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ELECTRONIC SUPPORTING INFORMATION

Efficient photon upconversion at remarkably low annihilator concentrations in liquid polymer matrix: when less is more

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Contents:

1. Synthetic methods and characterization data

Reagents and solvents were purchased from TCI Europe, Sigma Aldrich Co. or from VWR and were used without further purifications unless otherwise mentioned. Purification of the products was carried out either by column chromatography on Silica gel 60 or Silica gel 100 (Merck) or on preparative TLC plates (Merck) coated with neutral aluminum oxide 60 F254. NMR spectra were recorded using JEOL JNM-ECZ500R 500 MHz spectrometer using TMS as internal standard. HRMS measurements were done with Waters LCT Premier XE ESI-TOF bench top mass spectrometer. Lock-mass correction (leucine enkephaline as a reference compound), centering and calibration were applied to the result raw data to obtain accurate mass.

[2-(3-[10,15,20-tris(3,5-di-tert-butylphenyl)porphyrin-5-yl-k^2*N*^{21},*N*^{23}]phenoxy]ethanolato(2-)]zinc

A total of 56 mg (0.55 mmol) of 2-(3-(10,15,20-tris(3,5-di-tert-butylphenyl)porphyrin-5-yl)phenoxy)ethan-1-ol was dissolved in 10 ml of dichloromethane . To this solution 44 mg (0.2 mmol) of $Zn(OAc)_2 \bullet 2H_2O$ was added, and the rm was stirred overnight. The rm was washed with water (2×10 ml), and the product was purified by flash chromatography on Silica 60 (50 ml of sorbent, eluted with $CHCl_3$). Yield 55 mg, 92%.

HRMS (ESI-TOF): [M+] calcd for $C_{70}H_{80}N_4O_2Zn$ 1072.5573; found 1072.5546

^{1}H NMR (500 MHz, $CDCl_3$, TMS): 9.00 (s, 4H, 12,13,17,18-H), 8.98-8.94 (m, 4 H, 2,3,7,8-H), 8.08 (m, 6H, 2,5-H@10,15,20-phenyls), 7.84 (d, J=7.6 Hz, 1H, 6-H@5-phenyl), 7.78 (br s, 3H, 4-H@10,15,20-phenyls), 7.75 (br s, 1H, 2-H@5-phenyl), 7.6 (t, J=7.6 Hz, 1 H, 5-H@5-phenyl), 7.28-7.25 (m, 1H, 4-H@5-phenyl), 4.06 (t, J=4.6 Hz, 2H, 2-CH_2), 3.82-3.73 (m, 2H, 1-CH_2), 1.81 (t, J=6.1 Hz, 1H, OH), 1.52 (s, 18H, H-tBu), 1.51 (s, 36 H, H-tBu)

^{13}C NMR (126 MHz, $CDCl_3$, TMS): 156.83, 150.53, 150.49, 150.43, 149.97, 148.61, 144.53, 141.89, 132.39 (β-pyrrole), 132.34 (β-pyrrole), 132.23 (β-pyrrole), 131.69, 129.78, 129.68, 127.92, 127.47, 122.72, 122.54, 120.84, 120.62, 120.17, 114.06, 69.11, 61.42, 35.13, 31.85 ppm

[2-(3-[10,15,20-tris(3,5-di-tert-butylphenyl)porphyrin-5-yl-N^{21},N^{23}]phenoxy]ethanolato(2-)]platinum

A total of 20 mg (0.02 mmol) of 2-(3-(10,15,20-tris(3,5-di-tert-butylphenyl)porphyrin-5-yl)phenoxy)ethan-1-ol and 30 mg (0.11 mmol) of $PtCl_2$ was suspended in 15 ml of benzonitrile in a 40 ml vial under septum. The vial was vacuumed down to 3.2 mbar and filled up with argon; the procedure was repeated twice. The rm was stirred at 178 degC for 15 h. The solvent was removed on a rotavapor, the dry product was dissolved in dichloromethane and purified twice by preparative TLC (20×20 cm plate Merck Silica 60 on aluminium sheet, eluent CH_2Cl_2). Yield 15 mg, 71%.

