

Supporting Information For

Circularly polarized blue fluorescence based on chiral heteroleptic six-coordinate *bis*-pyrazolonate-Zn²⁺ complexes

Jiaxiang Liu,^a Yuzhen Zhao,^a Zhe Zhang,^a Manni Li,^a Wenqi Song,^a Wentao Li,^{*b} and Zongcheng Miao^{*c}

^a*Xi'an Key Laboratory of Advanced Photo-Electronics Materials and Energy Conversion Device, Technological Institute of Materials & Energy Science (TIMES), Xijing University, Xi'an 710123, P.R. China.*

^b*College of Big Data and Information Engineering, Institute of Advanced Optoelectronic Materials and Technology, Guizhou University, Guiyang 550025, P.R. China.*

^c*School of Artificial Intelligence, Optics and Electronics (iOPEN), Northwestern Polytechnical University, Xi'an 710072, P. R. China.*

To whom correspondence should be addressed.

Email address: wqli@gzu.edu.cn (Wentao Li); miaozongcheng@nwpu.edu.cn (Zongcheng Miao)

Spectroscopic Measurements.

Structural Measurements. The C, H, and N microanalyses were carried out with an elemental analyzer (Elementar vario EL, Germany). Fourier transform infrared (FTIR) spectra were obtained using an infrared spectrometer (Bruker, INVENIO, Germany). The nuclear magnetic resonance hydrogen spectra (^1H NMR) were recorded with a JEOL JNM-ECZ400S nuclear magnetic resonance spectrometer (Japan Electronics Corporation, 400 MHz) in CDCl_3 at room temperature, and the tetramethylsilane (TMS) was used as an internal standard. ^1H NMR spectra assignments are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet. MALDI-TOF mass spectra were recorded on an Applied Biosystems 4800 Plus MALDI-TOF/TOF Analyzer (Applied Biosystems). A suitable single crystal of **S,S-Zn²⁺** was obtained by recrystallization from absolute methanol. The crystal data of **S,S-Zn²⁺** were collected on a Bruker APEX-II CCD diffractometer with Ga-K α radiation ($\lambda = 1.34139 \text{ \AA}$) at 200 K. The structures were solved by the direct method SHELXS and then refined using the full-matrix least-squares method, i.e., SHELXL-2015, implemented in the OLEX2 package.¹ All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were refined isotropically. The absolute configuration of **S,S-Zn²⁺** was conclusively established using anomalous scattering of Ga-K α radiation with Flack parameter = 0.05(3). More details concerned with constraints and the refinements have been supplied in the cif files, and crystallographic data and selected bond lengths (\AA) and angles ($^\circ$) are presented in **Tables S2-S3**, respectively. Crystallographic data of **S,S-Zn²⁺** have been deposited in the Cambridge Crystallographic Data Centre (CCDC) with the CCDC number of 2300136.

Optical Measurements. UV-vis absorption spectra were recorded on a PerkinElmer LAMBDA

950 UV-Vis spectrophotometer (PerkinElmer, Waltham, MA, USA), and the experimental HOMO–LUMO energy gaps of the two chiral Zn²⁺ enantiomers (***R,R***-Zn²⁺ and ***S,S***-Zn²⁺) were calculated by the UV-vis edge absorption ($\lambda_{\text{abs}} = 333\text{-}334$ nm). Excitation and emission spectra were recorded using an FLS 1000 spectrofluorometer (Edinburgh Instruments, UK). Luminescence lifetimes were recorded on the FLS 980 (Edinburgh Instruments, England) transient fluorescence spectrometer (Edinburgh Instruments, England). Photoluminescence quantum yields (Φ_{PL}) were determined using a FLS 980 absolute photoluminescence quantum yield measurement system and integrating sphere as a sample chamber. Circular dichroism (CD) spectra were measured on a ChiraScan CD spectrometer (Applied Photophysics, UK). The CPL spectra were measured on a Jasco CPL-300 spectrophotometer based on ‘Continuous’ scanning mode at 100 nm/min scan speed. The test mode adopts “Slit” mode with the Ex and Em slit width 2500 μm and the digital integration time (D.I.T.) is 2.0 s with multiple accumulations (3 times) and their g_{PL} values were read from the curves recorded with the software bundled on the equipment. The Commission Internationale de L’Eclairage (CIE) coordinate of the complexes ***R,R***-Zn²⁺ and ***S,S***-Zn²⁺ were calculated by the International Commission on Illumination (CIE) system.

