

The influence of morphology and dispersion on the emission properties of materials based on lanthanide complexes

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Introduction

In recent decades, interest in lanthanide coordination compounds has been exponential. This is due to both fundamental and applied aspects. The first is related to the establishment of the relationship between the composition, structure, properties and structural features, and the second - to the use of luminescent coordination compounds as precursors of electroluminescent materials in organic light-emitting diodes [1-4], liquid crystal displays [5], sensors [6, 7], molecular thermometers [8, 9], fluorescent labels in biology and analytical chemistry [10, 11]. It is no secret that the dispersity and morphology have a decisive influence on the properties of nanomaterials. If certain regularities have already been established for nanopowders of metals and oxides, there are also few studies for coordination compounds. Depending on the electronic structure of the central ion, compounds can exhibit emission in the visible or IR spectral range. In this work, the synthesis of mono- and heterometallic, monomeric and metallopolymer complexes of lanthanides with unsaturated β -diketonates was carried out. Copolymers based on styrene, vinylcarbazole and methyl methacrylate were obtained. The composition, structure, morphology, dispersity and spectral-luminescence properties of all synthesized compounds were studied.

Materials and methods

Ligands were synthesized by Claisen condensation according to the scheme described by [12]. As starting compounds are chosen β -diketonate ligands (2,5-dimethylheptene-1-3,5-dione (dmhpd), (2,6-dimethyloctene-1-3,5-dione (dmokd), (2-methyl-5-phenylpentene-1-3,5-dione (mphpd) (2-methyl-5-biphenyl pentene-1-3,5-dione (mbphpd) are shown in fig. 1a. The synthesis of complexes was performed by the interaction of aqueous solutions of metal salts) with an aqueous solution of sodium salt of the corresponding ligand at a molar ratio of reagents 1: 3 (pH 8-9) at room temperature Fig. 1b.

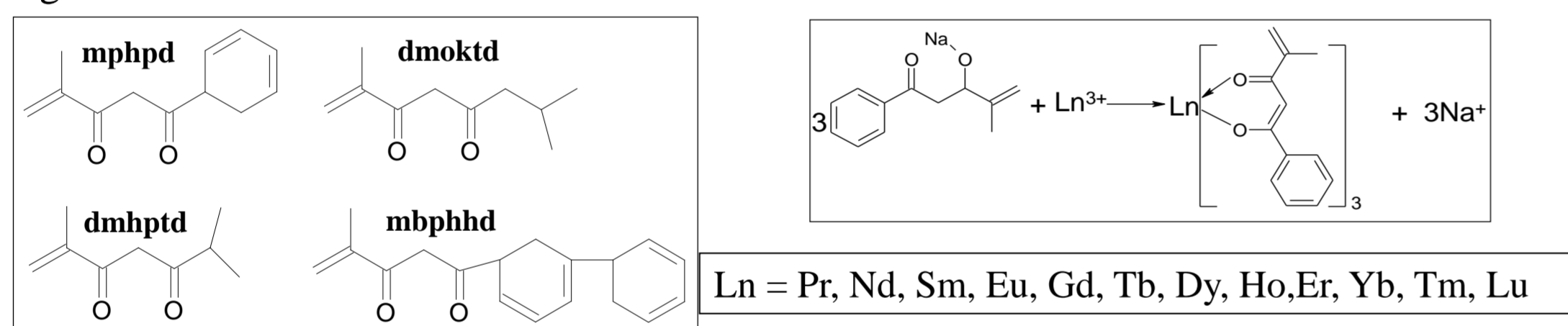
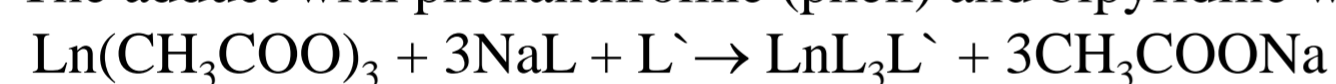


Figure 1 – Molecules of ligands used in the work (a), scheme of syntheses (b).

The adduct with phenanthroline (phen) and bipyridine was synthesized by reaction:



where L= dmhpd, dmokd, mphpd, mbphpd, L' = phen, dipy.

