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Synthesis, Spectral Characterization, Thermal Studies and DC Electrical Conductivity of Poly[di(2,5-dimercapto-1,3,4-thiadiazole)-Platinum (IV)] Complex

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[Poly[di(2,5-dimercapto-1,3,4-thiadiazole)]-Pt(IV)] complex [PDMT-Pt(IV)] was prepared by the reaction 2,5-dimercapto-1,3,4-thiadiazole with hydrogen hexachloroplatinate (IV) hydrate in a 2:1 molar ratio in mixture of methanol and water (1:8) under reflux for 24 h. The complex was characterized by elemental analyses, electronic spectra, FTIR spectroscopy, magnetic susceptibility, thermal analyses (TGA and DTA) and X-Ray diffraction. The results obtained are consistent with the proposed structure. The DC electrical conductivity variation with a temperature in the range 300–500 K was studied after annealing for 24 h at 100ºC and after doping with 5% I_2, for comparison. The complex behaved as a typical semiconductor with regard to an increase of conductivity with heat. The annealed and doped complex gave a DC electrical conductivity of 10^{-9} S cm^{-1} and 5.6×10^{-9} S cm^{-1} at high temperature, respectively. The DC electrical conductivity behavior was interpreted using the band theory.

Keywords: poly[di(2,5-dimercapto-1,3,4-thiadiazole)-platinum(IV)] complex; 2,5-dimercapto-1,3,4-thiadiazole; DC electrical conductivity; doping, thermal analysis; X-ray diffraction; activation energy

1 Introduction

The successful commercial applications of the polymeric materials and electrically conducting polymers have attracted the attention of researchers for decades and triggered intensive research in protective coatings, semiconductors, catalysis and analytical applications (1–4). The 2,5-dimercapto-1,3,4-thiadiazole (DMT) and metal-macromolecule complexes attracted the attention of researcher for decades (5–11).

The polymer-platinum complex under study is interesting for various reasons. For example, the presence of donor atoms such as N and S in the polymer backbone contributes greatly to its thermal and environmental stability and enhances the electrical conductivity (12). Other important features include the nature of palladium-sulfur bonding interaction and the biological activity of this material (13–15).

The objective of this study is: i) to synthesize and characterize poly[di(2,5-dimercapto-1,3,4-thiadiazole)-Pt(IV)] complex, ii) to present a comparative study of the DC electrical conductivity of the polymer complex and its change with temperature at 300–500 K, in the intrinsic and doped states, iii) to investigate the thermal properties of the polymer metal complex using TGA and DTA, iv) to calculate the activation energies (Ea) from the DC electrical conductivity and thermal analyses.

2 Experimental

2,5-Dimercapto-1,3,4-thiadiazole was purchased from Aldrich chemicals and was recrystallized twice before use. The hydrogen hexachloroplatinate(IV) hydrate ($H_2PtCl_6 \cdot xH_2O$) was used as received from BDH. The solvents were reagent grade: 99% absolute ethanol, DMF (BDH, Analar).

2.1 Instrumentation

The FTIR spectra were recorded using a KBr disc on a Shimadzu 8101 FTIR Spectrophotometer. The inherent viscosity of the polymer-metal complex was measured in DMSO using a suspended level Cannon-Ubbelohde viscometer. The melting points were measured on an electrothermal melting point apparatus. The elemental (CHNS) analyses were performed on an Elemental Analyses system GmbH VARIOEL $V_{2.3}$ 1998 CHNS Mode. The thermal analyses (TGA and DTA) were carried out on a Shimadzu

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TGA-50H and a Shimadzu DTA-50 at 23 to 600°C under 20 ml nitrogen per minute and a heating rate of 10°C per minute. The UV and visible absorption spectra were measured in DMSO using a PU 8800 UV-Visible Philips Automatic Scanning Spectrophotometer. The magnetic susceptibility was determined at room temperature by the Gouy Method. The X-Ray diffraction was carried out on a Bruker Axs Da Advance, Germany. The electrical conductivity measurements were measured on a Keithley Picoammeter/Voltage Source Model 6487. Doping and annealing were performed as described previously (16).

