Dyes and Pigments 80 (2009) 67–72

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

The synthesis and characterization of Cu(II) phthalocyanine bearing peripheral monoazacrown ethers and a spectral investigation of its film forming character

Tamara V. Basova [a],*, Irina V. Jushina [a], Ayse G. Gürek [b], Devrim Atilla [b], Vefa Ahsen [b,c]

[a] Nikolaev Institute of Inorganic Chemistry, Novosibirsk, Russia
[b] Gebze Institute of Technology, Department of Chemistry, P.O. Box 141, 41400 Gebze, Kocaeli, Turkey
[c] TUBITAK – Marmara Research Center, Materials Institute, P.O. Box 21, 41470 Gebze, Kocaeli, Turkey

ARTICLE INFO

Article history:
Received 6 March 2008
Received in revised form 20 May 2008
Accepted 20 May 2008
Available online 27 May 2008

Keywords:
Phthalocyanine
Thin film
Liquid crystal
Metallomesogen
Crown ether

ABSTRACT

The synthesis, liquid crystalline behavior and self-organizing properties of Cu(II)Pc bearing monoazacrown ether moieties that contain long alkyloxyphenyl N-pivotal groups are described. The Cu(II) phthalocyanine derivative has a hexagonal, columnar structure; optical absorption and vibrational spectroscopy revealed a predominantly co-facial interaction between the chromophores and their orientation parallel to a NaCl surface. It is proposed that such homeotropic alignment is attributable to the ability of the pendant monoazacrown ether groups to coordinate the Na^+ ions within the NaCl surface.

1. Introduction

Supramolecular structures having well-defined geometries have possible applications in diverse fields such as materials science, molecular electronics, and sensor development. Metallophthalocyanines (MPcs) have been extensively studied in the area of gas sensors [1], liquid crystals [2], organic semiconductors [3,4] and field effect transistors [5]. One of the strategies to create ordered materials originates from self-assembly of molecules, especially macromolecules with tailored architectures [6–9].

It is well understood that crown ether containing compounds can form a well-defined structure due to the specific affinity between the crown ether rings [8]. Crown ether containing phthalocyanines (Pcs) have been shown to possess a combination of three very useful properties [9], namely, they have an extended p-conjugated core which plays a key role in the charge-transfer properties of stacked Pcs, they contain crown ethers which can host alkaline ions and they possess alkyl side chains which can induce liquid crystalline behavior. Furthermore, crown ether-substituted phthalocyanines can be stacked to create ion-conducting channels [8,10–15].

Aza-crown, ether-substituted Pcs have been previously described in literature [16–19]. Different substituents have been introduced on the nitrogen atom of the aza-crown moiety to improve the solubility, liquid crystal properties as well as the intrinsic amphiphilic character of the compounds.

This paper concerns the synthesis, liquid crystalline behavior and self-organizing properties of Cu(II)Pc bearing monoazacrown ether moieties at peripheral positions that contain long alkyloxyphenyl N-pivotal group. The ability of the compound to form oriented films on NaCl was investigated using different spectroscopic methods.

2. Experimental section

2.1. Materials

4,5-Dibromo-1,2-[7-(3,4,5-tri-decyloxyphenyl-1-carbonyl)-7-aza-1,4,10,13-tetraoxatridecamethylene]-benzene (**1**) (Fig. 1) was prepared following the procedures described in literature [20]. All other reagents and solvents of reagent-grade quality were obtained from commercial suppliers, and were dried as described in Perrin and Armarego [21] before use.

---

* Corresponding author.
E-mail addresses: basova@che.nsk.su (T.V. Basova), ahsen@gyte.edu.tr, vefa.ahsen@mam.gov.tr (V. Ahsen).

0143-7208/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2008.05.002

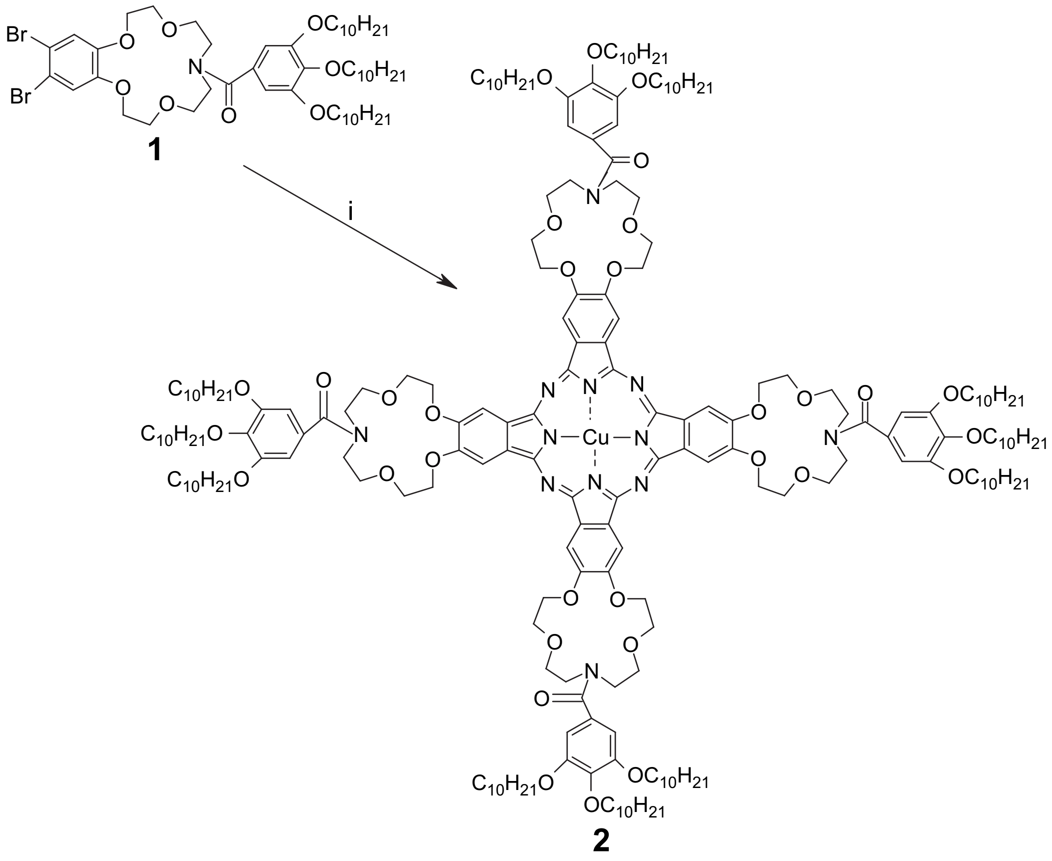

Fig. 1. Synthesis route for the preparation of the CuPc (**2**); (i) CuCN, pyridine, reflux.

2.2. Synthesis

2.2.1. 2,3;9,10;16,17;23,24-Tetrakis-[1,4,10,13-tetraoxatridecamethylene-7-aza-(3,4,5-tri-decyloxyphenyl-1-carbonyl) phthalocyaninato] copper(II) (2)

A mixture of **1** (0.73 g, 0.73 mmol), CuCN (0.20 g, 2.17 mmol), and dry pyridine (4.50 ml) was heated for 18 h under argon. The solvent was removed by vacuum distillation, the crude product was diluted with CH_2Cl_2 and filtered to remove inorganic impurities. The crude green product was then purified by column chromatography over silica gel with CH_2Cl_2. The dark green product was soluble in CH_2Cl_2 and $CHCl_3$, slightly soluble in ethyl acetate, *n*-hexane, and *n*-heptane, insoluble in ethanol, methanol, acetone, and DMF. Yield 150 mg (23%). Calc. for $C_{212}H_{332}N_{12}O_{32}Cu$ (3622) C, 70.25; H, 9.23; N, 4.64%. Found: C, 70.35; H, 9.29; N, 4.61%. IR (KBr): ν_{max} (cm^{-1}) 3054, 2924–2854 (CH_2, CH_3), 1634 (C=O), 1582 (C_{ar}=N), 1355 (C–N), 1282 (C–O–C), 1263, 1208, 1172 (C–N). MS (ES-MS), *m*/*z* (%): 3623 (60) $[M+H]^+$, 2721 (100).

2.3. Compound characterization

Elemental analysis was performed using Carlo Erba 1106 Instrument. Electrospray full scan spectra, in the range of *m*/*z* 50–2000 amu or *m*/*z* 2000–3000 amu, were obtained by infusion through fused silica tubing at 2–10 μl min^{-1}. The solutions were analyzed in the positive mode. The LCQ calibration (*m*/*z* 50–2000) was achieved according to the standard calibration procedure from the manufacturer (mixture of caffeine, MRFA and Ultramark 1621). An ES-Tuning Mix solution (Agilent) was used to calibrate the spectrometer between 2000 and 3000 amu. Matrix-assisted laser desorption/ionisation time-offlight mass spectrometry (MALDI-TOF MS) measurements were performed on a Bruker Daltonics micrOTOF (Bremen, Germany). Positive ion and linear mode MALDI-TOF-MS spectrum of compound **2** was obtained in 2,5-dihydroxy benzoic acid MALDI matrix using nitrogen laser accumulating 50 laser shots. Thermogravimetric analysis was carried out using Mettler Toledo Stare 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 Mettler Toledo Stare Thermal Analysis System/DSC 822e differential scanning calorimeter calibrated with indium from 3 to 4 mg samples under nitrogen atmosphere. Optical textures were observed with the polarizing microscope Leitz Wetzler Orthoplan-pol equipped with the hot stage Linkam TMS 93 and temperature-controller Linkam LNP.

Infrared spectra in KBr pellets were recorded using a Bio-Rad FTS 175C FT-IR spectrophotometer. Optical absorption spectra in the UV–visible region were recorded with a Schimadzu 2001 UV Pc spectrophotometer using 1 cm pathlength cuvettes at room temperature.

2.4. Film preparation and characterization

A small volume of solution of the CuPc (**2**) derivative in chloroform (5 mg/ml) was dispensed via a glass pipette onto an ultrasonically cleaned substrate held onto photoresist spinner (Microsystem model 4000). The speed of substrate rotation was 2000 rpm. Spinning was continued for 30 s during which time the solvent had evaporated to generate a film of the phthalocyanine derivative. Some films were heated to 322 °C in nitrogen atmosphere and then allowed to cool down at the rate of 5 °C min^{-1} to room temperature for comparison with as-deposited layers. The heating temperature was carefully controlled, so that the value should not exceed decomposition temperature (325 °C). Thin NaCl plates were used as substrates.

The thickness of deposited films was measured by ellipsometry. Spectroscopic ellipsometric measurements on the films on silicon substrates were performed by using a Woolam M-2000V™ rotating analyser spectroscopic ellipsometer in the spectral range of 400–800 nm.

Electronic absorption spectra of the films on quartz and NaCl substrates were recorded with a UV–VIS–NIR scanning spectrophotometer (UV–VIS-3101PC "Shimadzu") in the range from 400 to 900 nm. Polarized spectra in which the incident angle of the light beam was at 90° and 45° to the substrate, were recorded by using a gold wire grid polarizer and a goniometer. Excitation is called p-polarized when the electric field component of the incoming radiation is in the plane defined by the surface normal and the excitation direction. That is, there is a component of the electrical field normal to the sample surface. On the other hand, s-polarized excitation is defined when the electrical field is parallel to the surface of the sample.

Infrared spectra of CuPc (**2**) powder in NaCl pellets and its films on NaCl substrates were recorded using a Vertex 80 FTIR spectrometer.

Raman spectra were recorded with a Triplemate, SPEX spectrometer equipped with CCD detector in back-scattering geometry. The 488 nm, 40 mW line of an Ar-laser was used for the spectral excitation.

3. Results and discussion

3.1. Synthesis and general properties

The starting compound 4,5-dibromo-1,2-[7-(3,4,5-tridecyloxyphenyl-1-carbonyl)-7-aza-1,4,10,13-tetraoxatridecamethylene]-benzene (**1**) was obtained as described in literature [20]. Dibromo compound (**1**) was treated with CuCN in dry pyridine at reflux temperature to prepare the copper phthalocyanine derivative (**2**). The synthesis route is shown in Fig. 1.

Spectral investigation of the newly synthesized intermediates and Pcs are in accordance with the proposed structures. In the IR spectrum of CuPc (**2**), CH_2, CH_3 groups give rise to absorptions at 2924, 2854 cm^{-1} and amidic C=O group stretched around 1634 cm^{-1}. The investigation of the mass spectrum of the CuPc (**2**) confirmed the proposed structure. The mass spectra of **2** were obtained by means of two different techniques: Electron Spray (ES) and MALDI-TOF MS. The protonated molecular ion peaks were observed, respectively, at 3623 $[M+H]^+$ and 3636.92 $[M+4H]^+$. In the electronic absorption spectrum of the CuPc (**2**) solution in chloroform, intense Q absorption band was observed at 676 nm with a weaker absorption at 620 nm. The weaker absorptions on the higher energy side of Q bands are generally observed in the case of metallophthalocyanines, indicating the presence of aggregated species together with the monomeric ones which are essentially responsible for the intense absorption occurring in the main Q bands [22]. B band in the CuPc (**2**) spectrum was observed at 345 nm.

3.2. Characterization of the mesophase

The phase transition behavior of CuPc (**2**) was determined by differential scanning calorimetry (DSC) as well as by polarizing microscopic observations. The DSC measurement of **2** shows a broad peak at about 100 °C for the first heating cycle ($\Delta H = 12.64$ kJ/mol). The cooling cycle shows a broad peak at about 90 °C ($\Delta H = 13.30$ kJ/mol). The heating cycles were interrupted before reaching a clearing point to avoid decomposition. Decomposition temperature of the CuPc (**2**) is about 325–400 °C (determined by Thermal Gravimetric Analysis, TGA). We assume that the peak of **2** in the heating cycles is related to the transition from the crystalline phase to the mesophase and the peak of **2** in the cooling cycle is related to the transition from the mesophase to the crystalline phase. These investigations indicate that compound **2** exhibits a thermotropic liquid crystalline behavior above 97 °C.

The texture observed by polarizing optical microscopy for compound **2** is very similar to that obtained for other columnar mesophases described in literature [20–25]. Good mosaic texture of CuPc (**2**) mesophase was obtained by slow cooling, at the rate of 5 °C min^{-1}, from the isotropic melt. Temperature of the phase transition of **2** from mesophase to isotropic liquid is 322 °C. The texture of compound **2** under polarizing optical microscopy at 130 °C is presented in Fig. 2.

3.3. Spectral characterization of the films

It has already been shown that the thermal treatment of phthalocyanine films at temperatures higher that the temperature of phase transition to liquid crystalline phase for several hours or slow cooling from the isotropic melt leads to the formation of films with ordered structure [26–28].

To obtain the ordered structure, the CuPc (**2**) spun films were slowly cooled (5 °C min^{-1}) from the isotropic melt (322 °C). The thickness of the CuPc (**2**) film spun onto NaCl substrate, determined by ellipsometry was 18 nm, the index of refraction and extinction coefficient at 633 nm were 1.52 and 0.16, respectively.

The UV–visible spectra of the CuPc (**2**) film on NaCl and its solution in chloroform are shown in Fig. 3. The characteristic absorption peak observed in CuPc (**2**) solution at approximately 676 nm has been assigned to π–π^* transition and shows that monomers dominate in chloroform solutions. In the case of the films, a peak around 620 nm has been enhanced, indicating the occurrence of co-facial molecular aggregation in the film structure [29]. It is necessary to mention that co-facial molecular organization is observed not only for films subjected to heat-treatment but also for unheated films.

In order to study the orientation of CuPc (**2**) macrocycles in the film, the phthalocyanine ring is considered as a flat circular plate on which π–π^* transition dipole is uniformly distributed according to Yoneyama and co-workers [30]. Polarized UV–visible spectroscopy technique was used for the investigation of phthalocyanine films in a number of publications [31–33].

The polarized visible absorption spectra of CuPc (**2**) film are presented in Fig. 4. The absorbance of the p-polarized spectrum of

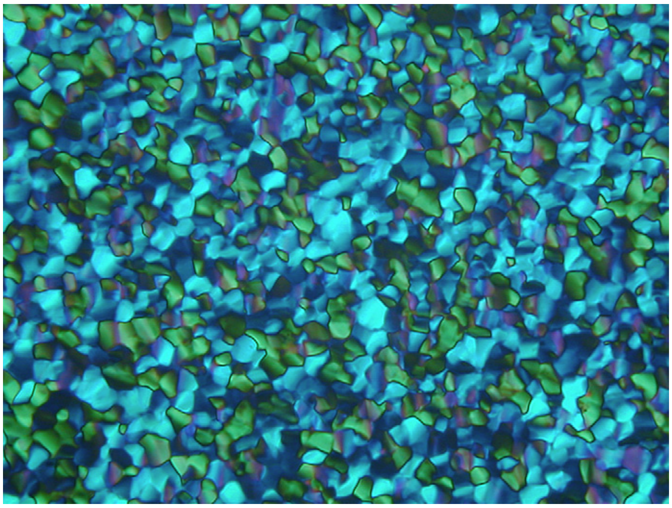

Fig. 2. Optical texture of the CuPc (**2**) observed at 130 °C (magnification 16×).

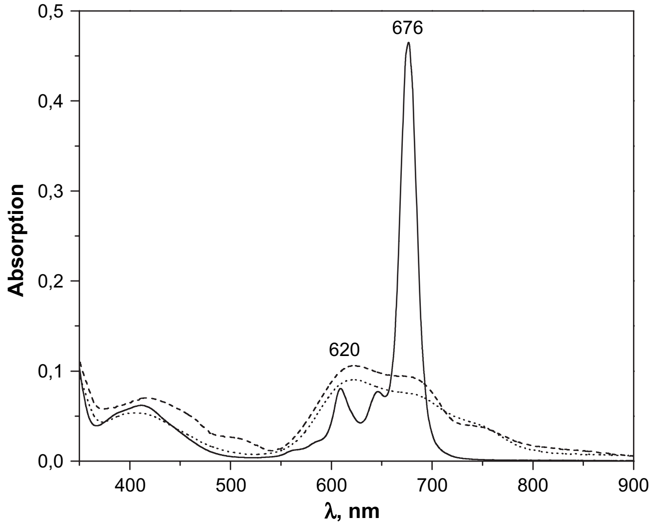

Fig. 3. Visible absorption spectra for the CuPc (**2**) solution in chloroform (solid line), film on NaCl substrate before (broken line) and after heating (dotted line).

