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AN OVERVIEW OF ORGANIC CHARGE-TRANSFER SOLIDS: INSULATORS, METALS, AND THE NEUTRAL-IONIC TRANSITION

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Abstract This presents a simple framework for studying the basic properties of the broad class of organic charge-transfer solids. It is shown that many of the differences in behavior of these materials can be described and understood in terms of a single, physical variable: ΔE_{REDOX}, the difference between the electrochemical oxidation potential of the donor and the reduction potential of the acceptor. Differences in this parameter are shown to be largely responsible for the difference between organic metals and insulators. ΔE_{REDOX} also determines whether the solids are neutral or ionic and has led to the discovery of a neutral-ionic transition between these two types of ground states.

INTRODUCTION

All organic molecules condense into solids (at sufficiently low temperatures), but most of them do not exhibit interesting physical properties in the solid state. We shall focus on a special class of organic solids called charge-transfer compounds.[1] These compounds are composed of two types of organic molecules: one, an electron donor, and the other, an electron acceptor. These solids are singled out because of the possibility that an electron may be transferred (or excited) from the donor to the acceptor, which may result in unpaired electrons which can potentially cause these solids to have interesting electronic, magnetic, and/or optical properties not found in the separate donor or acceptor solids. These molecules are often π-electron donors and acceptors and are usually planar, (in order to facilitate packing), but we shall also consider inorganic anions and cations,[2] such as Br^-, PF_6^-, K^+, and TEA^+.

In a solid, there are generally two different ways of stacking donor and acceptor molecules: (1) into Mixed Stacks, in which donor and acceptor molecules alternate along the stack; and (2) into Segregated Stacks, in which the molecules form separated donor stacks and acceptor stacks. The potential ability of these two types of stacks to conduct electricity is very different. For example, in order to conduct down a mixed stack, an unpaired electron on, say, a donor molecule would have to start by hopping to the adjacent molecule - an acceptor. Since the molecular potential of this acceptor is very different from that of the donor, this difference in potential will act as a large activation energy to conduction. For this reason, mixed stack solids are expected and found to be insulating. In contrast, for conduction along a segregated stack, an unpaired electron on one donor would again have to start by hopping to a neighboring molecule, but in this case the neighbor is also a donor. Thus, there would be no large molecular potential difference to limit the conductivity, and all compounds which have high conductivity also have segregated stacks, such as TTF-TCNQ. But the converse is not true: There are many insulating solids with segregated stacks, such as K-TCNQ.

In addition to differences in stacking types, organic solids are found with differences in the stoichiometric ratio of donor to acceptor. Some solids have a 1:1 ratio as in TTF-TCNQ and K-TCNQ, or a 1:2 ratio as in Qn-$TCNQ_2$; or 2:1 ratio as in $TMTSF_2PF_6$. There are even examples of incommensurate stoichiometry, such as in TTF-$Br_{0.79}$.

The most fundamental questions concern the factors that determine the stacking type and the stoichiometry. As in inorganic solids, our understanding of these factors in very limited and, in general, we must treat the stacking type and stoichiometry as given. (A few important exceptions will be noted later.) The most general questions that we can attempt to answer and which we shall address here are the following:

I. Mixed Stacking solids are found in two types: Those composed of neutral molecules, and those composed of cations and anions. What factors determine which is present, *i.e.* determine the ionicity of the solid?

II. Segregated Stacking solids with 1:1 stoichiometry are generally found to be either metallic or insulating, with a factor of 10^6 difference in conductivity at 300K. What factors determine this difference?

III. Are there some radical cation and radical anion salts for which we can understand what factors determine the stoichiometry?

Any discussion of such broad questions as these, in such a new and complex field as organic solids, and in such a short review as this is of necessity oversimplified. Only the most important effects will be considered and many relevant factors and features must be neglected. In this review, we shall present such an oversimplified, but unified and useful picture. Specifically, we shall attempt to show how:

(1) The above three major features of organic charge-transfer solids are largely determined by the degree of charge transferred from the donor to the acceptor; and

(2) The degree of charge transfer is largely determined by a competition between two factors: The cost (I-A) of ionizing the donor-acceptor pair and the electrostatic Madelung energy E_M gained by an ionic solid.

