

Synthesis and investigations of copper hexadecafluorophthalocyanine CuPcF_{16}

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Abstract

In this work, the results of synthesis and characterization of hexadecafluorinated copper phthalocyanine CuPcF_{16} are reported. The results of mass spectrometric studies of the composition of gaseous phase under solid compound and thermal properties of CuPcF_{16} are presented. The vapour pressure of this phthalocyanine is determined as a function of temperature by the Knudsen effusion method, in which the rate of effusion of the equilibrium vapour through a small orifice was measured. It was shown that hexadecafluorinated copper phthalocyanine exhibits lower volatility than its unsubstituted analogue. Besides, the spectral characterization of CuPcF_{16} powder and films is carried out.

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1. Introduction

Phthalocyanines have a great technological potential in areas related to intrinsic semiconductors, chemical sensors, nonlinear optics, laser recording materials, information storage systems, electrochromic display devices, and liquid–crystal colour display applications, among others.

Metal hexadecafluorophthalocyanine, MPcF_{16} , from the class of coordination compounds which are currently receiving a great deal of attention due to their interesting electron-transporting characteristics [1]. Synthesis of fluorinated iron, zinc and copper phthalocyanines was described long ago [2,3], however, an interest in the investigation of the properties of these compounds was rekindled last 5 years. While unsubstituted phthalocyanines exhibit p-type behaviour due to the doping with electron accepting molecules, thin films of some MePcF_{16} exhibit n-type behaviour. These properties resulted in a number of studies aiming at different applications like photovoltaic cells, rectifying junction and gas sensors.

Synthesis, spectral and electrochemical properties of vanadyl hexadecafluorophthalocyanine were described in Ref. [4]. Schlettwein et al. in Refs. [5,6] consider a possibility of epitaxial growth of VOPcF_{16} and ZnPcF_{16} films

on NaCl, KCl and KBr surfaces by organic molecular beam deposition (OMBD) technique. In these papers and in Ref. [7], it was shown that ZnPcF_{16} film structure depends not only on substrate materials but also on film thickness and substrate temperature. The electrical properties of ZnPcF_{16} films were investigated and n-type of conductivity was confirmed in Ref. [8].

The authors of Ref. [9] reported the electrochemical characteristics of vapour deposited films of ZnPcF_{16} , the kinetics of the reaction including charge transport in the film and structural changes occurring in the film on the basis of the results of cyclic voltammetry and spectroelectrochemistry.

Investigation of an interaction of CuPcF_{16} molecule with Si(1 1 1) and Si(1 0 0) substrates surface by means of monochromatic X-ray photoemission spectroscopy was carried out by Ottaviano et al. and Lozzi et al. in Refs. [10,11], correspondingly. High-resolution photoelectron spectra of CuPcF_{16} films and their interpretation may be found in the paper of the same group of authors [12]. The films of CuPcF_{16} were also characterized by X-ray diffraction and an influence of their disorder on the electron transport properties were studied in Ref. [13]. Besides, some authors investigated the effect of hexadecafluorinated phthalocyanines for photodynamic therapy [14]. So, the majority of papers are devoted to investigation of structural features and electrical characteristics of the films. At the same time, the fundamental properties of hexadecafluorinated phthalocyanines have not been sufficiently studied.

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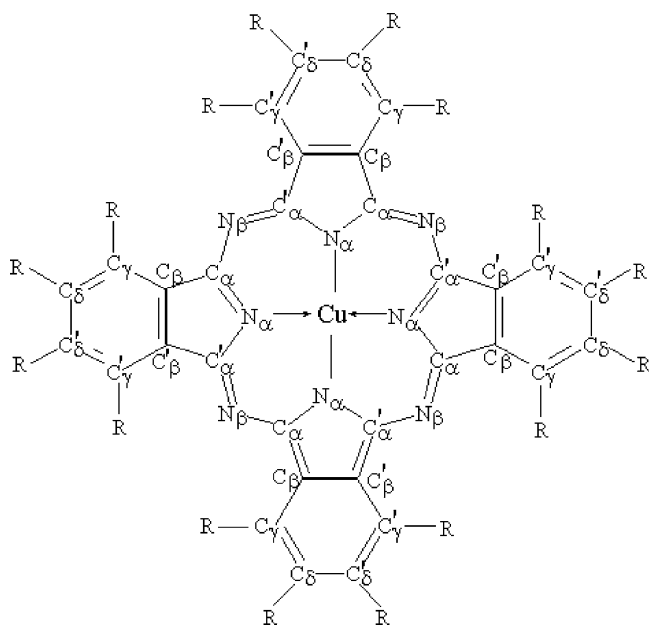


Fig. 1. Chemical structure of copper phthalocyanines, R = H, F.

