

# Organic Polymer Hosts for Triplet–Triplet Annihilation Upconversion Systems

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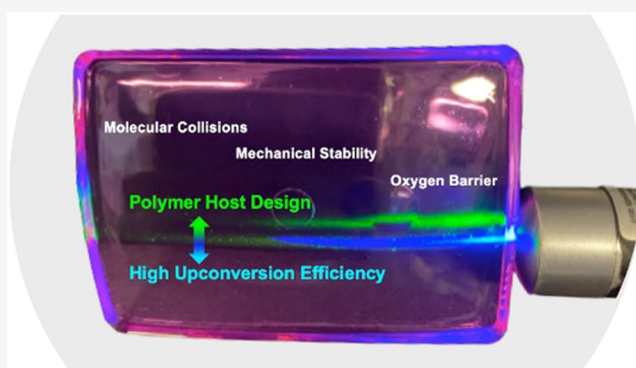
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**ABSTRACT:** Triplet–triplet annihilation upconversion (TTA-UC) is a process by which a lower energy photon can be upconverted to a higher energy state. The incorporation of TTA-UC materials into solid-state hosts has enabled advances in solar energy and many other applications. The choice of host system is, however, far from trivial and often calls for a careful compromise between characteristics such as high molecular mobility, low oxygen diffusion, and high material stability, factors that often contradict one another. Here, we evaluate these challenges in the context of the state-of-the-art of primarily polymer hosts and the advantages they hold in terms of material selection and tunability of their diffusion or mechanical or thermal properties. We encourage more collaborative research between polymer scientists and photophysicists in order to further optimize the current systems and outline our thoughts for the future direction of the field.



## INTRODUCTION

Photon upconversion (UC) through sensitized triplet–triplet annihilation (TTA) was first reported almost 60 years ago<sup>1</sup> but has seen growing interest in the past decade<sup>2,3</sup> due to its potential use in applications such as solar energy harvesting,<sup>4</sup> anti-Stokes fluorescence bioimaging,<sup>5</sup> high-sensitivity oxygen detection,<sup>6</sup> sensing,<sup>7,8</sup> night vision,<sup>9</sup> and anticounterfeiting.<sup>10</sup> TTA-UC systems work at low power ( $<100 \text{ mW cm}^{-2}$ ) and with both coherent and incoherent light, meaning sunlight can activate the process, making it particularly noteworthy.<sup>11</sup> A key requirement for efficient TTA-UC is rapid energy transfer between sensitizer and emitter chromophores. While respectable efficiencies have been achieved for liquid-state TTA-UC systems, translation to the solid state has proven more challenging but is essential for real-world use.<sup>12</sup> A promising solution is to embed TTA-UC systems in a solid-state polymeric host, allowing tuning and optimization of diffusion and mechanical and thermal properties to a specific application.

From an applications standpoint, TTA-UC offers a number of advantages over lanthanide-based UC systems, including high absorption coefficients and upconversion efficiencies, low excitation thresholds, and lower toxicity.<sup>12–15</sup> In the field of photovoltaics (PV), the power conversion efficiency of single-junction solar cells is limited by the well-known Shockley–Queisser limit, which accounts for a combination of losses including thermalization, intrinsic resistance leading to fill factor losses, and inefficient spectral harvesting.<sup>16,17</sup> The latter

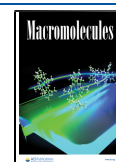
cause arises due to the inability to harvest photons with energy below the band gap of the solar cell, leading to significant wastage of potential energy. When TTA-UC materials are combined with conventional solar cells, transmitted low-energy photons can be converted to the favored high-energy photons, reflected back into the cell, and subsequently absorbed, thus improving the spectral harvesting efficiency.<sup>18–21</sup> TTA-UC systems have also been demonstrated in bioimaging,<sup>22,23</sup> sensing,<sup>7,8</sup> and anticounterfeiting<sup>10</sup> applications, where the unique anti-Stokes emission of TTA-UC systems is used to improve contrast. It also offers significant advantages in biological applications by reducing irradiation damage and increasing the penetration depth due to the longer wavelengths used to reach the target area.<sup>24</sup>

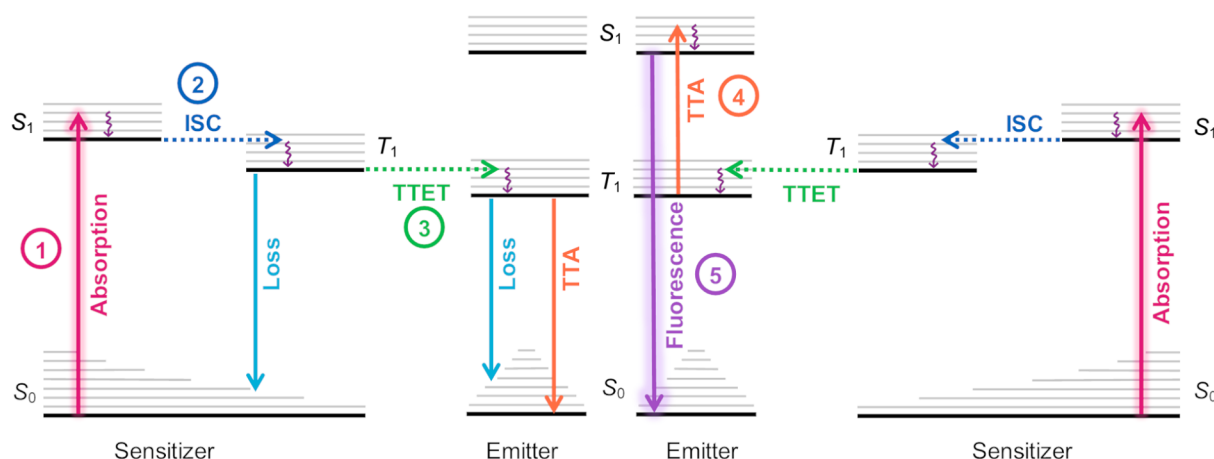
For practical use, many applications require TTA-UC chromophores to be incorporated in a solid matrix.<sup>25</sup> Though studies in solution have enabled understanding of the process, liquid host systems are not usually suitable for real-world use in PV cells or indeed many other of the aforementioned applications. The inclusion of a liquid layer within a device

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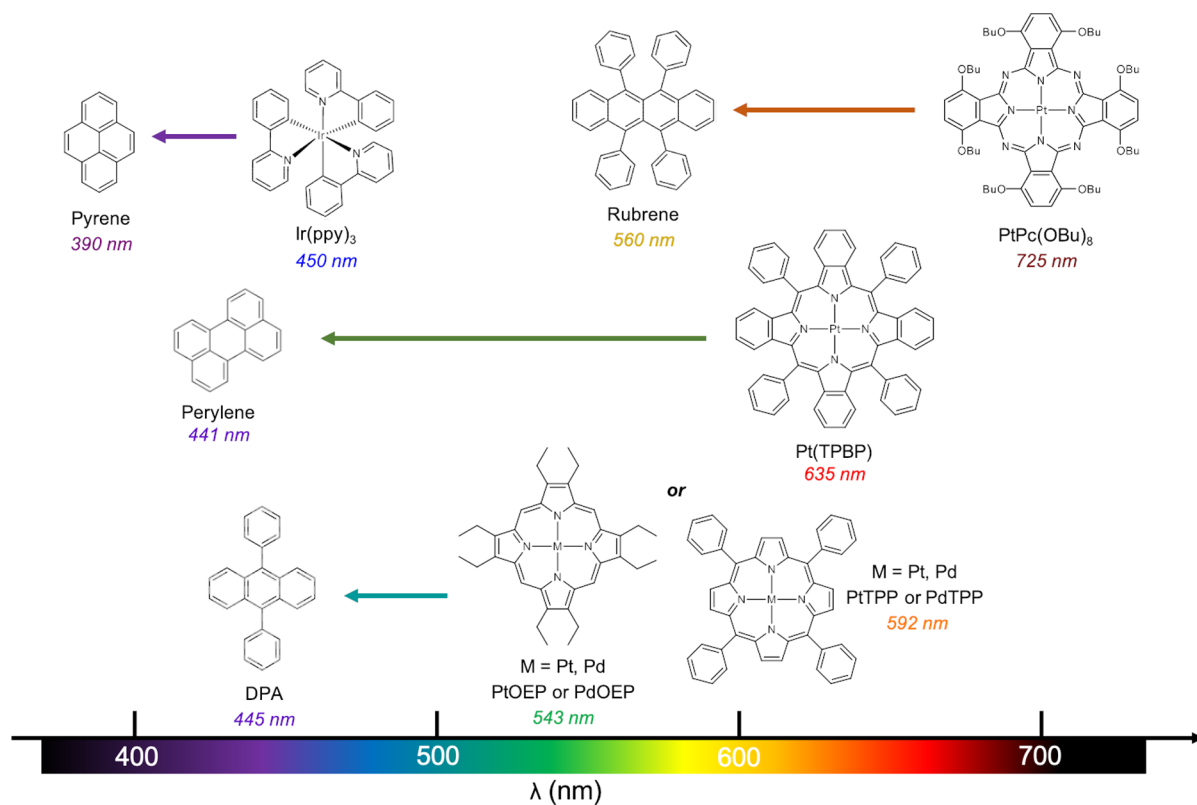
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**Figure 1.** Energy level diagram showing the steps of the radiative and nonradiative processes involved in triplet–triplet annihilation upconversion. (1) The absorption of photons by the sensitizers (glowing pink arrows) with vibrational nonradiative relaxation (squiggly purple arrows). (2) ISC (blue dashed arrow) over to the excited triplet state. (3) TTET (green dashed arrow) then occurs between the emitter and sensitizer in both pairs, and once the two emitters collide, (4) TTA occurs (orange lines), exciting one molecule to a higher energy singlet state with the second relaxing to the ground state. (5) The excited singlet relaxes radiatively via fluorescence (glowing purple line). The pale blue line represents potential energy losses during the process of TTA-UC.



