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# High Efficiency Low-Power Upconverting Soft Materials

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Supporting Information

**KEYWORDS:** photon upconversion, triplet—triplet annihilation, triplet fusion, soft materials, photonic materials

Tpconversion (UC), a process that can convert two or more photons with low energy to a single photon of higher energy, has the potential for overcoming the thermodynamic efficiency limits of sunlight-powered devices and processes, including photovoltaic cells, photocatalytic reactions, and photoelectrosynthetic processes. The UC phenomenon not only is traditionally synonymous with second-harmonic generation (SHG) using nonlinear inorganic crystals<sup>2</sup> and the sequential excitation of inorganic host materials doped with rare-earth metals<sup>3</sup> but also includes sensitized UC relying on the fusion of two energized triplet molecules.<sup>4</sup> This latter technology exhibits several distinctive features making it directly amenable for sunlight powering, 1,4 which can be accomplished at much higher efficiencies with noncoherent continuous-wave excitation at extremely low power densities (<1 mW cm<sup>-2</sup>). In this process, the photon energy absorbed by a sensitizer is transferred to an acceptor through triplet-triplet energy transfer, and two excited acceptor molecules undergo annihilation, producing (upconverted) singlet fluorescence. Although sensitized UC was first reported in the early 1960s,<sup>5</sup> this phenomenon was only sparingly investigated over the decades that followed. However, since 2003/2004, this field has experienced a resurgence by the recognition that long-lived metal-containing triplet sensitizers enable (near) quantitative yields of acceptor triplets immediately postured for fusion-producing singlet fluorescence. 4,6-8

To date, the majority of sensitized UC studies have been carried out in deoxygenated solution at rt, yet it remains highly desirable that appropriate sensitizer/acceptor molecules are embedded in suitable solid materials for potential device integration. Since our original report describing green-to-blue UC in a rubbery polymer film using palladium(II) octaethylporphyrin (PdOEP) and 9,10-diphenylanthracene (DPA) as sensitizer and acceptor/annihilator molecules, respectively,5 several groups have reported UC pairs embedded into various polymeric host matrices including polyurethane, <sup>10</sup> polyethylene glycol, <sup>11</sup> poly(methylmethacrylate), <sup>12</sup> and cellulose acetate. <sup>13</sup> It is important to note that the polymer matrix itself can be used as a direct participant in the UC reaction. 6,14 However, the isolated materials were fabricated by either dissolving or soaking the preformed polymeric host structure into an organic medium containing the UC pair followed by solvent removal. These procedures are limiting due to the obvious difficulties in achieving precisely doped, systematically variable materials in addition to the severe restrictions imposed on the dimensions and shapes of the materials that are ultimately fabricated. This year, Monguzzi et al. demonstrated that polystyrene upconverting nanoparticles formed via photopolymerization produced record solid-state upconversion efficiencies of 3.0 and 3.7%. 15

Here we present a facile fabrication technique for producing upconverting polymers that are easily molded into a variety of forms under ambient conditions with minimal processing using commercially available polyurethane precursors (Clear Flex 50, CLRFLX). In combination with the benchmark green-to-blue UC pair (PdOEP/DPA) dissolved in THF, the polymerization reaction readily proceeds under ambient conditions producing free-standing transparent rubbery solids that exhibit high flexibility (low  $T_g$ )<sup>16</sup> and good mechanical properties. To the best of our knowledge, this is the first report describing moldable upconverting polymers that can be precisely doped, enabling complete control over the resulting photonics. These combined attributes resulted in upconverting transparent materials exhibiting linear incident power dependence with record quantum efficiencies exceeding 20%.

