INTRODUCTION

The unique physicochemical properties of phthalocyanines and their metal complexes have made them subjects of numerous fundamental and applied studies. In recent years, phthalocyanines, which involve organic fragments of diverse chemical nature as peripheral substituents, were actively studied. Varying the structure of the fragments is a productive way of obtaining phthalocyanine compounds with desirable characteristics, among which water-soluble phthalocyanines are of primary interest. Such compounds are most promising for practical use, e.g., in production of electro-active materials and sensitizing agents for photodynamic therapy of cancer diseases [1]. In order to provide water solubility, peripheral substituents of anionic or cationic kind are introduced in phthalocyanine molecules. Among anionic substituents, sulfo groups [2, 3] and carboxyl-containing substituents [4, 5] are the most popular. As cationic substituents, pyridine derivatives [6, 7] and tetraalkylammonium salts [8] are usually used. The introduction of neutral ethylene glycol fragments to promote the solubility of phthalocyanines in water was also described [9]. In addition to the application of phthalocyanines, which involve ionogenic substituents, in photodynamic therapy of cancer diseases, a peculiar interest to water-soluble phthalocyanine complexes is determined by the possibility of immobilizing them on electrodes in the form of coatings composed of ultrathin self-assembled oppositely charged ionic layers on quartz and conductive glasses are considered. Based on the spectral, electrochemical, and electrocatalytic properties, the role of noncovalent interactions in the synthesis and operation of the composite systems is clarified.

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MODERN PROBLEMS OF THE PHYSICAL CHEMISTRY OF SURFACES, MATERIALS SCIENCE, AND MATERIALS PROTECTION


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Abstract—Methods of synthesis of a number of new functionalized phthalocyanines, as well as MgII, CoII, CuII, ZnII, and NiII phthalocyaninates, that involve benzo-15-crown-5-, phosphoryl-, or pyridine-containing fragments as peripheral substituents, which were developed and tested in IPCE RAS in the last five years, are reviewed and systematized. Methods of synthesis of the original phthalogens, which involve substituents of diverse composition, are considered. Results of an investigation of the aggregate states of the compounds in water and aqueous solutions of salts are generalized. The possibilities of electrostatic immobilization of the synthesized phthalocyanines in the form of self-assembled systems composed of ultrathin ionic layers on quartz and conductive glasses are considered. Based on the spectral, electrochemical, and electrocatalytic properties, the role of noncovalent interactions in the synthesis and operation of the composite systems is clarified.

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INTRODUCTION

A novel technique of producing water-soluble phthalocyanine-based systems has been developed at the Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences (IPCE RAS). The approach is based on special noncovalent interaction between phthalocyanine fragment or additional peripheral coordinating substituents and organic or inorganic cations. Benzo-15-crown-5, phosphoryl-, and pyridine-containing fragments are used as peripheral substituents. The presence of benzo-15-crown-5 substituents promotes the inclination of molecules to form diverse complexes [11–14], the phosphoryl group is easily polarizable and can serve as a good coordination unit [15], and pyridine rings can form salt-like compounds due to the lone electron pairs of nitrogen atoms. Therefore, phthalocyanines, which involve such peripheral substituents, are of special interest. These
features make it possible to create directionally new supramolecular structures with desirable properties.

However, despite the promising prospects, data on methods of synthesis and properties of the water-soluble metal-complex systems based on crown-, phosphoryl-, and pyridine-containing phthalocyanines are very poor and unsystematic.

METHODS OF PRODUCTION OF TETRA- AND OCTA-SUBSTITUTED PHTHALOCYANINES

1. Synthesis of Initial Phthalonitriles

As an initial compound in the synthesis of tetraoxy-(benzo-15-crown-5)-substituted phthalocyanines, (benzo-15-crown-5)-oxy-phthalonitrile (1), which was synthesized from commercial 4-nitrophthalonitrile and 4-oxy-benzo-15-crown-5 in dry DMSO in the presence of dehydrated $K_2CO_3$ according to a technique outlined in [16], was taken. Using similar schemes [17], we have obtained 4-(diphenyl-phosphoryl-methoxy) phthalonitrile (2), 4-[4-tertbutyl-2-(diphenylphosphoryl)-phenoxy]phthalonitrile (3), diethyl[2-(3,4-dicyanophenoxy)phenyl]phosphonate (4), 4-[2-(diphenylphosphorylmethyl)phenoxy]phthalonitrile (5), 4-(pyridin-4-ylmethoxy)phthalonitrile (6), and 4-(pyridin-3-ylmethoxy)phthalonitrile (7), which were not described earlier.

Although the method used is quite simple, we discovered a number of essential aspects that should be taken into account. For example, phthalonitrile 2 was obtained at a yield of 84%. When a reaction between 4-nitrophthalonitrile and 2-(diphenylphosphoryl)methylphenol was carried out under the same conditions, compound 2 was obtained with a yield of 25% instead of expected compound 5. The structure of the product was reliably determined with the use of $^1H$ NMR spectroscopy and mass spectrometry. $^{31}P$ NMR spectroscopy showed that 2-(diphenylphosphoryl)methylphenol degrades in the presence of $K_2CO_3$ excess in DMSO: upon exposure for 2 h at a temperature of 70°C, three phosphoryl-containing compounds were found in the reaction system in nearly equivalent amounts. During interaction between 4-nitrophthalonitrile and 4-tertbulyl-2(diphenylphosphoryl)phenol, which has no methylene group between a phosphoryl group and a phenol fragment, the corresponding phthalonitrile 3 was obtained with a yield of 76%. When diethyl(2-hydroxyphenyl)phosphonate is used for synthesis, the alkaline environment determines the partial hydrolysis of diethoxyphosphonate substituent, which results in the formation of an acidic half-ester, namely, o-ethyl(2-hydroxyphenyl)phosphonate, which should be treated with triethylorthophosphoramide during distillation of ethanol from the reaction volume for the formation of the target nitrile 4.

Di(oxybenzo-15-crown-5)phthalonitrile 8 was synthesized from dichlordicyanobenzene according to the procedure described in [18]: