TIPS-Naphthalene for Efficient Visible-to-UV Photon Upconversion under Sunlight and Room Light

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ABSTRACT: Until now, the efficiency of triplet-triplet annihilation-based photon upconversion (TTA-UC) from visible to ultraviolet (UV) light has been limited to ca. 10% due to the absence of high-performance acceptors (emitters). Here, we present the first example of visible-to-UV TTA-UC internal efficiency η_{UC} beyond 20% by developing a novel UV emitter, 1,4-bis((triisopropylsilyl)ethynyl)naphthalene (TIPS-Nph), and sensitizing its triplet by a donor Ir(C6)$_2$(acac) with strong visible absorption and weak UV absorption. Under optimized conditions, 97% of the excitation light is absorbed, the threshold excitation intensity (I_{th} = 1.1 mW cm^{-2}) is lower than the solar irradiance (1.4 mW cm^{-2} for 445 ± 5 nm), and significantly, the highest external UC efficiency $\eta_{UC,ext}$ of 17.4% for vis-to-UV TTA-UC is achieved. Upconverted UV emission can also be obtained with weak light sources such as an AM 1.5 solar simulator and room LEDs, paving the way for a variety of solar and indoor applications.

Triplet-triplet annihilation-based photon upconversion (TTA-UC) has attracted much interest because of its potential to efficiently convert lower-energy photons to higher-energy photons at a weak excitation intensity.[1-19] TTA-UC occurs in multi-chromophore systems wherein the excited triplet energy of a donor (sensitizer) is transferred to an acceptor (emitter), and sensitized acceptor triplets annihilate to show an upconverted emission (Figure 1a).

While the conversion of visible light (vis, $\lambda > 400$ nm) to ultraviolet light (UV, $\lambda < 400$ nm) is crucial for artificial photosynthesis and photocatalytic environmental cleanup, the efficiency of vis-to-UV TTA-UC (η_{UC}) at solar irradiance has been limited.[20-30] Relatively high vis-to-UV η_{UC} values of 5.2% and 10.2% have been observed by using semiconductor nanocrystals as donor and 2,5-diphenyloxazole (PPO) as acceptor.[31,32] However, their threshold excitation intensities (I_{th}), at which half of the maximum η_{UC} is obtained, were much higher (ca. 2 W cm^{-2}) than solar irradiance (a few mW cm^{-2}). It was difficult to lower the I_{th} value without dropping the η_{UC} since the broad absorption of semiconductor nanocrystals in the UV region inevitably induces the re-absorption and back energy transfer at higher donor concentrations.

Here, we show the first example of vis-to-UV TTA-UC efficiency η_{UC} over 20% by developing a novel acceptor 1,4-bis((triisopropylsilyl)ethynyl)naphthalene (TIPS-Nph, Figure 1a) with a high singlet generation probability f by TTA and combining it with a molecular donor we developed earlier, Ir(C6)$_2$(acac) (C6 = coumarin 6, acac = acetylacetone).[22] The highest η_{UC} value is certified by absolute quantum yield measurements.[33,34] Thanks to the strong visible absorption over 80,000 M^{-1} cm^{-1} and weak UV absorption of Ir(C6)$_2$(acac),[22,35,36] the I_{th} value reaches a sub-solar irradiance without dropping the η_{UC}, resulting in the highest external UC efficiency $\eta_{UC,ext}$ of 17.4% for vis-to-UV TTA-UC. Remarkably, an upconverted UV emission was also observed under an AM 1.5 solar simulator and desk LED light (Figure 1b-e).

