

Spectroscopy of pyrene (TNF)₂, perylene (TNF)₂ and (DPPD)₅I₁₂

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Abstract : The UV-visible and infrared spectra of three conducting charge transfer complexes namely (DPPD)₅I₁₂ pyrene (TNF)₂ and perylene (TNF)₂, where DPPD = N,N,N',N'-diphenyl-p-phenylenediamine and TNF = 2,4,5,7-tetranitro-9-fluorenone, have been studied. Spectra are analyzed to evaluate band gaps and to understand nature of transitions. Optical conductivity spectra are calculated using Kramers-Kronig relations. Two absorption envelopes at 1600 cm⁻¹ and 3400 cm⁻¹ are found to be Gaussians. The UV-visible spectra show plasma edges.

Keywords : Infrared spectra, UV-visible spectra, conducting charge transfer complexes

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1. Introduction

Many charge transfer complexes were found to be semiconducting [1,2]. Recently, highly conducting radical-ion salts have been studied [3]. (DPPD)₅I₁₂ [where DPPD = N,N,N',N'-diphenyl-p-phenylenediamine] is known and complex is found to be semiconducting with an activation energy of 0.07 eV from the resistivity measurement [4]. Its structure was also studied [5]. TNF (2,4,5,7-tetranitro-9-fluorenone) was used as acceptor to prepare pyrene (TNF)₂ and perylene (TNF)₂. Molecular structures of the chemicals used are shown in Figure 1.

2. Experimental details

(DPPD)₅I₁₂ has been prepared from mixed solutions of DPPD and iodine in hot chloroform. It is a blue material which turns green slowly after a long exposure to air. Pyrene (TNF)₂ and perylene (TNF)₂ are prepared from solutions in acetonitrile. TNF has been obtained from Aldrich Chemical Co., pyrene (TNF)₂ is green-blue and perylene (TNF)₂ is dark blue.

Both of the complexes are crystallized from solutions in xylene by evaporation at a constant temperature in a temperature-controlled hot water bath.

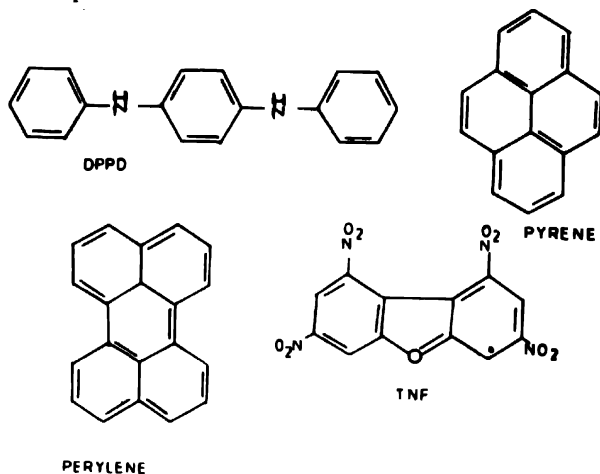


Figure 1. Molecular structures of donors and acceptors.

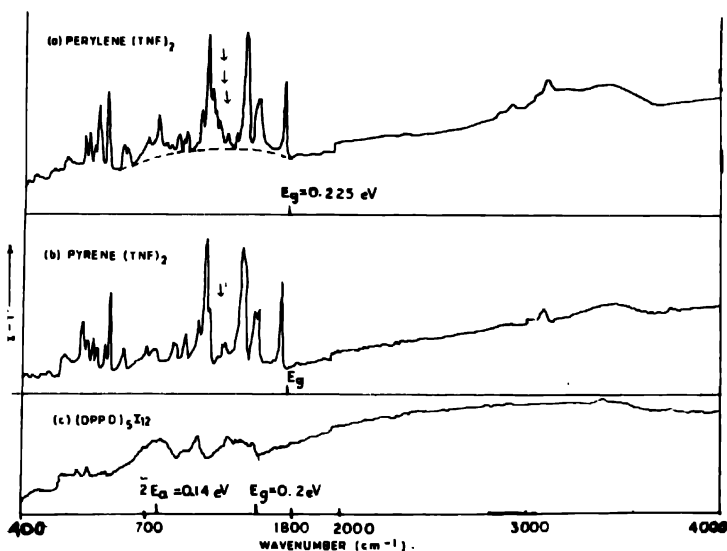


Figure 2. Infrared spectra of (DPPD)₅I₂, pyrene (TNF)₂ and perylene (TNF)₂. Broad Gaussian in the background absorption in perylene (TNF)₂ is shown with broken line which is not found for other two complexes.

