Modular Synthesis and Photophysical and Electrochemical Properties of 2,3,5,6-Tetraaryl-Substituted Benzo[1,2-*b*:5,4-*b*']difurans

Hayato Tsuji,¹ Chikahiko Mitsui,¹ Yoshiharu Sato,² and Eiichi Nakamura^{1,2}

¹Department of Chemistry, School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

²Nakamura Functional Carbon Cluster Project, ERATO, Japan Science and Technology Agency, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Received 16 August 2010; revised 14 October 2010

ABSTRACT: We developed a versatile synthesis of tetraaryl-substituted benzo[1,2-b:5,4-b']difurans (m-BDFs) via a zinc-mediated intramolecular double cyclization reaction of 4,6-bis(phenylethynyl)-1,3benzenediol, followed by a palladium-catalyzed crosscoupling reaction. In comparison with the corre*sponding benzo*[1,2-*b*:4,5-*b*']*difuran* (*p*-*BDF*) *isomers* reported previously, the m-BDFs are slightly wider between HOMO and LUMO, as well as a lower energy level of the former. These differences in properties between the structural isomers can be ascribed to the difference in the conjugation type. The compounds had high charge carrier mobility up to 1×10^{-3} cm²/Vs, which makes them attractive materials for organoelectronics applications. © 2011 Wiley Periodicals, Inc. Heteroatom Chem 22:316-324, 2011; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20682

INTRODUCTION

Benzofuran and congeners have recently received growing attention because of their useful photophysical and electric properties [1,2,3,4,5]. We recently reported the synthesis of a variety of tetraaryl-substituted benzo[1,2-*b*:4,5-*b'*]difurans (*p*-BDFs), their p-type semiconductor characteristics and high hole mobility (up to 10^{-3} cm²/Vs for amorphous film), and their versatility in organic light-emitting diodes [1]. These findings led us to study the *m*-isomer benzo[1,2-*b*:5,4-*b'*]difuran (*m*-BDF) **4**. In this article, we describe the preparation, photophysical, and electrochemical properties, and carrier mobilities of *m*-BDF.

RESULTS AND DISCUSSION

Synthesis of m-BDF

The present synthesis of *m*-BDF relies on the zincmediated cyclization of an ortho-alkynyl phenol into 3-zinciobenzofuran that we developed recently and extended to the synthesis of a variety of heterocyclic π -electronic compounds [6,7,8,9,10]. As shown in Scheme 1, dialkynylbenzenediol **2**, which is readily available from dibromobenzenediol **1**, was treated sequentially with butyllithium and zinc chloride to effect twofold intramolecular oxozincation of the

Dedicated to Professor Kin-ya Akiba on the occasion of his 75th birthday.

Correspondence to: H. Tsuji; e-mail: tsuji@chem.s.u-tokyo.ac.jp. E. Nakamura; e-mail: nakamura@chem.s.u-tokyo.ac.jp. © 2011 Wiley Periodicals, Inc.



SCHEME 1

triple bonds and provide quantitatively 3,5-dizincio*m*-BDF **3** as a stable intermediate that serves as a synthetic module to obtain a variety of derivatives. Upon quenching with water, this intermediate gave 3,5-protonated *m*-BDF **4a** in 99% isolated yield.

The Negishi coupling of **3** with iodobenzene, *p*-bromo-*N*,*N*-dimethylaniline *p*-bromo-*N*,*N*diphenylaniline, and *N*-(*p*-bromophenyl)carbazol afforded the corresponding 3,5-diarylated *m*-BDF derivatives **4b**-**4e** in 63%, 62%, 58%, and 65% isolated yields, respectively. Interestingly, the reaction with pentafluorophenyl bromide gave *m*-BDF dimer **5** in 57% isolated yield in preference to the desired 3,5-bis(pentafluorophenyl)-*m*-BDF **4f**, which was obtained in 20% yield. This is an indication that the first pentafluorophenyl group at the 3-position has a strong electron-withdrawing effect on the remote organozinc moiety at the 5-position and promotes the homocoupling reaction.

Crystal Structure

We performed single-crystal X-ray crystallographic analysis of β , β' -bis(dimethylanilino)-*m*-BDF **4c** and β , β' -bis(pentafluorophenyl)-*m*-BDF **4f**, and found interesting structural characteristics. The ORTEP drawings of these molecules are shown in Fig. 1. In *p*-BDFs that we previously reported, both α - and



FIGURE 1 ORTEP drawings of *m*-BDF derivatives (30% probability for thermal ellipsoids). The solvent molecule and crystallographically independent molecule are omitted for clarity. (a) p-Me₂N-C₆H₄-substituted *m*-BDF **4c** and (b) C₆F₅-substituted *m*-BDF **4f**.

