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Comparative Studies on Electronic Spectra and Redox Behaviors of Isomeric Benzo[1,2-*b*:4,5-*b*′]difurans and Benzo[1,2-*b*:5,4-*b*′]difurans

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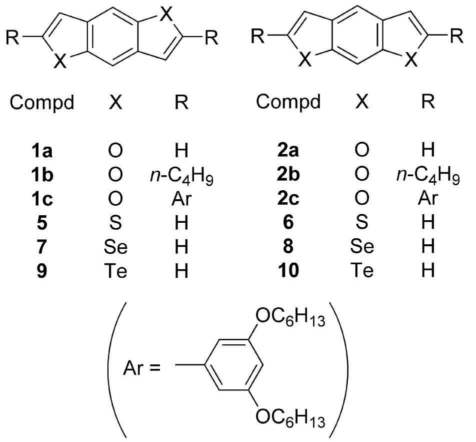
Electronic absorption/emission spectra, absolute fluorescence quantum yields, and oxidation potentials of isomeric benzo[1,2-*b*:4,5-*b*′]difurans (**1a**) and benzo[1,2-*b*:5,4-*b*′]difurans (**2a**) along with their α,α′-di-*n*-butyl (**1b** and **2b**) and bis(3,5-dihexyloxyphenyl) derivatives (**1c** and **2c**) were studied. The longest wavelength absorption maxima were very close between **1a** and **2a** and between **1b** and **2b**; however, the maximum absorption of **1c** was significantly red-shifted compared to that of **2c**, due to cross-conjugation in the latter. Unlike related compounds, the fluorescence quantum yields of syn (**1a**−**c**) and anti (**2a**−**c**) isomers were virtually identical. On the other hand, the oxidation potentials of the syn isomers were significantly lower than those of the anti isomers. Molecular orbital calculations revealed that this is likely to be characteristic of benzodifurans, because HOMO energy levels of the [1,2-*b*:4,5-*b*′] and [1,2-*b*:5,4-*b*′] isomers were estimated to be virtually identical in the other benzodichalcogenophenes.

1. Introduction

One of the characteristics of fused heteroaromatic compounds is the existence of structural isomers with respect to the orientation of fused heterorings.[1] Several structural parameters, such as bond length and molecular volume, may be similar in these isomers because they are assemblages of identical aromatic rings, but the chemical and physical properties are generally diverse. In order to understand the nature of heteroaromatic compounds, it is fundamental to elucidate the structure−property relationships. Hence, a number of comparative studies on isomeric fused heteroaromatic compounds, including UV/vis spectroscopy,[2] IR spectroscopy,[3] NMR spectroscopy,[4] mass spectroscopy (fragmentations),[5] X-ray diffraction analysis,[6] and reactivities,[7] were intensively conducted during the 1960s through 1980s. However, since the studies were performed from the perspective of fundamental heteroaromatic chemistry, most investigations focused on small molecules consisting of two (or occasionally three) fused rings.

Recently, fused heteroaromatic compounds consisting of three, four, or more fused rings have attracted much attention. This is partly because of the remarkable progress made in computer hardware and in the development of new theories, which have enabled us to calculate a wide variety of structural and electronic properties of large molecules with high accuracy and short computation time.[8−13] Essentially, these compounds have potential application in organic devices, such as organic field-effect transistors (OFETs), organic light emitting diodes (OLEDs), and photovoltaic cells,[14] due to an advantage of facile synthesis, chemical stability, and solubility compared to hydrocarbon compounds. A number of examples are reported where heteroaromatic compounds have behaved as good substituents for hydrocarbon analogues. For example, 5,11-bis(triethylsilylethynyl)anthradithiophene showed OFET performance superior to 6,13-bis(triisopropylsilylethynyl)pentacene, in spite of a similar 2-D π-stacking arrangement, high mobility (μ), and the I_{on}/I_{off} ratio of the former being attributed to the close π-stacked interactions in the crystal.[15] Another advantage of heteroaromatic compounds is that their performance may be tuned by substituting them with the structural isomers. Consequently, the effects of the orientation of fused heterorings on the molecular properties and device performance were investigated for several S-containing heteroaromatic compounds. Wex and Neckers studied electronic spectra, fluorescence quantum yields, oxidation potentials, and vibronic couplings of isomeric benzodithiophenes and thienobisbenzothiophenes[16,17] and subsequently examined their OFET performance.[18] Perepichka synthesized isomeric tetrathienoanthracenes and investigated their basic physical properties, X-ray structures, and performances as OFET devices.[19]

