Two-photon excited fluorescence materials usually suffer from inefficient two-photon absorption (TPA) and non-radiative excited states. Here, upconversion fluorescence in an electron donor-acceptor (DA) exciplex doped with fluorescent emitters are systematically investigated. It has been found that the undoped DA exciplex exhibits enhancements of $\sim 129\%$ and $\sim 365\%$ in upconversion fluorescence compared to donor- and acceptor-only systems, respectively. Interestingly, photoluminescence quantum yields (PLQYs) up to $\sim 98.65\%$ were measured and immensely enhanced upconversion fluorescence was observed after doping various fluorescent emitters into the DA exciplex. Our results reveal the existence of two-photon excited energy harvesting in a thermally activated delayed fluorescence (TADF) DA exciplex doped with fluorescent emitters, via reverse intersystem crossing followed by rapid Förster resonance energy transfer. Moreover, the additional gain mechanism related to intermolecular CT interaction that occurs at the TPA stage is found in the TADF DA exciplex system.

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1. INTRODUCTION

In last few decades, two-photon excited fluorescence (TPEF) has attracted increasing research interest for its growing list of applications that include two-photon imaging. Researchers are attracted by its tremendous advantages: high three-dimensional resolution, strong penetrability to biological tissues, and restricted photobleaching and phototoxicity [1–3]. Technically, TPEF materials with excellent two-photon absorption and light emission properties are essential and highly desired for two-photon imaging applications. Unfortunately, two-photon excitation is intrinsically much less efficient than a one-photon process [4–6]. To solve this problem, great efforts have been devoted to the design and discovery of dye molecules with large two-photon absorption cross-sections; particularly, complicated molecular architectures in view of the relationship between the two-photon absorption cross-section and the dipole moment [7–9]. However, this often results in inefficient radiative excited states due to the fast "internal conversion" mechanism, together with a great increase in the cost of commercial products caused by increased synthetic steps [10,11]. As a result, developing a facile, efficient strategy to obtain low-cost, highly efficient TPEF dyes with enhanced performance remains a challenge [12–14].

Besides two-photon absorption, there is another key parameter that is crucial for TPEF dyes: the fluorescence quantum efficiency. The fluorescence quantum efficiencies of organic chromophores are greatly restricted by the nonradiative excited states [15,16]. Recently, great advances have been made in the new emerging field of thermally activated delayed fluorescence (TADF) materials by minimizing the energy splitting, $\Delta E_{ST}$, between singlet and triplet states to efficiently facilitate the reverse intersystem crossing (RISC) process from triplet to singlet states [17–19]. This energy harvesting mechanism is ideal for TPEF dyes, although very few intrinsic (single-component) TADF molecules have been discovered to show two-photon absorption (TPA) properties. The energy harvesting becomes even more efficient in extrinsic TADF materials in which RISC occurs in exciplexes (EX) of designed electron donor (D) and acceptor (A) [20–22]. In particular, the light emission can be further enhanced by adding a tiny amount of fluorescent dopant into TADF hosts [23,24]. The rapid Förster resonance energy transfer (FRET) from the singlet EX states to the lowest
sight wavelength of 280.6 nm, pulse width of 945.1 ps, and
photoluminescence (PL) decay characteristics were measured with a
and the excitation wavelength is set to 330 nm. Transient pho-
light source is a xenon lamp, ultraviolet ranges, respectively, and we set it at 375 nm to
General Instrument Co., Ltd., Beijing). A tungsten lamp and
luminescence technology (TAPC) as the donor and
a deuterium lamp are used as the light sources in the visible and
a UV-vis spectrophotometer (TU-1901, Beijing Purkinje
vent at a concentration of 20 mg/mL. Subsequently, the solu-
3TPYMB, the green fluorescent emitter molecule TTPA
method. The donor molecule TAPC and acceptor molecule
TAPC:3TPYMB blends were prepared using a drop-casting
Luminescence Technology Corp. (Lumtec), New Taipei City,
the advantages of two-photon absorption and a high quantum
yield, so that they may have broad application prospects in the
field of two-photon fluorescence imaging.

