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Synthesis, characterization, electrospinning and antibacterial studies on triphenylphosphine-dithiophosphonates Copper(I) and Silver(I) complexes

Mehmet Karakus^{1*}, Yuksel Ikiz², Halil Ibrahim Kaya³ and Omer Simsek³

Abstract

Background: The novel amido and O-ferrocenyldithiophosphonates $[\text{FcP}(\text{S})(\text{SH})(\text{NHR}^1)]$ ($\text{Fc} = \text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4)$, $\text{R}^1 = 1\text{-}(4\text{-fluorophenylethyl and benzyloxycyclopentyl})$ and $[\text{FcP}(\text{S})(\text{OR}^2)\text{S}^-][\text{H}_3\text{N}^+\text{C}(\text{CH}_3)_3]$ ($\text{R}^2 = \text{myrtanyl})$ were synthesized by the reaction of $[(\text{FcPS}_2)]_2$ ($\text{Fc} = \text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4)$) and chiral amines, such as (S)-(–)-1-(4-fluorophenylethyl) amine and (1S,2S)-(+)-benzyloxycyclopentyl amine, and of (1S), (2S), (5S)-myrtanol in toluene. The reaction of ferrocenyldithiophosphonates and $[\text{Cu}(\text{PPh}_3)_2]\text{NO}_3$ or AgNO_3 and PPh_3 gave rise to copper(I) and silver(I) complexes in THF. $[\text{Ag}_2\{\text{FcP}(\text{OMe})\text{S}_2\}_2(\text{PPh}_3)_2]$ and $[\text{Cu}(\text{PPh}_3)_2]\text{NO}_3$ were embedded into nanofibers and their antimicrobial activities on fibers were also investigated.

Results: The compounds have been characterized by elemental analyses, IR, NMR (^1H -, ^{31}P -) spectroscopy as well as MS measurements. Nanofibers were obtained by electrospinning method which is the simplest and most effective method to produce nanoscale fibers under strong electrical field. Antimicrobial activity of the compound **5**, $[\text{Ag}_2\{\text{FcP}(\text{OMe})\text{S}_2\}_2(\text{PPh}_3)_2]$, and $[\text{Cu}(\text{PPh}_3)_2]\text{NO}_3$ on fibers were studied.

Conclusions: In this study, the new dithiophosphonate ligands were synthesized and utilized in the preparation of copper(I) and silver(I) complexes with ferrocenyldithiophosphonate and triphenylphosphine. Then, the compounds $[\text{Ag}_2\{\text{FcP}(\text{OMe})\text{S}_2\}_2(\text{PPh}_3)_2]$ and $[\text{Cu}(\text{PPh}_3)_2]\text{NO}_3$ were added into the PAN solutions (Co-PAN dissolved in dimethylacetamide) and the solutions were electrospun onto microscope slides and PP meltblown surfaces. Antimicrobial activity of the compounds $[\text{Ag}_2\{\text{FcP}(\text{OMe})\text{S}_2\}_2(\text{PPh}_3)_2]$ and $[\text{Cu}(\text{PPh}_3)_2]\text{NO}_3$ on fibers were determined in vitro against two indicator strains; *M. luteus* NCIB and *E. coli* ATCC25922. The obtained results indicated that these metals showed moderate level antimicrobial activities.

Keywords: Dithiophosphonates, Triphenylphosphine, Copper(I) and Silver(I) complexes, Nanofiber, Electrospinning, Antibacterial

Introduction

Metallic silver and copper are natural antimicrobial agents and historically recognized [1,2]. These agents have been added into many polymer solutions, such as polyacrylonitrile (PAN), polyvinyl alcohol (PVA), Poly(N-vinylpyrrolidone), polylactic acid (PLA), to produce nanofibers with electrospinning method [3-10].

Electrospinning is a simple method to produce micro or nanoscale fibers. Nanofibers, due to their high surface area and porosity, find applications in energy storage, healthcare, biotechnology, environmental engineering, defense and especially filtration [11]. Electrospinning process uses a high voltage electric field to produce electrically charged jets from polymer solution. Polymer solution on tip of a syringe or pipette ejects toward opposite charged collector when overcome surface tension. Polymer chain entanglements prevent jets from breaking off and create fiber form. Because of evaporation

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and air drag, jets split into smaller diameters [12]. Process parameters are divided into; solution parameters which include viscosity, surface tension, electrical conductivity; processing conditions which include applied voltage, tip to collector distance, feeding amount and type; and ambient conditions which include temperature and moisture [13].

Dithiophosphonates are an important class in organophosphorus chemistry due to utilising in agricultural, medicinal and technological field [14-35]. It has been known that a considerable number of dithiophosphonates and their metal complexes have been easily synthesized by the reaction Lawesson's reagent or Ferrocenyl Lawesson's reagent and the respective alcohols or amines due to a ring opening reaction by nucleophilic attack [30-32]. However, there is no study on nanofibers of dithiophosphonates by using electrospinning method.

In the present work, we report the synthesis of novel dithiophosphonates and their metals complexes with dithiophosphonates and triphenylphosphine. All compounds were characterized by elemental analyses, IR, NMR (^1H -, ^{31}P -) spectroscopy as well as MS measurements. The compounds $[\text{Ag}_2\{\text{FcP}(\text{OMe})\text{S}_2\}_2(\text{PPh}_3)_2]$ and $[\text{Cu}(\text{PPh}_3)_2]\text{NO}_3$ added into PAN polymer solutions and mixed. Mixed polymer solutions were electrospun onto microscope slides and PP (polypropylene) meltblown

surfaces. Meltblown is very commonly used textile non-woven structure to support and protect fine fibers, especially in filtration. Antibacterial activities of those nanofibers were investigated.

