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SYNTHESIS, STRUCTURE, AND π-DONOR PROPERTIES OF TRIS(ETHYLENEDIOXY)BENZENE AND BIS(ETHYLENEDIOXY)THIOPHENE

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Dedicated to Professor Yasuyuki Kita on the occasion of his 77th birthday

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Abstract – Tris(ethylenedioxy)benzene **3** and bis(ethylenedioxy)thiophene **4** have been synthesized starting from 2,3-dibromo-1,4-dioxene in 25 and 38% overall yields, respectively. These ethylenedioxy-fused benzene and thiophene can be easily oxidized to produce the corresponding radical cations $\mathbf{3}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$ because of their high-lying HOMO levels. Interestingly, the radical cation $\mathbf{3}^{\bullet+}$ exhibits a fairly strong fluorescent emission at λ_{max} 602 and 590 nm ($\Phi_F = 0.40$ in MeCN and 0.50 in H_2SO_4).

INTRODUCTION

Alkoxy substituents of aromatic rings act as a strong resonance-electron-donating unit and significantly stabilize radical cations generated from the aromatic molecules. Hexamethoxybenzene (**1**),[1,2] benzotris[1.3]dioxole (tris(methylenedioxy)benzene, **2**),[3,4] and tris(ethylenedioxy)benzene (**3**)[5,6] have been synthesized in order to investigate their unique redox behavior (Figure 1). Although a number of reports on **1** and **2** have been published up to date,[1-4] the properties of **3** did not fully characterized due to the difficulty in synthesizing **3** in a reasonable yield.[5] 3,4-Ethylenedioxythiophene[7] and 4,5-ethylenedioxytetrathiafulvalene[8] have been investigated to obtain widely applicable donor molecules, because ethylenedioxy-substituted donors are endowed with enhanced donor ability, stability of radical cations, and moderate solubility in common organic solvents. In the course of our studies on ethylenedioxy-substituted molecules,[9-11] we are interested in the synthesis and donor properties of tris(ethylenedioxy)benzene (**3**) and bis(ethylenedioxy)thiophene (**4**) (Figure 1). Here, we report an improved synthesis of **3** by using cyclotrimerization of organotin molecules in a one-pot procedure as well as the first synthesis of **4** with insertion of sulfur to 1,4-dilithio-1,3-butadiene unit. Furthermore, we report the properties of radical cations derived from **3** and **4**. It is noteworthy that the radical cation derived from **3** exhibits a fairly strong fluorescent emission.

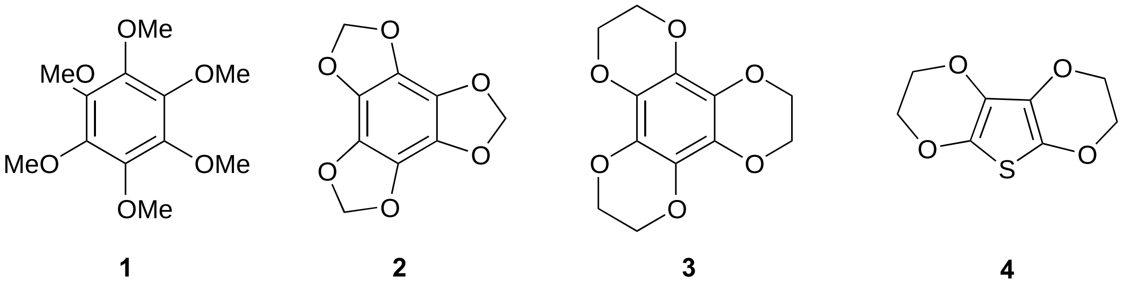
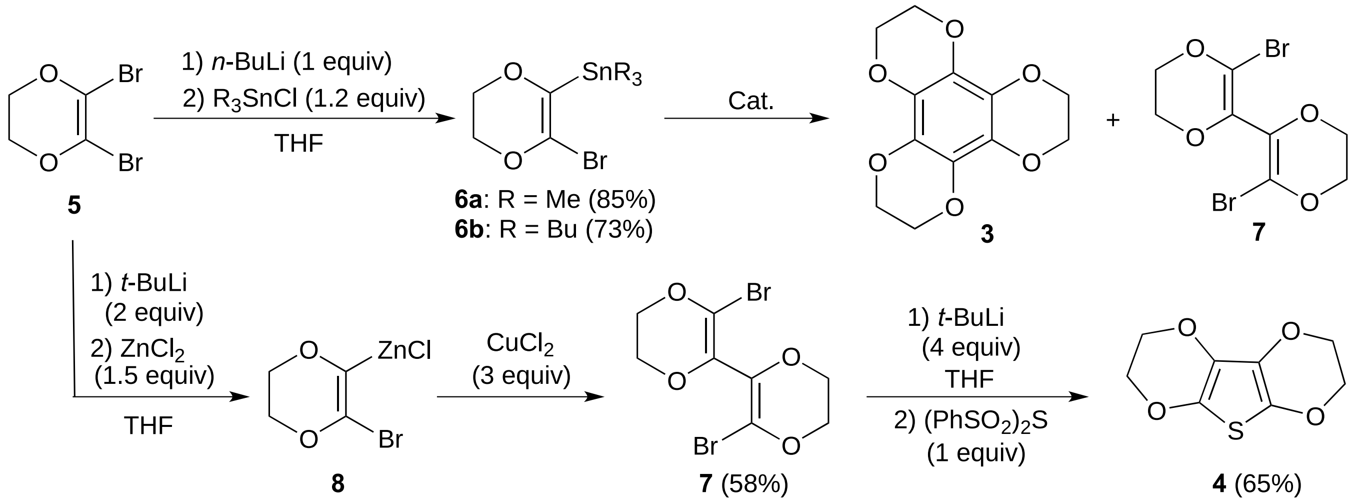


