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Electrical and Optical Properties of Conducting TCNQ Salts

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Electrical and Optical Properties of Conducting TCNQ Salts

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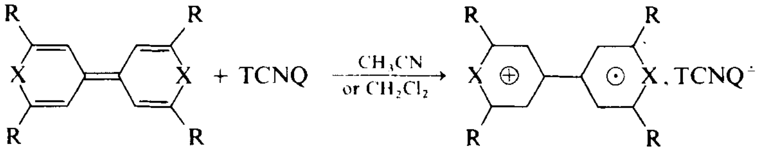
New series of TCNQ molecular complexes and organic radical-ion salts are presented. Their electrical behavior is related to their optical properties; characteristic parameters, such as the plasma frequency and the relaxation time, are deduced.

New series of TCNQ molecular complexes and organic radical-ion salts have been synthetized, in order to clarify the relationships between chemical structure and physical properties. In the first section, we shall describe these new series from a chemical point of view, then in Sections 2 and 3, we shall discuss the electrical and optical results obtained on those compounds which appeared most interesting.

1 SYNTHESIS

A Molecular complexes

Dipyranylidene and dithiopyranylidene complexes



1 2

R = H, CH_3, Ar,  ... X = O, S, NCH_3

The donors **1** are easily accessible by a one step synthesis from bisubstituted 2, 6 pyrylium or thiopyrylium salts.[1]

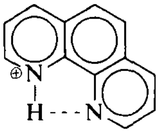
2 $X = O, R = C_6H_5$: DIPϕ_4-TCNQ
$X = S, R = C_6H_5$: DIPSϕ_4-TCNQ

B Organic radical-ion salts

1) Salts of TCNQ and of heterocyclic amines conjugated acids

Using the redox reaction of heterocyclic amines (or imines) with TCNQ and hydroquinone, we were able to synthetize several radical salts having interesting properties.

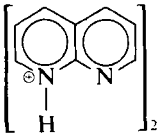
For example:



$, (TCNQ)_2^{\dot{-}}$;

3

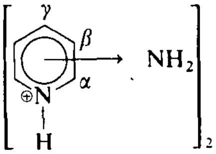
Oph$(TCNQ)_2$



$, (TCNQ)_3^{\dot{-}}$

4

1.8 $Nph_2(TCNQ)_3$



$, (TCNQ)_3^{\dot{-}}$

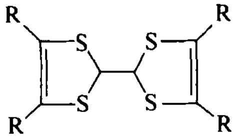
5

$Ap_2(TCNQ)_3$

This method leads directly to high purity products. A systematic study of this process as a function of amine structure, reagents concentration, solvent effect, etc. will be published elsewhere.* (See page [621]/317.)

2) Radical cation salts

Direct oxidation of TTF-type donors by $(SCN)_2$ leads to salts whose stoichiometry varies with the molecular ratio of the reagents. Some of the salts obtained in this way are good conductors.[4]



$$+ x(SCN)_2 \xrightarrow[\text{or } CH_3CN]{CH_2Cl_2} \begin{matrix} TTF_mSCN_n & \mathbf{6} \\ TMTTF_mSCN_n & \mathbf{7} \end{matrix}$$

R = H : TTF
R = CH_3 : TMTTF

$0.25 \leqslant x \leqslant 0.5, m = 2, n = 1$

2 ELECTRICAL CONDUCTIVITY

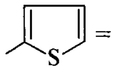
Electrical d-c conductivity measurements have been performed on powders at room temperature as well as, in favourable cases, on single crystals as a function of temperature.

2.1

All dipyranylidene complexes except one exhibit low conductivity. For example, on powders, we found[2] for σ with different R:

$R = CH_3$ 10^{-7} $(\Omega\,\mathrm{cm})^{-1}$

$R = pC_6H_4OCH_3$ $2.5 \cdot 10^{-4}$ $(\Omega\,\mathrm{cm})^{-1}$

R =  = Th 10^{-6} $(\Omega\,\mathrm{cm})^{-1}$

$R = pC_6H_4CH_3$ 10^{-1} $(\Omega\,\mathrm{cm})^{-1}$

However, with $R = C_6H_5$ we obtained a promising value on the powder, 1.7 $(\Omega\,\mathrm{cm})^{-1}$, which was confirmed on single crystals, $\sigma \simeq 25$–40 $(\Omega\,\mathrm{cm})^{-1}$ (this complex is labelled DIPϕ_4-TCNQ). Though having a good conductivity, DIPϕ_4-TCNQ shows a semiconducting behavior as a function of temperature with a low activation energy, 0.04 eV, until it undergoes a reversible transition to an insulating state at 240°K.[3]

