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Helical Oligonaphthodioxepins Showing Intense CPL in Solution and in the Solid State

Kazuto Takaishi*, Takahiro Yamamoto, Sakiko Hinoide, and Tadashi Ema*

Abstract: A series of oligonaphthodioxepins was synthesized, revealing a helically arranged octamer, (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3**, which showed intense circularly polarized luminescence (CPL) both in solution and in the solid state. The fluorescence quantum yields (Φ_{FL}) in solution and in the solid state were 0.90 and 0.22, respectively, and the g_{lum} values in solution and in the solid state were $+2.2 \times 10^{-3}$ and $+7.0 \times 10^{-3}$, respectively. This is one of the highest solid-state CPL g_{lum} values yet reported. The high Φ_{FL} and g_{lum} values were due to the rigidity as well as to the fact that (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3** was a non-planar molecule. Moreover, (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3** was highly stable both chemically and stereochemically.

Circularly polarized luminescence (CPL) is potentially useful in displays,[1] memory,[2] and bioimaging[3] applications because it produces three types of signals: left-handed CPL, right-handed CPL, and non-CPL (+, –, and 0). Over the past decade, several organic helical polymers and supramolecules with CPL activity have been developed.[4] Small monomolecular CPL dyes such as helicenes,[5] cyclophanes,[6] and binaphthyl compounds[7] have also attracted attention for use in certain applications. Solid-state CPL is preferred in many applications; however, almost all known monomeric dyes display CPL only in solution. Exceptional cases were reported by Imai and coworkers, who observed solid-state CPL from BINOL-derived phosphoric acids ($\Phi_{FL,solid} = 0.26$, $|g_{lum,solid}| = 1.5 \times 10^{-3}$; the Kuhn's anisotropy factor g_{lum} is defined as $2(I_L - I_R)/(I_L + I_R)$).[8] Commercial applications would require novel organic dyes that display much larger solid-state g_{lum} values.

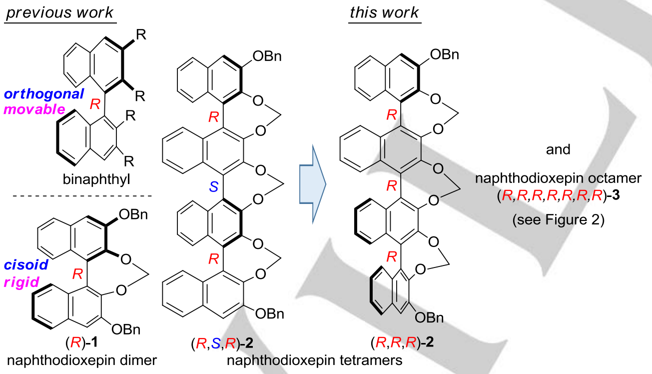

Figure 1. A typical binaphthyl and naphthodioxepin oligomers.

