Electronic Supplementary Information (ESI):

Highly Efficient Triplet–Triplet Annihilation Upconversion in Polycaprolactone: Application to 3D Printable Architecture and Microneedles

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Experimental section

Materials. Perylene, PCL (M.W. = 45000), and tetrahydrofuran (THF) were purchased from Sigma-Aldrich. Palladium(Pd)(II) meso-tetraphenyl-tetrabenzo-porphyrin (PdTPBP) was synthesized according to a procedure reported in the literature.[39]

Preparation of UC PCL coupon. Prior to the fabrication of the 3D UC structure using PCL, we first fabricated a 2D UC PCL using a drop-casting method to obtain its photochemical properties. PdTPBP and perylene stock solutions were prepared in THF (0.897 mM and 23.68 mM, respectively, and stored in the dark). PCL (3 g) was dissolved in 20 mL of THF (PCL solution). To fabricate the UC PCL, 50 μL of PdTPBP stock solution and 300 μL of perylene stock solution were mixed with 10 mL of PCL solution in a 50 mL falcon tube to obtain uniform concentration. After mixing, the mixture was placed in an oven at 60 °C for 30 min to remove air bubbles. UC PCL was then fabricated by casting the mixture onto a glass petri dish and storing at 70 °C in an oven for 18 h to completely evaporate the residual THF.

Characterization of UC PCL. The absorption, Stokes emission spectra, and the lifetimes of phosphorescence and UC emission were recorded using a spectrofluorometer (FS5-TCSPC, Edinburgh Instruments). UC emission spectra were recorded using a custom laser setup in which the UC PCL was excited at an angle of approximately 45°, using a 635 nm commercial diode laser with a 6 mm-diameter beam. The emission of the UC PCL was modulated with an optical chopper (120 Hz) and directed to a monochromator (Oriel Cornerstone, Newport) using a series of focusing lenses, and the scattered laser light was removed using a 632 nm notch filter. The signal was then detected by an Oriel photomultiplier tube and processed using a lock-in amplifier (SRB10 DSP, Stanford Research Systems). The incident laser intensity was adjusted with a continuously variable neutral density filter and measured using a power meter (843-R, Newport).

Fabrication of 3D UC structure. The 3D structure (rook-shaped; 17 × 17 × 34 mm, length × width × height) was downloaded from Thingiverse and printed using a 3D printer (Rokit INVIVO, Korea) with a 10 mL syringe (0.4

mm nozzle; Rokit, Korea). UC PCL was loaded into the syringe and heated at 120 °C for 30 min to melt it. Then, the 3D UC structure was printed on a glass slide according to a programmed G-code (NewCreatorK) with the following parameters: bed temperature = 10 °C, layer height = 0.7 mm, and output speed = 6 mm/s.

Fabrication of UC MNs. To fabricate UC MNs, a polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning, Midland, MI) mold was initially fabricated using laser and molding techniques to produce a series of conical MN cavities. The PDMS mold was piled with UC PCL, placed in a vacuum oven under 85 kPa, and heated at 200 °C for 2 h to completely melt the polymer. The UC MNs were then cooled to room temperature and removed from the mold for further use. The dried MN arrays were gently peeled off from the mold. The morphology of the fabricated MN arrays was characterized using a digital (AM413ZT, Dino-Lite, Taiwan) and optical (Eclipse TS100, Nikon, Japan) microscope.

Text S1. UC quantum yield measurement

The UC quantum yield (Φ_{UC}) of UC PCL ([PdTPBP] = 0.03 μmol g^{-1} and [perylene] = 4.7 μmol g^{-1}) was measured relative to the phosphorescence quantum yield of PdTPBP PCL ([PdTPBP] = 0.03 μmol g^{-1}) in response to laser excitation at 635 nm (Φ_{std}=7.5%, measured using C9920−02G instrument, Hamamatsu) and calculated using Equation S1.

$$\Phi_{UC} = \Phi_{std}\left(\frac{A_{std}}{A_{UC}}\right)\left(\frac{I_{UC}}{I_{std}}\right)\left(\frac{\eta_{UC}}{\eta_{std}}\right)^2 \#(S1)$$

A, I, and η denote the absorbance at 635 nm, integrated photoluminescence profile, and refractive index of the medium, respectively. The subscript “std” and “UC” refers to the phosphorescence of the reference standard (PdTPBP PCL, integrated over 750–850 nm) and the UC emission of the UC PCL (integrated over 420–570 nm), respectively. In this calculation, the absorbance and the refractive index of the medium are considered to be equal because both samples were fabricated by an identical synthetic procedure (identical concentration of PdTPBP in PCL).

