Electronic structure, optical and magnetic properties of
tetraphenylporphyrins-fullerene molecular complexes

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Abstract. This work presents optical, magnetic properties and quasi-equilibrium condensation processes of thin composite films based on C_{60}-MeTPP complexes. The elemental composition, surface morphology and distribution uniformity of the elements were investigated by SEM and energy-dispersive analysis. Different results were obtained for various types of MeTPP. Photoluminescence results showed decrease of intensity with C_{60} adding. The temperature dependence of magnetization M(T) and the field cooling (FC) and zero-field cooling (ZFC) curves for powder samples of CuTPP and CuTPP-C_{60} were measured to determine the changes in the magnetic behavior. Quantum-chemical calculations were performed to elucidate the experimental results.

1. Introduction

One of the most promising materials for organic optoelectronic devices, such as artificial photosynthesis systems and solar cells, are the molecular complexes of fullerenes with organic donors (e.g. porphyrins, phthalocyanines, pentacene) [1-3]. Fullerene is known as an acceptor with strong π-electron accepting ability, thus fullerene-based structures may be important for the study of photoinduced electron transfer. There are two basic approaches to the creation of such systems: synthesis of dyad molecules with C_{60} covalently bonded to porphyrins [4] and developing the self-assembled non-covalent complexes [2, 5, 6].

Intensively developed area of electronic devices based on carbon requires as physical as technological research of new materials. Composite materials and devices based on porphyrins attract a particular interest. Moreover, such devices can replace (or surpass in characteristics) usual silicon-based electronic devices. Tetraphenylporphyrin (TPP, the chemical formula is C_{44}H_{30}N_{4}) and its complexes with metal are p-type semiconductors and have high hole mobility, which determines its great application perspectives in organic optoelectronics [6]. The main type of these materials is fullerene (acceptor) and MeTPP complexes, which can be used in photovoltaic devices [6-8]. Noncovalent and covalent bonded fullerene complexes with various types of porphyrins have a good ability of self-organization because the energy minimum corresponds to the position where fullerene is located under TPP macrocycle. It became possible to create supramolecular structures, but usually they are studied only in solutions [8] or theoretically [9].
This work is devoted to experimental study of tetraphenylporphyrins –fullerene MeTPP-C$_{60}$ complexes (in which Me is Zn(II), Cu(II), Fe(II)).

2. Obtaining and investigation methods

MeTPP and MeTPP-C$_{60}$ thin films were produced by vacuum deposition in quasi-equilibrium conditions on Si, KBr and glass substrates. The film thickness was 200-500 nm. Surface morphology and phase composition of prepared films were investigated by secondary electron microscopy with an energy-dispersive X-ray console. Porphyrins: Zn(II)TPP, Cu(II)TPP, coordinated complex FeClTPP and its composites with fullerene were made by co-deposition in quasi-closed volume and by crystallization from solutions. It was shown that ZnTPP-C$_{60}$ and FeClTPP–C$_{60}$ films have a homogeneous structure with crystallite sizes in the lateral plane of about 1 mkm (see figure 1 (a)). In contrast, CuTPP-C$_{60}$ films have two different phases: CuTPP nanowire (of 20 nm in diameter) and C$_{60}$ cubic crystallites (of about 100 nm) (see figure 1 (b)). In this case, C$_{60}$ crystallites grow only over porphyrin nanowires that leads to the nanostructured films formation.

![Figure 1. SEM results. (a) – surface morphology of ZnTPP-C$_{60}$ film, (b) – CuTPP-C$_{60}$ film](image-url)

The method of crystallization from solutions gave the same result. Composition analysis by an energy-dispersive X-ray console showed that at most the composition does not change for ZnTPP, CuTPP –based films and corresponds to the stoichiometry. A depletion of Cl atoms (approximately halved) was found for FeClTPP-based films as compared with the original composition. In the same time, there was an indication of an appreciable amount of oxygen (about 3 wt% when background is 0.7%). Quantum-chemical calculations showed a weak bond of Cl atoms with the core of the porphyrin macrocycles. It can be assumed that Cl atoms partly detached from complexes during the thermal evaporation. Wherein, vacant Fe atoms bond with oxygen. The possible transition from Fe(II) to Fe(III) can lead to changes in magnetic properties. This fact requires further study.

Photoluminescence (PL) spectra for films of both types were measured. PL spectra are shown in figure 2. The reduction in emission intensity in MeTPP-C$_{60}$ as compared with pure MeTPP films is due to the photoinduced charge transfer between C$_{60}$ and MeTPP molecules. Fullerene adding leads to negligible changes in vibrational spectra of MeTPP because the distance between molecules in donor-acceptor couple is big enough (about 3Å). Emission in porphyrins is possible from various types of energy levels (for example, $S_1 \rightarrow S_0$ or $S_2 \rightarrow S_0$, which are prohibited for fullerenes). Due to these facts, the photoinduced charge transfer decreases a possibility of transfer with photon emission.

The temperature dependence of magnetization M(T) and the field cooling (FC) and zero-field cooling (ZFC) curves for powder samples of CuTPP and CuTPP-C$_{60}$ were measured to determine the changes in the paramagnetic behavior of (Cu$^{2+}$) under the complex formation. The intensity of M(T)
and M(H) dependences was found to decrease for the CuTPP-C\textsubscript{60} sample. Decrease in magnetization can be explained by interaction between CuTPP and C\textsubscript{60} after molecular complexes formation.

![Figure 2. Photoluminescence spectra of ZnTPP (solid line) and ZnTPP-C\textsubscript{60} (dash line).](image)

Density functional theory DFT/B3LYP calculations for MeTPP, C\textsubscript{60} and MeTPP-C\textsubscript{60} complexes were performed to elucidate some experimental results. The electronic structures of electron densities with energy levels at HOMO and LUMO were investigated. The calculations give the optimized geometry, formation energy and HOMO-LUMO gap for molecular complexes. Formation energy E(C\textsubscript{60})+E(MeTPP)–E(MeTPP-C\textsubscript{60}) equals to 0.21 eV for ZnTPP and 0.17 eV for CuTPP and HOMO-LUMO gap equals to 1.8–1.6 eV. Charge transfer between the components of the complex in the ground state is very small being of the order of 0.03 qe. Good agreement was found between the experimental measurements, the results of our DFT calculation and the data from [7].

3. Conclusions
MeTPP-based composite structures were obtained by two techniques. Complex experimental and theoretical analyses were performed for these samples. Energy-dispersive analysis found changes in FeClTPP composition after heating (i.e. during the thermal evaporation process). There was a Cl amount depletion. Fe showed active interaction with oxygen after destroying of bonds with Cl. For other MeTPP the composition did not change. Various types of MeTPP have different surface morphology. CuTPP-based films grow as nanowires with phase separating on C\textsubscript{60} crystallites and CuTPP wires. ZnTPP and FeCITPP samples have a smooth and homogenous surface. Photoluminescence and magnetic measurements showed intensity decrease for samples with fullerene. It can be explained by interaction between MeTPP and C\textsubscript{60} molecules. Quantum-chemical calculations confirm this conclusion.

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