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Enhanced Circularly Polarized Luminescence Dissymmetry of $[Ru(bpy)_3]^{2+}$ Complexes in a 3D Chiral Framework: A Study of Transparent Thin Films

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Supporting Information

Materials. Tris(2,2'-bipyridyl) dichlororuthenium (II) hexahydrate ($[Ru(bpy)_3]$ $Cl_2 \cdot 6H_2O$) (Sigma-Aldrich, 99.95% trace metals basis), zinc nitrate hexahydrate ($Zn(NO_3)_2$ $6H_2O$) (Sigma-Aldrich, 99.0% reagent grade), oxalic acid ($H_2C_2O_4$) (Sigma-Aldrich, 99.0% reagent grade), polyvinylpyrrolidone (PVP) (Sigma-Aldrich, powder, average Mw ~29,000), L-(+)-tartaric acid diammonium salt (Sigma-Aldrich), D-(-)-tartaric acid (Sigma-Aldrich) and ammonium hydroxide solution (Sigma-Aldrich) were used as received.

Synthesis. Synthesis of **[Λ-Ru(bpy)$_3$] tartrate salt**. To an aqueous solution (5 ml) containing 4 g (21.7 mmol) of L-(+)-tartaric acid diammonium salt, an aqueous solution (5 ml) of 250 mg (0.41 mmol) $[Ru(bpy)_3]$ $Cl_2 \cdot 6H_2O$ was added at room temperature. No crystallization happened at room temperature. The solution was cooled down at 4 °C and held for 1 day. Orange crystals formed on the bottom, washed with cold water and collected by vacuum filtration.

Synthesis of **[Δ-Ru(bpy)$_3$] tartrate salt**. To an aqueous solution (5 ml) containing 3.27 g (21.7 mmol) of D-(-)-tartaric acid, ammonium hydroxide solution was added with vigorously stirring until the precipitate totally disappeared and pH of the solution was 7~8. To this solution, 250 mg (0.41 mmol) $[Ru(bpy)_3]$ $Cl_2 \cdot 6H_2O$ was added. The solution was sonicated until all the solids were totally dissolved, and then cooled down at 4 °C and held for 1 day. Orange crystals formed on the bottom, washed with cold water and collected by vacuum filtration.

Synthesis of **[Λ/Δ-Ru(bpy)$_3$] [Zn$_2$(C$_2$O$_4$)$_3$]**. To a solution of an aqueous solution (15 ml) containing 37.8 mg of oxalic acid (0.3 mmol) was slowly added with stirring to an aqueous solution (10 ml) containing 77.9 mg of enantiomerically-pure [Λ/Δ-Ru(bpy)$_3$] tartrate (0.105 mmol), and 49.8 mg of Zn(NO$_3$)$_2$ 6H$_2$O (0.2 mmol). An orange precipitate starts to appear after a few minutes. After 30 min stirring, the precipitate is filtered off, washed with water and acetone, and vacuum-dried overnight to yield an orange solid.

Film fabrication. The [Λ/Δ-Ru(bpy)$_3$] [Zn$_2$(C$_2$O$_4$)$_3$] powder was first synthesized with addition of polyvinylpyrrolidone (PVP) (15 wt%). The crude product was collected by centrifuge and redispersed into 2 ml PVP ethanol solution. The resulting mixture was then sonicated for 30 min to achieve an orange precursor suspension. The substrate (FTO or quartz slide) was sonicated in acetone, ethanol, and isopropyl alcohol for 15 min. Dried by N$_2$, FTO or quartz slide were treated by UV ozone for 15 min. Then, the clean substrate was transferred to a spin-coater (Laurell Technologies Corporation) for film fabrication. The as-prepared [Λ/Δ-Ru(bpy)$_3$] [Zn$_2$(C$_2$O$_4$)$_3$] suspension (450 µL) was placed on the substrate, then had spin-coating for 30 s at 2500 rpm. Finally, the [Λ/Δ-Ru(bpy)$_3$] [Zn$_2$(C$_2$O$_4$)$_3$] films were dried at 70 °C for 20 min to remove residual solvent.