Table 1
Vibrational assignments of the absorption modes in IR spectrum of the CuPc (**2**) derivative

Frequency, cm^{-1}	Assignment
3076	Aromatic ν (CH)
2957	ν_{as} (CH_3)
2923	ν_{as} (CH_2)
2874	ν_s (CH_3)
2852	ν_s (CH_2)
1636	Amidic C=O stretching
1607	Benzene C=C stretching
1582	Ring stretching (C–C + C–N)
1508	Pyrrole stretching
1482	Ring stretching
1468	δ (CH_2)
1458	δ_{as} (CH_3) + in-plane pyrrole stretching
1421	In-plane pyrrole stretching
1388	δ_s (CH_3)
1353	Isoindole stretching
1333	C–H bending
1281	C–O stretching
1210	C–N stretching
1108	C–O in azacrown + in-plane C–H deformation
1068	In-plane C–H deformation
1035	Skeletal mode of central ring
935	Benzene wagging
855	Benzene wagging
803	Macrocycle deformation
745	Out-of-plane C–H deformation
737	Out-of-plane C–H deformation
720	Out-of-plane C–H deformation + out-of-plane ring deformation
671	Pc breathing

the film with the angle of incidence of 45° is significantly weakened in comparison with those observed at normal incidence and the s-polarized spectrum at 45°. Similar behavior was observed for multilayers of the other phthalocyanine derivatives [34]. These data indicate that the phthalocyanine macrocycles are oriented nearly parallel to the substrate surface.

The vibrational spectroscopies (IR and Raman) were used to confirm the preferential orientation of molecules relative to the substrate surface. The experimental frequencies in the IR spectra and assignments for the normal modes of CuPc (**2**) derivative are listed in Table 1. The IR spectra of CuPc (**2**) powder in NaCl pellet and the film deposited on NaCl surface are presented in Fig. 5. The assignment of the vibrations was made on the basis of comparison with the vibrational spectra of other unsubstituted [35,36] and substituted phthalocyanines [37,38].

A comparison of the relative intensities of in-plane and out-of-plane modes in the IR spectra of NaCl pellet and films indicates the molecular organization and preferential orientation of molecules in the film. In the NaCl pellet there exists a random distribution of phthalocyanine molecules with no preferred orientation. Transition dipoles parallel to the substrate surface are only observed in a normal incidence transmission spectrum.

The IR spectrum of CuPc (**2**) derivative is obscured by the overlap between the modes belonging to the phthalocyanine ring and those of the substituents; some bands, however, can provide good reference for the investigation of film orientation. The significant difference between the spectra of the pellet and those of the film is due to the C–H out-of-plane deformation modes in the range from 745 to 720 cm^{-1} (see Fig. 5 and Table 1). The intensity endures a significant reduction in the film spectrum, meanwhile the in-plane C–H deformation modes (1108 cm^{-1}) and in-plane pyrrole stretching modes (1421 and 1458 cm^{-1}) become more

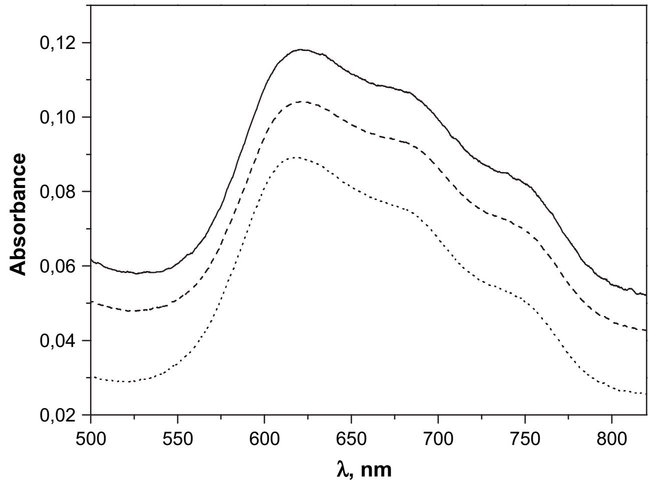

Fig. 4. Polarized visible absorption spectra for the CuPc (**2**) film: s-polarized spectrum at 45° incidence (solid line), p-polarized spectrum at normal (broken line) and 45° (dotted line) incidence.

