Electronic Supplementary Information (ESI) for

Porous film impregnation method for record-efficiency visible-to-UV photon upconversion and subsolar light harvesting

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Materials

All reagents and solvents were used as received without further purifications otherwise noted. The synthesis and characterizations of TIPS-Nph are described in the literature.[1, 2] $Ir(C6)_2(acac)$ was purchased from NARD Institute, Ltd. and recrystallized by ethanol and chloroform. For TTA-UC measurements, all samples were prepared in an argon-filled glovebox ($[O_2] < 0.1$ppm). Hexyl benzoate was purchased from TCI and deaerated by vacuuming with an oil-sealed rotary pump (TSW-150, SATO VAC INC.). As a porous film, Microporous Film (CMZ-05076, catalog thickness 38 μm) was purchased from 3M and used as received. A microlens array was provided by Ushio Inc. A focus diameter of the microlens array (ca. 3.0 μm) was obtained by geometric optical calculation using a single wavelength of 445 nm.

Experimental apparatuses

UV-vis absorption spectra were measured on a JASCO V-670 and a JASCO V-770. Photoluminescence (PL) spectra were obtained using a JASCO FP-8700. The absolute PL quantum yield was measured in an integrating sphere by a multichannel analyzer C10027-01 (Hamamatsu Photonics). Time-resolved PL lifetime measurements were performed using a TCSPC lifetime spectroscopy system, Quantaurus-Tau C11367-02 and C11567-01 (Hamamatsu Photonics). The viscosity of hexyl benzoate was obtained by VM-10A-L (SEKONIC CORPORATION) using an NCB2500 (EYELA) as a constant-temperature bath. The validity of viscosity was confirmed by comparing the experimental value of 1-hexanol (4.28 cP at 25 °C) with the reported values (4.436[3], 4.594[4], 4.403[5]). Scanning electron microscopy (SEM) images were recorded at the Ultramicroscopy center, Kyushu University. SEM was performed on a Zeiss Ultra55 instrument. Thermogravimetric analysis (TGA) was performed under a flow of N_2 gas (ca. 100 mL min^{-1}) using a Thermo plus EV02 TG8120 (Rigaku). A micrometer MCD130-25 (Niigata Seiki) was used to measure the thickness of porous films.

A diode laser of a wavelength at 445 nm (75 mW, RGB Photonics) was used as an excitation light source in TTA-UC measurements. For measuring excitation light intensity and the laser beam profile, a PD300-UV photodiode sensor (OPHIR Photonics) and a CCD beam profiler SP620 (OPHIR Photonics) were used. The diameter of the laser beam ($1/e^2$) was measured to be 3.9×10^{-4} cm^2 and 1.2×10^{-3} cm^2 with and without a focus lens, respectively, at the sample position. The laser power was controlled by rotating variable ND filters, and the emission was detected by an MCPD-9800 (Otsuka Electronics) with achromatic lenses in front of the detector in the TTA-UC measurements. In the measurement, the detector captures the TTA-UC emission

from the same face where the laser hits. PL spectra above 350 nm were calibrated by a standard lamp HL-3 plus-CAL (Ocean Optics).

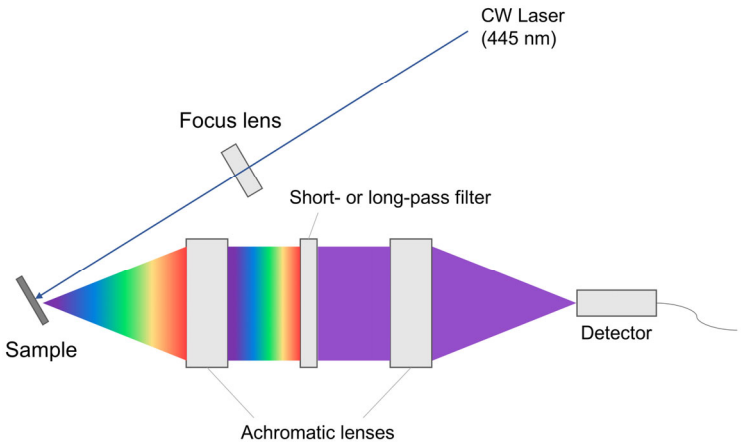

Figure S1 The illustration of the measurement setup of TTA-UC spectra.

