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Aggregation of *slipped-cofacial* phthalocyanine J-type dimers: Spectroscopic and AFM study

Alexander Yu. Tolbin [a,b,*], Victor E. Pushkarev [a,b], Marina V. Sedova [c], Sergey S. Maklakov [c], Larisa G. Tomilova [a,b]

[a] *Institute of Physiologically Active Compounds, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation*
[b] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*
[c] *Institute for Theoretical and Applied Electrodynamics RAS (ITAE RAS), Izhorskaya St., 13, 125412 Moscow, Russian Federation*

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ABSTRACT

Direct metallation of 2-hydroxyphthalocyanine J-type *slipped-cofacial* dimeric ligand by Mg, Zn, Cu, Ni and Co salts has been carried out to obtain corresponding metal complexes selectively without any noticeable dissociation or polymerization of the starting ligand. Integrated analysis of aggregation properties in the synthesized series has been conducted with the involvement of AFM microscopy, UV/Vis spectroscopy and theoretical assessment. As a result, a nonlinear relationship between absorption and concentration was found, with aggregation beginning to appear at concentrations above 3.3×10^{-5} mol L^{-1} with predominant formation of trimers from the dimeric molecules in THF solutions.

1. Introduction

Aggregation of macrocyclic dyes in most cases is represented as a combination of two or more molecules in a coplanar configuration, and is well known for phthalocyanines [1]. The disordered association of macrocyclic dyes usually weakens their useful properties and limits possible applications in catalysis [2], dye-sensitized solar cells [3], as well as in the photodynamic therapy [4]. Decreased solubility of the phthalocyanines susceptible to aggregation not only prevents their isolation in individual state but also often negatively affects spectral properties. Commonly, aggregation can be suppressed by chemical modifications. Thus, bulky peripheral substituents [5, 6] and/or axial groups coordinated by the metal center [7] can be introduced, which protect the π-conjugated chromophores from the undesirable intermolecular interactions. On the other hand, aggregation can sometimes lead to an unexpected increase in emission of organic compounds (AIE - aggregation induced emission) in the solid state, which opens a possibility for their use in light-emitting technology [8]. Thus, studies of the aggregation behavior of phthalocyanines and related dyes are crucial for the correct assessment of their applied potential.

Recently, we have demonstrated the ability of stable phthalocyanine J-type dimers to form ordered assemblies in the solid state, represented as globules with a narrow size distribution [9]. This result is not typical for the most of planar phthalocyanines and is likely due the specific relative arrangement of macrocycles in these dimers determined by the presence of peripheral OH-groups and characterized by a value of the so-called *slip angle* [10]. Thus, the in-depth study of the aggregation behavior of *slipped-cofacial* phthalocyanine J-type dimers is extremely important for further understanding of their intrinsic properties. In this work, we implemented an integrated approach to the study of the aggregation properties of these macrocyclic dyes, including UV/Vis spectroscopy, mathematical analysis and AFM study to determine the relationship between their spectral parameters and structural features.

2. Experimental

2.1. Materials and Methods

All solvents were of reagent-grade quality and were obtained directly from Aldrich. Phthalocyanine J-type dimeric ligand **1** was synthesized according to our previously published procedure [11]. UV/Vis spectra were recorded on a Hitachi U-2900 spectrophotometer in 300–900 nm range in THF using quartz cuvettes with a thickness of 0.1, 0.2, 0.5 and 1 cm. All solutions were freshly prepared just before optical experiments. Series of the spectra for each compound at different concentrations are given in the ESI (Figs. S1(a)–S6(a)).

Analyzed J-dimers **1–6** were weighed to the sixth decimal place. Concentrations of the initial solutions were in the range of 1.70

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[*] Corresponding author at: Institute of Physiologically Active Compounds, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation.
E-mail address: tolbin@ipac.ac.ru (A.Y. Tolbin).

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$\times 10^{-6}$–5.03×10^{-4} mol L^{-1}. Each subsequent solution was prepared by successive dilution of the previous one to level the volume measurement error at dilution. Absorption curves (Figs. S1(b)–S6(b) in the ESI) of J-dimers **1**–**6** are plotted in coordinates (k; C), where k is the absorption coefficient (cm^{-1}) associated with the optical density D by the relation: $k = D/d$, in which d is the optical path length (cm).

Images of Atomic Force Microscopy (AFM) were taken by means of a Solver P47H (NT-MDT) microscope in a tapping mode. Polycrystalline silicon ETALON© (NT-MDT) probe (tip radius of curvature <10 nm) was applied. The films were obtained by deposition on the cover glass from solutions in THF with a concentration of about 10^{-5} mol L^{-1} by analogy with the conditions elaborated for the recently described phthalo- and naphthalocyanine complexes [12]. 2D Images were converted to inverted bitmaps and processed with *Digimizer* Software (www.digimizer.com) to estimate average size of aggregates.

2.2. Synthesis

2.2.1. Common Procedure for Bis(2-hydroxy-9(10),16(17),23(24)-tri-tert-butylphthalocyanine) Complexes of Mg, Zn, Cu, Ni, Co

To a solution of dimeric ligand **1** (50 mg, 0.036 mmol) in 2-Dimethylaminoethanol (DMAE, 15 mL) corresponding metal acetate salt (0.09 mmol) was added followed by keeping the reaction mixture under reflux for 30 min. After the reaction was finished (UV/Vis control), the reaction mixtures were poured onto ice, and the residues were centrifuged, washed with methanol/water 1:1. Chromatography on Bio-Beads SX-1 (BIORAD) using THF as a solvent has revealed no polymeric impurities and starting ligand **1**. Target complexes **2**–**6** were obtained in the yields of 95% and more. Analytical characteristics for J-dimers **1**–**6** were reported previously in the works, where they were obtained for the first time [11, 13].

