

Frontiers of Organic Conductors and Superconductors

Gunzi Saito and Yukihiro Yoshida

Abstract We review the development of conductive organic molecular assemblies including organic metals, superconductors, single component conductors, conductive films, conductors with a switching function, and new spin state (quantum spin liquid state). We emphasize the importance of the ionicity phase diagram for a variety of charge transfer systems to provide a strategy for the development of functional organic solids (Mott insulator, semiconductor, superconductor, metal, complex isomer, neutral-ionic system, alignment of chemical potentials, etc.). For organic (super) conductors, the electronic dimensionality of the solids is a key parameter and can be designed based on the self-aggregation ability of a molecule. We present characteristic structural and physical properties of organic superconductors.

Keywords Charge transfer solid · Electronic dimensionality · Functional organic solid · Ionicity diagram · Organic metal · Organic superconductor · Phase transition · Quantum spin liquid state · Switching

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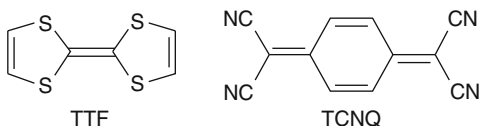
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1 Introduction

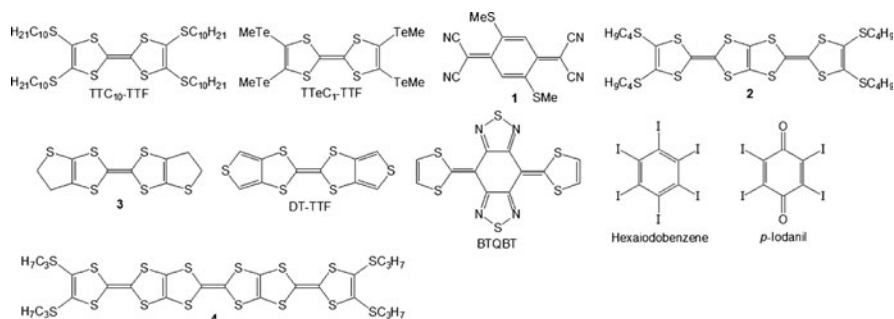
In this review we introduce the present status of conducting organic assemblies including single component conductors, organic metals and superconductors of the charge transfer type, exotic conductors having switching function, and new spin state (quantum spin liquid state) that neighbors a superconducting phase, with a focus on our achievements. We also briefly describe metallic and superconducting polymers. Ionic conduction, including proton conduction, is one of the essential transport phenomena in organic materials and has already been extensively reviewed [1] and therefore will not be discussed further in the present review.

2 Single Component Conductors

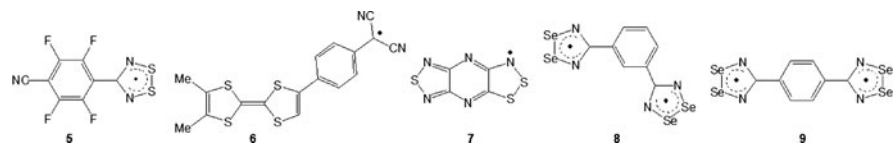
Since the discovery of the first metallic charge transfer (CT) solid, TTF·TCNQ (Scheme 1) by Ferraris, Cowan, et al. in 1973 [2], much attention has been devoted to organic (super)conductors by studies of several component CT solids based on TTF and TCNQ derivatives [3–18]. Besides numerous studies on multicomponent CT solids, several single-component organic conductors have been demonstrated based on (1) closed shell organic solids under high pressure [19–23] and those having peripheral chalcogen atoms [24, 25] or long alkyl chain (fastener effect) [26–29] functionalized TTF derivatives (Scheme 2), (2) organic neutral π -radicals (Scheme 3) [30–37], (3) betainic (zwitterionic) radicals of TCNQ [38–40] and TTF derivatives [41–45] (Scheme 4), and (4) transition metal complexes of phthalocyanine (Pc) [46, 47] and TTF-dithiolate [48, 49] ligands (Scheme 5). Among them, metallic behavior has been reported on three kinds of materials: closed shell organic solids under extremely high pressure [19–23], transition metal complexes of



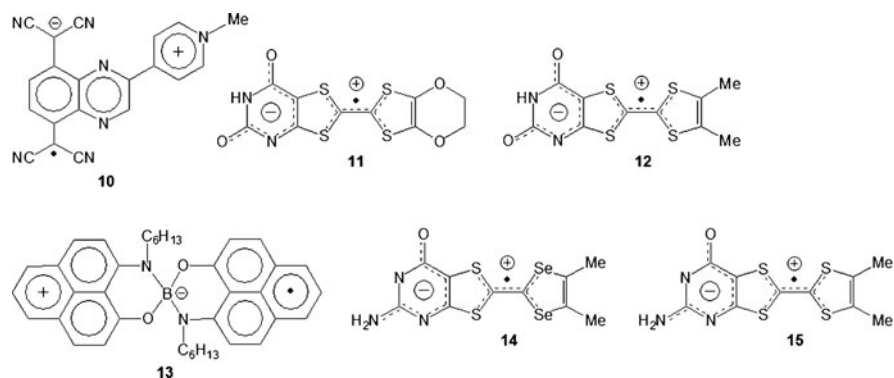
Scheme 1 Chemical structures of TTF and TCNQ



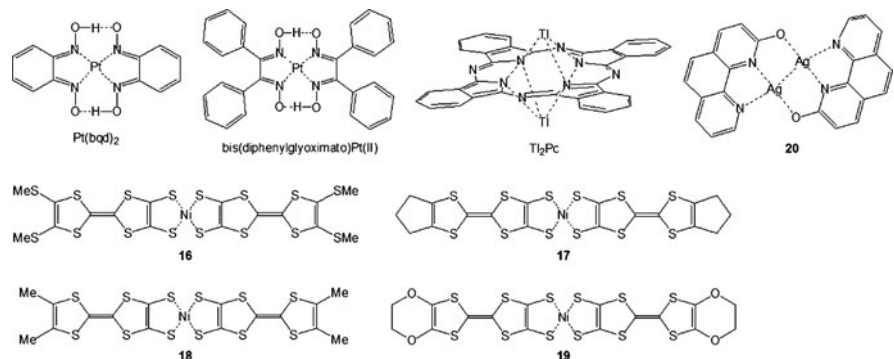
Scheme 2 Chemical structures of closed shell molecules of organic conductors



Scheme 3 Chemical structures of neutral π -radical and biradical molecules of organic conductors



Scheme 4 Chemical structures of betainic π -radical molecules of organic conductors



Scheme 5 Chemical structures of transition metal complexes of organic conductors

phthalocyanines [46], and transition metal complexes of TTF-dithiolate ligands [48, 49]. Superconductivity was observed in closed shell organic solids under high pressure [20, 21, 23].

2.1 Closed Shell Neutral Solids

Even though pentacene is known to be the first organic metal (semimetal) showing a decrease of resistivity down to ca. 200 K at 21.3 GPa [19], no superconductivity has been reported so far for solids composed only of aromatic hydrocarbons. Though Schön et al. reported superconductivity on polyacenes (anthracene, tetracene, and pentacene) in field effect transistor (FET) devices at low temperatures ($T_c < 4$ K), the paper was retracted [50]. Electric conductivity increases by the enhancement of intermolecular interactions by appropriate use of hetero-atomic contacts [24, 25, 51–56] to exert an atomic-wire effect and by peripheral addition of alkyl or alkylchalcogen groups [26–29, 53, 56, 57] to exert a fastener effect. The atomic-wire effect [51, 56] or fastener effect [26] afforded conduction paths in the solids, giving rise to high-mobility materials [24, 25, 29, 51, 55–59]. Table 1 summarizes selected conductors of closed shell molecules. However, so far at ambient pressure, the conductivity has only reached $\sim 10^{-3}$ S cm $^{-1}$ (bis(thiadiazolo)quino-TTF (BTQBT) and **4**). There are two single-component superconductors under extremely high pressure, *p*-iodanil ($\sigma_{RT} = 1 \times 10^{-12}$ S cm $^{-1}$

Table 1 Selected organic conductors of closed shell molecules

Molecule	$\sigma_{RT}/\text{S cm}^{-1}$ at ambient pressure (AP) ^a	Characteristics ^b	Reference
TTC ₁₀ -TTF	2.7×10^{-6}	Fastener effect, $\mu = 9\text{--}20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (time of flight)	[28, 29]
TTeC ₁ -TTE	1.4×10^{-5}	Hetero-atomic contacts, $\mu = 19\text{--}29 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (time of flight)	[51]
1	2×10^{-5}	Hetero-atomic contacts, $\mu = 6 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	[52]
2	1.7×10^{-4}	Fastener effect	[53]
3	2.7×10^{-4}	Hetero-atomic contacts	[54]
DT-TTF	6×10^{-4}	Hetero-atomic contacts, $\mu = 1.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (FET)	[55]
BTQBT	1×10^{-3}	Hetero-atomic contacts, $\mu = 0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (FET)	[24, 25]
4	2.5×10^{-3}	Fastener effect	[57]
<i>p</i> -Iodanil	1×10^{-12} at AP $\rightarrow 2 \times 10$ at 25 GPa, $T_c = \text{ca. } 2 \text{ K}$ at 52 GPa	Hetero-atomic contacts	[20]
Hexaiodobenzene	$T_c = 0.6 - 0.7 \text{ K}$ at ca. 33 GPa, $T_c = \text{ca. } 2.3 \text{ K}$ at 58 GPa	Hetero-atomic contacts	[21]

^a σ_{RT} electric conductivity at room temperature (RT)

^b μ mobility

Table 2 Selected organic conductors of neutral π -radical molecules

Molecule	$\sigma_{\text{RT}}/\text{S cm}^{-1}$ at AP	Characteristics	Reference
5	No data, Mott insulator	Push–pull effect, weak ferromagnet ($T_{\text{c}} = 35.5$ K at AP, $T_{\text{c}} = 64.5$ K at 1.6 GPa)	[60–62]
6	5.7×10^{-6}	Push–pull effect	[63]
7	10^{-4}	Dimer	[30]
8	2×10^{-4}	Extension of π -system, α -form: zigzag chain, β -form: dimer	[64, 65]
9	$<10^{-2}$ (polymerized)	Extension of π -system, dimer	[66]

at ambient pressure, $\sigma_{\text{RT}} = 2 \times 10 \text{ S cm}^{-1}$ at 25 GPa, and superconductivity at $T_{\text{c}} = \text{ca. } 2 \text{ K}$ at 52 GPa), and hexaiodobenzene ($T_{\text{c}} = 0.6\text{--}0.7 \text{ K}$ at around 33 GPa and $\text{ca. } 2.3 \text{ K}$ at 58 GPa). Both have peripheral chalcogen atoms, iodine, which may increase the electronic dimensionality of the solid under pressure.

2.2 Neutral π -Radical Solids

When the effective on-site Coulomb repulsive energy (U_{eff}) of the solid composed of π -radical molecules is smaller than the bandwidth (W), then the solid becomes a half-filled metal provided that the molecules stack uniformly without dimerization and can be described by a band picture. So far, no such radical molecules have been prepared. In order to decrease U_{eff} and stabilize radical molecules chemically, a push–pull effect and an extension of the π -system have been implemented, though a large U_{eff} and high reactivity (polymerization) are still crucial for the metallic transport. Table 2 summarizes selected organic conductors of neutral π -radical molecules.

2.3 Zwitterionic (Betainic) π -Radical Solids

A betainic structure is very effective in decreasing U_{eff} according to the LeBlanc's proposal for the TCNQ anion radical salt (eq. 1), where α is the molecular polarizability of the cation and r is the distance between TCNQ anion radical and a cation [67]:

$$U_{\text{eff}} = (1 - \alpha/r^3)U. \quad (1)$$

For a single component betaine, the cation moiety is connected or fused with the anion moiety by chemical bond and this fusion is more appropriate to decrease r . Pyrimido fused TTF betaines (**11**, **12**, **14**, and **15** in Scheme 4, $r = 4 - 5 \text{ \AA}$) are such examples compared with the single-bonded betaine (**10**, $r > 10 \text{ \AA}$). Table 3 summarizes selected organic conductors of betainic π -radical molecules. Very high σ_{RT} values for **12**, **14**, and **15** even on compacted pellet sample have been ascribed to strong intermolecular interactions through complementary hydrogen bonds (see Sect. 3.4.3). A phenalenyl-based betainic radical **13** shares one radical electron

Table 3 Selected organic conductors of betainic π -radical molecules

Molecule	$\sigma_{RT}/S\text{ cm}^{-1}$ at AP	Characteristics	Reference
10^a	3.2×10^{-5}	Connected by single bond	[38]
11^a	5×10^{-4}	Fused	[42, 44, 45]
12^a	1.2×10^{-3}	Fused	[41, 43]
13^b	5×10^{-2}	Fused, sharing one electron by two phenalenyl groups	[31, 34]
14^a	5×10^{-2}	Fused	[44, 45]
15^a	1.4×10^{-1}	Fused	[44, 45]

^aMeasured on compacted pellet^bMeasured on single crystal

between two phenalenyl groups leading to +0.5 charge on each phenalenyl group that may give rise to high mobility for the radical electron even for a large- U system. This resembles the concept of mixed valence or partial charge.

2.4 Transition Metal Complex Solids

Some transition metal complexes are excellent conductors. Thin films of cytochrome- c_3 , which contains four heme moieties coordinated by protein, exhibited a high conductivity with mixed valence state ($\text{Fe}^{2+}/\text{Fe}^{3+}$) and showed an increase in conductivity as the temperature was decreased ($2 \times 10^{-2}\text{ S cm}^{-1}$ at 268 K) [68–70]. The temperature dependence of conductivity in the highly conductive region is the opposite of that of semiconductors and may preclude the ionic conduction as a dominant contribution. However, since the high conductivity is realized in the presence of hydrogenase and hydrogen, the system is not strictly a single but rather a multicomponent molecular solid.

Although numerous reports on highly conductive single component transition metal compounds have appeared since 2000 (Table 4), the characterization of some compounds is insufficient to claim being a metallic single molecular solid because of issues of purity, measurement conditions, experimental information, etc. Many transition metal complexes of phthalocyanines or TTF-dithiolate ligands (Scheme 5) were insoluble in conventional solvents that rendered purification very difficult and the residual impurity might act as dopant to form a CT solid. Note that most authors stated that their material is the first single-component metal or good conductor without mentioning preceding studies on pentacene, *p*-iodanil, and [bis(benzoquinone dioximato)Pt(II): Pt(bqd)₂] under pressure or Tl₂Pc at ambient pressure done before 2000.

Metallic behavior down to low temperatures was reported on a compacted pellet of Tl₂Pc [46] with very high conductivity of $\sigma_{RT} \sim 10^4\text{ S cm}^{-1}$ (four-probe method using indium lead wires). A specific three-dimensional crystal architecture of Tl₂Pc is anticipated to form a three-dimensional semimetallic band. However, the

Table 4 Selected transition metal complex solids claimed to be metal composed of single component

Molecule	$\sigma_{RT}/S\text{ cm}^{-1}$ at AP	Characteristics	Reference	Year
Pt(bqd) ₂	3.3×10^{-3} at AP [71], insulator–metal–semiconductor under 1.7 GPa		[72, 73]	1989
Tl ₂ Pc	$>10^4$, metal >5 K	Poor reproducibility	[46]	1994
16	10^{-1} , metal (300–275 K)	Analytically pure	[74]	1996
17	4×10^2 , metal >0.6 K	dHvA oscillations	[48, 75]	2001
18	$3 - 4 \times 10^2$, metal >230 K		[76]	2001
19	8, metal >120 K	Dysonian EPR signal, no elemental analysis data	[77]	2003
20	14, metal	Measured by two-probe method, no SQUID signal	[78]	2003

reproducibility of the transport properties and even of the synthesis of the molecule is poor [79].