β-aromatic groups are twisted against the BDF ring (twist angles of 34.83° and 43.26° for tetraphenyl-*p*-BDF). On the other hand, in *m*-BDFs, the α-phenyl groups lie almost in the plane of the BDF ring (9.48° and 11.40° for **4c** and 1.29° and 4.33° for **4f**) [11] and the β-aryl rings are highly twisted (74.51° and 78.63° for **4c** and 64.76° and 67.30° for **4f**). This is likely the result of steric hindrance among the aromatic rings at α- and β-positions, and the hydrogen atom at the 5-position of the BDF core. Naturally, the effect of the packing force cannot be discounted.

Photophysical Properties

We next measured the ultraviolet (UV)–visible absorption and fluorescence spectra of *m*-BDFs **4a–4f** and found that these *m*-BDFs have a slightly wider bandgap than the *p*-BDF analogue. The spectra are shown in Fig. 2 and the data are summarized in Table 1. The longest wavelengths of the absorption maxima of these compounds are 340–356 nm and the absorption onset wavelengths (λ_{onset}) are 373–382 nm for the *m*-BDFs except dimethyl- and diphenylanilino-*m*-BDFs **4c** and **4d**, which have a significantly red-shifted onsets ($\lambda_{onset} = 400$ nm and 399 nm for **4c** and **4d**, respectively). Both absorption maxima and onset wavelengths of the *m*-BDFs are slightly blue-shifted (860–1470 cm⁻¹) compared with the corresponding *p*-BDF derivatives.

To explain the absorption spectra, we analyzed the structure-property relationships of *p*- and *m*-BDFs as discussed below for α, α' -diphenyl-BDFs. One can consider two thought experiments in discussing the conjugation of two BDF isomers (Fig. 3): (a) cyclic bridging of the *m*- and *p*-styrylstilbene system with two oxygen atoms and (b) replacement of two π -electrons of a C=C bond with two nonbonding electrons of an oxygen atom; that is, replacement of two double bonds in 2,7- and 2,6diphenylanthracene with two oxygen atoms. As the former is cross-conjugation, the difference in the



FIGURE 2 UV-visible absorption and fluorescence spectra of *m*-BDFs measured in dichloromethane at room temperature. (a) **4a**, **4b**, and **4f** and (b) **4c**–**4e**.

wavelengths of absorption maximum of the *m*– and *p*-styrylstilbene isomers is rather large (Fig. 3a, calculated absorption wavelengths: $\lambda_{max} = 316$ nm and 386 nm, respectively, $\Delta E = 0.71$ eV) [12] whereas that for diphenylanthracene isomers is small (calculated absorption wavelengths: $\lambda_{max} = 302$ nm and 319 nm for 2,7- and 2,6-isomer, respectively, $\Delta E = 0.22$ eV) [13]. Considering the small difference in absorption wavelengths: $\lambda_{max} = 346$ nm and 367 nm for *m*- and *p*-BDFs, respectively, $\Delta E = 0.20$ eV), the electronic structure of α, α' -diphenyl-BDFs may be considered to be more similar to that of diphenylanthracene isomers than to that of styrylstilbenes.

The phenyl- and pentafluorophenyl-substituted *m*-BDFs (**4a**, **4b**, and **4f**) have a series of sharp fluorescence bands with fine vibration structures between 1150 and 1200 cm⁻¹. The Stokes shift was very small (840 cm⁻¹ for **4a**, 1420 cm⁻¹ for **4b**, and 1290 cm⁻¹ for **4f**). The fluorescence quantum yields were rather high (0.81–0.93) for these compounds. On the other hand, the arylamino-*m*-BDFs **4c** and **4d** had a broad and structureless emission band accompanying a large Stokes shift (6260 cm⁻¹ for **4c**)

Compound	λ ^a abs (nm)	λ ^a onset (nm)	λ ^b emis (nm)	Stokes Shift (cm ⁻¹)	Φ_{F}^{c}	E ^d _{ox} (V)
4a	292, 341, 356	373 (392)	367, 385	840	0.92	0.82 (ir)
4b	343, 357 (sh)	378 (396)	376 (sh), 393	1420	0.93	0.89 (r)
4c	272, 299, 346, 359 (sh)	400 (428)	463	6260	0.67	0.29 (r)
4d	301, 343, 358 (sh)	399 (419)	455	5950	0.73	0.48 (r)
4e	342, 357 (sh)	382 (402)	402	3140	0.74	0.82 (ar)
4f	271, 297, 340, 354 (sh)	373 (393)	371, 388	1290	0.81	1.18 (ir)

TABLE 1 Summary of Photophysical and Electrochemical Properties of m-BDF derivatives 4a-4f

^aAbsorption spectra measured in CH₂Cl₂ at room temperature. sh: shoulder.

