Electronic Supplementary Information (ESI†) for

Photon Upconverting Bioplastics with High Efficiency and In-Air-Durability

Pankaj Bharmoria,[a,b] Shota Hisamitsu,[a] Yoichi Sasaki,[a] Tejwant Singh Kang,[a,c] Masa-aki Morikawa,[a] Biplab Joarder,[a,d] Kasper Moth-Poulsen,[b] Hakan Bildirir,[b] Anders Mårtensson,[b] Nobuhiro Yanai,*[,a,e] Nobuo Kimizuka*[,a]

[a] Department of Chemistry and Biochemistry, Graduate School of Engineering, Center for Molecular Systems (CMS), Kyushu University 744 Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan.

[b] Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Kemivägen 4,412 96 Gothenburg, Sweden.

[c] Department of Chemistry, UGC-centre for Advance Studies – II, Guru Nanak Dev University, Amritsar, 143005, India.

[d] Functional Materials, Design, Discovery & Development (FMD3), Advanced Membrane & Porous Materials Center, King Abdullah University of Science and Technology, Thuwal 23955-6900, Kingdom of Saudi Arabia.

[e] JST-PRESTO, Honcho 4-1-8, Kawaguchi, Saitama 332-0012, Japan.

**To whom correspondence should be addressed:* E-mail: yanai@mail.cstm.kyushu-u.ac.jp ; n-kimi@mail.cstm.kyushu-u.ac.jp; Phone: +81-92-802-2832; Fax: +81-92-802-2838

Experimental Section

Materials. All the solvents and reagents were used as received. Platinum (II) octaethylporphyrin (PtOEP), DMF, and gelatin type A from porcine skin were purchased from Sigma Aldrich. Triton X-100 was purchased from Chameleon. All the chemicals were used as obtained otherwise noted. Sodium 9,10-diphenylanthracene-2-sulfonate (DPAS) was synthesized according to our previous work.[1]

Methods

Preparation of G-TX-PtOEP-DPAS Film. 1 g of 20 wt% hot gelatin solution was added to 2.2 mg of DPAS, to which 0.025 g of liquid TX containing 0.95 mM of PtOEP was further added. The resulting solution was stirred at 90 ^{o}C until the solution became homogeneous. The hot solution was kept for 3 min at room temperature, followed by casting 260 µl of the solution on a glass plate and drying at room temperature in air for 48 hr. Final composition of the film after drying was [gelatin] = 88 wt%, [TX100] = 11 wt %, [DPAS] = 22 mmol kg^{-1} and [PtOEP] = 100 µmol kg^{-1}. The scheme of UC film preparation is provided in Fig. S2.

Optical Measurements. UV-Vis absorption spectra were recorded on JASCO V-670 and V-770 spectrophotometers in transmittance mode. The dried films were sandwiched between glass plats during measurements. The background correction was done with dried G-TX film. Luminescence spectra were measured by using a PerkinElmer LS 55 fluorescence spectrometer. Time-resolved photoluminescence lifetime measurements were carried out by using a time-correlated single-photon counting lifetime spectroscopy system, HAMAMATSU Quantaurus-Tau C11367-02 (for fluorescence lifetime)/C11567-01(for delayed luminescence lifetime). The quality of the fit has been judged by the fitting parameters such as χ^2 (<1.2) as well as the visual inspection of the residuals. For fluorescence lifetime analysis, the excitation and detection wavelengths were set at 365 nm and 437 nm, respectively. For TTA-UC emission lifetime analysis of G-TX-PtOEP-DPAS film, excitation and detection wavelengths were set at 531 nm and 437 nm, respectively. The absolute photoluminescence quantum yields were measured using a Hamamatsu C9920-02G instrument having an integration sphere for sample

excitation with a Xe excitation source and a monochromator, Hamamatsu A10080-01. For TTA-UC emission measurements of G-TX-PtOEP-DPAS film, a diode laser (532 nm, 200 mW, RGB Photonics) was used as the excitation source. The typical laser spot area estimated for 532 nm laser by using the diameter was 1.2 $x10^{-3}$ cm^2. The emitted light was collimated by an achromatic lens, the excitation light was removed using a notch filter (532 nm) or short pass filter (610 nm), and the emitted light was again focused by an achromatic lens to an optical fiber connected to a multi-channel detector MCPD-9800 (Otsuka Electronics). The thermoreversibility of TTA-UC in the G-TX-PtOEP-DPAS film and air stability of TTA-UC in TX-PtOEP-DPAS liquid were measured using a SPEX 1681 0.22m spectrometer with OBIS 532 nm -100LS 20 mW, Coherent laser with a spot area of 3.84 $x10^{-3}$ cm^2.

