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Self-Assembled Nanostructures Formation in Hybrid Metal-Mesogenic Systems

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Abstract

This chapter reviews the methods of supramolecular chemistry and cryochemistry to study the formation, morphological and structural properties, and possible applications of hybrid nanostructures and nanosized aggregates comprising plasmonic metals (silver and copper) and several mesogenic compounds, which exhibit different liquid crystalline mesophases—nematics, smectics, and cholesterics. Low-temperature vacuum co-condensation of reagent vapors on cooled surfaces of quartz, KBr, CaF_2, or polished copper was used to synthesize hybrid nanosystems including silver and copper and long-chain mesogenic derivatives of alkylcyanobiphenyls under molecular beam conditions. Controlled thermal treatment of the samples allowed the directed formation of metal nanoparticles of definite size from 2 up to 100 nm. It was shown that the procedures of temperature treatments and molecular self-organization of different liquid crystalline phases controlled the size and morphology of nanoparticles and their aggregates, which were formed in the system. Transmission electron microscopy (TEM) and atomic force microscopy (AFM) data of the samples show the formation of orientationally ordered structures in nematic mesophases. Formation of flat 2D aggregates was found in layered smectic mesophases. Optical absorbance spectra of silver/4-pentyl-4-cyanobiphenyl (Ag/5CB) and copper/4-pentyl-4-cyanobiphenyl (Cu/5CB) samples encapsulated in polymer poly-para-xylylene at 300 K contained characteristic bands of plasmonic absorbance of metal nanoparticles at 420–440 nm and 560–600 nm. Rising metal concentration in the sample led to the performable growth of rod-like metal particles with anisometric ratio l/d > 20 and intensive absorbance at higher wavelengths ($\lambda \geq 650$ nm). New hybrid nanosystems based on biomolecules of cholesterol or its heteroatomic analog thiocholesterol including nanosized silver particles of d = 5.0 ± 0.5 and d = 2.5 ± 0.5 nm, respectively, were obtained. Highly ordered 1D-, 2D-, and 3D structures containing silver nanoparticles were formed from concentrated organic sols at different support surfaces by removing the inert solvent from triple metal/ligand/solvent system and by cooling the binary metal/ligand system from isotropic state to the cholesteric liquid crystalline mesophase. The microstructure and composition of the hybrid nanosystems were characterized by FTIR, UV-Vis spectroscopy, TEM, and selected area electron diffraction (SAED). It was shown that hybrid

nanosystems based on silver nanoparticles covered by a stabilizing layer of mesogenic molecules of thiocholesterol display selectivity in adsorption of optical isomers of the selected compounds.

1. Introduction

This chapter reviews the methods of supramolecular chemistry and cryochemistry applied to study hybrid nanostructures and nanosized aggregates formed on plasmonic metals (silver and copper) and some mesogenic (liquid crystalline) compounds, which, in certain temperature ranges, reveal various liquid crystalline mesophases—orientationally ordered nematics, smectics with translationally ordered layer structure, and cholesterics exhibiting the space helix structures due to the chirality of their molecular structure and specifics of their helix supramolecular ordering. Attention was also paid to the peculiarities of morphological and structural behavior of such hybrid nanosystems, of their optical and adsorptive properties as well as perspectives of their possible applications.

Hybrid nanosystems comprising nanosized metal particles stabilized in functionalized organic matrices are scientifically interesting due to their highly promising applications in nanoelectronics, photonics, and sensor systems [1–6]. The use of mesogenic compounds in different liquid crystalline states as soft ordered template matrices opens new possibilities for the synthesis of anisotropic metal particles and their highly ordered assemblies. The presence of metal atoms and ions in liquid crystalline systems significantly extended the possible practical areas of their exploitation. The most prospective are hybrid metal-mesogenic nanosystems, combining molecular ordering of mesogenic matrix compounds and quantum-size properties of nanometals, which are different from both the characteristics of the single atoms and the properties of bulk materials. The properties of such systems are dependent not only on the size and shape of individual nanoparticles of the formed system, but also on the character of their joint organization and formation of the hybrid ordered structure [7, 8]. Among different methods of metal particles' incorporation into the organic systems and formation of hybrid nanosystems, the most original and useful are methods of low-temperature condensation of metal atoms with the molecular beam of organic component's vapors under high-vacuum conditions [9, 10]. The use of low temperatures and technique of vacuum condensation of metal atoms and organic molecular beams on the cooled support surfaces allowed researchers to stabilize and study such highly active species as metal clusters and nanoparticles and their labile complexes. This approach allowed us to realize the formation of hybrid nanosystems by bottom-up method and to carry out the directed metal atom and small clusters aggregation, controlled by structural and dynamic properties of molecular organized matrices, and also to create new ordered assemblies of nanoparticles.

In this work, the formation of new hybrid metal-mesogenic nanosystems was exemplified by two d-metals of the 11th group—silver and copper with mesogenic derivatives of long-chain

alkylcyanobiphenyls. Nanoparticles of silver and copper possess the intensive plasmonic bands in the visible region of spectrum and can be used for the visualization and marking of different biological objects. Mesogenic compounds of the alkylcyanobiphenyl row are widely used nowadays as components of active layers for liquid crystalline displays and indicators. These compounds form ordered liquid crystalline phases of two types—nematic, characterized by the existence of molecular orientations of long-range order, and smectic—with layered molecular ordering. The existence of molecular associates and formation of dimeric structures in solid and liquid crystalline phases is known for these compounds at low temperatures. They form several metastable and stable solid phases with a local structure similar to the liquid crystalline mesophases with a different molecular organization [11, 12]. A terminal cyano group and an aromatic core of the molecules can be considered as ligands suitable for the formation of complexes of π- and σ-types with atoms and clusters of the metals under consideration [13].

Controlled formation of anisometric nanoparticles and ordered hybrid nanostructures is one of the main objectives of this work. The role and mutual influence of self-organization processes of metal species and organic component's molecules were considered. The phase-structural transitions and physico-chemical properties that appear for new hybrid metal-mesogenic nanosystems were demonstrated on the example of a combination of silver and copper metal nanoparticles formed in mesogenic matrices of long-chain ($n \geq 5$) alkylcyanobiphenyls 4-pentyl-4-cyanobiphenyl (5CB) and 4-octyl-4-cyanobiphenyl (8CB).

Mesogenic derivatives of cholesterol possess unique liquid crystalline mesophases named cholesteric mesophases at definite temperature ranges [1]. The molecules in such a mesophase are arranged in prolonged 3D helix structures with special optical properties depending on the pitch of the helix, such as selective reflection of visible light. Introduction of metal atoms and clusters in cholesteric mesophase changes the intermolecular interactions in the system and leads to the induction of new liquid crystalline and isotropic phases. We can also find the formation of self-assembled nanosized aggregates with different morphology and hybrid nanostructures, including metal species of different sizes arranged by a mesogenic matrix in highly ordered assemblies with modified optical properties. Special attention will be paid to analyzing the possibilities of their use in modulation of optical signals and obtaining systems with tunable optical plasmonic resonance.

Self-organization of nanosized metal particles in highly ordered assemblies with definite structural and morphological characteristics is nowadays one of the most promising areas of nanoscience and nanotechnology [2, 3]. The unique quantum-size properties and the appearance of new collective modes open new possibilities for their application in such fields as microelectronics, optics, catalysis, information recording systems, and data storage systems [4, 5, 7]. The physical and chemical properties of such nanohybrid systems depend both on the size and shape of the structural elements (nanoparticles), and on the manner of their organization into the joint structure [8, 9]. Development of new synthesis methods of nanohybrid aggregates possessing special order in regular placement of the particles of the same size is an important task in modern nanochemistry. For the synthesis of nanoparticles having a certain size, it is necessary to physically or chemically isolate nanoparticles from one another and from the external environment to prevent aggregation. In many cases, the stability of such systems

is achieved through the introduction of functionalized organic ligands aryl- and alkylthiols, organic amines, alcohols, and other compounds capable of specific interactions with the surface of the nanoparticles [10, 11]. Hybrid nanosystems including biomolecules or their chemical analogs attract the increasing interest of researchers due to their compatibility with natural systems [12–14]. In the present chapter, we show the possibilities of using two new silver-containing nanosystems based on biomolecule of cholesterol and its heteroatomic analog—thiocholesterol. Supramolecular organization of the ligand molecules allows us to use the obtained nanoparticles for self-assembling in binary superlattices and for the formation of ordered 1D-, 2D-, and 3D nanostructures.

Cholesterol and its derivatives are optically active molecules and form helical liquid crystalline structures—cholesteric mesophases—at definite conditions. It is known that the effects of "guest-host" interactions are very important for the practical applications of composite liquid crystalline systems, including guest molecules of organic and inorganic compounds [15, 16]. At the same time, these compounds contain such functional groups as –OH and –SH, which are able to the effective interaction with the surface atoms of metal nanoparticles and form a mesogenic ligand stabilizing and selecting layers on the surface of metal nanoparticles. Recently, we have intensively developed investigations on the creation of new methods of producing hybrid metal-mesogenic nanosystems and the study of their physical and chemical properties [17–20].

