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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Formation of Organo-Inorganic Hybrid Networks in the System Consisting of Tris(2,2'-bipyridine)ruthenium Complexes and Silica

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Abstract—Organo-inorganic composites consisting of mutually linked ruthenium complexes with organic ligands and an inorganic SiO_2 network were synthesized by the sol-gel method. The luminescence and photosensitive properties of the resulting compounds were studied.

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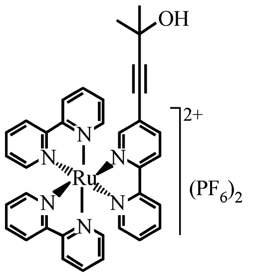
Thermally and chemically stable ruthenium(II) complexes with 2,2'-bipyridine derivatives have interesting photophysical, photochemical, and electrochemical properties. This allows them to be used for constructing photosensitive and electroluminescent devices, sensors, luminescent transducers, and catalysts [1–3]. Practical application of such structures is associated with their incorporation in a polymeric organic or inorganic matrix.

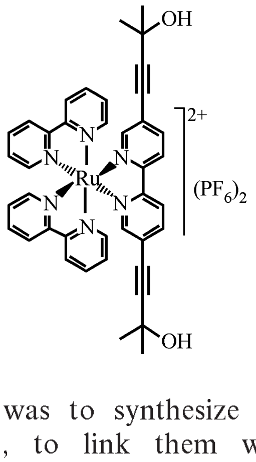
In case of organo-inorganic hybrids, the homogeneity and stability of the resulting structures is determined by the stability of the organic component of the system and by the possibility of its chemical binding with the inorganic network.

Tris(2,2'-bipyridine)ruthenium(II) complexes have unique thermal (500°C) and chemical stability: They are inert to concentrated sulfuric acid and to a 50% alkali solution [4]. The possibility of their chemical binding with an inorganic matrix by using special cross-linking agents has been shown earlier [5–8].

At the same time, further prospects for using organic complexes of transition metals, in particular, Ru^{2+}, in the form of organo-inorganic hybrids are associated with the possibility of the formation of a supramolecular organic structure based on them. In this structure, separate discrete centers of complex molecules should be connected with each other by chemical, preferentially double, bonds. An organic network synthesized in such a way opens principally new possibilities for electron movements, inaccessible for solutions of organic molecules. The most obvious method of preparing such structures is sol-gel synthesis of interpenetrating organo-inorganic hybrid networks.

To examine the basic possibility of the synthesis of such nanohybrid structures, we used ruthenium complexes containing in one of ligands substituents with triple bonds:



