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Taymour Hamdalla (✉ taymour_76@yahoo.com)

University of Tabuk <https://orcid.org/0000-0002-0807-7956>

A.A.A. Darwish

University of Tabuk

S.A. Al-Ghamdi

University of Tabuk

Ahmed Obaid M. Alzahrani

King Abdulaziz University

E.F.M. El-Zaidia

University of Tabuk

Nasser A. Alamrani

Tabuk university

Mohamed A. Elblbesy

tabuk university

I.S. Yahia

king Khaled university

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

Taymour A. Hamdalla^{1,2,*}, A.A.A. Darwish^{1,3}, S.A. Al-Ghamdi⁴, Ahmed Obaid M. Alzahrani^{5,6}, E.F.M. El-Zaidia^{4,7}, Nasser A. Alamrani⁸, Mohamed A. Elblbesy^{9,10} and I.S. Yahia^{11,12}

- 1) Department of Physics and Nanotechnology Research Unit, Faculty of Science, University of Tabuk, Tabuk 71491, Saudi Arabia
- 2) Department of Physics, Faculty of Science, Alexandria University, Alexandria, Egypt
- 3) Department of Physics, Faculty of Education at Al-Mahweet, Sana'a University, Al-Mahweet, Yemen.
- 4) Department of Physics, Faculty of Science, University of Tabuk, Tabuk 71491, Saudi Arabia
- 5) Center of Nanotechnology, King Abdulaziz University, Jeddah, Saudi Arabia
- 6) Physics Department, Faculty of Science, King Abdulaziz, University, Jeddah, Saudi Arabia
- 7) Department of Physics, Faculty of Education, Ain Shams University, Roxy 11757, Cairo, Egypt.
- 8) Department of Chemistry, Faculty of Science, University of Tabuk, Tabuk 71491, Saudi Arabia
- 9) Department of Medical Laboratory Technology, Faculty of Applied Medical Sciences, University of Tabuk, Tabuk 71491, Saudi Arabia.
- 10) Department of Medical Biophysics, Medical Research Institute, Alexandria University, Alexandria 21561, Egypt
- 11) Research Center for Advanced Materials Science (RCAMS), King Khalid University, and Advanced Functional Materials & Optoelectronic Laboratory (AFMOL), Department of Physics, Faculty of Science, King Khalid University, P.O. Box 9004, Abha, Saudi Arabia.
- 12) Nanoscience Laboratory for Environmental and Biomedical Applications (NLEBA), Semiconductor Lab., Department of Physics, Faculty of Education, Ain Shams University, Roxy 11757, Cairo, Egypt.

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 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

*Corresponding author: Taymour A. Hamdalla

E-mail address: taymour_76@yahoo.com

1. Introduction

Phthalocyanine (Pc) dyes are photosensitizers in the near IR region with unique photochemical, electrochemical, and thermal properties [1]. 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 [2,3]. Pc properties are attractive due to long-range periodic order, free of grain boundaries, and minimal traps and defects [4].

Pc chemical structure comprises varying numbers of single and multiple bonds, so molecules exist in high-grade electronically excited states [5]. 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 [6-8]. Metal phthalocyanine (MPc) dyes have significant linear and nonlinear optical properties that can be employed in optical sensors, optical elements, and protect human eyes from high-intensity lasers [9].

There have been very few studies of halogenated MPc, mainly limited to indicating that they have ideal properties for gas sensing applications [10]. The films of AlPcCl [11] and GaPcCl [12, 13] 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 [14]. Rajesh and Menon have examined the electrical conductivity of MnPcCl films [15]. It has been found that the impact of oxygen on electrical parameters was significant. As a high-performance limiter, Darwish *et al.* [16] 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.* [17]

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 [18]. Cherian and Menon presented a study of TiPcCl₂ films prepared by thermal evaporation [19]. 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 [19]. 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 subsequent TiPcCl₂ films were then deposited with different thicknesses of 100, 170, 270, and 377 nm onto a highly cleaned glass utilizing the vacuum coating system (HHV Auto 306) at the pressure of 2.5×10^{-4} Pa. We used a quartz monitor to control the thin-film thickness, and the deposition rate was at 1.5 nm/s. The interferometric process was applied to determine the exact thickness of the TiPcCl₂ film [20].

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 , and reflectance, R , in the wavelength range between 200-2500 nm for the TiPcCl₂ films. Then, T and R were used to calculate the optical constants [21, 22].

3. Results and discussion

3.1 Raman spectroscopy

Raman spectroscopy is used to investigate the molecular structure of the TiPcCl₂ films, such as group structure, functional groups, and structural parameter changes with the change of film thickness. The experimental data of Raman spectra of TiPcCl₂ thin films for TiPcCl₂ powder

sample and films of the thickness of 100, 170, 270, and 377 nm are shown in Fig. 1 (a-e). The most intense vibrational peaks of the Raman spectrum of TiPcCl_2 thin films are listed in Table 1. 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} [23]. 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 [23].

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. Fig. 2 showed 2D grain size patterns of TiPcCl_2 thin films with various thicknesses. TiPcCl_2 thin films show a uniformly nano spherical particle. The values of grains size for TiPcCl_2 thin films at different thicknesses are listed in Table 1. 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 [24]. 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 [12]. 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 [25].

3.3 Optical and dielectric constants

The optical transmittance and reflectance of the thin films of TiPcCl_2 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 [26]. On the other hand, TiPcCl₂ thin films' reflectance spectra are distinguished by specific peaks for $\lambda < 1000$ nm in the region associated with the electronic transitions in TiPcCl₂ thin films. At $\lambda > 1400$ 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 [27]. The complex refractive index, n^* , is given by [28]:

$$n^* = n + i k \quad (1)$$

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 [21, 22]:

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

$$k = \alpha \lambda / 4 \pi \quad (3)$$

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

where α : 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 [29]. 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 [30], as they show three absorption regions, which are the C-band at 225 nm, the B-band at 350 nm, and the last area is the Q-band at 715 nm.

The design of highly efficient optoelectronic devices depends on the complex dielectric constant ($\epsilon^* = \epsilon_1 + i \epsilon_2$) 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 [31]. The optical and electrical properties of the materials are related using the dielectric properties. The dielectric constant, ϵ_1 , and dielectric loss, ϵ_2 , of TiPcCl₂ could be calculated, respectively as [32, 33]:

$$\epsilon_1 = n^2 - k^2 \quad (5)$$

$$\epsilon_2 = 2nk \quad (6)$$

Fig. 5 shows the spectral distribution of ϵ_1 and ϵ_2 with $h\nu$. There is a remarkably different behavior that has appeared in the figures of both ϵ_1 and ϵ_2 . This conduct may be attributed to the different interactions in the center of electrons in TiPcCl₂ film and the incident photons that cause a difference in the spectrum shapes of ϵ_1 and ϵ_2 [34]. Two dielectric maximums that inferred the possibility of dielectric applications of TiPcCl₂ films could also be observed. According to Zhang *et al.* [35], 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 TiPcCl₂ 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. Fig. 6 depicts the absorption coefficient of TiPcCl₂ 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 [36]. The increased material thickness causes a reduction in inter-atomic spacing within our synthesized thin film, and this affects the material absorption [36].

However, the Q-band consists of a 1.74 eV peak and a 1.87 eV shoulder. The peak of the Q-band was allocated to the first π - π^* transition of the phthalocyanine macrocycle [37]. The Q-

band's shoulder was explained differently, as a second π - π^* transition, as an excitation peak [37] 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 large variations in the phthalocyanine absorption spectrum in that area suggests the existence of a d-band correlating with the central metal atom [37]. In the high energy region (5.59 eV), the absorption of TiPcCl₂ appears a band known as C-band like other MPc, which is attributed to the π -d transitions [37].

Researchers study the absorption edge for phthalocyanine and its derivatives thin film to provide information on inner band transitions [11-13, 19]. 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 [38]:

$$(\alpha hv)^L = H (hv - E_g) \quad (7)$$

where H is a constant, hv is photon energy, and E_g is the energy band gap. The constant L depends on the transition type and takes the value $\frac{1}{2}$ and 2 for an indirect transition and a direct transition, respectively. Fig. 7 shows the relation between $(\alpha hv)^{1/2}$ and photon energy for TiPcCl₂ 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 [39]. The higher band gap energy is called the fundamental band energy gap (E_{g2}) and the transition from π to π^* generally explains this [39]. The band gap energies values for various TiPcCl₂ 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 TiPcCl₂ deposited materials. The average energy gap, E_{g1} , is 1.5 eV, whereas the average E_{g2} is 2.95 eV. The comparison with other related compounds of phthalocyanine [11, 12, 40] of band gap energy value was shown in Table 2.

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 (ϵ_∞), the carrier concentration (N), and the lattice dielectric constant (ϵ_L), and they increase the understanding of the optical properties of TiPcCl₂ 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 [40]. The refractive index is analyzed using the following equations [41, 42]:

$$n^2 - 1 = \frac{E_d E_s}{E_s^2 - (h\nu)^2} \quad (8)$$

$$n^2 = \varepsilon_L - \frac{e^2 N}{4 \pi \varepsilon_0 m^* c^2} \lambda^2 \quad (9)$$

where ε_0 : the free space dielectric constant, m^* : the electron effective mass, and e : the electron's charge. Fig. 8a shows the change of $(n^2-1)^{-1}$ with $(h\nu)^2$, while Fig. 8b shows the evolution of n^2 with λ^2 . All the optical parameters are listed in Table 2. 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 [43]. Table 2 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 fields of science, such as optical fiber cables, optical gadgets modulators [44]. In nano-photonics science, the nonlinear optical materials also play a critical turn. 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 [45].

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 [46], the $\chi^{(3)}$ and n_2 values for $h\nu \rightarrow 0$ can be evaluated as follows:

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

$$n_2 = \frac{12\pi\chi^{(3)}}{n_0} \quad (11)$$

where n_0 : the linear refractive index at $h\nu \rightarrow 0$. Fig. 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 TiPcCl₂ 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 π -electron and the aligned chains in the direction of the induced electric field [47]. Also, the values of $\chi^{(3)}$ are 10^{-12} esu, which is compatible with other phthalocyanines [11-13]. The obtained results of $\chi^{(3)}$ and n_2 indicate that TiPcCl₂ films are excellent nonlinear optical materials, mainly if used as optical limiters.