SCHEME 1



Compd	X	R	Compd	X	R
1a	O	H	**2a**	O	H
1b	O	*n*-C$_4$H$_9$	**2b**	O	*n*-C$_4$H$_9$
1c	O	Ar	**2c**	O	Ar
5	S	H	**6**	S	H
7	Se	H	**8**	Se	H
9	Te	H	**10**	Te	H

In the field of material chemistry, S-containing heteroaromatic systems have been frequently used as described above. This is partly because of the expected S···S contact for those compounds, which would enhance electronic interactions between the adjacent molecules in molecular assemblies. There is no

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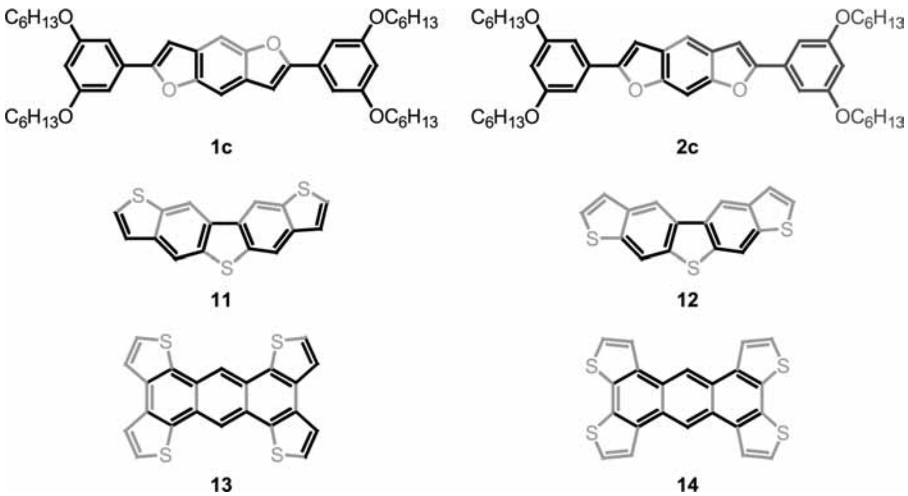
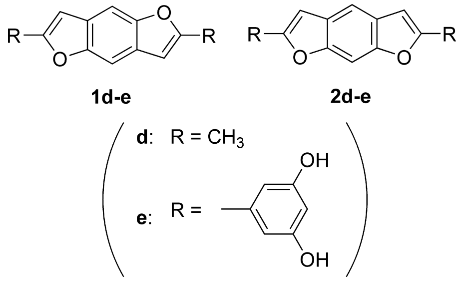
SCHEME 2



SCHEME 3



doubt that S···S contacts are advantageous, but recent reports suggest that heteroaromatic compounds that bear oxygen atoms instead of sulfur are capable of efficient intermolecular interactions that afford high performances as devices.[20] Two additional important features can be attributed to O-containing heteroaromatic systems. First, they should prefer π-stacking molecular assembly. This supposition is based on theoretical studies, according to which the interaction energies in a face-to-face molecular arrangement are similar in furan[21] and benzene dimers,[22] while they are very small or even repulsive in thiophene[23] and pyrrole dimers,[24] respectively. Thus, we expect strong intermolecular packing in O-containing heteroaromatic compounds, which would enhance intermolecular electronic interactions. Second, O-containing heteroaromatic systems can impart intense fluorescence, unlike those containing S, Se, and Te, whose weak fluorescence should be due to the heavy-atom effect, as previously reported by Zander et al.[25] Therefore, O-containing heteroaromatic systems may have potential use in organic light-emitting (field-effect) transistors (OLETs).[7,26] However, O-containing heteroaromatic systems have rarely been studied.

