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# Significant Enhancement of Absorption and Luminescence Dissymmetry Factors in the Far-red Region: Zinc(II) Homoleptic Helicate Formed by a Pair of Achiral Dipyrromethene Ligands

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**Abstract:** A homoleptic zinc(II) helicate organized by a pair of achiral dipyrromethene ligands through zinc(II)-coordination were synthesized to evaluate the chiroptical properties. This zinc complex afforded strong exciton-coupled chiroptical responses from the helical configuration with a strong absorption dissymmetry factor  $|g_{abs}|$  (up to 0.20). More importantly, an intense polarized luminescence in the far-red region (700-850 nm) with a fluorescence quantum yield  $\mathcal{D}_{FL}$  of 0.23 was observed for this helicate with a dissymmetry factor  $|g_{lum}|$  of 0.022, the largest value among the rare earth- and precious metal-free small molecules, to the best of our knowledge. These unprecedentedly large *g* values were supported by theoretical calculations.

## Introduction

and years, simple sophisticated In recent chiral molecules/materials that possess large anisotropy in circular dichroism (CD) and circularly polarized luminescence (CPL) have been considerably attracted.<sup>[1]</sup> In contrast with well-known efficient chiral properties (i.e., large dissymmetry factors) of lanthanide-[1h, 2] and precious metal-[3] based complexes and molecular assemblies, rare earth and precious metal-free helicenoids are one of the most promising organic molecules for higher dissymmetry factors for absorption and luminescence (i.e.,  $g_{abs}$  and  $g_{lum}$ ,<sup>[3c, 4]</sup> which are the differential absorption and emission of left- and right-circularly polarized light. However, the values for rare earth- and precious metal-free helicenes and helicenoids are generally small  $(10^{-3} \sim 10^{-5} \text{ range})^{[1b, 1d, 3c, 4]}$ although the several systems with higher values were reported.<sup>[5]</sup> To remedy the situation, researches on covalentlyfused double helicenes<sup>[4a, 6]</sup> and dimeric metallohelicenes have been reported with some success.<sup>[7]</sup>

Although extending  $\pi$ -conjugation is a straightforward strategy for the enhanced absorption and fluorescence properties in the far-red region,<sup>[8]</sup> a degree of red-shift by such an approach is relatively small in the case of carbohelicenes; for

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example, [16]carbohelicene<sup>[9]</sup> only shows the absorption maximum at ca. 430 nm (compare, e.g., 324 and 390 nm for [6] and [9]helicenes, respectively).<sup>[10]</sup> To make matters worse, fluorescence quantum yields ( $\Phi_{FL}$ ) of [*n*]carbohelicenes significantly decrease by increasing the size n ( $\Phi_{FL} \leq 0.02$  when  $n \geq 7$ ),<sup>[11]</sup> discouraging the utilization of simple helicenes for CPL in the far-red region.<sup>[19, 12]</sup> In contrast, improved chiroptical properties of dipyrromethene chromophores have been recently reported,<sup>[13]</sup> and the supramolecular dimer was shown to be more promising.<sup>[14]</sup> Accordingly, we envisioned that coordination-driven molecules with helical chirality composed of a pair of dipyrromethene chromophores are better suited for efficient CD and/or CPL properties.



**Scheme 1.** A formation of chiral homoleptic zinc(II) helicate organized by a pair of achiral phenanthrene-fused dipyrromethene ligands.

Herein we report the synthesis and strong chiroptical properties of rare earth- and precious metal-free homoleptic zinc(II) helicate organized by a pair of achiral benzo[a]phenanthrene-fused dipyrromethene ligands (Scheme 1). A selective formation of chiral helicate is elicited by the possibility of tetrahedral conformation utilizing two unsymmetrical bidentate ligands.

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The helicate exhibits the strong chiroptical responses with unprecedentedly large dissymmetry factors both in absorption and emission ( $|g_{abs}| = 0.20$  and  $|g_{lum}| = 0.022$ ), the latter of which appears in the far-red region (700-850 nm).



**Figure. 1** Single crystal structures of Zn(Phena-dpm)<sub>2</sub>. (A) Side and (B) top views in ORTEP drawing with 50% probability. Substructures of (C) zinc complexation and (D) one of the phenanthrene units.