2.2 Synthesis of Poly[di(2,5-dimercapto-1,3,4-thiadiazole)-Pt(IV)] Complex (PDMT-Pt)

A solution of ($H_2PtCl_6 \cdot xH_2O$) (1 gm, 2.5 mmol) in a mixture of methanol (25 ml) and water (3 ml) was added to a solution of 2,5-dimercapto-1,3,4-thiadiazole (0.737 gm, 5.0 mmol) in methanol (25 ml). The mixture was refluxed with stirring for 24 h under a thin stream of nitrogen gas. The precipitated polymer was separated by filtration, then washed several times with hot ethanol and dried in the air for 24 h.

2.3 Thermal Analyses of the Poly[di(2,5-dimercapto-1,3,4-thiadiazole)-Pt(IV)] Complex

The thermal decomposition behavior of the poly[di(2,5-dimercapto-1,3,4-thiadiazole)-Pt(IV)] complex was investigated by thermogravimetric analysis (TGA).

For each step in the decomposition sequence, the parameters were determined as explained in the literature (17). The activation energy E_a was calculated from the slope of a plot of the Coats-Redfern equation (18) for the reaction order $n \neq 1$, which when linearized for a correctly chosen n yields the activation energy from the slope;

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log\frac{ZR}{qE}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.303RT}$$

where: α = fraction of weight loss, T = temperature (K), n = order of reaction, Z = pre-exponential factor, R = molar gas constant, E_a = activation energy and q = heating rate. The order of reaction (n) is the one for which a plot of the Coats-Redfern expression gives the best straight line among various trial values of n that are examined, i.e., by trial and error for various trial values of n, estimated by the Horovitz-Metzger method (19).

2.4 The DC Electrical Conductivity Measurements of the Poly[Di(2,5-dimercapto-1,3,4-thiadiazole)-Pt(IV)] Complex

Samples of 200 mg were thoroughly ground and pressed into circular discs, 12.5 mm in diameter and 0.8 to 1 mm thick under 10^4 kg cm^{-1} pressure. To ensure good conductivity contact, the two surfaces of the disks were covered with conducting graphite. The electrical conductivity measurements were performed under vacuum (10^{-2}–10^{-4} mm Hg). The evacuated cryostat was placed inside a heating coil furnace, which could reach a temperature of 500 K. The DC electrical conductivity of the polymer was systematically measured while increasing the ambient temperature of the samples. All samples showed a linear behavior between the voltage applied (less than 30 V) and the current. In this study, the voltage was kept at 10 V. The system was allowed to stabilize for an hour prior to taking the readings; this was to eliminate any accumulated electrostatic charges. The rate of temperature change with time was kept to a minimum (2°C min^{-1}) to ensure an equilibrium state as far as possible.

The sample resistance-measuring device used was a picoammeter. The doped polymer was prepared by mixing 5% (w/w) I_2 with 200 mg of the polymer, then ground well and pelleted. More experimental details are given elsewhere (20, 21).

3 Results and Discussion

3.1 Synthesis and Characterization

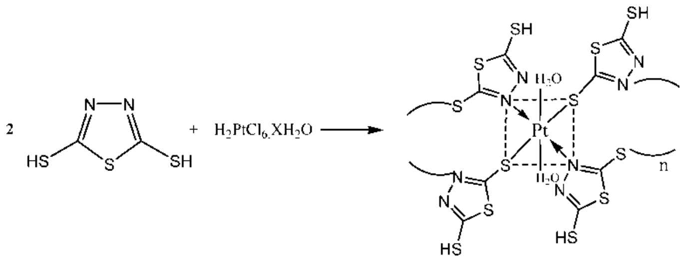
The PDMT-Pt was prepared by the reaction of 2,5-dimercapto-1,3,4-thiadiazole (2 mole) with $H_2PtCl_6 \cdot xH_2O$ (IV) (1 mole). The Pt(IV)-polymer complex is formed (Scheme 1). The PMDT-Pt is soluble in DMSO and insoluble in most other organic solvents, so that all attempts to recrystallize PDMT-Pt (IV) complex was unsuccessful. The yield is 34%. The melting point is >300°C. Elemental analyses as calculated for $C_4H_2N_4S_6Pt.2H_2O.2MeOH$ (Mol. wt. = 592.9): C, 12.14%; H, 2.38%; N, 9.44%; S, 32.41%. Found: C, 12.50%; H, 2.1%; N, 9.50%; S, 33.1%. The inherent viscocity of the polymer-metal was found to be 0.48 dl/g showing a fairly low molecular weight.

