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# Thin Films of Chlorosubstituted Vanadyl Phthalocyanine: Charge Transport Properties and Optical Spectroscopy Study of Structure

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## **Abstract**

Electrophysics and structure of thin films of chlorosubstituted vanadyl phthalocyanine (VOPcCl<sub>16</sub>) were studied using complementary experimental and theoretical techniques. To study charge transport properties of the latter films, organic field-effect transistors were fabricated by physical vapor deposition. The device exhibited good air stability without any extent of degradation after a storage in air for two months. The charge carrier mobility was measured to be  $(2.0\pm 0.1)\times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. This value was rationalized by poor ordering of the VOPcCl<sub>16</sub> films revealed with the use of polarization dependent Raman and UV-vis spectroscopies as well as by X-ray diffraction. Apart from this, we performed a detailed assignment of all intense bands in the vibrational spectra of VOPcCl<sub>16</sub>. To this end, the experimental IR and Raman data were complemented by quantum chemical (DFT) calculations at the B3LYP/6-311++G(2df,p) level of theory.

**Keywords:** Organic field-effect transistors; thin films; charge carrier mobility; chlorosubstituted oxometal phthalocyanines; vibrational spectroscopy; DFT calculations.

## 1. Introduction

Metallophthalocyanines (MPcs) have numerous applications in chemistry and materials science due to their enhanced thermal stability and facile and cheap synthetic procedures. Among numerous applications of thin films of metallophthalocyanines (MPcs), these species are widely used as active layers in molecular electronic devices [1]. More specifically, halogenated MPc derivatives (viz., hexadecafluoro- and hexadecachlorosubstituted compounds) are currently of significant interest due to their relatively high mobility of charge carriers and n-type semiconducting nature [2, 3]. More specifically, the electron mobility was measured to be  $(3-8)\times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  (depending on the procedure of the dielectric layer preparation) in the air-stable organic field-effect transistors (OFET) multilayer structures based on hexadecafluorosubstituted copper phthalocyanine ( $\text{CuPcF}_{16}$ ) [2, 4]. Apart from this, OFETs fabricated with the use of  $\text{CuPcF}_{16}$  nanoribbons exhibited electron mobility of  $(2-4)\times 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  depending on particular dielectric layers employed [5, 6]. Among the similar MPc congeners, the highest mobility ( $1.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) was achieved for organic single crystal field-effect transistors based on  $\text{ZnPcF}_{16}$  [7]. Note that the structure and interface properties of thin films of fluorinated 3d-metal phthalocyanines  $\text{MPcF}_{16}$  ( $M = \text{Cu}, \text{Co}, \text{Zn}$ ) were studied using a number of experimental structural techniques (e.g., X-ray photoelectronic spectroscopy and X-ray diffraction) [7-11].

On the other hand, the films of chlorosubstituted phthalocyanines of 3d-metals have attracted profoundly less attention. E.g., chlorine substitution in MPc was shown to modify solubility, conductivity, nonlinear optical and photochemical properties of MPc films [12, 13]. In a recent work, the authors [14] studied the annealing temperature dependence of the optical band gap of the  $\text{FePcCl}_{16}$  thin films and considered possible applications of the latter as components of molecular electronic devices. Furthermore, the array of rectangular microtubes of  $\text{CuPcCl}_{16}$  with a large interior width of  $1.4 - 1.8 \text{ }\mu\text{m}$  and thin walls ( $80 - 100 \text{ nm}$ ) was synthesized and characterized by means of scanning and transmission electron

microscopies, XRD, FTIR, and X-ray photoelectron spectroscopy [15]. Apart from this, the charge carrier mobility in the air-stable n-channel CuPcCl<sub>16</sub> transistor was determined to be  $\sim 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for the thin films deposited at an elevated substrate temperature [12].