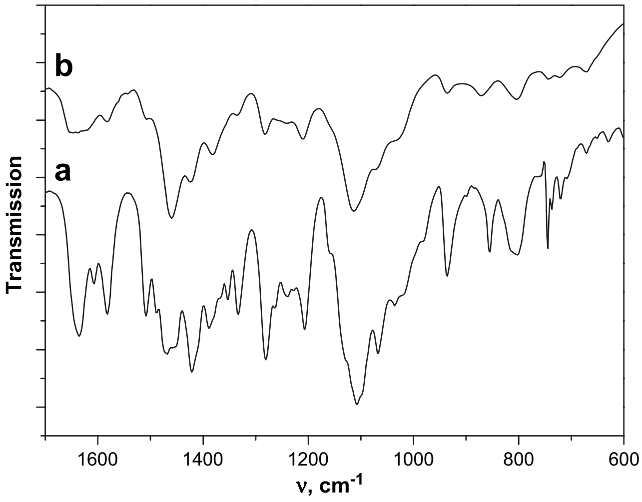

Fig. 5. (a) IR spectrum of the CuPc (**2**) in a NaCl pellet; (b) IR spectrum of the CuPc (**2**) film on NaCl surface.

prominent. These features, where the in-plane modes in the transmission spectrum are clearly enhanced, correlate with an average preferential flat-on orientation of the CuPc (**2**) molecules on the NaCl substrate.

It has already been established that no intensive bands in the range 300–1650 cm^{-1}, belonging to the organic substituents, were observed in Raman spectra of substituted phthalocyanines, due to the resonance nature of the Raman spectra excited by a laser beam in the visible region [39]. Thus, all bands in the Raman spectrum belong to the bending and stretching vibrations of the phthalocyanine macrocycle.

The polarized Raman spectra may also be used for the investigation of films' orientation. The dependence of measured intensities on the angle of incidence and beam polarization were used to probe the preferred molecular orientation of phthalocyanine thin films [40–42]. The principles of this approach were also described in detail in earlier publications [28,39,43].

A phthalocyanine molecule is characterized by D_{4h} group symmetry where A_{1g}, B_{1g}, B_{2g}, E_g modes are Raman active [44,45]. The determination of the symmetry types of all observed modes was made on the basis of the polarized spectra of CuPc solution in $CHCl_3$ and by analogy with Raman spectra of metal phthalocyanines with other substituents [28,46].

The symmetry types of the most intensive bands used for the determination of film orientation are indicated in Fig. 6. For the determination of molecules' orientation, it is necessary to derive the analytical expression of the components of Raman tensors for various types of molecule orientation. The detailed analysis of the Raman tensors for D_{4h} symmetry group and the determination of the molecular orientation are described in an earlier publication [43]. It is necessary to identify the I_{ii}/I_{ij} ratios of each symmetry type of vibration because the Raman intensities are proportional to the square of matrix elements. I_{ii}/I_{ij} is the ratio of average Raman intensities in parallel (I_{ii}) and cross (I_{ij}) polarizations of incident and scattered light.

The Raman spectra of the films of CuPc in parallel (*ii*) and cross (*ij*) polarizations are shown in Fig. 6. The intensities of the strongest lines with known symmetry types are measured. The average values of I_{ii}/I_{ij} ratios for each symmetry type of vibration are listed in Table 2. Knowing the experimental I_{ii}/I_{ij} ratio for A_{1g}, B_{1g} and B_{2g} modes, the α and β angles of molecule inclination relative to the substrate surface may be derived. The inclination angles are close to zero, which clearly indicates that the molecules are practically oriented parallel to the substrate surface.

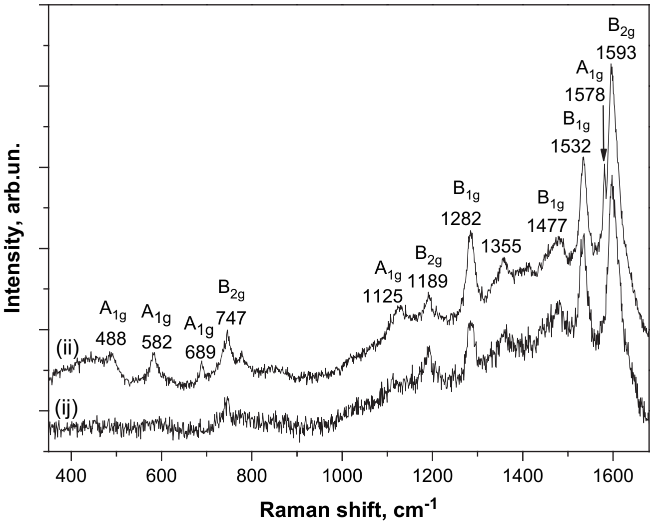

Fig. 6. Polarized Raman spectra of the CuPc (**2**) films in parallel (*ii*) and cross (*ij*) polarizations of incident and scattered light.

