Supplementary Information

Organogels for Low-Power Light Upconversion

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1. Materials and Methods

PdMesoIX [Pd(II) mesoporphyrin IX] was purchased from Frontier Scientific. PVOH [poly(vinyl alcohol), $M_w = 31\text{-}50 \text{ kg/mol}$, 98-99% hydrolyzed, $\rho_{20^\circ\text{C}} = 1.2\text{-}3 \text{ g cm}^{-3}$], HMDI [hexamethylene diisocyanate, >99% (GC)], rhodamine 101 and palladium(II) octa-ethylporphyrin were purchased from Sigma-Aldrich. $N,N$-dimethylformamide (DMF, 99.8%, dry over molecular sieves, $\rho_{20^\circ\text{C}} = 0.95 \text{ g cm}^{-3}$) and dimethyl sulfoxide (DMSO, 99.7%, dry over molecular sieves, $\rho_{20^\circ\text{C}} = 1.1 \text{ g cm}^{-3}$) were purchased from Acros Organics. 9,10-Diphenylanthracene [99%] was purchased from ABCR. All chemicals were used as received.
2. Preparation of solutions and gels

2.1. Solutions

2:1 w/w DMF/DMSO solutions containing the upconverting chromophores were prepared by first dissolving DPA (see solution IIIb), PdMesoIX (see solution IIIa) or both (see solution IIIc) in DMF (4 g, ~4.2 mL, \( \rho_{20} = 0.95 \text{ g/mL} \)) and subsequently diluting this mixture with DMSO (2 g, ~1.8 mL, \( \rho_{20} = 1.1 \text{ g/mL} \)). Note that no visible volume contraction was observed upon combination of DMF and DMSO solutions.

Upconverting toluene solutions were prepared by first dissolving PdOEP (0.64 mg) in toluene (10 mL) to prepare a stock solution with a chromophore concentration of \( 10^{-4} \text{ M} \). In a 10 mL measuring flask, the stock solution (2 mL) was diluted with additional toluene (8 mL) to adjust the chromophore concentration to \( 2 \cdot 10^{-5} \text{ M} \). DPA (20 mg) was then dissolved in the latter PdOEP solution (6 mL) by stirring the mixture for at least 10 min at 50 °C to prepare a solution with a chromophore concentration of \( 2 \cdot 10^{-5} \text{ M} \) PdOEP and \( 10^{-2} \text{ M} \) DPA.

All solutions were prepared under ambient conditions and either directly measured (ambient conditions) or purged with argon for 30 min (air-free conditions, solvent evaporation neglected due to the low volatility of the solvents).

2.2. Standard solutions for quantum yield measurements

A Rhodamine 101 standard solution \(^1\) \( 10^{-6} \text{ M} \) was produced by dissolving rhodamine 101 (4.96 mg) in ethanol (10 mL, \( 10^{-3} \text{ M} \)) and subsequently diluting three times 1 mL of this solution with 9 mL of solvent. Absorption and emission spectra were taken under ambient conditions due negligible O₂-quenching (Fig. S2). \(^1\)
An upconverting toluene standard solution was prepared by first dissolving PdOEP (0.64 mg) in toluene (10 mL) to prepare a stock solution with a chromophore concentration of $10^{-4}$ M. The stock solution (0.5 mL) was then diluted with additional toluene (9.5 mL) to adjust the chromophore concentration to $5 \cdot 10^{-6}$ M. DPA (33 mg) was dissolved in the latter PdOEP solution (10 mL) by stirring the mixture for at least 10 min at 50 °C to prepare a solution with chromophore concentrations of $5 \cdot 10^{-6}$ M PdOEP and $10^{-2}$ M DPA. This solution was transferred to a custom-made cuvette connected to a round-bottom flask, vacuum-degassed by three freeze-pump-thaw cycles and finally upconversion emission and absorption spectra were measured (Fig. S2).

