

SELF-ASSEMBLED NANOSTRUCTURES, FORMED BY YTTRIUM CROWN-PHTHALOCYANINATE IN SOLUTIONS

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Abstract

Optical and electrochemical properties of materials, based on phthalocyanines, are strongly influenced by their supramolecular organization in solid phase (crystals, polymeric composites, thin films). However, the understanding of the behavior of phthalocyanine complexes in solutions and their tendency to aggregation due to weak intermolecular interactions allows to predict the assembling of molecules in the solid state.

Herein, we performed systematic investigation of self-assembly of yttrium(III) tetra-15-crown-5-phthalocyaninato-acetate (**1**) in tetrachloroethane (TCE) solution. Studies were performed by means of transmission electron and atom force microscopy (TEM and AFM), as well as UV-Vis spectroscopy and dynamic light scattering (DLS).

DLS studies revealed that successive heating/cooling cycles, applied to solution of (**1**) in TCE resulted in formation of nanoparticles that was observed even after the first cycle. The growth of particles further occurred in next cycles and followed by hypsochromic shift of Q-band in UV-Vis spectra of investigated solutions from 680 to 640 nm, suggesting formation of cofacial supramolecular assemblies (H-aggregates). The diameter (15 nm) and length (250 nm) of assembled nanoparticles were determined by AFM technique. TEM studies of these particles suggest their crystalline structure, due to characteristic electron diffraction pattern.

The proposed approach can be used for elaboration of novel optoelectronic materials with controllable structure. For example, polyvinylcarbazole composites doped with the similar nanoparticles based on Ru(II) complexes reveal enhanced nonlinear optical properties. The study of optoelectronic properties of composites based on obtained nanoparticles is in the progress.

Keywords: phthalocyanine, yttrium(III), nanoparticle, aggregation, DLS, AFM and TEM techniques.

1. INTRODUCTION

Phthalocyanines (Pc) produced for 75 years as blue and green pigments are the most important organic colorants due to high intensity of light absorption together with high photo-, electro-, thermal and chemical stability. In the recent years it was found that the Pc can be also used as optoelectronic materials, photovoltaic cells, data storage devices, agents for photodynamic therapy, etc. [1]

Optical and electrochemical properties of Pc are strongly influenced by their *molecular* structure, namely the nature of metal center, as well as number, nature and arrangement of substituents on the periphery of the macrocycle. On the other hand, *supramolecular* interactions predetermine such properties of bulk materials as electronic conductivity, nonlinear optical properties, etc., since they play leading role in the ordering of molecules in solid state. Moreover, Pc can form supramolecular assemblies in solution because these aromatic compounds tend to aggregate by means of the stacking interactions. These aggregates formed in solution act as “precursors” for assembling in solid phase materials – polymeric composites, thin films, etc.

One of the most powerful tools to control Pc aggregation is introduction of crown-ethers at the periphery of the Pc macrocycle. Two last decades of crown-phthalocyanine chemistry have been marked by comprehensive studies of synthesis of novel crown-Pc's, their assembly induced by various factors, fabrication of thin films, incorporation into opto- and iono-electronic devices, and synthesis of biomimetic models, sensing applications, photovoltaics and photorefractive materials [2].

Recently it was demonstrated that solvent-induced aggregation of ruthenium(II) 15-crown-5-phthalocyaninates resulted in formation of nano-sized aggregates, which reveal strong increase of nonlinear optical susceptibility in comparison with monomeric compounds [3,4]. When introduced into a conducting polyimide with a high glass transition temperature, these aggregates demonstrated near-IR photorefractive properties, which were not observed in the case of monomeric complexes. These polymer composites, responsive to near-IR absorption, were proposed as materials for laser-beam correction and amplification for biomedical diagnosis and telecommunication devices. Further investigation evidenced that replacement of ruthenium ion with gallium(III) and indium(III) resulted in increase of nonlinear optical susceptibility of composites [5-7].

In the present work, the behavior of Yttrium(III) crownphthalocyaninato acetate (1) (Fig. 1) in solutions, thin films and polymeric composites was investigated since Y(III) complex is an analogue of previously investigated Ga(III) and In(III) complexes, therefore, the correlations between the nature of metal ion and photophysical characteristics of its complex can be established.

