New organic picolylamine-type ligands and electrochemical study of their complexation with $Cu(MeCN)_4ClO_4$

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A series of novel organic ligands with dipicolylamine and disulfide groups connected by polymethylene, alkylaryl, alkoxyaryl, or alkoxycarbonyl linker was synthesized. The electrochemical study by cyclic voltammetry was carried out for two synthesized ligands, and the formation of the complexes with $Cu(MeCN)ClO_4$ in the solution or on the gold electrode surface was established. The complex of Cu^I with 1,24-bis[*N*,*N*-bis(2-pyridylmethyl)-glycinoyloxy]-12,13-dithiatetracosane chemisorbed on the Au electrode is capable of binding molecular oxygen from solution.

Key words: dipicolylamines, disulfides, copper(I) complexes, chemisorption, gold, cyclic voltammetry.

Copper complexes with nitrogen-containing ligands can be used as low-molecular-weight models of enzymes hemocyanine, tyrosinase, and catechol oxidases (see, *e.g.*, Refs 1—5). These redox enzymes act as oxygen carriers (hemocyanine[6—8]), catalyze the *ortho*-hydroxylation of phenols to the corresponding pyrocatechols (tyrosinase[7,9]), or the oxidation of pyrocatechols to *o*-quinones (catechol oxidase[9,10]). Di- and tripyridylalkylamines are presently considered to be among the most promising models of active centers of copper-containing oxygenases.[1—5,11,12] The copper(I) complexes with these ligands have been synthesized to date and show a high capability of binding oxygen.[11,12]

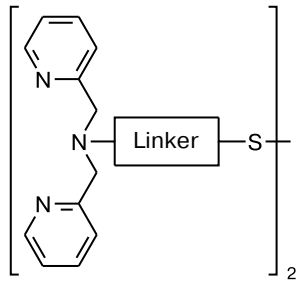
Metal complex catalysts immobilized on the metallic surface have several advantages for the use in catalysis. The immobilization of a homogeneous catalyst on the surface imparts practical advantages of heterogeneous catalysis to the performed reaction and retains advantages of homogeneous catalytic reactions. A doubtless advantage of immobilized catalysts is the easiness of catalyst separation from reactants and reaction products and the simplification of the procedure of their repeated use. It is important that catalysts with high molecular weight immobilized on the polymer or metal support are non-toxic and safe and, hence, they are insoluble in water and organic solvents (in some cases, this makes it possible to assign these reactions to the area of "green chemistry").[13] Self-organized monolayers capable of binding metal ions are formed upon adsorption of thiols and disulfides containing additional donor groups on the gold surface. The examples of performing catalytic reactions using metal complexes immobilized on the solid surface are described (see, *e.g.*, Refs 14—16).

In the present work, we describe the synthesis of novel organic ligands containing the dipicolylamine and disulfide groups. Such a combination of structural fragments imparts to the molecules the ability to both form coordination bonds of the nitrogen atoms of the amino groups and to chemisorb on the gold surface with the formation of the Au—S bond. The formation of the copper(I) complexes with such ligands, including those chemisorbed on the Au electrode surface, and molecular oxygen binding by the complex immobilized on the Au surface were studied.

Results and Discussion

Synthesis of the ligands. The general structure of the target organic ligands is given below. All synthesized compounds contain the dipicolyl fragment connected with the disulfide group by a linker being the polymethylene, alkylaryl, alkoxyaryl, or alkoxycarbonyl group.

Two methods were used for the synthesis of the target ligands with different linkers (Scheme 1). One of the methods is based on the alkylation of dipicolylamine (**1**) with alkyl halide (route *A*), and another method is based on the reductive amination of the corresponding aldehyde with dipicolylamine **1** (route *B*).



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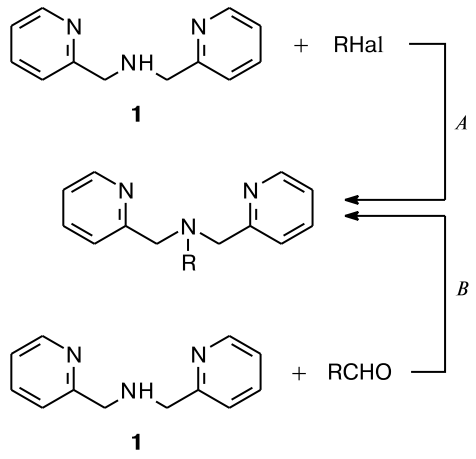
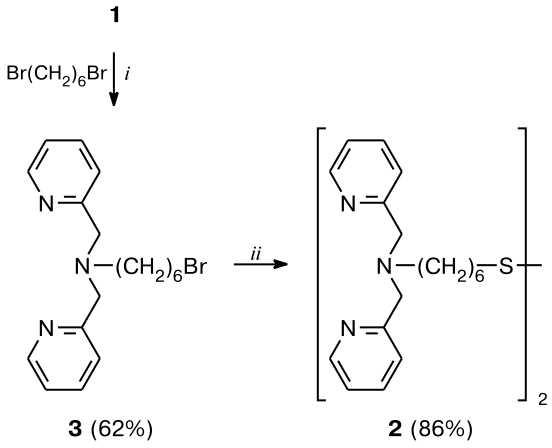
Scheme 1



RHal = $BrC_6H_{12}Br$, $4\text{-}ClCH_2C_6H_4SMe$, $BrCH_2COOH$
RCHO = $4\text{-}MeSC_6H_4CHO$, $[4\text{-}HC(O)C_6H_4S]_2$,
$[4\text{-}HC(O)C_6H_4OC_{11}H_{22}S]_2$

Compound **2** containing the alkanediyl linker was synthesized following route *A* (Scheme 2). First, the reaction of dipicolylamine **1** with 1,6-dibromohexane in the presence of Bu^nLi at −70 °C afforded monobromide **3**. A threefold excess of the alkylating reactant was used to obtained the product of substitution of only one bromine atom in α,ω-dibromoalkane. The nucleophilic substitution of the sulfur-containing group for the second bromine was performed by the treatment with potassium thioacetate in MeOH; when the reaction product is isolated, the primarily formed thiol is oxidized with air oxygen to disulfide **2**.