2.3. Gels

2.3.1. Reference gels without chromophores prepared under ambient conditions

Solution I was prepared as follows: In a 250 mL round-bottom flask, PVOH (30 g) was dissolved in DMSO (170 g) at 70 °C under constant agitation for 2 h in order to obtain a 15 wt% solution (solution I). This solution was kept over Drierite™ in a desiccator.

Solution II was prepared as follows: In a 25 mL vial, HMDI (57 mg) was dissolved in DMF (4 g) by shaking gently.

To prepare the reference gels, solution I (2 g) was mixed with the freshly prepared solution II (4 g), the viscous mixture was rapidly stirred with a glass rod for 30 s, and filled either into a spectroscopy cuvette (optical glass) for quantitative measurements or a poly(tetrafluoroethylene) mould (25 x 25 x 15 mm) for preparation of self-standing gels. Gel formation was observed after allowing the mixture to stand for ca. 10 min at room temperature. Quantitative measurements were performed at least 1.5 h after gelation.
2.3.2. Chromophore-containing gels prepared under ambient conditions

*Solution IIIa* was prepared as follows: PdMesoIX (0.67 mg) was dissolved in DMF (10 mL) to prepare a stock solution with a chromophore concentration of $10^{-4}$ M. In a 10 mL measuring flask, the stock solution (2.9 mL) was diluted with additional DMF (7.1 mL) to adjust the chromophore concentration to $2.9 \cdot 10^{-5}$ M (*solution IIIa*).

*Solution IIIb* was prepared as follows: DPA (20 mg) was dissolved in DMF (4 g) by stirring the mixture for at least 10 min at 50 °C to prepare a solution with a chromophore concentration of $1.4 \cdot 10^{-2}$ M. In order to measure undistorted absorption and direct emission spectra of DPA embedded in gels (Fig. 3), a 500-time diluted solution *IIIb* was used for the preparation of this specific gel.

*Solution IIIc* was prepared as follows: DPA (20 mg) was dissolved in a portion of *solution IIIa* (4 g) by stirring the mixture for at least 10 min at 50 °C.

To prepare the chromophore-containing gels, freshly prepared *solutions IIIa-c* (4 g) were each used to dissolve HMDI (57 mg) and the resulting solutions were each mixed with a portion of *solution I* (2 g each), the viscous mixtures were rapidly stirred with a glass rod for 30 s, and filled either into a spectroscopy cuvette (optical glass) for quantitative measurements or a poly(tetrafluoroethylene) mould (25 x 25 x 15 mm) for the preparation of self-standing gels. Gel formation was observed after allowing the mixture to stand for ca. 10 min at room temperature. Quantitative measurements were performed at least 1.5 h after gelation.

2.3.3. Chromophore-containing gels prepared under air-free conditions

*Solution IV* was prepared as follows: A flame-dried 25 mL Schlenk flask was charged with PVOH (3 g), which was subsequently dissolved in dry DMSO (20 g) at 70°C under constant
agitation for 2 h in order to obtain a 15 wt% solution. The resulting solution was then transferred into a nitrogen glove-box for further use.

*Solution V* was prepared as follows: In a flame-dried 20 mL Schlenk flask, PdMesoIX (1.34 mg) was dissolved in anhydrous DMF (20 mL) to prepare a stock solution with a chromophore concentration of $10^{-4}$ M. A portion of this solution (14.5 mL) was subsequently transferred to a flame-dried 100 mL Schlenk flask using a syringe and the solution was diluted with additional DMF (35.5 mL) to adjust the chromophore concentration to $2.9 \cdot 10^{-5}$ M. DPA (236 mg) and HMDI (677.32 mg, 0.65 mL, $\rho^{20^\circ C} = 1.05$ g cm$^{-3}$) were subsequently added and the mixture was heated to 50 °C for 10 min in order to dissolve the DPA. The resulting solution was then transferred into a nitrogen glove-box for further use.

In the glove-box, gels were prepared by combining portions of *solution IV* (2 g) and *solution V* (4 g), and quickly stirring the mixture with a glass rod for 30 s. The viscous mixture was then filled into a fluorescence cuvette (optical glass), which was capped and additionally sealed with Parafilm M®, and allowed to gel for at least 1.5 h in the glove-box prior to removal from the box and subsequent measurement.

