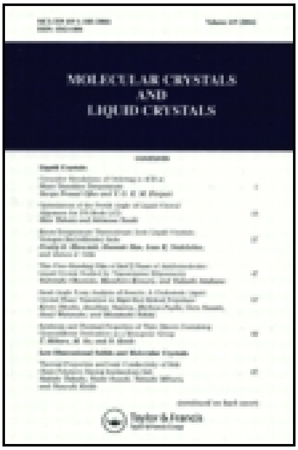

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Optical Properties of Vacuum Sublimed Cobalt Phthalocyanine (CoPc) Thin Layers

M. Wojdyła [a], M. Rębarz [a], W. Bała [a], B. Derkowska [a] & Z. Łukasiak [a]

[a] Nicolaus Copernicus University, Toruń, Poland

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M. Wojdyła, M. Rębarz, W. Bała, B. Derkowska, and Z. Łukasiak
Nicolaus Copernicus University, Toruń, Poland

In this article the temperature dependence of absorption spectra of vacuum sublimed cobalt phthalocyanine (CoPc) thin layer is presented. For comparison the optical properties of CoPc solution were also investigated. Absorption measurements revealed strong intermolecular interaction in the solid form as well as the presence of intramolecular charge transfer excitation below the B exciton band. Spectral distribution of complex refractive index (n) and extinction coefficient (k) as well as thickness of the layer were found basing on reflection and transmission measurements by minimization appropriately defined error function. Corresponding values of dielectric constants were also calculated.

Keywords: absorption; cobalt phthalocyanine (CoPc); complex refractive index; dielectric contants; reflection; transmission

INTRODUCTION

Metallophthalocyanines (MPcs) are very attractive materials because of their large number of unique optical and electrical properties which can be exploited in production and development of novel optoelectronic devices. Some of their unusual properties, like for example the deep hue, have been known for a long time, practically since their discovery in 1907 [1]. Owing to extraordinary properties of MPcs, it is not surprising that these compounds have been called as “a gift to molecular physics” by McKeown [2]. The new potential applications considerably intensified research concerning excited states of MPcs [3,4]. Recently the greatest efforts have been done to construct high efficient and stable organic light emitting devices (OLED), organic solar cells and

Address correspondence to Michał Wojdyła, Nicolaus Copernicus University, Institute of Physics, Grudziądzka 5, 87-100, Toruń, Poland. E-mail: mwojdyla@fizyka.umk.pl

field effect transistors (OFETs). Differently substituted metallophthalocyanines play a crucial role in development such new organic devices [5–11]. In majority applications these materials are used in the form of thin layers, that is why research concerning their basic optical properties is particularly important. For example the refractive index and absorption coefficient of particular layers in OLED determine the waveguide effect and absorption process in such structures [12]. On the other hand comparison between solution and thin film spectra may supply important information about interactions which are characteristic of solid state only. The nature of excited states of thin layers is very interesting because straightforwardly relate to processes such as: absorption, emission, electroluminescence or photoconductivity. It should be pointed out that the understanding of mechanisms which are responsible for these processes in molecular crystals is still limited and theoretical model are controversial. Although the optical properties of metallophthalocyanines with closed shell, like ZnPc or MgPc, are relatively well documented there is a little known about the electronic structure of other MPcs with open shell configuration. The example of such material can be phthalocyanine complex with cobalt ion (Co^{2+}) which contains seven electrons on 3d subshell. The electronic structure of such compounds is usually more complicated because open shell configuration promotes participation of transitions with intramolecular charge transfer. As a result optical spectra of these compounds can contain extra bands in comparison with closed shell metallophthalocyanines.

EXPERIMENTAL

The investigated material was purchased from Sigma-Aldrich Co. and used without further purification. The molecular structure of cobalt phthalocyanine (CoPc) is presented in the inset of Figure 1. Thin layers of CoPc were prepared using the conventional thermal sublimation method under the base pressure about 2×10^{-5} Tr. The temperature of CoPc source was about 350°C. Thin layers were deposited on quartz glass substrates, which during sublimation process were kept at room temperature. The transmission and reflection spectra were measured using SPM-2 (Zeiss Jena) prism monochromator as well as 250 W tungsten-halogen and 20 W deuterium lamp for measurements in IR-VIS and UV range, respectively. Sensitive Si photodiode with preamplifier (S8745-01 Hamamatsu) was used for light detection. The low temperature measurements were recorded using helium refrigerator (Cryogenic Inc.)

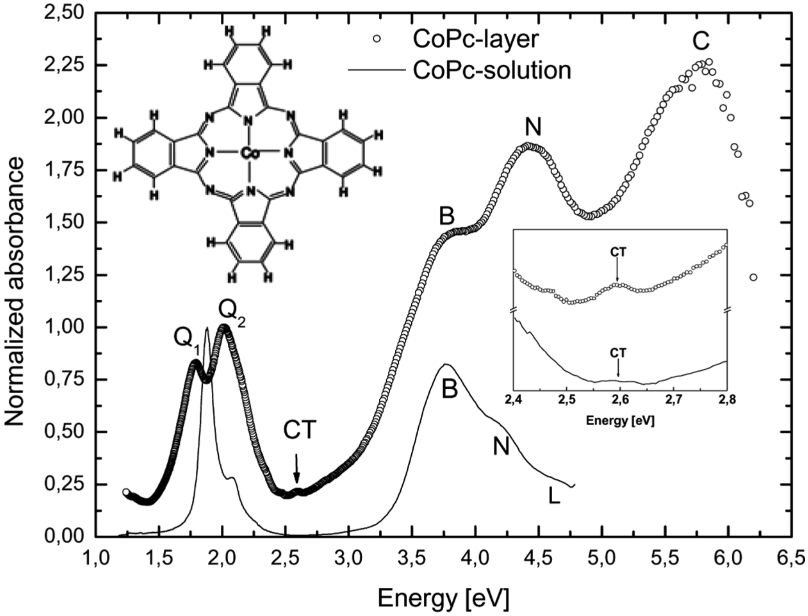

FIGURE 1 Absorption spectra of CoPc thin layer (circle) and solution (solid line). Both spectra were normalized to the unity at the maximum of Q band.

