Triazole-containing terpyridines with terminal aurophilic groups and their complexes with Rh^{III} for adsorption on the surface of gold

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We synthesized substituted phenylterpyridines containing one or two terminal disulfide groups and triazole-containing fragments in the linker between the terpyridine and sulfur-containing functional groups, as well as coordination compounds of the obtained terpyridines with Rh^{III}. The possibility of the ligands and complexes under study to be chemisorbed on the surface of gold electrodes with the formation of an Au—S bond was shown.

Key words: 2,2′:6′, 2″-terpyridines, aurophilic ligands, rhodium(III) complexes.

Interest in the synthesis of metal-containing organic derivatives with one or two terminal sulfur-containing groups is explained by the possibility of using such molecules in one-electron single molecular nanotransistors or charge-sensitive biosensors,[1—3] as luminescent probes,[4,5] as well as for design nanotransistors, light-emitting diodes, and various photovoltaic devices.[6]

In a number of works devoted to the study of transition metal complexes with nitrogen-containing ligands used as an island molecule in the development of nanotransistors, pyridine and polypyridine derivatives are used as *N*-donors. Thus, there are described ruthenium *S*-alkyl- and 4-pyridyl-substituted terpyridine complexes,[7] Fe^{II} and Ru^{II} complexes with 4,4′-bipyridine,[8] as well as a series of coordination compounds based on substituted terpyridines containing different metals (Fe, Co, Cr, Ru). Di- and tetrapyridyl-substituted pyrazine, 4′-pyridylterpyridine, and 4′-*S*-methylarylated terpyridines were used as ligands.[9] The Ru^{II} complexes with *N*,*N*′-bis(6-mercaptohexyl)-4,4′-bipyridine were also obtained.[10] Complexes containing terpyridine ligands have interesting photophysical properties,[11] therefore they are widely studied as materials for the design of light-emitting devices, organic light-emitting diodes,[12] and molecular magnets.[13]

Earlier, we showed the possibility of obtaining single molecular nanotransistors using gold nanoelectrodes placed at a distance of 4 nm from each other and interconnected by a molecule of an aurophilic Rh^{III} coordination compound with 4-([2,2′:6′,2″-terpyridin]-4′-yl)phenyl-5-(1,2-dithiolan-3-yl)pentanoate chemisorbed on the electrode surface due to the Au—S bonds. It has been shown that in the nanotransistors obtained, electron tunneling occurred through the rhodium atom, which was an intramolecular charge center.[14] In addition, aurophilic terpyridine ligands with one or two terminal disulfide groups and polymethylene linkers between functional fragments, as well as their coordination compounds with Rh^{III}, have been recently[15] synthesized, for which the ability to be adsorbed on the surface of gold electrodes and to carry out tunneling conduction has been shown. Among the ligands and complexes obtained, compounds with the minimum time of chemisorption on the surface of Au electrodes were identified, which turned out to be derivatives of 3,4- and 3,5-disubstituted phenylterpyridines.[15] However, the possibility of practical application of the obtained rhodium complexes in molecular nanodevices was found to be significantly limited by their poor solubility in most tested organic solvents, including DMF and DMSO.

The purpose of the present work is to synthesize a series of new organic ligands containing a terpyridine fragment as a rhodium ion chelator, disulfide fragments as the groups responsible for chemisorption of molecules on Au electrodes, and a linker fragment between them. In contrast to the previously described aurophilic terpyridines containing a polymethylene linker,[15] compounds obtained in this work contain a triazole fragment in the linker. The introduction of such a fragment increases the solubility of compounds in a number of organic solvents while maintaining the tunneling conductivity and the required distance between functional groups (4—6 nm[14]). Note that the presence of an additional conducting fragment in the molecules of triazole-containing terpyridines can also reduce the potential required for electron transfer in a one-electron nanodevice. The synthesized ligands were used as a basis for the preparation of coordination compounds with Rh^{III}, which were studied for their ability to be adsorbed on the gold surface.

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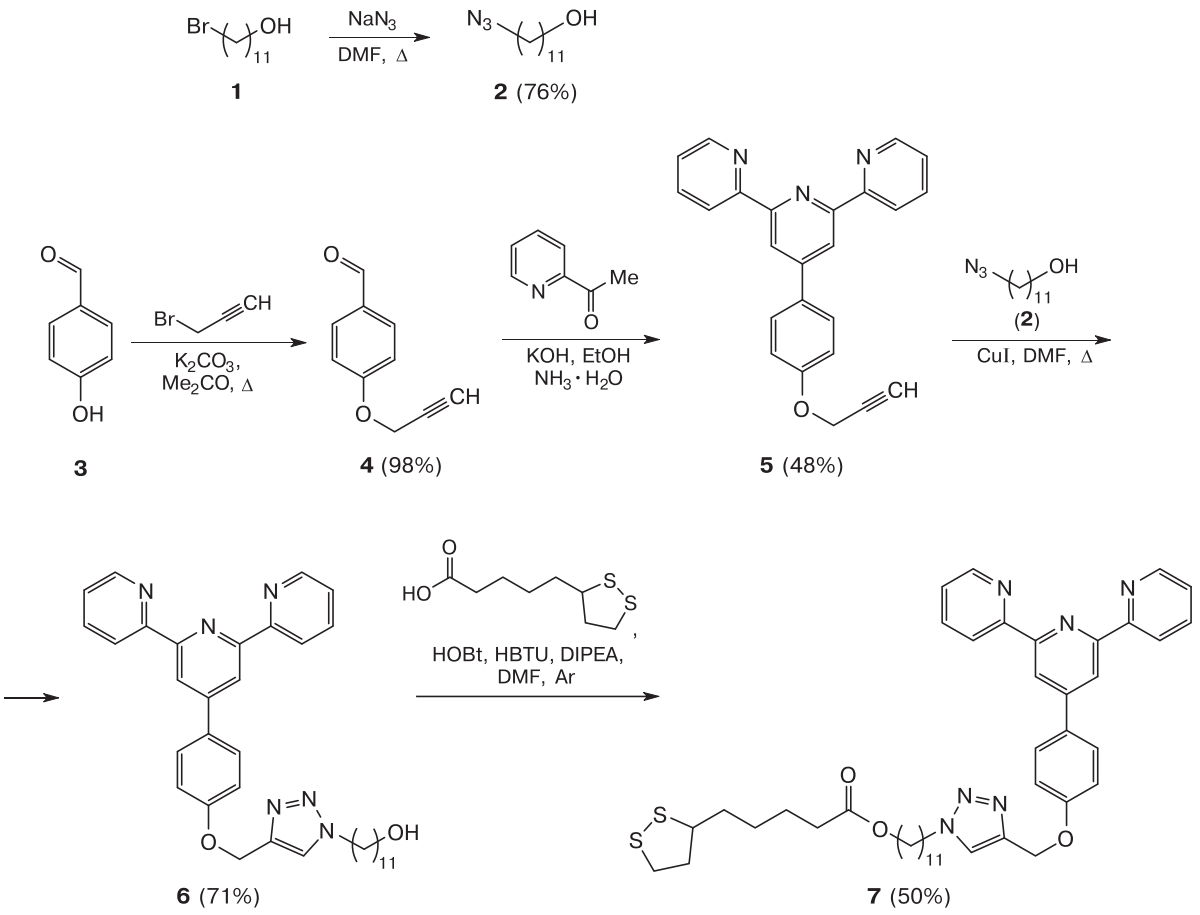
Scheme 1



