Synthesis and Functions of Binaphthyl Derivatives with Comprehensive Introduction of Phenylethynyl Groups

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Abstract: In this study, compounds with phenylethynyl (PE) groups introduced at all of the possible positions of the methylene-bridged structure of the 1,1'-bi-2-naphthol backbone (**3-PE** to **8-PE**) were synthesized. Compounds with four or six phenylethynyl groups (**3,6-PE**, **4,6-PE**, **5,6-PE**, **6,7-PE**, and **3,4,6-PE**) were also synthesized. The key reaction for the synthesis of these compounds was the Sonogashira reaction using halogen scaffolds. The new transformation methods include (1) selective bromination of the 5-position of the binaphthyl skeleton and (2) bromination of the 6-position and then iodination of the 4-position, followed by the Sonogashira reaction of iodine at the 4-position and lithiation and protonation of bromine at the 6-position. The optical properties of the compounds were evaluated. The extension of the π system greatly differed depending on the position of the phenylethynyl group. **4-PE**, **4,6-PE**, and **3,4,6-PE**, in which the phenylethynyl groups were introduced in the extended direction of the naphthalene linkage axis, showed longer absorption and emission wavelengths and higher fluorescence quantum yields than the other compounds. In circularly polarized luminescence measurements, **7-PE** showed a relatively large g_{lum} value, an interesting finding that reverses the sense.

Introduction

The binaphthyl skeleton is extensively used as a catalyst for asymmetric reactions and as a mother framework for functional materials owing to its adaptability in altering the dihedral angle in response to external conditions[1,2]. Notably, as a useful ligand for asymmetric reactions[3,4], this skeleton is used in 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) [5,6], organic catalysts, such as phosphoric acid catalysts [7,8], and quaternary ammonium catalysts[9,10]. Moreover, it is used as the core of dendrimers and serves as a source of chirality in chiral π compounds[11]. However, when contemplating the use of the chiral binaphthyl skeleton as a fluorescent dye, the challenge often lies in its low quantum yield. Effective strategies to overcome this limitation include converting the naphthalene ring to a larger π system, such as a pyrene ring[12–14], and enhancing the π system by introducing a phenylethynyl group onto the naphthalene ring[15]. Recently, many studies on the use of compounds linked to the binaphthyl skeleton as chiral luminescent molecules, including molecules with circularly polarized luminescence (CPL), have been reported[16–20].
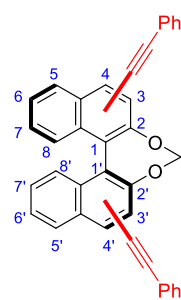
3-PE = 3,3'-di(phenylethynyl)
4-PE = 4,4'-di(phenylethynyl)
5-PA = 5,5'-di(phenylethynyl)
6-PA = 6,6'-di(phenylethynyl)
7-PA = 7,7'-di(phenylethynyl)
8-PA = 8,8'-di(phenylethynyl)
3,6-PE = 3,3',6,6'-tetra(phenylethynyl)
4,6-PE = 4,4',6,6'-tetra(phenylethynyl)
5,6-PE = 5,5',6,6'-tetra(phenylethynyl)
6,7-PE = 6,6',7,7'-tetra(phenylethynyl)
3,4,6-PE = 3,3',4,4',6,6'-hexa(phenylethynyl)

Figure 1. Binaphthyl derivatives **3-PE** to **3,4,6-PE** bearing phenylethynyl groups at all of the possible ring positions.

In this study, a series of compounds (denoted **3-PE** to **8-PE**) was synthesized, involving the bridging of the two hydroxy groups of 1,1'-bi-2-naphthol (BINOL) by a methylene unit (*i.e.*, one carbon atom) and the incorporation of two phenylethynyl groups at all of the feasible substitution positions. Subsequently, compounds possessing four or six phenylethynyl groups (**3,6-PE**, **4,6-PE**, **5,6-PE**, **6,7-PE**, and **3,4,6-PE**) were also synthesized, and their optical properties were systematically evaluated (Figure 1).

Results and Discussion

1. Synthesis

3-PE to **3,4,6-PE** were synthesized by two distinct methods: (1) by introducing halogens at the desired positions using readily available chiral BINOL as the starting compound, followed by the introduction of a phenylethynyl group via the Sonogashira reaction and (2) by synthesizing naphthols with appropriate substituents and subsequently performing oxidative dimerization to obtain racemic compounds, followed by the introduction of chiral auxiliary leading to diastereomeric mixtures, followed by separation using column chromatography or separation of racemic compounds using chiral columns.

1.1. Route using halogenation of (*S*)-BINOL
The two hydroxy groups of BINOL were protected with methyl groups (**1-Me**), hexyl groups (**1-Hex**) [21], methoxymethyl groups (**1-MOM**), acetyl groups (**1-Ac**), or trifluoromethanesulfonyl groups (**1-Tf**), and the positions of the halogens were controlled according to the characteristics of the introduced protecting groups (Scheme 1A). The desired compound was synthesized by a subsequent Sonogashira reaction[22–24].

1.1.1 Synthesis of 6-PE (Scheme 1B) [25,26]
Selective iodination at the 6-position of **1-Me** using 1,3-diiodo-5,5-dimethylhydantoin (DIH) yielded compound **2** (83% yield). The subsequent removal of the methyl groups using boron tribromide (**3**, quantitative yield) [27] and then one-carbon bridging of the two phenol hydroxy groups using dibromomethane gave compound **4** in 63% yield. The phenylethynyl groups were then introduced by the Sonogashira reaction to afford the desired compound **6-PE** in 28% yield.

1.1.2. Synthesis of 4,6-PE (Scheme 1C)
1-Hex was reacted with bromine by a method described in the literature to obtain compound **5** with bromine at the 4, 4′, 6, and 6′ positions in 73% yield[21]. The removal of the hexyl group (**6**, 98% yield), one-carbon bridging (**7**, 63% yield), and the introduction of phenylethynyl groups by the Sonogashira reaction gave the desired compound **4,6-PE** in 67% yield.

1.1.3. Synthesis of 4-PE (Scheme 1D)
The above method was modified to synthesize **4-PE**. After bromination of the 6-position of **1-Me** using *N*-bromosuccinimide (NBS) (**8**, quantitative yield) [28], selective iodination of the 4-position was performed using DIH (**9**, 70% yield). A switch from the methoxy group to a one-carbon bridge was performed (**11**, quantitative yield), giving compound **12** through an iodine-selective Sonogashira reaction, albeit in a low yield (15% yield). Finally, lithiation of the bromine atom with butyllithium followed by trapping with water gave **4-PE** in 84% yield.

