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Infrared spectra of charge transfer complexes of tetramethylbenzidine

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Abstract . The infrared spectra of six charge transfer (CT) complexes of N, N, N', N' – tetramethylbenzidine were obtained after the preparation of these complexes. Various organic acceptors like chloranil, tetracyanoethylene, tetracyanoquinodimethane, tetranitro-9-flourenone, dichloro-dicyano p benzoquinone and iodine were used It has been found that the complexes are semiconducting with either direct or indirect band gap lying in the infrared range Electronic Gaussian profiles are also found in which electronic motions are strongly coupled with intramolecular vibrations

1. Introduction

The interest continues in studying organic semiconductors with reports of novel materials. Physical properties of many organic conductors prepared by chemists or scientists who are working in this interdisciplinary subject, have not been studied thoroughly [1-3].

A novel organic semiconductor BTQBT was found to have conductivity of 10^{-3} S cm^{-1} [4]. The optical properties of ordered and disordered α-sexithiophene thin films have been studied recently [5]. Conducting complex salts N-C$_n$H$_{2n+1}$ isoquinoline (TCNQ)$_2$ have been synthesized [6]. Porphyrin films have been studied with impedance spectroscopy [7]. Bispyrrolotetrathiafulvalene donor is used to form complexes with TCNQ, TCNQF$_4$ and DDQ, which are anisotropic semiconductors [8]. (BEDT-TTF)$_2$I$_3$(β) is transformed in superconducting phase in the form of polymeric films [9]. Ultraviolet photoemission spectra and inverse photoemission spectra are measured on thin films of N, N'-dimethyl perylene-3,4,9,10- tetracarboxylic dianhydride [10]. A new conjugated Schiff-base macrocycle containing 1,3,4-oxidiazole ring is also prepared which formed conducting complex with iodine [11]. Photomodulation techniques are used for studying linear trans-

quinacridine [12]. High field electrical conduction and Seeback coefficient are studied on the derivatives of aspargic acid and some more organic semiconductors [13]. A series of coordination compounds based on macrocyclic tetraaza derivatives is found to form metallic or semiconducting compounds. These compounds are analyzed by Raman spectroscopy [14]. With this background, we have studied charge transfer complexes of N,N,N',N'-tetramethtylbenzidine with infrared spectroscopy.

2. Experimental

N,N,N',N'-tetramethylbenzidine (Tmbine) is a brass-bronze coloured material which act as a donor. N,N,N',N'-tetramethtylbenzidine (Tmbine) formed a violet coloured 1:1 complex with chloranil (tetrachloro-p-benzoquinone) by grinding in a mortar. Similarly Tmbine formed a black 1:1 complex with TCNQ (tetracyanoquinodimethane) and brown complex with TNF (2,4,5,7-tetranitro-9-fluorenone). It formed blue 1:1 complex with DDQ (2,3-dichloro-5,6-dicyano-p-benzoquinone), black complex with TCNE (tetracyanoethylene) and blue complex with iodine. The molecular structures of the donors and the acceptors used are shown in Figure 1.

IR spectra of the complexes were recorded in the range 400-4000 cm^{-1} in KBr pellets using Nicolet 400 D spectrophotometer. Semitransparent pellets were prepared by compressing the

material in a die. Nicolet 400 D spectrophotometer was used for recording the spectra of the complexes in the range 400–4000 cm⁻¹. The purity of isolated CT complexes was very high because donors and acceptors both were analytic reagents.
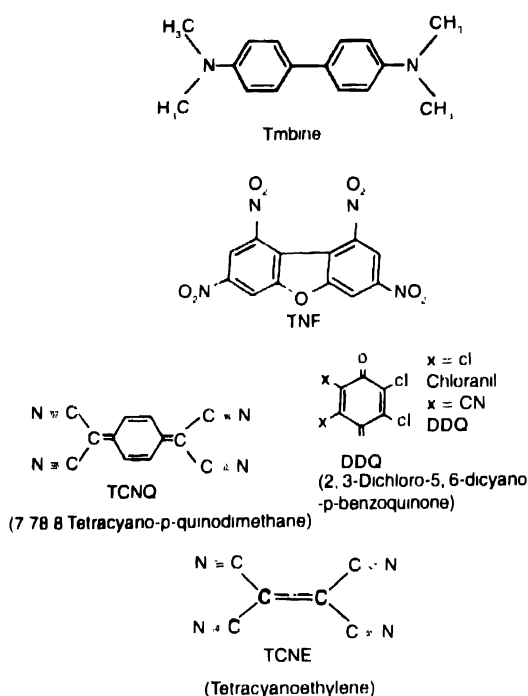

