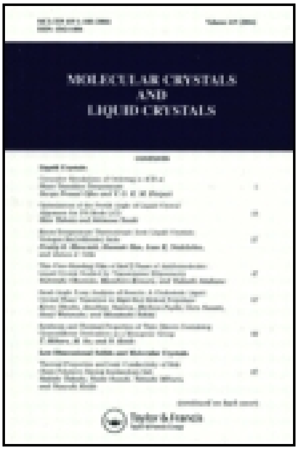

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Organic Superconductors: Present Status and Clue to Future

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Organic Superconductors: Present Status and Clue to Future

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Superconductivity in organic materials has been realized in charge transfer salts. Category of the materials has been expanded from TMTSF cation salts to BEDT-TTF and DMET cation salts and to Ni(dmit)$_2$ anion salts. The organic superconductors are characterized by highly anisotropic nature and low carrier density. The influence of the on-site Coulomb energy has been the subject of arguments and the relations to the copper oxide superconductors are discussed with this respect. The organic superconductors so far are sensitive to disorders even if they are nonmagnetic. Conducting polymers and organic films have been expected to be superconductors with high potential use, but, to substantiate these, defect-free materials are demanded.

1. INTRODUCTION: EVOLUTION OF ORGANIC SUPERCONDUCTORS AND CONDUCTORS

Superconductivity in organic material was first discovered in charge transfer salt (TMTSF)$_2$PF$_6$ with the critical temperature of $T_c = 0.9$ K under pressure in 1979.[1] Since then efforts to develop the organic superconductors have succeeded in bringing about more than 30 kinds of organic superconductors, as shown in Table I, and the T_c has exceeded 10 K. Surprisingly one third of them has emerged in these two years. Category of materials has also expanded as well as number of materials.

The types of the organic superconductors, however, are quite different from that proposed by Little,[2] which is a polymeric material and is designed to give high T_c superconductors. Following Bardeen-Cooper-Schrieffer's theory in metals based on the coherent motion of paired electrons with a phonon-mediated interaction, he proposed an extension of the electron pairing to the electrons moving along an organic polymer with side chains of high electrical polarizability. The proposal associating a possible molecular structure to substantiate the superconductor had stimulated scientists to realize the organic superconductors. Although the proposal has not been embodied even today, it has given great impact to material science.

A stream of the organic superconductor has been also supported by another branch. This goes back to the organic semiconductors, where the macroscopic electron mobility in organic molecules has been one of main subjects. A marked

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TABLE I

List of organic superconductors

Materials	P_c(kbar)	T_c(K)
$(TMTSF)_2PF_6$	6.5	1.2
$(TMTSF)_2AsF_6$	12	0.9
$(TMTSF)_2SbF_6$	11	0.4
$(TMTSF)_2TaF_6$	12	1.4
$(TMTSF)_2ClO_4$	0	1.4
$(TMTSF)_2ReO_4$	12	1.3
$(TMTSF)_2FSO_3$	6	3
$(BEDT\text{-}TTF)_4(ReO_4)_2$	4.5	2
$\beta\text{-}(BEDT\text{-}TTF)_2I_3$#	0	1.4
$\beta\text{-}(BEDT\text{-}TTF)_2I_3$	0.5	7.6
$\gamma\text{-}(BEDT\text{-}TTF)_3I_{2.5}$	0	2.5
$\varepsilon\text{-}(BEDT\text{-}TTF)_2I(I_8)_{0.5}$	0	2.5
$\alpha\text{-}(BEDT\text{-}TTF)_2I_3$: I_2-doped	0	3.3
$\alpha_t\text{-}(BEDT\text{-}TTF)_2I_3$	0	8
$\varepsilon \rightarrow \beta\text{-}(BEDT\text{-}TTF)_2I_3$	0	6
$\theta\text{-}(BEDT\text{-}TTF)_2I_3$	0	3.6
$\kappa\text{-}(BEDT\text{-}TTF)_2I_3$	0	3.6
$\beta\text{-}(BEDT\text{-}TTF)_2IBr_2$	0	2.5
$\beta\text{-}(BEDT\text{-}TTF)_2AuI_2$	0	4.2
$(BEDT\text{-}TTF)_4Hg_{2.89}Cl_8$	0	4.2
$(BEDT\text{-}TTF)_4Hg_{2.89}Br_8$	12	1.8
$(BEDT\text{-}TTF)_3Cl_2(H_2O)_2$	16	2
$(BEDT\text{-}TTF)_2Cu(NCS)_2$	0	10.4
$(DMET)_2Au(CN)_2$	1.5	0.9
$(DMET)_2AuI_2$	5	0.6
$(DMET)_2AuBr_2$	1.5	1.7
$(DMET)_2AuCl_2$	0	0.9
$(DMET)_2I_3$	0	0.6
$(DMET)_2IBr_2$	0	0.7
$TTF[Ni(dmit)_2]_2$	7	1.6
$(CH_3)_4N[Ni(dmit)_2]_2$	7	5