1.1.4. Synthesis of 3-PE (Scheme 1E)
Using **1-MOM** as the starting material, iodination at the 3-position of **1-MOM** using the neighboring group effect of the OMOM group (**13**, 62% yield) [29,30] was performed to removal the MOM group (**14**, quantitative yield), followed by one-carbon cross-linking (**15**, 41% yield). The introduction of the phenylethynyl groups were achieved using the Sonogashira reaction, resulting in the synthesis of **3-PE** in 17% yield.

1.1.5. Synthesis of 3,6-PE (Scheme 1F)
3,6-PE was synthesized by applying the above method to compound **3** possessing iodine at position 6. Initially, the hydroxy groups of **3** were converted to MOM groups (**16**, quantitative yield), and phenylethynyl groups were introduced at the 6,6'-positions by the Sonogashira reaction (**17**, 98% yield). Subsequent steps included iodination at the 3-position (**18**, 77% yield), replacement of the MOM group with a one-carbon bridge (**20**, 58% yield for two steps), and a final Sonogashira reaction, yielding the desired compound **3,6-PE** in 45% yield.

1.1.6. Synthesis of 5,6-PE (Scheme 1G)
Selective bromination at the 5-position was attempted using **1-Ac** according to a reported method[31,32]; however, a mixture of compounds with bromine at the 5-position and 5,6-positions was obtained, which was difficult to separate. Instead, this reaction was used for the 5,6-position selective bromination reaction to produce tetrabrominated **21** from **1-Ac** (37% yield). Subsequently, the obtained **5,6-PE** underwent conversion to a one-carbon bridge followed by the Sonogashira reaction to synthesize the desired compound **5,6-PE** in 28% yield.

#### 1.1.7. Synthesis of 5-PE (Scheme 1H)
We thought that 5-position selective bromination would be possible by converting the acetyl group of **1-Ac** to a trifluoromethanesulfonyl group and using **1-Tf**, a compound with reduced reactivity of the naphthalene ring, and thus we performed the bromination reaction using **1-Tf**. As anticipated, the reaction yielded the desired outcome of 5-position selective bromination, leading to the formation of compound **24** with a yield of 43%. **5-PE** was synthesized from compound **24** through a sequential process involving the removal of the trifluoromethanesulfonyl groups, one-carbon cross-linking, and a Sonogashira reaction.

1.2. Route using the dimerization of naphthalene with appropriate substituents
7-PE, **6,7-PE**, and **8-PE** were synthesized by a route using the dimerization of naphthalenes with appropriate substituents (Scheme 2).
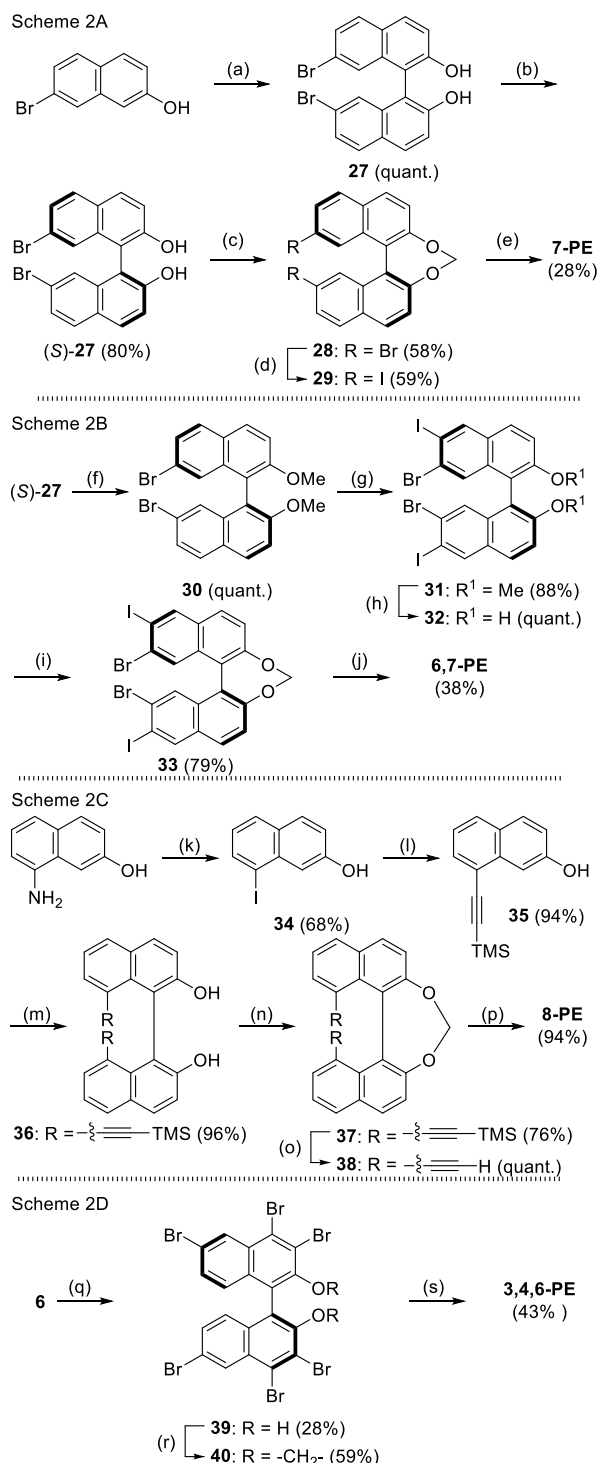
1.2.1. Synthesis of 7-PE (Scheme 2A)
(*S*)-**27** was synthesized by the oxidative dimerization of 7-bromo-2-naphthol followed by optical resolution using (–)-menthylformate according to established literature procedures[33]. (*S*)-**27** was subjected to the Sonogashira reaction after one-carbon cross-linking (**28**, 58% yield), but the reaction yield was low, probably because of steric hindrance. The target compound **7-PE** was synthesized by the lithiation of the bromine atom of (*S*)-**28**, followed by iodine trapping to form **29**, and then **29** was subjected to the Sonogashira reaction to give **7-PE** in 28% yield.