3.2 FTIR Spectra

Figure 1 shows the FTIR spectra of the DMT and PDMT-Pt. The main FTIR bands are summarized in Table 1. The assigned absorption bands are reasonably consistent with the suggested structures.

The starting material (DMT) showed many bands and broadband absorptions in the 3100–1800 cm^{-1} range. These bands are attributed to overtones and combinations, except two bands that appeared at 2519 and 2485 cm^{-1}, corresponding to the ν_{as}(S-H) and ν_s(S-H), respectively. The broadening of these features might be due to the presence of extensive hydrogen bonding of SH groups (22).

In the case of DMT, the stretch ν(S-H) weak band showed up weakly at (2491 cm^{-1}) and the deformation antisymmetric (δ_{as}) (C-SH) in-plane (ip) and deformation symmetric (δ_s) $(C\text{-}SH)_{ip}$ were noted also as weak bands at (948 cm^{-1}, 923 cm^{-1}), consecutively (10). All these bands showed up as very weak bands in the products or disappeared. The noticeable shift in position of the ν_{as}(C=N), ν_s(C=N) and δ ring for the PDMT-Pt compared to DMT, is as



Sch. 1. The synthesis of the poly[di(2,5-dimercapto-1,3,4-thiadiazole)-Pt(IV)] complex.

assurance of the formation of the polymeric product. The bands observed in 440–500 cm^{-1} region are assignable to ν(M-N) (23).

The adsorbed water absorption bands appeared at 3000–3500 cm^{-1} for $\nu(H_2O)$ and the bending (H_2O) around (1630 cm^{-1}) (24).

3.3 *The Electronic Spectra*

The main UV-visible absorptions of poly[di(2,5-dimercapto-1,3,4-thiadiazole)-Pt(IV)] complex and DMT are summarized in Table 2.

Figure 2 illustrates the electronic spectra of the DMT and PDMT-Pt. In the present study, the PDMT-Pt(IV) complex is diamagnetic. The PDMT-Pt showed three, π-π^* (K-band) λ_{max} at 213, 233 and 256 nm (47000, 43000 and 39000 cm^{-1}) and another two n-π^* (R-band) at λ_{max} 338 and 420 nm (29500 and 23800 cm^{-1}).

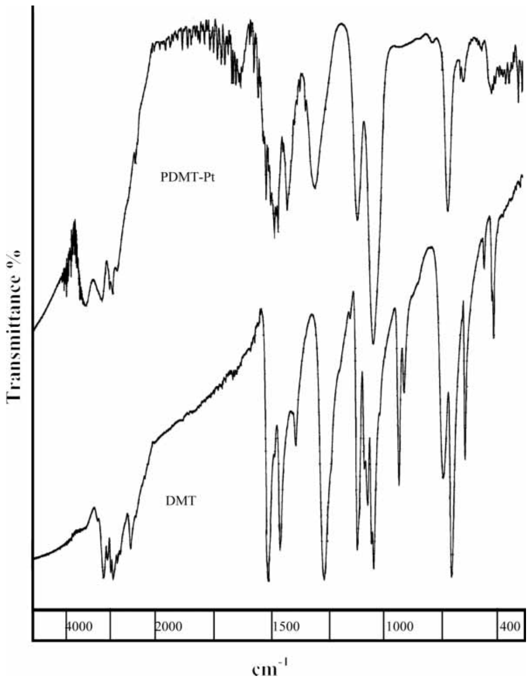


Fig. 1. The FTIR spectra of the DMT and PDMT-Pt complex.

