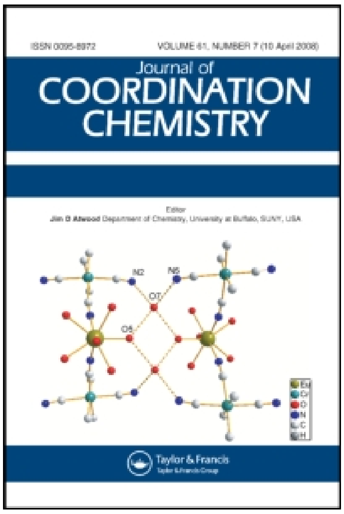

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Host-guest supramolecular polymers constructed of aniline derivatives and three-dimensional coordination polymers [(n-$Bu_3Sn)_2(R_3Sn)Fe(CN)_6$]_n, R = n-Bu or Ph

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Host–guest supramolecular polymers constructed of aniline derivatives and three-dimensional coordination polymers $[(n\text{-Bu}_3\text{Sn})_2(\text{R}_3\text{Sn})\text{Fe(CN)}_6]_n$, R = *n*-Bu or Ph

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The straightforward self-assembly reaction of R_3Sn^+ and $[Fe(CN)_6]^{3-}$ affords three-dimensional (3-D) coordination polymers $[(n\text{-Bu}_3\text{Sn})_2(\text{R}_3\text{Sn})\text{Fe(CN)}_6]_n$, R = *n*-Bu(I) or Ph(II). The architecture of these coordination polymers is closely related to zeolite and acts as a host with wide internal cavities or channels capable of encapsulating voluminous organic compounds. Aniline derivatives acting as guest are encapsulated within the cavities of the 3-D-polymeric hosts **I** and **II** by tribochemical reaction producing host–guest supramolecular polymers. The structures and physical properties of these hosts and their host–guest systems were investigated by elemental analysis, X-ray powder diffraction, IR, UV-vis, EPR, and magnetic measurements. The morphology of these systems was examined by scanning electron microscopy (SEM). The interesting feature of these host–guest supramolecular polymers is the enhanced electrical conductivities over those of the 3-D-coordination polymeric hosts upon encapsulation of conductive polymers within their cavities.

Keywords: Coordination polymers; 3-D-Supramolecular polymers; Host–guest systems; Self assembly; Encapsulation; Tribochemical reaction

1. Introduction

Coordination polymers or metal-organic coordination networks are metal–ligand compounds that extend infinitely into 1-D, 2-D, or 3-D, respectively via more or less covalent metal–ligand bonding. In at least one extended dimension the metal must be bridged by this organic ligand ([1, and references therein] and [2]). Coordination polymers are of particular interest to mimic the structure and host–guest behavior of natural, porous systems such as zeolites. 3-D-Coordination networks can form large, robust, and mesoporous networks that closely resemble zeolites in their structure and activity [3]. Such networks are able to incorporate a large variety of guests. Organometallic coordination polymers involving cyanide-linked repeat units of the super-Prussian blue type $[(R_3Sn)_3Fe(CN)_6]_n$ (R = methyl, *n*-butyl, or phenyl) have attracted considerable attention [4–7]. The structures of these coordination polymers, confirmed by single X-ray crystal structure [4–6], are based on 3-D-network of octahedral $[Fe(CN)_6]^{3-}$ building blocks and the trigonal bipyramidal R_3Sn^+

