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## Introduction

Light upconversion (UC) by triplet–triplet annihilation (TTA) employs a sensitizer-emitter pair to convert incident radiation into higher-energy photons. Unlike traditional upconversion approaches, such as second-harmonic generation, TTA-UC is unique in that upconversion can be achieved using non-coherent low-power energy sources ( $<0.1 \text{ W cm}^{-2}$ ).<sup>1–5</sup> In this process, low-energy light excites a sensitizer to its first excited singlet state, which undergoes intersystem crossing (ISC) to a triplet state and triplet–triplet energy transfer (TTET) to an emitter. Diffusion and collision of two excited emitter triplets generates a higher energy excited singlet state through TTA, from which upconverted delayed fluorescence that is higher in energy than the incident light source is emitted.

Although TTA-UC was established in the 1960s,<sup>6,7</sup> it has only been in the past decade that solid-state systems have been realized,<sup>8,9</sup> enabling practical application toward technologies such as photovoltaics,<sup>2,10–12</sup> optical data storage,<sup>13</sup> organic light-emitting diodes,<sup>14,15</sup> biological imaging,<sup>16,17</sup> and photocatalysis.<sup>18,19</sup> Polymeric host materials have been at the forefront of these advances owing to their wide range of chemical

# Thiol—ene click chemistry: a modular approach to solid-state triplet—triplet annihilation upconversion<sup>†</sup>

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The advancement of triplet-triplet annihilation based upconversion (TTA-UC) in emerging technologies necessitates the development of solid-state systems that are readily accessible and broadly applicable. Here, we demonstrate that thiol-ene click chemistry can be used as a facile cure-on-demand synthetic route to access elastomeric films capable of TTA-UC. Photopolymerization of multifunctional thiols in the presence of a thiol-functionalized 9,10-diphenylanthracene (DPA) emitter results in covalent DPA integration and homogenous crosslinked polymer networks. The palladium(II) octaethylporphyrin (PdOEP) sensitizer is subsequently introduced into the films through solution immersion. Upon excitation at 544 nm, green-to-blue upconversion is observed with compositional tuning resulting in an optimal upconverted emission intensity at 1.0 wt% DPA and 0.02 wt% PdOEP. The effectiveness of thiol-ene networks to function as robust host materials for solid-state TTA-UC is further demonstrated by improved photostability in air.

compositions, tunable mechanical properties, and ease of processing.<sup>8,20–24</sup> Examples of TTA-UC in diffusion restricted polymer matrices demonstrate that higher molecular mobility more effectively facilitates intermolecular energy transfers (TTET and TTA) and leads to greater upconversion efficiencies.<sup>24–28</sup> Excess mobility, however, results in dye leaching and phase separation resulting in nonradiative decay.<sup>29</sup> In glassy polymeric hosts, where the diffusion of dye molecules is restricted, very high emitter concentrations are required to facilitate TTET and TTA and result in aggregation and component separation.<sup>21,30</sup>

The design of solid-state systems is further complicated by the sensitivity of excited triplet states to the presence of very small amounts of molecular oxygen.<sup>31</sup> Only a few strategies have been demonstrated to address this challenge in the solidstate such as employing specific matrices to reduce the oxygen concentration,<sup>32</sup> or by incorporating oxygen scavengers.<sup>31</sup> Recently, robust TTA-UC was demonstrated in air-saturated solvent mixtures containing thioether functionalities which exhibit efficient oxygen scavenging.<sup>33</sup>

The dependence of TTA-UC on the chromophore concentration, their relative proximity, and air instability continues to hamper the realization of practically applicable solid-state systems. In this work, we demonstrate that thiol–ene click chemistry can be used as a facile cure-on-demand synthetic route to fabricate homogenous, optically transparent networks with covalently attached emitters. The sensitizer is subsequently introduced into the network *via* a simple solution immersion

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process resulting in films capable of TTA-UC. This strategy synergistically combines the favorable molecular diffusion within rubbery polymers,<sup>24–28</sup> hinders performance limiting dye aggregation,<sup>20,22,23</sup> imparts facile control over emitter and sensitizer concentrations, and affords fine-tuning of crosslink density (mechanical properties) and chemical functionality.<sup>34</sup> Lastly, a high-density of thioether linkages results in improved photostability in air enabling broad applicability.

