Supporting Information

Environment-responsive upconversion based on dendrimer-supported efficient triplet-triplet annihilation in aqueous media

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Experimental Section.

General. ^{1}H NMR and ^{13}C NMR spectra were measured with a JEOL EX-400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometer. ^{29}Si NMR spectra were measured with a JEOL JNM-A400 (80 MHz) spectrometer. Coupling constants (*J* value) are reported in hertz. The chemical shifts are expressed in ppm downfield from tetramethylsilane, using residual chloroform (δ = 7.24 in ^{1}H NMR, δ = 77.0 in ^{13}C NMR) as an internal standard. Masses of dendrimers were determined with a MALDI-TOF mass spectroscopy (acceleration voltage 21 kV, negative mode) with DHB (2,5-dihydroxybenzoic acid) as a matrix. UV–vis absorption spectra were obtained at 25 °C using 1 cm path length cell with a SHIMADZU UV-3600UV-vis-NIR spectrophotometer. The fluorescence emission under excitation at 537 nm was monitored using a Perkin Elmer LS50B at 25 °C using 1 cm path length cell with a 480-nm cut-off filter. The excitation bandwidth was 15 nm. The emission bandwidth was 5 nm. The DLS measurements were carried out at 90° scattering angle and 25 ± 0.2 °C using a FPAR-1000 particle analyzer with a He-Ne laser as a light source. The CONTIN program was used for data analysis to extract information on the average hydrodynamic size.

Octaammonium POSS (1). G2 POSS-core dendrimer was prepared according to the reference, *Chem. Commun.* **1997**, 1185. (3-Aminopropyl)triethoxysilane (100 mL, 0.427 mol) and 35–37% HCl (135 mL) in MeOH (800 mL) produced **1** as a white precipitate after 2 days at room temperature. The crude product was obtained after filtration, washing with cold MeOH, and drying. The product was spectroscopically pure in 30% yield (18.8 g). Recrystallization from hot MeOH afforded **1** (4.29 g, 3.66 mmol, 7%) as a white solid. ^{1}H NMR ($(CD_3)_2SO$, 25 °C): δ 8.23 (s, 24H), 2.76 (t, 16H), 1.71 (m, 16H), 0.72 (t, 16H). ^{13}C NMR ($(CD_3)_2SO$, 25 °C): δ 40.53, 20.13, and 7.96. ^{29}SiNMR($(CD_3)_2SO$, 25 °C): δ –66.4 (s).

Methyl ester-terminated POSS-core dendrimer (2). Amberlite IRA-400 ion-exchange resin (100 g) was prepared by successive washing with water (4 × 150 mL), 1 M NaOH (3 × 150 mL), water (6 × 150 mL), and MeOH (6 × 150 mL), which was the elution solvent; the resin was suspended in eluent and chilled (–10 °C, 2 h) before use. Half of the resin beads were loaded onto a column (3.5 cm outside diameter), and the other half were used to dissolve a suspension of neutralized POSS-NH_3^+ (5.0 g, 4.27 mmol) in the minimum amount of eluent below 0 °C. Elution across the column produced a MeOH solution of neutralized **1**. Immediately, methyl acrylate (100 mL, 1.11 mol) was added via syringe to the solution of neutralized **1**, and the resulting mixture was heated for 48 h at 80 °C. The reaction solution was concentrated *in vacuo*, and extracted with ethyl acetate. The organic phase was washed with brine and dried over $MgSO_4$. The product **2** (6.10 g, 2.60 mmol, 63%) as a colorless oil was obtained after evaporation: ^{1}H NMR (CD_3OD, 25 °C) δ 3.62 (s, 24 H),

2.18 (s, 16 H), 1.40 (m, 16 H), 0.96 (s, 48 H), 0.57 (m, 16 H): ^{13}C NMR(CD_3OD, 25 °C) δ 174.48, 57.24, 52.17, 50.39, 33.13, 21.39, 10.19: ^{29}Si NMR (D_2O, 25 °C) δ –66.2: MALDI–TOF [$(M+H)^+$] calcd. 1811.08, found 1812.01.

