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Axially Chiral *peri*-Xanthenoxanthenes as a Circularly Polarized Luminophore

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Supporting Information Placeholder

ABSTRACT: A series of axially chiral *peri*-xanthenoxanthenes (PXXs) were synthesized from BINOL without optical resolution. These are the first examples of chiral PXXs. Among them, PXX **5** with two naphthalene rings connected via a methylenedioxy bridge and a chiral axis displayed intense fluorescence (FL) and circularly polarized luminescence (CPL) both in solution (Φ_{FL} of 0.72 and $|g_{lum}|$ of 1.4×10^{-3}) and in the solid state (Φ_{FL} of 0.13 and $|g_{lum}|$ of 4.8×10^{-3}). The bridged structure of PXX **5** adjusts the angle between the vectors of the electric and magnetic transition dipole moments, which is essential for showing intense CPL activity.

Heteroatom-embedded polycyclic aromatic hydrocarbons (PAHs) have been actively investigated owing to the unique optical, physical, and chemical properties that are often superior to those of PAHs themselves.¹ Among the heteroatom-embedded PAHs, the *peri*-xanthenoxanthene (PXX) structure (1 in Figure 1), which was first reported by Pummerer and co-workers in 1926,² has recently been of research interest because of potential utility in devices such as light-emitting diodes, photovoltaic cells, field-effect transistors, and rollable displays.^{1a,3–5} For example, Bonifazi and co-workers reported several π -extended PXXs with narrow HOMO–LUMO gaps.⁵ In contrast, chiral PXXs have great potential for use in chiroptical materials science, but have yet to be reported.

The development of circularly polarized luminescence (CPL) organic dyes has been a recent focus of research,⁶ and CPL dyes are recognized to be next-generation materials.⁷ PXXs are an ideal target in this research due to their high fluorescence (FL) both in solution and in the solid state.^{3f,i,j,5b,c} Because synthetic methods for PXXs are limited and hydroxy group-appended PXXs are highly unstable,^{5c} development of CPL-active PXXs is challenging.

We have developed several CPL-active PAH dyes with axial chirality.⁸ Among them, naphthalene tetramers have been very useful as dyes or chiral scaffolds.^{8a,b,e} We envisioned that axially chiral PXXs could be synthesized by application of our previous synthetic strategy for naphthalene tetramers. Here, we report fluorescent PXXs 2–5 as the first examples of chiral PXXs (Figure 1); 2 and 3 are PXX dimers with a chiral axis, and PXXs 4 and 5 contain two naphthalene rings with two chiral axes. PXXs 2 and 4 possess butoxy groups, while 3 and 5 possess methylenedioxy-bridges between adjacent aryl rings. Among them, PXX 5, which could be synthesized from BINOL in only three steps, exhibited intense FL and CPL both in solution and in the solid state. Although solid-state CPL is advantageous in many applications, such dyes are quite rare.^{8a,b,d,9} The bridged structure in PXX 5 leads to a narrow angle between the adjacent aryl rings and is essential for achieving CPL activity.



Figure 1. (a) Chemical structures of PXX (1) and axially chiral PXXs 2–5 and (b) photographs of solutions of 1–5 and powdered 5. Conditions for solutions: 1,4-dioxane, 5.0×10^{-6} M, rt. The values in an 1-octanol solution are given in parentheses.

Scheme 1. Synthesis of Chiral PXXs 2 and 5



PXXs 2–5 had to be synthesized without using hydroxy PXXs as intermediates due to their instability.¹⁰ The synthetic route to 2 from (*R*)-BINOL is shown in Schemes 1a and S1. Mono-ol (*R*)-6 was obtained by conventional protection and hydroxylation of (*R*)-BINOL (71% in 2 steps). Oxidative coupling¹¹ of (*R*)-6 gave a diastereomer pair of naphthalene tetramers, (*R*,*R*,*R*)-7 (71%) and (*R*,*S*,*R*)-7 (13%), which could be easily separated by silica gel column chromatography. Subsequent butylation and deprotection afforded tetraols 9. The Kamei–Shimada oxidation¹² of 9 gave 2 (23– 36%). It should be noted that a pair of diastereomers 9 was converted into a pair of enantiomers 2; (*R*,*R*,*R*)-9 and (*R*,*S*,*R*)-9 were converted into (*R*)-2 and (*S*)-2, respectively. Dimer 3 was prepared by a similar method (Scheme S1). However, dimers 2 and 3 required a six-step synthesis with relatively low yields due to multiple oxidations in the final step.

The synthetic route to **5** is shown in Schemes 1b and S2. (*R*)-**10** was obtained by sequential methylene-bridging and hydroxylation of (*R*)-BINOL (69% in 2 steps). Oxidative coupling of (*R*)-**10** gave (*R*,*R*,*R*)-**11** (26%) and (*R*,*S*,*R*)-**11** (60%). (*R*,*S*,*R*)-**11** obtained in a larger amount was converted into (*R*,*R*)-**5** in a high yield (77%). Moreover, (*R*,*R*)-**5** could be obtained from (*R*)-**10** directly, although the yield was modest (7%). (*R*,*R*)-**4** also could be prepared easily (Scheme S2).