2. Morphology of metal nanoparticles, formed in alkylcyanobiphenyl matrices at low temperatures

TEM study of the film samples of hybrid nanosystems "silver-4-pentyl-4-cyanobiphenyl" (Ag/5CB) and "copper-4-pentyl-4-cyanobiphenyl" (Cu/5CB), obtained by low-temperature co-deposition of components and annealing at 150–200 K for 1–2 h, shows the possibility of the formation and stabilization of mesogenic matrix by 5CB practically monodispersed spherical metal nanoparticles 1–2 nm in size (**Figure 1**). These metal species were formed in the solid nanostructured matrix of 5CB as a result of thermal decomposition of unstable dimeric biligand π-complexes of metal atoms M(5CB)$_2$ [16]. The metal atoms liberated by degradation of the complexes localize and can interact with each other in the local areas formed by mobile alkyl chains of a terminal substituent in 5CB dimeric structures existing at such low temperatures. Results of the study of different small areas of the film sample by selected area electron diffraction (SAED) show the formation of metal nanoparticles with fcc lattice. The size of metal nanoparticles formed in mesogenic matrices at these temperatures was close to the critical crystal size of the metal particles.

These small metal particles are stable at low temperatures under the conditions of limited molecular mobility of mesogenic matrix particles and can play a role of the initial crystalline particles (the embryo of a new phase) by raising the temperature. These small metal crystals appear in ESR spectra of the samples as broadened singlets with g-factor close to the value for free electron, $g_e = 2003$, which could be referred to conducting electrons spin resonance in metal nanosized species [16].
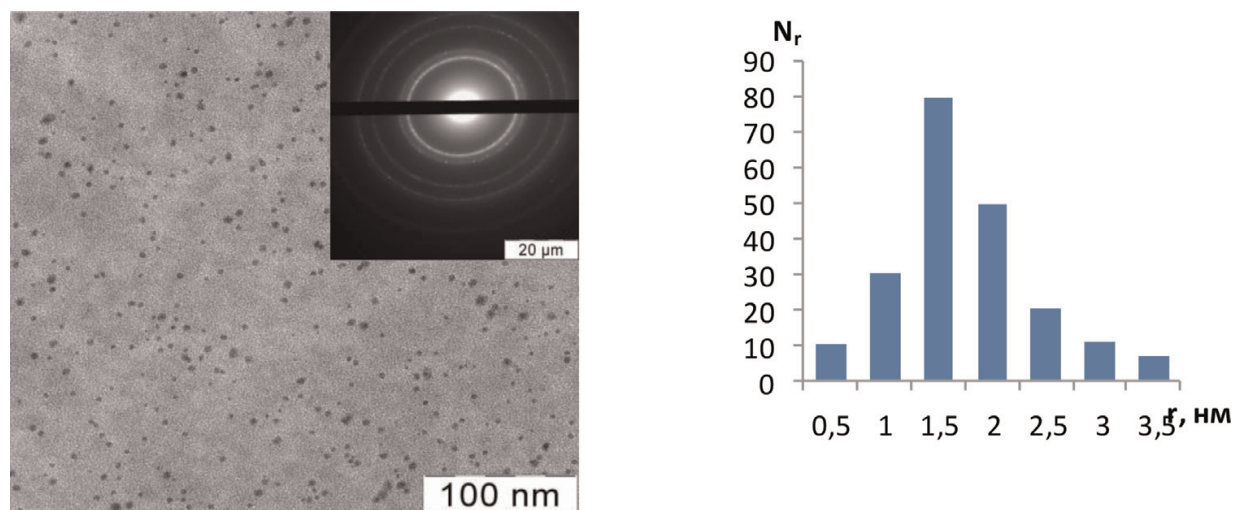
Figure 1. TEM pictures and electronic diffraction of the samples, including silver nanoparticles stabilized in mesogenic 5CB matrix at 200 K and histogram of their size distribution.

By annealing the samples from 90 up to 150 K, the relative intensity of the central component in ESR spectra increases, which reveals the thermal decomposition of the metastable complexes and the simultaneous growth of metal nanoclusters. UV-Vis spectroscopic study of silver/CB and copper/CB systems showed the appearance of new plasmonic absorbance bands in the visible region with a maximum at 400 and 560 nm, respectively.

On further heating of the samples up to temperatures more than 200 K, matrix crystallization process took place, which led to a sharp increase of matrix molecular mobility and rapid coalescence of nanoclusters followed by forming bigger aggregates, which was not recorded by the ESR technique. Such thermal behavior of the hybrid system can be deduced from the specifics of self-assembling processes and supramolecular organization of mesogenic cyanobiphenyl matrix at different temperatures. The combination of rigid aromatic core and flexible hydrocarbon chains of terminal substituents in ligand molecules leads to the formation of dimeric cyanophenyl structures in solid and liquid crystalline states at low temperatures. Such supramolecular structures could stabilize metal atoms due to the formation of metastable complexes. Thermal degradation of the complexes by increasing the temperature of the co-condensate samples followed by metal atoms escape into more soft domains formed by hydrocarbon chains and their rapid aggregation. Stabilization of nanosized metal clusters of size 1–2 nm formed at this stage is possible due to their low diffusion mobility in the solid cyanophenyl matrix. Warming of co-condensate systems up to the temperatures more than 200 K (T > 200 K), corresponding to CB crystallization, causes matrix softening and rise in the translational mobility of matrix molecules. This process is followed by metal nanoclusters' coalescence and formation of higher nanoparticles. Rapid heating up of the co-condensates up to the room temperature followed by the phase transition of the system in nematic (orientationally ordered molecular long-axes) and smectic phases (molecular ordering layered structure) led to the performable formation of the anisometric nanoparticles. In metastable crystal state of 5CB at 273–293 K, the temperatures close to the crystal to nematic phase transition point for hybrid metal-mesogenic "Ag-5CB" nanosystem, under the conditions of maximal ordering of liquid crystalline matrix molecules, the directed growth of highly anisotropic metal
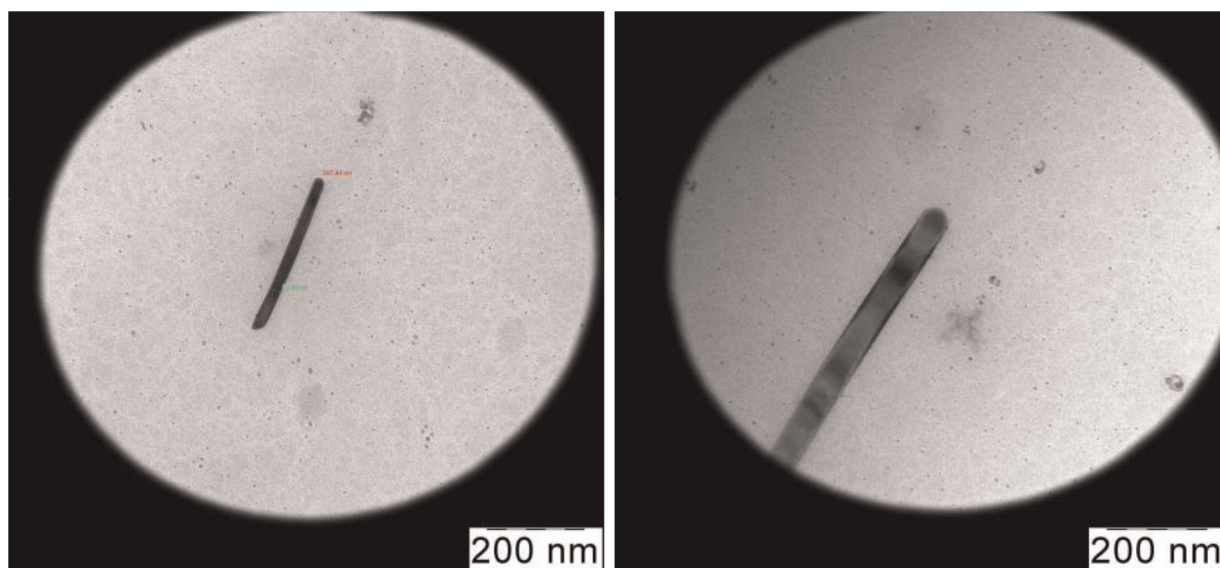
Figure 2. TEM pictures of silver nanorods, growing in 5CB matrix at 273–290 K.

nanorods took place, their lengths (l, nm) were more than 200 nm and their widths (d, nm) were about 15 nm, so anisometric l/d ratio was more than 10 (**Figure 2**). Mechanism of such almost single-dimensional growth of metal nanorods, in this case, is connected with the rapid growth of the molecular matrix mobility and maintaining high orientational order of the system.

Study of the samples by X-ray diffraction shows the exact crystal character of metal nanoparticles formed at these conditions. The samples possess texture that appeared due to the directed growth of rods along the crystallographic plane (100) and perpendicular to crystallographic plane (111). Observed mechanism of nanoparticles' growth can be explained by concurrent interaction of terminal functional cyano (CN) group of ligand molecules with metal atoms belonging to different crystallographic planes of forming nanoparticles. The interaction of ligand molecules with metal centers of highly packed bulky Ag (111) is slower in comparison with more loose Ag (100); so, the preferential growth of nanorods can be realized just in this direction due to the effective accession of small metal clusters and atom-by-atom addition formed in newly added layers and formation of highly anisometric metal nanoparticles.

3. Self-assembling of metal nanoparticles in nematic and smectic phases of mesogenic alkylcyanobiphenyls

It was shown by the combination of transmission electron microscopy (TEM) data with the results of selected area electron diffraction (SAED) and X-ray diffraction that hybrid metal-mesogenic nanosystems formed by low-temperature co-condensation of silver and copper with mesogenic cyanobiphenyls and followed by controlled annealing of the samples constitute of nanohybrid materials including metal nanoparticles stabilized and organized by matrix of mesogenic ligands. Depending on the phase of hybrid nanosystems Ag/5CB and

Ag/8CB, nanoparticles of different sizes and morphology—globular with main diameter 15 nm, anisometric rods, and flat 2D aggregates—were formed. Rapid heating of metal-mesogenic co-condensate samples up to 313 K was followed by phase transition of the hybrid system to the isotropic state and formation of globular metal particles of average diameter 15 nm. The data of FTIR study of the system show the formation of monomeric alkylcyano-biphenyl molecules stabilizing layer on the surface of nanoparticles due to donor-acceptor interactions of terminal CN group of ligand with surface metal atoms. The rising metal concentration and carrying out the nanoparticles' self-assembling processes in orientationally ordered nematic mesophase led to the formation of anisometric metal nanoparticles (anisometric factor l/d = 3–4) and their highly ordered assemblies. The results of AFM study of the samples show the formation of linear aggregates and regular orientationally ordered structures of anisometric nanoparticles in nematic phase 5CB at 300 K (**Figure 3**). Histogram of bimodal size distribution for metal nanoparticles in this case is also presented in **Figure 3**.

