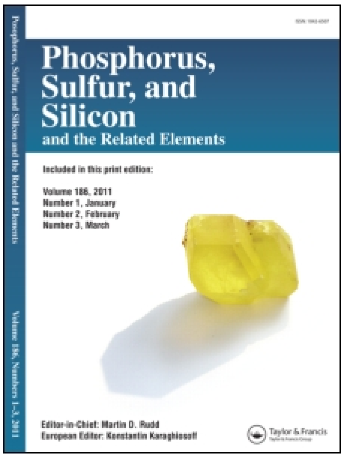

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# NOVEL SUPRAMOLECULAR DERIVATIVES CONTAINING TWO $R_3Sn^+$ (R = Me, n-Bu, or Ph) CONNECTING UNITS: THE FORMATION OF NOVEL HOST-GUEST SYSTEMS BY THE FACILE ENCAPSULATION OF GUEST THIOPHENE COMPOUNDS

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# NOVEL SUPRAMOLECULAR DERIVATIVES CONTAINING TWO $R_3Sn^+$ (R = Me, n-Bu, or Ph) CONNECTING UNITS: THE FORMATION OF NOVEL HOST–GUEST SYSTEMS BY THE FACILE ENCAPSULATION OF GUEST THIOPHENE COMPOUNDS

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*New supramolecular complexes* $[(Me_3Sn)(Ph_3Sn)_2Fe(CN)_6]$ ***(I)*** *and* $[(n\text{-}Bu_3Sn)(Ph_3Sn)_2Fe(CN)_6]$ ***(II)*** *are readily accessible by straightforward self-assembly of* $[Fe(CN)_6]^{3-}$ *and hydrated* $\{R_3Sn^+\}/\{R'_3Sn^+\}$*ions (R = Ph, and R′ = Me or n-Bu). The structural characterization of (**I**) and (**II**) is compared with well-documented supramolecular complex containing only* $\{Ph_3Sn^+\}$ *unit,* $[(Ph_3Sn)_3Fe(CN)_6]$*. These novel compounds have wide internal cavities capable of encapsulating voluminous organic compounds, and they behave as host acceptors forming charge transfer complexes (CTC). Thiophene compounds acting as guest donor species are encapsulated within the cavities of the three-dimensional (3D) supramolecular hosts. The structure and physical properties of these hosts and host–guest systems were studied by X-ray powder diffraction, IR, UV/Vis., and magnetic measurements.*

*Keywords:* Charge transfer complexes; host–guest systems; supramolecular hosts

## INTRODUCTION

The supramolecular compounds containing only one type of $\{R_3Sn^+\}$unit $[(R_3Sn)_3Fe^{III}(CN)_6]_\infty = {}_\infty[Fe(\mu\text{-}CNSn(R_3)NC)_3]$ (R = Me, n-Bu, or Ph) are well-documented coordination polymers,[1–5] whose iron(III) atoms may be considered as nodes of six-connected nets. The

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Address correspondence to Moustafa Sh. Ibrahim, Chemistry Department, Faculty of Science, Tanta University, 31527 Tanta, Egypt. E-mail: mshehatai2003@yahoo.com five-atoms metal connectors —CN→Sn←NC— usually result by rapid self-assembly when dissolved $[Fe(CN)_6]^{3-}$ ions meet hydrated $R_3Sn^+$ ions. The resulting compounds adopt an unprecedented type of spacious, three-dimensional (3D) framework devoid of any pseudocubes as basic structural building blocks.[4,6] The framework structure of this class of compounds creates wide parallel channels or cavities with diameters typically of ca. 8.8–9.5 Å. These large empty channels enclosed by the 3D frameworks exhibit some interesting zeolite-like host–guest systems.[6,7] Also, this family of the supramolecular compounds has different potential applications because the compounds act as oxidative materials by partial or complete reduction of the isostructural Fe(III) homologue $[(R_3Sn)_3Fe^{III}(CN)_6^-]_\infty$, forming charge transfer (CT) host–guest systems.[8–15] One interesting feature of these host–guest systems is the enhanced electronic conductivities exhibited by encapsulation of the conductive polymers within the cavities of these 3D hosts.

