Organic LETTERS

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Synthesis and Photophysical Properties of a 13,13′-Bibenzo[*b*]perylenyl Derivative as a π-Extended 1,1′-Binaphthyl Analog

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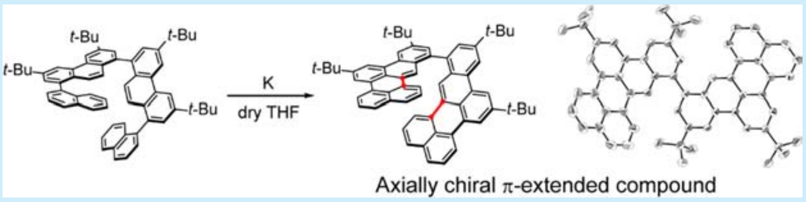
Supporting Information



ABSTRACT: A 13,13′-bibenzo[*b*]perylenyl derivative—an axially chiral π-extended compound in which two perylene subunits fused to 1,1′-binaphthyl scaffold—has been synthesized from 1,8-dibromophenanthrene using an anionic cyclodehydrogenation reaction in the presence of potassium metal as the key step. The pair of enantiomers can be separated by chiral high-performance liquid chromatography (HPLC), which showed a strong circular dichroism (CD) ($\Delta\varepsilon$ = 330 M^{-1} cm^{-1} at 449 nm, $|g_{CD}| = 5.8 \times 10^{-3}$ at 453 nm), high fluorescence quantum yield (Φ_f = 64%), and strong circular polarized luminescence (CPL) ($|g_{CPL}| = 5 \times 10^{-3}$ at 454 nm) in solution phase.

Controlling the interchromophoric interaction can provide design principles for diverse photophysical and chiroptical properties that are difficult to realize using only one chromophore.[1−4] Spatial arrangement of two chromophores is a determining factor in their interchromophoric interactions including interactions between transition electronic/magnetic dipole moments.[5−7]

Extension of the π-electron system by condensing aromatic rings is a current emerging yet challenging issue in the field of organic chemistry.[8−11] By expanding π-conjugation, desired properties for application to functional materials can be expected, such as high photoluminescence quantum yield, photophysical response in the visible and near-infrared wavelength regions, low redox potentials, and adequate $\pi-\pi$ stacking in the solid state causing a high carrier transportation.

1,1′-Binaphthyl[12−15] is a typical scaffold having axial chirality, which has been widely used as a chiral ligand for asymmetric organic syntheses,[16−18] a recognition unit of chiral molecules,[19−21] and a skeleton for asymmetric compounds.[22−25] Several 1,1′-binaphthyl-based polycyclic aromatic hydrocarbons (PAHs), such as 1,1′-bianthryl,[26,27] 1,1′-biphenanthryl,[28,29] 1,1′-bipyrenyl,[30−32] and 3,3′-biperylenyl,[33,34] have been synthesized (Figure 1) and are reported to have weak intramolecular interaction between the two aromatic subunits connected by a single C−C bond, especially in the ground state, due to the dihedral angle between the two π-conjugation planes close to 90° in solution. On the other hand, significant induction of chiroptical properties (i.e., circular dichroism (CD) and circular polarized luminescence (CPL)) can be successfully achieved by introducing the axial chirality.[23−25,32,35]