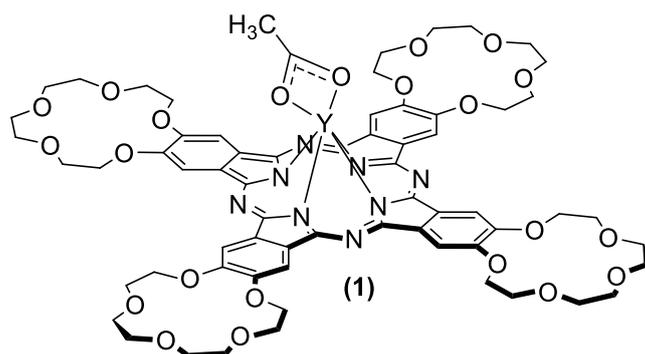


Fig. 1. Chemical structure of Yttrium(III) tetra-15-crown-5-phthalocyaninato acetate (1)

2. EXPERIMENTAL

Complex (1) was synthesized in quantitative yield via interaction of tetra-15-crown-5-phthalocyanine with yttrium acetate and 1,8-diazabicyclo[5.4.0]octadecene-7 in refluxing o-dichlorobenzene with subsequent preprecipitation from chloroform-hexane mixture.

Solution of complex (1) in tetrachloroethane (TCIE, Aldrich) was heated in Peltier cell to 70 °C and cooled to 5 °C with simultaneous measurements of UV-Vis spectra in 300-900 nm range. Heating-cooling cycles were repeated for three times. DLS measurements were performed after each cycle by means of DelsaNano C (Beckman Coulter, USA) particle size and analyzer at light wavelength 685 nm. The AFM investigation was carried out with AFM model Enviroscope and controller Nanoscope V from Bruker. Transmission electron microscopy was performed using LEO 912 AB OMEGA (Karl Zeiss) with accelerating voltage 100 kV.

3. RESULTS AND DISCUSSION

3.1 Investigation of aggregation of yttrium crownphthalocyaninato-actete in solutions

Measurements of UV-Vis spectra of (1) dissolved in TCIE upon heating and cooling were performed in spectrophotometer equipped with Peltier cell. Being in monomeric state, the complex revealed single Q-band

at 678 nm in UV-Vis spectrum (Fig.2a, dashed). Cooling of this solution to 5°C resulted in broadening of the Q-band with appearance of new band at 647 nm (Fig.2a, solid), which corresponds to formation of aggregates with cofacial arrangement of molecules – H-aggregates. Similar behavior was observed previously for other crown-phthalocyaninates [3-6].

At this step, DLS measurements revealed formation of 10-30 nm in diameter nanoparticles (average size – 15 nm, Fig.2b), which were absent in starting solution. One more heating and cooling of solution cycle resulted in further aggregation of complex **(1)** which was followed by increase of intensity of Q-band at 645 nm (Fig.2c) as well as growth of size of nanoparticles up to 20-60 nm (average size – 35 nm, Fig.2d). One more cycle of heating and cooling of the solution did not result in changing of UV-Vis spectra and increase of size of nanoparticles (Fig.2e,f), suggesting that the formation of nanoparticles was essentially finished at the second heating-cooling cycle. Notably, the obtained colloidal system was stable and the size of nanoparticles did not change upon storage of the solution (for how many hours, days). Therefore, application of simultaneous UV-Vis spectroscopy and DLS measurements evidenced of the formation of supramolecular assemblies by **(1)** in TCIE solutions.

