# **Electronic Supplementary Information**

# A new concept of a pseudo-Janus structure: employing a Yin-Yang fish structure film with up/down conversion fluorescence and bi-anisotropic conduction to represent the pseudo-Janus structure as a case study

Haina Qi, Yunrui Xie, Xiuling Yang, Liu Yang, Qianli Ma, Jiao Tian, Wensheng Yu, Dan Li, Guixia Liu, Xiangting Dong\*

Key Laboratory of Applied Chemistry and Nanotechnology at Universities of Jilin Province, Changchun University of Science and Technology, Changchun 130022, China. Fax: 86 0431 85383815; Tel: 86 0431 85582574; E-mail: dongxiangting888@163.com.

[\*] Prof Xiangting Dong

Key Laboratory of Applied Chemistry and Nanotechnology at Universities of Jilin Province, Changchun University of Science and Technology, Changchun 130022, China.

Tel.: +86-0431-85582574

Fax: +86-0431-85383815

E-mail: dongxiangting888@163.com.cn (Xiangting Dong)

# **Experimental sections**

## **Chemical reagents**

 $Y_2O_3$  (99.99 %),  $Yb_2O_3$  (99.99 %),  $Er_2O_3$  (99.99 %),  $Eu_2O_3$  (99.99 %),  $Tb_4O_7$  (99.99 %), 1,10phenanthroline (phen), ethylene glycol (EG), NaF, polyethylene glycol (PEG, Mw=20000), NH<sub>4</sub>F, NaNO<sub>3</sub>, polyethyleneimine (PEI), methylmethacrylate (MMA), NH<sub>4</sub>NO<sub>3</sub>, benzoic acid (BA), CHCl<sub>3</sub>, (1S)-(+)-10camphorsulfonic acid (CSA), *N*,*N*-dimethylformamide (DMF), benzoylperoxide (BPO), ammonium persulfate (APS), aniline (ANI), polyvinylpyrrolidone (PVP, Mr  $\approx$  1, 300, 000), anhydrous ethyl alcohol were used, and all of the chemicals were of analytic grade and purchased from Aladdin reagent Co. LTD, Shanghai, China. Distilled water was made in our laboratory.

## **Preparation of PMMA**

100 mL of MMA and 0.1 g of BPO were added into a 250-mL three-necked bottle with reflux device. The above solution was stirred vigorously at 110 °C to achieve a viscosity similar to that of glycerin. Heating was stopped and the solution was naturally cooled to the room temperature with continuous stirring. Then the above solution was poured into a tube with a filling height of 5-7 cm. The solution in the tube was kept for 2 days until no bubble was observed, then the above tube was transferred to a drying oven at 30 °C for 48 hours, and the solution in the tube was hardened into a transparent solid. Finally, the temperature of the drying oven was elevated to 110 °C and kept at the temperature for 2 hours to complete the polymerization reaction, and then solid PMMA was prepared after the temperature was naturally cooled down to room temperature.

#### **Construction of spinning liquids**

PANI/PMMA nanoribbon was used as the conductive material in the conductive side of the Janus nanoribbon, the process for preparing the spinning liquid containing PANI was as follows. CSA and ANI were dispersed in the mixture liquid of CHCl<sub>3</sub> and DMF with varying PANI/PMMA ratios, the liquid was stirred at ambient temperature for 12 hours (called as liquid A), and APS was dispersed into the DMF and stirred for 1 hour (called as liquid B). Liquid A and liquid B were refrigerated for 25 min at 0 °C. Liquid B was poured into liquid A and the obtained mixture was stirred in an ice-water for 3.5 hours. Finally, the reaction system was kept at 0 °C for 36 hours to obtain spinning liquid I and the Table S1 gives the practical components of spinning liquid I (S<sub>a</sub>). The color of the spinning liquid I is dark green, which accords with the characteristics of PANI of emeraldine form.

To fabricate NaYF<sub>4</sub>:Eu<sup>3+</sup>/PMMA nanoribbon as the insulative and red-fluorescent side of the Janus nanoribbon, in a typical procedure, NaYF<sub>4</sub>:Eu<sup>3+</sup> NPs and PMMA were dispersed into a mixed liquid of DMF and CHCl<sub>3</sub> under magnetic stirring for 12 hours to form spinning liquid II, the actual components were shown in Table S2. The spinning liquid (marked as spinning liquid III) for preparing (NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup>)/PMMA nanoribbon used as the insulative and green-fluorescent side of the Janus nanoribbon was obtained by using the similar approach and the components were summarized in Table S3.

