Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

A green solvent for operating highly efficient low-power photon upconversion in air

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Experimental Section

General: All reagents and solvents were used as received without further purification unless otherwise indicated. Platinum(II)-octaethylporphyrin (PtOEP), 9,10-diphenylanthracene (DPA) and 9,10-bisphenylethynylanthracene (BPEA) were purchased from J&K. Platinum(II)-tetraphenyltetrabenzoporphyrin (PtTPBP) was purchased from Frontier Scientific. D-limonene was purchased from Sigma Aldrich. Citronellol, Geraniol, Linalool, Nerol, Squalene, Myrcene, alpha-Pinene, L(-)-Carvone were purchased from Aladdin. Spectroscopic samples were placed in a 1 cm path length quartz cuvette. For luminescence lifetime tests, samples were bubble-degassed with nitrogen gas for at least 30 min, or by photochemical deoxygenation with a 532 nm CW laser. Absorption spectra were measured using a SHIMADZU UV-2600 spectrophotometer. The Photoluminescence decay curves were performed on an Edinburgh FLS-920 instrument using single photon counting measurement (Samples were irradiated by a modulated pulse laser excitation obtained by the SuperK EXTREME supercontinuum white light lasers, NKT Photonics). Noncoherent solar light (AM 1.5G) was achieved by a Solar Simulator (Newport 94043A). Static emission spectra were collected from FLS-920 spectrofluorometer (Edinburgh Instruments). Photographs were taken with an Olympus digital camera.

TTA-UC Power Dependence Experiment: The TTA-UC photoluminescence detected from FLS-920 spectrofluorometer was a result of a continuous laser-beam excitation from a 532 nm green laser (MLL-III-532, Changchun New Industries Optoelectronics Tech, Co., Ltd.) attenuated by a neutral density filter. Laser power was measured with a power meter (VLP-2000 20 mW, Beijing Ranbond Technology Co., Ltd.). The concentration of the UC pair was 1×10^{-4} M for PtOEP and 1×10^{-2} M for DPA. The power dependence data were plotted as a double logarithmic graph showing the integrated upconverted emission (390-525 nm) as a function of incident power densities.

Deoxygenation Cycling Experiment: PtOEP/DPA/D-limonene solution was placed in a quartz cuvette. Air was bubbled into the solution intermittently. The UC spectra were recorded while the bubbling (UC minimum) and after the deoxygenation process (UC maximum) in each cycle.

The Yield of the Triplet-Triplet Energy Transfer $\Phi_{\mathrm{TT\text{-}ET}}$ and Predicted Lifetimes of Sensitizer in D-limonene UC Pair: The $\Phi_{\mathrm{TT\text{-}ET}}$ was calculated by using Eq.S1 and predicated lifetimes of sensitizer in D-limonene UC pair was calculated by using Eq.S2 (PtOEP=1×10^{-5} M, DPA=2×10^{-3} M).

$$\Phi_{\mathrm{TT-ET}} = 1 - \frac{I_{\mathrm{S/E}}}{I_{\mathrm{S}}} \qquad \text{Eq.S1}$$

Where $I_{\mathrm{S/E}}$ and I_{S} represent integrated PL intensity of sensitizer in the prescence and absence of emitter.

$$\tau_{\mathrm{S/E}} = (1 - \Phi_{\mathrm{TT-ET}}) \times \tau_{\mathrm{S}} \qquad \text{Eq.S2}$$

Where $\tau_{\mathrm{S/E}}$ and τ_{S} (12.73 μs) represent the lifetimes of sensitizer in the presence and absence of emitter, $\Phi_{\mathrm{TT\text{-}ET}}$ was achieved in Eq.S1.

Quantum Yield Measurements: Upconversion quantum yield (UCQY) of PtOEP/DPA dissolved in D-limonene was measured relative to the fluorescence QY of rhodamine 6G in ethanol (Φ_{std} = 0.95).[1] Upconverting D-limonene solution was prepared in 1 cm^2 quartz optical cell. The concentrations of sensitizer and emitter were 1.25×10^{-5} M and 2×10^{-3} M respectively. The emission spectra were collected with the FLS-920 fluorometer. The UCQY was calculated using Eq.S3.[2]

$$\Phi_{\text{uc}} = 2\Phi_{\text{std}}\left(\frac{A_{\text{std}}}{A_{\text{uc}}}\right)\left(\frac{I_{\text{uc}}}{I_{\text{std}}}\right)\left(\frac{\eta_{\text{uc}}}{\eta_{\text{std}}}\right)^2 \qquad \text{Eq.S3}$$

