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Synthesis and Characterization of Dibenzodioxadiselenafulvalene

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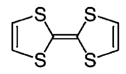
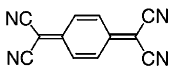
Abstract: Dibenzodioxadiselenafulvalene (DBOSF) was prepared and the cis and trans isomers were separated. X-ray crystallographic analysis revealed the presence of Se- - -H and O- - -H hydrogen bonds in both crystals. The electrochemical properties of *cis*- and *trans*-DBOSFs together with dibenzotetraoxafulvalene (DBTOF) and *cis*- and *trans*-dibenzodioxadithiafulvalenes were investigated by means of cyclic voltammetry and DFT calculation. The electron-donating ability and the stability of oxidized forms of DBOSFs are improved compared with those of DBTOF.

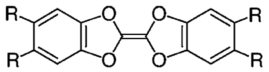
A large number of tetrachalcogenafulvalenes have been synthesized for donor molecules in organic conducting materials[1] since the discovery of the first organic metal tetrathiafulvalene−tetracyanoquinodimenthane (TTF−TCNQ).[2] Replacement of sulfur atoms with selenium and tellurium has been well investigated, whereas the oxygen analogues were relatively rare,[3] because of the instability of the tetraoxafulvalene core.[4] We have reported the preparation and characterization of the first tetraoxafulvalenes, DBTOF and DNTOF (dibenzo- and dinaphthotetraoxafulvalene, respectively),[5] with the aid of stabilization from benzene rings. The intimate chalcogen−chalcogen contacts play an important role in organic conducting materials. To improve the intermolecular interaction of oxygen-containing donor molecules, we introduced sulfur atoms in the fulvalene core, and the *cis*- and *trans*-dibenzodioxadithiafulvalenes (DBOTF) were synthesized and characterized.[6] The oxidized or partially charge-transferred forms were also stabilized, and actually we obtained the molecular complex of *trans*-DBOTF−TCNQ.[6] Substitution of selenium atoms attracts our attention with respect to electron-donor properties and stability of the cationic forms. We will report here the preparation and characterization of new donor molecules containing two oxygen and two selenium atoms in the fulvalene core, namely, *cis*- and *trans*-dibenzodioxadiselenafulvalenes (DBOSF).



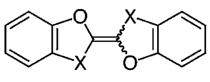
TTF



TCNQ

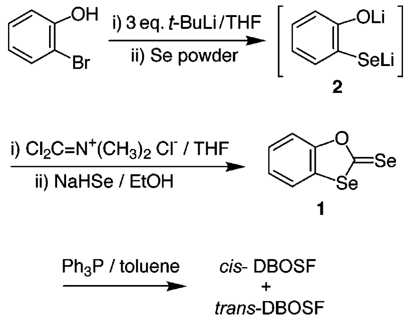


DBTOF (R = H)
DNTOF (R = CH=CH-CH=CH)



DBOTF (X = S)
DBOSF (X = Se)

SCHEME 1. Synthesis of DBOSF



The selenocarbonate precursor, benzo-1,3-oxaselenole-2-selone (**1**), was prepared according to one-pot methods for the preparation of the corresponding benzo-1,3-dioxole-2-selone[5] and benzo-1,3-oxathiole-2-selone[6] (Scheme 1). The dilithium salt of *o*-hydroxybenzeneselenol (**2**) was obtained from *o*-bromophenol according to a modified method for *o*-dimercaptobenzene and its selenium analogues,[7] and **2** was used for the next step without isolation. The reaction of **2** and (dichloromethylene)dimethylimmonium chloride (Viehe's salt)[8] followed by the treatment of the resultant mixture with NaHSe[9] gave **1** in 9% yield from *o*-bromophenol. We applied the synthetic procedure of DBTOF and DBOTF to the preparation of DBOSF, i.e., the central double bond was formed via a coupling reaction of **1** with triphenylphosphine as a dechalcogenating reagent. The isolated yield of DBOSF was 39% from **1**. Coupling reactions with tributylphosphine or trialkyl phosphites gave only unidentified products.

