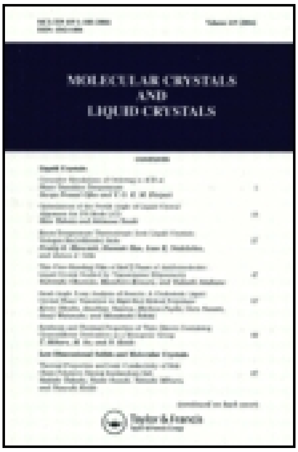

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Cryoformation of Hybrid Metal-Mesogenic Nanosystems

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Cryoformation of Hybrid Metal-Mesogenic Nanosystems

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Mesogenic nanosystems including silver and copper, and long-chain alkylcyanobiphenyls (CB) and alkylcyanophenylpyridines (PPy) have been obtained by low-temperature vacuum co-condensation of reagent vapors on cooled support surfaces. The formation of metastable bi-ligand π*-complexes of metal atoms and small clusters during co-condensation at low temperatures have been shown by FTIR, ESR and UV-Vis spectroscopy combining with the results of quantum chemistry calculations at HF/MP2 and DFT/B3LYP levels. Controlled thermal treatment of co-condensate samples allowed the directed formation of metal nanoparticles of definite size from 2 up to 100 nm. Formation of silver nanoclusters was also caused by UV-irradiation of co-condensate films.*

Keywords ESR and VIS-UV-spectroscopy; FTIR; hybrid metal-mesogenic nanosystems; low temperature deposition; metal nanoparticles

1. Introduction

Highly ordered systems including nanosized objects such as nanosized metals and semiconductors are of great interest due to the appearance of new collective physical and chemical properties in comparison to the bulk materials [1–5]. The use of mesogenic compounds as self-organizing organic template matrices opens new possibilities for synthesis of anisotropic metal particles and their highly ordered assemblies including ordering systems of nanorods and growth of nanowires and nanowhiskers. Cryochemical methods, i.e., low temperature joint and layer-by-layer vapor deposition and co-deposition [6–8], allow researchers to introduce metal atoms and clusters directly in the interaction with organic or inorganic compounds by low temperature co-condensation of component's vapors. In this case we can introduce metal atoms and small clusters directly into the mesogenic matrix and obtain hybrid metal-mesogenic nanosystem at atomic-molecular level. The possibilities of new metal-mesogenic nanosystems formation via low temperature co-deposition technique were demonstrated on the example of silver and copper with long chain ($n \geq 5$) alkylcyanobiphenyls (5CB, 8CB) and alkylcyanophenylpyridines (5PPy).

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2. Experimental Methods

Metal-containing film samples of l = 20–50 μm in thick were obtained by reagent's vapor co-condensation on the cooled surfaces of special spectral cryostats under molecular beam conditions. We used the quartz, KBr or CaF_2 spectral windows for transmission UV-Vis and FTIR-spectroscopy and a polished copper cube for reflection IR-spectroscopy studies. For ESR-spectroscopy we used the reagent vapors condensation on the cooled surface of quartz tube supplied by vacuum moving part, which allowed us to place the sample in the ESR resonator. The construction of cryostats allowed us to carry out the spectroscopic study of the film samples in situ under vacuum conditions both during co-condensation at low temperatures and by further heating of the samples up to 350 K. After co-condensation the FTIR and UV-Vis spectra were recorded using Specord M-80 and Specord M-40 spectrometers (Carl Zeiss Jena, Germany) in transmission mode. The ESR spectra were registered on the X-band ESR spectrometer (model P-1307) at 100 kHz modulation field of 2 Gs amplitude All equipment was functioning under computer programme suit in OS-2 Warp 4.0 operating system. The metal/ligand ratio was controlled with the aim of special calibration procedure of the evaporation cells and varied from 1:1 to 1:100, metal contents in the sample was determined by photometric analysis and via ICP – mass-spectrometry technique.