2.2

In order to investigate the influence of the heteroatom X, we have considered the dithiodipyranylidene DIPSϕ_4 with the same substituant $R = C_6H_5$ as a donor. The TCNQ complex has a very good conductivity: $\sigma_{RT} \simeq 250$–300 $(\Omega\,\mathrm{cm})^{-1}$ at room temperature and shows a metallic behavior above 145°K with $\sigma_{max}/\sigma_{RT} = 1.6$, but this ratio decreases by cycling the samples with respect to temperature.[3]

2.3

The TCNQ salt obtained with orthophenantroline as a donor, Oph-$(TCNQ)_2$, has also been studied on single crystals. The conductivity is about 75 $(\Omega\,\mathrm{cm})^{-1}$ at room temperature and metallic-like above 150°K with a ratio $\sigma_{max}/\sigma_{RT} = 1.2$, i.e. of the same order of magnitude as in NMP-TCNQ and Qn$(TCNQ)_2$.

2.4

In the case of naphtiridine and aminopyridine salts, measurements on powders only have been made. $Nph_2(TCNQ)_3$ exists in two forms: an insulating form and a conducting one. For this later one, we find $\sigma = 1.4$ $(\Omega\,cm)^{-1}$. For the amino-pyridine salts, we have investigated the influence of the position of NH_2 on the ring. With NH_2 in γ position we obtained an insulating compound, with NH_2 in α and β positions, the salts are conducting, in α, $\sigma = 1$ $(\Omega\,cm)^{-1}$, and in β, $\sigma = 3.4$ $(\Omega\,cm)^{-1}$. As we shall see in the next section, from the optical properties we can assume that these latter salts have a metallic behavior.

2.5

For $TMTTF_2SCN_1$, we obtain on powder $\sigma = 5$ $(\Omega\,cm)^{-1}$.

3 OPTICAL PROPERTIES

3.1 Optical absorption

Our optical density measurements are performed between 0.1 or 0.5 eV and 4 eV (i.e., 800 or 4000 cm^{-1} and 32,000 cm^{-1}) on disks made by pressing a mixture of powdered KBr and the desired compound. Figures 1 to 5 show

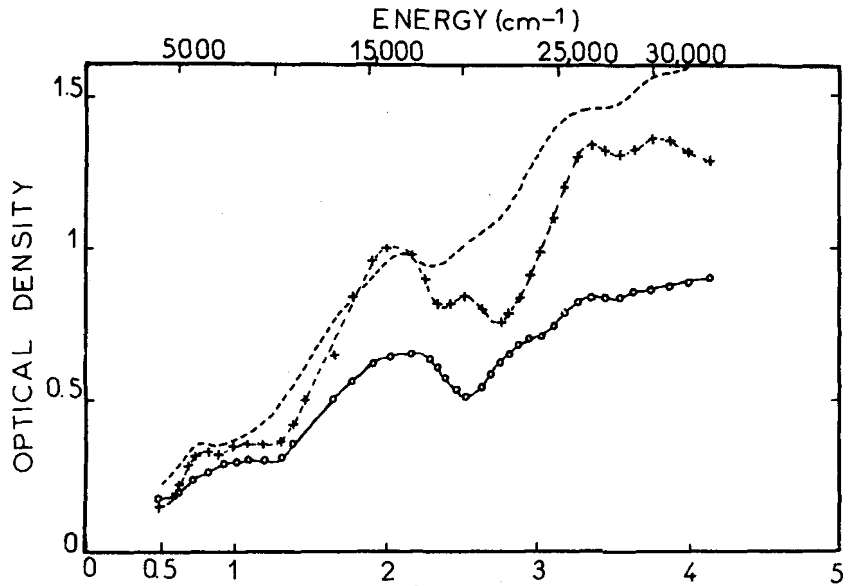


FIGURE 1 Powder absorption spectra of dipyranylidene complexes with R = Th (– – –), R = $C_6H_4OCH_3$ (+ + +), R = $C_6H_4CH_3$ (o–o–o).