## Experimental

#### Materials

All solvents and reagents were purchased from commercial sources and used as received. 9,10-Dibromoanthracene and 4-vinylbenzeneboronic acid were purchased from Alfa Aesar. Palladium(II) octaethylporphyrin (PdOEP) and poly(ethylene glycol)divinyl ether were obtained from Sigma-Aldrich. Pentaer-ythritol tetrakis(3-mercaptopropionate) and 3,6-dioxa-1,8-octane-dithiol were purchased from TCI, and 2,2-dimethoxy-2-phenyl-acetophenone was purchased from Acros. 9,10-Bis(4-vinylphenyl)-anthracene (1) was prepared according to literature procedures.<sup>35</sup>

#### Characterization

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Ascend 600 MHz spectrometer and chemical shifts were referenced to the residual solvent peak. Fourier transform infrared (FTIR) measurements were obtained using a Nicolet 6700 spectrometer equipped with an attenuated total reflectance (ATR) accessory. The glass transition temperatures  $(T_g)$  were measured by differential scanning calorimetry (DSC) using a TA Instruments Q200 with heating and cooling rates of 10  $^{\circ}$ C min<sup>-1</sup>.  $T_{g}$  was defined as the maximum of the first derivative plot of the first heating cycle from -80 °C. UV-vis absorption spectra were recorded using an Agilent Technologies Cary 5000 UV-vis-NIR spectrophotometer. Steady-state photoluminescence measurements were recorded using a PTI-Horiba QuantaMaster 400 spectrofluorimeter equipped with a 75 W Xe arc lamp. Quantum yields were obtained using a PTI K-Sphere "Petite" integrating sphere. Fluorescence decay profiles were recorded using a Horiba PPD-850 time-correlated single-photon counting (TCSPC) detector using a Fianium WhiteLase SC-400 laser at a repetition rate of 2 MHz.

#### Synthesis

**Compound 2.** 9,10-Bis(4-vinylphenyl)anthracene (0.500 g, 1.31 mmol), 3,6-dioxa-1,8-octanedithiol (12 mL, 65 mmol) and 2,2'-azobis(2-methylpropionitrile) (6.4 mg, 0.039 mmol) were added to a Schlenk tube, dissolved in CHCl<sub>3</sub> (20 mL), and stirred for 1 h at 60 °C. The solution was cooled to room temperature and poured into methanol (100 mL). Upon cooling to 0 °C light yellow crystals formed, which were filtered, washed with excess methanol, and dried under vacuum to afford 2 (0.55 g, 78%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.73 (4H, dd, J = 6.8, 3.3 Hz), 7.47–7.45 (8H, m), 7.36 (4H, dd, J = 6.9, 3.2 Hz), 3.78 (4H, t, J = 6.8 Hz), 3.70 (8H, m), 3.67 (4H, t, J = 6.4 Hz), 3.12 (4H, m), 3.03 (4H, m), 2.87 (4H, t, J = 6.9 Hz), 2.73

(4H, dt, J = 8.2, 6.4 Hz), 1.62 (2H, t, J = 8.2 Hz). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 139.72, 137.05, 136.90, 131.43, 129.96, 128.54, 126.99, 124.96, 72.98, 71.23, 70.38, 70.31, 36.44, 34.17, 31.83, 24.32. EA found: C, 67.35; H, 6.72. Calc. for C<sub>42</sub>H<sub>50</sub>O<sub>4</sub>S<sub>4</sub>: C, 67.50; H, 6.75%.

Thiol-ene polymer networks with DPA. When calculating the 9,10-diphenylanthracene (DPA) concentration for the various networks only the DPA core was considered and the amounts of 2 were chosen such that the resulting films contained 0, 0.25, 0.5, 1.0, 1.8, 2.5, and 5.0 wt% DPA. The following is a typical experimental procedure performed for the network containing 1.0 wt% of DPA. Dithiol 2 (39 mg, 0.052 mmol), 3,6-dioxa-1,8-octanedithiol (0.495 g, 2.72 mmol), poly(ethylene glycol) divinyl ether (0.940 g, 4.60 mmol), and pentaerythritol tetrakis(3-mercaptopropionate) (0.459 g, 0.1 mmol) (to achieve a 3:1 dithiol to tetrathiol molar ratio) were combined in a 1:1 thiol to alkene molar ratio in the presence of 1 wt% photoinitiator (2,2-dimethoxy-2-phenylacetophenone). The monomer solution was pipetted between glass slides separated by a 0.265 mm Teflon spacer and cured 14 inches away from a Cure-Tek UVA-400 lamp for 8 min. The films were subsequently soaked overnight in CHCl<sub>3</sub> solutions containing 0, 0.038, 0.075, and 0.15 mg  $mL^{-1}$  PdOEP and dried under vacuum for 24 h prior to optical characterization.

