Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information

Luminescence-baced circular polarization convertor: Polarization conversion of linearly polarized photoluminescence from one-dimensionally aligned quantum rods by retardation film

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1 Experimental details

1.1 Materials and instrumentations

Cadmium oxide (CdO, 99.99%), Trioctylphosphine oxide (TOPO, 99%), Trioctylphosphine (TOP, 97%), Tetradecylphosphonic Acid (TDPA, 98%), Selenium (99.99%), Sulfur (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 Inc. and used as received. Other chemicals were purchased from commercial chemical suppliers and were used without further purification. Polymer Zero-Order Quarter-Wave Plate (WPQ10E-633) and $\lambda/4$ Retarder film (WP140HE) were purchased from Thorlabs Inc. and Edmund Optics Inc., respectively, and were used as quarter-wave plate. UV-visible absorption spectra were measured with a V-650 (JASCO). Angular dependence of absorbance was evaluated using a V-650 (JASCO) with linear polarizer. PL spectra were measured with a FP-8600 (JASCO). The setups for evaluating LPL and CP light are described in the section **1.8** and **1.9**, respectively. All the spectral measurements were carried out at room temperature. Photographs were taken by compact digital camera Tough TG-6 (OLYMPUS).

1.2 Synthesis of yellow-color-emissive CdSe/CdS core/shell quantum rods (yellow-QR)

< Synthesis of CdSe quantum dots (**QD-1**) >

TOPO (1.5 g), ODPA (0.140 g), and CdO (0.031 g) were mixed in a 100 mL three-necked flask and were heated up at 150 ˚C for 1 h under vacuum. After the atmosphere in the flask was purged by nitrogen gas, the mixture was completely dissolved to be colorless transparent solution by heating up to 320 ˚C. The mixture was further heated up to 350 ˚C and TOP (0.75 mL) was injected into the flask. Then, after Se/TOP solution (1.0 mol L^{-1}, 0.33 mL) was injected to the flask, the reaction mixture was immediately cooled down by removing the mantle heater and was left to be room temperature. The obtained precipitate was purified by centrifugation using toluene (3 mL) for 1st step, methanol (3 mL) for 2nd step, and toluene/methanol mixed solvent (1/1 vol/vol, 6 mL) for 3rd step, respectively. After removal of supernatant, the precipitate was dissolved into TOP (1.5 mL). Concentration of the obtained **QD-1**/TOP solution was calculated by using previously reported method.[1] The detail calculation procedure is summarized in the section **1.5**.

< Synthesis of yellow-QR >

TOPO (1.0 g), ODPA (0.093 g), HPA (0.026 g), and CdO (0.015 g) were mixed in a 100 mL three-necked flask and were heated up at 150 ˚C for 1 h under vacuum. After the atmosphere in the flask was purged by nitrogen gas, the mixture was completely dissolved to be colorless transparent solution by heating up to 320 ˚C. TOP (0.50 mL) was injected into the flask. The synthesized **QD-1**/TOP solution (0.170 mol L^{-1}, 0.32 mL) and S/TOP solution (2.5 mol L^{-1}, 0.50 mL) were injected to the flask at 310 ˚C. Temperature was carefully kept at 310 ˚C for 6 minutes, then the reaction mixture was immediately cooled down by removing the mantle heater and was left to be room temperature. The obtained precipitate was purified by centrifugation using toluene (3 mL) for 1st step, and toluene/methanol mixed solvent (1/1 vol/vol, 6 mL) for 2nd step, respectively. After removal of supernatant, the precipitate was dissolved into toluene (1.5 mL). Concentration of the obtained yellow-QR/toluene solution was calculated using weight value of the dried powder per 0.5 mL.

1.3 Synthesis of orange-color-emissive CdSe/CdS core/shell quantum rods (orange-QR)

< Synthesis of CdSe quantum dots (**QD-2**) >

TOPO (4.0 g), TDPA (0.373 g), and CdO (0.080 g) were mixed in a 100 mL three-necked flask and were heated up at 150 ˚C for 1 h under vacuum. After the atmosphere in the flask was purged by nitrogen gas, the mixture was completely dissolved to be colorless transparent solution by heating up to 320 ˚C. The mixture was further heated up to 350 ˚C and TOP (2.0 mL) was injected into the flask. Then, after Se/TOP solution (1.0 mol L^{-1}, 0.88 mL) was injected to the flask at 370 ˚C, the reaction mixture was immediately cooled down by removing the mantle heater and was left to be room temperature. The obtained precipitate was purified by centrifugation using toluene (5 mL) for 1st step, methanol (8 mL) for 2nd step, and toluene/methanol mixed solvent (1/1 vol/vol, 10 mL) for 3rd step, respectively. After removal of supernatant, the precipitate was dissolved into TOP (4.5 mL). Concentration of the obtained **QD-2**/TOP solution was calculated by using previously reported method.[1] The detail calculation procedure is summarized in the section **1.5**.