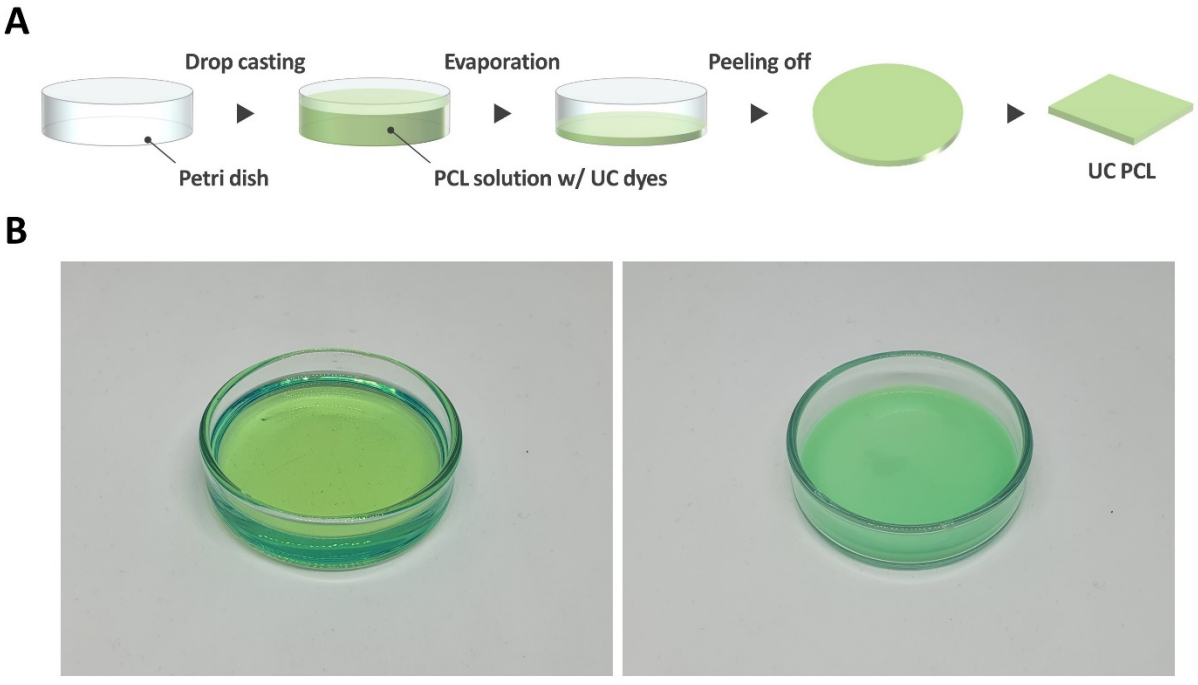

Figure S1. (A) Schematic illustration of the fabrication of upconverting polycaprolactone (UC PCL) coupon by using the drop-casting method**.** (B) Photographs of UC PCL coupon before and after the evaporation of tetrahydrofuran (THF).

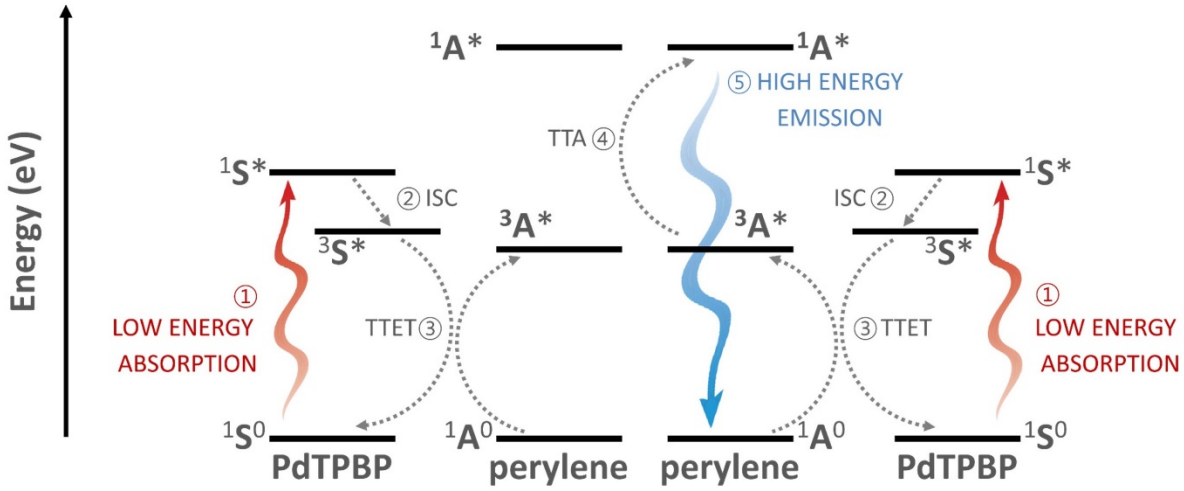

Figure S2. Schematic illustration of the steps in the triplet–triplet annihilation upconversion (TTA-UC) process.