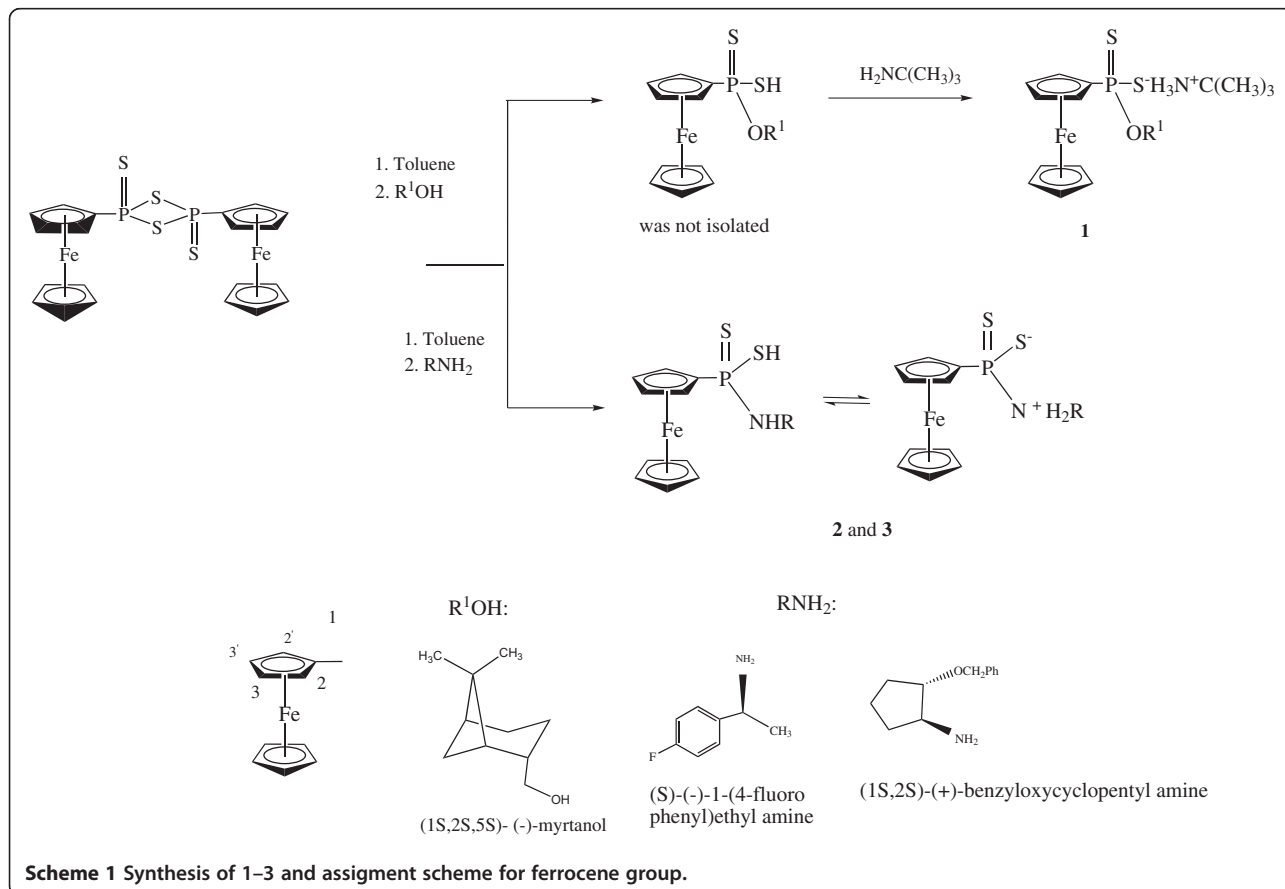
Result and discussion

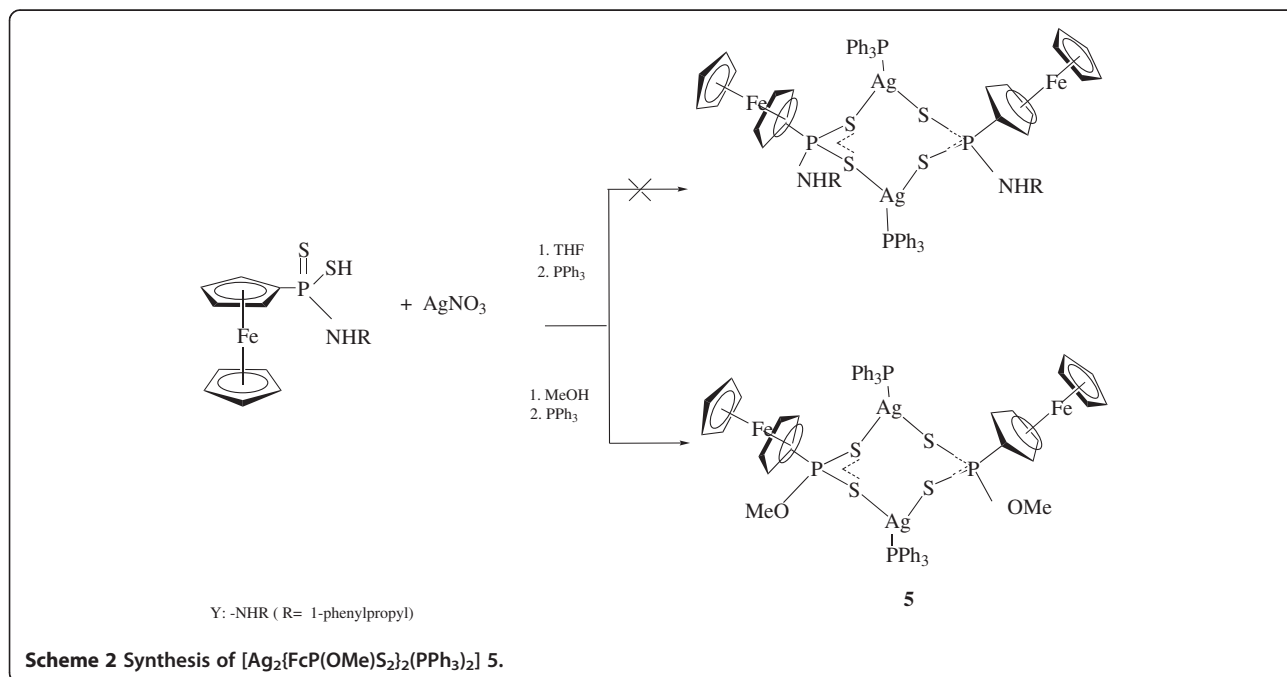
Synthesis and characterization

Amido and O-ferrocenyldithiophosphonates have been synthesized from Ferrocenyl Lawesson's reagent and amines or (1S,2S,5S)- (-)- O-myrtanol (Scheme 1). The Ferrocenyl Lawesson's reagent was reacted with (1S,2S,5S)- (-)- O-myrtanol and a crude dithiophosphonic acid was formed and then was treated with *tert*-butyl amine in order to convert it to its suitable salt **1**. In the case of amidodithiophosphonates **2** and **3** (Scheme 1), they were obtained as air stable solids [35]. The compound **5** was prepared by the reaction of (R) - (+) - 1 - phenylethyl amidoferrocenyldithiophosphonate [35] and AgNO_3 in toluene and MeOH mixture (Scheme 2).