< Synthesis of orange-QR >

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 were heated up at 150 ˚C for 1 h under vacuum. After the atmosphere in the flask was purged by nitrogen gas, the mixture was completely dissolved to be colorless transparent solution by heating up to 320 ˚C. TOP (1.0 mL) was injected into the flask. The synthesized **QD-2**/TOP solution (0.263 mol L^{-1}, 0.20 mL) and S/TOP solution (0.5 mol L^{-1}, 1.0 mL) were injected to the flask at 350 ˚C. Temperature was carefully kept at 350 ˚C for 8 minutes, then the reaction mixture was immediately cooled down by removing the mantle heater and was left to be room temperature. The obtained precipitate was purified by centrifugation using toluene (3 mL) for 1st step, and toluene/methanol mixed solvent (1/1 vol/vol, 6 mL) for 2nd step, respectively. After removal of supernatant, the precipitate was dissolved into toluene (3.5 mL). Concentration of the obtained orange-QR/toluene solution was calculated using weight value of the dried powder per 0.5 mL.

1.4 Synthesis of red-color-emissive CdSe/CdS core/shell quantum rods (red-QR)

< Synthesis of CdSe quantum dots (**QD-3**) >

TOPO (4.5 g), TDPA (0.420 g), and CdO (0.090 g) were mixed in a 100 mL three-necked flask and were heated up at 150 ˚C for 1 h under vacuum. After the atmosphere in the flask was purged by nitrogen gas, the mixture was completely dissolved to be colorless transparent solution by heating up to 320 ˚C. The mixture was further heated up to 350 ˚C and TOP (2.25 mL) was injected into the flask. Then, after Se/TOP solution (1.11 mol L^{-1}, 0.99 mL) was injected to the flask at 370 ˚C and was mixed for 10 seconds, the reaction mixture was immediately cooled down by removing the mantle heater and was left to be room temperature. The obtained precipitate was purified by centrifugation using toluene (5 mL) for 1st step, methanol (10 mL) for 2nd step, and toluene/methanol mixed solvent (1/1 vol/vol, 14 mL) for 3rd step, respectively. After removal of supernatant, the precipitate was dissolved into TOP (4.0 mL). Concentration of the obtained **QD-3**/TOP solution was calculated by using previously reported method.[1] The detail calculation procedure is summarized in the section **1.5**.

< Synthesis of red-QR >

TOPO (6.0 g), TDPA (0.600 g), HPA (0.157 g), and CdO (0.061 g) were mixed in a 100 mL three-necked flask and were heated up at 150 ˚C for 1 h under vacuum. After the atmosphere in the flask was purged by nitrogen gas, the mixture was completely dissolved to be colorless transparent solution by heating up to 320 ˚C. TOP (3.0 mL) was injected into the flask. The synthesized QD-3/TOP solution (0.160 mol L^{-1}, 1.21 mL) and S/TOP solution (2.5 mol L^{-1}, 1.5 mL) were injected to the flask at 340 ˚C. Temperature was carefully kept at 340 ˚C for 8 minutes, then the reaction mixture was immediately cooled down by removing the mantle heater and was left to be room temperature. The obtained precipitate was purified by centrifugation using methanol (5 mL x 2 times). After removal of supernatant, the precipitate was dissolved into toluene (6.0 mL). Concentration of the obtained red-QR/toluene solution was calculated using weight value of the dried powder per 0.5 mL.

1.5 Calculation of concentration of QD/TOP solution

The concentration of QD/TOP solution was calculated by the following procedure.[1] Firstly, diameter of 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 was the wavelength of the first excitonic absorption peak obtained by experimentally measured absorption spectra (Figures S1-S3). By using diameter (*D*) value, the extinction coefficient (ε) was calculated using equation (eq2):

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

By using extinction coefficient (ε), absorption at first excitonic peak (*A*), and path length (*L*) values, the concentration (*C*) was calculated using Lambert-Beer's law (eq3):

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

The calculated concentration (*C*) value was used for synthesis of QR.

1.6 TEM observation

A drop of QR/toluene solution was cast on the grid. After removal of excess solution by filter paper, grids were air-dried at room temperature. After vacuum drying, these grids were used for TEM observation. Triacetylcellulose-coated cupper grid with a carbon-coated surface was used for solution samples. For a 1D stretched film sample, thin film was directly attached on a TEM microgrid. TEM and HRTEM observation were performed with JEM-2200FS at 200 kV. Fast Fourier transform analysis was carried out by using Image J. Element mapping was performed on JEM-ARM200F (JEOL) with JED-2300T (JEOL).

1.7 Uniaxial stretching of QR/EVA composite film

A QR/toluene solution was mixed with poly(ethylene-*co*-vinyl acetate) (EVA)/toluene solution. The mixture was casted on a glass substrate and was air-dried at room temperature under. After detached from the substrate, the obtained film was sticked on a vernier caliper and was stretched to be certain length. Stretching ratio was defined as following equation (eq4):

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

where l_0 and l are length of the film before and after uniaxial stretching, respectively. The 1D stretched film was attached on a glass substrate and was used for LPL spectral measurements. For the CP convertor, the 1D stretched film was attached on a retardation film. The obtained film was used for CP light spectral measurements.

