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SYNTHESIS AND PROPERTIES OF FUSED TRIAD DONORS COMPOSED OF TWO 1,3-DITHIOLE[5]RADIALENES AND EXTENDED TETRATHIAFULVALENE

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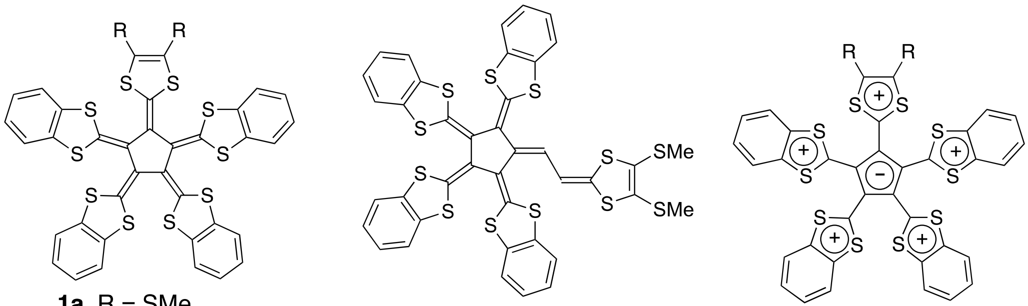
Abstract – Synthesis of fused triad donors composed of two 1,3-dithiole[5]radialenes and one vinyl-extended or thiophene-inserted teterathiafulvalene (**5**, **6**) have been successfully synthesized. Both donors exhibited simultaneous eight-electron oxidation attributed to simultaneous oxidation of two extended 1,3-dithiole[5]radialene units.

[n]Radialene is a class of cyclic π-conjugated hydrocarbons, which are composed of *n*-membered ring and n of exocyclic double bonds.[1] [n]Radialenes with electron-donating 1,3-dithiol-2-ylidene (DT) units are of interest, because they are expected to show multi-electron redox behavior accompanied with large structural changes to aromatic or anti-aromatic ring in the central *n*-membered ring.[2-5] They have also received considerable attention as possible components for functional materials such as molecular organic conductors and magnets because of their unique molecular and electronic structures as well as strongly electron-donating ability.[6] In particular, the [5]radialene with quintuple DTs (DT[5]radialene, **1**) and its vinyl-extended analog (**2**) exhibit unique redox behavior of a simultaneous four-electron transfer process.[3] A combination of spectroscopic investigations of the oxidized species and digital simulation of cyclic voltammogram indicated the tetracationic states of **1** and **2** were considerably stabilized due to the significant contribution of an aromatic cyclopentadienyl anion in the central five-membered ring, whereas simultaneous four-electron redox waves of them were composed of an apparent overlap of two pairs of two-electron redox waves.[3,7,8]