Thermodynamic Measurements. Thermogravimetric (TG) analysis was performed using a Q500 thermogravimetric analyzer (TA instruments, USA) at a heating speed of 10 °C/min in a nitrogen gas atmosphere.

Electrochemical Measurements. Cyclic voltammetry measurements were conducted on an Autolab PGSTAT302N in degassed MeCN solution at room temperature under a N₂ atmosphere (scan rate = 100 mV/s).

DFT and TD-DFT Theoretical Calculations. To further interpret the UV-vis spectral behaviour of the two chiral Zn²⁺ enantiomers *R,R*-Zn²⁺ and *S,S*-Zn²⁺, the original computational models of *R,R*-Zn²⁺ and *S,S*-Zn²⁺ were built on the basis of the crystal structure (*S,S*-Zn²⁺). Their minimum energy structures based on the ground-state (S₀) were obtained from density functional theory (DFT) calculations which were carried out employing the popular B3LYP functional theory in Gaussian 09.² The 6-31G (d, p) basis set³ was employed for C, H, O and N atoms, whereas the LANL2DZ basis set, together with the related effective core potentials 94, was used for Zn atoms.⁴ After that, their time-dependent DFT (TD-DFT) calculations were performed to explore energy transitions. Excited states are categorized into single/triple ligand-to-ligand, intra-ligand, ligand-to-metal or metal-to-ligand charge transfer states (LLCT, ILCT, LMCT or MLCT) by the interfragment charge transfer (IFCT) analysis.

Preparation and characterization of the pyrazolone ligand HPMBP (1-phenyl-3-methyl-4-benzoyl-5-pyrazolone)

The pyrazolone ligand, **HPMBP**, was synthesized according to a modified procedure described in the literature.⁵ In more detail, 1-phenyl-3-methyl-5-pyrazolone (**PMP**; 7.5 g, 43.1 mmol) was added to 1,4-dioxane (35 mL) and heated until the solid was completely dissolved. After the solution cooled slightly, Ca(OH)₂ (6.0 g, 81.1 mmol) was added to the reaction system, which was further stirred for 10 min. Subsequently, benzoyl chloride (5.86 mL, 55.0 mmol) was added dropwise over 5 min, and the reaction mixture was refluxed for 18 h and thereafter cooled to 25 °C. Ice-cold hydrochloric acid (15 mL, 12 mol/L) was added to the mixture, followed by 176 mL of distilled water. The brownish-red precipitate was filtered and purified by

recrystallization from CH₃OH and H₂O to give the light-yellow microcrystalline products. The target ligand was prepared *via* the synthetic route presented in **Scheme 1**. The analysis data for **HPMBP**: Yield = 10.5 g, 88%. Anal. Calcd for C₁₇H₁₄N₂O₂: C, 73.37; H, 5.07; N, 10.07%. Found: C, 73.42; H, 5.14; N, 10.03%. FTIR (KBr, cm⁻¹): 3448 (w), 3061 (w), 3043 (w), 2893 (w), 2581 (m), 1646 (vs), 1598 (m), 1578 (m), 1533 (s), 1497 (s), 1458 (m), 1399 (m), 1349 (s), 1310 (m), 1196 (w), 1107 (w), 1074 (w), 1024 (w), 949 (w), 932 (w), 832 (m), 798 (w), 755 (m), 727 (w), 706 (w), 687 (w), 670 (w), 610 (w), 532 (w). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.80 (d, 2H, -Ph), 7.57 (d, 2H, -Ph), 7.50 (t, 1H, -Ph), 7.45 (d, 2H, -Ph), 7.40 (t, 2H, -Ph), 7.24 (t, 1H, -Ph), 7.19 (s, 1H, -H of five-membered rings), 2.03 (s, 3H, -CH₃).