3. Results and Discussion

3.1. *Formation of the Metal-Mesogenic Nanosystems at Low Temperatures*

The spectroscopic study of Ag–/CB systems with different components ratios $(1/1 - 1/1000)$ at low temperatures shows the existence of metastable complexes due to metal interaction with π-system of ligand dimer. It was indicated by the appearance of two new bands in the IR-spectra of Ag-CB condensate film in the field of CN-stretching vibrations at 2030 and 2130 (2080) cm^{-1} compared to the neat ligand film [9,10]. The shift of about 100–200 cm^{-1} to lower frequencies is similar to π-complexes of zero-valent transition metals with unsaturated organic molecules. We also recorded the appearance of a new band at 650–660 cm^{-1}, which can be considered as metal-ligand vibration. Similar results were obtained for higher CB homology 8CB and 5PPy. In order to provide more careful interpretation of spectroscopic data ab initio quantum chemistry calculations have been carried out for model systems. The GAMESS quantum chemistry package and the conventional Stevens-Bash-Krauss (SBK) pseudopotentials on all heavy atoms with the corresponding basis sets have been employed. The complete ab initio geometry optimization and vibrational analysis was performed for the 5CB molecule, then a series of calculations has been carried out for linear and sandwich-like complex $Me(CB)_2$. The analysis of electron density distributions as well as the curvatures of the potential energy surfaces along the C-N coordinates have been performed. The sandwich-like π-complex structure has been considered as a model for the metal-cyanobiphenyl system (Fig. 1). The system is almost planar with anti-parallel arrangement of ligand molecules, that is according to the x-ray data for the cyanobiphenyls in the solid and liquid crystalline films, the molecules are arranged in pairs by the "head-to-tail" principle. And the silver atom placed between the center of CN fragment of ligand (1) and the center of the ring of ligand (2). In calculations, almost

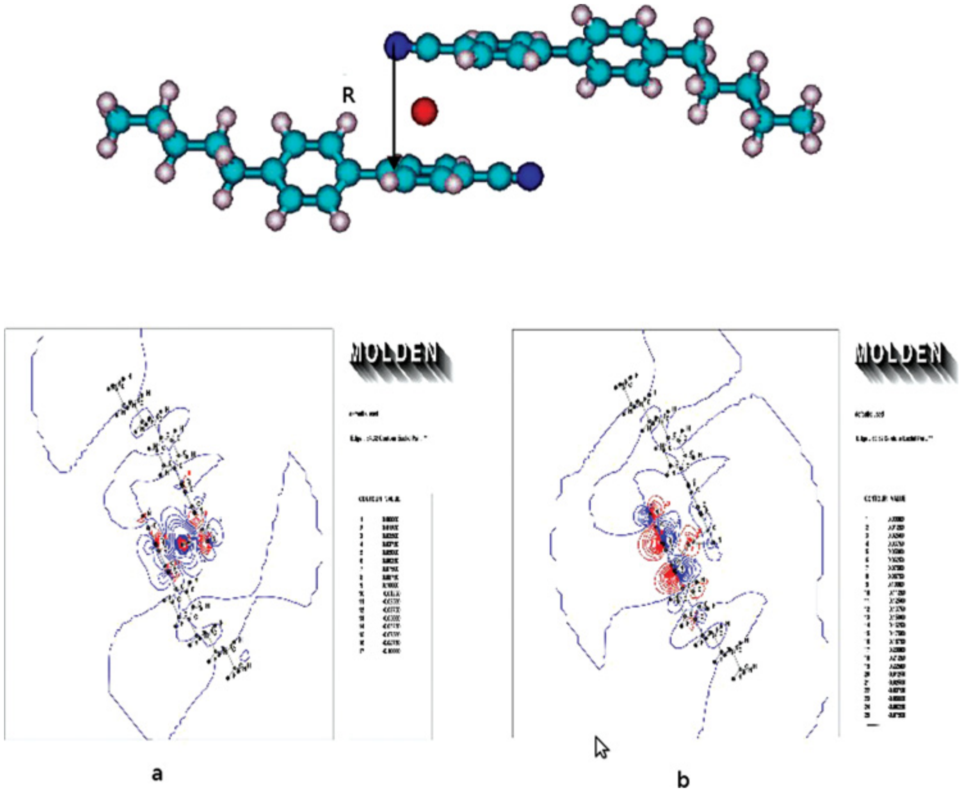
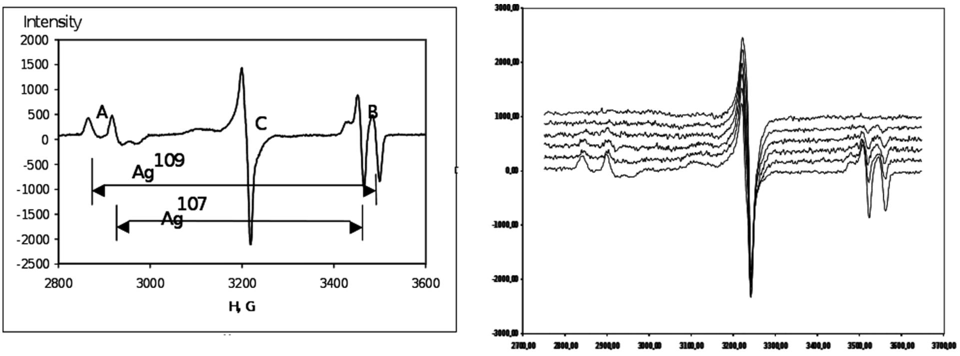