The final concentrations of all the components in air-free gels are given in Table S1, taking into account the mixing of *solutions IV* and *V*.

**Table S1.** Summary of components and concentrations in UC-gels.

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVOH</td>
<td>5 wt%</td>
</tr>
<tr>
<td>DPA</td>
<td>$10^{-2}$ M</td>
</tr>
<tr>
<td>PdMesoIX</td>
<td>$2 \cdot 10^{-5}$ M</td>
</tr>
<tr>
<td>HMDI</td>
<td>10 mol% hydroxyl-groups crosslinked</td>
</tr>
</tbody>
</table>
2.3.4. Chromophore-containing gels prepared under air-free conditions with varying polymer and crosslinker-contents

Solution VI was prepared as follows: The procedure for Solution V was followed, omitting the addition of HMDI.

In the glove-box, gels containing 2.5 wt% PVOH with 10 mol% crosslinked hydroxyl-groups were prepared as follows: A portion of solution IV (1 g) was diluted with air-free dry DMSO (1 g). To portion of solution VI (4 g), dry and air-free HMDI (29 mg) was added. Both solutions were then combined and the resulting mixture quickly stirred with a glass rod for 30 s. The viscous mixture was then filled into a fluorescence cuvette (optical glass), which was capped and additionally sealed with Parafilm M®, and allowed to gel for at least 1.5 h in the glove-box prior to removal from the box and subsequent measurement.

In the glove-box, gels containing 5 wt% PVOH with 2.5, 5 or 10 mol% crosslinked hydroxyl-groups were prepared as follows: To portion of solution VI (4 g), dry and air-free HMDI (14, 29 or 57 mg) was added. The resulting mixture was then combined with portion of solution IV (2 g) and quickly stirred with a glass rod for 30 s. The viscous mixture was then filled into a fluorescence cuvette (optical glass), which was capped and additionally sealed with Parafilm M®, and allowed to gel for at least 1.5 h in the glove-box prior to removal from the box and subsequent measurement.
**Fig. S1.** FTIR spectra monitoring the gelation of a 2:1 w/w solution of DMF/DMSO containing 5 wt% PVOH and HMDI as a cross-linker (5 mol% with respect to the PVOH-hydroxy groups) under ambient conditions over the course of 1.5 h. The characteristic isocyanate signal at 2271 cm\(^{-1}\) disappears 20 min after mixing.
3. Optical measurements

3.1. General

Steady-state photoluminescence (PL) experiments were carried out on a Photon Technology International (PTI) C720 spectrophotometer equipped with a Hamamatsu R928P photomultiplier. Upconversion was accomplished with a 2 mW non-polarized 543 nm green HeNe laser (Thorlabs HGR020, 1/e² beam diameter 0.83 mm) equipped with a laser line filter (543.5 ± 2 nm, FWHM = 10 ± 2 nm). Power densities were varied using reflective power density filters (Thorlabs) and measured with an optical power meter (Thorlabs PM100USB with photodiode power sensor S120VC). All samples were measured in 10 x 10 mm quartz (liquid) or optical glass (gels) cells. Vacuum-degassed solutions were prepared and measured in a custom-made quartz glass cuvette bearing a side arm round bottom flask for degassing. Emission spectra were corrected for the spectral response of the detector using the manufacturer’s correction files. UV-Vis absorption spectra were recorded on a Shimadzu UV-2401PC using 10 mm path quartz (liquid) or optical glass (gels) cells.

3.2. Quantum yield measurements

The upconversion quantum yield of a degassed solution containing PdMesoIX (2·10⁻⁵ M) and DPA (10⁻² M) in 2:1 w/w DMF/DMSO was determined under excitation with a power density of 180 mW cm⁻² at 543 nm by comparison of the absorption and upconverted emission spectra with the corresponding spectra (down- or upconverted emission) of solutions of rhodamine 101 in ethanol (10⁻⁶ M, Φᵣ = 0.915)¹,² and PdOEP (5·10⁻⁶ M) and DPA (10⁻² M) in toluene, for which an upconversion quantum yield of Φ_UC = 0.36 (excitation wavelength λ_ex = 515.5 nm, power density = 350 mW cm⁻²) was reported.