The first stage of the work included the development of methods for obtaining a model terpyridine **7** containing one disulfide fragment and a triazole fragment as part of the linker (Scheme 1). Commercially available 11-bromoundecanol **1**, 4-hydroxybenzaldehyde **3**, propargyl bromide, and lipoic acid were used as starting compounds.

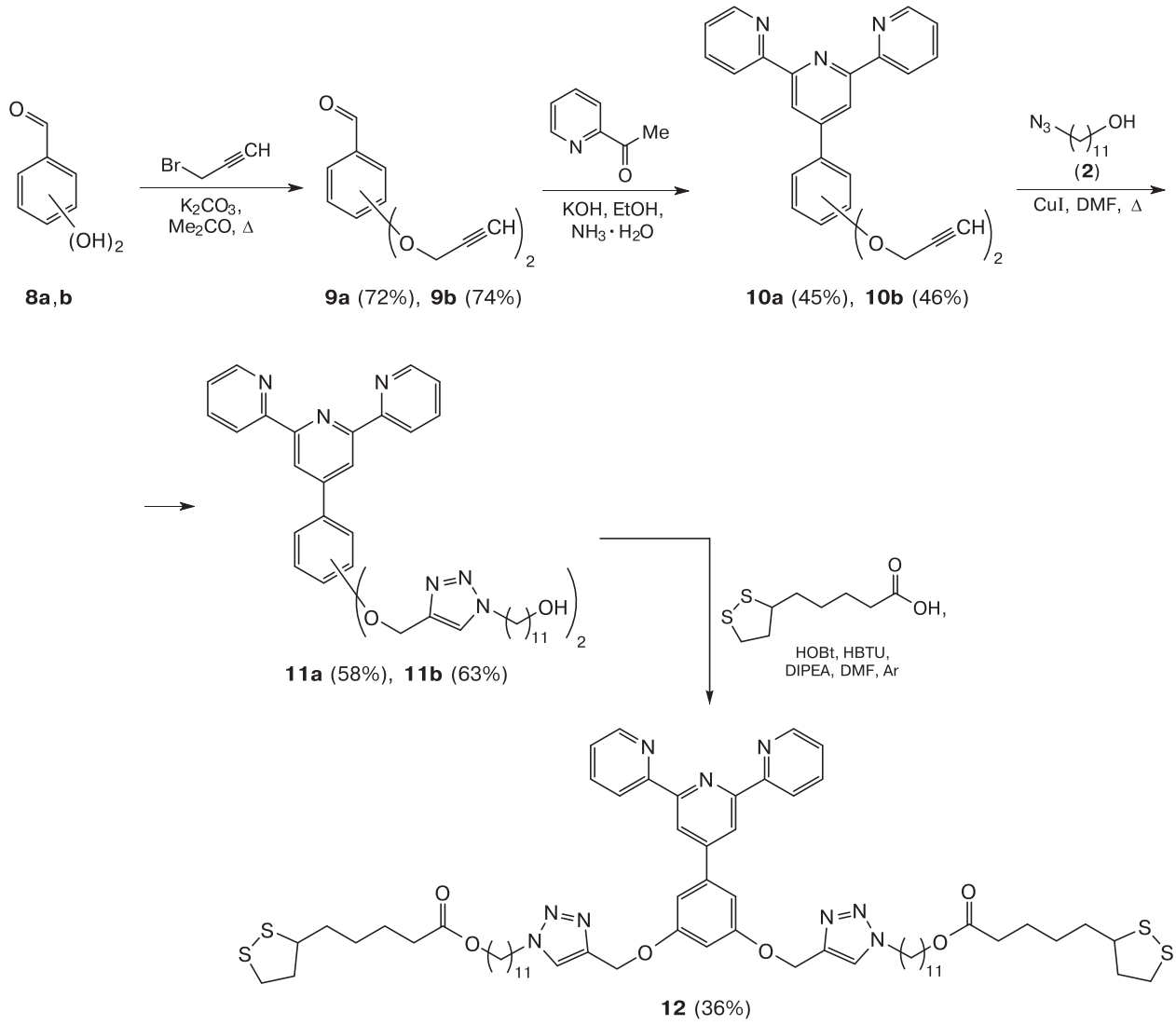
To obtain ligand **7**, 4-hydroxybenzaldehyde **3** was first alkylated with propargyl bromide. Next, the obtained aldehyde **4** was introduced into the base-catalyzed condensation with 2-acetylpyridine. Then the condensation product 4′-[4-(prop-2-yn-1-yloxy)phenyl]-2,2′:6′,2″-terpyridine (**5**) was subjected to azide-alkyne cycloaddition with azide **2** (obtained according to a known procedure[16]) in the presence of CuI. The thus obtained 4′-substituted terpyridine **6** with a terminal hydroxy group was esterified with lipoic acid in the presence of hydroxybenzotriazole (HOBt), 2-(1*H*-benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (BTUH), and diisopropylethylamine (DIPEA) to obtain the target ligand **7** in 50% yield.

Aurophilic ligand **12** containing two disulfide groups was synthesized according to the procedures developed for compound **7** (Scheme 2). Note that the last stage of the synthesis, the reaction of 3,5-disubstituted terpyridine **11b** with lipoic acid, yielded only product **12**, while in the case of 3,4-disubstituted phenylterpyridine **11a**, the esterification product of 3,4-disubstituted terpyridine at one hydroxy group and the starting phenylterpyridine **11a** were predominantly present in the reaction mixture even when the reaction time and temperature were increased. No desired product was obtained upon increasing either the amount of lipoic acid or the activator. It can be assumed that in the case of 3,4-disubstituted derivative **11a**, the reaction is hindered by steric effects arising from the formation of two closely spaced triazole rings.

The structure and composition of the compounds obtained were confirmed by ^{1}H and ^{13}C NMR spectroscopy, HPLC, and high-resolution mass spectrometry. Aldehydes **4** and **9** are characterized by the presence in the ^{1}H NMR spectra of signals for the aldehyde protons at δ ~9.7. Terpyridines **5** and **10** exhibit singlets at δ ~7.6 characteristic of the triazole ring protons. The ^{1}H NMR spectra of aldehydes and terpyridines with a terminal C≡C triple bond are characterized by the presence of triplets at δ ~2.6.

