

Sensitizer–host–annihilator ternary-cascaded triplet energy landscape for efficient photon upconversion in the solid state

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ABSTRACT

In this paper, we introduce a new strategy for improving the efficiency of upconversion emissions based on triplet–triplet exciton annihilation (TTA-UC) in the solid state. We designed a ternary blend system consisting of a triplet sensitizer (TS), an exciton-transporting host polymer, and a small amount of an annihilator in which the triplet-state energies of the TS, host, and annihilator decrease in this order. The key idea underpinning this concept involves first transferring the triplet excitons generated by the TS to the host and then to the annihilator, driven by the cascaded triplet energy landscape. Because of the small annihilator blend ratio, the local density of triplet excitons in the annihilator domain is higher than those in conventional binary TS/annihilator systems, which is advantageous for TTA-UC because TTA is a density-dependent bimolecular reaction. We tracked the triplet exciton dynamics in the ternary blend film by transient absorption spectroscopy. Host triplet excitons are generated through triplet energy transfer from the TS following intersystem crossing in the TS. These triplet excitons then diffuse in the host domain and accumulate in the annihilator domain. The accumulated triplet excitons undergo TTA to generate singlet excitons that are higher in energy than the excitation source, resulting in UC emission. Based on the excitation-intensity and blend-ratio dependences of TTA-UC, we found that our concept has a positive impact on accelerating TTA.

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INTRODUCTION

Photon upconversion (UC) is a phenomenon that converts two low-energy photons into a high-energy photon.^{1–9} UC has attracted considerable attention in recent years because of its potential applications in a number of fields, including solar cells, artificial photosynthesis, and bioimaging.^{5,10,11} Conventional UC based on triplet–triplet exciton annihilation (TTA-UC) takes place through a sequence of fundamental photophysical processes.^{1–9} First, a triplet sensitizer (TS) absorbs a low energy photon to generate a singlet exciton that rapidly converts into a triplet exciton through intersystem crossing (ISC). Triplet energy transfer (TET) between the TS and a triplet-accepting annihilator material with low-lying triplet and high-lying singlet state energies then occurs. Annihilator

triplet excitons diffuse randomly and undergo TTA when a triplet exciton meets another one, resulting in the creation of singlet excitons of higher energy than those of the TS. The singlet excitons rapidly decay to the ground state by emitting upconverted photons, i.e., UC emission.

Efficient TTA-UC in solution systems has been previously reported.¹² A UC quantum efficiency Φ_{UC} of up to 76% has been reported for red-to-blue conversion in a solution system (we set 100% as the maximum Φ_{UC} in this study), which corresponds to internal UC efficiency approaching its thermodynamic limit of 100%.¹² In contrast, solid state UC efficiencies lag behind those of solution systems^{8,9} because the materials are frozen in the solid state and cannot diffuse. Instead, excitons diffuse as quasi-particles in annihilator domains. Previous studies have reported UC emissions