Synthesis and characterization of the Zn²⁺ precursor complex [Zn(PMBP)₂(CH₃OH)₂]

To a stirred solution of **HPMBP** (0.056 g, 0.2 mmol) in 10 mL absolute CH₃OH, solid Zn(OAc)₂·2H₂O (0.022 g, 0.1 mmol) was added. After two minutes, a white precipitate appeared in the solution, and the resulting mixture was stirred for 4 h at 60 °C. Then, the colorless insoluble product was filtered and washed two times with absolute CH₃OH and H₂O. The crude product was recrystallized from CH₃OH to obtain a pure compound. The analysis data for **[Zn(PMBP)₂(CH₃OH)₂]**: Yield = 0.058 g, 85%. Anal. Calcd for C₃₆H₃₄N₄O₆Zn: C, 63.21; H, 5.01; N, 8.19%. Found: C, 63.15; H, 5.12; N, 8.24%. FTIR (KBr, cm⁻¹): 3429 (w), 3211 (w), 3062 (w), 2930 (w), 1610 (vs), 1595 (s), 1577 (s), 1531 (m), 1485 (vs), 1434 (s), 1401 (m), 1371 (m), 1235 (w), 1157 (w), 1135 (w), 1062 (m), 1025 (m), 1000 (w), 951 (m), 909 (w), 840 (w), 795 (w), 764 (m), 736 (m), 702 (w), 660 (w), 641 (w), 613 (m), 553 (w), 511 (w). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.73 (d, 4H, -Ph), 7.42 (m, 2H, -Ph), 7.34 (d, 8H, -Ph), 7.18 (t, 4H, -Ph), 7.05 (t, 2H, -Ph), 3.44 (s, 6H, -CH₃ of CH₃OH), 1.73 (s, 6H, -CH₃), 1.37 (1H, d, -OH for CH₃OH).

Figure S1. 400 MHz ^1H NMR spectra of the free ligands (**1S,2S-Chxn** and **HPMBP**) and the chiral complex **S,S-Zn $^{2+}$** in CDCl_3 at room temperature.

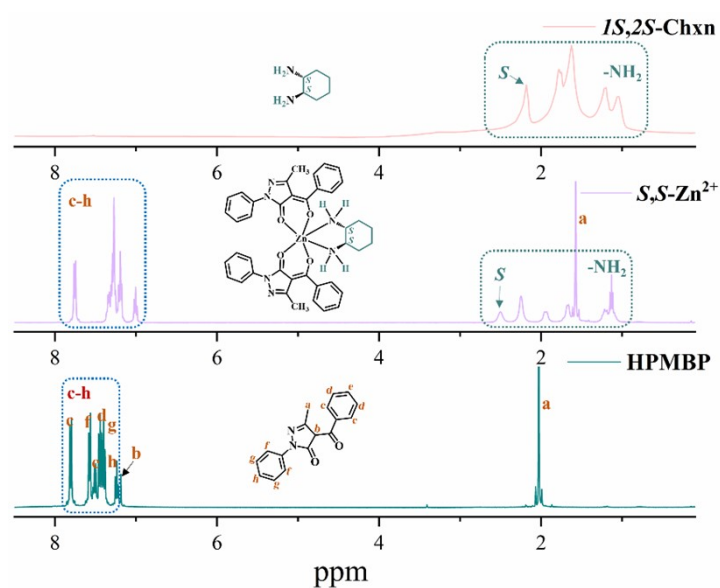


Figure S2. The octahedral coordination geometry of Zn^{2+} ion for complex **S,S-Zn $^{2+}$** (maroon: oxygen, dark blue: nitrogen, magenta: zinc).

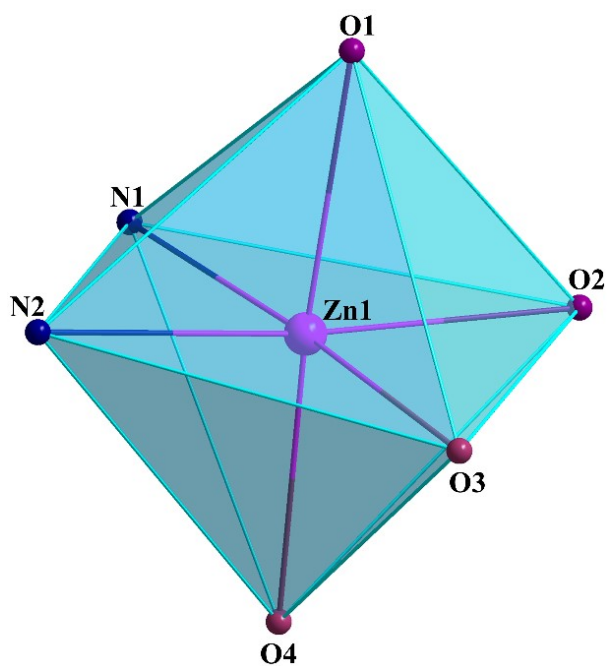


Figure S3. Thermogravimetric (TG) curves of the two chiral Zn²⁺ enantiomers (*R,R*-Zn²⁺ and *S,S*-Zn²⁺).