It is possible and very convenient for this review to make the above approach even more simple by introducing some reasonably good approximations (discussed in more detail in the following section). The values of the gas phase (I-A) of the molecules can be approximated by the electrochemical oxidation (donor) and reduction (acceptor) potentials of the isolated molecules in solution. This has been established[3] as a quantitatively reasonable approximation. In Fig. 1, we show the oxidation potentials for a wide variety of donor molecules and reduction potentials for a similar variety of acceptors. These variations are seen to be large compared with the typical variations of 0.1 eV in E_M between compounds.[4] Thus, we shall make the further approximation that E_M is relatively constant for all solids, compared with the wide ranges of values ΔE_{REDOX} for different compounds. Thus, the over-simplified proposal is that:

The major features of these materials (I, II, III above) are largely determined by the differences in the redox potentials of the constituent molecules.

This statement is clearly exaggerated, but nevertheless useful: both as a framework for dealing with the great variety and breadth phenomena in this field and also as a starting point for more extensive and precise work in the future. This picture has an added advantage for physicists: according to this picture, all one needs to know about a complex organic molecule, is its oxidation and reduction potentials. In the following sections, I, II, and III, we shall examine the above three questions from the point of view of this over-simplified picture. The degree of success in making sense out of the data will justify the guarded use of such a simple picture.