The cis and trans isomers of DBOSF were separated by means of gel-permeation column chromatography after recycled purification and characterized unequivocally by

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TABLE 1. Selected Crystallographic Parameters of *cis*- and *trans*-DBOSFs

	cis-DBOSF	*trans*-DBOSF
formula	$C_{14}H_8O_2Se_2$	$C_{14}H_8O_2Se_2$
habit	yellow needle	pale yellow needle
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a/Å	16.040(2)	8.9159(7)
b/Å	3.9690(3)	4.3310(3)
c/Å	19.179(1)	15.3642(9)
β/deg	107.158(4)	93.535(2)
V/Å^3	1166.6(2)	592.15(8)
Z	4	2
D_{calcd}/g cm^{-3}	2.084	2.053
μ(Mo Kα)/mm	6.327	6.233
no. of reflns	2594	1211
$R_1(F)$ $(I > 2\sigma(I))^a$	0.0384	0.0358
$R_w(F^2)$ (all data)^b	0.1441	0.1202

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

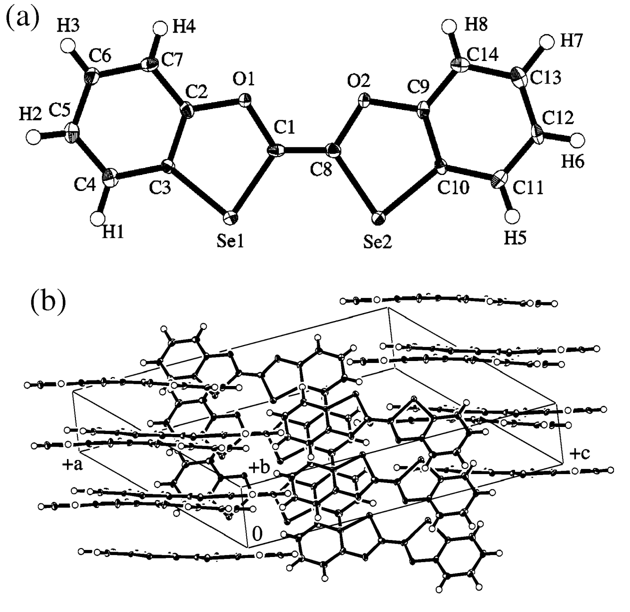

FIGURE 1. (a) Ortep drawing of *cis*-DBOSF with thermal ellipsoids at the 50% probability level. Atomic numbering is also shown. (b) Molecular arrangement in the crystal of *cis*-DBOSF.

means of the single-crystal X-ray crystallographic analysis. *cis*- and *trans*-DBOSFs are yellow and faintly yellow, respectively, in solids and in solutions. The cis/trans ratio was determined to be 5/8 by the peak areas in the chromatogram, but *cis*-DBOSF was found to undergo isomerization to *trans*-DBOSF in solutions on heating.

The X-ray crystal structure analysis (Table 1) reveals the almost planar molecular skeletons for both *cis*- and *trans*-DBOSFs. Figure 1 shows the Ortep drawing of *cis*-DBOSF and molecular arrangement in the crystal. Relatively short intermolecular chalcogen contacts are found to be 3.4493(6) Å for Se2- - -Se2$^{(\mathrm{i})}$ and 3.587(3) and 3.592(3) Å for Se2- - -O2$^{(\mathrm{ii})}$ and Se1- - -O1$^{(\mathrm{ii})}$, respectively. The intermolecular hydrogen-bonding interactions were pointed out for DBTOF and DNTOF,[4] and similarly hydrogen bonds CH- - -O are found in the crystal of *cis*-DBOSF: 2.9–3.0 Å for O1- - -H7$^{(\mathrm{iii})}$, O1- - -H7$^{(\mathrm{iv})}$, O2- - -H8$^{(\mathrm{iii})}$, and O2- - -H8$^{(\mathrm{iv})}$. Hydrogen bonds CH- - -Se are also found: 3.3–3.4 Å for Se1- - -H1$^{(\mathrm{v})}$, Se1- - -H2$^{(\mathrm{v})}$, Se2- - -H5$^{(\mathrm{ii})}$, and Se2- - -H5$^{(\mathrm{vi})}$. The symmetry operation codes for (i)–(vi) are $(^3/_2 - x, {}^1/_2 + y, {}^1/_2 - z)$, $(x, -1 + y, z)$, $(2 - x, -y, 1 - z)$, $(2 - x, 1 - y, 1 - z)$, $(1 - x, -y, 1 - z)$, and $(^3/_2 - x, -{}^1/_2 + y, {}^1/_2 - z)$, respectively.

