van der Waals solid solution crystals for highly efficient in-air photon upconversion under subsolar irradiation†

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Introduction

Photon upconversion (UC) creates high-energy photons that are useful for many purposes from less-useful, longer-wavelength photons. UC based on triplet–triplet annihilation (TTA) is an active area of research because of broad applicability spanning solar energy harvesting,1–3 optoelectronics,4,5 photochemistry,6–8 photoelectrochemistry,9–11 and bio-related applications.12,13 To date, the majority of reports on TTA-UC have studied liquid samples.1–3 However, liquid samples have risks of freezing, evaporation, and ignition, although some samples have high stability even against a flame.14,15 Furthermore, the large gas diffusivity in liquids requires suppression of damaging singlet oxygen.12,16–18 To resolve these issues, a solid UC system is being quested where triplet energy transfer (TET) from the sensitizer to the annihilator and triplet exciton diffusion should be efficiently designed (Fig. 1a).

After some initial works,23–28 the major obstacle has been the segregation of the sensitizer from the condensed phase of the annihilator,29–38 which forms an aggregate of the sensitizer and greatly diminishes the UC quantum yield (ΦUC) defined as
a maximum of 50% in this report), as typically reported for the combination of platinum octaethylporphyrin (PtOEP, Fig. 1b) and 9,10-diphenylanthracene (DPA, Fig. 1b).\textsuperscript{29–33}

To avoid this segregation issue, previous studies used a kinetically controlled approach\textsuperscript{30–38} where organic solids were quickly formed. For example, Simon and coworkers\textsuperscript{30} reported the fabrication of molecular glasses by rapidly cooling a hot melt of a sensitizer–annihilator mixture, but suppression of the aggregate was incomplete. Other studies\textsuperscript{31–38} formed organic thin films by casting a solvent solution on a flat substrate, where researchers, to an effective extent, suppressed the segregation of the sensitizer from the annihilator chromophores.

Some mechanistic studies showed, however, that the grain boundary and thus the grain size were the limiting factors for triplet exciton diffusion.\textsuperscript{39,40} Mikhnenko\textsuperscript{41} pointed out a significant degree of disorder in amorphous and polycrystalline organic thin films, in particular when the films were cast from solution.

Although the number of reports is limited, some studies used nonkinetic approaches.\textsuperscript{13,42–45} For example, Oldenburg \textit{et al.}\textsuperscript{42} fabricated sensitizer–annihilator heterojunctions of thin metal–organic framework (MOF) layers and reported $\Phi_{\text{UC}} < 0.1\%$ and an excitation threshold intensity ($I_\text{th}$) of ca. 1 mW cm$^{-2}$. Ogawa \textit{et al.}\textsuperscript{43} reported an aggregation-free dispersion of an anionic sensitizer in the crystal of an ionic annihilator utilizing ionic interactions between the chromophores ($\Phi_{\text{UC}} = 3\%$ and $I_\text{th} = 49$ mW cm$^{-2}$ in Ar), in which the photographs of the crystals, photostability data, and information on whether or not the crystals included the solvent methanol were not presented. Recently, Roy \textit{et al.}\textsuperscript{45} reported MOF crystals with $\Phi_{\text{UC}} = 1.95\%$ and $I_\text{th} = 5.1$ mW cm$^{-2}$. However, these values were, as in other MOF-based reports,\textsuperscript{13,44} for a liquid suspension and no photostability data were shown, whereas ref. 13 ($\Phi_{\text{UC}} = 0.64\%$ and $I_\text{th} = 2.5$ mW cm$^{-2}$) showed photodegradation data.

Surprisingly, van der Waals crystals formed by dispersion forces, representing the simplest class of organic crystals, have been nearly unexplored in the quest for high-performance UC solids. This lack of study may be because of the impact of the initial work\textsuperscript{29} that showed considerable segregation of PtOEP from the molecular crystal of DPA, which was also found in subsequent reports;\textsuperscript{10–13} the authors of ref. 43 described that dispersion-force based strategies sacrifice the advantages of crystalline systems.

The dispersion force approach has, however, many inherent advantages. First, by use of a weak dispersion force, the cost of the chromophores can be minimized because there is no need for elaborate moieties or ligands that cause specific interactions. Second, by use of a defined phase, samples can gain thermodynamic stability. This is in contrast with the previous strategy of using kinetically controlled methods because solids formed by such rapid methods rely on a nonequilibrium state.

Herein, we show, to our best knowledge, the first explicit exploitation of van der Waals forces to unequivocally resolve the long-standing sensitizer segregation problem by means of the classical but resurging concept of solid solutions.\textsuperscript{46} In solid solutions, represented by $\alpha$ and $\beta$ phases in Fig. 1b, mixing entropy is the driving force that molecularly disperses one component into a solid of the other component.\textsuperscript{46,47} Thus, the strategy envisaged here is to selectively generate dispersion-force-based $\alpha$ crystals and avoid emergence of a $\beta$ phase that is the sensitizer aggregate (Fig. 1b). We generated such solid solution crystals with an extremely low sensitizer: annihilator mole ratio (ca. 1:50000). Note that the similar term mixed crystal can include heterogeneous systems, such as a mixture of $\alpha$ and $\beta$ phases,\textsuperscript{47} which was not targeted here.
One of the key factors of the success here is attributable to our discovery of an excellent hydrocarbon annihilator, 9-(2-naphthyl)-10-[4-(1-naphthyl)phenyl]anthracene (ANNP, Fig. 1c), originally developed as a blue organic light-emitting diode (OLED) chromophore. Researchers often choose an asymmetric structure in OLED molecules. The key mechanism responsible for successful formation of θ-phase crystals is attributable to the 4-(1-naphthyl)phenyl side group, which features two distinct conformations and provides an interstitial site in the crystal. The sample was generated by a recrystallization method (Fig. 1d and Experimental section, ESI†) over 2–3 days. We thereby generated crystals that display extraordinary performance in air, as shown below.

Results and discussion

The crystals were pinkish (color of PtOEP) and transparent (Fig. 2a), with a flat-plate shape and thickness between ca. 50 and 250 μm (Fig. 2b). Polarization microscopy indicated twin-like multiple single-crystalline domains (Fig. 2b). The results were highly reproducible and we found no polymorph.

Optical absorption measurements of a crystal were straightforward because of the flat shape (Fig. S1, ESI†). The absorption spectrum of the single crystal (Fig. 2c) was identical to that of a dilute toluene solution of PtOEP, albeit with a 3.5 nm redshift of the peak. Fig. 2c also shows a spectrum of an over-saturated suspension of PtOEP in toluene, exhibiting an aggregation feature at 550 nm. The absence of the aggregation feature in the UC crystal indicates molecular dissolution of PtOEP in the crystal of ANNP and thus formation of a solid solution. Optical microscopic observations at a high magnification did not indicate aggregates (Fig. S2, ESI†). The spectrum did not depend on the light polarization (Fig. S3, ESI†) and thus PtOEP had no preferential orientation, at least for the direction normal to the largest crystal plane. From the absorption spectra, the concentration of PtOEP in the crystals was ca. 5 × 10⁻³ M (Table S1, ESI†). This corresponds to a significantly low sensitizer:annihilator mole ratio of ca. 1:50 000, which also supports that the crystals in Fig. 2 are a solid solution.

Below, we conducted all of our experiments in air. We excited the samples with a laser at 542 nm, which was 3.5 nm away from the absorption peak at 538.5 nm (Fig. 2c), unless otherwise stated. In this report, an excitation of 1 mW cm⁻² intensity at 542 nm corresponds to a sensitizer excitation density of 4.8 × 10⁻⁵ M s⁻¹. We used a microsphere-based setup (Fig. S4, ESI†) to investigate the photoemission from a single crystal.

During excitation at 542 nm, we observed an UC emission peaked at 434 nm (Fig. 3a). Conversely, we observed no UC emission from a reference crystal prepared with DPA by the same method (Fig. 3a and S3, ESI†). This demonstrates that the side groups of ANNP (Fig. 1c) played a key role in accommodating PtOEP in the crystal, as discussed below. The quantum yield of the phosphorescence of PtOEP (inset of Fig. 3a) was ca. 1 × 10⁻², indicating that the TET from PtOEP to ANNP was quantitative.