Figure 1. Hexamethoxybenzene (**1**), benzotris[1.3]dioxole (**2**), tris(ethylenedioxy)benzene (**3**), and bis(ethylenedioxy)thiophene (**4**)

RESULTS AND DISCUSSION

The synthesis of **3** was performed starting from 2,3-dibromo-1,4-dioxene (**5**) (Scheme 1). Lithiation of **5** with butyllithium (1 equiv) in THF, followed by treatment with trialkyltin chloride afforded **6** (**6a**, 85%; **6b**, 73%). Cyclotrimerization of **6** was carried out by using palladium or copper catalyst (Table 1).



Scheme 1. Synthesis of tris(ethylenedioxy)benzene (**3**) and bis(ethylenedioxy)thiophene (**4**)

As shown in Table 1, the reaction of **6a** in the presence of 5 mol% of $Pd(PPh_3)_4$ in toluene at 110 °C for 48 h afforded the desired cyclic trimer **3** in 20% yield (Entry 1). A similar reaction of **6a** in the presence of 10 mol% of $Pd(PPh_3)_4$ produced **3** (29%) with **7** (2%) (Entry 2). However, the reaction of **6a** by using

20 mol% of $Pd(PPh_3)_4$ gave **3** (8%) with **7** (2%) (Entry 3). As for solvent, the reaction of **6a** in DMF by using 10 mol% of $Pd(PPh_3)_4$ afforded **3** in 9% yield (Entry 4). On the other hand, the reaction of **6b** in toluene by using 10 mol% of $Pd(PPh_3)_4$ gave **3** (7%) with **7** (2%) (Entry 5). Therefore, for the cyclotrimerization of **6a**, the use of 10 mol% of $Pd(PPh_3)_4$ in toluene lead to **3** in the best yield. Furthermore, the reaction of **6a** with 3 equiv of CuTC (copper(I) thiophenecarboxylate) in NMP (1-methyl-2-pyrrolidone) at 110 °C for 48 h produced **3** in 9% yield (Entry 6).

Table 1. Reaction of **6a** or **6b** in the presence of $Pd(PPh_3)_4$ or CuTC[a]

Entry	Compd.	Catalyst	Equiv	Solvent	Temp. and Time	Products (%) **3**	**7**
1	**6a**	$Pd(Ph_3)_4$	0.05	toluene	110 °C, 48 h	20	–
2	**6a**	$Pd(PPh_3)_4$	0.1	toluene	110 °C, 48 h	29	2
3	**6a**	$Pd(PPh_3)_4$	0.2	toluene	110 °C, 48 h	8	2
4	**6a**	$Pd(PPh_3)_4$	0.1	DMF	140 °C, 48 h	9	–
5	**6b**	$Pd(PPh_3)_4$	0.1	toluene	110 °C, 48 h	7	2
6	**6a**	CuTc	3	NMP	130 °C, 48 h	9	–

[a] To a solution of **6a** or **6b** in toluene, DMF, or NMP was added $Pd(PPh_3)_4$ or CuTC (copper(I) thiophenecarboxylate) under argon at room temperature, and the mixture was heated for 48 h

For the synthesis of **4**, 2,3-dibromo-1,4-dioxacyclohexene (**5**) was reacted with 2 equiv of *tert*-butyllithium, followed by treatment with zinc chloride (1.5 equiv) to give organozinc intermediate (**8**). The reaction of **8** with excess amounts of copper(II) chloride afforded **7** in 58% yield. Lithiation of **7** with 2 equiv of *tert*-butyllithium, followed by treatment with $(PhSO_2)_2S$ (1 equiv) produced **4** in 64% yield (Scheme 1). Tris(ethylenedioxy)benzene **3** and bis(ethylenedioxy)thiophene **4** are stable at room temperature under air.