The samples for measurements in infrared range are prepared by grinding the materials along with KBr powder in a mortar and then pressing in a die to prepare pellets

of regular shape and size. For nujol mull spectra, suspensions are prepared in paraffin oil. The infrared spectra using KBr are shown in Figures 2 and 3. The nujol mull spectrum of

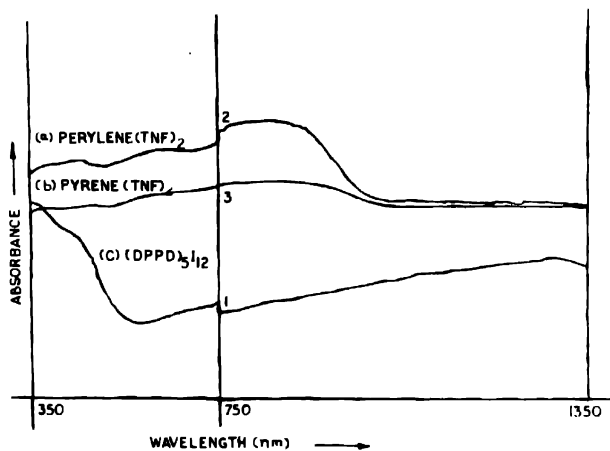


Figure 3. UV-visible spectra of (DPPD)₅I₂, pyrene (TNF)₂ and perylene (TNF)₂. Vertical line at 750 nm indicates change in filter.

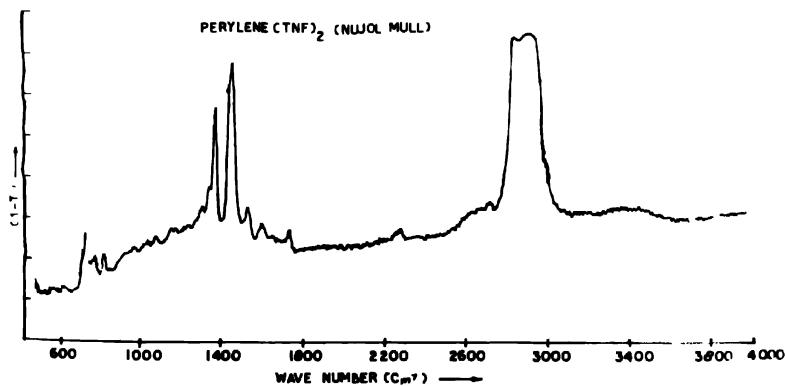


Figure 4. Nujol mull infrared spectrum of perylene (TNF)₂

peryene (TNF)₂ is shown separately (Figure 4). Standard spectrophotometer SP 700 A of Beckmann Co. has been used for UV-visible range and that of Perkin Elmer Co. is used for infrared range.

The mark at 750 nm by a vertical line in Figure 3 shows a change in filter of the spectrophotometer.

3. Results and discussion

The band gap of $(\text{DPPD})_5\text{I}_{12}$ is found to be 0.20 eV from the end of featureless absorption in the range 1600–3000 cm^{-1} for which absorbance is minimum. There are about 12 vibrational bands below 1600 cm^{-1} and continuous absorption ends here. These are tabulated in Table 1. Band gap should be twice the activation energy, *i.e.* 0.14 eV, if it is an

Table 1. Vibrational bands.

$(\text{DPPD})_5\text{I}_{12}$ (cm^{-1})	Pyrene $(\text{TNF})_2$ (cm^{-1})	Perylene $(\text{TNF})_2$ (KBr mull) (cm^{-1})
680	710	700
720	730	720
830	760	770
1020	780	800
1080	830	820
1120	850	920
1300	910	1040
1470	1040	1080
1500	1070	1200
1600	1150	1240
	1240	1320
	1280	1340
	1340	1450
	1440	1540
	1530	1620
	1580	1750
	1740	

Difference between KBr and nujol mull spectra of perylene $(\text{TNF})_2$.