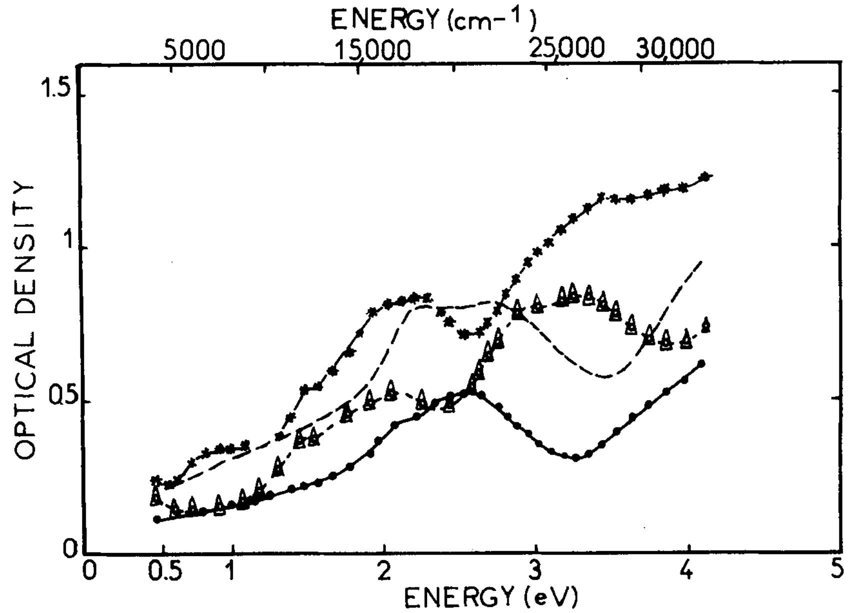


FIGURE 2 Powder absorption spectra of DIPϕ_4-TCNQ (∗-∗-∗), DIPSϕ_4-TCNQ (△-△-△), and the donors DIPϕ_4 (+ + +) and DIPSϕ_4 (● ● ●).

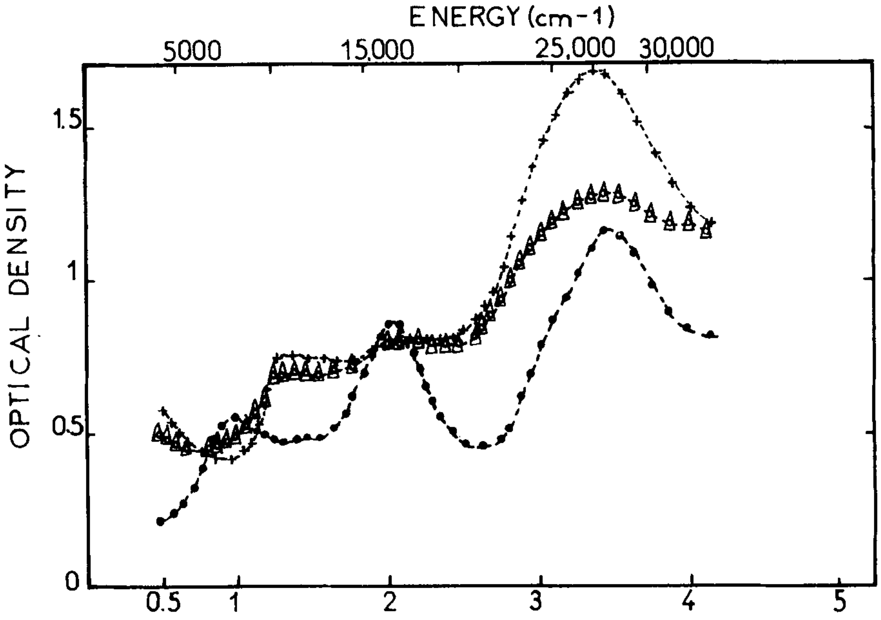


FIGURE 3 Powder absorption spectra of Qn(TCNQ)$_2$ (+ + +) and Nph$_2$(TCNQ)$_3$ in its conducting form (△-△-△) and its insulating form (●-●-●).

