

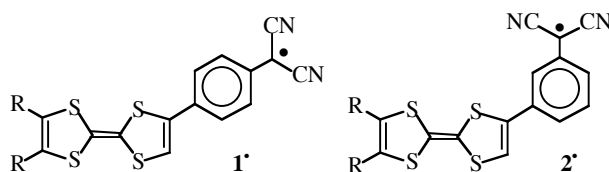
GENERATION AND AMPHOTERIC REDOX PROPERTIES OF NOVEL NEUTRAL RADICALS WITH THE TTF-TCNQ HYBRID STRUCTURE¹

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Abstract - One electron oxidation of 4-(2-tetrathiafulvalenyl)phenyl substituted dicyanomethylides (**1**⁻) gave black solids of the title radicals (**1**[•]). They exhibit quite high electrochemical amphotericity, which may be responsible for their good electrical conductivities ($\sigma = ca. 10^{-7} \text{ S cm}^{-1}$) as a single component. Isomeric radicals (**2**[•]) with a *m*-phenylene spacer could not be obtained under the similar conditions probably due to insufficient delocalization of the unpaired electron.

Recently much attention has been focused on multi-stage organic redox systems in the field of materials science.² Among them, a series of compounds showing electrochemical amphotericity is of special interest,³ where one electron-oxidation and reduction occur within an easily accessible potential window. Beside the topics as NLO materials⁴ or molecular electronic devices,⁵ another unique property is electrical conductivity⁶ as a single component.^{7,8} Graphite is the definitive example that exhibits the ultimate amphotericity with $E^{\text{sum}} \equiv E^{\text{ox}} + (-E^{\text{red}}) = 0$. Although it is quite difficult to endow the closed-shell species with pretty high amphotericity ($E^{\text{sum}} < 0.5 \text{ V}$),³ it would be much easily achieved in neutral radicals as suggested by our previous study.⁸ On the basis of these results, we have now designed novel neutral radicals which may exhibit very high amphotericity ($E^{\text{sum}} < 0.2 \text{ V}$) by incorporating both very strong electron-donating and -accepting subunits. Tetrathiafulvalene (TTF)⁹ is an electron-rich skeleton of choice ($E_1^{\text{ox}} = +0.36 \text{ V}$), whose donating property is finely tuned by substituents such as Me groups (2,3-Me₂-TTF: $E_1^{\text{ox}} = +0.31 \text{ V}$). Phenyldicyanomethyl [$\text{PhC}(\text{CN})_2^{\cdot}$] is selected as an open-shell acceptor. Its electron affinity is as high as tetracyanoquinodimethane (TCNQ) ($E_1^{\text{red}} = +0.18 \text{ V}$), which is shown by measuring the oxidation potential of $\text{PhC}(\text{CN})_2^-$ [$E^{\text{ox}} = +0.19 \text{ V}$ (irrev.)]. Connection of these two subunits furnishes the novel radicals (**1**[•] and **2**[•]) having a *p*- or *m*-phenylene unit, respectively. Although the irreversible oxidation wave of $\text{PhC}(\text{CN})_2^-$ suggests the poor stability of $\text{PhC}(\text{CN})_2^{\cdot}$ itself, the newly designed radicals with the TTF-TCNQ hydride structure (**1**[•] and **2**[•]) are expected to be much more stable due to delocalization of the unpaired electron over the enlarged π -system.



