SUPPORTING INFORMATION

Efficient NIR-to-vis photon upconversion in binary rubrene films deposited by simplified thermal evaporation

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SEM was utilized to reveal morphological changes between the cold-deposited rubrene films and the annealed ones. Fig. S1 and S2 below show surface and cross section SEM images, respectively. The images of the reference film containing sensitizer layer (**PdPc**/PS) only are also presented for comparison. The images clearly show that the sensitizer layer is uniform and it can be well distinguished from the cold-deposited rubrene, which takes spherical nano-droplet shape (300 – 1200 nm in size). A clear boundary between rubrene and sensitizer layer confirms that these layers are not intermixed. However, after the annealing the symmetrical shape of rubrene particles is lost and rubrene diffuses into the sensitizer layer making the boundary between these two layers to disappear.



Fig. S1. Surface SEM images of the sensitizer layer as a reference film (left column), cold deposited (middle column) and annealed (right column) UC films. The measurements were performed using 1 kV acceleration voltage and no additional coating. The sensitizer layer thickness, 260nm.



Fig. S2. Cross section SEM images of the sensitizer layer as a reference film (left column), cold deposited (middle column) and annealed (right column) UC films. The measurements were performed using 1 kV acceleration voltage and no additional coating. The sensitizer layer thickness, 260nm.



Fig. S3. Phosphorescence spectra measurements of **PdPc** sensitizer carried out by placing the sample inside the integrating sphere. Inset shows the spectra with background subtracted. $TET\{PdPc \rightarrow Rub\}$ efficiency was calculated according to Eq. 2.

We carried out phosphorescence intensity measurements across the film to check the uniformity, and subsequently, the variation in ϕ_{TET} . Phosphorescence intensity of **PdPc** sensitizer was found to change a little along X direction in the emitter-free films (used for reference), however it varied significantly in the UC films with rubrene present (see Fig. S4 below). This is explained by inhomogeneous rubrene distribution in UC film as there is more rubrene in the center than at the edges after evaporation and annealing. Correspondingly, the phosphorescence of the sensitizer is more quenched in the center due to more efficient TET{**PdPc** \rightarrow **Rub**}. The spatial variation of ϕ_{TET} reflects that of UC intensity (shown in Y-log scale in Fig.7a).

Phosphorescence and Φ_{TET} data for 3 different films fabricated under the same conditions are also displayed in the Fig. S4. The estimated error bars for Φ_{TET} are indicated.

Taking into account the simplified thermal evaporation technique employed for the fabrication of the UC films, the reproducible Φ_{TET} values could be obtained within the central area of ~4mm in size.



Fig. S4. a) Spatial variation of the phosphorescence intensity of **PdPc** sensitizer in reference emitter-free films (empty symbols) and UC films with emitter present (solid symbola). b) $TET\{PdPc \rightarrow Rub\}$ efficiency of UC films estimated from phosphorescence data according to Eq. 2.



Fig. S5. Optimization of rubrene thickness in the *'hot deposition'* mode. Thicker films were obtained by increasing a volume of the **Rub** stock solution, which was drop-casted on the bottom glass plate (see UC film fabrication scheme in Fig. 2). The first row shows digital photos of obtained films; the second row contains optical microscope images captured in the centre of the film; the third row displays FL transients with average FL lifetime (τ) indicated; the last row shows FL spectra of the films.



Fig. S6. a) Absorption spectra of UC films prepared by varying **Rub** evaporation time, and consequently, a thickness of **Rub** layer. Evaporation temperature was fixed at 280°C. The thickness (260nm) and concentration (0.1%) of the underneath sensitizer layer were kept constant. b) Normalized UC spectra of the same films.



Fig. S7. a) FL transients of the annealed **PdPc**/PS/**Rub** film recorded at 0 – 240 days after film fabrication. Solid line represents single-exponential fit of the dominant prompt decay component. FL lifetime, indicated. b) Optical microscopy images of the same film captured 0 and 240 days after film fabrication. **PdPc**-doped PS (sensitizer layer) thickness, 110nm.



Fig. S8. Pictures of cold-deposited UC films post-annealed at 100 °C and 200 °C for different durations (indicated).



Fig. S9. Thickness of the spin-coated sensitizer layers as determined by AFM. a) Thickness dependence on the mass and volume ratio (viscosity) between polymer and solvent (Toluene); b) thickness variation by using different spin-coating speeds while maintaining constant viscosity.



Fig. S10. The experimental scheme used to evaluate UC performance across the film. The UC film was excited with a focused 730nm laser beam, while spectral emission was collected on CCD detector. The film was scanned by moving the precision stage in X direction.



Fig. S11. UC intensity *vs* excitation power density of the cold-deposited and post-annealed UC film prepared under optimal conditions. UC threshold, indicated. **PdPc** concentration in the sensitizer layer, 0.1 wt%. Sensitizer layer thickness, 110 nm. Excitation wavelength, 730 nm.

