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Liquid crystal behavior of Ag(I) complexes based on a series of mesogenic 1,3,4-thiadiazole ligands

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ABSTRACT

2-(4-Alkoxyphenyl)-5-(*p*-tolyl)-1,3,4-thiadiazoles (alkoxy: $O(CH_2)_nH$, $n = 1–8$) (***6a–h***) (as a series of 1,3,4-thiadiazole derivatives) and their silver(I) complexes: bis(2-(4-alkoxyphenyl)-5-(*p*-tolyl)-1,3,4-thiadiazole)-silver(I) complexes (alkoxy: $O(CH_2)_nH$, $n = 1–8$) (***7a–h***) were prepared and characterized with different techniques: microelemental analysis, FTIR, UV–Vis, ^1H NMR, ^{13}C NMR and mass (for the organic compounds) spectra, in addition to the molar conductivity measurements (for Ag(I) complexes). Liquid crystal behavior of the two series of compounds was evaluated using polarized light optical microscopy (POM). The study revealed that both series are enantiotropic liquid crystalline materials (exhibiting wide mesomorpic temperature ranges) with different behavior and properties. ***6a–f*** displayed only nematic mesophase upon heating and cooling, while ***6g*** and ***6h*** exhibited both of SmC and nematic mesophases upon heating and cooling. Upon complexation of 1,3,4-thiadiazoles (***6a–h***) to silver(I), the liquid crystal behavior and properties are significantly changed (different mesophases, and lower mesophase and clearing temperatures). However, ***7b–h*** exhibited SmA mesophase upon heating and cooling, while ***7a*** shows no mesomorphic properties (simply melted to isotropic liquid).

KEYWORDS
Mesogens; Metallomesogens; 1,3,4-Thiadiazoles; Silver(I) complexes; Liquid cystalline materials

Introduction

Hydrophobic materials are a class of compounds with a low affinity to water (water repellents). The hydrophobicity of such materials is mainly due to the presence of one or more of hydrocarbon chains. These materials have shown some remarkable applications in several fields, such as chemistry, biology and material science [1–3].

Among various classes of organic compounds, heterocyclic derivatives have received special interest due to their versatile applications in different fields. These compounds have been already used as pharmaceutical drugs due to their high efficacy against a wide range of bacterial and fungal strains [4–8]. Furthermore, the heterocyclic compounds have many other industrial applications, such as corrosion inhibitors,

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surfactants, sanitizers, antioxidants, dyestuff [9,10]. The presence of oxygen, nitrogen and/or sulfur as hetroatoms gave these compounds high capability for electron-donating which related to being used as organic chelate ligands [11–13].

The fascinating applications (especially in medicine and industry) of mesogens and metallomesogens are majorly contributed in the expansion of this field by attracting the attention of the researches around the world. Due to that and since 1888 (first observation of a liquid-crystalline birefringent medium), thousands of researchers are so interested in designing materials with liquid crystal properties. In the ten recent years, a numerous number of articles have been reported, describing the liquid crystal properties of a wide range of organic derivatives [14–28] and metal-containing materials especially with aluminum [29], nickel [30], zinc [31,32], palladium [33,34], silver [35–40], iridium [41], platinum [34,42–44], and gold [45,46], as well as some lanthanide ions [47–49]. The most characteristic of metallomesogens is that the fundamental properties of the metal ions (magnetism, electrical conductivity, carrier mobility, etc.) can be combined with the liquid crystalline properties.

Silver(I) complexes based on different organic derivatives have shown some fascinating liquid crystal properties. In 2004, Ching K. Lee *et al.* [36] prepared a homologous series of silver(I) complexes based on a serious of 1-alkylimidazole (ID) compounds (R-ID, $R = C_nH_{2n+1}$, where $n = 10$, 12, 14, 16 and 18). The X-ray crystal structure of $[Ag(C_{12}H_{25}\text{-ID})_2]^{\cdot} NO_3$ displayed that the Ag center is two-coordinate, adopting a U-shaped conformation with bilayer packing. All of these compounds (except for $n = 10$) exhibited liquid crystalline properties with smectic A (SmA) mesophase, while, in 2010, María José Mayoral *et al.* [37] reported the synthesis of a series of Ag(I) complexes supported by 3,5-bis(4-alkyloxyphenyl)pyrazole (Py) compounds with the general formula: $[Ag\ (R\text{-Py})_2]^{\cdot}\ X$ ($R = C_nH_{2n+1}$, where $n = 12$, 14, 16 and 18; $X = CH_3\text{-p-}C_6H_4SO_3$-(PTS), CF_3SO_3-(OTf)) as metallomesogens. Beside the liquid crystalline properties, these compounds displayed photoluminescence properties in the solid state, in the mesophase and in solution. Recently, we prepared three series of silver(I) complexes based on symmetrical azines ($[Ag_2(SA)(NO_3)_2]$, SA: 1,2-bis[4-(*n*-alkoxy)benzylidene] hydrazine (where, *n*-alkoxy: $O(CH_2)_nH$, $n = 1$–10 or 12)) [38], asymmetrical azines ($[Ag_2(AA)(NO_3)_2]$, AA: [1-(4-(*n*-alkoxy))-2-(4′-dodecyloxy)benzylidene]hydrazine (where *n*-alkoxy: $O(CH_2)_nH$, $n = 1$–8)) [39] and pyrazoles ($[Ag\ (PY)_2]^{\cdot}NO_3$, PY: 3,5-bis[4-(*n*-alkoxy)-phenyl]-1H-pyrazole (where, *n*-alkoxy: $O(CH_2)_nH$, $n = 6$–10)) [40] as photoluminescent materials. Some of these complexes showed some remarkable liquid crystal properties. We report herein the synthesis and liquid crystal behavior of a series of 1,3,4-thiadiazoles and their silver (I) complexes.

Experimental

Physical measurements

Varian Cary 100 Conc. spectrophotometer was used to record the electronic spectra of the prepared compounds in the region (200–800 nm) for (1×10^{-4} M) in dichloromethane (DCM) at room temperature. Elemental analyses (C, H and N) were carried out by using a EuroEA 3000 Elemental Analyzer, while Ag was measured using a 7300 V ICP-OES PerkinElmer-Optima Spectrometer. Mass spectra were recorded using a

MS-SCI Shimadzu QP 1000EX spectrometer. Infrared spectra were obtained in the region (4000–600 cm^{-1}) by using a 8400S-FT–IR Shimadzu spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were performed in DMSO for precursors (**1**, **2**, **3** and **5**), and $CDCl_3$ for ligands (***6a–h***) and complexes (***7a–h***) using a Bruker 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR spectrometer. PW-BK5000R microscope supplied with HS-400 (KER3100-08S) heating stage was used to obtain the liquid crystal mesophases of 1,3,4-thiadiazoles and their silver(I) complexes. Molar conductivity of Ag(I) complexes in acetone (1×10^{-3} M) was measured at 25 C$^{\circ}$ using a WTW 82362-Weilheim digital conductometer.

Materials

The reagents used in this work were purchased from Aldrich Co. (Germany) and used as it is, without further purification: 1-iodomethane (98%), 1-bromoethane (99%), 1-bromopropane (99%), 1-bromobutane (98%), 1-bromopentane (99%), 1-bromohexane (99%), 1-bromoheptane (99%), 1-bromooctane (99%), *p*-toluic acid (98%), hydrazine hydrate (80%), phosphorus pentasulfide (99%), aluminum chloride (98%), potassium permanganate (99%). Methyl 4-methylbenzoate (**1**) and *p*-toluic hydrazide (**2**) were prepared following the synthetic procedure described in our previous work [23].

Synthesis of 4-methoxy-N′-(4-methylbenzoyl)benzohydrazide (3)

The synthetic procedure of this compound was slightly modified from that described in the literatures [23,50]. To a solution of *p*-toluic hydrazide (18 g, 120 mmol) in anhydrous pyridine (100 mL), 4-methoxybenzoyl chloride (20.5 g, 120 mmol) was added dropwise at −5 °C. The reaction mixture was kept overnight at room temperature, and then poured into cold aqueous solution of HCl (10%, 250 mL) to give a pale yellow microcrystalline solid. This solid was boiled in water for 15 min to remove the unreacted materials, and the remaining solid was collected by filtration. The final solid was recrystallized from ethanol to give the desired product. Yield (91%); m.p.= 210–212 °C. FTIR (υ/cm^{-1}): 3207 (w, υ(N–H)), 3151 (w, υ(N–H)), 2943 (w, υ_{as}(C–H) of CH_3 group), 2845 (w, υ_s(C–H) of CH_3 group), 1614 (m, υ(C = O)), 1593, 1558 and 1512 (s,m,m, υ(C = C) aromatic), 1251 (s, υ(C–O)). ^{1}H NMR (δ/ppm): 2.35 (3H, s, CH_3), 3.68 (3H, s, OCH_3), 6.88–6.91 (2H, d, $J = 8.8$ Hz, aromatic protons), 7.15–7.18 (2H, d, $J = 8.0$ Hz, aromatic protons), 7.60–7.63 (2H, d, $J = 8.0$ Hz, aromatic protons), 7.75–7.78 (2H, d, $J = 8.8$ Hz, aromatic protons), 10.17 (1H, s, NH), 10.20 (1H, s, NH). ^{13}C NMR (δ/ppm): 20.09 (CH_3), 55.86 (OCH_3), 114.19 ((C–H) aromatic), 125.22 ((C) aromatic), 129.48 ((C–H) aromatic), 130.32 ((C–H) aromatic), 142.25 (($\underline{C}$–CH_3) aromatic), 162.47 (($\underline{C}$–OCH_3) aromatic), 165.80 (C = O), 166.24 (C = O). Mass spect. (m/z): 284.

