

Supplementary Information

Thermoresponsive low-power light upconverting polymer nanoparticles

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Experimental section

Materials. ϵ -caprolactone was stirred over CaH_2 overnight, distilled under reduced pressure and stored in a glovebox under nitrogen atmosphere. 9-Bromo-10-phenylanthracene (**1**) and (4-(10-phenylanthracen-9-yl)phenyl)methanol (**2**) were synthesized following a previously reported procedure.^{1,2} All other reagents were purchased from Sigma Aldrich and were used as received.

Methods. ^1H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra were recorded on a Bruker Ascend 400 in CDCl_3 (from Cambridge Isotope Laboratories). The signal of residual CHCl_3 (^1H -spectra: δ 7.26 ppm, ^{13}C -spectra: δ 77.16 ppm) was used as reference and the end-group analysis experiments were performed using a relaxation delay time of 5 seconds to ensure the relaxation of all protons. The number-average molecular weights (M_n) were determined using end-group analysis and compared to MALDI-TOF mass spectroscopy results that were carried out on a MALDI-TOF ultrafleXtreme spectrometer from Bruker. A Polymerix software from Sierra Analytics was used for the data analysis and allowed calculating the weight-average molecular weight (M_w) and the molar mass dispersity (D_M) of the polymers. Size-exclusion chromatography (SEC) experiments were performed on a series 1200 HPLC system equipped with a 5 μm PLgel mixed guard column and two 5 μm PLgel mixed-D columns from Agilent. The data were recorded using an Optilab REX interferometric refractometer (Wyatt Technology Corp.) and a UV detector. An Astra software (Wyatt Technology Corp.) was used for the data analysis and the average molecular weights as well as polymer molar mass dispersities were determined against poly(styrene) standards ($M_p = 2,340\text{-}275,300 \text{ g mol}^{-1}$).

Thermogravimetric analysis (TGA) data were recorded on Mettler-Toledo STAR thermogravimetric analyzer from 25 to 500 °C at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. The decomposition temperature corresponding to 5 % weight loss, T_d , is reported. Differential scanning calorimetry (DSC) measurements were performed using a Mettler-Toledo DSC 2 system under nitrogen atmosphere from -80 to 100 °C with a heating and cooling rate of 10 °C min⁻¹. The reported data for the melting points (T_m) of organic compounds were obtained from the first-heating cycle and for polymeric species the thermal history was suppressed by extracting the values from the second heating cycle.

DPA-PCL-OH, 3. A flame-dried 10 mL microwave vial was charged with **2** (0.32 g, 0.9 mmol) and ϵ -caprolactone (0.71 mL, 6.4 mmol) under nitrogen atmosphere. The vial was sealed, placed in an oil bath at 110 °C and the reaction mixture was stirred for 15 min in order to obtain a clear yellow solution. Two drops of tin(II) 2-ethylhexanoate (Sn(oct)₂) were added and the resulting solution was stirred under argon atmosphere for 3 h at 110 °C. The reaction mixture was cooled in an ice-bath and diluted with dichloromethane (2 mL) at room temperature. The product was then precipitated into cold stirring diethyl ether (300 mL) and recovered by *vacuum* filtration. The product was dried overnight *in vacuo* at 40°C and obtained as an off-yellow solid (0.54 g, 51 %). ¹H NMR (400 MHz, CDCl₃, δ): 7.68-7.31 (m, 17H, ArH), 5.31 (s, 2H, Ar-CH₂), 4.07-4.04 (t, 25H, -CH₂CH₂O-), 3.66-3.63 (t, 2H, -CH₂CH₂OH), 2.50-2.46 (t, 2H, DPA-CH₂-CO₂CH₂CH₂-), 2.32-2.28 (t, 25H, -CO₂CH₂CH₂-), 1.67-1.60 (m, 50H, -CH₂CH₂CH₂CH₂CH₂-), 1.39-1.36 (m, 25H, -CH₂CH₂CH₂-). ¹³C NMR (101 MHz, CDCl₃, δ): 173.67, 139.22, 139.13, 137.45, 136.59, 135.42, 131.70, 131.42, 129.98, 128.56, 128.31, 127.64, 127.16, 126.93, 125.22, 125.15, 66.22, 64.28, 62.80, 34.25, 32.43, 28.48, 25.66, 25.42, 24.76, 24.71.