The IR spectrum of the ligands and their complexes showed two characteristic bands at around $692\text{--}642\text{ cm}^{-1}$ and $582\text{--}515\text{ cm}^{-1}$ which are assigned to $\nu_{\text{as}}(\text{PS}_2)$ and $\nu_{\text{s}}(\text{PS}_2)$, respectively [36,37].

Mass spectra of the compound **1** - **5** exhibited m/z values for identifiable certain fragments. Specific rotations





of all compounds showed that only one optical isomer was formed.

The ^{31}P NMR spectra of the ligands **2** and **3** were measured in DMSO-d_6 and showed two separate sets of signals which were shifted to 61.80 ppm ($J_{\text{PN-H}} = 41.7$ Hz for **2**) and 62.09 ppm ($J_{\text{PN-H}} = 38.2$ Hz for **3**) [35,38]. A very small signal was observed in the ^{31}P NMR spectra of the ligands **2** and **3** due to probably neutral and zwitter ion form in the DMSO-d_6 solution (see Scheme 1 for two isomer of **2** and **3**).

All ligands **1–3** reported here have been characterized by elemental analysis, IR, NMR and mass spectroscopy (Additional file 1). However, the ^{13}C -NMR spectra of the ligands **2** and **3** did not measured due to decomposed in the DMSO-d_6 .

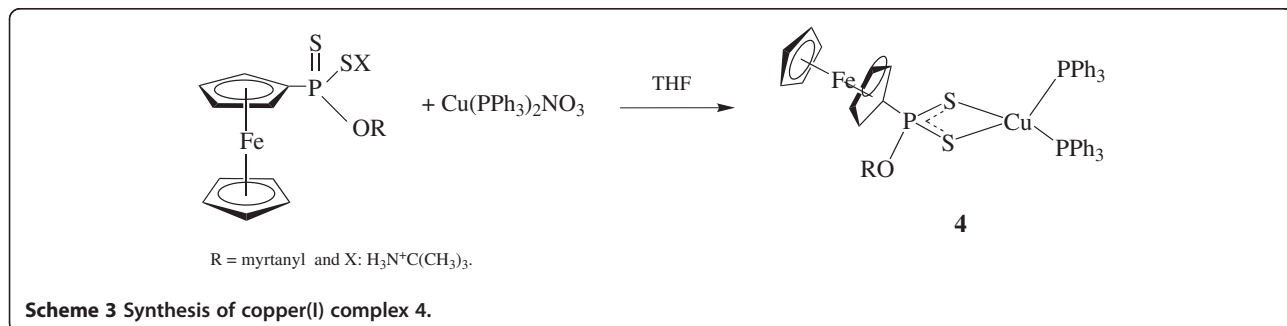
The synthesis of copper(I) and silver(I) complexes with ferrocenyldithiophosphonate and triphenylphosphine have been described and also characterized by elemental analyses, IR, NMR and MS spectroscopies (Additional file 1). The synthesis of copper(I) complexes were performed

by the reaction of $[\text{Cu}(\text{PPh}_3)_2]\text{NO}_3$ and the ligands (Scheme 3).

The complex **4** was obtained as yellow-orange solid. The ^{31}P NMR spectrum of **4** showed two signals at 97.8 and -2.9 ppm as expected [36] which were assigned to PS_2 and PPh_3 , respectively. The Cu(I) and Ag(I) complexes of **2** and **3** also showed two signals in the ^{31}P NMR spectrum as expected. However, other spectroscopic data were not satisfied. The ^{31}P NMR spectra of $[\text{Ag}_2\{\text{FcP}(\text{OMe})\text{S}_2\}_2(\text{PPh}_3)_2]$ **5** was measured in CDCl_3 and observed two signal at 92.82 (PS_2) and 6.03 (PPh_3) ppm.

Electrospinning studies

A comparative study on Silver(I) and Copper(I)- triphenylphosphine derivatives was performed and developed for the application of electrospun nanofibers. Figure 1 shows the compound $[\text{Ag}_2\{\text{FcP}(\text{OMe})\text{S}_2\}_2(\text{PPh}_3)_2]$ added PAN nanofibers on a microscope slide and PP meltblown surface. Average fiber diameter on microscope slide was measured



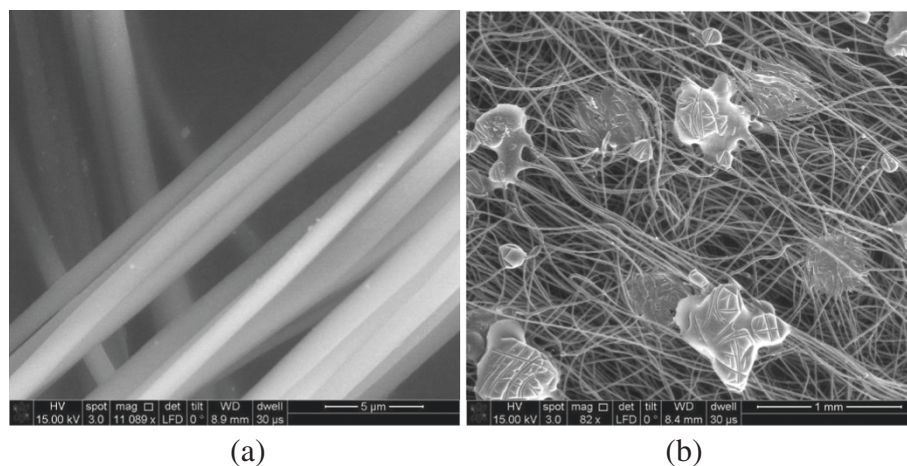


Figure 1 $[\text{Ag}_2\{\text{FcP}(\text{OMe})\text{S}_2\}_2(\text{PPh}_3)_2]$ added; a) electrospun PAN fibers on glass, b) electrospayed PAN particles on nonwoven surface.

about 1 micron which was higher than expected average fiber diameter. Occasional electrospaying occurred as in Figure 1-b, because of aggregation of the compound $[\text{Ag}_2\{\text{FcP}(\text{OMe})\text{S}_2\}_2(\text{PPh}_3)_2]$ particles.

