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Fourier-transform infrared and optical absorption spectra of 4-tricyanovinyl-*N*,*N*-diethylaniline thin films

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Abstract

Thin films of 4-tricyanovinyl-*N*,*N*-diethylaniline (TCVA) were prepared for the first time using thermal evaporation technique. The molecular structure and electronic transitions of TCVA films were investigated by Fourier-transform infrared (FTIR) and ultraviolet–visible (UV–vis) spectra. The observed vibrational wavenumbers in FTIR spectra were analysed and assigned to different normal modes of the molecule. UV–vis electronic absorption spectral measurements of TCVA films were analysed to obtain the electronic transitions and optical band gap (E_g). Other important optical parameters such as molar extinction coefficient ($\varepsilon_{\text{molar}}$), the oscillator strength (f), and the electric dipole strength (q^2) were also reported.

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Keywords: Organic thin film; FTIR spectra; Optical absorption

1. Introduction

The electronic and structural properties of the donor–acceptor substituted π-conjugated organic compounds are of considerable interest because of their applicability to optoelectronic devices and in fields of non-linear optics such as data storage [1]. Many donor–acceptor-conjugated organic molecules reported in the literature fall into the following categories: substituted benzene, biphenyls, stilbenes, azobenzenes ferrocenyl and schiff bases [2,3]. Disubstituted benzenes of the type D–Ph–A constitute a broad class of organic molecules with both technological and biological interest where D is an electron donor and A is an electron acceptor. Such compounds have been used in many applications such as dyeing of fabric, coloring of toners, and performing as dyes in photographic and optical information storage technologies.

4-Tricyanovinyl-*N*,*N*-diethylaniline (TCVA) is disubstituted benzenes of the type donor–acceptor with an electron donor (diethylamino group) and an electron acceptor (tricyanovinyl group) [4,5]. The molecular structure of TCVA is given in Fig. 1. This dye belongs to a class of organic compounds known as molecular rotors [5–7], which have a great importance as fluorescence probes of the flexibility of surrounding media [5–12]. It is used for coloring synthetic polymer fibers [13]. Also, it is applied as a sublimable dye in heat-transfer recording materials [14] and in photoconductive recording materials [15]. It has received some interest as a cytotoxic agent against tumours, as an X-ray protective agent and as a stabilizer in plastics against ultraviolet radiation [16].

The spectroscopic properties of organic electron-donor–acceptor complexes have received considerable attention [17–21]. Large changes in the polarity of molecules on electronic excitation had been early predicted by Förster [17] and were then found by Mülliken and Person [18] in charge-transfer complexes and by Nagakura and Tanaka [19] in intramolecular charge-transfer complexes. Conjugation of the donor and acceptor groups seemed to be the first condition for a significant contribution of the intramolecular charge-transfer interaction.

For organic compounds, energy gap can be evaluated by the energy interval between the highest occupied molecular orbital (HOMO) and the first excited states in the lowest unoccupied molecular orbital (LUMO) instead of the energy interval between valence band and conduction band for traditional crystalline semiconductors. The absorption spectra in

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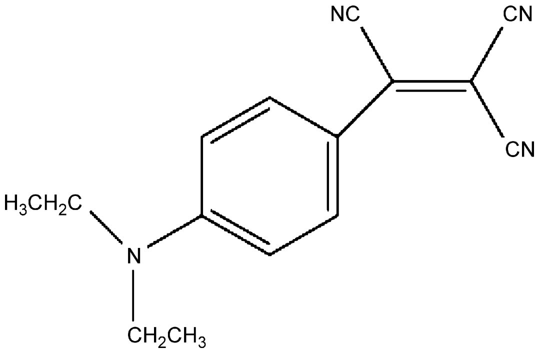

Fig. 1. The molecular structure of TCVA.

ultraviolet–visible (UV–vis) regions give important information about interacting conjugated π-electrons which obviously are also the basis of the relevant luminescent and electroluminescent properties of the organic materials [22]. The absorption and emission spectroscopic properties of TCVA have been investigated in the vapour phase [23] and in liquid solutions [24].