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connecting units. The framework structures create wide parallel channels or cavities with diameters typically of *ca* 9.5 Å, in which many intercalations have been explored. Guest absorption is not the only use of coordination polymers. The ordered solid also displays interesting physical properties such as oxidative properties, which can be attributed to the presence of octahedral building blocks $[Fe(CN)_6]^{3-}$ [8], whose reduction potential remains essentially constant at *ca* 0.41 v [9]. These 3-D-coordination polymers are insulators at room temperature. Conducting polymers as matrices within the cavities of these conventional polymers make them capable of charge flow through the 3-D-network. Polyaniline (PANI) is one of the most promising conducting polymers [10–12] because of good stability, high-electrical conductivity in doped state and easy preparation by chemical [13], electrochemical [14], and photochemical methods [15]. Inorganic redox systems such as Prussian blue and related metal hexacyanoferrates with conducting polymers present composites with properties such as electrochromism ([16, and references therein] and [17]), sensing properties [18, 19], ability to mediate redox reactions [20, 21], electronic (mixed-valence electron hopping) conductivity [22], capability to store charge [23], and molecular magnetism [24]. The current study is concerned with the synthesis and structural characterization of novel 3-D-coordination polymer $[(n\text{-}Bu_3Sn)_2(Ph_3Sn)Fe(CN)_6]_n$ and its well-documented parent system $[(n\text{-}Bu_3Sn)_3Fe(CN)_6]_n$. The *in situ* intercalative oxidation of aniline derivatives within the channels of the 3-D-coordination polymers was investigated to produce host–guest supramolecular polymers.

2. Experimental

The solid materials were of reagent grade from Aldrich or Merck and were used without purification. Aniline derivatives were doubly distilled under reduced pressure before use and stored in a refrigerator.

2.1. *Preparation of the coordination polymers*

An aqueous solution of $K_3[Fe(CN)_6]$ was added to a stirred solution of $n\text{-}Bu_3SnCl$ or $n\text{-}Bu_3SnCl/Ph_3SnCl$ in $H_2O : Me_2CO$ mixture in 1 : 3 and 1 : 2 : 1 molar ratios to produce 3-D-coordination polymers **I** and **II**, respectively. The precipitates which formed immediately after mixing were filtered off and washed with water, acetone, and diethyl ether, then finally dried under vacuum at room temperature before use. The purity and identity of the coordination polymers were checked by elemental analysis, IR, UV-vis spectroscopy, and X-ray powder diffraction.

2.2. *Preparation of host–guest supramolecular polymers*

The host–guest supramolecular polymers **1–10** were obtained by tribochemical reaction of aniline derivatives and the dry freshly prepared 3-D-coordination polymers **I** and **II**, in a molar ratio of 3 : 1, in the presence of a few drops of 2M HCl solution. The rate of reaction is enhanced by slight grinding. The products were isolated, washed with ethanol, and dried under vacuum.

2.3. *Instruments*

Elemental analyses were performed on a Perkin–Elmer 2400 automatic elemental analyzer. IR spectra were recorded on a Bruker Vector 22 spectrophotometer as KBr discs. UV-vis absorption spectra were recorded on a Shimadzu 3101 PC spectrophotometer as Nujol mulls. The thermogravimetric analyses (TGA) were performed on a Shimadzu AT-50 thermal analyzer in the range 25°C up to 1000°C with heating rate 10°C/min in a nitrogen atmosphere. The X-ray diffractograms were measured on a Bruker Axs-D8 ADVANCE (target Cu-Kα with secondary monochromator). The solid powder EPR spectra were recorded on Bruker ELEXSYS E500-Germany. The magnetic susceptibility was determined with a magnetic susceptibility balance 436 Devon Park Drive (USA) using $Hg[Co(SCN)_4]$ as calibrant. The electrical conductivity was measured by the two-probe technique on discs, obtained by pressing the samples at pressure of *ca* 600 kg cm^{-2} to form a cylindrical disc of diameter *ca* 0.6 cm and thickness of *ca* 0.15 cm. The current was recorded using a Kiethly 175 A autoranging multimeter. The morphologies of the coordination polymers, authentic sample of free PANI and the host–guest system were examined using scanning electron microscopy (SEM) JEOL (JXA-840A) Electron Probe Microanalyzer-JAPAN.