4. Conclusions

In this paper, the morphology and the optical properties of TiPcCl₂ thin film with different thicknesses have been studied. These films were prepared in the usual manner by thermal evaporation. The molecular structure was analyzed by a Raman spectrometer. The films' surface morphology was examined by atomic force microscope, and then the linear and nonlinear optical properties were studied. From this study, we conclude the following:

- The molecular structure of the prepared films is identical to the powder, and this indicates that homogeneous films can be obtained from the TiPcCl₂ compound by the thermal evaporation method.
- The morphology studied showed that TiPcCl₂ thin film has an average grain size and roughness of 223 and 41 nm, respectively.
- The dielectric constants inferred the possibility of dielectric applications of TiPcCl₂ films could also be observed. They also showed maximums released within the energy range of 1.5-2.2 eV, indicating an energy storage area. This shines a spotlight on the application of TiPcCl₂ films for energy storage.
- The band gap energy values for different TiPcCl₂ thin films are not affected by the film's thickness. The average energy gap is 1.5 eV, which makes these films attractive for photovoltaic applications.

- Nonlinear third susceptibility values are 10^{-12} esu, which is compatible with other phthalocyanines. The obtained results of nonlinear optical parameters indicate that TiPcCl₂ films are excellent nonlinear optical materials, mainly if used as optical limiters.

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Conflict of Interest:

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

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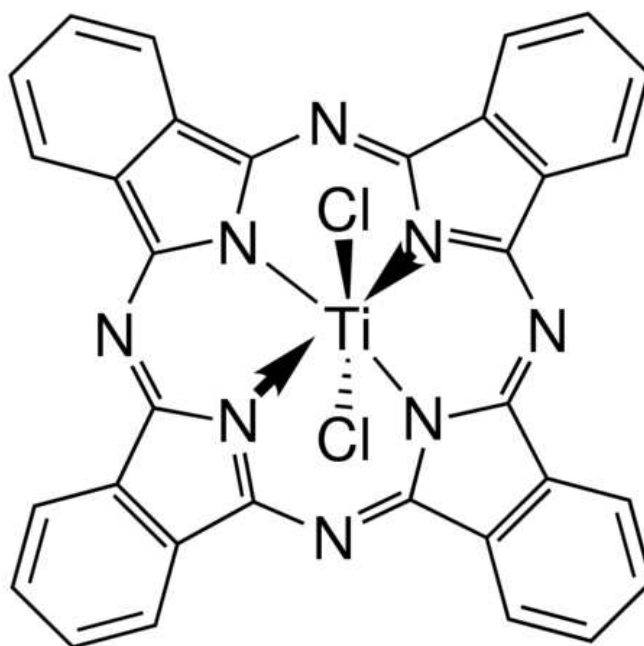
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Figures



Scheme 1: The molecular structure of TiPcCl₂ compounds

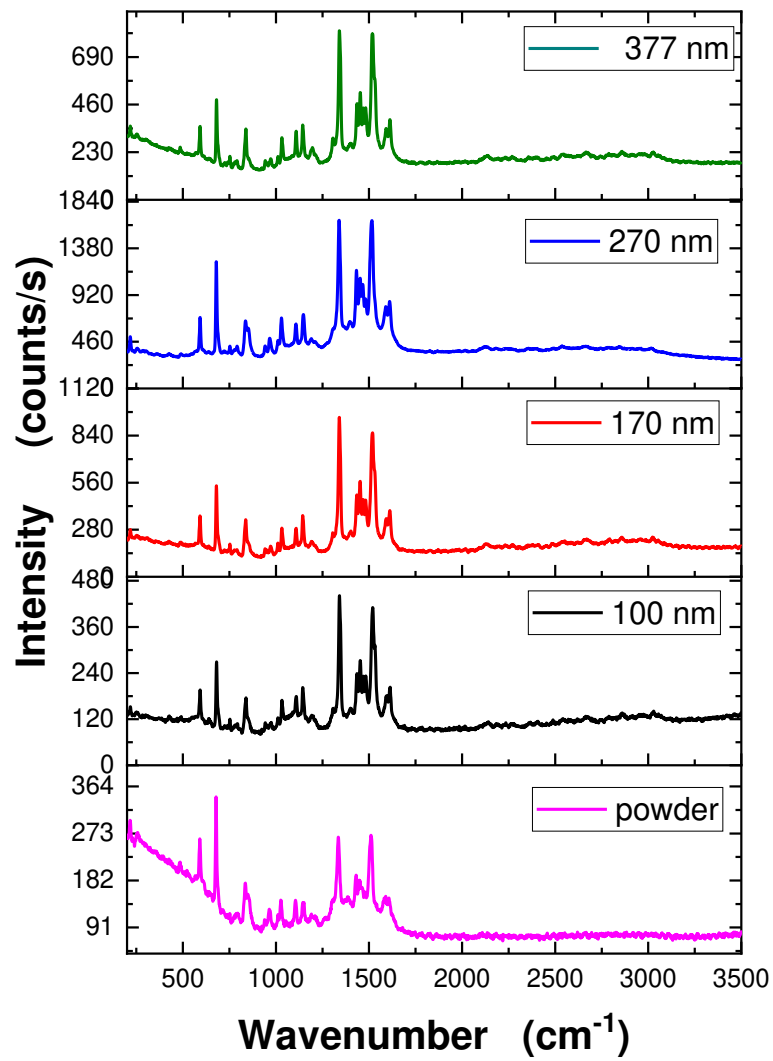


Fig. 1: Raman spectroscopy of powder and TiPcCl₂ film with different thickness

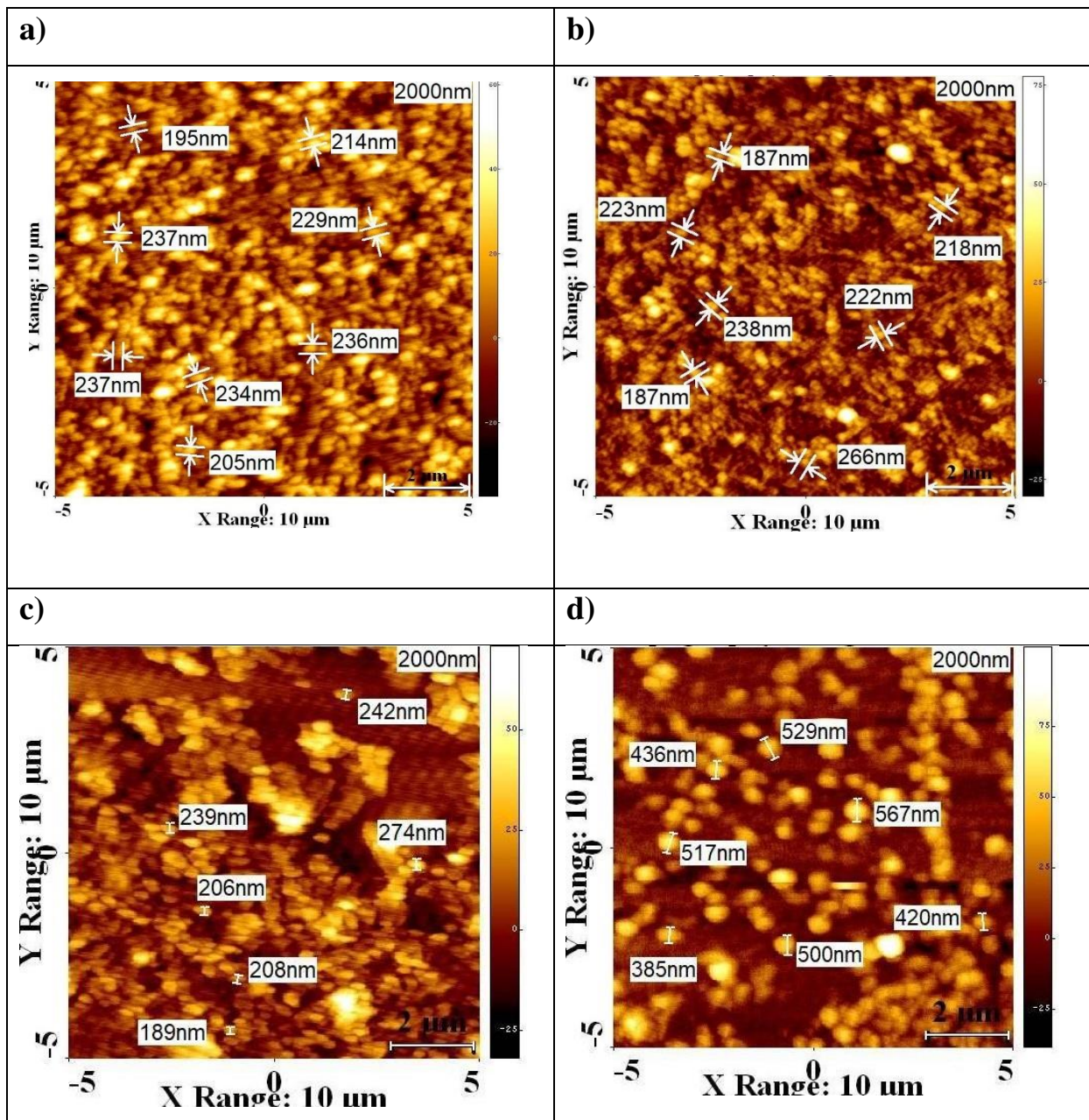


Fig. 2: 2D AFM images of TiPcCl_2 film with different thickness (a) 100 nm (b) 170 nm (c) 270 nm and (d) 377 nm

