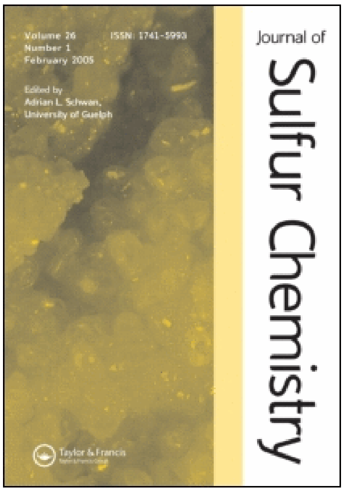

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Synthesis, properties, and CT complex formation of highly polarized thiocyanotetrathiafulvalenes[†]

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This paper is dedicated to Professor Juzo Nakayama on the occasion of his 65th birthday and retirement.

Highly polarized 4′5′-bis(methylthio), 4′,5′-ethylenedithio, and 4′,5′-ethylenedioxy-4,5-dithiocyanotetrathiafulvalenes [BMT-TTF$(SCN)_2$, EDT-TTF$(SCN)_2$, and EDO-TTF$(SCN)_2$] were synthesized in moderated yields from 2-cyanoethylthio-TTF derivatives. EDO-TTF$(SCN)_2$ formed a CT complex with $TCNQF_4$ due to its moderate electron donating ability. The packing structure of the CT complex obtained by X-ray analysis shows many intermolecular interactions through the S•••S, S•••N, C•••N, and N•••O contacts. The strong intermolecular interactions composed of the donor–donor, donor–acceptor, and acceptor–acceptor combinations enhance the dimensionality of the molecular network in the CT-complex.

Keywords: tetrathiafulvalene; polarized electron donor; oxidation potential; charge transfer complex; X-ray packing structure

1. Introduction

Highly polarized tetrathiafulvalenes (TTFs) have received considerable attention owing to several advantages as components for constructing supramolecular structures and nanonetworks, as well as molecular conductors (*1–4*). In these TTFs, intermolecular interactions can be enhanced by electrostatic dipole–dipole interactions forming close molecular networks. Furthermore, the S•••S, S•••N, C•••N, and N•••O contacts in crystals of polarized TTFs may be useful for crystal engineering. Therefore, TTFs having polarizable substituents such as ester groups (*5–8*), halogen

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[†] Crystallographic data for **1c** • $TCNQF_4$ have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC 715536.

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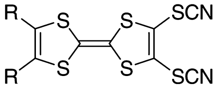
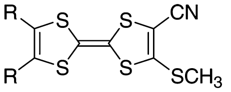
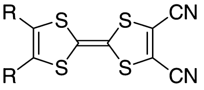
atoms (*9–21*), and cyano groups (*22, 23*) have been studied to date. Taking into account these considerations, we designed novel polarized TTFs **1** and **2** with thiocyano (SCN) substituent, which can show moderate electron-withdrawing ability, although polarized TTFs may sometimes form no CT complexes. We report here the synthesis and redox properties of new polarized TTFs **1** and **2** with SCN substituents, together with the X-ray structure of their CT complexes.



1a (R = SCH_3)
1b (R = $-SCH_2CH_2S-$)
1c (R = $-OCH_2CH_2O-$)



2a (R = SCH_3)
2b (R = $-SCH_2CH_2S-$)
2c (R = $-OCH_2CH_2O-$)



