Nanodroplet-Containing Polymers for Efficient Low-Power Light Upconversion

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Sensitized triplet–triplet-annihilation-based photon upconversion (TTA-UC) permits the conversion of light into radiation of higher energy and involves a sequence of photophysical processes between two dyes. In contrast to other upconversion schemes, TTA-UC allows the frequency shifting of low-intensity light, which makes it particularly suitable for solar-energy harvesting technologies. High upconversion yields can be observed for low viscosity solutions of dyes; but, in solid materials, which are better suited for integration in devices, the process is usually less efficient. Here, it is shown that this problem can be solved by using transparent nanodroplet-containing polymers that consist of a continuous polymer matrix and a dispersed liquid phase containing the upconverting dyes. These materials can be accessed by a simple one-step procedure that involves the free-radical polymerization of a microemulsion of hydrophilic monomers, a lipophilic solvent, the upconverting dyes, and a surfactant. Several glassy and rubbery materials are explored and a range of dyes that enable TTA-UC in different spectral regions are utilized. The materials display upconversion efficiencies of up to $\approx 15\%$, approaching the performance of optimized oxygen-free reference solutions. The data suggest that the matrix not only serves as mechanically coherent carrier for the upconverting liquid phase, but also provides good protection from atmospheric oxygen.

Triplets–triplets–annihilation (TTA) permits the conversion of light into radiation of higher energy and involves a sequence of photophysical processes between two dyes. In contrast to other upconversion schemes, TTA-UC allows the frequency shifting of low-intensity light, which makes it particularly suitable for solar-energy harvesting technologies. High upconversion yields can be observed for low viscosity solutions of dyes, but in solid materials, which are better suited for integration in devices, the process is usually less efficient. Here, we show that this problem can be solved by using transparent nanodroplet-containing polymers that consist of a continuous polymer matrix and a dispersed liquid phase containing the upconverting dyes. These materials can be accessed by a simple one-step procedure that involves the free-radical polymerization of a microemulsion of hydrophilic monomers, a lipophilic solvent, the upconverting dyes, and a surfactant. Several glassy and rubbery materials are explored and a range of dyes that enable TTA-UC in different spectral regions are utilized. The materials display upconversion efficiencies of up to $\approx 15\%$, approaching the performance of optimized oxygen-free reference solutions. Since oxygen is known to interfere with the TTA-UC process, the data suggest that the matrix not only serves as mechanically coherent carrier for the upconverting liquid phase, but also provides good protection from atmospheric oxygen.

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significant translational mobility and the collisional probability is high. However, the use of liquids (solutions or emulsions) complicates the fabrication of technologically useful devices. To enable TTA-UC in solid materials, UC dyes were included in rubbery polymers and polymer-based or supramolecular gels. Efficient TTA-UC has indeed been demonstrated in gels, but as their composition is dominated by a solvent, these materials suffer from the same limitations as solutions. Alternatively, the emitter can be incorporated in high concentration, for example, in organic or polymeric glasses. In this case, no molecular motion is needed, as excitons can migrate between nearby chromophores before they eventually annihilate. This sequence is particularly efficient in ordered chromophore arrays. Nevertheless, the highest TTA-UC efficiency reported for rigid materials (<5%) is much lower than that of solutions containing the same chromophores. Upconversion efficiencies of >15% have been reported for several dye systems in deaerated organic solvents (e.g., 9,10-diphenylanthracene (DPA)/palladium(II) octaethylporphyrin (PdOEP): 18% in toluene, PdOEP/platinum(II) octaetylporphyrin (PtOEP): >23% in ethanol or tetrahydrofuran (THF), perylene/palladium(II)-meso-tetraphenyl tetra-benzoporphine (PdTPBP): 38% in tetrahydrofuran), whereas microemulsions (e.g., 9,10-dinaphthylanthracene/palladium(II) tetratolylporphyrin: 16%, oil-in-water) have been proposed for efficient upconversion under ambient conditions. Suspensions of nanoparticulate or encapsulated systems and some organic solutions display good but usually lower TTA-UC efficiencies when operated under ambient conditions.