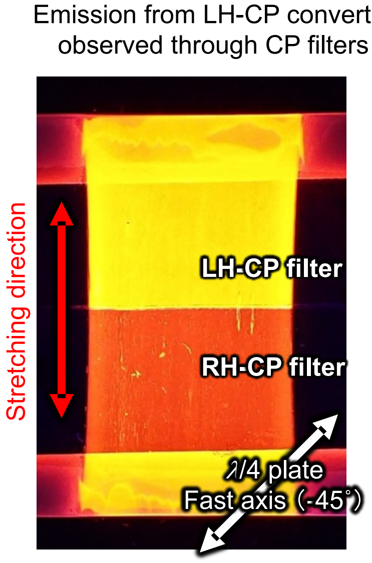
1.8 Spectral measurement of LPL

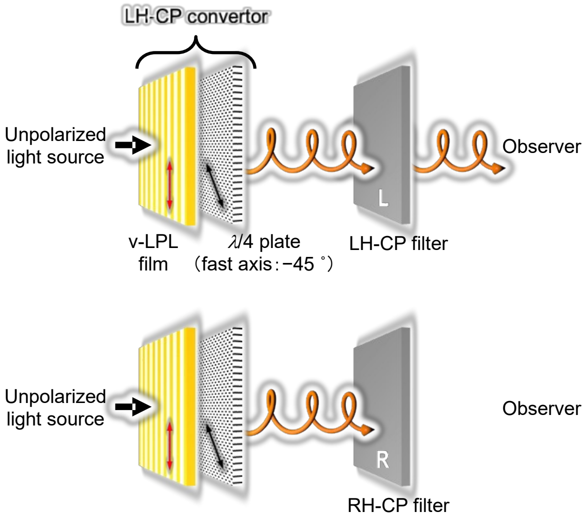
LPL spectra were recorded with a CCS200/M Compact Spectrometer (Thorlabs) with LPL detection optical setup. A 150W-xenon lump (150W) and monochromator of FP-8600 (JASCO) was used as a light source. A focused monochromatic light from light source was depolarized by passing through an optical fiber (M114L02, Thorlabs). The light beam was focused on the sample by Bi-Convex Lens (LB4879, Thorlabs). The light emission from samples was collimated by Plano-Convex Lens (LA4052, Thorlabs) and was passing through linear polarizer (WP25M-UB, Thorlabs) at fixed angle controlled by Indexing Rotation Mount (RSP1X15/M, Thorlabs). After passing through the linear polarizer, the light was focused on an optical fiber (M133L01, Thorlabs) by using Plano-Convex Lens (LA4052, Thorlabs) and the spectra was recorded by spectrometer. By comparing PL intensities of parallel (//) and perpendicular (⊥) LPL components against 1D stretching direction, degree of linear polarization in the photoluminescence ($P_{\text{LP-lum}}$) was calculated.

1.9 Preparation of luminescence-based CP convertor

< LH- (or RH-) CP convertor >

1D stretched QR/EVA composite film was laminated with a quarter-wave plate where the fast axis was placed at −45˚ (or +45˚) to the stretching direction. The example of LH-CP convertor is illustrated as indicated below.





1.10 Spectral measurement of CP light

CP light spectra were recorded with a CCS200/M Compact Spectrometer (Thorlabs) with CP light detection optical setup. A 150W-xenon lump (150W) and monochromator of FP-8600 (JASCO) was used as a light source. A focused monochromatic light from light source was depolarized by passing through an optical fiber (M114L02, Thorlabs). The light beam was focused on the sample by Bi-Convex Lens (LB4879, Thorlabs). The light emission from samples was collimated by Plano-Convex Lens (LA4052, Thorlabs) and was passing through $\lambda/4$ Fresnel Rhomb Retarder (FR600QM, Thorlabs) and linear polarizer (WP25M-UB, Thorlabs) at fixed angle controlled by Indexing Rotation Mount (RSP1X15/M, Thorlabs). After passing through the $\lambda/4$ Fresnel Rhomb Retarder and linear polarizer, the light was focused on an optical fiber (M133L01, Thorlabs) by using Plano-Convex Lens (LA4052, Thorlabs) and the spectra was recorded by spectrometer. The angle of fast axis of $\lambda/4$ Fresnel Rhomb Retarder was fixed at -45°. Detection of left-handed (LH-) and right-handed (RH-) CP light were performed by selecting the polarization axis of linear polarizer to be vertical (for LH-CP) and horizontal (for RH-CP), respectively. By comparing light intensities of LH- and RH- CP light components, degree of circular polarization in the photoluminescence (P_{CP}) was calculated.

2. Supplementary figures

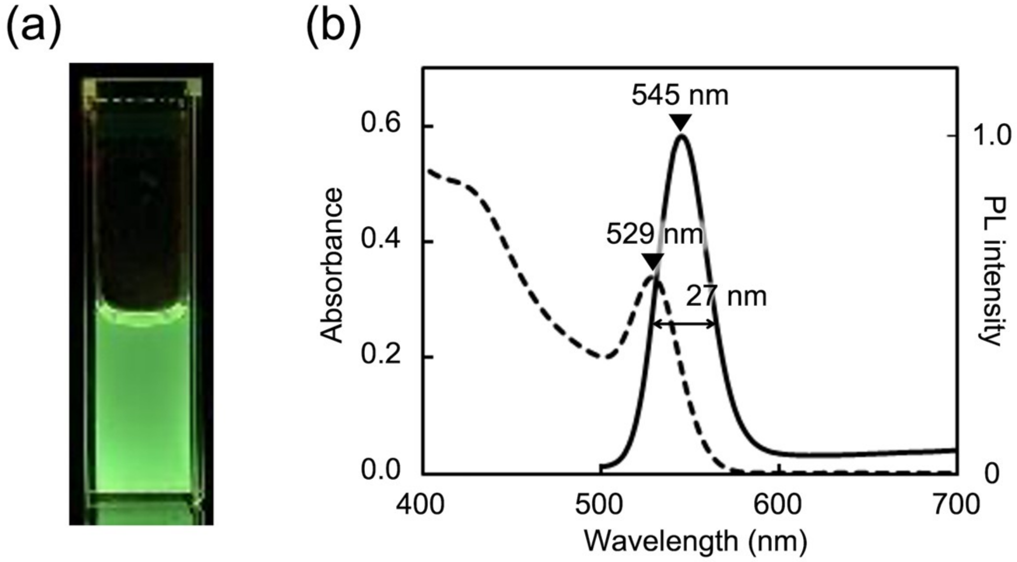


Figure S1 (a) Photograph of **QD-1**/toluene solution under UV light irradiation at 365 nm. (b) UV-vis (dotted lines) and PL (solid lines) spectra of **QD-1** suspended in toluene. Excitation wavelength was 450 nm. The PL peak is adjusted to be 1.