3. Results and discussion

3.1. *Analytical data*

The stoichiometric ratios of the hosts and host–guest systems were calculated from the elemental analyses data (table 1). The stoichiometric ratios depend on the nature and position of the substituents in the aniline ring, nature of the 3-D-coordination polymeric hosts, and the conditions used for the reaction.

3.2. *X-ray powder diffraction*

The 3-D-coordination polymers **I** and **II** exhibit X-ray diffraction patterns with numerous pronounced and sharp reflection peaks. The experimental powder X-ray

Table 1. Elemental analyses of the 3-D-coordination polymeric hosts and their host–guest supramolecular polymers.

		Elemental analysis found (Calcd) (%)		
No.	Composition	C	H	N
I	$[(n\text{-}Bu_3Sn)_3Fe(CN)_6]_n$	46.9 (46.6)	7.9 (7.5)	7.1 (7.8)
II	$[(n\text{-}Bu_3Sn)_2(Ph_3Sn)Fe(CN)_6]_n$	50.7 (50.5)	6.7 (6.1)	7.4 (7.4)
1	$[(\text{Aniline}) + (\text{I})]_n \cdot 2H_2O$	48.4 (47.6)	7.3 (7.7)	8.5 (8.1)
2	$[(\text{Aniline}) + (\text{II})]_n \cdot 8H_2O$	46.6 (47.0)	6.3 (6.7)	7.7 (7.1)
3	$[(o\text{-Toluidine HCl}) + (\text{I})]_n \cdot 5H_2O$	44.1 (44.8)	7.4 (7.7)	8.0 (7.5)
4	$[(o\text{-Toluidine HCl}) + (\text{II})]_n \cdot 10H_2O$	44.4 (45.1)	6.5 (6.8)	6.0 (6.7)
5	$[(o\text{-Chloroaniline})_{0.8} + (\text{I})]_n \cdot 2H_2O$	46.6 (47.0)	6.3 (6.7)	7.7 (7.1)
6	$[(o\text{-Chloroaniline})_{0.8} + (\text{II})]_n \cdot 4H_2O$	47.5 (48.2)	5.8 (6.3)	8.0 (7.2)
7	$[(\text{2,5-Dichloroaniline})_{0.9} + (\text{I})]_n$	45.8 (46.4)	6.8 (7.0)	8.2 (7.9)
8	$[(\text{2,5-Dichloroaniline})_{0.9} + (\text{II})]_n \cdot 3H_2O$	48.0 (47.8)	5.3 (5.9)	7.7 (7.2)
9	$[(\text{6-Chloro-2,4-dinitroaniline})_{0.9} + (\text{I})]_n \cdot 7H_2O$	39.8 (40.6)	7.6 (7.1)	8.2 (8.7)
10	$[(\text{6-Chloro-2,4-dinitroaniline})_{0.9} + (\text{II})]_n \cdot 5H_2O$	44.4 (44.9)	5.6 (5.8)	8.2 (8.5)

diffraction of **I** is compared with the simulated diffractogram (supplementary material), the latter being based on data resulting from the structure analysis of single crystal [5]. Satisfactory agreement is found between the experimental powder X-ray diffractogram and the simulated diffractogram, suggesting that the finely powdered bulk sample of **I** should be structurally closely related to the crystalline form. The X-ray powder diffraction of **II** is compared with that of **I** and $[(Ph_3Sn)_3Fe(CN)_6]_n$. The X-ray diffraction patterns differ notably, suggesting the presence of a new solid phase (alloyed polymer) and not a mixture of the two polymers [25]. The common features of these compounds are the presence of guest free, cyanide bridged 3-D-neutral networks. The 3-D-networks are composed of nearly planar R_3Sn (R = alkyl or aryl) units linked together with slightly distorted octahedral $Fe(CN)_6$ building blocks through N atoms, forming three infinite zigzag chains [4, 5]. The alkyl or aryl groups are disordered over three positions with their trigonal arrangement preserved. The 3-D-networks involve unusually wide internal cavities of diameters 8.8–9.5 Å [4–6]. These channels are large and expandable and show intercrystalline reaction chemistry [4]. The host attractive properties of the 3-D-coordination polymers, which demonstrated chemically [26–28], arise from the availability of large cavities for trapping voluminous organic and organometallic guest cations into the negatively charged host lattice $[(R_3Sn)_3Fe^{II}(CN)_6^-]_n$ accessible by complete reduction of the isostructural iron homologue $[(R_3Sn)_3Fe^{III}(CN)_6]_n$ [6], forming host–guest supramolecular coordination polymers. The X-ray diffraction patterns of host–guest supramolecular polymers under investigations figure 2 exhibit reflection peaks corresponding to those of their free hosts. The relative intensity of these peaks suffers dramatic decrease, indicating that the encapsulation of aniline derivatives within the cavities of the polymeric hosts decreases the degree of crystallinity.

