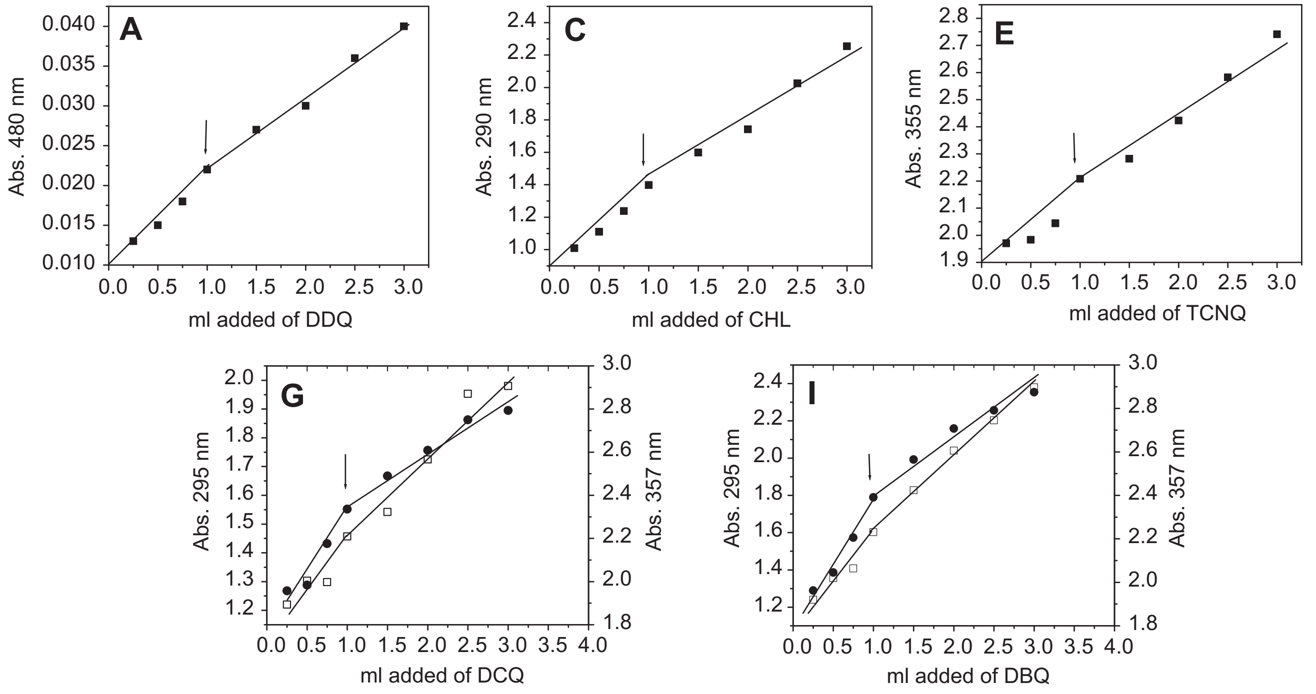


Figure 3 Photometric titration curves for: (A) BHENDI/DDQ, (C) BHENDI/CHL, (E) BHENDI/TCNQ, (G) BHENDI/DCQ and (I) BHENDI/DBQ systems.

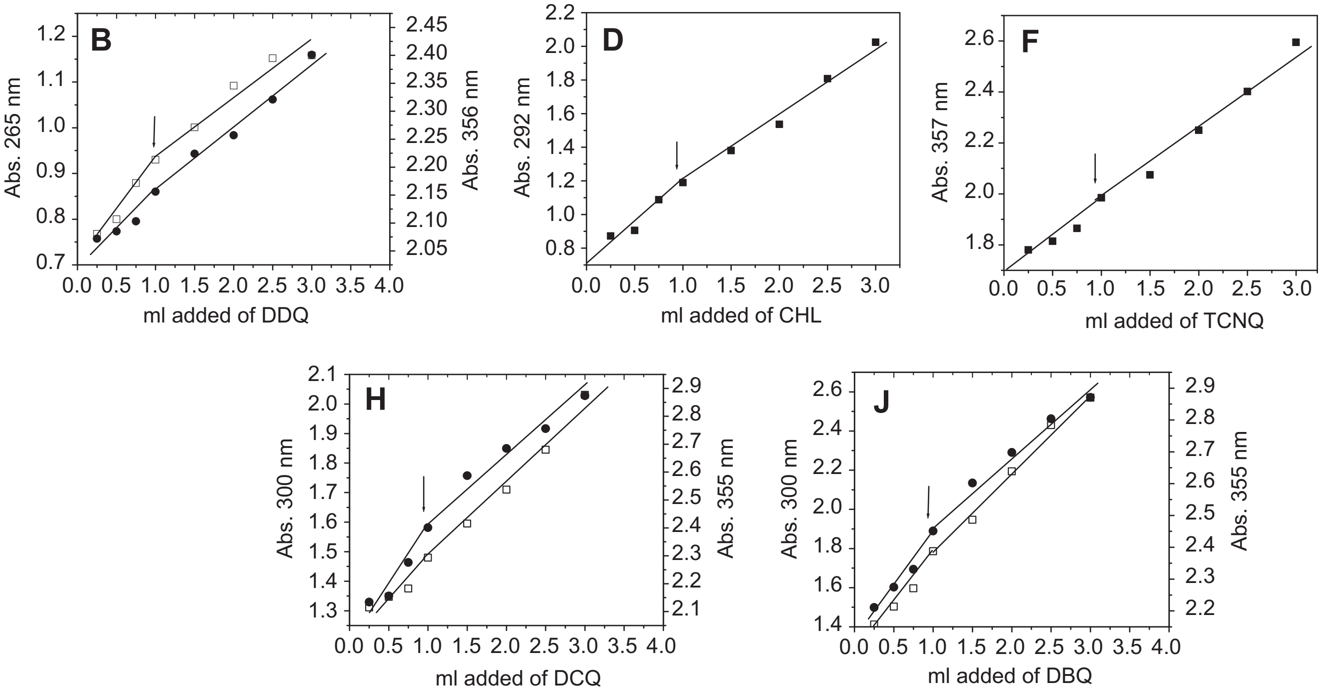


Figure 4 Photometric titration curves for: (B) BDMAENDI/DDQ, (D) BDMAENDI/CHL, (F) BDMAENDI/TCNQ, (H) BDMAENDI/DCQ and (J) BDMAENDI/DBQ systems.