#### Preparation of films for photostability experiments

**Neat thiol-ene polymer networks.** 3,6-Dioxa-1,8-octanedithiol (0.516 g, 2.83 mmol), poly(ethylene glycol) divinyl ether (0.961 g, 4.75 mmol), and pentaerythritol tetrakis(3-mercaptopropionate) (0.461 g, 0.943 mmol) (to achieve a 3:1 dithiol to tetrathiol molar ratio) were combined in a 1:1 thiol to alkene molar ratio in the presence of 1 wt% photoinitiator (2,2-dimethoxy-2-phenylacetophenone). The monomer solution was pipetted between glass slides separated by 0.265 mm Teflon spacers and cured 14 inches away from a Cure-Tek UVA-400 lamp for 8 min.

**Oxidation of neat thiol-ene polymer network.** Thiol-ene networks were oxidized following a previously reported procedure.<sup>36,37</sup> Thiol-ene films were submerged for 24 h in 30%  $H_2O_2$  in water. The samples were immersed in neat DI water 3 times for 1 h to remove any  $H_2O_2$ . The films were dried on a hotplate at 150 °C until no mass loss was observed.

Incorporation of DPA and PdOEP into thiol–ene networks. The neat and oxidized thiol–ene networks were submerged in  $CHCl_3$  solutions containing 1.33 mg mL<sup>-1</sup> DPA and 0.075 mg mL<sup>-1</sup> PdOEP for 24 h. The films were dried under vacuum for 24 h to remove any residual solvent prior to optical characterization.

**Preparation of tecoflex films.** DPA and PdOEP containing Tecoflex films were prepared following previously reported methods.<sup>8,25</sup> To a Teflon beaker was added 2.0 g of a Tecoflex EG-80A solution (5 wt% in DMF), 2 mL DPA solution (0.5 mg mL<sup>-1</sup> in DMF), and 1 mL PdOEP solution (0.01 mg mL<sup>-1</sup> in DMF). The beaker was placed on a hotplate at 90 °C for 2 h and further dried at 90 °C under vacuum overnight.

### **Results and discussion**

In this work, solid-state TTA-UC was achieved by covalently incorporating a DPA derivative (2), along with unbound PdOEP, into elastomeric networks prepared using thiol-ene click chemistry. To prevent aggregation of the DPA units, emitters bearing two reactive thiols were synthesized allowing covalent integration within the polymer network upon curing (Fig. 1). Our synthetic approach begins with the functionalization of 1 to promote solubility in the thiol-ene monomer formulation. This was achieved through the reaction of 1 and 3,6-dioxa-1,8octanedithiol (50 equiv.) in the presence of AIBN at 60 °C in CHCl<sub>3</sub> to give 2 in 78% yield. The absorption and emission spectra of PdOEP and 2 are shown in Fig. 2. PdOEP has two regions of absorption, a high-energy Soret band centered at 393 nm and lower-energy metal-to-ligand charge transfer (MLCT) bands at 512 and 546 nm. Upconversion occurs when the MLCT band of PdOEP is excited and blue emission from the DPA is observed. The characteristic absorption fingerprint and strong blue emission of 2 are similar to unmodified DPA (Fig. S5, ESI<sup>†</sup>), indicating that the solubilizing groups do not interfere with the optical properties of the DPA core and 2 can act as an efficient emitter when paired with PdOEP.

The method by which the thiol–ene films were prepared is shown in Fig. 1. The thiol–ene monomer mixture containing 2 was cured *via* photopolymerization under ambient conditions using a Cure-Tek UVA-400 lamp. The thiol–ene resin and solid networks were analyzed using ATR-FTIR to determine the degree of conversion. Prior to irradiation, the ==C-H and -S-H stretches were detected between 3130–3100 cm<sup>-1</sup> and 2675–2500 cm<sup>-1</sup>, respectively as shown in Fig. 3a. After curing, the peaks disappear indicating the thiol–ene reaction achieved full conversion. The resulting films were optically clear, flexible, and exhibited  $T_g$  values at  $-53 \pm 1$  °C as measured by DSC (Fig. 3b and c).

