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REVIEW



Photon Upconversion: From Two-photon Absorption (TPA) To Triplet-triplet Annihilation (TTA)

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ABSTRACT: Organic upconversion is a unique process in which low-energy light (usually NIR light) is converted to high-energy light through either two-photon absorption (TPA) or triplet-triplet annihilation (TTA) mechanism. Both TPA upconversion (TPA-UC) and TTA upconversion (TTA-UC) have been actively investigated in recent years due to their showing many intriguing applications in optics, biophotonics, and solar energy utilization. Although they show somewhat similarity (i.e., belonging to nonlinear twoquantum process and needing focusing excitation light), TPA-UC and TTA-UC are very different, such as in mechanism, characteristics involved, molecular design and potential applications. Here, we collectively reviewed these two kinds of upconversion and compare their respective characteristic and merits. We also present recent advances made in the areas of TPA- and TTA-UC, the remaining challenges and opportunities, with a particular emphasis on molecular engineering of these two active upconversion materials.

1. Introduction

Organic molecular photon-upconversion (UC) can convert two lowenergy photons into one higher-energy photon by either twophoton absorption (TPA) mechanism¹ or triplet-triplet annihilation (TTA) mechanism.² The two-photon absorption (TPA) can be described by the two-state model³ or the three-state model^{4, 5} that a molecule can be excited from the ground state (S₀) to the first excited singlet state (S₁) or to the second excited singlet state (S₂) by simultaneous absorption of two photons, via a virtual state. It is the virtual state (see Fig. 1a) that makes two-photon absorption require high excitation power density as large as more than MW·cm⁻², which only achieved by an ultrafast laser. After two photons are absorbed to produce an excited state, the relaxation of electron would give rise to the emission of a photon with frequency

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greater that those of the absorbed photons, that is, TPA upconversion (TPA-UC). Importantly, the TPA shows quadratic intensity dependence and possesses the overwhelming advantages of high spatial resolution and deep medium penetration, which can bring about numerous potential applications in biophotonics (fluorescence bioimaging⁶⁻⁹ and photodynamic therapy¹⁰), optics (two-photon data storage¹¹ and frequency upconverted lasing^{12, 13}) and nano-micro fabrication¹⁴.

The other organic upconversion is triplet-triplet annihilation upconversion (TTA-UC) (see Fig. 1b). This TTA-UC needs a bimolecular system containing triplet sensitizer and triplet acceptor (i.e., emitter).¹⁵ The sensitizer firstly absorbs low-power light, then undergoes intersystem crossing (ISC) and further transfers its triplet energy to the triplet of acceptor (TTT). Subsequently two nearby triplet acceptors undergo the triplet-triplet annihilation (TTA), producing a frequency-upconverted fluorescence (i.e. TTA upconversion).¹⁵ Since TTA-UC undergoes the inter-molecular two respective one-photon process that is transition allowance and just needs low excitation intensity (less than 100 mW·cm⁻², solar energy is enough).¹⁶ Thus, the acctrative solar energy applications, including photovoltaics,¹⁷⁻¹⁹ photosynthesis²⁰ and photocatalysis²¹ would be possible.



Fig. 1 Jablonski diagrams of TPA-UC (dual energy level model) (a) and TTA-UC (b).

Although TPA-UC and TTA-UC possess different mechanisms, both belong to nonlinear two-quantum process and need the focusing excitation light. The former involves a one-step intramolecular two-photon excitation process through a virtual state which imposes certain symmetry restrictions. It also requires a high excitation intensity thus necessitating the use of short pulse lasers with high peak intensities. In contrast, triplet-triplet annihilation upconversion utilizes an intermolecular process in which two neighboring molecules in triplet excited states produced by respective one photon excitation, interacting to lead one molecule to the emitting higher energy state and the other dropping to the ground state. Thus even though the annihilation behaves like a nonlinear process, it actually involves coupling of two linear excitations, which can be generated by using an intensity cw laser or even an incoherent lamp. There is no symmetry requirement for TTA.

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Currently, there are several reviews already existing, which deal with these two upconversion processes independently, none have described them collectively. This review described comparatively these two kinds of the photon upconversion (UC) concluding their characteristics, measurements and the active materials as well as notable applications.

2. Two-photon absorption upconversion (TPA-UC)

The concept of two-photon absorption (TPA) was firstly put forward by M. Goppert-Mayer in 1931.²² She theoretically predicted that a molecule could simultaneously absorb two photons from the ground state (S₀) to the excited state (S₁) under the very intensity excitation. Then, the intensity change (*dI*) of the light beam shows quadratic dependence of the input light intensity (Eq. 1),²³ where β is the two-photon absorption coefficient (in unit of cm/GW). The relationship of β and two-photon absorption cross-section (σ_{TPA} , in unit of cm⁴/GW) is expressed in Eq. 2,²⁴ where *N*_A is Avogadro's number and *d*₀ is the molar concentration of the absorbing molecules (in units of mol·dm⁻³). With different unit for two-photon absorbability, organic molecular TPA cross-section can be expressed by Eq. 3,²⁵ where *h*v is the photon energy of the excitation light. δ_{TPA} is the TPA cross-section in units of GM, i.e., the name abbreviation of Goppert-Mayer (1 GM=10⁻⁵⁰ cm⁴ ·s·photon⁻¹).

$$\frac{dI(z)}{dz} = \infty - \beta I^{2}(z) \qquad (1)$$
$$\beta = 10^{-3} N_{A} d_{0} \sigma_{TPA} \qquad (2)$$
$$\delta_{TPA} = h v \sigma_{TPA} \qquad (3)$$

When two photons were absorbed by chromophore, the produced excited state would relaxed and give rise to the emission with the frequency greater than those of the absorbed photons. Usually, the two-photon excited emission (TPA-UC) includes two kinds: i.e., the stimulated lasing (TPA lasing) and the upconverted fluorescence (TPA fluorescence), which depend on the direction of collectible emission. The strong TPA-UC is extremely attractive for

numerous applications such as light-emitting diodes (LEDs), photovoltaics and biomedicine. Besides, the most intriguing application is that it can offer high-energy coherent light sources in the short wavelength region which could create new advantages and breakthroughs in various laser-based applications.²⁶ Compared to conventional one-photon lasing, the two-photon lasing can make the two-photon excitation wavelength shift to longer wavelengths where organic molecules are relatively photo-stable.

$$\eta_{TPA} = \frac{E_{out}}{E_{in}} \times 100\% = \frac{I_{out}}{I_{in}} \times 100\%$$
(4)
$$\delta_{TPF} = \delta_{TPA} \times \Phi_{f}$$
(5)