Polymer metal complexes are obtained by the thermally initiated radical polymerization. All synthesised complexes was investigatigstion. Quantum-chemical calculations of molecules of ligands and metal complexes were carried out: enthalpy of formation, total energy of the molecule and bond lengths, parameters of electronic pop ulation of ligands. The geometry of β -diketonate molecules and complexes was calculated using the MOPAC2016 program. The PM7 method was chosen for the calculation. The use of this method in combination with the SPARKLE model, in which the lanthanide atom is represented as a point charge, allows obtaining reliable data on the geometry of lanthanide complexes with both aliphatic and aromatic ligands.

Results and discussion

Using physicochemical methods of analysis (IR, UV-Vis, DTG, elemental and DLS analyses, SEM microphotogtaphy) the composition of the complexes and the structure of the nearest coordination environment of the metal ion in the complex were determined. The quantum chemical calculations made it possible to geometrically optimize the molecules of some β -diketonate complexes (Fig. 2). The results showed that regardless of the nature and geometric structure of the substituent in the β -diketonate molecule, the complexes are characterized by a non-planar structure, and the ligands are located in different planes. Ligands are coordinated to the central ion by two oxygen atoms in a bidentate-chelate manner.

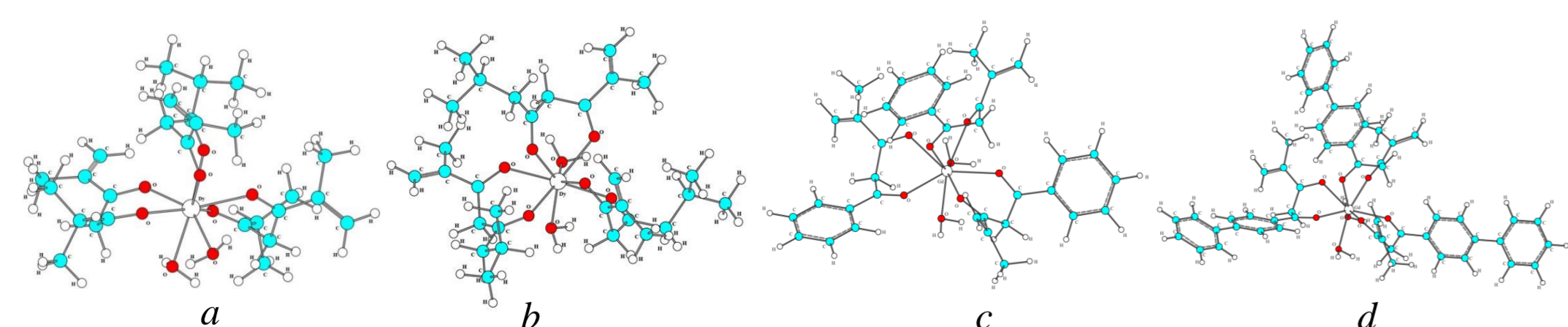


Figure 2 – Geometrically optimized structures of complexes a- Dy(dmhpd)₃, b- Dy(dmokd)₃, c- Gd(mphpd)₃, d-Gd(mbphpd)₃.

Thus, the shape and position of the bands in the IR spectra of monomeric and metallopolymer complexes are characteristic of bidentate-cyclically coordinated β -diketonate ligands (fig.3). The shift in the position of the bands of metallopolymer complexes compared to monomers in the low-frequency region indicates a weakening of the metal-ligand bond, which is caused by an increase in the covalency of the M-O bond in the latter [31-33].

