

Supporting Information (SI)

Conjugated electrospinning towards dual conductive network Janus-shape microfibers array film with enhanced green luminescence and high aeolotropic conduction

Yaolin Hu^{1,2}, Haina Qi^{1,2}, Qianli Ma², Liu Yang^{1,2}, Hong Shao^{1,2}, Yuqi Sheng^{1,2}, Yunrui
Xie^{1,2}, Wensheng Yu², Dan Li², Xiangting Dong^{1,2*}

1. College of Materials Science and Engineering, Changchun University of Science and Technology, Changchun 130022, China
2. Key Laboratory of Applied Chemistry and Nanotechnology at Universities of Jilin Province, Changchun University of Science and Technology, Changchun 130022, China

* Corresponding author. E-mail: xtdong@cust.edu.cn

2.1 Chemicals

Methyl methacrylate (MMA), benzoyl peroxide (BPO), *N,N*-dimethylformamide (DMF), CHCl₃, aniline (ANI), NaOH, ammonium persulfate (APS), (1*S*)-(+)-10-camphorsulfonic acid (CSA), carbon black (CB, size: 30 nm), Tb₄O₇ (99.99 %), 5-Sulfosalicylic acid dihydrate (SSA), triphenylphosphine oxide (TPPO), anhydrous ethanol were used, and all of the chemicals were of analytic grade and purchased from Aladdin reagent Co. LTD, Shanghai, China. Ultrapure water was prepared by Mili-QAdvantageA10 ultrapure water machine in our laboratory.

* Corresponding author. E-mail address: xtdong@cust.edu.cn, (Xiangting Dong).

2.2 Synthesis of PMMA and Tb(SSA)₃(TPPO)₂

A certain amount of BPO and MMA were added into a 500-mL three-necked flask with a reflux device and stirred with a speed of 340 r·min⁻¹ at 95-105 °C. After the mixed solution was stirred to reach a certain viscosity just like that of glycerin, the heating was stopped and the mixed solution was poured into test tubes with an influx height of 7-9 cm. The test tubes were placed in air to cool naturally to room temperature. Finally, the test tubes were placed in an electric vacuum oven at 35 °C for 60 h, and the gelatinous solution was solidified. Then the temperature was raised to 100 °C for 2 h, and PMMA was obtained after natural cooling down to room temperature.

A certain amount of Tb₄O₇ was dissolved in excessive concentrated nitric acid and then crystallized *via* evaporation of excess nitric acid and water by heating, and Tb(NO₃)₃·6H₂O powders were acquired and stored it for standby. Solution A was obtained by dissolving 1 mmol of Tb(NO₃)₃·6H₂O in 30 mL of anhydrous ethanol. SSA (3 mmol) and TPPO (2 mmol) were dissolved in anhydrous ethanol (50 mL), 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 6.5-7.5 with NaOH (1 mol·L⁻¹), the mixture was agitated for 5 h at 50 °C, then the precipitation was washed five times with anhydrous ethanol. Finally, the product was collected by centrifugation, and dried in a dryer for 36 h at 55 °C.

2.3 Synthesis of spinning liquids

[Tb(SSA)₃(TPPO)₂/PMMA]//[PANI/CB/PMMA] Janus-shape microfibers were used as the construction blocks to prepare the conjugated electrospinning manufactured Janus-shape microfibers array film (denoted as C-JMAF), conjugated electrospinning manufactured Janus-

