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Tetrasubstituted copper phthalocyanines: correlation between liquid crystalline properties, films alignment and sensing properties

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Abstract

Copper phthalocyanines (CuPc) containing alkylthio ($-\text{S}(\text{CH}_2)_n\text{CH}_3$, $n=7$ and 15), alkyloxy ($-\text{O}(\text{CH}_2)_n\text{CH}_3$, $n=7$ and 15) and polyoxo ($-\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$ and $-\text{S}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$) substituents were synthesized and investigated to reveal the effects of substituents type (alkylthio, alkyloxy and polyoxo) and the type of the connecting heteroatom (oxygen or sulphur) on the mesogenic properties, films alignment and sensing behaviour. The liquid crystalline properties of these phthalocyanines were investigated by differential scanning calorimetry, polarizing optical microscopy and X-ray diffraction techniques. The structure and morphology of spun thin films of copper phthalocyanine derivatives were studied by the UV-Vis and Raman spectroscopies as well atomic force microscopy. The sensing properties of CuPc films were studied by the measurement of conductivity change upon interaction with ammonia in the range 10-50 ppm. All investigated films of CuPc derivatives display thermotropic columnar mesomorphism. It was shown that the films with polyoxo- ($-\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$ and $-\text{S}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$) substituents as well as with alkylthio $-\text{S}(\text{CH}_2)_n\text{CH}_3$ ($n=7$) substituents, which are liquid crystalline at room temperature, form ordered films with a random planar alignment of columns. Their films exhibit the better sensor performance with the maximal sensor response for the films of CuPc containing ($-\text{S}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$) substituents.

Keywords: Copper phthalocyanines; chemical sensors; ammonia sensors; liquid crystals; film alignment

1. Introduction

Phthalocyanines are numerous and interesting group of synthetic analogues of the naturally occurring porphyrins such as chlorophyll or hemoglobin. By now thousands of phthalocyanines containing various substituents and central metal atoms have been synthesized and characterized. They have attracted considerable interested due to the perspectives of their application in such areas as photodynamic therapy, catalysis, chemical sensors and so on [1].

In order to improve the utility of phthalocyanine films in electronic and optical devices, it is important not only to suggest the molecule design but also to produce the uniform thin films with controllable architecture and ordering. In addition to physical gas deposition [2] and Langmuir-Blodgett (LB) technique [3], spin-coating technology is a suitable method of preparing uniform phthalocyanine films [4-6] due to the associated low cost and simplicity. This method could yield best quality films, especially if the deposited metal phthalocyanines films are able to form mesophases [7, 8]. Slow cooling from isotropic melt or sometimes heating the phthalocyanine films above the temperature of phase transition from crystal to mesophase can make better the long-range ordering of the films without destroying their homogeneity [7-10].

It has been shown that liquid crystalline phthalocyanines demonstrate high sensitivity to various analytes. Sensor response of a series of liquid crystalline (LC) phthalocyanine thin films toward NO₂ was studied by Kılınç et al. [11] and Shi et al. [12]. Sensor properties of spun films of octabutoxysubstituted zinc (II) phthalocyanine have been investigated; their response towards chlorine was shown to be significantly larger than that exhibited by thermally deposited unsubstituted ZnPc [13]. It was demonstrated that films' sensitivity of this ZnPc towards a range of analytes changes in the following order: Cl₂>NO₂>NO>NH₃ with the detection limit of Cl₂ was determined to be 5 ppb. The effect of oxidizing gases, such as O₂, NO₂ and O₃ on LC copper octakisalkylthio phthalocyanine thin film was also studied in the temperature range of 25–150 °C [14].

It is known that sensor properties depend on the type and number of peripheral

substituents, central metal ion and on film's morphology. While the influence of central metal on the sensor response has been extensively studied [15, 16] data on the investigation of the influence of substituents in LC phthalocyanines are rather scarce.

In a previous study [17] we have addressed the liquid crystalline behavior of octasubstituted phthalocyanine derivatives (CuPcR_8) substituted with alkylthio-, alkyloxy-, (trioxyethylene)thio- and (trioxyethylene)oxy- substituents in peripheral positions over a wide range of temperatures. The significant dependence of crystal-to-mesophase and mesophase-to-isotropic phase transition temperatures on the number of alkyl substituents was revealed for these phthalocyanines [17]. It was also known that both the mesophase type and the transition temperature also depend on the length of the alkyl chains [18-21]. The nature of the linking heteroatom between the side chains and aromatic core has also been shown to have a noticeable influence on the phthalocyanine properties [22, 23].

One of the main preferences of tetra-substituted liquid crystalline copper phthalocyanines over their octa-substituted analogues is that the tetra-substituted phthalocyanines can usually be synthesized as a mixture of four regioisomers [24, 25]. The occurrence of the isomers mixture decreases the phase transition temperatures as compared with the octasubstituted analogues. Furthermore, crystallisation of the liquid crystalline phthalocyanines is prevented for the same reason [26].

Despite the many examples of liquid crystalline CuPc described in the literature [7 and refs. therein] the investigation of the effect of the substituents type on the films alignment and sensor properties was not systematically carried out.

