# Synthesis of Diazafluorene-functionalized TTF Donors

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Synthesis and X-ray structure of novel ligands containing tetrathiafulvalene (TTF) are reported. These compounds have been prepared by condensation between diazafluorene coordination site and TTF moiety as conductivity site.

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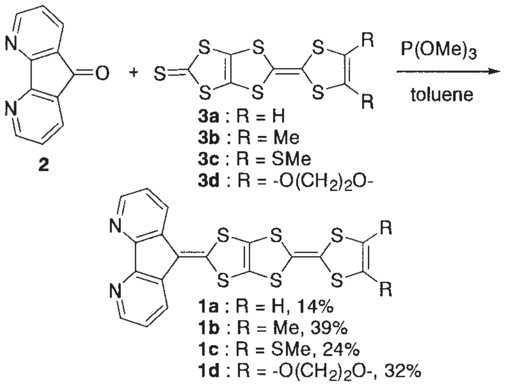
The transition metal complexes with organic donors such as tetrathiafulvalene have attracted current attention because of the various properties (their conductivity, magnetism, and optical property).[1,2] There is a possibility that functionalizes $\pi$-donor with coordination functions as ligand part for various metals. Recently, metal-coordinated TTF derivatives with phosphine,[3] acetylacetone,[4] or dithiolate moiety[5] have been developed with this purpose. Tetrathiafulvalene based ligands fused with diazafluorene moiety as a powerful chelating unit with various transition metals are possible ligands which form hybrid materials containing electron transfer, conductivity, and optical properties. In this paper, we report synthesis, electrochemical properties, and X-ray crystal structure of TTF-based ligands fused with diazafluorene unit (**1**).

The synthesis of **1a**–**d** were carried out using cross-coupling reaction of **2** and **3** with trimethylphosphite as shown in Scheme 1. 4,5-Diazafluoren-9-one (**2**) and the appropriate TTF derivatives (**3a**–**d**)[6] fused with 1,3-dithiole-2-thione ring were allowed to react in trimethylphosphite at 60–80 °C for 2 h under Ar atmosphere. After workup, column chromatography and recrystallization, the target "diazafluorene functionalized TTF ligands **1a**–**d** (DAF-DT-TTF)" were obtained as red or dark red powder in 14–39% yields (Scheme 1).[7]



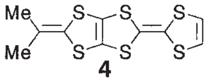
**Scheme 1.**

The redox potentials of **1a**–**d**, (2-methylidene-1,3-dithiolo[4,5-*d*])-tetrathiafulvalene (DT-TTF, **4**),[8] measured by cyclic voltammetry are summarized in Table 1. The cyclic voltammograms of **1a**–**d** in benzonitrile consisted of two-pairs of reversible waves (the first and the second steps) and one-pair of irreversible waves (the third step). The first redox potentials ($E_1$) of **1a**, **1b**, and **1d** were almost same with each other and also equal to that of **4**, while that of **1c** was ca. 0.1 V higher than those of other DAF-DT-TTFs as shown in Table 1. The $E_1$ values of DAF-DT-TTFs except for **1c** were higher by 0.10–0.13 V compared with that of TTF. On the other hand, the $E_3$ values of **1a**–**d** were almost equivalent and ca. 0.3 V higher than that of **4** according to electron-accepting nature of diazafluorene moiety. The $\Delta E (= E_2 - E_1)$ values (0.35, 0.32, and 0.28 V for **1a**, **1b**, and **1d**, respectively) were almost similar to that of **4** and ca. 0.07–0.14 V smaller than that of TTF. Particularly, the $\Delta E (= E_2 - E_1)$ value of **1c** was ca. 0.2 V smaller than that of TTF due to heteroatom (sulfur) stabilization effect of methylthio-substituents. The fact suggests that the on-site Coulombic repulsion in their dication states are decreased by delocalization of two positive charges in the whole molecule such as DT-TTFs.