shape microfibers non-array film (denoted as C-JMNF), di-axial parallel electrospinning manufactured Janus-shape microfibers array film (denoted as D-JMAF), di-axial parallel electrospinning manufactured Janus-shape microfibers non-array film (denoted as D-JMNF), the processes for preparing the spinning liquids were as follows. To fabricate $\text{Tb}(\text{SSA})_3(\text{TPPO})_2/\text{PMMA}$ microfibers, as the insulative and green-luminescent side of the Janus-shape microfiber, in a typical procedure, $\text{Tb}(\text{SSA})_3(\text{TPPO})_2$ and PMMA were dispersed into a mixed liquid of DMF and CHCl_3 under magnetic stirring for 18 hours to form spinning liquid I, the actual components were shown in Table S1. PMMA, CSA and ANI with varying ratios were dispersed in the mixing liquid of CHCl_3 and DMF, the mixed liquid was magnetically stirred at ambient temperature for 12 hours (called as liquid A), and APS was dispersed into the DMF and stirred for 1 hour (named as liquid B). Liquid A and liquid B were refrigerated for 60 min at 0 °C. Liquid B was poured into liquid A and the obtained mixture was stirred in an ice-water for 6 hours. Then CB nanoparticles (NPs) was added into the above liquid and the mixture was stirred for 6 hours to obtain spinning liquid II, and the practical components of spinning liquid II were summarized in Table S2. The spinning liquid II was used to prepare the conductive side of the $[\text{Tb}(\text{SSA})_3(\text{TPPO})_2/\text{PMMA}]/[\text{PANI}/\text{CB}/\text{PMMA}]$ Janus-shape microfiber. CB NPs were added into the mixture of DMF, CHCl_3 and PMMA and then magnetically stirred for 18 h to obtain the conductive spinning liquid III, the actual components were shown in Table S3. The preparative process of spinning liquid IV was the same as that preparing spinning liquid II except that CB was not added, the actual components were shown in Table S4. Spinning liquid V was obtained by mixing spinning liquid I(C_{1-i}) and spinning liquid II(L_{1-d}) in isopyknic, which was used to prepare the S-CMAF and S-CMNF.

Table S1 Compositions of the spinning liquid I

Spinning liquid I	Tb(SSA) ₃ (TPPO) ₂ /PMMA(wt %)	Tb(SSA) ₃ (TPPO) ₂ (g)	PMMA (g)	DMF (g)	CHCl ₃ (g)
L _{1-a}	5	0.06	1.20	4.00	13.00
L _{1-b}	10	0.12	1.20	4.00	13.00
L _{1-c}	15	0.18	1.20	4.00	13.00
L _{1-d}	20	0.24	1.20	4.00	13.00
L _{1-e}	25	0.30	1.20	4.00	13.00

Table S2 Composition of Spinning liquid II

Spinning liquid II	[(PANI/PMMA) +(CB/PMMA)] (wt %)	ANI (g)	CSA (g)	APS (g)	CB (g)	PMMA (g)	DMF (g)	CHCl ₃ (g)
C _{1-a}	5+1	0.06	0.24	0.12	0.012	1.20	3.00	12.50
C _{1-b}	5+2.5	0.06	0.24	0.12	0.03	1.20	3.20	12.50
C _{1-c}	5+5	0.06	0.24	0.12	0.06	1.20	3.50	12.50
C _{1-d}	5+7.5	0.06	0.24	0.12	0.09	1.20	4.00	12.50
C _{1-e}	5+10	0.06	0.24	0.12	0.12	1.20	4.50	12.50
C _{1-f}	15+1	0.18	0.72	0.36	0.012	1.20	3.00	12.50
C _{1-g}	15+2.5	0.18	0.72	0.36	0.03	1.20	3.20	12.50
C _{1-h}	15+5	0.18	0.72	0.36	0.06	1.20	3.50	12.50
C _{1-i}	15+7.5	0.18	0.72	0.36	0.09	1.20	4.00	12.50
C _{1-j}	15+10	0.18	0.72	0.36	0.12	1.20	4.50	12.50
C _{1-k}	30+1	0.36	1.44	0.72	0.012	1.20	3.00	12.50
C _{1-l}	30+2.5	0.36	1.44	0.72	0.03	1.20	3.20	12.50
C _{1-m}	30+5	0.36	1.44	0.72	0.06	1.20	3.50	12.50
C _{1-n}	30+7.5	0.36	1.44	0.72	0.09	1.20	4.00	12.50
C _{1-o}	30+10	0.36	1.44	0.72	0.12	1.20	4.50	12.50
C _{1-p}	50+1	0.60	2.40	1.20	0.012	1.20	3.00	12.50
C _{1-q}	50+2.5	0.60	2.40	1.20	0.03	1.20	3.20	12.50
C _{1-r}	50+5	0.60	2.40	1.20	0.06	1.20	3.50	12.50
C _{1-s}	50+7.5	0.60	2.40	1.20	0.09	1.20	4.00	12.50
C _{1-t}	50+10	0.60	2.40	1.20	0.12	1.20	4.50	12.50

