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Synthesis and properties of hetero-halogenated TTFs†

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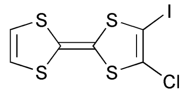
Novel hetero-halogenated TTFs containing both chlorine and iodine atoms were prepared and their unique characters based on the halogen atoms were examined.

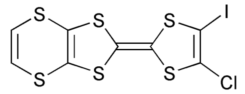
Since the discovery of "organic metal" TTF–TCNQ,[1] a great number of TTF derivatives have been synthesized during the last three decades.[2] Among them, halogenated TTFs[3,4] have attracted much attention in relation to the unique crystal and electronic structures of their cation radical salts. In contrast to the other halogenated TTFs, iodinated TTFs have special ability to construct an "iodine bond", which is the strong and directional I···X intermolecular interaction (X is a substituent including lone pair electrons). It originates in the smaller electronegativity of the iodine atom (2.2) compared with that of the carbon atom (2.5),[5] and also in the large coefficient of the $p\sigma^*$ LUMO on the iodine atom which interacts with the lone pair electrons. Since the physical properties of organic conductors are greatly influenced not only by the properties of a single molecule but also by the crystal structure, introduction of an "iodine bond" is one of the most effective methods of *crystal engineering*[6] in organic conductors.[4c–e] On the other hand, chlorinated or brominated TTFs were synthesized from the viewpoint of geometrical equivalence to the methyl group at first,[3c–e] however, cation radical salts including halogen-based intermolecular interactions are also reported as well as the iodinated TTFs.

In the course of our study on halogenated TTFs, we considered a simple but essential question: what is the difference in roles between the iodine and other halogen atoms in halogenated TTFs? This question prompted us to investigate the hetero-halogenated TTFs containing both iodine and chlorine atoms. In this paper, we report the first synthesis of hetero-halogenated TTFs together with their unique crystal and electronic character, which originates in the different nature between the chlorine and iodine atoms.

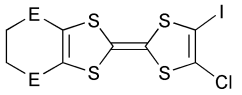
Synthesis of the key unit 4-chloro-5-iodo-[1,3]dithiole-2-thione **3** was accomplished by the stepwise halogenation outlined in Scheme 1. First, we attempted to introduce the chlorine atom into 4-iodo-[1,3]dithiole-2-thione **5**[7] because the synthesis of **5** has been already established. The reaction of **5** with various amounts of LDA followed by treatment with hexachloroethane (HCE) afforded, however, not only the desired product **3** but also 4,5-dichloro-[1,3]dithiole-2-thione **6**[8] and 4,5-diiodo-[1,3]dithiole-2-thione **7**.[4b] Competition between the chlorination of **5** and the disproportionation of 4-iodo-5-lithio-[1,3]dithiole-2-thione is suggested as shown in Scheme 2. Similar disproportionation has already been reported in a solution of lithio-TTF or halogenated thiophene derivatives[9,10] and it is difficult to separate these three compounds from the mixture by conventional column chromatography. These results prompted us to investigate another synthetic strategy, *i.e.* the iodination of 4-chloro-[1,3]dithiole-2-thione **2**. Mono-lithiation of **1** with 1.1 equiv. LDA in THF at −78 °C, followed by treatment with HCE (1.1 equiv.) afforded the dichloro derivative **6** and no trace of **2** was detected. It was assumed that disproportionation of 4-lithio-[1,3]dithiole-2-thione occurs according to the reported ring-opening reactions[11] and we modified the amounts of the reagents as follows: **1** (2.53 g) was di-lithiated by 2.2 equiv. of LDA in THF at −78 °C and following chlorination by quick treatment with HCE (3.30 g, 0.75 equiv. *vs.* thione) and subsequent hydrolysis at −78 °C afforded **2** as yellow crystals (1.38 g, 43%). The molecular structure of **2** was confirmed by NMR,



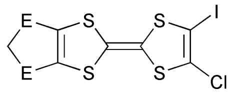
CII-TTF



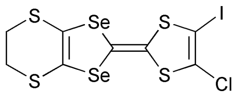
CIIVT



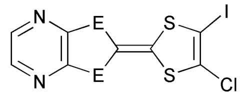
CIIEDO: E = O
CIIET: E = S
CIIEDS: E = Se