Solid polymers containing the TTA-UC sensitizer/emitter pair in a dispersed liquid phase could merge the efficient upconversion properties of solutions with the features offered by solid matrices. Initial embodiments of this general idea involved multistep encapsulation procedures or afforded opaque materials with limited mechanical properties. These obstacles can be overcome by fabricating nanodroplet-containing polymers that consist of a polymer matrix and a dispersed liquid phase, in which the upconverting dyes are dissolved (Figure 2a). Such materials can be accessed by a simple one-step process that was inspired by protocols used to create polymerizable lyotropic liquid-crystalline (LC) assemblies and polymerization-induced phase separation techniques. The former requires LC building blocks and typically afford gels, while the latter uses macromonomers to achieve nano-phase separation. By contrast, the nanodroplet-containing polymers introduced here can be made by polymerization of microemulsions of hydrophilic monomers, a lipophilic solvent, and a surfactant.

A first series of nanodroplet-containing polymers with a cross-linked glassy polymer matrix was prepared under ambient conditions by the redox-initiated free-radical polymerization of a mixture of the hydrophilic monomers 2-hydroxyethyl methacrylate (HEMA), methacrylic acid (MAA), and triethylene glycol dimethacrylate (TEG-diMA, cross-linker), a small amount of the lipophilic, low-volatility liquid 1-tert-butyl-3,5-dimethyl benzene (BMB), and the surfactant cetyltrimethylammonium bromide (CTAB, Figure 2c). The mixture also contained ethylene glycol as refractive-index modifier and plasticizer for the polymer matrix, and the well-known TTA-UC sensitizer/emitter pair PdOEP (2 × 10^{-5} m) and DPA (1.5 × 10^{-2} m) (Figure 1). The reaction afforded a rigid, tough material that was almost colorless if the dyes were omitted (Figure 2b; Figure S1 and Movie S1, Supporting Information). The dye-free nanodroplet-containing glassy polymer shows a transmittance of >75% over a path of 1 cm in the entire visible regime, which confirms that the matching of the refractive indices of the amorphous
matrix and the dispersed liquid phase allows suppressing interfacial scattering effects (Figure S2, Supporting Information). Scanning electron microscopy (SEM) images of the dye-free (Figure 2d) and dye-containing materials (Figure S3a, Supporting Information) reveal similar nanophase-separated structures. The images show clearly that the continuous polymer phase contains the solvent (BMB) in the forms of nanodroplets that have feature dimensions of \( \approx 20–100 \) nm and occasionally appear to merge into elongated channels. The absence of phase segregation observed in a reference material prepared without the surfactant (Figure S3b, Supporting Information) and the differences in the small-angle X-ray scattering data (Figure S4, Supporting Information) indicate that the surfactant is essential for the formation of the liquid nanodroplets even though no detailed structural information could be extracted from the latter measurement. The differential scanning calorimetry (DSC) trace displays only one glass transition at \( \approx 48–52 \) °C (Figure S5, Supporting Information), which is consistent with the formation of an amorphous, ethylene-glycol-plasticized poly(HEMA-co-MAA-co-TEG-diMA) copolymer.