Up to our knowledge, no study has been done on spectroscopic of TCVA thin films. This has given us the motivation to study in detail the Fourier-transform infrared (FTIR) and the UV–vis spectroscopes of TCVA in the form of thin films. In this paper, TCVA thin films were prepared for the first time using thermal evaporation technique. Also, we present the utility of FTIR spectroscopy in the molecular structure analysis of TCVA thin films and the spectra have been analysed in terms of peak positions and intensities. Moreover, we studied its UV–vis spectra in an attempt to obtain information about its electronic transitions. We have also extended our measurements to examine carefully the main optical absorption edge and the optical energy gap in the UV–vis spectral range.

2. Experimental details

The TCVA compound was prepared by direct reaction between *N*,*N*-diethylaniline and tetracyanoethylene [25] and the synthesis was described as follows:

A solution of *N*,*N*-diethylaniline (10 mmol) was dissolved in *N*,*N*-dimethylformamide, DMF, (20 ml) and cooled to 0 °C. Tetracyanoethlene, TCNE, (10 mmol) was also dissolved in DMF (10 ml) and it was then added drop wise to the aromatic amine solution with stirring at 0 °C. After it has been completely added, the solution was then heated at 90 °C for 3 h with continuous stirring. The solvent was removed under reduced pressure and the crude dye was dissolved in chloroform and chromatographied on silica gel using a mixture of chloroform ethyl acetate (3:7) as eluent. Recrystallization from toluene gave TCVA as dark brown crystals in 85% yield. ^{1}H NMR (CDCL$_3$): δ 8.06 (d, $J = 10$ Hz), 6.73 (d, 2H, $J = 10$ Hz), 3.53 (q, 4H, $J = 7$ Hz, CH$_2$), 1.29 (q, 6H, $J = 7$ Hz, CH$_3$). Elemental analysis: found C, 71.85; H, 5.72; N, 22.31; calculated for $C_{15}H_{14}N_4$: C, 72.00; H, 5.60; N, 22.40.

In addition, thermal analysis is carried out by differential scanning calorimeter (DSC) using Shimadzu DSC-50. The results of this investigation are presented in Fig. 2, which showed that this compound is stable up to 150 °C. Also, a sharp endothermic peak at 168 °C was observed, which corresponds to the melting point of the material. The X-ray diffraction patterns of TCVA in powder form show that there are several peaks with different intensities indicating that the material is polycrystalline.

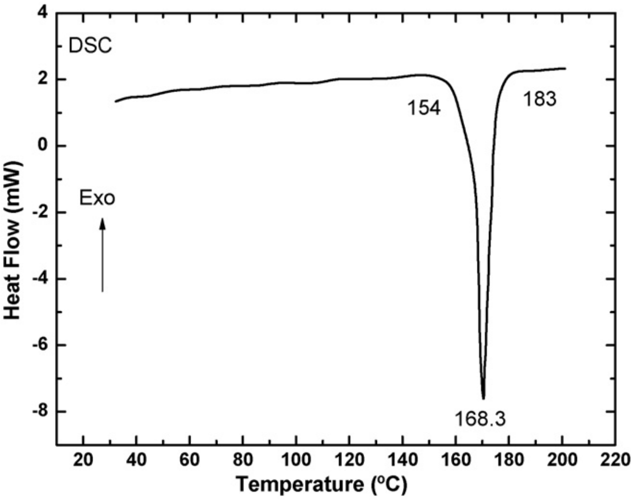

Fig. 2. The differential scanning calorimeter, DSC, thermogram of TCVA compound at a heating rate of 10 °C/min.

TCVA films were prepared by thermal evaporation technique using a high vacuum coating unit (Edwards, E306A). Thin films were deposited from a titanium evaporator charged by TCVA in a vacuum of 10^{-4} Pa. The material was heated up by passing a suitable current through the titanium evaporator. The deposition rate (5 nm s^{-1}) was controlled using a quartz crystal thickness monitor (Edwards, FTM4). Some of these films were annealed at 150 °C for 2 h in air. After annealing, the temperature was slowly reduced to the ambient temperature. X-ray diffraction patterns (not represented) recorded for the as-deposited TCVA film, showed that there are several peaks with background of amorphity indicating that the film is in a certain degree of crystallinity. Also, X-ray diffraction patterns of the annealed film show that the peaks increased in their intensities, which indicated that annealing enhanced its degree of crystallinity.