The aim of the present work is to study the correlation between liquid crystalline properties of tetrasubstituted copper phthalocyanines, their films alignment and sensing properties. The alkylthio- ($-\text{S}(\text{CH}_2)_n\text{CH}_3$, $n=7$ and 15), alkyloxy- ($-\text{O}(\text{CH}_2)_n\text{CH}_3$, $n=7$ and 15) and polyoxo- ($-\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$ and $-\text{S}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$) substituents were chosen to study the effect of the nature of connecting heteroatom between side chains and the aromatic core as well

as the influence of the substituent type. Structures and notations of the investigated tetrasubstituted phthalocyanines are given in Fig. 1. A comparative analysis of the mesogenic properties and films alignment of these peripherally tetrasubstituted copper phthalocyanines has also been performed. The mesogenic properties of these CuPc derivatives were studied by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction (XRD) techniques. The structure and morphology of the CuPc spun thin films were studied by Raman and UV-Vis spectroscopies as well atomic force microscopy.

2. Experimental

2.1. Materials

4-Nitrophthalonitrile [27], 4-(n-octyloxy)phthalonitrile (**1a**) [28], 4-(n-hexadecyloxy)phthalonitrile (**1b**) [29], 4-(n-octylthio)phthalonitrile (**1c**) [30], 4-(n-hexadecylthio) phthalonitrile (**1d**) [31], 4-(4,7,10-trioxaundecane-1-oxyl)phthalonitrile (**1e**) [32] and 4-(4,7,10-trioxaundecane-1-sulfanyl)phthalonitrile (**1f**) [33] were synthesized according to procedures described in the literature. CuPcs, **4d** [34], **4e** [35] and **4f** [35] were prepared by using the method described in the literature. Other solvents and reagents were obtained from commercial suppliers and dried as described in Perrin and Armarego [36].

2.2. Measurements

The IR spectra ($650\text{-}4000\text{ cm}^{-1}$) were recorded using a Perkin Elmer Spectrum 100 FT-IR spectrometer with an attenuated total reflection (ATR) accessory with ZnSe crystal. Electronic absorption spectra were recorded with Shimadzu UV-Vis-2101 spectrometer using 1 cm pathlength cuvette at room temperature. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) measurements were performed on a Bruker Daltonics micrOTOF (Bremen, Germany) by using 2,3-dihydroxybenzoic acid as a MALDI matrix. Elemental analysis was performed with a Thermo Finnigan Flash 1112 instrument

(ThermoFisher Scientific, Waltham, MA). The phase transitions of CuPcs **4a-f** were observed by means of a polarizing optical microscope (POM) (Leitz Wetzler Orthoplan-pol.) equipped with a hot stage (Linkam TMS 93) and a temperature controller (Linkam LNP). Thermogravimetric analysis (TGA) was carried out on a Mettler Toledo Star^c Thermal Analysis System at a rate of 10°C min⁻¹ in a nitrogen flow (50 mL min⁻¹). Transition temperatures were determined at a scan rate of 10 °C min⁻¹ using a Mettler Toledo Star Thermal Analysis System/DSC 822. The differential scanning calorimeter (DSC) system was calibrated with 3 mg indium samples under a nitrogen atmosphere. X-ray diffraction measurements (XRD) (Cu-K_α radiation) were performed using a Bruker Advanced D8 diffractometer at room temperature. Raman spectra were recorded with a Triplemate, SPEX spectrometer equipped with CCD detector in back-scattering geometry. The 488 nm, 20 mW line of an Ar-laser was used for the spectral excitation.

Spectroscopic ellipsometric measurements were used for the measurements of the thickness of films deposited on Si(100) substrates using a Woolam *M-2000VTM* rotating analyser spectroscopic ellipsometer in the spectral range of 400-800 nm. The surface morphology of the films was investigated by AFM using Nanoscope IIIa multimode atomic force microscope.

2.3. General procedure for the preparation of the CuPcs (4a-4c)

CuPcs (**4a-c**) were prepared by using the method described for **4d** in our previous paper [34]: Corresponding monosubstituted phthalonitrile (**1a-c**) and anhydrous PbO were stirred at 210 °C for 5 h under Ar atmosphere in solvent-free conditions. The reaction mixture was then dissolved in dichloromethane:acetic acid (3:1) mixture to remove lead metal ion from the cavity and the corresponding metal-free derivatives were obtained. This acidic mixture was extracted with water and organic phase was dried over anhydrous sodium sulfate. The formation of metal-free derivative was confirmed by UV-Vis spectroscopy by the observation of split Q-band of these Pcs. Metal-free derivatives of tetra-substituted phthalocyanines (**3a-c**) were refluxed under an

argon atmosphere with excess of anhydrous CuCl_2 in anhydrous n-hexanol for 2 hours and the reaction mixtures of **3a-c** were poured into ethanol. The precipitates were filtered and washed with ethanol. The crude products were purified using column chromatography over silica gel by using dichloromethane:ethanol (50:1) mixture for **4a** and **4c**; dichloromethane:hexane (50:1) mixture for **4b** as eluents.