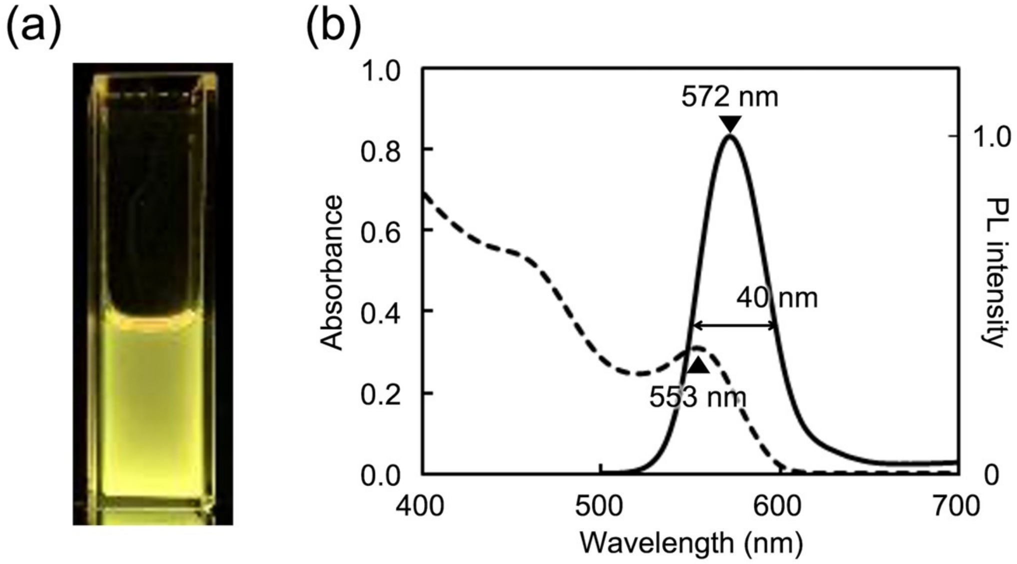


Figure S2 (a) Photograph of **QD-2**/toluene solution under UV light irradiation at 365 nm. (b) UV-vis (dotted lines) and PL (solid lines) spectra of **QD-2** suspended in toluene. Excitation wavelength was 450 nm. The PL peak is adjusted to be 1.

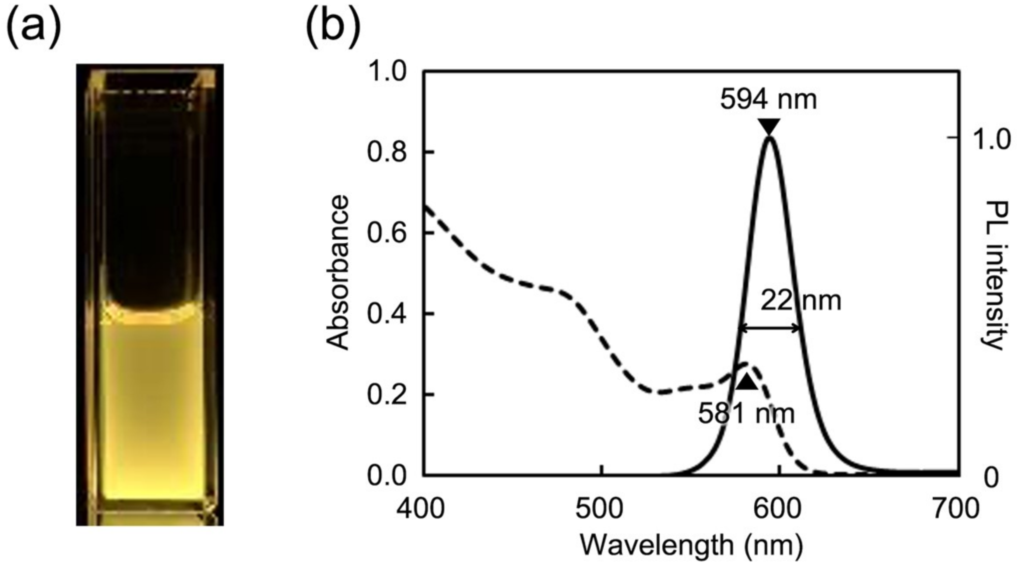


Figure S3 (a) Photograph of **QD-3**/toluene solution under UV light irradiation at 365 nm. (b) UV-vis (dotted lines) and PL (solid lines) spectra of **QD-3** suspended in toluene. Excitation wavelength was 450 nm. The PL peak is adjusted to be 1.

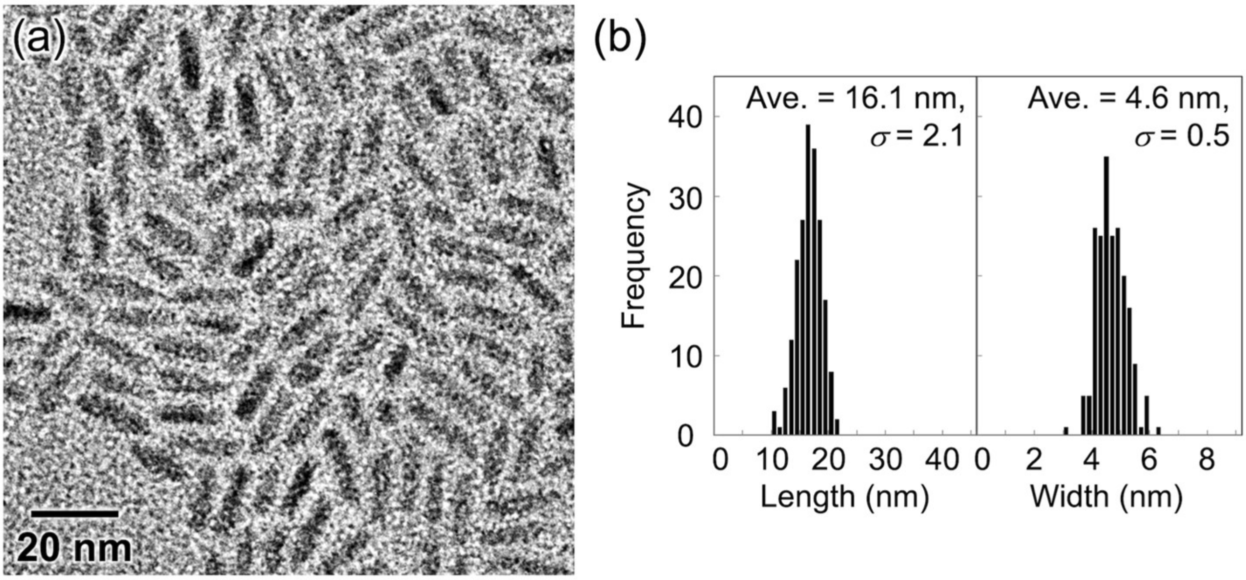


Figure S4 (a) TEM image of yellow-QRs. (b) Length (left) and width (right) distribution of yellow-QRs.

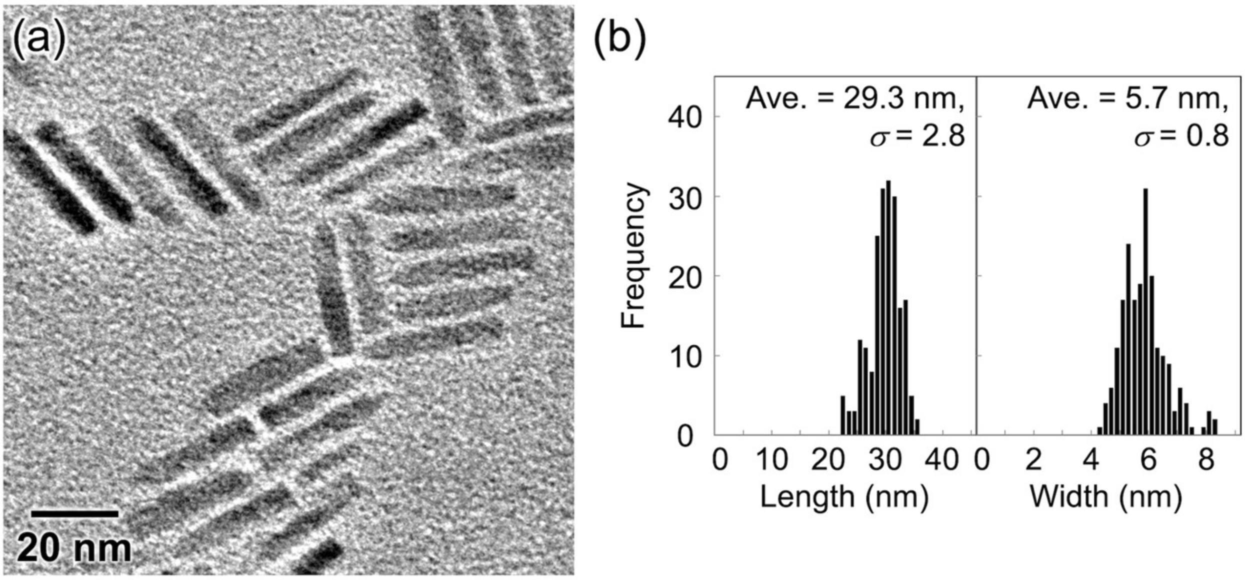


Figure S5 (a) TEM image of red-QRs. (b) Length (left) and width (right) distribution of red-QRs.

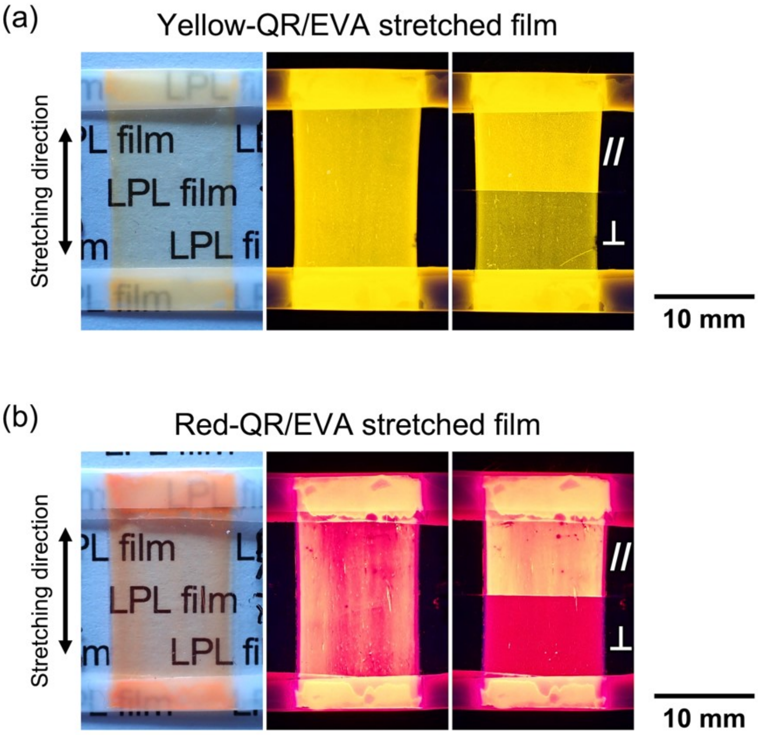


Figure S6 Photographs of 1D stretched (a) yellow-, and (b) red- QR/EVA composite films taken under room light (left) and UV light at 365 nm (middle and right). In the case of right photos, luminescence were observed through a linear polarizer placed in parallel (//) and perpendicular (⊥) directions to the stretching direction.

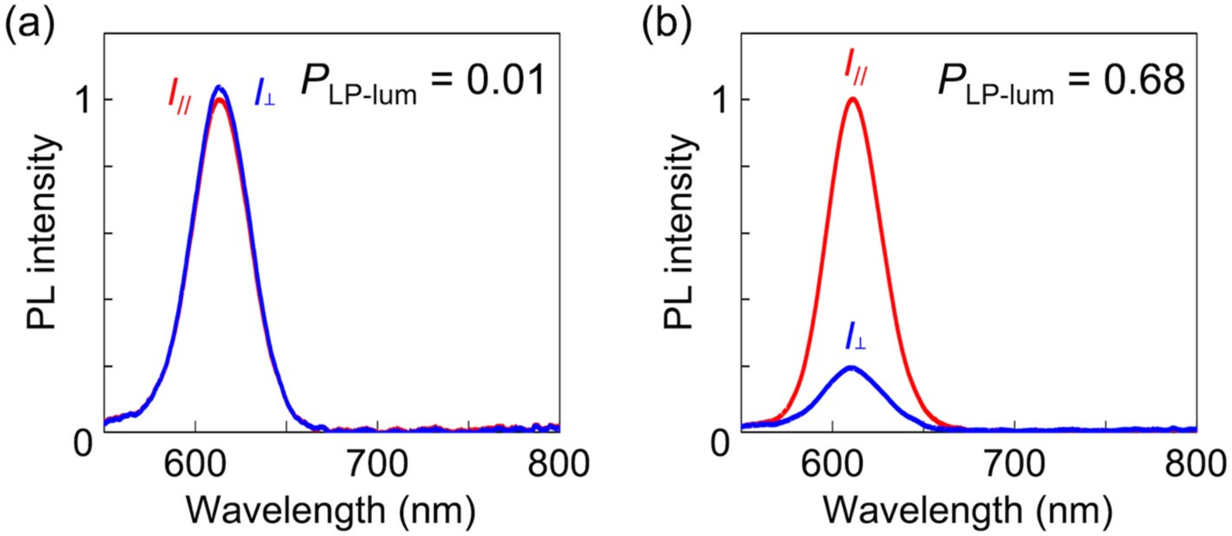


Figure S7 PL spectra of orange-QR/EVA composite films (a) before and (b) after 1D stretching. Red and blue lines indicate parallel (//) and perpendicular (⊥) LPL components against 1D stretching direction, respectively. Excitation wavelength, 450 nm.