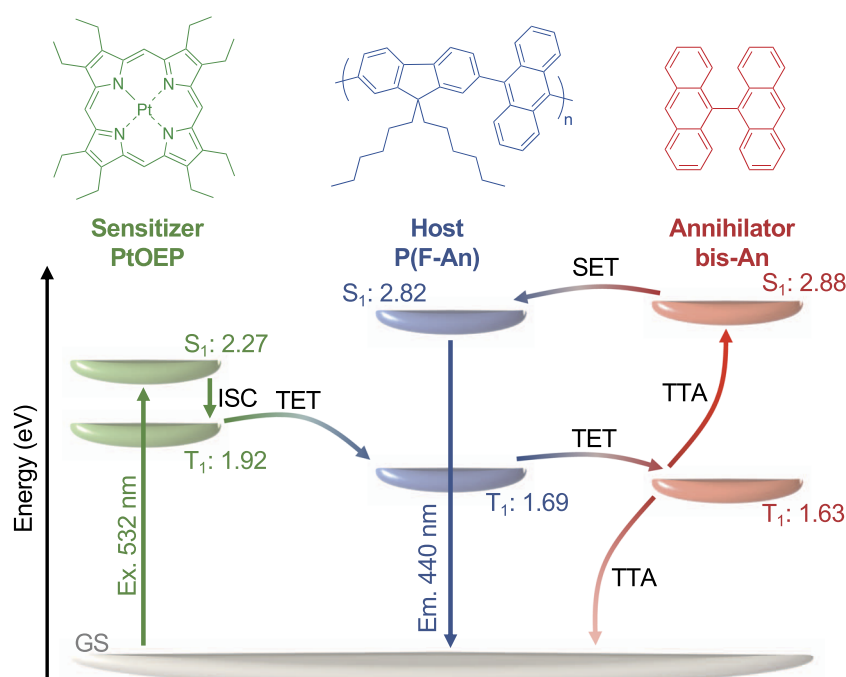


FIG. 1. Chemical structures and the energy landscape of the materials used in this study. ISC, TET, TTA, and SET refer to intersystem crossing, triplet energy transfer, triplet-triplet exciton annihilation, and singlet energy transfer, respectively. S_1 , T_1 , and GS are the lowest excited singlet, triplet, and ground states, respectively. The provided numbers are the energies of these states.

from solid thin films consisting of a TS and a triplet-accepting conjugated polymer as an annihilator.^{13,14} For example, blue UC emission was observed from a copolymer of spirofluorene and anthracene units doped with Pt(II)octaethylporphyrin (PtOEP).¹⁴ Because the diffusion constants of triplet excitons in organic amorphous solids are generally considerably smaller than those of materials in low-viscosity solutions, UC efficiency in the solid state is very poor; hence, an efficient solid state TTA-UC system is highly desired.

The rate equation for triplet excitons including TTA can be written as

$$\frac{dn_T}{dt} = G_T - \frac{n_T}{\tau} - \gamma n_T^2, \quad (1)$$

where G_T is the triplet generation rate through TET from the TS, n_T is the triplet exciton density, τ is the triplet exciton lifetime, and γ is the TTA rate coefficient, which is a function of the triplet exciton diffusion constant.¹ When we assume three-dimensionally isotropic exciton diffusion, γ is given by the following equation:^{15–18}

$$\gamma = 8\pi DR, \quad (2)$$

where D and R are the diffusion constant and effective reaction radius of triplet excitons, respectively. As maximum TTA efficiency is observed when $1/\tau \ll \gamma n_T$, a smaller γ due to slow triplet exciton diffusion in the solid state is disadvantageous for UC.

Herein, we report a new strategy for improving TTA-UC efficiency in the solid state. We designed a ternary blend system consisting of a TS, an exciton-transporting host conjugated polymer, and a small amount of an annihilator in which the triplet-state energies of the TS, host, and annihilator decrease in this order.

The key idea underpinning this ternary blend concept involves first transferring the triplet excitons generated in the TS to the host and then to the annihilator, driven by the cascaded triplet-energy landscape. Because of the small annihilator blend ratio, the local triplet exciton density in the annihilator domain is higher than the overall n_T , which is advantageous for TTA-UC because TTA is a bimolecular reaction. In this study, we demonstrate this strategy using PtOEP as the TS, poly[(9,9'-dihexylfluorenyl-2,7-diyl)-*alt*-(9,10-anthracene)] [P(F-An)], an alternative copolymer of fluorene and anthracene units, as the host and 9,9'-bianthracene (bis-An) as the annihilator (Fig. 1). We show that triplet excitons accumulate in bis-An domains through a sequence of TET. Based on the excitation-intensity and blend-ratio dependences of TTA-UC, we found that the effective TTA rate coefficient γ^{eff} in the ternary blend system is larger than that of the binary system, suggesting that triplet accumulation in small domains has a positive impact on accelerating TTA.

EXPERIMENTAL METHODS

Sample preparation

PtOEP, P(F-An), and bis-An were purchased from Frontier Scientific, Inc., American Dye Source, Inc., and Tokyo Chemical Industry Co., Ltd., respectively, and used without further purification. Thin films were prepared on quartz substrates by spin-coating from chloroform (CF) solutions. The blend ratio of PtOEP/P(F-An) binary blend films was 1:10 by weight, whereas that of PtOEP/P(F-An)/bis-An ternary blend films was 1:9:1 by weight, unless otherwise noted. Films were $\sim 1 \mu\text{m}$ thick, which corresponds to an

absorbance of ~ 0.4 at 532 nm. Sample films were encapsulated in a N_2 -purged glovebox for transient absorption (TA) and UC-emission measurements.

