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Supplementary Information for

**Transparent and flexible resins functionalized by lanthanide-based
upconversion nanocrystals**

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Experimental section

Synthesis of NaGdF₄:Yb,Er UCNCs.

NaGdF₄:Yb,Er UCNCs were synthesized by thermal decomposition method according to the previous report¹. The oleic acid (OA) and 1-octadecene (ODE) were utilized as the coordinating ligand and non-coordinating solvent, respectively. In a typical preparation of NaGdF₄:Yb,Er UCNCs, 1 mmol Ln(CF₃COO)₃ (0.78 mmol Gd³⁺, 0.20 mmol Yb³⁺, 0.02 mmol Er³⁺) and CF₃COONa were combined with OA (6.4 mL) and ODE (12.8 mL) in a three-neck flask. The mixture was heated at 110 °C for 40 min to obtain a transparent solution, and residual water and oxygen were removed by vacuum. Subsequently, it was further heated to 300 °C under Ar flow for 1 h. Finally, the resultant white products can be collected through centrifugation with cyclohexane/alcohol (1:1) several times.

Synthesis of NaGdF₄:Yb,Tm UCNCs.

NaGdF₄:Yb,Tm nanoparticles were synthesized via a similar procedure except that 1 mmol Ln(CF₃COO)₃ (0.795 mmol Gd³⁺, 0.20 mmol Yb³⁺, 0.005 mmol Tm³⁺) was used during the preparation.

Synthesis of content-dependent Au/NaGdF₄:Yb,Er hybrids.

Au-modified NaGdF₄:Yb,Er (Au/NaGdF₄:Yb,Er) UCNCs were synthesized with a simple reduction method², and the ascorbic acid (AA) and poly(vinylpyrrolidone) (PVP) were chosen as reducing agent and capping agent. 25 mg of the prepared NaGdF₄:Yb,Er UCNCs were dispersed in 10 mL H₂O, and mixed with 2 mL PVP₅₅₀₀₀ solution (2.4 mM) under magnetic stirring. Then 10 mM HAuCl₄ with different volumes were added to the mixture. Finally, Au/NaGdF₄:Yb,Er could be obtained after the addition of 0.9 mL 100 mM AA into the solution and reaction for 30 min. The contents of the Au were set to be 0.08 wt% (Au (0.08%)/NaGdF₄:Yb,Er), 0.16 wt% (Au (0.16%)/NaGdF₄:Yb,Er), 0.47 wt% (Au (0.47%)/NaGdF₄:Yb,Er) and 0.63 wt% (Au (0.63%)/NaGdF₄:Yb,Er).

UCNCs-functionalized PE slices.

UCNCs-functionalized PE slices were synthesized using the hot compaction method under 140 °C³. Typically, the PE resins were adequately mixed with Au/NaGdF₄:Yb,Er following the ratio of 50:1. Then the mixtures were fused under 140 °C for 4 min and vacuumed several times to reduce bubbles, and then further moulded under 6 MPa pressure. These final doped PE slices were shaped up in round tablets with a radius of 4.5 mm and thickness

of 1 mm. The NaGdF₄:Yb,Tm functionalized PE resins were also prepared using a PE to NaGdF₄:Yb,Tm ratio of 20:1.

Flexible UCNCs-functionalized PDMS resins.

UCNCs-functionalized PDMS resins were synthesized according to the previous work⁴. The 3.5 mg Au (0.16%)/NaGdF₄:Yb,Er hybrid was dispersed into 2 mL curing agent by sonication. The epoxy resin was added to the mixture with a volume ratio of 8:1 and then loaded onto the PDMS resins with a diameter of 3.5 cm and different thicknesses of 2, 3, 4 and 5 mm. The final molarity of UCNCs was about 0.76 mM in resins. Subsequently, the mold was heated at 80 °C for 10 h to cure the epoxy.

Material characterization.

Transmission electron microscopy (TEM) images were taken on a Hitachi Model H-7700 microscopy at an accelerating voltage of 100 kV.

High-resolution TEM (HRTEM) image and elemental mapping profiles were recorded by the field-emission high-resolution transmission electron microscope assembled with the energy dispersive x-ray spectrometry (EDX) systems (JEOL JEM-2100F) and operated at 200 kV.

