ABSTRACT
Triplet-triplet annihilation based upconversion (TTA-UC), the special photochemical process of converting two or more photons of lower energy into one photon of higher energy in multichromophore systems, has attracted much attention due to its potential in various applications including solar-based technologies and biophotonic application as well. Despite these advantages of TTA-UC, the development of effective UC host material for practical devices has been difficult due to the prerequisite for TTA-UC such as high diffusivity and anoxic conditions. This research reports a new TTA-UC host material: polycaprolactone (PCL) and polylactic acid (PLA) polymer blends for highly efficient, processable, and bio-compatible solid-phase TTA-UC. The photochemical properties of the prepared TTA-UC sample were fully characterized and fabrication of three-dimensional upconverting architecture using commercially available 3D-printer was demonstrated for the first time.

KEYWORDS
upconversion, triplet-triplet annihilation, 3D printing, polycaprolactone, polylactic acid, solid-phase upconversion

1. INTRODUCTION
Photon upconversion (UC) is becoming increasingly important in enhancing the efficiency of solar-based technologies as well as in pioneering unconventional biophotonic applications, owing to its capability of converting lower energy photons into one higher energy photon. Among several UC mechanisms, Triplet-Triplet Annihilation based UC (TTA-UC) is more competitive than other UC mechanisms because it can be activated at even weak excitation and continuous wavelength source such as sunlight. TTA-UC can be achieved through a series of energy transfer between two organic chromophores called as sensitizer and acceptor, so it is important to select the pair of sensitizer and acceptor. Additionally, the selection of proper media, which has a good diffusivity and low oxygen permeability, also should be considered for the successful TTA-UC process. Because the energy transfer in sensitizer and acceptor occurs via diffusion mechanism and to prevent oxygen-quenching of the excited chromophore’s triplet states. In earlier studies, TTA-UC was achieved in deoxygenated liquid organic solvents, but these solvents are not suitable for practical applications owing to its toxicity and poor oxygen protection. To overcome these problems, several works have reported TTA-UC in solid-state by using polymers as media. However, it also faced other problems: its low UC efficiency and its difficulty in the fabrication of desired shapes. Here, we overcome these limitations by using PCL/PLA polymer blends as media for the first time. The PCL/PLA polymer blend with UC chromophore pair was precisely prepared to aim to generate UC emission (~470nm) under 635nm laser irradiation. Additionally, we fabricated UC filament for commercially available 3D-printer by manipulating the PCL/PLA polymer blend with UC pair and produced UC-3D structures with desired-shape, successfully.

2. RESULTS AND DISCUSSION
2.1 Characterization of UC film
To analyze photochemical properties, we first fabricated UC films using the drop-casting method. Palladium(II) mesotetraphenyltetraphenylporphyrin (PdTPBP) and perylene, which have frequently been utilized for red-to-blue UC, were selected as sensitizer and acceptor, respectively and their absorption and photoluminescence spectra in PCL/PLA films were shown in Fig.1A. PdTPBP has characteristic Soret band at 440 nm and Q-band at 630 nm and emits phosphorescence at 792 nm, so red photons were efficiently captured by its Q-band absorption. Perylene is well known as an ideal TTA-UC acceptor due to its fluorescence peak at 470 nm and its high fluorescence quantum yield (Φf = 0.98)3, so this combination of sensitizer and acceptor can successfully achieve red-to-blue UC. Fabricated UC film with UC pair showed a notable upconverted blue emission in the ambient condition (Fig.1B), which can be observed without any filter. A quantum yield (QY) of UC film, which is defined as the ratio of absorbed photons to emitted photons, was calculated as a reference to the following equation6 and measured as a function of the excitation intensity.

$$\Phi_{UC} = 2 \times \Phi_{UC} = 2 \times \Phi_{exc} \left( \frac{I_{abs}}{I_{em}} \right) \left( \frac{F_{em}}{F_{exc}} \right) \left( \frac{m}{n} \right)^2$$

where $\Phi_{UC}$, $\Phi_{UC}$, $\Phi_{exc}$, $A$, $I$, $F$, and $n$ are upconversion quantum yield with 100% theoretical maximum, upconversion quantum yield with 50% theoretical maximum, absorbance, excitation intensity, integrated photoluminescence profile, and refractive index, respectively. The QY reached
about 6% (Fig. 1C) and it is comparable to the highest UC QY of PdTPBP and perylene obtained to date in solid-state and ambient condition; the multilayer UC film (ΦUC’ = 7%).

Fig.1: (A) Molecular structures and normalized absorption (solid) and emission (dashed) spectra of sensitizer (PdTPBP, red) and acceptor (Perylene, blue) in PCL/PLA blends. (B) (a) Photographs of UC PCL/PLA film with and without 635nm laser excitation. (C) A QY of UC film (ΦUC’) as a function of excitation intensity in ambient and room temperature condition.

2.2 Fabrication of UC-3D structure

The success of UC film also introduced new opportunities for fabrication of UC films or 3D structures using a fused deposition modeling (FDM) type 3D printer because PCL and PLA are commonly used as filaments for FDM 3D printer. Focusing on this characteristic, we manipulated UC film into the form of UC filaments which exhibit flexibility and fair mechanical properties to be used in 3D-printer. As a result, we can fabricate shape-controlled UC films or UC-3D structures and provide additional physical properties. Moreover, we implement effective TTA-UC on these fabricated UC-3D structures even under low-powered red LED (Fig.2).

Fig.2: Photographs of upconverting 3D-matrix with and without 630nm commercial LED excitation.

3. CONCLUSIONS

In summary, we fabricated 3D printable upconverting polymer blends (conjunction of PCL/PLA) that can be readily controlled in its shapes with a commercially available 3D-printer. By manipulating the polymer blends, we also produced UC filaments for 3D-printed structures. The 3D-printed structures showed intense UC emission even under ultra-low excitation power such as a commercial LED light source and moderate photochemical stability without any additional coating in ambient conditions owing to its low oxygen-permeability. To the best of our knowledge, this is the first report describing 3D-printable upconverting polymer blends, thus paving the new way toward various applications in solar and biophotonic devices by integrating UC materials with complex 3D shapes.

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