Surfactant-Assisted Lateral Self-Assembly of One-Dimensional Supramolecular Aggregates of Lutetium Double-Decker Phthalocyaninates

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In memory of bright organic chemist and dedicated teacher of colorful beauty of life, Larisa Tomilova

The development of feasible strategies for integrating 1D organic semiconductors into films is a challenging issue for organic electronics exploiting planar architectures of microelectronic devices. Herein we describe the method of planar organization of 1D supramolecular aggregates assembled from lutetium crown-substituted double-decker phthalocyaninate into ordered ultrathin films. The method utilizes the Langmuir-Blodgett technique in combination with adding tert-butylamine during the synthesis of the supramolecular aggregates. The atomic force microscopy examination of the resulting films shows that the introduction of surfactant promotes spreading of hydrophobic aggregates on the water subphase yielding ordered ultrathin layers. The size of aggregates can be controlled by varying the ratio of the phthalocyanine ligands and surfactant in the system. The size of the aggregates increases with the concentration of the surfactant, whereas the morphology of the films evolves from a filamentary continuous structure to individual nanowires immobilized in the surfactant layer. The proposed strategy can be used to obtain ordered coatings from 1D aggregates from various organic discotics with semiconductor properties.

Keywords: Langmuir-Blodgett films, phthalocyanine, organic nanowires, self-assembly.

Латеральная самосборка одномерных супрамолекулярных агрегатов двухпалубного краун-замещенного фталоцианината лютеция в присутствии ПАВ

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Разработка подходов к созданию упорядоченных покрытий из одномерных органических полупроводников представляет собой одну из актуальных проблем органической электроники, решение которой позволит интегрировать органические проводники в реально работающие устройства с планарной архитектурой. В данной статье продемонстрирована возможность организации одномерных супрамолекулярных агрегатов из двухпалубного краун-замещенного фталоцианината лютеция в упорядоченные ультратонкие пленки с помощью технологии Ленгмюра-Блоджетт за счет добавления трет-бутиламина при синтезе супрамолекулярных агрегатов. По данным атомно-силовой микроскопии введение ПАВ не только способствует
Self-Assembly of One-Dimensional Supramolecular Aggregates of Double-Decker Phthalocyaninates

Introduction

Fabrication of new semiconductor materials as an alternative for silicon electronics nowadays becomes increasingly important, particularly on the background of COVID-19 pandemic due to the reduced production of semiconductor silicon microchips. The advancements in organic electronics in recent decades have already led to the replacement of silicon by organic semiconductor materials in a number of electronic devices. The most striking example is the widespread adoption of OLED displays.

However, the development of organic nanostructured assemblies comprising separated working nanoelements of electronic circuits into a consolidated architecture remains a challenging issue. Most important difficulties are associated with the structural control during the synthesis as well as with the lack of methods for the lateral manipulations of the already prepared solid nanostructures on solid supports.

Phthalocyanines constitute one of the most promising classes of organic compounds for creating nanostructures for organic electronics. These compounds possess an extensive conjugated electronic system for effective charge transfer, thermal and chemical stability, as well as the possibility of fine-tuning their physical and chemical properties by the introduction of functional groups and metal ions into the molecule. Due to their discotic shape, phthalocyanines are prone to one-dimensional (1D) aggregation. The double-decker phthalocyanates of rare earth metals, in particular the complex with lutetium, which is known to have high among phthalocyanines semiconducting properties, are of special interest. In turn, the double-decker crown-substituted phthalocyaninates can undergo intermolecular aggregation in the presence of alkali metal ions through their coordination interactions with crown-ether groups yielding the particles with a length of several hundreds of nanometers. These supramolecular 1D aggregates are expected to be candidates for fabricating semiconductor nanowires, because in the aggregates, the orientation of the rings is perpendicular to the stacking direction, which provides the appearance of a conduction band. The most commonly applied methods for ordering phthalocyaninates and their complexes on solids are the deposition from solutions by drop-casting onto the atomically flat surfaces such as pyrolitic graphite and some metals and a Langmuir-Blodgett technique providing an opportunity to arrange insoluble molecules and aggregates on the surface of aqueous subphases with further transferring of the resulting well-defined arrangements onto solids. There have been a number of reports demonstrated the ordering of the phthalocyanine molecules and their metal complexes in thin films by a fine tuning of the orientation and lateral organization of macrocyclic monomer units in Langmuir monolayers. However, the organization of nearly micrometer long 1D aggregates of phthalocyaninates into ordered structures on solid surfaces has not been yet reported. Typically, the films of solid nano- and microparticles are obtained with drop-casting and spin-coating or electric-field solution atomization of colloid solution of aggregates. However, these methods do not allow appropriate control of orientation of the aggregates in thin films. Template synthesis and lithographic methods allow to fix an orientation of particles on a substrate, although their applicability is very limited due to their high cost and elaborated manufacturing.