RESULTS AND DISCUSSION

Figure 1 presents the comparison between absorption spectra of CoPc thin layer and solution prepared in DMSO solvent. The concentration of investigated solution was about 10^{-5} M. While the solution spectrum of CoPc is limited to the 4.75 eV because of cut-off DMSO solvent, the material deposited on the quartz substrate enable to carry out absorption measurements in wider spectral range, up to the 6.2 eV.

There are many features which are common for electronic spectra of differently substituted metallophthalocyanines (MPcs). In general for all MPcs in the spectral range 1.5–6.2 eV theory predicts at least five dominating electronic transitions which are usually labeled Q, B, N, L and C [13]. All mentioned transitions are π to π^* in nature and are associated with the heteroaromatic, 16 atom, 18 π-electron inner perimeter cyclic polyene [14]. All these transitions can be clearly resolved in absorption spectra of MPc gas phase [13]. Nevertheless in solid state absorption spectrum we can observe only one distinct band between B and C bands, which was labeled by letter N (Fig. 1). Probably both N and L transitions observed in gas and solution phase take part in creation of this band. According four-orbital LCAO

Gouterman's calculation [15,16] first two $\pi \rightarrow \pi^*$ bands are due to $a_{1u} \rightarrow e_g$ (Q) and $a_{2u} \rightarrow e_g$ (B) transitions. In contradiction to Gouterman's calculation, spectral band deconvolution analysis based on magnetic circular dichroism (MCD) and absorption spectroscopy [14] provided evidence of the presence of a second transition in the B band region, which was associated with $b_{2u} \rightarrow e_g$ transition. More advanced calculations based on self -consistent field theory for CoPc molecule predict 21 different transitions with nonzero oscillator force in the spectral range between 1.24 eV and 6.2 eV [17]. Moreover transitions involved 3d central metal ion are predicted because Co^{2+} has partially occupied 3d subshell which lie between Pc HOMO(π) and LUMO(π^*) orbitals. Majority of these intramolecular charge transfer transitions (LMCT or MLCT) lie in the same spectral range where strongly allowed $\pi \rightarrow \pi^*$ transitions so their identification is rather troublesome. It was also suggested that intramolecular charge transfer transitions have a large contribution in N and C absorption bands for thin films of CoPc [18]. Between Q and B bands of CoPc absorption spectrum we observe weak peak at energy about 2.6 eV. In the inset of Fig. 1 this structure is clearly visible in absorption spectra for both thin layer and solution, although for thin layer it is more sharply outlined. Density functional calculations for CoPc molecule predict one ligand to metal charge transfer transition (LMCT) between Q and B bands [19]. This transition involve orbitals $a_{2u}(\pi)$ and $d(e_g)$. CT type transition for CoPc in this spectral range was observed also in work [20]. That is why we suppose that peak at energy about 2.6 eV can be associated with intramolecular charge transfer transition (CT) however the attribution to an impurity level can not be completely excluded. The maxima positions of all observed absorption bands for thin layer and solution of CoPc were collected in Table 1. In the visible spectral range we observe two distinct peaks for both solution and thin layer spectra. Strong and sharp band at energy 1.88 eV (Q_1-Table 1), which is visible in solution spectrum is associated with first electronic transition between lowest lying vibrational levels of ground and excited state of molecule (Q_{00}). Absorption peak to the blue of the Q_1 band of CoPc solution is assigned as vibrational components of first electronic transition. In the Q-band region of CoPc film two absorption

TABLE 1 The Absorption Bands Positions for CoPc Solution and Thin Layer

CoPc	Q_1 [eV]	Q_2 [eV]	B [eV]	N [eV]	L [eV]	C [eV]
Solution	1.88	2.08	3.77	~4.2	~4.6	–
Thin layer	1.80	2.01	~3.8	4.42	–	5.80

peaks are also clearly visible. The second peak Q_2 cannot be attributed to the vibronic band of the Q_1 transition because the intensity of the Q_2 band is larger than the intensity of the Q_1 band and any molecular vibration in CoPc molecule does not show such strong coupling strength. Therefore, it is more probable that appearance of two bands Q_1 and Q_2 in solid state is due to Davydov effect, which causes splitting Q_1 ($a_{1u} \rightarrow e_g$) transition observed in solution into two distinct components. According Davydov theory each of the electronic transitions observed in solution (or gas phase) is broadened and splitted in the solid [21]. This effect occurs mainly due to resonance interaction between translationally inequivalent molecules in the unit cell. Comparison between absorption spectrum of solution and thin layer leads to the conclusion that aside from Q band splitting the other results of intermolecular interaction in solid are broadening and the shift of particular bands. The spectral shift can be either to the blue or to the red regions, depending on the mutual orientation of the monomer transition moments [22]. The broadening effect can be explained by aggregation and exciton (Davydov) coupling effect as well as interaction with phonons and molecular distortion in lattice. Transfer of intramolecular vibrations energy to lattice vibrations cause the broadening of absorption bands which depends on the rate of energy migration. Another reason for band broadening is the violation of lattice periodicity.