The upconverted quantum yield of the PdMesoIX/DPA solution was first determined using equation (E1)¹ and using the UC-standard PdOEP/DPA in toluene as reference. Φ, A, I and η represent the quantum yield, the integrated absorbance from λ = 533-543 nm (λ_ex = 543 nm),
the integrated upconverted emission intensity from $\lambda = 400-535$ nm and the refractive index, respectively. The subscripts $std$ and $unk$ refer to the PdOEP/DPA standard and the PdMesoIX/DPA unknown, respectively. The refractive indices used were $\eta_{\text{toluene}} = 1.496$, $\eta_{\text{DMF}} = 1.430$ and $\eta_{\text{DMSO}} = 1.479$ as per the Sigma-Aldrich product page. $\eta_{\text{DMF/DMSO}} = 1.446$ for 2:1 w/w DMF/DMSO solutions was calculated by linear combination of $\eta_{\text{DMF}}$ and $\eta_{\text{DMSO}}$.

Based on the absorption (Fig. S2a) and emission spectra (Fig. S2b) shown, a quantum yield $\Phi_{\text{PdMesoIX/DPA}} = 0.21$ was determined.

$$\phi_{\text{UC,PdMesoIX/DPA}} = \Phi_{\text{UC,PdOEP/DPA}} \left( \frac{A_{\text{std}}}{A_{\text{unk}}} \right) \left( \frac{l_{\text{unk}}}{l_{\text{std}}} \right) \left( \frac{\eta_{\text{DMF/DMSO}}}{\eta_{\text{toluene}}} \right)^2$$  \hspace{1cm} (E1)

The PdMesoIX/DPA solution quantum yield $\Phi_{\text{PdMesoIX/DPA}}$ was also determined by comparison with the standard rhodamine 101 (R101) by using equation (E2)$^2$. Here, $I$ represents the integrated upconverted emission intensity from $\lambda = 400-535$ nm ($I_{\text{unk}}$) or the integrated R101 emission intensity from $\lambda = 545-750$ nm ($I_{\text{std}}$); $\eta_{\text{ethanol}} = 1.362$ was used.

Based on the absorption (Fig. S2a) and emission spectra (Fig. S2b) shown, a quantum yield $\Phi_{\text{PdMesoIX/DPA}} = 0.22$ was determined.

$$\phi_{\text{UC,PdMesoIX/DPA}} = 2\Phi_{f,R101} \left( \frac{A_{\text{std}}}{A_{\text{unk}}} \right) \left( \frac{l_{\text{unk}}}{l_{\text{std}}} \right) \left( \frac{\eta_{\text{DMF/DMSO}}}{\eta_{\text{ethanol}}} \right)^2$$  \hspace{1cm} (E2)
Fig. S2. a) Absorption spectra of an argon-degassed solution containing PdMesolIX (2·10⁻⁵ M) and DPA (10⁻² M) in a 2:1 w/w DMF/DMSO mixture as well as of vacuum-degassed reference solutions containing PdOEP (5·10⁻⁶ M) and DPA (10⁻² M) in toluene or rhodamine 101 (10⁻⁶ M) in ethanol. b) Emission spectra of the same samples excited at 543 nm with a 2 mW HeNe laser operated at an incident power density of 180 mW cm⁻².
The quantum efficiencies of a solution containing PdMesoIX \( (2 \times 10^{-5} \text{ M}) \) and DPA \( (10^{-2} \text{ M}) \) that was prepared and handled under ambient conditions and of upconverting PVOH-HDMI/DMF/DMSO organogels containing PdMesoIX \( (2 \times 10^{-5} \text{ M}) \) and DPA \( (10^{-2} \text{ M}) \) were determined in a manner similar to the above protocol using a degassed solution containing PdMesoIX \( (2 \times 10^{-5} \text{ M}) \) and DPA \( (10^{-2} \text{ M}) \) in 2:1 w/w DMF/DMSO as reference, under excitation with a power density of 180 mW cm\(^{-2}\) at 543 nm.

Quantum yields were calculated using equation (E4)\(^1\), which was derived from (E3) assuming similar refractive indices \( \eta \) for 2:1 w/w DMF/DMSO gels and solutions.

\[
\phi_{UC, unk} = \phi_{UC, std} \left( \frac{A_{std}}{A_{unk}} \right) \left( \frac{I_{unk}}{I_{std}} \right) \left( \frac{\eta_{unk}}{\eta_{DMF/DMSO}} \right)^2
\]  
(E3)

\[
\phi_{UC, unk} = \phi_{UC, std} \left( \frac{A_{std}}{A_{unk}} \right) \left( \frac{I_{unk}}{I_{std}} \right)
\]  
(E4)

Based on the absorption \( A \) (Fig. S3) and the integrated upconverted emission \( I \) (Fig. 3b, S8-S11) quantum yields \( \phi_{UC, soln \ ambient} = 0.10 \), \( \phi_{UC, gel \ air-free} = 0.14 \) and \( \phi_{UC, gel \ ambient} = 0.006 \) were determined.
Fig. S3. a) Absorption and b) emission spectra of solutions containing PdMesoIX (2·10⁻⁵ M) and DPA (10⁻² M) in a 2:1 w/w DMF/DMSO and of PVOH-HDMI/DMF/DMSO organogels containing PdMesoIX and DPA in concentrations of 2·10⁻⁵M and 10⁻² M, respectively. The solutions and the gels were prepared under ambient and air-free conditions, respectively.
**Fig. S4.** Graphic illustration, picture, and UV-Vis transmission spectrum of an undoped gel consisting of a 2:1 w/w DMF/DMSO mixture that had been gelated with 5wt% PVOH and HMDI as a cross-linker (5 mol% with respect to PVOH-hydroxyl groups). The gel has a transmittance of >95% at 543 nm (green HeNe laser wavelength used for excitation).
**Fig. S5.** Normalized absorption and emission spectra of solutions of PdMesoIX and PdOEP (2·10^{-5} M) in a 2:1 w/w DMF/DMSO mixture. The emission spectra were recorded by exciting the samples under ambient conditions at 543 nm. The two porphyrins display identical spectra.
**Fig. S6.** Upconverted emission spectra recorded upon excitation of a) argon-degassed and b) non-degassed (prepared under ambient conditions) solutions containing $2 \cdot 10^{-5}$ M PdMesoIX and $10^{-2}$ M DPA in 2:1 w/w DMF/DMSO (black line) and $2 \cdot 10^{-5}$ M PdOEP and $10^{-2}$ M DPA in toluene. Both samples were excited at 543 nm with a 2 mW HeNe laser operated at an incident power density of 180 mW cm$^{-2}$, unless noted otherwise.
**Fig. S7.** Normalized emission spectrum of a $10^{-2}$M DPA DMF/DMSO solution (2:1 w/w) excited at 375 nm and normalized upconverted emission spectra of a DMF/DMSO solution (2:1 w/w) and a PVOH-HMDI/DMF/DMSO organogel containing $2 \cdot 10^{-5}$ M PdMesoIX and $10^{-2}$M DPA, irradiated with 543 nm green laser. All emission spectra are nearly identical.
**Fig. S8.** Upconverted emission spectra recorded upon excitation of a degassed solution containing 2·10⁻⁵ M PdMesoIX and 10⁻² M DPA in 2:1 w/w DMF/DMSO. The sample was excited at 543 nm with a 2 mW HeNe laser operated at incident power densities of between 4 and 180 mW cm⁻².

