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Conductivity of polyaniline and its derivatives incorporated within the cavities of the three dimensional [tris(trimethyltin)hexacyano-ferrate]$_\infty$

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Abstract

The dependence of the electrical conductivity of aniline and its derivatives in situ intercalated within the cavities of the three dimensional polymeric host $[(Me_3Sn)_3Fe(CN)_6]_\infty$, on temperature has been investigated. The conductivity values at 303 K, the activation energies and the energy gaps have been calculated. These novel polymeric intercalated complexes behave as good semiconductors. The conductivity depends on the structure of the aniline derivative and the conditions of the reaction.

INTRODUCTION

The three dimensional (3D) coordination polymer [tris(trimethyltin)hexacyanoferrate]$_\infty$ (**I**) is one of the novel family of 3D polymeric complexes recently prepared and characterized by spectroscopic studies and by X-ray single crystal diffraction spectroscopy [1, 2]. These polymeric complexes have a large cavity capable of encapsulating organic and organometallic guest cations [2–7]. Also, **I** behaves as good oxidative reagent towards phenols [8]. These attractive characteristic features of **I** offered the idea that organic molecules such as aniline, pyrrole, pyridine, thiazole or even thiophene could be encapsulated within its cavity to yield conductive or semiconductive intercalated polymeric complexes [6, 7].

It is well known that aniline, pyrrole and thiophene yield upon chemical or electrochemical oxidation technologically promising, electrically conductive, polymers [9]. Among these electrically conductive polymers, polyaniline is a particularly attractive material because it has a moderately

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high conductivity upon doping with simple Brönsted acids [10, 11], is easily synthesized by chemical or electrochemical oxidation of aniline [12, 13], and has good environmental stability [11]. It is now well established that the structure of polyaniline, in the base form, is that of a para-linked phenyleneaminimine [14, 15]. The conductive form of polyaniline is associated with intermediate oxidation state, e.g. emeraldine, which features an equal number of imine and amine nitrogens in the free-base form [16]. In the neutralized free-base form, the polymer is an insulator. However, a polyradical cation nature has been postulated for the conductive salt [17].

In the present work we present the successful in situ intercalation of aniline and its derivatives in the cavities of the three dimensional polymeric host $[(Me_3Sn)_3Fe(CN)_6]_\infty$ **I** to yield novel conductive or semiconductive polymeric or charge transfer molecular complexes. To the best of our knowledge nothing was mentioned about the electrochemical oxidation and conductivity of aniline derivatives, in spite of the fact that the chemical oxidation of some primary amines was studied under the same conditions as employed in the preparation of emaraldine [14].

EXPERIMENTAL

Aniline derivatives (Table 1) were doubly distilled under reduced pressure while the solid materials were of highly pure grade purchased from Aldrich or Merck. The polymeric host was prepared in the dark under nitrogen atmosphere and characterized as described elsewhere [18]. The polymeric guest–host intercalative complexes were prepared under nitrogen atmosphere at room temperature by direct addition of the polymeric host with aniline or its derivatives in addition to a few drops of 1 M HCl. The reaction with aniline **I** is spontaneous, but with respect to aniline derivatives, the rate of reaction is enhanced by grinding or sonication. In case of 3-chloroaniline, the reaction is also carried out at 40°C and in the vapour state at 60°C. The products of the intercalated complexes were washed with ethanol several times and dried under vacuum. The purity and identity of these intercalative complexes have previously been investigated [18] (Table 1).

Electrical conductivities ($\sigma\ \Omega^{-1}\ cm^{-1}$) were measured on the test sample, which was compressed under a pressure of about 600 kg cm^{-2} to form a cylindrical disc of diameter about 0.5 cm and thickness about 0.1 cm, through the temperature range 298–500 K and the current I for a series of applied voltages V, within the range $5\ V < V < 200\ V$, using a Super Megohmmeter Model RM 170 (Avo Ltd., Dover, England). The temperature was controlled to within 0.25 K of the desired value, and it was possible to determine the electrical characteristics of two discs of the test sample simultaneously as further check for reproducibility of results. The DTA

TABLE 1

The electrical conductivity at 303 K (σ_{303K}), activation energy (ΔE), energy gap (E_g) and transition temperature (T_s) for **I** and the intercalated polymeric complexes **1–14**