Characterization. X-ray powder diffraction was conducted on Bruker D8 Advanced Powder with a Cu Kα radiation. UV-vis absorption of films was measured by PerkinElmer Lambda 950 spectrometer. The morphologies of films which were deposited on glass slides with a dimension of 2.0×2.0 cm, sputter-coated with a gold layer and characterized on the scanning electron microscopy (SEM, FEI Quanta 200). CD spectra were recorded on a JASCO J-1500 spectrophotometer using a Xe lamp as the excitation source. Fluorescence spectra were recorded on a Fluoromax-4 spectrophotometer using a Xe lamp as the excitation source.

CPL spectra and subsequently derived g_{lum} values were recorded using an OLIS CPL Solo spectrofluorometer and the GlobalWorks software suite. Reported as g_{lum} (wavelength).

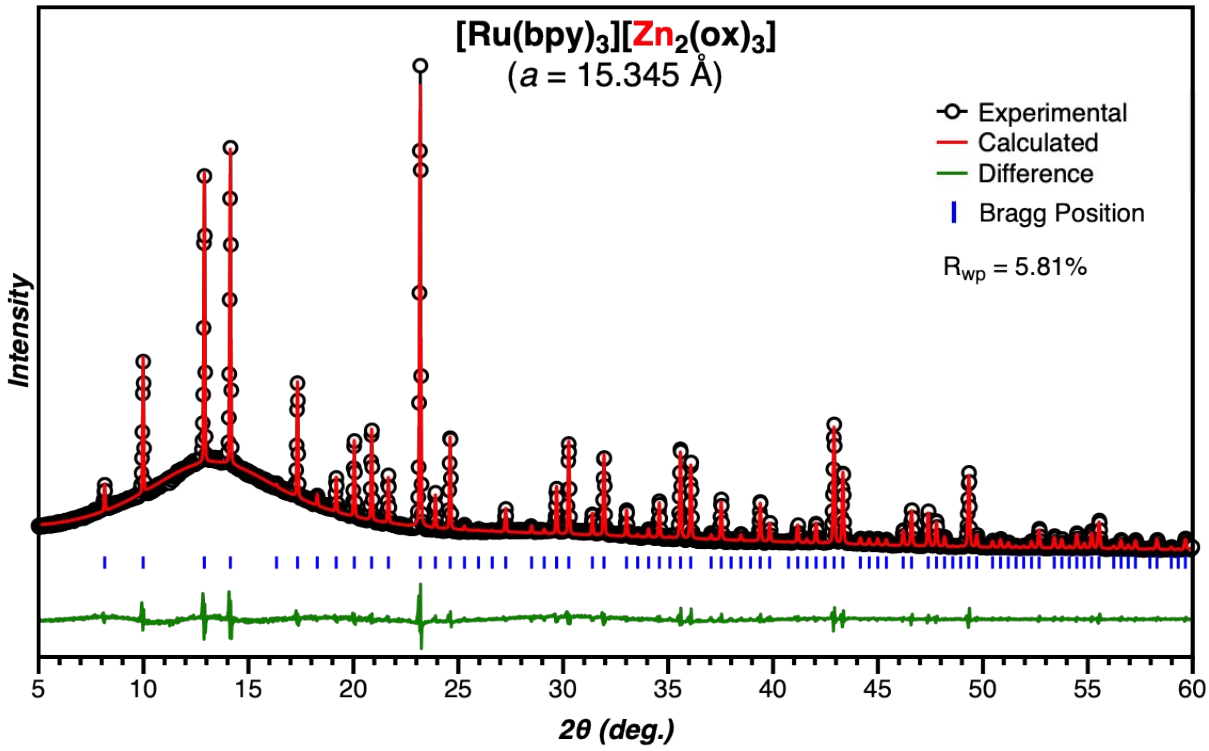

Figure S1. Rietveld refinement of PXRD for $[Ru(bpy)_3]$ $[Zn_2(C_2O_4)_3]$

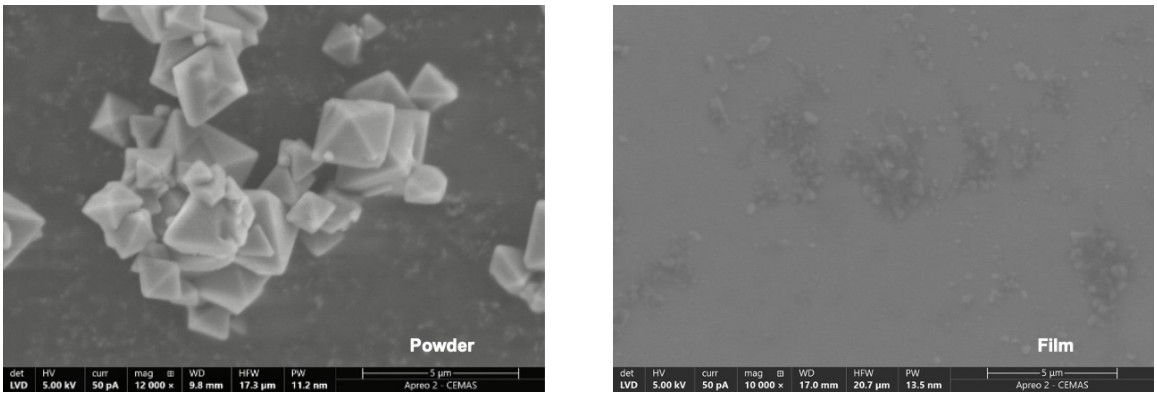

Figure S2. SEM images of $[Ru(bpy)_3]$ $[Zn_2(C_2O_4)_3]$ powder (left) and film (right).

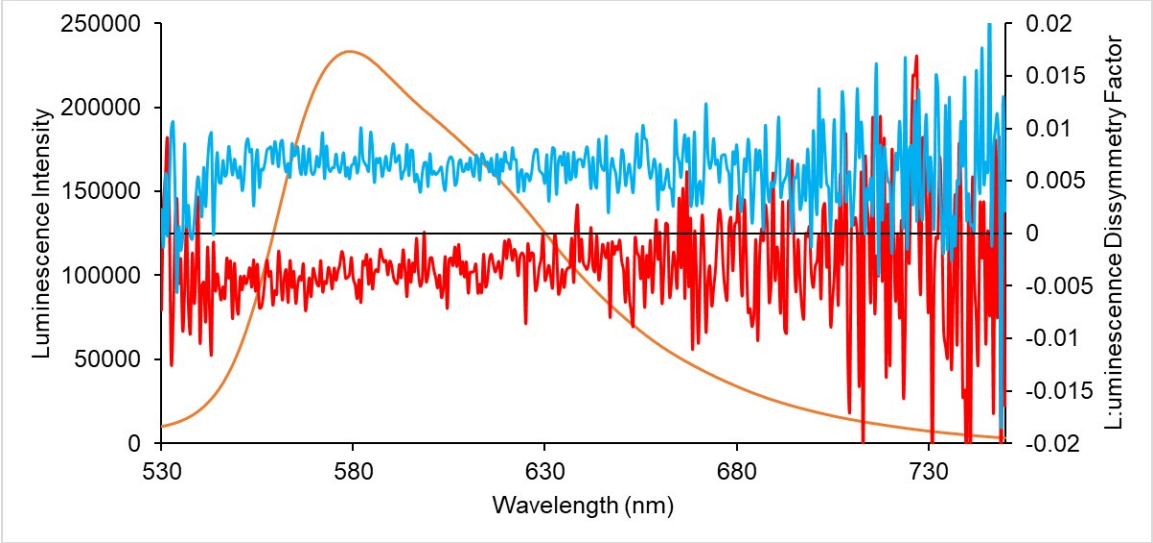

Figure S3. g_{lum} vs wavelength plot for the films.

