SYNTHESIS AND TRANSPORT CHARACTERIZATION OF POLY ANILINE FORMALDEHYDE COPOLYMER RESINS

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Abstract

The present work includes the synthesis of two samples of copolymer-resins prepared with aniline and formaldehyde in their various molar proportions, using the process of condensation and direct chemical blending (AF.1 and AF.3); and the transport properties investigated through temperature dependent d.c. electrical conductivity measurements with four probe instrument. The transport parameters like d.c. electrical-conductivity, activation energy, charge localization length, most probable hopping distance and charge hopping energy have been calculated at room temperature with the two theories i.e. band theory and hopping mechanism theory, and temperature dependent transport and electrical behavior is discussed for these samples AF.1 and AF.3. The values of calculated transport parameters suggested that these co-polymeric materials have immense potential for application as power source material in the fuel- cell.

Keywords: electrical-conductivity, amino-resins, transport-characterization, copolymers.

1. Introduction

The transport studies combined with electrical conduction mechanism of copolymers are enviable to realize its use in the applications related to electrode techniques and power industries. With the development of fuel cells, the electro-catalytic oxidation of small organic molecules such as methanol and formaldehyde has attracted immense interest of the researchers in the last two decades [1-5]. Formaldehyde is often preferred for the electro-catalytic activity of electrodes due to its simplest structure. Most of the research on the electrochemical behaviour of formaldehyde has been directed towards poly aniline (PAN) films in H_2SO_4 solution containing formaldehyde and Platinum, however, Pt particles on the PAN found not suitable for electro-deposition can cause a mass loss of the PAN film [6]. The copolymer poly aniline formaldehyde amino resin synthesized in the course of two different methods employed by us *i.e.* direct chemical blending and poly-condensation, is an approach to enhance the efficiency and activity of formaldehyde as novel electrode material with higher activity and stability. Besides, the objective of present study is also to identify the transport parameters like charge localization length, activation energy, *d.c.* electrical conductivity, most-probable hopping distance and charge hopping energy of the prepared samples of poly aniline formaldehyde copolymer at room temperature as well as at higher temperatures, for a meaningful device application.

2. Materials and methods

We have synthesized two new copolymers of aniline (*A*) and formaldehyde (*F*) in different molar proportions with acid or base catalysts by employing two different methods, where all the chemicals used were of Analytical Reagent Grade.

2.1. Solution Polymerization of Aniline and Formaldehyde in 1:2 molar proportions:

Mixture of 1 mole aniline (4.56ml) and 2 mole formaldehyde of 37% (3ml) were taken in a round bottom flask, and then 2M HCl (6 ml) and 2-3 porcelain pieces were added. These mixture were refluxed in an oil bath at

maintained temperature 120ºC ± 2ºC for 3 hours with constant stirring until the resinous mass yielded of dark brown color in poly condensation process. It was washed with cold water, dried, and powdered repeatedly and this powder was lastly washed with hot water to remove un-reacted monomers. The air dried copolymer resin was extracted with solvent either to remove unwanted traces of monomers which might be present along with aniline-formaldehyde co-polymer (AF). Now, it was purified by dissolving in 8% NaoH, re-filtered and re-precipitated by gradual drop wise addition of (1.1 v/v) conc. HCl using as acid catalyst. So obtained copolymer-resinous yield was filtered, washed with hot water, dried in air, powdered and kept in vacuum over anhydrous $CaCl_2$. Yield of resin was nearly 65%. In the present work, the sample abbreviation used for the sample prepared by this method is as AF-3.

2.2. Direct Blending by Chemical Synthesis of Aniline and Formaldehyde in 1:1 molar proportions:

In this method, formaldehyde in one molar ratio is slowly added to the solution of one molar aniline which is dissolved in aqueous solution of hydrochloric acid at low temperature. Stirring of the solution continued for 1-12 hours. The time of initial coloration on mixing of the reactants depends on temperature and the protonic acid used. The precipitated emeraldine salt is filtered, washed with water and then methanol. It is then dried in oven at 70-80ºC for 8 hours. In this way, we have prepared another sample of AF (1:1) by direct chemical synthesis method, using an acid catalyst. The yield of the copolymer depends upon the quality in molar ratio (1:1) of the reactants. In the present work, the sample abbreviation used for the sample prepared by this method is as AF-1.