Powder X-ray diffraction (XRD) patterns were recorded with a Philips X'Pert Pro Super X-ray diffractometer with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$).

Ultraviolet-visible-near-infrared (UV-vis-NIR) absorption spectra were collected in the spectral region of 300-2000 nm with a Shimadzu SolidSpec-3700 spectrophotometer.

Quantitative characterization of photoluminescence (PL) spectra.

This quantitative characterization of PL spectra was realized according to our prior method⁵. In detail, powder samples in the groove ($3 \times 3 \times 1 \text{ mm}^3$) on the silicon wafer were used to ensure the same thickness and area. The laser spot size ($\approx 1 \times 2 \text{ mm}^2$) was fixed during the measurement to ensure that the interaction volume and laser intensity were consistent throughout the test. The position of the laser relative to the samples was identical during the measurements.

Pump power-dependent UC emission.

The calculation of pump power-dependent UC emission was according to the following relation⁶,

$$I_{PL} \propto P^n$$

where I_{PL} is the PL intensity, P is the pump laser power, and n is the slope value which represents the number of the laser photons under unsaturated conditions.

Upconversion luminescence lifetime measurement.

The upconversion luminescence lifetimes of Er ions were measured using a Tektronix TDS2024 digital storage oscilloscope and a tunable laser system (Model Opolette 355LD OPO system) was used as the excitation source (980 nm).

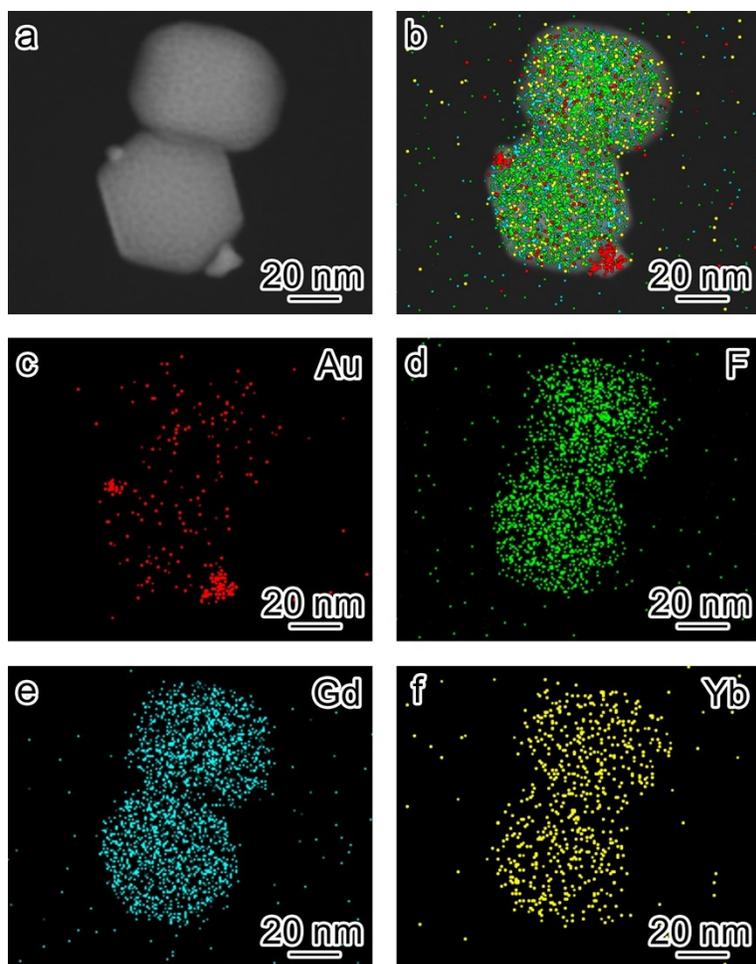


Figure S1. EDX elemental mapping profiles of Au/NaGdF₄:Yb,Er nanostructures. (a) TEM image of Au/NaGdF₄:Yb,Er nanostructures. (b) Merge image of elements. (c–f) Elemental mapping profiles of Au (c), F (d), Gd (e) and Yb (f) elements.