Table 2
Measured I_{ii}/I_{ij} ratios for A_{1g}, B_{1g} and B_{2g} modes in the Raman spectra of the CuPc (**2**) film on NaCl and calculated angles of molecule inclination

CuPc film	I_{ii}/I_{ij} ratios for A_{1g}, B_{1g} and B_{2g} modes			Angles, °	
	A_{1g}	B_{1g}	B_{2g}	α	β
	>10	1.0	1.0	~0	~0

Two typical alignments of the films of discotic liquid crystals are well-described as homeotropic and homogeneous alignments; in the former the disks lie horizontally on a plate while in the latter the disks stand perpendicularly on a plate. Usually, homeotropic alignment can be generated by thermal annealing; that is by slow cooling of the isotropic melt confined between two substrates [47]. Recently de Cupere and co-workers have studied the influence of the nature and number of solid interfaces on the alignment of the columns in a discotic liquid crystal [48]. However, some phthalocyanines display homeotropic alignment both for films confined between two substrates and for films deposited on one substrate. Homeotropic alignment was observed for films of crown ether-substituted phthalocyanine on the basal plane of graphite substrate [8]. Phthalocyanine derivatives of the octakis(dialkoxyphenoxy)-phthalocyaninatocopper(II) complexes forming $\mathrm{Col_{tet}}$ mesophase also exhibited spontaneous uniform homeotropic alignment on soda-lime glass and quartz plates [49]. The latter type of orientation was explained by the interaction of lone pairs of the phenoxy group in phthalocyanine derivatives with the dangling bonds of silicon atoms on the surface of glass or quartz. The first phthalocyanine disk adhered to the surface may trigger the stacking of the disks one after another.

The first monolayer of CuPc (**2**) molecules adheres to the NaCl surface due to the ability of the pendant monoazacrown ether groups to coordinate alkali ions and trigger the homeotropic alignment of molecular columns.

4. Conclusions

In the present work, the synthesis of the Cu(II) phthalocyanine with monoazacrown ether moieties on the periphery containing long alkyloxyphenyl N-pivotal group was described. The Cu(II) phthalocyanine derivative (**2**) exhibits a hexagonal columnar structure. From the optical absorption and vibrational spectroscopic studies a predominantly co-facial interaction of chromophores and their orientation parallel to the NaCl surface were concluded. It was suggested that the homeotropic alignment is due to the ability of the pendant monoazacrown ether groups to coordinate the alkali ions of the NaCl surface.

Acknowledgement

The authors wish to thank Colette Lebrun (CEA Grenoble) and Bünyemin Çoşut (Gebze Institute of Technology) for the mass spectrum. This work was financed by NATO Collaborative Linkage Grant N CBP.NR.NRCLG.983171.

References

[1] Snow AW, Barger WR. In: Leznoff CC, Lever ABP, editors. Phthalocyanines: properties and applications, vol. 1. New York: VCH; 1989. p. 341–92.
[2] Simon J, Bassou P. In: Leznoff CC, Lever ABP, editors. Phthalocyanines: properties and applications, vol. 2. New York: VCH; 1993. p. 223.
[3] Simon J, Andre J-J. In: Lehn JM, Rees CW, editors. Molecular semiconductors. Berlin: Spinger-Verlag; 1985.
[4] Simon J, Bassoul P. Design of molecular materials. Supramolecular engineering. Chichester: John Wiley & Sons, Ltd; 2000.
[5] Van de Craats AM, Stutzmann N, Bunk O, Nielsen MM, Watson M, Müllen K, et al. Adv Mater 2003;15(6):495–9.
[6] Fu J, Cong Y, Yu X, Pan C, Yang Y, Li B, et al. Polymer 2004;45(22):7389–94.

