

Supporting information (SI)

Electrospun Dual-aeolotropic Conductive Exceptional Janus membrane and Janus Tubule Functionalized by Up-/Down-Converting Fluorescence and Magnetism

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Materials

Y₂O₃ (99.99 %), Er₂O₃ (99.99 %), Yb₂O₃ (99.99 %), Tb₄O₇ (99.99 %), Co(acac)₂ (97 %), Fe(acac)₃ (98 %), Oleic
acid (OA, AR), Oleylamine (OM, 80-90 %), Dibenzyl ether, NH₄F, Polyethylenimine (PEI), Ethylene glycol (EG),
Anhydrous ethanol, Methyl alcohol, *N, N*-dimethylformamide (DMF), CHCl₃, NaNO₃, Sodium hydroxide (NaOH),
Acetylacetone (acac, AR), 2, 2'-Bipyridyl (bipy, AR), Nitric acid (HNO₃, AR), Thiophene, FeCl₃, Methyl

methacrylate (MMA), Benzoyl peroxide (BPO) are the reagents used in this work. All the reagents were of analytical grade and were directly used as received without further purification. The deionized water and PMMA are homemade.

Preparation of monodispersed CoFe₂O₄ NPs, NaYF₄:Yb³⁺, Er³⁺ NPs and Tb(acac)₃bipy complexes

Tb(acac)₃bipy (acac=acetylacetonone, bipy=2, 2'-Bipyridyl), NaYF₄:Yb³⁺, Er³⁺ NPs and CoFe₂O₄ NPs were prepared according to our previous reports. Briefly, Fe(acac)₃ (7.06 g), Co(acac)₂ (2.57 g), Oleic acid (19 mL), OA (60 mL) and Dibenzyl ether (100 mL) were added into a three-necked bottle and mixed evenly under magnetic stirring. The mixture was maintained at 200 °C for 2 h, then, heated to 300 °C and refluxed for 1 h. The entire process was completed under N₂ conditions. The mixed solution was cooled to room temperature, and then methyl alcohol was added into the mixture to obtain precipitation. Then, the subsidence was washed three times with ethanol and magnetic separation. Finally, the subsidence was dried at 60 °C in a dryer for 48 h to obtain OA modified monodisperse CoFe₂O₄ NPs.

The specific preparation of NaYF₄:Yb³⁺, Er³⁺ NPs is as follows: RE₂O₃ (n_{RE}=2.25 mmol, RE₂O₃=Y₂O₃, Yb₂O₃, Er₂O₃, the molar rate of Y:Yb:Er is 78:20:2) was added into a 100-mL beaker and dissolved in 20-mL HNO₃, excess HNO₃ was removed by heating evaporation to obtain RE nitrate crystals. And then, RE nitrate crystals were dissolved by adding the EG (30 mL) to obtained the EG solution of RE nitrate crystals. Finally, 0.7568 g of NaNO₃ was added into the above solution. Solution B was obtained by dissolving NH₄F and PEI in 45-mL EG. Solution A was added into solution B by drop and drop to form a mixture. Subsequently, the mixture was agitated for 10 min. Then, the pH value of the solution was adjusted to be neutral, and the mixture was transferred to a hydrothermal kettle of 100 mL for 120 min at 200 °C. The resultant was washed with anhydrous ethanol three times and DMF three times. The resultant was dried in an oven at 60 °C for 12 h to obtain NaYF₄:Yb³⁺, Er³⁺ NPs.

The synthesis method of Tb(acac)₃bipy complexes was described below, where the molar ratio of Tb³⁺: acac:

bipy was maintained at 1:3:1 ($n_{\text{Tb}}=2.5$ mmol). Tb_4O_7 was dissolved in 20-mL HNO_3 , excess HNO_3 was removed by heating evaporation to obtain Tb nitrate crystals, and solution A was obtained by dissolving Tb nitrate crystals in 30 mL anhydrous ethanol. acac and bipy were dissolved in anhydrous ethanol (50 mL), NaOH solution (10 mL, $1 \text{ mol}\cdot\text{L}^{-1}$) was added into the above mixture, and the mixture was stirred in indoor temperature to obtain solution B. The solution A was added to solution B drop by drop to get the suspension, adjust the pH value to 6.5-7 with NaOH ($1 \text{ mol}\cdot\text{L}^{-1}$), the mixture was agitated for 1 h at 50°C , then the precipitation was alternately washed three times with deionized water and anhydrous ethanol. Finally, the product was collected by centrifugation, and dried in a dryer at 60°C for 12 h.