Absolute configurations of 7 and 11 were determined by an Xray structure of their common derivative, bridged naphthalene tetramer 12 (Figure S1). The solubilities of 4 and 5 were higher than those of 2 and 3; 3 mg/mL for 1, 0.6 mg/mL for 2, 0.3 mg/mL for 3, 3 mg/mL for 4, and 2 mg/mL for 5 in CHCl₃ at room temperature. DFT-optimized structures of PXXs **2–5** are shown in Figure 2.¹³ Each aryl ring maintained planarity, and the dihedral angles between the adjacent aryl rings are completely dependent on the substituents. The aryl rings of **2** and **4** possessing butoxy groups are orthogonal (81–92°), the angles of which are typical for biaryls. In contrast, the bridges of **3** and **5** create a *cisoid* conformation (49°). These narrow angles were very close to the corresponding dihedral angles of X-ray structures of (*R*,*R*)-**5** (Figure 3) and (*R*,*S*,*R*)-**12** (Figure S1) (46–48°). DFT calculations suggested that angular ranges within 2.7 kcal/mol from the most stable structure were 50– 120° for **2** and 35–65° for **3**, indicating that the bridge leads to rigid structures (Figure S3). The difference between orthogonal and *cisoid* conformations should lead to different chiroptical characteristics. It is empirically known that the CPL intensities of binaphthyl compounds are correlated with their dihedral angles.^{8a,c,14}



Figure 2. DFT-optimized structures and dihedral angles of adjacent aromatic rings of **2–5** at the B3LYP/6-31G(d,p) level. The angles between the adjacent aryl rings are shown.



Figure 3. X-ray crystal structure of (R,R)-5. Left: space-filling model. Right: ORTEP diagrams (thermal ellipsoids at 50% probability).

We next analyzed the (chir)optical properties of solutions of 2– 5 (Figures 1b and 4). The absorption edges and the spectral shapes of 2 and 4 are very similar to those of 1, suggesting that the adjacent aryl rings are electronically independent due to the orthogonal twisting (Figure 4b). In contrast, the absorption edges of bridged PXXs 3 and 5 were red-shifted by partial conjugation between adjacent aryl rings. Time-dependent (TD) DFT calculations indicated the longest absorptions were optically permitted and caused by the transition from HOMO to LUMO. Gaps were 3.32 eV for 1, 3.29 eV for 2, 2.90 eV for 3, 3.28 eV for 4, and 2.99 eV for 5 (Figure

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S4). The HOMO levels of 1–5 were similar (–4.51 to –4.74 eV) while the bridged PXXs **3** and **5** had lower LUMO levels (–1.75 to –1.77 eV) than 1, 2, and 4 (–1.23 to –1.41 eV). This is probably due to the partial conjugation between adjacent aryl rings in the excited state.

CD intensities of 2–5 differed due to the type and dihedral angles of the aromatic rings (Figure 4a). It is noted that the signs at the longest absorption wavelength (450–500 nm) of (*R*)-2 ($\Delta \varepsilon = -3$) and (*R*)-3 ($\Delta \varepsilon = +5$) were opposite from each other despite the fact that they had the same absolute configuration. Salvadori and coworkers reported the relationship between the dihedral angle of the naphthalene rings and the theoretical CD intensity of 1,1'-binaphthyl.¹⁵ For PXX dimer 2, we investigated the relationship by TD DFT calculations (Figure S5). The CD intensities at the longest wavelength signals were significantly affected by the angle, and the sign was inverted at the angle of 80°.

PXXs 2–5 showed light-blue or bluish-green fluorescence with high fluorescence quantum yields in 1,4-dioxane ($\Phi_{FL,dioxane}$) of 0.56–0.89, and they are comparable or superior to 1 ($\Phi_{FL,dioxane}$ of 0.66)^{3f} (Figures 1b and 4d). The λ_{em} values of 3 and 5 were redshifted as compared to those of 2 and 4, respectively, which reflected the λ_{abs} . The Stokes shifts of bridged PXXs 3 (710 cm⁻¹) and 5 (600 cm⁻¹) were smaller than those of 2 (1580 cm⁻¹) and 4 (740 cm⁻¹), suggesting that the bridge leads to rigidity in the excited states. Indeed, each of the optimized structures of 3 and 5 in the excited states were very similar to those in the ground states (Figure S6). Dihedral angles of the biaryls for 2 and 4 are changed somewhat by the excitation; the values of the angle change were 26° for 2, 4° for 3, 30–34° for 4, and 2° for 5.

To our delight, the bridged PXXs, (*R*)-3 and (*R*,*R*)-5, displayed clear (+)-CPL (Figure 4c). The $g_{lum,dioxane}$ values were +1.3 × 10⁻³ for (*R*)-3 and +1.0 × 10⁻³ for (*R*,*R*)-5, where the dissymmetry factor g_{lum} is defined as $2(I_L - I_R)/(I_L + I_R)$; I_L and I_R represent the intensity of left and right CPL, respectively. The signs of the CPL agreed with those of the CD at the longest signals, suggesting that the ground and excited states have similar conformations. In contrast, CPL intensities of **2** and **4** were below the detection limit, strongly suggesting that the bridged structure is essential for CPL. When the solvent was changed to 1-octanol, the $\Phi_{FL,octanol}$ and $g_{lum,octanol}$ of (*R*,*R*)-**5** increased to 0.72 and +1.4 × 10⁻³, respectively.¹⁶ probably due to the higher viscosity.^{3f} The CPL and FL intensities were not very sensitive to temperature (-10 to 80 °C) (Figure S8). The stable CPL and FL are one of the merits for various applications.