Absorption spectrum of CoPc thin layer was measured in the wide temperature range from 13 K to 320 K. The temperature dependence of absorption is presented in Figure 2. We can see that broadening and positions of particular bands slightly depend on temperature. On the other hand the intensities of all bands, especially at high energy spectral region, are strongly affected by temperature. The changes of intensities of observed Q_1, Q_2, CT, B, N and C bands versus temperature are shown in Figure 3. Since the thermal behavior of bands is quite complicated and their conclusive interpretation remains difficult we suppose that a variety processes contribute to the observed changes. Among these processes the most important are [23]: intermolecular interactions which depends on crystal packing and relative orientation of neighboring molecules, participation of phonons which should leads to the increase of absorption intensities with temperature raise and finally the temperature deformation of molecules. It should be pointed out that though CoPc molecule was found to be planar with central metal ion being in the same plane with Pc macrocycle [24], we cannot exclude the change of metal positions relative to Pc rings due to decrease of temperature of solid. Such thermal deformation of molecules in crystal was observed for phthalocyanine coordinated with magnesium [25]. It is obvious that strong deformation of molecules in crystal can lead to the change of probability

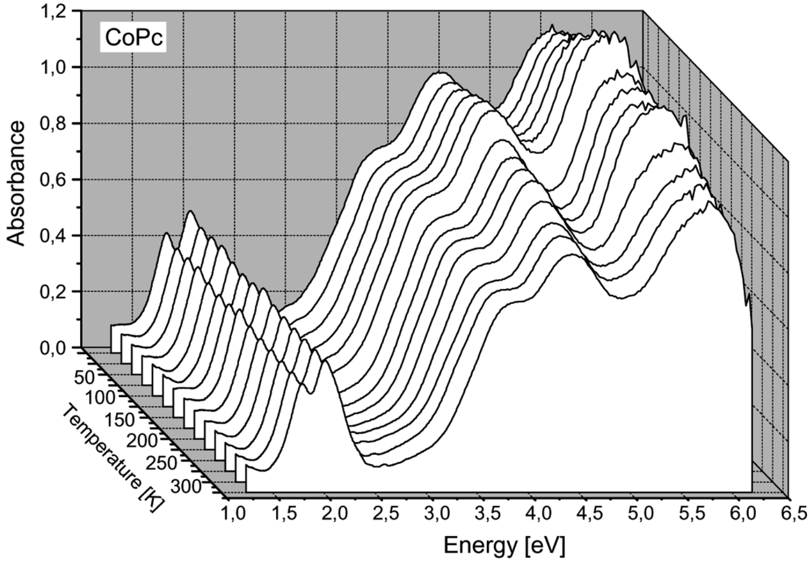

FIGURE 2 Absorption spectra of CoPc thin film measured at different temperatures.

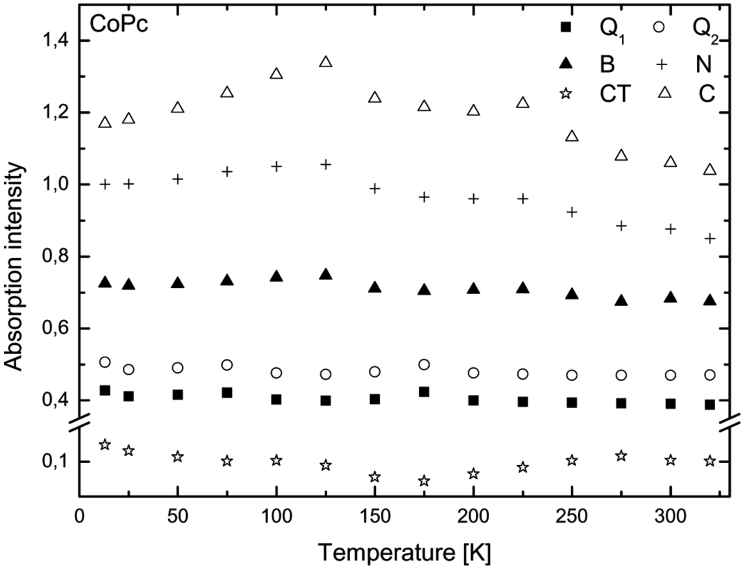

FIGURE 3 The thermal dependence of particular absorption bands intensities taken as maxima of the observed absorbance peaks.

of particular transitions even though the change of the molecular symmetry from D_{4h} for planar system to C_{4v} for non-planar, pyramidal structure. It is worth to note that observation of considerable thermal dependence of absorption spectra confirm polycrystalline nature of investigated layer. Only ordered arrangement of molecules in crystalline grain can lead to such strong intermolecular interaction. For amorphous layers this interaction is negligible and absorption spectra almost do not depend on temperature [26].