TPA lasing efficiency (η_{TPA}) can be calculated by the ratio of E_{out}/E_{in} or the the ratio of I_{out}/I_{in} (Eq. 4),²⁷ where E_{out} and E_{in} are the lasing energy and the excitation light energy, respectively; Iout and I_{in} are the lasing intensity and the excitation light intensity, respectively. While the TPA-UC efficiency (Φ_{TPA}) can be evaluated by the two-photon fluorescence (TPF) cross-section (δ_{TPF}) that is defined by $\delta_{\text{TPA}} \times \Phi_{\text{f}}$ (see Eq. 5),²⁸ where δ_{TPA} and Φ_{f} are the molecular TPA cross-section and one-photon fluorescence quantum yield, respectively. An active TPA-UC chromophore should possess large TPA cross-section (δ_{TPA}) with high fluorescence quantum yield (Φ_f) , which presents a useful criterion to design and synthesize new active chromophores. Theoretically, organic molecular δ_{TPA} value is related to the imaginary part of the third-order polarizability γ (- ω ; $(\omega, \omega, -\omega)$, as shown in Eq. 6,^{29, 30} where *h* is Plank's constant, n is the index of refraction of the medium, L is a local field factor (equal to 1 for vacuum), and c or ω is the speed of light or the frequency of light. As for material scientists and chemists, Equation (7)^{29, 30} is possibly more comprehensible, where M_{ge} or $M_{ee'}$ is the transition dipole moment between the ground state (S_0) and the excited state (S_1) or between S_1 and the higher excited state (S_2) . E_{ge} or $E_{ge'}$ is the energy difference between S_0 and S_1 or the S_1 and the higher excited state (S2). $\Delta \mu_{ge}$ is the molecular dipole moment difference between S_0 and S_1 . Except the third term in Eq. (7), the first two terms make positive contribution to the TPA process. These parameters can be calculated by theoretical calculations.³¹ Also, the parameter $\Delta \mu_{ge}$ can be obtained according to Lippert-Mataga equation (8),³² where Δv and Δf represent the molecular Stokes shift in different solvent and the orientation polarizability of solvent, respectively; $\Delta \mu_{ge}$ is the molecular dipole moment difference between S_0 and $S_1.$ C is the constant, while c and α are the light speed and the molecular cavity radius. ħ is Plank's constant divided by 2π . One can see from Eq. 9 that Δf is related with the dielectric constant (ϵ) and the refractive index (n) of solvent. So, the linear relationship of Δv and Δf can be plotted and the $\Delta \mu_{ge}$ value can be obtained in slope.

$$\delta(\omega) = \frac{4\pi\hbar\omega^2}{n^2c^2} L^4 \operatorname{Im}\gamma(-\omega;\omega,\omega,-\omega)$$
(6)
$$\delta_{\text{TPA}} \propto \frac{M_{ge}^2}{E_{ge}^2} \left[\frac{\Delta u^2_{ge}}{E_{ge}} + \sum_{e'} \frac{M_{ge'}^2}{E_{ge'}^2} - \frac{M_{ge}^2}{E_{ge}} \right]$$
(7)

$$\Delta v = \frac{\Delta \mu_{ge}^2}{c\hbar \alpha^3} \Delta f + C$$

$$\left(\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right)$$
(9)

Based on these parameters such as $M_{ee'}$ and $\Delta \mu_{ge}$ *etc*, the TPA cross-section can be predicted. Since small TPA cross-section of molecular dyes needs to use more intense laser beams, developing various active materials for enhancement TPA cross-section (δ_{TPA}) is necessary. As for the molecule engineering, chromophore design strategies aim at extending the conjugated length, changing the character of the conjugated bridge and increasing the molecular planarity as well as enhancing the donor (D) and acceptor (A) strength, which more often than not can augment TPA-UC. So far, principles and guidelines for molecular engineering that can enhance the TPA cross-section of dipolar,^{33, 34} quadrupolar,^{35, 36} octupolar^{37, 38} and dentritic^{39, 40} chromophores have been well developed. Among them, the linear conjugation structures and the branching/dendritic motifs are the typical candidates.

2.1 The Linear Structures

Generally, there are two molecular types for linear structures, i.e., asymmetrical D- π -A type and symmetrical D- π -D (or A- π -A) type. From the 1990s on, Prasad's group has done lots of pioneering works in developing D- π -A dyes,⁴¹⁻⁴⁴ where the typical upconverted lasing chromophores are (E)-4-[p-(N-hydroxyethyl-N-methyl)amino] styryl]-N-methylpyridinium iodide (ASPI), 4-(dimethylamino)-Nmethylstilbazoliumtosylate (DAST) and (E)-4-[N-(2-hydroxyethyl-Nmethyl)aminophenyl]-4'(6-hydroxyhexylsulphon-yl) stilbene (APSS) (Fig. 2). The reported TPA lasing efficiency (η_{TPA}) for **ASPI** in benzyl alcohol was as high as ~17% (at 600 nm), when excited by a focused 1064 nm laser (~10 ns).⁴¹ Dye ASPT doped bulk polymer rods presents TPA lasing at ~600 with efficiency of 3.5% (η_{TPA}) when pumped at 1064 nm (~10 ns).⁴² As an extension of this work, we have synthesized a series of styrylpyridine derivatives (Fig. 2), in order to further understand the structure-performance correlations.⁴⁵ These styrylpyridine chromophores in DMF solution present red upconversion lasing with the largest efficiency (η_{TPA}) at 10.7% for DEASPI and the smallest one at 0.13% for CSPI, when excitation by 1064 nm (40 ps) mode-locked Nd:YAG laser (at 2.14 mJ input energy). Experiments have demonstrated that the anion such as iodine ion (I⁻), CH₃SO₄⁻ and CH₃PhSO₄⁻, the molecular environments and the solution concentration have an important influence upon the TPA lasing efficiency.⁴⁶ Further investigation by the quantum chemical calculations, we found that the TPA lasing (n_{TPA}) show positive correlation to intramolecular charge-transfer, expressed by the decreasing bond length alternation (BLA) and the increasing charge density distribution ($\Delta \rho_{1,2}$).⁴⁵



Fig. 2 D- π -A chromophores with TPA lasing efficiency (η_{TPA}).

In 1998, M. Albota and co-workers put forward the concept of symmetrical charge-transfer and further reasoned that symmetrical bis(styryl)benzene derivatives (Fig. 3) could dramatically enhance TPA absorbing in comparison with model (E)-bis(di-nbutylamino)stilbene (BDBAS).⁴⁷.The TPA cross-section of bis(styryl)benzene derivative (R=OMe, n=2) is as large as 1250 GM at 775 nm, showing almost 6-fold increase, relative to model BDBAS (210 GM at 600 nm) (Fig. 3). This is interpreted to increase the change in the transition dipole moments.⁴ Using the extending symmetrical D- π -D chromophores, B. H. Compston and his coworkers48 investigated the structure-property with TPA crosssection and the application of two-photon-initiated polymerization. Experimental and theoretical studies confirmed that enhanced δ_{TPA} was correlated with the degree of symmetrical intramolecular charge-transfer. By nanosecond pulse excitation, they observed that bis(styryl)benzene derivatives present a combination of large δ_{TPA} and high fluorescence or triplet yield quantum yield. Such merits are especially available in TPA polymerization based threedimensional (3D) microfabrication. Since TPA possesses the advantages of high spatial resolution and deep medium penetration, they can achieve high density three-dimensional (3D) optical data storage by writing bits in a thick medium (> 100 μ m).⁴⁸



Fig. 3 Symmetrical bis(styryl)benzene derivatives and TPA properties



Fig. 4 Symmetrical and asymmetrical pn-junction chromophores.

In development of new large TPA molecules, we have synthesized some pn-junction based "D-A-D'-A-D" and "(D-A)_n" chromophores (Fig. 4).^{49, 50} Relative to **NT-G1** (215 GM),⁵⁰ pn-junction style chromophores **SO-G1** (δ_{TPA} , 377 GM) and **NO-G1** (δ_{TPA} , 454 GM) present higher TPA cross-section values, according to the two-photon fluorescence (TPF) method by the Ti:sapphire femtosecond laser. As such, triphenylamine-based pn-junction oligomer **P1** displays the greatest TPA coefficient (β , 2.5×10⁻¹¹ cm/W) among oligomers **P1-P3** due to **P1** presenting more obvious pn-junction feature and larger intramolecular charge-transfer from triphenylamine (as donor) to naphthalene (as acceptor).⁵¹ Since the TPA cross-section is determined by two-photon fluorescence measurement, large δ_{TPA} means high upconversion, which would have potential applications in fluorescence microscopy and bioimaging.