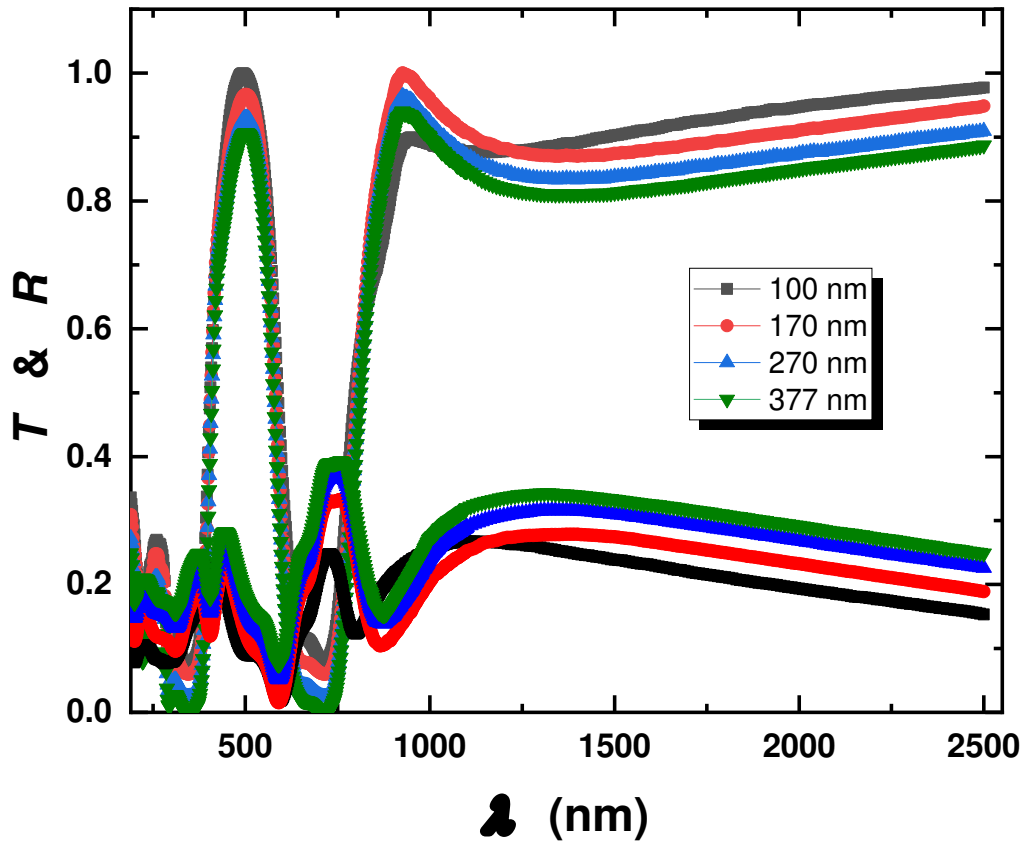


Fig. 3: Spectra of T and R of TiPcCl_2 films with different thicknesses

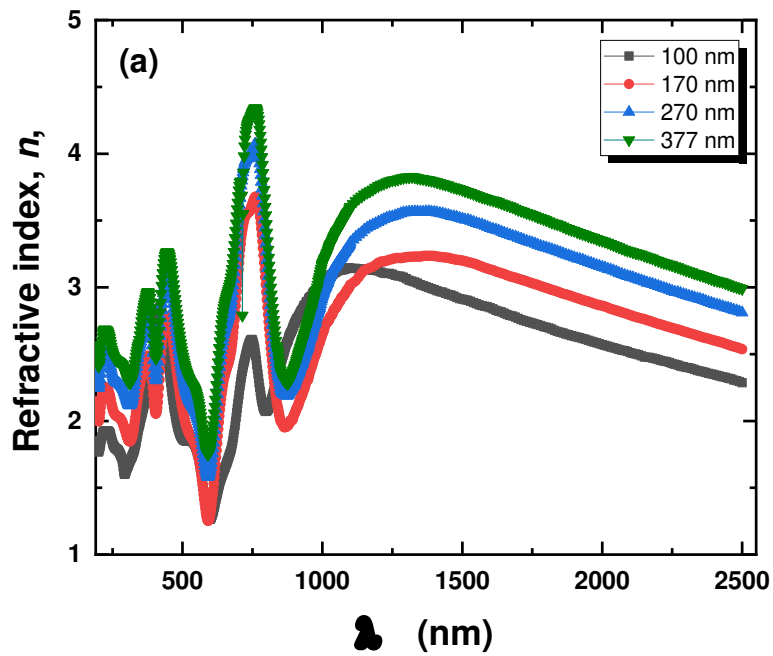
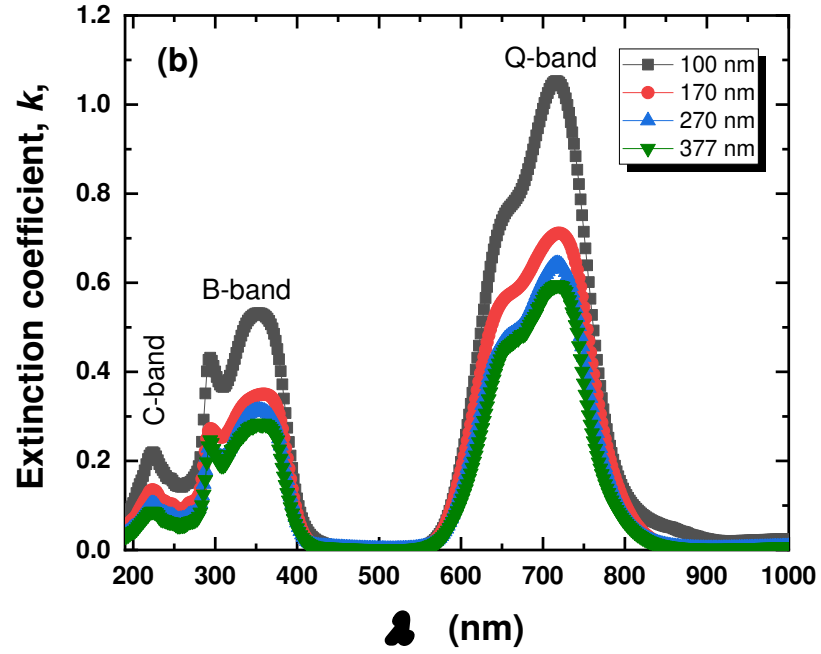


Fig. 4: Spectra of (a) the refractive index, n , and (b) extinction coefficient, k , of TiPcCl_2 films with different thicknesses.

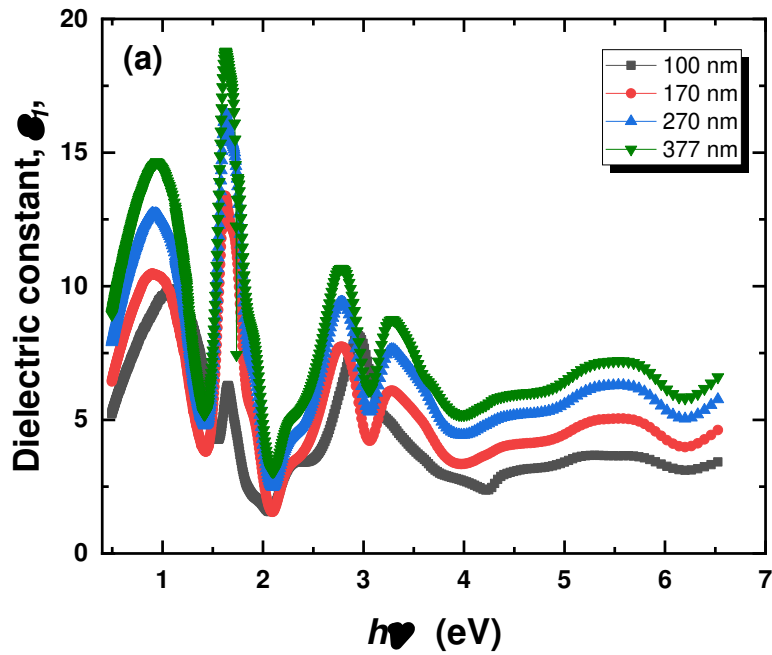
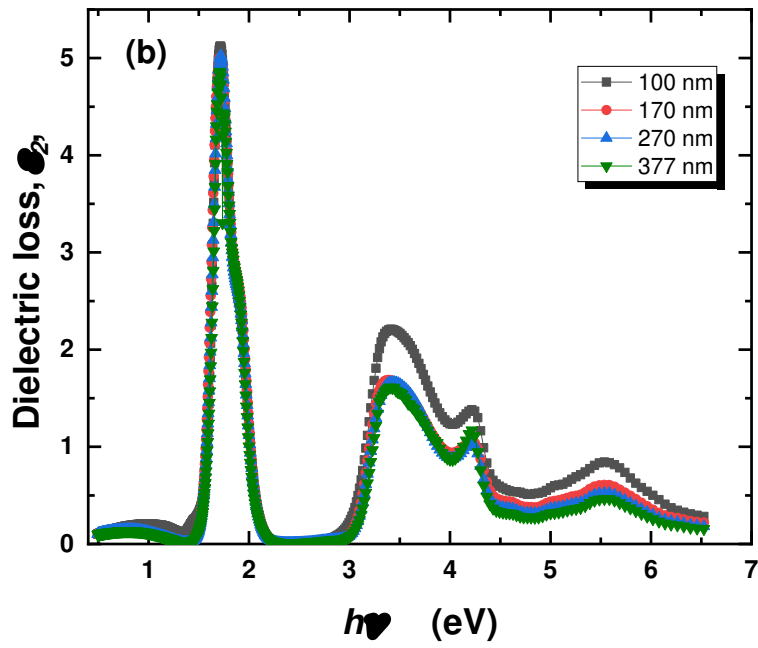


Fig. 5: Spectra of (a) the dielectric constant, ϵ_1 , and (b) dielectric loss, ϵ_2 , of TiPcCl₂ films with different thicknesses.