The optical constants of investigated layer can be calculated using reflection (R) and transmission (T) spectra by minimization of appropriately defined error function. It is commonly known that for optical spectra of very thin layers, which do not exhibit interference fringes the envelope methods proposed by Swanepoel [27] for transmission and Minkov [28] for reflection cannot be applied. However continuity of solutions obtained using typical single wavelength methods in the transparent region of sample should be much better in case of absence of the interference effect. In general optical constants of thin layer can be found by the numerical minimization of function [29,30]:

$$F_0 = \sum_{j=1}^{N} \Big[w_T (T_{\exp}(\lambda_j) - T_{calc}(n(\lambda_j), k(\lambda_j), d, \lambda_j))^2 + w_R (R_{\exp}(\lambda) - R_{calc}(n(\lambda_j), k(\lambda_j), d, \lambda_j))^2 \Big] \quad (1)$$

where N is the number of spectral points and w_T and w_R are weight factors which are proportional to the square of the reciprocal of transmission and reflection experimental error, respectively. The equations, which determine transmission and reflection of thin layer-substrate system are given elsewhere (see. appendix). Stenzel and Petrich [29] imposed additional constraints on the solution contours of n and k modifying the error function (1) in order to guarantee continuity and smoothness of solutions. The mentioned method connects advantages of both curve-fitting and single-wavelength techniques. In this work we propose similar approach, that is combination of single-wavelength and multi-wavelength methods but we impose more restricted additional constraints on the solution contours. In this connection we propose to minimize error function in the form:

$$F = F_0 + B_{nk} \quad (2)$$

where functional B_{nk} is described by equation:

$$B_{nk} = \beta_{nk} \sum_{j=1}^{N} \left[(n(\lambda_j) - \mathrm{Re}\sqrt{\varepsilon})^2 + (k(\lambda_j) - \mathrm{Im}\sqrt{\varepsilon})^2 \right] \quad (3)$$

where n is the refractive index, k-extinction coefficient of layer. β_{nk} in Eq. (3) is a weight factor while ε is the complex dielectric function which for highly absorptive materials like metallophthalocyanines can be written in the Lorentz-Lorenz form [31]:

$$\frac{\varepsilon-1}{\varepsilon+2}=A+BE^2+\frac{1}{\pi}\sum_{j}^{M}J_j\left[\frac{1}{E_{0j}-E-i\Gamma_j}+\frac{1}{E_{0j}+E+i\Gamma_j}\right] \tag{4}$$

where E_{oj}, Γ_j and J_j are resonant photon energy, linewidth and an intensity factor of jth transition, respectively. M denotes the number of resonance lines. The A and B are parameters, which gave consideration to absorption bands above measured spectral range. It means that favored solutions are those which fulfill simultaneously theoretical equations describing reflection and transmission layer-substrate system as well as Lorentz-Lorenz model. It should be pointed out that formulation of additional constraints on n and k contours leads to a mutual correlation between the dispersion and absorption behavior of the solutions as well as partially guarantee their continuity. The latter is caused by the fact that analytical function must be continuous and B_{nk} functional becomes large if discontinuities in the solution contours occur. However in contradiction to Stenzel technique, in presented method, we used in advance postulated dispersion and absorption laws in the form of the Lorentz-Lorentz function. For the sake of universality of used model, this method can be applied for materials with complicated dispersion and absorption behaviors such as organic materials for which optical spectra are characterized by few single or overlapping bands.

Figure 4 presents experimental and calculated transmission (T) and reflection (R) spectra for investigated CoPc thin layer. The T and R spectra were measured at normal and quasi-normal incidence, respectively in the spectral range 1.08–2.76 eV. The preliminary analysis of optical behavior leads to the conclusions that for smaller energies of photons (E $<$ 1.4 eV) the investigated layer is transparent and incident light is not absorbed and scattered ($T+R\approx 1$). For higher energy regions (E $>$ 1.4 eV) the inequality $R+T<1$ is fulfilled so process of absorption takes place. Optical constants (n, k, d) were calculated by minimization of error function (2) using conjugated gradient method. During calculations we assumed that two resonance lines ($M=2$, Eq. (4)) contribute to the observed bands in the measured spectral region. A weight factor (β_{nk}) was assumed equal 10^{-3}. The minimum of error function was found for layer thickness equal 36 nm. As we can see in Figure 4 the experimental and calculated spectra are almost identical. This fact is confirmed by a very small value of

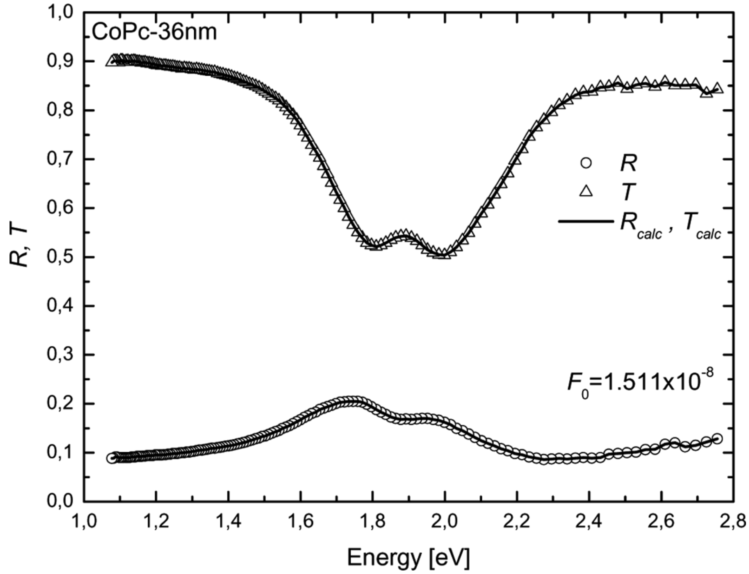

FIGURE 4 Experimental reflection (circle) and transmission (triangle) spectra for CoPc thin layer. Solid lines show spectra which were calculated basing on the minimization procedure.