Preparation of nanoparticles. A representative procedure, which was adapted from a previously reported protocol³ is provided for **3**/PtOEP nanoparticles:

Compound **3** (25 mg, 14.3 μmol) was dissolved in dichloromethane (1.9 mL) and an aliquot of a 0.32 mM PtOEP solution in dichloromethane (0.12 mL, $3.72 \cdot 10^{-8}$ mol) was added. After stirring the mixture for 5 min, an aqueous solution of sodium dodecyl sulfate (SDS) (5 mL, 3 mg mL⁻¹) was added, the mixture was stirred for another 5 min in order to form a pre-emulsion, and finally sonicated for 10 min using a Hielscher sonicator UP 400S at 60% intensity and cycles of 0.5 s pulses and 0.5 s delays. The dichloromethane was subsequently removed under reduced pressure under gentle stirring and milli-Q water was added so that the volume reached 5 mL and the nanoparticle concentration was 5 mg mL⁻¹ (2.86 $\mu\text{mol mL}^{-1}$). PCL/PtOEP and PCL nanoparticles were synthesized by replacing **3** with poly(ϵ -caprolactone) diol ($M_n = \sim 2,000$ g mol⁻¹, Sigma Aldrich) in presence and in absence of the sensitizer, respectively. A control experiment was performed by replacing **3** by **2** (4.3 mg, 12.0 μmol) to study the particle formation in the absence of polymer; however no stable suspension was obtained.

Nanoparticle characterization. *Dynamic light scattering (DLS).* The nanoparticle suspensions were diluted with Milli-Q water to a concentration of ~ 0.5 mg mL⁻¹ and filtered through 0.45 μm PVDF filters. Measurements were performed in cylindrical glass cells at 90° scattering angle for 120 s at 25 °C using a commercial goniometer instrument (3D LS Spectrometer, LS Instruments AG, Switzerland) equipped with a collimated laser beam ($\lambda = 660$ nm). The auto-correlation functions were fitted to a Schultz-Zimm distribution^{4,5} in order to obtain the mean diffusion coefficient and the polydispersity (std/mean). The Stokes-Einstein relation was used to determine the average hydrodynamic radius of the nanoparticles from the mean diffusion coefficient, a solid-sphere morphology was assumed, and the number-weighted distributions were determined using a previously described procedure.³

Cryogenic Transmission Electron Microscopy (CryoTEM). The samples were deposited (5 μL) on a carbon-coated copper grid (Lacey carbon film grids, Plano GmbH). The liquid was

removed by blotting with filter paper (Whatman qualitative filter paper, grade 1) before dropping the sample into a liquid ethane bath that was cooled by liquid nitrogen. After vitrification the specimen were immediately transferred to a Gatan (Pleasanton, California, USA) 626 cryo transfer holder and analyzed in a FEI Tecnai Spirit (Hillsboro, Oregon, USA) at 120 kV equipped with a 4k Eagle CCD device. Recording was done using serialEM⁶ at an electron dose of 100 e⁻/Å or lower.

Optical experiments. Optical measurements were conducted in QS Quartz SUPRASIL cuvettes (length pass = 1 mm, volume = 350 μL from Hellma Analytics) without any specific sealing procedure and the samples were excited using a 150 mW 532 nm Nd:YAG duplicated laser from Roithner Lasertechnik equipped with a laser line filter (532 nm, FWHM = 10 nm, FL532-10 from Thorlabs). The excitation laser beam has a Gaussian shape and the spot diameter which contains 90% of the intensity was 340 μm. The shape and the spot size were determined using the knife-edge method. The CW photoluminescence signals were recorded using a nitrogen-cooled CCD coupled with a double monochromator Triax-190 (Horiba Jobin Yvon), which has a spectral resolution of 0.5 nm and the recorded spectra were corrected for the setup optical response. The excitation power density was controlled with a variable neutral density filter (NDC-50C-2M-A from Thorlabs) and monitored with an optical power-meter (Thorlabs PM100USB with photodiode power sensor S120VC). The time-resolved PL experiments were performed using a square-wave modulated excitation laser with a temporal resolution < 0.2 μs and the spectra of the samples and of the DPA standard solution were detected in photon-counting mode using a Edimburgh L900 Flash Photolysis setup, which has a temporal resolution < 1 ns. The upconversion luminescence quantum efficiency of the polymeric upconverting nanoparticles was determined against a standard solution of DPA-PtOEP dye pair in deoxygenized tetrahydrofuran ([DPA] = 10 mM, [PtOEP] = 100 μM, $\Phi_{std} = 0.26$) according to:

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

where Φ_{UC} is the quantum yield, A_{uc} is the absorbance at the excitation, I_{uc} is the integrated upconverted photoluminescence spectral profile, P_{uc} is the excitation power density and η_{uc} is the refractive index of the medium. The theoretical maximum UC quantum efficiency is 0.50 since the *s*TTA-UC process uses two low energy photons to produce one higher energy photon. For comparison, the Φ_{UC} was measured by using an integrating sphere (Labsphere) according to the method reported by de Mello *et al.*⁷ UV-vis absorption spectra were recorded on a Cary Varian or a Shimadzu UV-2401PC spectrophotometer.

