

SOLUBLE PHTHALOCYANINES – NEW MATERIALS FOR OPTOELECTRONICS

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A new class of soluble phthalocyanines was synthesized and their electrical properties were studied. Their UV-VIS spectra consist of two strong Q and Soret bands at about 650 – 800 and 300 – 400 nm, respectively, showing an enhanced broad optical window with lower linear absorption at about 500 nm. The energy of the long-wavelength absorption is in good agreement with activation energy of dark conductivity; thus, the band gap energy can be estimated as 1.7 eV. The phthalocyanines under study are salts, and hence, due to the dissociation of ionic groups, the electrical conductivity is strongly dependent on the air humidity. This effect can be utilized for the construction of humidity sensors. Because of quite a high charge carrier mobility, of the order $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, the phthalocyanines were used for the construction of field-effect transistors.

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1. Introduction

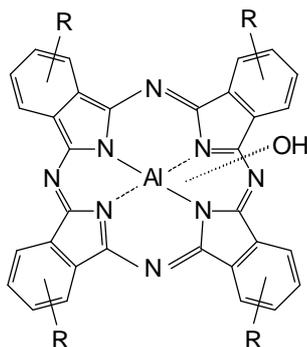
Organic and polymeric electronic devices have enjoyed increasing interest because of their potential low-cost applications, easy processing, great opportunities in modification of their chemical structures and good compatibility with a variety of substrates. Out of them, phthalocyanines (Pcs) play an important role as low-gap semiconducting materials. Many electrical and optical applications of Pcs can be mentioned: fuel cells, gas sensors, organic metals, electronic media, photoelectrical detectors, xerographic media, field-effect transistors, light-emitting diodes, optical recording, optical memories, information displays, hole-burning memories, light-limiters, lasers, non-linear optical elements, etc. However, Pcs prepared in a usual way [1] are not soluble in usual solvents; thus thin films can be prepared by vacuum evaporation or as mixtures of Pc microcrystals in polymer matrices. Because Pcs are very stable functional organic semiconductors, there is a strong interest in synthesizing substituted soluble materials.

2. Material synthesis and characterization

Sodium(hydroxyaluminium)phthalocyaninesulfonate $[\text{Al}(\text{OH})\text{Pc}(\text{SO}_3\text{Na})_{1,4}]$, see Scheme 1] was prepared from (hydroxyaluminium)phthalocyanine $[\text{Al}(\text{OH})\text{Pc}]$ dissolved in

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sulfuric acid containing 10 % SO_3 and subsequently heated to 85 °C for 6 h. The reaction mixture was poured into a mixture of water and ice, filtered and washed. The filter cake was dispersed in water and pH was adjusted with NaOH to ca. 11. Thus, $[\text{Al}(\text{OH})\text{Pc}(\text{SO}_3\text{Na})_{1-4}]$, was changed into a dark blue water-soluble sodium salt, which was isolated by vacuum evaporation of water on a water bath. The product was analyzed and purified by high-pressure liquid chromatography. Chemical compositions of the prepared materials are given in Table 1.



Scheme 1. Structure of $\text{Al}(\text{OH})\text{PcS}_{1-4}$ ($\text{R} = \text{SO}_3\text{Na}$ or H).

Table 1. Chemical composition of the studied sodium(hydroxyaluminium)phthalocyaninesulfonates.

Sample	$\text{Al}(\text{OH})\text{PcSO}_3$ Na (wt. %)	$\text{Al}(\text{OH})\text{Pc}(\text{SO}_3\text{Na})_2$ (wt. %)	$\text{Al}(\text{OH})\text{Pc}(\text{SO}_3\text{Na})_3$ (wt. %)	$\text{Al}(\text{OH})\text{Pc}(\text{SO}_3\text{Na})_4$ (wt. %)
1012/210	97.9	-	-	-
939/274-B	-	99.35	-	-
951/188	-	-	98.6	-
951/371	-	-	-	98.2
1012/143	47.3	45.9	6.2	0.7
975/301-2	5	46.6	43	5.3
1012/212	25.7	56.7	16.3	1

The absorption spectra of a water solution and of solid film are given in Fig. 1a. The fluorescence is very strong, the action spectra are given in Fig. 1b.