Measurements

UV-visible absorption and photoluminescence (PL) spectra were acquired on a UV-visible spectrometer (Hitachi, U-4100) and a fluorescence spectrometer (Horiba Jobin Yvon, Nanolog), respectively, equipped with a photomultiplier tube (Hamamatsu, R928P). A xenon lamp with a monochromator was used as the weak excitation source for normal PL measurements, whereas a 532-nm CW laser (RGB photonics, λ beam 532-200 DPS) was used as the high-power excitation source for UC-emission measurements. The relative quantum yields (QYs) of the UC emissions were determined relative to that of pristine PtOEP doped in a polystyrene (PS) film according to the following equation:¹⁹

$$\Phi_{UC} = 2\Phi_{std} \left(\frac{1 - 10^{-A_{std}}}{1 - 10^{-A_{UC}}} \right) \left(\frac{I_{UC}}{I_{std}} \right) \left(\frac{P_{std}}{P_{UC}} \right) \left(\frac{n_{UC}}{n_{std}} \right)^2, \quad (3)$$

where Φ , A , I , P , and n are the QY, absorbance at the excitation wavelength (532 nm), the integrated PL intensity, the excitation intensity, and the refractive index of the medium, respectively. Subscripts “UC” and “std” refer to the UC-emission film and the standard pristine PtOEP/PS film, respectively. Here, the n values of P(F-An) and PS were assumed to be 1.75 and 1.59, respectively.^{20–22} Φ_{ref} was determined with an integrating sphere using an absolute QY measuring system (Bunko-keiki, BEL-300).

TA data were collected using a highly sensitive microsecond TA system. A Nd:YAG laser (Elforlight, SPOT-10-200-532) operating at a wavelength of 532 nm was used as the excitation source. White light provided by a tungsten lamp with a stabilized power source was used as the probe light. Two monochromators and appropriate optical cut-off filters were placed before and after the sample to increase the signal-to-noise ratio. Further details of our TA setup are presented elsewhere.²³

RESULTS AND DISCUSSION

Excited-state energy landscape

Figure 2 shows the absorption and PL spectra of the materials employed in this study. As shown in Fig. 2(a), PtOEP exhibits two characteristic absorption bands at 350 nm–400 nm and 500 nm–550 nm that are attributable to the Soret and Q bands, respectively.^{24,25} P(F-An) and bis-An absorb below 450 nm, with the absorption onset of bis-An slightly blue-shifted compared to that of P(F-An). P(F-An) and bis-An exhibit fluorescence bands with peaks at ~ 440 nm and ~ 430 nm, respectively, whereas PtOEP shows a sharp phosphorescence band at ~ 645 nm.^{24–26} The peak wavelength of the fluorescence from the bis-An/PS film is red-shifted compared to that in a cyclohexane solution, suggesting that bis-An aggregates in the ternary blend film (see Fig. S2 for more details), which is beneficial for our strategy because triplet excitons accumulate in the bis-An domain. The lowest excited singlet state energy E_{S1} of P(F-An) and bis-An were determined to be 2.82 eV and 2.88 eV, respectively,

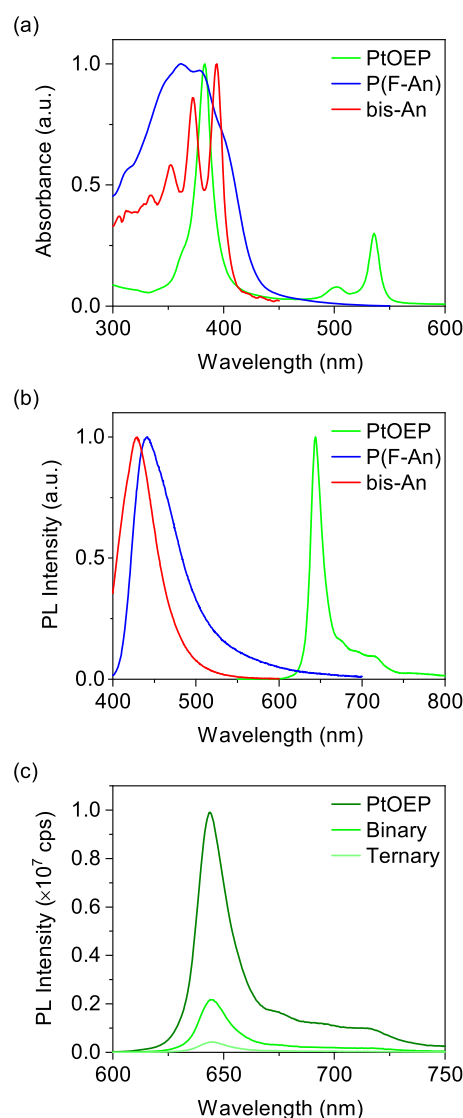


FIG. 2. (a) Absorption spectra of pristine P(F-An), bis-An/PS, and PtOEP/PS films. (b) PL spectra of pristine P(F-An), bis-An/PS, and PtOEP/PS films. (c) Phosphorescence spectra of the PtOEP/PS, PtOEP/P(F-An) binary, and PtOEP/P(F-An)/bis-An ternary blend films. Phosphorescence intensities were corrected for differences in absorbance at 530 nm.