Preparation of spinning liquors for constructing 2D special Janus membrane and 3D Janus tubule

For the sake of prepare Janus tubule, several different spinning liquors were prepared. Spinning liquor I was the spinning liquor with different $\text{NaYF}_4:\text{Yb}^{3+}$, Er^{3+} /PMMA mass ratios. A certain amount of $\text{NaYF}_4:\text{Yb}^{3+}$, Er^{3+} NPs were added to a mixed solution of DMF and CHCl_3 . The mixture was stirred for 30 min before PMMA was added. Spinning liquor I was obtained by stirring the mixed solution at room temperature for 24 h. Spinning liquor I containing $\text{NaYF}_4:\text{Yb}^{3+}$, Er^{3+} NPs with different mass percent was respectively defined as S_{a-1} , S_{a-2} and S_{a-3} . The specific amounts of each substance were summarized in **Table S1**.

The preparation process of spinning liquor II was described below: CoFe_2O_4 NPs (0.6000 g) were added into a tapered flask with a certain amount of DMF (0.6000 g) and CHCl_3 (6.0000 g) and the suspension was treated with ultrasonic dispersion treatment for 20 min. Then, PMMA (0.6000 g) was added to the above mixed solution, and it was agitated at ambient temperature for 24 h.

Spinning liquor III was composed of DMF, CHCl_3 , FeCl_3 , EDOT, CSA and PMMA. Among them, FeCl_3 was an oxidizer and CSA was used as dopant and surfactant. Firstly, a certain amount of EDOT, CSA and PMMA were mixed with CHCl_3 to obtain solution A. Solution B was obtained by mixing DMF with CSA. The solution A and

solution B were kept at 4 °C for 30 min. Afterwards, solution B was added into solution A and the mixture were agitated for 3 h under ice-water bath condition. The color of the blend solution gradually turned to dark green. Finally, the mixed solution was kept at 4 °C for 12 h to gain spinning liquor I. The spinning liquors containing PEDOT with different mass percent were named as S_{b-1} , S_{b-2} , S_{b-3} and S_{b-4} , respectively. The specific dosage of each substance was summarized in **Table S2**. Spinning liquor IV containing $Tb(acac)_3bipy$ (0.3000 g), DMF (0.6000 g), $CHCl_3$ (6.0000 g) and PMMA (0.6000 g).

Table S1. Composition and dosage of spinning solution I

Samples	NaYF ₄ :Yb ³⁺ , Er ³⁺ :PMMA	NaYF ₄ :Yb ³⁺ , Er ³⁺	PMMA/g	DMF/g	CHCl ₃ /g
	(mass ratio)	NPs/g			
S_{a-1}	1:1	0.6000	0.6000	0.6000	6.0000
S_{a-2}	1.5:1	0.6000	0.6000	0.6000	6.0000
S_{a-3}	2:1	0.6000	0.6000	0.6000	6.0000

Table S2. Composition and dosage of spinning solution III

Samples	PEDOT:PMMA		PMMA/g	CSA/g	FeCl ₃ /g	DMF/g	CHCl ₃ /g
	(wt/%)	EDOT/ μ L					
S_{b-1}	40	181	0.6000	0.2146	0.2738	0.6000	6.0000
S_{b-2}	50	226	0.6000	0.2684	0.3424	0.6000	6.0000
S_{b-3}	60	271	0.6000	0.3220	0.4108	0.6000	6.0000
S_{b-4}	70	316	0.6000	0.3755	0.4791	0.6000	6.0000

Spinning liquor I and spinning liquor III were separately infused into two 10-mL squirts; following a 5-mL syringe including spinning liquor II was injected into a 10-mL squirt to assemble the spinning device as shown in