2. EXPERIMENTAL SECTION

Materials preparation: The thin films of pristine TAPC [99.5%,
Luminescence Technology Corp. (Lumtec), New Taipei City],
3TPYMB (99%, Lumtec), TAPC:3TPYMB blend, TTPA-
doped TAPC:3TPYMB blends, and DCM-doped
TAPC:3TPYMB blends were prepared using a drop-casting
method. The donor molecule TAPC and acceptor molecule
3TPYMB, the green fluorescent emitter molecule TTPA
(99%, Lumtec) and the orange fluorescent emitter molecule
DCM (99%, Lumtec) were dissolved in tetrahydrofuran sol-
vent at a concentration of 20 mg/mL. Subsequently, the solution
was stirred overnight prior to film preparation. Quartz
substrates were selected for optical property measurements.
A tetrahydrofuran solution of each emitter dopant
(10−3 mol/L) was used for the measurement of absorption.

Measurements: The absorption spectra were measured using a
UV-vis spectrophotometer (TU-1901, Beijing Purkinje
General Instrument Co., Ltd., Beijing). A tungsten lamp and
datherium lamp are used as the light sources in the visible and
ultraviolet ranges, respectively, and we set it at 375 nm to
change the lamp. The photoluminescence spectra were mea-
sured using a fluorescence spectrophotometer (F-4500,
Hitachi, Ltd., Tokyo). The light source is a xenon lamp, and the excitation wavelength is set to 330 nm. Transient pho-
toluminescence (PL) decay characteristics were measured with a
fluorescence spectrometer (FLS920, Edinburgh Instruments
Ltd., Livingston, Scotland) using an EPLED-280 laser (excita-
tion wavelength of 280.6 nm, pulse width of 945.1 ps, and
bandwidth of 11.0 nm). Photoluminescence quantum yields
(PLQYs) were measured by an absolute PL quantum yield mea-
surement system (FLS920, Edinburgh Instruments) with an
integrating sphere under an excitation wavelength of
330 nm (xenon lamp). For the measurement of two-photon
induced fluorescence spectrum, a Ti:sapphire femtosecond
pulse amplification system (Legend Elite series, pulse width of
25 fs, repetition rate of 1000 Hz, Coherent Inc., Santa
Clara, CA) was used to excite the samples. The upconverted
emission was measured using a monochromator (Omi-
lambda300, Zolix Instruments Co., Ltd., Beijing) together with a
PMTH-S1C1-CR131 photomultiplier tube.

3. RESULTS

A. TPEF Studies of DA Exciplex

Molecular structures of the donor TAPC and acceptor 3TPYMB
are shown in Fig. 1(a). For TAPC, two electron-rich tri(p-tolyl)
amine groups are chemically bridged by a cyclohexane ring
formed by a D−π-D structure [27,28]; for 3TPYMB, a starburst
structure is formed by an electron-deficient trimesitylborane
core and pyridyl branches [29,30]. These TPA-active molecular
structures indicate that an effective TPA may exist in these two com-
ponents [31–33]. Figure 1(b) shows the energy-level alignment of
TAPC and 3TPYMB, in which the highest occupied molecular
orbital (HOMO) and the lowest unoccupied molecular orbital
(LUMO) energies are taken from literature [34−36]. The large
energy offsets between HOMO (1.2 eV) and LUMO
(1.3 eV) enable an efficient charge separation and the following
cexciplex formation processes after being excited [37].

Figure 1(c) shows the normalized room temperature PL and
optical absorption spectra of films of the pristine TAPC and
optical absorption spectra of the donor TAPC and acceptor 3TPYMB,
and the TAPC:3TPYMB (1:1) DA blend. The PL
emission spectra of TAPC and 3TPYMB peak at 384 nm and
385 nm, respectively; whereas the PL emission spectrum from
the blend shows a significantly red-shifted single peak at
≈460 nm. This indicates near 100% formation of photoexcited
DA exciplexes in the blend [38,39]. Based on a modified
Rehm–Weller equation: −ΔG_{CS} = E_{exciton} − E_{exciplex} [40], a
suitable value (≈0.6 eV) of the driving force −ΔG_{CS} for exci-
plex formation was estimated [41,42]. This may explain the
observed PL emission spectrum from the DA blend. In com-
parison, the optical absorption spectrum from the blend shows
contributions entirely from D and A molecules. No obvious
optical absorption in the range of the DA exciplex, which is
significantly red-shifted compared to that of excitons of D
or A, can be observed. This reveals that the exciplexes in the
blend originate from a photoexcited D and/or A instead of
optical transitions from the ground states to the EX states
[43]. We note that this is different with another DA-type
material named ground state charge-transfer (CT) cocrystals,
in which the optical absorption occurs via transitions from
the ground states to the CT exciton states instead of the exciton
states of D or A, leading to significantly red-shifted optical
absorption edges in their optical absorption spectra [44].
Accordingly, this difference in the optical absorption mecha-
nism may bring about a different design strategy for the
TPEF material. For ground state CT cocrystals, TPEF materi-
als can be designed based on TPA-free components in view of
the relationship between TPA and intermolecular CT interactions [45]; however, TPA components are necessary for the design of exciplex-based TPEF material since the photons in the exciplex blend are absorbed by D or A components.

