Supplementary Information

Generation of time-multiplexed chiroptical information from multilayer-type luminescence-based circular polarization conversion films

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1 Experimental

1.1 Materials and instrumentation

Cadmium oxide (CdO, 99.99%), trioctylphosphine oxide (TOPO, 99%), trioctylphosphine (TOP, 97%), tetradecylphosphonic acid (TDPA, 98%), selenium (99.99%), sulphur (99.98%), hexylphosphonic acid (HPA, 95%), octadecylphosphonic acid (ODPA, 97%), and poly(ethylene-*co*-vinyl acetate) (vinyl acetate 40 wt%) were purchased from Sigma-Aldrich Incorporated and used as received. Other chemicals were purchased from commercial chemical suppliers and used without further purification. A polymer zero-order quarter-wave plate (WPQ10E-633) and a $\lambda/4$ retarder film (WP140HE) were purchased from Thorlabs Incorporated and Edmund Optics Incorporated, respectively, and were used as a quarter-wave plate. UV-visible absorption spectra were obtained using a V-650 system (JASCO). Angular dependence of absorbance was evaluated using a V-650 system (JASCO) with a linear polarizer. PL spectra were obtained using a FP-8600 system (JASCO). PL lifetimes were measured using a C11367 Quantaurus-Tau fluorescence lifetime spectrometer (Hamamatsu Photonics). The setups for evaluating LPL, CP light, and time-resolved CP light spectra are described in Sections **1.6**, **1.7**, and **1.9**, respectively. All spectral measurements were obtained at room temperature. Photographs were obtained using a Tough TG-6 compact digital camera (OLYMPUS).

1.2 Synthesis of CdSe/CdS core/shell quantum rods (QRs)

< Synthesis of CdSe quantum dots (QDs) >

TOPO (4.0 g), TDPA (0.373 g), and CdO (0.080 g) were mixed in a 100 mL three-necked flask and heated at 150 °C for 1 h under vacuum. The flask was purged with nitrogen gas. A colorless transparent solution was formed by completely dissolving the mixture by heating it to 320 °C. The solution was then further heated to 350 °C and TOP (2.0 mL) was injected into the flask. A Se/TOP solution (1.0 mol L^{-1}, 0.88 mL) was injected into the flask at 370 °C, and the reaction mixture was immediately cooled by removing the mantle heater. The mixture was left at room temperature. The obtained precipitate was purified by centrifugation using toluene (5 mL), followed by methanol (8 mL), and finally a toluene/methanol mixed solvent (1/1 vol/vol, 10 mL). After removing the supernatant, the precipitate was dissolved in TOP (4.5 mL). The concentration of the obtained QD/TOP solution was calculated using a previously reported method.[1] Details of the calculation are provided in Section 1.5.

< Synthesis of QRs >

TOPO (2.0 g), TDPA (0.200 g), HPA (0.052 g), and CdO (0.030 g) were mixed in a 100 mL three-

necked flask and heated at 150 °C for 1 h under vacuum. The flask was purged with nitrogen gas, and the mixture was completely dissolved by heating it to 320 °C to form a colourless transparent solution. TOP (1.0 mL) was injected into the flask. The synthesized QD/TOP solution (0.263 mol L^{-1}, 0.20 mL) and the S/TOP solution (0.5 mol L^{-1}, 1.0 mL) were injected into the flask at 350 °C. The temperature was carefully maintained at 350 °C for 8 min, then the reaction mixture was immediately cooled by removing the mantle heater and left at room temperature. The obtained precipitate was purified by centrifugation using toluene (3 mL), followed by a toluene/methanol mixed solvent (1/1 vol/vol, 6 mL). After removing the supernatant, the precipitate was dissolved in toluene (3.5 mL). The concentration of the obtained QR/toluene solution was calculated using the weight of the dried powder per 0.5 mL.

1.3 Calculation of concentration of QD/TOP solution

The concentration of the QD/TOP solution was calculated using the following procedure.[1] First, the diameter of the CdSe QD (D) was calculated using equation (eq1):

$$D = (1.6122 \times 10^{-9})\lambda^4 - (2.6575 \times 10^{-6})\lambda^3 - (1.6242 \times 10^{-3})\lambda^2 - (0.4277)\lambda + (41.57), \quad \text{(eq1)}$$

where λ is the wavelength of the first excitonic absorption peak from the experimentally obtained absorption spectra (Figure S1). D was used to obtain the extinction coefficient (ε) via equation (eq2):

$$\varepsilon = 5875\ (D)^{2.65} \quad \text{(eq2)}$$

Using the extinction coefficient (ε), the absorption at the first excitonic peak (A), and the path length (L), the concentration (C) was calculated using the Lambert–Beer law (eq3):

$$A = \varepsilon CL \quad \text{(eq3)}$$

The calculated concentration (C) was used for the synthesis of the QRs.

