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Comparative Optical Investigations on the One-Dimensional Organic Metals (Perylene)₂ (PF₆)_{1.1} × 0.8CH₂Cl₂, (Pyrene)_{1 2} (SbF₆)₇ and (Fluoranthene)₂ (AsF₆)_{0.2} (PF₆)_{0.8}

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COMPARATIVE OPTICAL INVESTIGATIONS ON THE ONE-DIMENSIONAL ORGANIC METALS (PERYLENE)₂(PF₆)_{1.1} × 0.8CH₂Cl₂, (PYRENE)₁₂(SbF₆)₇ AND (FLUORANTHENE)₂(AsF₆)_{0.2}(PF₆)_{0.8}.⁺

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Abstract The reflectance spectra of different radical cation salts of the type (arene)₂XF₆ are reported (X=P,As,Sb). For light polarised perpendicular to the molecular stacks, the crystals exhibit the optical behaviour of an insulating molecular crystal, whereas for light polarised parallel to the stacks a pronounced plasma edge is observed. Compared to other organic metals the crystals show remarkably high values of the plasma energy. Because the concentration of the free carriers is obtained from the charge transfer between the radical cations and the inorganic counter ions, the effective mass of the free carriers may be calculated from the plasma frequency. The analysis of the reflectance data by a Lorentz-Drude model yields as well the values of the mean collision time, the electrical conductivity, and the bandwidth.

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INTRODUCTION

The discovery of organic charge-transfer salts with 1-dimensional (1d) metallic conduction about twenty years ago^{1,2} triggered an intense search for further organic metals. The greatest success of these investigations has been the synthesis of organic superconductors by Bechgaard and coworkers³⁻⁵. In these superconducting compounds the metallic conduction is effected by stacks of tetramethyl-tetraselenafulvalene (TMTSF) molecules. These donor molecules form the organic superconductor in conjunction with inorganic anion complexes, such as hexafluorophosphate or perchlorate.

Since these compounds are not readily synthesised, one has looked out for simpler donor molecules. The efforts in this direction resulted in the synthesis of a new group of 1d organic metals. In these compounds the molecular stacks exhibiting the metallic conduction are formed by simple aromatic molecules, like naphthalene (Na), fluoranthene (Fa), pyrene (Py), or perylene (Pe)⁶⁻⁹. In the present paper the metallic transport properties of some of these new compounds are analysed by means of optical investigations.

EXPERIMENTAL

Single crystals of $(\text{Pe})_2(\text{PF}_6)_{1.1} \times 0.8\text{CH}_2\text{Cl}_2$, $(\text{Py})_{12}(\text{SbF}_6)_7$ and $(\text{Fa})_2(\text{AsF}_6)_{0.2}(\text{PF}_6)_{0.8}$ were grown by electrocrystallisation in form of shiny black platelets or needles. Details about the crystal preparation and the crystal structure are found

in ref.7-9. For the optical measurements crystals with well-reflecting growth surfaces were selected. The reflectance data were obtained by a single-beam spectrometer especially adapted to tiny crystals.

RESULTS AND DISCUSSIONS

Fig.1 shows the reflectance spectra under polarised light for all investigated compounds. The spectra are typical for 1d organic metals. If the direction of polarisation is perpendicular to the axis of the molecular stacks, the crystals exhibit the optical behaviour of an insulating molecular crystal. For light polarised parallel to the stack axis the reflectance values reach 70 to 80 percent at low photon energies. At higher energies a steep plasma edge with a pronounced minimum is observed. This is characteristic for the optical absorption by free charge carriers. As Fig.2 shows, the spectral position of the plasma edge is shifted towards higher energies, if the donor molecules are changed from perylene to pyrene to fluoranthene.