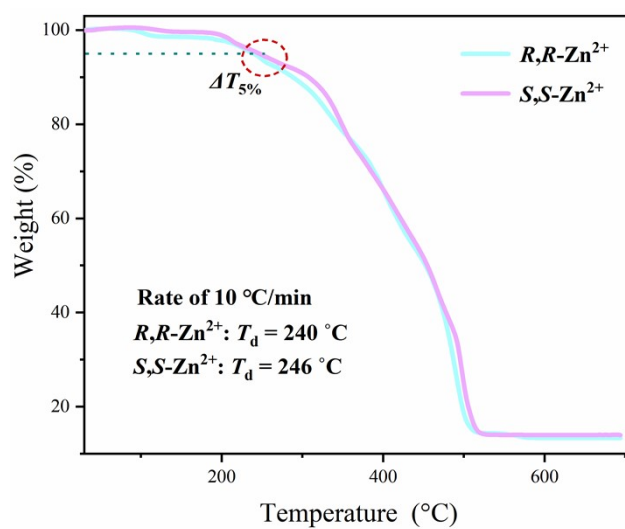


Figure S4. Normalized UV–vis absorption spectra of the chiral 1,2-diamine ligands (*1R,2R*-Chxn and *1S,2S*-Chxn) and pyrazolone ligand **HPMBP** in CH₂Cl₂ (1×10^{-5} M) at room temperature.

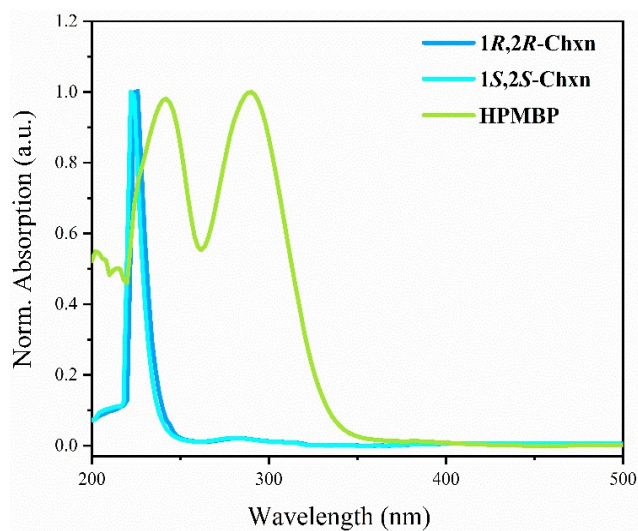


Figure S5. (a) Excitation spectra of the two chiral Zn²⁺ enantiomers (*R,R*-Zn²⁺ and *S,S*-Zn²⁺) recorded by monitoring the emissions at *ca.* 460 nm in CH₂Cl₂ (1 × 10⁻⁵ M); (b) Photoluminescence color coordinates on the CIE chromaticity diagram of the two chiral Zn²⁺ enantiomers (*R,R*-Zn²⁺ and *S,S*-Zn²⁺).

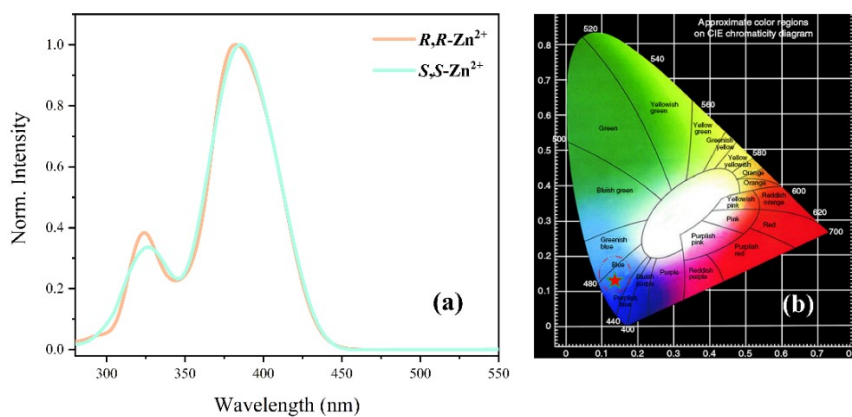


Figure S6. Room temperature decay curves of the two chiral Zn²⁺ enantiomers (*R,R*-Zn²⁺ and *S,S*-Zn²⁺) in CH₂Cl₂ (1×10⁻⁵ M) monitored at *ca.* 460 nm.

