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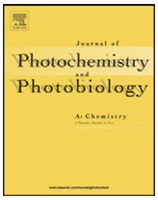

Molecular orientation and spectral investigations of Langmuir–Blodgett films of selected copper phthalocyanines

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ABSTRACT

Various spectral methods (IR absorption and reflectance-absorption, Raman scattering and UV–Vis absorption) were used for investigations of a family of copper phthalocyanines in non-polarized and polarized light. The spectra of bulk and thin film samples were compared and discussed; an orientation of selected copper phthalocyanines in Langmuir–Blogdett layers and interaction between the phthalocyanine dyes with solid substrates were studied and discussed. Molecular arrangement of the molecular skeleton on the solid substrates was also evaluated. The presence of dye aggregates in the Langmuir–Blodgett layers was shown confirming the data obtained in concentrated solutions and in Langmuir layers.

1. Introduction

Phthalocyanine pigments are most widely known as colorants but recently they are used as materials for application to photovoltaics, electrochemistry, electrocatalysis, non-linear optics, gas-sensing, data-storage devices, organic transistors and protectors [1–5]. Application of phthalocyanine nanowires for fast photoswitches and organic field transistors seems to be particularly promising [6]. Various phthalocyanines have also attracted considerable interest due to their applications in modern science and nanotechnology on the basis of their special photoelectric and electric properties [7]. For most of these applications, which largely rely on the electronic excited state properties, phthalocyanines are involved in the form of thin films or solid-layered structures. This makes a detailed recognition and understanding of the thin film properties highly desirable.

Phthalocyanines (**Pc**s) represent a large family of heterocyclic conjugated molecules with high chemical stability [1,8] however, they were found to undergo photooxidative cleavage, particularly in the solution. They are macrocyclic complexes whose π electron systems, localized over an arrangement of alternated carbon and nitrogen atoms, provide their unique chemical and physical properties. Mainly owing to the π system, **Pc**s and metalled **Pc**s display excellent thermal stability [7,8]. Metal complexes of **Pc**s, generated by the replacement of the hydrogen atoms in central cavity by metal atoms, are usually called metallophthalocyanines (**MPc**s). Central metals play a critical role in tuning the properties of **MPc**s; it results also in the alternation of molecular conformation. **MPc**'s conformation is determined by the size and location of the metal centre with respect to the mean plane of the aromatic **Pc** ligand. Between various **MPc**s applied for construction of modern solar cells [9–11] the copper phthalocyanines (**CuPc**s) present a special interest due to their potential photoelectronic properties. For example, one of the **CuPc**s has been used to fabricate the thin film photovoltaic devices with enhanced efficiencies [12]. The essentially planar conformation of **Pc**s can also be distorted by substituents alone through conformational stress [13]. Physical properties of substituted **Pc**s strongly depend on the chemical properties and spatial conformation of the substituents. This is why several substituted **CuPc**s with various side groups have been selected for our spectral investigations.

Pc films may be deposited by various means: spin coating, physical vapour deposition, molecular beam deposition, Langmuir–Blodgett deposition (LB), electrodeposition or covalent anchoring. Except for the last method, the orientation of the macrocycles with respect to the substrate can be evaluated. For our investigations LB films of various phthalocyanines were applied.

Abbreviations: **Pc**, phthalocyanine; **CuPc**, copper phthalocyanines; LB, Langmuir–Blodgett; IR, infrared; IRRA, infrared reflection–absorption; FWHM, full width at half maximum.

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On the other hand, for the characterization of the thin films of **Pc**s in related solid state devices, vibrational spectroscopies (IR and Raman) have proved to be versatile methods among various spectroscopic techniques. Since the first report in 1951 [14], infrared spectra of free-base phthalocyanine have been recorded by various research groups [15–17]. In this paper we add the IR spectra of eight **CuPc**s to the literature collection. All investigated **CuPc**s are characterized also by Raman scattering, visible and ultraviolet, as well as fluorescence and electronic spectroscopies. Usually, we recorded solid state spectra in KBr pellet but some of them were recorded in solution. Particular attention was devoted to IR reflection–absorption (IRRA) spectra of Langmuir–Blodgett films of selected **CuPc**s.

2. Experimental

To learn more about the influence of the chemical properties and spatial conformation of various substituents, which results in an extension of the π-electron system, we systematically investigated the spectroscopic response of bulk and thin film samples of a family of **CuPc**s (see Table 1). All **CuPc**s samples were obtained from Aldrich Chemical Company and were used as received. Sample **1** is a metal-free phthalocyanine (**H_2-Pc**) serving in these studies as reference sample. Sample **2** plays the similar role; it is the simplest copper(II) phthalocyanine (**CuPc**). All other samples: copper(II) 4,4′,4″,4‴-tetraaza-29H,31H-phthalocyanine (**3**), copper(II) 2,9,16,23-tetra-tert-butyl-29H,31H-phthalocyanine (**4**), copper(II) phthalocyanine-tetrasulfonic acid tetrasodium salt (**5**), copper(II) 2,3,9,10,16,17,23,24-octakis(octyloxy)-29H,31H-phthalocyanine, (**6**), copper(II) tetrakis(4-cumylphenoxy)phthalocyanine (**7**) and copper(II) 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecafluoro-29H,31H-phthalocyanine (**8**) are symmetrical substituted **CuPc**s bearing various lateral groups with different molecular structures and chemical properties. Thermodynamics of selected Langmuir monolayers and their absorption as well electronic absorption fluorescence properties in solution (chloroform) at the wide dye concentrations (10^{-3} to 10^{-6} M) is presented elsewhere [18].