**Fig. S9.** Upconverted emission spectra recorded upon excitation of a solution containing 2·10⁻⁵ M PdMesoIX and 10⁻² M DPA in 2:1 w/w DMF/DMSO. The solution was prepared under ambient conditions. The sample was excited at 543 nm with a 2 mW HeNe laser operated at incident power densities of between 10 and 325 mW cm⁻².
**Fig. S10.** Emission spectrum recorded from 350-750 nm upon excitation of the air-free PVOH-HMDI/DMF/DMSO organogel shown in Fig. 4 at 543 nm with a power density of 180 mW cm$^{-2}$. No significant emission was detected red-shifted with respect to the exciting light, showing complete energy transfer from the sensitizer to the emitter.
**Fig. S11.** Upconverted emission spectra recorded upon excitation of a PVOH-HDMI/DMF/DMSO organogel containing PdMesoIX (2·10⁻⁵ M) and DPA (10⁻²M). The gel was prepared under ambient conditions. The sample was excited at 543 nm with a 2 mW HeNe laser at incident power densities of between 30 and 250 mW cm².
Fig. S12. a) Double logarithmic plot of the integrated upconverted emission intensities of PVOH-HMDI/DMF/DMSO organogels with a PVOH content of 2.5 wt% (black) and 5 wt% (blue). The crosslink density (mol% of crosslinked PVOH hydroxyl-groups) was kept constant at 10 mol%. The gels containing PdMesoIX (2·10⁻⁵ M) and DPA (10⁻² M) were prepared under air-free conditions and excited at 543 nm with a 2 mW HeNe laser at incident power densities of between 6 and 325 mW·cm⁻². Portions (b) and (c) show least-square fits (solid lines) to the data shown in (a). A transition from quadratic (slopes ca. 1.78 and 1.93) to linear (slopes ca. 1.05) regime is observed at a power density of ca. 100 mW·cm⁻². Gels with a lower PVOH content seem to show a somewhat higher UC intensity at very low power densities.
Fig. S13. a) Double logarithmic plot of the integrated upconverted emission intensities of PVOH-HMDI/DMF/DMSO organogels with crosslinking densities (mol% of crosslinked PVOH hydroxyl-groups) of 2.5 mol% (red), 5 mol% (black) and 10 mol% (blue). The PVOH content was kept constant at 5 wt%. The gels contain PdMesoIX ($2 \times 10^{-5}$ M) and DPA ($10^{-2}$ M), were prepared under air-free conditions and excited at 543 nm with a 2 mW HeNe laser at incident power densities of between 6 and 325 mW·cm$^{-2}$. Portions (b) and (c) show least-square fits (solid lines) to the data shown in (a). A transition from quadratic (slopes ca. 1.92 and 1.93) to linear (slopes ca. 1.08 and 1.05) regime is observed at a power density of ca. 100 mW·cm$^{-2}$. 
**Fig. S14.** Upconversion emission intensity monitored at 433 nm upon continuous excitation of a PVOH-HDMI/DMF/DMSO organogel containing PdMesoIX (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 an incident power density of 180 mW cm⁻². There is a slight decay in upconversion intensity after 500 sec.
Fig. S15. Upconversion emission intensity monitored at 433 nm upon continuous excitation of a PVOH-HDMI/DMF/DMSO organogel containing PdMesoIX ($2 \cdot 10^{-5}$ M) and DPA ($10^{-2}$ M). The gel was prepared under ambient conditions. The sample was excited at 543 nm with a 2 mW HeNe laser at an incident power density of 180 mW cm$^{-2}$. Upconversion experiences a pronounced decay upon continuous excitation but recovers after four days in the dark.
**Fig. S16.** Pictures of liquid nitrogen-frozen, self-standing PVOH-HDMI/DMF/DMSO containing a) PdMesoIX (2·10⁻⁵ M) and b) PdMesoIX (2·10⁻⁵ M) and DPA (10⁻² M) irradiated at 543 nm with a 2 mW green HeNe laser. Both pictures display scattered green incident light and red downconverted sensitizer phosphorescence. c) Picture of the sample shown in b) taken upon thawing the sample. In this case green upconverted blue emission is clearly visible.
4. References