In this work, we suggest the approach to solve this problem exploiting supramolecular assembly of lutetium double-decker (15-crown-5)-substituted phthalocyaninate (LuL15, Figure 1a) by coordination of the crown ether groups with potassium ions in the presence of surfactants. The resulting 1D structures are spread on the water surface for ordering through lateral compression and further transferring onto solid substrates by using the Langmuir-Blodgett technique.

It is known that the presence of surfactant may prevent the aggregation of hydrophobic molecules and supramolecular amines and pyridines that are prone to one-dimensional (1D) aggregation. It was shown that surfactants may prevent the aggregation of hydrophobic molecules and suppress the orientation of the rings in Langmuir monolayers by changing the ratio of surfactant and phthalocyaninates.

**Figure 1.** a) Structure of the lutetium bis(tetra-15-crown-5) phthalocyaninate (LuL15) and scheme of coordination of crown ether groups with K⁺ ions. b) Schematic illustration of the formation of supramolecular aggregates LuL15-K⁺ in the presence of t-BA.
molecular structures and promotes their spreading on the water surface during the formation of Langmuir monolayers. In this work we used tert-butylamine (t-BA), a branched amphiphilic molecule that is also commonly used in the synthesis of metal-organic frameworks as a structure-directing agent assisting the formation of uniformly sized crystals. Atomic force microscopy was applied to studying how the concentration of t-BA in the LuL₂ solution influences the size of supramolecular aggregates and their organization in the monolayer on the aqueous subphase.

Experimental

Materials. Chloroform, acetonitrile, potassium tetraphenylborate (KBPh₄) were obtained from abcr GmbH, tert-butylamine (t-BA) was obtained from Sigma Aldrich. All chemicals used were of analytical reagent grade. Tetra-15-crown-5-phthalocyanine H₂L was synthesized using the previously reported procedure. Chloroform was used as a solvent for the preparation of the LuL₂ solution (1·10⁻⁵ M) and t-BA solution (1·10⁻³ M). Acetonitrile was used for the preparation of KBPh₄ solution (1·10⁻² M).