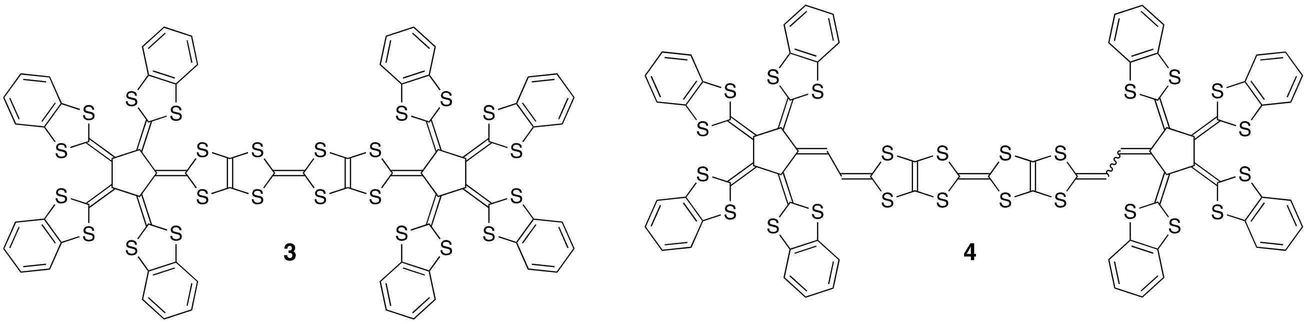
1a, R = SMe
1b, 2R = $(CH=CH)_2$

2

$\mathbf{1}^{4+}$

Figure 1. Chemical structures of **1**, **2** and $\mathbf{1}^{4+}$

Fused tetrathiafulvalene (TTF) donors are also of interest as candidates for functional materials such as conducting components for molecular conductors and positive electrode materials for rechargeable batteries.[9-11] We have reported the synthesis of several diad and triad π-electron donors composed of **1** (or **2**) and TTF (or thiophene-inserted TTF).[12,13] Among them, the triad donors with two DT[5]radialenes (**3**, **4**) exhibited a simultaneous eight-electron transfer process. In general, molecules exhibiting simultaneous multi-electron processes might be promising for utilization of positive electrode materials for rechargeable batteries, because they are expected to show a plateau discharge curve with the constant voltage and the large capacity in the batteries. However, **3** and **4** have a disadvantage as positive electrode materials, that is, utilization of maximum electrons (ten electrons) might be difficult because the ten-electron oxidation potentials of them are so high that the electrolyte solutions decompose. On the other hand, extended TTF analogs in which π-electron spacer inserted are known to have lower two-electron oxidation potentials than those of pristine-TTF because of reducing on-site Coulomb repulsion by increase the distance between two positive charges.



3

4

Figure 2. Chemical structures of **3** and **4**

In this paper, we report the synthesis of fused triad donors composed of vinyl- and thiophene-extended TTF and two units of **2** (**5**, **6**). Their redox behavior investigated by cyclic voltammetry and spectroelectrochemistry are also reported.

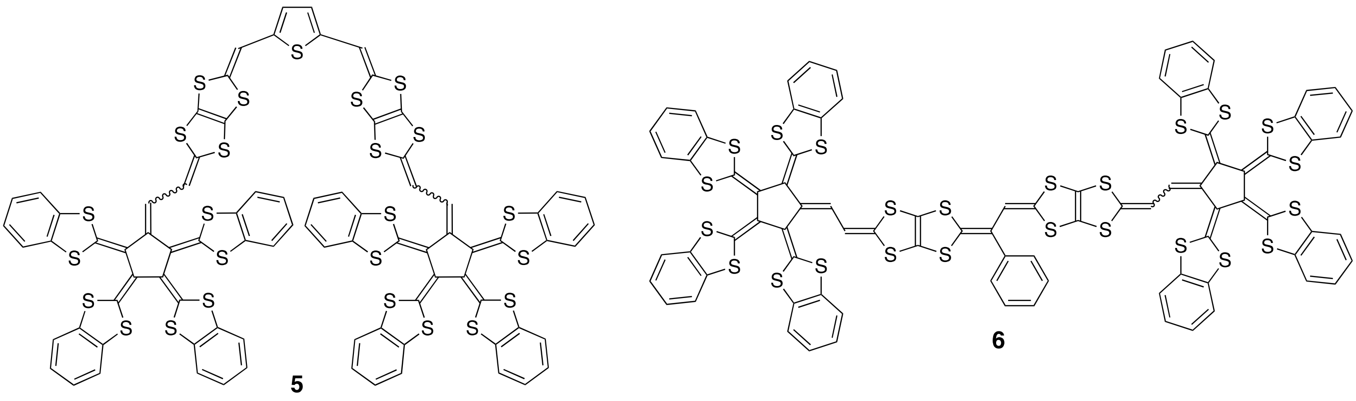
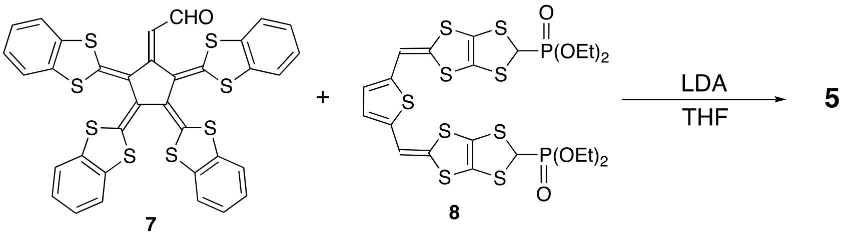
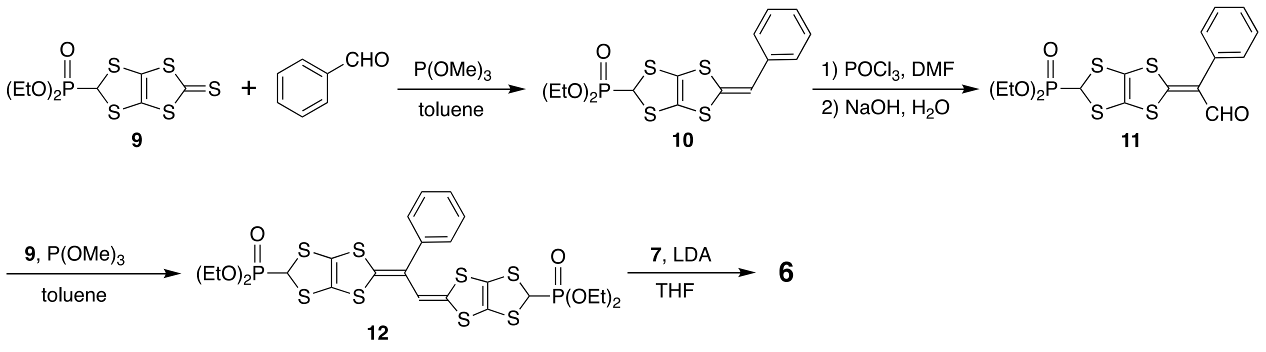


