Aggregation-Induced Emission

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Aggregation-Induced Photon Upconversion through Control of the Triplet Energy Landscapes of the Solution and Solid States**

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***Abstract:** Aggregation-induced photon upconversion (iPUC) based on control of the triplet energy landscape is demonstrated for the first time. When a triplet state of a cyano-substituted 1,4-distyrylbenzene derivative is sensitized in solution, no upconverted emission based on triplet–triplet annihilation (TTA) was observed. In stark contrast, crystalline solids obtained by drying the solution revealed clear upconverted emission. Theoretical studies unveiled an underlying switching mechanism: the excited triplets in solution immediately decay back to the ground state through conformational twisting around a C=C bond and photoisomerization, whereas this deactivation path is effectively inhibited in the solid state. The finding of iPUC phenomena highlights the importance of controlling excited energy landscapes in condensed molecular systems.*

The development of smart photofunctional materials with controlled multiexciton processes has been one of the central issues in photochemistry and photophysics, which requires the ability to control excited-state energy landscapes. In this context, photon upconversion (UC) through annihilation between two long-lifetime excited triplets (TTA) has recently come into the spotlight because of its wide applications that range from renewable energy productions to bioimaging and phototherapy.[1] TTA-UC processes occur in association with a series of photochemical events (see Figure S1 in the Supporting Information). First, a triplet excited state of a donor (sensitizer) is formed by intersystem crossing (ISC) from a photoexcited singlet state, and the formed donor triplets populate acceptor (emitter) excited triplets by triplet–triplet energy transfer (TTET). When two acceptor molecules in the triplet state diffuse and come into collision during their lifetime, a higher singlet energy level is formed by TTA, which consequently produces delayed upconverted fluorescence. To date, efficient TTA-UC has been achieved for a molecularly dispersed solution state, as it allows fast diffusion and collision of excited molecules.[2] However, the use of volatile organic solvents hampers the development of TTA-UC for practical applications, and thus it is highly desired to develop solid-state TTA-UC systems. Although amorphous polymer films have been employed as solid matrixes, they inevitably restrict the diffusion of excited triplet molecules, thereby necessitating the undesired use of high-power incident light to ensure effective concentration of excited triplets.[3] Condensed chromophore systems are attractive since they allow the high mobility of excitons instead of molecular diffusion,[1k,n,o] and organic crystals are a particularly promising class of materials with high triplet diffusivity.[1e,4] In this regard, molecules showing aggregation-induced emission (AIE) or aggregation-induced enhanced emission (AIEE) are particularly attractive, because they are highly emissive even in the neat crystalline state.[5] To date, however, the studies on AIE phenomena have largely been focused on the excited singlet states of molecular aggregates, and their triplet photochemistry especially in relation to TTA-UC phenomena has been unexplored. It is of great significance if the excited triplet energy levels undergo changes by aggregation, thereby allowing control over TTA-UC to be achieved.

Here we report the first example of aggregation-induced photon upconversion (iPUC) which is based on the controlled potential energy landscape of the excited triplet state. As a proof of concept, we employed one of the best-known structural motifs for AIE, cyano-substituted oligo(*p*-phenylenevinylene), as an acceptor.[5b,6] When triplet states of this acceptor were populated by a triplet sensitizer in solution, the TTA-UC emission was not observed. In contrast, crystalline powder samples obtained after drying this mixed solution showed a clear UC emission. Theoretical studies and control experiments unveiled an underlying mechanism: in solution, an enhanced conformational twisting around the double bond and photoisomerization in the excited triplet state (T_1) results in immediate intersystem crossing to the ground state (S_0),

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whereas this large structural change is effectively prohibited in the solid state. The difference in the energy landscape of excited triplet states between the solution and solid states was further amplified through the multiexciton TTA process as a remarkable ON/OFF switching of the UC emission depending on the molecular environment (Figure 1).

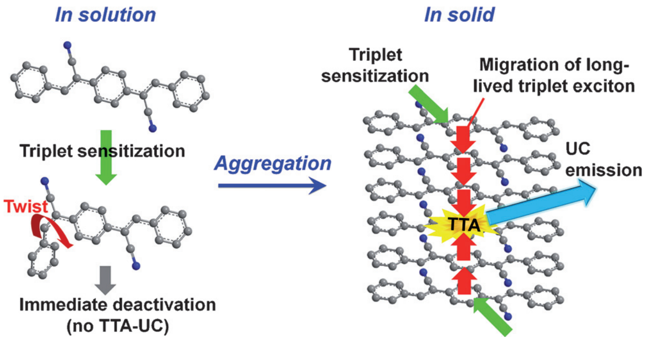

Figure 1. A schematic representation of aggregation-induced photon upconversion (iPUC). In solution, a sensitized triplet of the acceptor (emitter) immediately undergoes nonradiative deactivation by conformational twisting around a C=C bond and photoisomerization, thereby resulting in no upconverted emission. On the other hand, such a deactivation pathway is effectively prohibited in crystals. Sensitized triplet excitons can migrate between the regularly aligned acceptors and eventually annihilate (TTA) to give upconverted emission.

