



Review

Photon upconversion based on sensitized triplet–triplet annihilation

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ABSTRACT

Photon upconversion, the process wherein light of long wavelength is frequency converted to photons of higher energy, is readily achieved at low incident power through sensitized triplet–triplet annihilation (TTA) in various chromophore combinations spanning the UV to the near-IR. This emerging wavelength-shifting technology truly represents a viable route towards converting low energy terrestrial solar photons into light adequate to drive electron transfer in operational photovoltaics. Generalized molecular design constraints, all operational examples reported to date, and measurement techniques applied to these low power nonlinear processes are reviewed in this contribution. In many instances, direct visualization of this phenomenon is presented in solution and within various polymeric host materials.

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1. Introduction

1.1. Original experimental observations of TTA in solution

Photon upconversion accomplished through sensitized TTA was first introduced by Parker and Hatchard over 40 years ago wherein upconverted fluorescence was observed from donor/acceptor solution mixtures containing phenanthrene/naphthalene or proflavin hydrochloride/anthracene [1]. Selective excitation of the donor

chromophores produced photoluminescence blue-shifted with respect to the exciting light and the emission intensity displayed nonlinear incident light fluence dependence. The results of these original findings were interpreted as a two-quantum process involving triplet excited states leading to anti-Stokes delayed fluorescence emanating from the acceptor's singlet excited state. Investigators remained fixated on utilizing various combinations of aromatic hydrocarbons to generate upconverted photons through this sensitized TTA mechanism for many of the years that followed [2–5]. Some of the initial research in this area incorporating metal-containing chromophoric species included the observation of S_2 delayed fluorescence in metalloporphyrins [6] and TTA-producing delayed fluorescence in $K_4[Pt_2(P_2O_5H_2)_4]$, “platinum pop” [7]. Outside of these latter spurious reports, further developments in

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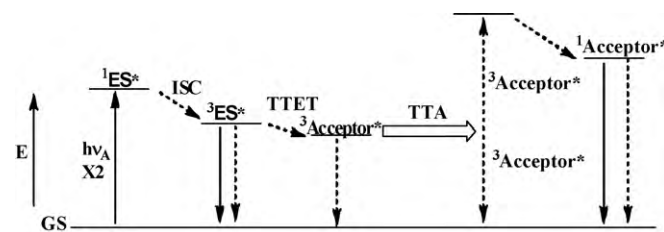
TTA-sensitized photon upconversion would not emerge until the 21st century.

Most recently, this field has experienced a significant rejuvenation spawned by the introduction of various metallated triplet sensitizers used in conjunction with appropriate acceptors/annihilators spanning the visible-to-near-IR region of the spectrum. These combinations of chromophores have successfully generated upconverted photons that can now be routinely discerned by the naked eye. The visualization of these newly conceived sensitized TTA-producing compositions in solution and a variety of polymeric media at low excitation power are reviewed herein. Molecular design constraints and measurement techniques that are applied to these low power nonlinear processes are also presented.

1.2. Requirements for the sensitizer and acceptor/annihilator molecules

The sensitized triplet–triplet annihilation mechanism involves the transfer of energy between a sensitizer (donor) molecule and an acceptor/annihilator. Hence, several factors are considered when determining the proper combination of chromophores in a viable upconverting scheme. Sensitizers are selected based on their ability to absorb light in the visible-to-near-IR region of the spectrum allowing for low energy excitation and must possess a relatively long triplet excited state lifetime, typically on the order of several microseconds and beyond. This latter requirement is necessary to facilitate conditions enabling efficient diffusional-based quenching. In our research group, metallated sensitizers including those that exhibit metal-to-ligand charge transfer (MLCT) excited states as well as heavy metal-containing porphyrins and phthalocyanines are generally studied since the presence of the π -conjugated aromatic rings in the latter shift their respective absorption and emission maxima towards the red and near-IR region of the spectrum. The heavy metal present in the porphyrins and phthalocyanines (Pd or Pt) strongly enhances the spin-orbit coupling which yields singlet–triplet intersystem crossing (ISC) efficiencies near unity. In order to observe bimolecular quenching of the triplet excited state of the sensitizer the triplet acceptor energy must be lower than the triplet energy of the sensitizer. The greater the energy difference between the triplet sensitizer and triplet acceptor, the greater the driving force for this reaction and generally speaking, the more favorable the triplet energy transfer process. It is also advantageous to use acceptors/annihilators with near unity fluorescence quantum yields since this value ultimately contributes to the overall upconversion quantum efficiency. The sensitizer (donor) molecule is chosen so that its singlet excited state lies below that of the acceptor's singlet manifold while the sensitizer's triplet state lies above that of the acceptor. In essence, the singlet and triplet excited states of the sensitizer should be strategically nested between the singlet and triplet excited states of the acceptor/annihilator. As long as these specific energy criteria are met and the combined triplet energy from two acceptor molecules is greater than or equal to the acceptor's singlet state energy, then conditions are appropriate for the observation of upconverted fluorescence from the sample.

A generalized Jablonski diagram summarizing the processes that are involved in photon upconversion via sensitized TTA is presented in Scheme 1. Following long wavelength selective excitation of the sensitizer and ISC, this molecule transfers its triplet energy to the acceptor, regenerating the ground state sensitizer. This process repeats and another long-lived excited triplet acceptor is formed, a stoichiometry now suitable to support one TTA event. In reality, the sensitization process cycles many times yielding a substantial population of long-lived sensitized triplets enabling TTA to take place rather efficiently. The primary evidence supporting TTA typically involves the observation of singlet fluorescence observed



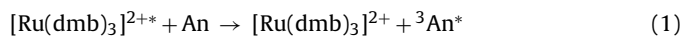
Scheme 1. Generalized energy level diagram of the upconversion processes between the triplet states of the sensitizer molecule and the triplet acceptor molecule leading to the singlet delayed fluorescence. Colored solid lines represent radiative processes. GS is ground state, ES is excited state, ISC is intersystem crossing, TTET is triplet–triplet energy transfer, and TTA is triplet–triplet annihilation.

anti-Stokes to the excitation light possessing a spectral profile identical to the acceptor molecule. The intensity of this singlet fluorescence displays a quadratic (x^2) incident light power dependence as TTA requires reaction between two sensitized triplet acceptor molecules.

2. Photon upconversion in solution

2.1. Development of metal–organic upconverting compositions

The first example of photon upconversion that emerged from our research group involved observations resulting from long wavelength excitation of $[\text{Ru}(\text{dmb})_2(\text{bpy-An})]^{2+}$ (dmb is 4,4'-dimethyl-2,2'-bipyridine and bpy-An is 4-methyl-4'(9-anthryl)-2,2'-bipyridine) in CH_3CN [8]. Here the triplet MLCT excited state is higher in energy than the triplet state of anthracene, while the singlet excited state of anthracene is higher in energy than that of the $^1\text{MLCT}$ and is lower than two times the triplet state of anthracene [9–13], thereby satisfying the energy requirements for sensitized TTA. Upon selective excitation of the MLCT transition at 450 nm, intramolecular energy transfer produces long-lived triplet anthracene and when two energized chromophore-quencher molecules diffuse to form an encounter complex leading to TTA, one ground state and one excited singlet state chromophore is generated. The latter decays radiatively to the ground state as evidenced by delayed fluorescence emission from anthracene [8]. It should be noted that although intramolecular singlet energy transfer provides an efficient nonradiative deactivation pathway [11,14–16], upconverted anthracene fluorescence was easily detected in our initial experiments. However, the MLCT ground state served as an intramolecular singlet state quencher of the anthracene fluorescence thereby resulting in rather low upconversion efficiency. Hence, the intermolecular processes using equimolar concentrations of $[\text{Ru}(\text{dmb})_3]^{2+}$ and anthracene were also investigated. The direct comparison between the intramolecular and the intermolecular systems under identical experimental conditions resulted in a ~ 2.9 -fold increase, likely resulting from suppression of Förster-type singlet-singlet transfer subsequent to TTA. In essence the simpler non-covalent donor-acceptor system in dilute solutions was found to be superior in generating the anti-Stokes delayed anthracene fluorescence [8]. The pertinent bimolecular triplet quenching and triplet–triplet annihilation reactions following low energy light excitation are shown in Eqs. (1) and (2).



A key feature of this sequence is the requirement to efficiently produce two sensitized triplets in order to observe upconverted light emission from singlet anthracene. In a later investigation, it was shown that the substitution of anthracene by 9,10-diphenylanthracene (DPA) further improved the upconversion

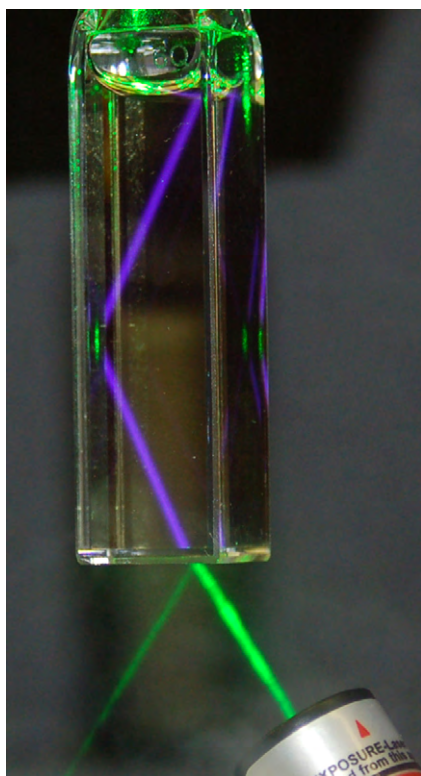


Fig. 1. Digital photograph of the upconverted fluorescence produced in a CH_3CN solution containing $[\text{Ru}(\text{dmb})_3]^{2+}$ and DPA. Excitation was afforded by a commercial green laser pointer ($\lambda_{\text{exc}} = 532 \text{ nm}$).

fluorescence yield, resulting in approximately a 24-fold enhancement of green-to-blue frequency conversion [17]. Stern–Volmer and bimolecular quenching constants revealed that the observed enhancement did not simply result from differences in quenching efficiency. In fact, a larger quenching constant was measured in the case of anthracene ($K_{\text{sv}} = 4492 \text{ M}^{-1}$; $k_{\text{q}} = 5.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) relative to DPA ($K_{\text{sv}} = 3465 \text{ M}^{-1}$; $k_{\text{q}} = 4.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) [17], meaning that at identical quencher concentrations, the efficiency in the former would necessarily be greater. Hence, it was believed that DPA's increased singlet fluorescence quantum yield ($\Phi = 0.95$) with respect to anthracene ($\Phi = 0.27$) [18] afforded the modest increase in relative upconversion efficiency. It is important to note that the green-to-blue photon upconversion can be easily visualized in $[\text{Ru}(\text{dmb})_3]^{2+}$ /DPA system with a commercial green laser pointer ($\lambda_{\text{exc}} = 532 \text{ nm}$, $<5 \text{ mW}$ peak power) as shown by the digital photograph in Fig. 1.

The synthetic utility of sensitized TTA reactions was later demonstrated where selective excitation of $[\text{Ru}(\text{dmb})_3]^{2+}$ at 457.9 nm in a degassed concentrated solution of anthracene in acetonitrile leads to the sensitized [4+4] photodimerization of anthracene [19]. Extending the reactions presented in Eqs. (1) and (2) to include Eq. (3), the anthracene dimer (An_2) is produced when singlet excited anthracene encounters an anthracene ground state molecule, which only occurs at high anthracene concentration.



It should be noted that identical photolysis of this reaction in aerated CH_3CN results in no precipitation after 130 min of continuous irradiation at low energy. However, the anthracene absorption bands monotonically disappeared as a function of irradiation time suggesting efficient endoperoxide formation [19]. A digital photograph taken after 40 min of visible light irradiation in deaerated CH_3CN illustrates the extent of the reaction and the ease at which

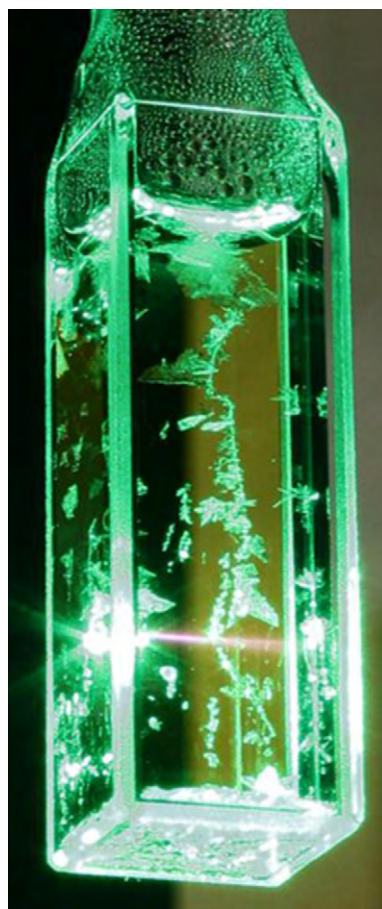


Fig. 2. Digital photograph of the optical cell containing crystallized anthracene photodimer produced by Ar^+ laser photolysis ($\lambda_{\text{exc}} = 514.5 \text{ nm}$) of an acetonitrile solution containing $[\text{Ru}(\text{dmb})_3]^{2+}$ ($5.25 \times 10^{-5} \text{ M}$) and anthracene ($\sim 1.4 \times 10^{-2} \text{ M}$). Photograph was adapted from reference [19].

the sensitized photochemical upconversion takes place (Fig. 2). The ability to afford chemical transformations via sensitized TTA is potentially valuable for energy storage in addition to organic synthesis. In relation to the latter, several recent reports have focused attention on using photoexcited $[\text{Ru}(\text{bpy})_3]^{2+}$ to promote synthetic transformations, including cycloadditions [20,21].

Sensitized upconverted fluorescence in non-covalent triplet energy transfer assemblies utilizing $\text{Ir}(\text{ppy})_3$ ($\text{ppy} = 2$ -phenylpyridine) as the sensitizer and pyrene or 3,8-di-*tert*-butylpyrene as the triplet/annihilator have also been investigated. The absorption spectrum of $\text{Ir}(\text{ppy})_3$ shows an intense band in the wavelength range 250–320 nm which is due to the π – π^* transitions localized on the ppy ligands. A weaker MLCT absorption band extends from 330 nm and tails into the visible. The MLCT emission of $\text{Ir}(\text{ppy})_3$ is centered near 515 nm and this particular study assumed a quantum yield of 0.61 in CH_2Cl_2 [22]. Recently it has been shown that the $\text{Ir}(\text{ppy})_3$ quantum yield is a remarkable 1.0 at room temperature [23]. The fluorescence quantum yields of pyrene and *tert*-butylpyrene are 0.35 and 0.39 respectively [22]. Upconverted fluorescence from pyrene and 3,8-di-*tert*-butylpyrene resulting from TTA following selective excitation of $\text{Ir}(\text{ppy})_3$ in deaerated dichloromethane using 450 nm laser pulses was observed. In both systems the TTA process was confirmed by the near quadratic dependence of the upconversion fluorescence intensity measured as a function of incident light power. However, in the upconverting cocktail utilizing pyrene as the acceptor/annihilator, pyrene excimer formation was detected by its characteristic broad emission centered at 470 nm. This

is a result of the relatively high concentrations of pyrene that was utilized in this study. Nevertheless, selective excitation of $\text{Ir}(\text{ppy})_3$ resulted in simultaneous sensitization of both singlet pyrene and pyrene excimer, the latter degrades the energy stored in the pyrene singlet excited state [22]. Excimer formation was completely suppressed in the case of 3,8-di-*tert*-butylpyrene due to the presence of the steric hindering *tert*-butyl groups [22].

The simultaneous detection of the upconverted singlet fluorescence and strong downconverted excimer emission emanating from pyrene [22] inspired us to develop a system that produces both upconverted and downconverted emission with respect to monochromatic incident photons. Given that many organic light emitting devices (OLED's) and electroluminescence (EL) materials utilize annihilation processes for light generation, it is plausible that such a technology would be adaptable in these applications and may result in devices with low drive voltages. Hence, we investigated a molecular assembly composed of $[\text{Ru}(\text{dmb})_3]^{2+}$, and 9,10-dimethylanthracene (DMA), an aromatic hydrocarbon known to produce low energy excimer emission out to ~ 700 nm [24,25]. With 514.5 nm laser excitation at low photon flux, selective excitation of $[\text{Ru}(\text{dmb})_3]^{2+}$ sensitizes $^3\text{DMA}^*$ which undergoes TTA, producing photon emission that spans almost the entire visible spectrum, 425–700 nm, with emission color that is systematically variable with excitation power [26]. The triplet excited state of $[\text{Ru}(\text{dmb})_3]^{2+}$ is efficiently quenched by 11 mM DMA in DMF resulting in photon upconversion but no excimer formation. The bimolecular quenching constant of the dynamic quenching process is $1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. However, at 90 mM DMA, both upconversion and downconversion processes are readily observed in DMF solutions [26]. The TTA process was confirmed by the quadratic dependence of the upconverted and downconverted emission emanating from the entire integrated photoluminescence profile (400–700 nm) of DMA measured with respect to incident light power. Time-resolved emission spectra of $[\text{Ru}(\text{dmb})_3]^{2+}$ and 90 mM DMA in both aerated and deaerated DMF clearly illustrated the time delayed nature of both types of singlet state emission which interestingly displayed similar decay kinetics on the order of 14 μs [26]. The emission quantum yields (Φ) measured using relative actinometry based solely on absorbed photons, increased with increasing DMA concentration, reaching a plateau at 3.0 mM DMA ($\Phi = 4.0\%$) while at 90 mM DMA the overall quantum yield diminished to 0.5%. The dominant process occurring at 3.0 mM DMA is upconversion from the singlet excited state of DMA, whereas, at 90 mM DMA both upconversion and excimeric emission are observed in almost equal portions, thereby resulting in an overall broad-band emission profile appearing white in color [26].

In an attempt to expand the range of chromophores applicable for upconversion, other molecules possessing long-lived triplet excited state lifetimes and whose absorption extend into the lower energy region of the spectrum were investigated as sensitizers. Serving the role of acceptor/annihilator, chromophores with very high fluorescence quantum yields, preferably those approaching unity were investigated. Our group and others have studied a range of porphyrins and phthalocyanines as sensitizers in upconverting schemes. We reported the first example of a phthalocyanine used in an upconverting scheme. In this study, 11,15,18,22,25-octabutoxyphthalocyanine ($\text{PdPc}(\text{OBU})_8$) was used as the sensitizer in combination with 5,6,11,12-tetraphenylanthracene (rubrene) as the acceptor/annihilator in toluene [27]. $\text{PdPc}(\text{OBU})_8$ is a photochemically stable compound with intense absorption in the red to deep-red region of the electromagnetic spectrum with a phosphorescence quantum yield of 77%, $\lambda_{\text{em}} = 996$ nm ($\tau_{\text{T}} = 3.5 \mu\text{s}$), energetically suitable for exothermic energy transfer to the rubrene acceptor [28,29]. Rubrene has been shown to exhibit a fluorescence quantum yield of near unity [18], rendering it an attractive acceptor/annihilator for upconversion. Most notably, rubrene is currently

used as a yellow dopant in light emitting diodes (LEDs) [30] as well as in organic photovoltaics (OPVs) [31]. Upconverted yellow singlet fluorescence from rubrene was generated from selective excitation ($\lambda_{\text{ex}} = 725$ nm) of the red-light-absorbing triplet sensitizer palladium $\text{PdPc}(\text{OBU})_8$ in vacuum-degassed toluene solutions using a Nd:YAG/OPO laser system in concert with gated iCCD detection [27]. An inherent disadvantage to rubrene lies in its propensity to photooxidize in solution forming rubrene endoperoxide which reduces the stability and lifetime of devices where it served as an active component [32,33]. However, in vacuum-degassed toluene solutions, the red-to-yellow upconversion process is stable under continuous long wavelength irradiation and is readily visualized by the naked eye even at modest laser fluence (0.6 mJ/pulse) as shown in Fig. 3a.