Figure 2 shows $[\text{Cu}(\text{PPh}_3)_2]\text{NO}_3$ added PAN nanofibers on a microscope slide and PP meltblown surface. Cu particles on nanofiber surface can be seen from SEM images as in Figure 2-a. Average PP meltblown fiber diameter was measured about 15 micron.

Antibacterial activities

Antimicrobial activities of the compounds $[\text{Ag}_2\{\text{FcP}(\text{OMe})\text{S}_2\}_2(\text{PPh}_3)_2]$ and $[\text{Cu}(\text{PPh}_3)_2]\text{NO}_3$ were determined first on agar media against two indicator strains; *M. luteus* NCIBM and *E. coli* ATCC25922. According to the well diffusion assay on agar media, $[\text{Ag}_2\{\text{FcP}(\text{OMe})\text{S}_2\}_2(\text{PPh}_3)_2]$ and $[\text{Cu}(\text{PPh}_3)_2]\text{NO}_3$ showed medium level of antimicrobial activities against both strains (Figure 3). When the control compounds (not including Cu or Ag

derivatives) were used for the same method, no inhibition zone or no antibacterial activity was occurred meaning that the relevant antimicrobial activities were mainly due to incorporated elements of Cu or Ag.

The control compounds and the compounds embedded fibers on meltblown surfaces were tested for inhibition of *E. coli* ATCC25922 in submerged bacterial solution. The highest inhibition ($32.5 \pm 2.1\%$) on *E. coli* was achieved with the compound $[\text{Ag}_2\{\text{FcPS}_2(\text{OMe})\}_2(\text{PPh}_3)_2]$. On the other hand, $[\text{Cu}(\text{PPh}_3)_2]\text{NO}_3$ provided $19.4 \pm 3.2\%$ inhibition on *E. coli* while the control compounds showed no inhibition.

In this study, the compounds showed better antibacterial activities on agar media because of diffusion. However when the compounds embedded into fibers, they showed antibacterial activities only in contact with bacteria. Even though there was limited antibacterial activity, these metals could be used on fibers with dithiophosphate and phosphine complexes for antibacterial applications.

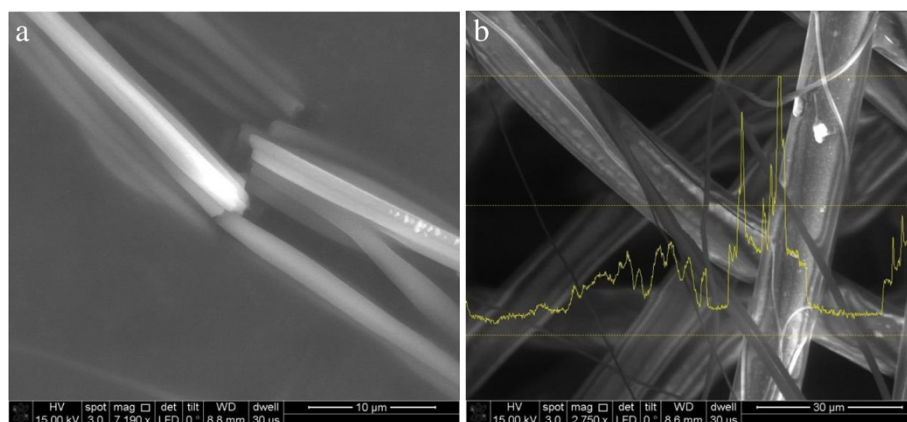
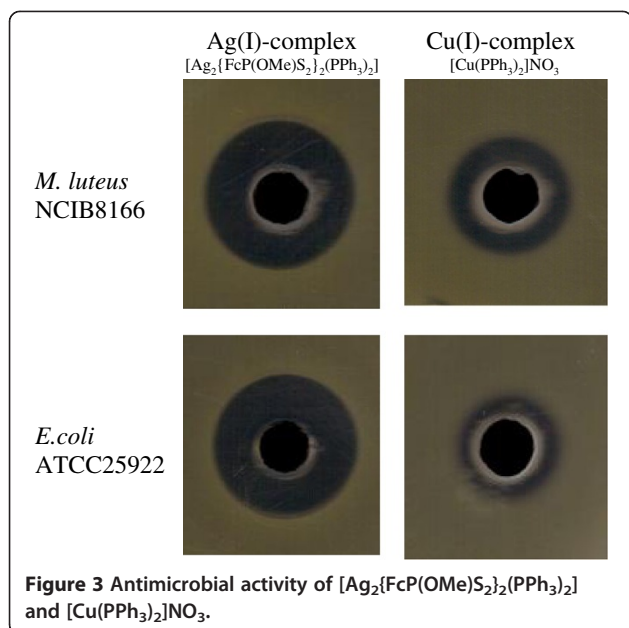


Figure 2 $[\text{Cu}(\text{PPh}_3)_2]\text{NO}_3$ added electrospun PAN fibers; a) on glass, b) on nonwoven surface.



It is generally believed that heavy metals react with proteins by combining the thiol (SH) groups, which leads to the inactivation of the proteins [39]. Therefore Ag and Cu could maintain their antimicrobial activity in the complexes of dithiophosphate and phosphine. This is significant especially for using these metals as embedded in fibers, although they have limited antibacterial activity [40,41].

Experimental

Materials and method

Solvents were distilled before used. The compounds 4 and 5 were carried out under N_2 atmosphere. All other chemicals were purchased from commercial sources and used directly without further purification. $[FcPS_2]_2$ (Fc: $Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4)$) and $[Cu(PPh_3)_2]NO_3$ were prepared as described in the literature [32,42], respectively. Elemental analyses were determined with a GmbH vario-MICRO CHNS apparatus. Melting points were determined by using Electrothermal apparatus. NMR spectra were recorded on a Bruker AVANCE DRX 400 NMR spectrometer and Jeol GSX 270 in $CDCl_3$ and d_6 -DMSO. IR spectra was measured on a Perkin-Elmer 2000 FTIR spectrophotometer ($4000 - 400\text{ cm}^{-1}$). Mass spectra were recorded with an AGILENT 1100 MSD and Waters machines. Optical rotation values were determined with an automatic digital ADP 440+ polarimeter.

