

Electronic Supplementary Information (ESI)

**Modularization Design Philosophy for Multifunctional Materials: A Case  
Study of Janus Film Affording Concurrent Electrically Conductive  
Anisotropy-Magnetism-Fluorescence Multifunctionality**

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## Experimental Sections

### Chemicals

The following chemicals were analytically pure reagents and directly used as received without further purification.  $\text{Eu}_2\text{O}_3$  (99.99 %),  $\text{Tb}_4\text{O}_7$  (99.99 %), concentrated nitric acid, benzoic acid (BA), 1,10-phenanthroline (phen), anhydrous ethanol,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{NH}_4\text{NO}_3$ , polyethylene glycol (PEG,  $M_r \approx 20\,000$ ), ammonia, oleic acid (OA), methylmethacrylate (MMA), benzoylperoxide (BPO), aniline (ANI), (1S)-(+)-camphor-10 sulfonic acid (CSA), ammonium persulfate (APS),  $\text{CHCl}_3$ , *N, N*-dimethylformamide (DMF), polyvinylpyrrolidone (PVP,  $M_r \approx 1,300,000$ ). Deionized water was homemade.

### Synthesis of $\text{Tb}(\text{BA})_3\text{phen}$ complexes, oleic acid coated $\text{Fe}_3\text{O}_4$ NPs and PMMA

$\text{Tb}(\text{BA})_3\text{phen}$  complexes, oleic acid coated  $\text{Fe}_3\text{O}_4$  NPs and PMMA were fabricated in accordance with the reference.<sup>37</sup>

### Synthesis of $\text{Eu}(\text{BA})_3\text{phen}$ complexes

$\text{Eu}(\text{BA})_3\text{phen}$  complexes were synthesized in line with the reference.<sup>40</sup>

### Preparation of spinning fluid for preparing F module

The preparation process of the spinning fluid A for F module was as following: 0.1500 g of  $\text{Eu}(\text{BA})_3\text{phen}$  and 1.0000 g of PVP were dissolved into 4.0000 g of DMF and a uniform solution was formed under magnetic stirring for 12 h at room temperature.

### Fabrication of spinning fluids for preparing M-F module

$[\text{Fe}_3\text{O}_4/\text{PMMA}]||[\text{Tb}(\text{BA})_3\text{phen}/\text{PMMA}]$  Janus nanobelt was acted as building unit for constructing M-F module affording fluorescence and magnetism. Fluorescent spinning fluid (marked as spinning fluid B) was prepared as following: a certain amount of  $\text{Tb}(\text{BA})_3\text{phen}$  and 1.0000 g of PMMA were dissolved into the mixed solvent of DMF (1.0000 g) and  $\text{CHCl}_3$  (10.0000 g) under magnetic stirring for 24 h at room temperature. Magnetic spinning fluid (named as spinning fluid C) was synthesized as following: a certain amount of  $\text{Fe}_3\text{O}_4$  NPs was ultrasonically dispersed into the mixed solvent of DMF (1.0000 g) and  $\text{CHCl}_3$  (10.0000 g) for 20 min to acquire spinning fluid C, and then 1.0000 g of PMMA was added into the above mixture under mechanically stirring for 24 h at room temperature. The specific amounts of materials for fabricating two spinning fluids were summarized in Table S1 and Table S2.

Table S1 Compositions of the spinning fluid B

Spinning fluid B	$\text{Tb}(\text{BA})_3\text{phen}/\text{PMMA}$ [wt %]	$\text{Tb}(\text{BA})_3\text{phen}$ [g]	PMMA[g]	DMF[g]	$\text{CHCl}_3$ [g]
S <sub>b1</sub>	5	0.0500	1.0000	1.0000	10.0000
S <sub>b2</sub>	10	0.1000	1.0000	1.0000	10.0000
S <sub>b3</sub>	15	0.1500	1.0000	1.0000	10.0000
S <sub>b4</sub>	20	0.2000	1.0000	1.0000	10.0000
S <sub>b5</sub>	25	0.25000	1.0000	1.0000	10.0000

Table S2 Compositions of the spinning fluid C

Spinning fluid C	Fe <sub>3</sub> O <sub>4</sub> /PMMA [mass ratio]	Fe <sub>3</sub> O <sub>4</sub> [g]	PMMA[g]	DMF[g]	CHCl <sub>3</sub> [g]
S <sub>c1</sub>	1:1	1.0000	1.0000	1.0000	10.0000
S <sub>c2</sub>	2:1	2.0000	1.0000	1.0000	10.0000
S <sub>c3</sub>	3:1	3.0000	1.0000	1.0000	10.0000