Solutions of DMT in DMSO feature a strong band at ca. 355 nm because of the n → π^* transition for the azomethine function with shoulders at higher and lower energy. This value showed a great shift in the polymer complex to 338 nm (29500 cm^{-1}). One absorption band observed at ca. 270 nm (37040 cm^{-1}), is assigned to the π-π^* intraligand electron transition, N=C=S. This band shifted in the case of the polymer complexation to 256 nm (39000 cm^{-1}), revealing involvement of the C=S group in polymer complexation (25).

The PDMT-Pt (IV) complex must be octahedral. Its geometry is supported by the electronic spectra. The ground state of platinum(IV) belongs to a d^6 system (26, 27). The band at ca. 420 nm (23800 cm^{-1}) is assignable to a combination of ligand sulphur → metal charge-transfer ($L\pi \rightarrow M_{CT}$) and d–d bands (28).

3.4 *Thermal Analysis*

Thermogravimetric analysis is a very useful method to study the thermal decompositions of solid substances. The thermal behavior of PDMT-Pt complex was followed up to 600°C in nitrogen flux. For each step in the decomposition sequence, it was possible to determine the following thermal parameters; T_i, T_f, TDTG, Δm and Ea, which are summarized in Table 3.

The TGA and DTG curves (Figure 3) obtained depict the decrease in sample mass with linear increase in treatment temperature. In the present investigation, the heating rate was fixed at 10°C min^{-1}. For the 23–200°C range, T_{max} is at 45°C from DTG curve, indicating the loss of a half molecule of methanol from PDMT-Pt (29), which means that it is stable in that range (first step). The range 200–475°C showed two steps as seen clearly from DTG curve.

In the 200–426°C range (second decomposition step), a mass loss of about 50.19% occurred. Qualitatively, this reflects the loss of 1.5 moles of methanol, 2 moles of H_2O

Table 1. The main FTIR bands of the poly[di(2,5-dimercapto-1,3,4-thiadiazole)-Pt(IV)] complex

	DMT	PDMT-Pt
ν(S-H)	2491 w	2491 vvw
ν_{as}(C=N)	1512 s	1512 w
ν_s(C=N)	1457, 1393 m	1478,1461, 1427
δ ring	1273 s	1303
δ $(CNNC)_{ip}$	1128, 1098 w	1119
ν(N-N)	1085, 1055 m	1055
δ_{as} $(C\text{-}SH)_{ip}$	954 w	948 vvw
δ_s $(C\text{-}SH)_{ip}$	923 w	923 vvw
ν_{as}(C-S)	756,722 s	730
ν_s(C-S)	662 vw	662
ν_{as}(C-S′)	585 w	575 w
ν_s(C-S′)	542 vw	541
H_2O Bend. H_2O	—	3453 vw 1623 w

v, very; w, weak; m, medium; ν, stretch; δ, deformation; s, symmetric; as, antisymmetric; ip, in-plane, bend.; bending.

Table 2. The main UV-visible absorptions of poly[di(2,5-dimercapto-1,3,4-thiadiazole)-Pt(IV)] complex

	π-π^*			n-π^*		
Material	ν_{max} nm	ν_{max} (cm^{-1})	E$_a$(eV)	ν_{max} nm	ν_{max} (cm^{-1})	E$_a$(eV)
DMT	220	45500	5.6	355	28200	3.5
	230	43500	5.4			
	270	37040	4.6			
PDMT-Pt	213	47000	5.8	338	29500	3.7
	233	43000	5.3	420	23800	3.0
	256	39000	4.9			