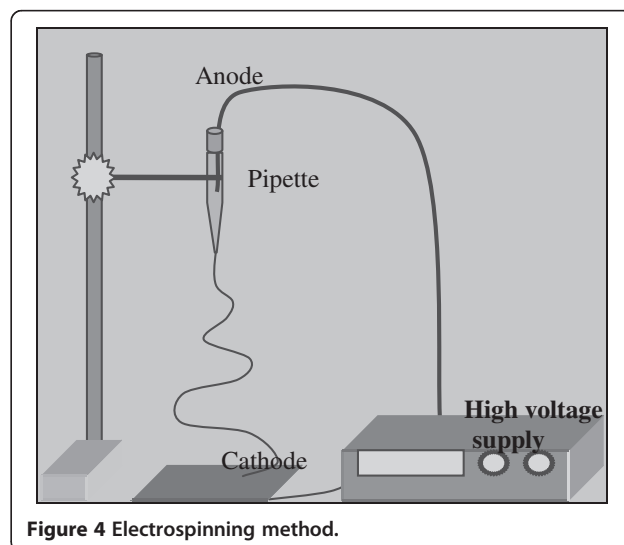
Electrospinning

The co-polymer polyacrylonitrile (PAN) and solvent dimethylacetamide (DMAc) were obtained from "AKSA acrylic chemistry company". 15% polymer was dissolved in 85% solvent (w/w-weight by weight basis) at 80–

100°C and stirred at least 4 hours. Polymer solution was prepared for electrospinning process by feeding into a pipette. Matsusada AU-40-0.75 high voltage supply were used to create electric field. Tip to collector distance was adjusted for 12 cm and voltage was adjusted 30 kV between the electrodes (Figure 4).

Antibacterial activity

Two different antimicrobial test methods were used. Firstly the antimicrobial activity of synthesized compounds was determined by using well diffusion assay [43]. After filter sterilization of relevant compounds, approximately 100 μl was filled to the wells which had been prepared previously by overlaying LB soft agar including the indicator strains *Micrococcus luteus* NCIB8166 and *Escherichia coli* ATCC25922 on to the Müller-Hilton agar plates, then 5 mm wells were created with cork borer respectively. DMSO was used for controlling. To test antimicrobial efficiency of relevant compounds on fibers, the dynamic assessment of antimicrobial activity was carried out according to the standard test method released from American Society for Testing and Materials (ASTM) for immobilized antimicrobial agents under dynamic contact (E2149-01). Test bacteria (*Escherichia coli* ATCC25922) were cultured in LB broth (Fluka) overnight inoculations at 37°C. Subsequently, bacterial culture was diluted in 0.3 mM KH_2PO_4 buffer until the solution has an absorbance of 0.28 ± 0.02 at 475 nm as measured spectrophotometrically to reach bacterial suspension ($1.5\text{--}3.0 \times 10^5\text{ CFU ml}^{-1}$). Rounds of fibers having total 4 in.^2 treated surface area were inoculated with $50 \pm 0.5\text{ ml}$ of bacterial suspension and incubated at 37°C 1 h $\pm 5\text{ min}$. Standard plate counts were performed after decimal dilution of the samples in 9 ml of 0.1% peptone water. The percent inhibition rate



(%) was calculated as formula of $(N1-N2/N1) \times 100$, where N1 and N2 represent the number of colonies on the plates before and after inhibition, respectively. Untreated fibers were used as a negative control.

Synthesis of ^t-Butyl ammonium salt of (1S,2S,5S)-(-)-O-myrtanyl ferrocenyl dithiophosphonate (1)

2,4-Bis(ferrocenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide [FcPS(μ -S)]₂ (1.80 g, 3.21 mmol) was reacted with 1S,2S,5S)-(-)-myrtanol (1.05 g, 6.42 mmol) in toluene (20 mL). The mixture was refluxed until all solids had dissolved. The dark brown solution was cooled to rt, filtered and treated with excess *tert*-butyl amine. The product was precipitated in freezer from toluene as a yellow solid, which was isolated by filtration, washed with toluene and *n*-hexane and then dried in air. Yield: 2.10 g 65%, m.p.: >187(dec.)°C. $[\alpha]_{589}^{25} = -3.61$ (c = 0.55 in THF). IR(KBr, cm⁻¹) ν_{max} : 648 (s, PS₂, asym) and 582 (m, PS₂, sym). ¹H NMR (DMSO-d₆, ppm) δ : 4.42 (br, 2H, C₅H₄), 4.23 (s, 5H, C₅H₅), 4.21 (br, 2H, C₅H₅), 4.18 (br, 2H, OCH₂), 1.80-1.25 (m, 9H in myrtanyl group), 1.18 (s, 9H, *t*Bu), 1.02 (s, 3H, CH₃), 1.01(s, 3H, CH₃). ¹³C NMR (DMSO-d₆, ppm) δ : 90.94 (d, C¹; *ipso*-C in C₅H₄, ¹J_{PC} = 124.7 Hz), 84.23(d, ²J_{PC} = 7.9 Hz), 71.30 (d, C² and C^{2'}, ²J_{PC} = 13.9 Hz), 70.06 (s, C₅H₅), 69.71(d, ⁴J_{PC} = 2.7 Hz), 68.91 (d, C³ and C^{3'}, ³J_{PC} = 4.9 Hz), 49.81 (s, *t*But), 49.12 (d, ³J_{PC} = 5.2 Hz), 48.37, 41.50, 29.95 (s, *t*Bu), 29.71, 26.78, 26.41, 22.23, 20.8 ppm. ³¹P NMR (DMSO-d₆, ppm) δ : 105.46. MS (ESI): m/z 433.1 [M-(H₃N⁺C(CH₃)₃)]. Anal. Calcd. for C₂₄H₃₈FeNOPS₂: C, 56.80; H, 7.55; N, 2.76; S, 12.64%. Found: C, 57.08; H, 7.38; N, 2.72; S, 12.18%.