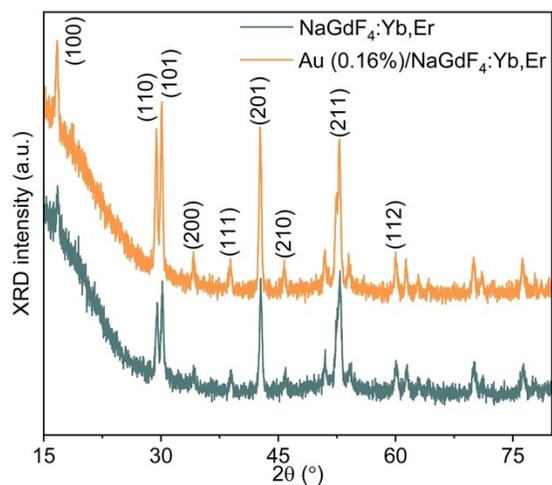


Figure S2. XRD patterns of NaGdF₄:Yb,Er and Au (0.16%)/NaGdF₄: Yb, Er hybrids.

Figure S1 shows the XRD patterns of NaGdF₄:Yb,Er and Au-modified NaGdF₄:Yb,Er. The characteristic peaks of both prepared samples match well with those for hexagonal NaGdF₄ (standard PDF#27-0699).

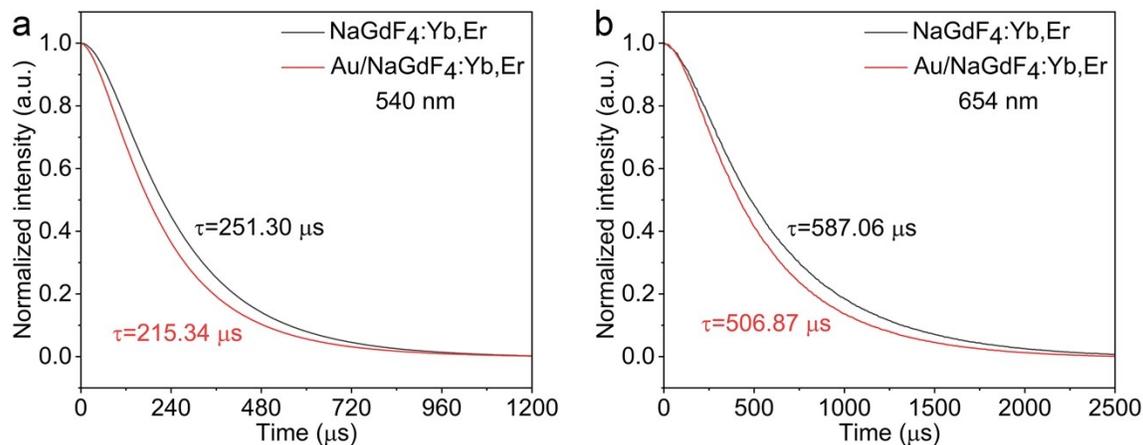


Figure S3. Upconversion luminescence lifetimes of NaGdF₄:Yb,Er with and without Au nanocrystals under 980 nm excitation. (a) Luminescence lifetimes of Er ions on green band (~540 nm). (b) Luminescence lifetimes of Er ions on red band (~654 nm).

Lifetime (τ) can be obtained from the fitting results using the single exponential function⁷:

$$I(t) = I_0 \exp(-t/\tau),$$

where I_0 is the initial emission intensity at $t = 0$. The decreases of luminescence lifetimes can be observed in both green band (from 251 to 215 μ s) and red band (from 587 to 507 μ s), demonstrating the enhanced excitation and radiative rates of Er ions induced by the plasmonics effect of Au nanocrystals.