In this work, the results of synthesis and characterization of hexadecafluorinated copper phthalocyanine CuPcF_{16} (Fig. 1) are reported. The results of mass spectrometric studies of the composition of gaseous phase under solid compound and thermal properties of CuPcF_{16} are presented. The vapour pressure of this phthalocyanine is determined as a function of temperature by the Knudsen effusion method, in which the rate of effusion of the equilibrium vapour through a small orifice is measured. These data are needed for improving the operating conditions of the growth of thin films by OMBD. Besides, the spectral characterisation of CuPcF_{16} powder and deposited films is carried out.

2. Experimental

CuPcF_{16} was synthesized by two different techniques. In the first case, the vacuum-sealed glass tube (0.13 Pa) with the mixture containing sublimed 3,4,5,6-tetrafluorophthalonitrile and copper powder in an equimolar amount 4:1 was heated during 7 h at 220 °C. In the second technique, hexadecafluorophthalocyaninacopper(II) was synthesized as in the first one; however, anhydrous copper(I) chloride was used instead of copper powder. Then the tube was opened and the mixture was washed by ethanol and acetone to remove soluble organic admixtures. The precipitate was purified by gradient sublimation in vacuum (1.33×10^{-3} Pa) at 450 °C. The resulting purple crystals were identified as hexadecafluorophthalocyaninacopper(II) (found: C, 44.6%; N, 13.0%; Cu 7.3%; calculated for CuPcF_{16} : C, 44.5%; N, 13.0%; Cu 7.4%). The yield of the product after sublimation was 15% in the first technique and 44% in the second one.

The composition of vapour of phthalocyanines was investigated by mass spectrometry technique in the temperature

range up to 600 °C. Mass spectra were obtained by means of MI-1201 and MX-1310 mass spectrometers. The molecules effusing from the cell were ionized by means of electrons of 35 eV energy. The evaporation temperature was risen by a step of 20–30 °C. The whole spectrum to 1000 mass units was recorded at each temperature. The sample weights were about 2×10^{-3} g.

The vapour pressures of these phthalocyanines were determined as a function of temperature by the Knudsen effusion method by means of MI-1201 mass spectrometer [15]. The Knudsen cells of 0.7 cm i.d. and depth were constructed from molybdenum and quartz. The diameters of the orifice were 0.020, 0.025, 0.030 cm and the channel length was 0.02 cm. The ratio of evaporation area to the area of the orifice was about 1000. The temperature of the effusion cell was risen by a step of 5–10 °C and measured by Pt/PtRh 10% thermocouple. The powder samples of 2–25 mg were set in the cell. The temperature error was ± 2 °C. The experimental error of pressure measurements was 10%.

Thermal investigation of the compound was carried out in inert media at atmospheric pressure on Q-1500 derivatograph (MOM, Hungary). The thermal study of the phthalocyanine in vacuum (1.33 Pa) was performed using derivatograph TA-7000. Heating rate was 5 grad min^{-1} in both cases.

The layers of CuPcF_{16} were obtained by OMBD technique using home made special installation at a room substrate temperature. The evaporation was carried out at a residual pressure 1.33×10^{-3} Pa. The evaporation temperature of copper phthalocyanine was 450 °C. Silicon and quartz plates were used as substrates.

The thickness of deposited films was measured by ellipsometry. Spectroscopic ellipsometric measurements on CuPcF_{16} films on silicon substrates were performed by using a Woolam M-2000TM rotating analyser spectroscopic ellipsometer in the spectral range of 400–800 nm. The angle of incidence was fixed at 70°. The dedicated software is used for data acquisition and analysis of the measured ellipsometric parameters $\psi(\lambda)$ and $\Delta(\lambda)$. Using the Levenberg–Marquardt multivariate regression algorithm, the measured data were fitted to the Cauchy model:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \quad k(\lambda) = \beta \exp \left[\gamma \left(\frac{1}{\lambda} - \frac{1}{L} \right) \right]$$

where n and k are the index of refraction and extinction coefficient at wavelength λ and A , B , C , β , γ and L are the model parameters.