Figure 3. Chemical structures of **5** and **6**

The Horner-Wadsworth-Emmons reaction of two equimolar amounts of the aldehyde **7**[14] with a thiophene-extended TTF derivative with bisphosphonate (**8**)[15] in the presence of LDA in THF at –78 °C afforded **5** in 35% yield (Scheme 1). On the other hand, the synthesis of the vinyl-extended donor **6** was carried out according to Scheme 2. The $P(OMe)_3$-mediated cross-coupling[16] between a 1,3-dithiole-2-thione with phosphonate ester (**9**)[17] and benzaldehyde in toluene at 110 °C gave a 5-phenyl-1,4-dithiafulvenyl derivative **10** in 85% yield. The Vilsmeier-Haack formylation on **10** with an excess of phosphoryl chloride in DMF at 0 °C, followed by treatment with aqueous sodium hydroxide solution afforded the formylated compound at 5-position (**11**) in 62% yield. A vinyl-extended TTF derivative with two phosphonate esters (**12**) was obtained in 20% yield by the $P(OMe)_3$-mediated cross-coupling reaction of **11** with **9** in toluene at 110 °C. The Horner-Wadsworth-Emmons reaction of **12** with **7** in the presence of LDA in THF at –78 °C gave the target compound **6** in 35% yield. Both the triad donors were presumably obtained as mixtures of *(E)*- and *(Z)*-isomers.



Scheme 1. Synthesis of **5**



Scheme 2. Synthesis of **6**

Redox behavior of **5** and **6** was investigated by cyclic voltammetry. The deconvoluted cyclic voltammograms of **5** and **6** are shown in Figure 4. The thiophene-extended [5]radialene **5** exhibit two-pairs of redox waves at –0.01 and +0.44 V (V vs. Fc/Fc$^+$), respectively, whereas **6** shows three pairs of redox at +0.01, +0.52, and +0.62 V, respectively. The peak currents of the first redox waves are more than ten times as large as those of the others, suggesting that the first redox waves of **5** and **6** correspond to eight-electron transfer processes.