Figures S1-S3 present the chemical structures of PdOEP and DPA along with their normalized absorption and emission spectra, when combined as a UC composition in THF, in addition to the relevant energetics of the associated UC process. Since CLRFLX can be precisely doped with both chromophores, we quantified the triplet-triplet quenching reaction kinetics using the dynamic Stern-Volmer relation with average lifetimes calculated from biexponential fits of the phosphorescence decay of PdOEP at 650 nm (Figure S4 and Table S1). The average  $\tau_0$  of PdOEP phosphorescence in CLRFLX was 1.29 ms, similar to that determined in other rigid media including polystyrene nanoparticles (0.99 ms), <sup>17</sup> PMMA (1.53 ms), <sup>18</sup> and cellulose acetate (1.2 ms) <sup>19</sup> but much longer than that for precast polyurethane matrices (314  $\mu$ s). This result implies that CLRFLX effectively diminishes <sup>3</sup>PdOEP\* deactivation by dioxygen, rendering it more susceptible to energy transfer quenching by DPA. The  $K_{SV}$  of 1762  $M^{-1}$ (Figure S5) corresponds to a bimolecular quenching constant,  $k_{\rm q}$ , of 1.37  $\times$  10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup>, 2 to 3 orders of magnitude smaller than the corresponding values reported in toluene, <sup>20</sup> indicating

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that the polymeric host material greatly restricts chromophore diffusion that is essential for both energy transfer and TTA. Despite the restricted mobility in comparison to the liquid phase, DPA concentrations necessary to achieve nearly quantitative quenching of PdOEP ( $\tau_0/\tau > 10$ ) are easily realized. Time-resolved emission spectra of these films illustrates that the upconverted <sup>1</sup>DPA\* fluorescence intensity systematically increases and the PdOEP phosphorescence decays faster as a function of DPA concentration, Figure S6, consistent with consecutive bimolecular reactions taking place in the polymer film, i.e. triplet sensitization followed by TTA.

In general, upconverted light intensity induced through sensitized TTA possesses a quadratic dependency to incident light power (i.e., slope in a log-log plot = 2) as sensitized UC is based on two-sequential one-photon absorptions followed by TTA.4 However, it has been recently shown that this observation results when experiments are performed in the weak-annihilation kinetic limit and most of the sensitized triplets decay prior to fusion.<sup>8,21</sup> Fortunately, strategies have been formulated leading to the strong annihilation (saturation) regime where the upconversion efficiency is maximized, indicated by the onset of linear incident power dependence. 8,21 Linearization occurs when the sensitized <sup>3</sup>DPA\* population decays almost exclusively through TTA at rates exceeding those typically controlling triplet state decay, i.e. first-order and pseudo-first-order quenching processes.<sup>21</sup> Consequently, identification of this crossover point is crucial for achieving the highest possible efficiency upconversion photonic materials. Figure 1a presents the double logarithm plot for the static intensity of the singlet fluorescence emanating from DPA at 430 nm  $\pm$  6 nm in a representative CLRFLX film measured as a function of incident light power density when PdOEP was selectively excited using the 514.5 nm line from an Ar+ laser. These results provide the first experimental evidence for incident light power dependence ranging from quadratic to linear in a polymer host material. It is noteworthy that the upconversion onset was observed under ultralow excitation conditions (0.22 mW cm<sup>-2</sup>) and that the crossover threshold was achieved at a relatively low light fluence ( $\sim$ 20 mW cm<sup>-2</sup>).

We subsequently quantified the UC efficiency in this material in the strong annihilation regime for this UC pair. We initially selected two distinct power densities at 514.5 nm (202 and 245 mW cm<sup>-2</sup>) and evaluated the UC quantum yields using relative actinometry in five distinct films against four different emission standards (CLRFLX films doped with only PdOEP) whose phosphorescence quantum yields ( $\Phi = 0.338 \pm 0.002$ ) were determined using a commercially available absolute system from Hamamatsu (see Supporting Information for complete details). We assumed that the PdOEP in CLRFLX quantum efficiency under laser excitation was identical to that determined from the absolute efficiency measurements. Based on 60 total experiments performed at each excitation power, we generated extremely reliable upconversion efficiencies of 0.207  $\pm$  0.005 and 0.208  $\pm$  0.005, respectively, as compared to 0.34 in vacuum degassed toluene. <sup>20</sup> As anticipated, both sets of data conspire to yield precisely the same quantum yield within experimental error, consistent with sensitized UC behavior occurring in the strong annihilation limit.<sup>8,21</sup> It is noteworthy that the current UC efficiencies exceed the current champion polymer host by a factor of 6–7, 15 exemplifying the notion that rubbery materials intended to function at rt are ideal hosts for supporting sensitized triplet fusion. With such convincing statistics, UC yields in a single film were measured as a function