High conductivity for transition metal complexes of TTF-dithiolate ligands have long been known, due to the mixing of π - d orbitals resulting in a small HOMO–LUMO gap [80]. At present, **17** is the most reliable metal in this category ($\sigma_{RT} = 4 \times 10^2\text{ S cm}^{-1}$, metallic down to 0.6 K) based on its purity, temperature dependencies of resistivity and magnetic susceptibility, and de Haas-van Alphen (dHvA) oscillations [48, 75].

Compound **20** was reported to be the first highly conductive (14 S cm^{-1} on compaction pellet sample) single-component molecular metal different from the dithiolate-type; however, the conductivity was measured by a two-probe method and no SQUID response was observed for $200\text{ K} > T > 5\text{ K}$ [78].

A metal complex Pt(bqd)₂ exhibited an insulator–metal–semiconductor transition under pressure [72, 73]. A continuous color change was observed in bis (diphenylglyoximate)Pt(II), Scheme 5 [81] under pressure and thus has been used as a pressure indicator. For these cases it is not clear that π - d orbital mixing is critical for the transport.

3 Organic Metals of Charge Transfer Type

3.1 Basic Concept for Organic Conductors

A metallic band structure is realized when the CT solids have a partial CT state and molecules form uniform segregated columns or layers. Figure 1 shows electrical conductivity data for 1:1 low-dimensional TTF·TCNQ system, as a function of redox potentials [82]. The two lines **a** and **b** are related to the equation expressing the relationship between I_D , E_A , and the Madelung energy $M(\delta)$ (δ = degree of CT) between partially charged component molecules (eq. 2) [83], where I_D and E_A are

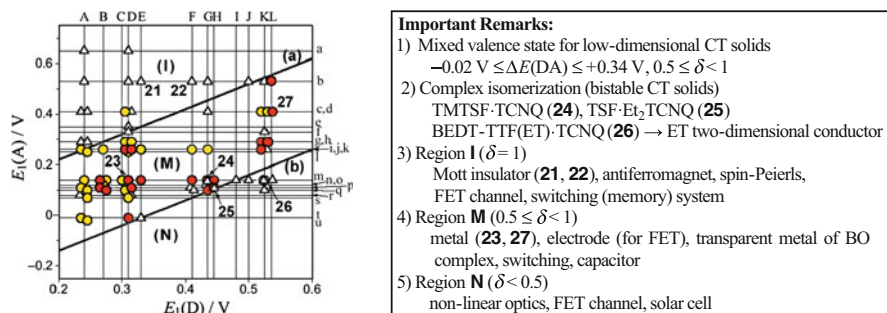
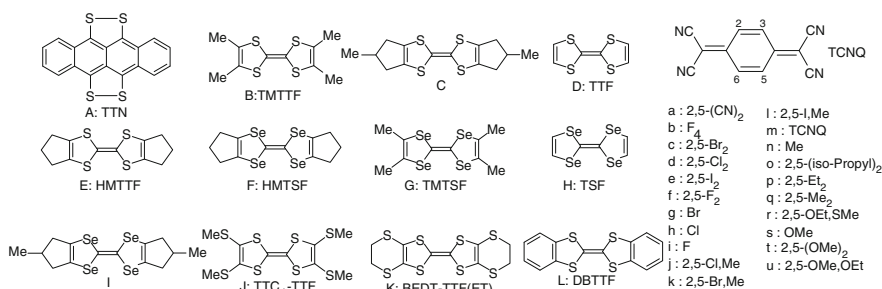


Fig. 1 Ionicity diagram for TTF-TCNQ system plotted as $E_1(\text{A})$ vs $E_1(\text{D})$ vs SCE after modification of the original diagram in [82]. *Open triangles* insulators or semiconductors; *yellow circles* highly conducting in compaction studies; *red circles* organic metals. Donors and acceptors are depicted in Scheme 6. Complexes **21–27** are HMTTF- F_4TCNQ , HMTSF- F_4TCNQ , TTF-TCNQ, TMTSF-TCNQ, TSF-Et₂TCNQ, ET-TCNQ, and DBTTF- Cl_2TCNQ , respectively. $E_1(\text{A})$ and $E_1(\text{D})$ in this figure are the peak values. Region N: neutral, M: partial CT, I: fully ionic. Line a: $\Delta E(\text{DA}) = -0.02 \text{ V}$, b: $\Delta E(\text{DA}) = 0.34 \text{ V}$



Scheme 6 Chemical structures of electron donor and acceptor molecules in Fig. 1

the ionization potential of an electron donor (D) and electron affinity of an electron acceptor (A), respectively (Scheme 6). The mixed valence region (M) is located between fully ionic (I) and neutral (N) regions. In the region M, the CT solids are either highly conductive (yellow circles) or metallic (red circles) when they have segregated stacks. The solids in the regions I and N are insulators (triangles), in general.

$$I_D - E_A = M(\delta). \quad (2)$$

So the partial CT state can be predicted and controlled by $(I_D - E_A)$ or $\Delta E(\text{DA})$ [$\Delta E(\text{DA}) = E_1(\text{D}) - E_1(\text{A})$; E_1 , first redox potential; $-0.02 \text{ V} \leq \Delta E(\text{DA}) \leq +0.34 \text{ V}$ for TTF-TCNQ system] for a combination of specific D and A, and the complex D·A exhibits a low lying CT band below $5 \times 10^3 \text{ cm}^{-1}$.

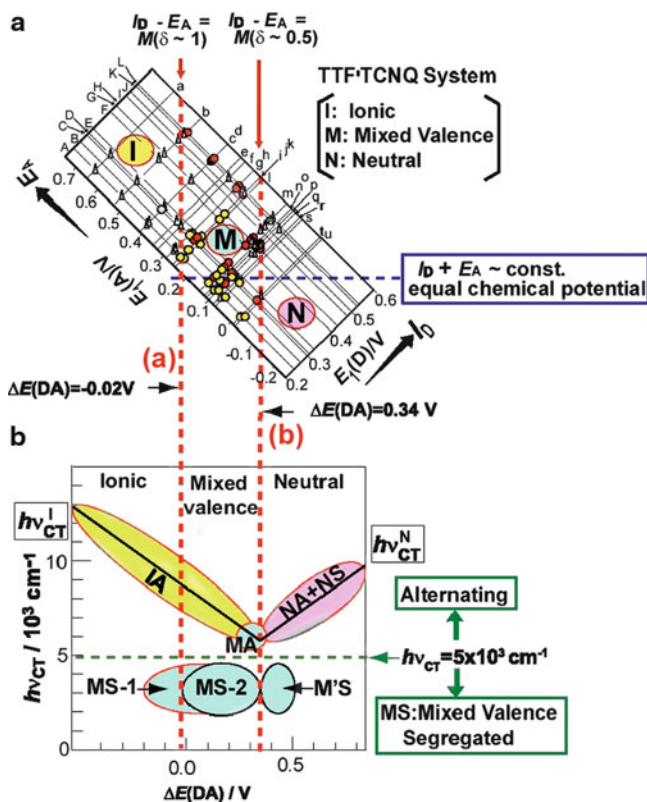
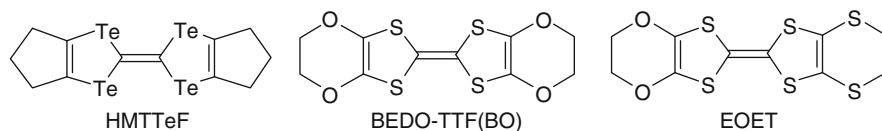


Fig. 2 (a) The same figure as Fig. 1 except for the scale of $E_1(\text{D or A})$. Organic metals on the blue dotted line have the same chemical potential ($I_D + E_A = \text{constant}$). (b) Schematic phase diagram of ionicity, conductivity and stacking of DA CT solids. The first optical transition energy in solid ($h\nu_{\text{CT}}$) is plotted against the $\Delta E(\text{DA})$ value. Left- and right-hand sides of the V-shaped line correspond to $h\nu_{\text{CT}}^{\text{I}} = I_D - E_A - C$ (eq. 3) and $h\nu_{\text{CT}}^{\text{N}} = -I_D + E_A + (2\alpha - 1)C$ (eq. 4) respectively, where C and αC are the Coulomb attractive energy between D^{++} and A^{*-} and the Madelung energy, respectively. IA ionic alternating, MA mixed valence alternating, NA neutral alternating, NS neutral segregated, MS mixed valence segregated (MS-1: non 1:1 (minor component is fully ionic), MS-2: 1:1 low-dimensional, M'S: 1:1 high-dimensional). An appropriate V-shaped line for the *p*-quinone system was obtained by a parallel shift of the V-shaped line for the TCNQ system towards the lower side by 0.13–0.16 V

Figure 2 shows the relationship between Fig. 1 and another kind of ionicity phase diagram (V shaped line in Fig. 2b) proposed by Torrance for the neutral-ionic (N–I) phase transition for the alternating stacks [84]. Figure 2a was made by rotating Fig. 1 ($E_1(\text{D})$ and $E_1(\text{A})$ have the same scale here) so as to make the two borderlines **a** and **b** vertical. Then all CT solids that lie on a horizontal line in Fig. 2a have the same chemical potential ($I_D + E_A = \text{constant}$). The organic metals in the region **M** residing on several different horizontal lines in Fig. 2a were employed as the source and drain electrodes to control the Fermi level alignment



Scheme 7 Chemical structures of HMTTeF, BEDO-TTF(BO) and EOET

between electrodes and channel for FET, making the injection of carriers smooth and giving varied polarity in FET behavior (see Sect. 3.4.1) [85].

In the neutral region near the bottom of the V-shaped line (region **MA**), an enantiotropic phase transition system (N–I transition) is located [84]. The CT solids that have $h\nu_{\text{CT}}$ bands below $5 \times 10^3 \text{ cm}^{-1}$ (horizontal green dotted line) belong to a different class (region **MS**) that usually includes (super)conductors and narrow-gap semiconductors having mixed valence segregated stacks or layers. The important point here is that **M'S** is for high-dimensional 1:1 CT solids, which usually extend their metallic regime toward lower δ values (higher $\Delta E(\text{DA})$ values), like the HMTTeF [86] and BEDO-TTF (BO) [87] systems (Scheme 7), owing to their strong self-aggregation ability (see Sect. 3.3). Even with $\delta = 1/3$, some BO complexes have segregated stacks and show metallic behavior. Figures 1 and 2 illustrate a prediction on the modes of molecular stacking: alternating and segregated, and information on the chemical potentials and other functionalities as described below.

3.2 Organic Metals and Related Functional Solids

Ionicity diagrams as depicted in Figs. 1 and 2 are clues to explore functional conductors of CT type, such as molecular metals, Mott insulators, N–I systems, complex isomers, and self-aggregated two-dimensional conductors (see comments in Fig. 1 and [3]).

1. The fully ionic solids (region **I**) afforded band insulators, 1:1 Mott insulators with ground states of antiferromagnets (E·b(**21**) and F·b(**22**) in Fig. 1) or spin-Peierls systems, ferroelectrics, ferromagnets, spin-ladders, and nonlinear transport materials (switching and memory).
2. The mixed valence solids (region **M** in Fig. 1a, and **MA**, **MS-1**, **MS-2** and **M'S** in Fig. 2b) afforded (super)conductors and the following various kinds of insulators: (1) a (nearly) uniform segregated stack having spin density wave (SDW), and anion or charge ordered (=charge disproportionation) state, (2) a non-uniform segregated stack showing Peierls-type distortion, spin-Peierls distortion, and dimer-type Mott insulators including antiferromagnets, quantum spin liquid and spin-ladders, and (3) an alternating stack including N–I systems, ferroelectrics, and highly conductive semiconductors. There are hybrids from the combination of ferro-, ferri-, or paramagnetic species based on transition

metal compounds as one component and mixed valence counterparts to form magnetic CT conductors.

3. The neutral solids (regions **N** and **NA + NS**), in general, exhibit a CT band represented by eq. 3 in the caption to Fig. 2, regardless of the stacking modes. Since most of the CT solids in the region **N** prefer alternating stacks with a few exceptions, they are band insulators with low ionicity. Very weak CT solids having segregated stacks are potential candidates for FET channel and solar cell materials since they have good conduction paths. Hydrogen-bonding and proton-transfer between the components manifest many interesting functions: switching, ferroelectrics, etc.
4. Near the borderline **b** in Fig. 1, the bistability concerning the ionicity between the neutral and partial CT states is realized, i.e., the monotropic complex isomers G-m, H-p, and K-m (**24**, **25**, and **26** in Fig. 1, respectively). Even though K-m (ET·TCNQ) is expected to afford a neutral insulator based on its $\Delta E(\text{DA})$ value, a highly conductive complex isomer has been prepared. This result indicates that the ET molecule has a significant self-aggregation ability to form a segregated column with increased dimensionality, which is a nature of the solids in the region **M'S** in Fig. 2b (see next section). The insulating CT solids residing near the borderline **a** or **b** have the potential to exhibit a phase transition into a highly conducting phase induced by external stimuli (electric field, photons, etc.) with smaller threshold than those placed far from the borderlines.

3.3 Molecular Design for Dimensionality: Self-Aggregation Ability

Since the metallic state in the one-dimensional electronic system is unstable, an increase in the electronic dimensionality is necessary to prevent the nesting of Fermi surfaces. Several attempts have been made through “pressure”, “heavy atom substitution”, “peripheral addition of alkylchalcogen groups”, or “fusion of TTF skeletons” [88] (Fig. 3, Scheme 8). The latter three correspond to the enhancement of the self-aggregation ability of the molecules and hence increase the electronic dimensionality of molecular assemblies. The HMTTeF molecules afforded a stable metallic phase without any trace of superconductivity [86]. The BO molecules also afforded stable two-dimensional metals having two-dimensional Fermi surfaces (b in Fig. 3) owing to the strong self-aggregation ability (see Sect. 3.4.2) [87]. The substitution of an ethylenedioxy group with an ethylenedithio group (BO $\rightarrow$ EOET (Scheme 7) [89] $\rightarrow$ ET) destabilized the stable metallic state of BO compounds and provided unstable two-dimensional conductors (d in Fig. 3). The elimination of one ethylenedioxy group (BO $\rightarrow$ EDO) [90, 91] was found to be very effective in making a one-dimensional Fermi surface (e in Fig. 3) to afford localized (magnetic) phase or metal–insulator (MI) transition (see Sect. 4.2). Several superconductors

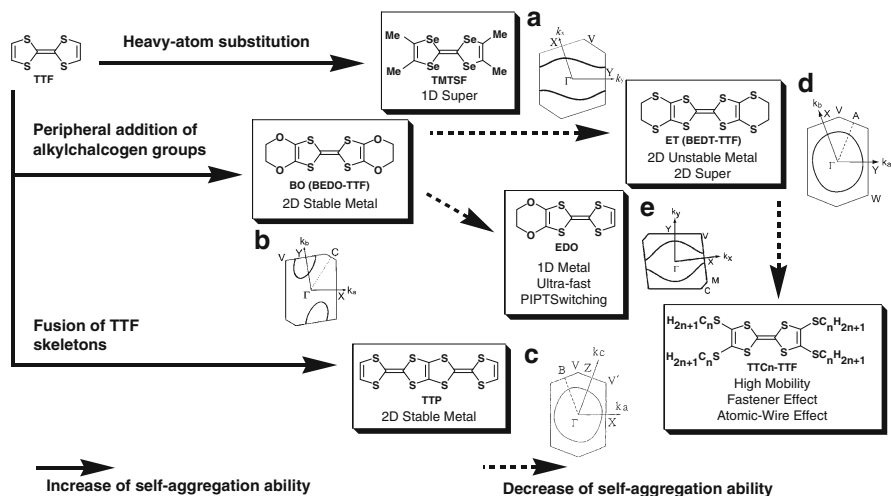
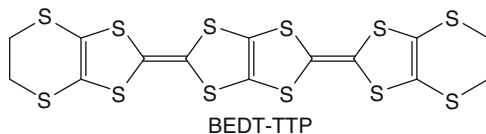


Fig. 3 Strategy for chemical modification of the TTF molecule to increase or decrease the electronic dimensionality (D) by the aid of enhance or suppress the self-aggregation ability of the donor molecules, respectively. Typical Fermi surfaces of TMTSF (a: (TMTSF) $_2$ NbF $_6$), BO (b: (BO) $_2$ I $_3$), TTP (c: (BEDT-TTP) $_2$ I $_3$, Scheme 8) [88], ET (d: β -(ET) $_2$ I $_3$), and EDO (e: (EDO) $_2$ PF $_6$) CT solids are depicted. PIPT: photo-induced-phase-transition



Scheme 8 Chemical structure of BEDT-TTP

have been prepared based on TMTSF having warped one-dimensional Fermi surface (a in Fig. 3), and on two-dimensional metals of ET, BO and a variety of analogs of TTF, even though TTF itself did not afford superconductors (see Sect. 5.1).

