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# Three-dimensional organotin – hexacyanoferrate polymers as effective oxidizing reagents towards phenols

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Three-dimensional organotin-hexacyanoferrate polymers of the type  $_{\infty}^{3}[(R_{3}Sn)_{3}Fe^{III}(CN)_{6}]$  where R = Me (I), *n*-butyl (II) and phenyl (III), represent members of the family of supramolecular coordination polymers (SCPs) which have zeolitic-like structure containing micropores. The structures of I–III contain wide channels capable of encapsulating resorcinol, which undergoes *in situ* oxidation to 1,3,4-trihydroxy benzene (THB) or *p*-nitrophenol (PNP), which converts to 1,4-benzoquinone (BQ) and 2-hydroxybenzoquinone (2-HBQ). The oxidation products were investigated by spectroscopic methods and by HPLC. The SCP III was found to be a more effective oxidizing reagent than I and II due to the presence of terminal Sn-OH<sub>2</sub> groups hydrogen bonded to one-sixth of the terminal CN groups, causing more wide expandable channels. In addition, mechanisms of the oxidation processes of resorcinol and PNP have been proposed. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: oxidation of phenols; supramolecular coordination polymer; organotin polymers; hexacyanoferrate polymers

## Introduction

Phenolic compounds are typical biorefractory organic materials included in the 114 priority toxic pollutants listed by US Environmental Production Agency. They represent an environmental problem because of their toxicity, poor biodegradability and accumulation potential in plant and animal tissues. Hence, it is clear that environmental pollution caused by such endocrine-disrupting chemicals is an issue that necessitates the development of an efficient and economical method for destroying endocrine-related chemicals.

Removal of phenols using biological methods is difficult, since they are very time- consuming and operate well only in the case of relatively dilute wastes. Chemical and advanced oxidation processes of phenolic wastes now offer alternative treatment methods when the concentration of the phenol compounds is too high for direct biological systems.<sup>[1-7]</sup>

The attractive properties of the supramolcular coordination polymers (SCPs) of the type  $[(R_3Sn)_3Fe(CN)_6]$  allow them to be used as effective oxidizing reagents.<sup>[8]</sup> These SCPs have zeolite-like structures with remarkably wide parallel channels capable of encapsulatig organic and organomatallic guest cations.<sup>[9]</sup> The purpose of this study was to investigate the oxidative property as a potential application of the well-characterized SCPs  $[(R_3Sn)_3Fe(CN)_6]$ , where R = Me (I), *n*-butyl (II) and phenyl (III),<sup>[10-12]</sup> towards the degradation of resorcinol and *p*-nitrophenol. The SCPs and the oxidation products were investigated spectrophotometrically. The oxidation products were also detected by HPLC.

## **Experimental**

#### Materials

All reagents used in this study were of analytical grade and used without further purification. The solvents used for the preparation

of the mobile phases for HPLC analyses were of HPLC grade from Sigma/Aldrich.

#### Synthesis of the SCPs I–III and the HGSCPs 1–6

The polymeric hosts  $[(R_3Sn)_3Fe^{III}(CN)_6]$  where R = Me(I), *n*-butyl (II) and phenyl (III), were formed by spontaneous precipitation from aqueous solutions containing Me<sub>3</sub>SnCl or Ph<sub>3</sub>SnCl, or from an H<sub>2</sub>O-Me<sub>2</sub>CO mixture containing *n*-Bu<sub>3</sub>SnCl and excess of potassium hexacyanoferrete. The precipitates were filtered off, washed with water and acetone and dried under vacuum at room temperature.

Anal. calcd for I ( $C_{15}H_{27}N_6Sn_3Fe$ ): C, 25.6; H, 3.8; N, 11.9%. Found: C, 25.5; H, 3.9; N, 11.8%. Anal. calcd for II ( $C_{42}H_{81}N_6Sn_3Fe$ ): C, 46.6; H, 7.5; N, 7.7%. Found: C, 46.5; H, 7.9; N, 7.75%. Anal. calcd for III ( $C_{60}H_{47}N_6Sn_3Fe$ ): C, 56.3; H, 3.7; N, 6.6%. Found: C, 56.5; H, 3.7; N, 6.7%.

The HGSCPs **1–6** were obtained by adding 1 mmol freshly prepared **I–III** to 1 mmol of resorcinol or PNP with continuous grinding and stirring in the presence of small amounts of water. The HGSCPs **1–6** were isolated, washed with water and ethanol and dried under vacuum.