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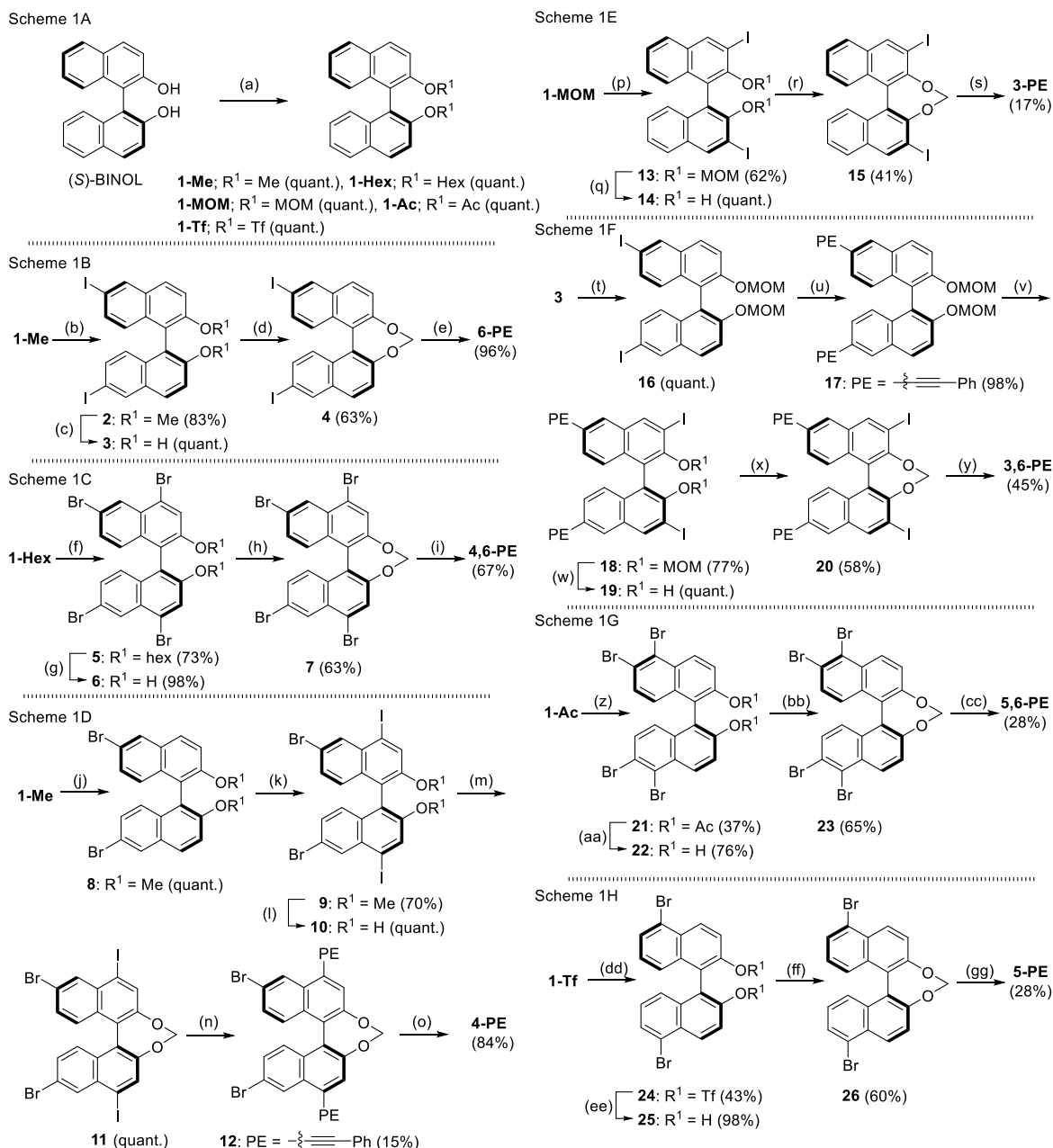
Scheme 1. Synthetic routes for **3-PE**, **4-PE**, **5-PE**, **6-PE**, **3,6-PE**, **4,6-PE**, and **5,6-PE**.

Conditions. (a) For **1-Me**; MeI (2.4 eq), K$_2$CO$_3$ (2.6 eq), DMF, rt, 5 h, quant. For **1-Hex**; 1-bromohexane (3.0 eq), K$_2$CO$_3$ (4.0 eq), DMF, 80 °C, quant. For **1-MOM**; MOMCl (2.2 eq), NaH (2.5 eq), DMF, 0 °C, quant. For **1-Ac**; AcCl (2.2 eq), NEt$_3$ (2.5 eq), CH$_2$Cl$_2$, 0 °C, quant. For **1-Tf**; Tf$_2$O (2.2 eq), DIPEA (2.5 eq), CH$_2$Cl$_2$, 0 °C, quant. (b) DIH (1.1 eq), TfOH (2.0 eq), 1,4-dioxane, 3 h, 83%, (c) BBr$_3$ (2.2 eq), CH$_2$Cl$_2$, 0 °C to rt, 1 h, quant., (d) CH$_2$Br$_2$ (5.0 eq), K$_2$CO$_3$ (6.0 eq), DMF, 80 °C, 63%, (e) Ethynylbenzene (2.2 eq), PdCl$_2$(PPh$_3$)$_2$ (0.05 eq), CuI (0.05 eq), NEt$_3$ (5.0 eq), THF, rt, 1 h, 96%, (f) Br$_2$ (5.0 eq), CH$_2$Cl$_2$, 0 °C, 10 min., 73%, (g) BBr$_3$ (2.2 eq), CH$_2$Cl$_2$, 0 °C to rt, 1 h, 98%, (h) CH$_2$Br$_2$ (5.0 eq), K$_2$CO$_3$ (6.0 eq), DMF, 80 °C, 12 h, 63%, (i) Ethynylbenzene (5.0 eq), PdCl$_2$(PPh$_3$)$_2$ (0.05 eq), CuI (0.05 eq), NEt$_3$ (5.0 eq), DMF, 80 °C, 14 h, 67%, (j) NBS (2.2 eq), CH$_2$Cl$_2$, rt, 2 h, quant., (k) DIH (1.1 eq), TfOH (2.0 eq), 1,4-dioxane, 3 h, 70%, (l) BBr$_3$ (2.2 eq), CH$_2$Cl$_2$, 0 °C to rt, 1 h, quant., (m) CH$_2$Br$_2$ (5.0 eq), K$_2$CO$_3$ (6.0 eq), DMF, 80 °C, 12 h, quant., (n) Ethynylbenzene (2.2 eq), PdCl$_2$(PPh$_3$)$_2$ (0.05 eq), CuI (0.05 eq), NEt$_3$ (5.0 eq), THF, 0 °C, 1 h, 15%, (o) n-BuLi (2.2 eq), THF, –78 °C, 30 min., 84%, (p) n-BuLi (3.0 eq), I$_2$ (3.0 eq), THF, –78 °C to rt, 5 h, 62%, (q) 4 M HCl in dioxane (excess.), 2 h, quant., (r) CH$_2$Br$_2$ (3.0 eq), NaH (4.0 eq), DMF, 0 °C to 80 °C, 41%, (s) Ethynylbenzene (2.2 eq), PdCl$_2$(PPh$_3$)$_2$ (0.05 eq), CuI (0.05 eq), NEt$_3$ (5.0 eq), THF, rt, 3 h, 17%, (t) MOMCl (2.2 eq), NaH (2.5 eq), DMF, 0 °C, quant., (u) Ethynylbenzene (2.2 eq), PdCl$_2$(PPh$_3$)$_2$ (0.05 eq), CuI (0.05 eq), NEt$_3$ (5.0 eq), THF, rt, 2 h, 98%, (v) n-BuLi (3.0 eq), I$_2$ (3.0 eq), THF, –78 °C to rt, 5 h, 77%, (w) 4 M HCl in dioxane (excess.), 2 h, quant., (x) CH$_2$Br$_2$ (3.0 eq), NaH (4.0 eq), DMF, 0 °C to 80 °C, 58%, (y) Ethynylbenzene (2.2 eq), PdCl$_2$(PPh$_3$)$_2$ (0.05 eq), CuI (0.05 eq), NEt$_3$ (5.0 eq), THF, 40 °C, 14 h, 45%, (z) Br$_2$ (10 eq), AcOH, rt, 5 h, 37%, (aa) 15% NaOH aq/THF/MeOH=1:2:1, 80 °C, 76%, (bb) CH$_2$Br$_2$ (5.0 eq), K$_2$CO$_3$ (6.0 eq), DMF, 80 °C, 13 h, 65%, (cc) Ethynylbenzene (5.0 eq), PdCl$_2$(PPh$_3$)$_2$ (0.05 eq), CuI (0.05 eq), NEt$_3$ (5.0 eq), DMF, 50 °C, 14 h, 28%, (dd) Br$_2$ (10 eq), AcOH, 100 °C, 5 h, 43%, (ee) 15% NaOH aq/THF/MeOH=1:2:1, 80 °C, 98%, (ff) CH$_2$Br$_2$ (5.0 eq), K$_2$CO$_3$ (6.0 eq), DMF, 80 °C, 12 h, 60%, (gg) Ethynylbenzene (2.2 eq), PdCl$_2$(PPh$_3$)$_2$ (0.05 eq), CuI (0.05 eq), NEt$_3$ (5.0 eq), DMF, 80 °C, 14 h, 28%