3.4 Variety of Conductive Charge Transfer Solids

3.4.1 Tuning of Fermi Level of FET Electrodes

Figure 4 demonstrates the control of p-, n-, and ambipolar-type FET operations in prototypical single-crystal organic FETs by “chemically tuning” the Fermi energy in TTF-TCNQ-based organic metal electrodes [85]. Figure 4a shows a device, where the organic channel is a neutral CT solid DBTTF-TCNQ, which has an alternating stack and the valence and conduction bands are mainly derived from the

HOMO of DBTTF and the LUMO of TCNQ, respectively (Fig. 4b). Source and drain electrodes are several organic metals of the TTF·TCNQ type having different chemical potentials predicted using Fig. 4c which is the same as Fig. 2a. For the electrodes whose chemical potentials are set within the conduction band of the channel material, FET exhibited *n*-type behavior (A in Fig. 4d). When the chemical potentials of organic metals are allocated within or near the valence band of the channel, *p*-type behaviors were observed (E, F in Fig. 4d). When the chemical potentials of the electrodes are within the gap of the channel, FET exhibited ambipolar-type behavior (B–D in Fig. 4d). Since the channel material is the alternating CT solid, the drain current is not excellent and a Mott type insulator of DA type or almost neutral CT solid having segregated stacks is much preferable in this context.

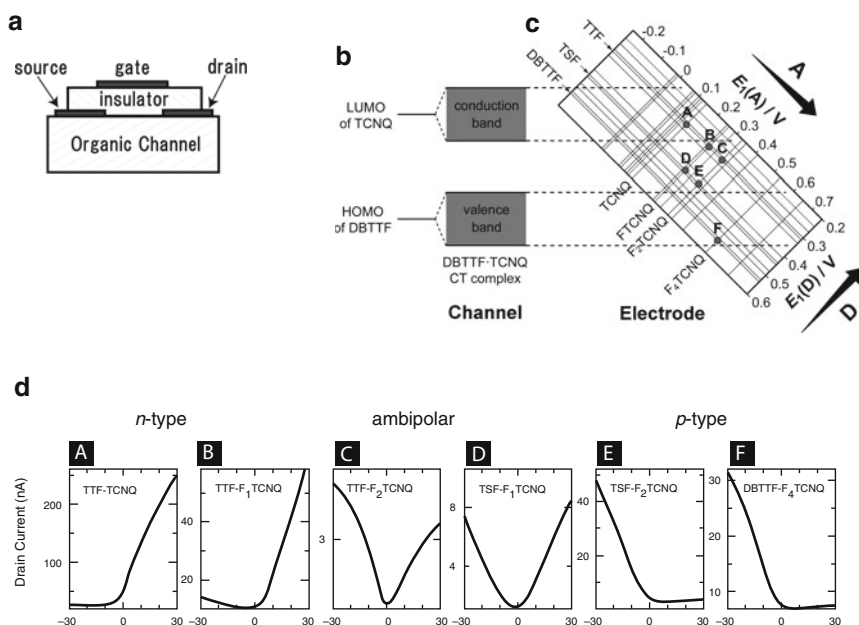


Fig. 4 Organic FET (OFET) composed of CT-complex-based organic metal electrodes. (a) An illustration of the device. (b) Interface band diagram of metal/semiconductor contact in DBTTF·TCNQ single crystal OFET with a variety of organic metal electrodes. (c) Modified figure of Fig. 2a. The conductive complexes A–F are drawn as functions of both I_D [or $E_1(D)$] and E_A [or $E_1(A)$]. (d) Transfer characteristics at $V_D = 5$ V of DBTTF·TCNQ single-crystal field effect transistors with the source and drain electrodes, composed of A: TTF·TCNQ, B: TTF·FTCNQ, C: TTF·F₂TCNQ, D: TSF·FTCNQ, E: TSF·F₂TCNQ, and F: DBTTF·F₄TCNQ, measured along the crystal long axes [85]

3.4.2 Two-Dimensional Stable Metals in Various Shapes

The related elements, proton (H^+), hydrogen ($\text{H}^\bullet$), and hydride (H^-) change their physical properties (including their size) drastically by the change of the number of electrons. Hydrogen-bond and proton-transfer interactions are the key to understanding many chemical reactions, biological activities, structure of molecular assemblies and supramolecules, functionalities in the solid state, etc.

As shown in Fig. 3 the peripheral addition of alkylchalcogen groups to the TTF skeleton increases the self-aggregation ability of the molecules and hence the electronic dimensionality of molecular assemblies increases. The typical example is the BO system [87]. Figure 5a,b shows one of the common packing patterns of the BO molecules. The strong self-aggregation ability of the BO molecules arises from both the $\text{CH}\cdots\text{O}$ hydrogen bonds in the face-to-face direction (Fig. 5a) and robust transfer interactions in two different oblique directions owing to the strong $\text{S}\cdots\text{S}$ atomic contacts (Fig. 5b) since inner chalcogen atoms have much higher electronic density than outer chalcogen atoms. These afford both a wide valence range of metallic state ($0.33 \leq \delta$) and a limited number of preferable packing patterns giving rise to a stable two-dimensional metallic state.

These robust intermolecular interactions provide a wide metallic band even in strongly disordered systems such as Langmuir–Blodgett (LB) films (BO complexes of $(\text{MeO})_2\text{TCNQ}$, C_nTCNQ ($n = 10, 14$), behenic acid, and stearic acid) [92–95], polycarbonate films dispersed with BO complexes (reticulate doped polymer (RDP) films with I_3 or Br salt, surface resistivity $1 \times 10^{-3} \text{ S}/\square$ at RT corresponding to ca. $10^2\text{--}10^3 \text{ S cm}^{-1}$) some of which are transparent (Br salt) [96, 97], compressed pellets with ferrimagnetic behavior $[(\text{BO})_3[\text{FeCr}(\text{oxalate})_3](\text{H}_2\text{O})_{3.5}]$ [98], films sensitive to the moisture in air $[(\text{BO})_2\text{ReO}_4(\text{H}_2\text{O})]$, $(\text{BO})_2\text{Br}(\text{H}_2\text{O})_3$ [99–101], etc., regardless of the sort, shape, and size of acceptor or anion molecules. As a result, the BO complexes hardly exhibit any phase transition including the superconducting one (only two superconducting salts with $T_c \leq 1.5 \text{ K}$; $(\text{BO})_3\text{Cu}_2(\text{NCS})_3$ [102] and $(\text{BO})_2\text{ReO}_4(\text{H}_2\text{O})$ [103]).

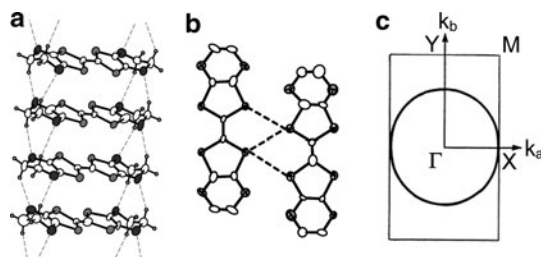


Fig. 5 Donor packing and Fermi surface for BO compounds. (a) Face-to-face packing (dotted lines indicate the $\text{CH}\cdots\text{O}$ hydrogen bonds), (b) side-by-side contacts (dotted lines indicate the short $\text{S}\cdots\text{S}$ atomic contacts), and calculated Fermi surfaces of (c) $(\text{BO})_2\text{Cl}(\text{H}_2\text{O})_3$. Calculated Fermi surface of $(\text{BO})_{2.4}\text{I}_3$ is depicted in Fig. 3b

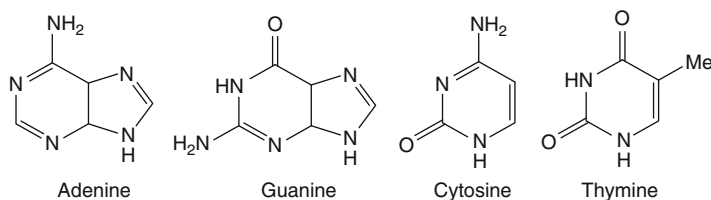
3.4.3 Conductors Based on Biological Materials

A variety of transport properties of biological materials, such as hemoglobin, amino acids, proteins, polypeptides, and so on, have been investigated, started with the pioneering works by Eley et al. [18, 104–113] (see also Chap. 12 in [18]). Most of them are insulating ($<10^{-11}$ S cm $^{-1}$ at 400 K) [18, 104–113] except cytochrome- c_3 (see Sect. 2.4) [68–70]. In recent studies on biomolecular conductors, DNA is one of the most active target molecules, and numerous experiments concerning the transport properties of DNA molecule have been carried out [114–122]. In the double-stranded DNA molecules, nucleobases establish a one-dimensional π -stacking structure which was proposed to be an efficient charge conduction path within DNA.

This past decade has seen numerous controversial studies regarding electrical conduction of DNA. Some reported high conductivity [115, 116, 118] with σ_{RT} of at most 10^4 S cm $^{-1}$ [115] or even superconducting properties [119], while others claimed that the carefully deionized DNA molecules are insulating [117, 120] in agreement with the old reports [121, 122] with σ_{RT} less than 10^{-6} S cm $^{-1}$. The controversy seems to have settled on a wide consensus that, apart from ionic conduction by the sodium gegenions, double-stranded DNA is an electrical insulator.

Several conductive CT solids with nucleobase skeletons have been developed in the TTF systems having uracil moieties ($\sigma_{RT} = 10^{-1}$ – 2 S cm $^{-1}$) [123–127]. Also several attempts have been undertaken to investigate the CT complexes in a variety of biochemical systems, especially using nucleobases (Scheme 9) [18, 104]. Estimation of I_P of the nucleobases, as potential components in CT complexes, indicate that they are reasonably effective π -donors particularly in the case of guanine (G); $I_D = 7.64$ – 7.85 eV vs adenine (A, 7.80– 8.26 eV), cytosine (C, 8.45– 8.74 eV), and thymine (T, 8.74– 8.87 eV) [128–131].

In the complex formation of nucleobases with *p*-chloranil, only G gave a CT solid which is in the neutral ground state estimated from the optical spectrum [132]. The mobility of electrons was described with regard to the transport properties on the CT solid of TCNQ with G [133]. C and 1-methylcytosine gave dark blue TCNQ radical anion salts with a 2:1 stoichiometry [134]. The examination of the CT solids of C, which has a weak electron donating ability ($E_p^{\text{ox}} = +1.90$ V vs SCE in water) as well as medium proton donating and strong proton accepting abilities ($\text{p}K_a = 4.55$ and 12.2) [135] with several TCNQs (RTCNQ) revealed the following [136–140].



Scheme 9 Chemical structures of nucleobases; adenine, guanine, cytosine, and thymine

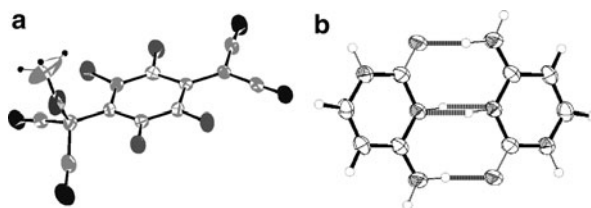


Fig. 6 Molecular structures of F₄TCNQ-OMe⁻ (a) and hemiprotonated cytosine pair CHC⁺ (b): dotted lines indicate the hydrogen bonds

Reaction between **C** in methanol and RTCNQ in acetonitrile yielded three kinds of ionic solids: (1) insulators composed of methoxy substituted RTCNQ anions such as (CHC⁺)[F₄TCNQ-OMe⁻](H₂O) (Fig. 6) [136], (2) semiconducting CT solids with fully ionic RTCNQ radical anions such as (CHC⁺)(TCNQ^{•-}) [137, 138], and (3) conducting CT solids of partially ionic or mixed valent RTCNQ radical anions such as (CHC⁺)(MeTCNQ^{0.5•-})₂ [138], where CHC⁺ is the hemiprotonated cytosine pair (Fig. 6b). Cation units in all products were found to be protonated cytosine species, most commonly CHC⁺, where H⁺ comes from methanol. This result suggests that the intrinsic transport properties of DNA should be studied not in protic solvents but under strictly dried conditions.

Crystal structural analysis of (CHC⁺)(TCNQ^{•-}) revealed the segregated structure with a uniform stacking pattern (Fig. 7a). The interplanar separations of TCNQ and CHC⁺ columns were 3.14 and 3.32 Å, respectively. The CHC⁺ pairs formed a one-dimensional ribbon structure (Fig. 7b). The hydrogen bonds between CHC⁺ ribbon and TCNQ molecules constructed the layered structure. In addition, the self-aggregation ability of **C** strengthened the uniform arrangement of the crystal resulting in both the high conductivity ($\sigma_{RT} = 3.2 \times 10^{-2} \text{ S cm}^{-1}$ on single crystal), which is one of the best among the conventional Mott type TCNQ salts and the absence of spin-Peierls type structural distortion down to 10 K. Transport property of (CHC⁺)(TCNQ^{•-}) was examined under high pressures up to about 7 GPa using a diamond anvil cell. The activation energy ε_a of 0.14 eV at ambient pressure decreased monotonically by a rate of 0.013 eV GPa⁻¹ [140]. The partially ionic salt of MeTCNQ in Group 3 exhibited the highest conductivity of 2 S cm⁻¹ so far observed for CT complexes based on biological molecules. This study revealed that the protonated states of **C**, especially the CHC⁺ species, are extraordinary stable and furthermore the characteristic pattern of the complementary hydrogen bonds between the cytosine molecules contribute to allow effective molecular packing and to control the electronic structure of TCNQ molecules for electronic conductors.