In contrast to the most part of planar MPc, oxometal phthalocyanines, viz., vanadyl and titanyl phthalocyanines (VOPc and TiOPc, respectively), are prone to a particular polymorphism, which is notably different from that of the former species [16, 17]. VOPc species with a permanent electrical dipole moment are prone to two-dimensional  $\pi$ - $\pi$  stacking, which leads to the presence of convex and concave pairs of these molecules in the crystal structure [17]. This results in a shorter intermolecular distance in comparison with planar phthalocyanines and larger  $\pi$ - $\pi$  stacking overlap, which, in turn, render promising the high-performance organic thin film transistors (OTFT) based of these species [2, 18-21]. Recently some of us have studied the structure and polymorphism of thin films of vanadyl hexadecafluorophthalocyanine (VOPcF<sub>16</sub>) prepared by physical vapor deposition (PVD) using X-ray and optical spectroscopy techniques [22]. The pristine VOPcF<sub>16</sub> films had a linear co-facial structure with average tilt angles of a phthalocyanine macroring plane with respect to the substrate plane of  $\sim 60^\circ$ . Annealing at the temperatures  $\sim 200^\circ \text{C}$  led to irreversible polymorphic phase transition to a slipped dimeric structure with mean values of a tilt angle of  $\sim 30^\circ$ . Note that after this phase transition the in-plane conductivity in the films of VOPcF<sub>16</sub> decreased noticeably (up to  $\sim 100$  times) [22].

It is therefore reasonable to scrutinize another promising species in the halogenated VOPc series, viz., VOPcCl<sub>16</sub> (Fig. 1). To our knowledge, electrophysics and other properties of the thin films of this species have never been scrutinized so far. Therefore, in the present contribution, we fabricated the organic field-effect transistors and studied charge transport properties of the thin films of VOPcCl<sub>16</sub>. To rationalize the observed facts, we also studied the molecular organization in the VOPcCl<sub>16</sub> thin films prepared by PVD using optical spectroscopy techniques (UV-vis and polarization dependent Raman spectroscopy). Apart from this, to apply properly the latter methodology, we studied all corresponding

normal coordinates and assigned all intense IR and Raman bands of VOPcCl<sub>16</sub> using complementary experimental (spectroscopic) and theoretical (density functional theory calculations) techniques.

## 2. Experimental and computational details

### 2.1. Synthesis

Vanadyl hexadecachlorophthalocyanine (VOPcCl<sub>16</sub>) was synthesized in line with the literature procedures proposed for other MPcCl<sub>16</sub> derivatives [13]. The 4:1 mixture of sublimed 3,4,5,6-tetrachlorophthalato-1,2-dinitrile (supplied from Aldrich) and crystalline V<sub>2</sub>O<sub>5</sub> was heated in a vacuum-sealed glass tube (10<sup>-3</sup> Torr). The obtained VOPcCl<sub>16</sub> was purified by vacuum gradient sublimation at a residual pressure of 10<sup>-5</sup> Torr.

### 2.2. Preparation of thin films and transistor structures

Thin films of VOPcCl<sub>16</sub> were prepared by physical vapor deposition (PVD) using ultra-high vacuum conditions (10<sup>-8</sup> mbar). A quartz crystal microbalance was used for measurements of a nominal thickness of deposited films. The latter value was estimated to be about 100 nm for all films studied. To make a bottom gate organic thin film transistor (OTFT) with a channel length  $L=10\ \mu\text{m}$  and width  $W=1\ \text{mm}$ , a 100 nm thick VOPcCl<sub>16</sub> film was deposited on a prefabricated gold (thickness of 50 nm) drain and source electrode systems. An Ohmic gate terminal was formed by applying a Ga–In eutectic layer on the reverse side of the Si wafer after etching the layer of a native oxide. The gate dielectric was a 300 nm thick silicon dioxide (capacitance per unit area  $C_i=10\ \text{nF cm}^{-2}$ ) thermally grown on an n-doped Si(100) wafer with a resistivity of 0.005  $\Omega\ \text{cm}$ . In order to improve the quality of the interface between the organic semiconductor and gate dielectric layers, an octadecyltrichlorosilane (OTS) monolayer was self-assembled on the oxide layer by dipping the substrates in 1% solution of OTS in ethanol. This procedure was shown to improve remarkably the performance of the OTFTs built on CuPc and CuPcCl<sub>16</sub> [12, 23]