No.	Intercalated polymeric complexes	Colour	σ_{303K}/ Ω^{-1} cm^{-1}	$\Delta E_1 \times 10^{22}$/ kJ	$E_g \times 10^{22}$/ kJ	$\Delta E_2 \times 10^{22}$/ kJ	$E_g \times 10^{22}$/ kJ	T_s/ K
I	$[(Me_3Sn)_3Fe(CN)_6]_\infty$	Orange	3.81×10^{-8}	0.831	1.662			
1	$[(\mathbf{I})_2$ + (aniline)$_3]$	Black	4.66×10^{-2}	0.253	0.506			
2	$[(\mathbf{I})_2$ + (aniline)$_3]$ [a]	Black	1.51×10^{-4}	0.793	1.589			
3	$[(\mathbf{I})_2$ + (*m*-toluidine)$_3]$	Black	2.82×10^{-4}	1.016	2.032	1.746	3.493	366.3
4	$[(\mathbf{I})_2$ + (*p*-toluidine)$_3]$	Dark brown	1.86×10^{-3}	0.697	1.394			416
5	$[(\mathbf{I})_2$ + (*p*-anisidine)$_3]$	Dark blue	6.31×10^{-5}	0.982	1.964			463
6	[**I** + 2,4,6-trimethylaniline]	Greenish brown	5.01×10^{-7}	0.513	1.026	1.330	2.660	357
7	[**I** + 3-chloroaniline](RT) [b]	Dark green	1.79×10^{-5}	0.897	1.794	1.913	3.826	338–353
8	[**I** + (3-chloroaniline)$_{0.75}$] (313 K)	Green	4.20×10^{-6}	2.275	4.550	0.833	1.666	335.5–350.8
9	[**I** + (3-chloroaniline)$_{0.5}$] (333 K)	Faint green	5.62×10^{-6}	2.221	4.442	0.793	1.586	361
10	[**I** + (4-chloroaniline)$_{0.9}$]	Brown	3.16×10^{-6}	0.942	1.884	0.181	0.362	416.6–476.2
11	[**I** + (2,5-dichloroaniline)$_{0.5}$]	Green	7.08×10^{-7}	0.961	1.922	2.125	4.250	429–488
12	[**I** + (2,4-dinitro-6-chloroaniline)$_{0.75}$]	Canary yellow	1.25×10^{-7}	0.570	1.140	3.317	6.634	406.5
13	[**I** + (2,3,4-trichloroaniline)$_{0.5}$]	Green	5.01×10^{-8}	0.237	0.474	0.538	1.076	376
14	[**I** + (2,4,6-tribromoaniline)$_{0.5}$]	Greenish yellow	1.26×10^{-8}	0.221	0.442	0.538	1.076	484.6

[a] In absence of HCl. [b] RT, room temperature.

measurements were made using a Du Pont 900 thermal analyser in the 50 mV cm^{-1} range with scan rate 20°C/min.

RESULTS AND DISCUSSION

The dependence of the electrical conductivity on temperature for the intercalated polymeric complexes **1–14** (Table 1) satisfies the conventional equation $\sigma = \sigma_0 \exp^{-\Delta E/KT}$, where σ_0 is constant, ΔE is the activation energy and K is Boltzmann's constant. The plots of log σ versus $1000/T$ gives, in the case of complexes **1**, **2**, **4** and **5**, straight lines within the investigated temperature range with scattering of data points above about 433 K, while the other cases show discontinuity at variable temperatures (Figs. 1 and 2). It is evident that the conductivity increases as the tem-

