Supporting Information

Effect of Crystallinity in Stretched PVA Films on Triplet-
Triplet Annihilation Photon Upconversion

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Fabrication of stretched UC-PVA films

A chromophore-blended PVA solution was prepared by adding 1.4 mL of an aqueous solution of chromophore [containing 23.9 mM of WS-DPA and 33.9 µM of WS-TPP] to 7 g of 10 wt% PVA (7 g, DP 2000, 98.5–99.5 mol% hydrolyzed, Kishida chemical, Co., Ltd., Japan) aqueous solution. The molar ratio of WS-TPP to WS-DPA was 1:706. A centrifugal mixer was used to achieve homogeneous blending and remove air bubbles. The samples were prepared using the wet-stretching process as shown in Figure S1. The PVA solution with chromophores was cast onto a carefully washed glass substrate. Next, the UC-PVA film on a glass substrate was heated in an oven for 15 min at 90 °C. The as-cast film (i.e., without immersion or stretching), referred to as “100%” film, was cut to the appropriate dimensions and mounted on a device for stretching. Then, the stretching device was immersed in a bath filled with a 3 wt% boric acid aqueous solution at 25 °C. Next, the film was stretched to obtain the stretching ratios ranging from 200% (two times) to 500% (five times). After stretching, the device with the film was dried in an oven at 60 °C for 5 min to obtain transparent, flexible, and thin UC-PVA films. All of the processes were performed under atmospheric air conditions.

Figure S1. Sample preparation: (a) cast PVA containing chromophores, (b) coat and dry in an oven, (c) cut films and set with a stretching device, (d) immerse and stretch in a boric acid aqueous solution, (e) dry in an oven.
Measurement of transmission spectra for different stretching ratios

Transmission spectra were measured using UV-VIS-NIR Spectrophotometer (UV-3600, Shimadzu, Corp., Japan). The scanning speed was medium and the sampling pitch was 1 nm.

![Transmission spectra for different stretching ratios](image)

**Figure S2.** Transmission spectra for different stretching ratios.

Measurement of fluorescence spectra of the UC-PVA films and the PVA film containing only the emitter

Upon excitation of 350 nm, the fluorescence spectra of the UC-PVA and PVA films containing only the emitter (WS-DPA PVA film) were obtained using an absolute photoluminescence quantum yield measurement system (C9920, Hamamatsu Photonics, Corp., Japan). Upon excitation with 350 nm light, the wavelength that corresponds to the absorption of WS-DPA, the main emission peak of UC-PVA films appeared at around 450 nm and a small peak was also observed at around 710 nm, which were assigned to the fluorescence of WS-DPA and phosphorescence of WS-TPP, respectively. The observed peak at longer wavelength could be generated by energy transfer from the emitter to the sensitizer since the fluorescence spectrum of WS-DPA was overlapped with Q-band of WS-TPP. Therefore, this back-energy transfer decreased emitter fluorescence quantum yield of UC-PVA compared with that of WS-DPA PVA film at the same emitter concentration.
Measurement of absorption spectra for different stretching ratios of UC-PVA film

Absorption spectra were measured using a UV-VIS-NIR spectrophotometer (UV-3600, Shimadzu, Corp., Japan). The scanning speed was medium and the sampling pitch was 1 nm. Moreover, the obtained absorption spectra were deformed primarily due to scattering throughout the films. The baseline drift was corrected by subtracting the offset for the WS-DPA PVA film without WS-TPP. The WS-TPP-COOH (before adding TBAOH) was used to prepare THF solution.

Figure S3. (a) Fluorescence spectra of UC-PVA film for different stretching ratios. (b) Fluorescence spectra of WS-DPA PVA film for different stretching ratios.
Measurement of fluorescence and phosphorescence quantum yield

Fluorescence quantum yield upon excitation of 350 nm and phosphorescence quantum yield upon excitation of 532 nm were obtained using an absolute photoluminescence quantum yield measurement system (C9920, Hamamatsu Photonics, Corp., Japan). The integral range of the emitting area was 400–850 nm for fluorescence and 650–850 nm for phosphorescence, respectively.

Measurement of the emission and absorption spectra of UC and determination of UC quantum yield ($\Phi_{UC}$)

The emission and absorption spectra of the UC-PVA films were measured using a bright-field confocal microscope (BX50, Olympus, Corp., Japan) with an objective lens (20×, N.A. = 0.50), and were detected using a spectrometer (USB2000-FLG, Ocean Optics, Inc., USA) with a multimode optical fiber (core diameter 400 µm, NA 0.48). To measure the UC emission spectrum, a continuous wave (CW) laser from a solid-state green laser module (MatchBox, Integrated Optics, UAB, Lithuania) centered at 532 nm (spectral width 8 nm FWHM) was used to irradiate the films. The polarization direction of the laser output was parallel to the stretched direction of the UC-PVA films. A neutral density (ND) filter was used to regulate the intensity. The excitation power at the sample surface was measured using a calibrated microscope photodiode power sensor (S170C, Thorlabs Inc., USA) connected to an optical power meter (PM200, Thorlabs Inc.,

Figure S4. Normalized absorption spectra for different stretching ratios.
USA). For measurements of the absorption spectrum, an unpolarized halogen lamp was used as the light source. Artifacts caused by the possible overtones of the laser were determined to be negligible by placing a shortcut filter (Y44, HOYA, Corp., Japan) in the excitation path.

