

Donor-Donor'-Acceptor Triads based on [3.3]Paracyclophane with 1,4-Dithiafulvene Donor and Cyanomethylene Acceptor: Synthesis, Structure, Electro- and Photo-physical Properties

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Abstract: Donor-donor'-acceptor triads (**1**, **2**) based on [3.3]paracyclophane ([3.3]PCP) as a bridge with electron-donating property (D') with 1,4-dithiafulvene (DTF; TTF half unit) as a donor and dicyanomethylene (DCM; TCNE half unit) or an ethoxycarbonyl-cyanomethylene (ECM) as an acceptor were designed and synthesized. The pulse radiolysis study of **1a** in 1,2-dichloroethane allowed the clear assignment of the absorption bands of the DTF radical cation (**1a**^{•+}), while the absorption bands due to the DCM radical anion could not be observed by γ -ray radiolysis in 2-methyltetrahydrofuran rigid glass at 77K. Electrochemical oxidation of **1a** first generates the DTF radical cation (**1a**^{•+}), whose absorption bands are in agreement with those observed by the pulse radiolysis study, followed by dication (**1a**²⁺). The ESR spectrum of **1a**^{•+} showed a symmetrical signal with fine structure and ESR simulation predicted that the spin of **1a**^{•+} is delocalized over S and C atoms of

the DTF moiety and the central C atom of the trimethylene bridge bearing DTF moiety. Pulse radiolysis, ESR, and electrochemical studies indicate that the DTF radical cation of **1a**^{•+} is more stable than that of **6**^{•+}, and the latter shows strong tendency to dimerize. This result indicates that [3.3]PCP moiety as a bridge can stabilize the DTF radical cation more than 1,3-diphenylpropane moiety because of kinetic stability due to its rigid structure and the weak electronic interaction of DTF and DCM moieties through [3.3]PCP.

Introduction

Tetrathiafulvalene (TTF) is known as the strong electron donor (D) that possesses highly reversible oxidation states and is successfully used as a building block for organic conductors.^[1] Aviram and Ratner proposed the concept of the unimolecular rectifier based on the TTF(D)-bridge(B)-TCNQ(A) dyad with bicyclooctane as a rigid σ -bridge.^[2] Particularly, since their proposal, many TTF(D)-B-A dyads with a σ - or π -bridge have been synthesized. These dyads offer considerable potential to develop molecular electronics materials that applied intramolecular charge transfer (ICT) process between D and A.^[3-6] Molecular electronics as nonlinear optical (NLO) materials and display electrochromic materials are based on ICT process between D and A through bridges.^[7] As the stable charge separated state D⁺-B-A⁻ with fixed D⁺ and A⁻ distance and the electron tunneling between D and A are prerequisite for in TTF(D)-B-A molecular rectifier proposed by Aviram and Ratner, the development of intramolecular rectification electronics requires the D-B-A dyads with a rigid σ -bridge. In the past decades, flexible σ -bridges have been used in TTF(D)-B-A dyads so far,^[4] and there has been no report on those with a rigid σ -bridge (i.e. bicyclooctane) such as the Aviram-Ratner model^[2]. Recently, the Langmuir-Blodgett monolayer of TTF(D)-B-A dyads containing trinitrofluorene (A) were reported to be the a few examples of the molecular rectifier in many TTF(D)- σ (B)-A dyads.^[4a, f]

1,4-Dithiafulvene (DTF; TTF half unit, 1,3-dithiole-2-ylidene) serves as an electron donating building block for diverse organic materials such as organic superconductors,^[8] and its radical cation has thermodynamic stability (Chart 1). In the reported DTF(D)-B-A dyads, π -spacers have been used as bridges mostly, and these dyads have been applied to dye-sensitized solar cells and nonlinear optical materials.^[9] In DTF(D)- σ (B)-DCM(A) dyads, only a few examples employed rigid σ -bridge.^[10]

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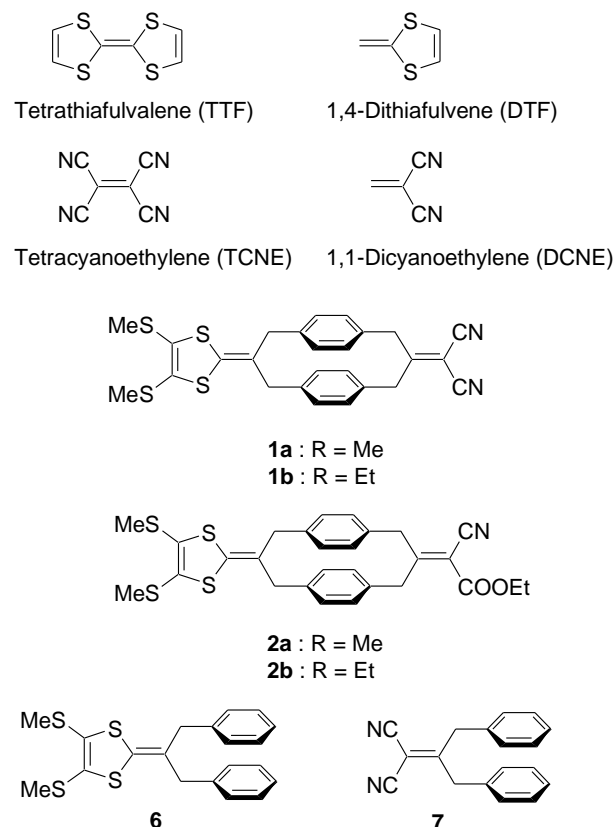


Chart 1. Molecular structures of TTF, DTF, TCNE, DCM, the target molecules (**1**, **2**), and the reference compounds.

The use of [2.2]- or [3.3]PCP as a bridge can promote ICT and control electronic interaction by the π - π stacking within cyclophane.^[11] Thus, D-B(PCPs:D')-A triads are interesting candidates for molecular electronics materials, and these D-A systems based on PCPs can be classified into three types according to the ways of introducing D and A into PCP as follows (Chart 2); type A: the CT (D-A) cyclophanes, type B: the cyclophanes substituted with D and A at the *psudopara* positions, type C: cyclophanes with D and A incorporated into the bridge chains.

Over three decades, rigid two- to four-layered CT (D-A) cyclophanes (type A) were synthesized by Staab's group,^[12] Misumi's group,^[13] and Shinmyozu's group,^[14] and they were used as model compounds for the clarifications of the dependence of CT interaction on transannular distance and relative orientation of A and D. In the past decade, there has been a growing interest in the use of [2.2]- or [3.3]PCP as a bridge in the D-B(PCP)-A triads (type B), in which D-PCP([2.2]PCP or [3.3]PCPs)-A triads are expected to show photoinduced charge separation phenomena with long lifetime, and these triads have been applied as organic solar cell^[15] and NLO materials.^[16]

On the other hand, there have been no reports of D-B(D')-A triads (type C), where π -systems of A and D are orthogonal to the benzene rings of the cyclophane, which is different from spiro π -conjugation. As far as we know, there are a few

examples of D-B(D')-D triads and B(D)-A dyads^[17] which can be categorized as type C. Previously, we reported that electronic interaction between orthogonal arranged DTF and benzene rings of [3.3]PCP in D-B(D')-D triads.^[17e] We have expected that these triads show unique electronic interaction between D and A through cyclophane moiety to generate stable charge separated states.