## **Result and Discussion**

#### **Synthesis**

We synthesized the achiral dipyrromethene ligand (Phena-dpm-H) by Suzuki-Miyaura coupling followed by Scholl reaction, which was complexed by zinc(II) to afford the chiral helicate  $Zn(Phena-dpm)_2$  as racemate in overall 2% yield (for 5 steps in Scheme 2). The detailed synthetic procedures are described in the experimental section (also see Figures S1-S9 in Supporting Information, SI).

#### Crystallographic analyses

Crystals of racemic Zn(Phena-dpm)<sub>2</sub>, which are suitable for X-ray diffraction analysis, were obtained by slow evaporation of CH<sub>2</sub>Cl<sub>2</sub> solution of the racemate. Although benzophenanthrene unit was nearly planar in its monomeric form, the helically chiral configuration was successfully developed by zinc(II) complexation with two Phena-dpm-H ligands (Figure 1A). Remarkably, an effective overlap between two terminal phenanthrene units in Zn(Phena-dpm)<sub>2</sub> was noticed with a separation distance smaller than the vdW contact (< 3.4 Å, Figure 1B). A skewed structure in this relatively congested complex was evident considering the dihedral angle of 71.0° between the dipyrromethene units (N1-N2-N3-N4), which was much smaller than that for the conventional tetrahedral geometry (Figure 1C). The torsion angle between the dipyrromethene and phenanthrene units (C22-C24-C25-N1) of 46.7° suggested the nonplanar structure of the ligand units (Figure 1D), which is most likely due to the intramolecular distortion interaction between the two ligands. The angle was in sharp contrast with the corresponding torsion angle (18.4°) in free Phena-dpm-H (Figure S10 in SI), although the bond lengths remained almost constant.



**Figure 2.** (A) Absorption spectra of (a)  $Zn(Phena-dpm)_2$  and (b) free Phena-dpm-H. (B) CD Spectra and (C) dissymmetry  $(g_{abs})$  factor profiles of  $Zn(Phena-dpm)_2$  in toluene. Red and blue lines correspond to (M,M)- and (P,P)-forms, respectively.

Thus, the cooperative effect between coordination and noncoordination (e.g.,  $\pi$ - $\pi$  stacking) bonds are essential for Zn(Phena-dpm)<sub>2</sub>, although the structure cannot solely be determined by intramolecular forces (*vide infra*).

#### Spectroscopic measurements

As expected, absorption spectrum of  $Zn(Phena-dpm)_2$ (Figure 2A, spectrum a) was red-shifted and broadened relative to that of free Phena-dpm-H (spectrum b). More importantly, an original absorption maximum at 522 nm was found as split peaks in the helicate at 548 and 615 nm, due to the excitonic **Figure 3.** (A) Fluorescence and (B) CPL spectra and (C) dissymmetry ( $g_{lum}$ ) factor profiles of Zn(Phena-dpm)<sub>2</sub> in toluene ( $\lambda_{ex} = 580$  nm). Red and blue lines correspond to (*M*,*M*)- and (*P*,*P*)-forms, respectively. The spectra were corrected by smoothing method because of poor detector response in the far-red region.

coupling.<sup>[15]</sup> A forbidden peak at 575 nm in  $Zn(Phena-dpm)_2$  (among the couplet) is assigned as distinct transition originated from the distorted geometry (Figures S10 and S11 in SI).

For chiroptical measurements, chiral HPLC equipped with DAICLE CHIRALPAK IE (Figure S12 in SI) was used to obtain the enantiopure samples. Figure 2B shows the CD spectra of (*P*,*P*)- and (*M*,*M*)-forms of Zn(Phena-dpm)<sub>2</sub> in toluene. The enantiomers exhibited mirror-imaged Cotton effects (CEs) in the UV and visible regions, with negative, positive, and negative CEs (from low to high excitation energy) for the (*P*,*P*)-isomer, and vise versa. The molar CD ( $\Delta \varepsilon$ ) in the visible region (~3,000

 $M^{-1}$  cm<sup>-1</sup> at 500-650 nm) was much larger than that in the UV (~160  $M^{-1}$  cm<sup>-1</sup> at 360 nm). Thus, the absorption dissymmetry factors  $g_{abs}$  of (*P*,*P*)-form were calculated to be +0.022 at 360 nm, +0.054 at 540 nm and -0.20 at 615 nm, respectively (Figure 2C).