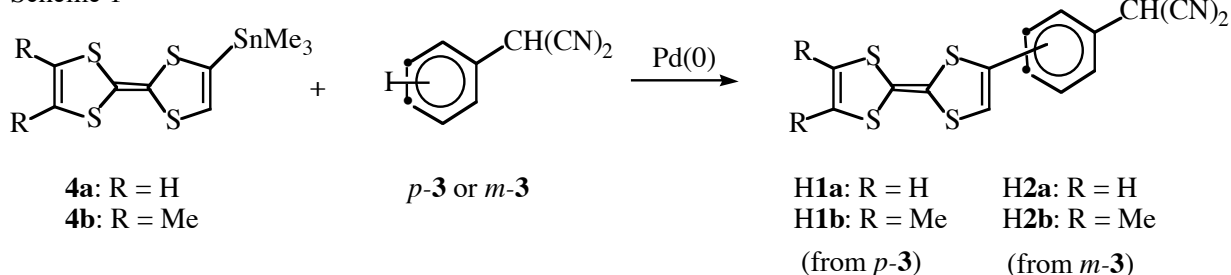
RESULTS AND DISCUSSION

Preparation, structure, and redox properties of (4- and 3-dicyanomethylphenyl)tetrathiafulvalenes (H1 and H2) with the TTF-TCNQ hydride structure. *p*- and *m*-Diiodobenzenes were subjected to Takahashi's arylmalononitrile preparation,¹⁰ and the resultant iodophenylmalononitriles (*p*-**3** and *m*-**3**) were coupled with 2-trimethylstannyl-TTF (**4a**)¹¹ to give **H1a** and **H2a** with the TTF-TCNQ hydride structure in 34 and 35% yields, respectively (Scheme 1). Similar cross-coupling reactions of 6,7-dimethyl-2-trimethylstannyl-TTF (**4b**) with *p*-**3** and *m*-**3** afforded **H1b** (y. 36%) and **H2b** (y. 39%), respectively.

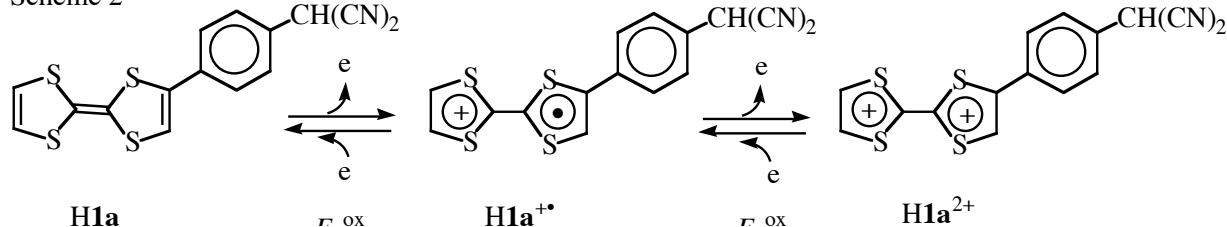
X-Ray structural analysis on **H2b** at 123 K has revealed that the substituents on TTF cause no significant distortion of the TTF skeleton (Figure 1). The whole π -electron system of **H2b** adopts a planar geometry; the dihedral angle between the TTF unit and the benzene nucleus is 3.7°. Furthermore, the largest deviation of non-hydrogen atoms from the least-square molecular plane excluding CN groups is only 0.17 Å. Therefore, there exist no steric reasons that may prevent the π -conjugation between the TTF unit and the phenylene group in the compounds studied here. Another important feature is that the bond length of the central tetrathio-substituted olefin [1.352(3) Å] is comparable with that of the parent TTF [1.349(3) Å].¹³ Considering that this bond length is sensitive to the degree of charge-transfer on TTF,¹⁴ the similarity of these values shows absence of any electronic effects from the dicyanomethyl group¹⁵ in these neutral donors.

In accord with negligible CT interaction between two subunits, redox behaviors of **H1a** and **H2a** resemble that of the parent TTF (Table 1). Their oxidation potentials measured in MeCN are essentially identical to each other, indicating that C₆H₄CH(CN)₂ moiety gives no effects on the reversible two-stage one electron-oxidation process of TTF (Scheme 2). This idea was also supported by comparisons among **H1b**, **H2b**, and Me₂-TTF. Again, the E^{ox} values are insensitive to the substituted position of dicyanomethyl group on the benzene nucleus. On the contrary, quite different behaviors were observed for the anions (**1**^{•-} and **2**^{•-}) having a *p*- or *m*-phenylene unit as shown in the next section.

