Synthesis of a Donor Molecule with Metal Coordination Sites toward Multifunctional Complexes

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We have synthesized a donor-type ligand **1a**–**1f** containing a 1,3-dithiol ring as the donor site and an *N*,*N*,*N*-tridentate ligand for metal complexation. In the crystal phase, the planar **1a** molecules stack along the *b* axis in the "head-to-tail" fashion. The $\mathrm{Fe^{II}}$ complex **2** shows typical paramagnetic behavior.

The interactions among localized d electron spins through delocalized π electrons have attracted much attention in the field of molecular magnetism and conduction.[1] Recently, TTF-based derivatives with coordination function have been synthesized to investigate π–d systems which have metal–ion binding groups attached at the periphery.[2] In this paper, we report the synthesis of a donor-ligand **1a**–**1f** in order to examine the chelate ability of a novel *N*,*N*,*N*-tridentate moiety (Figure 1). Such a π-donor equipped with coordination sites is expected to function as a ligand for transition metals.

We have synthesized donor-ligands **1a**–**1f**[3] using the phosphate-mediated cross-coupling reaction with triethyl phosphite, Route A, as shown in Scheme 1. 3-(2-Pyridyl)-4,5-diazafluoren-9-one (**3**)[3] were allowed to react with 1,3-dithiol thione derivatives **4a**–**4f**[4] in triethyl phosphite–dry toluene at 80–90 °C for 2 h under argon atmosphere. The yields of **1a**–**1f** depend on the reaction conditions to scatter in a wide range. The reactivity of **4a**–**4f** with the ketone **3** appears to be affected by the 1,3-dithiol thione moieties. Furthermore, it is notable that the solubility, chemical stability, and thermal stability were dependent on the substituents. The Wittig–Horner reaction,[5] Route B was carried out by adding 1.2 equiv. of *n*-butyllithium to a stirred solution of the corresponding phosphonate derivatives **5a**–**5b**[5] in dry tetrahydrofuran at −78 °C under argon atmosphere. A solution of **3** in dry dichloromethane was added to a solution of the highly nucleophilic phosphonate carbanion. This carbanion attacks the inactive carbonyl site of **3**. The products were purified with column chromatography and recrystallization, giving compounds **1a**–**1f** as stable orange or yellow solids in 1–65 and 60% yields for Route A and B, respectively (Table 1). Route B generally gives the desired **1a** and **1b** in a high yield compared with Route A.

The redox potentials ($E_{1/2}$) of **1a**–**1f** measured with differential pulse voltammetry (DPV)[6] and the synthetic yields are summarized in Table 1. The DPV of **1a**–**1f** exhibited a one-electron oxidation wave corresponding to the successive generation of the cation of the 1,3-dithiol-ring moiety. The order of the donor abilities (**1a** > **1b** > **1d** > **1c** > **1f** > **1e**) is consistent with that in the electron-releasing nature of the 1,3-dithiol ring. On the other hand, **1d** demonstrated not only a one-electron oxidation wave but also a poorly resolved one-electron reduction wave at $E_{1/2}{}^{\mathrm{red}} = -1.43$ V.[3] This reduction process was previously observed for the anion radical of [1,2,5]thiadiazole moiety.[4a]