FTIR on TCVA films was performed using Bruker, Vector 22 infrared spectrophotometer in the infrared spectral range 400–4000 cm^{-1}. For FTIR measurements of the powder form, 1 mg of TCVA powder was mixed with 50 mg of vacuum dried IR-grad KBr. However, for film form, a film of thickness 636 nm was deposited onto optically flat KBr single crystal substrate. The UV–vis absorption spectra of TCVA films deposited onto optically flat fused quartz substrates were recorded on spectrophotometer (JASCO model V-570 UV–vis–NIR). All the spectra were recorded at room temperature.

3. Results and discussion

3.1. Infrared spectra

The infrared spectrum is the unique characteristic of functional groups stacking the molecule and is found to be the most

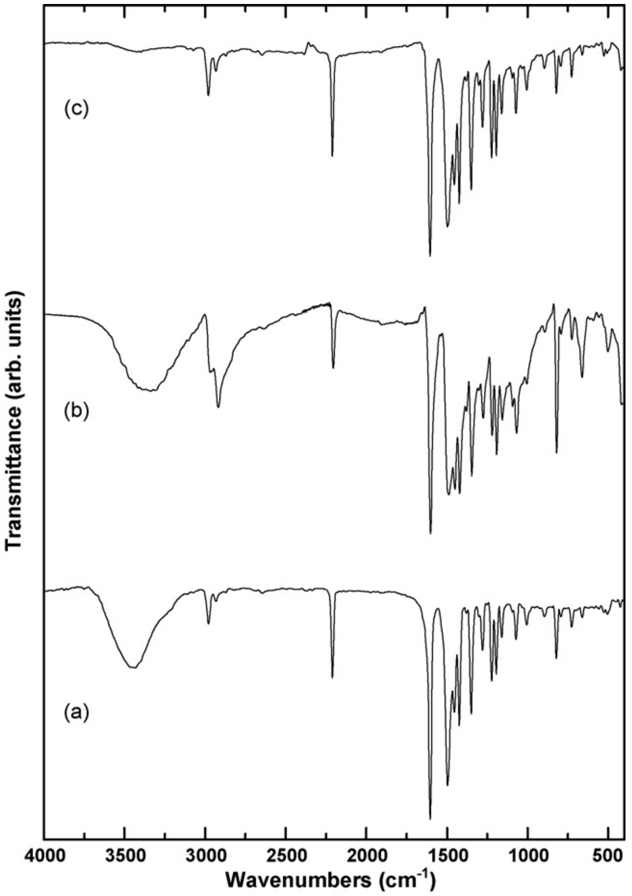

Fig. 3. Infrared spectra of TCVA for (a) powder form, (b) as-deposited film and (c) annealed film at 150 °C for 2 h.

Table 1
The position of band in FTIR spectra of different forms of TCVA

Powder	Film		Assignment
	As-deposited	Annealed	
3432.7	3368.2	3424.9	O–H stretching vibration.
3100	3100	3100	C–H aromatic
2977.6	2967.9	2979.5	C–H asymmetric stretching in CH_3
2931.3	2917.8	2933.2	C–H asymmetric stretching in CH_2
2210.0	2206.2	2210.0	C≡N stretching vibration
1602.6	1602.6	1604.5	C=C stretching vibration
1494.6	1488.8	1490.5	C=C bending vibration
1449.9	1449.9	1449.9	CH_3 asymmetric deformation
1423.2	1421.3	1423.2	CH_2 in-plane deformation
1348.0	1346.1	1348.0	C–H symmetric deformation in CH_3
1278.6	1276.7	1278.6	C–H in plane bending
1220.7	1218.8	1220.7	CH_2 wagging
1199.7	1191.8	1185.4	CH_2 twisting
1156.8	1153.2	1142.5	CH_3 wagging
1070.3	1068.4	1070.3	C–C stretching
1004.7	1004.7	1004.7	C–C stretching
914.2	894.8	894.8	CH_3 rocking
819.6	819.6	819.6	C–H out of plane bending
792.7	794.5	794.5	CH_2 rocking
725.1	725.1	725.1	CH_2 rocking
663.9	661.5	658.8	C–C in plane bending
571.0	595.9	585.8	C–C in plane bending
542.9	553.9	557.2	C–C in plane bending
503.0	501.4	505.3	C–C in plane bending
442.8	428.0	428.5	C–C in plane bending