Thiophene compounds have reduction potential of ca. 1.7 V (with respect to a saturated calomel electrode SCE)[16] compared with ca. 0.41 V for $[Fe(CN)_6]^{3-}$ anion.[17] This trend in the reduction potentials is in agreement with the reducing ability of thiophene compounds towards 3D-supramolecular hosts containing the $[Fe(CN)_6]^{3-}$ building blocks.

The current study is concerned with the synthesis and structural characterization of two novel supramolecular compounds. The interaction of these hosts with thiophene compounds confirmed the host attractive properties of both hosts, which arise from the availability of large cavities of hosts for trapping, under ambient conditions, voluminous thiophene molecules into the negatively charged host lattices.

# RESULTS AND DISCUSSION

## X-Ray Powder Diffraction (XRD)

Both novel supramolecular hosts **I** and **II** gave rise to satisfactory $XRD_s$ with numerous pronounced and sharp reflection. The $XRD_s$ of **I** and **II** are compared with the XRD of the parent compound $\{[(Ph_3Sn)_3Fe(CN)_6]\}$ (Figure 1). The $XRD_s$ look quite different from that of the parent system. The changes of the framework architecture are likely to result as the volume of R (alkyl or aryl) increases.[1] The different framework connectivities arise from the constraints imposed by packing the ligands within the framework defined by the Fe—CN—Sn bonds.[3] Both supramolecular hosts **I** and **II** are examples of guest-free cyanide-bridged 3D networks $[(R_3Sn)_nM(CN)_{2n}]$. These 3D neutral networks are composed of trigonal bipyramids (tbp) $R_3Sn$ units linked