Scheme 1



Scheme 2



Generation and redox properties of 4- and 3-(2-tetrathiafulvalenyl)phenyldicyanomethylides (1⁻ and 2⁻): the anionic precursors of the radicals. Figure 2 shows the cyclic voltammogram of the anion (1a⁻) generated *in situ* by adding 1 eq of Et₃N to an MeCN solution of H1a. Three pairs of reversible or quasi-reversible waves are observed. The first process was assigned to the one electron-oxidation of C₆H₄C(CN)₂⁻ moiety by comparisons with the potentials of reference compounds. The TTF unit in 1a⁻ undergoes two-stage one electron-oxidation at E₂^{ox} and E₃^{ox} (Scheme 3). Stronger donating property of 1a⁻ than that of PhC(CN)₂⁻ is due to the substitution effect of the electron-rich TTF skeleton. On the other hand, slight difficulty in oxidizing TTF unit in 1a⁻ at E₂^{ox} is attributable to the strong electron-withdrawing effect of C₆H₄C(CN)₂⁻ moiety. Similar behavior was observed in the dimethyl derivative (1b⁻). The differences between E₁^{ox} and E₂^{ox} in 1⁻ correspond to the E^{sum} values of 1[•] by definition. Thus, the radicals (1[•]) derived by the one electron-oxidation of the anionic precursors (1⁻) are shown to exhibit quite high amphotericity with E^{sum} of 0.29 V for 1a[•] and 0.24 V for 1b[•], respectively.

Table 1. Oxidation potentials^a of neutral donors (H1 and H2) and TTFs

	E ₁ ^{ox}	E ₂ ^{ox}
H1a	+0.37	+0.72
H1b	+0.32	+0.67
H2a	+0.36	+0.73
H2b	+0.32	+0.68
TTF	+0.36	+0.74
Me ₂ -TTF	+0.31	+0.68

^a E / V vs SCE, 0.1 mol dm⁻³ Et₄NClO₄ in MeCN, 100 mV s⁻¹. Values in Table 2 were obtained under the same conditions.

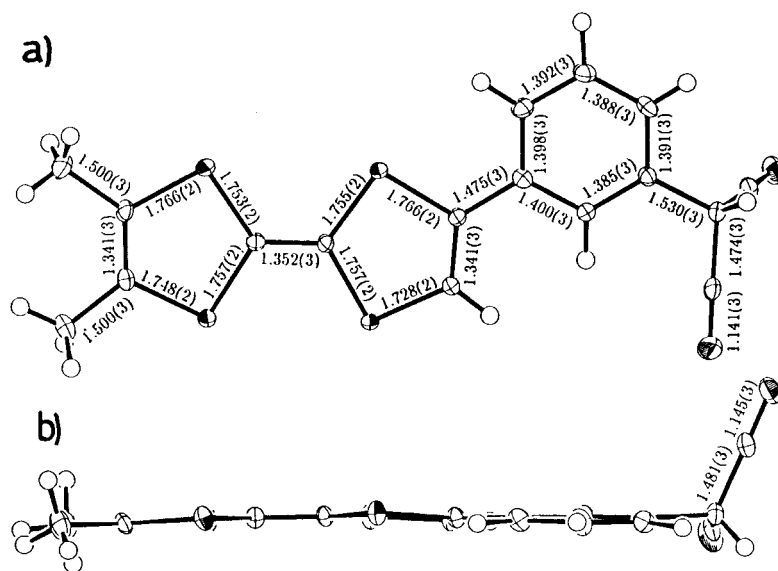


Figure 1. Molecular structure of H2b determined by X-Ray analysis at 123 K: a) top view; b) side view

Table 2. Oxidation potentials of anionic precursors (1⁻ and 2⁻) generated *in situ*^a

	E ₁ ^{ox}	E ₂ ^{ox}	E ₃ ^{ox}
1a ⁻	+0.12	+0.41 ^b	+0.73
1b ⁻	+0.10	+0.34 ^b	+0.70
2a ⁻	+0.17 ^c	(+0.35) ^d	(+0.75) ^d
2b ⁻	+0.18 ^c	(+0.32) ^d	(+0.69) ^d
PhC(CN) ₂ ⁻	+0.19 ^c	-	-

^a Anions were generated by addition of 1 eq of Et₃N to H1 or H2, respectively. ^b Quasi-reversible waves. ^c Irreversible waves. ^d Oxidation potentials of the products formed at the first oxidation process.