Fig. S1a. A positive high-voltage power supply (HVPS) is used to provide a high voltage of around 7-8 kV. The spinneret is connected to the positive pole of the HVPS. The receiving device of the microbelts array membrane is connected to the ground wire of the HVPS. The spinning distance, that is, the distance between the nozzle and the roller, is kept at 15 cm. The temperature and humidity of the environment are 20-30 % and 20-25 °C, respectively. The HVPS is adjusted to 7-8 kV. Subsequently, the electrospinning process was implemented. USJF of SJM was successfully prepared when the three spinning liquors were completely consumed. Afterwards, USJF was removed from the roller and cut to a certain size, and then the tailored USJF was fixed on the roller with tinfoil according to the length direction of the microbelt perpendicular to the rotation direction of the roller. The preparation of [PEDOT/PMMA]/[Tb(acac)₃bipy/PMMA] Janus microbelts array film as down-converting fluorescence of SJM (shorted for DJF) was carried out by an ordinary parallel spinneret. Spinning liquor III and spinning liquor IV were respectively infused into 10-mL squirt to assemble an electrospinning device diagram as shown in **Fig. S1b**. After electrospinning, DJF was successfully prepared when the above two spinning liquors were consumed. The electrospinning requirements of DJF on the right side of SJM are the same as those of USJF.

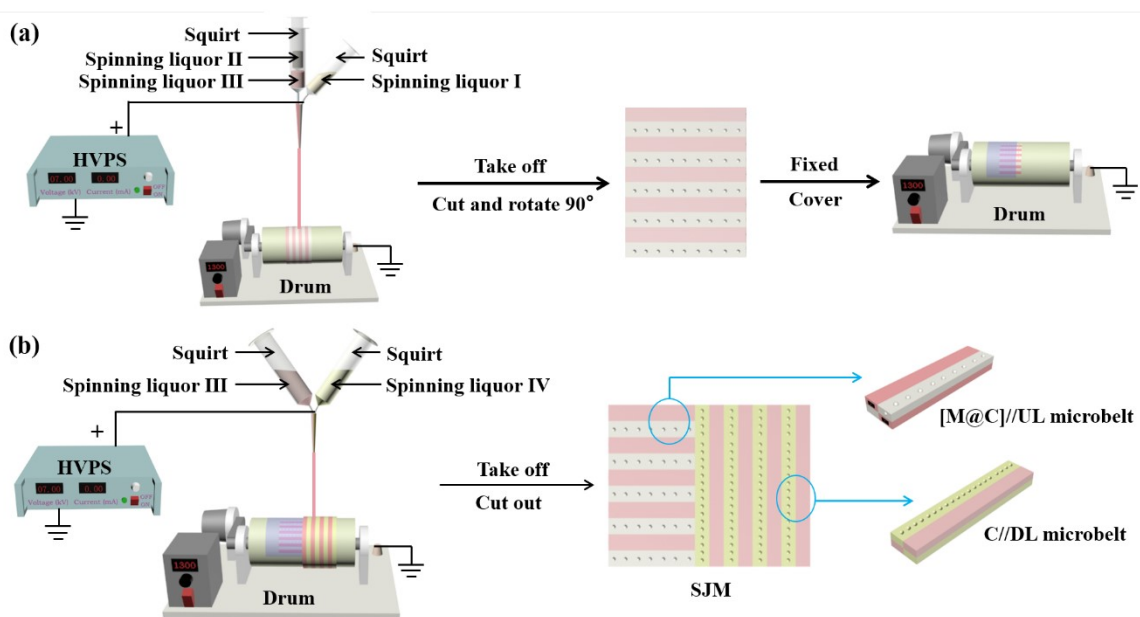


Fig. S1 Schematic diagram and electrospinning process for preparing SJM

Results and discussion

Morphology, XRD analysis and magnetism properties

The XRD patterns of $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ NPs and CoFe_2O_4 NPs are manifested in **Fig. S2**. The XRD patterns of the resultant $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ NPs and CoFe_2O_4 NPs conform to the cubic structure of NaYF_4 (PDF#77-2042) and cubic structure of CoFe_2O_4 (PDF#79-1744), respectively. **Fig. S2** shows the XRD pattern of SJM and Janus tubule. All resultant samples contain characteristic diffraction peaks of $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ NPs and CoFe_2O_4 NPs, indicating that $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ NPs and CoFe_2O_4 NPs have been successfully introduced into all the samples. Besides, the broad diffraction peak in the range of $15^\circ\sim 20^\circ$ is put down to amorphous PMMA.

