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NEW ORGANIC LIGANDS OF THE TERPYRIDINE SERIES: MODIFICATION OF GOLD NANOPARTICLES, PREPARATION OF COORDINATION COMPOUNDS WITH Cu(I), CATALYSIS OF OXIDATION REACTIONS*

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Organic ligands containing terpyridine and disulfide groupings linked between one another by a bonding –$O(CH_2)_n$- (n = 6, 12) fragment have been synthesized. Gold nanoparticles of mean size 1.8 nm modified with the indicated ligand were obtained by the method of Brust. By methods of electron spectroscopy and cyclic voltamperometry, the possibility of forming of coordinated compounds on the surface of gold nanoparticles modified by a terpyridine ligand, on interaction with $Cu(MeCN)_4ClO_4$ has been shown. The obtained nanoparticles catalyze the oxidation of 2,4-di-tert-butylphenol into 3,3',5,5'-tetra(tert-butyl)biphenyl-2,2'-diol.

Keywords: disulfides, complexes of metal peroxides, copper(I), Au nanoparticles, terpyridines, catalysis, electrochemistry.

The search for low molecular analogs of natural metalloenzymes as catalysts of organic reactions is an urgent problem of contemporary bioinorganic chemistry. Copper-containing redox-enzymes of type **3** (hemocyanine, tyrosinase, and catechol oxidase) are capable of reversibly binding molecular oxygen, fulfilling in the animal organism the function of transferers of oxygen (hemocyanine), catalysts of phenolic hydroxylation in the *o*-position (tyrosinase) or oxidation of pyrocatechols into the corresponding *o*-quinones (catechol oxidase) [1-3]. The first attempts to imitate the monooxygenase activity of type **3** copper-containing enzymes were undertaken in the fifties of the twentieth century [4]. It was then discovered that the simplest salts of monovalent copper were capable of catalyzing the oxidation of phenols. Later, similar catalytic activity was shown for coordination compounds of Cu(I) with pyridine and phenanthroline [5-8]. However, as a rule, the reactions led to the formation of mixtures of products and the mechanism of carrying out the conversions remained unclear. For example it was shown at the same time that copper(I) complexes with organic ligands were capable of catalyzing the oxidation of pyrocatechols to *o*-quinones [6]. Later Karlin and co-workers [9-11] synthesized a series of binuclear coordination compounds of copper with trimethylpyridylamine (TMPA) and

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* Dedicated to Academician of the Russian Academy of Sciences N. S. Zefirov on the occasion of his jubilee.

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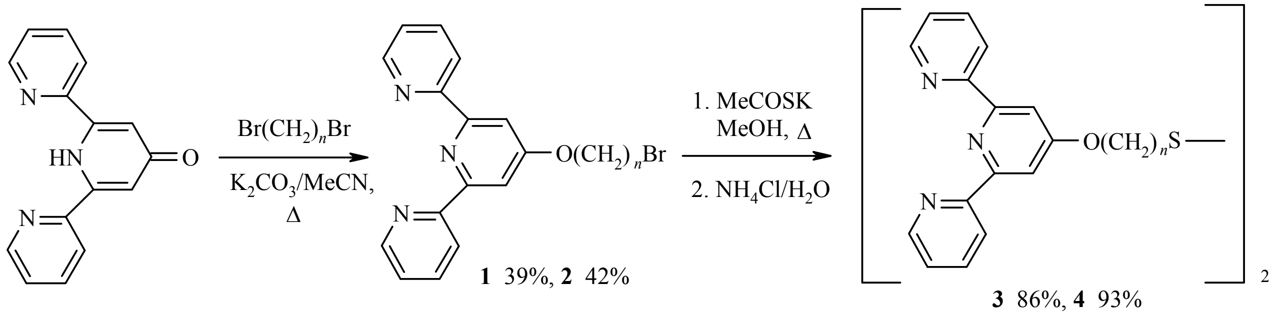
its derivatives, which react reversibly with oxygen. The activation of oxygen with binuclear complexes of copper(I) was also effected with the aid of coordination compounds containing a *m*-xylyltetrapyridyl grouping [12, 13], ligands of the imidazole series [14], pyrazole, anddimethylpyrazole [15-18]. The last of the indicated compounds displayed high catalytic activity in the oxidation of 3,5-di-*tert*-butylpyrocatechol to 3,5-di-*tert*-butyl-*o*-quinone [16, 17]. The binuclear copper-containing complexes of bis-imidazole-substituteddiimines display monooxygenase activity [19]. Ligands of the N-(2-hydroxybenzyl)amino acid series [20] form complexes with copper(I) ions, which display catechol oxidase activity.