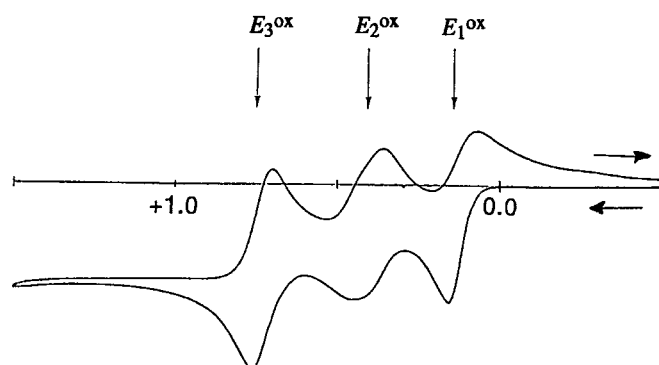
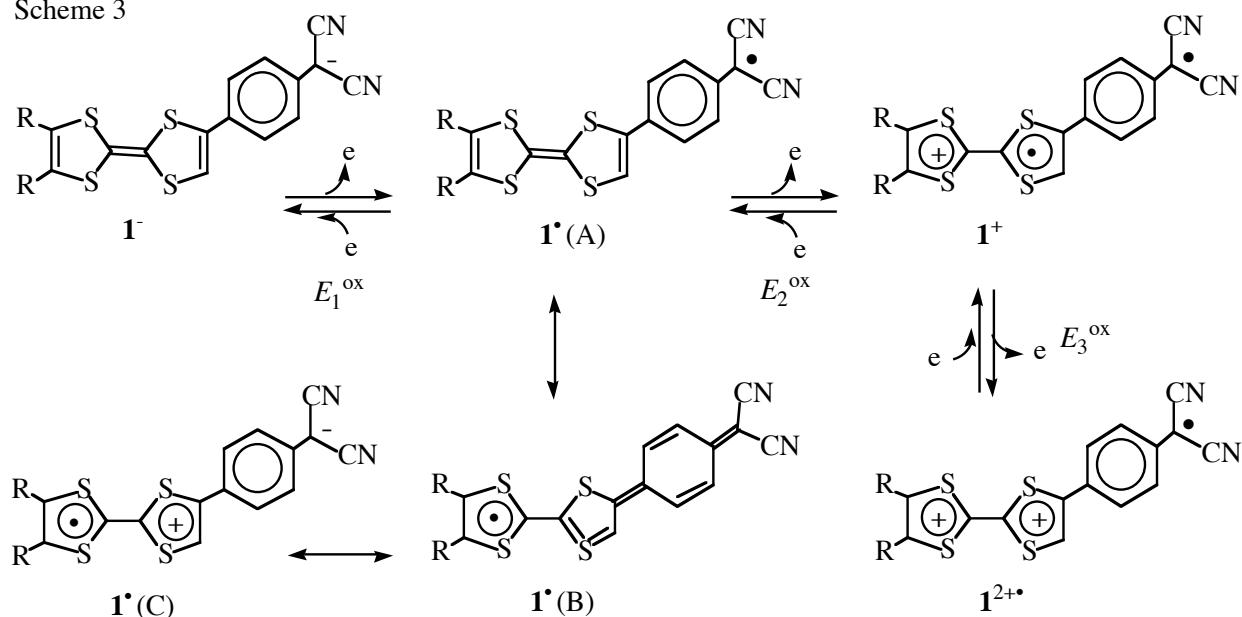


Figure 2. Cyclic voltammogram of 1a⁻ (E/V vs SCE, 0.1 mol dm⁻³ Et₄NClO₄ in MeCN)