**Figure 2.** Structures of common sensitizer–emitter pairs. The sensitizers are shown on the right-hand side, labeled with their name and absorption wavelength maximum. The emitters are shown on the left-hand side, labeled with their name and emission wavelength maximum.

presents mechanical problems such as leakage, spilling, and the evaporation of solvent over time, especially in warmer climates. The use of a solid-state system would offer a solution to these device-construction problems. However, the key limitation for solid-state TTA-UC is the significantly lower TTA-UC quantum yield ( $\Phi_{UC}$ ) when compared to the liquid state. For example, the highest reported  $\Phi_{UC}$  of the benchmark 9,10-diphenylanthracene (DPA)/platinum(II) octaethylporphyrin (PtOEP) emitter/sensitizer system is  $26 \pm 2\%$  (for an intensity excitation threshold,  $I_{th} = 0.64 \text{ mW cm}^{-2}$ ,

and excitation wavelength,  $\lambda_{exc} = 532 \text{ nm}$ ) in solution,<sup>4</sup> yet the  $\Phi_{UC}$  of the same system in the neat solid state is only 3% ( $I_{th} = 6.8 \pm 2.8 \text{ mW cm}^{-2}$ ,  $\lambda_{exc} = 532 \text{ nm}$ ).<sup>26</sup> This low upconversion efficiency in the solid state can be attributed to a combination of factors including inhomogeneous dye distribution, limited triplet diffusion, and oxygen quenching.<sup>27</sup>

The blending of TTA-UC chromophores in a polymeric host matrix can alleviate some of these issues by combining the attractive qualities of both liquid- and solid-state systems, allowing device design issues to be overcome, as well as

**Table 1.** Selected Polymeric Host Materials Reported for TTA-UC Applications, Detailing a Comparison of the Sensitizer and Emitter Used in Each Case, and the Glass Transition Temperature ( $T_g$ ), Upconversion Energy Shift ( $\Delta E$ ), Excitation Threshold Intensity ( $I_{th}$ ), and Measured Upconversion Quantum Yield ( $\Phi_{UC}$ )

host material	state	$T_g$ (°C)	sensitizer	emitter	$\Delta E$ [eV] <sup>a</sup>	$I_{th}$ (mW cm <sup>-2</sup> )	$\Phi_{UC}$ (%)	ref
<i>N,N'</i> -bis(octadecyl)- <i>L</i> -boc-glutamic diamide	organo-gel	( $T_c = 43.9$ ) <sup>b</sup>	PtOEP	DPA	0.53	1.5	3.5 <sup>c</sup>	32
poly(vinyl alcohol) (PVA)	organo-gel		PdMesoIX	DPA	0.58	180	>0.3 <sup>d</sup> 7 <sup>e</sup>	54
PVA	film	80	PtOEP	DPA	0.53	200	0.09 <sup>f</sup>	55
PVA	film	80	Os complex	Rubrene	0.85	10000	0.21	56
PVA	film	80	Os(btpy) <sub>2</sub> <sup>2+</sup>	tetra- <i>tert</i> -butylperylene	0.97	320	1.4	57
poly(DPAMA- <i>co</i> -MMA)	film	123–150	PdOEP	DPA	0.54	<32		36
PMMA	film	105	PtOEP	DPA	0.53	0.9	0.02	58
polyurethane	film		PtOEP	DPA	0.53	30	1.7	59, 60
polyurethane	film		Ir(ppy-DBP)	DBP	0.35	16.5	1.3	61
poly(olefin sulfone)	film	42	PtOEP	perylene		50	2.1	62
polyoctyl acrylate	elastomer	-62	PtOEP	DPA	0.53	0.3	21	63
sodium polyacrylate	porous hydrogel		PdTPP	DPA	0.49	24.0	1.6	64
epoxy resin	cross-linked polymer	31	PtOEP	P <sub>66614</sub> DPAS <sup>f</sup>	0.53	40	1.9	65
poly(HEMA- <i>co</i> -MAA- <i>co</i> -TEG-diMA)	liquid nanodomains in glassy polymer	50–52	PdOEP	DPA	0.54	2100	23 <sup>g</sup>	66

<sup>a</sup> $\Delta E$  in each reference was reported by the authors as the difference in the peak-to-peak energy from the excitation wavelength of the sensitizer to the emission maximum of the emitter. We note that the apparent anti-Stokes shift (i.e., the difference between the lowest energy absorption peak of the sensitizer and the emission peak of the emitter) would be more informative.<sup>33</sup> <sup>b</sup> $T_c$  is the crystallization temperature. <sup>c</sup>The triplet diffusion constant,  $D_T$ , was measured to be  $1.2 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>.  $D_T$  values were not reported for any other entries in this table. <sup>d</sup>In air. <sup>e</sup>In oxygen-free conditions. <sup>f</sup>P<sub>66614</sub>DPAS = 9,10-diphenylanthracene-2-sulfonate (DPAS) anion and trihexyl(tetradecyl)phosphonium cation. <sup>g</sup>Chromophores located in liquid nanodomains.

enhancing the stability of the TTA-UC system under ambient conditions.<sup>28</sup> However, when considering the properties of the ideal host, it can be challenging to reconcile the somewhat contradictory requirements of high molecular mobility, structural integrity, and oxygen barrier properties in a single material. This is further complicated by the different possible mechanisms for TTA-UC and the lack of consistent terminology in the field. Herein, recent and significant works, which use polymeric hosts to achieve upconversion in the solid state, will be discussed and compared in order to assess the best approaches to achieve harmony between these complex requirements. We will also offer our own perspective views as a suggestion to the future directions of TTA-UC in polymeric hosts in the coming years.

## MECHANISM OF TTA-UC

In order to identify the requisite characteristics of a suitable host material, we first need to understand the mechanism of TTA-UC. Figure 1 depicts an energy level diagram for the process, broken down into its individual steps. Two different lumophores, a sensitizer (or donor) and an emitter (also referred to as an annihilator or acceptor), with suitably matched energy levels are required for TTA-UC to occur.<sup>1,14</sup> Figure 2 shows the chemical structures of some commonly used sensitizer and emitter pairs. In a typical TTA-UC process, the sensitizer absorbs incident photons and is excited to its singlet excited state. As the sensitizer usually has a high intersystem crossing (ISC) rate, this singlet excited state is then efficiently converted to the triplet excited state, which then transfers from the sensitizer to the emitter through a process called triplet–triplet energy transfer (TTET), before the nonradiative decay of the sensitizer back to the ground state. When two triplet excited emitters meet, the TTA

process can take place, leading to one emitter being excited to the singlet state with the other relaxing to the ground state. The singlet excited emitter then emits a photon via fluorescence.

Depending on the mobility of the lumophores, two different TTA mechanisms may operate. The typical *molecular diffusion* mechanism is observed in systems with high molecular diffusion rates, such as solutions or soft hosts, where triplet excited emitters mobilize through the matrix and collide within their triplet lifetime. In other cases, when the donor lumophores are immobilized in an array of acceptors, the TTA process can only occur if a pair of neighboring emitters are both excited to the triplet state following TTET within the acceptor array, which is known as the *triplet energy migration* mechanism. Here, we meet our first challenge: how do we determine which mechanism operates in a given system? Surprisingly, the mode is not explicitly identified in many research articles. Upon closer inspection, this is likely to be a consequence of the lack of well-defined experimental methods to characterize the mechanism. Often, the mechanism is assigned somewhat intuitively; for example, in a highly rigid host such as a polymer with a very high glass transition temperature,  $T_g$ , or a metal–organic framework, it would be almost impossible to consider molecular diffusion as the probable mechanism. Moreover, in many circumstances, it is possible that both mechanisms could operate, for example, should donor–acceptor crystallites precipitate out within a mobile medium.

Both mechanisms ideally require a high quantum yield of donor-to-acceptor TTET, which necessitates a high triplet diffusion constant,  $D_T$ . However, the triplet diffusion coefficient can be used to differentiate the two mechanisms to some extent.<sup>29</sup> Typical values of  $D_T$  are in the order of  $\sim 1$

$\times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  in solution,<sup>30</sup> which is the upper limit for the molecular diffusion mechanism in a low glass  $T_g$  host. In the solid state or high  $T_g$  hosts,  $D_T$  ranges from  $\sim 1 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  for molecular diffusion<sup>31</sup> to values  $> 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  (i.e., greater than in solution) if the energy migration mechanism operates.<sup>29,32</sup> As these values are sufficiently different, the determination of  $D_T$  from the threshold excitation intensity (see below) could be used to more appropriately assign the mechanism, although this is still only rarely reported.<sup>29</sup>

As highlighted recently, an additional challenge arises from inconsistency in the terminology used in the field to report the efficiency of the TTA-UC process.<sup>33</sup> In this Perspective, we follow the conventional description for the upconversion quantum yield,  $\Phi_{\text{UC}}$ , namely, as the number of UC photons emitted divided by the number of photons absorbed by the sensitizer. Since TTA-UC requires two photons to release one photon of higher energy, the theoretical efficiency of upconversion cannot exceed 50%. All reported  $\Phi_{\text{UC}}$  values in Table 1 follow this conventional description for measured quantum yields where the original source reports the normalized yield (i.e., multiplication by a factor of 2 to scale from 50% to 100%); we have reversed the normalization for the ease of comparison.<sup>33</sup>

In practice, there are a number of additional factors that influence the measured upconversion quantum yield; for example, oxygen-quenching of excited triplet states can pose a massive obstacle when designing TTA-UC systems for use in atmospheric conditions. Back-energy transfer between emitter and sensitizer pairs and experimental output losses such as waveguiding, scattering, and inner-filter effects also have to be considered.<sup>34</sup> This means that  $\Phi_{\text{UC}}$  is often lower than the quantum yield of photons generated,  $\Phi_{\text{UC}_g}$ , which combines the yields of several different processes as described in eq 1, where  $\Phi_{\text{ISC}}$ ,  $\Phi_{\text{TTET}}$ ,  $\Phi_{\text{TTA}}$ , and  $\Phi_{\text{F}}$  are the quantum yields for ISC of the sensitizer, TTET from the sensitizer to the emitter, TTA, and fluorescence of the emitter, respectively, and  $\Phi_{\text{ET}}$  is the quantum yield for back-energy transfer from the  $S_1$  state on the emitter to the  $S_1$  state on the sensitizer (a source of loss).

$$\Phi_{\text{UC}_g} = \Phi_{\text{ISC}} \Phi_{\text{TTET}} \Phi_{\text{TTA}} \Phi_{\text{F}} (1 - \Phi_{\text{ET}}) \quad (1)$$

To maximize  $\Phi_{\text{UC}}$ , the solid-state matrix of the TTA-UC system should be designed in a way to allow efficient TTET and TTA processes. A useful figure-of-merit is the threshold excitation intensity,  $I_{\text{th}}$ , at which  $\Phi_{\text{TTA}}$  becomes 0.5, which can be described using the fundamental parameters of the system as<sup>35</sup>

$$I_{\text{th}} = (\alpha \Phi_{\text{TTET}} 8\pi D_T a_0)^{-1} (\tau_T)^{-2} \quad (2)$$

where  $\alpha$  is the absorption coefficient at the excitation wavelength,  $a_0$  is the annihilation distance between the emitter triplets, and  $\tau_T$  is the lifetime of the emitter triplet state.  $D_T$  is the triplet diffusion constant described earlier in the discussion of the mechanism.