Scheme 2. Synthetic routes for **7-PE**, **8-PE**, **6,7-PE**, and **3,4,6-PE**.

Scheme 2A

27 (quant.)

(*S*)-**27** (80%)

28: R = Br (58%)
29: R = I (59%)

7-PE
(28%)

Scheme 2B

(*S*)-**27**

30 (quant.)

31: R¹ = Me (88%)
32: R¹ = H (quant.)

33 (79%)

6,7-PE
(38%)

Scheme 2C

34 (68%)

35 (94%)

8-PE
(94%)

36: R = –≡–TMS (96%)
37: R = –≡–TMS (76%)
38: R = –≡–H (quant.)

Scheme 2D

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39: R = H (28%)
40: R = -CH₂- (59%)

3,4,6-PE
(43%)

Conditions; (a) FeCl₃ (1.7 eq), H₂O, 100 °C, 5 h, quant., (b) (-)-Menthyl Chloroformate (2.2 eq), NEt₃ (2.6 eq), CH₂Cl₂, 0 °C, 10 min., 15% NaOH aq./THF/MeOH=1:2:1, 80 °C, 80%, (c) CH₂Br₂ (5.0 eq), K₂CO₃ (6.0 eq), DMF, 80 °C, 12 h, 60%, (d) *n*-BuLi (2.2 eq), I₂ (2.2 eq), THF, –78 °C, 30 min., 59%, (e) Ethynylbenzene (2.2 eq), PdCl₂(PPh₃)₂ (0.05 eq), CuI (0.05 eq), NEt₃ (5.0 eq), THF, rt, 2 h, 28%, (f) MeI (2.4 eq), K₂CO₃ (2.6 eq), DMF, rt, 5 h, quant., (g) DIH (1.1 eq), TfOH (2.0 eq), 1,4-dioxane, rt, 3 h, 88%, (h) BBr₃ (2.2 eq), CH₂Cl₂, 0 °C to rt, 1 h, quant., (i) CH₂Br₂ (5.0 eq), K₂CO₃ (6.0 eq), DMF, 80 °C, 12 h, 79%, (j) Ethynylbenzene (10 eq), PdCl₂(PPh₃)₂ (0.05 eq), CuI (0.05 eq), NEt₃ (10.0 eq), DMF, 80 °C, 8 h, 38%, (k) NaNO₂ (1.0 eq), H₂SO₄ (6.6 eq), KI (2.0 eq), THF/H₂O=1:3, –10 °C, 68%, (l) TMS-acetylene (1.2 eq), PdCl₂(PPh₃)₂ (0.05

eq), CuI (0.05 eq), NEt₃ (1.5 eq), THF, rt, 1 h, 94%, (m) Cu-TMEDA (0.03 eq), CH₂Cl₂, rt, 2 h, 96%, (n) CH₂Br₂ (5.0 eq), K₂CO₃ (6.0 eq), DMF, 80 °C, 12 h, 76%, (o) TBAF (4.0 eq), THF, 0 °C, 1 h, quant., (p) PhI (2.2 eq), Pd(PPh₃)₄ (0.05 eq), CuI (0.05 eq), NEt₃/DMF=1:2, 80 °C, 1 h, 94%. (q) Br₂ (10 eq), CH₂Cl₂, 0 °C, 14 h, 28% (r) CH₂Br₂ (5.0 eq), K₂CO₃ (6.0 eq), DMF, 80 °C, 12 h, 59%, (s) Ethynylbenzene (10 eq), PdCl₂(PPh₃)₂ (0.05 eq), CuI (0.05 eq), NEt₃ (10.0 eq), DMF, 80 °C, 14 h, 43%

1.2.2. Synthesis of 6,7-PE (Scheme 2B)

The hydroxy group of (*S*)-**27** was protected by a methyl group (**30**, quantitative yield), and the 6-position was iodinated using DIH (**32**, 88% yield), followed by a series of reactions, including the Sonogashira reaction, to synthesize **6,7-PE** in 38% yield.

1.2.3. Synthesis of 8-PE (Scheme 2C)

Starting from 8-amino-2-naphthol, the synthesis of **8-PE** involved the iodination of the amino group via the diazonium group (**34**, 68% yield) [34], introduction of trimethylsilylacetylene via the Sonogashira reaction (**35**, 94% yield), and oxidative dimerization to yield **36** (96% yield). After one-carbon cross-linking (**37**, 76% yield), the TMS group was removed (**38**, quantitative yield) and racemic **8-PE** was synthesized by the Sonogashira reaction with benzene iodide in 94% yield. Finally, optical resolution was performed by chiral column chromatography with a portion of the synthesized racemic **8-PE** to obtain (*S*)-**8-PE** (see the Experimental Section for the details).