based on the peak positions of their respective fluorescence spectra, indicating that E_{S1} of bis-An in the ternary blend is slightly higher than that of P(F-An). E_{S1} of PtOEP was determined to be 2.27 eV based on the absorption onset because fluorescence from PtOEP was not observed due to efficient ISC.²⁵ The lowest excited triplet state energy E_{T1} was determined to be 1.92 eV, 1.69 eV, and 1.63 eV for PtOEP, P(F-An), and bis-An, respectively, based on the peak positions in their phosphorescence spectra [the phosphorescence spectra of P(F-An) and bis-An are found in the [supplementary material](#)]. The excited-state energies are summarized in Fig. 1. PtOEP,

P(F-An), and bis-An form a cascaded triplet energy landscape in the ternary blend film, as shown in Fig. 1. Note that phosphorescence from the PtOEP dimers in the PtOEP aggregate, which shows the phosphorescence band with the lowest energy at ~ 1.59 eV that may act as trap sites for triplet excitons, was marginal in both the binary and ternary blend films (see the [supplementary material](#)), indicating that most PtOEP molecules in the blend films disperse in the host P(F-An) matrix.

To determine the TET quantum yield Φ_{TET} from the TS to the host and/or the annihilator, we compared the phosphorescence intensities of the pristine PtOEP/PS and binary PtOEP/P(F-An) or ternary PtOEP/P(F-An)/bis-An blend films. Figure 2(c) reveals that the blend films still exhibit PtOEP phosphorescence; however, their intensities were considerably lower than that of the pristine PtOEP/PS film, indicating that TET from PtOEP to P(F-An) and/or bis-An occurs. Φ_{TET} was determined to be 78% and 96% for the binary and ternary blend films, respectively, based on the phosphorescence quenching yield, suggesting efficient TET from the TS. Although the reason why the ternary blend film exhibits a slightly enhanced Φ_{TET} is not clear yet, it may be due to suppression of back-TET from P(F-An) to PtOEP in the ternary blend owing to the cascaded energy landscape.

Triplet exciton dynamics

Figure 3(a) shows the TA spectra of the PtOEP/PS film. Photo-induced absorption (PIA) bands were observed ranging from 450 nm to 900 nm, whereas a negative hollow was observed at 500 nm–550 nm, which are assigned to T_1 – T_n absorption and ground state bleaching (GSB) of PtOEP, respectively, as reported previously.²⁴ The lifetime of PtOEP triplet excitons was determined to be 46 μs (see the [supplementary material](#)).²⁴ On the other hand, the TA spectra of the PtOEP/P(F-An) binary blend film are shown in Fig. 3(b). At 1 μs after photoexcitation, a broad PIA band ranging from 450 nm to 900 nm and a hollow at ~ 540 nm were observed, which are assigned to PtOEP triplet excitons. The GSB due to PtOEP then recovered rapidly (time constant is less than 2 μs), while a PIA band ranging from 450 nm to 900 nm remained over the 100 μs time scale. Although this long-lived PIA band is similar to that of PtOEP triplet excitons, we can safely distinguish this new PIA band from that of PtOEP triplet excitons because the characteristic GSB hollow of PtOEP at ~ 540 nm was not observed in the new long-lived PIA band, meaning that the new band observed in the binary blend is attributable to transient species originating from P(F-An). The new PIA band decayed faster in an O_2 atmosphere (see the [supplementary material](#)), indicating that the PIA band can be assigned to T_1 – T_n absorption of P(F-An). The triplet exciton lifetime of P(F-An) was determined to be ~ 570 μs (see the [supplementary material](#)).

The PIA band attributable to P(F-An) triplet excitons was also observed for the ternary blend film (see the [supplementary material](#)); however, it decayed considerably faster than that of the binary blend film, as shown in Fig. 3(c), suggesting that TET from P(F-An) to bis-An occurs rapidly. P(F-An) triplet excitons decay with a time constant of ~ 3 μs in the ternary blend film, which is more than two orders of magnitude faster than the intrinsic decay time of P(F-An) triplet excitons (~ 570 μs), indicating that TET from P(F-An) to bis-An undergoes with a QY of close to unity.

