Electronic Supporting Information

All-or-None Switching of Photon Upconversion in Self-Assembled Organogel Systems

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Scheme S1. Synthesis of donor and acceptors



Synthesis of DCS-Ac.

The ester form DCS-Es was synthesized according to the reported procedures.¹ Briefly, the mixture of methyl terephthalaldehydate (3.28 g, 2 mmol) and 1,4-phenylenediacetonitrile (1.57 g, 1 mmol) in *tert*-butyl alcohol (30 mL) was stirred at 50 °C. Potassium *tert*-butoxide (2.31 g, 2.05 mmol) powder was dropped into the mixture and stirred for 2 hours. The resulting precipitate was used for next step without purification. The hydrolysis of DCS-Es was carried on the general procedure. To a suspension of 2.24 g (0.5 mmol) DCS-Es in 75 mL 1:1 mixture of THF/MeOH, 15 mL of a 2 M KOH aqueous solution was added. The mixture was allowed to reflux for 3 h. THF was removed under reduced pressure and the resulting suspension was diluted with water. The precipitate formed by acidification with aqueous HCl (2 M) was collected by filtration, washed several times with water, yielding 1.80 g (86 %) of a yellow solid. The obtained DCS-Ac was washed several times by water, ethanol and acetone because of the poor solubility. It was used for next step without further purification.

Synthesis of L-1/D-1.

LGAm and DGAm were synthesized according to the previously reported methods.² LGAm/DGAm (2.40 g, 0.5 mmol) and DCS-Ac (1.01 g, 0.24 mmol) were dispersed into a solution

of THF/CHCl₃ (100 mL, 2:1, v/v). Then EDC•HCl (1.15 g, 0.6 mmol) and HOBt (0.81 g, 0.6 mmol) were added. The reaction mixture was stirred at 50 °C for 12 h. After removal of solvents, the remained solids were dissolved in THF (20 mL) and then poured into 1% Na₂CO₃ aqueous solution (500 mL). The collected precipitate was purified by column chromatography (CHCl₃) over silica gel to yield a yellow powder (0.85 g, yield: 26%). L-1: ¹H NMR (300 MHz, CDCl₃): δ = 8.17-8.19 (d, 2H), 7.99-8.02 (m, 7H), 7.81 (s, 4H), 7.63 (s, 2H), 6.88 (s, 2H), 5.82 (s, 2H), 4.59-4.63 (m, 2H), 3.28-3.34 (m, 8H), 2.59-2.67 (m, 2H), 2.35-2.43 (m, 2H), 2.17-2.26 (m, 4H), 1.53-1.58 (m, 7H), 1.48 (s, 9H), 1.30-1.33 (m, 62H), 0.89-0.94 (m, 12H). MALDI-TOF-MS, (dithranol matrix): calculated for C₈₄H₁₃₀N₈O₆ 1347.01; found 1347. Elemental analysis: calculated for C₈₄H₁₃₀N₈O₆ H 9.72, C 74.85, N 8.31; found H 9.70, C 74.81, N 8.39. D-1: ¹H NMR (300 MHz, CDCl₃): δ = 8.17-8.19 (d, 2H), 7.99-8.02 (m, 7H), 7.81 (s, 4H), 7.63 (s, 2H), 6.88 (s, 2H), 5.82 (s, 2H), 4.59-4.63 (m, 2H), 3.28-3.34 (m, 8H), 2.59-2.67 (m, 2H), 2.35-2.43 (m, 2H), 2.17-2.26 (m, 4H), 1.53-1.58 (m, 7H), 1.48 (s, 9H), 1.30-1.33 (m, 62H), 0.89-0.94 (m, 12H). MALDI-TOF-MS, (dithranol matrix): calculated for C₈₄H₁₃₀N₈O₆ 1347.01; found 1347. Elemental analysis: calculated for C₈₄H₁₃₀N₈O₆ (m, 2H), 2.35-2.43 (m, 2H), 2.17-2.26 (m, 4H), 1.53-1.58 (m, 7H), 1.48 (s, 9H), 1.30-1.33 (m, 62H), 0.89-0.94 (m, 12H). MALDI-TOF-MS, (dithranol matrix): calculated for C₈₄H₁₃₀N₈O₆ 1347.01; found 1347. Elemental analysis: calculated for C₈₄H₁₃₀N₈O₆ H 9.72, C 74.85, N 8.31; found H 9.70, C 74.87, N 8.37.

Synthesis of L-2.

The synthesis method of **L-2** was similar to those of above compounds with a different starting material, Pt(II) mesoporphyrin IX. The obtained crude product was purified by column chromatography with CHCl₃/methanol = 50/1 (v/v) as the elution solvents. The final product was dark red power. ¹H NMR (300 MHz, CDCl₃): $\delta = 8.12-8.16$ (m, 2H), 8.25 (s, 2H), 6.69 (s, 2H), 6.25 (s, 2H), 5.88 (s, 2H), 4.56 (s, 2H), 4.33-4.45 (m, 2H), 3.64-3.83 (m, 8H), 2.59-2.67 (m, 4H), 2.35-2.43 (m, 4H), 2.17-2.26 (m, 4H), 1.92-2.10 (m, 14H), 1.56 (s, 14H), 1.18-1.33 (m, 83H), 0.91-0.93 (m, 12H), 0.43 (s, 1H). MALDI-TOF-MS, (dithranol matrix): calculated for C₉₄H₁₅₄N₁₀O₆Pd H 9.46, C 69.12, N 8.76; found H 9.63, C 69.28, N 8.54.



Figure S1. Outline of the TTA-UC process, showing the energy levels involved in the TTA-UC (S = singlet, T = triplet). The TTA-UC involves a donor (sensitizer) with high intersystem crossing (ISC) efficiency and an acceptor (emitter) with high fluorescence quantum yield. First, the donor absorbs the low energy light to produce the excited singlet state (S₁). Second, the triplet state (T₁) of donor is populated through ISC. Third, triplet-triplet energy transfer (TTET) from donor T₁ to the triplet state of acceptor *via* the Dexter mechanism. Finally, the collision and annihilation (TTA) between two acceptor triplets produce a higher-energy singlet excited state of the acceptor S₁ which radiates upconverted delayed fluorescence.



Figure S2. (a) Absorption spectra of L-1 supramolecular organogels in various solvents ([L-1] = 1 mM, $\lambda_{ex} = 375$ nm). Fluorescence spectra of L-1 in (b) DMF and (c) ethanol ([L-1] = 1 mM, $\lambda_{ex} = 355$ nm).



Figure S3. CD spectra of L-1 and D-1 in (a) DMF gel and (b) ethanol gel. (c) CPL spectra of L-1 and D-1 in ethanol gel. In all measurements, [L-1] = [D-1] = 1 mM.



Figure S4. SEM images of xerogel L-2/L-1 (a) and L-2/D-1 (b) made from DMF gels ([L-2] = 20 μ M, [L-1] = [D-1] = 10 mM).



Figure S5. (a) Photoluminescence spectra of the binary L-2/L-1 gel in deaerated DMF at room temperature ([L-2] = 20 μ M, [L-1] = 10 mM) with different incident light intensity of 532 nm laser in deaerated toluene. A short pass filter (510 nm) was used to remove the scattered incident light. (b) UC emission intensity observed for the binary L-2/L-1 gel in deaerated DMF as a function of excitation intensity of the 532 nm laser. The dashed lines are fitting results with slopes of 2 (blue) and 1 (red). The I_{th} was determined as 113 mW cm⁻² from the crossing point of these two lines. (c) Photoluminescence spectra of the binary L-2/L-1 gel in deaerated ethanol at room temperature ([L-2] = 20 μ M, [L-1] = 10 mM) with different incident light intensity of the 532 nm laser. A short pass filter (510 nm) was used to remove the scattered incident light. (d) UC emission intensity observed for the binary L-2/L-1 gel in deaerated the binary L-2/L-1 gel in deaerated the scattered incident light. (d) UC emission intensity observed for the binary L-2/L-1 gel in contensity of the scattered incident light. (d) UC emission intensity observed for the binary L-2/L-1 gel in deaerated ethanol as a function of excitation intensity of the scattered incident light. (d) UC emission intensity observed for the binary L-2/L-1 gel in deaerated ethanol as a function of excitation intensity of the scattered incident light.

532 nm laser. The dashed lines are fitting results with slopes of 2 (blue) and 1 (red). The $I_{\rm th}$ was determined as 1110 mW cm⁻² from the crossing point of these two lines. UCPL: upconverted photoluminescence.



Figure S6. (a) UC emission decay at 480 nm of the binary L-2/L-1 gel in deaerated ethanol under pulsed excitation at 531 nm ([L-2] = 20 μ M, [L-1] = 10 mM). The red fitting curve, obtained by the relationship of $I_{UC}(t) \propto \exp(-t/\tau_{UC}) = \exp(-2t/\tau_{A,T})$ (τ_{UC} : UC emission lifetime, $\tau_{A,T}$: acceptor triplet lifetime), gave $\tau_{UC} = 28 \ \mu$ s. (b) UC emission decay at 490 nm of the binary L-2/L-1 gel in deaerated DMF under pulsed excitation at 531 nm ([L-2] = 20 μ M, [L-1] = 10 mM). The red fitting curve gave $\tau_{UC} = 35 \ \mu$ s.



Figure S7. Photoluminescence spectra of the binary L-2/L-1 gels in deaerated toluene, ethanol and DMF ([L-2] = 20 μ M, [L-1] = 10 mM). A 532 nm laser was used as an excitation light source. A short pass filter (510 nm) was used to remove the scattered incident light.

References:

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(2) Li, Y.; Wang, T.; Liu, M.: Gelating-induced supramolecular chirality of achiral porphyrins: chiroptical switch between achiral molecules and chiral assemblies. *Soft Matter* **2007**, *3*, 1312-1317.