With incommensurate lattice modulation.

increase in conductivity was found in perylene bromine complex by Akamatsu-Inokuchi-Matsunaga[3] and this has led the highly conducting organic materials. The degeneracy of current carriers, which is regarded as a prerequisite to identify as metallic conduction in modern solid state physics, has been confirmed.[4]

The organic conductors have been stages to make interplay between chemistry and physics, in other words cooperation of chemists and physicists is indispensable to carry out research. The molecular orbital theory as well as the interests in low dimensional material have bridged two parties. A door to control function in molecular level has been open to chemistry and that to meet new material with attractive properties has been open to physics.

The recent revolutionary evolution of the high T_c copper oxide superconductors has tempted the fields stimulated further by removing pessimistic clouds coming from misgivings about the high T_c superconductivity in itself.[5] Common physical aspects between the organic materials and the oxides, such as the reduced dimensionality and mechanisms relevant to the evolution of novel concepts, may hopefully feed nourishment with each other.

Here we review briefly the present status of the organic superconductors by placing emphasis on its specific features. Then we will compare the situations between the copper oxides and the organic materials to find a clue to make further development in organic superconductors, hopefully the advancement in T_c. One of the principal points for the high T_c copper oxides, at least at present day, is the large on-site Coulomb interaction. Status of the organic conductors will be discussed concerning with this respect.

2. SUPERCONDUCTIVITY IN ORGANIC CHARGE TRANSFER SALTS

Following the discovery of the organic superconductors in $(TMTSF)_2PF_6$, a series of isomorphous organic superconductors have been realized by replacing PF_6 with AsF_6, ClO_4, FSO_3, etc., as shown in Table I. The crystal consists of combination of stacked TMTSF molecules and counter anions, where columns of TMTSF dominate the electronic properties. As a result the system possesses low dimensional structure, either quasi one-dimensional or two-dimensional depending on the amount of interactions between the columns. The reduced dimensional system has attracted attentions since it yields ordered phases such as charge density waves (CDW), spin density waves (SDW), singlet superconductivity and triplet superconductivity. In TMTSF salts the superconducting ground states are in close contact to either the SDW (for $(TMTSF)_2PF_6$, $(TMTSF)_2ClO_4$ etc.) or the CDW (for $(TMTSF)_2FSO_3$, $(TMTSF)_2ReO_4$ etc.), which have brought about various interesting aspects in the nature of the superconductivity and the mechanism. In particular, an antiferromagnetic interaction among the columns has been considered to be a possible mechanism to mediate electron pairing.[6]

As the second donor molecule constructing the organic superconductors, BEDT-TTF molecule made its debut as a constituting molecule of $(BEDT\text{-}TTF)_4(ReO_4)_2$. In contrast to the TMTSF molecule forming isomorphous crystal structures irrespective to anions, the BEDT-TTF forms various types of compounds: Even for the same composition ratio, different types of the crystal structures are realized.[7] Among them β-$(BEDT\text{-}TTF)_2I_3$ and its analogues exhibit the superconductivity at ambient pressure. Furthermore, by pressure of an order of 1 kbar, T_c is raised as high as 8 K.[8] For composition of $(BEDT\text{-}TTF)_2I_3$, not only the β-type crystal with linear stacking but other ones such as κ-type with cross-checked stacking has been found to show the superconductivity.[9] In particular, κ-type crystal with the counter anion of $Cu(NCS)_2$ possesses T_c as high as 10.4 K.[10]

As mechanisms for TMTSF type superconductors, based on the quasi one-dimensionality, it has been proposed that a fluctuating superconductivity emerges at temperature much higher than T_c where three-dimensional ordering is stabilized.[11] This had arisen from the experiments on the tunneling junction spectroscopy and the infrared reflectance spectra, suggesting a large superconducting parameters gap. The thermal conductivity had exhibited a corresponding anomaly. In the metallic state, the resistivity decreases monotonically dow to 2 K without exhibiting residual resistivity and the magnetoresistance is extraordinary.