Here, electronic absorption/emission spectra, absolute fluorescence quantum yields, and oxidation potentials of benzo[1,2-*b*:4,5-*b*′]difurans (**1a**−**c**; see Scheme 1 for structures) and benzo[1,2-*b*:5,4-*b*′]difurans (**2a**−**c**) were studied to elucidate the structure−property relationship of isomeric O-containing heteroaromatic compounds. To evaluate the substituent effects, α,α'-di-*n*-butyl (**1b** and **2b**) and bis(3,5-dihexyloxyphenyl) derivatives (**1c** and **2c**) were also studied, where the *n*-butyl and 3,5-dihexyloxy groups provided facile synthesis and increased solubility, respectively. The characteristic features of benzodifurans (**1** and **2**) are compared both experimentally and theoretically to those of benzodithiophenes (**5** and **6**), benzodiselenophenes (**7** and **8**), and benzoditellurophenes (**9** and **10**).

2. Experimental Section

2.1. Materials. Several synthetic procedures for benzodifurans are known.[20a,27] In the present study, we used Sonogashira coupling giving *o*-alkynylphenols followed by cyclization under basic conditions (Supporting Information, Figure S1) to obtain the target compounds. Diiododiacetoxybenzene was subjected to Sonogashira coupling to yield bis(trimethylsilylethynyl)diacetoxybenzenes (**3a** and **4a**), which were treated with tetra-*n*-butylammonium fluoride (TBAF) in the presence of 4A molecular sieves[28] to undergo continuous deacetylation and desilylation to obtain **1a** and **2a**, respectively. Cyclization of bisethynylated dimethoxybenzenes **3b**,**c** and **4b**,**c**, which were

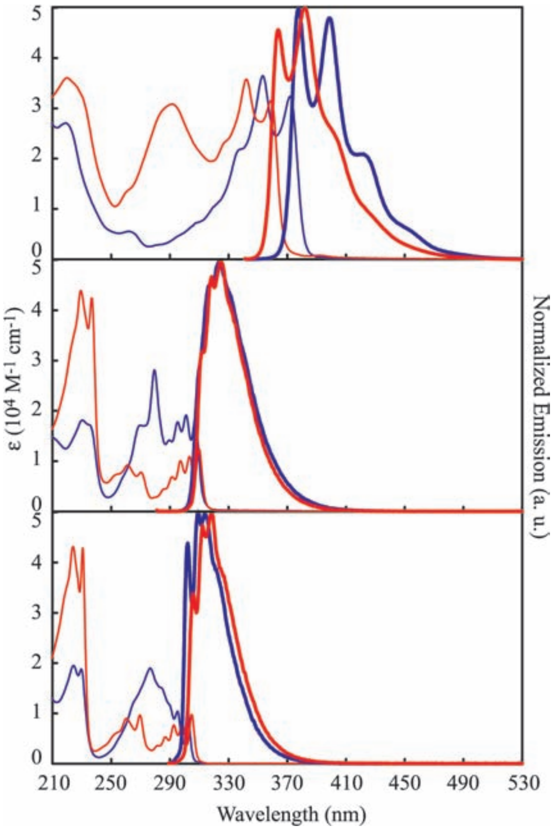


Figure 1. Electronic absorption (thin lines) and normalized emission (thick lines) spectra of **1a** (lower, blue), **2a** (lower, red), **1b** (middle, blue), **2b** (middle, red), **1c** (upper, blue), and **2c** (upper, red) in EtOH.