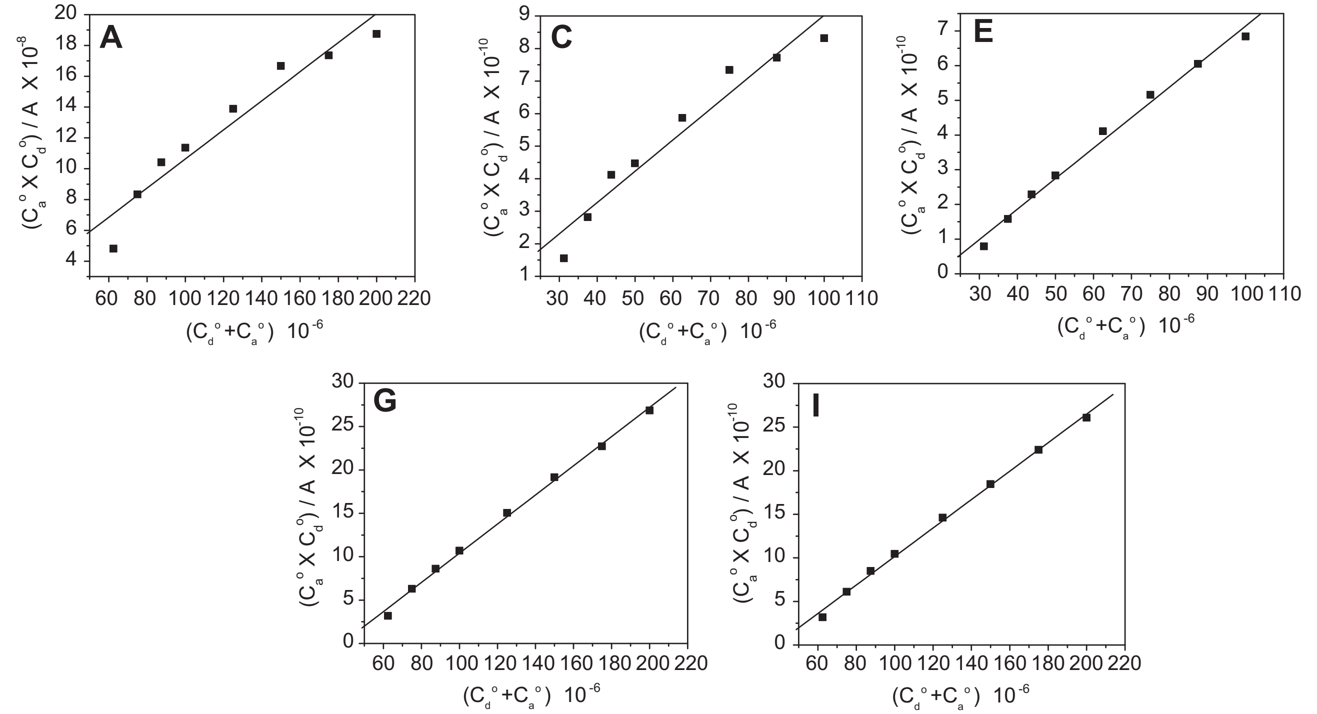


Figure 5 The plot of $(C_d^o + C_a^o)$ against $C_d^o \cdot C_a^o / A$ for the (A) BHENDI/DDQ, (C) BHENDI/CHL, (E) BHENDI/TCNQ, (G) BHENDI/DCQ and (I) BHENDI/DBQ systems.

spectrophotometer (400–4000 cm^{-1}). The compositions of the complexes were confirmed from mass spectra at 70 eV by using AEI MS 30 mass spectrometer. The thermal analysis (TGA&DTG) was carried under nitrogen atmosphere with a heating rate of 10 °C/min using a Shimadzu TGA-50H thermal analyzers.

4. Results and discussion

The elemental analysis and physical measurements data of the CT complexes formed [(BHENDI)(DDQ)], [(BDMAENDI)(DDQ)], [(BHENDI)(CHL)], [(BDMAENDI)(CHL)], [(BHENDI)(TCNQ)], [(BDMAENDI)(TCNQ)], [(BHENDI)

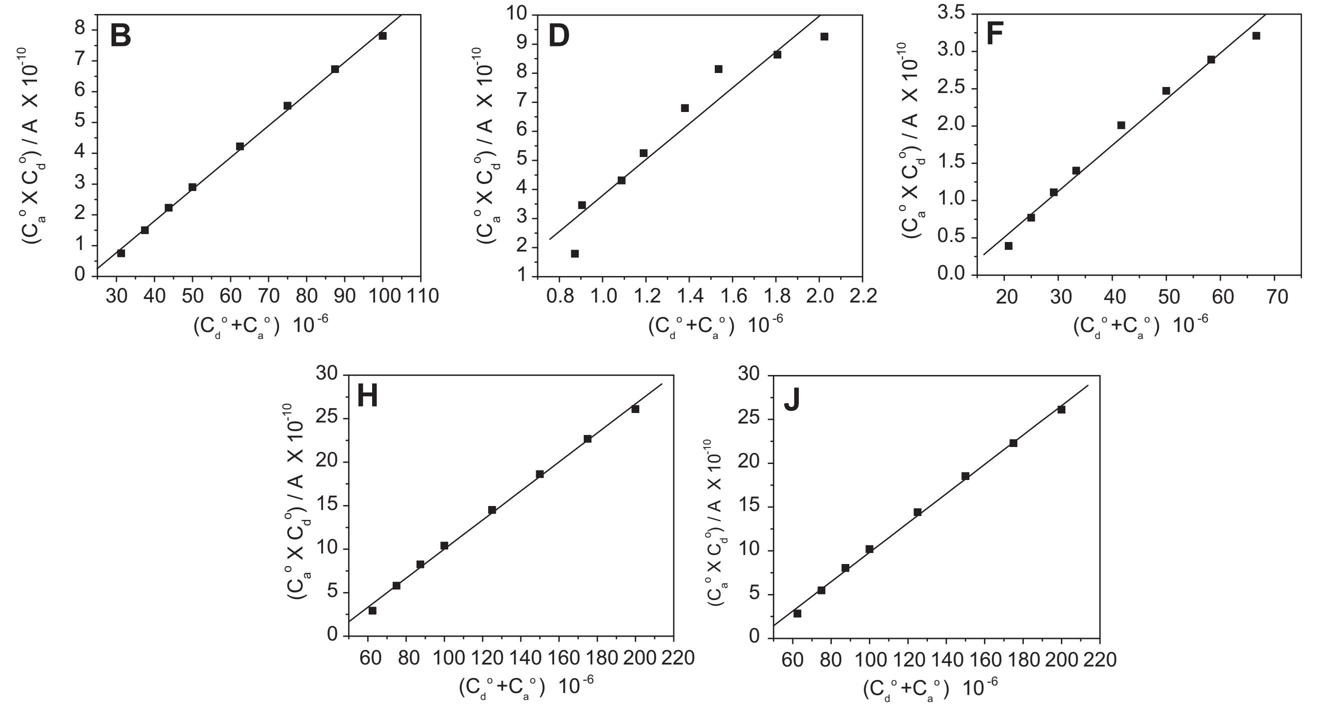


Figure 6 The plot of $(C_d^o + C_a^o)$ against $C_d^o \cdot C_a^o/A$ for the (B) BDMAENDI/DDQ, (D) BDMAENDI/CHL, (F) BDMAENDI/TCNQ, (H) BDMAENDI/DCQ and (J) BDMAENDI/DBQ systems.

(DCQ)], [(BDMAENDI)(DCQ)], [(BHENDI)(DBQ)] and [(BDMAENDI)(DBQ)] are listed in Table 1. All the reactions of (BHENDI) and (BDMAENDI) with DDQ, CHL and TCNQ were carried out in chloroform as a solvent except for the reactions of DCQ and DBQ with two N,N′-bis-alkyl derivatives of 1,4,6,8-naphthalenediimide donors were carried out in methanol. The N,N′-bis-alkyl derivatives of 1,4,6,8-naphthalenediimide charge-transfer complexes are stable in air, soluble in DMSO and DMF.

4.1. Electronic absorption spectra

The electronic absorption spectra of the reactants; donors N,N′-bis-alkyl derivatives of 1,4,6,8-naphthalenediimide (donor = (BHENDI) and (BDMAENDI) (1.0×10^{-4} M) and acceptors (DDQ, CHL, TCNQ, DCQ and DBQ) (1.0×10^{-4} M)) in $CHCl_3$ (in the case of DCQ and DBQ CT complexes, the CH_3OH was used) along with those of the formed 1:1 CT complexes are shown in Figs. 1 and 2A–E, respectively. The spectra demonstrate that the formed CT complexes show new absorption bands as follow; do not exist in the spectra of the reactants. These bands are attributed to charge-transfer complexes formation and can be assigned as follow:

(i) The spectra of the complex of the general formula [(BHENDI)(acceptor)] (acceptor = DDQ, CHL, TCNQ, DCQ and DBQ) show new bands at 480 nm for DDQ, 290 nm for CHL, 355 nm for TCNQ, 295 and 357 nm for DCQ and at 295 and 357 nm for DBQ complexes.

Table 2 Spectrophotometric results of the CT complexes of (A) [(BHENDI)(DDQ], (B) [(BDMAENDI)(DDQ)], (C) [(BHENDI)(CHL)], (D) [(BDMAENDI)(CHL)], (E) [(BHENDI)(TCNQ)], (F) [(BDMAENDI)(TCNQ)], (G) [(BHENDI)(DCQ)], (H) [(BDMAENDI)(DCQ)], (I) [(BHENDI)(DBQ)] and (J) [(BDMAENDI)(DBQ)] CT complexes.

