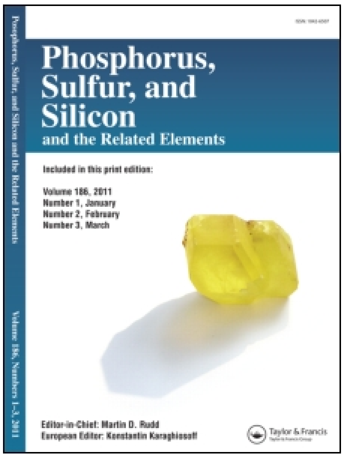

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Syntheses, Structures, and Thermal, Transport and Nonlinear Optical Properties of Tyc -Txf Compounds

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SYNTHESES, STRUCTURES, AND THERMAL, TRANSPORT AND NONLINEAR OPTICAL PROPERTIES OF TYC_n-TXF COMPOUNDS

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Abstract The syntheses, electric and structural properties of a series of uncapped $C_6X_4Y_4$ compounds (tetrakis(n-alkylchalcogeno)-tetrachalcogenafulvalenes; TYC_n-TXF) and nonlinear electric and optical properties of their CT complexes are described.

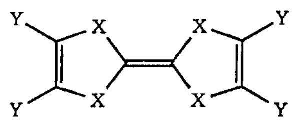
INTRODUCTION

Chalcogens in a molecule are known to increase molecular polarizability and reduce on-site Coulomb repulsion. In a solid, chalcogens have been used to increase dimensionality by the formation of intermolecular atomic contacts. These characteristics have provided many intriguing features on organic materials such as metallic, superconducting, non-linear transport properties, etc.

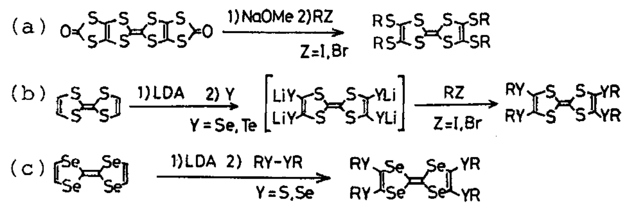
RESULTS AND DISCUSSION

Syntheses and Donor Abilities of TYC_n-TXF

The synthetic schemes of TYC_n-TXF are shown in Scheme 1. TTC_n-TTF(n=1-18) were synthesized from dithiapendione(Scheme 1a),[1] $TSeC_n$-[2] and $TTeC_n$-TTF(n=1-18)[3] were from TTF(Scheme 1b) and TTC_n-(n=1-14)[4,5] and $TSeC_n$-TSeF(n=1-12)[4,6] were by using dialkyldichalcogenide(Scheme 1c). It is noteworthy that the redox potentials of TYC_n-TXF are independent of the length of the alkyl chains.[7] The average redox potentials(E^1,



$C_6X_4Y_4$ compounds



Scheme 1

E^2 V vs SCE) of TYC_n-TXF are (0.64, 0.94, for X=Y=S),[7] (0.58, 0.93 for X=S,Y=Se),[2] (0.51, 0.91 for X=S,Y=Te),[3] (0.80, 1.08 for X=Se,Y=S),[5] and (0.75, 1.07 for X=Y=Se).[6] The donor ability of TYC_n-TXF increases from X=Se to S by 0.16-0.17eV, which is comparable to that from TSeF to TTF(0.59 vs 0.45V for E^1, respectively). The E^1 values of the TYC_n-TXF are not so much different from that of BEDT-TTF(0.63 V) indicating that the donor ability of TYC_n-TXF is moderately good.

Melting Points(T_m) and Thermal Properties of TYC_n-TXF

TYC_n-TXF exhibit the following three characteristics of melting:[1-10] 1)The carbon number dependences of T_m(Fig.1) show almost the same behavior among the series. 2)The cabon number n, where T_m shows minimum within a series, depends on Y and increases in the order of Y=S, Se, Te. 3)Generally T_m becomes higher in the order of Y=S, Se, Te.

These behaviors were analyzed by considering the enthalpy and entropy changes at T_m, $\Delta H_m=H_0+4nH^*$ and $\Delta S_m=S_0+4nS^*$, for the TYC_n-TTF series,[8-10] where nH*(or nS*) is the enthalpy(or entropy) ascribed to one of the four flexible alkyl chains, and H_0(or S_0) is the enthalpy (or entropy) which is independent of n. ΔH_m and ΔS_m were found to have linear relations with n for large n($\gtrsim$6-7), whereas these quantities show rather irregular dependence on n for small n(Fig.5 in Ref.9). From the linear part, H_0, H*(kJ/mol), S_0 and S*(J/K mol) were deduced and compared with those of n-alkanes.[11] It is noticed that H*(3.3~4.8 kJ/mol) and S*(8.3~12.1 J/Kmol) are almost the same to those of n-alkans(H*=3.0~4.1, S*=7.7~10.8) but H_0(-16.0~-58.6) and S_0(-14.0~-105.0) are considerably enhanced in the negative direction compared to those of n-alkanes(H_0=-11.2~-11.7, S_0=5.0~10.0). Both the negative values of H_0 and S_0 for large n and irregular deviation of ΔH_m and ΔS_m for small n together with the behaviors 2 and 3 above mentioned indi-