The ^{1}H NMR spectra of ligands **7** and **12** exhibit signals of a lipoic acid fragment: a triplet for the CH_2COO group

Scheme 2



8—11: 3,4-disubstituted (**a**), 3,5-disubstituted (**b**)

(δ ~2.31, J = 7.4 Hz) and multiplets for the CHS group (δ ~3.5) and two CH_2 groups of dithiolane (δ ~3.1 and δ ~2.5).

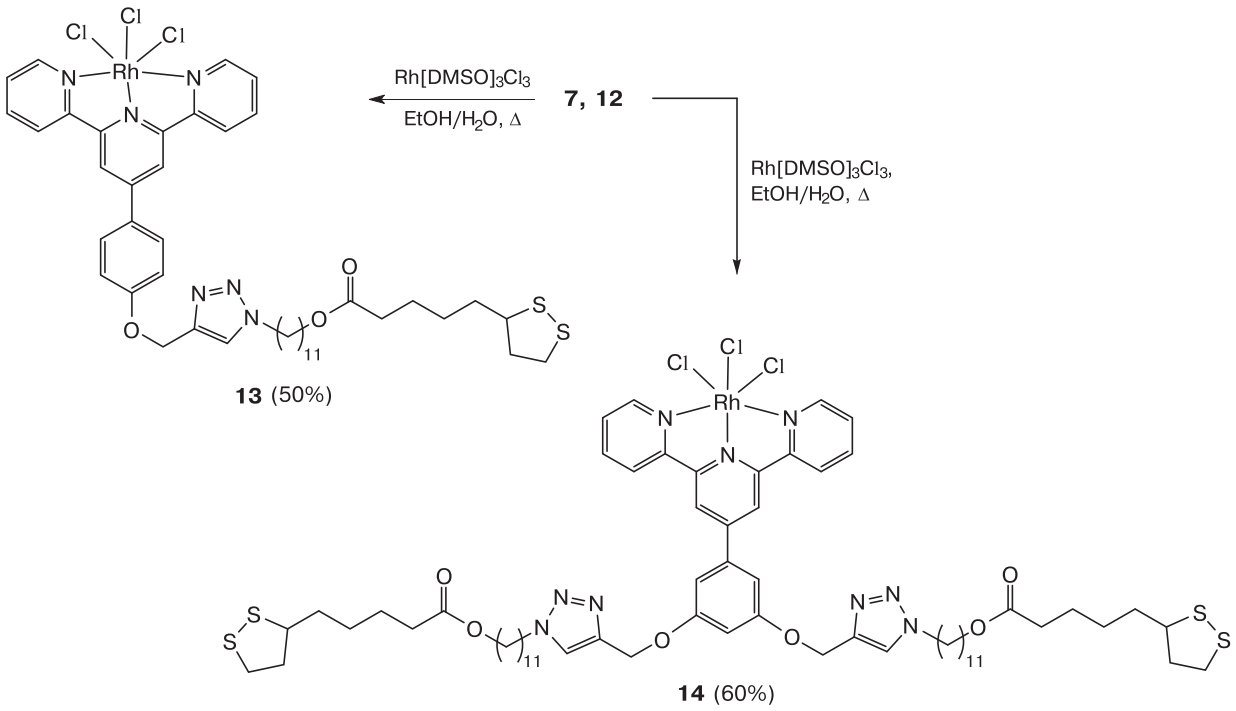
Rhodium-containing coordination compounds **13** and **14** were obtained by reflux of ligands **7** and **12** with $[Rh(DMSO)_3]Cl_3$[17] in ethanol (Scheme 3).

The formation of coordination compounds is accompanied by a downfield shift of the proton signals of the terpyridine fragment in the ^{1}H NMR spectra of molecules **13** and **14** by about 0.9 ppm compared to the starting ligands. The structure and composition of the complexes obtained were also confirmed by elemental analysis and mass spectrometry, as well as by electronic absorption spectroscopy.

The electronic spectra of ligands **7** and **12** exhibit strong bands in the UV range between 250 and 300 nm with an absorption maximum at ~290 nm, which belong to the ligand-centered π—π*-transitions in the organic fragment. Such bands are present also in the UV spectra of complexes **13** and **14**, but, besides, the spectra of coordination compounds exhibit additional bands of lower intensity in the range of 320—400 nm, which characterize the Rh(d)→L(π) transition with the metal-to-ligand charge transfer typical of the Rh^{III} polypyridyl complexes.[18,19]

Ligand **12** and its rhodium complex **14** were also studied by IR spectroscopy. The IR spectrum of the ligand exhibits a characteristic absorption band at 1732 cm^{-1} corresponding to the carbonyl groups, as well as a band at

Scheme 3



2926 cm^{-1} corresponding to the vibrations of the CH bond of the triazole ring. In the spectrum of complex **14**, the characteristic peak corresponding to the triazole ring retains its position, which indicates that the triazole fragment is not involved in the coordination with the metal.

Coordination compounds **13** and **14** expectedly turned out to be less soluble in organic solvents than free ligands **7** and **12** (Table 1). Ligands **7** and **12** are moderately soluble in most organic solvents, including $CHCl_3$, CH_2Cl_2, methyl and ethyl alcohols, acetone, while their rhodium complexes **13** and **14** can be dissolved only in DMSO and DMF. Nevertheless, the solubility of complexes **13** and **14** in DMSO was approximately twice as high as the solubility of rhodium-containing complexes of structurally similar ligands with polymethylene linkers,[15] the solubility of which does not exceed $0.6 \cdot 10^{-3}$ g mL^{-1}.

It is known[20] that disulfides are able to spontaneously chemisorb on the gold surface to form self-organizing monolayers (SOM) due to the formation of stable covalent Au—S bonds. The possibility of adsorption of sulfur-containing terpyridines **7** and **12** and their rhodium-containing coordination compounds **13** and **14** on the Au surface was studied by cyclic voltammetry on an Au electrode. The data of the electrochemical study are summarized in Table 2, typical current-voltage curves are shown in Fig. 1.