In contrast with the monomeric Phena-dpm-H (Figure S13 in SI), an efficient fluorescence spectrum of Zn(Phena-dpm)<sub>2</sub> in the far-red region was observed in toluene at 25 °C (Figure 3A), with a good fluorescence quantum yield ( $\Phi_{FL}$ ) of 0.23 and the lifetime ( $\tau_{FL}$ ) of 3.0 ns (Figure S14 in SI). Although a mirrorimaged relationship between absorption and emission spectra was noticed, a Stokes shift of 1100 cm<sup>-1</sup> suggests the moderate excited-state relaxation for the coordination-driven helicate (vide infra). Strong and exactly mirror-imaged CPL responses were observed for (P,P)- and (M,M)-Zn(Phena-dpm)<sub>2</sub> in the fluorescence spectrum (Figure 3B). The signs of CPL were consistent with those of CD at the lowest-energy band, which is in agreement with the general trends for the ECD and CPL spectra, including the reported exciton-coupled systems.<sup>[16]</sup> The  $q_{\text{lum}}$  value of (P,P)-form was calculated to be -0.022 at 660 nm (Figure 3C). Moreover, it should be emphasized that the  $q_{lum}$ profiles extended up to ca. 850 nm (i.e., far-red region) as shown in Figure 3C.

#### **Theoretical calculations**

To better understand the origins for the intense chiroptical responses in Zn(Phena-dpm)<sub>2</sub>, we analyzed the relevant electronic transitions with an aid of the density functional theory (DFT) calculations, detailed below. A similar approach has been successfully employed for some simple organic molecules.<sup>[1c, 17]</sup> Thus, we first obtained the optimized structures of Zn(Phena-dpm)<sub>2</sub> in the ground and excited states at the (TD)-DFT-M062X/def2-QZV(GD3) level.<sup>[18]</sup> Based on these calculated geometries in the  $S_0$  and  $S_1$  states, we then evaluated the relevant electronic  $(\mu)$  and magnetic (m)transition dipole moments, responsible for the rotational strength R for the CD and CPL spectra (Figure 4 and Table S1 in SI). We confirmed that small structural variation between the single crystal and calculated structures in the ground state did not considerably affect the predicated chiroptical responses (Figures S15-S18 in SI). In contrast, the structural relaxation was found to be substantial upon photoexcitation, which subsequently affected the chiroptical responses. Thus, the overall structural distortion around zinc(II) atom was somewhat reduced in the excited state because the dihedral and torsion angles of dipyrromethene units became smaller (53.7° and 39.2°, respectively). More interestingly, the degree of overlap between the phenanthrene ligands was considerably altered in the excited state (Figure 4), while the interplane distances were kept nearly constant (3.40 Å vs 3.25 Å). Such a structural change is well explained by the exciplex that generally requires sufficient π-overlap between two aromatic groups, while this is usually avoided in the ground state due to electrostatics and/or Pauli-repulsion.<sup>[19]</sup> As such, a slightly poorer chiroptical response was predicted for the  $S_1$ -to- $S_0$  transition (R = 770,

responsible for CPL) with respect to the reverse  $S_0$ -to- $S_1$  transition (R = 1013, for CD).

According to Rosenfeld equation,<sup>[20]</sup> R is the imaginary part of the scalar product of  $\mu$  and m of the relevant electronic transition (i.e.,  $R = |\mu| |m| \cos \theta$ ). Among the possible factors contributing to the large R values for both CD and CPL responses (and thus the dissymmetry factors  $g_{abs}$  and  $g_{lum}$ ), small angle between the moments ( $\theta$ ) was found to play a decisive role (Figure 4 and Table S1 in SI). Indeed, these factors for the S<sub>0</sub>-to-S<sub>1</sub> and S<sub>1</sub>-to-S<sub>0</sub> transition in the complex was calculated as 0.94 ( $\theta$  = 20.6°) and 0.96 ( $\theta$  = 15.7°), respectively, which are in sharp contrast with the much lower value: 0.027 ( $\theta$  = 91.6°) in free Phena-dpm-H (Figure S19 in SI). Such an enormous improvement is established by the  $C_{2}$ symmetrical alignment of two identical phenanthrene-fused helical units in Zn(Phena-dpm)<sub>2</sub>. In addition, the increase in absolute |m| was also due to the dimeric structure of Zn(Phenadpm)<sub>2</sub>. In brief, a proper alignment of two identical helical components through the coordination-driven molecules serves as a general strategy to achieve the strong chiroptical responses. This may have been apparent in CD where an effective exciton coupling should be observed, but now turned out to be also applicable to the materials that emit strong CPL in the far-red wavelength region. Recently, a related approach has been reported, in which conjugated diketopyrrolopyrrole units were covalently incorporated into the chiral helicene scaffold to provide intense chiroptical responses.<sup>[21]</sup>