The absolute TTA-UC efficiency of G-TX-PtOEP-DPAS films were measured by using an absolute quantum yield measurement system Quantaurus-QY Plus C13534-01 (Hamamatsu Photonics). The integrating sphere has an inner diameter of ca. 84 mm and a baffle between the sample and the detection port to avoid the direct observation of scattered excitation light and photoluminescence from a sample. The diode laser (532 nm, 200 mW, RGB Photonics) was used as an excitation source for TTA-UC quantum yield measurements. The laser power was controlled by combining a software (Ltune) and neutral density filters and measured using a PD300-UV photodiode sensor (OPHIR Photonics). The diameter of the laser beam ($1/e^2$) was estimated as 6.8×10^{-4} cm^2 for 532 nm laser at the sample position using a charge-coupled device (CCD) beam profiler SP620 (OPHIR Photonics). The G-TX-PtOEP-DPAS film samples were placed in an integrating sphere and excited by the laser excitation sources. The scattered excitation light was attenuated by using a 500 nm short-pass filter. The spectrometer was calibrated, including the integrating sphere and the short-pass filters using deuterium and halogen standard light sources. These standard light sources were calibrated in accordance with measurement standards traceable to primary standards (national standards) located at the National Metrology Institute of Japan.

Determination of TTA-UC efficiency η_{UC} by the absolute method. Since the UC emission intensity measured with the integrating sphere is strongly affected by re-absorption processes. The obtained spectra were corrected by considering re-absorption probability in the integrating sphere based on the previously reported protocol.[2] The measurements were carried out in three different instrument/sample configurations. In Experiment (A), the upconverting sample is placed inside the integrating sphere and the laser beam is directed on to the sample. Experiment (B) is similar to Experiment (A) except that the integrating sphere is removed mechanically without changing other configurations. In Experiment (C), the upconverting sample is placed inside the integrating sphere but its height is above the laser beam so that the laser is directed on the sphere wall. The TTA-UC emission spectra in the configurations of Experiment (A) and (B) ($P_A(\lambda)$ and $P_B(\lambda)$) were normalized by using the integrated phosphorescence profiles from 620 nm to 680 nm. By using these normalized spectra $P_A'(\lambda)$ and $P_B'(\lambda)$, the reabsorption probability a was obtained by the relationship,

$$\int P_A'(\lambda)\, d\lambda \,/\, \int P_B'(\lambda)\, d\lambda = 1 - a \qquad (1)$$

The re-absorption probability a of 0.639 was obtained by taking the ratio of the integrated area of the two normalized TTA-UC emission spectra from 380 nm to 500 nm. In the TTA-UC process, the absolute TTA-UC efficiency η_{UC} can be obtained by the following equation using the experimentally obtained UC efficiency $\eta_{UC,obs}$,[2]

$$\eta_{UC,obs} \approx \eta_{UC}\,(1 - a) \qquad (2)$$

Other Measurements. The thickness of the film was measured by Mitutoyo caliper ABSOLUTE AOS DIGIMATIC. Three different film samples were measured to get an average thickness of 0.2 mm. X-ray powder diffraction (X-RPD) measurements were carried out with a Rigaku SmartLab. Differential scanning calorimetry (DSC) traces were obtained by using a DSC1 STARe system (METTLER TOLEDO) under N_2 atmosphere. Before performing measurements, samples were completely dried under vacuum for at least 15 h. The scanning rate was 10 ^oC min^{-1}. After the first cycle, both film and TX-100 samples were kept at the isothermal condition at 100 ^oC before any further measurement. Reproducible thermograms of 7^{th} and 8^{th} cycles of both the samples were considered for presentation. The cross-section Scanning electron microscopy (SEM) images of the G-TX-PtOEP-DPAS film were obtained using JEOL JSM-7800F Prime FEG SEM. The acceleration voltage was set to 10 kV and a secondary electron detector was used. Before SEM observation, the sample was dried under vacuum for two days and coated with gold using Edwards S150B gold sputter. The cross-section was obtained by breaking the film in half with hands. Confocal laser scanning microscope (CLSM) imaging was performed on a Carl Zeiss LSM 510 confocal microscope. Thin-film samples were prepared on glass-bottomed dishes (Matsunami Glass Ind., Ltd.). Blue fluorescence images were obtained through a 505-530 nm bandpass filter using Ar laser at λ_{ex} = 405 nm. DMA analysis was performed on TA-instrument DMAQ800 in tensile film mode at a strain of 0.05 % and frequency of 1Hz and temperature of 30 ^oC. Prior to the measurement, a strain sweep was performed on G film to ensure that the applied strain is within the linear viscoelastic region (Fig. S6a). FT-IR spectra of the films were recorded on a SHIMADZU IRTracer-100 instrument. For each spectrum, 32 scans were made with a selected resolution of 4 cm^{-1}. An optical polarized microscopic image of the film was obtained using a Nikon optical microscope (Nikon Eclipse 80i). The measurement has been made at 10X magnification.