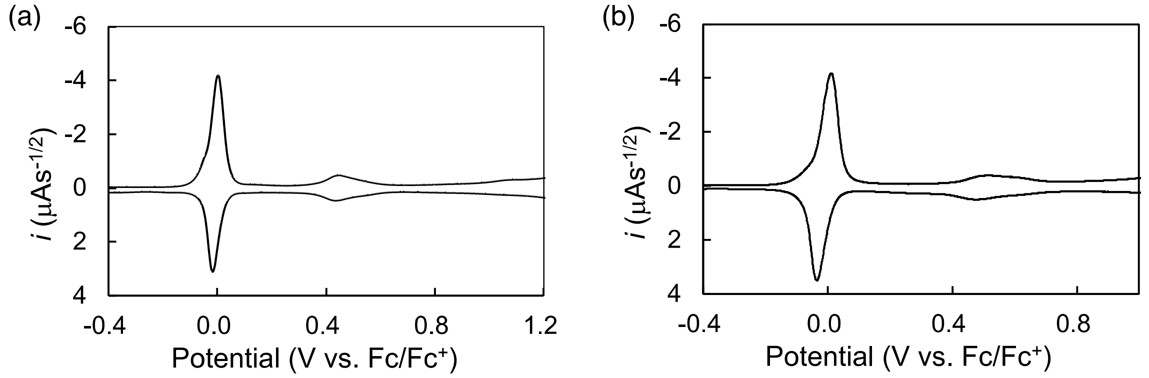


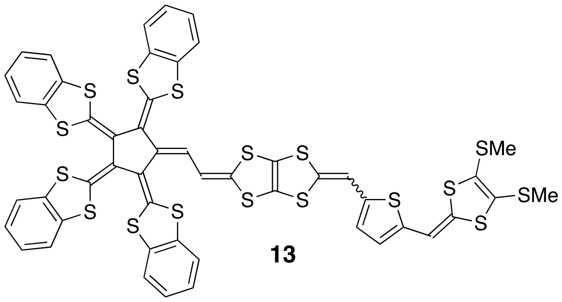
Figure 4. Deconvoluted cyclic voltammograms of **5** and **6**

The redox potentials of **5** and **6** are summarized in Table 1 together with their related compounds. The first eight-electron redox potentials of **5** and **6** are comparable to the four-electron redox potential of **2** (E_{m1} = –0.02 V), indicating that eight positive charges formed by the first oxidation processes are distributed on the two DT[5]radialene moieties at both ends, four each. The remaining extended TTF moieties presumably contribute to the subsequent redox processes. The redox potentials of **5** and **6** corresponding to the redox processes involving the extended TTF units are higher by 0.48–0.59 V than those of **14** and **15**.[18,19] On the other hand, the highest redox potentials of **5** and **6** are lower than those of **3** (+0.83 V) and **4** (+1.07 V). These results might be attributed to that the on-site Coulomb repulsion of **5** and **6** in decacation states is reduced, because the positively charged DT units are separated from each other by the insertion of the π electron system.

Table 1. Redox potentials of **5** and **6** and related compounds[a]

Donor	E_1	E_2	E_3	E_4	E_5	E_6	E_7	E_8	E_9	E_{10}
		E_{m1}[b]		E_{m2}[b]					E_{m3}[b]	
5				–0.01 (8e$^-$)					+0.44 (2e$^-$)	
6				+0.01 (8e$^-$)					+0.52	+0.62
3				–0.03 (8e$^-$)					+0.64	+0.83
4				–0.05 (8e$^-$)					+0.86	+1.07
2		–0.02 (4e$^-$)								
13		–0.02 (4e$^-$)			+0.17	+0.32				
14	–0.04	+0.11								
15	–0.07	+0.09								

[a]Condition: ^{n}Bu$_4$N·PF$_6$ (0.1 M), benzonitrile, 25 ºC, Pt working and counter electrodes. Potentials were measured against Ag/Ag$^+$ electrode and converted to the value vs. Fc/Fc$^+$. [b]$E_{\mathrm{m1}} = (E_1 + E_2 + E_3 + E_4)/4$. $E_{\mathrm{m2}} = (E_1 + E_2 + E_3 + E_4 + E_5 + E_6 + E_7 + E_8)/8$. $E_{\mathrm{m3}} = (E_9 + E_{10})/2$.



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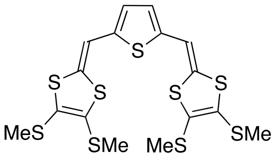

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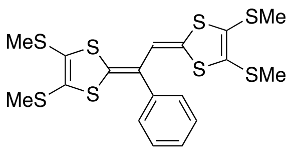