Figure 1. Molecular structures of Tmbine and the acceptors used

3. Results and discussion

N,N,N',N'-tetramethylbenzidine (Tmbine) is a brassy bronze coloured material compared to dull brown benzidine. Benzidine is an insulator but Tmbine is a semiconductor with a small band gap of 0.225 eV. It is a rare homomolecular material of such a less band gap. It shows direct forbidden transition across a band gap between the valence and conduction bands. The reason of low band gap is large dipole moment because of easy quaternization of N-atoms in N-(CH₃)₂ groups on both the sides of the biphenyl rings. The dipole-dipole interaction of attractive kind lowers intermolecular distance among neighbouring molecules. Charge density waves are confined in rectangular potential barrier.

Among the six charge transfer complexes of Tmbine studied here, two complexes namely Tmbine-I₂ (1:1) and Tmbine-TCNQ (1:1) have shown very small band gap of about 0 11-0.12 eV because of conducting stacks of $I_1 - I_2$ species and of TCNQ molecules, respectively (Table 1) There seems to be segregated stacks of donor and acceptor molecules in these two complexes.

Other four complexes are Peierls semiconductors with band gaps lying between 0.215 and 0.228 eV. Here either Tmbine stacks are conducting or the electrical conduction occurs in a charge

Table 1. Band gaps and nature of transitions.

Material	Colour	v_g (cm⁻¹)	hv_g (eV)	Absorption Function
Tmbine	Brass bronze	1720	0.215	$Ahv = B(hv-E_g)^{1/2}$
Tmbine-I₂	Blue	900 580	0.1125 0.0725	$Ahv = B(hv-E_g)^2$
Tmbine-CA	Violet	1800	0.225	$Ahv = B(hv-E_g)^{1/2}$
Tmbine-DDQ	Blue	1800	0.225	$Ahv = B(hv- E_g)^1$
Tmbine-TCNQ	Black	950 500	0.11875 0.0625	$Ahv = B(hv-E_g)^{1/2}$
Tmbine-TCNE	Black	1820	0 2275	$Ahv = B(hv-E_g)^2$
Tmbine-TNF	Brown	1800	0 225	$Ahv = B(hv-E_o)^{1/2}$

transfer band along mixed stacks or perpendicular to stacking direction. The increase of absorption edge in these four salts is because of possibility of Burstein- Moss shift as band-filling effect in heavily doped semiconductors. Coulomb repulsion along the stacks due to partial or full charge transfer can also be a reason for this slight increase of band gap compared to that of homomolecular Tmbine. There is crystallographic steric hindrance due to the presence of acceptor molecules, which increases intermolecular distance along Tmbine stacks. Perfectly half-filled band case can also lead to such a semiconducting behaviour. Also charge density waves in a rectangular potential barrier in only Tmbine tunnel in the complexes in the presence of electric field of acceptors. Regarding the nature of transition, three Tmbine complexes namely Tmbine-chloranil, Tmbine-TCNQ and Tmbine-TNF show a direct transition without involving any phonon as it is usually found for organic semiconductors shown in Figure 2 and Table 1. However, Tmbine-I₂, Tmbine-DDQ and Tmbine-TCNE show indirect transitions involving a phonon (Figure 2 and Table 1). This is because of polarizable acceptor molecule emitting a polar optical phonon. I_3^- and I_2 are highly polarizable. DDQ is polarizable because of possibility of forming an asymmetric semiquinone ion or because of two types of electron accepting groups (Cl and CN) on the benzoquinone and TCNE is distortable in three dimensions or polarizable because of aliphatic nature rather than having a coplanar benzene ring as in TCNQ. Thus, iodine, DDQ and TCNE furnish polar optical phonons to be absorbed by electronic motions.

Since the equation $\alpha hv = B(hv - E_g)^n$ is satisfied for transition in amorphous materials, In αhv vs $\ln(hv - E_g)$ is a straight line with n as a slope. These straight lines are also plotted for the complexes (Figure 3). The nature of transitions is summarized in Table 1.