Cyano-substituted oligo(*p*-phenylenevinylene)s represent an important family of chromophores showing AIE properties.[5b,6,7] The introduction of a bulky cyano group on the vinylene moieties leads to a twisted conformation around the double bonds in solution, which enables torsional nonradiative deactivation of excited singlets. We prepared (2*Z*,2′*Z*)-2,2′-(1,4-phenylene)bis(3-phenylacrylonitrile) (**1**, Figure 2 a) according to the reported procedure.[8] Yoon and Park reported that **1** shows an enhanced fluorescence quantum yield in the aggregated state compared with the molecularly dispersed solution.[9] For sensitization of the triplet of **1**, Pt^{II} octaethylporphyrin (PtOEP) was chosen as a donor, because its absorption spectrum reveals a small overlap with the emission of **1** (Figure 2 b). PtOEP in THF exhibited a typical Soret band at 403 nm and Q bands at 510 and 550 nm in the absorption spectra, and a phosphorescence peak was observed at 645 nm. The spectra of **1** in THF showed a typical π-π^* absorption band at 352 nm, with its fluorescence at 426 nm. On the other hand, a powder sample of **1** prepared by drying its THF solution showed a blue-shifted absorption band at 295 nm with a shoulder at 366 nm, and a slightly red-shifted emission was observed at 441 nm. These spectra are in accord with the previous observations.[9] We then doped the crystals of **1** with PtOEP by simply casting a mixed solution of **1** and PtOEP ([**1**]/[PtOEP] = 500:1) in THF. Microscopy images of the cast sample showed weak red phosphorescence of PtOEP and blue-green fluorescence of **1** from the same area, thus indicating the absence of macroscopic phase segregation (see Figure S2 in the Supporting Information). A fluorescence spectrum of the obtained powder showed a band at 485 nm (see Figure S3a in the Supporting Information) which is red-shifted compared with the emission of pure **1** powder. This result suggests a change in the molecular packing of **1** upon doping of the donor PtOEP. To investigate this point, we carried out X-ray powder diffraction (XRPD) measurements of **1** in the absence and presence of PtOEP (see Figure S3b in the Supporting Information). It was confirmed that the diffraction peaks of **1** were not affected by the addition of PtOEP, while several new peaks emerged, for example at $2\theta = 13.8, 16.3, 17.8$, and 18.4°. This emergence of new peaks is not ascribed to the presence of different polymorphs or macroscopic phase separation of donor PtOEP, because all the peaks are assignable to the simulation patterns obtained from the crystal structure of **1**,[9] that is, the addition of PtOEP served to change the packing structure of **1** to make it even closer to the previously solved crystal structure of **1**. These spectroscopic and XRPD results strongly support that the donor PtOEP was successfully doped in the crystals of **1**.

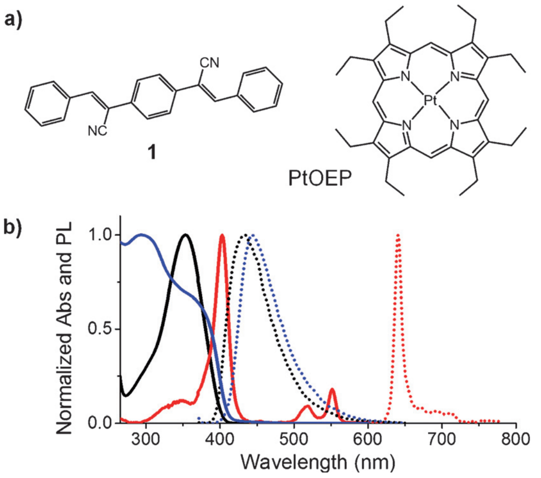

Figure 2. a) Molecular structures of acceptor (emitter) **1** and donor (sensitizer) PtOEP. b) Normalized absorption (solid lines) and luminescence (dotted lines) spectra of solutions of **1** (black, 0.1 mM) and PtOEP (red, 0.1 mM) in THF, and of a solid powder of **1** made from its THF solution (blue).