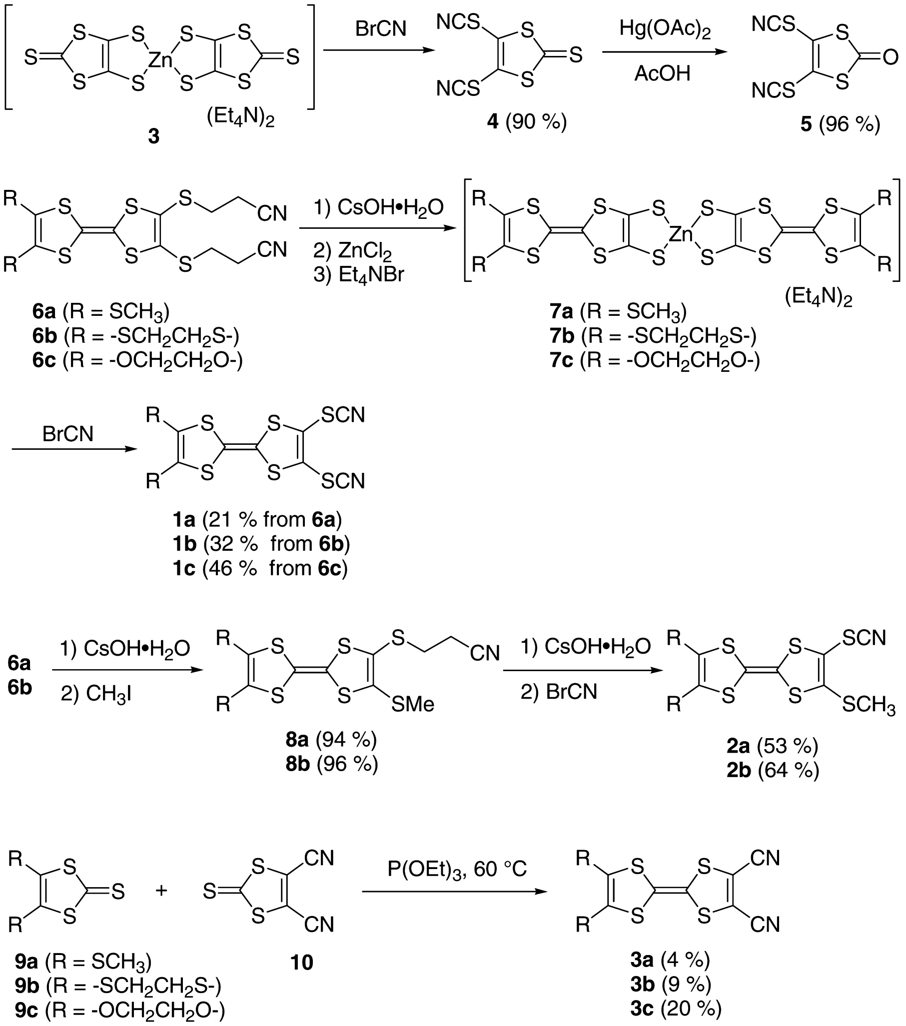
3a (R = SCH_3)
3b (R = $-SCH_2CH_2S-$)
3c (R = $-OCH_2CH_2O-$)

2. Result and discussion

As shown in Scheme 1, the thiocyano derivatives **1**, **2**, and **4** were synthesized by the reaction of thiolates with BrCN. Thus, the reaction of $Zn(dmit)_2(Et_4N)_2$ **3** with BrCN gave the 4,5-dithiocyano-1,3-dithiole-2-thione **4** in 90% yield. The thione **4** was easily converted to the ketone **5** in 96% yield. However, the synthesis of polarized TTFs **1a**–**1c** using the $P(OEt)_3$-mediated coupling of **4** or **5** with 1,3-dithiole-2-thiones under standard conditions was unsuccessful, presumably due to high reactivity of **5**. Therefore, we tried another route to synthesize **1**. Cyanoethyl substituted TTFs (**6a**–**6c**) were readily prepared starting from $Zn(dmit)_2(Et_4N)_2$ **3** using the literature procedure (*24*). Successive treatments of a DMF solution of **6a**–**6c** with $CsOH•H_2O$, $ZnCl_2$, and Et_4NBr produced the corresponding zinc complexes **7a**–**7c**. The complexes **7a**–**7c** were easily converted to TTF-dithiocyanates **1a**–**1c** by treatment with BrCN in moderated yields. For the synthesis of unsymmetrical TTFs **2a** and **2b**, the reaction of **6a** and **6b** with 1.0 equivalent of $CsOH•H_2O$ and CH_3I gave **8a** and **8b** in each 96% yield, respectively. Further conversion of **8a** and **8b** to **2a**–**b** was carried out by the successive reactions with $CsOH•H_2O$ and BrCN. In addition, the dicyanoTTFs **3a**–**3c** were also synthesized by the coupling of 1,3-dithiole-2-thiones **9a**–**9c** with 4,5-dicyano-1,3-dithiole-2-thione **10** in the presence of $P(OEt)_3$ (*23*).