1.2.4. Synthesis of 3,4,6-PE (Scheme 2D)

Hexaphenylethynyl **3,4,6-PE** was synthesized by further bromination of tetrabromine **6** to afford compound **39** (28% yield), followed by one-carbon cross-linking (**40**, 59% yield) and Sonogashira reaction at six reaction sites to synthesize **3,4,6-PE** in 43% yield.

2. X-ray structure analysis of 8-PE-MOM and 8-PE

We succeeded in synthesizing **3-PE** to **3,4,6-PE** by the above synthetic routes, in which phenylethynyl groups were introduced onto the binaphthyl derivatives in a comprehensive manner. Among these compounds, particular focus was placed on X-ray structural analysis of (*S*)-**8-PE** because of its intriguing structure featuring a highly twisted π system. Additionally, racemic **8-PE-MOM**, in which the hydroxy groups were protected by MOM groups instead of a one-carbon bridge, was investigated. The X-ray structures of **8-PE-MOM** and **8-PE** are shown in Figure 2, and a concise summary of selected carbon–carbon distances, characteristic bond angles, and dihedral angles of these compounds is given in Table 1. [34]
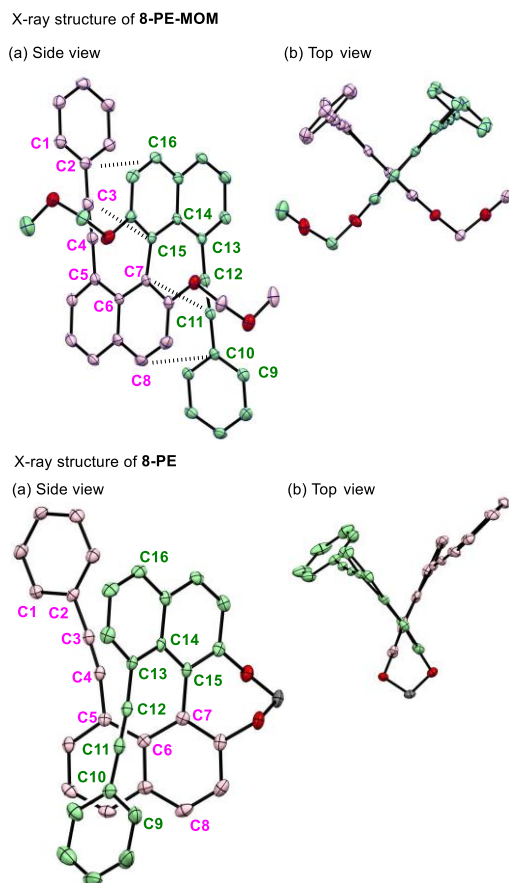
X-ray structure of **8-PE-MOM**

(a) Side view   (b) Top view

X-ray structure of **8-PE**

(a) Side view   (b) Top view

Figure 2. X-ray structures of compounds **8-PE-MOM** and **8-PE**: (a) side view and (b) top view.

Table 1. Distances (Å), angles (°), and dihedral angles (°) of compounds **8-PE-MOM** and **8-PE**

		8-PE-MOM	8-PE
Distance (Å)	C2-C16	3.353(3)	4.302(6)
	C3-C15	3.275(3)	3.539(7)
	C4-C15	2.822(3)	2.958(7)
	C7-C12	2.800(2)	2.928(5)
	C7-C11	3.254(3)	3.407(4)
	C8-C10	3.412(3)	3.885(5)
Angle (°)	C2-C3-C4	174.9(2)	176.7(4)
	C3-C4-C5	174.0(2)	167.7(4)
	C10-C11-C12	176.7(2)	175.4(4)
	C11-C12-C13	173.9(2)	172.7(4)
Dihedral angle (°)	C1-C2-C5-C6	−85.2(2)	157.9(4)
	C6-C7-C15-C14	−85.1(2)	60.6(6)
	C9-C10-C13-C14	−94.8(2)	87.0(4)

The structural features of **8-PE-MOM** revealed by X-ray structural analysis were as follows. Normally, two aromatic rings linked by a triple bond are oriented in the same plane for resonance stabilization[36–38]. However, the naphthalene and benzene rings linked by a triple bond in **8-PE-MOM** showed nearly orthogonal alignment (dihedral angles of C1–C2–C5–C6 = −85.2(2)° and C9–C10–C13–C14 = −94.8(2)°). Notably, the intramolecular distances between the specific carbon pairs C2 and C16, C3 and C15, C8 and C10, and C7 and C11 were 3.353(3), 3.275(3), 3.412(3), and 3.254 (3) Å, respectively, which are shorter than the standard π–π interplane distance of 3.5 Å. In other words, this indicates that π–π interactions between the another naphthalene and benzene rings take precedence over resonance stabilization through the triple bond between the naphthalene and benzene rings The angle of the triple bond connecting the benzene and naphthalene rings was 173.9(2)° to 176.7(2)°, indicating a nearly linear structure.

Conversely, the X-ray structure of compound **8-PE**, in which the two hydroxy groups were bridged by a single carbon atom, showed that the dihedral angle between the two naphthalene rings narrowed to 60.6(6)° because of the bridging. As a result, the molecule was greatly distorted. For example, the angle of the triple bond, ∠ C3–C4–C5, was significantly bent (167.7(4)°). Furthermore, the dihedral angle between the naphthalene and benzene rings through the triple bond was almost orthogonal with a C9–C10–C13–C14 dihedral angle of 87.0(4)°, while the C1–C2–C5–C6 dihedral angle was 157.9(4)°. Therefore, the distances C2–C16 and C8–C10 increased to 4.302(6) Å and 3.885(5) Å, respectively, indicating that these atoms were not in contact.

3. Optical properties of 3-PE to 3,4,6-PE

3.1. Optical properties of 3-PE to 8-PE

Next, the optical properties of the compounds were investigated. The ultraviolet–visible (UV-vis), circular dichroism (CD), fluorescence (FL), and CPL spectra of **3-PE** to **8-PE**, each featuring two phenylethynyl groups, are shown in Figure 3a–d. In this section, we focus on the UV-vis spectra of these compounds (Figure 3a). These compounds possess a binaphthol skeleton bridged by a single carbon, with the sole distinction being the positioning of the phenylethynyl groups. Despite these structural similarities, their UV-vis spectra exhibited significant diversity. The compounds with no phenylethynyl groups parallel to the axis connecting the two naphthalene rings (**3-PE**, **6-PE**, and **7-PE**) showed similar spectral shapes, with weak absorption intensity at the longest wavelength of around 360 nm. In contrast, **5-PE** with a phenylethynyl group at position 5 showed a marked increase in the absorption intensity at the longest wavelength, and **8-PE** with a phenylethynyl group at position 8 exhibited elongation in the longest wavelength absorption and an increase in the absorption intensity. Furthermore, **4-PE** with a phenylethynyl group on the line of the binaphthyl bond axis showed both a significant increase in the absorption intensity and an increase in the wavelength, indicating that the π system was most effectively extended.