### 2.3. Instruments

The X-ray diffraction patterns of VOPcCl<sub>16</sub> films were obtained using Shimadzu XRD-7000 powder diffractometer (Cu-anode sealed tube, Bragg-Brentano geometry, out-of-plane scan,  $\theta$ -2 $\theta$  goniometer, scintillation counter). The Raman spectra were recorded with a HR 800 spectrometer (Horiba Jobin Yvon). The spectra were measured in a backscattering geometry using a BX 41 microscope. Nd:YAG laser line (532 nm) was used for spectral excitation. The spectral resolution of various diffraction gratings was 1.5 - 3 cm<sup>-1</sup>. To determine the depolarization ratios, the parallel and perpendicular polarized Raman spectra were recorded using the corresponding polarizers. In order to protect samples from damage, the laser power was attenuated with the use of D1 laser filters. IR spectra were recorded in polyethylene and KBr pellets using a Vertex 80 FTIR spectrometer. The UV/Vis spectra were recorded using a Shimadzu UV-3101PC spectrophotometer. The OTFT characteristics were measured at room temperature under air atmosphere for the transistors comprised of VOPcCl<sub>16</sub> films using a microprocessor controlled Keithley 93 I-V measurement system. The drain voltage was varied from 0 to 40 V with a rate of 50 mV s<sup>-1</sup>.

### 2.4. Quantum chemical calculations

Vibrational spectra of VOPcCl<sub>16</sub> were computed using density functional theory at the B3LYP/6-311++G(2df,p) level [24, 25]. Ultrafine integration grids were employed for numerical solving of the Kohn-Sham equations. Due to strong mixing of collective lattice modes and intramolecular vibrations in the low wavenumber region, we did not consider the experimental bands below 150 cm<sup>-1</sup>. Almost all metal phthalocyanines have strong electronic absorption lines in the UV-vis spectral region used for excitation. Due to this fact, their Raman spectra have strong resonant nature, which we did not consider

and therefore did not calculate the Raman intensities. Gaussian 09 program package was used for quantum chemical calculations [26].

### 3. Results and discussion

#### 3.1 Field-effect mobility of charge carriers in the VOPcCl<sub>16</sub> film

To study the electrophysical properties of VOPcCl<sub>16</sub> films, we fabricated the organic thin film transistor (OTFT). Fig. 2 shows a source-drain current ( $I_{DS}$ ) as a function of a drain-source voltage ( $V_{DS}$ ) characteristics at various versus source-gate voltage values ( $V_G$ ) of the OTFT studied. As seen from Fig. 2, the linear dependence is followed by a saturation region upon the increase of drain-source voltage ( $V_{DS}$ ). The source current  $I_{DS(sat)}$  was found to saturate at  $V_{DS}$  values about 70 V at all  $V_G$  values used. Consequently, in the saturation regime the field-effect mobility can be directly obtained from the well known quadratic dependence of the saturated drain-source current  $I_{DS(sat)}$  on  $V_G$  [27, 28]:

$$I_{DS(sat)} = \mu \frac{W}{2L} C_i (V_G - V_T)^2 \quad (1)$$

where  $C_i$  is the capacitance per unit area of the insulator layer (in our case, 10 nF cm<sup>-2</sup>),  $V_T$  is the threshold voltage of a transistor switching, and  $\mu$  is the field-effect mobility.

The plots in Fig. 3 show the transfer curves of  $I_{DS}$  versus source-gate voltage  $V_G$  for the same OTFT measured in the saturation regime at  $V_{DS} = 80$  V. In a good accord with (1), the square root of  $I_{DS}$  as a function of  $V_G$  was found to be linear (Fig. 3b, black squares). The values of  $\mu$  and  $V_T$  were estimated from the slope and the intercept at  $I_{DS(sat)} = 0$  of the linear graphs, respectively. Finally, the charge carrier mobility in the VOPcCl<sub>16</sub> films was found to be  $(2.0 \pm 0.1) \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. Note that all measurements were performed under ambient conditions.