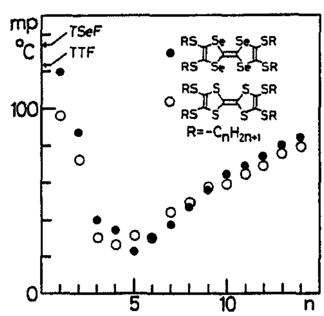


FIGURE 1 Melting points of TTC_n-TTF (o) and TTC_n-TSeF (•).

cate that the intermolecular atomic contacts using chalcogen Y play significant role in stabilizing the crystals in the small n region and the molecular associations of $C_6X_4Y_4$ moieties are more ordered in the large n region than those in the small n region.

Structures and Transport Properties

The molecular structures of TYC_n-TXF so far determined are classified into four types(Fig.2). The chair forms are usually observed for large n. The angle between the flat $C_6X_4Y_4$ plane and the alkyl chains is ca.50° for the form I and about 90° for the form II. With these conformations, a bundle of long alkyl chains assembles the central $C_6X_4Y_4$ moieties in a fashion that the flat π-electron system can pile up one after the other very tightly(Fig. 2). Some of them exhibit tight atomic contacts not only within the column but also between the adjacent columns so that they show 2-dimensional(2D) electronic natures. These features give low ionization potentials[12] and high conductivity with small activation energy as a single component material(e.g. σ_{RT} Scm^{-1} and E_aeV are $2.7x10^{-6}$, 0.13 for TTC_{10}-TTF, $6.7x10^{-6}$, 0.17 for TTC_{10}--TSeF, respectively).[5,13] High drift mobility(μ_e=6.8,μ_h=6.4cm^2/V s at RT) was observed in TTC_8-TTF.[14] This phenomenon; fastener effect,[15] is a concerted one between the van der Waals interactions of the long alkyl chains and the resonance interactions of the π-electron moieties.

When the alkyl chain is short, either boat or modified chair form

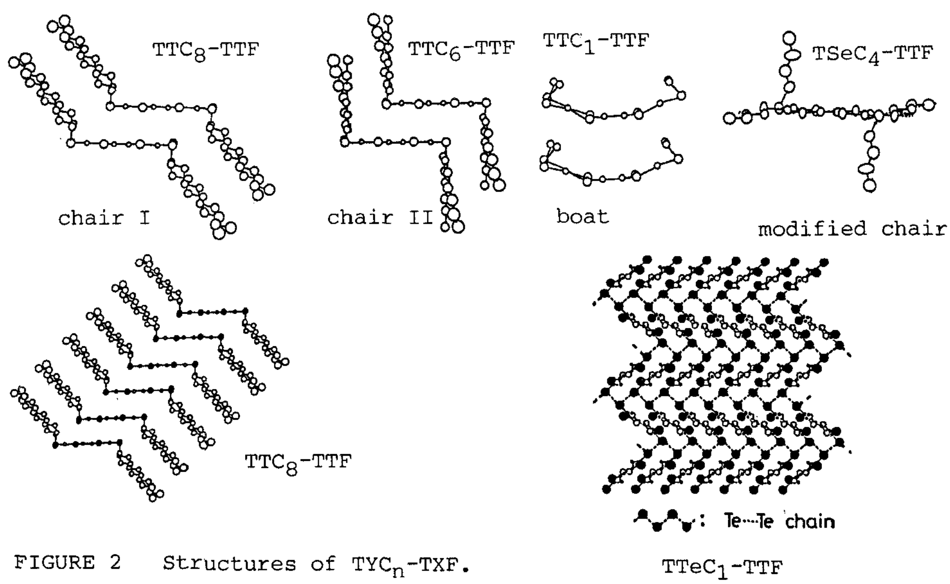


FIGURE 2 Structures of TYC_n-TXF.

is realized. Usually the alkyl chains prevent the proximate approach of $C_6X_4Y_4$ moieties in the boat form which results in poor σ_{RT} with high E_a (e.g. 3.4×10^{-11} Scm^{-1}, 0.38eV for TTC_1-TTF, 7.7×10^{-10}, 0.60 for TTC_1-TSeF). In the modified chair form, short intermolecular atomic contacts are formed often, especially using Y. $TTeC_1$-TTF is such compound with particular features. It forms 1D regular columns. Both the relatively large distances between the neighboring $C_6S_4Te_4$ planes (3.76A) and Te..Te atomic contacts($\geq$5.48A) within the column indicate that the direct face-to-face interactions are not responsible for the high conductivity(1.4×10^{-5} Scm^{-1}) and mobilities(μ_h=28.5, μ_e=18.6 cm^2/V·s). Between the neighboring columns were found remarkably short Te..Te contacts(3.64A, vdW sum=4.12A) which form a number of infinite zigzag atomic wires of ..Te..Te.. through the crystals(Fig.2).[16] Therefore, the novel transport of $TTeC_1$-TTF is most likely associated with the conductive Te..Te..Te infinite chains cooperated with the highly polarizable TTF segments which mediate the chains.