## ■ CURRENT APPROACHES TO POLYMERIC HOST DESIGN FOR TTA-UC

As mentioned above, the most significant issues facing the translation of TTA-UC from solution to the solid state include the difficulty of achieving sufficient mechanical integrity to enable inclusion into a final device design, while retaining

sufficient contact between the incorporated lumophores to enable the TTA-UC process.

For all systems that we will discuss in the following sections, there are a number of common challenges. First, it should be noted that achieving a homogeneous distribution of organic fluorophores in a host medium is often difficult.<sup>11</sup> For TTET and TTA to occur effectively (steps 3 and 4 in Figure 1), a high concentration of sensitizers and emitters is required. Such conditions in a solid-state host matrix often lead to severe aggregation of the chromophores. This may result in the introduction of new nonradiative pathways that lead to aggregation-caused quenching (ACQ) of the emission and a reduction in  $\Phi_{\text{F}}$  of both the sensitizer and the emitters.<sup>11,36,37</sup> Alternatively, such aggregation may switch-on or amplify the triplet energy migration mechanism, which may or may not be desirable, depending on the final requirements. Certainly, any uncontrolled precipitation should be avoided.

Second, molecular diffusion is typically very slow in solid-state TTA-UC systems. The rate of TTET is reliant upon collision between an emitter and excited sensitizer and may be diminished by low molecular diffusion rates as the triplet exciton may relax before achieving collision with an emitter (represented by the blue “loss” line in Figure 1).<sup>38</sup> Equally, limited molecular diffusion also affects the TTA process, which requires the collision of a pair of triplet emitter excitons.<sup>28,39,40</sup> Both of these diffusion-limited processes have a direct effect on the number of upconverted photons generated (eq 2), leading to a loss of efficiency as the molecular mobility decreases.

Finally, the parasitic quenching of the triplet-excited states by oxygen is another consideration in the design of practical TTA-UC systems. While both sensitizer and emitter triplets may be quenched, it predominately affects the emitter triplets due to their longer excited-state lifetime and typically higher population density. This presents an immediate dichotomy as a fully oxygen-impermeable medium necessarily implies a low molecular diffusion rate, which would decrease the efficiency of TTET. Unfortunately, the deoxygenating methods employed in solution to remove atmospheric oxygen are not immediately transferable to solid-state matrices. Oxygen-scavenging molecules may be embedded into the polymer matrix to mitigate this problem.<sup>41–44</sup> Alternatively, oxygen barrier materials may be used to prevent oxygen penetration, which may be either inherently oxygen-impermeable host media or external encapsulation architectures.<sup>45–48</sup>

Generally speaking, molecular diffusion in polymers is primarily reliant on three factors, the size of the diffusant, the temperature at which the system exists, and the availability of free volume within the host polymer.<sup>49,50</sup> Smaller diffusants inherently have a larger diffusion rate, being subject to less steric hindrance in their movement. For TTA-UC pairs, it is difficult to significantly change the size of the molecules used without adversely affecting the activity of the system. Variations in temperature affect the diffusion rate on two fronts.<sup>51,52</sup> First, there is, as may be expected, a steady increase in rate as temperature increases. Second, the rate of diffusion increases sharply as the temperature of the polymer passes above its glass transition temperature ( $T_g$ ). While the operational temperature of a TTA-UC system may not be subject to change, particularly in certain sensitive applications, it is possible to tune the  $T_g$  of the host to allow for suitable diffusion rates at a given temperature. Finally, the diffusion process itself is inherently dependent on the availability of free

volume within a polymer environment into which a diffusant is able to move; this volume may be increased by utilizing polymeric systems with lower crystallinity and density.

There is an inherent relationship between each of these three factors: below the glass transition temperature, reduced polymer mobility leads to a reduction in free volume, which in turn makes it harder for diffusion to take place, especially for large molecules. Experimentally, the glass transition temperature is the easiest parameter to tune in this respect. For small molecules dispersed in rubbery polymers above their respective  $T_g$ , diffusion rates may be as high as  $10^{-5}$   $\text{cm}^2 \text{s}^{-1}$ ,<sup>53</sup> comparable to diffusion rates in solution. Conversely, for glassy polymers below their  $T_g$ , molecular diffusion rates are several orders of magnitude lower, as low as  $10^{-13}$   $\text{cm}^2 \text{s}^{-1}$  in certain systems.<sup>52</sup> It is this large variance in diffusion rates across the glass transition that dictates the requirement for the use of different TTA-UC mechanisms.

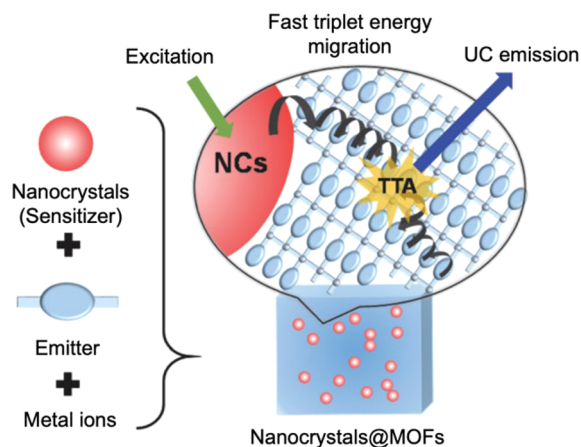
Given the importance of the glass transition on both molecular diffusion and oxygen ingress, we will now discuss pertinent examples of TTA-UC systems in the literature, organizing them based on the  $T_g$  of the host material. First, we will look at high  $T_g$  rigid hosts that introduce mechanical strength to the system, before discussing the merits of low  $T_g$  flexible hosts that promote the molecular diffusion of lumophores. Table 1 summarizes some of the key features of the solid-state TTA-UC systems discussed throughout the text.

### ■ TTA-UC PARTICLES IN HIGH $T_g$ POLYMERIC HOSTS

Polymers with a high  $T_g$  can be used as rigid host materials to provide the mechanical strength for samples using TTA-UC chromophores in aggregated forms such as particles and crystals. Unlike in solution,<sup>4</sup> in this instance, both the sensitizer and emitter are immobilized in the solid-state matrix. As such, the TTA step is no longer reliant on the molecular diffusion of emitters, and instead, the process relies on triplet exciton transfer between neighboring molecules in the emitter domains, i.e., the triplet energy migration mechanism.<sup>21,28,67</sup> Energy migration-based TTA-UC can often be found in rigid solid-state systems, for example, nanocrystal-doped metal–organic frameworks (Figure 3),<sup>68</sup> where molecular diffusion is not available due to the rigid, crystalline structure. In such systems, the TTET rate between the sensitizer and the emitter is highly dependent on the blending of the two components, as phase separation of the sensitizer and emitter may trap the triplet exciton in the sensitizer domains, preventing the TTET process.

It should be noted that, while for this mechanism TTA-UC can occur even in the absence of any matrix, the host material fulfills several important roles: facilitating the even distribution of particles, reducing scattering by improving the surface morphology, blocking oxygen, and perhaps most importantly, offering mechanical structure and stability, thereby enabling the integration into larger devices. TTA-UC systems using solid-state lumophore nanocrystals or particles have been widely reported in research fields including bioimaging,<sup>22–24</sup> photovoltaics,<sup>69,70</sup> and light emission.<sup>71,72</sup> A number of studies also embed solid-phase TTA-UC chromophores in high  $T_g$  polymeric hosts, which are further discussed below.

Aggregated TTA-UC chromophores in high  $T_g$  polymer hosts often lead to phase separation, which reduces the rate of TTET. One such example was reported by Karpicz et al. in



**Figure 3.** Typical mechanism of triplet energy migration-based TTA-UC demonstrated by an example where nanocrystals of the sensitizer are doped into a metal–organic framework (MOF) of the emitter. The nanocrystals are excited to produce triplet excitons, which migrate rapidly to the emitter causing TTA. The upconverted photon is emitted out of the system. Adapted with permission from ref 68. Copyright Royal Society of Chemistry 2018.

2014 who studied the exciton dynamics in poly(methyl methacrylate) (PMMA) using the bench-mark DPA and PtOEP emitter/sensitizer pair.<sup>58</sup> Film samples with DPA in a 5-fold concentration excess compared to PMMA were prepared by either evaporation or spin-coating from a chloroform solution. Here, PMMA is used as a binder for the lumophores rather than as a true host material. Phosphorescence lifetime measurements performed in the PtOEP emission band suggested that a fraction of the excited sensitizer was not quenched due to inhomogeneous blending of the DPA/PMMA/PtOEP films. Another example that used PMMA as the host material with a DPA concentration of 25% w/w paired with up to 0.5% w/w of PdOEP was reported by Lee et al. in 2013, where two very different approaches were used to produce the TTA-UC PMMA blend film samples.<sup>39</sup> In the first method, powdered PdOEP and DPA were mixed with PMMA by melt-pressing and subsequent stir-extrusion. The second method involved dissolving DPA, PdOEP, and PMMA in dimethylfuran, followed by precipitation by the addition to water. Both resulting PMMA blends were melt-pressed again to give thin films (100–180  $\mu\text{m}$  thickness), showing TTA-UC emission in ambient conditions for 6 months. In both of the above reports, the efficiency of TTET was limited by the phase separation between the sensitizer and the emitters.

It is worth noting here that, although TTA-UC lumophores are typically expected to achieve homogeneous distribution in high diffusion (low  $T_g$ ) hosts, such as poly(urethane) (PU),<sup>45</sup> there are several reported examples of particle formation in such media.<sup>73,74</sup> In 2019, Gao et al. reported a series of dimer and trimer derivatives of DPA and their TTA-UC properties when paired with PtOEP.<sup>59</sup> We note that the solvents used to prepare the samples were deoxygenated before use. The resulting TTA-UC pairs were observed to coaggregate into particles when embedded in the PU matrix with a  $\Phi_{\text{UC}}$  of 1.7% being reported later in the author's doctoral thesis.<sup>60</sup> Thin film samples were prepared by dissolving the DPA derivatives, PtOEP, and PU in THF, which was drop-cast between two glass slides. The resulting samples were cured for 12 h under ambient conditions and subsequently at 60 °C for

a further 12 h. Particles of the luminophores were observed in the resulting thin films by dark-field optical microscopy. Although not confirmed in this work, it indicates the possibility that both molecular diffusion and triplet energy migration can coexist in the same polymeric host matrix.

