Electronic Supplementary Information

Modulation of circularly polarized luminescence by swelling of microgels functionalized with enantiopure [Ru(bpy)₃]²⁺ luminophores

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Material and method

Resolution of racemic ruthenium complex

Enantiomeric separation of racemic (4-vinyl-4-methyl-2,2'-bipyridine)bis(2,2-bipyridine)ruthenium(II) complex, simply abbreviated $[Ru(bpy)_3]^{2+}$ for commodity, was performed as follows: 2.2 equiv. of P(V) TRISPHAT (TT) salts of Delta (Δ) configuration [S1,S2] were added to racemic solutions of $[Ru(bpy)_3](PF_6)_2$ in a CH_2Cl_2/acetone mixture (2:1) and the resulting diastereomeric complexes were separated by chromatography over silica gel (CH_2Cl_2 as eluent) [S3,S4,S5]. The collected fractions displayed a diastereomeric ratio >30:1 in ^{1}H NMR spectroscopy. Then isolated salts $[\Delta-Ru(bpy)_3][\Delta-TT]_2$ and $[\Lambda-Ru(bpy)_3][\Delta-TT]_2$ were transformed into $[\Delta-Ru(bpy)_3](PF_6)_2$ and $[\Lambda-Ru(bpy)_3](PF_6)_2$ (ee >95%) by i) extractions in aqueous layers with $[^nHex_4N][Br]$ as phase transfer agent and ii) precipitations of the hexafluorophosphate salts with saturated solutions of KPF_6 [S6]. $[\Delta-Ru(bpy)_3](PF_6)_2$: $[\alpha]_{Na} = -880$ (c=0.011, CH_2Cl_2); $[\Lambda-Ru(bpy)_3](PF_6)_2$: $[\alpha]_{Na} = +830$ (c=0.010, CH_2Cl_2).

4-vinyl-4-methyl-2,2'-bipyridine   =
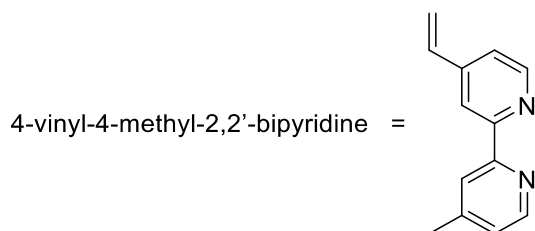
Microgel synthesis

The Δ- ruthenium complex and Λ- ruthenium complex were incorporated into pNIPAM microgels according to the previously reported procedure[S7]. Two types of pNIPAM microgel incorporating Δ-ruthenium complex were synthesized. One has phenylboronic acid in the pNIPAM microgel (pNIPAM-Δ-Ru-PBA). The other does not have the phenylboronic acid (pNIPAM-Δ-Ru). All pNIPAM microgel incorporating Λ-ruthenium complex has phenylboronic acid (pNIPAM-Λ-Ru-PBA).

Preparation of the luminescent microgel solution

A phosphate buffer solution was prepared as follows: 687.7 mg of $Na_2HPO_4 \cdot 12H_2O$ (Sigma-Aldrich) and 10.35 mg of $NaH_2PO_4 \cdot H_2O$ (Sigma-Aldrich) were dissolved in 500 ml of water. The pH of the phosphate buffer was adjusted to be pH 8.5 by 0.1 M HCl or 0.1 M NaOH.

The luminescent microgel solution was prepared by mixing the microgel and the phosphate buffer solution with or without fructose. The aqueous suspension of the synthesized pNIPAM microgel (1 ml) is mixed with phosphate buffer (1.5 ml) at room temperature. The mixture was shaken by the hand.

In the luminescent microgel solution with fructose, D-(−)-Fructose ((>99%, Fluka BioChemika) was dissolved to be 20 mM.

Measurements of the optical and chiroptical properties

A quartz cuvette was used for the investigation of the optical and chiroptical properties (UV-visible absorption (UV), circular dichroism (CD), fluorescence (FL) and circularly polarized luminescence (CPL)). UV and CD spectra were obtained on a JASCO J-815. FL and CPL spectra were investigated using a JASCO CPL-300. The temperature at the spectroscopic measurement was controlled at 15 °C by water chiller. The luminescent microgel solution was stirred with 2000 rpm during the measurement. The excitation wavelength of the FL and CPL measurements was 420 nm. The fluorescence lifetime was obtained on a Hamamatsu Photonics K.K. C11367-01. The temperature and excitation wavelength of fluorescence lifetime measurement were 25 ˚C and 405 nm.