3.3. *IR spectra*

The IR spectra of the 3-D-coordination polymeric hosts and their host–guest supramolecular polymers are shown in figure 1. The IR spectra of the 3-D-coordination polymeric hosts **I** and **II** display strong to medium bands at 2132 and 408 cm^{-1} due to the stretching vibrations of $[Fe(CN)_6]^{3-}$ building blocks. These bands reflect the covalent nature of the $Fe–C\equiv N \rightarrow Sn$ bridging unit due to their positions at higher wavenumbers than those of the corresponding salt $K_3[Fe(CN)_6]$ [29]. The medium bands at 515–517 and 598 cm^{-1} were assigned to the stretching vibrations of Sn–C bonds of *n*-butyl and phenyl groups, respectively. Also, the main bands for *n*-Bu_3Sn group are the C–H stretching vibrations in the region of 2953–2960 and 2922–2925 cm^{-1}. The presence of two ν_{CH} bands could arise from crystallographic non-equivalence of *n*-butyl groups in the distorted trigonal bipyramidal structure of the zigzag chains combined with *n*-butyl groups in linear chains [30]. On the other hand, the medium band at 3053 cm^{-1} in 3-D-coordination polymeric host **II** was assigned to ν_{CH} of the phenyl group. Upon encapsulation of the aniline derivatives within the cavities of the 3-D-coordination polymeric hosts **I** and **II**, the IR spectra of the hosts reveal drastic changes. The main changes in the spectra of **1**–**4** are the disappearance of the bands assigned to the stretching vibrations of $[Fe^{III}(CN)_6]^{3-}$ building blocks and the appearance of a strong intense band at 2078 cm^{-1} due to stretching vibrations of $[Fe^{II}(CN)_6]^{4-}$ building blocks, indicating that the 3-D-coordination polymeric hosts **I** and **II**