Coordination of transition metal ions by ligands, secured on the surface of nanoparticles of noble metals, opens a route to metal-complex catalysts combining the merits of homogeneous catalysis (high activity and comparative simplicity for establishing the reaction mechanism) with the merits of heterogeneous catalysts (ease of separation from reaction products and the possibility of repeated use) [21]. At the present time, only individual examples of reactions proceeding under catalysis by nanoparticles modified by metal complexes are described in the literature [22, 23].

The aim of the present work was to synthesize new organic ligands of the terpyridine series to stabilize gold nanoparticles and to investigate their complex formation on the gold surface with $Cu(MeCN)_4ClO_4$, and also to study the catalytic properties of nanoparticles modified in this way in the oxidation of 2,4-di-*tert*-butylphenol.

To obtain terpyridine derivatives **3, 4** the bromoalkyloxy-substituted terpyridines **1, 2** were first synthesized by the alkylation of 2,6-dipyridylpyridone with α,ω-dibromoalkanes with MeCN in the presence of K_2CO_3 as base:



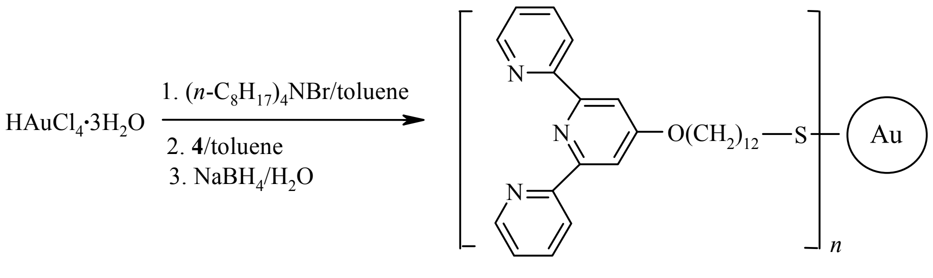
1 39%, **2** 42%

3 86%, **4** 93%

1, 3 $n = 6$, **2, 4** $n = 12$

To obtain a predominance of the monooxidation products **1, 2** and suppression of the formation of products of nucleophilic substitution of both bromine atoms in the dibromoalkane, a threefold excess of the alkylating agent was used. Compounds **1** and **2** were then reacted by nucleophilic substitution with potassium thioacetate. After hydrolysis, in the course of which oxidation of the initially formed alkanethiol to disulfide by oxygen of the air occurred, disulfides **3** and **4** were isolated in high yield.

Synthesis of gold nanoparticles modified by ligand **4** was carried out by the method of Brust [24].



According to the data of transmitting electron microscopy (Fig. 1), the nanoparticles obtained have a mean size of 1.8 nm.

To confirm the adsorption of terpyridine derivative **4** on the gold surface and its interaction with $Cu(MeCH)_4ClO_4$ the synthesized nanoparticles were investigated by IR spectroscopy. Bands were observed in the IR spectrum of the gold nanoparticles modified with disulfide **4** for the stretching vibrations of C=C(Ar) and C=N(Ar) groups at 1662, 1581, and 1562 cm^{-1}. On interacting the indicated nanoparticles with Cu(I) a displacement occurred in the vibrational bands of fragments C=C(Ar) and C=N(Ar) into the region of 1656, 1606, and 1565 cm^{-1}, which confirms the formation of a coordinated compound on the gold surface.