To prepare the pellet of both these synthesized samples, the copolymer powder was well dried, grounded and pressed in 11mm steel die-set by applying 7000 $kg.cm^{-2}$ pressure with the help of hydraulic compressor. To maintain the good contacts, both the sides of pellet are thin layered by colloidal graphite in acetone. The *d.c* electrical conductivity of the samples (AF-1 and AF-3) measured by four probe arrangement, purchased from SES Instrument Pvt. Ltd. Roorkee, India (model No. DFP-RM, Rev. 2/6/10). A PID controlled over unit, model PID-200 is used for stable and accurate temperature control, in which set displayed on 3½ digit DPM through selector switch, with measurement accuracy ±0.5ºC (typical). The resolution of used constant current source is 10µA with measurement accuracy ±0.25% while the resolution of low current source is 1µA with measurement accuracy ± 0.25%. The digital micro voltmeter is also very sensitive having resolution 1µV with measurement accuracy ±0.2% in this four probe equipment.

3. Results and Discussion

The electrical conductivity ($\sigma = 1/\rho$) varies with absolute temperature and temperature dependence of conductivity was fitted to Arrhenius type equation known by band theory [7];

$$\sigma_T = \sigma_0 \, e^{-(Ea/2kT)} \quad \text{..... (1)}$$

Where σ_T = electrical conductivity at temperature T, σ_o= electrical conductivity at absolute zero, E_a = activation energy thermal conduction of sample, k = Boltzmann's constant.

The logarithmic form of equation (1) with the extrapolation as straight line equation enable us to calculate the slope of straight line, and the activation energy E_a of thermal conduction can be calculated from this calculated slope. The measured values of 'σ' for sample AF-1 and AF-3 are plotted semi-logarithmically as a function of reciprocal of temperature term under four different theories, shown in Fig.1 (a-d) and Fig.2 (a-d). It is clear from the graphs, the electrical conductivity increases with temperature and Arrhenius behaviour shown as a good approximation with the band theory, so the conduction mechanism in these copolymers could be explained by well-known energy band theory. Since the organic polymers are generally insulators, it means mobile charge carrier shouldn't be readily available here in appropriate numbers to participate the conduction mechanism. If these charge carriers may be created by partial oxidation (*i. e.* by removal of electron from completely filled valance band) or partial reduction (*i. e.* by adding of electrons to empty conduction band) with the help of appropriate oxidant or reluctant, then there is a possibility to observe

the conduction behaviour in these organic polymers.

However, many investigators were suggested [8-10] the various other modes for electrical conduction involving different mechanism (other than the band theory) such as hopping, involvement of grain boundary barriers, tunnelling conduction by carriers *etc.* For example:

Electrical conductivity was explained on the basis of hopping of electrons and as the function of temperature [8] by Greave's equation (2);

$$\sigma T^{1/2} = e^{-BT^{1/4}} \quad \ldots\ldots\ldots (2)$$

Where B is a constant related to variable range hopping mechanism for conduction of electrons [8].

According to *Matare etal.* [9], conduction mechanism was also explained as a function of temperature including grain boundary barriers and deduced by the following expression;

$$\sigma = AT^{1/2} e^{-Ea/kT} \quad \ldots\ldots\ldots (3)$$

Where A is a const. and E_a is height of potential barrier.

Zeller [10] also reported the tunneling conduction mechanism and expressed it by following equation;

$$\sigma_T = \sigma_0 \, e^{-A/T^{1/2}} \quad \ldots\ldots\ldots (4)$$

In the present article, plots of log σ Vs 1000/T are presented for synthesized samples AF-1 and AF-3 of poly aniline formaldehyde to evaluate their transport properties with the help of temperature dependence behavior of *d.c.* electrical conductivity. These plots are showing the variation of d.c. electrical conductivity with temperature-term based on a particular theory [7-10] discussed above, i.e. band theory, hopping theory, grain boundary theory and tunneling conduction theory depicted in Fig. 1 (a - d) and Fig. 2 (a - d). In fact, it is observed that graphs shown in Fig.1 (b) and Fig.2 (b) exhibit better linearity for both the samples AF-1 and AF-3 as compared to the graphs by other theories, implies that the electrical conduction is these copolymers are predominantly occurred by hopping mechanism. The polarans are hopping from state to state and act as charge carriers in these two synthesized copolymers of poly aniline formaldehyde amino resin

