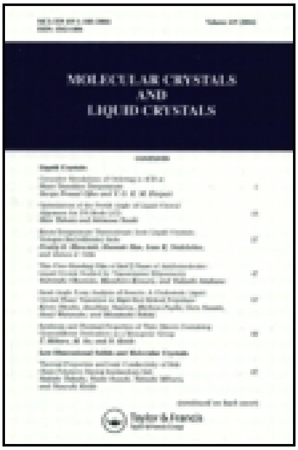

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SYNTHESIS AND PROPERTIES OF NEW DONORS WITH AN ABILITY OF METAL-COORDINATION

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Abstract Synthesis and properties of new donors with the function to control the electrical conductivity by coordination with various metal ions were described. Red shifts in the absorption spectra of donors were observed by coordination with ferrous ion and cyclic voltammetry suggested the ability of electron donation were slightly decreased by metal coordination. Metal complexes with both of ferrous and nickel ions were isolated.

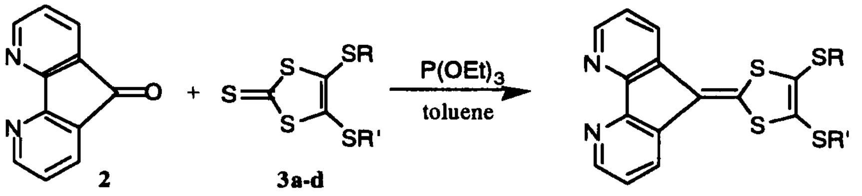
INTRODUCTION

Many studies on the synthesis of new donors have been reported with the modification of tetrathiafulvalene (TTF) framework or its analogues leading to show the highly conductive or superconducting properties. These investigations were not aimed to find new types of organic superconductors but also established the basic principles for their molecular design.[1] We have already reported the synthesis of some TTF derivatives to which the new function was added exhibiting the new types of physical properties containing the reproducible electrical conductivity controlled with external stimuli such as irradiation of UV or visible light, or heating.[2] These properties are attributable to the reversible changes by cis-trans isomerization. Therefore, these compounds might become a new type of electrical switching devices controlled by light or heating.[3] Recently, J. Becher et al. reviewed new role of TTF derivatives as building-blocks in supramolecular chemistry including some ligand systems.[4] We are now studying the another function which affects the electrical conductivities by changing the relative orientation of donor molecules in the crystals.

From the facts that many studies about the metal-coordination of 1,10-phenanthroline or 2,2'-bipyridyl derivatives are appeared, 4,5-Diaza-9-(4,5-disubstituted-1,3-dithiol-2-ylidene)-fluorenes **1a-d** in which two pyridine rings are involved by annelation are promised to exhibit highly coordination ability with various metal ions. Therefore, these compounds are one of the best candidates for studying the relationship between electrical conductivities and orientation of the donor molecules. These molecules incorporating bipyridyl group as metal binding sites are expected to change their relative orientation by coordination of metal ions, and consequently resulted to change their electrical conductivities.

RESULTS AND DISCUSSION

The synthetic routes to new donors **1a-d** are shown below.



1a : R = R' = Et
1b : R = R' = Bu
1c : R, R' = $-CH_2CH_2-$
1d : R = R' = Me

FIGURE 1 The synthetic routes to **1a-d**.

4,5-Diazafluoren-9-one **2** was synthesized by the oxidation of 1,10-phenanthroline with alkaline potassium permanganate in 29% yields with some modification of the procedure reported in the literature.[5] Cross coupling reaction of **2** with corresponding 4,5-disubstituted-trithiocarbonates **3a-d** in the presence of triethyl phosphite in argon atmosphere afforded **1a-d** along with the mixture of self-coupling product of **3a-d**, respectively. Compounds **1a-d** were isolated by column chromatography on silica gel using dichloromethane-methanol to give yellow crystals in a moderate yield.

All new compounds were characterized by NMR, UV, and Mass spectra. The electronic absorption spectra of **1a** are shown in Figure 1 and 2. And the spectral data are summarized in Table1. The absorption maxima of **1a** in methanol appeared at longer wavelength in all cases in comparison of those in cyclohexane. These facts were attributable to the presence of hydrogen bonds among two nitrogen atoms and methanol. However the details about these results are not clear.
To a solution of **1a** in methanol was added one-third molar amount of ferrous sulfate, the yellow solution was turned reddish yellow in color and orange precipitates were formed indicating the presence of coordination with Fe^{2+} ion. These data were also shown in Table 1. Red shifts were observed in all peaks by metal coordination and the tailing end were also appeared at longer wavelength region. The electronic

spectra of **1a** were shown in Figure 2 and those of coordinated species were in Figure 3.