Calculation of TTA-UC efficiency

TTA-UC efficiency (η_{UC}) in hexyl benzoate was calculated by a relative method using a standard, according to the following equation,[6, 7]

$$\eta_{UC} = 2\Phi_{Std}\left(\frac{1-10^{-A_{Std}}}{1-10^{-A_{UC}}}\right)\left(\frac{E_{UC}}{E_{Std}}\right)\left(\frac{I_{Std}}{I_{UC}}\right)\left(\frac{n_{UC}}{n_{Std}}\right)^2$$

where Φ, A, E, I, and n are quantum yield, absorbance at 445 nm, integrated PL spectral profile, excitation light intensity, and refractive index of the solvent, respectively. The subscripts UC and Std denote the system of upconversion and standard. In the measurements of the TTA-UC material in the form of the film, donor phosphorescence (Phos) was used as an internal standard, and the efficiency was calculated by the following equation.

$$\eta_{UC} = 2\Phi_{Phos}\left(\frac{E_{UC}}{E_{Phos}}\right)\left(\frac{I_{Phos}}{I_{UC}}\right)$$

The phosphorescence quantum yield of the donor was 8.6% at the spectral region from 500 nm to 800 nm excited by 445 nm.

Sample preparation for TTA-UC

A hexyl benzoate solution of TIPS-Nph and $Ir(C6)_2(acac)$ ([TIPS-Nph] = 10 mM, $[Ir(C6)_2(acac)]$ = 100 μM) was prepared in an argon-filled glovebox. A porous film was impregnated with the solution in the glovebox. The excess solution was removed from the surface of the film. The porous film was sandwiched between two quartz substrates, sealed with epoxy resin glue, and left overnight inside the glovebox. In a measurement using a microlens

array, the porous film was sandwiched between a quartz substrate on one side and the microlens array on the other, sealed with glue, and left overnight inside the glovebox.

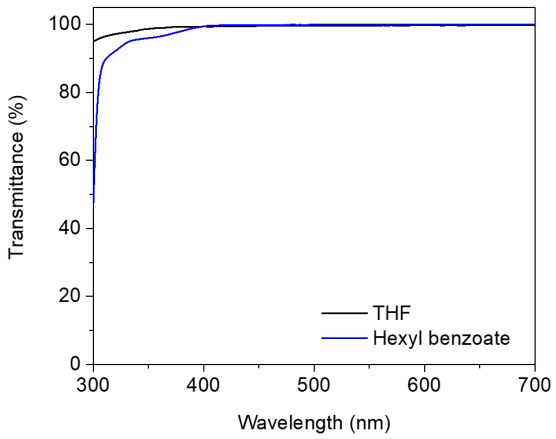

Figure S2 Transmittance of THF and hexyl benzoate in a quartz cell with a 5 mm effective optical path length.