The instability of rubrene as the acceptor/annihilator in solution partially inspired us to seek out an air-stable solution-based acceptor that could be employed in an upconverting scheme as the acceptor/annihilator while shifting the excitation energy towards the red region of the spectrum with retention of a large anti-Stokes energy shift. Due to the remarkably high emission efficiency of 2-chloro-*bis*-phenylethynylantracene (2CBPEA) in the visible region of the spectrum, good solubility in a variety of solvents, chemical and thermal stability, and inertness towards dioxygen [34], we proposed this “light-stick” compound to be a viable acceptor/annihilator for use in upconversion schemes. Upconverted singlet fluorescence of 2CBPEA resulting from sensitized TTA is observed following selective excitation of platinum(II)tetraphenyltetraabenzoporphyrin (PtTPBP) at 635 nm. Stern–Volmer analysis of the photoluminescence quenching of PtTPBP by 2CBPEA yields a bimolecular quenching constant of $1.62 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, slightly below the diffusion limit in DMF at room temperature [35]. The quenching pathway is presumed to proceed through triplet–triplet energy transfer and the upconverted fluorescence that was observed resulted from TTA implying efficient triplet production in the porphyrin quenching step. Up to this point, most of the efficiently functioning upconverting systems based on sensitized TTA generally possess energy gaps on the order of ~ 0.5 eV between the excitation light and the maximum singlet fluorescence emission band exhibited by the acceptor/annihilator. The PtTPBP/2CBPEA experimental system offers one of the largest energy differences reported by us (0.58 eV) that places both the absorption of the donor (red) and the upconverted fluorescence of the acceptor/annihilator (blue–green) in the visible region of the electromagnetic spectrum [35]. It is important to note that upon selective excitation of the metalloporphyrin sensitizer with 635 nm light, the blue–green upconverted fluorescence is clearly discernible to the naked eye even in a well-illuminated room as shown in the digital photograph in Fig. 3b.

Inspired by the need to further expand the anti-Stokes energy shifts obtainable from sensitized TTA, we identified a composition that achieved this goal while simultaneously affording visible-to-UV photon upconversion. Selective 442 nm excitation of the triplet sensitizer 2,3-butanedione (biacetyl) in the presence of the laser dye 2,5-diphenyloxazole (PPO) in deaerated benzene results in the observation of singlet fluorescence from the latter in the UV centered at 360 nm, anti-Stokes shifted by a record 0.64 eV with respect to the excitation [36]. As shown in Table 1, among the several upconverting systems that have been investigated both by us and others and apart from the $[\text{Ru}(\text{dmb})_3]^{2+}/\text{An}$ system which at this time represents the greatest anti-Stokes shift of 0.69 eV, the biacetyl/PPO system is the next in line. The anticipated anti-Stokes shift of 0.74 eV for biacetyl/PPO system was unfortunately not realized as a result of the inner filter effect mandated by the extremely large concentrations of PPO necessary to afford reasonable yields of triplet sensitization. The TTA process was confirmed by the quadratic dependence of the upconverted integrated PPO

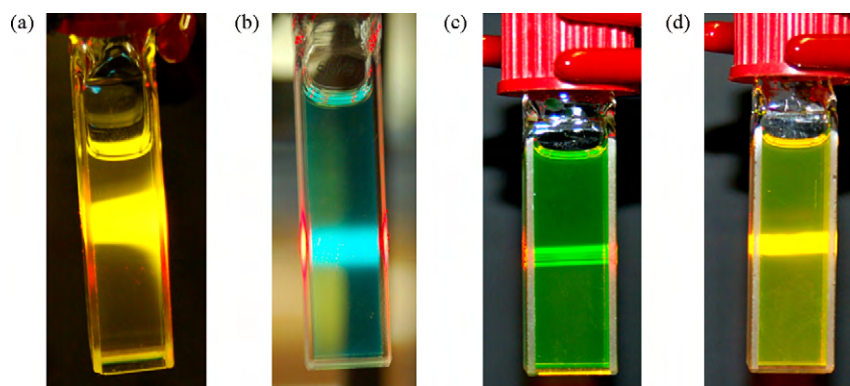


Fig. 3. Digital photographs of (a) 1.61×10^{-5} M PdPc(OBu)₈ and 5.86×10^{-4} M rubrene in deaerated toluene upon 725 nm excitation, (b) 3.40 μ M PtTPBP and 1 mM 2CBPEA in deaerated DMF with laser diode excitation at 635 nm, (c) 3.20 μ M PtTPBP and 6.5×10^{-4} M **BD-1** in deaerated benzene with laser diode excitation at 635 nm (d) 3.20 μ M PtTPBP and 4.2×10^{-4} M **BD-2** in deaerated benzene with laser diode excitation at 635 nm.

emission intensity measured with respect to incident 442 nm light power density [36]. Most recently, our group has reported sensitized red-to-blue upconversion utilizing PtTPBP as the sensitizer and perylene as the acceptor/annihilator in deaerated benzene [37]. This resulted in a record anti-Stokes shift of 0.80 eV with respect to the excitation wavelength and the peak of the upconverted perylene emission [37].

Other research groups have also reported solution-based photon upconversion utilizing PdOEP as the sensitizer and DPA as the acceptor [38]. The green region of the terrestrial solar spectrum in combination with collimating lenses, and long pass filters as well as broad-band interference filters with a central wavelength at 550 nm was used as the excitation source [38]. The blue upconverted DPA fluorescence was observed with an optical fiber spectrometer with excitation intensity at the focal point in the order of 10 W cm^{-2} [38]. Later on, photon upconversion was also reported in a system comprising two sensitizers and a single emitter molecule [39]. Here, palladium *meso*-tetraphenyltetraabenzoporphyrin (PdPh₄TBP) and palladium(II) *meso*-tetraphenyl-octamethoxide-tetranaphtholporphyrin [PdPh₄MeO₈TNP], the sensitizers utilized in this study, were excited with 635 and 695 nm, respectively and the yellow upconverted rubrene emission centered at 560 nm

was observed in toluene [39]. The energy difference between the excitation wavelength and the upconverted singlet rubrene emission in the former is 0.43 eV and in the latter is 0.26 eV (Table 1). It was reported that the red region of the solar spectrum was utilized as the excitation source. This was achieved using a 12 in. Dobsonian telescope to collect and couple the sunlight into a fiber. The infrared tail of the solar spectrum was rejected by a large scale interference filter before focusing at the fiber surface [39]. The use of both sensitizers in the same reaction mixture was reported to be additive in regards to the triplet-triplet annihilation assisted upconversion [39]. To also demonstrate that photon upconversion is a generalized phenomenon and to utilize various regions of the solar spectrum as the excitation source various sensitizer/acceptor combinations were selectively chosen that emits across the entire visible region of the solar spectrum and were investigated. These include sensitizer/acceptor combinations of PdOEP/DPA, PdPh₄TBP/9,10-bis(phenylethynyl)anthracene (BPEA), and PdPh₄MeO₈TNP/9,10-bis(phenylethynyl)naphthalene (BPEN) producing blue, green and orange upconverted emission in toluene upon 532, 635 and 695 nm excitation, respectively [40]. Here, the energy difference between the excitation wavelength and the upconverted maxima of the acceptor/annihilator are 0.51, 0.58 and 0.43 eV for the PdOEP/DPA, PdPh₄TBP/BPEA and

Table 1
Relevant energetics of sensitizer and acceptor/annihilator molecules investigated to date.

Sensitizer	Acceptor	λ_{ex} (nm)	E_{ex} (eV)	λ_{obs} (nm)	E_{obs} (eV)	$E_{\text{obs}} - E_{\text{ex}}$ (eV)	References
PtTPBP	Perylene	635	1.95	451	2.75	0.80	[37]
[Ru(dmb) ₃] ²⁺	An	514.5	2.41	400	3.10	0.69	[17]
Biacetyl	PPO	442	2.80	360	3.44	0.64	[36]
PdTAP	Rubrene	780	1.59	560	2.21	0.62	[41]
PtTPBP	2CBPEA	635	1.95	490	2.53	0.58	[35]
PdPh ₄ TBP	BPEA	635	1.95	490	2.53	0.58	[40,98]
PdOEP	DPA	544	2.28	445	2.79	0.51	[40,80]
PdPc(OBu) ₈	Rubrene	725	1.71	560	2.21	0.50	[27]
PtOEP	DPA	533	2.33	440	2.82	0.49	[97]
ZnTPP	Perylene	532	2.33	441	2.81	0.48	[42]
ZnTPP	C343	532	2.33	443	2.80	0.47	[42]
[Ru(dmb) ₃] ²⁺	DMA	514.5	2.41	431	2.88	0.47	[26]
PdTPBP	BPEA	633	1.96	515	2.41	0.45	[40]
PdPh ₄ OMe ₈ TNP	Rubrene	695	1.78	560	2.21	0.43	[39]
PdPh ₄ OMe ₈ TNP	BPEN	695	1.78	560	2.21	0.43	[40]
2MeOTX	PPO	410	3.02	360	3.44	0.42	[97]
Ir(ppy) ₃	Pyrene	450	2.76	390	3.18	0.42	[22]
Ir(ppy) ₃	<i>tert</i> -Butylpyrene	450	2.76	392	3.16	0.40	[22]
PtTPBP	BD-1	635	1.95	527	2.35	0.40	[47]
[Ru(dmb) ₃] ²⁺	DPA	514.5	2.41	445	2.79	0.38	[17]
PtTPBP	BD-2	635	1.95	556	2.30	0.28	[47]
PdPh ₄ TBP	Rubrene	635	1.95	560	2.21	0.26	[39]

ex = excitation; obs = peak observed emission wavelength.

PdPh₄MeO₈TNP/BPEN mixtures respectively, Table 1. The relative upconverting efficiency for PdPh₄TBP/BPEA was determined and the results are discussed in the quantum yield section later in this review. Others have also reported the use of a palladium(II) tetraanthraporphyrin (PdTAP) in an upconverting scheme, thereby allowing near-IR excitation of this chromophore at 780 nm [41]. Yellow upconverted rubrene emission was observed upon selective excitation of PdTAP at 780 nm in toluene resulting in a net energy shift of 0.62 eV between the excitation wavelength and the emitted photons, see Table 1 for a compilation of anti-Stokes energy shifts realized to date [41].