^bEmission spectra excited at 320–340 nm measured in CH₂Cl₂ at room temperature. sh: shoulder.

^{*c*}Determined employing the absolute method.

^dFor **4b–4d**: determined by the half-wave voltage of cyclic voltammetry (CV) measurement (vs. Fc/Fc⁺). For **4a**, **4e**, and **4f**: determined by differential pulse voltammetry (DPV) measurement (vs. Fc/Fc⁺). Both measurements were performed in dichloromethane (0.5 mM) using TBAP (0.1 M) as an electrolyte. r: reversible, ir: irreversible, qr: quasi reversible.



FIGURE 3 Schematic representation of the effective conjugation lengths of styrylstilbenes, BDFs, and anthracene derivatives, together with their absorption maximum wavelengths (calculated at the TD B3LYP/6–31G*//B3LYP/6–31G* level assuming planarity of the conjugation system) and experimental data (shown in parentheses).

and 5950 cm⁻¹ for **4d**) and moderate quantum yield (0.67 and 0.73 for compounds **4c** and **4d**, respectively). We can ascribe this large shift to the well-known charge-transfer character of the emission of arylamines [14]. The carbazole-substituted derivative **4e** also had a broad and structureless emission band accompanying a moderate Stokes shift (3140 cm⁻¹) and quantum yield (0.74), the magnitude of which is between those of tetraphenyl derivative **4a** and arylamino derivatives **4c** and **4d**.

Electrochemical Properties

Cyclic voltammetry (CV) measurements presented in Fig. 4 reveal that most of the tetraarylsubstituted *m*-BDFs are electrochemically stable, whereas diphenyl-*m*-BDF **4a** is not. Their oxidation potentials are summarized in Table 1. Tetraphenylsubstituted *m*-BDF **4b** had a reversible first oxidation wave with a slight shift of E_{ox} to the positive side as compared with diphenyl-*m*-BDF **4a** (0.89 V for **4b** and 0.82 V for **4a**). As expected, electrondonating amino substituents caused a shift in the first oxidation potential to the negative side ($E_{ox} =$ 0.29 and 0.48 V for **4c** and **4d**), whereas an electronwithdrawing pentafluorophenyl group caused a shift to the positive side ($E_{ox} = 1.18$ V for **4f**), although compound **4f** failed to show reversibility of the first oxidation wave for an unknown reason. These oxidation potentials shift approximately 0.1–0.15 eV to the positive side as compared with the corresponding *p*-BDF isomers (e.g., 0.74 for tetraphenyl*p*-BDF and 0.88 V for tetraphenyl-*m*-BDF), [1a] suggesting increased stability of the *m*-isomers against oxidation.

Carrier Mobility

We performed carrier drift mobility measurements for **4b**, **4d**, and **4e** and found moderate to high



FIGURE 4 Cyclic voltammograms of *m*-BDFs 4a-4f measured in dichloromethane.

carrier mobilities of these compounds. The mobilities were obtained by the time-of-flight (TOF) method using the amorphous films prepared by vacuum deposition. Figure 5 plots the carrier mobility against the applied electric field. Tetraphenyl-m-BDF 4b and diphenylanilino-*m*-BDF 4d had hole mobilities of 5.3 \times 10⁻⁵ and 2.5 \times 10⁻⁴ cm²/Vs, respectively, for an electric field (E) of 2.5×10^5 V/cm. The carbazolyl-substituted derivative 4e showed ambipolarity like the corresponding *p*-isomer, [1b] having hole and electron mobilities of $\mu_h = 1.7\,\times\,10^{-3}$ cm²/Vs and $\mu_e = 1.4 \times 10^{-3} \text{ cm}^2/\text{Vs},$ respectively, at $E = 2.5 \times 10^5$ V/cm. We attribute this increase in the hole mobility to a synergistic effect between the BDF unit and the carbazole moiety. These carrier mobilities are lower than those of the *p*-BDF analogues ($\mu_h = 6.4 \times 10^{-4} \text{ cm}^2/\text{Vs}$ for tetraphenyl-*p*-BDF; $\mu_h = 2.8 \times 10^{-3} \text{ cm}^2/\text{Vs}$ for diphenylanilino-*p*-BDF; and $\mu_h=3.7\times 10^{-3}~cm^2/Vs$ and $\mu_e=4.4\times 10^{-3}$ cm²/Vs for carbazolyl-*p*-BDF) but still high enough

for applications in organic electronic devices. Notably, the amorphous films of *m*-BDFs used in the TOF measurements did not crystallize in more than half a year after fabrication, whereas the amorphous film of tetraphenyl-*p*-BDF crystallized in less than 1 month upon standing on a shelf. We consider that the stability of the amorphous state of the *m*–BDF is due to the lower symmetry of this isomer.

CONCLUSION

We developed a versatile synthesis of tetraarylsubstituted benzo[1,2-b:5,4-b']difurans (m-BDF) via a zinc-mediated intramolecular double cyclization reaction. Comparison between the p- and m-BDF isomers revealed (a) similarity of the mode of the conjugation in BDFs to that in substituted anthracenes rather than styrylstilbenes, (b) a wide-gap and slightly lower oxidation potential of m-BDFs, which should increase resistance to oxidation, and



FIGURE 5 Carrier (hole and electron) drift mobilities of 4b, 4d, and 4e plotted against the square root of the electric field measured employing the TOF method at room temperature.

(c) high stability of the amorphous films. Applications of *m*-BDFs in organic electronic devices are now in progress.

EXPERIMENTAL

All of the reactions dealing with air- or moisturesensitive compounds were carried out in a dry reaction vessel under a positive pressure of nitrogen or argon. Proton nuclear magnetic resonance (¹H NMR) and carbon nuclear magnetic resonance (¹C NMR) spectra were recorded on a JEOL ECA-500 (500 MHz for ¹H and 125 MHz for ¹³C) NMR spectrometer using CDCl₃ as a solvent at ambient temperature unless otherwise noted. Tetramethylsilane was used as an internal reference.

2-[4,6-Dibromo-3-(tetrahydro-2H-2-pyranyloxy)*phenoxy]tetrahydro-2H-pyran.* To а 20 mL two-necked flask were added 4,6-dibromo-1,3benzenediol (268 mg, 1.00 mmol) and 3,4-dihydro-2*H*-pyran (DHP) (911 µL, 10.0 mmol). After stirring at ambient temperature for 10 min, pyridinium *p*-toluenesulfonate (PPTS) (5.0 mg, 0.020 mmol) was added to the mixture. After stirring at ambient temperature for 11 h, the reaction was guenched with saturated sodium bicarbonate solution. The organic layer was extracted twice with ethyl acetate, washed with brine, and dried over Na₂SO₄. After removal of the solvent in vacuo, the crude material was subjected to flash column chromatography on silica gel (hexane/toluene = 80/20 to toluene 100%)

to afford the title compound (diastereomer mixture A and B) as a white powder (353 mg, 81%). ¹H NMR: δ 1.60–1.74 (m, 6H for A and 6H for B, overlapped), 1.82–1.88 (m, 2H for A and 2H for B, overlapped), 1.94–1.97 (m, 2H for A and 2H for B, overlapped), 2.02-2.10 (m, 2H for A and 2H for B, overlapped), 3.58–3.63 (m, 2H for A and 2H for B, overlapped, OCH_2CH_2) 3.82–3.85 (m, 2H for A, OCH_2CH_2), 3.87–3.92 (m, 2H for B, OCH₂CH₂), 5.42 (s, 2H for B, OCHO), 5.51 (s, 2H for A, OCHO), 7.02 (s, 1H for A, Ar), 7.09 (s, 1H for B, Ar), 7.66 (s, 1H for A and 1H for B, overlapped, Ar). ¹³C NMR of diastereomer A: & 18.3, 25.2, 30.2, 61.9, 97.5, 105.5, 106.6, 135.5, 153.7. ¹³C NMR of diastereomer B: δ 18.2, 25.2, 30.1, 61.8, 96.8, 104.9, 105.2, 135.6, 153.3. MS (APCI+): 435 (M+H). Anal. Calcd for C₁₆H₂₀Br₂O₄: C, 44.06; H, 4.62. Found: C, 43.86; H, 4.60.