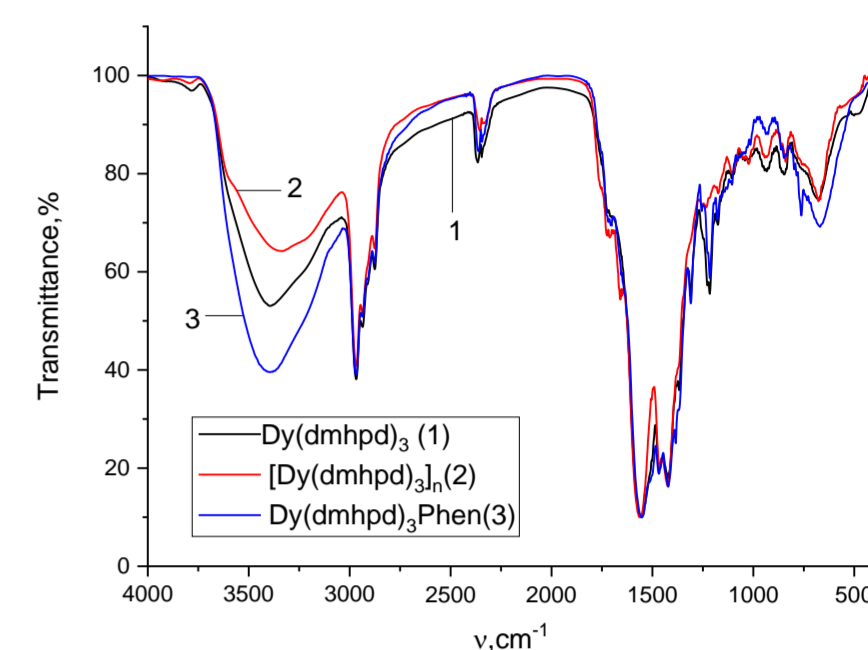


Figure 3 IR spectra of coordination compounds of dysprosium (III)

In general, the results of chemical and thermal analysis, the IR spectroscopy method allow us to depict the structure of the complexes as follows (Fig.4):

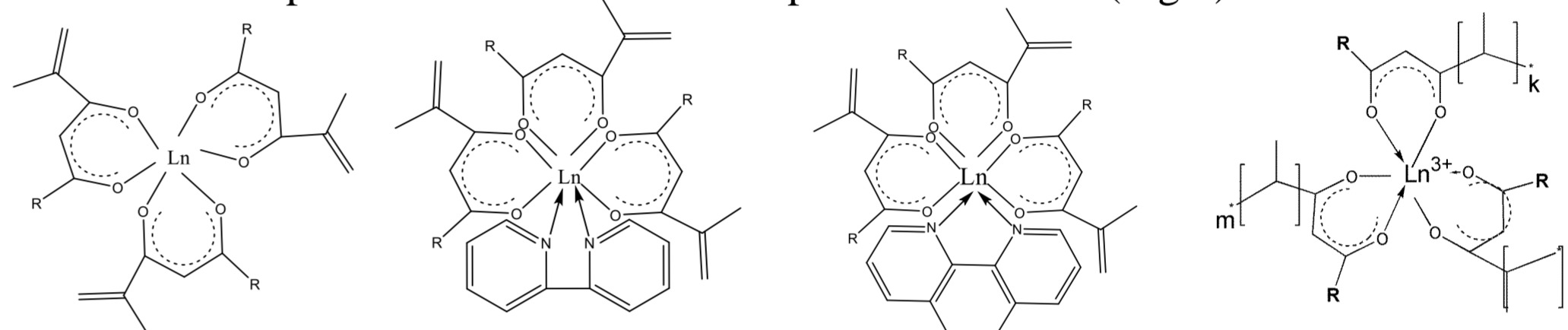


Figure 4 Structure of complexes R=, -C₆H₅; C₁₂H₉; -CH(CH₃)₂; -CH₂CH(CH₃)₂

Let us consider the influence of morphology and dispersion on the luminescence properties using the example of some lanthanides. As can be seen from Fig. 5 for complexes and metallopolymer based on dmokd and dmhpd, all emission transitions $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ are present; J = 9, 11, 13, 15 are characteristic of the Dy³⁺ ion. The absence of significant displacement and splitting of the metallopolymer bands confirms the same structure and symmetry of the coordination polyhedron of the monomer and metallopolymer complexes.

Comparative analysis of microphotographs of powders with different ligand systems confirms the existence of a relationship between the nature of the substituents in the ligands and their physicochemical properties. This seems to be an obvious fact, since the nature of the substituents mostly determines the properties. If dysprosium complexes with alkyl substituents have fairly high emission characteristics, then for compounds with aryl substituents, they are 10 times lower Fig. 5a,b. Thus, powders of all complexes based on dmokd and dmhpd can be classified as nanopowders (Fig. 6 a-d). At the same time, compounds based on aryl substituents (fig.6 e,f) have a layered agglomerated structure. As a result, there is no emission.