Recently the d¹⁰ metalloporphyrin, zinc(II) *meso*-tetraphenylporphyrine (ZnTPP), was also investigated in the context of sensitized TTA. The S₁ fluorescence intensity of ZnTPP was used to monitor the initial rate of porphyrin triplet state production while the S₂ fluorescence intensity was used to monitor the initial rate of TTA of the porphyrin in benzene [42]. Two blue-emitting compounds, perylene and coumarin 343 (C343), were investigated as triplet acceptors to study the mechanism of TTA and energy transfer in deaerated benzene solutions of ZnTTP. Perylene and coumarin 343 both have similar singlet energies, 2.81 and 2.80 eV respectively, that lie slightly below the S₂ energy of ZnTPP (2.9 eV) as well as having similar singlet excited state lifetimes of 5.5 ns and 4.0 ns, respectively. However, the triplet excited state energy of perylene (1.53 eV) is lower than the triplet energy of ZnTPP (1.59 eV) whereas, the triplet energy of coumarin 343 (2.06 eV) is significantly higher than that of triplet excited perylene [42]. Both emitter molecules are reported to exhibit photon upconversion upon selective excitation of ZnTPP at 532 nm resulting in a net energy difference between the excitation wavelength and the upconverted perylene and C343 emission of 0.48 and 0.47 eV, respectively (Table 1). In the ZnTTP/peryene system, upconversion involves the triplet energy transfer from the ZnTTP to triplet perylene followed by TTA of perylene thereby resulting in the singlet excited state of perylene which radiatively decays to the ground state. However, in the ZnTTP/C343 system, emission from the S₂ state of ZnTTP is quenched while fluorescence from C343 grows in. The preferred upconversion mechanism in the latter was reported to involve the formation of a triplet exciplex between the porphyrin triplet and the acceptor/annihilator, followed by TTA of the triplet exciplex with a second porphyrin triplet in a three-center process [42], in opposition to the mechanism involving singlet electronic energy transfer that was previously reported [38,43].

2.2. Upconversion quantum yields

Upconversion quantum yields have been determined for several of the experimental systems that have been investigated to date. It is important to note that these efficiencies are controlled by a variety of factors including relative chromophore concentrations along with the quadratic excitation power dependence which makes quantification of an absolute quantum yield for the relevant process difficult. Therefore, we and other investigators have initially approached this problem by defining quantum efficiencies measured under very precise experimental conditions. Most measurements from our laboratory have utilized relative actinometry, Eq. (4) [44], where Φ_{unk} , A_{unk} , I_{unk} and η_{unk} represents the quantum yield, absorbance, integrated photoluminescence intensity and refractive index of the sample. The corresponding terms for the subscript std are for the reference quantum counter, which

$$\Phi_{\text{unk}} = 2\Phi_{\text{std}} \left(\frac{A_{\text{std}}}{A_{\text{unk}}} \right) \left(\frac{I_{\text{unk}}}{I_{\text{std}}} \right) \left(\frac{\eta_{\text{unk}}}{\eta_{\text{std}}} \right)^2 \quad (4)$$

varied in each donor/acceptor system investigated. Eq. (4) incorporates an additional multiplicative factor of 2 since the absorption of 2 photons is required for the observation of 1 upconverted photon

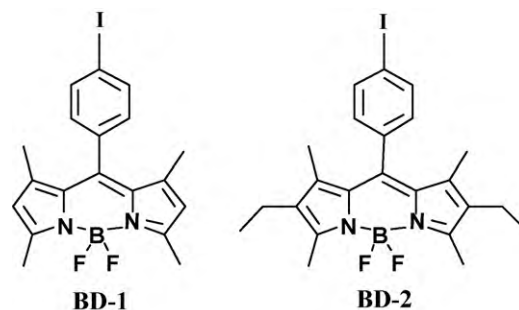


Chart 1. Chemical structures of the BODIPY chromophores successfully applied in upconversion schemes.

(in the emission actinometer this ratio is 1:1), thereby guaranteeing a maximum conversion efficiency of unity. This approach will be discussed further below as we have come to the realization that some of our own reported upconversion quantum efficiencies were originally underestimated resulting from omission of this factor.

The phosphorescence quantum yield of the red-light-absorbing sensitizer, PtTPBP, in conjunction with the singlet fluorescence of two distinct iodophenyl-bearing boron dipyrromethene (BODIPY) derivatives **BD-1** [45] ($\Phi_{\text{f}} = 0.69$) and **BD-2** [46] ($\Phi_{\text{f}} = 0.78$) were determined experimentally [47]. The chemical structures of **BD-1** and **BD-2** are shown in Chart 1. The nature of the PtTPBP/**BD-1** and **BD-2** photochemical systems afforded a highly reproducible upconversion quantum efficiency determination under select conditions which to the best of our knowledge was the first time such quantitative measurements were reported in the literature [47]. **BD-1** and **BD-2** afforded stable green ($\Phi_{\text{UC}} = 0.0313 \pm 0.0005$, corrected value of 0.0626) and yellow ($\Phi_{\text{UC}} = 0.0753 \pm 0.0036$, corrected value of 0.151) upconverted emissions in benzene, respectively, the corrected data being presented in Fig. 4 [47]. The percent quantum efficiency of upconverted fluorescence was measured as a function of the concentration of both **BD-1** and **BD-2**, determined relative to a methylene blue quantum counter ($\Phi_{\text{f}} = 0.03$) [48] with excitation at 635 nm. Although the emission profile of methylene blue does not effectively overlap that of **BD-1** or **BD-2**, highly reproducible quantum yield data were readily obtained in both instances over many independent measurements in our conventional single photon counting fluorimeter [47]. With measured upconversion quantum efficiencies in hand and dynamic Stern–Volmer quenching parameters established, the TTA quantum efficiency with a theoretical maximum of 11.1% [49], can be calculated from these data. Assuming that $\Phi_{\text{UC}} = \Phi_{\text{q}} \Phi_{\text{TTA}} \Phi_{\text{f}}$, where the upconversion quantum efficiency is the product of the quantum efficiencies of PtTPBP triplet quenching, BODIPY triplet–triplet annihilation, and singlet BODIPY fluorescence, respectively, then Φ_{TTA} is readily calculated from the remaining three experimentally determined quantities, yielding $\Phi_{\text{TTA}} = 0.098$ and 0.198 for **BD-1** and **BD-2**, respectively [47]. The corrected **BD-1** value still remains below the theoretical spin-statistical TTA maximum of 11.1%, however, the corrected **BD-2** value now stands at 19.8%, greatly exceeding the TTA spin-statistical limit. This is not completely unreasonable as recent work published by Schmidt and coworkers have experimentally demonstrated a related sensitized homo-TTA process (PQ₄Pd sensitizer and rubrene acceptor/annihilator) also exceeding spin-statistical limitations with photon upconversion efficiency attaining 16% [50]. Given these two distinct experimental systems, it appears that upconversion quantum yields can indeed surpass the theoretical boundary of 11.1% which is quite appealing in terms of translating this phenomenon towards real world applications. A more detailed discussion of spin statistics will be presented in Section 2.3.

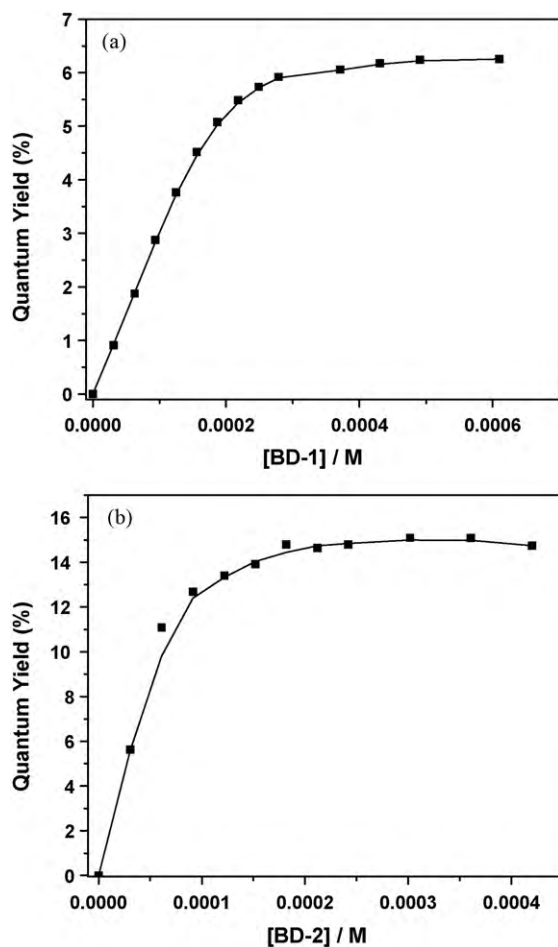


Fig. 4. Relative upconverted fluorescence quantum yield of (a) **BD-1** and (b) **BD-2** as a function of increasing concentration of the dyes under selective excitation of PtTPBP (635 nm) in deaerated benzene.

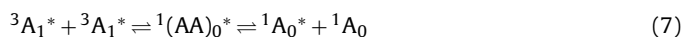
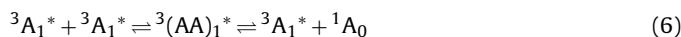
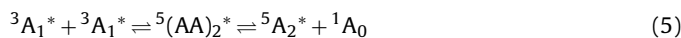
The relative quantum efficiency of the upconverted PPO fluorescence for the biacetyl/PPO system was also measured as a function of the PPO concentration, determined relative to 1,8-diphenyl-1,3,5,7-octatetraene (DPO) as the quantum counter using 442 nm excitation in benzene [51]. These experiments measured a maximum quantum yield of 0.0058 ± 0.0002 (now corrected to 0.016), a substantially lower quantum efficiency relative to the BODIPY chromophores described above. This is likely a result of the sluggish initiating triplet energy transfer process between excited biacetyl and ground state PPO chromophores, as nanosecond transient flash photolysis performed under pseudo-first order conditions revealed a bimolecular triplet–triplet quenching constant of only $9.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ [36]. Note that this value is well below the diffusion rate constant of benzene, $1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ [18]. Since the overall upconversion quantum efficiency is the product of the efficiencies of triplet energy transfer quenching, PPO triplet–triplet annihilation, and singlet PPO fluorescence, a shortfall in one of these quantities ultimately results in low upconversion quantum yield.