**Table 1.** Redox Potentials[a] of **1** and related compounds

| Compound | $E_1$ | $E_2$ | $E_3$ | $E_2 - E_1$ |
|---|---|---|---|---|
| **1a** | +0.07 | +0.42 | +1.32 | 0.35 |
| **1b** | +0.05 | +0.37 | +1.27 | 0.32 |
| **1c** | +0.17 | +0.38 | +1.32 | 0.21 |
| **1d** | +0.08 | +0.36 | +1.31 | 0.28 |
| **4** | +0.05 | +0.36 | +1.01 | 0.31 |
| TTF | - 0.05 | +0.37 | | 0.42 |

[a] Conditions: 0.1 M$^{-1}$ $n$-Bu$_4$NClO$_4$, benzonitrile, 25° C, Pt working and counter electrodes. Potentials were measured against an Ag/Ag$^+$ electrode. $E$ in $V$ vs Fc/Fc$^+$.



**4**

The molecular and crystal structures of **1c** were determined by X-ray diffractional analysis.[9] A general view of the molecular structure of **1c**, together with the crystallographic atom-numbering scheme, is shown in Figure 1. The diazafluorene and central $C_2S_4$ (S1-C13-S3-S4-C14-S2) in tetrathiapentalene moiety of the molecule is almost planar and **1c** possesses dihedral angles of 17.7 ° between $S_4$ (S1-S3-S4-S2) plane of tetrathiapentalene and $S_4$ (S3-S5-S6-S4) one of outer TTF. The rest of the outer TTF moiety bends outwards with folding along **S**···**S** lines by 20.5 (S3-S4) and 16.2 ° (S5-S6), respectively. The C-C bond lengths of five-membered ring (C3-C9-C11-C10-C4) in diazafluorene moiety of **1c** are almost equal (1.42–1.48 Å) and the bond angles are 106–108 °. Each C-C bond length of the five-membered ring is longer by 0.03–0.09 Å than that of cyclopentadienyl ring in ferrocene (1.39 Å)[10] and C = C bond length of cyclopentadiene (ca. 1.37 Å),[11] although it is almost equal to C-C bond length of cyclopentadiene in fulvalene derivatives (1.45–1.47 Å). These facts suggest that the five-membered ring in diazafluorene moiety of **1c** is almost ideal pentagon form and the C-C bonds have some

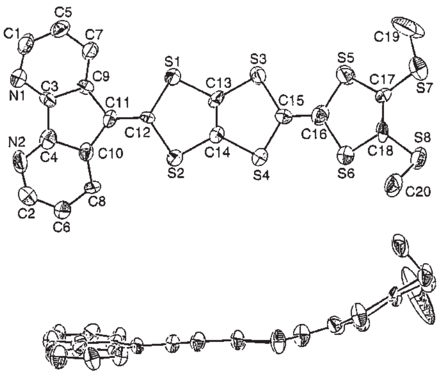


**Figure 1.** The molecular structure of **1c** with labeling scheme. Selected bond lengths (Å) and angels (°) are: C(3)–C(4) 1.45(2), C(3)–C(9) 1.42(2), C(9)–C(11) 1.47(2), C(10)–C(11) 1.48(2), C(4)–C(10) 1.46(2), C(4)–C(3)–C(9) 108(1), C(9)–C(11)–C(10) 107(1), C(4)–C(10)–C(11) 106(1), C(3)–C(4)–C(10) 109(1).

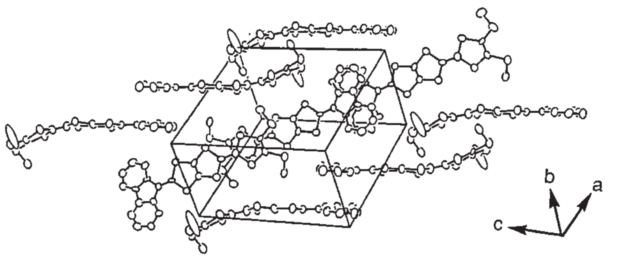


**Figure 2.** Molecular packing structure of **1c**.

double bond character. The packing structure of **1c** is shown in Figure 2. There are two $\pi$-$\pi$ stacking types in stair structure. One overlap mode in stair structures is head-head overlap type (diazafluorene ring is regarded as head moiety), another is tail-tail overlap type (tail moiety regard as outer 1,3-dithiole ring). The interplannar distances between the diazafluorene planes (head-head) of DAF-DT-TTFs is ca. 3.61 Å. Those between the outer 1,3-dithiole rings (tail-tail) is ca. 3.64 Å. The two stair structures are orthogonally arranged to each other.