On account of their nonpolar nature, the upconverting dyes were expected to preferably reside in the hydrophobic liquid nanodroplets (accounting for 10–15 wt% of the material) and exhibit solution-like TTA-UC. To test this hypothesis, the optical properties of dye-doped nanodroplet-containing polymer glasses were studied by means of continuous wave and time-resolved optical spectroscopy, employing BMB solutions of the dyes as reference system. The absorption and steady-state photoluminescence (PL) spectra of samples containing either PdOEP or DPA, or the DPA/PdOEP mixture match the spectra of corresponding solutions well (Figure 3a and Figure S6, Supporting Information),\(^{[17]}\) demonstrating that the inclusion process did not affect the electronic properties of the chromophores. The dynamics of the characteristic blue DPA fluorescence at 431 nm and red PdOEP phosphorescence at 666 nm were studied using time-resolved PL spectroscopy and provided insights about the location of the dyes. The time-resolved intensity decay of the blue DPA emission shows a biexponential behavior in nanodroplet-containing polymers comprising either both dyes or DPA only (Figure 3b). This suggests the coexistence of two subpopulations of emitters having characteristic PL lifetimes of \( \approx 6 \) and \( \approx 14 \) ns, respectively. The faster lifetime is similar to the one observed for a DPA solution in BMB (7.2 ns, Figure 3b), whereas the longer decay appears to be associated with aggregated DPA molecules embedded in the rigid matrix. The relative contributions of the two decay components obtained from biexponential fits of the data indicate that \( \approx 35\% \) of the emitter molecules reside in the liquid phase. Their majority appears to be included in the solid matrix, where they neither contribute to nor hamper the TTA-UC process because the sensitizer molecules appear to reside predominantly in the liquid phase (vide infra).

Upon irradiation with green laser light at 543 nm (275 mW cm\(^{-2}\)), the DPA/PdOEP doped nanodroplet-containing polymer displayed, even under ambient conditions, bright blue emission (Figure 3c, left), while the reference materials

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**Figure 2.** Nanodroplet-containing polymers. a) Rendering of the materials morphology. b) Chemical structures of the constituents forming the glassy polymer, the surfactant, and the liquid phase. c) Photograph and d) scanning electron microscopy images of a dye-free nanodroplet-containing glassy polymer. The SEM images reveal a continuous polymer phase featuring partially interconnected pores with typical diameter of \( \approx 20–100 \) nm; the inset is a magnification of a portion of the SEM image.
containing either PdOEP or DPA only displayed red phosphorescence or scattered green light, respectively (Figure 3c, right). While dominated by the upconverted blue emission, the PL spectrum of the DPA/PdOEP-containing material shows a weak emission band at 666 nm (Figure 3d), which is associated with residual PdOEP phosphorescence and suggests that the sensitizer–emitter TTET is not quantitative. Time-resolved phosphorescence experiments revealed a single exponential decay with a lifetime $\tau_{\text{ph}} = 1.50$ ms, which is much higher than the value of 20 $\mu$s observed in the degassed BMB solution, but comparable to the radiative decay of PdOEP.\(^{[48]}\) Thus, these findings suggest that the weak red luminescence belongs to a small portion of the sensitizer that is embedded in the polymer phase, where it is well protected from oxygen and solvent quenching (Figure S7, Supporting Information).\(^{[3]}\) No fast emission component could be detected, which indicates that for the sensitizer molecules incorporated in the liquid phase, the TTET yield is 100% and that emitter-to-sensitizers back energy transfer is negligible.\(^{[3]}\)

The same excitation conditions were used to acquire the upconversion emission spectra of degassed and non-degassed DPA/PdOEP reference solutions in BMB (Figure 3d). The non-degassed solution showed neither up- nor downconverted emission at 543 nm laser excitation at 543 nm (PdOEP, DPA/PdOEP). b) Decay dynamics of the blue PL at 435 nm detected in the dye-doped polymer and in a reference solution of DPA ($10^{-2}$ M) in BMB under pulsed laser excitation at 340 nm. In the polymer, the PL decays in a double exponential manner with a fast and a slow component. In solution, the PL decays according to a single exponential function. c) Pictures of the DPA/PdOEP doped polymer under 543 nm laser excitation in the dark (1) and under ambient light (2) showing bright blue upconverted emission. In a polymer that was only doped with PdOEP (3), red PL is observed through a 600 nm long-pass filter, while no PL is observed if only DPA is present (4). d) PL spectra of the DPA/PdOEP doped polymer (solid line) as well as degassed (dotted line) and non-degassed (dashed line) BMB solutions containing the same concentration of dyes ($1.5 \times 10^{-2}$ M$/2 \times 10^{-5}$ M). The laser stray light has been removed for clarity. The inset shows the decay of the upconverted emission from the polymer at 435 nm under modulated 532 nm excitation (30 mW cm$^{-2}$). The red and the blue solid lines show fits of data with the analytical functions used to describe the decay dynamic at high and low densities of triplet exciton, respectively. e) TTA-UC quantum yield ($\Phi_{\text{UC}}$) of the DPA/PdOEP doped nanodroplet-containing polymer (triangles) and a standard system in solution (dots) as a function of the excitation intensity. The vertical line marks the excitation intensity threshold $I_{\text{th}}$, where $\Phi_{\text{UC}}$ is half of its maximum value.