F_0 error. Calculated refractive index and extinction coefficient as a function of photon energy are illustrated in Figures 5 and 6, respectively. As we expected the refractive index presents an anomalous dispersion in the absorption region as well as normal dispersion in the transparent region. The solid lines in these figures represent the Lorentz-Lorenz model which was simultaneously fitted to the real (n) and imaginary (k) part of complex refractive index. The corresponding fitting parameters are collected in Table 2. The presented fitting is quite satisfactory. The small misfit can be due to dimensional effects. The corresponding real (ε_1) and imaginary (ε_2) parts of dielectric constants were also calculated using well know equations:

$$\varepsilon_1 = n^2 - k^2 \tag{5}$$

$$\varepsilon_2 = 2nk \tag{6}$$

The spectral dependences of dielectric constants are presented in Figure 7. It is known that the real part of complex dielectric function describes dispersion and the imaginary part absorption process in matter. We can see that calculated real and imaginary parts of

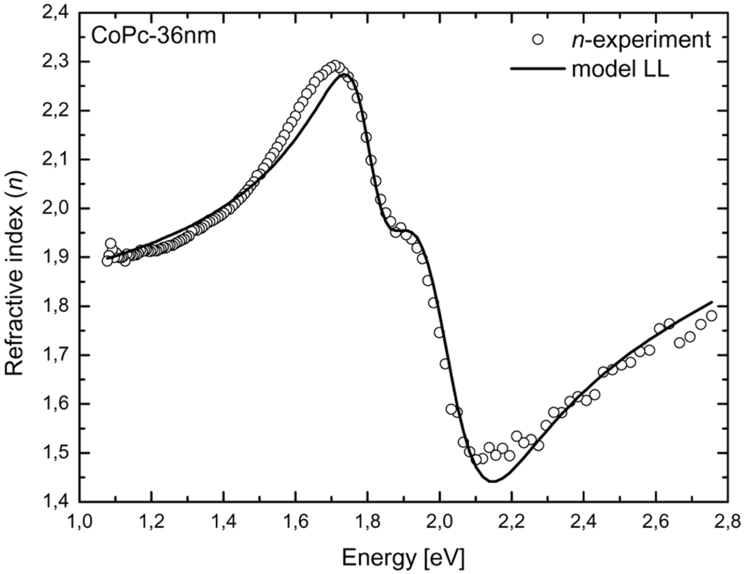

FIGURE 5 Refractive index of CoPc layer as a function of photon energy. Solid line represents Lorentz-Lorenz model fitted to the dispersion spectrum.

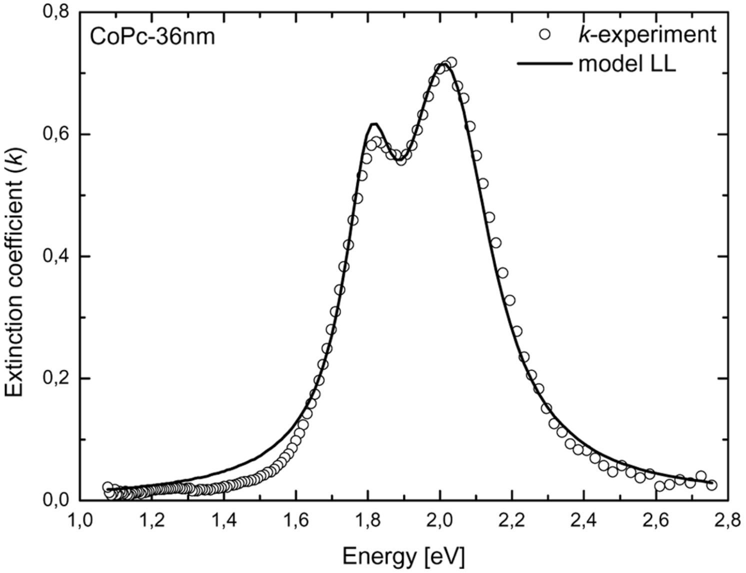

FIGURE 6 Extinction coefficient of CoPc layer as a function of photon energy. Solid line represents Lorentz-Lorenz model fitted to the absorption spectrum.

TABLE 2 Values Obtained from Fitting Lorentz-Lorenz Formula to Real and Imaginary Part of Complex Refractive Index

	Fitting parameters		
Band	J [eV]	E [eV]	Γ [eV]
Q_1	0.029	1.822	0.082
Q_2	0.126	2.055	0.138
A = 0.380; B = 0.014 $[\mathrm{eV}]^{-2}$			

dielectric constants resemble quite well refractive index and extinction coefficient spectral behavior, respectively.