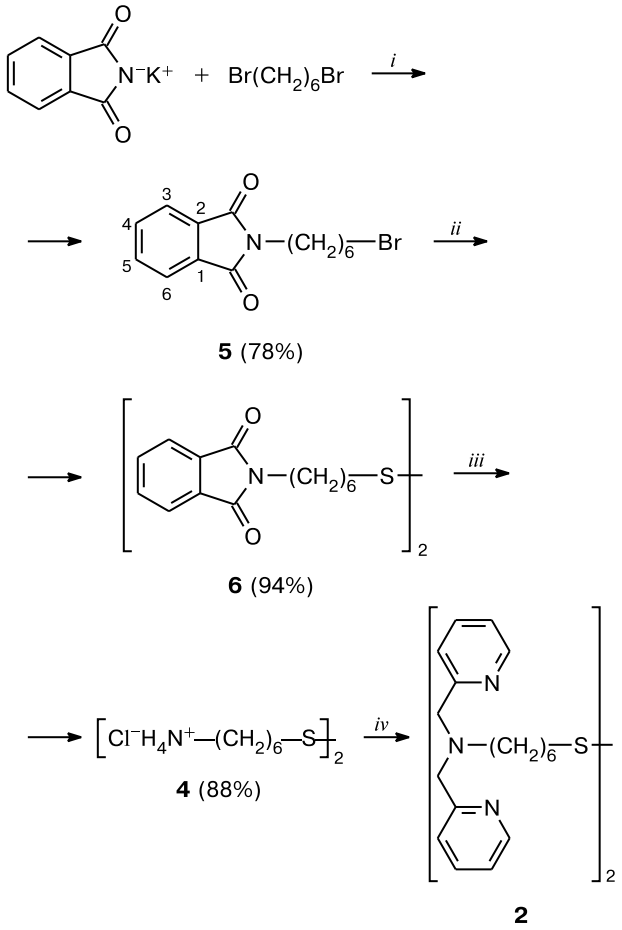
Scheme 2



Reagents and conditions: *i.* Bu^nLi, THF; *ii.* (1) AcSK, MeOH, 65 °C, (2) NH_4Cl, H_2O, O_2 (air).

An alternative method of synthesis of ligand **2** (Scheme 3) is the reductive amination of two equivalents of 2-pyridinecarbaldehyde with diamino disulfide **4**, which was obtained, in turn, from 1,6-dibromohexane and potassium phthalimide according to the Garbriel method.

Scheme 3

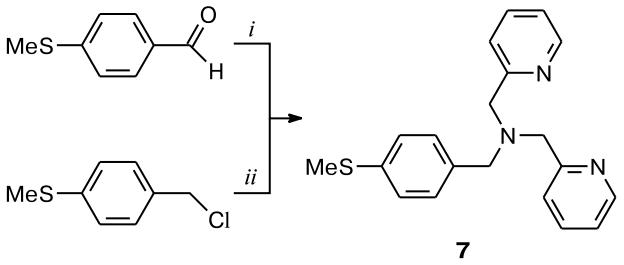


Reagents and conditions: *i.* DMF; *ii.* (1) $Na_2S_2O_6$, MeOH, H_2O, (2) I_2; *iii.* $NH_2NH_2 \cdot H_2O$, EtOH, 80 °C; *iv.* (1) KOH, EtOH, (2) $NaBH_3CN$, 2-PyCHO, AcOH, MeOH.

Apart the ligands bearing the disulfide group, we synthesized compound **7** containing the methylthio group (Scheme 4). It is known that aryl alkyl sulfides, similarly to thiols and disulfides, are capable of chemisorbing on the Au surface to form self-organized monolayers, which are usually less ordered and are formed with a lower rate than alkanethiols and dialkyl disulfides.[17] Compound **7** can be synthesized by two alternative routes (see Scheme 1).

The first route (see Scheme 4) is the condensation of 4-methylthiobenzaldehyde with dipicolylamine **1** in the presence of sodium cyanoborohydride and produces compound **7** in 73% yield. The second route is the nucleophilic substitution of the chlorine atom in 4-methylthiobenzyl chloride under the action of **1** in the presence of potassium carbonate. A higher yield (84%) of target product **7** is achieved in the second case.

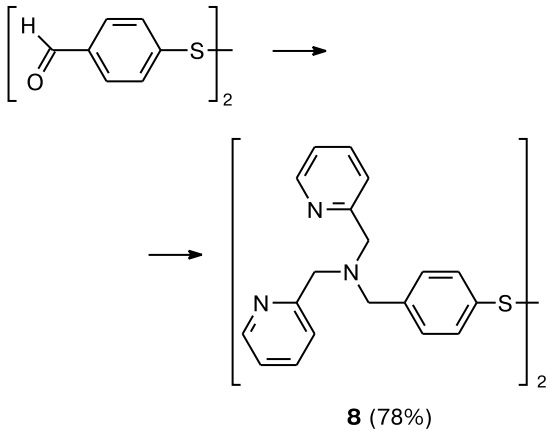
Scheme 4



Reagents and conditions: *i.* **1**, $NaBH_3CN$, AcOH, MeOH; *ii.* **1**, K_2CO_3, DMF.

Ligand **8**, being close in structure to compound **7** and differing by the presence of the disulfide group instead of the methylsulfide one, was synthesized in 78% yield by the reaction of bis(4-formylphenyl) disulfide with dipicolylamine **1** in the presence of sodium cyanoborohydride (Scheme 5).

Scheme 5

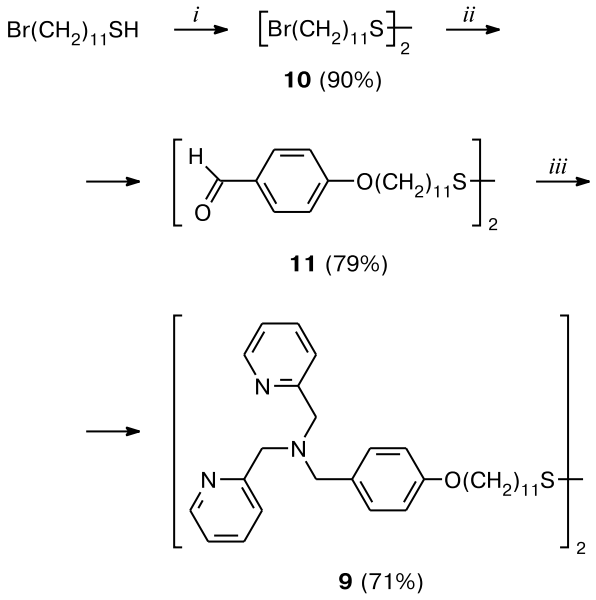


Reagents and conditions: **1**, $NaBH_3CN$, AcOH, MeOH.