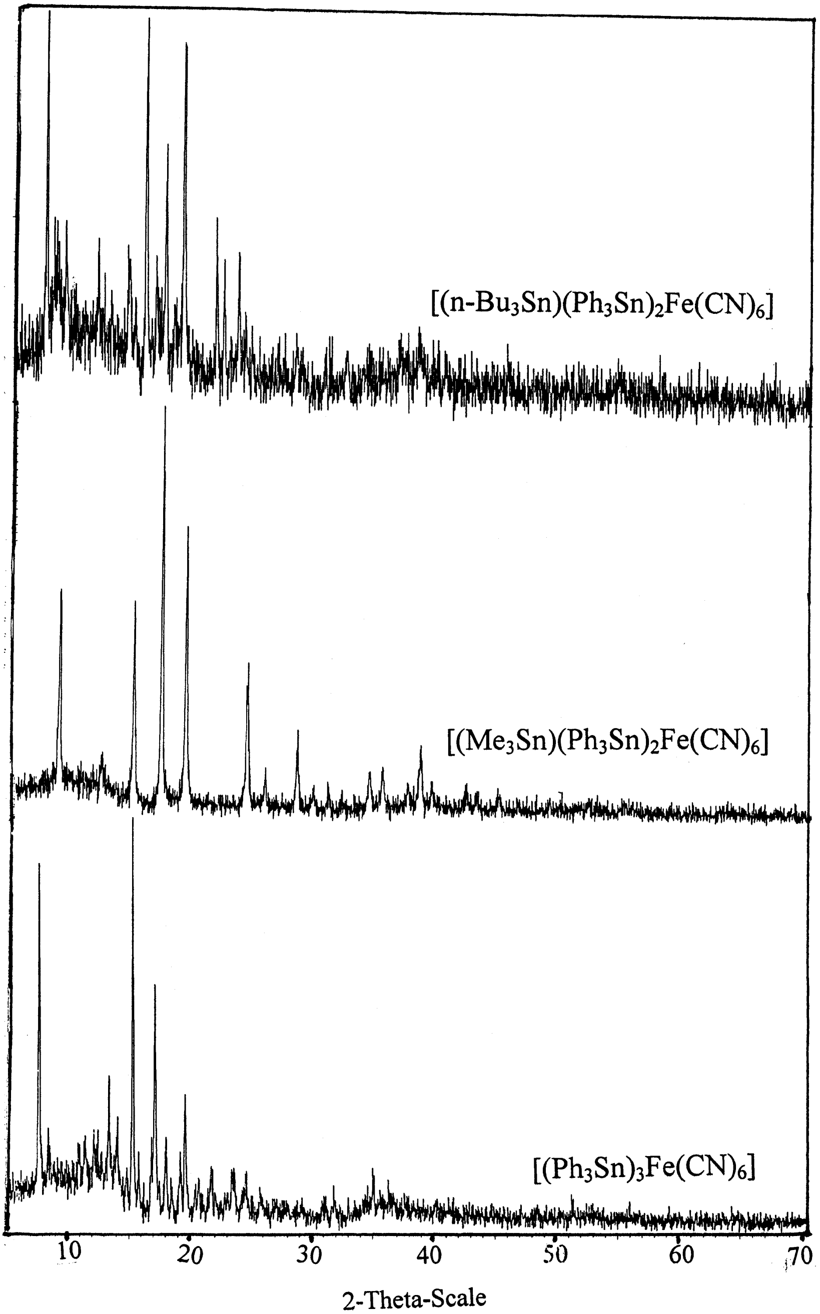

**FIGURE 1** The experimental powder X-ray diffractograms of the supramolecular hosts.

**TABLE I** Elemental Analyses Data and Composition of Hosts and Host–Guest Systems

| Compound | Donor guest | Composition | Found (Calcd.) (%) C | H | N |
|---|---|---|---|---|---|
| Parent | — | $[(Ph_3Sn)_3Fe(CN)_6]\cdot H_2O$ | 56.5 (56.3) | 3.7 (3.7) | 6.7 (6.6) |
| **I** | — | $[(Me_3Sn)(Ph_3Sn)_2Fe(CN)_6]$ | 49.4 (50.2) | 3.5 (3.6) | 7.3 (7.8) |
| **II** | — | $[(n\text{-}Bu_3Sn)(Ph_3Sn)_2Fe(CN)_6]$ | 53.0 (53.9) | 5.5 (4.7) | 6.0 (6.9) |
| **1** | T | $[(T)_{0.5} + (\mathbf{I})]\cdot 2H_2O$ | 47.4 (47.3) | 4.1 (4.0) | 7.1 (7.1) |
| **2** | T | $[(T)_{0.5} + (\mathbf{II})]\cdot 2H_2O$ | 52.3 (52.5) | 4.8 (4.9) | 6.2 (6.6) |
| **3** | 3-MeT | $[(3\text{-}MeT)_{0.5} + (\mathbf{I})]$ | 50.0 (50.7) | 3.8 (3.7) | 7.0 (7.5) |
| **4** | 3-MeT | $[(3\text{-}MeT)_{0.5} + (\mathbf{II})]\cdot 2H_2O$ | 52.1 (52.5) | 4.8 (4.9) | 5.3 (6.5) |
| **5** | $2\text{-}NO_2$ | $[(2\text{-}NO_2T)_{0.5} + (\mathbf{I})]$ | 50.6 (49.6) | 3.6 (3.6) | 7.2 (7.9) |
| **6** | $2\text{-}NO_2$ | $[(2\text{-}NO_2T)_{0.5} + (\mathbf{II})]\cdot 2H_2O$ | 51.6 (51.6) | 4.2 (4.8) | 7.0 (6.9) |
| **7** | 3-BrT | $[(3\text{-}BrT)_{0.5} + (\mathbf{I})]$ | 49.6 (48.8) | 4.1 (3.5) | 6.5 (7.2) |
| **8** | 3-BrT | $[(3\text{-}BrT)_{0.5} + (\mathbf{II})]\cdot H_2O$ | 52.1 (51.7) | 4.7 (4.7) | 6.0 (6.7) |

T, Thiophene.