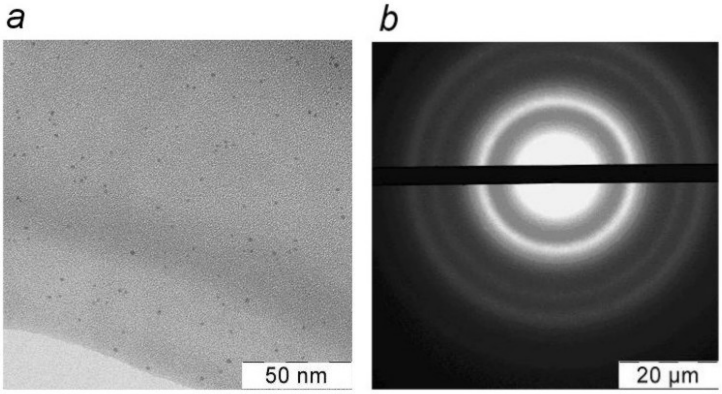


Fig. 1. Gold nanoparticles modified with disulfide **4** according to transmission electron microscopy: *a* electron photomicrograph; *b* electron diffractogram.

Study of the complex formation of ligand **4** on the surface of gold nanoparticles with $Cu(MeCN)_4ClO_4$ in MeCN solution, and the possibility of binding molecular oxygen to the resulting complex, was carried out by optical spectroscopy. The present method is one of the most available and convenient for the analysis of nanoparticles, enabling indirect assessment of their size, and also to fix the progress of complex formation and changes in the coordination sphere of the metal ion on the surface of the nanoparticles.

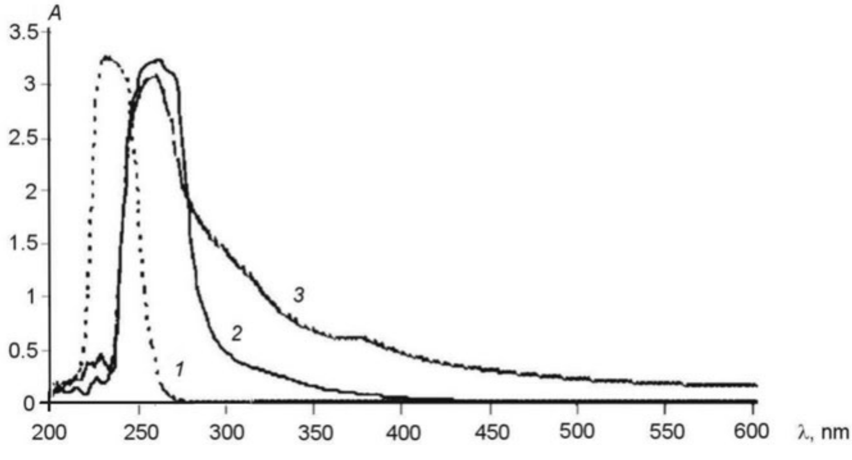


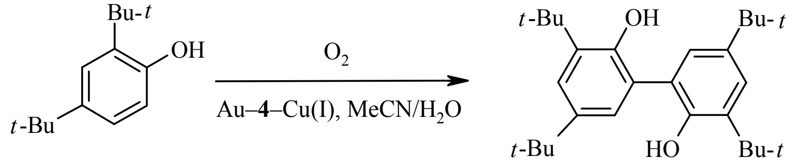
Fig. 2. Electronic spectra of solutions of *1* – $Cu(MeCN)_4ClO_4$; *2* – ligand **4**; *3* – ligand **4** after adding $Cu(MeCN)_4ClO_4$ and passing air through for 1 h (conc. 10^{-3} M, MeCN).