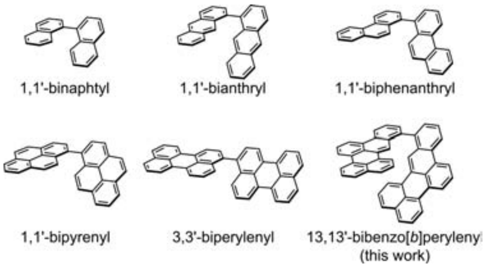


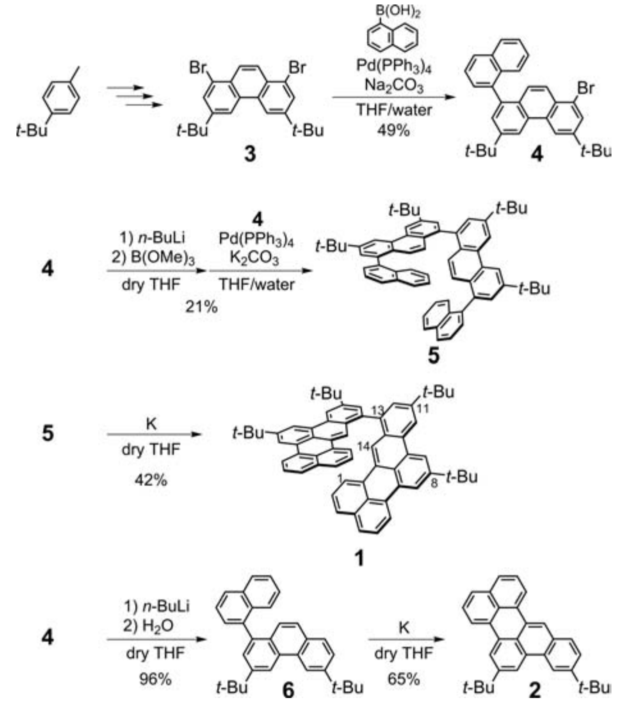
Figure 1. Chemical structures of 1,1′-binaphthyl-based polycyclic aromatic hydrocarbons.

In this context, we envisioned that further strong chiroptical properties could be achieved while retaining good photophysical properties in the monomer state by connecting even more π-extended PAHs. We focused on perylene as fluorescence chromophores because of its high fluorescence quantum yield and outstanding photostability.[1,33,36,37] Here, we report the synthesis and photophysical properties of a 13,13′-bibenzo[*b*]perylenyl derivative **1** (Scheme 1).

Received: March 15, 2016
Published: April 27, 2016

DOI: 10.1021/acs.orglett.6b00747
Org. Lett. 2016, 18, 2118−2121

Scheme 1. Synthesis of 8,8′,11,11′-Tetra-*tert*-butyl-13,13′-bibenzo[*b*]perylenyl



Compound **1** was synthesized according to the route shown in Scheme 1. 1,8-Dibromo-3,6-di-*tert*-butylphenanthrene (**3**) was prepared from commercially available 4-*tert*-butyltoluene in five steps according to the literature.[38] Mononaphthyl-substituted phenanthrene derivative **4** was synthesized by Suzuki–Miyaura coupling of compound **3** with 1-naphthylboronic acid. One half of compound **4** was lithiated, borylated, and then reacted with the other half of **4** in the presence of $Pd(PPh_3)_4$ and potassium carbonate, affording 8,8′-di(1-naphthyl)-1,1′-biphenanthryl (**5**). For the cyclodehydrogenation of the precursor **5**, a conventional photochemical reaction was attempted in the presence of iodine as an oxidant;[39] however, no reaction occurred upon UV irradiation during 12 h in cyclohexane. The Scholl reaction (i.e., oxidative aryl–aryl coupling reactions) of **5** using iron(III) chloride[40] resulted in a complicated mixture of unidentified byproducts. Instead, the intramolecular aryl–aryl bond formation of compound **5** was successfully achieved by an anionic cyclodehydrogenation induced by potassium metal,[41] affording the desired compound **1** in 42% yield. In this reaction, the two C–C bonds between the naphthyl and phenanthryl groups (i.e., the carbon atoms at the 8-position of the naphthyl group and at the 9-position of the phenanthryl group) were selectively formed and the 10- and 10′-positions of the product were not reacted.[42] Reference compound **2** was synthesized by lithiation of compound **4** followed by the same anionic cyclodehydrogenation induced by potassium metal. The structure of compounds **1** and **2** was fully characterized by ^{1}H NMR, ^{13}C NMR, and HMQC/HMBC measurements and high-resolution mass spectrometry (see the Supporting Information).

The axially chiral structure of **1** was suggested by ^{1}H NMR spectroscopy in $CDCl_3$ (Figure 2). The proton signals of H-a, H-c, and H-f, which are laterally distant from the C–C bond at the 13,13′-positions of compound **1**, were shifted to downfield by 0.18, 0.04, and 0.01 ppm, respectively, compared to the chemical shifts of compound **2**. On the other hand, slight upfield shifts were observed for the signals of protons H-g and H-h (0.05 and 0.08 ppm, respectively), which were more prominent for the protons H-j, H-k, and H-l (0.14, 0.30, and 0.63 ppm, respectively). The prominent upfield shifts for the protons H-j, H-k, and H-l imply that these protons locate on top of the π-plane of the other benzo[*b*]perylene unit. Therefore, the dihedral angle between the two benzo[*b*]perylene moieties (ϕ) is less than 90° and the two perylene subunits of compound **1** are in proximity in solution, which was consistent with the optimized structure calculated by a DFT method (ϕ = 77.5°) in the gas phase (Figure S1, Supporting Information).