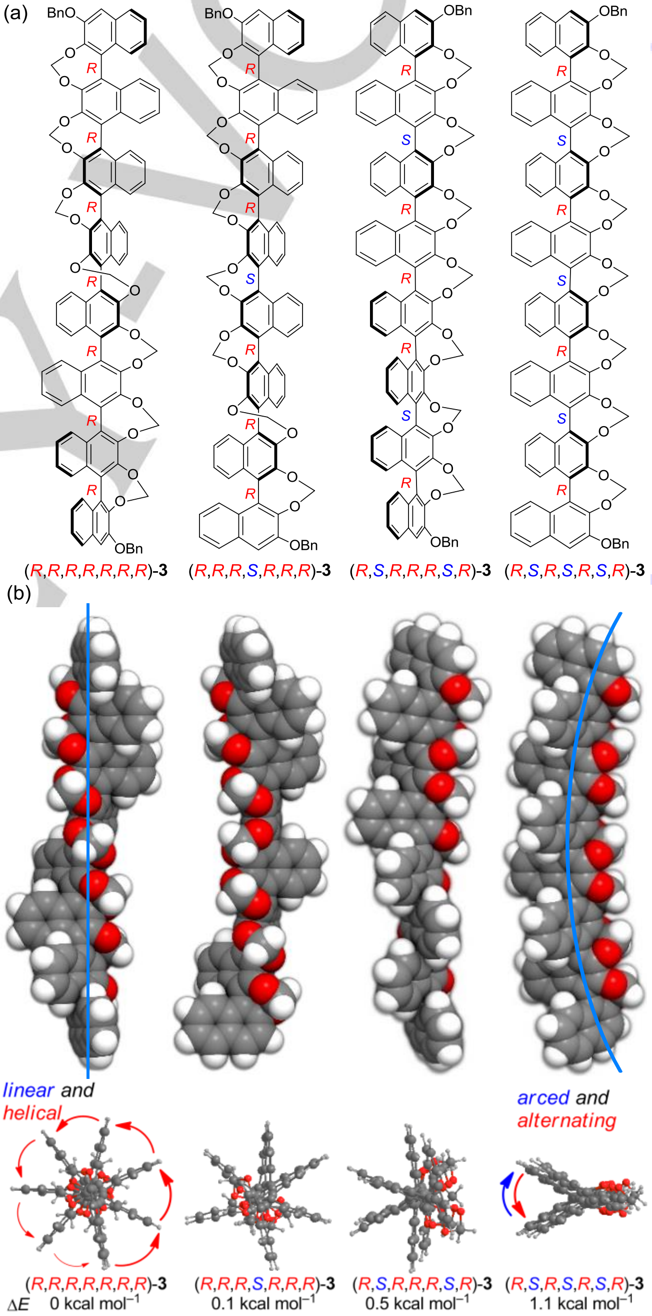

Figure 2. a) Selected stereoisomers **3**. b) Top and side views of the DFT-optimized structures of **3** (B3LYP/6-31G(d,p) level). The terminal benzyloxy groups were replaced with hydrogen atoms.

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Dinaphthodioxepins exhibit unique optical properties compared to other 1,1'-binaphthyls.[9] We previously synthesized the (*R*)-naphthodioxepin dimer **1**, (*R*,*S*,*R*)-tetramer **2**, and (*R*,*S*,*R*,*S*,*R*,*S*,*R*)-octamer **3** (Figures 1 and 2).[10] The dioxepin ring structure leads to a rigid and cisoid conformation that enabled partial conjugation along the chiral axis involving the ^1L_a transition[11]. Therefore, the absorption and fluorescence maxima red-shifted as the degree of oligomerization increased. The compounds also fluoresced both in solution ($\Phi_{\mathrm{FL,1,4\text{-}dioxane}}$ of up to 0.79) and in the solid state ($\Phi_{\mathrm{FL,solid}}$ of up to 0.29), unlike typical binaphthyl compounds. Naphthalene oligomers without the dioxepin moiety exhibited neither solid-state fluorescence nor red-shifted absorption properties because their naphthalene rings were movable and orthogonal.[12]

In this study, we focused on a particular set of stereoisomers of **2** and **3**. Seventy-two stereoisomers (36 enantiomeric pairs) of **3** exist, and the optimized structures of four representative examples, (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3**, (*R*,*R*,*R*,*S*,*R*,*R*,*R*)-**3**, (*R*,*S*,*R*,*R*,*R*,*S*,*R*)-**3**, and (*R*,*S*,*R*,*S*,*R*,*S*,*R*)-**3**, are shown in Figure 2.[13] Although the overall structures of the stereoisomers **3** differed significantly from one another, the dihedral angles between adjacent naphthalene rings (C2–C1–C1'–C2') were about 49°. The calculated potential energy (an index of the molecular strain) did not differ significantly among the stereoisomers: (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3** was the most stable (e.g., Δ*E* between (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3** and the most unstable stereoisomer, (*R*,*S*,*R*,*S*,*R*,*S*,*R*)-**3**, was calculated to be 1.1 kcal mol^{-1} at the B3LYP/6-31G(d,p), 3.3 kcal mol^{-1} at the M062X/6-31G(d,p), and 1.5 kcal mol^{-1} at the B97D/TZVP levels of theory). The axes of (*R*,*S*,*R*,*S*,*R*,*S*,*R*)-**3** were bent to form an arc due to an accumulation of strain. The naphthalene rings of (*R*,*S*,*R*,*S*,*R*,*S*,*R*)-**3** displayed an alternating arrangement similar to that observed in the *meso*-form. Therefore, (*R*,*S*,*R*,*S*,*R*,*S*,*R*)-**3** was not expected to display significant chiroptical properties. On the other hand, the naphthalene rings of (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3** took a left-handed helical shape with linearly aligned chiral axes.[14] This helical (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3** was expected to display excellent CPL properties. Here, we report that (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3** showed intense FL and CPL both in solution and in the solid state.