If we compare these reflectance spectra with those of the well-known 1d metals, we can draw the following conclusions: Up to now, there has been a broad gap between the spectral position of the plasma edge of organic metals, like tetrathiafulvalene-tetracyano-p-quinodimethane (TTF-TCNQ) and its derivatives including the organic superconductors on one hand^{10,11}, and the spectral position of the plasma edges of inorganic 1d metals

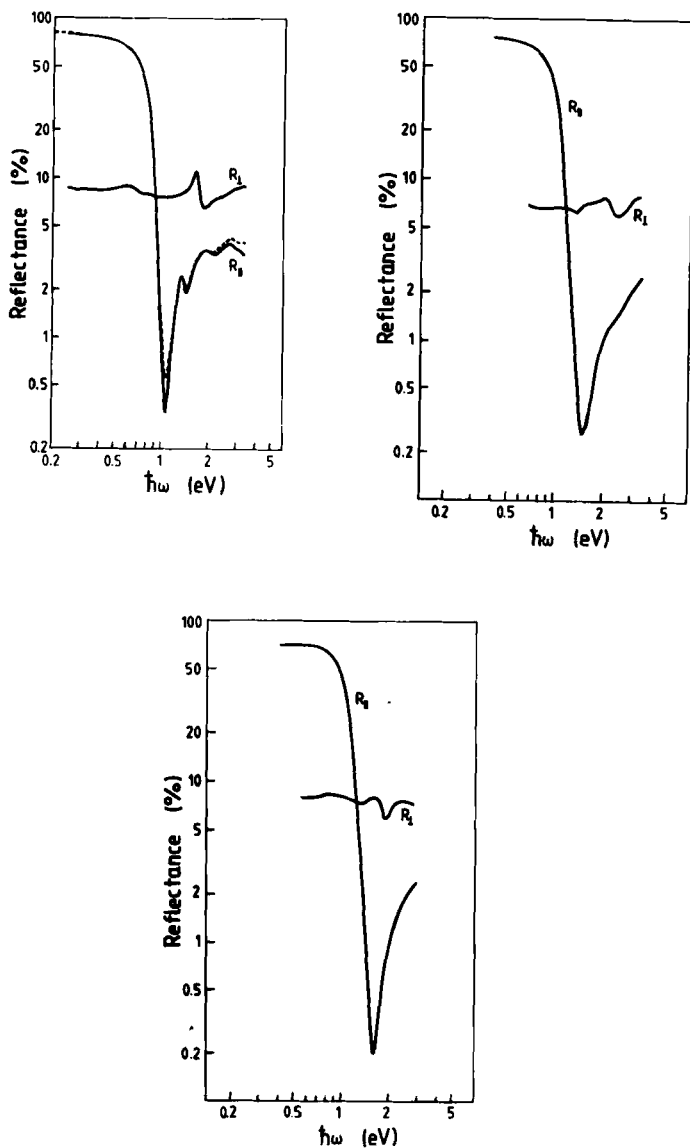


FIGURE 1. Polarised reflectance spectra of $(\text{Pe})_2(\text{PF}_6)_{1.1} \times 0.8\text{CH}_2\text{Cl}_2$ (dashed Line: Lorentz-Drude fit), $(\text{Py})_{12}(\text{SbF}_6)_7$ and $(\text{Fa})_2(\text{AsF}_6)_{0.2}(\text{PF}_6)_{0.8}$