Two envelopes are found in four salts namely Tmbine-chloranil, Tmbine-DDQ, Tmbine-TCNE and Tmbine-TNF which

are Gaussians around 1500-1600 cm⁻¹ and 3400 cm⁻¹ as listed in Table 2. No envelopes are found in Tmbine-I₂ and Tmbine-TCNQ

where the quadrupole splitting is absent and there is two band transport. The spectra are of the type of those of TMPD-KI-I₂
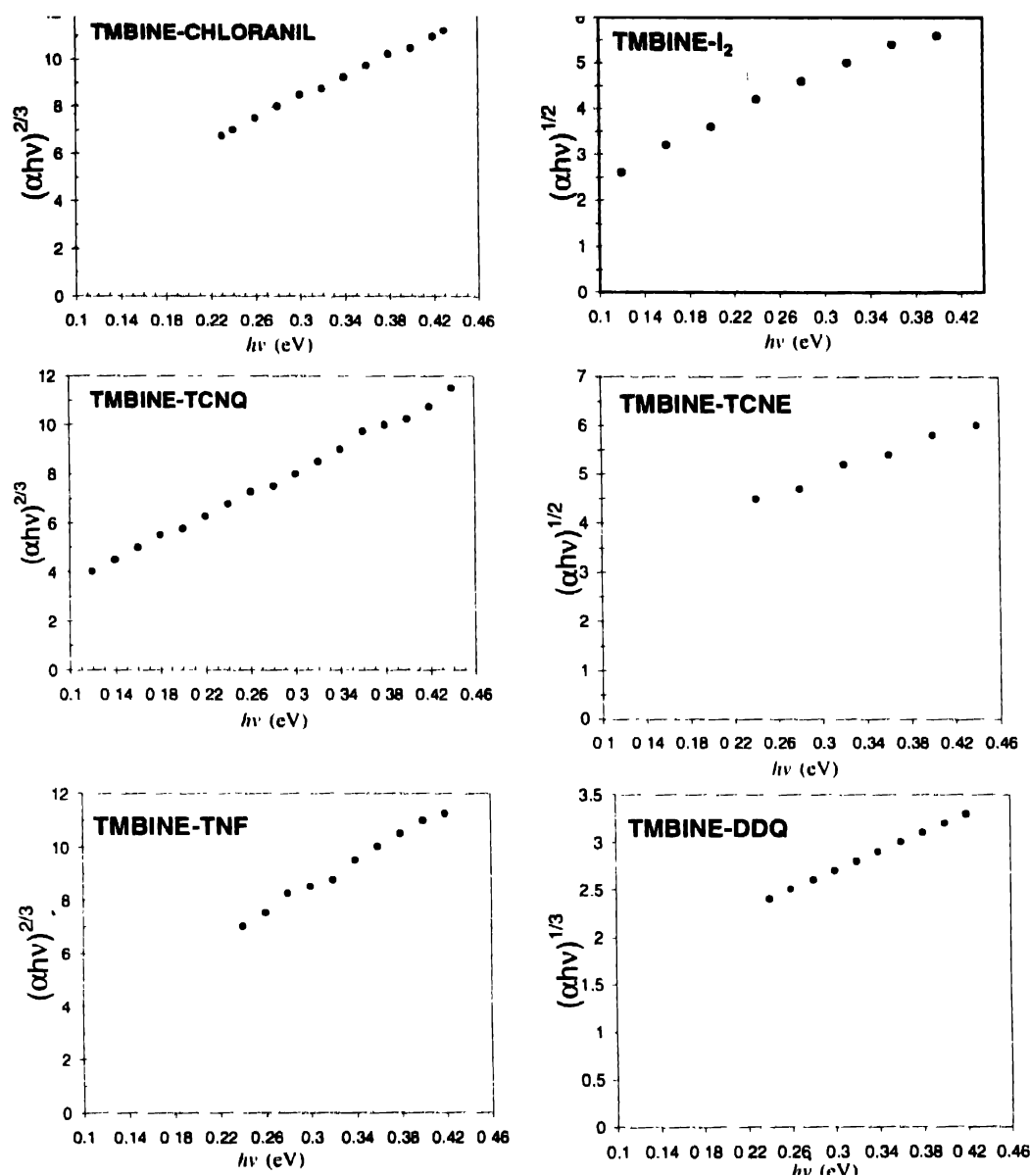

Figure 2. Forbidden direct transition in (a) Tmbine-Chloranil, (b) Tmbine-TCNQ, and Figure and (c) Tmbine-TNF Indirect transitions in (d) Tmbine-I₂, (e) Tmbine-TCNE and (f) Tmbine-DDQ.