In this paper we are particularly interested in the spectra of Langmuir–Blodgett (LB) layers of investigated **CuPc**s. Thin films of **CuPc**s were produced by the use of a KSV 2000 minitrough (KSV Instruments Ltd.) equipped with a temperature control system. The Langmuir trough area was 380 mm × 90 mm. The temperature of subphase was achieved and kept constant (22 °C) with a cooling circulator. The subphase was deionized water (resistivity 18.2 MΩ cm) obtained with a Mili-Q water purification system (Milipore Corp.). The samples were dissolved in chloroform and 10^{-4} M solutions were spread onto the subphase and let chloroform to be evaporated (15 min). The floating film of a Langmuir layer was compressed symmetrically from both sides with motion barrier speed of 3 mm/min.

The transfer of a molecular layer was done onto substrates of hydrophilic Au plates. In the experiment we used a 1000 Å gold layer deposited on a 160 Å chrome on the glass plate. The transfer of the molecular layer onto the substrates was performed at a surface pressure of about 20 mN/m and with speed of 2 mm/min during an upstroke and downstroke; the dipping stroke was 20 mm. Five or ten layers were deposited on Au substrates for the IR studies and two or twenty layers (i.e. one or ten layers on each quartz plate side) for electronic absorption investigations of the dyes on the quartz plate. The transfer ratio (TR) was estimated as a ratio of decreased number of dye molecules on the subphase area to the area of amount of dye molecules deposited on the substrate coated with the floating layer. We have tried to make LB layers of all dyes under investigations. However, for making LB layers and discussing results we have chosen only these dyes which are well dissolved in chloroform. For this purpose the dyes **4**, **6** and **7** are the best ones because they are perfectly soluble in chloroform and are characterized by good TR values; therefore these dyes are the subject of our study with the use of polarized light. The TR values of these dye layers range from close to 1 to about 0.7 (depending on number of layers and the type of samples).

For vibrational analysis of the LB films a reflection–absorption method was applied. In this experiment the sample to be analyzed is placed on a mirror (e.g. gold) so that the absorption of the sample reduced the reflectance, and a sort of transmission spectrum of the sample results. The reflection–absorption spectra for unpolarized and polarized light, with electric vector of the light wave parallel (0°; *p*-polarization) and perpendicular (90°; *s*-polarization) to the plane of incidence, were recorded with a FT IR Bruker Equinox 55 spectrometer, in the range 400–4000 cm^{-1}.

For spectral investigations we have chosen the films of five or ten layers; those of ten layers give more intense signals. For the unpolarized light the relative intensity increases monotonously with an incidence angle increase; the strongest bands have been recorded if the incidence angle equals 80°. For polarized light, with the electric vector parallel to the incident plane (*p*-polarization), a maximum of the normalized band intensity is observed for several bands.

Electronic and vibrational spectra of **1**–**8** were also investigated at bulk, thin layer and liquid samples. The spectra of the solid samples were recorded at room temperature, in the KBr pellets containing dispersed compounds. Electronic and vibrational absorption spectra were recorded in the range between 200 and 3500 nm with Perkin Elmer UV-Vis-NIR Lambda 19 spectrometer and in the range 400–17 000 cm^{-1} with FT-IR Bruker Equinox 55 spectrometer. Raman scattering spectra, with He–Ne laser excitations, were recorded with a LabRAM HR 800 spectrometer (HORIBA Jobin Yvon) in pure **Pc**s powder. Although the electronic and vibrational spectra were recorded in the large spectral region (400–50 000 cm^{-1}) our interest was focused on two ranges: between 200 and 600 nm, were the electronic excitations of **CuPc**s occur, and between 400 and 1800 cm^{-1}, where the intramolecular vibrations of the dyes components are observed.

Electronic absorption spectra were performed with the use of a spectrophotometer Carry 4000 in the range of 250–800 nm. Steady-state emission spectra were investigated with a spectrofluorometer Hitachi F4500 in the same way as described in [18].

3. Results and discussion

3.1. IR reflection–absorption spectra

Our particular attention is focused on orientation of phthalocyanine molecules in Langmuir–Blodgett layers, determined from IR reflection–absorption spectra (IRRA) of selected **CuPc**s films. The subject is very important because the ordered thin organic films deposited on solid substrates by the Langmuir–Blodgett (LB) technique [19] can be applied in modern technology to produce functional molecular devices.

Orientation of organic chain molecules grafted to a metal surface is commonly determined using electron or IRRA spectroscopies. In our investigations we will use the second method. This method is dependent upon the optical constants of the thin film and substrate, the angle of incidence, as well as the polarization of the incident IR radiation (*p*-component refers to radiation polarized parallel and *s*-component – to radiation polarized perpendicularly, with respect to the plane of incidence). The phase shift of the *s*-component exhibits no significant dependence upon the variation of the angle of incidence. In contrast, the phase shift of the *p*-component strongly depends upon the angle of incidence.

Table 1
Molecular structures and chemical names of the investigated phthalocyanines.