**Figure 4.** Calculated structures of (*P*,*P*)-Zn(Phena-dpm)<sub>2</sub> in (A) ground and (B) excited states. Hydrogen atoms are omitted for clarity. Electric ( $\mu$ ) and magnetic (*m*) transition dipole moments for S<sub>0</sub>-to-S<sub>1</sub> or S<sub>1</sub>-to-S<sub>0</sub> state are also shown.

## Conclusions

In conclusion, we successfully demonstrated that the homoleptic chiral zinc(II) helicate selectively formed by a pair of achiral benzo[a]phenanthrene-fused dipyrromethene ligands

afforded unusually strong chiroptical responses with absorption and luminescence dissymmetry factors of  $|g_{abs}| = 0.20$  (at 615 nm) and  $|g_{lum}| = 0.022$  (at 660 nm), respectively. The  $g_{lum}$ profiles also extended up to ca. 850 nm. They are highest values among the rare earth- and precious mental-free small molecules that emit in the far-red wavelength region. We believe that a synthetic strategy exemplified herein for enhanced chiroptical properties will provide a new perspective for future development of advanced luminescent materials.

## **Experimental Section**

#### General and materials

The best available grade solvents and reagents were purchased from commercial suppliers such as Tokyo Chemical Industry, Kanto Chemical Co., Inc., Nacalai Tesque, and Wako Pure Chemical Industries. All commercial reagents were used without further purification. Column flash chromatography was performed on silica gel (Fuji Silysia Chemical Itd. PSQ60B or PSQ100B, 60 µm or 100 µm). Preparative recycling gel permeation chromatography was performed with high pressure liquid chromatography apparatus Japan Analytical Industry LC-9204 using chloroform as eluent at room temperature. We used an LC-9204 apparatus equipped with a pump (JAI PI-60, flow rate 2.5 mL / min), a UV detector (JAI UV-3740) and two columns (JAIGEL 2H and 1H, 40 × 600 mm for each). Racemic Zn(Phena-dpm)<sub>2</sub> were separated bv usina hexane/dichloromethane/diethylamine (60/40/0.1, v/v/v) as eluent at room temperature on a DAICEL CHIRALPAK® IE column. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a 400 MHz spectrometer JEOL ECX-400, AL-400, or ALPHA-400 using the solvent peak as the reference standard, with chemical shifts given in parts per million (ppm). CDCl<sub>3</sub> and C<sub>6</sub>D<sub>6</sub> were used as the solvents. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a JEOL JMS-S3000. Electron ionization (EI) mass spectra were recorded on a JEOL JMS-700. The DFT and TD-DFT calculations of molecular orbitals were performed with Gaussian 09 at the M062x/def2QZV/def2QZV (GD3) level of theory. The molecular geometries were optimized by TPSSTPSS/def2TZVP/def2TZVP (GD3BJ). 2-(2-Bromophenyl)naphthalene<sup>[22]</sup> and Br-BDP<sup>[23]</sup> were synthesized by referring the reported synthetic methods.

#### Preparation and analysis of single-crystal structures

Single crystals of the racemic mixtures: Zn(Phena-dpm)<sub>2</sub> for packing formation analysis were prepared by concentration of dichloromethane (DCM) solution at -10 °C. Analyses of crystal structures were performed on a Rigaku R-AXIS RAPID diffractometer with graphite monochromated Mo K  $\alpha\,$  radiation. The structures were solved by direct methods (SHELXS-97). Computation of molecular graphics was performed with ORTEP-3 for Windows. Additional crystallographic information is available in SI (vide infra). CCDC-1826041 (rac-Zn(Phena-dpm)<sub>2</sub>) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Crystallographic Data Center Cambridge via www.ccdc. cam.ac.uk/data\_request/cif.

#### Spectroscopic measurements

**Spectroscopy**: UV-vis absorption spectra were recorded on Parkin Elmer (Lamda 750) UV-VIS-NIR spectrophotometer. Fluorescence spectra were recorded on HORIBA (FluoroMax Plus) spectrophotometer.

