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Optically Active Phenylethene Dimers Based on Planar Chiral Tetrasubstituted [2.2]Paracyclophane

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Abstract

Optically active phenylethene dimers based on a planar chiral 4,7,12,15tetrasubstituted [2.2]paracyclophane were synthesized. We succeeded in controlling the molecular motion by binding luminophores in close proximity with the [2.2]paracyclophane scaffold. For example, aggregation-induced emission (AIE)-active luminophores were converted to show intense photoluminescence (PL) even in a diluted solution at room temperature and the resulting compound worked as a single-molecule thermo-responsible material around room temperature. Because of the AIE-active unit, the molecular motion could be easily activated by heating, leading to variable and reversible PL intensity. Furthermore, the π -conjugated systems with the planar chirality of 4,7,12,15-tetrasubstituted [2.2]paracyclophane provided excellent characteristics on circular dichroism (CD) and circularly polarized luminescence (CPL). The obtained dimers showed high CPL performances both in a diluted solution and in an aggregation state. We succeeded in proving that the simple molecular designs composed of only carbon and hydrogen atoms can create versatile optical functionalities.

Introduction

The establishment of molecular design for controlling luminescent properties in π conjugated systems is of much importance for the applications not only to improve performances of organic opto-electronic devices^[1] but also to produce optical sensors.^[2] In the most of organic luminescent molecules, strong emission can be observed only in a diluted solution, and weak or no emission in an aggregation state. This behavior is called aggregation-caused quenching (ACQ).^[3] Especially, in planar molecules, ACQ is critically induced by strong intermolecular $\pi - \pi$ interaction which promotes radiation-less deactivation via exciton delocalization or excimer formation.^[4] In contrast, recent reports presented another class of compounds which exhibits the opposite luminescent characteristics. Aggregation-induced emission (AIE)-active molecules show subtle emission in the solution state, whereas bright emission can be observed in the aggregation state. It has been proposed that radiation-less deactivation processes should be caused by vigorous intramolecular motion in the solution state. By suppressing the molecular motion in the aggregation state, strong emission can be recovered, leading to significant solid-state emissions.^[5] Because of versatility of this switching properties, a wide variety of optical sensors have been developed.^[6]

A large number of stimuli-responsive materials based on AIE behaviors have been accomplished.^[5e] The target-selective emission enhancements can be achieved by the immobilization of the movable units in AIE-active molecules with covalent or non-covalent bonds triggered by the target recognition.^[7] Additionally, AIE properties were also varied corresponded to drastic environmental changes such as freezing of matrices,^[8] polarity alteration^[9] and addition of external forces.^[10] These systems were applicable for sensitive environmental sensors. Although various methodologies have been established

so far, there are much room to explore precise control of molecular stacking and reflect external stimuli in the degree of stacking as optical property changes. Our target is to develop the single molecular system involving the stacking unit with luminescent property and to realize the stimuli-responsive materials toward environmental factors. 4,7,12,15-Tetrasubstituted [2.2]paracyclophane framework^[11] makes it realized to achieve controlling the orientation and the number of stacking molecules. In addition, the behavior was easily detected by the optical and chiroptical properties because the [2.2] paracyclophane scaffold can arrange two luminophores in close proximity at the chiral position without losing the PL performance.^[12] Chiroptical properties, such as CD and CPL spectra measurements, provide detail information about the molecular conformation and intermolecular interaction in the ground state and in the excited state, respectively.^[13] Exploring the system is important not for understanding interaction of π -conjugated molecules but also for producing functional materials, for example, high-performance CPL ones or stimuli-responsive ones. CPL is the phenomenon that chiral compound emits circularly polarized light and it is available for optically active light. In these days, CPL has received much attention for the potential application to a light source of 3D display, biochemistry, chirality induction in the field of organic synthesis and optical cryptography. For those reasons, we selected the optically active [2.2]paracyclophane framework and investigated the behaviors of ACQ and AIE monomers and dimers both in the dilute solution state and in the aggregation state.