Quantum chemical calculations supported the above findings. [39] The highest occupied molecular orbitals (HOMOs), lowest unoccupied molecular orbitals (LUMOs), and HOMO–LUMO

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energy gaps of **3-PE** to **8-PE** by DFT at the B3LYP/6-31+G(d,p) level of theory are shown in Figure 4. The HOMO–LUMO coefficients are spread over the entire molecule for all of the compounds, there is no significant difference in the extension of the π system depending on the position of the phenylethynyl group. However, the oscillator strengths of the HOMO–LUMO transition and the HOMO–LUMO energy levels reveal that **4-PA** and **5-PA** exhibit large oscillator strengths, which is consistent with the large measured molar absorption coefficients of **4-PE** and **5-PE**. Furthermore, the increases in the HOMO levels and the decreases in the LUMO levels of **4-PA** and **8-PA**, accompanied by decreases in the HOMO–LUMO gaps, indicate that the absorption at the longest wavelengths of these compounds shifts toward longer wavelengths, which is consistent with the actual measurements.

Next, we describe the FL spectra of compounds **3-PE** to **8-PE** (Figure 3b). Among the compounds studied, **4-PE** exhibited the most extensive π system, showing the largest molar absorption coefficient and the longest absorption wavelength in the UV-vis spectrum. Consequently, in the FL spectrum, **4-PE** also emitted at significantly longer wavelengths (411 and 436 nm) than the other compounds.

The CD and CPL spectra of **3-PE** to **8-PE** are shown in Figure 3c and 3d, respectively. In the CD spectra, all of the compounds featuring *S* axial chirality exhibited a negative sign at the maximum absorption wavelength, except for (*S*)-**7-PE**, which notably showed a significantly larger positive signal. Moreover, (*S*)-**7-PE** showed a positive signal in the CPL spectrum. This intriguing observation will be subjected to in-depth discussion in a forthcoming paper, in which considerations based on computational chemistry will be presented to shed light on this phenomenon.
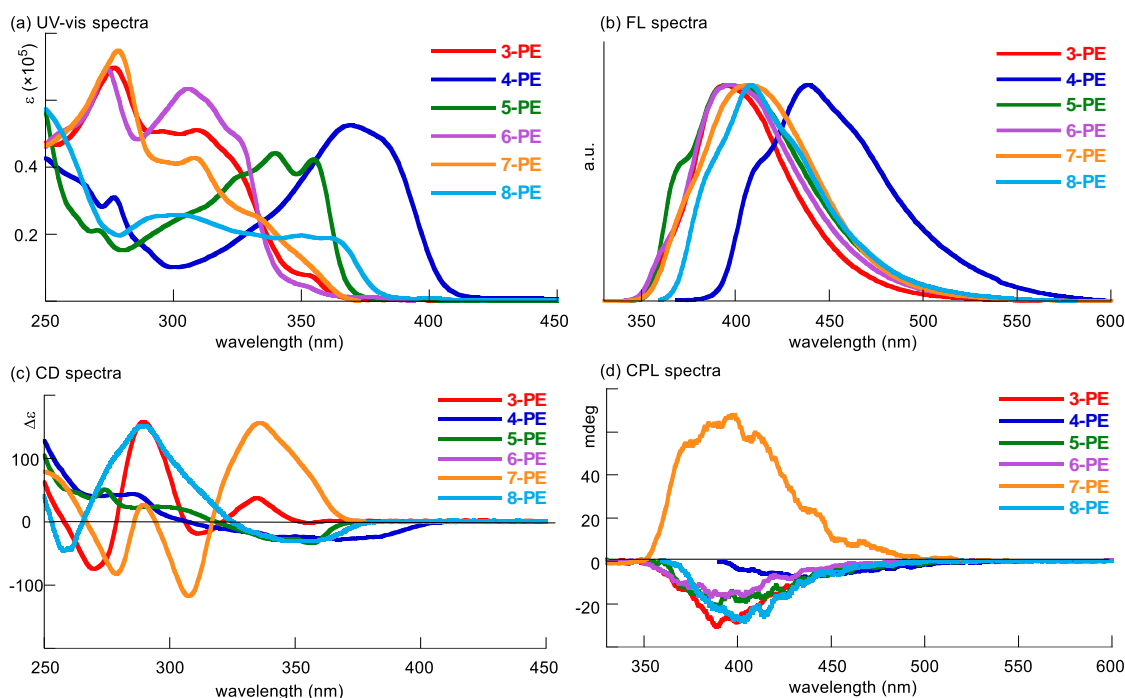

Figure 3. UV-vis, CD, FL, and CPL spectra of **3-PE** to **8-PE**.

Conditions; (a) UV-vis; CHCl$_3$, 1.0×10^{-5} M, 25 °C. (b) FL; 1.0×10^{-5} M in CHCl$_3$, 25 °C, **3-PA** (λ_{Ex}=330 nm), **5-PA** ((λ_{Ex} =330 nm), **4-PA** ((λ_{Ex} =359 nm), **6-PA** ((λ_{Ex} =274 nm), **7-PA** ((λ_{Ex} =279 nm), and **8-PA** ((λ_{Ex} =350 nm). (c) CD; CHCl$_3$, 1.0×10^{-5} M, 25 °C. (d) CPL; CHCl$_3$, 1.0×10^{-5} M, 25 °C.
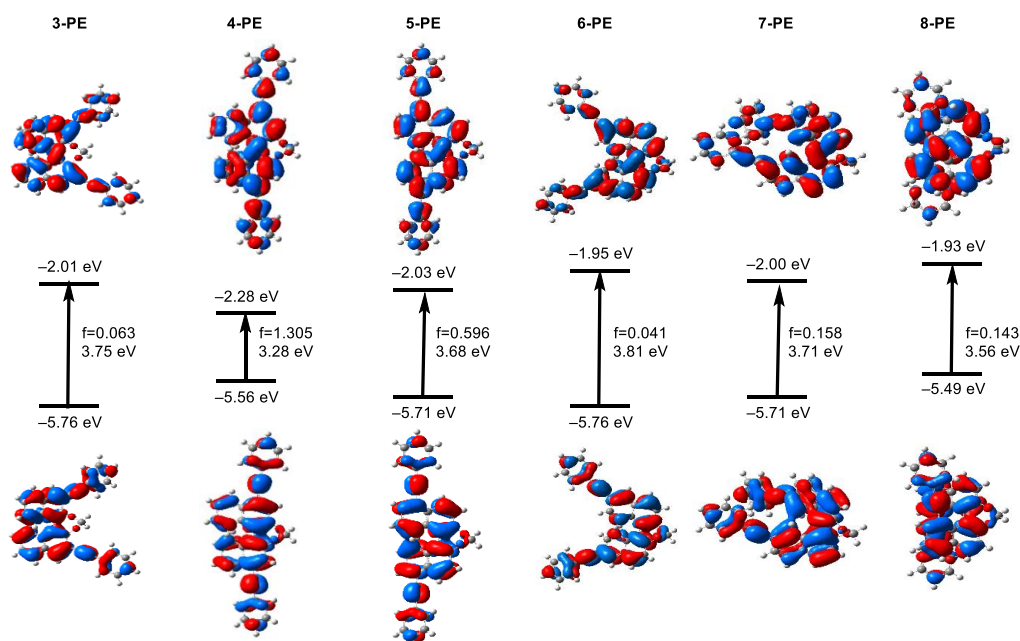
Figure 4. HOMOs, LUMOs, and HOMO–LUMO energy gaps of compounds **3-PE** to **8-PE** by DFT at the B3LYP/6-31+G(d,p) level of theory.