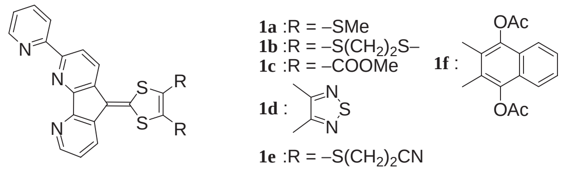
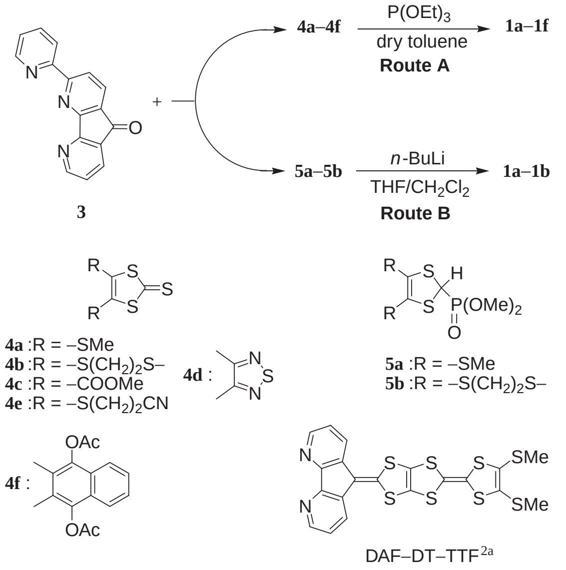


Figure 1. Molecular structure of donor-ligands with metal coordination sites.

A single crystal of **1a** was obtained with recrystallization from chloroform–diethyl ether, and the crystal structure was determined with X-ray diffraction analysis.[7] As shown in Figure 2, the molecule **1a** is almost planar except for the methyl group attached to S(3), while the torsion angle (S1–C2–S3–C4) is 83.8°.



Scheme 1.

Table 1. The synthetic yields of **1a**–**1f** and their redox potentials

Compound	Yield[a]/%	Yield[b]/%	$E_{1/2}$[6]/V
1a	1	60	+1.14
1b	6	59	+1.16
1c	20	—	+1.23
1d	24	—	+1.21[c]
1e	43	—	+1.27
1f	65	—	+1.24

[a] Route A: phosphate-mediated cross-coupling reaction. [b] Route B: Wittig–Horner reaction. [c] One-electron reduction wave at $E_{1/2}{}^{\mathrm{red}} = -1.43$ V.[3]

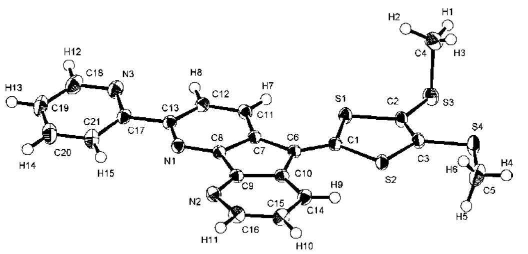


Figure 2. The molecular structure of **1a** with labeling scheme.

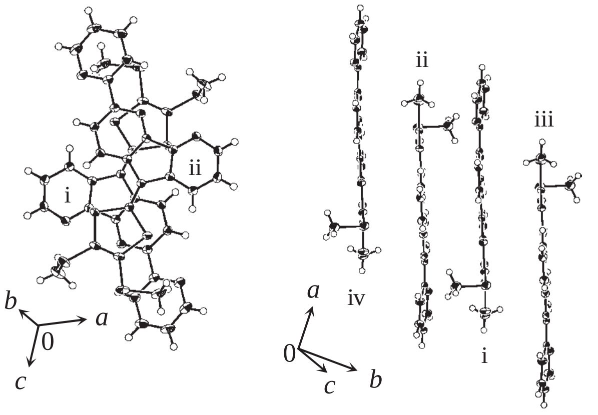


Figure 3. The molecular packing manners of **1a**: head-to-tail manner (left) and dimer chain structure (right). Symmetry operations: i (x, y, z), ii ($-x+1$, $-y+1$, $-z+1$), iii ($-x+1$, $-y$, $-z+1$), iv (x, $y+1$, z).