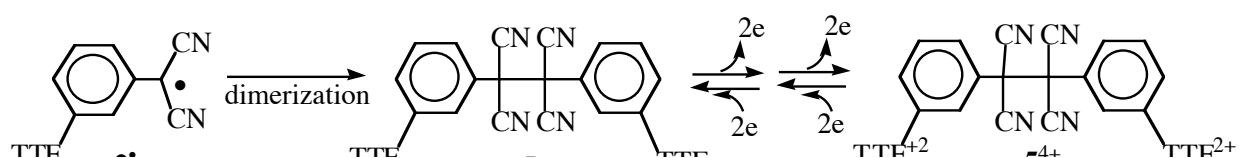
Although generation and isolation of highly amphoteric molecules have been proven very difficult,^{9,16} electrochemical reversibility observed in the interconversion between 1^- and $1^\bullet$ prompted us to preparative-scale oxidation of 1^- . When a brown MeCN solution of $1a^-$ generated from **H1a** and 1.2 eq Et_3N was reacted with 1.5 eq I_2 , a black powder precipitated immediately; it weighed 58% of the theory for the radical ($1a^\bullet$). Similar I_2 -treatment on $1b^-$ also afforded a black solid, and the same material was obtained by the electrochemical oxidation in MeCN. Although full characterization of these solids was hampered due to the very low solubility and instability in polar solvents, they were assigned to the desired radicals ($1^\bullet$) based on the combustion analyses and MS spectra. In the IR spectra, both radicals show two distinct $\text{C}\equiv\text{N}$ stretching bands at 2204 and around 2170 cm^{-1} , suggesting the contribution of neutral forms (A and B in Scheme 3) as well as a zwitterionic form (C).

The electrical conductivities of $1a^\bullet$ or $1b^\bullet$ measured by a two-probe method at room temperature are 1.1×10^{-7} and $5.7 \times 10^{-6} \text{ S cm}^{-1}$, respectively. These values are high as a single component, thus confirming our idea that the unpaired electrons of neutral radicals can act as conduction electrons in the solid when the amphotericity is high enough.⁸ In seeking for a higher conductivity of the radicals, regulation of the electronic structure toward a smaller E^{sum} becomes important beside controlling of the crystal packing.¹⁷ The electronic interaction between the donating and accepting subunits through the *p*-phenylene spacer results in the lower electron affinity of $1^\bullet$ than $\text{PhC}(\text{CN})_2^\bullet$. In the same manner, the donating properties of $1a^\bullet$ or $1b^\bullet$ become weaker than TTF or $\text{Me}_2\text{-TTF}$, respectively. This is the reason for much greater E^{sum} values of $1^\bullet$ than expected by the simple calculation from the redox potentials of reference compounds (hypothetical E^{sum} : 0.17 V for $1a^\bullet$ and 0.12 V for $1b^\bullet$).

Scheme 3



Scheme 4



Accordingly, the *m*-phenylene derivatives (**2**[•]) with smaller mesomeric interaction between subunits are expected to show higher amphotericity than **1**[•]. In fact, the E_1^{ox} values of **2**[•] are much higher than those of **1**[•] and rather close to the value of PhC(CN)₂[•] itself (Table 2). To our regret, however, the first oxidation step is irreversible both in **2a**[•] and **2b**[•], indicating the high reactivity of **2**[•]. It should be mentioned that two pairs of reversible waves are observed in the more anodic region, which are assigned to the oxidation processes of the products derived from **2**[•] (Table 2). Such voltammograms are best accounted for by formation of dimer (**5**) with two TTF moieties (Scheme 4). The limited delocalization of the unpaired electron in **2**[•] cannot afford the sufficient stabilization to the radicals for isolation.

CONCLUSION

This work has revealed that the novel TTF derivatives bearing *p*-C₆H₄C(CN)₂[•] group could be generated and isolated as stable solids. They exhibit quite high electrical amphotericity, and their E^{sum} values are two of the smallest values ever reported. The radicals (**1**[•]) were formed as insoluble powders, thus difficult to obtain as crystalline materials for measuring physical properties or crystallographic study. By introduction of proper substituents and/or slight modification of the framework, however, this class of neutral radicals would serve as good candidates for intramolecular CT materials⁹ or conducting magnetic multifunctional materials.¹⁹

