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Photochromism of 1,2-Bis(2-alkyl-1-benzofuran-3-yl)perfluorocyclopentene Derivatives

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1,2-Bis(2-*n*-alkyl-1-benzofuran-3-yl)perfluorocyclopentene derivatives have been synthesized and their photochromic performance has been studied in solution as well as in the single-crystalline phase. All derivatives undergo photochromism in hexane solution. The introduction of long alkyl chains at the 2-positions of the benzofuran rings of the bis(1-benzofuran-3-yl)ethenes enhances the cyclization quantum yield. This is attributed to the increase in the population of the antiparallel conformers. The derivatives with methyl, propyl, butyl, pentyl, and hexyl substituents exhibit photochromism even in the single-crystalline phase. An X-ray crystallographic analysis reveals that the ethyl-substituted derivative is packed in a parallel conformation, while the other derivatives are in an antiparallel conformation. This conformational difference controls the reactivity in the crystalline phase.

Introduction

Various types of photochromic compounds have been synthesized to date in an attempt to apply these compounds to optoelectronic devices.[1–4] Among these compounds, diarylethene derivatives are the most promising candidates for such applications because of their fatigue resistance and thermally irreversible properties.[4]

Most of the diarylethene derivatives synthesized so far are composed of thiophene, benzothiophene, or thiazol heteroaryl groups.[4–17] The photochromic performance of these derivatives is superior to that of other derivatives having pyrrole or indole groups from the viewpoint of thermal stability[16] as the latter derivatives undergo thermally reversible photochromic reactions and cannot be used for optical memories and switches.

In a previous paper we reported that 1,2-bis(2-methyl-1-benzofuran-3-yl)perfluorocyclopentene (**1a**) and 1,2-bis(2-butyl-1-benzofuran-3-yl)perfluorocyclopentene (**4a**) undergo thermally irreversible and fatigue-resistant photochromic reactions in solution.[18] Replacement of benzothiophene heteroaryl groups with benzofuran groups increased the cyclization quantum yield in solution. Both **1a** and **4a** show photochromism even in the crystalline phase. In this paper, we report on diarylethene derivatives having 2-*n*-alkyl-1-benzofuranyl groups. The derivatives having long alkyl chains show favorable photochromic performance in solution as well as in the single-crystalline phase.

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Results and Discussion

Synthesis of the Diarylethene Derivatives

Diarylethene derivatives **1a**–**8a** were synthesized by a coupling reaction of 2-*n*-alkyl-3-bromo-1-benzofuran with perfluorocyclopentene derivatives according to a procedure described previously.[18] The structures of **1a**–**8a** were confirmed by ^{1}H NMR spectroscopy, mass spectrometry, and elemental analysis. The structures of **1a**–**6a** were also determined by X-ray crystallographic analysis.

Photochromic Reactions in Hexane Solution

Figure 1 shows the absorption spectral change of **2a** in hexane upon irradiation with 313-nm light. Compounds **2a** and **2b** have absorption maxima at 275 (ε = 1.12×10^4 M^{-1}cm^{-1}) and 489 nm (ε = 1.51×10^4 M^{-1}cm^{-1}), respectively. The conversion rate upon irradiation with 313-nm light is 58%. Compounds **2a**, **3a**, and **5a**–**8a** all show photochromism in hexane solution (see Supporting Information). Table 1 summarizes the absorption maxima and the absorption coefficients of open- and closed-ring isomers in hexane. The cyclization and cycloreversion quantum yields were also measured and are included in Table 1. The absorption maximum of **2b** (489 nm) shows a bathochromic shift of as much as 20 nm upon replacement of methyl substituents with ethyl substituents. The absorption maxima of **2b**–**8b** are almost constant (489–490 nm). The conversion

rate upon irradiation with 313-nm light increases from 48% for compound **1** to 67% for compound **8** (Scheme 1).

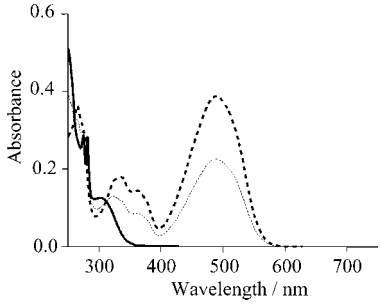
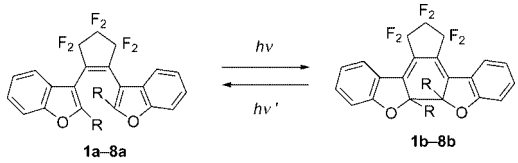


Figure 1. Absorption spectra of **2** (2.5×10^{-5} M) in hexane solution. Solid, dashed, and dotted lines represent **a** (open form), **b** (closed-ring form), and the photostationary state under irradiation with 313-nm light, respectively.



1: R= CH_3
2: R= C_2H_5
3: R= C_3H_7
4: R= C_4H_9
5: R= C_5H_{11}
6: R= C_6H_{13}
7: R= C_7H_{15}
8: R= C_8H_{17}

Scheme 1.