UV-Vis spectra of the solutions and films on quartz substrates were recorded with a UV-Vis-NIR scanning spectrophotometer (UV-Vis-3101PC “Shimadzu”) in the range from 400 to 900 nm.

Raman spectra were recorded with a Triplemate, SPEX spectrometer equipped with a O-SMA, Si-diode array in back-scattering geometry. The 488 nm, 150 mW line of an Ar-laser was used for the spectral excitation.

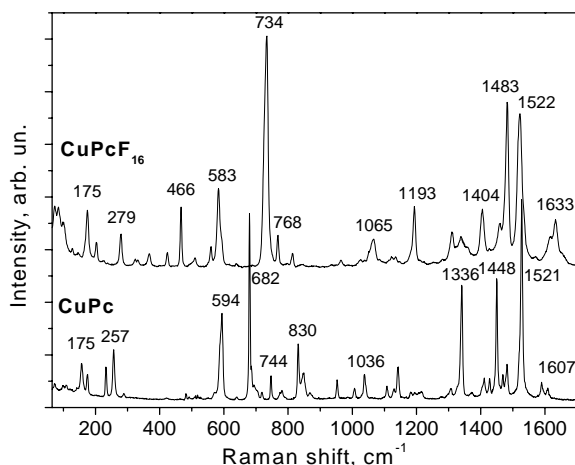


Fig. 2. Raman spectra of CuPc and CuPcF₁₆.

3. Results and discussion

3.1. Vibrational spectra

The Raman spectra of CuPcF₁₆ are presented in Fig. 2. The assignment of the vibrations was made on the basis of comparison with the Raman spectra of unsubstituted copper phthalocyanine. Normal coordinate analysis for the in-plane gerade modes of the CuPc confirmed by the measurement of the isotopic frequency shifts upon ¹⁵N substitution for nitrogen atoms was carried out in Ref. [16]. The experimental frequencies in the Raman spectra and assignments for the normal modes of CuPc and CuPcF₁₆ are listed in Table 1.

Compared to the unfluorinated phthalocyanine, it is observed that the fluorine atoms induce the essential shift of C=C benzene stretching vibrations to high frequency region. Electron-withdrawing substituents also lead to shift of the modes with a predominant contribution of copper–nitrogen vibrations.

3.2. Thermal properties

The thermal properties of CuPcF₁₆ were investigated by differential thermal analysis DTA in vacuum (1.33 Pa) and in helium. The temperatures of the beginning of sublimation and decomposition of CuPcF₁₆ are compared with those of unsubstituted copper phthalocyanine in Table 2.

The data of high thermal mass spectrometry show that CuPcF₁₆ sublimates without thermal decomposition until 600 °C, as is also the case with other phthalocyanines [17–20]. The analysis of the mass spectra shows that CuPcF₁₆ sublimates in the form of monomer. The parent ion CuPcF₁₆⁺ (*m/e* = 863) gave the most prominent peak. These ions were accompanied by the corresponding doubly charged ions.

The vapour pressures of these phthalocyanines were determined as a function of temperature by the Knudsen effusion method. The principle of this technique was

Table 1

Experimental frequencies in the Raman spectra and assignments for the normal modes of CuPc and CuPcF₁₆

