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The Design of Organic Metals. Dibenzotetrathiafulvalene-2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DBTTF-DDQ)

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The electrical and optical properties of the four charge-transfer salts formed between the two donors tetrathiafulvalene (TTF) and dibenzotetrathiafulvalene (DBTTF) and the two acceptors tetracyanoquinodimethan (TCNQ) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) are compared. The differences are rationalized on the basis of electrochemical considerations. DBTTF–TCNQ, the compound composed of the weakest donor and acceptor, is found to be a neutral complex. However, TTF–TCNQ and the new material DBTTF–DDQ are mixed valence and highly conducting. The latter material, which is the first highly conducting salt to contain the common acceptor DDQ, has a room temperature pellet electrical conductivity of 8 Ω^{-1} cm^{-1}. Finally, the combination of best donor and acceptor, TTF–DDQ, forms an insulating, completely ionic salt. The structure of this salt has been determined and found to crystallize with relatively isolated dimers of TTF and strongly distorted stacks of DDQ.

For the past few years we have been engaged in a program aimed at gaining a systematic understanding of the electronic and structural properties of organic charge-transfer complexes. As part of this work we have attempted to expand the range of materials that will form organic metals. We now report the electrical and optical properties of the new highly conducting salt DBTTF–DDQ,¹⁾ the first²⁾ such material containing the common acceptor DDQ. In order to understand why DBTTF–DDQ is highly conducting, we will compare the electrical and optical properties of the four charge-transfer salts formed between the two donors DBTTF and TTF and the two acceptors DDQ and TCNQ.¹⁾ This comparison will illustrate the dependence of the solid state electrical properties of organic charge-transfer complexes on the redox properties of the individual molecules and, consequently, will illustrate guidelines for how to make organic metals.

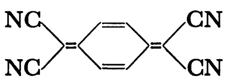
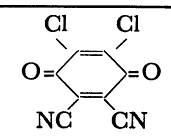
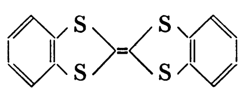
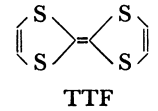
High conductivity requires that two conditions be fulfilled: first, the donor and acceptor must crystallize in separate (segregated) stacks and, second, the degree of charge transfer, ρ, from donor to acceptor must be fractional ($\rho<1$), *i.e.*, the resulting complex must be mixed valence. The criteria we use in selecting donors and acceptors that will meet these conditions have been discussed in detail elsewhere.²⁻⁴⁾ However, we will briefly mention under what conditions the criterion of incomplete charge-transfer is met³⁾ since it is of central importance to the results reported here.

The total binding energy of these materials per donor/acceptor pair, expressed as a function of ρ, the degree of charge-transfer, is given in Eq. 1,

$$E_B(\rho) = -\rho[\rho E_M - (I-A)], \qquad (1)$$

where E_M is the Madelung (electrostatic binding) energy of the completely ionized lattice, I is the ionization potential of the donor, and A is the electron affinity of the acceptor. Since variations in E_M are smaller than variations in $(I-A)$ for the types of materials under discussion, differences in ρ between different materials should depend mainly on the quantity $(I-A)$. Since the values of I and A are generally not well known for organic molecules, however, we use the more readily obtained values of the electrochemical half-wave potentials ($E_{1/2}$) as a measure of relative donor/acceptor strength. Since $\Delta E_{\mathrm{REDOX}}$, the difference between the $E_{1/2}$ values of any donor/acceptor pair, can be related⁵⁾ to the quantity $(I-A)$ in Eq. 1, values of $\Delta E_{\mathrm{REDOX}}$ can be used to predict the degree of charge-transfer in a given material. In particular, if $\Delta E_{\mathrm{REDOX}}$ is large

Table 1. Properties of donor/acceptor combinations: $\Delta E_{\mathrm{REDOX}}$, valence, and room temperature pellet electrical conductivity

	 TCNQ ($E_{1/2}$=0.23 V)	 DDQ ($E_{1/2}$=0.56 V)
 DBTTF ($E_{1/2}$=0.55 V)	+0.32 V Neutral 10^{-7} Ω^{-1} cm^{-1}	−0.01 V Mixed valence 8 Ω^{-1} cm^{-1}
 TTF ($E_{1/2}$=0.29 V)	+0.06 V Mixed valence 70 Ω^{-1} cm^{-1}	−0.27 V Ionic 10^{-8} Ω^{-1} cm^{-1}

and positive, a neutral charge-transfer complex results, *i.e.*, for a poor donor/acceptor combination, $\rho=0$. If $\Delta E_{\mathrm{REDOX}}$ is large and negative, a fully ionic charge-transfer salt results, *i.e.*, for a good donor/acceptor combination, $\rho=1$. For intermediate values of $\Delta E_{\mathrm{REDOX}}$, estimated3) as $-1/4\,\mathrm{V}\lesssim\Delta E_{\mathrm{REDOX}}\lesssim 1/4\,\mathrm{V}$, there is incomplete charge-transfer and a mixed-valence, and therefore highly conducting, compound results.