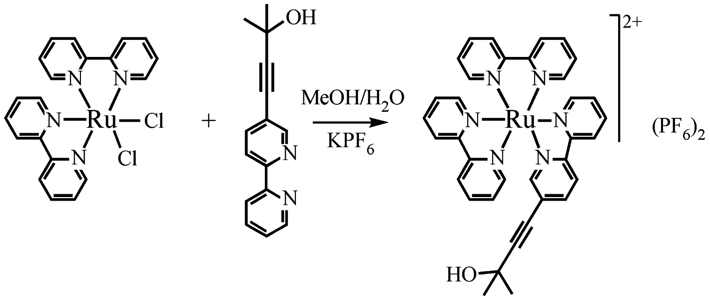


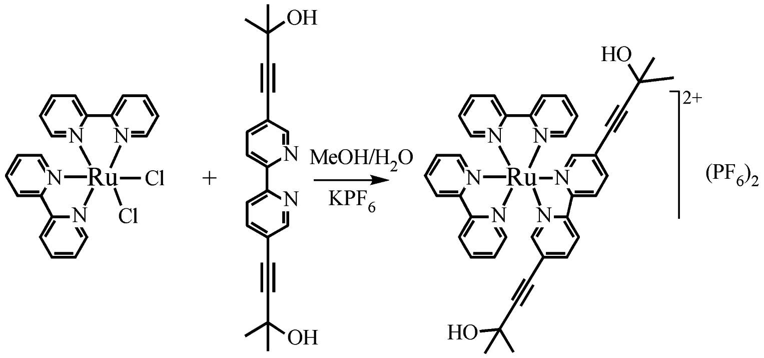
The goal of this study was to synthesize the above-mentioned complexes, to link them with each other by copolymerization with trimethoxysilicylacetylene (TMOSA), to incorporate the resulting structure into a silica matrix obtained by hydrolytic copolycondensation of tetramethoxysilane and TMOSA, and also to study physicomechanical and optical properties of the resulting materials.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 instrument, working frequencies 300.13 and 75.5 MHz, respectively, internal reference TMS. The absorption spectra were measured on an SF-56 spectrophotometer; the IR spectra, on a Bruker IFS-88 Fourier spectrometer; and the mass spectra, on an MKh5303 instrument equipped with an electrospraying ionization source (Institute of Analytical Instrument Making, Russian Academy of Sciences). The composition of reaction mixtures and purity of compounds were determined by thin-layer chromatography (TLC) on Silica gel 60 F254 and Armsorb TSKh-AN-UF 254 plates. In the synthesis we used Favorskii's carbinol and potassium hexafluorophosphate purchased from Aldrich. *cis*-[Bis-(2,2'-bipyridine)]ruthenium dichloride [9, 10], bis-(triphenylphosphine)palladium dichloride [11], copper(I) iodide [12], 5-bromo-2,2'-bipyridine, and 5,5'-dibromo-2,2'-bipyridine [13, 14] were prepared by the procedures described previously. The light sensitivity and quantum yields of photogeneration of charge carriers η were measured in the electrophotographic mode [15, 16] in the spectral range 400–800 nm at a field intensity E = (0.1–1.0)E_0, where E_0 is the limiting electric field strength for a material under study. The light sensitivity $S_{0.1}$ was determined by the criterion of a 10% decrease in the surface potential layer V in relation to the initial value ($\Delta V/V$ = 0.1) for illumination both by a monochromatic light with a wavelength from 400 to 700 nm and with a KGM-300 halogen lamp (integral light sensitivity).

Stable tris(2,2'-bipyridine)ruthenium complexes containing triple bonds conjugated with the bipyridine system were prepared with 5-(2-hydroxyisopropylethynyl)-2,2'-bipyridine and 5,5'-bis(2-hydroxyisopropylethynyl)-2,2'-bipyridine:





For this purpose, a suspension of 500 mg of [bis-(2,2'-bipyridine)]ruthenium dichloride and 1.05 equiv of functionally substituted 2,2'-bipyridine in a mixture of 40 ml of water and 40 ml of methanol was refluxed for 2 h until the complex bipy$_2$RuCl$_2$ disappeared (monitoring by TLC on aluminum oxide). The resulting solution was cooled and filtered, and 2.1 equiv of potassium hexafluorophosphate in 30 ml of water was added to the filtrate. The precipitate formed was filtered off, dried, dissolved in 2 ml of acetonitrile, and reprecipitated into 20 ml of absolute diethyl ether.

[Rubipy$_2$(bipy–C≡C–CMe$_2$OH)](PF$_6$)$_2$, yield 58%. ^{1}H NMR spectrum [(CD$_3$)$_2$SO], δ, ppm: 1.39 s (6H, CH$_3$), 5.57 s (1H, OH), 7.55 m (6H, 1H^6 + 5H$^{5,5'}$), 7.66–7.73 m (3H, $H^{6,6'}$), 7.78 d (1H, $H^{6'}$), 7.86 d (1H, H^{6}), 8.18 q (6H, $H^{4,4'}$), 8.83 t (6H, $H^{3,3'}$). ^{13}C NMR spectrum [$(CD_3)_2SO$], δ_C, ppm: 31.9 (CH_3), 64.6 (C–OH), 76.8 (C≡C), 104.1 (C≡C), 123.8, 125.0, 125.3, 125.5, 125.8, 128.7, 128.8, 128.9, 129.6, 138.9, 140.9, 151.9, 152.1, 152.3, 152.6, 152.8, 156.6, 156.8, 157.2, 157.4, 157.5. UV spectrum (CH_3CN), λ, nm (ε, l mol^{-1} cm^{-1}): 245 (23 800), 255 (21 100), 285 (68 700), 401 (5800), 453 (13 400). IR spectrum (KBr), ν, cm^{-1}: 3641 s, 3554 s, 3394 s, 3095 m, 3078 m, 2977 m, 2856 m, 2324 w, 2229 w (C≡C), 1604 m, 1467 s, 1369 m, 1311 m, 1271 m, 1240 m, 1166 m, 837 s, 761 s, 729 s, 557 s. Mass spectrum (solution in $CH_3CN : H_2O$ = 50 : 50, electrospray ionization): 797.11 ($[M–PF_6]^+$), 326.08 ($[M–2PF_6]^{2+}$).

