Preparation, Raman spectroscopy, surface morphology and optical properties of TiPcCl₂ nanostructured films: thickness effect

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Received: 28 January 2021 / Accepted: 15 July 2021 / Published online: 14 August 2021
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Abstract
Phthalocyanines are of a broad interest in photovoltaic applications. In this study, films of titanium-phthalocyanine-chloride (TiPcCl₂) were prepared by the thermal evaporation method. The molecular structure was studied by a Raman spectrometer, showing a match between the spectra of the powder and the prepared films. The films’ surface was examined by the atomic force microscope, revealing grain size and surface roughness of TiPcCl₂ thin films to be 223 and 41 nm, respectively, for a 100 nm thickness. The energy gap was determined to be 1.5 eV, with no observable effect by the thickness change. Additionally, the linear and nonlinear optical constants were calculated from reflectance and transmittance measurements. The values of third nonlinear susceptibility are in order of 10⁻¹² esu, which is compatible with other phthalocyanines. The nonlinear optical constants indicate that TiPcCl₂ films could also be used for optical laser limiters.

Keywords Organic films · Nanostructure · Optical properties · Dielectric constants · Nonlinear optical

1 Introduction
Phthalocyanine (Pc) dyes are photosensitizers in the near IR region with unique photochemical, electrochemical, and thermal properties (Odabaş et al. 2012). Pc is an aromatic dye with different colors determined by the substitution of the benzene rings. Pc is widely used in various scientific fields such as optical communication, electronic, optoelectronic, and solar cell (Zhang and Lovell 2017; Basova et al. 2014). Pc properties are attractive due to long-range periodic order, free of grain boundaries, and minimal traps and defects (Wang et al. 2018).

Pc chemical structure comprises varying numbers of single and multiple bonds, so molecules exist in high-grade electronically excited states (Darwish et al. 2016). Several
metals, such as Zn, Pb, Cu, Ga, etc., are integrated into Pc’s side group to improve its structural and desirable properties. Different studies have shown that Pc’s optical properties and applications are influenced by central metal nature (Wang et al. 2020; Viswanath et al. 2020; Kaur et al. 2020). Metal phthalocyanine (MPc) days have significant linear and nonlinear optical properties that can be employed in optical sensors, optical elements and protect human eyes from high-intensity lasers (Zhu et al. 2001).

There have been very few studies of halogenated MPc, mainly limited to indicating that they have ideal properties for gas sensing applications (Dogo et al. 1992). The films of AlPcCl (El-Nahass et al. 2015) and GaPcCl (El-Zaidia et al. 2020; Darwish et al. 2020) were analyzed to investigate their optical properties. These films exhibit indirectly allowed transitions, and different dispersion and absorption parameters were calculated. In addition, the electrical measurement of AlPcCl was performed to determine the energy gap by cyclic voltammetry and was found to be 1.42 eV (Soliman et al. 2016). Rajesh and Menon have examined the electrical conductivity of MnPcCl films (Rajesh and Menon 2005). It has been found that the impact of oxygen on electrical parameters was significant. As a high-performance limiter, Darwish et al. (Darwish et al. 2015) studied the highly branched synthesis parameters in (III)Pc polymer. The investigation of the characterization of the lifetime of GaPcCl was carried out by Chauke et al. (Chauke et al. 2007).

One of the halogenated MPc is Titanium-phthalocyanine-dichloride (TiPcCl₂), where Ti⁺⁴ has many more advantageous properties than other metals, which have high corrosion resistance and a high strength-to-density ratio (Zhang and Chen 2019). Cherian and Menon presented a study of TiPcCl₂ films prepared by thermal evaporation (Cherian and Menon 2008). The thermal activation energy of the electrical conduction is affected by annealing and the presence of oxygen. Nevertheless, the energy gap was not affected by annealing (Cherian and Menon 2008). Titanium-phthalocyanine-dichloride (TiPcCl₂) compound has not received extensive research and study, although it is essential for optoelectronic applications.