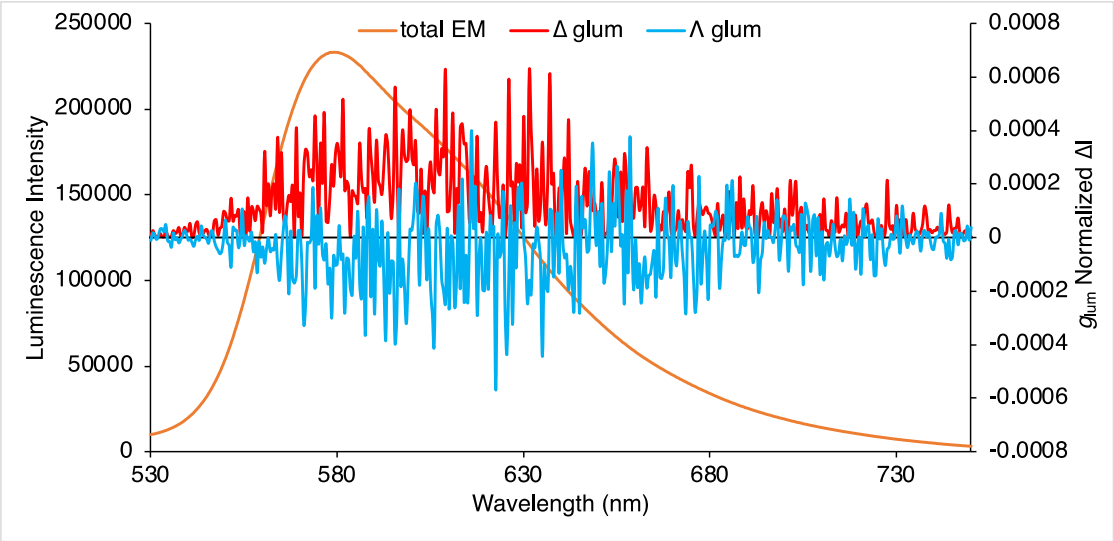

Figure S4. CPL spectra of [Λ/Δ-Ru(bpy)$_3$] tartrate in an aqeous solution

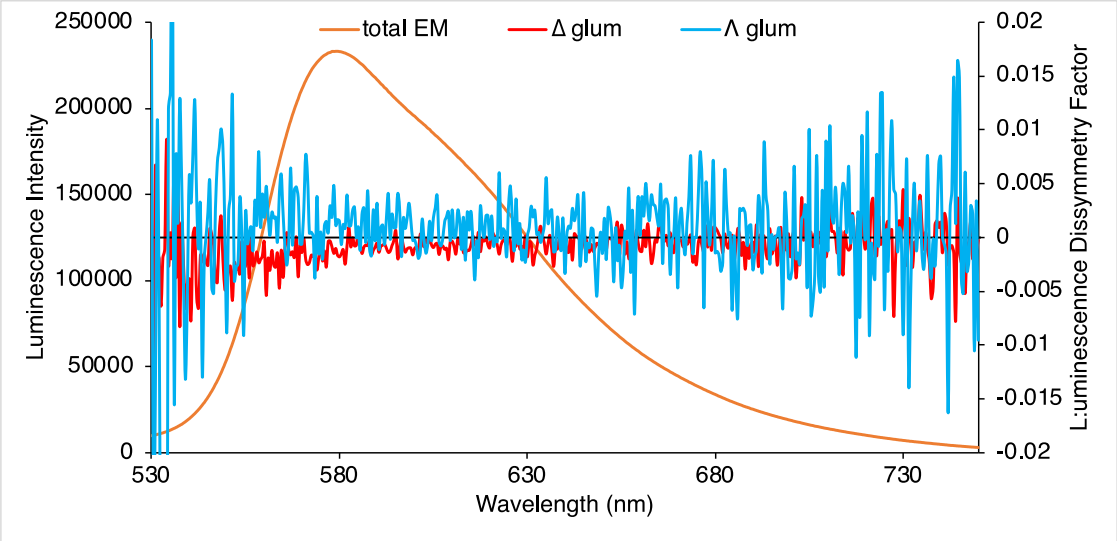

Figure S5. g_{lum} vs wavelength plot for the solutions.