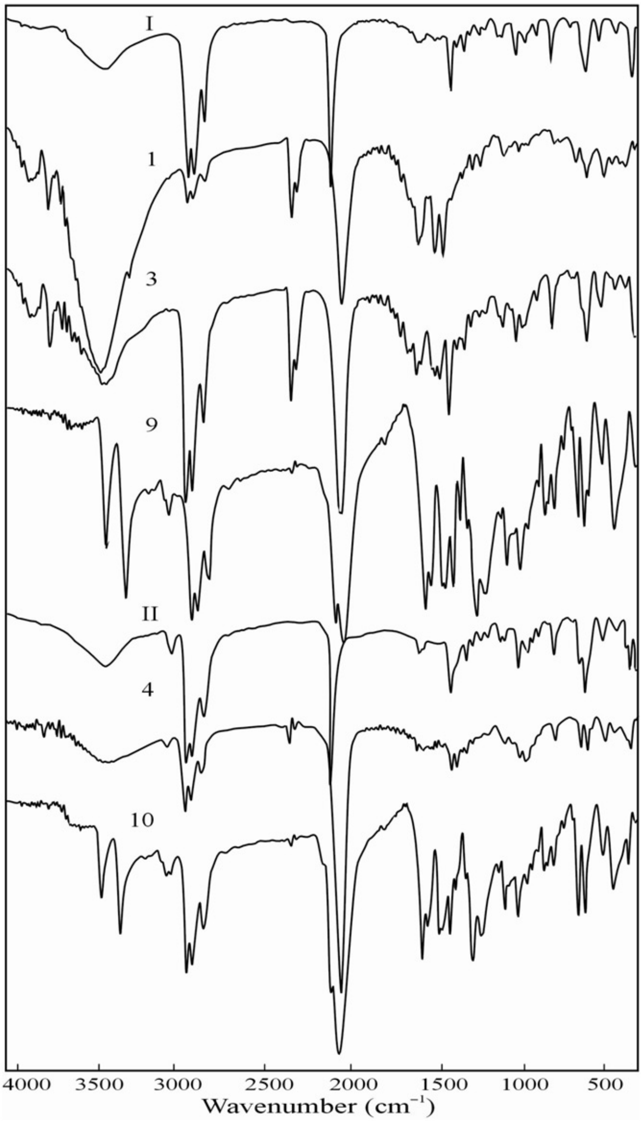

Figure 1. IR spectra of the 3-D-coordination polymer **I**, **II** and some of their host–guest supramolecular polymers.

were completely reduced by aniline and *o*-toulidine hydrochloride as guests. The single weak intensity band at 3280–3295 cm^{-1} was assigned to the stretching vibrations of the N–H, which suggests the presence of secondary amino group. The appearance of this band indicates the oxidative polymerization of aniline and *o*-toulidine within the cavities of the 3-D-coordination polymeric hosts **I** and **II** [31]. The weak band of NH was covered by the broad band of great intensity at 3400–3447 cm^{-1} which corresponds to the stretching vibrations of water molecules. The oxidative polymerization of aniline can also be justified from bands at 1626–1648 and 1550–1560 cm^{-1} assigned to $\nu_{C=N}$ and $\nu_{C=C}$ of quinoid-diimine; the band at 1504 cm^{-1} corresponds to $\nu_{C=C}$ of quinoiddiamine [32]. IR spectra of the host–guest supramolecular polymer **5–10** display bands around 2087 and 2135 cm^{-1} due to $[Fe^{II}(CN)_6]^{4-}$ and $[Fe^{III}(CN)_6]^{3-}$ building blocks, respectively, indicating partial reduction of Fe^{III} to Fe^{II} by aniline derivatives. Bands around 3379 cm^{-1} correspond to stretching vibrations of the NH_2 group. In such cases, these aniline derivatives are trapped within the channels of the polymeric hosts in the monomeric state, forming charge-transfer (CT) intercalated complexes. The IR spectra of all host–guest systems reveal medium bands around 520 and 598 cm^{-1} due to the various stretching vibration modes of Sn–C bonds, indicating that the trigonal bipyramidal R_3Sn groups still play the role of linking pairs of iron-bonded cyanide ligands forming the 3-D-network structure. Bands around 1295 cm^{-1} were assigned to the C–N stretching vibrations of the aniline derivatives. Combination bands observed in the region of 2340–2370 cm^{-1} correspond to the stretching vibrations of amine hydrochloride [33].

3.4. *Thermogravimetric analysis*

The thermograms of **I** (supplementary material) and **II** comprise two steps. The release of two molecules of *n*-Bu_3SnCN from **I**, and (*n*-Bu_3SnCN)(Ph_3SnCN) from **II**, in addition to the gradual loss of cyanide groups as cyanogen molecules $(CN)_2$ from 150°C up to 250°C [34]. Above 250–450°C, the structural breakdown occurs and a mixture of Fe_2O_3 and SnO_2 is formed. The thermogram of **1** (supplementary material) displays four steps. The first from room temperature to 150°C corresponds to the release of two water molecules of crystallization. Two molecules of *n*-Bu_3SnCN are released in the temperature range 150–640°C. The decomposition of aniline occurs in the temperature range 640–800°C. This high temperature is because the 3-D-host protects the encapsulated guest from undergoing degradation. Above 800°C, the cyanide-linked framework is no longer stable and a structural breakdown occurs, leaving the stable mixed oxides.