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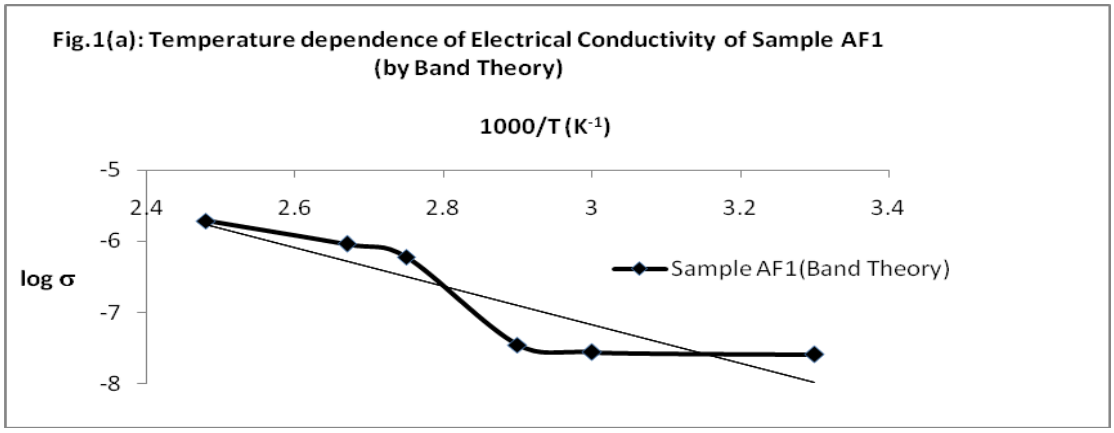

Fig. 1(a). Temperature dependence of Electrical Conductivity of Sample AF-1 by Band Theory

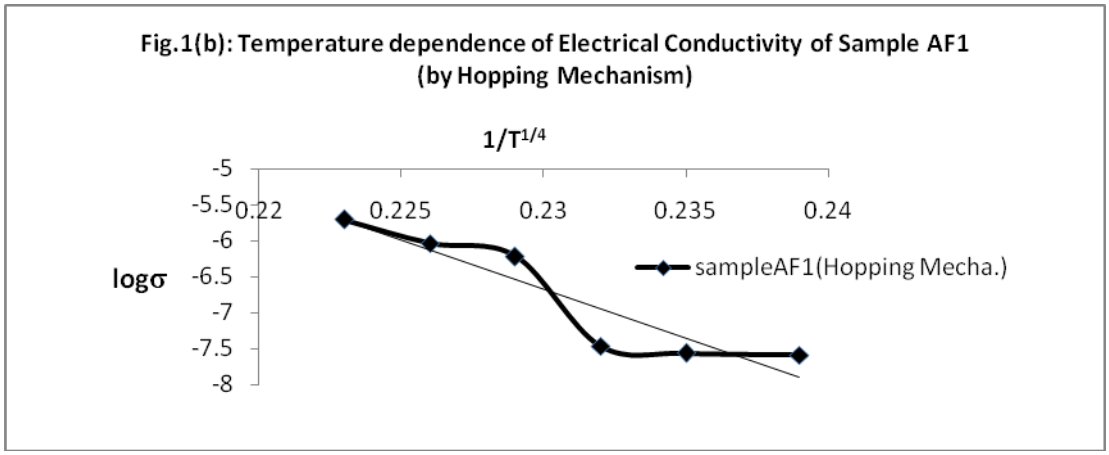

Fig. 1(b). Temperature dependence of Electrical Conductivity of Sample AF-1 by Hopping Theory