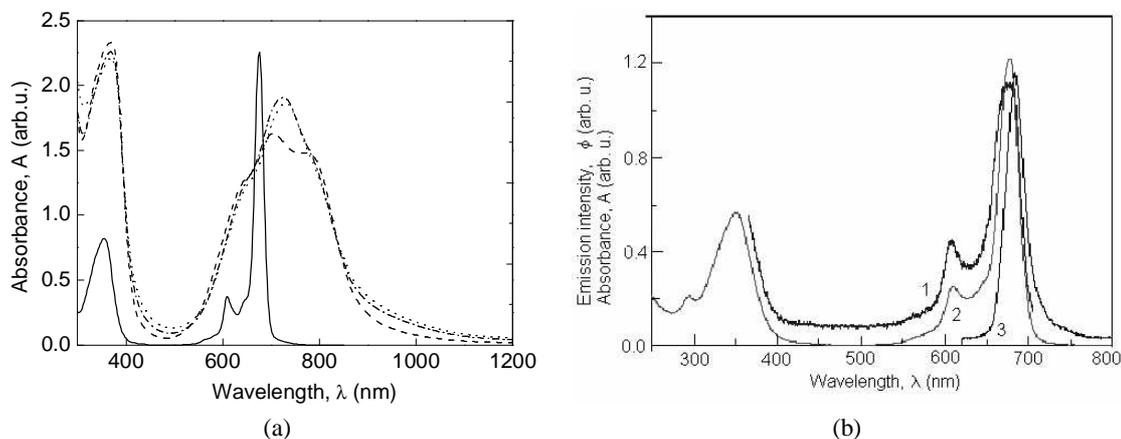


Fig. 1. (a) Absorption spectra of $\text{Al}(\text{OH})\text{Pc}(\text{SO}_3\text{Na})_2$ in water solution (full line) and in solid film (dash line). Dot-and-dash line – spectrum of BaCl_2 -treated $\text{Al}(\text{OH})\text{Pc}(\text{SO}_3\text{Na})_2$, dot line – spectrum of the CT complex $\text{Al}(\text{OH})\text{Pc}(\text{SO}_3\text{Na})_2$ – tetrachloro-1,4-benzoquinone. (b) Photoluminescence of $\text{Al}(\text{OH})\text{Pc}(\text{SO}_3\text{Na})_2$ in water. Curve 1 – excitation spectrum, curve 2 – absorption spectrum, curve 3 – emission spectrum.

The UV-VIS spectra consist of two strong Q and Soret bands at about 650 – 800 and 300 – 400 nm, respectively, showing an enhanced broad optical window with lower linear absorption at about 500 nm. The long-wavelength absorption band is a consequence of π -electron transitions from the highest occupied orbital to the lowest unoccupied orbital. The triplet state formed by intersystem crossing is quite efficient in phosphorescence. Electronic structure of neutral free Pc molecule is conserved also in the solid phase. Here, also ionized states are formed; they are characterized by narrow valence band E_v and conduction band E_c , similarly to inorganic semiconductors. In Pcs, however, these levels are actually self-energy levels of quasi-free charge carriers determined by their polarization, many-electron interactions with the crystal, and have nothing in common with the one-electron conduction bands of traditional solid-state physics. The conduction band is located slightly above the first singlet state (Q-band). A characteristic feature of solid Pcs (and generally of all molecular crystals) is the existence of charge-transfer (CT) states, non-conducting polar states formed by pairs of electrons and holes which are localized on different Pc molecules. The CT level is situated below the conduction band. These states play an important role in the charge carrier photogeneration. Similarly to unsubstituted Pcs, the substituted ones can also form charge-transfer complexes with a characteristic CT band in the long-wavelength part of the spectrum, at 900 – 1000 nm (cf. Fig. 1a, dot line).