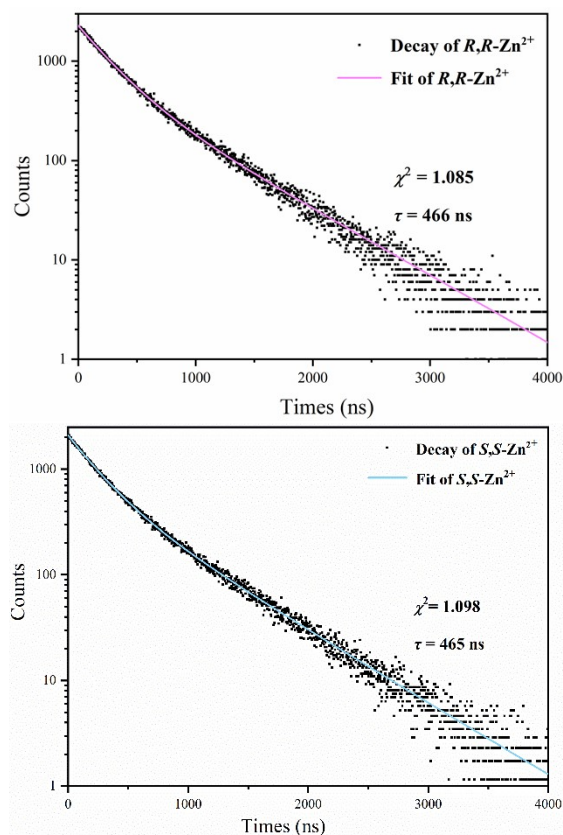


Figure S7. CD spectra of the chiral 1,2-diamine ligands (**1R,2R-Chxn** and **1S,2S-Chxn**) in CH₂Cl₂

(1×10^{-5} M) at room temperature.

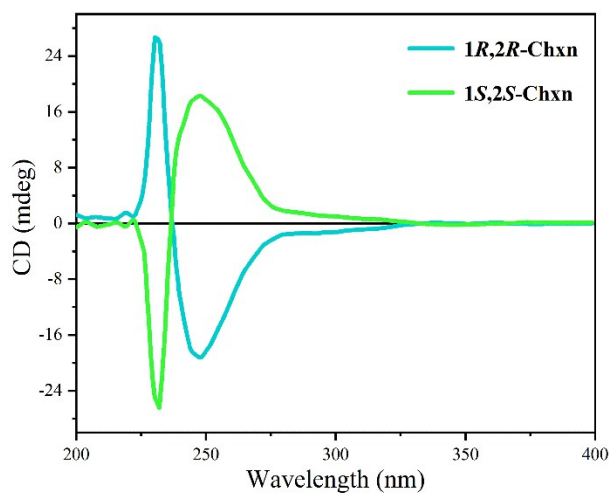


Figure S8. The g_{lum} curves of the two chiral Zn²⁺ enantiomers (**R,R-Zn²⁺** and **S,S-Zn²⁺**) in CH₂Cl₂

(1×10^{-5} M).

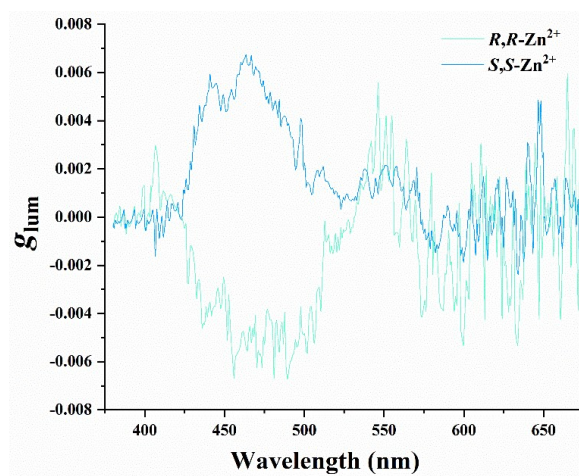


Figure S9. The CV curves of the two chiral Zn²⁺ enantiomers (*R,R*-Zn²⁺ and *S,S*-Zn²⁺) recorded versus Fc⁺/Fc in degassed MeCN solution at room temperature under a N₂ atmosphere (scan rate = 100 mV/s).