Using higher homology 4-octyl-4-cyanobiphenyl (8CB) molecules as stabilizing ligands gives us the possibility to carry out metal nanoparticles' formation in layered molecular structured smectic mesophase also. In this case, we saw the formation of quasi-fractal flat metal aggregates intercalated between smectic layers of 8CB due to higher interacting energy in the smectic layers and microphase segregation (**Figure 4**).

Thus, fulfilling the self-organization and self-assembly processes during the formation of hybrid nanosystems in liquid-crystalline mesophases of different types led to the production of metal nanoparticles of different sizes and morphology and their supramolecular organization in highly ordered nanostructures, including anisometric nanoparticles and rod-like aggregates stabilized in nematic mesophases and flat 2D metal aggregates in layered structured smectic phases of long-chain alkylcyanobiphenyls. Increasing the ligand molecules' concentration led to the stabilization of metal nanoparticles of smaller size. Increasing metal concentration in the orientationally ordered nematic system supported the formation of anisometric rod-like metal nanoparticles and their aggregates. The scheme of phase-structural states for Ag/
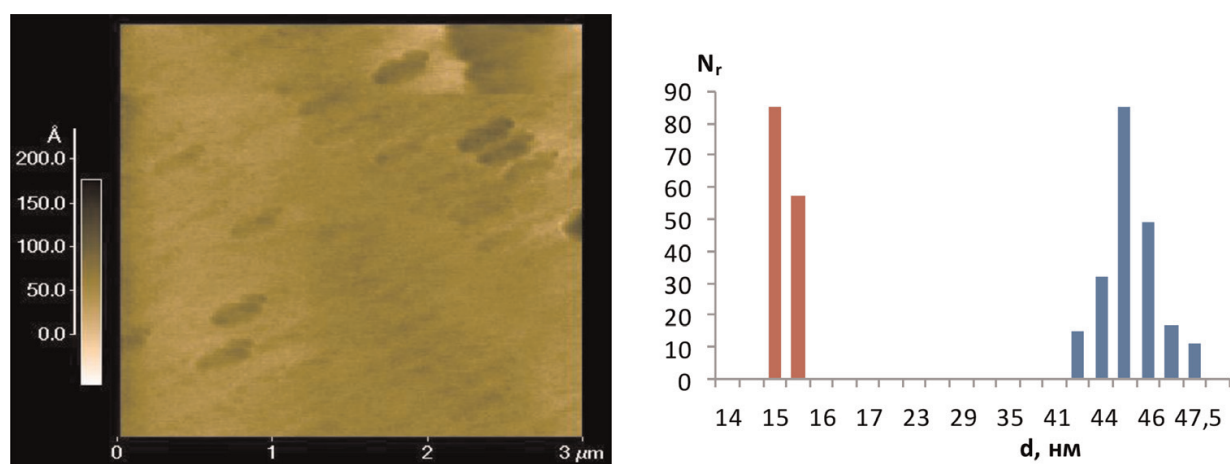

Figure 3. An AFM image (tapping mode) of the sample of hybrid metal-mesogenic nanosystem "Ag-5CB" (1/10) in nematic phase 5CB (left) and histogram of size distribution (right) for silver nanoparticles, red—cross size of nanoparticles, blue—linear length of nanoparticles.

5CB hybrid nanosystem indicating the conditions for the formation of metal nanoparticles with definite morphology is presented in **Figure 5**. This scheme is considered the combination of the result of thermal analysis, polythermal polarization spectroscopy, and electronic and atomic force microscopy.
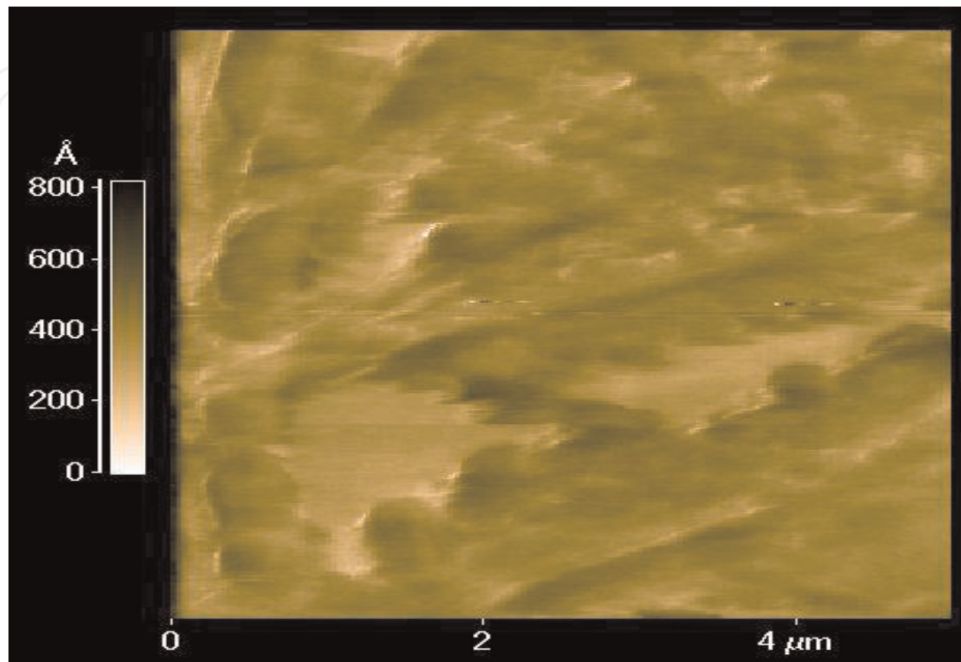

Figure 4. An AFM image (tapping mode) of the sample of hybrid metal-mesogenic nanosystem "Ag-8CB" (1/10) in smectic phase.
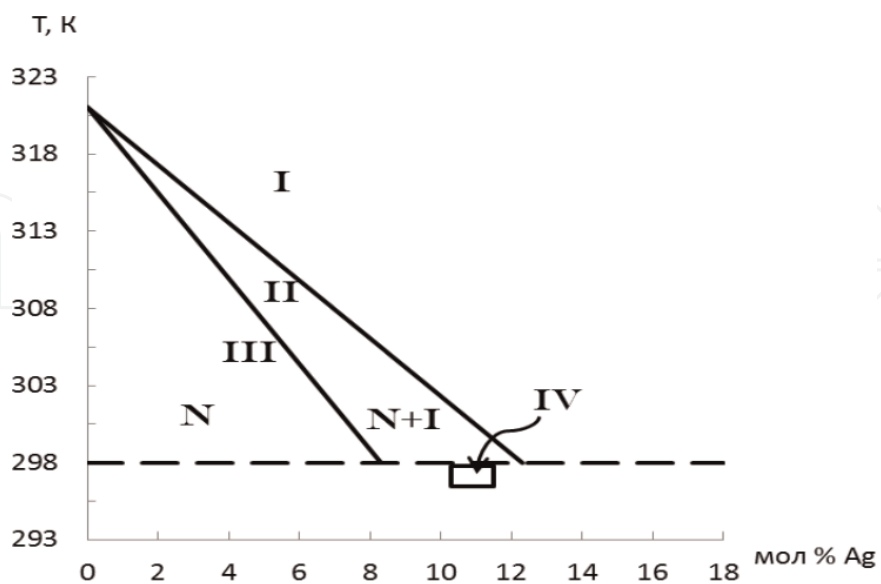

Figure 5. The scheme of phase-structural states for "silver-5CB" hybrid nanosystem: I—isotropic phase; II—two-phase region: isotropic phase including the fluctuations of nematic ordering; III—nematic phase; IV—the temperature region in nematic phase close to phase transition from crystalline to nematic; and V—solid phase at 150–200 K.

The data presented in **Figure 5** show the formation of nanoparticles with different morphology and sizes, stabilized by mesogenic ligands depending on the phase of mesogenic matrix and metal concentration in the system. The shape of the particles is in general the result of competition between general tendency for the minimization of particle's surface energy and elastic energy of liquid crystal. Rapid heating (more than 100 K/min) of the co-condensate Ag/5CB sample to temperatures of isotropic phase (T > 318 K)—region I—led to the formation and stabilization of global nanoparticles with d = (15 ± 10) nm. Transition to the nematic phase of 5CB gives us anisometric metal nanoparticles and their orientationally ordered assemblies—region III. In the bi-phase region II, including the co-existence of isotropic phase with fluctuations of nematic ordering, the formation of both isotropic globular and anisometric rods is possible. Maintaining the samples at 273–283 K and increasing the metal content in the sample from 1 up to 10 w/w % (region IV in **Figure 5**) led to the preferential growth of rod-like metal nanoparticles with l/d ratio more than 10. Small metal nanoparticles 1–2 nm in size are formed in diluted systems in the solid phase at 150–200 K.