Where Φ, A, I, and η represents the quantum yield, absorbance at λ_{ex} (532 nm), integrated photoluminescence spectral profile, and refractive index of the medium (1.36 for ethanol, 1.474 for D-limonene) respectively. The corresponding terms for the subscript "std" are for the reference quantum counter, rhodamine 6G, in ethanol at the identical excitation wavelength. The fluorescence of the standard solution and the upconverted emission spectra of UC solution were integrated over 500-680 nm for rhodamine 6G and 390-525 nm for DPA to calculate quantum yield. Two absorbed photons are needed to generate one emitted photon through TTA; therefore, the factor 2 is included in Eq.S3 to make the theoretical maximum quantum yield unity rather than 50%.

Determination of the Bimolecular Quenching Constant According to the Smoluchowski theory: The diffusion-controlled bimolecular rate constant (k_0) was calculated using the Smoluchowski Equation (Eq.S4).[3]

$$k_0 = 4\pi RDN/1000 = \frac{4\pi N}{1000}(R_{\text{S}} + R_{\text{E}})(D_{\text{S}} + D_{\text{E}}) \qquad \text{Eq.S4}$$

Where R is the collision radius, D is the sum of the diffusion coefficients of the sensitizer (D_{S}) and emitter (D_{E}), and N is Avogadro's number. The collision radius is generally assumed to be the sum of the molecular radii of the sensitizer (PtOEP: R_{S} = 8.7 Å) and emitter (DPA: R_{E} = 4.5 Å).[4] The factor of 1000 is necessary to keep the units correct when the concentration is expressed in terms of molarity. The term $N/1000$ converts molarity to molecules/cm^3. Diffusion coefficients were obtained from the Stokes-Einstein equation (Eq.S5).[3]

$$D = kT/6\pi\eta R \qquad \text{Eq.S5}$$

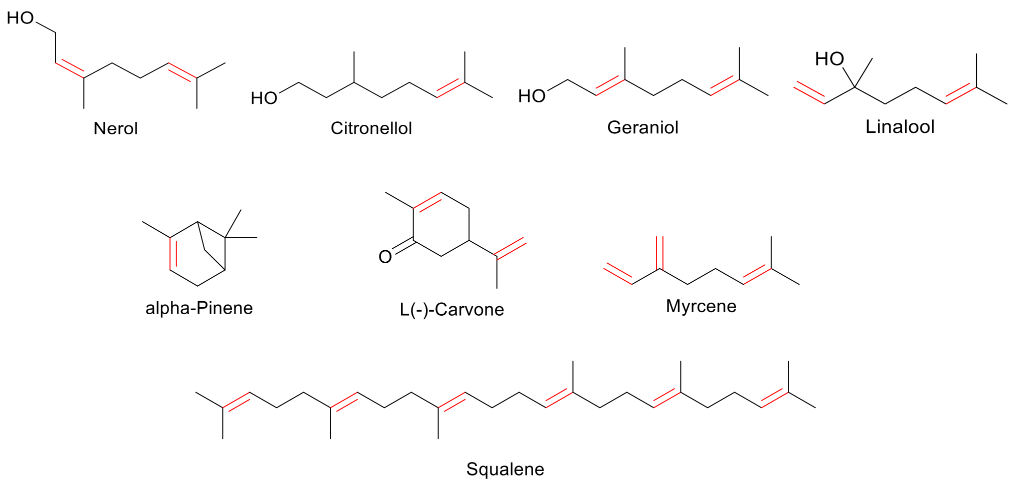
Where k is Boltzmann's constant, η is the solvent viscosity (D-limonene: 0.95 cP), and R is the molecular radius, T=298 K.

Determination of the Bimolecular Quenching Constant According to Stern-Volmer Equation :

$$\frac{F_0}{F} = 1 + K_{\text{q}}\tau_0[C_{\text{E}}] \qquad \text{Eq.S6}$$

Where F_0 represents integrated PL intensity of sensitizer in the absence of emitter. F represents the integrated PL intensity of sensitizer in the presence of emitter. K_{q} is quenching rate under a selected concentration of sensitizer in the presence of emitter (PtOEP=1×10^{-5} M, DPA=2×10^{-3} M). The lifetimes in the absence (τ_0 =12.73 μs) of emitter is acquired by tested PL decay of sensitizer in the absence of emitter. [C_E] is the concentration of emitter (DPA=2 × 10^{-3} M).

Chart S1. Selected natural solvents for TTA-UC function in air. Unsaturated carbon-carbon double bond of terpene-based solvents molecular structures were marked red.