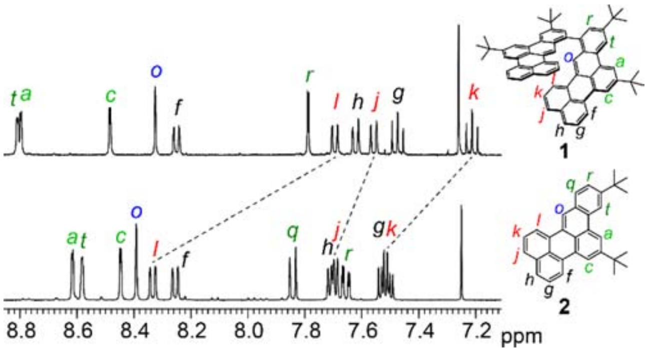


Figure 2. ^{1}H NMR spectra of compounds **1** (top) and **2** (bottom) in $CDCl_3$ at room temperature (for details of chemical shifts, see Table S1, Supporting Information).

The structure of compound **1** was unambiguously determined by X-ray crystallography. A single crystal suitable for X-ray analysis was obtained by a liquid–liquid diffusion method using a toluene solution of a racemic mixture of **1** and acetonitrile as a poor solvent. The dihedral angle (ϕ) was 119.8° (Figure 3a). Considering the results of ^{1}H NMR and DFT calculation, the large dihedral angle in the crystal structure is likely due to a packing effect.

X-ray analysis revealed that compound **1** is arranged in a 1-D chain through a slipped π–π stacking along the *c*-axis, in which the axially chiral enantiomers (i.e., (*P*)- and (M)-isomers) are alternately stacked with the π–π distance of 3.28–3.47 Å (Figure 3b,c). Besides the π–π stacking interaction, the CH···π interaction was observed between the *tert*-butyl group and benzo[*b*]perylene moiety in the crystal structure (see Figure S2, Supporting Information).

The absorption and steady state fluorescence spectra of compounds **1** and **2** were recorded in methylcyclohexane (MCH) (Figure 4 and Table 1). The absorption and fluorescence spectra of **1** were quite similar in shape to those of **2**. Absorption and fluorescence maxima of **1** (446 and 454 nm, respectively) appeared at slightly longer wavelengths by ca. 10 nm than those of **2** (438 and 445 nm, respectively). The Stokes shifts for both **1** and **2** were very small (only 395 and 359 cm^{-1}, respectively), suggesting a remarkably small geometrical relaxation of **1** in the excited state. The similarity in the ground- and excited-state geometries of **1** is in marked contrast to the previously reported 3,3′-biperylenyl derivative.[34] The fluorescence quantum yield and fluorescence lifetime of **1** ($\Phi_f = 0.64$, $\langle\tau_f\rangle = 3.4$ ns) were comparable to those of **2** ($\Phi_f = 0.74$, $\langle\tau_f\rangle = 3.6$ ns). Thus, the photophysical properties of the benzo[*b*]perylene subunit can be well retained after dimerization by linking with a single C–C bond at the 13,13′-positions.

Enantiomers of compound **1** were separated from a racemic solution by a chiral high-performance liquid chromatography

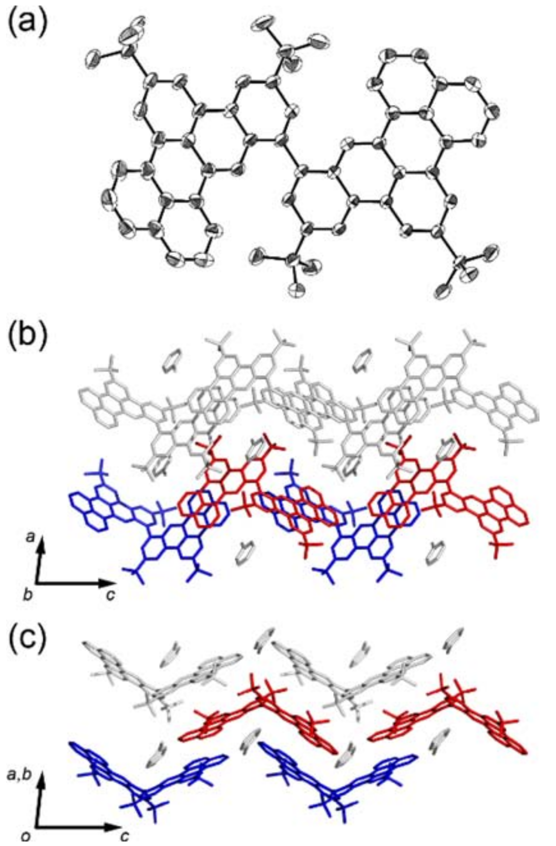


Figure 3. (a) ORTEP drawing of **1**, showing 50% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity. (b) Crystal packing structure of **1** viewed normal to the (010) face. Red and blue represent the (*P*)- and (*M*)-isomers, respectively. (c) Crystal packing viewed normal to the ($\bar{1}$10) face.