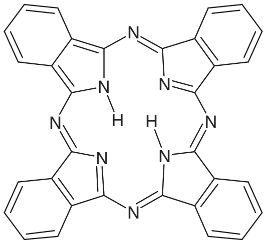
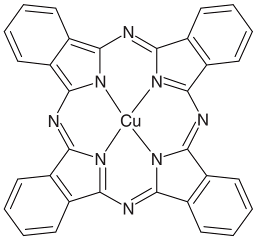
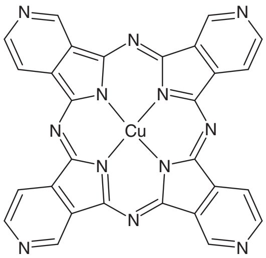
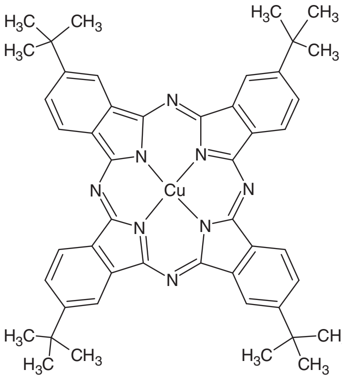
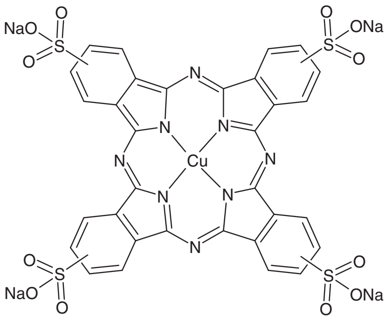
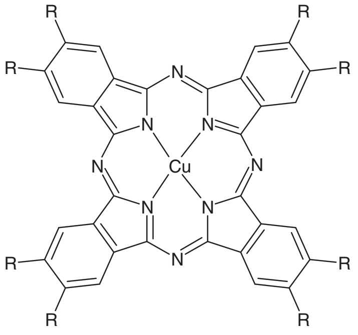
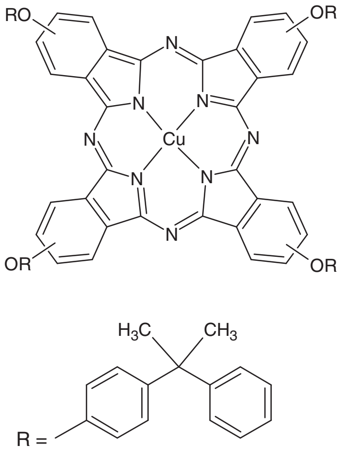
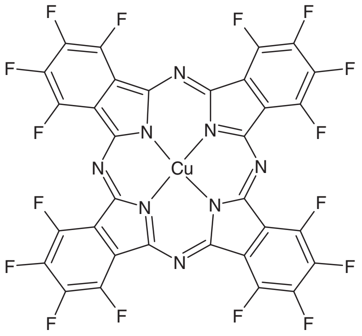
Molecular structure	Chemical name	Short name
	Phthalocyanine	**1**
	Copper(II) phthalocyanine	**2**
	Copper(II) 4,4′,4″,4‴-tetraaza-29H,31H-phthalocyanine	**3**
	Copper(II) 2,9,16,23-tetra-tert-butyl-29H,31H-phthalocyanine	**4**
	Copper(II) phthalocyanine-tetrasulfonic acid tetrasodium salt	**5**

Table 1 (*Continued*)

Molecular structure	Chemical name	Short name
 R = —OCH$_2$(CH$_2$)$_6$CH$_3$	Copper(II) 2,3,9,10,16,17,23,24-octakis(octyloxy)-29H,31H-phthalocyanine	**6**
	Copper(II) tetrakis(4-cumylphenoxy)phthalocyanine	**7**
	Copper(II) 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecafluoro-29H,31H-phthalocyanine	**8**

There are several methods of molecular orientation determination [20–25]. Whereas the acquisition of the IR spectrum itself is rather straightforward, the determination of orientation parameters is complicated by the requirement to use the bulk reference spectrum. At present, mainly two methods have been used to extract orientation information from spectral data. However, both methods have some requirements and limitations. Application of the absolute method requires the precise knowledge of the complex refractive index. On the other hand, the application of the method using relative intensities requires a second IR-active vibration with differently oriented transition dipole moment to eliminate the relative concentration. In our evaluations we applied the simplified method discussed by Arnold et al. [20]. Since the intensity of a band is proportional to the absolute value of the transition dipole moment M of the band, the ratio $(M_i/M_j)^2$ of two bands can be supposed to be the ratio of the band intensities, $I_i^{\mathrm{bulk}}/I_j^{\mathrm{bulk}}$ of the bulk spectrum. Furthermore, the ratio $(M_i/M_j)^2$ is equal to the ratio $I_i^{\mathrm{LB}}/I_j^{\mathrm{LB}}$ of the band intensities in the spectrum of LB film. Thus, one can determine the tilt angle Θ between the transition moment M_i and the normal to the substrate (Fig. 1) using following equation:

$$\mathrm{tg}^2\Theta = \frac{I_i^{\mathrm{bulk}} I_j^{\mathrm{LB}}}{I_j^{\mathrm{bulk}} I_i^{\mathrm{LB}}}. \qquad (1)$$

This relative method was described in detail by Debe [21] and Arnold et al. [20]. The method has been applied by us for determination of the perylenediimide–fullerene dyads [26].

Spectral determination of the orientation of the planar **CuPc**'s cycles was successfully performed for ten layer samples of **4**, **6**, and **7**. The typical IRRA spectrum of **6**, for two perpendicular light polarizations, restricted to the most informative region from 800 to 1800 cm^{-1} is shown in Fig. 2. It is necessary to mention that the IRRA spectrum for p-polarization or recorded in unpolarized light practically approximate the absorption spectrum recorded in KBr pellet.

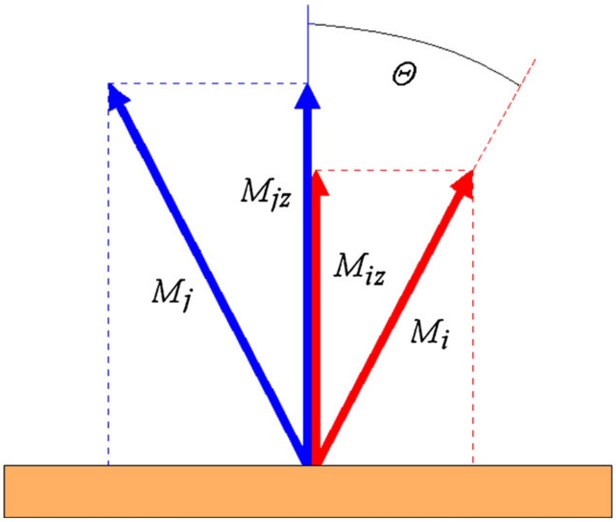


Fig. 1. Schematic representation of an orientation of the transition moments M_i and M_j at the surface of the metal substrate.