Table S3 Compositions of the spinning liquid III

Spinning liquid III	CB/PMMA (wt %)	CB (g)	PMMA (g)	DMF (g)	CHCl ₃ (g)
C _{2-a}	1.0	0.012	1.20	2.00	12.50
C _{2-b}	2.5	0.03	1.20	2.50	12.50
C _{2-c}	5.0	0.06	1.20	3.00	12.50
C _{2-d}	7.5	0.09	1.20	3.50	12.50
C _{2-e}	10.0	0.12	1.20	4.00	12.50

Table S4 Compositions of the spinning liquid IV

Spinning liquid IV	PANI/PMMA (wt %)	ANI (g)	CSA (g)	APS (g)	PMMA (g)	DMF (g)	CHCl ₃ (g)
C _{3-a}	5	0.06	0.24	0.12	1.20	3.00	12.50
C _{3-b}	15	0.18	0.72	0.36	1.20	3.50	12.50
C _{3-c}	30	0.36	1.44	0.72	1.20	4.00	12.50
C _{3-d}	50	0.60	2.40	1.20	1.20	4.50	12.50

2.4 Construction of contrast samples

To highlight the performance advantages of the prepared C-JMAF, the counterpart C-JMNF, D-JMAF, D-JMNF, S-CMAF and S-CMNF were also prepared as the contrast samples (as illustrated in Fig. S1). For C-JMNF, conjugated electrospinning preparative process was the same as that for preparing of C-JMAF except that a piece of wire netting was applied as a collecting device instead of the revolving roller. D-JMAF and D-JMNF were prepared by using conventional di-axial parallel electrospinning. The C-JMNF, D-JMAF and D-JMNF were prepared by using the same spinning liquids as those for preparing the C-JMAF (C_{1-i}//L_{1-d}). S-CMAF and S-CMNF were prepared by using spinning liquid V. The collecting for preparing the S-CMAF and S-CMNF were the revolving roller and wire netting, respectively. Other spinning conditions were the same as those for the preparation of C-JMAF.

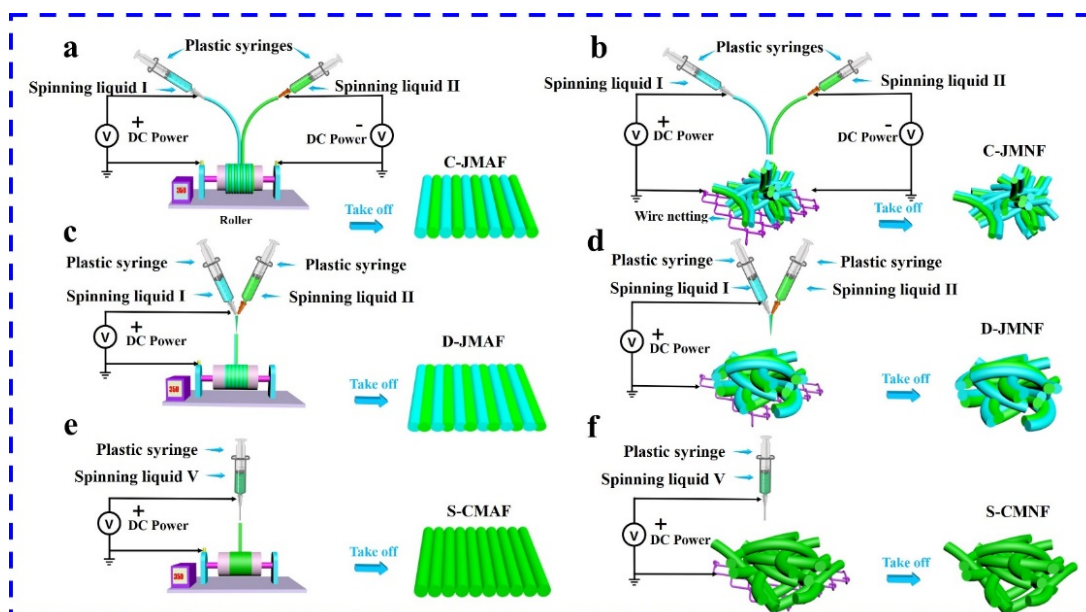


Fig. S1 Illustrative diagram of electrospinning instruments and procedures for preparing C-JMAF and the contrast samples