Herein, we synthesized the mono and diphenylethene-derivative monomers (**MPh1** and **MPh2**) and dimers (**DPh1** and **DPh2**) based on a planar chiral 4,7,12,15-tetrasubstituted [2.2]paracyclophane (Figure 1). **MPh1** includes a scaffold for exhibiting ACQ property, while **MPh2** possesses a framework for showing AIE property.¹⁴ By

connecting two **MPh1** molecules to form the [2.2]paracyclophane framework, the resulting **DPh1** provided strong emission in the diluted solution and weak emission in the aggregation state, which was the same property of **MPh1**. In contrast, the **DPh2** showed strong emission even in the diluted solution and moderate emission in the aggregation state. This result means that the stacking formation with **MPh2** induced distinct different optical properties from the single molecular unit. Furthermore, it was demonstrated that **DPh2** showed thermo-responsive photoluminescence (PL) changes around room temperature in the diluted solution. Moreover, because of planar chirality of the dimers, **DPh1** and **DPh2** presented high performance CPL profiles in diluted solutions and in the aggregation state. From these results, it can be expected that the tetrasubstituted [2.2]paracyclophane framework is promised to be a fundamental molecular unit with the simple composition of the only carbon and hydrogen atoms for receiving stimuli-responsive material as well as optically active materials.

Figure 1

Synthesis

The optical resolution of planar chiral 4,7,12,15-tetrasubstituted [2.2]paracyclophane was carried out using the diastereomer method that we previously developed, and the obtained enantiopure compounds were converted to the corresponding (S_p) - and (R_p) -4,7,12-tribromo-15-(trifluoromethanesulfonate)[2.2]paracyclophanes ((S_p) -CpOTf, (R_p) -**CpOTf**).^[12d] The synthetic routes to the target optically active cyclic compounds are shown in Schemes 1 and 2. According to the previous study on the syntheses of **DPh1** and **MPh1**,^[15] we modified the synthetic route to obtain optically active dimer compounds. A bromide of compound $\mathbf{1}^{[16]}$ was converted to a boronate ester to obtain compound 2 in 97% isolated yield. Compound 2 was readily used in the Suzuki-Miyaura coupling^[17] (Scheme 1). Scheme 2 shows the synthesis of the target planar chiral dimers **DPh1** and **DPh2**. In this scheme, only the reactions of the (S_p) -isomers are shown; the (R_p) -isomers were synthesized under identical conditions with (R_p) -CpOTf. Suzuki-Miyaura coupling of (S_p) -CpOTf was carried out with *trans*-2-(4,4,5,5tetramethyl-1,3,2-dioxaborolan-2-yl)styrene 3 in the catalytic system of Pd2(dba)3/PPh3 using $CsCO_3$ as a base to afford (S_p) -**DPh1** in 54% isolated yield. Using the same procedure, (S_p)-**DPh2** was also prepared in 67% isolated yield. In the case of (S_p)-**DPh2**, unreacted OTf groups were converted to OH groups to remove byproducts by silica gel column chromatography. The details are shown in the Supporting Information. Scheme 3 shows the syntheses of the monomeric model compounds, MPh1 and MPh2, which are the half units of the dimers, **DPh1** and **DPh2**, respectively. As shown in Scheme 3, the same procedure as Scheme 1 was available for MPh1 and MPh2, and the isolated yields of these molecules were 74% and 46%, respectively. The structures of all new compounds in this study were confirmed by ¹H and ¹³C NMR spectroscopies, high-resolution mass

spectrometry (HRMS), and elemental analysis. The detailed synthetic procedures and NMR spectra are shown in the Supporting Information.