We then measured upconverted emission spectra of the THF solution and solid powder of PtOEP/**1** mixture in deaerated conditions under excitation at 532 nm by a green laser (Figure 3 a). Scattered incident light could be removed effectively by using a short pass filter. As a result, no upconverted emission was observed in solution regardless of the excitation power (measured up to 220 mW cm^{-2}). Very interestingly, on the other hand, the solid powder clearly showed upconverted emission at 485 nm. The PtOEP/**1** mixed powder showed a microsecond-scale lifetime, which supports the observed UC emission being produced from long-lifetime triplet species (Figure 3 b).[1c] A lifetime of an acceptor triplet $\tau_{A,T}$ of 90 μs was obtained by considering the relationship of $I_{UC}(t) \propto \exp(-t/\tau_{UC}) = \exp(-2t/\tau_{A,T})$ (τ_{UC}: UC emission lifetime, $\tau_{A,T}$: acceptor triplet lifetime) in the longer timescale region, when the annihilation efficiency becomes negligible compared with the spontaneous decay of the triplets.[3d,10]

In general, the upconverted emission intensity through annihilation between sensitized acceptor triplets (TTAs)

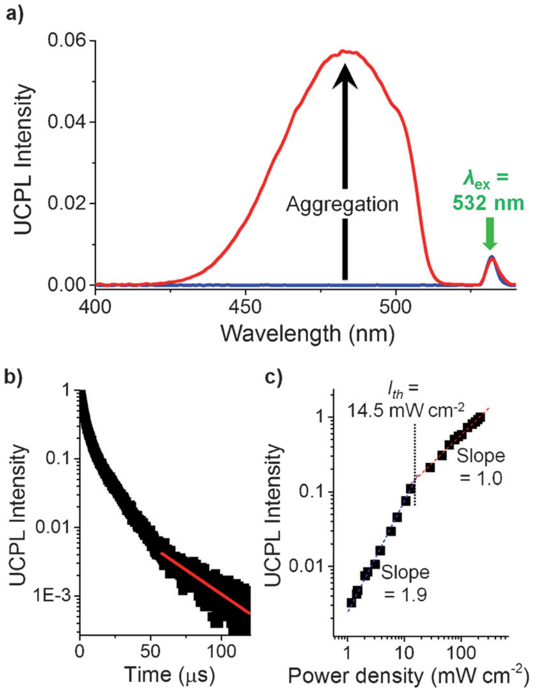

Figure 3. a) Photoluminescence spectra of the PtOEP/**1** pair in THF deaerated by repeated freeze-pump-thaw cycles (blue line, [PtOEP] = 0.1 mм, [**1**] = 10 mм) and in the solid powder under vacuum (red line, PtOEP/**1** = 1:500). A 532 nm laser was used as an excitation light source. A short pass filter (510 nm) was used to remove the scattered incident light. b) UC emission decays at 480 nm of the PtOEP/**1** mixed powder (PtOEP/**1** = 1/500) under pulsed excitation at 531 nm. The red fitting curve was obtained by considering the relationship of $I_{UC}(t) \propto \exp(-t/\tau_{UC}) = \exp(-2t/\tau_{A,T})$. c) UC emission intensity observed for the PtOEP/**1** mixed powder (PtOEP/**1** = 1/500) as a function of the power density of the 532 nm excitation. The dashed lines are fitting results with slopes of 1.9 (blue) and 1.0 (red), and I_{th} was determined as 14.5 mW cm^{-2} from the crossing point of these two lines. UCPL: upconverted photoluminescence.

shows a quadratic dependence to the incident light power at a weak excitation region, as expected for the bimolecular annihilation process.[1b,h,11] In this regime, TTA is inefficient because of the prevailing nonradiative decay of acceptor triplets. Meanwhile, by increasing the incident power above the threshold excitation intensity I_{th}, TTA becomes the main deactivation channel for the acceptor triplets, where the overall UC process is optimized. This changes the excitation power dependence from quadratic to linear. The mechanistic details of these TTA-UC kinetics have been well documented in previous reports.[1b,h,11] Figure 3c presents a double logarithm plot for the UC emission intensity of the PtOEP/**1** mixed powder as a function of the power density of the incident light. At the lower-power regime (< 14.5 mW cm^{-2}), a slope close to 2 was observed, whereas it changed to 1 at the higher-power density (> 14.5 mW cm^{-2}). These observations provide decisive evidence for the TTA-based UC mechanism in the solid state, and a relatively low I_{th} value of 14.5 mW cm^{-2}.[3d–f] This provides the first demonstration that AIE chromophores are applicable for aggregation-induced photon upconversion (iPUC) phenomena.