Among these experimental facts the tunneling junction data and the anomaly in the thermal conductivity had not been reproduced by later experiments: Later tunneling junction experiment deduced the gap parameter in agreement with the BCS formula.[12] The infrared data had turned out not to be specific to the superconducting material but rather common nature relevant to a specific vibrational mode of the charge transfer salt.[13]

The specific heat has been consistent with the BCS theory[14] and the magnetic field effects to the superconductivity have been described with the second kind superconductivity with pronounced anisotropy.[15]

It has been revealed that the superconductivity is very sensitive to defects even if they are nonmagnetic. By making alloys such as $(TMTSF)_2(ClO_4)_{1-x}(ReO_4)_x$,[16] $(TMTSF)_{2-x}(TMTTF)_xClO_4$, β-$(BEDT\text{-}TTF)_2(I_3)_{1-x}(IBr_2)_x$ etc.,[17] the superconductivity is suppressed with low content of x, e.g. less than 10%. For $(BEDT\text{-}TTF)_2A_{1-x}B_x$, where A, B = I_3, I_2Br, IBr_2, the alloying modulates the system either by giving the variation of the intermolecular interactions or by introducing the random potentials. Figure 1 shows the composition dependence of T_c and residual resistivity.[17]

It is confirmed that the lattice spacing changes continuously with alloy composition x, indicating that the intermolecular interaction and hence the electronic structure changes continuously. This suggests that the T_c which is a representative parameter of the superconductivity changes with x connecting the situations for I_3 salt and IBr_2 one. The experimental data, however, differ drastically from this expectation by exhibiting the suppression of T_c with increase of $x \geqq 0.1$ for $(BEDT\text{-}TTF)_2(I_3)_{1-x}(IBr_2)_x$, as shown in Figure 1.

Corresponding to the T_c versus x relation it turns out that the residual conductance σ_R observed just above T_c or at low temperature, plotted in the upper part of the figure, shows a good coincidence with the variation of T_c. This situation is true also for the cases with other anion combinations. Since the carrier concentrations in these materials are considered to be kept constant against temperature change, the decrease in the conductivity is directly correlated with the reduction of the collision time of the carriers due to the random potentials induced by the anion mixing. In fact the residual resistance dependences of T_c are in good agreement with the calculation carried out by Hasegawa-Fukuyama for the effect of weak localization by nonmagnetic impurities to T_c.[18]

The sensitivity of the superconductivity to nonmagnetic defects has been manifested for alloys of TMTSF salts also. For example, in the case of $(TMTSF)_2(ClO_4)_{1-x}(ReO_4)_x$, the superconductivity has disappeared for $x \geqq 0.05$, indicating that nonmagnetic defects give important influence.[16] The sensitivity is extraordinary in a sense that usual superconductors so far, caused by the singlet pairing, are rather insensitive to the nonmagnetic defects. For this reason it had been speculated that the superconductivity in the organic charge transfer salt might be of triplet type. This speculation, however, has got no other support and instead it contradicts with the upper critical field H_{c2}, which is limited by the value of H_{c2} (Tesla) = 1.82 T_c (K), suggesting that the singlet is more plausible.[19] In fact in TMTSF salts