To obtain ligand **9** containing the aryloxyalkyl fragment as a linker, we used the sequence of reactions (Scheme 6) including the synthesis of dibromo disulfide **10** by the oxidation of 11-bromo-1-undecanethiol with iodine, the alkylation of 4-hydroxybenzaldehyde with compound **10** in the presence of potassium carbonate in DMF, and the subsequent condensation of obtained product **11** with dipicolylamine **1** in MeOH in the presence of sodium cyanoborohydride.

The synthesis of ligand **12** bearing the ester group was performed in two stages from dipicolylamine **1**, bromoacetic acid, and dibromo disulfide **10** (Scheme 7). At the first stage, dipicolylamine **1** was alkylated with bromoacetic acid in the presence of potassium hydroxide. Isolated potassium salt **13** was used in the nucleophilic substitution

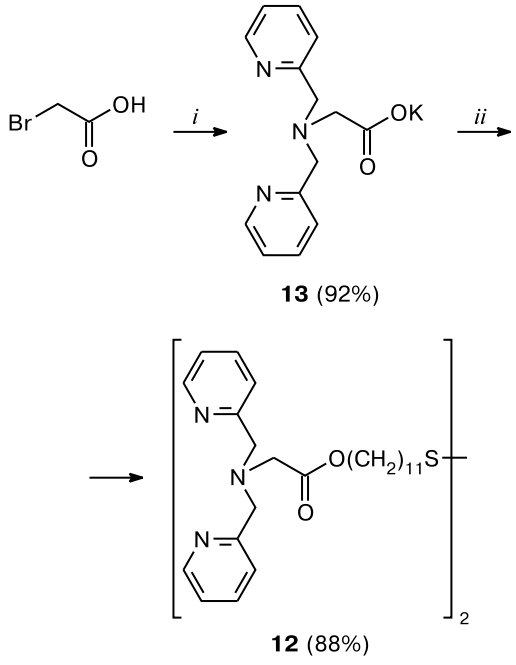
Scheme 6



Reagents and conditions: *i.* I_2, MeOH; *ii.* 4-HOC_6H_4CHO, K_2CO_3, DMF; *iii.* **1**, $NaBH_3CN$, AcOH, MeOH.

reaction with dibromide **10**. Ligand **12** was synthesized in 88% yield at the second stage of the synthesis.

Scheme 7



Reagents and conditions: *i.* **1**, KOH, H_2O; *ii.* **10**, K_2CO_3, DMF.

Electrochemical properties of ligands 7 and 12 and their complexes with Cu^I. The possibility of formation of coor-

dination compounds with $Cu(MeCN)_4ClO_4$ by ligands **7** and **12**, chemisorption of ligand **12** and its copper-containing complex on the Au electrode, and binding of molecular O_2 by the latter in solution was studied by the methods of cyclic voltammetry (CV) and rotating disk electrode (RDE). The electrochemical oxidation and reduction potentials measured *vs* Ag/AgCl/KCl (sat.) are listed in Table 1.

The reduction of ligand **7** in MeCN proceeds as one two-electron stage, while the oxidation proceeds in three stages for the CV method and in two stages for the RDE method with the current ratio 1 : 1.5, which indicates its stepwise oxidation (see Table 1, Fig. 1).

The starting copper(I) salt, $Cu(MeCN)_4ClO_4$, on the GC electrode in MeCN is oxidized quasi-reversibly at $E_{pa} = 1.08$ V and is reduced at $E_{pc} = -0.60$ V (see Table 1). The Cu^0 complex formed upon the electroreduction of $Cu(MeCN)_4ClO_4$ is restrictedly stable, which is confirmed by the presence of the low-intensity oxidation peak of $Cu^0 \rightarrow Cu^I$ (−0.46 V) and the peak of desorption of metallic copper from the electrode surface at −0.13 V in the reverse scan of the CV curve. Note that at the Au electrode the oxidation of $Cu(MeCN)_4ClO_4$ proceeds reversibly ($E_{pa}/E_{pc} = 1.04/0.97$), whereas the reduction occurs with the formation of metallic copper ($E_{pc}/E_{pa} = -0.49/-0.20$ (desorption).

Immediately after mixing solutions of ligand **7** and $Cu(MeCN)_4ClO_4$ in a solution of MeCN, the peaks of oxidation and reduction of the free salt disappear from the CV curve (see Fig. 1) and the peaks of the complex appear. The reversible oxidation peak of $Cu^I \rightarrow Cu^{II}$ for the complex is observed at $E_{pa}/E_{pc} = 0.30/-0.23$ V, *i.e.*, a very considerable shift of the potential to the cathodic region (by 780 mV) compared to the oxidation of the salt is observed. The potential of the reduction peak of $Cu^I \rightarrow Cu^0$ changes insignificantly (shift by 30 mV to the cathodic region of potentials, see Table 1). As the starting salt, the Cu^0 complex formed in this process is restrictedly stable (the low-intensity oxidation peak of $Cu^0 \rightarrow Cu^I$ at −0.52 V

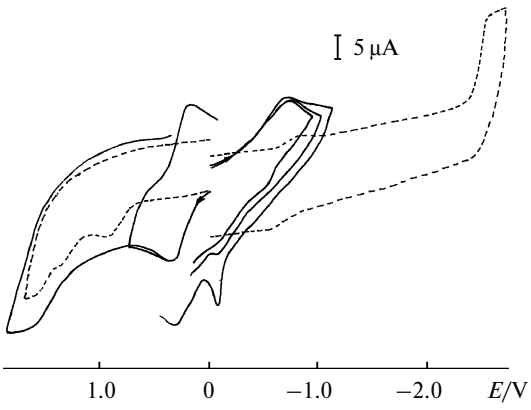


Fig. 1. Cyclic voltammograms (GC electrode, MeCN, Bu_4NClO_4) of ligand **7** (dashed lines) and its complex with $Cu(MeCN)_4ClO_4$ (solid lines); concentration 10^{-3} mol L^{-1}. The curve at the left was obtained by the anodic scan, and the curves at the right are the cathodic scan.

Table 1. Oxidation (E^{Ox}) and reduction (E^{Red}) potentials of $Cu(MeCN)_4ClO_4$, ligands **7** and **12**, and their complexes with $Cu(MeCN)_4ClO_4$ measured by the CV and RDE methods (MeCN, 0.1 *M* Bu_4NClO_4, *vs* Ag/AgCl/KCl (sat.))