Cyclic voltammograms (CV) of ligands **7** and **12** in a DMSO solution in the presence of 0.1 *M* Bu_4NClO_4 were recorded first on a glassy carbon (GC) electrode, on which chemisorption does not occur, and then on an Au electrode. The CV curves of ligands **7** and **12** on the GC electrode show reduction peaks at $E_{pc} = -1.67 \div -1.92$ V corresponding to the reduction of terpyridine fragments of ligands[20–22] and an oxidation peak at ~1.20 V (see Fig. 1, *a*). Beside them, the CV curves of complexes **13** and **14** recorded on the GC electrodes show additional

Table 1. Solubility of ligands **7** and **12** and their complexes **13** and **14** in organic solvents*

Ligand	Solubility in $CHCl_3$/g mL^{-1}	Complex	Solubility in DMSO/g mL^{-1}
7	0.04	**13**	$1.4 \cdot 10^{-3}$
12	0.05	**14**	$1.2 \cdot 10^{-3}$

* The solubility was determined by a portion-wise addition of the corresponding compound to 5 mL of $CHCl_3$ or DMSO with stirring until a stable suspension formed persisted for 30 min; the resulting solution was filtered and concentrated *in vacuo*, the residue was weighed. The weighing accuracy was ±0.5 mg.

Table 2. Electrochemical reduction (E_p^{Red}) and oxidation (E_p^{Ox}) potentials on the GC and Au electrodes of ligands **7** and **12** and their coordination compounds **13** and **14** measured by CVA*

Compound	E_p^{Red}/V		E_p^{Ox}/V	
	GC electrode	Au electrode	GC electrode	Au electrode
7	−1.71	1.33	1.20	1.19
	−1.90	−1.74	—	—
	−1.92	—	—	—
12	−1.73	−1.36	1.23	1.25
	−1.89	−1.73	—	—
	−1.89	—	—	—
13	−0.67	−0.63	1.10	0.99
	−1.75	−1.38	1.25	1.20
	−1.92	−1.92	—	—
14	−0.63	−0.61	1.04	0.96
	−1.73	−1.38	1.26	1.21
	−1.89	−1.90	—	—

* Solvent DMSO, supporting electrolyte 1 *M* Bu_4NClO_4, potential sweep rate 200 mV s^{-1}, 25 °C.

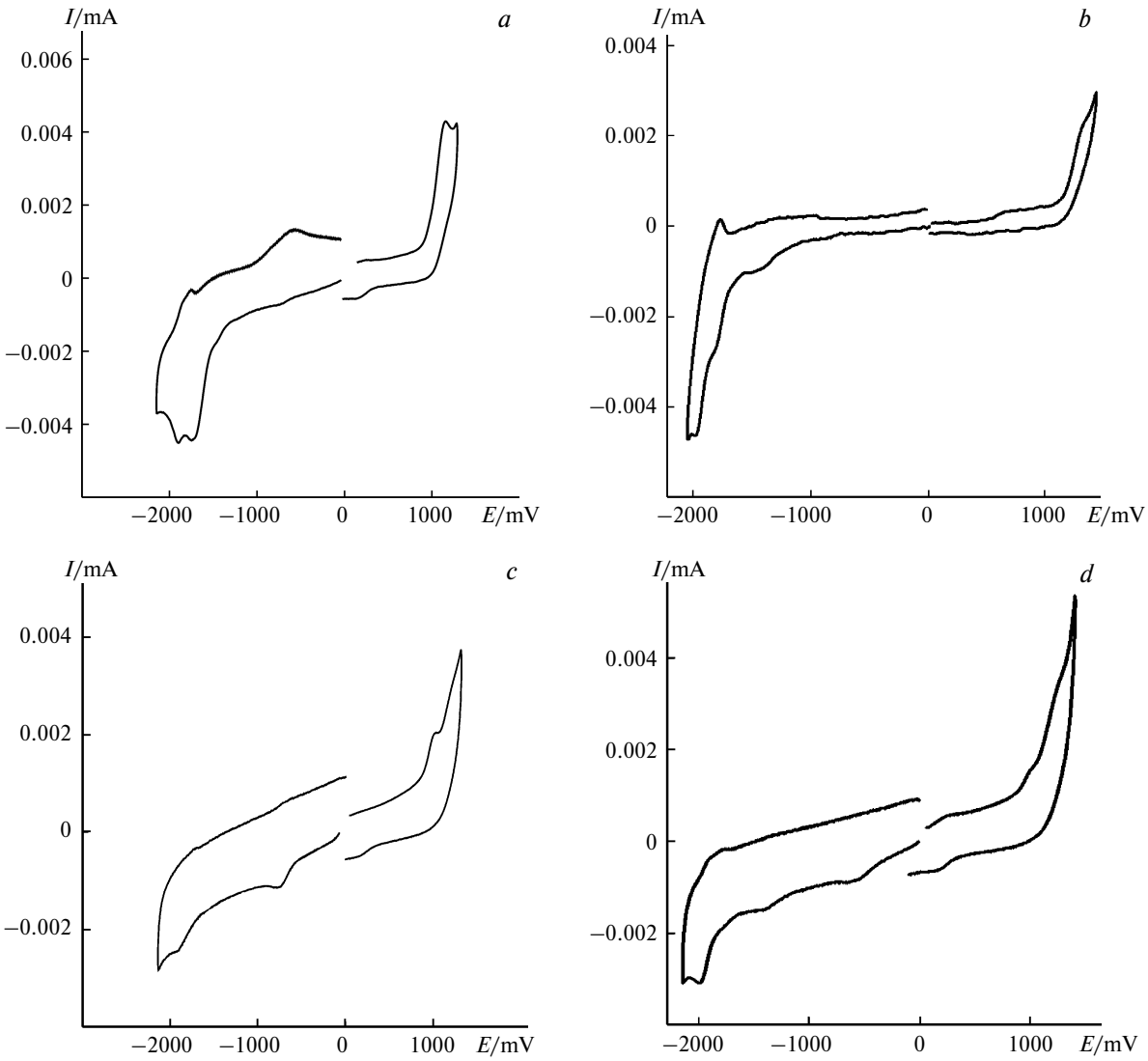


Fig. 1. Cyclic voltammograms of ligand **12** (*a*, *b*) and rhodium complex **14** (*c*, *d*) recorded on the GC (*a*, *c*) and Au electrodes (*b*, *d*) (concentration of compounds $5 \cdot 10^{-4}$ mol L^{-1}, solvent DMSO, supporting electrolyte 1 *M* Bu_4NClO_4, 25 °C, reference electrode Ag/AgCl/KCl (sat.)).

cathodic peaks in the range of −0.61÷−0.63 V corresponding to the reduction $Rh^{III} \rightarrow Rh^{I}$ (see Fig. 1, *c*).

The CV curves of all ligands and complexes recorded on the Au electrode show a peak of the reduction of the Au—S bond at −1.33÷−1.38 V (see Fig. 1, *b, d* and Table 2), which confirms that the compounds are covalently bonded to the electrode surface.[23]

To estimate the time of a monolayer formation, the Au electrodes were placed in solutions of test compounds **12** and **14** in DMSO with a concentration of $5 \cdot 10^{-4}$ mol L^{-1} and the times after which the intensity of the peaks at −1.3—1.4 V on the CV curves corresponding to the reduction of the Au—S fragment ceased to change were determined. For all the compounds studied, an average duration of the monolayer formation was 12 h, which agrees with the results obtained for complexes of similar ligands with polymethylene linkers.[15] Thus, a change in the nature of the linker does not significantly affect the ability of ligands and coordination compounds to chemisorb on the gold surface and does not change the duration of the adsorption layer formation.