To construct a series of stereopure oligonaphthodioxepins, we selected a bottom-up method using chiral BINOL as a starting material (Scheme S1). The absolute configuration of the octamers **3** was determined using the exciton chirality method with two TPP(Zn) chromophores.[15] The X-ray crystal structure of (*R*,*R*,*R*)-**2**, shown in Figure 3, revealed a cisoid conformation (47–49°) similar to the half structure of the DFT-optimized (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3**. The solubilities of the stereoisomers **3** showed more significant differences. (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3** was highly soluble in CH_2Cl_2, whereas (*R*,*S*,*R*,*S*,*R*,*S*,*R*)-**3** was relatively insoluble. At 20 °C in CH_2Cl_2, the solubility limits of (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3**, (*R*,*R*,*R*,*S*,*R*,*R*,*R*)-**3**, (*R*,*S*,*R*,*R*,*R*,*S*,*R*)-**3**, and (*R*,*S*,*R*,*S*,*R*,*S*,*R*)-**3** were ≥200, 120, 90, and 1 mg mL^{-1}, respectively. The stacking interactions likely increased in this order. The dipole moments may also have significantly influenced solubility. Each dipole moment in the helically arranged naphthalene rings was dispersive and cancelled other dipole moments out, whereas those of the alternating naphthalene ring were parallel and intensified. Indeed, TLC on silica gel 60 (Merck, $CHCl_3$/EtOAc = 50/1) indicated that the R_f values were 0.63, 0.48, 0.35, and 0.05 for (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3**, (*R*,*R*,*R*,*S*,*R*,*R*,*R*)-**3**, (*R*,*S*,*R*,*R*,*R*,*S*,*R*)-**3**, and (*R*,*S*,*R*,*S*,*R*,*S*,*R*)-**3**, respectively. VT NMR studies and DFT calculations indicated that the oligonaphthodioxepins were highly stable both chemically and stereochemically (see the Supporting Information for details).

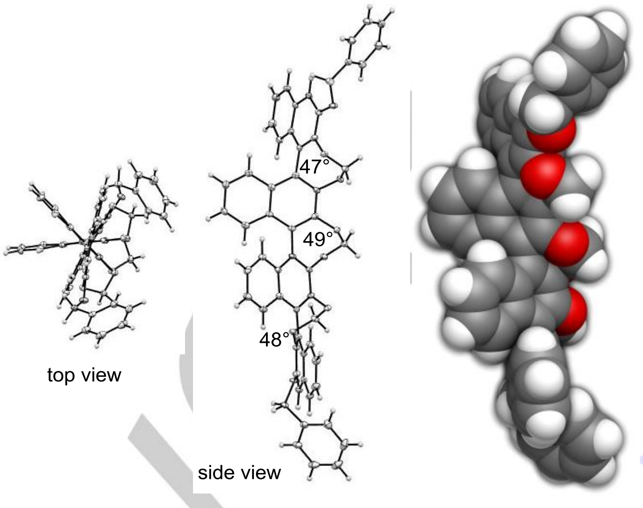

Figure 3. X-ray crystal structure of (*R*,*R*,*R*)-**2** (the solvent molecules are omitted for clarity): (left) ORTEP diagrams (thermal ellipsoids at 50% probability) and (right) a space-filling model.