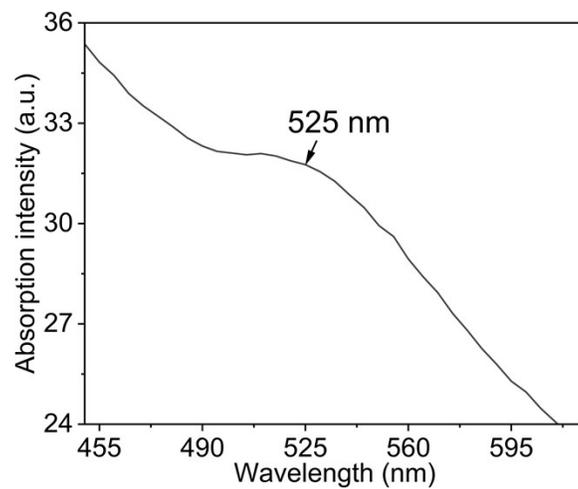


Figure S4. UV-vis-NIR absorption spectrum of pure Au nanocrystals.

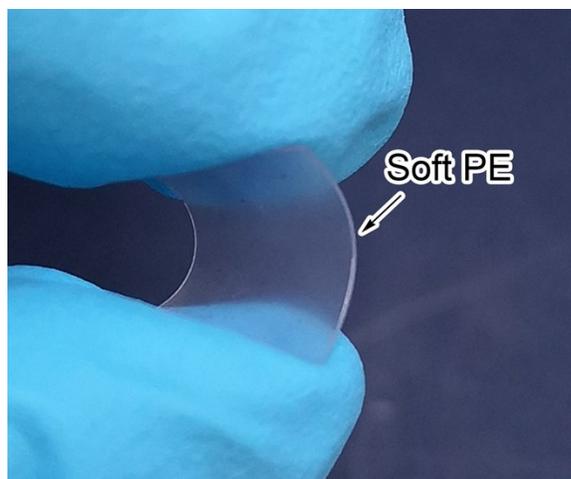


Figure S5. Photograph image of the PE resin after bending.

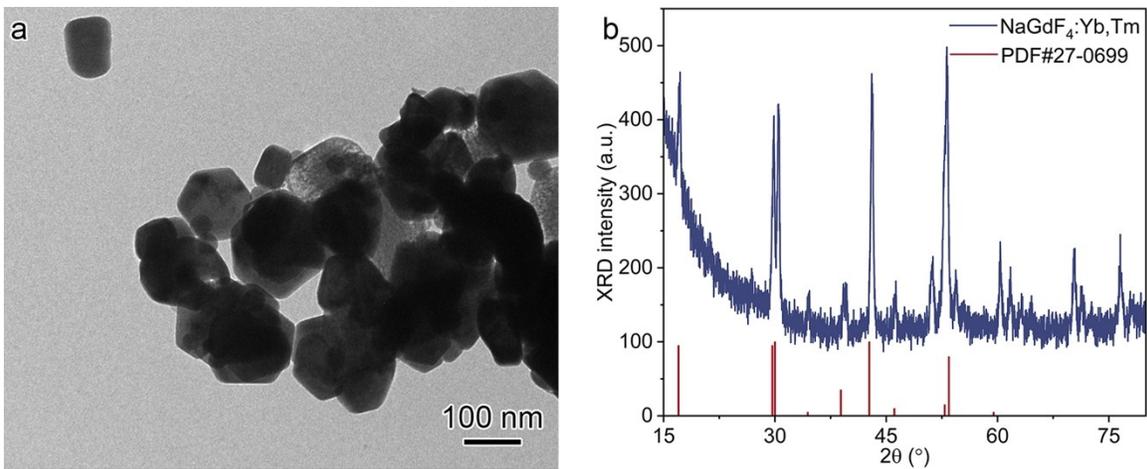


Figure S6. (a) TEM image of NaGdF₄:Yb,Tm nanostructures. (b) XRD pattern of NaGdF₄:Yb,Tm UCNCs and the standard diffraction pattern of hexagonal NaGdF₄ (PDF#27-0699).