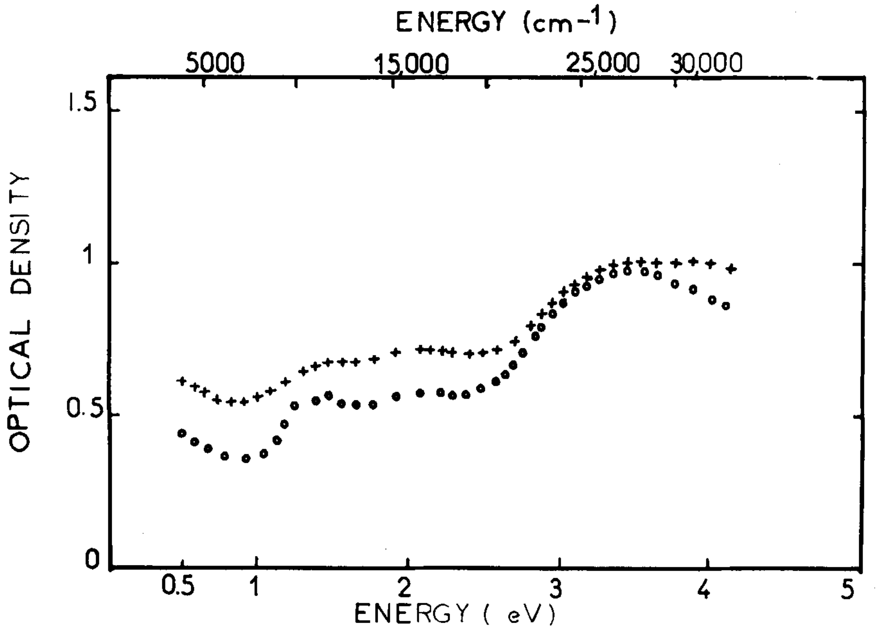


FIGURE 4 Powder absorption spectra of aminopyridine$_2$ TCNQ$_3$ salts: —NH$_2$ in α position (+ + +), in β position (○–○–○).

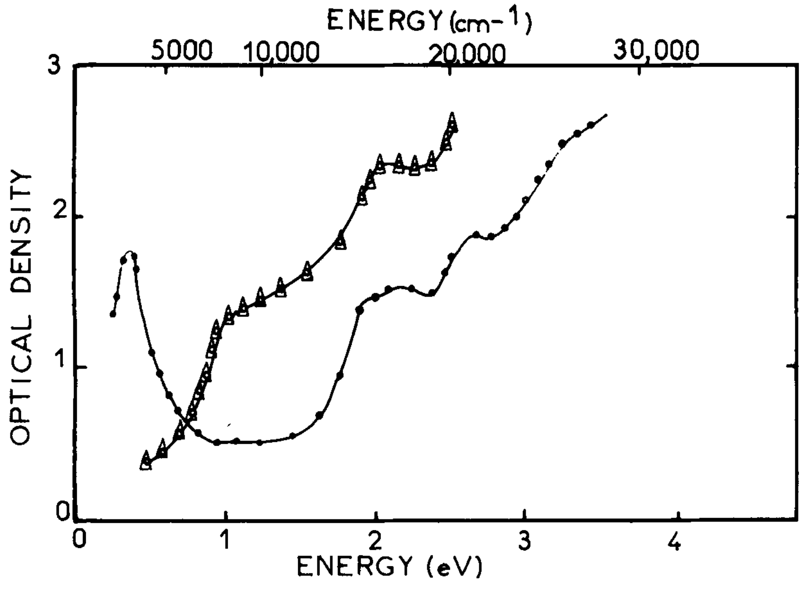


FIGURE 5 Powder absorption spectra of TMTTF$_1$(SCN)$_2$ (△-△-△) and TMTTF$_2$(SCN)$_1$ (●-●-●).

the optical density as a function of energy for the different series described in Section 1. We can distinguish two parts in the spectra.