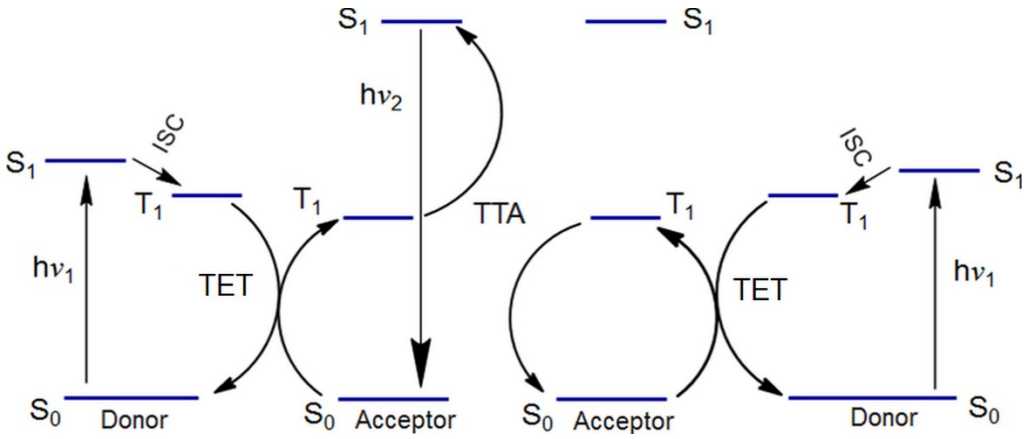

Fig. S1. Outline of the TTA-UC process, showing the energy levels involved in the TTA-UC (S = singlet, T = triplet). The TTA-UC involves a donor (sensitizer) with high intersystem crossing (ISC) efficiency and an acceptor (emitter) with high fluorescence quantum yield. First, the sensitizer absorbs the low energy light to produce the excited singlet state (S_1). Second, the triplet state (T_1) of the sensitizer is populated through ISC. Third, triplet energy transfer (TET) from donor T_1 to the triplet state of acceptor via the Dexter mechanism. Finally, the collision and annihilation (TTA) between two acceptor triplets produce a high-energy singlet excited state of the acceptor S_1, which radiates upconverted emission.

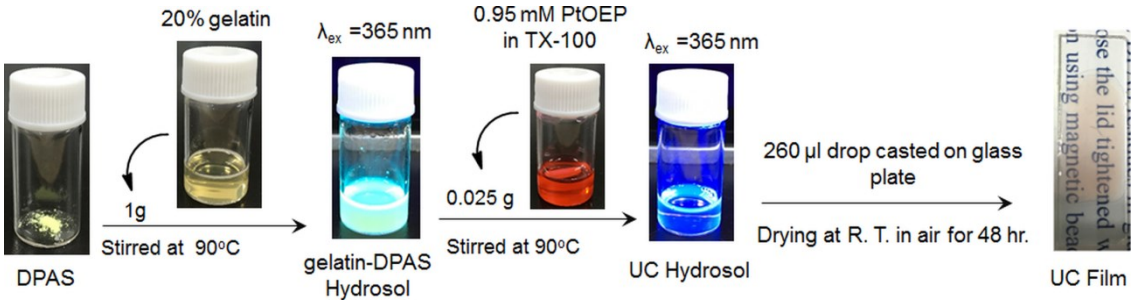

Fig. S2. Scheme of the preparation of G-TX-PtOEP-DPAS upconverting film.

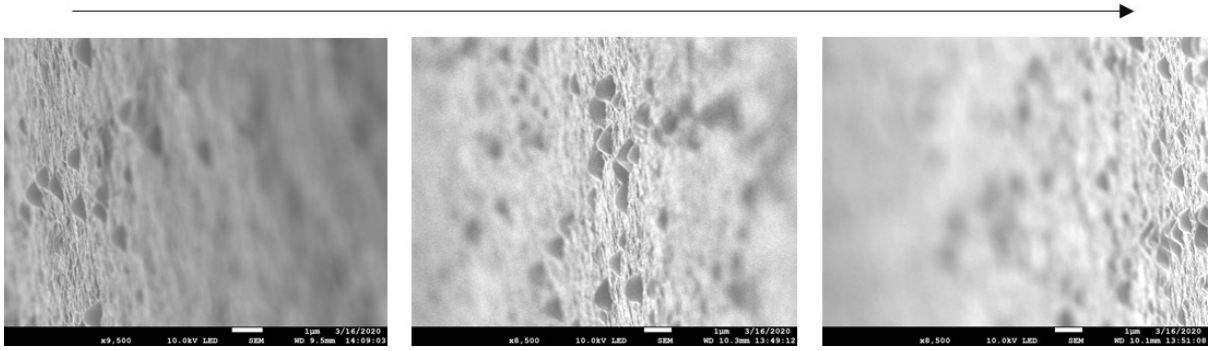

Fig. S3. Cross-sectional SEM images of the G-TX-PtOEP-DPAS film from different parts of the cross-section starting from left to right (Scale bar = 1µm).