One solution to overcome molecular aggregation is to add solubilizing chains to the archetypical TTA-UC chromophore structures. Kashino et al. recently reported a solid-state TTA-UC system based on films of epoxy thermoset resins incorporating an ionic liquid emitter composed of 9,10-diphenylanthracene sulfonate and lipophilic phosphonium ions bearing long alkyl chains in combination with PtOEP as the sensitizer.<sup>65</sup> The ionic moieties and solubilizing chains resulted in a significantly increased dispersibility of the emitter within the resin (up to 1000 mM). Moreover, the rigid environment resulted in a surprisingly long emitter triplet lifetime of 17.8 ms, which in combination with high TTET, allows for effective triplet exciton diffusion and annihilation, resulting in a  $\Phi_{UC}$  of 1.9% with low threshold excitation intensity ( $I_{th} = 40 \text{ mW cm}^{-2}$ ). Notably, almost no difference was observed between the  $\Phi_{UC}$  values of films prepared and sealed in a glovebox ( $< \sim 0.2\%$  deviation).<sup>65</sup> Epoxy resins are known for their low permeability to moisture and oxygen, which has led to their common use as encapsulants for LEDs and PV cells.<sup>75</sup> This work demonstrates that modification of the lumophore structure may also provide a useful strategy to improve molecular mobility (through solubilization), while retaining the low oxygen permeability of the host.

### ■ TTA-UC IN LOW $T_g$ POLYMERIC HOSTS

As discussed above,  $\Phi_{UC}$  for TTA-UC systems using aggregated lumophores is often limited by phase separation and inefficient TTET. The issue may be addressed by utilizing polymeric host materials with glass transition temperatures below ambient temperature. These materials are typically flexible elastomers at room temperature, enabling their potential use in applications where stiffer, high  $T_g$  host materials would be unsuitable. In such materials, the polymeric host exhibits enough free space volume to enable an appreciable rate of molecular diffusion for any incorporated small molecules, which in the case of polymer-hosted TTA-UC systems, enables sensitizer/emitter collisions and the corresponding energy transfer required for TTA-UC to occur. Unfortunately, this molecular diffusion is not limited to the embedded lumophores and may also facilitate oxygen ingress.

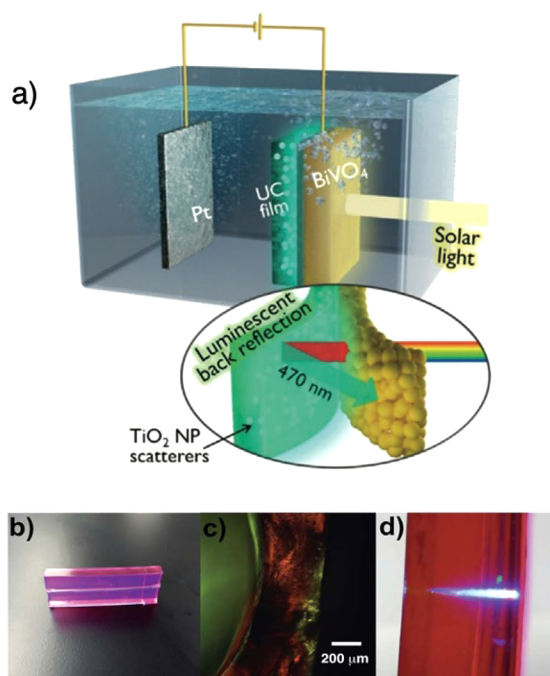
Castellano and co-workers demonstrated the first example of TTA-UC in a rubbery polymer host in 2007 using a 50:50 copolymer of poly(ethylene oxide) and poly(epichlorohydrin) (PEO-PEI) with a glass transition temperature of  $-43 \text{ }^\circ\text{C}$ .<sup>76</sup> The oxygen permeability of the samples was not described. In 2009, the same team established the diffusion-related dependence in polymeric hosts by investigating the TTA-UC process in the same copolymer ( $T_g$  of  $-37 \text{ }^\circ\text{C}$ ) and several commercially available poly(urethane)s, Texin 270, Texin 285, and Tecoflex EG-80A ( $T_g$ 's of 0,  $-32$ , and  $-70 \text{ }^\circ\text{C}$ , respectively), both above and below the glass transition temperatures of the respective systems.<sup>77</sup> In both reports, the sensitizer/emitter pair of palladium(II) octaethylporphyrin (PdOEP) and DPA was used, and a reasonable distribution of the lumophores within the host was achieved by casting a common initial solution of the polymer and chromophores in dimethylformamide (DMF). This DMF solution was cast onto

glass slides and dried to yield films with a typical thickness of  $90\text{--}100 \text{ }\mu\text{m}$ . While the study was limited due to the lack of structural details regarding the commercial polymers, it firmly established that the intensity of the upconverted emission was enhanced with an increasing temperature above the  $T_g$  for each polymer tested. Unfortunately, upconversion quantum yields were not reported in this study.

More recently, Schlenker and co-workers have demonstrated a metal-free solid-state TTA-UC system using the same PEO-PEI copolymer host.<sup>78</sup> This metal-free system used a novel thiosquaraine sensitizer paired with rubrene as the emitter, eliminating the need for heavy metals, while allowing conversion of red light ( $\lambda_{ex} = 685 \text{ nm}$ ) to a yellow emission ( $\lambda_{em} = 570 \text{ nm}$ ); unfortunately,  $\Phi_{UC}$  was not reported for the polymer-hosted system. Such a metal-free approach has advantages for potential cost reduction as well as a reduction in environmental impact during both sample production and disposal.

Following the initial investigative work conducted by Castellano and co-workers,<sup>77</sup> poly(urethane)s have received a substantial amount of interest as polymeric host materials for TTA-UC.<sup>81</sup> This interest is seemingly driven by a combination of favorable properties (such as inherent flexibility, clarity, and high transmittance) and the widespread availability of commercial two-component kits, allowing for the manufacture of devices without the need for any significant synthetic investment. The ease of TTA-UC device manufacture using poly(urethane)s has seen them applied widely to a number of practical applications. For example, Moon and co-workers recently reported the use of a poly(urethane) back-reflecting TTA-UC layer to enhance the yield of both hydrogen and oxygen from a photoelectrochemical water-splitting system (see Figure 4a).<sup>79</sup> The layered electrode was prepared under ambient conditions and incorporated both perylene and palladium(II) meso-tetraphenyltetraabenzoporphyrin (PdTPBP) lumophores in a polymeric host of the commercially available poly(urethane) ClearFlex 50, enabling absorbance of wavelengths at  $600\text{--}650 \text{ nm}$  and re-emission of upconverted light with a wavelength of  $470 \text{ nm}$ ; again,  $\Phi_{UC}$  was not reported for this system. The team used the TTA-UC layer to enhance the amount of incident light that was available for absorption by a Mo:BiVO<sub>4</sub> electrode, which has an upper absorbance wavelength of  $610 \text{ nm}$  by positioning the poly(urethane) TTA-UC layer underneath the electrode allowing for upconversion of any transmitted photons and utilizing titania nanoparticles to enable back-scattering of this upconverted light toward the electrode. The upconversion-enhanced device showed a significant improvement when compared to the bare Mo:BiVO<sub>4</sub> electrode, yielding an increase of approximately 16% for the production of both hydrogen and oxygen, which corresponds to the increased photocurrent density observed in the enhanced electrode.

A ClearFlex poly(urethane) host has also been used by Steinhardt and co-workers to produce a photocatalytic microfluidic device that enabled photochemical oxidation reactions in flow through the use of TTA-UC chromophores embedded in the reactor walls (see Figure 4b).<sup>80</sup> The poly(urethane) was doped with DPA and PdOEP as the emitter/sensitizer pair and cast into a reactor mold, which was degassed under vacuum. The upconverted photons were used to generate singlet oxygen via excitation of  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ , and the reactor was run using a plug-flow methodology,



**Figure 4.** Applications of solid-state TTA-UC systems using commercially available ClearFlex poly(urethane) hosts. (a) An upconversion-based luminescent back reflector is used to assist photoelectrochemical water-splitting at Mo:BiVO<sub>4</sub> photoelectrodes. Adapted with permission from ref 79. Copyright John Wiley and Sons 2019. (b–d) Images showing an upconversion-based photocatalytic microreactor demonstrating (b) upconversion enrichment of blue photon flux in diffuse sunlight; (c) a cross-section of the reactor surface; (d) a dye-doped reactor upconverting a 532 nm (green) laser. Adapted with permission from ref 80 under Creative Commons license CC-BY-3.0.

alternating the reaction solution and oxygen gas plugs for better mixing. This system was used to synthesize the antihelmintic drug ascaridole by oxidation of  $\alpha$ -terpine. Under diffuse low illumination ( $113 \text{ W}\cdot\text{m}^{-2}$ ), the upconverting system showed a drastic improvement in product yield ( $\sim 400\%$  increase) when compared to the same system manufactured from an undoped poly(urethane); however, the authors again do not state the  $\Phi_{\text{UC}}$  of the dye-sensitizer-polymer combination.

Overall, poly(urethane)s have shown good utility as TTA-UC hosts with typically high optical clarity, flexibility, and glass transition temperatures significantly below room temperature, as well as the wide commercial availability of ready-to-mix kits suitable for sample manufacture. However, they are not without their limitations. The reliance in the literature on such commercially available mixtures, typically with extremely limited, if any, structural information, makes it difficult to fully develop an understanding of the structure–property relationships at work in hosted TTA-UC systems. This, coupled with the typical transmittance cutoff of 400–500 nm for aromatic, or hemiaromatic, poly(urethane) materials, could impose limitations for some applications. The variation in structures for poly(urethane) hosts also has an effect on both the rate of molecular diffusion and that of oxygen ingress. While the rates of both are tied, given the overall good oxygen resistance of poly(urethane)s compared to other polymer families, this does offer some room for finding a sweet spot via tuning of the molecular structure.

