1. Introduction

Spiro-fused polycyclic aromatic compounds (PACs), in which two planarized biaryls are connected perpendicularly by a tetragonal spiro atom, have been intensively studied in the last few decades, owing to their unique three-dimensional structure, high thermal stability, superior processability, and promising photophysical and electronic properties [1–3]. These intriguing characteristics offer advantages in (opto)electronic applications, such as organic field effect transistors [4,5], organic light emitting diodes [6–8], and organic solar cells [9–12]. The prototypical motif of spiro-fused PACs is 9,9′-spirobi[fluorene] (SBF). A variety of SBF-based compounds with functional substituent(s) and/or a π-extended structure have been developed for the purpose of tuning the photophysical and electronic properties [1,2]. Incorporation of heterocycle unit(s) into π-conjugated systems or a heteroatom as a spiro atom has also been a promising strategy to achieve the desired functions of spiro-fused PACs [3,13–16].

When two dissymmetric biaryls are linked by a spiro atom, the resulting spiro compound is chiral. Two different dissymmetric biaryls give a C1-symmetric spiro compound, while two identical dissymmetric biaryls afford a C2-symmetric one. Although chiral spiro-fused PACs have attracted less attention until recently, there have been several reports on their applications to molecular recognition [17,18], diastereoselective self-assembly [19,20], and asymmetric catalysts [21,22]. In 2016, Kuninobu, Takai, and co-workers reported the first example of a chiral spiro-fused PAC [23] that exhibited circularly polarized luminescence (CPL), which has received significant interest, owing to its potential applications [24–28]. This report has triggered many studies on spiro-fused PACs that exhibit CPL [29–37]. We have also developed a series of chiral spiro-fused PACs, such as spiro-SS, -SS(O)2, and -SN (Figure 1) [16,38–42]. These spiro-fused PACs exhibit CPL
and their optical properties were found to depend on the substituents and the incorporated heterocycle units. The recent studies clearly demonstrate the excellent potential of spiro-fused PACs as chiral materials, and further investigations are still required for elucidating the structure–property relationship, and thus developing spiro-fused PACs with tailored properties.

![Previous work](image1.png) ![This work](image2.png)

**Figure 1.** Molecular structures of previously reported chiral spiro-fused PACs and 1–3 in this study.

In the course of our studies, we have focused on incorporating a furan unit in a chiral spiro-fused PAC skeleton. Furan, the oxygen analog of thiophene, has reduced aromaticity and is more electron-rich compared to thiophene [43]. Therefore, the electronic perturbation of a furan unit to a π-conjugated system would be different from that of a thiophene unit, inducing unique electronic and photophysical properties. To date, a wide range of furan-containing π-conjugated compounds have been reported as organic functional materials [44–48]. However, the synthetic attempt of spiro-fused PACs containing furan unit(s) have been quite limited. In 2010, Ohe and co-workers reported the first examples of furan-containing spiro-fused PACs [49,50]. These compounds were found to be highly emissive. More recently, the chiral spiro-fused PAC with a furan unit has been reported by Nakamura and co-workers, demonstrating CPL properties [35]. Herein, we report the synthesis and photophysical properties of furan-containing chiral spiro-fused PACs 1–3, which are oxygen analogs of spiro-SS, -SS(O)$_2$, and -SN (Figure 1). The $S,S$-dioxide derivative 2 and the pyrrole-containing compound 3 can be synthesized from 1 through aromatic metamorphosis. Incorporation of a furan unit in place of a thiophene unit was found to have great impact on photophysical properties.

**2. Results**

Our first attempt to prepare racemic 1 (rac-1) is illustrated in Scheme 1. 3-Bromo-2-(bromophenyl)-1-benzothiophene (4) was dilithiated with BuLi, and then treated with the ester 5. The subsequent Friedel–Crafts cyclization of the resulting tertiary alcohol 6 successfully gave the desired compound rac-1 (37% yield from 4). The structure was confirmed by X-ray crystallographic analysis (Figure 2). Both enantiomers were found to be contained in the unit cell. The two spiro-linked π-conjugated planes are almost completely perpendicular (87.3°). Screening of optical resolution conditions with HPLC on a chiral stationary phase (chiral HPLC) showed that baseline separation of enantiomers cannot be achieved.
In order to prepare each enantiomer of 1, we designed the hydroxy-substituted spiro compound 11, which would be converted into 1 via a two-step reaction (Scheme 2). Previously, Lützen and co-workers have reported the efficient optical resolution of 9,9'-spirobi[fluorene]-2,2'-dilol and its derivatives with chiral HPLC [51]. We have also demonstrated that the dihydroxylated derivative of spiro-SS can be separated into enantiomers with chiral HPLC more efficiently than its parent compound spiro-SS [39]. Furthermore, Nakamura and co-workers reported the optical resolution of the furan-containing chiral spiro-fused PAC with one hydroxy group by using chiral HPLC [35]. Accordingly, we envisaged that incorporation of a hydroxy group on 1 would make an efficient optical resolution with chiral HPLC possible.

The synthesis of the hydroxy-substituted compound 11 and its transformation to 1 are illustrated in Scheme 2. First, 2-(2-bromo-4-methoxyphenyl)-1-benzothiophene (7) was lithiated with BuLi, and then treated with 10H-indeno[1,2-b][1]benzofuran-10-one (8). The resulting tertiary alcohol 9 was converted into the methoxy-substituted spiro compound rac-10 via acid-promoted Friedel–Crafts cyclization (66% yield from 8). Finally, demethylation of rac-10 with BBr₃ gave the hydroxy-substituted compound 11 (58% yield) in a racemic form. As expected, the optical resolution of rac-11 was achieved by HPLC with a CHIRALPAK® IA column with hexane/CHCl₃ (50/50) as an eluent (Figure S18). In addition, the hydroxy group of 11 was found to be cleaved off via the transformation to the triflate 12 (85% yield with rac-11; 87% yield with (+)-11) and the following palladium-
catalyzed reduction with formic acid (96% yield with rac-12, 89% yield with (+)-12) [39]. This two-step reaction should not affect the chiral center. Therefore, the transformation of enantiopure 11 can give the corresponding enantiomer of 1 without racemization.