Compound	E_p^{Red}	$E_{1/2}^{Red}$	E_p^{Ox}	$E_{1/2}^{Ox}$
		GC electrode		
$Cu(MeCN)_4ClO_4^-$	−0.60	−0.48	1.08	1.10
	/−0.46		/0.92	
	−0.13 [a]	—	—	—
7	−2.51	−2.50 (2e)	0.94	0.99 (1e)
	—	—	1.33	1.42
				(1.5e)
	—	—	1.60	—
7 + $Cu(MeCN)_4ClO_4^-$	−0.63	−0.65	0.30	0.24
	/−0.52		/0.23 [b]	
	−0.12 [a]	−0.86	0.80	1.47
	—	−1.62	1.60	—
12 [c]	−0.75 [d]	—	0.37	—
	−1.51	—	0.74	—
	−1.98	—	—	—
	−2.31	—	—	—
		Au electrode		
12 [e]	−0.73 [d]	—	0.53	—
	−1.46	—	0.95	—
	−1.67	—	—	—
12 [d]	−0.93	—	0.28	—
12 + $Cu(MeCN)_4ClO_4^-$ [f]	−0.53	—	0.25	—
			/0.14	
	−0.98	—	0.92	—
	−1.66	—	—	—
	−1.76	—	0.92	—
	/−0.60			
12 + $Cu(MeCN)_4ClO_4^-$ [g]	0.23	—	0.96	—
	/0.14			
	−0.51	—	—	—
	−0.98	—	—	—
12 + $Cu(MeCN)_4ClO_4^-$ [h]	0.28	—	0.94	—
	/0.14			
	−0.88	—	—	—

Note. E_p are the cathodic peak potentials measured by the CV method (200 mV s^{-1}); the potentials of the peaks at reverse scans of the CV curves are presented under slashes; $E_{1/2}$ are the half-wave potentials measured by the RDE method (2800 rpm); the number of electrons transferred at each stage is given in parentheses.

[a] Desorption potential.
[b] The initial potential is 0.7 V.
[c] Solution in DMF.
[d] Adsorption potential.
[e] In solution.
[f] In monolayer.
[g] In monolayer after purging with O_2.
[h] In monolayer after removal of O_2.

and the peak of desorption of Cu^0 at −0.12 V are detected on the reverse scan of the voltammetric curve).

The prolong O_2 purging through a solution of the complex does not result in a change in the peak potentials of the transitions $Cu^I \rightarrow Cu^{II}$ and $Cu^I \rightarrow Cu^0$ or the appearance of any new peaks in the CV curve. Evidently, this complex does not react with oxygen under the experimental conditions.

Disulfide **12** has a very low solubility in MeCN and, hence, its electrochemical behavior was studied in DMF, where the peaks observed in the CV curves are most distinct. Compound **12** is oxidized in two stages, whereas its reduction proceeds in three stages, the first of which (−1.51 V) corresponds to the reduction of the S—S bond, and the second stage (−1.98 V) corresponds to the reduction of the ester moiety.[18] Note that the reduction of compound **12** in MeCN on the Au electrode is accompanied by the formation of three peaks, the first of which is the adsorption one and the second and third peaks correspond to the reduction of the S—S bond and the ester group, respectively, and the potentials are shifted to the anodic region compared to the GC electrode (see Table 1, Fig. 2).

The chemisorption of disulfide **12** on the Au electrode surface results in the disappearance of the adsorption prepeak at −0.75 V and the peak of S—S bond reduction in the CV curve, whereas the reduction peak of the S—Au bond appears at −0.93 V (see Table 1 and Refs 19—21).

The behavior of chemisorbed complex **12** with Cu^I in MeCN was studied after the Au electrode was stored in a solution of compound **12** in DMF (10^{-3} mol L^{-1}) for 3 h. In this case, according to the literature data, disulfide is chemisorbed on the metal surface with the S—S bond cleavage and the formation of the Au—S bond. Then the electrode was consequently washed with DMF and MeCN and placed in a solution of $Cu(MeCN)_4ClO_4$ in MeCN for 6 h to form the coordination compound on the electrode surface.

The formation of chemisorbed complex **12** with $Cu(MeCN)_4ClO_4$ is confirmed by the appearance in the

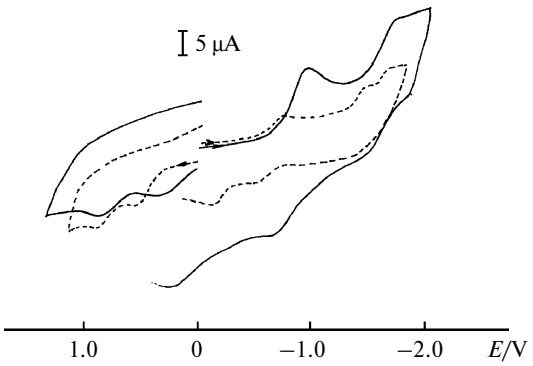


Fig. 2. Cyclic voltammograms (MeCN, Bu_4NClO_4) of ligand **12** on the Au electrode in solution (dashed lines) and in the monolayer (solid lines).