At the final stage of the electrochemical study, we demonstrated the stability of the formed monolayers of coordination compounds on the Au electrodes. For this purpose, the electrodes, kept for 24 h in solutions of complexes **13** and **14** to remove non-chemisorbed molecules from the surfaces, were sequentially washed with a solution of supporting electrolyte and DMSO (thrice) and dried in air, after which the electrodes were immersed in a pure solution of supporting electrolyte, and the cyclic voltammograms were recorded. Identical CV curves were obtained before and after washing and drying the electrodes.

In conclusion, we developed approaches for the preparation of terpyridine ligands with two terminal sulfur-containing groups and a triazole ring in the linker between the coordinating and sulfur-containing fragments, as well as their coordination compounds with Rh^{III}. For the ligands and rhodium complexes obtained, we showed the possibility of chemisorption on the surface of Au electrodes with the formation of stable adsorption layers.

Experimental

Reaction progress and purity of compounds were monitored by thin layer chromatography (TLC) on silica gel precoated Silufol-UV-254 plates. Melting points were determined in an open capillary tube using a heating block and were not corrected. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance and Agilent 400-MR instruments (400 and 101 MHz, respectively). Chemical shifts are given relative to hexamethyldisiloxane used as an internal standard. IR spectra were recorded in KBr pellets on a Nicolet IR200 Fourier-transform IR spectrometer (Termo Scientific, USA) with a resolution of 4 cm^{-1}. UV spectra were recorded on a Hitachi U-2900 instrument. Electrospray ionization high resolution mass spectra (ESI HRMS) were recorded on a Bruker microTOF II instrument in positive ion mode (the capillary voltage was 4500 V). Mass scanning range *m/z* 50—3000 Da, external or internal calibration was used (Electrospray Calibration Solution, Fluke). Compounds were injected as solutions in acetonitrile, the flow rate was 3 μL min^{-1}. The nebulizer gas was nitrogen (4 L min^{-1}), the interface temperature was 180 °C. Laser ionization mass spectra (LI-MS) were recorded on a Bruker Autoflex II (FWHM 18000) instrument using a nitrogen laser (337 nm) and a time-of-flight mass analyzer. The accelerating voltage was 20 kV. The samples were applied to a polished steel substrate. The spectra were obtained in the positive ion mode. The resulting spectrum was a sum of 50 spectra obtained at different points in the sample.

High performance liquid chromatography (LC-MS) was used for preparative isolation of reaction products and analysis of their purity. The instrument was a Shimadzu Prominence LC-20 chromatograph with a Phenomenex Luna 3 μm C18 90A column (150×4.6 mm) at 40 °C with a fraction collector connected to the Shimadzu LCMS-2020 quadrupole mass spectrometer with a DUIS-ESI-APCI dual ionization source. Mobile phases: A (0.1% formic acid in water) and B (acetonitrile). LC parameters for analyzes: gradient flow 1 mL min^{-1} (0—0.5 min 5% of eluent B, 0.5—9.5 min from 5% to 90% of eluent B, 9.5—12 min 90% of eluent B, and 12—14.5 min from 90% to 5% of eluent B). Mass spectrometry parameters: drying gas 15.0 L min^{-1}, nebulizing gas 1.5 L min^{-1}, drying gas temperature 250 °C, heating block temperature 400 °C, interfacial voltage −3.5 kV, corona discharge needle voltage −3.5 kV. Positive (mass range 250—2000 Da) and negative ions (mass range 90—2000 Da) were recorded.

Electrochemical studies were carried out at 25 °C on an IPC-2000 potentiostat with a refinement software package (developed at the A. N. Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences by V. E. Kasatkin, vadim_kasatkin@mail.ru; see also http://www.expo.ras.ru/base/prod_data.asp?prod_id=4687). Glassy carbon and Au disks 2 mm in diameter polished with Al_2O_3 (<10 mm) were used as electrodes, supporting electrolyte was 0.1 *M* solution of Bu_4NClO_4 in DMSO; Ag/AgCl/KCl (sat.) was used as a reference electrode. Potentials are given with allowance for *iR* compensation. All measurements were carried out under an argon atmosphere. The samples were dissolved in a pre-deoxygenated solvent. For chemisorption of sulfur-containing ligands and complexes on the surface of an Au electrode, the electrode was immersed in a saturated solution of the corresponding compound for 1—3 days and then washed 5—10 times with a DMSO solution.

Compound **2** was obtained according to the known procedure,[16] salt $[Rh(DMSO)_3]Cl_3$ was obtained as described.[17]

Synthesis of mono- and bis(prop-2-yn-1-yloxy)benzaldehydes 4 and 9a,b (general procedure). Potassium carbonate was added to a solution of the corresponding benzaldehyde **3** или **8** in acetone (100 mL) and the resulting mixture was heated to reflux (56 °C). Propargyl bromide was slowly added dropwise to the refluxing solution. The reaction mixture was refluxed for 4 h, cooled to room temperature, the solvent was evaporated, the residue was recrystallized from ethanol.

4-(Prop-2-yn-1-yloxy)benzaldehyde (4) was obtained from 4-hydroxybenzaldehyde (**3**) (1.0 g, 8.2 mmol), K_2CO_3 (4.53 g, 32.8 mmol), and propargyl bromide (3.9 g, 32.8 mmol). The yield was 1.28 g (98%), a dark yellow powder. ^{1}H NMR ($CDCl_3$), δ: 9.91 (s, 1 H, CH=O); 7.84—7.88 (m, 2 H, H_{Ar}); 7.08—7.11 (m, 2 H, H_{Ar}); 4.79 (d, 2 H, OCH_2, J = 2.4 Hz); 2.58 (t, 1 H, C≡CH, J = 2.4 Hz). LC-MS, *m/z*: 161 $[M + H]^+$.

3,4-Bis(prop-2-yn-1-yloxy)benzaldehyde (9a) was obtained from 3,4-dihydroxybenzaldehyde (**8a**) (1.0 g, 7.25 mmol), K_2CO_3 (4.0 g, 29.0 mmol), and propargyl bromide (3.45 g, 29.0 mmol). The yield was 1.12 g (72%), a dark yellow powder. ^{1}H NMR ($CDCl_3$), δ: 9.87 (s, 1 H, CH=O); 7.56 (d, 1 H, H_{Ar}, J = 1.7 Hz); 7.52 (dd, 1 H, H_{Ar}, J_1 = 8.3 Hz, J_2 = 1.8 Hz); 7.17 (d, 1 H, H_{Ar}, J = 8.3 Hz); 4.84 (dd, 4 H, OCH_2, J_1 = 12.9 Hz, J_2 = 2.4 Hz); 2.58 (dt, 2 H, C≡CH, J_1 = 7.9 Hz, J_2 = 2.3 Hz). LC-MS, m/z: 215 $[M + H]^+$.