3.4.4 Two-Dimensional Metal Based on C₆₀

CT solids of fullerene C₆₀ with a number of different inorganic cations have shown metallic or superconducting properties (for superconductivity, see Sect. 5.2.3). Among the fullerene metals, the best known families are MC₆₀ anion radical salts

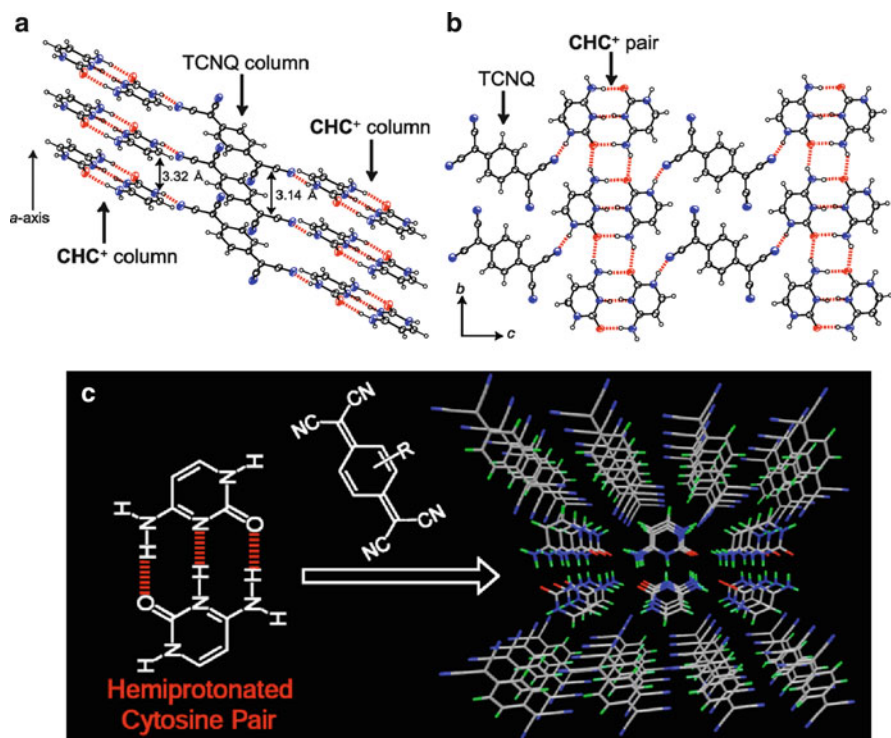
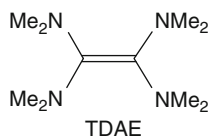


Fig. 7 Crystal structure of $(\text{CHC}^+)(\text{TCNQ})$ salt. (a) Uniform segregated stacks of CHC^+ and TCNQ. (b) CHC^+ ribbons by complementary hydrogen bonds and TCNQ form a layer within a bc -plane (hydrogen bonds: red dotted lines). (c) Formation of three-dimensional structure ($//a$) between hemiprotonated cytosine pair and RTCNQ species

($M = \text{K}, \text{Rb}, \text{and Cs}$), which contain linearly polymerized $\text{C}_{60}^{\bullet-}$, and superconducting M_3C_{60} salts ($M = \text{alkali metals}$), obtained by doping C_{60} with alkali metals [141–143]. As metal cations expand the three-dimensional lattice of the initial C_{60} framework, M_3C_{60} salts exhibit three-dimensional metallic conductivity, whereas MC_{60} salts are either three-dimensional (when $M = \text{K}$) or quasi-one-dimensional metals (when $M = \text{Rb}$ or Cs) [144]. Two-dimensional fullerene metals have not been obtained by conventional doping methods except for Na_4C_{60} where C_{60} has a two-dimensional polymeric structure [145], whilst the various possible ways of modifying M_xC_{60} CT solids have almost been exhausted. With conventional organic donor molecules, C_{60} is too weak an acceptor molecule to afford ionic solids. A very strong organic donor molecule, tetrakis(dimethylamino) ethylene (TDAE, Scheme 10), did yield a completely ionic solid – a ferromagnet with $T_c = 16 \text{ K}$ [146].

A multicomponent approach for synthesizing ionic fullerene compounds $\text{D}_I^+ \cdot \text{D}_{II} \cdot (\text{fullerene})^{\bullet-}$ is very effective in developing various functional and structural fullerene CT solids, including σ - and π -type dimers of fullerenes and an η -type



Scheme 10 Chemical structure of TDAE

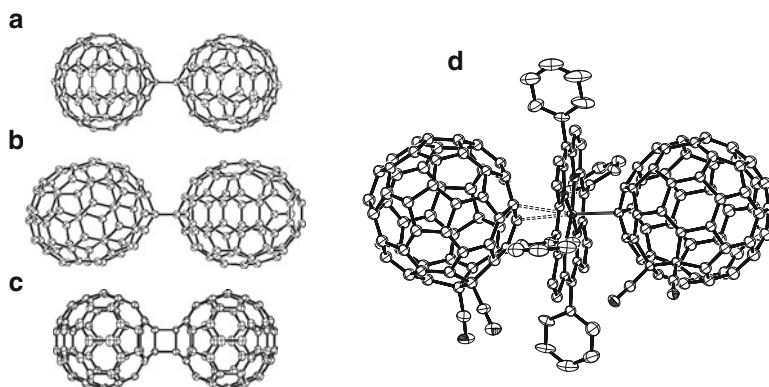
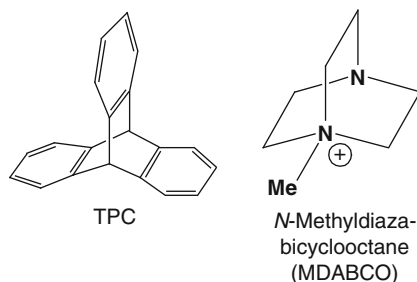


Fig. 8 (a) σ -type C_{60} dimer, (b) σ -type C_{70} dimer, (c) π -type C_{60} dimer, and (d) η^1 -coordination of cobalt(II) tetraphenylporphyrin with $C_{60}(\text{CN})_2$

complex (Fig. 8), where D_{I}^+ is a small, strong donor or cation that ionizes fullerene and determines its charged state, whereas D_{II} is a large, neutral molecule that defines the crystal packing of the complex [147–154]. In order to exhibit metallic properties, the C_{60} sublattice should have a close-packed structure with appropriate $C_{60}\cdots C_{60}$ distances. Otherwise, diamagnetic single-bonded $(C_{60}^-)_2$ dimers were formed when the distance is short, or strong spin frustration will be created based on the trilateral triangle spin geometry of $C_{60}^{\bullet-}$ when the distance is large just like $\kappa\text{-(ET)}_2\text{Cu}_2(\text{CN})_3$ in Sect. 6.1. The triptycene (TPC) molecule (Scheme 11) afforded a suitable geometrical space and spatial regulation as the D_{II} component for $C_{60}^{\bullet-}$ ions, giving rise to a close-packed fullerene two-dimensional sublattice in which the $C_{60}^{\bullet-}$ monomers preferentially form a two-dimensional honeycomb network of $C_{60}^{\bullet-}$. Namely, the TPC molecules form hexagonal layers with voids that accommodate the *N*-methyldiazabicyclooctane cation (MDABCO^+ , D_{I}^+) (Scheme 11, Fig. 9a). Docking $C_{60}^{\bullet-}$ into the periodic hollow sites in the $(\text{MDABCO}^+)\cdot\text{TPC}$ network (Fig. 9b,c) leads to the two-dimensional organic metal $(\text{MDABCO}^+)\cdot\text{TPC}\cdot(C_{60}^{\bullet-})$ [154]. There are two kinds of C_{60} layers, layer A (Fig. 9f) and layer B. $C_{60}^{\bullet-}$ molecules in layer B are rotationally disordered above 200 K and layer B is not metallic and exhibits spin frustration. The ordering of $C_{60}^{\bullet-}$ in the B layers with MDABCO^+ at around 200 K triggers a transition from a nonmetallic and antiferromagnetically frustrated state to a metallic state in layer B, whilst the ordered $C_{60}^{\bullet-}$ in layer A keeps its two-dimensional itinerancy over the entire temperature range. It exhibits a metallic state down to 1.9 K, which was



Scheme 11 Chemical structures of TPC and MDABCO

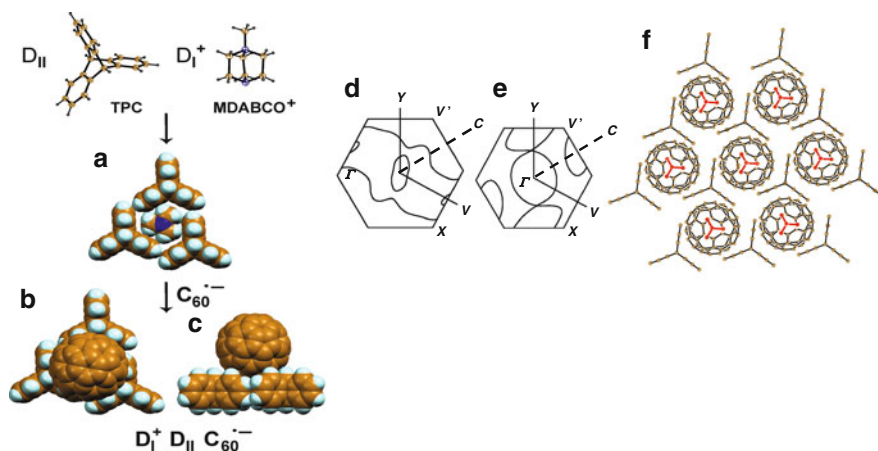


Fig. 9 Molecular structures of TPC (D_{II}) and MDABCO⁺ (D_I^+) [154]. Crystal structure packing in (MDABCO⁺)·TPC·(C_{60}^{*-}). (a) TPC molecules form a hexagonal hollow and the MDABCO⁺ cation fits into the hollow; the C_{60}^{*-} molecules are docked into the hollow in TPC layer in a key–keyhole relationship [top view (b) and side view (c)] to form $D_I^+ D_{II} C_{60}^{*-}$. Colors: C, dark yellow; H, pale blue; and N, dark blue. Calculated Fermi surface at 160 K in (d) layer A and (e) layer B. (f) Projection of the (MDABCO⁺)·TPC layer on the C_{60} layer A (red color: MDABCO⁺)

consistent with the calculated Fermi surfaces (Fig. 9d,e). This metal is composed of only light elements (C, H, and N).

4 Exotic Conductors with a Switching Function

4.1 Basic Aspects

All of the organic molecules have multifunctional natures and provide plural intermolecular interactions depending on the nature of counter component,

morphology (solid, films, uni-molecule, etc.), and external circumstances. For example, the CT interaction between D and A molecules in solid are broken down into two kinds of interactions: Interaction I – electron transfer from neutral D to A molecules that costs $(I_D - E_A)$ and Interaction II – Madelung energy M , as described in Sect. 3.1 (Fig. 10a). One can expect that the balance between the interactions I and II can be controlled easily by external stimuli. The controllability increases as the system approaches to a boundary area and the system shows a variety of phase transitions (i.e., metal $\leftrightarrow$ insulator, Mott insulator $\leftrightarrow$ metal, quantum spin liquid $\leftrightarrow$ superconductor, neutral $\leftrightarrow$ ionic, valence tautomerization), monotropic (e.g., complexes **24–26** in Fig. 1) and enantiotropic (e.g., TTF-*p*-chloranil) complex isomerizations, and switching or memory effect depending on the potential depths and barrier height ΔE in Fig. 10b. Therefore, possible candidates for such phase transition can be selected based on the diagrams in Fig. 10c, d.

The switching or memory phenomena induced by electric field application or photo irradiation have been studied on Mott insulators, charge ordered insulators, and N–I transition systems and were found to be fast phase transitions in general. For the former two systems, the phase transitions caused a pronounced change in reflectance and conductivity from insulating to metallic features. The third system also exhibited a change in conductivity and dielectric response connected with the transports of solitons and/or domain walls, dynamic dimerization, and

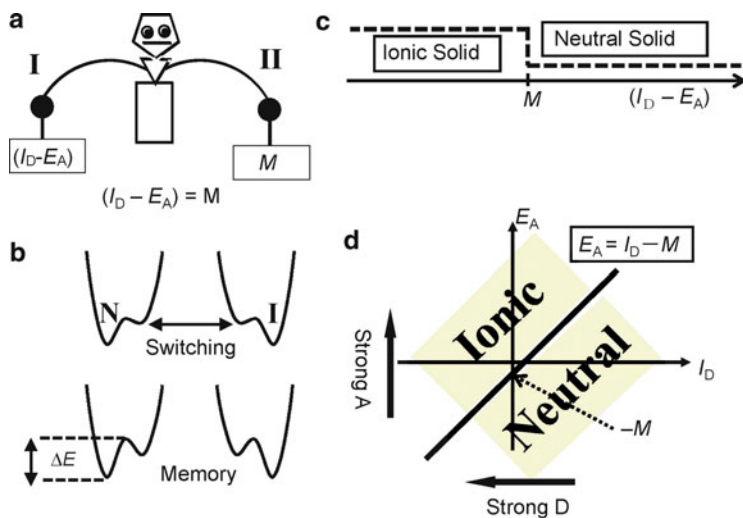


Fig. 10 (a) A schematic balance between ionization energy $(I_D - E_A)$ and Madelung cohesive energy M for CT solids. (b) Model double minimum potential for the N–I system for switching (upper, potential barrier between stable and metastable states is small and thermally accessible) and memory (lower, potential barrier is rather high $\Delta E \gg k_B T$). One- (c) and two-dimensional (d) diagrams for searching for the boundary zone and functional materials. (d) is a schematic diagram corresponding to Fig. 1

ferroelectricity. It should be emphasized that most of the π -molecules are, in Pearson nomenclature, soft acids or soft bases. Thus they have a huge electronic polarizability, and are susceptible to external stimuli when the ionicity and mutual orientation of the molecules are appropriately designed. Table 5 summarizes CT solids having switching behavior and are compared with superconductor (TMTSF)₂ClO₄ showing sliding SDW. So far among the switching systems by electric-field, (NT)₃GaCl₄ (Scheme 12) exhibited the lowest threshold (1×10^2 V cm⁻¹) [166], which is smaller by one order of magnitude than the well known Cu·TCNQ [155, 156], but much larger than that of sliding SDW. As for the response to the electric field, the ability to show thyristor action was demonstrated for the charge-ordered systems based on TTF derivatives [167].

For these transition systems, the following five parameters are important for the development of materials:

1. *Response time* which can be controlled by taking into account the origin of the transition (1) fs for pure electronic transition, (2) addition of molecular deformation leads to ps response time, (3) further addition of lattice deformation leads to a slower response time > ps.
2. *Coherence* (transition efficiency) depends on the degree of electron–phonon or electron–molecular vibration coupling.
3. *Response temperature* (operating temperature) may decrease in the following order: bond formation and cleavage → molecular deformation → lattice deformation → electronic deformation such as SDW and charge-order melting.
4. *Threshold* of the external stimuli should not be zero to have clear switching and memory.
5. *Durability* of the system.

4.2 Ultrafast Photo-Induced Phase Transition in (EDO)₂X

To destabilize the metallic state of the BO complexes, the elimination of one ethylenedioxy group (BO → EDO) [90, 91] was very efficient owing to the weakened self-aggregation ability (Fig. 3). The (EDO)₂X salts (X = PF₆, AsF₆, and SbF₆) are three-quarters-filled band conductors with a quasi-one-dimensional Fermi surface (Fig. 3e) and exhibit a first-order MI transition (Fig. 11a, b) at rather high temperatures (240–280 K) [90, 173]. The T_{MI} was tuned by chemical modifications. Deuteration of EDO (d₂-EDO, Scheme 13) increased T_{MI} by ca. 2.5 K, while complexation with larger counter anions decreased T_{MI} in the order X = ClO₄ (>337 K) > PF₆ (278 K) > AsF₆ (ca. 268 K) > SbF₆ (ca. 240 K) [173–176].