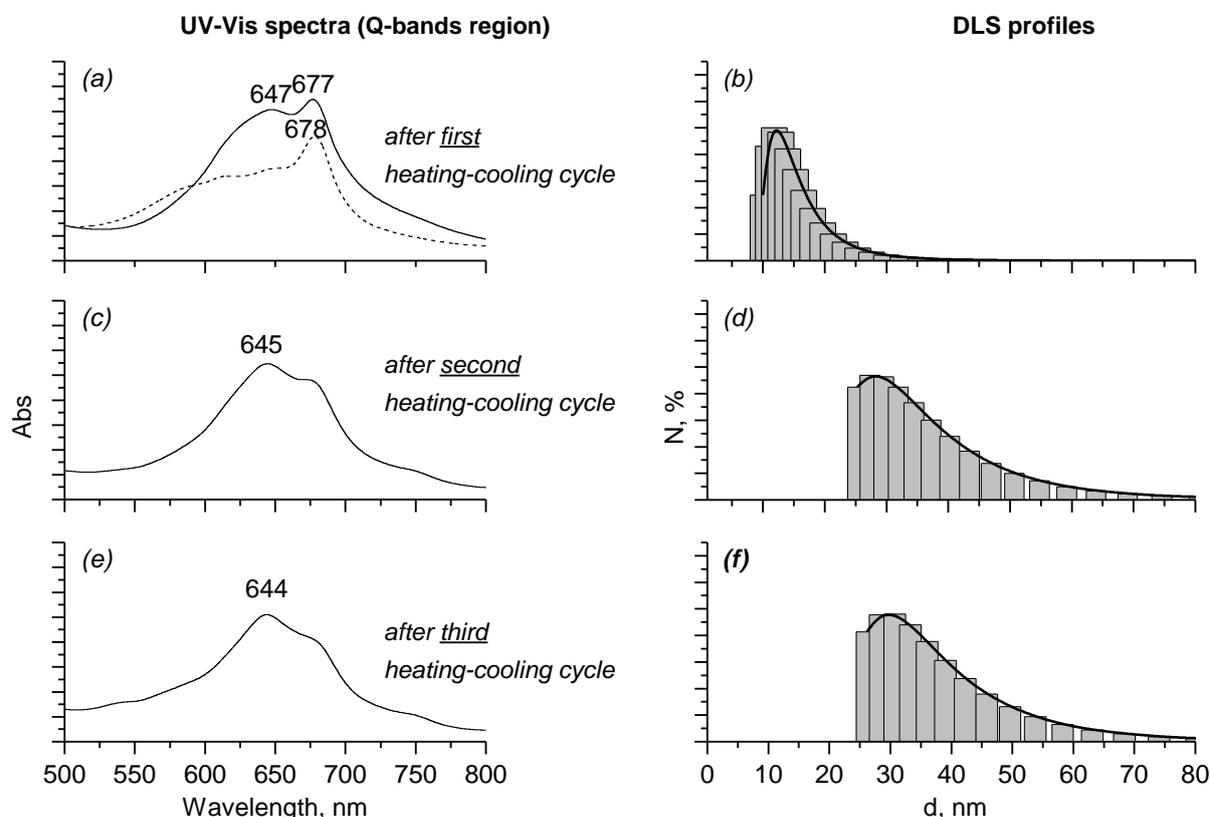


Fig. 2. Results of DLS measurements and Q-bands region of UV-Vis spectra of solution of **(1)** in TCIE before (dashed line) and after one (a,b) two (c,d) and three (e,f) cycles of heating to 70°C and cooling to 5°C.

3.2 Morphology of aggregates, formed by yttrium crownphthalocyaninato actete in cast films

Investigation of morphology of aggregates was performed by AFM and TEM techniques.

TEM studies of powdered **(1)** evidenced that it consists of amorphous phase that did not reveal electron diffraction (Fig.3a). When **(1)** was dissolved in TCIE and freshly prepared solution was casted onto graphite without proceeding heating-cooling, the formation of amorphous film was observed (Fig.3b). This film contained only minor amount of crystalline phase with weak electron diffraction (Fig. 3c). Probably, the

formation of this phase was due to local increase of concentration upon evaporation of solvent and subsequent crystallization of **(1)** on graphite surface.

AFM studies of cast film obtained from freshly prepared solution of **(1)** on mica did not evidence of formation of any supramolecular assemblies. However, when solution of **(1)** in TCIE was heated and cooled for three times and cast on mica surface, the formation of aggregates was observed by AFM. The average size of these aggregates was 500x20 nm. The morphology of cast film depended on concentration of **(1)** – application of diluted solution (10^{-5} M) resulted in formation of isolated aggregates (Fig.4a); increase of concentration up to 10^{-4} - 10^{-3} M resulted in formation of ribbons, composed of stacked aggregates (Fig.4c). Formation of such assemblies result in appearance of electron diffraction pattern with intensive reflexes which evidenced of their crystallinity (Fig.5).

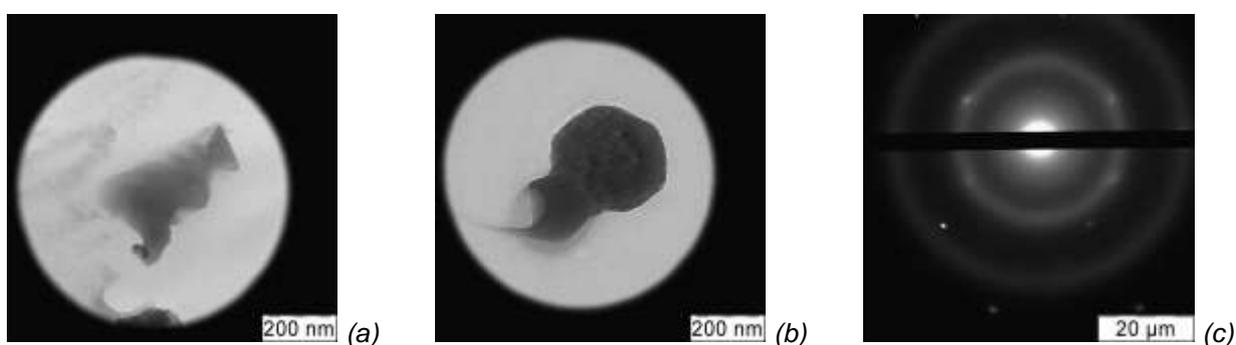


Fig. 3. TEM images of complex **(1)**: (a) – powder; (b) – cast film obtained from freshly prepared solution on graphite surface; (c) – electron diffraction pattern from cast film.