2.3.1. 2(3),9(10),16(17),23(24)-Tetrakis(*n*-octyloxy) phthalocyaninato copper (II) (**4a**)

4a was prepared by the procedure described above by starting with 4-(*n*-octyloxy) phthalonitrile (**1a**) (0.50 g, 1.95 mmol) and anhydrous PbO (0.218 g, 0.97 mmol) to obtain PbPc **2a** as intermediate. This PbPc derivative was converted to the corresponding metal free derivative **3a** (130 mg, 0.08 mmol) by the treatment of acetic acid. Then this metal free phthalocyanine **3a** was refluxed in anhydrous n-hexanol (2 mL) with anhydrous CuCl_2 (20 mg, 0.16 mmol) to obtain CuPc **4a** in a good yield of 84%. IR [(ATR) $\nu_{\text{max}}/\text{cm}^{-1}$]: 3078 (Aromatic-CH), 2918-2850 (Aliphatic-CH), 1609 (C=C), 1508, 1487, 1464, 1389, 1344, 1259, 1241, 1095 (C-O-C), 1055, 1017. UV-Vis (THF): λ_{max} nm (log ϵ) 340 (5.17), 612 (4.86), 677 (5.48). MALDI-TOF-MS m/z : Calcd. for: $\text{C}_{64}\text{H}_{80}\text{CuN}_8\text{O}_4$: 1088.94, found 1090.09 $[\text{M}+\text{H}]^+$ (100). Calcd. for $\text{C}_{64}\text{H}_{80}\text{CuN}_8\text{O}_4$: C% 70.59, H% 7.40, N% 10.29; Found: C% 70.53, H% 7.73, N% 9.79.

2.3.2. 2(3),9(10),16(17),23(24)-Tetrakis(*n*-hexadecyloxy) phthalocyaninato copper (II) (**4b**)

4b was prepared by the procedure described for the synthesis of **4a** by starting with 4-(*n*-hexadecyloxy) phthalonitrile (**1b**) (0.50 g, 1.36 mmol) and anhydrous PbO (0.151 g, 0.68 mmol) to obtain PbPc **2b** as intermediate. This PbPc derivative was converted to the corresponding metal free derivative **3b** (180 mg, 0.12 mmol) by the treatment of acetic acid. Then this metal free phthalocyanine **3a** was refluxed in anhydrous n-hexanol (2 mL) with anhydrous CuCl_2 (20 mg, 0.16 mmol) to obtain CuPc **4b** in a good yield of 81%. IR [(ATR) $\nu_{\text{max}}/\text{cm}^{-1}$]: 3059 (Aromatic-CH), 2922-2862 (Aliphatic-CH), 1594 (C=C), 1570, 1498, 1465, 1391, 1312, 1262,

1232, 1150, 1109 (C-O-C), 1044. UV-Vis (THF): λ_{\max} nm (log ϵ) 342 (5.30), 611 (5.00), 677 (5.60). MALDI-TOF-MS m/z: Calcd. for: $C_{96}H_{144}CuN_8O_4$: 1537.80, found 1537.88 $[M]^+$ (100). Calcd. for $C_{96}H_{144}CuN_8O_4$: C% 74.98, H% 9.44, N% 7.29; Found: C% 74.80, H% 8.77, N% 6.93.

2.3.4. 2(3),9(10),16(17),23(24)-Tetrakis(*n*-octylthio) phthalocyaninato copper(II) (4c)

4c was prepared by the procedure described for the synthesis of **4a** by starting with 4-(*n*-octylthio) phthalonitrile (**1c**) (0.50 g, 1.83 mmol) and anhydrous PbO (0.140 g, 0.61 mmol) to obtain PbPc **2c** as intermediate. This PbPc derivative was converted to the corresponding metal free derivative **3c** (200 mg, 0.18 mmol) by the treatment of acetic acid. Then this metal free phthalocyanine **3a** was refluxed in anhydrous *n*-hexanol (2 mL) with anhydrous $CuCl_2$ (48 mg, 0.36 mmol) to obtain CuPc **4c** in a good yield of 89%. IR [(ATR) ν_{\max}/cm^{-1}]: 3066 (Aromatic-CH), 2953-2852 (Aliphatic-CH), 1601 (C=C), 1507, 1442, 1388, 1340, 1310, 1260, 1197, 1143, 1102, 1070, 1086 (C-S-C), 1037. UV-Vis (THF): λ_{\max} nm (log ϵ) 343 (5.07), 628 (4.98), 694 (5.42). MALDI-TOF-MS m/z: Calcd. for: $C_{64}H_{80}CuN_8S_4$: 1153.20, found 1153.53 $[M]^+$ (100). Calcd. for $C_{64}H_{80}CuN_8S_4$: C% 66.66, H% 6.99, N% 9.72; Found: C% 66.44, H% 7.18, N% 8.82.

2.4. Preparation and characterization of thin films

Small volumes (10 μ l) of copper phthalocyanine solutions in dichloromethane (5×10^{-3} g/cm³) were dispensed by a glass pipette onto an ultrasonically cleaned substrate held on a photoresist spinner. The substrate was rotated for 60 s at a speed 2000 rpm. The solvent was evaporated upon rotation and thin films of the species were prepared. The substrates were varied according to the experimental requirements.

2.5. Study of the sensor properties

To test their electrical resistance, the copper(II) phthalocyanine films were spun onto glass substrates with deposited interdigitated Pt electrodes (DropSens, G-IDEPT10). The dimension of gaps is 10 μm ; the number of digits is 125 x 2 with a digit length equal to 6760 μm ; the cell constant is 0.0118 cm^{-1} . The resistance of the CuPc films was measured with Keithley 236 electrometer by applying a constant dc voltage (10 V).