The study of film thickness’s influence on optical properties and film morphology gives us a detailed insight into many new conditions that have taken place during the material deposition in substrates. The alteration of bandgap with a change in the film thickness can be a useful tool for examining how oxide layers can be produced within the film structure. The present work is focused on studying the influence of film thickness on characterization, linear, and nonlinear optical properties of TiPcCl₂ thin films.

2 Experimental techniques

TiPcCl₂ powder was purchased from Sigma-Aldrich Company. The molecular structure of TiPcCl₂ has been introduced in Scheme 1. The TiPcCl₂ films were deposited onto a highly cleaned quartz glass utilizing the vacuum coating system (HHV Auto 306) at the pressure of 2.5 × 10⁻⁴ Pa. Different weight of TiPcCl₂ powder was used each time to prepare films of different thicknesses, and a quartz monitor was used to control the deposition rate at 1.5 nm/s. Then, the interferometric process was applied to determine the exact thickness of the TiPcCl₂ film (Richardson, 1972). Four samples with different thicknesses of 100, 170, 270, and 377 nm were obtained.

The vibrational properties of TiPcCl₂ films have been recorded by Raman spectroscopy using a Dilor XY modular spectrometer. The morphology of TiPcCl₂ films with
different thicknesses was investigated utilizing an Atomic Force Microscope (AFM) mode NT-MDT-Type Next, Russia.

Optical spectroscopic characterization was studied by a double-beam spectrophotometer (JASCO, V-570), which was utilized to record the spectra of transmittance, $T_m$, and reflectance, $R_m$, in the wavelength range between 200 and 2500 nm for the TiPcCl$_2$ films. The reflectance, $R$, and transmittance, $T$, of TiPcCl$_2$ films were calculated using the equations shown below (El-Nahass, 1992):

\[
T = T_m(1 - R_q)
\]

\[
R = R_m R_{Al} [(1 - R_q)^2 + 1] - T^2 R_q
\]

where $R_q$: the reflectance of reference quartz substrate and $R_{Al}$: the of the reference aluminum mirror. Then, $T$ and $R$ were used to calculate the optical constants (Rashad et al. 2018).

### 3 Results and discussion

#### 3.1 Raman spectroscopy

Raman spectroscopy is used to investigate the molecular structure of the TiPcCl$_2$ films, such as group structure, functional groups, and structural parameter changes with the change of film thickness. The experimental data of Raman spectra of TiPcCl$_2$ thin films for TiPcCl$_2$ powder sample and films of the thickness of 100, 170, 270, and 377 nm are shown in Fig. 1a–e. This figure shows that the Raman spectra of the deposited films are like the powder spectra and do not alter with evaporation, suggesting that the thermal evaporation approach is an excellent way to obtain non-dissociated TiPcCl$_2$ films. However, the phthalocyanine ring’s characteristic vibration absorption peaks were assigned to 596 and 1337 cm$^{-1}$. The peaks related to the C=C bond existed at the wavenumber of 1612 and 1519 cm$^{-1}$. At wavenumber 1430 cm$^{-1}$, a high peak related to C=C bonds appears within our fabricated materials. At wavenumber corresponding to 681 cm$^{-1}$, the presence of C-O bonds appears to be strong. The Raman spectra of TiPcCl$_2$ are close to other MPc with different central metals (Zhang et al. 2018).
3.2 Morphological studies

AFM is utilized for examining the surface of organic thin films, and it was used in this study to calculate the grain size and the roughness. Figure 2 showed 2D grain size patterns of TiPcCl$_2$ thin films with various thicknesses. TiPcCl$_2$ thin films show a uniformly nano spherical particle. It can be observed that the grain size increased with increasing the film thickness. Also, an increase in grain size may be due to an improvement in crystallinity and an increase in clusters’ development, contributing to small grain agglomeration (Öztas 2008). Such agglomerated grains merge to create larger grains with better crystallinity. The grain size and roughness surface for TiPcCl$_2$ thin films were measured and found to be 223 and 41 nm, respectively, for a thickness of 100 nm. TiPcCl$_2$ films have a larger grain size and a lower surface roughness than those reported for GaPcCl (El-Zaidia et al. 2020). In thin films, the composition of the surfaces significantly affects the transport of conduction electrons. In the case of mesoscopic roughness in the range of a few nanometers, this because of the film’s varying thickness, which results in a spatially variable conductivity. Also, microscopic roughness can lead to electrons’ dispersion and further improves the thin film’s resistance (Reiss and Brückl, 1992).
3.3 Optical and dielectric constants