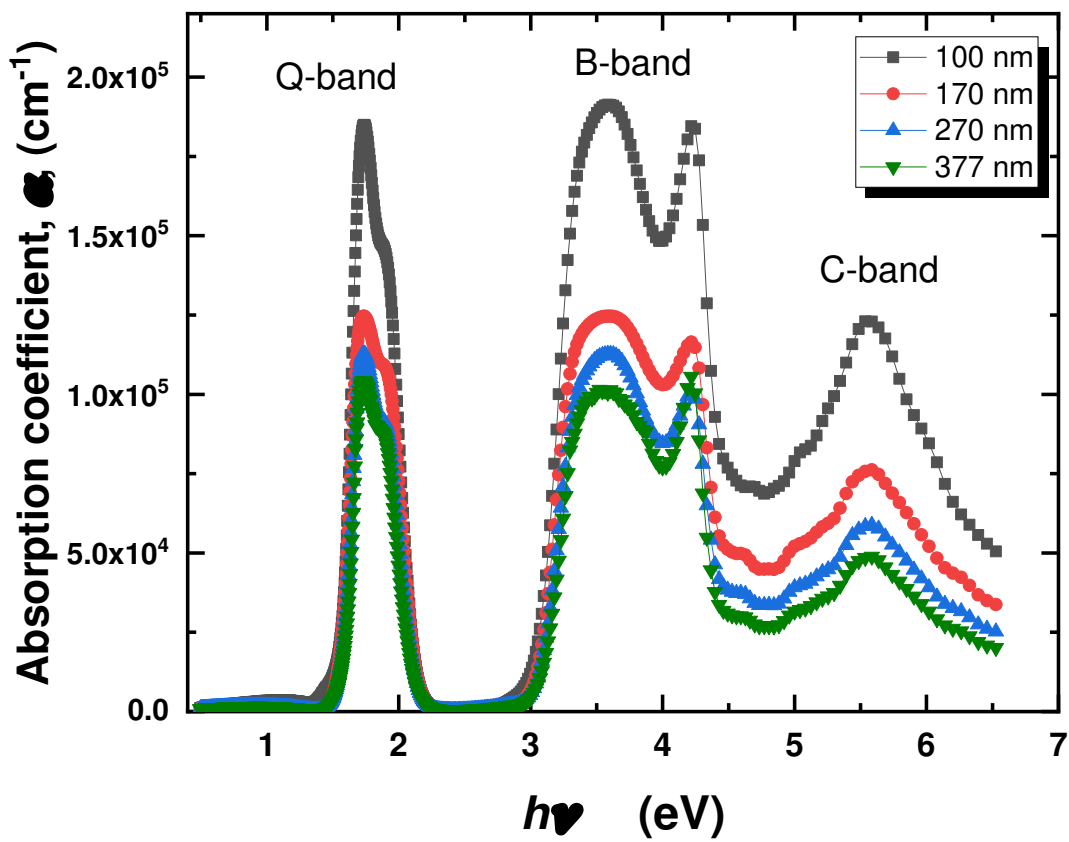


Fig. 6: Spectra of the absorption coefficient, α , of TiPcCl₂ films with different thicknesses.

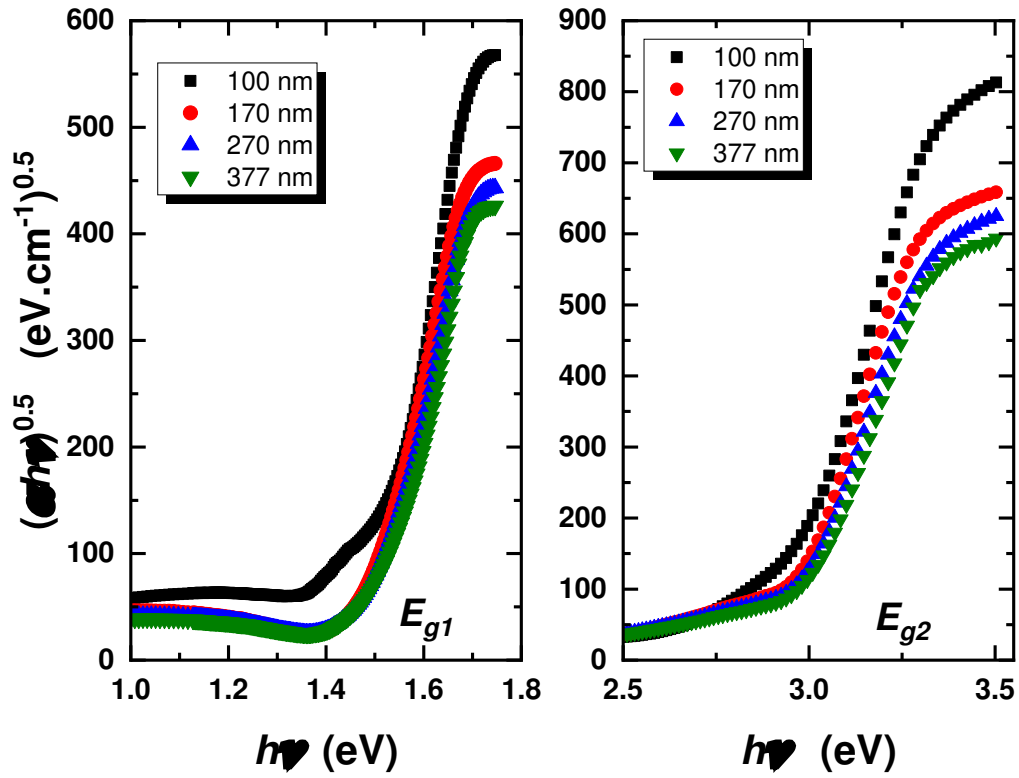


Fig. 7: The relation between $(\alpha h\nu)^{0.5}$ and $h\nu$ for TiPcCl₂ films with different thicknesses

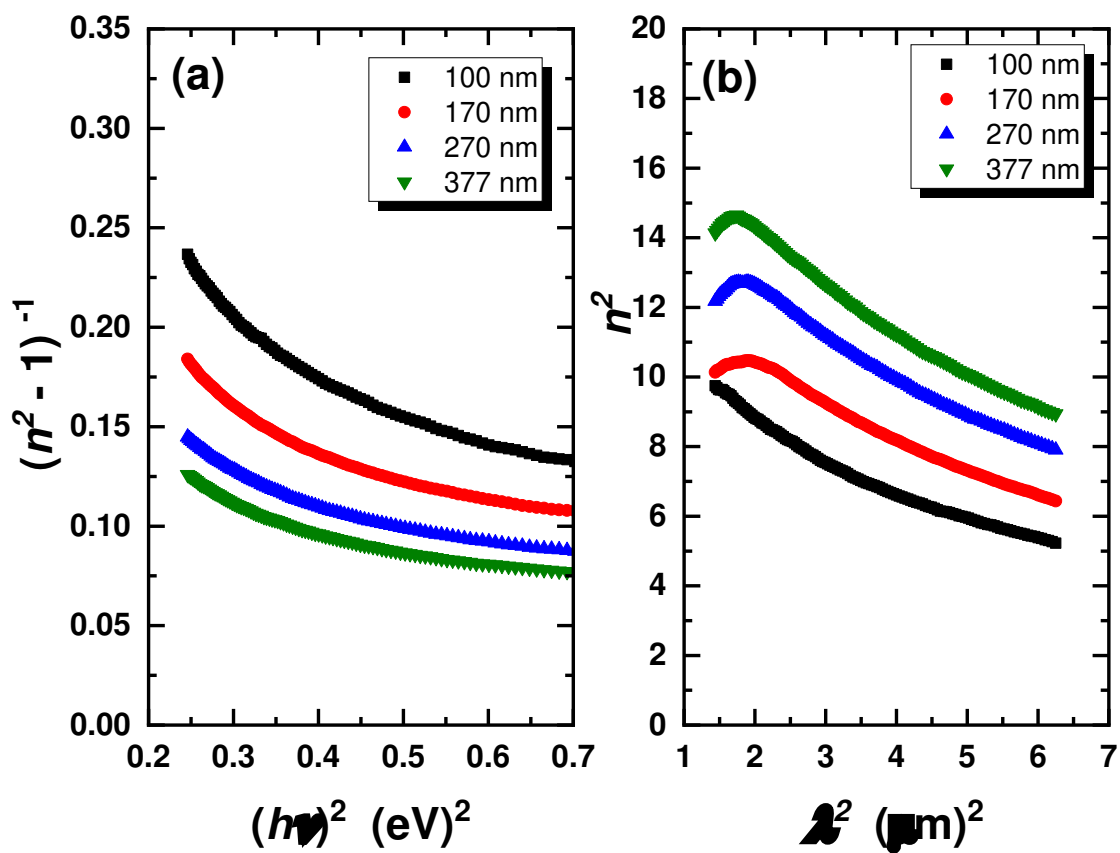


Fig. 8: a) the relation between $(n^2-1)^{-1}$ and $(h\nu)^2$, b) the relation between n^2 and λ^2 for TiPcCl₂ films

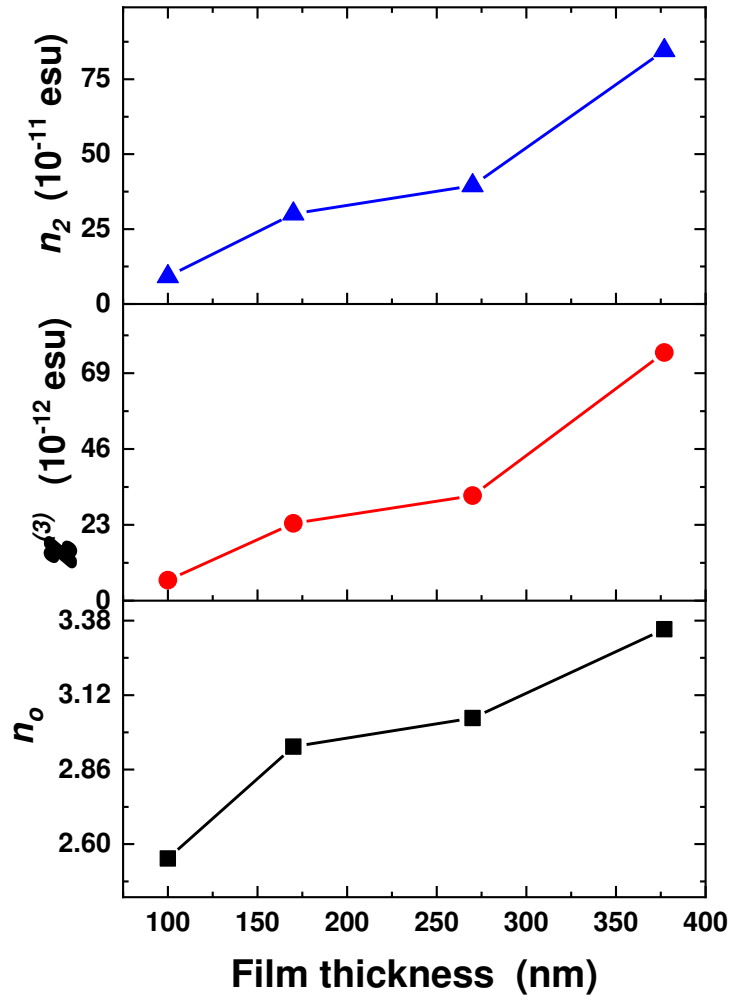


Fig. 9: The nonlinear optical parameters of TiPcCl₂ films as a function of film thickness