KBr mull (cm^{-1})	Nujol mull (cm^{-1})
700	No Band
1540	1480 (Red Shift)
1620	1540 (Red Shift)

intrinsic semiconductor. There are three absorption envelopes in the range 600–1600 cm^{-1} , one at 700 cm^{-1} , other at 1100 cm^{-1} and the third at 1400 cm^{-1} . The envelope at 1400 cm^{-1} is twice the activation energy. Thus $(\text{DPPD})_5\text{I}_{12}$ shows characteristic of an infrared photoconductor in which there is a peak in absorption at the value of the real band gap. Optical absorption edge at 0.2 eV is shifted by 0.06 eV with respect to this peak corresponding to transitions across the gap. This blue shift is mainly because of band-filling

effects and electron-electron interactions like heavily doped semiconductor [6]. There is a fine-structure of the peak at 1100 cm⁻¹ (0.14 eV) which is related with multi-electron hopping as discussed elsewhere [7]. This hopping is related with resonating polyiodine chain in (DPPD)₅I₁₂. In the entire range 1600–4000 cm⁻¹, there is only one indentation of a band at 3400 cm⁻¹. Band filling effect leads to a blue shift of absorption edge which is called Burstein-Moss shift. Electron-electron interaction increases the band gap due to Coulomb repulsion.

Resistance of the order of 10⁵ ohms has been measured for the crystals of pyrene (TNF)₂ using a digital multimeter. Similarly, perylene (TNF)₂ shows a resistance of the order of 10² ohms on the crystal of almost same size as pyrene (TNF)₂. Thus perylene (TNF)₂ is 1000 times more conducting than pyrene (TNF)₂. Both the electrical resistivities lie in the semiconducting range. These results should be compared with those of pyrene-TCNQ and perylene-TCNQ which are insulators [1]. Thus TNF is better than TCNQ for more conducting complexes for donors like pyrene and perylene. The nitro groups in TNF helps in forming electrically conducting complexes than cyano groups of TCNQ. Thus, TNF is better than TNB (Trinitro-benzene) and the latter always gives insulating complexes with organic donors [1].

Pyrene (TNF)₂ and perylene (TNF)₂ both show featureless absorption above 1800 cm⁻¹. The optical absorption edge for both lie at 0.225 eV (1800 cm⁻¹). But the spectra differ in the formation of envelope around 1400 cm⁻¹. There is a clear peak in the background at 1500 cm⁻¹ in perylene (TNF)₂ which is not found in pyrene (TNF)₂.

Table 2. Frequency shifts of the bands in an electronic absorption in perylene (TNF)₂ in nujol mull spectrum.

Frequency of the band in perylene (TNF) ₂ (cm ⁻¹)	Frequency of the expected band of normal mode of TNF (cm ⁻¹)	Total shift (cm ⁻¹)
1000	900	100
1100	990	110
1180	960	120
1260	1135	125
1320	1190	130
1360	1225	135
1400	1260	140
1475	1325	150
1540	1385	155
1620	1460	160
1670	1505	165
1710	1540	170
1770	1595	175

This peak is more clearly seen in the nujol mull spectrum (Figure 4) of perylene (TNF)₂ because liquid-solid interactions are weaker in paraffin oil than solid-solid interactions in KBr pellets. The sharp band at 1440 cm⁻¹ has a large number of side bands towards high-frequency side in perylene (TNF)₂, while this is not found in pyrene (TNF)₂. The side-bands are marked by arrows in Figure 2. There are charge density waves in perylene (TNF)₂ while these are not present in pyrene (TNF)₂ and (DPPD)₅I₁₂. The charge transfer contact move when a current flows through the sample [8]. The crystals conduct along the direction of charge transfer. The crystal structures are not known but it seems there are mixed stacks in pyrene (TNF)₂ and perylene (TNF)₂. An envelope of 10 bands is found in perylene (TNF)₂ around 1400 cm⁻¹ which also show 10% frequency shifts according to Rice's model [9]. These frequency shifts are noted separately (Table 2).