Notably, we greatly enhanced the emission intensity (Fig. 3a), ΦUC (Fig. 3b), and Ih (Fig. 3c) of the as-generated crystals by annealing at 90 °C for 4 days to ΦUC = 16.4% and Ih = 0.77 mW cm⁻² for the maximum and lowest values, respectively, for measurements of 10 samples. The average values were 13.4% and 2.1 mW cm⁻², respectively; Table S1 and Fig. S6 and S7 (ESI†) present the entire data. This dramatic enhancement is attributable to the improved crystallinity, as supported by the selective increase of the intensities of higher-angle peaks in the powder X-ray diffraction patterns by annealing (Fig. S8, ESI†). This hypothesis is further supported by the drastic increase of the triplet lifetime τ, from a value of 470 μs to a value of 5.1 ms (Fig. 3d). We also found a slight increase in the fluorescence quantum yield ΦFL (from a value of 38.7% to a value of 41.7%, Table S2, ESI†). Note that these values were lower than the ΦFL of ANNP in a toluene solution (3 × 10⁻⁶ M, deaerated by three freeze–pump–thaw cycles), which was measured to be 84.3%; refer to Fig. S9 in the ESI† for the fluorescence spectra of ANNP in the crystal and toluene solution. Therefore, the UC in the present materials system is largely limited by ΦFL in the crystalline state.

In Fig. 3c, we regarded 2.31 mW cm⁻², obtained by integrating an AM1.5 solar spectrum over the range of 538.5 ± 7 nm, as an equivalent solar irradiance for monochromatic excitation at 542 nm (542 nm) based on eqn (1):

\[ I_{542\text{nm}} = \frac{1}{545.5 - 531.5} \int_{531.5}^{545.5} I_{542\text{nm}} \, \text{d}z, \]

where I₅₄₂ₙₘ is the solar irradiance at 542 nm.
We passed the simulated sunlight through a 510 nm long-pass filter. We corrected the fluctuation of the excitation laser power during the measurement (refer to Fig. S14, ESI†). In panels (c) and (e), we acquired the data represented by open marks first by increasing the excitation light power, and then we acquired the data represented by filled marks to check the quantitative reproducibility.

The reproducibility check carried out using another sample batch (batch #2, 3.2 mg) reproduced the results with a slightly different $I_{th} = 0.216 \tau$. There are two additional features of the crystals. First, the crystals exhibit high photostability under continuous photo-irradiation in air (Fig. 3f, at 542 nm and 20 mW cm$^{-2}$). Such photostability may come from the close-packed molecular arrangement that is attributable to the high crystallinity. Second, thermo-gravimetric analysis (TGA) showed that the crystals contained 2.1 wt% solvent, and this quantity did not change by annealing (Fig. S11, ESI†). This indicates stable accommodation of the solvent, which can escape at a temperature greater than 150 °C (Fig. S11, ESI†).

We analyzed single-crystal X-ray diffraction (sc-XRD) data for a single crystal of the as-received ANNP (Fig. 4a) and a single domain cut out of the UC crystal (Fig. 4b). For the latter, only the case after annealing is shown here because the change in the crystallographic parameters caused by annealing is too small to be clearly evident pictorially (see Table S3 for these crystallographic data, ESI†). In Fig. 4b, PtOEP is not seen because of its significantly low concentration.

These data indicate that the 2-naphthyl group had two slightly different conformations, displayed in green and light pink whose ratio was 72 : 28 for both Fig. 4a and b. Conversely, in the spectrum shown in Fig. 2c, where $\varepsilon_\lambda$ is the molar absorption coefficient of PtOEP in the crystal at wavelength $\lambda$. However, such an equivalent irradiance has an unclear meaning, which can be also recognized by the lack of a clear definition for it.52 One clear problem of such an equivalent irradiance is that is outside the integration range of eqn (1).

We thus resort to direct evaluation using a solar simulator. We passed the simulated sunlight through a 510 nm long-pass filter and irradiated onto an ensemble (3.2 mg) of the crystals (batch #1) (Experimental section and Fig. S10, ESI†). We obtained the UC emission from the sample under one-sun (1 $\odot$) irradiance, whereas we observed no emission when we replaced the crystals by the same quantity of ANNP (inset of Fig. 3e). This verified that the blue fluorescence exclusively originated from UC. From the dependence of the UC emission intensity on the irradiance (Fig. 3e), to an ensemble (3.2 mg) of the UC crystals. Refer to the Experimental section for details. The inset shows the emission spectra acquired under 1 $\odot$ irradiance after being passed through a 510 nm long-pass filter, where the results obtained with the as-supplied ANNP powder (3.2 mg) are also presented. (f) Photostability test under continuous photo-irradiation in air (Fig. 3f, at 542 nm and 20 mW cm$^{-2}$).
the 4-(1-naphthyl)phenyl group had two substantially different conformations, displayed in light blue and orange whose ratio was 51:49 for both Fig. 4a and b. As evident in the center of the graphics, simultaneously adopting light-blue configurations by two adjacent ANNP molecules is prohibited because of their spatial overlap. Only “light blue + orange” or “orange + orange” pairs are allowed. This large conformational freedom suggests the presence of an interstitial space near it.