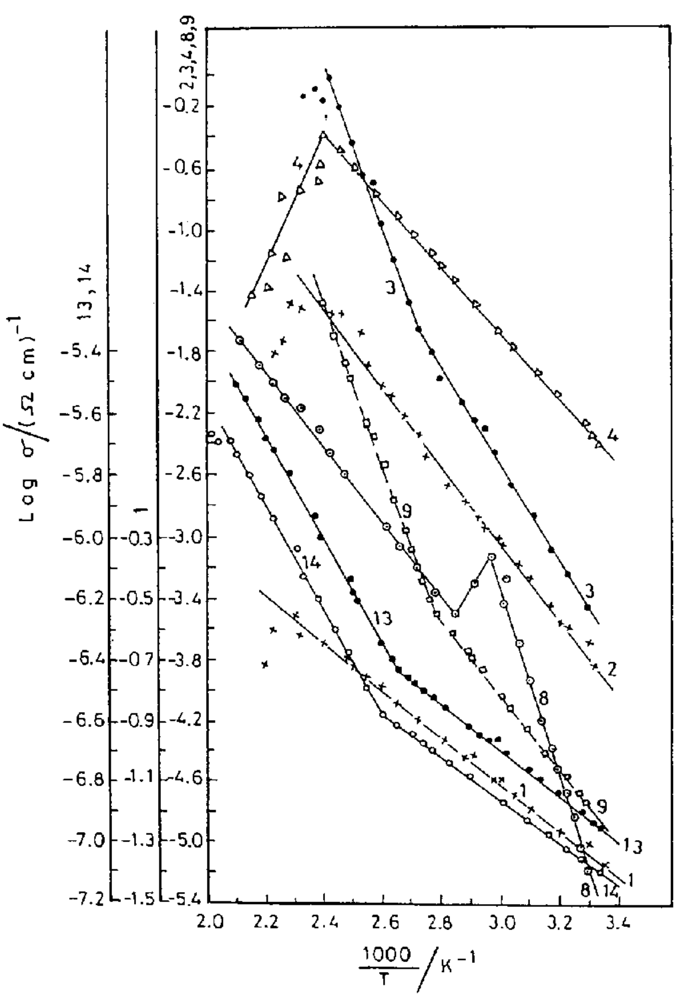

Fig. 1. Log σ versus $1000/T$ for intercalated polymeric complexes **1–4**, **8**, **9**, **13** and **14**.

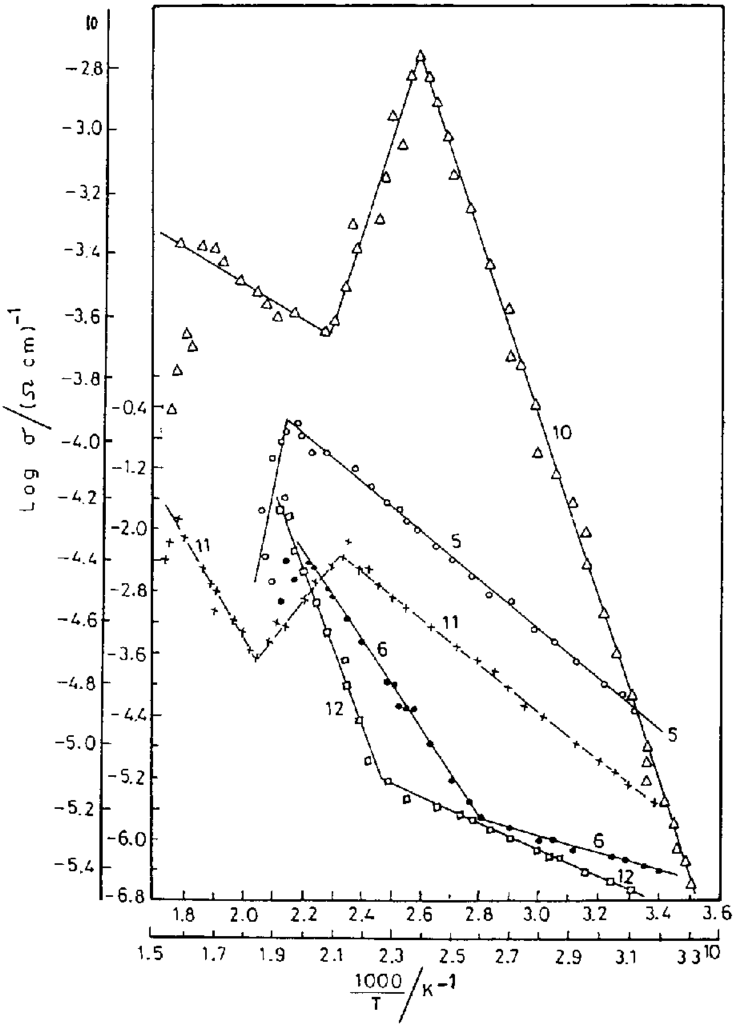

Fig. 2. Log σ versus $1000/T$ for intercalated polymeric complexes; **5**, **6** and **10–12**.

perature is increased; hence these intercalative complexes possess semiconductive properties. The conductivity values at 303 K and the activation energies ΔE as well as the energy gaps E_g are given in Table 1. The variation of the d.c. electrical conductivity as a function of temperature for the intercalative complexes **1**, **2**, **4** and **5** indicates the gradual increase of conductivity with increasing temperature. At temperatures higher than about 433 K, the conductivity suddenly falls and scattering of data points is observed. The straight line obtained for each complex shows the unique behaviour of the conduction mechanism. The DTA curves of these intercalative complexes exhibit a marked stability up to temperature values 473, 440 and 415 K after which an exothermic peak starts to appear at 534, 489 and 498 K for the complexes **2**, **4** and **5** respectively. However, a