CT complexes	λ (nm)	K (l mol^{-1})	ε (l mol^{-1} cm^{-1})	E (eV)	f	I_p	μ
A	480	7.980×10^4	10.58×10^2	2.59	0.714	6.93	0.766
B	356	4.440×10^4	9.700×10^4	3.49	1.05	7.56	89.00
C	290	16.72×10^4	10.41×10^4	4.28	1.20	8.11	83.20
D	292	2.590×10^6	16.19×10^2	4.25	1.75	8.09	10.40
E	355	5.320×10^4	11.37×10^4	3.50	1.23	7.56	96.20
F	357	8.500×10^4	16.20×10^4	3.48	1.25	7.55	97.40
G	357	2.620×10^4	5.940×10^4	3.48	0.642	7.55	69.80
H	355	2.490×10^4	5.990×10^4	3.50	0.404	7.56	55.20
I	357	2.640×10^4	6.120×10^4	3.48	0.802	7.55	78.00
J	355	2.410×10^4	5.970×10^4	3.50	0.645	7.56	21.60

(ii) The spectra of the [(BDMAENDI)(acceptor)] complexes show new bands at 265 and 356 nm for DDQ, 292 nm for CHL, 357 nm for TCNQ, 300 and 355 nm for DCQ and at 300 and 355 nm for DBQ complexes.

All of these CT bands do not exist in the spectra of both donor and acceptor or become shifted to red or blue wavelength, which indicate the formation of the charge-transfer complexes. The stoichiometry of the [(donor)(acceptor)] (donor = (BHENDI) and (BDMAENDI)) reactions were shown in all cases to be of ratio 1:1. This was concluded on the bases of the obtained elemental analysis data of the isolated solid CT complexes as indicated in the Table 1, as well as from the complexes infrared spectra, which indicate the existence of the bands characteristic for both the N,N′-bis-alkyl derivatives of 1,4,6,8-naphthalenediimide and the acceptors. The stoichiometry of 1:1 is also strongly supported by photometric titration measurements. These measurements were based on strong absorption bands at 480 nm for DDQ, 290 nm for CHL, 355 nm for TCNQ, (295 and 357 nm) for

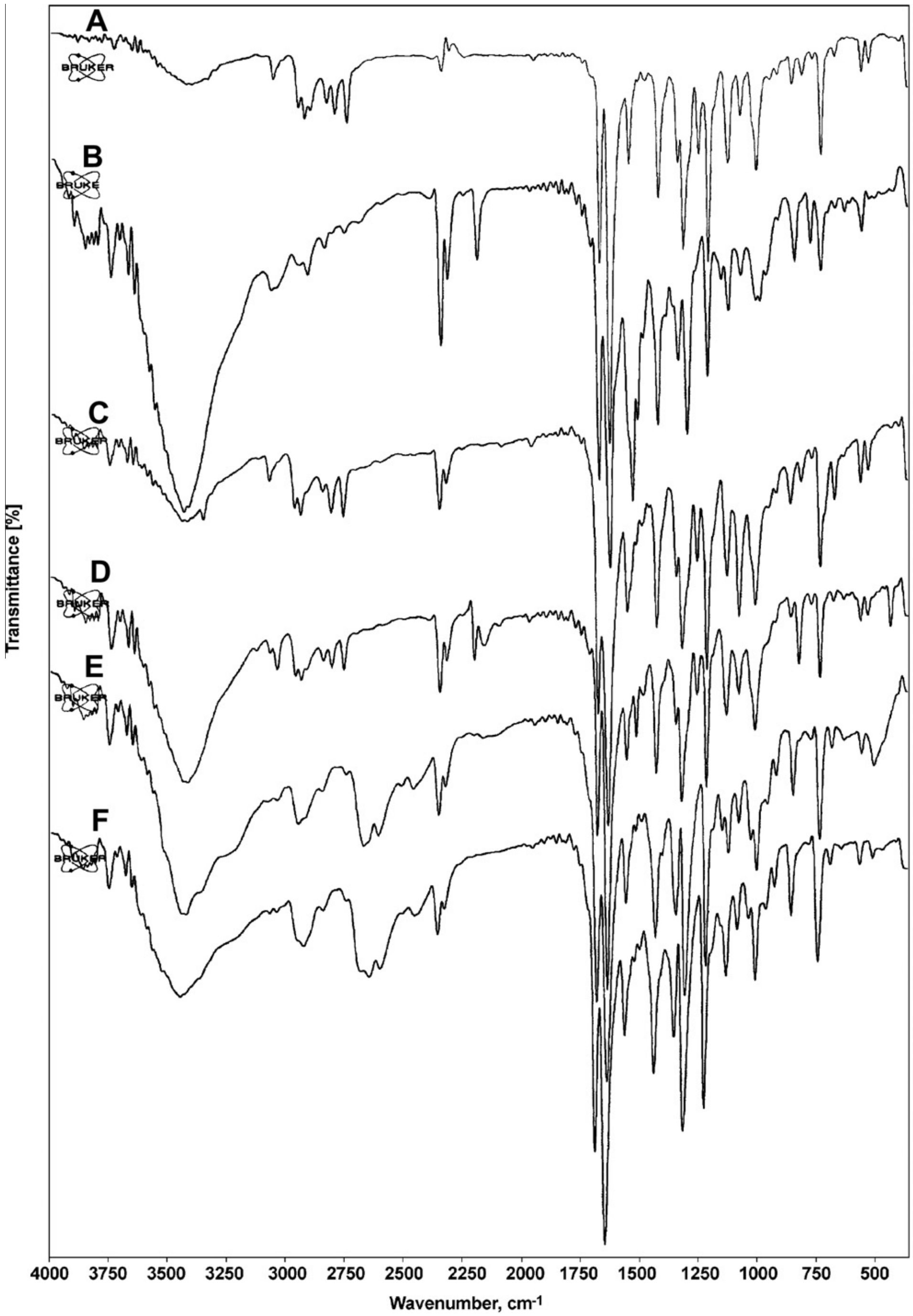


Figure 7 Infrared spectra of (A) BHENDI, (B) BHENDI/DDQ, (C) BHENDI/CHL, (D) BHENDI/TCNQ, (E) BHENDI/DCQ and (F) BHENDI/DBQ compounds.

DCQ and at 295 and 357 nm for DBQ in the general formula of [(BHENDI)(acceptor)] complexes and at (265 and 356 nm) for DDQ, 292 nm for CHL, 357 nm for TCNQ, (300 and 355 nm) for DCQ and at 300 and 355 nm for DBQ with the general formula [(BDMAENDI)(acceptor)] complexes.

In these measurements the concentration of donor was kept fixed at 0.25×10^{-4} M while the concentration of the acceptors was varied over the range of 0.0625×10^{-4}–0.750×10^{-4} M with respecting of [(BDMAENDI)(DDQ)], [(BHENDI)(CHL)], [(BDMAENDI)(CHL)] and [(BHENDI)(TCNQ)]. Concerning of [(BHENDI)(DDQ)], [(BHENDI)(DCQ)], [(BDMAENDI)(DCQ)], [(BHENDI)(DBQ)] and [(BDMAENDI)(DBQ)] charge-transfer complexes, the donor was kept fixed at 0.50×10^{-4} M while the concentration of the acceptors was varied over the range of 0.125×10^{-4}–1.500×10^{-4} M. Exceptional, the [(BDMAENDI)(TCNQ)] complex, the donor was kept fixed at