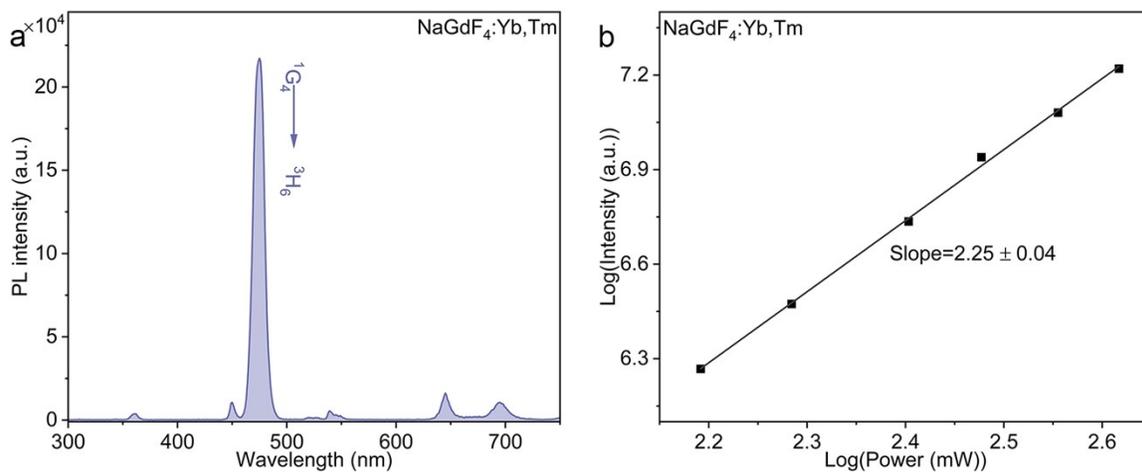


Figure S7. (a) UC emission spectra of NaGdF₄:Yb,Tm UCNCs excited under 980 nm laser irradiation. The blue band (around 475 nm) is attributed to the ¹G₄ \rightarrow ³H₆ transitions. (b) Pump power-dependent UC emission of NaGdF₄:Yb,Tm from 155.5 to 414 m W under 980 nm pump irradiation.

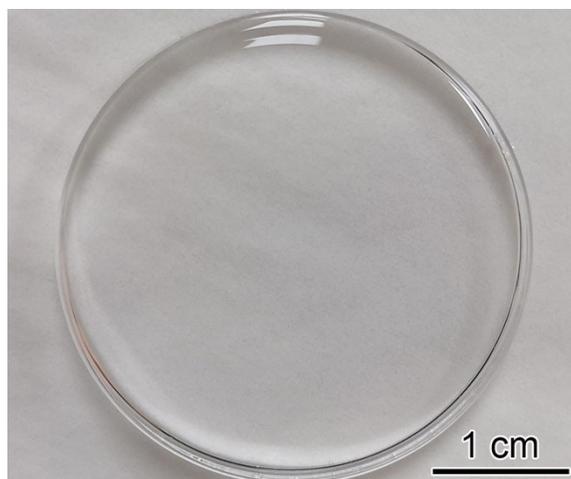


Figure S8. Photograph image of transparent PDMS resin with a diameter of 3.5 cm.

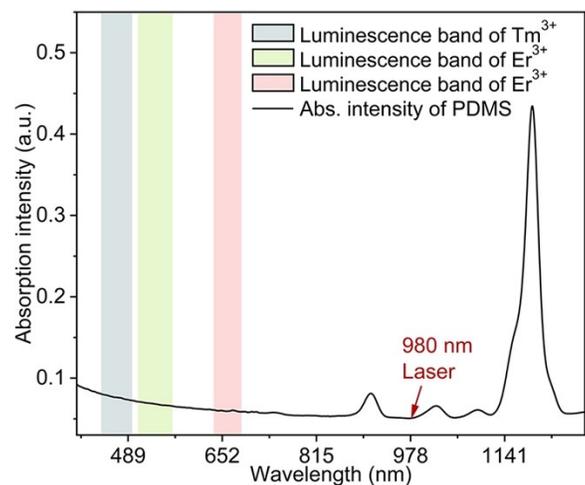


Figure S9. UV-vis-NIR absorption spectrum of PDMS resin.