TABLE 2

DTA data of the intercalated polymeric complexes

Intercalated polymeric complexes	DTA peaks/°C	
	Endotherm	Exotherm[a]
$[(Me_3Sn)_3Fe(CN)_6]_\infty$		60.4(s), 148.5, 217.7
$[(Me_3Sn)_4Fe(CN)_6]_\infty$	87(s)	205, 254.6(sb), 307.9(sb),
1	110(s)	245, 336
2	70(s)	186(sb), 264, 345
3	69(s), 87(s)	229, 340
4	113(s)	150.8(sb), 216.5, 292
5	124(s)	225, 284
6	109(s)	150(sb), 224, 345
7		65.6(s), 143(sb), 229, 315, 365(sb), 411
8		62.6(s), 161.4(sb), 222, 335, —, 430
9	61(s), 91(s)	80(s), 166.8(sb), 219, 319, —, 425.5
10	117(s)	68.3(s), —, 209, 318, 374.4(sb)
11	61(s)	131.4(sb), 240, 319, 370(b), 495
12	102(s), 125(s)	59.2(s), 139.9(s), 217.5, 284, 308(sb)
13	141(s)	152(s), 195.4(sb), 235.5, 305, 335
14	85(s)	147.5(s), 222.5, 253, 315.5

Key: b, broad peak, s, small peak; sb, small broad peak.

small endothermic peak appears around 348 K due to release of impurities of aniline derivatives (Table 2). This thermal stability, as well as the activation energy values, indicate an intrinsic conduction mechanism within the investigated temperature range. The decrease of conductivity at temperatures equal to or higher than those of the exothermic peak, can be referred to the decomposition of the intercalative complexes.

The plots of log σ versus $1000/T$ of the intercalative complexes **3**, **6**, **9**, **12**, **13** and **14** reveal a discontinuity of the straight lines at 366.3, 357, 361, 406.5, 376 and 384.6 K, respectively, and therefore they have two activation energies ΔE_1 and ΔE_2. The discontinuity phenomenon can be ascribed to a molecular rearrangement, crystallographic transition, volume change or changes in conduction mechanism [19].

The DTA curves of the intercalative complexes **3**, **6** and **9** exhibit thermal stability until temperatures of 484, 473 and 463 K, respectively, after which a strong exothermic peak started to appear. However, endothermic peaks at 342 and 360 K (complex **3**) 382 and 334 K (complex **6**) and 364 K (complex **9**) are observed in the DTA curves. However the DTA curves of **12**, **13** and **14** show endothermic peaks at 375 and 398 K, 414 K and 358 K, respectively, and exothermic peaks at 412.9 and 490.5 K, 468.4 and 508.5 K and 420.5 and 495.5 K, respectively (see Table 2). The endothermic peaks could be attributed to the release of the molecules of water of crystallization and the impurities of the unreacted aniline derivatives. The temperatures of the endothermic peaks and the transition temperatures T_s have more or less the same values however, so the difference observed can be ascribed to the different heating rates used.

The activation energy values ΔE_1 are lower than those of ΔE_2. Thus, from the DTA data and the activation energy values, it could be concluded that the observed ΔE values of these intercalative complexes are due to changes in the conduction mechanism. For the first segment with ΔE_1, the presence of impurities is playing the role of existing the probability for valence band electrons to be injected into the conduction band. This is accompanied by the formation of a delocalized electron in the conduction band and a hole in the valence band providing the so called intrinsic electronic conductivity. After the transition temperature, for the second segment, where no impurities are present, the valence-band electrons transfer into the conduction band under the action of temperature providing an extrinsic electronic conductivity.

In contrast, the conductivity curves of the complexes **7**, **8**, **10** and **11** exhibit three regions A, B and C with two transition temperatures. Regions A and C exhibit a positive temperature coefficient of electrical conductivity, indicating semiconducting behaviour. Region B is characterized by a decrease of conductivity as the temperature is increased. This region is narrow and appears at relatively low temperature for complexes **7** and **8**, but a wide range of transition temperature (416.6–476.2 and 429.2–487.8 K) is observed for complexes **10** and **11**, respectively.

For complexes **7** and **8** a small exothermic peak appears at 338.6 K and 335.6 K, respectively, which corresponds to the transition temperature range. In this case, the molecules of compounds **7** and **8**, which in the vapour state are incorporated within the cavities of the polymeric host, undergo rearrangement within these cavities. Hence carriers suffer scattering as a result of lattice rearrangement within the temperature range of this region. This is also supported by the low activation energy of region C compared to that of region A.