Scheme 2. Synthesis of the hydroxy-substituted spiro compound 11 and its transformation to 1.

A benzothiophene skeleton can be transformed to an indole one by aromatic metamorphosis, which includes oxidation of a thiophene unit and the inter/intra molecular S\textsubscript{N}Ar reaction of the resulting S,S-dioxide unit with a primary amine [52]. Recently, we applied this transformation to spiro-SS [40]. The resulting spiro-fused compounds with one [spiro-SS\textsubscript{O}\textsubscript{2}] or two S,S-dioxide units or with one (spiro-SN) or two pyrrole units showed photophysical properties that were quite different from the parent compound spiro-SS. In this context, we investigated the transformation of 1 to the S,S-dioxide derivative 2 and the pyrrole-containing compound 3 (Scheme 3). The oxidation of rac-1 was readily achieved by using an excess amount of 3-chloroperbenzoic acid (mCPBA) as an oxidant, affording rac-2 in high yield (96%). Furthermore, the reaction of rac-2 with aniline in the presence of KHMDS (potassium hexamethyldisilazide) successfully gave rac-3 in a moderate yield (64%). Enantiomers of 2 and 3 were also prepared from enantiopure 1. The oxidation and the inter/intra molecular S\textsubscript{N}Ar reaction should not affect the chiral center. Therefore, these transformations could proceed without racemization to afford enantiopure 2 and 3.

Scheme 3. Synthesis of the S,S-dioxide derivative 2 and the pyrrole-containing compound 3.

The UV–vis absorption and photoluminescence (PL) spectra of spiro-fused PACs 1–3 are shown in Figure 3. The photophysical data are summarized in Table 1, together with those of the previously reported spiro-SS, spiro-SS\textsubscript{O}\textsubscript{2}, and spiro-SN for comparison.
We also performed theoretical calculations by density functional theory (DFT) and time-dependent (TD) DFT methods at the B3LYP/6-31G(d) level of theory to understand the experimental photophysical properties.

![Figure 3. (a) UV–vis absorption and (b) PL spectra of rac-1–3 in CH₂Cl₂.](image)

|             | λ<sub>abs</sub> (nm) | λ<sub>em</sub> (nm) | Φ  |
|-------------|----------------------|---------------------|----|
| rac-1       | 337                  | 369 (320)           | 13 |
| rac-2       | 332, 355 (sh)        | 480, 519 (330)      | <1 |
| rac-3       | 335, 353 (sh)        | 402 (330)           | 16 |
| rac-SS<sup>d</sup> | 340                | 368 (330)           | 6  |
| rac-SS(O)<sub>2</sub><sup>d</sup> | 336, 356 (sh) | 459 (380) | 1   |
| rac-SN<sup>c</sup> | 334, 350 (sh) | 414 (330) | 2   |

<sup>a</sup> The longest absorption maximum in CH₂Cl₂. sh: shoulder. <sup>b</sup> Emission maximum in CH₂Cl₂. Excitation wavelength in parenthesis. <sup>c</sup> Absolute quantum yield in CH₂Cl₂. <sup>d</sup> Reference [38].<sup>c</sup> Reference [40].

Compound rac-1 gave a well-resolved absorption spectrum, with the longest absorption maximum (λ<sub>abs</sub>) at 337 nm (Figure 3a). In contrast, the absorption spectrum of the S,S-dioxide derivative rac-2 exhibited well-resolved absorption bands in the <340 nm range and broad absorption bands in the longer wavelength range. Such a difference in the absorption properties between rac-1 and rac-2 is the same as that observed for spiro-SS and spiro-SS(O)<sub>2</sub> [38]. By analogy with the discussion on spiro-SS and spiro-SS(O)<sub>2</sub> in our previous report, the well-resolved absorption bands and the broader absorption bands were derived from the indeno[1,2-b][1]benzofuran subunit and the indeno[1,2-b][1]benzothiophene S,S-dioxide subunit, respectively. Each of these two subunits works as an almost-independent chromophore, since their perpendicular arrangement through a spiro carbon atom allows a limited orbital interaction between them in the ground state. The absorption spectrum of rac-3 is slightly broader and red-shifted in comparison to that of rac-1, exhibiting a shoulder peak at 353 nm. The absorption spectra of rac-1–3 are almost independent of solvent polarity (Figure S19a–c). The TD-DFT calculations demonstrated that the spiro-fused PACs rac-1–3 exhibit the calculated longest absorption bands at 352 nm, 428 nm, and 361 nm, respectively, all of which are assigned to the transitions dominated by the HOMO→LUMO transition (Table S5). The obtained calculation results are qualitatively coincident with their experimental absorption spectra. The absorption spectra of rac-1–3 are very similar to those of their thiophene analogs spiro-SS, -SS(O)<sub>2</sub>, and -SN, respectively [38,40]. Therefore, the replacement of a thiophene unit with a furan unit was found to have little impact on absorption properties.