3.5. *Electronic absorption spectra*

Electronic absorption spectra of the 3-D-coordination polymeric hosts **I**, **II** and their host–guest systems are shown in figure 2. The UV-vis spectra of **I** and **II** have five intense absorptions around 220, 275, 300, 320, and 420 nm. These bands were observed in the absorption spectrum of $K_3[Fe(CN)_6]$ [35]. The first band at 220 nm is due to π–π^* transitions from the metal to cyanide, while the three bands around 275, 300, and 420 nm correspond to CT transitions from the filled bonding orbitals of the cyanide ligand to the hole in the shell of iron. The low-intensity band at 320 nm is due to the ligand field (d–d) transitions. Electronic absorption spectra of the host–guest supramolecular polymers **1–10** show absorption bands in the range 210–750 nm due to the electronic transitions of aniline derivatives and the 3-D-coordination polymeric hosts. The two absorption bands at 220 and 260 nm are due to the $^1L_a \leftarrow {}^1A$ and $^1L_b \leftarrow {}^1A$ transitions within the individual benzenoid rings in aniline derivatives [19]. The redox reaction between the 3-D-coordination polymers and aniline derivatives as guest was confirmed by the composite band around 330 nm due to electronic transitions of the $[Fe^{II}(CN)_6]^{4-}$ building blocks. The band around 410 nm corresponding to the electronic transition of $[Fe^{III}(CN)_6]^{3-}$ is completely disappeared in host–guest

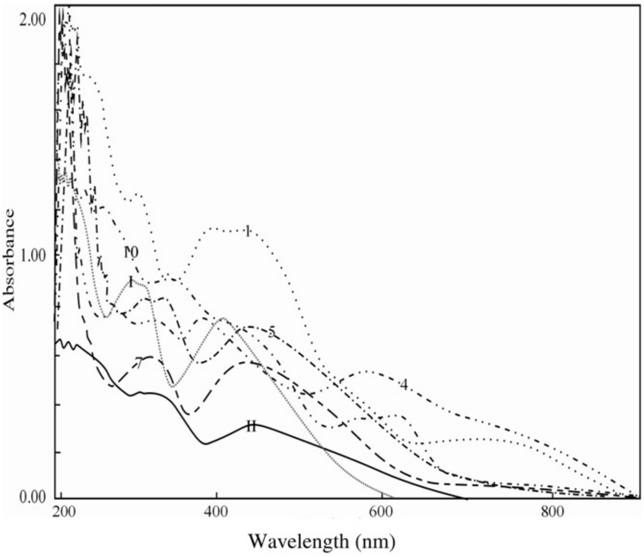

Figure 2. UV-vis spectra of the 3-D-coordination polymers **I**, **II** and some of their host–guest supramolecular polymers.

supramolecular polymers **1**–**4**, indicating that the 3-D-coordination polymeric hosts **I** and **II** are completely reduced to the isostructural Fe^{II} anion homologue $[(R_3Sn)_3Fe^{II}(CN)_6^-]_n$ by aniline. However, the appearance of this band in host–guest supramolecular polymers **5**–**10** supports the presence of mixed-valance iron hexacyano building blocks which is also indicated by IR. The new absorption bands at 435 and 750 nm in host-guest supramolecular polymers **1**–**4**, observed as broad or shoulder bands, can be attributed to polaron absorption band and the dication absorption band (bipolaron form), respectively. These bands are characteristic for emeraldine salt form of PANI ([16, and references therein] and [36]). Moreover, the CT character of the host–guest supramolecular polymers was supported by the appearance of bands within the range 505–700 nm corresponding to intermolecular CT transitions between the negatively charged cavities of the 3-D-coordination polymeric hosts and aniline derivatives [37]. The 3-D-coordination polymeric hosts **I** and **II** are optically transparent in the visible region of 430–900 nm.