TABLE 1: Collection of Spectroscopic Properties and Oxidation Potentials of 1a−c and 2a−c

	1a	1b	1c	2a	2b	2c
$\lambda_{\max}$ (log ε)^{a}, nm	224 (4.29), 295 (4.00), 302 (4.04)	279 (4.45), 295 (4.24), 301 (4.28), 307 (4.27)	336 (sh, 4.33), 353 (4.56), 372 (4.51)	223 (4.63), 292 (3.88), 299 (3.22), 305 (3.99)	229 (4.64), 297 (3.99), 303 (4.02), 310 (4.09)	291 (4.49), 327 (sh, 4.37), 341 (4.55), 358 (4.49)
$\lambda_{\mathrm{F,max}}{}^{a,b}$, nm	303, 310, 315	311 (sh), 319, 325, 333 (sh)	379, 399, 423, 456 (sh)	307, 313, 319	313, 319, 326, 334 (sh)	365, 383, 404 (sh), 430 (sh)
$\Phi_{\mathrm{F}}{}^{a}$	0.43	0.42	0.76	0.41	0.41	0.73
E_{ox}(anodic)^{c}, V	+1.08 (sh), +1.23	+0.85	+0.73	+1.18, +1.29	+1.04	+0.82
E_{ox}(onset)^{c}, V	+0.92	+0.71	+0.56	+1.00	+0.82	+0.71

[a] In ethanol. [b] Excitation wavelength was 280 nm for **1a**,**b** and **2a**,**b** and 340 nm for **1c** and **2c**. [c] Electrode: Pt (working), Pt (counter), and Ag/AgCl (reference). Supporting electrolyte: n-Bu_4NPF_6. Solvent: CH_3CN. Scan rate: 100 mV/s. Versus ferrocene/ferricinium.

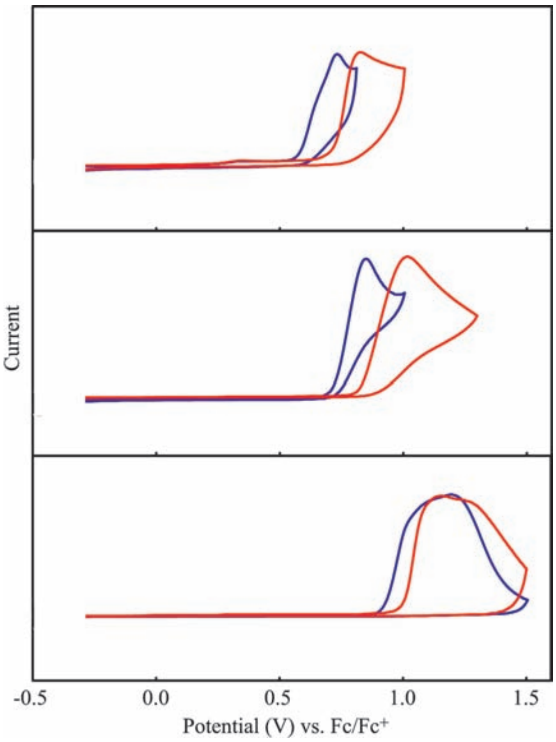


Figure 2. Comparison of cyclic voltammograms of **1a** (lower, blue), **2a** (lower, red), **1b** (middle, blue), **2b** (middle, red), **1c** (upper, blue), and **2c** (upper, red) in CH_3CN at a scan rate of 100 mV s^{-1}.

also synthesized by means of Sonogashira coupling, was performed in the presence of LiI in 2,6-dimethylpyridine (collidine)[29] to provide **1b**,**c** and **2b**,**c**.

2.2. Electronic Absorption/Emission Spectra. Electronic absorption spectra were acquired on a Shimadzu UV-2400PC spectrometer. Fluorescent spectra were recorded in ethanol on a Shimadzu RF-5300PC spectrometer using a 450 W xenon short arc and sample detection in 90° geometry. Fluorescence quantum yields were measured using an absolute PL quantum yield measurement system (C9920-02, Hamamatsu Photonics K.K.).[30]

2.3. Electrochemical Analyses. Cyclic voltammetry (CV) was performed in 1 mM of substrate on a BAS-600 electrochemical analyzer. All oxidation CV measurements were carried out in anhydrous acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate ($n$$Bu_4NPF_6$) as a supporting electrolyte and purged with argon prior to conducting the experiment. A platinum working electrode was used and platinum wire was used as a counter electrode. All potentials were recorded against an Ag/AgCl reference electrode and calibrated with the standard ferrocene/ferricinium redox couple ($E^{1/2} = +0.46$ V) measured under identical conditions.