Absorption frequencies are in cm^{-1}.

useful physical method of investigation in identifying functional groups and to know the molecular structure. The absorption of IR radiation causes the various bands in a molecule to stretch and bend with respect to one another. The most important range (400–4000 cm^{-1}) is of prime importance for the study of an organic compound by spectral analysis [26]. The infrared spectrum has two regions. The fingerprint region is unique for a molecule and the functional group region is similar for molecules with the same functional groups.

Fig. 3 shows FTIR spectra of powder, as-deposited and annealed film of TCVA and all the wavenumber values of peaks values are listed in Table 1. A comparison of FTIR spectra of powder and as-deposited film forms indicates that thermal evaporation technique is a good one to obtain undissociated TCVA films. In addition, the FTIR spectrum of the annealed TCVA film is similar to the spectra of powder and as-deposited film, which indicated that TCVA film has good thermal stability.

Absorption bands found in the high-frequency (4000–2700 cm^{-1}) region of spectrum are usually associated with O–H and C–H stretching modes. Fig. 3 shows a broad intensity band at 3432.7 cm^{-1} for TCVA powder and at 3368.2 cm^{-1} for as-deposited film. This band can be logically assigned to a hydroxyl group O–H stretching vibration. The presence of the O–H band in IR spectrum indicates that the material contains hydroxyl group despite the molecular structure dos not contain this group. This means that hydroxyl group could be interred due to the absorption of water (H_2O) by the material. However, the spectrum of TCVA annealed films shows that this peak is removed indicating that when the material is heated and at a certain temperature water will be removed. The 3100 cm^{-1} absorption band is assigned to C–H aromatic. In addition, the 2977.6 cm^{-1} absorption band is assigned to an asymmetric C–H stretching mode of the CH_3 group and the 2931.3 cm^{-1} absorption can be assigned to C–H asymmetric stretching in CH_2.

A sharp absorption band appearing at 2210 cm^{-1} is assigned to the stretching vibration of C≡N group that forms conjugated bond with benzene ring. The strong band appearing at 1602.6 cm^{-1} is due to C=C stretching vibration. These bands point to the incorporation of the tricyanovinyl group. The peaks at 1450 and 1367.8 cm^{-1} indicate to the CH_3 bending modes. The CH_2 in-plane deformation and CH_2 wagging were observed at 1423.2 and 1344 cm^{-1}, respectively. The C–H deformation bands of aromatic C–H groups are observed at 819.6 and 792.7 cm^{-1}. The bands in the 792.7–679 cm^{-1} region can be assigned to C–H and C–C vibrations.

3.2. *The electronic absorption spectra*

The absorption spectra of as-deposited and annealed TCVA films are shown in Fig. 4. The energies corresponding to the absorption maximum presented in these spectra are listed in Table 2. The electronic absorption spectra of TCVA display four main bands. The first band (*A*) at 200–230 nm is assigned to the

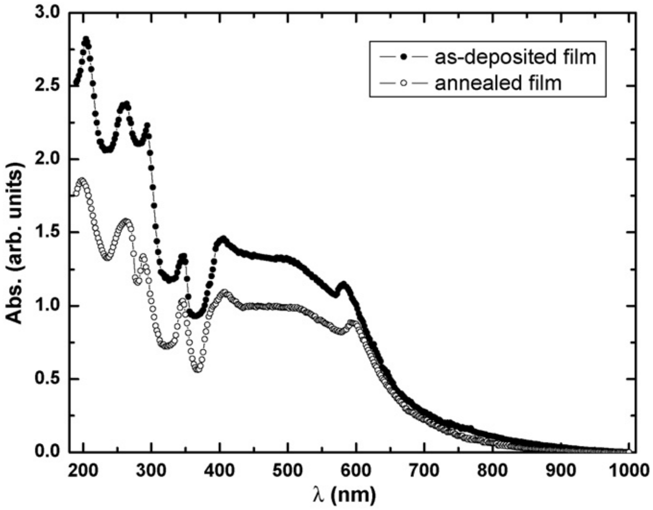

Fig. 4. The absorption spectra of as-deposited and annealed TCVA films.