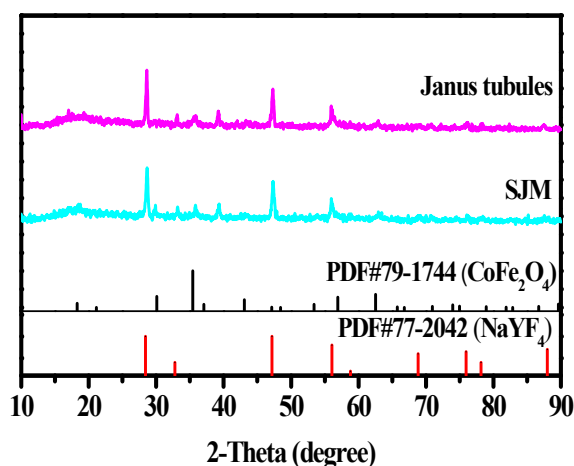


Fig. S2 XRD patterns of CoFe_2O_4 NPs, SJM and 3D Janus tubule with standard profiles of CoFe_2O_4

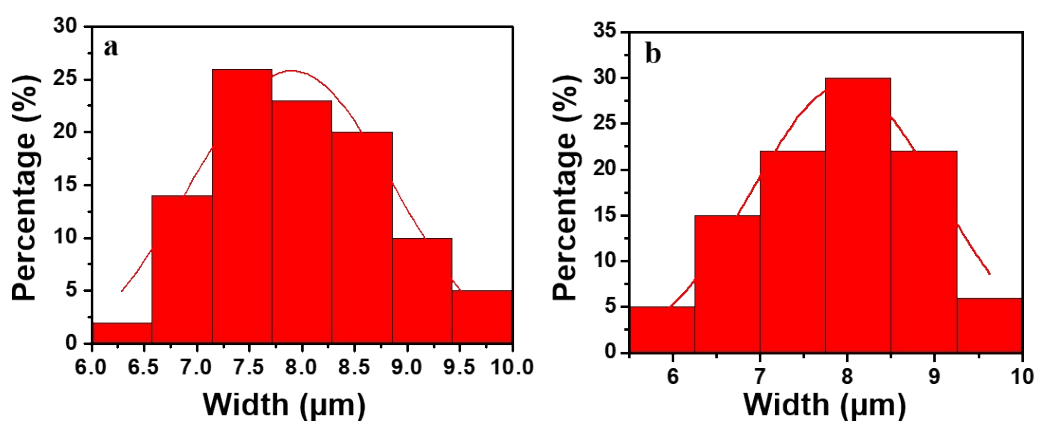


Fig. S3 Histograms distribution histogram of the width of Janus microbelt

Fluorescence performance

Fig. S4 gives the up-conversion luminescence spectra of samples; it can be concluded that the emission of

strong green light is located at 541 nm and the emission of weak red light is located at 655 nm, which corresponds to the $^2H_{11/2}/^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$ energy level transitions of Er^{3+} ions, respectively. The up-conversion luminescence spectrum at various pump powers is shown in **Fig. S4a**, the up-conversion luminescence intensity increases, as the pump power increases. In the up-conversion process, the intensity of each emission peak has a certain relationship with the pump power of the infrared excitation light (**Fig. S4b**). The formula is as follows:

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

Where, I_{up} represents the up-conversion emission intensity, P represents the pump power, and n (the slope) is the number of photons generated during each up-conversion emission process. The slopes of green-emission light and red-emission light are respectively 1.670 and 1.882, closed to 2, illustrating that the up-conversion luminescence process of $NaYF_4:Yb^{3+}, Er^{3+}$ NPs is a two-photon process. Besides, the saturation magnetization of 3D Janus tubule is $8.20 \text{ emu} \cdot \text{g}^{-1}$ when the mass ratio of $CoFe_2O_4$ to PMMA is 1:1 and the corresponding hysteresis loop is shown in **Fig. S5**. It can be concluded that 3D Janus tubule almost has the same saturation magnetization as 2D SJM.