Kinetics of delayed fluorescence upon *s*TTA

According to Cheng *et al.*, the equation describing the evolution of the *s*TTA-UC intensity is:

$$DF_{UC}(t) = [T]^2 \left(\frac{1 - \phi_{TTA}}{\exp[k_T t] - \phi_{TTA}} \right)^2,$$

where ϕ_{TTA} , T , and k_T are the TTA yield, the triplet density and the triplet spontaneous decay rate, respectively.

Note about the evaluation of molecular weight

The value calculated by end-group analysis matches well the one obtained by MALDI-TOF spectroscopy. Although the molecular weight determined by SEC via comparison against poly(styrene) standards may be slightly overestimated (the assumption that both polymers of a given length have the same hydrodynamic volume is most probably not correct), this method was deemed more reliable than the data obtained by SEC-LS, since the refractive index increment (dn/dc) is not necessarily constant for short polymers and was not known for the material investigated.⁸

Table S1. Molecular weight data measured by ^1H NMR end-group analysis, MALDI-MS and SEC against poly(styrene) standards for polymer **3**.

Polymer	M_n (NMR)	M_n MALDI	M_n (SEC)	M_w (SEC)	\mathcal{D}_M
3	1,750	1,900	2,650	3,300	1.24

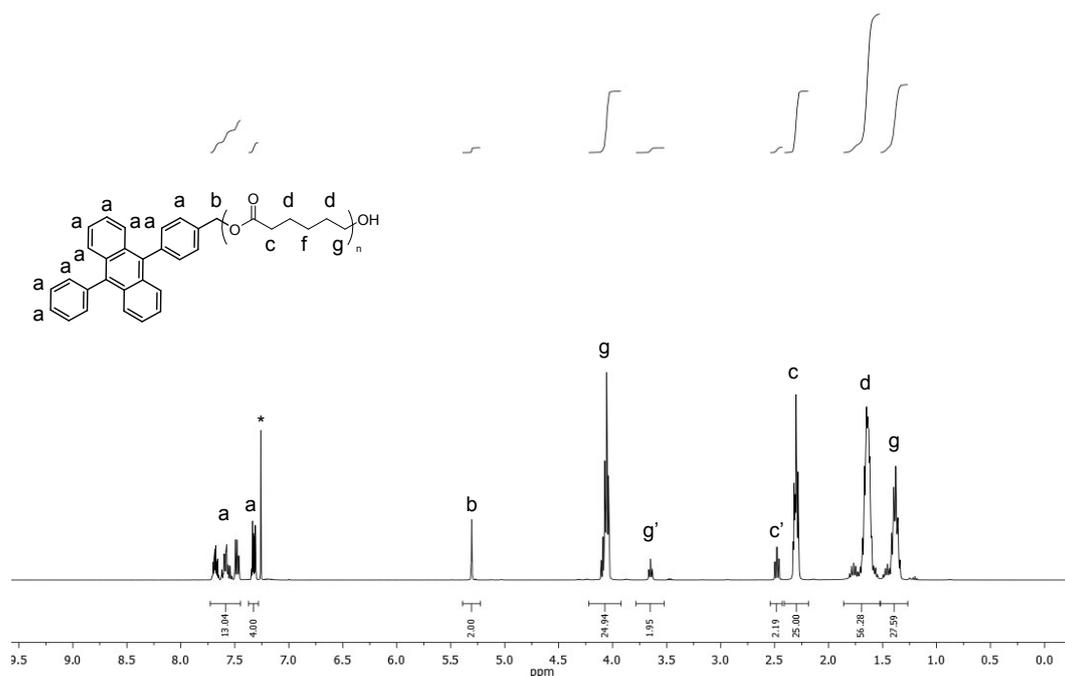


Fig. S1. ^1H NMR spectrum of DPA-PCL-OH, **3** (400 MHz, CDCl_3 , δ): 7.68-7.31 (m, 17H, ArH), 5.31 (s, 2H, Ar- CH_2), 4.07-4.04 (t, 25H, $-\text{CH}_2\text{CH}_2\text{O}-$), 3.66-3.63 (t, 2H, $-\text{CH}_2\text{CH}_2\text{OH}$), 2.50-2.46 (t, 2H, DPA- $\text{CH}_2-\text{CO}_2\text{CH}_2\text{CH}_2-$), 2.32-2.28 (t, 25H, $-\text{CO}_2\text{CH}_2\text{CH}_2-$), 1.67-1.60 (m, 50H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$), 1.39-1.36 (m, 25H, $-\text{CH}_2\text{CH}_2\text{CH}_2-$). Number-average molecular weight determined by end-group analysis, $M_n = 1,750 \text{ g mol}^{-1}$.

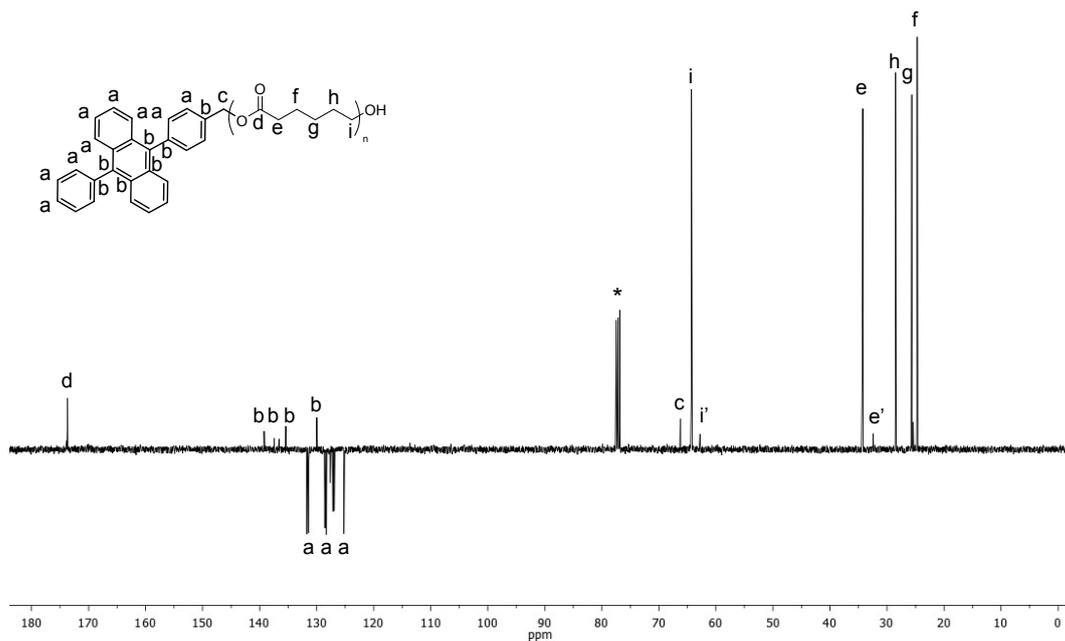


Fig. S2. ^{13}C NMR spectrum of DPA-PCL-OH, **3** (101 MHz, CDCl_3 , δ): 173.67, 139.22, 139.13, 137.45, 136.59, 135.42, 131.70, 131.42, 129.98, 128.56, 128.31, 127.64, 127.16, 126.93, 125.22, 125.15, 66.22, 64.28, 62.80, 34.25, 32.43, 28.48, 25.66, 25.42, 24.76, 24.71.