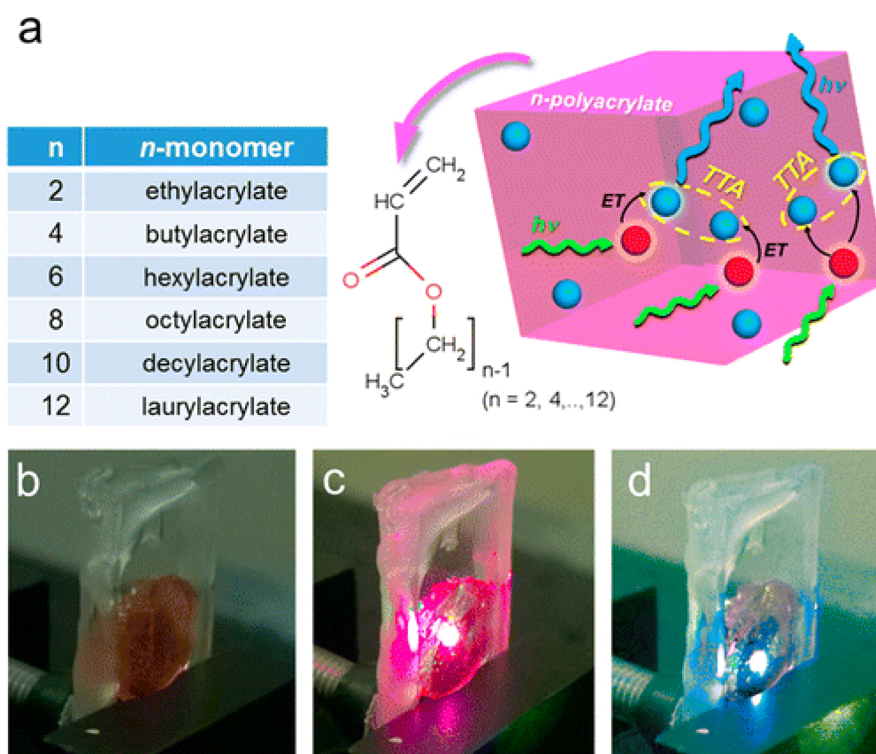
In contrast, poly(alkyl methacrylate)s typically possess low transmittance cutoffs between 250 and 400 nm, which when coupled with their low glass transition temperatures, makes them useful polymeric hosts. The viability of alkyl acrylates as host materials for TTA-UC was demonstrated in 2016 by Monguzzi et al., whose initial interest was spurred by the combination of both flexibility and low glass transition temperatures.<sup>63</sup> A range of side-chain lengths were investigated, ranging from 2 to 12 carbons as shown in Figure 5, which gave a selection of materials with varying  $T_g$ 's from  $-11$  to  $-55$  °C. A lower  $T_g$  was shown to correlate with an increase in molecular diffusion and upconversion quantum yield, reaching a maximum  $\Phi_{\text{UC}}$  of 22% (comparable to the currently reported record for  $\Phi_{\text{UC}}$  in solution of 26%).<sup>4</sup> This study therefore supports that the relationship between the  $T_g$ , diffusion rate, and quantum yield demonstrated by Castellano and co-workers is not specific to a given system<sup>76,77</sup> but instead is applicable to a broad selection of polymeric hosts.

Poly(hexyl methacrylate) has recently been demonstrated as a host material for a stress-sensing system based on TTA-UC.<sup>8</sup> This report used a covalently grafted anthracene emitter alongside freely dispersed PtOEP as the sensitizer. The anthracene was masked with a Diels–Alder cross-linkage, as depicted in Figure 6, preventing participation in the TTA-UC process in the resting state. When the system was subjected to mechanical stress, this Diels–Alder linkage was cleaved and the exposed anthracene was able to participate in TTA-UC, providing a system that offers sensitive, stress-fracture sensing capabilities. Significantly, the use of TTA-UC as a detection method, rather than the simple fluorescence, increased the range of concentrations over which a proportional relationship existed between concentration and emission intensity. This relationship allowed for quantification of the fracture level of the material, increasing by an order of magnitude to  $10^{-4}$  M or greater for TTA-UC detection, compared to ca.  $10^{-5}$  M for fluorescence, capped primarily due to self-quenching. It is perhaps worth noting that the system used in this work, while an interesting and novel application of TTA-UC, is reported to have a  $\Phi_{\text{UC}}$  of only 0.041%; no comment is made on why the efficiency is seemingly so low, although measurements were conducted using a xenon arc lamp rather than a laser.

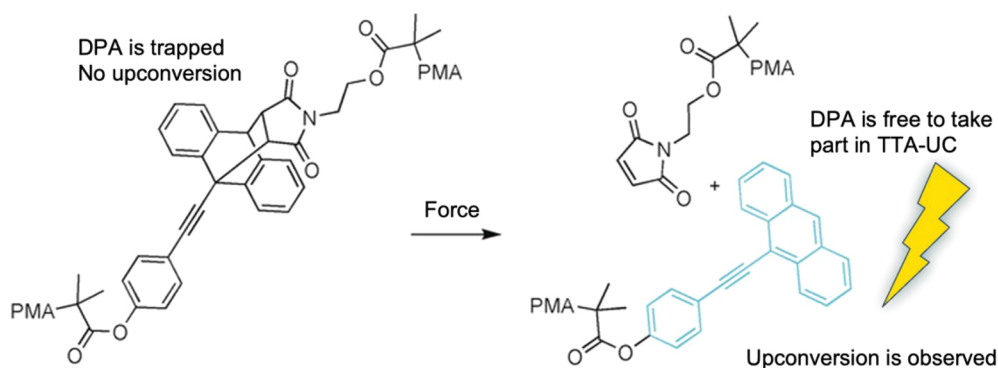
In summary, low  $T_g$  polymeric host systems are currently one of the more established and promising classes of hosts for TTA-UC based on molecular diffusion. They can offer favorable mechanical properties, such as flexibility or compressibility, important in a range of potential applications that would be unsuitable for a stiffer high  $T_g$  material. Importantly, they still allow for the ready diffusion of their hosted chromophore pairs, enabling the realization of significantly higher quantum efficiencies than those observed for the embedded particle approaches required by high  $T_g$  polymeric hosts.

## ■ GEL HOSTS AND MIXED-PHASE SYSTEMS

While the use of bulk polymer hosts is well-established, there remains a compromise to be made in the mobility of the dispersed chromophores when compared to solution-phase systems. The use of gelled hosts is an emerging area of investigation with only a handful of examples reported to date but offers the potential for a combination of good mechanical stability with high rates of molecular diffusion for the chromophore pairs maintained through the presence of the dispersed liquid phase.<sup>82,83</sup> The application of a gelled host



**Figure 5.** Poly(acrylate) host system doped with DPA and PdOEP for TTA-UC. (a) Scheme showing the structures of the poly(acrylate) de-loaded system and an outline of the physical processes occurring during TTA-UC. The red circles represent the sensitizer PtOEP and the blue circles, the emitter DPA. A DPA:PtOEP ( $10^{-2}$  M: $10^{-4}$  M) doped poly(octyl acrylate) sample (b) under daylight and under (c) low intensity (0.01 suns) and (d) high intensity (10 suns) laser excitation at 532 nm. Adapted from ref 63. Copyright American Chemical Society 2016.



**Figure 6.** Stress-sensing system based on TTA-UC. The scheme depicts the Diels–Alder linkage on the DPA derivative covalently attached to the poly(hexyl methacrylate) host. The linkage can be cleaved under force, resulting in the DPA derivative being free to act as an emitter to enable TTA-UC to occur within the system, producing a fluorescence response to sense stress. Adapted from ref 8 under Creative Commons license CC-BY-3.0.

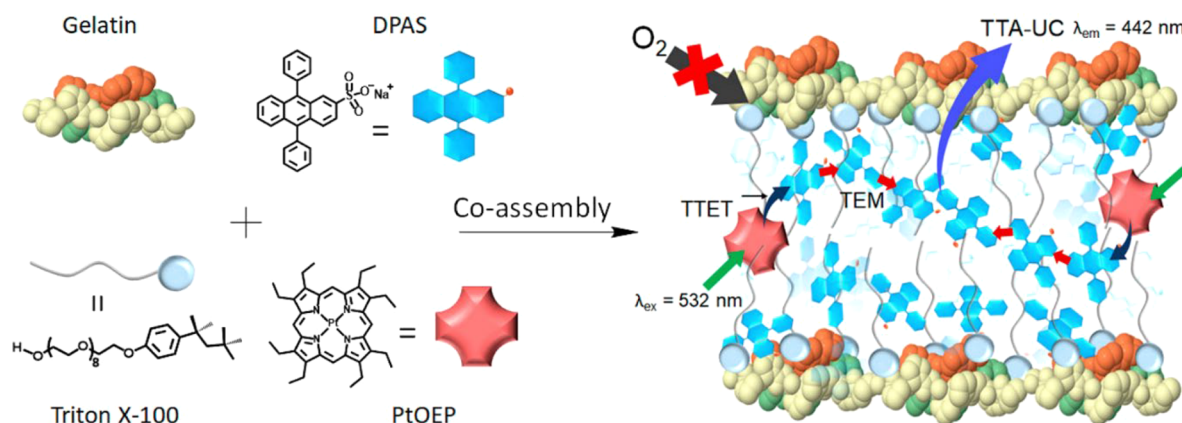
system for TTA-UC was first demonstrated by Schmidt and co-workers in 2015 using a small organogelator, 1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol.<sup>84</sup> Using a chromophore pair of DPA and PdTPP dissolved in tetralin, the authors reported no discernible difference in performance between the gelled system and the equivalent solution with a  $\Phi_{UC}$  of  $\sim 4\%$  observed in both cases. This work demonstrated the potential advantages of using a gel host compared to a bulk polymer host.

More recently, work by Kimizuka and coauthors has reported a biobased hydrogel system that uses the synergistic interaction between gelatin and the commercially available surfactant Triton X-100,<sup>85</sup> whereby the polar chain of the surfactant inserts within the gelatin layer, and both the donor

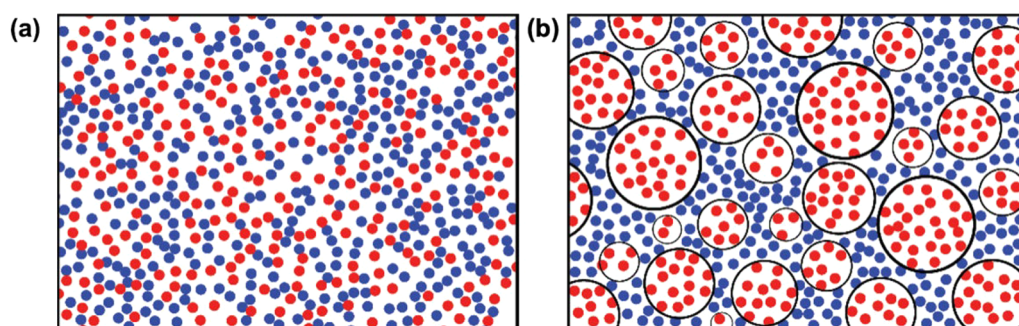
and acceptor molecules are accumulated in the nonpolar surfactant domains, as shown in Figure 7. This study used PtOEP as the sensitizer, pairing it with two different emitters, DPA and a sulfonated variant, DPAS. The sulfonated emitter exhibited a longer triplet lifetime (4.9 ms) compared to DPA (3.3 ms), resulting in an increased upconversion quantum yield for the PtOEP/DPAS pair compared to PtOEP/DPA ( $\Phi_{UC} = 6.75\%$  vs 5.1%). Significantly, the strong hydrogen-bonding network of the gelatin layer acts as an effective oxygen barrier layer, reducing the quenching as a result of oxygen penetration into the system.