2.4. Theoretical studies. Theoretical investigation of **1a**, **1d**, **1e**, **2a**, **2d**, **1e** (Scheme 3), and **5−8** was performed on the basis of optimized structures by HF/3-21G*, HF/6-31G**, and B3LYP/6-31G** methods using Spartan ‘04 Windows (version 1.0.3, Wavefunction, Inc.) run on Microsoft Windows XP, while that of **9** and **10** was conducted by the HF/3-21G* method, because 6-31G** basis sets are not available for tellurium. As shown in Figures 3 and S2 (Supporting Information), the atomic orbital (AO) coefficients in the HOMOs of **1a**, **2a**, and **5−8** calculated by B3LYP/6-31G** methods are very close to those obtained by HF/3-21G* methods, indicating that they may be compared to the AO coefficients in the HOMOs of **9** and **10** by HF/3-21G* methods in a qualitative manner. During all calcula-

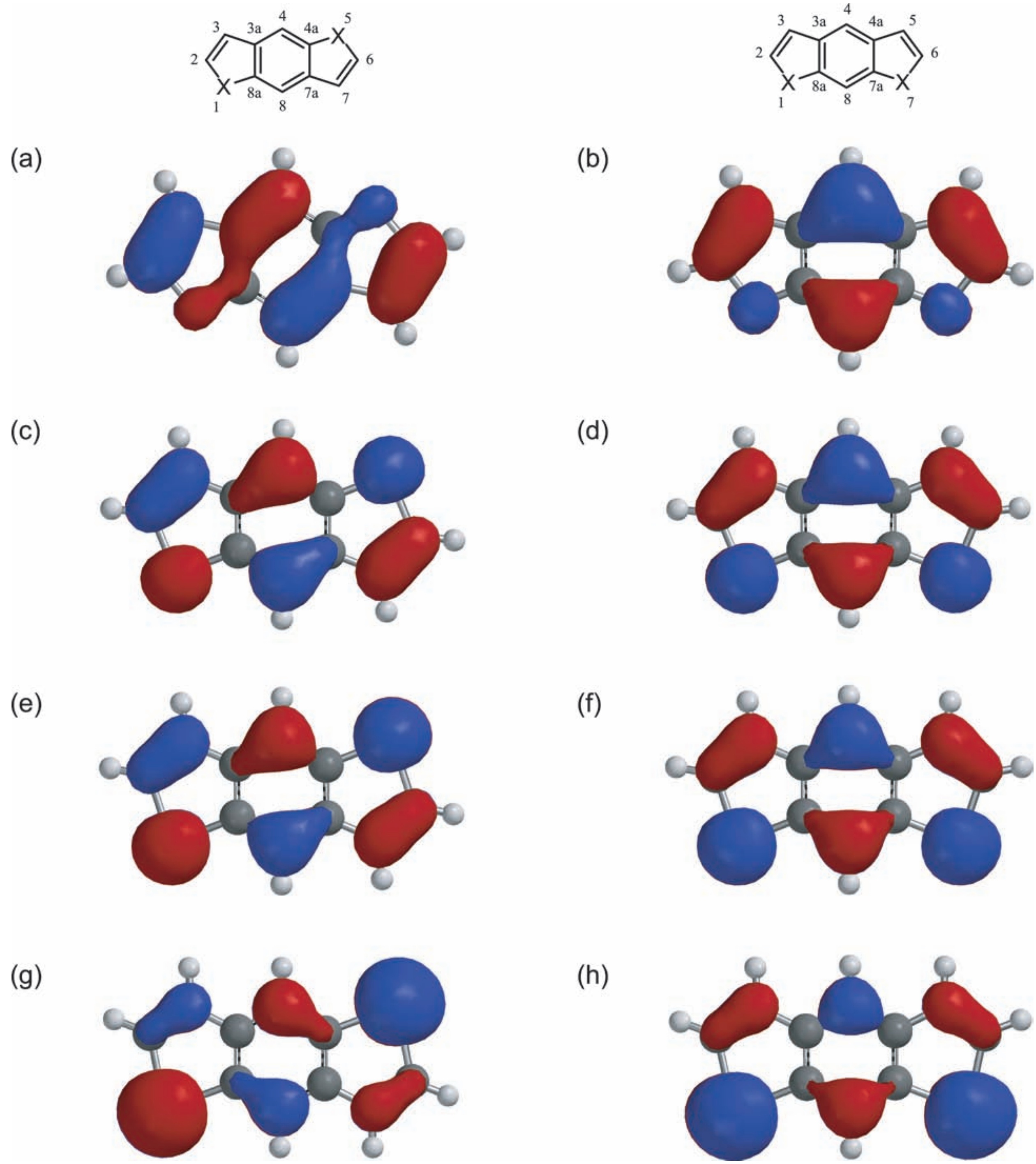


Figure 3. HOMO orbitals of **1a** (a), **2a** (b), **5** (c), **6** (d), **7** (e), **8** (f), **9** (g), and **10** (h) calculated by B3LYP/6-31G** (**1a**, **2a**, **5**−**8**) and HF/3-21G* (**9**, **10**) methods.

tions, the C_{2h} (for **1a**, **1d**, **1e**, **5**, **7**, **9**) and C_{2v} (for **2a**, **2d**, **2e**, **6**, **8**, **10**) symmetries of the molecular structure were postulated.

3. Results and Discussion

Electronic absorption and emission spectra of **1a**−**c** and **2a**−**c** in EtOH are shown in Figure 1. The shapes of the absorption spectra of **1a** and **2a** were very close in the longer wavelength regions (290−310 nm) but considerably different in the shorter wavelength regions (210−290 nm). This gave rise to the