Schemes 1–3

Results and Discussion

Optical Properties

The optical properties of both enantiomers of π -conjugated dimers, **DPh1** and **DPh2** as well as their monomeric model compounds MPh1 and MPh2 were evaluated (Table 1). Figure 2 shows the UV-vis absorption spectra of the compounds in diluted solutions (1,4-dioxane, 1.0×10^{-5} M) and the aggregation state produced in the poor solvent system $(1,4-\text{dioxane/H}_2\text{O} = 1/99 \text{ v/v}, 1.0 \times 10^{-5} \text{ M})$. Maximum values of molar extinction coefficient of **DPh1** and **MPh1** in diluted solutions were larger than those in the aggregation state. In addition, the edges in the absorption band were observed in the redshifted wavelength region in the aggregation state. It is likely that intermolecular interaction should occur in the aggregation state. In the aggregation state of MPh1, the shoulder peak was observed at around 400 nm which was longer than the peak top wavelength of the dimer, **DPh1**, in the dilute solution state. Two reasons were probable for the explanation of the phenomenon. One is the difference of stacking formation between **DPh1** in the dilution state and **MPh1** in the aggregation state. **MPh1** could form face-to-face stacking whereas DPh1 formed X-shape stacking and the former interaction was stronger than the latter one. The other is the number of the interacted molecules. In the aggregation state of **MPh1**, two or more molecules could interact each other. Conversely, from the comparison with **DPh2** and **MPh2**, smaller change of maximum values of molar extinction coefficient was obtained than those with **DPh1** and **MPh1**. In the DPh2 and MPh2 systems, intermolecular interaction could be disturbed because of steric hindrance. The peak top wavelengths of absorption bands of **DPh1** (395 nm) and DPh2 (403 nm) were red-shifted in comparison to those of the monomers MPh1 (353 nm) and MPh2 (337 nm), respectively. Through-space conjugation via the [2.2]paracyclophane framework should be responsible for the red-shifts of the absorption bands in the dimers.^[18] The peak top wavelength of **MPh2** was shorter than that of **MPh1** although **MPh2** possesses larger numbers of the phenyl rings than those in **MPh1**. It is suggested that structural distortion could be induced in **MPh2** by steric hindrance, resulting in the restriction of conjugation length. However, peak top wavelength of **DPh2** was observed in the longer wavelength region than that of **DPh1**. It is proposed that the molecular planarity could be improved by the dimerization via the [2.2]paracyclophane framework. Those data imply the existence of the restriction of molecular motion.

Table 1 and Figure 2

Figure 3 shows the PL spectra of the compounds in the diluted solution (1,4-dioxane, 1.0×10^{-5} M) and the aggregation state (1,4-dioxane/H₂O = 1/99 v/v, 1.0×10^{-5} M). ACQ was clearly observed from **DPh1** ($\Phi_{lum} = 0.78$ in diluted solution, $\Phi_{lum} = 0.03$ in aggregation state) and **MPh1** ($\Phi_{lum} = 0.87$ in diluted solution, $\Phi_{lum} = 0.13$ in aggregation state). Intermolecular interaction should occur in the planar conformations. Interestingly, **MPh2** showed AIE property ($\Phi_{lum} = 0.04$ in diluted solution, $\Phi_{lum} = 0.56$ in aggregation state), however **DPh2** provided good PL properties in both solution and aggregation states ($\Phi_{lum} = 0.58$ in diluted solution, $\Phi_{lum} = 0.24$ in aggregation state). To comprehend unique optical properties of **MPh2** and **DPh2**, detailed analyses were executed.

Figure 3

In the most of AIE-active molecules, the degree of molecular motion in the excited

state plays a significant role in AIE properties. In order to confirm the effect of molecular motion, kinetic information was gathered from the calculations of radiative (k_r) and nonradiative rate constants (k_{nr}) with PL lifetime measurements (Table 1 and Figure S11). In diluted solutions, the k_rs of **DPh2** and **MPh2** were almost same ($k_r = 2.2 \times 10^8$ for **DPh2**, 2.1×10^8 for MPh2), whereas the k_{nr} of DPh2 was much smaller than that of MPh2 (k_{nr} = 1.6×10^8 for **DPh2**, 5.1×10^9 for **MPh2**). These data clearly indicate that intramolecular motion should occur in MPh2. In addition, the rigid and stable [2.2]paracyclophane framework suppressed molecular motion in the excited state, leading to smaller $k_{\rm nr}$ than that of **MPh2**. In the relationship of the k_{nrs} of **DPh1** ($k_{nr} = 6.7 \times 10^7$) and **MPh1** ($k_{nr} =$ 9.3×10^7), the same tendency was observed. In summary, **DPh2** should intrinsically have luminescent properties both in the solution and aggregation states. However, because of molecular planarity as suggested in the UV-vis absorption spectrum, some degree of ACQ was induced via the intermolecular π - π interaction in the aggregation state. Therefore, the moderate level of emission can be observed. The k_{nr} of **DPh1** was smaller than that of **DPh2** because the highly planar structure of **DPh1** made efficient extension of π -conjugated system and that contributed to the rigid conformation. In the PL spectra, the wavelength of the peak top of MPh2 was shorter than that of MPh1 in spite of the fact that the opposite result was obtained in the UV-vis absorption spectra. Considering that the PL spectrum of **MPh1** exhibited vibrational structure whereas that of **MPh2** did not show it, in the case of MPh2, structure relaxation occurred in the excited state, which led to a red-shifted PL spectrum.