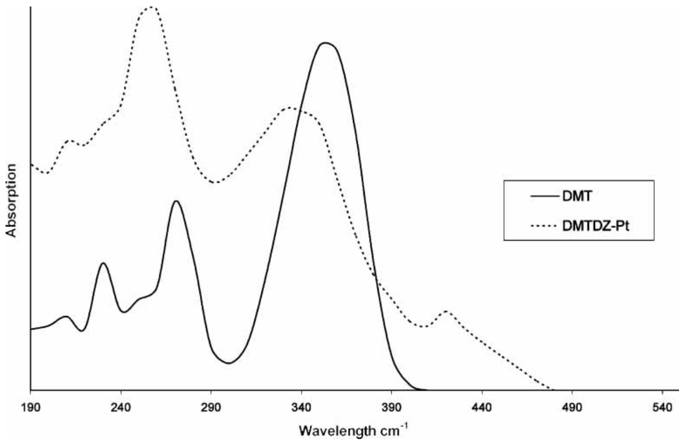


Fig. 2. The main UV-visible absorptions of poly[di(2,5-dimercapto-1,3,4-thiadiazole)-Pt(IV)] complex.

and 42.4% of the backbone. The third decomposition step in the range 426–475°C is due to the loss of 18% from the backbone. The degradation of the metal complex was complete below 475°C, and the final residue was corresponding to platinum metal as typically seen in the literature (30, 31).

The details of decomposition and the associated activation energies are summarized in Table 3. Figure 3 illustrates the TGA and DTG curves of poly[di(2,5-dimercapto-1,3,4-thiadiazole)-Pt(IV)] complex and the insert is the DTA in the temperature range studied in the DC electrical conductivity.

3.5 X-Ray Diffraction Patterns

The direct method of investigation of the crystallinity or amorphous behavior of a polymer is the X-ray diffraction analyses (32). The X-ray diffractograph of the PDMT-Pt was determined at room temperature in the region $2\theta = 10^\circ - 80^\circ$ and is illustrated in Figure 4. The X-ray diffractograph indicated that the PDMT-Pt is amorphous.

3.6. DC Electrical Conductivity

Figure 5 displays the DC electrical conductivity vs. $1/T$ for the annealed and doped (5% I_2) poly[di(2,5-dimercapto-1,3,4-thiadiazole)-Pt(IV)] complex. The DC electrical conductivity of the PDMT-Pt complex was measured vs. $1/T$ in the 300–500 K range. The effect of the annealing and the acceptor doping with 5% I_2 is measured and compared. The annealed and doped PDMT-Pt showed four and two stages, respectively. Each step has its own activation energy. The PDMT-Pt responded to heat by an increase in the DC electrical conductivity and behaved almost similarly; this is a typical behavior of semi-conductor materials (33).

The enhancement of DC electrical conductivity of annealed and doped PDMT-Pt started at ambient temperature at about 10^{-14} S cm^{-1}. The annealed and doped PDMT-Pt gave a DC electrical conductivity at high temperature of 10^{-9} S cm^{-1} and 5.6×10^{-9} S cm^{-1}, respectively. The highest DC electrical conductivity at ambient temperature is noticed for the annealed PDMT-Pt. However, the highest DC electrical conductivity at higher temperature is noticed for the doped PDMT-Pt. The acceptor dopant (I_2) does not

Table 3. The thermal gravimetric data of poly[di(2,5-dimercapto-1,3,4-thiadiazole)-Pt(IV)] complex

	TGA						
Step no.	Wt. Loss % found (calcd.)	T$_i$/°C	T$_f$/°C	T$_{DrTGA}$	Res. % found (calcd.)	Ea kJmol^1 (Ea eV)	React
1st	2.826 (2.7)	23	200	48	97.172 (97.3)	138.5 (1.44)	0.5 CH_3OH
2nd	50.193 (49.4)	200	426	340	46.979 (47.9)	90.13 (0.93)	1.5 CH_3OH 2 H_2O 42.4 % bb
3rd	14.384 (14.87)	426	475	447	32.594 (33.03)	663 (6.87)	18 % bb

bb, backbone.

