Polyhedron 200 (2021) 115149

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Design and synthesis of novel terpyridine-based ligands with one and two terminal aurophilic moieties and their Rh(III) and Ru(II) complexes for the adsorption on metal surfaces

Irina O. Salimova, Anna V. Berezina, Ilona A. Shikholina, Nikolai V. Zyk, Elena K. Beloglazkina *

M.V. Lomonosov Moscow State University, Chemistry Department, Moscow 119991, Russia

ARTICLE INFO

Article history:
Received 18 November 2020
Accepted 5 March 2021
Available online 17 March 2021

Keywords:
2.2′:6′,2″-Terpyridine
Aurophilic ligands
Ruthenium
Rhodium
Electrochemistry

ABSTRACT

Novel terpyridine ligands with one and two terminal aurophilic sulfur containing fragments, (S)-11-(4-([2,2′:6′,2″-terpyridin]-4′-yl)phenoxy)undecyl 5-(1,2-dithiolan-3-yl)pentanoate (**7**), (S)-((4-([2,2′:6′,2″-terpyridin]-4′-yl)-1,3-phenylene)bis(oxy))bis(undecane-11,1-diyl) bis(5-((S)-1,2-dithiolan-3-yl)pentanoate) (**11a**), (S)-((4-([2,2′:6′,2″-terpyridin]-4′-yl)-1,2-phenylene)bis(oxy))bis(undecane-11,1-diyl) bis(5-((S)-1,2-dithiolan-3-yl)pentanoate) (**11b**), (S)-((5-([2,2′:6′,2″-terpyridin]-4′-yl)-1,3-phenylene)bis(oxy))bis(undecane-11,1-diyl) bis(5-((S)-1,2-dithiolan-3-yl)pentanoate) (**11c**) were synthesized and employed to synthesis of mononuclear ruthenium(II) and rhodium(III) complexes. Electrochemical studies of the obtained ligands and coordination compounds and their ability to chemisorb on gold electrodes surfaces have been carried out. Among the obtained metal complexes, compounds with the minimum time of chemisorption with the formation of Au-S bonds were revealed, which are complexes of 3,4- and 3,5-substituted phenylterpyridines.

1. Introduction

The interest in the development of metal-containing aurophilic organic derivatives with one or two terminal sulfur-containing groups in ligand fragments is associated with the promise of such molecules for the creation of single-electron single-molecule transistors or charge-sensitive biosensors [1–7] and luminescent probes [8,9]. In particular, the polypyridyl complexes of ruthenium(II) and rhodium(III) are used as luminophores in DNA-based biosensors [10–13].

The presence of two sulfur-containing groups in the organic ligand, used to obtain the metal complexes, give possibility to such coordination compounds chemosorb on two closely spaced gold electrodes to form strong Au-S covalent bonds. One of the promising using of these compounds may be the single-molecular sequencing based on charge-sensitive sensors. It is proposed to use metal complexes fixed between planar nanoelectrodes as a bridge-molecule in the sensors for detecting the one charge pair separation as a result of DNA/RNA polymerization [14–16]. The key to the practical implementation of such sequencing is the development of reliable methods for producing organic ligands with three functional groups, while one is able to coordinate a metal atom, and the other two groups can bind to electrodes.

Coordination compounds of ruthenium with bipyridine ligands have been offered as sensors for various amino acid fragments (phenylglycine, valine), as well as phosphate anions [17–19]. There are works devoted to the creation of single-molecule sensors based on aurophilic nitrogen-containing coordination compounds 4,4′-bipyridine, N′-bis(6-mercaptohexyl)-(4,4′-bipyridine) and N,N′-bis(6-acetoxythio)-(4,4′-bipyridine) [20–22], as well as S-alkyl- and ruthenium 4-pyridyl substituted terpyridine complexes [23] and complexes of terpyridines with Zn(II) [24,25].

Coordination compounds of Fe, Co, Cr, Ru with ligands based on substituted aurophilic terpyridines showed higher conductivity compared to 4,4′-bipyridine and its analogues. These results have evidenced the terpyridine coordination compounds are highly perspective for using in single-molecule devices as an island [26,27]. Earlier, we proposed the method of single-molecule nanotransistors producing based on gold electrodes located at the 4 nm distance. The gap between electrodes is occupied by the chemically-formed symmetric aurophilic coordination compound of Rh(III) with (S)-4-([2,2′:6′,2″-terpyridin]-4′-yl)phenyl 5-(1,2-dithiolan-3-yl)pentanoate. It is shown that in the obtained molecular nanotransistors the electrons tunneling was carried out through the rhodium atom was the only intramolecular charge center [28].

* Corresponding author.
E-mail address: bel@org.chem.msu.ru (E.K. Beloglazkina).

https://doi.org/10.1016/j.poly.2021.115149
0277-5387/

The development of the above-mentioned single-molecule devices requires the developing a convenient synthetic procedure for the preparation of suitable organic ligands and their *bis*-ligand coordination compounds that can be chemisorbed on two gold electrodes located at a distance of several nm. It was previously proved that when such a pair of electrodes is immersed in a solution of a *bis*-(S-containing ligand) coordination compound with the distances between two terminal sulfur-containing groups no less than the interelectrode gap, some of the molecules of the symmetric aurophilic coordination compound can be adsorbed with Au-S bonds formation on two different electrodes, connecting them among themselves [28].

In this article, novel terpyridine ligands with one and two terminal aurophilic fragments was designed to provide the following criteria: (1) the ligand possibility to bound second-row transition metal ions, in particular rhodium and ruthenium, forming mononuclear coordination compounds [29,30]; (2) the presence of the stable disulfide fragment, which at the same time provides the possibility of rapid chemosorption on gold electrodes surface with the formation of Au-S bonds; (3) the distance between the sulfur-containing fragments is about 4 nm, which corresponds to the achievable interelectrode gap in the nanoelectrode device [28]. The target ligands (L) were synthesized and employed to synthesize of ruthenium(II) and rhodium(III) complexes with the Ru(L) $DMSOCl_2$ or $RhM(L)Cl_3$ composition. The possibility of the resulting complexes adsorption on the gold electrodes surface was demonstrated.

2. Experimental

2.1. Materials and methods

All starting materials were obtained from commercial sources and used without additional purification. ^1H and ^{13}C NMR spectra were obtained on a Bruker Avance spectrometer (400 and 100 MHz respectively) instrument, internal standard was HMDS (δ 0.05 ppm).

Preparative chromatographic separation of the reaction mixtures was carried out using the INTERCHIM puriFlash 430 chromatograph.

High resolution mass spectra were recorded on the Orbitrap Elite high resolution mass spectrometer. Solutions of samples in DMSO with 1% formic acid were introduced into the ionization source by electrospray. HRMS spectra of rhodium-containing coordination compounds **13** and **14** were recorded with the addition of 1% silver nitrate.

Mass spectra with laser ionization (LI MS) were recorded on a Bruker Autoflex II instrument (FWHM 18000) with the 337 nm nitrogen laser, a time-of-flight mass analyser operating in reflectron mode, and an accelerating voltage of 20 kV. Samples were applied to a polished steel substrate. Spectra were recorded in positive ion mode. The resulting spectrum was a sum of 50 spectra obtained at different points in the sample.

For HPLC analysis system with Shimadzu Prominence LC-20 column and a convection fraction collector connected with a single quadrupole mass spectrometer Shimadzu LCMS-2020 with dual ionization source DUIS-ESI-APCI were used. The analytical and preparative column was Phenomenex Luna 3u C18 100A.

Elemental analyses were performed on a Vario MICRO cube CHNS Elementar.

Electronic spectra in the UV and visible regions were recorded on a Hitachi U-2900 instrument. Mass spectra with laser ionization (LI-MS) recorded on a Bruker Autoflex II instrument (FWHM 18000) with the 337 nm nitrogen laser and a time-of-flight mass analyzer operating in the reflection mode. Accelerating voltage 20 kV. Samples were applied to a polished steel substrate. Spectra were recorded in positive ion mode. The resulting spectrum was a sum of 50 spectra obtained at different points of the sample.

4-([2,2′:6′,2″-Terpyridin]-4′-yl)phenol syntheses was described in [31]; the synthesis of $[Rh(DMSO)_3]Cl_3$ and $[Ru(DMSO)_4]Cl_2$ were described in [32–34].

Electrochemical studies were performed at 25 °C using a IPC-2000 potentiostat with the refinement program complex (developed in A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, RAS; author V. E. Kasatkin, vadim_kasatkin@mail.ru; see, for example http://www.expo.ras.ru/base/prod_data.asp?prod_id=4687). Glass carbon and Au disks (both 2 mm in diameter) polished with Al_2O_3 (<10 mm) were used as the working electrodes, and a 0.1 m Bu_4NClO_4 solution in DMSO served as the supporting electrolyte. Ag/AgCl/KCl(sat.) was used as the reference electrode. The potentials are given with allowance for iR compensation. All measurements were carried out under argon. The samples were dissolved in pre-deoxygenated solvent. For the ligands and complexes chemisorption on gold electrode surface electrode was immersed of in a saturated solution of corresponding disulfide-derivatized compound for 1–3 days, then the electrode was removed, washed 2 times with DMSO and dried in air.

2.2. Synthesis

2.2.1. Synthesis of 4-((11-hydroxyundecyl)oxy)benzaldehyde (**2**)

To the solution of 4-hydroxybenzaldehyde **1** (0.5 g, 4.1 mmol) in 50 ml of acetonitrile K_2CO_3 (1.1 g, 8.2 mmol) were added and the resulting mixture was heated to 80 °C. After that, 11-bromoundecanol (2.2 g, 8.6 mmol) was introduced into the reaction mixture. The mixture was stirred under heating for 25 h. After the reaction completed, the solvent was distilled off, the resulting mixture was suspended in water, extracted with $CHCl_3$, and the organic fraction was dried over Na_2SO_4. After the solvent removing the target substance was recrystallized from a methanol:diethyl ether mixture (1:1), washed with ethanol and dried in air. Thus, 0.98 g (82%) of compound **2** was obtained as a white powder. M. p. 68–70 °C.

