Supporting Information

Tunable Fluorescence Emission Based on Multilayered MOF-on-MOF

Qing-Qing Xia [a], Xing-Huo Wang [a], Jia-Lin Yu [a], Zhi-Yuan Xue [a], Juan Chai [b], Ming-Xue Wu [a,*], Xiaomin Liu [a,*]

[a] *School of Chemistry and Chemical Engineering, Qingdao University, Qingdao 266071, Shandong, P. R. China*

[b] *Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, 1219 Zhongguan West Road, Ningbo, Zhejiang 315201, P. R. China*

** E-mail: wmx517@qdu.edu.cn, liuxiaomin@qdu.edu.cn*

1. Synthesis of Dyes and ZIF-8 Based Composites

1.1 Synthesis of ZIF-8@perylene@ZIF-8@RhB

Initially, 446.2 mg (1.5 mmol) of $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in 3 mL methanol (solution 1) followed by adding 250 μL of methanol solution of perylene with a concentration of 1mmol/L to prepare solution A. Next, 369.5 mg (4.5 mmol) of 2-methylimidazole was dissolved in 3 mL of methanol to prepared solution B. Finally, solution B, 625 μL of triethylamine and solution A was stirred and reacted at room temperature for 3 hours. ZIF-8@perylene precipitate was obtained through centrifugal purification with methanol. Subsequently, solution 1 and 250μL of 1mmol/L methanol solution of RhB were added into the above paste ZIF-8@perylene and mixed into a homogeneous state followed by adding solution B and 625μL of triethylamine into the mixture. The mixture was stirred and reacted at room temperature for another 3 hours. Final product ZIF-8@perylene@ZIF8@RhB was obtained by washing and centrifugating with methanol. Then, the ZIF-8@perylene@ZIF8@RhB precipitate obtained by centrifugation was redispersed in 5 mL methanol for subsequent experiment.

1.2 Synthesis of ZIF-8@RhB@ZIF-8@perylene

The preparation of ZIF-8@RhB@ZIF-8@perylene was similar to that of ZIF-8@perylene@ZIF-8@RhB, but reversed the order of the addition of RhB and perylene.

1.3 Synthesis of ZIF-8@perylene+RhB

Firstly, 446.2 mg (1.5 mmol) of $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in 3 mL of methanol to obtained solution A, and then added 250 μL of 1 mmol/L perylene methanol solution and 250 μL of 1 mmol/L RhB methanol solution to solution A under stirring. Then, solution B obtained by dissolving 369.5 mg (4.5 mmol) of 2-methylimidazole in 3 mL of methanol and 625 μL of triethylamine were added to the previous obtained mixture, and the reaction was stirred at room temperature for 3 hours. After that, the dye adsorbed on the surface of the product was removed by centrifugating and washing. Finally, the precipitate obtained by centrifugation was dispersed in 5 mL of methanol for subsequent experiments.

1.4 Synthesis of ZIF-8@0.25perylene@ZIF-8@10RhB

The preparation procedure was similar to that of Section 1.1, except that the concentration of the methanol solution of perylene used in Section 1.1 was changed to 0.25 mmol/L and the concentration of the methanol solution of RhB was changed to 10 mmol/L.

1.5 Synthesis of ZIF-8@0.125perylene@ZIF-8@10RhB

To preparation of ZIF-8@0.125perylene@ZIF-8@10RhB, the concentration of the methanol solution of perylene was changed to 0.125mmol/L, and

the others were the same as Section 1.4.

1.6 Synthesis of ZIF-8@0.125perylene@ZIF-8@20RhB

The preparation method of this material was the same as the preparation method of ZIF-8@0.125perylene@ZIF-8@10RhB mentioned in Section 1.5, but the methanol solution of RhB used in the preparation of the outer MOF@dye was 20mmol/L, the other steps remain unchanged.

1.7 Synthesis of ZIF-8@0.125perylene+25RhB

The synthesis of ZIF-8@0.125perylene+25RhB was the same as the method mentioned in Section 1.3, but the concentration of the methanol solution of perylene was changed to 0.125mmol/L and the concentration of the methanol solution of RhB was 25mmol/L.