As stated earlier, the relative quantum efficiency of PdPh₄TBP/BPEA was also investigated [40]. This was accomplished by comparing the overall upconverted emission of PdPh₄TBP/BPEA to a reference of known quantum efficiency according to Eq. (4). Here, a 10^{-5} M toluene solution of BPEA with a fluorescence quantum yield of 85% was used as the quantum counter and was excited at 407 nm [40]. The dependence of the quantum yield was investigated as a function of emitter concentration at a constant sensitizer concentration of 10^{-4} M as well as by maintaining a constant molar ratio

of sensitizer/emitter of $\sim 1/10$. A collimated beam with a diameter of 3.9 mm at a power density of 80 mW cm^{-2} was used in excitation of the sample. When the sensitizer concentration is maintained at 10^{-4} M , the upconverted emission intensity increases with increasing BPEA concentration up to 1 mM (1.8%) after which a decrease in the upconverting efficiency was observed. In the latter case, when the ratio of the concentration of the sensitizer/emitter is $\sim 1/10$, the upconverting efficiency was greatest at $0.2 \times 10^{-4} \text{ M}$ PdPh₄TBP (3.2%). The authors reported that the highest upconversion quantum yield of 3.2% was observed for $2 \times 10^{-5} \text{ M}$ PdPh₄TBP and $2 \times 10^{-4} \text{ M}$ BPEA at an excitation of 80 mW cm^{-2} [40]. No further discussion of these results was provided by the authors.

2.3. Triplet–triplet annihilation rate constants in solution

In 1988, Saltiel and Atwater published a comprehensive review on spin-statistical factors in diffusion-controlled reactions which are at the heart of the sensitized homo-TTA reactions presented herein [52]. Briefly, when two distinct molecules ^mA and ⁿB with spin multiplicities of *m* and *n*, respectively, diffusively encounter, the product of these spin multiplicities (*mn*) directly gives the number of possible encounter-pair spin states. In a TTA reaction, this value is 9 (3×3). In the absence of an applied magnetic field, the encounter-pair spin states become equally populated under equilibrium conditions at ambient temperatures, implying that the formation probability of each individual state is simply the inverse of the product of the two reactant spin multiplicities (*mn*)⁻¹; this is the so-called spin-statistical factor. The spin multiplicities of the encounter-pair sublevels produced are determined by the Clebsch–Gordan series, where *S* ($M = 2S + 1$) can have a maximum value of $s_1 + s_2$, a minimum value of $|s_1 - s_2|$, and intermediate values incremented by 1, i.e. $s_1 + s_2 - 1$, and so on. When two excited triplets (³A₁^{*}) interact ($s_1 = s_2 = 1$), nine encounter-pair spin states are produced with equal probability which are composed of three distinct sublevels, five of which are quintet ($S = 2$), three are triplet ($S = 1$), and one is of singlet ($S = 0$) character as outlined in Eqs. (5)–(7) [52,53]. Therefore, spin statistics predicts that as long each encounter-pair preserves their multiplicity, one would expect that only Eq. (7) would produce upconverted singlet fluorescence from TTA, representing 1/9 or 11.1% of the annihilation events, $(2S + 1)/9$. The two sensitized TTA examples described above (Section 2.2) clearly exceed this limit suggesting that the triplets and possibly the quintets are conspiring to yield additional singlet fluorescing products.



In order to determine the TTA rate constant (k_{TT}) in solution, the nanosecond excited state dynamics of the sensitizer before and after adding the acceptor chromophore were investigated. In our group, this was first explored in the PtTPBP/2CBPEA system. Nanosecond transient absorption (TA) measurements of only the sensitizer and the acceptor were collected in deaerated DMF solutions as well as upon the addition of sufficient amount of acceptor to efficiently quench the triplet excited state of the sensitizer were obtained. The latter resulted in excited state features that were predominantly due to the triplet acceptor/annihilator molecule (Fig. 5a) [35]. Transient absorption decays monitored at the peak of the characteristic 2CBPEA triplet–triplet excited state absorption (490 nm) measured as a function of incident nanosecond 630 nm pump laser fluence recovered the rate constant for the sensitized TTA process, $k_{TT} = 5.64 \pm 0.08 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Fig. 5). The triplet–triplet annihilation rate constant (TTA) was calculated

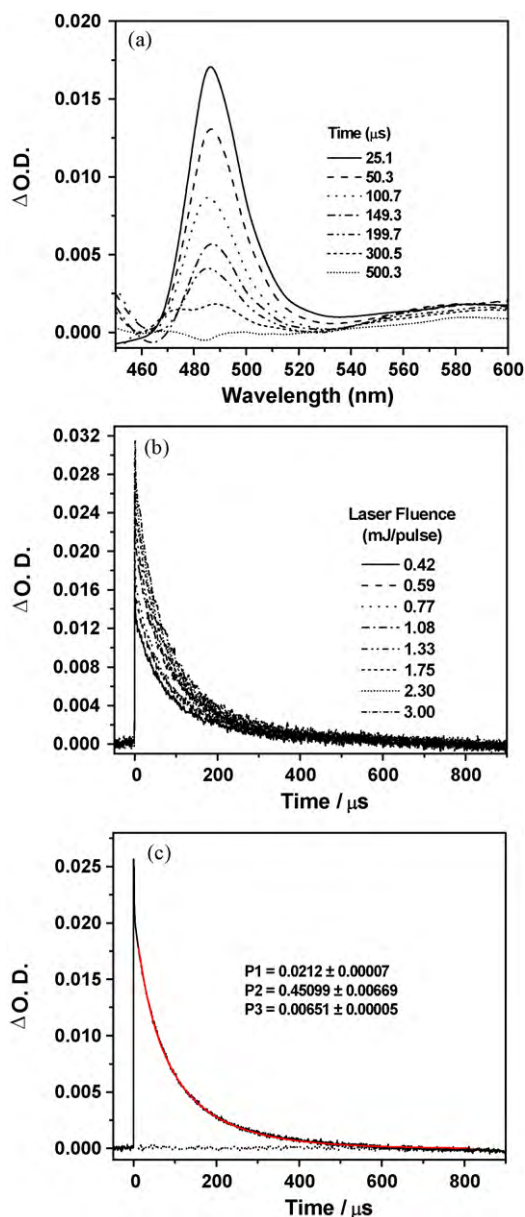


Fig. 5. (a) Transient absorption difference spectrum of 3.40 μM PtTPBP and 1 mM 2CBPEA measured as a function of delay time in deaerated DMF, 2.0 mJ/pulse, $\lambda_{\text{ex}} = 630$ nm. (b) Time-resolved absorption kinetics at 490 nm of the data in part (a). (c) Representative kinetic fit (1.75 mJ/pulse data) to Eq. (3) (red line) and the residuals of this fit (dotted line). Figure was adapted from reference [35].

by fitting the transient absorption decay observed at 490 nm as a function of the laser power to Eq. (8).

$$\frac{d[{}^3\text{M}^*]}{dt} = -k_{\text{T}}[{}^3\text{M}^*] - k_{\text{TT}}[{}^3\text{M}^*]^2 \quad (8)$$

Here $[{}^3\text{M}^*]$ is the concentration of the triplet excited state of 2CBPEA, k_{TT} is the triplet–triplet annihilation rate constant and k_{T} is the triplet decay rate constant. This kinetic scheme was first introduced by Birks in studies of triplet–triplet interactions in concentrated fluid solutions [5]. Integration of Eq. (8) produces Eq. (9) which readily translates into a convenient 3-parameter expression (Eq. (10)) that was used to fit the experimental data, minimized by nonlinear least squares in Origin 8.0.

$$[{}^3\text{M}^*] = \frac{[{}^3\text{M}^*]_0 e^{-k_{\text{T}}t}}{1 + [{}^3\text{M}^*]_0 (k_{\text{TT}}/k_{\text{T}})(1 - e^{-k_{\text{T}}t})} \quad (9)$$

$$y = \frac{p_1}{1 + (p_1 \times p_2/p_3) \exp(p_3 \times x) - (p_1 \times p_2/p_3)} \quad (10)$$

The terms of Eq. (10) are defined as $y = [{}^3\text{M}^*]$, $x = t$ (time), $p_1 = [{}^3\text{M}^*]_0$, $p_2 = k_{\text{TT}}$, and $p_3 = -k_{\text{T}}$. It should be noted that the measured decay curve for $[{}^3\text{M}^*]$ is in absorbance units, hence to convert this to molar concentration, the triplet–triplet extinction coefficient of 2CBPEA was employed, $1.25 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. This was calculated from the triplet energy transfer method utilizing the triplet energy transfer donors, $[\text{Ru}(\text{bpy})_3]^{2+}$ and 2-acetonaphthone, with known excited state extinction coefficients [35]. We note that the k_{TT} values of 2CBPEA approach the diffusion limit in DMF, $k_{\text{diff}} = 8.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at 25 $^\circ\text{C}$ [18], thereby indicating that triplet–triplet annihilation is a diffusion controlled process under the presented experimental conditions.

We have also determined the PPO triplet–triplet annihilation rate constant of the biacetyl/PPO combination from transient absorption decays of deaerated benzene solution. The peak characteristic to the triplet-to-triplet excited state absorption (500 nm) maxima of PPO was monitored as a function of the incident pulsed laser fluence and was fitted according to Eq. (10). This process attains the diffusion limit in benzene at room temperature, $k_{\text{TT}} = 1.1 \pm 0.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ [36], again indicating that the TTA process is indeed diffusion controlled under the experimental conditions that were present.