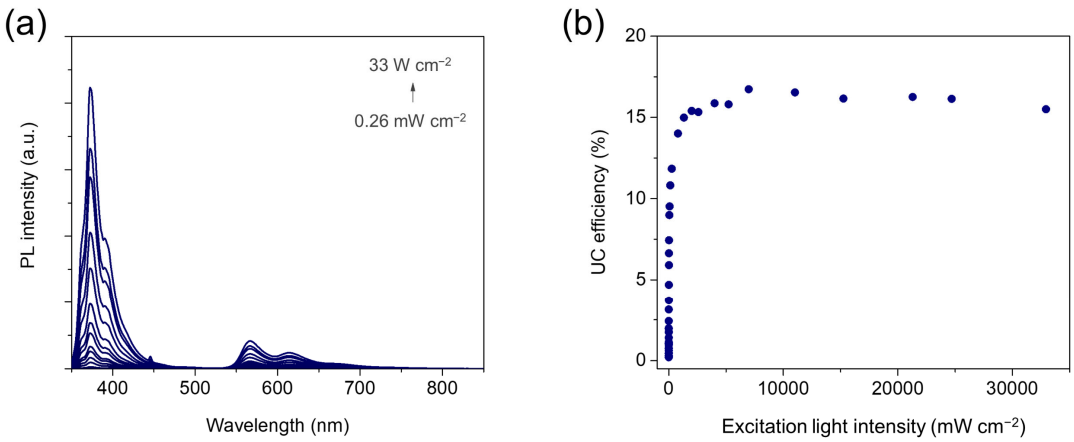

Figure S3 (a) Photoluminescence (PL) spectra and (b) TTA-UC efficiencies of a deaerated hexyl benzoate solution of TIPS-Nph (10 mM) and $Ir(C6)_2(acac)$ (100 μM) at various intensities of the laser of a wavelength at 445 nm.

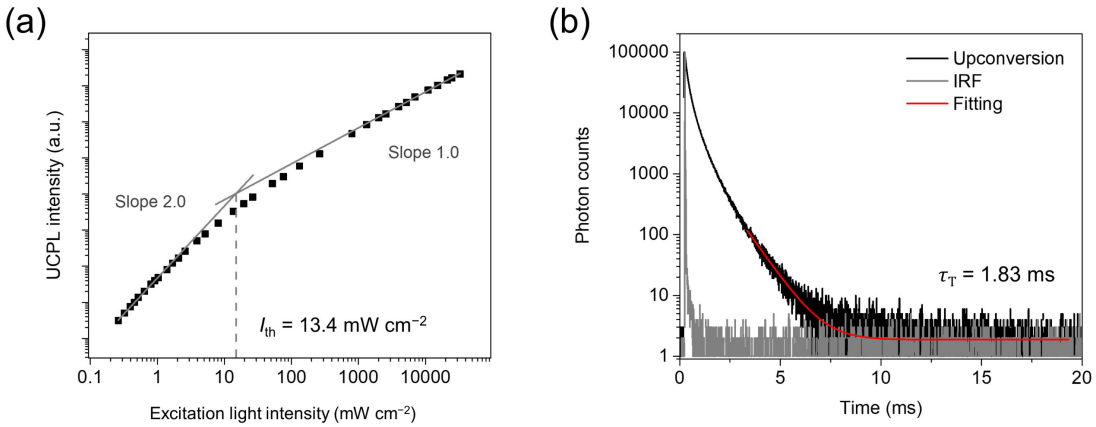

Figure S4 (a) Upconversion PL intensities of TIPS-Nph (10 mM) and $Ir(C6)_2(acac)$ (100 μM)in deaerated hexyl benzoate with different excitation intensities under a laser (λ_{ex} = 445 nm). (b) Upconversion emission decay (black line) of the hexyl benzoate solution at 380 nm under pulsed excitation light with a band-pass filter of 445 nm. The gray line shows an instrumental response function (IRF). The red line is a fitting curve for the tail part of the decay using the following relationship,[8]

$$I(t) \propto \exp(-\frac{t}{\tau_{UC}}) = \exp(-\frac{2t}{\tau_T})$$

where τ_{UC} and τ_T are the upconversion emission lifetime and the triplet lifetime of the acceptor, respectively.