Cyclic voltammetric analyses of polarized TTFs **1a**–**1c**, **2a**–**2b**, and **3a**–**3c** were carried out in PhCN (Table 1). All compounds showed two reversible redox waves assigned to the formation of cation radicals and dications. As expected, the first oxidation potentials of **1a**–**1c** are, by 0.08–0.09 V, lower than those of **3a**–**3c** owing to the lower electron-withdrawing effect of thiocyano group than cyano group. Especially, **1c** ($E^1_{1/2} = 0.22\,V$ *vs* Fc/Fc^+) can be expected to form CT-complexes with π-acceptors. As for **2a** and **2b**, the redox potentials showed more negative values in both $E^1_{1/2}$ and $E^2_{1/2}$, *i.e.* **2a** and **2b** are much better π-donors.

Since the new donor **1c** showed moderate electron-donating ability, **1c** was subjected to form the CT complexes with acceptor molecules. After several attempts, **1c** was found to form single crystals with tetrafluorotetracyanoqunodimethane ($TCNQF_4$) by slow mixing **1c** and $TCNQF_4$ in a MeCN-chloroform solution. From the X-ray crystallographic analysis, the CT complex consists of **1c** and $TCNQ-F_4$ (1:1) in the unit cell (Figure 1). The donor **1c** molecules have a crystallographic C_2 symmetry with a two-fold axis passing through the central C=C bond and the acceptor $TCNQ-F_4$ molecules have a crystallographic C_i symmetry with an inversion center. The donor **1c** adopts planar central TTF skeleton with vertical SCN groups, and there are 13 kinds of the van der Waals contacts in the crystal. The length of the central C–C bond was found to be 1.384 Å, which is a little longer than that of neutral TTFs. These results suggest a certain charge transfer in the donor molecule. Interestingly, although the donor molecules are stacked in segregate manner with S•••S van der Waals contacts along the *c* axis in head-to-tail mode, the packing style is mainly attributed to the dipole interactions at the terminal SCN groups (Figures 2 and 3). Thus,



Scheme 1. Synthesis of TTF-thiocyanates **1a–1c** and **2a–2b** together with related compounds **3a–3c**.

Table 1. Redox potentials of **1a–1c**, **2a**, **2b** and **3a–3c**.[a]

	$E_1^{1/2}$	$E_2^{1/2}$	ΔE
TTF	−0.09 (1e$^-$)	0.27 (1 e$^-$)	0.36
1a	0.30 (1e$^-$)	0.51 (1e$^-$)	0.21
1b	0.31 (1e$^-$)	0.54 (1e$^-$)	0.23
1c	0.22 (1e$^-$)	0.48 (1e$^-$)	0.26
2a	0.06 (1e$^-$)	0.31 (1e$^-$)	0.25
2b	0.20 (1e$^-$)	0.47 (1e$^-$)	0.27
3a	0.39 (1e$^-$)	0.60 (1e$^-$)	0.21
3b	0.43 (1e$^-$)	0.64 (1e$^-$)	0.21
3c	0.30 (1e$^-$)	0.58 (1e$^-$)	0.28

Notes: [a]Conditions: $^n\mathrm{Bu_4NClO_4}$, PhCN, Pt working electrode and counter electrodes. Potentials were measured against an Ag/Ag$^+$ electrode and converted to the value *vs* Fc/Fc$^+$.

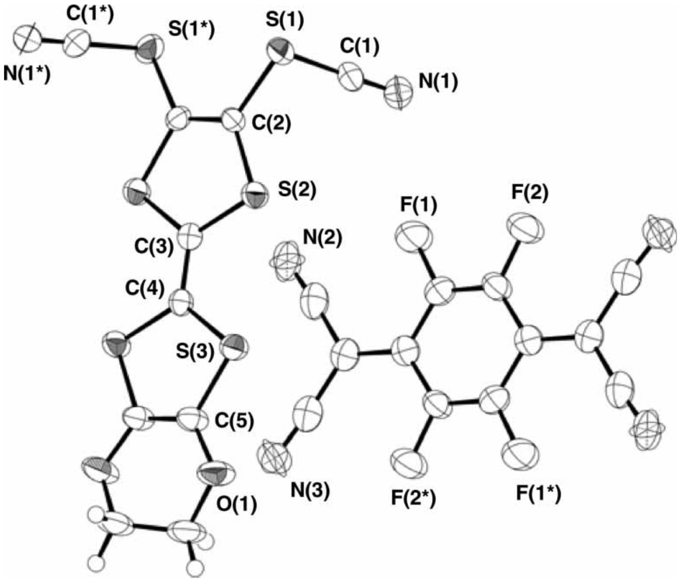


Figure 1. ORTEP drawing of **1c** • $TCNQF_4$ (50% probability).

