Crystal structures and electrical conducting properties of the first molecular metals based on a novel electron acceptor, 4-oxo-2,6-bis(dicyanomethylene)-2,6-dihydrocyclopentadithiophene (CPDT)

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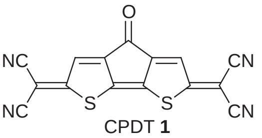
A novel electron acceptor CPDT has been synthesized; the Fermi surfaces of the metallic anion radical salts of CPDT are purely one-dimensional, while the acceptor molecules form rigid and tight two-dimensional networks in the crystal structures of the salts.

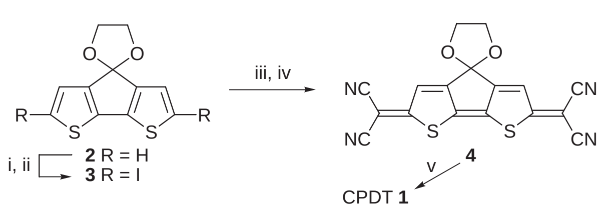
Electron-accepting molecules with three terminal electron-withdrawing groups appear to be promising components for organic conductors because they would have high electron accepting abilities as well as highly rigid and coplanar conformations, giving stable anion radicals and dianions owing to the effective conjugation of the three terminal groups.[1] We have now designed and successfully synthesized such a novel acceptor molecule, 4-oxo-2,6-bis(dicyanomethylene)-2,6-dihydrocyclopenta[2,1-*b*;3,4-*b*′]dithiophene (CPDT) **1**. Furthermore, we have obtained metallic anion radical salts of **1** and have clarified the conducting properties and crystal structures of the metallic salts. These are the first examples of molecular metals of the heterophene–TCNQ family.[2]



CPDT **1**

CPDT was synthesized starting from the ketal **2**[3] (Scheme 1). CPDT‡ is reduced reversibly in three successive one-electron transfer reactions to give the stable anion radical, dianion and trianion radical species which demonstrate, by cyclic voltammetry, three pairs of single-electron redox waves with good reversibility at half-wave reduction potentials of +0.04, −0.27 and −1.43 V (*vs*. SCE in CH_2Cl_2 at 25 °C). The first reduction potential is more positive by 0.18 V than that of **4** (−0.14 V). The log K_{sem} value[4] of CPDT (5.26) is larger by 1.36 than that of **4** (3.90), indicating that the anion radical of CPDT is thermodynamically stabilized by delocalization of the unpaired electron over the three terminal electron-accepting groups.

Interestingly, the crystalline anion radical salts $(Me_4N)[CPDT]_2$, $(Et_4N)[CPDT]_2$, $(Me_4P)[CPDT]_2$ and $(Me_4As)[CPDT]_2$, prepared by electrochemical reduction, are metallic at room temperature and their conductivities reach maximum values (σ_{max}) of 170, 290, 55 and 55 S cm^{-1} at the $T_{\sigma\mathrm{max}}$ values listed in Table 1. $T_{\sigma\mathrm{max}}$ becomes lower as the size of the counter cation in these four salts is increased. Below $T_{\sigma\mathrm{max}}$, the metallic states gradually become unstable, and drastic decreases in the conductivities with the transition to the semiconducting phases occurred at *ca*. 130 K for the Me_4N salt, 150 K for the Et_4N salt, 165 K for the Me_4P salt and 173–185 K for the Me_4As salt [Table 1 and Fig. 1(*a*)]. The metallic properties were also confirmed by the temperature dependence of the magnetic susceptibility measurement using a SQUID susceptometer [Fig. 1(*b*)]. The magnetic susceptibilities of the Me_4N and Me_4As salts are invariable from room temperature down to T_{DIA} = 135 and 50 K, respectively, which are regarded as Pauli-like, and decrease drastically at these temperatures with the transition to the diamagnetic phases. The phase transition mechanisms seem to be significantly different from each other, although the crystal structures are isomorphous, as described below. Occurrence of the Peierls type transition is suggested in the Me_4N salt, since T_{MI} is almost identical with T_{DIA}. However, in the Me_4As salt, the magnetic susceptibility does not decrease even after the M–I transition has occurred [Fig. 1(*b*)], and the magnitude of the magnetic susceptibility of the Me_4As salt (8×10^{-4} emu mol^{-1}) is significantly large when compared with those of ordinal molecular metals. These phenomena suggest the existence of a $4k_F$ charge density wave (CDW) growing phase[5] at the temperature region between 150 (T_{MI}) and 50 K (T_{DIA}) in the Me_4As salt.



Scheme 1 *Reagents and conditions*: i, LiBu, THF, −40 °C, then 0 °C, 30 min; ii, I_2, Et_2O, −78 °C, then room temp., 30 min, 56%; iii, $NaCH(CN)_2$, THF, $Pd(PPh_3)_4$, THF, reflux, 4 h; iv, Br_2, H_2O, room temp., 74%; v, 70% aq. $HClO_4$, CH_2Cl_2, 0 °C, 3 h, 96%

Table 1 Properties of anion radical salts of CPDT

Cation	Ratio[a]	σ_{rt}[b]/S cm^{-1}	$T_{\sigma\mathrm{max}}$/K	T_{MI}/K
Me_4N	1 : 2	160	250	130
Et_4N	1 : 2	260	220	150
Me_4P	1 : 2	47	215	165
Me_4As	1 : 2	42	173	173–185

[a] By elemental analysis. [b] Measured by four probe method on a single crystal.