In the PL spectra, rac-1 exhibited emission maximum (λ<sub>em</sub>) at 369 nm in CH₂Cl₂ (Figure 3b). A slight red-shift was observed with an increase in solvent polarity (λ<sub>em</sub>: 361 nm (hexane), 366 nm (toluene), 366 nm (THF), 369 nm (CH₂Cl₂), and 381 nm (acetonitrile) Figure S19d). The S,S-dioxide derivative rac-2 exhibited emission maximum at
434 nm in non-polar hexane, which is largely red-shifted compared to that of rac-1. With the increase in solvent polarity, a significant positive solvatochromic shift was observed (Figure 4a). In addition, the second emission band clearly appeared at the longer wavelength (519 nm) in CH₂Cl₂ and became predominant in the most polar acetonitrile (542 nm). According to our previous report [38], the shorter-wavelength emission band reflects the feature of the indeno[1,2-b][1]benzothiophene S,S-dioxide subunit. On the other hand, the longer-wavelength one could be ascribed to the photo-induced intramolecular charge transfer (ICT), in which the indeno[1,2-b][1]benzofuran and the indeno[1,2-b][1]benzothiophene S,S-dioxide subunits work as electron-donating and electron-accepting units, respectively. Indeed, the HOMO and LUMO estimated by DFT calculation are mainly localized in indeno[1,2-b][1]benzofuran and indeno[1,2-b][1]benzothiophene S,S-dioxide subunits, respectively, by reflecting the donor–acceptor-type structure (Figure 5). The emission band of the pyrrole-containing compound rac-3 is also red-shifted compared to that of rac-1. In addition, the PL spectrum of rac-3 exhibited a stronger dependence on solvent polarity than that of rac-1 (Figure 4b). The HOMO of rac-3 is delocalized both on indeno[1,2-b][1]benzofuran and indeno[1,2-b]indole subunits, but the apparently larger distribution is demonstrated on the latter subunit. In contrast, the LUMO is mainly located on the indeno[1,2-b][1]benzofuran subunit. Therefore, indeno[1,2-b][1]benzofuran and indeno[1,2-b]indole subunits act as electron-accepting and electron-donating units, respectively, inducing an ICT character of rac-3 in its emissive state and a clear positive solvatochromic shift in the PL spectrum.

![Figure 4](image-url)  
**Figure 4.** Solvent effect on PL spectra of (a) rac-2 and (b) rac-3.

![Figure 5](image-url)  
**Figure 5.** Frontier molecular orbitals of (R)-1–3.
Next, the effect of the furan unit on the emission properties of rac-1–3 was evaluated through a comparison with those of the thiophene analogs spiro-SS, SS(O)2, and -SN. As described above, the PL spectrum of rac-2 in CH2Cl2 clearly shows the longer-wavelength emission band, owing to a photo-induced ICT, and it is predominant in acetonitrile (Figure 4a). On the other hand, such an emission band is less clear and observed only as a shoulder in the case of spiro-SS(O)2 [38]. This difference could be attributed to the more electron-rich furan unit, which works as a stronger electron-donating unit and allows more efficient photo-induced ICT. The degree of the solvatochromic shift of rac-3 (λem: 374 nm (hexane) and 421 (acetonitrile)) (Figure 4b) is slightly smaller than that of the thiophene analog spiro-SN (λem: 375 nm (hexane) and 430 (acetonitrile)) [40].

The indeno[1,2-b]indole unit is the electron-donating unit both in rac-3 and spiro-SN, and the indeno[1,2-b][1]benzofuran and the indeno[1,2-b][1]benzothiophene subunits work as electron-accepting units in rac-3 and spiro-SN, respectively. Therefore, the smaller solvatochromic shift of rac-3 could be due to the less efficient electron-accepting character of the more electron-rich indeno[1,2-b][1]benzofuran unit. The absolute quantum yields of rac-1 and rac-3 are 0.13 and 0.16, respectively (Table 1), which are much higher than those of spiro-SS (0.06) and spiro-SN (0.02) [38,40]. The S,S-dioxide derivative rac-2 is merely emissive (<0.01), similar to spiro-SS(O)2 [38].

Chiroptical properties of 1–3 were investigated by CD and CPL spectroscopies (Figure 6 and Table 2). The CD spectrum of (+)-1 exhibited two large positive Cotton effects at 340 nm and 328 nm and several negative and positive ones around 305 nm and 260 nm, respectively, which are quite similar to those of (+)-(S)-spiro-SS [38,39]. Therefore, the absolute configuration of (+)-1 is considered to be S. The TD-DFT calculation results also support this assignment. CD spectra of (+)-2 and (+)-3 are slightly different from those of the thiophene analogs spiro-SS(O)2 and spiro-SN, respectively, but the sign of the first Cotton effect of (+)-2 and (+)-3 is identical to that of (+)-(S)-isomers of spiro-SS(O)2 and spiro-SN [38,40]. The dissymmetry factors in absorption, gabs (Δε/ε = (εL − εR)/(εL + εR))/2, were estimated to be approximately 1.2 × 10−3 for (+)-1, 1.4 × 10−3 for (+)-2, and +1.4 × 10−3 for (+)-3. In the CPL spectra, (+)- and (−)-1–3 gave mirror-image CPL spectra with each other. The dissymmetry factors in luminescence, glum [2ΔI/I = 2(Ie − IL)/(IL + IR)], IL and IR: luminescence intensities of left and right circularly polarized light, respectively) [24], of (+)-1–3 were estimated to be +0.90 × 10−3, +2.8 × 10−3, and +0.97 × 10−3, respectively, which are comparable to those of spiro-SS, SS(O)2, and -SN [38,40] and the previously reported chiral small organic molecules with significant CPL activity. The solvent effect on CPL was also investigated for (+)-2, since its PL spectrum exhibits significant positive solvatochroism. As expected, with the increase in solvent polarity, the CPL maximum shifted to the longer wavelength range (Figure 6b).

Figure 6. CD and CPL spectra of (a) 1, (b) 2, and (c) 3 in CH2Cl2 (red and blue lines for CD; pink and green lines for CPL; purple and orange lines in (b) for CPL in toluene and acetonitrile, respectively).
Table 2. Chiroptical data of spiro-fused PACs 1–3 in CH$_2$Cl$_2$.

|     | $g_{abs}$ ($\times 10^{-3}$) $^a$ | $g_{lum}$ ($\times 10^{-3}$) $^b$ | $|\alpha|_{D}^{25}$ $^c$ |
|-----|---------------------------------|---------------------------------|--------------------------|
| (+)-1 | +1.2 (341 nm)                   | +0.90 (381 nm)                  | 154 ($\pm 0.298$)        |
| (+)-2 | +1.4 (378 nm)                   | +2.8 (517 nm)                   | 151 ($\pm 0.150$)        |
| (+)-3 | +0.31 (351 nm)                  | +0.97 (394 nm)                  | 175 ($\pm 0.094$)        |

$^a$ Calculated at the longest CD maximum. Wavelength for the calculated $g_{abs}$ in parentheses. $^b$ Calculated at the CPL maximum. Wavelength for the calculated $g_{lum}$ in parentheses. $^c$ In CH$_2$Cl$_2$. Concentration in parentheses.

