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Proton transfer complexes based on some π -acceptors having acidic protons with 3-amino-6-[2-(2-thienyl)vinyl]-1,2,4-triazin-5(4H)-one donor: Synthesis and spectroscopic characterizations

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ABSTRACT

Charge transfer complexes based on 3-amino-6-[2-(2-thienyl)vinyl]-1,2,4-triazin-5(4H)-one (ArNH₂) organic basic donor and pi-acceptors having acidic protons such as picric acid (PiA), hydroquinone (Q(OH)₂) and 3,5-dinitrobenzene (DNB) have been synthesized and spectroscopically studied. The $-NH_{2}^{+}$ ammonium ion was formed under the acid-base theory through proton transfer from an acidic to basic centers in all charge transfer complexes resulted. The values of formation constant (K_{CT}) and molar extinction coefficient (ε_{CT}) which were estimated from the spectrophotometric studies have a dramatic effect for the charge transfer complexes with differentiation of pi-acceptors. For further studies the vibrational spectroscopy of the $[(ArNH_3^+)(PiA^-)]$ (1), $[(ArNH_3^+)(Q(OH_2^-)]$ (2) and $[(ArNH_3^+)(DNB^-)]$ (3) of (1:1) charge transfer complexes of (donor: acceptor) were characterized by elemental analysis, infrared spectra, Raman spectra, ¹H and ¹³CNMR spectra. The experimental data of elemental analyses of the charge transfer complexes (1), (2) and (3) were in agreement with calculated data. The IR and Raman spectra of (1), (2) and (3) are indicated to the presence of bands around 3100 and 1600 cm^{-1} distinguish to $-NH_{4}^{+}$. The thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) techniques were performed to give knowledge about thermal stability behavior of the synthesized charge transfer complexes. The morphological features of start materials and charge transfer complexes were investigated using scanning electron microscopy (SEM) and optical microscopy.

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1. Introduction

Biological activities of the organic compounds containing thiophene are well known to exhibit various biological activities like anti-HIV PR inhibitors [1], anti-breast cancer [2], anti-inflammatory [3], anti-protozoal [4], antitumor [5], antitubercular with antimycobacterial activity [6]. On the other hand, 1,2,4-triazine have attracted the attention of most chemists because many of 1,2,4-triazines are biologically active [7] and were used in medicine especially as anti AIDS, anticancer agents [8], antitubercular agents [9], anti-anxiety and anti-inflammatory activities [10], as well as in agriculture [11]. Intermolecular charge transfer (CT) complexes are formed when electron donors and electron acceptors interacted as general phenomenon in organic chemistry branch [12]. Mulliken and Person [13] considered such complexes to arise from a Lewis acid-Lewis base type of interactions. The bonding between the components of the complex being postulated to arise from the

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partial transfer of a π -electron from the base to an unoccupied orbital of the acid [14]. Literature survey [15,16] concerning the importance of charge transfer complexes of many donating centers, reveals a great attention as solar cells [15] and analysis of an active ingredient or pharmaceutical dosages [16]. To continue our investigation in this research area [17-19], we report here the formation of the three new (1:1) CT-complexes $[(ArNH_3^+)(PiA^-)]$ (1), $[(ArNH_3^+)(Q(OH)_2^-)]$ (2) and $[(ArNH_3^+)(DNB^-)]$ (3), respectively. The main task of the work is to discuss the reaction stoichiometries, spectroscopic characterizations of the new CT-complexes and predict the place of interaction between the ArNH₂ donor and acceptors (PiA, Q(OH)₂ and DNB).

2. Experimental

2.1. Chemical and reagents

All chemicals and reagents used in this study were of analytical grade. Picric acid, hydroquinone and 3,5-dinitrobenzene were obtained from Aldrich Chemical Company.