To fabricate Tb(BA)<sub>3</sub>phen/PVP as the green-fluorescence area of the eyes of the pseudo-Janus structure film, in a typical procedure, Tb(BA)<sub>3</sub>phen and PVP were dissolved in a mixed solvent of DMF and CHCl<sub>3</sub> under magnetic stirring for 12 hours to form spinning liquid IV, the real components were shown in Table S4. The spinning liquid (marked as spinning liquid V) for preparing Eu(BA)<sub>3</sub>phen/PVP used as the red-fluorescence area of the eyes of the pseudo-Janus structure film was obtained by using the

similar approach and the components were summarized in Table S5.

Spinning liquid I	PANI/PMMA/wt%	ANI/g	CSA/g	APS/g	DMF/g	CHCl <sub>3</sub> /g	PMMA/g
S <sub>a1</sub>	15	0.09	0.22	0.22	1.8	8.2	0.6
$S_{a2}$	30	0.18	0.44	0.44	1.8	8.2	0.6
$S_{a3}$	50	0.30	0.74	0.73	1.8	8.2	0.6
$S_{a4}$	70	0.42	1.04	1.02	1.8	8.2	0.6

Table S1 Compositions of the spinning liquid I.

Table S2 Compositions of the spinning liquid II.

Spinning liquid II	NaYF4:Eu3+:PMMA/wt%	NaYF <sub>4</sub> :Eu <sup>3+</sup> /g	DNF/g	CHCl <sub>3</sub> /g	PMMA/g
S <sub>b1</sub>	0.5:1	0.5	4.0	12.0	1.0
S <sub>b2</sub>	1:1	1.0	4.0	12.0	1.0
S <sub>b3</sub>	1.5:1	1.5	4.0	12.0	1.0

Table S3 Compositions of the spinning liquid III.

Spinning liquid III	(NaYF4:Yb <sup>3+</sup> ,Er <sup>3+</sup> ):PMMA/wt%	(NaYF <sub>4</sub> :Yb <sup>3+</sup> ,Er <sup>3+</sup> )/g	DNF/g	CHCl <sub>3</sub> /g	PMMA/g
S <sub>c1</sub>	0.5:1	0.5	4.0	12.0	1.0
$S_{c2}$	1:1	1.0	4.0	12.0	1.0
S <sub>c3</sub>	1.5:1	1.5	4.0	12.0	1.0

Table S4 Compositions of the spinning liquid IV.

Spinning liquid IV	Tb(BA)3phen/PMMA/wt%	Tb(BA) <sub>3</sub> phen/g	DMF/g	CHCl <sub>3</sub> /g	PMMA/g
S <sub>d1</sub>	5	0.025	0.80	7.20	0.50
S <sub>d2</sub>	10	0.050	0.80	7.20	0.50
S <sub>d3</sub>	15	0.075	0.80	7.20	0.50
S <sub>d4</sub>	20	0.100	0.80	7.20	0.50
S <sub>d5</sub>	25	0.125	0.80	7.20	0.50

Table S5 Compositions of the spinning solution V.

Spinning liquid V	Eu(BA)3phen/PMMA/wt%	Eu(BA) <sub>3</sub> phen/g	DMF/g	CHCl <sub>3</sub> /g	PMMA/g
S <sub>e1</sub>	5	0.025	0.80	7.20	0.50
S <sub>e2</sub>	10	0.050	0.80	7.20	0.50
S <sub>e3</sub>	15	0.075	0.80	7.20	0.50
S <sub>e4</sub>	20	0.100	0.80	7.20	0.50
S <sub>e5</sub>	25	0.125	0.80	7.20	0.50

#### Synthesis of pseudo-Janus structure film

The electrospinning conditions were as follows: the distance between the spinneret and the collector was 15 cm and a direct-current voltage of 8 kV was provided. The rotational speed of the rotary drum was 1200 r min<sup>-1</sup> and the spinning speed was 1 mL h<sup>-1</sup>. The spinning process was carried out at ambient temperature of 20-22 °C and relative air humidity of 23-25 %.

The U-JDF and D-JDF were fabricated under the same conditions and steps as those for preparing U-PF and D-PF. First of all, spinning liquid I ( $S_{a1}$ ) and III ( $S_{c2}$ ), the spinning liquid I ( $S_{a1}$ ) and II ( $S_{b2}$ ) were respectively electrospun into disordered Janus nanoribbons mat by using parallel electrospinning *via* employing a wire-netting as the collector, and thus U-JDF and D-JDF were obtained. Next, spinning liquid IV and spinning liquid V were respectively electrospun into disordered nanofibers to obtain the G-PF and R-PF, and finally the JDF was obtained. To prepare composite nanoribbons array film and composite nanoribbons disordered film, mixed liquid of spinning liquid I ( $S_{a1}$ ) and III ( $S_{c2}$ ) was used as the spinning liquid and spinning liquid I ( $S_{a1}$ ) and II ( $S_{b2}$ ) were also blended as the spinning liquid. In the above processes, the new spinning liquids were electrospun into composite nanoribbons array film (U-CAF and D-CAF) and composite nanoribbons disordered film (U-CAF and D-CAF) and composite nanoribbons disordered film (CAF and CDF) by traditional single-axial electrospinning. The steps of preparing CAF and CDF were the same as those for fabrication of PF and





Figure S1 Diagrammatic drawing of electrostatic spinning instruments and procedures for preparing three control samples of JDF (a), CAF (b) and CDF (c).