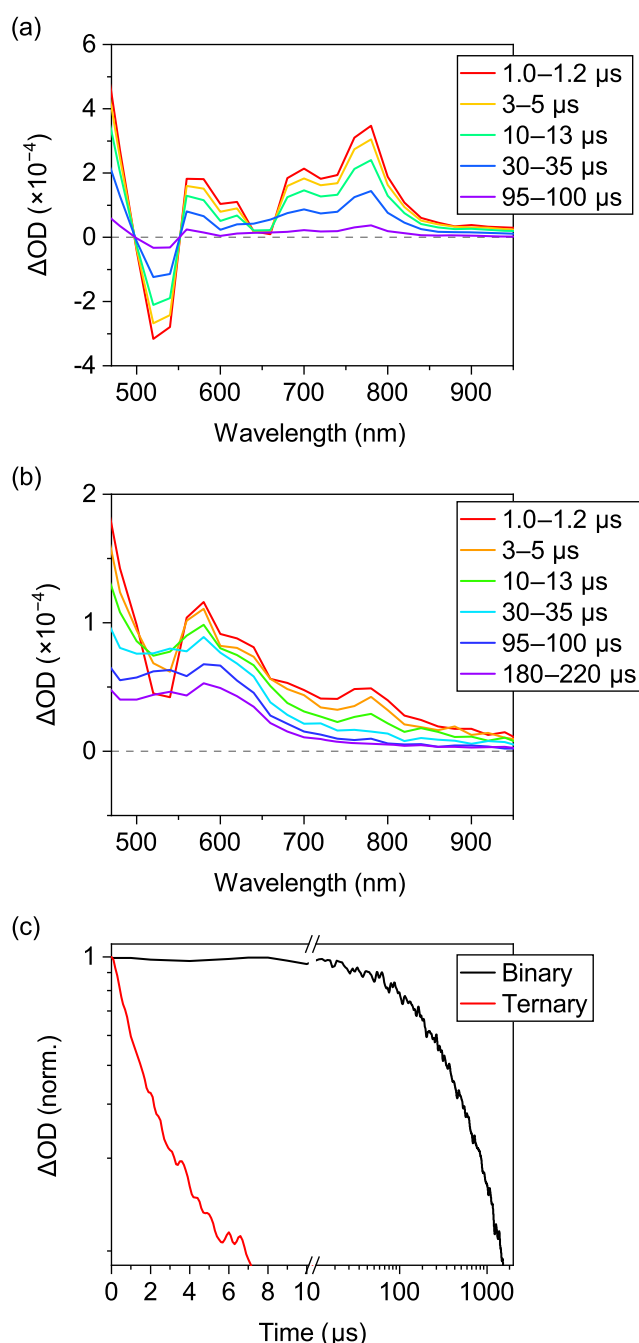


FIG. 3. TA spectra of (a) PtOEP/PS and (b) binary blend films excited at 532 nm. (c) Time evolution of P(F-An) triplet excitons in the binary and ternary blend films monitored at 600 nm. The excitation wavelength was set at 532 nm with a fluence of $12 \mu\text{J cm}^{-2}$.

Note that bis-An should have a triplet PIA at ~ 430 nm according to previous studies;^{27,28} however, this PIA band was not able to be detected in this study because the large steady-state absorption band of P(F-An) fully overlaps this region, making it difficult

to probe below 450 nm in this study. Instead, we observed a very faint TA signal attributable to bis-An triplet excitons in the near-IR region (see Fig. S9 in the [supplementary material](#)). Figure S9 shows the TA spectra and decay kinetics monitored at 900 nm for a PtOEP/bis-An mixture in a CF solution. After decaying rapidly within 5 μ s, which is attributable to TET from PtOEP to bis-An, a faint but long-lived PIA signal was observed, which is attributable to bis-An triplet excitons. The lifetime of bis-An triplet excitons was determined to be ~ 110 μ s. Because the absorption cross section of the faint bis-An triplet PIA was too small to be observed in the ternary blend film where the large P(F-An) triplet PIA tail overlaps, the lifetime of bis-An triplet excitons in the ternary blend is assumed to be the same as that in the PtOEP/bis-An solution, meaning that the triplet exciton lifetime of the annihilator is approximately five times shorter than that of P(F-An). To briefly summarize, we revealed exciton dynamics in the ternary blend system. PtOEP singlet excitons are promptly generated upon photoexcitation and are rapidly converted into triplet excitons through ISC, followed by TET from PtOEP to P(F-An). The triplet excitons in the P(F-An) domain diffuse randomly and undergo TET to bis-An when excitons reach P(F-An)/bis-An interfaces. As the blend ratio of bis-An is lower than that of P(F-An), triplet excitons accumulate in small bis-An domains, meaning that the local triplet exciton density in the annihilator domain in the ternary blend is higher than the overall triplet density. This is in sharp contrast to previously reported TS/host/annihilator ternary systems where TS and annihilator molecules are dispersed into electronically inert polymer host matrices such as cellulose acetate and poly(methyl methacrylate).^{29–33} Triplet excitons diffuse when high concentrations of TS/annihilator molecules are loaded into the inert host matrix in these systems in which triplet excitons diffuse through hopping between nearest TS or annihilator molecules. Because the rate constant of the Dexter-type energy transfer scales exponentially with the decrease in the distance between two chromophores,¹ ternary systems that use inert host polymers are disadvantageous for TET. In contrast, as we used an exciton-transporting conjugated polymer as a host material, triplet excitons can diffuse in the host domain, resulting in faster and more efficient exciton transport to the annihilator domain than that when an inert host is used (see the [supplementary material](#)).