1.4 TEM observation

A cellulose triacetate-coated copper grid with a carbon-coated surface was used for TEM. A drop of the QR/toluene solution was cast on the grid. After removing excess solution using filter paper, the grid was air-dried at room temperature. The grid was then dried in vacuum and used for TEM, which was performed using a JEM-2200FS electron microscope at 200 kV.

1.5 Uniaxial stretching of luminogen/EVA composite films

Each luminogen/toluene solution was mixed with a poly(ethylene-*co*-vinyl acetate) (EVA)/toluene solution. The mixture was cast on a glass substrate and air-dried at room temperature. After detaching

it from the substrate, the obtained film was placed on a pair of vernier calipers and stretched to a specific length. The stretching ratio was defined by the following equation (eq4):

$$\text{Stretching ratio} = (l - l_0) / l_0, \qquad \text{(eq4)}$$

where l_0 and l are the lengths of the film before and after uniaxial stretching, respectively. The 1D stretched film was attached to a glass substrate and used to obtain the various spectra.

1.6 Acquisition of LPL spectra

The LPL spectra were obtained using a CCS200/M compact spectrometer (Thorlabs Inc.) with an LPL detection optical setup. An NIJI-3KF variable wavelength light source (Bunkoukeiki Co., Ltd) was used as a monochromatic depolarized light source. The light beam was focused on the sample using a bi-convex lens (LB4879, Thorlabs Inc.). The light emission from each sample was collimated using a plano-convex lens (LA4052, Thorlabs Inc.), and was passed at a fixed angle through a linear polarizer (WP25M-UB, Thorlabs Inc.) controlled by an indexing rotation mount (RSP1X15/M, Thorlabs Inc.). After passing through the linear polarizer, the light was focused on an optical fibre (M133L01, Thorlabs Inc.) using the plano-convex lens (LA4052, Thorlabs Inc.), and the spectra were recorded by the spectrometer. All spectral measurements were done by placing front face to the incident light side and back face to the detector side. The degree of linear polarization of the photoluminescence ($P_{\text{LP-lum}}$) was calculated by comparing the PL intensities of the parallel (//) and perpendicular (⊥) LPL components.

1.7 Acquisition of CP light spectra

The CP light spectra were obtained using a CCS200/M compact spectrometer (Thorlabs Inc.) with a CP light detection optical setup. An NIJI-3KF variable wavelength light source (Bunkoukeiki Co., Ltd) was used as a monochromatic depolarized light source. The light emission from the samples was collimated using a plano-convex lens (LA4052, Thorlabs Inc.), and was passed through a $\lambda/4$ Fresnel rhomb retarder (FR600QM, Thorlabs Inc.) and a linear polarizer (WP25M-UB, Thorlabs Inc.) at a fixed angle controlled by an indexing rotation mount (RSP1X15/M, Thorlabs Inc.). After passing through the $\lambda/4$ Fresnel rhomb retarder and linear polarizer, the light was focused on an optical fibre (M133L01, Thorlabs Inc.) using a plano-convex lens (LA4052, Thorlabs Inc.), and the spectra were recorded using the spectrometer. The fast axis angle of the $\lambda/4$ Fresnel rhomb retarder was fixed at −45°. Left-handed (LH-) and right-handed (RH-) CP light was detected by selecting vertical (for LH-CP) and horizontal (for RH-CP) polarization axes with the linear polarizer. All spectral measurements were done by placing front face to the incident light side and back face to the detector side. We calculated the degree of circular polarization in the photoluminescence (P_{CP}) by comparing the light

intensities of the LH- and RH- CP light components.