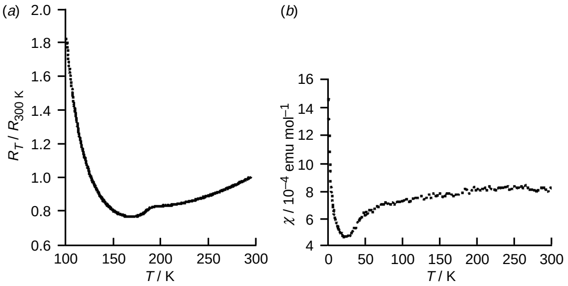


Fig. 1 Temperature dependence of (*a*) the resistivity and (*b*) the magnetic susceptibility of $(Me_4As)[CPDT]_2$

The crystal structures of the metallic salts $(Me_4N)[CPDT]_2$, $(Me_4P)[CPDT]_2$ and $(Me_4As)[CPDT]_2$, which are isomorphous with each other, were determined by X-ray analysis.§ The unit cell contains four crystallographically equivalent acceptor molecules and two equivalent cations, giving a cation to acceptor ratio of 1 : 2. The formal charge on CPDT is −0.5. The unit cell contains two acceptor columns stacking along the *b*-axis and each column is separated by a cation layer [Fig. 2(*a*)].

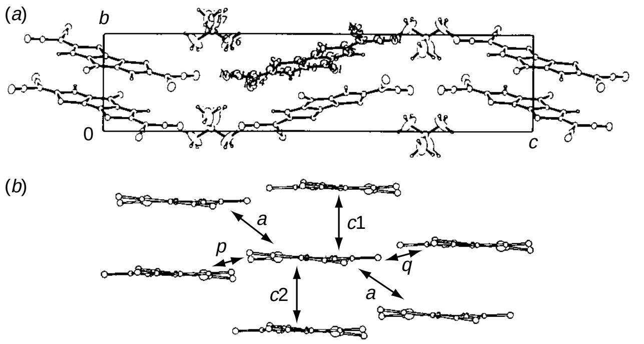


Fig. 2 Crystal structure of Me$_4$N[CPDT]$_2$: (*a*) projection onto the *bc*-plane and (*b*) overlap mode viewed along the acceptor short axis

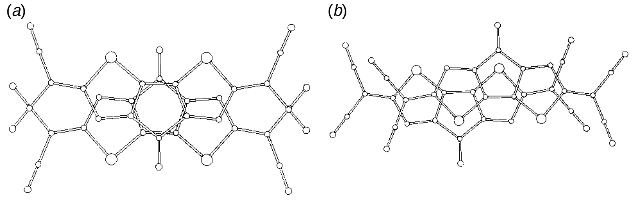


Fig. 3 Overlaping modes of CPDT molecules in (Me$_4$N)[CPDT]$_2$: (*a*) intra-dimer overlap, (*b*) inter-dimer overlap

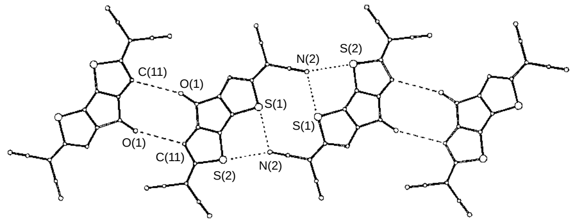


Fig. 4 Side-by-side interaction of CPDT in (Me$_4$N)[CPDT]$_2$

The acceptor column is constituted by weakly dimerised CPDT molecules with intra-dimer interplanar distances of 3.20–3.21 Å [*c*1 in Fig. 2(*b*)] and inter-dimer interplanar distances of 3.32–3.33 Å [*c*2 in Fig. 2(*b*)]. The overlapping mode is the so-called 'ring-over-ring' type in the intra-dimer overlap and the 'ring-over-bond' type in the inter-dimer overlap (Fig. 3). Interestingly, there are two S1–N2 (3.01–2.97 Å) and two S2–N2 (3.04–2.99 Å) contacts, and there are two short intermolecular hydrogen bonds between O1··H11 (3.25–3.28 Å) along the acceptor short axis in the crystal structures of these salts (Fig. 4). Thus rigid and tight two-dimensional layered intermolecular networks are constructed along the *ab*-plane.