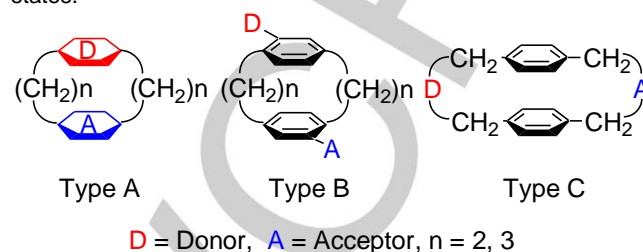


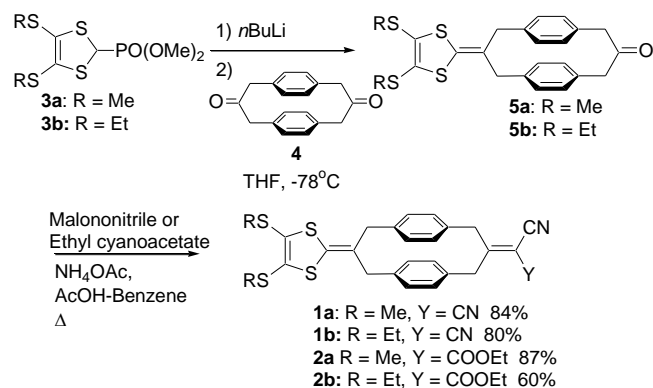
Chart 2. Three types of donor-cyclophane-acceptor triads.

Thus, we focused on a cylindrical and rigid structure of [3.3]PCP as a rigid spacer of D-B-A triads, instead of the bicyclooctane bridge, in order to construct the rigid triads with fix D-A distance (Chart 1). We synthesized DTF(D)-[3.3]PCP(B)-DCM or ECM (A) triads, in which [3.3]PCP was used as a σ -spacer with electron-donating property (D'). In this paper, we report the synthesis, structure, electrochemical and photophysical properties of the triads **1** and **2**, and properties of the DTF radical cation **1a⁺** based on pulse radiolysis, electrochemical, and ESR studies.

Results and Discussion

Synthesis

The synthesis of DTF-[3.3]PCP-DCM triads **1a-b** and DTF-[3.3]PCP-ECM triads **2a-b** is shown in Scheme 1. The corresponding 1,3-dithiole phosphonate esters **3a-b**^[18] and [3.3]paracyclophane-2-11-dione **4**^[19] were prepared according to the literature procedures. Cyclophane **4** was reacted with the anion generated from phosphonate esters **3a-b** by *n*BuLi in dry THF at -78°C , and the reaction mixture was slowly warmed up to room temperature. After the solvent was evaporated, the reaction mixture was purified by column chromatography on silica gel with CH_2Cl_2 /hexane (2/1) as an eluent to afford the triad precursor cyclophane monoketones **5a-b** in 47 and 57% yield, respectively. Then the cyclophanes **5a-b** were reacted with malononitrile or ethyl cyanoacetate in the presence of ammonium acetate and acetic acid in benzene at reflux. After removal of the solvents, the reaction mixture was purified by column chromatography on silica gel with CH_2Cl_2 as an eluent or recrystallization from CH_2Cl_2 -MeOH. The target triads **1a-b** and **2a-b** were obtained 84, 80, 87, and 60% yields, respectively. All compounds synthesized were fully characterized by ^1H -NMR, ^{13}C -NMR, IR, and MS data.



Scheme 1. Synthesis of the triads **1a-b** and **2a-b**.

Molecular structure

Single crystals of **1a** were grown by recrystallization from benzene solution and the molecular structure of **1a** was determined by single crystal X-ray diffraction analysis. The side and top views of the structure of **1a**, together with the crystallographic atom-numbering scheme of D and A moieties are shown in Figure 1. The interplanar distance between two benzene rings of **1a** was 3.269 Å. The trimethylene bridges of the cyclophane take a chair conformation and the 1,4-dithiafulvene bends outwards with planes A(C4–C3–S3–S4) and B(C5–S3–S4) folding along the S3–S4 lines by 4.24°. The dihedral angles of the DTF moiety (planes A and B) with the benzene rings of [3.3]PCP are 85.39 and 85.58°, respectively, indicating the almost orthogonal relationship between the DTF moiety and the benzene rings of [3.3]PCP. Similar orthogonal structure is observed in the benzene rings of [3.3]PCP and DCM moiety as an acceptor. Because our effort to prepare single crystals of **2a** and **2b** was unsuccessful, their molecular structures were optimized by B3LYP/6-31G* level of theory, and the calculations predicted similar molecular structures to that of **1a** (Figure 1S).

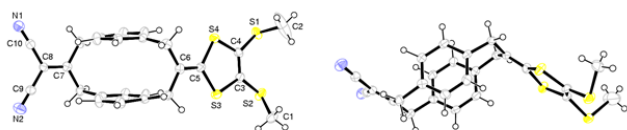


Figure 1. The molecular structure of **1a** with side and top views.

Absorption spectra

The absorption spectra of the triads (**1a**, **2a**) and the related compounds (**6**, **7**) were measured in CH₂Cl₂ at room

temperature (Figure 2). The absorption spectra of **1** and **2** are nearly identical. The triad **1a** exhibits two strong absorption peaks at 292 (ε 14100 M⁻¹cm⁻¹) and 324 (ε 7800) nm and a shoulder at around 365 (ε 4200) nm, and **2a** shows similar absorption spectrum to that of **1a** [λ_{max} 288 (ε 16700), 325 (ε 9600), and 365 (sh, ε 4300) nm], while the bis(benzyl)DTF **6** absorbs at 257 (ε 13600), 286 (ε 15200), 332 (ε 6100), and around 365 (sh, ε 3100) nm and the bis(benzyl)DCM **7** exhibits a peak at 277 (ε 5000) nm. The spectral shape of **1a** is a simple combination of those of **6** and **7** (Figure 2), while the intensity of the peak at 334 nm of **1a** is higher than that of **6**, suggesting the presence of weak electronic interaction between the DTF and DCM moieties through [3.3]PCP (i.e. both of intramolecular electronic interaction between the DTF and benzene rings of [3.3]PCP, and intramolecular electronic interaction between the DCM and benzene rings of [3.3]PCP).^[17e]

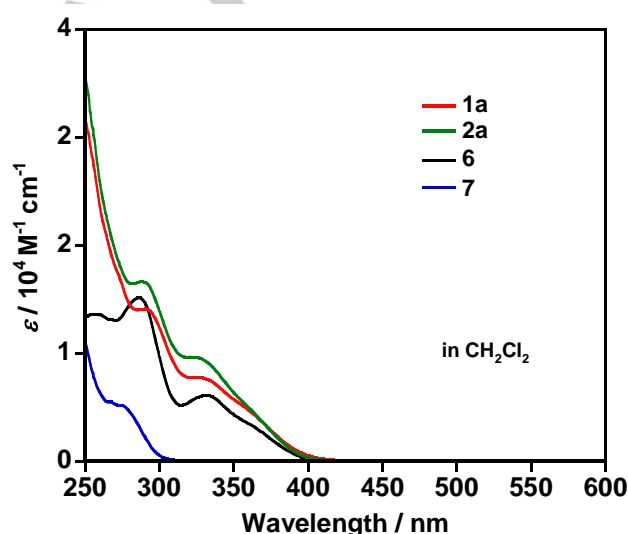


Figure 2. Electronic spectra of **1a** and **2a**, and the reference compounds **6** and **7** in CH₂Cl₂.