The phase transition consists of a cooperative mechanism with charge-ordering, anion order–disorder, Peierls-like lattice distortion, which induces a doubled lattice periodicity giving rise to $2k_{\text{F}}$ nesting, and molecular deformation (Fig. 11c). The high temperature metallic phase is composed of flat EDO molecules with +0.5 charge, while the low temperature insulating phase is composed of both flat monocations

Table 5 Selected CT solids having switching behavior under electric field and/or photon irradiation are compared with the sliding SDW^a

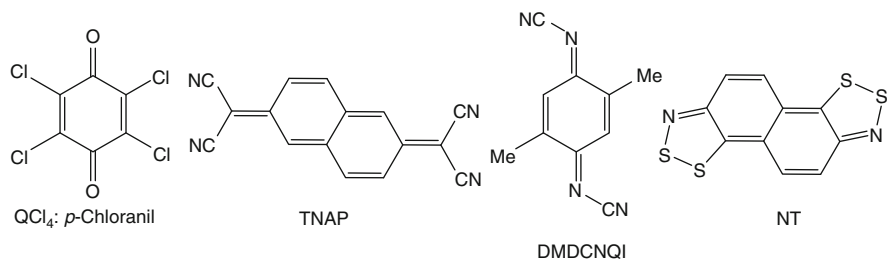
Mechanism	CT solid	Electric field		Photon irradiation				Reference
		E_{th} (V cm ⁻¹)	T_{oper} (K)	Reference	Photon density	Sensitivity	Response time	
Mott or spin-Peierls Insulator↔Mixed valency or metal ^b	Cu·TCNQ	4×10^3	RT	[155, 156]	1,500 W cm ⁻²	—	RT	[157]
	Cu·TNAP	8×10^3	RT	[155]	—	—	—	—
	K·TCNQ	$>10^3$	<230	[158]	—	20 dimers	ps ^c	<394 [159]
	Rb·TCNQ	—	—	—	—	<10	1.5 ps	RT Okamoto H private communication
Mott + Peierls Insulator ↔ Metal CO insulator↔Metal	Ag(DMDCNQI) ₂	—	—	—	—	—	3–5 days	[160]
	Cu(d _g -DMDCNQI) ₂	—	—	—	~10 ⁸ W cm ⁻²	100e	20 ps	<78 [161]
	(EDO) ₂ PF ₆	—	—	—	2 × 10 ¹⁸ cm ⁻³	500	1.5–2 ps	270 [162, 163]
	α-(ET) ₂ I ₃	—	—	—	—	—	120 ns	4 [164]
Neutral↔Ionic	θ-(ET) ₂ CsZn(SCN) ₄	3×10^2	<20	[165]	—	—	—	—
	(NT) ₃ GaCl ₄	1×10^2	RT	[166]	—	—	—	—
	θ-(ET) ₂ CsCo(SCN) ₄	1.4×10^2	4.2	[167]	—	—	—	—
	TTF·QCl ₄	3×10^3	190	[168, 169]	1.8×10^8 cm ⁻³	280–2,800	20–100 ps	77 [170, 171]
Sliding SDW	TTeC ₁ -TTF·TCNQ	—	—	—	—	—	ps ^c	<300 [159]
	(TMTSF) ₂ ClO ₄	$<5 \times 10^{-4}$	1.5	[172]	—	—	—	—

CO⁻: charge ordered; E_{th} threshold electric field; T_{oper} operating temperature

^aNo experiments

^bMixed valency or metallic behavior has not been observed by thermal variation except Ag(DMDCNQI)₂

^cAccording to the time-dependence of photo-induced reflectivity change [159], the response times for TTeC₁-TTF·TCNQ and K·TCNQ are a few times and a few hundred times faster, respectively, than that for TTF-*p*-chloranil



Scheme 12 Chemical structures of p -chloranil, TNAP, DMDCNQI, and NT

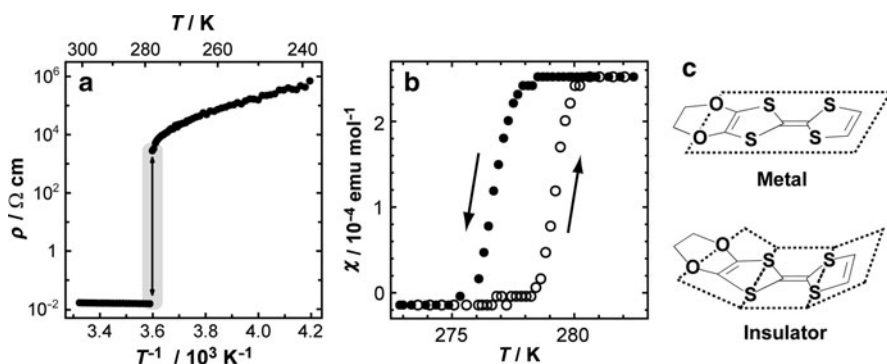
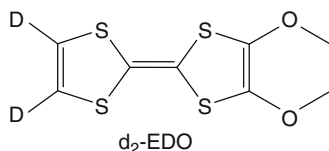


Fig. 11 Temperature dependence of (a) resistivity and (b) magnetic susceptibility of $(\text{EDO})_2\text{PF}_6$. Gray shadow in (a) and arrows in (b) indicate the MI transition. (c) Molecular structures of neutral and monocationic EDO molecules [90]. Calculated Fermi surface of $(\text{EDO})_2\text{PF}_6$ is depicted in Fig. 3e



Scheme 13 Chemical structure of d_2 -EDO

and bent neutral EDO molecules with charge-ordered stripes (+1, +1, 0, 0) [177, 178]. This stripe is different from the so far known (0, +1, 0, +1) stripe for θ -(ET)₂MM'(SCN)₄ [179], indicating that the neighbor-site Coulomb repulsion energy is not dominant compared to the transfer energy within the $(\text{EDO}^{1+})_2$ dimer.

Laser irradiation onto the insulating $(\text{EDO})_2\text{PF}_6$ crystal induces a phase transition to the highly conductive state within a few picoseconds [162, 180]. The crystal surface was excited by laser irradiation with a pulse width of 0.12 ps. The excitation photon energy (1.55 eV) was nearly resonant to the CT band at $11.1 \times 10^3 \text{ cm}^{-1}$ (1.37 eV), directly reflecting the excitation of the charge ordered state.

The reflectance change $\Delta R/R$ from insulating to conductive states exhibits negative and positive maxima at the probe photon energy of 1.38 and 1.72 eV, respectively (Fig. 12). The life-time of the photo-induced conductive phase strongly depends on the excitation intensity. In case of $2 \times 10^{18} \text{ cm}^{-3}$ excitation condition, the reflectance change occurred within only about 1.5 ps. Therefore, it is said that the melting of the charge ordered state accompanied by the insulator-to-conductor phase conversion occurs within 1.5 ps just after excitation with threshold-like behavior (threshold photon density is 10^{18} cm^{-3}). The excitation intensity corresponds to a single excitation photon for ca. 500 molecules. Within the resolution time (1 μs), the electric conductivity was largely enhanced (more than five orders of magnitude) just after photo-excitation.

So far, among the switching systems by photo irradiation, TTF-*p*-chloranil, which is known to have strong electron–lattice coupling, has the highest sensitivity (280–2,800 molecules per photon) and fast response time (20–100 ps), though the operating temperature is low (77 K). The EDO system has high sensitivity (500 molecules per photon), fast response time (1.5–2 ps), and moderately high operating temperature (270 K for X = PF₆). To realize a molecular phase-switching device controllable by light irradiation with 1 ps response time (i.e., THz region), it is essential to develop a material that shows highly sensitive and ultra-fast PIPT phenomena near RT with high repeatability and durability. Such an ultra-fast transition has been observed in a purely electronic origin. Although the ultra-fast transition (within a few hundred fs) accompanied by the molecular conformational change has been observed for systems such as retinal in rhodopsin [181], this is a unimolecular nano-system. As for the meso-size scale switch, an electron–lattice coupled coherent system is necessary for an ultra-fast transition.

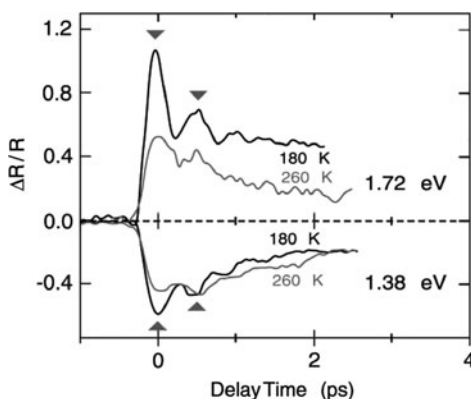


Fig. 12 Probe photon energy dependence of the time profile for the reflectance change $\Delta R/R$ observed at 180 K and 260 K. The pump photon energy ($E//b$) was 1.55 eV and the probe photon energy ($E//b$) was 1.72 and 1.38 eV for the *upper* and *lower panels*, respectively. The oscillations in $\Delta R/R$ relate molecular deformation modes [162]

5 Organic Superconductors of Charge Transfer Type

There are several comprehensive textbooks and review articles devoted to organic superconductors [3, 4, 182–186] which describe design and preparation, crystal and band structures, chemical, transport, magnetic, optical, and thermal properties, and theory.

5.1 Superconductors Based on Donor Molecules

5.1.1 TMTSF Superconductors

The most successful molecule by “heavy atom substitution” (Fig. 3) is TMTSF. Since the discovery of the first organic superconductor (TMTSF)₂PF₆ ($T_c = 1.1$ K at 0.65 GPa) by Jérôme and Bechgaard [187, 188], eight quasi-one-dimensional superconductors (TMTSF)₂X (X = PF₆, AsF₆, SbF₆, NbF₆, TaF₆, ClO₄, ReO₄, and FSO₃) with $T_c < 3$ K have been prepared [187–189]. Among them, the superconducting NbF₆ salt can only be prepared by using ionic liquid (1-ethyl-3-methylimidazolium)NbF₆ [189] and others by using more common tetrabutylammonium salts as the electrolyte. Salts with octahedral anions exhibited an MI transition at 11–17 K at ambient pressure due to SDW; superconductivity appeared with an on-set T_c of ca. 1 K at 0.6–1.2 GPa. Salts with (pseudo)tetrahedral anions exhibited an order–disorder transition for the anions which induced an MI transition for X = ReO₄ and FSO₃ at 177 K and 88 K, respectively, and superconductivity appeared at 1.2 K and 3 K, respectively, under 0.5–1 GPa. The isomorphous (TMTTF)₂X salts displayed superconductivity under high pressure of 2.6–9 GPa with T_c less than 3 K for X = PF₆, SbF₆, BF₄, and Br [190–193].

(TMTSF)₂ClO₄ is the only ambient pressure superconductor among them; it did not show the Hebel–Slichter coherence peak, indicating that its superconductivity is of the non-*s*-wave type [194]. A generalized phase diagram, including (TMTTF)₂X and (TMTSF)₂X, indicates that the superconducting phase neighbors the magnetic SDW phase (Fig. 13) [195].

5.1.2 ET Two-Dimensional Conductors and Superconductors

κ -Type Superconductors

TTF derivatives with peripheral addition of alkylchalcogen groups were found to be effective in increasing dimensionality of CT solids and suppressing the Peierls-type MI transition. The first ET two-dimensional organic metal down to low

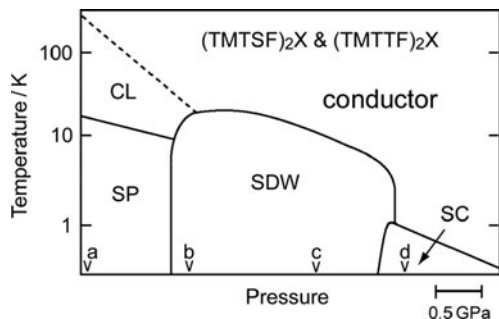


Fig. 13 Generalized phase diagram for the $(\text{TMTSF})_2\text{X}$ and $(\text{TMTTF})_2\text{X}$ by Jérôme [195]. CL, SP, SDW, and SC refer to charge-localized (which corresponds to charge-ordered state), spin-Peierls, spin density wave, and superconducting states, respectively. (a) $(\text{TMTTF})_2\text{PF}_6$, (b) $(\text{TMTTF})_2\text{Br}$, (c) $(\text{TMTSF})_2\text{PF}_6$, (d) $(\text{TMTSF})_2\text{ClO}_4$

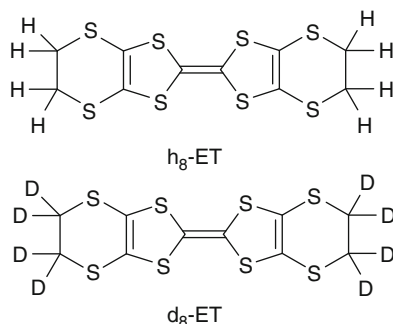
temperatures was $(\text{ET})_2\text{ClO}_4$ (1,1,2-trichloroethane) [196]. Since then, hundreds of ET solids have been prepared. Different kinds of $\text{ET}\cdots\text{ET}$ (π - π , S- $\cdots$ S) and $\text{ET}\cdots\text{anion}$ (hydrogen bonds) intermolecular interactions, large conformational freedom of ethylene groups, flexible molecular framework, fairly narrow bandwidth (W), and strong electron correlations (U_{eff}) gave a rich variety of complexes with different crystal and electronic structures ranging from insulators to superconductors. About 60 ET superconductors are known so far. Currently $\beta'-(\text{h}_8\text{-ET})_2\text{ICl}_2$ (on-set $T_c = 14.2$ K at 8.2 GPa [197], mid-point T_c of 13.4 K is estimated), and $\kappa-(\text{d}_8\text{-ET})_2\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$ ($T_c = 13.1$ K at 0.03 GPa) [198] show the highest T_c under pressure, while both are Mott insulators at ambient pressure. At ambient pressure, $\kappa-(\text{d}_8\text{-ET})_2\text{Cu}(\text{CN})[\text{N}(\text{CN})_2]$ shows the highest T_c of 12.3 K [199] followed by $\kappa-(\text{h}_8\text{-ET})_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ ($T_c = 11.8$ K) [200].

The four κ -type superconductors $\kappa-(\text{ET})_2\text{CuL}_1\text{L}_2$ ($\text{L}_1, \text{L}_2 = \text{Cl}, \text{Br}, \text{NCS}$, and $\text{N}(\text{CN})_2$), which were discovered by us and the Argonne group [200–203], share some common structural and physical properties. Table 6 summarizes the two kinds of ligand in a salt, T_c of H- and D-salts (salt using $\text{h}_8\text{-ET}$ and $\text{d}_8\text{-ET}$, respectively; Scheme 14), ratio of transfer interactions t'/t for triangle geometry of ET dimers (see Sect. 6.1), U/W , and year of discovery. Figure 14 shows the crystal structure of the prototype $\kappa-(\text{ET})_2\text{Cu}(\text{NCS})_2$, anion structures, calculated Fermi surface, and micrograph of single crystals. Although these ET salts have similar structural aspects, their transport properties differ (Fig. 15). $\kappa-(\text{ET})_2\text{Cu}(\text{CN})[\text{N}(\text{CN})_2]$ (29) showed a monotonic decrease of resistivity with upper curvature down to T_c . $\kappa-(\text{ET})_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ (31) exhibited a similar behavior to that of $\kappa-(\text{ET})_2\text{Cu}(\text{NCS})_2$ (30) except that a metallic regime near RT was observed in 30. $\kappa-(\text{ET})_2\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$ (32) showed a semiconductor ($\varepsilon_g = 24$ meV)–semiconductor ($\varepsilon_g = 104$ meV) transition at ca. 42 K due to an antiferromagnetic (AF) fluctuation resulting in a weak ferromagnet below 27 K [208, 209]. Under a weak pressure, it showed a similar temperature dependence to that of $\kappa-(\text{ET})_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$.