The intermolecular overlap integrals of the metallic salts are summarized in Table 2. There is no significant difference between *c*1 and *c*2, which indicates that the degree of the dimerization is very weak in these salts. On the other hand, the overlap integrals along the acceptor shot axis are less than 1/300 of *c*1 or *c*2 (Table 2), in spite of the existence of the inter-column S–N and O–H contacts. This is ascribed to the extremely small π-atomic orbital coefficients of the O and the S atoms in the LUMO of CPDT. From the tight-binding band calculations[6] using the overlap integrals shown in Table 2, it is demonstrated that these salts have highly one-dimensional Fermi surfaces opened along the *a**-axis [Fig. 5(*a*)]. These salts have a split band structure due to their dimerized crystal structures and the lower energy band is half filled [Fig. 5(*b*)]. The calculated band widths are 0.73, 0.67 and 0.68 eV in the Me$_4$N, Me$_4$P and Me$_4$As salts, respectively. The phase transition of the Me$_4$N salt at 130 K appears to be caused by a Peierls transition, since salts with a large band width can obtain a large energy benefit by forming the band gap.

Table 2 Intermolecular overlap integrals (*S*) of the anion radical salts[a]

	$S/10^{-3}$		
Overlap direction[b]	Me$_4$N salt	Me$_4$P salt	Me$_4$As salt
*c*1 (intra-dimer)	−19.65	−18.83	−18.83
*c*2 (intra-dimer)	16.53	14.37	15.14
a (inter-column)	0.0744	0.0559	0.0713
p (S1–N2 contact)	0.00429	0.0913	0.00393
q (O1–H11 contact)	0.00672	0.0104	0.0260

[a] Calculated with π-atomic orbital coefficients obtained by the extended Hückel MO method using bond angles and bond lengths obtained from the X-ray analysis. [b] The overlap directions are indicated in Fig. 2(*b*).

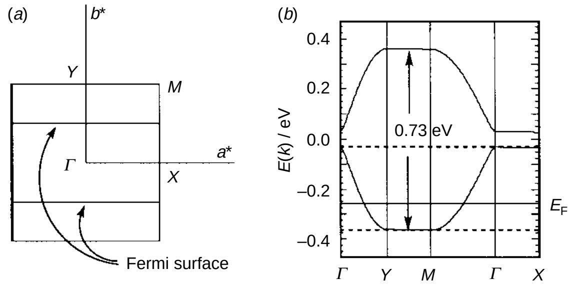


Fig. 5 (*a*) Fermi surface and (*b*) band structure of (Me$_4$N)[CPDT]$_2$, calculated by the tight binding approximation method

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Notes and References

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‡ *Selected data* for CPDT **1**, mp > 300 °C; ν_{max}(KBr)/cm^{-1} 3047, 2218, 1732, 1504, 1460, 1325, 1252, 1225, 957, 897, 760; λ_{max}(CH$_2$Cl$_2$)/nm (log ε) 553 (sh, 4.32), 520 (4.93), 489 (4.74), 458 (sh, 4.37), 360 (3.48), 341 (3.62), 323 (sh, 3.75), 314 (sh, 3.89), 297 (4.27), 286 (4.26), 274 (4.16); *m*/*z* (70 eV) 321 (M$^+$ + 3, 2.23%), 320 (M$^+$ + 2, 11.47), 319 (M$^+$ + 1, 19.38) and 318 (M$^+$, 100) [HRMS: 317.9673 (M$^+$]. Calc. 317.9670] (Calc. for $C_{15}H_2N_4OS_2$: C, 56.60; H, 0.63; N, 17.60. Found: C, 56.44; H, 0.78; N, 17.39%).

§ *Crystal data* for (Me$_4$N)[CPDT]$_2$: monoclinic, space group *P*2/n, a = 7.4763(7), b = 6.9411(7), c = 30.428(4) Å, β = 91.523(10)°, V = 1578.5(3) Å^3, Z = 4, $\rho_{calc.}$ = 1.495 g cm^{-1}, μ(Cu-Kα) = 31.81 cm^{-1}, R (R_w) = 0.062 (0.067) for independent 2129 reflections [$I > 5.00\sigma(I)$]. For (Me$_4$P)[CPDT]$_2$: monoclinic, space group *P*2/n, a = 7.446(2), b = 6.984(2), c = 31.596(2) Å, β = 92.33(2)°, V = 1641.7(6) Å^3, Z = 4, $\rho_{calc.}$ = 1.472 g cm^{-1}, μ(Cu-*K*α) = 35.10 cm^{-1}, R (R_w) = 0.035 (0.038) for independent 2203 reflections [$I > 3.00\sigma(I)$]. For (Me$_4$As)[CPDT]$_2$: monoclinic, space group *P*2/n, a = 7.430(1), b = 6.994(2), c = 31.922(2) Å, β = 92.50(1)°, V = 1657.2(5) Å^3, Z = 4, $\rho_{calc.}$ = 1.546 g cm^{-1}, μ(Cu-Kα) = 41.30 cm^{-1}, R (R_w) = 0.034 (0.036) for independent 2446 reflections [$I > 3.00\sigma(I)$]. The data were collected on a Rigaku AFC-5R diffractometer with graphite monochromated Cu-Kα radiation (λ = 1.54178 Å, ω–2θ scan technique). After absorption correction, the structures were solved by direct methods (SIR92) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotopically. Some hydrogen atoms were refined isotopically, the others were included in fixed positions. CCDC 182/836.

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