Figure 1. Two electronic configurations: neutral molecular complex and charge transfer for the ground state of biligand Ag(5CB)2 System and molecular model of complex structure and topography of electron spin density distribution. (Figure appears in color online.)

all the geometry parameters have been fixed at the values of the free CB molecule, the distance R between the planar ligands (1) and (2) has been varied.

Pilot calculations showed that two Hartree-Fock solutions could compete for the ground state of the complex, one corresponded to the $(PhCN)_2Ag$ and another to the charge-transfer $(PhCN)_2^-Ag^+$ configurations. Multiconfigurational self-consistent field method (MCSCF) was used in order to take into account such a pronounced effect of electron density distributions in the complex structure. The computed dependence of the total energy on the interligand distance (R) indicates a drastic modification in the electron density distribution in the vicinity of $R = 4.7$ Å. At large R ($R > 4.7$ Å), the neutral silver atom is embedded into the cavity between the ligands, the charge-transfer $(PhCN)_2^-Ag^+$ configuration dominates at $R < 4.7$ A. (Fig. 1).

It is important that two CN-groups are non-equivalent in the complex structure, and it reflects in two CN-stretching vibrations band in IR-spectra. Donation of the smaller fraction of electron density of metal to the antibonding orbitals of CN of one ligand results in an increase of the corresponding internuclear C-N distance and decrease of the vibrational frequency. Interaction of Ag atom with the phenyl $-\pi$ system of another ligand leads to a redistribution of the electron density following by a decrease of the corresponding CN frequency by another value. The simulated



a) b)

Figure 2. ESR spectra of silver-5CB co-condensate film: a) at 80 K and b) at different temperatures, from bottom to top 80 K, 108 K, 120 K, 140 K, 150 K, 182 K, 200 K.

red shifts in the CN vibrations (-150 and $-175\,\mathrm{cm}^{-1}$) correlate well with the observed experimentally for the Ag/5CB films (-150 and $-200\,\mathrm{cm}^{-1}$).

The ESR-spectrum of Ag co-condensate with 5CB at 80 K (Fig. 2) showed two doublets lines at the higher and lower fields due to silver atoms with two isotopes Ag^{107} ($J = 1/2$) and Ag^{109} ($J = 1/2$) [11–12]. The magnetic resonance parameters of these signals obtained via computer treatment of the experimental spectra are characteristic for π-complexes of silver atoms. The comparison of isotropic splitting constants for complexes with the values for undisturbed silver atoms $A(Ag^{107}) = 611$ G and $A(Ag^{109}) = 705{,}4$ G isolated in hydrocarbon matrix using common procedure allowed us to estimate the electron spin density on silver as $\rho_M = 0.89$ for Ag/5CB and $\rho_M = 0.78$ for Ag/5PPy systems. These values are characteristic for metal atom π-complexes and show the electron density donation from silver atom to ligand π-system.