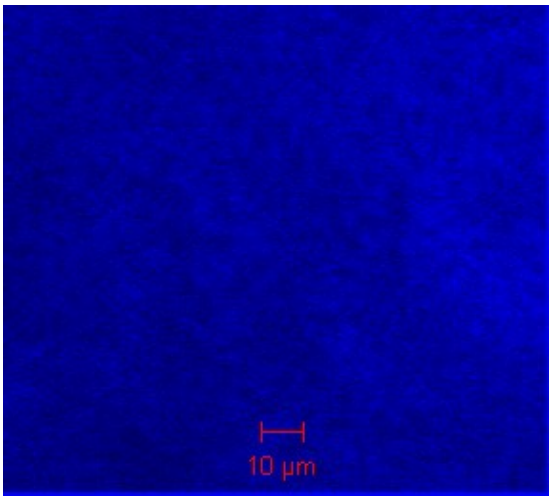

Fig. S4. CLSM image of the G-TX- PtOEP-DPAS film (λ_{ex} = 405 nm).

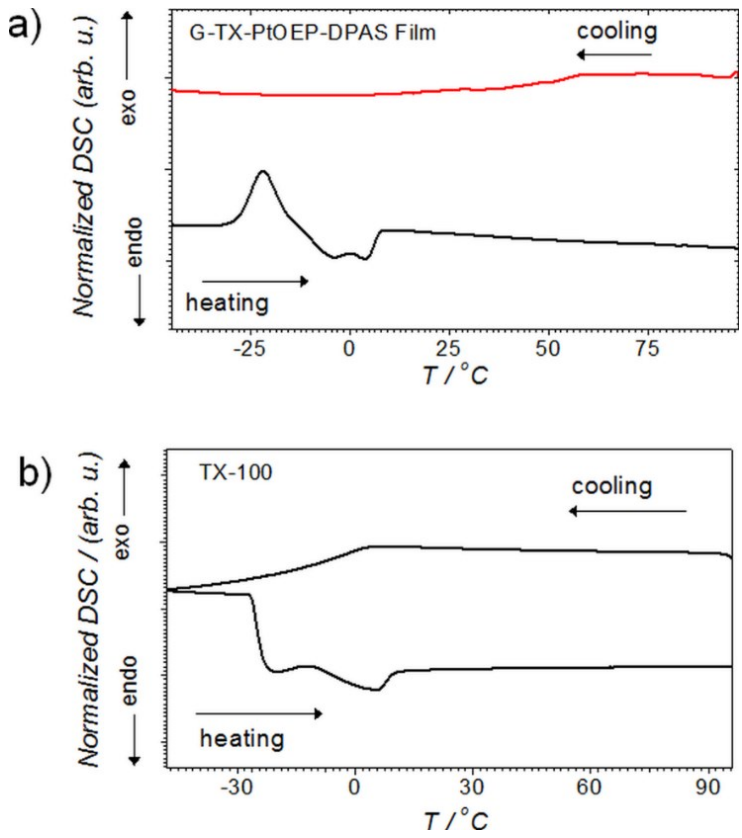

Fig. S5. DSC thermograms of a) the G-TX-PtOEP-DPAS film and b) neat TX (scan rate = 10 °C min^{-1}, N_2 atmosphere). The endothermic peaks of the G-TX-PtOEP-DPAS film and neat TX at around 6 °C are assignable to the melting of TX. The freezing peak of neat TX was not detected, probably due to the gradual crystallization of TX. The exothermic peak of the G-TX-PtOEP-DPAS film at –22 °C during the heating process can be assigned to the freezing of the TX microdroplets. The TX microdroplets would show the supercooling phenomenon in the film.