The samples were placed in a homemade measurement cell 40 mL in volume, through which a gas was passed. A cylinder of NH_3 was used as the source of gas, while a cylinder of air was used as the dilution and carrier-gas source. The concentration of ammonia was adjusted by mixing with the carrier gas using computer driven mass flow controllers. Before starting any measurements, CuPc films were held for 10 min under air flow until the resistance reached a steady state value. NH_3 gas (10-50 ppm) was then diluted with air and injected into the measurement cell. All gas sensing measurements were carried out at the temperature of 22 $^\circ\text{C}$. For humidity measurements, the wet carrier gas was prepared by bubbling the carrier gas through distilled water. The relative humidity (RH) inside the measurement cell was controlled with a commercially available humidity meter (MPE-202.013).

3. Results and Discussion

3.1. Synthesis

Monosubstituted phthalonitriles (**1a-f**) were synthesized by nucleophilic substitution reaction of 4-nitrophthalonitrile with alkylthiols or alcohols in the presence of K_2CO_3 in DMF at room temperature under an argon atmosphere. However, phthalonitrile **1b** was synthesized by heating the reaction mixture at 80 $^\circ\text{C}$ due to the low solubility of hexadecanol in DMF.

Generally, CuPcs can be obtained either by cyclotetramerization of phthalonitriles in the presence of copper salt [35] or *via* insertion of the Cu(II) metal ion into the cavity of the corresponding metal-free derivatives which can be prepared by establishing lithium pentanolate procedure [37] or *via* demetallization of the corresponding Pb(II) derivative [34]. In this work,

the alkyloxy and alkylthio substituted CuPcs (**4a-c**) were prepared by inserting Cu(II) metal ion into metal free derivatives (**3a-c**) which were prepared *via* demetallization of Pb(II) phthalocyanine analogues (**2a-c**) (Fig. 1). The synthesis of **4c** was previously reported but it was prepared by different method in this study [37, 38]. CuPcs (**4a-c**) were characterized by using UV-Vis, FT-IR and MALDI-TOF mass spectroscopic techniques as well as elemental analysis. The obtained data were in agreement with the theoretically expected values for all studied CuPcs and in the case of reported values for **4c** [37].

3.2. Mesomorphism

The thermotropic mesomorphism behaviors of CuPcs (**4a-f**) were investigated by POM, TGA, DSC, and XRD at room temperature. All these phthalocyanines displayed thermotropic columnar (Col) mesomorphism. POM measurements showed no changes of the birefringent textures upon heating from 25 to 300°C. Liquid crystalline textures typical for columnar discotic mesophases were observed for all CuPcs derivatives (Fig. 2). Optically visible decomposition could not be seen during POM investigations of all CuPcs.

Decomposition temperatures were independently determined by TGA at a heating rate of 10°C min⁻¹ in a nitrogen flow. For oxygen linked CuPcs **4a**, **4b** and **4e**, the start of weight loss values were observed at 320°C, 300°C and 350°C, respectively, whereas those values were observed at 250°C, 270°C and 250°C for sulphur linked CuPcs **4c**, **4d** and **4f**, respectively, suggesting that the S-alkyl bond breaks more easily than the O-alkyl bond.

DSC measurements revealed that melting transitions for all CuPcs (**4a-f**) took place in their first heating run (Figs. S1-S6). The melting transitions of **4c** and **4f** are broad in their first heating run and crystallisation is suppressed at studied cooling rate of 10°Cmin⁻¹ in their first cooling run (Figs. S3 and S6). Second heating-cooling cycle of **4c** and **4f** gave no transitions confirming that these two CuPc derivatives remain at liquid crystalline phase in a large temperature range from -30°C and to their decomposition temperatures including room temperature as well. Broad bands

in the first heating cycle of the DSC curve of **4a** suggest additional thermal transitions between 60 and 150°C that could not be observed by POM (Fig. S1). DSC measurements showed transitions from mesophase to crystalline phase at 70.6°C for **4a**, 37.0°C for **4b**, 34.1°C for **4d** and 7°C for **4f** in their first cooling run (Figures S1, S4, S2 and S6). Additionally, **4b** showed one more transition at 19.9°C, which is attributed to crystal-crystal transition that indicates polymorphism (Fig. S2). The phase behaviors of CuPcs **4a-f** were summarized in Table 1.

The identification of mesophases was performed by XRD measurements (Fig. 3 and Figs. S7-S12). The XRD data are given in Table 2. In order to prepare samples for XRD, dichloromethane solutions of **4a-f** were dropped on glass slides and left at room temperature for the solvent evaporation. These drop-casted films were then heated at 150°C in an oven for 2 hours and then measured directly without cooling. The XRD patterns of **4a-f** contain reflections typical of a Col mesophase of substituted phthalocyanines. The XRD pattern of **4a** at room temperature revealed five reflections at 25.25, 13.03, 8.77, 6.61 and 5.19 Å with the reciprocal spacing ratio of 1 : 1/2 : 1/3 : 1/4 : 1/5, assigned as (001), (002), (003), (004) and (005) reflections, indicating a layered structure with lamellar ordering [39]. XRD of **4b** is scattered in many directions leading to a large band split into two distributed over a wide range instead of high intensity narrower peaks (Fig. S8). It can therefore be concluded that **4b** is amorphous in the drop casted prepared film at room temperature. **4d** is crystalline at room temperature. The XRD patterns of **4c**, **4e** and **4f** contain typical reflections of a Col mesophase. In the low angle region, **4c** gave sharp peaks with the ratio of 1 : 1/√3 : 1/√4 : 1/√7 while **4f** gave peaks with the ratio of 1 : 1/√3 : 1/√4 : 1/√7 : 1/√9. These results indicate to a 2D hexagonal lattice with disc-like molecules stacked in columns in the hexagonal arrangement for both **4c** and **4f**. Mesomorphic properties of **4c** have already been described elsewhere [37]. XRD pattern of **4e** shows two reflections which can be indexed as (11) and (20), indicating to a two-dimensional rectangular lattice with disc-like molecules stacked in columns in a rectangular arrangement. The lattice constants a and b