The cyclization quantum yield increases with an increase in the chain length. To reveal the origin of this increase, the conformation of **1a**–**4a** was determined by NMR spectroscopy for solutions in CD_3OD at –90 °C. Figure 2(a) shows the spectrum of **1a**. In this figure, "p" indicates the proton signal of the parallel conformation and "ap" the proton signal of the antiparallel conformation. Although the signal of the methyl protons connected at the 2-position of the benzofuran ring are observed at δ = 2.11 ppm at room temperature, this signal is split into two, at δ = 2.29 (parallel) and 1.85 ppm (antiparallel), at –90 °C. The intensity ratio of the two signals indicates that the relative population of antiparallel and parallel conformers of **1a** is 53:47 at –90 °C.

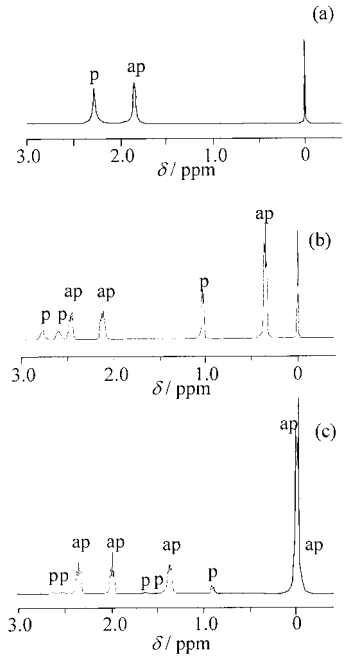


Figure 2. ^{1}H NMR spectra of (a) **1a**, (b) **2a**, and (c) **3a** in CD_3OD at –90 °C. The signals of the parallel conformation are labeled "p" and those of the antiparallel conformation "ap".

Figure 2(b) shows the spectrum of **2a** at –90 °C. The ethyl signals of the antiparallel conformation are observed at δ = 2.46 (CH_2) and 2.12 ppm (CH_2), and at δ = 0.35 ppm (CH_3), whereas those of the parallel conformation are observed at δ = 2.76 (CH_2) and 2.59 ppm (CH_2), and at δ = 1.04 ppm (CH_3). The intensity ratio of these signals indicates that the relative population of the antiparallel and parallel conformers of **2a** is 73:27 at –90 °C.

Figure 2(c) shows the spectrum of **3a** at –90 °C. The propyl signals of the antiparallel conformation are observed at δ = 2.35 (CH_2), 1.99 (CH_2), and 1.37 ppm (CH_2), and at δ = –0.02 ppm (CH_2 and CH_3), whereas the signals of the parallel conformation are observed at δ = 2.64 (CH_2), 2.52 (CH_2), 1.63 (CH_2), and 1.41 ppm (CH_2), and at δ =

Table 1. Absorption maxima and the coefficients of the open- and closed-ring forms of **1**–**8**, quantum yields of cyclization and cycloreversion reactions, and conversion under irradiation with 313-nm light in hexane solution.

	Absorption spectra		Quantum yield		Conversion (313 nm)
	Open form ε/$M^{-1}cm^{-1}$ (λ_{max}/nm)	Closed-ring form ε/$M^{-1}cm^{-1}$ (λ_{max}/nm)	Cyclization (313 nm)	Cycloreversion (517 nm)	
1	1.00×10^4 (274)	1.44×10^4 (469)	0.38	0.35	48%
2	1.12×10^4 (275)	1.51×10^4 (489)	0.40	0.25	58%
3	1.23×10^4 (275)	1.61×10^4 (489)	0.42	0.25	63%
4	1.14×10^4 (275)	1.46×10^4 (489)	0.49	0.24	66%
5	1.18×10^4 (275)	1.51×10^4 (490)	0.52	0.25	66%
6	1.20×10^4 (275)	1.52×10^4 (490)	0.55	0.24	64%
7	1.20×10^4 (275)	1.52×10^4 (490)	0.55	0.24	66%
8	1.21×10^4 (275)	1.52×10^4 (490)	0.56	0.24	67%

0.91 ppm (CH_3). The intensity ratio of these signals indicates that the relative population of antiparallel and parallel conformers of **3a** is 91:9 at –90 °C.

The populations of the antiparallel conformers **1a**, **2a**, **3a**, and **4a** were determined to be 53%, 73%, 91%, and 98%, respectively, in CD_3OD at –90 °C. When the alkyl chain length increases, the populations of the antiparallel conformers increase. The increase in the populations of the antiparallel conformers is thought to enhance the cyclization quantum yield.

The cycloreversion quantum yields of **2**–**8** remain constant (0.25), therefore the alkyl chain does not affect the cycloreversion yield.

X-ray Crystallographic Analysis

In a previous paper[18] we reported the structure determinations of **1a** and **4a** by X-ray crystallography. The molecules are packed in a photoactive parallel conformation, and the distances between the reactive carbon atoms are 0.356 (**1a**) and 0.372 nm (**4a**). Both compounds show photochromism in the single-crystalline phase.