Whether symmetrical or asymmetrical structures have larger TPA cross-section? In 2000, Kim and co-workers synthesized D- π -D and D- π -A dithienothiophene (DTT)-centered chromophores (101-104) (Fig. 5a).⁵² The measurements are carried out at the identical conditions and the results showed that the $\delta_{\textit{TPA}}$ value of symmetrical 101 (1050 GM) is more than 3-fold larger than the asymmetrical **102** (335 GM); while the δ_{TPA} of symmetrical **103** (1990 GM) shows a 1.7-fold increase, relative to the asymmetrical analogues 104 (1190 GM). The finding that symmetrical intramolecular charge-transfer possesses larger TPA cross-section is of importance since it would be helpful for active TPA molecule engineering. In 2001, we investigated the influence of molecular symmetry upon active TPA based on theoretical calculations correlative with the corresponding experimental measurements.53 Calculations results showed that symmetrical stilbene derivatives exhibit larger transition dipole moment ($M_{ee'}$ =12~15D) than the asymmetrical counterparts (Mee'=6~10D), while asymmetrical structures have larger dipole moment difference ($\Delta \mu_{ge}$ =3~12D) than symmetrical ones ($\Delta \mu_{ge}$ =~0D) (Fig. 5b), which revealed that the TPA cross-section mainly depend on the amount of transition dipole moment (M_{ee'}).53,54

In 2008, Prasad group reported that the symmetrical ladder-type fluorine-based chromophores (nFL, n=1~4) presented highly enhanced TPA cross-section (Fig. 6a).⁵⁵ Measured by the nonlinear transmission method, the δ_{TPA} values were increased from 1FL (584 GM), 2FL (853 GM), 3FL (1280 GM) till to 4FL (1846 GM). Due to their enhanced two-photon response, these ladder-type

oligofluorene chromophores provide the advantages of a higher signal/noise ratio, better optical limiting and lower power requirement for the excitation source.⁵⁵ Later on, Blanchard-Desce group synthesized two prolonged phenanthrene-based chromophores **10** and **11** (Fig. 6a) for the application of the two-photon upconverted imaging in the biological membranes.⁶ Under excitation of a mode locked Ti/sapphire laser (80-fs pulses, 80 MHz), the δ_{TPA} values are measured to be 3310 GM for **10** and 3760 GM for **11**, showing more than 2 orders of magnitude larger than the standard fluorophore fluorescein (30 GM).⁶ This noticeable increase is due to their semi-rigid extending conjugation to nanoscale rod.⁶



Fig. 5 (a) Molecular structures of **101-104** and the TPA cross-sections, (b) the transition dipole moment ($M_{ee'}$) and dipole moment difference ($\Delta \mu_{ge}$) for symmetrical and asymmetrical stilbene derivatives.

Usually, two-photon absorption property exhibited by the organic molecules in the solution is quenched in the solid state due to aggregation. However, efficiently luminescent materials in the solid-state form are highly desired in many photonic applications such as TPA lasing and light emission of OLED. In order to development new chromophores with high aggregation-induced upconversion, Prasad group synthesized a kind of symmetrical 9,10bis[4'-(4"-aminostyryl)styryl]anthracene (BDSA-Bz) with enhanced TPA-UC by nanoaggregation. (Fig. 6b).⁵⁶ BDSA-Bz showed weak fluorescence in organic solvent owing to its large internal rotation in the monomer form; however, once its nanoaggregation is formed in water, the internal rotation is considerably hindered and leads to significant increases of TPA cross-section (δ_{TPA} =217 GM) and fluorescence quantum yield (Φ_F =13%), relative to it in solution $(\delta_{TPA}=172 \text{ GM}, \Phi_F=2\%)$. And the TPF cross-section (δ_{TPF}) is increased from 15 (in solution) to 101 (in aggregation), which shows the three-dimensional potential application in fluorescence bioimaging.⁵⁶ Also, they found that BDSA-Bz modified silica nanoparticles can obviously exhibit the aggregation-enhanced TPA-

UC which can act as an energy donor to react with the acceptor of a photosensitizing PDT drug.⁵⁶ In 2007, they have prepared the stable aqueous dispersions of co-encapsulating nanoparticles in the nonpolar interior of micelles by co-precipitating an organically modified silica sol with the photosensitizer (BDSA, Fig. 6b).⁵⁷ Using a multidisciplinary nanophotonic approach, indirect excitation of this photosensitizer can achieve intrapaticle energy-transfer from the dye aggregates and generates singlet oxygen that produces vitro cytotoxic effect in tumour cells by photosensitization under twophoton irradiation.⁵⁷ Another interesting nanoaggregation molecule is 1,4-bis(cyanostyryl)benzene-based triphenylamine isomer (CSB-TP).⁵⁸ Changing the position of cyano group within CSB-TP obtained α -CSB-TP and β -CSB-TP isomers (Fig. 6b). The resulting fluorescence wavelength was shifted to 586 nm and the TPA cross-section was increased at 357 nm for β -CSB-TP, relative to α -CSB-TP (530 nm, 297 GM), when using Ti-sapphire laser with 130 femtosecond (fs) pulses, which can be used to prepare the fluorescent organic nanoparticles with readily tunable emission colour.58



Fig. 6 Symmetrical chromophores and TPA cross-sections

2.2 The Branch/Dendrimer Structures

In 1999, Prasad and co-workers reported that triphenylamine-based branched chromophores has shown its TPA cross-section increasing with the branching number.⁵⁹.This phenomenon was firstly recognized to be the cooperative enhancement effect. As shown in Fig. 7a, the TPA cross-sections of one-branched (**PRL-101**), two-

branched (PRL-501) and three-branched (PRL-701) chromophores in tetrachloroethane solvent were measured at 60×10⁻²⁰, 208×10⁻²⁰ and 587×10⁻²⁰ cm⁴/GW, determined with nanosecond pulses at 810 nm.⁵⁹ Later on, this "cooperative effect" has found in many other branched or dendrimeric systems, such as triazine-based,⁶⁰⁻⁶² 2,4,6alkylpyridinium-based,63, 64 1,3,5-tricyanobenzene-based,65-67 truxene-based⁶⁸ porphyrins-based.^{69,70} Among and them. triphenylamine group is regarded as the most typical "core",⁷¹⁻⁷⁵ since triphenylamine group possesses more active site that makes the branching synthesis be easy and it is a perfect donor that can effectively enhance intramolecular charge transfer with result that increasing TPA cross-section. For instance, the triphenylaminebased branch-2 possesses 17-fold increase in TPA cross-section (1562 GM), relative to the branch-1 (Fig. 7b).⁷⁶ Combination the theoretical calculations and experimental measurements, we found that only one of the three branches within triphenylaminebranched chromophores shows larger excited charge redistribution, while other branch(es) show(s) negligible excited charge-transfer (Fig. 7c, T1~T3).77



Fig. 7 Triphenylamine-based branched chromophores and TPA cross-sections

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In 2003, Rebane group also confirmed that strong cooperative enhancement of TPA in triphenylamine-based dendritic systems (Fig. 8).^{78, 79} After systematic measurements, they found that the maximum TPA cross-section (δ_{TPA}) was increased from compd. **2** (320 GM), to **4** (1330 GM) till to **6** (2700 GM), in proportion to N^2 (where *N is* triphenylamine group). By a femtosecond pulses laser, the measured two-photon absorption cross-section (δ_{TPA}) of dendrimer **8** (**4SG2**) was as high as 1×10^4 GM. This enhancement is facilitated by the quasi-planar conjugated structure that presents direct inter-branch charge-transfer throughout the molecules.^{78, 79} Using the small substituent group attached to branched chromophore has no obvious contribution to TPA enhancement.⁸⁰