Table 6 Four typical κ -type superconductors with T_c above 10 K (29 – 32) and a Mott insulator (34)

Number in Fig. 15 and Anion	Ligand		T_c/K		t'/t	U/W	Year	Reference
	L_1	L_2	H-salt	D-salt				
(30) Cu(NCS) ₂	SCN	NCS	10.4	11.2 [3]	0.81–0.86	0.94	1988	[201]
(31) Cu[N(CN) ₂]Br	N(CN) ₂	Br	11.8	11.2 [204]	0.67	0.92	1990	[200]
(32) Cu[N(CN) ₂]Cl	N(CN) ₂	Cl	12.8 (0.03GPa)	13.1 [198]	0.75	0.90	1990	[202]
(29) Cu(CN)[N(CN) ₂]	CN	N(CN) ₂	11.2	12.3 [3, 199]	0.66–0.71	0.87	1991	[203]
(34) Cu ₂ (CN) ₃	CN	CN (or NC)	6.8–7.3		1.06	0.9	1991	[203, 205–207]

Ligand L_1 forms infinite chain by the coordination to Cu(I). Ligand L_2 coordinates to Cu(I) as pendant
The t and t' values were calculated by the extended Hückel method



Scheme 14 Chemical structures of $h_8\text{-ET}$ and $d_8\text{-ET}$

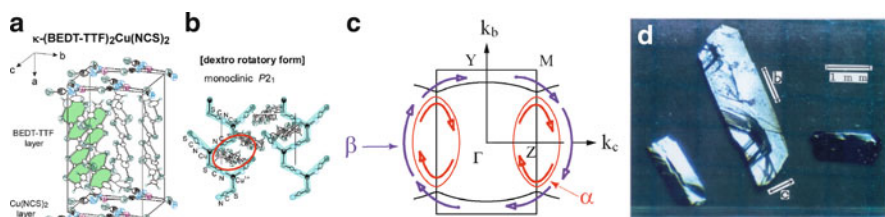


Fig. 14 $\kappa\text{-(ET)}_2\text{Cu(NCS)}_2$. (a) Crystal structure: two-dimensional conducting ET layer is sandwiched by the insulating anion layers along the a -axis (bc -plane is two-dimensional conducting plane). Two kinds of layers are Josephson coupled. (b) Anion structure: $\text{Cu}\cdots\text{SCN}\cdots\text{Cu}\cdots\text{SCN}\cdots$ forms zigzag infinite chain along the b -axis and other ligand SCN (Ligand L_2 in Table 6) coordinates to Cu(I) by N atom to make a space (indicated by *red ellipsoid*) to which an ET dimer fits. Picture is the dextrorotatory form. (c) Reflecting the crystal symmetry, the calculated Fermi surfaces of the $P2_1$ salts ($\kappa\text{-(ET)}_2\text{Cu(NCS)}_2$, $\kappa\text{-(ET)}_2\text{Cu(CN)[N(CN)}_2]$) showed the certain energy gap between a one-dimensional electron like Fermi surface and a two-dimensional cylindrical hole-like one (α -orbit), while such a gap is absent in the $Pnma$ salts ($\kappa\text{-(ET)}_2\text{Cu[N(CN)}_2]\text{Br}$, $\kappa\text{-(ET)}_2\text{Cu[N(CN)}_2]\text{Cl}$). For $\kappa\text{-(ET)}_2\text{Cu(NCS)}_2$, electrons move along the closed ellipsoid (α -orbit) then at higher magnetic field (>20 T) electron hops from the ellipsoid to open Fermi surface to show circular trajectory (β -orbit, Magnetic breakdown). (d) Single crystals by electrooxidation

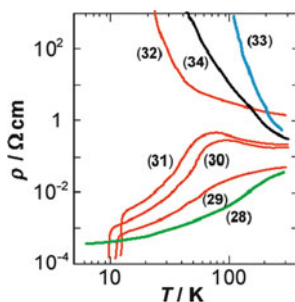


Fig. 15 Temperature dependences of resistivity of 10 K class superconductors $\kappa\text{-(ET)}_2\text{Cu(CN)[N(CN)}_2]$ (29), $\kappa\text{-(ET)}_2\text{Cu(NCS)}_2$ (30), $\kappa\text{-(ET)}_2\text{Cu[N(CN)}_2]\text{Br}$ (31), and $\kappa\text{-(ET)}_2\text{Cu[N(CN)}_2]\text{Cl}$ (32) are compared with those of a good metal with low T_c $\beta\text{-(ET)}_2\text{AuI}_2$ (28), strongly electron correlated insulator $\theta\text{-(ET)}_2\text{Cu}_2\text{(CN)[N(CN)}_2)_2$ (33), and a Mott insulator $\kappa\text{-(ET)}_2\text{Cu}_2\text{(CN)}_3$ (34) at ambient pressure

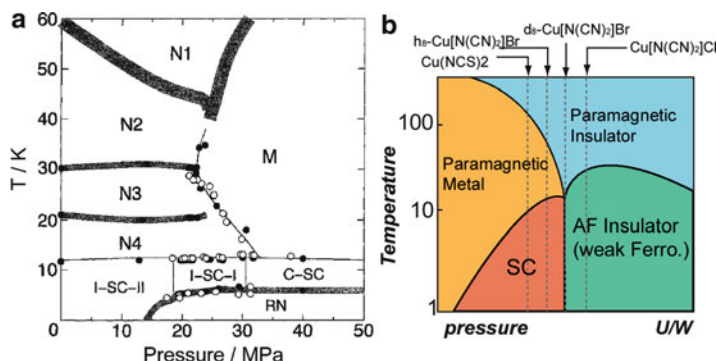


Fig. 16 (a) Phase diagram of κ -(h₈-ET)₂Cu[N(CN)₂]Cl determined from conductivity and magnetic measurements [213, 217, 218]. N1–N4: nonmetallic phase, M: metallic phase, RN: reentrant nonmetallic phase, I-SC-I, II: incomplete superconducting phase, S-SC: complete superconducting phase. N2 shows the low-dimensional AF fluctuation. N3 shows growth of three-dimensional AF ordered phase. N4: weak ferromagnetic phase. (b) Proposed phase diagram [211, 212]

κ -(h₈-ET)₂Cu[N(CN)₂]Cl showed a complicated T - P phase diagram as elucidated by Ishiguro and Ito et al. (Fig. 16a) [213–222]. Thoroughgoing studies under He gas pressure showed firm evidence of the coexistence of superconducting (I-SC-II phase: I-SC = incomplete superconducting) and AF phases [210, 216, 223, 224], where the radical electrons of ET molecules played both roles of localized and itinerant ones. Under a pressure of ca. 20–30 MPa another incomplete superconducting phase (I-SC-I) appeared and the complete superconducting (C-SC) phase resides adjacent to this phase at higher pressures. Below these superconducting phases, a reentrant nonmetallic (RN) phase was observed. Similar T - P phase diagrams were obtained for κ -(d₈-ET)₂X (X = Cu[N(CN)₂]Cl [218] and X = Cu[N(CN)₂]Br [219–221]) with a parallel shift of pressure. They occur at the higher and lower pressure sides of the κ -(h₈-ET)₂Cu[N(CN)₂]Cl for the Br and Cl salts, respectively. In contrast to the H salt, κ -(d₈-ET)₂Cu[N(CN)₂]Cl did not exhibit a coexistence of the superconducting and AF phases, and hence afforded AF resonance [222]. Increasing the distance between the ET dimers in Fig. 14a,b causes the transfer interactions between ET dimers to decrease; this may correspond to the decrease of band-width and to the increase of density of states at Fermi level $D(\epsilon_F)$, and consequently T_c is expected to increase. According to this line of thought, higher T_c is expected for the salt having a larger anion spacing. Such a κ -type salt may be found near the border between poor metals and Mott insulators.

The Fermi surfaces of these salts have been studied by measuring the quantum oscillations [183] such as SdH (Shubnikov–de Haas) and dHvA and geometrical oscillations (AMRO, angle-dependent magnetoresistance oscillation) ([4], Appendix, pp 445–448). The Fermi surface of κ -(ET)₂Cu(NCS)₂ (Fig. 14c) calculated based on the crystal structure is in good agreement with those observed data [225].

Superconducting Characteristics of κ -Type Superconductors

1. H_{C2} . κ -(ET)₂Cu(NCS)₂ gave higher upper critical magnetic field H_{C2} values in the two-dimensional plane than the Pauli limited magnetic field H_{Pauli} [226, 227].
2. *Symmetry of superconducting state*. No Hebel–Slichter coherence peak was observed in either κ -(ET)₂Cu(NCS)₂ or κ -(ET)₂Cu[N(CN)₂]Br in ¹H NMR measurements, ruling out a BCS *s*-wave state. The symmetry of the superconducting state of κ -(ET)₂Cu(NCS)₂ had been controversially described as normal BCS-type or non-BCS type; however, scanning tunneling spectroscopy showed *d*-wave symmetry with line nodes along the direction near $\pi/4$ from κ_a - and κ_c -axes [228, 229], and thermal conductivity measurements were consistent with this result [230]. κ -(ET)₂Cu [N(CN)₂]Br showed the same symmetry [231].
3. *Inverse isotope effect*. The inverse isotope effect has so far been observed for κ -(ET)₂Cu(NCS)₂ [3–18, 232] (Fig. 53 in [3]), κ -(ET)₂Cu(CN)[N(CN)₂] [3, 199], and κ -(ET)₂Cu[N(CN)₂]Cl [198], and the normal isotope effect for κ -(ET)₂Cu[N(CN)₂]Br [204, 233].
4. *Phase diagram*. A proposed *T*–*P* phase diagram for κ -(ET)₂CuL₁L₂ by Kanoda (Fig. 16b), where only the parameter U/W is taken into account, includes the salts κ -(ET)₂Cu(NCS)₂, κ -(ET)₂Cu[N(CN)₂]Br, and κ -(ET)₂Cu[N(CN)₂]Cl [211, 212]. However, the metallic behaviors of κ -(ET)₂Cu(NCS)₂ **30** above 270 K and of κ -(ET)₂Cu(CN)[N(CN)₂] **29**, the whole nature of κ -(ET)₂Cu₂(CN)₃ **34**, and the low-temperature reentrant behavior of κ -(ET)₂Cu[N(CN)₂]Br and κ -(ET)₂Cu[N(CN)₂]Cl cannot be allocated in this diagram. This diagram is a simplified one, compared with the experimentally observed phase diagram [213, 222], but is convenient and useful to explain the general trends for these salts. The phase diagram and “geometrical isotope effect” [234] point out that T_c decreases with increasing pressure if only the parameter U/W or $D(\varepsilon_F)$ is taken into account. This tendency has been observed under hydrostatic pressure but not under uni-axial pressure (see next Section and Sects. 5.1.3 and 6.2).

Other ET Superconductors

One of the most intriguing ET superconductors is the salt with I₃ anion, which afforded α , α_t , β_L , β_H , δ , ε , γ , θ , and κ -type salts with different crystal and electronic structures. Among them, α , α_t , β_L , β_H , γ , θ , and κ -type salts are superconductors with $T_c = 7.2$, ~ 8 , 1.5, 8.1, 2.5, 3.6, and 3.6 K, respectively [235–249]. The α -(ET)₂I₃ exhibited nearly temperature independent resistivity down to 135 K [235], at which charge-ordered MI transition occurred [236]. It has been claimed that α -(ET)₂I₃ has a zero-gap state with a Dirac cone type energy dispersion, hence with zero-effective mass and infinite mobility in the metallic state like graphene [237, 238]. Under hydrostatic pressure it became two-dimensional metal down to low temperatures (at 2 GPa). Very interestingly, however, it became superconductor under the uniaxial pressure along the *a*-axis (0.2 GPa, $T_c = 7.2$ K on-set), though along the *b*-axis it remained metal down to low temperature

(0.3–0.5 GPa) [239]. α -(ET)₂I₃ was able to be converted to mosaic polycrystal with $T_c \sim 8$ K by tempering at 70–100 °C for more than 3 days. The $T_c \sim 8$ K phase thus obtained exhibited a similar NMR pattern to that of the β_H -salt; however, it was isolated at ambient pressure so was designated as α_t -salt [240]. RDP films composed of ET in polycarbonate (2 wt%) were treated with CH₂Cl₂/I₂ vapors and then annealed at 137 or 155 °C to convert the α -(ET)₂I₃ to the superconducting α_t -(ET)₂I₃. The film is metallic and exhibits a broad superconducting transition below 7 K [241].

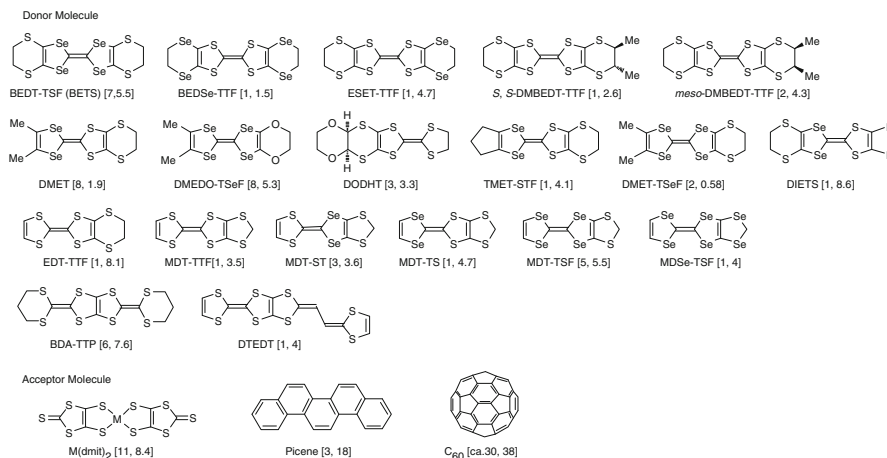
The β_L -salt was the first ambient pressure superconductor in the ET family with $T_c = 1.5$ K, reported by Yagubskii et al. [242]. The β_L -salt is characterized by having a superlattice appearing at 175 K with incommensurate modulations of ET and I₃ to each other [243]. Then the orientationally disordered ethylene groups near I₃ are ordered so as to make a new periodicity according to the incommensurate superlattice periodicity. The β_L -salt was converted to the high T_c phase, β_H -salt $T_c = 8.1$ K, by pressurizing (hydrostatic pressure) above 0.04 GPa by the suppression of the superlattice and then by depressurizing while keeping the sample below 125 K [244, 245]. The β_H -salt returned to β_L -salt when the salt was kept above 125 K at ambient pressure. The T_c of β_H -salt decreased with hydrostatic pressure monotonically; however, under the uniaxial stress the further T_c increase taking a maximum at a piston pressure of 0.3–0.4 GPa is observed for both directions parallel and perpendicular to the donor stack [246].

5.1.3 Superconductors of Other Donor Molecules

Besides ET, BO (two low T_c superconductors; see Sect. 3.4.2), TMTSF, and TMTTF superconductors, there are other superconductors (Scheme 15, numbers in bracket are the total members of each superconductor and the highest T_c) of CT salts based on symmetric (BETS [250], BEDSe-TTF [251], and BDA-TTP [252–255]) and asymmetric donors (ESET-TTF [256], *S,S*-DMBEDT-TTF [257], *meso*-DMBEDT-TTF [258, 259], DMET [260], DMEDO-TSeF [261, 262], DODHT [263], TMET-STF [264], DMET-TSeF [265], DIETS [266], EDT-TTF [267], MDT-TTF [268, 269], MDT-ST [270, 271], MDT-TS [272], MDT-TSF [273–276], MDSe-TSF [277], and DTEDT [278]). The reported T_c s of most superconductors recently prepared are the on-set T_c values that are approximately 0.5–1 K higher than the mid-point T_c values. T_c s of them are less than 10 K.