[7] Engelkamp H, Middelbeek S, Nolte RJM. Science 1999;284:785–8.
[8] van Nostrum CF, Picken SJ, Schouten A-J, Nolte RJM. J Am Chem Soc 1995; 117(40):9957–65.
[9] Samorí P, Engelkamp H, de Witte P, Rowan AE, Nolte RJM, Rabe JP. Angew Chem Int Ed 2001;113(12):2410–2.
[10] Simon J, Sirlin C. Pure Appl Chem 1989;61(9):1625–9.
[11] Koray AR, Ahsen V, Bekaroglu Ö. J Chem Soc Chem Commun 1986;12:932–3.
[12] Ahsen V, Yilmazer E, Ertaş M, Bekaroğlu Ö. J Chem Soc Dalton Trans 1988;2: 401–6.
[13] Bardin M, Bertounesque E, Plichon V, Simon J, Ahsen V, Bekaroğlu Ö. J Electroanal Chem 1989;271(1–2):173–80.
[14] Toupance T, Ahsen V, Simon J. J Am Chem Soc 1994;116(12):5352–61.
[15] Musluoğlu E, Ahsen V, Gül A, Bekaroğlu Ö. Chem Ber 1991;124(11):2531–6.
[16] Ahsen V, Gürek AG, Musluoğlu E, Gül A, Bekaroğlu Ö. Chem Ber 1989;122(6): 1073–4.
[17] Kandaz M, Bekaroğlu Ö. J Porphyrins Phthalocyanines 1999;3(5):339–45.
[18] Cabezon B, Quesada E, Esperanza S, Torres T. Eur J Org Chem 2000;15: 2767–75.
[19] Atilla D, Ahsen V. J Porphyrins Phthalocyanines 2002;6(9):593–6.
[20] Yılmaz F, Atilla D, Ahsen V. Polyhedron 2004;23(11):1931–7.
[21] Perrin DD, Armarego WLF. Purification of laboratory chemicals. Oxford: Pergamon; 1989.
[22] Stilmann MJ, Nyokong T. In: Leznoff CC, Lever ABP, editors. Phthalocyanines: properties and applications, vol. 1. New York: VCH; 1993. p. 133–290.
[23] Kroon JM, Koehorst RBM, van Dijk M, Sanders GM, Sudhölter EJR. J Mater Chem 1997;7(4):615–24.
[24] Duro JA, de la Torre G, Barbera J, Serrano JL, Torres T. Chem Mater 1996;8(5): 1061–6.
[25] Sleven J, Görller-Walrand C, Binnemans K. Mater Sci Eng C 2001;18(1–2): 229–38.
[26] Cook MJ. J Mater Chem 1996;6(5):677–89.
[27] Treacher KE, Clarkson GJ, Ali-Adib Z, McKeown NB. J Chem Soc Chem Commun 1996;(1)::73–5.
[28] Basova T, Gürek AG, Ahsen V. Mater Sci Eng C 2002;22(1):99–104.
[29] Kasha M, Rawls HR, El-Bayoumi A. Pure Appl Chem 1965;11:371–7.
[30] Yoneyama M, Sugi M, Saito M, Ikegami K, Kuroda S, Iizima S. Jpn J Appl Phys 1986;25(7):961–5.
[31] Fujiki M, Tabei H, Kurihara T. Langmuir 1988;4(5):1123–8.
[32] Pasimeni L, Meneghetti M, Rella R, Valli L, Granito C, Troisi L. Thin Solid Films 1995;265(1–2):58–65.
[33] Yan W, Zhou Y, Wang X, Chen W, Xi S. J Chem Soc Chem Commun 1992;12: 873–5.
[34] Nakahara H, Sun KZ, Fukuda K, Azuma N, Nishi H, Uchida H, et al. J Mater Chem 1995;5(3):395–9.
[35] Liu Z, Zhang X, Zhang Y, Jiang J. Spectrochim Acta A 2007;67(5):1232–46.
[36] Debe MK. J Appl Phys 1984;55(9):3354–66.
[37] Revell DJ, Chambrier I, Cook MJ, Russel DA. J Mater Chem 2000;10(1):31–7.
[38] Rodriquez-Mendez ML, Souto J, De Daja JA. J Raman Spectrosc 1995;26(8–9): 693–8.
[39] Basova TV, Kolesov BA, Gürek AG, Ahsen V. Thin Solid Films 2001;385(1–2): 246–51.
[40] Aroca R. J Mol Struct 1986;143:131–4.
[41] Aroca R, Jennings C, Loutfy RO, Hor A-M. J Phys Chem 1986;90(21):5255–7.
[42] Dowdy J, Hoagland JJ, Hipps KW. J Phys Chem 1991;95(9):3751–5.
[43] Basova TV, Kolesov BA. Thin Solid Films 1998;325(1–2):140–4.
[44] Jennings C, Aroca R, Hor A-M, Loutfy RO. J Raman Spectrosc 1984;15(1): 34–7.
[45] Aroca R, Zeng ZQ, Mink J. J Phys Chem Solids 1990;51(2):135–9.
[46] Basova T, Kol'tsov E, Gürek AG, Atilla D, Ahsen V, Hassan AK. Mater Sci Eng C 2008;28(2):303–8.
[47] Iino H, Hanna J, Bushby RJ, Movaghar B, Whitaker BJ, Cook MJ. Appl Phys Lett 2005;87:132102-1–132102-3.
[48] de Cupere V, Tant J, Viville P, Lazzaroni R, Osikowicz W, Salaneck WR, et al. Langmuir 2006;22(18):7798–806.
[49] Hatsusaka K, Ohta K, Yamamoto I, Shirai H. J Mater Chem 2001;11(2): 423–33.