1.8 Synthesis of mechanically mixed ZIF-8@0.125perylene+ZIF-8@25RhB

Dissolving 446.2 mg (1.5 mmol) of $Zn(NO_3)_2 \cdot 6H_2O$ in 3 mL methanol and then added 250 μL of methanol solution of perylene with a concentration of 0.125mmol/L to the above solution to obtain solution A. Next, 369.5 mg (4.5 mmol) of 2-methylimidazole was dissolved in 3 mL of methanol to prepared solution B. Finally, solution B, 625 μL of triethylamine and solution A was stirred and reacted at room temperature for 3 hours. ZIF-8@0.125perylene precipitate was obtained through centrifugal purification and redispersed in 5 mL methanol. ZIF-8@25RhB was prepared in similar method but replaced 0.125mmol/L of perylene with 25mmol/L of RhB. Finally, equal volume of ZIF-8@0.125perylene and ZIF-8@25RhB were mixed together for subsequent fluorescence experiment.

1.9 Synthesis of solid ZIF-8@perylene@ZIF-8@3RhB

Except that the concentration of the added methanol solution of perylene became 1mmol/L and the concentration of the methanol solution of RhB became 3mmol/L, the other steps were the same as that in Section 1.1. However, in the last step, the paste-like solid product obtained by centrifugation should be dried at 50°C for 6 hours and then grinded it to obtain a solid white light material ZIF-8@perylene@ZIF-8@3RhB.

1.10 Synthesis of mixed ZIF-8@perylene+ZIF-8@3RhB

First of all, ZIF-8@perylene solid powder and ZIF-8@3RhB solid powder need to be prepared separately according to the similar method mentioned in Section 1.9. Then, the same amount of ZIF-8@perylene powder and ZIF-8@3RhB powder were mechanically mixed to obtain ZIF-8@perylene+ZIF-8@3RhB solid.

1.11 Synthesis of solid ZIF-8@perylene+3RhB

Similar to the preparation method in Section 1.7, but the preparation of solid ZIF-8@perylene+3RhB needed to change the methanol solution of perylene to 1mmol/L and the concentration of methanol solution of RhB to 3mmol/L. In addition, another difference was that the paste ZIF-8@perylene+3RhB obtained after washing should be dried.

2. Characterizations

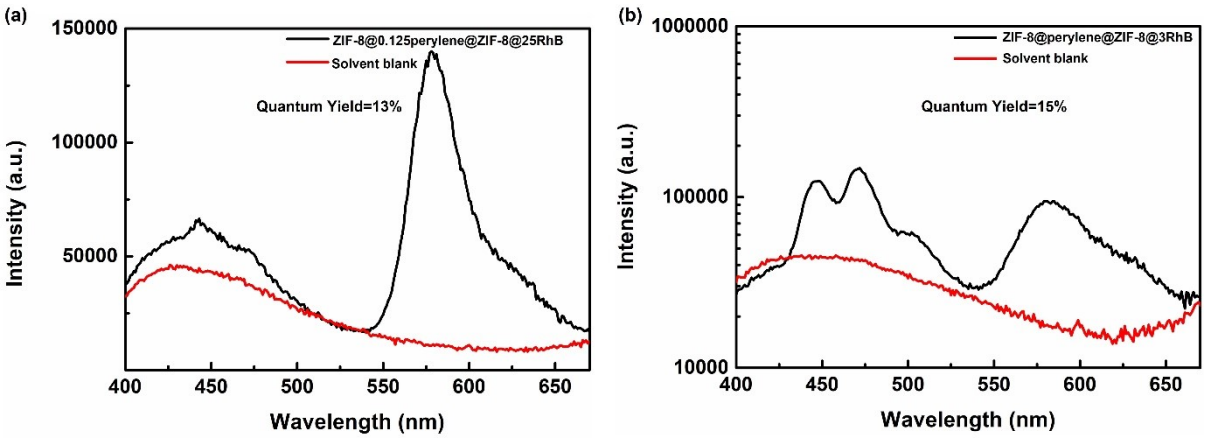


Fig. S1 Absolute fluorescence quantum yield of dispersed ZIF-8@0.125perylene@ZIF-8@25RhB and solid ZIF-8@perylene@ZIF-8@3RhB.