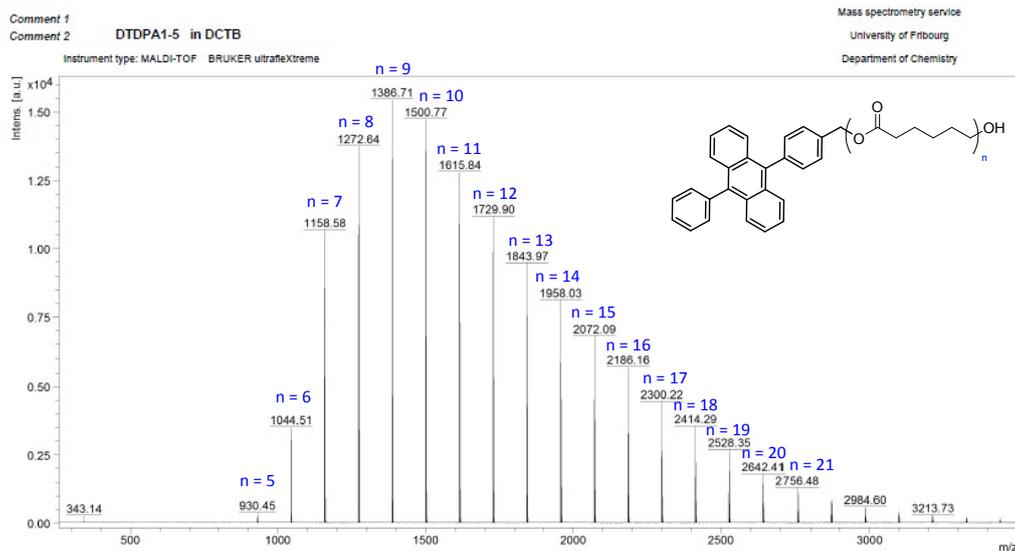


Fig. S3. MALDI-TOF mass spectrum of DPA-PCL-OH, **3**. Estimated number-average molecular weight, M_n , = 1,744 g mol^{-1} , weight-average molecular weight, M_w , = 1,899 g mol^{-1} , molar-mass dispersity, D_M = 1.09.

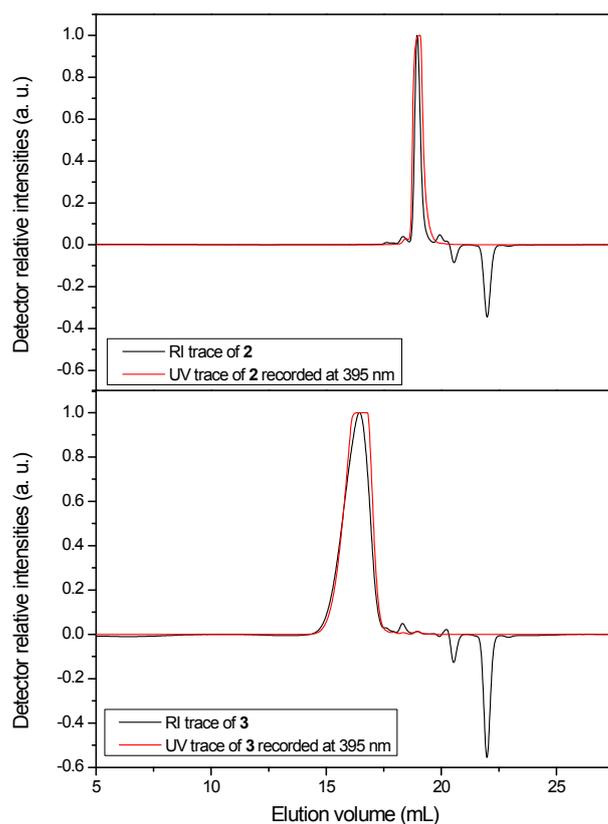


Fig. S4. Size exclusion chromatography (SEC) traces of (4-(10-phenylanthracen-9-yl)phenyl)methanol (**2**) (top) and DPA-PCL-OH (**3**) (bottom) in THF (1 mL min⁻¹). Traces of the differential refractive index (black) and of the UV detector (red, detection wavelength = 395 nm) are shown.

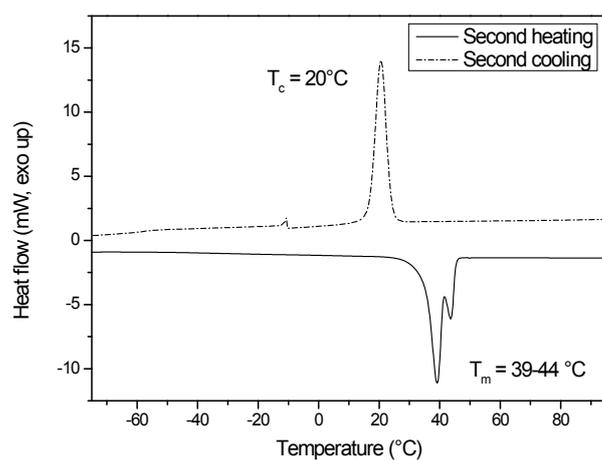


Fig. S5. Differential scanning calorimetry (DSC) curves of DPA-PCL-OH (**3**). The experiment was conducted with heating and cooling rates of 10 °C min⁻¹ under N₂ atmosphere and data from the second heating cycle are reported.

