Novel Complexes With New Electro-optic Properties

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Thin films of different complexes based on tetrathiafulvalene and copper maleonitrile were electrodeposited onto indium tin oxide coated glass and it was found that the application of a potential across the length of the sample resulted in a change of the visible absorption spectrum in samples where the ions in the complex had a permanent dipole moment.

Since their discovery about 40 years ago, a lot of research has been carried out into the preparation and properties of conducting organic and organometallic complexes. The main area of application for these materials has been in the microelectronics industry as alternatives to silicon and germanium semiconductors.[1,2] The crystal structure of these organic conductors consists of segregated stacks of planar donors and planar acceptors or radical ion stacks with closed shell counter ions. The stacks are partially charged and result in pseudo-one-dimensional conduction, where the conductivity in the plane of the stacks can be as high as that for graphite.[3]

The aim of the present work is to study changes that occur in the visible spectrum for a series of novel complexes when a potential is applied across the length of the sample and a current flows through the material. The work investigates the difference between complexes with non-centrosymmetric and centrosymmetric ions.

In the current study two types of charge transfer complexes were grown: those with a planar cation (based on tetrathiafulvalene [TTF]) with different anions, and those with a planar anion (based on metal dithiolenes) with different cations.

A complex of disodium copper maleonitrile dithiolate, $Na_2Cu(S_2C_4N_2)_2$ $[Na_2Cu(mnt)_2]$ (5×10^{-3} mol dm^{-3}) was electroreduced in a solution of acetonitrile containing 0.1 mol dm^{-3} of an electrolyte (Table 1). The $[Na_2Cu(mnt)_2]$ was prepared as described in the literature.[4] Cyclic voltammetry showed that the $[Cu(mnt)_2]^{2-}$ complex was reduced to $[Cu(mnt)_2]^{3-}$ irrespective of the electrolyte used. A thin film of the $[Cu(mnt)_2]^{3-}$ complex was electrodeposited as an amorphous material on a glass slide coated with indium tin oxide [ITO]. Electrical contacts were made to the material using conducting silver paint. A series of potential differences was applied across the length of the sample in the solid state and the visible spectrum was recorded when each voltage was applied. The high conductivity of the sample and the large contact resistance between the ITO and sample ensured that the potential drop was almost entirely across the sample. The spectra were measured using a Hewlett Packard HP8452A diode array spectrophotometer which could measure the spectrum from 300 to 800 nm in 0.5 s. A similar process was used for the TTF compounds, but the TTF was oxidised at the ITO electrode rather than reduced.

Fig. 1 shows the visible spectrum of the α-methyl benzylammonium $[Cu(mnt)_2]^{3-}$ complex after the background spectrum of ITO coated glass had been subtracted. The peaks at 450, 540 and 700 nm are believed to be interference fringes which result from the thin films used. Measurements could not be made below 300 nm because the ITO coated glass absorbs strongly in this region. The electrochromic properties of the ITO were measured but found to be negligible in the region of the spectrum studied.

There is a significant decrease in the absorption maxima of the various bands with an increase in applied potential. The absorbance at 390 nm decreased by approximately 40% upon the application of 10 V across the length of the sample. These materials turn visibly clearer when a potential is applied across them, and therefore may form the basis of solid state electro-optic devices. This decrease in absorbance is not reversible, *i.e.* when the potential is removed, the spectrum of the material does not return to its original form. Heating the sample to about 70 °C before a potential was applied had no effect on the spectrum in the region 350–810 nm, demonstrating that this phenomenon is not a thermal effect caused by resistive heating of the film. Annealing the sample in an oven at 100 °C for 30 min after a potential had been applied across it allowed the initial spectrum of the material to be re-obtained.

The above experiment was repeated for a similar film grown using tetraethylammonium tetrafluoroborate as the electrolyte. The visible absorption spectra of the material did not change when a potential difference was applied across the sample.

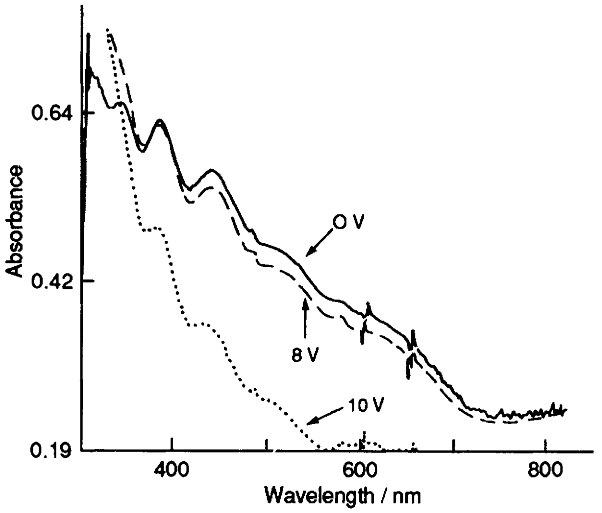

Fig. 1 A graph of the changes in the visible spectrum of a α-methyl benzylammonium $[Cu(mnt)_2]^{3-}$ complex grown on to ITO coated glass when a potential is applied across it in the solid state