Tables

Table 1: Raman peaks of the TiPcCl₂ powder and its films

No	Wavenumber (cm ⁻¹)			Bonds
	Powder	Films (100 nm)	Films (377 nm)	
1	593	592	592	*****
2	677	681	681	C-O
3	832	838	839	*****
4	967	964	970	*****
5	1030	1032	1033	*****
6	1105	1110	1108	C-C
7	1150	1144	1143	*****
8	1336	1340	1340	C-O
9	1430	1432	1451	C-H
10	1514	1517	1519	C=C
11	1589	1613	1612	C=C

Table 2: Surface and linear optical parameters of TiPcCl₂ films

Film	Grain size (nm)	Roughness (nm)	E_{g1} (eV)	E_{g2} (eV)	E_o (eV)	E_d (eV)	ϵ_∞	ϵ_L	N/m^* ($\times 10^{46} \text{g}^{-1} \text{cm}^{-3}$)	Ref
TiPcCl ₂ (100 nm)	223	41.0	1.50	2.93	1.21	8.85	6.49	9.35	5.45	Current work
TiPcCl ₂ (170 nm)	233	42.0	1.49	2.94	1.33	15.60	8.66	11.75	7.17	Current work
TiPcCl ₂ (270 nm)	240	53.8	1.49	2.94	1.21	13.25	9.27	13.57	7.48	Current work
TiPcCl ₂ (377 nm)	479	57.9	1.51	2.96	1.28	18.83	11.25	15.52	8.73	Current work
AlPcCl	---	---	1.42	2.87	1.59	4.04	3.53	4.86	8.9	[11]
GaClPc	125.5	82.9	1.49	2.92	1.09	5.62	5.46	9.87	10.3	[12]
SnPcCl ₂	---	---	1.51	2.97	---	---	---	---	---	[40]

Figures

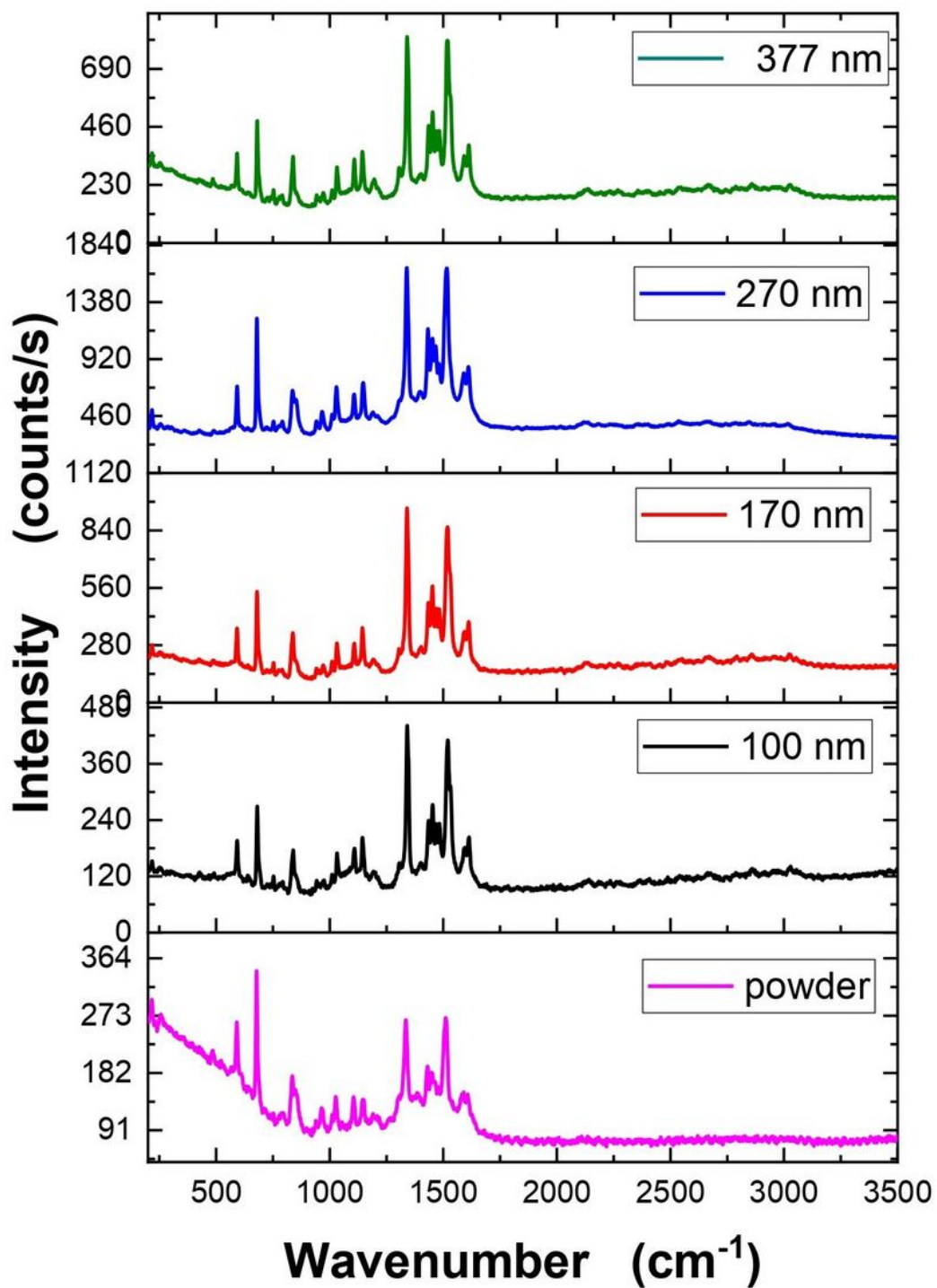


Figure 1

Raman spectroscopy of powder and TiPcCl₂ film with different thickness

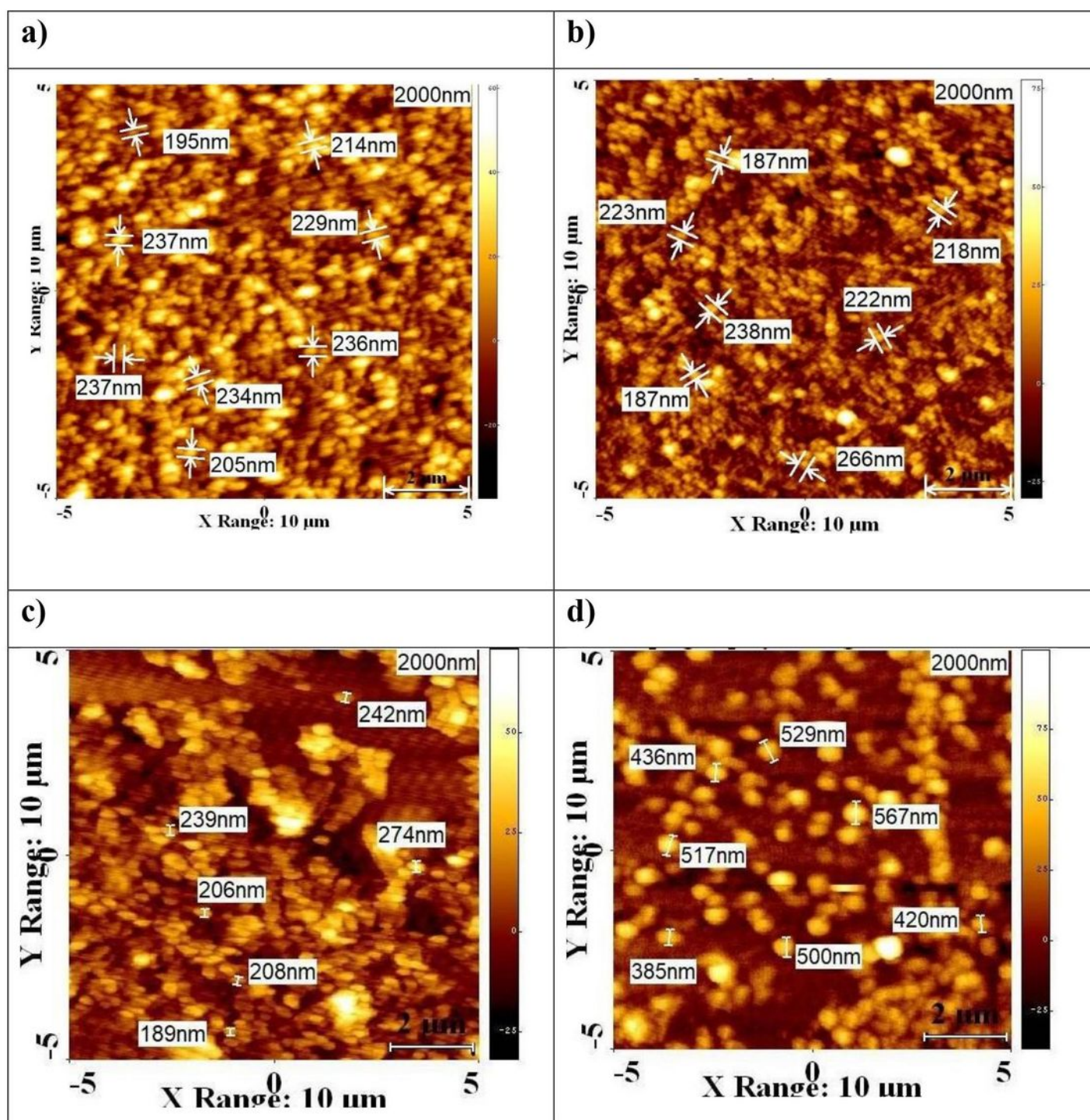


Figure 2

2D AFM images of TiPcCl₂ film with different thickness (a) 100 nm (b) 170 nm (c) 270 nm and (d) 377 nm