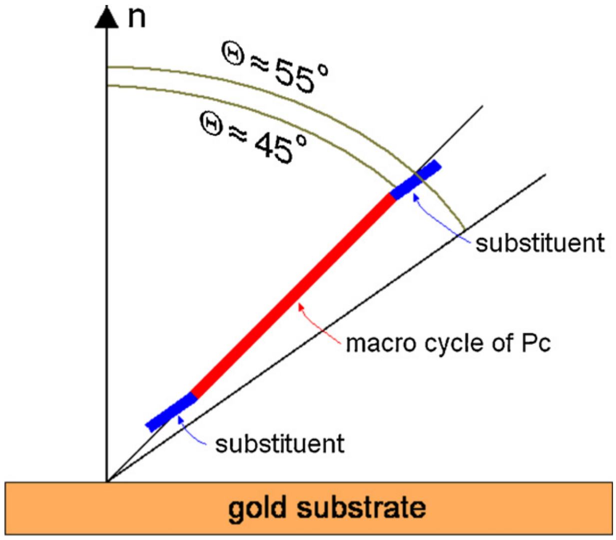


Fig. 3. Schematic illustration of the molecular orientation of substituted phthalocyanine.

For example, the spectrum of **6** in the KBr pellet is dominated by the bands at 1507, 1463, 1419, 1385, 1280, 1203, 1110, 1100, and 745 cm^{-1} assigned among others to C–N and C–C stretching, in-plane C–N–C, C–N, N–H, C–H, and C–C bending, out-of-plane C–C and C–H bending, as well as N–N heaving vibrations (see Table 3 for details). There are also several bands of medium intensities, for instance 1713, 1606, 1489, 1354, 1070, 1053, and 853 cm^{-1}. Similar bands but insignificantly shifted and changed in their intensities are observed in thin films of **6** deposited on the gold substrate. Wavenumbers of the strongest bands mentioned above are: 1608, 1559, 1507, 1490, 1467, 1420, 1389, 1283, 1205, and 1113 cm^{-1}. These small band shifts reflect changes in the charge distribution on the **Pc** molecule after deposition on gold. The changes of electron density in porphyrin, phthalocyanine and perylene dye's layers were discussed in our previous papers [26,27] and are related to possible electron transfer between a solid substrate and a dye. It seems that this effect is mainly responsible for modifications of IR spectra of the LB layers of investigated dyes with regard to those in the KBr pellet. On the other hand, different intermolecular interactions in LB layers could also modify their vibrational spectra. It is necessary to mention that IRRA spectra, even for ten molecular layers, are weak in comparison with the absorption ones for the favourable concentration of the investigated compounds in the pellet. On the other hand, the investigated layered samples show more or less heterogeneous structure. One can detect relatively flat enclaves, containing probably 10 layers – from theses regions the IRRA spectra were recorded.

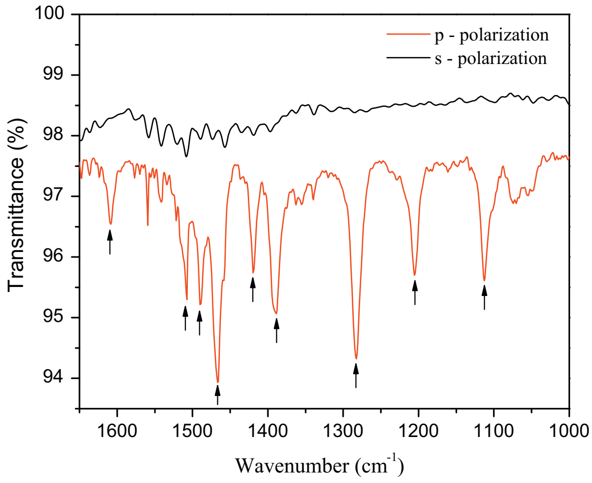


Fig. 2. Polarized reflection–absorption spectra for 10 layers of LB film of sample **6** on Au, at the angle of incidence 80° (bands used for calculation of the tilt angles are marked by arrows).

Absorption spectra of the investigated samples were recorded for KBr pellets, but the IRRA spectra of LB films were taken as *p*-polarized one. In our estimations the most intensive bands at 1280 cm^{-1} of the samples **6** and **4** were assumed as reference bands. As it is given in Tables 2 and 3, these bands are assigned to vibrations of the central **Pc** cycle; according to Basova et al. its assignment is E_u modes of C–C–H and C_α–C_β–C_β [16]. Similarly, the strong band at 1235 cm^{-1} was chosen as a reference band for the sample **7**. For estimation of the molecular orientation of the macrocyclic central part of **Pc**s, expressed by the tilt angle θ, the selected most intensive and relatively good resolved reflection–absorption bands characterizing only the central part of **Pc**s have been used (Table 2); the absolute values of absorbances and reflectances of the reference bands are given in parenthesis. In contradiction to macrocycle vibrations, only the bands assigned to the vibrations of substituents were used for evaluation of an orientation of substituents – the tilt angles of their planes are also indicated in Table 2. The tilt angles were calculated using Eq. (1) and normalized (or absolute) band intensities are collected in Table 2. Analyzing the data gathered in Table 2 one can see that the angles θ of the central parts of the investigated **Pc**s, determined on the basis of various absorption–reflection bands are between 38 and 47°. In particular, the average angle θ of the sample **4** is $(42 \pm 3)°$, of **6** – $(45 \pm 3)°$, and of **7** – also $(42 \pm 3)°$. These data were evaluated taking into consideration only the bands assigned to bending or deformations of the macrocycle; for the sample **6** the used bands are marked by arrows (see Figs. 2 and 4). The bands typical for vibrations of the substituents (e.g. 1257 cm^{-1} of **4**, 1490 and 1100/1113 cm^{-1} of **6**, and 1030 cm^{-1} of **7**) were used for determination of the orientation of substituent groups. The data collected in Table 2 show that these groups are inclined from the plane of the central cycle by about 10°. Thus, we can conclude that the investigated **Pc**s layers are similarly oriented, with the tilt angle Θ between 42° and 45°; only the external groups of substituents are slightly inclined to the central plane. Schematic illustration of the molecular orientation of a substituted phthalocyanine is shown in Fig. 3.