Pulse radiolysis

The formation of DTF radical cation or DCM radical anion of **1a** was examined by pulse- or γ-ray radiolysis (Figure 3, additional spectra can be found in the ESI†: Figure 2S - Figure 4S). The transient absorption spectra of **1a** in 1,2-dichloroethane (DCE) during pulse radiolysis are shown in Fig. 3. In transient absorption spectrum observed at 50 ns after an electron pulse, **1a** shows two broad bands, in which the band in the region of 400–500 nm exhibits the maximum at 415 nm and a shoulder at 467 nm, while the very broad band in the region of 600–850 nm consists of the maximum at 750 nm and a shoulder at 677 nm.

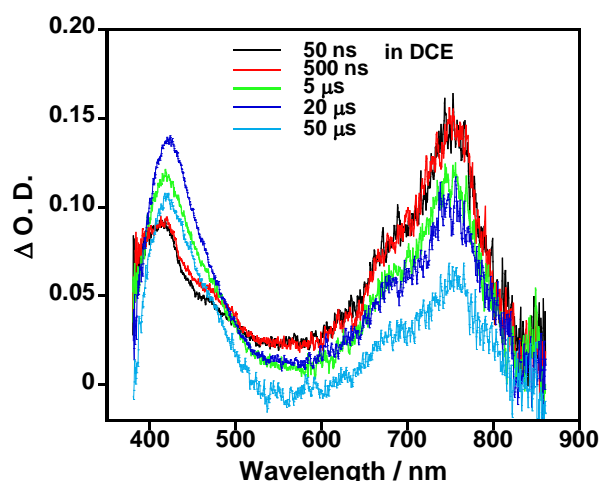


Figure 3. Transient absorption spectra observed at 50, 500 ns and 5, 20, 50 μ s after an electron pulse the triad **1a** (2.5 mM) in DCE under Ar atmosphere at 295 K.

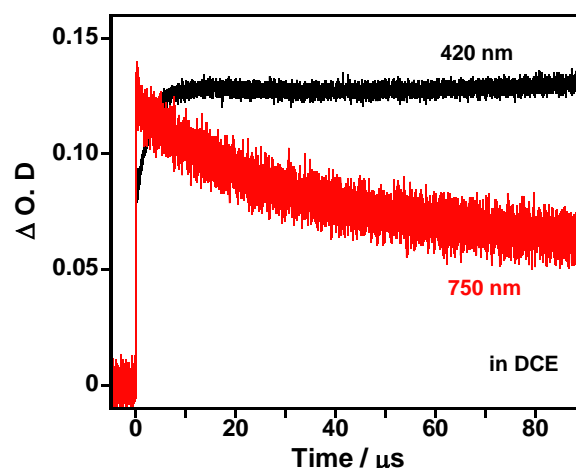
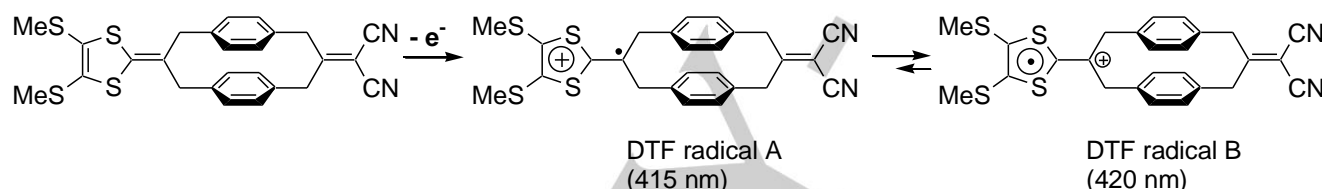


Figure 4. Kinetic traces of Δ O.D. at 420 and 750 nm during the pulse radiolysis of the triad **1a** (2.5 mM) in DCE under Ar atmosphere at 295 K.



Scheme 2. Possible DTF radical cations of the triad **1a**.

The intensity of the bands at 677 and 750 nm gradually decreased and shifted to the longer wavelength region by ca. 10 nm until 50 μ s. On the other hand, the intensity of the band in the region of 400 – 500 nm gradually increased up to 50 μ s and shifted to 420 nm. The absorption spectrum at 50 ns after an electron pulse can be assigned to the first generated DTF radical cation **1a**^{•+} (DTF radical A) [λ_{max} : 415, 467 (sh), 677 (sh), and 750 nm], and the new band at 420 nm at 20 μ s after an electron pulse is due to another structure of the DTF radical cation **1a**^{•+} (DTF radical B) (Scheme 2).^[20] Because of the presence of intramolecular electronic interaction between the DTF and benzene rings of [3.3]PCP in the ground state, positive charge of DTF radical cation would be partly located on [3.3]PCP. The radical cation of bis(benzyl)DTF **6** [λ_{max} : 414, 467 (sh), 676 (sh), and 750 nm] exhibited similar transient absorption bands to those of **1a** at 415 and 750 nm as well as the shoulders at ca. 467 and 677 nm (Figure 5S). Although the intensity of the bands at 676 and 750 nm in **6**^{•+} gradually decreased, these bands as well as the band at 414 nm did not shift to the longer wavelength region.

The time profiles of **1a** and **6** at 420 (415) and 750 nm during the pulse radiolysis are shown in Figure 4, Figure 6S, and Table 1. The decay profiles of **1a** and **6** monitored at 750 nm showed multicomponent decay up to 90 μ s, indicating the presence of the components with shorter and longer time decays. The time decay constants of **1a** and **6** were evaluated as τ_1 (**1a**: 16.5 μ s, **6**: 4.4 μ s) and τ_2 (**1a**: 82.8 μ s, **6**: 34.7 μ s). As

Table 1. The decay lifetimes of the triad **1a** and the related compound **6** at 750 nm and 420 or 415 nm.

Compound	τ_1 (μ s) ^[a]	τ_2 (μ s) ^[a]	τ (μ s) ^[b]
1a	16.5	82.8	>90
6	4.4	34.7	33.4

[a] The decay lifetimes at 750 nm were measured in in DCE under Ar atmosphere at 295 K and double exponential decay fitting (eqn (1)) was used. [b] The decay lifetimes at 420 or 415 nm were measured in in DCE under Ar atmosphere at 295 K and single exponential decay fitting (eqn (2)) was used.

$$\Delta\text{OD} = A_1 \exp\left[-\frac{(t-t_0)}{\tau_1}\right] + A_2 \exp\left[-\frac{(t-t_0)}{\tau_2}\right] + A_{\text{off}} \quad (1)$$

$$\Delta\text{OD} = A_1 \exp\left[-\frac{(t-t_0)}{\tau_1}\right] + A_{\text{off}} \quad (2)$$

shown in Figure 4, the decay rate of the DTF radical B observed at 420 nm is faster than the decay rate of the DTF radical A, and the concentration of the DTF radical B is constant after 10 μ s, while the concentration of the DTF radical A is decreased even after 10 μ s. These data indicate that the first generated DTF radical cation (DTF radical A) converts to another structure of

the DTF radical cation (DTF radical B) under the pulse radiolysis conditions (Figure 4 and Scheme 2). Different from the time profile of **1a**, the concentration of the DTF radical cation of **6** (415 nm) is decreased even after 80 μ s, indicating its instability compared to that of **1a**^{•+} (Figure 6S). Clearly, the lifetime of the DTF radical cation of **1a** is longer than that of the bis(benzyl)DTF **6**, indicating that the DTF radical cation is stabilized by rigid structure of [3.3]PCP. The absorption spectrum of **1a** in 2-methyltetrahydrofuran (MTHF) rigid glass at 77K after γ -radiolysis is similar to that of **1a** at 50 ns after an electron pulse (Figure 3S and Figure 4S), but the absorption band due to the DCM radical anion was not observed.