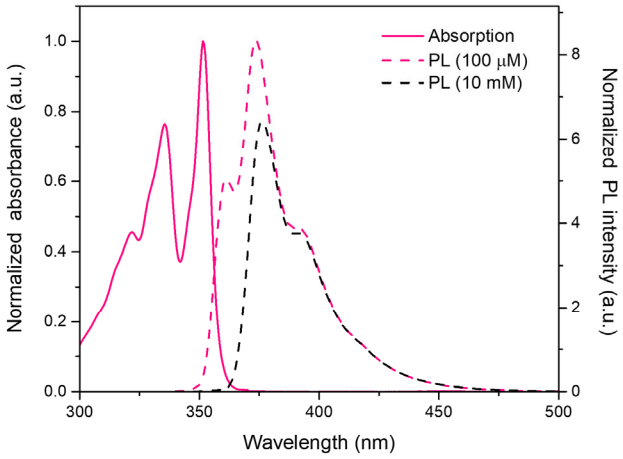

Figure S5 Normalized absorption (solid pink line) and PL (dashed pink line, λ_{ex} = 320 nm) spectra of TIPS-Nph in deaerated hexyl benzoate with the concentration of 100 μM, and normalized PL spectrum of TIPS-Nph with the concentration of 10 mM (dashed black line, λ_{ex} = 320 nm). PL spectra were normalized at 420 nm. The fluorescence quantum yield of TIPS-Nph (100 μM) was 76.3% (λ_{ex} = 320 nm).

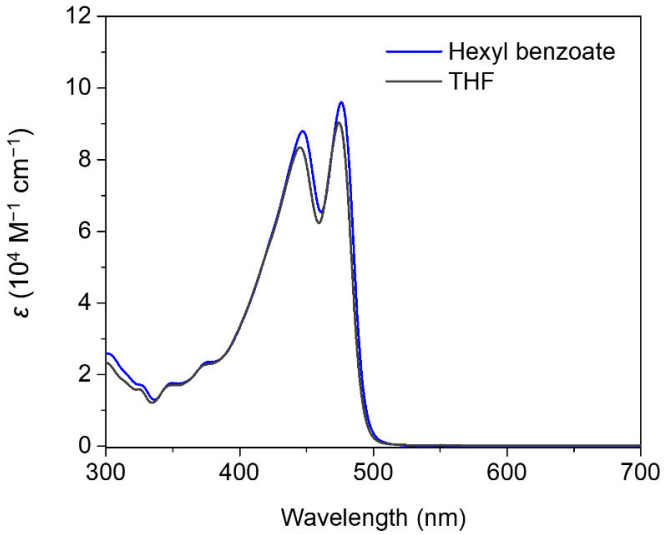

Figure S6 Absorption spectra of $Ir(C6)_2(acac)$ in hexyl benzoate and THF (100 μM).

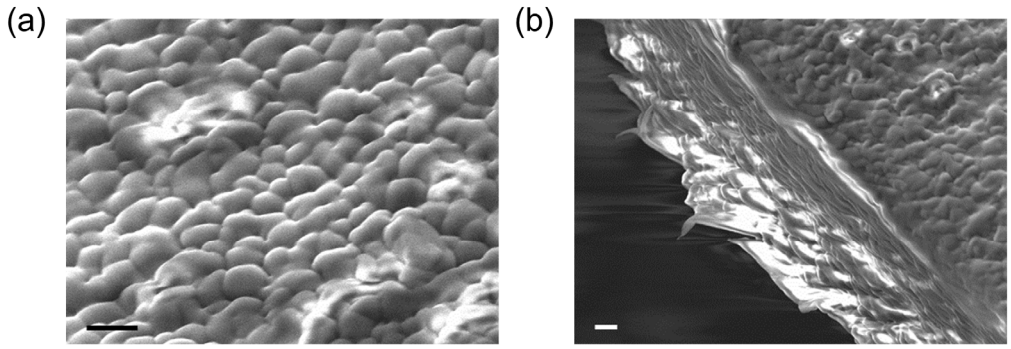

Figure S7 SEM images of (a) the surface and (b) the cross-section of a porous film. Scale bars indicate 2 μm.

Table S1 Mean and standard deviation (SD) values of porous films. The minimum scale value is 0.001 mm (1 μm).