The room temperature PL decay curves of films of the pristine TAPC and 3TPYMB, and the TAPC:3TPYMB (1:1) DA blend measured at their PL emission peaks are shown in Figs. 1(d) and 1(e). The short PL lifetimes ($\tau = 1.9$ ns and 1.4 ns for TAPC and 3TPYMB, respectively) and mono-exponential decay of PL intensities of D and A indicate fluorescent emission from singlet excitons [46]. However, the transient PL decay curve of the blend shows an extremely long lifetime that contains double exponential components, $\tau = 251.1$ ns and 950.4 ns with proportions of 53% and 47%, respectively. The prolonged fluorescence lifetimes of the blend reveal effective TADF RISC processes from the triplet states ($^3$EX) to the singlet states of DA exciplex ($^1$EX) in the blend [47].

Figures 2(a) and 2(b) illustrate one-/two-photon excited fluorescence processes in conventional exciton-type molecules and TADF exciplex-type materials, respectively. For conventional exciton-type molecules, for example, pristine D molecules, the initial one-/two-photon excitation decay occurs very fast from the excited donor states to the singlet exciton ($^1$D), followed by fluorescent emission. It is tempting to assume that all of the photo-generated $^1$D produces fluorescent emission; under this condition, the PLQYs of exciton-type molecules would be 100%. However, energy loss mechanisms such as the intersystem crossing (ISC) from $^1$D to the triplet exciton ($^3$D) is quite feasible since the energy level of $^3$D is much lower than that of $^1$D [48]. This leads to substantial population of nonradiative $^3$D that is generated in parallel with the fluorescent emission process of $^1$D. This may explain the reported low PLQY (much lower than 100%) of most molecules. For TADF exciplex-type materials, however, the $\Delta E_{ST}$ between $^1$EX and $^3$EX is rather small, giving rise to efficient RISC from $^3$EX to $^1$EX and thus an increased PLQY of 5%–100% [49]. This provides a possibility to achieve enhanced TPEF in TADF exciplex-type materials.

To explore the nonlinear optical properties of TADF exciplex-type material, long-wavelength-excited fluorescence measurements of the DA blend (1:1) were investigated using a near-infrared femtosecond laser. As shown in Fig. 3(a), the
DA blend shows a strong blue emission with a peak at \( \approx 470 \text{ nm} \) upon 760 nm excitation, revealing an efficient upconversion process in the blend. The upconversion PL spectra of the blend exhibit almost the same shape and wavelength distribution as that of downconversion PL measurement [Fig. 1(c)], indicating that the upconversion fluorescence originates from radiative transition from the EX states also to the ground states [45]. In addition, the intensities of the upconversion fluorescence from the DA blend increase gradually with the power of the excitation laser. From the log–log plot of the integrated area of emission spectra versus the power intensity of input laser [Fig. 3(b)], a slope of 2.0 is obtained. This implies that the upconversion fluorescence stems from a two-photon absorption process [50]. We have also measured the long-wavelength-excited fluorescence properties of pristine D and A, and the results exhibit that both D and A show TPEF upon 760 nm excitation by using a near-infrared femtosecond laser operating at 1 kHz. Combined with the optical absorption and PL analysis mentioned above, we speculate that the TPEF in the film of TADF DA blend originates from a two-photon-excited exciplex formation process that is composed of a TPA process of D and/or A and a following exciplex formation process. It is found that the intermolecular CT interactions between two-photon excited donors and ground state acceptors (or vice versa) give rise to a near 100% formation of DA exciplex under the influence of the driving force \( -\Delta G_{\text{CS}} \) because the TPEF spectra of the DA blend only show exciplex emission bands, and no obvious fluorescence contributions from the D or A molecules can be observed.