Fig. 8 Molecular structures of BDPAS (2)-based dendrimers 4, 6 and 8

One of the advantages of triphenylamine-based branched molecules is that triphenylamine "core" can connect more functional branching, which usually bring about the optimized properties by TPA-UC detection. More recently, we synthesized three triphenylamine-based molecules containing one, two and three of 7-pyridinylbenzo[c][1,2,5] thiadiazole group(s) (TPTZ-n, n=1~3, Fig. 9a).81 Relative to TPTZ-1, the TPA-UC showed 2-fold enhancement for TPTZ-3 and 1.5-fold enhancement for TPTZ-2. The cross-section values (δ_{TPA}) are increased from TPTZ-1 (121 GM) to TPTZ-2 (184 GM) to TPTZ-3 (254 GM). Using TPA-UC detection, Choosing TPZ-1 to detect Cu2+ by TPA-UC and down-conversion fluorescence, respectively, the former showed 10-fold enhanced sensitivity relative to the later since the quenching constant of TPA-UC (k_{SV}^{2P}) is at 13.6 mM $^{\cdot 1}$ and that of down-conversion fluorescence (k_{SV}^{1P}) at 1.77 mM^{-1.81} Also, the branched molecules with functional branching possess more sensitivity. For example, when detecting Ni²⁺, the quenching constants ($k_{\scriptscriptstyle SV}^{\scriptscriptstyle 1P}$) of TPZ-1, TPZ-2 and TPZ-3 are demonstrated at 1.70 mM⁻¹, 2.32 mM⁻¹ and 4.30 mM⁻¹, respectively.⁸¹



Fig. 9 The branched structures of TPTZ-n (n=1~3) (a) and ET-101, PRL-501 and PRL-406 (b).

For the purpose of investigating the influence of branching, "core" and the resulting dendritic molecule upon TPA cross-section (σ_{TPA}) , respectively, Prasad and co-workers investigated three newly chromophores (PRL-501, PRL-406 and ET-101, Fig. 9b) using the femtosecond Z-scan technique.⁸² The σ_{TPA} values of **PRL-501** (branching), PRL-406 (cored-unit) and ET-101 (dendrimer) are at 0.73×10⁻²⁰, 0.26×10⁻²⁰ and 1.52×10⁻²⁰ cm⁴/GM, respectively. That is, the σ_{TPA} value is in the order of dendrimer > branching > core. For the conjugated dendrimers, they would display efficient fluorescence resonance energy transfer (FRET) from the branching to the "core", which bright out a significant increasing emission of the "core" unit when excitation of the branching, compared to direct excitation of the "core".71 This "antenna effect" can occur other branching systems such as porphyrin-cored⁶⁹ and dibenzothiophene-cored⁸³ branching chromophores. As shown in Fig. 10, using one-photon excitation (at 420 nm, Xe lamp) and twophoton excitation (at 800 nm, laser), respectively, the porphyrincored molecule emits not only strong down-conversion but also strong TPA-UC fluorescence, locating at ~650 and ~725 nm. Meanwhile, with indirect excitation by either 300 nm (Xe lamp) or 532 nm (laser), this branched sample also presented the same

down- and up-conversion fluorescence, resulting from intramolecular energy transfer and "antenna effect". 69



Fig. 10 The scheme of up-conversion and down-conversion based on two-photon excitation and one-photon excitation, when excitation of the "branching" and the "core", respectively.



Fig. 11 The dendritic chromophores of TOZ-2 and TOZ-4

As described above, the branched and dendritic molecules have the merits such as TPA enhancement and optimized performances. Their other important benefit is that it can provide an effective approach to enhance TPA without the maximum TPA absorption shifting. In 2008, we found that chromophores TOZ-2 and TOZ-4 (Fig. 11) in THF emit strong TPA-UC, when pumped by Ti: sapphire femtosecond laser pulse at 800 nm.⁸⁴ Using the TPF methods, TOZ-4 possesses δ_{TPA} value as large as 5254 GM, showing ~3 times larger than that of TOZ-2 (1804 GM), while both have the identical maximum absorption including one-photon and two-photon peaks.⁸⁴ In search of the trade-off effect between two-photon absorptivity and the maximum absorption position, we also synthesized the naphthaline-cored dendrimers⁸⁵ that exhibit increasing TPA with the generation number from 1 (Np-G1, 959 GM), to 2 (Np-G2, 5582 GM), to 3 (NP-G3, 9575 GM) (Fig. 12a). Their maximum linear absorption positions are proved to fixing at ~415 nm, indicating that a trade-off between optical transparency and NLO performance (two-photon absorption) can be existed in dendritic architectures (Fig. 12b). Moreover, these dendrimers can successfully initiate the acrylate resins to two-photon

polymerization (TPP) with the efficiency increasing with the generation number. As shown in Fig. 13, the TPP processes were involved in two-photon absorption (excitation), then intramolecular energy transfer and intermolecular electron transfer between initiator and MMA monomer to obtain very regular diamond structure with submicron size.⁸⁵



Fig. 12 Linear absorption (a) and TPA cross-sections (b) of naphthaline-cored dendrimers from Np-G1 till to Np-G3.



Fig. 13 Two-photon polymerization (TPP) resulting submicron structure involved in TPA, intramolecular charge-transfer and intramolecular energy-transfer as well as intermolecular electron-transfer.

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3. Triplet-triplet Annihilation Upconversion (TTA-UC)

Different from the TPA-UC, the other organic upconversion is triplet-triplet annihilation based upconversion (TTA-UC) that was first introduced by Parker and Hatchard over 50 years ago.⁸⁶ TTA-UC phenomenon undergoes a series of quantum process that involves in a bimolecular system containing sensitizer and acceptor.⁸⁷ Firstly, the sensitizer harvests the excitation energy toward its triplet excited state by the intersystem crossing (ISC). Secondly, the sensitizer shifts its triplet energy to the acceptor, which is called triplet-triplet energy transfer (TTT). Thirdly, two excited triplet acceptors encounters each other and produce one excited singlet state (S_1) and one ground state (S_0) , which is called triplet-triplet annihilation (TTA). Lastly, the S₁ state decays from the excited state to the ground state and irradiates the upconversion fluorescence. Since the processes mentioned above, including ISC, TTT and TTA etc. are transition-allowed, the TTA-UC can achieve at ultra-low excitation power less than the terrestrial solar radiation (ca. 100 mW·cm⁻²). The overall upconversion capability (η_{TTA}) can be evaluated by Eq. 10,^{88.} where ε and Φ_{ISC} are the molar extinction coefficient and the intersystem crossing (ISC) of sensitizer; Φ_{UC} is the upconversion efficiency of the acceptor.

$$\eta_{\text{TTA}} = \varepsilon \times \Phi_{\text{ISC}} \times \Phi_{UC}$$
(10)
$$\Phi_{UC} = 2\Phi_r \left(\frac{A_r}{A_s}\right) \left(\frac{F_s}{F_r}\right) \left(\frac{\eta_s}{\eta_r}\right)^2$$
(11)
$$\Phi_{UC} = \Phi_{TTI} \times \Phi_{TTA} \times \Phi_F$$
(12)

The upconversion efficiency (Φ_{uc}) can be calculated based on the equation (11),⁸⁹ where the subscript "s" and "r" represent the sample (i.e., sensitizer or acceptor) and the reference (for example, rhodamine 6G or coumarin etc), respectively. Φ_r is the fluorescence quantum yield of the reference. Ar and As are the absorbance of the reference and sensitizer, respectively. Fr and Fs are the integrated emission of the reference and the acceptor under the excitation of the sensitizer. n_r and n_s are the refractive indices of the solvent dissolving sample and the reference, respectively. The factor 2 accounts for the fact that two absorbed photons are required to produce one upconverted photon.² According to Eq. 12,⁹⁰ one can see that the upconversion efficiency (Φ_{UC}) is relevant to the fluorescence quantum yield (Φ_F) of acceptor, the triplet-triplet energy transfer efficiency (Φ_{TTT}) and the triplet-triplet annihilated efficiency (Φ_{TTA}). Qualitatively, sensitizer with long-lived triplet state (T1) will present high TTT efficiency (Φ_{TTA}) since the successful TTT process needs large Dexter distance and resulting effective diffusion in order to insure the contact of sensitizer and acceptor. Quantitatively, TTT efficiency (Φ_{TTT}) can be evaluated by the Stern-Volmer equation (Eq. 13),⁹¹ where I₀ and I are the phosphorescence intensities of sensitizer without and with acceptor, respectively. K_{sv} , [Q] and τ_0 are the Stern-Volmer constant, the concentration (mol·dm⁻³) of acceptor and the lifetime of the triplet excited state of the sensitizer, respectively. k_a is the phosphorescence quenching constant that is proportional to the TTT efficiency (Φ_{TTA}).