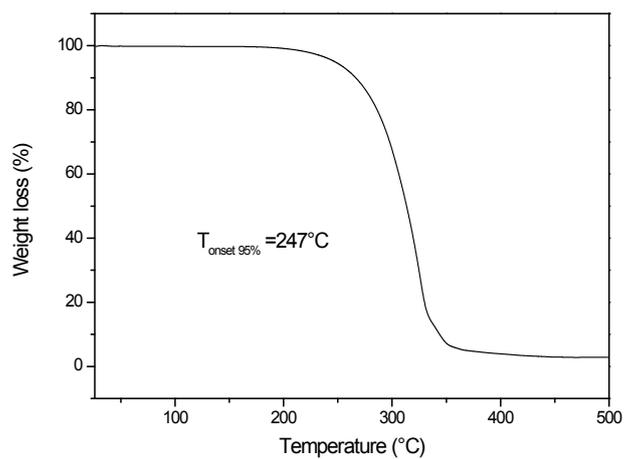


Fig. S6. Thermogravimetric analysis (TGA) traces of DPA-PCL-OH (**3**). The experiment was conducted at a heating rate of $10^{\circ}\text{C min}^{-1}$ under a N_2 atmosphere.

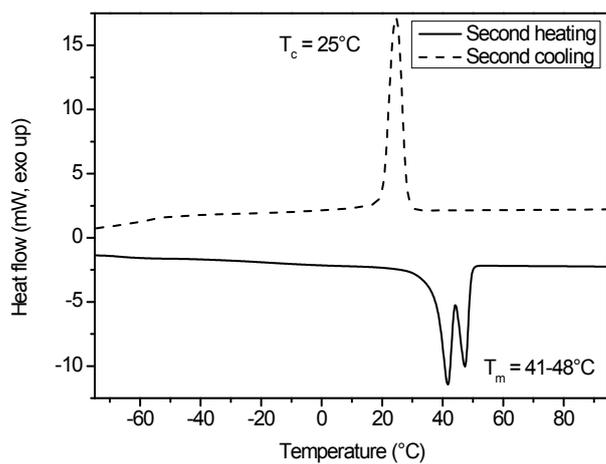


Fig. S7. Differential scanning calorimetry (DSC) curves of commercial PCL (Sigma Aldrich, $M_n = \sim 2,000 \text{ g mol}^{-1}$). The experiment was conducted at a heating rate of $10^{\circ}\text{C min}^{-1}$ under a N_2 atmosphere.

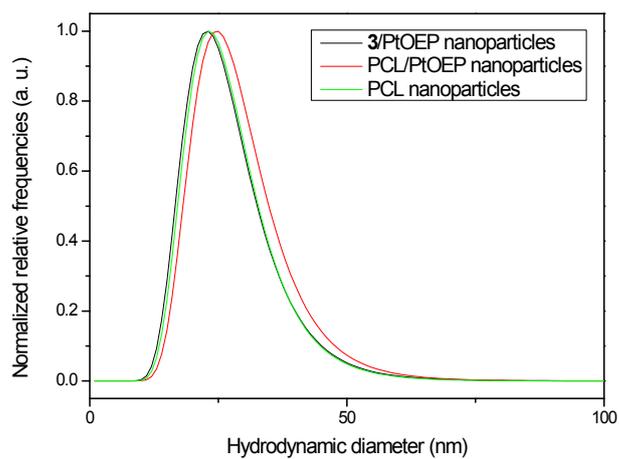


Fig. S8. Size distributions of **3**/PtOEP nanoparticles (black), PCL/PtOEP nanoparticles (red), and PCL nanoparticles (green) in dilute aqueous suspensions ($\sim 0.5 \text{ mg mL}^{-1}$) measured by DLS at a scattering angle of 90° . The distributions were converted to number-weighted distribution by assuming solid-sphere morphology.