2.5 Characterizations

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 was utilized to investigate luminescence properties of the films. Electrically conductive properties of the specimens were measured *via* a Hall effect measurement system (ECOPIA HMS-3000). A Thermogravimetric analyzer (TG, TAQ600) was used to measure the thermal stability of the C-JMAF. A Universal mechanical testing machine was used to test the mechanical strength of C-JMAF.

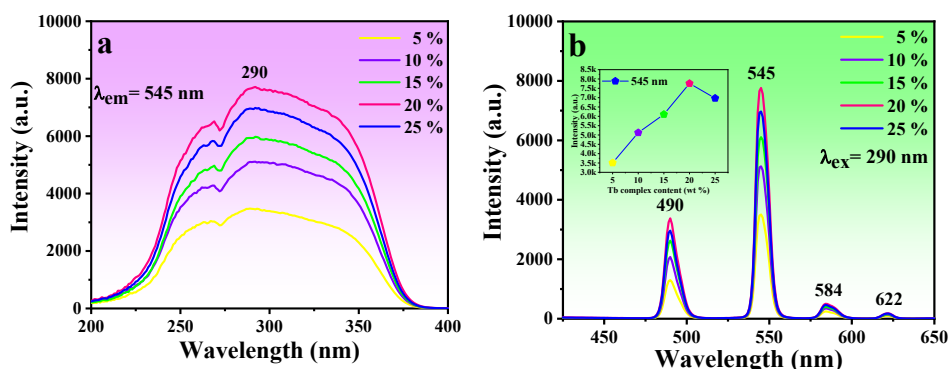


Fig. S2 Excitation spectra (a) and emission spectra (b) of $\text{Tb}(\text{SSA})_3(\text{TPPO})_2/\text{PMMA}$ microfiber with different contents of $\text{Tb}(\text{SSA})_3(\text{TPPO})_2$ complex

In order to explore the optimal content of $\text{Tb}(\text{SSA})_3(\text{TPPO})_2$ complex in PMMA, a series of $\text{Tb}(\text{SSA})_3(\text{TPPO})_2/\text{PMMA}$ microfibers array containing different mass percentages of $\text{Tb}(\text{SSA})_3(\text{TPPO})_2$ complex were prepared *via* using spinning liquids I though conventional single-axis electrospinning. From the excitation spectra of the $\text{Tb}(\text{SSA})_3(\text{TPPO})_2/\text{PMMA}$ microfibers (Fig. S2a), it can be observed that there is a wide excitation band between 225 and 375 nm, and the optimal excitation wavelength is 290 nm. Taking 290 nm as the excitation wavelength, the emission spectra of the samples are obtained (Fig. S2b). It is found that the emission peaks of $\text{Tb}(\text{SSA})_3(\text{TPPO})_2/\text{PMMA}$ are located at 490, 545, 584 and 622 nm respectively, corresponding to $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$ and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ energy levels transitions of Tb^{3+} . The strong sharp line emission at 545 nm is the supersensitive transition of Tb^{3+} , and emission intensity at 545 nm is much higher than that at 490 nm. With the increase of doping concentration of terbium complex, the shape of emission peaks does not change a lot, but the emission peaks intensity first increases and then decreases (inset of Fig. S2b). When the mass percentage of $\text{Tb}(\text{SSA})_3(\text{TPPO})_2$ to PMMA is 20 %, the luminescence intensity reaches the maximum. When the mass percentage of $\text{Tb}(\text{SSA})_3(\text{TPPO})_2$ to PMMA is greater than 20

%, too many rare earth complex will aggregate into clusters, causing luminescence quenching, which leads to a decrease in luminescence intensity. Therefore, in the subsequent study, a mass fraction of $\text{Tb}(\text{SSA})_3(\text{TPPO})_2$ to PMMA of 20 % is selected as the best ratio to construct related samples.