Synthesis of 2-(4-methoxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole (4 = 6a)

The title compound was prepared by the previously reported procedure [23,51]. Compound **3** (25 g, 87 mmol) and phosphorous pentasulfide (24.9 g, 87 mmol) were dissolved in anhydrous pyridine (150 mL), and the reaction mixture was heated under reflux for 24 h. The mixture was then poured into cold water (500 mL) and a precipitate deposited. This precipitate was collected by filtration, washed thoroughly with water and finally recrystallized from ethyl acetate to give the desired product in pure form. Yield (87%); m.p.= 209–210 °C. FTIR (υ/cm^{-1}): 3066 (w, υ(C–H) aromatic), 2964 (w, υ_{as}(C–H) of CH_3 group), 2837 (w, υ_s(C–H) of CH_3 group), 1602 (m, υ(C = N)), 1577 and 1516 (w,s, υ(C = C) aromatic), 1255 (s, υ(C–O)). UV–Vis (λ/nm): 232 (n–σ^*), 326 (π–π^*). ^{1}H NMR (δ/ppm): 2.40 (3H, s, CH_3), 3.86 (3H, s, OCH_3), 6.96–6.99 (2H, d, $J = 8.7$ Hz, aromatic protons), 7.26–7.28 (2H, d, $J = 7.9$ Hz, aromatic protons), 7.85–7.88 (2H, d, $J = 8.0$ Hz, aromatic protons), 7.91–7.94 (2H, d, $J = 8.7$ Hz, aromatic protons). ^{13}C NMR (δ/ppm): 21.50 (CH_3), 63.80 (OCH_3), 114.49 ((C–H) aromatic), 122.94 ((C) aromatic), 127.57 ((C) aromatic), 127.73 ((C–H) aromatic), 129.40 ((C–H) aromatic), 129.79 ((C–H) aromatic), 141.33 (($\underline{C}$–CH_3) aromatic), 161.80 (($\underline{C}$–OCH_3) aromatic), 167.44 (C = N), 167.47 (C = N). Mass spect. (m/z): 282.

Synthesis of 4-(5-(p-tolyl)-1,3,4-thiadiazol-2-yl)phenol (5)

This compound was prepared following the procedure described in our previous work [23]. Anhydrous aluminum chloride (1.00 g, 7.5 mmol) was added to a solution of compound **4** = **6a** (0.68 g, 2.4 mmol) in dry benzene (25 mL), and the reaction mixture was heated by reflux for 24 h. After evaporation of the solvent and pouring the residue into cold water, an off-white microcrystalline solid was formed. The obtained solid was collected by filtration, and then dissolved in an aqueous solution of potassium hydroxide (10%, 30 mL). The solution was filtered, and the filtrate was neutralized with HCl (10%). The precipitate formed was washed thoroughly with water and dried under vacuum. The final solid was recrystallized from ethanol to obtain compound **5**. Yield (81%); m.p.= 221–223 °C. FTIR (υ/cm^{-1}): 3045 (w, υ(C–H) aromatic), 2966 (w, υ_{as}(C–H) of CH_3 group), 2850 (w, υ_s(C–H) of CH_3 group), 1608 (m, υ(C = N)), 1583 and 1523 (m,w, υ(C = C) aromatic), 1244 (s, υ(C–O)). ^{1}H NMR (δ/ppm): 2.18 (3H, s, CH_3), 6.77–6.79 (2H, d, $J = 8.65$ Hz, aromatic protons), 7.13–7.16 (2H, d, $J = 8.17$ Hz, aromatic protons), 7.64–7.66 (4H, d, $J = 8.43$ Hz, aromatic protons), 10.09 (1H, s, OH). ^{13}C NMR (δ/ppm): 21.44 (CH_3), 116.65 ((C–H) aromatic), 121.04 ((C) aromatic), 127.46 ((C) aromatic), 127.81 ((C–H) aromatic), 129.84 ((C–H) aromatic), 130.37 ((C–H) aromatic), 141.57 (($\underline{C}$–CH_3) aromatic), 160.85 ((C–OH) aromatic), 166.88 (C = N), 167.84 (C = N). Mass spect. (m/z): 268.

Synthesis of 2-(4-alkoxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole (6a–h) (general procedure)

These compounds were prepared based on the synthetic procedure described in our previous work [23]. To a mixture of compound **5** (2.68 g, 10 mmol) and anhydrous potassium carbonate (1.38 g, 10 mmol) in acetone (50 mL), *n*-alkyl bromide (11 mmol) was added. The reaction mixture was refluxed for 12 h and then left to cool at room temperature. The crude product was then poured into cold water, and the solid formed was collected by filtration. This solid was washed with aqueous solution of potassium hydroxide (5%), then with water several times, and finally recrystallized from ethyl acetate.

2-(4-Methoxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole (6a), see compound 4

2-(4-Ethoxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole (6b)

Yield (85%). FTIR ($\upsilon/\mathrm{cm}^{-1}$): 3080 (w, υ(C–H) aromatic), 2982 (w, υ_{as}(C–H) of CH_3 group), 2929 (w-m, υ_{as}(C–H) of CH_2 group), 2866 (w, υ_s(C–H) of CH_3 group), 2825 (w-m, υ_s(C–H) of CH_2 group), 1605 (m, υ(C=N)), 1573 and 1518 (s,m, υ(C=C) aromatic), 1251 (s, υ(C–O)). UV–Vis (λ/nm): 231 (n–σ*), 324 (π–π*). ^{1}H NMR (δ/ppm): 1.41-1.45 (3H, t, -$OCH_2\underline{\mathbf{CH_3}}$), 2.42 (3H, s, CH_3), 4.02-4.06 (2H, q, -$\underline{\mathbf{OCH_2}}CH_3$), 6.97-7.00 (2H, d, $J=8.73$ Hz, aromatic protons), 7.25–7.27 (2H, d, $J=7.91$ Hz, aromatic protons), 7.88–7.90 (2H, d, $J=7.95$ Hz, aromatic protons), 7.92–7.95 (2H, d, $J=8.75$ Hz, aromatic protons). ^{13}C NMR (δ/ppm): 14.73 (-$OCH_2\underline{\mathbf{CH_3}}$), 21.16 ($CH_3$), 63.74 (-$\underline{\mathbf{OCH_2}}CH_3$), 114.99 ((C–H) aromatic), 122.80 ((C) aromatic), 127.61 ((C) aromatic), 127.65 ((C–H) aromatic), 129.43 ((C–H) aromatic), 129.81 ((C–H) aromatic), 141.34 (($\underline{\mathbf{C}}$–CH_3) aromatic), 161.26 (($\underline{\mathbf{C}}$–OCH_2) aromatic), 167.41 (C=N), 167.57 (C=N). Mass spectrum (m/z): 296.

2-(4-Propyloxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole (6c)

Yield (84%). FTIR ($\upsilon/\mathrm{cm}^{-1}$): 3066 (w, υ(C–H) aromatic), 2964 (w, υ_{as}(C–H) of CH_3 group), 2931 (m, υ_{as}(C–H) of CH_2 group), 2866 (w, υ_s(C–H) of CH_3 group), 2826 (w-m, υ_s(C–H) of CH_2 group), 1602 (m, υ(C=N)), 1575 and 1516 (s,m, υ(C=C)aromatic), 1255 (s, υ(C–O)). UV–Vis (λ/nm): 230 (n–σ*), 325 (π–π*). ^{1}H NMR (δ/ppm): 1.04-1.09 (3H, t, -$OCH_2CH_2\underline{\mathbf{CH_3}}$), 1.88-1.90 (2H, m, -$OCH_2\underline{\mathbf{CH_2}}CH_3$), 2.42 (3H, s, CH_3), 3.97-4.01 (2H, t, -$\underline{\mathbf{OCH_2}}CH_2CH_3$), 6.95–6.97 (2H, d, $J=8.74$ Hz, aromatic protons), 7.26–7.27 (2H, d, $J=7.91$ Hz, aromatic protons), 7.85–7.87 (2H, d, $J=7.93$ Hz, aromatic protons), 7.89–7.91 (2H, d, $J=8.75$ Hz, aromatic protons). ^{13}C NMR (δ/ppm): 10.49 (-$OCH_2CH_2\underline{\mathbf{CH_3}}$), 21.52 (-$OCH_2\underline{\mathbf{CH_2}}CH_3$), 22.50 ($CH_3$), 69.73 (-$\underline{\mathbf{OCH_2}}CH_2CH_3$), 115.02 ((C–H) aromatic), 122.75 ((C) aromatic), 127.60 ((C) aromatic), 127.65 ((C–H) aromatic), 129.42 ((C–H) aromatic), 129.81 ((C–H) aromatic), 141.33 (($\underline{\mathbf{C}}$–CH_3) aromatic), 161.47 (($\underline{\mathbf{C}}$–OCH_2) aromatic), 167.39 (C=N), 167.59 (C=N). Mass spectrum (m/z): 310.

2-(4-Butyloxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole (6d)

Yield (88%). FTIR ($\upsilon/\mathrm{cm}^{-1}$): 3068 (w, υ(C–H) aromatic), 2953 (w, υ_{as}(C–H) of CH_3 group), 2935 (m, υ_{as}(C–H) of CH_2 group), 2868 (w, υ_s(C–H) of CH_3 group), 2852 (w, υ_s(C–H) of CH_2 group), 1600 (m, υ(C=N)), 1578 and 1514 (s,m, υ(C=C)aromatic), 1251 (s, υ(C-O)). UV–Vis (λ/nm): 229 (n–σ*), 322 (π–π*). ^{1}H NMR (δ/ppm): 0.96-1.02 (3H, t, -$OCH_2(CH_2)_2\underline{\mathbf{CH_3}}$), 1.48-1.61 (2H, m, -$OCH_2CH_2\underline{\mathbf{CH_2}}CH_3$), 1.82-1.85 (2H, m, -$OCH_2\underline{\mathbf{CH_2}}CH_2CH_3$), 2.41 (3H, s, CH_3), 3.97-4.05 (2H, t, -$\underline{\mathbf{OCH_2}}CH_2CH_2CH_3$), 6.97–6.99 (2H, d, $J=8.77$ Hz, aromatic protons), 7.27–7.30 (2H, d, $J=7.92$ Hz, aromatic protons), 7.86–7.88 (2H, d, $J=7.90$ Hz, aromatic protons), 7.91–7.93 (2H, d, $J=8.76$ Hz, aromatic protons). ^{13}C NMR (δ/ppm): 13.86 (-$OCH_2(CH_2)_2\underline{\mathbf{CH_3}}$), 19.23

($\mathrm{-OCH_2CH_2}\underline{\mathbf{CH_2}}\mathrm{CH_3}$), 21.54 ($\mathrm{CH_3}$), 31.54 ($\mathrm{-OCH_2}\underline{\mathbf{CH_2}}\mathrm{CH_2CH_3}$), 67.95 ($\mathrm{-}\underline{\mathbf{OCH_2}}\mathrm{(CH_2)_2CH_3}$), 115.00 ((C–H) aromatic), 122.72 ((C) aromatic), 127.64 ((C) aromatic), 127.77 ((C–H) aromatic), 129.42 ((C–H) aromatic), 129.82 ((C–H) aromatic), 141.34 (($\underline{\mathbf{C}}\mathrm{-CH_3}$) aromatic), 161.31 (($\underline{\mathbf{C}}\mathrm{-OCH_2}$) aromatic), 167.40 (C = N), 167.56 (C = N). Mass spectrum (m/z): 324.