3. Materials and Methods

3.1. General Procedures

All manipulations that involved air- and/or moisture-sensitive compounds were carried out with the standard Schlenk technique under argon. Analytical thin-layer chromatography was performed on glass plates coated with 0.25-mm 230–400 mesh silica gel that contained a fluorescent indicator. Column chromatography was performed by using silica gel (spherical neutral, particle size 63–210 $\mu$m). The recycling preparative HPLC was performed with YMC–GPC T–2000 and T–4000 columns (chloroform as an eluent). Most of the reagents were purchased from commercial suppliers, such as Sigma-Aldrich Co. LLC (St. Louis, MO, USA), Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), and Kanto Chemical Co., Inc. (Tokyo, Japan), and used without further purification, unless otherwise specified. Commercially available anhydrous solvents were used for air- and/or moisture sensitive reactions. Compound 4 was prepared according to the literature [53].

NMR spectra were recorded in CDCl$_3$ on a JEOL-ECX400 spectrometer (JEOL Ltd., Tokyo, Japan) (1$^H$ 400 MHz; 13$^C$ 101 MHz; 19$^F$ 376 MHz). Chemical shifts were reported in ppm relative to the internal standard signal (0 ppm for Me$_4$Si in CDCl$_3$ and acetone-d$_6$) for $^1$H and the deuterated solvent signal (77.16 ppm for CDCl$_3$ and 29.84 ppm for acetone-d$_6$) for 13$^C$. Data are presented as follows: chemical shift, multiplicity (s = singlet, brs = broad singlet, d = doublet, t = triplet, m = multiplet and/or multiple resonances), coupling constant in hertz (Hz), and signal area integration in natural numbers. Melting points were determined on SRS OptiMelt melting point apparatus (Stanford Research Systems, Sunnyvale, CA, USA). High resolution mass spectra were taken with a Bruker Daltonics microTOF–QII mass spectrometer (Bruker Corporation, Billerica, MA, USA) by the atmospheric pressure chemical ionization-time-of-flight (APCI–TOF) method. UV–vis absorption spectra were recorded on a JASCO V-650 spectrophotometer (JASCO Corporation, Tokyo, Japan). Photoluminescence spectra were recorded on a JASCO FP–6500 spectrofluorometer (JASCO Corporation, Tokyo, Japan). Absolute quantum yields were determined by an absolute quantum yield measurement system with a JASCO ILF–533 integrating sphere (JASCO Corporation, Tokyo, Japan). HPLC analyses and optical resolution were carried out using a DAICEL CHIRALPAK® IA-3 column (4.6 mm $\times$ 250 mm) and a DAICEL CHIRALPAK® IA column (20 mm $\times$ 250 mm) (Daicel Corporation, Tokyo, Japan), respectively. Circular dichroism (CD) spectra were recorded on a JASCO J–725 spectrometer (JASCO Corporation, Tokyo, Japan). CPL spectra were measured by using a JASCO CPL–300 spectrometer (JASCO Corporation, Tokyo, Japan). Optical rotations were measured on a JASCO P–2200 polarimeter (JASCO Corporation, Tokyo, Japan) using a 50-mm cell.

3.2. Synthesis

3.2.1. Methyl 2-(1-Benzofuran-2-yl)benzoate (5)

A mixture of methyl 2-bromobenzoate (0.97 mL, 6.9 mmol), (1-benzofuran-2-yl)boronic acid (1.23 g, 7.6 mmol), Pd$_2$(dba)$_3$ (0.13 g, 0.14 mmol), SPhos (0.22 g, 0.53 mmol), and K$_2$CO$_3$ (2.86 g, 21 mmol) in anhydrous MeCN (30 mL) and deionized water (3 mL) was placed in a 100-mL Schlenk tube and degassed by three freeze–pump–thaw cycles. After stirring at 80 °C for 24 h under argon, the reaction mixture was cooled to room temperature. To the reaction mixture, 1 M aqueous HCl was slowly added, and the resulting mixture was extracted with CH$_2$Cl$_2$ (10 mL $\times$ 3). The combined organic layers were dried over
anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The resulting crude residue was purified by silica-gel column chromatography with hexane/CH₂Cl₂ (3/2, Rf = 0.48) as an eluent to give 5 as a colorless oil (1.55 g, 89% yield). The ¹H and ¹³C NMR data were identical to those reported in the literature [54].

3.2.2. rac-Spiro[indeno[1,2-b][1]benzofuran-10,10′-indenol[1,2-b][1]benzothiophene] (rac-1)

A mixture of 4 (0.74 g, 2.0 mmol) and N,N,N′,N′-tetramethylethylenediamine (1.2 mL, 8.0 mmol) in anhydrous THF (15 mL) was placed in a 50-mL Schlenk tube and cooled to −78 °C. To the mixture was added BuLi (2.3 M in hexane, 1.8 mL, 4.2 mmol) dropwise, and the resulting mixture was stirred at −78 °C for 1 h. Compound 5 (0.56 g, 2.2 mmol) in anhydrous THF (15 mL) was slowly added to the reaction mixture at −78 °C, and the resulting mixture was stirred at −78 °C for 1 h, warmed to ambient temperature, and then stirred for 18 h, before being quenched with water. The resulting mixture was extracted with EtOAc (5 mL × 3), and the combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The resulting crude residue containing the tertiary alcohol 6 was used in the following step without purification.