n–σ* transitions of *N*,*N*-diethylaniline group and second band (*B*) at 235–365 nm is assigned to the π–π* transitions of the aromatic rings; this band appears splitted. The third band (*C*) at 370–565 nm involves n–π* transition of the C≡N groups. The longer wavelength band (*D*) at 570–900 nm can be assigned to an intramolecular charge-transfer interaction. The charge transfer will originate from *N*,*N*-diethylaniline group as an origin to the C≡N group as a sink.

This absorption is in agreement with that obtained for 4-tricyanovinyl-*N*,*N*-dimethylaniline whose absorption spectrum was recorded in different solvents [25]. The bands are assigned as a charge-transfer bands arising from the resonance of the lone pair of nitrogen atom of the aniline to the tricyanovinyl substituents. An intense absorption band in the visible region was also obtained for 4-dicyanovinyl-*N*,*N*-dimethylaniline (*p*-*N*,*N*-dimethylaminobenzylidenemalononitrile) in different solvents [5] where they explained their results by π–π* transition with a considerable amount of intramolecular charge-transfer character.

Generally the spectra of the molecule possessing phenyl–cyan complexes demonstrate extremely large intra-molecular charge transfer [22], which substantially changes both linear as well as non-linear optical properties. So one can expect an occurrence of the large range of the optical properties with the enhanced non-linear optical susceptibilities. This is unambiguously confirmed by the annealing spectral features presented in Fig. 4, probably due to contribution of enhanced number of the electron-vibration anharmonic modes.

The absorption bands are due to electronic transition from the ground states to excited states. During such a transition in a molecule, electrons are promoted from HOMO to LUMO. In a semiconductor bulk solid, the transitions occur between the valence band and conduction band. The valence band and conduction band are the solid-state analogue of the HOMO and LUMO of a molecule. E_g is the band gap or difference between the valence and conduction bands. The optical absorption coefficient (α) of a solid describes the exponential decay of light intensity with the distance into solid ($I_t = I_0\,e^{-\alpha d}$). It can be described using the expression:

$$\alpha = \frac{2.303 \times \text{Abs}}{d} = \frac{2.303 \times \text{OD}}{d} \tag{1}$$

Here d is the film thickness and

$$\text{Abs} \equiv \text{OD} = \log_{10}\left(\frac{I_0}{I_t}\right) = \log_{10}\left(\frac{1}{T}\right) \tag{2}$$

where T is transmittance and Abs is the absorbance or the optical density OD.

In many organic materials, it is usual to analyse the optical absorption at the fundamental edge in terms of band-to-band transitions theory [27–32]. In this treatment, the absorption data follows a power law, which is given by [33]:

$$(\alpha h\nu)^{\mathrm{m}} = g(h\nu - E_g) \tag{3}$$

and yield values of the optical energy band (E_g). Here g is a constant and m is an index which can assume values of 2, 1/2, 1/3 or 3/2 depending on the nature of the band-to-band electronic transitions and the profile of the electron density in the valance and conduction bands. The experimental data have been fitted with the theoretical equation (3) for different values of m. As expected, the best fit is obtained for $m = 1/2$. This behaviour indicated that the transitions are indirect allowed transitions, which are expressed by the following modified equation:

$$(\alpha h\nu)^{1/2} = g(h\nu - E_g \pm E_{ph}) \tag{4}$$

where E_{ph} is the energy of phonons assisted. Fig. 5 shows the functional dependence of $(\alpha h\nu)^{1/2}$ on $h\nu$ for as-deposited and annealed TCVA films. The obtained values of E_g and E_{ph} from these curves are listed in Table 2.