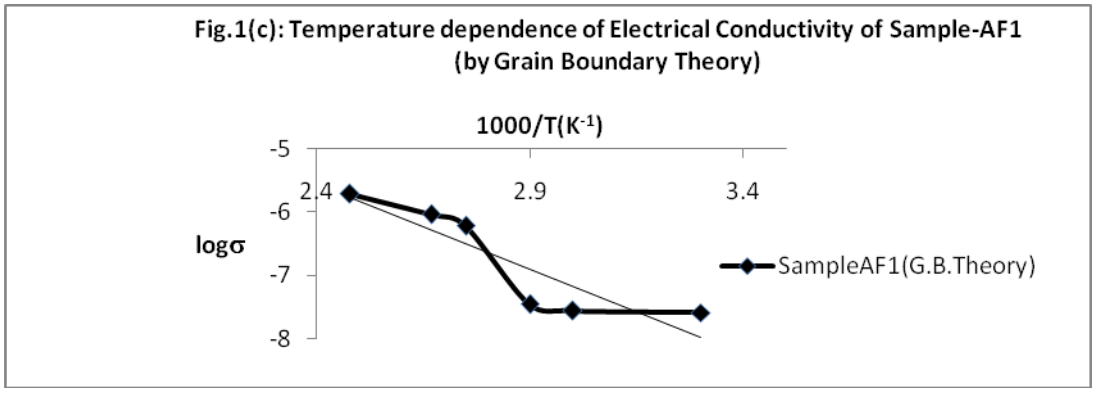

Fig. 1(c). Temperature dependence of Electrical Conductivity of Sample AF-1 by Grain Boundary Theory

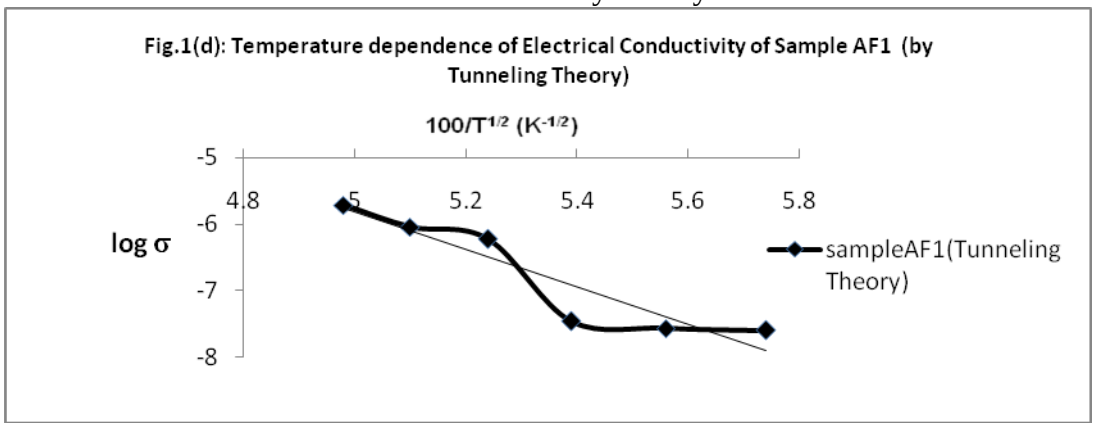

Fig. 1(d). Temperature dependence of Electrical Conductivity of Sample AF-1 by Tunneling Theory

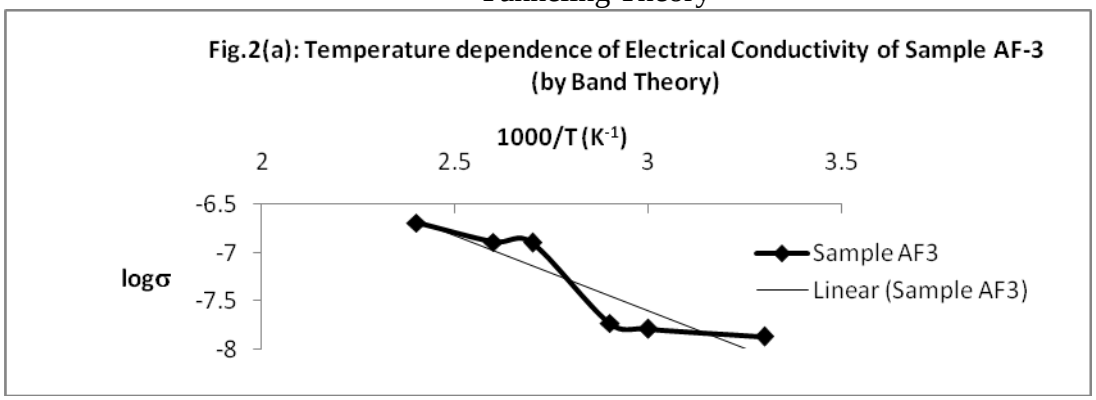

Fig. 2(a). Temperature dependence of Electrical Conductivity of Sample AF-3 by Band Theory