Electronic spectra of the intermediates formed on linking molecular oxygen with Cu(I) complexes always contain intense absorption maxima corresponding to O→Cu charge transfer. The position of these absorption maxima are characteristic and enable discrimination of structural types of the resulting complexes [*trans*-1,2-peroxo-, μ-η^2:η^2-peroxo-, bis(μ-oxo)- etc.] [25-28].

There was a single absorption band in the electronic spectrum of ligand **4** in the UV region at 261 nm. A solution of $Cu(MeCN)_4ClO_4$ also absorbs only in the UV region of the spectrum (Fig. 2). After mixing solutions of **4** and $Cu(MeCN)_4ClO_4$ insignificant displacements of the absorption maximum of the ligand into the long-wave region of the spectrum (258 nm). After passing air through the solution obtained for 1 h two additional maxima appeared in the spectra at 316 and 379 nm, which were not observed for the free ligand or for monovalent copper perchlorate. These absorption bands are characteristic of binuclear bis(μ-oxo) complexes of copper(III) [27, 28] (Fig. 2).

In the electronic spectra of solutions of nanoparticles modified with ligand **4** (concentration 10 mg/ml, toluene) plasma resonance bands were observed at 558 nm. After treatment of this solution with $Cu(MeCN)_4ClO_4$ the plasma resonance band was displaced into the long-wave region to 660 nm, which indicates the formation of aggregates larger-sized.

It is known from literature data that intermediates of similar structure may be used for catalysis of the oxidation of phenols and pyrocatechols [13, 14]. The catalytic properties of gold nanoparticles modified with ligand **4** in the presence of monovalent copper perchlorate were investigated by us in a model reaction of oxidizing 2,4-di-*tert*-butylphenol by oxygen of the air. After passing air for 4 h at room temperature into a solution containing 2,4-di-*tert*-butylphenol and nanoparticles modified by coordination compounddisulfide **4** with $Cu(MeCN)_4ClO_4$, 4,4',6,6'-tetra-*tert*-butylphenyl-2,2'-diol **5** was obtained in 25% yield.



5, 25%

We note that no formation of other possible oxidation products of the initial phenol (*o*-quinones, hydroquinones, etc.) was observed. The complex formed therefore selectively catalyzes the oxidation of 2,4-di-*tert*-butylphenol to the corresponding biphenyl in moderate yield.

Complex formation between ligand **4** and $Cu(MeCN)_4ClO_4$ was also investigated by us on the surface of a gold electrode by cyclic voltamperometry (CVA). It is known that thiols anddisulfides form self-organizing monolayers (SOM) on the surface of noble metals [29]. To obtain SOM of compound **4** on the Au surface, the gold electrode was stored in an acetonitrile solution of the ligand (conc. = 10^{-6} M) for 12 h. After this the electrode was washed several times with solvent, with acetone, and CVA curves were drawn. The obtained results are shown in Table 1 and in Fig. 3.

Ligands **3** and **4** on the surface of the Au electrode were oxidized at 1.62 and 1.24 V respectively, but were reduced in three stages. For the first stage of reduction $\Delta E = E_p^{Red} - E_p^{Ox}$ between the first and the reversible peak was 150 and 270 mV respectively (see Table 1).

After maintaining the Au electrode with ligand **4** adsorbed onto it in $Cu(MeCN)_4ClO_4$ solution for 12 h the CVA curves were changed (Table 1 and Fig. 3). Three oxidation peaks were observed on the anodic curve. Peak **A** at 0.37 V probably corresponds to the oxidation of Cu(I) to Cu(II) in the composition of the complex compound with ligand **4**. Oxidation of Cu(I) to Cu(II) for $Cu(MeCN)_4ClO_4$ occurs at a potential of 0.46 V under the conditions of the investigation (see Table 1).