Because $\text{Al(OH)Pc(SO}_3\text{Na)}_{1-4}$ are salts, it is expected that, due to the dissociation of ionic groups, the electrical conductivity will be a strong function of the air humidity. The change of the conductivity with fluctuating relative humidity from 5 to 98 % is given in Fig. 2. In this way $\text{Al(OH)Pc(SO}_3\text{Na)}_{1-4}$ molecules behave as fast humidity sensors with good reproducibility. However, from the viewpoint of electronic applications the humidity instability is a disadvantage. This problem was overcome in two ways:

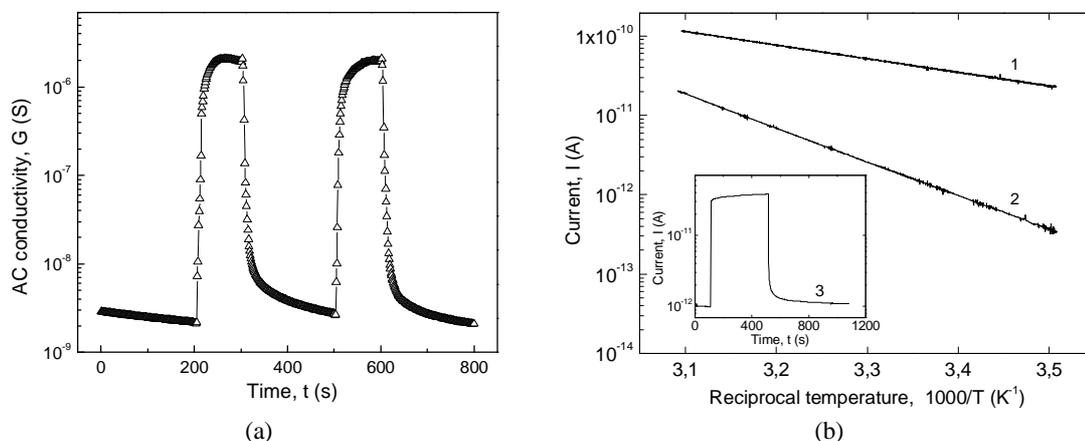


Fig. 2. (a) Changes of AC electrical conductivity of surface sample $\text{Al(OH)Pc(SO}_3\text{Na)}_{1-2}$; distance of Pt electrodes on ceramics was 50 μm . (b) Dependence of dark current (curve 2) and photocurrent (curve 1) on temperature; inset: photoconductivity kinetics.

- (i) The $\text{Al(OH)Pc(SO}_3\text{Na)}_{1-4}$ film was exposed to a 5 % water solution of BaCl_2 (pH 2 – 3). During the processing sodium ions were replaced by barium ones; their sensitivity to humidity was much lower. As it follows from absorption spectra shown in Fig. 1a (dot-and-dash line), the electron structure conserved; no important changes were observed.
- (ii) The other way consisted in encapsulation of Pc molecules in a conductive (due to charge carrier transport) polymer. The composite film poly[3,4-(ethylenedioxy)thiophene] (PEDOT)| $\text{Al(OH)Pc(SO}_3\text{Na)}_{1-4}$ was prepared by dipping in a solution consisting of phthalocyanine and prepolymers prepared in situ by oxidative polymerization of 3,4-(ethylenedioxy)thiophene and methyl methacrylate in the presence of iron(III) tosylate as oxidant and a mixture of *N*-methylpyrrolidone, ethanol, isopropyl alcohol and butyl alcohol as solvents at room temperature.