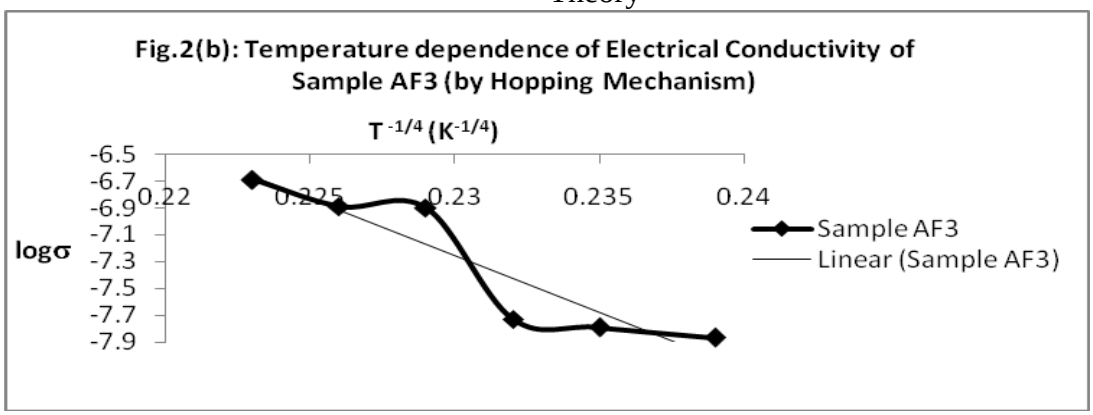

Fig. 2(b). Temperature dependence of Electrical Conductivity of Sample AF-3 by Hopping Theory

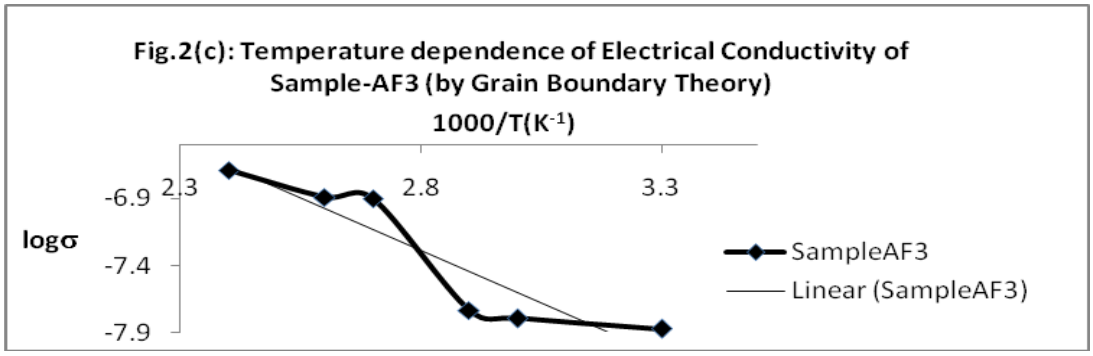

Fig. 2(c). Temperature dependence of Electrical Conductivity of Sample AF-3 by Grain Boundary Theory

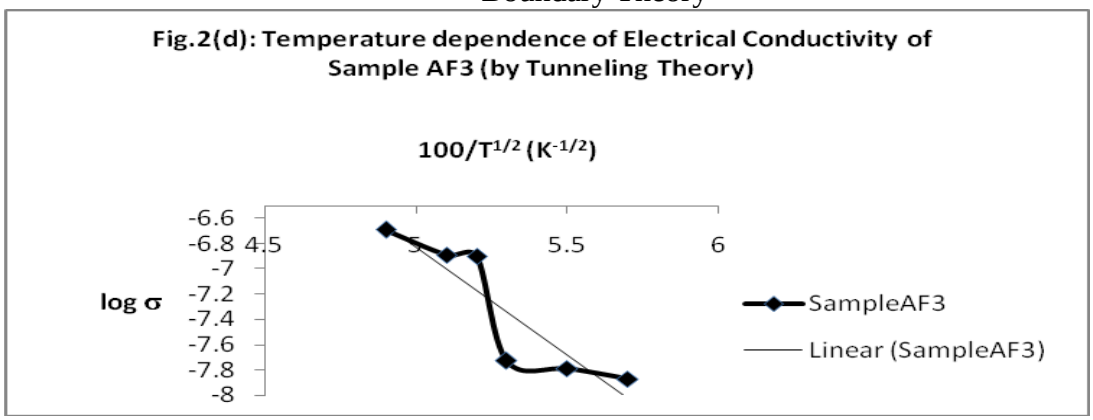

Fig. 2(d). Temperature dependence of Electrical Conductivity of Sample AF-3 by Tunneling Theory