UC emission via TTA

Figure 4(a) shows the excitation intensity dependence of the PL spectrum of the PtOEP/P(F-An) binary blend film, which exhibits PL at wavelengths below that of the excitation wavelength (532 nm). Because the spectral shape is consistent with the fluorescence spectrum of P(F-An), as shown in Fig. 2(b), this emission is attributable to delayed fluorescence from P(F-An) singlet excitons generated through the TTA of P(F-An) triplet excitons. The PtOEP/P(F-An)/bis-An ternary blend film also exhibits anti-Stokes-shifted emission, as shown in Fig. 4(b), which indicates that bis-An triplet excitons undergo TTA after TET from P(F-An). Singlet excitons of bis-An generated via the TTA, then, undergo singlet energy transfer (SET) to P(F-An), followed by delayed fluorescence from P(F-An). The UC emission intensity of the ternary blend is higher than that of the binary blend, as shown in Figs. 4, 5(c), and 5(d), suggesting efficient TTA in the ternary blend. The external quantum

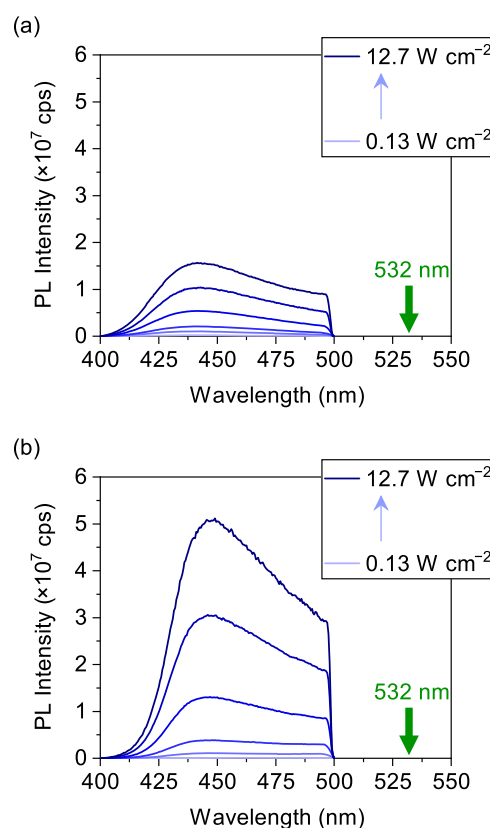


FIG. 4. PL spectra of the (a) PtOEP/P(F-An) binary and (b) PtOEP/P(F-An)/bis-An ternary blend films excited at 532 nm. The excitation intensity was varied over 0.13 W cm^{-2} – 12.7 W cm^{-2} from bottom to top. Emission above 500 nm is cut using a short-pass filter.

efficiency (EQE) of the UC emission, which is defined as the ratio of the number of upconverted photons emitted to the number of irradiated low-energy photons to the sample and can be written as $\text{EQE} = \Phi_{\text{UC}}/2 \times (1 - 10^{-A})$,³⁴ of the ternary device was determined to be 0.075%.