2. Electronic absorption envelopes for the charge transfer complexes

	Low energy Gaussian Kmax (cm⁻¹)	Full width at half maximum cm⁻¹	High energy Gaussian kmax (cm⁻¹)	Full width at half maximum cm⁻¹
Tmbine	1500	680	3450	300
Tmbine chloranil	1500	520	3450	400
Tmbine DDQ	1470	400	3430	280
			3250	150
Tmbine-TCNE	1600	600	3400	340
Tmbine-TNF	1350	720	3400	400

and TMPD-HI-I₂ [15]. Here, charge transfer is more and band gap is about 0.11 eV only. There is a possibility of charge density waves in both of these complexes and 0.11eV is the pinning gap for pinned CDW.

The featureless (without having any fine structure) Gaussians around 3400 cm⁻¹ are fitted to be

$$A = A_0 e^{-\frac{(K-K_0)^2}{2M_2}},$$

where K_0 is the central wave number and M_2 is the second moment of the distribution (Figure 4). The widths of the
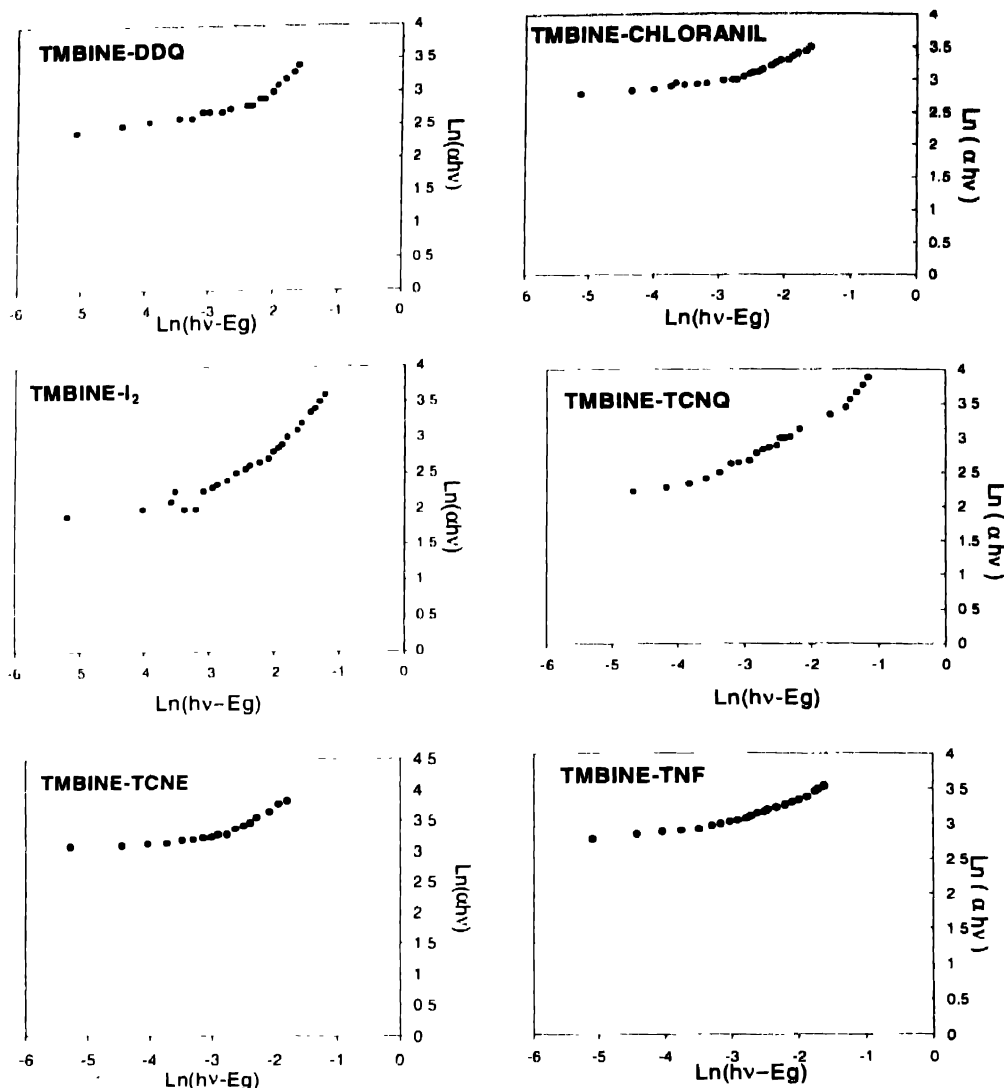
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Figure 3. In αhv vs ln (hv -E_r) plots for (a) Tmbine-DDQ, (b) Tmbine-I₂, and (c) Tmbine-TCNE In αhv vs ln (hv E_r) plots for (d) Tmbine-Chloranil, (e) Tmbine-TCNQ and (f) Tmbine-TNF