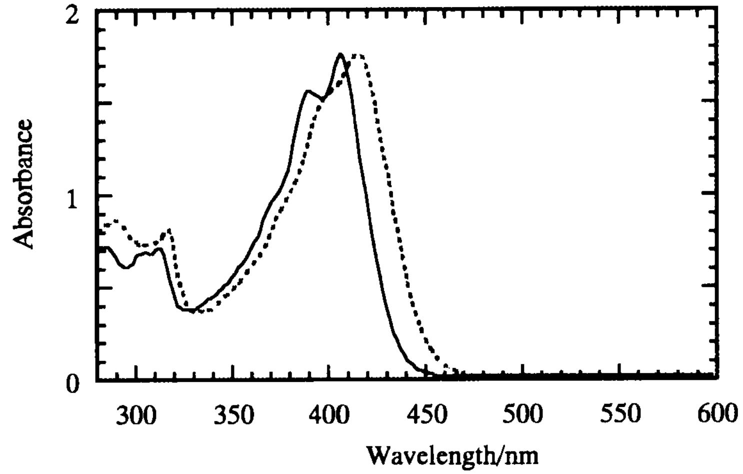


FIGURE 2 The electronic absorption spectra of **1a**. The solid line and the dashed line denote the spectra measured in cyclohexane and in methanol, respectively.

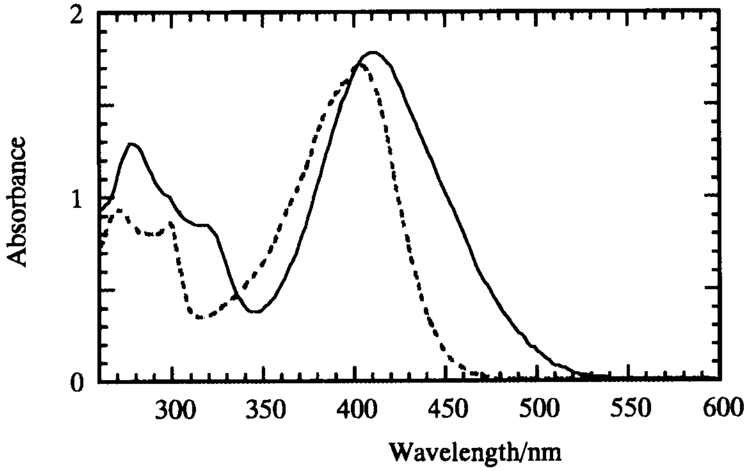


FIGURE 3 The electronic absorption spectra of **1a** in methanol. The solid line and the dashed line denote metal free and Fe^{2+}-coordination, respectively.

Metal coordination of **1a** with other metal ions was also investigated but no coordination with cupric ion was occurred by the fact that the color of the solution was unchanged in the reaction mixture. Nickel chloride was mixed with a solution of **1a** to afford two kinds of precipitates with different in color, and the details about these results are now in progress.

TABLE 1 Electronic absorption maxima of **1a** (λmax in nm).

Solvent	metal free	Fe^{2+} -coordination
methanol	290 302(sh) 317 416	298 316(sh) 334 422
cyclohexane	378 392 407	

Redox potentials were measured by cyclic voltammetry in dichloromethane at room temperature under argon atmosphere and the results were summarized along with that of TTF in Table 2. Cyclic voltammograms of **1a-d** showed the reversible one-electron redox waves in the sweep region from +0.70 to +1.00V in which the redox reaction of dithiolate ring was involved. The values of first redox potentials (E_1) of **1a-d** were lower by about 0.65V than those of tetrathioalkyl-TTF derivatives. These tendencies indicate **1a-d** have the lower ability of electron donating than those of TTF derivatives.

TABLE 2 First redox potentials of donors in dichloromethane.

Compound	E_1	with Fe^{2+} ion
1a	0.81	0.98
1b	0.80	
1c	0.80	
1d	0.78	
TTF	0.15	

V vs. Ag/Ag^+, Pt electrode, 0.1M Bu_4NClO_4, scan rate 100mV/s.

Figure 4 shows the cyclic voltammogram of **1a**. In the case of coordination with Fe^{2+} ion, the remarkable higher shift of the first redox potential was observed in **1a** compared with that of uncoordinated **1a**. This shift are attributable to the evidence of metal coordination at the sites of pyridine moieties resulting the decrease of electron density in dithiolate ring. Consequently the ability of electron donation in **1a** was to be lower by coordination with metal ions.