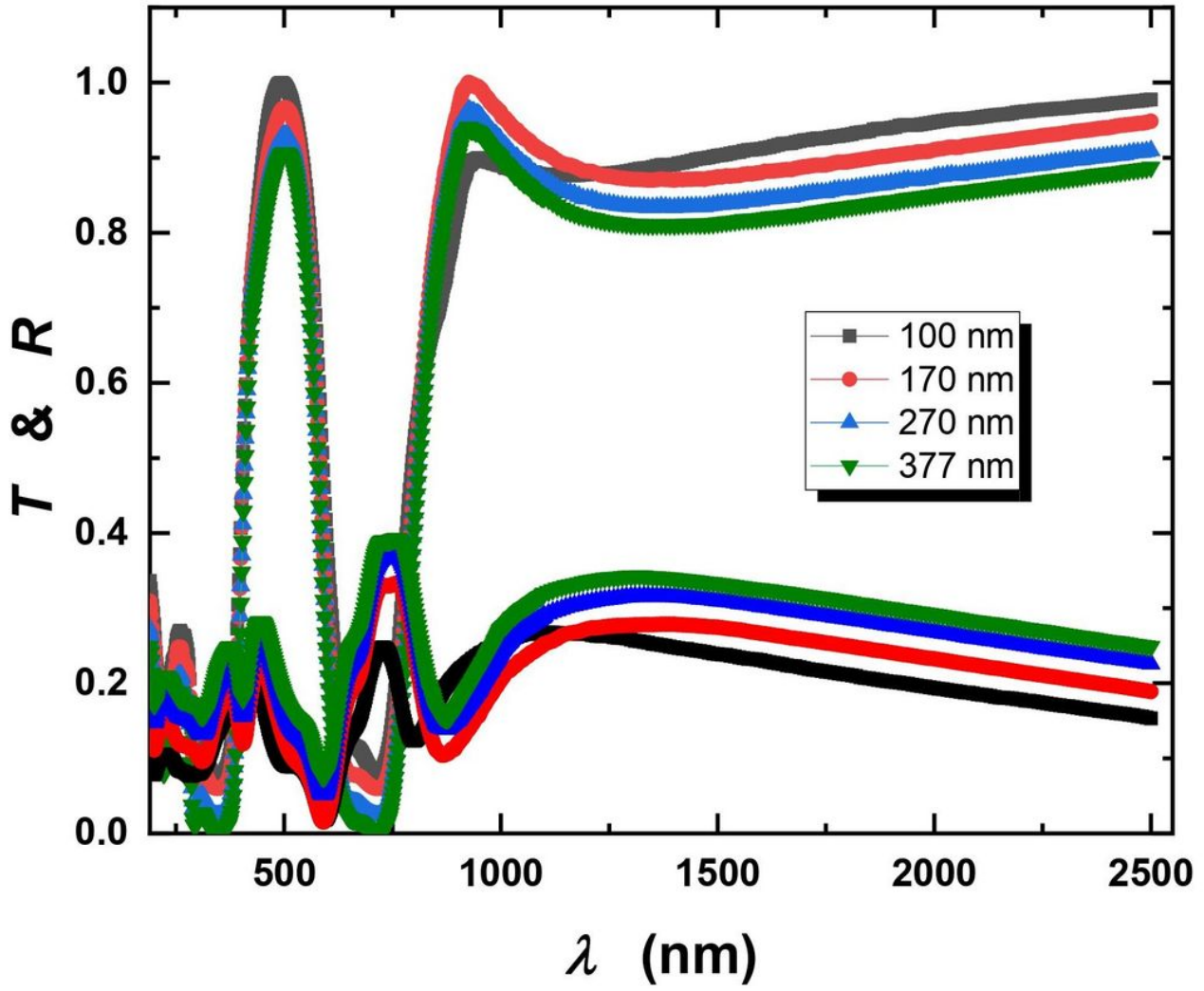


Figure 3

Spectra of T and R of TiPcCl₂ films with different thicknesses

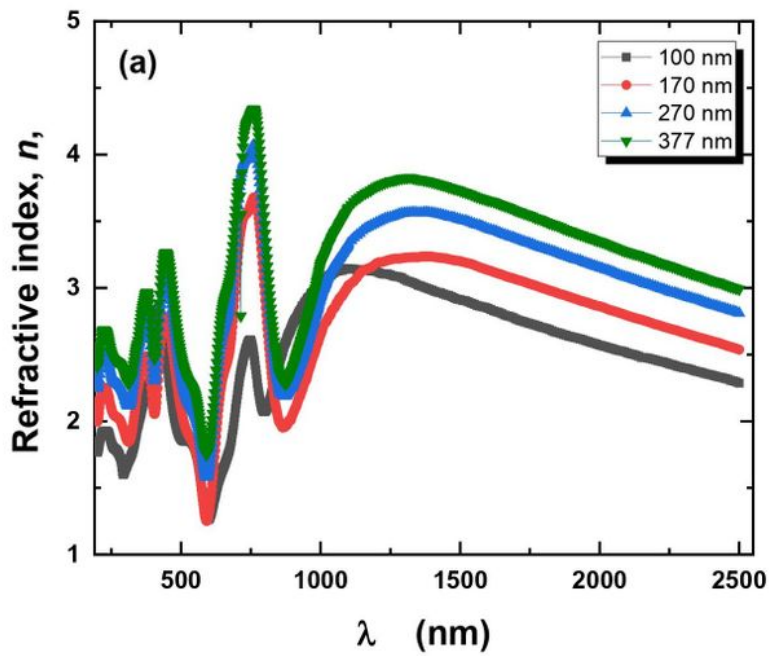
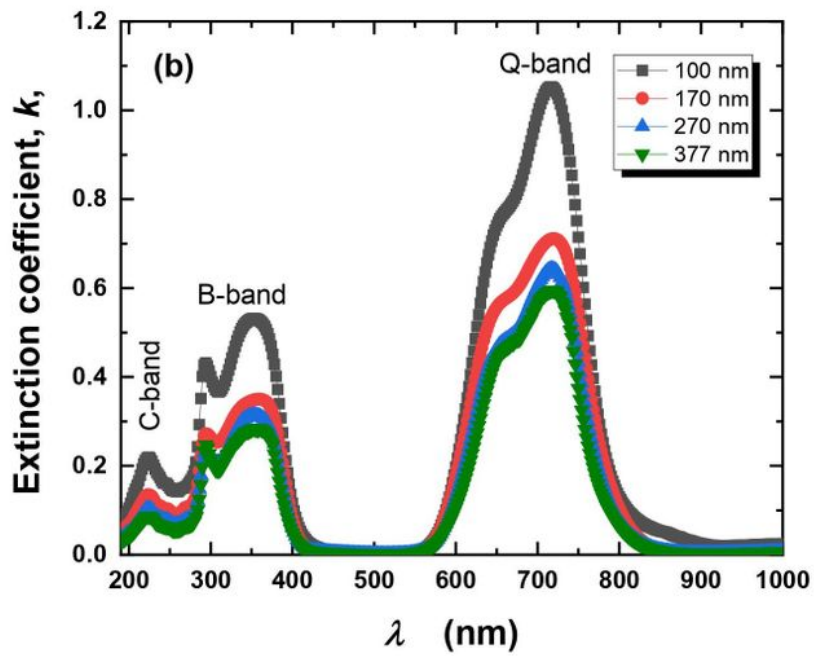


Figure 4

Spectra of (a) the refractive index, n , and (b) extinction coefficient, k , of TiPcCl_2 films with different thicknesses.

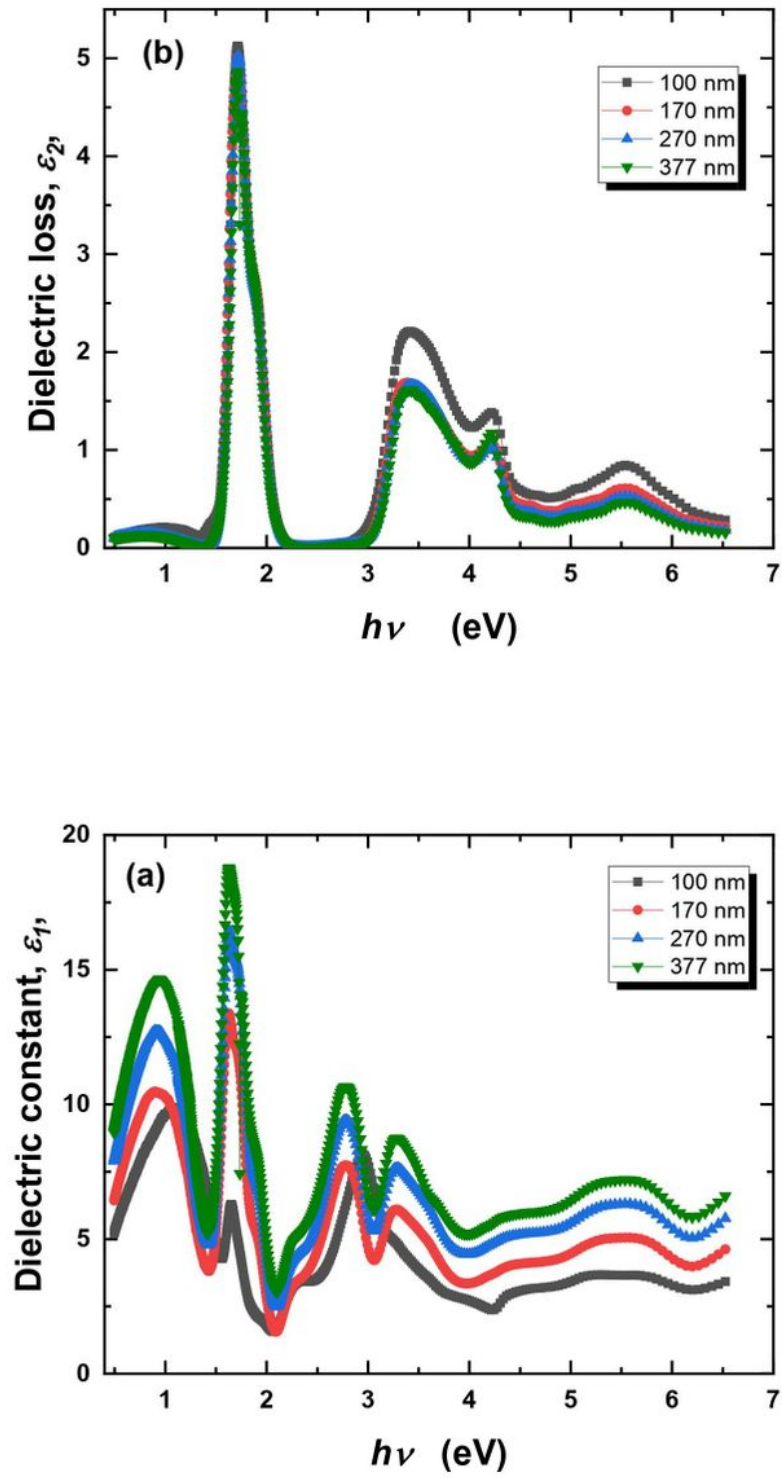


Figure 5

Spectra of (a) the dielectric constant, ϵ_1 , and (b) dielectric loss, ϵ_2 , of TiPcCl₂ films with different thicknesses.