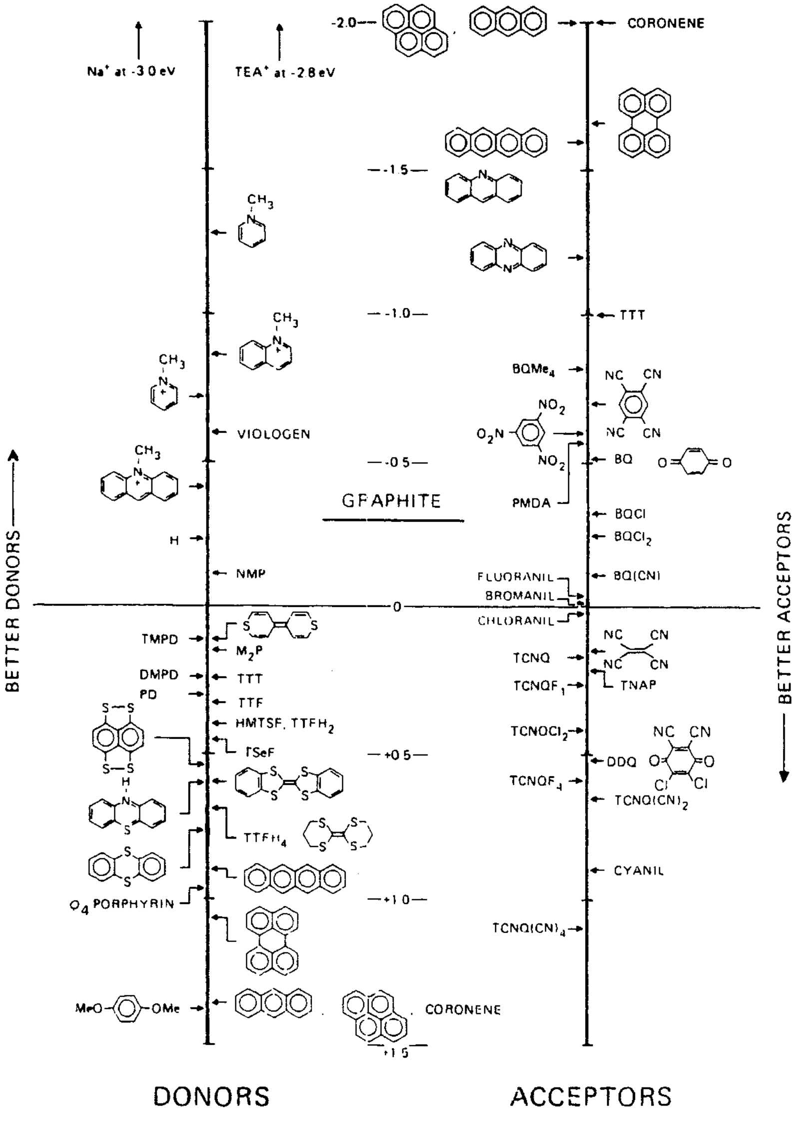

FIGURE 1. Values of the oxidation potential for a wide variety of donors (on left) and the reduction potential for a number of acceptors (on right) in Volts. (For meaning of symbols, see References.)

I. NEUTRAL *VERSUS* IONIC MIXED STACKS

The vast majority of organic charge-transfer solids have the donor and acceptor molecules arranged in mixed stacks[1]. In these structures, the molecules are found to be either nominally neutral (usual case) or cations and anions. The simplest description of this situation was first discussed by McConnell and coworkers,[5] who pointed out that this behavior could be understood by simply considering the competition between two energies (discussed earlier): The cost of ionizing a donor-acceptor pair, and the electrostatic (or Madelung) energy E_M of the solid that is gained by forming ions. The cost of ionization (I-A) is given by the difference between the ionization energy (I) of the donor and the electron affinity (A) of the acceptor. The electrostatic energy can be expressed as $E_M=\alpha\langle e^2/a\rangle$; that is, a constant (the Madelung constant) times the Coulomb attraction within a neighboring donor-acceptor pair at a nominal distance a apart. For similar values of E_M, a poor donor and a poor acceptor will tend to form a neutral solid, whereas a great donor and a great acceptor will tend to form an ionic solid. A simple calculation[5] shows that the boundary between the neutral and ionic ground states is sharp (actually discontinuous) and occurs where:

$$(I-A) = \alpha\langle e^2/a\rangle . \qquad (1)$$

Implicitly, McConnell's description neglects the overlap between molecules along the stack. This interaction has been included by Soos and coworkers,[6] who find that a well defined, sharp transition still exists, but now the transition is between states which are only nominally neutral and nominally ionic. In order to recognize this effect, we shall define the words Neutral and Ionic (with capital letters) to mean nominally neutral and nominally ionic.

In order to experimentally study this behavior, we shall examine one of the earliest studied measurements on these materials; namely, the charge-transfer absorption bands. The observation of this type of absorption initially lead to the discovery of these charge-transfer interactions and causes the color of these solids (or solutions) composed of often colorless donors and acceptors. In a Neutral solid, this absorption is associated with exciting an electron from the (neutral) donor to the acceptor. The energy of this transition is given by:

$$h\nu_{CT}^{N} = (I - A)-\langle e^2/a\rangle , \qquad (2)$$

i.e., the net cost of ionizing the pair, less the electrostatic attraction between the pair of charges created by this excitation. Similarly, for an Ionic mixed stack, one can excite an electron from the anion to the cation, which will involve net energy:

$$h\nu_{CT}^{I} = (2\alpha-1)\langle e^2/a\rangle-(I-A)\ , \qquad (3)$$

being careful to correctly count all the electrostatic interactions.

In order to compare Eqs. (2) and (3) to experimental values of $h\nu_{CT}$, we need experimental numbers for the molecular energies I and A, as well as for the Madelung constant and Coulomb energy $\langle e^2/a\rangle$. Values of I and A can be found for a number of organic donors and acceptors, but not all. Data for the electrochemical oxidation and reduction potentials are much more available and readily measured, and it is well established that these potentials are linearly related to I and A. Thus, we shall use the difference in redox potentials ΔE_{REDOX} as a measure of (I-A). In order to find α and $\langle e^2/a\rangle$, on the other hand, one must know the crystal structure and have done the necessary calculation. Generally speaking, the structures are not known and only a few Madelung calculations have been carried out on organic mixed stack compounds. Fortunately, the values calculated vary only slightly (~0.1 eV out of 3.5 eV) from compound to compound. In a comparison of different materials with values of ΔE_{REDOX} varying over a range of 0-3 eV, these variations in the electrostatic parameters are small. Thus, we shall treat them as constant for all mixed stack compounds.