EXPERIMENTAL

Preparation of iodophenylmalononitriles (*p*-3 and *m*-3). Mineral oil of NaH (960 mg, 60%, 24 mmol) was removed by washing with *n*-hexane. To its suspension in dry THF (40 mL) was added a solution of malononitrile (1.38 g, 20.9 mmol) in 10 mL of THF over 10 min at 0 °C under Ar. The mixture was stirred for 30 min at rt. To the resultant solution of sodium dicyanomethylide were added *p*-diiodobenzene (4.98 g, 15.1 mmol) and (Ph₃P)₂Pd(II)Cl₂ (550 mg, 0.78 mmol). The whole mixture was heated at reflux for 34 h under Ar. After quenching by pouring over ice water (100 mL), the basic aqueous layer was washed with CHCl₃ (50 mL x 3). Unreacted *p*-diiodobenzene (2.73 g, 55% recovery) was obtained from the combined organic layers. Acidifying the aqueous layer with HCl and extraction with CHCl₃ (50 mL x 3) gave a gray solid (761 mg) of *p*-iodophenylmalononitrile (*p*-3) containing a small amount of *p*-phenylenebis(malononitrile). Chromatographic separation on SiO₂ (CHCl₃) gave pure *p*-3 (605 mg) as faintly yellow crystals in 15% yield. Similar procedure on *m*-diiodobenzene gave *m*-iodophenylmalononitrile (*m*-3) as a pale yellow solid in 25% yield along with 58% recovery of the starting material.

Data of *p*-3: mp 99-100.5 °C (EtOH); ¹H NMR (90 MHz, CDCl₃) δ 5.00 (1H, s), 7.25 (2H, AA'XX'), 7.90 (2H, AA'XX'); IR (KBr) 3432, 3084, 2872, 2256, 1584, 1486, 1402, 1062, 1008, 920, 838, 782, 522, 440 cm⁻¹; MS (EI) *m/z* 268 (M⁺); Anal. Calcd for C₉H₅N₂I: C, 40.32; H, 1.88; N, 10.45; I, 47.34. Found: C, 40.40; H, 2.08; N, 10.33; I, 47.04. Data of *m*-3: colorless solid, mp 94.5-96.5 °C (benzene/*n*-hexane); ¹H NMR (400 MHz, CDCl₃) δ 5.02 (1H, s), 7.25 (1H, dd, *J* = 8.5, 8.5 Hz), 7.50 (1H, d, *J* = 8.5 Hz), 7.85 (1H, d, *J* = 8.5 Hz), 7.86 (1H, s); IR (KBr) 2888, 2256, 1752, 1588, 1570, 1472, 1420, 1256, 1234, 1166, 1104, 1086, 1068, 1004, 928, 875, 818, 774, 694, 672, 422 cm⁻¹; Anal. Calcd for C₉H₅N₂I: C 40.32, H 1.88, N 10.45, I 47.34. Found: C 40.36, H 2.05, N 10.36, I 47.58.

Preparation of (4- and 3-dicyanomethylphenyl)tetrathiafulvalenes (H1a and H2a) and their dimethyl derivatives (H1b and H2b) . Unsubstituted TTF¹⁸ and the 2,3-dimethyl derivative (Me₂-TTF)¹² were prepared according to the literature. 2-Trimethylstannyl-TTF (**4a**)¹¹ was obtained as an orange oil *via* 2-lithio-TTF and used without further purification for the cross-coupling. 2-Trimethylstannyl-6,7-dimethyl-TTF (**4b**) was similarly prepared from Me₂-TTF in nearly quantitative yield. Because of easy destannylation during the purification process, **4b** was also used as prepared after checking its purity by ¹H NMR [(90 MHz, CDCl₃) δ 0.33 (9H, s), 1.92 (6H, s), 6.23 (1H, s)].

To a solution of 2-trimethylstannyl-TTF (**4a**, 546 mg, 1.49 mmol) in toluene (20 mL) were added *p*-iodophenylmalononitrile (**p-3**, 324 mg, 1.21 mmol) and (Ph₃P)₄Pd(0) (142 mg, 0.123 mmol). The mixture was heated at reflux for 6 h. After evaporation of solvent, the residue was diluted with AcOEt (50 mL) and washed with water (50 mL x 3) and brine (50 mL). Drying over Na₂SO₄ and evaporation of solvent gave a brown solid, from which 140 mg of 2-(4-dicyanomethylphenyl)tetrathiafulvalene (**H1a**) was obtained as orange crystals in 34 % yield by chromatographic separation on SiO₂.