The structures of **3** and **4** were unambiguously determined by X-ray analysis. Single crystals of **3** were obtained by recrystallization from THF. Benzene derivative **3** with three-fold fusion of dioxacyclohexene units has either C_2 or D_3 symmetric structure depending on the inversion of ethylenedioxy moiety. According to DFT calculations at the B3LYP/6-31G(d) level, the energy difference between these isomers is negligibly small, but only the C_2 symmetric structure was observed in the crystal (Figure 2). The central benzene moiety of **3** is planar, and the C–C bond lengths exhibit a delocalized structure in spite of slightly disordered deformation. Interestingly, the packing diagram shows an intermolecular stacking of benzene rings, forming a columnar structure in the crystal. Furthermore, weak hydrogen bonds between oxygen atoms of ethylenedioxy group and hydrogen atoms in the neighboring column were observed (O(6)–H(7) 2.50 Å, van der Waals radii: O, 1.40 Å and H, 1.2 Å) (Figure 2b).

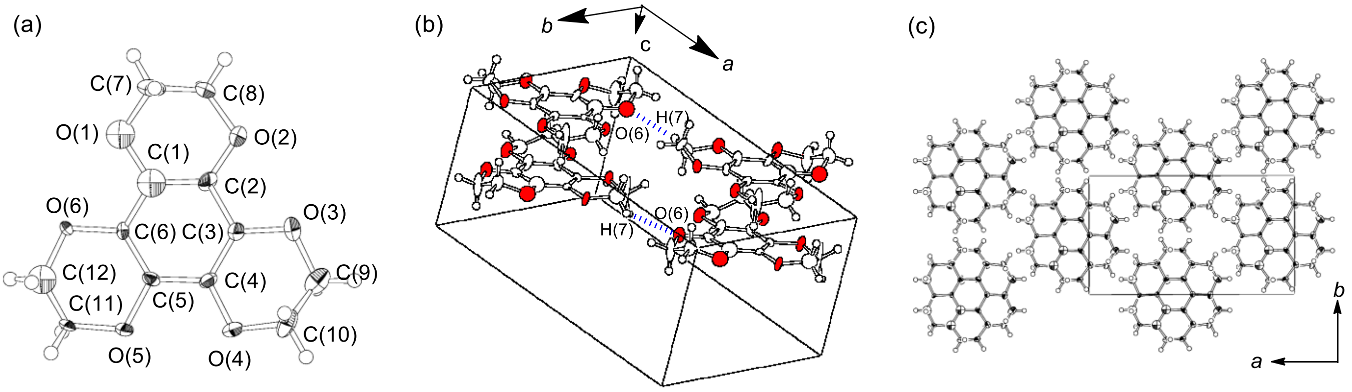


Figure 2. (a) Crystal structure of **3**. The C–C bond lengths (Å): C(1)–C(2) 1.383, C(2)–C(3) 1.420, C(3)–C(4) 1.390, C(4)–C(5) 1.399, C(5)–C(6) 1.380, C(6)–C(1) 1.380. (b) Packing structure of **3** with O(6)–H(7) hydrogen bonds (2.50 Å). (c) Packing diagram of **3** along the *c*-axis.

Single crystals of **4** were obtained by recrystallization from diisopropyl ether/benzene. Although the B3LYP calculations predicted that the C_2 symmetric optimized structure of **4** was more stable than the C_s structure by 0.26 kcal mol^{-1}, the C_s symmetric structure was observed in the solid state (Figure 3). The central five membered ring of **4** is planar, and the C–S and C–C bond lengths (S(1)–C(1) 1.747 Å, C(1)–C(2) 1.348 Å, and C(2)–C(3) 1.434 Å) exhibit a delocalized structure like thiophene (Figure 3a,b). Weak hydrogen bonds between oxygen atoms of ethylenedioxy group and hydrogen atoms of the neighboring molecules were observed. However, there are no intermolecular π–π interaction between the thiophene rings in the crystal (Figure 3c).

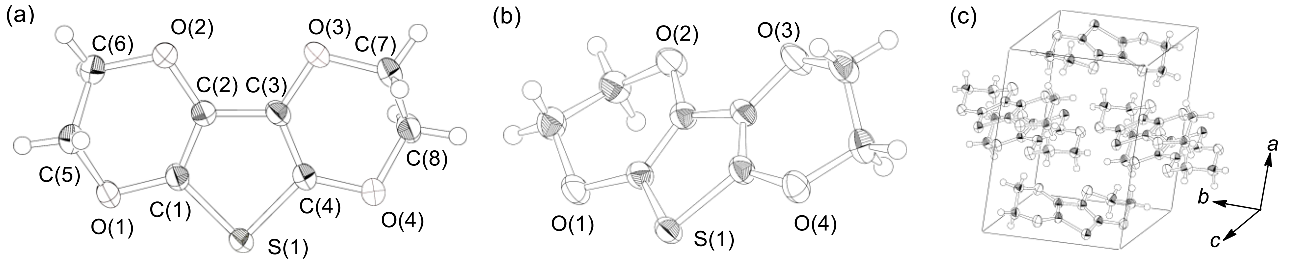


Figure 3. (a, b) Crystal structure of **4**. (c) Packing diagram of **4**.