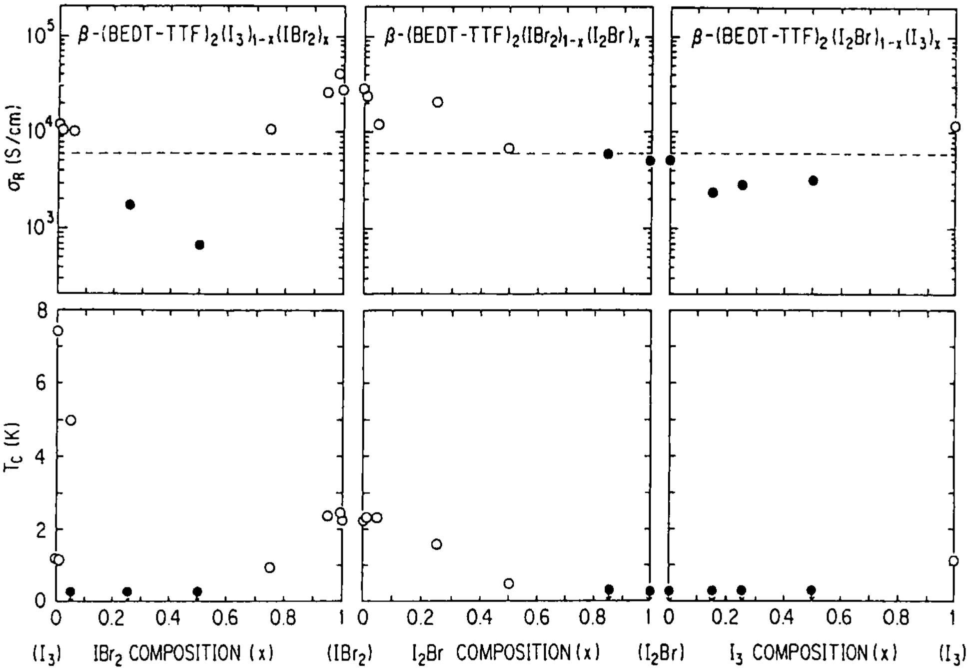

FIGURE 1 Alloy composition dependence of T_c and the residual conductance at low temperatures σ_R. Open and closed circles are for the superconducting and not-superconducting, respectively. The measurements for β(BEDT-TTF)$_2$(I$_3$)$_{1-x}$(IBr$_2$)$_x$ with $x \leq 0.26$ were carried out under pressure. (Ref. 17)

also the effect of the nonmagnetic defects has been interpreted in terms of the electron localization in low dimensional system.[18] The effect of the localization to the superconductivity is thus specific to the low dimensional organic superconductors. In other words, the effect of the imperfections to the superconductivity is serious for organic conductors possessing the low dimensional structure.

Concerning the microscopic structure of the superconductors, it should be remarked that (TMTSF)$_2$ClO$_4$ is of the order parameter having lines of zero on the Fermi surface, reminiscent of the heavy electron superconductors with the *f* electrons.[20] This has been deduced from the temperature dependence of the proton spin resonance relaxation time T_1 just below T_c, which does not exhibit the enhancement of $1/T_1$ below T_c in contrast to the BCS superconductors.

Recently two new kinds of charge transfer salts, DMET cation salts and Ni(dmit)$_2$ anion salts have been included as organic superconductors. An unsymmetrical molecule DMET, which is shown in Figure 2, is formed by jointing halved TMTSF and BEDT-TTF molecules. The DMET radical salts have variety of crystal types as found in BEDT-TTF salts and six kinds of salts have been found to be superconducting as shown in Table I. These crystals have quasi one-dimensional stacking of DMET molecules whose long axes are alternatively reversed, in other words, TMTSF part and BEDT-TTF part face with each other within a stack, and hence the resultant crystal is of centrosymmetry. In this case also salts with I$_2$Br as counter anion did not show superconductivity, though those with IBr$_2$ did as in BEDT-

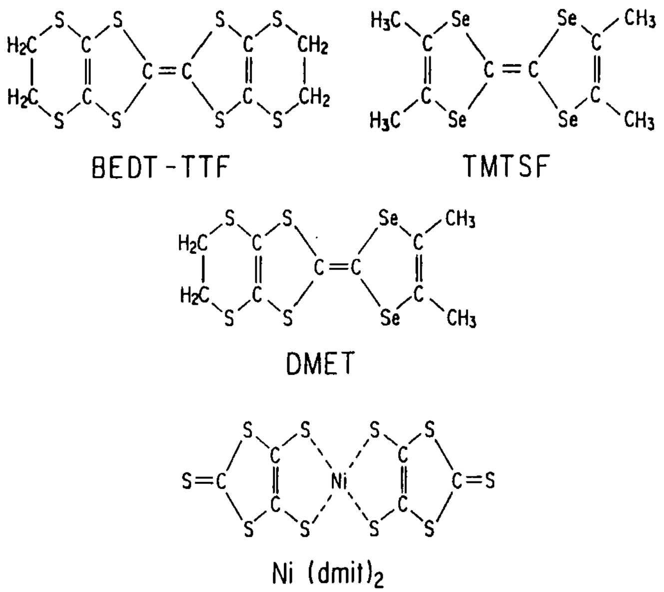

FIGURE 2 Chemical formulae of molecules constituting organic superconductors.

TTF salts.[22] The superconductivity in salts with $Au(CN)_2$, AuI_2 and $AuCl_2$ is reminiscent of the TMTSF salt, in which the competition with the SDW ordering is controlled by anion size and pressure.