4. Hybrid metal-mesogenic nanosystems encapsulated in polymer films and their optical properties

The layer-by-layer co-condensation of vapors of para-xylylene monomer, metal silver, and cyanobiphenyl ligand followed by controlled heating or UV irradiation of the sample led to the formation of hybrid metal-mesogenic compositions with varied metal contents from 1 up to 10 w/w %, encapsulated in polymer film:
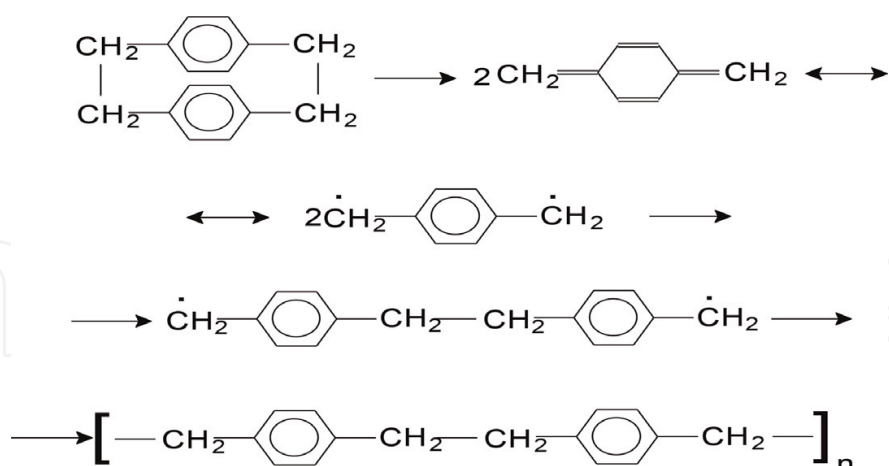
The results of TEM study of the Ag/5CB samples encapsulated in poly-para-xylylene (PPX) films show that increasing metal contents in the sample up to 10 w/w% led to the growth and stabilization of elongated rod-like metal particles with anisometric ratio l/d more than 10 (where l is the length and d is the cross diameter of particles). X-ray diffraction pictures of the Ag/5CB (w/w 1:10) sample, formed at 200 K followed by annealing up to 450 K, are shown in
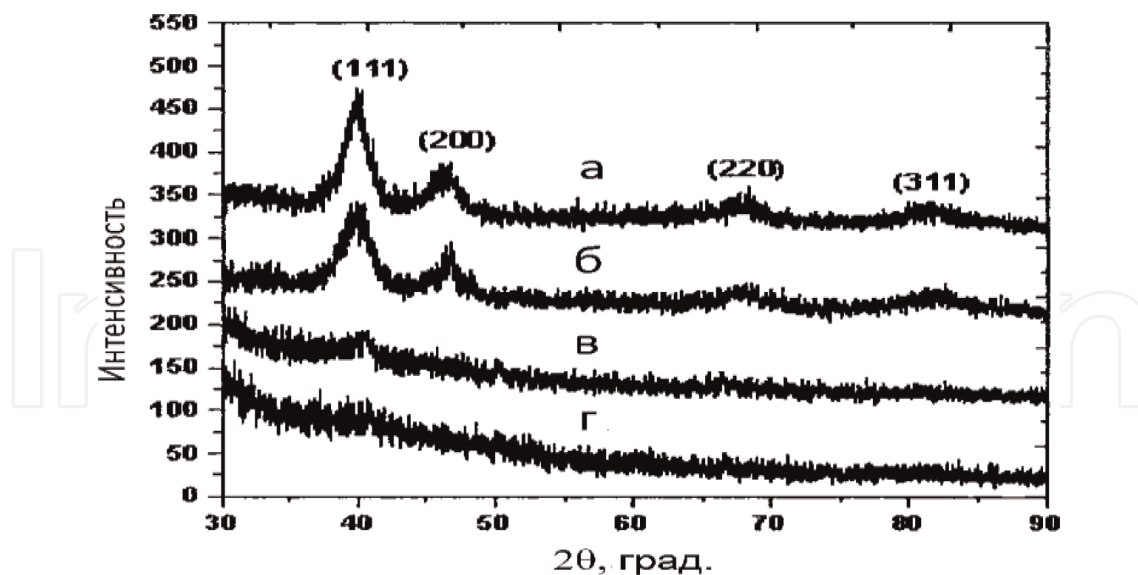
Figure 6. X-ray data for sample of hybrid metal-mesogenic nanosystem Ag/5CB (1:10), encapsulated in polymer (PPX) film at 450 K (a), 300 K (b), 250 K (c), and 200 K (d).

Figure 6. The results obtained show the formation of metal nanoparticles with fcc lattice, with lattice constant similar to that of crystal silver, a = 0.408 nm; the crystallographic planes were identified as (111), (200), (220), and (311). TEM data for the Ag/5CB (10 w/w %) sample encapsulated in polymeric film showed the formation of regular nanostructures stabilized by liquid crystalline matrix of anisometric metal nanoparticles (**Figure 7**), and their optical spectra are presented in **Figure 8**. Optical spectra contained the intensive absorbance bands of bimodal plasmonic resonance of anisometric silver nanoparticles (**Figure 8**).
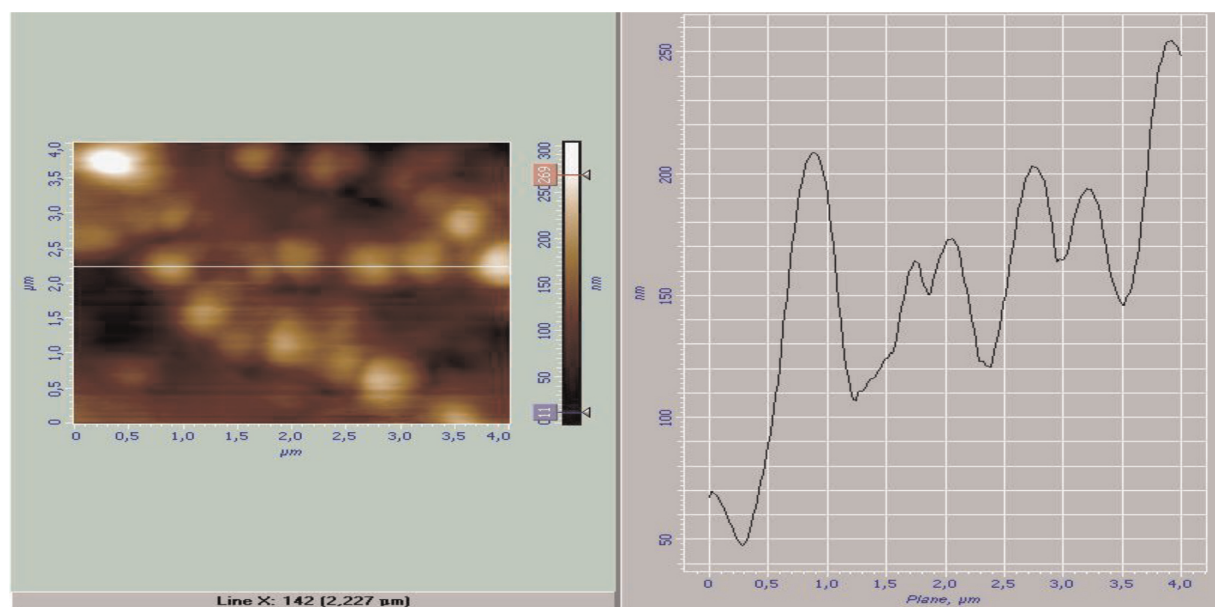

Figure 7. AFM data for the sample of hybrid metal-mesogenic nanosystem Ag/5CB (1:10 w/w%) encapsulated in poly-para-xylylene polymeric film.
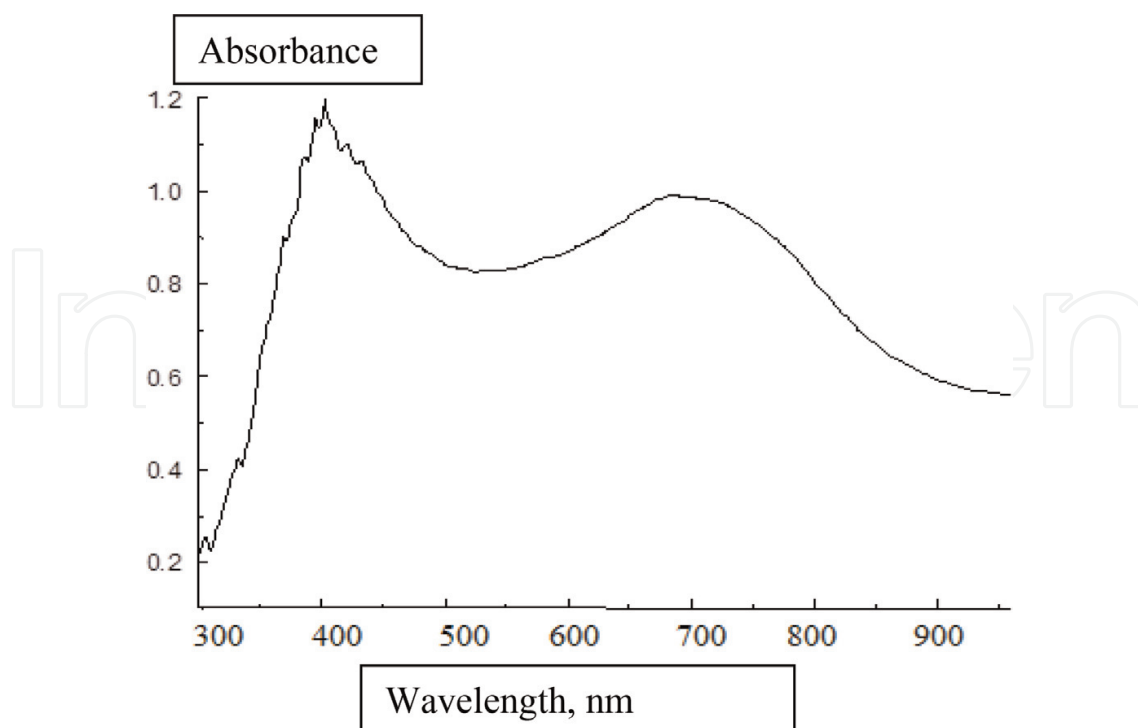
Figure 8. An optical spectrum for the sample of hybrid metal-mesogenic nanosystem Ag/5CB (1:10 w/w %) encapsulated in poly-para-xylylene polymeric film.