The error in determining optical constants can be estimated by considering the effect of small changes in the input transmission and reflection data on the calculated optical constants. For this purpose we extract n, k and d values from test dataset of R and T (generated from known n, k, d values) which contain random noise up to ±1.5% for R and ±0.5% for T, simulating random experimental errors. It is commonly known that in the transparent region where absorption is very small the relative error in determining extinction coefficient can be very large [28]. However we found that in the region

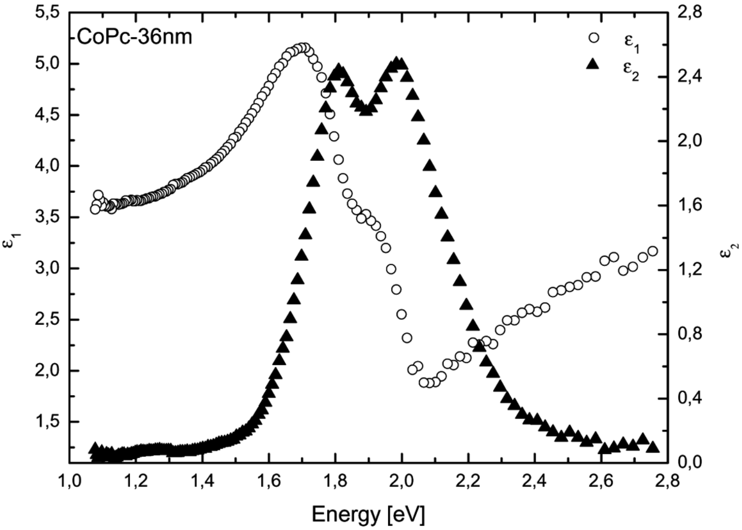

FIGURE 7 Real ε_1 and imaginary ε_2 part of complex dielectric constants as a function of photon energy.

of medium and high absorption ($k > 0.1$) the relative error in determining extinction coefficient do not exceeds 7.0%. The error in determining refractive index in the whole investigated spectral range is considerably smaller than that for extinction coefficient and it is less than 3.7%. The thickness of the layer was calculated with 1 nm accuracy.

The knowledge of extinction or absorption coefficient ($\alpha = 4\pi k/\lambda$) enables us to determine optical band gap of investigated material according procedure proposed by Tauc. In both amorphous and crystalline materials in the high absorption region ($\alpha > 10^4\,\mathrm{cm}^{-1}$) the absorption coefficient α depends on the photon energy E according the relation [32,33]:

$$\alpha E = A(E - E_g)^m \tag{7}$$

where A is a constant and E_g is optical band gap (Tauc band gap). Parameter m is equal 1/2 for allowed direct transitions and 3/2 for forbidden direct transitions. For indirect transitions and amorphous materials $m = 2$. The plot of $(\alpha E)^2$ versus E give a straight line what suggests that the fundamental absorption edge in investigated film is formed by the direct allowed transitions. The band gap was determined as the intersection with the energy axis of the straight line through the high-energy points of a graph of $(\alpha E)^2$ vs. E (see Fig. 8).

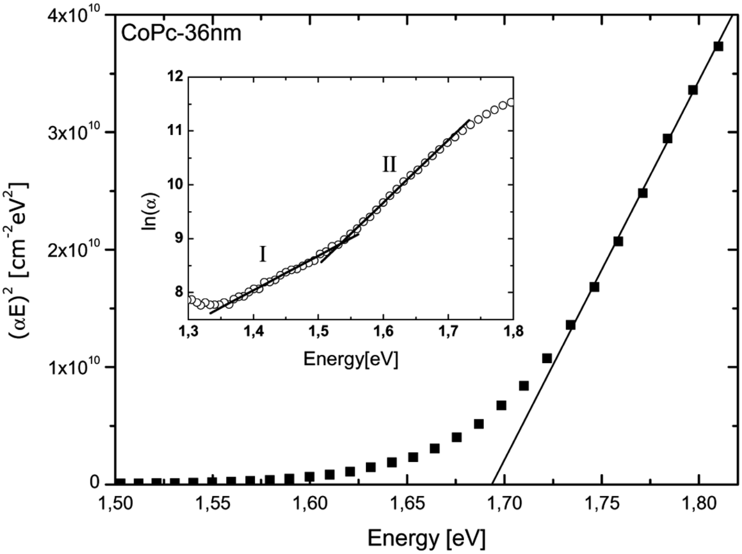

FIGURE 8 The dependence of $(\alpha E)^2$ versus the photon energy. In the inset the Urbach plot is presented.

We found that optical band gap for CoPc thin layer is equal 1.69 eV. Below optical band gap, where absorption is relatively low, the behavior of absorption curve exhibits exponential character. However the plot of ln(α) vs. photon energy shows two energy regions with different slope in which absorption grows exponentially (see the inset of Fig. 8). In this connection absorption spectrum below optical band gap can be described by two-exponential Urbach-like dependence [34]:

$$\alpha = \alpha_{01}\exp(E/E_{u1}) + \alpha_{02}\exp(E/E_{u2}) \tag{8}$$

where α_{01} and α_{01} are constants whereas E_{u1} and E_{u2} are Urbach energies for spectral region I and II in which the plot of ln(α) is linear. The values of E_{u1} and E_{u1} were calculated from the slope of linear fitting to the rectilinear segment of the ln(α) graph. The obtained Urbach energies are equal $E_{u1} = 0.156$ eV and $E_{u2} = 0.086$ eV for spectral region I and II, respectively. According to Schreiber and Toyozava [35] the Urbach tail of excitonic transitions can be explained as an effect of exciton-phonon coupling including the localization of exciton. Since we observe two distinct excitonic transitions (Q_1 and Q_2) in the considered spectral range, each of these transitions can produce exponential Urbach tail with different slope. However we cannot exclude that exponential increase of absorption is also connected with structural disorder and local field fluctuations in crystal.