Table 2
Determined angles Θ and other parameters for selected LB samples (absolute values of absorption and reflection band intensities of reference ones are in parenthesis).

Short name	Sample name	Wavenumber [cm^{-1}]	Band assignment	Normalized band intensity		Angle Θ [°]
				In bulk	In LB film	
4	Copper(II)2,9,16,23-tetra-tert-butyl-29H,31H-phthalocyanine	1322	Central cycle vibration	1.09	0.83	41
		1280	Central cycle vibration	1.00 (0.36)	1.00 (0.31)	45
		1257	Substituent vibration	1.18	1.72	50
		1201	Central cycle vibration	0.62	0.50	42
		1092	Central Cycle vibration	2.93	1.895	39
6	Copper(II) 2,3,9,10,16,17,23,24-octakis(octyloxy)-29H,31H-phthalocyanine	1608	Central cycle vibration	0.29	0.33	47
		1507	Central cycle vibration	0.36	0.44	46
		1490	Substituent vibration	0.20	0.38	54
		1467	Central cycle vibration	0.94	1.13	47
		1420	Central cycle vibration	0.48	0.48	45
		1389	Central cycle vibration	0.72	0.66	44
		1280	Central cycle vibration	1.00 (0.51)	1.00 (0.43)	45
		1205	Central cycle vibration	0.69	0.56	42
		1100/1113	Substituent vibration	0.42	0.59	56
7	Copper(II) tetrakis(4-cumylphenoxy) phthalocyanine	1235	Central cycle vibration	1.00 (0.29)	1.00 (0.26)	45
		1175	Central cycle vibration	0.21	0.18	43
		1118	Central cycle vibration	0.14	0.15	46
		1093	Central cycle vibration	0.33	0.20	38
		1052	Central cycle vibration	0.23	0.15	39
		1030	Subsituent vibration	0.07	0.12	53
		1015	Central cycle vibration	0.20	0.15	41

In fact, some molecular groups in relatively large organic molecules are inclined in relation to adjacent groups. It was shown e.g. for azobenzene-containing long-chain fatty acids and their salts [24]. The molecular orientation determined by various authors [26–29] in self-assembled monolayers of octadecanethiol and *p*-terphenylthiol is between (23 ± 1°) and 38°. On the other hand it was found by Zhao et al. [30] that the **Pc**s molecules are arranged with an angle of 49.8° and 63.6° to the substituents. Just recently, Benten et al. [31] have investigated the copper phthalocyanine derivative and found that the tilting angles Θ are up to 40°. Our results are in reasonable agreement with the literature data for similar films. One can notice that the orientation of the molecules depends not only on the molecular structure of the central cycle but also on the chemical nature, flexibility and ability to incline from the plane of the central macrocycle.

3.2. IR absorption spectra

The IR absorption spectra of various phthalocyanines depend on two main aspects. Firstly, the vibrations of planarmacro cycle of **Pc** or **CuPc** molecules. These vibrations are strongly modified if the molecule contains various substituent groups. Thus, the second aspect is nature and structure of substituents. For us, the basic is the IR spectrum of **CuPc**; it acts as a reference. The **CuPc** molecule consists of 57 atoms and possessing D_{4h} point group symmetry. The vibrations of **CuPc** can be classified into following irreducible representation [32,33]:

$$\Gamma_{\text{vib}} = 14A_{1g} + 13A_{2g} + 14B_{1g} + 14B_{2g} + 13E_g + 6A_{1u} + 8A_{2u} + 7B_{1u} + 7B_{2u} + 28_{Eu} \quad (2)$$

where A_{1g}, B_{1g}, B_{2g}, and E_g modes are Raman active. The nodegenerated A_{1g}, B_{1g}, and B_{2g} modes are in-plane vibrations, and double degenerate E_g are out-of-plane vibrations [34].

The experimental spectra of **Pc** (**1**) and **CuPc** (**2**) are shown in Fig. 4 (absolute values of absorption and reflection band intensities of reference ones are in parenthesis, Table 2). It has been found that some of the vibrational modes of **CuPc** lie at the same or close positions with corresponding vibrational modes for **Pc**; it is perfectly seen for the bands at 1611, 1590, 1508, 1480, 1466, 1421, 1334, 1288, 1120, 1091, 755, 730, 506, 434 cm^{-1} and few bands assigned to C–H stretching vibrations (3059, 3049, 3029 and 3013 cm^{-1}). However, other bands are shifted and changed in their intensities. It is an example showing that relatively small change in the molecule composition distinctly changes IR spectrum of the molecule. The strong bands of **Pc**s, at similar wavenumbers were also observed e.g. in the papers [16,35–37]. Supplied documentary evidence with tentative band assignment is shown in Table 3. As one can see some

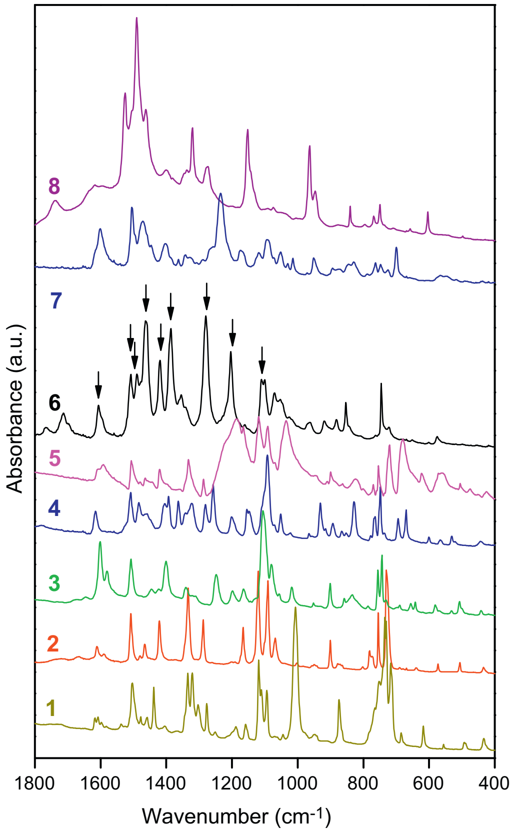


Fig. 4. IR absorption spectra of the investigated phthalocyanines in KBr pellet (bands of the sample **6** used for calculation of the tilt angles are marked by arrows).