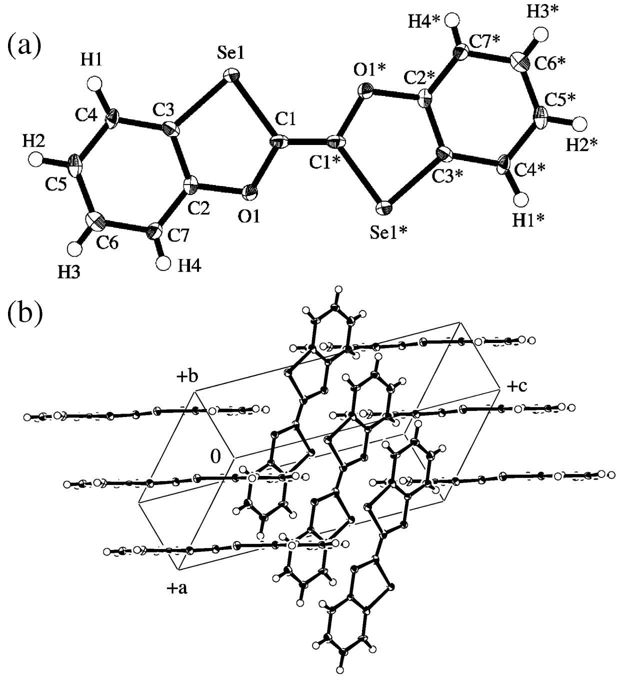

FIGURE 2. (a) Ortep drawing of *trans*-DBOSF with thermal ellipsoids at the 50% probability level. Atomic numbering is also shown. Symmetry operation code for * is 1-*x*, *y*, 1-*z*. (b) Molecular arrangement in the crystal of *trans*-DBOSF.

Figure 2 shows the molecular and crystal structures of *trans*-DBOSF. A half of *trans*-DBOSF is crystallographically independent, and the counterpart is related with the inversion symmetry. The shortest intermolecular distance is 3.579(3) Å for Se1- - -O1† (the symmetry operation code for † is $1 - x, 1 - y, 1 - z$). Other interatomic distances concerning Se atoms are longer than 3.6 Å. Instead, relatively short hydrogen bonds are found: 2.73(4) Å for O1- - -H4‡ and 3.04(6) Å for Se1- - -H1§ (the symmetry operation codes for ‡ and § are $(1 - x, -{}^1/_2 + y, {}^3/_2 - z)$ and $(-x, 1 - y, 1 - z)$, respectively).

In both crystals, the nearest molecules within a $\pi-\pi$ stack are related to the *b*-axis translation. The Se- - -O interactions seem to be substantial in the stacking direction, while the Se- - -H and O- - -H hydrogen-bonding interactions work in the intercolumnar contacts. Both face-to-face and side-by-side interactions are known to be essential for the conducting properties of the tetrachalcogenafulvalenium salts.[1] The hydrogen-bonding contact would be important in DBOSF ion radical salts when they are prepared.

We investigated electron-donating properties on *cis*- and *trans*-DBOSFs by means of cyclic voltammetry (CV). Figure 3 summarizes the CV results on the DBOXF series, DBTOF, and DBTTF (dibenzoTTF). The first oxidation processes were reversible for DBOTFs and DBOSFs whereas that of DBTOF was irreversible. This finding suggests that the introduction of S and Se atoms in place of O atoms improves the stability of their cation radical states. From a close look at the cathodic peaks, the oxidation processes of DBOTF were more clearly

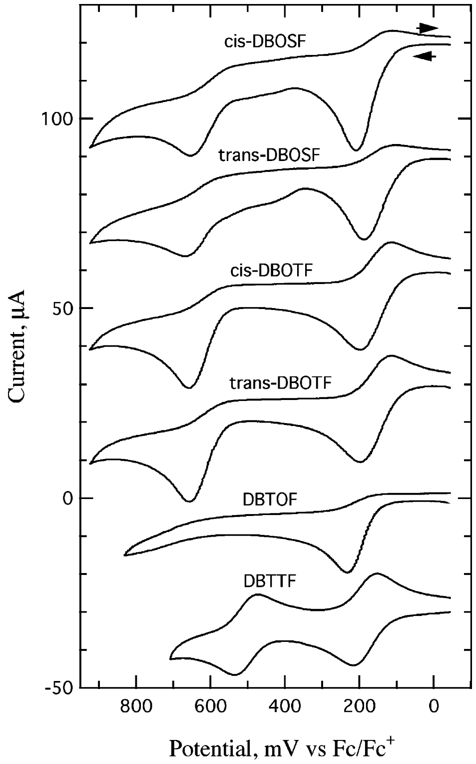

FIGURE 3. Cyclic voltammograms of *cis*- and *trans*-DBOSFs together with DBOTFs, DBTOF, and DBTTF measured in acetonitrile solutions.