DMEDO-TSeF afforded eight superconductors. Six of them are κ -(DMEDO-TSeF)[Au(CN)₂](solvent) and their T_c s (1.7–5.3 K) are tuned by the use of cyclic ethers as solvent of crystallization [262].

β -(BDA-TTP)₂X (X = SbF₆, AsF₆) exhibited a slight T_c increase at the initial stage of uniaxial strain parallel to the donor stack and interlayer direction while T_c decreased perpendicular to the donor stack [253]. θ -(DIETS)₂[Au(CN)₄] exhibited superconductivity under uniaxial strain parallel to the *c*-axis ($T_c = 8.6$ K at 1 GPa), though under hydrostatic pressure a sharp MI transition remained even at 1.8 GPa [266].



Scheme 15 Component molecules for molecular superconductors except TMTSF, TMTTF, ET and BO systems. *Numbers in bracket* are the total members of each superconductor and the highest T_c (in K)

MDT-ST, MDT-TS, and MDT-TSF superconductors have noninteger ratio of donor and anion molecules such as (MDT-TS)(AuI₂)_{0.441} making the Fermi level different from the conventional 3/4 filled band for TMTSF and ET 2:1 salts [270–276]. The Fermi surface topology of (MDT-TSF)X (X = (AuI₂)_{0.436}, (I₃)_{0.422}), and (MDT-ST)(I₃)_{0.417} has been studied by SdH and AMRO [271, 274–276].

κ -(MDT-TTF)₂AuI₂ (T_c = 3.5 K) exhibited a Hebel–Slichter coherent peak just below T_c , indicating a BCS-type gap with s -symmetry [269], while d -wave like superconductivity has been suggested for β -(BDA-TTP)₂SbF₆ [254, 255].

The most intriguing phenomenon is the reentrant superconductor–insulator–superconductor transition under a magnetic field for (BETS)₂FeCl₄. Kobayashi et al. have developed BETS salts formed with tetrahedral anions MX₄ (M: Fe and Ga, X: Cl and Br) [279–283]. Especially salts with λ -[284, 285] or κ -type packings [279–281] have been studied in terms of the competition of magnetic ordering and superconductivity. The initial notable finding is for λ -(BETS)₂GaCl₄ with a superconducting transition at 8 K (mid-point 5.5 K) and for λ -(BETS)₂FeCl₄ with a coupled AF and MI transitions at 8.3 K. For the FeCl₄ salt, a relaxor ferroelectric behavior in the metallic state below 70 K [286] and a firm nonlinear electrical transport associated with the negative resistance effect in the magnetic ordered state have been observed [287]. Moreover, it has been found by Uji et al. that the FeCl₄ salt shows a field-induced superconducting transition under a magnetic field of 18–41 T applied exactly parallel to the conducting layers [285]. Interestingly, the λ -(BETS)₂Fe_xGa_{1-x}X₄ passes through a superconducting to insulating transition on cooling [288]. The κ -(BETS)₂FeX₄ (X = Cl, Br) are AF superconductors, where the transition temperatures were T_N = 2.5 K and T_c = 1.1 K for the Br salt, and T_N = 0.45 K and T_c = 0.17 K for the Cl salt [289]. Similar phenomena, namely AF,

ferromagnetic, or field induced superconductivity, have been observed in several inorganic solids such as the Chevrel phase [290] and heavy-fermion systems [291]. Recently it has been reported that λ -(BETS)₂GaCl₄ exhibited superconductivity in the minute size of four pairs of (BETS)₂GaCl₄ based on the scanning tunneling microscopy study [292].

5.2 Superconductors Based on Acceptor Molecules

There are three kinds of superconductors based on acceptor molecules: M(dmit)₂ (Scheme 15, M = Ni, Pd) [293], picene [294], and C₆₀ [141–143]. C₆₀ system has the highest T_c for molecular superconductors (T_c = 38 K) followed by the picene one (T_c = 18 K); however, those two systems are very unstable chemically (caused partly by very weak electron accepting ability) and decompose immediately at ambient condition.

5.2.1 dmit System

Eleven superconductors were prepared based on M(dmit)₂ (three for M = Ni, eight for M = Pd) and their T_c s are less than 8.4 K. Only one showed superconductivity at ambient pressure (EDT-TTF[Ni(dmit)₂], T_c = 1.3 K) [295]. Superconducting LB films of dimethylbis(tetradecyl)ammonium[M(dmit)₂] (T_c < 3.9 K) have been reported [296].

5.2.2 Picene System

Very recently, Kubozono and his coworkers reported new organic superconductors: alkali-metal doped picene compounds [294]. Although their shielding fractions are relatively small (<15%), the bulk superconducting phase was observed below 7.0 K for K_{2.9}picene, 18 K for K_{3.3}picene, and 6.9 K for Rb_{3.1}picene, in which the LUMO + 1 orbital for picene would be in a half-filled electronic state. For K_{3.3}picene, T_c is significantly higher than that of K-doped graphite (T_c ~ 5.5 K) [297] and comparable to that of K₃C₆₀ (T_c = 18 K) [141]. The Pauli-like paramagnetic susceptibility is higher than that of K_{2.9}picene with lower T_c , suggesting BCS-type superconductivity. At present, although the crystal structures of the doped compounds are unclear, the refined lattice parameters are indicative of the deformation of the herringbone structure of pristine picene and the intercalation of alkali dopants within the two-dimensional picene layers [294].

5.2.3 C₆₀ System

The icosahedral C₆₀ molecule with I_h symmetry has triply degenerate LUMO and LUMO + 1 orbitals with t_{1u} and t_{1g} symmetries, respectively, and C₆₀ can accept up to 12 electrons.

Immediately after the isolation of macroscopic quantities of C₆₀ solid [298], highly conducting [299] and superconducting [141] behaviors were verified for the K-doped compounds prepared by a vapor–solid reaction (Haddon, Hebard, et al.). Crystallographic study based on the powder X-ray diffraction profile revealed that the composition of the superconducting phase is K₃C₆₀ and the diffraction pattern can be indexed to be a face-centered cubic (fcc) structure with a three-dimensional electronic pathway [300]. The lattice parameter ($a = 14.24$ Å) is apparently expanded relative to the undoped cubic C₆₀ ($a = 14.17$ Å). The superconductivity has been observed for many A₃C₆₀ (A: alkali metal), e.g., Rb₃C₆₀ ($T_c = 29$ K [301]), Rb₂CsC₆₀ ($T_c = 31$ K [302]), and RbCs₂C₆₀ ($T_c = 33$ K; the highest T_c among the ambient pressure C₆₀ superconductors, reported by Tanigaki et al. [302]), and their structures are analogous to that of K₃C₆₀ with varying lattice constants. The T_c varies monotonically with the lattice constant, independently of the type of the alkali dopant [302, 303]. This behavior can be interpreted in terms of BCS theory, in agreement with the observation of Hebel–Slichter coherence peaks for NMR [304] and μ SR [305] and the normal isotope effect; namely T_c decreases by the isotopic substitution $^{12}\text{C} \rightarrow ^{13}\text{C}$ [306].

Keeping the C₆₀ valence invariant (−3), the intercalation of NH₃ molecules (e.g., (NH₃)K₃C₆₀) results in a lattice distortion from cubic to orthorhombic, accompanied by the appearance of AF ordering instead of superconductivity [307]. Changing the valence in cubic system also has a pronounced effect on T_c . For example, T_c in Rb_{3−x}Cs_xC₆₀ prepared in liquid ammonia gradually increases as the mixing ratio approaches $x = 2$ [308]. Further increasing the nominal ratio of Cs leads to a sizable decrease of T_c , despite the fact that the lattice keeps the fcc structure for $x < 2.65$. Such a band-filling control has been realized for Na₂Cs_xC₆₀ ($0 \leq x \leq 1$) [309] and Li_xCsC₆₀ ($2 \leq x \leq 6$) [310], and shows that T_c decreases sharply as the valence state on C₆₀ deviates from −3.

According to the relationship between the lattice volume and T_c as described, cubic Cs₃C₆₀ would be an ultimate candidate for a higher T_c superconductor, but the conventional vapor–solid reaction affords only the thermodynamically stable CsC₆₀ and Cs₄C₆₀ phases. In 1995, noncubic Cs₃C₆₀ was obtained by a solution process in liquid ammonia, and the superconductivity was observed below 40 K under an applied hydrostatic pressure of 1.4 GPa [311].

In 2008, the A15 or body-centered cubic (bcc) Cs₃C₆₀ phase, which shows bulk superconductivity under applied hydrostatic pressure, was obtained, together with a small amount of by-products of body-centered orthorhombic (bco) and fcc phases, by a solution process in liquid methylamine (Prassides, Rosseinsky, et al.) [312]. Interestingly, the lattice contraction with respect to pressure results in an increase in T_c up to around 0.8 GPa, above which T_c gradually decreases. The highest T_c is

38 K, which exceeds the value of $\text{RbCs}_2\text{C}_{60}$ (33 K). The trend in the initial pressure range is not explicable within the simple BCS theory. Under an ambient pressure, on the other hand, the A15 Cs_3C_{60} shows an AF ordering below 46 K, verified by means of ^{133}Cs NMR and μSR [313]. Very recently, it has been found that the fcc phase also shows an AF ordering at 2.2 K under an ambient pressure, and a superconducting transition at 35 K under an applied hydrostatic pressure of about 0.7 GPa [314]. Note that T_c of both phases follows the universal relationship for A_3C_{60} superconductors in the vicinity of the Mott boundary.

Some noncubic superconductors have been obtained for $\text{Yb}_{2.75}\text{C}_{60}$ ($T_c = 6$ K) [315], $\text{Sm}_{2.75}\text{C}_{60}$ ($T_c = 8$ K) [316], Ba_4C_{60} ($T_c = 6.7$ K) [317, 318], and Sr_4C_{60} ($T_c = 4.4$ K) [318]. Eu_6C_{60} with bcc packing undergoes a ferromagnetic transition at 12 K, arising from Eu^{2+} cations with $S = 7/2$ spin [319], and shows a giant negative magnetoresistance arising from a significant π - f coupling between the conduction electrons on C_{60} and localized $4f$ -electrons on Eu [320]. Ce_xC_{60} shows a coexistence of superconductivity and ferromagnetism below 13.5 K, although its crystal structure and composition are currently unclear [321].

C_{60} doped with K ($T_c < 8.1$ K) [322] and Rb ($T_c < 23$ K) [323] exhibit superconductivity on LB films, which was detected by the AC complex magnetic susceptibility or low magnetic field microwave absorption measurements. However, both the structural disorder inherent to the LB films and the low-dimensional nature of the thin-layer structure severely prohibit the observation of superconductivity by resistivity measurements.

As mentioned, the (super)conductors based on C_{60} and picene are chemically very unstable, and immediately decompose on exposure to air. Crystal engineering to protect such (super)conductors against air and moisture is essential for further investigation.

5.3 *Metallic Doped Polymers and Unidentified Organic Superconductors*

5.3.1 Polymer Superconductors and Metallic Polymer

Little's 1964 proposal for high T_c superconductivity was based on a polymer system having both a conduction path and highly polarizable pendants, which mediate the formation of Cooper pairs in the conduction path by electron–exciton coupling [324]. There are at least two inorganic polymer superconductors, poly(sulfur nitride) $(\text{SN})_x$ [325–327] and black phosphorus [328], with crystalline forms. The covalent bond of the golden crystal of $(\text{SN})_x$ has an ionic character by a partial electron transfer ($0.4 e$) from S to N. Weak interchain interactions between SN polymer chains give it a quasi-one-dimensional nature. Along the polymer chain, the σ_{RT} value is $1\text{--}4 \times 10^3 \text{ S cm}^{-1}$, rising by a factor of ca. 10^2 at 4.2 K and superconductivity appeared at $T_c = 0.26$ K and T_c increased under pressure ($T_c \leq 3$ K). Black phosphorus has a two-dimensional

layer structure with $\sigma_{RT} \sim 1 \text{ S cm}^{-1}$ and exhibited superconductivity under pressure ($T_c \sim 6 \text{ K}$, 16 GPa). When the sample was pressurized after cooling the sample at ambient pressure to 4.2 K, T_c increased considerably ($T_c = 10.7 \text{ K}$, 29 GPa). These are metallic and superconducting polymers without doping.

After Little's proposal, many researchers have pursued such an exciting system in vain. Even metallic behavior was rarely seen in doped organic polymers, gels, and actuators. As mentioned in Sect. 3.4.4, MC_{60} with linearly polymerized $\text{C}_{60}^{\pm}$ exhibited one-dimensional ($M = \text{Rb}, \text{Cs}$) or three-dimensional ($M = \text{K}$) metallic behavior [144]. Recently a doped polyaniline was reported to exhibit a metallic temperature dependence for a crystalline polymer; chemical oxidation of monomers grew crystallite polyaniline [329]; early doping studies on polypyrrole (PF_6) and poly(3,4-ethylene-dioxythiophene)X ($X = \text{PF}_6, \text{BF}_4, \text{and CF}_3\text{SO}_3$) prepared by electrooxidation at low temperatures also showed a metallic temperature dependence below 10–20 K (Scheme 16) [330, 331].

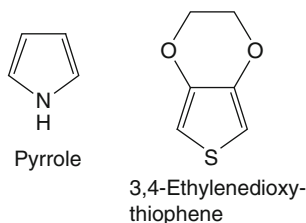
So far no organic polymers have been confirmed to show superconductivity, in spite of several unconfirmed polymer superconductors mentioned below. It should be remembered that the sample should be well oriented, otherwise the disorder inherent to organic polymers will destroy the superconductivity.

5.3.2 Unidentified Superconducting Organics

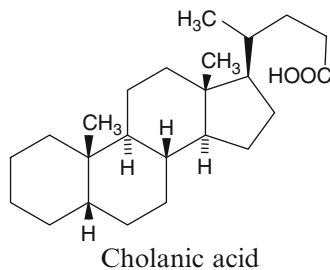
There have been several experimental reports describing very high T_c s or very fascinating materials with low T_c though these data are not reproducible.

The most puzzling one was the Na salt of cholanate with $T_c = 277.0 \text{ K}$ reported in 1976, though cholanic acid does not have π -electrons (Scheme 17) [332]. The superconductivity was detected by conductivity and magnetic measurements. The authors mentioned that the salt showed an insulator to superconducting transition and the transition was fractional. Very recently, a biological compound (double-stranded DNA) was reported to exhibit proximity-induced superconductivity below 1 K [119]. The deionized DNA molecules are insulating and superconductivity cannot be expected.

In 1978, aniline black was reported to show possible superconductivity by the irreversible drop of resistivity by 10^6 in the I – V measurements at RT around 250 V ($T_c = 295.5 \text{ K}$) [333]. In 1989, a resistance drop by nine orders of magnitude and a strong



Scheme 16 Chemical structures of pyrrole and 3,4-ethylene-dioxythiophene



Scheme 17 Chemical structure of cholic acid

diamagnetism which was destroyed by magnetic field were reported on polypropylene oxidized for 3 years ($T_c = 293$ K) [334]. Oligo- and polyphthalocyanines have been reported to exhibit T_c of 83 and 92 K, detected by LFMA (low-field magnetic absorption) [335], which is very sensitive but sometimes gives false signals.

