

Electronic Supplementary Information (ESI) for

**Heavy metal-free visible-to-UV photon upconversion with over
20% efficiency sensitized by a ketocoumarin derivative**

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Materials

All reagents and solvents were used as received and no further purification was performed unless otherwise noted. CBDAC was purchased from TCI and purified by recrystallization with ethanol. The synthesis and characterizations of TIPS-Nph and Ir(C6)₂(acac) are described in our previous reports.^[1,2] For TTA-UC measurements, the solutions were prepared in an Ar-filled glove box ([O₂] < 0.1 ppm) using deoxidized toluene purchased from Wako.

General characterization

UV-vis absorption spectra were recorded on a JASCO V-670/V-770 spectrophotometer. Photoluminescence spectra were measured by using JASCO FP-8300 and FP-8700 spectrofluorometers. The absolute fluorescence quantum yield was measured in an integrating sphere using a HAMAMATSU multichannel analyzer C10027-01. Time-resolved photoluminescence lifetime measurements were carried out by using a time-correlated single-photon counting lifetime spectroscopy system, HAMAMATSU Quantaaurus-Tau C11367-21, C11567-02 and M12977-01.

Nano-second transient absorption spectra were measured by the pump-probe method. We employed a white-light continuum generated from an ultrafast laser as a probe pulse. An output pulse from a Ti:sapphire regenerative amplifier (Spectra-Physics, Spitfire Ace, pulse duration: 120 fs, repetition rate: 1 kHz, pulse energy: 4 mJ/pulse, central wavelength: 800 nm) seeded by an output pulse from Ti:sapphire femtosecond mode-locked oscillator (Spectra-Physics, Tsunami) was led to the optical parametric amplifier (OPA) (Spectra-Physics, TOPAS-prime), and a signal light with a wavelength of 1200 nm was generated. The signal light was focused on a sapphire crystal (3 mm thickness) and generated a white-light continuum utilized to the probe pulse. We employed third-harmonic generation (THG: 355 nm) lights of a Nd:YAG laser (EKSPLA NT242, central wavelength: 1064 nm, pulse duration: 6 ns) or output pulses from an optical parametric oscillator (central wavelength: 450 and 480 nm, pulse duration: 3 ns) using the THG of the Nd:YAG laser as the excitation pulse. The delay time was electrically controlled by a delay generator (Stanford Research Systems DG645), synchronized to the regenerative Ti:sapphire amplifier. The polarization of the light for the pump and probe pulses were set to the magic angle (54.7°). The pump and probe pulses were focused on the sample solution in a quartz cell (1 mm path length). The fluence of the pump pulse at the sample position was 1.9 mJ cm⁻² ($\lambda_{\text{ex}} = 355$ nm), 0.05 mJ cm⁻² ($\lambda_{\text{ex}} = 450$ nm) or 0.19 mJ cm⁻² ($\lambda_{\text{ex}} = 480$ nm). The probe pulse passed through the sample solution was dispersed by a polychromator (JASCO, CT-10, 300 grooves / 500 nm), and the spectra were recorded by a multichannel detection system with CMOS sensors (UNISOKU, USP-PSMM-NP).

DFT calculations

Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were conducted with the B3LYP exchange-correlation functional as implemented in the Gaussian 16W.^[3] The optimized ground-state structure of CBDAC was obtained with 6-311+G(d,p) basis set. Then, TD-DFT was employed with 6-311+G (d,p) basis set to obtain the singlet and triplet excited-state properties. All calculations were associated with the PCM model and toluene was chosen as a solvent.

Determination of TTA-UC efficiency η_{UC} by the relative method

For TTA-UC emission spectra, a 445 nm diode laser (75 mW, RGB Photonics) was used as the excitation source. The laser power was controlled by combining a software (Ltune) and a variable neutral density filter and measured using a PD300-UV photodiode sensor (OPHIR Photonics). The laser beam was focused on a sample using a lens. The diameters of the laser beam ($1/e^2$) were measured at the sample position using a CCD beam profiler SP620 (OPHIR Photonics). A typical area of the laser beam spot estimated from the diameter was $2.1 \times 10^{-4} \text{ cm}^2$. The emitted light was focused by an achromatic lens to an optical fiber connected to a multichannel detector MCPD-9800 (Otsuka Electronics). 425 nm short-pass filter was used between the sample and the detector. TTA-UC emission spectra above 350 nm were calibrated by using a standard lamp Ocean Optics HL-3 plus-CAL.