Conductive PEDOT films are usually prepared by a two-step procedure [2]. The solubility problem was subsequently circumvented by using a water-soluble polyelectrolyte, sulfonated polystyrene (PSS), as the charge-balancing dopant in polymerization to yield the PEDOT/PSS system [3]. Here, we present a new simple one-step synthetic route for the preparation of conductive PEDOT films. Figures 3a and 3b show the SEM patterns for samples consisting of one and five PEDOT layers, respectively. The films were prepared by dipping in prepolymerized solutions consisting of a monomer and oxidant in the ratio 1 : 1. The typical film thickness was 7 μm per layer. The five-layer film showed AC conductivity $\sigma = 264 \text{ S cm}^{-1}$. Before the measurements the samples were heated to 110 $^{\circ}\text{C}$ (thermal stability was improved). The conductivity was frequency-independent in the range from 100 Hz to 100 kHz. From the temperature dependence of the conductivity followed that the tunneling conductivity mechanism is the most probable for the description of charge carrier transport. If the five-layer sample was washed in ethanol, the resulting thickness was 12 times lower. The conductivity was found much lower, $\sigma = 35 \text{ S cm}^{-1}$. The value is typical of many films prepared by different techniques as reported in literature [4]. The SEM patterns for one- and five-layer washed samples are presented in Figs. 3c and 3d, respectively. The patterns show the ethanol-insoluble phase of the films, which is disordered, quite homogeneous, but less conductive. It could be pointed out that this procedure did not substantially change the sensing properties of the film.

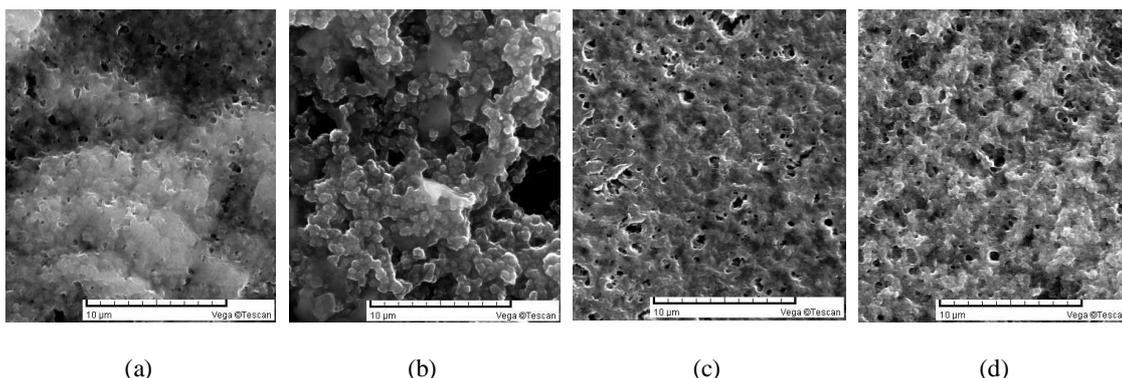


Fig. 3. SEM patterns of PEDOT one-layer (a), and five-layers (b) as-prepared films, as well as one-layer (c) and five-layers (d) films washed in ethanol.

3. Electrical properties

The current-voltage ($j \sim U$) characteristic of sandwich sample ITO/Al(OH)Pc(SO₃Na)_{1.2}/Al showed ohmic behaviour at low voltages; a non-linearity at higher voltages suggested a hole injection from ITO electrode. From the temperature dependence of the dark current (see Fig. 2b), the activation energy 0.84 eV was found. This value represents the Fermi level position; thus, the band gap energy 1.7 eV can be evaluated. This value agrees well with the value obtained from absorption spectra.

The Pcs under study were sensitive to light, their electrical conductivity increased under illumination. Thus, photodetectors could be constructed. The fast change of the conductivity occurred by more than one order of magnitude in the illumination with light of $\lambda = 670 \text{ nm}$ of suitable intensity (surface Pt electrode configuration with gap 50 μm). The activation energy of the fast photoconductivity was determined as 0.34 eV; this value represents a typical depth of charge carrier traps in Pcs. In addition to a fast photoresponse (see inset of Fig. 2a), a slow relaxation was observed. This process was more pronounced at higher temperatures. According to preliminary measurements the slow process could be ascribed to photoinduced reorientation of Pc molecules.