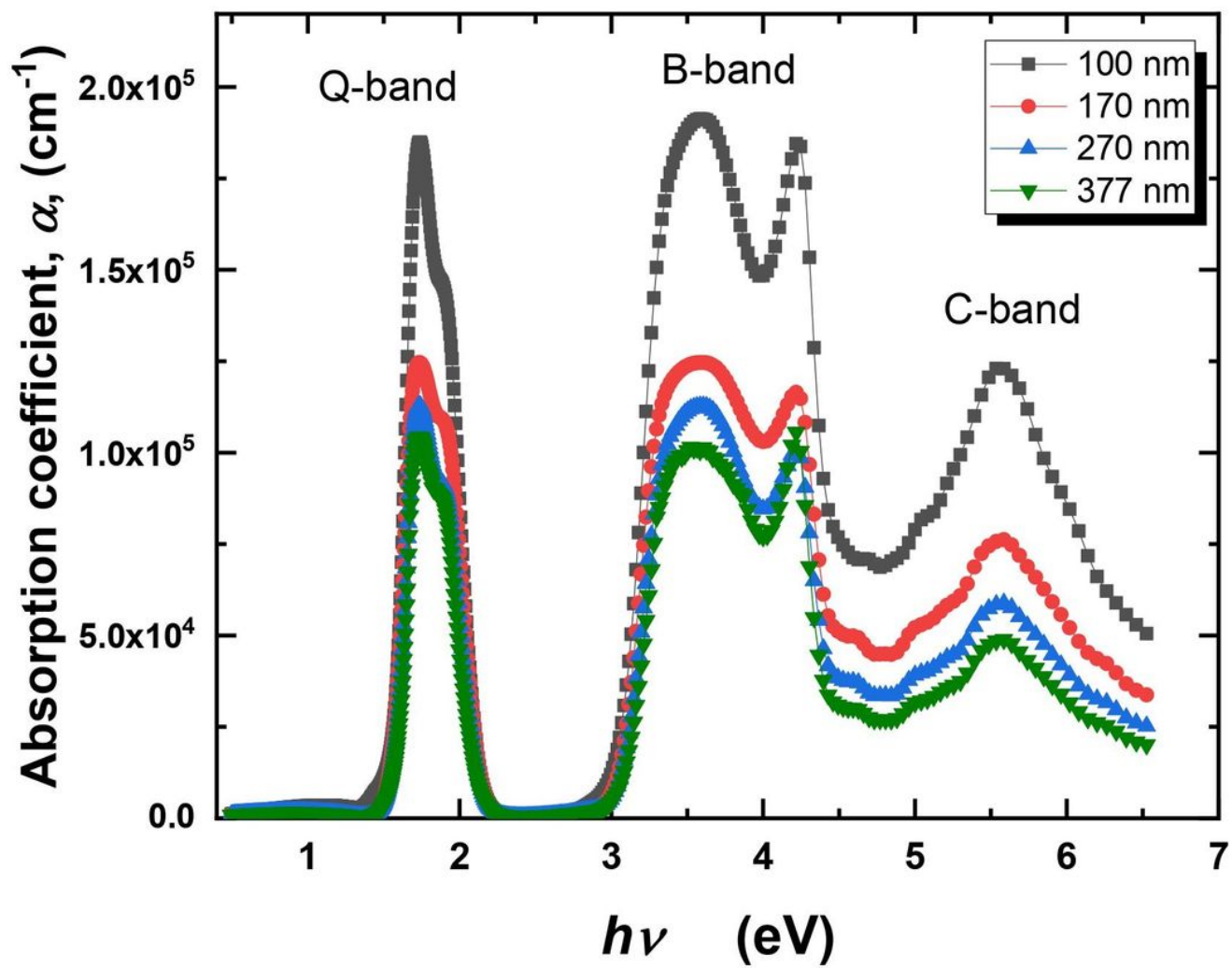


Figure 6

Spectra of the absorption coefficient, α , of TiPcCl₂ films with different thicknesses.

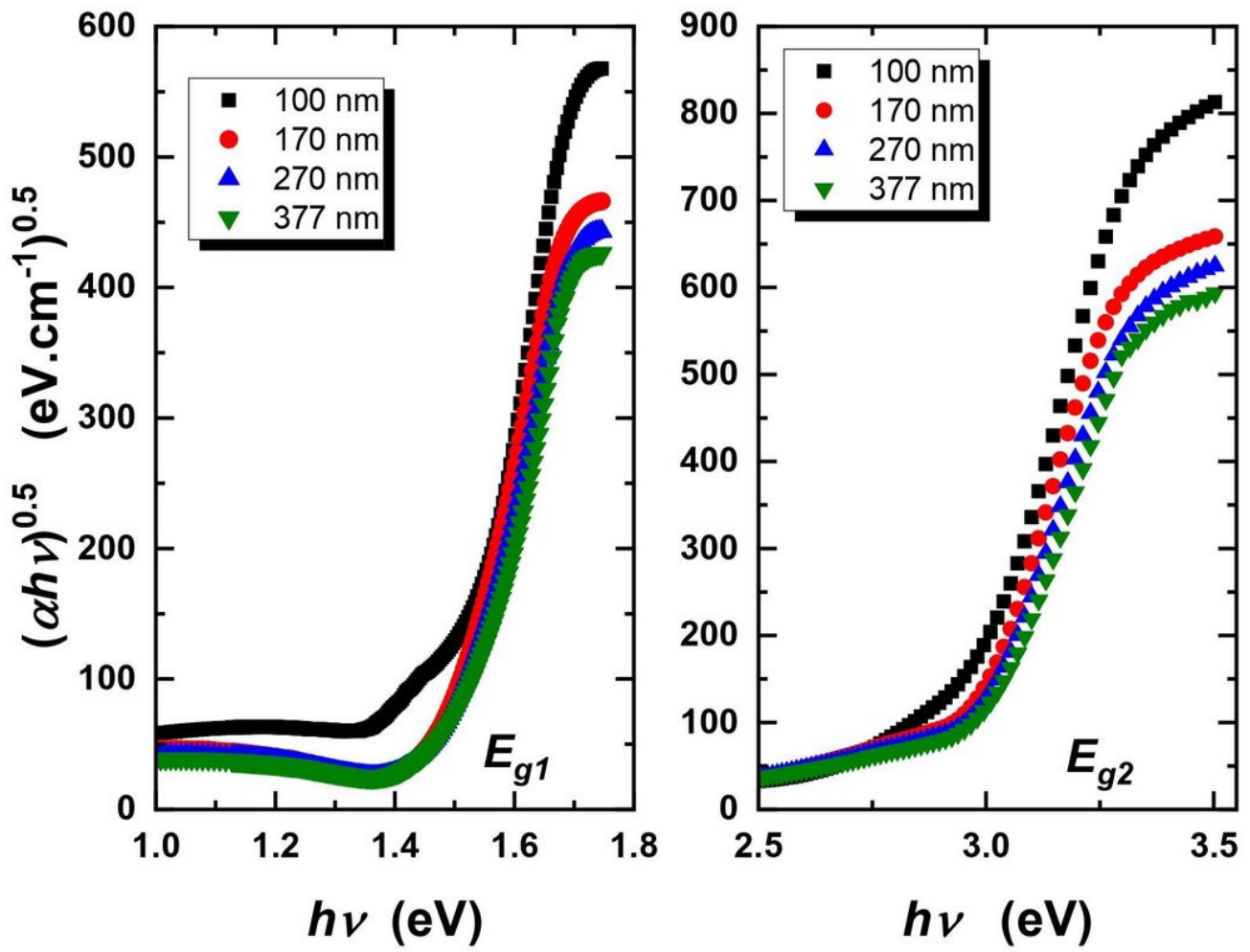


Figure 7

The relation between $(\alpha h\nu)^{0.5}$ and $h\nu$ for TiPcCl₂ films with different thicknesses