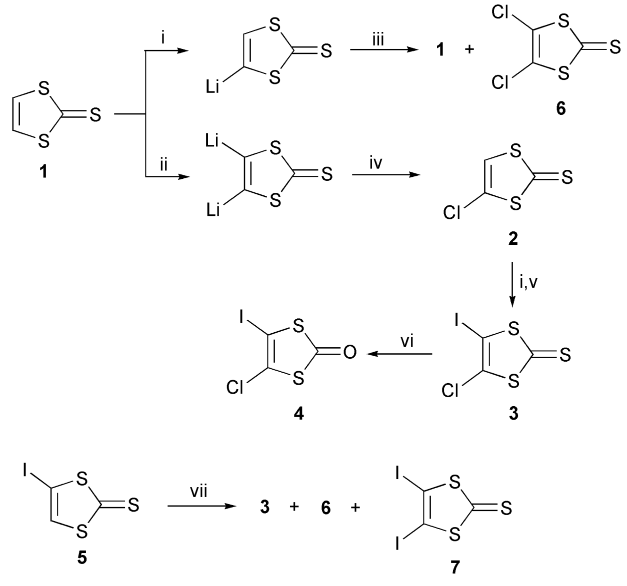
CIIMT: E = S
CIIMDS: E = Se



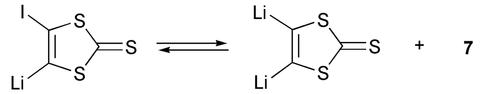
CIIETS



CIIP: E = S
CIIPS: E = Se



Scheme 1 *Reagents and conditions*: i, LDA (1.1 equiv.), THF, −78 °C; ii, LDA (2.2 equiv.), THF, −78 °C; iii, C_2Cl_6 (1.1 equiv.); iv, C_2Cl_6 (0.75 equiv.) then H_2O (43%); v, ICl (84%); vi, $Hg(OAc)_2$, $CHCl_3$–AcOH, r.t., (97%); vii, LDA then C_2Cl_6, THF, −78 °C.



Scheme 2 Disproportionation of 4-iodo-5-lithio-1,3-dithiole-2-thione.

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/ob/b3/b310822h/

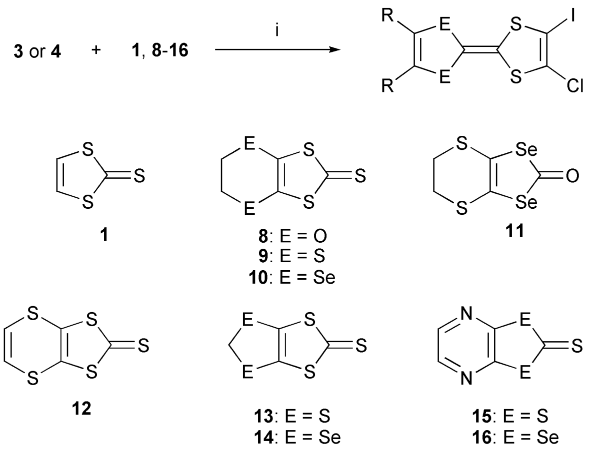
Table 1 Results of the cross-coupling reactions and cyclic voltammetry data[a] for new hetero-halogenated TTFs and related compounds

Donor	Materials	Solvent	Yield (%)[b]	Color	$E_1^{1/2}$/V	$E_2^{1/2}$/V	ΔE (= $E_2^{1/2} - E_1^{1/2}$)
TTF					−0.10	0.32	0.42
IEDT[12]					0.08	0.41	0.34
DIET[12]					0.14	0.47	0.33
ClI–TTF	**4** + **1**	Toluene	14	Orange	0.12	0.47	0.35
ClIEDO	**4** + **8**	Benzene	53	Red	0.11	0.44	0.33
ClIET	**4** + **9**	Toluene	70	Red	0.18	0.49	0.31
ClIEDS	**4** + **10**	Toluene	47	Orange	0.16	0.47	0.31
ClIETS	**3** + **11**	Toluene	44	Purple	0.26	0.52	0.26
ClIVT	**4** + **12**	Toluene	48	Orange	0.26	0.54	0.28
ClIMT	**4** + **13**	Toluene	44	Red	0.16	0.45	0.29
ClIMDS	**4** + **14**	Toluene	59	Red	0.13	0.43	0.30
ClIP	**4** + **15**	Toluene	67	Orange	0.45	0.73[c]	—
ClIPS	**4** + **16**	Toluene	83	Orange	0.47	0.71[c]	—