Determination of Φ_{UC} using internal reference method

The internal reference method is essentially very similar to emission quantum yield determination by using comparative (relative) method, which is a standard in the community and was extensively described in the literature¹:

$$\Phi = \Phi_R \frac{I O D_R n^2}{I_R O D n_R^2}$$

Here Φ is FL quantum yield, *I* - integrated FL intensity, *OD* – optical density and *n* is the refractive index. Label '*R*' refers to a reference material with known FL quantum yield.

In the case of internal reference **PdPc** with known Φ_{FL} , $n=n_R$ and $OD=OD_R$, and the Eq. above can be simplified to

$$\Phi_{UC} = \Phi_{FL} \frac{I_{UC}}{I_{FL}}$$

Here I_{UC} and I_{FL} are the integrals of UC and FL spectra, respectively.

Reproducibility data of FL quantum yield of the sensitizer (ϕ_{FL}^{PdPc}) and evaluation of an error for ϕ_{UC}

We performed over 40 measurements on different samples to determine Φ_{FL} of **PdPc** using the integrating sphere method. The samples ranged from those containing sensitizer layer only to UC films prepared by different evaporation modes (hot deposition, cold deposition, annealed) used in this work. Additionally, **PdPc** concentration in PS and sensitizer layer thickness were varied from 0.1 to 1 wt% and from 110nm to 500nm, respectively. Each sample was measured multiple times at different spots. Different sample excitation geometries (perpendicular and edge excitation) in the sphere were utilized to result in low (5-10%) and high (10-40%) absorption. Moreover, the reliability of the Φ_{FL} estimates was verified by employing two different setups with different integrating spheres. All the data is summarized and plotted as a histogram in Fig. S12 below. The average FL quantum yield of **PdPc** was estimated to be 0.1% with a standard deviation of 0.03%. The results confirmed the eligibility and versatility of the sensitizer **PdPc** as an internal reference for quantum yield determination.

The error of Φ_{UC} can be found by estimating the errors of each term in the following equation $\Phi_{UC} = \Phi_{FL} \frac{I_{UC}}{I_{FL}}$.

The largest error in evaluation of I_{UC} and I_{FL} comes from the correct subtraction of the background signal (Fig. 8). For I_{UC} it is a few percent only and thus can be neglected, meanwhile for I_{FL} with much larger impact of the background, the absolute error is ±11% (=22%/2) at most (see Fig. S13 below). An evaluation of the background signal was carried for the UC film with the thinnest sensitizer layer of 110 nm, hence having the largest impact of the background. The calculated relative error for Φ_{UC} in the case of internal reference method is 32%, which implies $\Phi_{UC} = (1.0 \pm 0.32)\%$.



Fig. S12. Distribution of absolute FL quantum yield of **PdPc**-doped polystyrene films at the concentration of 0.1 - 1 wt%. The samples included in the histogram represent various preparation conditions (thickness, concentration etc.) as well as different sample excitation geometries in the integrating sphere. The average FL quantum yield of PdPc was found to be 0.1% with the standard deviation of 0.03%.



Fig. S13. Emission spectrum of **PdPc**/Ps/**Rub** film (black line) from Fig.8 with sensitizer layer thickness of 110 nm. I_1 and I_2 indicate spectral integrals of FL_{PdPc} and background signals, respectively.

Confirmation for achieving TTA domination regime ($\phi_{TTA} \approx 100\%$)

According to the theoretical work of K. Murakami et al,² UC vs excitation intensity dependence can be expressed as

$$\Theta = 1 + \frac{1 - \sqrt{1 + 2\Lambda}}{\Lambda}$$

where Θ is normalized UC quantum yield $(\Phi_{UC}/\Phi_{UC}^{\omega})$ and Λ is dimensionless excitation intensity. Evidently, max. Φ_{UC} (Θ =1) is reached when Λ approaches infinity. It is also discussed that commonly used UC threshold (I_{th}) determined by the intersection of quadratic and linear excitation regimes corresponds to Λ =2, which substituted into the expression above gives Θ =0.382. Therefore, Λ =4 (2×I_{th}) is suggested to be used to describe the true I_{th} as corresponding to Θ =0.5 by definition.

In the case of our rubrene-based UC films $I_{th} = 1.4W/cm^2$ as determined from the intersection of quadratic and linear regimes (Fig. S11), thus corresponding to $\Lambda=2$. The statistical probability (*f*) was evaluated at the excitation density of 100 W/cm², exceeding the true I_{th} by a factor of $100/(2\times1.4) \approx 36$ and corresponding to $\Lambda \approx 143$. Such high excitation results in $\Theta=0.89$ indicating that no significant Φ_{UC} can be gained using higher pump levels. Even if slightly non-saturated excitation conditions with $\Theta=0.89$ instead of 1.0 are assumed, the change in the *f* will be minor, from 19.5% to 21.9%.

References

- 1. Lakowicz, J. R. Principles of Fluorescence Spectroscopy (Kluwer Academic / Plenum Publishers 1999).
- 2. Murakami, Y. and Kamada, K. Phys. Chem. Chem. Phys., 2021, 23, 18268.