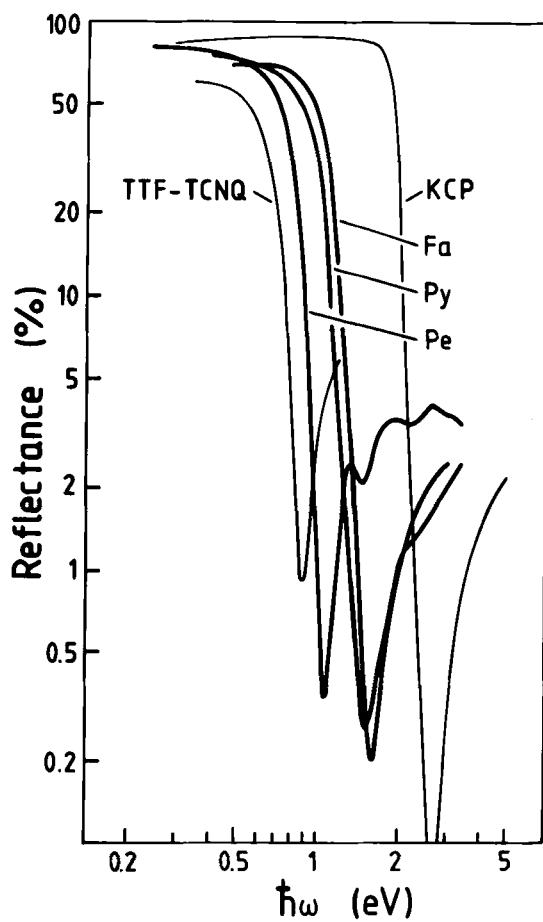


FIGURE 2. R_{\parallel} of TTF-TCNQ; $(\text{Pe})_2(\text{PF}_6)_{1.1} \times 0.8\text{CH}_2\text{CL}_2$; $(\text{Py})_{12}(\text{SbF}_6)_7$; $(\text{Fa})_2(\text{SbF}_2)_{0.2}(\text{PF}_6)_{0.8}$ and KCP.

like $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3} \times 3.2\text{H}_2\text{O}$ (KCP) and other Krogmann salts on the other hand. The new 1d organic metals, built up from aromatic molecules, have higher plasma energies than the other 1d organic metals, and tend to fill this gap between organic and inorganic 1d metals.

For a quantitative analysis of R_{\parallel} we used in the case of $(\text{Py})_{12}(\text{SbF}_6)_7$ and $(\text{Fa})_2(\text{AsF}_6)_{0.2}(\text{PF}_6)_{0.8}$ a simple Drude model. In the case of $(\text{Pe})_2(\text{PF}_6)_{1.1} \times 0.8\text{CH}_2\text{Cl}_2$ this model was extended by a Lorentz term in order to take into account the electronic transitions between 1.3 and 4 eV. A fit of R_{\parallel} on the basis of these models yields the values of the plasma energy $\hbar\omega_p$, of the dielectric constant of the lattice ϵ_g , and of the mean collision time τ . Furthermore, from the relation

$$\sigma_0 = \omega_p^2 \epsilon_0 \epsilon_g \tau \quad (1)$$

optical values for the electrical conductivity may be determined. The charge transfer to the inorganic counter ions leads to a depletion of the highest band of the molecular stacks and hence to p-type conductivity. Knowing the values of the carrier concentration N_p from the charge transfer ρ we may also calculate the values for their effective mass m^* from the plasma frequency ω_p

$$\omega_p^2 = \frac{N_p e^2}{\epsilon_0 \epsilon_g m^*} \quad (2)$$

On the basis of the tight binding model follows

further the bandwidth $4t$ from the overlap integral t

$$4t = \frac{\hbar^2 \rho \pi}{m^* a^2 \sin \rho \pi / 2}$$

where a is the distance between the organic molecules in the direction of the metallic axis.

The values thus obtained for the three different compounds are compiled in Table I. For a comparison the corresponding data of TTF-TCNQ, (TMTSF)₂PF₆ and KCP are also given.

TABLE I Transport properties of some 1d metals.

	$\hbar\omega_p$ (eV)	$\sigma_{0,opt}$ ($10^3 \Omega^{-1} \text{cm}^{-1}$)	τ (10^{-15}sec)	N_p (10^{21}cm^{-3})	$\frac{m}{m_0}$	$4t$ (eV)
TTF-TCNQ	0.76	1.2	4	2.8	3	0.43
(TMTSF) ₂ PF ₆	0.87	1.1	2.7	1.4	1	1
(Pe) ₂ (PF ₆) _{1.1} $\times 0.8 \text{CH}_2\text{Cl}_2$	0.91	1.9	4.4	1.42	0.91	1.1
(Py) ₁₂ (SbF ₆) ₇	1.08	1.6	3.3	1.77	0.87	1.8
(Fa) ₂ (AsF ₆) _{0.2} (PF ₆) _{0.8}	1.18	1.9	2.9	1.63	0.71	2.25
KCP	1.98	7.5	4.3	1.1	0.2	

As already indicated by the shift of the plasma edge the effective masses of the new compounds are smaller than those of other organic metals. This is due to a stronger overlap of the molecu-

lar orbitals along the stacks resulting in broader bands. The largest bandwidth with a value of more than 2eV is found in the fluoranthene salt. With these properties the radical cation salts built up from simple aromatics represent a transition between the usual narrow-band organic conductors and the large number of broad-band inorganic conductors.

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