With constant $\langle e^2/a\rangle$ and α in Eqs. (2) and (3), we can consider the variation of $h\nu_{CT}$ as a function of (I-A), or equivalently ΔE_{REDOX}. In Fig. 2, we show this variation by the straight lines which form the V-shaped curve (see top scale). In order to compare with experiment, we have plotted[7] on the same figure the frequencies of the charge-transfer bands observed in 25 organic mixed-stack solids versus ΔE_{REDOX} of the constituent donor and acceptor pairs. (For names of specific compounds, see Ref. 7). The theory (V-shaped curve obtained from Eqs. (2) and (3)) has been shifted to best fit and the data. Note that the slope is unity. The agreement evident in Fig. 2 is good evidence that there is both meaning and usefulness in the simplest approach. Clearly, the value of $h\nu_{CT}$ and the distance away from the Neutral-Ionic boundary are largely determined by (and hence predictable from) the difference in the redox potentials. Recall also that Fig. 2 is a plot of a solid state measurement ($h\nu_{CT}$) *versus* a measurement on isolated molecules in solution. Thus, deviations from perfect agreement (particularly for

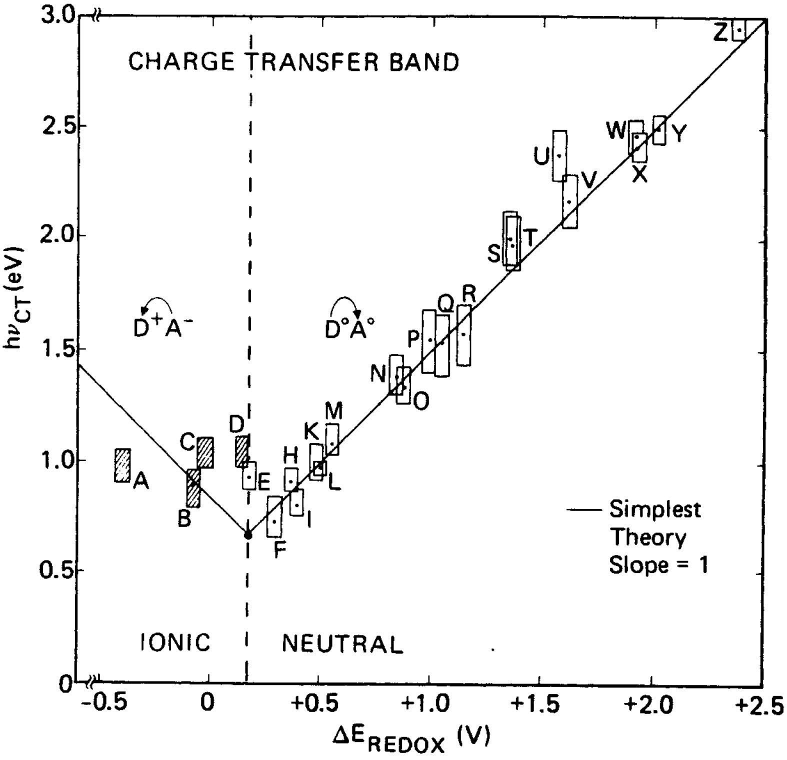

FIGURE 2. Comparison of the prediction of the simplest model (straight lines forming V-shaped curve) with plot $h\nu_{CT}$ *versus* ΔE_{REDOX}. Vertical dashed line in Neutral-Ionic boundary.

the ionic compounds!) should not be surprising; also considering the simplicity of the assumption behind the plot in Fig. 2.

But there is something else to be realized from Fig.?2. Note that the neutral compounds near the neutral-ionic boundary, for example those labelled E, F, H, and I, are Neutral, but on the verge of becoming Ionic. What would happen to these materials under pressure? As the molecules are forced closer together, the electrostatic energy the Ionic ground state would increase, thus favoring Ionic phase. Thus, one might hope that at sufficiently high pressure, the Ionic phase would become lowest and these materials would undergo a transition from Neutral to an Ionic ground state.

Indeed, such a Neutral-Ionic phase transition has been recently discovered[7] in 10 of these compounds which lie near the boundary. The experiment consisted of mounting thin crystals in a pressurizing fluid in a diamond anvil high pressure cell. One then monitors the color of these crystals as the pressure is increased. Neutral molecules, having closed shells, tend to be yellow (absorbing in the ultraviolet only) while ions tend to be strongly colored dyes with absorption in the visible associated with the unpaired electrons. Under pressure, these materials exhibited a distinct change in color, from yellow to (usually) red. In TTF-chloranil, the changes in the optical spectrum[7] of the solid are closely related to the differences between the solution spectrum of neutral TTF and chloranil molecules and that of the ions. In addition, for different compounds, the pressure required for this transition was found to be higher for materials lying farther from the Neutral-Ionic boundary (Fig. 2).

This observation represents the first observation in any type of material of a Neutral-Ionic transition not complicated by structural effects. In a CdTe and a series of related inorganic compounds a transition was found[8] nearly 20 years ago, at which the ground state changed from covalent (neutral) to ionic. At this transition, however, the structure also changed from tetrahederal to octahedral coordination, with a ~20% contraction in volume. For these transitions, it is somewhat difficult to separate how much of the transition is structural and how much is electronic. In SmS and related compounds[9] an unrelated transition is observed, although it is called a "valence" transition. The difference here is that the effects are concentrated almost entirely on the donor (Sm) and the sulfur generally remains unaffected.

II. METALS VERSUS INSULATORS

The most exciting property of organic solids has always been their electrical conductivity. Some of the original TCNQ compounds[10] had conductivities as high as 10^2 Ω^{-1}cm^{-1}. At low temperatures, TTF-TCNQ and more recently $TMTSF_2PF_6$ show conductivities of ~10^4 and ~10^5 Ω^{-1}cm,$^{-1}$ respectively, and most dramatically $TMTSF_2ClO_4$ is superconducting for $T<1K$. The vast majority of work in organic solids has focused on attempting to measure and understand the details of these highly conducting compounds. It is important in an overview of charge-transfer compounds, however, to recognize that high conductivity is extremely rare; the vast majority of these compounds have 300K conductivities of $<10^{-6}$ Ω^{-1}cm.$^{-1}$ Focusing on the compounds with 1:1 stoichiometry for the remainder of this section, only a very few are highly conducting ($\sigma(300K) \geq 10$ Ω^{-1}cm^{-1}) and these compounds are ~10^5 times larger than all of the insulating majority. Originally, all of these highly conducting materials contained TCNQ as the acceptor, indicating something special and unique about this molecule, although there are also insulating TCNQ compounds.

The explanation for this sharp and dramatic separation into either metals or insulators involves[11-14] the difference in redox potentials (as promised in the introduction). Focusing on TCNQ salts with a variety of different donors, a very poor donor will contribute no unpaired electrons to a TCNQ stack and hence, no electrons to give conductivity in such a neutral solid. A stack of excellent donors, on the other hand, will donate one unpaired electron to each TCNQ. In order for a stack of such TCNQ radical anions to conduct, one of the unpaired electrons must hop to an adjacent TCNQ anion, forming a dianion. Since electrons repel each other, there is a disproportion energy which acts like a barrier to limit the conductivity in such a stack. For a stack of intermediate donors, there will be a degree of charge-transfer in between the extremes of zero (very poor donors) and unity (excellent donors), giving rise to a stack of TCNQ molecules, some of which are neutral and some anions. Such an incomplete charge-transfer gives rise to a mixed valence TCNQ stack (and a mixed valence donor stack). The unpaired electrons in this stack can now easily conduct, not limited by the disproportion energy.