The tail of the absorption edge is exponential indicating the presence of localized states in the energy band gap and supporting the amorphous background obtained in the X-ray pattern. The origin of this band tailing is still a matter of conjecture but according to Dow and Redfield [34] it arises from the random fluctuations of the internal fields associated with structural disorder which are considerable in many amorphous solids. The amount of tailing can be estimated to a first approximation by plotting the absorption edge data in terms of an equation originally given by Urbach [35] and which has been applied to many

Table 2
The electronic transitions in TCVA film

	A (eV)	B			C		D (eV)	E_g (eV)	E_{ph} (meV)	E_t (meV)
		B_1 (eV)	B_2 (eV)	B_3 (eV)	C_1 (eV)	C_2 (eV)				
As-deposited film	6.08	4.73	4.22	3.56	3.05	2.49	2.13	1.45	114	217
Annealed film	6.26	4.73	4.30	3.58	3.04	2.50	2.09	1.51	91	141

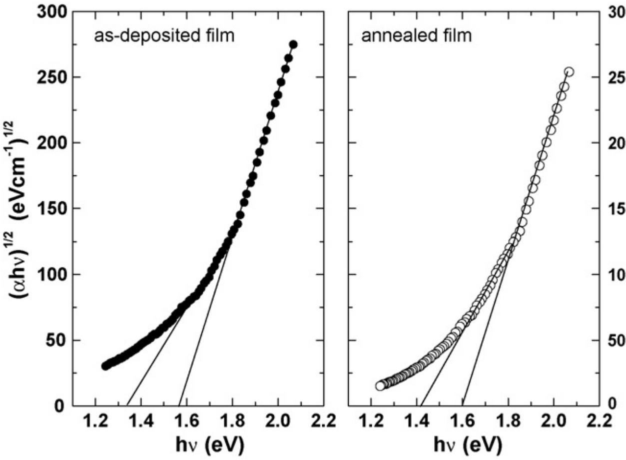

Fig. 5. Plot of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ for as-deposited and annealed TCVA films.

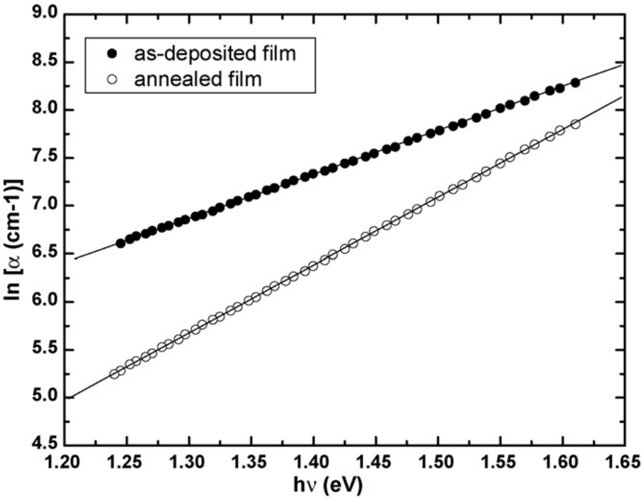

Fig. 6. Plot of $\ln(\alpha)$ vs. $h\nu$ for as-deposited and annealed TCVA films.

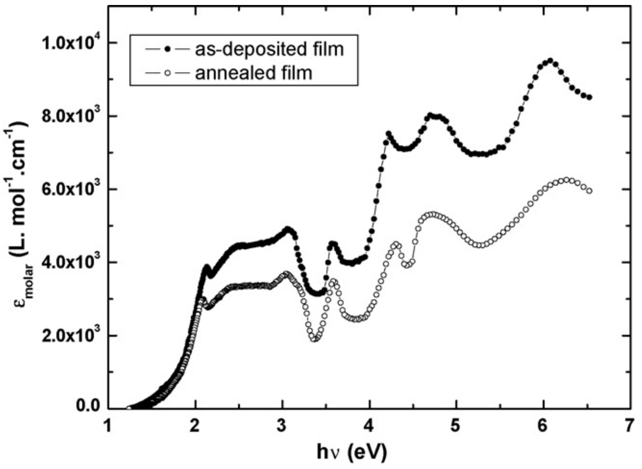

Fig. 7. Plot of $\varepsilon_{\text{molar}}$ vs. $h\nu$ for as-deposited and annealed TCVA films.

glassy materials. The absorption edge of non-metallic materials gives a measure of the energy band gap and the exponential dependence of the absorption coefficient, $\ln(\alpha)$, on photon energy, $h\nu$, is found to hold over several decades for a glassy material and takes the form [35]:

$$\ln(\alpha) = \ln(\alpha_0) - \left(\frac{h\nu}{E_t}\right) \tag{5}$$

where α_0 is a constant and E_t is interpreted as the width of the tail of localized states in the forbidden band gap. Fig. 6 represents the linear dependence of the natural logarithm of absorption coefficient, $\ln(\alpha)$, on the photon energy, $h\nu$, for as-deposited and annealed TCVA films. The reciprocal of the slope of each line yields the magnitude of E_t and its values for as-deposited and annealed films are listed in Table 2. It is clear that annealing process increases the energy gap of TCVA film and decreases both phonon energy and width of the tail of localized states.