The structures of **2a**, **3a**, **5a**, and **6a** were determined by X-ray crystallographic analysis. Single crystals of **2a**, **3a**, **5a**, and **6a** were obtained by recrystallization from a mixed solution of diethyl ether and hexane. X-ray crystallographic data for **2a**, **3a**, **5a**, and **6a** are given in the Experimental Section. Figure 3(a) shows an ORTEP drawing of **2a**. This figure indicates that **2a** is packed in a photo-inactive parallel conformation in the crystal. Although the crystal of **2a** is photochemically inactive, **1a**, **3a**, **4a**, **5a**, and **6a** undergo photochromism in the single-crystalline phase.

Figure 3(b) shows an ORTEP drawing of **3a**. The crystal has four molecules in the asymmetric unit. Although the conformation of these four molecules differs slightly, they

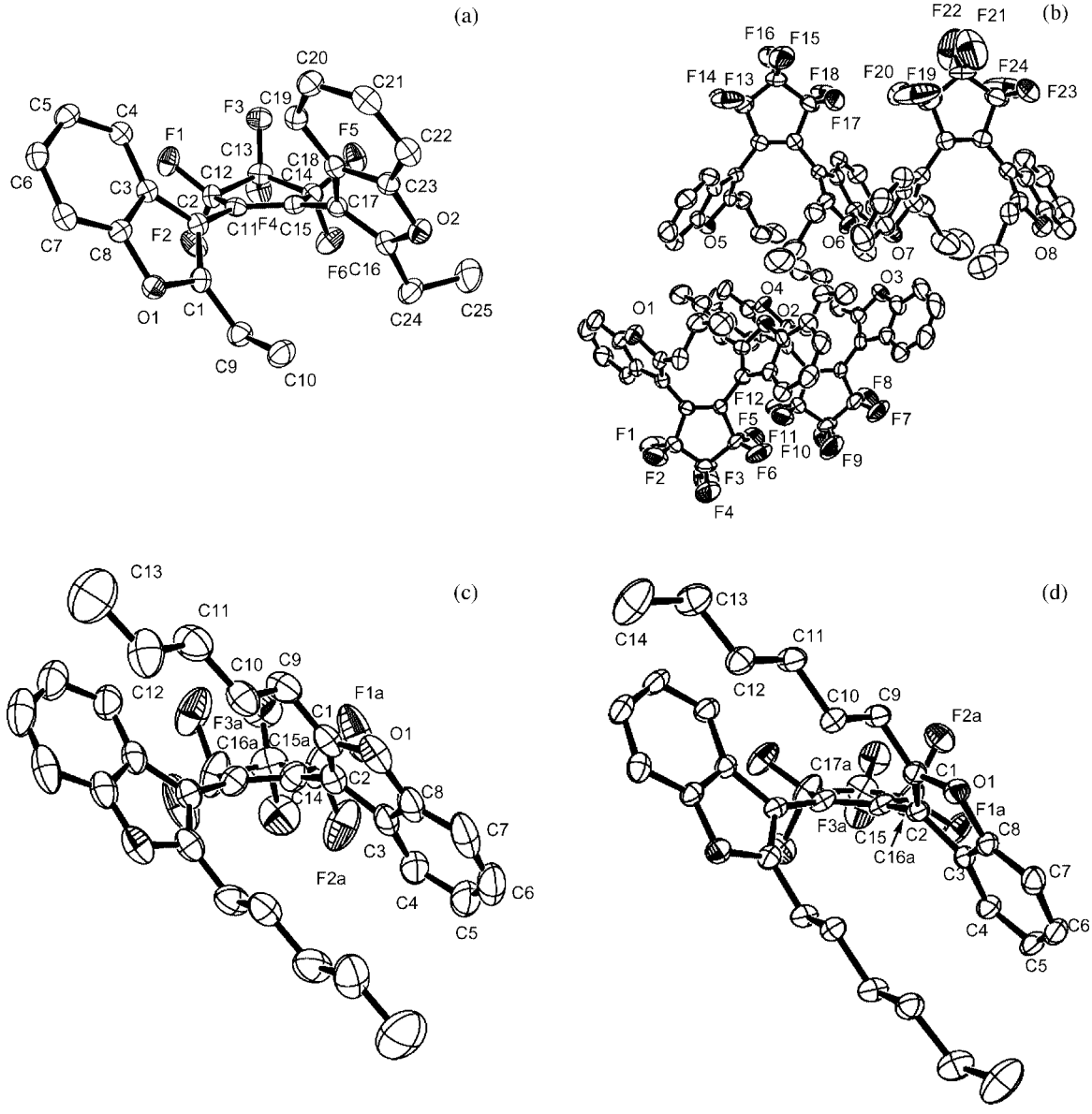


Figure 3. ORTEP drawings of (a) **2a**, (b) **3a**, (c) **5a**, and (d) **6a** showing 50% probability displacement ellipsoids. Hydrogen atoms have been omitted for clarity.

all have benzofuran rings in a photoactive antiparallel conformation. The distances between the reactive carbon atoms were found to be 0.367, 0.370, 0.372, and 0.375 nm. These distances are all shorter than the value of 0.42 nm which allows a photochromic reaction in the crystal.[19]

Figures 3(c) and (d) show ORTEP drawings of **5a** and **6a**, respectively. They indicate that **5a** and **6a** are also packed in a photoactive antiparallel conformation in the crystal. The distances between the reactive carbon atoms were found to be 0.373 and 0.373 nm, respectively; these distances are short enough for the molecules to undergo photochromism.