## **Characterization techniques**

The phase compositions of as-prepared NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> NPs, NaYF<sub>4</sub>:Eu<sup>3+</sup> NPs, U-PF, D-PF and control samples were analysed *via* X-ray diffractometer (XRD, made by Bruker Corporation with the model of D8 FOCUS and Cu Kα radiation) at the acceleration voltage of 40 kV and current of 20 mA. The energy dispersive spectroscopy (EDS, produced by Oxford Instruments) was used for elemental analyses of the films. A scanning electron microscope (SEM, JSM-7610F) and optical microscope (OM, CVM500E) were utilized to observe the morphology and internal structure of the products. The Hitachi fluorescent spectrophotometer F-7000 and ZF-20D dark box ultraviolet analyzer were utilized to investigate fluorescence properties of the films. A xenon lamp and a 980 diode laser were respectively used as

excitation sources for down-conversion and up-conversion fluorescence tests, and the slit width was fixed at 2.5 nm for the excitation determination. A Hall effect measurement system (ECOPIA HMS-3000) was applied to study electrical property.

# **Results and discussion**

**XRD** analysis



Figure S2 XRD results of the U-JDF, D-JDF, U-CAF, D-CAF, U-CDF and D-CDF.

# Morphology observation



Figure S3 (a-e) SEM images of NaYF4:Eu<sup>3+</sup> NPs (a), NaYF4:Yb<sup>3+</sup>,Er<sup>3+</sup> NPs (b), disordered Janus

nanoribbons (c), composite nanoribbons in array (d) and disordered composite nanoribbons (e). (f-g) Histograms of the diameter distribution of the NaYF<sub>4</sub>:Eu<sup>3+</sup> NPs (f), NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> NPs (g). (h-j) Histograms of the width distribution of disordered Janus nanoribbons (h), composite nanoribbons in array (i) and disordered composite nanoribbons (j).



Figure S4 Breaking strength of PF is tested in different directions.



### **Fluorescence performance**

Figure S5 (a) Up-conversion emission spectra of NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> NPs excited by a 980-nm diode laser

with different pumped powers. (b) Plots of natural logarithm intensity of the up-conversion emission versus natural logarithm pumped power of the NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> NPs. (c) Excitation spectrum and (d) emission spectrum of NaYF<sub>4</sub>:Eu<sup>3+</sup> NPs. (e) UV-Vis absorbance spectrum of PANI.

The up-conversion fluorescence spectra of NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> NPs are shown in Figure S5a. The NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> NPs emit obvious green (524, 544 nm) and red (656 nm) emissions, and the intensity of red emission is higher than that of green emission. The emission peak at 524 nm and 544 nm respectively belongs to the  ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$  and  ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$  transition of Er<sup>3+</sup>, and the emission peak at 656 nm corresponds to the  ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$  transition of Er<sup>3+</sup>. In the up-conversion process, the intensity of each emission peak is proportional to the power of the infrared excitation light. The formula is expressed as following:

#### $I \propto P^n$

where *I* and *P* respectively represent up-conversion emission intensity and pump energy, n is the number of excitation photons required for each up-conversion photon emitted. The relationship between the natural logarithm of up-conversion emission intensity and the natural logarithm of pump power of NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> NPs is shown in Figure S5b. The slope of the curve is 2.06 (red emission) and 1.72 (green emission), respectively, close to 2, proving that the up-conversion emissions of NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> NPs are two-photon process.