Considering the triplet harvesting mechanism existing in the TADF exciplex, an enhanced TPEF from exciplex can be theoretically expected [51]. We thus investigate the TPEF properties of pristine D, A, and DA blend under the same conditions. As shown in Fig. 3(c), all the TPEF spectra of the DA blends show a giant enhancement compared to that of pristine D and A, confirming experimentally the existence of the TPEF enhancement mechanism in exciplex systems. By integrating and averaging the intensities of TPEF bands of D, A, and DA blend [Fig. 3(d)], average enhancements of \( \sim 129\% \) and \( \sim 365\% \) are calculated for D and A, respectively. It is reasonably deduced that RISC processes from the triplet states \( ^3\text{EX} \) to the singlet states of DA exciplex \( ^1\text{EX} \) in the blend enhanced the TPEF. We also measured the PLQY of the pristine D, A, and DA blend, and the results show that the PLQY of the DA blend (7.40%) is higher than that of the pristine D (6.45%) and A (4.01%). We note that the obtained TPEF enhancement is larger than that of PLQY, indicating there may exist another possible enhancement mechanism for TPEF in the exciplex DA blend. We speculate that the intermolecular CT interaction may be responsible for the enhancement of TPEF, because it has been found to facilitate two-photon absorption [52], and it exists in the excited state of the DA blend and gives rise to the formation of the exciplex [53].

B. TPEF Studies of DA Exciplex Doped with Fluorescent Emitters

Figure 4(a) shows the molecular structures of two fluorescent emitters: TTPA and DCM. In the host-dopant system, an effective FRET process occurs only when the absorption peak of the dopant overlaps with the emission band of the host [54]. To verify the suitability of the fluorescent emitters, we selected the normalized optical absorption for the TAPC:3TPYMB exciplex system, and the PL spectra of TTPA and DCM were measured at room temperature and shown in Fig. 4(b). As a reference, the normalized PL emission band of the TAPC:3TPYMB (1:1) DA blend host is also provided as a dark area. The PL spectra of TTPA and DCM each show a single emission band with peaks at 532 nm and 570 nm, respectively. We note that the absorption bands of both TTPA and DCM overlap perfectly with the PL emission band from the exciplexes in the blend host, indicating that an effective FRET process may occur from the
singlet state of the exciplex (1EX) to the singlet state of the fluorescent emitter (1EM).

Figures 4(c) and 4(d) show the normalized PL spectra of the DA blend hosts doped with various concentrations of TTPA and DCM fluorescent emitters, respectively. It can be found that the emission intensities from the fluorescent emitters exceed that of the DA blend host at a concentration of 0.2% for both TTPA and DCM. This reveals that the FRET process is very efficient in these systems. As the concentrations of the fluorescent dopants increase to 0.5%–1%, most of the fluorescence results from the emitter. This may partially explain why most of the reported concentrations of fluorescent emitters in the TADF-based organic light-emitting diodes (OLEDs) are 1% [24,25,55]. As the concentration of the dopants increased to 2%, only fluorescence contributed by fluorescent emitters was observed. Therefore, we use 2% as the dopant concentration to study the TPEF mechanisms of the DA exciplex doped with fluorescence emitters in this work.

Figure 4(e) shows the room temperature PL decay curves of TTPA- and DCM-doped DA blends measured at their PL emission peaks. Both TTPA- and DCM-doped DA blends show double lifetime components. For the TTPA-doped DA blend, $\tau = 37.4$ ns and $245.3$ ns are obtained; for DCM-doped samples, the lifetime components are $\tau = 4.3$ ns and $19.8$ ns, respectively. We note that these values are much shorter than that of undoped DA blends (251.1 ns and 950.4 ns), indicating an efficient rapid FRET process from the singlet 1EX state of the exciplex host to the singlet 1EM state of the dopant emitter [56]. It is also found that the proportions of prompt components are 97.4% and 83.3% for TTPA- and DCM-doped DA blends, respectively. We note that these values are much higher than that of the undoped DA blend discussed above, revealing that the majority of singlet exciplex states of the host directly transfer to the singlet exciton states of the dopant via FRET and then give rise to prompt fluorescence [57]. Thus, the energy loss during the mutual conversion between the singlet state and the triplet state of the exciplex may be weakened and the fluorescence quantum efficiency can therefore be further increased. We thus expect that enhanced TPEF may also be achieved in a TADF DA blend doped with fluorescent emitters, because a similar FRET process may occur on the two-photon excited exciplexes. In addition, we prepared organic light-emitting devices based on exciplex doped with 2% TTPA and measured the electroluminescence spectrum [Fig. 4(f)]. The devices have obvious green light emissions with an emission peak at 528 nm. We believe that this fluorescent doped exciplex system with ultra-high PLQYs may also have broad application prospects in the field of light-emitting devices.