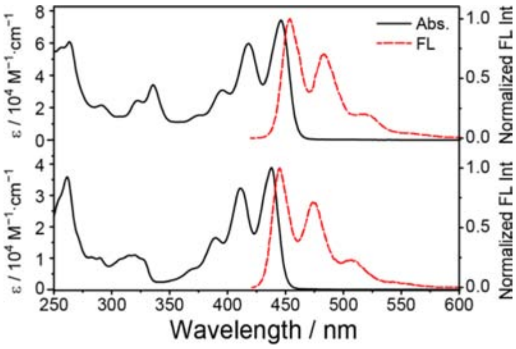


Figure 4. Absorption and fluorescence spectra of compounds **1** (top) and **2** (bottom) in MCH.

(HPLC) (Figure S6, Supporting Information), and then CD spectra were measured in MCH (Figure 5a). The first fraction in the chiral HPLC was (+)-**1**, which showed a positive Cotton effect at the longest wavelength ($\Delta\varepsilon$ = 330 M^{-1} cm^{-1} at 449 nm, $|g_{CD}|$ = 5.8 × 10^{-3} at 453 nm), while the second fraction was (−)-**1** showing a negative Cotton effect as the mirror image. On the basis of the comparison of experimental CD spectra with theoretically calculated rotatory strength (at the M062X/6-311G(2d,p) level) (Figure 5b), the axial chirality of **1** was determined as (*P*)-(+)-**1** and (*M*)-(−)-**1**. The assignment of chirality is consistent with that estimated by the exciton chirality method.[43−45]

Table 1. Photophysical Properties of Compounds 1 and 2 in MCH

compd	$\lambda_{max,abs}$/nm (ε/$M^{-1}cm^{-1}$)	$\lambda_{max,FL}$/nm	Φ_f[a]	$\langle\tau_f\rangle$/ns[b]	k_f/ns^{-1}[c]	k_{nr}/ns^{-1}[c]
1	446 (7.3 × 10^4)	454	0.64	3.4	0.19	0.11
2	438 (3.9 × 10^4)	445	0.74	3.6	0.21	0.073

[a] Measured by an absolute method using an integrating sphere. [b] The area-weighted mean fluorescence lifetime $\langle\tau_f\rangle$ was calculated as follows: $\langle\tau_f\rangle = \Sigma(A_n\tau_n^2)/\Sigma(A_n\tau_n)$, where A_n is the coefficient of the exponential function for the *n*th component. [c] Fluorescence emission rate constant (k_f) and nonradiative decay rate constant (k_{nr}) were calculated as follows: $k_f = \Phi_f/\langle\tau_f\rangle$, $k_{nr} = (1 - \Phi_f)/\langle\tau_f\rangle$.

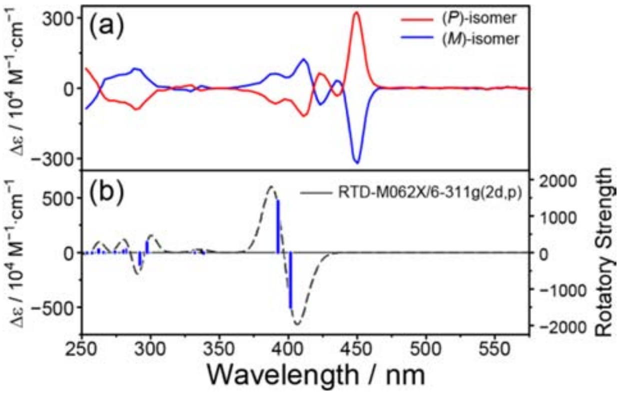


Figure 5. (a) Experimentally observed CD spectra of compounds in MCH at 15 °C (red, (*P*)-(+)-**1**; blue, (*M*)-(−)-**1**). (b) Rotatory strengths of (*M*)-(−)-**1** calculated at M062X/6-311g(2d,p) level. Gray dashed line denotes the simulated CD spectra from the calculated rotatory strengths.