Photochromic Reactions in the Crystalline Phase

Compounds **1a**, **3a**, **4a**, **5a**, and **6a** undergo photochromic reactions in the single-crystalline phase. Figure 4 shows the color change of **6**. Before photoirradiation the crystal is colorless [Figures 4(a) and (b)]. Upon irradiation with 365-nm light for 3 s, however, the crystal turns red [Figure 4(c)]. When the crystal is rotated by 90°, the color of the crystal changes to pale red [Figure 4(d)]. The color disappears upon irradiation with visible light ($\lambda > 400$ nm).

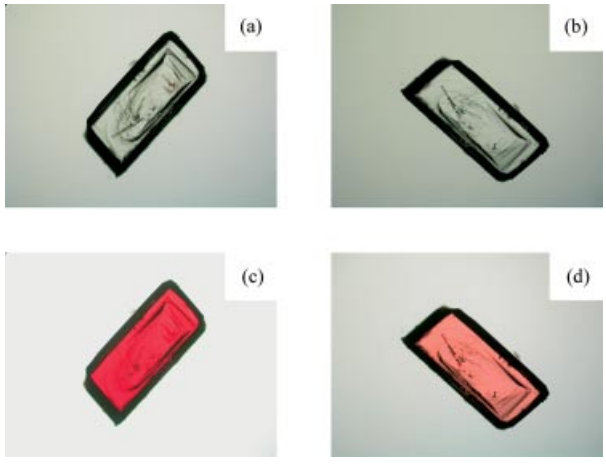


Figure 4. Photographs of a single crystal of **6** under polarized light before (a: $\theta = 0°$; b: $\theta = 90°$) and after (c: $\theta = 0°$; d: $\theta = 90°$) irradiation with 365-nm light. θ is the rotation angle of the crystal.

Figure 5(a) shows the polarized absorption spectra of the colored crystal of **6**. Upon rotating the crystal sample under polarized light, the absorption intensity at 520 nm changes. The change of the color from red to pale red upon rotating the crystal indicates that the closed-ring isomers are oriented regularly in the crystal. Figure 5(b) shows the polar plot at 520 nm. The absorption maximum does not change upon rotation, but the intensity changes dramatically.

Compounds **3** and **5** also undergo photochromic reactions in the single-crystalline phase. Just as for compound **6**, a color change from orange to pale orange is observed for **5** upon rotating the crystal sample. However, in the case of **3** the absorption intensity at 503 nm does not change upon rotating the sample under polarized light. Figures 6(a) and (b) show the polarized absorption spectra of the colored crystal of **3**. The observed crystal face is the (001) face,

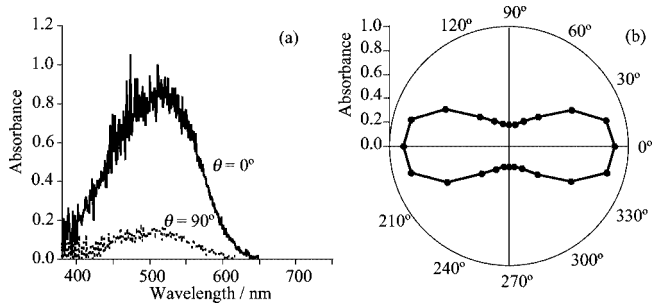


Figure 5. Polarized absorption spectra of the colored crystal of **6**: (a) polarized absorption spectra and (b) direction of polarizer at 520 nm.

which is the well-developed one. The crystal of **3a** has four molecules in the asymmetric unit. The two molecules on the surface are almost perpendicular to the other two molecules in the unit. This means that the absorbance of the crystal does not change upon rotating a crystal of **3** under polarized light.

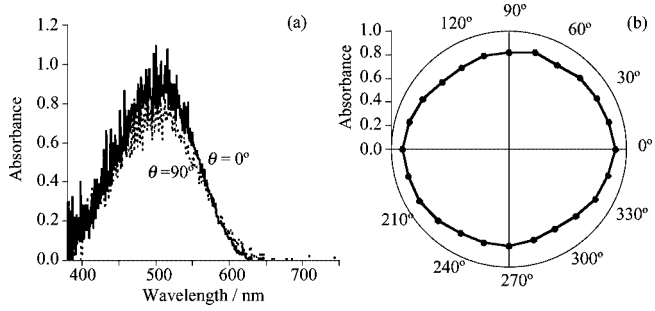


Figure 6. Polarized absorption spectra of the colored crystal of **3**: (a) polarized absorption spectra and (b) direction of polarizer at 500 nm.

Compound **2a** does not show any photochromism in the single-crystalline phase. This reactivity is strongly dependent on the conformation of the molecule. X-ray crystallographic analysis of the crystals of **2a** revealed that it is packed in a photo-inactive parallel conformation in the crystal. This conformation prevents the diarylethene from undergoing photochromism in the single-crystalline phase.