2-[4, 6-Bis(phenylethynyl)-3-(tetrahydro-2H-2*pyranyloxy)phenoxy]tetrahydro-2H-pyran.* Nitrogen was bubbled through a solution of piperidine (36 mL) and triethylamine (100 mL) for 30 min. To this solution was added 2-[4,6-dibromo-3-(tetrahydro-2*H*-2-pyranyloxy)phenoxy]tetrahydro-2*H*-pyran (8.67 g, 19.9 mmol) followed by CuI (380 mg, 1.99 mmol), PPh₃ (1.05 g, 3.98 mmol), and Pd(PPh₃)₄ (2.31 g, 1.99 mmol). The mixture was stirred at 90°C for 22 h. After cooling to ambient temperature, additional CuI (76 mg, 0.40 mmol), PPh₃ (210 mg, 0.80 mmol), and $Pd(PPh_3)_4$ (461 mg, 0.40 mmol) were added and stirred at 90°C for 18 h. The reaction mixture was cooled to ambient temperature, and piperidine and triethylamine were removed in vacuo. After the reaction was quenched with water, the organic layer was extracted with CHCl₃, washed with brine, and dried over MgSO₄. After removal of the solvent in vacuo, the crude mixture was subjected to flash silica gel column chromatography (hexane/ethyl acetate = 99/1 to 95/5) to afford the title compound (8.27 g, 17.3 mmol, 87%) as a white solid. ¹H NMR: δ 1.60–1.64 (m, 2H for A and 2H for B, overlapped), 1.70-1.74 (m, 4H for A and 4H for B, overlapped), 1.86–1.91 (m, 2H for A and 2H for B, overlapped), 2.00–2.10 (m, 2H for A and 2H for B, overlapped), 2.13-2.18 (m, 2H for A and 2H for B, overlapped), 3.61-3.65 (m, 2H for A and 2H for B, overlapped, OCH_2CH_2), 3.94–4.03 (m, 2H for A and 2H for B, OCH_2CH_2), 5.58 (s, 2H for A, OCHO), 5.64 (s, 2H for B, OCHO), 6.9 (s, 1H for B, Ar), 7.03 (s, 1H for A, Ar), 7.29-7.36 (m, 6H for A and 6H for B, overlapped, Ph), 7.49-7.51 (m, 4H for A and 4H for B, overlapped, Ph), 7.64 (s, 1H for A and 1H for B. overlapped, Ar). ¹³C NMR of diastereomer A: δ 18.2, 25.2, 30.2, 61.7, 85.2, 92.2, 96.9, 104.4, 107.7, 123.9, 127.9, 128.3, 131.3, 136.8, 158.8. ¹³C NMR of diastereomer B: δ 18.1, 25.2, 30.0, 61.6, 85.2, 92.3, 96.2, 103.1, 107.3, 123.9, 127.8, 128.3, 131.3, 136.8, 158.5. MS (APCI+): 479 (M+H). Anal. Calcd for $C_{32}H_{30}O_4$: C, 80.31; H, 6.32. Found: C, 80.25; H, 6.28.

4,6-Bis(phenylethynyl)-1,3-benzenediol(2). To a solution of 2-[4,6- bis(phenylethynyl)-3-(tetrahydro-2H - 2 - pyranyloxy)phenoxy]tetrahydro - 2H - pyran (957 mg, 2.0 mmol) in 20 mL of CH_2Cl_2 was added trifluoroacetic acid (TFA) (148 µL, 2.0 mmol) at 0°C. The mixture was stirred at this temperature for 30 min and passed through a short pad of silica gel employing CH₂Cl₂ as an eluent. After removing the solvent in vacuo, the crude mixture was subjected to flash silica gel column chromatography employing hexane/CH₂Cl₂/ethyl acetate = 90/5/5 as an eluent to give the title compound (576 mg, 93%) as a white powder. Mp: 124–125°C. ¹H NMR: δ6.00 (s, 2H, OH), 6.63 (s, 1H, Ar), 7.35-7.39 (m, 6H, m- and *p*-Ph), 7.50–7.55 (m, 5H, *o*-Ph and Ar). ¹³C NMR: δ 82.0, 95.6, 101.4, 103.0, 122.3, 128.5, 128.8, 131.5, 134.6, 158.4. MS (APCI+): 311 (M+H). Anal. Calcd for C₂₂H₁₄O₂: C, 85.14; H, 4.55. Found: C, 85.03; H, 4.66.

2,6-Diphenylbenzo[1,2-b:5,4-b']difuran (**4a**). To 4,6-bis(phenylethynyl)-1,3solution of а benzenediol(150 mg, 0.483 mmol) in THF (0.5 mL) was added a solution of *n*-butyllithium in hexane (620 µL, 1.57 mol/L, 0.97 mmol) at 0°C. The resulting mixture was allowed to warm to ambient temperature and stirred for 30 min. A solution of zinc chloride in THF (0.97 mL, 1.0 mol/L, 0.97 mmol) and toluene (2.0 mL) was added. The yellow solution was heated to 120°C and stirred for 2 h at this temperature. After cooling to ambient temperature, the reaction mixture was quenched with saturated ammonium chloride aqueous solution. The crude material was filtrated and washed several times with H₂O and acetone to afford the title compound (149 mg, 99%) as white powder. Mp: 272–273°C. ¹H NMR: δ 7.09 (s, 2H, furan), 7.36 (dd, *J* = 7.5, 7.5 Hz, 2H, *p*-Ph), 7.46 (dd, *J* = 7.5, 7.5 Hz, 4H, *m*-Ph), 7.67 (s, 2H, BDF), 7.88 (d, J = 7.5 Hz, 4H, *o*-Ph). ¹³C NMR (60°C): δ 94.3 (CH), 101.3 (CH), 110.8 (CH), 124.9 (CH), 126.4 (C), 128.4 (CH), 128.8, (CH) 130.8 (C), 153.7 (C), 156.5 (C). MS (APCI+): 311 (M+H). Anal. Calcd for C₂₂H₁₄O₂: C, 85.14; H, 4.55. Found: C, 84.95; H, 4.62.