It is worth noting that the blend ratio of the PtOEP sensitizer is relatively high in this study (~ 9.1 wt. %) to increase PtOEP absorption. As the main aim of this study is to introduce a new strategy and demonstrate the concept, we prioritized improving the signal-to-noise ratios of the TA measurements. As a result, back-SET and re-absorption of the UC emission caused by the sensitizer as well as self-absorption by the host became large bottlenecks in enhancing Φ_{UC} in this study (see the [supplementary material](#)).^{34,35} In other words, there is still room to improve Φ_{UC} of our ternary systems by reducing the blend ratio of PtOEP. We obtained a higher Φ_{UC} of 0.36% from a ternary blend film with the blend ratio of 0.1:9:1. On the other hand, the EQE of the low-PtOEP content blend film decreased to 0.020% due to poor green light absorption. Simultaneously achieving sufficient light harvesting and suppressed back-SET is a major challenge to overcome and beyond the scope of this study.

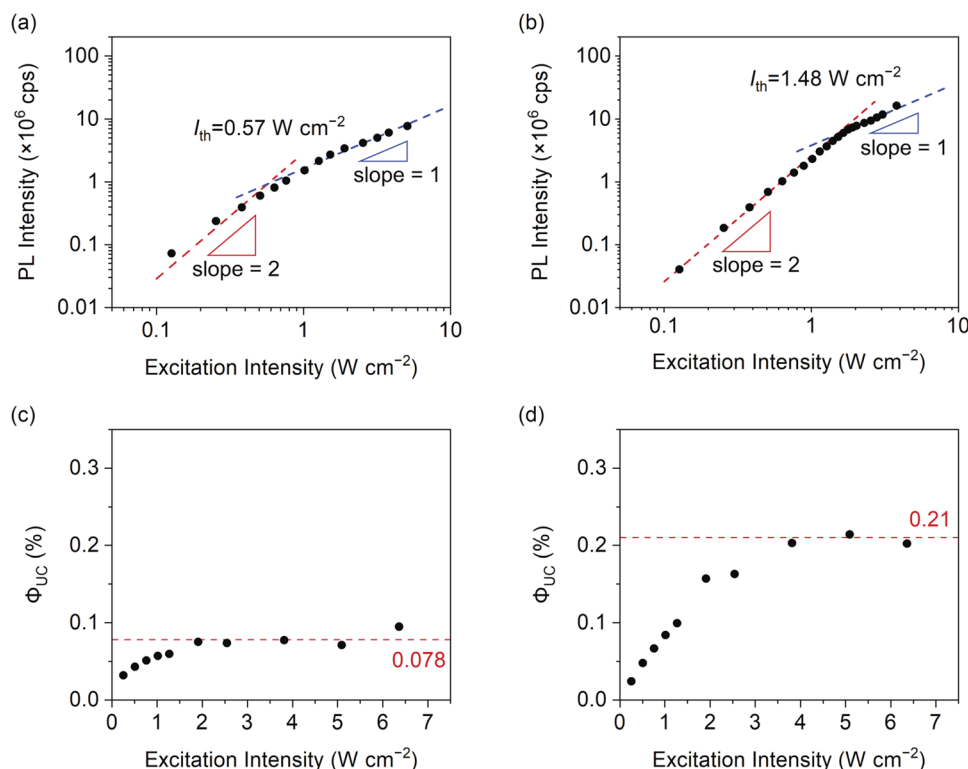


FIG. 5. Log-log plots of UC emission intensity I_{UC} as a function of excitation intensity I_{ex} for the (a) binary and (b) ternary blend films. The broken lines represent fitting curves with slopes of 2 (red) and 1 (blue). Φ_{UC} as a function of I_{ex} for the (c) binary and (d) ternary blend films.

Finally, we measured the excitation-intensity dependence of the UC emission to verify that our hypothesis that the ternary blend concept is beneficial for improving TTA efficiency is correct. Figures 5(a) and 5(b) show log-log plots of the UC emission intensity I_{UC} as a function of excitation intensity I_{ex} . The UC emission intensity increases quadratically at lower excitation intensities ($I_{UC} \propto I_{ex}^2$, red line), whereas it increases linearly at higher excitation intensities ($I_{UC} \propto I_{ex}$, blue line).^{4,36} The intersection of the two lines in each case led to characteristic threshold intensities I_{th} of 0.57 W cm⁻² and 1.48 W cm⁻² for the binary and ternary blend films, respectively. The threshold intensity I_{th} provides a useful figure-of-merit of TTA-UC, above which Φ_{UC} approaches its maximum value.^{4,36} I_{th} is expressed as