Similarly, 2-(4-dicyanomethylphenyl)-6,7-dimethyltetrathiafulvalene (**H1b**), 2-(3-dicyanomethylphenyl)-tetrathiafulvalene (**H2a**), 2-(3-dicyanomethylphenyl)-6,7-dimethyltetrathiafulvalene (**H2b**) were obtained in 36, 35, and 39% yields, respectively, by the cross-coupling reactions of the following combinations, **4b** with **p-3**, **4a** with **m-3**, and **4b** with **m-3**.

Data of **H1a**: mp 188.5-190 °C (benzene); ¹H NMR (400 MHz, CDCl₃) δ 5.07 (1H, s), 6.35 (2H, s), 6.64 (1H, s), 7.51 (2H, AA'BB'), 7.52 (2H, AA'BB'); IR (KBr) 3076, 2904, 2888, 1578, 1538, 1506, 1414, 924, 840, 824, 794, 778, 756, 736, 668, 432 cm⁻¹; MS (EI) m/z 344 (M⁺); Anal. Calcd for C₁₅H₈N₂S₄: C, 52.29; H, 2.34; N, 8.13; S, 37.24. Found: C, 52.14; H, 2.45; N, 7.89; S, 37.04. Data of **H1b**: brown crystals, mp 189.5-191 °C (benzene/*n*-hexane); ¹H NMR (400 MHz, CDCl₃) δ 1.97 (6H, s), 5.07 (1H, s), 6.63 (1H, s), 7.50 (2H, AA'BB'), 7.51 (2H, AA'BB'); IR (KBr) 3064, 2916, 2164, 1570, 1532, 1506, 1436, 1412, 780, 768 cm⁻¹; MS (FD) m/z 372 (M⁺); Anal. Calcd for C₁₇H₁₂N₂S₄: C, 54.80; H, 3.25; N, 7.52; S, 34.43. Found: C, 54.42; H, 3.45; N, 7.36; S, 33.89. Data of **H2a**: orange crystals (CHCl₃), mp 149.5-152 °C; ¹H NMR (400 MHz, CDCl₃) δ 5.08 (1H, s), 6.35 (2H, s), 6.64 (1H, s), 7.43-7.53 (4H, m); IR (KBr) 3068, 2884, 2856, 1604, 1584, 1564, 1540, 1482, 1436, 1212, 1154, 984, 872, 798, 780, 736, 688, 666, 660, 436 cm⁻¹; MS (FD) m/z 344 (M⁺); Anal. Calcd for C₁₅H₈N₂S₄: C, 52.29; H, 2.34; N, 8.13; S, 37.24. Found: C, 51.70; H, 2.47; N, 7.84; S, 36.92. Data of **H2b**: orange crystals, mp 151-153.5 °C (benzene); ¹H NMR (400 MHz, CDCl₃) δ 1.97 (6H, s), 5.07 (1H, s), 6.63 (1H, s), 7.44-7.52 (4H, m); IR (KBr) 2912, 2888, 1604, 1580, 1556, 1530, 1478, 1440, 1272, 1254, 1210, 1180, 1154, 1090, 994, 912, 892, 872, 848, 802, 780, 742, 684, 650, 624, 586, 438, 418 cm⁻¹; MS (FD) m/z 372 (M⁺); Anal. Calcd for C₁₇H₁₂N₂S₄: C, 54.80; H, 3.25; N, 7.52; S, 34.43. Found: C, 54.79 H, 3.32; N, 7.42; S, 34.40.

Preparation of 4-(2-tetrathiafulvalenyl)phenyldicyanomethyls (1'). To a suspension of neutral precursor (**H1a**) (50 mg, 0.145 mmol) in 10 mL dry MeCN was added Et₃N (25 μL, 0.17 mmol) under Ar. The resulting brown solution turned deep green immediately upon addition of iodine (55 mg, 0.217 mmol). After stirring for 1 h, 4-(2-tetrathiafulvalenyl)phenyldicyanomethyl (**1a'**, 29 mg) was obtained as black precipitates in 58% yield. Similarly, 4-(6,7-dimethyl-2-tetrathiafulvalenyl)phenyldicyanomethyl (**1b'**) was obtained in quantitative yield.