### Fabrication of spinning fluid for preparing AF module

Tb(BA)<sub>3</sub>phen/Eu(BA)<sub>3</sub>phen/PMMA nanobelt was acted as building unit for constructing AF module and prepared by the spinning fluid containing Tb(BA)<sub>3</sub>phen and Eu(BA)<sub>3</sub>phen. The mass percentage of Tb(BA)<sub>3</sub>phen and Eu(BA)<sub>3</sub>phen to PMMA is designated as 15 %. The compositions of the spinning fluid were shown in Table S3. The specific preparation process was as following: a certain mass of Tb(BA)<sub>3</sub>phen, Eu(BA)<sub>3</sub>phen and PMMA (1.0000 g) were dissolved into the mixed solvent of DMF (1.0000 g) and CHCl<sub>3</sub> (10.0000 g). Then the mixed solutions were magnetically stirred for 24 h at room temperature (defined as spinning fluid D).

Table S3 Compositions of the spinning fluid D

Spinning fluid D	Tb(BA) <sub>3</sub> phen:Eu(BA) <sub>3</sub> phen	Tb(BA) <sub>3</sub> phen[g]	Eu(BA) <sub>3</sub> phen[g]	PMMA[g]	DMF[g]	CHCl <sub>3</sub> [g]
	[mass ratio]					
S <sub>d1</sub>	10:0	0.1500	0.0000	1.0000	1.0000	10.0000
S <sub>d2</sub>	9:1	0.1350	0.0150	1.0000	1.0000	10.0000
S <sub>d3</sub>	7:3	0.1050	0.0450	1.0000	1.0000	10.0000
S <sub>d4</sub>	5:5	0.0750	0.0750	1.0000	1.0000	10.0000
S <sub>d5</sub>	3:7	0.0450	0.1050	1.0000	1.0000	10.0000
S <sub>d6</sub>	1:9	0.0150	0.1350	1.0000	1.0000	10.0000
S <sub>d7</sub>	0:10	0.0000	0.1500	1.0000	1.0000	10.0000

### Synthesis of spinning fluid for preparing E-F module

[PANI/PMMA]||[Eu(BA)<sub>3</sub>phen/PMMA] Janus nanobelt acted as building unit for constructing E-F module was constructed by two spinning fluids which included fluorescent spinning fluid (defined as spinning fluid E) and conductive spinning fluid (marked as spinning fluid F). The spinning fluid E was prepared similarly to spinning fluid B. The spinning fluid F was synthesized as following steps. First of all, a certain amount of ANI, CSA and PMMA (1.0000 g) were dissolved into the mixed solvent of DMF (1.0000 g) and CHCl<sub>3</sub> (10.0000 g) under magnetic stirring for 48 h at room temperature (defined as solution 1). Subsequently, a certain amount of APS was dissolved into DMF (1.0000 g) and stirred for 1 h at room temperature (marked as solution 2). Two solutions were frozen for 20 min at 0 °C in a refrigerator. Then solution 2 was added into solution 1 by inches under magnetic stirring for 3 h in an ice-water bath, and then the mixture was refrigerated for 24 h at 0 °C to obtain spinning fluid F. The specific amounts of used materials for fabricating two spinning solutions were summarized in Table S4 and Table S5.

Table S4 Compositions of the spinning fluid E

Spinning fluid E	Eu(BA) <sub>3</sub> phen/PMMA[wt %]	Eu(BA) <sub>3</sub> phen[g]	PMMA[g]	DMF[g]	CHCl <sub>3</sub> [g]
S <sub>e1</sub>	5	0.0500	1.0000	1.0000	10.0000
S <sub>e2</sub>	10	0.1000	1.0000	1.0000	10.0000
S <sub>e3</sub>	15	0.1500	1.0000	1.0000	10.0000
S <sub>e4</sub>	20	0.2000	1.0000	1.0000	10.0000
S <sub>e5</sub>	25	0.25000	1.0000	1.0000	10.0000