Electrochemical properties

In order to study the electrochemical properties of **1a-b** and **2a-b**, cyclic voltammograms and differential pulse voltammograms of **1** and **2** were measured in CH₂Cl₂ (Figure 5, ESI†). The redox potentials of **1** and **2** are summarized in Table 2 along with those of the references, bis(benzyl)DTF **6** and bis(benzyl)DCM **7**. The first and second oxidation processes of **1** and **2** (E_{ox1} : +0.32 to +0.34 V, E_{ox2} : +0.73 to +0.74 V, V vs. Fc/Fc⁺) correspond to the formation of the radical cation and dication of the DTF moiety (Scheme 1S), respectively, based on the pulse radiolysis study as described above. The first oxidation potentials (E_{ox1} : +0.32 to +0.34 V) of **1** and **2** are slightly higher than that of **6** (E_{ox1} : +0.30V; Figure 14S). This result suggests that weak intramolecular electronic interaction between DTF donor and

[3.3]PCP is present, and positive charge of the DTF radical cation would be mostly localized over the 1,3-dithiole ring. The

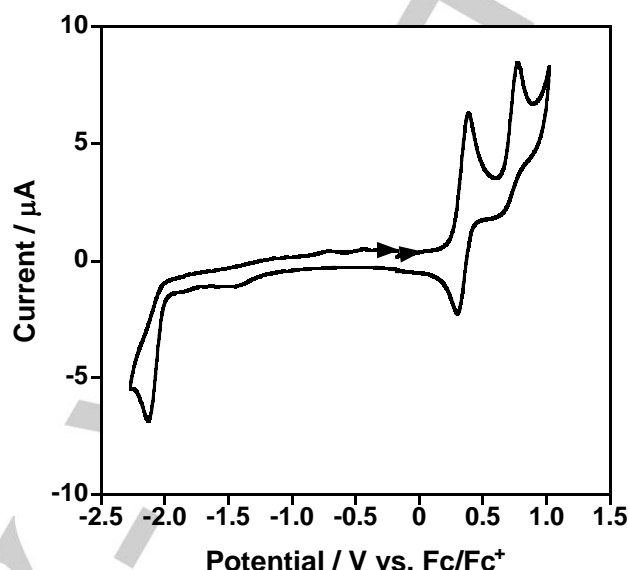


Figure 5. Cyclic voltammogram of **1a** under the conditions (in CH₂Cl₂/0.1M *n*Bu₄NPF₆, Ag/AgNO₃ as the reference electrode, Pt as the working and counter electrode at the potential scan rate of 0.1V/s. Potentials are referred to vs. Fc/Fc⁺(V)).

Table 2. Electrochemical data of triads **1**, **2**, and the related compounds.

Compound	E_{ox1} / [V] ^[a]	E_{ox2} / [V] ^[a]	E_{ox3} / [V] ^{[b][c]}	E_{red} / [V] ^{[b][d]}	HOMO / [eV] ^[e]	HOMO / [eV] ^[f]	LUMO / [eV] ^[e]	LUMO / [eV] ^[f]	E_g exp ^[g]
1a	+0.34	+0.74	+1.45	-2.12	-5.35	-5.41	-3.16	-2.29	2.19
1b	+0.33	+0.75	+1.46	-2.12	-5.36	-5.35	-3.15	-2.28	2.21
2a	+0.32	+0.73	+1.36	-2.28	-5.34	-5.26	-3.03	-1.95	2.31
2b	+0.34	+0.74	+1.38	-2.26	-5.36	-5.20	-3.06	-1.94	2.30
5a	+0.32	+0.72	+1.40		-5.35				
5b	+0.33	+0.73	+1.39		-5.35				
6	+0.30	+0.74			-5.32				
7				-2.15			-3.15		

[a] Determined from the cyclic voltammograms in CH₂Cl₂/0.1M *n*Bu₄NPF₆, Ag/AgNO₃ as the reference electrode, Pt as the working and counter electrode at the potential scan rate of 0.1V/s. Potentials are referred to vs. Fc/Fc⁺(V), reversible step. [b] irreversible step. [c] E_{ox3} is anodic peak potential. [d] E_{red} is cathodic peak potential. [e] HOMO = - (E_{pc}^{onset} + 5.1) and LUMO = - (E_{pc}^{onset} + 5.1). [f] HOMO and LUMO are estimated by DFT methods (B3LYP/6-31G* level). [g] E_g^{exp} = HOMO – LUMO.

third oxidation potentials of **1** and **2** (E_{ox3} : +1.36 to +1.46 V), which are assigned to one electron oxidation of [3.3]PCP moiety to its cation radical species, are higher than that of [3.3]PCPs (E_{ox} : +1.07 V).^[21] Probably, this anodic shift is due to an introduction of A and D into the central carbon of the trimethylene bridges and electrostatic repulsion from the dication species of the DTF moiety. Thus, [3.3]PCP serves as a bridge with electron-donating properties (D'). The reduction process of **1a** (E_{red} : -2.12 V), **1b** (E_{red} : -2.12 V) or **2a** (E_{red} : -2.26 V), and **2b** (E_{red} : -2.28 V) can be attributed to the formation of the radical anion species of DCM or ECM moiety, respectively. As the electron accepting ability of ECM substitute was weaker than that of DCM substitute,^[10] the reduction potentials of **2** are lower than that of **1**. The reduction potentials (E_{red} : -2.12 V) of **1a** and **1b** are slightly lower than that of the bis(benzyl)DCM **7** (E_{red} : -2.15 V; Figure 15S), and this suggests the presence of intramolecular electronic interaction between DCM and [3.3]PCP.