At high energies, roughly above 1.5 eV, many similarities are observed, as already mentioned by several authors.[5,6] The peaks in the optical density are attributed to intra-molecular excitations and correspond in general to peaks found in the optical spectra of $TCNQ^-$ and $(TCNQ^-)_2$ in solution. On Figures 3 and 4, we have represented the spectra of conducting salts: $Qn(TCNQ)_2$, $Nph_2(TCNQ)_3$, aminopyridine$_2$(TCNQ)$_3$ and also of $Nph(TCNQ)_n$ in its insulating form. In these cases, the peaks appearing above 1.5 eV have the same positions as the ones of $(TCNQ^-)_2$ in solution (the location of the main absorption peaks of $TCNQ^0$, $TCNQ^-$ and $(TCNQ^-)_2$ are reported in Table I.[7] We must emphasize that such a comparison between optical spectra relative to solid state on the one hand, to solutions on the other hand, may be very uncertain, because the last one may be strongly dependent on the solvent. In spite of this fact, the peaks at 3.35 eV (27,000 cm^{-1}) and at about 2 eV (16,000 cm^{-1}) are generally attributed to the presence of the dimer $(TCNQ^-)_2$. Some new features are seen on the spectra of dipyranylidene complexes (Figures 1 and 2) with R = p-$C_6H_4OCH_3$ (peak at 2.5 eV) and with R = *p*-$C_6H_4CH_3$ (shoulder at 3 eV), of DIPϕ_4-TCNQ (at 2.25 eV) and of DIPSϕ_4-TCNQ (a well defined peak at 3 eV (24,000 cm^{-1}). The optical properties of donors are not always known, but for DIPϕ_4 and DIPSϕ_4 some information is available for the neutral donors D^0 in solid state (Figure 2) and for D^+ and D^{++} in acetonitrile.[8] We have indicated the positions of their main absorption maxima in Table II. As seen on Figure 2, the peaks at 2.25 eV in DIPϕ_4-TCNQ and at 2.1 eV in DIPSϕ_4-TCNQ may be related to the presence of the neutral donor, but the origin of the peak observed at 3 eV remains unclear. It cannot be attributed to the donor without assuming a shift with respect to peaks existing in solution; another possibility is to attribute it to TCNQ: from Table I, we see that in solution $TCNQ^-$ presents a peak at 2.94 eV and $TCNQ^0$ at 3.15 eV. It is difficult to conclude, but this peak can reasonably be considered to be related to $TCNQ^0$ species.

At low energies, we distinguish two kinds of behavior in the optical density curves. For insulating compounds (on Figure 3, $Nph(TCNQ)_n$ and on Figure 5, $TMTTF(SCN)_2$), the absorption rises rapidly as the energy increases and reaches a maximum at about 1 eV (8000 cm^{-1}); this is an interband transition corresponding to excitations of electrons along the chain, as interpreted by Tanner *et al.*[9] for K-TCNQ from reflectance measurements with polarized light on single crystals. For conducting salts, the absorption in this energy range decreases to a minimum corresponding roughly to the plasma frequency (which is more precisely defined from reflectance curves), then rises again to peaks at about 1.2–1.5 eV (11,000 cm^{-1}) due to intra-

TABLE I

Optical properties of TCNQ. Energy of the maxima of absorption bands. (After Ref. 7)

	Energy (eV)	Energy (cm^{-1})
TCNQ^0 in solution	3.15	25,400
in solid state	2.9	23,500
	3.6	29,000
TCNQ$^-$ in solution	1.48	12,000
	1.66	13,400
	2.94	23,700
(TCNQ$^-$)$_2$ in solution	1.43	11,500
	1.94	15,600
	3.36	27,100

molecular transitions of the TCNQ$^-$ anion and possibly of the radical cation (see Tables I and II).