Table S5 Compositions of the spinning fluid F

Spinning fluid F	PANI/PMMA[wt %]	ANI[g]	CSA[g]	APS[g]	PMMA[g]	DMF[g]	CHCl <sub>3</sub> [g]
S <sub>f1</sub>	15	0.1500	0.3000	0.8822	1.0000	2.0000	10.0000
S <sub>f2</sub>	30	0.3000	0.6000	1.1033	1.0000	2.0000	10.0000
S <sub>f3</sub>	50	0.5000	1.0000	1.3232	1.0000	2.0000	10.0000
S <sub>f4</sub>	70	0.7000	1.4000	1.5437	1.0000	2.0000	10.0000

#### Preparation of spinning fluid for preparing Fe<sub>3</sub>O<sub>4</sub>/Tb(BA)<sub>3</sub>phen/PMMA composite nanobelts

The method to obtain spinning fluid for preparing Fe<sub>3</sub>O<sub>4</sub>/Tb(BA)<sub>3</sub>phen/PMMA composite nanobelts was as following: a certain amount of Fe<sub>3</sub>O<sub>4</sub> NPs was dispersed into the mixed solvent of DMF (1.0000 g) and CHCl<sub>3</sub> (10.0000 g) and ultrasonically dispersed for 20 min, and then a certain amount of Tb(BA)<sub>3</sub>phen and 1.0000 g of PMMA were added into the mixture under mechanically stirring at room temperature (marked as spinning fluid G). During this process, the amounts of related substances were the same as those for preparing [Fe<sub>3</sub>O<sub>4</sub>/PMMA]||[Tb(BA)<sub>3</sub>phen/PMMA] Janus nanobelts.

#### Synthesis of spinning fluid for preparing PANI/Eu(BA)<sub>3</sub>phen/PMMA composite nanobelts

A certain amount of ANI, CSA, Eu(BA)<sub>3</sub>phen and PMMA (1.0000 g) was dissolved into the mixed solvent of DMF (1.0000 g) and CHCl<sub>3</sub> (10.0000 g) under magnetic stirring for 48 h at room temperature to obtain spinning fluid (marked as spinning fluid H ). The rest of the experimental procedures and the amounts of related substances were the same as those for preparation of [PANI/PMMA]||[Eu(BA)<sub>3</sub>phen/PMMA] Janus nanobelts.

#### Fabrication of contrast samples

In order to demonstrate the superiority of 4M-EMF Janus film, three contrast samples including [Fe<sub>3</sub>O<sub>4</sub>/PMMA]||[Tb(BA)<sub>3</sub>phen/PMMA] Janus nanobelts non-array (marked as M-F JN), Fe<sub>3</sub>O<sub>4</sub>/PMMA/Tb(BA)<sub>3</sub>phen composite nanobelts array (denoted as M-F CA), Fe<sub>3</sub>O<sub>4</sub>/PMMA/Tb(BA)<sub>3</sub>phen composite nanobelts non-array (defined as M-F CN) were prepared. The electrospinning devices for preparing three contrast samples were respectively illustrated in Fig. S1a, S1b and S1c. We selected spinning fluids S<sub>b3</sub> and S<sub>e1</sub> and replaced the roller with wire-netting to obtain M-F JN. Similarly, we selected spinning fluid G and severally used the roller and wire-netting as the collector to gain M-F CA and M-F CN. In the same way, spinning fluids S<sub>e3</sub> and S<sub>f1</sub> were selected and wire-netting was used as the collector for getting the [PANI/PMMA]||[Eu(BA)<sub>3</sub>phen/PMMA] Janus nanobelts non-array (marked as E-F

JN). We chose spinning fluid H and respectively used the roller and wire-netting as the collector to gain Eu(BA)<sub>3</sub>phen/PMMA/PANI composite nanobelts array (denoted as E-F CA) and Eu(BA)<sub>3</sub>phen/PMMA/PANI composite nanobelts non-array (defined as E-F CN). Fig. S1d to S1f respectively showed the electrospinning devices for fabricating the three contrast samples.