Anal. calcd for  $[(1,2,4-THB)(Me_3Sn)_4$  Fe  $(CN)_6]_n$ .H<sub>2</sub>O **1**  $(C_{24}$  H<sub>44</sub> N<sub>6</sub> Sn<sub>4</sub> Fe O<sub>4</sub>): C, 28.5; H, 4.3; N, 8.3%. Found: C, 28.7; H, 4.3; N, 8.1%. Anal. calcd for  $[(1,2,4-THB)(n-Bu_3Sn)_{3.5}$  Fe  $(CN)_6]_n$ .H<sub>2</sub>O **2**  $(C_{54}$  H<sub>102.5</sub> N<sub>6</sub> Sn<sub>3.5</sub> Fe O<sub>4</sub>): C, 47.3; H, 7.5; N, 6.1%. Found: C, 47.0; H, 7.4; N, 6%. Anal. calcd for [(1,2,4-THB) (Ph<sub>3</sub>Sn)<sub>4</sub> Fe  $(CN)_6]_n^3$ H<sub>2</sub>O **3**  $(C_{84}$  H<sub>72</sub> N<sub>6</sub> Sn<sub>4</sub> Fe O<sub>6</sub>): C, 56.2; H, 4.7; N, 5.0%. Found: C, 55.8; H, 4.8 N, 5.0%. Anal. calcd for for  $[(BQ)_{0.067}(2-HBQ)_{0.933}$  (Me<sub>3</sub>Sn)<sub>3.5</sub> Fe  $(CN)_6]_n^6$ H<sub>2</sub>O **4**  $(C_{22.5}$  H<sub>37.5</sub> N<sub>6</sub> Sn<sub>3.5</sub> Fe O<sub>4</sub>): C, 29.2; H, 4; N, 9.1%. Found: C, 28.6;

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H, 4; N, 9.3%. Anal. calcd for  $[(BQ)_{0.067}(2-HBQ)_{0.933} (n-Bu_3Sn)_{3.5}$  Fe  $(CN)_6]_n^{\bullet}H_2O$  **5**  $(C_{54} H_{100.5} N_6 Sn_{3.5}$  Fe O<sub>4</sub>): C, 48.0; H, 7.5; N, 6.2%. Found: C, 47.7; H, 7.2; N, 6.3%. Anal. calcd for  $[(BQ)_{0.1}(2-HBQ)_{0.90} (Ph_3Sn)_4$  Fe  $(CN)_6]_n^{\bullet}3H_2O$  **6**  $(C_{48} H_{70} N_6 Sn_4$  Fe O<sub>6</sub>): C, 56.8; H, 3.9; N, 4.7%. Found: C, 56.4; H, 3.9; N, 4.8%.

#### Instruments

The IR and UV-vis spectra were recorded on Perkin Elmer SP 1430 and Shimadzu 3101 PC spectrophotometers, respectively. Elemental analyses were carried out on a Perkin Elmer 2400 automatic elemental analyzer. The X-ray powder diffraction patterns were recorded using a Philips PW-1729 (Cu<sub>x</sub> – K<sub> $\alpha$ </sub> radiation using Ni filter). The simulated X-ray diffraction patterns were obtained using a Mercury 2.2 program. The magnetic susceptibility was determined with Johnson-Matthey susceptometer. HPLC experiments were carried out on HPLC, Waters 2690 series. HPLC experiments for PNP were conducted using an X-bridge C18 column (5  $\mu$ m particle size, 150  $\times$  4.6 mm) with a flow rate of 1.5 ml min<sup>-1</sup> at room temperature. The mobile phases used were acetonitrile and methanol-water (1:1, v/v). HPLC experiments for resorcinol were carried out using a reverse-phase C<sub>18</sub> Atlantis column (250  $\times$  4.6 mm) with a flow rate of 1.5 ml min<sup>-1</sup> at room temperature. The mobile phase used consisted of 10 mM ammonium formate, with pH adjusted to 3.0 using formic acid. The solid materials were heated in methanol using ultrasonic bath. A 20 µL volume of each solution was filtered off and then injected into the column. The concentrations of resorcinol and *p*-nitrophenol were determined by HPLC.

