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Experimental and theoretical studies on circularly polarized phosphorescence of a [2.2]paracyclophane-based platinum(II) complex[†]

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An optically active binuclear platinum(II) complex based on planar chiral [2.2]paracyclophane was synthesized. The corresponding enantiomers exhibited red circularly polarized phosphorescence (CPP) with the dissymmetry factor $|g_{lum}| = 1.0 \times 10^{-3}$. We report, for the first time, theoretical estimation of the CPP $|g_{lum}|$ value using relativistic calculations.

Circularly polarized luminescence (CPL) from organic¹ and inorganic² materials has attracted much attention owing to its broad range of photochemical applications. In particular, chiral transition metal complexes including platinum,³ iridium,⁴ ruthenium,⁵ and chromium⁶ which show circularly polarized phosphorescence (CPP), have been intensively studied to develop efficient organic light emitting diodes.⁷ The right- and left-handed luminescence properties are quantified using the dissymmetry factor g_{lum} , given by the equation: $g_{\text{lum}} = 2(I_{\text{left}} - I_{\text{right}})/(I_{\text{left}} + I_{\text{right}})$, where I_{left} and I_{right} are the intensities of the left- and right-handed emitted light, respectively. The CPP value has been controlled by the introduction of various organic chiral building blocks to the ligand of metal complexes including helicenes, ^{3a-c,4a,5} binaphthyls, ^{3d,e,4b} and pinenes.^{3f,4c} However, the guidelines for creating chiral transition complexes with high g_{lum} values are insufficient. Therefore, novel chiral motifs for transition metal complexes are required for the development of efficient CPP materials. In order to create novel functional materials based on chiral [2.2]paracyclophanes,⁸ we developed optical resolution methods for di- and tetra-substituted [2.2]paracyclophanes by using diastereomer methods.^{8a-d} In addition, the separated enantiopure [2.2] paracyclophanes have been used as chiral building blocks for a variety of organic molecules with second order structures such as two-blades-propeller-,^{8b} V-,^{8e} X-,^{8f,g} double-helical,^{8c} and

†-shaped structures,⁸^h leading to excellent circularly polarized fluorescence. Herein, we describe the synthesis, structure, optical and chiroptical properties of a phosphorescent binuclear bipyridineplatinum(II) complex linked with planar chiral bis-(*para*)-pseudo-*ortho*-[2.2]paracyclophane. Moreover, theoretical studies of the $|g_{lum}|$ value of CPP, which has not been estimated theoretically, were peformed using relativistic calculations.

The synthetic route to obtain the binuclear Pt complex, Pt₂ $(\mu$ -o-cy)₂(dtbpy)₂] (o-cy = 4,12-diethynyl-7,15-dimethoxy[2.2]paracyclophanes, dtbpy = 4.4'-di-tert-butyl-2.2'-bipyridyl) (2) is shown in Scheme 1. Enantiopure chiral building blocks 4,12-diethynyl-7, 15-dimethoxy[2.2] paracyclophanes $((R_p)$ - and (S_p) -1) were prepared using a previously developed method.^{8e} (R_p) -1 was reacted with [PtCl₂(dtbpy)] in the presence of CuI/Et₃N in CH₂Cl₂ to afford $(R_{\rm p},R_{\rm p})$ -2 in a 31% isolated yield. The enantiomer $(S_{\rm p},S_{\rm p})$ -2 was prepared using the same procedure as the opposite enantiomer. Complexes $(R_{\rm p},R_{\rm p})$ -2/ $(S_{\rm p},S_{\rm p})$ -2 were characterized using ¹H and ¹³C nuclear magnetic resonance (NMR; Fig. S1 and S2, ESI⁺) and infrared spectroscopy. The structure of $(R_{\rm p}, R_{\rm p})$ -2 was established by single-crystal X-ray diffraction (SXRD) analysis. ORTEP drawings and crystallographic data of (R_{p}, R_{p}) -2 are shown in Fig. 1 and Table S1 (ESI[†]), respectively. The front and side views of $(R_{\rm p}, R_{\rm p})$ -2 (Fig. 1A) show that the complex was stabilized as a chiral cyclic conformation in the crystalline state. The angle of two platinum coordination planes was 62.2° on average for all fragments in the crystal. This





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Fig. 1 (A) ORTEP representations of (R_p, R_p) -**2**. Thermal ellipsoids are shown at the 50% probability level. C: gray, N: blue, O: red, Pt: white. (B) Crystal packing structure of (R_p, R_p) -**2**. CCDC 2022660.†

unique chiral cyclic structure was attributed to the bridging coordination of the two optically pure pseudo-*ortho*-cyclophane skeletons. A total of 7.5 molecules of ($R_{\rm p}$, $R_{\rm p}$)-2 were helically aligned along the *B* axis in the large unit cell (*a*, *b*, *c* = 21.8, 51.3, 22.4 Å) *via* multiple intermolecular CH– π and π – π interactions (Fig. 1B). The helical bundles were aligned in the same direction to form grid-shaped pores (Fig. S5, ESI†). PLATON analysis showed that the solventaccessible volume of the crystal was *ca*. 53%, suggesting that the volume of the pore was 12 200 Å³ in the unit cell (22 993 Å³).

