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Organogels for Low-Power Light Upconversion

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We herein report new organogels that permit efficient optical upconversion (UC) by triplet-triplet annihilation. The materials studied consist of a liquid organic phase composed of a mixture of N,N-dimethylformamide and dimethyl sulfoxide in which the UC chromophore pair Pd(II) mesoporphyrin IX and 9,10-diphenylanthracene was dissolved, and a three-dimensional polymer network was formed by covalently cross-linking poly(vinyl alcohol) with hexamethylene diisocyanate. The new gels are highly transparent, shape-persistent, and display efficient green-to-blue upconversion with UC quantum yields of >0.6 and 14% under ambient and oxygen-free conditions, respectively. The design approach presented here permits the fabrication of a hitherto unexplored class of materials with a unique combination of properties. The framework can easily be extended to other materials based on other solvents, polymer networks, and/or chromophore pairs.

Conceptual insights

Optical upconversion by triplet-triplet annihilation is a process that is potentially useful for a plethora of applications that range from solar harvesting to in-vivo bioimaging. While this effect had been demonstrated in organic solutions already over 50 years ago, its adaptation to the solid state is more recent. However, the quantum efficiency of solid-state upconverting materials is usually low. We herein report upconverting organogels, which combine the best features of upconverting solutions and solids, i.e., high quantum efficiency, transparency, low dye-content, shape persistence, and considerable oxygen tolerance. The design approach appears to be general and applicable to other materials.

Fig. 1 Energy-level diagram displaying energy states and electronic processes occurring during sensitized triplet-triplet annihilation upconversion (TTA-UC). ISC: intersystem crossing, TTET: triplet-triplet energy transfer, TTA: triplet-triplet annihilation, GS: ground state. $^1\text{S}^*$, $^1\text{E}^*$ first singlet excited states of the sensitizer S and the emitter E, $^3\text{S}^*$, $^3\text{E}^*$: first triplet excited states of these species. Green light with a 543 nm wavelength is used for excitation, red sensitizer phosphorescence (667 nm) is observed in case of incomplete energy transfer, and blue fluorescence (433 nm) is observed in case of successful TTA-UC.
Herein we present a novel design concept for upconverting organogels, which combine several attractive features of upconverting solutions and solids, i.e., high quantum efficiency, and shape persistence. The materials consist of a continuous polymer network and a liquid organic phase in which the upconverting chromophores are dissolved (Fig. 2). This architecture proves to be ideal for efficient UC by providing simultaneously good mechanical integrity, high molecular mobility, low dye content and efficient light harvesting. Furthermore, we speculated that the use of DMF and/or DMSO, which both exhibit low oxygen solubility (equilibrium concentration = 0.65 mM\(^2\) and 0.33 mM,\(^2\) respectively), as the liquid phase may impart substantial tolerance against triplet-quenching by oxygen.

![Graphic representation of the structure of the upconverting organogels studied and chemical structures of the constituents used.](image)

High optical quality gels were created by cross-linking poly(vinyl alcohol) (PVOH) in a 2:1 w/w DMF/DMSO mixture by reaction with hexamethylene disiocyanate (HMDI).\(^3\) This was readily achieved, either under ambient or under air-free conditions, by vigorous mixing of a DMSO solution containing PV OH with a poly(vinyl alcohol) (PVOH) in a 2:1 w/w DMF/DMSO mixture and to limit aggregation of this sensitizer, the dicarboxylate derivative palladium(II) meso-porphyrin IX (PdMesoIX) (Fig. 2) was employed instead of PdOEP. PdMesoIX exhibits UV-Vis absorption and emission spectra that are identical to those of palladium octaethylporphyrin (PdOEP) (ESI Fig. S5, Fig. 3) and the two porphyrins have comparable phosphorescence lifetimes (PdMesoIX in THF: 1.33 ms at 298 K,\(^3\) PdOEP in toluene: 0.65 ms at 295 K\(^2\)). Thus, we surmised that PdMesoIX can be used to sensitize the blue-light emitting DPA (Fig. 3) and that the upconversion characteristics of this hitherto unexplored sensitizer/emitter pair are similar to those of PdOEP/DPA.