The obtained crude residue was dissolved in CH₂Cl₂ (7 mL). To the solution, trifluoroacetic acid (1.5 mL) was added at ambient temperature, and the reaction mixture was stirred at ambient temperature for 6 h, before being quenched with aqueous saturated NaHCO₃. The resulting mixture was extracted with CH₂Cl₂ (10 mL × 4), and the combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The resulting crude residue was purified by silica-gel column chromatography with hexane (Rf = 0.38) as an eluent to give rac-1 as a colorless solid (0.30 g, 37% yield); mp 245.5–246.6 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, J = 8.2 Hz, 1H), 7.74 (d, J = 7.3 Hz, 1H), 7.66 (d, J = 7.8 Hz, 1H), 7.58 (d, J = 8.2 Hz, 1H), 7.39–7.35 (m, 2H), 7.18–7.12 (m, 2H), 7.07 (td, J = 7.3, 0.9 Hz, H), 7.04 (td, J = 7.8, 0.9 Hz, H), 7.01–6.93 (m, 2H), 6.83 (d, J = 7.3 Hz, 1H), 6.77–6.73 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 162.4, 160.2, 149.8, 148.7, 144.4, 144.0, 141.7, 139.2, 133.4, 128.3, 128.2, 127.2, 126.9, 125.5, 124.9, 124.4, 124.2, 124.0, 123.9, 123.8, 123.5, 123.3, 121.1, 120.1, 119.3, 118.2, 112.4, 57.4 (one missing signal for an aromatic carbon is presumed to overlap one of the signals that was observed); HRMS–APCI⁺ (m/z) calcd for C₂₀H₁₇O₅⁺ [(M + H)⁺], 413.0995, found 413.0994.

3.2.3. 2-(2-Bromo-4-methoxyphenyl)-1-benzothiophene (7)

A mixture of (1-benzothiophen-2-yl)boronic acid (99 mg, 0.55 mmol), 2-bromo-1-iodo-4-methoxybenzene (0.15 g, 0.49 mmol), Na₂CO₃ (0.11 g, 1.1 mmol), and Pd(PPh₃)₄ (29 mg, 25 μmol) in anhydrous 1,4-dioxane (2.1 mL) and deionized water (0.30 mL) was placed in a 30-mL Schlenk tube and degassed by three freeze–pump–thaw cycles. After stirring at 90 °C for 48 h under argon, the reaction mixture was cooled to room temperature. To the reaction mixture, 1 M aqueous HCl was slowly added, and the resulting mixture was extracted with CH₂Cl₂ (5 mL × 3). The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The resulting crude residue was purified by silica-gel column chromatography with hexane/EtOAc (9/1, Rf = 0.52) as an eluent and preparative HPLC to give 7 as a colorless solid (0.11 g, 67% yield): mp
82.3–84.1 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.84 (dd, $J = 8.2, 0.9$ Hz, 1H), 7.80 (dd, $J = 7.3, 1.4$ Hz, 1H), 7.46 (d, $J = 8.2$ Hz, 1H), 7.42 (s, 1H), 7.37 (td, $J = 6.9, 1.4$ Hz, 1H), 7.32 (td, $J = 7.3, 1.4$ Hz, 1H), 7.25 (d, $J = 2.7$ Hz, 1H), 6.92 (dd, $J = 8.7, 2.7$ Hz, 1H), 3.85 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 160.0, 142.1, 140.2, 140.0, 132.9, 127.8, 124.5, 124.4, 124.2, 123.8, 123.6, 122.2, 118.9, 113.8, 55.8; HRMS–APCI$^+$ (m/z) calcd for C$_{15}$H$_{12}$BrOS$^+$ ([M + H]$^+$), 318.9787, found 318.9791.

3.2.4. 2-(1-Benzofuran-2-yl)benzoic Acid (13)

To a solution of 5 (1.75 g, 6.9 mmol) in methanol (20 mL), a mixture of NaOH (1.68 g, 42 mmol) and water (20 mL) was added at room temperature. After stirring at 60 °C for 4.5 h, the reaction mixture was cooled to room temperature and acidified with 1 M aqueous HCl. The resulting mixture was extracted with Et$_2$O (10 mL × 4). The combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The resulting crude residue was purified by chromatography with hexane/(101 MHz, CDCl$_3$) δ 169.6, 155.93, 155.88, 132.8, 131.9, 130.4, 130.2, 130.1, 130.0, 129.7, 125.3, 123.8, 123.6, 118.9, 113.8, 55.8; HRMS–APCI$^+$ (m/z) calcd for C$_{15}$H$_{12}$BrOS$^+$ ([M + H]$^+$), 318.9787, found 318.9791.

3.2.5. 10H-Indeno[1,2-b][1]benzofuran-10-one (8)

A mixture of 13 (3.83 g, 16 mmol) and thionyl chloride (1.4 mL, 19 mmol) in anhydrous CH$_2$Cl$_2$ (160 mL) was placed in a 300-mL three-neck flask with a condenser at ambient temperature. To the mixture, anhydrous DMF (100 μL) was added, and the resulting mixture was stirred for 1.5 h at 40 °C. The volatiles were removed under reduced pressure to afford the acid chloride intermediate.

A mixture of AlCl$_3$ (3.26 g, 24 mmol) and anhydrous CH$_2$Cl$_2$ (180 mL) was charged in a 500-mL three-neck flask with a condenser and a dropping funnel and cooled at 0 °C. To the mixture, a solution of the acid chloride intermediate in anhydrous CH$_2$Cl$_2$ (160 mL) was slowly added via the dropping funnel over 2 h at 0 °C under argon atmosphere. The reaction mixture was stirred for 18 h at 40 °C, cooled to ambient temperature, and then poured into ice-cooled 1 M aqueous HCl. The resulting mixture was extracted with CH$_2$Cl$_2$ (100 mL × 3), and the combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The resulting crude residue was purified by silica-gel column chromatography with hexane/EtOAc (9/1, $R_f = 0.49$) as an eluent to give 8 as an orange solid (1.44 g, 41% yield). The $^1$H and $^{13}$C NMR data were identical to those reported in the literature [55].