Conclusions

Diarylethene derivatives having various benzofuranyl groups, namely 1,2-bis(2-*n*-alkyl-1-benzofuran-3-yl)perfluorocyclopentene, have been synthesized. All derivatives undergo photochromism in hexane solution, and the introduction of long alkyl chains at the 2-positions of the benzofuran rings of 1,2-bis(1-benzofuran-3-yl)perfluorocyclopentene enhances the cyclization quantum yields. The ratio of antiparallel/parallel conformers was determined by ^{1}H NMR spectroscopy in CD_3OD. The long alkyl chain increases the population of the antiparallel conformers. The derivatives having methyl, propyl, butyl, pentyl, and hexyl substituents exhibit photochromism even in the single-crystalline phase. The derivative with ethyl substituents, how-

ever, does not show any photochromism in the single-crystalline phase. An X-ray crystallographic analysis of the open-ring isomer having ethyl substituents has revealed that the molecules are packed in a photo-inactive parallel conformation.

Experimental Section

General: All solvents used were spectrograde and were purified by distillation before use. Absorption spectra were measured with a spectrophotometer (Shimadzu, UV-2100). The quantum yields were determined by comparing the reaction rates of the diarylethene derivatives in hexane against that of furylfulgide in toluene. The samples were not degassed. Absorption spectra in the single-crystalline phase were measured using an OPTI-POL 2POL (Nikon) polarizing microscope connected to a Hamamatsu PMA-11 detector. Photoirradiation for single-crystal measurements was carried out using a 100-W mercury lamp (Nikon, C-SHG1 and LH-M100CB-1) as a light source. For solution measurements, a super-high-pressure mercury lamp (Ushio, 500W) was used as the light source. Light of appropriate wavelength was isolated by passing it through a monochromator (RITSU MC-10N) or through L-29 and Y-44 filters. ^{1}H NMR spectra were recorded with a Gemini 200 spectrometer (200 MHz) at room temperature with $CDCl_3$ or CD_3OD as solvent and tetramethylsilane as an internal standard. For low-temperature analysis, the spectra were recorded with a JEOL ECA400 (400 MHz) or JEOL ECA600 (600 MHz) spectrometer at –90 °C with CD_3OD as solvent and tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded with a Bruker AVANCE 400 (100 MHz) instrument at room temperature. Mass spectra were recorded with a Shimadzu GCMS-QP5050A gas chromatography/mass spectrometer. X-ray crystallographic analysis was carried out using a Bruker SMART CCD X-ray diffractometer. Good-quality crystals (**2a**: 0.3×0.2×0.2 mm; **3a**: 0.2×0.15×0.15 mm; **5a**: 0.2×0.1×0.1 mm; **6a**: 0.2×0.1×0.1 mm) were selected for the X-ray diffraction study. The data collection was performed with a Bruker SMART 1000 CCD-based diffractometer (60 kV, 30 mA) equipped with an Mo-K_α radiation source. Further details can be found in Table 2.[20] HPLC was carried out with a Shimadzu LC-10AD liquid chromatograph coupled with a Shimadzu SPD-10AV spectrophotomeric detector. A silica gel column (Wako Wakosil-5SIL) was used to analyze diarylethene isomers.

Materials: The starting materials 3-bromo-2-ethyl-1-benzofuran (CAS no. 325465-53-0), 2-propyl-1-benzofuran (13141-47-4), 2-pentyl-1-benzofuran (4265-12-7), 2-hexyl-1-benzofuran (39195-67-0), 2-heptyl-1-benzofuran (92654-58-5), and 2-octyl-1-benzofuran (39195-68-1) were obtained according to literature procedures.[21–23] Compounds **1a** and **4a** were prepared according to a method described previously.[18]

1,2-Bis(2-methyl-1-benzofuran-3-yl)perfluorocyclopentene (1a): ^{1}H NMR (400 MHz, CD_3OD, –90 °C): δ = 1.84 (br. s, 3.2 H), 2.28 (br. s, 2.8 H), 7.08–7.71 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.42, 156.47, 154.49, 126.71, 124.95, 123.98, 120.25, 120.22, 120.20, 111.44, 105.68, 13.78 ppm.

1,2-Bis(2-butyl-1-benzofuran-3-yl)perfluorocyclopentene (4a): ^{1}H NMR (400 MHz, CD_3OD, –90 °C): δ = –0.15–0.00 (m, 4 H), 0.35 (t, J = 7.1 Hz, 5.9 H), 0.72–0.77 (m, 2 H), 0.90–0.92 (m, 0.1 H), 1.29–1.34 (m, 2 H), 2.00–2.03 (m, 2 H), 2.40–2.73 (m, 4 H), 7.05–7.27 (m, 0.1 H), 7.39–7.47 (m, 3.9 H), 7.58–7.60 (m, 2 H), 7.74–7.78 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.89, 159.42, 154.61, 127.10, 124.96, 123.99, 120.49, 120.45, 120.40, 111.49, 104.81, 29.56, 27.46, 22.51, 13.96 ppm.