Fig. 2 shows the UV/vis absorption and circular dichroism (CD) spectra in toluene solutions (2.0 \times 10⁻⁴ M) of ($R_{\rm p}$, $R_{\rm p}$)-2, (S_{p}, S_{p}) -2 and the UV/vis absorption spectrum of a corresponding model compound $Pt(dtbpy)(C \equiv CC_6H_4OMe)_2$ 3 (see ESI[†]); the related data are listed in Table S2 (ESI[†]). The absorption spectra of $(R_{\rm p}, R_{\rm p})$ -, $(S_{\rm p}, S_{\rm p})$ -2, and 3 exhibited broad absorption bands attributable to a singlet ligand-to-ligand charge transfer (¹LLCT) at approximately 400–600 nm. The appearance of new absorption band at 500–600 nm for (R_p, R_p) and (S_p, S_p) -2 indicates that the two coordination systems in 2 interacted electronically via through-space interactions of cyclophanes. The CD spectra showed mirror images with a molar circular dichroism ($\Delta\epsilon$) on the order of $10^2 \text{ M}^{-1} \text{ cm}^{-1}$. The dissymmetry factors of absorbance $|g_{abs}|$ of 2 (1.0 × 10⁻³) at 510 nm were slightly lower than those of a series of pure organic cyclophane-based molecules previously reported.⁸ The photoluminescence (PL) and CPL spectra of (R_p, R_p) -, (S_p, S_p) -2 and PL spectrum of 3 in degassed toluene solutions $(2.0 \times 10^{-4} \text{ M})$ are shown in Fig. 3 with corresponding data in Table S2 (ESI⁺). Complex 3 exhibited phosphorescent properties with an estimated quantum efficiency of 0.025. The PL decay curve was fitted using a double exponential curve with the PL lifetimes (τ) of 0.10 and 0.45 µs (Fig. S6a, ESI[†]). In contrast,



Fig. 2 UV/vis absorption and CD spectra of (R_p, R_p) - and (S_p, S_p) -**2** and UV/vis absorption spectrum of **3** in toluene (2.0 × 10⁻⁴ M).



Fig. 3 PL and CPL spectra of (R_p, R_p) - and (S_p, S_p) -**2** in toluene (2.0 × 10⁻⁴ M) and in the PMMA film (10 wt%) and PL spectrum of **3** in toluene (2.0 × 10⁻⁴ M). The CPL spectra were scaled on the maximum intensity of its corresponding non-polarized emission.

complex (R_p, R_p) - and (S_p, S_p) -2 exhibited a broad emission band with peaks at 656 nm, which were red-shifted by 55 nm compared to that of 3. The Φ_{298K} of 2 was estimated to be 0.001. The variable temperature experiment in 2-MeTHF (Fig. S7, ESI[†]) showed that Φ_{298K} of 2 was <0.001, compared to 0.070 at 77 K. A significant bathochromic shift from $\lambda_{\text{max},77\text{K}}$ = 604 nm to $\lambda_{\text{max},298\text{K}}$ = 685 nm was observed. These results indicate that the emission of complex 2 was significantly heat quenchable owing to large structural distortions in the excited state. (R_p,R_p)- and (S_p,S_p)-2 emitted CPP with an estimated absolute $|g_{\text{lum}}|$ value of 1.0 \times 10⁻³ by eqn (S1) and (S2) (ESI^{\dagger}), the charts of g_{lum} are shown in Fig. S8 (ESI^{\dagger}). Optical properties in the solid state were examined and 2 was dispersed in a spin-coated poly(methyl methacrylate) (PMMA) film (10 wt% 2 in PMMA). The UV/vis absorption and CD spectra were identical to those in the solution state (Fig. S9, ESI⁺). In

contrast to the non-emissive properties observed in the toluene solution, the absolute Φ value of **2** in the film state slightly increased to 0.007, while λ_{max} was hypsochromically shifted to 610 nm due to the suppression of structural distortion in the excited state (Fig. 3). The PL decay curve was fitted using a double exponential curve and the PL lifetimes (τ) were 0.02 and 0.07 µs (Fig. S6b, ESI†). The $|g_{\text{lum}}|$ value of **2** was 1.0×10^{-3} , the same as the value obtained in toluene.