## **Results and Discussion**

The powder X-ray diffractions of I-III were compared with simulated X-ray diffractions based on data resulting from the structure analyses of single crystals of I-III<sup>[10-12]</sup> (Fig. 1). The experimental and simulated X-ray diffraction diffractograms look very similar, suggesting immediately that the final powdered bulk samples of I-III should be structurally closely related to the crystalline forms. The common feature of these SCPs is the polymeric nonlinear  $[Fe-C \equiv N-Sn-N \equiv C-Fe]_n$  chains which intersect to build up the 3D-network structure. The alkyl or phenyl groups are disordered over three positions with their trigonal arrangement preserved. The difference between the structures of the methyl-, n-butyl- and phenyl-tin SCPs arises from the constraints imposed by packing the ligands with the framework defined by the Fe-CN-Sn bonds. The presence of remarkable wide channels whose walls are internally coated by constituents of the lipophilic R<sub>3</sub>Sn groups allows encapsulation of resorcinol or PNP, which undergoes *in situ* oxidation forming new HGSCPs.<sup>[10–12]</sup>

The IR spectra of **I–III** display a strong intensity band at 2145, 2133 and 2141 cm<sup>-1</sup>, respectively, due to  $\nu_{C \equiv N}$ . These values are much higher than those of the genuine salts of the corresponding  $[Fe^{III}(CN)_6]^{3-}$  anions ( $\nu_{C \equiv N} = 2116 \text{ cm}^{-1}$ ). This increase in the vibration wavenumbers of the cyanide bond suggests the presence of a nonlinear chain with anticipated bridges  $[Fe-C \equiv N-Sn-N \equiv C-Fe]$ . The  $\nu_{Fe-C}$  band of **I–III** at 407, 403 and 411 cm<sup>-1</sup>, respectively, reflects the presence of the octahedral  $[Fe^{III}(CN)_6]^{3-}$  building blocks.<sup>[13]</sup> The IR-active  $\nu_{Sn-C}$  vibrations at 547, 519 and 582 cm<sup>-1</sup> for **I–III**, respectively, reflect the presence of Sn–C bonds, while the absence of the symmetric  $\nu_{Sn-C}$  band advocates the exclusive presence of trigonal planar



**Figure 1.** Comparison of the simulated and experimental X-ray diffractograms of the host supramolecular coordination polymers I–III.

 $\mathsf{R}_3\mathsf{Sn}$  units owing to their axial anchoring to two cyanide N atoms.^{[14]}

The electronic absorption spectra of **I**–**III** in Nujol mull matrices reveal mainly three absorption bands in the region 220–432 nm. The first band at 220 nm is due to  $\pi - \pi^*$  transitions from iron to the cyanide ligand (M  $\rightarrow$  L). The composite band at 310–330 nm corresponds to ligand field (d–d) transitions ( $^2A_{2g} \rightarrow {}^2T_{1g}$ ).<sup>[15]</sup> The low energy band at 419–430 nm corresponds to  $\pi - \pi^*$  transitions of the [Fe<sup>III</sup>(CN)<sub>6</sub>]<sup>3–</sup> building blocks. The SCPs I–III exhibit paramagnetic behavior with magnetic values,  $\mu_{eff}$  equal to 2.036, 2.32 and 2.291 BM, respectively, supporting the presence of [Fe<sup>III</sup>(CN)<sub>6</sub>]<sup>3–</sup> building blocks.

#### Spectral characterstics of the HGSCPs 1-6

Resorcinol and PNP undergo *in situ* oxidation within the channels of the SCPs **I–III** while in some cases the SCPs exhibit partial reduction. The IR spectra of **1–3** reveal a broad band at 3420, 3423 and 3410 cm<sup>-1</sup>, respectively, corresponding to  $\nu$ H<sub>2</sub>O. The IR spectrum of resorcinol exhibits two strong bands at 3257 and 3208 cm<sup>-1</sup> due to stretching vibrations of the two hydroxyl groups. On the other hand, the IR spectra of **1–3** reveal a broad band around 3250 cm<sup>-1</sup> due to  $\nu_{OH}$  of the oxidation product.  $\gamma_{CH}$  vibrations of resorcinol appear at 843 and 680 cm<sup>-1</sup> due to the isolated CH bond and the three adjacent CH bonds, respectively, while they appear in the IR spectra of **1–3** at 860 and 790 cm<sup>-1</sup> due to the isolated CH bond and the two adjacent CH bonds, respectively. These IR bands indicate that resorcinol is oxidized to the corresponding 1,2,4-trihydroxy benzene (THB). This opinion was further supported by the presence of the bands of the benzene