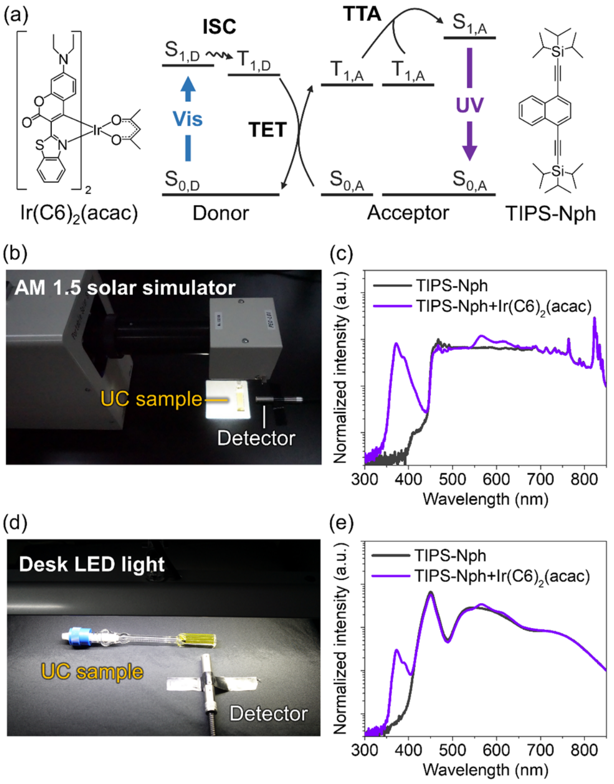

Figure 1. (a) Energy diagram of vis-to-UV TTA-UC using a donor Ir(C6)$_2$(acac) and a novel acceptor TIPS-Nph. Pictures and spectra (normalized at 850 nm) of TIPS-Nph (10 mM) with (purple)/without (gray) Ir(C6)$_2$(acac) (100 μM) in deaerated THF under (b, c) an AM1.5 solar simulator (450 nm long-pass filter is included) and (d, e) a desk LED light without using any further lens and filter.

Considering that TIPS-tetracene/anthracene are well-studied compounds,[16,37,38] it is a bit surprising that TIPS-Nph is a new compound. We synthesized TIPS-Nph and fully characterized it (see Supporting Information (SI)). A THF solution of TIPS-Nph (100 μM) showed a 0-0 absorption peak at 350 nm (3.54 eV) and a vibronic fluorescence spectrum in the UV region (Figure S4) with an absolute fluorescence quantum yield $\Phi_{\rm FL}$ of 74% ($\lambda_{\rm ex}$ = 320 nm). Ir(C6)$_2$(acac) shows two absorption bands at 445 and 474 nm and phosphorescence at 567 nm (2.19 eV) (Figure S4). As we discussed previously, the sharp and intense ligand-centered π-π* absorption bands of Ir(C6)$_2$(acac) are useful to avoid the quenching of upconverted UV emission.[22]

Under excitation by a 445 nm laser, an upconverted emission in the UV region was observed in a deaerated THF solution of Ir(C6)$_2$(acac) and TIPS-Nph (Figure 2a, [Ir(C6)$_2$(acac)] = 100 μM, [TIPS-Nph] = 10 mM). The ms-scale delayed emission supports the triplet-mediated mechanism (Figure S5). The TTA-UC efficiency $\eta_{\rm UC}$ is standardized to a theoretical maximum of 100%.[39] The $\eta_{\rm UC}$ value of Ir(C6)$_2$(acac) and TIPS-Nph was determined as 20.5% by the relative method (Figure 2b, see SI for details). The reliability of the highest $\eta_{\rm UC}$ was confirmed by a similar value of 21.4% at 17.2 W cm^{-2} obtained by the absolute method in the integrating sphere (see SI for details).[33,34] This $\eta_{\rm UC}$ is the highest value for vis-to-UV TTA-UC ever reported and twice higher than the previous record (10.2%).[32] On the other hand when the previous best acceptor PPO[21,27,30-32] was combined with Ir(C6)$_2$(acac) in THF, no upconverted emission was observed (Figure S6).

The triplet energy transfer (TET) efficiency $\Phi_{\rm TET}$ was estimated by measuring the sensitizer phosphorescence quantum yield (see SI for details). The efficiency of Ir(C6)$_2$(acac)-to-TIPS-Nph and Ir(C6)$_2$(acac)-to-PPO TET were 97% and almost 0%, respectively. The absence of TET is the reason for no TTA-UC emission from the Ir(C6)$_2$(acac) and PPO solution.

To explain the difference of $\Phi_{\rm TET}$ values between TIPS-Nph and PPO, we carried out density functional theory (DFT) calculations of TIPS-Nph and PPO. The estimated S$_1$ energy level of TIPS-Nph was 3.44 eV, which agrees well with the observed absorption peak at 3.54 eV. The estimated T$_1$ energy levels of TIPS-Nph (2.10 eV) was lower than that of PPO (2.51 eV), which would be responsible for the observed differences in the TET efficiency and the occurrence of TTA-UC. Therefore, it was necessary to use the donor with large UV absorption for sensitizing PPO triplet, which has limited the $\eta_{\rm UC}$ and $I_{\rm th}$ values.