To estimate HOMO levels of **3** and **4**, redox potentials were measured by cyclic voltammetry (CV) in acetonitrile. As shown in Figure 4, **3** shows reversible one-electron redox process ($E^{ox}_{1/2}$: 0.55 V vs

Fc/Fc$^+$), whereas **4** exhibits quasi reversible one-electron redox process ($E^{ox}_{1/2}$: 0.31 V vs Fc/Fc$^+$). Based on the relation that Fc/Fc$^+$ redox couple corresponds to –4.80 eV to vacuum, HOMO levels of **3** and **4** are evaluated as –5.35 eV and –5.11 eV, respectively. Therefore, **3** and **4** are estimated to possess fairly high-lying HOMO levels for 6π-aromatic systems. The DFT calculations predicted that the HOMO levels of **3** (D_3) and **4** (C_2) are –5.00 eV and –4.84 eV, respectively, and these values are in reasonable agreement with the experimentally estimated HOMO levels. Furthermore, the calculated HOMO levels of **3** and **4** are higher by 1.70 eV and 1.49 eV than the calculated values of parent benzene and thiophene, respectively. Interestingly, in contrast to the low oxidation potential of **3**, the oxidation potential ($E^{ox}_{1/2}$ = 1.24 V vs SCE and 0.86 V vs Fc/Fc$^+$) of hexamethoxybenzene (**1**) in benzene with Pr_4NClO_4 as supporting electrolyte[12] is ca. 0.3 V higher than the oxidation potential of **3** **(**$E^{ox}_{1/2}$: 0.55 V vs Fc/Fc$^+$**)** in acetonitrile with Bu_4NClO_4 as supporting electrolyte. This 0.31 V higher HOMO level of **3** compared with **1** is considered to be caused by the difference in the rigidity of oxy-substituents. As depicted in Figure 5, the degenerated HOMOs of **3** and **1** are spread over oxygen atoms and the lobes over oxygen atoms in **3** are larger than those of **1**. Consequently, the high electron-donating ability of ethylenedioxy fusion was confirmed.

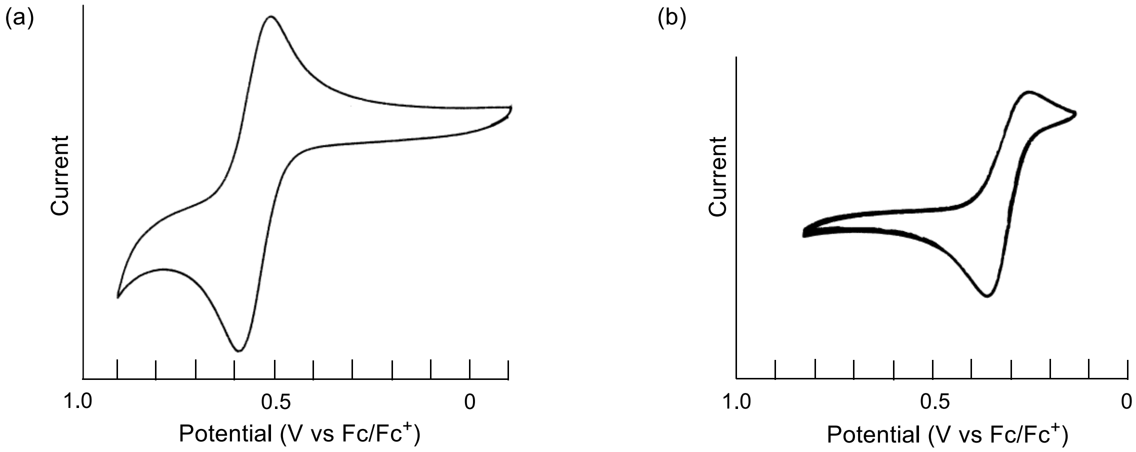


Figure 4. Cyclic voltammograms of **3** (a) and **4** (b): 0.1M Bu_4NClO_4 in MeCN under argon at room temperature, Pt working and counter electrodes, scan rate 50 mV s^{-1}.

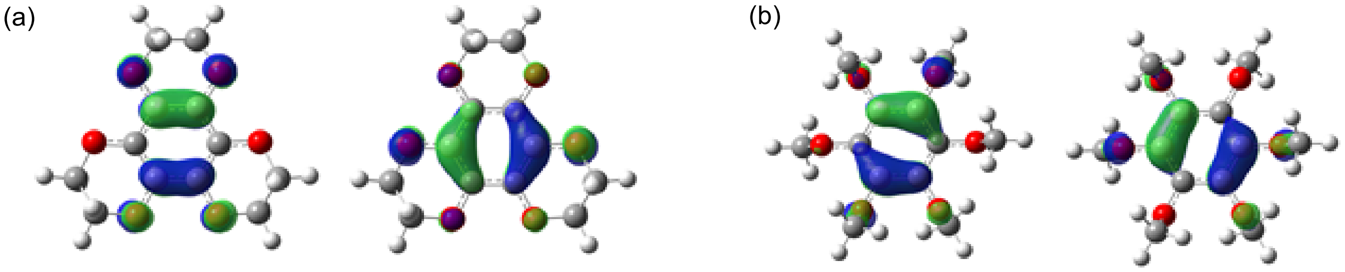


Figure 5. HOMOs of (a) **3** and (b) hexamethoxybenzene (**1**) (Isoval = 0.05)