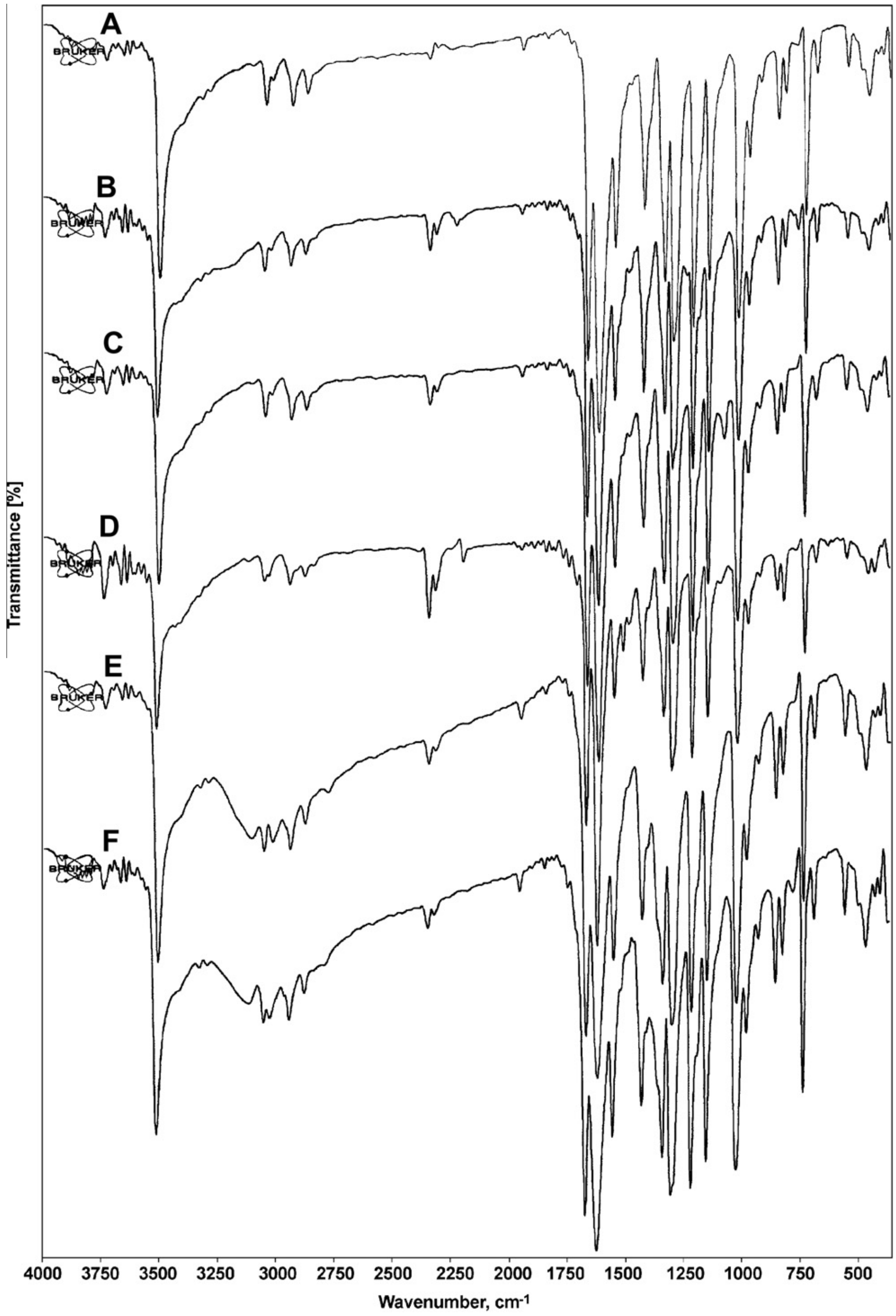


Figure 8 Infrared spectra of (A) BDMAENDI, (B) BDMAENDI/DDQ, (C) BDMAENDI/CHL, (D) BDMAENDI/TCNQ, (E) BDMAENDI/DCQ and (F) BDMAENDI/DBQ compounds.

0.1667×10^{-4} M while the concentration of the TCNQ acceptor was varied over the range of 0.0417×10^{-4}–0.500×10^{-4} M as described.

Photometric titration curves based on these measurements are shown in Figs. 3 and 4A–E. The donor–acceptors equivalence points indicate that the donors:acceptors molar ratio in all cases is 1:1 and this result agrees quite well with the elemental analysis and infrared spectra of the solid CT complexes. Accordingly, the formed CT complexes upon the reaction of (BHENDI) and (BDMAENDI) as donors with π-acceptors (DDQ, CHL, TCNQ, DCQ and DBQ) under investigation have the general formula [(donors)(acceptors)]. The 1:1 modified Benesi–Hildebrand equation (Skoog, 1985) was used in calculating the values of the equilibrium constant, K and the extinction coefficient, ε. The values C_a^o and C_d^o are the initial concentrations of the π-acceptors (DDQ, CHL, TCNQ, DCQ and DBQ) and the donors (BHENDI) and (BDMAENDI), respectively, while A is the absorbance at the CT bands. Plotting the values of the $C_a^o \cdot C_d^o / A$ against the $C_a^o + C_d^o$ values for each acceptor, a straight line is obtained with a slope of $1/\varepsilon$ and intercept of $1/K\varepsilon$ as shown in Figs. 5 and 6A–E. For the reactions of the two N,N′-bis-alkyl derivatives of 1,4,6,8-naphthalenediimide donors with (DDQ, CHL, TCNQ, DCQ and DBQ), the obtained values of both K and ε associated with these complexes are given in Table 2. These complexes show high values of both the formation constants (K) and the extinction coefficients (ε). These high values of K confirm the expected high stabilities of the formed CT complexes as a result of the expected high donation of the two N,N′-bis-alkyl derivatives of 1,4,6,8-naphthalenediimide donors; N,N′-bis-[2-hydroxyethyl)]-1,4,6,8-naphthalenediimide (BHENDI) and N,N′-bis-[2-N,N-dimethylaminoethyl)]-1,4,6,8-naphthalenediimide (BDMAENDI) which contains oxygen and nitrogen atoms as well as the aromatic rings. The values of the equilibrium constants are strongly dependent on the nature of the used acceptor but, there is clear relationships can be obtained

Table 3 Infrared frequencies[a] (cm^{-1}) and band assignments for (A) *BHENDI*, (B) [(*BHENDI*)(DDQ)], (C) [(*BHENDI*)(P-CHL)], (D) [(*BHENDI*)(TCNQ)], (E) [(*BHENDI*)(DCQ)] and (F) [(*BHENDI*)(DBQ)] compounds.

A	B	C	D	E	F	Assignments[b]
3424 br	3446 vs br	3424 br	3424 s br	3425 s br	3446 br	ν(O–H); BHENDI, and H_2O of KBr
		3356 w				
3080 ms	3076 m br	3080 ms	3050 m	–		ν_{as}(C–H); $CH_2 + CH_3$ ν(C–H); aromatic
2974 w	2925 w	2973 w	2972 w	2955 m	2928 m	ν(C=C); CH aromatic
2949 w	2924 w	2949 w	2972 w	2680 ms	2653 ms	ν_s(C–H); CH_2
2855 w	2854 w	2856 vw	2855 w	2619 w	2607 ms	
2821 ms	2770 w	2821 ms	2770 w			
2770 ms		2770 ms				
–	2213 ms	–	2221 w	–	–	ν(C=N); DDQ and TCNQ
			2181 w			
–	2730 vw	–	2700 vw	2681 m br	2653 m br	Hydrogen bonding
	2700 vw		2630 vw	2619 m	2607 m	
	2660 vw					
	2500 vw					
1702 s	1704 s	1701 s	1702 s	1702 s	1702 s	ν(C=O); donors, DDQ and P-chloranil
1658 vs	1660 vs	1657 vs	1658 vs	1658 vs	1660 vs	
1581 ms	1564 s	1579 s	1580 ms	1581 ms	1580 ms	ν(C=C); aromatic
1514 vw	1543 ms	1519 w	1541 m			
1456 s	1457 s	1455 s	1456 ms	1457 s	1456 s	δ(CH); CH def.
1375 w	1372 ms	1374 w	1374 w	1372 ms	1373 ms	δ(CH); aromatic
1350 s	1334 s	1348 s	1349 s	1333 vs	1333 vs	ν_{as}(CN)
1287 ms	1249 s	1287 ms	1287 ms	1246 vs	1246 vs	ν(C-O); C-OH
1244 s		1244 s	1245 s	1178	1155 m	
1163 ms		1161 ms	1162 ms	1153 ms		
1111 m	1191 w	1110 ms	1112 m	1110 m	1109 w	ν_s(CN)
1043 ms	1161 ms	1042 ms	1042 ms	1034 ms	1032 ms	
	1109 w					
	1029 ms					
986 vw	883 ms	956 vw	894 vw	953 w	989 vw	δ(CH); in-plan bend
957 vw	816 ms	896 vw	860 ms	882 ms	951 w	
895 w		851 vw	808 vw	808 vw	882 m	
852 w		809 vw				
808 vw						
771 s	773 ms	770 ms	770 ms	770 s	770 s	δ(CH); CH- rock
714 w		711 mw	714 vw	721 w	720 w	
602 mw	601 mw	601 mw	601 mw	596 m	596 mw	δ(CH); out-of-plan
571 mw	570mw	570 mw	570 mw	542 ms	540 w	
445 vw			474 m			
410 ms						

[a] br, broad; m, medium; s, strong; sh, shoulder; w, weak.