| CuPc [16] | CuPcF ₁₆ | Assignment |
|-----------|---------------------|---|
| 234 | 225 | Cu–N _α , C _α –N _β –C _α |
| 257 | 279 | Cu–N _α |
| | 466 | C _δ –C _δ –F |
| 490 | 509 | C _β –C _γ –C _δ , C _γ –C _δ –C _δ |
| | 559 | C _δ –C _δ –F |
| 594 | 583 | C _α –N _β –C _α , C _β –C _γ –C _δ |
| 682 | | C _δ –C _γ –H, C _β –C _γ –C _δ , C _α –N _β |
| 692 | | C _δ –C _γ –H, C _α –N _β –C _α , C _δ –C _δ –H |
| 717 | | C _δ –C _δ –H |
| 744 | 734 | C _α –N _β –C _α |
| 773 | 768 | C _β –C _β –C _γ , C _α –N _β |
| 780 | | C _γ –C _δ , C _β –C _β , C _δ –C _γ –H |
| 830 | 814 | C _γ –C _δ , C _β –C _β , C _α –N _β –C _α |
| | 1025 | C _δ –F |
| 1036 | 1065 | C _δ –C _δ , C _γ –C _δ , C _α –C _β , N _α –C _α |
| 1106 | | C _β –C _β , C _δ –C _δ , C _γ –C _δ , N _α –C _α |
| 1142 | 1135 | C _γ –C _δ , C _α –N _β , C _α –C _β |
| 1193 | 1193 | N _α –C _α , C _β –C _β , C _δ –C _δ |
| 1336 | 1334 | C _α –N _β , C _β –C _β , C _α –C _β |
| 1339 | 1338 | C _γ –C _δ , C _β –C _γ –C _δ , C _α –C _β |
| 1410 | 1404 | C _α –N _β , C _γ –C _δ , C _δ –C _δ |
| 1427 | 1427 | C _α –C _β , C _β –C _β , C _γ –C _δ |
| 1448 | 1459 | C _α –C _β , C _β –C _β –C _γ , C _β –C _γ –C _δ |
| 1482 | 1483 | C _γ –C _δ , C _β –C _β –C _γ |
| 1522 | 1522 | N _α –C _α , C _α –N _β , C _γ –C _δ |
| 1526 | 1572 | C _γ –C _δ , C _β –C _β , C _α –C _β |
| 1589 | 1618 | C _γ –C _δ , C _β –C _β , C _α –C _β |
| 1607 | 1633 | C _γ –C _δ , C _β –C _β , C _α –C _β |

The notation of atoms in phthalocyanine molecule is in Fig. 1.

described in Refs. [20–23]. It is well known that the dependence of vapour pressure on temperature is expressed by the Clapeyron–Clausius equation as

$$\log P \text{ (atm)} = -\frac{A}{T} + B \quad (1)$$

where $A = \Delta H_T^\circ/R$ and $B = \Delta S_T^\circ/R$ [22,23]. The results of vapour pressure measurement are plotted in Fig. 3. Least-squares constants A and B corresponding to Eq. (1), the enthalpies and entropies of sublimation are presented in Table 3. These data were originally obtained. The references devoted to the investigation of thermal behaviour in the gaseous phase and vapour pressure data are available only for a limited number of phthalocyanines [24–26]. Using the effusion method, the vapour pressure of copper phthalocyanine in the temperature range from 384 to 449 °C was found 30 years ago by Curry and Shaw [24]. Vapour pressures of some unsubstituted phthalocyanines have been measured by

Table 2

Temperatures of the beginning of sublimation (T_{subl}) and decomposition (T_{decomp}) for copper phthalocyanines

| Compound | T_{subl} (°C in vacuum (1.33 Pa)) | T_{subl} (°C in helium) | T_{decomp} (°C in helium) |
|---------------------|--|----------------------------------|------------------------------------|
| CuPc | 395 | 430 | >600 |
| CuPcF ₁₆ | 470 | 450 | 550 |

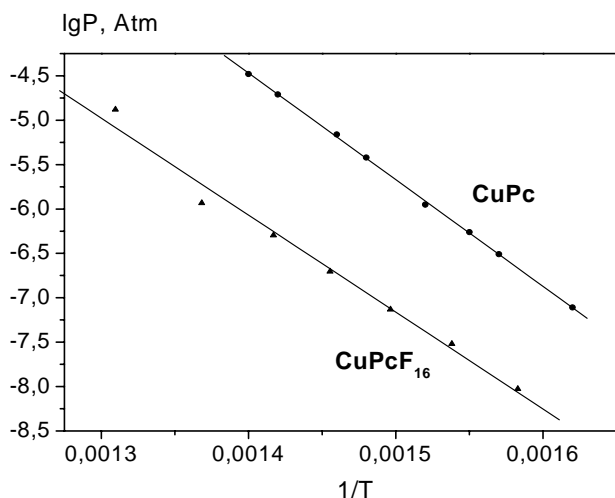


Fig. 3. Vapour pressure of CuPc and CuPcF₁₆.

Knudsen effusion technique in our early publication [20], and heat and entropy of sublimation were obtained. As for hexadecasubstituted phthalocyanines, only the vapour pressure of chloro- and bromo-phthalocyanines were measured by effusion method in Ref. [25].