We next analyzed the optical properties of solutions of **1**–**3**. The optical spectra of the 1,4-dioxane solutions are shown in Figure 4, and the luminescence properties are summarized in Table 1. The absorption edges shifted to the red upon oligomerization, and the stereoisomers displayed few differences (Figure 4b). TD-DFT calculations of any of the octamers **3** indicated that both the HOMO and LUMO were delocalized across the molecule with a gap of 3.5 eV, without exception. Figure 4d plots the fluorescence spectra. All compounds exhibited a high fluorescence quantum yield ($\Phi_{\mathrm{FL,1,4\text{-}dioxane}}$), (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3** showed the highest FL ($\Phi_{\mathrm{FL,1,4\text{-}dioxane}}$ = 0.90) (Table 1). The stereoisomers displayed similar FL spectra with somewhat different Stokes shifts. (*R*,*R*,*R*)-**2** and (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3** provided smaller Stokes shifts than the other stereoisomers, e.g., 1700 cm^{-1} for (*R*,*R*,*R*)-**2**, 3200 cm^{-1} for (*R*,*S*,*R*)-**2**, 1100 cm^{-1} for (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3**, and 2500 cm^{-1} for (*R*,*S*,*R*,*S*,*R*,*S*,*R*)-**3**. In both the ground and excited states, (*R*,*R*,*R*)-**2** and (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3** were more rigid than the other stereoisomers, and the rigidity decreased the Stokes shift and increased the fluorescence quantum yield. Although the optimized ground and excited (S_1) state structures of (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3** were very similar to one another, the structure of the excited (S_1) state of (*R*,*S*,*R*,*S*,*R*,*S*,*R*)-**3** was linear and did not assume an arc form (Figure S4).[16] Excitation energy may be lost through the small structural change.

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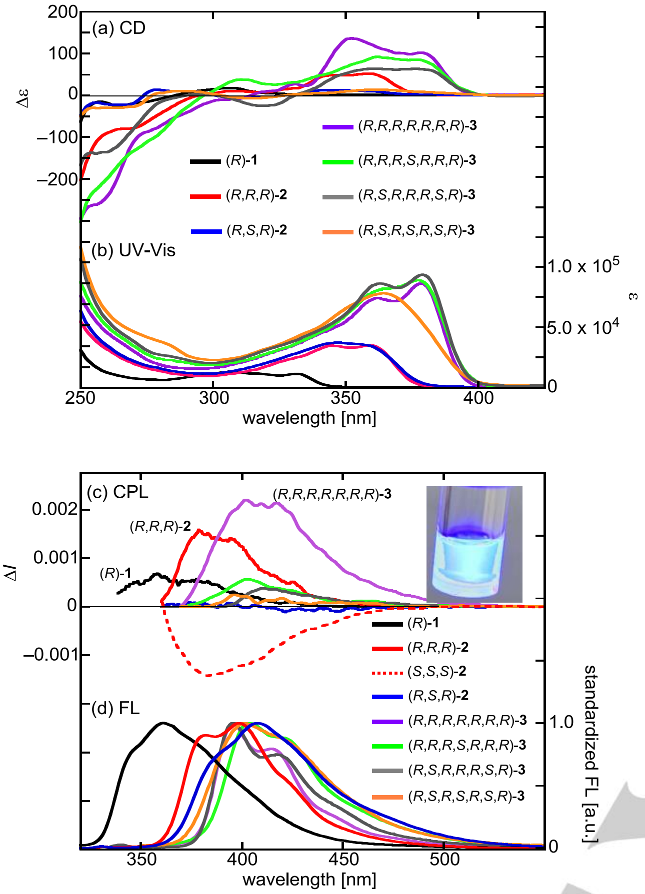

Figure 4. a) CD, b) UV-Vis, c) CPL, and d) FL spectra of **1**–**3** in 1,4-dioxane. Conditions: [**1**] = 1.0 × 10^{-5} M, [**2**] = 5.0 × 10^{-6} M, [**3**] = 2.5 × 10^{-6} M, 20 °C, λ_{ex} = 310 nm for **1**, 330 nm for **2** and **3**. The inset presents a photograph of a picture of 2.5 × 10^{-6} M (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3** solution under UV (365 nm) light.