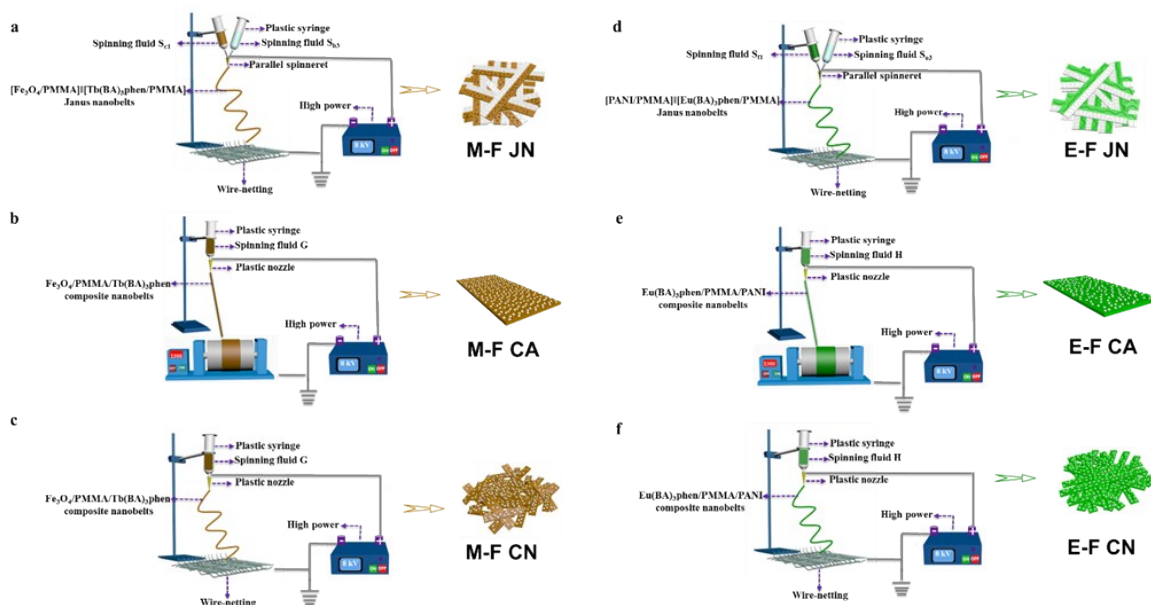


Fig. S1 Electrospinning devices for preparing (a) M-F JN, (b) M-F CA, (c) M-F CN, (d) E-F JN, (e) E-F CA and (f) E-F CN

## Characterization techniques

Phase compositions were analyzed by X-ray diffractometer (XRD, Bruker D8 FOCUS) by using a Cu *K* $\alpha$  radiation. The magnetic performance of the samples was detected by a vibrating sample magnetometer (VSE, MPMS SQUID XL). The morphologies and structures of the samples were characterized *via* a field emission scanning electron microscope (FESEM, XL-30) equipped with an energy-dispersive X-ray spectroscopy (EDS). An optical microscope (OM, CVM500E) was employed to observe the morphologies of the samples. A Hitachi fluorescence spectrophotometer F-7000 was used to investigate the fluorescence (PL) properties. The conductive determinations were conducted on a Hall Effect measurement system (ECOPIA HMS-3000). All the above tests were performed at room temperature.

## Results and Discussion

### Fluorescent properties

In order to obtain the optimum percentage of Tb(BA)<sub>3</sub>phen to PMMA, a series of Tb(BA)<sub>3</sub>phen/PMMA nanobelts array were fabricated by using spinning fluids from S<sub>b1</sub> to S<sub>b5</sub>. Excitation and emission spectra of Tb(BA)<sub>3</sub>phen/PMMA nanobelts array doped with different percentages of Tb(BA)<sub>3</sub>phen are illustrated in Fig. S2. As found from the excitation spectra (Fig. S2a), the strongest peak at 291 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, 622 nm are obtained under the excitation of 291-nm light, as seen in Figure S2b. These characteristic emission peaks come from  $^5D_4 \rightarrow ^7F_6$  (489 nm),  $^5D_4 \rightarrow ^7F_5$  (545 nm),  $^5D_4 \rightarrow ^7F_4$  (586 nm) and  $^5D_4 \rightarrow ^7F_3$  (622 nm) energy level transitions of Tb<sup>3+</sup>, and  $^5D_4 \rightarrow ^7F_5$  hypersensitive transition leads to the strongest green light emission at 545 nm. The maximum fluorescence intensity is obtained when the