Recall that the thin film of a closely related hexadecahalogenated copper phthalocyanine (CuPcF<sub>16</sub>) deposited on a substrate heated to 125 °C behaved as an air-stable n-channel transistor with a maximum

electron field-effect mobility of  $3 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [2]. The air-stable transistor performance with a charge carrier mobility of  $\sim 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  was also observed for the films of  $\text{CuPcCl}_{16}$  organic semiconductor [12]. The disordered  $\text{FePcCl}_{16}$  films also demonstrated good stability in air atmosphere, however, their field-effect mobility was profoundly lower, viz.,  $\sim 2.7 \cdot 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [2]. On the other hand, the devices based on unsubstituted vanadyl phthalocyanine (VOPc) films deposited on the pure  $\text{Si/SiO}_2$  substrates and their counterparts modified by various silane derivatives (e.g., octadecyltrichlorosilane, (3-chloro)propyltriethoxysilane, and vinyltriethoxysilane) exhibited the mobility ranging from  $3 \times 10^{-3}$  to  $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  depending on the morphology and orientation of the films [19]. It is seen that the field-effect mobility of  $\text{VOPcCl}_{16}$  films measured in the present work ( $2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) is *ca.* order of magnitude lower in comparison with the halogenated CuPc species [2], but is close to that of the VOPc films. More generally, the observed mobility value is common of phthalocyanine films grown under typical conditions without particular efforts spent toward obtaining oriented films [29-31].

We also scrutinized the air-stability of the  $\text{VOPcCl}_{16}$ -based OTFT. To this end, the devices were exposed to air (under ambient light) for 60 days. The charge carrier mobility was measured every 10 days in accordance with the above-described procedure (Fig. S1, Supporting Information). As seen from Fig. S1, the devices exhibited good air stability without a notable degradation even upon two-month exposure to air.

At the same time, the structure (e.g., molecular ordering, crystal phase composition, and molecular orientation) and morphology (grain size and boundary) of semiconductor film are crucial for carrier mobility in OTFT [19]. In order to rationalize on the molecular level the observed values of charge carrier mobility in the  $\text{VOPcCl}_{16}$  films, we scrutinized the structural organization of the latter. However, the conventional out-of-plane X-ray diffraction technique did not clarify any issues in the present case.

The XRD pattern of VOPcCl<sub>16</sub> film exhibits only a diffuse peak with the maximum at about 6° (Fig. S2, Supporting Information), indicating a low extent of crystallinity of the film.

Nevertheless, among various experimental approaches, the methodology based on vibrational spectroscopy (e.g., polarization dependent Raman spectroscopy) may offer valuable insights into structure and molecular arrangement of thin films. The latter method is particularly useful in the case of partially oriented films and/or species possessing unknown crystal structure, because the widely used X-ray diffraction methods are not directly applicable in this case [22, 32-37]. However, for proper application of Raman spectroscopy in structural studies, the detailed assignment of vibrational spectra (more specifically, the symmetry irreducible representations of all intense Raman active bands) is absolutely crucial. Unfortunately, to our knowledge, the vibrational spectra of VOPcCl<sub>16</sub> have not been discussed in the literature. Therefore, to obtain a comprehensive outlook and assign clearly all intensive vibrational bands, in the present contribution we complemented the experimentally measured IR and Raman spectra with insights from theory (viz., DFT calculations).

### 3.2. *Experimental and theoretical vibrational spectra of VOPcCl<sub>16</sub>*

Fig. 4 represents the DFT optimized structure of VOPcCl<sub>16</sub> corresponding to the global minimum on the potential energy surface. The full structural description of the latter species is available in the Supporting Information (Table S1). Note that bulky Cl substituents lead to the non-planar distortion of the phthalocyanine macrocycle (Fig. 4). As a result, VOPcCl<sub>16</sub> has a lower symmetry ( $C_{2v}$ ) in comparison with the VOPc and VOPcF<sub>16</sub> counterparts ( $C_{4v}$ , respectively) [22]. Assuming the  $C_{2v}$  point group for the VOPcCl<sub>16</sub> comprised of 58 atoms, the corresponding vibrational representation reads as  $\Gamma = 44 A_1 + 40 A_2 + 42 B_1 + 42 B_2$ . The modes of all symmetry type are Raman active, and the  $A_1$ ,  $B_1$  and  $B_2$  modes are IR active.