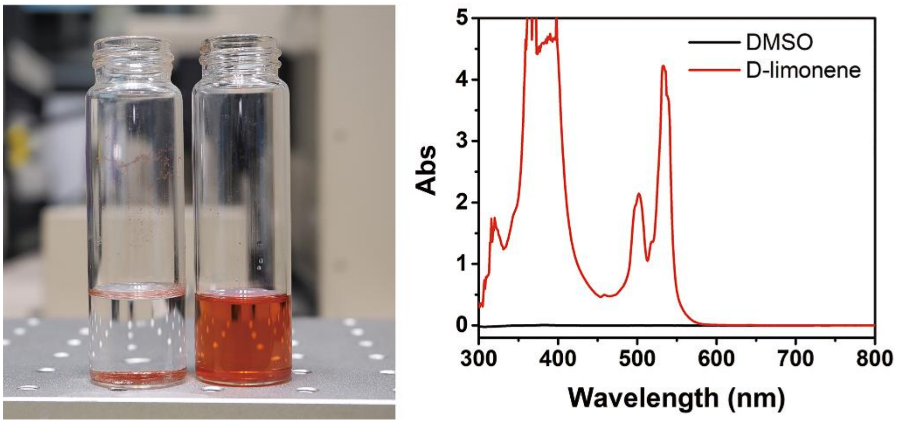


Fig. S1 Absorption spectrum of PtOEP/DMSO and PtOEP/D-limonene reflected the solubility of sensitizer (PtOEP) in DMSO and D-limonene. The left picture indicated that the D-limonene has good solubility compared to DMSO. All samples are directly prepared without any cosolvent.

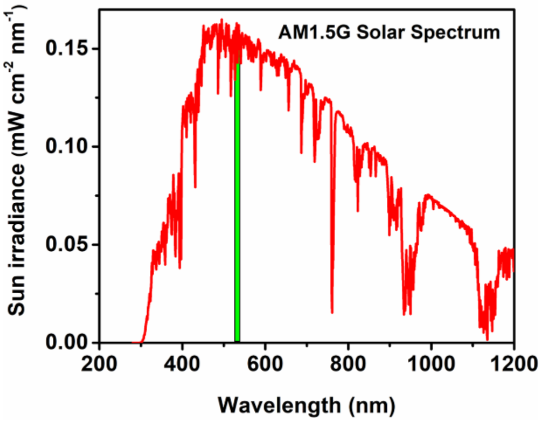


Fig. S2 Air-mass 1.5 global (AM1.5G) standard solar spectrum. The integrated irradiance supplied by the sun across the absorption spectrum of the PtOEP sensitizer (527-537 nm, green area) is 1.54 mW cm^{-2}.

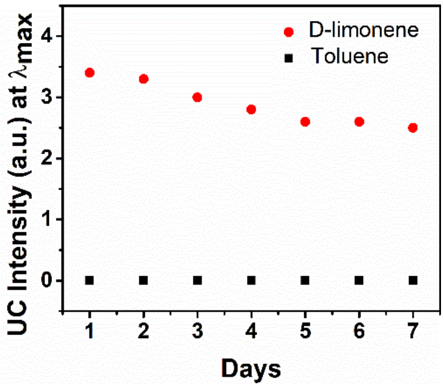


Fig. S3 Time dependence of UC emission intensity at λ_{max} = 430 nm of DPA/PtOEP in D-limonene (red circle) and toluene (black square) (PtOEP = 1×10^{-4} M, DPA = 2×10^{-2} M, λ_{ex} = 532 nm). All the samples were kept and measured in air at room temperature.

