Support Information for:

Water-soluble, upconverting $Sr_2Yb_{0.3}Gd_{0.7}F_7:Er^{3+}/Tm^{3+}$@$PSI_{oAm}$ bio-probe for *in vivo* trimodality imaging

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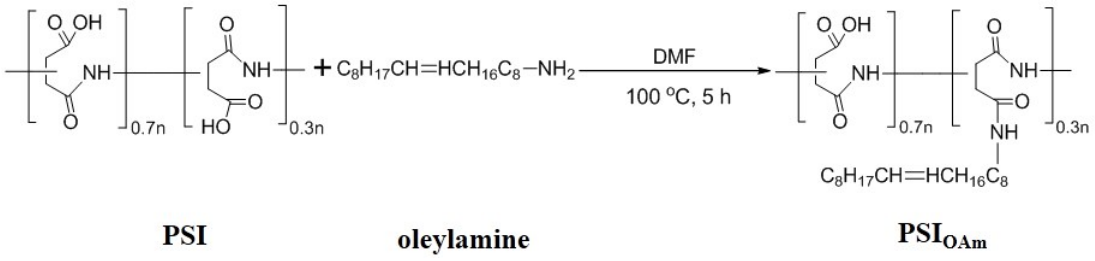
Content

S1. Materials

NH_4F (99.99%), $SrCl_2$ (99.99%), $Ln(NO_3)_3{\cdot}6H_2O$ (Ln = Gd, Yb, Er and Tm), oleylamine and oleic acid were purchased from Sigma-Aldrich. Polysuccinimide (PSI) was purchased from Shijiazhuang Desai Chemical Company. Other chemicals are of analytical grade and used as received without further purification.

S2. Preparation of the oleylamine modification of polysuccinimide

1.6 g of polysuccinimide (PSI) was dissolved in 32 mL of N, N-Dimethylformamide (DMF) at 60 °C under magnetic stirring followed by the addition of oleylamine (1.63 mL). The mixture was treated at 100 °C for 5 h before cooling to room temperature. Then methanol (80 mL) was added to precipitate the product (PSI_{OAm}). Finally, the PSI_{OAm} was collected after centrifugation and evaporating the residual methanol.



Scheme S1. Synthetic routine of PSI_{OAm}

S3. Characterization

The crystal structures of as-prepared samples were characterized by a powder X-ray diffraction (XRD) apparatus (D/Max 2500). The morphology, and element constitution of the samples were characterized by transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM, JEOL 2100) equipped with an Oxford instrument energy dispersive X-ray spectroscopy (EDS) system at the accelerating voltage of 200 kV. Upconversion emission spectra were recorded by a fluorescence spectrophotometer (R500) under the excitation of a 980 nm laser. The surface structure of PSI_{OAm}-modified UCNCs was tested by Fourier transform infrared spectra (Vertex80+Hyperion2000/Vertex80+ Hyperion2000). The magnetic properties of the samples were evaluated by Physical Property Measurement

Systerm (PPMS- 9/PPMS EC Ⅱ-9T). Upconversion optical bioimaging was performed under a confocal laser scanning microscope (ZEISS710). In vivo UCL imaging was performed by in vivo imaging system (Berthold Technologies: NightOWL LB983). CT and MRI experiments were conducted in AnHui Provincial Hospital (Hefei, China).

S4. The characterization of as-prepared $Sr_2Yb_xGd_{1-x}F_7$ nanocrystals

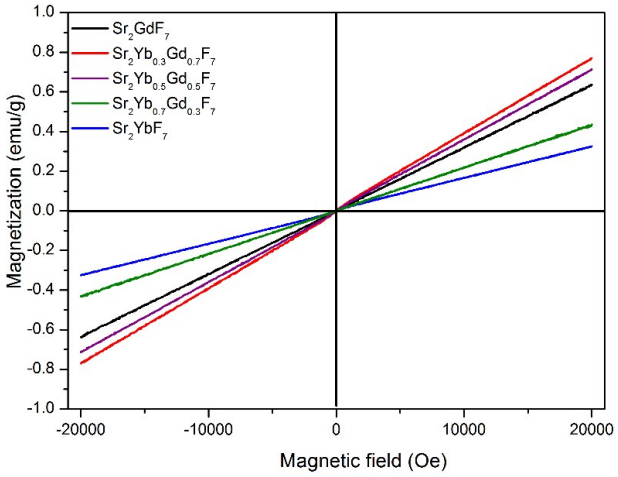


Fig. S1 Magnetization as a function of an applied field for $Sr_2Yb_xGd_{1-x}F_7$: 0.2%Er^{3+}/0.2%Tm^{3+} doped with different Gd^{3+} contents.