Synthesis of (S)-(-)-1-(4-fluorophenylethyl)-amidoferrocenyldithiophosphonate (2)

[FcP(S)(μ -S)]₂ 1.50 g (2.67 mmol) was treated with (S)-(-)-1-(4-fluorophenylethyl) amine (0.745 g, 5.35 mmol) in a 1:2 ratio in toluene (25 mL) to give the corresponding amidoferrocenyldithiophosphonate. The reaction was carefully heated until all the solids dissolved and a brown solution was obtained and then a solid product was formed, which was isolated by filtration. The product was washed with petroleum ether (40–60°C). The yellow crystalline product was dried under vacuum. Yield: 1.57 g, 70%, m.p.: 169°C. $[\alpha]_{589}^{25} = 75$ (c = 0.08 in THF). IR(KBr, cm⁻¹) ν_{max} : 645 (s, PS₂, asym) and 526 (m, PS₂, sym). ¹H NMR (DMSO-d₆, ppm) δ : 7.63 (br, 2H, arom.), 7.25 (br, 2H, arom.), 4.56 (br, 2H, C₅H₄), 4.43 (br, 2H, C₅H₄), 4.37 (s, 5H, C₅H₅), 2.50 (s, 3H, CH₃), 1.59 (s, 1H, CH). ³¹P NMR (DMSO-d₆, ppm) δ : 61.80 (d, J_{PNH} = 41.7 Hz) ppm. MS (ESI): m/z = 401.95 [M-F]⁺. Anal. Calcd. for C₁₈H₁₉NF₂PS₂Fe: C, 51.56; H, 4.57; N, 3.34; S, 15.29%. Found: C, 51.71; H, 5.07; N, 3.54; S, 14.20%.

Synthesis of (1S,2S)-(+)-benzyloxycyclopentyl-amidoferrocenyldithiophosphonate (3)

Compound 3 was prepared in the same manner as compound 2, from [FcP(S)(μ -S)]₂ (1.00 g, 1.78 mmol) and 1S,2S-(+)-benzyloxycyclopentyl amine 0.68 g (3.56 mmol) in toluene (25 mL). Yield: 1.19 g (76%), m.p.: 174–176°C. $[\alpha]_{589}^{25} = 53.33$ (c = 0.15 in THF). IR(KBr, cm⁻¹) ν_{max} : 645 (s, PS₂, asym) and 525 (m, PS₂, sym). ¹H NMR (DMSO-d₆, ppm) δ : 8.29(br, 1H, NH), 7.37(br, 5H, arom.), 4.54 (br, s, 2H, C₅H₄), 4.21 (br, s, 5H, C₅H₅), 4.18 (br, s, 2H, C₅H₄), 3.99 (br, 2H, OCH₂), 3.80 – 1.69 (br, m, 8H, C₅H₈ group). ³¹P NMR (DMSO-d₆, ppm) δ : 62.09 ppm (J_{PN-H} = 38.2 Hz) ppm. MS (ESI): m/z = 296.86 [M-C₅H₈OCH₂C₆H₅]⁺. Anal. Calcd. for C₂₂H₂₇NOPS₂Fe: C, 56.06; H, 5.59; N, 2.97%. Found: C, 60.07; H, 6.34; N, 3.30%.

Synthesis of [Cu{Fe(η^5 -C₅H₅)(η^5 -C₅H₄P(OR)S₂)(PPh₃)₂}] (R = myrtanyl) (4)

A solution of [Cu(PPh₃)₂NO₃] (0.13 g, 0.20 mmol) in THF (10 mL) was added dropwise to a solution of (1S, 2S, 5S)-O-myrtanyl-ferrocenyldithiophosphonate 1 (0.10 g, 0.20 mmol) in THF (10 mL) and stirred at r.t. for 2 h. A yellow-orange solution was observed. The reaction mixture was filtered and the solvent was removed under reduced pressure. A yellow-orange crystalline product was isolated. Yield: 0.12 g, 60%, m.p.: 179–180°C. $[\alpha]_{589}^{25} = 120$ (c = 0.05 in THF). IR (KBr, cm⁻¹) ν_{max} : 642 (s, PS₂, asym) and 515 (m, PS₂, sym). ¹H NMR (CDCl₃, ppm) δ : 7.43 – 7.25 (m, 30H, arom.), 4.36 (br, 2H, C₅H₄), 4.25 (s, 2H, C₅H₅), 4.21 (s, 2H, C₅H₄), 3.80 (m, 2H, OCH₂), 2.40–1.10 (m, 9H, in myrtanyl group), 1.24 (s, 3H, CH₃), 0.87 (s, 3H, -CH₃). ³¹P NMR (CDCl₃, ppm) δ : 97.85 (PS₂) and -2.87 (PPh₃) ppm. Anal. Calcd. for C₅₆H₅₆OP₃S₂FeCu (1021.51 g.mol⁻¹): C, 65.84; H, 5.52; S, 6.27%. Found: C, 65.49; H, 5.54; S, 5.93%.

Synthesis of [Ag{Fe(η^5 -C₅H₅)(η^5 -C₅H₄P(OR)S₂)(PPh₃)₂}]₂ (R = CH₃) (5)

A mixture of AgNO₃ (0.12 g, 0.70 mmol) and PPh₃ (0.18 g, 0.70 mmol) in MeOH (20 mL) was added dropwise to a solution of the compound (R) - (+) - 1 - Phenylethyl amidoferrocenyldithiophosphonate [35] (0.28 g, 0.70 mmol) in toluene (25 mL) and stirred for 2 h. A yellow precipitate product was immediately formed. The product was filtered, washed with petroleum ether(40–60°C) and dried in air. Yield: 0.38 g (79%). M.p.: >160°C (dec.). IR(KBr, cm⁻¹) ν_{max} : 649 (ν_{asym} PS₂) and 560 (ν_{sym} PS₂). ¹H NMR (CDCl₃, ppm) δ : 7.36 – 7.02 (m, 30H, arom.), 4.55 (br, 4H, 2x C₅H₄), 4.36 (br, 4H, 2xC₅H₄), 4.16 (s, br, 10H, 2xC₅H₅), 1.39 (d, br, 6H, 2xOCH₃, ³J_{PH} = 5.4 Hz). ³¹P NMR (CDCl₃, ppm) δ : 97.82 (PS₂) and 6.03 (PPh₃). MS (ESI) (m/z): 279.1 [FePS₂]⁺. Anal. Calc. for C₅₈H₅₄O₂P₄S₄Fe₂Ag₂: C, 51.12; H, 3.99; S, 9.41. Found: C, 50.76; H, 3.96; S, 9.87%.