It is interesting to compare CuPcF₁₆ vapour pressure with the analogous results obtained early for the unsubstituted β -copper phthalocyanine [20]. Hexadecafluorosubstituted copper phthalocyanine exhibits lower volatility than its unsubstituted analogue. Because enthalpy and entropy are functionally related, it is not surprising that the progression is similar for ΔH and ΔS . A difference in CuPc and CuPcF₁₆ volatility may be explained by different crystal packing and therefore different intermolecular bonding in the solids. Unfortunately, we have not succeeded to grow single crystal of CuPcF₁₆ to compare their crystal structures in detail. However, a comparison of X-ray diffraction data for β -CuPc [27] and CuPcF₁₆ powder (Table 4) testify to similar crystal packings of these compounds.

3.3. Absorption spectra

As unsubstituted CuPc, CuPcF₁₆ is characterized by low solubility. Fig. 4 shows the absorption spectra of CuPcF₁₆ solutions in pyridine and DMFA (dashed and dotted lines, correspondingly). The concentration of phthalocyanine was $5 \times 10^{-6} \text{ mol l}^{-1}$. Absorption maxima for Q-band are seen at 679 nm with shoulders at 647 and 614 nm for CuPcF₁₆ solutions in pyridine (Fig. 4, dashed line). This

Table 4
X-ray diffraction peaks of CuPcF₁₆ powder

| 2θ (°) | D (Å) | Height (%) |
|---------------|---------|------------|
| 6.1 | 14.5 | 100 |
| 9.1 | 9.7 | 8.7 |
| 9.4 | 9.4 | 2.9 |
| 10.3 | 8.5 | 1.5 |
| 12.0 | 7.3 | 0.7 |
| 12.5 | 7.1 | 5.1 |
| 17.5 | 5.1 | 3.6 |
| 19.2 | 4.6 | 3.1 |
| 19.6 | 4.5 | 1.8 |
| 21.9 | 4.1 | 2.2 |
| 24.7 | 3.6 | 2.3 |
| 24.9 | 3.6 | 3.3 |
| 25.5 | 3.5 | 1.9 |

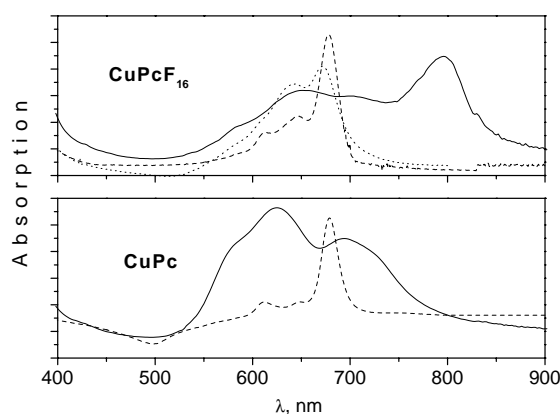


Fig. 4. Optical absorption spectra of CuPcF₁₆ dissolved in DMFA (dotted line), pyridine (dashed line) and as a film on quartz substrate (solid line) and CuPc dissolved in 1-chloronaphthalene (dashed line) and as a film on quartz substrate (solid line).

spectrum is very similar to the spectrum of CuPc solution in 1-chloronaphthalene (Fig. 4, dashed line). The absence of aggregation effects indicates monomer behaviour of CuPcF₁₆ in pyridine. The spectrum of CuPcF₁₆ in DMFA (Fig. 4, dotted line) differs from the spectrum of this compound in pyridine and shows a strong absorption peak at 643 nm, which indicates to aggregation in solution [4].

The films of CuPcF₁₆ were deposited at deposition rate of 0.6 nm s^{-1} and room substrate temperature. This regime is very close to the conditions reported in [7,9,12]. The film thickness determined by ellipsometry was 68 nm, the index of refraction and extinction coefficient at wavelength 633 nm were 1.62 and 0.11, correspondingly. These values of the refractive index obtained in this work for CuPcF₁₆

Table 3
Least-squares constants A and B corresponding to the equation $\log P$ (atm) = $B - A/T$, the enthalpies and entropies of vaporization

| Compounds | Temperature range (K) | $\log P$ (atm) = $B - A/T$ | | ΔH° (kcal mol ⁻¹) | ΔS° (kcal mol ⁻¹) |
|---------------------|-----------------------|----------------------------|---------|--|--|
| | | B | A | | |
| β -CuPc | 618–713 | 12.47 | 12110.8 | 55.4 ± 0.5 | 57.1 ± 0.7 |
| CuPcF ₁₆ | 631–763 | 8.53 | 10493.1 | 48.0 ± 1.7 | 39.0 ± 2.2 |

film are in good agreement with those calculated with different methodology for the polycrystalline films of unsubstituted CuPc in Refs. [28,29].