together with slightly distorted octahedral $Fe(CN)_6$ fragments through the cyanide N atoms.[2–4] The R groups are disordered over three positions with their trigonal arrangement preserved. Increasing the steric bulk of the R group might force all C—N—Sn angles to become 180°C[6]. Some of the intraframework of the host might be too narrow to accommodate $R_3Sn$ units with larger than Me, since the van der Waals spheres of the closest-lying aryl or alkyl C and cyanide N atoms are not far from overlapping.[1] The "formula weight volume," $V_f = M_r/D_c$ ($M_r$ = formula weight, $D_c$ = calculated density), of the two novel supramolecular hosts **I** and **II** are compared with the parent (Table II). The density-based formula volumes $V_f$ increase gradually with the space demand of the tin-bonded group. R changes of the framework architecture are likely to result as the volume of R increases.[6] In the case of **I**, $V_f$ values decrease than those of **II** and the parent system due to the presence of smaller R (Me) group. The drastic change of $V_f$ from the parent $\{[(Ph_3Sn)_3Fe^{III}(CN)_6]\}$ should be due to the unique architecture of the lattices of **I** and **II** in which the $R_3Sn$ connecting units function as spatially well-oriented spacers.[4]

**TABLE II** Formula Volume $V_f$ ($cm^3\ mol^{-1}$) of Various Host Systems Calculated from Pyknometric Density Values

| Host system | Volume (V) $cm^3$ | Density (d) | $V_f$ |
|---|---|---|---|
| $[(Ph_3Sn)_3Fe(CN)_6]$ | 0.232 | 1.3866 | 910.13 |
| $[(Me_3Sn)(Ph_3Sn)_2Fe(CN)_6]$ | 0.2920 | 1.3414 | 801.98 |
| $[(n\text{-}Bu_3Sn)(Ph_3Sn)_2Fe(CN)_6]$ | 0.2124 | 1.1235 | 1069.87 |

The powder $XRD_s$ of the novel supramolecular host–guest systems (**1–8**) indicate that they are isostructural compounds to the corresponding supramolecular hosts **I** and **II**. Also, the XRD lines as well as relative intensities remain constant when going from the supramolecular hosts to the supramolecular host–guest systems. This indicates that there is no change in the supramolecular nature of the hosts and that the frameworks are little affected by the presence of thiophene guest molecules; this phenomenon can be justified from the following spectra.

## Infrared Spectra

The IR spectra of supramolecular hosts **I** and **II** reveal the presence of $[Fe^{III}(CN)_6]$ building blocks and the different $R_3Sn$ (R = Me, n-Bu or Ph) connecting units (Figure 2, Table III). The IR spectra display one intense band in the $\nu_{CN}$ region, which is likely to reflect the significantly perturbed surrounding of their $R_3Sn$-interlinked $Fe(CN)_6$ octahedra.[4] Also, the position of this band at 2133–2144 $cm^{-1}$ reflects the covalent nature of the $Fe{-}C{\equiv}N{\rightarrow}Sn$ bridging units.[10] The stretching vibrations of $\nu_{CN}$ bands of **I** and **II** usually occur at higher wave numbers than

**TABLE III** IR Spectral Data ($cm^{-1}$) for Supramolecular Hosts and Host–Guest Systems

| | Guest | | | Host | | | | |
|---|---|---|---|---|---|---|---|---|
| No. | $\nu_{H_2O}$ | $\delta_{C-H}$ | $\nu_{C=C}$ | $\nu_{Fe^{III}-CN}$ | $\nu_{Fe^{II}-CN}$ | $\nu_{Sn-C}$ | $\nu_{Fe^{III}-C}$ | $\nu_{Fe^{II}-C}$ |
| Parent | | | | 2141 | — | 582 | 411 | — |
| **I** | | | | 2144 | — | 552<br>580 | 409 | — |
| **II** | | | | 2133 | — | 521<br>589 | 405 | — |
| **1** | — | 1468 | — | 2184 | 2077 | 552<br>586 | 411 | 449 |
| **2** | 3427<br>1629 | 1469 | 1556 | 2183 | 2076 | 544<br>589 | — | 448 |
| **3** | — | 1478 | 1581 | 2145 | 2083 | 552<br>590 | 411 | 446 |
| **4** | 3437<br>1627 | 1472 | 1578 | 2184 | 2080 | 555<br>589 | 411 | 448 |
| **5** | — | 1482 | 1578 | 2145 | 2085 | 554<br>589 | 411 | 446 |
| **6** | 3426<br>1628 | 1473 | 1578 | 2185 | 2079 | 539<br>591 | — | 448 |
| **7** | — | 1478 | 1589 | 2144 | 2083 | 553<br>589 | 411 | 447 |
| **8** | 3440<br>1628 | 1471 | 1589 | 2184 | 2080 | 540<br>589 | — | 448 |