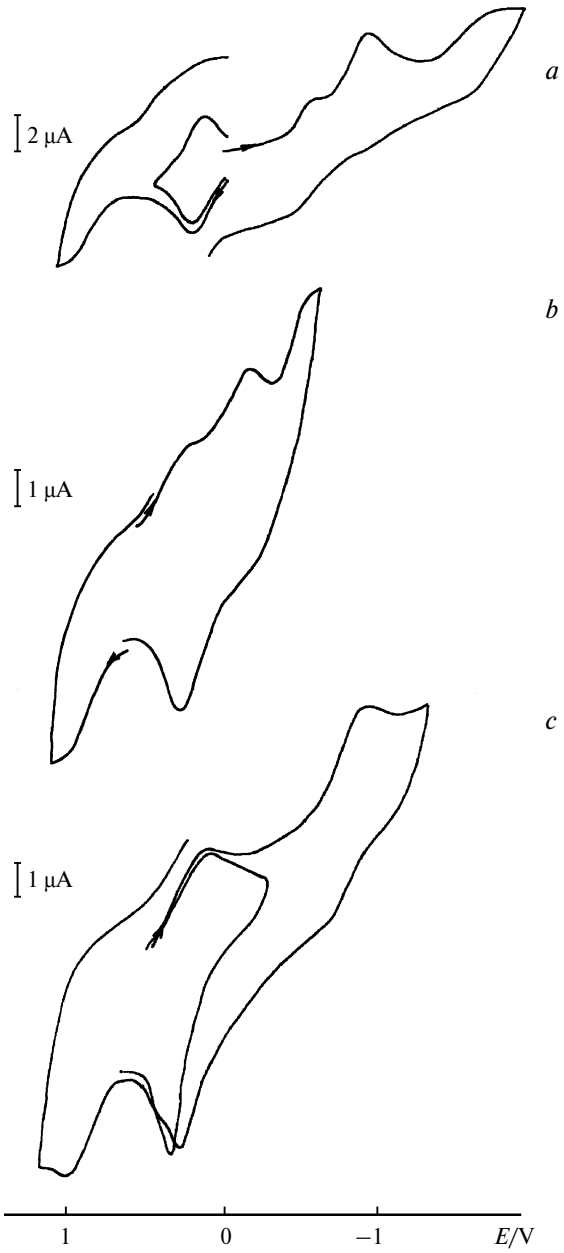


Fig. 3. Cyclic voltammograms (MeCN, Bu_4NClO_4, monolayers on the Au electrode) of the complex of ligand **12** with $Cu(MeCN)_4ClO_4$ before (*a*) and after purging of the solution with oxygen for 40 min (*b*) (the CV curve was detected for the solution containing an excess of oxygen; therefore, after passing a potential of ~0.6 V, a very intense peak of O_2 reduction is observed in the cathodic region) and after oxygen was removed from the solution with argon for 40 min (*c*).

CV curve of the oxidation $Cu^I \rightarrow Cu^{II}$ (E_{pa}/E_{pc} = = 0.25/0.14) and reduction $Cu^I \rightarrow Cu^0$ (E_{pc} = −0.53 V) peaks (Fig. 3, *a*).

After the electrochemical cell containing the Au electrode with the monolayer of the complex of ligand **12** with Cu^I was purged with O_2 for 40 min, the shape of the CV

changes dramatically: a cathodic peak corresponding to the transition $Cu^{II} \rightarrow Cu^{I}$ (E_{pc} = 0.23 V) appears. The presence of this peak shows that, when binding with O_2, the copper in the composition of the complex is oxidized to Cu^{II}. In addition, in the voltammetric curve, the reduction peak of $Cu^{I} \rightarrow Cu^{0}$ is shifted to the anodic region and a new peak appears at −0.18 V (see Fig. 3, *b*), which probably corresponds to the reduction of the oxygen-containing moiety of the product.

When the cell is purged with argon for 40 min after the formation of the oxygen-containing complex, the reduction peak of $Cu^{II} \rightarrow Cu^{I}$ (E_{pc} = 0.28 V) is observed in the CV curve (see Fig. 3, *c*) and the reduction peak of $Cu^{I} \rightarrow Cu^{0}$ of the starting complex at −0.53 V is absent. These data indirectly indicate that the oxidation with oxygen of the starting copper-containing complex of ligand **12** is irreversible under these conditions.

Thus, the electrochemical data confirm the possibility of formation of the chemisorbed complex of ligand **12** with $Cu(MeCN)_4ClO_4$ on the Au electrode surface and the binding of molecular oxygen by this complex. It seems promising to study this complex as a catalyst of redox reactions, first of all, phenol and pyrocatechol oxidation. At the same time, according to the CV data, ligand **7** containing the methylthio group and benzyl linker, which links the latter with the dipicolylamine fragment, forms no complexes with Cu^{I} in a MeCN solution.

Experimental

The reaction course and individual character of products were monitored by thin layer chromatography on an immobilized silica gel layer (Silufol). ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance instrument at 400 and 100 MHz, respectively. IR spectra were measured on a UR-20 instrument in Nujol, and electronic spectra in the UV and visible regions were recorded on a Hitachi U-2900 instrument. Mass spectra were obtained on a Finnigan MAT 95 XL instrument (direct inlet, electron impact, 70 eV).

A PI-50-1.1 potentiostat switched to a PR-8 programmer was used for electrochemical studies. The working electrodes were glassy carbon (GC) (d = 2 mm), platinum (d = 3 mm), and gold (d = 2 mm) disks, the supporting electrolyte was a 0.1 *M* solution of Bu_4NClO_4 in MeCN, the reference electrode was Ag/AgCl/KCl (sat.), and a Pt plate served as an auxiliary electrode. The surface of working electrodes was polished with an alumina powder with the particle size less than 10 μm (Sigma—Aldrich). For CV studies, the potential sweep rate was 200 mV s^{-1}, and for the RDE method it was 20 mV s^{-1}. The potentials are presented with allowance for *iR*-compensation. All measurements were carried out under dry argon; and the samples were dissolved in a beforehand deaerated solvent. The number of transferred electrons in redox processes was determined by comparing the limiting current of the wave in RDE experiments with the current of one-electron oxidation of ferrocene taken in an equal concentration.

11-Bromo-1-undecanethiol[22] and bis(4-formylphenyl) disulfide[23] were synthesized following the known procedures.

***N*-(6-Bromohexyl)-*N*,*N*-bis(2-pyridylmethyl)amine (3).** A two-necked flask pre-heated and then cooled to room temperature in an argon flow was filled with a solution of dipicolylamine **1** (0.5 g, 2.5 mmol) in absolute THF (15 mL). The flask was cooled to −70 °C, and a 1.6 *M* solution of *n*-butyllithium in hexane (1.73 mL, 2.8 mmol) was syringed. The reaction mixture was stirred for 15 min at the same temperature, and then 1,6-dibromohexane (1.5 g, 6.3 mmol) in absolute THF (5 mL) was added. The resultant solution was stirred for 12 h, gradually raising temperature to ambient. Water (20 mL) was added to the solution, and organics was extracted with CH_2Cl_2 (3×20 mL). The organic fractions were dried with anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the product was isolated by column chromatography on silica gel (petroleum ether—ethyl acetate, 6 : 1). Compound **3** was obtained as a yellow oil in a yield of 0.56 g (62%). ^1H NMR ($CDCl_3$), δ: 8.49 (d, 2 H, HC(6), HC(6′), Py, J = 4.9 Hz); 7.77 (td, 2 H, HC(4), HC(4′), Py, J_1 = 1.7 Hz, J_2 = 7.7 Hz); 7.52 (d, 2 H, HC(3), HC(3′), Py, J = 7.7 Hz); 7.25 (td, 2 H, HC(5), HC(5′), Py, J_1 = 1.5 Hz, J_2 = 6.3 Hz); 3.75 (s, 4 H, CH_2Py); 3.47 (t, 2 H, CH_2Br, J = 6.7 Hz); 2.46 (t, 2 H, CH_2N, J = 7.1 Hz); 1.73 (m, 2 H, CH_2); 1.48 (m, 2 H, CH_2); 1.25 (m, 4 H, $(CH_2)_2$). MS, m/z (I_{rel} (%)): 362 (10%) $[M]^+$.