In our previous works [23,36] we showed that phthalocyanine complexes coordinated with Mg^{2+} or Zn^{2+} ions exhibit photoluminescence even in solid phase. We also tried to measure photoluminescence properties of CoPc layer and solution, however the signal in both cases was undetectable even though we applied very sensitive phase resolved technique. Non-measurable photoluminescence of CoPc molecules can be explained by very strong spin-orbit coupling caused by the mixing of metal and ligand orbitals [37].

CONCLUSIONS

This work contains investigation results of the fundamental optical properties of CoPc thin layer which was grown by the thermal sublimation method on transparent, quartz substrate. For comparison this compound was also investigated in the solution form. The comparison of absorption spectra in solution and solid form leads to the conclusion that the dominant effects of crystallization are broadening and splitting of monomeric bands. These effects mainly result from intermolecular interaction in the layer. It was found that openshell configuration for CoPc molecule influence on the contribution of intramolecular charge transfer transitions in absorption spectra and non-measurable fluorescence in both solid and solution form. The temperature dependence investigations of absorption spectra revealed a polycrystalline nature of CoPc layer and a large influence of intermolecular interaction on its spectral properties. Optical constants of thin CoPc layer were determined using transmission and reflection spectra. Basing on computer simulations the errors of used method in determining optical constants were also estimated. It was found that in the whole investigated spectral region, the error in determining refractive index is considerably smaller than that for extinction coefficient. The knowledge of absorption coefficient enabled us to determine the optical band gap of CoPc layer. Optical transition connected with Q band was found to be direct and allowed. We found that for energy smaller than optical band gap absorption coefficient increase exponentially. This effect was explained by exciton-phonon interaction.

APPENDIX

Equations describing transmission and reflection of thin layer-substrate system can be obtained by summing the electric fields of the multiply reflected beams in the coherent limit in layer as well as summing of the multiply reflected beams intensities in the incoherent limit in the substrate. Consequently, normal transmission and reflection of layer-non-absorbing substrate system in air medium are given by quite complicated equations [28,38,39,40]:

$$T = \frac{Ax}{B - (C\cos 2\delta - D\sin 2\delta)x + Ex^2} \tag{9}$$

$$\begin{aligned} R = {} & \frac{A' - (B'_1\cos 2\delta - B'_2\sin 2\delta)x + C'x^2}{A'' - (B''_1\cos 2\delta - B''_2\sin 2\delta)x + C''x^2} \\ & + \frac{A'''x^2}{[A'' - (B''_1\cos 2\delta - B''_2\sin 2\delta)x + C''x^2]} \\ & \times \frac{1}{[D'' - (E''_1\cos 2\delta - E''_2\sin 2\delta)x + F''x^2]} \end{aligned} \tag{10}$$

where

$A = 16n_s(n^2 + k^2)$

$B = [(n+1)^2 + k^2][(n+1)(n+n_s^2) + k^2]$

$C = 2[(n^2 - 1 + k^2)(n^2 - n_s^2 + k^2) - 2k^2(n_s^2 + 1)]$

$D = 2k[2(n^2 - n_s^2 + k^2) + (n_s^2 + 1)(n^2 - 1 + k^2)]$

$$
\begin{aligned}
E &= [(n-1)^2 + k^2][(n-1)(n-n_s^2) + k^2]\\
A' &= [(n-1)^2 + k^2][(n+n_s)^2 + k^2]\\
B'_1 &= 2[(n^2+k^2-1)(n^2+k^2-n_s^2) + 4k^2 n_s]\\
B'_2 &= 4k[n_s(n^2+k^2-1) - (n^2+k^2-n_s^2)]\\
C' &= [(n^2+1)^2 + k^2][(n-n_s)^2 + k^2]\\
A'' &= [(n+1)^2 + k^2][(n+n_s)^2 + k^2]\\
B''_1 &= 2[(n^2+k^2-1)(n^2+k^2-n_s^2) - 4k^2 n_s]\\
B''_2 &= 4k[n_s(n^2+k^2-1) + (n^2+k^2-n_s^2)]
\end{aligned}
$$

$$
\begin{aligned}
C'' &= [(n-1)^2 + k^2][(n-n_s)^2 + k^2]\\
A''' &= 64 n_s (n_s-1)^2 (n^2+k^2)^2\\
D'' &= [(n+1)^2 + k^2][(n+1)(n+n_s^2) + k^2]\\
E''_1 &= 2[(n^2+k^2-1)(n^2+k^2-n_s^2) - 2k^2(n_s^2+1)]\\
E''_2 &= 2k[(n^2+k^2-n_s^2) + (n_s^2+1)(n^2+k^2-1)]\\
F'' &= [(n-1)^2 + k^2][(n^2-1)(n-n_s^2) + k^2]\\
x &= \exp(-\alpha d), \alpha = \frac{4\pi k}{\lambda}, \ \delta = \frac{2\pi n d}{\lambda}.
\end{aligned}
$$

In above equations n, n_s, k, α, δ and d are refractive indices of layer and substrate, extinction and absorption coefficient of layer, phase shift and layer thickness, respectively.

REFERENCES

[1] Braun, A. (1907). *J. Tcherniac. Ber. Deut. Chem. Ges.*, *40*, 2709.

[2] McKeown, N. B. (1998). *Phthalocyanine Materials: Synthesis, Structure and Function*, Cambridge University Press: Cambridge.

[3] Wojdyła, M., Derkowska, B., Rębarz, M., Bratkowski, A., & Bała, W. (2005). *J. Opt. A: Pure Appl. Opt.*, *7*, 463.