mass percentage of Tb(BA)<sub>3</sub>phen to PMMA is 15%. Therefore, the spinning fluid S<sub>b3</sub> is applied to prepare M-F module in this study. In order to obtain the optimum percentage of Eu(BA)<sub>3</sub>phen to PMMA, a series of Eu(BA)<sub>3</sub>phen/PMMA nanobelts array were prepared by using spinning fluids from S<sub>e1</sub> to S<sub>e5</sub>. As seen from the excitation spectra (Fig. S2c), the strongest peak at 289 nm can be assigned to  $\pi \rightarrow \pi^*$  electron transition of ligands when the monitoring wavelength is 615 nm. Characteristic emission peaks located at 580, 593, 615, 620 nm are obtained at the excitation of light with a wavelength of 289 nm, as observed in Fig. S2d. These characteristic emission peaks are originated from  $^5D_0 \rightarrow ^7F_0$  (580 nm),  $^5D_0 \rightarrow ^7F_1$  (593 nm),  $^5D_0 \rightarrow ^7F_2$  (615 nm and 620 nm) energy level transitions of Eu<sup>3+</sup>, and  $^5D_0 \rightarrow ^7F_2$  hypersensitive transition results in the strongest red light emission at 615 nm. The maximum fluorescence intensity is obtained when the mass percentage of Eu(BA)<sub>3</sub>phen to PMMA is 15%. Therefore, the spinning solution S<sub>e3</sub> is applied to prepare E-F module in this work.

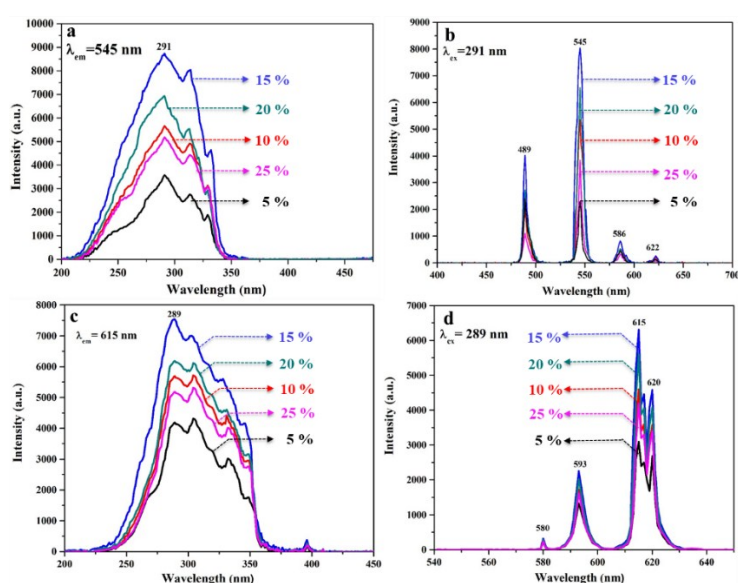


Fig. S2 Excitation (a, c) and emission (b, d) spectra of (a, b) Tb(BA)<sub>3</sub>phen/PMMA nanobelts array doped with different percentages of Tb(BA)<sub>3</sub>phen and (c, d) Eu(BA)<sub>3</sub>phen/PMMA nanobelts array doped with different percentages of Eu(BA)<sub>3</sub>phen

In order to prove that the Janus structure of 4M-EMF Janus film has no obvious influence on the fluorescence performance of the F module, the fluorescence property of single F module is compared with that of the F module in 4M-EMF Janus film. The fluorescence of single F module is almost the same as that of F module of 4M-EMF Janus film, as shown in Fig. S3a and S3b. Fig. S4a and S4d are the schematic diagrams revealing fluorescent properties of the two films. It displays that the Janus structure of 4M-EMF Janus film also has no obvious interference on the fluorescence performance of the F module. For single M-F module and M-F module of 4M-EMF Janus film, no difference in the fluorescence intensity between the two films is found, as shown in Fig. S3c and S3d. Figure S4b and S4e are the schematic diagrams revealing fluorescent properties of the two films. It indicates that the Janus structure of 4M-EMF Janus film also has no remarkable influence on the fluorescence performance of M-F module. For single E-F module, the fluorescence intensity is closed to that of E-F module of 4M-EMF Janus film, as shown in Fig. S3e and S3f. Fig. S4c and S4d present the schematic diagrams revealing fluorescent properties of the two films. It reveals that the Janus structure of 4M-EMF Janus film also has no evident effect on the fluorescent

performance of E-F module. From what has been discussed above, we can safely arrive at the conclusion that no apparent interferences among various modules are found owing to macro-partition actualized by modularization, fully demonstrating that the modularization design philosophy has preponderances in constructing multifunctional materials.