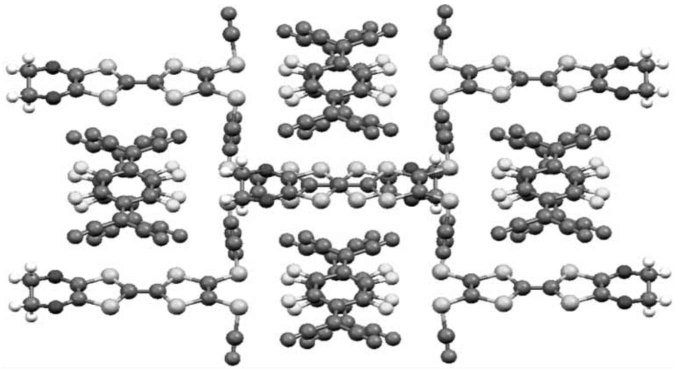


Figure 2. Packing diagram along the *c* axis.

each SCN group of **1c** contacts with other donor molecules of another column in head-to-tail manner through many N•••S, N•••C, and N•••O contacts (Figure 3). The N•••S distances are, in particular, 14% shorter than the sum of van der Waals radii (3.4 Å), and the strong intermolecular interactions along the *a*, *b*, and *c* axes enhance the dimensionality. On the contrary, $TCNQF_4$ molecules stack along the *c* axis with several C•••C contacts. Although many short contacts were found in the crystal, the room temperature electric conductivity of the CT complex was less than 1.0×10^{-6} S cm^{-1}, presumably due to the poor eclipsed structure.

3. Conclusion

New TTFs **1a**–**1c** having SCN groups were synthesized. The redox potentials of the highly polarized **1a**–**1c** showed better electron donor ability as compared with **3a–3c**. In accordance with this result, the new donor **1c** formed the 1:1 complex with $TCNQF_4$, and the structure of the

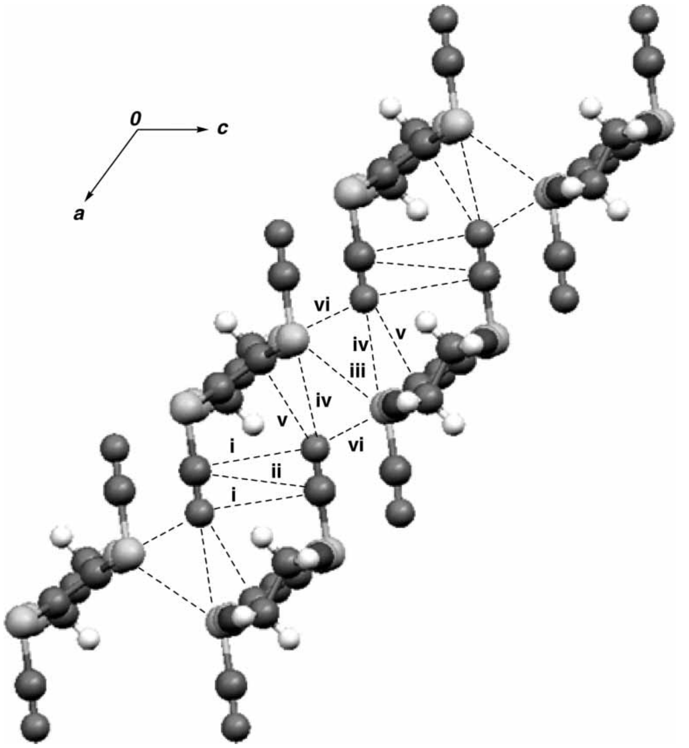


Figure 3. Packing diagram along the *b* axis. $TCNQF_4$ molecules are omitted for clarity. Dotted lines indicate selected intermolecular interactions: (i) N(1)•••C(1)^1 3.243(8) Å ($1 = -1/2 - x, -1/2 - y, -z$); (ii) C(1)•••C(1)^1 3.350(7) Å; (iii) S(2)•••S(3)^2 3.668(2) Å ($2 = x, -y, 1/2 + z$); (iv) N(1)•••S(1)^3 2.964(5) Å ($3 = -1/2 + x, -1/2 - y, -1/2 + z$); (v) N(1)•••C(2)^1 3.106(6) Å; (vi) N(1)•••O(1)^4 2.976(6) Å ($4 = -1/2 + x, -1/2 + y, z$).