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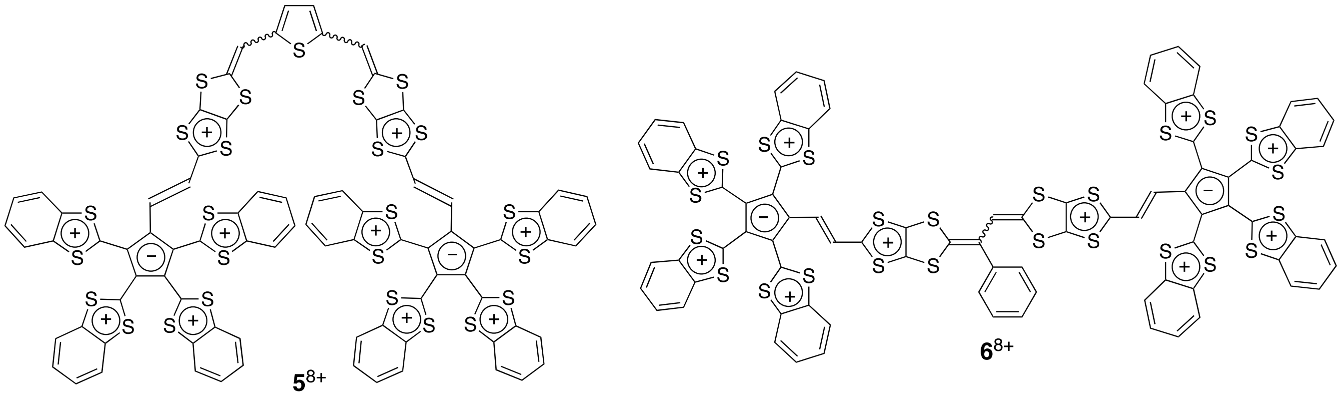

Figure 5. Plausible structures of $\mathbf{5}^{8+}$ and $\mathbf{6}^{8+}$

The electronic structures of the oxidized species of **5** were investigated by spectroelectrochemistry. Figure 6 shows the UV-vis-NIR spectra of **5** and its oxidized species generated by electrochemical oxidations in a PhCN solution containing 0.1 M ^{n}Bu$_4$NPF$_6$ at constant voltages. The neutral **5** shows absorption maxima at 375 and 513 nm. By applying the voltage at +0.07 V (vs. Fc/Fc$^+$), new absorption bands appeared at 588 and 1192 nm. The spectrum has a resemblance to those of $\mathbf{2}^{2+}$, $\mathbf{13}^{2+}$ (1182 nm), and $\mathbf{4}^{4+}$ (1177 nm), indicating that two positive charges are mainly distributed on each extended DT[5]radialene moiety similar to $\mathbf{2}^{2+}$, $\mathbf{13}^{2+}$ and $\mathbf{4}^{4+}$.[7,13] The absorption maximum at 588 nm grew by further application of the voltage, whereas the absorption maxima at 1192 nm gradually decayed. The subsequent application of a constant voltage at +0.77 V afforded a spectrum presumably ascribable to $\mathbf{5}^{8+}$ at 568 and 725 nm together with a shoulder absorption at 832 nm. The shoulder absorption band at 832 nm might be assigned to an intramolecular charge-transfer from the strongly donating thiophene-extended TTF moiety.[20]

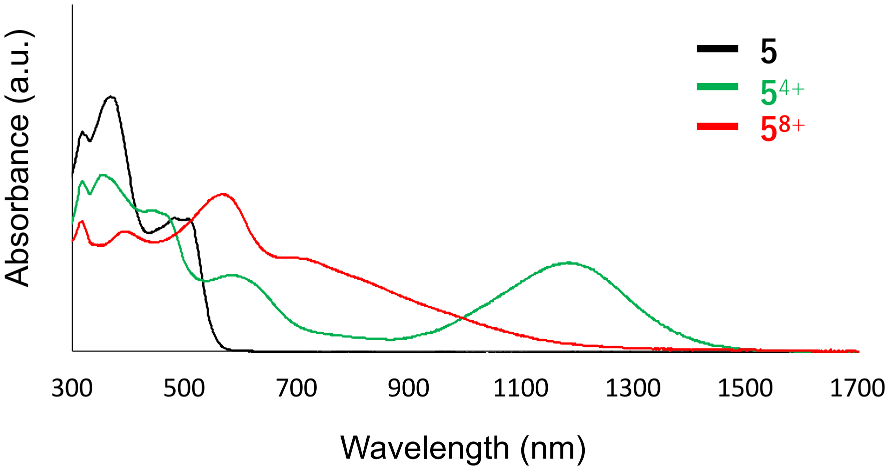

Figure 6. UV-vis-NIR spectra of **5** and its oxidized species in a PhCN solution