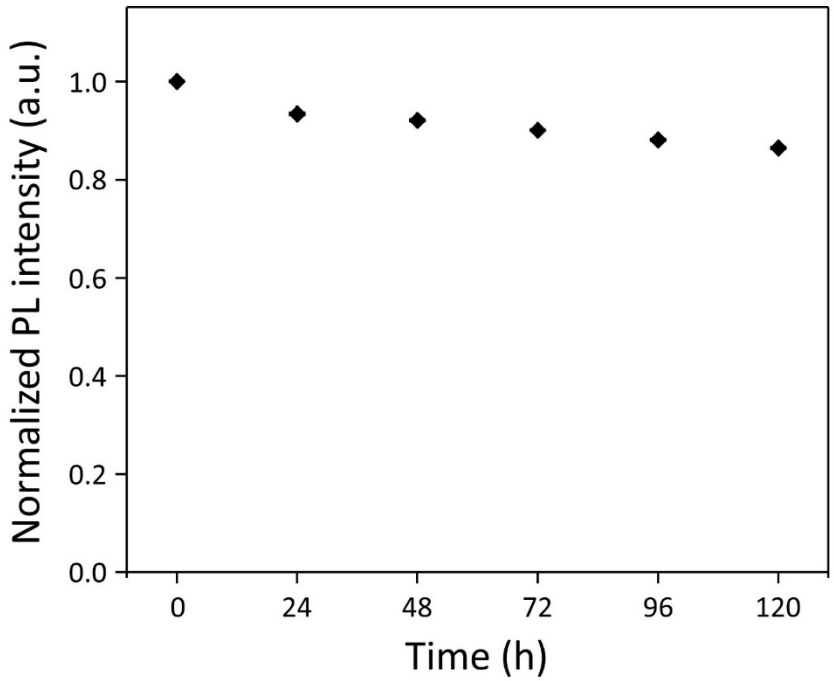

Figure S3. Shelf-life of the UC PCL ([PdTPBP] = 0.03 μmol g^{-1} and [perylene] = 4.7 μmol g^{-1} in PCL). The UC PCL was stored in a dark room and UC emission intensity (centered at 470 nm) of the UC PCL was measured every 24 h under 66.6 mW cm^{-2} laser irradiation at 635 nm.

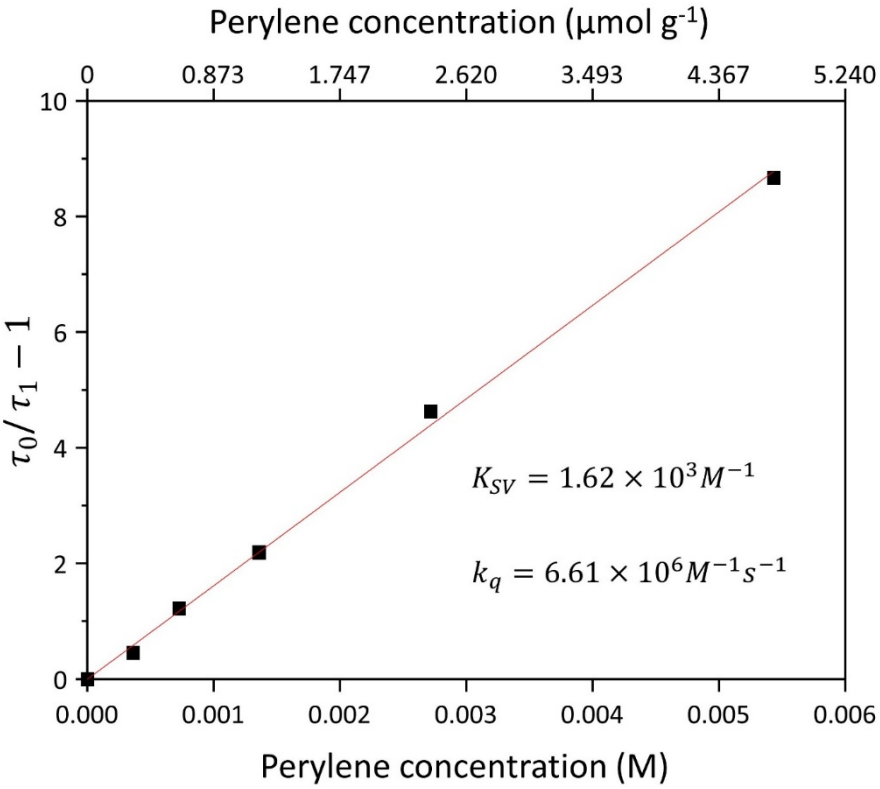

Figure S4. Stern–Volmer plot (generated from phosphorescence lifetime analysis) where K_{SV} (the slope of the plot) and k_q (K_{SV}/τ_0) represent the Stern–Volmer constant and bimolecular quenching constant, respectively. The density of PCL is 1.145 g mL^{-1}