The presence of a weak electronic interaction between D and A through B([3.3]PCP) is further suggested by DFT (B3LYP/6-31G*) theoretical calculations using GAUSSIAN 09 (Figure 6).^[22] The HOMO and LUMO energies were also estimated by experimental redox potentials^[23] and theoretical calculations (Table 2 and Figure 6), which indicate that HOMO energies of **1a-b** and **2a-b** are almost same as those of the DTF-[3.3]PCP-one **5** and bis(benzyl)DTF **6**. The trends of theoretically estimated HOMO and LUMO energies are well agreed with experimental data of cyclic voltammogram values. The LUMO orbitals of **1a** and **2a** are mostly localized over DCM and ECM, respectively, and partly over the benzene rings of the [3.3]PCP and the trimethylene bridge bearing the DCM or ECM

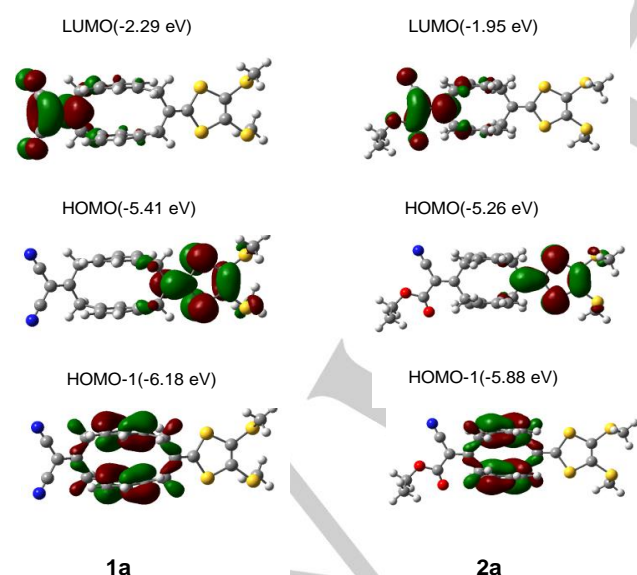


Figure 6. Molecular orbitals of the triads **1a** and **2a** calculated by the DFT method at the B3LYP/6-31G* level.^[22]

moiety, while the HOMO orbitals are mostly localized over the DTF moiety and partly over the trimethylene bridge bearing DTF moiety and the benzene rings of [3.3]PCP. The HOMO-1 orbitals are completely localized over the cyclophane moiety (Figure 6). These results show that the positive charge of the radical cation species of the triads **1a** and **2a** predominantly present on the DTF ring and partly on the benzene rings and the trimethylene bridge bearing the DTF moiety. These results indicate the presence of indirect weak orbital interaction between DTF and DCM or ECM through [3.3]PCP in the ground state.

Stability and characterization of the radical cation species

Spectroelectrochemistry

Figure 7 shows absorption spectra of **1a** in CH_2Cl_2 recorded by applying potential ranging from 0 to +1.25 V. At the potential of +0.8 V, **1a** exhibits three λ_{max} 's at 415, 676 (sh), and 750 nm and shoulders at around 367 and 466 nm, which are quite similar to those of the radical cation **1a^{•+}** generated by pulse radiolysis (Figure 7). The bis(benzyl)DTF **6** also shows the λ_{max} 's at 413, 676 (sh), and 750 nm at a potential of +0.8 V and these bands are assigned to those of the DTF radical cation **6^{•+}** (Figure 8). The bands at 415, 676, and 750 nm of **1a** were found from TD-DFT calculation of **1a^{•+}** to be assigned to the DTF radical cation (Table 1S, Figure 16S, and Figure 17S). The band at 415 nm, which is assigned to the excited transitions of DTF radical cation and DTF radical cation-[3.3]PCP, corresponded with the λ_{max} at 380 nm obtained by TD-DFT calculations ($110\beta \rightarrow 128\beta$, $126\alpha \rightarrow 130\alpha$). The bands at 676 and 750 nm can be assigned to the excited transition of DTF radical cation-[3.3]PCP (TD-DFT; λ_{max} 626 nm, $122\beta \rightarrow 128\beta$) and that of **1a^{•+}** molecule – DTF radical cation (TD-DFT; λ_{max} 712 nm, $124\beta \rightarrow 128\beta$), respectively.

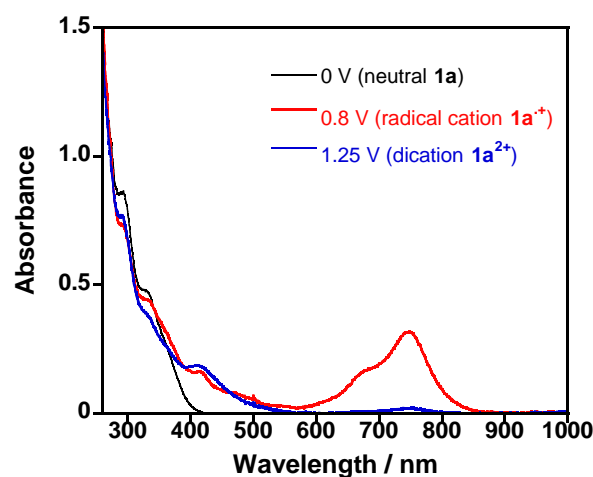


Figure 7. Absorption spectra of **1a** in CH_2Cl_2 (0.1M $n\text{Bu}_4\text{NPF}_6$) under the potential voltages of 0, 0.8, and 1.25 V vs. Ag/Ag^+ .

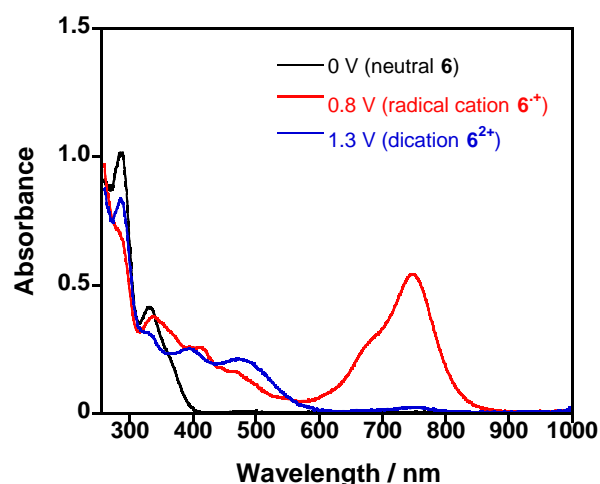
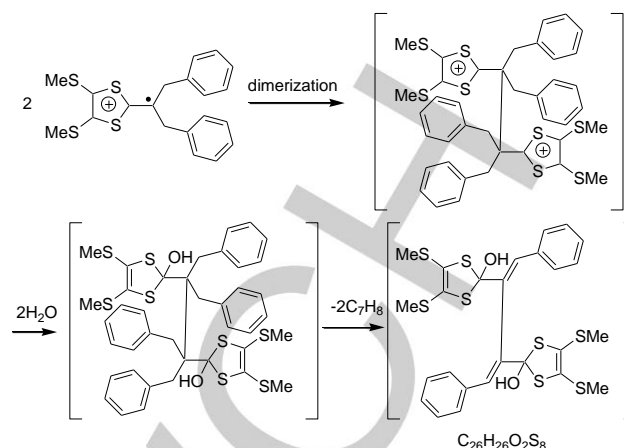


Figure 8. Absorption spectra of **6** in CH_2Cl_2 (0.1M $n\text{Bu}_4\text{NPF}_6$) under the potential voltages of 0, 0.8, and 1.3 V vs. Ag/Ag^+ .