The nujol mull spectrum of perylene (TNF)₂ (Figure 4) should be compared with the spectra of pyridine (TCNQ)₂, quinoline (TCNQ)₂ and triethylammonium (TCNQ)₂ [10]. In TCNQ salts, damped-driven oscillators are found for two absorption envelopes, which are two Gaussian envelopes situated at 1400 cm⁻¹ and 3450 cm⁻¹. The Gaussians at 3450 cm⁻¹ in pyrene (TNF)₂ and perylene (TNF)₂ are fitted here (Figure 5). The electron-phonon coupling is weaker in TNF complexes than TCNQ complexes. As a result, continuous electronic absorption remains Gaussian and is not distorted to shape of an oscillator by riding upon intramolecular vibrations. The vibrations fling the charge carriers from one molecule to the neighbouring molecules.

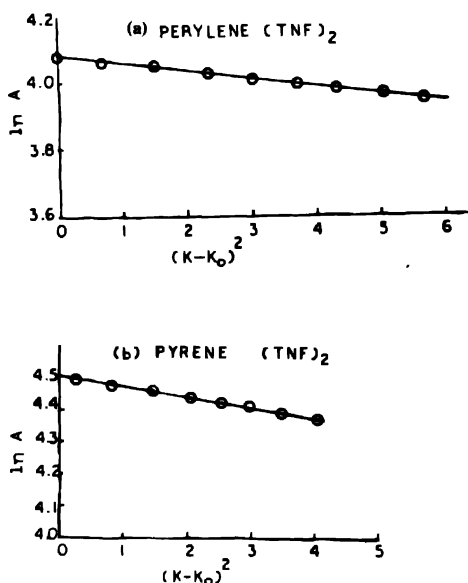


Figure 5. Gaussian fits for (a) perylene (TNF)₂ and (b) pyrene (TNF)₂ at 3430 cm⁻¹.

Optical conductivity spectra for the three complexes were calculated using Kramers-Kronig relations which are as follows :

$$\epsilon_1 = 1 - \frac{2}{\pi} \int_0^\infty \frac{\omega \epsilon_2 - \omega_0 \epsilon_2(\omega_0)}{\omega^2 - \omega_0^2} d\omega,$$

$$\epsilon_2 = - \frac{2}{\pi} \int_0^\infty \frac{\omega \epsilon_1 - \omega_0 \epsilon_1(\omega_0)}{\omega^2 - \omega_0^2} d\omega,$$

$$\sigma(\omega) = \frac{\omega \epsilon_2(\omega)}{4\pi},$$

where ω is frequency, ϵ_1 and ϵ_2 are real and imaginary parts of dielectric constant, ω_0 is natural frequency and $\sigma(\omega)$ is optical conductivity.

These relations are discussed in detail elsewhere [11]. Optical conductivities show peaks for the envelopes at 1500 cm⁻¹ in all the three complexes (Figure 6). Since

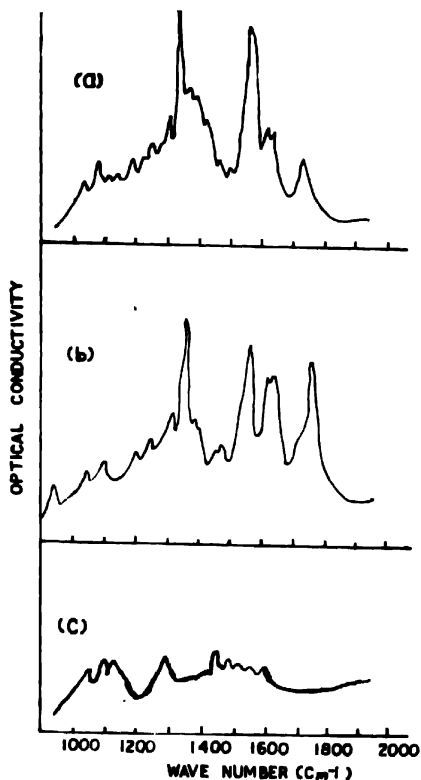


Figure 6. Optical conductivity spectra of (a) perylene (TNF)₂, (b) pyrene (TNF)₂ and (c) (DPPD)₂I₁₂. Background peak in pyrene (TNF)₂ arises from the Lorentzian Shape of $\mu_1(\omega)$.

$\sigma(\omega) = \alpha(\omega)n_1(\omega)c / 4\pi$ where $\alpha_1(\omega)$ is absorption coefficient, $n_1(\omega)$ is real part of refractive index and c is the velocity of light and $n_1(\omega)$ has a Lorentzian shape in the region of anomalous dispersion; there is a tail of the envelope towards low-frequency side. The tails are clearly seen for all the complexes for both the envelopes. The Gaussian envelope does not remain symmetric because of this.