Complex Formation and Nonlinear Properties

A variety of complexes was prepared from TYC_n-TXF of short alkyl chain (mainly n=1-3).[1,4,7,13,17] TYC_n-TXF of long alkyl chain do not form complexes with common acceptors indicating strong steric hindrance.

$TTeC_1$-TTF·TCNQ(1:1, σ_{RT}=1.0×10^{-2} Scm^{-1}, E_a=0.11eV) shows two kinds of equivalent regular mixed stacks with different stacking directions (dihedral angles of 55.3°).[18] Since there are short atomic contacts between them, the resistivity anisotropy is quasi 3D(1:1:10). The regular stack dimerizes at 240K(Tc). The crystal ionicity was estimated to be ionic but very close to the neutral-ionic(N-I) boundary.

It has been known that regular mixed stack complexes such as TTF·p-chloranil(CA) show a phase transition between the neutral and ionic ground states,[19] and several anomalous physical properties have been observed,[20] most of which relate with the dimerization. Among them, a nonlinear transport where current density(J) increases with decreasing applied field(E) has attracted much attentions in connection with the switching effect. The conductivity in TTF·CA has been explained by the term of solitonic or domain-wall-like charge carriers.[21]

Figure 3 shows J-E characteristics of $TTeC_1$-TTF·TCNQ.[22] Below Tc the J-E curves exhibit a discontinuous jump to the negative resistance region which occurs at the critical point(J_T, E_T). With decreasing temperatures further, a switching effect with a large hysteresis was observed(Fig.2 in Ref.22b). A comparison of E_T values of several complexes which show the same phenomenon revealed a linear correlation between E_T and E_a values for neutral(or ionic) crystals.[22a] It was found that the E_T value decreases linearly as the ionicity approaches the N-I boundary from both the neutral and ionic sides. So far, $TTeC_1$-TTF•TCNQ has the lowest E_T value.

The inclusion of polarizable chalcogens in a molecule and the ionicity increase due to the complex formation are thought to be favorable to enhance the optical nonlineality. A preliminary study on the TYC_n-TXF complexes by third-order harmonic generation(THG) was done with a powder method at a pump-light wavelength of 1900 nm. Each component was inactive in THG and CT complexes did not show second harmonic generation. The THG intensities of p-nitroaniline and PTS[23] were taken as the references as 1 and 47, respectively. So far $TTeC_1$-TTF•DTNF(relative THG intensity=25), $TTeC_1$-TTF•BTDA-TCNQ(15), $TTeC_1$-TTF•TCNQ(ca.25), $TTeC_2$-TTF•TCNQ(ca.40), $TSeC_1$-TSeF•F_4TCNQ(25), $TSeC_1$-TTF•DTNF(0) and $TSeC_1$-TTF•TCNQ(0) have been examined in the TYC_n-TXF series. Some of them have fairly high THG activity but the most active complex was HMTTeF•DCAQ(>50) in our study. However, the THG intensity is still smaller than the reported value of perylene•TCNQ(4.1 times than that of PTS) which does not contain chalcogens.[24]

These optically active complexes above mentioned have neutral ground state except the F_4TCNQ complex. So one may expect that mixed stack with low ionicity is essential to give high THG intensity due to the high electronic polarization. But this statement is too vague to define THG active complexes. In fact there are so many exceptions. Some are inactive in THG even though they belong to the above category. Others are active even though they are ionic with segregated

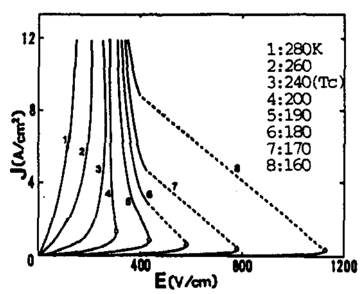


FIGURE 3 Nonlinear transport of $TTeC_1$-TTF•TCNQ, O indicates (J_T, E_T).[22]

stacks(e.g. κ-(BEDT-TTF)$_2$ Cu(NCS)$_2$ (40)). Since the quantitative and systematic investigations of the molecular and crystal polarizability and structural analyses are not sufficient, the understanding of the origin of the large THG intensity of CT complexes is the future work.

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