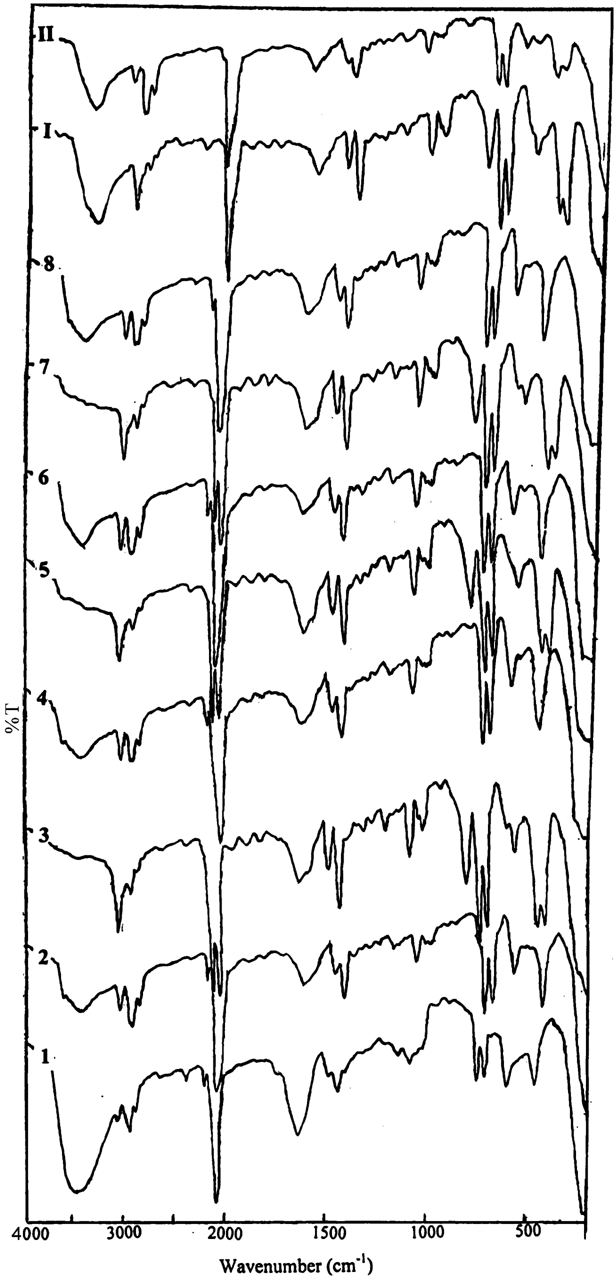

FIGURE 2 IR spectra of hosts and host–guest systems.

the corresponding salts (ca. $\nu_{CN} = 2116\ \text{cm}^{-1}$ for $K_3[Fe(CN)_6]$), which indicates the presence of linear bridging between metal centers.[18,19] In addition, the IR spectra exhibit a medium intense band in the range 405–409 $\text{cm}^{-1}$ due to the stretching vibrations of the $Fe^{III}$—C bond. The $\nu_{(Fe^{III}-C)}$ vibration increases along with that of $\nu_{CN}$ due to the anticipated, gradual reorientation of the partially $\pi$-antibonding "lone" electron pair on each cyanide N atom towards a suitable vacant orbital of the lewis acid $A^+$ ($Fe{-}C{\equiv}N{:} + A \leftrightarrow Fe{-}C{\equiv}N^{\delta+} \rightarrow A^{\delta-} \leftrightarrow Fe{=}C{=}N{-}A$).[20]