2-(4-Pentyloxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole (6e)

Yield (89%). FTIR ($\upsilon/\mathrm{cm}^{-1}$): 3067 (w, υ(C–H) aromatic), 2958 (w, υ_{as}(C–H) of $\mathrm{CH_3}$ group), 2930 (m, υ_{as}(C–H) of $\mathrm{CH_2}$ group), 2870 (w, υ_s(C–H) of $\mathrm{CH_3}$ group), 2858 (m, υ_s(C–H) of $\mathrm{CH_2}$ group), 1602 (m, υ(C = N)), 1575 and 1518 (s,m, υ(C = C)aromatic), 1253 (s, υ(C–O)). UV–Vis (λ/nm): 231 (n–σ*), 325 (π–π*). ^{1}H NMR (δ/ppm): 0.88-0.96 (3H, t, $\mathrm{-OCH_2(CH_2)_3}\underline{\mathbf{CH_3}}$), 1.42-1.57 (4H, m, $\mathrm{-OCH_2CH_2}\underline{\mathbf{(CH_2)_2}}\mathrm{CH_3}$), 1.81-1.84 (2H, m, $\mathrm{-OCH_2}\underline{\mathbf{CH_2}}\mathrm{(CH_2)_2CH_3}$), 2.42 (3H, s, $\mathrm{CH_3}$), 3.98-4.03 (2H, t, $\mathrm{-}\underline{\mathbf{OCH_2}}\mathrm{(CH_2)_3CH_3}$), 6.95–6.98 (2H, d, $J = 8.74$ Hz, aromatic protons), 7.26–7.28 (2H, d, $J = 7.94$ Hz, aromatic protons), 7.84–7.87 (2H, d, $J = 7.96$ Hz, aromatic protons), 7.92–7.94 (2H, d, $J = 8.73$ Hz, aromatic protons). ^{13}C NMR (δ/ppm): 14.05 ($\mathrm{-OCH_2(CH_2)_3}\underline{\mathbf{CH_3}}$), 21.53 ($\mathrm{-OCH_2(CH_2)_2}\underline{\mathbf{CH_2}}\mathrm{CH_3}$), 22.57 ($\mathrm{CH_3}$), 29.13 ($\mathrm{-OCH_2CH_2}\underline{\mathbf{CH_2}}\mathrm{CH_2CH_3}$), 31.58 ($\mathrm{-OCH_2}\underline{\mathbf{CH_2}}\mathrm{(CH_2)_2CH_3}$), 68.28 ($\mathrm{-}\underline{\mathbf{OCH_2}}\mathrm{(CH_2)_3CH_3}$), 114.96 ((C–H) aromatic), 122.72 ((C) aromatic), 127.77 ((C) aromatic), 128.03 ((C–H) aromatic), 129.37 ((C–H) aromatic), 129.82 ((C–H) aromatic), 141.33 (($\underline{\mathbf{C}}\mathrm{-CH_3}$) aromatic), 161.33 (($\underline{\mathbf{C}}\mathrm{-OCH_2}$) aromatic), 167.40 (C = N), 167.61 (C = N). Mass spectrum (m/z): 338.

2-(4-Hexyloxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole (6f)

Yield (80%). FTIR ($\upsilon/\mathrm{cm}^{-1}$): 3064 (w, υ(C–H) aromatic), 2961 (w, υ_{as}(C–H) of $\mathrm{CH_3}$ group), 2933 (m, υ_{as}(C–H) of $\mathrm{CH_2}$ group), 2862 (w, υ_s(C–H) of $\mathrm{CH_3}$ group), 2851 (m, υ_s(C–H) of $\mathrm{CH_2}$ group), 1601 (m, υ(C = N)), 1575 and 1516 (s,m, υ(C = C) aromatic), 1256 (s, υ(C–O)). UV–Vis (λ/nm): 230 (n–σ*), 324 (π–π*). ^{1}H NMR (δ/ppm): 0.89-0.95 (3H, t, $\mathrm{-OCH_2(CH_2)_4}\underline{\mathbf{CH_3}}$), 1.40-1.59 (6H, m, $\mathrm{-OCH_2CH_2}\underline{\mathbf{(CH_2)_3}}\mathrm{CH_3}$), 1.78-1.82 (2H, m, $\mathrm{-OCH_2}\underline{\mathbf{CH_2}}\mathrm{(CH_2)_3CH_3}$), 2.40 (3H, s, $\mathrm{CH_3}$), 3.98-4.02 (2H, t, $\mathrm{-}\underline{\mathbf{OCH_2}}\mathrm{(CH_2)_4CH_3}$), 6.95–6.97 (2H, d, $J = 8.79$ Hz, aromatic protons), 7.23–7.25 (2H, d, $J = 7.96$ Hz, aromatic protons), 7.84–7.86 (2H, d, $J = 7.92$ Hz, aromatic protons), 7.95–7.97 (2H, d, $J = 8.76$ Hz, aromatic protons). ^{13}C NMR (δ/ppm): 14.08 ($\mathrm{-OCH_2(CH_2)_4}\underline{\mathbf{CH_3}}$), 21.55 ($\mathrm{-OCH_2(CH_2)_3}\mathbf{CH_2}\mathrm{CH_3}$), 22.62 ($\mathrm{CH_3}$), 28.84 ($\mathrm{-OCH_2(CH_2)_2}\underline{\mathbf{CH_2}}\mathrm{CH_2CH_3}$), 29.13 ($\mathrm{-OCH_2CH_2}\underline{\mathbf{CH_2}}\mathrm{(CH_2)_2CH_3}$), 31.62 ($\mathrm{-OCH_2}\underline{\mathbf{CH_2}}\mathrm{(CH_2)_3CH_3}$), 68.31 ($\mathrm{-}\underline{\mathbf{OCH_2}}\mathrm{(CH_2)_4CH_3}$) 114.99 ((C–H) aromatic), 122.76 ((C) aromatic), 127.81 ((C) aromatic), 128.13 ((C–H) aromatic), 129.41 ((C–H) aromatic), 129.87 ((C–H) aromatic), 141.30 (($\underline{\mathbf{C}}\mathrm{-CH_3}$) aromatic), 161.46 (($\underline{\mathbf{C}}\mathrm{-OCH_2}$) aromatic), 167.44 (C = N), 167.62 (C = N). Mass spectrum (m/z): 352.

2-(4-Heptyloxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole (6g)

Yield (83%). FTIR ($\upsilon/\mathrm{cm}^{-1}$): 3060 (w, υ(C–H) aromatic), 2962 (w, υ_{as}(C–H) of $\mathrm{CH_3}$ group), 2927 (m, υ_{as}(C–H) of $\mathrm{CH_2}$ group), 2852 (w, υ_s(C–H) of $\mathrm{CH_3}$ group), 2847 (m, υ_s(C–H) of $\mathrm{CH_2}$ group), 1603 (m, υ(C = N)), 1575 and 1518 (s,m, υ(C = C)aromatic), 1259 (s, υ(C–O)). UV–Vis (λ/nm): 230 (n–σ*), 322 (π–π*). ^{1}H NMR (δ/ppm): 0.87-0.96

(3H, t, $\text{-OCH}_2(\text{CH}_2)_5\underline{\mathbf{CH_3}}$), 1.45-1.62 (8H, m, $\text{-OCH}_2\text{CH}_2\underline{\mathbf{(CH_2)_4}}\text{CH}_3$), 1.76-1.79 (2H, m, $\text{-OCH}_2\underline{\mathbf{CH_2}}(\text{CH}_2)_4\text{CH}_3$), 2.41 (3H, s, CH_3), 3.99-4.05 (2H, t, $\text{-}\underline{\mathbf{OCH_2}}(\text{CH}_2)_5\text{CH}_3$), 6.96–6.99 (2H, d, $J = 8.76$ Hz, aromatic protons), 7.26–7.29 (2H, d, $J = 7.99$ Hz, aromatic protons), 7.85–7.88 (2H, d, $J = 7.94$ Hz, aromatic protons), 7.93–7.95 (2H, d, $J = 8.79$ Hz, aromatic protons). ^{13}C NMR (δ/ppm): 14.03 ($\text{-OCH}_2(\text{CH}_2)_5\underline{\mathbf{CH_3}}$), 21.54 ($\text{-OCH}_2(\text{CH}_2)_4\underline{\mathbf{CH_2}}\text{CH}_3$), 22.57 ($\text{CH}_3$), 28.59 ($\text{-OCH}_2(\text{CH}_2)_3\underline{\mathbf{CH_2}}\text{CH}_2\text{CH}_3$), 29.77 ($\text{-OCH}_2(\text{CH}_2)_2\underline{\mathbf{CH_2}}(\text{CH}_2)_2\text{CH}_3$), 29.17 ($\text{-OCH}_2\text{CH}_2\underline{\mathbf{CH_2}}(\text{CH}_2)_3\text{CH}_3$), 31.65 ($\text{-OCH}_2\underline{\mathbf{CH_2}}(\text{CH}_2)_4\text{CH}_3$), 68.37 ($\text{-}\underline{\mathbf{OCH_2}}(\text{CH}_2)_5\text{CH}_3$) 114.83 ((C–H) aromatic), 122.83 ((C) aromatic), 127.90 ((C) aromatic), 128.10 ((C–H) aromatic), 129.38 ((C–H) aromatic), 129.81 ((C–H) aromatic), 141.35 (($\underline{\mathbf{C}}\text{–CH}_3$) aromatic), 161.37 (($\underline{\mathbf{C}}\text{–OCH}_2$) aromatic), 167.56 (C = N), 167.67 (C = N). Mass spectrum (m/z): 366.