It is useful to relate the absorption coefficient, α, to the molar extinction coefficient, $\varepsilon_{\text{molar}}$, which is often used to describe the absorption of light by non-solid molecular media. The spectral distribution of the molar extinction coefficient was calculated from the relation [36]:

$$\alpha = \frac{\rho}{M} \times 10^3 \ln(10)\varepsilon_{\text{molar}} \tag{6}$$

where ρ is the solid mass density; M the molecular weight; $\varepsilon_{\text{molar}}$ is in units of $\mathrm{L\,mol^{-1}\,cm^{-1}}$. The spectral distributions of $\varepsilon_{\text{molar}}$ for as-deposited and annealed TCVA films are shown in Fig. 7.

The two most important parameters are the oscillator strength, f, and the electric dipole strength, q^2 where their values were calculated by using the following mathematical expression [32]:

$$f = 4.32 \times 10^{-9} \int \varepsilon_{\text{molar}}(\nu)\,\mathrm{d}\nu \tag{7}$$

Table 3
The spectral parameters of TCVA film at different bands

Band	$\lambda_{\max}$ (nm)		$\varepsilon_{\text{molar}}$ ($\mathrm{L\,mol^{-1}\,cm^{-1}}$)		q^2 (Å)		f	
	As-deposited	Annealed	As-deposited	Annealed	As-deposited	Annealed	As-deposited	Annealed
A	204	198	9515	6254	0.67	0.48	0.30	0.37
B_1	262	262	8019	5313	0.20	0.12	0.01	0.17
B_2	294	288	7518	4499	0.21	0.13	0.05	0.03
B_3	348	346	4508	3483	0.08	0.06	0.01	0.01
C_1	406	408	4914	3680	0.60	0.16	0.04	0.01
C_2	498	496	4404	3354	0.76	0.58	0.14	0.10
D	582	592	3876	2922	0.25	0.13	0.05	0.02

$$q^2 = \left(\frac{1}{2500}\right)\varepsilon_{\text{molar}}\left(\frac{\Delta\lambda}{\lambda}\right) \tag{8}$$

where $\Delta\lambda$ is the absorption half bandwidth. In order to evaluate the oscillator strengths and the electric dipole strength, a Gaussian fit was performed to each peak. The calculated parameters for as-deposited and annealed TCVA films are listed in Table 3. A comparison of these results shows that all parameters vary in the band regions, and have a slight change by annealing process.

4. Conclusion

TCVA thin films were prepared for the first time using thermal evaporation technique. A comparison of FTIR spectra of powder and as-deposited thin film forms indicated that the thermal evaporation technique is a good one to obtain undissociated TCVA films. In addition, the IR spectrum of the annealed TCVA film is similar to the spectra of powder and as deposited film, which indicated that TCVA film has good thermal stability. According to the optical absorption spectra, TCVA thin film has a wide absorption range spectrum in UV–vis region, which is appropriate for application of TCVA thin films in photovoltaic devices. Furthermore, the analysis of absorption coefficient revealed indirect transitions with 1.45 eV as energy band gap.