calculated using the equation: $1/(d_{hkl})^2 = h^2/a^2 + k^2/b^2$ and the indexation of the Col_r mesophase of **4e** is given in Table 2.

3.3. Films characterization

Thin films of the studied CuPcR₄ derivatives exhibit typical optical absorption spectra for the most of metal phthalocyanines [40]. The spectra are characterised by two bands in visible and ultraviolet spectral regions, one in the range of 650-800 nm (Q-band) and another in the range of 300-450 nm (B-band). Q-band arises from the electron transitions from highest occupied molecular orbital (HOMO) a_{1u} to the lowest unoccupied molecular orbital (LUMO) e_g. B-band is attributed to the transitions from the (HOMO) a_{2u} to the (LUMO) e_g [40]. The visible region of the spectrum of the CuPc films gives an indication of the type of molecular packing in the investigated film. It has already been shown that usually four basic types of MPc molecules arrangement are observed in spun films; these are cofacial (face-to-face), herringbone, edge-to-edge and isolated arrangements [6]. They are determined by the nature and extent of the intermolecular exciton coupling between the aromatic cores of neighboring Pc molecules [41].

It is known that films of discotic mesogens are able to self-organize spontaneously and adopt a long-range oriented structure upon their heating followed by slow cooling [7, 8]. The electronic absorption spectra of the investigated CuPc films before and after heating are given in Fig. 4. Q-bands in the spectra of as-deposited CuPc films are split giving bands at both higher and lower wavelengths relative to the Q-band in the solution phase. This indicates to the herringbone arrangement of CuPc molecules. The herringbone arrangement is typical for a number of crystalline M(II)Pcs with translationally non-equivalent molecules in the unit cell [6].

The Q-band splitting does not disappear in the spectra of the **4a**, **4b** and **4d** films after heating, confirming the persistence of herringbone arrangement. In the spectra of **4a** and **4d**, only the ratio of Q_I and Q_{II} intensities change, whereas spectrum changes are more pronounced in the case of the **4b** film. The Q-band contains two components at 617 and 688 nm in the spectrum of

the **4b** film before heating. After annealing the intensity of the Q-band at 617 nm decreases, while the shoulder at 688 nm shifts to 747 nm and its intensity increases (Fig. 4). These changes in the optical absorption spectrum of the **4b** film appear to be connected with the formation of a new phase according to the DSC measurements (Table 1).

The Q-bands in the spectra of the **4c**, **4e** and **4f** films both before and after heating are blue shifted relative to the spectra of their corresponding solution spectra. This gives clear indication to the formation of cofacial (face-to-face) arrangement of CuPc molecules in the films. It is interesting to mention that the **4c**, **4e** and **4f** derivatives tend to form ordered films with the cofacial arrangement of phthalocyanine macrocycles even without heating. This type of ordering is similar to that of the films of octaalkyl analogues which also form Col mesophases [17, 42].

Fig. 5 shows AFM images of the films of the studied CuPc derivatives. The surfaces of **4a** and **4b** consist of small elongated aggregates. The films of **4c**, **4d**, **4e** and **4f** (Fig. 5) demonstrate fibrous-like porous morphology. The rms roughness for the films is given in Table 3. The film thicknesses along with their refractive indices (n) and extinction coefficients (k) measured using spectroscopic ellipsometry are also presented in Table 3.

The Raman spectroscopy was used to characterize the preferential orientation of CuPc molecules relative to the substrate surface. The application of polarized Raman spectroscopy method for investigation of the molecular orientation of thin films has already been described elsewhere [8, 43]. This method allows to estimate the angles of molecule inclination relative to the substrate surface in the case of ordered films. The non-polarized Raman spectra of CuPc derivatives (**4a-f**) are presented in Fig. S13 (Supplementary Information). The polarized Raman spectra of **4b** and **4d** films are shown in Fig. 6 as examples. The average values of I_{ii}/I_{ij} ratios (where I_{ii} and I_{ij} are the intensities of the bands in the Raman spectra recorded in parallel (ii) and cross (ij) polarization of incident and scattered light) for each symmetry type of vibrations in the polarized spectra of the films for all CuPc derivatives are given in Table 4. The symmetry types

of vibrations were assigned by analogy with similar phthalocyanine molecules [17, 44]. The analysis of I_{ii}/I_{ij} ratios shows that the film of **4b** does not demonstrate any preferential orientation of molecules relative to the substrate surface because the values of I_{ii}/I_{ij} ratios of the bands in its Raman spectra are close to those in the spectra of its solutions. The inclination angle of CuPc macrocycles relative to the substrate surface was calculated to be $65\pm 5^\circ$ for the films of **4a** and **4d** derivatives deposited on the surface of glass slides. As was shown above that **4a** and **4d** are crystalline at room temperature. A herringbone arrangement of macrocycles inclined relative to the substrate surface is observed for a number of unsubstituted and substituted metal phthalocyanines [45, 46].