Variable Temperature PL Measurement

Variable temperature UV-vis absorption and PL measurements were carried out to

obtain further information on the suppression of the molecular motion by the [2.2]paracyclophane framework. These spectra were obtained in the diluted toluene solution (1.0×10^{-5} M for absorption and 1.0×10^{-6} M for PL measurements) at 20, 40, 60 and 80 °C. Relative PL quantum efficiencies were calculated by using the absolute PL quantum efficiency in 1,4-dioxane at 25 °C as a standard (Table 2). In the UV-vis absorption spectra (Figures 4A and 4B), by increasing the temperature, the molar extinction coefficients of **DPh1** and **DPh2** decreased, and the wavelengths of absorption maxima were blue-shifted. The effective conjugation length should be shortened by the molecular motion of the phenyl rings. In the PL spectra, the intensity of **DPh2** drastically decreased by increasing the temperature (Figures 4C and 4D). The PL quantum efficiencies of **DPh1** and **DPh2** decreased 9% and 43% by increasing the temperature from 20 °C to 80 °C, respectively and they were recovered by cooling. These results represent that the molecular motion of the phenyl rings in **DPh2** was suppressed at room temperature. By increasing the solution temperature, the molecular motion should be activated, resulting in acceleration of non-radiative deactivation. Taking advantage of the sensitivity of AIE-active molecules and rigidity of [2.2] paracyclophane frameworks, we successfully synthesized the single-molecule thermo-responsive material. Although several thermo-responsive systems with AIE-active molecule were reported, most of all were constructed based on a sol-gel transition or a composite system.^[19] Threedimensionally binding AIE-active molecules in close proximity with covalent bonds is a new strategy and the results are expected to contribute to a development of singlemolecule optical sensors.

Figure 4 and Table 2

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Dispersion of the Dimers in Polystyrene Film

To investigate the effect of molecular motion on ACQ, DPh1 and DPh2 were dispersed in polystyrene ($M_n = 80,000$, PDI = 2.6) films, and their optical properties were monitored. The films including 1, 2, 5, 10, 20, 40, 60, 80 and 100 wt% of **DPh1** and **DPh2** in polystyrene were prepared with a spin-coat method from 40 μ L CHCl₃ solution (1.0 × 10^{-3} M of **DPh1** and **DPh2** in polystyrene). The results are summarized in Figure S12 and Table S1. **DPh1** and **DPh2** exhibited high absolute PL quantum efficiencies in the 1 wt% films ($\Phi_{lum} = 0.86$ and 0.80, respectively). The Φ_{lum} value of the 1 wt% film of **DPh2** was much higher than that in the diluted solution ($\Phi_{\text{lum}} = 0.58$). This result indicates that the molecular motion of **DPh2** was largely stopped in the film and that was active in the dilute solution. Conversely, the molecular motion of **DPh1** was highly restricted even in the dilute solution state because similar Φ_{lums} were obtained both in the dilute solution state ($\Phi_{\text{lum}} = 0.79$) and in the 1 wt% film state. The Φ_{lum} of **DPh1** dropped rapidly from 2 wt% to 20 wt% films ($\Phi_{lum} = 0.79$ for 2 wt%, 0.55 for 5 wt%, 0.42 for 10 wt%, 0.26 for 20 wt%), and the 40, 60, 80 and 100 wt% films showed low Φ_{lum} values ($\Phi_{\text{lum}} < 0.1$). It is likely that ACQ should occur in these films. On the other hand, increasing the rate of **DPh2** in polystyrene films, the decrease of the Φ_{lum} was moderately. High Φ_{lum} was kept in the 2 wt% film ($\Phi_{\text{lum}} = 0.82$) and it decreased from the 5 wt% film ($\Phi_{\text{lum}} = 0.69$). Finally, the Φ_{lum} value reached 0.27 in the 100 wt% film, which was pure **DPh2**. This value was almost identical to the aggregate of **DPh2** ($\Phi_{\text{lum}} = 0.24$). Therefore, it was suggested that the decrease of Φ_{lum} in the aggregate of **DPh2** was caused by ACQ. Although decrease of Φ_{lum} occurred, the obtained **DPh2** films provided good PL quantum efficiencies even in the condensed state and those results can be advantage for obtaining high brightness films.