To validate this hypothesis, a degassed solution containing PdMesoIX (2 \(\times\) 10\(^{-5}\) M) and DPA (10\(^{-5}\) M) in a 2:1 w/w DMF/DMSO mixture was prepared and the upconverted emission upon excitation with a green laser emitting at 543 nm (incident power density 180 mW cm\(^{-2}\)) was monitored (ESI, Fig. S6). The PdMesoIX concentration was chosen to efficiently harvest the irradiated light (absorbance \(A = 0.9\) ) and to obtain maximum upconverted light output. The PdMesoIX:DPA ratio (1:500) was selected to maximize sensitizer-to-emitter energy transfer and minimize energy back-transfer.\(^4\) The comparison with the upconverted emission spectrum of a corresponding solution of PdOEP (2 \(\times\) 10\(^{-5}\) M) and DPA (10\(^{-5}\) M) in toluene reveals identical emission spectra, which exclusively display the characteristic blue DPA emission (ESI Fig. S7), although the high DPA concentration caused some self-absorption on the high-energy end of the spectrum. Using the reported upconversion quantum yield of 36% for a vacuum-degassed PdOEP/DPA solution in toluene\(^11\) and the fluorescence quantum yield of 91.5% for a rhodamine 101 solution in ethanol as references,\(^2\) a quantum yield of 22% was determined for the argon-degassed PdMesoIX/DPA solution in DMF/DMSO by comparison of the respective absorbances, integrated emission intensities, and refractive indices (ESI Fig. S2, section 3.2, Eqs. E1-2). The PdMesoIX/DPA solution was subsequently used as quantum yield standard for DMF/DMSO-based gels and solutions (ESI Fig. S3, Eqs. E3-4).

We further investigated the upconversion characteristics of the PdMesoIX/DPA pair in DMF/DMSO solution by probing the upconverted emission intensity as a function of excitation power density (ESI Fig. S8). A log-log plot of the respective data for air-free solutions (Fig. 4b) shows two different regimes, in which the data can be fitted with two separate linear regressions. The...
intersection of the corresponding lines marks the transition from a quadratic (low excitation intensity, slope: 1.86 +/- 0.03) to a linear regime (high excitation intensity, slope: 1.20 +/- 0.01) and denotes the power density where TTA becomes the dominant decay pathway for the DPA triplets, ca. 30 mW·cm⁻² (Fig. 4b). The experiment was repeated with solutions prepared under ambient conditions (ESI Fig. S9). In this case, the upconverted emission intensity was, at all excitation power densities probed, lower than that of the corresponding air-free solutions and all data fit well to a single quadratic function (Fig. 4b, slope: 1.90 +/- 0.03). These results indicate that triplet quenching, likely from dissolved O₂, is at play for the samples prepared under ambient conditions. However, we note that also in the case of samples prepared and handled under ambient conditions TTA-UC is observed at an excitation power density as low as 10 mW·cm⁻² and that the quantum yield of 10% at 180 mW·cm⁻² is very appreciable. This behaviour is in stark contrast to that of a corresponding solution of PdOEP (2·10⁻⁵ M) and DPA (10⁻² M) in toluene, which if prepared under ambient condition displays no detectable upconversion at excitation power densities up to 350 mW·cm⁻² (ESI Fig. S6b), and supports the conclusion that the DMF/DMSO mixture chosen for the present indeed contributes to a reduction of the triplet-quenching by oxygen.

We next prepared cross-linked PVOH-HMDI/DMF/DMSO gels containing PdMesolIX (2·10⁻⁵ M) and DPA (10⁻² M) in the same concentration as the DMF/DMSO solutions discussed above and studied the gels’ upconverting capabilities in an analogous manner. Gratifyingly, the UC organogels prepared under air-free conditions exclusively displayed the characteristic blue upconverted DPA emission (Fig. 4a, full spectrum ESI Fig. S10), even if excited at power densities as low as 6 mW·cm⁻². Similarly to the air-free solutions, the log upconversion intensity vs. log excitation power density plot displays quadratic (slope: 1.81 +/- 0.02) and linear (slope: 1.09 +/- 0.01) regimes, with a transition at a power density of ca. 100 mW·cm⁻² (Fig. 4b). Particularly at high-excitation densities, the process is very efficient; using degassed PdMesolIX/DPA in a 2:1 w/w DMF/DMSO solution as a reference (vide supra), we estimated a quantum yield of 14% at an excitation power density of 180 mW·cm⁻² (ESI Fig. S3, Eqs. E3,4). We suspect that molecular mobility is somewhat restricted by the presence of the cross-linked polymer network, which results in a lower efficiency and in a higher transition power density compared to the air-free solutions. Interestingly, no major changes of transition power densities or UC intensities in the linear regime were observed when the cross-link density of the gel was reduced to 5 or 2.5 mol% or when the PVOH content was reduced to 2.5 wt% (ESI Fig. S12 and S13).

Fig. 4 a) Upconverted emission spectra recorded upon excitation of a PVOH-HMDI/DMF/DMSO organogel containing PdMesolIX (2·10⁻⁵ M) and DPA (10⁻² M). The gel was prepared under air-free conditions. The sample was excited at 543 nm with a 2 mW HeNe laser at incident power densities of between 6 and 275 mW·cm⁻². b) Double logarithmic plot of the integrated upconverted emission spectra of DMF/DMSO solutions (black) and PVOH-HMDI/DMF/DMSO organogels (blue) containing PdMesolIX (2·10⁻⁵ M) and DPA (10⁻² M). The samples were prepared under air-free (triangles) or ambient (squares) conditions. Solid lines represent least-square fits to the data.