[a] *vs.* $Cp_2Fe–Cp_2Fe^+$ couple, in PhCN with 0.1 M *n*-Bu_4NBF_4, glassy carbon working electrode, 100 mV s^{-1}, r.t. [b] Isolated yield. [c] E_2^{ox} (irreversible).

MS, X-ray diffraction and elemental analyses.‡,§ Subsequent reaction of **2** (3.03 g) with 1.1 equiv. LDA in 200 ml of THF at −78 °C, followed by treatment with iodine monochloride (3.9 g, 1.3 equiv. *vs.* thione) at −78 °C gave **3** as yellow wool (4.46 g, 84%). Iodination of **2** using perfluorobutyl iodide instead of iodine monochloride was unsuccessful. Owing to the larger electronegativity of the chlorine atom, and the higher stability of the C–Cl bond rather than that of the C–I bond, the disproportionation does not occur and the iodination of **2** proceeded smoothly. The thione **3** was easily converted to the corresponding ketone **4** quantitatively according to the conventional $Hg(OAc)_2–CHCl_3$ method. All new compounds were characterized by NMR, MS and elemental analyses.‡

Hetero-halogenated TTFs listed in Table 1 were prepared by the cross-coupling reaction under the condition of $P(OEt)_3$–toluene (or benzene) reflux in moderate to high yield (Scheme 3). All molecular structures of the new donors were characterized by NMR, MS, and elemental analyses.†



Scheme 3 *Reagents and conditions*: i, $P(OEt)_3$, toluene or benzene, reflux (1–1.5 h).

The donor abilities of hetero-halogenated TTFs were examined by measuring their redox potentials (Table 1). The $E_1^{1/2}$ values of the new ClI-donors are higher than those of the corresponding monoiodo or diiodo derivatives (for example ClIET, IEDT and DIET in Table 1).[7,12] This is ascribable to stabilization of the energy level of the highest occupied molecular orbital (HOMO) by the electron-withdrawing nature of the chlorine atom. On the other hand, ΔE values are smaller than those of the corresponding monoiodo and diiodo derivatives.[7,12] It is suggested that the on-site Coulomb repulsion is reduced by more extension of HOMO toward the chlorine atom than the iodine atom on the edge of the skeleton. These results are also consistent with the results of MO calculations as shown in Fig. 1.

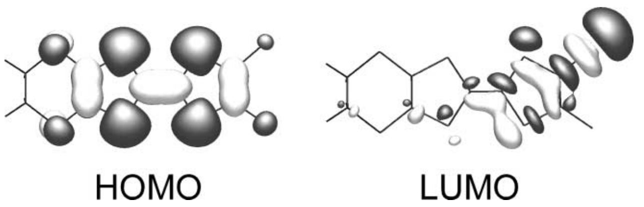


Fig. 1 Frontier orbitals of ClIET calculated by the MNDO-PM3 method.

Fig. 2 shows the crystal structure of ClIPS.§ A supramolecular chain structure is constructed by the strong iodine bond ($d_{I\cdots N}$ = 3.08(3) Å) along the crystallographic *a* + *c* direction. Interestingly, short intermolecular contacts exist only between the iodine and nitrogen atoms and similar shortening of the intermolecular distance was not observed between the chlorine and nitrogen atoms. The intrastack I···I distance is 4.09 Å and it is almost the same as the sum of the van der Waals radii. Furthermore, the space group of ClIPS is chiral *Pn* and this must result from an asymmetry of the donor molecule and a strong anisotropy of the iodine bond.