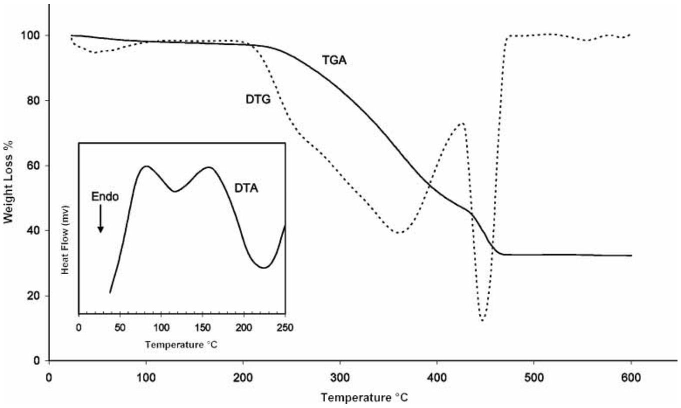


Fig. 3. The TGA and DTG curves of the poly[di(2,5-dimercapto-1,3,4-thiadiazole)-Pt(IV)] complex. The insert is the DTA in temperature range studied in the DC electrical conductivity.

show any notable features in DC electrical conductivity. This may be attributed in the case of doping with acceptor I_2 to its role in decreasing in the crystallinity in this configuration. Furthermore, this material has metal in its backbone. Thus, this material is doped internally (34), and the external doping would not enhance the DC electrically conductivity much (35).

3.7 *Activation Energies*

Table 4 summarizes the calculations of the bulk activation energies (E_a) at different temperature ranges for all the segments of the curves of the annealed and doped PMDT-Pt. The carriers available for the DC electrical conductivity are electrons and holes.

The annealed PDMT-Pt gave four segments, while the doped PDMT-Pd gave two segments.

The activation energy (E_a) calculated from the electrical conductivity measurements (log σ vs. T^{-1}) curves by the Arrhenius equation, $\sigma = \sigma_{\circ} \exp - \Delta E/kT$, where ΔE is the activation energy (related to the gap energy), k is the Boltzmann constant, and T is the absolute temperature.

All these segments are due to physical reactions (phase transitions or chain conformation) as shown in DTA. These are in accordance with the small peaks near these ranges as a T_i or T_{max} in the DTA, which does not correspond to weight loss in the TGA (36). Consequently, there is some kind of phase transition across this specific temperature (20).

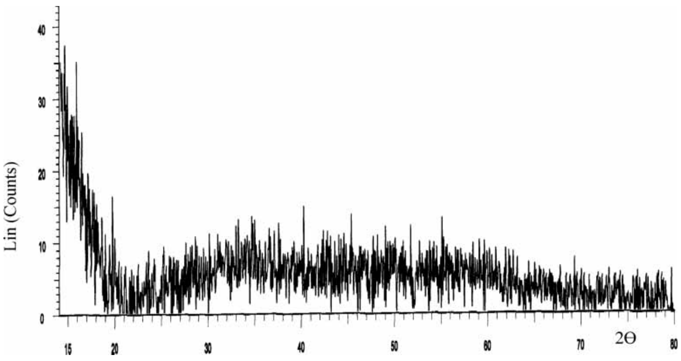


Fig. 4. X-ray diffraction patterns of PDMT-Pd.

