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Optical properties of soluble phthalocyanines

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The optical properties of a new group of soluble phthalocyanines (Pc), containing sulpho-, amino- and sulphonamide groups are presented. The optical absorption spectrum consists of two main bands, Q and Soret ones, with maxima at about 600 – 700 and 350 – 400 nm, respectively, and of a broad optical window with a lower linear absorption at about 500 nm. The oxidation energies for different sulphonamide substituted phthalocyanines were determined using cyclic voltammetry. They ranged from -5.46 to -5×10 eV. Thus, the positions of the LUMO levels are in the region -3.85 to -4.27 eV. The band gap energies were determined from optical absorption spectra, and ranged from 1.69 to 1.75 eV. The thin films, after deposition by spin coating or dipping, were usually amorphous, but they could be converted into crystalline films by thermal treatment, as shown by WAXS studies.

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1. Introduction

Phthalocyanines (Fig. 1) are stable molecular semiconductors suitable for many electronic applications, like photodetectors, gas sensors, field effect transistors, solar cells, non-linear optical media, etc [1]. However, they are not soluble in the usual organic solvents. Thin film preparation from non-soluble materials needs a complicated technique, which is quite expensive. The use of soluble phthalocyanines should help to overcome this problem, because they can be deposited by cold technologies (e.g., spin-coating, drop-casting, inkjet printing, etc.)

The presence of Soret and Q bands in absorption spectra is usually reported in literature. The Q-band is split into a doublet, which corresponds to the π-π* transitions (low energy) with the participation of vibronic levels (higher energy). However, there is no information in the literature concerning the optical properties of sulphonamide-substituted phthalocyanines.

There are several possible ordered structures of phthalocyanine stacks; the main are the α-, β- and x-forms, which differ by distances among molecules and the angle to the stack normal [2].

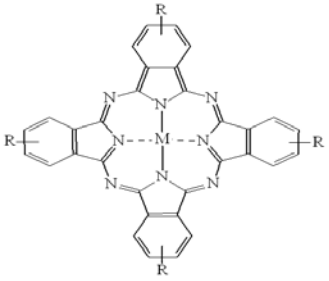
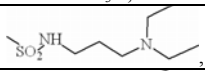
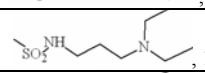
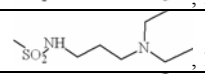
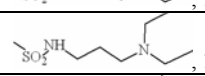
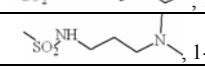


Fig. 1. Structural formula of a phthalocyanine molecule. A list of studied materials with different substituents R and central metal atoms M is given in Table 1.

It is known [3] that the oxidation potential E_{ox} correlates with the energy of the HOMO level, and the reduction potential E_{red} with the energy of the LUMO level. It is possible to use cyclic voltammetry for the determination of the E_{ox} and E_{red} potentials.

Phthalocyanines form charge-transfer complexes with acceptor molecules, which can be detected by means of the absorption spectra [4]. Depending on the acceptor electron affinity, the dark conductivity or photoconductivity increases [5].

Table 1. List of the materials under study. The digits refer to the number of substituents.

No	Material	Structure		Solvent
		M =	R =	
1	$CuPc(SO_3Na)_{1-3}$	Cu	SO_3Na, 1-3	H_2O
2	$Al(OH)Pc(SO_3H)_{1-3}$	Al(OH)	SO_3H, 1-3	H_2O + NaOH
3	$CuPc(Sulphonamide)_{1-2}$	Cu	 , 1-2	Chloroform
4	$ZnPc(Sulphonamide)_{1-2}$	Zn	 , 1-2	Chloroform
5	$FePc(Sulphonamide)_{1-2}$	Fe	 , 1-2	Chloroform
6	$NiPc(Sulphonamide)_{1-2}$	Ni	 , 1-2	Chloroform
7	$CuPc(Sulphonamide)_{1-2}$	Cu	 , 1-2	Chloroform

2. Experiment

Sulphonamide-substituted phthalocyanines were synthesized by chlorsulphonation from non-substituted phthalocyanines, and the products were reacted with an appropriate amine. Metallophthalocyanine polysulphonic acid polysodium salts were synthesized by sulphonation of non-substituted phthalocyanines (Table 1). Fluorinated indium tin oxide (FITO) glasses were used for the cyclic voltammetry. Phthalocyanines were deposited by spin-coating or drop-casting. The thicknesses of the thin films varied from 150 to 1000 nm.

Solutions for measuring the absorption spectra were prepared from the respective phthalocyanine and a spectral grade solvent (Table 1); the concentration was $c = 1x10^{-5}$ mol/l. The optical absorption spectra were measured using a UV-VIS-NIR Perkin-Elmer Lambda 950 spectrophotometer. A HZG4 X-ray diffractometer was used for structure detection. An AMEL instruments MOD 7050 potentiostat was used for electrochemical redox potential measurements.

3. Results and discussions

3.1. Absorption spectra

The typical absorption spectrum of model Zn 3-diethylamino-1-propylsulphonamide phthalocyanine is presented in Fig. 2. There are two main characteristic bands; the Soret or B-band and the Q-band. Their maxima are located at 338 and 680 nm, respectively. The first band is related to the d-π* electronic transition, and the second one to the π-π* electronic transitions of carbon atoms [6]. There are also vibrational and dimeric bands located at 606 and 628 nm, respectively. The spectrum of the thin film is slightly shifted to the red region.

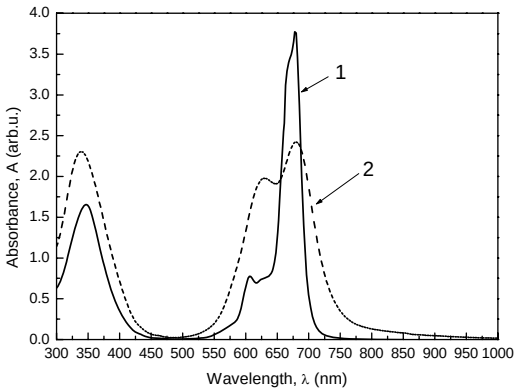


Fig. 2. The absorption spectra of Zn 3-diethylamino-1-sulphonamide phthalocyanine. Solution (1), thin film (2).

The absorption spectra of phthalocyanines are dependent on central metal atoms. For comparison, the influences of Cu, Zn, Fe and Ni cations are presented in Fig. 3. The positions of the absorption bands are slightly shifted to lower energies with increasing cation radius.

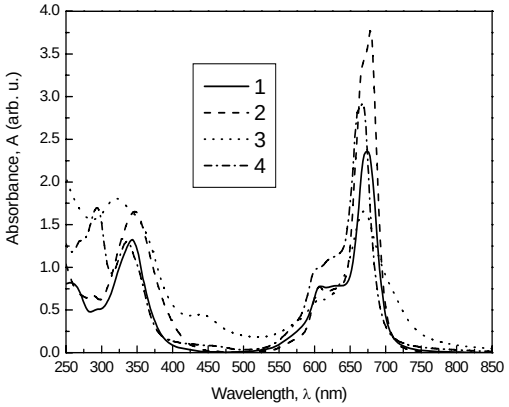


Fig. 3. Optical absorption spectra of sulphonamide-substituted phthalocyanines with different central metal atoms. Chloroform solution. The central metal atoms were: 1 – Cu, 2 – Zn, 3 – Fe, 4 – Ni.

The band positions are not strongly dependent upon the character of the substituents (Fig. 4). The band gap energies were calculated using the long-wavelength part of the absorption spectra. The values are summarized in Table 2.

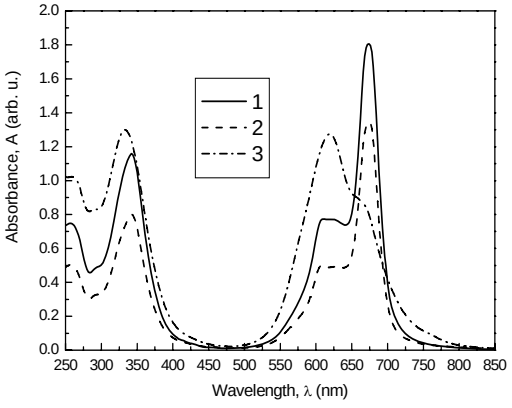


Fig. 4. Influence of substituents on the absorption spectum of pthtalocyanine. 1 – $CuPc(SO_2NHCH_2CH_2CH_2N(C_2H_5)_2)_{1-2}$; 2 – $CuPc(SO_2NHCH_2CH_2CH_2N(CH_3)_2)_{1-2}$; 3 – $CuPc(SO_3Na)_{1-3}$.

3.2. Structural changes during heating

It was found that the morphology of phthalocyanine thin films changes from an amorphous to a highly ordered structure during thermal treatment. This is reflected in the absorption spectra (see Fig. 5). When the film was heated to 140°C for 5 hours, the peak at 800 nm disappeared.