Typical Procedure for Pd(0)-Catalyzed Cross-Coupling of the Benzodifuranzinc Intermediate with Aryl Halides

2, 3, 5, 6 - Tetraphenylbenzo[1, 2 - b:5, 4 - b']difuran (**4b**). To a solution of 4,6-bis(phenylethynyl)-1,3-

benzenediol (1.24 g, 4.00 mmol) in THF (4.0 mL), a solution of *n*-butyllithium in hexane (4.82 mL, 1.66 mol/L, 8.00 mmol) at 0°C was added. The resulting mixture was allowed to warm to ambient temperature and stirred for 30 min. A solution of zinc chloride in THF (8.0 mL, 1.0 mol/L, 8.0 mmol) and toluene (8.0 mL) was added to the reaction mixture. The resulting pale yellow solution was heated to 120°C in a sealed tube and stirred for 3 h at this temperature. After cooling to ambient temperature, $Pd_2(dba)_3$ ·CHCl₃ (414 mg, 0.40 mmol), P(t- Bu_{3} in toluene (1.6 mL, 1.0 mol/L, 1.6 mmol), and then iodobenzene (1.07 mL, 9.60 mmol) were successively added. After stirring at ambient temperature for 20 h, the reaction mixture was guenched with a saturated ammonium chloride aqueous solution. The organic layer was extracted with CHCl₃ and washed with H₂O. After evaporating the solvent in vacuo, crude material was purified by flash column chromatography on silica gel employing a gradient from hexane/chloroform = 95/5 to hexane/chloroform = 70/30 as an eluent to give the title compound. Final purification by high vacuum (pressure under 20 mTorr) train sublimation at 230– 250°C afforded the title compound as white powder (1.16 g, 2.51 mmol, 63%). Mp: 222–223°C. ¹H NMR: δ 7.26–7.33 (m, 6H, *m*-and *p*-Ph), 7.39 (dd, J = 7.5, 7.5 Hz, 2H, p-Ph), 7.42 (s, 1H, BDF), 7.45 (dd, J =7.4, 7.4 Hz, 4H, *m*-*Ph*), 7.49 (d, *J* = 7.4 Hz, 4H, *o*-Ph), 7.65 (d, J = 7.4 Hz, 4H, o-Ph), 7.72 (s, 1H, BDF). ¹³C NMR: δ 93.9 (CH), 109.2 (CH), 117.4 (C), 126.8 (CH), 127.4 (C), 127.6 (CH), 128.2 (CH), 128.4 (CH), 129.1 (CH), 129.9 (CH), 130.7 (C), 132.9 (C), 150.8 (C), 152.8 (C). MS (APCI+): 463 (M+H). Anal. Calcd for C₃₄H₂₂O₂: C, 88.29; H, 4.79. Found: C, 88.46; H, 4.92.

3,5-Bis(4-N,N-dimethylaminophenyl)-2,6-diphenylbenzo[1,2-b:5,4-b']difuran (**4c**). White powder. Mp: 277–278°C. ¹H NMR: δ 3.03 (s, 12H, NMe₂), 6.81 (d, J = 8.6 Hz, 4H, Ar), 7.26 (dd, J = 7.5, 7.5 Hz, 2H, Ar), 7.32 (dd, J = 7.5, 7.5 Hz, 4H, Ar), 7.36 (d, J = 8.6 Hz, 4H, Ar), 7.50 (s, 1H, BDF), 7.67 (s, 1H, BDF), 7.71 (d, J = 7.5 Hz, 4H, Ar). ¹³C NMR: δ 40.5, 93.6, 109.7, 112.9, 117.7, 120.4, 126.6, 127.7 (two carbons are overlapped), 128.3, 130.5, 131.3, 149.8, 150.0, 152.8. HRMS (APCI+) calcd for C₃₈H₃₃N₂O₂ (M+H): 549.2542. Found: 549.2568.

3, 5-Bis(4-N, N-diphenylaminophenyl)-2,6-diphenylbenzo[1,2-b:5,4-b']difuran (4d). Pale yellow powder. Mp: 241–242°C. ¹H NMR (CD₂Cl₂): δ 7.06 (dd, J = 7.5 Hz, 7.5 Hz, 4H, *p*-Ph), 7.12 (d, J =8.6 Hz, 4H, phenylene), 7.17 (d, J = 7.5 Hz, 8H, *o*-Ph), 7.29 (d, J = 8.6 Hz, 4H, phenylene), 7.29–7.39 (m, 14H, *m*- and *p*-Ph), 7.53 (s, 1H, BDF), 7.72 (s, 1H, BDF), 7.72 (d, J = 7.5 Hz, 4H, *o*-Ph). ¹³C NMR (CD₂Cl₂): δ 93.4 (CH), 109.3 (CH), 116.8 (C), 122.7 (CH), 122.9 (CH), 124.5 (CH), 125.6 (C), 126.4 (CH), 127.0 (C), 127.8 (CH), 128.1 (CH), 129.0 (CH), 130.1 (CH), 130.6 (C), 147.0 (C), 147.1 (C), 150.3 (C), 152.5 (C). MS (APCI+): 797 (M+H). Anal. Calcd for C₅₈H₄₀N₂O₂: C, 87.41; H, 5.06; N, 3.52. Found: C, 87.45; H, 5.16; N, 3.39.