3.2.6. rac-2′-Methoxyspiro[indeno[1,2-b][1]benzofuran-10,10′-indeno[1,2-b][1]benzothiophene] (rac-10)

A mixture of 7 (0.48 g, 1.5 mmol) and $N,N,N′,N′$-tetramethylethylenediamine (0.45 mL, 3.0 mmol) in anhydrous THF (12 mL) was placed in a 100-mL Schlenk flask and cooled to −78 °C. To the mixture, BuLi (2.6 M in hexane, 0.59 mL, 1.5 mmol) was added dropwise, and the resulting mixture was stirred at −78 °C for 1 h. Compound 8 (0.27 g, 1.3 mmol) in anhydrous THF (12 mL) was slowly added to the reaction mixture at −78 °C, and the resulting mixture was stirred at −78 °C for 1 h, warmed to ambient temperature, and then stirred for 18 h, before being quenched with water. The resulting mixture was extracted...
with CH$_2$Cl$_2$ (10 mL $\times$ 3), and the combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The resulting crude residue was roughly purified by silica-gel column chromatography with hexane/EtOAc (9/1) as an eluent. The fractions ($R_f = 0.16$) that contained the tertiary alcohol 9 and some impurities were concentrated under reduced pressure.

The resulting residue was dissolved in CH$_2$Cl$_2$ (10 mL) and cooled to 0 °C. To the solution, trifluoroacetic acid (0.4 mL) was added at 0 °C, and the reaction mixture was stirred at 0 °C for 1 h, before being quenched with aqueous saturated NaHCO$_3$. The resulting mixture was extracted with CH$_2$Cl$_2$ (10 mL $\times$ 3), and the combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The resulting crude residue was purified by silica-gel column chromatography with hexane/EtOAc (9/1) as an eluent to give rac-10 as a colorless solid (0.37 g, 66% yield from 8); mp 216.4–221.6 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.78 (ddd, $J = 8.2, 1.8, 0.9$ Hz, 1H), 7.36 (ddd, $J = 7.6, 0.9$ Hz, 1H), 7.15 (ddd, $J = 8.2, 6.9, 1.4$ Hz, 1H), 7.10 (ddd, $J = 8.2, 6.9, 1.4$ Hz, 1H), 7.04 (td, $J = 7.6, 1.4$ Hz, 1H), 6.98–6.94 (m, 2H), 6.89 (dd, $J = 8.2, 2.3$ Hz, 1H), 6.79–6.77 (m, 2H), 6.69 (ddd, $J = 7.8, 1.4, 0.9$ Hz, 1H), 6.39 (d, $J = 2.3$ Hz, 1H), 3.63 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.3, 160.2, 155.1, 151.1, 150.0, 144.4, 143.5, 140.1, 133.7, 133.4, 132.2, 128.2, 127.2, 125.9, 124.8, 124.4, 124.1, 123.9, 123.7, 123.6, 123.5, 123.0, 120.7, 120.6, 119.4, 118.1, 113.4, 112.4, 109.9, 57.4, 55.6; HRMS−APCI$^+$ (m/z) calcd for C$_{30}$H$_{19}$O$_2$S$^+$ ([M + H$^+$]), 443.1100, found 443.1103.

3.2.7. rac-Spiro[indeno[1,2-b][1]benzofuran-10,10′-indenob[1,2-b][1]benzo[b]thiophene]-2′-ol (rac-11)

To a mixture of rac-10 (1.04 g, 2.4 mmol) and anhydrous CH$_2$Cl$_2$ (24 mL), BBr$_3$ (1 M in CH$_2$Cl$_2$, 4.7 mL, 4.7 mmol) was added dropwise at 0 °C. After stirring at 0 °C for 2.5 h, the reaction was quenched with water. The resulting mixture was extracted with CH$_2$Cl$_2$ (15 mL $\times$ 3) and the combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The resulting crude residue was purified by silica-gel column chromatography with hexane/EtOAc (3/1, $R_f = 0.46$) as an eluent to give rac-11 as a colorless solid (0.59 g, 58% yield). rac-11 can be separated into enantiopure (−)-11 and (+)-11 by HPLC equipped with an analytical DAICEL CHIRALPACK® IA-3 column (Φ 4.6 mm $\times$ 250 mm) ($t_R = 12.7$ min for (−)-11 and 14.5 min for (+)-11) (flow rate: 1.0 mL/min; eluent: hexane/CHCl$_3$ = 50/50): $[\alpha]_D^{25}$ for (+)-11 +175 ($c = 0.112$, CH$_2$Cl$_2$); mp 261.2–265.7 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.80 (d, $J = 8.0$ Hz, 1H), 7.74 (d, $J = 7.4$ Hz, 1H), 7.58 (d, $J = 8.6$ Hz, 1H), 7.52 (d, $J = 8.0$ Hz, 1H), 7.38 (t, $J = 7.2$ Hz, 1H), 7.18 (dd, $J = 8.0$, 1.2 Hz, 1H), 7.12 (td, $J = 8.0$, 1.2 Hz, 1H), 7.06 (td, $J = 7.5$, 1.2 Hz, 1H), 7.00–6.96 (m, 2H), 6.84 (dd, $J = 8.0$, 2.3 Hz, 1H), 6.80–6.79 (m, 2H), 6.70 (d, $J = 8.0$ Hz, 1H), 6.32 (d, $J = 2.6$ Hz, 1H), 4.54 (brs, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.3, 160.2, 155.1, 151.1, 150.0, 144.4, 143.5, 140.0, 133.6, 133.3, 132.3, 128.2, 127.2, 125.7, 124.8, 124.4, 124.1, 123.4, 123.0, 120.7, 120.6, 119.3, 118.2, 115.0, 112.4, 111.2, 57.3; HRMS−APCI$^+$ (m/z) calcd for C$_{29}$H$_{18}$O$_2$S$^+$ ([M + H$^+$]), 429.0944, found 429.0931.