2-(4-Octyloxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole (6h)

Yield (90%). FTIR (υ/cm^{-1}): 3072 (w, υ(C–H) aromatic), 2972 (w, υ_{as}(C–H) of CH_3 group), 2928 (m, υ_{as}(C–H) of CH_2 group), 2853 (w, υ_s(C–H) of CH_3 group), 2835 (m, υ_s(C–H) of CH_2 group), 1604 (m, υ(C = N)), 1576 and 1516 (s,m, υ(C = C)aromatic), 1257 (s, υ(C-O)). UV–Vis (λ/nm): 229 (n–σ^*), 325 (π–π^*). ^{1}H NMR (δ/ppm): 0.87-0.91 (3H, t, $\text{-OCH}_2(\text{CH}_2)_6\underline{\mathbf{CH_3}}$), 1.37-1.59 (10H, m, $\text{-OCH}_2\text{CH}_2\underline{\mathbf{(CH_2)_5}}\text{CH}_3$), 1.78-1.81 (2H, m, $\text{-OCH}_2\underline{\mathbf{CH_2}}(\text{CH}_2)_5\text{CH}_3$), 2.43 (3H, s, CH_3), 4.00-4.04 (2H, t, $\text{-}\underline{\mathbf{OCH_2}}(\text{CH}_2)_6\text{CH}_3$), 6.97–6.99 (2H, d, $J = 8.69$ Hz, aromatic protons), 7.28–7.30 (2H, d, $J = 7.81$ Hz, aromatic protons), 7.87–7.90 (2H, d, $J = 7.97$ Hz, aromatic protons), 7.91–7.94 (2H, d, $J = 8.75$ Hz, aromatic protons). ^{13}C NMR (δ/ppm): 14.29 ($\text{-OCH}_2(\text{CH}_2)_6\underline{\mathbf{CH_3}}$), 21.66 ($\text{OCH}_2(\text{CH}_2)_5\underline{\mathbf{CH_2}}\text{CH}_3$), 22.34 ($\text{CH}_3$), 26.28 ($\text{-OCH}_2(\text{CH}_2)_4\underline{\mathbf{CH_2}}\text{CH}_2\text{CH}_3$) 28.69 ($\text{-OCH}_2(\text{CH}_2)_3\underline{\mathbf{CH_2}}(\text{CH}_2)_2\text{CH}_3$), 29.42 ($\text{-OCH}_2(\text{CH}_2)_2\underline{\mathbf{CH_2}}(\text{CH}_2)_3\text{CH}_3$), 29.62 ($\text{-OCH}_2\text{CH}_2\underline{\mathbf{CH_2}}(\text{CH}_2)_4\text{CH}_3$), 31.44 ($\text{-OCH}_2\underline{\mathbf{CH_2}}(\text{CH}_2)_5\text{CH}_3$), 68.41 ($\text{-}\underline{\mathbf{OCH_2}}(\text{CH}_2)_6\text{CH}_3$) 114.75 ((C–H) aromatic), 122.73 ((C) aromatic), 127.95 ((C) aromatic), 128.23 ((C–H) aromatic), 129.43 ((C–H) aromatic), 129.99 ((C–H) aromatic), 149.72 (($\underline{\mathbf{C}}\text{–CH}_3$) aromatic), 161.39 (($\underline{\mathbf{C}}\text{–OCH}_2$) aromatic), 167.59 (C = N), 167.73 (C = N). Mass spectrum (m/z): 380.

Synthesis of bis(1,3,4-thiadiazole)-silver(I) complexes (7a–h) (general procedure)

To a solution of appropriate 1,3,4-thiadiazole compound (2.36 mmol) in DCM (50 ml), AgNO_3 (0.2 g, 1.18 mmol) was added as a solid. The reaction mixture was stirred at room temperature in the absence of light, and under inert conditions until all the AgNO_3 solid disappeared. The solvent was removed under vacuum, and the residue was dissolved in DCM. A colorless solid was appeared after the addition of hexane. This solid was collected by filtration, washed subsequently with water and hexane, and finally dried in vacuum.

Bis[2-(4-methoxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole] silver(I) nitrate (7a)

Yield (75%). Elemental analysis (%) calc.: C 52.3, N 9.5, H 3.8, Ag 14.7; found: C 52.1, N 9.4, H 3.6, Ag 14.4. Molar conductivity (Λ): 69 S.cm^2.mol^{-1}. FTIR (υ/cm^{-1}): 3059 (w, υ(C–H) aromatic), 2948 (w, υ_{as}(C–H) of CH_3 group), 2826 (w, υ_s(C–H) of CH_3 group), 1614 (m, υ(C = N)), 1598 and 1510 (w,s, υ(C = C) aromatic), 1253 (s, υ(C–O)). UV–Vis (λ/nm): 234 (n–σ^*), 330 (π–π^*). ^{1}H NMR (δ/ppm): 2.43 (6H, s, $2\times CH_3$), 3.89 (6H, s, $2\times OCH_3$), 7.00–7.03 (4H, d, J = 8.71 Hz, aromatic protons), 7.29–7.32 (4H, d, J = 7.47 Hz, aromatic protons), 7.87–7.90 (4H, d, J = 8.10 Hz, aromatic protons), 7.93–7.96 (4H, d, J = 8.50 Hz, aromatic protons). ^{13}C NMR (δ/ppm): 21.02 (CH_3), 55.00 (OCH_3), 114.29 ((C–H) aromatic), 123.01 ((C) aromatic), 127.28 ((C) aromatic), 127.89 ((C–H) aromatic), 128.96 ((C–H) aromatic), 129.40 ((C–H) aromatic), 143.51 (($\underline{\mathbf{C}}$–CH_3) aromatic), 160.89 (($\underline{\mathbf{C}}$–OCH_3) aromatic), 167.14 (C = N), 167.39 (C = N).

Bis[2-(4-ethoxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole] silver(I) nitrate (7b)

Yield (74%). Elemental analysis (%) calc.: C 53.6, N 9.2, H 4.2, Ag 14.1; found: C 53.3, N 9.0, H 4.1, Ag 13.9. Molar conductivity (Λ): 70 $S.cm^2.mol^{-1}$. FTIR (υ/cm^{-1}):, 3068 (w, υ(C–H) aromatic), 2955 (w, υ_{as}(C–H) of CH_3 group), 2931 (w-m, υ_{as}(C–H) of CH_2 group), 2853 (w, υ_s(C–H) of CH_3 group), 2839 (w-m, υ_s(C–H) of CH_2 group), 1613 (m, υ(C = N)), 1599 and 1512 (s,m, υ(C = C) aromatic), 1250 (s, υ(C–O)). UV–Vis (λ/nm): 229 (n–σ^*), 322 (π–π^*). ^{1}H NMR (δ/ppm): 1.44-1.48 (6H, t, $2\times(\text{-}OCH_2\underline{\mathbf{CH_3}})$), 2.43 (6H, s, $2\times CH_3$), 4.08-4.12 (4H, q, $2\times(\text{-}\underline{\mathbf{OCH_2}}CH_3)$), 6.98-7.01 (4H, d, J = 8.51 Hz, aromatic protons), 7.29–7.31 (4H, d, J = 7.34 Hz, aromatic protons), 7.86–7.89 (4H, d, J = 7.72 Hz, aromatic protons), 7.91–7.94 (4H, d, J = 8.41 Hz, aromatic protons). ^{13}C NMR (δ/ppm): 14.59 ($\text{-}OCH_2\underline{\mathbf{CH_3}}$), 20.14 ($CH_3$), 63.99 ($\text{-}\underline{\mathbf{OCH_2}}CH_3$), 114.62 ((C–H) aromatic), 121.89 ((C) aromatic), 126.46 ((C) aromatic), 127.45 ((C–H) aromatic), 128.56 ((C–H) aromatic), 129.97 ((C–H) aromatic), 142.09 (($\underline{\mathbf{C}}$–CH_3) aromatic), 162.07 (($\underline{\mathbf{C}}$–OCH_2) aromatic), 167.32 (C = N), 167.88 (C = N).

Bis[2-(4-propyloxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole] silver(I) nitrate (7c)

Yield (72%). Elemental analysis (%) calc.: C 54.7, N 8.9, H 4.6, Ag 13.6; found: C 54.5, N 8.8, H 4.3, Ag 13.2. Molar conductivity (Λ): 69 $S.cm^2.mol^{-1}$. FTIR (υ/cm^{-1}):, 3061 (w, υ(C–H) aromatic), 2959 (w, υ_{as}(C–H) of CH_3 group), 2933 (m, υ_{as}(C–H) of CH_2 group), 2855 (w, υ_s(C–H) of CH_3 group), 2834 (w-m, υ_s(C–H) of CH_2 group), 1611 (m, υ(C = N)), 1600 and 1510 (s,m, υ(C = C)aromatic), 1254 (s, υ(C–O)). UV–Vis (λ/nm): 228 (n–σ^*), 322 (π–π^*). ^{1}H NMR (δ/ppm): 1.03-1.09 (6H, t, $2\times(\text{-}OCH_2CH_2\underline{\mathbf{CH_3}})$), 1.81-1.88 (4H, m, $2\times(\text{-}OCH_2\underline{\mathbf{CH_2}}CH_3)$), 2.42 (6H, s, $2\times CH_3$), 3.97-4.01 (4H, t, $2\times(\text{-}\underline{\mathbf{OCH_2}}CH_2CH_3)$), 6.97–7.00 (4H, d, J = 8.53 Hz, aromatic protons), 7.28–7.30 (4H, d, J = 7.94 Hz, aromatic protons), 7.86–7.89 (4H, d, J = 7.89 Hz, aromatic protons), 7.91–7.94 (4H, d, J = 8.58 Hz, aromatic protons). ^{13}C NMR (δ/ppm): 9.98 ($\text{-}OCH_2CH_2\underline{\mathbf{CH_3}}$), 21.02 ($\text{-}OCH_2\underline{\mathbf{CH_2}}CH_3$), 22.99 ($CH_3$), 69.27 ($\text{-}\underline{\mathbf{OCH_2}}CH_2CH_3$), 114.60 ((C–H) aromatic), 121.97 ((C) aromatic), 124.94 ((C) aromatic), 127.27 ((C–H) aromatic), 128.94 ((C–H) aromatic), 129.38 ((C–H) aromatic), 141.06 (($\underline{\mathbf{C}}$–CH_3) aromatic), 161.68 (($\underline{\mathbf{C}}$–OCH_2) aromatic), 168.03 (C = N), 168.34 (C = N).