	Mean (μm)	SD (μm)
Pristine film	40.2	2.04
Immersed film	40.8	1.86

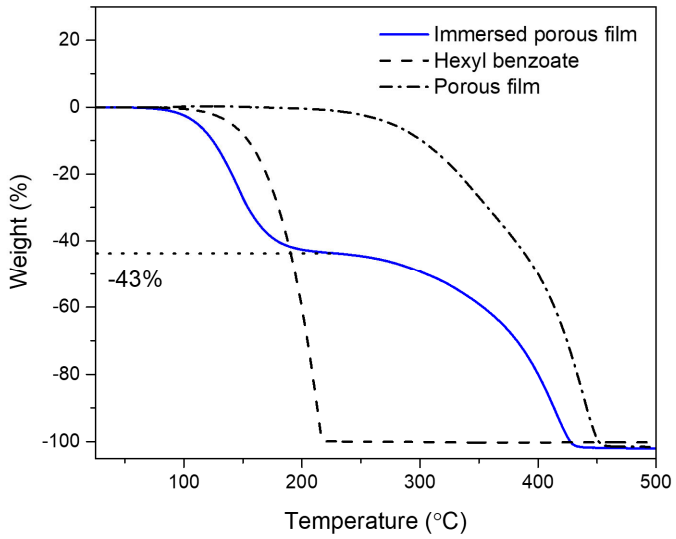

Figure S8 TGA curves of an immersed porous film in hexyl benzoate (blue, solid), hexyl benzoate (black, dashed), and pristine porous film (black, dash-dotted).

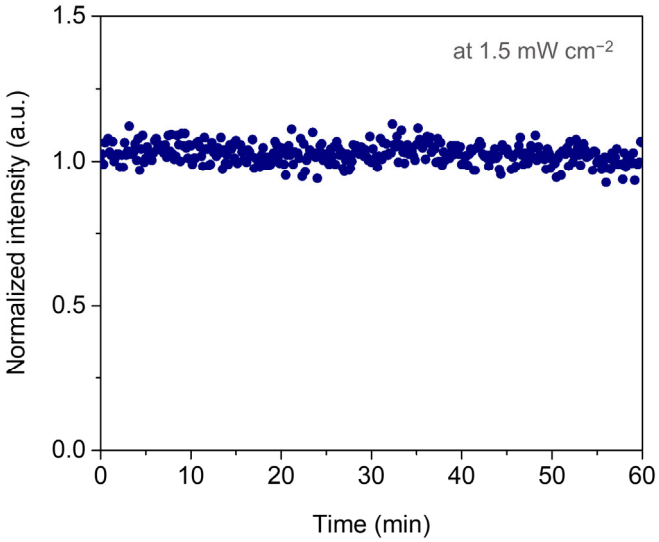

Figure S9 UCPL intensities (λ_{det} = 372 nm) normalized at 0 min of a film sealed with quartz substrates at 1.5 mW cm^{-2} of a laser for one hour.

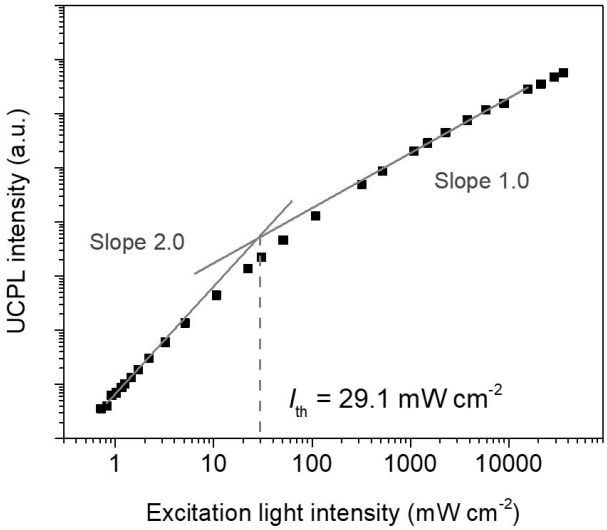

Figure S10 UCPL intensities of a film stored in the dark for 9 days at different excitation intensities under a laser of a wavelength at 445 nm.

References

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