3,5-Bis[4-(9H-carbazolyl)phenyl]-2,6-diphenylbenzo[1,2-b:5,4-b']difuran (**4e**). White powder. Mp: 312–313°C. ¹H NMR: δ 7.30 (dd, J = 8.0 Hz, 8.0 Hz, 4H, Ar), 7.37 (dd, J = 7.5 Hz, 7.5 Hz, 2H, Ar), 7.40–7.44 (m, 8H, Ar), 7.55 (d, J = 8.0 Hz, 4H, Ar), 7,71 (d, J = 8.0 Hz, 4H, Ar), 7,72 (s, 1H, BDF), 7.76 (d, J = 7.5 Hz, 4H, Ar), 7.80 (d, J = 8.0 Hz, 4H, Ar), 7.80 (s, 1H, BDF), 8.15 (d, J = 8.0 Hz, 4H, Ar). ¹³C NMR (CDCl₂CDCl₂): δ 94.6, 109.2, 110.0, 116.6, 120.4, 120.5, 123.4, 126.3, 127.2, 127.3, 128.8, 130.5, 131.3, 131.8, 137.1, 140.5, 151.7, 153.0 (three carbons are overlapped). MS (APCI+): 793 (M+H). Anal. Calcd for C₅₈H₃₆N₂O₂: C, 87.86; H, 4.58; N, 3.53. Found: C, 88.03; H, 4.81; N, 3.39.

3, 5-*Bis*(*pentafluorophenyl*) - 2, 6-*diphenylbenzo*-[1,2-*b*:5,4-*b'*]*difuran* (**4f**). White powder. Mp: 245– 246°C. ¹H NMR: δ 7.01 (s, 1H, BDF), 7.40–7.42 (m, 6H, Ph), 7.60–7.62 (m, 4H, Ph), 7.83 (s, 1H, BDF). ¹³C NMR (125 MHz, CD₂Cl₂): δ 94.6, 101.1, 107.3 (m), 108.2, 125.9, 126.0, 128.7, 129.3, 138.0 (dm, J = 251.6 Hz), 141.2 (dm, J = 254.0 Hz), 144.6 (dm, J = 248.0 Hz), 152.6, 154.3. MS (FAB) calcd for C₃₄H₁₂N₂O₂ [M]⁺: 642, found: 642. Anal. Calcd for C₃₄H₁₂F₁₀O₂: C, 63.56; H, 1.88. Found: C, 63.54; H, 2.15.

5, 5'-Bis(pentafluorophenyl)-2,2',6,6'-tetraphenyl-3,3'-bibenzo[1,2-b:5,4-b']difuran (5). Mp: 347– 348°C. ¹H NMR (CDCl₂CDCl₂, 130°C): δ 6.76 (s, 2H, BDF), 7.21–7.24 (m, 6H, Ph), 7.31–7.34 (m, 6H, Ph), 7.50–7.52 (m, 4H, Ph), 7.65–7.68 (m, 4H, Ph), 7.80 (s, 2H, BDF). ¹³C NMR could not be measured owing to poor solubility. HRMS (APCI+) calcd for C₅₆H₂₅F₁₀O₄ (M+H): 951.1593. Found: 951.1571.

Cyclic voltammetry and differential pulse voltammetry (DPV) were performed using HOKUTO DENKO HZ-5000 voltammetric analyzer. All measurements were carried out in a one-compartment cell under N_2 gas, equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and an Ag/Ag⁺ reference electrode. The supporting electrolyte was a 0.1 mol/L dichloromethane solution of tetrabutylammonium perchlorate (TBAP). All potentials were corrected

against Fc/Fc⁺. CV was measured with a scan rate of 100 mV/s.

Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-788664 (**4c**) and CCDC-788663 (**4f**). 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).

ACKNOWLEDGMENTS

The authors would like to thank MEXT (KAKENHI for E.N., No. 22000008, H.T., No. 20685005) and the Global COE Program for Chemistry Innovation. This work was partly supported by the Strategic Promotion of Innovative R&D, JST. CM thanks JSPS for the Research Fellowship for Young Scientists (No. 21.9262).