The proposed method allows encapsulation from several molecular layers up to several microns. In the optical spectra of such hybrid metal-containing mesogenic systems encapsulated in PPX films at 300 K, the plasmonic bands appear at 420–440 and 500–600 nm, characteristic of the formation of silver nanoparticles and their ordered aggregates, respectively. Increasing the metal concentration led to the formation of anisometric rod-like particles with multimodal plasmonic resonance related to cross and linear resonance. The formation of rod-like metal nanoparticles with anisometric ratio l/d > 10 enhanced plasmonic absorbance in the long-wave spectral range ($\lambda \geq 650$ nm). In this case, the value of dichroic ratio $D_{\parallel}/D_{\perp}$ in the plasmonic band for Ag/5CB (1:10) samples uniformly oriented by magnetic field rises by 5 times in comparison with pure 5CB samples. Optical properties of the samples are stable for several months.

5. Self-organization processes in organosols and cholesteric mesophases of cholesterol- and thiocholesterol-based nanosystems

Hybrid "silver-cholesterol" and "silver-thiocholesterol" nanosystems were produced by cryochemical synthesis via low-temperature co-condensation of components' vapors or two-phase chemical reduction of the silver nitrate salt by $NaBH_4$ and metal-organic complex transferring into toluene environment using inter-phase zwitter-ionic carrier $N^+(C_8H_{17})_4Br^-$ and functionalized cholesteric ligands [21, 22]. Cholesterol (a) and thiocholesterol (b) molecules were also used in order to form protective surface layers on silver nanoparticles formed in the system, their chemical structures are presented below.

(a)   (b)
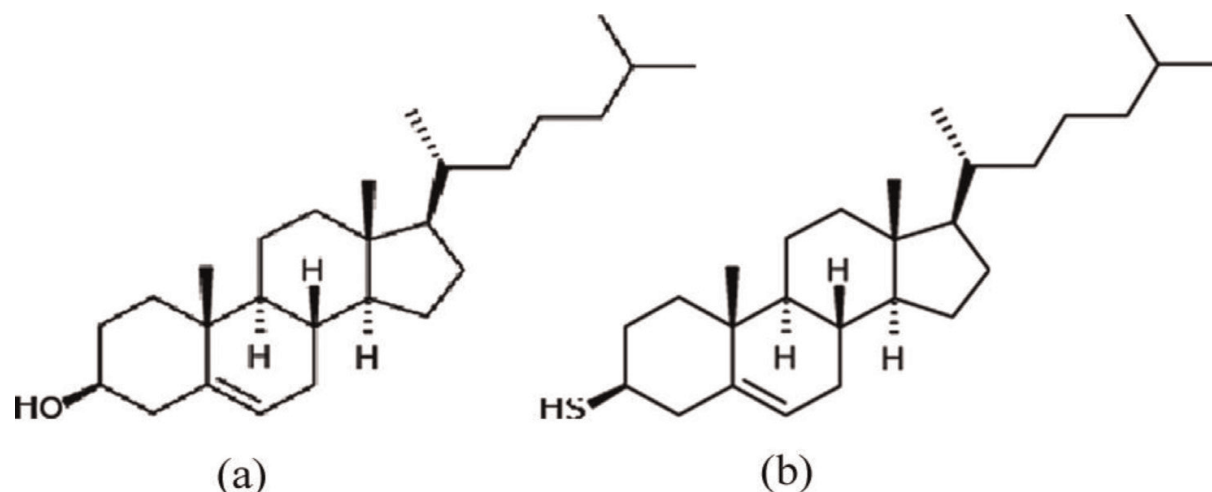
The organic silver nanoparticle's sols prepared after drying and dissolution had been used for FTIR-and UV-Vis spectroscopic studies. The FTIR spectra of the samples were recorded using Tensor II FTIR spectrometer Bruker (Germany), and UV-Vis spectra were recorded by the V770 spectrometer, JASCO (Japan). The chemical composition of the samples obtained was controlled using selected area electron diffraction (SAED) and direct chemical analysis by ICP-MS spectrometer. The internal structure of the samples and the size distribution of the stabilized silver particles were obtained using transmission electron microscopy (TEM) instrument LEO 912 AB Omega (Germany); differential scanning calorimetry (DSC) instrument STA 449C, Netzsch (Germany); and X-ray diffraction instrument D/MAX-2600, Rigaku (Japan).

Understanding the mechanism of interaction between metal species and stabilizing agents—cholesterol and thiocholesterol ligand molecules—was one of the purposes of this study. The most typical bands of O–H group stretching vibrations at ν = 3490–3500 cm^{-1} and O–H group δ-deformation vibrations at ν = 1090–1140 cm^{-1} and also of S–H group stretching vibrations at ν = 2540–2590 cm^{-1} are almost absent in the FTIR spectra of the silver-containing hybrid nanosystem's samples, and the bands stretching vibrations for CH$_3$–, CH$_2$–, and S(O)–CH$_2$ groups at ν = 2920–2880 cm^{-1} and ν = 1415–1440 cm^{-1} are appear in the spectra. This fact could be considered at the spectral confirmation of the interaction of the thioxy group of thiocholesterol ligand and hydroxy group of cholesterol ligand molecules with the surface atoms of silver nanoparticles [16] and of the existence of stabilizing ligand monolayers on the surface of the metal nanoparticles [17].

The morphology and size distributions of metal species primarily formed in "silver-cholesterol-toluene" and "silver-thiocholesterol-toluene" triple hybrid nanosystems are presented in **Figures 9A** and **B** and **10A** and **B**, respectively. The main diameter values of silver nanoparticles were d = (6.5 ± 1.5) nm for cholesterol-stabilized organosols of silver nanoparticles and d = (2.5 ± 0.5) nm for thiocholesterol-stabilized organosols of silver nanoparticles.

The formation of dispersions of stabilized nanoparticles and their regular surface structures took place by withdrawal of organic solvent from the film samples. The chemical nature of stabilizing ligand molecules and concentration of metal nanoparticles in the hybrid system determined the manner of metal species packing in 2D- and 3D superlattices. By removing the
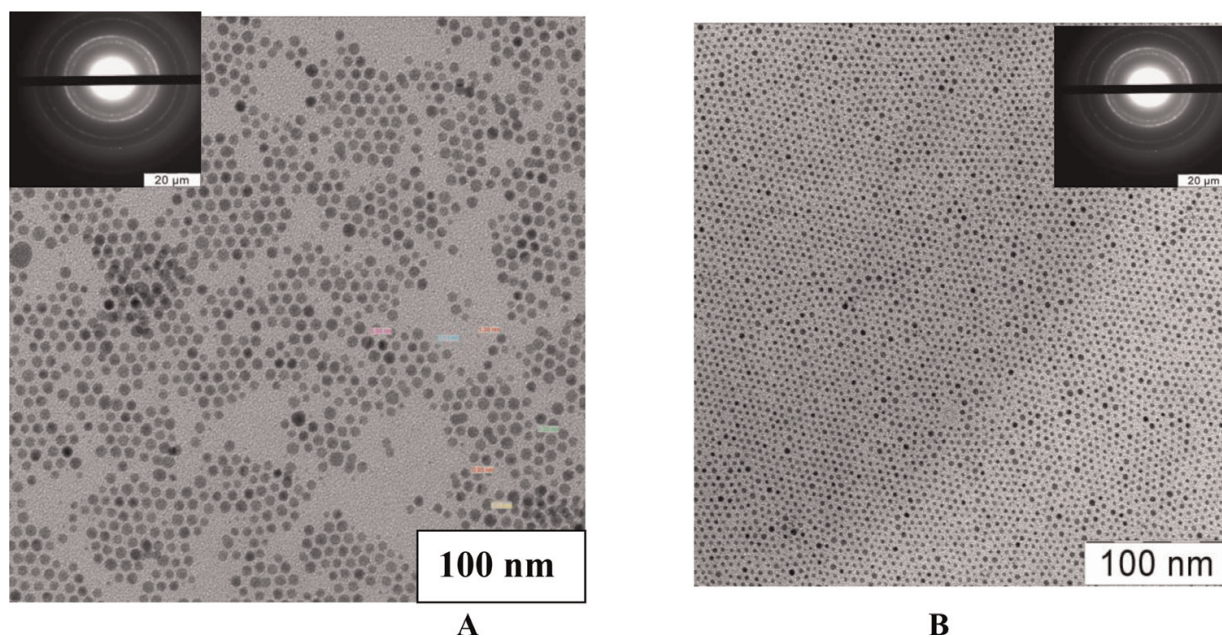
Figure 9. TEM pictures for silver nanoparticles stabilized by cholesterol (A) and thiocholesterol (B) ligand molecules.
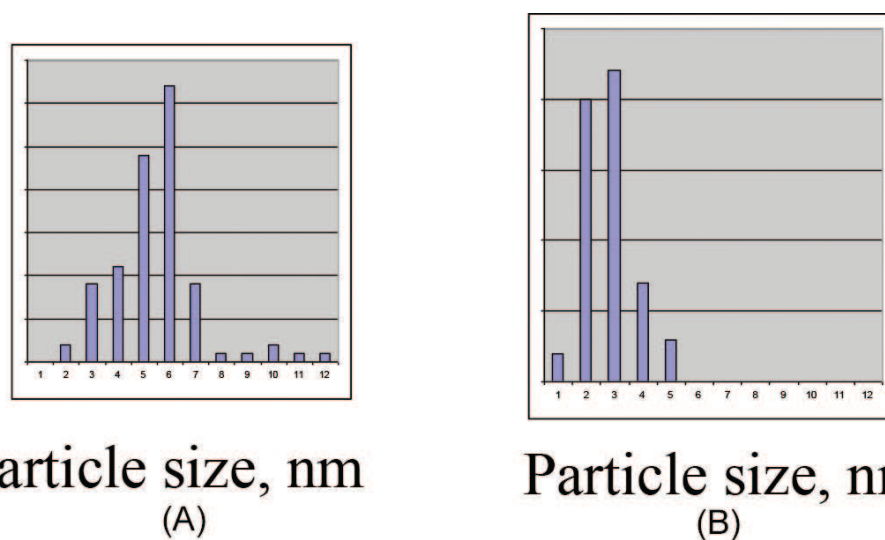