[Rubipy$_2${bipy(C≡C–CMe$_2$OH)$_2$}](PF$_6$)$_2$, yield 49%. ^1H NMR spectrum [$(CD_3)_2SO$], δ, ppm: 1.38 s (6H, CH_3), 5.55 s (2H, OH), 7.51 s (2H, $H^{6,6'}$), 7.55 t (4H, $H^{5,5'}$), 7.72 d (2H, $H^{6,6'}$), 7.82 d (2H, $H^{6,6'}$), 8.20 t (6H, $H^{4,4'}$), 8.84 d (6H, $H^{3,3'}$). ^{13}C NMR spectrum [$(CD_3)_2SO$], δ_C, ppm: 31.9 (CH_3), 64.6 (C–OH), 76.8 (C≡C), 104.4 (C≡C), 118.9, 119.0, 123.9, 125.3, 125.4, 125.5, 128.8, 139.1, 140.9, 152.2, 152.7, 152.9, 156.0, 157.1, 157.5. UV spectrum (CH_3CN), λ, nm (ε, l mol^{-1} cm^{-1}): 255 (25 300), 285 (75 100), 320 (50 400), 345 (32 600), 401 (7600), 446 (13 000), 480 (10 200). IR spectrum (KBr), ν, cm^{-1}: 3626 s, 3550 s, 3394 s, 3101 s, 3076 s, 2927 s, 2864 m, 2231 (C≡C) m, 1600 s, 1471 s, 1367 m, 1274 s, 1242 s, 1168 s, 840 s, 763 s, 729 s, 557 s. Mass spectrum (solution in $CH_3CN : H_2O$ = 50 : 50, electrospray ionization): 879.15 ($[M–PF_6]^+$), 367.10 ($[M–2PF_6]^{2+}$).

According to the published data [17–22], TMOSA is prepared in two steps:

$$Si(OMe)_4 \text{ (or } SiCl_4) \rightarrow Si(OMe)_3Cl \rightarrow HC{\equiv}C{-}Si(OMe)_3.$$

Despite apparent simplicity of these transformations, this synthesis involved serious problems. Initially we thoroughly tested all the three known procedures [17–21] for preparing trimethoxychlorosilane:

$$3Si(OMe)_4 + SiCl_4 \overset{AlCl_3}{\rightleftarrows} 4Si(OMe)_3Cl,$$

$$Si(OMe)_4 + CH_3COCl \overset{AlCl_3}{\rightleftarrows} Si(OMe)_3Cl + CH_3COOMe,$$

$$SiCl_4 + 3MeOH \rightleftarrows Si(OMe)_3Cl + 3HCl.$$

The boiling points and refraction indices of thus obtained samples completely corresponded to the published values [17–21], and the elemental analysis seemed to confirm the trimethoxychlorosilane formation. However, detailed examination of their structure by NMR spectroscopy and mass spectrometry showed that the synthesized samples were mixtures containing at least three compounds: $Si(OMe)_2Cl_2$, $Si(OMe)_3Cl$, and $Si(OMe)_4$.

This result can be accounted for by closeness of their boiling points, possible formation of azeotropes, and/or disproportionation of methoxychlorosilanes on heating to boiling points.

The reaction of silicon tetrachloride with methanol appeared to be practically the most convenient. Analysis by chromatography–mass spectrometry showed that this reaction yielded a mixture of methoxychlorosilanes of the following composition (%): $Si(OMe)Cl_3$ 5, $Si(OMe)_2Cl_2$ 30, $Si(OMe)_3Cl$ 50, and $Si(OMe)_4$ 15.