Absorption spectrum of CuPcF₁₆ film on quartz is given in Fig. 4. The spectrum of unsubstituted CuPc is also included for comparison. The bands in the film spectra split into at least two bands with apparent maxima at 626 and 694 nm for CuPc and at 654 and 796 nm for CuPcF₁₆ typical for the interaction of adjacent molecules in molecular crystals [30].

The spectrum of CuPc film deposited at the same conditions corresponds to α -modification of copper phthalocyanine [31]. The spectrum obtained for the film of CuPcF₁₆ is significantly broader which appears to point toward the presence of a mixture of different modifications. A small absorption near that of the solution shows the presence of an amorphous fraction. It is interesting to note that this spectrum does not practically differ from that of the film deposited by rubbing of the CuPcF₁₆ powder obtained after sublimation.

According to the molecular exciton theory [32], the red shift of Q-band in CuPcF₁₆ (at 796 nm) points to edge-to-edge interaction between neighbouring phthalocyanine moieties. The splitting energy of this band which may be determined from the difference to the band in solution and yields 0.27 eV considerably larger than this value of CuPc. Following the model of Kasha et al. [32] the larger splitting energy points towards a quiet stronger interaction between adjacent CuPcF₁₆ molecules in the unit cell. Very similar conclusions were made in Ref. [8], where the films of ZnPcF₁₆ had been investigated. Interactions in molecular crystals are known to be of the van der Waals type. Obviously from our data and results of Ref. [8], the introduction of 16 electronegative fluorine atoms into phthalocyanine ring leads to the preferred edge-to-edge arrangement at a higher interaction energy for MPcF₁₆ in comparison with unsubstituted MPc. It allows to suggest that this stronger intermolecular interaction in condense phase may be the reason of the lower volatility of CuPcF₁₆ as compared with CuPc (Fig. 3).

It was shown in Refs. [5–7] that the films structure depends on film thickness, substrate material, substrate temperature during deposition and subsequent annealing. In Ref. [7], the ZnPcF₁₆ films deposited on ITO and quartz glass at room substrate temperature have optical absorption spectra with Q-band at about 667 nm blue shifted from the monomer absorption. The band at 820 nm appears only after annealing of these films at 473 K during 50 h. In our case, the CuPcF₁₆ films with red shifted Q-band at 796 nm (Fig. 4) dominated in the absorption spectra are obtained when deposited at room temperature of quartz substrate without subsequent annealing. It is interesting to note that the absorption spectrum does not practically change after heating at 493 K during 10 h. The noncoincident results appear to connect with different deposition techniques: evaporation from open crucible in Ref. [7] and OMBD in our case. Additional study is necessary to understand an influence of experimental conditions of deposition in the CuPcF₁₆ film structure.

Such investigations based on the data of temperature dependence of vapour pressure obtained in this work will be a subject of the following study.

4. Conclusions

The assignment of vibrations in the Raman spectra of CuPcF₁₆ was made on the basis of comparison with the spectra of unsubstituted copper phthalocyanine. The data of high thermal mass spectrometry show that CuPcF₁₆ sublimes in the form of monomer without thermal decomposition until 600 °C, as is also the case with other monophthalocyanines. The vapour pressure of copper hexadecafluorophthalocyanine was determined as a function of temperature by the Knudsen effusion method. It was shown that hexadecafluorosubstituted copper phthalocyanine exhibits lower volatility than its unsubstituted analogue. In accordance with X-ray data, a difference in CuPc and CuPcF₁₆ volatility appears to be explained by different crystal packing and therefore different intermolecular bonding in the solids.

The absorption spectra of CuPcF₁₆ solutions and films were compared with those of unsubstituted copper phthalocyanine. Obviously from the absorption spectra, the introduction of 16 electronegative fluorine atoms into phthalocyanine ring leads to the preferred edge-to-edge arrangement at a higher interaction energy for CuPcF₁₆ in comparison with unsubstituted CuPc. This allows us to suggest that this stronger intermolecular interaction in condense phase may be the reason of the lower volatility of CuPcF₁₆ as compared with CuPc.