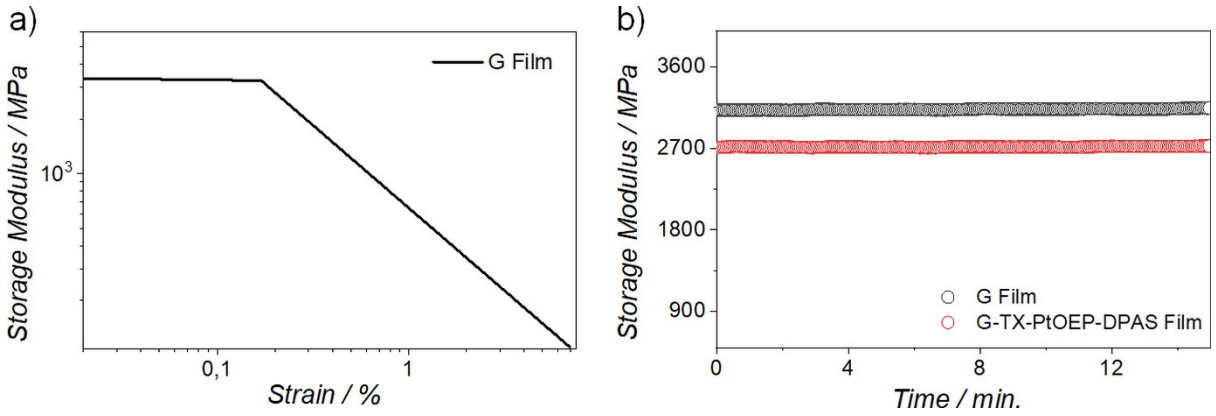

Fig. S6. DMA profiles of a) the G film showing strain sweep plot and b) time sweep plots of the G film and the G-TX-PtOEP-DPAS film at 30 °C, a strain of 0.05 % and frequency of 1 Hz.

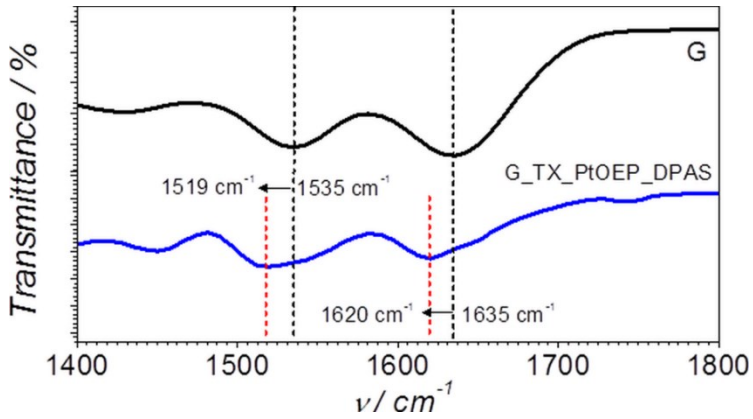

Fig. S7. FT-IR spectra of G (black) and G-TX-PtOEP-DPAS (blue) films showing red shifts of 15 cm^{-1} in the amide-I region and 16 cm^{-1} in the amide-II region of G due to interactions of gelatin with other components in G-TX-DPAS film.

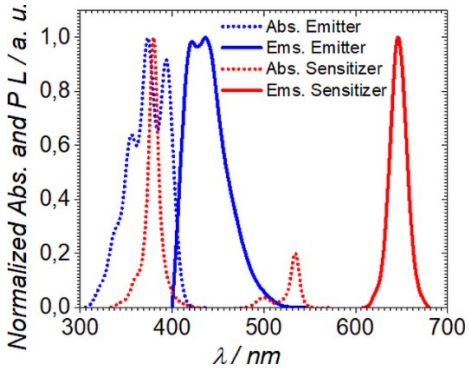

Fig. S8. Absorption (dotted line) and photoluminescence (solid line) spectra of DPAS (blue line, 500 µM) and PtOEP (red line, 23 µM) in THF. The absorption spectrum of DPAS showed peaks at 356, 373.5, and 394.5 nm, whereas its fluorescence maximum was observed at 436.5 nm. In the case of PtOEP, the absorption peaks were observed at 380, 500.5, and 534.5 nm, and phosphorescence maximum at 646 nm. Excitation wavelengths were 379 and 532 nm for DPAS and PtOEP, respectively.

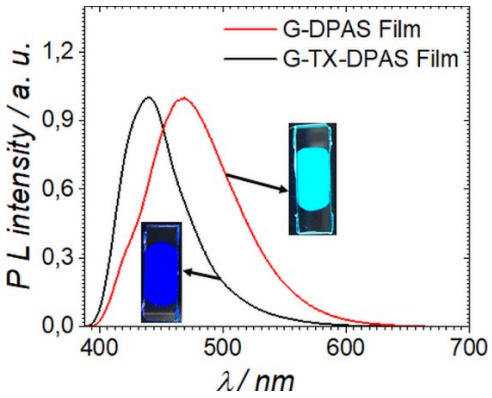

Fig. S9. Photoluminescence spectra of G-DPAS and G-TX-DPAS films (λ_{ex} = 365 nm).