The molecule inclination angles in the films of **4c**, **4e** and **4f** derivatives were calculated to be about 90° . According to the DSC data (Table 1), **4c**, **4e** and **4f** are liquid crystalline at room temperature. It has already been shown elsewhere [7] that most LC phthalocyanines form films with random planar alignment of columns in which the molecules are oriented perpendicular to the substrate surface with air constituting the upper interface but azimuthally disordered.

3.4. Comparative study of the sensor properties of CuPc films

The sensor properties of CuPc films were studied by the measurement of conductivity change upon interaction with ammonia. The conductivities of **4a-f** films deposited onto the interdigitated electrode structures were measured in the direction parallel to the films plane; the results are summarized in Table 3. The lateral conductivity tends to decrease with the increase of chain length (films **4a** and **4b**; **4c** and **4d**) similar to the films of phthalocyanine molecules described by other researchers [17, 47].

The conductivity of alkylthio-substituted phthalocyanines (**4c**, **4d** and **4f**) measured in dry air is higher in comparison with their alkyloxy-substituted analogues (**4a**, **4b** and **4e**) (Table 3). This effect was explained by Ban *et al.* [48] where the larger sulphur atom bridging the alkyl chains to the macrocycle hinders the structural disorder in the molecular stacks during the melting of the

hydrocarbon chains upon transition from crystalline to mesophase and therefore enhances the electron mobility of charge carriers.

The sensor response of CuPc films was determined after alternation of NH₃ exposure and recovery periods. Air was allowed to flow through the test chamber until the resistance reached a steady state value, and then the valves of the chamber were closed and NH₃ gas (10-50 ppm) diluted with air was injected into the measurement cell. The resistance was recorded during a period of time sufficient to obtain a saturated current reading and the response time of the sensor was calculated. The test chamber was then opened and purged with air flow. A typical response curve of the film of **4c** to ammonia gas at concentrations of 10-50 ppm is given in Fig. 7(a) as an example.

The resistance of the sensing film has increased as a result of exposure to NH₃ due to the adsorption of the electron donating ammonia molecules on the CuPc causing a charge transfer between the phthalocyanine and the analyte molecules. The result clearly demonstrates that all investigated CuPc films exhibit p-type conductivity.

To evaluate the sensor performance at different humidity, the measurements were repeated in the same way, but with the gas mixture with relative humidity (RH) of 50 and 75%. The response curves of the film of **4c** and **4f** to ammonia gas at the concentration of 30 ppm, measured at room temperature (298 K) and at different RH are given in Figs. 7(b) and 7(c) as examples. The initial conductivity of all investigated films increases with the increase of RH. Fig. 7(b) shows that the sensor response of **4c** to NH₃ gas decreases by about 1.4 times with increasing RH from 0 to 50%. Similar behavior is observed for the films of all derivatives bearing alkyloxy- (**4a**, **4b**) and alkylthio- (**4c**, **4d**) substituents. CuPc **4e** and **4f** bearing polyoxo -O(CH₂CH₂O)₃CH₃ and -S(CH₂CH₂O)₃CH₃ substituents exhibit stronger dependence on humidity and the decrease in their sensor response is much larger than in the case of **4a**, **4b**, **4c** and **4d** films (Fig. 7(c)). The higher sensitivity of CuPcs with poly(oxyethylene) substituents to humidity can be explained by their hydrophilic character. The main reason for the decrease in sensitivity to ammonia gas

appears to be a competitive sorption of ammonia and water molecules on the surface of the sensing layer.

The normalised sensor responses R_n ($R_n = (R - R_0)/R_0$; where R_0 is the resistance value at the start of an exposure/recovery cycle and R is the resistance of the CuPc film at a certain NH_3 concentration) of the films of all investigated CuPc derivatives towards NH_3 at different concentrations, measured at RH 50% are depicted in Fig. 8 as examples. The deviations shown on the graphs were estimated taking into account the measurements of 5 different samples of the films of each CuPc derivative. It is noteworthy to mention that for the series of the sensing measurements carried out here the procedure of films preparation should be strictly controlled in order to obtain films with reproducible thickness. The concentration of the solutions (5×10^{-3} g/cm³), the rotation time (60 s) and spin speed (2000 rpm) were the same for all prepared films. The variation in film thickness of the different samples of the same CuPc derivative was no more than 3 nm. The obtained results show that the response values for the different CuPc derivatives, measured at RH 0% and 50% vary in the following order: **4f** > **4e** > **4c** > **4a** > **4d** > **4b**. It is worth mentioning that this order slightly changes if the RH increases to 75% with **4c** ~ **4f** > **4e** > **4a** > **4d** > **4b**. The normalised sensor responses of **4c** and **4f** films versus NH_3 concentration, measured at RH 0, 50 and 75% are shown in Fig. 9. It is seen from the graphs that **4f** films still exhibit sensor response to ammonia at RH 75% but the value of their sensor response becomes lower than that of **4c** film measured at the same RH.