We gained insight into the chiroptical absorption properties of 2 using time-dependent density functional theory (TD-DFT) calculations⁹ (LC-BLYP^{10*a*}/ZORA-def2-SVP, SARC-ZORA-SVP with relativistic ZORA Hamiltonian¹¹) based on the optimized structure in the ground state (MN15^{10*b*}/6-31G(d), LanL2DZ¹²). Fig. 4A shows the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of (R_p , R_p)-2. HOMO(a)/HOMO(b) and LUMO(a)/LUMO(b) are degenerate with the phase reversal of the π -d-mixed orbital localized on a diethynylcyclophane-Pt unit for HOMOs and π^* -d-mixed orbitals localized on a bipyridine-Pt unit for



Fig. 4 (A) Frontier orbitals and major configurations of S_1 and S_2 transition. (B) TEDM (blue) and TMDM (purple) of S_1 and S_2 for (R_p, R_p) -**2** estimated from TD-DFT calculation.

LUMOs. Hence, the transition energies of the lowest excited states of S1 and S2 were similar. The major electronic configurations of S₁ and S₂ were determined to be the HOMO(a)-to-LUMO(a)/ HOMO(b)-to-LUMO(b) and HOMO(a)-to-LUMO(b)/HOMO(b)-to-LUMO(a) transitions, indicating that the absorption (ca. 550 nm) could be attributed to ¹LLCT transitions (Table S3, ESI⁺). These ¹LLCT transitions dominate the chiroptical absorption properties. The transition electronic dipole moment (TEDM) and transition magnetic dipole moment (TMDM) as well as θ of S₁ and S₂ transitions for $(R_{\rm p},R_{\rm p})$ -2 are shown in Fig. 4B. The $g_{\rm abs}$ values were theoretically determined using $g_{abs} = 4|\boldsymbol{\mu}||\boldsymbol{m}|\cos\theta/(|\boldsymbol{\mu}|^2 + |\boldsymbol{m}|^2)$, where μ and m are the TEDM and TMDM, respectively, while θ is the angle between μ and m. In the S₁ transition, both dipole moments were oriented along the C_2 axis owing to the C_2 symmetric ¹LLCT character. The angle θ was calculated to be 0.0°. Although the small angle θ maximizes the g value, the large TEDM arising from the LLCT character reduced the g_{abs} value. In the S₂ transition, the angle θ was calculated to be 80° owing to the asymmetric ¹LLCT character, minimizing the g_{abs} value. These calculated θ s theoretically give positive CD signs, supporting the experimentally observed results presented in Fig. 2.

Spin-orbit coupling-(SOC-)TD-DFT calculation¹³ (LC-BLYP/ ZORA-def2-SVP, SARC-ZORA-SVP with relativistic ZORA Hamiltonian) was performed for $(R_{\rm p},R_{\rm p})$ -2 based on the optimized structure in the lowest triplet state (unrestricted (U)MN15/6-31G(d), LanL2DZ) to estimate CPP properties. SOC-TD-DFT calculations were used to analyze triplet excited properties including phosphorescent lifetimes and zero-field splitting energies. The calculation was applied to estimate the phosphorescent $|g_{lum}|$ value. Fig. 5A shows the frontier orbitals and major configurations of the T_1 and T_2 transitions. As well as the ground state, the HOMOs and LUMOs were degenerate. In addition, transition characteristics of T1 and T2 were the same as the asymmetric transition of the S_2 and C_2 symmetric transition of S1, respectively. Fig. 5B shows the energy diagrams of the SOC states. The low-level SOC states were a cluster of multiple states consisting of T_1 and T_2 transitions. The $|g_{lum}|$ value of the most bright-state SOC₃ was 3.3×10^{-3} , consistent with the experimental results. The SOC₃ state consisted of a large contribution of $T_{1,0}$ (53%), indicating that the observed CPP dominated the asymmetric LLCT transition with a large TEDM. Table S6 (ESI[†]) summarizes the absolute values of TEDM, TMDM, and major configurations consisting of the SOC states. In $SOC_{2,3,6}$, both dipole moments were similar to the asymmetric S_2 transition, decreasing the $|g_{lum}|$ values. In $SOC_{1,4,5}$, both dipole moments were oriented along the C_2 axis, similar to the C_2 symmetric S₁ transition. Therefore, the $|g_{lum}|$ values were maximized, on the order of 10^{-2} . However, the oscillator strengths f of SOC_{1,4,5} were significantly lower than those of SOC₃. These results provide guidelines for preparing CPP materials with high dissymmetry factors. (1) The LLCT transition reduced the $|g_{lum}|$ value owing to the large TEDM. Intraligand charge transfer with a small TEDM is suitable. (2) Frontier MOs symmetries should be higher than C_2 without the degeneracy of asymmetric orbitals to create pure and wellseparated symmetric triplet transitions. Further preparation





of optically active [2.2]paracyclophane-based platinum complexes is currently underway.

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Conflicts of interest

There are no conflicts of interest to declare.

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