1.8 Fluorescence polarization microscopy

The fluorescence polarization images were obtained by quantum rod orientation microscopy (QROM) technique, as described elsewhere.[2] Briefly, for each pixel of an image, a value for the complete angular dependence of polarization is obtained, which is defined as $P = (I_V - I_H)/(I_V + I_H)$, where the subscripts V and H stand for vertically and horizontally polarized emission, respectively. Maps of orientation and degree of linear polarization (DOLP) are obtained from the angular dependence of polarization and are represented by false color codes. In the present study, the exciting light source was a 490 nm LED (M490L3, Thorlabs Inc.) set at a light intensity ($I_{excitation}$) of 765 μW, and it was used in combination with an excitation filter (ET492/25x, Chroma Technology). Exciting light was diverted to an inverted oil immersion objective (UPLSAPO100XO, NA1.40, Olympus) by a dichroic mirror (510dcxr), and fluorescence was collected by the same objective and filtered by an emission filter (ET520LP, Chroma). Subsequently, it was imaged on the camera (ORCA Flash4, Hamamatsu Photonics) by the QROM optics, which consisted of a rotating superachromatic half waveplate (SAHWP05M-700, Thorlabs Inc.) and polarization beamsplitters (PBS101, Thorlabs Inc.). The magnification of the system yielded a pixel size corresponding to 36.3 nm in the sample plane. The integration time per camera frame was adapted to the brightness of the sample.

1.9 Acquisition of time-resolved CP light spectra

Time-resolved CP light spectra were recorded using a C11367 Quantaurus-Tau fluorescence lifetime spectrometer (Hamamatsu Photonics) with a CP light detection setup. Monochromatic pulsed light (470 nm) from the built-in LED light source was depolarized by passing it through an optical fibre (M93L01, Thorlabs Inc.), and was subsequently used to irradiate the multi-layered luminescence-based CP convertors. The light emission from each convertor was passed through a polymer zero-order quarter-wave plate (WPQ10E-633, Thorlabs Inc.) and a linear polarizer (WP25M-UB, Thorlabs Inc.). The azimuthal angles of WPQ10E-633 and WP25M-UB were controlled using an index rotation mount (RSP1X15/M, Thorlabs Inc.). The angle of the polarization axis of WP25M-UB was fixed to vertical. LH- and RH-CP light was detected by selecting WPQ10E-633 fast axis angles of −45° (for RH-CP) and +45° (for LH-CP). After passing through the WPQ10E-633 and WP25M-UB, the spectra were recorded using a C11367 detection system equipped with a monochrometer and a photomultiplier tube. The emission was recorded at 10 nm increments from 550 to 700 nm. In the present study, the time corresponding to the maximum PL intensity was defined as 0 ns. The digital integration time was fixed at 1 ns for the preparation of Figures 6, 7, and S6.

2. Supplementary figures

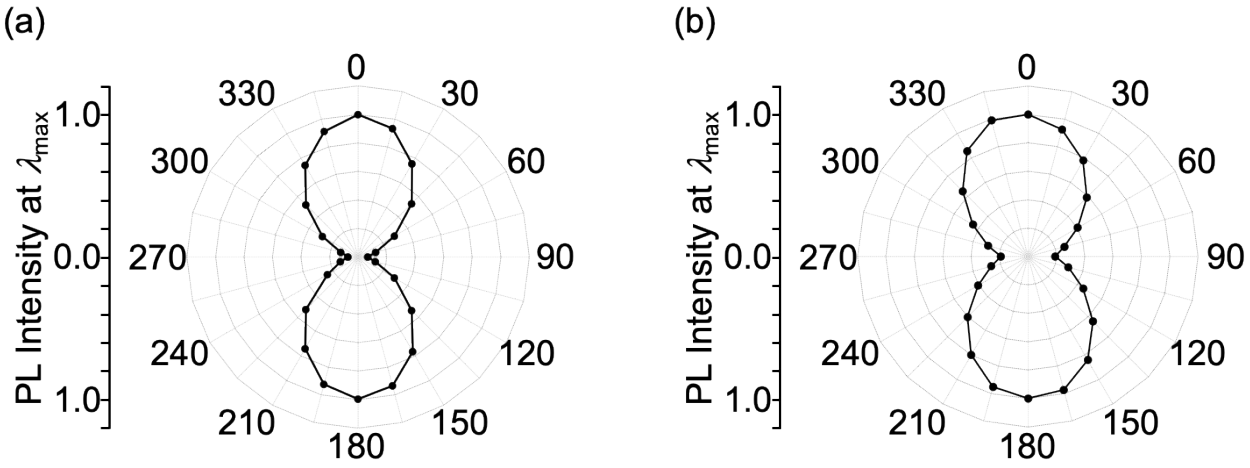

Figure S1 Angular dependence of PL intensity at λ_{max} of (a) the $LPL_{MEH\text{-}PPV}$ film and (b) the LPL_{QR} film. The excitation wavelength was 470 nm. The PL peak was adjusted to 1.