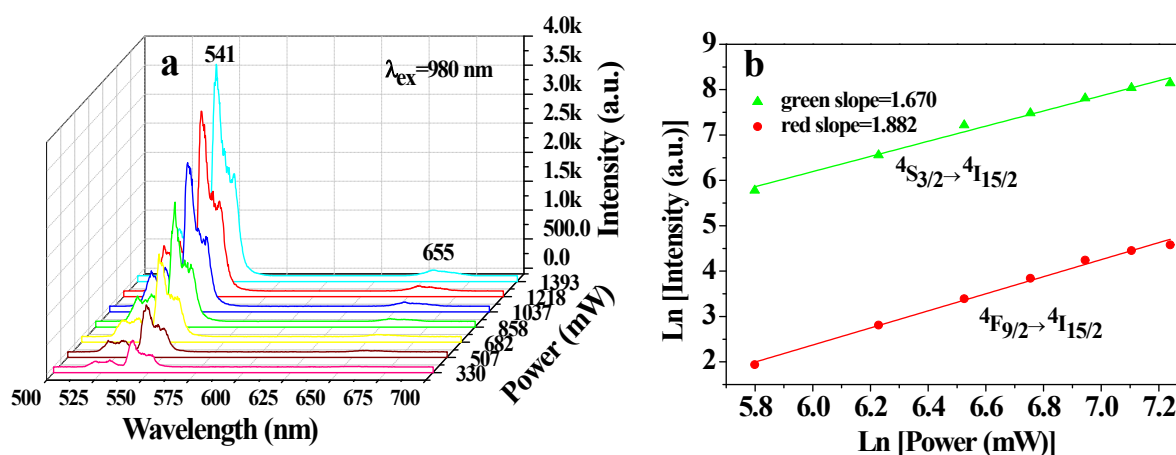


Fig. S4 Up-conversion luminescence spectra of $NaYF_4:Yb^{3+}, Er^{3+}$ NPs at different pump power (a), and double natural logarithm diagrams between up-conversion luminescence intensity ($\ln I$) and pump power ($\ln P$) (b)

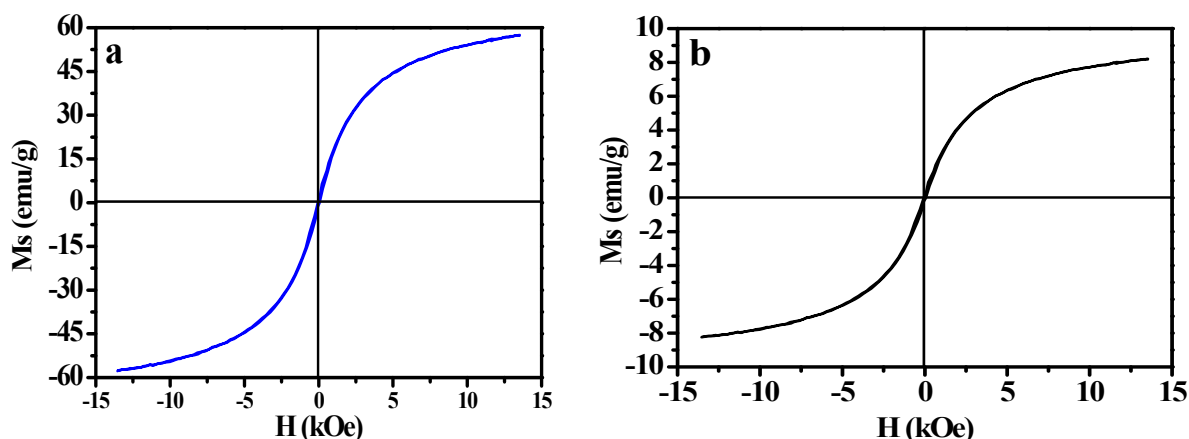


Fig. S5 Hysteresis loops of CoFe₂O₄ NPs (a) and Janus tubule (b)

Electrical conduction

The conductance of SJM containing different contents of PEDOT and contrastive samples was measured. SJM consists of two parts: USJF and DJF. Therefore, the conducting test of SJM is divided into three main parts: the conductive direction (i.e. length direction of nanobelt, named as CD) and insulative direction (i.e. width direction of nanobelt, abbreviated as ID) of USJF, the CD and ID of DJF, and the length direction of SJM (from left to right). Besides, the conductive test method in all array samples in contrastive samples is the same as that of the SJM. The conductance in two perpendicular directions is also measured for non-array samples. For USJF and DJF, the conductance of CD and ID of USJF and DJF are separately defined as U_{CD} , U_{ID} , D_{CD} and D_{ID} . The degree of anisotropy of USJF and DJF are respectively represented by U_{CD}/U_{ID} and D_{CD}/D_{ID} . $(U-D)_{ID}$ express as the conductance tested from left to right on the surface of SJM. Taking USJF as an example, the schematic diagrams of the conductive test are manifested in **Fig. S6**.