Absorbance (A) was calculated from transmittance (T) according to

$$A = \log_{10}(1/T) \times 2.303.$$

Then the functions $A^{1/2}$, $A^{1/3}$, $A^{2/3}$, A^2 , $(Ah\nu)^{1/2}$, $(Ah\nu)^{1/3}$, $(Ah\nu)^{2/3}$, $(Ah\nu)^2$ and $\ln A$ were calculated which are well known functions for various transitions (Table 3). In A was calculated for knowing band tailoring. These functions were plotted against $h\nu$.

Table 3. Functions for various transitions.

Type of transition	Absorption function
Allowed direct transition in crystals	$\alpha = A(h\nu - E_g)^{1/2}$
Allowed direct transition in amorphous material	$\alpha h\nu = A(h\nu - E_g)^{1/2}$
Forbidden direct transition in crystals	$\alpha = A(h\nu - E_g)^{3/2}$
Forbidden direct transition in amorphous material	$\alpha h\nu = A(h\nu - E_g)^{3/2}$
Allowed indirect transition in crystals	$\alpha = A(h\nu - E_g)^2$
Allowed indirect transition in amorphous material	$\alpha h\nu = A(h\nu - E_g)^2$
Forbidden indirect transition in crystals	$\alpha = A(h\nu - E_g)^3$
Forbidden indirect transition in amorphous materials	$\alpha h\nu = A(h\nu - E_g)^3$

In (DPPD)₅I₁₂, $Ah\nu = C(h\nu - E_g)^{3/2}$, where E_g is the band gap and C is a constant. This expression is found to fit over the longest range and shows best least square fit (Figure 7a). This reveals forbidden direct transition (forbidden at $K = 0$ but allowed for $K \neq 0$) across the band gap.

In pyrene (TNF)₂, $Ah\nu = C(h\nu - E_g)^3$ is the best fit, indicating forbidden-indirect transition across the gap along a disordered lattice (Figure 7b). Perylene (TNF)₂ shows a strongly correlated behaviour and none is a good fit. All graphs show curvature because of strong correlation among electrons due to electron-phonon coupling.

Table 4. Band assignment in the spectra of (a) (DPPD)₅I₂, (b) pyrene (TNF)₂ and (c) perylene (TNF)₂.

(a)		(b)		(c)	
Frequency (cm ⁻¹)	Vibration	Frequency (cm ⁻¹)	Vibration	Frequency (cm ⁻¹)	Vibration
3400	N-H stretching	3100	C-H stretching	3100	Ring C-H stretching
1420-1740	Ring C-C vibration	1720	C=O stretching	1800	C=O stretching
1320	C-H bending	1620	Ring C-C vibrations	1640	Ring C-C vibration
940-1200	C-C vibrations	1420	Ring C-C vibrations	1550	NO ₂ stretching
700-860	Ring C-H bending	1420	Ring C-C vibrations	1440-1500	Ring C-C vibration
400-600	Raman active mode	1365	Ring C-H bending	1370-1440	C-H bending
		1340	NO ₂ stretching	1340	NO ₂ stretching
		1325	C-H bending	1100-1250	C-O bending
		1020-1240	C-H vibrations and C-O stretching	720-850	Ring C-H bending
		700-920	Ring C-H bending	400-600	Raman active modes
		400-600	Raman active modes		

Band assignments were carried out after taking a guidance from elsewhere [12]. These assignments are tabulated (Table 4). In both pyrene (TNF)₂ and perylene (TNF)₂, C-H bending (deformation) vibrations show resonating effects with NO₂ vibrations of TNF. Thus charge density waves are formed, particularly in perylene (TNF)₂ through charge transfer interactions and vibronic coupling. Molecular vibrations couple with electronic motions and delocalize charge carriers. Electron-optical phonon coupling related with bond dipoles gives rise to overall electron-phonon coupling in the solid state.