reversible than those of DBOSF. Measurements in short-range cycles around the first oxidation wave did not improve the appearance of the cathodic peaks. The second oxidation processes are irreversible for DBOSFs and DBOTFs. DBTOF exhibited no second oxidation wave, probably owing to the immediate decomposition of the DBTOF cation radical.[5]

The first half-wave redox potentials are 0.17 V (vs Fc/ Fc^+) for DBOSFs and DBOTFs. From comparison with the potentials of the first anodic peaks because we could not define the half-wave potentials ($E^{(1)}{}_{1/2}$) of DBTOF, DBTOF was a poorer donor than the others by ca. 0.03 V. Thus, the electron-donating properties of DBOTF and DBOSF are slightly improved compared with DBTOF. Cowan et al. reported that $E^{(1)}{}_{1/2}$ of dibenzooxatrithiafulvalene exhibited a shift by 0.01 V compared with those of DBTTF.[3] We can summarize that the introduction of oxygen atoms causes a nearly 0.01 V shift per one oxygen in the TTF core.

From the quite similar profiles of the CV results on DBOSFs and DBOTFs, the substitution of S with Se hardly affected the donating properties. Furthermore, the magnitude of the on-site Coulomb repulsion for DBOSFs was very close to that of DBOTFs as suggested by the gap observed between the first and second redox waves.

TABLE 2. HOMO Energy of DBOSFs, DBOTFs, and DBTOF Calculated on the DFT B3LYP Level, Using the 6-311+G(2d,p) Basis Set

geometry	E_{HOMO}/eV X-ray structure	E_{HOMO}/eV B3LYP/6-31G(d) optimized
cis-DBOSF	−4.903	−4.952
trans-DBOSF	−4.877	−4.902
cis-DBOTF	−4.864	−4.926
trans-DBOTF	−4.970	−4.900
DBTOF	−4.927	−4.990

Assuming that the electronegativity is dominantly operative, the electron-donor property of DBOSF would be stronger than that of DBTOF owing to the intrinsic nature of Se. On the other hand, the acquirement of aromaticity in oxidized forms is usually supposed as a driving force of electron-donating properties of 1,3-dichalcogenole 7π systems. From the π-orbital overlap point of view, we can expect that DBTOF might be a stronger donor than DBOSF. The experimental results revealed that the former explanation was plausible or the two contributions were almost balanced.

The electron-donating abilities were confirmed by theoretical MO calculations. We applied semiempirical calculations in MOPAC,[10] only giving unsatisfactory results. The Se parameters are included in the MNDO-PM3 Hamiltonian but we assumed that the Se parameters were inadequate for the calculation on the peculiar dioxadiselenafulvalene systems. Thus, we performed ab initio calculations[11] for the present systems.

We applied single-point calculation for the present donor molecules whose structures were determined in the crystals, using the density functional B3LYP theory[12,13] with the 6-311+G(2d,p) basis set. Table 2 summarizes the HOMO energies of the donors investigated here. The CV experiments were performed in solution phases, and accordingly the calculation results are better compared with those of the computationally optimized geometries (B3LYP/6-31G(d)). The calculation results show that the HOMO energies are rather insensitive to the substitution between S and Se and that DBTOF has the lowest HOMO energy, in good agreement of the experimental CV results. The HOMO level of *cis*-DBOSF is slightly lower than that of *cis*-DBOTF because the HOMO surfaces are localized at the Se and S atoms (Figure 4a) and intramolecular through-space Se- - -Se bonding interaction in the cis form seems to stabilize the HOMO level. The HOMOs are largely dependent on the chalcogen character, being consistent with the argument that the electronegativity scale of the chalcogen atoms dominates the order of the electron-donating ability.

In summary, we have exploited the preparation method for oxygen-containing donor molecules, DBTOF, DBOTF, and DBOSF, and evaluated their electrochemical properties. For development of conducting materials, DBOTF and DBOSF are more promising than DBTOF because the stability of the oxidized forms is improved by partial replacement with S and Se atoms. We could prepare the DBOTF−TCNQ complex[6] but no CT complex of DBOSF has been characterized so far. The difficulty in the preparation of the latter may be related to the instability of oxidized DBOSF species compared with that of DBOTF. Conducting solids containing oxidized DBOSF and DBOTF may have a hydrogen-bonded network and chalcogen−oxygen contacts.