Bis[2-(4-butyloxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole] silver(I) nitrate (7d)

Yield (71%). Elemental analysis (%) calc.: C 55.7, N 8.6, H 4.9, Ag 13.2; found: C 55.6, N 8.4, H 4.7, Ag 13.0. Molar conductivity (Λ): 67 $S.cm^2.mol^{-1}$. FTIR (υ/cm^{-1}):, 3065 (w, υ(C–H) aromatic), 2951 (w, υ_{as}(C–H) of CH_3 group), 2938 (m, υ_{as}(C–H) of CH_2

group), 2857 (w, υ_s(C–H) of CH_3 group), 2853 (w, υ_s(C–H) of CH_2 group), 1612 (m, υ(C = N)), 1601 and 1512 (s,m, υ(C = C)aromatic), 1254 (s, υ(C-O)). UV–Vis (λ/nm): 234 (n–σ^*), 331 (π–π^*). ^{1}H NMR (δ/ppm): 0.97-1.02 (6H, t, $2\times(\text{-}OCH_2(CH_2)_2\underline{\mathbf{CH_3}})$), 1.48-1.58 (4H, m, $2\times(\text{-}OCH_2CH_2\underline{\mathbf{CH_2}}CH_3)$), 1.76-1.85 (4H, m, $2\times(\text{-}OCH_2\underline{\mathbf{CH_2}}CH_2CH_3)$), 2.42 (6H, s, $2\times CH_3$), 4.01-4.05 (4H, t, $2\times(\text{-}\underline{\mathbf{OCH_2}}CH_2CH_2CH_3)$), 6.97–6.99 (4H, d, $J = 8.53$ Hz, aromatic protons), 7.27–7.30 (4H, d, $J = 7.64$ Hz, aromatic protons), 7.87–7.89 (4H, d, $J = 8.08$ Hz, aromatic protons), 7.91–7.94 (4H, d, $J = 8.58$ Hz, aromatic protons). ^{13}C NMR (δ/ppm): 13.33 ($\text{-}OCH_2(CH_2)_2\underline{\mathbf{CH_3}}$), 18.72 ($\text{-}OCH_2CH_2\underline{\mathbf{CH_2}}CH_3$), 21.01 ($CH_3$), 30.70 ($\text{-}OCH_2\underline{\mathbf{CH_2}}CH_2CH_3$), 67.46 ($\text{-}\underline{\mathbf{OCH_2}}(CH_2)_2CH_3$), 114.53 ((C–H) aromatic), 122.59 ((C) aromatic), 127.27 ((C) aromatic), 128.91 ((C–H) aromatic), 129.31 ((C–H) aromatic), 129.66 ((C–H) aromatic), 140.84 (($\underline{\mathbf{C}}$–CH_3) aromatic), 161.82 (($\underline{\mathbf{C}}$–OCH_2) aromatic), 167.77 (C = N), 169.01 (C = N).

Bis[2-(4-pentyloxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole] silver(I) nitrate (7e)

Yield (69%). Elemental analysis (%) calc.: C 56.7, N 8.3, H 5.2, Ag 12.7; found: C 56.5, N 8.0, H 5.0, Ag 12.4. Molar conductivity (Λ): 68 $S.cm^2.mol^{-1}$. FTIR (υ/cm^{-1}):, 3063 (w, υ(C–H) aromatic), 2952 (w, υ_{as}(C–H) of CH_3 group), 2937 (m, υ_{as}(C–H) of CH_2 group), 2874 (w, υ_s(C–H) of CH_3 group), 2858 (m, υ_s(C–H) of CH_2 group), 1613 (m, υ(C = N)), 1597 and 1515 (s,m, υ(C = C)aromatic), 1255 (s, υ(C–O)). UV–Vis (λ/nm): 229 (n–σ^*), 323 (π–π^*). ^{1}H NMR (δ/ppm): 0.89-0.95 (6H, t, $2\times(\text{-}OCH_2(CH_2)_3\underline{\mathbf{CH_3}})$), 1.43-1.58 (8H, m, $2\times(\text{-}OCH_2CH_2\underline{\mathbf{(CH_2)_2}}CH_3)$), 1.82-1.87 (4H, m, $2\times(\text{-}OCH_2\underline{\mathbf{CH_2}}(CH_2)_2CH_3)$), 2.41 (6H, s, $2\times CH_3$), 3.99-4.05 (4H, t, $2\times(\text{-}\underline{\mathbf{OCH_2}}(CH_2)_3CH_3)$), 6.97–7.00 (4H, d, $J = 8.62$ Hz, aromatic protons), 7.27–7.29 (4H, d, $J = 7.91$ Hz, aromatic protons), 7.86–7.89 (4H, d, $J = 7.92$ Hz, aromatic protons), 7.93–7.96 (4H, d, $J = 8.69$ Hz, aromatic protons). ^{13}C NMR (δ/ppm): 13.53 ($\text{-}OCH_2(CH_2)_3\underline{\mathbf{CH_3}}$), 21.01 ($\text{-}OCH_2(CH_2)_2\underline{\mathbf{CH_2}}CH_3$), 22.09 ($CH_3$), 28.63 ($\text{-}OCH_2CH_2\underline{\mathbf{CH_2}}CH_2CH_3$), 31.06 ($\text{-}OCH_2\underline{\mathbf{CH_2}}(CH_2)_2CH_3$), 67.78 ($\text{-}\underline{\mathbf{OCH_2}}(CH_2)_3CH_3$), 114.52 ((C–H) aromatic), 122.49 ((C) aromatic), 127.77 ((C) aromatic), 128.91 ((C–H) aromatic), 129.31 ((C–H) aromatic), 129.99 ((C–H) aromatic), 140.93 (($\underline{\mathbf{C}}$–CH_3) aromatic), 162.02 (($\underline{\mathbf{C}}$–OCH_2) aromatic), 167.62 (C = N), 167.83 (C = N).

Bis[2-(4-hexyloxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole] silver(I) nitrate (7f)

Yield (68%). Elemental analysis (%) calc.: C 57.7, N 8.0, H 5.5, Ag 12.3; found: C 57.5, N 7.9, H 5.4, Ag 12.0. Molar conductivity (Λ): 67 $S.cm^2.mol^{-1}$. FTIR (υ/cm^{-1}):, 3065 (w, υ(C–H) aromatic), 2967 (w, υ_{as}(C–H) of CH_3 group), 2942 (m, υ_{as}(C–H) of CH_2 group), 2861 (w, υ_s(C–H) of CH_3 group), 2855 (m, υ_s(C–H) of CH_2 group), 1612 (m, υ(C = N)), 1599 and 1511 (s,m, υ(C = C)aromatic), 1253 (s, υ(C-O)). UV–Vis (λ/nm): 229 (n–σ^*), 329 (π–π^*). ^{1}H NMR (δ/ppm): 0.87-0.93 (6H, t, $2\times(\text{-}OCH_2(CH_2)_4\underline{\mathbf{CH_3}})$), 1.42-1.61 (12H, m, $2\times(\text{-}OCH_2CH_2\underline{\mathbf{(CH_2)_3}}CH_3)$), 1.76-1.84 (4H, m, $2\times(\text{-}OCH_2\underline{\mathbf{CH_2}}(CH_2)_3CH_3)$), 2.42 (6H, s, $2\times CH_3$), 3.99-4.04 (4H, t, $2\times(\text{-}\underline{\mathbf{OCH_2}}(CH_2)_4CH_3)$), 6.98–7.01 (4H, d, $J = 8.82$ Hz, aromatic protons), 7.25–7.28 (4H, d, $J = 7.82$ Hz, aromatic protons), 7.85–7.87 (4H, d, $J = 7.88$ Hz, aromatic protons), 7.98–8.01 (4H, d, $J = 8.79$ Hz, aromatic protons). ^{13}C NMR (δ/ppm): 13.52 ($\text{-}OCH_2(CH_2)_4\underline{\mathbf{CH_3}}$), 21.04 ($\text{-}OCH_2(CH_2)_3\mathbf{CH_2}CH_3$), 21.94