The TTA-UC efficiency η_{UC} in deaerated toluene was determined relative to a standard, coumarin 6 in deaerated toluene (50 μM), according to the following equation,^[4,5]

$$\eta_{UC} = 2 \phi_{std} \left(\frac{1 - 10^{-A_{std}}}{1 - 10^{-A_{UC}}} \right) \left(\frac{I_{std}}{I_{UC}} \right) \left(\frac{F_{UC}}{F_{std}} \right) \left(\frac{n_{UC}}{n_{std}} \right)^2 \quad (S1)$$

where ϕ , A , I , F and n represent quantum yield, absorbance at 445 nm, excitation intensity, integrated photoluminescence spectral profile, and refractive index of the solvent, respectively. The subscripts UC and std denote the parameters of the upconversion and standard systems. Note that the theoretical maximum of η_{UC} is standardized to be 1 (100%).

Determination of TTA-UC efficiency η_{UC} by the absolute method

The absolute TTA-UC efficiency was measured by using the absolute quantum yield measurement system C13534-01 (Hamamatsu Photonics).^[5] The sample was introduced into an integrating sphere and excited with a 445 nm laser (75 mW, RGB Photonics). The scattered excitation light was removed using a 410 nm short-pass filter, and the emitted light was monitored by a multichannel detector. The spectrometer, including the integrating sphere and short-pass filter, was calibrated by Hamamatsu Photonics.

The observed TTA-UC efficiency ($\eta_{UC,obs}$) of CBDAC and TIPS-Nph in deaerated toluene ([CBDAC] = 100 μM , [TIPS-Nph] = 10 mM) was obtained by the procedure reported by de Mello et al.^[6,7] The effect of reabsorption upon $\eta_{UC,obs}$ was further corrected by our previously developed method to obtain the absolute η_{UC} value.^[5] The methods of measurement and the calculation of each parameter required to obtain the reabsorption probability α are described in our previous report.^[1] Note that we corrected the reabsorption due to multiple excitations within the integrating sphere, but we did not correct the inner-filter effect within the sample in both the relative and absolute methods.

The measurements were carried out in four different instrument/sample configurations. In Experiment (A), The upconverted sample is placed in the integrating sphere and the laser beam is irradiated directly onto the sample. Experiment (B) is the same as Experiment (A), except that the integrating sphere is mechanically removed without changing the other configurations. In experiment (C), the sample for upconversion is placed in the integrating

sphere, but its height is above the laser beam, so the laser is irradiated on the wall of the sphere. Experiment (D) is the same as experiment (A) except that a reference sample containing only the solvent toluene without dye is used. To minimize the effect of reabsorption, a small sample volume of $1 \times 4 \times 8$ mm was used.

The first-pass absorbance (*Abs*) was estimated by the following equation,

$$Abs = 1 - \frac{L_A}{L_C} \quad (S2)$$

Here, L is the number of laser photons emitted from the sphere, and the subscript indicates the type of experimental configuration. $\eta_{UC,obs}$ is estimated as follows,

$$\frac{\eta_{UC,obs}}{2} = \Phi_{UC,obs} = \frac{P_A - (1 - Abs) P_C}{L_D Abs} \quad (S3)$$

where P is the emitted photon. The deaerated toluene solution of CBDAC and TIPS-Nph showed a $\eta_{UC,obs}$ value of 6.1% at 9.1 W cm^{-2} . Note that in order to minimize the inner-filter effect, the laser beam is irradiated at the edge of the sample close to the detector.^[8] The TTA-UC emission spectra in the configurations of Experiment (A) and (B) ($P_A(\lambda)$ and $P_B(\lambda)$) were normalized by using the integrated fluorescence profile from 550 nm to 650 nm (Fig. S3a). Using these normalized spectra $P_A'(\lambda)$ and $P_B'(\lambda)$, the reabsorption probability a was determined by the following equation,

$$\frac{\int_0^{\infty} P_A'(\lambda) d\lambda}{\int_0^{\infty} P_B'(\lambda) d\lambda} = 1 - a \quad (S4)$$