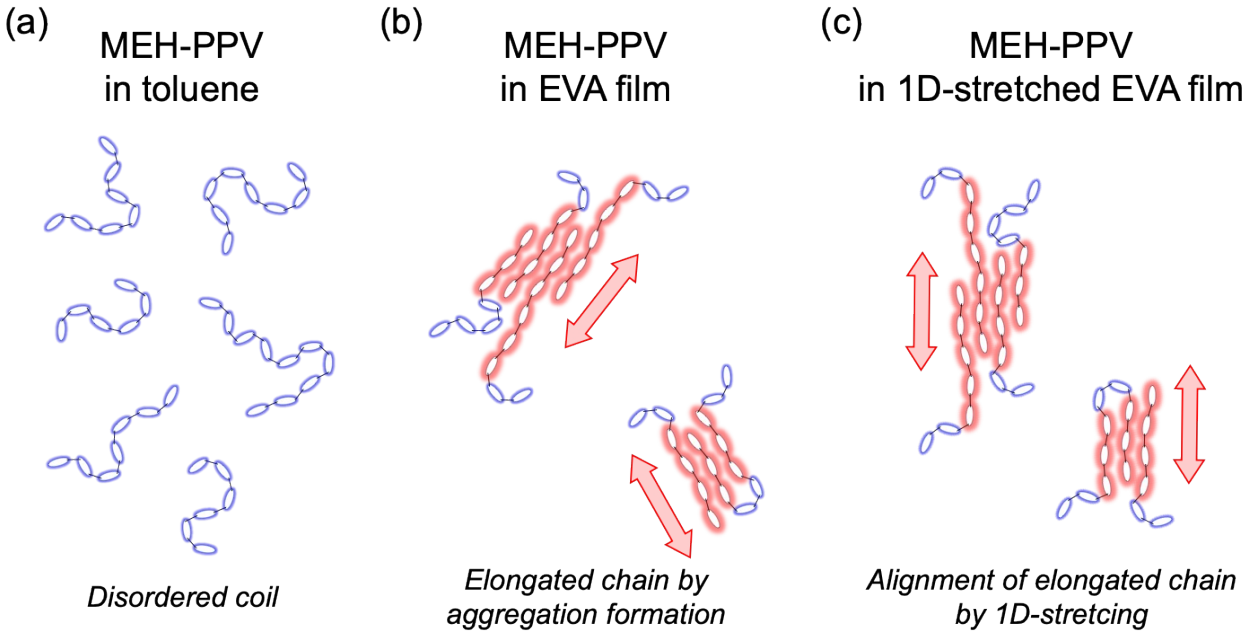

Figure S2 Schematic illustration of MEH-PPV polymer chains in (a) a toluene solution with and without EVA, (b) a composite EVA film before stretching, and (c) a composite EVA film after stretching ($LPL_{MEH\text{-}PPV}$ film).