Table 1 gives $E_{1/2}$ values6) (in parentheses) for the two donors, TTF and DBTTF, and the two acceptors, TCNQ and DDQ, as well as the $\Delta E_{\mathrm{REDOX}}$ values for the four donor/acceptor combinations. Since donor strength increases as $E_{1/2}$ decreases, it is apparent that TTF is a considerably stronger donor than DBTTF. On the other hand, since acceptor strength increases as $E_{1/2}$ increases, it can be seen that DDQ is a much stronger acceptor than TCNQ. Thus, for TTF–TCNQ, $\Delta E_{\mathrm{REDOX}}$ is $+0.06$ V and the material is a mixed-valence, highly conducting salt. Because of its small value (-0.01 V) of $\Delta E_{\mathrm{REDOX}}$, one would predict that DBTTF–DDQ would also be a mixed-valence, highly conducting solid. This is what we have found. DBTTF–TCNQ, however, has a large, positive ($+0.32$ V) value of $\Delta E_{\mathrm{REDOX}}$. Hence, it is a neutral insulating ($\rho=0$) solid. The $\Delta E_{\mathrm{REDOX}}$ value of -0.27 V for TTF–DDQ lies too near the ionic boundary ($\Delta E_{\mathrm{REDOX}}\approx-1/4$ V) to allow one to predict whether TTF–DDQ would be mixed-valence or ionic. We have found it to be, in fact, completely ionic.

The reaction of DBTTF with DDQ in toluene results in a 1 : 1 compound7) with the relatively high room temperature powder electrical conductivity of 8 Ω^{-1} cm^{-1}, compared to values in the range of 10^{-4}—10^{-10} Ω^{-1} cm^{-1} for any of the previously known compounds of DDQ, and compared to a value of 70 Ω^{-1} cm^{-1} for TTF–TCNQ. Although we have not been able to obtain single crystals of DBTTF–DDQ suitable for X-ray diffraction, the high electrical conductivity leaves no doubt that the material is composed of mixed-valence, segregated stacks of donors and acceptors. Convincing evidence for the mixed-valence nature of DBTTF–DDQ can also be obtained from its optical spectrum, Fig. 1. Like that of TTF–TCNQ, the spectrum consists of high energy bands largely characteristic of the individual ions. In addition, and most importantly, there is a low energy band at ≈0.4 eV which, in the case of TTF–TCNQ, has been shown to be a mixed-valence, intrastack charge-transfer transition.8) This mixed-valence charge-transfer band is found in and is characteristic of all known organic metals.8) Thus, DBTTF–DDQ is mixed-valence and is the first highly conducting material that contains DDQ. This compound is one of the rare examples4) of a highly conducting organic charge-transfer salt that does not contain TCNQ or one of its derivatives as the acceptor molecule. This compound is also significant as one of the first highly conducting materials containing DBTTF, the oldest TTF-like molecule.9) Metallic DBTTF compounds with BF_4^- and $TCNQCl_2$ have recently been reported.10,11)

Slow diffusion of an acetonitrile solution of TTF into a DDQ solution of the same solvent yields small, dark red crystals of almost cubic habit. A projection of the structure (space group $P\bar{1}$ with $a=10.227(4)$, $b=12.195(5)$, $c=6.609(2)$ Å, $\alpha=77.51(2)$, $\beta=81.93(2)$, and $\gamma=87.30(4)$°, with 2 formula units per unit cell) onto the (001) plane is shown in Fig. 2(a). It consists of

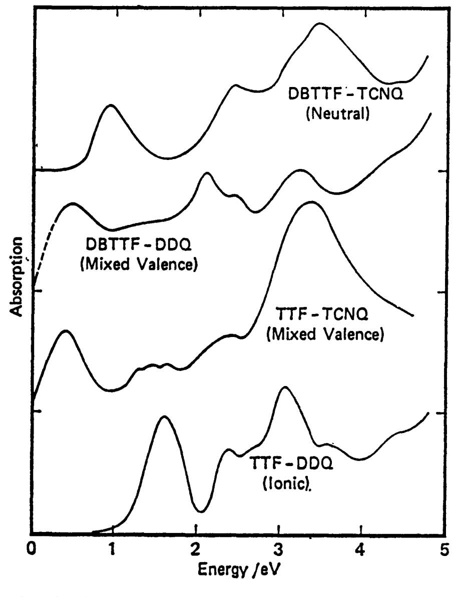


Fig. 1. Optical absorption spectra of the four complexes formed between the two donors TTF and DBTTF and the two acceptors DDQ and TCNQ.