NMR ^1H (400 MHz, $CDCl_3$, δ, ppm): 9.87 (s. 1H), 7.81–7.83 (m, 2H), 6.99 (d, 2H, J = 8.7 Hz), 4.03 (t, 2H, J = 6.6 Hz), 3.63 (t, 2H, J = 6.7 Hz), 1.79–1.83 (m, 2H), 1.54–1.58 (m, 2H), 1.29–1.46 (m, 14H).

NMR ^{13}C (100 MHz, $CDCl_3$, δ, ppm): 190.62, 164.28, 131.90, 129.88, 114.78, 68.44, 63.01, 33.80, 32.79, 29.50, 29.42, 29.35, 29.26, 29.04, 28.70, 28.13, 25.91, 25.71.

LC-MS: Calculated, m/z: 292.20. $C_{18}H_{28}O_3$. Found: ($[M+H]^+$) 293.24.

2.2.2. Synthesis of 11-(4-([2,2′:6′,2″-terpyridin]-4′-yl)phenoxy) undecan-1-ol (**3**)

To the solution of KOH (0.16 g, 2.06 mmol) in 10 ml of ethanol 4-((11-hydroxyundecyl)oxy)benzaldehyde **2** (0.3 g, 1.03 mmol), then 2-acetylpyridine (0.235 ml, 2.06 mmol) and after 10 min an excess (0.4 ml, 10.3 mmol) of 25% aqueous ammonia were added. The reaction mixture was stirred at 50 °C for two days. After the reaction completed, the solvent was distilled off, and the residue was recrystallized from methanol, washed with diethyl ether and dried in air. Thus, 0.21 g (42%) of the compound **3** was obtained as a white powder. M.p. 161–163 °C.

NMR ^1H (400 MHz, $CDCl_3$, δ, ppm): 8.68–8.74 (m, 6H), 7.88–7.90 (m, 4H), 7.37 (d, 2H, J = 3.5 Hz), (dd, 2H, J_1 = 8.3 Hz, J_2 = 3.5 Hz), 4.04 (d, 2H, J = 4.2 Hz), 3.63–3.67 (m, 2H), 1.74–1.82 (m, 2H), 1.32–1.57 (m, 16H).

NMR ^{13}C (100 MHz, $CDCl_3$, δ, ppm): 160.14, 156.45, 155.82, 149.81, 149.07, 136.81, 130.50, 128.47, 123.71, 121.37, 118.25, 114.91, 68.14, 63.00, 32.81, 29.47, 29.26.

LC-MS: Calculated, *m*/*z*: 495.29. $C_{32}H_{37}N_3O_2$. Found: ($[M+H]^+$) 496.30.

*2.2.3. Synthesis of (S)-11-bromoundecyl 5-(1,2-dithiolan-3-yl) pentanoate (**5**)*

To the solution of lipoic acid (0.206 g; 1 mmol) in 20 ml of dichloromethane DMAP (0.012 g; 0.1 mmol), EDC·HCl (0.210 g; 1.1 mmol) and 11-bromo-undecanol-1 (0.251 ml; 1 mmol) were added. The mixture was stirred for 24 h in the inert atmosphere. The solvent was removed under reduced pressure and the residue was purified by column chromatography (Puriflash 15 μ 25 g, eluent: P.E. (100%)/EtOAc (0%) = > P.E. (90%)/EtOAc (10%) for 15 min). Thus, 0.360 g (82%) of the compound **5** was obtained as yellow oil.

NMR ^{1}H (400 MHz, $CDCl_3$, δ, ppm): 4.05 (t, 2H, *J* = 6.7 Hz), 3.51–3.62 (m, 1H), 3.40 (t, 2H, *J* = 6.7 Hz), 3.05–3.23 (m, 2H), 2.41–2.51 (m, 1H), 2.31 (t, 2H, *J* = 7.4 Hz), 1.80–1.96 (m, 3H), 1.57–1.75 (m, 6H), 1.37–1.54 (m, 4H), 1.23–1.37 (m, 12H).

LC-MS: Calculated, *m*/*z*: 297.97. $C_{19}H_{35}BrO_2S_2$. Found: ($[M+H]^+$) 298.93.

*2.2.4. Synthesis of (S)-11-(4-([2,2′:6′,2″-terpyridin]-4′-yl)phenoxy) undecyl 5-(1,2-dithiolan-3-yl)pentanoate (**7**)*

2.2.4.1. Method I. To the solution of lipoic acid (0.17 g, 0.84 mmol) in 20 ml of DMF HOBt (0.17 g, 1.26 mmol), HBTU (0.48 g, 1.26 mmol) and DIPEA (0.3 ml, 1.68 mmol) were added and the mixture was stirred in the inert atmosphere for 40 min. After that 11-(4-([2,2′:6′,2″-terpyridin]-4′-yl)phenoxy)undecan-1-ol **3** were added and the reaction mixture was stirred in the inert atmosphere for 48 h. Then the solvent was removed under reduced pressure and the residue was purified by column chromatography (Puriflash 15μ 25 g, eluent: petroleum ether => petroleum ether (50%)/EtOAc + $NH_3{\cdot}H_2O$ (50%) =>EtOAc + $NH_3{\cdot}H_2O$ (100%) for 26 min. The ratio of EtOAc and $NH_3{\cdot}H_2O$ is 1:0.0025. Thus, 0.18 g (66%) of the compound **7** was obtained as white-green oily crystals.

2.2.4.2. Method II. To the suspension of 4-(2.2:6′,2″- terpyridin-4′-yl) phenol (0.4 g, 1.23 mmol), and cesium carbonate (4.0 g, 12.3 mmol) in 100 ml of acetonitrile 11-bromoundecyl-5-(1,2-dithiolan-3-yl)pentanoate **5** (0.81 g, 1.85 mmol) was added. The resulting mixture was boiled with stirring for 40 h. Then the solvent was distilled off under reduced pressure, the resulting mixture was suspended in water and extracted with chloroform. The combined organic fractions were dried over Na_2SO_4 and the solvent was distilled off. The residue was purified by column chromatography (Puriflash 15μ 40 g, eluent: P.E. (100%)/EtOAc + $NH_3{*}H_2O$ (0%) => P.E. (50%)/EtOAc + $NH_3{\cdot}H_2O$ (50%) => P. E. (0%)/EtOAc + $NH_3{*}H_2O$ (100%) for 20 min. The ratio of EtOAc and $NH_3{*}H_2O$ is 1:0.0025). Thus, 0.46 g (54%) of the compound **7** was obtained as white-green oily crystals.

NMR ^{1}H (400 MHz, $CDCl_3$, δ, ppm): 8.76–8.79 (m, 6H), 7.93–8.00 (m, 4H), 7.43 (dd, 2H, J_1 = 6.6 Hz, J_2 = 5.3 Hz), 7.01 (d, 2H, *J* = 8.8 Hz) 4.04 (dt, 4H, J_1 = 17 Hz, J_2 = 6.6 Hz), 3.53–3.60 (m, 1H), 3.07–3.20 (m, 2H), 2.41–2.49 (m, 2H), 2.31 (t, 2H, *J* = 7.4 Hz), 1.24–1.94 (m, 24H).

NMR ^{13}C (100 MHz, $CDCl_3$, δ, ppm): 173.67, 160.11, 156.37, 155.79, 149.81, 149.09, 136.91, 130.43, 128.50, 123.79, 121.40, 118.24, 114.83, 68.11, 64.56, 56.36, 40.23, 38.50, 34.62, 34.14, 29.72, 29.53, 29.28, 28.80, 28.65, 26.07, 25.96, 24.74.

LC-MS: Calculated, *m*/*z*: 683.32.$C_{40}H_{39}N_3O_3S_2$. Found: ($[M+H]^+$) 684.35.

HRMS: Calculated ($[M+H]^+$): 684.3294. $C_{40}H_{49}N_3O_3S_2$. Found: ($[M+H]^+$) 684.3298.

UV–vis: (λ, nm, (ε, $l{\cdot}mol^{-1}{\cdot}cm^{-1}$)): 289 (43650).

2.2.5. Synthesis of bis((11-hydroxyundecyl)oxy)benzaldehydes (general procedure).

To the solution of dihydroxybenzaldehyde **8a-c** in 60 ml of acetonitrile K_2CO_3 was added and the mixture was heated to 80 °C. After that, 11-bromoundecanol was introduced into the reaction mixture. The mixture was stirred under heating for 40 h. After the reaction complete, the solvent was distilled off, the resulting mixture was suspended in water and extracted from chloroform. The combined organic fractions were dried over Na_2SO_4, the solvent was remover and the residue was recrystallized from a methanol:diethyl ether mixture (1:1), washed with diethyl ether and dried in air.

*2.2.5.1. Synthesis of 2,4-bis((11-hydroxyundecyl)oxy)benzaldehyde (**9a**).* From 1.0 g of 2,4-dihydroxybenzaldehyde **8a** (7.25 mmol),1.0 of potassium carbonate (29.0 mmol) and 4.0 g of 11-bromoundecanol (15.9 mmol),1.32 g (38%) of the compound **9a** was obtained as a light brown powder. M.p. 94–97 °C.

NMR ^{1}H (400 MHz, $CDCl_3$, δ, ppm): 9.70 (s, 1H), 7.42 (d, 1H, *J* = 8.6 Hz), 6.53 (d, 1H, *J* = 6.5 Hz), 6.41 (s, 1H), 4.00 (t, 4H, *J* = 6.5 Hz), 3.64 (t, 4H, *J* = 6.6 Hz), 1.30–1.89 (m, 36H).

NMR ^{13}C (100 MHz, $CDCl_3$, δ, ppm): 188.59, 165.83, 163.40, 130.21, 118.81, 106.17, 98.90, 68.44, 63.04, 32.78, 29.43, 29.06, 26.02, 25.75.