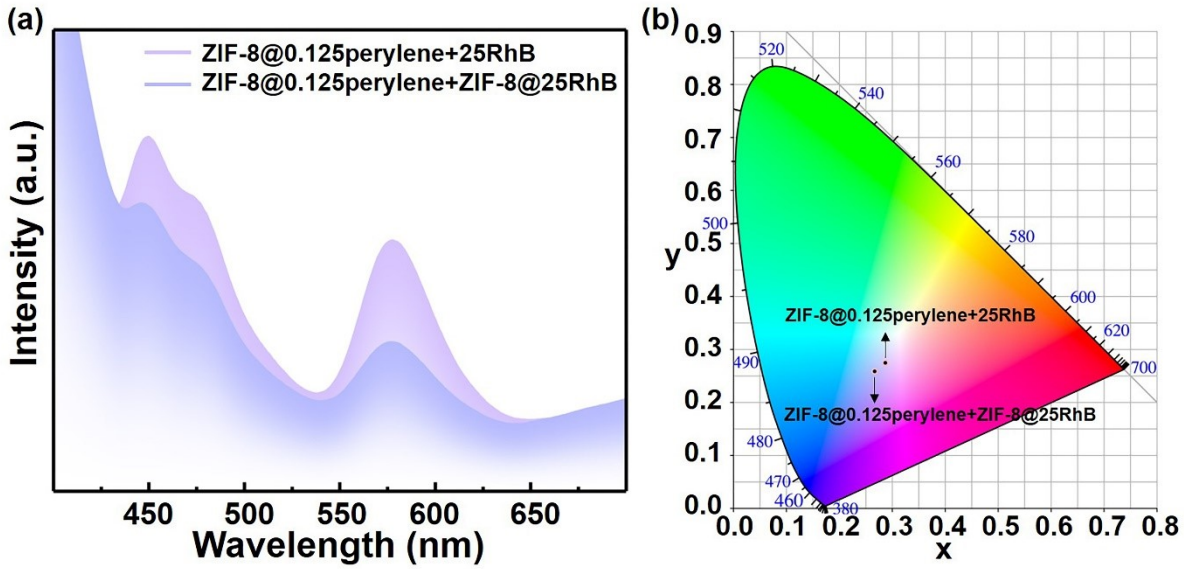


Fig. S2 (a) Fluorescence emission of ZIF-8@0.125prylene+25RhB and mechanically mixed ZIF-8@0.125prylene+ZIF-8@25RhB in dispersed state. (b) CIE chromaticity coordinates of ZIF-8@0.125prylene+25RhB and mechanically mixed ZIF-8@0.125prylene+ZIF-8@25RhB in dispersed state.

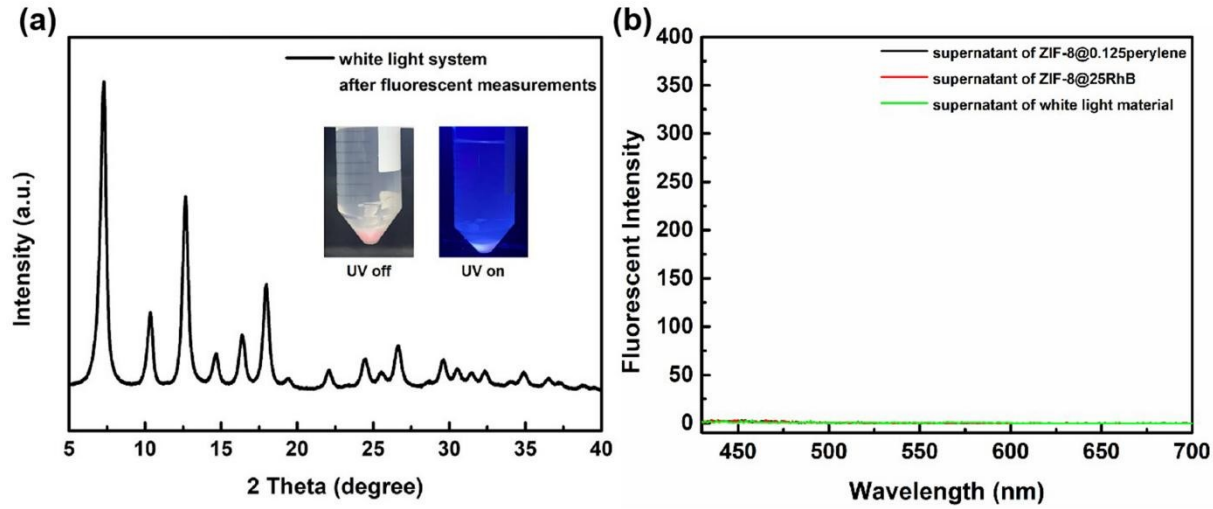


Fig. S3 (a) XRD patterns of the white light material after the fluorescent test, the inset is the photo of the white light material with or without 365nm UV light after the fluorescent test. (b) The fluorescence spectra of supernatants of ZIF-8@0.125perylene, ZIF-8@25RhB and ZIF-8@0.125perylene@ZIF-8@25RhB soaked methanol solution after fluorescent measurements.