This proposal for the occurrence of high conductivity can be tested straightforwardly: Plot the conductivity versus ΔE_{REDOX}. Small ΔE_{REDOX} will give ionic (Mott) insulators, while large ΔE_{REDOX} will give neutral insulators, and the metals will lie in between. Figure 3 is such a plot[14] and shows that the highly conducting compounds exist only over a very narrow-range of ΔE_{REDOX}, inbetween one group of compounds which can be shown to be neutral and another which is ionic.

A number of other explanations[15,16] had been proposed to account for the large 10^6 difference in 300K conductivities of the 1:1 compounds. Among these was a model related to Little's mechanism of superconductivity, which supposed that the electronic polarizability of the donor molecule, for example, screened out the Coulomb interactions on the TCNQ stack, allowing conductivity for compounds with polarizable donors. Indeed, the conductivity and polarizability of TTF^+ and NMP^+ are much larger than those K^+ and TEA^+. However, a more crucial test is provided by the examples[17,18] of the HMTTF and HMTSF salts of TCNQ and $TCNQF_4$. All four salts are isostructural and all the molecules involved are highly polarizable. Nevertheless, the $TCNQF_4$ salts are $\sim 10^6$ times less conducting at 300K. The explanation is found in the differences in ΔE_{REDOX} and not in polarizability: the TCNQ salts are highly conducting because they are mixed valence. The effect of fluorine substitution is to increase the electron affinity of $TCNQF_4$, which increases the charge transfer to unity, making the $TCNQF_4$, salts Mott insulators. The highly polarizable molecules are not polarizable enough of screen of Coulomb interactions. This is the only explanation consistent with all the data. Thus, TTF and NMP make good conductors with TCNQ, not because they are more polarizable than K^+ and TEA^+, but because they are poorer donors (and they are larger - hence smaller Madelung eneryg).[11,13,14]

If the explanation is really so simple, there should be nothing special about TCNQ and one should be able to make other highly conducting charge transfer salts. Using these guidelines, such compounds have recently been made[19,20] using the familiar (but hitherto unsuccessful) acceptors chloranil, bromanil, fluoranil and DDQ.

III. STOICHIOMETRY

Charge-transfer compounds with large organic donors and acceptors form in various stoichiometries; *e.g.*, TTF-TCNQ, $TTT\text{-}TCNQ_2$, $Morph_2$ $TCNQ_3$. It is difficult to imagine how the stoichiometry could be viewed as a variable to be optimized;