3,5-Bis(prop-2-yn-1-yloxy)benzaldehyde (9b) was obtained from 3,5-dihydroxybenzaldehyde (**8b**) (1.0 g, 7.25 mmol), K_2CO_3 (4.0 g, 29.0 mmol), and propargyl bromide (3.45 g, 29.0 mmol). The yield was 1.15 g (74%), a white powder. ^{1}H NMR ($CDCl_3$), δ: 9.91 (s, 1 H, CH=O); 7.13 (d, 2 H, H_{Ar}, J = 2.3 Hz); 6.87 (t, 1 H, H_{Ar}, J = 2.3 Hz); 4.74 (d, 4 H, OCH_2, J = 2.4 Hz); 2.57 (t, 2 H, C≡CH, J = 2.4 Hz). LC-MS, m/z: 215 $[M + H]^+$.

Synthesis of mono- and bis-4′-(prop-2-yn-1-yloxy)phenyl-2,2′:6′,2″-terpyridines 5 and 10 (general procedure). Mono- or bis(prop-2-yn-1-yloxy)benzaldehyde **4** or **9** (1 equiv.) and 2-acetylpyridine (2 equiv.) were added to a solution of KOH (2 equiv.) in ethanol (30 mL). The mixture was stirred for 10 min, followed by the addition of an excess (10 equiv.) of 25% aqueous ammonia and stirring for 15 h with heating at 50 °C. The precipitate formed was collected by filtration and recrystallized from a mixture of methanol—diethyl ether (1 : 1), filtered, washed with diethyl ether, and dried in air.

4′-[(Prop-2-yn-1-yloxy)phenyl]-2,2′:6′,2″-terpyridine (5) was obtained from KOH (0.7 g, 12.5 mmol), compound **4** (1.0 g, 6.25 mmol), 2-acetylpyridine (1.4 mL, 12.5 mmol), and 25% aqueous ammonia (2.4 mL, 62.5 mmol). The yield was 1.1 g (48%), a white powder. ^{1}H NMR ($CDCl_3$), δ: 8.71—8.73 (m, 4 H, 3′,5′,3,3″-tpyH*); 8.67 (d, 2 H, 6,6″-tpyH, J = 7.9 Hz); 7.85—7.89 (m, 4 H, 4,4″-tpyH, H_{Ar}); 7.31—7.34 (m, 2 H, 5,5″-tpyH); 7.08 (d, 2 H, H_{Ar}, J = 8.8 Hz); 4.74 (d, 2 H, OCH_2, J = 2.4 Hz); 2.55—2.56 (m, 1 H, C≡CH). ^{13}C NMR ($CDCl_3$), δ: 158.36, 156.28, 155.84, 149.60, 149.12, 136.90, 131.67, 128.58, 123.83, 121.38, 118.37, 115.24, 78.30, 75.87, 55.86. LC-MS, m/z: 364 $[M + H]^+$.

4′-[3,4-Bis(prop-2-yn-1-yloxy)phenyl]-2,2′:6′,2″-terpyridine (10a) was obtained from compound **9a** (1.0 g, 4.7 mmol), KOH (0.53 g, 9.4 mmol), and 2-acetylpyridine (1.05 mL, 9.4 mmol). The yield was 0.8 g (43%), a pale yellow powder. ^{1}H NMR ($CDCl_3$), δ: 8.75—8.77 (m, 6 H, 6,6″-tpyH, 3′,5′,3,3″-tpyH); 7.96 (t, 2 H, 4,4″-tpyH, J = 7.3 Hz); 7.59—7.63 (m, 2 H, H_{Ar}); 7.42 (t, 2 H, 5,5″-tpyH, J = 5.8 Hz); 7.18 (d, 1 H, H_{Ar}, J = 8.4 Hz); 4.96 (d, 2 H, OCH_2, J = 1.8 Hz); 4.85 (d, 2 H, OCH_2, J = 1.8 Hz); 2.58 (br.s, 2 H, C≡CH). ^{13}C NMR ($CDCl_3$), δ: 156.25, 155.91, 149.73, 149.14, 148.47, 147.66, 136.92, 132.56, 123.86, 121.40, 118.63, 114.73, 114.14, 78.34, 78.25, 76.27, 76.19, 57.28, 56.82. LC-MS, m/z: 418 $[M + H]^+$.

4′-[3,5-Bis(prop-2-yn-1-yloxy)phenyl]-2,2′:6′,2″-terpyridine (10b) was obtained from compound **9b** (1.0 g, 4.7 mmol), KOH (0.53 g, 9.4 mmol), and 2-acetylpyridine (1.05 mL, 9.4 mmol). The yield was 0.9 g (47%), a light pink powder. ^{1}H NMR ($CDCl_3$), δ: 8.72—8.73 (m, 2 H, 6,6″-tpyH); 8.65—8.69 (m, 4 H, 3′,5′,3,3″-tpyH); 7.89 (td, 2 H, 4,4″-tpyH, J_1 = 7.7 Hz, J_2 = 1.7 Hz); 7.36 (ddd, 2 H, 5,5″-tpyH, J_1 = 7.4 Hz, J_2 = 4.8 Hz, J_3 = 1.0 Hz); 7.12 (d, 2 H, H_{Ar}, J = 2.2 Hz); 6.74 (t, 1 H, H_{Ar}, J = 2.2 Hz); 4.79 (d, 4 H, OCH_2, J = 2.4 Hz); 2.58 (t, 2 H, C≡CH, J = 2.4 Hz). ^{13}C NMR ($CDCl_3$), δ: 161.10, 155.91, 155.37, 152.03, 149.26, 143.46, 137.21, 123.63, 121.40, 118.08, 105.56, 102.93, 78.75, 76.42, 56.91. LC-MS, m/z: 418 $[M + H]^+$.

Synthesis of mono- and bis([2,2′:6′,2″-terpyridin]-4′-yl)-phenoxymethyl-1*H*-triazol-1-yl)undecan-1-ols 6 and 11 (general procedure). 11-Azidoundecan-1-ol (**2**) and CuI were added to a solution of mono- or bis[4′-(prop-2-yn-1-yloxy)phenyl]-2,2′:6′,2″-terpyridine **5** or **10** in DMF (15 mL). The mixture was heated at 70 °C for 24 h under an inert atmosphere, the solvent was evaporated, the residue was suspended in water and extracted with chloroform. The combined organic fractions were dried with Na_2SO_4 and the solvent was evaporated. The resulting mixture was dissolved in DMF, followed by a slow dropwise addition of a solution of EDTA in water. The ratio DMF : EDTA solution = 1 : 4 (v/v). The mixture was stirred for 24 h, extracted with chloroform, and dried with Na_2SO_4. The solvent was evaporated and the residue was recrystallized from diethyl ether.