The experimental IR and Raman and calculated IR spectra of VOPcCl<sub>16</sub> are shown in Fig. 5. Table S2 (Supporting Information) represents a comparison of the experimental and calculated wavenumbers of the strongest vibrational bands of VOPcCl<sub>16</sub>. The assignment of experimental fundamental bands was performed using the DFT calculated wavenumbers and intensities. In several unclear cases, the IR intensities were used along with the Raman data. Apart from this, Supporting Information also contains the experimental far IR spectra of VOPcCl<sub>16</sub> (Figure S3).

As seen from Table S2 and Fig. 5, the experimental wavenumbers of VOPcCl<sub>16</sub> fundamentals are in a good agreement with their DFT calculated counterparts (the RMS difference between theory and experiment is 16 cm<sup>-1</sup>). It is instructive to compare the vibrational spectra of VOPcCl<sub>16</sub> with its closest congeners, viz., VOPcF<sub>16</sub> and VOPc [22]. Note that more bands were observed in the IR and Raman spectra of the VOPcCl<sub>16</sub> in comparison with the VOPc and VOPcF<sub>16</sub> (Fig. 5) [22]. This fact is in line with the lower symmetry (*C*<sub>2v</sub> point group) of this species in comparison with VOPc and VOPcF<sub>16</sub> (*C*<sub>4v</sub> symmetry).

It is natural to expect that the introduction of heavy chlorine substituents to the phthalocyanine macrocycle leads to the red shift of wavenumbers of some modes in comparison with the case of VOPc [22]. However, the changes in the electronic structure upon substitution render the spectral changes more complicated. Let us consider the instructive example: viz., the mode at 1609 cm<sup>-1</sup> in the experimental IR spectrum of VOPc corresponding to benzene ring stretching vibrations [22]. Upon Cl-substitution in VOPcCl<sub>16</sub> this band shifts down to 1563 cm<sup>-1</sup> (Table S2), while in the case of VOPcF<sub>16</sub>, the wavenumber of this mode *increases* to 1637 cm<sup>-1</sup> [22]. Therefore, along with the naturally expected modifications in the reduced mass values, the force constants changes also play an important role. This fact can be explained by a tiny interplay of mesomeric (+M) and induction (-I) effects: +M dominates over -I effect in the case of F substituents, and the electron-withdrawing nature of chlorine atoms renders -I effect stronger than +M [38]. Apart from this, the normal coordinates of some modes (viz., those at

236, 294, 670, 819, 1082, 1088, and 1184  $\text{cm}^{-1}$ ) also change, mainly due to an increasing contribution of C-C-Cl bendings and C-Cl stretching vibrations (Table S2).

Note that there are four strong bands at 1208, 1273, 1302 and 1390  $\text{cm}^{-1}$  (Fig. 5a) in the IR spectral range 1200–1400  $\text{cm}^{-1}$  of VOPcCl<sub>16</sub>. The isoindole and pyrrole deformations mainly contribute to the normal coordinates of these vibrational bands (Table S2). It is also instructive to consider the V=O stretching mode of VOPcCl<sub>16</sub>. According to DFT predictions, it lies at 1068  $\text{cm}^{-1}$  (Table S2), while in the experimental IR spectrum this band is located at 1020  $\text{cm}^{-1}$  (Fig. 5a, Table S2). Similar to the case of VOPc [22], the notable disagreement between the experiment and computations can be explained by the intermolecular interactions in the crystal, which shift the wavenumber of this band.