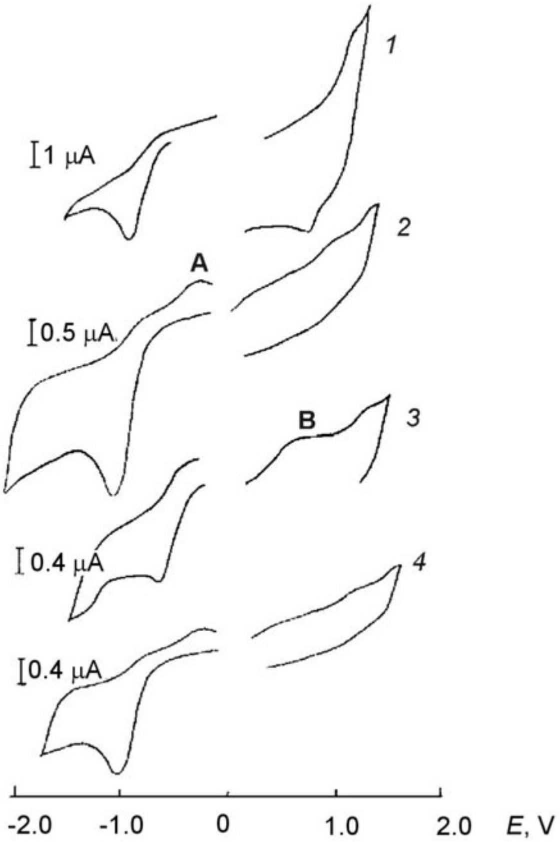


Fig. 3. Cyclic voltamperograms (DMF, conc. = 10^{-3} M, 0.1 M Bu_4NBF_4); *1* – ligand **4** adsorbed on the Au electrode; *2* – ligand **4** adsorbed on the Au electrode after treatment with $Cu(MeCN)_4ClO_4$; *3* – and *4* – ligand **4** on the Au electrode after sequential treatment with $Cu(MeCN)_4ClO_4$ and blowing oxygen through the solution for 40 min, (*3*) first scanning of potential and (*4*) fourth scanning of potential.

TABLE 1. Oxidation and Reduction Potentials of Terpyridines **3**, **4** Adsorbed on the Au Electrode, and of Products of Their Interaction with $Cu(I)(MeCN)_4ClO_4$, measured by CVA (relative to the Ag/AgCl/KCl saturated electrode; DMF; 0.1 M Bu_4NBF_4).

Compound	Oxidation (reversible peaks) E_p^{Ox}, V	Reduction (reversible peaks) E_p^{Red}, V
3	1.62 (1.18)	-0.74 (0.59); –1.68 (1.40)
4	1.24 (0.72)	-0.92 (0.65); –1.50
4 + $Cu(MeCN)_4ClO_4$	0.37; 1.12; 1.36 [0.36; 1.15 V]*	-0.85 (0.12; 0.67); -1.56 [-0.82/–0.16; -0.62; -1.58]*
4 + $Cu(MeCN)_4(ClO_4)$ after passing oxygen through the solution for 40 min		
first scanning of potential	1.02 [1.14/0.6]*	-0.70 (0.50); -1.26; -1.59
fourth scanning of potential	0.44; 1.06	-1.00 (0.68); –1.60
$Cu(MeCN)_4ClO_4$	0.46 (0.23); 1.20*	-0.32 (0.06)*

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*For a solution in MeCN

To demonstrate the binding of oxygen on the surface of the electrode by the complex copper(I) compound with ligand **4,** the electrode, modified by sequential treatment with ligand **4** and Cu(MeCN)$_4$ClO$_4$ was placed in pure base solution through which a stream of oxygen was passed for 40 min (Table 1 and Fig. 3). On the CVA oxidation curve taken after passing oxygen the anodic peak (E_p^{Ox} ~ 0.4 V) corresponding to the Cu(I)/Cu(II) transition was absent. Only one peak **B** was observed on the anodic curve at 1.02 V, corresponding to the oxidation of the Cu(II) complex. On numerous scannings of potential from 0.00 to 1.10 V in the anodic region the peak at ~0.4 V was displayed , i.e. the initial Cu(I) complex was regenerated, which was oxidized on the surface of the gold electrode by oxygen of the air to the Cu(II) complex. The obtaineddata confirm the possibility of reversibly binding molecular oxygen with the complex of ligand **4** with Cu(I) on the gold surface.