We discuss two notable points. First, as shown in Fig. 4b, there are ethanol molecules, shown in magenta color, near this conformational freedom with a mole ratio of ANNP: ethanol = 5:1. This ratio did not change by annealing, which agrees with the constant quantity of the included solvent (2.1 wt%) by annealing found by TGA. Here, 2.1 wt% ethanol corresponds to the mole ratio of ANNP: ethanol ≥ 4:1, which roughly agrees with the ratio determined by the sc-XRD analysis. Second, the crystal structure of the UC crystal did not change from that of the as-supplied ANNP, except for slight changes in the crystallographic parameters (Table S3, ESI†). This implies the rigidity of the ANNP arrangement in the crystal. From the sc-XRD data, the density of ANNP was 2.44 × 10^3 mol m^{-3}, which is much lower than those of anthracene (6.99 × 10^3 mol m^{-3})^15 and DPA (3.72 × 10^3 mol m^{-3})^26. We surmise that POEP molecules were also accommodated near that side group, although not directly evident by this analysis. Thus, the rigid and low-density network of ANNP and the movable 4-(1-naphthyl)phenyl side group are the key factors for realizing the concept we targeted. Notably, analysis of the sc-XRD data assuming toluene instead of ethanol was impossible. However, a trace quantity of toluene could have also been included. The inclusion of a much lesser quantity of toluene could be ascribed to the larger molecular volume of toluene in organic crystals (Voronoi–Dirichlet polyhedron volume, 157.5 Å^3) than that of ethanol (86.4 Å^3)^57.

Triplet exciton diffusion characterizes the properties of a solid TTA-UC system.^{41,58} Monguzzi et al. derived^59

\begin{equation}
I_{th} = \frac{1}{2\Phi_{TET}^\Sigma a_0 D_T \tau_T},
\end{equation}

where z is the sensitizer absorption coefficient at the excitation wavelength, $\Phi_{TET}$ is the quantum efficiency of the TET (assumed to be unity), $a_0$ is the minimum distance required for the annihilation of two annihilator triplets, and $D_T$ is the diffusion coefficient of the triplet exciton. For $a_0$, we used the average value of the nearest-neighbor and second-nearest-neighbor distances (7.44 and 8.84 Å, respectively, Fig. S12, ESI†). Using the average value of $I_{th}$ for monochromatic excitation at 542 nm (2.1 mW cm^{-2}), $\alpha$ (3.5 × 10^{-3} cm^{-1}), and $\tau_T$ (5.1 ms), $D_T$ was 9.22 × 10^{-7} cm^2 s^{-1}. The triplet exciton diffusion length $L_T$ is given by^{41,58}

\begin{equation}
L_T = \sqrt{2ZD_T\tau_T},
\end{equation}

where $Z$ is the dimensionality (from 1 to 3). We assume $Z = 3$, although this must be elucidated by future work. Depending on the custom, the other form

\begin{equation}
L_T = \sqrt{ZD_T\tau_T},
\end{equation}

is also used.^{41,58} From these relations, the present UC crystals have an $L_T$ ($L_T^\Sigma$) of 1.68 (1.19) μm. These values are approximately two orders of magnitude larger than the previously reported values for solid TTA-UCs,^{13,40,60,61} except $L_T \sim 1.6$ μm for water-suspended MOF nanoparticles of ca. 55 nm size.^{13} We compared these reported $L_T$ and $D$ values in Table S4 (ESI†). Thus, within a sphere with radius $L_T$ ($L_T^\Sigma$), there are approximately $1.25 \times 10^6$ (4.43 × 10^5) PtOEP molecules. Therefore, the significantly low concentration of POEP caused by our use of the z-phase (cf. Fig. 1b) was not problematic. These results reconfirm previous suggestions^39,40,43 that high crystallinity and a large crystalline domain are important for efficient UC in solids.