The replacement of chlorine by the ethynyl group according to the known procedure [22] became the second step of the synthesis:

$$Si(OMe)_3Cl + HC{\equiv}CNa \rightarrow Si(OMe)_3C{\equiv}CH.$$

Unfortunately, here again the results were poorly reproducible and the yield of the final product was low. Variation of reaction conditions did not give a positive result. Therefore, we developed a new synthesis method using ethynylmagnesium bromide, which allowed us to considerably increase the yield of the target product:

$$Si(OMe)_3Cl + HC{\equiv}CMgBr \rightarrow Si(OMe)_3C{\equiv}CH.$$

According to the data of NMR spectroscopy, gas chromatography–mass spectrometry, and elemental analysis, the product obtained was a mixture of mono-, di-, and triethynylmethoxysilanes free from chlorine.

Attempts to separate this mixture failed. We could not increase the TMOSA content in the distillate to a value over 70%. However, this fact should not influence the formation of an organo-inorganic hybrid, as all the components contain building blocks necessary for it, namely, triple bonds and methoxy groups, allowing organic and inorganic networks, respectively, to be formed.

Polymerization via triple bonds was carried out by the modified procedure from [23]. The initial system consisted of tetramethoxysilane (0.5 equiv), a mixture of methoxysilylacetylenes (0.5 equiv), palladium chloride (0.01 equiv), and a solution of ruthenium complexes in propionitrile. The reaction mixture was left for two days at room temperature, and then the polycondensation process was carried out. For this purpose, 4 equiv of water and 0.1 equiv of trifluoroacetic acid were added to the system.

The resulting solutions were placed in sealed polypropylene test tubes and kept at 60°C for 2 days. Then hermetic stoppers to the tubes were replaced by perforated stoppers (hole diameter about 1 mm), and crude gels were dried for 10 h at 60°C, 14 h at 75°C, 24 h at 90°C, and 24 h at 110°C. The temperature was raised at a rate of 5 deg h^{-1}. After that, the gels were placed in glass test tubes with perforated stoppers, heated to 110°CC (15 deg h^{-1}), and kept for 12 h at this temperature.

The samples were synthesized in the form of monolithic structures: disks of width 3–7 mm and diameter 15–30 mm and cylinders of length 15–30 mm and diameter 4–6 mm, and also 1–2-μm-thick films on a polymeric support. The conditions for the hydrolysis of methoxy groups of the components and for polycondensation of the formed compounds were optimized by varying the acidity of the medium in the course of the sol–gel process and by simultaneously removing the formed alcohol in the form of volatile compounds [24].

The absorption spectra of the composites practically coincide with the spectra of the initial ruthenium complexes (Fig. 1).

All the synthesized samples show strong luminescence in the region of 610–630 nm (excitation with xenon lamp radiation with λ = 450 nm). The normalized luminescence spectra of the composites (Fig. 2) contain one emission band broadened as compared to solutions. Its position depends on the concentration of the ruthenium complex in the hybrid.

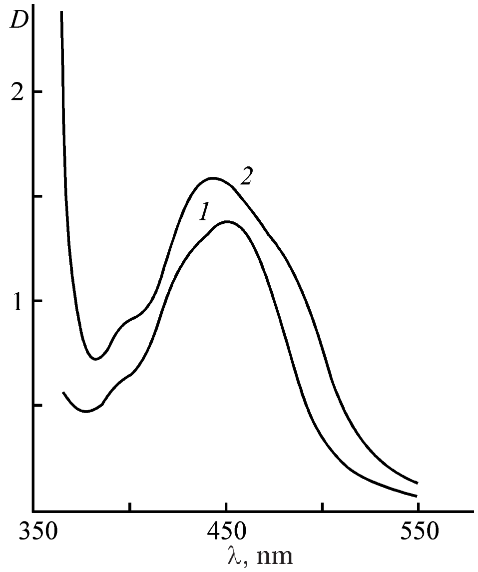


Fig. 1. Absorption spectra of ruthenium complexes. (*D*) Optical density and (λ) wavelength. Complex: (*1*) [Ru-bipy$_2$(bipy–C≡C–CMe$_2$OH)](PF$_6$)$_2$ and (*2*) [Ru-bipy$_2${bipy(C≡C–CMe$_2$OH)$_2$}](PF$_6$)$_2$; the same for Fig. 2.