3.6. *Magnetic properties*

The effective magnetic moments μ_{eff} of the 3-D-coordination polymeric hosts **I** and **II** indicate that they are paramagnetic (μ_{eff}, *ca* 2.32 and 2.23 BM, respectively), due to presence of low-spin iron(III) which have one unpaired electron in the d_{yz} orbital in the distorted octahedral $[Fe^{III}(CN)_6]^{3-}$ structure. All the host–guest supramolecular polymers **1**–**10** exhibit paramagnetic character with μ_{eff} values less than that of the corresponding hosts. The host–guest systems **5**–**10** show paramagnetic behavior with μ_{eff} values in the range 0.94–1.43 BM, due to the presence of mixed iron environment, d^5 for iron(III) and d^6 for iron(II), indicating partial reduction of the 3-D-coordination polymeric hosts. The host–guest systems **1**–**4** exhibit paramagnetic character with

Table 2. Electrical conductivities of the 3-D-coordination polymeric hosts and their host–guest supramolecular polymers.

Compound	$\sigma_{303\mathrm{K}}$ (s cm^{-1})	Compound	$\sigma_{303\mathrm{K}}$ (s cm^{-1})
I	6.0×10^{-12}	**5**	1.0×10^{-4}
II	7.0×10^{-12}	**6**	2.5×10^{-5}
1	1.8×10^{-4}	**7**	1.9×10^{-9}
2	1.1×10^{-4}	**8**	7.9×10^{-9}
3	4.1×10^{-5}	**9**	9.2×10^{-9}
4	1.2×10^{-4}	**10**	8.9×10^{-9}

μ_{eff} values 1.25–1.58 BM, due to the free radical cation of the corresponding PANI. This is also supported by EPR spectra (Supplementary material) which reveal only one strong symmetrical signal with g-value at 2.0. This signal corresponds to the free radical cation of the aniline derivatives [38–40] and is observed in EPR spectra of the authentic sample of PANI prepared by oxidation of the monomers with ferric chloride. The presence of such strong signal presents good evidence for polymerization of the aniline derivatives and for the paramagnetic nature of these host–guest systems.

3.7. *Electrical conductivity*

The electrical conductivity values are given in table 2. The 3-D-coordination polymers **I** and **II** behave as insulators having conductivity values in the range of 10^{-12} s cm^{-1}. A significant increase in the conductivity of the host–guest supramolecular polymers **1**–**6** is observed, which behave as semiconductors having conductivities in the range of 10^{-4}–10^{-5} s cm^{-1}. The semiconducting character of these compounds was supported by studying the variation of DC-electrical conductivity as a function of temperature. Positive temperature coefficients of electrical conductivity indicate semiconducting behavior of these host–guest systems. However, the conductivity of the host–guest supramolecular polymers is lower than that of the PANI prepared by conventional methods without host polymers. This is because the host–guest supramolecular polymers result from the assembly of conducting polymers separated by a 3-D-polymeric network of insulating character. Moreover, the constrained PANI in the intracrystalline region can impose chain conformational changes that also contribute to a decrease in the conductivity of the system. Host–guest supramolecular polymers **7**–**10** behave as insulators with conductivity values in the range of 10^{-9} s cm^{-1}. Generally, the conductivity decreases with increasing number of substituents on the aniline ring.

3.8. *Scanning electron microscope*

The scanning electron micrographs (supplementary material) of the 3-D-coordination polymeric host **I** (Supplementary material) show that it has lumpy aggregates of porous cuboidal texture. The authentic sample of free PANI (supplementary material) has a flaky texture. This flaky texture of PANI was observed in the scanning electron micrograph of the host–guest supramolecular polymer **1** (supplementary material).

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