6,6′-Dithiobis[*N*,*N*-(2-pyridylmethyl)hexane-1-amine] (2). ***A.*** Potassium thioacetate (0.53 g, 4. 6 mmol) was added to a solution of compound **3** (0.56 g, 1.6 mmol) in MeOH (25 mL). The mixture was refluxed for 12 h and cooled to ~20 °C. A saturated solution of NH_4Cl (30 mL) was added, and organics was extracted with CH_2Cl_2 (3×20 mL). The organic fractions were dried with Na_2SO_4, and the solvent was evaporated under reduced pressure. Compound **2** was obtained as a yellow oil in a yield of 0.43 g (86%). ^1H NMR ($CDCl_3$), δ: 8.49 (d, 2 H, HC(6), HC(6′), Py, J = 4.5 Hz); 7.66 (td, 2 H, HC(4), HC(4′), Py, J_1 = 1.8 Hz, J_2 = 7.8 Hz); 7.57 (d, 2 H, HC(3), HC(3′), Py, J = 7.8 Hz); 7.16 (td, 2 H, HC(5), HC(5′), Py, J_1 = 1.3 Hz, J_2 = 5.7 Hz); 3.91 (s, 4 H, CH_2Py); 2.77 (t, 2 H, CH_2S, J = 7.2 Hz); 2.62 (t, 2 H, CH_2N, J = 6.7 Hz); 1.56 (m, 2 H, CH_2); 1.40 (m, 2 H, CH_2); 1.25 (m, 4 H, $(CH_2)_2$). MS, m/z (I_{rel} (%)): 629 (12%) $[M]^+$.

B. 2-(6-Bromohexyl)-1*H*-isoindole-1,3(2*H*)-dione (**5**). A solution of 1,6-dibromohexane (10 g, 43.2 mmol) in DMF (5 mL) was added to a suspension of potassium phthalimide (1.94 g, 10.5 mmol) in DMF (10 mL). The reaction mixture was stirred for 48 h. After reaction completion, water (5 mL) was added to the mixture, and organics was extracted with CH_2Cl_2 (3×10 mL). The combined organic extracts were washed with brine and water and dried with anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure. Compound **5** was obtained as a white powder, m.p. 63 °C, in a yield of 2.5 g (78%). Found (%): C, 53.96; H, 5.12; N, 4.35; Br, 25.53. $C_{14}H_{16}BrNO_2$. Calculated (%): C, 54.21; H, 5.20; N, 4.52; Br, 25.76. ^1H NMR ($CDCl_3$), δ: 7.87 (d, 2 H, HC(3), HC(6), Ph, J = 5.4 Hz); 7.74 (d, 2 H, HC(4), HC(5), Ph, J = 5.4 Hz); 3.71 (t, 2 H, CH_2N, J = 7.3 Hz); 3.42 (t, 2 H, CH_2Br, J = 6.8 Hz); 1.88 (m, 2 H, CH_2); 1.72 (m, 2 H, CH_2); 1.51 (m, 2 H, CH_2); 1.40 (m, 2 H, CH_2).

2,2′-[Dithiobis(hexane-1,6-diyl)]bis[1*H*-isoindole-1,3(2*H*)-dione] **(6).** A solution of sodium thiosulfate (0.5 g, 3.14 mmol) was added to a solution of compound **3** (1 g, 3.2 mmol) in a MeOH—water (1 : 1) mixture. The reaction mixture was refluxed for 24 h with stirring. Iodine was added to the resultant solution under reflux until stable color appeared, and then the

mixture was refluxed for 4 h. Sodium sulfite was added until the solution decolorized to remove a iodine excess. The precipitate formed was filtered off and purified by flash chromatography (hexane—diethyl ether, 1 : 1). Compound **6** was obtained as a white powder, m.p. 59 °C, in a yield of 0.79 g (94%). Found (%): C, 63.87; H, 5.02; N, 5.12; S, 12.09. $C_{28}H_{32}N_2O_4S_2$. Calculated (%): C, 64.09; H, 6.15; N, 5.34; S, 12.22. ^{1}H NMR ($CDCl_3$), δ: 7.83 (d, 2 H, HC(3), HC(6), Ph, J = 5.4 Hz); 7.70 (d, 2 H, HC(4), HC(5), Ph, J = 5.4 Hz); 3.67 (t, 2 H, CH_2N, J = 7.6 Hz); 2.64 (t, 2 H, CH_2S, J = 7.1 Hz); 1.65 (m, 4 H, $(CH_2)_2$); 1.40 (m, 2 H, $(CH_2)_2$).

1,14-Diammonio-7,8-dithiatetradecane dichloride (**4**). A mixture of compound **6** (0.79 g, 1.5 mmol), hydrazine hydrate (0.24 g, 4.8 mmol), and EtOH (10 mL) was refluxed for 1 h under argon. After the starting compounds were completely dissolved, the formation of a colorless precipitate of the reaction production was observed. The solvent was removed under reduced pressure, and 1 *M* HCl (15 mL) was added to the residue. The mixture was refluxed with stirring for 1 h. The solvent was evaporated *in vacuo*, and EtOH (30 mL) was added to the residue. The undissolved precipitate was filtered off, and the product was precipitated from the filtrate with an Et_2O—AcOEt (1 : 1) mixture, filtered off, and recrystallized from an EtOH—Et_2O—AcOEt (1 : 2 : 2) mixture. Compound **4**, m.p. 230 °C, was obtained as a white powder in a yield of 0.45 g (88%). Found (%): C, 42.51; H, 8.54; N, 8.12. $C_{12}H_{30}Cl_2N_2S_2$. Calculated (%): C, 42.72; H, 8.96; N, 8.30. ^{1}H NMR (DMSO-d_6), δ: 8.02 (s, 3 H, NH_3^+); 2.75 (t, 2 H, CH_2N, J = 6.6 Hz); 2.71 (t, 2 H, CH_2S, J = 7.7 Hz); 1.62 (m, 2 H, CH_2); 1.56 (m, 2 H, CH_2); 1.34 (m, 4 H, $(CH_2)_2$).