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References

[1] R.W. Boyd, Nonlinear Optics, Academic Press, New York, 1992.
[2] K.D. Singer, J.E. Sohn, L.A. King, H.M. Gordon, H.E. Katz, C.W. Dirk, J. Opt. Soc. Am. B 6 (1989) 1339.
[3] C.F. Shu, Y.K. Wang, J. Mater. Chem. 8 (1998) 833.
[4] A. Safarzadeh-Amiri, Can. J. Chem. 62 (1984) 1895.
[5] R.O. Loutfy, K.Y. Law, J. Phys. Chem. 84 (1980) 2803.
[6] R.O. Loutfy, Pure Appl. Chem. 58 (1986) 1239.
[7] M.S.A. Abdel-Mottaleb, R.O. Loutfy, R. Lapouyade, J. Photochem. Photobiol. A 48 (1989) 87.
[8] R.O. Loutfy, K.Y. Law, Macromolecules 14 (1981) 587.
[9] K.Y. Law, Chem. Phys. Lett. 75 (1980) 545.
[10] K.Y. Law, Photochem. Photobiol. 33 (1981) 799.
[11] R.O. Loutfy, B.A. Arnold, J. Phys. Chem. 86 (1982) 4205.
[12] R.O. Loutfy, Macromolecules 16 (1983) 678.
[13] A.T. Peters, M.S. Wild, J. Soc. Dyers Colour 93 (1977) 126.
[14] N. Taguchi, A. Imai, T. Niwa, Y. Murata, Eur. Pat. Appl. EP. 163 (1984) 145.
[15] H.E. Wright, M.A. Berwick, Res. Discl. 158 (1977) 62.
[16] S.S.M. Hassan, J.M. Abdella, N.E. Nashed, Mikrochim. Acta 83 (1984) 27.
[17] R. Förster, Organic Charge-Transfer Complexes, Academic Press, London, 1969.
[18] R.S. Mülliken, W.B. Person, Molecular Complexes, Wiley-Interscience, New York, 1969.
[19] S. Nagakura, J. Tanaka, J. Chem. Phys. 22 (1954) 236.
[20] T.P. Carsey, G.L. Findley, S.P. McGlynn, J. Am. Chem. Soc. 101 (1970) 4502.
[21] Z.R. Grabowski, K. Rotklewicz, A. Siemiarczuk, D.J. Cowtey, W. Nouv. Baumann, J. Chim. 3 (1970) 443.
[22] E. Koscien, J. Sanetra, E. Gondek, B. Jarosz, I.V. Kityk, J. Ebothe, A.V. Kityk, Spectrochim. Acta Part A 61 (2005) 1933.
[23] A.V. Deshpande, A. Beidoun, A. Penzkofer, G. Wagenblast, Chem. Phys. 142 (1990) 123.
[24] A.V. Deshpande, A. Beidoun, A. Penzkofer, G. Wagenblast, Chem. Phys. 148 (1990) 141.
[25] A.M. Asiri, J. Saudi Chem. Soc. 6 (1) (2002) 51.
[26] J.R. Dyer, Applications of Absorption Spectroscopy of Organic Compounds, Prentice-Hall of India (P), New Delhi, 1987.
[27] M.M. El-Nahass, K.F. Abd-El-Rahman, A.A.M. Farag, A.A.A. Darwish, Int. J. Modern Phys. B 18 (2004) 421.
[28] M.M. El-Nahass, K.F. Abd-El-Rahman, A.A. Al-Ghamdi, A.M. Asiri, Physica B 344 (2004) 398.
[29] G.B. Kamath, C.M. Joseph, C.S. Menon, Mater. Lett. 57 (2002) 730.
[30] K.R. Rajesh, C.S. Menon, Mater. Lett. 51 (2001) 266.
[31] G.A. Kumar, J. Thomas, N. George, N.V. Unnikrishnan, P. Radhakrishnan, V.P.N. Nampoori, C.P.G. Vallabhan, J. Mater. Sci. 35 (2000) 2539.
[32] G.A. Kumar, J. Thomas, N. George, B.A. Kumar, P. Radhakri, V.P.N. Shnan, C.P.G. Poori, N.V. Vallabhan, Unnikrishnan, Phys. Chem. Glasses 41 (2000) 89.
[33] J. Bardeen, F.J. Blatt, L.H. S Hall, Proceedings of the Conference on Photoconductivity, Atlantic City, November 4–6, 1965, p. 149.
[34] J.D. Dow, D. Redfield, Phys. Rev. B 5 (1972) 594.
[35] F. Urbach, Phys. Rev. 92 (1953) 1324.
[36] B.H. Schechtman, W.E. Spicer, J. Mol. Spect. 33 (1970) 28.