similar shapes of the emission spectra of **1a** and **2a**. This is in contrast to those of benzodithiophenes **5** and **6**, whose absorption spectra in the longer wavelength regions (290−320 nm) and emission spectra had considerably different shapes.[16] Moreover, the longest wavelength absorption maximum ($\pi-\pi^*$) was red-shifted (8 nm) in **5** compared to **6**, while it was blue-shifted (3 nm) in **1a** compared to **2a**. The Stokes shifts in **1a**,**b** and **2a**,**b** were as small as those in **5** and **6** (<3 nm), indicating the rigidity of their π moieties. Remarkably, the fluorescence quantum yields (Φ_Fs) of **1a** and **2a** (Table 1) were much larger than those of **5** ($\Phi_F = 0.014$, in ethanol) and **6** (0.009).[16] It is also noted that **7** and **9** are less intensely fluorescent than **5**.[31] This may be due to the absence of the heavy atoms in **1a** and **2a**. The Φ_Fs of **1a** and **2a** were also larger than that of anthracene (0.27, in ethanol).[32]

TABLE 2: HOMO/LUMO Energies (in eV) of 1a, 1d, 1e, 2a, 2d, 2e, and 5−10 Calculated by HF/3-21G*, HF/6-31G, and B3LYP/6-31G** Methods**

	HF/3-21G*	HF/6-31G**	B3LYP/6-31G**
1a	−8.03/2.69	−7.63/2.90	−5.54/−0.82
2a	−8.28/2.93	−7.93/3.11	−5.70/−0.70
1d	−7.62/2.94	−7.26/3.13	−5.23/−0.58
2d	−7.97/3.19	−7.56/3.34	−5.46/−0.46
1e	−7.47/1.59	−7.09/1.82	−5.15/−1.56
2e	−7.78/1.85	−7.38/2.03	−5.39/−1.42
5	−7.67/2.44	−7.58/2.52	−5.48/−1.10
6	−7.68/2.78	−7.60/2.85	−5.50/−0.90
7	−7.50/2.42	−7.51/2.43	−5.42/−1.15
8	−7.51/2.90	−7.51/2.89	−5.44/−0.86
9	−7.22/2.28	—[a]	—[a]
10	−7.23/2.24	—[a]	—[a]

[a] Gaussian basis sets are not available.