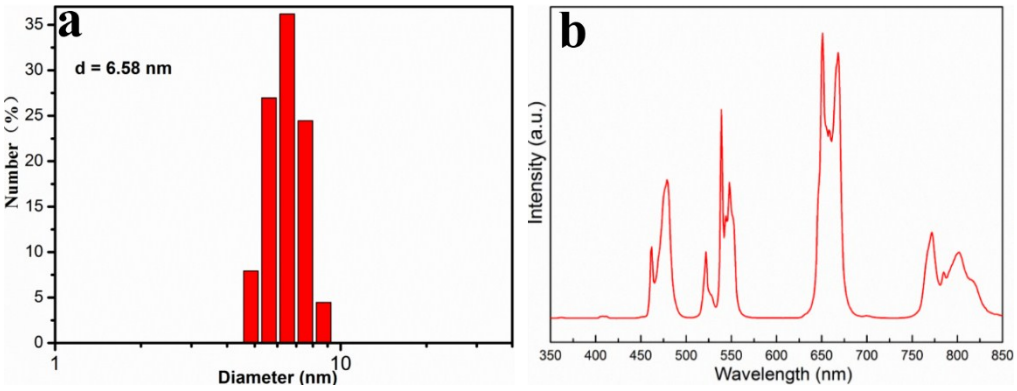


Fig. S2 (a) The size distribution diagram of $Sr_2Yb_{0.3}Gd_{0.7}F_7$: 0.2%Er^{3+}/ 0.2% Tm^{3+}; (b) Upconversion luminescence spectra of $Sr_2Yb_{0.3}Gd_{0.7}F_7$: 0.2%Er^{3+}/ 0.2% Tm^{3+}

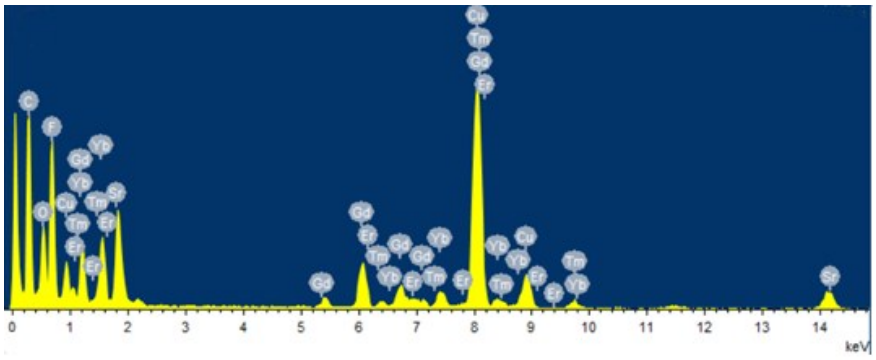


Fig. S3 EDS spectra of as-synthesized $Sr_2Yb_{0.3}Gd_{0.7}F_7$: 0.2%Er^{3+}/0.2%Tm^{3+}.

Element	Weight percentage	Atom percentage
C K	8.84	34.93
O K	1.80	5.36
F K	4.44	11.10
Cu K	48.83	36.45
Sr L	6.59	3.56
Gd L	15.85	4.79
Er L	3.31	0.95
Tm L	3.52	1.00
Yb L	6.82	1.85
Total	100.00	

Table S1 the EDS spectrum analysis of the content of the elements of $Sr_2Yb_{0.3}Gd_{0.7}F_7$: Er^{3+}/Tm^{3+}

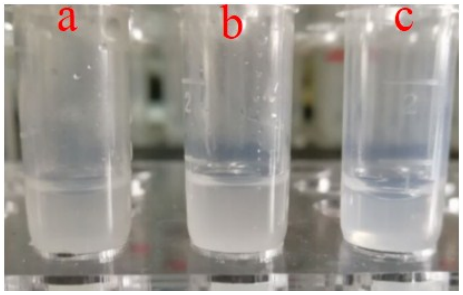


Fig. S4 The images of $Sr_2Yb_{0.3}Gd_{0.7}F_7$: 0.2%Er^{3+}/0.2%Tm^{3+} with different modifiers aqueous solution of 2500 μg/mL: (a) $Sr_2Yb_{0.3}Gd_{0.7}F_7$: 0.2%Er^{3+}/0.2%Tm^{3+}@SiO_2, (b) $Sr_2Yb_{0.3}Gd_{0.7}F_7$: 0.2%Er^{3+}/0.2%Tm^{3+}@PEG and (c) $Sr_2Yb_{0.3}Gd_{0.7}F_7$: 0.2%Er^{3+}/0.2% Tm^{3+}@PSI_{OAm}.