The totally symmetric band ( $A_1$ ) with dominating contributions from a macroring breathing coordinate and V-N<sub>α</sub> bond stretching (the atoms are denoted in accordance with Fig. 1) lies at 593 and 589  $\text{cm}^{-1}$  in the Raman spectra of VOPc and VOPcF<sub>16</sub>, respectively [22]. The corresponding wavenumber shifts to 519  $\text{cm}^{-1}$  upon Cl-substitution VOPcCl<sub>16</sub> (Table S2). Finally, the strongest band in the far IR spectral region (100-450  $\text{cm}^{-1}$ ) of VOPcCl<sub>16</sub> was observed at 417  $\text{cm}^{-1}$  (Fig. S3, Supporting Information). This band can be assigned to V-N<sub>α</sub> stretching together with N<sub>α</sub>-V=O deformation vibration (Table S2).

### 3.3. Structure of the thin films of VOPcCl<sub>16</sub>

After the detailed assignment of Raman active bands of VOPcCl<sub>16</sub>, we applied the polarization dependent Raman spectroscopy to shed more light on the molecular orientation in the thin films of VOPcCl<sub>16</sub>. To this end, we recorded the polarized Raman spectra of VOPcCl<sub>16</sub> films in both parallel (in the Porto notation,  $z(xx)\bar{z}$ ) and cross polarizations ( $z(xy)\bar{z}$ ), respectively. The technical details of this experimental approach are described elsewhere [39-41]. Note that the molecular orientation is described in the Euler coordinates [42]. The detailed description of the methodology employed is also given elsewhere [42, 43]. The use of the azimuthally averaged molecular orientation model [43] is justified by the observed absence of azimuthal anisotropy in the depolarization ratio  $\rho = I(z(xy)\bar{z})/I(z(xx)\bar{z})$ . Thus,

after the proper azimuthal averaging, the intensity ratio transformed from the molecular to substrate coordinates reads as:

$$I_{\parallel\perp} = \int_0^{2\pi} (e_i^\parallel \cdot (R(\varphi, \theta, \psi)^T \cdot A_1^{\parallel\perp} \cdot R(\varphi, \theta, \psi)) \cdot e_s^{\parallel\perp})^2 d\varphi \quad (2)$$

where  $e_i$  and  $e_s$  denote the unit electric field vectors of the incident ( $i$ ) and scattered ( $s$ ) light w.r.t. the polarization vector (in the Porto notation, these are  $z(xx)\bar{z}$  ( $\parallel$ ) and  $z(xy)\bar{z}$  ( $\perp$ ), respectively) [40].

Note that the Euler angle  $\theta$  refers to the tilt angle between the plane of a molecule and a substrate in the chosen coordinate system. Consequently, for the modes of the given symmetry type, there is a one-to-one correspondence between the tilt angle  $\theta$  and the depolarization ratios  $\rho$  in accordance with (2) [40].

Fig. 6 represents the polarized Raman spectra recorded in the parallel and cross polarizations of VOPcCl<sub>16</sub> films with a nominal thickness of 100 nm deposited on a glass substrate. The A<sub>1</sub>, B<sub>1</sub> and B<sub>2</sub> modes, which are well separated from other counterparts in the Raman spectra of VOPcCl<sub>16</sub> (Table S2), were used to determine the molecular orientation in the thin films. Note that the A<sub>1</sub> modes (viz. those at 320, 684, 742, 850, 962, 1172, 1302, and 1500 cm<sup>-1</sup>) exhibit a distinct dependence of the depolarization ratio on the orientation (Fig. 6). As mentioned in the previous section, in contrast to the VOPc and VOPcF<sub>16</sub>, the VOPcCl<sub>16</sub> molecule has a C<sub>2v</sub> symmetry. Therefore, in the present case the tilt angle should be estimated using the polarizability tensor for C<sub>2v</sub> point group. However, this would introduce a third tensor element due to the additional twist between the benzene rings [44]. Thus, we assumed the polarizabilities of the VOPcCl<sub>16</sub> in  $x$  and  $y$  directions to be the same. In other words, to simplify the calculations of the tilt angles, we treated the VOPcCl<sub>16</sub> as if it were of the C<sub>4v</sub> symmetry.