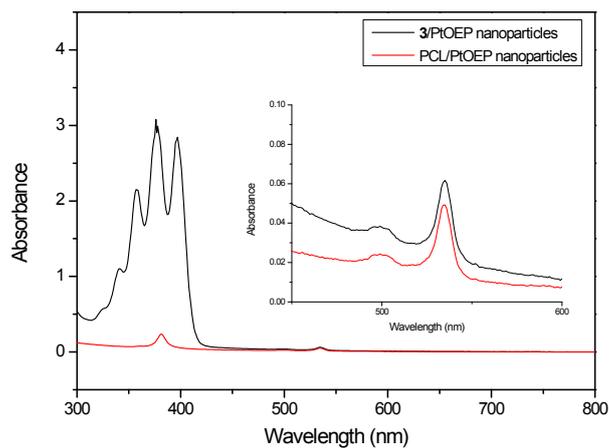


Fig. S9. Absorption spectra of **3**/PtOEP nanoparticle (black) and PCL/PtOEP nanoparticle (red) suspensions ($\sim 5 \text{ mg mL}^{-1}$) in a quartz cuvette with an optical path of 1 mm. The inset is a magnification showing the absorption peak used to excite (532 nm) the sensitizer.

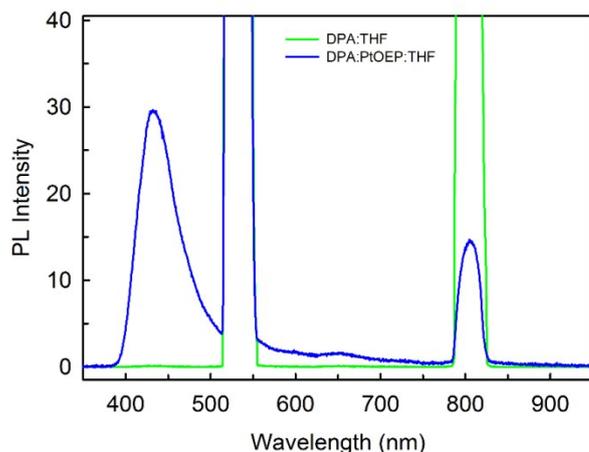


Fig. S10. Photoluminescence spectra of THF solutions of DPA/PtOEP (blue line) and DPA (green line) upon continuous wave laser (CWL) excitation at 532 nm (10 mW cm^{-2}). In absence of the light-harvesting sensitizer PtOEP, no blue luminescence can be observed. The stray-light signal at 800 nm comes is the residual emission of the diode used to pump the Nd:Yag crystal to produce the 532 nm laser light used as excitation source in our experiments.

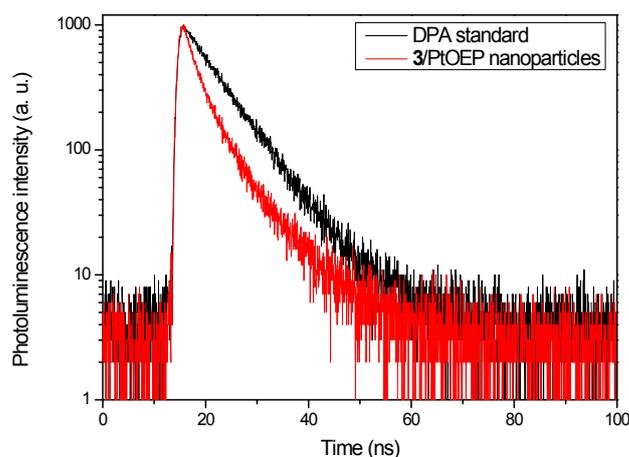


Fig. S11. Time-resolved fluorescence decay at 435 nm of DPA in a standard solution (degassed THF, 10^{-6} M) (black), and a **3**/PtOEP nanoparticle suspension (5 mg mL^{-1}) in water (red) under pulsed UV excitation at 340 nm and ambient conditions (not degassed). The fluorescence decay follows a multi-exponential function and is faster than that of the DPA in solution, which demonstrates the presence of quenching centers for singlet excitons with a consequent reduction of the emitter emission yield ($\Phi_E = 30\%$ in the **3**/PtOEP nanoparticles, whereas $\Phi_E = 96\%$ for the DPA solution).⁹

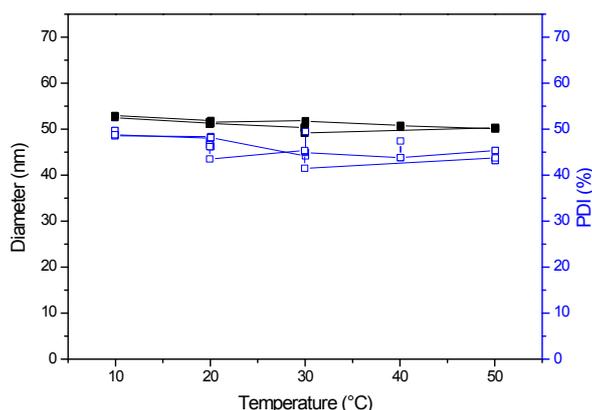


Fig. S12. Average intensity-weighted hydrodynamic diameter and polydispersity of the 3/PtOEP nanoparticles measured by DLS in an aqueous dispersion at temperatures from 10 to 50 °C. The particle size was not significantly affected by temperature.