To unveil the reason why TTA-UC is inhibited in solution, each photochemical process was scrutinized. First, we examined the donor-to-acceptor TTET process. In the presence of acceptor **1**, the phosphorescence of PtOEP around 650 nm was almost quenched (Figure 4a). A comparison of phosphorescence intensities obtained with and without acceptor gives a donor-to-acceptor energy-transfer efficiency of 99 %. This was further supported by measurements of the phosphorescence lifetime. Without acceptor, the phosphorescence of PtOEP at 650 nm in THF solution showed a single exponential decay with a lifetime of 66 μs (Figure 4b). However, in the presence of the acceptor **1**, the phosphorescence decay became significantly faster and almost overlapped with the instrument response function (IRF), which is consistent with the phosphorescence quenching data.[12] Thus, the triplet energy is almost quantitatively transferred to the acceptor. We then investigated the generation of acceptor triplets by measuring transient absorption spectra of the PtOEP/**1** mixed solution (see Figure S4 in the Supporting Information).[13] No detectable signal was observed over the examined time scale, thus implying that the triplet lifetime of **1** in solution is shorter than 100 ns. This is in remarkable contrast with the observed triplet lifetime $\tau_{A,T}$ of 90 μs in the solid crystalline state (Figure 3b). From these results, the acceptor triplets should be produced in solution, but their lifetime seems to be too short for them to come into collision for bimolecular annihilation.

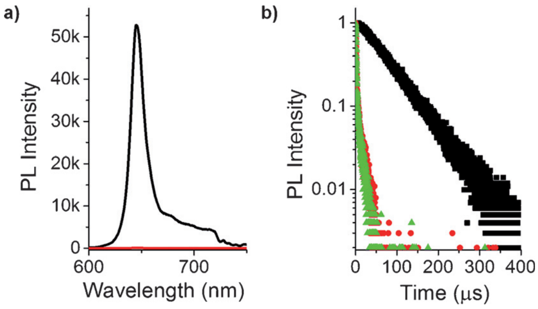

Figure 4. a) Phosphorescence spectra of PtOEP in the absence (black) and presence (red) of **1** in deaerated THF ([PtOEP] = 0.1 mм, [**1**] = 10 mм) under excitation by a 532 nm laser. b) Decays of the donor PtOEP phosphorescence at 650 nm in the absence (black) and presence (red) of acceptor **1** in deaerated THF ([PtOEP] = 0.1 mм, [**1**] = 10 mм), together with instrument response function (IRF, green), under a pulsed excitation at 531 nm.

To understand the underlying mechanism for the iPUC phenomena newly found in this study, we carried out geometry optimization at the DFT level on the ground state (S_0) and the excited triplet state (T_1) of **1** both in solution and in the crystal. S_0min and T_1min represent the most-stable optimized structures in the S_0 and T_1 states. In THF, S_0min of **1** shows a dihedral angle of one of the two C=C bonds, $\theta(C_1C_2C_3C_4)$, of 178° (see Tables S1 and S2 in the Supporting Information). On the other hand, T_1min of **1** has a drastically altered $\theta(C_1C_2C_3C_4)$ value of 78°. The C_2–C_3 bond was found to be longer in T_1min (1.47 Å) than that in S_0min (1.36 Å). This reflects that the $\pi \rightarrow \pi^*$ transition character of T_1 state adds single bond nature to the $C_2{-}C_3$ bond, which stabilizes the twisted T_1 conformation. To check the possibility of intersystem crossing (ISC) from T_1 to S_0, it is necessary to calculate the energy levels of T_1 and S_0 at the same structure in the vicinity of the T_1 equilibrium. Therefore, we calculated these energy levels at the T_1min structure. Interestingly, the energy level of the T_1 state (1.62 eV) was found to be lower than that of the S_0 state (1.88 eV) at the T_1min structure in THF (see Table S1 in the Supporting Information), which suggests the crossing of the T_1 and S_0 energy levels.