The UC efficiency $\eta_{\rm UC}$ is described by the following expression,[6]

$$\eta_{\rm UC} = f\Phi_{\rm ISC}\Phi_{\rm TET}\Phi_{\rm TTA}\Phi_{\rm FL} \tag{1}$$

where $\Phi_{\rm ISC}$ and $\Phi_{\rm TTA}$ represent the quantum yields of donor ISC and TTA. In the current system, the $\Phi_{\rm ISC}$ and $\Phi_{\rm TTA}$ values are assumed to be close to 1 since there is no donor fluorescence and the excitation intensity is in the linear regime as shown later. By increasing the acceptor concentration from 100 μM to 10 mM, the $\Phi_{\rm FL}$ value decreased from 74% to 66%. This decrease is due to the inner filter effect, as confirmed by the disappearance of the short-wavelength fluorescence component at 10 mM (Figure S7). From these parameters, the relatively high f value of 32% was estimated for TIPS-Nph, and this is the main reason for the highest vis-to-UV TTA-UC efficiency. The high f value may be associated with the reduction of nonradiative loss in the TTA process by the rigid bonding of the ethynyl group, as recently suggested by Rao and coworkers.[38] Ethynyl naphthalene can be the promising structural unit for vis-to-UV TTA-UC, and we expect that the TTA-UC efficiency can be further improved by increasing the fluorescence quantum yield through the optimization of the acceptor structure.

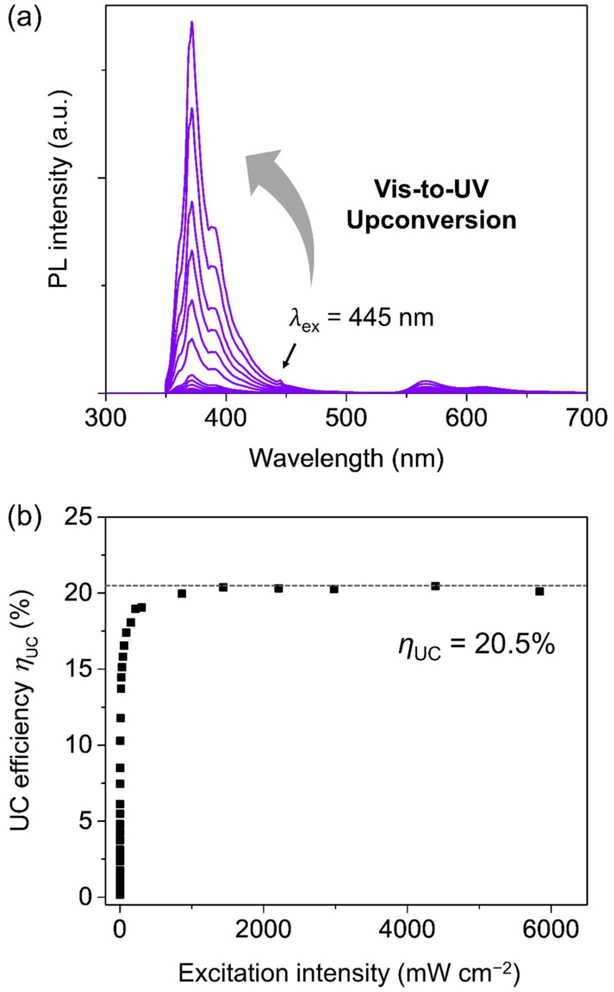

Figure 2. (a) Photoluminescence (PL) spectra of Ir(C6)$_2$(acac) and TIPS-Nph in deaerated THF ([Ir(C6)$_2$(acac)] = 100 μM, [TIPS-Nph] = 10 mM) at various excitation intensities from 0.030 mW cm^{-2} to 5.8 W cm^{-2} ($\lambda_{\rm ex}$ = 445 nm, no filter). (b) UC efficiency $\eta_{\rm UC}$ of 100 μM Ir(C6)$_2$(acac) and 10 mM TIPS-Nph in deaerated THF at various excitation intensities of the 445 nm laser.

Besides the high $\eta_{\rm UC}$, the threshold excitation intensity $I_{\rm th}$ is the key parameter to characterize TTA-UC. In the typical TTA-UC systems, the UC emission intensity shows a quadratic and a linear dependence on the excitation intensity at low- and high-intensity regimes, respectively.[40-42] The intersection of the two fitting lines provides $I_{\rm th}$. The log-log plot of UC emission intensity of 100 μM Ir(C6)$_2$(acac) and 10 mM TIPS-Nph against the excitation intensity showed a transition of slope from ca. 2.0 to 1.0, giving a $I_{\rm th}$ value of 2.3 mW cm^{-2} (Figure 3a). To further reduce the $I_{\rm th}$ value, we increased the donor concentration from 100 μM to 300 μM. Remarkably, the obtained $I_{\rm th}$ of 1.1 mW cm^{-2} with 300 μM of the donor is lower than the solar irradiance of 1.4 mW cm^{-2} for 445 ± 5 nm (Figure 3a).