These results reveal that the chlorine atom mainly contributes to the electronic property of the single molecule and the iodine atom contributes to the intermolecular interaction through the iodine bond. Appropriate application of the different roles of the halogen atoms in TTF derivatives would be useful for designing novel supramolecular organic conductors based on the TTF derivatives. Research on cation radical salts of the new hetero-halogenated TTFs is in progress.

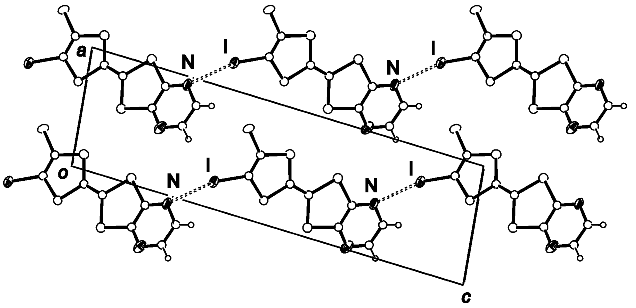


Fig. 2 Crystal structure of ClIPS ($d_{I\cdots N}$ = 3.08(3) Å).

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Notes and references

‡ *Selected data of new compounds*: **2**: yellow crystals, mp 74.5 °C; *m*/*z* (EI, 70 eV): 168 (M^+ for $C_3H^{35}ClS_3$); δ_H (270 MHz, $CDCl_3$) 6.84 (s, 1H); δ_C (67.8 MHz, $CDCl_3$) 210.0 (C=S), 124.3 (C–H), 123.9 (C–Cl);

Elemental analysis: Calc. for C_3HClS_3: C, 21.36; H, 0.60. Found: C, 21.46; H, 0.54%; **3**: yellow wool, mp 111 °C; *m*/*z* (EI, 70 eV): 294 (M^+ for $C_3{}^{35}ClIS_3$); δ_C (67.8 MHz, $CDCl_3$) 210.8 (C=S), 127.1 (C–Cl), 72.7 (C–I); Elemental analysis: Calc. for C_3ClIS_3: C, 12.23. Found: C, 12.27%; **4**: off-white wool, mp 84.0 °C; *m*/*z* (EI, 70 eV): 278 (M^+ for $C_3{}^{35}ClIOS_2$); δ_C (67.8 MHz, $CDCl_3$) 190.6 (C=O), 119.4 (C–Cl), 65.7 (C–I); Elemental analysis: Calc. for C_3ClIOS_2: C, 12.94. Found: C, 13.04%.

§ *Crystal data for* **2**: C_3HClS_3, $M = 168.67$, yellow prism (0.60 × 0.40 × 0.20 mm), *monoclinic*, $P2_1/c$ (#14), $a = 4.0483(10)$, $b = 10.844(3)$, $c = 13.748(3)$ Å, $\beta = 97.190(5)°$, $V = 598.8(3)$ Å^3, $T = 293$ K, $\mu = 1.543$ mm^{-1}, $Z = 4$, 4173 reflections measured, 1479 unique (Rint = 0.0223). Final R indices [$I > 2\sigma(I)$]: $R1 = 0.0378$, $wR2 = 0.1098$. R indices (all data): $R1 = 0.0403$, $wR2 = 0.1112$. CCDC 219243. See http://www.rsc.org/suppdata/ob/b3/b310822h/ for crystallographic data in .cif or other electronic format.

Crystal data for **ClIPS**: $C_8H_4ClIS_4Se_2N_2$, $M = 510.51$, orange plate (0.60 × 0.15 × 0.02 mm), *monoclinic*, Pn (#7), $a = 6.7584(15)$, $b = 4.0939(9)$, $c = 22.946(5)$ Å, $\beta = 97.097(4)°$, $V = 630.0(2)$ Å^3, $T = 293$ K, $\mu = 8.833$ mm^{-1}, $Z = 2$, 2464 reflections measured, 1391 unique (Rint = 0.0264). Final R indices [$I > 2\sigma(I)$]: $R1 = 0.0602$, $wR2 = 0.1572$. R indices (all data): $R1 = 0.0628$, $wR2 = 0.1595$. CCDC reference number 219244. See http://www.rsc.org/suppdata/ob/b3/b310822h/ for crystallographic data in .cif or other electronic format.

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