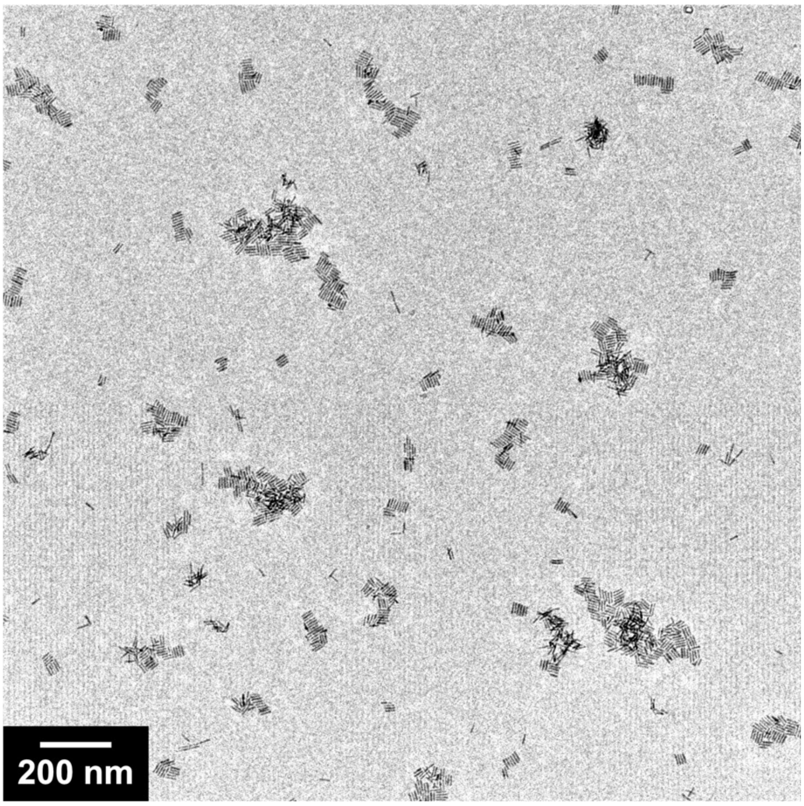


Figure S8 TEM images of orange-QR/EVA composite films without 1D stretching.

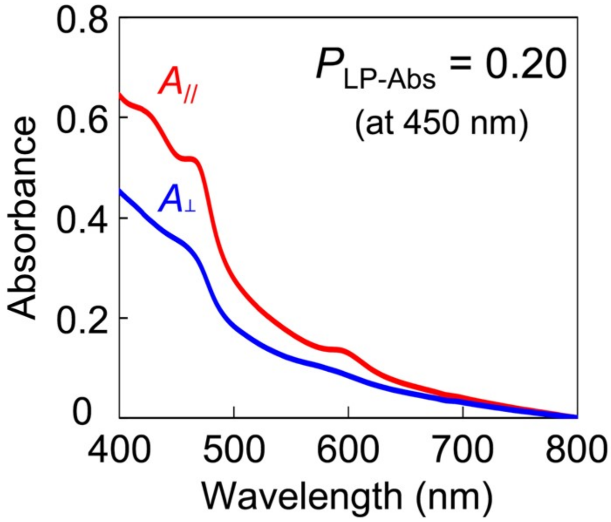


Figure S9 Absorption spectra of orange-QR/EVA stretched film under parallel (red line) and perpendicular incident LP light (blue line).

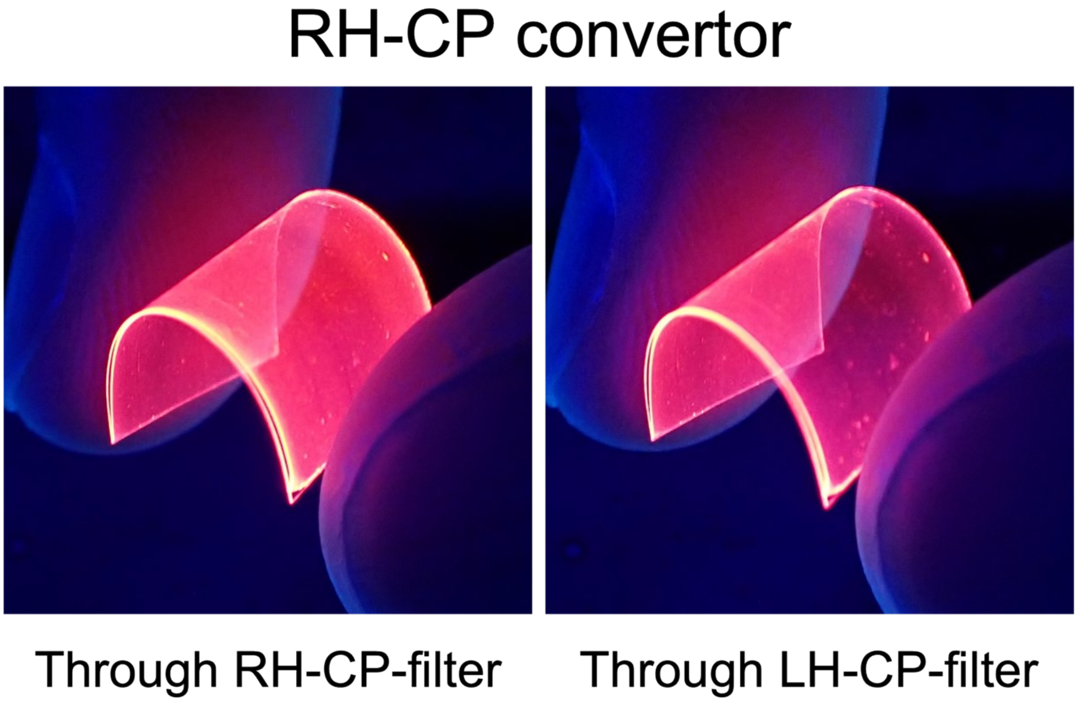


Figure S10 Photograph of flexible-type luminescence-based CP convertor.