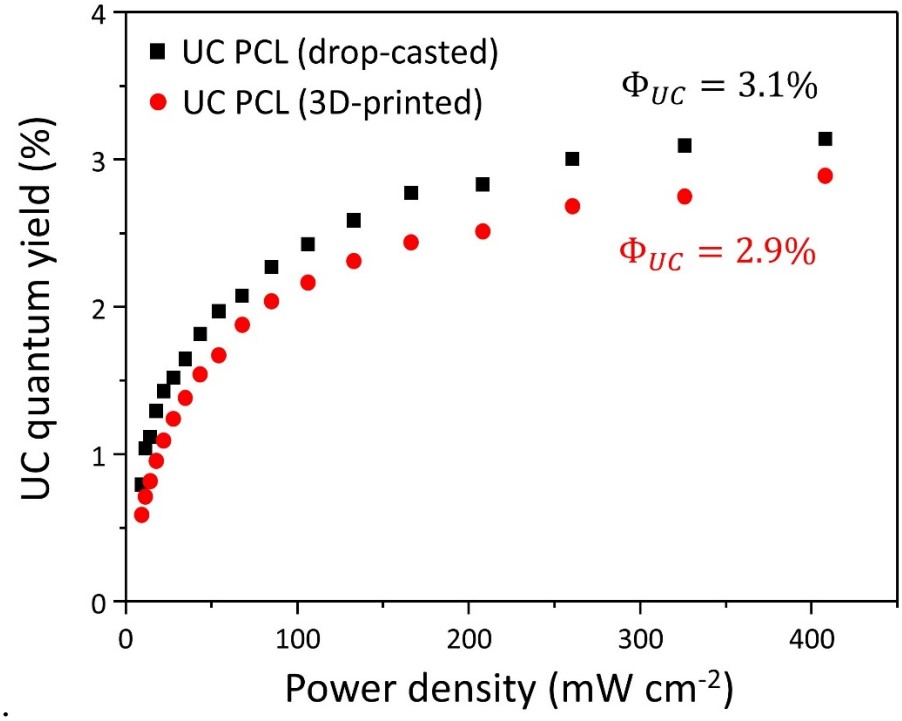

Figure S5. UC quantum yield of the UC PCL and 3D UC structure as a function of the power density of 635 nm laser excitation ([PdTPBP] = 0.03 μmol g^{-1} and [perylene] = 4.7 μmol g^{-1} in PCL).

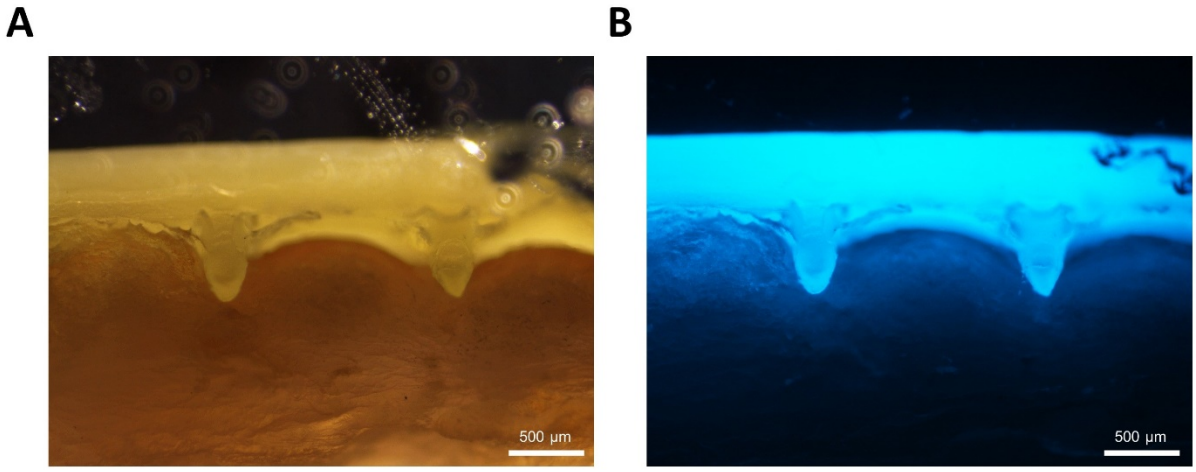

Figure S6. Cross-sectional optical images of upconverting microneedles (UC MNs) inserted into the porcine skin under (A) white light and (B) 635 nm laser excitation, acquired through a 600 nm shortpass filter.

References

[S1] R. Tao, J. Zhao, F. Zhong, C. Zhang, W. Yang and K. Xu, *Chem. Comm.*, 2015, **51**, 12403-12406.