The optical transmittance and reflectance of the thin films of TiPcCl₂ with a thickness of 100, 170, 270, and 377 nm have been illustrated in Fig. 3. This figure shows the homogeneity of TiPcCl₂ thin films. It can be noted from Fig. 3, at wavelengths (λ) greater than 960 nm, that the transmission increases steadily until it reaches approximately 96%. The light transmission within TiPcCl₂ thin films was affected by the thickness, as shown in Fig. 3. Therefore, we can conclude that the absorption of light within TiPcCl₂ films augments with increasing material thickness. The decrease in the transmission is due to the grain size change, where a larger grain size acts to increase the absorption of the fabricated material (Ebrahimi et al. 1999). On the other hand, TiPcCl₂ thin films’ reflectance spectra are distinguished by specific peaks for λ < 1000 nm in the region associated with the electronic transitions in TiPcCl₂ thin films. At λ > 1400 nm, the film’s reflectance decreases with an increase in wavelength and increases with increasing the film thickness. In this wavelength range, the TiPcCl₂ thin films become transparent for light, where the sum of T and R is approximately equal to unity.

A deep understanding of optical constants is a valuable method to learn the photonic and optoelectronic behavior (Munekata and Kukimoto 1983). The complex refractive index, \( n^* \), is given by:

\[
 n^* = n + ik
\]  

(3)
where \( n \) is the real part and called the refractive index while \( k \) is the imaginary part and called the extinction coefficient. These parameters were calculated as (Rashad et al. 2018):

\[
\alpha = \frac{1}{d} \ln \left( \frac{1 - R^2}{2T} + \sqrt{R^2 + \frac{1 - R^2}{4T^2}} \right)
\]

(4)

\[
k = \alpha \lambda / 4 \pi
\]

(5)

\[
n = \frac{1 + R}{1 - R} + \sqrt{\frac{4R}{(R - 1)^2} - k^2}
\]

(6)

where \( \alpha \): the absorption coefficient, and \( d \): the thickness of TiPcCl₂ film.

The variation of refractive index, \( n \), with the wavelength for TiPcCl₂ thin film at various thicknesses are shown in Fig. 4a. There are different high-energy peaks at \( \lambda < 1000 \) nm, which exhibit a multi-oscillator behavior. At \( \lambda > 1000 \) nm, the refractive index decreases by about 19% as the wavelength increases, indicating dispersion increase in this wavelength range. Further, the values of \( n \) increase with increasing the thickness, which could be explained by the film’s discontinuity formed during the deposition’s initial stages (Zeypada et al. 2010).