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$$I_0/I = K_{sv}[Q] + 1 = k_q \cdot \tau_0[Q] + 1$$
 (13)

$$\frac{{}^{3}\varepsilon_{A}}{{}^{3}\varepsilon_{S}} = \frac{\Delta A_{A}}{\Delta A_{S}}$$
(14)

$$[{}^{3}M^{*}]_{t} = \frac{[{}^{3}M^{*}]_{0}}{1 - (e^{-tk_{T}} - 1) \times \frac{[{}^{3}M^{*}]_{o} \times k_{TTA}}{k_{T}}}$$
(15)

On the other hand, triplet-triplet annihilation efficiency (Φ_{TTA}) can be estimated according to Eq. 14 and Eq. 15.⁹² By means of the laser flash photolysis measurements, the absorption difference spectra of sensitizer (ΔA_s) and acceptor (ΔA_a) can be obtained. Then, the triplet extinction coefficient (${}^{3}\varepsilon_{A}$) of acceptor can be obtained if the triplet molar extinction coefficient (${}^{3}\varepsilon_{S}$) of the sensitizer is known. So, the TTA rate constant (k_{TTA}) that can stand for the TTA annihilation efficiency (Φ_{TTA}) can be calculated according to Eq. 15. ⁹³ Here, [${}^{3}M^{*}$]₀ and [${}^{3}M^{*}$]_t represent the concentration (in the units of mol·dm⁻³) of the triplet acceptor when *t*=0 and *t*=*t* (*t* is the time). The latter (${}^{3}[M^{*}]_{t}$) is equal to molar extinction coefficient (${}^{3}\varepsilon_{A}$) value. k_{T} is the triplet decay rate constant of acceptor can be obtained by fitting the transient absorption decay also the laser flash photolysis measurements.⁹³



Theoretically, two triplet acceptor $({}^{3}A_{1}^{*})$ undergoes TTA process that are governed by the spin statistic law (Eq. 16).⁹⁴ That is, when two excited triplets $({}^{3}A_{1}^{*})$ interact, nine encounter-pair spin states are produced with equal probability that is composed of three distinct sublevels: i.e., five of which are quintet (${}^{5}[AA]_{2}^{*}$), three of which are triplet (${}^{3}[AA]_{1}^{*}$) and one of which is singlet (${}^{1}[AA]_{0}^{*}$). Based on this spin statistics, the quintet state (${}^{5}A_{2}^{*}$), the triplet state (${}^{3}A_{1}^{*}$) and the singlet state (${}^{1}A_{0}^{*}$) will have 5/9 (55.6%), 3/9 (33.3%) and 1/9 (11.1%) chance, respectively, to decay into the triplet excited state (${}^{3}A_{1}^{*}$),⁹⁵ thus the maximal upconversion quantum yield from the singlet state (${}^{1}A_{0}^{*}$) will be no higher than 11.1% (1/9).² However, many groups report the results that the obtained Φ_{UC} exceeds this limit (11.1%)⁹⁶⁻¹⁰¹ and suggest that both the triplets and the quintets have also contribution to the upconversion efficiency.

3.1 Solution-based Upconversion

Castellano group made a lot of pioneering work to develop different upconversion systems that emission short wavelength in the range of UV~visible by excitation longer wavelength even to the near-infrared regions.^{93, 102-105} Among them, the green-to-blue upconversion based on bimolecular PdOEP/DPA (octaethyl-porphyrinatopalladium(II)/9,10-diphenylanthracene) has been investigated extensively due to DPA possessing high fluorescence

autumn yield (Φ_F =0.95) and suitable triplet energy level (E_{TI} =1.77eV) matched with sensitizer PdOEP. In 2005, Castellano group comparatively investigated the upconversion efficiencies of DPA and anthracene (An) doped with the identical sensitizer $Ru(dmb)_{3}$.¹⁰² They found that the upconversion intensity of DPA approximately achieves 24.4-fold enhancement, relative to anthracene (An) as emitter, which is attributed to DPA's increased singlet fluorescence quantum yield (Φ_F =0.95) with respect to anthracene (Φ_F =0.27) (Table 1). This reveals that choosing the suitable triplet acceptor with high fluorescence quantum yield (Φ_F) is the key factor for the TTA-UC system. The other green-to-blue upconversion system is Ir(ppy)₃ (ppy=2-phenylpyridine)/pyrene bimolecular system (Fig. 14). Excitation the MLCT band of Ir(ppy)₃ can produce the blue upconverted fluorescence that originates from pyrene (Table 1).¹⁰³ If high concentrations of pyrene was using, the upconverting located at 470 nm was observed, which results from the pyrene excimer.¹⁰³ So, the effective simultaneous sensitization of both singlet pyrene and pyrene excimer is valuable since it would compose white light with respect to monochromatic incident photons. Meanwhile, Castellano group designed covalent binding sensitizer-acceptor chromophore and investigated the upconversion efficiency in comparison with the sensitizer/acceptor bimolecular system. Under identical experimental conditions, the efficiency (Φ_{UC}) of intermolecular [Ru(dmb)₃]²⁺/anthracene (An) is almost 3-fold increased relative to that of intramolecular [Ru(dmb)₃]²⁺/anthracene (An) (Fig. 14).^{104, 105} This suggests that sensitizer-acceptor containing chromophore tends to undergo Foster type singlet-singlet transfer, where the Dexter energy-energy transfer is made against.¹⁰⁶



Fig. 14 Molecular structures of sensitizers and acceptors generating green-to-blue upconversion.

Recently, we reported several green-to-blue systems containing DPA-derivative (such as DTA, DTACI DTACN and DTACO₂Me). (Fig. 14).¹⁰⁷ Selective excitation of PdOEP (532 nm, 0.5 W/cm²) in DMF resulted in anti-Stokes blue emission at 430~450 nm. The maximum upconversion quantum yield (Φ_{UC} =17.4%) was obtained for the pair PdOEP/DTACI, concomitantly combining high fluorescence quantum

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yield of DTACI (Φ_{F} , 70%) and the effective Stern-Volmer quenching constant (k_{sv}, 8.9×10⁴ M⁻¹).¹⁰⁷ Having considered that much less attention is paid to the development of new triplet acceptors, we synthesized some new 9,10-dinaphthylanthracenes (Figs. 15).¹⁰⁸ The results showed that with the same sensitizer such as PdMeTPP, the 9,10-dinaphthylanthracene with donating group exhibits a higher upconversion efficiency than that with withdrawing group. The results have shown that 9,10-dinaphthylanthracene (DNAMe) showed high fluorescence quantum yield (Φ_F , 78%) and larger quenching efficiency (k_q , 554.9 M⁻¹·s⁻¹), in comparison with DNACI $(\Phi_F=69\%, k_q=390.0 \text{ M}^{-1} \cdot \text{s}^{-1})$ and DNACN $(\Phi_F=63\%, k_q=98.1 \text{ M}^{-1} \cdot \text{s}^{-1})$. Consequently, their upconversion efficiencies (Φ_{UC}) were in the order of DNAMe (33.68 %) >DNACI (24.57 %) > DNACN (21.03 %), under excitation at ultralow power density of 60 mW·cm² (532 nn). Dynamics data showed that the increasing phosphorescence lifetime (τ_p) accompanied by decreasing non-phosphorescence decay rate constant (knp) has contribution to the triplet-triplet energy transfer (TTT), confirmed by the Stern-Vlomer equation.¹⁰⁸