HRMS (ESI-TOF): [M+] calcd for $C_{70}H_{80}N_4O_2Pt$ 1202.5908; found 1202.5938.

^{1}H NMR (500 MHz, CHLOROFORM-D) δ 8.85-8.72 (m, 8H), 8.06-7.94 (m, 6H), 7.81-7.74 (br s, 4H), 7.74-7.72 (m, 1H), 7.61 (t, J = 8.0 Hz, 1H), 7.31 (dd, J = 8.0, 1.9 Hz, 1H), 4.25 (t, J = 4.2 Hz, 2H), 4.02 (t, J = 4.6 Hz, 2H), 1.54-1.45 (br s, 56H)

^{13}C NMR (126 MHz, CHLOROFORM-D) δ 157.13, 148.92, 143.14, 141.13, 141.04, 140.59, 140.54, 131.07, 130.99, 130.90, 130.38, 129.17, 129.06, 127.81, 127.33, 123.63, 121.17, 120.21, 114.37, 69.42, 61.65, 35.14, 31.82

2. Photophysical Measurements

a) Steady-state spectroscopy

All the measurements were carried out using freshly prepared dichloromethane (DCM) or PEG-200 solutions. UV-Vis absorption spectra were recorded using a Shimadzu UV-3600PC (Shimadzu, Japan) spectrophotometer with a 1-cm quartz cell. Molecular extinction coefficients of PtTPPOH and ZnTPPOH in both DCM and PEG-200 are summarized in the Table S1.

Table S1. Molar extinction coefficients of PtTPPOH and ZnTPPOH in DCM and PEG-200

Compound	DCM		PEG-200	
	λ_{max}	Value ($M^{-1}cm^{-1}$)	λ_{max}	Value ($M^{-1}cm^{-1}$)
ZnTPPOH	421	710000	427	689000
	549	26000	559	22000
	588	6500	599	11000
PtTPPOH	404	448000	405	438000
	511	42500	511	41000
	540	7700	539	11000

Steady-state fluorescence and phosphorescence spectra were recorded with a FLS1000 spectrofluorometer (Edinburgh Instruments, UK). Xe arch or μF flash lamp were utilized to obtain either fluorescence or phosphorescence spectra. Time-gating modality of FLS1000 was applied to discriminate fluorescence and phosphorescence spectra for ZnTPPOH.

Phosphorescence emission spectra for PtTPPOH and ZnTPPOH in PEG-200-oleic acid mixture was measured after 1 hour of N_2-purging upon excitation at their respective absorption maximums.

b) Phosphorescence lifetime measurement.

Phosphorescence lifetimes were measured using a FLS1000 equipped with μF flash lamp. PtTPPOH solutions in presence and absence of TTBPer were excited at 540 nm and ZnTPPOH's ones at 560 nm. The decays were monitored at the wavelengths of the sensitizers phosphorescence spectrum maximum . Depending on the resulting decays the frequency of the lamp was adjusted from 10 to 100 Hz. Phosphorescence lifetimes were calculated with Fluoracle software.

c) Stern−Volmer quenching experiments.

The Stern−Volmer constants (K_{SV}) and the bimolecular triplet-triplet energy transfer rate constants (k_{TTET}) were obtained using the dynamic quenching Stern−Volmer equation:

$$\boldsymbol{\tau}_0/\boldsymbol{\tau}_a = 1 + K_{SV}[Q] = 1 + k_{TTET}\boldsymbol{\tau}_0[Q] \qquad (1),$$

where $\boldsymbol{\tau}_0$ and $\boldsymbol{\tau}_a$ are the sensitizer emission intensities in the absence and presence of the quencher, respectively. K_{SV} is the Stern−Volmer quenching constant, k_{TTET} is bimolecular triplet-triplet energy transfer rate constant, and [Q] is the molar concentration of the quencher. The concentration of sensitizer was chosen to give an

absorbance of 0.1 at the excitation wavelength.

d) Upconversion fluorescence measurement.