The extinction index, \( k \), of different TiPcCl₂ thin film thicknesses as a function of the wavelength is introduced in Fig. 4b. Three peaks in the absorption curve have been found at 225, 350, and 715 nm. These peaks are like the phthalocyanine compounds, as they show three absorption regions, the C-band at 225 nm, the B-band at 350 nm, and the last area is the Q-band at 715 nm. The Q-band, in particular, is associated with excitations between the states of HOMO (\( \pi \)-state) and LOMO (\( \pi^* \)-state) (Wang et al. 2010). In the case of all films with different thicknesses, the Q-band is split into two peaks. As much literature points, the Metallo-phthalocyanine and Metallo-phthalocyanine chloride are categorized into two forms (i.e. dimer and monomer) (Dolphin 2012). The proximity of the two rings in dimer form can motivate two identical molecules between the transition moments.
This interaction leads to two new levels of energy and is attributable to the exciton dividing energy. If there are two molecules in the cell unit, the spectrum presents two exciton bands, producing the corresponding Davydov splitting (ΔQ). Another aspect is the importance of assessing the multi-morphic phase of the layer produced in vacuum sublimation. The changes in the film layers reveal changes in film structure in the α-phase. The relative changes in the intensity of the different peaks in the Q bands can check this (El-Zaidia et al. 2020). Further, if the intensity of the individual bands is negligible, then the β-phase is dominant. However, there is no shift of the Q-band peaks for the prepared TiPcCl₂ films. So, the ΔQ value does not change with the thickness of the films, which it found equal to 0.16 eV. This means that ΔQ of the current sample is comparable to the relative value of the majority of Phthalocyanine compounds. The experimental ΔQ values of GaClPc, AlClPc, and SnPcCl₂ were evaluated to be 0.18, 0.18 and 0.20 eV, respectively (El-Zaidia et al. 2020; Zawadzka et al. 2015; El-Nahass et al. 2004).
The design of highly efficient optoelectronic devices depends on the complex dielectric constant \( \varepsilon^* = \varepsilon_1 + i \varepsilon_2 \) as a significant quantity, due to the knowledge associated with the dielectric constant that it offers a relaxed view of the interactions between photons and electrons in a material (El-Nahass et al. 2012). The optical and electrical properties of the materials are related using the dielectric properties. The dielectric constant, \( \varepsilon_1 \), and dielectric loss, \( \varepsilon_2 \), of TiPcCl\(_2\) could be calculated, respectively as (Zahedi and Dorranian 2013):

\[
\varepsilon_1 = n^2 - k^2
\]

\[
\varepsilon_2 = 2nk
\]

Figure 5 shows the spectral distribution of \( \varepsilon_1 \) and \( \varepsilon_2 \) with \( h\nu \). There is a remarkably different behavior that has appeared in the figures of both \( \varepsilon_1 \) and \( \varepsilon_2 \). This conduct may be attributed to the different interactions in the center of electrons in TiPcCl\(_2\) film and the incident photons that cause a difference in the spectrum shapes of \( \varepsilon_1 \) and \( \varepsilon_2 \). Two dielectric maximums that inferred the possibility of dielectric applications of TiPcCl\(_2\) films could also be observed. According to Zhang et al. (Zhang et al. 2016), the maximums released within the energy range of 1.5–2.2 eV, as shown in Fig. 5, indicate an energy storage area where energy can be stored. This shines a spotlight on the application of TiPcCl\(_2\) films for energy storage.

### 3.4 Absorption and dispersion analysis

The absorption of light from organic materials provides a great insight into the knowledge of the transfer of electrons between energy levels. Figure 6 depicts the absorption coefficient of TiPcCl\(_2\) thin film spectra against the photon energy in the Q, B, and C bands. In the three-band, the wavelength affects the absorption coefficient. The absorption coefficient decreased at the C-band due to the band absorption generated by direct Coulomb encounters with lattice constituents. The increased material thickness causes a reduction in inter-atomic spacing within our synthesized thin film, and this affects the material absorption (Mistrik et al. 2017).

However, the Q-band consists of a 1.74 eV peak and a 1.87 eV shoulder. The Q-band peak was allocated to the first \( \pi-\pi^* \) transition of the phthalocyanine macrocycle (El-Nahass et al. 2005). The Q-band’s shoulder was explained differently, as a second \( \pi-\pi^* \) transition, as an excitation peak as an internal vibrational interval, and as a surface state. In the high-energy region of the Soret band around 3.58 and 4.24 eV, the critical indicator of the significant variations in the phthalocyanine absorption spectrum in that area suggests the existence of a d-band correlating with the central metal atom. In the high energy region (5.59 eV), the absorption of TiPcCl\(_2\) appears a band known as C-band like other MPC, which is attributed to the \( \pi-d \) transitions (El-Nahass et al. 2005).