In summary, we have developed new fused triad donors possessing two extended DT[5]radialene units and vinyl- and thiophene-extended TTF (**5** and **6**). Both the donors show a simultaneous eight-electron transfer wave, in which two DT[5]radialene units are involved. Spectroelectrochemistry suggested that the simultaneous eight-electron oxidation of **5** and **6** proceeded by way of a tetracation with two dicationic vinyl-extended DT[5]radialene moieties. The negative shift of the highest oxidation potentials compared to **4** might bring an expectation of ten-electron utilization in the rechargeable batteries. Further investigations, in particular, fabrication and charge-discharge properties of rechargeable batteries using **5** and **6** as a positive electrode material are in progress.

EXPERIMENTAL

General. $POCl_3$, NaOH, dry THF, and dry DMF were purchased from commercial suppliers and used without further purification. Toluene, $P(OMe)_3$, and diisopropylamine were dried and/or distilled by standard methods. LDA was prepared by treatment of dry diisopropylamine with ^{n}BuLi in dry THF at –78 °C. ^{1}H NMR spectra were recorded on a Bruker Biospin AVANCE 400 spectrometer equipped with a CryoProbe (400 MHz) using $CDCl_3$, C_6D_6-CS_2, or CD_3COCD_3-CS_2 solvent. The chemical shifts were referenced to tetramethylsilane (0 ppm) for ^{1}H NMR. MS spectra, including high resolution mass spectra (HRMS) were recorded on Thermo Scientific, Exactive Plus Orbitrap Mass Spectrometer for electrospray ionization (ESI). Only the more intense or structurally diagnostic mass spectral fragment ion peaks were reported. Melting points were determined with a Yanaco MP-J3. Cyclic voltammetries (CV) were carried out using ALS/chi 617B Electrochemical analyzer. The CV cell consisted of Pt working electrode, Pt wire counter electrode, and an Ag/$AgNO_3$ reference electrode. The measurements were carried out in 0.3 mM PhCN, and the sample solution also contained 0.1 M $^n Bu_4NPF_6$ as a supporting electrolyte. All redox potentials were measured against Ag/Ag^+ and converted to values vs. Fc/Fc^+. Spectroelectrochemistry was performed on the sample placed within a quartz cuvette with a path length of 1 mm. Pt gauze (100 mesh) was used as an optically transparent electrode.

Compound 5: To a mixture of **7** (89 mg, 0.124 mmol) and **8** (42 mg, 0.056 mmol) in THF (5 mL) was added 0.5 M LDA (0.25 mL, 0.125 mmol) at –78 °C under an argon atmosphere. The mixture was stirred for 4 h during warming up to room temperature. After the addition of MeOH, the resultant red precipitate was filtered and washed with MeOH. The precipitation was purified by column chromatography on silica gel with CS_2 to afford **5** (70 mg, 0.038 mmol) in 67% yield as red powder. mp 257–258 °C (dec), ^{1}H NMR (C_6D_6-CS_2) δ 7.32–7.30 (m, 2H), 7.29–7.26 (m, 2H), 7.19–7.10 (m, 11H), 7.09–7.03 (m, 4H), 7.02–6.89 (m, 13H), 6.70 (t, *J* = 3.6 Hz, 2H), 6.59 (q, *J* = 3.3 Hz, 2H), 5.95□5.92 (m, 4H); HRMS (ESI): calcd for $C_{84}H_{40}S_{25}$ $[M]^{2+}$: 1849.6106; found: 1849.6094.

Compound 10: To a solution of **9** (500 mg, 1.46 mmol) and benzaldehyde (63 μL, 0.61 mmol) in toluene (15 mL) was added $P(OMe)_3$ (15 mL). The reaction mixture was refluxed for 2 h under an argon atmosphere. After cooling to room temperature, $P(OMe)_3$ and toluene were removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2-AcOEt (10:1, v/v) to afford **10** (519 mg, 1.24 mmol) in 85% yield as brown oil. ^{1}H NMR ($CDCl_3$) δ 7.36 (t, *J* = 7.8 Hz, 2H), 7.21–7.18 (m, 3H), 6.55 (s, 1H), 5.35 (d, *J* = 6.4 Hz, 2H), 4.29–4.27 (m, 4H), 1.38 (t, *J* = 7.0 Hz, 6H). This compound was used for the subsequent reaction without further purification; HRMS (ESI): calcd for $C_{15}H_{18}O_3PS_4$ $[M+H]^+$: 404.9871; found: 404.9871.