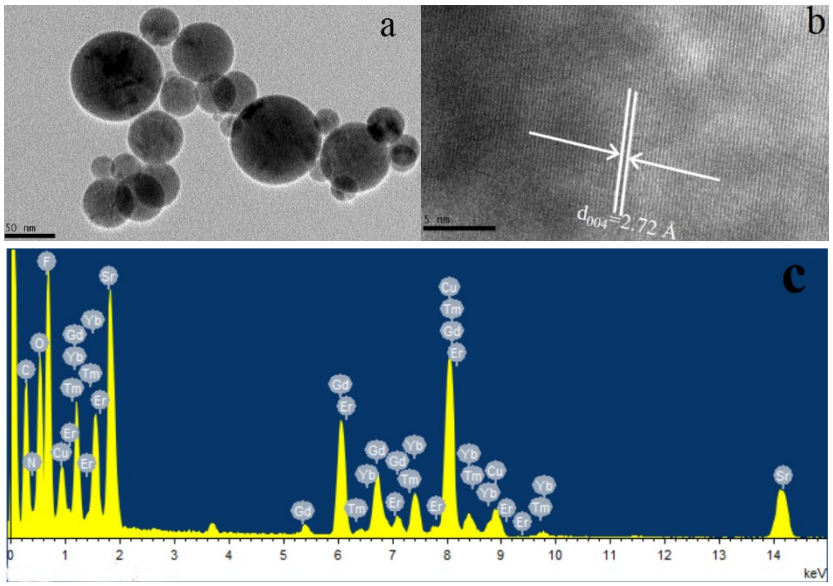


Fig. S5 TEM, HRTEM and EDS of the UCNCs@$PSI_{OAm.}$: (a) TEM image, (b) HRTEM image and (c) EDS spectra.

Element	Weight percentage	Atom percentage
C K	4.72	22.64
N K	0.04	0.17
O K	3.20	11.52
F K	5.26	15.96
Cu K	27.80	25.23
Sr L	11.42	7.49
Gd L	33.13	12.15
Er L	0.78	0.29
Tm L	0.83	0.29
Yb L	12.82	4.26
Total	100.00	

Table S2 the EDS spectrum analysis of the content of the elements of the UCNCs@$PSI_{OAm.}$

S5. The application in MR and CT imaging

Materials	$r_1/[Gd^{3+}](mM^{-1}s^{-1})$	References
our sample	2.88	/
Gd-DTPA	3.587	*Nanoscale*, 2017, 9, 4620-4628.
Sr_2LuF_7:Yb/Er@Sr_2GdF_7@SrF_2	0.1515	*ACS Appl. Mater. Interfaces*, 2017, 9, 5748-5758.
$NaYbF_4$: Tm^{3+}/Gd^{3+}	0.8	*Biomaterials*, 2017, 115, 90-103.
$NaGdF_4$:Yb,Er,Mn,Co@mSiO_2-CuS	1.1	*Nanoscale*, 2017, 9, 4759-4769.
$BaYbF_5$: Gd^{3+}/Er^{3+}	1.053	*Mater. Sci. Eng., C*, 2017, 75, 510-516.
$NaYF_4$:Yb^{3+}/Tm^{3+}@$NaGdF_4$:Yb^{3+}-DPP-PEG	1. 3725	*J. Am. Chem. Soc*., 2013, 135, 18920-18929.
Fe_3O_4@ß-$NaGdF_4$:Yb/Er	2.9	*COORDIN. CHEM. REV.*, 2018, 364, 10–32.
PEG-GdF_3:Fe	3.3	*Nanoscale*, 2018, 10, 1394-1402.
$NaYbF_4$:Tm@$NaGdF_4$:Yb-PVP	3.58	*Science Bulletin*, 2017, 62, 903–912.
$NaGdF_4$:Yb/Tm@SiO_2@TiO_2@FA	4.53	*Biomaterials,* 2015, 44, 82-90.
PBMn-52	4.9	*ACS Appl. Mater. Interfaces*, 2017, 9, 13875−13886.
(PEG-NaGd$(WO_4)_2$Eu	7.3±0.3	*Nanoscale*, 2018, 10, 1607–1612.
AuGds	12.39	*Nanoscale*, 2017, 9, 4620-4628.
Gd-FA-PFBT	16.98	*Adv. Funct. Mater.* 2018, 28, 1707174-1707192.