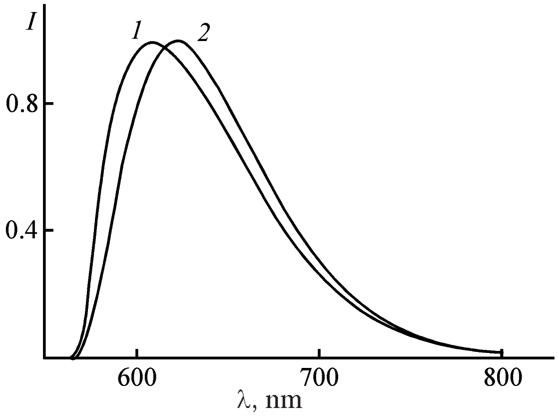


Fig. 2. Normalized luminescence spectra of composites containing various complexes. (*I*) Normalized intensity and (λ) wavelength.

The light sensitivity $S_{0.1}$ of the synthesized samples (Fig. 3) is at a level of (1–2) × 10^4 cm^2 J^{-1} in the spectral range 400–550 nm; the quantum yield of charge carriers is 0.005±0.001. These values are 2–4 times higher than the analogous value found previously for composites in which ruthenium complexes are covalently bonded with the silica matrix, but are not a part of an organic network and are not bonded with each other.

An insignificant bathochromic shift in absorption spectra (~10 nm), and also a weak decrease in the intensity of absorption bands of the –C≡C– bond in the IR spectra show that the structure connecting ruthenium complexes with each other is primitive and imperfect. However, a substantial growth of

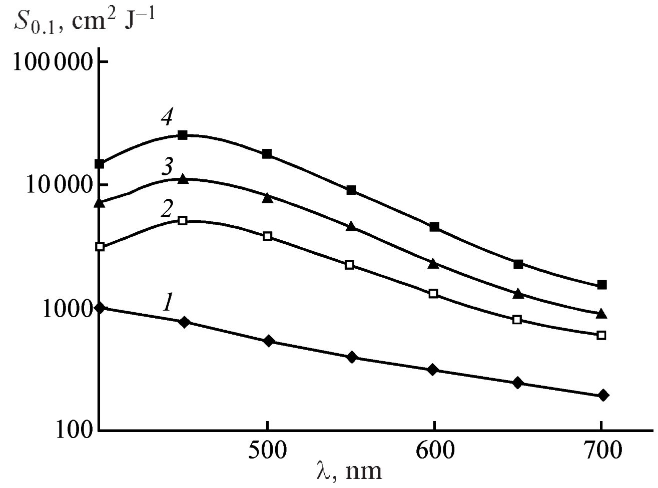


Fig. 3. Spectra of light sensitivity of composites. ($S_{0.1}$) Light sensitivity and (λ) wavelength. (*1*) Sample free of ruthenium complexes, (*2*) composite in which ruthenium complexes are not a part of a supramolecular structure [6], and (*3, 4*) composites with the ruthenium complexes under consideration: (*3*) $[\mathrm{Rubipy_2(bipy{-}C{\equiv}C{-}CMe_2OH)}](\mathrm{PF_6})_2$ and (*4*) $[\mathrm{Rubipy_2\{bipy(C{\equiv}C{-}CMe_2OH)_2\}}](\mathrm{PF_6})_2$.

light sensitivity of the composites, and also a 20–40 nm long-wave shift of the emission band maximum with increasing concentration of the ruthenium complex, as compared to composites in which the components are chemically bonded with each other but are not incorporated in a supramolecular structure, suggest the formation of a supramolecular organic network linking the ruthenium complexes.

CONCLUSIONS

(1) The new organo-inorganic hybrids based on Ru(II) complexes containing substituents with triple bonds in one of ligands were synthesized.

(2) Even incomplete binding of ruthenium complexes with each other with the formation of a supramolecular structure strongly enhances the luminescence and photosensitive properties of the synthesized samples.

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