Fig. 5 Pictures of free-standing PVOH-HMDI/DMF/DMSO organogels irradiated with a 2 mW green HeNe laser at 543 nm (power density = 350 mW cm⁻²). The sample shown in a) and b) contains PdMesolIX (2·10⁻⁵ M) and DPA (10⁻² M) and emits blue upconverted light that is clearly visible, even under ambient illumination. The samples shown in c) and d) contain only PdMesolIX (c, 2·10⁻⁵ M) or DPA (d, 10⁻³M) and display diffused porphyrin phosphorescence (c) or excitation light (d). All gels were produced in a mould under ambient conditions and were probed under ambient conditions after release from the mould.
Most intriguingly, also the chromophore-containing gels prepared and operated under ambient conditions displayed appreciable upconversion (ESI Fig. S11, Fig. 5). The pictures shown in Fig. 5a,b show strikingly that the materials are shape-persistent when removed from the moulds and display, in contrast to reference gels that contain only the sensitizer (Fig. 5c) or only the emitter (Fig. 5d), bright upconverted blue emission when excited at 543 nm with a power density of 350 mW cm$^{-2}$. Interestingly, a strong decay of the upconverted emission intensity over time was observed upon continuous irradiation (ca. 5 min) at 180 mW cm$^{-2}$ (ESI Fig. S15). Such decay might be attributed to local photo-bleaching (e.g. reaction of PdOEP-sensitized singlet oxygen with DPA)$^{37,38}$ and/or the formation of polymer degradation products since it was not observed in the air-free gels (ESI Fig. S14), which displayed only minor intensity reduction under the same conditions. However, the effect was fully reversible; if the sample was left to rest for 4 days and excited anew, the original upconversion properties were restored, likely on account of diffusion of degradation products out of the irradiated volume as well as diffusion of “fresh” chromophores into that zone. The initial UC-intensity peak-values of ca. 10$^6$ counts (ESI Fig. S15) are slightly lower than the peak-values found for the corresponding solutions prepared under ambient conditions (ESI Fig. S3b and S6b), suggesting a maximum quantum efficiency of ca. 10%. However, in view of the above-discussed transient behavior, TTA-UC intensities were measured after >4 min of continuous irradiation, estimating the quantum efficiency to 10 > $\Phi$ > 0.6% at an excitation power density of 180 mW cm$^{-2}$ (ESI Fig. S3, Eqs. E3.4). Very much like the solutions prepared under ambient conditions, the TTA-UC intensity, detectable at power densities ≥30 mW cm$^{-2}$, increased in a quadratic fashion (slope: 1.81 +/- 0.04) with the incident power density, although a deviation towards linear behaviour appears to be at play at power densities above 100 mW cm$^{-2}$ (Fig 4b). We speculate that this deviation originates from mild photobleaching taking place during the timeframe of the measurement.

Liquid nitrogen freezing of the UC gel into glasses led to the immediate suppression of upconversion and the appearance of phosphorescence (ESI Fig. S16b and c). This disappearance thus demonstrates the importance of molecular mobility for upconversion in organogels doped with low dye concentrations. By contrast, the red phosphorescence of the sample containing only the porphyrin was not affected by freezing the gels (Fig. 5c and ESI Fig. S16a).

Conclusions

In summary, we have presented the first examples of very efficient upconverting gels. These systems consist of a small weight fraction of a cross-linked network, which bestows the material with mechanical integrity, and a solvent phase, which provides high chromophore diffusivity and protects the process to a certain extent from oxygen quenching. Such organogels are easily accessible and can be readily be transformed in any desirable shape. The materials should lend themselves to (two-photon) 2D or even 3D photopatterning$^{39,40}$ and appear to be particularly useful for soft actuators,$^7$ gels for guided 3D cell-growth,$^{29}$ or as a matrix for upconversion enhancing photonic structures, which are impossible or difficult to realize with liquid or solvent-free solid UC material.$^{41-43}$ It appears that the general concept can readily be applied to gels based on other solvents, polymer networks, and chromophore systems. In particular the hygroscopic and volatile nature of the solvents employed call for further improvements. Upconverting organogels broaden the range of upconverting materials

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Notes and references

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TOC Text and Figure
Low-power green-to-blue upconverting poly(vinyl alcohol)/DMF/DMSO-based organogels containing palladium(II) mesoporphyrin IX sensitizer and diphenylanthracene emitter are presented as a versatile new approach for efficient, self-standing solid-state upconverting materials.