Compound **2.** A solution of KOH (0.075 g, 1.3 mmol) in EtOH was added to a solution of ammonium salt **4** (0.45 g, 1.3 mmol) in EtOH. The mixture was stirred for 15 min at room temperature. A precipitate of KCl was filtered off, and the solvent was removed under reduced pressure. The residue was dissolved in anhydrous dichloroethane (10 mL), and sodium triacetoxyborohydride (0.83 g, 3.9 mmol) in dichloroethane (10 mL) and pyridine-2-carbaldehyde (0.31 g, 2.9 mmol) were added to the resultant solution. The mixture was stirred for 18 h at ~20 °C, a saturated solution of $NaHCO_3$ (20 mL) was added, and organics was extracted with ethyl acetate (3×10 mL). The organic fractions were dried with anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. Compound **2** was obtained in a yield of 0.66 g (81%).

N*-[4-Methylthiobenzyl]-*N*,*N*-bis(2-pyridylmethyl)amine (7).** ***A. A solution of dipicolylamine (**1**) (0.3 g, 1.5 mmol) in absolute MeOH containing AcOH (0.13 g, 2 mmol) was added to a solution of 4-methylbenzaldehyde (0.29 g, 1.9 mmol) in MeOH, and then $NaBH_3CN$ (0.14 g, 2 mmol) was added by portion, avoiding warming of the reaction mixture. Then the mixture was stirred for 24 h at ~20 °C under argon. Concentrated HCl was added to pH 2, and the mixture was stirred for 1 h. The solvent was removed under reduced pressure, and the residue was dissolved in water and washed with CH_2Cl_2. The aqueous phase was alkalized with a solution of $NaHCO_3$ to pH 8, and organics was extracted with CH_2Cl_2. The organic extracts were dried with anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. Compound **7** was obtained as a yellow oil in a yield of 0.37 g (73%). ^{1}H NMR ($CDCl_3$), δ: 8.48 (d, 2 H, HC(6), HC(6′), Py, J = 8.7 Hz); 7.58 (t, 2 H, HC(4), HC(4′), Py, J = 7.3 Hz); 7.52 (d, 2 H, HC(3), HC(3′), Py, J = 7.3 Hz); 7.28 (t, 2 H, HC(5), HC(5′), Py, J = 8.7 Hz); 7.16 (d, 2 H, HC(2), HC(6), Ph, J = 8.3 Hz); 7.08 (d, 2 H, HC(3), HC(5), Ph, J = 8.3 Hz); 3.93 (s, 4 H, CH_2Py); 3.75 (s, 2 H, CH_2Ph); 2.40 (s, 3 H, MeS). MS, m/z (I_{rel} (%)): 335 (12%) $[M]^+$.

B. Potassium carbonate (0.41 g, 3 mmol) was added to a solution of 4-methylthiobenzyl chloride (0.3 g, 1.7 mmol) and dipicolylamine (**1**) (0.4 g, 2 mmol) in DMF (5 mL). The reaction mixture was stirred at room temperature for 48 h. After reaction completion, water (3 mL) was added to the mixture, and organics was extracted with CH_2Cl_2 (3×5 mL). The organic extracts were dried with anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. Compound **7** was obtained in a yield of 0.48 g (84%).

Bis(4-{[*N*,*N*-bis(2-pyridylmethyl)amino]methyl}phenyl) disulfide (8). A solution of dipicolylamine **1** (0.24 g, 1.2 mmol) in absolute MeOH containing AcOH (0.23 g, 3.8 mmol) was added to a solution of bis(4-formylphenyl) disulfide (0.17 g, 0.6 mmol), and then $NaBH_3CN$ (0.24 g, 3.8 mmol) was added by portions, avoiding warming of the reaction mixture. The resultant mixture was stirred for 24 h at ~20 °C under argon. Concentrated HCl was added to pH 2, and the mixture was stirred for 1 h. The solvent was evaporated under reduced pressure, and the residue was dissolved in water and washed with CH_2Cl_2. The aqueous phase was alkalized with $NaHCO_3$ to pH 8 and extracted with CH_2Cl_2. The organic extracts were dried with anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. Compound **8** was obtained as a yellow oil in a yield of 0.3 g (78%). ^{1}H NMR ($CDCl_3$), δ: 8.48 (d, 2 H, HC(6), HC(6′), Py, J = 8.7 Hz); 7.58 (t, 2 H, HC(4), HC(4′), Py, J = 7.3 Hz); 7.52 (d, 2 H, HC(3), HC(3′), Py, J = 7.3 Hz); 7.28 (t, 2 H, HC(5), HC(5′), Py, J = 8.7 Hz); 7.16 (d, 2 H, HC(2), HC(6), Ph, J = 8.3 Hz); 7.08 (d, 2 H, HC(3), HC(5), Ph, J = 8.3 Hz); 3.87 (s, 4 H, CH_2Py); 3.65 (s, 2 H, CH_2Ph). MS, m/z (I_{rel} (%)): 641 $[M]^+$ (10%).

Bis(11-bromoundecyl) disulfide (10). A solution of 11-bromo-1-undecanethiol (1.49 g, 5.6 mmol) in MeOH (15 mL) was titrated with a 1 *M* solution of iodine in MeOH until the solution turned light yellow and this color did not disappear for several minutes. To remove a iodine excess, a small amount of sodium sulfite was added to the mixture, which was stirred to dissolution. The solution was cooled, and the precipitate that formed was filtered off and washed with EtOH. Disulfide **10**, m.p. 102—103 °C, was obtained as white crystals in a yield of 1.34 g (90%). Found (%): C, 50.05; H, 8.44; S, 12.34. $C_{22}H_{44}S_2Br_2$. Calculated (%): C, 49.62; H, 8.27; S, 12.03. ^{1}H NMR ($CDCl_3$), δ: 3.43 (t, 2 H, CH_2Br, J = 6.8 Hz); 2.70 (t, 2 H, CH_2S, J = 7.4 Hz); 1.87 (m, 2 H, CH_2); 1.69 (m, 2 H, CH_2); 1.42 (m, 2 H, CH_2); 1.31 (m, 12 H, $(CH_2)_6$).