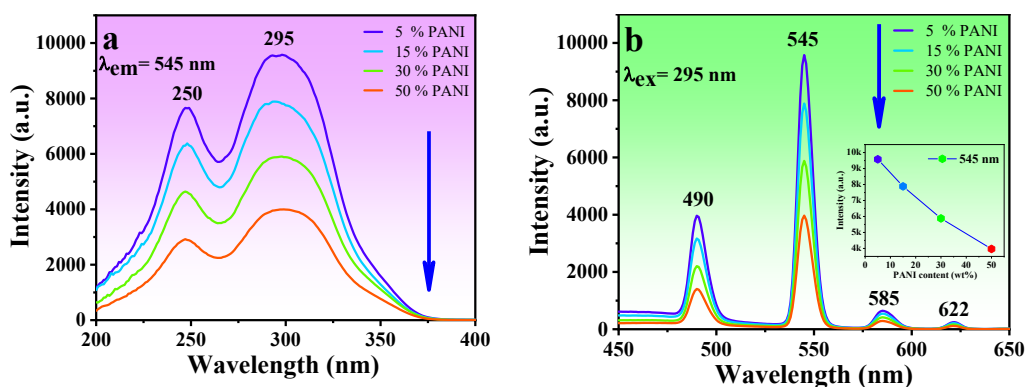


Fig. S3 Excitation spectra (a) and emission spectra (b) of C-JMAF-P with different PANI contents

The luminescence properties of C-JMAF-P and C-JMAF-C with different PANI contents and CB contents are respectively studied when the content of $\text{Tb}(\text{SSA})_3(\text{TPPO})_2$ are fixed at 20 %, PANI content changes from 5% to 50% and CB content changes from 1 % to 10 %, respectively. The excitation spectra (Fig. S3a and Fig. S4a) monitored by 545-nm and emission spectra (Fig. S3b and Fig. S4b) at the excitation of 295-nm and 310-nm ultraviolet light are respectively given in Fig. S3 and Fig. S4. The intensity of excitation and emission peaks of C-JMAF-P and C-JMAF-C decreases with the increase of PANI and CB contents, but the shape of peaks does not change largely. This is because the PANI in C-JMAF-P and CB in C-JMAF-C can strongly absorb the excitation light and the emitted light, and the more PANI and CB is added (inset of Fig. S3b and Fig. S4b), the more light is adsorbed by PANI and CB, and the

weaker excitation and emission light intensity becomes.

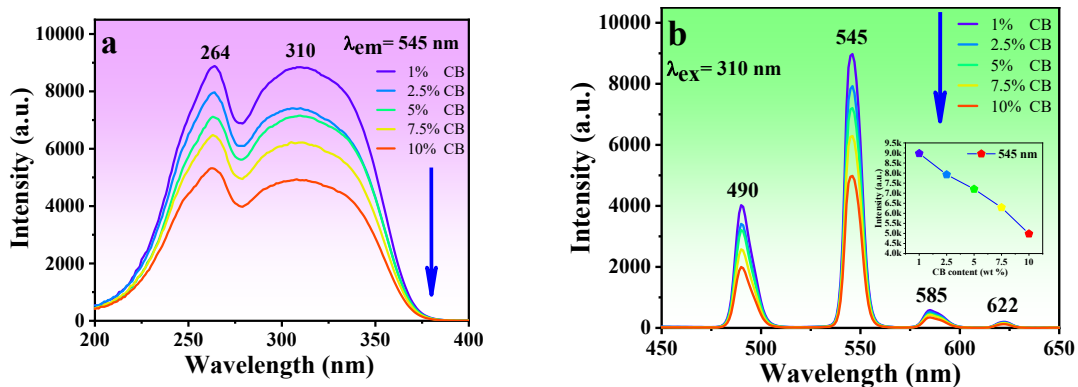


Fig. S4 Excitation spectra (a) and emission spectra (b) of C-JMAF-C with different CB contents