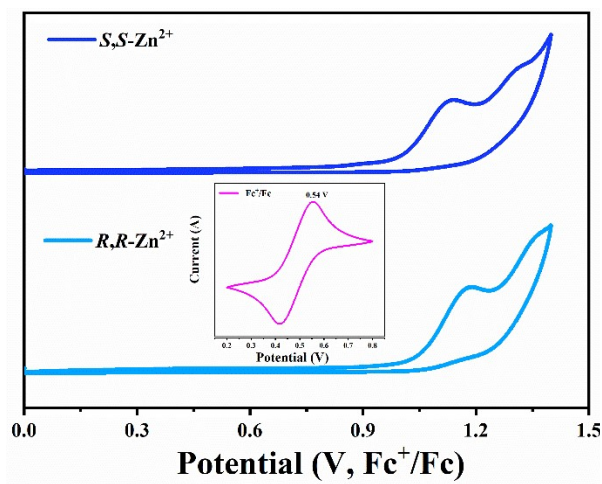


Table S1. The comparison of the CPL performance between this work and other reported homoleptic Schiff/2,2'-bipyridyl-base Zn²⁺ complexes.



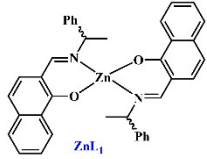
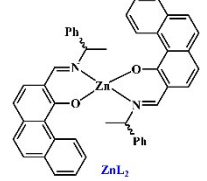

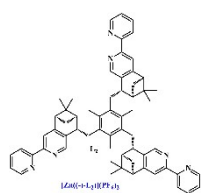
Compound	$\lambda_{\text{PL}}^{\text{max}}$ (nm)	τ	Φ_{PL} (%)	$ g_{\text{PL}} $	reference
 [Zn(PMBP) ₂ (Chiral-Chxn)]	458-460	225-254 ns	9-10	0.0065- 0.0068	This work
 R/S-ZnL	491	7.39-8.42 μs	14.8	3.0×10^{-3}	<i>Mater. Chem. Front.</i> , 2019, 3 , 867-873
 ZnL ₁	462	/	25	7.7×10^{-4}	<i>Chem. Commun.</i> , 2022, 58 , 7503-7506
 ZnL ₂	469	/	17	3.2×10^{-3}	
 [Chiral-ZnLBy(H ₂ O)(NO ₂) ₂]	490	/	/	2.5×10^{-3}	<i>Dalton Trans.</i> , 2023, 52 , 7646-7651
 Zn(+-)-10Ph-1	470	74 ns	10.8	2.4×10^{-3}	<i>J. Am. Chem. Soc.</i> , 2007, 129 , 210-217

Table S2. Crystal diffraction data and refinement statistics for the chiral Zn²⁺ complex[Zn(PMBP)₂(1*S*,2*S*-Chxn)] (*S,S*-Zn²⁺).

Compound	<i>S,S</i> -Zn ²⁺ ·CH ₃ OH
CCDC	2300136
Empirical formula	C ₄₁ H ₄₄ N ₆ O ₅ Zn
Formula weight	766.19
Crystal system	triclinic
Space group	<i>P</i> 1
<i>a</i> /Å	11.4625(6)
<i>b</i> /Å	13.1925(7)
<i>c</i> /Å	14.4678(7)
α /°	67.905(2)
β /°	83.474(2)
γ /°	70.309(2)
<i>V</i> /Å ³	1908.38(17)
<i>Z</i>	2
ρ /g·cm ⁻³	1.333
Crystal size/mm	0.21 × 0.18 × 0.17
μ (Mo/Ga-K α)/mm ⁻¹	0.858
Data/restraints/parameters	14292/3/964
Quality-of-fit indicator	1.073
No. unique reflections	14292
No. observed reflections	49066
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0385 <i>wR</i> ₂ = 0.0968
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0491 <i>wR</i> ₂ = 0.1016
Flack parameter	0.05(3)

Table S3. Selected bond lengths (Å) and angles (°) for [Zn(PMBP)₂(1*S*,2*S*-Chxn)]·CH₃OH (***S,S***-Zn²⁺·CH₃OH).