Researchers study the absorption edge for phthalocyanine and its derivatives thin film to provide information on inner band transitions (El-Nahass et al. 2015; Darwish et al. 2020; Cherian and Menon, 2008). The electronic transitions in organic materials occur mainly between the highest occupied molecular (HOMO) and the lowest molecular orbital (LUMO). The area between them is the band gap, and Tauc’s relation can detect the optical band gap (Herring, 1955):

\[
(\alpha h\nu)^{1/2} = H(h\nu - E_g)
\]

where \( H \) is a constant, \( h\nu \) is photon energy, and \( E_g \) is the energy band gap. The constant \( L \) depends on the transition type and takes the values \( \frac{1}{2} \) and 2 for an indirect transition and
a direct transition, respectively. Figure 7 shows the relation between $(\alpha h\nu)^{1/2}$ and photon energy for TiPcCl$_2$ thin films at various thicknesses, and two energy bands are described in this figure. These band energies describe the lowest values as the optical band gap energy ($E_{g1}$), which is a consequence of several factors, including dislocations and vacancies, within the microstructure film (Tichý et al. 1999). The higher band gap energy is called the fundamental band energy gap ($E_{g2}$) and the transition from $\pi$ to $\pi^*$ generally explains this (Darwish et al. 2018). The band gap energies values for various TiPcCl$_2$ films are not affecting by the thickness of the film, which confirms the thermal vacuum evaporation competence to prevent oxidation layers from occurring during the creation of the TiPcCl$_2$

Fig. 5 Spectra of (a) the dielectric constant, $\varepsilon_1$, and (b) dielectric loss, $\varepsilon_2$, of TiPcCl$_2$ films with different thicknesses
deposited materials. The average energy gap, $E_{g1}$, is 1.48 eV, whereas the average $E_{g2}$ is 2.83 eV. The comparison with other related compounds of phthalocyanine (El-Nahass et al. 2015, 2004; El-Zaidia et al. 2020) of band gap energy value was shown in Table 1.

With the magnitudes of the refractive index, several main linear optical parameters can be calculated. These parameters are the single oscillator energy ($E_s$), the dispersion energy ($E_d$), high-frequency dielectric constant ($\varepsilon_\infty$), the carrier concentration ($N$), and the lattice dielectric constant ($\varepsilon_L$) and they increase the understanding of the optical properties of TiPcCl$_2$ films. For example, $E_s$ symbolizes the single oscillator energy influenced by excitons’ formation through the material. At the same time, $E_d$ is used primarily to evaluate the optical interband transitions (El-Nahass et al. 2004). The
| Film     | Grain size (nm) | Roughness (nm) | $E_g1$ (eV) | $E_g2$ (eV) | $E_s$ (eV) | $E_d$ (eV) | $\varepsilon_\infty$ | $\varepsilon_l$ | $N/m^*(\times 10^{14} \text{ g}^{-1} \text{ cm}^{-3})$ | Ref |
|----------|----------------|----------------|-------------|-------------|------------|------------|----------------------|--------------|--------------------------------------------|-----|
| TiPcCl$_2$ (100 nm) | 223            | 41.0           | 1.48        | 2.83        | 1.28       | 1.67       | 4.56                 | 7.78         | 4.75 Current work                             |     |
| TiPcCl$_2$ (170 nm) | 233            | 42.0           | 1.49        | 2.83        | 1.36       | 1.85       | 5.66                 | 9.43         | 5.76 Current work                             |     |
| TiPcCl$_2$ (270 nm) | 240            | 53.8           | 1.46        | 2.82        | 1.40       | 2.03       | 6.75                 | 11.08        | 6.56 Current work                             |     |
| TiPcCl$_2$ (377 nm) | 479            | 57.9           | 1.49        | 2.81        | 1.42       | 2.17       | 7.68                 | 12.49        | 7.32 Current work                             |     |
| AlPcCl$_2$ | –              | –              | –           | –           | –          | –          | –                   | –            | – Current work                                 |     |
| GaClPc | –              | –              | –           | –           | –          | –          | –                   | –            | – Current work                                 |     |
| SnPcCl$_2$ | –              | –              | –           | –           | –          | –          | –                   | –            | – Current work                                 |     |
refractive index is analyzed using the following equations (Wemple and DiDomenico Jr, 1971):

\[ n^2 - 1 = \frac{E_d E_s}{E_s^2 - (\hbar \nu)^2} \]  
\[ n^2 = \varepsilon_L - \frac{\varepsilon^2 N}{4 \pi \varepsilon_0 m^* c^2 \lambda^2} \]