The reabsorption probability a of 0.72 was obtained by taking the ratio of the integrated area of the two normalized TTA-UC emission spectra from 350 nm to 415 nm (Fig. S3b). We confirmed that the reabsorption probability a does not almost depend on the excitation intensity in the examined excitation intensity range. We can approximate that the reabsorbed photons are lost, and the absolute efficiency η_{UC} of TTA-UC can be obtained by the following equation,

$$\eta_{UC,obs} \approx \eta_{UC} (1 - a) \quad (S5)$$

Substituting the values of $\eta_{UC,obs}$ and a value into the equation (S5), a η_{UC} value of 21.5% was obtained in the deaerated toluene solution of CBDAC and TIPS-Nph. This absolute η_{UC} value is close to the relative η_{UC} value of 20.3% (Fig. 3b), confirming the reliability of the relative TTA-UC efficiency.

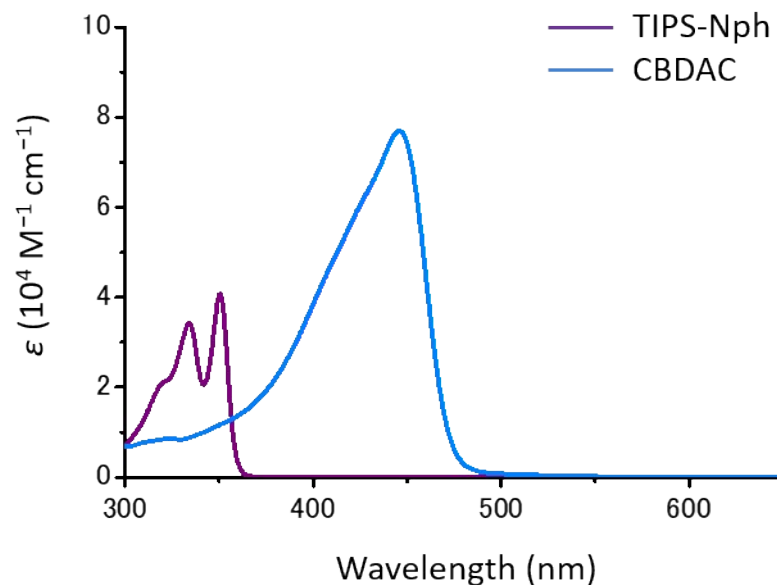


Fig. S1. Absorption coefficients of TIPS-Nph (purple line, 100 μM , $\epsilon_{350\text{nm}} \sim 41,000 \text{ M}^{-1} \text{ cm}^{-1}$) and CBDAC (blue line, 100 μM , $\epsilon_{446\text{nm}} \sim 77,000 \text{ M}^{-1} \text{ cm}^{-1}$) at room temperature in deaerated toluene.