Synthesis of lutetium(III) bistetra-15-crown-5phthalocyaninate, LuL₂. Tetra-15-crown-5-phthalocyanine H₂L (53 mg, 42 μmol) and DBU (189 mg, 1.2 mmol) were dissolved in the mixture of n-octanol (2 mL) and 1-chloronaphthalene (4 mL). The solution was brought to reflux under slow flow of argon and Lu(OAc)₃·4H₂O (26 mg, 62 μmol) was added to the boiling mixture. Control over the reaction by UV-Vis spectroscopy evidenced of complete conversion of H₂L to the sandwich complex within 1 h. After cooling to room temperature, reaction mixture was diluted with the mixture of 1:1 vol. EtOAc/hexane and the formed precipitate was filtered, washed with hexane and washed off the filter with chloroform. The resulting solution was partially evaporated, MnO₂ was added to oxidize the anionic form of the target complex to the neutral state, and the resulting suspension was transferred onto the alumina column packed with neutral alumina in chloroform. Target complex was isolated by gradient elution with the mixture of chloroform + 0 → 1.5 vol. % MeOH. Yield: 44 mg (78 %). MALDI-TOF MS, m/z: calc. for C₄₄H₃₄LuN₁₆O₁₆ 7279.9, found 7270.8 → [M]⁺. UV-Vis (CHCl₃) λmax nm (Δε rel. %): 666 (1.00), 603 (0.19), 477 (0.25), 367 (0.83), 291 (0.61). The physical-chemical characteristics were in agreement with the previously reported data. Formation of supramolecular structures. For preparation of LuL₂·K⁺-based structures the mixture of LuL₂ solution (1·10⁻⁵ M) and t-BA solution (1·10⁻³ M) with various ratios (1:2, 1:5, 1:10) was prepared. After that the KBPh₄ in acetonitrile (1·10⁻² M) was added to LuL₂-t-BA mixture with a molar ratio LuL₂:KBPh₄ molar ratio of 1:4 (Figure 1b). Supramolecular structures formed via the adding potassium salt to individual solution of LuL₂ were used as a control system. The reaction mixture was kept for 2 days in a dark place at room temperature. Spectrophotometric study of the reaction mixture in a course of the formation of aggregates showed that the presence of t-BA did not affect the optical properties of LuL₂, and the absorption spectrum of the mixed LuL₂-t-BA solution merged with that of the individual

Results and Discussion

To obtain supramolecular aggregates, a solution of potassium tetraphenylborate (KBPh₄) in acetonitrile was added to mixed solutions of LuL₂ and t-BA in chloroform with molar ratios of 1:2, 1:5, and 1:10 to achieve LuL₂·KBPh₄ molar ratio of 1:4 (Figure 1b). Supramolecular structures formed via the adding potassium salt to individual solution of LuL₂ were used as a control system. The reaction mixture was kept for 2 days in a dark place at room temperature.

Spectrophotometric study of the reaction mixture in a course of the formation of aggregates showed that the presence of t-BA did not affect the optical properties of LuL₂, and the absorption spectrum of the mixed LuL₂-t-BA solution merged with that of the individual

![Figure 2](image-url)
solution of this phthalocyaninate (Figure 2a, curve 1). This behaviour is an indication of the weakness of interactions between the surfactant and phthalocyanine, that is, the surfactant is not expected to interfere with the potassium-induced self-assembly of the LuL₂ complexes. Characteristic bands corresponding to π-π* transitions in the macrocyclic ligand are resolved in the spectrum: the Q-band at 666 nm, the unpaired electron band at 477 nm and the B- and N-bands at 366 and 332 nm, respectively.[13] Immediately after the addition of potassium salt, the opacity of the reaction mixture increases along with a shift of the Q-band from 666 to 658 nm (Figure 2a, curve 2). Such spectral changes suggest the intermolecular coordination of K⁺ ions with the crown ether groups of phthalocyaninate leading to the formation of the extended LuL₂-K⁺ supramolecular aggregates.[13,34]

To obtain nanostructured surface coatings on solid substrates, the portions of colloidal solution of the as-prepared LuL₂-K⁺ aggregates with various t-BA concentration in chloroform were spread onto the water surface, compressed to a surface pressure 30 mN/m close to that of the monolayer collapse (Figure 2b), and then vertically transferred onto the silica substrates. A film obtained from the solution of the ligand and salt without the surfactant was formed as a control sample through similar procedure.