$$I_{th} = \frac{1}{\alpha \Phi_{TET} \gamma \tau^2}, \quad (4)$$

where α is the absorption coefficient of the UC device at the excitation wavelength. Based on the experimental results presented above, α , Φ_{TET} , and τ are 7.8×10^3 cm⁻¹, 0.78, and 570 μ s, respectively, for the binary blend, which leads to a γ of 3.3×10^{-16} cm³ s⁻¹. Equation (4) is still valid for our ternary blend system (see the supplementary material). The effective TTA rate coefficient in the ternary system γ^{eff} , where we hypothesize that the accumulation of triplet excitons in the small annihilator domain will boost TTA, was determined to be 2.1×10^{-15} cm³ s⁻¹ from I_{th} , which is nearly one order of magnitude larger than that of the reference binary system. The larger γ^{eff} in the ternary blend indicates that the introduced strategy positively enhances TTA efficiency. Note that I_{th} of the

ternary blend film is higher than that of the binary blend film due to the five-times-shorter triplet exciton lifetime τ as I_{th} is inversely proportional to the square of τ .

Another interpretation of the larger γ^{eff} observed for the ternary blend film may involve that the diffusion constant for triplet excitons in the bis-An domain is higher than that in the P(F-An) domain. Therefore, we also measured the blend-ratio dependence of I_{th} and Φ_{UC} to corroborate our conclusion. The higher annihilator content will reduce the exciton accumulation effect, whereas the diffusion constant is not disturbed or may even increase due to increased bis-An aggregation. As shown in Fig. 6, I_{th} increases with increasing bis-An blend ratio, whereas Φ_{UC} decreases at the same time.

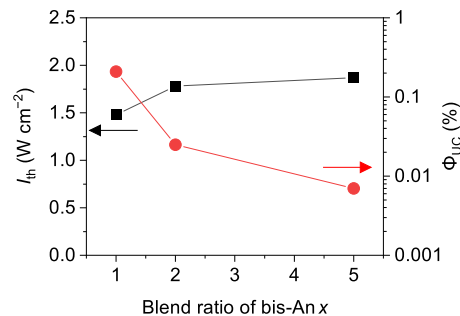


FIG. 6. Blend ratio dependence of I_{th} (black squares) and Φ_{UC} (red circles) for the PtOEP/P(F-An)/bis-An ternary blend films. The blend ratio was 1:(10 - x):x.

These results clearly rule out the second interpretation. Therefore, the origin of the enhanced γ^{eff} observed for the ternary blend can be rationalized by the accumulation of triplet excitons in small annihilator domains, which boosts the density dependent bimolecular reaction.

CONCLUSION

We introduced a new strategy for improving the efficiency of solid-state TTA-UC by designing a ternary-cascaded energy landscape for triplet excited states using PtOEP as the triplet sensitizer, P(F-An) as the exciton-transporting host, and bis-An as the annihilator. Spectroscopic measurements revealed that triplet excitons generated in PtOEP transfer to P(F-An) with a high QY of 96%, and subsequently to bis-An with a QY of close to unity, driven by the cascaded triplet energy landscape. As the amount of bis-An in the ternary blend film is low, the local triplet exciton density in the bis-An domain is higher than the overall density. Based on I_{th} values and the triplet exciton lifetimes of P(F-A) and bis-An, we found that exciton accumulation in the small annihilator domain has a positive impact on accelerating TTA. The annihilation rate coefficient of the ternary blend is nearly one order of magnitude higher than that of the binary counterpart. Although I_{th} of our ternary blend is relatively high at the moment, it is mainly due to the short lifetime of bis-An triplet excitons [five-times shorter than that of P(F-An)] and slower triplet diffusion. If we assume that the lifetime of the annihilator is 570 μs (same as the host) and D is one order of magnitude larger than that of bis-An, I_{th} will be reduced to 5.5 mW cm^{-2} , which is comparable to solar power in the 500 nm–550 nm region. To further improve our ternary blend concept, therefore, bis-An should be replaced with other annihilators that have longer triplet lifetimes as well as higher diffusion constants.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for phosphorescence spectra of P(F-An) and bis-An, PL spectra of bis-An, absorption and PL spectra of a PtOEP/bis-An binary blend film, back singlet energy transfer, re-absorption and self-absorption, triplet exciton decay kinetics in a PtOEP/PS film, assignment of P(F-An) triplet excitons, TA spectra of a ternary blend film, lifetime of bis-An triplet excitons, blend ratio dependence of I_{th} , blend ratio dependence of Φ_{UC} , UC emission from a PtOEP/PS/bis-An ternary blend film, and rate equations for ternary blend systems.

ACKNOWLEDGMENTS

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The authors declare no competing financial interests.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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