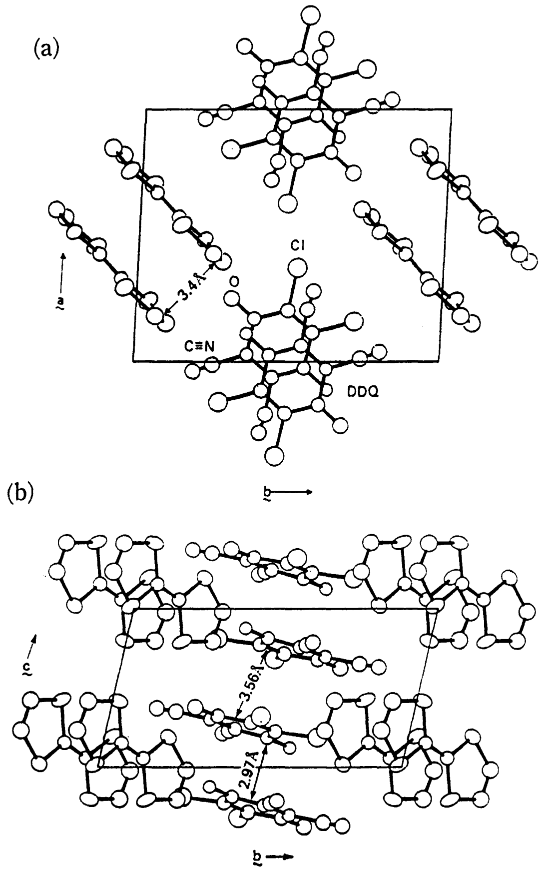


Fig. 2. Structure of TTF–DDQ projected onto the (a) (001) plane and (b) onto the (100) plane.

strongly distorted stacks of DDQ and isolated, eclipsed dimers of TTF. The interplanar spacing between the two TTF molecules comprising the dimer is ≈3.4 Å. There is virtually no overlap between adjacent dimers. The DDQ molecules also dimerize, but do so within the framework of infinite columns of DDQ stacked parallel to the c axis. The stacking of the DDQ molecules can be seen in the (100) projection of the structure, shown in Fig. 2(b). The interplanar spacing between molecules of the DDQ dimer is 3.0 Å. This is an extremely short distance. The interplanar spacing between molecules in adjacent dimers is 3.56 Å. This strong distortion of the DDQ stacks, as well as the existence of isolated dimers of TTF, accounts for the fact that there is no paramagnetic contribution to the magnetic susceptibility. The distortion of the acceptor stack is presumably caused by the same phenomenon[12] that causes the distortion in the low temperature phases of other fully ionic complexes, such as K–TCNQ.[13] The completion of the structural analysis ($R=12\%$) has been complicated by the fact that the DDQ molecule is disordered, exhibiting partial interchange of –Cl and –C–N groups. Such disorder has previously been seen in the charge-transfer complex of DDQ with benzo[*c*]-phenanthrene.[14]

That $\rho=1$ in TTF–DDQ can be seen in its optical spectrum, shown in Fig. 1. The absence of a mixed valence charge transfer band near 0.4 eV indicates that this compound is not mixed valence. The optical spectrum is dominated by the stronger absorption of the TTF molecule and is nearly identical to that of $(TTF^+)_2$ dimers,[15] consistent with the dimers evident in the structure (Fig. 2). The optical absorption indicates that they are not neutral, but completely ionic ($\rho=1$) in agreement with the conclusions of Ikemoto and co-workers.[16]

The optical spectrum of DBTTF–TCNQ, also shown in Fig. 1, shows no evidence of any absorption[17] due to $TCNQ^-$ and hence must be a neutral ($\rho=0$) complex. (Absorption due to $DBTTF^+$, if it were present, would also appear near 2.0 eV, but would be considerably weaker than the $TCNQ^-$ absorption.) Recent ESR experiments[18] also indicate that DBTTF–TCNQ is a neutral complex. This is expected from the large positive value (+0.32 V) of $\Delta E_{\mathrm{REDOX}}$ (Table 1). The energy of the charge transfer band at 0.91 eV is in agreement with a computed[19] value based on $\Delta E_{\mathrm{REDOX}}$. The second band near 2.4 eV is probably a second charge-transfer band.

In summary, it seems apparent that if the $\Delta E_{\mathrm{REDOX}}$ value of the donor/acceptor pair in a 1 : 1 charge-transfer complex differs significantly from zero, the degree of charge-transfer in the complex will be either zero or one ($\rho=0,1$). If, however, $\Delta E_{\mathrm{REDOX}}=0$, the complex will probably be mixed-valence. As described above, we have used the $\Delta E_{\mathrm{REDOX}}$ values in Table 1 to successfully predict that DBTTF–TCNQ would be neutral and that DBTTF–DDQ would be mixed-valence and, therefore, highly conducting. In so doing, we have convincingly demonstrated that by employing simple electrochemical considerations and readily obtainable data, one can reliably estimate the degree of charge-transfer which might be expected for a 1 : 1 compound. As a result, one can predict which combinations of donors and acceptors have a reasonable probability of giving rise to organic metals. This predictability has been used to obtain the first highly conducting salt of the common acceptor DDQ.

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1) Abbreviations used are: DBTTF, dibenzotetrathiafulvalene; TTF, tetrathiafulvalene; DDQ, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone; TCNQ, tetracyanoquinodimethan; $TCNQCl_2$, dichlorotetracyanoquinodimethan.

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