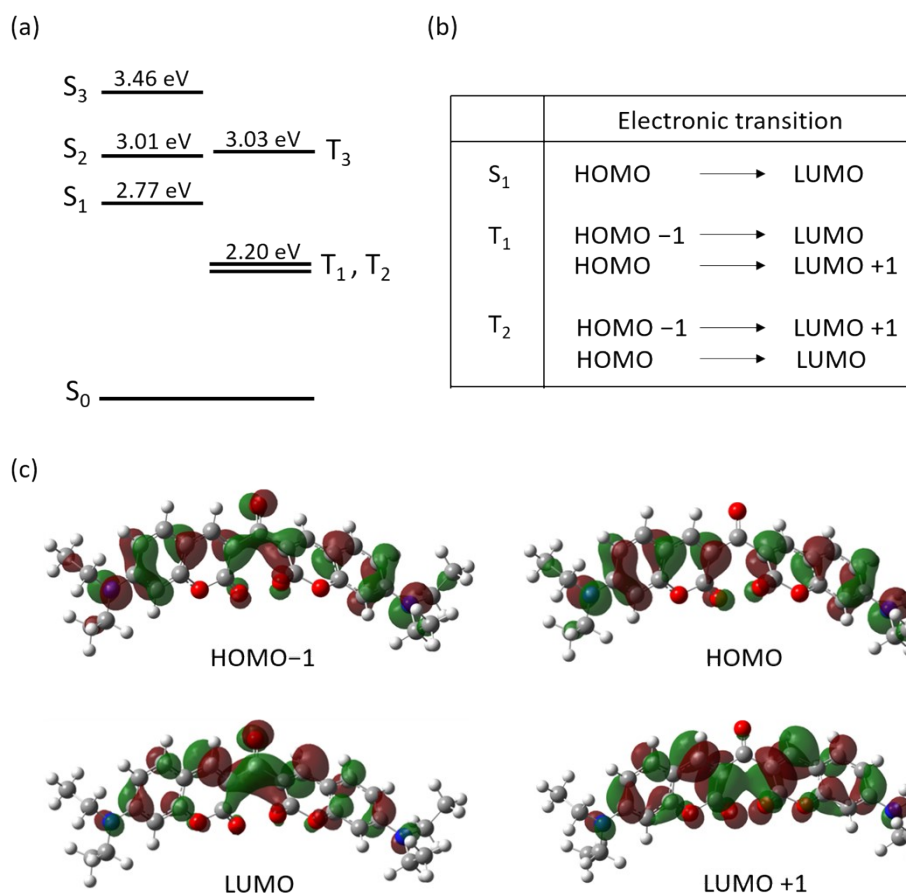


Fig. S2. (a) Calculated energy levels of singlet and triplet excited states of CBDAC. (b) Electronic transition involved in S_1 , T_1 and T_2 states of CBDAC. (c) Molecular orbitals of CBDAC in the ground state (isovalue = 0.025).

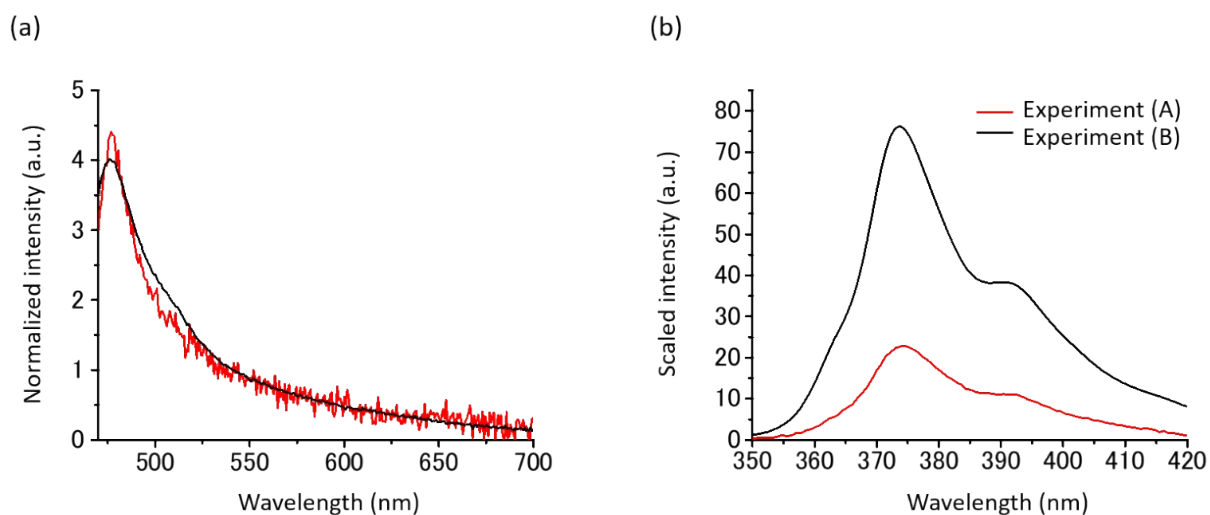


Fig. S3. (a) Normalized fluorescence and (b) scaled upconverted spectra of CBDAC and TIPS-Nph in deaerated toluene ([CBDAC] = 100 μM , [TIPS-Nph] = 10 mM) under excitation of 445 nm laser (excitation intensity = 580 mW cm^{-2}) in the experiment (A) (red) and (B) (black) scaled by using the integrated fluorescence profiles from 550 nm to 650 nm.