The $Ni(dmit)_2$ salt is specific in view of the composition of multi-sulfur π acceptor molecule (Figure 2). The first superconductor with $Ni(dmit)_2$ was $TTF[Ni(dmit)_2]$.[23] However, the role of the anion was not clear and the three-dimensional network structure spanned by the combination of donor and acceptor molecules was claimed as essential. For $(CH_3)_4N[Ni(dmit)_2]$ it is shown that $Ni(dmit)_2$ stacks construct the conducting path and two plane-like Fermi surfaces. The T_c as high as 5 K is observed under 7 kbar.[24] It is noted that the pressure dependence of T_c is positive in contrast to the cases of TMTSF and BEDT-TTF salts.[25] This opens a new subject on the relation between the superconductivity and the intermolecular distance.

3. COMPARISON WITH HIGH T_c OXIDE SUPERCONDUCTORS

The copper oxide with high T_c superconductivity has exhibited similarity with the organic superconductors in some phenomenological points of view. First these materials are of reduced dimensionality: The copper oxide superconductors are of two-dimensional nature and the dimensionality has been ascribed to networks of CuO_2. In the meantime the organic charge transfer salts undergoing the superconducting transition has quasi one-dimensional ($(TMTSF)_2X$) or two-dimensional ($(BEDT\text{-}TTF)_2X$) electronic structure, which is due to the crystal structure made of columns of stacked planar molecules. For polymeric materials which are expected to yield the superconductivity is of quasi one-dimensional nature.

The role of importance of the reduced dimensionality to the superconductivity has not been clarified yet. One can say, however, common aspects concerning the reduced dimensionality lay a bridge across the two types of materials, by offering countermeasures. Presumably we are permitted to say that the physics and chemistry relevant to the reduced dimensionality established through the study of the organic systems served as a basis for that of the high T_c superconductors.

The second is that the concentration of the carriers are lower by an order of magnitude compared to ordinary superconducting metals.[26] This is in part ascribed to the largeness in the unit cell giving one electron. In Table II we listed the calculated electron concentrations together with other representative parameters. According to the BCS formalism the high density of states is preferable to cause the high T_c transition. Form this viewpoint, the low electron concentration reflecting the low density of states at the Fermi surface seems to be inadequate for the high T_c in conventional superconductors, suggesting that a new mechanism dominates for the superconductivity in these material. For (BEDT-TTF)$_2$I$_3$ exhibiting T_c of 8 K, the estimated Debye temperature is as low as ca. 50 K: Taking account of these situations Yamaji considered pairing mechanism mediated by intramolecular vibration.[27]

The proximity to insulating states formed by some ordered phase is the third similarity. In TMTSF salts the superconductivity is in close contact with the SDW state in pressure phase diagram.[1] For BEDT-TTF salts, subtle modification in crystal structure separates the superconductivity from the insulating. The situation for $La_{2-x}Sr_xCuO_4$ is similar: The insulating La_2CuO_4 changes to be superconducting with $0 < x < 0.2$ giving highest T_c at $x = 0.15$. Further $YBa_2Cu_3O_{7-y}$ changes from the superconducting to insulating near $y = 0.6$ as increasing y.

The most specific feature of the copper oxide, which is notified at present, is the strong Coulomb repulsions. Photoelectron spectroscopy of $YBa_2Cu_3O_{6.8}$ has reduced the Coulomb energy between 3d-electrons U_{dd} reaches as high as ca. 5.eV.[28] For the organic charge transfer salts the magnitude of the on-site Coulomb

TABLE II

Comparison of parameters of organic and copper oxide superconductors.

	(TMTSF)$_2$ClO$_4$	β-(BEDT-TTF)$_2$I$_3$	$La_{1.85}B_{0.15}CuO_4$	$YBa_2Cu_3O_7$
T_c(K)	1.4	8	40	95
n(cm^{-3})	1.3×10^{21}	1.2×10^{21}	2.1×10^{21}	2×10^{21}
U(eV)	0.5(<2)	0.5(<2)	~5	~5
W(eV)	1	1	9*	7.5*
ξ_0 (Å)	900 ‖a	350 ‖	~10	16 ‖
	600 ‖b	23 ⊥		2 ⊥
	20 ‖c			
$2\Delta/k_BT_c$	~4	~15 ‖	4-8	4-8
		~ 4 ⊥		

* Cu(3d)-O(2p) band

repulsion has been argued. Through the analysis of spin susceptibility, the on-site Coulomb energy in these systems has been estimated to be ~1 eV (at most 2 eV).[29] The emergence of SDW ordering is supporting the dominance of the Coulomb interaction.