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2.2. Synthesis of ArNH₂ donor

The synthesis of the starting materials of 3-amino-6-[2-(2-thie-nyl)vinyl]-1,2,4-triazin-5(4H)-one (donor; ArNH₂) was carried out in order to gain access to the best appropriate methods with good

yield and high purity. First pathway, the conventional method by refluxing 2-aminoganidine carbonate with 2-oxo-4-(2-thienyl)but-3-enoic acid [20] in glacial acetic acid [21]. Second pathway, carrying out the reaction between the two above compounds (solvent free) under microwave irradiation as described in literature



Scheme 1. Pathway preparation of 3-amino-6-[2-(2-thienyl)vinyl]-1,2,4-triazin-5(4H)-one (donor; ArNH₂).

Table 1

Analytical and Physical data for 3-amino-6-[2-(2-thienyl)vinyl]-1,2,4-triazin-5(4H)-one (ArNH₂) and their charge transfer complexes.

Compound empirical formula (M. Wt.)	Color	$\Lambda m \left(\Omega^{-1} \operatorname{cm}^{-1} \operatorname{mol}^{-1} ight)$	Elemental analysis (%) found (calcd.)			
			С	Н	Ν	S
ArNH ₂ (C ₉ H ₈ N ₄ OS) 220.25	Yellow	15	48.98 (49.08)	3.14 (3.66)	25.32 (25.44)	14.55 (14.56)
[(ArNH ₃ ⁺)(PiA ⁻)] (449.35)	Yellow	45	39.89 (40.09)	2.39 (2.47)	21.77 (21.82)	7.11 (7.14)
$[(ArNH_3^+)(Q(OH)_2^-)](330.36)$	Light Yellow	51	54.38 (54.53)	4.20 (4.27)	16.87 (16.96)	9.65 (9.71)
[(ArNH ₃ ⁺)(DNB ⁻)] (388.36)	Light Yellow	39	46.22 (46.39)	3.08 (3.11)	21.43 (21.64)	8.15 (8.26)



Fig. 1. Electronic absorption spectra of ArNH₂–PiA, ArNH₂–Q(OH)₂ and ArNH₂–DNB charge transfer systems, where [ArNH₂] = 0.2×10^{-4} M, [Acceptors: PiA, Q(OH)₂ and DNB] = 0.2×10^{-4} M, Mixture, [(ArNH₂)(acceptor)] = 0.2×10^{-4} M.



Fig. 2. Titration spectra of (A) ArNH₂-PiA, (B) ArNH₂-Q(OH)₂ and (C) ArNH₂-DNB systems at detectable peaks of 345, 292 and 340 nm, respectively.

[22], (Scheme 1) the structure of donor was confirmed with its 1 H NMR, 13 C NMR, IR, as well as mass spectra.

- (i) First pathway: A mixture of 2-oxo-4-(2-thienyl)but-3-enoic acid (0.01 mol), 2-aminoganidine carbonate (0.01 mol) in glacial acetic acid (25 mL) was stirred under reflux for 2 h, cooled to room temperature, the precipitate separated while reflux collected by filtration on hot to give a yellowish crystals (yield 62%) m.p. over 300 °C.
- (ii) Second pathway: A mixture of 2-oxo-4-(2-thienyl)but-3enoic acid (0.01 mol) and 2-aminoganidine carbonate (0.01 mol) were dissolved in a mixture of methylene chloride/methanol ((80/20) (v/v)), 15 mL) then 1.0 g of silica gel (200-400 mesh) was added, the solvent was removed by evaporation, the dried residue was transferred into a glass beaker and irradiated for (1.5-2.0 min) in a domestic microwave oven. The product was chromatographed on a silica gel column, using methylene chloride as eluent. (Yield = 98%) m.p. over 300 °C. IR (KBr): 3353, 3107 cm⁻¹ (NH₂, NH), 1668 cm⁻¹ (C=O amide). ¹H NMR (DMSO-d₆): $\delta = 6.73$ (d, 1H, I = 15.9 Hz, CH=CH_e), 6.85 (s, 2H, NH₂), 7.08 (t, 1H, J = 3.60, 4.80 Hz, thiophene – H_b, 7.28 (d, 1H, J = 3.3 Hz, thiophene – H_c), 7.51 (d, 1H, J = 5.1 Hz, thiophene - H_a), 8.00 (d, 1H, J = 15.9 Hz, CH_d=CH) and 12.27 (s, 1H, NH). ¹³C NMR (DMSO-d₆): δ = 120.5, 120.6, 126.6, 127.5, 128.2, 128.4, 141.7, 142.4 and 155.3 (Ar-C, C=C, C=N and C=O), m/e (Int.%): 220 (14.27), 219 (64.24), 135 (100), 121 (20.20), 78 (13.51), 69 (12.99), 59 (15.14), 44 (15.69), 43 (32.57).