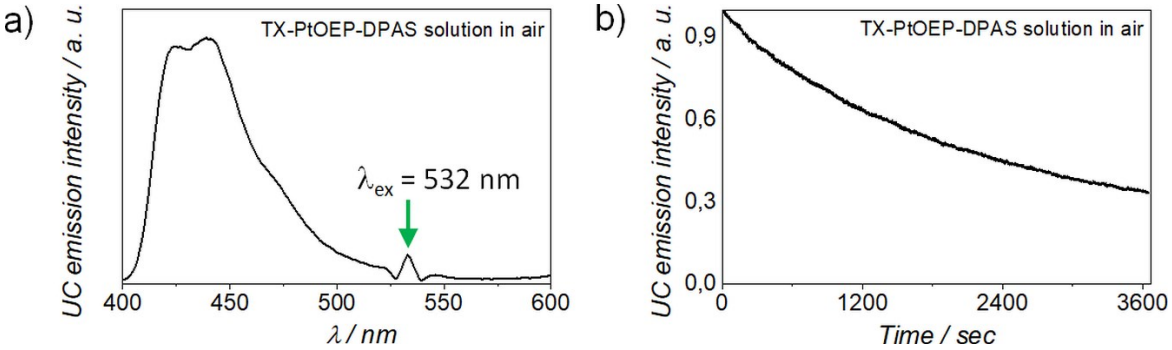

Fig. S10. a) UC emission profile of TX-PtOEP-DPAS liquid in air (λ_{ex} = 532 nm, I_{ex} = 52 mW cm^{-2}). b) Time-dependent UC emission intensity of TX-PtOEP-DPAS liquid in air at 437 nm upon the continuous 532 nm laser excitation. Chromophores concentrations are [PtOEP] = 23 mM and [DPAS] = 5 mM.

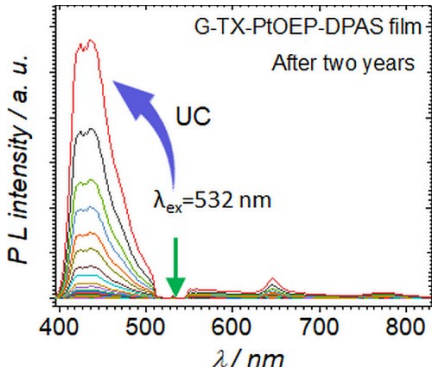

Fig. S11. Photoluminescence (PL) spectra of 2 years old G-TX-PtOEP-DPAS film at different excitation intensity of 532 nm laser at room temperature in air. A notch filter at 532 nm was used to remove the scattered incident light.