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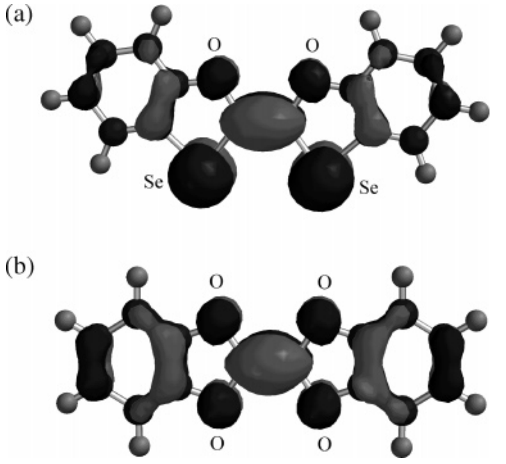

FIGURE 4. HOMO surfaces of *cis*-DBOSF and DBTOF based on the DFT calculation (B3LYP/6-311+G(2d,p)//B3LYP/6-31G-(d)).

Experimental Section

Benzo-1,3-oxaselenole-2-selone (1). To a tetrahydrofuran (THF) solution (30 mL) containing 2-bromophenol (12.1 mL; 20 mmol) was added 3.0 equiv of *tert*-butyllithium in pentane (28 mL) at −50 °C under a nitrogen atmosphere. After the mixture was stirred for 8 h at −50 °C to complete the dilithiation, a THF suspension (20 mL) containing powdery Se metal (1.58 g; 20 mmol) was added and the solution was stirred for a further 8 h at −50 °C. Portions of (dichloromethylene)dimethylimmonium chloride (Viehe's salt;[8] 2.54 g; 20 mmol) were added to the mixture at room temperature and the resultant mixture was warmed to ca. 40 °C until the mixture turned yellow. An ethanol solution (20 mL) containing 20 mmol of NaHSe (prepared from 1.58 g of Se powder and $NaBH_4$)[9] was added to the above mixture at −20 °C and the combined mixture was warmed to room temperature for 2 h. Pure **1** was obtained by passing through a short column repeatedly (SiO_2 eluted with 1/1 CH_2Cl_2−hexane and 1/9 CH_2Cl_2−hexane). Removal of the solvent gave yellow solids of **1** (473 mg; 9.0%). Mp 123−124°C (CH_2Cl_2−hexane). ^1H NMR (270 MHz, 1/1 CS_2−$CDCl_3$) δ 7.31 (1H, d of t, $J = 1.4$, 7.5 Hz), 7.39 (1H, d of t, $J = 1.6$, 7.7 Hz), 7.46−7.51 (2H, m). ^{13}C NMR (68 MHz, 1/1 CS_2−$CDCl_3$) δ 113.1, 124.4, 126.3, 128.0, 128.4, 158.6, 202.6. MS (EI, 70 eV) *m/z* 259, 260, 261, 262, 263, 264, 265 [M^+]. IR (KBr) ν 749, 958, 977, 1053, 1162, 1444, 1456 cm^{-1}. UV/vis ($CHCl_3$) λ_{max} /nm (ϵ /dm^3 cm^{-1} mol^{-1}) 362 (2.2×10^4). Anal. Calcd for $C_7H_4OSe_2$: C, 32.09; H, 1.54. Found: C, 32.80; H, 1.49.