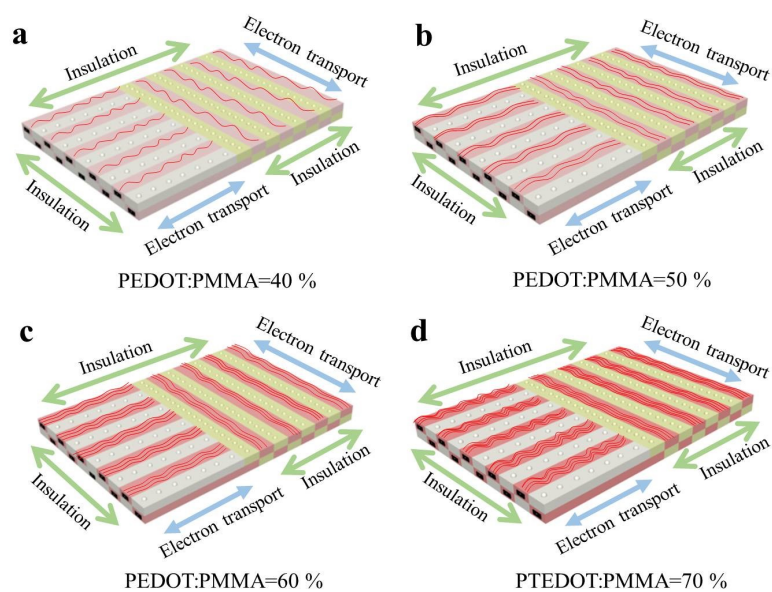


Fig. S6 Conductive schematic diagrams of SJM at different mass percent of PEDOT

To ensure that the shape of the tubule does not change during the test, a glass rod is inserted into the center of 3D Janus tubule as a bracket. For T-I, one half along the length direction and the circumferential direction of the tubule is respectively conductive (**Fig. S7a**) and insulated (**Fig. S7b**). The other half is conductive along the length direction (**Fig. S7c**) and insulated along the circumferential direction (**Fig. S7d**). Also, the length direction of 3D Janus tubule is insulated (**Fig. S7i**). For T-II, one half of tubule exhibits conductive along the circumferential (**Fig. S7e**) and insulated along the length (**Fig. S7f**). The other half along the length and the circumferential direction appears conductive (**Fig. S7g**) and insulated (**Fig. S7h**), respectively. Similarly, the length direction of 3D Janus tubule is insulated; the corresponding schematic diagram of conducting test is shown in **Fig. S7j**.

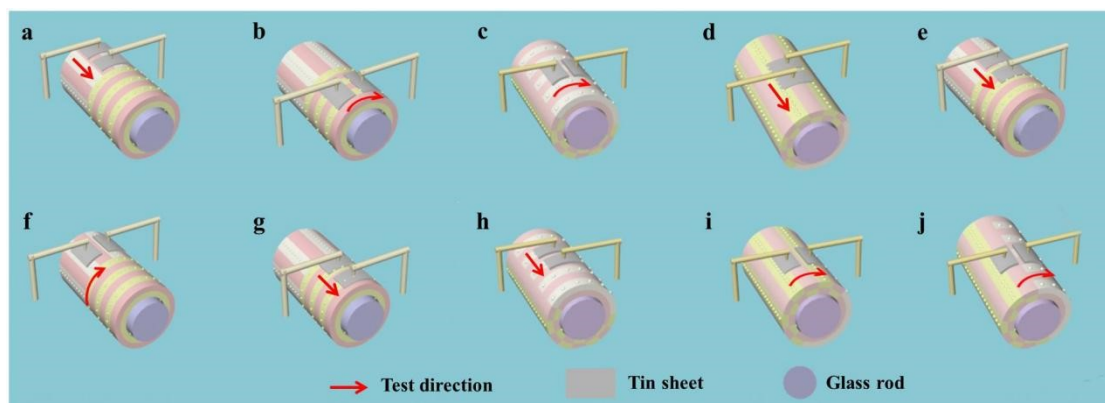


Fig. S7. Diagrammatic sketch for conductive test of the circumferential direction (a, b, c, d), length direction (f, g, h,

i) and interface (e, j) of Janus tubule