Conclusions

The new dithiophosphonate ligands were synthesized and utilized in the preparation of copper(I) and silver(I) complexes with ferrocenyldithiophosphonate and triphenylphosphine. Then, the compounds $[\text{Ag}_2\{\text{FcP}(\text{OMe})\text{S}_2\}_2\text{PPh}_3)_2]$ and $[\text{Cu}(\text{PPh}_3)_2\text{NO}_3]$ were added into the PAN polymer solution (Co-PAN dissolved in dimethylacetamide) and the solution was electrospun onto microscope slide and PP meltblown surface producing fibers, average about 1 micron diameter. SEM images of these fibers show that compounds did not evenly distribute on fiber surface along the fiber length, meaning also not evenly distributed in polymer solution because of particles aggregation which caused electrospinning, as well. Antimicrobial activity of the compounds ($[\text{Ag}_2\{\text{FcP}(\text{OMe})\text{S}_2\}_2(\text{PPh}_3)_2]$ and $[\text{Cu}(\text{PPh}_3)_2\text{NO}_3]$) on fibers were determined in vitro against two indicator strains; *M. luteus* NCIB and *E. coli* ATCC25922. The obtained results indicated that these metals could be immobilized with the dithiophosphonate-phosphine and showed moderate level antimicrobial activity.

Additional file

Additional file 1: Spectra of Compounds.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

MK has coordinated the experimental work, synthesized, characterized the structure of the all compounds and wrote the manuscript. YI has obtained nanofiber by electrospinning method. HK and OS carried out antibacterial studies. All authors have read and approved the final manuscript.

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References

1. Silvestry-Rodriguez N, Sicairos-Ruelas EE, Gerba EE, Bright KR: Silver as a disinfectant. *Rev Environ Contam Toxicol* 2007, **191**:23–45.
2. Grass G, Rensing C, Solioz M: Metallic copper as an antimicrobial surface. *Appl Environ Microb* 2011, **77**:1541–1547.
3. Yang QB, Li DM, Hong YL, Li ZY, Wang C, Qiu SL, Wei Y: Preparation and characterization of a pan nanofibre containing Ag nanoparticles via electrospinning. *Synthetic Met* 2003, **137**:973–974.
4. Lee HK, Jeong EH, Baek CK, Youk JH: One-step preparation of ultrafine poly(acrylonitrile) fibers containing silver nanoparticles. *Mater Lett* 2005, **59**:2977–2980.
5. Jin WJ, Jeon HJ, Kim JH, Youk JH: A study on the preparation of poly(vinyl alcohol) nanofibers containing silver nanoparticles. *Synthetic Met* 2007, **157**:454–459.
6. Hong KH: Preparation and properties of electrospun poly (vinyl alcohol)/ silver fiber web as wound dressings. *Polym Eng Sci* 2007, **47**:43–49.
7. Jin WJ, Lee HK, Jeong EH, Park WH, Youk JH: Preparation of polymer nanofibers containing silver nanoparticles by using poly (N-vinylpyrrolidone). *Macromol Rapid Comm* 2005, **26**:1903–1907.
8. Yousef A, Barakat NAM, Amna T, Al-Deyab SS, Hassan MS, Abdel-hay A, Kim HY: Inactivation of pathogenic *Klebsiella pneumoniae* by CuO/TiO₂ nanofibers: A multifunctional nanomaterial via one-step electrospinning. *Ceram Int* 2012, **38**:4525–4532.
9. Xu X, Yang Q, Wang Y, Yu H, Chen X, Jing X: Biodegradable electrospun poly(L-lactide) fibers containing antibacterial silver nanoparticles. *Eur Polym J* 2006, **42**:2081–2087.
10. Han XJ, Huang ZM, Huang C, Du ZF, Wang H, Wang J, He CL, Wu QS: Preparation and characterization of electrospun polyurethane/inorganic-particles nanofibers. *Polym Composites* 2012, **33**:33.
11. Ramakrishna S, Fujihara K, Teo WE, Yong T, Ma Z, Ramaseshan R: Electrospun nanofibers solving global issues. *Mater Today* 2006, **9**:40–57.
12. Reneker DH, Chun I: Nanometre diameter fibres of polymer, produced by electrospinning. *Nanotechnology* 1996, **7**:216–223.
13. Ramakrishna S: *Introduction to Electrospinning and Nanofibers*. Singapore: World Scientific Publishing; 2005.
14. Contarini S, Tripaldi G, Ponti G, Lizzit S, Baraldi A, Paolucci G: Surface investigation of lubricant-metal interactions by synchrotron photoemission spectroscopy. *Appl Surf Sci* 1997, **108**:359–364.
15. Fuller M, Yin Z, Kasrai M, Bancroft GM, Yamaguchi ES, Ryason PR, Willermet PA, Tan KH: Chemical characterization of tribochemical and thermal films generated from neutral and basic ZDDPs using X-ray absorption spectroscopy. *Tribol Int* 1997, **30**:305–315.
16. Ma Q, Wang X-Y, Chen Q, Leung W-H, Zhang Q-F: Dinuclear ruthenium complexes containing tripodal dithiophosphonate ligands. *Inorg Chimica Acta* 2011, **378**:148–153.
17. Karakus M, Loennecke P, Hildebrand M, Hey-Hawkins E: Chiral Heterobimetallic Gold(I) Ferrocenyldithiophosphonate Complexes. *Z Anorg Allg Chem* 2011, **637**:983–987.
18. Karakus M, Lönnecke P, Hey-Hawkins E: Zwitterionic ferrocenyldithiophosphonates: the molecular structure of $[\text{FcP}(\text{S})\text{S}(\text{OCH}_2\text{CH}_2\text{NH}_2\text{Me})] [\text{Fc} = \text{Fe}(\eta^5\text{-C}_5\text{H}_4)(\eta^5\text{-C}_5\text{H}_3)]$. *Polyhedron* 2004, **23**:2281–2284.
19. Karakus M: Synthesis and characterization of novel organothio phosphorus compounds: X-ray crystal structure of $\text{H}_3\text{COC}_6\text{H}_4\text{P}(\text{OC}_2\text{H}_4\text{S})(\text{S})$ synthesized by a new method. *Z Anorg Allg Chem* 2006, **632**(8–9):1549–1553.
20. Karakus M, Yilmaz H, Bulak E, Lönnecke P: Bis- $[\mu\text{-}[\text{O-cyclopentyl}(4\text{-methoxyphenyl})\text{dithiophosphonato}]1\kappa\text{S} 2\kappa\text{S} \text{-}[\text{O-cyclopentyl}(4\text{-methoxyphenyl})\text{dithiophosphonato}]1\kappa\text{2S}, \text{S}'\text{dizinc}(\text{II})]$. *Appl Organomet Chem* 2005, **19**:396–397.
21. van Zyl WE, Woollins JD: The coordination chemistry of dithiophosphonates: An emerging and versatile ligand class. *Coord Chem Rev* 2013, **257**:718–731.
22. van Zyl WE: Dithiophosphonates and related P/S-type ligands of group 11 metals. *Comments Inorg Chem* 2010, **31**:13–45.
23. van Zyl WE, Fackler JP Jr: A general and convenient route to dithiophosphonate salt derivatives. *Phosphorus, Sulfur, Silicon Relat Elem* 2000, **167**:117–132.
24. van Zyl WE, López-de-Luzuriaga JM, Fackler JP Jr: Luminescence studies of dinuclear gold(I) phosphor-1,1-dithiolate complexes. *J Mol Struct* 2000, **516**:99–106.
25. van Zyl WE, Staples RJ, Fackler JP Jr: Dinuclear gold(I) dithiophosphonate complexes: formation, structure, and reactivity. *Inorg Chem Commun* 1998, **1**:51–54.
26. Pillay MN, Omondi B, Staples RJ, van Zyl WE: A hexanuclear gold(I) metallatriangle derived from a chiral dithiophosphate: synthesis, structure, luminescence and oxidative bromination reactivity. *CrystEngComm* 2013, **15**:4417–4421.
27. Pollnitz A, Silvestru A, Gimeno MC, Laguna A: New gold(I) and silver(I) complexes with organophosphorus ligands with SPNSO skeleton. Crystal and molecular structures of monomeric $[\text{Au}(\text{SPPH}_2)(\text{O}_2\text{SR})\text{N}(\text{PPh}_3)]$ (R = Me, C₆H₄Me-4) and dimeric $[\text{Ag}(\text{SPPH}_2)(\text{O}_2\text{SPH})\text{N}(\text{PPh}_3)]_2 \cdot 2\text{CH}_2\text{Cl}_2$. *Inorg Chimica Acta* 2010, **363**:346–352.
28. Liu S-L, Wang X-Y, Duan T, Leung W-H, Zhang Q-F: Hydrolysis and coordination behavior of ferrocenyl-phosphonodithiolate: Synthesis and structure of $\text{Cu}_4[\text{FcP}(\text{OCH}_3)(\mu\text{-S})(\mu\text{-S})]_4 [\text{Fc} = \text{Fe}(\eta^5\text{-C}_5\text{H}_4)(\eta^5\text{-C}_5\text{H}_3)]$. *J Mol Struct* 2010, **964**:78–81.