The measurement of $\Phi_{\text{UC}}$ was performed in the same manner as the UC emission and absorption measurements under the microscope. The $\Phi_{\text{UC}}$ was determined relative to the fluorescence quantum yield ($\Phi_R$) of 100 µM rhodamine 101 (Rh101, Exciton Inc., USA) in ethylene glycol (EG, Sigma-Aldrich spectrometric grade, USA) solution according to the following equation,

$$\Phi_{\text{UC}} = 2\Phi_R \frac{I_R A_R E_{\text{UC}} \eta^2_{\text{UC}}}{I_{\text{UC}} A_{\text{UC}} E_R \eta^2_R},$$

where $\Phi$, $I$, $A$, $E$, and $\eta$ represent the quantum yield, excitation power, absorbance at 532 nm, the integrated intensity of the corrected emission spectrum and refractive index of the medium, respectively. A multiplication factor of 2 was used to achieve the maximum $\Phi_{\text{UC}}$ of 100%. The suffixes UC and R refer to the UC-PVA film and a reference (Rh101/EG), respectively. The $\Phi_R$ of Rh101/EG was taken to be 94% as described in Ref. 1. The refractive index values of the UC-PVA film and Rh101/EG were 1.49 and 1.43, respectively. The obtained absorbance of the stretched UC-PVA films at the excitation wavelength was quite small due to the low thickness of the films (20 – 30 µm). Therefore, we measured the UC emission and absorption spectra of stretched UC-PVA films using one layer for the 100% non-stretched film, two layers for the 200%-stretched film, and three layers for 400%-stretched film. Figure S5 shows the UC emission intensity dependence of the absorbance for different layers. Moreover, the obtained absorption spectra were deformed primarily due to scattering throughout the films. The baseline drift was corrected by subtracting the offset for the WS-DPA PVA film without WS-TPP (Figure S6).
Finally, we measured the dependence of UC emission on the excitation intensity ($I_{ex}$). Moreover, curve fitting for the UC emission intensity was performed using the following equation,

$$I_{UC} = K \frac{1 + (1 - \sqrt{1 + 4 \frac{I_{ex}}{I_{th}}})}{(2 \frac{I_{ex}}{I_{th}})} I_{ex},$$

(2)

where $K$, $I_{ex}$, and $I_{th}$ are the proportionality parameter, excitation intensity, and threshold intensity, respectively.

**Figure S5.** UC emission intensity dependence of the absorbance for different layers. Inset values: $\Phi_{UC}$ of the 400% UC-PVA film for different layers (the WSTPP to WS-DPA molar ratio was 1:70).

**Figure S6.** Absorbance spectra of the 400% UC-PVA film and the 400% WS-DPA PVA film.
Measurement of optical microscope images of ultraviolet-excited UC-PVA films

The optical microscopy images of the ultraviolet-excited UC-PVA films were measured using a bright-field confocal inverted microscope (IX83, Olympus, Corp., Japan) with an objective lens (40×, N.A. = 0.70), followed by excitation by 365 nm ultraviolet light (SLUV-4, AS ONE, Corp., Japan). The fluorescence images of films were recorded using a CCD (INFINITY 1, Lumenera, Corp., USA). The exposure times were 350 and 900 ms for the 100% film and 400% film, respectively.

Measurement of crystallinity index and molecular orientation

The crystallinity index $C$ of PVA was determined by attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy measurements (FT/IR-4700, ATR PRO610P-S, ZnSe prism, JASCO, Corp., Japan) using the following equation:

$$ C = \frac{Abs_{1140 \text{ cm}^{-1}}}{Abs_{1420 \text{ cm}^{-1}}} $$

where $Abs_{1140 \text{ cm}^{-1}}$ and $Abs_{1420 \text{ cm}^{-1}}$ are the absorbances associated with the crystalline sensitive peak and reference peak, respectively. Figure S7 shows the FTIR spectra of the 100% UC-PVA film.