2.3. Synthesis of charge transfer complexes of ArNH₂ donor

The three solid charge transfer complexes $[(ArNH_3^+)(PiA^-)]$ (1), $[(ArNH_3^+)(Q(OH)_2^-)]$ (2) and $[(ArNH_3^+)(DNB^-)]$ (3) were synthesized as a yellow-to-pale yellow colors by mixing a saturated solution (25 mL) of 3-amino-6-[2-(2-thienyl)vinyl]-1,2,4-triazin-5(4*H*)-one (donor; ArNH₂) to a saturated solution (25 mL) of each acceptors (PiA, Q(OH)₂ and DNB) in methanol. All mixtures were stirred for 45 min at 40 °C temperature and the solid products were filtered off, washed with minimum amounts of chloroform and dried under vacuum over anhydrous CaCl₂.

2.4. Physical measurements and analytical estimations

Elemental analyses (C, H, and N) were performed by the micro analytical unit, Cairo University. The electronic absorption spectra of the ArNH₂ donor and the acceptors (PiA, $Q(OH)_2$ and DNB) and the resulted charge transfer complexes were recorded in methanol within 800–200 nm range using a Perkin–Elmer Precisely Lambda 25 UV/Vis double beam Spectrometer fitted with a quartz cell of 1.0 cm path length. Infrared spectra within the range of 4000–400 cm⁻¹ for the free reactants and the resulted CT-complexes were recorded from KBr disks using a Shimadzu FT-IR Spectrometer with 30 scans and 2 cm⁻¹ resolution, while Raman laser spectra of samples were measured on the Bruker FT–Raman with laser 50 mW. ¹H, ¹³C NMR were recorded as DMSO solutions on a Bruker 600 MHz spectrometer using TMS as the internal standard. DSC thermograms of the ArNH₂ donor and its charge transfer complexes were



Fig. 3. The modified Benesi-Hildebrand plot of (A) ArNH₂-PiA, (B) ArNH₂--Q(OH)₂ and (C) ArNH₂-DNB systems at detectable peaks of 345, 292 and 340 nm, respectively.

Table 2

Spectorophotometric data of the $\rm ArNH_2-PiA, ArNH_2-Q(OH)_2$ and $\rm ArNH_2-DNB$ charge transfer systems in methanol.

Complex	$K (1 \text{ mol}^{-1})$	λ max (nm)	ε (l mol ^{-1} cm ^{-1})
[(ArNH ₃ ⁺)(PiA ⁻)] [(ArNH ₃ ⁺)(Q(OH) ₂ ⁻)] [(ArNH ₃ ⁺)(DNB ⁻)]	$\begin{array}{c} 1.26 \times 10^{4} \\ 0.78 \times 10^{4} \\ 0.595 \times 10^{4} \end{array}$	345 292 340	$\begin{array}{l} 9.44 \times 10^{4} \\ 3.31 \times 10^{4} \\ 5.66 \times 10^{4} \end{array}$

obtained on a SCINCO DSC 1500 STA. Samples in solid form were placed in aluminum pans with a pierced lid, and heated rate of 10 °C min⁻¹ under a nitrogen flow. TGA was carried out on a SCIN-CO TGA 1500 STA apparatus at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. Scanning electron microscopy (SEM) images and energy-dispersive X-ray detection (EDX) were taken in Joel JSM-6390 equipment, with an accelerating voltage of 20 kV. Microstructures of donor and charge transfer complexes were examined by Optical microscopy model Meiji 7800 Techno Microscopy.