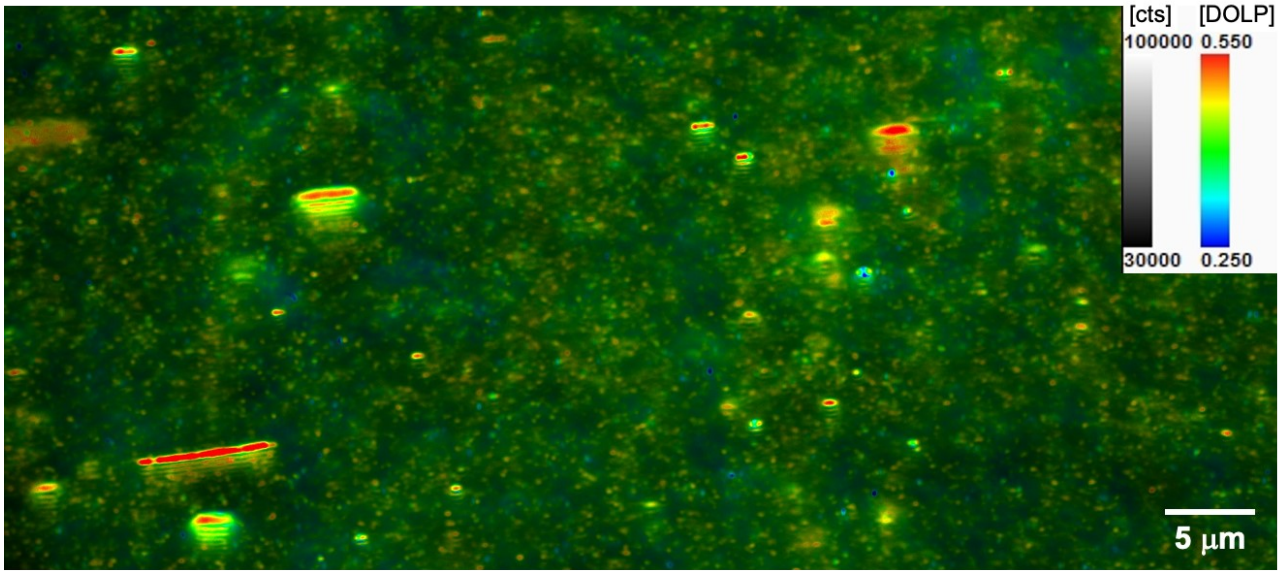

Figure S3 DOLP image of fluorescence of an LPL_{QR} film obtained using the QROM technique, as described in Section 1.8. The rainbow color scale is coded for degree of linear polarization (DOLP).

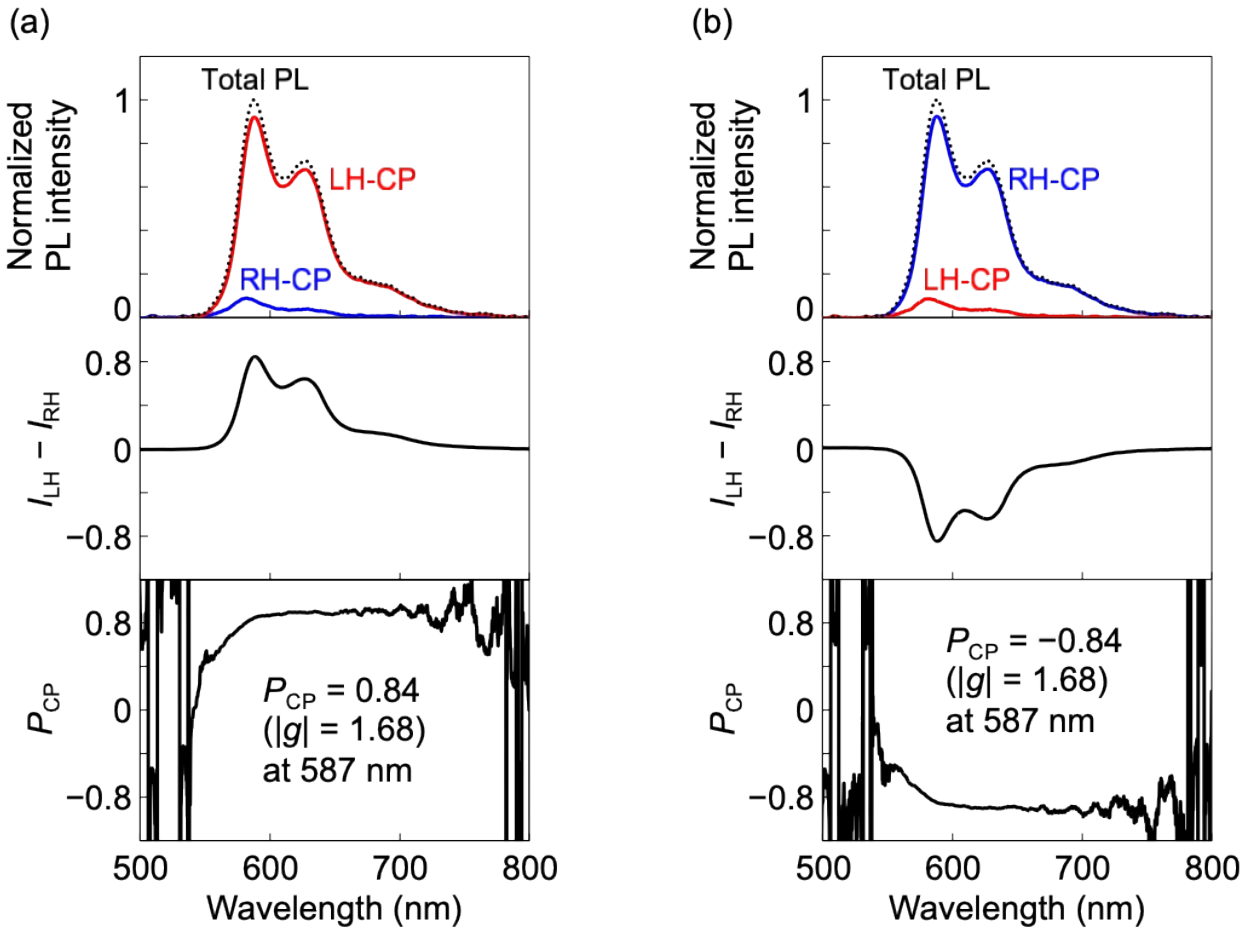

Figure S4 PL (top), CP light (middle), and P_{CP} (bottom) spectra of single-layered luminescence-based CP convertors fabricated from an $LPL_{MEH\text{-}PPV}$ film. The total PL values were normalized so that the highest peak equalled one. The azimuthal angles between the polarization axis of the $LPL_{MEH\text{-}PPV}$ film and the fast axis of the quarter-wave film were fixed at (a) −45° and (b) +45°. The excitation wavelength was 470 nm.