Absolute fluorescence quantum yield were recorded on Jasco (FP-8500) spectrofluorometer with an integrating sphere detector. Fluorescence lifetimes were also measured on HORIBA Scientific timecorrelated single-photon counting system (FluoroCube) with the laser light (DeltaDiode, laser diode head) as an excitation source. A laser operation wavelength, pulse width, and frequency were 404 nm, 50 ps and 1 MHz, respectively. The practical time resolution is 15 ps by deconvolution of an observed trace with the analytical software (DAS6).

# Circular dichroism (CD) and circularly polarized luminescence (CPL) measurements.

CD spectra were measured by Jasco (J-1500) CD spectrometer and CPL spectra were recorded on Jasco (CPL-300) CPL spectrophotometer. For chiroptical measurements, chiral HPLC equipped with Daicel Chiralcel IE column was used to obtain enantiopure samples (Figure S12 in SI). Regarding the chiral stabilities of Zn(Phena-dpm)<sub>2</sub>, the CD signal ( $\Delta \varepsilon$ ) in toluene was approximately reduced by half after several days. In a polar solvent such as THF, the half-lifetime slightly became accelerated.

#### Synthesis

Synthesis of compound 1: 2-(2-bromophenyl)-naphthalene (3.0 g, 10.6 mmol), 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.0 g, 31.3 mmol) and triethylamine (3.3 mL, 23.4 mmol) were solved in deoxidized toluene (45 mL), and then, Ni(dppp)Cl<sub>2</sub> (600 mg, 1.11 mmol) was added to the mixture solution under a nitrogen atmosphere. The mixture was stirred at 95 °C for 12 h. After cooling to room temperature, the mixture was poured into water, and then the organic layer was extracted with dichloromethane (DCM), washed with brine, dried over MgSO<sub>4</sub>, and evaporated. The residue was purified by column chromatography using hexane/ethyl acetate (50/1, v/v) as the eluent, finally, compound 1 (1.12 g, 32% yield) was obtained as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.98 (d, J = 13.2 Hz, 5H), 7.22 (d, J = 8.3 Hz, 1H), 7.48-7.60(m, 5H), 1.28 (s, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 147.25, 140.57, 134.59, 132.96, 132.30, 130.09, 129.20, 127.88, 127.72, 127.59, 127.50, 127.19, 126.24, 125.81, 125.43, 83.49, 24.42. High resolution MALDI-TOF-Mass: m/z = 330.178 [M] (Figures S1 and S2 in SI).

Synthesis of Nap-Ph-BDP: Cs<sub>2</sub>CO<sub>3</sub> (750 mg, 2.30 mmol) was dissolved in a degassed mixture solvent of water (2.4 mL) and THF (120 mL) under a nitrogen atmosphere.  $Pd_2(dba)_3$ ·CHCl<sub>3</sub> (120 mg, 0.116 mmol) and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (300 mg, 0.731 mmol), compound 1 (321 mg, 0.972 mmol) and bromo-substituted BODIPY (309 mg, 0.796 mmol) were added and stirred at room temperature for 48 h. After finishing the reaction, the mixture was filtered by using Celite pad, then rinsing Nap-Ph-BDP with DCM, and evaporated. The residue was purified by column chromatography using hexane/ethyl acetate (6/1, v/v) as the eluent, then, violet solid was obtained. In addition, obtained violet solid was purified by recycling GPC using only CHCl<sub>3</sub> as the eluent, finally, Nap-Ph-BDP (393 mg, 98% yield) was obtained as a violet solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.83-7.84 (m, 3H), 7.67-7.73 (m, 3H), 7.44-7.59 (m, 3H), 7.28-7.44 (m, 3H), 7.21 (dd, J = 8.4, 1.7 Hz, 1H), 6.40 (dd, J = 4.0, 1.6 Hz, 1H), 5.87 (s, 1H), 2.21 (s, 3H), 1.77 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 147.34, 144.15, 143.92, 140.61, 139.25, 138.46, 135.95, 135.54, 135.34, 133.57, 133.38, 132.46, 131.68, 131.04, 130.90, 130.14, 129.73, 129.26, 128.45, 128.07, 127.93, 127.78, 127.69, 127.62, 126.20, 126.05, 118.35, 21.10, 19.71. High resolution El-Mass: m/z = 512.226 (Figures S3 and S4 in SI).