The high-lying HOMO levels should cause the facile one-electron oxidation of **3** and **4**. In fact, ESR spectra of radical cation $\mathbf{3}^{\bullet+}$ have been intensively investigated.[6] In the present study, we also observed the similar ESR spectra of $\mathbf{3}^{\bullet+}$. In addition, despite of the quasi reversibility of CV in acetonitrile, ESR spectrum of $\mathbf{4}^{\bullet+}$ generated by the reaction of **4** with $SbCl_5$ in dichloromethane could be observed at room temperature (Figure 6a). The ESR signal showed a five-line signal (a_H = 0.15 mT, g = 2.0034), suggesting that the spin density mainly resides on one of two carbons (i.e., α- and β-carbons) in thiophene ring which conveyed the nearer methylene protons. The DFT calculations (UB3LYP/6–31G(d)) demonstrated that the coupling constants of methylene protons nearer to α-carbons of $\mathbf{4}^{\bullet+}$ (C_s) are 0.38 mT for proton in axial position and 0.02 mT for proton in equatorial position (Figure 6b). The average of the calculated values (0.2 mT) is reasonably consistent with the observed value.

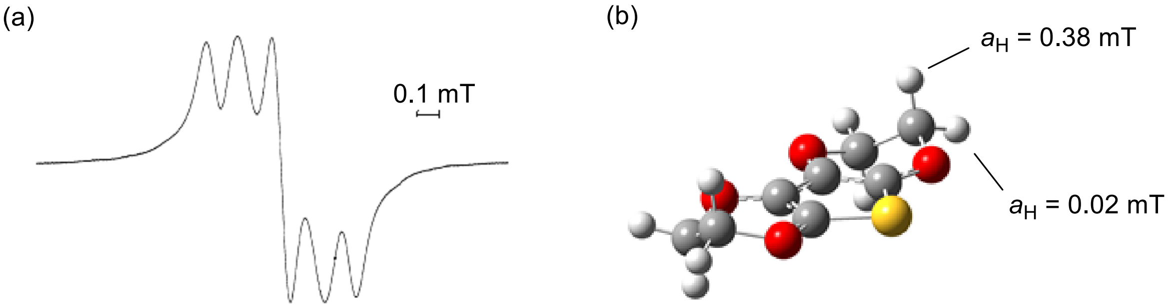


Figure 6. (a) ESR spectrum of **4** with $SbCl_5$ in CH_2Cl_2 at room temperature. (b) Optimized structure of $\mathbf{4}^{\bullet+}$ with calculated hyperfine coupling constants.

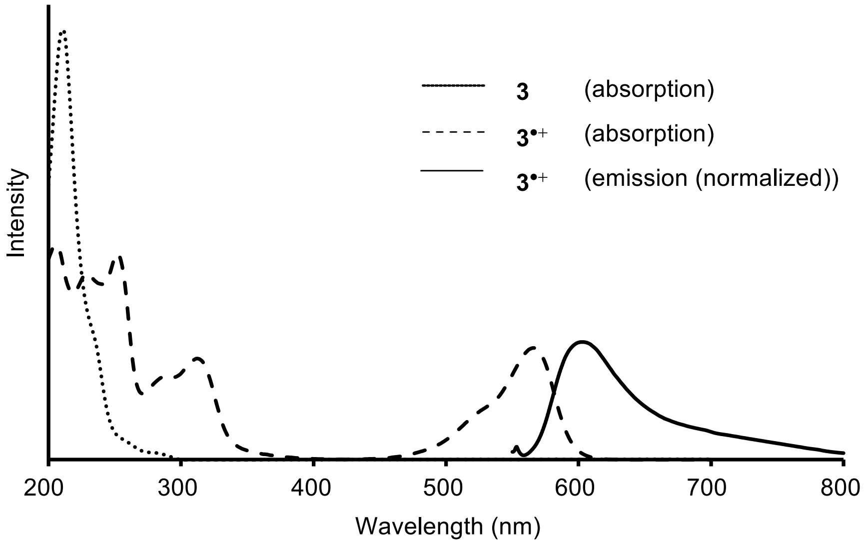


Figure 7. Absorption spectra of **3** and $\mathbf{3}^{\bullet+}$ with emission spectrum of $\mathbf{3}^{\bullet+}$ in MeCN at room temperature