REFERENCES

- [1] (a) Tsuji, H.; Mitsui, C.; Ilies, L.; Sato, Y.; Nakamura, E. J Am Chem Soc 2007, 129, 11902; (b) Tsuji, H.; Mitsui, C.; Sato, Y.; Nakamura, E. Adv Mater 2009, 21, 3776.
- [2] (a) Abdulaziz, M.; Auping, J. V.; Meador, M. A. J Org Chem 1995, 60, 1303; (b) Hwu, J. R.; Chuang, K.-S.; Chuang, S. H.; Tsay, S.-C. Org Lett 2005, 7, 1545; (c) Miyata, Y.; Terayama, M.; Minari, T.; Nishinaga, T.; Nemoto, T.; Isoda, S.; Komatsu, K. Chem Asian J 2007, 2, 1492; (d) Shukla, R.; Wadumethrige, S. H.; Lindeman, S. V.; Rathore, R. Org Lett 2008, 10, 3587; (e) Hayashi, N; Saito, Y.; Higuchi, H.; Suzuki, K. J Phys Chem A 2009, 113, 5342; (f) Baraldi, I.; Benassi, E.; Ciorba, S.; Šindler-Kulyk, M.; Škorić, I.; Spalletti, A. Chem Phys 2009, 361, 61; (g) Yi, C.; Blum, C.; Lehmann, M.; Keller, S.; Liu, S.-X.; Frei, G.; Neels, A.; Hauser, J.; Schürch, S.; Decurtins. S. J Org Chem 2010, 75, 3350.
- [3] Bunz, U. H. F. Angew Chem, Int Ed 2010, 49, 5037.
- [4] (a) Politis, J. K.; Nemes, J. C.; Curtis, M. D. J Am Chem Soc 2001, 123, 2537; (b) Gidron, O.; Diskin-Posner, Y.; Bendikov, M. J Am Chem Soc 2010, 132, 2148.
- [5] (a) Zhang, L.-Z.; Chen, C.-W., Lee, C.-F.; Wu, C.-C.; Luh, T.-Y. Chem Commun 2002, 2336; (b) Wu, C.-C.; Hung, W.-Y.; Liu, T.-L.; Zhang, L.-Z.; Luh, T.-Y. J Appl Phys 2003, 93, 5465; (c) Miyata, Y.; Nishinaga, T.; Komatsu, K. J Org Chem 2005, 70, 1147; (d) Lin, H.-C.; Lin, W.-Y.; Bai, H.-T.; Chen, J.-H.; Jin, B.-Y.; Luh, T.-Y. Angew Chem, Int Ed 2007, 46, 897; (e) Bai, H.-T.; Lin, H.-C.; Luh, T.-Y. J Org Chem 2010, 75, 4591.
- [6] (a) Tsuji, H.; Sato, K.; Ilies, L.; Itoh, Y.; Sato, Y.; Nakamura, E. Org Lett 2008, 10, 2263; (b) Tsuji, H.; Sato, K.; Sato, Y.; Nakamura, E. J Mater Chem 2009, 19,

3364; (c) Tsuji, H.; Sato, K.; Sato, Y.; Nakamura, E. Chem Asian J 2010, 5, 1294.

- [7] Tsuji, H.; Yokoi, Y.; Mitsui, C.; Ilies, L.; Sato, Y.; Nakamura, E. Chem Asian J 2009, 4, 655.
- [8] (a) Ilies, L.; Tsuji, H.; Sato, Y.; Nakamura, E. J Am Chem Soc 2008, 130, 4240; (b) Ilies, L.; Tsuji, H.; Nakamura, E. Org Lett 2009, 11, 3966; (c) Ilies, L.; Sato, Y.; Mitsui, C.; Tsuji, H.; Nakamura, E. Chem Asian J 2010, 5, 1376.
- [9] (a) Tsuji, H.; Yamagata, K.-i.; Fujimoto, T.; Nakamura, E. J Am Chem Soc 2008, 130, 7792; (b) Yoshikai, N.; Zhang, S.-L.; Yamagata, K.-i.; Tsuji, H.; Nakamura, E. J Am Chem Soc 2009, 131, 4099.
- [10] Zhu, X.; Mitsui, C.; Tsuji, H.; Nakamura, E. J Am Chem Soc 2009, 131, 13596.
- [11] Dihedral angles between the mean-planes of BDF and aromatic rings were calculated using MERCURY 2.3 (http://www.ccdc.cam.ac.uk/mercury().
- [12] Ito, Y.; Uozu, Y.; Matsuura, T. Tetrahedron Lett 1987, 28, 3493.
- [13] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery,

Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. Gaussian 03, Revision B.05; Gaussian, Inc., Pittsburgh PA, 2003.

[14] Grabowski, Z. R.; Rotkiewicz, K.; Rettig, W., Chem Rev 2003, 103, 3899.