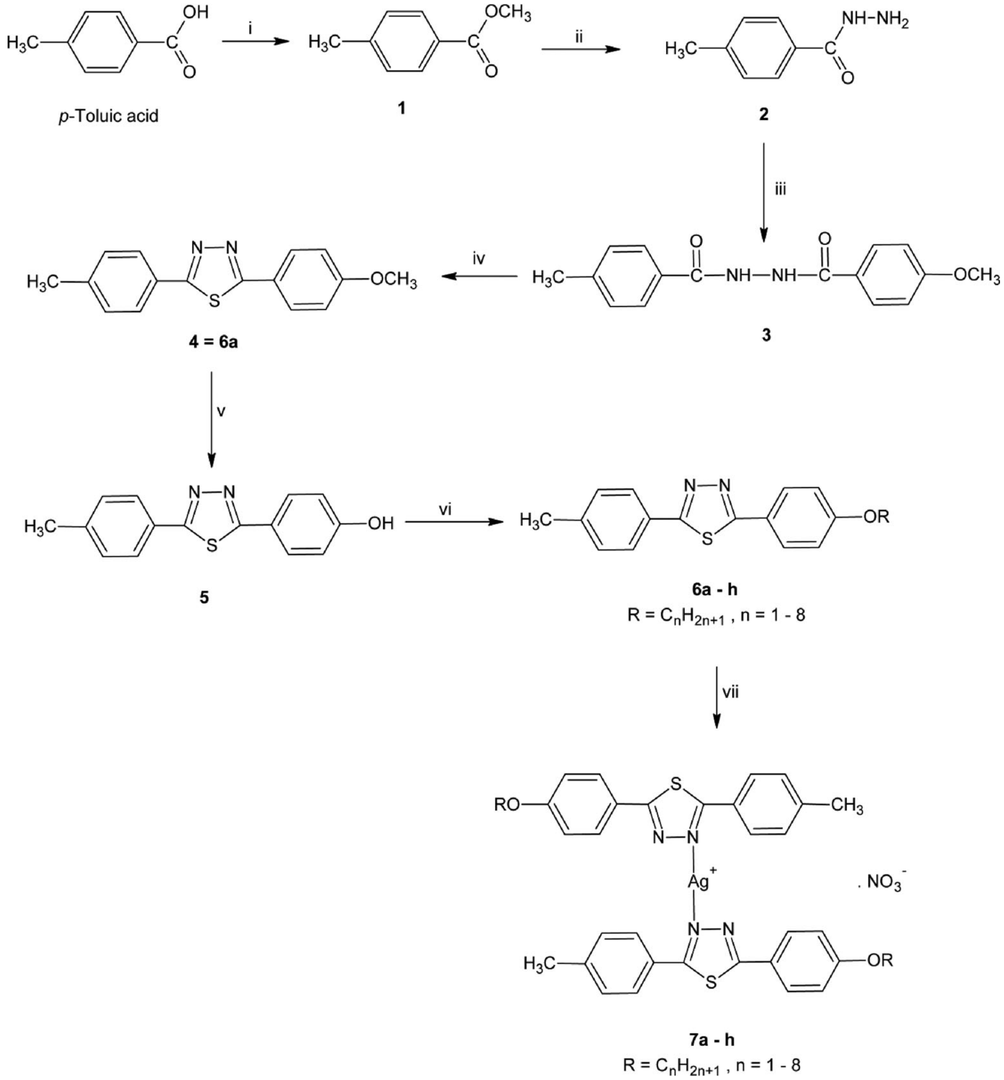
(CH_3), 27.66 (-$OCH_2(CH_2)_2\underline{\mathbf{CH_2}}CH_2CH_3$), 28.34 (-$OCH_2CH_2\underline{\mathbf{CH_2}}(CH_2)_2CH_3$), 31.99 (-$OCH_2\underline{\mathbf{CH_2}}(CH_2)_3CH_3$), 67.80 (-$\underline{\mathbf{OCH_2}}(CH_2)_4CH_3$), 114.64 ((C–H) aromatic), 122.31 ((C) aromatic), 127.24 ((C) aromatic), 128.87 ((C–H) aromatic), 129.43 ((C–H) aromatic), 130.03 ((C–H) aromatic), 141.06 (($\underline{\mathbf{C}}$–CH_3) aromatic), 161.11 (($\underline{\mathbf{C}}$–OCH_2) aromatic), 168.01 (C = N), 168.72 (C = N).

Bis[2-(4-heptyloxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole] silver(I) nitrate (7g)

Yield (65%). Elemental analysis (%) calc.: C 58.5, N 7.8, H 5.8, Ag 12.0; found: C 58.4, N 7.7, H 5.6, Ag 11.7. Molar conductivity (Λ): 66 $S.cm^2.mol^{-1}$. FTIR (υ/cm^{-1}):, 3063 (w, υ(C–H) aromatic), 2968 (w, υ_{as}(C–H) of CH_3 group), 2939 (m, υ_{as}(C–H) of CH_2 group), 2855 (w, υ_s(C–H) of CH_3 group), 2841 (m, υ_s(C–H) of CH_2 group), 1614 (m, υ(C = N)), 1600 and 1510 (s,m, υ(C = C)aromatic), 1254 (s, υ(C–O)). UV–Vis (λ/nm): 231 (n–σ^*), 328 (π–π^*). ^{1}H NMR (δ/ppm): 0.87-0.96 (6H, t, 2×(-$OCH_2(CH_2)_5\underline{\mathbf{CH_3}}$)), 1.45-1.62 (16H, m, 2×(-$OCH_2CH_2\underline{\mathbf{(CH_2)_4}}CH_3$)), 1.76-1.79 (4H, m, 2×(-$OCH_2\underline{\mathbf{CH_2}}(CH_2)_4CH_3$)), 2.41 (6H, s, 2 × CH_3), 3.99-4.05 (4H, t, 2×(-$\underline{\mathbf{OCH_2}}(CH_2)_5CH_3$)), 6.96–6.99 (4H, d, *J* = 8.76 Hz, aromatic protons), 7.26–7.29 (4H, d, *J* = 7.99 Hz, aromatic protons), 7.86–7.89 (4H, d, *J* = 7.91 Hz, aromatic protons), 7.92–7.94 (4H, d, *J* = 8.81 Hz, aromatic protons). ^{13}C NMR (δ/ppm): 13.51 (-$OCH_2(CH_2)_5\underline{\mathbf{CH_3}}$), 21.04 (-$OCH_2(CH_2)_4\underline{\mathbf{CH_2}}CH_3$), 21.94 ($CH_3$), 27.66 (-$OCH_2(CH_2)_3\underline{\mathbf{CH_2}}CH_2CH_3$), 28.34 (-$OCH_2(CH_2)_2\underline{\mathbf{CH_2}}(CH_2)_2CH_3$), 29.88 (-$OCH_2CH_2\underline{\mathbf{CH_2}}(CH_2)_3CH_3$), 31.91 (-$OCH_2\underline{\mathbf{CH_2}}(CH_2)_4CH_3$), 67.80 (-$\underline{\mathbf{OCH_2}}(CH_2)_5CH_3$), 114.64 ((C–H) aromatic), 119.87 ((C) aromatic), 127.27 ((C) aromatic), 128.87 ((C–H) aromatic), 129.44 ((C–H) aromatic), 130.07 ((C–H) aromatic), 141.06 (($\underline{\mathbf{C}}$–CH_3) aromatic), 161.12 (($\underline{\mathbf{C}}$–OCH_2) aromatic), 167.99 (C = N), 168.62 (C = N).

Bis[2-(4-octyloxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole] silver(I) nitrate (7h)

Yield (63%). Elemental analysis (%) calc.: C 59.4, N 7.5, H 6.1, Ag 11.6; found: C 59.3, N 7.2, H 6.2, Ag 11.8. Molar conductivity (Λ): 66 $S.cm^2.mol^{-1}$. FTIR (υ/cm^{-1}):, 3069 (w, υ(C–H) aromatic), 2970 (w, υ_{as}(C–H) of CH_3 group), 2941 (m, υ_{as}(C–H) of CH_2 group), 2855 (w, υ_s(C–H) of CH_3 group), 2838 (m, υ_s(C–H) of CH_2 group), 1612 (m, υ(C = N)), 1599 and 1513 (s,m, υ(C = C)aromatic), 1254 (s, υ(C–O)). UV–Vis (λ/nm): 230 (n–σ^*), 323 (π–π^*). ^{1}H NMR (δ/ppm): 0.85-0.90 (6H, t, 2×(-$OCH_2(CH_2)_6\underline{\mathbf{CH_3}}$)), 1.40-1.60 (20H, m, 2×(-$OCH_2CH_2\underline{\mathbf{(CH_2)_5}}CH_3$)), 1.79-1.83 (4H, m, 2×(-$OCH_2\underline{\mathbf{CH_2}}(CH_2)_5CH_3$)), 2.41 (6H, s, 2 × CH_3), 3.98-4.02 (4H, t, 2×(-$\underline{\mathbf{OCH_2}}(CH_2)_6CH_3$)), 6.99–7.02 (2H, d, *J* = 8.73 Hz, aromatic protons), 7.29–7.31 (2H, d, *J* = 7.88 Hz, aromatic protons), 7.89–7.92 (2H, d, *J* = 7.96 Hz, aromatic protons), 7.93–7.96 (2H, d, *J* = 8.82 Hz, aromatic protons). ^{13}C NMR (δ/ppm): 13.61 (-$OCH_2(CH_2)_6\underline{\mathbf{CH_3}}$), 21.02 ($OCH_2(CH_2)_5\underline{\mathbf{CH_2}}CH_3$), 22.17 ($CH_3$), 25.51 (-$OCH_2(CH_2)_4\underline{\mathbf{CH_2}}CH_2CH_3$) 28.66 (-$OCH_2(CH_2)_3\underline{\mathbf{CH_2}}(CH_2)_2CH_3$), 28.74 (-$OCH_2(CH_2)_2\underline{\mathbf{CH_2}}(CH_2)_3CH_3$), 28.85 (-$OCH_2CH_2\underline{\mathbf{CH_2}}(CH_2)_4CH_3$), 31.32 (-$OCH_2\underline{\mathbf{CH_2}}(CH_2)_5CH_3$), 67.80 (-$\underline{\mathbf{OCH_2}}(CH_2)_6CH_3$), 114.55 ((C–H) aromatic), 122.12 ((C) aromatic), 127.07 ((C) aromatic), 128.92 ((C–H) aromatic), 129.43



Scheme 1. Synthetic diagram for the preparation of compounds. Reactions and reagents: (i) methanol, H_2SO_4; (ii) ethanol, NH_2NH_2.H2O; (iii) pyridine, 0 °C; (iv) P_2S_5, pyridine; (v) $AlCl_3$, benzene; (vi) RBr, acetone; (vii) $AgNO_3$, CH_2Cl_2.

((C–H) aromatic), 129.34 ((C–H) aromatic), 140.92 (($\underline{C}$–CH_3) aromatic), 161.04 (($\underline{C}$–OCH_2), 167.77 (C = N), 168.32 (C = N).

Result and discussion

Synthesis and characterization of the compounds

A series of 2-(4-alkoxyphenyl)-5-(*p*-tolyl)-1,3,4-thiadiazoles (alkoxy: $O(CH_2)_nH$, $n = 1–8$) ***(6a–h)*** was prepared through several successive steps starting from *p*-toluic acid, while bis(2-(4-alkoxyphenyl)-5-(*p*-tolyl)-1,3,4-thiadiazole)-silver(I) complexes (alkoxy: $O(CH_2)_nH$, $n = 1–8$) ***(7a–h)*** were prepared by the stirring of a corresponding 1,3,4-thiadiazole compound with silver nitrate in DCM, in the absence of light, and under inert and ambient conditions. Scheme 1 shows the synthetic diagram of the prepared compound.