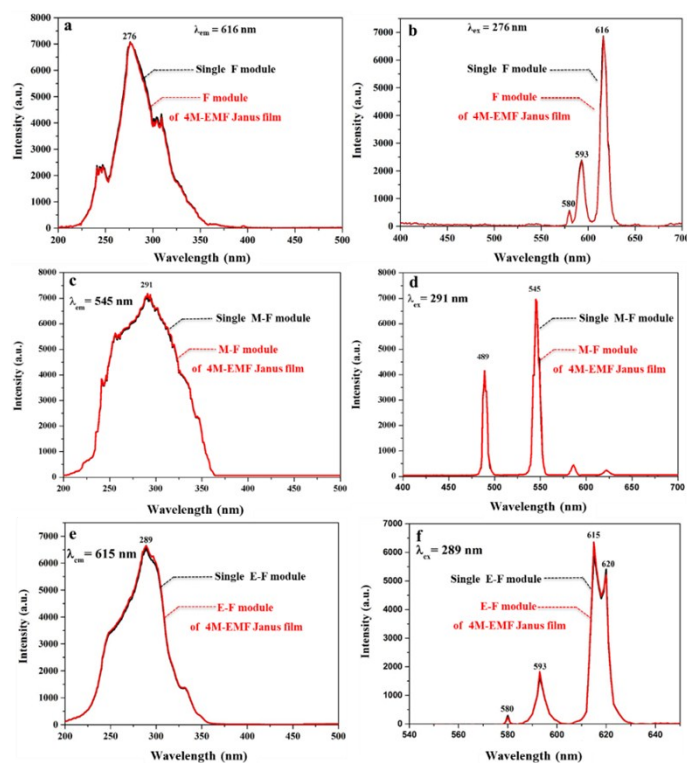


Fig. S3 Excitation (a, c, e) and emission (b, d, f) spectra of (a, b) single F module and F module of 4M-EMF Janus film, (c, d) single M-F module and M-F module of 4M-EMF Janus film, (e, f) single E-F module and E-F module of 4M-EMF Janus film

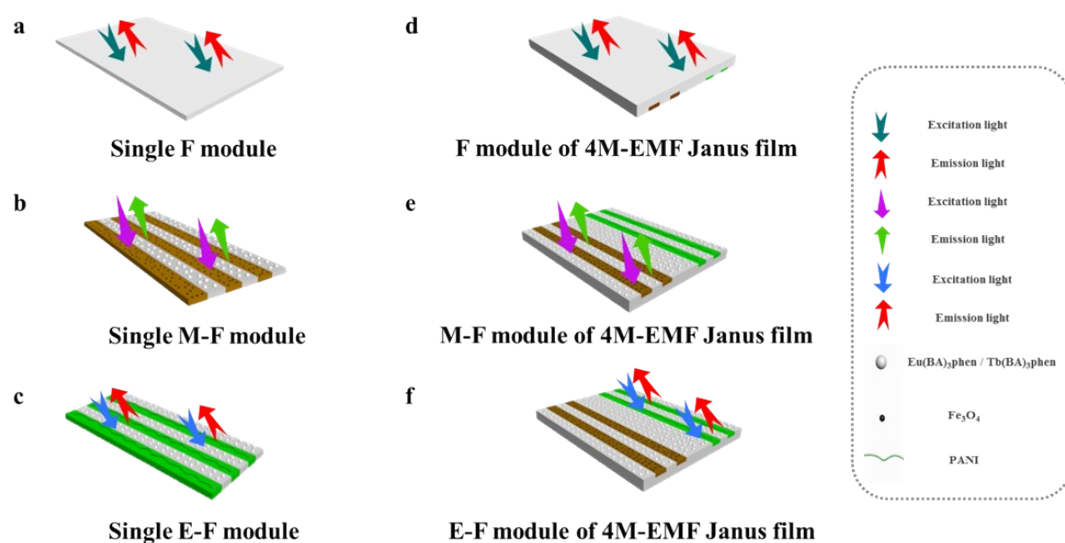


Fig. S4 Schematic illustrations of excitation light and emission light in (a) single F module, (b) F module of 4M-EMF Janus film, (c) single M-F module, (d) M-F module of 4M-EMF Janus film, (e) single E-F module and (f) E-F module of 4M-EMF Janus film