3. Alternative acceptor/annihilators

Recently, our group reported the first example of a molecule other than an aromatic hydrocarbon that has been used in an upconverting scheme as the acceptor/annihilator [47]. In general, the use of aromatic hydrocarbons as acceptor/annihilator chromophores represents a strategic choice since they conveniently possess large splitting in their singlet–triplet energy gaps, permitting the relevant sensitizer levels to be sandwiched between, facilitating the necessary thermodynamics for the observation of upconversion. This limiting experimental reality has severely restricted both fundamental research and the broader applicability of low power upconversion phenomena. Fortunately, recent efforts have revealed the presence of large singlet–triplet energy gaps in the BODIPY class of fluorophores, $E_{\text{T}} \approx 1.6 \text{ eV}$ [54,55]. BODIPY chromophores are popular molecular probes exhibiting high fluorescence quantum yields and are strongly resistant to photobleaching thereby making them suitable candidates for incorporation into upconversion schemes [56–58]. In our study, PtTPBP was used as the triplet sensitizer ($\Phi_{\text{P}} = 0.7$ [59], $\tau = 40.6 \mu\text{s}$ in benzene) in conjunction with **BD-1** [$\Phi_{\text{F}} = 0.69$] and **BD-2** [$\Phi_{\text{F}} = 0.78$] described earlier [47]. The fluorescence spectra of **BD-1** and **BD-2** exhibit an almost mirror-image symmetry with their corresponding absorption spectra, $\lambda_{\text{max}} = 527$ and 548 nm, respectively. Selective excitation of PtTPBP at 635 nm leads to the generation of long-lived phosphorescence at 766 nm, which has the ability to sensitize triplet state formation in either **BD-1** or **BD-2** through diffusive energy transfer, eventually leading to TTA of the ${}^3\text{BODIPY}^*$ chromophores. Triplet energy transfer rate constants from the PtTPBP sensitizer were established using dynamic Stern–Volmer analysis yielding bimolecular quenching constants of 4.18×10^8 and $1.06 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for **BD-1** and **BD-2**, respectively. The attenuated quenching constant in the former was attributed to the smaller driving force for triplet energy transfer from the PtTPBP sensitizer. The emission intensity power dependence plot of the sensitized upconverted fluorescence intensity of **BD-1** and **BD-2** upon 635 nm excitation of PtTPBP resulted in quadratic fits (x^2) which is illustrative of the nonlinear photochemistry driving the upconversion processes. These data clearly show that the upconverted fluorescence intensity is proportional to the square of the

incident light power at 635 nm and hence to the square of the triplet BODIPY concentrations. Digital photographs of the green and yellow upconverted fluorescence of **BD-1** and **BD-2** are shown in Fig. 3c and d, respectively, upon selective excitation of a deaerated PtTPBP benzene mixture containing the acceptor/annihilator at 635 nm excitation, thereby resulting in a net energy difference of 0.40 and 0.28 eV, respectively (Table 1).

4. Quartic incident light power dependence realized in photon upconversion

Simultaneous two-photon excitation (TPE) processes are generally accomplished through the use of high peak power ultrafast lasers with wavelengths ranging from the visible to the near-IR. TPE of various chromophores has led to widespread fundamental scientific progress along with notable applications in chemistry, materials science, imaging, photolithography, and micro-to-nanofabrication [60–73]. Inspired by the pursuit of new opportunities in photonics, we postulated whether the sensitized TTA process could be adapted to TPE technology. This would effectively replace the two-sequential one-photon excitations typically associated with TTA with two independent simultaneous two-photon excitations, the latter exhibiting an unprecedented quartic (x^4) incident light power dependence [74]. As it is well established that Ru^{II} metal-to-ligand charge transfer chromophores are susceptible to TPE [75–77] and the [Ru(dmb)₃]²⁺ excited state successfully promotes sensitized TTA with DPA [17], this molecular donor–acceptor pair represent a rational departure point for the present prototypical study.

Stern–Volmer analyses of the triplet quenching of [Ru(dmb)₃]²⁺ by DPA upon one-photon excitation at 430 nm (10 mW at 80 MHz) and TPE at 860 nm (1 W at 80 MHz) in argon-degassed CH₃CN obtained from two independent sets of experiments (<5% variation) under each excitation condition resulted in average K_{SV} values of 5121 and 5213 M⁻¹ with respective k_q 's of 5.56×10^9 and 5.66×10^9 M⁻¹ s⁻¹ using $\tau_0 = 0.92$ μ s [78]. The Stern–Volmer quenching data indicate that the triplet energy transfer kinetics of the [Ru(dmb)₃]²⁺/DPA donor/acceptor combination is the same regardless of the excitation pathway. The bimolecular energy transfer rate constants obtained are well below the diffusion limit of the solvent, 1.9×10^{10} M⁻¹ s⁻¹ at 25 °C [18].

As shown in Fig. 6, when a solution mixture containing 9.6 μ M [Ru(dmb)₃]²⁺ and 2.48×10^{-4} M DPA in deaerated CH₃CN was excited at 860 nm, TPE promoted TTA process initiated from two-sequential simultaneous two-photon excitations resulted in the sensitized upconverted singlet DPA fluorescence displaying an extraordinary quartic (x^4) incident light power dependence. Analysis of the integrated upconverted DPA emission intensity (high energy emission band) measured as a function of the incident laser power (Fig. 6a) resulted in the anticipated quartic power dependence as illustrated by the solid black squares and fit line (x^4) displayed in Fig. 6b. The residual unquenched photoluminescence intensity of [Ru(dmb)₃]²⁺ was also measured as a function of the incident 860 nm laser power in the same experiment (Fig. 6a, low energy emission band) resulting in the expected quadratic (x^2) dependence as illustrated by the solid red circles and fit line presented in Fig. 6b. The inset in Fig. 6b presents double logarithm plots of the data in order to better differentiate between the two- and four- ($x^2 \times x^2$)-photon excitation processes. Indeed the slopes of the solid red and black lines in the inset are 1.95 and 3.98 respectively, indicating that the photochemistry that drives the observed residual photoluminescence of [Ru(dmb)₃]²⁺ and the upconverted DPA fluorescence in the solution mixture upon 860 nm excitation are certainly two- and four-photon processes, respectively [78]. Triplet–triplet annihilation of the energy transfer products yields

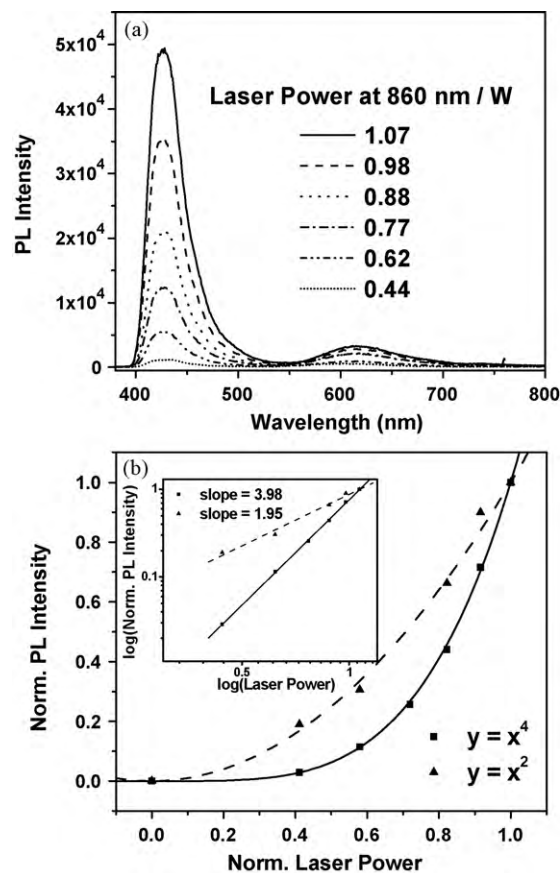


Fig. 6. (a) Emission intensity profile of upconverted DPA and residual photoluminescence of [Ru(dmb)₃]²⁺ following selective excitation of [Ru(dmb)₃]²⁺ at 860 nm in a deaerated CH₃CN mixture of 9.6 μ M [Ru(dmb)₃]²⁺/2.48 $\times 10^{-4}$ M DPA, measured as a function of incident optical power. The pulse repetition rate was 80 MHz. (b) Normalized integrated emission intensity from panel (a) plotted as a function of the normalized incident light power. The solid and dotted black lines represent the best quartic (x^4) and quadratic (x^2) fits to the data points, respectively. Inset: double logarithm plot of the data points in (b). Figure was adapted from reference [78].

upconverted blue fluorescence with a record anti-Stokes shift of 1.38 eV for the TTA process with respect to the 860 nm excitation light.

5. Photon upconversion in rubbery polymeric materials

In order to fully exploit the upconversion process it would be very attractive if solid materials could be developed that were capable of displaying this effect. This advance would, for example, permit the utilization of wavelength-shifting films in combination with solid-state lasers, or in photovoltaics [79], enabling more complete harnessing of the solar spectrum. This is particularly valuable for making better use of the near-IR region in real devices. With the notion that chromophore diffusion must be possible to allow for the annihilation of two triplets in low-concentration (\sim mM) polymer/dye blends, PdOEP and DPA were incorporated into a 1:1 copolymer of ethyleneoxide and epichlorohydrin (EO-EPI), which served as an example of a rubbery polymer host [80]. The quadratic incident power dependence as well as the static and time-resolved emission data previously reported for this material support the notion that the singlet DPA fluorescence observed in this polymeric material is indeed the result of the proposed sensitized TTA-based mechanism [80]. The fact that translational mobility of the chromophores in the matrix polymer is essential was supported by the fact that upconversion was completely suppressed at 77 K [80], i.e. well below the glass transition temperature of EO-EPI [81]. This is

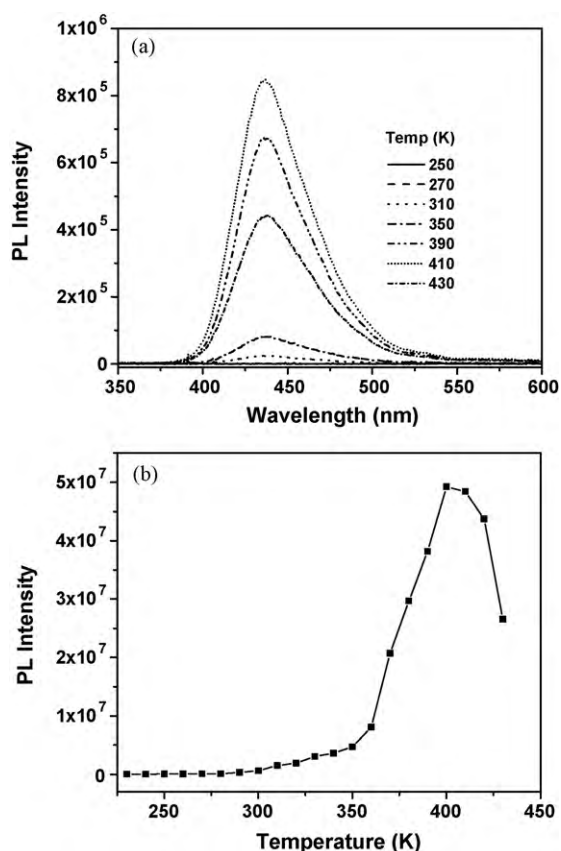


Fig. 7. (a) Select upconversion emission profiles of an EO-EPI film containing (0.22 mM) PdOEP and (18.1 mM) DPA measured at variable temperatures upon excitation at 544 nm with 2 mJ/pulses at a rate of 10 Hz. (b) Integrated upconverted emission intensity as a function of temperature for the plot shown in (a). The sampling width is 500 ns and the delay time ranged from 1 to 100 μ s. It should be noted that the integrated area at each temperature was obtained from the maximum intensity reached for each respective temperature thereby varying the delay time. Figure was adapted from reference [82].

consistent with the fact that chromophore diffusion is inhibited in the glassy state, preventing the necessary bimolecular interactions between sensitizer and acceptor/annihilator (required for energy transfer) and between two acceptor/annihilator molecules (required for TTA).