11-{4-[4-([2,2′:6′,2″-Terpyridin]-4′-yl)phenoxy]methyl-1*H*-1,2,3-triazol-1-yl}undecan-1-ol (6) was obtained from compound **5** (0.2 g, 0.55 mmol), CuI (0.021 g, 0.11 mmol), 11-azidoundecan-1-ol (**2**) (0.14 g, 0.66 mmol), EDTA (0.1 g, 0.33 mmol), DMF (1 mL), and H_2O (4 mL). The yield was 0.22 g (71%), an orange powder. ^{1}H NMR ($CDCl_3$), δ: 8.66—8.72 (m, 6 H, 6,6″-tpyH, 3′,5′,3,3″-tpyH); 7.89 (d, 4 H, 4,4″-tpyH, H_{Ar}, J = 5.1 Hz); 7.62 (s, 1 H, CHN); 7.36 (d, 2 H, 5,5″-tpyH, J = 4.9 Hz); 7.12 (d, 2 H, H_{Ar}, J = 8.4 Hz); 5.30 (s, 2 H, OCH_2); 4.37 (t, 2 H, $C\underline{H}_2OH$, J = 7.1 Hz); 3.63 (t, 2 H, NCH_2, J = 6.6 Hz); 1.25—1.92 (m, 19 H, $(CH_2)_9$, CH_2OH). LC-MS, m/z: 577 $[M + H]^+$.

11,11′-(4,4′-({[4-([2,2′:6′,2″-Terpyridin]-4′-yl)-1,2-phenylene]bis(oxy)}bis(methylene))bis(1*H*-1,2,3-triazol-4,1-diyl))-bis(undecan-1-ol) (11a) was obtained from compound **10a** (0.2 g, 0.48 mmol), CuI (0.037 g, 0.19 mmol), 11-azidoundecan-1-ol (**2**) (0.23 g, 1.06 mmol), EDTA (0.17 g, 0.57 mmol), DMF (2 mL), and H_2O (8 mL). The yield was 0.24 g (58%), a brown powder. ^{1}H NMR ($CDCl_3$), δ: 8.66—8.73 (m, 6 H, 6,6″-tpyH, 3′,5′,3,3″-tpyH); 7.88 (t, 2 H, 4,4″-tpyH, J = 7.4 Hz); 7.72 (d, 2 H, CHN, H_{Ar}, J = 1.7 Hz); 7.59 (s, 1 H, CHN); 7.52 (d, 1 H, H_{Ar}, J = 7.9 Hz); 7.34—7.37 (m, 2 H, 5,5′′-tpyH); 7.16 (d, 1 H, H_{Ar}, J = 8.3 Hz); 5.37 (d, 4 H, OCH_2, J = 14.1 Hz); 4.35 (t, 4 H, $C\underline{H}_2OH$, J = 7.1 Hz); 3.62 (t, 4 H, NCH_2, J = 6.0 Hz); 1.23—1.89 (m, 38 H, $(CH_2)_{18}$, CH_2OH). LC-MS, m/z: 844 $[M + H]^+$.

11,11′-(4,4′-({[5-([2,2′:6′,2″-Terpyridin]-4′-yl)-1,3-phenylene]bis(oxy)}bis(methylene))bis(1*H*-1,2,3-triazol-4,1-diyl))-bis(undecan-1-ol) (11b) was obtained from compound **10b** (0.2 g, 0.48 mmol), CuI (0.037 g, 0.19 mmol), 11-azidoundecan-1-ol (**2**) (0.23 g, 1.06 mmol), EDTA (0.17 g, 0.57 mmol), DMF (2 mL), and H_2O (8 mL). The yield was 0.25 g (63%), a light brown powder. ^{1}H NMR ($CDCl_3$), δ: 8.66—8.74 (m, 6 H, 6,6″-tpyH, 3′,5′,3,3″-tpyH); 7.89 (td, 2 H, 4,4″-tpyH, J_1 = 7.7 Hz, J_2 = 1.7 Hz); 7.67 (s, 2 H, CHN); 7.37 (dd, 2 H, 5,5″-tpyH, J_1 = 6.8 Hz, J_2 = 5.3 Hz); 7.16 (d, 2 H, H_{Ar}, J = 2.1 Hz); 6.76 (s, 1 H, H_{Ar}); 5.31 (d, 4 H, OCH_2, J = 14.1 Hz); 4.38 (t, 4 H, $C\underline{H}_2OH$, J = 7.2 Hz); 3.63 (t, 4 H, NCH_2, J = 6.6 Hz); 1.93 (t, 4 H, CH_2CH_2OH, J Hz = 7.0); 1.26—1.63 (m, 34 H, $(CH_2)_{16}$, CH_2OH). LC-MS, m/z: 844.54 $[M + H]^+$.

Synthesis of mono- and bis([2,2′:6′,2″-terpyridin]-4′-yl)-phenoxymethyl-1*H*-1,2,3-triazol-1-yl)undecyl-5-(1,2-dithiolan-3-yl)pentanoates 7 and 12 (general procedure). The agents HOBt, BTUH, and DIPEA were added to a solution of lipoic acid in

* tpyH are the protons of the 2,2′:6′,2″-terpyridine fragment.

DMF (15 mL), the resulting mixture was stirred for 40 min under an inert atmosphere, followed by the addition of compound **6** or **11** and stirring for 48 h under an inert atmosphere. The reaction progress was monitored by TLC. The solvent was evaporated and the residue was purified by column chromatography (chromatographic column: silica gel 15 μ (40 g), gradient elution: petroleum ether → petroleum ether —ethyl acetate + + $NH_3 \cdot H_2O$ (1 : 1) → ethyl acetate + $NH_3 \cdot H_2O$, 26 min. The ratio ethyl acetate : $NH_3 \cdot H_2O$ = 1 : 0.0025).