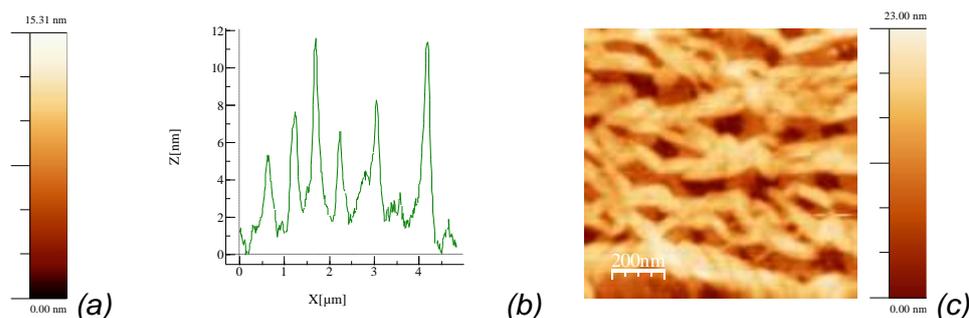


Fig. 4. AFM images of complex **(1)**: (a) – cast film prepared from 10^{-5} solution; (b) – line profile showing the size of aggregates; (c) – cast film prepared from 10^{-3} solution.

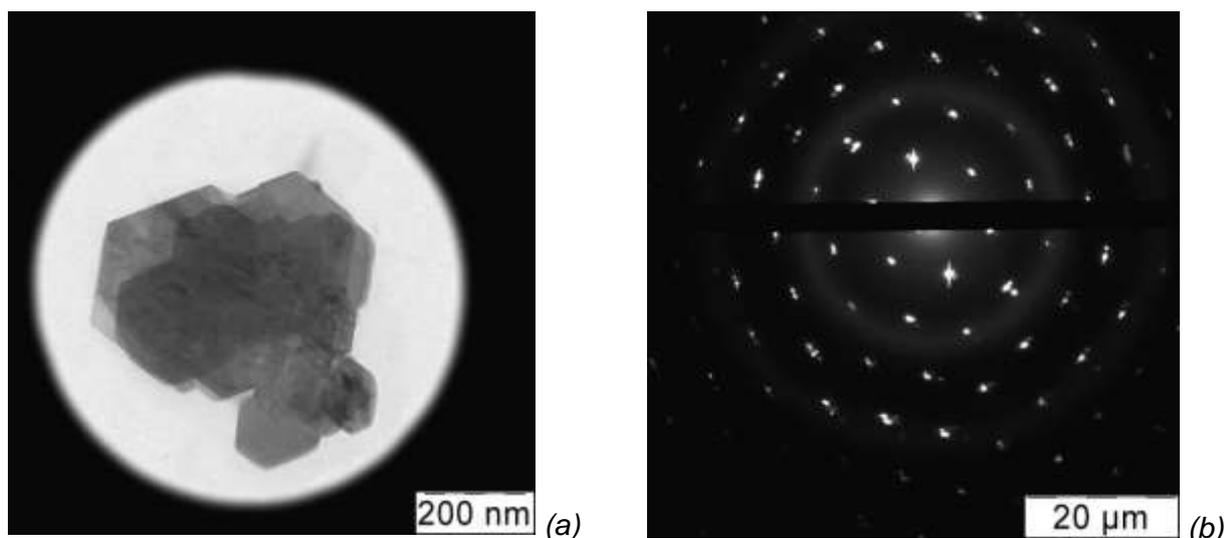


Fig. 5. TEM image of aggregates, formed from 10^{-3} M solution on graphite surface (a) and corresponding electron diffraction pattern (b).

3.3 Photoelectric and photorefractive properties of polymeric composites, doped with yttrium crownphthalocyaninato-acetate

Investigation of composites, formed by supramolecular aggregates of **(1)** and polyvinylcarbazole (PVC) at 1064 nm evidenced that these materials reveal photorefractive properties. The maximum coupling gain coefficient found for the material composed of PVC and **(1)** at an electric field intensity of $120 \text{ V}/\mu\text{m}$ was $\Gamma = 35 \text{ cm}^{-1}$. Quantum yield of formation of electron-hole pairs was $\phi_0 = 0.6$. Dielectric susceptibility of **(1)** measured by Z-scan method in TCIE solution (1mg/ml) was also determined – $\chi(3) = 4.2 \times 10^{-10}$ esu. More details can be found in paper [8].