3.2. Optical properties of the compounds with four and six phenylethynyl groups (3,6-, 4,6-, 5,6-, and 6,7-PE and 3,4,6-PE)

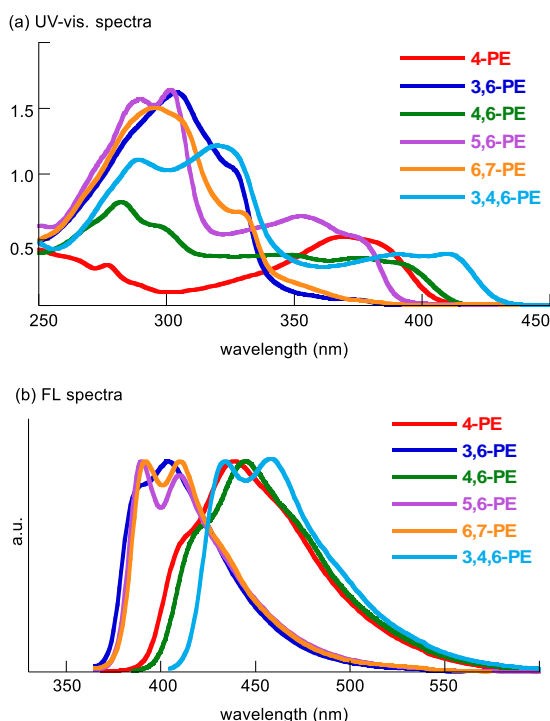The UV-vis and FL spectra of the compounds featuring four and six phenylethynyl groups, as well as those of **4-PE**, are shown in Figure 5a and 5b. **4-PE** exhibited absorption and emission at longer wavelengths than the other compounds, as mentioned above. Similar spectral characteristics were observed for the compounds in which the phenylethynyl groups were aligned parallel to the naphthalene axis, such as **4,6-PE**, **5,6-PE**, and **3,4,6-PE**, displaying absorption (Figure 5a) and emission (Figure 5b) predominantly in the longer wavelength region.
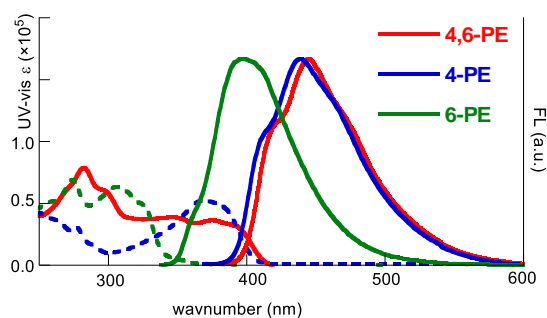

Figure 5. (a) UV-vis and (b) FL spectra of **4-PE**, **3,6-PE** to **6,7-PE**, and **3,4,6-PE**.

Conditions; (a) UV-vis; 1.0×10^{-5} M in $CHCl_3$, 25 °C, (b) FL; 1.0×10^{-5} M in $CHCl_3$, 25 °C, **4-PA** ((λ_{Ex} =359 nm), **3,6-PA** (λ_{Ex} =330 nm), **4,6-PA** (λ_{Ex} =370 nm), **5,6-PA** λ_{Ex} =330 nm), **6,7-PA** (λ_{Ex} =330 nm), and **3,4,6-PA** (λ_{Ex} =395 nm).

Figure 6. UV-vis (dashed) and FL (solid) spectra of **4,6-PE**, **4-PE**, and **6-PE**

Here, we focus on **4,6-PE** with four phenylethynyl groups and **4-PE** and **6-PE** with two phenylethynyl groups (Figure 6). The UV-vis spectrum of **4,6-PE** revealed no extended absorption wavelengths compared with that of **4-PE**, despite the presence of four phenylethynyl groups. In addition, the fluorescence spectrum of **4,6-PE** closely resembled that of **4-PE**. These results suggest that the addition of the phenylethynyl group at the 6-position of **4,6-PE** has a minimal effect on extending the π system in both the ground and excited states. This indicates that the absorption at longer wavelengths and the emission predominantly originate from the **4-PE** backbone. This observed phenomenon agrees with the results of computational chemistry. The HOMO and LUMO of **4,6-P**E are shown in Figure 7, demonstrating that the phenylethynyl group at position 6 makes a negligible contribution to both the HOMO and LUMO states. Likewise, for **6,7-PE** and

3,4,6-PE, the distributions of the HOMO and LUMO coefficients are poor for the phenylethynyl group at position 6, indicating their limited contribution to extending the π system.
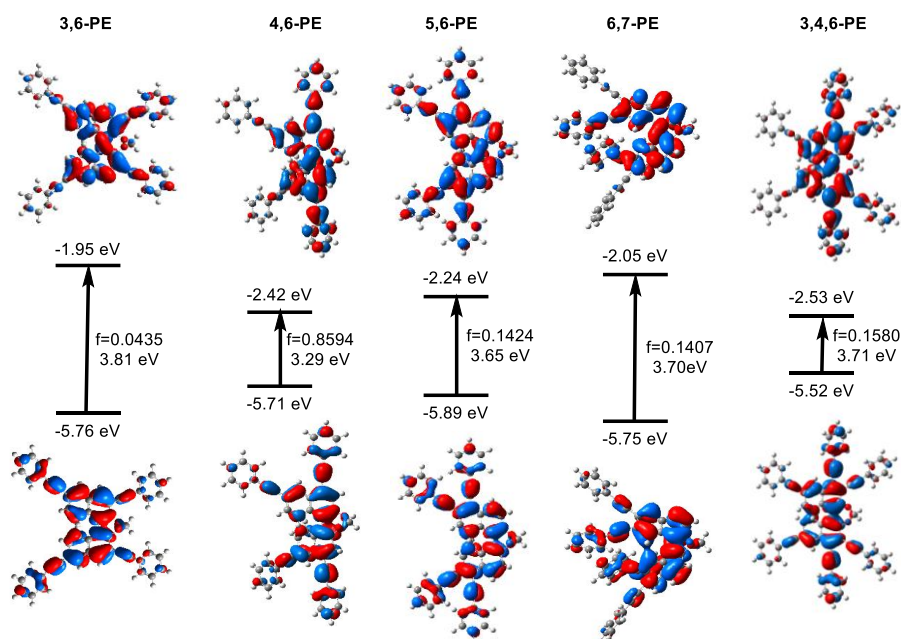