3. Results and discussion

3.1. Analytical data and conductivity measurements

Elemental analyses data of 3-amino-6-[2-(2-thienyl)vinyl]-1,2, 4-triazin-5(4*H*)-one (donor) and their charge transfer complexes

were reported in Table 1. The elemental analysis tool proved that the molar ratio between ArNH₂ (donor) and respective π -acceptors (PiA, Q(OH)₂ and DNB) is 1:1. The interaction process occurs through the proton transfer from acidic centers in the mentioned acceptors to the nitrogen atom of ArNH₂ donor. Conductivity meter type Jenway 4010 was used to measure conductivities of different charge transfer complexes of ArNH₂ donor in DMSO with 1.0×10^{-3} mol/dm³ concentration. The conductivities of the free reactants were also measured at a similar condition in order to make comparison between the free donor and acceptors with those of its charge transfer complexes. The molar conductances of ArNH₂ CT-complexes were reported in Table 1. The molar conductance values range from 15 to 51 Ω^{-1} cm⁻¹ mol⁻¹. The molar conductance values indicate that the charge transfer complexes have slightly electrolytic nature. Slightly electrolytic complexes assigned to the formation of positive and negative datives anions under the acid-base migration theory [23].

3.2. UV/Vis spectra and photometric titrations

The electronic absorption spectra of 0.2×10^{-4} M solutions of ArNH₂, PiA, Q(OH)₂, DNB, and their ArNH₂-acceptor mixtures in methanol are shown in Fig. 1. The charge transfer absorption bands which detectable after proton transfer were observed in the spectra of the reaction mixtures at 350 nm, (292 and 338 nm) and (277 and 340 nm) for the ArNH₂–PiA, ArNH₂–Q(OH)₂ and ArNH₂–DNB complexes, respectively. Based on the photometric titration processes represented in Fig. 2, the stoichiometry has 1:1 M ratio



Fig. 4. IR spectra of (A): $[(ArNH_3^+)(PiA-)]$, (B): $[(ArNH_3^+)(Q(OH)_2^-)]$ and (C): $[(ArNH_3^+)(DNB-)]$ charge transfer complexes.

for ArNH₂: acceptor. The 1:1 modified Benesi-Hildebrand Eq. (1) [24] was used in the calculations of formation constant, K, and the molar absorptivity, ε , values for each charge transfer complexes formed. Fig. 3 showed these straight lines plots and the obtained data were given in Table 2. The data reveals that ArNH₂-PiA, ArNH₂-Q(OH)₂ and ArNH₂-DNB charge transfer systems show high values of both the K and . The high values of K reflect the high stability of the formed CT-complexes as a result of the expected high electron donation from the ArNH₂ while the high value of agree quite well with the formation of CT-complexes which are known to have high absorptivity values [17-19]. The value of K for [(ArNH₃⁺)(PiA⁻)] is about twice times higher than that of $[(ArNH_3^+)(Q(OH)_2^-)]$ or $[(ArNH_3^+)(DNB^-)]$. Accordingly, the formed CT-complexes are formulated as [(ArNH₂)(acceptor)]. These results were supported by the elemental analysis data of the solid complexes as well as photometric titration.

$$\frac{C_a^o C_d^o l}{A} = \frac{1}{K\varepsilon} + \frac{C_a^o + C_d^o}{\varepsilon}$$
(1)

3.3. Infrared and Raman spectra

The infrared and Raman data for the $ArNH_2$ charge transfer complexes are shown in Figs. 4 and 5 and the observed absorption bands were listed in Table 3. The band assignments between 4000–



Fig. 5. Raman Laser spectra of (A) [(ArNH₃⁺)(DNB–)] and (B) [(ArNH₃⁺)(PiA–)] charge transfer complexes.