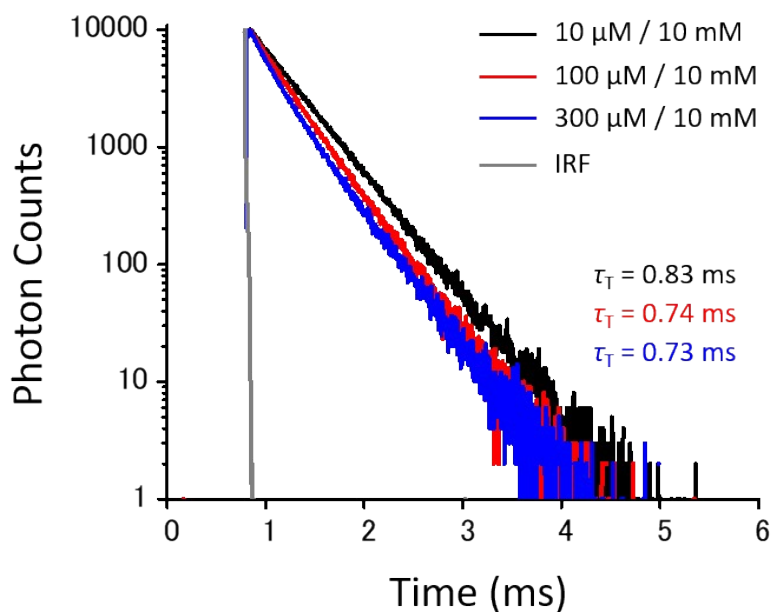


Fig. S4. UC emission decay of CBDAC/TIPS-Nph ([CBDAC] = 10, 100, 300 μM , [TIPS-Nph] = 10 mM) at 370 nm in deaerated toluene under pulsed excitation at 445 nm. The gray line shows instrumental response function (IRF). The red fitting curve for the tail part of the decay was obtained by the known relationship,^[9]

$$I_{\text{UC}}(t) \propto \exp\left(\frac{-t}{\tau_{\text{UC}}}\right) = \exp\left(\frac{-2t}{\tau_{\text{T}}}\right) \quad (\text{S6})$$

where τ_{UC} and τ_{T} are UC emission lifetime and acceptor triplet lifetime, respectively.

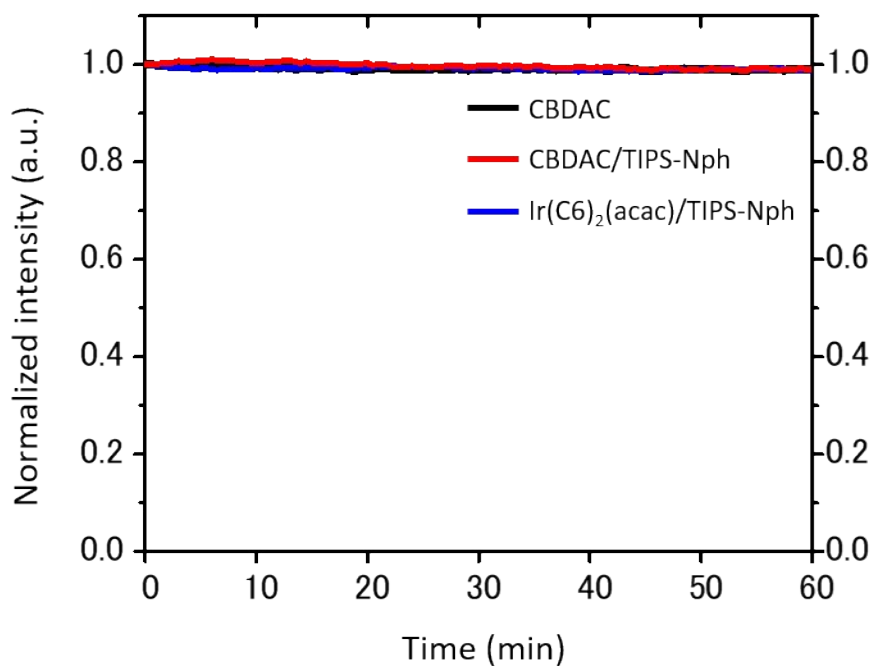


Fig. S5. Photoluminescence intensity of CBDAC (black line, [CBDAC] = 100 μ M, monitored at 482 nm, $I_{\text{ex}} = 500 \text{ mW cm}^{-2}$), CBDAC/TIPS-Nph (red line, [CBDAC] = 100 μ M, [TIPS-Nph] = 10 mM, monitored at 373 nm, $I_{\text{ex}} = 579 \text{ mW cm}^{-2}$) and Ir(C6)₂(acac)/TIPS-Nph (blue line, [Ir(C6)₂(acac)] = 100 μ M, [TIPS-Nph] = 10 mM, monitored at 373 nm, $I_{\text{ex}} = 438 \text{ mW cm}^{-2}$) in deaerated toluene under the continuous 445 nm laser excitation for one hour.