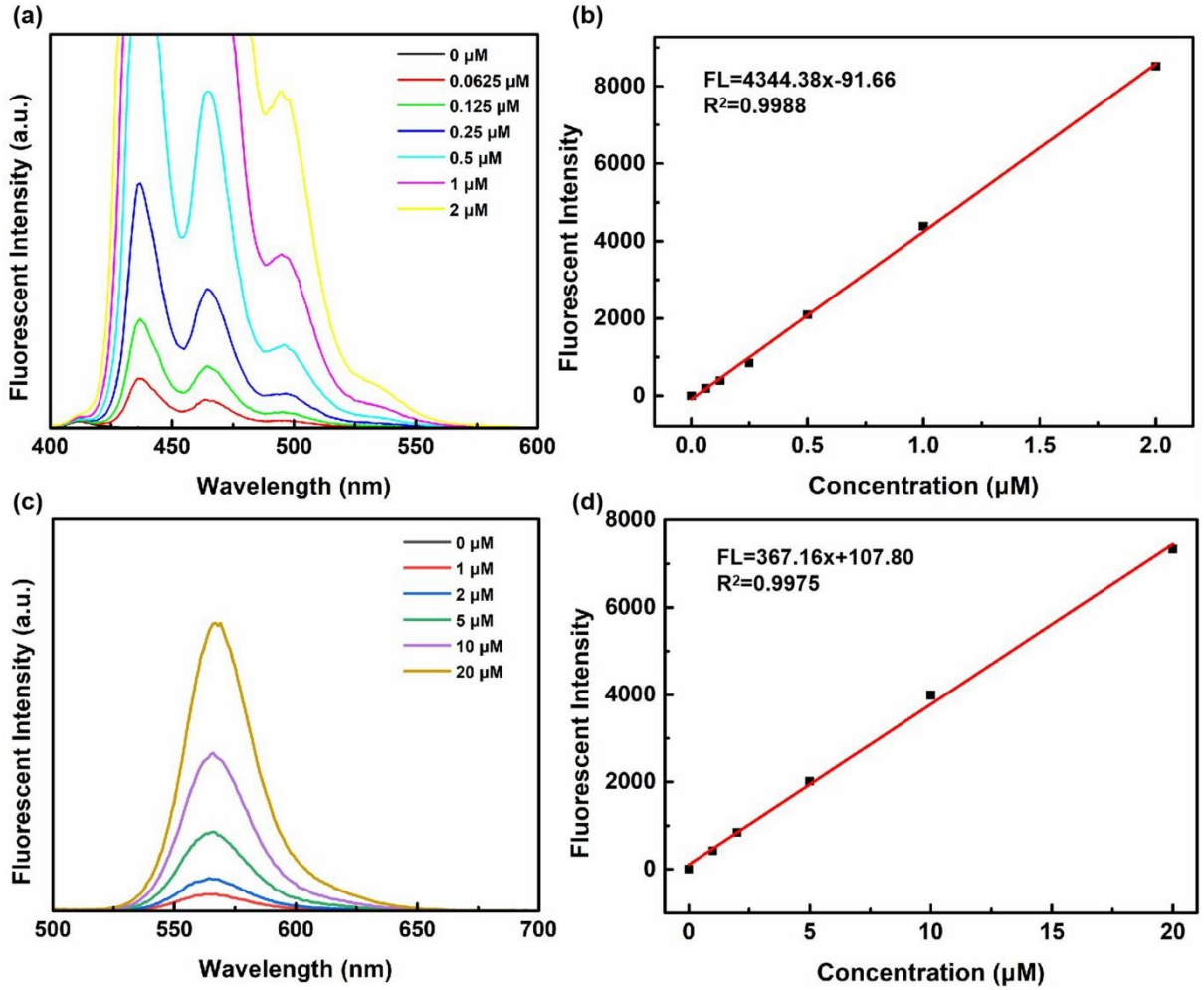