Further work by the same group has demonstrated the synthesis of a micelle-based hydrogel TTA-UC system and its subsequent use for optogenetic manipulations in deep





**Figure 7.** Hydrogel-based TTA-UC host system. The figure demonstrates the coassembly of gelatin and the surfactant Triton X-100, incorporating PtOEP and DPAS as the TTA-UC chromophore pair. Gelatin forms a strong hydrogen-bonded layer into which the PEO tail of Triton X-100 inserts itself, allowing the PtOEP and DPAS to accumulate in the corresponding internal nonpolar domain. The tight hydrogen-bonded gelatin-Triton network provides an effective oxygen barrier layer, allowing for efficient TTA-UC to occur within the hydrophobic domains. Adapted from ref 85. Copyright American Chemical Society 2018.



**Figure 8.** Computational studies demonstrate that the distribution of the sensitizer and emitter affect the TTA-UC efficiency. Two possible distributions of sensitizer and emitter molecules throughout an upconversion matrix are shown. (a) Randomly placed molecules, emitters in blue and sensitizers in red. Some emitters are very close to each other, whereas others are surrounded by sensitizers and have no partner to perform upconversion. (b) Correlated placement of molecules: A circle represents a cluster of sensitizers, whereas outside the circles only emitters are embedded in the host material. Reproduced with permission from reference 87. Copyright AIP Publishing 2014.

tissues.<sup>86</sup> This involved the development of a novel osmium-based sensitizer with a relatively long-lived triplet excited state (24  $\mu$ s) compared to other osmium complexes (0.2  $\mu$ s), allowing for triplet transfer even within viscous host systems. The osmium sensitizer and emitter (2,5,8,11-tetra-*tert*-butylperylene) were incorporated into micelles formed from the commercially available triblock copolymer Pluronic F127 by dissolution in DMF, with subsequent freeze-drying and dispersion in water leading to gelation. Unfortunately, while the authors report a  $\Phi_{UC}$  of 2.95% for the chromophore pair in DMF solution, they do not report an efficiency in the final hydrogel system. The gelled samples were further heat treated at 80 °C to enhance the oxygen barrier properties of the resulting gel with the annealed system retaining more than 90% of the upconversion intensity after 30 min of near-infrared (NIR) irradiation, compared to an almost total loss in the unannealed material. This micelle-based approach is a promising method for the formation of TTA-UC materials suitable for inclusion in manufactured devices, retaining the efficiency of solution-based systems while benefiting from improvements in oxygen barrier properties resulting from the use of a gel host.

One very recently reported approach used embedded liquid nanodroplets to achieve the high molecular diffusion rate of solution-based TTA-UC systems, while using a high  $T_g$

polymeric host.<sup>66</sup> Three commonly used TTA-UC dye pairs were tested: DPA:PtOEP, rubrene:palladium(II)-octabutoxyphthalocyanine (Pd(OBu)<sub>8</sub>Pc), and 2,5,8,11-tetra(*tert*-butyl)perylene (TBPe):PdTPBP. Lumophores were dissolved in hydrophobic butyl benzoate and distributed as nanodroplets stabilized with cetyltrimethylammonium chloride, about 40 nm in diameter, in a mixture of high  $T_g$  polymeric hosts such as poly(methacrylic acid), poly(2-hydroxyethyl methacrylate), poly(triethylene glycol), and poly(glycol dimethacrylate). Dimethylthiomethane was added to the system as an oxygen scavenger to prevent triplet quenching from residual oxygen within the nanodroplets. Among them, the DPA:PtOEP system gave a remarkable maximum  $\Phi_{UC}$  of  $23 \pm 3\%$  in ambient conditions. All tested TTA-UC systems showed only negligible performance losses over 3 months, indicating good stability to air.

The use of gels as host materials for TTA-UC applications is a promising, but challenging, area of investigation. While such systems offer the potential to reach quantum efficiencies comparable to those observed in solution, as inherently wet materials, they also suffer from many of the drawbacks that have been highlighted for solution-based UC systems. As such, careful engineering may be required in order to address challenges such as dehydration. Moreover, the risk of oxygen penetration in gelled hosts must also be carefully considered

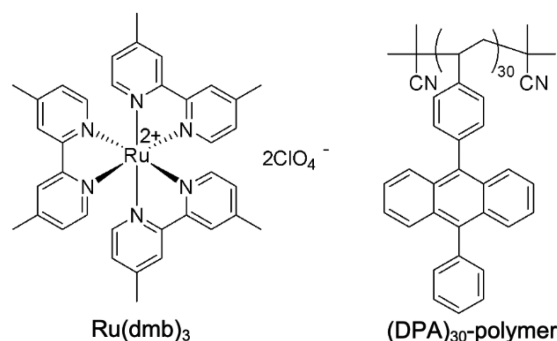
and managed, particularly when using systems with a low quantity of solid mass. However, as discussed in this section, there are a number of approaches that manage to overcome this and have been shown to approach the potential that such systems promise.

### ■ GRAFTED LUMOPHORES AND ASSEMBLED POLYMER SYSTEMS

A theoretical study conducted by Zimmermann et al.<sup>87</sup> suggests that the spatial positioning of the sensitizer and emitter is crucial for upconversion and improving their distribution can significantly improve their performance. They found that placing the sensitizers in clustered formations led to significantly higher upconversion efficiency compared to random distribution when modeled using rubrene as an emitter and a palladium porphyrin (PdPQ<sub>4</sub>) as a sensitizer (Figure 8). If this model can be followed when designing host systems by grouping sensitizers together, this could lead to a more efficient upconversion material.

This theory could be put into practice by covalently grafting chromophores to self-assembling polymers in order to group them in ordered clusters of enhanced sensitizer or emitter concentrations. This could be achieved through supramolecular interactions such as hydrogen bonding and  $\pi$ - $\pi$  stacking interactions or alternatively by covalent grafting. The local concentration of emitters can be kept high by grafting them into the backbone of a polymer; for example, in poly(methacrylate)s, the methacrylate monomer can be copolymerized with an emitter-functionalized version so that DPA can be incorporated into the polymer backbone.<sup>27,36,88</sup>

One example has been demonstrated by Tilley et al. in 2015, in which a polymer containing 30 pendant diphenylanthracene groups, named (DPA)<sub>30</sub>-polymer, was used as the emitter to demonstrate the intramolecular TTA process (Figure 9).<sup>89</sup> Ru(dmb)<sub>3</sub> was used as the sensitizer, and both



**Figure 9.** Chemical structures of the sensitizer Ru(dmb)<sub>3</sub> and the combined host and emitter (DPA)<sub>30</sub>-polymer, respectively. In this study, the DPA emitter is covalently grafted to the polymeric host to achieve rapid intramolecular TTA, yielding a 5% UC efficiency. Redrawn from ref 89.

lumophores were dissolved in chloroform at a relatively low concentration ( $\sim 10^{-5}$  M). The kinetics of each step in the TTA-UC process were analyzed. A rapid intramolecular TTA process was observed ( $\sim$ ns), contributing 5% to the UC efficiency of this system. Although the absolute UC efficiency was not reported in this work, this approach warrants further investigation.

Another example of DPA being grafted to a polymeric host framework was shown by Lee et al., who explored the

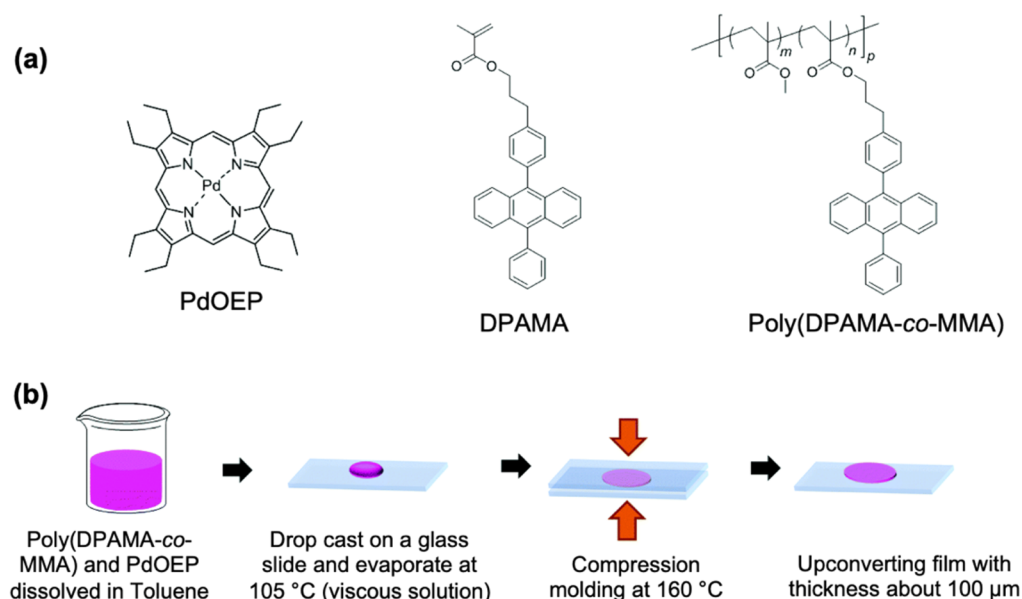
covalent-linking of the emitter to a high  $T_g$  host by copolymerization.<sup>36</sup> DPA was grafted to a methacrylate monomer, and the resulting diphenylanthracene methacrylate (DPAMA) was copolymerized with methacrylate in various ratios from 8 to 72 wt %, drop cast, and compression-molded into a thin film of around 100  $\mu$ m thickness, as depicted in Figure 10. The  $T_g$  of the polymer increased from 123 °C for pure PMMA to 150 °C for the DPAMA homopolymer. PdOEP was chosen as the sensitizer, and the concentration was kept low between 0.002 and 0.33 wt %. Green-to-blue upconversion was observed upon excitation with a HeNe laser at 543 nm at and above 32 mW cm<sup>-2</sup>, with a maximum upconversion emission intensity observed at an emitter/sensitizer ratio of 34:0.005 wt %. Notably, upconversion was only observed above the glass transition temperature (123–150 °C with increasing DPAMA content) of the material, which is impractically high for use in solar cells. This would imply that, although this is a high  $T_g$  host, TTA-UC proceeded via the diffusion mechanism usually observed in low  $T_g$  systems.