G2 POSS-core dendrimer (3). The solution containing **2** (6.1 g, 2.60 mmol) with an excess of ethylenediamine (100 mL, 1.48 mol) was stirred for 4 days at 4 °C. After removing ethylenediamine, washing with diethyl ether, and dialyzing in water, the G2 POSS-core dendrimer **3** was obtained in 92% yield (6.3 g, 2.39 mmol) as a colorless oil: ^{1}H NMR ($CDCl_3$, 25 °C) δ 3.23 (t, 32 H), 2.72 (t, 32 H), 2.66 (t, 32 H), 2.43 (t, 16 H), 2.39 (t, 32 H), 1.46 (m, 16 H), 0.54 (t, 16 H): ^{13}C NMR ($CDCl_3$, 25 °C) δ 171.97, 80.03, 49.19, 33.67, 28.18, 28.06, 21.12, 10.57: ^{29}Si NMR (D_2O, 25 °C) δ –66.2 (s). MALDI–TOF [$(M+H)^+$] calcd. 2722.86, found 2722.18.

Determinations of the enhancement solubilization factors (ESF). Samples containing the guest molecules and each dendrimer were mixed and allowed to equilibrate in darkness overnight. The absorption spectra were measured by using a Shimadzu UV-3600 at 25 °C. In the studies with anthracene the solute concentration was varied from 10 μM to 100 μM. In the studies with PtOEP the solute concentration was varied from 1 μM to 10 μM. All samples were measured in 50 mM sodium phosphate buffer. The ESF values were determined according to the reference, *Proc. Natl. Acad. Sci. USA* **1998**, 95, 15351. To quantify the effectiveness of a particular dendrimer in solubilizing the studied compounds, the ESF is defined as the number of moles of compound solubilized per number of moles of dendrimers was calculated, using Equation 1.

$$ESF = \frac{[H]_d}{[D]_W} = \frac{[H]_0 - S_W}{[D]_W} \qquad (1)$$

Where $[H]_d$ is the guest concentration in aqueous solutions, $[H]_0$ is the analytical concentration of the guest and S_W is the water solubility of the guest.

Fluorescence measurements with the dendrimer complexes. Fluorescence measurements were executed with the aqueous solutions containing 100 μM G2 POSS-core dendrimer, 100 μM anthracene, and 10 μM PtOEP in 50 mM sodium phosphate, 10% DMSO, and 1% THF at 25 °C with the excitation at 537 nm passing through a 480 nm cut-off filter. Samples were bubbled with nitrogen for 1 h before the measurements. The quantum yields were determined by comparing to the fluorescence intensities in the spectra of anthracene with the excitation at 376 nm in DMSO or water according to Equation 2.

$$\Phi_{up} = \Phi_{(An,em,DMSO,376ex)} \cdot I_{up}/I_{(An,em,DMSO,376ex)} \cdot \varepsilon_{(An,376)}/\varepsilon_{(complex,537)} \cdot c_{complex}/c_{An} \cdot (n_{(H2O)}/n_{(DMSO)})^2 \cdot S_{1nm}/S_{15nm} \cdot E_{376}/E_{537} \quad (2)$$

Here, $\Phi_{(An,em,DMSO,376ex)}$ is the quantum yield of the fluorescence emission from anthracene with the excitation at 376 nm in DMSO determined to be 0.18 as an absolute value with an integrating sphere. I is the emission area calculated from the spectrum, ε is the molar extinct coefficient, c is the concentration, n is the refractive index of each solvent, S is the light amplitude in each slit width, and E is the light amplitude in each wavelength.