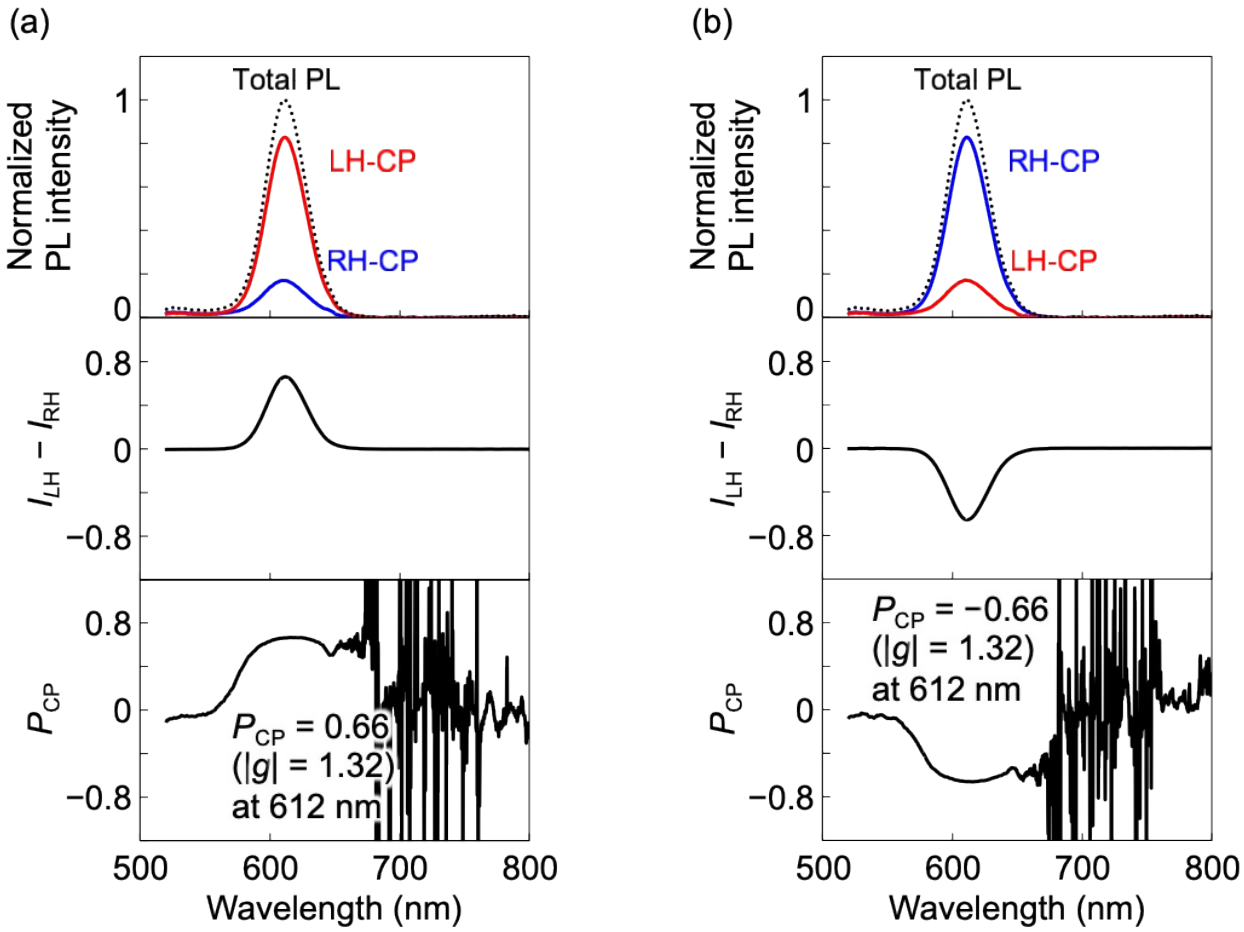

Figure S5 PL (top), CP light (middle), and P_{CP} (bottom) spectra of single-layered luminescence-based CP convertors fabricated from LPL_{QR} films. The total PL values were normalized so that the highest peak equalled one. The azimuthal angles between the polarization axis of the LPL_{QR} film and the fast axis of the quarter-wave film were fixed at (a) −45° and (b) +45°. The excitation wavelength was 470 nm.