The bridging double-bond length of **1a**, d(C1–C6) $= 0.137$ nm, is longer than that in the 1,3-dithiol-ring one, d(C2–C3) $=$ 0.134 nm. These values are closer to those of heptafulvalene[8] than those of the neutral TTF.[9] The C–C bond lengths of the five-membered ring (C6–C7–C8–C9–C10) in the diazafluorene moiety of **1a** are 0.141–0.147 nm and the bond angles are 106–108°, which are similar to those of DAF–DT–TTF.[2a] As shown in Figure 3, the molecular packing is a dimer chain stacked in a "head-to-tail" manner along the b axis. One of the two terminal methylthio groups extends out of the molecular plane, and the other is located in the plane (0.76°: S2–C3–S4–C5). The latter methylthio group is located just over the pyridine ring, with the closest distances of 0.359–0.405 nm[10] between methyl carbon (C5 (i)) and aromatic carbon atoms (C17–C18–C19–C20 (ii)). Furthermore, the hydrogen bond between a hydrogen atom of the methylthio group extended out of the molecular plane and a nitrogen atom of the diazafluorene unit is noticeable (0.274 nm: H2 (i)–N2 (ii)). The 1,3-dithiol-ring moieties do not stack with each other and no intermolecular S–S contacts were examined; these observations can be understood by the head-to-tail stacking of the molecules in this crystal.

The iron complex [Fe(**1a**)$_2$](BPh$_4$)$_2$ (**2**) was obtained as orange powder in 45% yield by treating a methanol solution of FeCl$_2$ containing 2 equiv. of NaBPh$_4$ with 2 equiv. of **1a** in dichloromethane.[3] The magnetic susceptibilities χT of **2** were measured between 2 and 350 K with a superconducting quantum interference device (SQUID) magnetometer in an external field of 0.5 T. The diamagnetic contributions were subtracted using Pascal's law. The complex **2** shows typical paramagnetic behavior; $\chi_{\mathrm{m}}T$ value (3.0 cm^3 K mol^{-1}) corresponds to a high-spin state ($S = 2$) due to iron(II) ion in octahedral coordination. Simulation of the experimental data using a spin-Hamiltonian, $H = D_z{}^2 + g\mu_{\mathrm{B}}SH$, yielded a zero-field parameter $|D| = 4.66$ cm^{-1} and g value of 2.02.[11] A precise information of the coordination geometry in **2** is not available, because its single crystals applicable to X-ray diffraction analysis have not been obtained. However, when taking account of the ligand structure of **1** and the size of the counter ion, **2** likely lies somewhere between a highly distorted six-coordinate complex and a four-coordinate compound with two additional weak interactions. The various steric interactions within the ligand array induce long Fe–N distances and a correspondingly weak ligand field.

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3 Experimental procedures, the analytical, spectral, voltammetric, and magnetic susceptibility data for **1a**–**1f** and **2** are compiled in the Supporting Information which is available electronically on the CSJ-Journal website, http://www.csj.jp/journals/chem-lett/.

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6 Condition: 3×10^{-4} mol L^{-1} in CH$_2$Cl$_2$, 13 °C, supporting electrode: 0.1 mol L^{-1} TBABF$_4$, reference: SCE, working and counter electrode: Pt, scan rate: 50 mV s^{-1}, pulse width: 50 ms, period: 0.1 s.

7 Crystal data of **1a** (CCDC 644738): C$_{21}$H$_{15}$N$_3$S$_4$, orange needle, fw 437.60, $T = 103(2)$ K, monoclinic, $P2_1/c$ (#14), $a =$ 1.33685(2), $b = 0.81699(2)$, $c = 1.88492(5)$ nm, $\beta =$ 109.5925(11)°, $V = 1.93950(8)$ nm^3, $Z = 4$, $\rho_{\mathrm{c}} = 1.499$ Mg m^{-3}, $F(000) = 904$, $\theta_{\max} = 25.49°$, μ (Mo Kα) $= 0.503$ mm^{-1}, Mo Kα ($\lambda = 0.071069$ nm), total data = 16473, unique data = 3597 ($R_{\mathrm{int}} = 0.0367$), R_1 ($I > 2\sigma(I)$) $= 0.0307$, wR_2 (all data) = 0.0730, GOF = 1.051.

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