3.2.8. rac-Spiro[indeno[1,2-b][1]benzofuran-10,10′-indenob[1,2-b][1]benzo[b]thiophene]-2′-yl Trifluoromethanesulfonate (rac-12)

A mixture of rac-11 (82 mg, 0.19 mmol) and anhydrous triethylamine (1.0 mL, 1.0 mmol) in anhydrous CH$_2$Cl$_2$ (2 mL) was placed in a 20-mL Schlenk tube and cooled to −78 °C. To the mixture, trifluoromethanesulfonic anhydride (45 µL, 0.27 mmol) was added dropwise, and the resulting mixture was stirred at −78 °C for 30 min. The reaction was quenched with water, and then the resulting mixture was extracted with CH$_2$Cl$_2$ (5 mL $\times$ 3). The combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The resulting crude residue was purified by silica-gel column chromatography with hexane/EtOAc (9/1, $R_f = 0.43$) as an eluent to give rac-12 as a colorless solid (92 mg, 85% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 (d, $J = 7.8$ Hz, 1H), 7.77 (d, $J = 7.3$ Hz, 1H), 7.70 (d, $J = 8.2$ Hz, 1H), 7.60 (d, $J = 8.2$ Hz, 1H), 7.42 (dd, $J = 7.6$, 6.6 Hz,
128.0, 127.8, 124.6, 124.3, 124.0, 123.8, 123.7, 122.9, 121.8, 121.6, 119.2, 118.8, 112.6, 57.7 (one
162.8, 160.2, 151.4, 147.7, 146.3, 144.5, 142.9, 134.0, 133.5, 133.3, 130.0, 129.2, 128.9, 128.5,
J
124.3, 124.2, 124.0, 123.92, 123.89, 121.5, 121.4, 120.8, 119.0, 118.70 (q, JCF = 321 Hz),

The crude product of (+)-12 was also obtained by using (+)-11 (62 mg, 0.14 mmol), anhydrous triethylamine (0.10 mL, 0.72 mmol), and trifluoromethanesulfonic anhydride (32 µL, 0.20 mmol), according to the procedure for rac-12. Purification by silica-gel column chromatography with hexane/EtOAc (9/1, Rf = 0.43) as an eluent gave (+)-12 as a colorless solid (70 mg, 87% yield); [α]D25 +128 (c 0.158, CH2Cl2). The 1H and 13C NMR spectra were identical to those of rac-12.

3.2.9. rac-Spiro[indeno[1,2-b][1]benzofuran-10,10′-indenofuran-1,2-b][1]benzo thiophene] (rac-1)

A mixture of rac-12 (56 mg, 0.10 mmol), Pd(OAc)2 (1.2 mg, 5.3 µmol), PPh3 (2.4 mg, 9.2 µmol), anhydrous triethylamine (85 µL, 0.61 mmol), formic acid (15 µL, 0.39 mmol), and anhydrous DMF (1.0 mL) was placed in a 20-mL Schlenk tube and degassed by three freeze–pump–thaw cycles. After stirring at 80 °C for 2 h under argon, the reaction mixture was allowed to cool to room temperature. The reaction was quenched by adding 1 M aqueous HCl slowly, and the resulting mixture was extracted with CH2Cl2 (5.0 mL × 3). The combined organic layers were dried over anhydrous Na2SO4, filtered, and concentrated under reduced pressure. The resulting crude residue was purified by silica-gel column chromatography with hexane/EtOAc (9/1, Rf = 0.70) as an eluent to give rac-1 as a colorless solid (40 mg, 96% yield). The 1H and 13C NMR spectra were identical to those of rac-1 described above.

The crude product of (+)-1 was also obtained by using (+)-12 (79 mg, 0.12 mmol), Pd(OAc)2 (1.4 mg, 6.2 µmol), PPh3 (3.1 mg, 12 µmol), anhydrous trimethylamine (0.12 mL, 0.83 mmol), formic acid (22 µL, 0.53 µmol), and DMF (1.4 mL), according to the procedure for rac-1. Purification by silica-gel column chromatography with hexane/EtOAc (9/1, Rf = 0.70) as an eluent gave (+)-1 as a colorless solid (52 mg, 89% yield); [α]D25 +154 (c 0.298, CH2Cl2). The 1H and 13C NMR spectra were identical to those of rac-1.

3.2.10. rac-Spiro[indeno[1,2-b][1]benzofuran-10,10′-indenofuran-1,2-b][1]benzo thiophene] 5,5′-Dioxide (rac-2)

To a mixture of rac-1 (0.12 g, 0.30 mmol) and CH2Cl2 (2.0 mL), m-chloroperoxybenzoic acid (contains ca. 30% water, 0.19 g, 1.1 mmol) was added at 0 °C. The resulting mixture was stirred at 0 °C for 24 h. The reaction was quenched with a mixture of an aqueous saturated Na2S2O3 and NaHCO3, and then the resulting mixture was extracted with CH2Cl2 (5.0 mL × 3). The combined organic layers were dried over anhydrous Na2SO4, filtered, and concentrated under reduced pressure. The resulting crude residue was purified by silica-gel column chromatography with CHCl3 (Rf = 0.81) as an eluent to give rac-2 as a colorless solid (0.13 mg, 96% yield); 1H NMR (400 MHz, CDCl3) δ 8.38 (3H, d, J = 7.8 Hz, 1H, 7.77 (3H, d, J = 7.3 Hz, 1H, 7.66 (3H, d, J = 7.3 Hz, 1H, 7.59 (3H, d, J = 8.2 Hz, 1H, 7.46–7.41 (1H, 7.28 (3H, d, J = 7.6 Hz, 1H, 7.24–7.20 (m, 1H, 7.18–7.10 (m, 1H, 7.06 (3H, d, J = 7.6 Hz, 1H, 6.94 (3H, d, J = 7.8 Hz, 1H, 6.35 (3H, d, J = 7.3 Hz, 1H, 13C NMR (101 MHz, CDCl3) δ 162.8, 160.2, 151.4, 147.7, 146.3, 144.5, 142.9, 134.0, 133.5, 133.3, 130.0, 129.2, 128.9, 128.5, 128.0, 127.8, 124.6, 124.3, 124.0, 123.8, 122.9, 121.8, 121.6, 119.2, 118.8, 112.6, 57.7 (one

The crude product of (+)-2 was obtained by using (+)-1 (27 mg, 65 µmol), m-chloroperoxybenzoic acid (41 mg, 0.17 mmol), and CH2Cl2 (0.7 mL), according to the procedure for rac-2. Purification by silica-gel column chromatography with CHCl3 (Rf = 0.81) as an eluent
gave (+)-2 as a colorless solid (28 mg, 96% yield): [α]D 25° +151 (c 0.15, CH2Cl2). The 1H and 13C NMR spectra were identical to those of rac-2.