Figure 3 shows the AFM images of the resulting surface coatings. The films obtained by the transfer of the monolayer without t-BA presents chaotically distributed separated crystallites with 5 µm width and 20 nm height (Figure 3a). Based on the size of the molecules of the lanthanide double-decker crown-substituted phthalocyaninates, which can be described by a disk of diameter 2.2–2.5 nm and height 0.8 nm,[16] we can assume that these crystallites are formed through non-controlled aggregation and separated into the bulky phase. The stacking of LuL₂ molecules in the presence of the salt and without the surfactant leads to rapid polydisperse nucleation and growth of the forming aggregates. The high nonuniformity of the coating is probably due to the strong electrostatic repulsion of the aggregates, preventing their tight packing and transferring onto the solid surface.

The addition of t-BA into the solution of the LuL₂ ligands before its mixing with potassium salt led to a striking change in the lateral ordering and the morphology

Figure 3. AFM images and corresponding profiles of LuL₂-K⁺-aggregates formed in systems with different molar ratios LuL₂-t-BA (a) 1:0, b) 1:2, c) 1:5, d) 1:10.
of the resulting monolayers. The surface packing density of the aggregates increases significantly (Figure 3b–d). This increase is a consequence of charge compensation on the outer surface of the aggregates because of the adsorption of the surfactant, as well as due to facilitated spreading of the aggregates on the water surface owing to the amphiphilic nature of t-BA. The most remarkable aspect of these systems is an effect of the surfactant concentration in the system on the morphology of the resulting surface coatings. When the LuL₂–t-BA molar ratio is close to 1:2, the entire surface is uniformly coated with thin interlaced filaments with larger aggregates intercalated between them (Figure 3b). The film thickness is about 2.5 nm, which corresponds to the height of the stacked LuL₂ molecule in the edge-on orientation with respect to the substrate surface. This morphology implies that the surfactant does not inhibit the formation of the LuL₂–K⁺ aggregates but rather effectively prevents direct contact between them due to the steric effect of the bulky structure of t-BA. An increase of the fraction of t-BA in the colloidal solution (LuL₂–t-BA 1:5) leads to a disappearance of thin filaments accompanied by an increase in the lateral size of the wires (Figure 3c). The thickness of the monolayer corresponds to the height of vertically stacked LuL₂ molecule. For this surfactant/ligand ratio, the surface packing density remains rather high. However, when the LuL₂–t-BA ratio is increased to 1:10, the size of the aggregates changed dramatically approaching tens of microns in length and 100–200 nm in height (Figure 3d). The packing density of the aggregates in this film reasonably decreases due to an increase of the amount of the surfactant separating into individual phase. The monolayer represents therefore a coexistence of the large supramolecular aggregates floating in the condensed film of the t-BA. This pattern of the concentration-dependent evolution of the system morphology provides a useful tool for tailoring the parameters of these supramolecular assemblies for targeted practical applications.

Besides the opportunity of manipulating the size of supramolecular aggregates during their formation, using t-BA makes it possible to obtain highly oriented films of the LuL₂–K⁺ particles. In all AFM images presented in Figure 3, the transfer line is nearly parallel to the upper edge of the image. Consequently, the long axis of the aggregates is oriented predominantly along the transfer direction in the films formed in the presence of t-BA.

Conclusions

In summary, we have demonstrated how to exploit the surfactant chemistry for fabricating ordered ultrathin coatings based on supramolecular aggregates from luteinum double-decker crown-substituted phthalocyaninate. A distinctive feature of this approach is that the surfactant performs two functions simultaneously. First, it acts as a structure-forming agent during the supramolecular synthesis. The concentration of surfactant in the reaction system determines the size and the aspect ratio of aggregates. Second, the surfactant assists spreading of the hydrophobic aggregates at the air/water interface making them processable for further transferring to solid substrates using the Langmuir-Blodgett technique. We believe that this facile approach can be used for a variety of 1D supramolecular structures, which are hydrophobic and thereby unsuitable for traditional compression-controlled Langmuir-Blodgett deposition. This can be particularly promising for obtaining organic semiconductor coatings from supramolecular aggregates assembled through both supramolecular and stacking interactions.

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