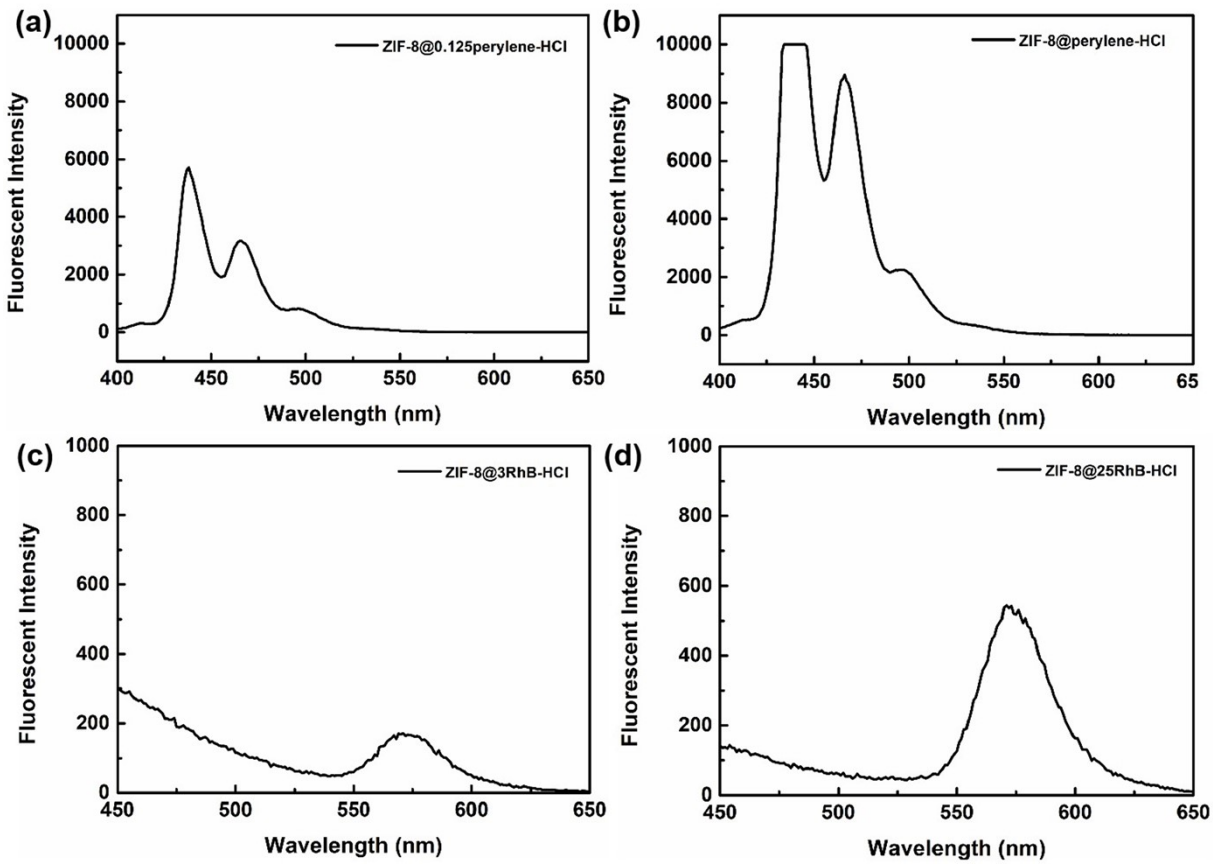