LC-MS: Calculated, *m*/*z*: 478.37.$C_{29}H_{50}O_5$. Found: ($[M+H]^+$) 479.35.

*2.2.5.2. Synthesis of 3,4-bis((11-hydroxyundecyl)oxy)benzaldehyde (**9b**).* From 1.0 g of 3,4-dihydroxybenzaldehyde **8b** (7.25 mmol), 1.00 g of potassium carbonate (29.0 mmol) and 4.0 g of 11-bromoundecanol (15.9 mmol) 2.63 g (76%) of the compound **9b** was obtained as a white powder. M.p. 88–90 °C.

NMR ^{1}H (400 MHz, $CDCl_3$, δ, ppm): 9.82 (s. 1H), 7.39–7.43 (m, 2H), 6.95 (d, 1H, *J* = 8.1 Hz), 4.03–4.09 (м, 4H), 3.64 (t, 4H, *J* = 6.6 Hz), 2.57 (br.s., 2H), 1.84 (sxt, 4H, *J* = 7.2 Hz), 1.56 (quin, 4H, *J* = 6.8 Hz), 1.46–1.49 (m, 4H), 1.25–1.34 (m, 24H).

NMR ^{13}C (100 MHz, $CDCl_3$, δ, ppm): 191.14, 154.66, 149.38, 129.80, 126.73, 111.68, 110.81, 69.08, 63.01, 32.78, 29.58, 29.41, 25.98, 25.78.

LC-MS: Calculated, *m*/*z*: 478.37. $C_{29}H_{50}O_5$. Found: ($[M+H]^+$) 479.35.

*2.2.5.3. Synthesis of 3,5-bis((11-hydroxyundecyl)oxy)benzaldehyde (**9c**).* From 1.0 g of 3,5-dihydroxybenzaldehyde **8c** (7.25 mmol), 1.00 g of potassium carbonate (29.0 mmol) and 4.0 g of 11-bromoundecanol (15.9 mmol) 3.05 g (88%) of the compound **9c** was obtained as a white powder. M.p. 96–99 °C.

NMR ^{1}H (400 MHz, $CDCl_3$, δ, ppm): 9.88 (s. 1H), 6.98 (d, 2H, *J* = 2.3 Hz), 6.69 (t, 1H, *J* = 2.2 Hz), 3.98 (t, 4H, *J* = 6.5 Hz), 3.64 (t, 4H, *J* = 6.6 Hz), 2.03 (br.s., 2H), 1.75–1.85 (m, 4H), 1.25–1.58 (m, 32H).

NMR ^{13}C (100 MHz, $CDCl_3$, δ, ppm): 191.95, 160.82, 138.40, 108.17, 107.68, 68.48, 63.01, 32.78, 29.44, 29.26, 29.10, 25.94, 25.71.

LC-MS: Calculated, *m*/*z*: 478.37. $C_{29}H_{50}O_5$. Found: ($[M+H]^+$) 479.35.

2.2.6. Synthesis of 11,11′-(([2,2′:6′,2″-terpyridin]-4′-yl)phenylene)bis (oxy))bis(undecan-1-ol)s (general procedure)

To the solution of KOH in 20 ml of ethanol bis((11-hydroxyundecyl)oxy)benzaldehydes **9a-c**, then 2-acetylpyridine and after 10 min an excess (0.8 ml, 21.0 mmol) of 25% aqueous ammonia were added. The reaction mixture was stirred at 50 °C for two days. After the reaction completed, the solvent was distilled off, the target substance was recrystallized from methanol, washed with diethyl ether and dried in air.

*2.2.6.1. Synthesis of 11,11′-((4-([2,2′:6′,2″-terpyridin]-4′-yl)-1,3-phenylene)bis(oxy))bis(undecan-1-ol) (**10a**).* From 1.0 g of 2,4-bis((11-hydroxyundecyl)oxy)benzaldehyde **9a** (2.1 mmol), 0.23 g of potassium hydroxide (4.2 mmol), 0.47 ml of 2-acetylpyridine (4.2 mmol) 0.66 g (46%) of the compound **10a** was obtained as a white powder. M.p. 170–171 °C.

NMR ^{1}H (400 MHz, $CDCl_3$, δ, ppm): 8.56–8.60 (m, 6H), 7.80 (t, 2H, *J* = 7.7 Hz), 7.41–7.44 (m, 1H), 7.26 (t, 2H, *J* = 5.6 Hz), 6.50 (d, 2H, *J* = 8.4 Hz), 3.90 (t, 4H, *J* = 6.3 Hz), 3.45 (qw, 4H, *J* = 7.0 Hz), 1.62–1.88 (m, 4H), 1.02–1.46 (m, 32H).

NMR ^{13}C (100 MHz, $CDCl_3$, δ, ppm): 160.89, 156.78, 155.01, 149.06, 136.65, 131.21, 123.40, 121.64, 121.21, 105.53, 100.30, 68.56, 68.15, 63.06, 32.81, 29.40, 26.14, 26.00, 25.74.

LC-MS: Calculated, *m*/*z*: 681.45. $C_{43}H_{59}N_3O_4$. Found: ([M+H]$^+$) 682.45.

*2.2.6.2. Synthesis of 11,11′-((4-([2,2′:6′,2″-terpyridin]-4′-yl)-1,2-phenylene)bis(oxy))bis(undecan-1-ol) (**10b**).* From 1.0 g of 3,4-bis((11-hydroxyundecyl)oxy)benzaldehyde **9b** (2.1 mmol), 0.23 g of potassium hydroxide (4.2 mmol), 0.47 ml of 2-acetylpyridine (4.2 mmol) 0.65 g (45%) of the compound **9b** was obtained as a white powder. M.p. 182–185 °C.

NMR ^{1}H (400 MHz, $CDCl_3$, δ, ppm): 8.56–8.61 (m, 6H), 7.78–7.85 (m, 2H), 7.30–7.36 (m, 4H), 6.84 (d, 1H, *J* = 8.4 Hz), 3.99 (t, 2H, *J* = 6.3 Hz), 3.89 (t, 2H, *J* = 6.3 Hz), 3.39 (dt, 4H, J_1 = 6.5 Hz, J_2 = 3.3 Hz), 3.22 (br.s., 2H), 1.60–1.67 (m, 4H), 1.12–1.35 (m, 32H).

NMR ^{13}C (100 MHz, $CDCl_3$, δ, ppm): 156.44, 155.78, 150.36, 149.52, 149.04, 136.90, 131.24, 123.75, 121.48, 120.37, 118.51, 113.87, 113.17, 69.71, 69.25, 62.98, 58.38, 50.73, 32.78, 29.45, 25.99, 25.74, 18.37.

LC-MS: Calculated, *m*/*z*: 681.45.$C_{43}H_{59}N_3O_4$. Found: ([M+H]$^+$) 682.45.

*2.2.6.3. Synthesis of 11,11′-((5-([2,2′:6′,2″-terpyridin]-4′-yl)-1,3-phenylene)bis(oxy))bis(undecan-1-ol) (**10c**).* From 1.0 g of 3,5-bis((11-hydroxyundecyl)oxy)benzaldehyde **9c** (2.1 mmol), 0.23 g of potassium hydroxide (4.2 mmol), 0.47 ml of 2-acetylpyridine (4.2 mmol) 0.65 g (45%) of the compound **10c** was obtained as a white powder. M.p. 187–188 °C.

NMR ^{1}H (400 MHz, $CDCl_3$, δ, ppm): 8.71 (d, 2H, *J* = 4.0 Hz), 8.64–8.67 (m, 4H), 7.88 (d, 2H, *J* = 1.5 Hz), 7.36 (d, 2H, *J* = 1.4 Hz), 7.01 (d, 2H, *J* = 2.1 Hz), 6.54 (s, 1H),4.03 (t, 4H, *J* = 6.4 Hz), 3.61(t, 4H, *J* = 6.7 Hz), 2.03 (br.s., 2H), 1.29–2.05 (m, 36H).

NMR ^{13}C (100 MHz, $CDCl_3$, δ, ppm): 160.78, 156.33, 155.86, 150.59, 149.10, 140.61, 136.84, 123.77, 121.41, 119.10, 106.13, 101.91, 68.28, 63.03, 32.81, 29.50, 29.35, 26.03, 25.72,

LC-MS: Calculated, *m*/*z*: 681.45.$C_{43}H_{59}N_3O_4$. Found: ([M+H]$^+$) 682.45.

*2.2.7. Synthesis of compounds **11a-c** (general procedure)*

To the solution of lipoic acid in 20 ml of DMF HOBt, HBTU and DIPEA were added and the mixture was stirred in the inert atmosphere for 40 min. After that bis(11-hydroxoundecyloxo)-2.2′:6′,2″-terpyridine **10a-c** were added and the reaction mixture was stirred in the inert atmosphere for 48 h. Then the solvent was removed under reduced pressure and the residue was purified by column chromatography (Puriflash 15μ 25 g, eluent: petroleum ether => petroleum ether (50%)/EtOAc + $NH_3{\cdot}H_2O$ (50%) =>EtOAc + $NH_3{\cdot}H_2O$ (100%) for 26 min. The ratio of EtOAc and $NH_3{\cdot}H_2O$ is 1:0.0025.

*2.2.7.1. Synthesis of (S)-((4-([2,2′:6′,2″-terpyridin]-4′-yl)-1,3-phenylene)bis(oxy))bis(undecane-11,1-diyl) bis(5-((S)-1,2-dithiolan-3-yl) pentanoate) (**11a**).* From 0.38 g of lipoic acid (1.8 mmol), DIPEA (0.6 ml, 3.7 mmol), HOBt (0.37 g, 2.7 mmol), HBTU (1.05 g, 2.7 mmol) and 0.3 g of 11,11′-((4-([2,2′:6′,2″-terpyridin]-4′-yl)-1,3-phenylene)bis(oxy))bis(undecan-1-ol) **10a** (0.44 mmol) 0.27 g (58%) of the compound **11a** was obtained as yellow oil.