In contrast, such unusual inversion behavior was not observed in the crystal. The dihedral angle $\theta(C_1C_2C_3C_4)$ shows only a small change from S_0min (175°) to T_1min (166°). Similar to **1** in THF solution, the elongation of the $C_2{-}C_3$ bond from 1.35 Å (S_0) to 1.47 Å (T_1) was observed in the crystal, however, the rotation around the $C_2{-}C_3$ bond was prohibited in the rigid crystalline environment. The energy level of the T_1 state (1.88 eV) is higher than that of the S_0 state (0.55 eV) at the T_1min structure (see Table S1 in the Supporting Information). Therefore, crossing between the T_1 and S_0 levels is prevented in crystals. This is consistent with the observed relatively long triplet lifetime and corresponding TTA-UC in the crystalline state.

Making potential energy curves is useful to investigate the details of the T_1-to-S_0 ISC process. We estimated the S_0 and T_1 potential energies of **1** in THF as a function of the C=C bond rotation by a series of constrained geometry optimization calculations with fixed dihedral angle $\theta(C_1C_2C_3C_4)$ values. The S_0 potential energy curve shows a large rotational energy barrier of 1.33 eV at $\theta(C_1C_2C_3C_4) = 90°$ (light blue line in Figure 5). As noted above, to follow the actual T_1-to-S_0 ISC process, it is necessary to calculate the energy level of the S_0 state at the T_1 structure (denoted as $S_{0(\mathrm{T1\ structure})}$, dark blue line in Figure 5). Reflecting the changes in the molecular structure, such as the $C_2{-}C_3$ bond length, the energy level of $S_{0(\mathrm{T1\ structure})}$ is always higher than that of S_0, while the angular dependence is basically maintained. Significantly, on the T_1 energy landscape (red line in Figure 5), passing from the initial state (point A) to the T_1 equilibrium does not involve any increase in potential energy, and thus this relaxation process should occur spontaneously.

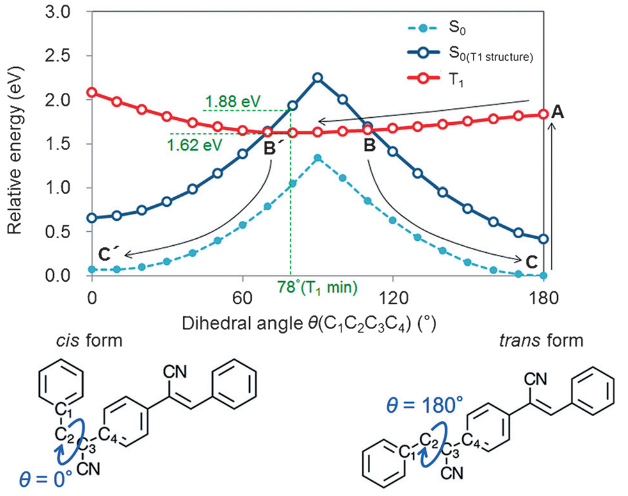

Figure 5. Potential energy curves of S_0 at its optimized structures (light blue line), S_0 at optimized structures of T_1 (denoted as $S_{0(\mathrm{T1\ structure})}$, dark blue line), and T_1 at its optimized structures (red line) as a function of the torsional angle $\theta(C_1C_2C_3C_4)$ around the $C_2{-}C_3$ bond for **1** in THF. All the energy levels were calculated relative to the energy of the S_0 state at the most-stable S_0 structure (S_0min, $\theta = 178°$, see Table S1 in the Supporting Information).

Consequently, the potential energy curves of T_1 and $S_{0(\mathrm{T1\ structure})}$ give two crossing points at around $\theta = 70°$ and 110° (points B and B′). These crossing points are located very close to the T_1 equilibrium geometry; the activation energies are less than only 0.03 eV. After passing the crossing points (B or B′), the formed S_0 state would naturally relax into stable conformations (points C or C′) through the potential energy curves of S_0. This barrier-free transition from the T_1 to S_0 state gives a clear account of the experimentally observed short triplet lifetime of acceptor **1** in solution.