Table 3 Assignments of the IR and Raman (R) spectral bands (cm^{-1}) for ArNH₂ and their charge transfer complexes.

Compound	v(NH)		$\delta(\mathrm{NH}_3^+)_{\mathrm{def}}$		$\delta(\mathrm{NH}_3^+)_{\mathrm{sym}}$		$\rho(\mathrm{NH}_3^+)$	
	IR	R	IR	R	IR	R	IR	R
[(ArNH ₃ ⁺)(PiA ⁻)]	3100	3085	1627	1616	1334	1337	797	827
$[(ArNH_3^+)(Q(OH)_2^-)]$	3065	3102	1546	1604	1350	1327	804	779
[(ArNH ₃ ⁺)(DNB ⁻)]	3107	3100	1614	1624	1350	1353	812	845

400 cm⁻¹ shows the main characteristic absorption bands of NH₃⁺ group. For example the ν (NH), δ_{def} (NH₃), δ_{sym} (NH₃), and ρ (NH₃) vibration of all charge transfer complexes occurs at about 3100, 1600, 1300 and 800 cm⁻¹, respectively. The presence of these bands confirmed that the proton transfer phenomena from the acidic center of each acceptor to the lone pair of electron of – NH₂ group to form NH₃⁺ ammonium ion upon complexation. Also, there is some small changes comparison between the spectra of the CT-complexes and those of the reactants, could also be notable from the expected changes in the symmetry and electronic configurations of both reactants upon charge transfer complexation.

3.3.1. ¹H and ¹³C NMR spectra

The reaction of ArNH₂ as donor with picric acid as acceptor gave a new charge transfer complex named by 5-oxo-6-[2-(2-thienyl) vinyl] -4,5-dihydro-1,2,4-triazin-3-aminium-2,4,6-trinitrobenzenolate (Scheme 2). The ¹H NMR showed disappearance of the signal of NH₂ in ArNH₂ donor with presence of a broad signal at δ = 4.8 ppm which assigned to NH₃⁺ through the formation of salt between ArNH₂ and picric acid. The signal at δ = 8.88 ppm in the free picric acid which assigned to aromatic proton was right shifted. This displacement due to the increase of the shielding of these protons with overall decrease in the value of the coupling constant because of the change of the magnetic environment of



Scheme 2. Formula of [(ArNH₃⁺)(PiA⁻)] charge transfer complex.

all proton as a result of complex formation. ¹H NMR (DMSO-d₆): δ = 4.8 (b, 3H, NH₃⁺), 6.40 (d, 1H, *J* = 14.2 Hz, CH=CH_e), 7.12 (t, 1H, *J* = 3.6, 3.6 Hz, thiophene – H_b), 7.31 (d, 1H, *J* = 3.6 Hz, thiophene – H_c), 7.59 (d, 1H, *J* = 5.4 Hz, thiophene – H_a), 7.75 (d, 1H, *J* = 14.7 Hz, CH_d=CH), 8.60 (s, 2H, H_f of benzene ring) and 12,01 (s, 1H, NH). ¹³C NMR (DMSO-d₆): δ = 120.5, 124.3, 125.2, 127.4, 128.3, 128.4, 129.1, 138.8, 141.2, 141.7, 155.1, 160.6 and 163.1 (Ar–C, C=C, C=N and C=O).