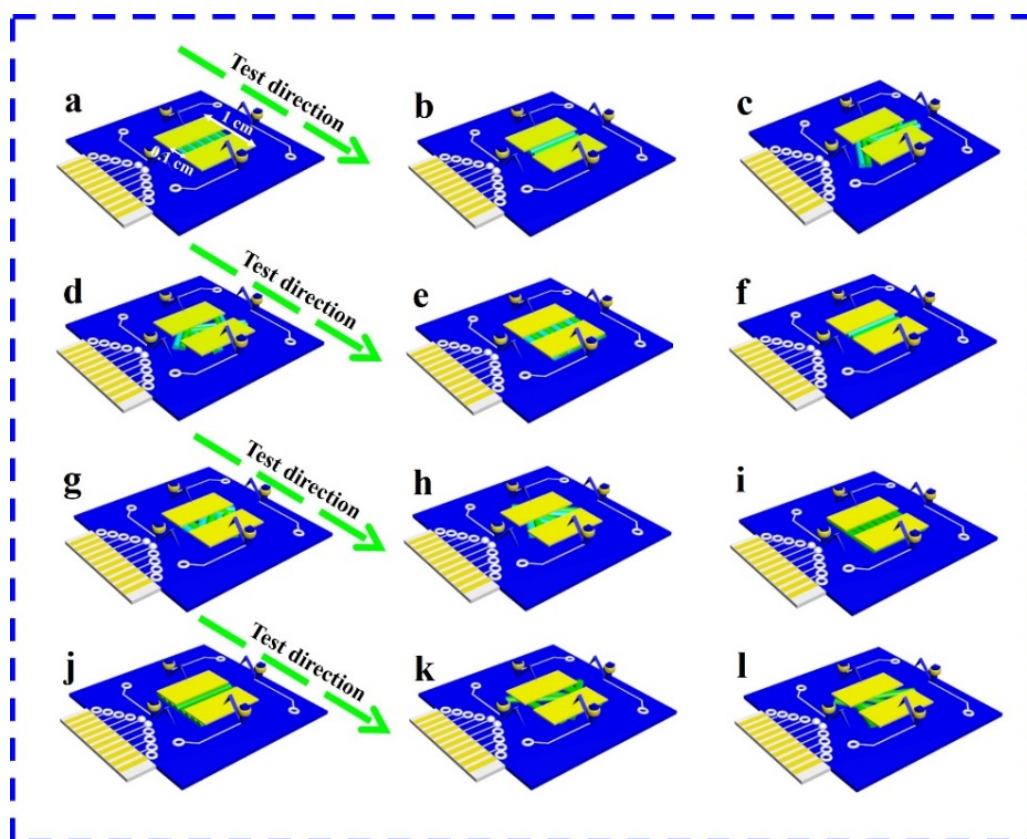


Fig. S5 Schematic illustration of the conductive test methods for C-JMAF (a and b), C-JMNF (c and d), D-JMAF (e and f), D-JMNF (g and h), S-CMAF (i and j) and S-CMNF (k and l)

All of the samples are tested for electrical conductance. Fig. S5 reveals the specific test method. Firstly, after the specimen is cut into a 1.0 cm×1.0 cm square, silver conductive adhesive is applied on both ends to minimize contact resistance. Secondly, two copper sheets (0.45 cm×1.0 cm) are used as electrodes to press on the silver conductive adhesive on the both ends of the specimen, and the two probes of the tester are placed on the two copper sheets. Finally, the conductance value of the specimen is tested.