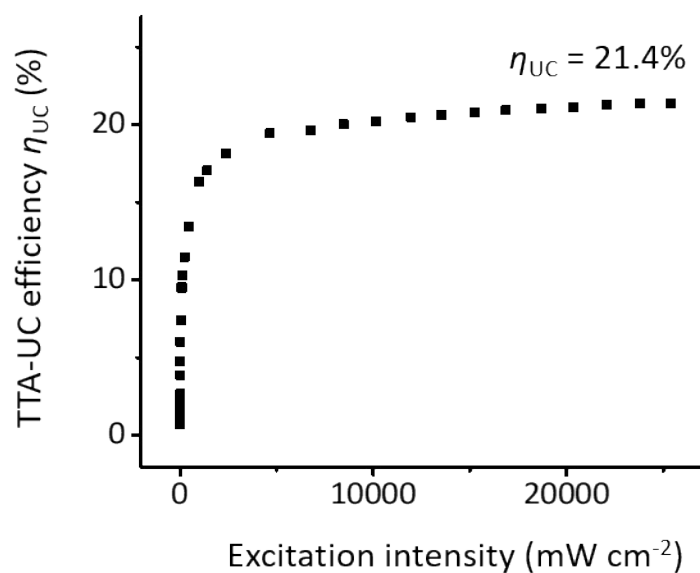


Fig. S6. TTA-UC efficiency η_{UC} of Ir(C6)₂(acac)/TIPS-Nph ([Ir(C6)₂(acac)] = 100 μ M, [TIPS-Nph] = 10 mM) in deaerated toluene.

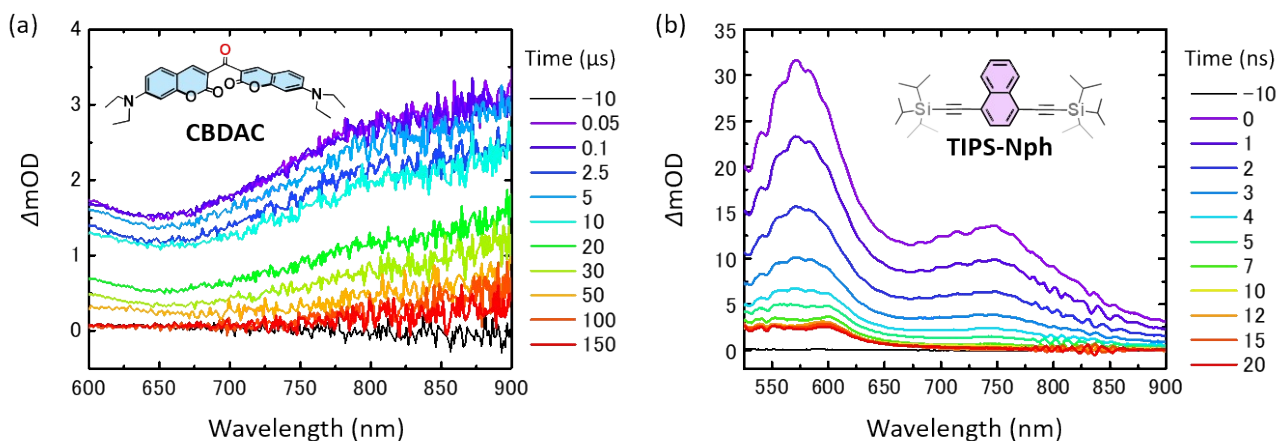


Fig. S7. Transient absorption spectra of (a) CBDAC (300 μM , $\lambda_{\text{ex}} = 480 \text{ nm}$) and (b) TIPS-Nph (10 mM, $\lambda_{\text{ex}} = 355 \text{ nm}$) in deaerated toluene. The pump pulse fluence were 0.48 mJ cm^{-2} for CBDAC and 1.9 mJ cm^{-2} for TIPS-Nph, respectively.

CBDAC showed a broad transient absorption in the observed region with a lifetime of 21.8 μs , which can be attributed to triplet absorption. TIPS-Nph showed ns-scale singlet absorption around 570 nm and 750 nm, and the signal around 600 nm remaining after 20 ns can be attributed to the triplet origin. Since the CBDAC triplet shows transient absorption around 800 nm, but the TIPS-Nph triplet does not, the Stern–Volmer analysis was performed at this wavelength.