Table 3
Approximate description of the main vibrational bands of the investigated phthalocyanines.

Samples of phthalocyanines								Band description [26,27]
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	
				425				
433	**434**	**442**	**444**			**437**		In-plane C–C–H bend.
				452				
				475				
493						492		In-plane N–H bend., in-plane pyrrole bend.
	506	**508**		**505**				Out-of-plane ring bend. and C–N–C bend., N–N heaving
						518		Out-of-plane ring bend.
		532	531					
						548		
556								In-plane N–H bend., isoindol strech. & def.
	573		**566**	**561**	**575**	**565**		Out-of-plane C–N–C and C–C bend.
				572				Out-of-plane C–C bend.
		582						
			600				**603**	
617				623				Out-of-plane C–N–C bend.
	639	642						
		655					658	
	669		669			669		
	679			680				N–N and C–C heaving.
685								
	690	690	694			700		Out-of-plane C–N–C and C–H bend.
717				**721**	**722**	**725**		Out-of-plane C–H, N–H bend.
730	**730**	**731**						In-plane N–H bend., isoindole strech. & def.
735								Out-of-plane C–H, N–H bend.
		744	**748**		**745**	**748**	**749**	
752	**755**	**756**		**754**		**763**		Out-of-plane C–C and N–H bend., in-plane C–N–C bend.
765			**764**			**768**	**768**	Out-of-plane C–N–C bend.
				770				Out-of-plane C–C bend. And ring and Cu–N stretch.
	781	**786**						Stretch. M–N
	802			801				Out-of-plane C–H bend., ring stretch., and N–N heaving.
	805							
		834	828	824		829		
						845	840	
		858	853		853			
			866	864				
874	871					875		Out-of-plane C–H bend.
	878				882			
	901	**901**	**893**	**900**	**919**			Ring stretch., C–C out-of-plane bend., N–N heaving.
			915	910				HeavingN–N.
			931					Ring stretch.
							946	Out-of-plane C–C bend.
	950	952			962	951		Out-of plane C–H bend.
			966			971	963	
1007	1002							In-plane C–H bend., C–C stretch.
		1017				1015		
			1023					
				1035		1030		
1045								In-plane N–H bend., isoindol def.
1049		1056	1052		1053	1052		
	1069			1070	1070	1073	1074	N–N and C–C heaving.
		1080						
	1091							In-plane C–H bend. and N–N heaving.
1100		**1106**	**1092**	**1091**	**1100**	**1093**		In-plane N–H, C–H bend.
1118	**1120**			**1118**	**1110**	**1118**		In-plane C–H bend.
			1148				1152	Stretch. C–C.
1159	1166	1165	1154	1165				In-plane-C–H bend.
						1175		
1188				1186				Out-of-plane C–H and N–Cu–N bend.
		1198						
			1201		1203			N–N heaving, out-of-plane C–H bend.
						1235		
1251		1248						In-plane N–H bend., C–N strech.
			1257			1257		
							1273	
1277								
	1288		**1280**	**1287**	**1280**	**1288**		In-plane C–C bend., out-of-plane C–H bend.
1303						1308		N–N heaving, in-plane C–N–C bend., C–C stretch.
1321			1322			1329	1320	In-plane C–C bend.
	1334	1340	1363	1333	1354	1342		Out-of plane C–H bend., C–C strech, N–N heaving.
				1361		1361		
				1375				
			1393	1400	1385			Cu–N stretch., in-plane C–N–C bend.
		1400	**1404**			**1404**	**1400**	C–C stretch., in-plane C–H bend.
	1421	**1423**		**1420**	**1419**			C–C stretch., in-plane C–H bend.

Table 3 (*Continued*)

Samples of phthalocyanines								Band description [26,27]
1	2	3	4	5	6	7	8	
1441		**1445**		**1443**		**1446**		C–C stretch., in-plane C–H bend.
1458	**1466**		**1459**	**1464**	**1463**	**1472**	**1462**	In-plane C–H, N–H bend., out-of-plane C–C bend.
1478	**1480**		**1483**	**1480**	**1489**		**1489**	In-plane C–H and C–N–C bend., out-of-plane C–C bend.
1504	**1508**	**1507**	**1508**	**1506**	**1507**	**1504**		C–N stretch., in-plane C–N–C bend.
							1525	
1538						1540		C–N stretch., in-plane C–N–C bend.
					1559			In-plane N–H bend., C–N strech.
1597	**1590**	**1580**		**1592**		**1559**		
1608		**1601**		**1608**	**1606**	**1601**		In-plane C–C bend.
1617	**1611**		**1616**				**1617**	
	1665							Stretch. C–C.
							1736	In-plane C–C bend.
					2852			
			2866					
			2902					
					2923			
			2956		2955			
						2996		
3014	3013			3012				C–H stretch.
3029	3029					3031		C–H stretch.
		3039	3036					
3049	3049			3047				C–H stretch.
3062	3059		3066		3057	3056		C–H stretch.
3076	3081		3077		3075	3084		C–H stretch.
3291								