Compound 11: To a mixture of **10** (222 mg, 0.530 mmol) in DMF (10 mL) was added $POCl_3$ (0.198 mL, 2.12 mmol) at 0 °C under an argon atmosphere. The mixture was stirred for 2 h at room temperature. After the reaction mixture was stirred for 2 h at 0 °C, 1 M NaOH aq. (20 mL, 20 mmol) was added. The reaction mixture was extracted with CH_2Cl_2. The combined organic layers were washed with H_2O, and dried over Na_2SO_4. After the solvent was evaporated in vacuo, the residue was chromatographed on silica gel with CH_2Cl_2-AcOEt (10:1, v/v) to afford **11** (142 mg, 0.329 mmol) in 62% yield as yellow powder. ^{1}H NMR ($CDCl_3$) δ 9.35 (s, 1H), 7.46 (t, *J* = 3.6 Hz, 2H), 7.39–7.36 (m, 3H), 5.44 (d, *J* = 3.2 Hz, 1H), 4.37–4.24 (m, 4H), 1.34 (t, *J* = 8.2 Hz, 6H); HRMS (ESI): calcd for $C_{16}H_{18}O_4PS_4$ $[M+H]^+$: 432.9820; found: 432.9819.

Compound 12: To a solution of **9** (44.5 mg, 0.130 mmol) and **11** (56 mg, 0.13 mmol) in toluene (5 mL) was added $P(OMe)_3$ (5 mL). After the reaction mixture was refluxed for 2 h under an argon atmosphere, an extra amount of **9** (44.5 mg, 0.130 mmol) was added to the reaction mixture. Then, **9** (44.5 mg, 0.130 mmol) was added three times every 2 h. After cooling to room temperature, $P(OMe)_3$ and toluene were removed under reduced pressure. The residue was column chromatographed on silica gel with CH_2Cl_2-AcOEt (10:1, v/v) to afford **12** (26 mg, 0.0351 mmol) in 27% yield as yellow powder. ^{1}H NMR ($CDCl_3$) δ 7.40 (t, J = 3.8 Hz, 2H), 7.24–7.22 (m, 3H), 6.02 (d, J = 2.0 Hz, 1H), 5.32 (q, J = 2.1 Hz, 1H), 5.23 (q, J = 6.6 Hz, 1H), 4.27–4.20 (m, 8H), 1.36–1.34 (m, 12H); HRMS (ESI): calcd for $C_{24}H_{28}O_6P_2S_8$ $[M]^+$: 729.9127; found: 729.9125.

Compound 6: To a mixture of **7** (28 mg, 0.040 mmol) and **12** 13 mg, 0.018 mmol) in THF (3 mL) was added 0.5 M LDA (0.25 mL, 0.125 mmol) at –78 °C under an argon atmosphere. The mixture was stirred for 4 h during warming up to room temperature. After the addition of MeOH, the resultant red precipitate was filtered and washed with MeOH. The precipitation was purified by column chromatography on silica gel with carbon disulfide to afford **4** (6.6 mg, 0.0035 mmol) in 20% yield as red powder. mp 246–247 °C (dec), ^{1}H NMR (CD_3COCD_3-CS_2) δ 7.44–7.23 (m, 21H), 7.18–7.07 (m, 16H), 6.11 (q, J = 4.1 Hz, 1H), 5.92–5.89 (m, 2H) 5.86–5.82 (m, 2H); HRMS (ESI): calcd for $C_{86}H_{42}S_{24}$ $[M]^{2+}$: 1843.6541; found: 1843.6542.

ACKNOWLEDGEMENTS

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20. Further increases in the voltage produced no further spectral change, probably due to the reduction

of oxidized species (**5**$^{9+}$, **5**$^{10+}$) by a reductant (e.g. H_2O) contained as an impurity. Otherwise, the voltage might not be applied properly owing to the large resistance between the working electrode and the reference electrode in the electrochemical cell.