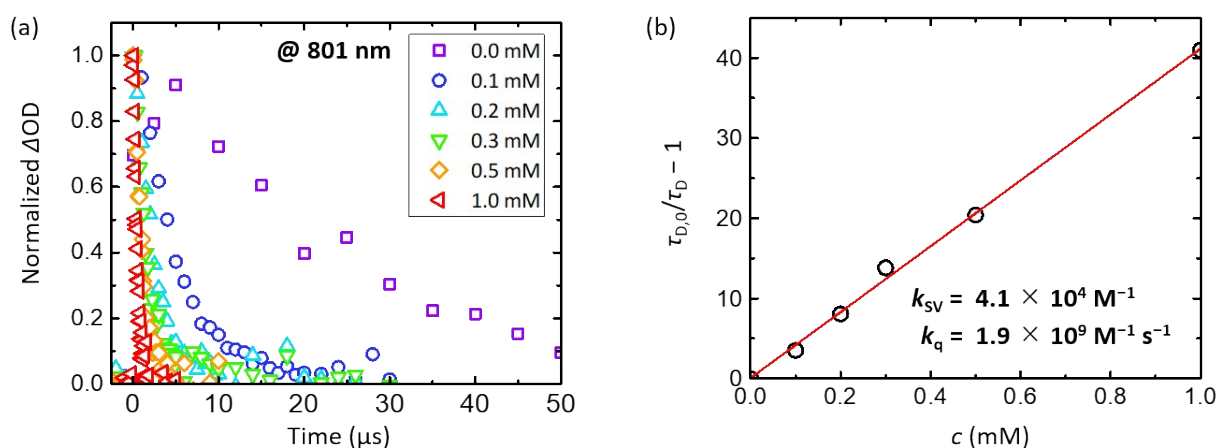


Fig. S8. (a) Transient decay for CBDAC (300 μM , $\lambda_{\text{ex}} = 480 \text{ nm}$, monitored at 801 nm) and CBDAC/TIPS-Nph ([CBDAC] = 100 μM , [TIPS-Nph] = 0.1, 0.2, 0.3, 0.5, 1.0 mM, $\lambda_{\text{ex}} = 450 \text{ nm}$, monitored at 801 nm, 450 nm long-pass filter) in deaerated toluene. (b) Lifetime-based Stern–Volmer plots at different TIPS-Nph concentrations. The pump pulse fluence were 0.19 mJ cm^{-2} for CBDAC and 0.05 mJ cm^{-2} for CBDAC/TIPS-Nph, respectively.

The time decay of the transient absorption signal at 801 nm was monitored by varying the concentration of the acceptor. Lifetime-based Stern–Volmer analyses yielded a quenching rate constant of $1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The high Φ_{TET} value of 99.8% was estimated from the obtained rate constants at the TIPS-Nph concentration of 10 mM. The

Φ_{TET} of 99.8% in CBDAC/TIPS-Nph was estimated by using triplet lifetime, $\Phi_{\text{TET}} = 1 - \frac{\tau_{D,0}}{\tau_D}$, where $\tau_{D,0}$ and τ_D are donor

triplet lifetime without and with acceptor, respectively.

Table S1. Summary of parameters related to η_{UC} . The TET efficiency of Ir(C6)₂(acac)/TIPS-Nph was estimated by the

equation $\Phi_{TET} = 1 - \frac{\Phi_p}{\Phi_{p,0}}$, where $\Phi_{p,0}$ and Φ_p are donor phosphorescence quantum yields without acceptor (80.3%) and with acceptor (2.6%), respectively.