3-Bromo-2-propyl-1-benzofuran (9): *N*-Bromosuccinimide (3.67 g, 20.6 mmol) was slowly added to a stirred THF solution (30 mL) of 2-propyl-1-benzofuran (3.00 g, 18.7 mmol) at 5 °C, and the reaction mixture was stirred for 15 h. The reaction mixture was then poured into a sodium thiosulfate solution and extracted with diethyl ether. The organic layer was dried with anhydrous magnesium sulfate, and the solution was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (hexane) to give 4.24 g of **9** in 95% yield as a colorless liquid. ^{1}H NMR

Table 2. Crystal data for **2a**, **3a**, **5a**, and **6a**.

	2a	**3a**	**5a**	**6a**
Empirical formula	$C_{25}H_{18}F_6O_2$	$C_{27}H_{22}F_6O_2$	$C_{31}H_{30}F_6O_2$	$C_{33}H_{34}F_6O_2$
Formula mass	464.39	492.45	548.55	576.60
Temperature/K	123(2)	293(2)	193(2)	123(2)
Crystal system	triclinic	orthorhombic	monoclinic	monoclinic
Space group	*P*–1	*P*2(1)2(1)2(1)	*C*2/*c*	*C*2/*c*
Unit cell dimensions:				
a/Å	10.190(4)	16.031(4)	11.865(4)	11.973(7)
b/Å	10.905(4)	16.157(4)	16.862(5)	17.251(7)
c/Å	11.162(4)	36.357(8)	13.827(4)	13.899(7)
α/°	72.813(6)	90	90	90
β/°	64.355(5)	90	91.272(5)	94.720(11)
γ/°	74.636(5)	90	90	90
Volume/Å^3	1054.6(6)	9417(4)	2765.6(15)	2861(3)
Z	2	16	4	4
Density (calcd.)/g cm^{-3}	1.462	1.389	1.317	1.339
Goodness-of -fit on F^2	1.018	0.943	1.081	1.085
Final *R* indices [I/2σ(I)]				
*R*1	0.0510	0.0600	0.0625	0.0627
*wR*2	0.1371	0.1359	0.1515	0.1521
R indices (all data)				
*R*1	0.0636	0.1422	0.0716	0.0706
*wR*2	0.1485	0.1743	0.1620	0.1605

(200 MHz, $CDCl_3$): δ = 1.00 (t, J = 7.8 Hz, 3 H), 1.79 (sext, J = 7.8 Hz, 2 H), 2.81 (t, J = 7.8 Hz, 2 H), 7.25–7.49 (m, 3 H), 7.61–7.81 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.07, 153.94, 128.82, 124.80, 123.50, 119.54, 111.50, 94.83, 28.99, 21.46, 14.10 ppm. MS (EI): m/z = 238 [M^+]. $C_{11}H_{11}BrO$ (239.1): calcd. C 55.25, H 4.64; found C 55.13, H 4.49.

3-Bromo-2-pentyl-1-benzofuran (10): Compound **10** was prepared from 2-pentyl-1-benzofuran (3.00 g, 15.9 mmol) according to a procedure similar to that used for **9**. The crude product was purified by column chromatography on silica gel (hexane) to give 3.96 g of **10** in 93% yield as a olorless liquid. ^{1}H NMR (200 MHz): δ = 0.84–0.99 (m, 3 H), 1.32–1.38 (m, 4 H), 1.68–1.79 (m, 2 H), 2.82 (t, J = 7.6 Hz, 2 H), 7.25–7.47 (m, 3 H), 7.65–7.81 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.95, 153.55, 128.47, 124.42, 123.14, 119.16, 111.14, 94.26, 31.30, 27.30, 26.67, 22.44, 14.04 ppm. MS (EI): m/z = 266 [M^+]. $C_{13}H_{15}BrO$ (267.2): calcd. C 58.44, H 5.66; found C 58.35, H 5.59.

3-Bromo-2-hexyl-1-benzofuran (11): Compound **11** was prepared from 2-hexyl-1-benzofuran (3.00 g, 14.8 mmol) according to a procedure similar to that used for **9**. The crude product was purified by column chromatography on silica gel (hexane) to give 3.82 g of **11** in 92% yield as a colorless liquid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.85–0.92 (m, 3 H), 1.26–1.38 (m, 6 H), 1.68–1.80 (m, 2 H), 2.82 (t, J = 7.8 Hz, 2 H), 7.24–7.47 (m, 3 H), 7.65–7.81 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.96, 153.55, 128.47, 124.41, 123.13, 119.16, 111.14, 94.24, 31.56, 28.82, 27.57, 26.70, 22.62, 14.14 ppm. MS (EI): m/z = 280 [M^+]. $C_{14}H_{17}BrO$ (281.2): calcd. C 59.80, H 6.09; found C 59.69, H 6.03.