![FTIR spectra](image)

**Figure S7.** FTIR spectra of the 100% UC-PVA films obtained using unpolarized incident light.
The orientation function value $f$ of the PVA films that contained chromophores was determined based on polarized ATR-FTIR using the following equations:\(^3\)

$$D = \frac{\text{Abs}_{\parallel} 1325 \text{ cm}^{-1}}{\text{Abs}_{\perp} 1325 \text{ cm}^{-1}}$$  \hspace{1cm} (4)

$$f = \frac{2(1 - D)}{(D + 2)}$$  \hspace{1cm} (5)

where $D$ is the dichroic ratio and $\text{Abs}_{\parallel}$ and $\text{Abs}_{\perp}$ are the parallel and perpendicular absorbances of the incident light for the polarization direction and the stretched direction, respectively. The peak at 1325 cm\(^{-1}\) corresponds to the coupling of the OH bending vibration ($\delta$(OH)) and other vibrations of PVA as shown in Figure S8.\(^4\)

**Figure S8.** FTIR spectra of the UC-PVA films using polarized incident light. (a) 100% UC-PVA film and (b) 400% UC-PVA film, black line: perpendicular, red line: parallel.

**X-ray diffraction measurements**

The wide-angle X-ray diffraction (XRD) patterns of UC-PVA films were obtained using the standard concentration beam method (SmartLab, Rigaku, Corp., Japan). The scanning speed and sampling intervals were 5°/min and 0.01°, respectively. The XRD pattern of the UC-PVA films was measured in a wide angle range (Figure S9). The result showed a typical diffraction peak of PVA at $2\theta = 19.6^\circ$ that gradually broadened with the increase in the stretching ratio while a sharp peak was observed for the non-stretched 100% film. This broad peak was also attributed to the reduced crystallinity of the PVA film.
Comparison between immersed and non-immersed 100% UC-PVA film

The non-stretched film was immersed for 10 seconds in a 3 wt% boric acid aqueous solution at 25 °C, and then the film was dried in an oven at 60 °C for 5 min. The upconversion emissions of the films were measured using a home-built measurement system with a 532-nm green laser. Film emissions were collected using a spectrometer (QE65000, Ocean Optics, Inc., USA) through an optical fiber (P200-2-UV-VIS, 200 μm diameter, Ocean Optics, Inc., USA) with a collimating lens (74-UV, 5 mm diameter and 10 mm focal length, Ocean Optics, Inc., USA) and a notch filter (86-120, center wavelength 532 nm and FWHM 17 nm, OD > 6.0, Edmund Optics, Inc., USA). A 532 nm CW laser (3010143, Laser Create, Corp., Japan) adjusted by a Keithley 2400 source meter was used as the light source. Laser power was measured by a power meter (LP1, Sanwa, Corp., Japan) calibrated with a Si photodiode. The $\Phi_{UC}$ of non-stretched immersed film was estimated using emission intensity spectra and compared with $\Phi_{UC}$ of the as-cast film.

Figure S9. X-ray diffraction patterns of the UC-PVA films.
**Figure S10.** Photographs of (a) the non-stretched immersed film and (b) as-cast film (i.e., non-immersed and non-stretched film). (c) Emission intensity spectra of the films irradiated with a 532 nm green laser at the illumination intensity of 259 mW/cm².

**1H and 13C NMR data**

1H NMR and 13C NMR were recorded on a Bruker AVANCE III HD 400 MHz using tetramethylsilane (TMS) as an internal standard in deuterated DMSO.

WS-DPA-COOH

1H NMR (DMSO, 400 MHz) δ(ppm) 12.10 (br, 2H), 7.63 (m, 4H), 7.41 (m, 4H), 7.34 (d, 4H, J = 8.6 Hz), 7.21 (d, 4H, J = 8.6 Hz), 4.13 (t, 4H, J = 6.2 Hz), 2.36 (t, 4H, J = 7.3 Hz) 1.84-1.74 (m, 16H). 13C NMR (DMSO, 100 MHz) δ(ppm) 173.8, 157.6, 135.7, 131.5, 129.3, 129.0, 125.9, 124.7, 114.0, 66.7, 32.8, 27.6, 20.7.
Figure S11. $^1$H NMR spectrum of WS-DPA-COOH

Figure S12. $^{13}$C NMR spectrum of WS-DPA-COOH
WS-TPP-COOH

$^1$H NMR (DMSO, 400 MHz) $\delta$(ppm) 12.12 (br, 4H), 8.82 (s, 8H), 8.03 (d, 18H, $J = 8.5$ Hz), 7.34 (d, 18H, $J = 8.5$ Hz), 4.25 (t, 8H, $J = 6.0$ Hz), 2.42 (t, 8H, $J = 7.3$ Hz), 1.94-1.80 (m, 16H). $^{13}$C NMR (DMSO, 100 MHz) $\delta$(ppm) 174.9, 159.1, 141.6, 135.4, 133.4, 131.6, 121.9, 113.5, 67.9, 33.9, 28.8, 21.9.

Figure S13. $^1$H NMR spectrum of WS-TPP-COOH
References