29. Barranco EM, Crespo O, Gimeno MC, Jones PG, Laguna A: **Unprecedented formation of novel phosphonodithioate ligands from ferrocenyldithiadiphosphetane disulfide.** *Inorg Chem* 2008, **47**:6913–6918.
30. Gray IP, Milton HL, Slawin AMZ, Woollins JD: **Synthesis and structure of [Fc(RO)PS₂]⁻ complexes.** *Dalton Trans* 2003, **17**:3450–3457.
31. Gray IP, Milton HL, Slawin AMZ, Woollins JD: **Synthesis and structure of [An(RO)PS₂]⁻ complexes.** *Dalton Trans* 2004, **16**:2477–2486.
32. Foreman MRSJ, Slawin AMZ, Woollins JD: **The reaction of dithiadiphosphetane disulfides with dienes, alkenes and thioaldehydes.** *J Chem Soc Dalton Trans* 1999, **7**:1175–1184.
33. Solak S, Aydemir C, Karakus M, Lönnecke P: **Novel Gold(I) and Silver(I) Complexes of Phosphorus-1,1-dithiolates and Molecular Structure of [O, O'-(Boronyl)2PS2]H3NC(CH3).** *Chem Cen J* 2013, **7**:89.
34. Hernandez-Galindo M del C, Jancik V, Moya-Cabrera MM, Toscano RA, Cea-Olivares R: **2D hydrogen bond networks in the crystals of [(NH₄ center dot H2O)(2)][(RO)(Fc)P(S)(2)](2) (R = 3-(BzO)-Bz, 4-(n-Bu)-Bz, Bz = benzyl).** *J Organomet Chem* 2007, **692**:5295–5304.
35. Karakus M: **Synthesis and Characterization of Chiral Gold(I) Phosphine Complexes with New Dithiophosphorus Ligands.** *Phosphorus, Sulfur, Silicon Relat Elem* 2011, **186**:1523–1530.
36. Haiduc I, Mezei G, Micu – Semeniac R, Edelman FT, Fisher A: **Differing coordination modes of (O-alkyl)-p-ethoxyphenyldithiophosphonato ligands in copper(I), silver(I) and gold(I) triphenylphosphine complexes.** *Z Anorg Allg Chem* 2006, **632**:295–300.
37. Haiduc I, Sowerby DB, Lu S-F: **Stereochemical aspects of phosphor-1,1-dithiolato metal complexes (dithiophosphates, dithiophosphinates): coordination patterns, molecular structures and supramolecular associations – I.** *Polyhedron* 1995, **14**:3389–3472.
38. Cui Z, Miao Z, Zhang J, Chen R-Y: **Synthesis of Diphenyl alpha-(O-phenyl bis(2-chloroethyl) amidophosphorylamino)- phosphonates.** *Phosphorus, Sulfur, Silicon Relat Elem* 2008, **183**:720–725.
39. Silver S, Phung LT: **Bacterial heavy metal resistance: new surprises** *Annu Rev Microbiol.* *Annu Rev Microbiol* 1996, **50**:753–789.
40. Windler L, Height M, Nowack B: **Comparative evaluation of antimicrobials for textile applications.** *Environ Int* 2013, **53**:62–73.
41. McArthur JV, Tuckfield RC, Baker-Austin C: **Antimicrobial textiles.** *Handb Exp Pharmacol* 2012, **211**:135–152.
42. Cotton FA, Goodgame DML: **Tetrakis(triphenylphosphine)-Silver(I) and (Triphenylphosphine)-Copper(I) Complexes.** *J Chem Soc* 1960:5267–5269.
43. Schillinger U, Lücke FK: **Lactic Acid Bacteria as Protective Cultures in Meat Products.** *Fleischwirtsch* 1990, **70**:1296–1299.

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