For compounds of intermediate conductivity (Figure 1), we observe a shift of the onset of interband transitions to lower energies. The energy gap is about 0.78 eV (6300 cm^{-1}) for dipyranylidene complexes with R = Th and R = $C_6H_4OCH_3$; with R = $C_6H_4CH_3$ it is not well defined but smaller, which is consistent with a higher conductivity. An interesting case is that of DIPϕ_4-TCNQ (Figure 2) where the metallic behavior breaks down because of the presence of low-lying interband transition. Figure 5 shows for comparison the low energy spectra of radical cation salts, an insulating one, TMTTF$_1$(SCN)$_2$ and a conducting one, TMTTF$_2$(SCN)$_1$ for which the optical density increases with decreasing energy to a peak centered at about 0.36 eV (2900 cm^{-1}). This peak, labelled A by Torrance,[5] is found in all

TABLE II

Optical properties of DIPϕ_4 and DIPSϕ_4. (After Ref. 8)

	DIPϕ_4		DIPSϕ_4	
D^0 (solid state[a])	2.2 eV	17,740 cm^{-1}	2.15 eV	17,340 cm^{-1}
in acetonitrile	2.7	21,770	2.5	20,160
D$^+$ in acetonitrile	1.58	12,740	1.43	11,530
	1.76	14,190	1.55	12,500
	2.48	20,000	2.70	21,770
	3.06	24,670	3.60	29,000
	3.44	27,740	3.84	30,970
	3.87	31,200		
D^{++} in acetonitrile	2.73	22,000	2.79	22,500
	3.47	27,980		

[a] This work.

conducting salts at about the same energy and might be attributed to excitation of an electron from a TCNQ$^-$ ion to a neighboring neutral TCNQ^0 molecule and described as an intraband transition. This interpretation has been questioned by Tanner *et al.*[9,10] from experiments on K-TCNQ and TTF-TCNQ. In the case of TTF-TCNQ, a Kramers-Krönig analysis of reflectance measurements allowed to calculate the real part of the conductivity which presents no peak around 0.3 eV, but instead, a strong peak at 0.14 eV (1130 cm^{-1}), while the absorption coefficient shows, like the optical density, a maximum around 3000 cm^{-1}. We follow this interpretation and conclude that these "organic metals" are not simple metals but have essentially the optical properties of semi-conductors with energy gaps of about 0.1 eV.

3.2 Reflectance measurements

Figure 6 shows the measured reflectance between 0.1 and 1.24 eV (800 and 10,000 cm^{-1}) on polycrystalline compactions of DIPSϕ_4-TCNQ, DIPϕ_4-TCNQ and TTF-TCNQ for comparison. If one excepts the structures between 0.1 and 0.3 eV arising from molecular vibrational modes, the

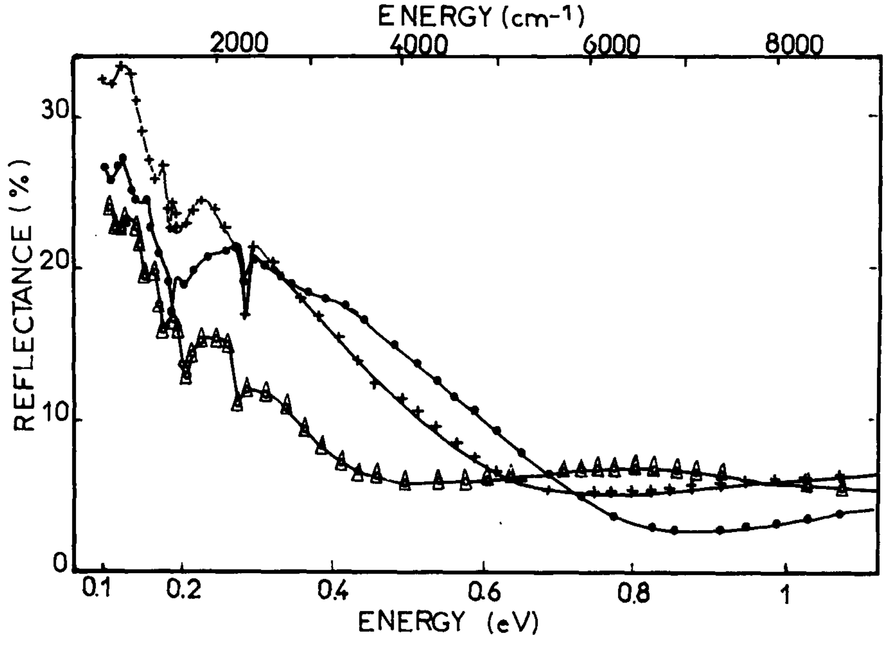


FIGURE 6 Reflectance spectrum of polycrystalline compactions of TTF-TCNQ (●-●-●), DIPSϕ_4-TCNQ (+ + +), DIPϕ_4-TCNQ (△-△-△).