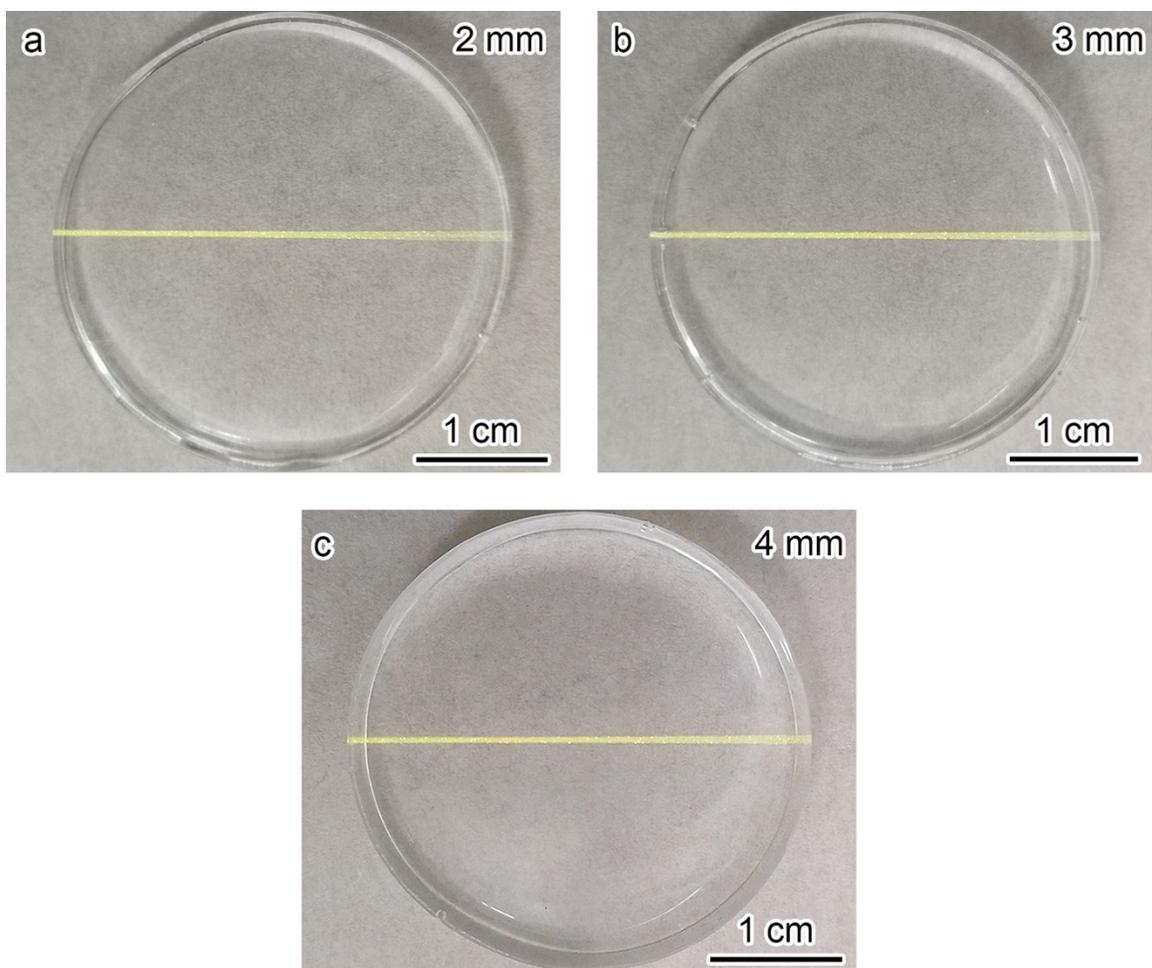


Figure S10. Emission image of Au (1.6%)/NaGdF₄:Yb,Er-modified PDMS resins with (a) 2 mm, (b) 3 mm and (c) 4 mm thickness under 980 nm laser (3 W) irradiation.

Table S1. Partial data of absorption peaks in Fig. S9.

Absorption band	Position/nm	Abs. intensity
Peak 1	475	0.0758
Peak 2	670	0.0604
Peak 3	742	0.0578
Peak 4	909	0.0811
Peak 5	1022	0.0658
Peak 6	1094	0.0609
Peak 7	1189	0.4346

Fig. S9 shows that the main absorption band of PDMS resin is located around 1189 nm, and shows negligible absorption at the wavelength of 980 nm. Therefore, it can be a perfect substrate for our study on UCNCs using a 980 nm light irradiation. The detailed data are converted into Table S1 for ease of comparison.

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