3-Bromo-2-heptyl-1-benzofuran (12): Compound **12** was prepared from 2-heptyl-1-benzofuran (3.00 g, 13.9 mmol) according to a procedure similar to that used for **9**. The crude product was purified by column chromatography on silica gel (hexane) to give 3.80 g of **12** in 93% yield as a colorless liquid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.85–0.88 (m, 3 H), 1.17–1.78 (m, 10 H), 2.82 (t, J = 7.8 Hz, 2 H), 7.25–7.47 (m, 3 H), 7.64–7.81 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.97, 153.55, 128.47, 124.41, 123.14, 119.16, 111.14, 94.25, 31.81, 29.11, 29.03, 27.62, 26.70, 22.72, 14.17 ppm. MS (EI): m/z = 294 [M^+]. $C_{15}H_{19}BrO$ (295.2): calcd. C 61.03, H 6.49; found C 60.94, H 6.44.

3-Bromo-2-octyl-1-benzofuran (13): Compound **13** was prepared from 2-octyl-1-benzofuran (3.00 g, 13.0 mmol) according to a procedure similar to that used for **9**. The crude product was purified by column chromatography on silica gel (hexane) to give 3.45 g of **13** in 86% yield as a colorless liquid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.84–0.88 (m, 3 H), 1.17–1.80 (m, 12 H), 2.82 (t, J = 7.8 Hz, 2 H), 7.25–7.47 (m, 3 H), 7.64–7.81 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.98, 153.56, 128.48, 124.42, 123.14, 119.16, 111.15, 94.25, 31.93, 29.33, 29.26, 29.16, 27.61, 26.71, 22.74, 14.18 ppm. MS (EI): m/z = 308 [M^+]. $C_{16}H_{21}BrO$ (309.2): calcd. C 62.14, H 6.84; found C 62.03, H 6.73.

1,2-Bis(2-ethyl-1-benzofuran-3-yl)perfluorocyclopentene (2a): Butyllithium (6.11 mL of a 1.6 M hexane solution, 9.77 mmol) was slowly added to a stirred THF solution (40 mL) of 3-bromo-2-ethyl-1-benzofuran (2.00 g, 8.89 mmol) at –78 °C, and the solution was stirred at –78 °C for 15 min. Octafluorocyclopentene (0.471 mL, 3.56 mmol) was then added slowly to the reaction mixture at –78 °C, which was stirred at –78 °C to 30 °C for 12 h. The reaction mixture was poured into concentrated sodium chloride solution and extracted with diethyl ether. The organic layer was dried with anhydrous magnesium sulfate and the solvents were evaporated in vacuo. The crude product was purified by column chromatography on silica gel (hexane) to give 0.908 g of **2a** in 44% yieldas colorless crystals; m.p. 110–111 °C. ^{1}H NMR (200 MHz, $CDCl_3$, room temp.): δ = 0.83 (t, J = 8.0 Hz, 6 H), 2.39 (t, J = 8.0 Hz, 4 H), 7.16–7.31 (m, 4 H), 7.37–7.42 (m, 2 H), 7.48–7.51 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.68, 158.67, 154.59, 127.11, 124.93, 123.95, 120.28, 120.24, 120.21, 111.52, 104.39, 21.10, 11.57 ppm. ^{1}H NMR (600 MHz, CD_3OD, –90 °C): δ = 0.35 (t, J = 6.8 Hz, 4.5 H), 1.03 (t, J = 6.5 Hz, 1.5 H), 2.09–2.17 (m, 1.5 H), 2.43–2.50 (m, 1.5 H), 2.58–2.63 (m, 0.5 H), 2.72–2.80 (m, 0.5 H), 7.11–7.15 (m, 0.5 H), 7.24–7.30 (m, 1.5 H) 7.40–7.46 (m, 3.0 H), 7.49–7.53 (m, 0.5 H), 7.57–7.61 (m, 1.5 H) 7.74–7.77 (m, 1.5 H) ppm. MS (EI): m/z = 464 [M^+]. $C_{25}H_{18}F_6O_2$ (464.4): calcd. C 64.66, H 3.91; found C 64.68, H 3.92.

1,2-Bis(2-propyl-1-benzofuran-3-yl)perfluorocyclopentene (3a): Compound **3a** was prepared from 3-bromo-2-propyl-1-benzofuran (2.00 g, 8.36 mmol) according to a procedure similar to that used for **2a**. The crude product was purified by column chromatography on silica gel (hexane) to give 0.843 g of **3a** in 41% yield as colorless crystals; m.p. 71–72 °C. ^{1}H NMR (200 MHz, $CDCl_3$, room temp.): δ = 0.54 (t, J = 7.2 Hz, 6 H), 1.17–1.32 (sext, J = 7.6 Hz, 4 H), 2.26 (t, J = 7.6 Hz, 4 H), 7.19–7.32 (m, 4 H), 7.38–7.43 (m, 2 H), 7.54–7.58 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.41, 158.15, 154.31, 126.81, 124.67, 123.65, 120.16, 120.12, 120.08, 111.20, 104.64, 29.19, 20.55, 13.29 ppm. ^{1}H NMR (600 MHz, CD_3OD, –90 °C): δ = –0.02–0.08 (m, 7.3 H), 0.91 (t, J = 7.0 Hz, 0.5 H), 1.36–1.43 (m, 2.0 H), 1.63 (br. s, 0.2 H), 1.97–2.02 (m, 1.8 H), 2.33–2.37 (m, 1.8 H), 2.50–2.56 (m, 0.2 H), 2.61–2.66 (m, 0.2 H), 7.04–7.07 (m, 0.2 H), 7.21–7.26 (m, 0.2 H) 7.35–7.41 (m, 1.8 H), 7.44–7.46 (m, 0.2 H), 7.54–7.59 (m, 1.8 H) 7.73–7.75 (m, 1.8 H) ppm. MS (EI): m/z = 492 [M^+]. $C_{27}H_{22}F_6O_2$ (492.4): calcd. C 65.85, H 4.50; found C 65.92, H 4.49.