The ESR spectra of copper-cyanobiphenyl (Cu/5CB) co-condensate samples obtained at 77 K consist at least of two signals. One is the quartet signal (marked as A in Fig. 3) due to copper-cyanobiphenyl π-complex structure formation. The other is anisotropicc singlet line at 3250 G (marked as B) with g-factor close to the

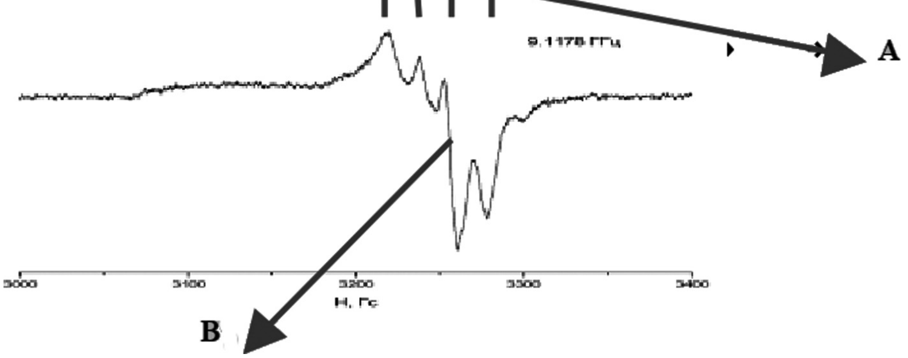


Figure 3. ESR spectra of copper-5CB co-condensate film at 80 K.

value for free electron $g_e = 2{,}0023$, which can be considered due to conducting electron's spin resonance of copper nanoclusters. Signal A has a strong anisotropy with perpendicular hyperfine splitting (HFI) constant of approximately 28 G. The splitting on two copper isotops: ^{63}Cu and ^{65}Cu was not resolved due to close values of their nuclear g-factors. These relatively small HFI constant values and strong signal anisotropy pointed out to p-type of semi-occupied orbital localized on copper atom. In this suggestion the value of anisotropic HFI interaction constant was $B = 51$ MHz. Comparing this value with $B_0 = 386$ MHz for the electron occupied p-orbital of copper atom [13] the unpaired electron spin density on $4p_z$ copper orbital can be estimated as $\rho_M = 0{,}13$. The process of electron promotion from "s" to "p" copper orbital is known for bi-ligand π-complexes of zero-valence copper [13].

3.2. *Thermal Evolution of the Samples at 80–350k*

In ESR spectra for all the systems there is also central signal (B) with g-factor close to 2.0032 (g-factor of free electron), that could be referred to conducting electrons spin resonance (CESR) of silver and copper nanosize clusters. This signal represents the superposition of a number of isotropic singlet lines of Lorentz shape. Such signals were observed also for highly concentrated co-condensates of silver and copper with hydrocarbons and inert gases. CESR signal's g-factors and line widths differ for metal clusters of different size due to variations in the values of spin-lattice relaxation time (T_1). Lowering the cluster size led to the limitation of the free electron movement in metal crystal and to increasing shift relatively to g-factor value 2.0032.Taking into the account the values of experimental shifts of central signal from free electron g-factor and the fact of absence of the well-known ESR-signals of small silver and copper clusters (3–7 atoms) in the experimental spectra of metal/CB co-condensates, the average size of metal clusters stabilized in cyanophenyl matrix at 90–120 K can be estimated as 1–2 nm (10–300 atoms). By warming of co-condensate samples from 90 K up to 150 K the relative integral intensity of multiple signals due to paramagnetic complexes decreases and the intensity of the central component increases), that reveals the thermal decomposition of the metastable complexes and the simultaneous growth of metal nanoclusters. ESR-signal of metal nanoclusters is stable in temperature range 150–200 K [14]. Further heating of the samples ($T > 200$ K) up to the temperatures of matrix crystallization led to sharp rising of molecular mobility and rapid coalescence of nanoclusters forming higher aggregates, which don't recorded by ESR-technique. TEM data show that annealing of co-condensate samples at low temperatures 150–200 K gives us almost monodiperse silver particles ($d = 2{,}0 \pm 0{,}5$)nm in size due to thermal decomposition of metastable complexes. So, the size estimated by ESR-data have been confirmed by the direct TEM data for the samples at these temperatures The same effect can be caused by UV-light irradiation of the film sample at 80 K.