Table S3 Comparison of Ionic Relaxivity (r_1) Values of Gd^{3+}-Based NPs.

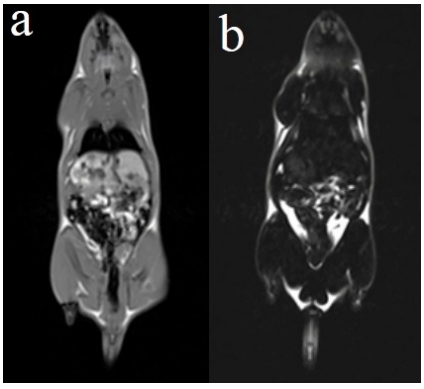


Fig. S6 *In vivo* T2-weighted MR images of the rat: (a) pre-injection, (b) post-intravenous injection.

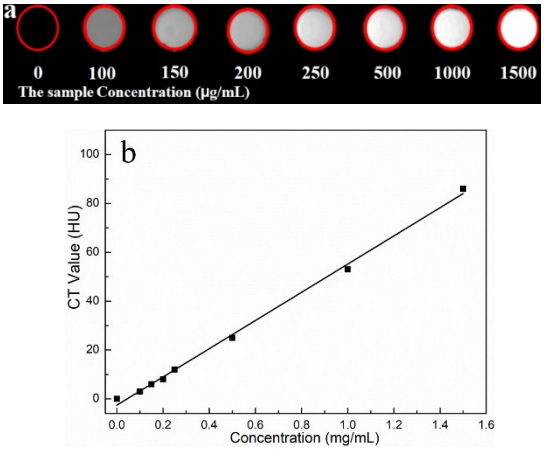


Fig. S7 (a) CT images of the UCNCs@PSI_{OAm} aqueous solution at various concentration; (b) CT value for the various concentrations of the UCNCs@PSI_{OAm}.

Materials	CT value (HU)	Concentration (mg/mL)	References
our sample	~53	1	/
iobitridol	~27.2	1	*Nanoscale*, 2018, 10, 1394-1402.
$K_{0.3}Bi_{0.7}F_{2.4}$:Yb^{3+}/Tm^{3+}	~30	1	*ACS Appl. Mater. Interfaces*, 2017, 9, 20426-20434.
$BaGdF_5$@MPN	~35	1	*J Mater Sci: Mater Med.*, 2017, 28, 74-84.
PEG-GdF_3:Fe	~44.2	1	*Nanoscale*, 2018, 10, 1394-1402.
$NaYF_4$:Yb/Tm@$NaGdF_4$:Yb^{3+}-DPP-PEG	~50	1	*J. Am. Chem. Soc*., 2013, 135, 18920 -18929.
AuGds	~55.1	1	*Nanoscale*, 2017, 9, 4620-4628.
GNCNs-Gd	~60	1	*Biomaterials*, 2017, 120, 103-114.
Fe-mTa_2O_5@CuSZnPc/PCM	~62.74	1	*Inorg. Chem*., 2018, 7, 136-145
$NaYbF_4$:Tm@$NaGdF_4$:Yb-PVP	~90	1	*Science Bulletin*, 2017, 62, 903–912.
MnO@Au	~91.15	1	*Nanoscale,* 2018,10, 3631–3638.

Table S4 Comparison of CT value of the existing CT contrast agent.

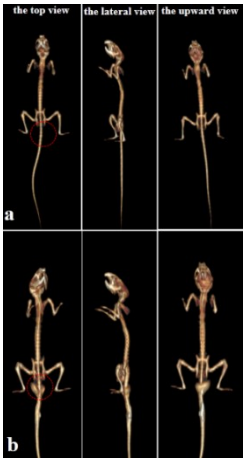


Fig. S8 The 3D renderings of *in vivo* CT images of a mice based on the UCNCs@PSI_{OAm}: (a) pre-injection and (b) post-injection.

Fig. S9 The photo of the injected mouse after 20 days.

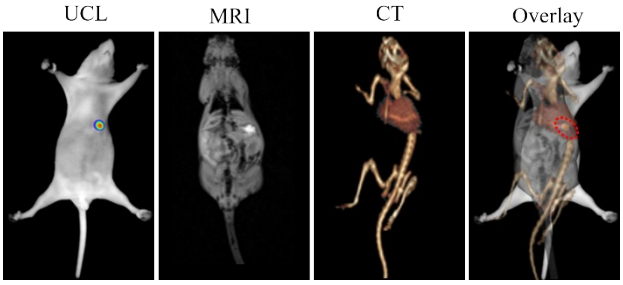


Fig. S10 The overly image of CT, MR and UCL.