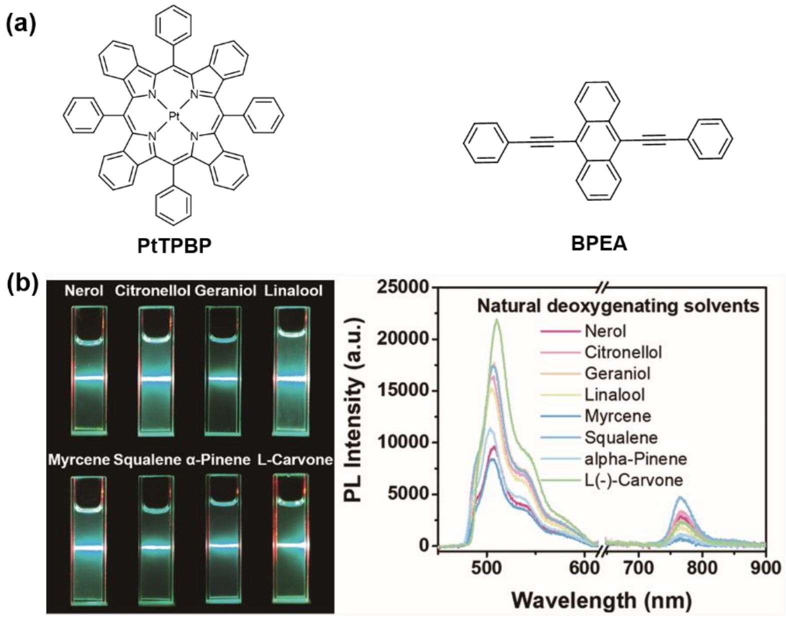


Fig. S4 (a) Molecular structures of PtTPBP and BPEA. (b) Photoluminescence spectra of BPEA/PtTPBP in natural deoxygenating solutions upon excitation at 635 nm in air. The left picture showed bright cyan UC emission in naturally protic and aprotic solvents. The stray laser light has been removed for clarity.

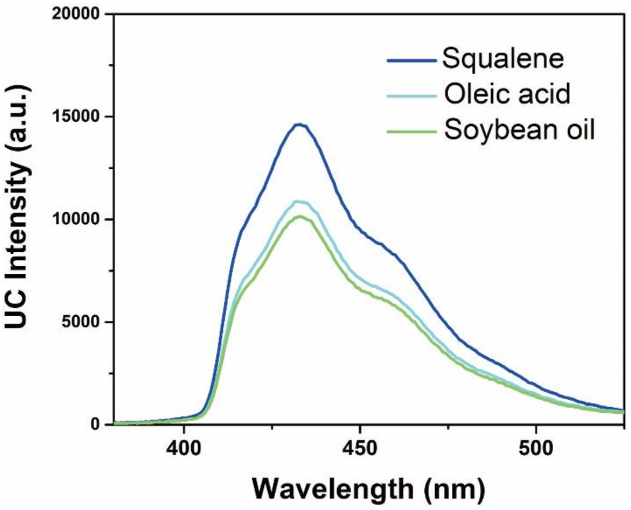


Fig. S5 A potential bioimaging application of an alternative terpene-based solvent (squalene). For clear observation of organism, the UC intensity are important in order to increase contrast. The oleic acid and soybean oil were selected to compare the UC intensity to a terpene-based solvent (squalene).

Table S1. Upconversion quantum yield of BPEA/PtTPBP in natural deoxygenating solvents at different conditions. The UCQY of red-green UC dye pair was calculated using Eq.S3.

solvent	Φ_{UC} N_2 (%)	Φ_{UC} air (%)
Nerol	10.9	12.5
Citronellol	20.3	20.4
Geraniol	24.2	20.7
Linalool	19.1	21.1
Myrcene	14.4	13.6
Squalene	22.6	23.0
Alpha-Pinene	16.6	16.5
L(-)-Carvone	26.4	26.4

Upconversion quantum yields (UCQY) of BPEA/PtTPBP (PtTPBP： 1×10^{-5} M, BPEA： 1×10^{-3} M) dissolved in different natural solvents were measured relative to the fluorescence QY of methylene blue cation in water (0.04). Refractive index of water and these selective natural solvents are 1.33 for water, 1.474 for Nerol, 1.456 for Citronellol, 1.474 for Geraniol, 1.462 for Linalool, 1.469 for Myrcene, 1.494 for Squalene, 1.465 for alpha-Pinene and 1.498 for L(-)-Carvone. All the red-to-green UC dye pair in selective natural solvents were irradiated by a modulated pulse laser excitation at the same testing conditions (635 nm, 20mW).

Video S1 Dynamic oxygen scavenging process in the cycles of air-bubbled PtOEP/DPA/D-limonene solution under 532 nm CW laser irradiation.

Video S2 Air-stable noncoherent UC in PtOEP/DPA/D-limonene solution under irradiation of a solar simulator.

Video S3 Dynamic oxygen scavenging process in the cycles of air-bubbled PtTPBP/BPEA/D-limonene solution under 635 nm CW laser irradiation.

References

1 M. Douglas, W. Roger and S. P. G., *Photochem. Photobiol.*, 2002, **75**, 327-334.
2 J. H. Kim and J. H. Kim, *J. Am. Chem. Soc.*, 2012, **134**, 17478-17481.
3 J. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer US, 2006.
4 A. Monguzzi, R. Tubino and F. Meinardi, *Phys. Rev. B*, 2008, **77**, 155122.