In the case of complexes **10** and **11**, the situation is completely different, where the data points suffer scattering even in region C. This can be attributed to the decomposition of the complexes, since the strong exothermic peak starts to appear at 482 K (complex **10**) and 513 K (complex **11**) (Table 2).

CONDUCTIVITY–STRUCTURAL CORRELATIONS

The addition of aniline to the polymeric host in the presence of 1 M HCl leads to redox reaction in which the aniline monomer is oxidatively polymerized while the polymeric host $[(Me_3Sn)_3Fe^{III}(CN)_6]_\infty$ is reduced to the isostructural iron homologue $[Me_3Sn)_3Fe^{II}(CN)_6^-]_\infty$ (ref. 18). The

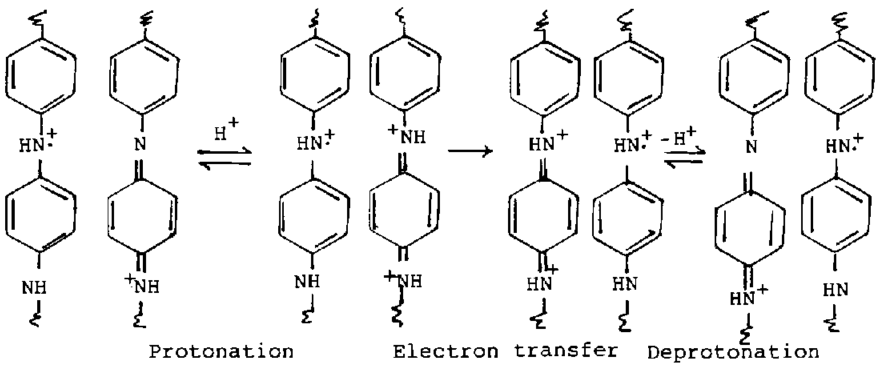

Chart 1.

conductivity of complex **1** is $4.66 \times 10^{-2}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ which is higher than that of complex **2** ($1.51 \times 10^{-4}\ \Omega^{-1}\ \mathrm{cm}^{-1}$) prepared in the absence of HCl solution. Thus, the protonated form of polyaniline intercalated within the cavities of the polymeric host shows a dramatic increase in conductivity by six orders of magnitude with respect to that of the polymeric host which is an insulator at room temperture, and also by two orders of magnitude with respect to that of complex **2**.

It was assumed that for $\mathrm{pH} > 1$ only imine nitrogens are protonated [20] and a partially oxidized and partially protonated sample of the polyaniline was considered, implying the presence of a dynamic equilibrium of protonation and deprotonation. This proton exchange in polyaniline has recently been demonstrated by NMR spectroscopy [21]. It may also facilitate intramolecular and intermolecular charge transport (Chart 1). This is the case for complex **2** where some of the protons produced by the oxidation of aniline compensate the charge of the reduced form of the polymeric host; the other protons link some of the unprotonated imine nitrogens forming the protonated polyaniline which is encapsulated within the negatively charged cavity of the reduced form of the polymeric host (Chart 2). On addition of 1 M HCl, in the case of **1** a high degree of

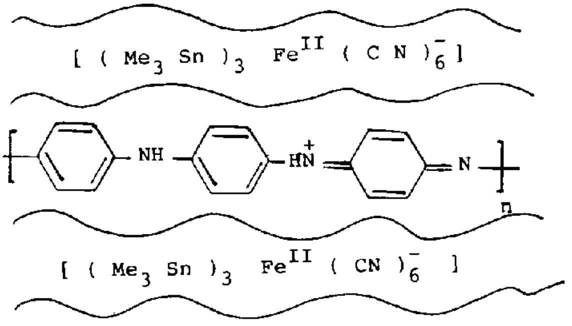

Chart 2.

protonation is expected which is supposed to be an essential prerequisite for high conductivity of polyaniline.

m-Toluidine, *p*-toluidene, *p*-anisidene, 2,4,6-trimethylaniline, 3-chloroaniline(RT) and 4-chloroaniline undergo oxidation within the cavities of the polymeric host forming black, dark brown, dark blue and green polymeric products [18]. The conductivity of these intercalated complexes **3**–**7** and **10** at 303 K are lower by some orders of magnitude with respect to that of **1**; in spite of this fact they behave as semiconductors. This can be attributed to the fact that the primary oxidation products are rather less stable than in the aniline series, being more prone to polymerization, and that the higher quinonoid products are less easily formed.