NMR ^{1}H (400 MHz, $CDCl_3$, δ, ppm): 8.74–8.83 (m, 6H), 8.03 (t, 2H, *J* = 7.7 Hz), 7.63 (d, 1H, *J* = 8.4 Hz), 7.45 (t, 2H, *J* = 5.9 Hz), 6.61 (dd, 1H, J_1 = 8.5 Hz, J_2 = 2 Hz), 6.55 (d, 1H, *J* = 2.1 Hz), 4.00–4.08 (m, 8H), 3.08–3.66 (m, 6H), 2.41–2.49 (m, 2H), 2.31 (t, 4H, *J* = 7.4 Hz), 1.10–1.94 (m, 48H).

LC-MS: Calculated, *m*/*z*: 1057.52. $C_{59}H_{83}N_3O_6S_4$. Found: ([M+H]$^+$) 1058.50.

HRMS: Calculated ([M+H]$^+$): 1058.5243, $C_{59}H_{83}N_3O_6S_4$. Found: ([M+H]$^+$) 1058.5236.

UV–vis: (λ, nm, (ε, l·mol^{-1}·cm^{-1})): 322 (26950), 305 (36650), 286 (51400).

*2.2.7.2. Synthesis of (S)-((4-([2,2′:6′,2″-terpyridin]-4′-yl)-1,2-phenylene)bis(oxy))bis(undecane-11,1-diyl) bis(5-((S)-1,2-dithiolan-3-yl) pentanoate) (**11b**).* From 0.38 g of lipoic acid (1.8 mmol), DIPEA (0.6 ml, 3.7 mmol), HOBt (0.37 g, 2.7 mmol), HBTU (1.05 g, 2.7 mmol)and 0.3 g of 11,11′-((4-([2,2′:6′,2″-terpyridin]-4′-yl)-1,2-phenylene)bis(oxy))bis(undecan-1-ol) **10b** (0.44 mmol) 0.28 g (61%) of the compound **11b** was obtained as light green oil.

NMR ^{1}H (400 MHz, $CDCl_3$, δ, ppm): 8.74 (d, 2H, *J* = 4.7 Hz), 8.66–8.68 (m, 4H), 7.89 (td, 2H, J_1 = 7.7 Hz, J_2 = 1,8 Hz), 7.48 (dd, 1H, J_1 = 8.3 Hz, J_2 = 2,1 Hz), 7.42 (d, 1H, *J* = 2.1 Hz), 7.36 (ddd, 2H, J_1 = 7.4 Hz, J_2 = 1,8 Hz, J_3 = 2.1 Hz), 6.99 (d, 1H, *J* = 8.3 Hz), 4.04–4.15 (m, 8H), 3.53–3.60 (m, 2H), 3.08–3.21 (m, 4H), 2.42–2.50 (m, 2H), 2.31 (td, 4H, J_1 = 7.4 Hz, J_2 = 2.6 Hz), 1.83–1.95 (m, 6H), 1.24–1.74 (m, 44H).

LC-MS: Calculated, *m*/*z*: 1057.52. $C_{59}H_{83}N_3O_6S_4$. Found: ([M+H]$^+$) 1058.50.

HRMS: Calculated ([M+H]$^+$): 1058.5243, $C_{59}H_{83}N_3O_6S_4$. Found ([M+H]$^+$): 1058.5214.

UV–vis: (λ, nm, (ε, l·mol^{-1}·cm^{-1})): 381 (4000), 331 (24,550), 306 (41,750), 287 (57,400), 256 (30,300).

*2.2.8. Synthesis of (S)-((5-([2,2′:6′,2″-terpyridin]-4′-yl)-1,3-phenylene)bis(oxy))bis(undecane-11,1-diyl) bis(5-((S)-1,2-dithiolan-3-yl)pentanoate) (**11c**)*

From 0.38 g of lipoic acid (1.8 mmol), DIPEA (0.6 ml, 3.7 mmol), HOBt (0.37 g, 2.7 mmol), HBTU (1.05 g, 2.7 mmol)and 0.3 g of 11,11′-((5-([2,2′:6′,2″-terpyridin]-4′-yl)-1,3-phenylene)bis(oxy)) bis(undecan-1-ol) **10c** (0.44 mmol) 0.29 g (63%) of the compound **11c** was obtained as yellow oil.

NMR ^{1}H (400 MHz, $CDCl_3$, δ, ppm): 8.73 (d, 2H, *J* = 4.2 Hz), 8.66–8.70 (m, 4H), 7.88 (td, 2H, J_1 = 7.7 Hz, J_2 = 1.7 Hz), 7.36 (ddd, 2H, J_1 = 7.4 Hz, J_2 = 4.8 Hz, J_3 = 1.1 Hz), 7.00 (d, 2H, *J* = 2.1 Hz), 6.55 (t, 1H, *J* = 2.1 Hz), 4.02–4.07 (m, 8H), 3.53–3.60 (m, 2H), 3.07–3.20 (m, 4H), 2.45 (td, 2H, J_1 = 12.3 Hz, J_2 = 6.5 Hz), 2.31 (t, 4H, *J* = 7.4 Hz), 1.86–1.94 (m, 2H), 1.78–1.85 (m, 4H), 1.58–1.74 (m, 14H), 1.24–1.54 (m, 30H).

NMR ^{13}C (100 MHz, $CDCl_3$, δ, ppm): 173.68, 160.73, 156.22, 155.81, 150.57, 149.10, 140.54, 136.97, 123.88, 121.45, 119.10, 106.00, 101.74, 68.24, 64.57, 60.44, 56.36, 40.23, 38.50, 34.62, 34.14, 29.54, 29.44, 29.28, 28.80, 28.64, 26.10, 25.96, 24.73, 21.11, 14.22.

LC-MS: Calculated, *m*/*z*: 1057.52. $C_{59}H_{83}N_3O_6S_4$. Found: ([M+H]$^+$) 1058.50.

HRMS: Calculated ([M+H]$^+$): 1058.5243, $C_{59}H_{83}N_3O_6S_4$. Found ([M+H]$^+$): 1058.5234.

UV–vis: (λ, nm, (ε, l·mol^{-1}·cm^{-1})): 317 (19300), 281 (64200), 259 (39400).

2.2.9. Synthesis of coordination compounds (general procedure)

The solution of ligands **7, 11a-c** in 2 ml of dry EtOH was heated to 70 °C. After that, the solution of metal salt in 2 ml dry EtOH was added. The mixture was stirred for 24 h under reflux. The formed

precipitate was filtered off, washed with ethanol, chloroform, diethyl ether and dried in air.

2.2.9.1. Coordination compound ***12a***. From 0.03 g of ligand **7** (0.04 mmol), 0.018 g of $[Rh(DMSO)_3]Cl_3$(0.04 mmol), 0.02 g (51%) of the compound **12a** was obtained as orange powder. M. p. > 250 °C.

Elemental analysis, calculated: C, 55.89; H, 6.60; N, 3.31. $C_{40}H_{49}Cl_3N_3O_3RhS_2$. Found: C, 56.16; H, 6.72; N, 3.62.

HRMS: Calculated ([M+Ag]): 998.0387. $C_{40}H_{49}N_3Cl_3O_3AgRhS_2$. Found: ([M+Ag]) 998.0372

UV–vis: (λ, nm, (ε, l·mol^{-1}·cm^{-1})): 381 (6250), 313 (26650), 288 (47500), 259 (31150).

2.2.9.2. Coordination compound ***12b***. From 0.03 g of ligand **7** (0.04 mmol), 0.019 g of $[Ru(DMSO)_4]Cl_2$(0.03 mmol), 0.02 g (50%) of the compound **12b** was obtained as dark brown powder. M. p. > 250 °C.

Elemental analysis, calculated: C, 54.01; H, 5.94; N, 4.50. $C_{42}H_{55}Cl_2N_3O_4RuS_3$. Found: C, 54.27; H, 5.84; N, 4.38.

LI-MS: Calculated ($[M+2H]^+$+CH_3CN): 976.2197 $C_{42}H_{55}N_3Cl_2O_4RuS_3H_2$. Found: ($[M+2H]^+$+$CH_3CN$) 976.2195

UV–vis: (λ, nm, (ε, l·mol^{-1}·cm^{-1})): 500 (7400), 332 (33300), 312 (38500), 291 (40800).

2.2.9.3. Coordination compound ***13a***. Elemental analysis, calculated: C, 55.89; H, 6.60; N, 3.31. $C_{59}H_{83}Cl_3N_3O_6RhS_4$. Found: C, 56.28; H, 6.48; N, 3.50.

From 0.03 g of ligand **11a** (0.03 mmol), 0.013 g of $[Rh(DMSO)_3]Cl_3$(0.03 mmol), 0.015 g (42%) of the compound **13a** was obtained as orange powder. M.p. > 250 °C.

UV–vis: (λ, nm, (ε, l·mol^{-1}·cm^{-1})): 381 (1750), 318 (35100), 285 (69550), 261 (44000).

2.2.9.4. Coordination compound ***13b***. From 0.03 g of ligand **11b** (0.03 mmol), 0.013 g of $[Rh(DMSO)_3]Cl_3$(0.03 mmol), 0.015 g (42%) of the compound **13b** was obtained as orange powder. M. p. > 250 °C.

Elemental analysis, calculated: C, 55.89; H, 6.60; N, 3.31. $C_{59}H_{83}Cl_3N_3O_6RhS_4$. Found: C, 55.94; H, 6.52; N, 3.09.

HRMS: Calculated ([M+Ag]): Exact Mass: 1372.2336 $C_{59}H_{83}N_3Cl_3O_6AgRhS_4$. Found: ([M+Ag]) 1373.2362

UV–vis: (λ, nm, (ε, l·mol^{-1}·cm^{-1})): 383 (11350), 329 (34200), 317 (42950), 284 (79600), 261 (58300).