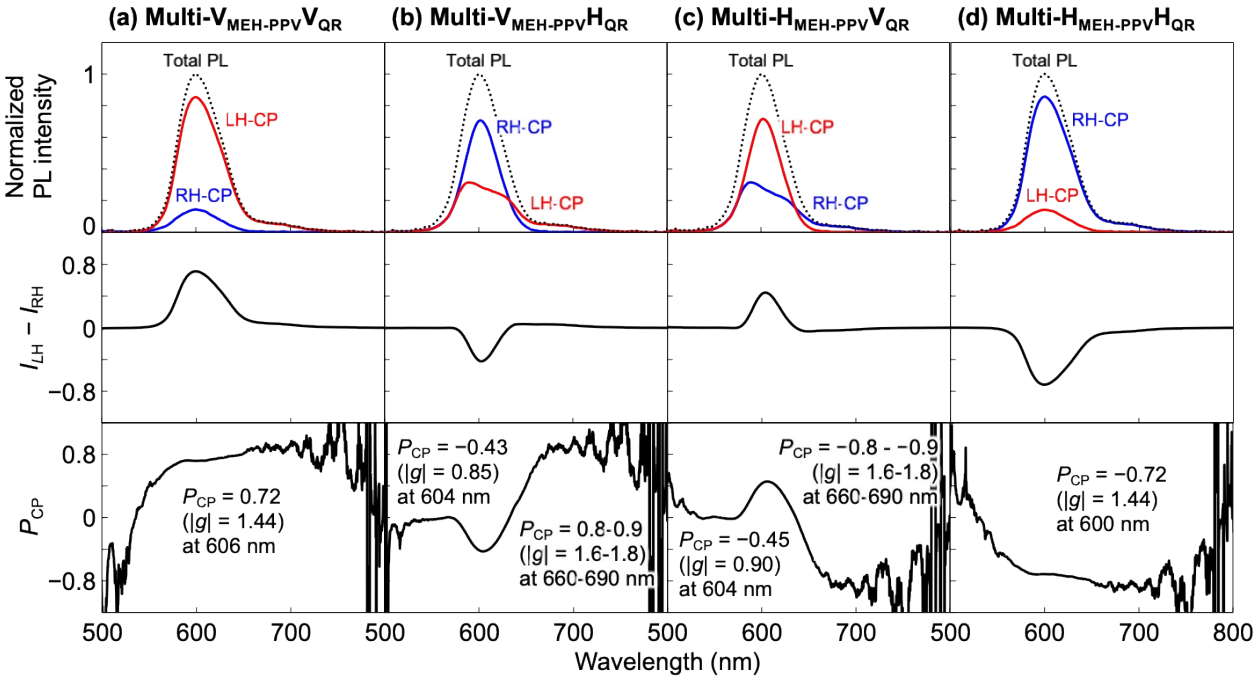

Figure S6 PL (top), CP light (middle), and P_{CP} (bottom) spectra of (a) **Multi-V$_{MEH-PPV}$V$_{QR}$**, (b) **Multi-V$_{MEH-PPV}$H$_{QR}$**, (c) **Multi-H$_{MEH-PPV}$V$_{QR}$**, and (d) **Multi-H$_{MEH-PPV}$H$_{QR}$**. The total PL values were normalized so that the highest peak equalled one. The excitation wavelength was 470 nm.