Various techniques were used to identify the mesogens ***(6a–h)*** and metallomesogens ***(7a–h)***: microelemental analysis, FTIR, UV–Vis, ^{1}H NMR, ^{13}C NMR and mass (for the organic compounds) spectra, in addition to the molar conductivity measurements (for Ag(I) complexes). The details of these data are illustrated in the experimental part.

Microelemental analyses (C, H and N) data show the good agreement of the actual and the proposed formulas.

In general, some characteristic bands belong to C–H, C = C, C = N and C–O functional groups [52] are observed in the FTIR spectra of ***6a–h***. The FTIR spectra of silver(I) complexes ***(7a–h)*** displayed almost, the same bands that detected in the spectra of their corresponding ligands (1,3,4-thiadiazole compounds) but with slight changes either in their appearance or positions. For example, the band due to the stretching vibration of C = N group that observed in the spectra of 1,3,4-thiadiazole compounds ***(6a–h)***, were found to be slightly shifted to higher frequencies in the spectra of the corresponding Ag(I) complexes***(7a–h)***. This gives an evidence that the binding of a thiadiazole molecule (organic ligand) to the silver(I) ion takes place through the N atom of the C = N group. Shifting the stretching vibration of a C = N group to higher frequencies upon coordination to a metal ion is already detected and reported earlier [53–56].

Several signals belonging to the various proton and carbon nuclei are observed in the ^{1}H NMR and ^{13}C NMR spectra of 1,3,4-thiadiazole compounds (for instance see Fig. 1a). In the spectra of Ag(I) complexes, some of these signals are found to be shifted, either to a lower or higher chemical shift, for example see Fig. 1b. The details of these signals and their assignment for all the prepared compounds are depicted in the experimental part.

UV–Vis spectra of 1,3,4-thiadiazoles ***(6a–h)*** displayed two absorption peaks at the ranges: (229–232 nm) and (322–326 nm). The first peak is attributed to the n–σ^* transition, while the second one is assigned to π–π^* transition. However, the spectra show no peak related to the n–π^* transition band which may be hidden by π–π^* band. Upon coordination of the prepared 1,3,4-thiadiazole compounds to Ag(I) ion, the n–σ^* and π–π^* were found to be shifted either to higher or lower wavernumbers. Moreover, the band due to the charge transfer (CT) transition in all complexes was located either merged or slightly separated from the strong π–π^* band. No d-d transitions are appeared in all the spectra of silver(I) complexes because of the filled d–orbitals of silver atom [57]. The details of the UV–Vis spectral data are listed in the experimental part.

The molar conductivity values of silver(I) complexes ***(7a–h)*** in acetone (1×10^{-3}M) are in the range (66–70) S. cm^2. mol^{-1}, confirming their (1:1) electrolytic nature [58].

The data provided by FTIR, UV–Vis, NMR (^{1}H and ^{13}C NMR) spectra, conductivity measurements and microelemental analysis, revealed the monodentate behavior of 1,3,4-thiadiazole compounds toward silver(I). Two molecules of 1,3,4-thiadiazoles are binding to the Ag atom through the N atom, produced a linear-mononuclear complex with the general formula [Ag $(L)_2$]. NO_3 (where L: 2-(4-alkoxyphenyl)-5-(*p*-tolyl)-1,3,4-thiadiazole derivative). Almost of the prepared thiadiazole complexes that investigated so far confirmed that the binding of thiadiazole ligand to a metal ion is took place through N atoms [59–62].

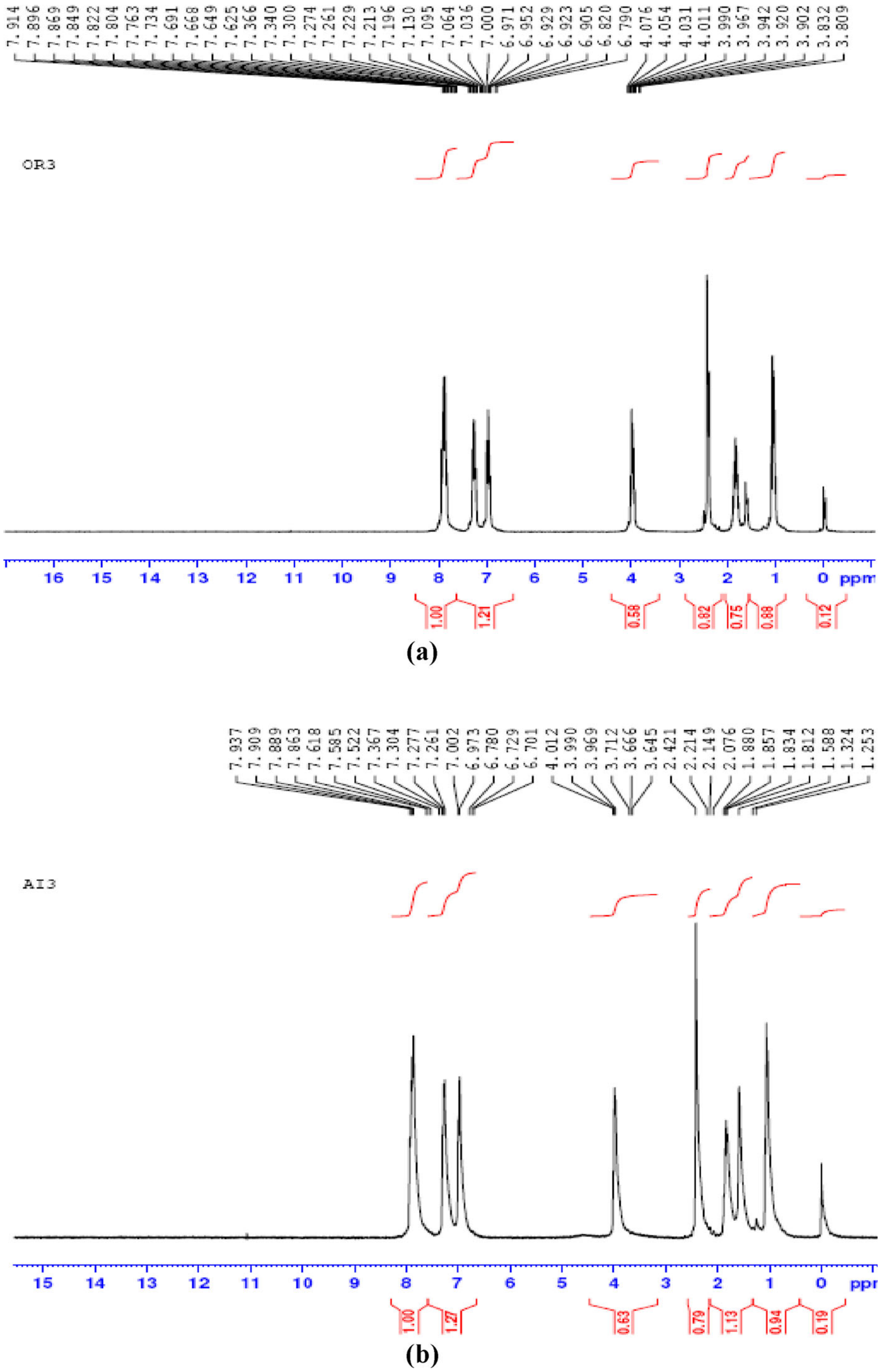


Figure 1. ^{1}H NMR spectra of **6c** (a) and **7c** (b).

Table 1. Phase transitions and their temperatures for the prepared compounds obtained by POM.

Compound	n	Phase transitions (T / °C) First heating	Phase transitions (T / °C) First cooling
6_a	1	Cr-N (154.0) N-I (216.0)	I-N (214.0) N-Cr (138.0)
6_b	2	Cr-N (141.0) N-I (224.0)	I-N (220.0) N-Cr (125.0)
6_c	3	Cr-N (146.0) N-I (200.0)	I-N (198.0) N-Cr (122.0)
6_d	4	Cr-N (138.0) N-I (204.0)	I-N (198.0) N-Cr (110.0)
6_e	5	Cr-N (122.0) N-I (192.0)	I-N (191.0) N-Cr (106.0)
6_f	6	Cr-N (117.0) N-I (196.0)	I-N (191.0) N-Cr (98.0)
6_g	7	Cr-SmC (113.0) SmC-N (121.0) N-I (186.0)	I-N (183.0) N-SmC (118.0) SmC-Cr (96.0)
6_h	8	Cr-SmC (110.0) SmC-N (134.0) N-I (183.0)	I-N (181.0) N-SmC (129.0) SmC-Cr (93.0)
7_a	1	Cr-I (204.00)	I-Cr (200.00)
7_b	2	Cr-SmA (147.0) SmA-I (210.0)	I-SmA (207.0) SmA-Cr (55.0)
7_c	3	Cr-SmA (133.0) SmA-I (185.0)	I-SmA (181.0) SmA-Cr (68.0)
7_d	4	Cr-SmA (127.0) SmA-I (191.0)	I-SmA (188.0) SmA-Cr (59.0)
7_e	5	Cr-SmA (125.0) SmA-I (181.0)	I-SmA (179.0) SmA-Cr (66.0)
7_f	6	Cr-SmA (112.0) SmA-I (186.0)	I-SmA (182.0) SmA-Cr (96.0)
7_g	7	Cr-SmA (107.0) SmA-I (178.0)	I-SmA (172.0) SmA-Cr (94.0)
7_h	8	Cr-SmA (113.0) SmA-I (180.0)	I-SmA (177.0) SmA-Cr (92.0)

Cr—crystalline solid, SmA—smectic A mesophase, SmC—smectic C mesophase, N—nematic mesophase, I—isotropic liquid, n—alkyl chain length.

Liquid crystalline behavior of the prepared compounds

Liquid crystalline behavior of the prepared compounds was evaluated using polarized light optical microscopy (POM) technique. The studies showed in general that all the compounds of 2-(4-alkoxyphenyl)-5-(*p*-tolyl)-1,3,4-thiadiazoles (alkoxy: $O(CH_2)_nH$, $n = 1–8$) ***(6a–h)*** and bis(2-(4-alkoxyphenyl)-5-(*p*-tolyl)-1,3,4-thiadiazole)-silver(I) complexes (alkoxy: $O(CH_2)_nH$, $n = 2–8$) ***(7b–h)*** are mesomorphic materials displaying enantiotropic liquid crystal properties, while ***7a*** ($n = 1$) shows no mesomorphic properties (simply melted to isotropic liquid). The details of the mesophase transitions are depicted in Table 1, and examples of optical micrographs of these compounds are illustrated in Fig. 2.