From the point view of the solar energy application, the red-toblue upconversion was more interesting since such the system can make the best of harvesting sun light over a near infrared range of the spectrum solar. The typical red-to-blue upconversion systems are reported to be PtTPBP doped with perylene and 2CBPEA, respectively (Fig. 16). These systems can produce upconvertion at 450~460 nm with respect to the excitation wavelength at 635 nm, showing larger anti-Stokes shift at 0.73-0.80 eV (Table 1).92, 110 Apart from the red-to-blue upconversion system, the red-to-yellow upconversion system was also interesting for solar energy application,112-114 where the systems were mainly fixed on the acceptor of rubrene (5,6,11,12-tetraphenylnaphthacene) doped with different triplet sensitizers. For example, when rubrene was combined with PdPh₄TBP and PdPh₄MeO₈TNP, respectively, the yellow upconverted emission centered at 560 nm was observed in toluene on the excitation at 635 and 695 nm, respectively, which can excite PdPh₄TBP and PdPh₄MeO₈TNP (Fig. 16).¹⁰⁰ Also, the

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yellow upconverted emission from rubrene in toluene was observed with selective excitation of PdTAP at 780 nm and 11,15,18,22,25-octabutoxyphthalocyanine (PdPc(OBu)₈) at 725 nm, respectively. (Fig. 16)^{115, 116} The above four upconverted systems resulted in net energy shift between the excitation wavelength and the emitted photons of 0.62 eV for PdTAP/rubrene, 0.26 eV for PdPh₄TBP/rubrene, 0.43 eV for PdPh₄MeO₈TNP/rubrene and 0.50 eV for PdPc(OBu)₈/rubrene, respectively.^{115, 116} As for the pairs of PdPh₄TBP/9,10sensitizer/acceptor bis(phenylethnyl)anthracene (BPEA) and PdPh₄MeO₈TNP/9,10bis(phenylethynyl)napthacene (BPEN) (Fig. 16), they can produce red-to-green (635 nm shifting 490 nm) and red-to-orange (695 nm shifting to 560 nm) upconversion in toluene, respectively, resulting in the net energy shift of 0.58 and 0.43 eV, respectively.¹¹⁷ Interestingly, in [Ru(dmb)₃]²⁺/9,10-dimethylanthracene (DMA) system (Fig. 14, Fig. 16), almost equal portions of DMA upconversion and its excimeric emission was presented, which resulted in an overall broad-band white emission.¹¹⁸ It was of critical importance to expand the upconversion blue-shifting to UV region so as to develop the solar utility of semiconductors (such as dye-sensitization. 2009. TiO_2 without In Castellano group⁹².reported a new bimolecular system, 2,3-butanedione (biacetyl)/2,5-diphenyloxazole (PPO) that can effect visible-to-UV photon upconversion. With selective 442 nm excitation of the triplet sensitizer of biacetyl, UV upconversion from PPO centered at 360 nm was recorded in deaerated benzene, which presents anti-Stokes shifted by a record 0.64 eV with respect to the excitation.



Fig. 16 Molecular structures of triplet sensitizers and acceptors.

Up to now, the triplet-triplet annihilated upconversion (TTA-UC) materials only work efficiently in solution with the

efficiency at 3~39% since the TTA-UC is diffusion controlled, the chromophore diffusion in solution can be significantly promoted. Usually, the employed TTA-UC solvents are benzene,⁹⁰ DMF,⁹² toluene,⁹⁰ acetonitrile¹¹⁸ and dichloromethane¹¹⁹ etc. More recently, we systematically investigated the both aprotic and protonic solvent-effects on the upconversion efficiency (Φ_{UC}).¹²⁰ The results showed that the Φ_{UC} of DPA/PdTPP in aprotic solvents decreased with the increasing of aprotic solvent polarity; while the Φ_{UC} in protonic solvents increased with the increasing of the protonic solvent polarity.¹²⁰ Importantly, we found that alcohol solvent in the presence of β -cyclodextrin can effectively enhance the phosphorescence lifetime (τ_P) of sensitizer (PdTPP) and the fluorescence quantum yield ($\Phi_{\rm F}$) of acceptor (DPA). In the presence of β -cyclodextrin (β -CD) (Fig. 17), the free rotation of DPA is restricted with the result that both the fluorescence deactivation and the triplet-triplet annihilation of acceptor (DPA) are enhanced. Thus, a increasing upconversion efficiency (Φ_{uc}) up to ~36% was obtained under excitation of low power density at 60 mW·cm⁻² $(\lambda_{ex}=532 \text{ nm})$,¹²⁰ which is simple way to effectively increase upconversion efficiency without environmental side effect of these volatile and deleterious organic solvents.



Fig. 17 The proposed mechanism TTA-UC in the presence of β -CD. Reprinted from ref.¹²⁰

The other simple way to increase upconversion efficiency is the external heavy atom effect.¹⁰⁸⁻¹¹⁰ Under low-powered excitation of 30 mW·cm⁻², the upconversion efficiencies (Φ_{UC}) of DPA/PdTPP) and DPA/PdBrTPP in the DMF were measured to be 12.33% and 30.18%, respectively. The latter is attributed to the heavy atom effect from the intramolecular effect. For the same system (DPA/PdBrTPP) in PhBr solvent, the measured Φ_{UC} value was as high as 35.17%, indicating that the solvent effect (i.e., the external heavy atom effect) is more efficient than the internal heavy atom effect to increase the upconversion. Due to TTA-UC showing strong dependence on the triplet state of both the sensitizer and the acceptor, the upconversion efficiency is susceptible to oxygen.¹²¹ Nowadays, lots of efforts have been made to achieve TTA-UC in an aerated environment by embedding chromophores in either rubbery or rigid polymeric matrices,^{2, 122} and loading chromophores into silica nanoparticles,123 as well as even incorporating the upconverting dyes in micellar carriers,¹²⁴ all of these techniques have shown some limitations in either their complicated

preparation processes or very low UC-efficiency (less than 6% at an excitation intensity of 100 mW cm⁻²). Recently, we found¹²⁵ that the oil-in-water (o/w) microemulsion containing 9,10dinaphthylanthracenes doped with Pd(II)tetratolylporphyrin (PdMeTPP) (Fig. 15) exhibits TTA-UC performance without degassing anymore. Under excitation at 60 mW·cm⁻¹ power density, the upconverted o/w microemulsion presented an increasing Φ_{UC} value accompanied by an increase in temperature.¹²⁵ This is attributed to the fact that oil-in-water (o/w) containing the nonionic emulsifier (Tween-20) can be converted reversibly to water-in-oil (w/o) microemulsion (Fig. 18a), which would promote the TTT and TTA processes with a result that the increasing upconverted efficiency as high as 33.12%. Importantly, the upconveted oil-inwater (o/w) microemulsion shows very stable in air for several days (Fig.18b).¹²⁵



Fig. 18 (a) Time-dependent upconversion efficiency for DNAMe/ PdMeTPP in o/w microemulsion (70°C) and DMF (25°C), respectively, under an air atmosphere; (b) Thermal-driven mechanism of effective o/w microemulsion medium for upconversion. Reprinted from ref.¹²⁵