The Ru(II) complexation of DAF-DT-TTF derivatives and *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$ was examined by use of **1c**. The formed Ru(II) complex is assigned $Ru(bpy)_2$**1c**$(PF_6)_2$ by $^1$H NMR and MS spectral data.[12] The longest wavelength absorption maximum of $Ru(bpy)_2$**1c**$(PF_6)_2$ in $CHCl_3$ exhibited red shifts (ca. 20 nm) and the tailing end was also appeared at longer wavelength region (ca. 150 nm) compared with the ligand **1c**. In summary, we have prepared diazafluorene functionalized TTF ligands (**1a**–**d**, DAF-DT-TTF), which formed Ru(II) complex $Ru(bpy)_2$**1c**$(PF_6)_2$ by treatment of *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$. We are now currently investigating routes to other Ru(II) DAF-DT-TTFs complexes.

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7 **1a**: red powder; mp. 215 °C (decomp.); $^1$H NMR ($CDCl_3/CS_2 = 1:1$, v/v, 400 MHz): $\delta$ 6.42 (2H, s), 7.39 (2H, dd, $J = 7.3$, 4.8 Hz), 8.02 (2H, dd, $J = 7.1$, 1.0 Hz), 8.68 (2H, dd, $J = 4.9$, 1.3 Hz); MS(EI): $m/z$ 444($M^+$). **1b**: dark red powder; mp. 223 °C (decomp.); $^1$H NMR ($CDCl_3/CS_2 = 1:1$, v/v, 400 MHz): $\delta$ 2.00 (6H, s), 7.35 (2H, dd, $J = 7.4$, 4.6 Hz), 7.99 (2H, dd, $J = 7.4$, 1.0 Hz), 8.63 (2H, dd, $J = 4.7$, 1.0 Hz), MS(EI): $m/z$ 472($M^+$). **1c**: dark red powder; mp. 218 °C (decomp.); $^1$H NMR ($CDCl_3/CS_2 = 1:1$, v/v, 400 MHz): $\delta$ 2.45 (6H, s), 7.34 (2H, dd, $J = 7.8$, 4.9 Hz), 7.95 (2H, dd, $J = 7.8$, 1.0 Hz), 8.64 (2H, dd, $J = 4.9$, 1.0 Hz); MS(EI): $m/z$ 536($M^+$). **1d**: dark red powder; mp. 219 °C (decomp.); $^1$H NMR ($CDCl_3/CS_2 = 1:1$, v/v, 400 MHz): $\delta$ 4.28 (4H, s), 7.34 (2H, dd, $J = 6.9$, 4.9 Hz), 8.00 (2H, dd, $J = 6.8$, 1.0 Hz), 8.67 (2H, dd, $J = 1.2$, 4.7 Hz); MS(EI): $m/z$ 502($M^+$).

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9 Crystal data of **1c**: $C_{20}H_{12}N_2S_8$, orange, prismatic, monoclinic, space group $P2_1/c$(# 14), $a = 15.536(4)$ Å, $b = 8.902(3)$ Å, $c = 15.785(3)$ Å, $\beta = 92.22(2)°$, $V = 2181.3(9)$ Å$^3$, $Z = 4$, $T = 23$ °C, $D_c = 1.634$ g/cm$^3$, $F(000) = 1096.00$, $\mu$(Mo K$\alpha$) = 8.31 cm$^{-1}$, graphite monochromated MoK$\alpha$ ($\lambda = 0.71069$ Å), $2\theta_{max} = 50°$, total data 3710, unique data 3577 ($R_{int} = 0.044$), $R = 0.076$ and $R_w = 0.084$.

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12 $Ru(bpy)_2$**1c**$(PF_6)_2$: dark red powder; $^1$H NMR ($CD_3COCD_3$, 200 MHz): $\delta$ 2.49 (6H, s), 7.80–7.53 (6H, m), 8.30–8.21 (12H, m), 8.82 (H, d, $J = 8.3$ Hz); MS(FAB): $m/z$ 1094.8 ($M^+$-$PF_6$), 949.9 ($M^+$-$2PF_6$).