At more positive potential of +1.25 V, the absorption bands at 676 and 755 nm disappeared, while the absorption intensity of the band at 411 nm increased, and this significant spectral change is assigned to the generation of the DTF dication 1a^{2+} from the radical anion $1\text{a}^{\bullet-}$. The related DTF diphenylpropane compound (**6**) also showed similar absorption bands at 340, 413, 466(sh), 676(sh), and 751 nm at a potential of +0.8 V by DTF radical cation formation (Figure 8). DTF diphenylpropane **6** showed two new bands at 395 and 473 nm and the long wavelength bands at 676 and 751 nm disappeared at potential of +1.3 V. The bis(benzyl)DTF **6** also showed similar spectral changes at the potential of +1.3 V, indicating the generation of the dication 6^{2+} (Figure 8). After electrochemical oxidation of **6** at +0.8 V for 5 min, however, the new intense λ_{max} 's appeared at 397 and 475 nm, which are different from the band due to the radical cation species of $6^{\bullet+}$, along with the λ_{max} 's at 676 (sh) and 755 nm due to the DTF radical cation (Figure 18S). As these new observed bands at 397 and 475 nm are similar to those of the dication 6^{2+} , this result suggests that the dication 6^{2+} species were generated by disproportionation or dimerization of $6^{\bullet+}$ species under electrochemical oxidation at +0.8 V for 5 min. FAB-MS spectrum of the solution showed two main molecular ion peaks at m/z 388.048 (M^+ , calcd. 388.045) that corresponds to the neutral reference **6** ($\text{C}_{20}\text{H}_{20}\text{S}_4$) and at m/z 629.551 ($(M-H)^+$, calcd. 629.001), which might correspond to the signal of the neutral dimer derivative obtained from the dimer dication 6^{2+} via $6^{\bullet+}$ (Scheme 3, Figure 19S, and Figure 20S).^[24]

In contrast, the absorption bands of the DTF radical cation species $1\text{a}^{\bullet+}$, which were generated by electrochemical oxidation at +0.8 V for 5 min, were intact (Figure 21S). These results indicate that the DTF radical cation $1\text{a}^{\bullet+}$ is more stable than the radical cation $6^{\bullet+}$ under the conditions and the radical cation $6^{\bullet+}$ tends to dimerize, probably because of the kinetic stability of $1\text{a}^{\bullet+}$ by steric hindrance of the rigid [3.3]PCP structure and the presence of weak electronic interaction between DTF and DCM moieties through [3.3]PCP.



Scheme 3. Dimerization mechanism of DTF reference **6** under electrochemical oxidation conditions.

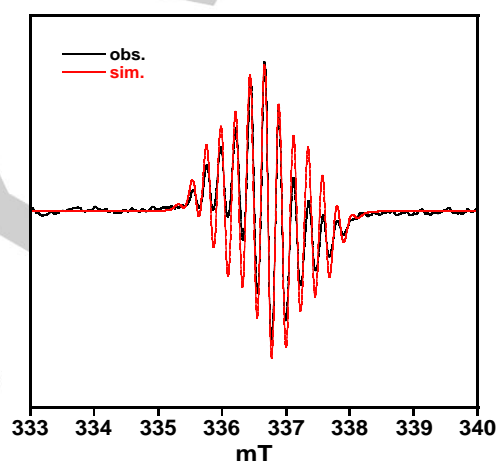


Figure 9. ESR spectrum of **1a** (1mM) in CH_2Cl_2 (0.1 M $n\text{Bu}_4\text{NPF}_6$); +0.8 V vs. Ag/Ag^+ .

ESR study

In order to characterize the DTF radical cation $1\text{a}^{\bullet+}$, ESR spectrum of the electrochemically oxidized species of **1a** in CH_2Cl_2 at a potential of +0.8 V (vs. Ag/Ag^+) was measured. The observed ESR shows a symmetrical signal with fine structure (Figure 9), and agreed with simulated ESR spectra of **1a**. The ESR signal of **1a** consists of eleven lines with g -value of 2.0072 and two coupling constants of $a(6\text{H}) = 0.22$ mT and $a(2\text{H}) = 0.68$ mT. The hyper interactions between six hydrogen atoms of methylthio groups and two benzylic hydrogen atoms of the trimethylene bridge were considered, since six methylthio hydrogens are equivalent by the rapid rotation of the methylthio group and four benzylic hydrogens are non-equivalent by slow conversion of the trimethylene bridge. Based on the DFT calculations (UB3LYP/6-31G), the spin distribution is delocalized over four sulfur atoms and two sp^2 carbons of 4,5-bis(methylthio)-1,3-dithiole-2-ylidene moiety, and the central

carbon atom of the trimethylene bridge bearing the DTF moiety (Figure 22S).

In contrast, the ESR spectrum of the radical cation $6^{+\bullet}$, which was generated by the same electrochemical oxidation at +0.8 V, is not symmetric and this indicates the presence of two or more different radical cation species (Figure 23S). Thus, the instability of the radical cation $6^{+\bullet}$ compared to that of $1^{+\bullet}$ was again demonstrated by the ESR study. By introducing rigid [3.3]PCP as B and D' in between DTF(D) and DCM(A), the DTF radical cation could be kinetically stabilized.

Molecular structure and spin distribution of **1a** were calculated on the basis of the DFT methods (UB3LYP/6-31G*) GAUSSIAN 09 Package (Figure 22S).^[22] There are two possible conformations of the radical cation of **1a**, namely the parallel and orthogonal conformations by relations between 1,3-dithiole ring and benzene rings of [3.3]PCP. The orthogonal conformation is defined that the 1,3-dithiole ring lies orthogonal to the benzene rings of [3.3]PCP, whereas the parallel one denotes parallel to the benzene rings of [3.3]PCP. The optimized molecular structure of **1a⁺** has the orthogonal conformation (Figure 24S), similar to the structure of neutral **1a**.

Conclusions

The new triads, DTF(D)-[3.3]PCP(D')-DCM or ECM **1** and **2**, in which the DTF and DCM moieties are orthogonal to the benzene rings of [3.3]PCP were synthesized and their structures were elucidated by single crystal X-ray analysis and DFT theoretical calculations. One electron oxidized species of **1a**, the radical cation **1a⁺**, was generated by pulse radiolysis and the first generated radical cation **1a⁺** converts to another structural radical cation species **1a⁺** in 50 μ s after an electron pulse. The **1a⁺** and **1a²⁺** species are generated by stepwise electrochemical oxidation processes, and **1a⁺** was found to be more stable than that of the bis(benzyl)DTF $6^{+\bullet}$, which shows tendency to dimerize. ESR spectral study indicates the homogeneity of **1a⁺**, whereas the ESR signal of $6^{+\bullet}$ contains a few radical species. The ESR study indicated that the stability of **1a⁺** is ascribed to delocalization of spin on four sulfur and two carbon atoms in the 1,3-dithiole ring and the central carbon atom of the [3.3]PCP trimethylene bridge. The electrochemical, and molecular orbital studies indicate the presence of weak electronic interaction between DTF and DCM moieties through [3.3]PCP. Thus, the higher stability of **1a⁺** compared to $6^{+\bullet}$ is ascribed to this weak electronic interaction, kinetic stability by steric hindrance and rigid cyclophane structure that prohibit dimerization of the DTF radical cation. The D-B(D')-A triads **1** and **2** can stabilize the DTF radical cation by introduction of rigid [3.3]cyclophane without substitution of sterically bulky substituents into the DTF radical cation and [3.3]PCP in these DTF-[3.3]PCP-A triads can be functioned as a rigid σ -bridge. These new D-B(D')-A triads offer potential opportunity for the design of new molecular rectifier model and orthogonal π -systems different from spiro π -conjugation.