We have shown therefore the possibility of binding molecular oxygen with a complex of ligand **4** with Cu(I) on the surface of both gold nanoparticles and the gold electrode. The nanoparticles modified by the coordination compound of ligand **4** with Cu(I) are capable of catalyzing the oxidation of phenols into the corresponding dihydroxybiphenyls.

EXPERIMENTAL

The IR spectra were obtained on a UR-20 instrument. The ^{1}H and ^{13}C NMR spectra were described on a Bruker Avance (400 and 100 MHz respectively) instrument in CDCl$_3$, internal standard was HMDS (δ 0.05 ppm). Electronic spectra in the UV and visible regions were recorded on a Hitachi U-2900 instrument. Analysis by GC-MS was effected on a Finnigan MAT SSQ 7000 chromato-mass spectrometer; ionization energy was 70 eV, quartz capillary column OV-1 (25 m), temperature regimen 70°C (2 min) then 20°C/min to 280°C (10 min).

Photomicrographs of samples were obtained on a LEO 912 AB OMEGA transmitting electron microscope (Carl Zeiss, Germany), operating accelerating voltage was 100 kV. Samples were prepared by applying a solution (1-2 μl) to copper mesh (d = 3.05 mm) coated with formvar, which was then air dried. A check on the progress of reactions and the homogeneity of compounds was effected by TLC on Silufol plates.

A PI-50-1.1 potentiostat, switched to a PR-8 programer, was used for electrochemical investigations. The operating electrode was a golddisk (d = 1 mm), base electrolyte was 0.1 M Bu$_4$NBF$_4$ solution in DMF, reference electrode a Ag/AgCl/KCl saturated, and auxiliary electrode a platinum plate. The rate of scanning the potential was 200 mV/s, potentials are given allowing for iR compensation. All measurements were carried out in an atmosphere of dry argon. Samples were dissolved in previously deaerated solvent. DMF of pure grade was purified by stirring with freshly calcined K$_2$CO$_3$ for 4 days, with subsequent distillation in vacuum initially over P$_2$O$_5$ and then over anhydrous CuSO$_4$.

2,6-Bis(2'-pyridyl)-4-pyridone was synthesized by the procedure of [30] from 1,5-di(2-pyridyl)pentan-1,3,5-tri-one [30] and ammonium acetate.

Interaction of 2,6-Bis(2-pyridyl)-4-pyridone with α,ω-Dibromoalkanes (General Method). 2,6-Bis(2-pyridyl)-4-pyridone was dissolved in absolute acetone and α,ω-dibromoalkane and potassium carbonate were added to the solution. The reaction mixture was boiled for 12 h. The precipitated solid was filtered off, and the solvent removed in vacuum. The reaction product was isolated by column chromatography in the system petroleum ether–ethyl acetate, gradient elution, initial ratio of solvents 4:1, final 2:1.

4'(6-Bromohexyloxy)[2,2'; 6',2"]terpyridine (1). As the result of the reaction of 2,6-bis(2-pyridyl)-4-pyridone (0.25 g, 1 mmol), 1,6-dibromohexane (0.49 g, 2 mmol), and potassium carbonate (0.28 g, 2 mmol), compound **1** (0.16 g, 39%) was obtained as a colorless oil. ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.55 (4H, m, (CH$_2$)$_2$); 1.90 (4H, m, (CH$_2$)$_2$); 3.44 (2H, t, J = 6.7, CH$_2$Br); 4.24 (2H, t, J = 7.5, CH$_2$O); 7.34 (2H, dd, J_1 = 3.9, J_2 = 7.2, H-5, H-5" Py); 7.86 (2H, t, J = 7.7, H-4, H-4" Py); 8.03 (2H, s, H-3', H-5' Py); 8.63 (2H, d, J = 7.9, H-3, H-3" Py); 8.71 (2H, d, J = 4.0, H-6, H-6" Py).