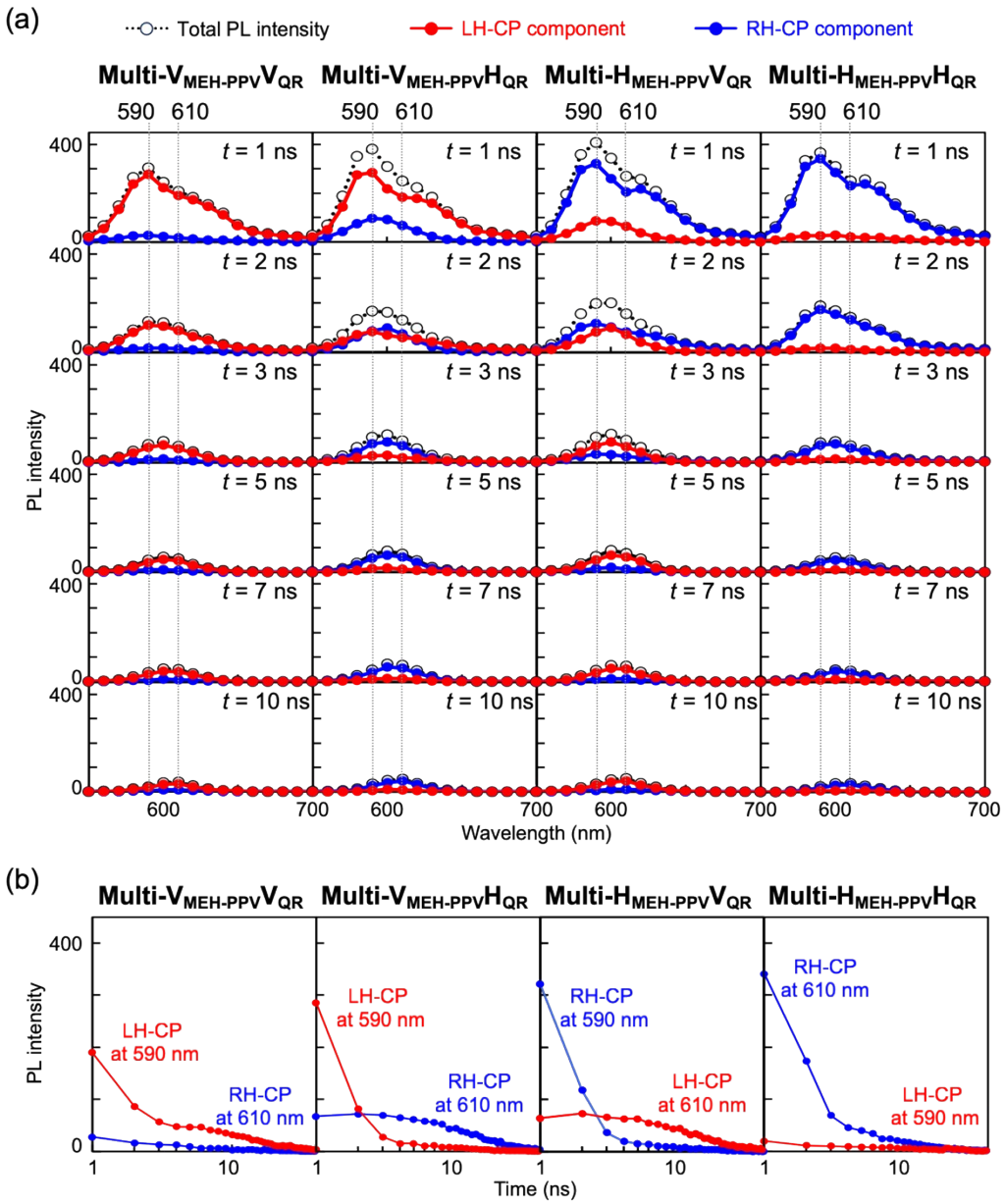

Figure S7 (a) Time-course changes in PL spectra of **Multi-V$_{MEH-PPV}$V$_{QR}$**, **Multi-V$_{MEH-PPV}$H$_{QR}$**, **Multi-H$_{MEH-PPV}$V$_{QR}$**, and **Multi-H$_{MEH-PPV}$H$_{QR}$**. The red and blue lines indicate LH- and RH-CP components, respectively. The black dotted lines indicate the total PL. The convertors were excited by depolarized pulsed light at 470 nm. (b) Time-course changes in PL intensity of LH-CP components at 590 nm (the blue lines in the left two graphs) and RH-CP components at 610 nm (the red lines in the left two graphs) from **Multi-V$_{MEH-PPV}$V$_{QR}$** and **Multi-V$_{MEH-PPV}$H$_{QR}$**. The time-course changes in PL intensity of the LH-CP components at 610 nm (the red lines in the right two graphs) and RH-CP components at 590 nm (the blue lines in the right two graphs) from **Multi-H$_{MEH-PPV}$V$_{QR}$** and **Multi-H$_{MEH-PPV}$H$_{QR}$**.

3. References

[1] W. W. Yu, L. Qu, W. Guo, X. Peng, *Chem. Mater.* 2003, **15**, 2854-2860.

[2] A. Chakrabarty, G. Raffy, M. Maity, L. Gartzia-Rivero, S. Marre, C. Aymonier, U. Maitra, and A. Del Guerzo, *Small*, 2018, **14**, 1802311.