4,4′-[Dithiobis(undecane-11,1-diyloxy)]dibenzaldehyde (11). Dibromide **10** (1.1 g, 2.05 mmol) was added to a suspension of 4-hydroxybenzaldehyde (0.5 g, 4.1 mmol) and anhydrous potassium carbonate (0.68 g, 4.9 mmol) in absolute DMF (10 mL). The reaction mixture was stirred for 18 h at 60 °C. The mixture was cooled to ~20 °C, water (20 mL) was added, and organics was extracted with CH_2Cl_2 (3×10 mL). The organic extracts were washed with brine and dried with anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure. Compound **11** was obtained as a yellow oil in a yield of 1 g (79%). ^{1}H NMR ($CDCl_3$), δ: 9.85 (s, 1 H, CHO); 7.80 (d, 2 H, HC(2), HC(6), Ph, J = 7.9 Hz); 6.96 (d, 2 H, HC(3), HC(5), Ph, J = 7.9 Hz); 4.01 (t, 2 H, CH_2O, J = 6.4 Hz); 2.66 (t, 2 H,

CH_2S, J = 7.9 Hz); 1.79 (m, 2 H, CH_2); 1.65 (m, 2 H, CH_2); 1.43 (m, 2 H, CH_2); 1.28 (m, 12 H, $(CH_2)_6$). MS, m/z (I_{rel} (%)): 615 (13%) $[M]^+$.

4,4´-[Dithiobis(undecane-11,1-diyloxy)]bis{[*N*,*N*-bis(2-pyridylmethyl)aminomethyl]benzene} (9). A solution of dipicolylamine **1** (0.26 g, 1.3 mmol) in absolute MeOH containing AcOH (0.31 g, 5 mmol) was added to a solution of dibenzaldehyde **11** (0.5 g, 0.8 mmol) in MeOH. Then $NaBH_3CN$ (0.31 g, 5 mmol) was added by portions, avoiding warming of the resultant mixture. The reaction mixture was stirred for 24 h under argon atmosphere at ~20 °C, concentrated HCl was added to pH 2, and the mixture was stirred for 1 h. The solvent was evaporated under reduced pressure, and the residue was dissolved in water and washed with CH_2Cl_2. The aqueous phase was alkalized to pH 8 by the addition of $NaHCO_3$ and organics was extracted with CH_2Cl_2. The organic extracts were dried with anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. Compound **9** was obtained as a yellow oil in a yield of 0.45 g (71%). ^{1}H NMR ($CDCl_3$), δ: 8.61 (d, 2 H, HC(6), HC(6´), Py, J = 4.5 Hz); 7.78 (t, 2 H, HC(4), HC(4´), Py, J = 7.8 Hz); 7.52 (d, 2 H, HC(3), HC(3´), Py, J = 7.8 Hz); 7.43 (t, 2 H, HC(5), HC(5´), Py, J = 5.7 Hz); 7.34 (d, 2 H, HC(2), HC(6), Ph, J = 7.9 Hz); 6.90 (d, 2 H, HC(3), HC(5), Ph, J = 7.9 Hz); 4.25 (s, 4 H, CH_2Py); 4.13 (s, 4 H, CH_2Ph); 3.74 (t, 2 H, CH_2O, J = 6.9 Hz); 2.68 (t, 2 H, CH_2S, J = 7.8 Hz); 1.76 (m, 2 H, CH_2); 1.67 (m, 2 H, CH_2); 1.44 (m, 2 H, CH_2); 1.27 (m, 12 H, $(CH_2)_6$). MS, m/z (I_{rel} (%)): 981 (12%) $[M]^+$.

Potassium *N*,*N*-bis(2-pyridylmethyl)glycinate (13). Bromoacetic acid (0.28 g, 2 mmol) and KOH (0.24 g, 4 mmol) were added to a solution of dipicolylamine **1** (0.8 g, 2 mmol) in water (20 mL). The mixture was stirred for 32 h under argon at ~20 °C and organics was extracted with CH_2Cl_2 (3×10 mL). The organic extracts were dried with anhydrous Na_2SO_4, the solvent was washed under reduced pressure, and the residue was washed with MeCN. Compound **13** was obtained as a brown powder in a yield of 0.56 g (92%). ^{1}H NMR (DMSO-d_6), δ: 8.45 (d, 2 H, HC(6), HC(6´), Py, J = 4.9 Hz); 7.72 (td, 2 H, HC(4), HC(4´), Py, J_1 = 1.7 Hz, J_2 = 7.7 Hz); 7.56 (d, 2 H, HC(3), HC(3´), Py, J = 7.7 Hz); 7.21 (td, 2 H, HC(5), HC(5´), Py, J_1 = 1.5 Hz, J_2 = 6.3 Hz); 3.88 (s, 4 H, CH_2Py); 2.86 (s, 2 H, CH_2CO). MS, m/z (I_{rel} (%)): 295 (9%) $[M]^+$.

1,24-Bis[*N*,*N*-bis(2-pyridylmethyl)glycinoyloxy]-12,13-dithiatetracosane (12). Potassium carbonate (0.41 g, 3 mmol) was added to a solution of salt **13** (0.5 g, 1.7 mmol) and disulfide **10** (0.55 g, 1 mmol) in DMF (10 mL), and the reaction mixture was stirred for 48 h at ~20 °C. Water (10 mL) was added and organics was extracted with CH_2Cl_2 (3×10 mL). The organic extracts were washed with brine and dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure. Compound **12** was obtained as a beige oil in a yield of 0.66 g (88%). ^{1}H NMR ($CDCl_3$), δ: 8.50 (d, 2 H, HC(6), HC(6´), Py, J = 5.8 Hz); 7.63 (td, 2 H, HC(4), HC(4´), Py, J_1 = 1.9 Hz, J_2 = 7.7 Hz); 7.55 (d, 2 H, HC(3), HC(3´), Py, J = 7.8 Hz); 7.13 (td, 2 H, HC(5), HC(5´), Py, J_1 = 1.4 Hz, J_2 = 5.8 Hz); 4.07 (t, 2 H, CH_2O, J = 6.9 Hz); 3.78 (s, 4 H, CH_2Py); 2.89 (s, 2 H, CH_2CO); 2.65 (t, 2 H, CH_2S, J = 7.5 Hz); 1.62 (m, 4 H, $(CH_2)_2$); 1.27 (m, 14 H, $(CH_2)_7$). MS, m/z (I_{rel} (%)): 884 (11%) $[M]^+$.

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