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References

- [1] Z. Bao, A.J. Lovinger, J. Brown, *J. Am. Chem. Soc.* 120 (1998) 207.
- [2] J. Jones, M.V. Twigg, *Inorg. Chem.* 8 (1969) 2018.
- [3] J.M. Birchall, R.N. Haszeldine, J.O. Morley, *J. Chem. Soc. C* (1970) 2667.
- [4] M. Handa, A. Suzuki, S. Shoji, K. Kasuga, K. Sogabe, *Inorg. Chim. Acta* 230 (1995) 41.
- [5] D. Schlettwein, H. Tada, S. Mashiko, *Langmuir* 16 (2000) 2872.
- [6] D. Schlettwein, K. Hesse, H. Tada, S. Mashiko, U. Storm, J. Binder, *Chem. Mater.* 12 (2000) 989.
- [7] D. Schlettwein, H. Graaf, J.-P. Meyer, T. Oekermann, N.I. Jaeger, *J. Phys. Chem. B* 103 (1999) 3078.
- [8] S. Hiller, D. Schlettwein, N.R. Armstrong, D. Wöhrle, *J. Mater. Chem.* 8 (4) (1998) 945.
- [9] K. Hesse, D. Schlettwein, *J. Electroanal. Chem.* 476 (1999) 148.
- [10] L. Ottaviano, L. Lozzi, F. Rispoli, S. Santucci, *Surf. Sci.* 402–404 (1998) 518.

- [11] L. Lozzi, L. Ottaviano, F. Rispoli, P. Picozzi, S. Santucci, *Surf. Sci.* 433–435 (1999) 157.
- [12] L. Ottaviano, L. Lozzi, F. Ramondo, P. Picozzi, S. Santucci, *J. Electron. Spectrosc. Relat. Phenom.* 105 (1999) 145.
- [13] J.H. Schön, Z. Bao, *J. Appl. Phys.* 89 (2001) 3526.
- [14] K. Oda, S.-I. Ogura, I. Okura, *J. Photochem. Photobiol. B* 59 (2000) 20.
- [15] V.M. Grankin, P.P. Semyannikov, *PTE* 4 (1991) 129.
- [16] T.V. Basova, B.A. Kolesov, *J. Struct. Chem.* 5 (2000) 770 (Engl. Transl.).
- [17] H.C. Hill, R.I. Reed, *Tetrahedron* 20 (1964) 1359.
- [18] K. Varmuza, G. Maresch, A. Meller, *Monatsh. Chem.* 105 (1974) 327.
- [19] J.P. Linsky, T.R. Paul, R.S. Nohr, M.E. Kenney, *Inorg. Chem.* 19 (1980) 3131.
- [20] P.P. Semyannikov, T.V. Basova, V.M. Grankin, I.K. Igumenov, *J. Porphyrins Phthalocyanines* 4 (2000) 271.
- [21] L.N. Sidorov, M.V. Korobov, L.V. Zhuravleva, *Mass Spectral and Thermodynamic Researches*, Moscow State University, Moscow, 1985.
- [22] M. Ingram, J. Drauart, *Investigations at High Temperatures*, Mir, Moscow, 1962.
- [23] M. Knudsen, *Ann. Physik.* 29 (1909) 179.
- [24] J. Curry, W. Shaw, *J. Phys. Chem.* 69 (1965) 344.
- [25] D. Bonderman, E.D. Cater, W.E. Barnnet, *J. Chem. Eng. Data* 15 (1970) 396.
- [26] K. Yase, Y. Takahashi, N. Ara-Kato, A. Jpn. *J. Appl. Phys.* 34 (1995) 636.
- [27] C.J. Brown, *J. Chem. Soc. A* 10 (1968) 2488.
- [28] M.K. Debe, *J. Vac. Sci. Technol. A* 10 (1992) 2816.
- [29] A.B. Djurišić, C.Y. Kwong, T.W. Lau, W.L. Guo, E.H. Li, et al., *Opt. Commun.* 205 (2002) 155.
- [30] A.S. Davydov, *Theory of Molecular Excitons*, Nauka, Moscow, 1968.
- [31] G.N. Meshkova, A.T. Vartanyan, A.N. Sidorov, *Optika i spektroskopiya* 43 (1977) 262.
- [32] M. Kasha, H.R. Rawls, A. El-Bayoumi, *Pure Appl. Chem.* 11 (1965) 371.