11-(4-{[4-([2,2′:6′,2″-Terpyridin]-4′-yl)phenoxy]methyl}-1*H*-1,2,3-triazol-1-yl)undecyl-5-(1,2-dithiolan-3-yl)pentanoate (7) was obtained from lipoic acid (0.11 g, 0.55 mmol), HOBt (0.11 g, 0.82 mmol), BTUH (0.31 g, 0.82 mmol), DIPEA (0.19 mL, 1.1 mmol), and alcohol **6** (0.15 g, 0.26 mmol), a white powder. ^{1}H NMR ($CDCl_3$), δ: 8.66—8.74 (m, 6 H, 6,6″-tpyH, 3′,5′,3,3′-tpyH); 7.86—7.90 (m, 4 H, 4,4″-tpyH, H_{Ar}); 7.63 (s, 1 H, CHN); 7.36 (ddd, 2 H, 5,5″-tpyH, J_1 = 7.4 Hz, J_2 = 4.8 Hz, J_3 = 1.2 Hz); 7.13 (d, 2 H, H_{Ar}, J = 8.4 Hz); 5.30 (s, 2 H, OCH_2); 4.37 (t, 2 H, CH_2OH, J = 7.3 Hz); 4.05 (t, 2 H, NCH_2, J = 6.8 Hz); 3.53—3.60 (m, 1 H, CHS); 3.08—3.21 (m, 2 H, CH_2S); 2.42—2.50 (m, 1 H, C<u>H</u>$_2$CHS); 2.31 (t, 2 H, CH_2C=O, J = 7.4 Hz); 1.26—1.94 (m, 25 H, $(CH_2)_9$, CHC<u>H</u>$_2$C<u>H</u>$_2$C<u>H</u>$_2$, C<u>H</u>$_2$CHS). ^{13}C NMR ($CDCl_3$), δ: 173.12, 159.56, 155.95, 155.33, 152.07, 149.24, 142.38, 137.23, 134.61, 129.66, 128.66, 123.68, 121.41, 118.17, 114.89, 72.32, 65.26, 56.31, 52.43, 40.21, 38.53, 34.65, 33.91, 29.62, 29.35, 29.09, 28.90, 28.49, 27.14, 25.82. MS, found: *m/z* 765.1615 $[M + H]^+$, calculated for $C_{43}H_{52}N_6O_3S_2$: 765.3627. UV (DMSO), λ_{max}/nm (ε): 292 (2132).

{4,4′-(([5-([2,2′:6′,2″-Terpyridin]-4′-yl)-1,3-phenylene)bis(oxy))bis(methylene))bis(1*H*-1,2,3-triazol-4,1-diyl))bis(undecan-11,1-diyl)bis[5-(1,2-dithiolan-3-yl)pentanoate] (12) was obtained from lipoic acid (0.15 g, 0.18 mmol), DIPEA (0.26 mL, 1.5 mmol), HOBt (0.15 g, 1.1 mmol), BTUH (0.43 g, 1.1 mmol), and alcohol **11b** (0.15 g, 0.18 mmol). The yield was 0.08 g (36%), a pale yellow powder. ^{1}H NMR ($CDCl_3$), δ: 8.73 (d, 2 H, 3,3″-tpyH, J = 4.0 Hz); 8.7 (s, 2 H, 3′,5′-tpyH); 8.66 (d, 2 H, 6, 6″-tpyH, J = 7.9 Hz); 7.87—7.91 (m, 2 H, 4,4′′-tpyH); 7.67 (s, 2 H, CHN); 7.37 (dd, 2 H, 5,5″-tpyH, J_1 = 6.9 Hz, J_2 = 5.3 Hz); 7.15 (d, 2 H, H_{Ar}, J = 2.1 Hz); 6.76 (s, 1 H, H_{Ar}); 5.30 (s, 4 H, OCH_2); 4.36—4.40 (m, 4 H, C<u>H</u>$_2$OH); 4.05 (t, 2 H, NCH_2, J = 6.7 Hz); 3.53—3.60 (m, 2 H, CHS); 3.08—3.21 (m, 4 H, CH_2S); 2.41 (dq, 2 H, C<u>H</u>$_2$CHS, J_1 = 12.3 Hz, J_2 = 6.3 Hz); 2.31 (t, 4 H, CH_2C=O, J = 7.3 Hz); 1.26—1.93 (m, 50 H, $(CH_2)_9$, CHC<u>H</u>$_2$C<u>H</u>$_2$C<u>H</u>$_2$, C<u>H</u>$_2$CHS). ^{13}C NMR ($CDCl_3$), δ: 173.18, 156.26, 156.21, 155.54, 152.09, 149.35, 143.34, 142.58, 137.23, 128.64, 123.61, 121.41, 118.07, 105.58, 100.91, 72.37, 65.36, 56.37, 52.46, 40.34, 38.52, 34.67, 33.83, 29.68, 29.41, 29.15, 28.98, 28.61, 27.24, 25.82. MS, found: *m/z* 1220.5891 $[M + H]^+$, calculated for $C_{65}H_{89}N_9O_6S_4$: 1220.5878. UV (DMSO), λ_{max}/nm (ε): 284 (2380), 315 (908).

Synthesis of coordination compounds 13 and 14 (general procedure). A solution of ligand **7** or **12** in anhydrous EtOH (2 mL) was heated to reflux, followed by the addition of a solution of $[Rh(DMSO)_3Cl_3]$ in anhydrous EtOH (2 mL). The mixture was refluxed for 24 h with stirring and cooled to room temperature. The formed precipitate was collected by filtration, washed with ethanol, chloroform, diethyl ether, and dried in air.

Coordination compound 13 was obtained from ligand **7** (0.03 g, 0.04 mmol) and the salt $[Rh(DMSO)_3]Cl_3$ (0.017 g, 0.04 mmol). The yield was 0.02 g (50%), an orange powder. Found (%): C, 53.10; H, 5.32; N, 8.70. $C_{43}H_{52}Cl_3N_6O_3RhS_2$. Calculated (%): C, 53.01; H, 5.38; N, 8.63. LI-MS, *m/z*: 939 $[M - {}^{37}Cl]^-$, 902 $[M - {}^{35}Cl]^{2-}$, 867 $[M - {}^{35}Cl]^{3-}$. UV (DMSO), λ_{max}/nm (ε): 382 (2880), 340 (6160), 290 (29840).

Coordination compound 14 was obtained from ligand **12** (0.03 g, 0.025 mmol) and the salt $[Rh(DMSO)_3Cl_3]$ (0.011 g, 0.025 mmol). The yield was 0.018 g (60%), a bright orange powder. Found (%): C, 52.57; H, 6.37; N, 8.34. $C_{65}H_{89}N_9Cl_3O_6RhS_4$. Calculated (%): C, 54.59; H, 6.27; N, 8.82. LI-MS, *m/z*: 1393 $[M - {}^{37}Cl]^-$, 1358 $[M - {}^{35}Cl]^{2-}$, 1322 $[M - {}^{35}Cl]^{3-}$. IR (CCl_4), ν/cm^{-1}: 1727 (C=O), 2926 (C_2N_3). UV (DMSO), λ_{max}/nm (ε): 380 (10960), 340 (18320), 318 (29400), 284 (50840).

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