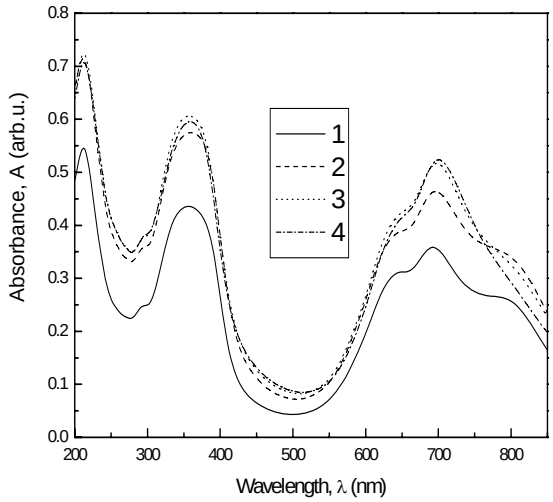


Fig. 5. Changes of the absorption spectra of the hydroxyaluminium phthalocyaninsulphate sodium salt thin film after heating. 1 – 2 h. in air after preparation; 2 – 2 h evacuation at 80 °C; 3 – 2 h evacuation at 140°C; 4 – 3 h evacuation at 140 °C.

The reason one can see is the change of the morphology of pthtalocyanine films: from an amorphous to a highly ordered stacking structure. The X-ray diffraction shows a strong peak characteristic of the crystalline structure (Fig. 6).

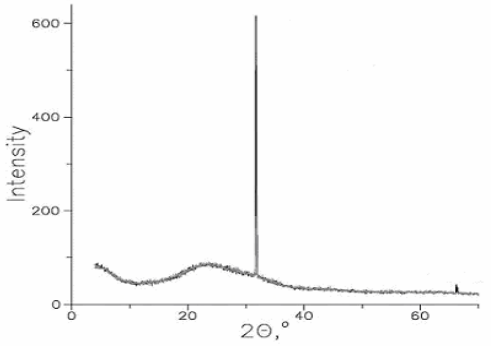


Fig. 6. The X-ray difractogram of a hydroxyaluminium phthalocyaninsulphonic acid sodium salt after 5 hours heating at 140°C.

3.3. Electronic structure

In Table 2, the values of the HOMO and LUMO levels and band gap energies obtained for different sulphonamide-substituted phthalocyanines are presented. The last ones were determined from the $(h\nu\times\alpha)^2$ vs. $h\nu$ dependences, where α is the absorption coefficient of the thin film. In this way the long-wavelength part of the absorption spectrum was linearized and from the cross point with energy axis the band gap energy was determined. The last ones were determined by the analysis of the absorption coefficients of phthalocyanines thin films. It was impossible to measure the reduction potentials because of the problems with the film stability. The oxidation potentials were calculated from the cyclic voltammetry curves.

Table 2. Maxima of the absorption bands and the electronic parameters of some phthalocyanines under study. LUMO position was determined, taking into account, that HOMO level is lower than E_{ox} on 0.5 eV [3].

Material	Thin films		Band gap, (eV)	E_{ox}, (V)	LUMO, (eV)
	B, (nm)	Q, (nm)			
CuPc(Sulphonamide)$_{1\text{-}2}$	339	625, 679	1.69	-5.46	-4.27
ZnPc(Sulphonamide)$_{1\text{-}2}$	338	630, 680	1.72	-5.30	-4.08
FePc(Sulphonamide)$_{1\text{-}2}$	336, 455	616, 682	1.75	-5.10	-3.85
NiPc(Sulphonamide)$_{1\text{-}2}$	338	619, 667	1.74	-5.35	-4.11

3.4. Charge transfer complexes

To improve the photoconductivity, some acceptor-like additives are needed. They participate in the charge carrier pair formation. A phthalocyanine molecule excited to the singlet state in the presence of an acceptor forms a non-relaxed exciplex. After the electron transfer, an ion pair is formed. It can dissociate into free charge carriers under the influence of an external electric field [7].

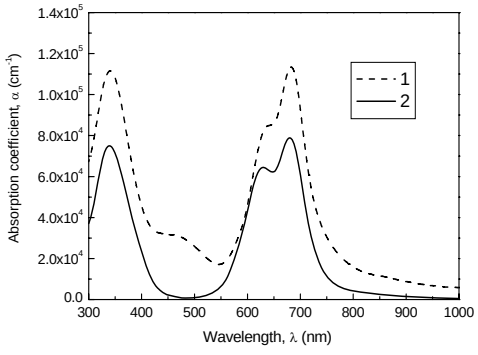


Fig. 7. Absorption spectra of Zn sulphonamide substituted phthalocyanine without (solid line) and with an acceptor (dash line) in thin film.

The charge-transfer complex can be detected by optical spectroscopy. The spectrum of a thin film of Zn sulphonamide phthalocyanine with tetracyano-1,4-quinodimethane shows two new bands at 450-500 nm, and weak band near 900 nm which can be related to the charge transfer complex formation. It is important for photoelectronic applications: as shown above, the presence of a charge transfer complex should improve the dark and photoconductivity.

4. Conclusions

The shapes of the absorption spectra of phthalocyanines depend on the type of the central metal atom. The values of the HOMO and LUMO levels depend on the central cations, and vary in the interval 0.3 to 0.5 eV. Using thermal treatment, oriented films structures can be obtained.

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