The samples were prepared in a 1 cm^2 special optical glass cuvettes with screw cap and septum (Starna Scientific Ltd., UK). Deoxygenation was performed using nitrogen purging for ca. 1 hour. The concentration of sensitizer was adjusted to give an absorbance of 1.0 at the excitation wavelength, and the concentration of TTBPer was adjusted high enough to quench at least 90% of sensitizer's phosphorescence. Laser power density dependence experiments were performed by using Verdi-V6 532 nm second-harmonic Nd:YAG laser (Coherent Inc., USA). Laser beam was focused in ca. 800 µm spot. Spot size was measured by using LBP2-H2-Vis2 Laser Beam Profiler (Ophir-Silicon LLC, USA).

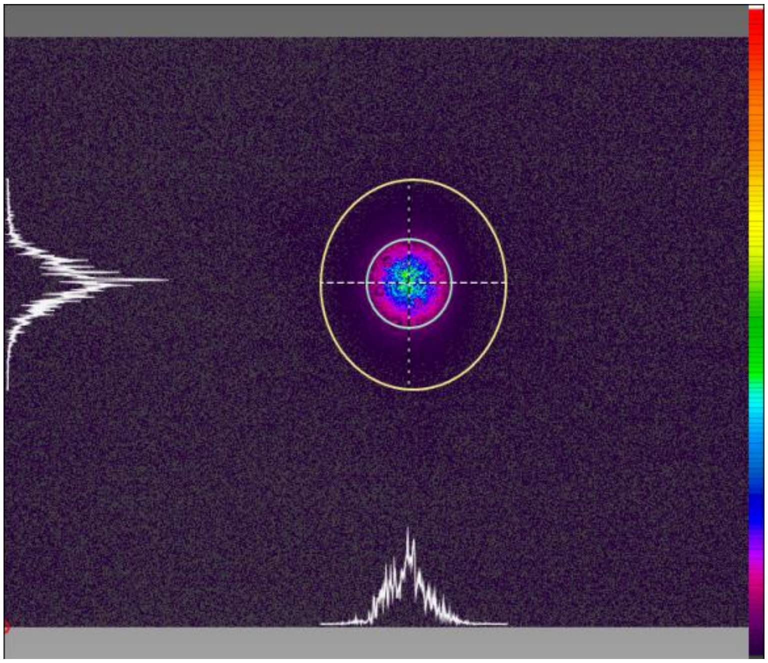

Fig. S1. 2D Beam display

Power meter head from Coherent Inc. was used to measure excitation power. An appropriate short-pass filter (520 nm) was mounted to filter the upconverted light. A set a neutral density filters was used to modulate the excitation power. Steady-state upconversion spectra were recorded on AvaSpec-2048 fiber-optic spectrometer (Avantes, Netherlands). FLS920 fluorimeter. The final emission intensities in these samples were corrected for the filter effects. The integrated emission intensities were plotted as a function of the measured excitation power density in double logarithmic fashion. Slopes of 1 and 2 were obtained corresponding to the weak and strong annihilation regimes, respectively (equation 2 and equation 3). The explanation of this behavior of upconversion intensity versus power density lies in the following equations and has been decribed in detail by Catellano and co-workers [1]:

$$I_{UC} = \frac{\Phi_{fl}^{A} k_{TTA} [A^3]^2}{2k_T} \qquad (2)$$

$$I_{UC} = \Phi_{fl}^{A} [A^3]^2 \qquad (3)$$

where k_T is the sum of all unimolecular and pseudofirst-order decay pathways for annihilator triplet state $[A^3]$, k_{TTA} is the bimolecular triplet-triplet annihilation rate constant, and $\Phi^{A}{}_{fl}$ is the annihilator fluorescence quantum yield. Thus, in the strong annihilation limit, the total upconversion intensity is linearly proportional to the laser power density and consequently to $[A^3]$, while for the weak annihilation regime it is proportional to $[A^3]^2$.