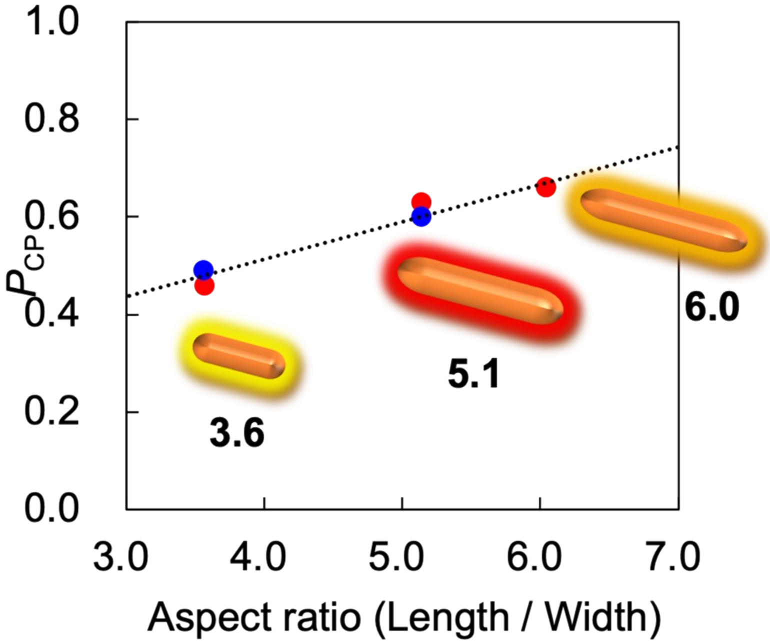


Figure S11 Correlation between the aspect ratio of QRs and the PCP value. Aspect ratios of yellow-, orange-, red- QRs are 3.6, 6.1, and 5.1, respectively.

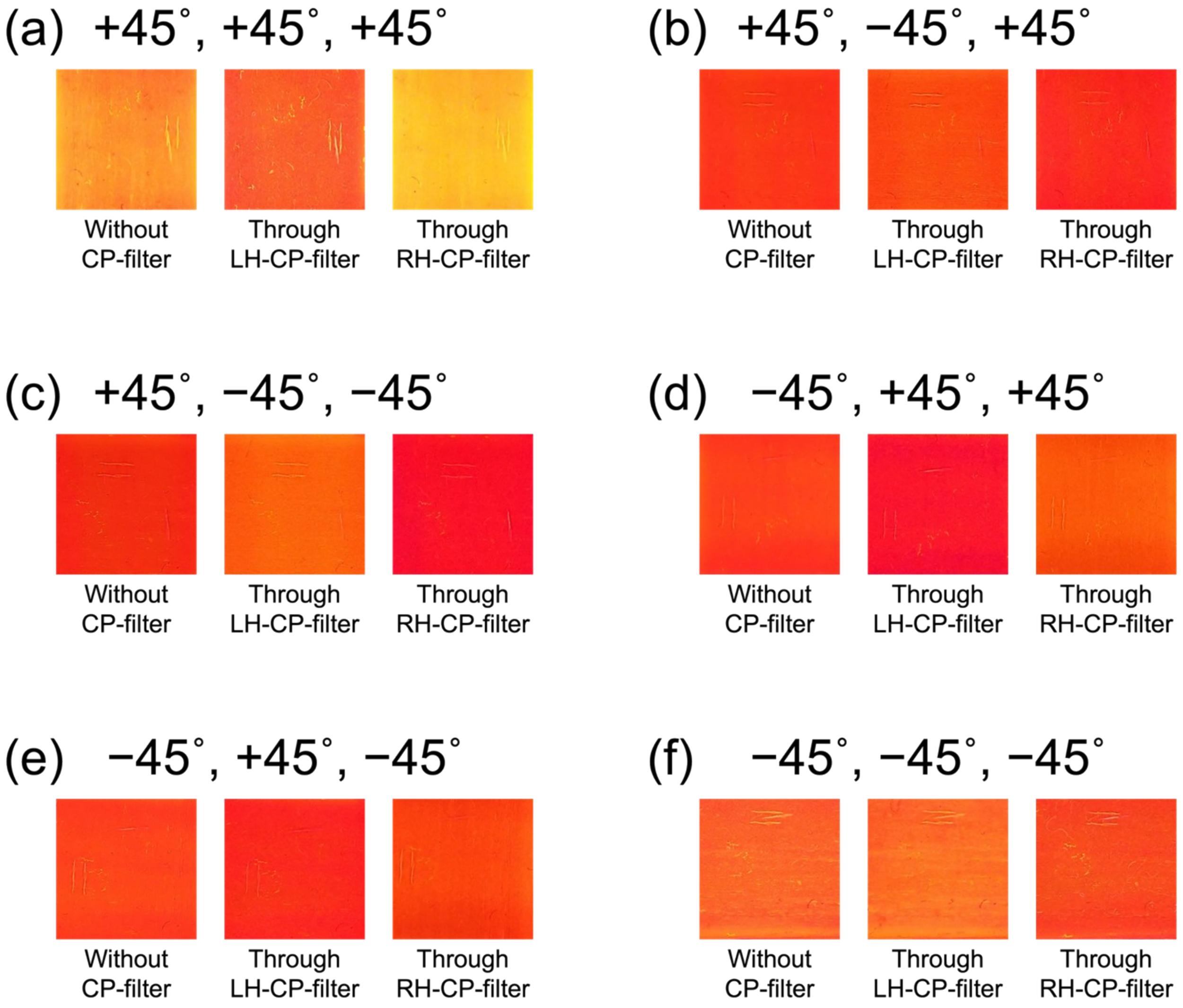


Figure S12 Photograph of three-layered luminescence-based CP convertor under UV light at 365 nm observed without CP-filter (left) and through LH- (middle) and RH- CP-filter (right). The three values above photos indicate each angles between the polarization plane of the red- (value on the left), orange- (value in the middle), and yellow-colored (value on the right) LPL films and fast axis of the quarter-wave plate, respectively.

3. References

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