UV-vis spectroscopy was used to quantitatively determine the DPA concentrations in the thiol–ene networks. For samples with greater than 0.5 wt% DPA, the film thickness in combination with the large extinction coefficient of DPA resulted in absorbances that were too high for quantitative measurement. Analysis of the 0.25 wt% DPA film was in excellent agreement



Fig. 2 Normalized absorption (solid lines) and photoluminescence spectra (dashed lines) of PdOEP and 2 in  $CHCl_3$  solutions. The photoluminescence from PdOEP and 2 were collected using excitation wavelengths of 393 and 375 nm, respectively.

with theoretical values (see ESI<sup>†</sup> for full details). To confirm covalent attachment of 2 into the polymer network, dye leaching experiments were performed<sup>23</sup> demonstrating >95% incorporation for all samples (see ESI<sup>†</sup> for full details). The results from both the leaching experiments and UV-vis indicate that concentration values used in the synthetic preparation accurately reflect the emitter concentrations in the films.

Once the DPA-bearing films were prepared and characterized, the sensitizer was incorporated into the thiol–ene films by overnight immersion into  $CHCl_3$  solutions of PdOEP. The films were subsequently dried under vacuum for 24 h to remove any residual solvent and analyzed by UV-vis to determine quantitative PdOEP concentrations (Fig. S8, ESI†). Soaking the films in solutions with PdOEP concentrations of 0.038, 0.075, and 0.15 mg mL<sup>-1</sup> repeatedly resulted in 0.005, 0.01, and 0.02 wt% PdOEP in the polymer network, respectively (Table S2, ESI†). A linear trend



Fig. 1 Synthesis of 2 and schematic representation of the process employed to produce thiol-ene networks. Thiol-ene monomers, photoinitiator and 2 were mixed, and cured under a Cure-Tek UVA-400 lamp for 8 min. The crosslinked networks were subsequently submerged in PdOEP CHCl<sub>3</sub> solutions to incorporate the sensitizer.



**Fig. 3** (a) ATR-FTIR spectra of thiol-ene monomer mixture before (solid lines) and after (dotted lines) UV-curing. The areas around the =C-H (blue) and -S-H (orange) stretches are highlighted. (b) Picture of a cured thiol-ene film to show the film flexibility and optical clarity. (c) DSC thermograph of thiol-ene films using a 10 °C min<sup>-1</sup> heating rate.

between the solution concentration and wt% PdOEP in the thiol-ene films demonstrates that sensitizer concentration can be controlled (Fig. S10, ESI<sup>†</sup>).

#### Optical characterization of films

Normalized direct fluorescence spectra of thiol–ene films prior to PdOEP incorporation are shown in Fig. 4. As the DPA concentration is increased, the maximum fluorescence wavelength shifts from 439 to 448 nm. The decrease in emission at the blue edge can be attributed to reabsorption,<sup>38</sup> whereas, the increase in lower energy emission most pronounced in the 5.0 wt% DPA sample is commonly attributed to the formation of excimer states.<sup>39,40</sup> Direct fluorescence measurements of PdOEP-doped films were also conducted (Fig. S11, ESI†), and negative peaks centered around 515 and 546 nm appear, consistent with reabsorption from PdOEP.

As shown in Fig. 5b, upon irradiating the PdOEP-doped thiolene films with green light (532 nm), blue emission (440 nm) can clearly be observed without the use of a 500 nm short-pass filter. Upconversion performance was analyzed *via* steady-state photoluminescence spectroscopy using a 544 nm excitation wavelength



Fig. 4 Normalized direct fluorescence spectra of thiol-ene films prior to doping with PdOEP ( $\lambda_{ex}$  = 375 nm).

to selectively excite the MLCT band of PdOEP. As an example, the photoluminescence spectra from the films comprised of 1.0 wt% DPA are shown in Fig. 5a (see Fig. S12 and S13 for a complete set of spectra, ESI<sup>†</sup>). Areas under the upconverted emission from DPA (400–520 nm) and phosphorescence from PdOEP (630–800 nm) are plotted in Fig. 5c and d for all samples.

The overall upconversion quantum efficiency is determined by the efficiencies of ISC of the photosensitizer (which can be assumed to equal 1),<sup>24</sup> TTET from the sensitizer to emitter, TTA between two emitters, and fluorescence quantum yield ( $\Phi_{\rm Fl}$ ) of the emitter.<sup>3,41</sup> As DPA concentration is increased the phosphorescence diminishes indicating the TTET from PdOEP to DPA becomes more efficient with maximum upconverted emission intensity observed at 1.0 wt% DPA (Fig. 5c and Fig. S12, ESI†). To rationalize the decrease in emission intensity above this point, the  $\Phi_{\rm Fl}$  of the thiol–ene films without sensitizer were measured using an integrating sphere. When progressing from 0.25 to 5.0 wt% DPA the  $\Phi_{\rm Fl}$  decreases from 68 to 56% (Fig. 5), which falls within the same reported range for similar systems and can be attributed to self-quenching effects.<sup>30</sup>