The radical cation **3**$^{\bullet+}$ was generated by the reaction of **3** either with $Fe(ClO_4)_3$ in acetonitrile or aerobic oxidation in H_2SO_4, and the absorption spectra were measured in acetonitrile and H_2SO_4. The absorption spectrum of **3**$^{\bullet+}$ in acetonitrile (Figure 7) is similar to the spectrum of **3**$^{\bullet+}$ in H_2SO_4. In contrast, clear absorption spectra of **4**$^{\bullet+}$ could not be obtained, because **4**$^{\bullet+}$ was not enough stable as anticipated from the result of CV. As shown in Figure 6 and summarized in Table 2, the absorption maxima of **3**$^{\bullet+}$ were observed at 566 nm in acetonitrile and at 558 nm in H_2SO_4. TD–DFT calculations at the same level predicted that HOMO–1→SOMO transition (93% contribution) is located at 589 nm with oscillator strength of 0.07, supporting the observed absorption maxima of **3**$^{\bullet+}$.

Table 2. Absorption maxima of **3** and **3**$^{\bullet+}$.[a]

Compound	Solvent	λ_{max} nm (logε)
3	acetonitrile	211 (4.47)
3$^{\bullet+}$	acetonitrile	312 (3.89), 566 (3.94)
3$^{\bullet+}$	H_2SO_4	314 (3.87), 558 (3.89)

[a] **3**$^{\bullet+}$ in MeCN was prepared by mixing a solution of **3** in MeCN with 1 equiv of $Fe(ClO_4)_3$, whereas **3**$^{\bullet+}$ in H_2SO_4 was prepared by dissolving **3** in H_2SO_4.

Although a large number of organic fluorophore have been known to date, almost all of them have closed-shell structures. In sharp contrast, fluorescence properties of radical ions remain undeveloped principally due to the intrinsic instability of open-shell molecule. Thus, limited examples of fluorescent radical ions have been investigated.[13-22] It is worth to note that **3**$^{\bullet+}$ shows a relatively strong fluorescence under irradiation of a 540 nm excitation wavelength (Figure 6). The fluorescence spectra of **3**$^{\bullet+}$ were measured in acetonitrile and in H_2SO_4, and the emission maxima in these solvents were detected at 602 nm and 590 nm, respectively. The quantum yield (Φ_f) was determined from the integrated fluorescence intensity and the absorbance of **3**$^{\bullet+}$ using the fluorescence of methanol solution of Nile Red as standard. The quantum yields ($\Phi_f = 0.40$ in MeCN and $\Phi_f = 0.50$ in H_2SO_4) are much higher than those reported for 1,3,5-trimethoxybenzene radical cation in solution ($\Phi_f = 2\times10^{-3}$).[20] The higher quantum yield of **3**$^{\bullet+}$ would be due to the enhanced rigidity of the oxy-substituents caused by the cyclic structures. To compare with the calculated values, the singlet excited state (S_1) of **3**$^{\bullet+}$ was optimized with TD-DFT calculations. From these calculations, the fluorescence maximum was predicted to be 725 nm which are in fair agreement with the experimental emission maxima.

In summary, we have shown an improved synthesis of **3** by using transition-metal-mediated cyclotrimerization of organotin molecules and the first synthesis of **4** with insertion of sulfur to

1,4-dilithio-1,3-butadiene unit. The full fusion of 1,4-dioxacyclohexene units was found to cause the considerable elevation of HOMO levels. As a result, these radical cations were facilely generated, and among them benzene radical cation was relatively stable. Furthermore, $\mathbf{3}^{\bullet+}$ showed a strong fluorescence (Φ_f = 0.40~0.50). This finding may stimulate development of a novel class of open-shell doublet fluorophores.

EXPERIMENTAL

JEOL JNM-EX 400 (400 MHz ^{1}H NMR and 100 MHz ^{13}C NMR) and JEOL JNM–EX 500 (500 MHz ^{1}H NMR and 125 MHz ^{13}C NMR) spectrometers using tetramethylsilane as an internal standard. Electronic spectra were recorded with SHIMADZU UV-VIS-NIR Scanning Spectrophotometer (Model UV-3101 PC). Fluorescence emissions were recorded on JASC FP-6500 Spectrofluorometer and ISR-3100 integrated share. The mass spectra (EI-MS) were determined on SHIMADZU GCMS-QP2010. Elemental analyses were performed in the micro analysis laboratory of Tokyo Metropolitan University. DFT calculations were performed with the Gaussian 09 program. All geometry optimizations were carried out at the B3LYP/6–31G(d) basis set. X-Ray crystal structure analysis was performed by using Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation and rotating anode generator. Gel permeation liquid chromatography (GPLC) was carried out using JAIGEL-1H column (20 mm×600 m ×2) and chloroform as eluent. Melting points were determined with Yanaco MP-500D melting point apparatus. Thin layer chromatography (TLC) was performed with a Merck 60 F254 (0.25 mm silica gel). Column chromatography was performed with Daisogel IR-60 (60/210 nm), or neutral alumina activity Ⅱ-Ⅲ, 70-230 mesh ASTM. The solvents used for synthesis were dried and purified by usual techniques prior to use.