Experimental Section

General

All dry solvents were distilled by standard procedures (THF from Na/benzophenone under N_2 , benzene from CaH_2 under N_2). The other chemicals were obtained commercially and used without further purification. Moisture-sensitive reactions were carried under an argon atmosphere. NMR spectra were recorded on JEOL AL-300 nuclear magnetic resonance spectrometer (300 MHz for 1H and 75 MHz for ^{13}C NMR). Chemical shifts are reported downfield from TMS, referenced to the chloroform-d solvent. Infrared spectra were measured on a JASCO FT/IR-460 plus. High resolution mass spectrometry was performed with a JEOL MSatation-700. Melting points are uncorrected and were obtained on a Mel-Temp apparatus.

Synthesis

Compound 5a. In a two necked flask, to a solution of the phosphonate **3a** (61 mg, 0.20 mmol) in dry THF (8 mL) at $-78^\circ C$ under Ar atmosphere, $nBuLi$ (0.16 mL, 0.24 mmol, 1.6 M) was slowly added dropwise. The mixture was stirred at $-78^\circ C$ for 20 min, while the mixture was turned into a red solution. Then, a solution of [3.3]paracyclophane-2,11-dione **4** (53 mg, 0.20 mmol) in dry THF (16 mL) was slowly added to the reaction mixture. After stirring for 1 h at $-78^\circ C$, the mixture was allowed slowly to warm to the room temperature and stand overnight. The solvent was removed under vacuum, water (15 mL) was added to the residue and obtained pale pink solid by filtration and washing with methanol. The resulting pale pink solid was purified by column chromatography on silica gel (eluents dichloromethane/*n*-hexane 2:1) to afford **5a** as a pale pink solid (47 mg, 47%). M.p. 206–208 $^\circ C$; 1H NMR (300 MHz, $CDCl_3$) δ 2.46 (s, 6H), 3.40 (s, 4H), 3.68 (s, 4H), 6.75 (s, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.8, 43.2, 51.9, 125.3, 126.8, 130.3, 133.7, 137.6, 137.6, 207.3; IR (KBr disk) ν (cm^{-1}) 804, 823, 837, 866, 890, 1109, 1428, 1509, 1631, 1687, 2851, 2919, 2952, 2991, 3016; FAB-HRMS m/z calcd. for $C_{23}H_{24}OS_4$: 442.0554; found: 442.0537 [M^+].

Compound 5b. Compound **5b** was obtained by the method similar to the preparation of **5a** using **3b** instead of **3a** as pale pink solid (yield: 58%). M.p. 142–144 $^\circ C$; 1H NMR (300 MHz, $CDCl_3$) δ 1.37 (t, $J = 7.3$ Hz, 6H), 2.89 (q, $J = 7.3$ Hz, 4H), 3.40 (s, 4H), 3.68 (s, 4H), 6.75 (s, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.1, 30.1, 43.2, 51.9, 125.0, 125.7, 129.8, 130.3, 133.6, 137.6, 207.3; IR (KBr disk) ν (cm^{-1}) 808, 824, 866, 1084, 1109, 1239, 1257 1430, 1509, 1630, 1691, 2853, 2921, 2955, 2999, 3022; FAB-HRMS m/z calcd. for $C_{25}H_{26}OS_4$: 470.0867; found: 470.0875 [M^+].

Compound 1a. In a flask was placed **5a** (37 mg, 0.080 mmol), malononitrile (170 mg, 2.6 mmol) and ammonium acetate (420 mg, 5.4 mmol) in a mixed solvent of benzene (17 mL) and glacial acetic acid (3 mL). The flask was equipped with a Dean-Stark apparatus, the mixture was stirred for 48h under reflux. After cooling to room temperature, the reaction mixture was diluted with water (10 mL), and extracted with CH_2Cl_2 (15 mL $\times 3$). The combined organic layer was washed with water (15 mL $\times 3$), dried over $MgSO_4$, and the solvent was removed under vacuum. The resulting yellow residue was purified with by column chromatography on silica gel (eluents dichloromethane) to afford **1a** as a pale yellow solid (37 mg, 90%). M.p. 230–232 $^\circ C$; 1H NMR (300 MHz, $CDCl_3$) δ 2.46 (s, 6H), 3.40 (s, 4H), 3.90 (s, 4H), 6.72 (dd, $J_1 = 8.2$ Hz, $J_2 = 23.1$ Hz, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.8, 43.1, 43.5, 88.1, 112.2, 124.9, 125.4, 127.4, 130.1, 130.2, 133.4, 138.4, 182.0; IR (KBr disk) ν (cm^{-1}) 802, 834, 889, 1109, 1185, 1260, 1384, 1419, 1432, 1508, 1572, 1587, 1606, 2230, 2852, 2921, 2959,

2998, 3018; FAB-HRMS m/z calcd. for $C_{26}H_{22}N_2S_4$: 490.0666; found: 490.0698 [M^+].

Compound 1b. Compound **1b** was obtained by the method similar to the preparation of **1a** using **5b** instead of **5a** as a pale yellow solid (yield: 80%). M.p. 174–176 °C; 1H NMR (300 MHz, $CDCl_3$) δ 1.35–1.40 (m, 6H), 2.85–2.93 (m, 4H), 3.40 (s, 4H), 3.89 (s, 4H), 6.72 (dd, $J_1 = 7.9$ Hz, $J_2 = 22.6$ Hz, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.1, 30.1, 43.0, 43.6, 88.1, 112.2, 123.6, 124.5, 124.6, 125.8, 127.5, 127.6, 130.1, 130.2, 133.4, 138.4, 182.0; IR (KBr disk) ν (cm^{-1}) 802, 836, 889, 1054, 1112, 1189, 1260, 1419, 1436, 1507, 1571, 1586, 1605, 2230, 2852, 2920, 2962, 2997, 3019; FAB-HRMS m/z calcd. for $C_{26}H_{26}N_2S_4$: 518.0979; found: 518.0994 [M^+].

Compound 2a. Compound **2a** was obtained by the method similar to the preparation of **1a** using ethyl cyanoacetate instead of malononitrile as pale pink solid (yield: 87%). M.p. 185–187 °C; 1H NMR (300 MHz, $CDCl_3$) δ 1.41 (t, $J = 7.2$ Hz, 3H), 2.45 (s, 6H), 3.38 (s, 4H), 3.90 (s, 2H), 4.12 (s, 2H), 4.38 (dd, $J_1 = 7.1$ Hz, $J_2 = 14.3$ Hz, 2H), 6.65–6.76 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 18.8, 40.3, 43.1, 43.2, 46.1, 62.4, 107.7, 116.1, 125.2, 125.5, 125.6, 126.8, 129.8, 130.0, 130.1, 130.4, 134.5, 135.5, 137.1, 137.8, 161.9, 175.3; IR (KBr disk) ν (cm^{-1}) 773, 799, 892, 1028, 1083, 1113, 1186, 1231, 1273, 1439, 1508, 1592, 1619, 1730, 2221, 2852, 2922, 2961, 2977, 3016; FAB-HRMS m/z calcd. for $C_{28}H_{27}O_2NS_4$: 537.0925; found: 537.0955 [M^+].