where \( \varepsilon_0 \): the free space dielectric constant, \( m^* \): the electron effective mass, and \( e \): the electron’s charge. Figure 8a shows the change of \( (n^2-1)^{-1} \) with \( (h\nu)^2 \), while Fig. 8b shows the evolution of \( n^2 \) with \( \lambda^2 \). All the optical parameters are listed in Table 1. The increase of these optical parameters with increasing film thickness could be interpreted by the variation in ionization, which occurs primarily due to the rise in the number of cations in coordination with nearby anions. Table 1 has also reported similarities with the relative compounds of phthalocyanine of these constants.

3.5 Calculated nonlinear optical constants

Studying the nonlinear optical properties of organic dyes is vital for different scientific fields, such as optical fiber cables and optical gadgets modulators (Ali and Palanisamy 2005). In nano-photonics science, nonlinear optical materials also play a critical role. The organically replaced molecules together demonstrate observable non-linear optics and electrooptical impact. These materials may be used for doubling or tripling the frequency of laser light. They are also desirable for high-speed data processing and essential to many emerging technologies, including digital and optical computing (Arivuoli, 2001).

![Fig. 8](image-url)

**Fig. 8**  a The relation between \( (n^2-1)^{-1} \) and \( (h\nu)^2 \), b the relation between \( n^2 \) and \( \lambda^2 \) for TiPcCl\(_2\) films
Nonlinear optical properties are primarily understood by the study of third nonlinear susceptibility ($\chi^{(3)}$) and nonlinear refractive index ($n_2$). From Miller’s generalized law (Tichý et al. 1999), the $\chi^{(3)}$ and $n_2$ values for $h\nu \rightarrow 0$ can be evaluated as follows:

$$\chi^{(3)} = 1.7 \times 10^{-10} \left(\frac{n_0^2 - 1}{4\pi}\right)^4$$

(12)

$$n_2 = \frac{12\pi \chi^{(3)}}{n_0}$$

(13)

where $n_0$: the linear refractive index at $h\nu \rightarrow 0$. Figure 9 presents the variance of $n_0$, $\chi^{(3)}$, and $n_2$ as a function of the film’s thickness. As shown in this figure, the values of $n_0$, $\chi^{(3)}$, and $n_2$ indicate an increase in the thickness of TiPcCl$_2$ thin film. The increase in the values of the three parameters with the increase in the thickness could be related to the change of the delocalization degree of $\pi$-electron and the aligned chains in the direction of the induced electric field (Stegeman et al. 1988). Also, the values of $\chi^{(3)}$ are $10^{-12}$ esu, which is compatible with other phthalocyanines (El-Nahass et al. 2015; Darwish et al. 2020). The obtained results of $\chi^{(3)}$ and $n_2$ indicate that TiPcCl$_2$ films are excellent nonlinear optical materials, mainly if used as optical limiters.

Fig. 9 The nonlinear optical parameters of TiPcCl$_2$ films as a function of film thickness.
4 Conclusions

Various characterization techniques investigated the morphology and the optical properties of TiPcCl₂ thin film with different thicknesses. The AFM and the Raman spectrometry analysis reveal a good dispersion of material structure. The morphology studied showed that TiPcCl₂ thin film has an average grain size and roughness of 223 and 41 nm, respectively. The average energy gap of our tested thin film was 1.5 eV, and it was found that the energy gap was not affected by the film’s thickness. The dielectric constants inferred the possibility of dielectric applications of TiPcCl₂ films could also be observed. They also showed maxima released within the energy range of 1.5–2.2 eV, indicating an energy storage area. Nonlinear third susceptibility values are 10⁻¹² esu, which is compatible with other phthalocyanines. The obtained results are of guidance, meaning the possibility of using such composites in various applications such as solar cells, light-emitting diodes, etc.

Acknowledgements The authors extend their appreciation to the Deanship of Scientific Research at University of Tabuk for funding this work through Research Group RGP-S-1441-008.

Declarations

Conflict of interest The authors declare that there is no conflict of interest regarding the publication of this paper.

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