### ■ OXYGEN RESISTANCE OF THE POLYMER HOST

Unfortunately, the molecular mobility that is enhanced through use of a low  $T_g$  polymer may also facilitate oxygen diffusion. As discussed earlier, quenching of excited triplet states due to oxygen penetration is a significant problem that reduces the efficiency of TTA-UC systems under ambient conditions. Oxygen permeability is highly structure dependent, and values were not reported for most of the examples described thus far. For comparison, poly(ester)-based PUs have an oxygen permeability of  $\sim 1$ –10 Barrer<sup>90</sup> (1 Barrer =  $3.348 \times 10^{-16}$  mol m/(m<sup>2</sup> s Pa)), while for PMMA, this is 0.15 Barrer.<sup>91</sup> For poly(ester)-based PUs, there is a noted positive correlation between oxygen permeability and the molecular weight ( $M_n$ ) of the “soft” segment, derived from the diol monomer: the longer the soft segment, the higher is the permeability.<sup>90</sup> This trend is also correlated with a decrease in the  $T_g$  of the soft segment (note, not the whole polymer) with more flexible segments showing higher permeability values. The structure of the “hard” segment of the PU structure also affects permeability with increased aromatic content, and therefore, higher crystallinity decreases the permeability.<sup>90</sup> Oxygen diffusion rates in PUs follow the same trends as observed for permeability with typical rates between  $\sim 10^{-5}$  and  $10^{-7}$  cm<sup>2</sup> s<sup>-1</sup><sup>90</sup>; as expected, this is lower than that reported for PMMA ( $1.9 \times 10^{-8}$  cm<sup>2</sup> s<sup>-1</sup>).<sup>92</sup>

The oxygen permeability of alkyl acrylates also shows a dependence on chain length, ranging from 1.06 Barrer for poly(methyl acrylate) and rising sharply to 19.0 Barrer with the addition of a single methylene unit for poly(ethyl acrylate).<sup>93</sup> A less dramatic, but continuous, increase in permeability is observed as the chain length is extended up to 76.3 Barrer for poly(docosyl acrylate).<sup>93</sup> This increase in permeability is attributed to the increase in the free volume within the amorphous domains formed by the alkyl side chains in comparison to the more rigid and crystalline-favoring backbone.<sup>93</sup> The marked change in oxygen permeability as a result of sometime subtle changes in the macromolecular structure suggests that this warrants further investigation in the context of their use as TTA-UC hosts.

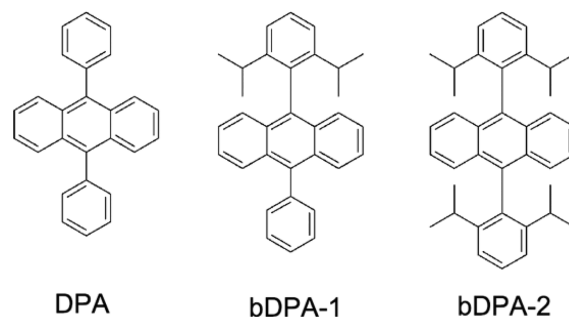
Since the diffusion length,  $L$ , is related to both the diffusion coefficient and the triplet lifetime ( $L = \sqrt{D\tau_T}$ ), it becomes



**Figure 10.** TTA-UC system design with the DPA emitter covalently grafted to the polymer host. (a) Structures of the PdOEP sensitizer, DPAMA monomer and emitter, and poly(DPAMA-co-MMA) copolymer matrix. (b) Schematic representation of thin film assembly via drop casting solution at 105 °C onto a glass slide and compression molding at 160 °C and light pressure. Reproduced with permission from ref 36. Copyright Royal Society of Chemistry 2014.

apparent that the relative magnitudes of  $D$  for the TTA lumophores versus oxygen and also the concentration of each species will determine whether the two species meet during the triplet lifetime. As discussed earlier, typical values of  $D_T$  range from  $10^{-5}$  to  $10^{-9}$  cm<sup>2</sup> s<sup>-1</sup>, depending on the medium and the TTA mechanism that operates. This range clearly overlaps with the exemplar oxygen diffusion rates given above. The concentration is therefore clearly very important. Thus, while a polymeric host with poor barrier properties may be compensated for, to some degree, by increasing the concentration of TTA-UC lumophore pairs, there will be an upper limit at which aggregation introduces further non-radiative decay pathways that decrease the TTA-UC efficiency. A more preferable approach would be to prepare the entire system under oxygen-free conditions and coat it with an oxygen-impenetrable barrier. We will now examine some examples from the literature where this strategy has been used.

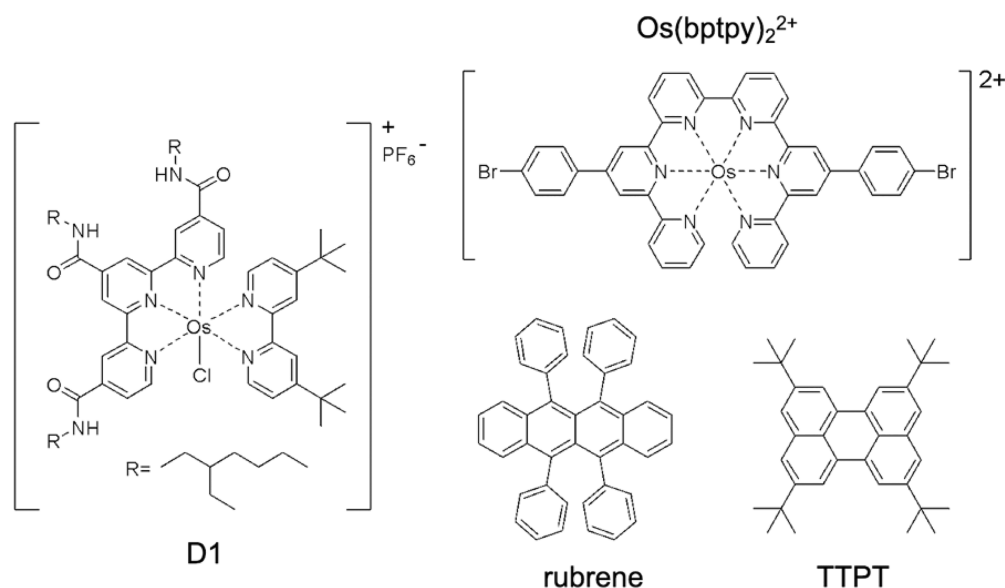
Oxygen permeability is typically lowest in polymers with high crystallinity, polarity, and density.<sup>94–96</sup> Poly(vinyl alcohol) (PVA) exhibits several of these attributes.<sup>97–100</sup> In 2020, Gao et al. reported a PVA-hosted TTA-UC system using a combination of DPA derivatives and PtOEP as the emitter/sensitizer pair (Figure 11).<sup>55</sup> TTA-UC active crystals were prepared via rapid recrystallization, whereby a THF solution of the lumophore mixture was rapidly injected into an aqueous solution of sodium dodecyl sulfate (SDS). The steric substituents reduced the recrystallization rate of bDPA-2, causing a decline in the crystallinity and improved mixing with PtOEP. Instead of obtaining crystals in the micrometer scale, as observed for DPA or bDPA-1, bDPA-2 yielded nanocrystals with a diameter less than 200 nm. The resulting TTA-UC crystals were then blended in an aqueous solution of PVA and drop-cast as thin film samples on glass slides. The bDPA-2-based PVA thin film showed a  $\Phi_{UC}$  of ~1% in comparison with ~0.3% for bDPA-1 and less than 0.1% for DPA. While these quantum yields may be considered low, it is worth



**Figure 11.** Chemical structures of DPA and the bulky substituted DPA derivatives bDPA-1 and bDPA-2. These bulky emitters were used to yield nanocrystals with a diameter of >200 nm to be mixed with sensitizer PtOEP to proceed via the aggregation mechanism of TTA-UC. Redrawn from ref 56.

considering that, in this example, the dye-hosting layer was directly exposed to the ambient atmosphere, suggesting that PVA acts as a suitably impervious oxygen barrier.

In 2016, Amemori et al. reported a NIR-to-visible TTA-UC system based on a lipophilic osmium complex (D1) as the sensitizer and rubrene as the emitter (Figure 12).<sup>56</sup> Unlike other TTA-UC sensitizers, D1 can be directly excited to a triplet excited state with a relatively strong  $S_0$ - $T_1$  absorption, which can potentially avoid the energy losses in the intersystem crossing of the conventional triplet sensitizers. PVA was again chosen as the host material to prevent triplet quenching by oxygen. To prepare film samples, both the sensitizer and the emitter were dissolved in THF and rapidly injected in an aqueous solution of SDS (10 mM) to give the TTA-UC nanoparticles (NP) with an average diameter of 220 nm. The resulting NPs were then dispersed in 15% w/w PVA and drop-cast on glass slides with the resulting thin film exhibiting a  $\Phi_{UC}$  of ~0.22% when excited at 938 nm in air. A similar approach of direct  $S_0$ - $T_1$  excitation in a PVA matrix was reported by Sasaki et al. from the same research group.<sup>57</sup>



**Figure 12.** Chemical structures of two pairs of lumophores used in TTA-UC systems: sensitizer lipophilic osmium complex D1 with the emitter rubrene and sensitizer Os(bptpy)<sub>2</sub><sup>2+</sup> with the emitter 2,5,8,11-tetra-*tert*-butylperylene (TTPT). Both pairs are able to facilitate direct S<sub>0</sub>-T<sub>1</sub> excitation in a PVA matrix, which can potentially sidestep the energy losses in the intersystem crossing step of TTA-UC. Redrawn from ref 57.

A new complex Os(bptpy)<sub>2</sub><sup>2+</sup> was paired with 2,5,8,11-tetra-*tert*-butylperylene (TTPT) as the sensitizer and emitter, respectively (Figure 12). Solid-state samples were prepared by precipitating TTPT with 5% w/w of Os(bptpy)<sub>2</sub><sup>2+</sup>, followed by mechanical grinding to improve the mixing. The resulting powder was then dispersed in aqueous SDS solution and recollected by centrifugation. The mixture was then blended with 10% w/w PVA and cast on glass substrate, giving a Φ<sub>UC</sub> of ~1.35% when excited at 724 nm in air.

Poly(urethane) was used by Hagstrom et al. to construct micropatterned flexible thin films based on TTA-UC.<sup>10</sup> Due to the thin film format of the sample, an additional barrier was required to limit oxygen diffusion with the requirement that the final system remain flexible; the team opted to sandwich the TTA-UC host (thickness of ~15 μm) between two layers of poly(vinyl acetate) as an encapsulating oxygen barrier deposited on a colorless polyethylene terephthalate substrate. The resulting UC system was a transparent flexible plastic sheet coated with TTA-UC materials, showing Φ<sub>UC</sub> of 7% at its maximum and I<sub>th</sub> at 70 mW/cm<sup>2</sup> under ambient conditions.