In general CuPc derivatives with alkylthio- ($-\text{S}(\text{CH}_2)_n\text{CH}_3$, $n=7$ and 15) and alkyloxy- ($-\text{O}(\text{CH}_2)_n\text{CH}_3$, $n=7$ and 15) substituents exhibit lower sensor response compared to those with polyoxo- ($-\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$ and $-\text{S}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$) substituents (Fig. 8). The sensor response tends to decrease with the increase of the chain length. This can be explained by the hydrophobic nature of alkylthio and alkyloxy substituents, which prevents the penetration of polar NH_3 molecules to reach the metal center of the phthalocyanine molecule. Film morphologies as well as molecules ordering in the film are other factors that influence the sensor

response. As it has already been stated earlier, the **4f**, **4e** and **4c** derivatives are liquid crystalline at room temperature (Table 1) and their films exhibit planar alignment.

The response and recovery times of all sensor layers are given in Table 5 for comparison. The films of **4f** and **4e** demonstrate faster response with the response time about 15 s at NH_3 concentration of 30 ppm, while the response times of **4a**, **4b**, **4c**, **4d** films are longer and vary from 35 to 55 s (Table 5). The recovery time of **4f** and **4e** films is also smaller than that of the films of CuPc derivatives with alkyl substituents. The humidity level practically does not influence the response and recovery times of the investigated sensing layers.

Using DFT calculations and spectral investigation, it has been shown that ammonia and amines interacts with the central metal ion inside the phthalocyanine ring and preferably forms a five-coordinated complex with MPcs with charge transfer to phthalocyanine molecule [49-52]. The electron charge transfers from electron donor NH_3 molecule to MPc resulting in a decrease of the holes density, hence causing a marked increase in the film's resistance [53]. Discotic liquid crystalline materials form more ordered and more efficient π - π molecular orbital overlap within columnar stacks that produces higher charge-carrier mobilities [54, 55]. Therefore in the case of LC **4f**, **4e** and **4c** phthalocyanine derivatives the charge can more favorably travel within the stack, resulting in a large and fast variation of the resistance.

Moreover, in a previous publication a comparison between the sensor properties of the ordered and disordered films [56] has shown that the ordered films demonstrate better sensor response to volatile organic compounds. Thin films of magnesium 5,10,15,20-tetraphenyl porphyrin (MgTPP) produced by spin coating subjected to slow heat treatment up to 280°C have shown improved molecular ordering with enhanced π - π interactions. The improved film structure was shown to exhibit better response to VOCs in comparison to the non-annealed MgTPP film [57].

Chemiresistive sensor response towards ammonia of several metal phthalocyanine and porphyrin species has been widely reported in the literature [15, 58, 59]. A comparison of the sensing characteristics of various phthalocyanine-based sensors shows that gas sensors based on CuPc layers investigated in the present work demonstrate response and recovery times about two times lower than those for films of unsubstituted metal phthalocyanines deposited on flexible biaxially oriented polyethylene terephthalate substrates [60] and spin-coated films of CuPc bearing shorter *t*-Bu [61] as well as iso-pentyloxyphthalocyanine substituents [15]. A slightly less recovery time of 47 s was observed for films of tetrafluorosubstituted cobalt phthalocyanine bearing electron withdrawing fluorine substituents [51] and for the advanced hybrid materials of pyrene substituted phthalocyanines with single-walled carbon nanotubes [62].

4. Conclusion

Copper(II) phthalocyanines substituted with alkylthio- ($-\text{S}(\text{CH}_2)_n\text{CH}_3$, $n=7$ and 15), alkyloxy- ($-\text{O}(\text{CH}_2)_n\text{CH}_3$, $n=7$ and 15) and polyoxo- ($-\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$ and $-\text{S}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$) substituents were investigated to reveal the effect of substituents type and the heteroatom connecting the substituents to the aromatic core on the mesogenic properties, films alignment and sensor performance of thin films of these derivatives. The sensing performance was studied against low-concentrations of NH_3 (10-50 ppm) by measuring changes in the films' conductivity at different humidity. All investigated CuPc films display thermotropic columnar mesomorphism. It was shown that the films of CuPc derivatives with polyoxo- ($-\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$) and ($-\text{S}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$) substituents as well as with alkylthio- $-\text{S}(\text{CH}_2)_n\text{CH}_3$ ($n=7$) substituents which are liquid crystalline at room temperature and they form ordered films with a random planar alignment of columns in which the molecules are oriented perpendicular to the surface of the substrate. They exhibited good sensing performance with the maximal sensor response for the films of CuPc derivative bearing $-\text{S}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$ substituents.

The other three CuPc derivatives substituted with alkylthio- ($-\text{S}(\text{CH}_2)_n\text{CH}_3$, $n=15$) and alkyloxy- ($-\text{O}(\text{CH}_2)_n\text{CH}_3$, $n=7$ and 15) substituents form polycrystalline films. They exhibit the lowest sensor response compared to those with polyoxo- ($-\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$ and $-\text{S}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$) substituents. The sensor response tends to decrease with the increase of the chain length of the alkyl substituents.

The effect of humidity on the ammonia gas detection capabilities of the spin coated CuPc films has also been investigated. The results showed that the presence of water vapour leads to the lowering of the NH_3 response of the sensors in humid atmosphere. It is necessary to mention that CuPcs bearing hydrophilic polyoxo- ($-\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$ and $-\text{S}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$) substituents exhibit stronger dependence on humidity and the decrease of their sensor response is much stronger than in the case of derivatives with alkylthio and alkyloxy substituents.