Figures 5(a) and 5(b) show the power-dependent long-wavelength-excited fluorescence spectra of TAPC:3TPYMB (1:1) blends doped with 2% (mass fraction) TTPA and 2% (mass fraction) DCM, respectively. Under 760 nm excitation, the TTPA-doped DA blends show strong green emission with their peaks at $\approx 555$ nm; the orange emission bands that peak at $\approx 625$ nm, however, are observed for the DCM-doped DA blends.
blends. This reveals the efficient upconversion processes in these films. Moreover, the upconversion PL spectra of the emitter-doped blends exhibit similar emission bands to that of the downconversion PL spectra, indicating that the upconversion and downconversion emission may originate from the same excited state [58]. As shown in Figs. 5(c) and 5(d), the slopes of the log–log plot of the integrated area of the emission spectra versus the input power intensities for TTPA- and DCM-doped DA blends are both calculated to be ~2.1, implying that the observed upconversion fluorescence from these samples stems from a two-photon absorption process [59].

Figure 6(a) shows the normalized long-wavelength-excited fluorescence spectra of the pristine A, undoped DA blend, TTPA-doped DA blend, and DCM-doped DA blend. Different emission colors of purple, blue, green, and orange were obtained by adjusting the material components. This is technically useful for many TPEF applications. We note that this method is theoretically extensible. More colors can be potentially obtained in this blend by adjusting the dopants, or in other TADF DA blend systems, through reasonable material design. In the case of the existence of an effective FRET process from the singlet exciplex state of the host to the singlet state of the fluorescent emitter, the color of TPEF can be theoretically adjusted by doping a tiny amount of fluorescent emitter.

To study the influence of FRET on TPEF, TPEF properties of DA blends with and without fluorescent dopants were investigated under the same conditions. We found that the intensities of TPEF are immensely increased after doping 2% TTPA and 2% DCM. We note that TPEF intensities of DA blends doped with fluorescent emitters exceed the full scale, like measuring with a convergent lens. Therefore, all the long-wavelength-excited fluorescence spectra of TTPA- and DCM-doped blends were measured without a convergent lens in this work. Under this condition, the intensities of undoped DA blend are too weak to be detected [Figs. 6(b) and 6(c)]. The PLQYs of TTPA- and DCM-doped DA blends also confirm the enhancement of fluorescence. After doping with 2% TTPA and DCM, PLQYS of 98.65% and 20.86% were measured, respectively. These values are greatly increased compared to that of an undoped DA blend, indicating the existence of a FRET-related one- and two-photon fluorescence enhancement mechanism in a fluorescent emitter-doped DA blend. As shown in Fig. 6(d), the rapid FRET process from the singlet state 1EX of the DA exciplex host to the singlet 1EM state of the fluorescent emitter reduces the loops between 1EX and 1EX and thus the nonradiative energy loss during the waiting period for RISC, leading to an extremely high PLQY of FRET-type TADF blends and immensely enhanced TPEF intensities [60]. We note that there is also an energy loss mechanism; namely, the Dexter energy transfer (DET) process from the triplet state 3EX of the DA exciplex host to the triplet 3EM state of the fluorescent emitter [26]. Unlike the long-range FRET process, DET is a short-range process that is remarkable only in those blends with high dopant concentrations [61,62]. We also note that the observed enhancement of TPEF is larger than the values of the corresponding PLQY. This indicates that there may exist an additional possible enhancement mechanism for TPEF. Because the PLQY of TTPA-doped DA blend is up to 98.65% and there is not much room to improve, we speculate that the additional fluorescence is coming from the TPA process. Besides the TPE by D or A components, the intermolecular CT interaction in the excited states of exciplex may also facilitate the two-photon absorption.

**4. CONCLUSION**

In conclusion, we studied upconversion fluorescence in thin films based on an electron DA exciplex of TAPC:3TPYMB (1:1) and blends doped with 2% TTPA or 2% DCM fluorescent emitters. It is found that the color-adjustable upconversion fluorescence could be immensely enhanced in a fluorescent emitter-doped TADF DA exciplex. The RISC processes from 3EX to 1EX and consequently the rapid FRET process from 1EX of the DA exciplex host to the singlet 1EM state of the fluorescent emitter reduce the nonradiative energy loss and lead to immensely enhanced TPEF intensities.
By analyzing the relationship between the TPEF enhancements and the PLQYs in a series of samples, we also identified a new TPA gain mechanism related to the intermolecular CT interaction in the TADF DA exciplex system. We believe our findings may provide a new avenue for a material design strategy for highly efficient TPEF materials.

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