## ■ FUTURE DIRECTIONS

In summary, the ideal polymeric host should be able to deliver high molecular mobility to enhance the TTA-UC efficiency (for the diffusion mechanism), strong mechanical strength to allow practical device fabrication, and high O<sub>2</sub> resistance to reduce or inhibit triplet quenching and improve the life-span of resulting devices under ambient conditions. As we have seen through our review of the literature, it is clear that a compromise must be found in order to manage these competing requirements. Herein, we propose some suggestions for the future development of polymeric host materials for solid-state TTA-UC.

**Reporting of Upconversion Quantum Yields, Mechanisms, and Measurements.** It is currently not possible to unequivocally determine the optimum materials' properties (e.g., T<sub>g</sub>, chemical structure, Young's modulus) required for efficient TTA-UC based on our review of the state-of-the-art.

In many cases, upconversion quantum yields are not reported for encapsulated lumophores, and as noted earlier, the mechanism is usually not equivocally assigned. This is further complicated by the lack of consistency in terminology used to report upconversion performance, as recently highlighted.<sup>33</sup> We advocate for the reporting and measurement protocols championed in the aforementioned article. We also recommend that, for solid-state systems, such as those described here, the measured upconversion quantum yield should be reported as a bare minimum and the measurement conditions, excitation wavelength, laser power, and particularly ambient conditions (i.e., has the oxygen been removed), must be clearly stated. The fundamentals of both the energy transfer and the molecular diffusion mechanisms, including the experimental methods used to differentiate them, also warrant further investigation. Measurement and reporting of triplet diffusion constants may help to unravel the underlying mechanism.

**Balancing Molecular Diffusion, Mechanical Strength, and Oxygen Ingression.** The achievement of a suitable balance between the rate of molecular diffusion and mechanical strength is a prevailing challenge in the development of low T<sub>g</sub> polymeric host for solid-state TTA-UC systems: generally speaking, a reduction of the T<sub>g</sub> is typically accompanied by a corresponding decrease in mechanical strength and an increase in flexibility. While there is high demand for the development of materials with a good balance between rates of molecular diffusion and mechanical strength, there has to date been surprisingly little investigation into systems such as gelled or mixed-phase host systems with the handful of examples discussed earlier in this Perspective showing the potential of such systems.

A lower T<sub>g</sub> also leads to an increased molecular diffusion rate, which facilitates the required molecular collisions for the diffusion-controlled mechanism but also promotes O<sub>2</sub> ingress. The effects of O<sub>2</sub> quenching can be drastically reduced, if not effectively eliminated, by introducing antioxidant materials, such as oleic acid, into the solid-state TTA-UC systems.<sup>41</sup> One close example was reported by

Mongin et al. in 2016, where the TTA-UC lumophores were dissolved in liquid poly(ethylene glycol)-containing oleic acid as the oxygen scavenger and encapsulated inside of a plastic shell (~2 mm thickness).<sup>42</sup> However, to our knowledge, this strategy of a direct combination of oxygen scavengers with polymeric hosts has not been demonstrated yet for TTA-UC systems.

It should be possible to use recent advances made in the field of controlled radical polymerization in which active oxygen-scavenging systems have been developed to allow for air-sensitive reactions to be conducted under a standard atmospheric environment. Systems have been demonstrated for both atom transfer radical polymerization (ATRP) and reversible addition–fragmentation chain-transfer polymerization (RAFT), on the basis of in situ deoxygenation using glucose oxidase in low concentrations (2–0.2  $\mu\text{M}$ ) to deoxygenate the solutions directly, even while open to the atmosphere.<sup>101,102</sup> Such an active oxygen-scavenging system could be incorporated into hydrogel systems with little modification and conceivably offer substantial improvements in the oxygen resilience of any hosted TTA-UC system.

It should be noted that the oxygen quenching of triplet states has the detrimental consequence of reactive oxygen species such as singlet oxygen, which may degrade organic lumophores over time. Elimination of oxygen from the system through the use of either scavengers or permanent oxygen barriers would thus extend the lifetime of the system, while also allowing for the use of polymer hosts that promote the desired lumophore mobility for TTA-UC.

**Homopolymer Blends and Copolymers.** The vast majority of systems investigated to date have used only a single homopolymer as the host. While this has yielded some good results thus far, the number of suitable homopolymeric materials is limited by the need to fulfill the multiple requirements of a good host. This limited selection could potentially be vastly expanded most simply by investigating blended polymer mixtures, utilizing the complementary properties of each component (e.g., oxygen barrier behavior from polymer A and favorable mechanical behavior from polymer B) to obtain a bulk host material that is superior to any individual component.<sup>103–106</sup> While more technically involved, the use of copolymers (either random or some more complex architecture) would likely open up a wide range of possibilities, perhaps even allowing for control of lumiphore dispersal via polymer domain formation.<sup>107,108</sup>

**Organic–Inorganic Hybrid Hosts.** A potentially promising avenue of research is the use of organic–inorganic hybrid materials as solid hosts, which could offer the benefits of both organic and inorganic systems. For example, doping inorganic nanoparticles into organic polymeric hosts has been shown to help to improve the photostability of both the substrate and the TTA-UC system.<sup>27</sup> Some studies have already been conducted on TTA-UC systems using semiconducting inorganic nanoparticles that can act as a sensitizer with an organic substrate grafted to the particle acting as an emitter.<sup>27,109,110</sup> Inorganic materials usually provide more mechanical structure and an improved barrier to oxygen for the system and are often more photostable, while the presence of a grafted organic polymer maintains the processability of lightweight polymeric materials.<sup>111</sup> There are many materials that show great promise to be developed into TTA-UC host systems.<sup>112,113</sup> One such example was reported by Kim et al., who developed a quantum dot/siloxane composite film, which

is exceptionally stable against heat and moisture.<sup>113</sup> The film showed excellent dispersion of the nanocrystals and favorable mechanical properties and could be potentially used to load chromophores, which could be encapsulated in the matrix by the high degree of siloxane bond formations and cross-linked bonding. It is optically clear and resistant to the rigors of the atmosphere, making it ideal for solar applications.<sup>113</sup>

**Molecular Alignment and Positioning.** An efficient intramolecular TTA process is highly reliant on both the molecular distance (usually requiring a separation of less than 1 nm) and molecular orbital overlap. To date, most reported TTA-UC systems are under isotropic molecular orientation, which may not be the optimal condition to maximize the TTA process. By aligning the molecules in the same orientation, one could improve the TTA process and potentially enhance the TTA-UC efficiency. As previously discussed, a computational paper by Zimmermann et al.<sup>87</sup> also demonstrated the potential benefits of a clustered formation of emitters and sensitizers to improve TTA-UC efficiency.

## CONCLUSIONS

This Perspective summarizes some recent works using polymeric host materials to produce solid-state TTA-UC systems. Standard polymers, such as poly(urethane)s, poly(methyl methacrylate), and poly(vinyl acetate), have been used as the host materials of TTA-UC, allowing the fabrication of relatively efficient solid-state TTA-UC systems in an ambient atmosphere. Although some such systems have already been reported, there is still significant scope for the optimization of solid-state TTA-UC systems. The major challenge in the field is to develop such host materials that balance the need for molecular diffusion with the mechanical strength of the sample substrate, while preventing the oxygen-caused triplet quenching. Several approaches already taken to overcome these challenges, including high  $T_g$  or low  $T_g$  polymers, mixed-phase systems, lumiphore-grafted systems, and oxygen resistance systems, have been discussed. Some future research directions are also suggested in this Perspective. Novel and advanced polymeric host materials with balanced molecular diffusion and mechanical strength and excellent oxygen restriction are still under development and should lead to an increase in the incorporation of TTA-UC in systems and applications in the near future.

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### Notes

The authors declare no competing financial interest.

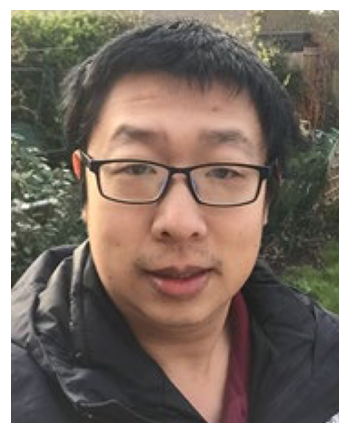
### Biographies



Michael J. Bennison received his MChem from the University of Sheffield (2009) and PhD on ring-opening polymerization from the University of Warwick (2013). He then worked with Prof. Andrew Cooper at the University of Liverpool on stimuli-responsive polymers in supercritical carbon dioxide before moving to the University of Manchester in 2018 with Dr. Samuel Jones to develop broad-spectrum antiviral polymeric materials. In 2019, Mike joined the Photoactive Materials Group at the University of Cambridge, where he is currently investigating polymeric hosts for triplet–triplet annihilation upconversion systems. Mike's broader research interests include functional materials synthesis and the use of renewable feedstocks.



Abigail R. Collins studied Chemistry at the University of St Andrews before going on to receive an MSc in Polymer Chemistry from the University of Warwick. Her dissertation, for which she received a distinction, was on self-healing hydrogels for wound therapies under the direction of Dr. Paul Wilson. Abi is currently completing her PhD at the University of Cambridge in the Photoactive Materials Group headed by Dr. Rachel Evans. Her research interests include the development and characterization of novel organic–inorganic hybrid polymers as solid-state triplet–triplet annihilation upconversion hosts for solar energy applications.



Bolong Zhang studied Chemistry at Fuzhou University and received his BSc in 2012. He obtained his MSc and PhD in Chemistry at the University of Melbourne in Dec 2019 under the direction of Dr. Wallace Wong, Dr. David Jones, and Prof. Kenneth Ghiggino. In early 2020, he joined the Photoactive Materials Group (lead by Dr. Rachel Evans) at the University of Cambridge as a postdoctoral Research Associate. Bolong has extended research experience in the design and synthesis of optically active organic materials, functional device fabrication, and spectroscopy analysis.



Rachel C. Evans is a Reader (Associate Professor) in Materials Chemistry at the University of Cambridge (UK). She obtained her MChem (2002) and PhD (2007) in Physical Chemistry from Swansea University (UK) and held an FCT research fellowship between the Universities of Coimbra and Aveiro (Portugal). From 2010 to 2017, she was an Assistant and then Associate Professor in the School of Chemistry at Trinity College Dublin (Ireland). Rachel's research is focused on the development of new photoactive materials and devices for harvesting solar and artificial light, solar–thermal energy storage, and stimuli-responsive soft matter.

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