To investigate in greater detail how the upconversion in the doped PdOEP/DPA EO-EPI blend depends on temperature, thin films comprising the chromophores in nominal concentrations of 0.2–0.3 mM PdOEP and 18–20 mM DPA were investigated by our group. The films were placed in a liquid nitrogen variable temperature cryostat and time-resolved emission spectra were measured at various temperatures [82]. The intensity of the upconverted fluorescence increases with increasing temperature up to a maximum at \sim 400 K after which a sharp decrease in the PL intensity was observed until the film no longer exhibited the upconversion phenomenon (Fig. 7). These observations are qualitatively consistent with sequential bimolecular chemical steps under diffusion control as predicted by the Stokes–Einstein relationship ($D = kT/6\pi\eta R$) where the chromophore diffusion coefficients (D) are directly proportional to the temperature (T) and inversely proportional to the viscosity (η) of the medium. 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 rendering improved upconversion yields at elevated temperatures.

Additional experiments were performed where separate PdOEP/DPA doped EO-EPI films were heated for 0, 30, or 60 min to temperatures between 290 and 400 K and the emission profiles were collected after each exposure [82]; these data show an irreversible reduction of the upconversion emission intensity for samples heated to 400 K (but not the ones exposed to lower temperatures) which scales with exposure time, suggesting that within the polymer matrix, the dye cocktail eventually loses its functionality at temperatures of 400 K or above. At present, the apparent decomposition mechanism is not understood but is postulated to be as a result of (1) segregation/compartmentalization inside the respective polymer matrix as the morphology of the polymer likely varies with temperature or potentially from (2) chromophore “sweating” where the matrix can no longer serve as a viable host for the chromophores above a certain temperature threshold. The latter concept has already been observed in closely related TPU materials [83]. Subsequently, the upconverted emission intensity increased with increasing temperature and was found to be completely reversible upon several heating and cooling cycles provided the temperature remained below 400 K [82].

In order to (i) demonstrate the generality of the approach, (ii) further explore the correlation between transport properties, temperature and upconversion, and (iii) extend the framework to matrix polymers with better mechanical properties than EO-EPI (which exhibits limited mechanical properties such as low Young’s modulus and low mechanical strength resulting in dimensional instability and failure of the films at low stresses) [81] the thermoplastic polyurethanes (TPUs) Texin 285, Texin 270 and Tecoflex EG-80A were also investigated as representative examples of other suitable rubbery host polymers. These thermoplastic elastomers exhibit a two-phase morphology, composed of hard segments – formed by the reaction of 4,4’-methylene-bis(phenylisocyanate) (MDI, in the case of both Texins) or hydrogenated MDA (in case of the Tecoflex) and butanediol as chain extender – and soft segments – polyester diols in case of the Texins and polytetramethyleneglycol in case of the Tecoflex [84–86]. The hard segments act as physical cross-links, and therefore the mechanical properties as well as the transport of small molecules through these materials depend on the ratio of hard-to-soft phase, i.e. the ratio of chain extender to polyol and the molecular weight of the latter [87–90]. Qualitatively, the upconversion characteristics of the TPU blends are similar to those of the EO-EPI blends as illustrated in Fig. 8. Fig. 8 clearly demonstrates that the onset temperature for upconversion is lowest for the Tecoflex, consistent with the fact that this material displays the lowest T_g . As was observed in the EO-EPI blend, the thermal ‘activa-

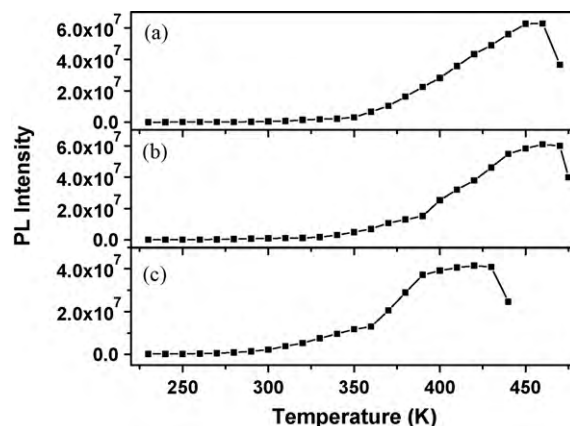


Fig. 8. Upconverted PL intensity as a function of temperature obtained from PdOEP/DPA doped thin films of (a) Texin 270, (b) Texin 285, and (c) Tecoflex EG-80A upon 544 nm excitation with a 2 mJ/pulse at 10 Hz. Figure was adapted from reference [82].

Table 2
Phosphorescence decay parameters of PdOEP in Tecoflex EG-80A.

Temperature (K)	KWW model ^a	Bi-exponential model	
	τ (μ s) (β)	τ_1 (α_1) (μ s); τ_2 (α_2) (μ s)	$\langle \tau \rangle$ (μ s) ^b
300	260 (0.93)	246 (0.87); 524 (0.13)	314
320	160 (0.83)	155 (0.77); 341 (0.23)	230
340	100 (0.76)	113 (0.89); 383 (0.11)	192
360	50 (0.61)	62.6 (0.72); 188 (0.28)	130

^a Decay parameters determined using Eq. (12).

^b Calculated using Eq. (11).

tion' of the upconversion is completely reversible for the TPU blends as long as the temperature remains below the critical threshold [82].

Attempts were made to further explore the dynamics of the bimolecular processes necessary for photon upconversion in the polymer host, Tecoflex EG-80A. The phosphorescence decay at 670 nm of a thin film of 0.17 mM PdOEP in Tecoflex EG-80A was measured as a function of temperature and the data were fitted to complex kinetic models since the residual fit of a monoexponential model was not good [82]. These models include the sum of two single exponential decays as well as the Kohlrausch–Williams–Watts (KWW) [91,92] stretched exponential model. In the former kinetic analyses, average lifetimes were calculated from a sum of two single exponentials as shown in Eq. (11):

$$\bar{\tau} = \frac{\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2} \quad (11)$$

where τ_1 and τ_2 are the two recovered lifetimes and α_1 and α_2 are the respective amplitudes of the two lifetime components [93]. The KWW function is shown in Eq. (12), where the stretching parameter β ($0 < \beta < 1$) is related to the width of an underlying Levy distribution of the relaxation rates and τ is the lifetime at the maximum amplitude of the distribution [33–35]. Smaller β values relate to a broader distribution of rates and hence more substantial heterogeneity. The fitting parameters recovered from these two modeling approaches are collected in Table 2. Fig. 9a is a digital photograph of a doped PdOEP/DPA thin film showing the upconverted blue DPA fluorescence upon 544 nm excitation.

$$A(t) = A_0 \exp \left[- \left(\frac{t}{\tau} \right)^\beta \right] \quad (12)$$

In both models a substantial decrease in lifetime/average lifetime of the triplet excited state of the porphyrin was clearly observed as the temperature increases in the polymer films. The β values correspondingly decrease due to increasing heterogeneity of the different microenvironments present in this TPU material

[82]. The work demonstrated that photon upconversion is viable at high temperatures in low T_g polymeric hosts despite significant kinetic complexities. Importantly, triplet sensitized upconversion has been shown to be enhanced as a function of increasing temperature in each polymer studied and that the softest material overall, Tecoflex EG-80A, afforded the best optical performance near room temperature, whereas, the Texin materials operate more efficiently above 400 K.

Doped PdPc(OBu)₈/rubrene thin films in the polymer host EO-EPI were also investigated in our group and were shown to decompose over several days under ambient aerated conditions as the intensity of the upconverted fluorescence slowly decreased over this time period [27]. This is a result of the decomposition of rubrene forming rubrene endoperoxide as was evident by the disappearance of the absorption bands of rubrene in addition to solution ¹H NMR evidence [27]. To circumvent this problem, blend films were prepared in an inert argon atmosphere using freeze-pump-thaw degassed solutions (three cycles) containing the sensitizer and acceptor [27]. The results show that blend polymer films that were fabricated under an inert atmosphere and maintained under a positive argon pressure shows a quadratic incident power dependence supporting the notion that similar to the solution-based phenomenon, nonlinear photochemistry drives the photon upconversion in these thin films through TTA. Films that were exposed to air deviated somewhat from this incident light power dependence [27]. A digital photograph of the upconverted yellow emission resulting from rubrene is shown in Fig. 9b upon 725 nm excitation.

It should be mentioned here, that we were able to incorporate several upconverting systems into thin films utilizing various polymers. We have also translated several of the upconverting systems investigated in our group into polymer bars (Tecoflex EG-80A) (Fig. 9c–e), thereby, illustrating that this phenomenon is possible not only in thin films but also in soft rubbery polymer bars that are about 5 mm thick. Here diffusion was still able to occur and the upconverted emission was clearly visible by the naked eye even in a well-illuminated room.