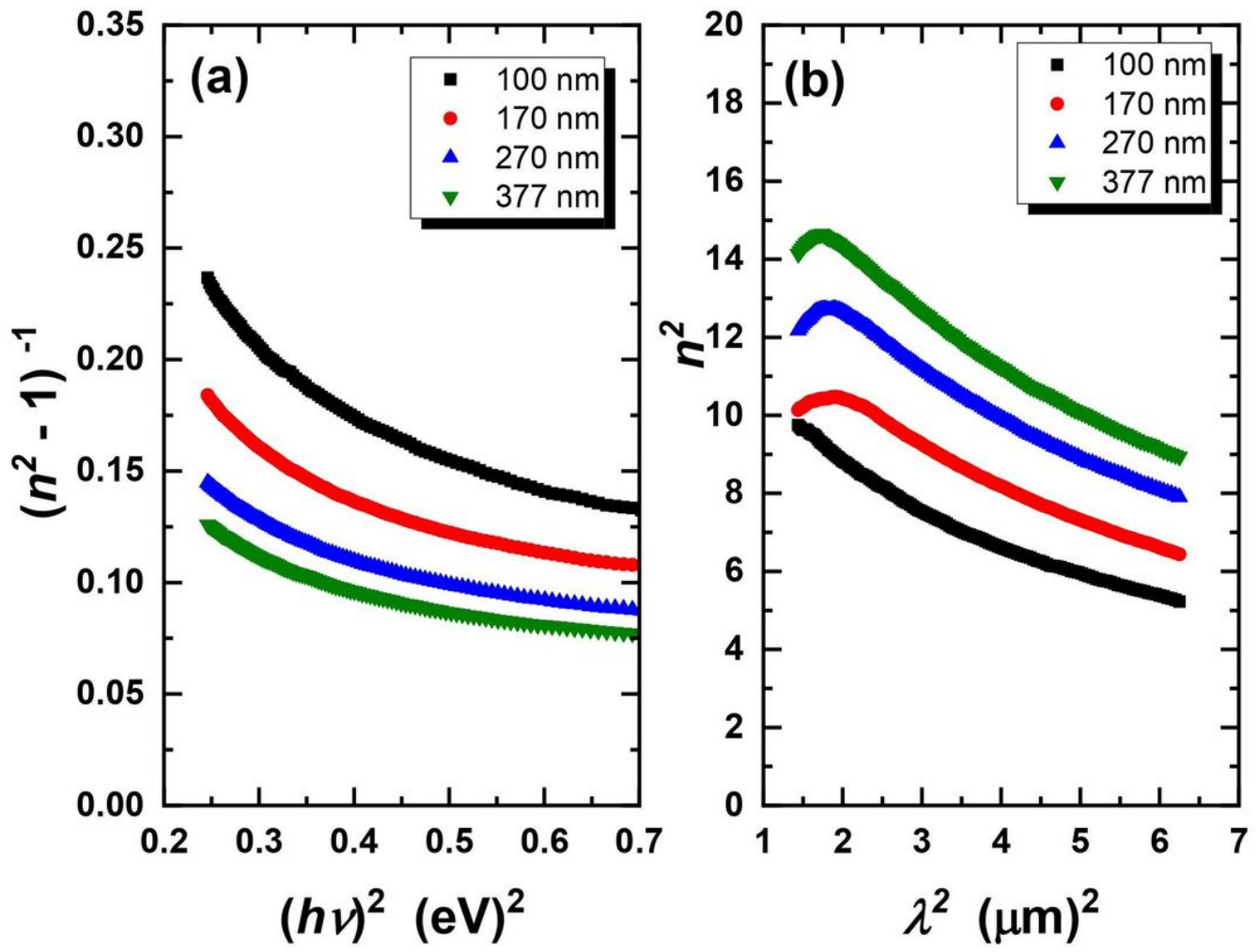


Figure 8

a) the relation between $(n^2 - 1)^{-1}$ and $(h\nu)^2$, b) the relation between n^2 and λ^2 for TiPcCl₂ films

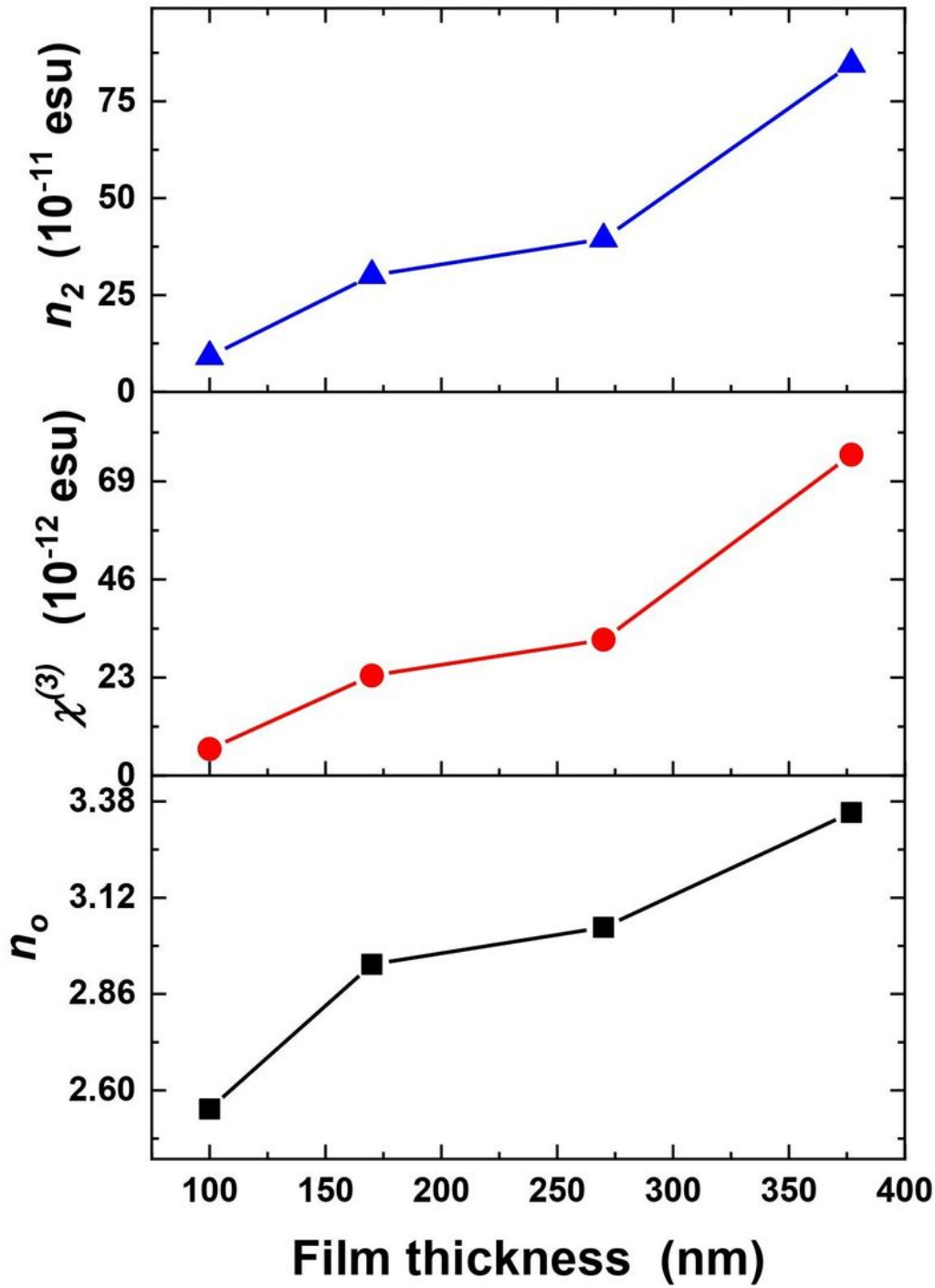


Figure 9

The nonlinear optical parameters of TiPcCl₂ films as a function of film thickness

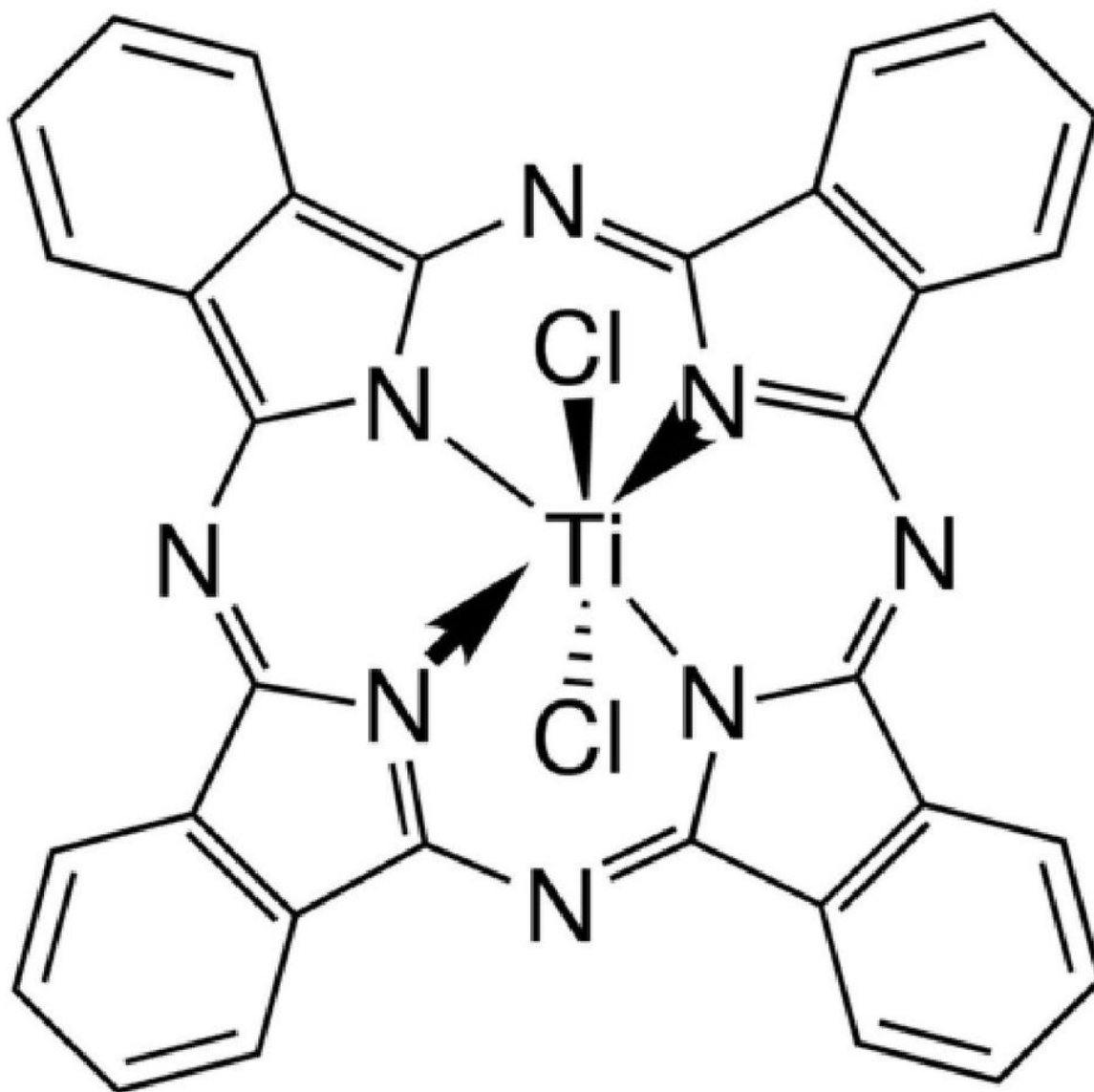


Figure 10

Scheme1-The molecular structure of TiPcCl_2 compounds