CONCLUSIONS

Comprehensive investigation of behavior of yttrium(III) crownphthalocyaninato-acetate **(1)** in solutions, cast films and polymeric composites was performed by means of UV-Vis spectroscopy, DLS, AFM, TEM and Z-scan techniques. The formation of nanosized aggregates in solution was observed upon heating and cooling of solution of **(1)** in tetrachloroethane. The polyvinylcarbazole composites doped with these aggregates reveal photorefractive properties. The proposed approach for fabrication of aggregates of **(1)** can be utilized in elaboration of novel optoelectronic materials and devices.

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LITERATURE

- [1] WÖHRLE, D., SCHNURPFEIL, G., MAKAROV, S. G., KAZARIN, A., SUVOROVA, O. N. Practical Applications of Phthalocyanines – from Dyes and Pigments to Materials for Optical, Electronic and Photo-Electronic Devices. *Macroheterocycles* 2012, 5, 191–202.

- [2] GORBUNOVA, Y. G., MARTYNOV, A. G., TSIVADZE, A. Y. Crown-Substituted Phthalocyanines: From Synthesis towards Materials. In *Handbook of Porphyrin Science*; Kadish, K. M.; Smith, K. M.; Guillard, R., Eds.; World Scientific Publishing, 2012; Vol. 24, pp. 271–388.
- [3] GRISHINA, A. D., GORBUNOVA, Y. G., ZOLOTAREVSKY, V. I., PERESHIVKO, L. Y., ENAKIEVA, Y. Y., KRIVENKO, T. V., SAVELYEV, V., VANNIKOV, A. V., TSIVADZE, A. Y. Solvent-Induced Supramolecular Assemblies of Crown-Substituted Ruthenium Phthalocyaninate: Morphology of Assemblies and Non-Linear Optical Properties. *J. Porphyrins Phthalocyanines* 2009, 13, 92–98.
- [4] GRISHINA, A. D., ZOLOTAREVSKY, V. I., GORBUNOVA, Y. G., PERESHIVKO, L. Y., ENAKIEVA, Y. Y., KRIVENKO, T. V., SAVELYEV, V., VANNIKOV, A. V., TSIVADZE, A. Y. The Influence of a Solvent on the Aggregation of ruthenium(II) Tetra-15-Crown-5-Phthalocyaninate. *Russ. J. Phys. Chem. A* 2009, 83, 1907–1912.
- [5] VANNIKOV, A. V., GRISHINA, A. D., GORBUNOVA, Y. G., KRIVENKO, T. V., LARYUSHKIN, A. S., LAPKINA, L. A., SAVELYEV, V., TSIVADZE, A. Y. Photoelectric, Nonlinear Optical, and Photorefractive Properties of Composites Based on poly(N-Vinylcarbazole) and Gallium Phthalocyaninate. *Polym. Sci. A* 2011, 53, 1069–1075.
- [6] VANNIKOV, A. V., GORBUNOVA, Y. G., GRISHINA, A. D., TSIVADZE, A. Y. Photoelectric, Nonlinear Optical, and Photorefractive Properties of Polymer Composites Based on Supramolecular Ensembles of Ru(II) and Ga(III) Complexes with Tetra-15-Crown-5-Phthalocyanine. *Prot. Met.* 2013, 49, 57–65.
- [7] GRISHINA, A. D., GORBUNOVA, Y. G., KRIVENKO, T. V., LAPKINA, L. A., SAVEL'EV, V. V., VANNIKOV, A. V., TSIVADZE, A. Y. Photorefractive and Nonlinear Optical Properties of indium(III) tetra(15-Crown-5)phthalocyaninate-Based Composites. *Prot. Met.* 2014, 50, 472–479.
- [8] VANNIKOV, A. V., GRISHINA, A. D., GORBUNOVA, Y. G., LAPKINA, L. A., SAVEL'EV, V. V., ZOLOTAREVSKY, V. I., KRIVENKO, T. V., LARYUSHKIN, A. S., TSIVADZE, A. Y. The Influence of the Central Atom on the Photoelectric, Nonlinear and Photorefractive Optical Properties of Phthalocyaninate. *High Energy Chemistry*, 2015, DOI: 10.7868/S0023119715010147.