Finally, we discuss back-energy transfer (BET, Fig. 5a). BET was previously regarded as inevitable in a binary sensitizer–annihilator solid based on the estimated BET efficiency ($\Phi_{BET}$) as high as 40%.^{35} When Förster resonance energy transfer (FRET)^62 is the dominant mechanism, $\Phi_{BET}$ can be estimated by comparing the fluorescence decay time-constant ($\tau_{1A}$) from

![Fig. 4 Crystal structures determined from the single crystal X-ray diffraction data. (a) As-supplied ANNP and (b) UC crystal after annealing. Here, the side groups of ANNP have two distinct conformations (4-(1-naphthyl)phenyl group in light blue and orange, and 2-naphthyl group in green and light pink) that coexist in both cases. In panel (b), ethanol molecules are shown in magenta. Refer to Table S3 (ESI†) for the crystallographic data for all the cases. CCDC deposition numbers 2109297 and 2109300 contain the supplementary crystallographic data for panels (a) and (b), respectively.](image-url)
the UC crystals and $\tau_{1A}$ from the crystals prepared without PtOEP (Fig. 5b). Note that this method cannot be used to evaluate the BET caused by simple reabsorption of UC photons by the sensitizer because this reabsorption does not change $\tau_{1A}$. Thus, here we assess the BET by FRET that actively quenches the $^{1}A^{*}$ state. Our double-exponential fits in Fig. 5b yielded fast and slow components, where the time-constants were 2.50 and 7.04 ns for the UC sample, and 2.45 and 7.18 ns for the crystals prepared without PtOEP (pink). We generated these curves by averaging the curves acquired from 10 crystals for each case. We multiplied the data for the "UC crystal" by 1.21 to match the heights of these curves at time = 0.

Conclusions

We demonstrated the concept of explicitly exploiting van der Waals solid solution crystals consisting of only an $\alpha$-phase to resolve the long-standing problem of sensitizer segregation and realize materials with outstanding UC performance. Compared with the existing concept of using kinetically controlled fast-solidification conditions, the present approach has the advantages of (i) higher thermodynamic stability because of the reliance on (near-)equilibrium states and (ii) higher UC performance because of the simultaneous achievements of a long triplet exciton diffusion length and suppression of detrimental BET from the $^{1}A^{*}$ states. The factors in (ii) were caused, respectively, by the large single-crystal domain with high crystallinity and the significantly low concentration of the sensitizer. To form crystalline solid solutions, the interstitial site created by the bulky and movable side group of ANNP has been found to be the key factor, as supported by the comparison with a reference crystal prepared with DPA. The elucidated high $\Phi_{UC}$, low $I_{th}$, and high photostability in air are promising for applications. In particular, the extraordinarily low $I_{th}$ demonstrated by using simulated sunlight indicates that solar concentration optics are no longer needed for efficient upconversion of terrestrial sunlight. Probably the most important advantage of this concept lies in its reliance on the versatile van der Waals force and hydrocarbon annihilators. Overall, the proof-of-concept here is a major technical leap forward in the quest for high-performance UC solids, which will open up diverse photonics technologies in the future.

Author contributions

Y. M. conceived the idea and supervised the project. Y. M., H. A., S. K., and H. K. led the project. R. E. and M. H. performed the experiments and analyzed the data. H. K. and S. K. contributed to searching for and selecting the annihilator. R. E. conducted single-crystal X-ray diffraction measurements. H. U. and H. O. analyzed the diffraction data and determined the crystal structure. Y. M. and R. E. wrote the manuscript. All authors commented on the manuscript and agreed with the submission of this manuscript.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

† When calculating $I_{th}$, the definition of the laser spot area is important. Some researchers used the $1/e^2$ diameter to calculate the spot area for Gaussian laser beams. However, as described in ref. 63, the laser spot area calculated by the $1/e^2$ diameter yields a 50% lower excitation intensity than the actual peak intensity in the laser spot. In all previous TTA-UC papers authored by Y. M., a $FWHM$ diameter of the Gaussian profile was used to calculate the spot area, yielding a 1.44 times higher intensity than the actual peak intensity; i.e., conservative calculation of $I_{th}$. In the present article, however, all excitation beams had a top-hat intensity profile (cf. Fig. 54, ESI†), and therefore the intensity values for
all laser-based experiments matched the actual excitation intensity on
the sample.