Donor/Acceptor	η_{UC} (%)	f (%)	Φ_{ISC} (%)	Φ_{TET} (%)	Φ_{TTA} (%)	Φ_{FL} (%)
CBDAC/TIPS-Nph (100 μ M/10 mM)	20.3	33.8	91.9	99.8	~100	65.5
Ir(C6) ₂ (acac) / TIPS-Nph (100 μ M/10 mM)	21.4	33.8	~100	96.7	~100	65.5

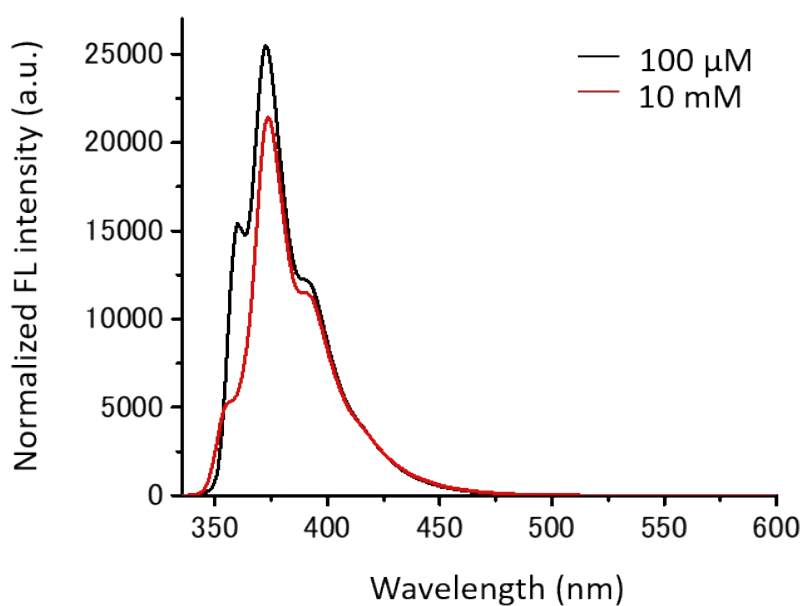


Fig. S9. Fluorescence spectra ($\lambda_{ex} = 320$ nm) of TIPS-Nph in deaerated toluene ($[TIPS-Nph] = 100$ μ M (black), 10 mM (red)) normalized at 420 nm. The peak at 360 nm on the short wavelength side becomes smaller at higher concentrations due to the inner-filter effect. Note that we show this comparison just to show the existence of reabsorption, and we did not use it for correcting the TTA-UC efficiency.

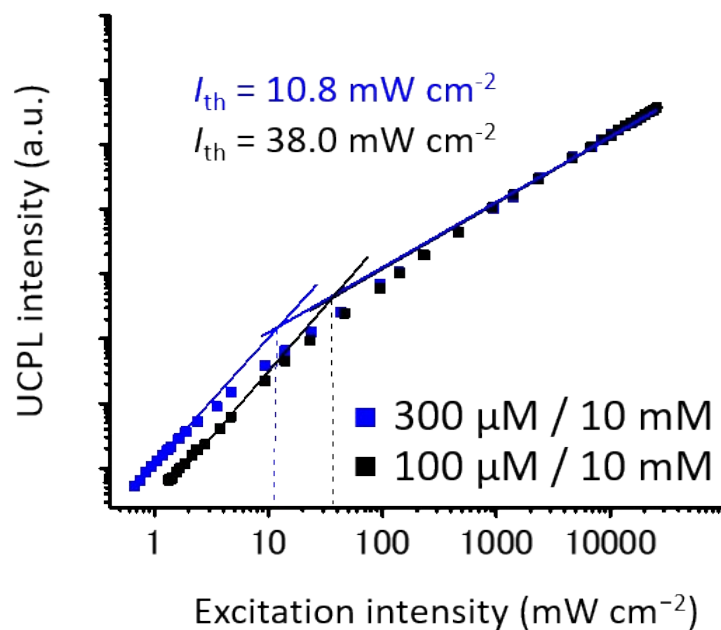


Fig. S10. UCPL intensity as a function of excitation intensity of the mixed solution of CBDAC (100 μM (black), 300 μM (blue)) and 10 mM TIPS-Nph in deaerated toluene ($\lambda_{\text{ex}} = 445 \text{ nm}$, 425 nm short-pass filter)

We have previously reported the lower I_{th} of 2.3 mW cm^{-2} for $\text{Ir}(\text{C6})_2(\text{acac})/\text{TIPS-Nph}$ in THF,¹ but we found that the same $\text{Ir}(\text{C6})_2(\text{acac})/\text{TIPS-Nph}$ system showed a higher I_{th} of 30.3 mW cm^{-2} in toluene, which is close to that of the current CBDAC/TIPS-Nph system in toluene. The detailed reason for the solvent dependence of I_{th} is unclear and needs further examination.

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