Similar results was obtained by the reaction of ArNH₂ with dinitrobenzene which, resulted in 5-hydroxy-6-(2-(thiophen-2-yl)vinvl)-1.2.4-triazin-3-aminium 2.6-dinitro benzen-1-ide (Scheme 3), the ¹H NMR showed disappearance of the signal of NH₂ in ArNH₂ donor with appearance of broad signal at δ = 4.5 ppm for NH₃⁺ referring to the formation of salt between the electron poor dinitrobenzene and the electron rich triazine derivative ArNH₂. The complex formed an activate NH–C=O \leftrightarrow N=C–OH tautomerization in triazine ring which, illustrated in the appearance of signal at δ = 14.72 ppm for OH group and disappearance of ring NH signal. ¹H NMR (DMSO-d₆): δ = 4.5 (b, 3H, NH₃⁺), 6.80 (d, 1H, $I = 10.2 \text{ Hz}, \text{ CH}=\text{CH}_{e}$, 7.13 (t, 1H, $I = 3.6, 3.6 \text{ Hz}, \text{ thiophene} - \text{H}_{b}$), 7.20 (d, 1H, J = 1.8 Hz, dinitrobenzene– H_f), 7.51 (d, 1H, J = 5.4 Hz, thiophene – H_c), 7.81 (d, 1H, J = 6.6 Hz, thiophene – H_a), 7.91 (t, 1H, J = 5.4, 5.6 Hz, dinitrobenzene – H_g), 8.65 (d, 1H, J = 10.2 Hz, CH_d=CH) and 14.72 (s, 1H, OH). ¹³C NMR (DMSO-d₆): δ = 118.5, 123.5, 126.3, 126.9, 127.9, 128.2, 129.3, 129.4, 131.5, 142.2, 147.9, 154.9 and 164.6 (Ar-C, C=C, C=N and C=O).

For the reaction between the electron rich 1,4-qinol acceptor and triazine derivative ArNH₂ donor, the (5-hydroxy-6-[2-(thiophen-2-yl)ethenyl]-1,2,4-triazin-3-aminium 4-hydroxy phenolate) (Scheme 4) is resulted with the same result that obtained from the electron poor picric acid and dinitrobenzene. The ¹H NMR showed signals at δ = 4.51, 6.56 and 8.66 ppm for NH₃⁺, four aromatic quinol protons and one quinol OH proton, respectively, with disappearance of NH₂ signal of ArNH₂ donor. ¹H NMR (DMSO-d₆): δ = 4.65 (b, 3H, NH₃⁺), 6.56 (s, 4H, ArH quinol), 6.81 (d, 1H, *J* = 16.2 Hz, CH=CH_e), 7.08 (t, 1H, *J* = 3.60, 4.80 Hz, thiophene – H_b), 7.20 (d, 1H, *J* = 1.5 Hz, thiophene – H_c), 7.52 (d, 1H, *J* = 2.4 Hz, thiophene – H_a), 7.82 (d, 1H, *J* = 15.9 Hz, CH_d=CH), 8.66 (s, 1H, OH quinol)



Scheme 3. Formula of [(ArNH₃⁺)(DNB⁻)] charge transfer complex.



Scheme 4. Formula of $[(ArNH_3^+)(Q(OH)_2^-)]$ charge transfer complex.

and 14,6 (s, 1H, OH). ¹³C NMR (DMSO-d₆): δ = 115.5, 123.5, 126.2, 126.8, 127.8, 128.1, 128.4, 142.1, 145.8, 149.6, 154.9 and 164.7 (Ar—C, C=C, C=N and C=O).

3.4. Optical and scanning electron microscopes

Surface image using optical microscope (Fig. 6) demonstrate to the porous structures of the surface of prepared charge transfer complexes. Analysis of these images shows the size of pores to be quite different with different acceptors. The chemical analysis results by EDX for the formed charge transfer complexes show a homogenous distribution of each acceptor. SEM examinations were checked the surfaces of these CT-complexes that show a small particles which tendency to agglomerates formation with different shapes comparison with the start materials. The chemical compositions of the free ArNH₂ donor and charge transfer complexes were determined using energy-dispersive X-ray diffraction (EDX). In the EDX profile of these complexes (Fig. 7A–D), the peaks of the carbon, nitrogen, oxygen, and sulfur elements, which constitute the molecules of ArNH₂, $[(ArNH_3^+)(PiA^-)]$, $[(ArNH_3^+)(Q(OH)_2^-)]$ and [(ArNH₃⁺)(DNB⁻)] charge transfer complexes, are clearly identified confirming the proposed structures.

3.5. Thermal analysis TGA/DSC

The simultaneous TGA/DSC analysis of the ArNH₂($C_9H_7N_4OS$] free donor and their respective [(ArNH₃⁺)(PiA⁻)], [(ArNH₃⁺)(Q(OH)₂⁻)] and [(ArNH₃⁺)(DNB⁻)] charge transfer complexes were studied from ambient temperature to 800 °C under nitrogen atmosphere using α -Al₂O₃ as the reference (Fig. 8. The free donor decomposed in three steps with seven (100, 225, 275, 400, 475, 530 and 750 °C) DSC peaks. The first decomposition step at DSC = 100 and 225 °C endothermic, it loses a fragment of NH₂ with a weight loss 7.73%. Then the endothermic peaks at 275 and 400 °C were assigned to the loss of H₂S and C₂H₂ after the decom-



Fig. 6. Optical microscopy photos of (A) ArNH2, (B) $[(ArNH_3^+)(PiA^-)]$, (C) $[(ArNH_3^+)(Q(OH_2^-))]$ and (D) $[(ArNH_3^+)(DNB^-)]$ complexes.



Fig. 7. SEM images and EDX spectra of (A) $ArNH_2$, (B) [$(ArNH_3^+)(PiA^-)$], (C) [$(ArNH_3^+)(QOH_2^-)$] and (D) [$(ArNH_3^+)(DNB^-)$] complexes.

position of thiophene moiety with weight loss 27.27%. The third step has a wide range 400–800 °C with three DSC maximum peaks at 475, 530 and 750 °C involves the removal of C_5 HN₃O with mass loss 54.09%.

The $[(ArNH_3^+)(PiA^-)]$ charge transfer complex was degraded by three decomposition steps from 25–250 °C, 250–400 °C and 400–

800 °C with DSC maximum peaks at (150 °C, 200 °C endothermic), 275 °C exothermic and 625 °C exothermic, respectively. The first decomposition step has a weight loss about 10.22% with librated one of NO₂ molecules from picric acid moiety. The second step is exothermically by fragments of $2NO_2 + NH_2 + OH$ moieties with 27.78% weight loss. The last step completed with the loss of rest or-



Fig. 7 (continued)



Fig. 8. A–D: TGA and DSC curves of (A) ArNH₂, (B) [(ArNH₃⁺)(PiA⁻)], (C) [(ArNH₃⁺)(Q(OH)₂⁻)] and (D) [(ArNH₃⁺)(DNB⁻)] complexes.

ganic moieties of both ArNH₂ donor and PiA acceptor, leaving a few residual carbon atoms.

The $[(ArNH_3^+)(Q(OH)_2^-)]$ charge transfer complex decomposes firstly in the range of 25–300 °C, endothermically evolved thiophene moiety with a weight loss 25.07%. The second step within range (300–400 °C, mass loss 13.00%) involves the exothermic peak with loss of acetylene and hydroxo moieties. The third decomposition step at DSC = 435 °C assigned to the losses of NH₂ and the second OH group of hydroquinone acceptor with a weight 10.00%. The last degradation step at DSC = (675 and 725 °C exothermically) has an extremely large scale of weight loss for about 42.00% due to libration of the rest of both donor and hydroquinone acceptor leaving few carbon atoms as residue.

The $[(ArNH_3^+)(DNB^-)]$ charge transfer complex decomposed in two major steps. The first degradation step contain four maximum

endothermically DSC peaks at 100, 150, 200 and 275 °C and one exothermic peak at 350 °C with a weight loss 71.21% which assigned to starts decomposed in the temperature range of 25–400 °C with the liberated of thiophene, acetylene and DNB fragments. The amino triazin moiety was decomposed in both endothermically and exothermically peaks at 450 and 700 °C, respectively, with a weight loss value equal 23.00%. Few carbon atoms remain as a final residual.

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