3. 3 Polymer-based Upconversion

Since the solution-based upconverted material is sensitive to oxygen, solid-state upconversion materials are much more attractive, which is convenient for real-world applications without solution toxicity and solvent evaporation. In 2011, Baluschev and Landfester reported the new nanocapsules by encapsulating perylene and PdOEP in polymeric matrixes (Fig. 19a).¹²⁶ Such nanocapsules show efficient UC emission at 450 nm when dispersed in aqueous environment and present potential application in the tissue and cells.¹²⁶ Later, Monguzzi group successfully obtained PtOEP/DPA-doped polymer nanoparticles (NPs) in aqueous suspension and drop-cast films (Fig. 19b).¹²¹ The up-conversion efficiency of the NPs was comparable to that of the corresponding dye solution and the excitation-power threshold (I_{th}) was as low as a few mW·cm⁻² (approaching solar irradiance).¹²¹ At the same time, Li et al also prepared the watersoluble upconversion nanoparticles by coloading PtOEP/DPA into silica nanoparticles with the help of surfactant (Fig. 19c).¹²³ These nanoparticles exhibit high upconversion efficiency at 4.5% (260 mW·cm⁻²) in pure water, which have shown low cytotoxicity and successfully used to label living cells with high signal-to-noise ratio.¹²³ Also, Kim et al obtained the TTA-upconversion (UC) materials achieved in the aqueous phase by encapsulating the

solvent phase (hexadecane, HD) containing PtOEP/DPA in a rigid polymer shell (polyisobutylene, PIB) in the form of aqueous dispersible microcapsules (Fig. 19d).²⁰ The green-to-blue upconversion efficiency of PtOEP/DPA system in HD/PIB were at 10% (at 100 mW·cm⁻²) and 28% (2000 mW·cm⁻²), respectively. These upconverted microcapsules eliminated the need for the deoxygenation step that is essential for existing TTA-based UC processes and enabled stable TTA-UC to occur even after a month of exposure to the ambient environment.

More recently, Castellano and Kim¹²⁷ developed a kind of colour tunable rigid polymeric microcapsules (MCs) that function both in aqueous and dry phases. Platinum(II) tetraphenyltetrabenzoporphyrin (PtTPBP) was used as a sensitizer and perylene, 9,10-bis(phenylethynyl)anthracene (BPEA), and a boron dipyrromethene derivative (BD-2) were employed as acceptors for red to blue, cyan, and green UC, respectively in oxygen-rich environments. Combined with the ability to indirectly sensitize a fluorophore using trivial energy transfer, the present soft material design affords colour tuning as well as broadband emission from a monochromatic light source. Facile magnetic separation also allows UC substrate retrieval particularly suitable for bioimaging and related applications in photonics.127



Fig. 19 TTA-UC nanoparticles composed of PdOE/perylene (a), PtOEP/DPA (b), PdOEP/DPA (c) and PtOEP/DPA (d) in different polymeric matrixes. Reprinted from refs^{20, 121, 123, 126}

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The dyes embedded within the NPs provided the crucial benefit of shielding both sensitizer and acceptor from the external environment, preventing quenching by oxygen and suggesting a more-general employment of this material as a dye-protective shell. In 2008, Castellano group reported that the red-to-yellow upconversion from the host EO-EPI doped bimolecular

 Table 1 Examples of combinations of sensitizers and emitters and the parameters of triplet-triplet annihilation upconversion performances

No.	Sensitizer (optimized concentration)	Acceptor (optimized concentration)	Wavelength- shift	λ_{ex}	λ_{uc}	Anti-Stocks (E _{ex} -E _{UC})	Solvent	Ref.
1	$(30 \mu M)^{3}$	DPA (1.3 mM)	green-to-blue	514.5 nm or 532 nm	430 nm	0.47 eV or 0.55 eV	CH₃CN	102
2	$(10 \ \mu M)$	pyrene (1 mM)	blue-to-UV	450 nm	390 nm	0.42 eV	CH ₂ Cl ₂	103
3	PdPh ₄ TBP PdPh ₄ TBP (100 μM)	C C C C C C C C C C C C C C C C C C C	red-to-yellow	635 nm	560 nm	0.26 eV	toluene	100
4	X X Y Y Y Y X Y Y Y Y Y X Y Y Y Y Y Y Y Y Y Y Y Y Y	rubrene (2 mM)	red-to-yellow	695 nm	560 nm	0.43 eV	toluene	100
5	$\begin{array}{c} + \\ + \\ + \\ + \\ + \\ + \\ + \\ + \\ + \\ + $	Bis(tetracene) (0.5 mM)	red-to-green	700 nm	480~58 0 nm	0.37~0.81	toluene	141
6	$\begin{array}{c} & OC_{4}H_{3} & OC_{4}H_{3} \\ C_{4}H_{3}O & N_{Pd} \\ C_{4}H_{3}O & N_{Pd} \\ C_{4}H_{3}O & N_{Pd} \\ C_{4}H_{3}O & C_{4}H_{3} \end{array} \\ (16.1 \ \mu M) \\ OC_{4}H_{3}OC_{4}H_{3} \end{array}$	rubrene (0.6 mM)	red-to-yellow	725 nm	560 nm	0.5 eV	toluene	116
7	$\begin{array}{c} & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\$	rubrene (1 mM)	red-to-yellow	790 nm	570 nm	0.61 eV	toluene	115
8	() + () + () + () + () + () + () + () +	2CBPEA (0.089 mM)	red-to-blue	635 nm	490 nm	0.58 eV	DMF	92

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9	Bu ^t H ^I Bu ^t H ^I H ^I	perylene (2.3 mM)	red-to-blue	655 nm	440 nm	0.93 eV	toluene	142
10	Ν PtOEP (100 μM)	DPA (1 mM)	green-to-blue	532 nm	435 nm	0.52 eV	polymeric matrices	121
11	$\begin{array}{c} Bu^{1} & F_{1} = R_{2} = H \\ Bu^{1} & H_{1} = R_{2} = H \\ Bu^{1} & H_{2} = H \\ Bu^{1} & H_{2} = H \\ H_{2} = H_{2} = H_{2} \\ H_{3} = H_{2} = H_{2} \\ H_{2} \\ H_{2} = H_{2} \\ H_{2} = H_{2} \\ H_{2} \\ H_{2} = H_{2} \\ H_{$	rubrene (5.1 mM)	red-to-yellow	600~75 Onm	550~60 0 nm	0.41~0.6 eV	toluene	143
12	$ \begin{pmatrix} N \\ N \\ N \\ Pd \\ N \\ $	DPA (2.4 mM)	green-to-blue	532 nm	436 nm	0.51 eV	OH- solvent	120
13	Me N-Pd-N Me Me Me Me	R = CH ₃ DNAMe R = CI DNACI R = CN DNACN (2.4 mM)	green-to-blue	532 nm	446~46 4 nm	0.34~0.45 eV	micro- emulsion	125
14	Br N-Pd-N Br Br Br Br	DPA (2.4 mM)	green-to-blue	532 nm	436 nm	0.51 eV	Br	108
15	$ \begin{array}{c} $	perylene (0.14 mM)	red-to-bule	635nm	440nm	0.87 eV	THF	144
16	$ \begin{array}{c} $	BPEA (0.13 mM)	red-to-blue	635nm	472nm	0.68 eV	THF	144
17	PtTPBP N Pt N N H (11 μM)	Bd-2 (0.14 mM)	red-to-yellow	635nm	536nm	0.36 eV	THF	144

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PdPc(OBu)₈/rubrene.¹¹⁶ Although rubrene was easy to decompose over several days under ambient aerated conditions, the intensity of yellow upconverted fluorescence was shown to slowly decreased in this solid system over this time period, demonstrating that the decomposition of rubrene can be effcectively depressed in host EO-EPI matrixes, as was evident by the disappearance of the absorption bands of rubrene.¹¹⁶ All of these solid TTA-UC materials were confirmed to keep stable upconversion emission for several months since the degassed solution containing the sensitizer/acceptor pairs were blended in films under the condition of nitrogen or argon atmosphere. However, these solid-based upconversion efficiency was quite low (less than 6% at an excitation intensity of 100 mW·cm⁻²), with respect to the counterpart in liquid solution. For example, using cellulose acetate as the inert host matrix doped with palladium(II)tetraphenyltetrabenzoporphyrin (PdTPBP)/9,10bis(phenylethylnyl)anthracene (BPEA), the red-to-green photon upconversion at 515 nm originating from BPEA was observed when selective excitation of PdTPBP at 633 nm, however, the upconverted efficiency was three orders of magnitude lower in the solid film than in liquid solution.¹²⁸ This indicates that the polymer matrix reduces the triplet excitons mobility and the diffusion coefficient to result in decreasing the TTA-upconversion. As predicted by the Stokes-Einstein relationship, molecular diffusion coefficients (D) is directly proportional to the temperature (T) and inversely proportional to the viscosity (η) of the medium, shown in Eq. 17.129

$$D = \frac{kT}{6\pi nR}$$
(17)