Figure 3. Optical properties of dye-doped nanodroplet-containing glassy polymers. a) Normalized absorption (black lines) and photoluminescence (PL) spectra of nanodroplet-containing glassy polymers doped with DPA ($10^{-5}$ M), PdOEP ($10^{-5}$ M), or DPA/PdOEP ($1.5 \times 10^{-5}$ M$/2 \times 10^{-5}$ M) excited at 375 nm (DPA) or under continuous wave laser excitation at 543 nm (PdOEP, DPA/PdOEP).
emission, whereas the degassed solution emits bright upconverted blue light, indicating triplet quenching by molecular oxygen in the former.\textsuperscript{[11]} The PL spectrum of the DPA/PdOEP nanodroplet-containing polymer mirrors the features observed for the degassed solution, and the upconverted emission intensities of the two samples are comparable, although the polymer had been prepared under ambient conditions. This material retained \textasciitilde 50\% of its initial upconversion efficiency after storage for six weeks or after 13.5 h of continuous operation under 10 mW cm\textsuperscript{-2} irradiation at 543 nm (Figures S8–S10, Supporting Information). A comparison of plots of the upconverted emission intensity versus time (Figures S9 and S10, Supporting Information) recorded for polymers prepared under ambient conditions and inert atmosphere, respectively, suggests that the former contain traces of oxygen, which are, however, rapidly consumed upon irradiation. Taken together, these results highlight that the glassy polymer matrix protects the liquid nanodroplet surprisingly well from atmospheric oxygen and that the use of a volatile liquid component is no fundamental obstacle for longevity, although the stability needs to be clearly improved before technological exploitation in devices is feasible. Strategies to achieve this include the use of dyes with better (photo) stability (DPA is well-known to undergo (photo)oxidation to an endoperoxide and dimerize, respectively\textsuperscript{[24,49,50]}, the addition of stabilizers\textsuperscript{[14,51,52]} a less volatile solvent\textsuperscript{[53,54]}, and perhaps additional barrier layers.\textsuperscript{[7]}

The fact that the upconversion observed in the dye-doped nanodroplet-containing polymer is the result of TTA-UC was confirmed by time-resolved PL measurements (inset of Figure 3d). Under modulated excitation, the blue PL shows the expected complex decay dynamics that range from the nanosecond to the millisecond time scale. As commonly observed in TTA-UC systems, in the short-time range, the upconverted light decay is fast, on account of the initially high density of emitter triplets, which enhances their annihilation rate. As a result, the TTA yield (\(\Phi_{\text{TTA}}\)) in this time domain is often close to unity. Conversely, at longer times, the triplet density becomes so low that TTA is a negligible dissipation channel. Thus, in this regime, the delayed emission decay follows a single exponential function, with a characteristic lifetime \(\tau_{\text{UC}}\) that follows the spontaneous recombination time of DPA triplets \(\tau_\text{T} = 2\tau_{\text{UC}}\).\textsuperscript{[55]} The analysis of the long-time component afforded \(\tau_\text{T}\) of 726 \(\mu\text{s}\). This value is typical for DPA in organic solvents, while a much higher \(\tau_\text{T}\) would be expected for TTA-UC in a rigid matrix.\textsuperscript{[26,29]} Indeed, upconversion was observed when the material was excited with noncoherent green light at 543 nm obtained from a filtered high-pressure xenon lamp (20–30 mW cm\textsuperscript{-2}) or with collimated solar light passed through a 515 nm long-pass filter (Figure S14, Supporting Information). Taken together, the present material concept displays characteristics that are useful for solar harvesting applications and appears to be a promising framework for further development into stable devices, especially by replacing the model UC dyes used here by more (photo)stable chromophores and/or the addition of stabilizers.\textsuperscript{[4,7]}