We also investigated the solid-state (well-ground powder) FL and CPL properties (Figures 1b, 5, and S9). All PXXs displayed yellow or greenish yellow fluorescence with good $\Phi_{FL,solid}$ values: 0.11 for 1, 0.07 for 2, 0.06 for 3, 0.16 for 4, and 0.13 for 5. In comparison to the FL of 1, the FLs of 2–5 did not quench greatly or instead enhanced. Compounds 2–5 are non-planar with substituents, and therefore they avoided efficient stacking with the π -plane of adjacent molecules. Indeed, the more axes and bulky butoxy groups there are, the higher the $\Phi_{FL,solid}$ values. In addition, the crystals of (*R,R*)-5 has a herringbone structure, and strong π – π stacking is not observed (Figure S2). (*R,R*)-5 showed intense CPL with a glum,solid value of +4.8 × 10⁻³, although the others did not show apparent CPL. Again, the bridging structure is important or essential for CPL in the solid state.



Figure 4. (a) CD, (b) UV-Vis, (c) CPL, and (d) FL spectra of solutions of **1–5**. Conditions: 1,4-dioxane, 5.0×10^{-6} M (5.0×10^{-5} M for insets), 20 °C, l = 1 cm, $\lambda_{ex} = 350$ nm. CPL spectra of **2** and **4** are omitted because of little or no signal.



Figure 5. CPL and FL spectra of **5** in the solid state. Conditions: KBr, 20 °C, $\lambda_{ex} = 400$ nm.

The g_{lum} is theoretically defined as $4(|\mu| \cdot |m| \cdot \cos \theta_{\mu,m})/(|\mu|^2 + |m|^2)$, where μ and m represent the electric and magnetic transition dipole moments, respectively, and $\theta_{\mu,m}$ represents the angle of vectors between μ and m.¹⁷ Therefore, keeping $\theta_{\mu,m}$ away from 90° is desirable for the development of excellent organic CPL dyes as demonstrated by Isobe.^{17b} Calculated $\theta_{\mu,m}$ values were 89.5° for **2**, 86.2° for **3**, 86.9° for **4**, and 78.0° for **5**, suggesting that the bridge leads to $\theta_{\mu,m}$ smaller than 90° (Figure S7). The $\cos \theta_{\mu,m}$ of bridged PXXs **3** and **5** were much larger than those of corresponding non-bridged PXXs: 0.009 for **2**, 0.063 for **3**, 0.054 for **4**, and 0.208 for **5**, while the $|\mu|$ and |m| were slightly altered by the bridging (Table 1). As a

Table 1. Transition Dipole Moments and glum Values of 2–5^a

compd	$ u ^b$	$ m ^c$	$\cos \theta_{\mu,m}{}^{d}$	$g_{ m lum,dioxane}$	
	$(10^{-18} \text{ esu} \cdot \text{cm})$	$(10^{-21} \text{ erg} \cdot \text{G}^{-1})$		theoretical	experimental
(R)- 2	9.29	10.2	0.009	$+4.1 \times 10^{-5}$	nd
(R)- 3	9.98	7.16	0.063	$+1.8 \times 10^{-4}$	$+1.3 \times 10^{-3}$
(R,R)-4	7.81	2.24	0.054	$+6.3 \times 10^{-5}$	nd
(<i>R</i> , <i>R</i>)- 5	8.60	3.40	0.208	$+3.3 \times 10^{-4}$	$+1.0 \times 10^{-3}$
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^{*a*}TD DFT calculation at the CAM-B3LYP/6-311+G(2d,p) level with the self-consistent reaction field (SCRF) method (1,4-dioxane) using the excited-state structures. ^{*b*}The electric transition moment. ^{*c*}The magnetic transition moment. ^{*d*} $\theta_{\mu m}$ is angle of vectors between μ and m.

In conclusion, we developed unprecedented axially chiral PXXs 2–5. They were synthesized from BINOL without optical resolution. All PXXs maintained high FL both in solution and in the solid state. Among the chiral PXXs, 5 with methylenedioxy bridges was synthesized in only three steps and displayed intense CPL both in solution and in the solid state. This methylenedioxy bridge is a key structure and is essential for achieving CPL activity. This development of axially chiral PXXs increases the possibility of the application of heteroatom-embedded PAHs to materials using chiroptical characteristics and will lead to new design of more powerful CPL materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: .

Synthesis, spectra, and computational details (PDF) X-ray crystallographic data for (R,R)-5 (CIF) X-ray crystallographic data for (R,S,R)-12 (CIF)

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Notes

The authors declare no competing financial interest.

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