Figure 10. Histograms of size distribution for silver nanoparticles stabilized by cholesterol (A) and thiocholesterol (B) ligand molecules.

organic solvent, the formation of 2D nanostructures with a hexagonal (**Figure 9**) or cubic symmetry was achieved (**Figure 11**).

The process of such ordered nanostructure formation can be described by the following scheme presented in **Figure 12** [20]. It began from the formation of individual metal nanoparticles in highly diluted organic sols stabilized by cholesterol or its heteroatomic derivative thiocholesterol and by raising the metal nanoparticles' concentration, which led to the production of 2D- and 3D nanoparticle superlattices with hexagonal and cubic symmetry.
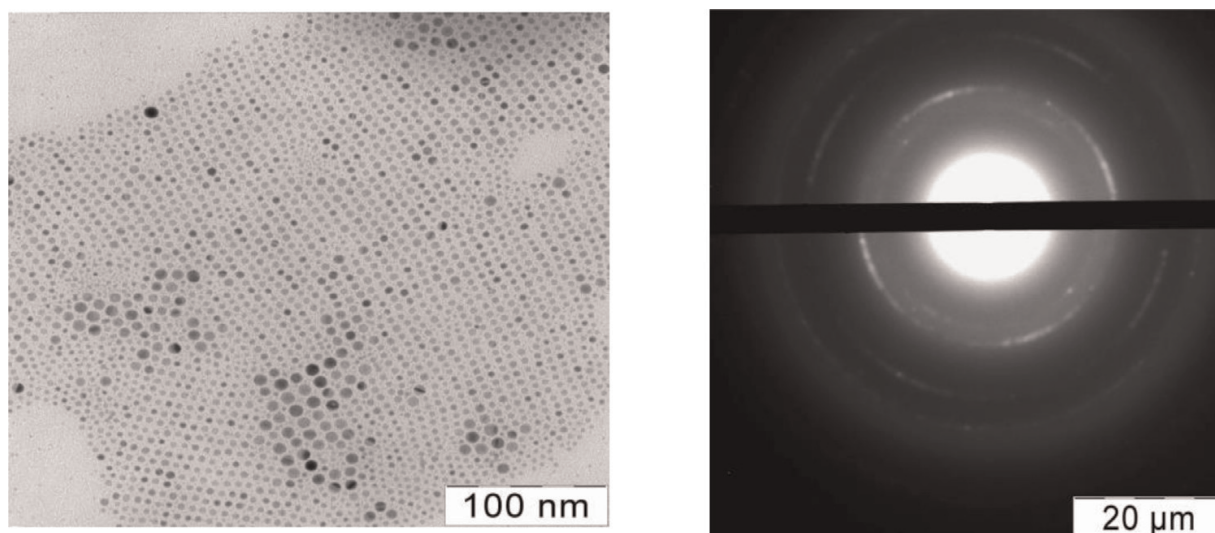
Figure 11. TEM and SAED pictures of silver-thiocholesterol samples obtained by deposition from triple "silver-cholesterol-toluene" system [20].

It is of interest that the interparticle distance (average distance between the centers of metal nanoparticles) in the nanostructures obtained is rather small and is practically equal to the size of organic layer shell from cholesterol or thiocholesterol molecules (about 2.5 nm). Such regular position of plasmonic metal small nanoparticles in highly ordered dielectric organic media promised possible applications of the hybrid systems obtained in nanooptics and molecular electronics.

Binary "silver-thiocholesterol" nanosystem, obtained after entire removal of the toluene solvent, was heated up to 70–80 C and then cooled down to ambient temperature. It possessed liquid crystalline cholesteric mesophase that could exist in a supercooled state for a long time. The formation of elongated nanotubular hybrid aggregates took place. The TEM pictures for the sample of the binary system stored at 293 K for 24 h for the silver nanoparticles formed in the system are presented in **Figure 13**.

Supramolecular ordering of hybrid nanosystem included the interaction of the surface centers of silver nanoparticles with the functional groups of cholesterol and thiocholesterol ligands and their helix supramolecular ordering in cholesteric mesophase. The scheme of molecular interactions is presented in **Figure 14**.

There were intensive plasmonic bands of ligand-stabilized silver nanoparticles at 420–450 nm (**Figure 15**, curve 1) in the UV-Vis spectra of hybrid "silver-cholesterol" and "silver-thiocholesterol" nanosystems. Rising of metal contents led to the red shift of these bands due to specific interactions of silver nanoparticles with ligand molecules and particle-particle dipole-dipole interactions. In the optical spectra of binary "silver-thiocholesterol" system (**Figure 15**, curve 2) along with the plasmonic absorption of individual silver nanoparticles at $\lambda = 450$ nm, the long-wave absorption also appears at 770–1000 nm, which is characteristic for chain aggregates of silver nanoparticles [23]. The hybrid aggregates' absorbance bands were
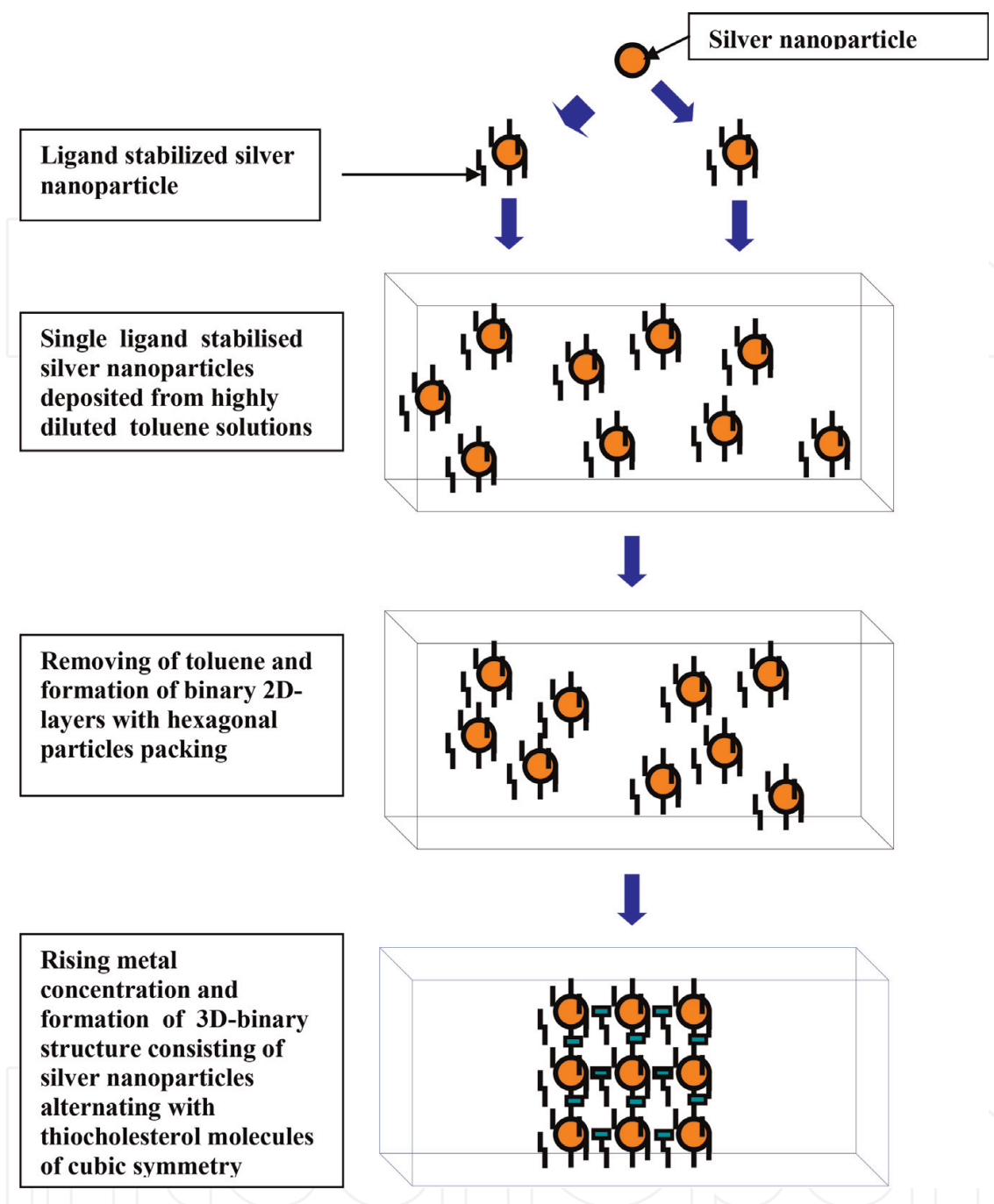
Figure 12. The scheme of formation of binary nanostructures of silver nanoparticles and thiocholesterol molecules in triple "silver-thiocholesterol-toluene" systems [20].

shifted to the near-infrared region and it is important for possible applications in in vivo imaging and sensing of different biomedical objects.