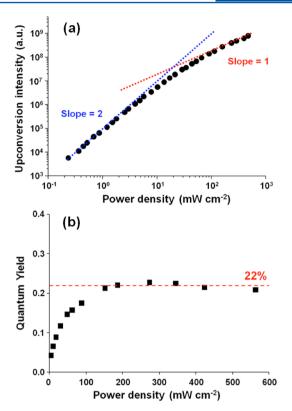
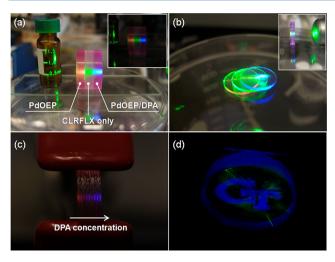


Figure 1. (a) Upconversion emission signal at  $430 \pm 6$  nm and (b) quantum yield measured as a function of 514.5 nm incident power in the PdOEP/DPA/CLRFLX blend film. [PdOEP]: 0.5 mM, [DPA]: 13.4 mM. The dashed lines in (a) are the linear fits with slopes of 1.0 (red, linear response) and 2.0 (blue, quadratic response) in the high and low power regimes, respectively. (b) Upconversion quantum yields in the same PdOEP/DPA/CLRFLX blend films measured as a function of incident light power density. The dashed red line in (b) indicates a 22% quantum yield obtained in the strong annihilation regime at the 6 highest incident powers.

of 514.5 nm power density, as shown in Figure 1b. The UC yields continuously increase until the strong annihilation limit was reached in this particular sample ( $\sim$ 100 mW cm $^{-2}$ ) at which time the quantum efficiencies level out to a constant value of 22%. Similar power-dependent quantum efficiency trends are established for several UC compositions in solution. We note that precast blank CLRFLX materials can also be impregnated with PdOEP and DPA; however, the final materials produce only a fraction of the UC quantum efficiency achieved in Figure 1b.

Figure 2a and b display photographs of RGB light emission from the CLRFLX samples (embedded with silica microparticles to promote facile light scattering) excited using a commercial green laser pointer ( $\lambda_{\rm ex}=532$  nm). By simply changing the composition of the chromophore in the polymer host (PdOEP only, blank, or PdOEP/DPA), a discrete and intense red, green, and blue color was observed by the unassisted eye. We were able to successfully tune the emission color from blue-to-purple-to-red by simply changing the DPA dosage as shown in Figure 2c. Finally, we can form this polymer into any desired shape by curing it in an appropriate mold (Figures 2d and S7). These combined attributes represent appealing traits necessary to realize facile device integration.

In summary, moldable upconverting polymers were fabricated in a straightforward manner resulting in the observation of linear incident light power dependence while Chemistry of Materials Communication



**Figure 2.** Photographs of the prepared polymer samples irradiated by a green laser pointer,  $\lambda_{\rm ex}=532$  nm (<10 mW incident power). RGB light emission from the (a) polymer disk and (b) the polymer film (thickness: ca. 100 mm). (c) Gradual change in light emission from blue to purple to red in the stacked polymer films containing different concentrations of DPA. (d) Blue light emission of the PdOEP/DPA blend polymer shaped as 'GT' imaged from expanded 514.5 nm Ar<sup>+</sup> laser output in concert with a 500 nm short-pass filter to minimize scattered excitation photons. In (a) and (b), hydrophobic silica particles were dispersed in the polymer mixture during the preparation step to facilitate scattering of green light.

achieving unprecedented solid-state quantum efficiencies exceeding 20%. We believe that the CLRFLX medium presently embodies the characteristics most suitable for achieving regenerative sensitized UC photochemistry in shapeable polymeric hosts and can readily accommodate a variety of nonpolar sensitizer-acceptor/annihilator compositions. These materials appear readily poised for photovoltaic device integration intended for the capture and conversion of sub-bandgap solar photons.

## ASSOCIATED CONTENT

#### Supporting Information

Details regarding sample preparation, spectroscopic measurements, and upconversion quantum yields. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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