Gaussians (W) are obtained using

$$M_2 = \frac{W^2}{8 \ln 2}$$

and are tabulated. The widths are related with electron-phonon coupling constants. The values are noted (Table 2).

The Gaussian envelope with fine structure below the Peierls gap was used to calculate maximum optical conductivity $\sigma = \omega n_1 c / 4\pi$ where α is the absorption coefficient, n_1 is the real part of refractive index and c is the velocity of light.

The ln σ_{max} values vs number of vibrations coupled with electronic motions, i.e lying within the envelope, has been plotted to be a straight line (Figure 5 and Table 3). This rectilinear behaviour is found for 35 Peierls semiconductors [16]. Counductivity increases exponentially with the number of

Table 3. Maximum optical conductivity vs no.of coupled bands

Material	No. of bands in the envelope(n)	σ_{max} (X10^10 sec^-1)	ln σ_{max}	Absorptn (Arb Uni
Tmbine	12	2.5	23.94	100
Tmbine-DDQ	7	2.05	23.74	82
Tmbine-chloranil	9	2 36	23.89	94 5
Tmbine-TCNE	10	2.41	23.91	96 2'
Tmbine-TNF	11	2.475	23.93	99

coupled vibrations. The molecular vibrations delocalize charge carries. The band assignments in the complexes carried by finger printing method by taking guidance from elsewhere (17-19) and are summarized here (Tables 4-6).

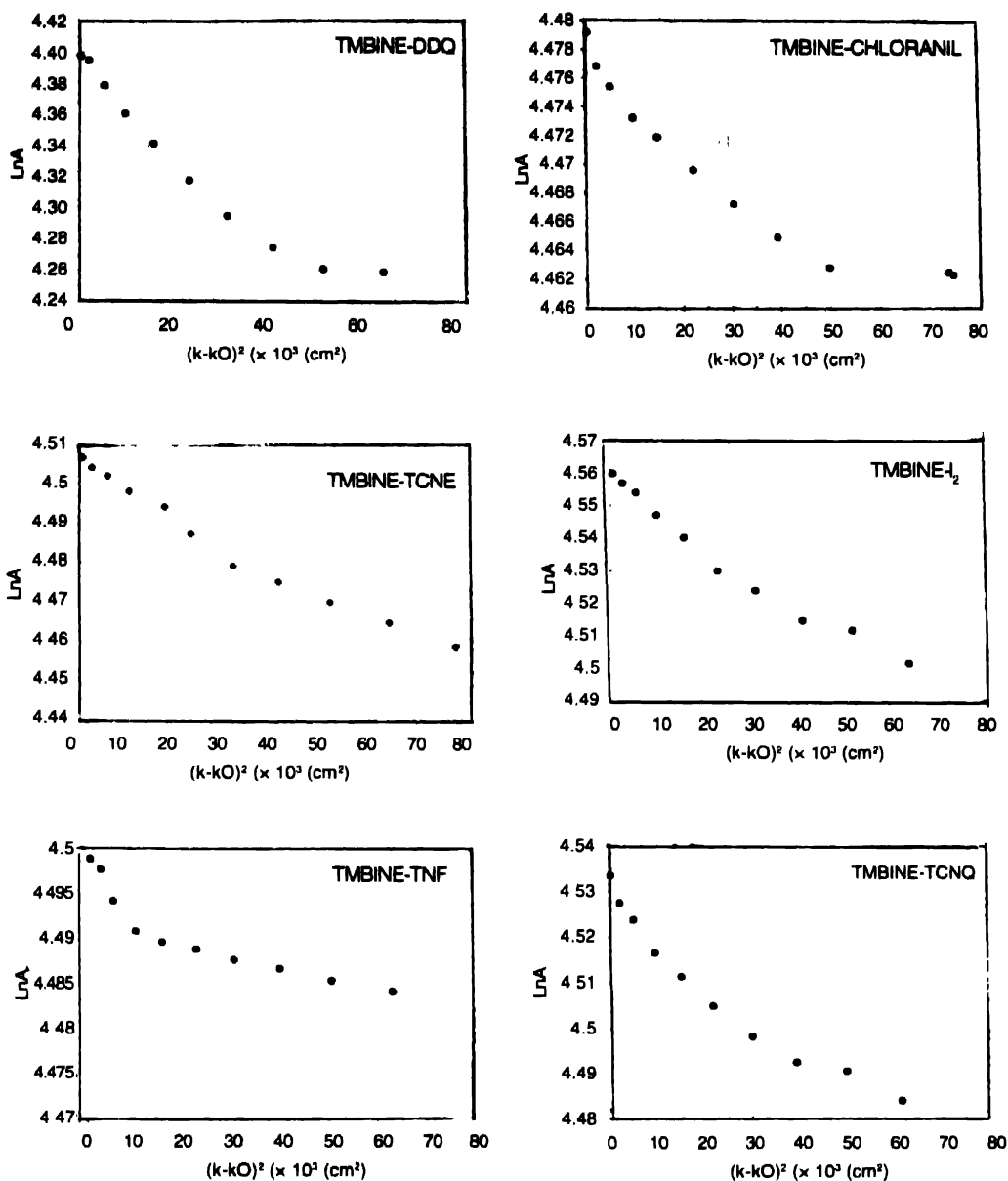Triethylammonium (TCNQ)₂ were studied earlier [20]. envelopes were damped oscillator model but here the envel

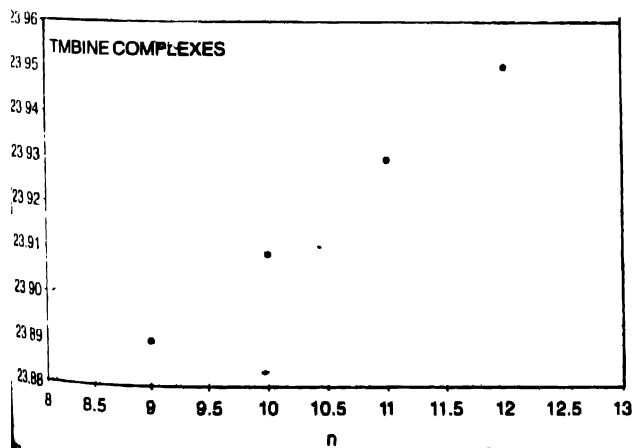**Figure 4.** Gaussian fitted around 3400 cm⁻¹ in the six charge transfer complexes of Tmbine.

are Gaussians. Recently, it is shown how to prove Gaussians from oscillator model using large damping coefficient [21]. When the damping coefficient is large, the energy transfer from the molecular vibrations to the electronic motions is large. Thus, the charge carries gain kinetic energy from damped vibrations and become free leading to the Gaussians shape of electronic absorption envelope. This is a first step towards the suppression of Peierls transition. Gaussian curves remain the same instead of the continuum jellium model of Frohlich superconductors because of optical phonons. In Tmbine-I_2 and Tmbine-TCNQ, these polarons are also dispersed and pinned charge density waves are formed having only a pinning gap rather than the Peierls gap.

e 5. $\ln \sigma_m$ vs n where σ_m is the maximum optical conductivity and n the number of bands in the envelope.