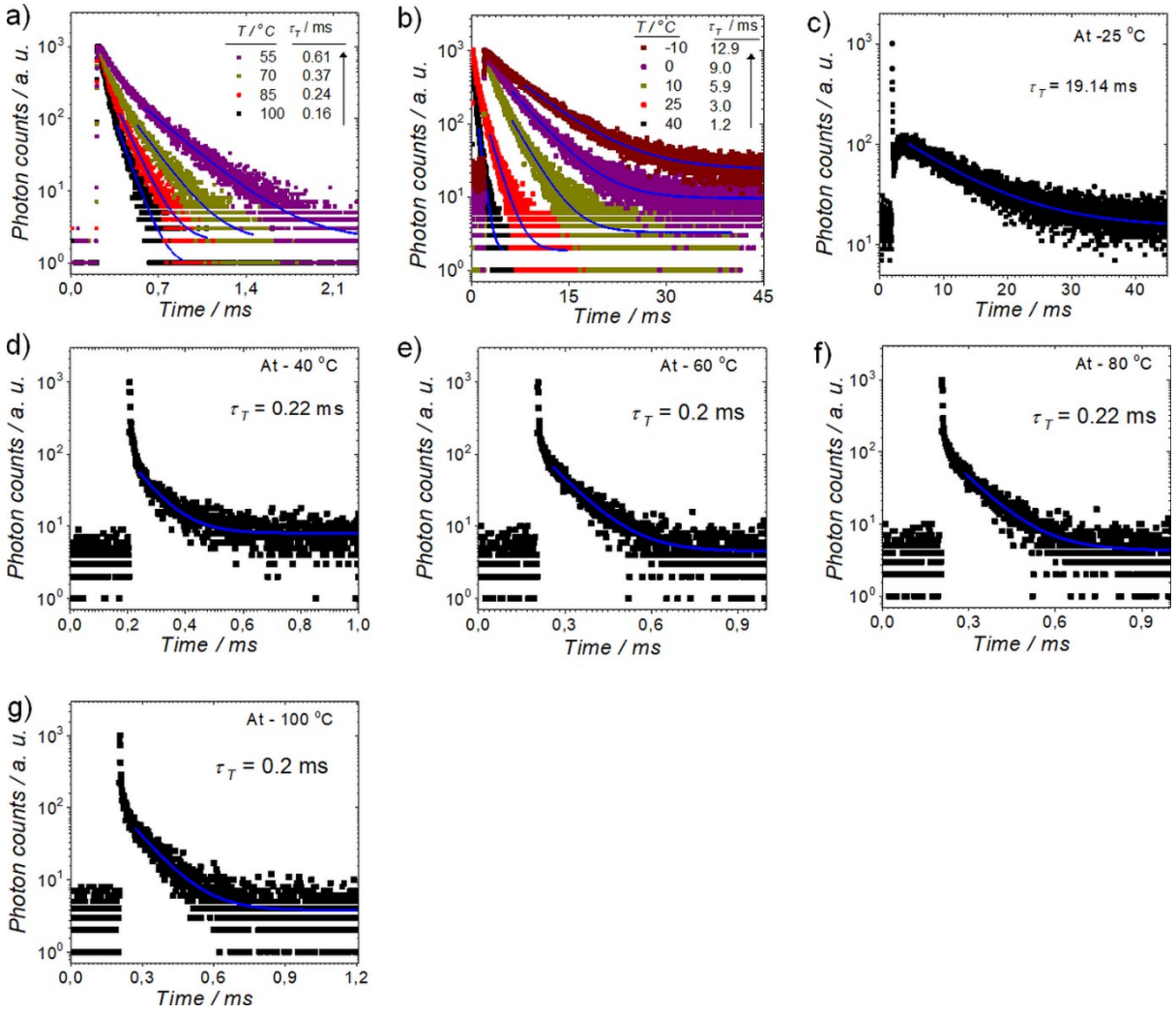

Fig. S12. Temperature-dependent emission decay profiles of vacuum-dried G-TX-PtOEP-DPAS film sealed under Ar from 100 °C to -100 °C. The blue fitting curves were obtained by tail fitting of decay profiles using a single exponential equation with Chi < 2. The triplet lifetimes in the film were measured after waiting for 10 min at each measurement temperature.