2.2.9.5. Coordination compound ***13c***. From 0.03 g of ligand **11c** (0.03 mmol), 0.013 g of $[Rh(DMSO)_3]Cl_3$(0.03 mmol), 0.014 g (4%) of the compound **13c** was obtained as orange powder. M. p. > 250 °C.

Elemental analysis, calculated: C, 55.89; H, 6.60; N, 3.31. $C_{59}H_{83}Cl_3N_3O_6RhS_4$. Found: C, 56.15; H, 6.95; N, 3.35.

HRMS: Calculated ([M+Ag]): Exact Mass: 1372.2336 $C_{59}H_{83}N_3Cl_3O_6AgRhS_4$. Found: ([M+Ag]) 1372.2331

UV–vis: (λ, nm, (ε, l·mol^{-1}·cm^{-1})): 380 (500), 339 (4450), 316 (15200), 281 (37950), 257 (24450).

2.2.9.6. Coordination compound ***14b***. From 0.03 g of ligand **11b** (0.03 mmol), 0.014 g of $[Ru(DMSO)_4]Cl_2$(0.03 mmol), 0.015 g (41%) of the compound **14b** was obtained as a dark brown powder. M.p. > 250 °C.

Elemental analysis, calculated: C, 55.98; H, 3.21; N, 6.85. $C_{61}H_{89}Cl_2N_3O_7RuS_5$. Found: C, 56.29; H, 3.40; N, 6.58.

LI-MS: Calculated ($[M+2H]^+$+CH_3CN): 1350,4147 $C_{61}H_{89}N_3Cl_2O_7RuS_5H_2$. Found: ($[M+2H]^+$+$CH_3CN$) 1350.4172

2.2.9.7. Coordination compound ***14c***. From 0.03 g of ligand **11c** (0.03 mmol), 0.014 g of $[Ru(DMSO)_4]Cl_2$(0.03 mmol), 0.016 g (43%) of the compound **14c** was obtained as a dark brown powder. M.p. > 250 °C.

Elemental analysis, calculated: C, 55.98; H, 3.21; N, 6.85. $C_{61}H_{89}Cl_2N_3O_7RuS_5$. Found: C, 56.09; H, 4.43; N, 3.32.

LI-MS: Calculated ($[M+2H]^+$+CH_3CN): 1350,4147 $C_{61}H_{89}N_3Cl_2O_7RuS_5H_2$. Found ($[M+2H]^+$+$CH_3CN$): 1350.4182

3. Results and discussion

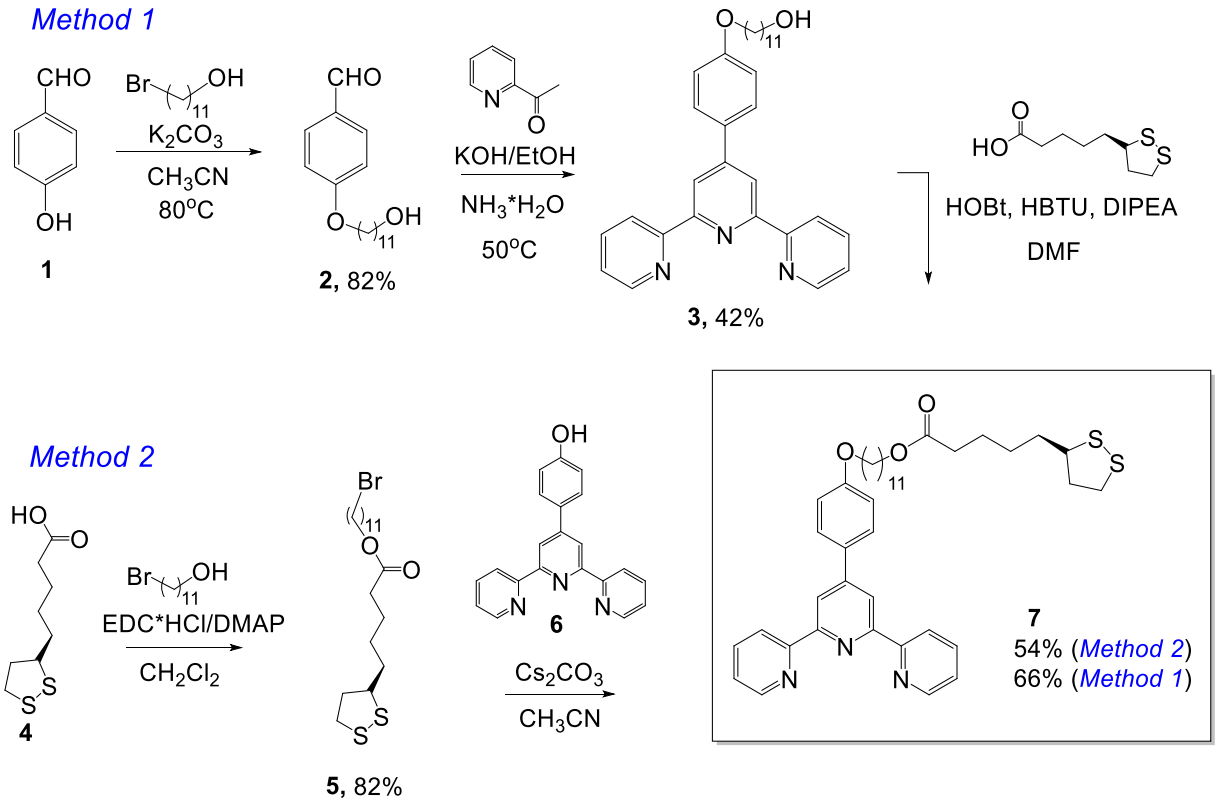
3.1. Ligands synthesis

The structure of the organic ligands **7**, **11a-c** synthesized in this work is shown in Schemes 1, 2. Compounds **7**, **11a-c** contain the terpyridine fragment for metal ion coordination, and two disulfide groups in the lipoic acid fragment, which allow adsorption on gold electrodes. The length of linker fragment between the two disulfide groups was selected in such way as to ensure a distance between them about 4 nm, corresponding to the achievable inter electrode gap in the nanoelectrode device [28]. The initial development of the synthetic scheme was carried out at the example ligand **7** with one disulfide fragment; this ligand can be used for the synthesis of mono- and bis-ligand coordination compounds with increased stability compared to previously described ligands of similar structure with thioacetate aurophilic moiety [30,31].

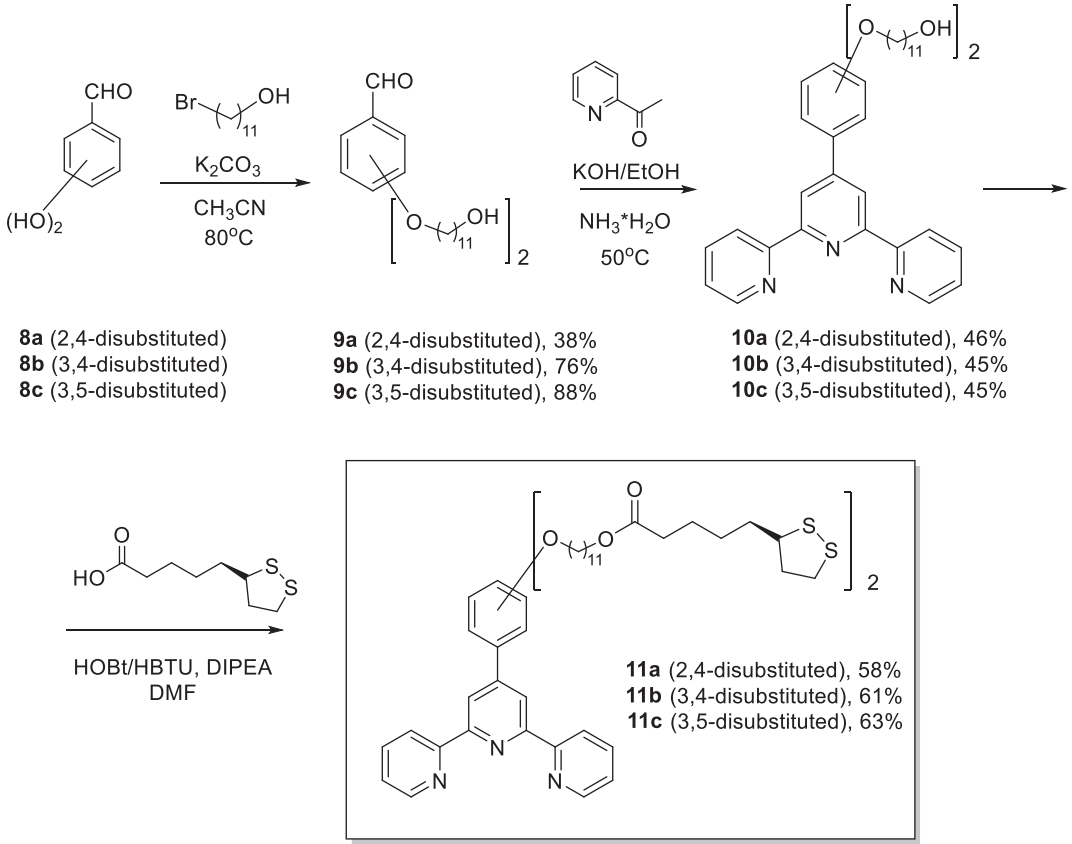
The strategy development for obtaining the target ligands using the example of model ligand **7** was carried out using two synthetic sequences, designated as Method 1 and Method 2 in Scheme 1. According to Method 1, the 4-hydroxybenzaldehyde **1** was first alkylated with 11-bromundecanol in the presence of base (K_2CO_3) according to S_N2 reactions to give substituted benzaldehyde **2**, which was further converted to 4′-substituted terpyridine **3** [35]; subsequent esterification with lipoic acid at the action of HOBt/HBTU mixture yielded the target ligand **7**. Method 2 consisted in the initial alkylation of lipoic acid with 11-bromundecanol to give ester **5**, and then the resulting product was reacted with 4-([2,2′:6′,2″-terpiridin]-4′-yl) phenol **6** obtained by the described procedure [31]. Generally, Method 1, despite a greater number of synthetic stages, gives a better yield of the target product, and is easier than the experimental plan. This method was further used to obtain ligands with two sulfur-containing fragments.