By contrast, 3-chloroaniline (313 and 333 K), 2,5-dichloroaniline, 2,4-dinitro-6-chloroaniline, 2,3,4-trichloroaniline and 2,4,6-tribromoaniline do not undergo polymerization; rather, they form charge transfer complexes (CTCs) giving green to yellow complexes [18]. These CTCs behave as weak

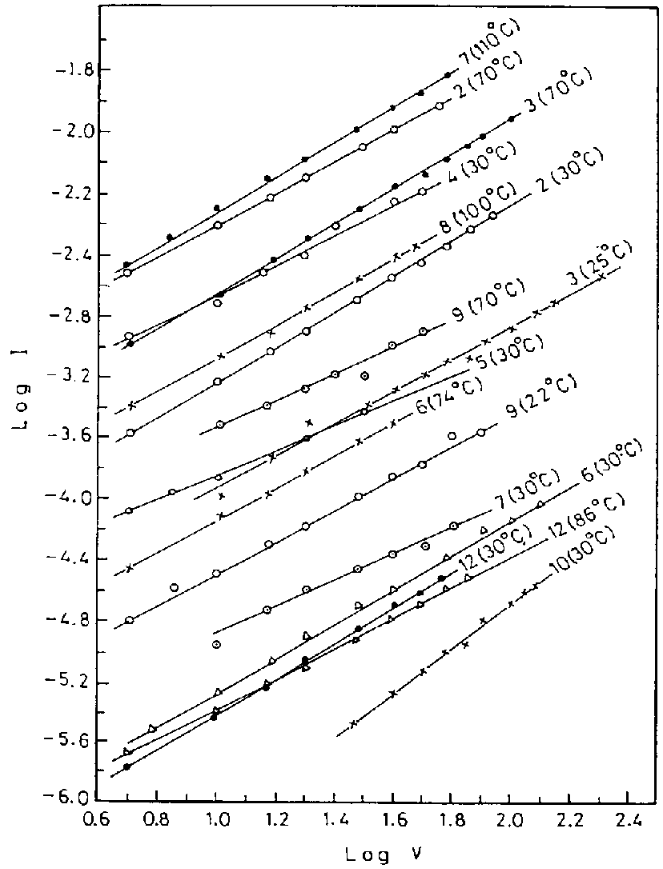

Fig. 3. Log *I* versus log *V* for intercalated polymeric complexes; **2**–**10** and **12** at different temperatures.

semiconductors with conductivity values lower than those of the other polyaniline derivatives. In the case of 3-chloroaniline, the conductivity of complex **7** is higher than those of complexes **8** and **9** and the colour is dark green indicating completion of the reaction in the former case. Generally, the conductivity decreases as the number of substituents increases at the aniline ring and it also depends on the conditions of the reaction.

I–V CHARACTERISTIC CURVES

The conventional technique of measuring conductivity needs certain precautions due to the contact effects which may lead to injection of carriers, considerable depletion of the layer at the contact area, or even space charge limited current effects. These effects cause false results and hence to ensure the validity of results presented here, the current against voltage characteristics of the intercalated polymeric complexes were obtained by maintaining the temperature constant and increasing the applied voltage. The obtained linear I–V characteristics prove the ohmic contacts where the effects which may arise from the above mechanisms are neglected. This is also supported by the plots of $\log I$ against $\log V$ at constant different temperatures (Fig. 3). They show a $I \propto V^n$ dependence with $n \approx 1$ (Table 3), indicating an ohmic character which is temperature independent over the range of temperatures and voltages applied.

TABLE 3

Values of n over different range of applied voltage and temperature of the intercalated polymeric complexes

Intercalated polymeric complex	Temperature/K	Applied voltage/V	n
I	303	10 130	1.07
1	299	20–170	1.15
2	303, 343	5–60, 5–100	1.13, 1
3	298, 343	10–199, 5–125	1, 1.04
4	303, 366	5–70, 5–32	1.06, 1
5	303	5–50	1
6	303, 347	6–125, 5–40	1, 1
7	303, 383	10–63, 5–60	1, 1
8	373	5–70	1.05
9	297, 343	5–80, 10–50	1.05, 1
10	303, 373	25–125, 5–50	1.38, 1
11	303	5–80	1.05
12	303, 359	5–63, 5–63	1.10, 1
13	299	5–150	0.92
14	299	5–140	1.05

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