Here, k is Boltzmann's constant. R is the radius of the spherical particle. Since small sized molecules are easy to diffuse, the sensitizer and acceptor should be small; meanwhile, the increased temperature and decreased viscosity (η) of the medium also promote diffusion, all of which would result in enhanced TTA-UC. For polymer-based materials, as the temperature of the film is increased, the polymer viscosity is reduced; these cooperative effects promote faster diffusion and more efficient energy transfer collisions with improved upconversion yields at elevated temperatures, probably due to the varied distance in the polymeric matrix.130

To exploit efficient solid upconverted materials, several rubbery polyurethanes are selected as the solid matrixes, such as copolymer ethyleneoxide/epichlorohydrin (EO-EPI, Fig. 20a),^{116, 131} cellulose acetate, rigid poly(methylmethacrylate) (PMMA),¹³² polyurethane precursors (Clear Flex 50, CLRFLX, Fig. 20b),133 and even a multicomponent polymeric film.¹²⁸ For example, Castellano group used copolymer of ethyleneoxide and epichlorohydrin (EO-EPI) as the host matrix doped with the bimolecular PdOEP/DPA.¹³¹ They found that TTA-upconversion efficiency was much lower in comparison with that in solution. This strongly suggests that enhancing mobility of PdOEP and DPA in the polymeric matrix is much more essential, since the chromophore diffusion is inhibited in the glassy state.¹³¹ When PtOEP/DPA was doped in rigid poly(methylmethacrylate) (PMMA) films, the obtained blue DPA upconversion efficiency was at 0.02%; however, within the rigid PMMA films doped with 2MeOTX, the blue DPA upconversion efficiency was enhanced. Also within the rigid PMMA films doped with 2MeOTX/PPO (2-methoxythioxanthone/2,5-diphenyloxazole), blue-to-UV photon upconversion was reported when selective excitation of 2MeOTX at 410 nm resulted in upconverted PPO emission in the region 350~380 nm.¹³² It was found that increasing doping concentrations of the emitter can facilitate the migration of triplet energy in the polymer host. Meanwhile increasing temperature could decrease the viscosity/rigidity of polymer and would improve the doped chromophore diffusion, which would significantly promote the polymer-based upconversion efficiency.



Fig. 20 (a) Chemical structure of EO-EPI and the optical picture of a blend film comprising of PdOEP and DPA in polymer; (b) photographs of CLRFLX samples doped with PdOEP/DPA. Reprinted from refs.^{106, 133}

4. Conclusions and outlook

So as to provide a comprehensive overview for investigators who are interesting in organic molecular photon up-conversion, we reviewed the two-photon absorption upconversion (TPA-UC) and triplet-triplet annihilation upconversion (TTA-UC) collectively, each of which has been actively investigated in recent years. Although TPA-UC and TTA-UC are all based on organic molecules, both are very different, such as in mechanism, characteristics and techniques involved. The distinguishing features between TPA-UC and TTA-UC are presented in Table 2.

Table 2 Distinguishing features of TPA-UC and TTA-UC

	TPA-UC	TTA-UC			
Optical effect	nonlinear	nonlinear			
Quantum transition	prohibition	allowance			
Excitation light	\geq 10 ⁶ W·cm ⁻²	< 0.1 W⋅cm ⁻²			
Excitation light	tight focusing light	Focusing light			
Influence factor	intramolecular	intermolecular			
initial internet internet	charge-transfer	energy-level			
	deep penetratior	, low excitation			
Advantages	high resolution, larg	e power, high UC			
	anti-Stokes emission	efficiency			
		susceptible to			
Drawbacks	high pump power	oxygen, small anti-			
		Stokes emission			

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In seeking for the active TPA-UC and TTA-UC chromophores, physical scientists, chemists and material scientists are required to play the critical roles in the investigation of materials and photophysical rules, because design of the new efficient chromophores are dependent on molecular engineering and optical operation. Recent TPA upconversion advance¹³⁴ shows that the metal-organic framework materials can effectively boosted their multiphoton absorption cross-sections and enhanced upconversion efficiency based on Förster resonance energy transfer. Within hostguest metal-organic frameworks consisting of encapsulated high quantum yielding guest molecules, the multi-photon upconversion can be effectively enhanced at 800, 1200, and 1500 nm femtosecond pulsed laser excitation.134 The multi-photon upconversion exhibits much more beneficial owing to the cubic or biquadratic dependence of the input light intensity and the use of much longer excitation wavelength. Also, multi-photon excitation would present better spatial confinement of the excitation volume and thus a higher resolution. Furthermore, the multi-photon lasing can result in the largest anti-Stokes emission so far.12 An other recent progress¹³⁵ in developing TPA materials showed that an organic single crystal of an oligo(phenylene vinylene) can exhibit strong two-photon excited fluorescence and stimulated emission, with large TPA cross sections spanning a wide wavelength range at 700~800 nm. The measured TPA cross-section is exceptionally large (3137 GM). Because of the very large TPA cross-sections, twophoton-excited fluorescence in either solution and in solid form can be unambiguously record even on a standard spectrofluorimeter with a Xeon lamp as excitation source,¹³⁵ showing potential TPA-UC applications in the fields of biophotonics and optics.

As for TTA-UC molecule engineering, the sensitizers with intense absorption of visible light in the red and near-IR range, accompanying with long triplet lifetime (τ_P) is aspired. Meanwhile developing acceptors with high fluorescence quantum yield ($\Phi_{\rm F}$) is also important. Moreover, the energy levels between sensitizer and acceptor should be matched, that is, $E_{T1(D)}>E_{T1(A)}$ and $2E_{T1(A)}>$ $E_{S1(A)} > E_{S1(D)}$ (i.e., the excited triplet state of the sensitizer ($E_{T1(D)}$) is higher in energy than the triplet state of the acceptor $(E_{T1(A)})$, the singlet excited state of the acceptor $(E_{S1(A)})$ should be higher in energy than that of the singlet excited state of the sensitizer $(E_{S1(D)})$ and lower than two times the triplet state energy of the acceptor itself).¹³⁶ Recent TTA upconversion advance¹³⁷⁻¹³⁹ reveals that developing the sensitizers with high triplet energy level (E_T) and the acceptors small singlet-triplet difference (ΔE_{ST}) is beneficial to triplet-triplet energy transfer efficiency (Φ_{TTT}) and especially to promoting triplet-triplet annihilation (Φ_{TTA}) .¹³⁷⁻¹³⁹ In addition, considering that the spin multiplicities of the other 5/9 and 3/9 of spin multiplicities can also be annihilated via the singlet pathway.¹⁴⁰ How to use these the spin multiplicities is worth the whistle.

Finally, it should be pointed out that the key to increase upconversion efficiency is to enhance the intramolecular chargetransfer for TPA-UC and the intermolecular energy-transfer for TTA-UC. Probably, in the framework of host-guest super-molecular system, the combination of the Förster energy-transfer for TPA-UC and Dexter electron-transfer for TTA-UC is new strategy of the molecule engineering. The investigation of relationship between TPA-UC and TTA-UC is challenging and is especially worth pursuing.

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Notes

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