Thus, silver and copper atoms form at low temperatures (80–90 K) metastable complexes with ligand molecules. Thermal degradation of the complexes at higher temperatures (120–150 K) or by UV-light irradiation resulted in metal atoms aggregation and simultaneous formation of metal nanoclusters (1–2 nm) in size at once. Such thermal behavior of the system can be deduced from the specifics of supramolecular organization of mesogenic cyanobiphenyl matrix. The combination of rigid aromatic core and flexible hydrocarbon chains of terminal substituents in ligand molecules leads to the formation of dimeric cyanophenyl structures at low temperatures, which stabilized metal atoms due to formation of metastable complexes. Thermal degradation of the complexes by rising 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 nanosize metal clusters of 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 crystallisation, causes matrix softening and rising the translational mobility of matrix molecules. This process followed by metal nanoclusters coalescence and formation of higher nanoparticles. Rapid heating up of the co-condensate up to the room temperature followed by the phase transition of the system in nematic (orientationally ordered) phase led to the formation of the anisotropic particles.

VIS-UV spectroscopic study of silver/CB and copper/CB systems confirmed the data of IR- and ESR spectroscopy. UV-spectra of silver/CB/decane system at 90 K show (Fig. 4, curve 1) the appearance of new structured absorbance band in visible region with maximum at 360 nm according to pale-yellow color of co-condensate films in comparison with colorless neat CB film. Quantum chemistry modeling of the complex exited states shows the existence of several intensive charge transfer transitions of metal-to-ligand and ligand-to-ligand types in the proposed sandwich-like π-complex structure in this spectral region. It should be mentioned that small silver clusters could also absorb at 380–420 nm.

This complex band (360 nm) disappeared by warming of the samples up to 200 K (Fig. 4, curve2,3), confirming complex thermal degradation at these temperatures. The new wide band with maximum at 440 nm simultaneously raised, that could be referred to absorbance of silver nanoparticle's surface plasmons [14]. The aggregation of silver atoms and small clusters via complex decomposition and formation of nanosize metal particles of could cause it. Rapid annealing of the co-condensate samples up to 300 K led to a red shift of this band maximum (increasing of the absorbance at higher wavelengths) (Fig. 4, curve 3), that could be connected both