Measurement of hydrodynamic diameter by dynamic light scattering

Particle size distributions were determined by photon correlation spectroscopy using a Malvern Instruments Zetasizer Nano S90 operating with a HeNe laser at 90˚. The hydrodynamic diameters dH were calculated from diffusion coefficients using the Stokes–Einstein equation. All correlogram analyses were performed using software supplied by the manufacturer. The polydispersity index (PDI) is given by the cumulant analysis method.

Calculation of g_{abs} with error

Dissymmetry factors of absorption (g_{abs}) and error of g_{abs} were calculated as follows: The g_{abs} was calculated by the following equation. ΔA and A are the CD and UV (DC voltage measured by CD spectrometer) intensities at λ nm, respectively.

$$g_{abs} = \frac{\Delta A(\lambda)}{A(\lambda) * 32982}$$

Curve fitting was carried out in CD spectra. The number of the peak component of fitting curve was determined by referring the shoulders in spectra and the number of peaks reported in the reference[S8]. Gaussian function was utilized for the fitting. In the fitting of CD spectra, the wavelength of peak component was determined (Fig. S1(a), Fig. S1(c), Fig. S2(a) and Fig. S2(c)).

The baseline correction of UV spectra was carried out by subtracting the exponential decay function from the raw UV spectra. The curve fitting of baseline-corrected UV spectra was carried out by Gaussian function. Then, the number and the wavelength of peak components of UV spectra were assimilated to those in CD spectra (Fig. S1(b), Fig. S1(d), Fig. S2(b) and Fig. S2(d)). The g_{abs} was calculated from the values of the fitting curves (red line in the UV and CD spectra) at 420 nm corresponding to the excitation photon wavelength.

The standard deviation of the fitting curves was defined as the error of g_{abs}, and was calculated by fitting the curves of CD and UV spectra as follows: the variance of ΔA (420 nm) and A (420 nm) was determined by dividing the residual sum of squares by the number of the data point. The standard deviation was calculated by taking the square root of the variance. The error of g_{abs} was determined from the standard deviation of ΔA and A by the error propagation law.

Calculation of g_{lum} with error

Dissymmetry factors of emission (g_{lum}) and the error of g_{lum} were calculated as follows: The g_{lum} was calculated by the following equation. ΔI and I are the CPL and FL (DC voltage measured by CPL spectrometer) intensities at λ nm, respectively.

$$g_{lum} = \frac{2\Delta I(\lambda)}{I(\lambda)}$$

Curve fitting of CPL and FL spectra was carried out to make the spectra smooth. Gaussian function was utilized for the curve fitting. In the fitting, each peak component of fitting curve was ignored on the calculation of g_{lum}. The FL and CPL intensities of the fitting curves at the wavelength which the CPL intensity is the highest was referred to calculate g_{lum}.

The standard deviation of the fitting curves was defined as the error of g_{lum}, and was calculated by fitting the curves of CPL and FL spectra as follows: the residual sum of squares was calculated from the fitting curves of CPL and FL spectra. The variance was determined by dividing the residual sum of squares by the number of the data point. The standard deviation was calculated by taking the square root of the variance. The error of g_{lum} was determined from the standard deviation of ΔI and I by the error propagation law.

Table S1 Hydrodynamic diameter and swelling ratio of the microgels in each condition (T = 15 °C). Swelling ratio is defined as the ratio of the diameters between a given microgel and the reference microgel (pNIPAM-Δ-Ru-PBA without fructose).

	pNIPAM-Δ-Ru-PBA with fructose	pNIPAM-Δ-Ru-PBA without fructose	pNIPAM-Δ-Ru
Hydro-dynamic diameter (nm)	263±5	122±4	161±4
Swelling ratio	2.16	1.00	1.32