It can be clearly seen from Table 1 that compounds ***6a–h*** displayed only nematic mesophase upon heating and cooling, which was attributed from the typical thread-like texture, droplet-like texture or schlieren-like texture, while ***6g*** and ***6h*** showed both of SmC and nematic mesophases upon heating and cooling. SmC mesophase was identified by the schlieren-like texture, while nematic mesophase assigned from the typical thread-like texture, droplet-like texture or schlieren-like texture. These results are quite similar to that obtained by Jie Han *et al.* [63].

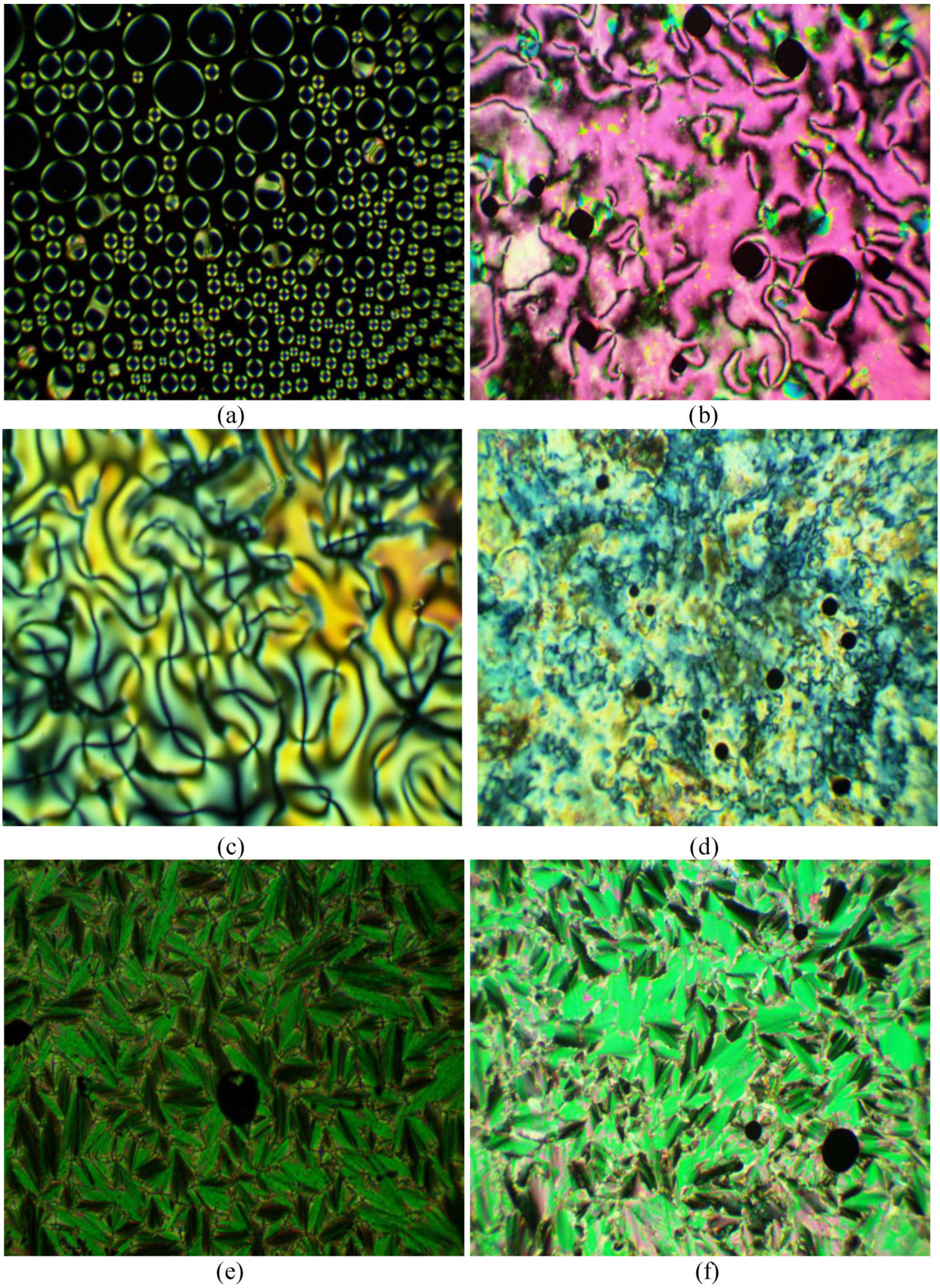


Figure 2. Optical micrographs (magnification:×300) of (a) the nematic droplet-like texture obtained for **6f**, at 120 °C upon cooling; (b) the nematic thread-like texture observed for **6g**, at 176 °C upon cooling; (c) the schlieren nematic texture detected for **6e**, at 183 °C upon heating; (d) the smectic C texture exhibited by **6g**, at 117 °C upon heating, (e) the fan-shape texture shown by **7e**, at 131 °C upon cooling; (f) the fan-shape texture observed for **7g**, at 113 °C upon cooling.

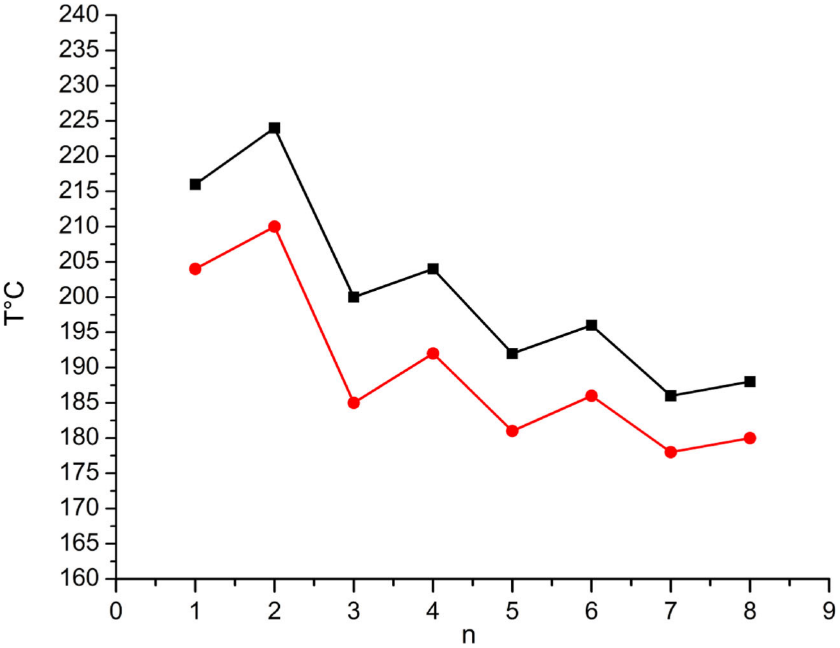


Figure 3. Clearing temperature (T_c) as a function of alkyl chain length for 1,3,4-thiadiazoles series (black line) and silver(I) complexes series (red line).

Upon complexation of 2-(4-alkoxyphenyl)-5-(*p*-tolyl)-1,3,4-thiadiazoles to silver(I), the liquid crystal behavior and properties are appreciably changed. In this context, silver(I) complexes ***7b–h*** exhibit SmA mesophase upon heating and cooling, while ***7a*** shows no mesomorphic properties (simply melted to isotropic liquid). This difference may be due to the different stereochemical structure of the two series of compounds.

In general, the length of hydrocarbon chain might have variable effects on the clearing temperature of a mesogen or metallomesogen. So, as the chain length of a compound increases, the van der Waals interactions increase and this would increase the clearing point. On the other hand, the flexibility of the hydrocarbon chain may disrupt the lateral core–core interactions, and consequently reduces the clearing point of a compound. The clearing temperatures of 2-(4-alkoxyphenyl)-5-(*p*-tolyl)-1,3,4-thiadiazoles (alkoxy: $O(CH_2)_nH$, $n = 1–8$) (**6a–h**) and bis(2-(4-alkoxyphenyl)-5-(*p*-tolyl)-1,3,4-thiadiazole)-silver(I) complexes (alkoxy: $O(CH_2)_nH$, $n = 1–8$) (**7a–h**) are found to be decreased with increasing the chain length, see Fig. 3 (the odd-even effect in both series can be clearly seen from this figure). Therefore, this indicates that the melting process seems to be governed by the random motion of hydrocarbon chains, and is less affected by the van der Waals interactions between chains [14,38,64]. Moreover, the clearing temperature of silver(I) complexes series (**7a–h**) were found to be lower than that of the corresponding 1,3,4-thiadiazoles series (**6a–h**). This may be due to the following reason: the structure of 1,3,4-thiadiazole compounds (**6a–h**) show only one tail of hydrocarbon chain, while the structure of silver(I) complexes (**7a–h**) displayed two tails. Consequently, the disruption of the lateral core–core interactions by flexibility of the alkyl chains would be more pronounced in silver(I) complexes.

Conclusions

Reaction of 2-(4-alkoxyphenyl)-5-(*p*-tolyl)-1,3,4-thiadiazoles (alkoxy: $O(CH_2)_nH$, $n = 1–8$) (***6a–h***) (as a series of 1,3,4-thiadiazole derivatives) with silver nitrate at room temperature, in the absence of light, and under inert conditions produced a series of organic-inorganic hybrids with two tails of hydrophobic hydrocarbon chains: bis(2-(4-alkoxyphenyl)-5-(*p*-tolyl)-1,3,4-thiadiazole)-silver(I) complexes (alkoxy: $O(CH_2)_nH$, $n = 1–8$) (***7a–h***). Both series are confirmed as liquid crystalline materials with different behavior and properties (different mesophases, and different melting and clearing temperatures). The prepared1,3,4-thiadiazoles behave as mesogens (***6a–f)*** show only nematic mesophase upon heating and cooling, while ***6g*** and ***6h*** display SmC and nematic mesophases upon heating and cooling. On the other hand, the silver(I) complexes behave as metallomesogens exhibiting SmA mesophase upon heating and cooling, except ***7a*** which shows no mesomorphic properties (simply melted to isotropic liquid).

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