While the IR-active $\nu_{(Sn-C)}$ absorptions of both samples clearly display two types of intense bands corresponding to the presence of alkyl and aryl carbon atoms, the supramolecular host **I** reveals two intense bands at 552 and 580 $\text{cm}^{-1}$ due to the stretching vibration of $Sn{-}C_{(CH_3)}$ and $Sn{-}C_{(Ph)}$, respectively. In the case of supramolecular host **II**, two bands are located at 521 and 589 $\text{cm}^{-1}$ due to $Sn{-}C_{(n-Bu)}$ and $Sn{-}C_{(Ph)}$, respectively, indicating that these groups still play the role of linking the $[Fe^{II}(CN)_6]^{3-}$ building blocks and acting as connecting units to form 3D networks.[4] Also, the main bands for $R_3Sn$ are at 2915–2922 (C—H valance), 1427–1480 ($CH_3$-deformation), and 731–791 $\text{cm}^{-1}$ (C—H-rocking).

The IR spectra of the supramolecular hosts suffer changes as a result of encapsulated thiophene compounds within their channels (Table III, Figure 2). The main changes are the appearance of two CN stretching bands from Fe—CN—Sn in the region 2145–2185 and a strong band at 2076–2085 $\text{cm}^{-1}$, indicating the partial reduction or transformation of $[Fe(CN)_6]^{3-}$ building blocks to $[Fe^{II}(CN)_6]^{4-}$ containing host–guest systems. In addition, the IR spectra exhibit medium intense bands at 411 $\text{cm}^{-1}$ due to the stretching vibrations of the $Fe^{III}$—C bond and a medium-to-weak intensity band at 446–449 $\text{cm}^{-1}$ due to the stretching vibrations of the $Fe^{II}$-C bond.

The IR spectra of the host–guest systems **1–8** exhibit intense bands in the range 1556–1589 $\text{cm}^{-1}$ due to stretching vibrations of C=C (aromatic ring), while the vibrations of C—H bond appear at 1468–1482 $\text{cm}^{-1}$. There is no evidence for the presence of polythiophene within the channels of the hosts due to the higher oxidation potential of thiophene molecules.[14,21,22]

The main structural framework appears to be still maintained in host–guest systems **1–8**, as indicated by the high degree of similarity between the spectra. Upon encapsulation, the IR spectra of the host–guest systems exhibit medium intensity bands of $\nu_{(Sn-C)}$ vibrations at 539–590 $\text{cm}^{-1}$. Some of the $\nu_{(Sn-C)}$ vibration bands occurred at higher wave numbers than the bands of their corresponding hosts, reflecting more covalent interaction between the cyanide N atoms and the $R_3Sn$ units under the influence of the electron-rich guest cations.[10]

Also, these bands reveal the presence of trigional bipyramidal (tbp)-configured $R_3Sn(NC)_2$ units, indicating that these groups still play the role of the linkages between pairs of iron-bonded cyanide ligands to form the 3D networks.

## Electronic Absorption Spectra

The electronic absorption spectra of the metal ion ($Fe^{III}$) with $d^5$ configuration in the ($^2T_{2g}$) of supramolecular hosts **I** and **II** as Nujol mull matrix reveal three broad bands around 230, 310, and 419 nm (Table IV). They resemble the bands observed in the absorption spectra of the parent $\{[(Ph_3Sn)_3Fe(CN)_6]\}$, and $K_3[Fe(CN)_6]$.[8,23] The first band at 220 nm is due to $\pi$-$\pi^*$ transitions from the metal to the cyanide ligand (M→L). The composite band at 310 nm corresponds to ligand field (d-d) transition ($^2A_{2g} \rightarrow {}^2T_{1g}$). The low energy band at 419 nm corresponds to $\pi$-$\pi^*$ transitions of $[Fe(CN)_6]^{3-}$ building blocks.[17]