It is interesting to note that the twisted conformation around the C=C bond is known to play an important role as a reaction intermediate in the *trans–cis* isomerization of stilbene and related compounds.[13,14] Similarly, our theoretical results (Figure 5) suggest the occurrence of triplet-mediated photoisomerization in our system. To confirm this experimentally, we measured absorption, ^{1}H NMR, and mass spectra after prolonged irradiation of the deaerated THF solution of the PtOEP/**1** pair ([PtOEP] = 0.1 mm, [**1**] = 10 mm, $\lambda_{ex} = 520$ nm) with light. The decrease in the absorbance at 350 nm and the increase in absorbance at around 290 nm were observed after 2 h irradiation with light, and longer irradiation (3 h) did not make further large changes (see Figure S5 in the Supporting Information). The NMR spectra showed an appearance of new signals at around 7.3 and 7.8 ppm together with decreases in the intensity of the corresponding original signals (see Figure S6 in the Supporting Information). These observations agree well with the previously reported *trans*-to-*cis* isomerization of cyanostilbene derivatives.[14d,e] The other side reactions, such as a [2+2] dimerization, did not occur, as confirmed by mass spectrmetry after photoirradiation for 3 h. From these results, the deactivation path from T_1 to S_0 involves photoisomerization in addition to nonradiative thermal deactivation.

To prove the validity of the above considerations, control examinations were performed using 1,4-distyrylbenzene without cyano substituents (**2**) and with methyl substituents (**3**; see Figure S7 in the Supporting Information. Figure S8 in the Supporting Information shows the theoretical potential curves of T_1 and S_0 of **2** in solution as a function of dihedral angle around a C=C bond. In contrast to the barrier-free T_1-to-S_0 transition observed for **1**, there is a small activation barrier (0.15 eV) for **2** to pass from the original T_1 state (point D) to the crossover point with the potential curve of $S_{0(\mathrm{T1\ structure})}$ (point E). Possible reasons for this behavior are the lower steric hindrance around the C=C bond (see Figure S8 in the Supporting Information) and the loss in stabilization of the T_1 state by electron-withdrawing cyano groups. The former reason is more plausible, because we observed the barrier-free T_1-to-S_0 transition for **3**, which has steric hindrance and weak electron-donating methyl substituents (see Figure S9 in the Supporting Information). These results predict the existence of a certain triplet lifetime for **2** even in solution. Actually, in THF solution as well as solution-cast crystals, the PtOEP/**2** pair showed upconverted delayed blue fluorescence with microsecond-scale lifetimes upon excitation with the green light (see Figures S10 and S11 in the Supporting Information). The log-log plots of UC emission intensities against excitation power density showed transitions from quadratic to linear dependences, which are characteristic of TTA-based UC (see Figure S10 in the Supporting Information). In addition, transient absorption measurements of the PtOEP/**2** mixture in THF showed T_1-T_n absorption bands from 450 nm to 500 nm in a microsecond timescale (see Figure S12 in the Supporting Information). Similar transient absorption behavior has been reported by Tokumaru and co-workers for T_1-T_n absorption of a 1,4-distyrylbenzene derivative.[13] These results confirm that the immediate deactivation of the excited triplet state in solution is responsible for the unique iPUC phenomena.

In summary, we have demonstrated the first example of aggregation-induced photon upconversion (iPUC) based on the control of triplet energy landscapes between the solution and solid states. The iPUC behavior observed for the PtOEP/**1** pair occurred as a consequence of the extremely short lifetime of the acceptor triplet in solution as a result of the barrier-free T_1-to-S_0 intersystem crossing (ISC) and the effective prohibition of this conformational-twisting-driven transition in the rigid crystalline state. Although there have been many reports on dynamic conformational changes in excited triplet states,[13,14] control of the multiexciton TTA-UC process based on a change of the molecular environment has been unprecedented. The UC emission by triplet energy migration and annihilation by using AIE molecules provides a powerful means to realize TTA-UC selectively in condensed states, which would be useful for imaging and sensing applications based on background-free UC emissions. From the perspective of controlling multiexciton phenomena in condensed molecular systems, the present study shows significant advances. First, it unlocked the latent opportunities of AIE molecules in the triplet state. The previous AIE systems in molecular crystals show fluorescence based on single-excitation processes, which naturally have a finite ON/OFF ratio between the solid and solution states.[5d,15] Meanwhile, since the UC emission requires two triplet excitons to meet, the complete OFF state can be realized under the common excitation power regime. Second, we observed TTA-UC in the crystalline state without macroscopic segregation of donor molecules. We instead observed the improved molecular alignment of **1** upon doping the donor molecules. This indicates that by properly tuning the intermolecular interactions between donors and acceptors, it might be possible to develop more efficient TTA-UC (or iPUC) in the solid state. We envisage the integration of these iPUC phenomena with recently developed soft supramolecular[1k,o] or phase cross-over molecular systems,[16] which would lead to synergistic control of the triplet energy landscapes and consequent regulation of the multiexcitation processes.

Keywords: aggregation · donor–acceptor systems · photochemistry · photon upconversion · triplet-triplet annihilation

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