1,2-Bis(2-pentyl-1-benzofuran-3-yl)perfluorocyclopentene (5a): Compound **5a** was prepared from 3-bromo-2-pentyl-1-benzofuran (2.00 g, 7.48 mmol) by a procedure similar to that used for **2a**. The crude product was purified by column chromatography on silica gel (hexane) to give 0.882 g of **5a** in 43% yield as colorless crystals; m.p. 59–60 °C. ^{1}H NMR (200 MHz): δ = 0.69–1.26 (m, 18 H), 2.26 (t, J = 8.0 Hz, 4 H), 7.20–7.33 (m, 4 H), 7.38–7.43 (m, 2 H), 7.54–7.61 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.92, 159.58, 154.62, 127.14, 124.95, 123.97, 120.52, 120.48, 120.43, 111.52, 104.81, 31.52, 27.66, 27.21, 22.65, 14.14 ppm. MS (EI): m/z = 548 [M^+]. $C_{31}H_{30}F_6O_2$ (548.6): calcd. C 67.87, H 5.51; found C 67.78, H 5.52.

1,2-Bis(2-hexyl-1-benzofuran-3-yl)perfluorocyclopentene (6a): Compound **6a** was prepared from 3-bromo-2-hexyl-1-benzofuran (2.00 g, 7.11 mmol) by a procedure similar to that used for **2a**. The crude product was purified by column chromatography on silica gel (hexane) to give 0.774 g of **6a** in 38% yield as colorless crystals; m.p. 82–83 °C. ^{1}H NMR (200 MHz): δ = 0.76–1.22 (m, 22 H), 2.26 (t, J = 7.8 Hz, 4 H), 7.20–7.33 (m, 4 H), 7.38–7.43 (m, 2 H), 7.55–7.61 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.96, 158.65, 154.63, 127.14, 124.96, 123.99, 120.52, 120.48, 120.45, 111.50, 104.82, 31.74, 29.09, 27.69, 27.46, 22.78, 14.35 ppm. MS (EI): m/z = 576 [M^+]. $C_{33}H_{34}F_6O_2$ (576.6): calcd. C 68.74, H 5.94; found C 68.75, H 5.95.

1,2-Bis(2-heptyl-1-benzofuran-3-yl)perfluorocyclopentene (7a): Compound **7a** was prepared from 3-bromo-2-heptyl-1-benzofuran (2.00 g, 6.77 mmol) according to a procedure similar to that used for **2a**. The crude product was purified by column chromatography on silica gel (hexane) to give 0.716 g of **7a** in 35% yield as a yellow liquid. ^{1}H NMR (200 MHz): δ = 0.81–1.27 (m, 26 H), 2.26 (t, J = 7.6 Hz, 4 H), 7.19–7.33 (m, 4 H), 7.38–7.43 (m, 2 H), 7.55–7.61 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.94, 158.59,

154.62, 127.13, 124.96, 123.98, 120.51, 120.47, 120.43, 111.51, 104.81, 31.97, 29.40, 29.26, 27.70, 27.52, 22.95, 14.44 ppm. MS (EI): m/z = 604 [M^+]. $C_{35}H_{38}F_6O_2$ (604.7): calcd. C 69.52, H 6.33; found C 69.67, H 6.26.

1,2-Bis(2-octyl-1-benzofuran-3-yl)perfluorocyclopentene (8a): Compound **8a** was prepared from 3-bromo-2-octyl-1-benzofuran (2.00 g, 6.47 mmol) according to a procedure similar to that used for **2a**. The crude product was purified by column chromatography on silica gel (hexane) to give 0.654 g of **8a** in 32% yield as a yellow liquid. ^{1}H NMR (200 MHz): δ = 0.81–1.29 (m, 30 H), 2.26 (t, J = 8 Hz, 4 H), 7.19–7.33 (m, 4 H), 7.38–7.43 (m, 2 H), 7.55–7.60 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.58, 158.53, 154.71, 127.20, 124.98, 124.01, 120.56, 120.52, 120.49, 111.53, 104.88, 32.21, 29.59, 29.49, 29.47, 27.75, 27.55, 23.05, 14.46 ppm. MS (EI): m/z = 632 [M^+]. $C_{37}H_{42}F_6O_2$ (632.7): calcd. C 70.24, H 6.69; found C 70.29, H 6.60.

Supporting Information (see footnote on the first page of this article): Absorption spectra of **2**, **3**, **5**, **6**, **7**, and **8** in hexane solution.

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