Figure S4 The relationship of concentration and fluorescent intensity of perylene (a-b) and RhB (c-d).



(e)

Quantity (mg)	ZIF-8@0.125perylene -10mg	ZIF-8@perylene -10mg	ZIF-8@3RhB -10mg	ZIF-8@25RhB -10mg
Fluorescent intensity	858	2263	200	546
massratio (wt%)	0.00056	0.0015	0.001	0.006

Fig. S5 (a-d) Fluorescent intensity of corresponding materials in methanol after destruction by HCl. (e) The related parameters of dyes in ZIF-8@dyes.

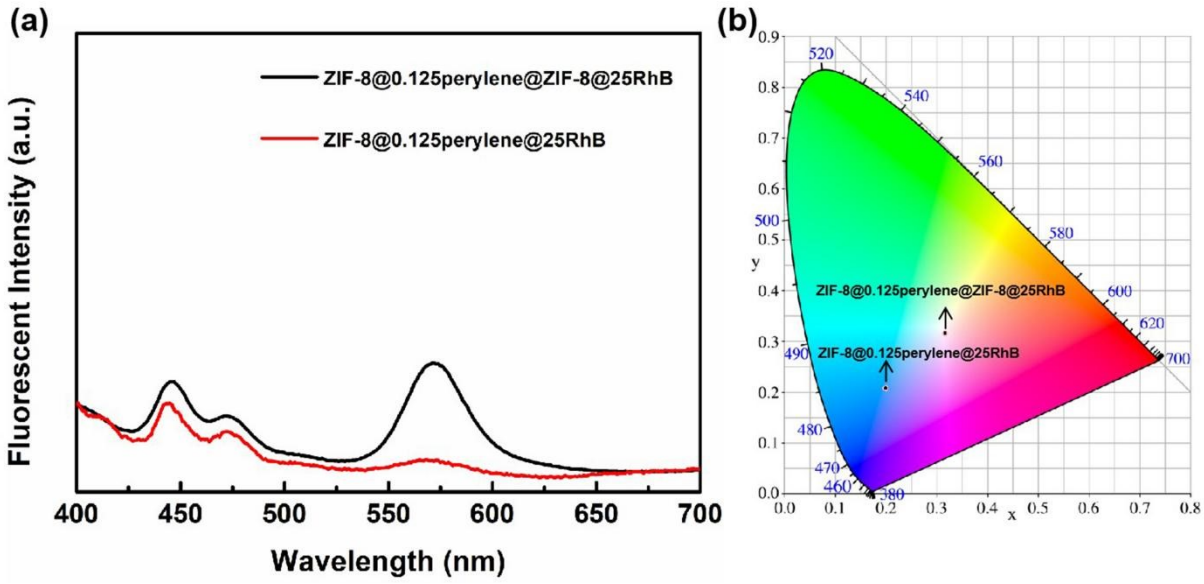


Figure S6 Fluorescence emission of white light ZIF-8@0.125perylene@ZIF-8@25RhB and ZIF-8@0.125perylene@25RhB as well as their CIE chromaticity diagram.

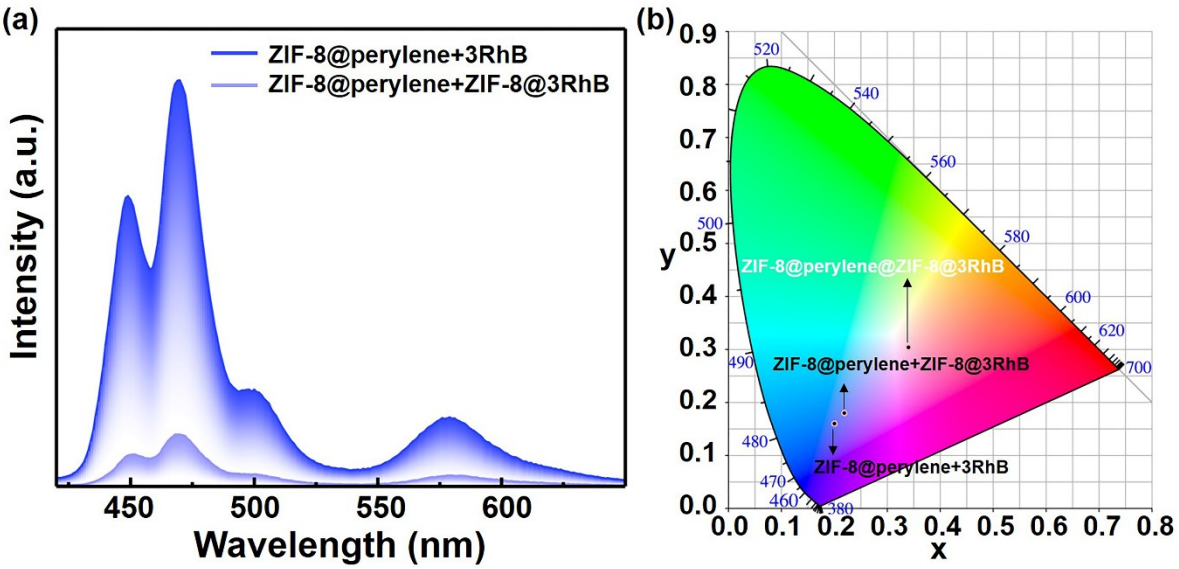


Fig. S7 (a) Solid state fluorescence of ZIF-8@prylene+3RhB and mechanically mixed ZIF-8@prylene+ZIF-8@3RhB. (b) CIE chromaticity coordinates of ZIF-8@prylene+3RhB and mechanically mixed ZIF-8@prylene+ZIF-8@3RhB in solid state.