CT complex **1c**·$TCNQF_4$ showed many intermolecular interactions based on the S•••S, S•••N, C•••N, and N•••O contacts at the terminal SCN moieties. Therefore, the CT complex **1c**·$TCNQF_4$ showed an enhanced dimensionality of the molecular network in the crystal.

4. Experimental

NMR spectra were recorded on a JEOL JNM-EX 500 instrument (500 MHz for ^1H NMR and 125 MHz for ^{13}C NMR). Spectra are reported (in δ) referred to internal $(CH_3)_4Si$. MS spectra were measured by a JEOL JMS-AX 500 instrument. X-ray crystal analysis was carried out using a Rigaku AFC-7R four-circle diffractometer with graphite monochromated Mo-Kα radiation. Cyclic voltammograms were recorded on a BAS CV-27 voltammeric analyzer. Electric conductivity was measured with a Fuso Electro Chemical System HECS 994C multi channel conductometer. All solvents were dried by conventional procedures and distilled before use. All new TTF derivatives reported here gradually decomposed when heated to determine their melting points.

4.1. *Synthesis of 4′,5′-bis(methylthio)-4,5-dithiocyanotetrathiafulvalene (1a)*

To a solution of **6a** (400 mg, 0.86 mmol) in DMF (3 ml) was added $CsOH \cdot H_2O$ (660 mg, 4.4 mmol) in MeOH (4 ml). After stirring for 30 min, $ZnCl_2$ (350 mg, 2.6 mmol) in MeOH (4 ml), aq. NH_3 solution (4 ml), and Et_4NBr (510 mg, 2.4 mmol) in water (4 ml) were added in this order. The mixture was stirred for 1 h. Then, the precipitate was collected by filtration, washed with water and hexane, and dried *in vacuo*. The zinc complex **7a** was used for the next reaction without further purification.

To a solution of the complex **7a** in DMF (5 ml) was added BrCN (220 mg, 2.1 mmol) in DMF (2 ml) at −40 °C. After warming to rt, the reaction mixture was stirred for 30 min. Then, the mixture was poured into water, and products were extracted with CH_2Cl_2. The organic layer was washed with saturated brine and dried over $MgSO_4$. Column chromatography on SiO_2 with CH_2Cl_2-hexane ($v/v = 4:1$) as eluent and additional purification with GPC gave a red powder of **1a** (75 mg, 21%). ^1H NMR ($CDCl_3$) δ 2.25 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 140.4, 127.8, 121.4, 121.0, 104.1, 19.2.

4.2. *Synthesis of 4′,5′-ethylenedithio-4,5-dithiocyanotetrathiafulvalene (1b)*

The synthesis of **1b** was carried out starting from **6b** in 32% yield in a similar manner as described for **1a**. **1b**: a purple powder; ^1H NMR ($CDCl_3$) δ 3.32 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 123.2, 122.0, 113.4, 105.5, 103.2, 66.4.

4.3. *Synthesis of 4′,5′-ethylenedoxy-4,5-dithiocyanotetrathiafulvalene (1c)*

The synthesis of **1b** was carried out in 46% yield starting from **6c** in a similar manner as described for **1a**. **1c**: purple powder; ^1H NMR ($CDCl_3$) δ 4.29 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 123.2, 122.0, 113, 105.5, 103.2, 66.4.

4.4. *Synthesis of 4-cyanoethylthio-4′,5,5′-tris(methylthio)tetrathiafulvalene (8a)*

To a solution of **6a** (600 mg, 1.3 mmol) in DMF (10 ml) was added $CsOH \bullet H_2O$ (220 mg, 1.5 mmol) under Ar atmosphere. After stirring for 10 min, CH_3I (275 mg, 1.9 mmol) was added dropwise, and the mixture was stirred for another 1 h at rt. Then, the mixture was poured into water and products were extracted with CH_2Cl_2. The organic phase was washed with brine and dried over $MgSO_4$. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel with CH_2Cl_2 as the eluent to give an orange powder of **7a** (534 mg, 96%). **7a**: ^1H NMR ($CDCl_3$) δ 3.03 (t, $J = 7.1$ Hz, 2H), 2.71 (t, $J = 7.1$ Hz, 2H), 2.47 (s, 6H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 128.1, 123.1, 117.4, 108.4, 107.3, 66.4, 66.3, 31.3, 18.9.