6 Spin Disordered State (Quantum Spin Liquid State) Neighboring Superconductivity

Figures 13 and 16b, and also the phase diagrams for electron-correlated C_{60} [336], cuprate oxide, iron pnictide, and heavy fermion systems [337], indicate that a magnetic ordered state (SDW, AF) can be located in a phase diagram next to the superconducting state. However, for the system having very strong electron frustrations a new exotic magnetic state (quantum spin liquid state without any magnetic order) appeared. That spin liquid state has only been predicted theoretically [338]. Furthermore, the superconducting state neighbors directly to the spin liquid state for the Mott insulator $\kappa-(ET)_2Cu_2(CN)_3$ **34** (in Table 6), which has a larger anion space than those for four 10 K class superconductors **29–32** in Table 6. Its Fermi surface has a similar shape to that of $\kappa-(ET)_2Cu(NCS)_2$ [339–341].

6.1 New Spin State Originated from Strong Spin Frustrations: Quantum Spin Liquid State

Figure 17a shows the packing motif of $\kappa-(ET)_2Cu_2(CN)_3$ where an ET dimer, which is encircled by an ellipsoid, is a unit with $S = 1/2$ spin. The geometry of the spin lattice (Fig. 17b) is a triangular lattice with two kinds of transfer integrals, $t = (|t_p| + |t_q|)/2$ and $t' = t_b/2$ [343, 344], suggesting that the system has a strong spin frustration. All κ -type salts have such triangular spin lattice, though the magnitude of the frustration depends on the shape of the triangle and the ratio t'/t is a good parameter to estimate the frustration. The t'/t values for $\kappa-(ET)_2X$ in Table 6 calculated by extended Hückel

method indicate that the spins in κ -(ET)₂Cu₂(CN)₃ ($t'/t = 1.06$) are severely frustrated compared with the other κ -type salts ($t'/t = 0.7$ – 0.9). Even though the previous density-function theory (DFT) calculations [345, 346] gave a little higher t'/t and the recent DFT calculations using a generalized-gradient-approximation gave the smaller t'/t (~ 0.8) [347, 348] than unity, κ -(ET)₂Cu₂(CN)₃ exhibited the unprecedented features caused by strong spin frustration.

Figure 17c,d compares the line shapes of ¹H NMR absorption of κ -(ET)₂Cu₂(CN)₃ and κ -(ET)₂Cu[N(CN)₂]Cl, respectively. κ -(ET)₂Cu[N(CN)₂]Cl exhibited a drastic change below 27 K owing to the formation of three-dimensional AF ordering, while, the absorption band of κ -(ET)₂Cu₂(CN)₃ remained almost invariant down to 32 mK, indicating a nonspin-ordered state: the quantum spin liquid state [342, 349–357].

The three Mott insulators, κ -(ET)₂Cu[N(CN)₂]Cl, deuterated κ -(ET)₂Cu[N(CN)₂]Br, and κ -(ET)₂Cu₂(CN)₃, have nearly the same U_{eff}/W (~ 0.9); however, the electronic ground states of them are different. The spins in the former two salts condensed into the AF state because of the less frustrated spin geometry in κ -(ET)₂Cu[N(CN)₂]Cl ($t'/t \sim 0.75$) and D-salt of κ -(ET)₂Cu[N(CN)₂]Br ($t'/t = 0.68$ for the H-salt). Since the spin frustration is quite significant in κ -(ET)₂Cu₂(CN)₃ because of the equilateral triangle spin geometry, the formation of the AF and superconducting states is suppressed at ambient pressure and the unprecedented spin liquid state appears instead.

Controversial discussions ensued concerning the magnitude of the gap of the spin liquid state. Specific heat measurements suggested a gapless nature [358], while thermal conductivity measurements suggested a small gap [359]. Furthermore, there is an abnormality in lattice near 5–6 K which was detected by ¹³C NMR [357] and thermal expansion [360] measurements, indicating that the lattice is not frozen even at 5–6 K.

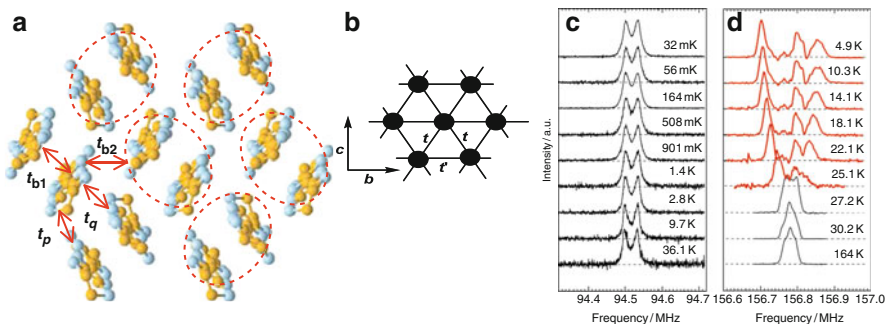


Fig. 17 (a) Donor packing pattern of κ -(ET)₂Cu₂(CN)₃ along the *a*-axis (transfer integrals; $t_{b1} = 22$ meV, $t_{b2} = 12$ meV, $t_p = 8$ meV, and $t_q = 3$ meV) and (b) triangular spin lattice ($t'/t = 1.06$; $t' = t_{b2}$, $t = (|t_p| + |t_q|)/2$) composed of the ET dimer which is encircled by an *ellipsoid* in (a) and represented by *closed circle* in (b). Line shape of ¹H NMR of (c) κ -(ET)₂Cu₂(CN)₃ [342] and (d) κ -(ET)₂Cu[N(CN)₂]Cl [209]

6.2 Emergence of Superconducting State Next to Spin Liquid State

The uni-axial strain method can apply strain only along one direction. For κ -(ET)₂Cu₂(CN)₃, uni-axial strain changed the temperature dependence of resistivity from that depicted in Fig. 15 to be similar to those of **30** and **31**, namely semiconductor–metal–superconducting behavior. A superconducting state readily appeared nearly above 0.1 GPa in both directions along the *b*- (Fig. 18 right figure: t'/t increases in this direction) and *c*- (Fig. 18 left figure: t'/t decreases in this direction) axes [361], without passing through the spin-ordered state. The appearance of the superconducting state is ascribed to the release of the strong spin frustrations since the t'/t deviates from unity in both directions. Within the *bc*-plane, the superconducting state appeared above 0.1 GPa [$T_c = 3.8$ K (*//b*), 5.8 K (*//c*)] and T_c increased up to 6.8 K (*//b*, 0.5 GPa) and 7.2 K (*//c*, 0.3 GPa). Along the *a**-axis, the superconducting state appeared above 0.3 GPa.

A plot of T_c vs T_{IM} (Fig. 19), which is a Mott insulator–metal transition temperature, indicates that the pressure dependence of T_c behaves similarly in both directions. However, the uni-axial results are considerably different from those resulting under hydrostatic pressure, which extinguish the superconducting phase above 0.3 GPa. κ -(ET)₂Cu₂(CN)₃ was converted to a metal and superconductor by applying hydrostatic pressure through a Mott insulator–metal transition at 13–14 K with a resistivity drop by 10^5 [354, 362]. The critical pressure and T_c under hydrostatic pressure differ within the literature [203, 205–207, 354, 362], reflecting anisotropic nature of T_c and high sensitivity to the inclusion of Cu²⁺ and N(CN)₂ anion as described in the next section. The uni-axial method afforded (1) a much higher T_c value, (2) an increase of T_c at the initial pressure region, (3) an anisotropic pressure dependence, and (4) superconducting phase remaining at higher pressure compared with that of hydrostatic results. There have been many hydrostatic pressure studies on systems having very anisotropic electronic structures. According to the results in Fig. 19 where the hydrostatic pressure results do not agree with

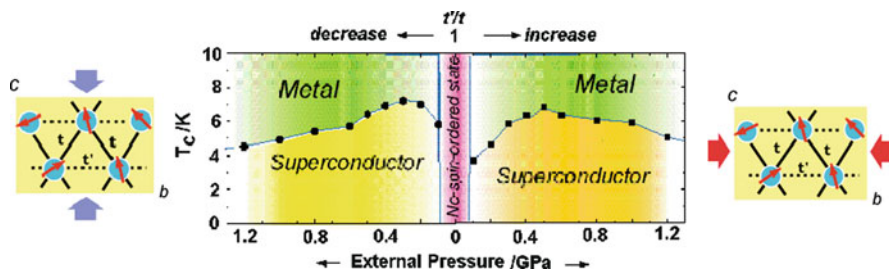
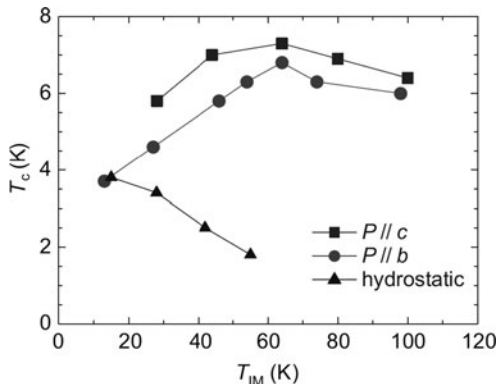


Fig. 18 Temperature–uniaxial pressure phase diagram in the low temperature region of κ -(ET)₂Cu₂(CN)₃ [361]. The strain along the *c*-axis corresponds to decrease t'/t (left side), while the stress along the *b*-axis increases t'/t (right side)

Fig. 19 Pressure dependence of on-set T_c of κ -(ET)₂Cu₂(CN)₃ by the uni-axial strain and hydrostatic pressure methods



any of those along the principal axes or their averaged ones, it is very difficult to understand logically the hydrostatic pressure results.

The emergence of the superconducting state is interpreted by both the increase of U_{eff}/W and the deviation of t'/t from unity. The increase of T_c in the initial pressure regime is ascribed to the reduction of the spin frustration. The following decrease of T_c in whole measured directions is explained by the decrease of $D(\varepsilon_F)$ owing to the increase of W . The appearance of superconducting state immediately after the release of the spin frustration in the spin liquid state is an indication of the importance of the magnetic mediation for superconductivity. The uni-axial strain experiments, which included other κ -type superconductors, clearly revealed that T_c increased as the U/W approaches unity and as the t'/t departs from unity (Fig. 20) [363].

Following κ -(ET)₂Cu₂(CN)₃, five materials [364], including EtMe₃Sb[Pd(dmit)₂]₂ as an organic solid [365], have been found to have quantum spin liquid states; however, superconductivity has been confirmed only for κ -(ET)₂Cu₂(CN)₃.

6.3 Control of U/W and Band Filling: κ' -(ET)₂Cu₂(CN)₃

The anion structure of the Mott insulator κ -(ET)₂Cu₂(CN)₃ **34** in Fig. 21 revealed the disorder in the position of C and N atoms of the C≡N groups (L₂ part; Table 6, Fig. 21a) [205–207, 370], due to the existence of an inversion center. However, ¹³C NMR experiments observed very sharp resonance lines due to the homogeneous local field in the metallic state [371], which suggests that the C/N disorder, if any, does not work as the disorder potential in the conduction layer.

Owing to the very similar geometrical shape, size, and equal charge between Cu(CN)₂[N≡C–Cu–C≡N for X–Cu–Y, with obtuse bond angle of 120.1°] and N(CN)₂[N≡C–N–C≡N, bond angle 116.7°], they were nearly freely replaceable with each other in the anion layer, resulting in comparable lattice parameters among κ -(ET)₂Cu(CN)₃, κ -(ET)₂Cu(CN)[N(CN)]₂, and their alloy, κ' -salt (Fig. 21a–c).

Fig. 20 T_c of κ -(ET)₂X salts are plotted as function of t'/t and U/W [363]. X = I₃ (a), Ag(CN)₂·H₂O (b), Cu(CN)[N(CN)₂] (c), and Cu[N(CN)₂]Cl (d). Blue and yellow arrows indicate the direction of t'/t decreases and U/W increases, respectively. Red arrows correspond to the change of T_c by applying uni-axial strain

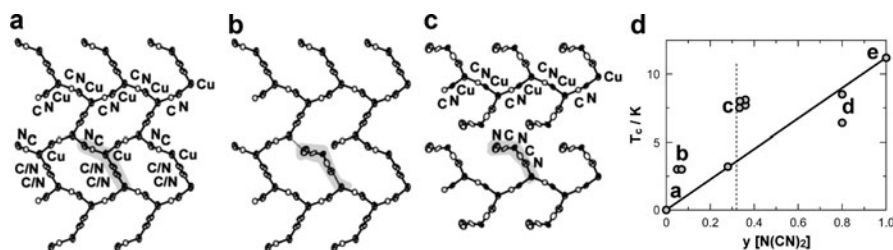
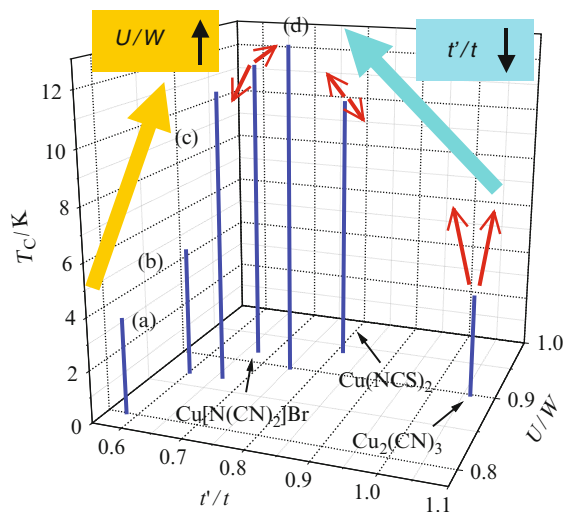


Fig. 21 The anion structures of (a) κ -(ET)₂Cu₂(CN)₃ and (c) κ -(ET)₂Cu(CN)[N(CN)₂]. (b) A schematic figure of κ -(ET)₂(Cu²⁺_{2-x-y}Cu¹⁺_x){(CN)_{3-2y}[N(CN)₂]_y} with $y \sim 0.1$. (d) Relation between the content of N(CN)₂, y and T_c in several crystals of κ' salt: κ -(ET)₂(Cu¹⁺)_{2-x-y}(Cu²⁺)_x(CN)_{3-2y}[N(CN)₂]_y. As for points a–e, see text. Dashed line indicates the samples of $y \sim 0.3$ [362, 366–369]

It was found that the exact chemical formula of κ' -(ET)₂Cu(CN)₃ was κ -(ET)₂(Cu¹⁺_{2-x-y}Cu²⁺_x){(CN)_{3-2y}[N(CN)₂]_y} and its transport natures were governed by the amount of Cu²⁺ (x) and ligand [NC–N–CN][−] (y) [368]. At $x = 0$ and $y = 0$, the salt is a Mott insulator κ -(ET)₂Cu₂(CN)₃ (point a in Fig. 21d), while the other extreme side ($x = 0$, $y = 1$) is κ -(ET)₂Cu(CN)[N(CN)₂] with $T_c = 11.2$ K at ambient pressure (point e). By changing both x (80–1,200 ppm) and y [preferential values of y are 0.05 (point b), 0.3–0.4 (c), 0.8 (d)], the T_c was tuned from 3 to 11 K. At $y = 0.3$ –0.4, the T_c ranged from 3 to 10 K and the crystals with different T_c had different x values, indicating that the charge of ET was modified from +0.5 to +0.5 (1 − x), that corresponds to the change of chemical potential, i.e., band-filling. T_c increased with increasing x (= the content of Cu²⁺) up to 400 ppm, and then T_c decreased.

These experimental facts indicate that this system can be an excellent model of band-filling control, and will be a good candidate for making a superlattice composed of Mott insulator/superconductor hetero-junctions. It should be emphasized that their lattice parameters are nearly kept constant through such an anion modification, which is the most essential feature for achieving the successful tuning of T_c in an organic superconductor.

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