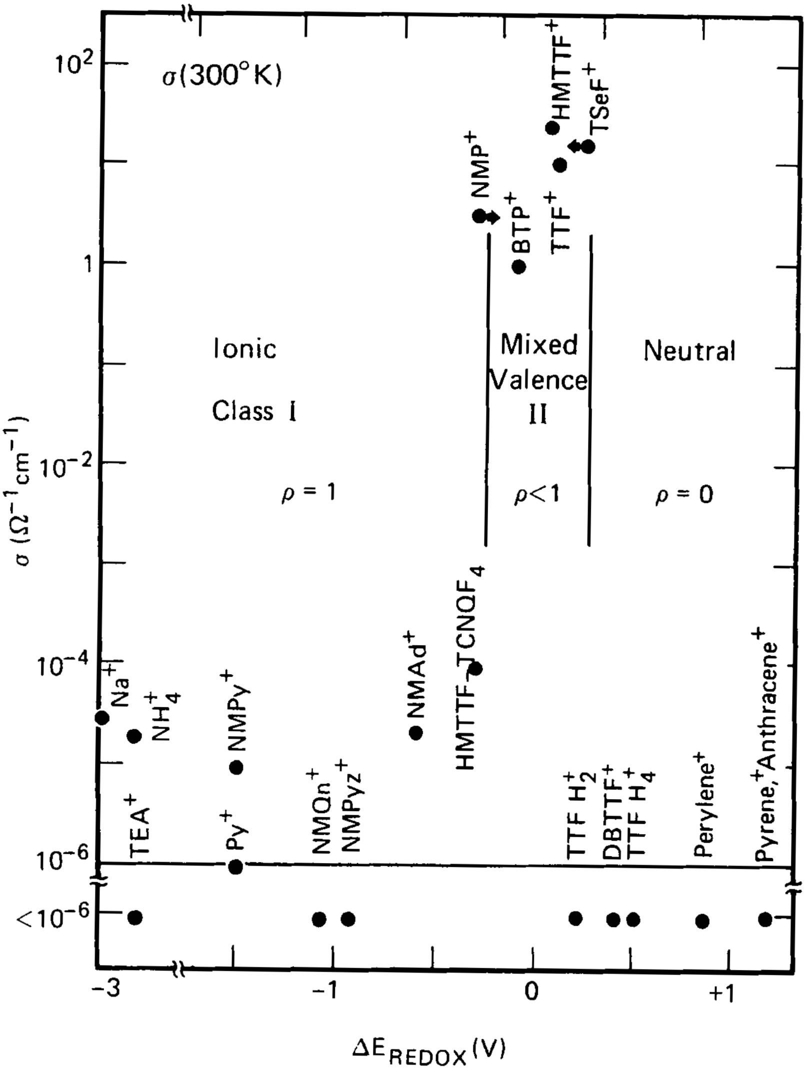

FIGURE 3. A plot of the 300K conductivity of a series of TCNQ compounds *versus* ΔE_{REDOX}, showing how the highly conducting compounds are found to occur over a narrow range of ΔE_{REDOX}.

rather, the stoichiometry is determined undoubtedly by packing considerations of the relevant strucures. In compounds with small inorganic counterions, such as $TMTSF_2ClO_4$, K-TCNQ, Cs_2TCNQ_3, TTF-$Br_{0.79}$, we might hope that the structure would allow a variety of different concentrations of these small counterions and that other factors would determine the observed stoichiometry. In the case of the $TMTSF_2X$ class of compounds (or Bechgaard phases), this is not the case. The zig-zag structure of the TMTSF stacks leaves a series of cages for the counterions - one cage for each two TMTSF molecules - hence the stoichiometry.

Another case is the halide salts of TTF. Here, there are no cages; rather, the structure contains channels without any clear steric requirements for the halide concentration. In fact, the bromide stoichiometry is found to vary over a narrow range (0.75-0.79) and the stoichiometry for the isostructural chloride (0.82) and iodide (0.71) salts are different. What factors determine the stoichiometry in this case? Again, it can be shown[13] that in this case the stoichiometry is determined by the competition between (I-A) and the Madelung energy. (The approximations of using ΔE_{REDOX} and neglecting variation of E_M are not good in this case.) For the bromide salt of TTF, the calculated stoichiometry is very close to the observed value. The closeness of this agreement may be fortuitous, but the quantitative agreement between the observed and calculated changes in stoichiometry between the I^-, Br^- and Cl^- salts (caused by changes in A) is excellent and indicates that the stoichiometry is indeed determined by these factors. Also, the general trend of the bromide salts of TMPD, TTF and naphthalene is also predicted: TMPD-Br (excellent donor, ionic salt), TTF-$Br_{0.79}$ (intermediate donor, mixed valence), and napthalene-Br_0 (poor donor, neutral). These factors work on some cases only, mainly in those compounds which form with channels. While there are a number of such compounds, most of the others cannot yet be understood on this (or any other) basis.

In conclusion, we have attempted to show that, at the simplest level, many of the basic features of organic charge-transfer solids are largely determined by the difference in the redox potentials of the constituent donor and acceptor molecules. This simple description is not the complete or final word. Nevertheless, it represents a simplified and unified view, useful for a first, crude understanding of the general behavior of these materials and provides the basic framework for expanding and building up a more complex and sophisticated understanding.

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