***cis-* and *trans*-DBOSFs.** A toluene solution (5 mL) containing **1** (413 mg; 1.58 mmol) and triphenylphosphine (432 mg; 1.65 mmol) was refluxed for 2.5 h. After hexane was added to the mixture at room temperature, triphenylphosphine and its selenide were solidified and separated by filtration. The solvent was removed from the filtrate and a mixture of *cis*- and *trans*-DBOSFs was separated by silica gel chromatography eluted with 1/9 CH_2Cl_2−hexane as a yellow fraction (224 mg). Subsequently, the cis and trans isomers were separated by a gel-permeation chromatography (JAI polystylene-gel columns 1H+1H, eluted with $CHCl_3$, detected with 254 nm absorption). The *cis*- and *trans*-DBOSFs were collected after 5 time recycles as fractions with the retention times of 56 and 58 min/cycle, respectively. The cis/trans ratio was nearly 5/8 estimated by the chromatogram peak heights. The isolated yields were 48 (17%) and 63 mg (22%) for *cis*- and *trans*-DBOSFs, respectively. Unchanged **1** was recovered (70 mg; 17%). *cis*-DBOSF: yellow needles, mp 156−157°C (CH_2Cl_2−hexane). ^1H NMR (270 MHz, $CDCl_3$) δ 6.99 (2H, d of t, $J = 1.3$, 7.7 Hz), 7.07 (2H, d of d, $J = 1.3$, 7.7 Hz), 7.17 (2H, d of t, $J = 1.3$, 7.7 Hz), 7.29 (2H, d of d, $J = 1.3$, 7.7 Hz). ^{13}C NMR (68 MHz, $CDCl_3$) δ 111.5, 121.1, 123.1, 123.2, 125.1, 127.1, 154.6. MS (EI, 70 eV) *m/z* 363, 364, 365, 366, 367, 368, 369 [M^+]. IR (KBr) ν 731, 956, 1131, 1233, 1458 cm^{-1}. UV/vis (hexane) λ_{max} /nm (ϵ /dm^3 cm^{-1} mol^{-1}) 322 (1.2×10^4), 229 (4.6×10^4). Anal. Calcd for $C_{14}H_8O_2Se_2$: C, 45.93; H, 2.20. Found: C, 45.44; H, 1.62. *trans*-DBOSF: slightly yellow needles, mp 192−193°C (CH_2Cl_2−hexane). ^1H NMR (270 MHz, $CDCl_3$) δ 6.96 (2H, d of t, $J = 1.3$, 7.7 Hz), 6.98 (2H, d of d, $J = 1.3$, 7.7 Hz), 7.14 (2H, d of t, $J = 1.3$, 7.7 Hz), 7.27 (2H, d of d, $J = 1.3$, 7.7 Hz). ^{13}C NMR (68 MHz, $CDCl_3$) δ 111.5, 120.8, 123.5, 124.3, 125.2, 127.3, 155.6. MS (EI, 70 eV) *m/z* 363, 364, 365, 366, 367, 368, 369 [M^+]. IR (KBr) ν 747, 977, 1144, 1156, 1444 cm^{-1}. UV/vis (hexane) λ_{max} /nm (ϵ /dm^3 cm^{-1} mol^{-1}) 320 (8.3×10^3), 244 (2.7×10^4), 226 (2.5×10^4). Anal. Calcd for $C_{14}H_8O_2Se_2$: C, 45.93; H, 2.20. Found: C, 45.84; H, 2.17.

X-ray Crystallographic Analysis. Diffraction data of a single crystal of *cis*- and *trans*-DBOSFs were collected on a Rigaku R-axis RAPID diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) at 90 K. The structures were directly solved by the SIR92 method in the teXsan program package.[14] Numerical absorption correction was used. All of the hydrogen atoms could be found in difference Fourier maps, and the parameters of the hydrogen atoms were included in the refinement. The thermal displacement parameters were refined anisotropically for non-hydrogen atoms and isotropically for hydrogen atoms. Full-matrix least-squares methods were applied by using all of the unique diffraction data. The selected crystallographic parameters are summarized in Table 1.

Cyclic Voltammetry Analysis. Cyclic voltammograms were recorded on a CypressSystems CS-1200 voltammeter. The acetonitrile solutions were prepared which contained 5 mmol/L of the specimen (nearly saturated concentrations) and 0.1 mol/L of tetra-*n*-butylammonium perchlorate as a supporting electrolyte. An Ag/Ag^+ electrode was used as the reference electrode and calibrated with the Fc/Fc^+ redox potential measured under the same conditions. Platinum working and counter electrodes were used. The scan rate was 200 mV/s. The half-wave potentials were reproduced with the scan rates of 100 and 400 mV/s.

MO Calculation. All the calculations were carried out with the Spartan02 program package.[11] Single-point calculations were performed with the hybrid B3LYP density functional theory method, where Becke's three-parameter exchange functional[12] and Lee−Yang−Parr's correlation functional[13] were used. The 6-311+G(2d,p) basis set was applied to the molecules whose geometry was determined by means of X-ray crystallographic analysis. Geometry optimizations were performed with the B3LYP method with the 6-31G(d) basis set. The HOMO surfaces were drawn at the static isovalue of 0.002.

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Supporting Information Available: ^1H and ^{13}C NMR spectra for **1** and *cis*- and *trans*-DBOSFs and CIF files for *cis*- and *trans*-DBOSFs. This material is available free of charge via the Internet at http://pubs.acs.org.

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