4'-(12-Bromododecanyloxy)[2,2';6',2"]terpyridine (2). As a result of the reaction of 2,6-bis(2-pyridyl)-4-pyridone (0.34 g, 1.4 mmol), 1,12-dibromododecane (0.89 g, 2.8 mmol), and potassium carbonate (0.37 g, 2.8 mmol), compound **2** (0.28 g, 42%) was obtained as a white powder; mp 97-98°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.40 (14H, m, $(CH_2)_7$); 1.56 (2H, m, CH_2); 1.88 (4H, m, $(CH_2)_2$); 3.37 (2H, t, *J* = 6.8, CH_2Br); 4.26 (2H, t, *J* = 6.4, CH_2O); 7.29 (2H, dd, J_1 = 4.7, J_2 = 7.4, H-5, H-5" Py); 7.81 (2H, t, *J* = 7.8, H-4, H-4" Py); 8.04 (2H, s, H-3', H-5' Py); 8.62 (2H, d, *J* = 7.5, H-3, H-3" Py); 8.66 (2H, d, *J* = 4.1, H-6, H-6" Py). ^{13}C NMR spectrum, δ, ppm: 167.0, 156.6, 156.2, 148.7, 136.1, 123.3, 121.0, 107.5, 67.8, 33.0, 32.8, 29.5, 29.4, 29.1, 28.8, 28.2, 26.1. Found, %: C 65.56; H 7.02; 8.31. $C_{27}H_{34}BrN_3O$. Calculated, %: C 65.32; H 6.85; N 8.47.

Preparation of Disulfides 3, 4 (General Method). Potassium thioacetate was added to a solution of 4'-(bromoalkyloxy)[2,2';6',2"]terpyridine in methanol. The reaction mixture was boiled for 10-12 h. After cooling, saturated ammonium chloride solution (20 ml) was added to the mixture, which was then extracted with methylene chloride (3 x 20 ml). The organic fraction was dried over anhydrous sodium sulfate, and the solvent removed in vacuum.

Bis[6'-1-([2,2';6',2"]terpyridyl)oxy]hexyl Disulfide (3). As a result of the reaction of compound **1** (0.16 g, 0.39 mmol) in methanol (10 ml) with potassium thioacetate (0.13 g, 1.2 mmol) for 10 h, compound **3** (0.12 g, 86%) was obtained as a pinkish oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.55 (4H, m, $(CH_2)_2$); 1.72 (2H, m, CH_2); 1.87 (2H, m, CH_2); 2.73 (2H, t, *J* = 7.3, CH_2S); 4.23 (2H, t, *J* = 6.3, CH_2O); 7.35 (2H, dd, J_1 = 4.8, J_2 = 6.8, H-5, H-5" Py); 7.84 (2H, t, *J* = 7.7, H-4, H-4" Py); 8.02 (2H, s, H-3', H-5" Py); 8.62 (2H, d, *J* = 7.9, H-3, H-3" Py); 8.69 (2H, d, *J* = 3.5, H-6, H-6" Py).