Compound 2b. Compound **2b** was obtained by the method similar to the preparation of **1b** using ethyl cyanoacetate instead of malononitrile as pale pink solid (yield: 60%). M.p. 134–135 °C; 1H NMR (300 MHz, $CDCl_3$) δ 1.35–1.44 (m, 9H), 2.85–2.92 (m, 4H), 3.38 (s, 4H), 3.90 (s, 2H), 4.12 (s, 2H), 4.38 (dd, $J_1 = 7.1$ Hz, $J_2 = 14.3$ Hz, 2H), 6.65–6.76 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 15.1, 30.1, 40.3, 43.1, 43.2, 46.1, 62.4, 107.7, 116.1, 125.2, 125.4, 125.8, 126.9, 127.0, 127.5, 129.8, 130.0, 130.1, 130.4, 134.4, 135.5, 137.9, 161.9, 175.3; IR (KBr disk) ν (cm^{-1}) 775, 800, 893, 1027, 1085, 1112, 1189, 1232, 1274, 1418, 1442, 1508, 1589, 1605, 1728, 2220, 2834, 2868, 2922, 2979, 3020; FAB-HRMS m/z calcd. for $C_{30}H_{31}O_2NS_4$: 565.1238; found: 565.1243 [M^+].

X-ray crystallography

X-ray diffraction data were collected on a Rigaku VariMax with Saturn diffractometer for **1a** with Mo $K\alpha$ radiation ($\lambda = 0.71070$ Å) to a maximum 2θ value of 55.0° . All computations were performed using Yadokari-XG 2009 program.^[25] The structures were solved by the direct method (SHELXS-97) and refined by the full-matrix least-squares method. Non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined using the riding model. Additional crystallographic data are as follows. **1a**: dimension $0.33 \times 0.09 \times 0.09$ mm³, formula $C_{26}H_{22}N_2S_4$, $M = 490.70$, monoclinic, space group $P2_1/c$ (No. 14), $a = 14.503(6)$, $b = 21.263(9)$, $c = 21.263(9)$ Å, $\beta = 99.405(6)^\circ$, $V = 2343.2(17)$ Å³, $Z = 4$, $D_c = 1.391$ g cm⁻³, μ (Mo $K\alpha$) = 0.423 mm⁻¹, $T = 120(2)$ K, $F(000) = 2000$, 5340 reflections, $R_1 = 0.0843$ ($I > 2.0\sigma(I)$), $wR_2 = 0.2426$. GOF 1.097. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1463789. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Cyclic voltammetry

Cyclic voltammetry experiments have been carried at room temperature with a BAS ALS6105 B electrochemical analyzer, in a three-electrode cell

(Ag/Ag⁺ reference) using Pt disk (1.6 mm diameter) as a working electrode and Pt wire as a counter electrode. 0.1 M nBu_4NPF_6 in CH_2Cl_2 was used as the electrolyte. All the potentials (except in the spectroelectrochemical section) are quoted vs. the ferrocene/ferrocenium (Fc/Fc⁺) couple.

Spectroelectrochemistry

Spectroelectrochemical data were recorded for compounds **1a** and **6** (ca. 10^{-4} M) in CH_2Cl_2 with nBu_4NPF_6 (0.1 M) as supporting electrolyte on an Ocean Optics SD 2000 fiber optic spectrophotometer between 200 – 1100 nm at ambient temperature. Spectra were corrected for background absorption arising from the cell, the electrolyte and the working electrode. The optical thin-layer electrochemical cell used a Pt mesh working electrode, Pt wire counter and Ag/Ag⁺ reference electrodes. The solutions were analyzed in situ: the working electrode was held at a potential at which no electrochemical work was being done in the cell and the spectrum of the neutral compound was recorded, which was identical to the spectrum recorded for open-circuit conditions. The potential was then increased in 50 ± 700 mV increments and held until equilibrium had been obtained, as evidenced by a sharp drop in the cell current. The cell used can be operated either under semi-infinite diffusion or thin-layer conditions.

Pulse-radiolysis and γ -radiolysis

Pulse radiolysis experiments were performed using an electron pulse (28 MeV, 8 ns, 0.7 kGy/pulse) from a linear accelerator at Osaka University. The probe light from 450 W Xe-lamp (Ushio, UXL-451-0) was detected with a multichannel spectrometer (Hamamatsu Photonics, S3904-1024F). In the present pulse radiolysis study, the sample (2.5 mM typically) was dissolved in 1,2-dichloroethane (DCE) or DMF in order to generate radical cation or radical anion of the sample, respectively. The kinetic traces were measured by using a photomultiplier (Hamamatsu Photonics, R2949). The sample for γ -ray radiolysis (1 mM typically) was dissolved in n -butyl chloride (BuCl) or 2-methyltetrahydrofuran (MTHF) to generate radical cation or radical anion, respectively. After the several freeze-pump-thaw cycles of the sample solution in a quartz cell (2 mm of optical path), the sample was kept at 77 K to form transparent glass, and then subjected to γ -ray irradiation (a ^{60}Co γ source: total dose, 1.54 kGy). The absorption spectra of the γ -ray irradiated sample at 77 K were measured using Shimadzu UV-3100.

ESR

The ESR measurements were carried out by using an electrochemical ESR based on a JEOL JES-FA200 spectrometer equipped a field frequency (F/F) lock accessory and a built in NMR gaussmeter. The electrochemical experiments were performed by in situ electrochemical oxidation using ALS 2323 bi-potentiostat. The electrochemistry experiments have been used on an ESR cell equipped with Pt wires as working and counter electrodes and Ag/Ag⁺ reference electrodes. Other experimental conditions were similar to spectroelectrochemistry experimental conditions.

Molecular orbital calculations

Optimized structures and electron densities of the neutral cyclophane triads and radical cation were estimated at the B3LYP/6-31G(d) level using GAUSSIAN 09 package. The optimized structures are confirmed to be the equilibrated most stable ones from the absence of imaginary frequencies.

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Keywords: paracyclophane • triad • donor-acceptor system • dithiafulvene • radical cation

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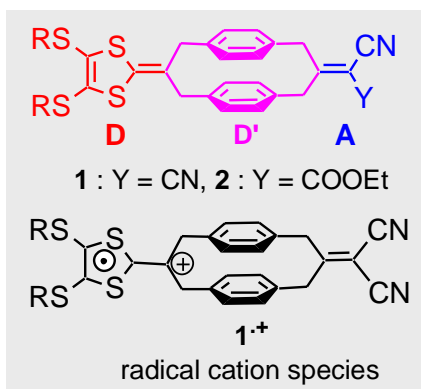
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Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

The new DTF(D)-[3.3]PCP(D')-DCM or ECM (**1**, **2**) triads, based on [3.3]paracyclophane ([3.3]PCP) as a bridge with electron-donating property (D') with 1,4-dithiafulvene (DTF) as a donor and dicyanomethylene (DCM) or an ethoxycarbonyl-cyanomethylene (ECM) as an acceptor were synthesized. The D-B(D')-A triad **1** can stabilize the DTF radical cation by introduction of rigid [3.3]PCP without substitution of sterically bulky substituents.



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Donor-Donor'-Acceptor Triads based on [3.3]Paracyclophane with 1,4-Dithiafulvene Donor and Cyanomethylene Acceptor: Synthesis, Structure, Electro- and Photo-physical Properties