Molecular Models

In **DPh2**, experimental optical data strongly suggested the existence of suppression of the molecular motion between two luminophores stacked at the [2.2]paracyclophane unit. Further information about the molecular motion was evaluated by density functional theory (DFT). The structures of **MPh2** and **DPh2** were optimized at the BLYP/def2-TZVPP level. Resulting molecular structures are shown in Figure 5. From the molecular models, it was clearly shown that the optimized structure of **MPh2** was highly twisted, whereas that of **DPh2** was relatively planar because of the intramolecular stacking. The two luminophores were located at the distance of 4–6 Å, which was sufficient to inhibit the free rotation. The restriction of the molecular motion was corresponded to the high Φ_{lum} value of **DPh2** in the diluted solution. However, in the aggregation state, the ACQ should occur. The highly-twisted structure of **MPh2** should be favorable for maintaining molecular motions in the solution and avoiding ACQ in the aggregation, leading to the AIE behavior. Thus, it is summarized that the stacking at the [2.2]paracyclophane unit should contribute to enhancing molecular planarity even in the presence of multiple hindered groups. Then, unique emission behaviors were obtained.

Figure 5

Chiroptical Properties

Finally, the chiroptical properties of the ground and excited states of **DPh1** and **DPh2** were investigated by CD and CPL spectroscopies, respectively. Chiroptical data such as CD and CPL dissymmetry factor^[20] (g_{abs} and g_{lum} , respectively) are summarized in Table 3. Figure 6 shows the CD and absorption spectra of both enantiomers of **DPh1** and **DPh2**

in the diluted solution (1,4-dioxane, 1.0×10^{-5} M) and in the aggregation state (1,4dioxane/H₂O = 1/99 v/v, 1.0×10^{-5} M). From both enantiomer solutions, mirror image Cotton effects were observed clearly in the CD spectra. In the diluted solution, the *g*_{abs} values of the first Cotton effect were estimated to be $+3.5 \times 10^{-3}$ for (*S*_p)-**DPh1** and $+1.0 \times 10^{-3}$ for (*S*_p)-**DPh2**, respectively. In the aggregation state, the *g*_{abs} values of the first Cotton effect were estimated to be $+3.0 \times 10^{-3}$ for (*S*_p)-**DPh1** and $+0.87 \times 10^{-3}$ for (*S*_p)-**DPh2**, respectively. When these compounds formed the aggregates, the *g*_{abs} values for (*S*_p)- and (*R*_p)-**DPh1** decreased and the pattern of Cotton effect was red-shifted in all regions, whereas those for (*S*_p)- and (*R*_p)-**DPh2** remained in almost all regions. This result also indicates stronger intermolecular interaction of **DPh1** and that of **DPh2** was twisted.

The CPL spectra of both enantiomers of **DPh1** and **DPh2** in the diluted solution (1,4dioxane, 1.0×10^{-5} M) and in the aggregation state (1,4-dioxane/H₂O = 1/99 v/v, 1.0×10^{-5} M) are shown in Figure 7. Mirror image CPL spectra were obtained from the enantiomers. The g_{lum} values were estimated to be $+3.7 \times 10^{-3}$ for (S_p)-**DPh1** and $+0.73 \times 10^{-3}$ for (S_p)-**DPh2** in the diluted solution, and $+4.3 \times 10^{-3}$ for (S_p)-**DPh1** and $+0.90 \times 10^{-3}$ for (S_p)-**DPh2** in the aggregation state. In the aggregation systems of (S_p)- and (R_p)-**DPh1**, CPL peak tops were red-shifted, and the g_{lum} values increased because of intermolecular interaction in the excited state. On the other hand, small changes were observed in the CPL peak top and g_{lum} values of (S_p)-**DPh2** due to weak intermolecular interaction in the excited state. In the diluted solution, **DPh1** exhibited excellent CPL profiles ($\varepsilon_{max} = 61,000 \text{ M}^{-1}\text{ cm}^{-1}$, $\Phi_{lum} = 0.78$ and $g_{lum} = +3.7 \times 10^{-3}$ for (S_p)-**DPh1**, ε_{max} : maximum of molar extinction coefficient) in comparison to the recent reported CPL