The TTA-UC quantum yield, \(\Phi_{\text{UC}}\), of the DPA/PdOEP doped nanodroplet-containing glassy polymer, defined as the ratio between the numbers of emitted and absorbed photons, was first measured as function of the excitation intensity at 532 nm, using an air-free TTA-UC standard solution (\(\Phi_{\text{UC}} = 26\%\)) as reference (see the Experimental Section and the Supporting Information). In order to compare the performance of the two systems, we show in Figure 3e the measured \(\Phi_{\text{UC}}\) as function of the excitation intensity. The log-log plots of the data reveal two distinct regimes; below a threshold value, the efficiency depends on the excitation power density, but at high excitation intensity, \(\Phi_{\text{UC}}\) of the DPA/PdOEP nanodroplet-containing glassy polymer is constant at \(\approx 15\%\). This behavior is common and related to the bimolecular nature of the TTA step, which makes the efficiency dependent on the density of annihilating triplets and therewith the excitation intensity. However, at a sufficiently high excitation intensity, the TTA rate is much faster than the spontaneous decay of triplet states and TTA becomes their main recombination pathway with a \(\Phi_{\text{TTA}}\) of 100%. In this case, \(\Phi_{\text{UC}}\) reaches a constant value provided that the efficiencies of the intersystem crossing, TTET, and of the emitter fluorescence remain constant.\textsuperscript{[3,21]}

An instructive figure of merit is the threshold excitation intensity \(I_{\text{th}}\), where the spontaneous decay rate of the emitter triplet equals the TTA rate and thus \(\Phi_{\text{UC}}\) reaches half of its maximum.\textsuperscript{[3,8,32,56]} The DPA/PdOEP nanodroplet-containing glassy polymer exhibits an \(I_{\text{th}}\) of \(\approx 1.4\) mW cm\textsuperscript{-2}, which corresponds to \(\approx 0.9\) suns (vertical line in Figure 3e and Figure S13, Supporting Information). This subsolar intensity threshold matches that of the reference solution well, and corroborates that the TTA-UC process in the nanodroplet-containing polymer occurs in the liquid phase. Another important figure of merit for solar harvesting applications is \(\Phi_{\text{UC}}\) at an excitation density of one solar irradiance; in the case of the DPA/PdOEP nanodroplet-containing polymer, this value is \(\approx 9\%\), the highest ever reported for TTA-UC in a rigid matrix.\textsuperscript{[26,29]} Indeed, upconversion was observed when the material was excited with noncoherent green light at 543 nm obtained from a filtered high-pressure xenon lamp (20–30 mW cm\textsuperscript{-2}) or with collimated solar light passed through a 515 nm long-pass filter (Figure S14, Supporting Information). Taken together, the present material concept displays characteristics that are useful for solar harvesting technologies and appears to be a promising framework for further development into stable devices, especially by replacing the model UC dyes used here by more (photo)stable chromophores and/or the addition of stabilizers.\textsuperscript{[4,7]}