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Table 1. Phase transition temperatures, [corresponding enthalpy changes in parentheses] of CuPc complexes (**4a-f**) determined by DSC for the first heating/cooling cycle. Heating and cooling rates: 10 °C min⁻¹, Phase nomenclature: Cr: crystal phase, Cr_L: crystalline lamellar phase, Col_h: hexagonal columnar mesophase, Col_r: rectangular columnar phase, dec: initial decomposition.

CuPc	T (°C) [ΔH (kJ mol ⁻¹)]
4a	$\text{Cr}_L \xrightleftharpoons[70.6 [6.4]]{57.6 [-2.9]} \text{Col}_h \xrightarrow{> 320} \text{dec}$
4b	$\begin{array}{ccc} \text{Cr} & \xrightarrow{41.8 [-15.1]} & \text{Col}_h \xrightarrow{> 300} \text{dec} \\ & & \downarrow 37.0 [2.9] \\ & & \text{Cr}_y \\ & \xleftarrow{19.9 [3.8]} & \text{Cr}_x \end{array}$
4c	$\text{Cr} \xrightleftharpoons[-]{53.4 [-23.0]} \text{Col}_h \xrightarrow{> 250} \text{dec}$
4d	$\text{Cr} \xrightleftharpoons[34.1 [48.0]]{51.0 [-72.0]} \text{Col}_h \xrightarrow{> 270} \text{dec}$
4e	$\text{Cr} \xrightleftharpoons[7.0 [10.5]]{83.0 [-19.5]} \text{Col}_r \xrightarrow{> 350} \text{dec}$
4f	$\text{Cr} \xrightleftharpoons[-]{58.1 [-27.79]} \text{Col}_h \xrightarrow{> 250} \text{dec}$

Table 2. XRD data for Cu(II)Pc complexes (**4a-f**) at room temperature.

Compound	Observed spacings, Å	Theoretical spacings, Å	Ratio	Phase & Lattice parameters	Miller Indices
4a	25.25	25.25	1	Cr _L	(001)
	13.03	12.63	2		(002)
	8.77	8.42	3		(003)
	6.61	6.31	4		(004)
	5.19	5.05	5		(005)
	4.54				
3.31					
4b	29.04(very broad) 15.94(very broad) 4.31			Amorphous	
4c	19.70	19.70	1	Col _h a: 22.75	(100)
	11.56	11.37	$\sqrt{3}$		(110)
	9.99	9.85	$\sqrt{4}$		(200)
	7.82	7.44	$\sqrt{7}$		(210)
4d	30.87			Cr	
	20.72				
	16.35				
	4.34				
	3.97				
3.33					
4e	20.07	20.07		Col _r a: 32.82 b: 25.37	(11)
	16.41	16.41			(20)
	10.20	10.05			(31)
	8.39	8.46			(03)
	6.85	6.89			(42)
5.59	5.82		(52)		
4f	19.52	19.52	1	Col _h a: 22.54	(100)
	11.48	11.27	$\sqrt{3}$		(110)
	9.97	9.76	$\sqrt{4}$		(200)
	7.60	7.38	$\sqrt{7}$		(210)
	6.71	6.50	$\sqrt{9}$		(300)

Table 3. The thicknesses, refractive indices (n), extinction coefficients (k), rms roughness and conductivity values (σ) of the CuPc (**4a-f**) films.

Sample	Film thickness, nm	Optical parameters, at $\lambda= 632.8$ nm		RMS, nm	$\sigma, \Omega^{-1} \text{ m}^{-1}$
		n	k		
4a	73.8	1.52	0.18	0.544	$1.1 \cdot 10^{-6}$
4b	57.8	1.50	0.29	1.177	$1.2 \cdot 10^{-7}$
4c	74.7	1.33	0.30	0.486	$4.8 \cdot 10^{-6}$
4d	57.4	1.57	0.32	0.463	$7.1 \cdot 10^{-7}$
4e	52.2	1.57	0.27	2.197	$2.6 \cdot 10^{-6}$
4f	53.1	1.52	0.36	2.153	$2.7 \cdot 10^{-6}$

Table 4. Measured I_{ii}/I_{ij} ratios for A_{1g} , B_{1g} and B_{2g} modes in the Raman spectra of the CuPc (**4a-f**) films and the film orientation data.

CuPc	I_{ii}/I_{ij} ratios for A_{1g} , B_{1g} and B_{2g} modes			Film orientation
	A_{1g}	B_{1g}	B_{2g}	
4a	5.1	1.4	1.4	Crystalline ordered film Inclination angle $65\pm 5^\circ$
4b	5.7	1.4	1.4	Disordered film
4c	3.5	3.3	1.2	LC ordered film Inclination angle $\sim 90^\circ$
4d	4.0	3.0	1.4	Crystalline ordered film Inclination angle $65\pm 5^\circ$
4e	3.4	3.3	1.2	LC ordered film Inclination angle $\sim 90^\circ$
4f	3.4	3.3	1.2	LC ordered film Inclination angle $\sim 90^\circ$

Table 5. Response and recovery times of the **4a-4f** films at the NH_3 concentration of 30 ppm.

Film	Response time, s.	Recovery time, s
4a	55	30
4b	35	50
4c	50	30
4d	35	45
4e	15	20
4f	15	20