[b] ν, stretching; δ, bending.

Table 4 Infrared frequencies[a] (cm^{-1}) and band assignments for (A) *BDMAENDI*, (B) [(*BDMAENDI*)(DDQ)], (C) [(*BDMAENDI*)(P-CHL)], (D) [(*BDMAENDI*)(TCNQ)], (E) [(*BDMAENDI*)(DCQ)] and (F) [(*BDMAENDI*)(DBQ)] compounds.

A	B	C	D	E	F	Assignments[b]
3521 vs	3521 vs	3521 vs	3522 vs	3520 vs	3521vs	ν(O–H); BHENDI, and H_2O of KBr
3067 mw	3067 mw	3068 mw	3067 mw	3122 w	3128 br	ν_{as}(C–H); CH_2 + CH_3
				3068 mw	3066 mw	ν(C–H); aromatic
				3033 mw	3040 mw	
2956 mw	2957 mw	2957 mw	2957 mw	2956 mw	2956 mw	ν(C=C); CH aromatic
2892 w	2892 w	2893 w	2893 w	2892 w	2892 mw	ν_s(C–H); CH_2 + CH_3
–	2252 mw	–	2221 mw			ν(C=N); DDQ and TCNQ
–	–	–	–	–	–	Hydrogen bonding
1695 s	1691 s	1693 s	1694 s	1694 s	1694 s	ν(C=O); donors, DDQ and P-chloranil
1646 vs	1646 vs	1646 vs	1646 vs	1645 vs	1456 vs	
1578 s	1578 s	1577 s	1577 ms	1578 s	1577 s	ν(C=C); aromatic
			1541w			
1455 s	1454 s	1456 s	1456 ms	1455 s	1454 s	δ(CH); CH def.
1367 s	1367 s	1367 s	1367 ms	1368 s	1367 s	δ(CH); aromatic
1329 vs	1332 v s	1329 vs	1331 vs	1328 vs	1331 vs	ν_{as}(CN)
1245 vs	1245 vs	1245 vs	1245 vs	1244 vs	1245 vs	ν(C–O); C–OH
1178 vs	1178 vs	1178 vs	1178 s	1778 vs	1178 vs	
1052 vs	1051 vs	1052 vs	1052 vs	1052 vs	1052 vs	ν_s(CN)
1009 w	1009 w	1009 w	1009 w	1009 mw	1009 ms	
960 vw	960 vw	960 vw	886 w	960 w	959 w	δ(CH); in-plan bend
886 mw	887 mw	886 mw	858 mw	885 ms	886 ms	
856 w	856 w	856 w		856 m	856 m	
768 s	768 s	768 s	768 ms	767 s	767 vs	δ(CH); CH-rock
722 w	772 w	720 w	772 w	721 m	721 m	
590 w	591 w	590 w	591 w	590 m	590 m	δ(CH); out-of-plan
502 m	502 m	502 m	501 w	501 m	501 m	
463 vw	462 vw	442 vw	473 w	462 vw	462 vw	
410 ms	410 ms	410 ms	410 ms		410 ms	

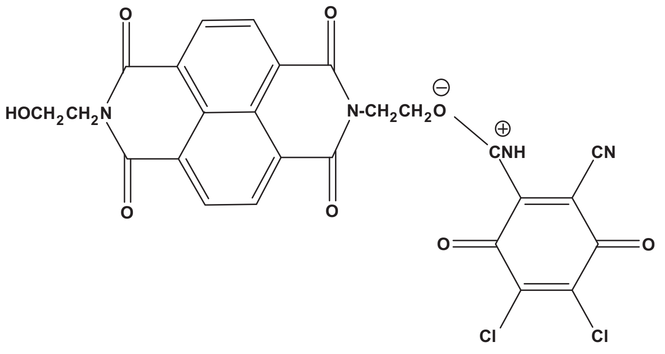
[a] br, broad; m, medium; s, strong; sh, shoulder; w, weak.
[b] ν, stretching; δ, bending.

between the *K* values and the electron withdrawing substituents to it such as cyano and halo groups. Furthermore, the all systems were also measured spectrophotometrically after 24 h to get an idea about the stability of the donor/acceptor systems in solution manner.

From Figs. 5 and 6, the values of (ε), (*K*), oscillator strength (*f*), which is dimensionless quantity, used to express the transition probability of the CT band and the transition dipole moment (μ) (Lever, 1985; Tsubomura and Lang, 1964; Aloisi and Pignataro, 1973; Foster, 1969; Kinoshita, 1962; Haynes, 2010–2011) of the CT complexes are evaluated and listed in Table 2. The dissociation energy (*W*) (Haynes, 2010–2011) can be calculated from the corresponding CT energy E_{CT}, ionization potential of the donor (I_p) and electron affinity of the acceptor (E_A). The energy of the $\pi-\pi^*$ interaction (E_{CT}) is calculated. Where λ_{CT} is the wavelength of the CT band of the complexes.

4.2. Infrared spectra

The infrared spectra of BHENDI, BDMAENDI and the formed CT complexes, [(BHENDI)(π-acceptors)] and [(BDMAENDI)(π-acceptors)] (where π-acceptors = DDQ, CHL, TCNQ, DCQ and DBQ) were recorded from KBr discs. These spectra are shown in Figs. 7A–E and 8A–E, respectively. The spectral bands are detected and assigned into their vibrational modes and given in Tables 3 and 4. The presence of the essential of

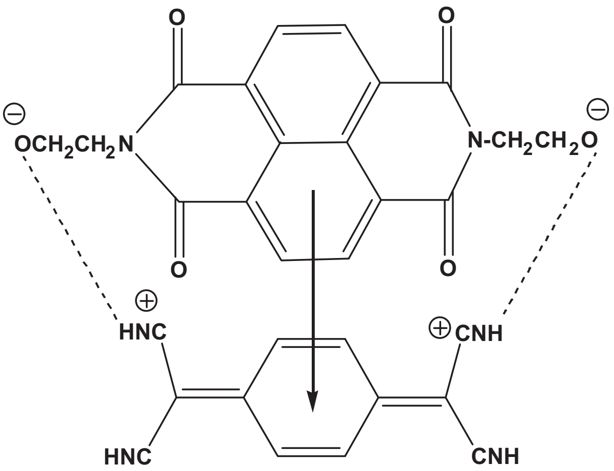


Scheme 2 Structure of [(BHENDI)(DDQ)] CT complex.

stretching and bending infrared bands of the (BHENDI), (BDMAENDI) donors and acceptors (DDQ, CHL, TCNQ, DCQ and DBQ) in the resulted CT complexes spectra strongly support the formation of CT complexation. It is clearly obviously that finding small sifts in both wavenumber values and the intensities of bands in comparison between the reactants and the CT complexes were formed. This fact is due to the structure configurations upon the complexation. For example:

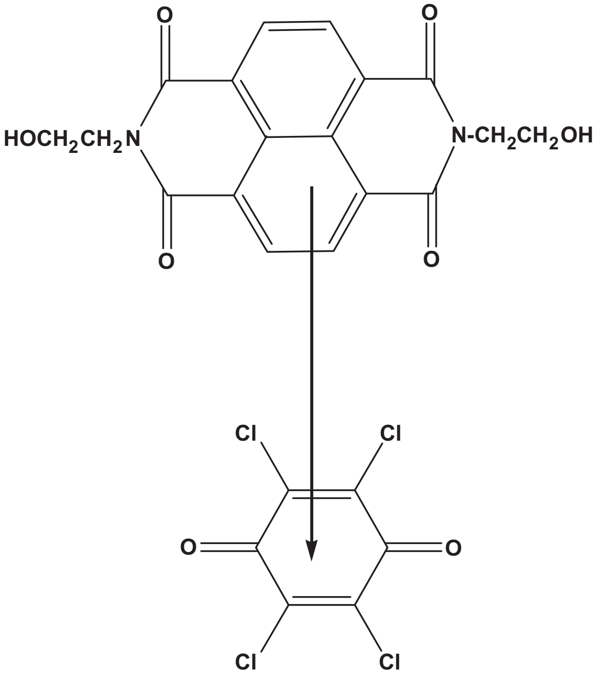
(i) As expected, the bands characteristic for the (BHENDI) donor in [(BHENDI)(DDQ)] CT complex are shown with small changes in band intensities and frequency values. For example, the ν(O–H) vibration occur at 3424 cm^{-1} for free donor (Bellamy, 1975) is shifted to 3446 cm^{-1} with very strong broadening in the IR spectrum of the CT complex. The vibration frequency of the C≡N group for DDQ observed at 2250 ad 2231 cm^{-1} is shifted to 2213 cm^{-1} in the charge-transfer complex. The other observation is the shifted in the ν(C=C); aromatic from 1581 cm^{-1} in the free donor toward blue shift at 1564 cm^{-1}. From the three mentioned items, we can be concluded that, the charge-transfer complexation occurs through the interaction between one of the hydroxyl groups of the donor and one of the cyano groups of the DDQ acceptor (Scheme 2).

(ii) In the infrared spectrum of [(BHENDI)(DDQ)] CT complex, the spectrum of the CT complex did not exhibit any new bands indicating that no chemical reaction occurred, other than electron transfer ($\pi-\pi^*$) from the BHENDI to CHL (Scheme 3). This suggestion is supported by the change in the intensities of the characteristic bands of aromatic rings.

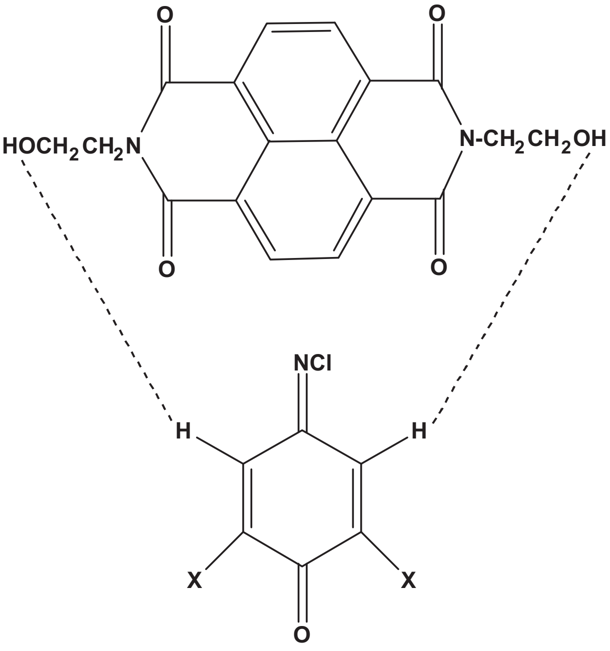


Scheme 4 Structure of [(BHENDI)(TCNQ)] CT complex.

(iii) In the case of [(BHENDI)(TCNQ)] CT complex, the IR spectrum of TCNQ shows strong bands at 2220, 1540 and 860 cm^{-1} corresponding to ν(C≡N) (Bellamy, 1975), aromatic ν(C=C) and 1,4-disubstituted benzene stretching, respectively (Fig. 6). These bands were shifted in the spectrum of the CT complex with the investigated compound to 2221, 2181, 1580, 1541, 1511, 894, 859 and 808 cm^{-1}. TCNQ is a π-acceptor and (BHENDI) is a rich donor that, this is contain nitrogen, oxygen and conjugated system with two aromatic groups. So CT complexes can be formed with this florescence dye. Molar ratio of the reactants in the CT complex was determined by molar ratio method and it was found to be 1:1 for studied donor with TCNQ. This



Scheme 3 Structure of [(BHENDI)(CHL)] CT complex.

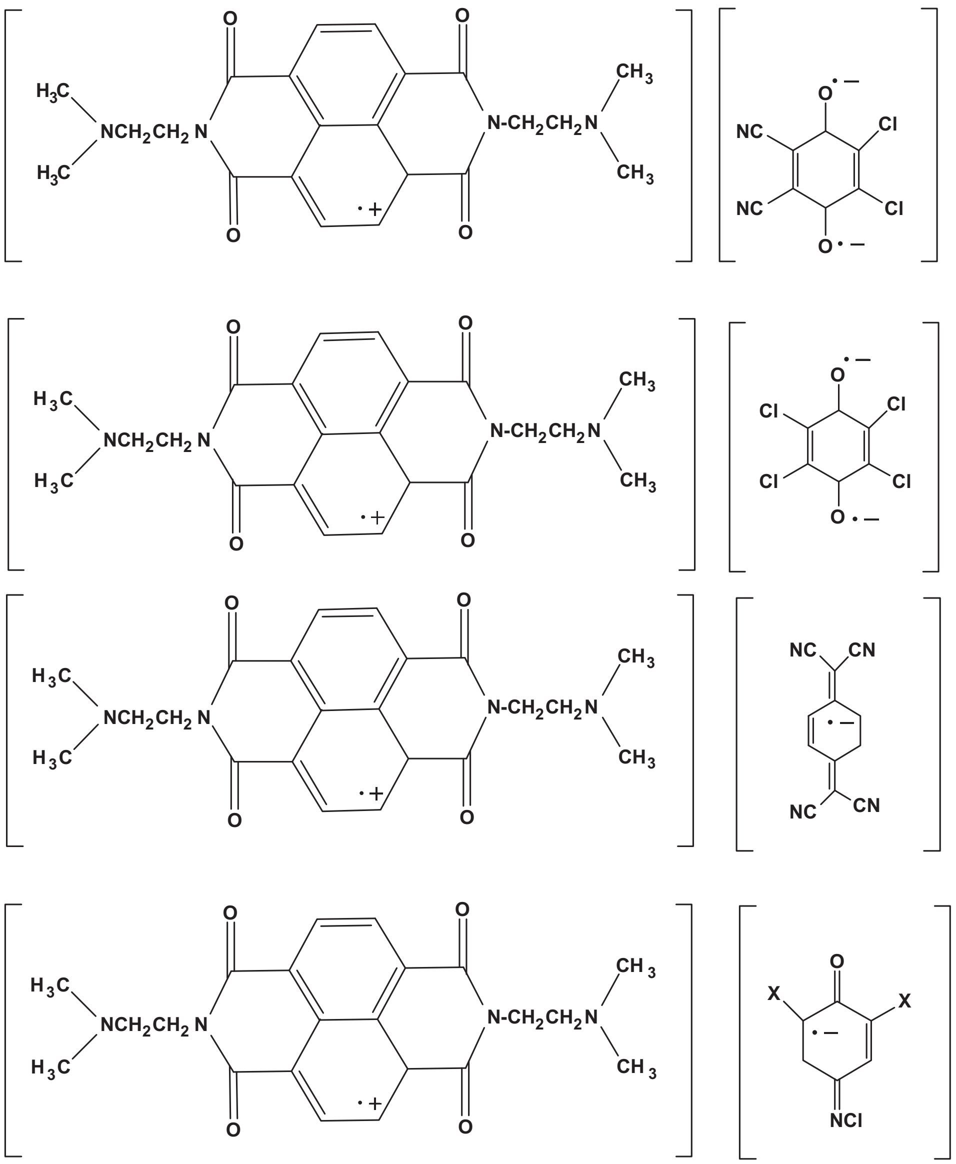


Scheme 5 Structures of [(BHENDI)(DCQ)] and [(BHENDI)(DBQ)] CT complexes (where X = Cl and Br in case of DCQ and DBQ, respectively).

ratio may be due to the presence of the steric hindrance. The nitrogen atoms have lower electron density, but aromatic rings and hydroxyl groups in the (BHENDI) have more electron density and less sterically hindered. So n–π* and $\pi-\pi$* CT complexes were formed (Scheme 4).