To further explore the efficiency, \(\Phi_{\text{UC}}\) was measured under high excitation intensity at 532 nm (100 mW cm\textsuperscript{-2}) using both an integrating sphere and a quasi-collinear PL setup for the detection of the emitted light (see the Experimental Section and the Supporting Information) and averaging data collected for three independently made samples.\textsuperscript{[3]} This yielded \(\Phi_{\text{UC}}\) values of 16 \(\pm\) 2\% and 14 \(\pm\) 3\%, respectively, confirming the data shown in Figure 3e. To our best knowledge, this is by far the highest TTA-UC efficiency ever reported for a rigid polymer prepared and operated under ambient conditions. The fact that the efficiency is substantially lower than that of a degassed DPA/PdOEP reference solution in THF (\(\Phi_{\text{UC}} = 26\%\)) is partially related to the reduced DPA fluorescence quantum yield...
in BMB (78%) vis-à-vis THF (96%) (Figure S26, Supporting Information) and likely due to quenching/photodegradation related to some residual oxygen, suggesting room for further improvement.

The generality and versatility of the material design concept were demonstrated by varying several parameters. PdOEP was replaced with PtOEP, another sensitizer that can be paired with DPA. This resulted in materials with a maximum green-to-blue $\Phi_{\text{UC}}$ of $\approx 8\%$. A detailed spectroscopic study shows that the characteristics are very similar to the DPA/PdOEP-doped system (see the Supporting Information). Three other dye pairs were incorporated in the nanodroplet-containing glassy polymer in order to extend the process to other spectral ranges (Figure 4a,b). The sensitizer PdTPBP was combined with the emitters 9,10-bis(phenylethynyl) anthracene (BPEA) and tetratert-butylperylene (TBPe) to achieve red-to-green and red-to-blue upconversion (Figure 4a), respectively.\textsuperscript{[2,21]} The integration of the sensitizer/emitter pair palladium(II)-octabutoxyphthalocyanine (Pd(OBu)$_8$Pc) and rubrene afforded a material that displayed red-to-yellow upconversion with a maximum $\Phi_{\text{UC}}$ of $15 \pm 3\%$ (Figure 4b and the Supporting Information).

Finally, the composition and mechanical properties of the matrix were varied. A thermoplastic upconverting material that could be reshaped upon heating above 50 °C was made by using the original recipe, but omitting the cross-linker TEG-diMA (Figure 4c). A rubbery material was made by replacing the methacrylic monomers with their acrylic counterparts, i.e., 2-hydroxyethyl acrylate, acrylic acid, and tetraethylene glycol diacrylate (Figure 4d). Other variations, such as the substitution of BMB with toluene, xylenes, or 1-[(2-ethylhexyl)oxy]-4-methoxybenzene also resulted in transparent upconverting materials (Figure S16, Supporting Information).

In summary, we have developed a simple and versatile one-step approach to create upconverting nanostructured polymers that combine the desirable and tailorable mechanical, thermal, and optical properties of polymer matrices with photophysical properties that are normally only observed in degassed solutions of upconverting dyes. The glassy polymer matrix investigated provides surprisingly good protection from atmospheric oxygen and permits operation under ambient conditions. Some of the materials made displayed record upconversion efficiencies under conditions that would be experienced in solar energy harvesting applications. Considering the generality of this material design strategy, and the robustness of the morphology formation, the framework presented here appears not only to be useful for the fabrication of upconversion materials and devices, but should be exploitable to access other types of advanced optical materials.

**Experimental Section**

*Synthesis of Upconverting Nanodroplet-Containing Glassy Polymers:* Chemicals were purchased from Sigma-Aldrich, ABCR, Acros Organics, TCI (Tokyo Chemical Industry Co., Ltd.), or Inochem, Ltd. (Frontier Scientific, Inc.) and were used as received. All nanodroplet-containing polymers were prepared under ambient conditions without prior deoxygenation of the mixture or its single components, unless specifically stated otherwise. A 20 mL vial equipped with a stir bar was charged under ambient conditions with CTAB (250 mg, 5 wt%), HEMA (2.66 g, 53.2 wt%), TEG-diMA (175 mg, 3.5 wt%), BMB (500 mg, 10 wt%), ethylene glycol (750 mg, 15 wt%), and MAA (665 mg, 13.3 wt%) (total weight: 5 g). Benzyl peroxide (10 mg, 0.2 wt%) was subsequently added and the mixture was heated to 80 °C and stirred for 10–15 min to appear clear and homogeneous, before it was filtered warm through a 0.2 µm polycarbonate filter to either an optical glass cuvette or a glass vial containing N,N-dimethyl aniline (10 mg, 0.2 wt%). The still clear mixture was briefly shaken and left to stand at 20 °C until gelation ($\approx$10–15 min), before it was placed into a water bath (15 °C), which served as a cooling medium.