Table 1: FL and CPL properties of **1**–**3**.

compound	1,4-dioxane sol. Φ_{FL}[a]	1,4-dioxane sol. g_{lum}	solid state Φ_{FL}[b]	solid state g_{lum}
(*R*)-**1**	0.44	+6.8 × 10^{-4}	0.13	–1.1 × 10^{-3}
(*R*,*R*,*R*)-**2**	0.78	+1.6 × 10^{-3}	0.29	+1.4 × 10^{-3}
(*R*,*S*,*R*)-**2**	0.79	nd[c]	0.21	+2.1 × 10^{-4}
(*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3**	0.90	+2.2 × 10^{-3}	0.22	+7.0 × 10^{-3}
(*R*,*R*,*R*,*S*,*R*,*R*,*R*)-**3**	0.79	+5.7 × 10^{-4}	0.24	nd[c]
(*R*,*S*,*R*,*R*,*R*,*S*,*R*)-**3**	0.84	+3.8 × 10^{-4}	0.17	nd[c]
(*R*,*S*,*R*,*S*,*R*,*S*,*R*)-**3**	0.64	+3.1 × 10^{-4}	0.13	nd[c]

Conditions: λ_{ex} = 310 nm for **1**, 330 nm for **2** and **3**, 20 °C, solution; [**1**] = 1.0 × 10^{-5} M, [**2**] = 5.0 × 10^{-6} M, [**3**] = 2.5 × 10^{-6} M. [a] The absolute fluorescence quantum efficiencies of (*R*,*R*,*R*)-**2** and (*R*,*R*,*R*,*S*,*R*,*R*,*R*)-**3** were measured as reference standards. [b] Absolute fluorescence quantum efficiency. [c] Not detected.

The CPL spectra are shown in Figure 4c. (*R*,*R*,*R*)-**2** and (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3** possessed significant (+)-CPL, and $g_{lum,1,4\text{-}dioxane}$ values were +1.6 × 10^{-3} for (*R*,*R*,*R*)-**2** and +2.2 × 10^{-3} for (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3**. The signs and the *g* values of the CPL and the CD related to the transition from the HOMO to LUMO (e.g., a g_{abs} value of (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3** was +1.5 × 10^{-3} at the first Cotton CD band in Figure 4a) agreed well, as is often the case, indicating that the structures in the ground and excited states were similar. (*R*,*R*,*R*)-**2** and (*S*,*S*,*S*)-**2** provided clear mirror images. The spectral shape and intensity of (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3** were not altered by the solvents (1,4-dioxane, CH_2Cl_2, CH_3CN, EtOAc, DMF, toluene) and the temperature ranging 20–80 °C (Figures S6 and S7). That is, the CPL properties were not affected by the environment.

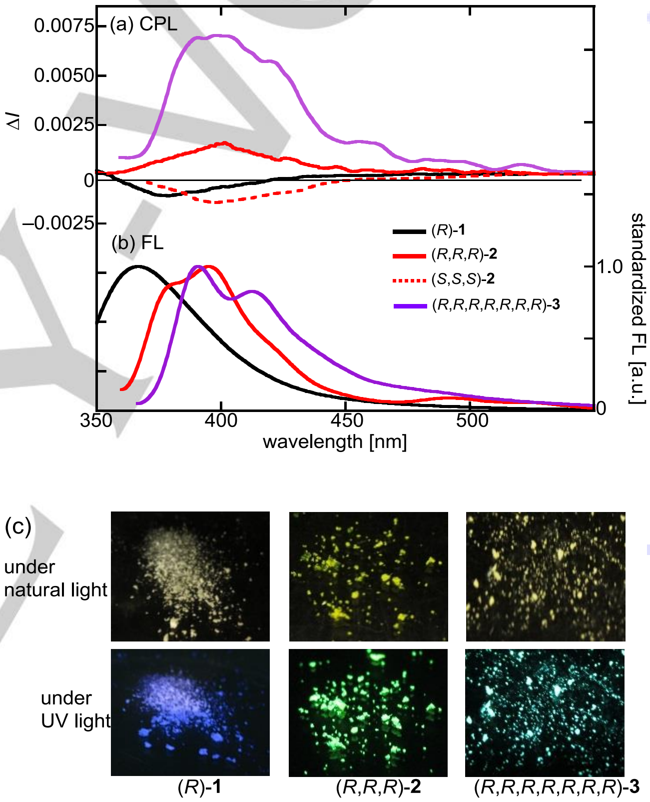

Figure 5. a) Solid-state CPL and b) FL Spectra of **1**–**3**. Conditions: λ_{ex} = 310 nm for **1**, 330 nm for **2** and **3**, 20 °C, nujol mull. c) Photographs showing the solid-state FL of **1**–**3**.