reflectance decreases with increasing energy as for a metal; the plasma edge is observable with a minimum of the reflectance at 0.88 eV for TTF-TCNQ, at 0.75 eV for DIPSϕ_4-TCNQ and at about 0.5 eV for DIPϕ_4-TCNQ. Then, although presenting a semi-conducting behavior in its d-c conductivity, DIPϕ_4-TCNQ shows optically metallic properties in this energy range. Susceptibility measurements also lead to the same conclusion.[2] The curves on Figure 6 are in fact an average over all crystalline orientations in the solid. The component $R_{\parallel}$, parallel to the conducting axis, may be extracted from the data of Figure 6 by subtracting the perpendicular reflectance $R_{\perp}$, assumed constant in the infra-red and roughly equal to the minimum value at the plasma edge. Then, the $R_{\parallel}$ values are fitted with a Drude expression for the dielectric function:

$$\varepsilon(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\omega/\tau}$$

ε_{∞} is the residual dielectric constant, which takes into account the core polarisability, $\omega_p = (4\pi Ne^2/m^*)^{1/2}$ is the plasma frequency, with N the electron density, m^* the optical mass, and τ is the electronic relaxation time. For DIPϕ_4-TCNQ, we did not try to fit our data, the metallic region being too small, for TTF-TCNQ our results are in agreement with the published values ($\varepsilon_{\infty} = 2.43$, $\omega_p = 1.20$ eV, $\tau^{-1} = 0.23$ eV)..For DIPSϕ_4-TCNQ, we obtain:

$$\varepsilon_{\infty} = 3.05, \quad \omega_p = 0.99\text{ eV}, \quad \tau^{-1} = 0.287\text{ eV},$$

and for Oph(TCNQ)$_2$:

$$\varepsilon_{\infty} = 2.05, \quad \omega_p = 0.85\text{ eV}, \quad \tau^{-1} = 0.364\text{ eV}$$

From these values we are able to calculate the d-c conductivity; $\sigma_{dc} = \omega_p^2\tau/4\pi$, which could also be obtained directly on single crystals. We find $\sigma_{dc} = 470$ $(\Omega\,\text{cm})^{-1}$ and 270 $(\Omega\,\text{cm})^{-1}$ for DIPSϕ_4-TCNQ and Oph(TCNQ)$_2$ respectively, which is to be compared with the measured values: 250 $(\Omega\,\text{cm})^{-1}$ and 75 $(\Omega\,\text{cm})^{-1}$. This slight discrepancy is not surprising, because we did not work on really good single crystals.

In conclusion, we have shown how absorption measurements in the visible and near infra-red range can easily bring information on the electronic properties of the compound. In addition, reflectance measurements on polycrystalline compactions give for conducting salts a realistic value of the d-c conductivity, which may be quite useful for characterizing the compound behavior before undertaking the growth of single crystals. Moreover, in the tight binding approximation, the plasma frequency is given by

$$\omega_p^2 = \frac{4e^2}{\hbar^2} b^2 N(\bar{B}_D + \bar{B}_A)$$

where b is the intermolecular distance along the stacking axis and $\overline{B_D}$ and $\overline{B_A}$ are related to the band widths of the donor and the acceptor respectively by $\bar{B} = B \sin \pi\rho/2$ where ρ is the charge transferred by molecule. It should be possible to determine $\overline{B_D} + \overline{B_A}$ and to compare the results with the band widths deduced from magnetic susceptibility measurements[11] and to obtain indications on the magnitude of the Coulomb repulsion U.

Acknowledgements

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* *Footnote added in proofs:* For synthesis of TCNQ salts of heterocyclic amines conjugated acids via redox reaction (amine, TCNQ, hydroquinone) and determination of stoichiometry of obtained salts, see Proceedings on Quasi One dimensional conductors (Dubrovnik 1978), to be published by Springer-Verlag.