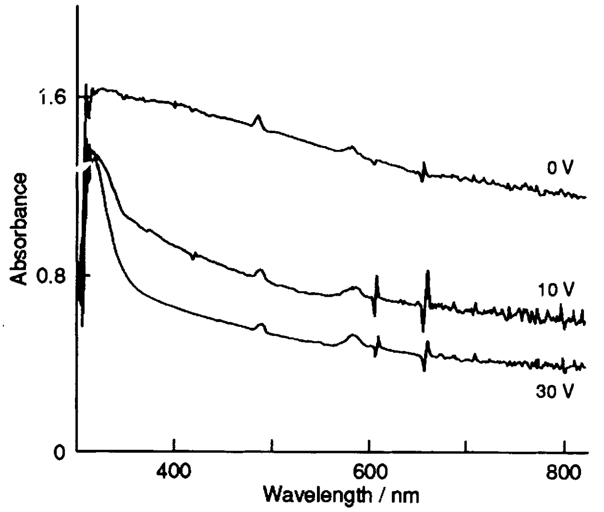

Fig. 2 A graph of the changes in the visible spectrum of a TTF mandelate complex grown on to ITO coated glass when a potential is applied across it in the solid state

Table 1 Percentage change in absorbance of various complexes

Cation	Anion	Electrolyte counter ion	Change in absorbance (%)
α-methylbenzyl ammonium	CuMNT	Cl^-	-40[a]
o-chlorophenyl ammonium		PF_6^-	-3
m-chlorophenyl ammonium		PF_6^-	-4
p-chlorophenyl ammonium		PF_6^-	-6
phenyl ammonium		PF_6^-	$+45$
triethyl ammonium		BF_4^-	-3
tetraethyl ammonium		BF_4^-	0
tetrabutyl ammonium		BF_4^-	0
TTF	Mandelate	Et_4N^+	-43[b]
	Tartrate	Et_4N^+	-52
	tetraphenyl borate	Bu_4N^+	0
	perchlorate	Et_4N^+	0
	adipate	Et_4N^+	0
	camphorate	Et_4N^+	-6

[a] Change in absorbance at 390 nm on application of 10 V. [b] Change in absorbance at 400 nm on application of 30 V.

Fig. 2 shows the visible spectrum of TTF mandelate as a function of applied potential. Again, large decreases in the absorption of the material are observed when a potential is applied. The observation that complexes based on planar cations show the same effect as those based on planar anions suggests that this is not a chemical change such as the dissociation of the amine. The reversibility of this effect by heating the material also suggests that it is not chemical in nature.

Table 1 lists the change in absorbance at a given wavelength for a series of $Cu(mnt)_2$ and TTF complexes when potentials are applied across a thin film of each material. It can be seen that a wide variety of these complexes show these novel electro-optic effects although the magnitude changes considerably. It should be noted that the change in absorbance can be quite significant and one material, phenylammonium $[Cu(mnt)_2]^{3-}$, actually became visibly darker when a potential was applied.

These data also show that all of the materials which do not demonstrate these electro-optic properties have centrosymmetric cations in the case of $Cu(mnt)_2$ complexes and centrosymmetric anions in the case of TTF complexes.

It is proposed that these novel and important observations arise from an alignment of the ion dipoles of the non-centrosymmetric ions in the film as a result of the applied potential. If the excited state is stabilized by an interaction between the anion and the cation then the intensity of the absorption band will be affected by the overlap of the molecular orbitals. It is suggested that in materials with non-centrosymmetric ions the application of a potential field causes an alignment of the dipoles which changes the overlap of the orbitals and hence the magnitude of the absorbance. If this idea is correct then the change in absorbance with applied potential will be dependent upon the orientation of the ion's dipole moment. Centrosymmetric ions do not have a dipole moment and are therefore, not significantly affected by a potential field.

The principle of dipoles becoming aligned in an electric field has previously been observed and utilized in electrochromic devices.[5] Submicron needles of chromium metal suspended in a gel or polymer have been aligned in an electric field, changing their optical properties. Removing the potential field causes the particles to randomize due to Brownian motion and revert to their original optical properties. In the current work, the materials are solid and hence there is a large barrier to rotation which will be dependent on the radius and dipole moment of the ion and the size of the cavity in which it rotates. The dipoles which are aligned in the electric field can only return to their random orientation when the sample is heated so that the ions can overcome the barrier to rotation.

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