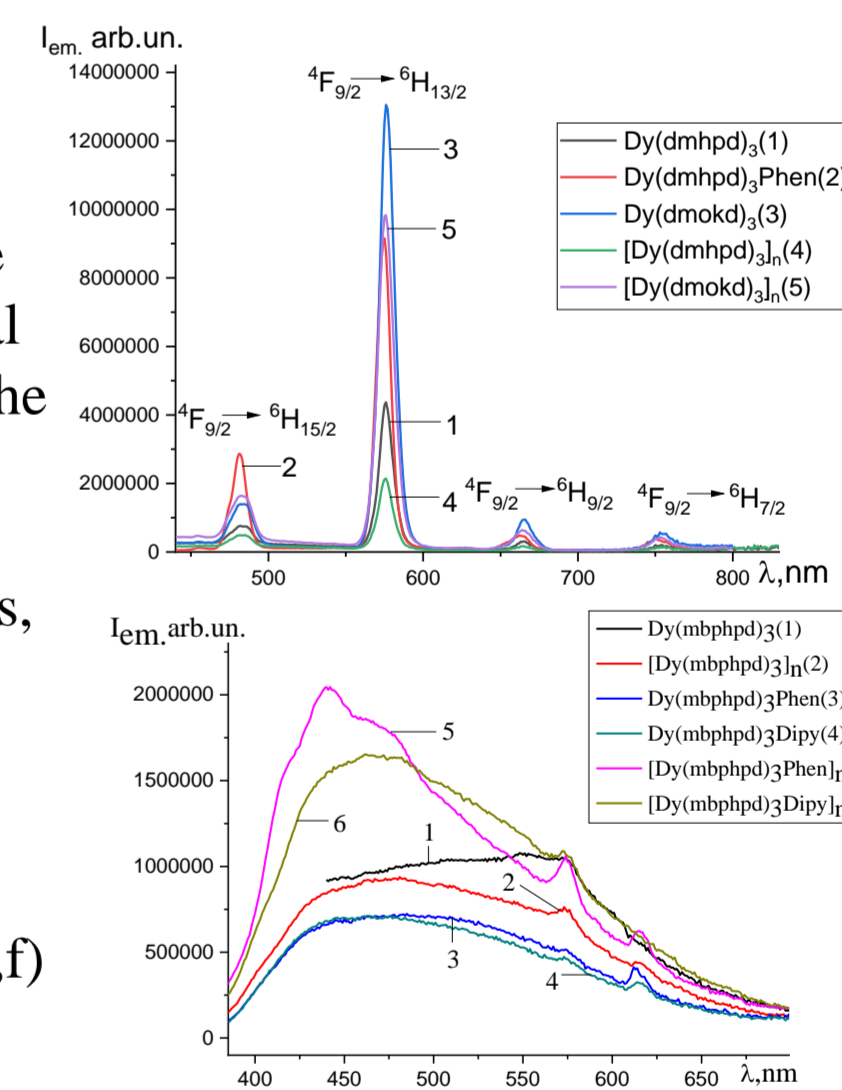


Figure 5 Emission spectra of Dy(III) compounds

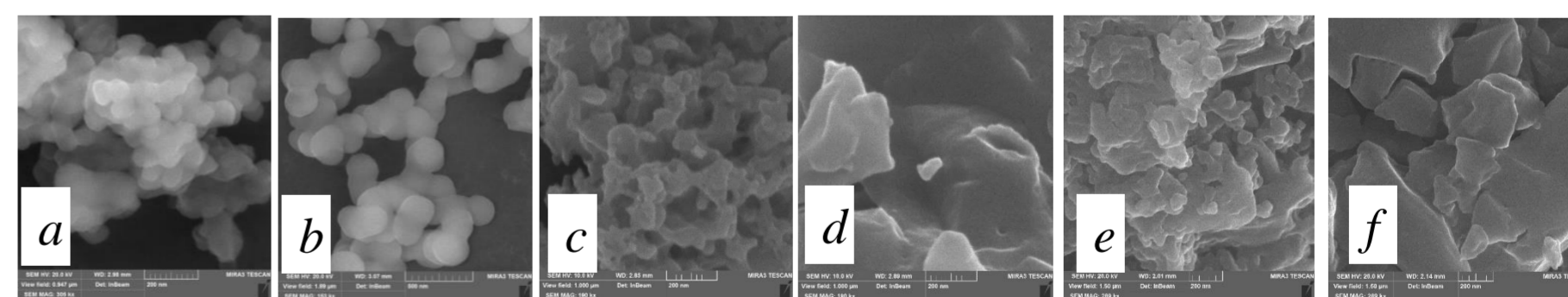


Figure 6 SEM microphotography Dy(dmokd)₃-a, [Dy(dmokd)₃]_n-b, Dy(dmhpd)₃-c, [Dy(dmhpd)₃]_n-d, Dy(mbphpd)₃-e, [Dy(mbphpd)₃]_n-f

As can be seen from Fig. 7, such correlations occur for compounds based on one ligand, methacryloacetophenone (mphpd).

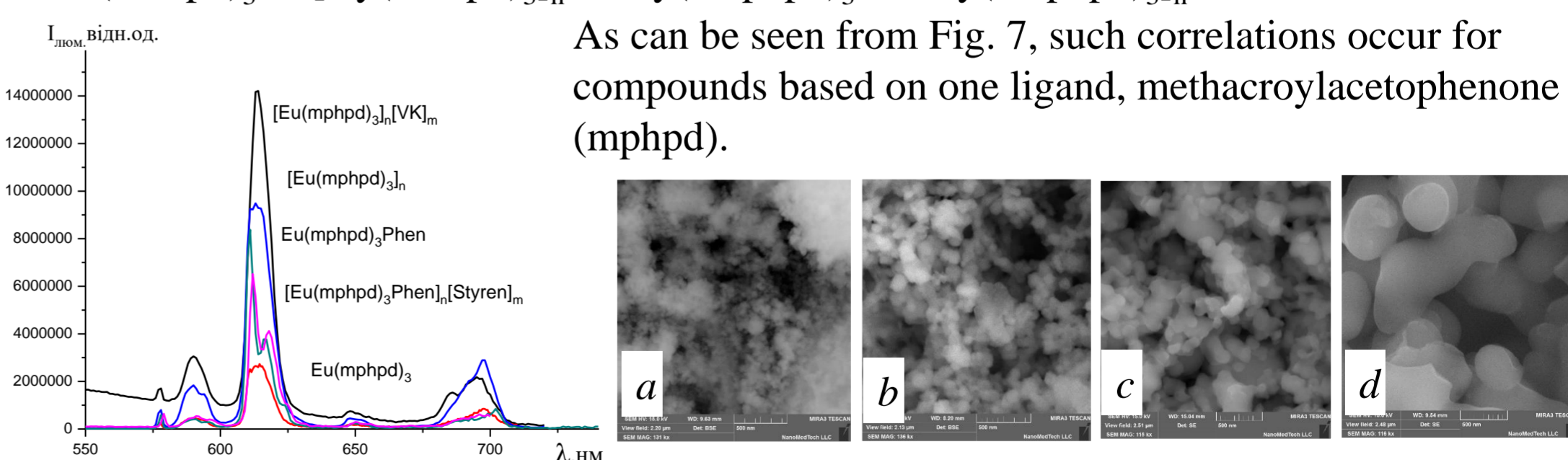


Figure 7 Emission spectra of Eu(III) compounds and SEM microphotography Eu(mphpd)₃ - a, [Eu(mphpd)₃]_n - b, [Eu(mphpd)₃]_n[VC]_m - c, [Eu(mphpd)₃]_n[Styrol]_m - d

Conclusion

The conducted studies showed that varying the substituents in the chelate rings allows for a purposeful influence on the emission properties of metal complexes. High disperse systems, which contain particles of spherical size, are characterized by a higher emission than similar polydisperse and microdisperse systems.