Finally, we measured the solid-state FL and CPL spectra of the all-(*R*)-**1**–**3** (Figure 5).[17] Compounds **1**–**3** fluoresced in the solid (powder) state. The fluorescent (*R*)-**1** was pale blue ($\Phi_{FL,solid}$ = 0.13), (*R*,*R*,*R*)-**2** was yellow green ($\Phi_{FL,solid}$ = 0.29), and (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3** was light blue ($\Phi_{FL,solid}$ = 0.22). The $\Phi_{FL,solid}$ values were very high, although they were lower than the corresponding values obtained in solution. The high values obtained from solid-state fluorescence were due to the rigidity as well as to the fact that the oligonaphthodioxepins, especially helical (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3**, were non-planar molecules. These molecules avoided efficient stacking with the π-planes of adjacent molecules in the solid state. In fact, the $\lambda_{em,solid}$ values were very close to $\lambda_{em,1,4\text{-}dioxane}$. The CPL of (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3** was characterized by a high $g_{lum,solid}$ of $+7.0 \times 10^{-3}$. It is thought that the influence of linearly polarized emission was small by the fact that (*R*,*R*,*R*)-**2** and (*S*,*S*,*S*)-**2** provided clear mirror images and the CPL had no dependency of the direction of excited light.[18] Non–dioxepin-fused oligonaphthalenes[12] did not display CPL properties, indicating that a helical and highly rigid structure in the excited state is essential for obtaining an intense CPL.

In conclusion, we developed helically arranged oligonaphthodioxepins with excellent chiroptical properties, solubility, structural rigidity, and (stereo)chemical stability. It should be noted that (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3** showed intense FL and CPL both in solution and in the solid state ($\Phi_{FL,1,4\text{-}dioxane} = 0.90$, $g_{lum,1,4\text{-}dioxane} = +2.2 \times 10^{-3}$, $\Phi_{FL,solid} = 0.22$, $g_{lum,solid} = +7.0 \times 10^{-3}$). The values of $g_{lum,solid}$ was one of the highest yet reported for monomeric organic compounds to our knowledge. The π-planes of adjacent (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3** molecules were incapable of forming efficiently stacked structures due to the non-planar molecular conformation, which led to a high $\Phi_{FL,solid}$ value.

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Conflict of interest

The authors declare no conflict interest.

Keywords: Axial chirality • Chiroptical property • Circularly polarized luminescence • Helical structure

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[16] The ground and excited states of a naphthalene tetramer without a dioxepin ring were calculated (Figure S5). The structures appeared to be distinct.

[17] a) Solid-state UV-Vis and CD spectra of (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3** are shown in Figure S8. These spectra were similar to the solution-state spectra; b) Powder XRD studies indicated that these materials assumed a typical amorphous form (Figure S19).

[18] The possibility that the linear polarization distorted the CPL signal of (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**3** cannot be denied.

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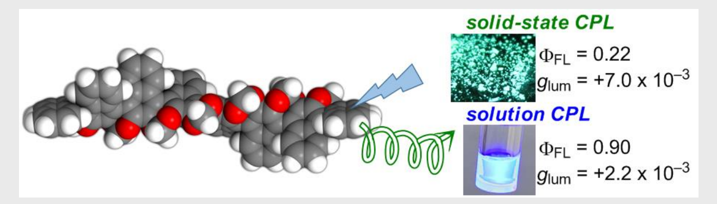

Solid-state CPL dyes: A (*R*,*R*,*R*,*R*,*R*,*R*,*R*)-naphthodioxepin (dioxepin-fused naphthalene) octamer was found to take a unique left-handed helical structure with high rigidity, (stereo)chemical stability, and solubility. Interestingly, the octamer emits strong circularly polarized luminescence (CPL) with high Φ_{FL} and g_{lum} values both in solution and in the solid state.

K.Takaishi, T. Yamamoto, S. Hinoide, T. Ema**

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Helical Oligonaphthodioxepins Showing Intense CPL in Solution and in the Solid State