The transport phenomenon of newly synthesized poly aniline formaldehyde copolymers can be evaluated by findings various parameters like *d.c.* electrical conductivity, activation energy, charge localization length, most probable hopping distance and charge hopping energy. These transport parameters *i.e. d.c.* electrical conductivity (σ), activation energy of thermal conduction (E_a), charge localization length (α^{-1}), most probable hopping distance (R) and charge hopping energy (W) for synthesized samples AF-1 and AF-3 of poly aniline formaldehyde copolymers are calculated from the hopping theory [8] as well as from the band theory [7] at room temperature, listed in Table-1.

TABLE-1

Polymer	**σ (Scm^{-1}) (from 303 to 403)^oK**	**E_a**	**T_o (^oK)**	**α^{-1} (nm)**	**R (nm)**	**W (eV)**
Sample **(AF1)**	$2.569x10^{-7}$ to $0.1926x\ 10^{-5}$	8.84×10^{-3} (H. T.)	2633.384 (H. T.)	5.566 (H. T.)	4.102 (H. T.)	0.05613 (H. T.)
		3.15×10^{-3} (B. T.)	333.756 (B. T.)	43.93 (B. T.)	11.52 (B. T.)	0.007 (B. T.)
Sample **(AF3)**	$0.1337x10^{-7}$ to $0.2016x\ 10^{-6}$	0.145×10^{-3} (B. T.)	0.7128 (B. T.)	$2.059x10^{4}$ (B. T.)	249.1 (B. T.)	$1.517x10^{-5}$ (B. T.)
		$11.392x10^{-3}$ (H.T.)	4372.95 (H.T.)	3.353 (H.T.)	3.183 (H.T.)	0.0931 (H.T.)

H.T. – Hopping Theory, B.T. – Band Theory

As almost all the plots of log σ *Vs* temperature term (1000/T *etc.*) according to various theories discussed above, are found to be linear where the *d.c.* electrical conductivity is in increasing

manner over a wide range of temperature [Fig. 1(a-d) & Fig.2(a-d)], point toward the semiconducting nature of these synthesized resinous co-polymers. Moreover, the calculated values of energy gap (E_a) are also substantiating the semiconducting nature of these poly-aniline-formaldehyde amino resins AF-1 and AF-3. The lesser values of probable hopping distance (R) for both the samples at room temperature suggested the dominant role of tunneling effects in the conductivity will be possible when thermal excitation fails to support hopping at higher temperatures. The evaluated values of charge localization length (α^{-1}) and charge hopping energy (W) for synthesized samples AF.1 and AF.3 of poly aniline formaldehyde copolymers are also corroborating this suggestion.

4. Conclusions

Two new copolymer-resins of aniline and formaldehyde are synthesized by condensation (AF-3) and direct chemical blending (AF-1) in the presence of 2M HCl as a catalyst. The *d.c.* electrical conductivity of AF-1 copolymer-resin varies from 2.569×10^{-7} to 0.1926×10^{-5} Siemens cm^{-1} in the temperature range from room temperature 303ºK to 403ºK. The *d.c*. electrical conductivity of AF-3 copolymer-resin varies from 0.1337×10^{-7} to 0.2016×10^{-6} Siemens cm^{-1} in the temperature range from room temperature 303ºK to 403ºK. The plots of log σ *Vs* temperature according to band-theory, hopping theory, grain-boundary theory and tunneling theory are found to be linear in the temperature range under study, indicates that the Wilson's exponential law $\sigma = \sigma_0 \exp(-E/kT)$ is obeyed. The compared values of various transport parameters such as activation energy of thermal conduction (E_a), charge localization length (α^{-1}), most probable hopping distance (R) and charge hopping energy (W) for synthesized samples AF-1 and AF-3 calculated according to band theory and hopping theory suggest that the charge transfer is temperature dependent one transpire by hopping and tunneling, between metallic or highly conducting islands embedded in an insulating matrix.

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