Figure 7. HOMOs, LUMOs, and HOMO–LUMO energy gaps of compounds **3,6-PE** to **3,4,6-PE** DFT at the B3LYP/6-31+G(d,p) level of theory.
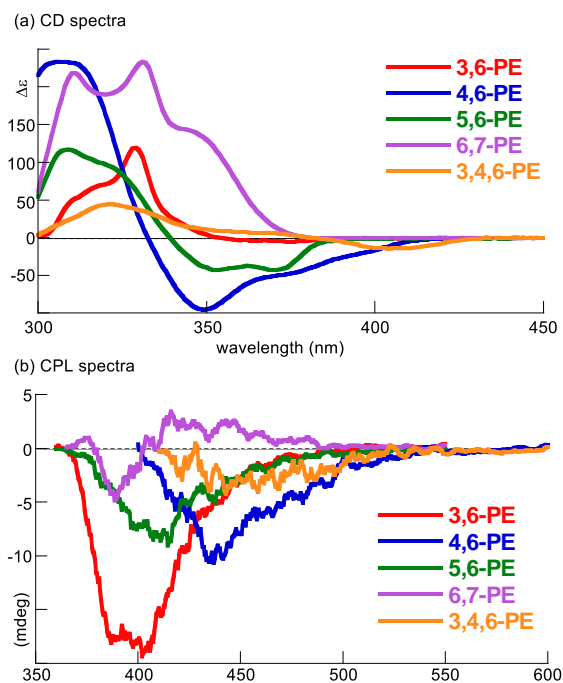

Figure 8. CD and CPL spectra of the compounds with four and six phenylethynyl groups.

Finally, the CD and CPL spectra of the compounds with four and six phenylethynyl groups are summarized in Figure 8, and the optical property data (absorption wavelengths (λ_{UV}), emission wavelengths (λ_{FL}), fluorescence quantum yields (Φ), fluorescence lifetimes (τ), fluorescence radiative rate constants (k_r), nonradiative rate constants (k_{nr}), absorption dissymmetry factors (g_{abs}), and luminescence dissymmetry factors (g_{lum})) for all of the compounds synthesized in this study are summarized in Table 2. The CD spectral intensities of the poly-substituted phenylethynyl compounds at the longest wavelengths were generally small and exhibited a negative sense. Their CPL intensities were also smaller than those of the corresponding di-substituted phenylethynyl compounds. Moreover, upon comparison of the *g* values among the di-, tetra-, and hexa-substituted compounds, the disubsutitued compounds showed approximately one order of magnitude larger *g* values.

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Table 1. Optical properties of **3-PE** to **3,4,6-PE**.

compound	λ_{UV} (nm)	λ_{FL} (nm)	Φ (%)	τ (ns)	$k_r \times 10^{-8}$	$k_{nr} \times 10^{-8}$	g_{abs} ($\times 10^3$)	g_{lum} ($\times 10^3$)
3-PA	277, 356	396	30	2.76	1.08	2.55	−0.22	−1.5
4-PA	369	411, 436	77	1.29	5.99	1.75	−0.50	−0.52
5-PA	355	370, 397	63	2.06	3.07	1.79	−0.84	−1.9
6-PA	275, 327	398	36	3.2	1.12	2.01	−1.5	−1.8
7-PA	279, 311	407	37	4.13	0.90	1.53	1.1	5.6
8-PA	302, 360	408	41	2.46	1.66	2.42	−1.2	−1.8
3,6-PA	304, 370	389, 404	34	5.7	1.65	1.15	−1.3	−1.3
4,6-PA	418	429, 445	80	1.7	4.81	1.18	−0.70	−0.63
5,6-PE	367	390, 410	88	2.1	4.04	0.57	−0.80	−0.65
6,7-PE	295, 333	392, 410	21	9.2	0.23	0.86	−0.79	−0.28
3,4,6-PE	410	433, 459	81	1.7	4.65	1.07	−0.27	−0.27

4. Conclusion

In this study, we synthesized and evaluated a series of compounds (**3-PE** to **3,4,6-PE**) obtained by cross-linking the hydroxy groups of BINOL with a methylene chain and integrating phenylethynyl groups in all of the possible substitution sites. In particular, in terms of the synthetic methodology, we developed a method for selectively introducing a bromine atom at the 5-position of the BINOL skeleton by triflation of the hydroxy group. In addition, after bromination of the 6-position followed by iodination of the 4-position, a new conversion method was developed, including the Sonogashira reaction of iodine at the 4-position and the removal of bromine at the 6-position. By combining these and conventional methods, **3-PE** to **3,4,6-PE** were synthesized. X-ray structural analysis of **8-PE** and **8-PE-MOM** revealed that the orientation of the phenylethynyl group differed depending on whether the hydroxy group of BINOL was bridged with a methylene chain or MOM. A meticulous examination of their optical properties was performed. The findings revealed that there were significant variations in the extent of the π-system extension contingent upon the position of the phenylethynyl group. Of particular note is the discovery that introducing phenylethynyl groups aligned parallel to the naphthalene ring connecting the axis is effective for extending the π system and enhancing the fluorescence quantum yield. This comprehensive study systematically elucidates the structural and optical property correlations within binaphthyl derivatives, providing insights into their design for specific functional applications.

Supporting Information

All Experimental procedures, X-ray data for 8-PE and 8-PE-MOM, spectroscopic data for all new compounds, and computational data (PDF).

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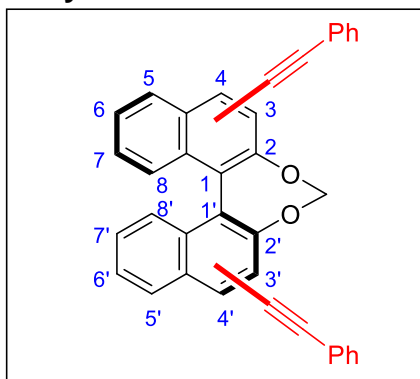
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