While the common “internal” UC efficiency $\eta_{\rm UC}$ gives an understanding of the basic UC properties, it is important to achieve a high "external" UC efficiency $\eta_{\mathrm{UC,ext}}$ for real-world applications. It is defined as

$$\eta_{\mathrm{UC,ext}} = \eta_{\mathrm{UC}} \times (1 - 10^{-A}) \qquad (2)$$

where A represents the absorbance at the excitation wavelength (445 nm). Figure 3b shows the excitation dependence of $\eta_{\mathrm{UC,ext}}$ for TIPS-Nph (10 mM) with different concentrations of Ir(C6)$_2$(acac) (100 and 300 μM). The highest $\eta_{\mathrm{UC,ext}}$ of 17.4% as vis-to-UV TTA-UC was achieved with 300 μM of the donor. Remarkably, even at the solar irradiance of 1.4 mW cm^{-2}, this sample shows a high $\eta_{\mathrm{UC,ext}}$ of about 6%.

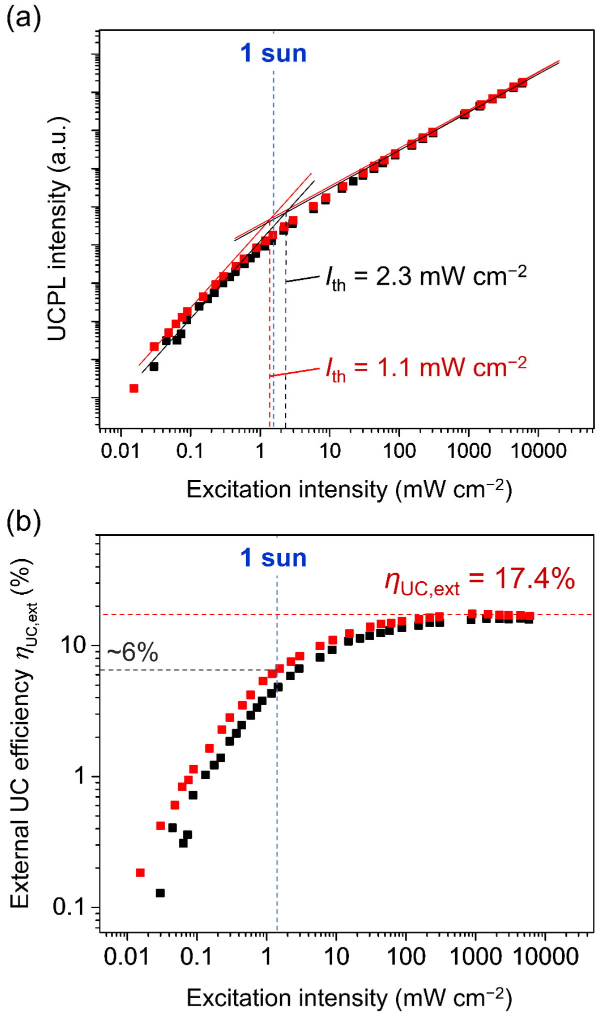

Figure 3. Excitation intensity dependence of (a) UC emission intensity and (b) external UC efficiency $\eta_{\mathrm{UC,ext}}$ of Ir(C6)$_2$(acac) (100 μM (black), 300 μM (red)) and TIPS-Nph (10 mM) in deaerated THF (λ_{ex} = 445 nm). Blue line indicates the intensity of sunlight (1.4 mW cm^{-2} for 445 ± 5 nm).