The synthetic sequence for the preparation of the target terpyridine ligands **11a-c** with two sulfur-containing fragments is shown in Scheme 2. Considering the data obtained for model ligand **7**, the synthesis of compounds **11a-c** was carried out according to the initial modification scheme of phenol fragments 2,4-, 3,4- and 3,5-dihydroxybenzaldehyde **8a-c** followed by conversion of the obtained **9a-c** esters to the corresponding terpyridines **10a-c** in ~45% yields. The ester bond formation with lipoic acid was carried out using the mixture of HOBt and HBTU in the presence of the base, similarly to the described methods [36,37].

When optimizing the preparation conditions ligands **11a-c**, it was found in all cases for the formation of bis-functionalization products of both OH groups of the initial dioles **10a-c**, a large excess of lipoic acid and the corresponding activators have to be used. Otherwise the mono-esterification productsat one of the hydroxyl groups of the starting compounds are mainly formed. Under the optimized conditions, target ligands **11a-c** were obtained in 58–63% yields from diols **10a-c** (10%, 21%, 25% from aldehydes **10a-c**). In the synthesis of intermediate compounds **9a-c,** the main by-products also were the monoalkylation product at one of the hydroxyl groups of starting compounds **8**; to suppress this undesirable reaction, a large excess of the starting 11-bro-



Scheme 1. Synthesis of the ligand **7**.



Scheme 2. Synthesis of ligands **11a-c**.

mundecanol-1 was used and the reaction time was increased to 40 h.

The structures and purity of all obtained organic compounds were confirmed by ^{1}H and ^{13}C NMR spectra, high performance liquid chromatography and mass-spectrometry. For compounds **2, 9a-c**, the characteristic signals in the ^{1}H NMR spectra are the aldehyde group signals at ~9.7 ppm and the triplets of CH_2O fragments at ~4.0 ppm with J ~ 6.5 Hz. Compounds **3** and **10a-c** are characterized by the presence of similar signals at ~4.0 ppm, as well as by the significant shift proton signals of the aromatic region to the weakly field region, which confirms the formation of the terpyridine system. The main characteristic features of the ^{1}H NMR spectra of target ligands **11a-c**, as well as model ligand **7**, are an increase in the integrated signal intensity in the region of ~4.0 ppm with the simultaneous change in their multiplicity, as well as the appearance of lipoic acid characteristic signals: the CH_2COO groups triplet at ~ 2.31 ppm with J = 7.4 Hz, CH-S group multiplet at ~3.5 ppm and two signals of cyclic CH_2 groups at ~3.1 and ~2.5 ppm.

3.2. Synthesis of coordination compounds

Based on the obtained ligand **7** with one aurophilic fragment, we investigated the possibility to preparate its rhodium-containing coordination compound using the reaction with rhodium (III) chloride hydrate. However, the isolation of individual product **12a** in this reaction turned out to be hindered by the extremely low solubility of $RhCl_3{\cdot}3H_2O$ in organic solvents and by the formation of the ester bond hydrolysis product of ligand **7** when the reaction is carried out in water-containing mixtures. Taking this into account, we used complexes $[Rh(DMSO)_3]Cl_3$ and $[Ru(DMSO)_4]Cl_2$, which are readily soluble in organic solvents, as the sources of Rh(III) and Ru(II). DMSO-containing complexes were obtained from the corresponding hydrates of metal chlorides using the described procedures [32–34]. Thus, coordination compounds **12a**,**b** were synthesized according to a procedure similar to that previously described for the preparation of monoterpyridine rhodium and ruthenium derivatives [38] by refluxing of the ligand and metal salt in ethyl alcohol (Scheme 3). To obtain coordination compounds based on ligands with two sulfur-containing fragments (**13a-c**, **14b**, **c**; Scheme 4), the same method was used.

The structures of coordination compounds **12** were confirmed by ^{1}H NMR spectra, where the signals of the ligand terpyridine protons were shifted to the down field region by approximately 0.8 ppm compared to free ligand. Also, the structures of compounds **12–14** were confirmed by HRMS and UV–vis spectra, and for the coordination compounds its composition was consistent with elemental analysis data.

Coordination compounds **12–14** are practically insoluble in water and in most organic solvents, with the exception of DMSO and DMF. However, even in these two solvents, the solubility of the ruthenium complexes does not exceed 10^{-5} M. Rhodium-containing complexes are somewhat better soluble and can be dissolved in DMSO at a maximum concentration of ~$5{\cdot}10^{-4}$ M.

3.3. Electrochemistry

The electrochemical behaviour of ligands **7**, **11** and complexes **12–14** in DMSO solutions using class carbon (GC) or Au electrodes was investigated by cyclic voltammetry. The electrochemical data are summarised in Table 1, typical CV curves are shown in Figs. 1–3 and in Supplementary Information.

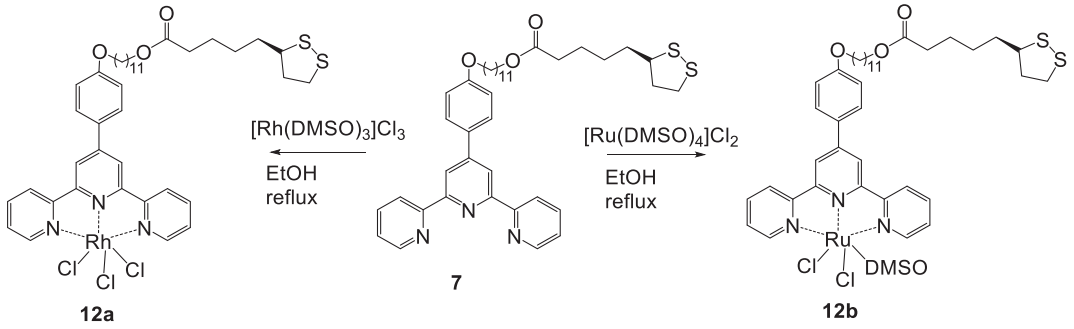
The oxidation and reduction potentials of the studied ligands and complexes are practically don't depend on the positions of the substituents in the benzene ring of the phenylterpyridine ligand. For all ligands there are two reduction peaks at E_{pc} = −1.70 to −2.00 V on CV curves recorded using GC electrodes (Fig. 1a); these peaks correspond to the reduction of the terpyridine ligands [38–41].

The same peaks corresponding to the reduction of terpyridine ligands were also observed on the CV of complexes **12–14**. In addi-

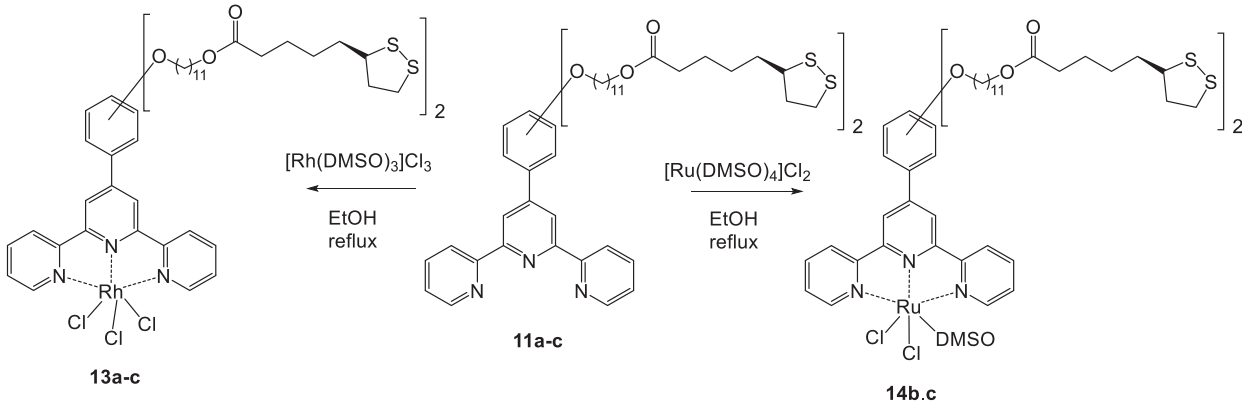
Table 1
Electrochemical reduction (E_p^{Red}) and oxidation (E_p^{Ox}) potentials of ligands and complexes measured by the CV technique in DMSO on GC and Au electrodes in the presence of 0.1 M Bu_4NClO_4. The potential scan rate was 200 mV/s*.

Compound	E_p^{Red}		E_p^{Ox}	
	GC electrode	Au electrode	GC electrode	Au electrode
7	-1.82 -1.96	-1.52 -1.80 -1.97	1.01 1.13	1.12
12a	-0.81 -1.97	-1.02 -1.36 -1.80 -1.99	1.12 1.29	0.96 1.26
12b	-1.33 -1.90	-1.46 -1.80 -1.97	1.12 1.29	0.75 1.27
11a	-1.70 -2.00		1.16 1.33	
13a	-0.70 -1.77 -2.00		1.03 1.26	
11b	-1.81 -1.92	-1.42 -1.66 -1.94	1.01 1.13	1.12
13b	-0.65 -1.73 -1.96	-0.96 -1.37 -1.76 -1.96	1.04	1.22
14b	-1.50 -1.94	-1.33 -1.75 -1.97	1.12 1.29	0.96 1.20
11c	-1.81 -1.88	-1.38 -1.62 -1.91	1.01 1.10	1.10
13c	-0.96 -1.76 -1.99	-0.84 -1.35 -1.75 -1.91	1.06 1.28	1.11
14c	-1.71 -1.95	-1.39 -1.87 -1.95	1.01 1.26	0.73 1.10

* The peaks corresponding to the oxidation and reduction of coordinated metal ions are shown in blue; peaks of Au-S bond reduction – in red.



Scheme 3. Synthesis of coordination compounds **12a, b**.



Scheme 4. Synthesis of coordination compounds **13a-c** and **14b**,**c**.

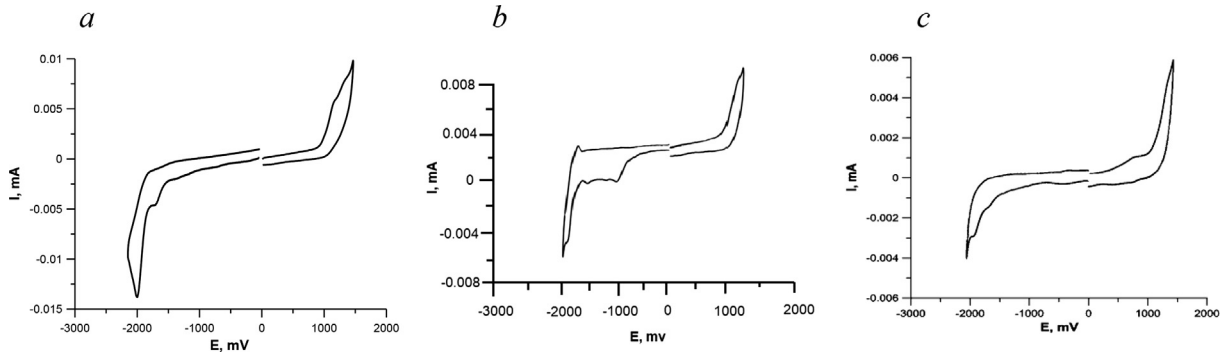


Fig. 1. Cyclic voltammograms of ligand **11b** (*a*), its Rh(III) complex **13b** (*b*) and Ru(II) complex **14b** (*c*). GC electrode, $5{\cdot}10^{-4}$ M, DMSO, Bu_4NClO_4.

tion to them, on GC electrodes for rhodium (III) complexes **12a** and **13** the additional cathodic peaks, corresponding to the $Rh^{III} \rightarrow Rh^{I}$ reduction [30,31] appear at CV in the region about −0.65 to −0.96 V (Fig. 1b). For the ruthenium (II) complexes **12b** and **14** the additional peaks at ~ 0.73 to 0.96 V were observed in the oxidation region, corresponding to the $Ru^{II} \rightarrow Ru^{III}$ oxidation [30,31]. No additional peaks of metal reduction were observed in the anodic region for complexes **14**, which is consistent with literature data. At deep reduction of complexes **12**–**14** (scanning the potential up to −2.1 V), a black metal powder deposition was observed on the electrode surface; thus, the reduced form of the complex is unable to retain zero-valent rhodium or ruthenium.

The use of a gold electrode makes it possible to explore the adsorption of synthesized compounds on Au surface with the formation of a covalent Au-S bond. It is known that disulfides are capable of spontaneously chemisorbing on the gold surface with the formation of self-assembled monolayers (SAM) with the formation of a stable covalent Au-S bonds [42]. When Au electrodes were used for CV registration, we observed a changes in the volt-ampere curves over time. Electrochemical monitoring of the changes when the gold electrode was kept in a solution of compounds **7**, **11** in DMSO showed that at the first moment after placing the gold electrode in the ligand solution, the CV curves were almost identical obtained on the GC electrode (Fig. 2, *blue and green curves*). However, already after 30 min, a very intense additional peak with a reduction potential of about −1.6 V was observed on CV, in the region less cathodic than the peak of the initial terpyride ligand (Fig. 2, *red curve*). Upon further keeping the electrode in the ligand solution, the intensity of the peak at ~−1.6 V gradually decreased and simultaneously a peak at ~−1.3 V appeared, corresponding to the reduction of the Au-S bond of the chemisorbed ligand. Finally, after 1–2 days, the intensity of the peak at −1.3 V reaches

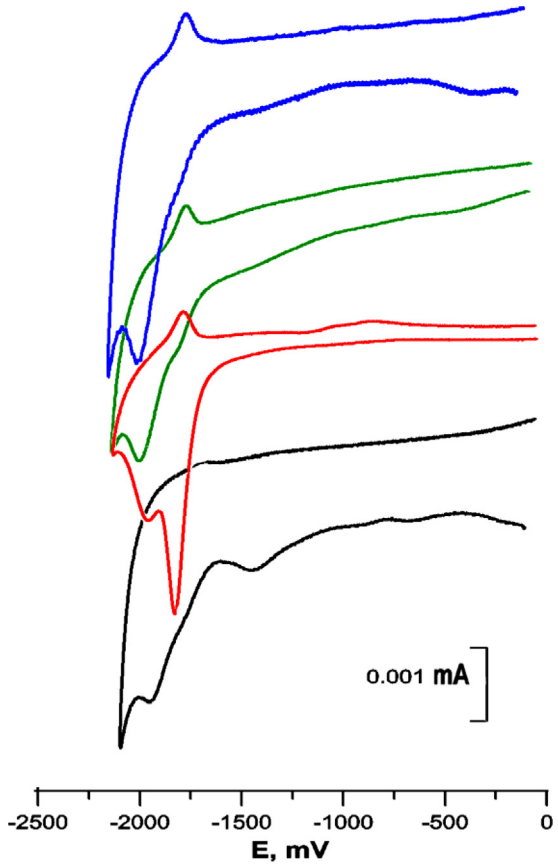


Fig. 2. Cathode part of cyclic voltammograms of ligand **11c** on Au electrode depending on the time the electrode is kept in solution, *Green curve* – after 1 min, *red curve* – after 30 min, *black curve* – after 24 h. The *blue curve* represents the CV on GC electrode.

a maximum and does not change further, and the peak at −1.6 V completely disappeared (Fig. 2, *black curve*).

To explain these changes, one should take into account the previously shown ability of terpyridines to adsorb on a gold surface due to the coordination of nitrogen atoms with Au [43]; this process proceeds faster than the breaking of the disulfides S—S bonds and the formation of the Au-S bonds, but it is reversible. Presumably, when a gold electrode is placed in a solution of terpyridine-containing ligands **7**, **11**, the ligand is rapidly adsorbed on gold with the participation of terpyridine nitrogen atoms, which is accompanied by a shift in the reduction peaks of the ligand fragment to the region of lower potentials (Scheme 1S). However, then the reorientation of the ligand relative to the gold surface occurs, and finally, there is a peak in the reduction of the Au-S bond and uncoordinated terpyridine on the CV curves.

At the final stage of the electrochemical study, we showed the stability of the formed SAM of coordination compounds on Au electrodes. For this, the electrodes, kept for a day in the solutions of complexes **13** and **14**, were sequentially washed with a solution of a supporting electrolyte and then DMSO (3 times) to remove non-chemisorbed molecules from the surface, dried in air, after which the electrodes were immersed in a clean solution of a supporting electrolyte and cyclic voltammograms were recorded. The results obtained showed almost complete identity of the volt-ampere curves obtained before and after washing and drying the electrodes (Fig. 3).

Taking into account the better solubility of rhodium complexes **13** as compared to ruthenium complexes **14**, in further experiments, the Rh(III) complexes **13a-c** were tested. We studied the time of complete adsorbtion of complexes **13** and their organic ligands **11** on gold electrodes surfaces in order to identify the optimal complex for potential practical use. To determine the time required for the complete course of adsorption, Au electrodes were placed in the solutions of ligands **11** or complexes **13** in DMSO at the same concentration of $5 \cdot 10^{-4}$ M for different times (12 h, 24 h, 36 h, etc. up to 3 days), after which the electrodes were removed from the solution of the testing compound, washed with DMSO, dried in air, placed in a solution of a supporting electrolyte in DMSO, and the intensity of the peaks at ~−1.35 V on the CV, corresponding to the reduction of the Au-S, was determined. The moment of completion of the formation of the adsorption layer was considered the time after which the intensity of the peaks at ~−1.35 V ceases to increase with an increase in the electrode keeping time in the solution of the adsorbed compound.

It was found that the complete adsorption on gold for different isomers of ligands and their complexes occurs at different times (Table 2). Thus, considering the ligands **11** chemisorption is completed the fastest for 3,5-disubstituted terpyridine **11c**. In the case of the complexes, compounds **13b** and **13c** are adsorbed much faster than the 2,4-disubstituted isomer **13a**, for which the peak of Au-S bond reduction remains extremely low-intensity even after 3 days of keeping the gold electrode in the test compound solution. Such differences, apparently, can be associated with steric hindrances arising during the adsorption of *ortho*-substituted phenylterpyridines. Thus, taking into account the data obtained, rhodium complexes of 3,5 and 3,4-disero-substituted terpyridines **13b** and **13c** are most suitable as a bridge molecule for the sensors.

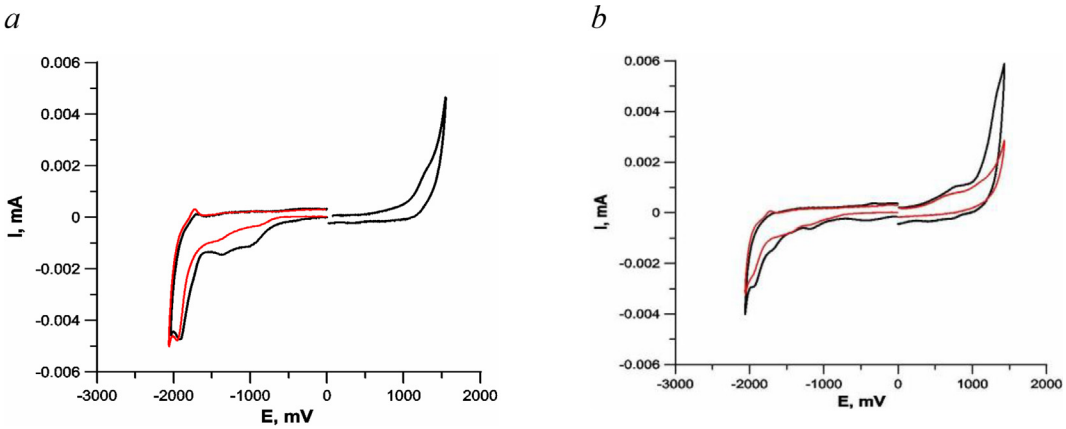


Fig. 3. Cyclic voltammograms of complexes **13c** (a) and **14c** adsorbed on Au electrode surface. *Black curves – before* and *red curves – after* the electrodes washing and drying.