As seen from Figure S5c, the excitation spectrum of NaYF<sub>4</sub>:Eu<sup>3+</sup> NPs monitored at 592 nm exhibits the optimal excitation wavelength at 395 nm, which is attributed to the  ${}^{7}F_{0}\rightarrow{}^{5}L_{6}$  energy levels transitions of Eu<sup>3+</sup> ions. There are also several weak excitation peaks, respectively attributed to the  ${}^{7}F_{0}\rightarrow{}^{5}H_{6}$  (318 nm),  ${}^{7}F_{0}\rightarrow{}^{5}D_{4}$  (362 nm),  ${}^{7}F_{0}\rightarrow{}^{5}G_{2}$  (380 nm) and  ${}^{7}F_{0}\rightarrow{}^{5}D_{1}$  (466 nm) energy levels transitions of Eu<sup>3+</sup> ions. The emission spectrum of NaYF<sub>4</sub>:Eu<sup>3+</sup> NPs is observed under the excitation of 395-nm ultraviolet light and exhibits characteristic emission peaks at 592 and 616 nm, which are corresponding to  ${}^{5}D_{0}\rightarrow{}^{7}F_{1}$  and  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  energy level transitions of Eu<sup>3+</sup>, respectively, as seen in Figure S5d.



Figure S6 Fluorescence schematic drawing of the PF and the control samples.



Figure S7 (a, c) Excitation and (b, d) emission spectra of Eu(BA)<sub>3</sub>phen/PVP nanofibers doped with different percentages of Eu(BA)<sub>3</sub>phen (a, b) and Tb(BA)<sub>3</sub>phen/PVP nanofibers doped with different percentages of Tb(BA)<sub>3</sub>phen (c, d).

In order to obtain the optimum percentage of Eu(BA)<sub>3</sub>phen to PVP, a series of Eu(BA)<sub>3</sub>phen/PVP nanofibers were prepared with different percentages of Eu(BA)<sub>3</sub>phen. As seen from the excitation spectrum (Figure S7a), the strongest excitation peak at 307 nm can be assigned to  $\pi \rightarrow \pi^*$  electron transition of ligands when the monitoring wavelength is 615 nm. Characteristic emission peaks of Eu<sup>3+</sup> ions located at 581, 592, 615 nm are obtained at the excitation of light with a wavelength of 307 nm, as observed in Figure S7b. These characteristic emission peaks are originated from  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  (581 nm),  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  (592 nm) and  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  (615 nm) energy level transitions of Eu<sup>3+</sup>. The Eu(BA)<sub>3</sub>phen/PVP nanofibers exhibit the strongest emission band at 615 nm. The maximum fluorescence intensity is obtained when the mass percentage of Eu(BA)<sub>3</sub>phen to PVP is 15 %. Therefore, the red eye region of PF (R-PF) was prepared by using mass percent of Eu(BA)<sub>3</sub>phen to PVP of 15 % in this work. In order to obtain the optimum percentage of Tb(BA)<sub>3</sub>phen to PVP, a series of Tb(BA)<sub>3</sub>phen/PVP nanofibers were fabricated with different percentages of Tb(BA)<sub>3</sub>phen to PVP. Excitation and emission spectra of Tb(BA)<sub>3</sub>phen/PVP nanofibers are illustrated in Figure S7 (c, d). As found from the excitation spectrum (Figure S7c), the strongest peak at 294 nm can be attributed to  $\pi \rightarrow \pi^*$  electron transition of ligands when the monitoring wavelength is 545 nm. Characteristic emission peaks situated at 489, 545, 586, 620 nm are obtained under the excitation of 294-nm light, as seen in Figure S7d. These characteristic emission peaks come from  ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$  (489 nm),  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  (545 nm),  ${}^{5}D_{4} \rightarrow {}^{7}F_{4}$  (586 nm) and  ${}^{5}D_{4} \rightarrow {}^{7}F_{3}$  (620 nm) energy level transitions of Tb<sup>3+</sup>. The Tb(BA)<sub>3</sub>phen/PVP nanofibers exhibit the strongest emission band at 545 nm. The maximum fluorescence intensity is obtained when the mass percentage of Tb(BA)<sub>3</sub>phen to PVP is 15%. Therefore, the green eye region of PF (G-PF) was prepared with mass percent of Tb(BA)<sub>3</sub>phen to PVP of 15 % in this study.

#### **Electrical Conduction Analysis**



Figure S8 Conductive schematic of the PF.

Schematic illustration depicted in Figure S9 is the examination methods for conductance of the films which are tailored to an area of  $1 \times 1$  cm<sup>2</sup>. At the distance of 0.1 cm, two tin sheets with the size of  $1 \times 0.45$  cm<sup>2</sup> are used as electrodes. Two tin sheets coated with conductive resin, as the electrodes, are respectively pressed on the surface of the samples. Then the two stylets of the Hall effect measurement system are respectively pressed against the two tin sheets. For the array films, the conductances along the nanoribbon

alignment direction, perpendicular to the nanoribbon alignment direction, and the whole film from left-toright direction are measured. For disordered films, the conductances of the samples in two perpendicular directions and the whole sample from left-to-right direction are tested.



Figure S9 Schematic illustration for conductance test of samples.



Figure S10 Schematic of conduction of the PF and the control samples.