(iv) If we examine the acceptors (DCQ) and (DCQ) we find out that two withdrawing halo groups in the para and ortho position, respectively, are relative to the 3H and 5H. These withdrawing groups give facility to liberate the protons in position 3H and 5H to make intermediate hydrogen bond with the lone pair of electron on the oxygen atoms for the two hydroxyl groups of BHENDI. The electron density around protons depends on the degree of electro negativity for atoms attached with protons; therefore, the withdrawing groups make decreasing in the electron density around protons. So the chemical transfer for these protons is higher than that of the protons attached to the atom that have a lesser electron negativity. This was supported by the elemental analysis, the photometric titration which make confirm that the ratio occurs by 1:1 (donor:acceptor) and infrared spectra which shows the appearance two peaks for hydrogen bond (Bellamy, 1975) at 2681 and 2619 cm^{-1} for [(BHENDI)(DCQ)] and at 2653 and 2607 cm^{-1} for [(BHENDI)(DBQ)] (Scheme 5).

(v) Even though the IR spectra of the isolated solid complexes formed from the interactions of (BDMAENDI) with DDQ, CHL, TCNQ, DCQ and DBQ are presented in Fig. 7 and Table 4. However, the bands of the donor and acceptors in these complexes reveals small shifts in both band intensities and wavenumber values from those of the free molecules. This is normal due to the expected symmetry and electronic structure changes upon complexation. For example, the $\nu(\text{C}\equiv\text{N})$ vibrations are observed as a very strong at 2220 cm^{-1} in the spectrum of free TCNQ and at doublet at 2250 and 2231 cm^{-1} with medium strong bands for free DDQ. These vibrations occur at single medium weak band at



Scheme 6 Structures of [(BDMAENDI)(π-acceptors)] complexes (where π-acceptors are DDQ, CHL, TCNQ, DCQ and DBQ).

2252 and 2220 cm^{-1} in the spectra of the corresponding [(BDMAENDI)(DDQ)] and [(BDMAENDI)(TCNQ)], respectively. The interaction between the donor and acceptor gave $\pi-\pi^*$ transitions by forming of radical ion pairs, such as donors form radical cation and acceptors form radical ions as shown in Scheme 6.

4.3. Mass spectra

The compositions of the [(BHENDI)(DDQ)], [(BHENDI)(CHL)] and [(BDMAENDI)(TCNQ)] CT complexes were confirmed using mass spectra at 70 eV by using AEI MS 30 mass spectrometer. Interestingly, the exhibited of both molecular ion peaks of donors and the acceptors (DDQ, CHL and TCNQ) at 354 and 227 u for the BHENDI and DDQ; at 354 and 249 u for the BHENDI and CHL and at 408 and 204 u for BDMAENDI and TCNQ, respectively. The presence of both peaks of donors and acceptor are strongly supported the formation of charge-transfer complexes. The other peaks may correspond to various fragments for complexes. The intensity of these peaks gives an idea of the stability of these fragments.

4.4. Thermal investigations

The [(BDMAENDI)(DCQ)] and [(BDMAENDI)(DBQ)] complexes were studied by thermogravimetric analysis from ambient temperature to 600 °C in nitrogen atmosphere. The TG curves were redrawn as % mass loss vs. temperature (TG) curves. Typical TG curves are presented in Fig. 9, and the temperature ranges and percentage mass losses of the decomposition reaction together with evolved moiety and the theoretical percentage mass losses were discussed below.

Thermal analysis curves of the [(BDMAENDI)(DCQ)] and [(BDMAENDI)(DBQ)] CT complexes show that decomposition takes places in four stages in temperature range 398–873 K for [(BDMAENDI)(DCQ)] complex and in between 423 and 873 K for [(BDMAENDI)(DBQ)] CT complex (Fig. 9A and B), respectively. The four endothermic decomposition stages correspond to decomposition of the donor and the acceptors. The TG curves of the two CT complexes show a weight losses (Found 51.70%, Calcd. 51.50% for

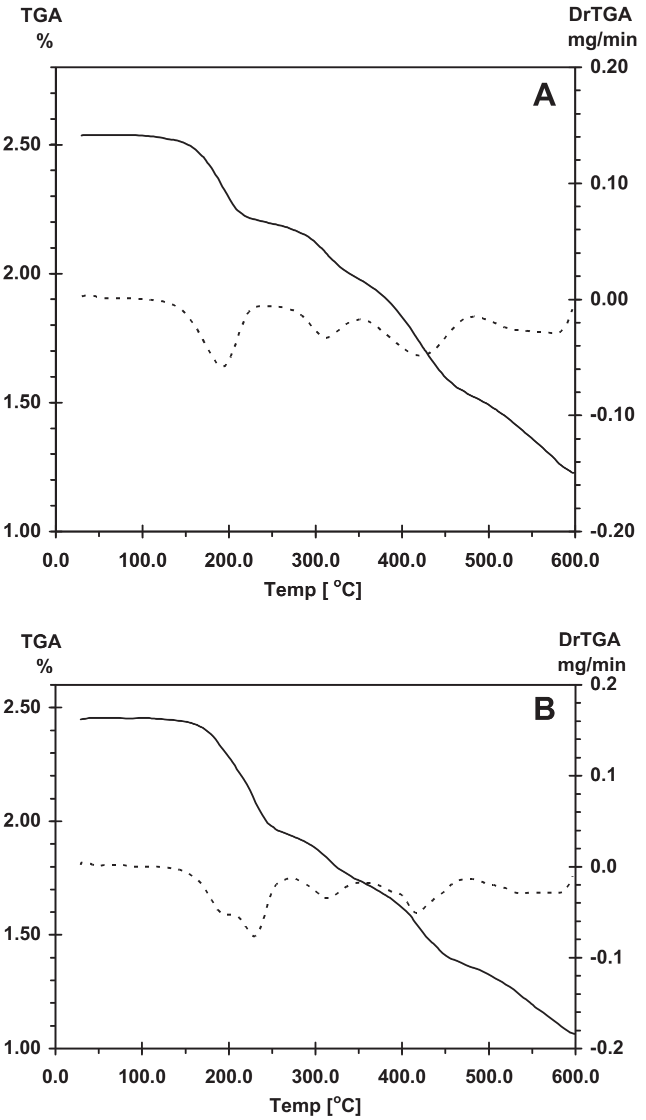


Figure 9 TGA/DTG curves of: (A) [(BDMAENDI)(DCQ)] and (B) [(BDMAENDI)(DBQ)] CT complexes.

Table 5 Kinetic parameters using the Coats–Redfern (CR) and Horowitz–Metzger (HM) operated for (A) [(BDMAENDI)(DCQ)] and (B) [(BDMAENDI)(DBQ)] CT complexes.