[4] Wojdyła, M., Derkowska, B., Bała, W., Bratkowski, A., Korcala, A. (2006). *Opt. Mater.*, *28*, 1000.

[5] Aziz, H., Popovic, Z. D., Hu, N. X., Hor, A. M., Xu, G. (1999). *Science*, *283*, 1900.

[6] Forsythe, E. W., Abkowitz, M. A., & Gao, Y. (2000). *J. Phys. Chem., B*, *104*, 3948.

[7] Vestweber, H. & Rie, W. (1997). *Synthetic Met.*, *91*, 181.

[8] Zhu, L., Tang, H., Harima, Y., Yamashita, K., Ohshita, J., & Kunai, A. (2002). *Synthetic Met.*, *126*, 331.

[9] Westphalen, M., Kreibig, U., Rostalski, J., Lüth, H., & Meissner, D. (2000). *Sol. Energ Mat. Sol. C.*, *61*, 97.

[10] Xue, J., Uchida, S., Rand, B. P., & Forrest, S. R. (2004). *Appl. Phys. Lett.*, *85*, 5757.

[11] Yasuda, T. & Tsutsui, T. (2005). *Chem. Phys. Lett.*, *402*, 395.

[12] Kalinowski, J. (2005). *Organic Light-Emitting Diodes*, Marcel Dekker: New York.

[13] Stillman, M. J. *et al.* (1989). Phthalocyanines properties and applications. Leznoff, C. C. & Lever, A. B. P. (Eds), VCH: New York, Chapter 3, 133.

[14] Mack, J. & Stillman, M. J. (2001). *Coord. Chem. Rev.*, *219*, 993.

[15] McHugh, A. J., Gouterman, & M., Weiss, C. (1972). *Theor. Chim. Acta*, *24*, 346.

[16] Gouterman, M., Wagniere, G. H., & Snyder, L. C. (1963). *J. Mol. Spectrosc.*, *11*, 2.

[17] Liang, X. L., Flores, S., Ellis, D. E., Hoffman, B. M., Musselman, R. L. (1991). *J. Chem. Phys.*, *95*, 403.

[18] El-Nahass, M. M., El-Gohary, Z., & Soliman, H. S. (2003). *Opt. Laser Technol.*, *35*, 523.

[19] Liao, M. S. & Scheiner, S. (2001). *J. Chem. Phys.*, *114*, 9780.

[20] Moigne, J. L., Even, R. (1985). *J. Chem. Phys.*, *83*, 6472.

[21] Davydov, A. S. (1962). *Theory of Molecular Excitons*, Mcgraw-hill: New York.

[22] Pope, M. *et al.* (1982). *Electronic Processes in Molecular Crystals*, Clarendon Press: Oxford.

[23] Wojdyła, M., Bała, W., Derkowska, B., Rębarz, M., & Korcala, A. (2007). *Opt. Mater.*, in Press.

[24] Tackley, D. R., Dent, G., & Smith, W. E. (2001). *Phys. Chem. Chem. Phys.*, *3*, 1419.

[25] Janczak, J. & Kubiak, R. (2001). *Polyhedron*, *20*, 2901.

[26] Endo, A., Matsumoto, S., & Mizuguchi, J. (1999). *J. Phys. Chem., A 103*, 8193.

[27] Swanepoel, R. (1983). *J. Phys. E: Sci. Instrum.*, 16, 1214.

[28] Minkov, D. A. (1989). *J. Phys. D: Appl. Phys.*, *22*, 1157.

[29] Stenzel, O., Petrich, R. (1995). *J. Phys. D: Appl. Phys.*, *28*, 978.

[30] Laghla, Y. & Scheid, E. (1997). *Thin Solid Films*, *306*, 67.

[31] Stenzel, O., Wilbrant, S., Stendal, A., Beckers, U., Voigtsberger, K., & von Borczyskowski, C. (1995). *J. Phys. D: Appl. Phys.*, *28*, 2154.

[32] Yakuphanoglu, F., Atalay, Y., Sekerci, M. (2005). *J. Mol. Struct.*, *779*, 72.

[33] El-Nahass, M. M., Farag, A. M., El-Rahman, K. F. A., & Darwish, A. A. A. (2005). *Opt. Laser Technol.*, *37*, 513.

[34] Yakuphanoglu, F., Cukurovali, A., & Yilmaz, I. (2004). *Physica B*, *353*, 210.

[35] Schreiber, M. & Toyozawa, Y. (1982). *J. Phys. Soc. Japan*, *51*, 1544.

[36] Wojdyła, M., Bała, W., Derkowska, B., Łukasiak, Z., Czaplicki, R., Luc, J., Sofiani, Z., Dabos-Seignon, S., Sahraoui, B. (2006). *Nonlin. Opt. Quant. Opt.*, *35*, 103.

[37] Huang, T. H., Rieckhopp, K. E., & Voigt, E. M. (1977). *Chem. Phys.*, *19*, 25.

[38] Kubinyi, M., Benkö, N., Grofcsik, A., & Jones, W. J. (1996). *Thin Solid Films*, *286*, 164.

[39] Birgin, E. G., Chambouleyron, I. E., Martinez, J. M., Ventura, S. D. (2003). *Appl. Numer. Math.*, *47*, 109.

[40] Birgin, E. G., Chambouleyron, I., & Martinez, J. M. (1999). *J. Comput. Phys.*, *151*, 862.