3.2.11. rac-5'-Phenyl-5'H-spiro[indeno[1,2-b][1]benzofuran-10,10'-indeno[1,2-b]indole] (rac-3)

A solution of KHMDs (0.5 M in toluene, 0.19 mL, 93 µmol) was charged in a 20-mL Schlenk tube, and toluene was removed under reduced pressure. The resulting residue was dissolved with anhydrous xylene (0.3 mL) under argon. The resulting xylene solution of KHMDs was added to a mixture of rac-2 (14 mg, 31 µmol) and aniline (5.7 µl, 62 µmol) in another 20-mL Schlenk tube under argon at ambient temperature. The resulting solution was stirred at 140 °C for 48 h. The reaction mixture was cooled to an ambient temperature, and 1 M aqueous HCl was added slowly to the reaction mixture. The resulting mixture was extracted with CH2Cl2 (5 mL × 4), and the combined organic layers were dried over Na2SO4, filtered, and concentrated under reduced pressure. The crude residue was purified by silica-gel column chromatography with hexane/EtOAc (9/1, Rf = 0.48) as an eluent to give rac-3 as a colorless solid (9.4 mg, 64% yield); mp 255.1–259.2 °C; 1H NMR (400 MHz, CDCl3) δ 7.75–7.66 (m, 5H), 7.60–7.54 (m, 2H), 7.40–7.34 (m, 2H), 7.18–7.13 (m, 3H), 7.08–7.03 (m, 2H), 7.00–6.94 (m, 2H), 6.89–6.78 (m, 5H); 13C NMR (101 MHz, CDCl3) δ 162.3, 160.2, 151.3, 150.6, 144.6, 142.5, 138.1, 135.4, 133.5, 129.8, 128.0, 127.5, 127.1, 127.0, 126.4, 126.2, 124.7, 123.8, 123.67, 123.34, 123.29, 122.8, 122.3, 120.9, 119.4, 119.0, 118.9, 117.9, 112.3, 111.1, 54.3; HRMS–APCI+ (m/z) calcd for C25H22NO+ ([M + H]+), 472.1696, found 472.1687.

The crude product of (+)-3 was obtained by using (+)-2 (16 mg, 36 µmol), aniline (7 µL, 77 µmol), KHMDs (0.5 M in toluene, 0.22 mL), and xylene (0.36 mL), according to the procedure for rac-3. Purification by silica-gel column chromatography with hexane/EtOAc (9/1, Rf = 0.48) as an eluent gave (+)-3 as a colorless solid (4.7 mg, 27% yield): [α]D 25° +175 (c 0.094, CH2Cl2). The 1H and 13C NMR spectra were identical to those of rac-3.

3.3. Computational Studies

The DFT and TD-DFT calculations were performed by using the Gaussian 09 program [56] at the B3LYP/6-31G(d) level of theory in the gas phase. The starting molecular models for DFT geometry optimizations were built and optimized with MMFF molecular mechanics by using the Spartan '08 package (Wavefunction, Inc., Irvine, CA, USA). Six singlet states were calculated in the TD-DFT calculations. The visualization of the molecular orbitals was performed using GaussView 5.

3.4. X-ray Crystallography

For X-ray crystallographic analysis, a suitable single crystal was selected under ambient conditions, mounted using a nylon loop filled with paraffin oil, and transferred to the goniometer of a RIGAKU R-AXIS RAPID diffractometer (Rigaku Corporation, Tokyo, Japan), with graphite-monochromated Cu–Kα irradiation (λ = 1.54187 Å). The structure was solved by a direct method (SIR 2008 [57]) and refined by full-matrix least-squares techniques against F2 (SHELXL-2014 [58,59]). The intensities were corrected for Lorentz and polarization effects. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions.

Crystal data for rac-1: formula: C20H16OS (M = 412.48 g/mol): monoclinic, space group P21/n (No. 14), a = 14.2753(3) Å, b = 9.8401(2) Å, c = 15.7643(3) Å, β = 114.4630(10)°, V = 2015.63(7) Å3, Z = 4, T = 193(2) K, μ(CuKα) = 1.566 mm-1, Dcalc = 1.359 g/cm3, 34,993 reflections measured (3.519° ≤ θ ≤ 68.226°), 3684 unique (Rint = 0.0448; Rsigma = 0.0213), which were used in all calculations. The final R1 was 0.0688 (I > 2σ(I)) and wR2 was 0.2028 (all data). CCDC 2,191,229 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures, accessed on 8 August 2022.
4. Conclusions

In summary, we have synthesized furan-containing chiral spiro-fused PACs 1–3. Aromatic metamorphosis strategy was applied to 1, affording the pyrrole-containing 3, as well as the S,S-dioxide derivative 2. The hydroxylated derivatives of 1 were found to be separated into enantiopure isomers by chiral HPLC, which allowed us to prepare enantiomers of 1–3. Introduction of a furan unit has proven to have a great impact on their photophysical properties. The observed impact could be attributed to the increased electron-richness of furan compared to thiophene. The synthesized furan-containing chiral spiro-fused PACs demonstrated CPL with a $g_{\text{lim}}$ value of $<2.3 \times 10^{-3}$, which is comparable to those of the reported chiral small organic molecules.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules27165103/s1, Figures S1–S17: $^1$H, $^{13}$C, and $^{19}$F NMR spectra for 1–3, 7, and 10–13; Table S1: Crystallographic data for rac-1; Figure S18: HPLC chart for optical resolution of 11; Figure S19: UV–vis (1–3) and PL (1) spectra in various solvents; Figures S20–S22: Molecular orbitals for (R)-1–3; Tables S2–S4: Coordinates and absolute energy of the optimized structures for (R)-1–3; Table S5: The selected absorption of (R)-1–3 calculated by TD-DFT method.

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Sample Availability: Samples of the compounds are available from the authors.

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