4.5. *Synthesis of 4-cyanoethylthio-5-methyl-4′,5′-ethylenedithiotetrathiafulvalene (8b)*

The synthesis of **8b** was carried out in 96% yield starting from **6b** in a similar manner as described for **8a**. **8b**: orange powder, ^1H NMR ($CDCl_3$) δ 3.32 (s, 4H), 3.0 (t, $J = 7.0$ Hz, 2H), 2.70 (t, $J = 7.0$ Hz, 2H), 2.47 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 128.1, 123.1, 117.4, 108.24, 107.3, 66.4, 66.3, 31.3, 18.9.

4.6. *Synthesis of 4′,5,5′-tris(methylthio)-4-thiocyanotetrathiafulvalene (2a)*

To a solution of **8a** (300 mg, 0.70 mmol) in DMF (10 ml) was added $CsOH \bullet H_2O$ (220 mg, 1.5 mmol) under Ar atmosphere. The mixture was stirred for 10 min, and then BrCN (80 mg, 0.75 mmol) in DMF (4 ml) was added at −40°C and stirred for 30 min at the same temperature.

After the temperature was warmed to rt, the mixture was stirred for a further 30 min. Then, the mixture was poured into water and products were extracted with CH_2Cl_2. The organic phase was washed with brine and dried over $MgSO_4$. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel with CH_2Cl_2 as the eluent to give an orange powder of **2a** (148 mg, 53%). **2a**: ^{1}H NMR ($CDCl_3$) δ 2.51 (s, 3H), 2.44 (s, 3H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 139.5, 128.2, 127.1, 115.9, 108.5, 107.6, 107.1, 19.3.

4.7. *Synthesis of 4′,5′-ethylenedithio-5-methyl-4-thiocyanotetrathiafulvalene (2b)*

The synthesis of **2b** was carried out in 64% yield starting from **8b** in a similar manner as described for **2a**. **2b**: orange powder; ^{1}H NMR ($CDCl_3$) δ 3.34 (s, 4H), 2.51 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 139.5, 114.2, 113.9, 113.7, 108.4, 107.5, 30.2, 19.3.

4.8. *Synthesis of 4,5-dicyano-4′,5′-ethylenedioxytetrathiafulvalene (3c)*

To a solution of **9c** (408 mg, 2.1 mmol) and **10** (340 mg, 1.8 mmol) in benzene (20 ml) was added $P(OEt)_3$(4 ml, 23 mmol) at 60 °C under Ar atmosphere. The mixture was stirred for 6 h at 60 °C under Ar atmosphere, and $P(OEt)_3$ and benzene were removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2-CS_2 ($v/v = 4:1$) as the eluent to give a purple powder of **3c** (110 mg, 20%). **3c**: MS (DI) $m/z = 312$ (M^+); ^{1}H NMR ($CDCl_3$) δ 4.30 (s, 4H).

5. X-ray structural determination of 1c • $TCNQF_4$

Single crystals suitable for X-ray analysis were obtained by slow mixing of a solution of **1c** in $CHCl_3$ with a solution of $TCNQF_4$ in MeCN. A black plate with a dimension of $0.30 \times 0.20 \times 0.06\,\mathrm{mm}^3$ was chosen for the analysis. Crystal data for **1c**: $C_{22}H_4N_6O_2F_4S_6$, *Mw* 652,69, monoclinic, space group $C2/c$ (#15), $a = 14.344(2)$ Å, $b = 20.441(3)$ Å, $c = 10.625(4)$ Å, $\beta = 127.401(11)°$, $V = 2474.7(10)$ Å^3, $Z = 4$, $D_c = 1.752\,\mathrm{g\,cm^{-3}}$, $R_1 = 0.0415$, $R_w = 0.095$, GOF = 1.029. Among a total of 2987 reflections measured, 2837 were unique, and the observed ($I > 2.00\sigma(I)$) 1297 reflections were used for the refinement. The crystal structure was solved by the SIR97 program, and refined by the full matrix least-squares method on Yadokari-XG software.

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