of the bands are distinctly shifted in substituted **Pc**s (**3**–**8**). On the other hand new bands connected with vibrations of various bonds of substituents are observed in the IR spectra. In all spectra the most intensive bands are connected with out-of-plane C–N or C–H bending (at the region of 700–730 $\mathrm{cm^{-1}}$), stretching C–C and in-plane C–H bending (between 1100 and 1120 $\mathrm{cm^{-1}}$), in-plane C–C bending and out-of-plane C–H bending (about 1300 $\mathrm{cm^{-1}}$), and C–N stretching and C–N–C in-plane bending (above 1500 $\mathrm{cm^{-1}}$). On the other hand, there are characteristic features of **Pc** under studies. In particular, the IR spectrum of **3** distinguishes oneself for relatively strong bands at 1580 and 1601 $\mathrm{cm^{-1}}$, and distinctly modified regions at about 1300 $\mathrm{cm^{-1}}$ (in-plane C–C and out-of-plane C–H bending), between 1100 and 1120 $\mathrm{cm^{-1}}$ (stretching C–C and in-plane C–H bending), and at the region of 700–730 $\mathrm{cm^{-1}}$ (out-of-plane C–N or C–H bending). The last region contains the vibrations typical for pyridine group; similarly, pyridine shows strong bands at about 600, 885, 1440, and 1570 $\mathrm{cm^{-1}}$. The next sample **4** contains four tertbutyl groups as **Pc** substituents. These groups are spatial and rotating; it creates several spatial hindrances and various intra- and intermolecular interactions. As a result the molecule shows low symmetry but its IR spectrum contains many supplementary absorption bands mainly connected with C–H stretching, bending and scissoring. The sample **5** contains four tetrasulfonic acid tetrasodium salts – it provokes activation of supplementary bands seen as distinct broadening of the bands centred at about 1620, 1200, 1090, 1020, and 680 $\mathrm{cm^{-1}}$. Long aliphatic chains in **6** give similar effects as the tertbutyl groups in **4**; the absorption spectrum of **6** is rich, with numerous bands typical for C–H vibrations, in principle similar to IR spectrum of **4**. Except absorption bands characteristic for **CuPc** (**2**), the IR spectrum of **7** is dominated by a few strong and relatively broad bands at about 1600, 1540, 1500, and 1260 $\mathrm{cm^{-1}}$. In opposite to the spectra discussed above, the IR spectrum of **8** contains rather weak bands of **Pc** macro ring but shows a few strong bands at about 1525, 1490, 1460, 1320, 1150, and 960/950 $\mathrm{cm^{-1}}$. These bands reflect the vibrations of the benzene ring substituted with four fluorine atoms.

From the above discussion one can see that the IR absorption spectra of various **Pc**s are different one to another. They are not a superposition of the spectra of central ring and substituents but they show features typical for completely new molecules: the substituted phthalocyanines.

3.3. *Raman spectra*

The Raman spectra of the investigated phthalocyanines (**1**–**8**), excited with radiation of $\lambda_{\mathrm{exc}} = 633$ nm, are gathered in Fig. 5; for better illustration, the spectra of basic phthalocyanines **Pc** (**1**) and **CuPc** (**2**) are supplementary shown in Fig. 6. All these spectra were recorded in pure **Pc**s powder. There are several similarities in the spectra. The most typical vibrations are observed for all the samples at about 1520, 1450, 1340, 1300, 950, 740, 670, 490, and 225 $\mathrm{cm^{-1}}$. Besides there are the lines characteristic for substituent, for example the large doublet centred at 1350 $\mathrm{cm^{-1}}$ and the line at 770 $\mathrm{cm^{-1}}$ for **8** as well as the line at 1240 $\mathrm{cm^{-1}}$ for **3**. Similar Raman bands were observed by other authors for selected **Pc**s [38,39]. However, it is necessary to stress that Raman spectra of the investigated **Pc**s are very similar one to another, more similar than the IR spectra. The same effect was observed recently by us for systems containing organic chromophore bonded to fullerene [40,41].

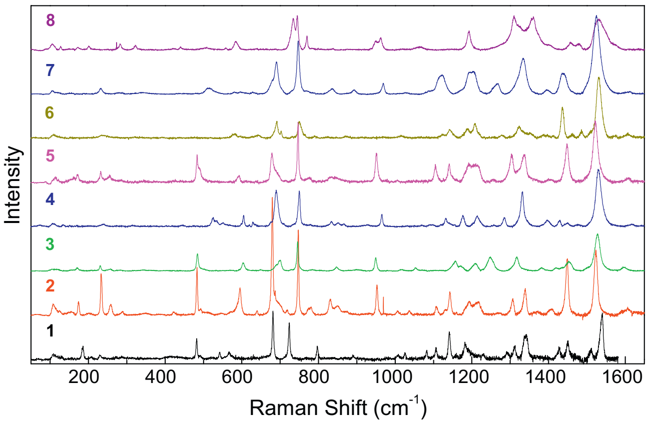


Fig. 5. Raman spectra of the investigated phthalocyanines excited with radiation of $\lambda_{\mathrm{exc}} = 633$ nm.

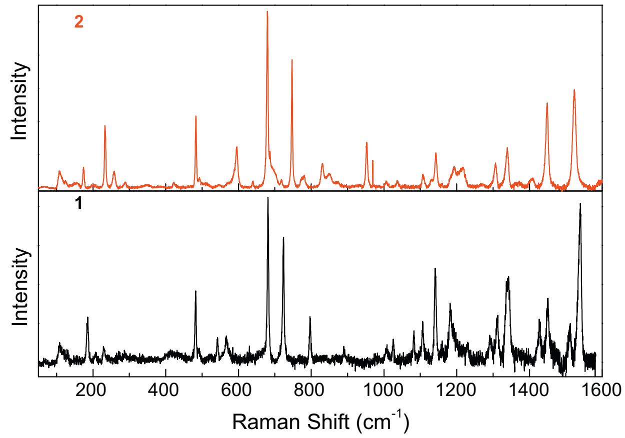


Fig. 6. Raman spectra of basic phthalocyanines **Pc** (**1**) and **CuPc** (**2**).