The chirality of active compounds is important for many biochemical processes [24–26], the study and separation of optical isomers of drugs are principal for pharmaceutical applications, and control of optical purity is necessary for the production of pharmaceutical components.
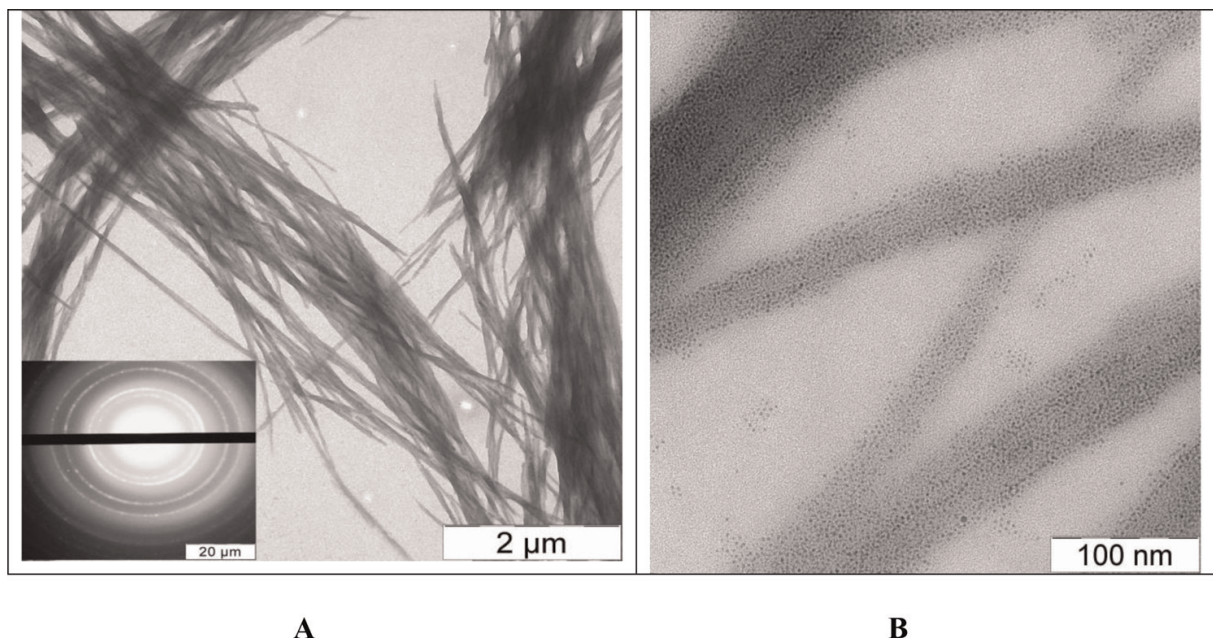
Figure 13. TEM pictures for hybrid silver-thiocholesterol aggregates after 24 h of storage in liquid crystalline mesophase: general view (A) and internal structure (B) [22].
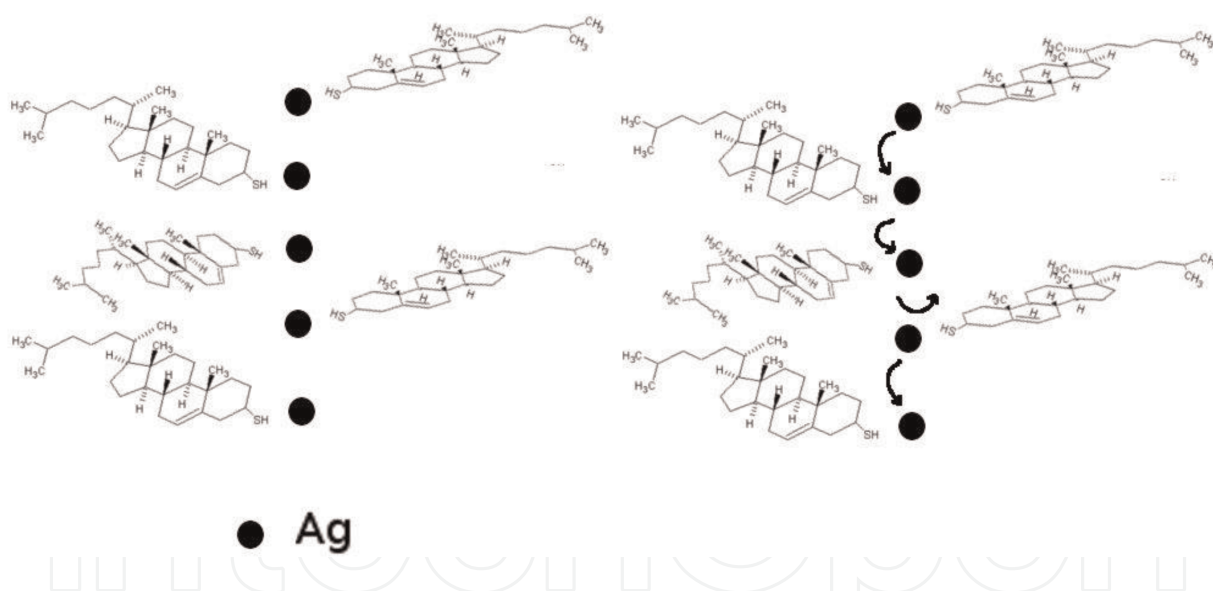

Figure 14. The scheme of silver-thiocholesterol tubular nanoaggregates formation.

Cholesterol and thiocholesterol ligands and their mesogenic derivatives are natural and modified chiral matrices, which adsorptive and selective properties only begin to study [27].

The synthesis of hybrid nanoparticles with silver core and stabilizing cholesterol/thiocholesterol shell layer of chiral ligand thiocholesterol was produced by modified of borohydride reduction method [28], including reduction of silver ions Ag^+ in bi-phase water-organic system in the presence of mesogenic ligands. This system was used to impregnate silica gel plates for thin-layer chromatography. The UV-Vis spectra of toluene sols of the hybrid
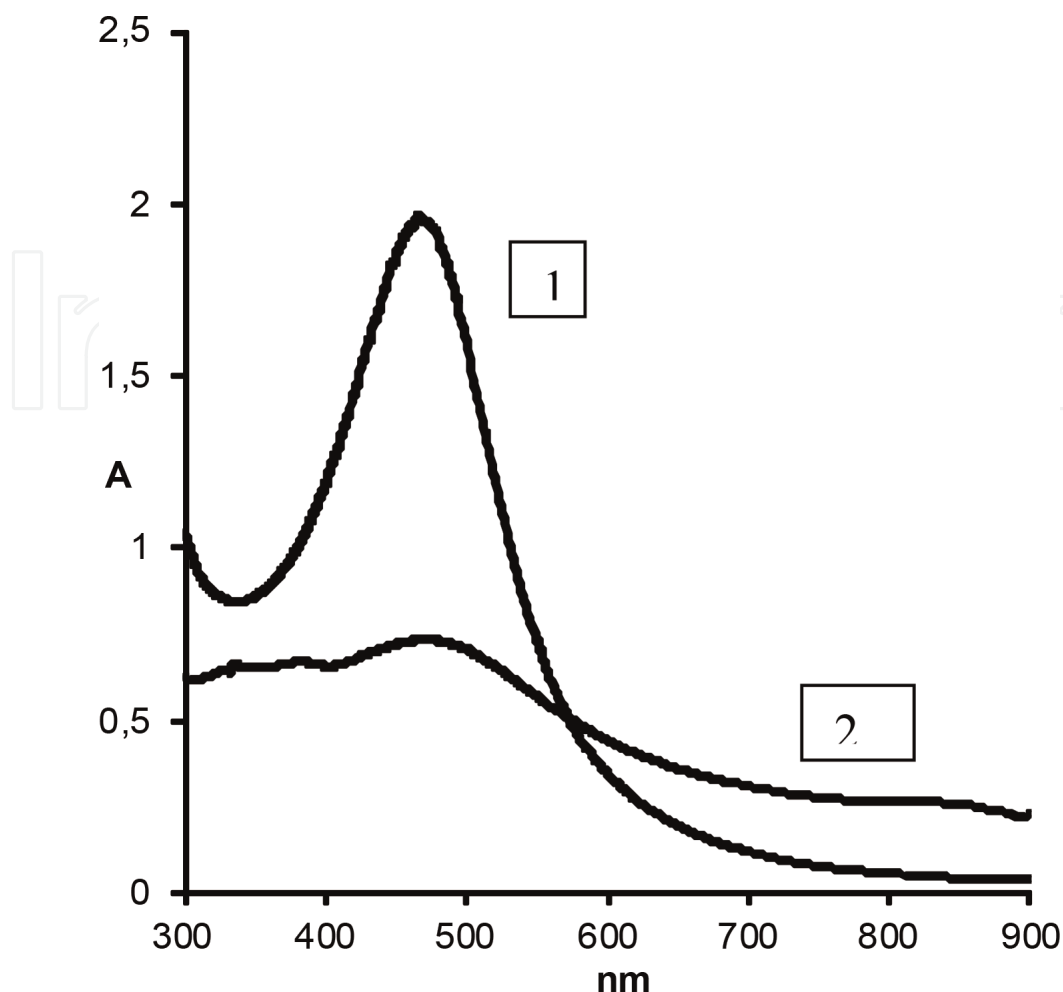
Figure 15. Optical absorbance spectra: 1—highly diluted sols of silver nanoparticles stabilized by thiocholesterol in toluene and 2—linear aggregates, formed in liquid crystalline mesophase of hybrid "silver-thiocholesterol" system.

system "silver-thiocholesterol" (Ag: L = 1:5) were recorded in silver concentration of range 0.2–2.0 mg/ml and show the characteristic silver nanoparticles' plasmonic band at 450 nm. The intensity of absorbance grows linearly by increasing the concentration of nanoparticles.