The rate of racemization of **1** was investigated by monitoring the time course of CD signal intensity at 449 nm at different temperatures (Figure S8, Supporting Information). Based on the Eyring plot of the CD signal decay rate, the activation free energy of the racemization was calculated as $\Delta G^\ddagger$ = 102.9 kJ·mol^{-1} at 25 °C ($\Delta H^\ddagger$ = 89.6 kJ·mol^{-1}, $\Delta S^\ddagger$ = −44.5 kJ·mol^{-1}) (Figure S9, Supporting Information). According to these parameters, the half-life of the isolated enantiomers is $\tau_{1/2}$ = 18 h at 25 °C.

Circular polarized luminescence (CPL) is a powerful tool to investigate the electronic structure of chiral molecules in the excited state.[24,35] Both enantiomers, (*P*)-(+)-**1** and (*M*)-(−)-**1**, showed positive and negative CPL signals around 454 nm with a dissymmetric factor of $|g_{CPL}|$ = (5 ± 3) × 10^{-3} (Figure 6). The sign of the CPL signal was consistent with the sign of the first Cotton effect observed in the CD spectra (Figure 5a). Interestingly, the dissymmetric factors of luminescence were comparable to that of absorption ($|g_{CD}|$ = 5.8 × 10^{-3}) for compound **1**, suggesting that the electronic structure of **1** in the excited state is similar to that in the ground state.

In conclusion, 13,13′-bibenzo[*b*]perylenyl derivative **1** was synthesized using 1,8-dibromo-3,6-di-*tert*-butylphenanthrene (**3**) as a key intermediate. The photophysical properties of benzo[*b*]perylene subunit can be well retained in the axially chiral dimer **1** by linking with the C−C bond at the 13,13′-positions. Bibenzo[*b*]perylenyl **1**—a *π*-extended molecule with axial chirality consisting of only carbon and hydrogen atoms without any heteroatoms—exhibited a strong emission (Φ_f = 0.64) and relatively large dissymmetric factors of both absorption and emission ($|g_{CD}|$ = 5.8 × 10^{-3}, $|g_{CPL}|$ = 5 × 10^{-3}, respectively)

DOI: 10.1021/acs.orglett.6b00747
Org. Lett. 2016, 18, 2118−2121

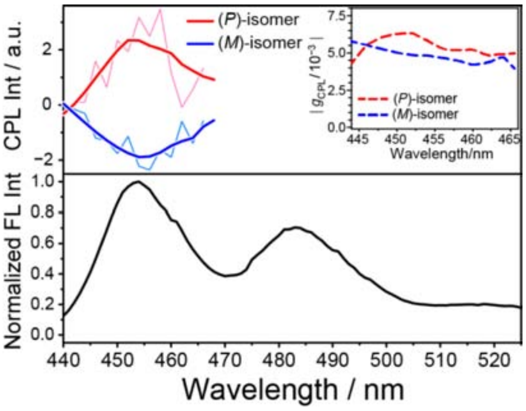


Figure 6. (a) CPL spectra of (*P*)-(+)-**1** and (*M*)-(−)-**1** in MCH. The Inset shows the corresponding g_{CPL} spectra of **1**. (b) Corresponding fluorescence spectrum of **1** in MCH.

compared to typical small organic molecules.[46] The substituent effect on the chiroptical properties, emission in the solid state, and chiral enrichment by addition of chiral guests are now under investigation in our group.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00747.

Experimental details, ^{1}H and ^{13}C NMR spectra, Cartesian coordinates of the optimized structures, and the calculated excited states (PDF)

X-ray crystallographic data of compound **1** (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by a Grant-in-Aid for Scientific Research on Innovative Areas “Photosynergetics” (No. 26107008) from the MEXT, Japan and a Grant-in-Aid for Young Scientists (B) (No. 25810048) from the JSPS, Japan.

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(46) The $|g_{CPL}|$ value of **1** is larger than those of 1,1′-bipyrenyl, 1,1′-bianthryl, and 1,1′-binaphthyl derivatives reported to be 4×10^{-4}, 1×10^{-4}, and 1×10^{-3}, respectively. A significantly large $|g_{CD}|$ value has been reported for a 1,1′-bianthryl derivative ($|g_{CD}| = 1.6 \times 10^{-2}$). For details, see Figure S10 in the Supporting Information.