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compounds.^{14a} On the other hand, in the aggregation state, **DPh2** showed good CPL profiles ($\varepsilon_{\text{max}} = 31,000 \text{ M}^{-1} \text{ cm}^{-1}$, $\Phi_{\text{lum}} = 0.24$ and $g_{\text{lum}} = +0.90 \times 10^{-3}$ for (S_p)-**DPh2**).

Table 3 and Figures 6 and 7

Conclusions

Optically active phenylethene dimers, **DPh1** and **DPh2**, were synthesized with a planar chiral 4,7,12,15-tetrasubstituted [2.2]paracyclophane. From the series of experimental data and theoretical calculation, it is strongly suggested that molecular motion can be efficiently regulated by stacking with two luminophores in close proximity by the [2.2]paracyclophane unit even in the presence of multiple steric hindered groups. As a result, unique luminescent behaviors were monitored during phase transition. By increasing the temperature, PL intensity of **DPh2** decreased sensitively. Subsequently, the intensity was recovered by cooling. Moreover, **DPh1** and **DPh2** showed good chiroptical properties and the dissymmetry factors on the order of approximately 10⁻³. **DPh1** had excellent CPL profiles in the diluted solution, and **DPh2** had good CPL profiles in the aggregation state. Those effects are originated from the planar chiral, rigid and stable 4,7,12,15-tetrasubstituted[2.2]paracyclophane scaffold. Since these results are realized only with carbon and hydrogen atoms, the [2.2]paracyclophane unit could be a versatile building block for constructing advanced optical materials with multiple functions.

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- [20]CD dissymmetry factor is defined as $g_{abs} = 2\Delta\varepsilon/\varepsilon$, where $\Delta\varepsilon$ indicates differences of absorbance between left and right handed circularly polarized light. CPL dissymmetry factor is defined as $g_{lum} = 2(I_{left} - I_{right})/(I_{left} + I_{right})$, where I_{left} and I_{right} indicate luminescence intensities of left and right handed CPL, respectively.

Scheme 1. Synthesis of compound 2.



Scheme 2. Synthesis of planar chiral dimers (*S*_p)-DPh1 and DPh2.



Scheme 3. Synthesis of model compounds MPh1 and MPh2.





Figure 1. Structures of MPh1, DPh1, MPh2 and DPh2.

	λ_{abs} c/ nm	$\lambda_{\text{lum}} d / \text{nm}$	$\tau^{e}/$ ns	χ^2	$arPsi_{ ext{lum}^f}$	$k_{\rm r}^{g}/{\rm s}^{-1}$	$k_{\rm nr} {}^{g} / {\rm s}^{-1}$
DPh1 ^a	395	455	3.28	1.02	0.78	2.4×10^{8}	6.7×10^{7}
DPh1-agg ^b	394	470	0.24 (80.9%) 1.59 (19.1%)	1.58	0.03	1.3×10 ^{8 h}	4.0×10 ^{9 h}
$\mathbf{MPh1}^{a}$	353	401, 424	1.40	1.09	0.87	6.2×10^{8}	9.3×10 ⁷
MPh1-agg ^b	344	443	0.24 (80.6%) 0.88 (19.4%)	1.44	0.13	5.4×10 ^{8 h}	3.6×10 ^{9 h}
DPh2 ^a	403	494	2.60	1.17	0.58	2.2×10^{8}	1.6×10^{8}
DPh2-agg ^b	403	503	1.40	1.13	0.24	1.7×10^{8}	5.4×10 ⁸
MPh2 ^a	337	468	0.19	1.19	0.04	2.1×10^{8}	5.1×10 ⁹
MPh2-agg ^b	341	473	2.30	1.07	0.56	2.4×10^{8}	1.9×10^{8}