3. Results and Discussion

3.1. Outlook and Synthesis

Metal-free *slipped-cofacial* J-dimer **1** was obtained previously by demetallation of corresponding magnesium complex **2** in acidic medium [11]. This was the first attempt to show that the stable J-type phthalocyanine ligand can also exist, despite the lack of metal oxygen binding between macrocycles, as it can be assumed in the starting magnesium complex **2**. Somewhat later, on an example of nickel and copper complexes (compounds **4**, **5**), in which axial coordination is also impossible due to the low coordination number of the metals, we found similar spectral and fluorescent properties with the dimeric complexes of magnesium, zinc and cobalt (compounds **2**, **3**, **6**) [13]. This allowed us to assume that the stability of J-dimers, which do not decompose into monomers, neither chemically nor thermally, is based on unusually strong interactions of the macrocycles. During formation of such structures in the synthesis, the monomeric units are successfully combined with a low energy of transition state, which leads to a global minimum at the contact surface of these macrocycles [14]. Dimeric complexes **2**–**6** were previously obtained in one-pot reactions starting from 2-hydroxy-9(10),16(17),23(24)-tri-*tert*-butylphthalocyanine [15], which is monomeric unit of J-dimer **1**. In this work we demonstrate an alternative approach to produce dimeric complexes on metallation of metal-free J-dimer **1** with corresponding metal acetate salts (Scheme 1).

During the metallation, no destruction of dimeric ligand **1** was observed. Chromatography revealed no polymer or monomeric impurities. This is one of the examples demonstrating stability of the phthalocyanine *slipped-cofacial* J-dimers in the chemical transformations. Dye compounds **1**–**6** were further used in spectroscopic and AFM experiments.

3.2. AFM Study

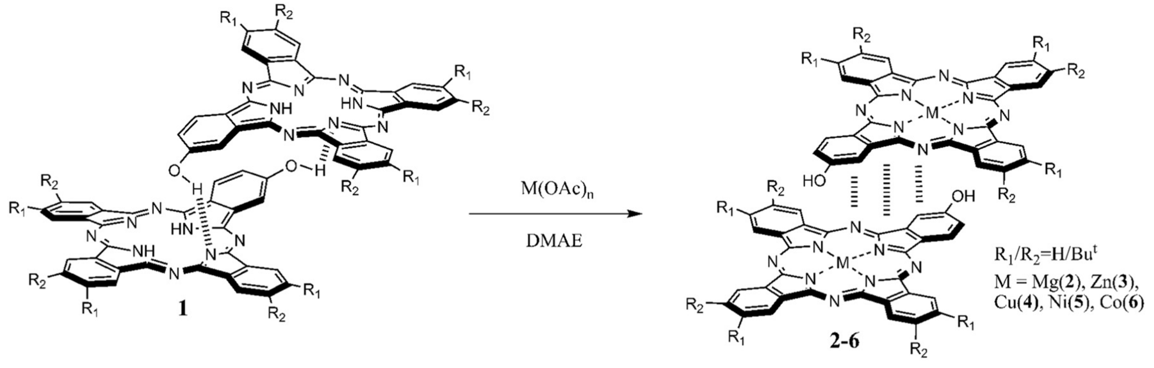
Investigation of J-dimers **1**–**6** by the AFM method is presented as 2D-micrographs in Fig. 1. The average dimensions of aggregates are listed in Table 2. For the metal-free and magnesium complex (J-dimers **1**,**2**), the aggregates are close to spherical type, which is consistent with the results obtained by us for these dyes with the field emission scanning electron microscopy (FE-SEM) [11]. In the case of zinc, nickel and cobalt complexes **3**, **5** and **6**, a part of the aggregates tends to the needle-like kind with a maximum length of about 500 nm. Copper complex **4** occupies an intermediate position in this series, which may be due to both the decreased distortion of macrocycles in this J-dimer [13] and its solvatophobic nature.

The size of the aggregates and their shape are an important characteristic of nanomaterials based on organic dyes for various optical technologies. In the next section, we establish a relationship between aggregation of J-dimers **1**–**6** and their spectral properties.

3.3. Beer's Law and Spectroscopic Analysis

Aggregation can be detected directly from the UV/Vis investigations, demonstrating appearance of the new bands (H– or *J*-), or broadening of the original ones [1, 5]. In non-polar solvents, such as CCl_4, $CHCl_3$, dimeric ligand **1** showed an aggregation pattern close to the H-type [16], while in THF no additional bands were observed. The UV/Vis spectra of *J*-dimers **1**–**6** in THF solutions (Fig. 2) almost do not change over a wide range of concentrations.

Absorption spectra of dyes **1**–**6** show B (or Soret), Q (Q_1 and Q_2 for ligand **1**) and J-band, which are characteristic of *slipped-cofacial* phthalocyanine J-type dimers [11]. To investigate the aggregation properties, we applied an integrated approach based on analyzing the absorption curves (Figs. S1(b)–S6(b) in the ESI) with determination of a point of deviation from linearity (*i.e.* from Beer's law) with the following calculation of the aggregation number and equilibrium aggregation constant at this point.



Scheme 1. Synthesis of dimeric complexes **2**–**6**: refluxing (30 min) in DMAE in the presence of metal acetate salts in slight excess, yields >95%.