Table 4
Absorption parameters of **4**, **6** and **7** LB layers on the quartz plate.

Dye	Langmuir–Blodgett			Langmuir layer[a]		
	Absorption band, λ [nm]	FWHM [cm^{-1}]	Absorption ratio	Absorption band, λ [nm]	FWHM [cm^{-1}]	Absorption ratio
4				218		
				265		
	332			334		
	623	2090		623		
	680	1170	0.54 (1)	680	2480	0.49 (2)
6	283			287		
	339			340		
	414			402		
				429		
	649	1630		654		
	695	1030	0.97 (3)	694	4090	1.09 (4)
7				217		
	335			277		
				334		
	619	2030		618		
	680	1280	0.43 (5)	680	2690	0.47 (6)

FWHM was evaluated with the use of Gaussian analyses. FWHM – full width at the half maximum; ΔFWHM = ±100 cm^{-1}, Δλ = ±1 nm. Absorption ratio: (1) – 680/623, (2) – 680/623, (3) – 695/649, (4) 694/654, (5) 680/619, and (6) – 680/618.

[a] The data on the basis of results in part 1, Fig. 4.

In general, both IR and Raman vibrational spectra of investigated **CuPc**s are dominated by the vibrations of the macrocycle; this is why all the spectra show numerous resemblances.

3.4. Langmuir–Blodgett layer UV–Vis absorption spectra

In this chapter absorption feature of the dyes (**4**, **6** and **7**) and their ability to aggregate creation are shown and discussed. On the basis of our investigations of absorption and thermodynamics behaviour of these dyes [18] we have concluded on the presence of H (**4** and **7**) and oblique (**6**) dimers. Absorption of the samples composed of two LB or twenty layers (one or ten layers on each side of the quartz plate, respectively) were measured. The results for the 2 layered samples of **4**, **6** and **7** are shown in Fig. 7. The absorption parameters (absorption band locations, full width at half maxima (FWHM), absorption intensity ratios) of the LB samples and the Langmuir layers were evaluated on the basis of the results presented in [18]. The shapes of the absorption spectra and locations of the bands and absorption ratios are strongly coherent with those of the Langmuir layers. The data are gathered in Table 4. Only some very small differences of these spectra in LB from those of the Langmuir layers are observed in the intensity ratios and shifts of the bands (within the range of experimental errors). The arrival of the strong bands at about 622 nm (**4**) and 618 nm (**7**) evidences the presence of the H aggregates in these dyes [42–44], which strongly dominate over monomers (seen as the humps at about 680 nm). In **6** the splitting of the bands in the range of 650–695 nm can be a proof of creation of the oblique dimers. These results convincible show and confirm the presence of aggregates in the LB layers – the H type in **4** and **7** and the oblique one in **6** of the very similar configuration as found in the Langmuir layers and concentrated solution. The only very spectacular differences between the spectra of the samples in the monolayers and in LB are the values of FWHM. These values reach up to about 4000 cm^{-1}; for the samples in chloroform these are 660 cm^{-1}. Additional experiment for the **6** sample with twenty layers (ten layers on the each quartz plate side) were also done; there are not particular differences between the spectra neither in the shape, the band positions nor in the intensity ratios. This result confirms the same arrangement of the dye molecules when they are spread as one layer interacting directly with the substrate and those of ten layers interacting through the first layer with the solid. On the basis of this part of our experiments we can claim the similar molecular organization of the dyes when they create the Langmuir monolayers and are transferred on the quartz plate as the LB layers. Thus, the close correlation between the Langmuir layer absorbance with those related to absorption of the LB films let us to conclude as to the presence of the H aggregates in **4** and **7** and the oblique one in **6**.

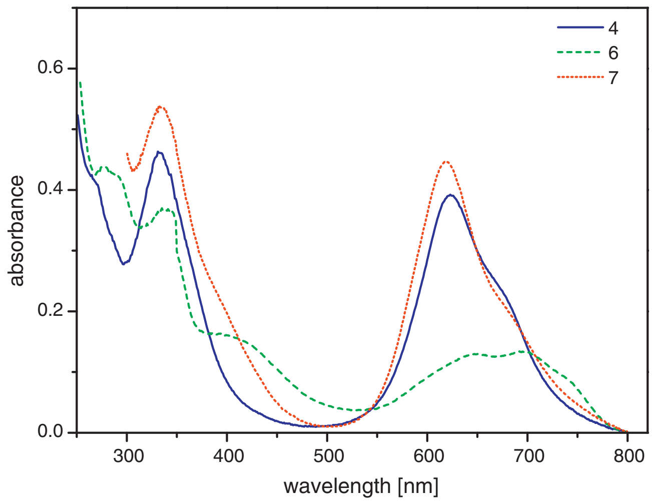


Fig. 7. Absorption spectra of **4**, **6** and **7** of two LB layers on the quartz plate.

4. Conclusions

It was stated that both vibrational (IR and Raman) spectra of investigated **CuPcs** are dominated by the vibrations of the **Pc** macro cycle. However, the spatial structure and properties of substituents influence distinctly the spectra. Some new bands characteristic for substituents, shifts of some bands and changes in their form were also observed. The role of interactions between the first monolayer and substrate was mentioned. Some suggestions on the interaction in the **CuPc**s layers were presented taking into account comparison of the bulk and thin layer spectra. From the IRRA spectra of LB films the tilt angles Θ for transitions of bending or deformations of macro cycles are between 42° and 45° but for remaining ones connected with vibrations of substituents they are $(53 \pm 3)^{\circ}$.

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