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*Figure 4.* Tuning upconversion in nanodroplet-containing polymers. a,b) Pictures of dye-doped nanodroplet-containing polymer glasses under laser excitation at the indicated wavelengths. The materials contain the sensitizers PdTPBP or Pd(OBu)$_8$Pc and the emitters BPEA, TBPe, or rubrene, as indicated. c) Pictures of a thermoplastic nanodroplet-containing polymer glass doped with DPA/PdOEP under green laser excitation, as prepared and after reshaping at elevated temperature. d) Pictures of a slice of a nanodroplet-containing elastomer doped with DPA/PdOEP under green excitation in dark and ambient light. Thanks to its rubbery properties, the slice could be prepared by cutting the material with a knife.
the polymerization was complete, a transparent, hard material was obtained, which was either kept in a polymer film sealed cuvette and used for quantitative optical measurements or released from the glass vial by breaking the latter with a hammer. Materials of similar appearance were also obtained when MMB was replaced with toluene, xylene, or 1,2-ethanediol (poly)4-methoxybenzene.

Green-to-blue upconverting nanodroplet-containing glassy polymers were prepared by substituting the BMB with a solution of PdOEP or PtOEP (2 × 10^-5 M) in MMB (500 mg, 10 wt% of total weight) and adding DPA (25 mg). Assuming a final density of 1 g cm^-3 for the final material, the chromophore concentrations were 2 × 10^-5 M for PdOEP or PtOEP and 1.5 × 10^-4 M for DPA. A reduction of the DPA concentration by a factor of 2 resulted in a virtually unchanged upconversion intensity (lower density of the material).

Red-to-blue or red-to-green upconverting nanodroplet-containing glassy polymers were prepared by using the same recipe and contained PdTTPB (2 × 10^-7 M) as sensitizer and TBe or BPA (2 × 10^-3 M) as emitters, respectively. The dark red-to-yellow upconverting nanodroplet-containing glassy polymers contained instead Pd(OBu)8Pc (10^-7 M) or PtOEP (2 × 10^-7 M) as sensitizer and TBPe or BPEA (2 × 10^-3 M) as emitters, respectively. The theoretical maximum UC quantum efficiency ΦUC of the nanodroplet-containing polymers was determined relative to the maximum upconversion quantum yield of the DPA/PtOEP UC pair in deaerated tetrhydrofuran ([DPA] = 10^-5 M, [PtOEP] = 10^-6 M) used as secondary standard in quasi-collinear and integrating sphere PL setups. This method has practical advantages over using a primary standard and is an accepted practice in the field.[28,55,57] The theoretical maximum UC quantum efficiency is 0.50, since the TTA-UC process uses two low energy photons to produce one high-energy photon. The maximum ΦUC of the secondary standard is 0.26, under excitation at 532 nm and a power density of 100 mW cm^-2; it was measured and calculated by using the laser dye rhodamine 6G (10^-5 M in ethanol) as reference material.[28]

The recorded spectra were corrected for the setup optical response. The secondary standard (or “reference”) solution was freshly prepared in a glovebox under nitrogen atmosphere (O2-level <0.1 ppm) and the cuvette was sealed with a hot melt adhesive before being characterized prior to each set of measurements outside of the glovebox. To confirm the results obtained, ΦUC measurements were also performed using an integrating sphere on a series of independently made samples (see the Supporting Experimental Section in the Supporting Information for further details).[37]

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

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