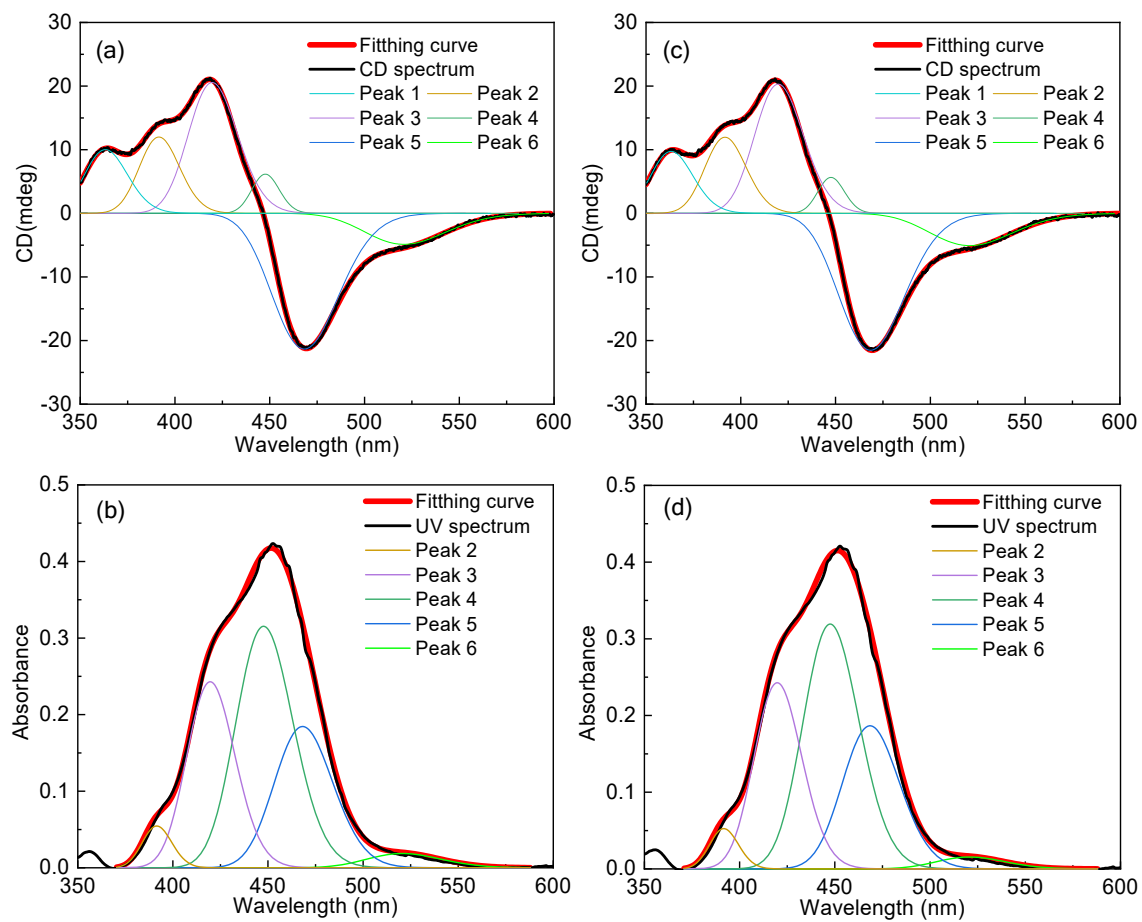Fig. S1 Fitting curves of CD and UV spectra of pNIPAM-Δ-Ru. (a) CD spectra without fructose, (b) UV spectra without fructose, (c) CD spectra with fructose, and (d) UV spectra with fructose.
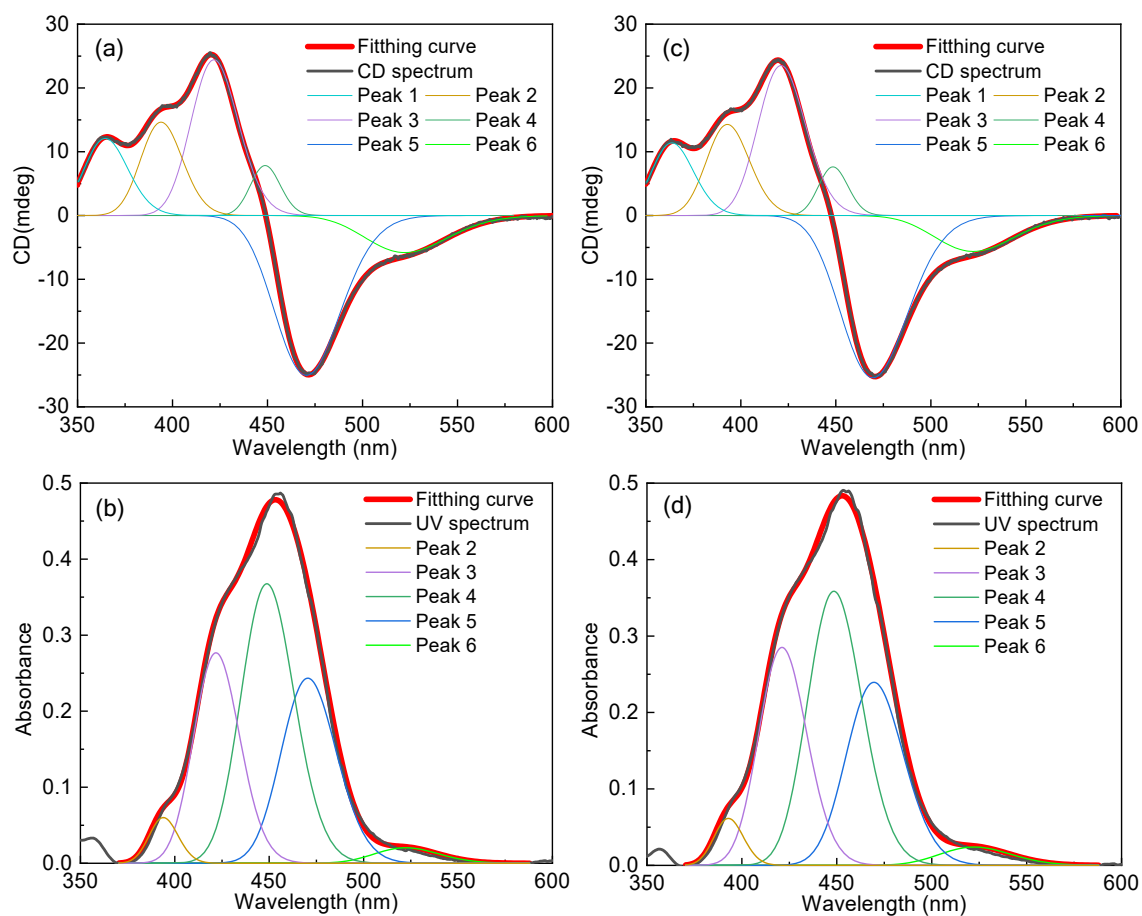
Fig. S2 Fitting curves of CD and UV spectra pNIPAM-Δ-Ru-PBA. (a) CD spectra☐without fructose, (b) UV spectra without fructose, (c) CD spectra with fructose and (d) UV spectra with fructose.