Bis[12'-1-([2,2';6',2"]terpyridyl)oxy]dodecanyl Disulfide (4). As a result of the reaction of compound **2** (0.25 g, 0.5 mmol) in methanol (15 ml) with potassium thioacetate (0.17 g, 1.5 mmol) for 12 h, compound **4** (0.22 g, 93%) was obtained as a pink-colored powder; mp 83-84°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.41 (14H, m, $(CH_2)_7$); 1.58 (2H, m, CH_2); 1.88 (4H, m, $(CH_2)_2$); 2.66 (2H, t, *J* = 7.3, CH_2S); 4.25 (2H, t, *J* = 6.3, CH_2O); 7.31 (2H, t, *J* = 4.8, H-5, H-5" Py); 7.83 (2H, t, *J* = 7.7, H-4, H-4" Py); 8.02 (2H, s, H-3', H-5' Py); 8.62 (2H, d, *J* = 8.1, H-3, H-3" Py); 8.68 (2H, d, *J* = 4.0, H-6, H-6" Py). ^{13}C NMR spectrum, δ, ppm: 167.2, 156.8, 156.2, 148.9, 136.4, 123.5, 121.2, 107.4, 68.0, 39.1, 34.0, 29.5, 29.3, 29.1, 28.4, 26.0, 24.6. Found, %: C 72.49; H 7.85; N 9.23; S 6.95. $C_{54}H_{68}N_6O_2S_2$. Calculated, %: C 75.32; H 7.59; N 9.38; S 7.14.

Synthesis of Nanoparticles Modified with Bis[12'-1-([2,2';6',2"]terpyridyl)oxy]dodecanyl Disulfide (4). A mixture of a solution (15 ml) of $HAuCl_4·3H_2O$ (0.17 g, 0.43 mmol) in distilled water and a solution of tetraoctylammonium bromide (0.26 g, 0.47 mmol) in toluene (10 ml) was stirred vigorously to transfer $HAuCl_4$ into the organic phase, which changed color from bright-yellow to dark-brown. The aqueous layer was separated, and disulfide **4** (0.035 g, 0.04 mmol) was added to the organic layer. A freshly prepared solution of $NaBH_4$ (0.18 g, 4.7 mmol) in distilled water (12 ml) was added dropwise with intense stirring. The reaction mixture was stirred for 3 h, the organic layer separated, evaporated to half volume, mixed with ethanol (50 ml) and maintained at -10°C for 4 h. The precipitated solid was filtered off and washed with ethanol. Modified nanoparticles of gold (0.2 g) were obtained. IR spectrum, ν, cm^{-1}: 1662, 1581, 1562 (C=C(Ar), C=N(Ar)).

Interaction of Gold Nanoparticles Modified with Bis[12'-1-([2,2';6',2"]terpyridyl)oxy]dodecanyl Disulfide (4), with $Cu(MeCN)_4ClO_4$. $Cu(MeCN)_4ClO_4$ (10 mg) was added to a suspension of gold nanoparticles (0.1 g) modified with ligand **4** in absolute MeCN (10 ml). The obtained mixture was stirred at room temperature for 1 day. The solid was filtered off and washed with ethanol. A black powder (0.08 g) was obtained. IR spectrum, ν, cm^{-1}: 1656, 1606, 1565 (C=C(Ar), C=N(Ar)).

Oxidation of 2,4-Di-*tert*-butylphenol Catalyzed by Modified Nanoparticles. A stream of air was passed through a solution of 2,4-di-*tert*-butylphenol (0.05 g, 0.2 mmol) in a mixture of MeCN–H_2O, 1:1, for 4 h in the presence of nanoparticles (1 mg) modified with coordination compound of disulfide **4** and $Cu(MeCN)_4ClO_4$ at room temperature. The reaction mixture was rinsed with concentrated aqueous ammonia solution (2 ml), and extracted with methylene chloride. The organic phase was dried over anhydrous sodium sulfate, and the solvent removed in vacuum.The reaction product (0.025 g) was obtained in the form of an oil. According to data of GC-MS it was a mixture of 4,4',6,6'-tetra-*tert*-butylphenyl-2,2'-diol (**5**) and the initial 2,4-di-*tert*-butylphenol in a ratio of 1:1.

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