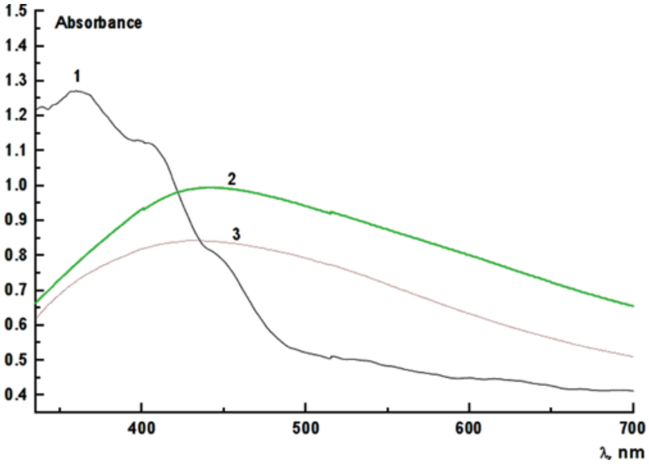


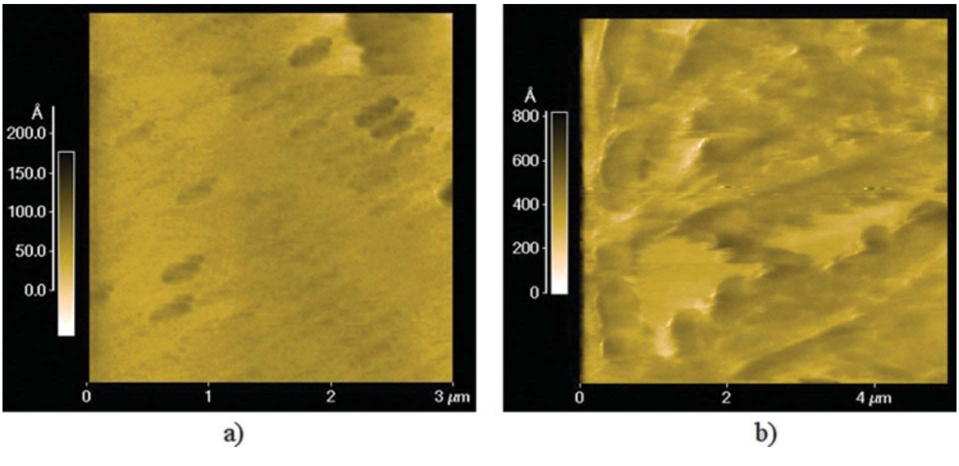
Figure 4. UV-VIS spectra of Ag/5CB co-condensates during annealing in temperature range 80–180 K: 1–80 K; 2–200 K, 3–300 K (the base spectrum of the neat cyanobiphenyl film is subtracted from the original co-condensate spectra). (Figure appears in color online.)

with rising of the size of the metal particles and with producing of the anisotropic metal particles in the liquid-crystalline mesophase of cyanobiphenyl matrix at room temperature. Analogous changes in optical spectra were recorded for Cu/5CB co-condensate systems. The copper nanoparticles plasmon resonance band was observed at 560 nm. [15].

3.3. *Morphology and Supramolecular Organization of Metal Nanoparticles in Nematic and Smectic Phases*

Transmission electron microscopy (TEM) data of metal-mesogenic nanosystems in thin film samples and encapsulated in polymeric poly-para-xylylene films show the formation of different morphology and size nanoparticles, stabilized by mesogenic ligands depending on the phase state of mesogenic matrix and metal concentration in the system [16]. The shape of the particles is in general the result of competition of general tendency of 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 5CB sample to the temperatures of isotropic phase existence ($T > 318$ K) led to the formation and stabilization of almost spherical nanoparticles with $d = (15 \pm 10)$ nm in size. Growth in the nematic phase of 5CB gives us anisometric nanoparticles. The maintaining of the samples at 273–283 K and increasing of the metal content in the sample from 1 up to 10 w/w % led to preferential growth of rod-like metal nanoparticles with higher l/d ratio more than 20.

Low temperature layer-by-layer co-condensation of silver, mesogenic compound 4-pentyl-4-cyanobiphenyl (5CB) and para-xylylene monomer followed by heating of the obtained film sample resulted in encapsulation of such hybrid metal-mesogenic system into polymer film. The data of AFM of the samples obtained in tapping mode show the formation of orientationally ordered assemblies of anisometric particles in nematic phase 5CB (Fig. 5a) and the formation of flat almost 2D-quazi-fractal nanometal aggregates in smectic (layered organized) phases of higher homology 4-octyl-4-cyanobiphenyl (8 CB) (Fig. 5b). Thus, metal clusters aggregation



a) b)

Figure 5. AFM-image (tapping mode) of silver-cyanobiphenyl mesogenic films: a) Ag/5CB (1/10) in nematic phase; b) Ag/8CB (1/10) in smectic phase. (Figure appears in color online.)

in nematic mesophase led to the formation of matrix governed formation of non-spherical nanoparticles and their ordered assemblies. In the case of formation of metal nanoparticles in the smectic phase of 8CB homology led to quasi-fractal 2D-structures growth (Fig. 5b) intercalating between smectic cyanobiphenyl bilayers due to higher interacting energy into the smectic layers and microphase segregation.