The substituent effects of the *n*-butyl groups on the electronic absorption/emission spectra and Φ_F are relatively small. In the electronic absorption spectra of **1b** and **2b**, the same magnitude of red-shifts (5 nm) was observed for the longest wavelength maxima. In contrast, peaks in the emission spectra ($\lambda_{F,max}$s) were red-shifted to a greater extent in **1b** (8−10 nm) than in **2b** (4−7 nm). Φ_Fs were virtually identical in **1b** and **2b**. Compared with the *n*-butyl group, the substituent effects of the 3,5-dihexyloxyphenyl group were significantly different. When compared to nonsubstituted compounds (**1a** and **2a**), the longest wavelength absorption maximum was red-shifted by 70 nm in **1c** and by 53 nm in **2c**. The different substituent effects should arise from cross-conjugation in **2c**. As depicted in Scheme 2, the right (black lines) and left aryl groups (dark gray lines) are in cross-conjugation in **2c**, while two aryl groups are linearly conjugated in **1c**. Different substituent effects on the absorption spectra stemming from cross conjugation were also observed in isomeric oligo(thieno[3,2-*b*]thiophene)s and oligo(dithieno[3,2-*b*:2′,3′-*d*]-thiophene)s.[33] The larger red-shift of the emission spectra of **1c** (76 nm) vs **2c** (58 nm) may be explained similarly. On the other hand, the Φ_Fs were very close between **1c** and **2c**. It is noteworthy that, while Φ_Fs were virtually identical in the isomeric benzodifurans (the [1,2-*b*:4,5-*b*′] and [1,2-*b*:5,4-*b*′] isomers), they appeared to be generally different in isomeric compounds as reported for **5** vs **6**, **11** (0.14) vs **12** (0.012),[16] and **13** (0.32) vs **14** (0.17),[19] where the isomers bearing a cross-conjugated π-system were less intensely fluorescent (see Scheme 2).

Cyclic voltammograms (CV) of **1a−c** and **2a−c** are shown in Figure 2. Similarly to **5**, **7**, and **9**,[31] irreversible oxidation waves were observed. The E_{ox}(onset) of **1a** was higher than that of **5**, **7**, and **9**,[31] which should relate to the more electronegative character of the oxygen atom. E_{ox}(onset)s of **1a** and **2a** were found to be different; that of the former was 0.08 V less than that of the latter (Table 1). The different oxidation potential of the [1,2-*b*:4,5-*b*′] and [1,2-*b*:5,4-*b*′] isomers should be characteristic of benzodifurans, and that of the other benzodichalcogenophenes ought to be virtually identical in the isomers. This is in part supported by the fact that the photoelectron spectra are nearly identical for the benzo[1,2-*b*:4,5-*b*′]-dithiophene and its [1,2-*b*:5,4-*b*′] isomer.[17] Moreover, MO calculations using HF/3-21G*, HF/6-31G**, and B3LYP/6-31G** methods revealed that the HOMO energy level of **1a** was higher than that of **2a** by 0.15−0.30 eV, regardless of the calculation methods, whereas the HOMO energies of the other benzodichalcogenophenes were comparable (**5** vs **6**, **7** vs **8**, and **9** vs **10**) with deviations of less than 0.02 eV (Table 2). This relates to the stepwise alternation of the atomic orbital (AO) coefficients observed in the HOMOs of the benzo[1,2-*b*:4,5-*b*′]dichalcogenophene and benzo[1,2-*b*:5,4-*b*′]dichalcogenophene, except for **1a** (Figure 3). In the [1,2-*b*:5,4-*b*′] isomers, the AO coefficients at the 1 and 7 positions (chalcogen atoms) increase, while those at all the other positions decrease monotonously in **2a**, **6**, **8**, and **10**, in that order (Figure 3, right). This is attributable to the different characteristics of the 2p, 3p, 4p, and 5p orbitals of oxygen, sulfur, selenium, and tellurium, respectively. Similar alternation of the AO coefficients is found in the HOMOs of **5**, **7**, and **9** (Figure 3, left). However, the AO coefficients of the HOMO of **1a** are considerably different from those of the [1,2-*b*:4,5-*b*′] isomers. The AO coefficients of the HOMO at the 4a and 8a positions are significantly larger in **1a**, while those in **5**, **7**, and **9** are essentially zero. In addition, those at the 3a and 7a positions have much larger than expected values based on the monotonous alternation of the AO coefficients of **5**, **7**, and **9**.