Other reports on photon upconversion in the solid state have recently appeared. This process was demonstrated in poly(9,9-bis(2-ethyl-hexyl)fluorene) (PF2/6) films doped with PdOEP. Upon 532 nm excitation of PdOEP the characteristic blue emission of PF2/6 was observed together with the expected phosphorescence of the PdOEP component [94]. However, in this report two mechanisms were postulated that could have resulted in the upconverted PF2/6 emission. This involves a sequential multiphoton absorption or TTA of the porphyrin followed by energy transfer. The authors were unable to distinguish between the two mechanisms but postulated that the mechanism involving sequential multiphoton absorption may be dominant but also noted that the pump

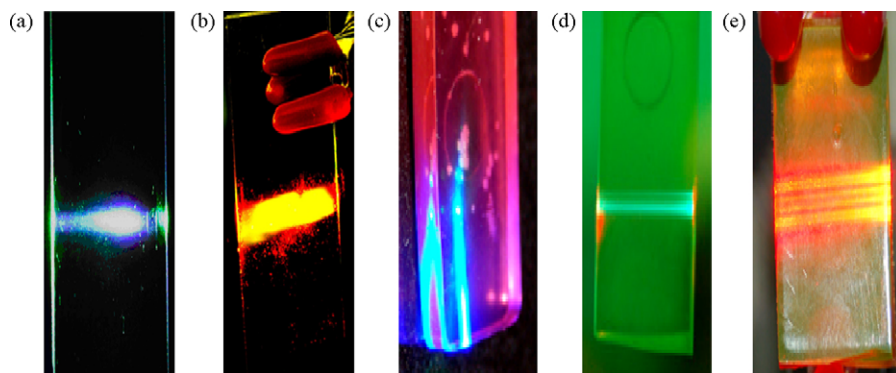


Fig. 9. Digital photographs of ethyleneoxide-epihydrochlorin (EO-EPI) thin films doped with (a) PdOEP/DPA upon 544 nm excitation, (b) PdPc(OBu)₈/rubrene upon 725 nm excitation and Tecoflex EG-80A polymer bars doped with (c) PdOEP/DPA upon 544 nm excitation, (d) PtTBPB/2CBPEA upon 635 nm excitation and (e) PtTBPB/BD-2 upon 635 nm excitation.

intensities used in their study were five orders of magnitude lower than that used by others to achieve two-photon excitation of similar magnitude in polyfluorene [94]. This approach was later extended to other blue-emitting conjugated polymer hosts involving the ladder-type polymer, poly(pentaphenylenes), (L-5Ph). A comparison of the photoluminescence efficiency in systems composed of PF2/6 and L-5Ph doped with platinum octaethylporphyrin (PtOEP) was reported [95]. The upconverting efficiency in the ladder-type pentaphenylene polymer showed a 5-fold increase compared to the PF2/6 system. The higher efficiency was reported to be partially attributed to the reduced reabsorption of the photoluminescence in the case of the ladder-type matrix [95]. A sample composition of another blue-light emitting poly(spirobifluorene-anthracene) copolymer doped with a low concentration of PtOEP was later demonstrated to show an order of magnitude increase in the upconverted fluorescence compared with an anthracene-free spirobifluorene copolymer and to the metallated porphyrin-doped polyfluorene thin films [96]. This increase was believed to originate from the triplet energy transfer from the phosphorescence of PtOEP to the polymer host, followed by TTA, thereby, resulting in the blue emission from the spirobifluorene host polymer [96]. A system was later investigated in which the triplets of two blue emitter molecules were strategically chosen to lie above and below the triplet of the sensitizer molecule [43]. The triplet of the blue emitter oligo(9,9-bis(2-ethylhexyl)fluorene) (OF7) molecule is essentially higher (2.16 eV) than the triplet PtOEP (1.91 eV) chromophore while the triplet energy of DPA (1.78 eV) is lower than that of PtOEP [43]. The upconverting efficiency of doped PtOEP solid-state films containing OF7 and DPA were investigated and compared. A 20-fold increase in the upconversion efficiency was observed in films containing PtOEP/DPA compared to films containing PtOEP/OF7 upon 532 nm excitation at 5 kW/cm² [43]. The increased upconversion efficiency in the former is a result of the high probability of the triplet–triplet energy transfer process as well as the long-lived triplet lifetime of DPA at room temperature (~3 ms) [18] compared to the triplet energy transfer process of PtOEP and OF7.

Recently, upconversion was demonstrated in rigid poly(methyl methacrylate) (PMMA) films containing the donor/sensitizer, PtOEP, and the acceptor/annihilator, DPA [97]. Blue DPA fluorescence was observed upon 533 nm excitation of PtOEP in the rigid PMMA films resulting in a net energy difference of 0.49 eV (Table 1). Very high concentrations of the emitter molecule were utilized in the PMMA films, in the order of 0.4 M to facilitate the migration of triplet energy in this rigid polymer host. An upconversion efficiency of 0.02% at 533 nm at a power density of 0.9 mW cm⁻² was also reported in the PMMA films [97]. The quantum efficiency was based on comparisons to the intensities of the directly excited DPA fluorescence or the phosphorescence of PtOEP. The TTA process was confirmed by a 2-fold reduction in the excitation intensity which produced a simultaneous 4-fold reduction in the upconverted blue DPA intensity. Blue-to-UV photon upconversion was also reported utilizing the sensitizer, 2-methoxythioxanthone (2MeOTX), and the emitter, PPO in the rigid PMMA films. Selective excitation of 2MeOTX at 410 nm filtered through a 385 nm cut-off filter in a PMMA film doped with 2MeOTX and 0.4 M PPO resulted in the upconverted PPO emission in the region 350–380 nm [97]. Based upon this and our own work in this area, we speculate that high *T_g* polymers such as PMMA could realize improved function as upconversion host materials if utilized at higher temperatures where polymer viscosity/rigidity would decrease and chromophore diffusion would be more significantly promoted.

Others have also reported the realization of red to green photon upconversion in solid polymeric film made of cellulose acetate [98]. Cellulose acetate is an inert host matrix and is transparent in the spectral range of the chromophores

[98]. Selective excitation of the red absorbing porphyrin, palladium(II)tetraphenyltetrabenzoporphyrin (PdTPBP), at 633 nm resulted in the green upconverted emission of 9,10-bis(phenylethynyl)anthracene (BPEA) at 515 nm resulting in a net energy difference of 0.58 eV (Table 1) [98]. The bimolecular processes that are involved in upconversion such as the triplet–triplet energy transfer reaction between the donor and the acceptor molecules as well as the TTA between the acceptor molecules were investigated in DMF solution before the reaction mixture was translated into thin films [98]. The overall upconverting efficiency rate was determined by the efficiency of diffusion assisted by energy transfer to the triplet acceptor as well as the rate of TTA between the triplet excitons. The efficiency of the energy transfer from PdTPBP to BPEA was evaluated by comparing the photoluminescence decay of the porphyrin in a solution/thin film mixture of PdTPBP/BPEA with a sample that only contained PdTPBP [98]. The upconverted quantum efficiency was reported to be three orders of magnitude lower in the solid film than in liquid solution [98]. The lower observed quantum efficiency in the solid state was proposed to be as a result of low triplet excitons mobility and hence it was concluded that polymer host with increased diffusion coefficient need to be considered.

Most recently, the influence of magnetic field effects on the TTA process in thin films doped with PtOEP/DPA was reported [99]. The theory of the magnetic field effects was developed by Merrifield and Suna and allows the mechanism of interaction between the triplet states in single crystals of polyacenes to be established [100–102]. The kinetics of triplet excitons of organic materials at high excitation intensity in thin films have been extensively investigated in the last decade and provide information about the overall TTA of different compounds [103,104]. However, the mechanism of interaction between the triplet excitons in disordered films of molecular materials is not well understood to date. It has not been understood how the positional disorder of the molecules affects the fusion of triplets or whether the rate of interaction of the triplets is limited by the diffusion or by the probability of annihilation after collision. To investigate this effect PtOEP/DPA doped thin films (100 nm thick) on silica substrates were placed between the poles of an electromagnet at a 50 ° angle to the direction of the magnetic field where the film was excited with 532 and 355 nm with photon flux ranging from 10¹⁸ to 10²⁰ photon cm⁻² s [99]. At this photon flux the intensity of the DPA photoluminescence remains proportional to the square of the excitation intensity. The measurements were taken under an argon atmosphere at room temperature. The delayed DPA fluorescence obtained in the presence of a magnetic field were reported to be strong due to favorable sensitization of the DPA triplets by the excited PtOEP sensitizer [99]. Analytical expressions were derived to estimate the overall annihilation probability, which outlined the peculiar role played by the disorder and demonstrate that the triplet–triplet fusion in solid films is indeed a diffusion controlled process [99]. The magnetic field modulation of the upconverted emission in doped PtOEP/DPA films was reported to be attributed to the Hamiltonian spin of the interacting triplet excitons [99]. The magnitude of the effect was determined by the positional disorder of the molecules and was found to depend on the branching ratio of the singlet and triplet fusion channel rates to the rate of triplet pair dissociation [99].

6. Concluding remarks

This review serves to illustrate that photon upconversion, based on sensitized triplet–triplet annihilation is truly a generalized phenomenon as long as all the proper energy requirements are met. Various combinations of sensitizers and acceptors/annihilators that span the near-IR to visible region of the solar spectrum have

been investigated and illustrate the broad-ranging potential of this wavelength-shifting phenomenon. Several solid polymeric materials exhibiting this phenomenon have been discovered, including the low glass transition temperature polyurethanes which allow diffusion of the relevant species, thereby enabling the necessary sequential bimolecular processes. The relative quantum yields of various systems in solutions have been investigated at low excitation power. To date, the BODIPY chromophore **BD-2** exhibits the highest reported upconversion efficiency presently known resulting from low power continuous-wave excitation, 15.1%. The reported upconversion quantum yields in solid-state host materials were significantly lower than that obtained in solution, nevertheless, the bimolecular processes necessary for upconversion were still able to function in these media. The triplet–triplet annihilation rate constants of several molecular systems in solution were analyzed and confirmed to be at or near diffusion controlled. Although numerous advances have been made in this area over the past couple of years, many questions still remain and several lines of investigation are worth pursuing. These include the potential for increasing the upconversion quantum efficiency both in solution and in various rubbery low T_g polymeric materials (or high T_g materials at high temperatures) as the possibility remains for harnessing the different spin products generated from the initial TTA encounter. The continuing exploration and evaluation of chromophores capable of expanding the net anti-Stokes energy difference between the excitation wavelength and the upconverted emission peak remains a valuable endeavor for energy-relevant research. Current work in our own laboratory continues to explore these ventures and is poised to merge these photon management systems with operational photovoltaics.

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