The spectra of the host–guest supramolecular complexes **1–8** reveal mainly five absorption bands at 229–515 nm (Table IV). These bands are due to the electronic transitions between thiophene compounds and the supramolecular hosts. The first two bands at 229–285 nm are attributed to the $^1L_a \leftarrow {}^1A$ and $^1L_b \leftarrow {}^1A$ transitions of the thiophene moieties within the channels of the hosts. However, the host–guest supramolecular complexes **1–8** consist of mixed-valence iron hexacyano building blocks (see IR spectra). The composite band around 300 nm corresponds to d-d transitions, $^1A_{1g} \rightarrow {}^1T_{1g}$ of the $[Fe^{II}(CN)_6]^{4-}$ building blocks.[25] The weak band at 410–423 nm can be attributed to d-d transitions of the $[Fe^{III}(CN)_6]^{3-}$ building blocks. These bands support the presence of

**TABLE IV** The Electronic Absorption Spectra (nm) and the Magnetic Moments (BM) of Hosts and Host–Guest Systems

| No. | $^1L_a \leftarrow {}^1A$ of thiophene moities | $^1L_b \leftarrow {}^1A$ of thiophene moities | $\pi$-$\pi^*$ transitions $Fe^{III}$—CN | $\pi$-$\pi^*$ transitions $Fe^{II}$—CN | CT | $\mu_{eff}$ |
|---|---|---|---|---|---|---|
| **I** | — | — | 430 | — | — | 2.46 |
| **II** | | | 432 | | | 2.43 |
| **1** | 235 | 269 | 419 | 335 | 498 | 1.79 |
| **2** | 236 | 268 | 419 | 331 | 495 | 1.04 |
| **3** | — | 270 | 423 | 324 | 505 | 1.42 |
| **4** | — | 271 | 419 | 347 | 495 | 1.12 |
| **5** | 240 | 259 | 418 | 310 | 515 | 2.06 |
| **6** | — | 285 | 413 | 322 | 515 | 1.10 |
| **7** | 229 | 270 | 412 | 330 | 515 | 1.45 |
| **8** | 230 | 268 | 410 | 325 | 515 | 1.63 |

mixed-valence iron hexacyano building blocks, as is also indicated by the weak paramagnetic behavior of these systems (Table IV). On the other hand, the diffuse reflectance spectra exhibit an additional broad band at 495–515 nm, corresponding to ion-pair charge transfer (CT) between the negatively charged cavity of the supramolecular hosts and thiophene guest molecules.[15,26] In addition, the spectra do not show any bands in the near IR region corresponding to intervalence transitions, indicating the localized interaction between the mixed-valence iron.[27] The electronic absorption bands are rather broad and may be composed of contributions from several species.

## Magnetic Properties

All hosts and host–guest systems are paramagnetic. This is typical of low-spin $Fe^{III}$ compounds (Table IV) which have $(d\varepsilon)^5$ electronic configuration with one unpaired electron in the $d_{yz}$ orbital, forming a distorted octahedral structure.[28] The paramagnetic behavior of host–guest systems (**1–8**) is less than that of the corresponding hosts, indicating the presence of mixed-iron environment ($d^5$ core for Fe(III) and $d^6$ core for Fe(II)), which is due to the partial reduction of hosts under the influence of guest molecules.

## Electrical Conductivity

The two novel host systems behave as insulators with conductivity values $0.213 \times 10^{-10}$ and $2.4 \times 10^{-10}$ $Scm^{-1}$ for **I** and **II**, respectively. The conductivity of the parent, $[(Ph_3Sn)_3Fe(CN)_6]$, is $0.124 \times 10^{-10}$ $Scm^{-1}$. On the other hand, the conductivity of the host–guest supramolecular systems is still weak semiconductors or insulators ($0.514–1.126 \times 10^{-10}$ $Scm^{-1}$). These results reveal that thiophene molecules are present in the neutral form within the cavity of the hosts.[14,15] The low conductivity is also reflected the absence of the metallic absorption bands (ca. 1100 nm) in the electronic absorption spectra of these host–guest systems.