Starting Material. 2,3-Dibromo-1,4-dioxene (**5**) was prepared by previously reported procedure.[5]

2-Bromo-3-trimethylstannyl-1,4-dioxene (6a). To a solution of **5** (5.00 g, 20.5 mmol) in THF (100 mL) was added dropwise a solution of butyllithium in hexane (1.56 M, 13 mL, 20.5 mmol) at –78 ºC during 10 min under argon atmosphere, and the mixture was stirred at the same temperature for 1 h. A solution of chlorotrimethylstannane (4.90 g, 24.6 mmol) in THF (50 mL) was added dropwise during 1 h. The mixture was stirred at –78 ºC for 1 h and then was gradually warmed to room temperature. The mixture was concentrated under reduced pressure. To the residue were added Et_2O (200 mL) and saturated aqueous $NaHCO_3$ (100 mL). The organic layer was separated and washed with brine (100 mL×2). The organic layer was dried over sodium sulfate, filtrated, and concentrated *in vacuo*, and the residue was distilled under reduce pressure to afford **6a** (5.72 g, 85%) as a colorless oil; bp 60–65 ºC/3 torr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.21–4.19 (m, 2H), 4.00–3.98 (m, 2H), 0.24 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ

138.8, 125.4, 67.5, 64.1, –8.6; GC–MS *m/z* 324 (M^+), 326 $(M+2)^+$, 328 $(M+4)^+$, 330 $(M+6)^+$, 332 $(M+8)^+$; IR (film) 2982, 2920, 2872, 1591, 1453, 1369, 1269, 1240, 1123, 931, 859, 775, 722 cm^{-1}. Anal. Calcd for $C_7H_{13}O_2BrSn$: C, 25.65; H, 4.00. Found: C, 25.87; H, 3.97.

2-Bromo-3-tributylstannyl-1,4-dioxene (6b). To a solution of **5** (2.00 g, 8.2 mmol) in THF (60 mL) was added dropwise a solution of butyllithium in hexane (1.56 M, 16.2 mL, 22.6 mmol) at –78 ºC during 10 min under argon atmosphere, and the mixture was stirred at the same temperature for 1 h. A solution of chlorotributylstannane (3.40 g, 10.4 mmol) in THF (20 mL) was added dropwise during 10 min. The mixture was stirred at –78 ºC for 1 h and then was gradually warmed to room temperature. The mixture was concentrated under reduced pressure. To the residue were added Et_2O (150 mL) and saturated aqueous $NaHCO_3$ (100 mL). The organic layer was separated and washed with brine (50 mL×2). The organic layer was dried over sodium sulfate, filtrated, and concentrated *in vacuo*, and the residue was separated by silica gel chromatography eluted with EtOAc–hexane (1:10) to afford **6b** (2.85 g, 73%). **6b**: colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.24–4.22 (m, 2H), 4.02–4.00 (m, 2H), 1.64–1.42 (m, 6H), 1.33 (sext, 6H, *J* = 7.4 Hz), 1.15-0.65 (m, 6H), 0.90 (t, 9H, *J* = 7.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.6, 125.7, 67.7, 64.1, 28.8, 27.1, 13.6, 10.5; DI-MS *m/z* 450 (M^+), 451 $(M+1)^+$, 452 $(M+2)^+$, 453 $(M+3)^+$, 454 $(M+4)^+$, 455 $(M+5)^+$, 456 $(M+6)^+$, 457 $(M+7)^+$, 458 $(M+8)^+$.

Tris(ethylenedioxy)benzene (3) (Table 1, Entry 2)**.** To a solution of **6a** (800 mg, 2.44 mmol) in toluene (5 mL) was added tetrakis(triphenylphosphine)palladium (282 mg, 0.244 mol, 10 mol%) under argon atmosphere. The mixture was refluxed for 48 h. The mixture was cooled to room temperature and filtered through Celite, and the residue was washed with CH_2Cl_2 (300 mL). The filtrate was washed with water (100 mL×3). The organic layer was dried over magnesium sulfate and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with CH_2Cl_2–hexane (1~5:10) to afford **3** (58 mg, 29%) and **7** (8 mg, 2%). **3**: colorless solid; sublimed at 390 ºC; IR (KBr) 2991, 2938, 2887, 1630, 1490, 1376, 1274, 1247, 1104, 958 cm^{-1}; UV (MeCN) λ_{max} 211 nm (ε = 29,300); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.29 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 127.2, 84.9; EI-MS *m/z* 252 (M^+), 224, 196, 140, 112. Anal. Calcd for $C_{12}H_{12}O_6$: C, 57.14; H, 4.80. Found: C, 57.25; H, 4.79. **7**: colorless powder; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.27–4.24 (m, 4H), 4.22–4.19 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 128.9, 121.6, 67.5, 64.3; EI-MS *m/z* 326 (M^+), 328 $(M+2)^+$, 330 $(M+4)^+$; IR (KBr) 2934, 1637, 1559, 1448, 1338, 1269, 1241, 1141, 1117, 1093, 947 cm^{-1}. Anal. Calcd for $C_8H_8O_4Br_2$: C, 29.30; H, 2.46. Found: C, 29.55; H, 2.51.