4. Thin film field-effect transistors (TFET)

A p^+ -doped silicon wafer was used as a substrate and a gate electrode. An insulating SiO_2 layer, 100 nm thick, was prepared by thermal oxidation. A system of source-drain electrodes was then photolithographically patterned using chromium (10 nm) as an adhesion layer, and gold (80 nm). The interdigital source-drain geometry is shown in Fig. 4: typical device width, $Z = 2$ mm, typical channel length, $L = 20$ μm . The device was fabricated by depositing the organic layer by spin coating from solution. Typically, the films were ca. 300 nm thick.

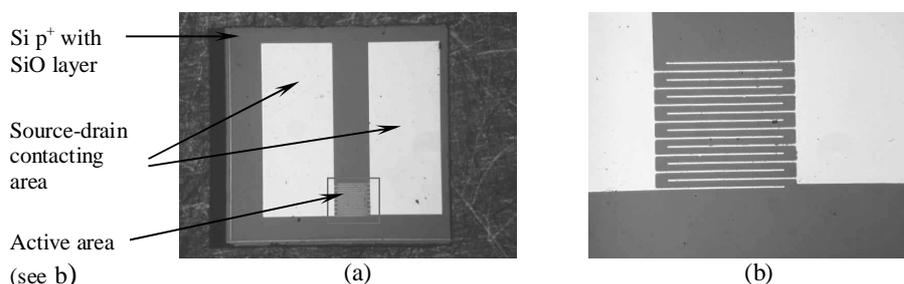


Fig. 4. (a) FET structure; (b) structure of the active area.

Typical source-drain current j_d vs. source-drain voltage U_d characteristics measured at different gate voltages U_g are shown in Fig. 5a. From the saturation U_d values of the source-drain currents vs. gate voltage plot, the charge carrier mobility was determined as $\mu_{FET} = 1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (cf. Fig. 5b). The saturation source drain current (j_d) fulfilled the usual conditions: the dependence of the square-root of j_d is proportional to the gate voltage U_g .

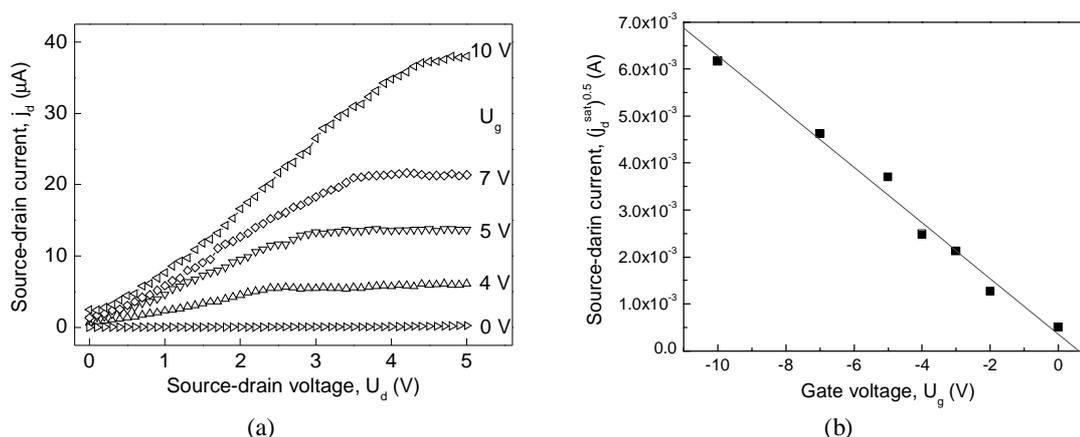


Fig. 5. (a) j_d vs. U_d characteristics for different gate voltages of the $[\text{Al}(\text{OH})\text{Pc}(\text{SO}_3\text{Na})_{1-2}]$ FET structure; (b) $(j_d^{\text{sat}})^{0.5}$ vs. U_g dependence.

5. Conclusions

It was shown that soluble derivatives of phthalocyanines with attractive electronic properties suitable for the fabrication of electronic devices can be prepared. These materials are acceptable for the preparation of thin films by cold technologies, e.g. by silk-screen and ink-jet printing, which opens a new era in the Pc research.

Acknowledgements

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