To further investigate these results and the effect of PdOEP, the direct fluorescence decay behavior of DPA was examined using TCSPC. Upon excitation at 400 nm, the time resolved emission at 425 nm was recorded. As shown in Fig. 6b, films without PdOEP exhibit a linear decrease in fluorescence lifetime which further supports the self-quenching effects observed in the  $\Phi_{\rm Fl}$  data. When PdOEP is present, fluorescence lifetimes shorten, signifying back energy transfer from DPA to PdOEP.<sup>42</sup> Interestingly, the fluorescence decay lengthens from 0.25 to 1.0 wt% DPA. This result may be due to the overlap area, between the PdOEP Soret band and DPA emission, decreasing as the emission red shifts upon increasing emitter concentration. This result demonstrates that spectral overlap between sensitizer absorption and emitter fluorescence is an important factor in governing the performance of TTA-UC systems.<sup>43,44</sup>

Fabricating upconverting materials via thiol-ene click chemistry is advantageous because the thioether linkages formed upon curing can act as oxygen scavengers to improve photostability.<sup>33</sup> To investigate this, the upconversion photostability of thiol-ene networks with thioether linkages was compared to thiol-ene films where the thioether groups were oxidized to sulfone groups. For these samples, thiol-ene films (without covalently tethered DPA) were synthesized and the DPA and PdOEP were infused into the network through solution immersion (1.0 wt% DPA and 0.01 wt% PdOEP). Thioether groups were oxidized prior to doping with PdOEP and DPA using a hydrogen peroxide solution according to previously reported procedures.<sup>36,37</sup> As a secondary comparison, DPA and PdOEP doped Tecoflex films, a well-studied aliphatic polyether-based thermoplastic polyurethane host material for TTA-UC, were also prepared according to previously reported methods.8 Fig. 7 shows the upconverted emission intensity at 440 nm measured under continuous irradiation at 532 nm in ambient conditions. The thiol-ene films with thioether functionality exhibit considerably better photostability compared to the thiol-ene networks with sulfone functionality and Tecoflex films, potentially indicating

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**Fig. 5** (a) Photoluminescence emission from PdOEP doped thiol-ene networks comprised of 1.0 wt% DPA showing the upconverted emission (400–520 nm) from DPA and phosphorescence from PdOEP (630–800 nm) ( $\lambda_{ex}$  = 544 nm). A break from 520 to 630 nm is present to exclude the excitation peak for clarity. (b) Picture of upconverting thiol-ene film upon irradiation with 532 nm laser in natural room light without aid from a shortpass filter. Integrated upconverted emission (c) and phosphorescence (d) intensities from thiol-ene films with various PdOEP concentrations as a function of DPA concentration.



**Fig. 6** (a) Direct fluorescence quantum yield of thiol-ene films prior to PdOEP addition as a function of DPA concentration ( $\lambda_{ex}$  = 375 nm). (b) Direct fluorescent lifetimes of thiol-ene films with various PdOEP concentrations as a function of DPA concentration ( $\lambda_{ex}$  = 400 nm,  $\lambda_{ex}$  = 425 nm).

that the thioether linkages scavenge molecular oxygen and can aid in long term upconversion performance.

## Conclusions

In summary, thiol-ene click chemistry was successfully used to create robust materials for solid-state TTA-UC. Functionalized DPA chromophores with pendant thiols allowed for near quantitative covalent incorporation into homogeneous, elastomeric polymer networks. This synthetic strategy resulted in



**Fig. 7** Normalized upconverted emission intensity from samples comprised of 1.0 wt% DPA and 0.01 wt% PdOEP under constant irradiation with a 10 mW 532 nm laser. Each plot corresponds to a different host material: thiol-ene network with thioether functionality (blue), thiol-ene network and sulfone groups (black), and Tecoflex (red).

optically transparent films using a quick solventless photopolymerization method. Upon addition of a PdOEP sensitizer, green-to-blue upconversion was observed with optimal upconverted emission intensity detected at 1.0 wt% DPA and 0.02 wt% PdOEP. Lastly, by using thiol–ene click chemistry, a high concentration of thioether linkages were present in the material resulting in increased photostability. These results provide a clear demonstration of the versatility of the thiol–ene approach toward creating upconverting polymers.

# Conflicts of interest

There are no conflicts to declare.

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