Compound	<i>S,S</i> -Zn ²⁺ ·CH ₃ OH
Zn(1)-O(1)	2.093(3)
Zn(1)-O(2)	2.144(4)
Zn(1)-O(3)	2.113(3)
Zn(1)-O(4)	2.093(4)
Zn(1)-N(1)	2.130(5)
Zn(1)-N(2)	2.107(5)
O(1)-Zn(1)-O(2)	87.14(14)
O(3)-Zn(1)-O(4)	87.32(15)
N(1)-Zn(1)-N(2)	82.33(19)

Table S4. Frontier orbitals and their corresponding electron cloud density distributions for the two chiral Zn²⁺ enantiomers (*R,R*-Zn²⁺ and *S,S*-Zn²⁺) on the basis of optimized S₀ geometries.

Complex	Orbital	Contribution of metal d _π orbitals and π orbitals of ligand to MOs (%)			
		Zn	(PMBP)-1	(PMBP)-2	Chiral-Chxn
<i>R,R</i> -Zn ²⁺	LUMO+2	0.43	0.03	99.47	0.07
	LUMO+1	0.45	97.39	2.02	0.15
	LUMO	0.47	1.93	97.49	0.11
	HOMO	0.49	1.77	97.60	0.14
	HOMO-1	0.57	97.45	1.67	0.31
	HOMO-2	0.21	0.28	99.25	0.25
<i>S,S</i> -Zn ²⁺	LUMO+2	0.47	0.03	99.45	0.05
	LUMO+1	0.45	97.60	1.83	0.13
	LUMO	0.41	1.75	97.63	0.21
	HOMO	0.51	2.47	96.89	0.13
	HOMO-1	0.54	96.79	2.36	0.30
	HOMO-2	0.19	0.29	99.21	0.30

Table S5. Electronic excitation energy and their corresponding transition types and properties

for the two chiral Zn²⁺ enantiomers (*R,R*-Zn²⁺ and *S,S*-Zn²⁺) by the IFCT analysis of TD-DFT calculations

Complex	State	λ (nm)	E (eV)	Oscillator f	transition (% contrib.)	Assignment (%)	
<i>R,R</i> -Zn ²⁺	S ₀ →S ₁	361	3.4310	0.0122	H→L (95.91);	¹ ILCT: 95.18	¹ LLCT: 3.85
						¹ MLCT: 0.49	¹ LMCT: 0.47
	S ₀ →S ₂	352	3.5196	0.0016	H→L+1 (96.03);	¹ LLCT: 95.37	¹ ILCT: 3.70
						¹ MLCT: 0.49	¹ LMCT: 0.45
	S ₀ →S ₃	348	3.5612	0.0272	H-1→L+1 (89.25);	¹ LLCT: 97.92	¹ ILCT: 3.17
					H-1→L (5.40);	¹ MLCT: 0.57	¹ LMCT: 0.53
S ₀ →T ₁	456	2.7152	0.0000	H→L (62.66);	³ ILCT: 95.14	³ LLCT: 3.74	
				H-2→L (27.32); H→L+5 (2.24);	³ LMCT: 0.46	³ MLCT: 0.66	
<i>S,S</i> -Zn ²⁺	S ₀ →S ₁	362	3.4221	0.0124	H→L (95.95);	¹ ILCT: 96.64	¹ LLCT: 4.46
						¹ MLCT: 0.51	¹ LMCT: 0.41
	S ₀ →S ₂	352	3.5188	0.0019	H→L+1 (93.85);	¹ LLCT: 95.22	¹ ILCT: 4.18
					H-1→L+1 (3.85);	¹ MLCT: 0.33	¹ LMCT: 0.27
	S ₀ →S ₃	349	3.5483	0.0215	H-1→L+1 (86.27);	¹ LLCT: 96.65	¹ ILCT: 2.59
					H-1→L (6.08);	¹ MLCT: 0.47	¹ LMCT: 0.29
S ₀ →T ₁	457	2.7106	0.0000	H→L (62.28);	³ ILCT: 94.79	³ LLCT: 4.18	
				H-2→L (27.47); H→L+5 (2.27);	³ MLCT: 0.65	³ LMCT: 0.38	

Supplementary References

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