Table 1. Optical p	properties of the co	ompounds.
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^{*a*} In 1,4-dioxane. ^{*b*} In 1,4-dioxane/H₂O = 1/99 v/v. ^{*c*} 1.0 × 10⁻⁵ M. ^{*d*} 1.0 × 10⁻⁶ M, excited at absorption maxima. ^{*e*} Emission lifetime at λ_{lum} . ^{*f*} Absolute PL quantum efficiency. ^{*g*} $k_{\text{r}} = \Phi_{\text{lum}}/\tau$, $k_{\text{nr}} = (1 - \Phi_{\text{lum}})/\tau$. ^{*h*} Calculated by using the major component.



Figure 2. UV–vis absorption spectra in 1,4-dioxane (solid line) and 1,4-dioxane/H₂O = 1/99 v/v (dotted line) ($1.0 \times 10^{-5} \text{ M}$); (A) **DPh1** and **MPh1**; (B) **DPh2** and **MPh2**.



Figure 3. PL spectra in 1,4-dioxane (solid line) and 1,4-dioxane/H₂O = 1/99 v/v (dotted line) ($1.0 \times 10^{-5} \text{ M}$); (A) **DPh1** and **MPh1**; (B) **DPh2** and **MPh2**.



Figure 4. UV–vis and PL variable temperature spectra in toluene $(1.0 \times 10^{-5} \text{ M for UV})$ where $1.0 \times 10^{-6} \text{ M}$ for PL, excited at absorption maximum) at 20 °C, 40 °C, 60 °C, 80 °C; (A) UV–vis spectra of **DPh1**; (B) UV–vis spectra of **DPh2**; PL spectra of **DPh1**; PL spectra of **DPh1**; PL spectra of **DPh2**.

	20 °C	40 °C	60 °C	80 °C
DPh1	0.70	0.68	0.65	0.63
DPh2	0.51	0.44	0.39	0.29

Table 2. Relative PL quantum efficiencies^{*a,b*}.

^{*a*} In toluene $(1.0 \times 10^{-6} \text{ M} \text{ excited at absorption maximum})$. ^{*b*} Relative PL quantum efficiencies were calculated from absolute PL quantum efficiencies of **DPh1** and **DPh2** in 1,4-dioxane (Table 1), respectively.



Figure 5. Molecular models of **MPh2** and **DPh2**. The structure was optimized by DFT at BLYP/def2-TZVPP levels.

	$g_{abs}{}^{a}/10^{-3}$	$g_{\rm lum}^{b}/10^{-3}$
(<i>S</i> _p)- DPh1	+3.5	+3.7
(Sp)- DPh1-agg	+3.0	+4.3
(<i>S</i> _p)- DPh2	+1.0	+0.73
(Sp)- DPh2-agg	+0.87	+0.90

Table 3. Chiroptical properties: Spectroscopic data of (*S*_P)-isomers.

^{*a*} $g_{abs} = 2\Delta\varepsilon/\varepsilon$, where $\Delta\varepsilon$ indicates differences of absorbance between left and right handed circularly polarized light, respectively. The g_{abs} value of the first peak top was estimated. ^{*b*} $g_{lum} = 2(I_{left} - I_{right})/(I_{left} + I_{right})$, where I_{left} and I_{right} indicate luminescence intensities of left- and right- handed CPL, respectively. The average g_{lum} value of the around peak top was estimated.



Figure 6. CD, g_{abs} , and absorption spectra in 1,4-dioxane (solid line) and in 1,4-dioxane/H₂O = 1/99 v/v (dotted line) (1.0×10^{-5} M); (A) (S_p)- and (R_p)-**DPh1**; (B) (S_p)- and (R_p)-**DPh2**.



Figure 7. CPL, g_{lum} , and PL spectra in 1,4-dioxane (solid line) and 1,4-dioxane/H₂O = 1/99 v/v (dotted line) (1.0×10^{-5} M); (A) (S_p)- and (R_p)-**DPh1**; (B) (S_p)- and (R_p)-**DPh2**. Excitation wavelength: 350 nm.

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