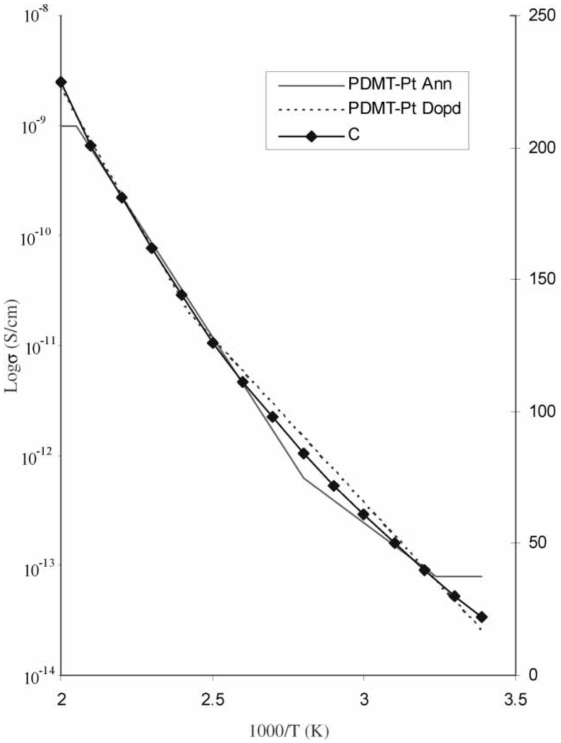


Fig. 5. The DC electrical conductivity vs. 1/T of the annealed and doped (5% I_2) poly[di(2,5-dimercapto-1,3,4-thiadiazole)-Pt(IV)] complex.

Figure 6 shows the energy schematic model based on the band theory. In this case, the bulk energy gap

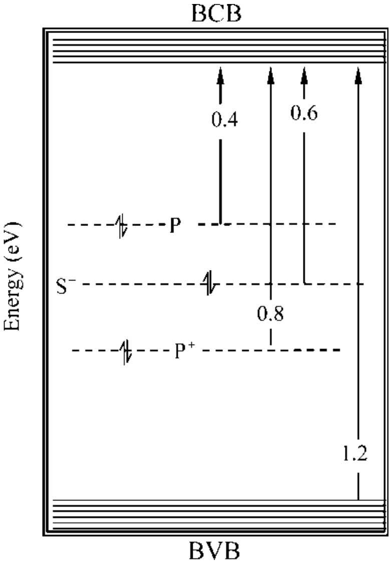


Fig. 6. The proposed energy schematic model based on the band theory of PDMT-Pt.

Table 4. The calculations for the bulk activation energies (Ea) at different temperature ranges of annealed and doped PDMT-Pt (IV) complex

Polymer-metal complex	Annealed (100°C/24 h)			Doped/annealed (5% I_2)		
	T(°C)	Ea eV		T(°C)	Ea eV	
PDMT-Pt	22–35	0.0	R	22–141	0.6	S
	35–84	0.4	P−	141–225	1.2	VB
	84–214	0.8	P+			
	214–225	0.0	R			

(BEG) is about 1.2 eV. This is the highest activation energy obtained.

For the annealed PDMT-Pt, the first segment is due to recombination or annihilation (R), which is 0.0 eV. The second segment (35–84°C), is due to excitation from the upper level of negative polaron (P^-), which is ~0.4 eV. The third segment (84–214°C) is due to excitation from the lower level of positive polaron (P^+), which is ~0.8 eV. The fourth segment is due to recombination or annihilation (R), which is 0.0 eV.

For the doped PDMT-Pt, the first segment (22–141°C), is due to soliton (S^-) level excitation (i.e. in the middle of (BEG) (37)) which is about 0.6 eV. The second segment (141–225°C) is due to the excitation from the bulk valance band (BVB), which is ~1.2 eV.

4 Conclusions

The following points can be concluded from this work:

1. Reaction of the 2,5-dimercapto-1,3,4-thiadiazole with $H_2PtCl_6 \cdot xH_2O$ formed a polymer-metal complex of the type $[ML_{2.}2H_2O]_n$. Its chemical and physical properties are studied.
2. The correlations between CHNS analysis, TGA, DTA, X-ray diffraction and DC electrical conductivity for the PDMT-Pt (IV) complex were followed.
3. The PDMT-Pt (IV) complex is thermally stable up to 500 K.
4. The electrical conductivity of the annealed and doped PDMT-Pt (IV) complex increased with increasing temperature. This is mainly due to the variation of the carrier concentration with temperature as in the case of typical semiconductors.
5. The PDMT-Pt (IV) complex has a metal in its backbone, thus this material is doped internally, so the annealed and doped PDMT-Pt (IV) complex are similar in the DC electrical conductivity at ambient and higher temperature.

5 Acknowledgments

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