Table 2
Time of the ligands **11** and their rhodium complexes **13** adsorption on the surface of gold electrodes with Au-S bond formation*.

	Compound					
	11a	**11b**	**11c**	**13a**	**13b**	**13c**
Adsorption time, h	>72	48	36	>72	12	12

* From a solution in DMSO with a concentration of $5{\cdot}10^{-4}$ M.

Interestingly, for complexes **13b** and **13c**, the time of complete adsorption on Au turns out to be shorter than for the corresponding ligands **11b** and **11c** (48 and 36 h for ligands and only 12 h for complexes). Presumably, this difference may be due to the fact that for coordination compounds in which the lone electron pairs of terpyridine nitrogen are coordinated with the Rh, it becomes impossible to orient the terpyridine fragment to the gold surface with the Au-N coordination (Scheme 1S) and the only possible option becomes the participation of disulfide groups. Therefore, the total adsorption time does not require additional period of re-orientation of the ligand fragment relative to the gold surface.

4. Conclusion

Thus, we have developed a convenient methods for the preparation of aurophilic terpyridine ligands with one or two terminal disulfide groups. On their basis, mononuclear coordination compounds with Rh(III) and Ru(II) were synthesized for the subsequent study of the possibility of their adsorption on the metal surfaces. Among the obtained metal complexes, compounds with the minimum time of chemisorption on the surface of gold electrodes with the formation of Au-S bonds were revealed, which are complexes of 3,4- and 3,5-substituted phenylterpyridines.

CRediT authorship contribution statement

Irina O. Salimova: Methodology, Formal analysis, Visualization, Writing - original draft. **Anna V. Berezina:** Validation. **Ilona A. Shikholina:** Investigation. **Nikolai V. Zyk:** Data curation, Supervision. **Elena K. Beloglazkina:** Conceptualization, Writing - review & editing, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We are grateful to the Russian Science Foundation (Project 19-73-00193) and Russian Foundation of Basic Research (Project 19-33-90146) for the financial support of this work. This work in part of NMR study was supported by the M.V. Lomonosov Moscow State University Program of Development.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2021.115149.

References

[1] M. Veldhorst, J. Hwang, C. Yang, A. Leenstra, B. de Ronde, J. Dehollain, J. Muhonen, F. Hudson, K. Itoh, A. Morello, A. Dzurak, Nat. Nanotechnol. 9 (2014) 981–985.
[2] V. Shorokhov, D. Presnov, S. Amitonov, Y.u. Pashkin, V. Krupenin, Nanoscale 9 (2) (2017) 613–620.
[3] S. Dagesyan, V. Shorokhov, D. Presnov, E. Soldatov, A. Trifonov, V. Krupenin, Nanotechnology 28 (2017) 225-304.
[4] R. Davidson, J. Liang, D. Milan, B. Mao, R. Nichols, S. Higgins, D. Yufit, A. Beeby, P. Low, Inorg. Chem. 54 (2015) 5487–5494.
[5] P. Gale, E. Howe, X. Wu, Chem. 1 (2016) 351–422.
[6] P. Gale, C. Caltagirone, Chem. Soc. Rev. 44 (2015) 4212.
[7] D. Barry, D. Caffrey, T. Gunnlaugsson, Chem. Soc. Rev. 45 (2016) 3244–3274.
[8] M. Saleem, K. Lee, RSC Adv. 5 (2015) 72150–72287.
[9] M. Mital, Z. Ziora, Coord. Chem. Rev. 375 (2018) 434–458.
[10] H. Xiang, J. Cheng, X. Ma, X. Zhoua, J. Chruma, Chem. Soc. Rev. 42 (2013) 6128–6185.
[11] J. Zhao, S. Ji, W. Wu, H. Guo, J. Sun, H. Sun, Y. Liu, Q. Li, L. Huang, RSC Adv. 2 (2012) 1712–1728.
[12] Z. Liu, W. He, Z. Guo, Chem. Soc. Rev. 42 (2013) 1568–1600.
[13] A. Ramdass, V. Sathish, E. Babu, M. Velayudham, P. Thanasekaran, S. Rajagopal, Coord. Chem. Rev. 343 (2017) 278–307.
[14] N. Pourmand, M. Karhanek, H. Persson, W. CD, T. Lee, A. Zahradníková, R. Davis, Pro. Natl. Acad. Sci. USA, 103(17) (2016) 6466-6470.
[15] V. Bashkirov, A. Grigoryev, M. Gutorov, E. Ilyichev, V. Kolesov, K. Krutovsky, A. Manturov, Patent 2679494, 2019.
[16] J. Pekola, O. Saira, V. Maisi, A. Kemppinen, M. Mottonen, Y. Pashkin, D. Averin, Rev. Mod. Phys. 85 (4) (2013) 1421–1432.
[17] Y. Hua, Y. Lib, J. Joung, J. Yind, S. Park, J. Yoon, M. Hyun, Sens. Actuators B 241 (2017) 224–229.
[18] H. Ali, S. Quinn, T. McCabe, P. Kruger, T. Gunnlaugsson, New J. Chem. 33 (4) (2009) 793–800.
[19] J. Kitchen, E. Boyle, T. Gunnlaugsson, Inorg. Chim. Acta 381 (2012) 236–242.
[20] Y. Tanaka, M. Kiguchi, M. Akita, Chem. Eur. J. 23 (2017) 4741–4749.
[21] R. Brooke, C. Jin, D. Szumski, R. Nichols, B. Mao, K. Thygesen, W. Schwarzacher, NanoLett. 15 (2015) 275–280.
[22] H. Osorio, S. Catarelli, P. Cea, J. Gluyas, F. Hartl, S. Higgins, E. Leary, P. Low, S. Martín, R. Nichols, J. Tory, J. Ulstrup, A. Vezzoli, D. Milan, Q. Zeng, J. Am. Chem. Soc. 137 (2015) 14319–14328.
[23] R. Farran, L. Quang, D. Jouvenot, F. Loiseau, R. Pansu, A. Deronzier, J. Chauvin, Inorg. Chim. Acta 454 (2017) 197–207.
[24] Q. Ma, P. Li, Z. Gao, S. Fong, Y. Li, Actuators B: Chem. 281 (2019) 424–431.
[25] V. Zwicker, B. Long, K. Jolliffe, Org. Biomol. Chem. 13 (28) (2015) 7822–7829.
[26] J. Granifo, R. Gavino, E. Freire, R. Baggio, J. Mol. Struct. 1006 (2011) 684–691.
[27] S. Chappell, C. Brooke, R. Nichols, L. Kershaw Cook, M. Halcrow, J. Ulstrup, S. Higgins, Faraday Discuss. 193 (2016) 113–131.
[28] V. Gaydamachenko, E. Beloglazkina, R. Petrov, S. Dagesyan, I. Sapkov, E. Soldatov, Moscow Univ. Phys. Bull. 73 (2018) 193–198.
[29] A. Majouga, E. Beloglazkina, E. Manzheliy, D. Denisov, E. Evtushenko, K. Maslakov, E. Golubina, N. Zyk, Appl. Surf. Sci. 325 (2015) 73–78.
[30] E. Beloglazkina, A. Majouga, E. Manzheliy, A. Moiseeva, Y. Lin'kova, N. Zyk, Polyhedron 85 (2015) 800-808.
[31] E. Beloglazkina, E. Manzheliy, A. Moiseeva, O. Maloshitskaya, N. Zyk, D. Skvortsov, I. Osterman, P. Sergiev, O. Dontsova, Y. Ivanenkov, M. Veselov, A. Majouga, Polyhedron 107 (2016) 27–37.
[32] T. Bora, M. Singh, J. Inorg. Nucl. Chem. 38 (1976) 1815–1820.
[33] I. Bratsos, E. Alessio, M. Ringenberg, T. Rauchfuss, Inorg. Synth. 35 (2010) 148–152.
[34] R. James, R. Morris, Can. J. Chem. 58 (1980) 399–408.
[35] C. Song, Z. Ye, G. Wang, J. Yuan, Y. Guan, Chem. Eur. J. 16 (2010) 6464–6472.
[36] J. Taunton, J. Collins, S. Schreiber, J. Am. Chem. Soc. 118 (1996) 10412–10422.
[37] S. Han, Y.-A. Kim, Tetrahedron 60 (2004) 2447–2467.
[38] H. Wolpher, S. Sinha, J. Pan, A. Johansson, M. Lundqvist, P. Persson, R. Lomoth, J. Bergquist, L. Sun, V. Sundstrom, B. Akermark, T. Polivka, Inorg. Chem. 46 (2007) 638–651.
[39] C. Mikel, P.G. Potvin, Polyhedron 21 (2002) 49–54.
[40] J. Paul, S. Spey, H. Adams, J.A. Thomas, Inorg. Chim. Acta 357 (2004) 2827–2832.
[41] S. Sovan, S. Sounik, M. Ritankar, M. Roy, R.R. Dighe, A.R. Chakravarty, Polyhedron 29 (2010) 3251–3256.
[42] A. Ulman, Chem. Rev. 96 (1996) 1533–1554.
[43] R.B. Romashkina, A.G. Majouga, E.K. Beloglazkina, D.A. Pichugina, M.S. Askerka, A.A. Moiseeva, R.D. Rakhimov, N.V. Zyk, Russ. Chem. Bull. 61 (2012) 2265–2281.