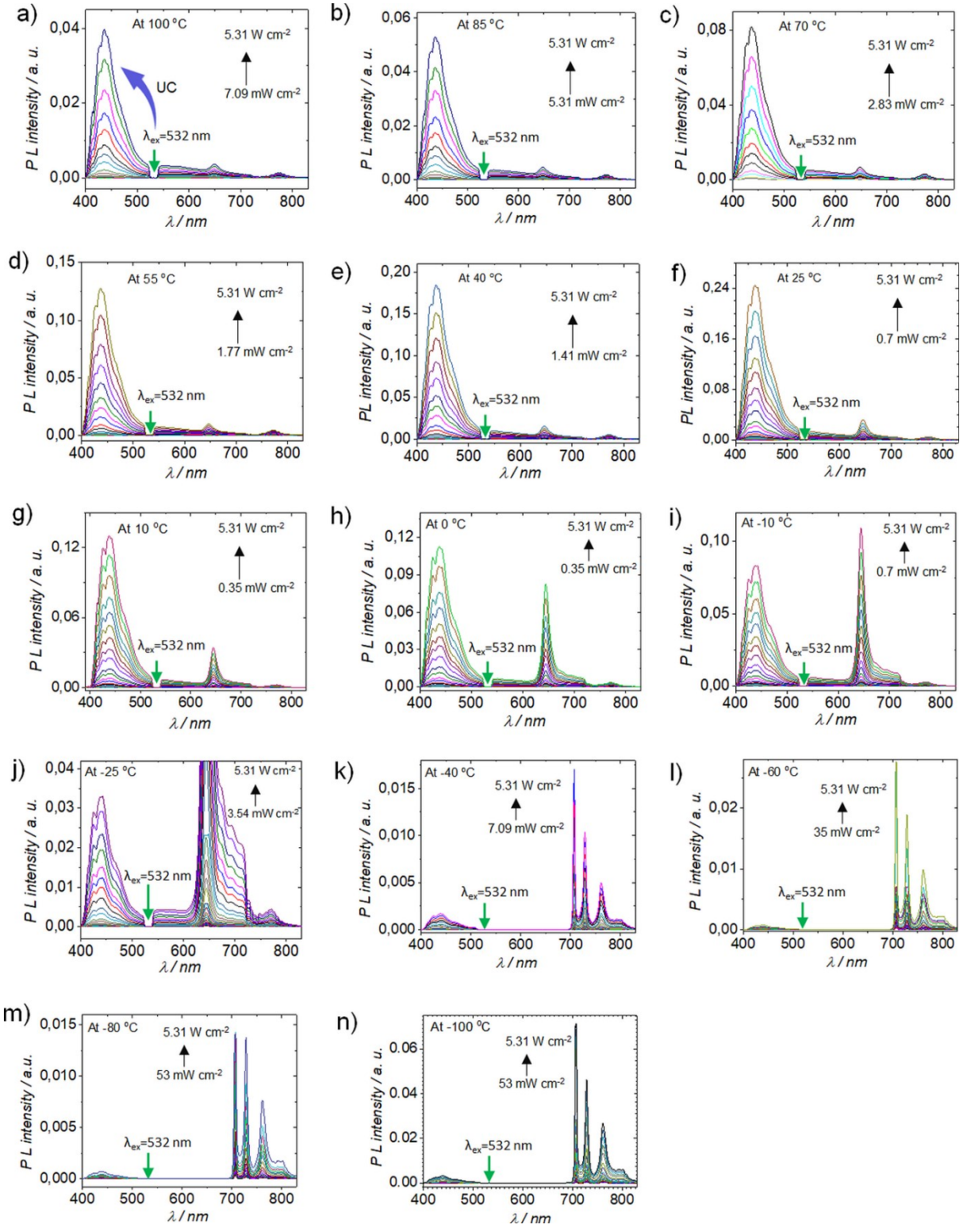

Fig. S13. Temperature-dependent UC emission intensity plots of vacuum-dried G-TX-PtOEP-DPAS film sealed under Ar from 100 °C to -100 °C. A notch filter at 532 nm was used to remove the scattered incident light. An additional short pass filter at 610 nm was used to record the data from -40 °C to -100 °C (k-n). The luminescence, which could not be cut by the short-pass filter, was observed above 700 nm. The UC emission spectra of the film were recorded after waiting for 10 min. at each measurement temperature.

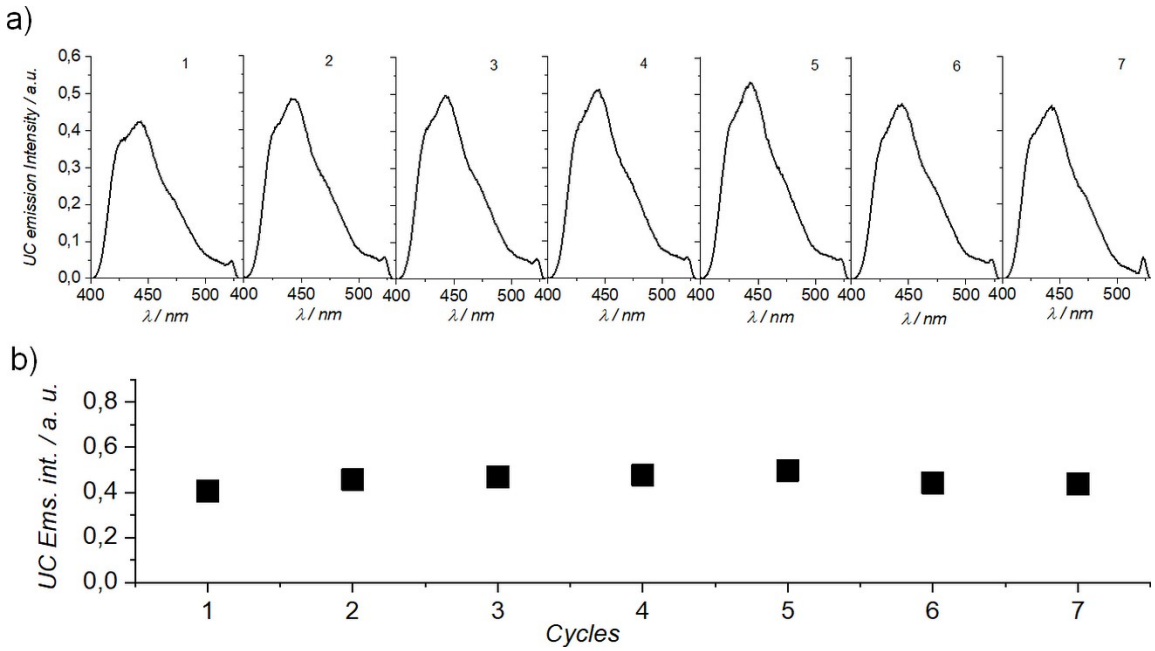

Fig. S14. Photoluminescence a) spectra and b) intensity at 437 nm of G-TX-PtOEP-DPAS film at 20 °C after repeatedly heating the film to 65 °C for 5 min, cooling it to 20 °C, and keeping it at 20 °C for 1hr (532 nm laser excitation (λ_{ex} = 532 nm, I_{ex} = 26 mW cm^{-2}).

References

1 S. Hisamitsu, N. Yanai, N. Kimizuka, *Angew. Chem. Int. Ed.*, 2015, **54**, 11550 – 11554.
2 N. Yanai, K. Suzuki, K. T. Ogawa, Y. Sasaki, N. Harada, N. Kimizuka, *J. Phys. Chem. A*, 2019, **123**, 10197 – 10203