To determine the quantum yields for each step, initially, we defined the quantum yield of upconversion (Φ_{up}) as Equation 3:

$$\Phi_{up} = \Phi_{ISC} \cdot \Phi_{sens} \cdot \Phi_{TTA} \cdot \Phi_{(An,em,DMSO,376ex)} \quad (3)$$

Here, the efficiency of the generation of the triplet-excited PtOEP (Φ_{ISC}) was evaluated as a relative value from the phosphorescence intensity according to Equation 4. From the decrease of the emission band from the triplet-excited state of PtOEP, the efficiency for sensitizing (Φ_{sens}) was calculated according to Equation 5. The quantum yield of upconversion (Φ_{up}) was calculated as a relative value compared to the fluorescence emission of anthracene with the excitation at 376 nm. Thus, the efficiency of TTA (Φ_{TTA}) was obtained.

$$\Phi_{ISC} = \Phi_{phos} \cdot I_{(phos,H2O)}/I_{(phos,DMSO)} \cdot \varepsilon_{(537,DMSO)}/\varepsilon_{(537,water)} \cdot S_{5nm}/S_{15nm} \quad (4)$$

Here, Φ_{phos} is the quantum yield of phosphorescence of PtOEP according to the reference 7 in the main text. I is the phosphorescence intensity from PtOEP in each solvent, ε is the molar extinct coefficient of the solution at 537 nm in each solvent.

$$\Phi_{sens} = 1-(I/I_0) \quad (5)$$

Here, the integration of the phosphorescence from PtOEP was represented as I_0 in the absence and I in the presence of anthracene.

Figures:

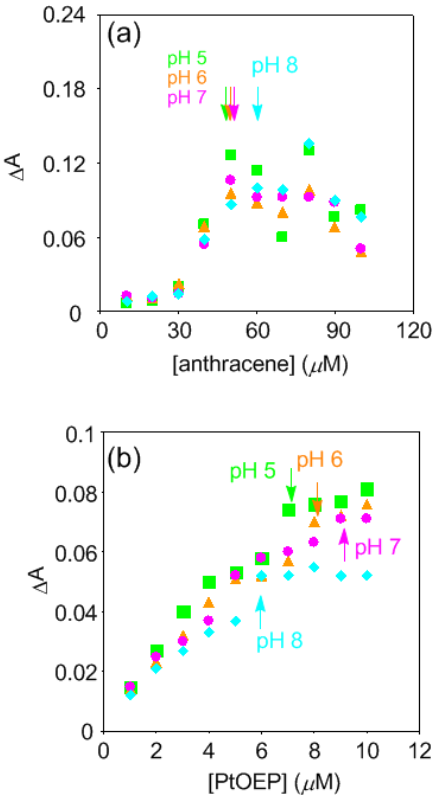

Figure S1. Comparisons of absorbance for various ratios of (a) anthracene and (b) PtOEP to the G2 POSS-core dendrimer with various pH. The maximum number of the guest molecules entrapped within the dendrimers indicated by the arrows was evaluated, and the ESF values were calculated.

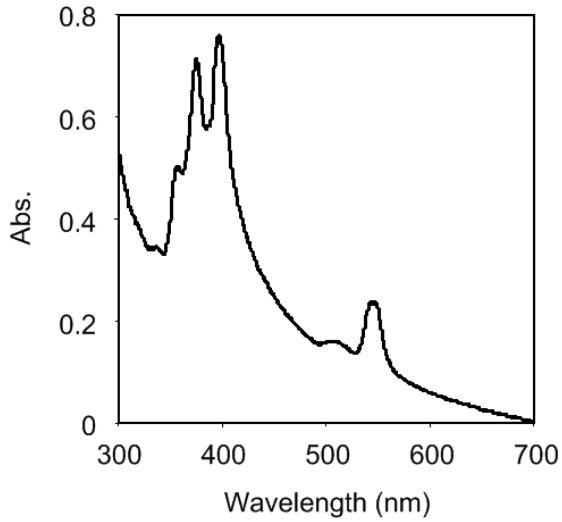

Figure S2. UV–vis absorption spectrum of the solution containing 100 μM anthracene, 10 μM PtOEP, and 100 μM G2 POSS-core dendrimer in 50 mM sodium phosphate buffer (pH = 7.0).