Optical spectra of silver/cyanobiphenyl and copper/cyanobiphenyl samples at 300 K contain characteristic bands of plasmon absorbance of metal nanoparticles at 420-440 nm and 560-600 nm. Increase of metal concentration in the sample led to the performable growth of rod-like metal particles with anisometric ratio $l/d > 20$ 20 and intensive absorbance at higher wavelengths ($\lambda \geq 650$ nm). The interaction of the samples with carbon tetrachloride vapor led to decrease of the absorbance at plasmon resonance band, that demonstrates the possibility of sensor applications of nanostructured films obtained.

4. Conclusions and Perspectives

New metal-mesogenic hybrid nanosystems were obtained based on silver and copper mesogenic alkylcyanobiphenyls derivatives, which formed diversely organized solid and liquid crystalline phases with different type of molecular organization. In temperature range 80-300 K the controlling of metal particles size in range 2-200 nm and their morphology and aggregation processes were made. Understanding the peculiarities controlling the size, shape and self-organization of nano- and subnanosized particles and the properties of hybrid metal-mesogenic materials including such particles is the main scope of our present and further investigations.

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References

[1] Lehn, J. M. (1995). *Supramolecular Chemistry*, VCH Verlags-gesellshaft: Weinheim, New York, Basel, Cambridge, Tokio, 328.
[2] Gleiter, H. (2000). *Acta Mater.*, *1*, 1.
[3] Gusev, A. I. (2005). *Nanomaterials, Nanostructures, Nanotechnologies*, Moscow.
[4] Suzdalev, I. P. (2006). *Nanotechnologies, Physico-Chemistry of Nanoclusters, Nanostructures and Nanomaterials*, Moscow.
[5] *Nanoscale Materials in Chemistry*, Klabunde, K. J. (Ed.), Wiley: New York.
[6] Sergeev, G. B. (2006). *Nanochemistry*, Elsevier, B. V., 248.
[7] Shabatina, T. I., & Sergeev, G. B. (2003). *Russ. Chem. Rev.*, *72*, 643.
[8] Shabatina, T. I., & Sergeev, G. B. (2008). *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 313–314, 18–22.
[9] Shabatina, T. I., Timoshenko, V. A., Morosov, Yu. N., & Sergeev, G. B. (2002). *Material science and Engineering*, C 22, 193.

[10] Shabatina, T. I. (2003). *Moscow University Chemistry Bulletin*, *57*(N5), 20–36.

[11] Sergeev, G. B., & Shabatina, T. I. (2002). In: *Frontiers in Surface and Interface Science*, Duke, Ch. B. & Plummer, E. V. (Eds.), Elsevier Science B.V., NHL, 628–655.

[12] Shabatina, T. I. (2007). *Struct. Chem.*, *18*, 511.

[13] Howard, J. A., Joly, H. A., & Mile, B. (1990). *J. Phys. Chem.*, *94*, 1275.

[14] Shabatina, T. I., Timoshenko, V. A., Belyaev, A. A., Morosov, Yu. N., & Sergeev, G. B. (2002). *Bull. Russian Acad. Sciences*, *387*, 193.

[15] Shabatina, T. I., Morosov, Yu. N., Timoshenko, V. A., & Sergeev, G. B. (2005). *Mol. Cryst. and Liq. Cryst.*, *440*, 325.

[16] Shabatina, T. I., & Sergeev, G. B. (2010). In: *Polymer Thin Films*, Hashim, A. A. (Ed.), Chapter 11, InTech Pub., 185–196.