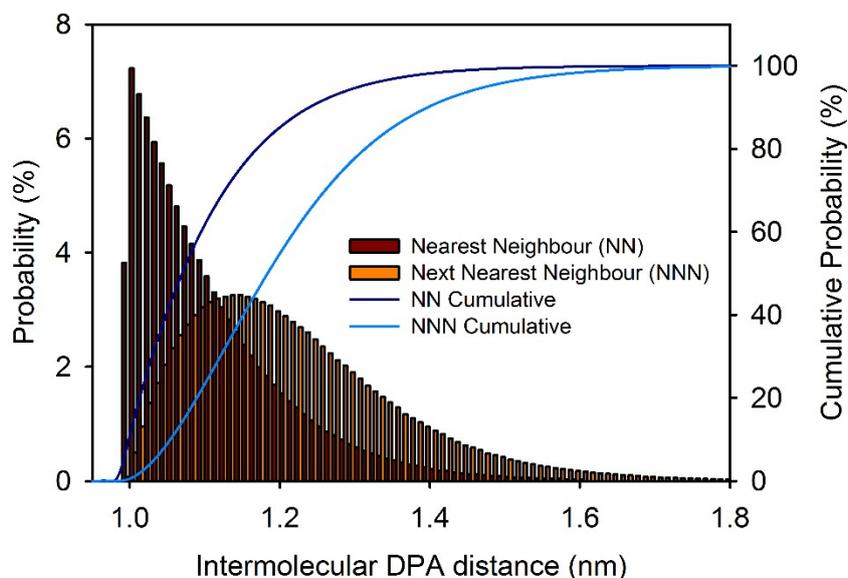


Fig. S13. Histogram of the intermolecular stochastic nearest-neighbor (NN) and next nearest-neighbor (NNN) distance distribution of an ensemble of 3186 DPA molecules embedded in a spherical nanoparticle of radius 13 nm. Continuous lines are the corresponding cumulative probabilities. The average number of emitters was calculated by assuming that the density of PCL in the particle core is the same as the one reported for the solid state and the average particle volume, calculated from the average hydrodynamic radius measured by DLS. This estimation corresponds to the situation in which the particles are above T_m , i.e., in the absence of crystalline/amorphous partitioning. Using a similar methodology, the average number of sensitizer molecules per particles was estimated to be nine, which represents a favorable scenario to have two or more excitons per particles available at the same time for triplet-triplet annihilation. The result of the Monte Carlo calculations has obtained imposing a minimum center-to-center intermolecular distance between two nearest neighbor molecules of 1.0 nm, in accordance with the steric hindrance of the DPA (molecular radius 0.45 nm). The distribution of nearest neighbor (NN) distances is peaked at 1.05 nm, with 100% of dyes having a nearest neighbor closer than 1.4 nm (blue line).

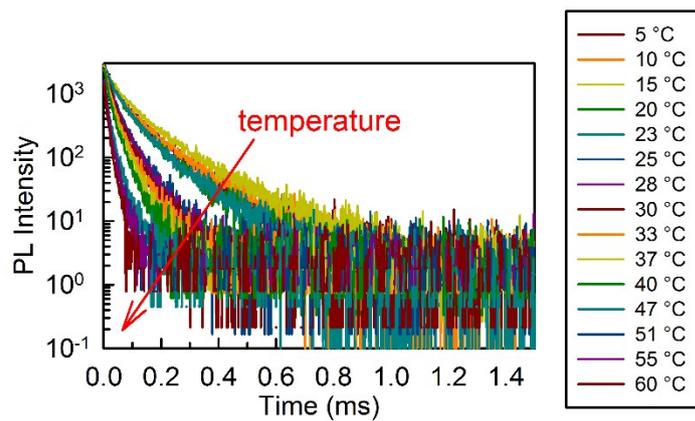


Fig. S14. Temperature dependence of the UC decay of the **3**/PtOEP nanoparticles in aqueous suspension (5 mg mL^{-1}) under pulsed excitation at 532 nm and ambient conditions (not degassed).

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