The selection of model optical isomers of tested compounds was made using silica plates modified by hybrid silver-thiocholesterol (Ag:L = 1:5) nanoparticles (**Figure 16**) with a concentration of 1.2 mg/ml. The chromatographic separation of tested substances was made using modified silica plates [29]. The eluent phase for the selection was chosen from several solvents that differed in their chemical structure and polarity—methanol, isopropanol, acetonitrile, acetone, and butyl acetate. It was shown that the most suitable eluent was the mixture aceto-nitrile/water (50:50 v/v), the yield mobility was found rising in the order: 1,1′-bi-2-naphtol <2,2′-diamino-1,1′-binaphtol (DABN) ≈ trifluoro antranyl ethanol (TFAE). The difference of the values of R_f was observed for S- and R-isomers of DABN and TFAE. The detection of the spots of separated enantiomers DABN and TFAE was made by UV irradiation at 360 nm of the chromatographic plates using the ability of these compounds for exhibiting fluorescence [30].
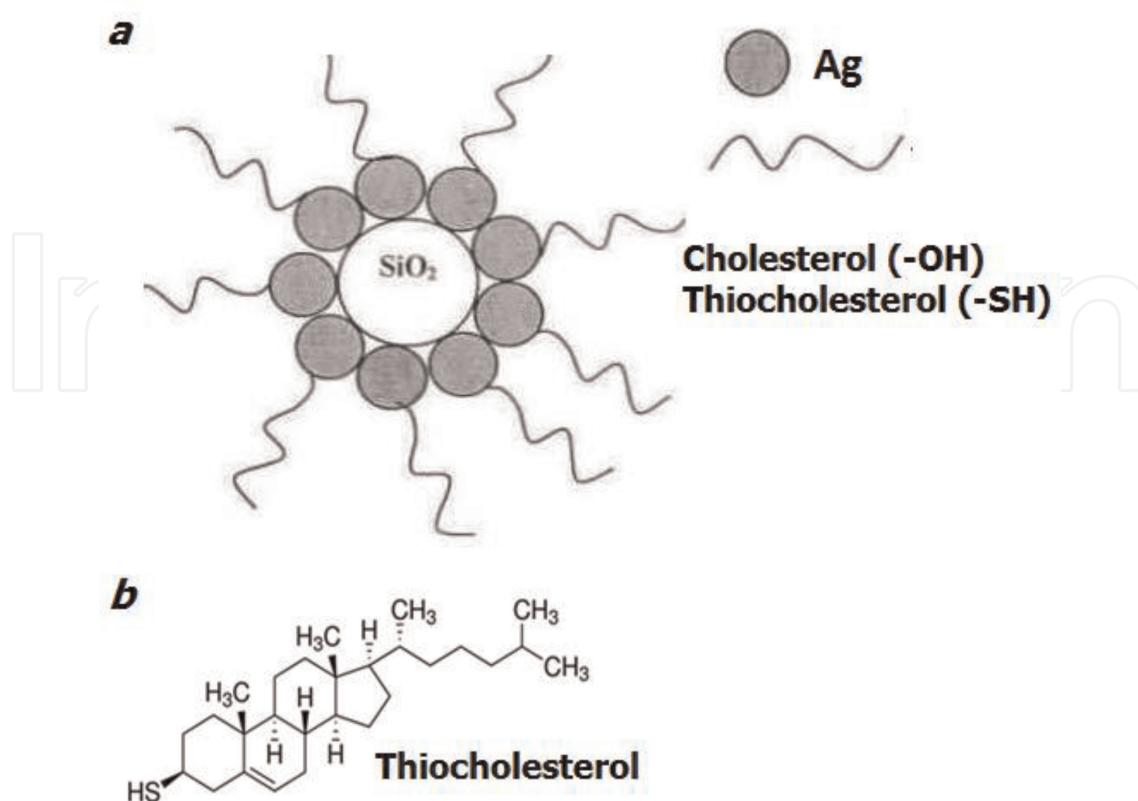
Figure 16. Schematic structure (a) of silica gel modified by silver nanoparticles stabilized by thiocholesterol (b).

The chromatographic separation was estimated by the value of R_f, which was calculated using the relation $R_f = x/L$, where x is the length, passed by the substance from the start line, and L is the length, passed by solvent up to front line [28]. The efficiency of separation was estimated by the value α (selection factor), which was calculated using the relation $\alpha = \frac{1/Rf_2 - 1}{1/Rf_1 - 1}$, where Rf_1 and Rf_2 are parameters of the two substances' retention. The data are presented in **Table 1**. It was shown that hybrid nanosystems based on silver nanoparticles covered by stabilizing layer of mesogenic molecules of thiocholesterol were selective in the separation of optical isomers of DABN and TFAE [31].

Test substances	Rf	α
2,2′-diamino-1,1′-binaphlene (R)	0.57	1.56
2,2′-diamino-1,1′-binaphlene (S)	0.46	
1,1-bi-2-naphthol (R)	0.49	1.07
1,1-bi-2-naphthol (S)	0.51	
TFA (R)	0.43	1.56
TFA (S)	0.54	

Table 1. The retention times (R_f) and separation factors (α) of test compounds in thin-layer chromatography experiments [31].

6. Conclusions and perspectives

A new approach was proposed and realized for the formation of highly ordered hybrid metal-mesogenic nanostructures based on the mesogenic matrix-governed self-organization of atomic-molecular systems obtained by low-temperature condensation of metal and mesogenic components' vapors followed by controlled annealing of the samples. The hybrid metal-mesogenic nanosystems have been obtained including plasmonic metal (silver and copper) nanoparticles stabilized and supramolecular structures organized by liquid crystalline matrix and their properties were studied in temperature range 80–350 K. The conditions that allowed the production of metal nanoparticles of different sizes and morphology were determined, and methods of creation of their ordered nanostructures using molecular self-organization and metal species self-assembly were developed.

Low-temperature co-deposition of metal (Ag, Cu) and mesogenic alkylcyanobiphenyl component (5CB, 8CB) vapors led to the formation of the first stage of metastable biligand complexes of metal atoms with functional CN group, stabilized in ligand matrices. Thermal degradation of the metastable complexes at 150–200 K led to the formation of small metal clusters, which initiate the growth of nanoparticles and their further aggregation and organization in anisotropic mesogenic matrix. The structural and dynamic properties of mesogenic matrix at different temperatures and different phases controlled metal atoms' and small clusters' self-assembling and aggregation and led to the formation of metal particles of different sizes and morphology and their ordered aggregates. The competition of the processes of matrix molecules self-association, metal atoms aggregation and metastable complexes formation between metal species of different size with ligand molecules and molecular aggregates determines the structure and physico-chemical properties of hybrid nanosystems formed in definite conditions. Highly ordered nanohybrid systems can be very promising for different applications in nanoelectronics and electro-optics, as they possess unusual optical and sensor properties.

Ligand-stabilized silver nanoparticles were obtained by biphase chemical synthesis using biomolecule of cholesterol and its heteroatomic analog thiocholesterol. Regular 2D- and 3D superlattices with hexagonal or cubic ordering of almost monodispersed silver nanoparticles with main size d = (6.0 ± 1.5) nm for "silver-cholesterol" and d = (2.5 ± 0.5) nm for "silver-thiocholesterol" systems were obtained by removing the solvent from surface layers of triple "silver-cholesterol (thiocholesterol)-toluene" sols and for binary "silver-thiocholesterol" systems. Hybrid nanosized tubular silver-thiocholesterol aggregates with linear size (length) of more than 10 μm and only 15–20 nm wide including practically monosized silver nanoparticles of d = (2.5 ± 0.5) nm have been formed for binary silver-thiocholesterol system in cholesteric liquid crystalline mesophase.

The optical properties of hybrid nanosystems obtained belong to the plasmon absorption of individual silver nanoparticles and also possess modified plasmonic bands of hybrid nanostructures and highly ordered nanoparticle superlattices formed under special concentration and temperature conditions. Such hybrid nanostructures should be of interest for the creation of new optical and electro-optical devices with adjustable light absorption and light reflection. Integrating silver nanoparticles of exact size and shape and their aggregates of

definite morphology with biological molecules and blocks opens new perspectives for obtaining new bio-compatible instruments for imaging and sensing biological objects in living organisms and targeted medical therapy.

The hybrid metal-mesogenic nanosystems obtained were also used as liquid crystalline component for modification of silica gel nanoparticles and production of chiral matrices for thin-film chromatography. The conditions that allowed the production of silica gel plates modified by chiral hybrid metal-mesogenic nanosystems from toluene sols were developed. The new chiral matrices for thin-film chromatography possessed enantioselectivity related to optical isomers of 2,2′-diamino-1,1′-binaphtol (DABN) and trifluoro antrenylethanol (TFAE). We have succeeded in selecting optical isomers of TFAE with selecting factor equal to 1.56. In the future, the hybrid silver-thiochlesterol systems obtained in this work can be used as chiral stationary phase also for high-performance liquid chromatography (HPLC). One can expect the higher values of selectivity effects due to the increasing pathway for selecting compounds in comparison with thin layer chromatography technique.

Acknowledgements

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