Table 1. The electronic absorption spectra (nm) of the SCPs I–III and HGSCPs 1–6					
SCP	(M $\rightarrow$ L) transition	d-d transition	<i>π</i> - <i>π</i> * [Fe	<sup>III</sup> (CN) <sub>6</sub> ] <sup>3-</sup>	
1	220	310	41	19	
н	218	315	42	25	
ш	222	330	43	30	
HGSCP	${}^{1}L_{a} \leftarrow {}^{1}A$	$^{1}L_{b} \leftarrow ^{1}A$	$\pi - \pi^* [\text{Fe}^{II}(\text{CN})_6]^{4-}$	$\pi - \pi^*  [Fe^{III}(CN)_6]^{3-}$	
1	225	280	335	-	
2	230	280	345	420	
3	230	285	350	-	
HGSCP	$\pi - \pi^* BQ$	$\pi - \pi^* [\text{Fe}^{II}(\text{CN})_6]^{4-}$	$\pi - \pi^*  [Fe^{III}(CN)_6]^{3-}$		
4	290	317	430		
5	285	335	425		
6	295	338	-		

ring at 1610, 1580, 1542 and 1514 cm<sup>-1</sup> due to  $\nu_{C=C}$  and the absence of any bands due to  $\nu_{C=0}$ . The IR spectra of **1** and **3** also exhibit bands due to  $\nu_{C=N}$  at 2087 and 2043 cm<sup>-1</sup> and at 2088 and 2062 cm<sup>-1</sup>, respectively, and the bands at 446 and 450 cm<sup>-1</sup> due to  $\nu_{Fe}^{II}_{-C}$ , indicating the reduction of the SCPs **I–III** by resorcinol. On the other hand, two bands appear at 2135 cm<sup>-1</sup> ( $\nu_{Fe}^{III}_{-C}$ ) and at 2085 cm<sup>-1</sup> ( $\nu_{Fe}^{II}_{-C}$ ), in addition to two bands at 408 cm<sup>-1</sup> ( $\nu_{Fe}^{III}_{-C}$ ) and 457 cm<sup>-1</sup> ( $\nu_{Fe}^{II}_{-C}$ ), indicating partial reduction of **I**–**3** also reveal the  $\nu_{Sn-C}$  band at 553, 535 and 545 cm<sup>-1</sup>, respectively, indicating the presence of HGSCPs, whose octahedral [Fe(CN)<sub>6</sub>] units are continuously interlinked by practically planar R<sub>3</sub>Sn fragments.

The IR spectrum of PNP is characterized by a strong band at 3325 cm<sup>-1</sup> due to  $v_{OH}$  and two strong bands at 1560 and 1325 cm<sup>-1</sup> due to  $v_{asym.}$  and  $v_{sym.}$  NO<sub>2</sub>, respectively. These bands disappear in the IR-spectra of 3-6, indicating that PNP is oxidized by the SCPs I-III. Also, two new bands appear at 3350-3360 and at 1640–1650 cm<sup>-1</sup> due to  $v_{OH}$  and  $v_{C=0}$ , respectively, indicating oxidation of PNP to BQ and 2-HBQ. The IR spectra of **4** and **5** exhibit the bands corresponding to the  $[Fe^{III}(CN)_6]^{3-1}$ and  $[Fe^{II}(CN)_6]^{4-}$  building blocks at 2135–2145, 2075–2082, 460 and 405 cm<sup>-1</sup>, indicating partial reduction of the SCPs I and II by PNP. On the other hand, the IR specrum of 6 reveals two bands at 2080 cm<sup>-1</sup> ( $\nu_{Fe}$ <sup>II</sup><sub>-C</sub>) and at 450 cm<sup>-1</sup> ( $\nu_{Fe}$ <sup>II</sup><sub>-C</sub>), indicating quantitative reduction of the SCP III by PNP. The IR spectra of 4-6 also display a band around 545 cm<sup>-1</sup> due to  $v_{\text{Sn-C}}$  supporting the polymeric nature of HGSCPs 4-6, as well as a broad band at 3420 cm<sup>-1</sup> due to  $v_{\rm H2O}$ .