It's not uncommon for only high internal TTA-UC efficiency η_{UC} to be reported by employing a low donor concentration (low absorbance), since the high donor absorbance leads to the undesirable re-absorption and back energy transfer. On the other hand, in the current system, the weak donor absorption at the UV region allows us to realize the high visible absorbance and the high internal UC efficiency η_{UC} at the same time, resulting in the high external UC efficiency $\eta_{\mathrm{UC,ext}}$. The 300 μM donor absorbs 97% of 445 nm light (A = 1.55, path length = 1 mm). Significantly, the internal UC efficiency η_{UC} was maintained as high as 18.0% even at such high donor concentration (Figure S8). The acceptor-to-donor back singlet/triplet energy transfers are suppressed thanks to the small UV absorption of donor and the lower T$_1$ energy level of the acceptor than the donor, which was supported by similar acceptor fluorescence lifetimes with/without the donor (Figure S9) and similar acceptor triplet lifetimes at the different donor concentrations (Figure S5).

As a simple demonstration, we placed the deaerated THF solution of Ir(C6)$_2$(acac) and TIPS-Nph under the AM 1.5 solar simulator (Figure 1b). A 450 nm short-pass filter was introduced into the solar simulator to avoid the direct excitation of the acceptor. At 1 sun, without any focusing of the excitation light, an upconverted UV emission was observed from the mixed solution of Ir(C6)$_2$(acac) and TIPS-Nph (Figure 1c). The fact that no upconverted emission was observed in the absence of the donor confirms the sensitized TTA-UC. A nearly 100% quantum yield of photocatalytic water splitting has been reported, but the absorption of the photocatalysts was limited to the UV range.[43] It is anticipated to add the visible light sensitivity to these ultimate photocatalysts by the vis-to-UV TTA-UC.

Indoor applications of vis-to-UV TTA-UC are challenging since the intensity of common room light is even weaker than sunlight. We tested our TTA-UC system by using the desk LED light whose intensity for the blue portion (λ < 500 nm) is ca. 0.7 mW cm^{-2} at a separation of about 7 cm from the LED surface (Figure 1d). Even at such a low excitation intensity, the deaerated THF solution of Ir(C6)$_2$(acac) and TIPS-Nph clearly showed an upconverted UV emission, while the TIPS-Nph solution without the donor did not show any UV emission (Figure 1e). Moreover, the upconverted emission was observed at different distances from the desk LED light from 5 cm to 50 cm, where the LED light intensity (λ < 500 nm) varied from 0.88 mW cm^{-2} to 0.065 mW cm^{-2} (Figure S10). By formulating the solid-state upconverters based on the current donor-acceptor dyes and combining them with photocatalysts, TTA-UC would contribute to improving the indoor environments.

In conclusion, we show the first example of vis-to-UV TTA-UC efficiency η_{UC} beyond 20%, which is two times higher than the previous record. The highest η_{UC} value was certified by the absolute quantum yield measurements. This new record originates from the high f value of the novel acceptor TIPS-Nph and the strong visible absorption and weak UV absorption of donor Ir(C6)$_2$(acac). This donor-acceptor pair gives the threshold excitation intensity I_{th} as low as 1.1 mW cm^{-2}, being lower than the solar irradiance. While it is usually challenging to achieve the high external UC efficiency $\eta_{\mathrm{UC,ext}}$ due to the severe quenching of UC emission at a high donor concentration, the favorable absorption feature of the donor and the lower triplet energy of acceptor than the donor realize the record external efficiency $\eta_{\mathrm{UC,ext}}$ of 17.4% for vis-to-UV TTA-UC. Even weak visible light within the sunlight and room LED light can be effectively converted to UV light, showing the promising potential of vis-to-UV TTA-UC for various solar and indoor applications.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publication website at DOI: xx.xxxx/jacs.xxxxxxx.

Experimental details, NMR spectra, UV-vis absorption spectra, photoluminescence spectra, decays and spectra of UC emission, excitation intensity dependence of UC efficiency, fluorescence decays.

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Notes

The authors declare no competing financial interest.

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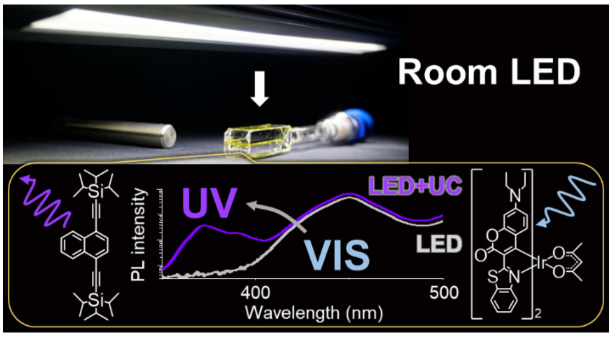
Room LED
UV
VIS
LED+UC
LED
PL intensity
400
500
Wavelength (nm)
Si
Si
N
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S
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