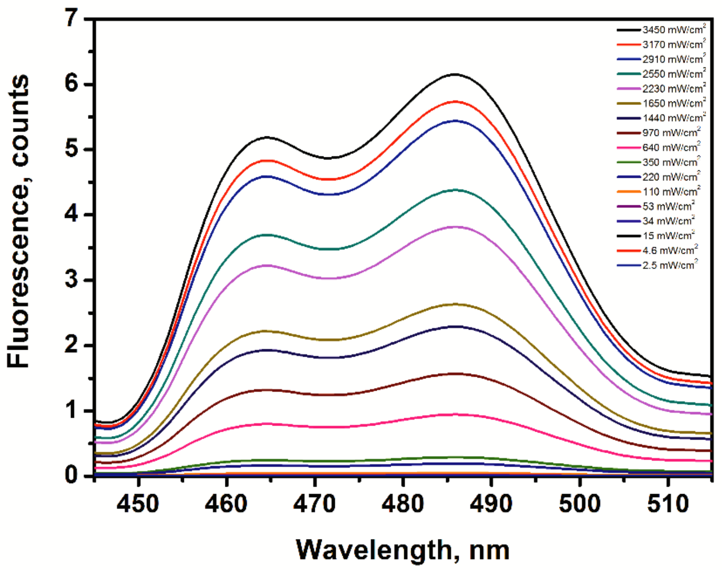

Fig. S2. Upconverted emission spectra of TTBper (3 mM) sensitized by PtTPPOH in deoxygenated PEG-OA solution.

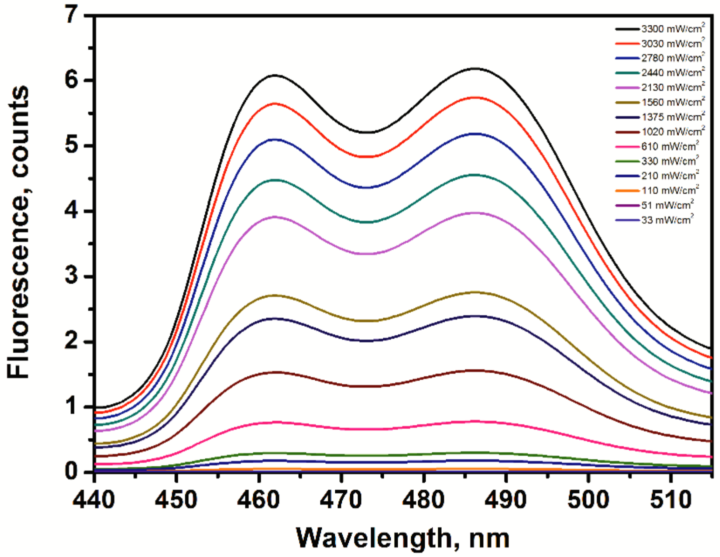

Fig. S3. Upconverted emission spectra of TTBper (3 mM) sensitized by ZnTPPOH in deoxygenated PEG-OA solution.

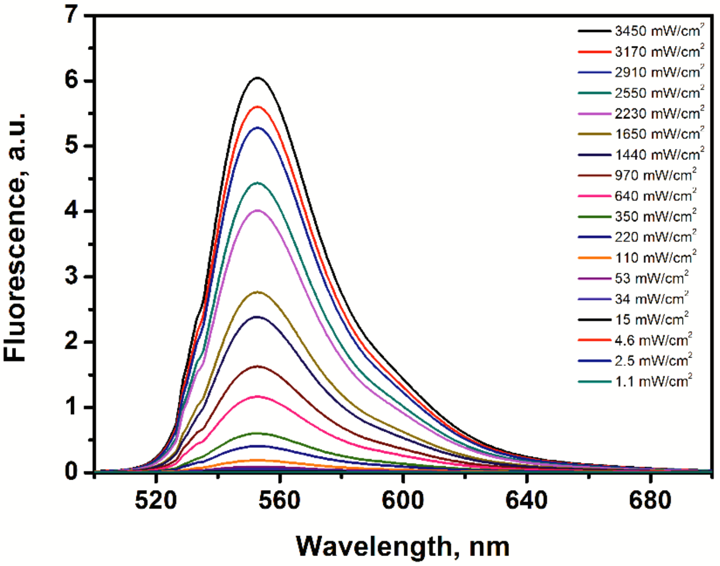

Fig. S4. Emission spectra of the Rhodamine 6G in ethanol upon 532 nm excitation.