The ratios of the intensities of the totally symmetric modes range between 0.12 and 0.15, while the ratios of the intensities of the B modes are equal to 0.75. The ratios of intensities of the corresponding vibrations in the  $z(xx)\bar{z}$  and  $z(xy)\bar{z}$  spectra were close to those in the spectra of solution or disordered samples [45]. Therefore, we concluded that the VOPcCl<sub>16</sub> films are *disordered*. This fact agrees well with the above discussed absence of any pronounced peaks in the XRD pattern of the VOPcCl<sub>16</sub> film.

Apart from this, we compared the UV-vis absorption spectra of VOPcCl<sub>16</sub> thin film (Fig. 7, red graphic) with that in the 1-chloronaphtalene solution (Fig. 7, blue graphic). The latter is comprised of the Q-band lying at 760 nm with a shoulder at 690 nm and differs from that of the VOPcF<sub>16</sub> film [22]. This Q-band is typical of phthalocyanine complexes and originates primarily from electronic promotions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) in the Pc core [46]. On the other hand, the shoulder at 690 nm is associated with the presence of aggregated species in the solution. The molecular organization in the MPc thin films notably affects the wavelength of the Q-band [47, 48]. At the same time, the films containing isolated Pc cores or amorphous films exhibit the spectra similar to those obtained from diluted MPc solutions. In the present case, the maximum of the Q-band (762 nm, Fig. 7) lies very close to that in the spectrum of a 1-chloronaphtalene solution (760 nm, Fig. 7). This fact is also in line with the amorphous nature of the VOPcCl<sub>16</sub> thin films studied.

It is worth mentioning that the unsubstituted VOPc and hexadecafluorinated VOPcF<sub>16</sub> phthalocyanine crystalline films grown under similar experimental conditions [22] exhibit a particular preferable orientation of crystallites w.r.t. a substrate surface. It is therefore seen that the chemical modification of a phthalocyanine ligand by introduction of chlorine electron withdrawing substituents significantly influences the molecular organization in thin films. In the particular case of VOPcCl<sub>16</sub>, the chlorine substituents make the intermolecular interactions (e.g.,  $\pi$ - $\pi$  in the stacks) so weak that the films with the ordered crystal domains cannot be formed at all.

#### 4. Conclusions

The organic field-effect transistors (OFET) were fabricated to study the charge transport properties of VOPcCl<sub>16</sub> thin films. An *n*-doped silicon was used as a substrate, with a gold contact functioning as the gate, and a SiO<sub>2</sub> layer of 300 nm as the gate dielectric with a capacitance per unit area of 10 nF cm<sup>-2</sup>.

Similarly to the parent MPc species and fluorinated MPcF<sub>16</sub> analogues [2, 5, 12], the device exhibited good air stability without any extent of degradation even after a storage in air for two months. The charge carrier mobility in the VOPcCl<sub>16</sub> thin films was found to be  $2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , which is well below than that of oriented MPc films grown on the surfaces with preliminarily deposited inducing or templating layers [49, 50]. This fact is in line with poor ordering of the VOPcCl<sub>16</sub> films revealed with use of polarization dependent Raman spectroscopy. However, the observed mobility value is comparable with that of phthalocyanine films grown under typical conditions without any special treatment of the substrate surface.

In a more general sense, thin films of chlorinated metal phthalocyanines are promising for further study due to their stability upon exposure to air and non-marginal values of electron mobility. More efforts are necessary toward preparing the ordered structures, which are expected to exhibit higher electron mobility.

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## **ASSOCIATED CONTENT**

### **Supporting Information**

Supporting Information is available free of charge on the Internet. DOI: xxxx.

Aging experiments and XRD pattern of the VOPcCl<sub>16</sub> films, DFT optimized geometry of VOPcCl<sub>16</sub>, detailed assignment of all intense bands in the IR and Raman spectra of VOPcCl<sub>16</sub>.

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