Tris(ethylenedioxy)benzene (3) (Table 1, Entry 6)**.** To a solution of **6a** (500 mg, 1.53 mmol) in *N*-methyl-2-pyrrolidone (8 mL) was added CuTC (cupper(I) thiophenecarboxylate) (873 mg, 4.58 mmol) under argon atmosphere. The mixture was gradually heated to 130 ºC. After stirring for 48 h, the mixture was cooled to room temperature. The mixture was filtrated through silica gel and the residue was washed with CH_2Cl_2 (200 mL). Then the filtrate was washed with 5% aqueous NH_3. The organic layer was washed with water two times. Then the organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed on silica gel with CH_2Cl_2–hexane (1~5:10) as eluent to give **3** (11 mg, 9%).

3,3'-Dibromo-2,2'-bi-1,4-dioxene (7). To a solution of **5** (1.00 g, 4.10 mmol) in THF (20 mL) was added dropwise a solution of *tert*-butyllithium in pentane (1.40 M, 6.2 mL, 8.68 mmol) at –78 ºC during 15 min under argon atmosphere, and the mixture was stirred at the same temperature for 2 h. A solution of dry zinc chloride (0.86 g, 6.14 mmol) in THF (10 mL) was added dropwise during 1 h. The mixture was stirred for 1 h at –78 ºC and gradually was warmed to –40 ºC. The mixture was cooled again to –78 ºC and 1.65 g (12.3 mmol) of copper(II) dichloride was added. The mixture was stirred at –78 ºC for 1 h and was gradually warmed to room temperature. The mixture was filtrated through a short column of alumina to remove insoluble products. The resultant solution was concentrated *in vacuo*, and the concentrate was chromatographed on silica gel with CH_2Cl_2–hexane (1~5:10) as eluent to give **7** (0.40 g, 58%).

Bis(ethylenedioxy)thiophene (**4**)**.** To a solution of **7** (1.00 g, 3.05 mmol) in THF (100 ml) and Et_2O (100 mL) was added dropwise a solution of *t*-butyllithium in pentane (1.49 M, 8.40 mL, 12.5 mmol) at –78 ºC during 10 min, and the mixture was stirred at the same temperature for 1.5 h. The solution of benzenesulfonic thioanhydride (880 mg, 3.30 mmol) in THF (10 mL) was added dropwise during 10 min, and the mixture was stirred at –78 ºC for 1 h and then was gradually warmed to room temperature. The mixture was concentrated under reduce pressure. CH_2Cl_2 and water were added to the residue. The organic layer was separated, dried over sodium sulfate, filtrated, and concentrated *in vacuo*. The residue was separated by column chromatography on silica gel with EtOAc–hexane (1:10) to afford **4** (390 mg, 65%). **4**: colorless solid, mp 98–99 ºC; ^1H NMR (500 MHz, $CDCl_3$) δ 4.30–4.28 (m, 4H), 4.25–4.23 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 125.3, 124.9, 67.0, 65.8; EI-MS *m/z* 200 (M^+); UV (acetonitrile) λ_{max} 229 nm (ε = 4,680); IR (KBr) 2975, 1630, 1482, 1370, 1241, 1230, 1132, 1061, 965, 864 cm^{-1}. Anal. Calcd for $C_8H_8O_4S$: C, 47.99; H, 4.03. Found: C, 48.07; H, 3.91.

X-Ray Crystallographic Analysis of 3: $C_{12}H_{12}O_6$, MW = 252.22, colorless crystal of 0.25 × 0.25 × 0.30 mm; monoclinic, C_c (#9), a = 16.038(2) Å, b = 9.294(2) Å, c = 7.161(2) Å, β = 93.02(2)˚, V = 1065.8(4) Å^3, T = 295 K, Z = 4, μ_{calcd} = 1.572 g cm^{-3}, 1223 unique reflections out of 1348 with $I > 2\sigma(I)$, 164 parameters, R_1 = 0.107, wR_2 = 0.1358.

X-Ray Crystallographic Analysis of 4: $C_8H_8O_4S$, MW = 200.21, colorless crystal of 0.45 × 0.30 × 0.20 mm; monoclinic, $P2_{1/a}$ (#14), a = 9.866(3) Å, b = 7.497(2) Å, c = 11.741(2) Å, β = 106.96(2)º, V = 830.7(4) Å^3, T = 295 K, Z = 4, μ_{calcd} = 1.60 g cm^{-3}, 1905 unique reflections out of 2166 with $I > 2\sigma(I)$, 118 parameters, R_1 = 0.028, wR_2 = 0.043.

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