The electronic absorption spectra of **1–6** exhibit mainly three absorption bands at 225-430 nm, except that of 2, which displays four absorption bands (Table 1). The spectra of 1-3 show two strong intensity bands at 230 and 280 nm due to (<sup>1</sup>La  $\leftarrow$  <sup>1</sup>A) and  $({}^{1}L_{b} \leftarrow {}^{1}A)$  transitions, respectively, of the benzenoid system. The band around 345 nm is due to  $\pi - \pi^*$  transitions of  $[Fe^{II}(CN)_6]^{4-1}$ building blocks while the spectrum of 2 shows an additional band at 420 nm due to  $\pi - \pi^*$  transitions of  $[Fe^{III}(CN)_6]^{3-}$  building blocks.<sup>[16]</sup> This indicates that the oxidation product of resorcinol still contains the benzene ring while the host SCP II undergoes partial reduction. On the other hand, the electronic spectra of 4 and **5** display a band at 290 nm corresponding to  $\pi - \pi^*$  transitions of benzoquinone in addition to the broad band at 317, 335 and 338 nm of **4**, **5** and **6**, respectively, due to  $\pi - \pi^*$  transitions of  $[Fe^{II}(CN)_6]^{4-}$  building blocks. The spectra of **4** and **5** also show a band at 430 and 425 nm, respectively, due to  $\pi - \pi^*$  transitions of [Fe<sup>III</sup>(CN)<sub>6</sub>]<sup>3–</sup> building blocks, indicating partial reduction to the mixed valence iron homologs. In this case, PNP was oxidized to the corresponding quinoniod structure. The spectra of **2**, **4** and **5** do not show any band in the near-IR region corresponding to an intervalence transition indicating the localized interaction between the mixed valence iron.<sup>[17]</sup> The presence of the mixed valence iron in the HGSCPs **2**, **4** and **5** was further supported by the paramagnetic nature with  $\mu_{eff}$  values of 1.6, 1.7 and 1.65 BM, respectively.

#### **HPLC study**

The chromatogram of resorcinol shows a peak with retention time 5.467 min which disappears in the chromatograms of HGSCPs **1–3** while a new peak appears with retention time 2.03 min corresponding to THB as supported by the peak of the standard THB sample, which appears at 2.108 min. On the other hand, the chromatogram of PNP exhibits a peak at retention time 2.779 min. This peak disappears in the chromatograms of **4–6** and instead two peaks appear at retention times 2.266 and 3.496 min. The new two peaks correspond to BQ and 2-hydroxy-benzoquinone (2-HBQ), respectively, as supported by the peaks of the standard BQ and 2-HBQ samples observed at 2.265 and 3.495 min, respectively. It is apparent that the ratio of the concentration of BQ to 2-HBQ within the channels of the SCPs I and II is 1:14.4 while that of the SCP III is 1:9.

## Discussion

The spectroscopic and HPLC data indicated oxidation of resorcinol to THB and PNP to BQ and 2-HBQ within the channels of the host SCPS I–III. THB is formed via the attack of the hydroxyl radical,<sup>[18]</sup> which possesses a strong electrophilic character and prefers to attack the carbon atom with the highest electron density at *ortho* and *para* positions on the benzene ring. Upon contact, a C–O bond will be formed, while a  $\pi$  bond of the aromatic ring is broken, generating a trihydroxycyclohexadienyl radical that undergoes further reaction with dissolved oxygen to yield THB<sup>[6]</sup> (Scheme 1).

On the other hand, PNP is mainly oxidized to 2-HBQ and a small amount of BQ by electrophilic addition of the hydroxyl radical to the double bonds of the benzene ring to form initially substituted aromatic products which lead to two pathways.<sup>[19]</sup> For one way, the hydroxyl radical would attack the benzene ring to produce



Scheme 1. Oxidation process of resorcinol within the channels of the host SCPS I-III.



 $\mbox{Scheme 2. Oxidation process of p-nitrophenol within the channels of the host SCPS I–III.$ 

Table 2.   The time and the oxidation conversion percent of resorcinol     and PNP by the SCPs I-III					
HGSCP	Reaction time (min)	Resorcinol or PNP conversion (%)			
1	12	90			
2	20	90			
3	10	98			
4	20	92			
5	25	87			
6	16	97			

4-nitrocatechol. For the other, the hydroxyl radical would attack the nitro group due to the relatively long length of the C–N bond. The former case predominantly forms 2-HBQ while the other leads to the formation of small amount of BQ according to Scheme 2.

The oxidative activity of the host SCPs I–III indicates that the host III has higher oxidative activity than the SCPs I and II (Table 2).

The conversions of resorcinol or PNP to the corresponding oxidation products are nearly complete in the case of the SCP **III** within 10 and 16 min, respectively. SCP **III** contains wider and more expandable rectangular channels than SCPs **I** and **II** due to the presence of a zigzag chain formed by hydrogen bonding.<sup>[12]</sup> On the other hand, SCP **II** has a lower oxidative activity than **I** and **III** due to the presence of different kinds of rings constructing the 3D-network while the bulky butyl groups fill most of the space of the channels. However, **I**–**III** can be considered as effective oxidizing reagents towards oxidation of resorcinol or PNP.

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