By a constant current electrolysis of the anionic precursor (**1b**⁻) in MeCN containing 0.1 mol dm⁻³ Et₄NClO₄, the radical (**1b**[•]) was also obtained in 56% yield. In the case of the electrolysis of *m*-phenylene derivative (**2a**⁻), however, the resulting brownish solid is not the desired radical (**2a**[•]) but tentatively assigned to the dimer (**5a**) (y. 50%) by the doubled molecular weight in the MS spectrum and absence of strong CN stretching frequencies in IR. Preparation of dimers from the *m*-phenylene-type anionic precursors (**2**⁻) was difficult to reproduce, probably due to the overoxidation of **5** to polycationic species.

Data of **1a**[•]: mp > 300 °C; IR (KBr) 3064, 2204, 2172, 1600, 1548, 1494, 1476, 1436, 1412, 1342, 1200, 1184, 1142, 1070, 1018, 830, 798, 780, 704, 652, 466 cm⁻¹; MS (FD) m/z 343 (M⁺); Anal. Calcd for C₁₅H₇N₂S₄·H₂O: C, 49.47; H, 2.51. Found: C, 49.47 H, 2.33. Data of **1b**[•]: black powder, mp 159-161.5 °C; IR (KBr) 2204, 2168, 1596, 1522, 1430, 1340, 1202, 1182, 1086, 928, 826, 782, 702 cm⁻¹; MS (FD) m/z 372 (M⁺+1); Anal. Calcd for C₁₇H₁₁N₂S₄: C, 54.95; H, 2.98; N, 7.54. Found: C, 54.77; H, 3.11; N, 7.71. Data of **5a**: mp >240 °C; IR (KBr) 3452, 2068, 1598, 1538, 1488, 1422, 1252, 1212, 1090, 998, 850, 798, 780, 748, 698, 658, 622 cm⁻¹; MS (FD, relative intensity) m/z 344 (100), 686 (M⁺, 31); Anal. Calcd for C₃₀H₁₄N₄S₈: C, 52.44; H, 2.05; N, 8.16. Found: C, 51.85; H, 2.39; N, 8.45.

Measurement of Redox Potentials. Oxidation (*E*^{ox}) and reduction (*E*^{red}) potentials were measured by cyclic voltammetry in dry MeCN containing 0.1 mol dm⁻³ Et₄NClO₄ as a supporting electrolyte. Ferrocene undergoes one electron-oxidation at +0.38 V under the same conditions. All of the values shown in the text are in *E*/V vs SCE, and Pt wire was used as a working electrode. In the case of irreversible waves, *E*^{ox} and *E*^{red} were calculated as *E*_(anodic peak) - 0.03 and *E*_(cathodic peak) + 0.03, respectively.

X-Ray Analysis of H2b: Red plate, 0.2 x 0.1 x 0.05 mm³, C₁₇H₁₂N₂S₄, *M* 372.54, triclinic *P*1bar, *a* = 6.772(4), *b* = 8.419(4), *c* = 14.729(7) Å, α = 78.03(2), β = 81.76(2), γ = 86.62(2)°, *V* = 812.6(7) Å³, ρ (*Z* = 2) = 1.522 g cm⁻³. A total of 3442 unique data (2θ_{max} = 55°) was measured at *T* = 123 K with a Rigaku Mercury CCD camera diffractometer (Mo-Kα radiation, λ = 0.71069 Å). Numerical absorption correction was applied (μ = 5.83 cm⁻¹). The structure was solved by the Patterson method and refined by the full-matrix least-squares method on *F* with anisotropic temperature factors for non-hydrogen atoms. All of the hydrogen atoms were picked up from the D-map and refined with isotropic temperature factors. The final *R* and *R*_w values are 0.059 and 0.070 for 3442 non-zero reflections and 255 parameters (GOF = 2.13). Maximum residual electron density is 1.14 e Å⁻³.

ACKNOWLEDGMENTS

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