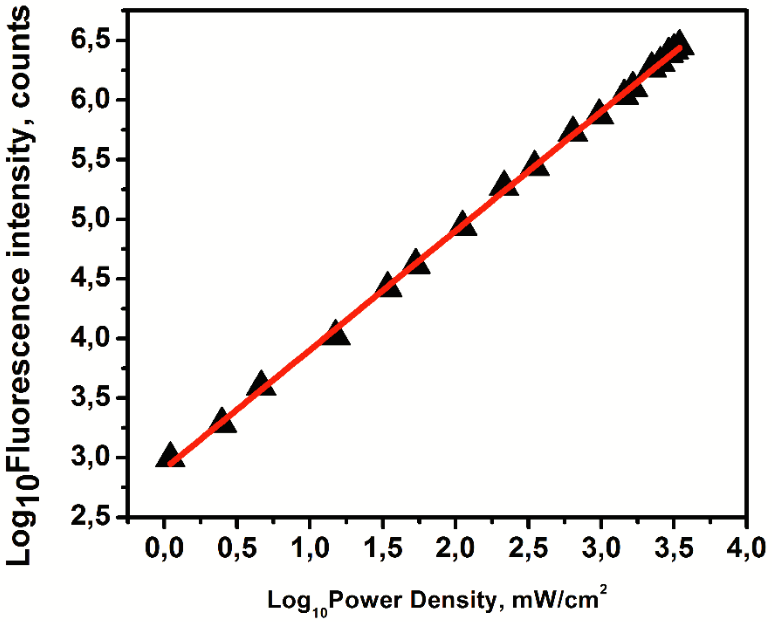

Fig. S5. Double-logarithmic plot of the Rhodamine 6G fluorescence in respect to laser power density.

e) Upconversion quantum yield calculations

For these measurements we focused the laser spot onto the edge of a 1 cm^2 cuvette to minimize the path length for the emitted light. Then, emission spectra were corrected using the equation to take into account all the types of inner filter effects[2]:

$$\frac{F_0}{F} = \frac{2{,}303 \times D_m \times \Delta l_m}{10^{-D_m \times l_m} \times (10^{D_m \times \frac{\Delta l_m}{2}} - 10^{-D_m \times \frac{\Delta l_m}{2}})} \qquad (4)$$

where F_0 is the corrected fluorescence intensity, F is the observed fluorescence intensity, D_m is the optical density at the emission wavelength, Δl_m is diameter of the laser spot, and l_m is the distance between the center of the laser spot and the edge of the cuvette (i.e. the path length of the emitted light).

Upconversion quantum yields Φ_{UC} were calculated by using dilute Rhodamine 6G (R6G) in ethanol as a reference (Φ_{fl} = 95%)[3] according to following equation:

$$\Phi_{UC} = 2\Phi_{std} \left(\frac{A_{std}}{A_{UC}}\right) \left(\frac{I_{UC}}{I_{std}}\right) \left(\frac{\eta_{UC}}{\eta_{std}}\right)^2 \qquad (5)$$

where Φ_{std} is the fluorescence quantum yield of the standard (Rhodamine 6G), I is the integrated emission intensity of the standard or upconversion solutions, A is the absorbance of the standard and upconversion solutions at 532 nm, and η is the refractive index of the solvents used. Two absorbed photons are needed to generate one emitted photon through TTA; therefore, the factor of 2 is included in eq 5 to make the theoretical maximum quantum yield unity rather than 0.5. Quantum yields were measured under optimized experimental conditions (linear response regime and $\Phi_{TTET} \geq 90\%$).

References

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3 R. F. Kubin and A. N. Fletcher, *J. Lumin.*, 1982, **27**, 455–462.