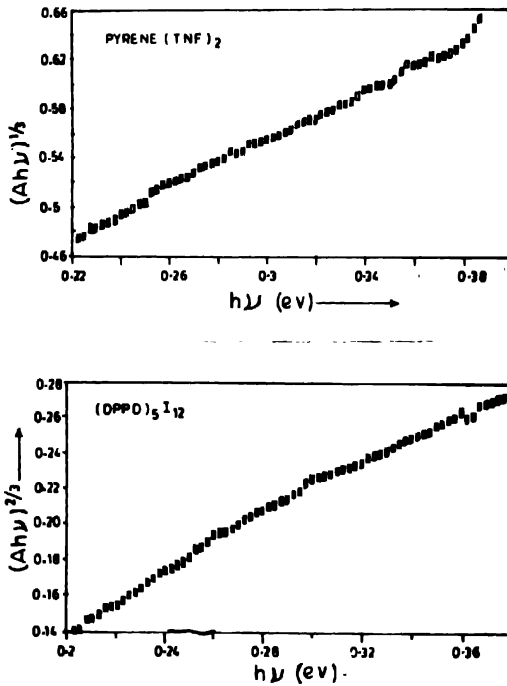


Figure 7. Absorption edges of (DPPD)₅I₁₂ and pyrene (TNF)₂.

The free-carrier absorption indicating whether the charge carriers are scattered by acoustic phonons or optical phonons or impurities could not be studied in the range above 3200 cm⁻¹ because of a broad band near 3450 cm⁻¹ indicating that these are strongly correlated electron systems. Free-carrier absorption relations are not applicable to correlated electron systems.

In UV-visible spectra (Figure 3) plasma edges are found. For opaque materials, $A = 1 - R$ (R is reflectance) or $R = 1 - A$ clearly shows shoulders in absorbance at 450 nm (2.7 eV) in (DPPD)₅I₁₂ and at 950 nm (1.26 eV) in perylene (TNF)₂. These are plasma edges in reflectivity. The plasma frequency is given by $\omega_p^2 = 4\pi n_s e^2/m^*$. ω_p is large/

because n_1 is large. n_1 is the number of charge carriers in a charge density wave. Pyrene (TNF)₂ is semiconducting and the plasma edge is not pronounced. In (DPPD)₅I₁₂, the absorption increases as the frequency increases in the visible range which indicates that there is a transition from impurity band to conduction band [6].

Table 5. Relation between optical conductivity and no. of bands

Name of the complex	No of band in the envelope (n)	Absorption %	Optical Conductivity σ (ω) (sec^{-1})	$\ln \sigma$
(DPPD) ₅ I ₁₂	7	50	0.5×10^{11}	26.94
Pyrene (TNF) ₂	9	70	7.0×10^{11}	27.27
Perylene (TNF) ₂	12	88	8.8×10^{11}	27.50

$\ln \sigma$ vs n where σ is the maximum (peak value) optical conductivity and n is no. of vibrations in the envelope is plotted here (Table 5 and Figure 8). It is found to be a straight

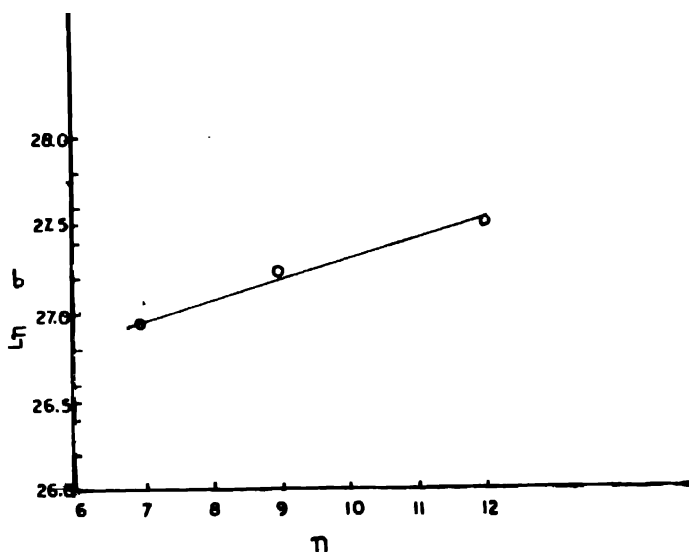


Figure 8. $\ln \sigma$ vs n where σ is the maximum optical conductivity and n is the no of bands in the envelope.

line The graph clearly shows that as the number of coupled vibrations increases, optical conductivity also increases. This means that the intramolecular vibrations delocalize the charge carriers.

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