LUMO energy levels of benzodichalcogenophenes were also estimated by means of MO calculations. In contrast to HOMO energy levels, they are commonly different in the [1,2-*b*:4,5-*b*′] and [1,2-*b*:5,4-*b*′] isomers, the former being lower than the latter (Table 2). As a result, the HOMO−LUMO gaps are smaller in the [1,2-*b*:4,5-*b*′] isomers. The energy gaps calculated by B3LYP/6-31G** methods decrease in the order of **1a/2a**, **5/6**, and **7/8**, and in fact, the longest wavelength absorption maxima were reported to be red-shifted in the order of **5**, **7**, and **9** (in THF).[31]

The *n*-butyl groups lowered the E_{ox}(onset)s of **1b** and **2b** compared with those of **1a** and **2a**, respectively. The effect of lowering the E_{ox}(onset) was larger in **1b** [ΔE_{ox}(onset) = −0.21 V, vs **1a**] than in **2b** (−0.18 V, vs **2a**). Although the difference in the observed E_{ox}(onset)s was slight, MO calculations (B3LYP/6-31G**) on the model compounds [α,α′-dimethylbenzo[1,2-*b*:4,5-*b*′]difuran (**1d**) and its [1,2-*b*:5,4-*b*′] isomer (**2d**)] also predicted that the substituent effect of alkyl groups in lowering the HOMO energy levels should be different in the isomers, E_{HOMO}(**1d**) − E_{HOMO}(**1a**) and E_{HOMO}(**2d**) − E_{HOMO}(**2a**) being 0.31 and 0.23 eV, respectively (Table 2). The substituent effect of lowering the E_{ox}(onset)s was more significant in **1c** [ΔE_{ox}(onset) = −0.36 V vs **1a**] and **2c** (−0.29 V vs **2a**), which is likely to be due to the resonance effect of the aryl (3,5-dihexyloxyphenyl) groups. MO calculations again predicted the larger substituent effect of the aryl groups: the E_{HOMO} of α,α′-di(3,5-dihydroxyphenyl)benzo[1,2-*b*:4,5-*b*′]difuran (**1e**) is 0.39 eV higher than that of **1a**, while the E_{HOMO} of the [1,2-*b*:5,4-*b*′] isomer **2e** is 0.30 eV higher than that of **2a**.

4. Conclusions

Electronic absorption/emission spectroscopy, electrochemical studies, and theoretical calculations revealed the different behaviors of isomeric benzodifurans (**1a−c** and **2a−c**) compared with the other isomeric benzodichalcogenophenes (**5−10**) and related compounds (**11−14**). While the oxidation potentials were different in benzodifurans, the longest wavelength absorption/emission maxima (except for **1c/2c**) and Φ_Fs were virtually identical in the [1,2-*b*:4,5-*b*′] and [1,2-*b*:5,4-*b*′] isomers. The present results likely indicate that the properties of materials consisting of benzodifuran and its derivatives should vary considerably depending on whether they consist of the [1,2-*b*:4,5-*b*′] isomer, the [1,2-*b*:5,4-*b*′] isomer, or (if available) their mixture, and the variation should be wider than in the other benzodichalcogenophene derivatives. Note that several S-containing fused heteroaromatic compounds, such as anthraditiohphenes,[34] alkyne-functionalized anthradithiophenes,[15] and alkyne-functionalized tetradithiophenes,[14a] were examined for their OFET performance without separation of the isomers. If they are substituted by benzodifurans, their properties may be more influenced by the isomeric ratio. Studies on the crystal structures of **1a**−**c** and **2a**−**c** and their performances as devices are currently underway.

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Supporting Information Available: Synthetic procedures and analytical and spectral characterization data of **1a**−**c** and **2a**−**c**, HOMO orbitals of **1a**, **2a**, and **5**−**10** calculated by HF/3-21G* methods, and molecular modeling coordinates of **1a**, **1d**, **1e**, **2a**, **2d**, **2e**, and **5**−**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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