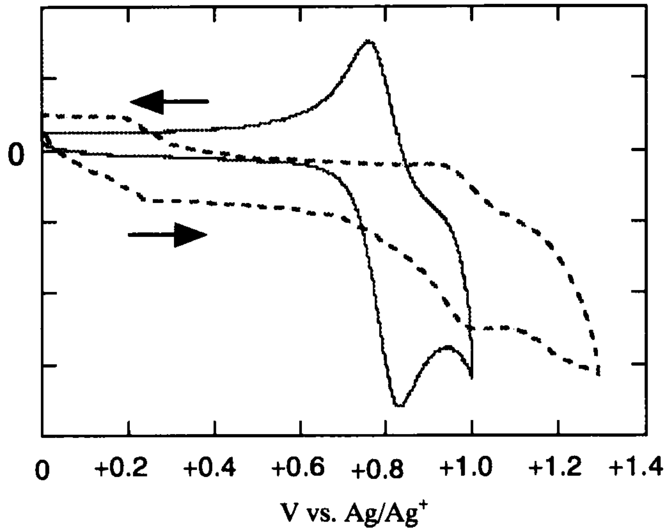


FIGURE 4 Cyclic voltammograms of **1a** in dichloromethane. The solid line and the dashed line denote metal free and Fe^{2+}-coordination, respectively.

EXPERIMENTAL

A typical procedure for 4,5-diaza-9-[4,5-bis(ethylthio)-1,3-dithiol-2-ylidene]-fluorene **1a** is as follows: A mixture of 182.3mg(1.00 mmol) of **2** and 380.9mg(1.5 mmol) of 4,5-bis(ethylthio)-1,3-dithiole-2-thione **3a** was dissolved in 50mL of toluene. After addition of 10mL of triethyl phosphite into the solution, the reaction mixture was refluxed for 4hr under argon stream. Evaporation of solvents under reduced pressure resulted yellow solids which were filtered, and washed with hexane. Recrystallization of the residue from benzene-hexane yielded 64.9mg of yellow microcrystals. The mother liquid was concentrated under reduced pressure. Column chromatography of the residue on silica gel eluting with dichloromethane-metanol(100:3) followed by recrystallization from the same solvent described above afforded another 142.7mg of crystals. Total amounts of **1a** was 207.6mg (53%). Mp 162.1-162.5°C; ^{1}H NMR (270MHz, CDCl$_3$,): δ 8.66 (dd, J= 1.0, 4.9Hz, 2H), 8.02(dd, J=1.2, 8.1Hz, 2H), 7.36(dd, J=8.1, 4.6Hz, 2H), 3.00(q, J=7.3Hz, 4H), 1.40(t, J=7.3Hz, 6H); ^{13}C NMR (67MHz, CDCl$_3$,): δ 15.0, 30.8, 114.4, 122.3, 129.2, 129.3, 131.2, 142.9, 147.2, 154.6; Mass: m/z 388(M$^+$).

4,5-Bis(buthylthio)-1,3-dithiole-2-thione **3b**, 4,5-ethylenedithio-1,3-dithiole-2-thione **3c**, and 4,5-bis(methylthio)-1,3-dithiole-2-thione **3d** were reacted to give 4,5-diaza-9-[4,5-bis(butylthio)-1,3-dithiol-2-ylidene]-fluorene **1b**, 4,5-diaza-9-(4,5-

ethylenedithio-1,3-dithiol-2-ylidene)-fluorene **1c**, and 4,5-diaza-9-[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-fluorene **1d**, respectively, in a similar manner to the reaction of **1a**. The physical and spectral data are as follows:

1b: Yellow microcrystals in 43% yield. Mp 79.2-80.9°C; ^{1}H NMR (270MHz, $CDCl_3$): δ 8.66 (dd, J= 1.0, 4.9Hz, 2H), 8.02(dd, J=1.2, 8.0Hz, 2H), 7.36(dd, J=4.9, 8.3Hz, 2H), 2.97(t, J=7.1Hz, 4H), 1.60(m, 8H), 0.96 (t, J=7.2Hz, 6H); ^{13}C NMR (67MHz, $CDCl_3$,) : δ 13.6, 21.7, 31.7, 36.3, 114.3, 122.4, 129.2, 129.3, 131.2, 143.1, 154.5; Mass: m/z 444(M^+).

1c: Reddish yellow microcrystals in 55% yield. Mp >280°C(decomp); ^{1}H NMR (270MHz, $CDCl_3$): δ 8.66 (dd, J= 1.5, 4.9Hz, 2H), 8.01(dd, J=1.2, 8.1Hz, 2H), 7.37 (dd, J=4.9, 8.3Hz, 2H), 3.43(s, 4H); ^{13}C NMR (67MHz, $CDCl_3$): δ 29.3, 114.0, 122.4, 129.4, 131.3, 147.2, 154.7; Mass: m/z 358(M^+).

1d: Yellow microcrystals in 44% yield. Mp >180°C(decomp); ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.66 (dd, J= 1.0, 4.9Hz, 2H), 8.03 (dd, J=1.2, 8.3Hz, 2H), 7.36(dd, J=4.9, 8.0Hz, 2H), 2.58(s, 3H); ^{13}C NMR (67MHz, $CDCl_3$,) : δ 19.3, 114.7, 122.4, 128.9, 129.3, 131.3, 142.7, 147.2, 154.7; Mass: m/z 360(M^+).

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