Based on the large on-site Coulomb energy the mechanisms of the high T_c in the copper oxide have been argued. The mainstream of the current study supports the remarkable dominance of U and on this basis the resonating valence bond (RVB) models and the Hubbard models have been insisted on as keys to understand the superconductivity. In these cases the systems are of insulating behavior without excess holes which are introduced either by alloying ($La_{1.85}Ba_{0.15}CuO_4$) or by oxidation ($YBa_2Cu_3O_{7-y}$).

Search for new organic superconductors has brought about vast numbers of the organic salts. Among them we have found semiconducting salts such as α'-(BEDT-TTF)$_2$IBr$_2$, α'-(BEDT-TTF)$_2$IBrCl, β'-(BEDT-TTF)$_2$ICl$_2$, with the magnetic susceptibility as high as -5×10^{-4} emu/mole which is kept in the order of this value down to a certain structural transition temperature.[30] By taking account of the charge transfer ratio of 0.5/BEDT-TTF and the calculated band structure by the extended Huckel method, we can imagine that these may be the Mott-Hubbard type insulators characterized by the strong Coulomb repulsion among the electrons satisfying the half-filling condition. Then, it is interesting to undertake to introduce excess holes or electrons to these insulators by doping or alloying with anions of different valence, in order to simulate one of the typical aspects of the high T_c copper oxide.

Note that the above mentioned does not necessarily mean that the superconductivity mechanisms are similar between the oxides and the organic charge transfer salts. The values of U are much higher for the copper oxides, while the band properties take still dominant roles for the present organic superconductors. In fact the phenomenological properties are different as represented by the values of the coherence length ξ_0: For the organic charge transfer salts ξ_0 reaches 30–100 times of the lattice parameter but for the oxides ξ_0 is of the order of the lattice parameter or less. However we should point out that the organic materials may form an useful prototype based on the similarity in the background and by making the best use of the chemical and molecular modifications. This may be helpful to specify the mechanism for the high T_c superconductivity and to find new interesting materials and phenomena in organic superconductors. In a sense, (BEDT-TTF)$_2$A$_{1-x}$B$_x$ system is an appropriate system to study the effect of doping, since by alloying conducting paths formed by BEDT-TTF are unchanged, in a first approximation, but only the counter anions giving carriers are modified. However, as mentioned in previous section the sensitivity to defects may be a crucial barrier to the realization of the superconductivity.

4. POLYMERS AND MOLECULAR FILMS

The organic superconductor was proposed first in polymeric materials, which has potentiality in designing with a wide variety of desired properties. Although the first proposed polymer possessed shortages such as the reduction in coupling due to the spacing between the relevant electrons and acting dipoles, this has been revised in some ways.[31] A possibility of superconductivity in polyacene $[(C_4H_2)n]$ has been pointed out, which may show an accidental degeneracy between the valence and conduction bands and thereby divergence of the density of states at the Fermi surface.[32]

More recently another possibility of superconductors by mixture of the strong repulsive electron-electron interactions and a weak retarded attractive interaction are discussed for a one-dimensional electron gas with an analogy to the short-ranged RVB picture of superconductivity. Polymers can be a basis for this mechanism and even the polyacetylenes may satisfy the requirement for the superconductivity in principle.[33] In reality, however, disorders in the material suppress its emergence. For this reason the preparation of the well-ordered or defect-free polymers should be a target for a current investigation for superconductivity in organic polymers.

Following the polymeric model of the superconductor with excitonic interaction, a sandwich structure combining thin metallic layer and semiconductor was proposed by Ginzburg.[34] The shortage of the one-dimensional system having a dislike to the long range order will be improved by adopting the two-dimensional system. Combining monomolecular layer with metallic conduction and that with high polarizability the sandwich type layered superconductor model will be constructed. In fact high electrical conductivity has been realized $(TMTTF)_3(C_{14}TCNQ)_2$ Langmuir Blodgett (LB) films.[35] At present, however, one meets two problems with LB film system: The range of molecular arrangement within a layer is not long enough and this will be serious for the defect-sensitive superconductors. Secondly, the distance between the conducting and the polarizing molecule should be short to insure strong coupling. The developments in preparation and control of monomolecular films are desirable.

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Note added in proof: After submitting this paper in June 1988, following two new organic superconductors were discovered:

(MDT-TTF)$_2$AuI$_2$ with $T_c = 3.5$ K (G. C. Papavassiliou et al., *Synth. Metals* **27** B379 (1988)) and TTF[Pd(dmit)$_2$]$_2$ with $T_c = 6.5$ K at $P_c = 19$ kbar (L. Brossard et al., *Synth. Metals* **27**, B157 (1988)).