Complex	Stage	Method	Parameter					r
			E (J^{-1})	A (s^{-1})	ΔS (J mol^{-1} K^{-1})	ΔH (J mol^{-1})	ΔG (J mol^{-1})	
A	1st	CR	9.01×10^4	1.45×10^8	-9.24×10^1	8.62×10^4	1.29×10^5	0.9967
		HM	9.56×10^4	6.02×10^8	-8.06×10^1	9.17×10^4	1.29×10^5	0.9998
		Average	9.28×10^4	3.73×10^8	-8.65×10^1	8.89×10^4	1.29×10^5	
	2nd	CR	1.14×10^5	7.50×10^7	-9.88×10^1	1.09×10^5	1.68×10^5	0.9921
		HM	1.24×10^5	1.14×10^9	-7.72×10^1	1.19×10^5	1.65×10^5	0.9953
		Average	1.19×10^5	6.07×10^8	-8.8×10^1	1.14×10^5	1.66×10^5	
B	1st	CR	1.32×10^5	1.08×10^{13}	-8.0×10^{-1}	1.28×10^5	1.27×10^5	0.9951
		HM	1.39×10^5	6.64×10^{13}	-1.59×10^1	1.35×10^5	1.28×10^5	0.9981
		Average	1.35×10^5	3.86×10^{13}	-4.49	1.31×10^5	1.27×10^5	
	2nd	CR	1.41×10^5	4.69×10^{12}	-6.71	1.37×10^5	1.4×10^5	0.9996
		HM	1.54×10^5	1.68×10^{14}	-2.3×10^1	1.5×10^5	1.38×10^5	0.99903
		Average	1.47×10^5	8.63×10^{13}	-1.48×10^1	1.43×10^5	1.39×10^5	

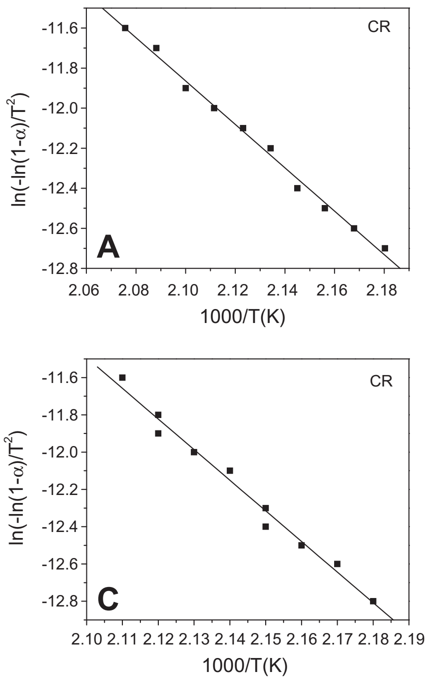


Figure 10 Kinetic diagrams of Coats–Redfern (CR) and Horowitz–Metzger (HM) equations for: (A and B) [(BDMAENDI)(DCQ)] and (C and D) [(BDMAENDI)(DBQ)] CT complexes.

[(BDMAENDI)(DCQ)] complex and Found 56.92%, Calcd. 57.60% for [(BDMAENDI)(DBQ)] complex) corresponding to the loss of ($C_3H_{26}N_5Cl_3O_5$) and ($C_3H_{26}N_5Br_2O_5Cl$) for [(BDMAENDI)(DCQ)] and [(BDMAENDI)(DBQ)] CT complexes, respectively. The final products, formed at 873 K, consist of black residual of carbon atoms because of limited oxygen for both the two charge-transfer complexes. Reported data on thermal analysis studies were collected in nitrogen atmosphere media.

4.5. Kinetic studies

In order to study the influence of the DCQ and DBQ as acceptors on the formation of charge-transfer complexes with N,N′-bis-[2-N,N-dimethylaminoethyl)]-1,4,6,8-naphthalenediimide (BDMAENDI) and the thermal stability behavior of the resulted CT complexes. This investigated were carried out kinetically using the Coats–Redfern and Horowitz–Metzger equations (Coats and Redfern, 1964; Horowitz and Metzger, 1963). The results are listed in Table 5, and shown in Fig. 10. The calculating of thermodynamic data applied on the first decomposition peak at around (DTG_{max} = 467 K) in both CT complexes. Accordingly, the kinetic data in Table 5, all of the CT complexes have negative entropy, which indicates that activated complexes have more ordered systems than reactants.

References

Aloisi, G.G., Pignataro, S., 1973. J. Chem. Soc. Faraday Trans. 69, 534.

Alp, S., Erten, S., Karapirem, C., Koz, B., Doroshenko, A., Icli, S., 2000. J. Photochem. Photobiol. A Chem. 135, 103.

Andric, G., Boas, J., Bond, A., Fallon, G., Ghiggino, K., Hogan, C., Hutchison, J., Lee, M., Langford, S., Pilbrow, J., Troup, G., Woodwar, C., 2004. Aust. J. Chem. 57, 1011.

Angadi, M., Gosztola, D., Wasielievski, M., 1998. J. Appl. Phys. 118, 6187.

Barros, T., Brochsztain, S., Troskano, V., Filho, P.B., Politi, M.J., 1997. J. Photochem. Photobiol. A Chem. 111, 97.

Bellamy, L.J., 1975. The Infrared Spectra of Complex Molecules. Chapman & Hall, London.

Coats, A.W., Redfern, J.P., 1964. Nature 201, 68.

Das, S.K., Krishnamoorthy, G., Dofra, S.K., 2000. Can. J. Chem. 78, 191.

Foster, R., 1969. Organic Charge Transfer Complexes. Academic Press, London.

Gosztola, D., Niemezyk, P., Svek, W., Lukas, A., Wasielievski, M., 2004. J. Phys. Chem. A 104, 6545.

Haynes, W.M., 2010–2011. Hand Book of Chemistry and Physics, 91st ed., CRC Press.

Horowitz, H.W., Metzger, G., 1963. Anal. Chem. 35, 1464.

Jones, G., Jimenez, J.A.C., 1999. Tetrahedron Lett. 40, 8551.

Kinoshita, M., 1962. Bull. Chem. Soc. Jpn. 1609.

Lee, S., Zu, Y., Hermann, A., Geerts, Y., Mullen, K., Bard, A., 1999. J. Am. Chem. Soc. 121, 3513.

Lever, A.B.P., 1985. Inorganic Electronic Spectroscopy, second ed. Elsevier, Amsterdam, p. 161.

Refat, M.S., El-Didamony, A.M., 2006. Spectrochim. Acta Part A 65 (3–4), 732.

Refat, M.S., Sadeek, S.A., Khater, H.M., 2006. Spectrochim. Acta Part A 64 (3), 778.

Refat, M.S., Grabchev, I., Chovelon, J.-M., Ivanova, G., 2006a. Spectrochim. Acta Part A 64 (2), 435.

Refat, M.S., Al-Didamony Ahmed, H., El-Zayat, L.A., 2006b. Can. J. Anal. Sci. Spectrosc. 51 (3), 147.

Refat, M.S., Killa, H.M.A., Grabchev, I., El-Sayed, M.Y., 2007. Spectrochim. Acta Part A 68 (1), 123.

Refat, M.S., El-Zayat, L.A., Yeşilel, Okan Zafer, 2008a. Polyhedron 27 (2), 475.

Refat, M.S., Ahmed, H.A., Grabchev, Ivo, El-Zayat, L.A., 2008b. Spectrochim. Acta 70 (4), 907.

Refat, M.S., El-Zayat, L.A., Yeşilel, Okan Zafer, 2010-a. Spectrochim. Acta Part A 75 (2), 745.

Refat, M.S., Didamony, Hamdy Al., El-Nour, Khlood M. Abou, Grabchev, Ivo, El-Zayat, Lamia, 2011. Arabian J. Chem. 4 105.

Skoog, D.A., 1985. Principle of Instrumental Analysis, third ed. Saunders College Publishing, New York, USA (Chapter 7).

Smith, G., Lynch, D.E., Byriel, K.A., Kennard, C.H.L., 1997. J. Chem. Crystallogr. 27, 307.

Smith, G., Lynch, D.E., Bott, R.C., 1998. Aust. J. Chem. 51, 159.

Smith, G., Bott, R.C., Rae, A.D., Willis, A.C., 2000. Aust. J. Chem. 53, 531.

Takenaka, S., Yamashita, K., Takagi, M., Uno, Y., Kondo, H., 2000. Anal. Chem. 72, 1334.

Tsubomura, H., Lang, R.P., 1964. J. Am. Chem. Soc. 86, 3930.

Usun, D., Ozser, M., Yunes, K., Icil, H., Demuth, M., 2003. J. Photochem. Photobiol. A Chem. 156, 45.

Wiederrecht, G., Wasielievski, M., 1998. J. Am. Chem. Soc. 120, 3231.

Yamashita, K., Takagi, M., Kondo, H., Takenaka, S., 2002. Anal. Biochem. 306, 188.