Table 4. Band assignments in the infrared spectrum of tetramethylbenzidine (hydrated)

Wave number cm^{-1}	Band assignments
3500 (m)	Water $v_{o\,H}$
2900	$v_{c\,H}$ of ring
2800 (s)	$v_{c\,H}$ of CH$_3$
1620 (s)	Water or $v_{c\,N}$
1510 (s)	Water or δ_{c-H} (asymmetric)
1450 (s)	δ_{CH2} (scissor) OF CH$_3$
1360 (s)	$\Delta\delta_{c-H}$ (symmetric)
1230	(s)
1200	
1150 (m)	
1100	
1060 (m)	
1040 (m)	δ_{c-c}
1000 (m)	δ_{c-N}
940 (s)	$\pi_{c\,H}$ of CH$_3$
800 (s)	CH$_2$ rocking of CH$_3$
520 (m)	
500	Water

+v is stretching δ is deformation and π is rocking or wagging. s = strong. m - medium

Table 5. Band assignments in the infrared spectra of CT complexes of Tmbine

Tmbine-chloranil		Tmbine-TCNQ		Tmbine- TNF	
Wave number (cm^{-1})	Band assignment	Wave number (cm^{-1})	Band assignment	Wave number (cm^{-1})	Band assignment
2911 (m)	v_{c-H}	3050 (s)	Vc-H	3150 (s)	v_{c-H}
2800 (m)	v_{c-H}	2200 (s)	Vc≡ N	2800 (m)	v_{c-H}
1700 (s)	ıc = 0	1600(m)	Water	1830(s)	New band (TNF band)
	ıc = 0				
1660 (s)		1620(m)	Water	1600(s)	$v_{c=o}$
1420 (m)	δ_{c-o}	1550(s)	New band (TCNQ band)	1480(s)	NO$_2$ group vibs
1380 (m)	δ_{CH} (Sym)	1350(m)	δ_{c-N} (Sym.)	1460(s)	
1280 (m)	New band (chloranil band)	1100(m)	$v_{c=c}$	1490(m)	
1100 (s)	$v_{c=c}$	900(s)	π_{c-H}	1400(s)	δ_{c-H}
860 (m)	v_{c-c}	520(s)	Water	900(m)	π_{c-H}
800 (s)	-CH$_2$ (rocking)			820(s)	CH$_2$ rocking
750 (m)	C-Cl			780(s)	CH$_3$
				640(m)	wagging
580 (m)	Water			520(m)	Water

Table 6. Band assignments in the infrared spectra of Ct complexes of Tmbine.

Tmbine-DDQ		Tmbine-I$_2$		Tmbine-TCNE	
Wave number (cm)	Band assignment	Wave number (cm)	Band assignment	Wave number (cm)	Band assignment
3400 (s)	Water V$_{o\,H}$	3450 (s)	Water V$_{o\,H}$	3459(s)	Water
3270 (s)	Water	2950 (s)	V$_{c-H}$	3000(s)	v_{c-H}
2900 (s)	v_{c-H}	2200 (m)	New band (I$_2$ chain band)	2350 (s)	
2250 (m)	V$_{c=N}$	1550 (s)	$v_{c=N}$	1600(s)	Water or
1500 (s)	$\delta_{c=o}$	1500 (s)	δ_{c-H}	1500(s)	v_{CH} (assy)
1400(m)	δ_{CH2}	1470(m)	δ_{CH2}	1300(s)	New band (TCNE)
		1450(m)	(Scissor)		
1300(m)	δ_{c-H}			1130(m)	vc-c
1200(s)	$v_{c=c}$	1350(m)	δ_{CH} (sym.)	1000(m)	δ_c
800(m)	CH$_2$ rocking	1200(w)	vc=c	820(s)	v_{c-c}
700(m)	$v_{c=o}$	800(w)	CH$_2$ rocking	750(m)	$\pi_{c\,H}$
600(m) 500(m) 470(w)	Lattice water or CH$_3$ rocking	500(m)	Lattice water or CH$_3$ Rocking	620(m) 530(m)	CH$_3$ rocking Lattice water

4. Conclusion

A donor like Tmbine having very low ionization potential, form highly conducting complexes with iodine and TCNQ-type strong acceptors and a Peierls transition is suppressed. The remaining four complexes are Peierls semiconductors. Gaussian curve rather than damped oscillators as envelopes can be considere as a first step towards the suppression of the Peierls transition.

Acknowledgment

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