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Review

Mix-substituted phthalocyanines of a “push–pull”-type and their metal complexes as prospective nanostructured materials for optoelectronics

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ABSTRACT

To study the influence of structural features of phthalocyanine (Pc) derivatives on their physico-chemical properties in bulk and thin films, 23 new phthalocyanines with different quantity and ratio of donor (alkyloxy-groups, in fragment “**A**”) and acceptor (Cl-, in fragment “**B**”) substituents in one molecule of the **A$_3$B**, **ABAB** and **AABB** types with varied length of alkyloxy-substituents and their metal complexes were designed and synthesized. A comparative analysis of spectral, mesomorphic and photoelectric properties of these mix-substituted phthalocyanines of a “push–pull” type was performed. It was shown that non-peripheral substitution by alkyloxy-fragments in hetero-substituted Pcs (similar to homo-substituted Pc) leads to red-shifting of the Q-band into near-IR region. The intensity of photoluminescence, position of peaks and their splitting are strongly connected with chemical structure of Pcs and the type of solvent. In contrast to non-mesogenic octyloxy-Pc (**A4**) having alkyloxy-substituents in non-peripheral positions, 22 of 23 synthesized compounds possess columnar mesomorphism. The change of donor–acceptor ratio can influence the type of mesophase. A new approach to the creation of materials for optoelectronics is proposed and implemented, which includes design of compounds possessing vitrification from mesophase with maintenance of a columnar order, absorption in the near IR-region of the spectrum and good performance electrophysical characteristics simultaneously.

1. Introduction

In the development of pioneering works of R.P. Linstead (1902–1966) concerning synthesis and application of phthalocyanine (29H,31*H*-tetrabenzo[*b*,*g*,*l*,*q*]-5,10,15,20-tetraazaporphine) and its derivatives (Pcs) as dyes and pigments [1], since the turn of the century these compounds have been attracting considerable interest as prospective nanostructured materials.

This interest was promoted by S. Chandrasekhar’s discovery of a new type of mesogens with a disk-like molecular shape [2], because Pcs with appropriate peripheral substituents around their molecular core obtain the opportunity to reveal unique liquid crystalline properties with a columnar arrangement of their aromatic cores, which gives rise to a one-dimensional conductivity pathway [3,4].

The relationship between a molecular structure of Pcs and their chemical and physical properties was widely investigated. Introduction of substituents increases solubility of phthalocyanines in organic and aqueous solvents and can induce liquid crystalline properties (thermotropic and lyotropic mesophase formation). At first, the most commonly used substituents were alkyl [5], alkyloxy [6], alkyloxymethyl [7] along with carboxy [8,9] and sulfo groups [10]. Then, the diversity of substituents was broadened by alkylthio [11], perfluoroalkyl [12], alkylsulfonyl [13], oligo(ethyleneoxy) [14] and aryloxy substituents [15], as well as by introduction of aromatic [16] or heteroaromatic groups [17], and even bulky substituents without aliphatic chains [18].

Moreover, phthalocyanine molecule can be substituted not only uniformly with the groups of one type, but heterosubstituted with substituents of different types (donor/acceptor, hydrophilic/hydrophobic etc.) [19]. In recent decades newly synthesized Pcs found more special interest due to excellent properties

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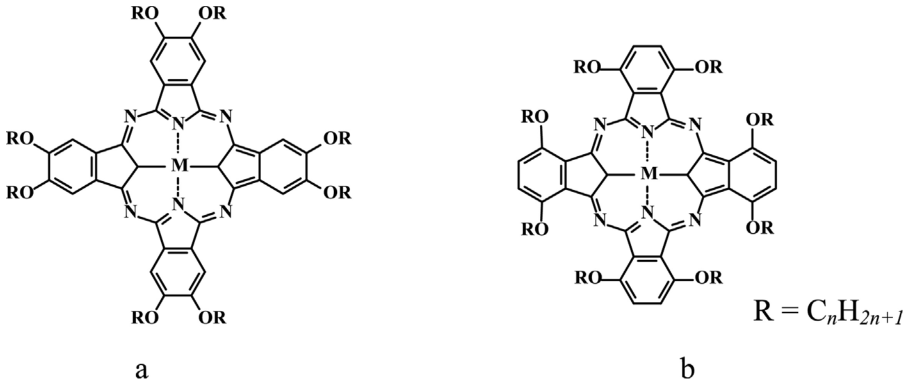


Fig. 1. Peripherally (a) and non-peripherally (b) substituted alkyloxy-phthalocyanines.

such as high thermal and chemical stability, lipophilicity and solubility in different solvents.

High solubility of Pcs is important for many reasons: e.g. for optical properties investigation and application, for film fabrication by spin-coating or Langmuir–Blodgett techniques. It is known that the number and type of the substituents, as well as their position in the molecule have a profound influence on optical and mesomorphic properties of Pcs [20].

The position of substitution (peripheral/non-peripheral) plays a very important role. Non-peripherally substituted phthalocyanines are important as they shift optical absorption spectra into infrared region. For example, optical spectra of peripherally substituted Pcs are characterized by two intense bands: Q-band centered at around 670 nm and the B-band located in the near-UV region, both correlated to π–π^* transitions [21]. λ_{max} values of non-peripherally substituted Pcs are red-shifted at about 50–70 nm, since the alkyloxy-groups take part in the macro π-conjugation system of the Pc moiety. The increase in the numbers of alkyloxy-groups leads to a decrease of the π^*-orbital energy; and the absorbance therefore shifts to a longer wavelength [22]. Besides, it was shown that peripherally substituted 2,3,9,10,16,17,23,24-octaalkyloxyphthalocyanines (Fig. 1a) exhibit liquid crystalline properties, while non-peripherally substituted 1,4,8,11,15,18,22,25-octaalkyloxyphthalocyanines (Fig. 1b) are non-mesogenic [23].

All abovementioned properties in combination with high thermal and chemical stability, relative easiness of synthesis, possibility of metal introduction, ability to be deposited in thin films give rise to intense interest to Pcs as attractive materials for many technologies: semiconductors, sensors, organic photovoltaics and others [24].

The organic photovoltaics is a promising alternative for high cost crystalline silicon cells in the renewable energy technology thanks to their low cost, light weight and large area fabrication of flexible substrates. The composition of key compounds is usually used in organic photovoltaic cells. Each component of such composition has its own responsibility: as a light absorber, a hole transport agent and an acceptor phase. For example, "small" molecule solar cells can contain Pcs or porphyrins as dyes, poly[2-methoxy-5-(3′,7′-dimetyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) or poly(hexylthiophene) (P3HT) as the p-type donor phase and glassy materials, simultaneously, and fullerene or perylene derivatives as electron acceptors [25].

Low bandgap polymers and fullerene derivatives have enabled fabrication of very high power conversion efficiencies (∼7%) in the bulk heterojunction organic solar cells [26].

But the current research concentrates on obtaining higher efficiency by designing and synthesizing new organic small molecules for organic solar cells: dendrimers, star-shaped compounds, phthalocyanine or porphin derivatives. The advantages of "small" molecule solar cells are the following: well defined molecular structure, definite molecular weight, easy purification, easy mass-scale production, better understanding of molecular structure – properties relationship, more predictable fabrication protocol [27].

We have chosen Pc-derivatives bearing alkoxy-substituents in non-peripheral positions because this type of substitution leads to red-shifting of Q-band of Pc-absorption spectrum in comparison with peripherally substituted analogues. In its return, it leads to the increase of light-harvesting ability of phtotovoltaic devices [28].

Mix-substituted Pcs of a "push–pull" type are the most promising compounds of the Pc-series and are very prospective material for "small" molecule organic cells. Since they contain both electron donating and electron withdrawing substituents in one molecule they have a polarized structure. Besides, as we have proved, the presence of donor and acceptor groups in other Pc-derivatives leads to formation of a columnar mesophase with vitrification without any crystallization on cooling [29,30].

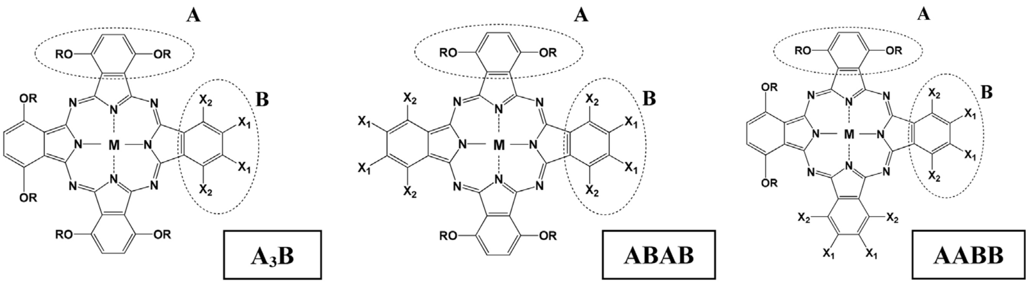
2. Experimental

Due to the ability of "push–pull" Pcs to reveal all the necessary properties required for key compounds of organic photovoltaic solar cells, we have designed and synthesized 23 new mix-substituted phthalocyanine derivatives (Fig. 2): ligands and metal complexes of **A$_3$B**, **A**B**A**B and **AA**BB types bearing donor substituents (alkyloxy-groups of different length) attached to the phthalonitrile fragment "**A**" in non-peripheral positions and acceptor substituents (two or four chlorines, –Cl) introduced into the phthalonitrile fragment "**B**".

For convenience we introduce the following abbreviation of the studied phthalocyanines (Fig. 2), which we are going to use throughout the text: (**A$_3$B**, **ABAB** or **AABB**) M–Pc–$(OC_nH_{2n+1})_yCl_m$, where we note the type of phthalocyanine on the first place in brackets; M = 2H$^+$, HoOH, InCl, Cu^{2+}, Zn^{2+}; Pc is phthalocyanine; *n* is the number of carbon atoms in the alkyloxy-substituent *(n* = 8, 16); *y* is the number of alkyloxy-substituents in molecule; *m* is the number of chlorine atoms introduced into molecule *(m* = 2, 4).

Synthesis of the studied 23 mix-substituted phthalocyanine derivatives: ligands and metal complexes composed of donor fragments "**A**" (bearing alkyloxy-groups in non-peripheral positions) and acceptor fragments "**B**" (bearing chloro-substituents) of **A**$_3$B, **A**B**A**B and **AA**BB types was performed by statistical condensation and described elsewhere [31–33].

Mesomorphic behaviour of the compounds under study was investigated by polarizing optical microscopy (Leitz LaborLux 12 Pol microscope equipped with a Mettler FP 82 hot stage) and differ-



M = $2H^+$, HoOH, InCl, Cu^{2+}, Zn^{2+}; X_1, X_2 = H, Cl; R = C_nH_{2n+1}, $n = 8, 16$

Fig. 2. Molecular structure of the studied mix-substituted phthalocyanine derivatives.

ential scanning calorimetry (calorimeter DSC 200 PC/1/M/H Phox of Netzsch company).

Electronic absorption spectra of chloroform solutions and thin films of the studied compounds were recorded at room temperature on the spectrophotometers HITACHI U-2001, Ava Spec-2048 Avantes and Cary 5000 (Varian) in the wavelength range of 200–1000 nm, with the spectral band width of 2 nm. Solutions concentrations were $1.3–1.6 \times 10^{-6}$ M.

Fluorescence spectra of bulk samples were registered at room temperature on the spectrophotometer SOLAR CM 2203 (Belarus) in the Institute of Solution Chemistry of the Russian Academy of Science (Ivanovo, Russia). The fluorescence spectra of films were recorded on Cary Eclipse (Varian) spectrofluorimeter in the wavelength range of 220–850 nm with the spectral band width of 5 nm.

Langmuir layers were formed from solutions of compounds (**A$_3$B**) H_2–Pc–$(OC_{16}H_{33})_6Cl_2$ (C = 0.014 wt.%) and (**A$_3$B**) H_2–Pc–$(OC_{16}H_{33})_6Cl_4$ (C = 0.0113 wt.%) in chloroform, where C is the mass fraction of the solute. The layer compression speed was 55 cm^2/min. The Langmuir–Schaefer films were obtained by transferring floating layers from water surface (horizontal lift, the number of transfers is $n = 50$ layers, the thickness of the produced thin films was 110 nm) onto oriented glass substrates with indium-tin oxide (ITO) electrodes at room temperature (293–295 K) and surface pressure of $\pi = 0.15–0.6$ mN/m. The glass substrates were oriented by rubbing with an abrasive material (crocus).

Semiconducting structures were obtained by a vacuum deposition from a quartz cuvette onto a glass substrate with ITO electrodes at room temperature and the residual pressure of 5×10^{-5} mm Hg. The sputtered Pc samples were spaced 20 cm from the substrates. Then, a system of aluminum contacts was sputtered onto the semiconductor film through a mask at room temperature and the same pressure. The absence of the effect of Al on the degradation of thin films was studied in Ref. [34]. The electrode geometry allowed one to determine both optical and photoelectric properties of the films.

Photoelectric measurements. To study the photocurrent of organic structures the light sources based on GaAs semiconducting light emitting diodes (LED) with two fixed wavelengths ($\lambda_1 = 660$ nm and $\lambda_2 = 940$ nm) were used. The film samples were illuminated by light square pulses of a different length. The photoelectric signals were registered by the broadband storage oscilloscope. The current pulse was measured through a calibrated resistance $R = 91$ kΩ sequentially connected to the photovoltaic cell. The bias voltage (U_b) varied a in wide diapason (up to 9 V).

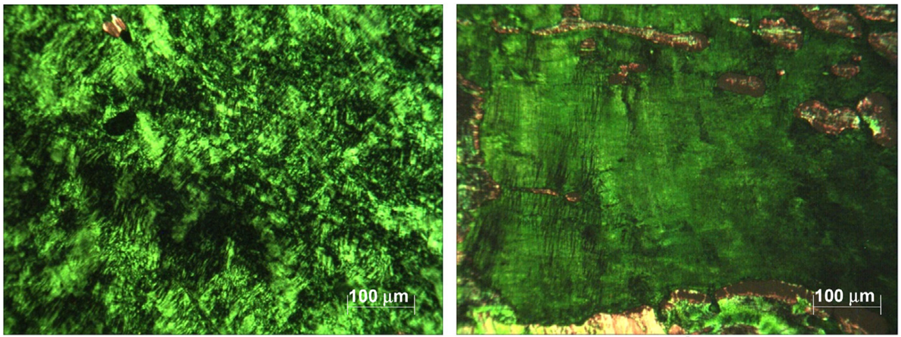
Calculation details. Geometry optimization, energies of frontier orbitals (HOMO/LUMO) and bandgaps of the molecules were obtained using a density functional theory method (DFT/B3LYP/6-311++G**) with the help of Gaussian 09 package.

3. Results and discussion

3.1. Mesomorphic properties

All the synthesized phthalocyanines were studied in regards of mesomorphic properties by polarizing microscopy and differential scanning calorimetry (DSC). Transition to isotropic liquid was not reached as compounds start to decompose around 250 °C, while mesomorphic textures were still preserved.

Octyloxy-substituted Pcs of **A$_3$B**, **ABAB** and **AABB** type H_2–Pc–$(OC_8H_{17})_yCl_{2,4}$ regardless of the number of chlorine atoms in the molecule (di- or tetra-chloro-substituted) – ligands, as well as their corresponding holmium complexes Ho–Pc–$(OC_8H_{17})_yCl_{2,4}$ (**A$_3$B-Ho**, **ABAB-Ho** and **AABB-Ho**) possess mesomorphism enantiotropically [28,31,35]. The observed typical textures prove the formation of a two-dimensionally ordered columnar mesophase (Fig. 3). On cooling below 100 °C all the above mentioned octyloxy-substituted Pcs vitrify with the preservation of the mesophase texture. Glass transitions were also detected by DSC. For example, for ligand (**AABB**) H_2–Pc–$(OC_8H_{17})_6$–Cl_2 $T_g = 98$ °C, and complexation with holmium did not influenced temperature of glass



a *b*

Fig. 3. Texture microphotographs of two-dimensionally ordered mesophase at heating T = 250 °C, ×100: (*a*) ligand (**A$_3$B**) H_2–Pc–$(OC_8H_{17})_6$–Cl_2; (b) holmium complex (**A$_3$B-Ho**) Ho–Pc–$(OC_8H_{17})_6$–Cl_2 [31].

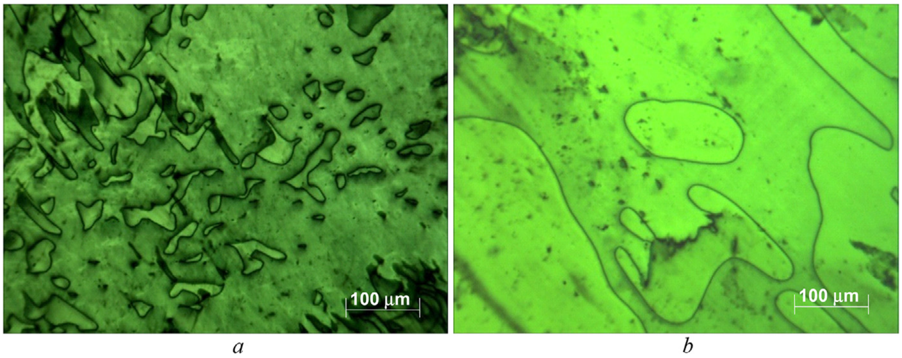


Fig. 4. Schlieren texture of ligand (**A**$_3$B) H_2–Pc–$(OC_{16}H_{33})_6$–Cl_4: (a) at heating, T = 145 °C, ×100; (b) on cooling, T = 45 °C, ×100 [33].

transition: (**AABB-Ho**) Ho–Pc–$(OC_8H_{17})_6$–Cl_2 $T_g = 98\,°C$. For ligands (**A**$_3$**B**) H_2–Pc–$(OC_8H_{17})_6$–Cl_4, (**ABAB**) H_2–Pc–$(OC_8H_{17})_6$–Cl_4 and (**AABB**) H_2–Pc–$(OC_8H_{17})_6$–Cl_4, glass transitions were detected at 92, 132 and 151 °C, correspondingly.

It was shown that the phase transition temperatures and the diapason of mesophase existence for tetra-chloro-substituted ligands H_2–Pc–$(OC_8H_{17})_y$–Cl_4 depend on the donor/acceptor ratio in the molecule and position of substitution [35]. If we designate the corresponding non-mesogenic non-peripheral homo-substituted Pc as **A**$_4$, the above characteristics are increasing in the following sequence: **A**$_4$ ($\Delta t_m = 0°$) < **A**$_3$**B** ($\Delta t_m = 92.4°$) < **ABAB** ($\Delta t_m = 135°$) < **AABB** ($\Delta t_m > 150°$) [28,35].

As octyloxy-substituted Pcs have low solubility in organic solvents we have synthesized higher homologues (hexadecyloxy-substituted), and since Pcs of **A**$_3$**B** type possessed the maximal solubility we have continued to work with this type of compounds. The presence of six aliphatic chains (this is the highest amount of chains in comparison with **ABAB** and **AABB** types) in these "push–pull" compounds enhances solubility in organic solvents. Therefore, in our further research we focused on the **A**$_3$B type compounds.

Mesomorphism investigation of hexadecyloxy-substituted ligands H_2–Pc–$(OC_{16}H_{33})_6$–Cl_2 and H_2–Pc–$(OC_{16}H_{33})_6$–Cl_4, as well as their metal complexes with copper, zinc or indium showed that all the studied compounds are mesomorphic, except the indium complex – In–Pc–$(OC_{16}H_{33})_6$–Cl_2. The absence of mesomorphic properties in the last case can be connected with the presence of extra-ligand at indium atom that violates the self-assembly of molecules into columns which are basic structural units of a columnar mesophase. The mesomorphic properties (texture characteristics, temperature diapason of mesophase existance) for hexadexyloxy-substituted Pcs depend on the number of chlorine atoms, as well as the metal introduced into molecule.

Pcs with ***tetra***-chloronitrile fragment (**A**$_3$**B**) M–Pc–$(OC_{16}H_{33})_6$–Cl_4 (M = 2H$^+$, Cu^{2+}, Zn^{2+}) formed a mesophase with thread-like defects (Fig. 4) which is typical for the nematic mesophase. Mesomorphic Pcs with ***di***-chloronitrile fragment (**A**$_3$**B**) M–Pc–$(OC_{16}H_{33})_6$–Cl_2 (M = 2H$^+$, Cu^{2+}, Zn^{2+}) showed a non-geometrical or herring-bone texture (Fig. 5) which is typical for the two-dimensional ordered columnar mesophase analogous to the one previously observed for octyloxy-substituted Pcs.

Structural organization in mesophases needs further investigation, however, the preliminary SAXS experiments showed that the mesophase with a thread-like texture is a nematic columnar mesophase.

On cooling copper complexes Cu–Pc–$(OC_{16}H_{33})_6$–Cl_m, regardless of the ratio of donor and acceptor groups in the molecule, retain in mesomorphic state even at room temperature while zinc complexes Zn–Pc–$(OC_{16}H_{33})_6$–Cl_m vitrify. Phase state of ligands also depends on the number of chlorine atoms in molecule: di-chloro-substituted compound H_2–Pc–$(OC_{16}H_{33})_6$–Cl_2 preserves mesophase with the herring-bone texture even at room temperature, while the analogue with four chlorine atoms H_2–Pc–$(OC_{16}H_{33})_6$–Cl_4 vitrifies keeping Schlieren-texture of the previous mesophase.

Therefore, in contrast to the studied octyloxy-substituted Pcs, the increase of the number of acceptor substituents significantly influences the type of formed mesophase of hexadecyloxy-substituted analogues. Thus, if octyloxy-substituted Pcs displayed only one two-dimensionally ordered columnar mesophase, hexadecyloxy-substituted Pcs formed two types of mesophases depending on the number of chlorine atoms in molecule.

3.2. Spectral properties

Since spectral properties of Pcs determine their light absorbing properties which are important for the light harvesting efficiency,

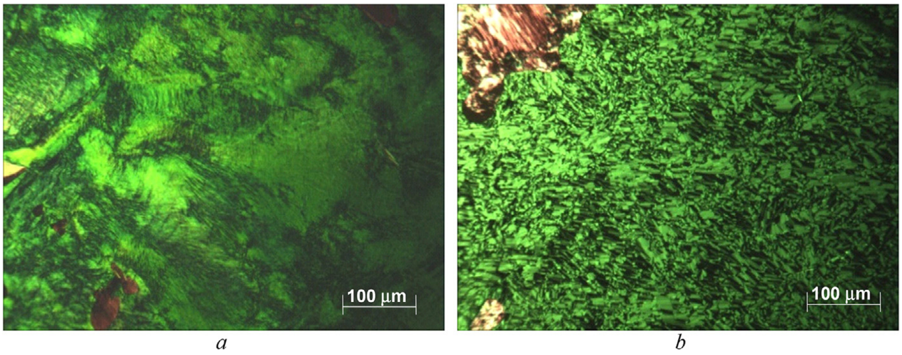
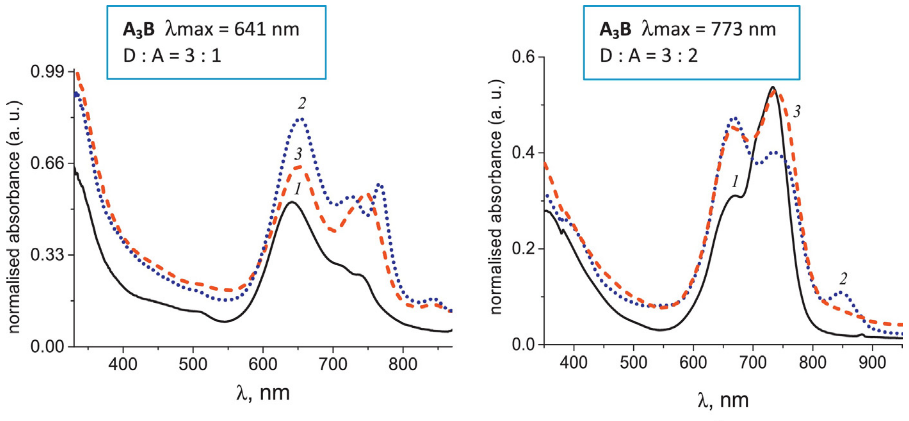


Fig. 5. Texture microphotographs of a two-dimensionally ordered columnar mesophase of ligand (**A**$_3$B) H_2–Pc–$(OC_{16}H_{33})_6$–Cl_2: (a) at heating T = 140°C, ×100; (b) on cooling, at T = 110 °C, ×100 [33].



a *b*

Fig. 6. Absorption spectra of ligands in chloroform: (a) H_2–Pc–$(OC_8H_{17})_2$–Cl_2; (b) H_2–Pc– $(OC_8H_{17})_2$–Cl_4. Designations of curves: 1 – **A**$_3$B, 2 – **A**B**A**B, 3 – **AA**BB [31].

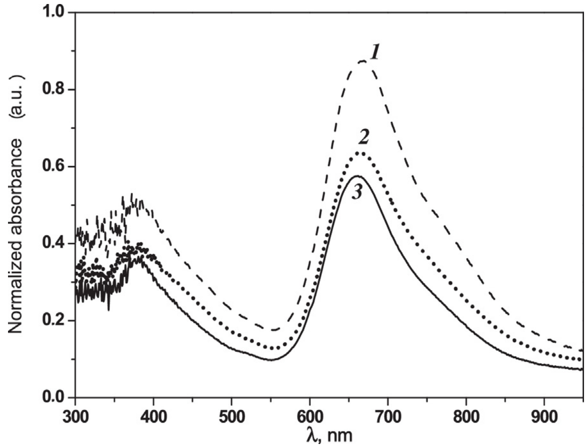


Fig. 7. Electronic absorption spectra of Langmuir–Blodgett films for H_2–Pc–$(OC_8H_{17})_y$–Cl_4. Designations of curves: 1 – **A**$_3$B, 2 – **A**B**A**B, 3 – **AA**BB [36].

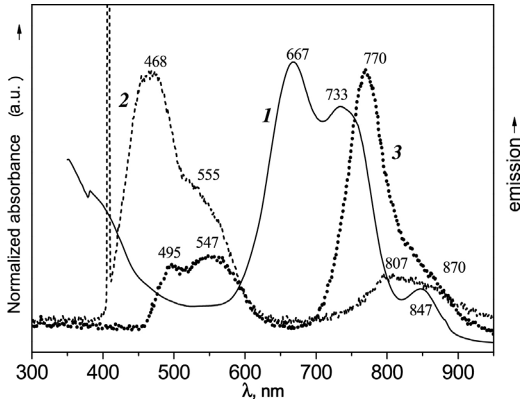


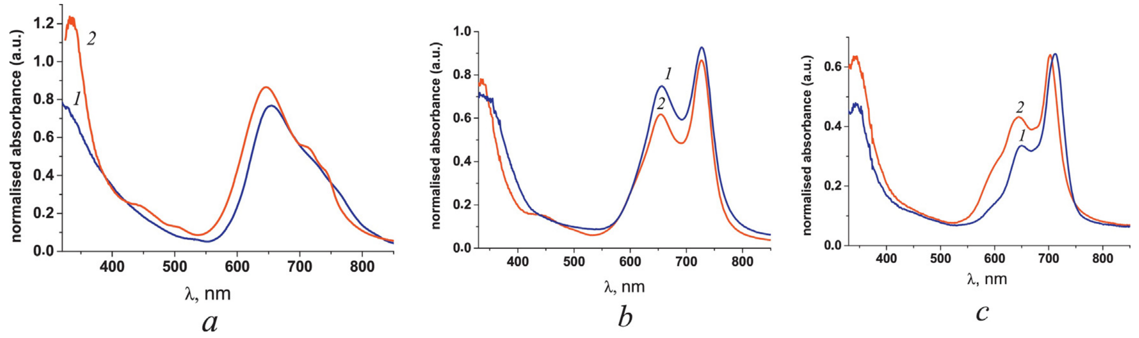
Fig. 9. Normalized spectra of compound (**ABAB**) H_2–Pc–$(OC_8H_{17})_4$–Cl_4: 1 – absorption in chloroform, 2 – photoluminescence in chloroform, 3 – photoluminescence in toluene [35,36].

we studied the effect of structural features of the compounds synthesized on the absorption spectra in solutions and thin films.

3.2.1. *Absorption properties of bulk and film samples*

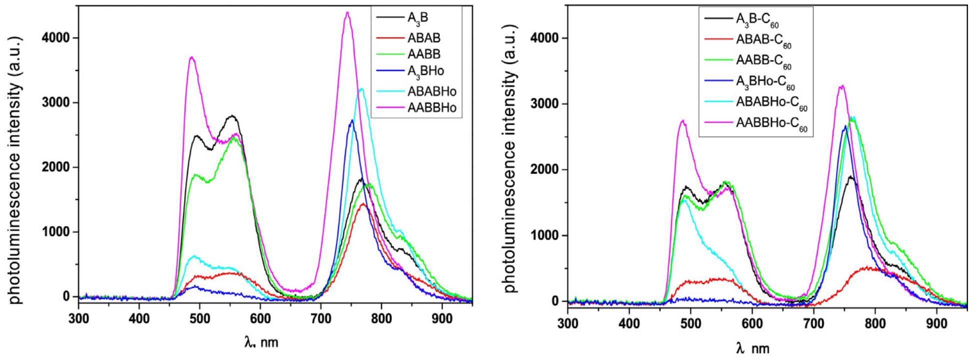
It was established that, likewise for symmetrical non-peripherally homo-substituted Pcs (of **A$_4$** type), the mix-substituted Pcs M–Pc–$(OC_nH_{2n+1})_y$–Cl_m of a "push–pull" type also show bathochromic shifts of Q-band of their absorption spectra. The comparison of electronic absorption spectra of ***octyloxy***-substituted Pcs H_2–Pc–$(OC_8H_{17})_y$–Cl_m of different types (**A$_3$B**, **ABAB** and **AABB**) showed that the increase of the number of chlorine atoms from two to four leads to batochromic shift in a Q-band position. Moreover, the value of this shift significantly depends on the donor/acceptor ratio. As it can be seen from Fig. 6, the maximum shift was observed for tetra-chloro-substituted Pcs H_2–Pc–$(OC_8H_{17})_y$–Cl_4 of **A$_3$B** and **AABB** types, i.e. when the donor and acceptor groups are located at the opposite sides of the molecule and the donor/acceptor ratio is 3:2 (Fig. 6b) [31]. For example, for di- and tetrachloro-substituted Pcs of **A$_3$B** type this shift is 641 and 773 nm, correspondingly. Film samples of the same compounds are characterized by fewer bands and hypsochromic shift of Q-band maximum in comparison with solutions (Fig. 7) [36]. Such changes can be explained by the amplification of the associative process in the plane to plane type films.

In contrast, the elongation of aliphatic chains (***hexadecyloxy***-substituted Pcs) decreases the manifestation of this effect (Fig. 8a). At the same time, the introduction of metal significantly influences



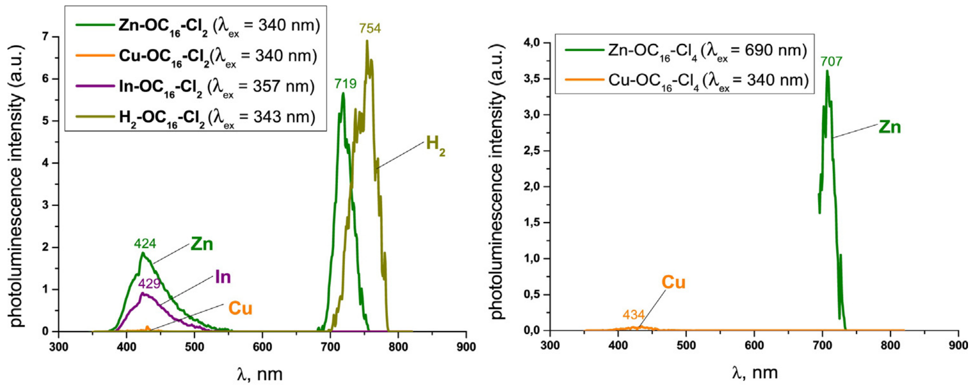
a *b* *c*

Fig. 8. Absorption spectra of (**A$_3$B**) M–Pc–$(OC_{16}H_{33})_6$–Cl_m in chloroform solutions: (a) H_2–Pc–$(OC_{16}H_{33})_6$–Cl_m; (b) Cu–Pc–$(OC_{16}H_{33})_6$–Cl_m; (c) Zn–Pc–$(OC_{16}H_{33})_6$–Cl_m. Designations of curves: 1 – $m = 2$, 2 – $m = 4$ [33].



a *b*

Fig. 10. Photoluminescence spectra of $\mathbf{A_3}$B, **A**B**A**B and **AA**BB types ligands and their holmium complexes M–Pc–$(OC_8H_{17})_y$–Cl_4, where M = $2H^+$, HoOH. (a) Toluene solutions, (b) toluene solutions with addition of C_{60} [35,36].



a *b*

Fig. 11. Photoluminescence spectra of $\mathbf{A_3}$B M–Pc–$(OC_{16}H_{33})_6$–Cl_m in chloroform solutions: (a) M–Pc–$(OC_{16}H_{33})_6$–Cl_2, (b) M–Pc–$(OC_{16}H_{33})_6$–Cl_4 [33].

the absorption maxima position (Fig. 8b, c) while the number of chlorine atoms (or donor/acceptor ratio) does not have such pronounces.

3.2.2. Photoluminescent properties

Knowing that photoluminescent properties are important for practical applications of the synthesized compounds we studied emission spectra of these compounds in solvents and thin films.

During laser illumination of octyloxy-substituted compounds in chloroform or toluene the photoluminescence of samples takes place (Fig. 9). But the intensity of photoluminescence and position of peaks are strongly connected with the chemical structure of Pc derivatives and with the solvent used.

Thus, for the studied compounds M–Pc–$(OC_8H_{17})_y$–Cl_4 maximum positions in toluene solutions are observed around 770 nm, while in chloroform – at 470 nm (Fig. 9). On example of all three types ($\mathbf{A_3B}$, **ABAB** and **AABB**) – ligands and their Ho-complexes it was shown that in toluene solutions the intensity of photoluminescence maxima depends on the structure of Pc-derivatives. The highest intensity of the long-wave maxima was observed for **AABB-Ho** complex, while the lowest – for **ABAB** ligand. Generally, the highest intensity of photoluminescence in longwave region was found for Ho-complexes.

Addition of fullerene C_{60} to the Pc solutions leads to a photoluminescence quenching (Fig. 10b). This significant reduction of photoluminescence intensity can be attributed to the efficient photoinduced charge generation between "push–pull" Pc and fullerene [35,36].

Compound M–Pc–$(OC_8H_{17})_y$–Cl_2 in chloroform solution has the maxima of emission at 770 nm. Unfortunately, at the first step of our work, the films obtained by Langmuir–Schaefer method did not show any emission under laser irradiation. Nevertheless, by selection of conditions of floating layers formation and their transfer onto the solid substrate under the constant control of the supramolecular organization in the films has allowed us to achieve photoluminescence in the films of the holmium complex ($\mathbf{A_3B}$) Ho–Pc–$(OC_8H_{17})_6$–Cl_2 [37].

In hexadecyloxy-substituted Pcs the change in donor–acceptor ratio, as well as the introduction of metals into the molecule, have a great influence on the photoluminescence properties. The metal-free Pc of $\mathbf{A_3B}$ type substituted with two chlorine atoms shows emission peaking at 754 nm; no emission has been observed for the Pc with four chlorines (Fig. 11). While Zn-complexes show photoluminescence, copper and indium complexes barely reveal it [28,33].

3.3. Photoelectric properties

To the best of our knowledge, there are practically no data concerning the effect of the phthalocyanine derivatives structure on the efficiency of solar cells. One of the few works in this direction reports on phthalocyanine metal complexes [38]. Analyzing photovoltaic parameters of solar cells based on different metal non-substituted phthalocyanines, G. Shaposhnikov and coauthors in Ref. [39] found that the efficiency of light transformation into electrical energy decreases in the series: ZnPc → MgPc → H_2Pc → OVPc, PbPc, CuPc > MnPc. In the same article it was shown that at the optimum thickness of the phthalocyanine layers is equal to 850 Å, the efficiency of solar cells varies between 0.1 and 0.066% for ZnPc and MgPc, respectively [39].

We studied photoelectric properties (photovoltaic effect and photoconductivity effect) in thin films obtained on the basis

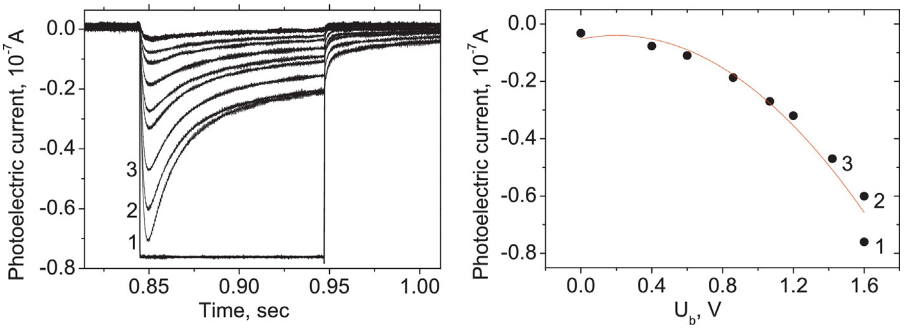


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Fig. 12. (a) Pulses of photoelectric current for the film of the compound (**A**$_3$**B**) H_2–Pc–$(OC_{16}H_{33})_6$–Cl_2 when exposed to light of a rectangular pulse of 100 ms duration. The numbers next to the curves correspond to different bias voltages (U_b). The light source is based on GaAs LED. The wavelength of the light pulses is of 660 nm. The power of the incident radiation is $W = 24\,mW/cm^2$. (b) The photocurrent in the photoconductivity effect for the film of the individual compound (**A**$_3$**B**) H_2–Pc–$(OC_{16}H_{33})_6$–Cl_2 according to the bias voltage U_b. The voltage was applied in the opposite direction [33].

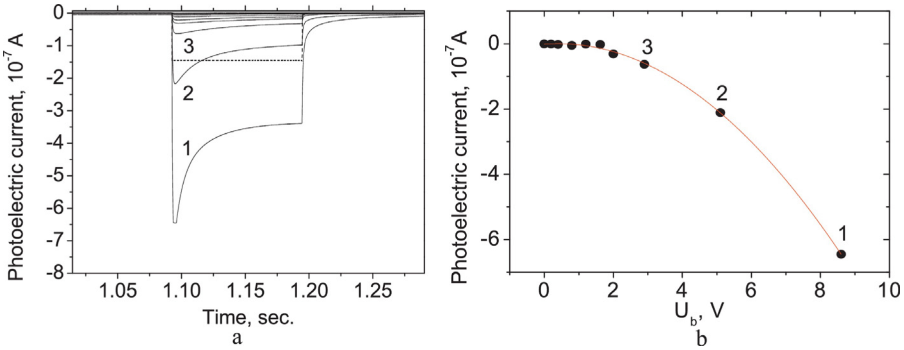

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Fig. 13. (a) Pulses of photoelectric current for the structure ITO/H_2–Pc–$(OC_{16}H_{33})_6$–Cl_2/C_{60}/Al illuminated by the rectangular light pulses (dashed curve); (b) voltage U_b for the photovoltaic cell: ITO/H_2–Pc–$(OC_{16}H_{33})_6$–Cl_2/C_{60}/Al. The voltage was applied in the opposite direction [33].

of individual semiconducting material H_2–Pc–$(OC_{16}H_{33})_6$–Cl_2 and its mixture with fullerene C_{60}. The results of photoconductivity investigation of ITO/H_2–Pc–$(OC_{16}H_{33})_6$–Cl_2/Al and ITO/H_2–Pc–$(OC_{16}H_{33})_6$–Cl_2/C_{60}/Al structures are shown in Figs. 12 and 13, respectively.

The pulse form of photoelectric current looks like the pulse form of pyroelectrics. Conversion efficiency *s* is equal to 10–100 mA/W. However, the upper limit is higher than in PZT-ceramics.

It is worth noting that the dependence of photoelectric current on the bias voltage in both cases (ITO/H_2–Pc–$(OC_{16}H_{33})_6$–Cl_2/Al and ITO/H_2–Pc–$(OC_{16}H_{33})_6$–Cl_2/C_{60}/Al) is described by a quadratic current dependence of the bias voltage: Figs. 12a and 13a, respectively. The quadratic dependence corresponds to the transient current model limited by the space charge [40]. However, the calculation of the charge mobility using the shape of impulse response curves according to [40] gives unusually low values of the order of 10^{-7} $cm^2/V\,s$, which is three orders of magnitude smaller than the conventional mobilities for organic materials. It seems that in this case the transient currents can be explained by discharge and charge of bulk charge traps inhomogeneously distributed in thin conducting layer [41,42]. The half-width of the transient current of the 20 ms order (Fig. 12b and 13b) reflects the photocurrent inertia typical for photoconduction effects in organic photoconductors.

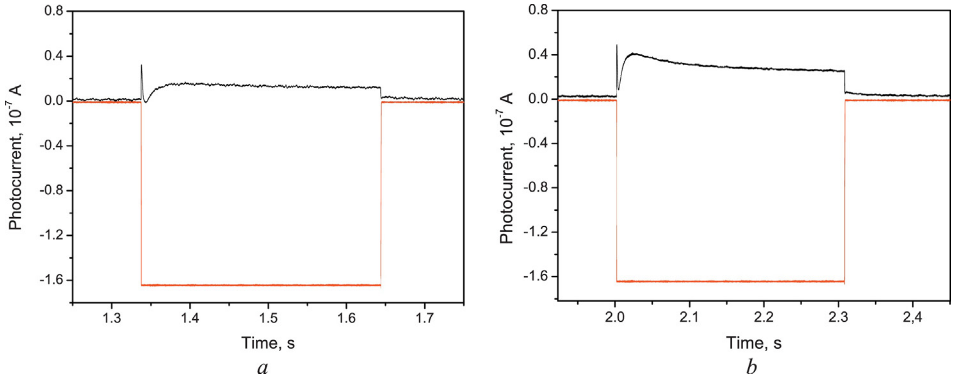

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Fig. 14. Pulses of photovoltaic current ($U_b = 0$) in the cells illuminated by the rectangular pulse of light. The light source is based on GaAs LED. The wavelength of the light pulses is of 660 nm. (a) ITO/H_2–Pc–$(OC_{16}H_{33})_6$–Cl_2/C_{60}/Al cell, (b) ITO/H_2–Pc–$(OC_{16}H_{33})_6$–Cl_4/C_{60}/Al cell.

The photoelectric current of the semiconducting heterophase systems composed by mix-substituted Pcs: H_2–Pc–$(OC_{16}H_{33})_6$–Cl_2 or H_2–Pc–$(OC_{16}H_{33})_6$–Cl_4 and fullerene C_{60} is shown in Fig. 14. In the experiment we measured photocurrent in film cells illuminated by the rectangular pulses of light and studied kinetics of the optical response of these semiconducting structures (Schottky diode) [43] and donor–acceptor transition [44].

The specific feature of obtained photodiode structures is the presence of a sufficiently intense transient current as compared to photovoltaic. This may be explained by the shallow discharge and charge traps at the interface between amorphous polycrystalline C_{60} and phthalocyanine.

Probably it is possible to control the number of charge traps in the films obtained (which are associated with the formed aggregates) and, accordingly, the photoelectric properties of these films by varying Pcs structure.

3.4. *Computational methods*

As it has been shown [45], the cascaded type of organic photovoltaic cells is quite promising for increasing the efficiency of light harvesting and conversion of light to electric current. To use the cascade type of cells with "push–pull" type Pcs synthesized by us, it was necessary to minimize the barriers to the hole injection from one Pc derivative to another.

In connection with it, we performed geometry optimization and density functional theory (DFT) calculations of phthalocyanines (**A_3B**) H_2–Pc–$(OC_nH_{2n+1})_6$–Cl_m ($m = 2, 4$) and fullerene C_{60} using the B3LYP method with the G-311++G** basis set. The calculations were performed with the help of Gaussian 09 package. The values of the frontier orbitals (HOMO/LUMO) and bandgap energies for "pull–push" Pcs of **A_3B** type containing two or four chlorine atoms in the molecule depending on the length of alkoxy-groups (from methoxy- to butyloxy-) were obtained and extrapolated for octyloxy- and hexadecyloxy-substituents [46]. Since the electrons from the frontier orbitals are located only within Pc macrocycle and do not spread into the aliphatic chains (Fig. 15) the elongation of the chains do not affect the HOMO/LUMO values significantly. Electron distribution of the frontier orbitals for fullerene C_{60} is shown in Fig. 16.

All the abovementioned let us to elaborate a cascade type of a solar cell with the following sequence of components: ITO/H_2–Pc–$(OC_{16}H_{33})_6$–Cl_2/H_2–Pc–$(OC_{16}H_{33})_6$–Cl_4/C_{60}/Al (Fig. 17). As we found out the photoelectric current has increased tenfold in this cascade cell in comparison with the single phthalocyanine H_2–Pc–$(OC_{16}H_{33})_6$–Cl_4/C_{60} system.

The next step of our work will be to determine the efficiency of this photovoltaic cell and to obtain such data as V_{oc}, I_{sc} and FF.

4. Conclusion

A new approach to the creation of materials for optoelectronics is proposed and implemented. It includes design of compounds possessing vitrification from mesophase with maintenance of columnar order, absorption in the visible region of the spectrum

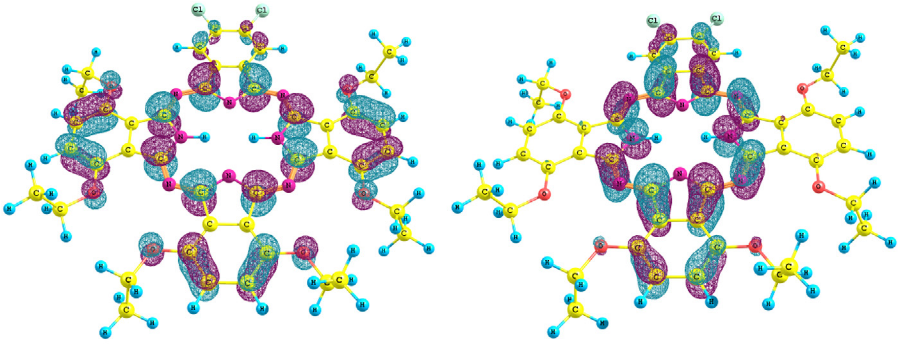
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Fig. 15. Electron distribution of the frontier orbitals of (**A_3B**) H_2–Pc–$(OC_2H_5)_6$–Cl_2: (a) HOMO orbitals, (b) LUMO orbitals [46].

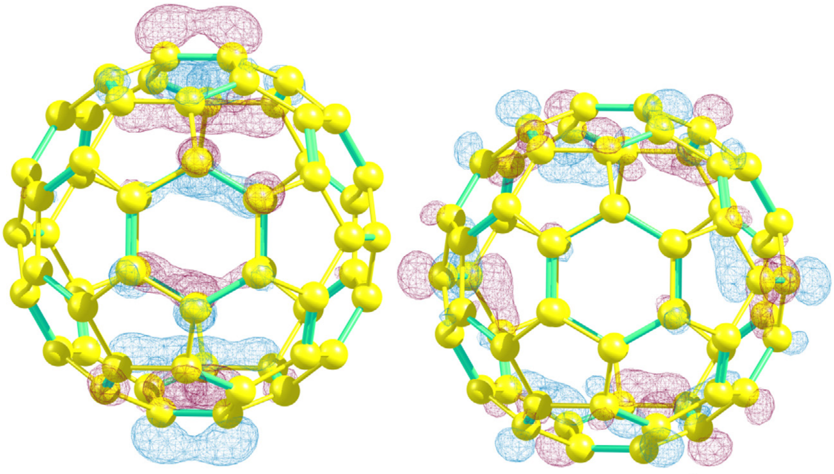
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Fig. 16. Electron distribution of the frontier orbitals for fullerene C_{60}: (a) HOMO orbitals, (b) LUMO orbitals [46].

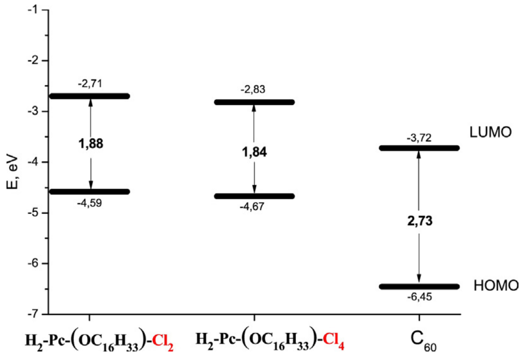

Fig. 17. Schematic energy levels of H_2–Pc–$(OC_{16}H_{33})_6$–Cl_2, H_2–Pc–$(OC_{16}H_{33})_6$–Cl_4 and fullerene C_{60} based on DFT calculations data [46].

and good performance electrophysical characteristics simultaneously.

Using this approach 23 new phthalocyanine (Pc) derivatives of a "push–pull" type and their metal complexes were designed and synthesized.

In contrast to non-mesogenic octyloxy-Pc (**A4**) having alkyloxy-substituents in non-peripheral positions, 22 of 23 synthesized compounds possess columnar mesomorphism.

The ratio of donor (–OC_nH_{2n+1}) and acceptor (–**Cl**) groups, their position in the molecule and the length of alkyloxy-substituents substantially influence thermotropic mesomorphic behavior.

On the example of hexadecyloxysubstituted metal-free Pc we showed that the change of the donor–acceptor ratio can influence the type of mesophase (from nematic columnar to two dimensional ordered columnar).

Non-peripheral substitution by alkyloxy-fragments in hetero-substituted Pcs (as it was found in the case of homo-substituted Pc) leads to red-shifting of the Q-band into near-IR region.

Introduction of ***four*** Cl-acceptors leads to *bathochromic* shift of absorption spectra in comparison to the analogues substituted with ***two*** Cl-acceptors. This phenomena is particularly evident for Pcs of **a A_3B** type.

During laser illumination of Pc-derivatives in chloroform or toluene the photoluminescence of samples takes place, but the intensity of photoluminescence, position of peaks and their splitting are strongly connected with the chemical structure of Pc-derivatives and the type of solvent.

The use of the synthesized Pcs in the experimental cascade cell increases the photoelectric current more than tenfold, and the conversion efficiency of individual compounds is comparable with silicon converters.

Acknowledgements

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