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**Synthesis of Nap-Ph-dpm**: ZrCl<sub>4</sub> (342 mg, 1.47 mmol) in methanol (4 mL) and Nap-Ph-BDP (150 mg, 0.292 mmol) in MeCN (30 mL) were mixed under a nitrogen atmosphere, and refluxed for 30 min. After cooling to room temperature, the mixture was poured into water, and then, Nap-Ph-dpm was extracted with DCM, washed with brine, dried over MgSO<sub>4</sub>, and evaporated. The residue was purified by column chromatography using hexane/ethyl acetate/triethylamine (20/1/1, v/v/v) as the eluent. Nap-Ph-dpm was proceeded next step without complete purification.

Synthesis of Phena-dpm-H: Nap-Ph-dpm (70 mg, 0.166 mmol) was dissolved in deoxidized DCM (40 mL) under a nitrogen atmosphere. Then, BF<sub>3</sub>·OEt<sub>2</sub> (0.1 mL, 0.793 mmol) and PIFA (222 mg, 0.516 mmol) in deoxidized DCM (4 mL) was added dropwise to the mixture at -55 °C (MeCN) under nitrogen atmosphere. The reaction mixture was stirred at -55 °C for 1 h. After quenching the reaction by MeOH and a Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aqueous solution, Phena-dpm-H was extracted with DCM, dried over MgSO<sub>4</sub>, and evaporated. The residue was purified by column chromatography using hexane/ethyl acetate/triethylamine (20/1/1, v/v/v) as the eluent, finally, Phena-dpm-H (39 mg, 51% yield) was afforded as a red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.43 (d, J = 8.8 Hz, 1H), 8.64-8.71 (m, 2H), 8.10-8.13 (m, 2H), 8.06 (d, J = 8.1 Hz, 1H), 8.02 (d, J = 9.0 Hz, 1H), 7.88-7.92 (m, 1H), 7.70 (t, J = 7.9 Hz, 1H), 7.55 (dt, J = 9.5, 3.5 Hz, 2H), 7.09 8s, 1H), 7.03 (s, 2H), 6.99 (dd, J = 4.5, 0.9 Hz, 1H), 6.55 (d, J = 4.5Hz, 1H), 2.44 (s, 3H), 2.20 (s, 6H). High resolution EI-Mass: m/z = 462.210 [M] (Figures S5 and S6 in SI).

**Synthesis of Zn(Phena-dpm)**<sub>2</sub>: Phena-dpm-H (28 mg, 60.6 μmol) and Zn(OAc)<sub>2</sub> (5.28 mg, 28.9 μmol) were dissolved in degassed THF (10 mL) under a nitrogen atmosphere, and stirred at 60°C for 48h. Next, the mixture was filtered by silica-gel pad, then rinsing Phena-dpm-H with DCM, and evaporated. The residue was purified by GPC by using neat CHCl<sub>3</sub> as the eluent to give Zn(Phena-dpm)<sub>2</sub> (18 mg, 36% yield) as a blue to gold solid. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 9.17 (dd, *J* = 8.0, 0.6 Hz, 1H), 8.28 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 9.2 Hz, 1H), 7.84 (s, 1H), 7.54 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.34-7.38 (m, 1H), 7.26 (s, 1H), 7.21-7.25 (m, 1H), 7.02 (s, 1H), 6.99 (d, *J* = 9.0 Hz, 1H), 6.87 (s, 1H), 6.76-6.80 (m, 2H), 6.64 (td, J = 7.7, 1.6 Hz, 2H), 6.19 (dd, J = 4.3, 0.9 Hz, 1H), 2.52 (s, 3H), 2.37 (s, 3H), 2.29 (s, 3H). High resolution MALDI-TOF-Mass: m/z = 986.327 [M] (Figures S7 and S8 in SI).

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Layout 1:

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A supramolecular homoleptic zinc helicate composed of a pair of achiral ligands demonstrated the unprecedented strong chiroptical responses with large dissymmetry factors ( $|g_{abs}| = 0.20$  and  $|g_{lum}| =$ 0.022) in the far-red region, largest among rare earth and precious mental -free small molecules.



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Significant Enhancement of Absorption and Luminescence Dissymmetry Factors in the Far-Red Region from Rare Earth-Free Zinc(II) Homoleptic Helicate Formed by a Pair of Achiral Dipyrromethene Ligands