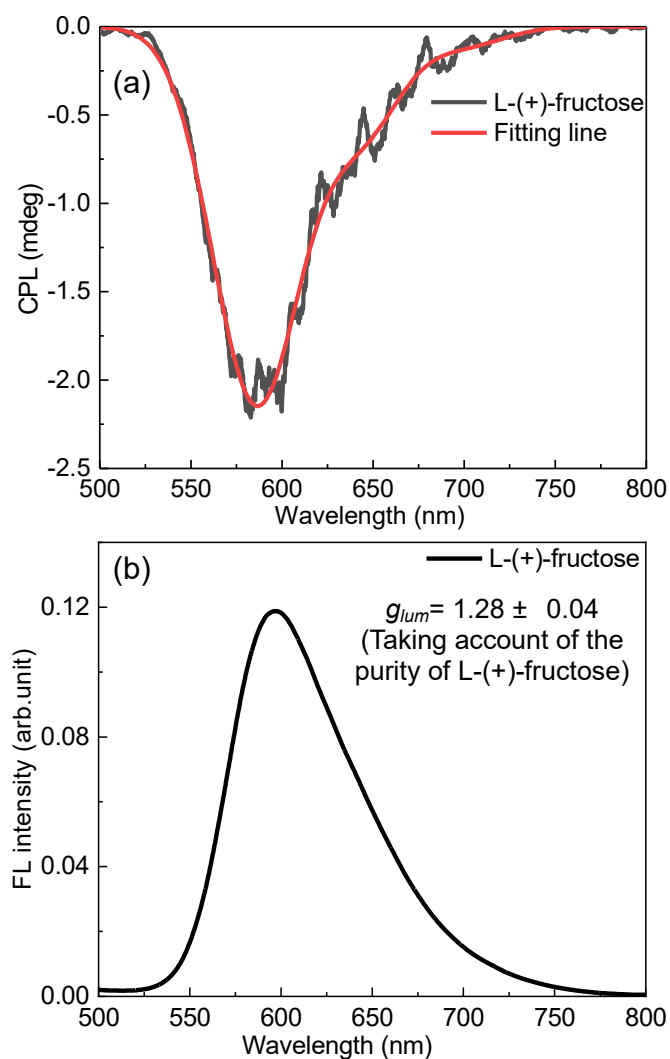
Fig. S3 CPL and Fluorescence spectra of pNIPAM-Δ-Ru-PBA with (L)-(+)-fructose.. (a) CPL spectra and (b) FL spectra. The black and red lines are the spectra and fitting line, respectively. Measurement temperature was 15 °C. Excitation wavelength of FL and CPL spectra was 420 nm.
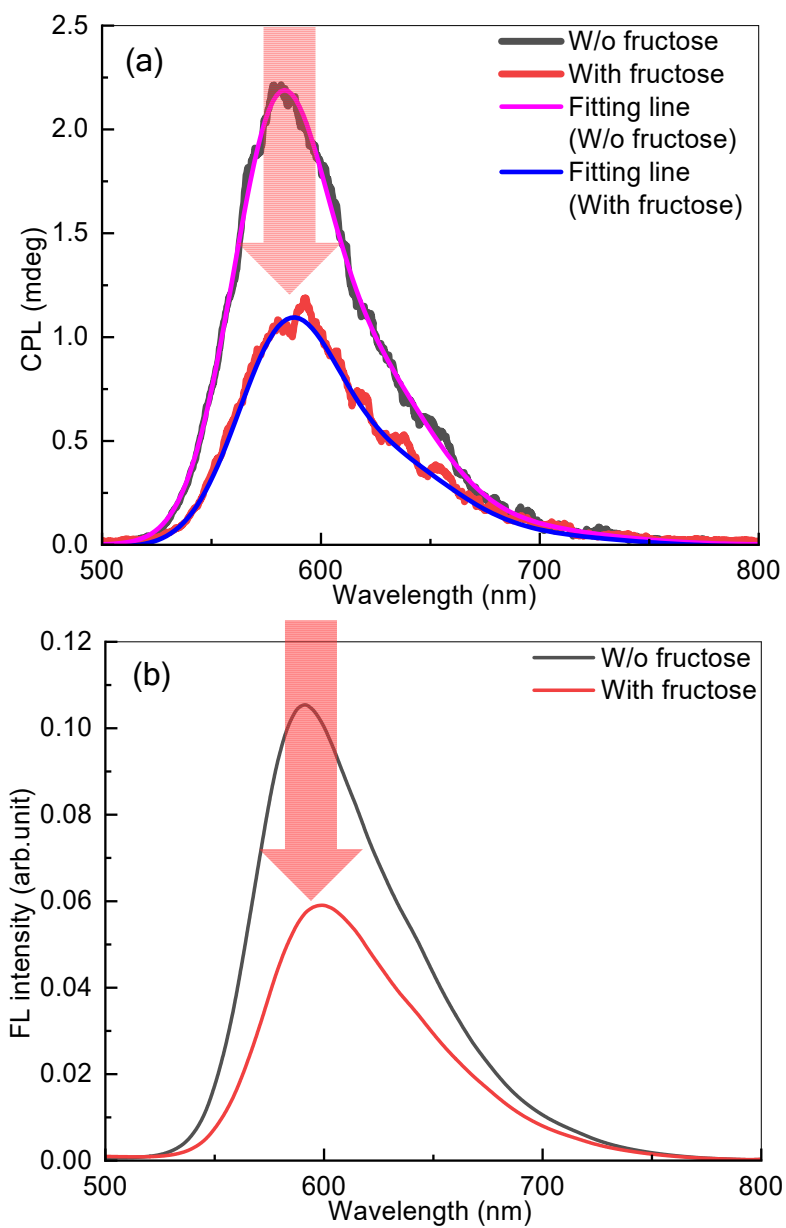
Fig. S4 CPL and fluorescence spectra of pNIPAM-Λ-Ru-PBA with or without fructose. (a) CPL spectra and (b) FL spectra. The red and black lines are the spectra with and without fructose, respectively. Blue and purple lines are the fitting line of CPL spectra with and without fructose, respectively. Measurement temperature was 15 °C. Excitation wavelength of FL and CPL spectra was 420 nm.

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