## EXPERIMENTAL

Elemental analyses were performed on a Perkin-Elmer 2400 automatic elemental analyzer. IR spectra were recorded as KBr-pellets in the 4000–200 $cm^{-1}$ range using a Perkin-Elmer sp 1430 spectrophotometer. UV/Vis. absorption spectra were recorded on a Shimadzu 3101 pc spectrophotometer as a Nujol mull matrix and reflectance. The X-ray diffractograms were measured on a Debye-Scherrer PW 1050 ($Cu_xk_\alpha$;

Ni-Filter) instrument (Philips). The magnetic susceptibility was determined with a Johnson-Matthey susceptometer. The electrical conductivity was measured by compressing the sample under a pressure of ca. 600 Kg $cm^{-2}$ to form a cylindrical disc of diameter ca. 0.6 cm and thickness ca. 0.2 cm. The current, I, for the applied voltage, V, was recorded at room temperature using a Keithly 175A autoranging multimeter.

## Supramolecular Hosts (I) and (II)

Supramolecular complex in the formula $[(Ph_3Sn)_3Fe^{III}(CN)_6]_\infty$ yielded as well defined, voluminous 3D tbp $Ph_3Sn(NC)_2$ units as M-connecting units.[8,9] A solution of $K_3[Fe(CN)_6]$ was prepared in doubly distilled water according to the required stoichiometry of the supramolecular complex. An excess of $K_3[Fe(CN)_6]$ was added to stirred solution of $Ph_3SnCl$ in water/acetone mixture (2: ratio) (Equation (1)). Color precipitate, forming immediately after mixing, were filtered off and repeatedly washed with distilled water and diethyl ether, then finally dried under vacuum at room temperature before use.

$$3\,Ph_3SnCl + K_3[Fe(CN)_6] \xrightarrow{\text{water/acetone}} [(Ph_3Sn)_3Fe^{III}(CN)_6]_\infty \downarrow + 3\,K^+ + 3\,Cl^- \qquad (1)$$

In this case, the chain-propagating $N_{cyanide} \rightarrow Sn$ bonds are energetically superior to the $O_{water} \rightarrow Sn$ bonds present in the $Ph_3Sn.aq^+$ ion in solution.[16]

In the corresponding $[(Ph_3Sn)_3Fe^{III}(CN)_6]_\infty$ system, the formation of two analytically pure and air-stable derivatives takes place in the presence of two tbp-connecting units. The $Ph_3SnCl$, $R'_3SnCl$ (R = Me or n-Bu), and $K_3[Fe(CN)_6]$ in 2:1:1 molar ratio were dissolved in the minimum amount of water/acetone mixture to yield $[(R'_3Sn)(Ph_3Sn)_2Fe^{III}(CN)_6]_\infty$ (R = Me or n-Bu). The color precipitates were filtered off and washed with water and diethyl ether, then finally dried under vacuum at room temperature before use (Equation (2)).

$$R'_3Sn^+ + 2\,Ph_3Sn^+ + [Fe^{III}(CN)_6]^{3-} \xrightarrow{\text{water/acetone}} [(R'_3Sn)(Ph_3Sn)_2Fe^{III}(CN)_6]_\infty$$

$$R' = Me\ (\mathbf{I})\ \text{or}\ n\text{-}Bu\ (\mathbf{II}) \qquad (2)$$

The products from this reaction were identical to the corresponding precipitate obtained according to Equation (1). Interestingly, throughout the reaction in Equation (2), the supramolecular products **I** and **II** remain virtually insoluble.

## Host–Guest Systems (1–8)

Freshly prepared supramolecular hosts **I** and **II** can be transferred into several host–guest systems (**1–8**), mainly by adding the dry, freshly prepared hosts to an excess of thiophene donor compounds with continuous grinding at room temperature. The color and composition of the products depended on the reaction time and grinding. The products were isolated, washed with ethanol, and dried in vacuum.

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