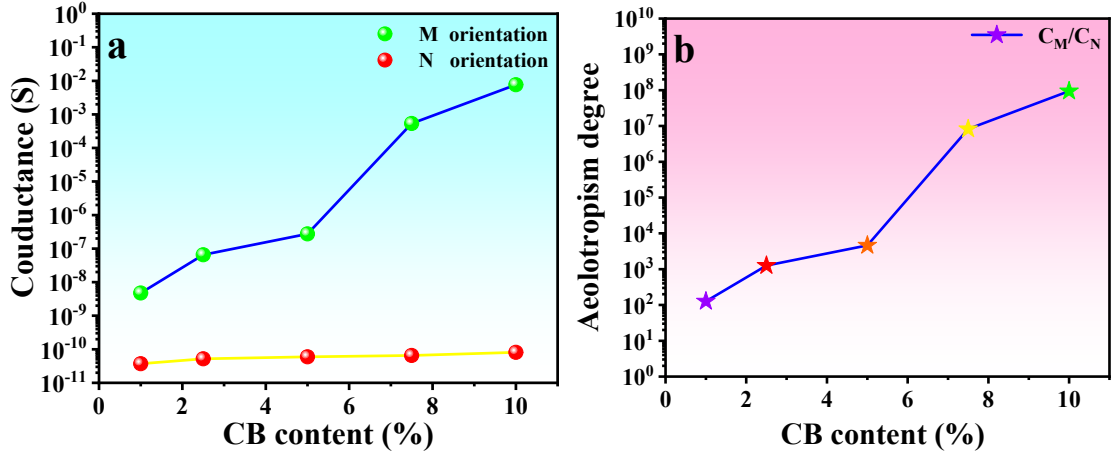


Fig. S6 Change of the conductances in different orientations (a) and conductive aeolotropism degree (b) with different CB contents for C-JMAF-C

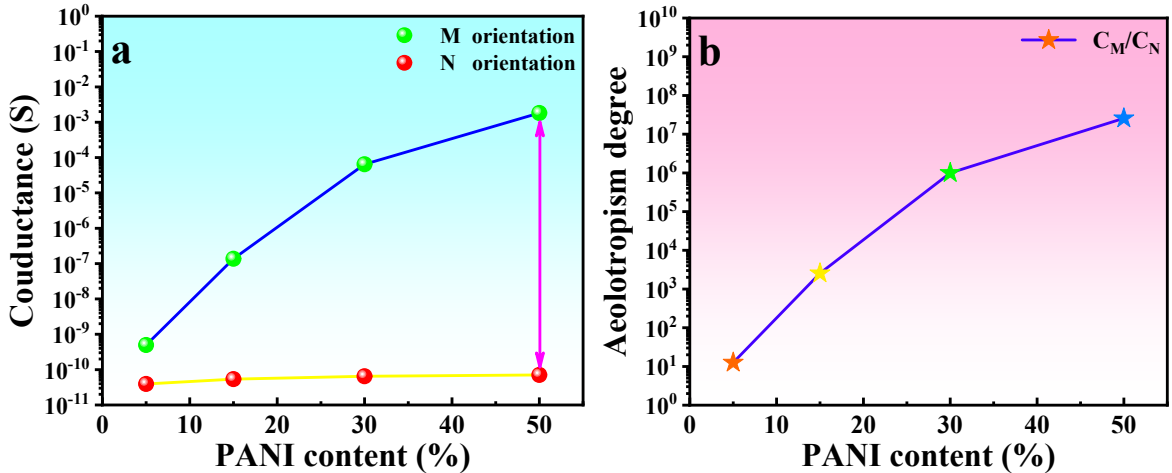


Fig. S7 Variation of the conductances in different orientations (a) and the conductive aeolotropism degree (b) with different PANI contents for C-JMAF-P

Table S5 Conductances of the C-JMAF (15% PANI+ 7.5% CB) bent for 100 times

Times	C_M (S)	C_N (S)	C_M/C_N
intial	1.56×10^{-2}	6.90×10^{-11}	2.26×10^8
20	1.44×10^{-2}	8.20×10^{-11}	1.76×10^8
40	1.35×10^{-2}	9.60×10^{-11}	1.41×10^8
60	1.26×10^{-2}	1.01×10^{-10}	1.25×10^8
80	1.12×10^{-6}	1.14×10^{-10}	9.82×10^7
100	1.06×10^{-6}	1.19×10^{-10}	8.91×10^7