Materials. All reagents and solvents were used as received without further purification unless otherwise indicated. Analytical grade N,N-dimethylformamide (DMF) was purchased from Wako Pure Chemical. 2,7-di-tert-butylpyrene (DBP) with a high purity >98% (GC) was purchased from TCI Co., Ltd.. Ir(C6)2(acac) (C6 = coumarin 6, acac = acetylacetone) was synthesized according to the reported methods. The purity of Ir(C6)2(acac) was confirmed by 1H NMR, mass spectra and elemental analysis prior to use. 1H NMR [300 MHz, (CDCl3)], δ: 7.89 [d, 2H, H(1)], 7.62 [d, 2H, H(4)], 7.36 [t, 2H, H(2)], 7.23 [t, 2H, H(3)], 6.31 [d, 2H, H(7)], 6.09 [d, 2H, H(5)], 5.84-5.88 [m, 2H, H(6)], 5.32 [s, 1H, H(10)], 3.15-3.32 [q, 8H, H(8)], 1.73 [s, 6H, H(11)], 1.06 [t, 12H, H(9)]. MALDI-TOF-MS: m/z calcd: 990.2, found: 990.2, 890.8 (without acac). Element analysis C45H45IrN4O8S2·2H2O: found C 52.6, H 4.21, N 5.39; calcd C 52.67, H 4.42, N 5.46.

The high purity of Ir(C6)2(acac) was further confirmed by that the phosphorescence lifetime of Ir(C6)2(acac) in DMF (16.0 µs, 0.5 mM) was close to the reported values (14 µs in 2-methyltetrahydrofuran; 11.3 µs in CHCl3).

Characterization. UV-vis absorption spectra were recorded on a JASCO V-670 spectrophotometer. Luminescence spectra were measured by using a PerkinElmer LS 55 fluorescence spectrometer. Time-resolved photoluminescence lifetime measurements were carried out by using time-correlated single photon counting lifetime spectroscopy system, HAMAMATSU Quantaaurus-Tau C11567-01. Upconversion luminescence spectra were recorded on Otsuka Electronics MCPD-7000 instrument with the excitation source using an external, adjustable semiconductor laser (445 nm, 0-78 mW).

Determination of TTA-UC quantum efficiency. The upconversion luminescence quantum efficiency (ΦUC) was determined relative to a standard, Coumarin 6 in DMF (Φstd = 0.72), according to the following equation:
\[ \Phi_C = \Phi_{std} \left( \frac{A_{std}}{A_{UC}} \right) \left( \frac{l_{UC}}{l_{std}} \right) \left( \frac{\eta_{UC}}{\eta_{std}} \right)^2 \]  

where \( \Phi \), \( A \), \( I \), and \( \eta \) represent the quantum yield, absorbance at 445 nm, integrated photoluminescence spectral profile, and refractive index of the solvent. The subscripts \( UC \) and \( std \) denote the parameters of the upconversion and standard systems. Since the standard and the upconversion system are both in the same solvent DMF, Eq. 1 is simplified to

\[ \Phi_{UC} = \Phi_{std} \left( \frac{A_{std}}{A_{UC}} \right) \left( \frac{l_{UC}}{l_{std}} \right) \]  

These quantum yield values were averaged by using at least three independent measurements. We measured several different batches, and similar values were obtained reproducibly.

Supporting figures:

**Fig. S1** Qualitative Jablonski diagram showing the triplet-triplet annihilation (TTA)-based upconversion (UC) emission, using Ir(C6)\(_2\)(acac) as the photosensitizer (triplet donor) and DBP as the emitter (triplet acceptor). ISC: intersystem crossing; TTET: triplet-triplet energy transfer.

**Fig. S2** Fluorescence spectra of DBP in DMF with different DBP concentrations under the identical measurement condition (\( \lambda_{ex} = 345 \) nm).
We estimated the singlet-singlet back energy transfer efficiency by calculating the spectral overlap integral between acceptor fluorescence and donor absorption. Molar extinction coefficient $\epsilon / \text{M}^{-1} \text{cm}^{-1}$ is usually used to calculate the overlap integral ($J / \text{nm}^4 \text{M}^{-1} \text{cm}^{-1}$). However, for TTA-UC processes, it is essential to consider how many photons are absorbed by donor (how many triplet species are formed) rather than molar concentration of donor. Therefore, to compare the efficiencies of different donor species, it is necessary to normalize the extinction coefficient at the excitation wavelength. The overlap integral was calculated according to the following equation,

$$J = \int_0^\infty f_A(\lambda)\epsilon_{D,\text{norm}}(\lambda)\lambda^4 d\lambda$$  \hspace{1cm} (3)

where $f_A$ is the wavelength dependent acceptor (DBP) emission spectrum normalized to an area of 1, $\epsilon_{D,\text{norm}}$ is the extinction coefficient of the donor in units of $\text{M}^{-1} \text{cm}^{-1}$ normalized at 445 nm, and $\lambda$ is the wavelength in nm. The ratio of the overlap integral for Ir(ppy)$_3$ ($J_{\text{Ir(ppy)$_3$}}$) and Ir(C6)$_2$(acac) ($J_{\text{Ir(C6)$_2$(acac)}}$) was $J_{\text{Ir(ppy)$_3$}} / J_{\text{Ir(C6)$_2$(acac)}} = 2.076 \times 10^{11} / 4.023 \times 10^{10} = 5.2$. Therefore, our new donor Ir(C6)$_2$(acac) has 5 times less spectral overlap with acceptor DBP compared with conventional donor Ir(ppy)$_3$. 

**Fig. S3** Absorption spectra (normalized at 445 nm) of Ir(ppy)$_3$ (0.05 mM), Ir(C6)$_2$(acac) (0.05 mM), and fluorescence spectrum of DBP (0.5 mM; $\lambda_{ex} = 335$ nm) in deaerated DMF.
We experimentally quantified back energy transfer rate using a modified Stern-Volmer analysis. As explained in Fig. S3, it is more essential to use donor absorbance than to use donor concentration for the characterization of TTA-UC systems. Therefore, we modified the Stern-Volmer relation as follows

\[
\frac{I_0}{I} = 1 + K_{SV}[D] = 1 + K_{SV}(A_D/\epsilon d) = 1 + K'_{SV}A_D
\]

where \(I_0\) and \(I\) represent the acceptor fluorescence intensities in the absence and presence of donor (quencher), \(K_{SV}\) is the Stern-Volmer constant, \([D]\) is the molar concentration of donor (quencher), \(A_D\) is the donor absorbance at the excitation wavelength for TTA-UC (445 nm), \(\epsilon\) is the molar excitation coefficient of donor at 445 nm, \(d\) is the cell thickness (0.1 cm), and \(K'_{SV}\) is the modified Stern-Volmer constant. Linear fitting results gave the \(K'_{SV}\) values of 18 and 1.1 for Ir(ppy)_3 and Ir(C6)(acac), respectively. This result supports that the unwanted acceptor-to-donor singlet-singlet back energy transfer was much suppressed for Ir(C6)(acac) compared with conventional Ir(ppy)_3 thanks to the less absorption of Ir(C6)(acac) in the UV region.
Fig. S5 Photoluminescence decay at 385 nm of the deaerated DMF solution of the Ir(C6)2(acac)/DBP pair under pulsed excitation at 445 nm ([Ir(C6)2(acac)] = 0.1 mM, [DBP] = 0.5 mM). The single exponential fitting of the tail parts (red line) provided the triplet lifetime of the acceptor DBP ($\tau_{A,T} = 270$ µs).

Supporting references: