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Supporting Information

Self-Assembly Dye-Encapsulated Metal-Organic Frameworks Coated with Thermoplastic Polyurethane for Highly-Stable Incandescent White Lighting

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1. Experimental section:

Materials and methods: Zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$] was purchased from Sinopharm Chemical Reagent Ltd. (Shanghai, China). 2-methylimidazolate (Hmim) N, N-dimethylformamide (DMF) and methanol were purchased from Aladdin Ltd. (Shanghai, China). Organic fluorescent dyes pm546, pm605 and SRh101 were purchased from Exciton. (Shanghai, China). TPU was purchased from Evermore Chemical Industry Ltd. (Taiwan, China). All the regents purchased were used without further purification.

The powder XRD patterns of the nanocrystals were recorded on a PANalytical X'Pert Pro X-ray diffractometer with Cu-Kα (λ = 1.54 Å). The luminescence spectra of dye solution and dye-encapsulated composites were collected by an Edinburgh Instrument F900 fluorescence spectrometer. Thermogravimetric analyses were performed on Netzsch TG209F3 with the heating rate at 10 °C·min^{-1} under N_2 atmosphere. Flourier transformation infrared (FTIR) spectra were obtained from KBr discs on a Nicolet iS10 FTIR spectrometer.

Synthesis of ZIF-8⊃pm546/pm605/SRh101:

The ZIF-8⊃pm546/pm605/SRh101 nanocrystals were synthesized under ambient temperature via an *in situ* method according to the previous reported protocol but with slight modification. At first, pm546, pm605 and SRh101 were prepared as DMF solution in the molar ratio of 10^{-2} mol·L^{-1}, 5×10^{-4} mol·L^{-1} and 5×10^{-3} mol·L^{-1}, respectively. For phosphor synthesis, 0.2 g $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in 8 g methanol first. Then the dyes were added with different amounts and the stock solution was kept stirring for 10 min. Afterwards, 8.6 g of a solution containing 0.6 g Hmim was added dropwise. The reaction solution was kept stirring for 3 hours. The obtained composites were collected by centrifugation (12000 rpm/3min) and washed thoroughly with methanol for five times to remove the residual dye molecules absorbed on the surface of ZIF-8. The ZIF-8⊃pm546, ZIF-8⊃pm605, ZIF-8⊃SRh101 composites were also prepared by utilizing the similar method.

Preparation of ZIF-8⊃pm546/pm605/SRh101@TPU and fabrication of remote-type WLED:

At first, 3 g TPU was added into a 20-mL glass bottle containing 5 mL DMF and stirred at 60 ℃ with a speed of 300 rpm for 2 hours until completely dissolved. Then, 300 mg of as prepared ZIF-8⊃pm546/pm605/SRh101 nanocrystals were added into 1 mL TPU/DMF colloidal solution and uniformly dispersed and coated with continuous magnetic stirring for 3 hours. Subsequently, the mixture was poured into a previously prepared mold, gently cooled to room temperature and left overnight for the evaporation of extra solvent. At last, a hemispherical phosphor layer was obtained. For the fabrication of remote-type WLED, the prepared hemispherical phosphor layer was coated on a commercial 460-nm blue LED chip and fixed by highly transparent silicone.

2. Additional Characterization Figures and Table.

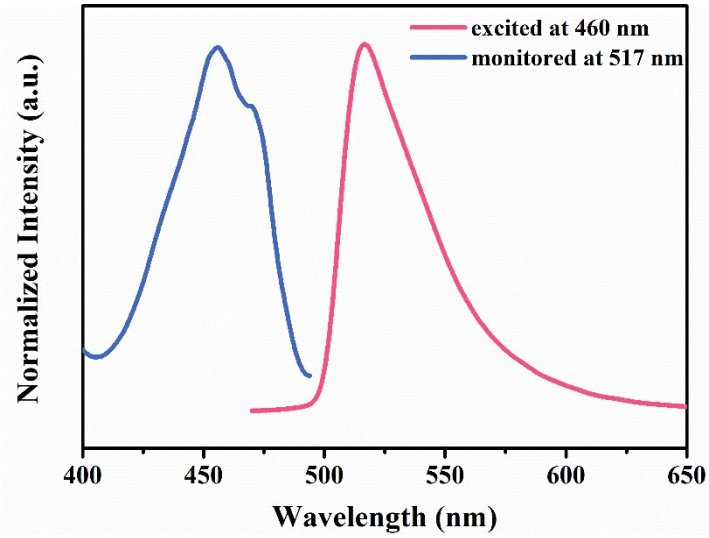

Fig. S1. The emission and excited spectrum of pm546 dilute solution.

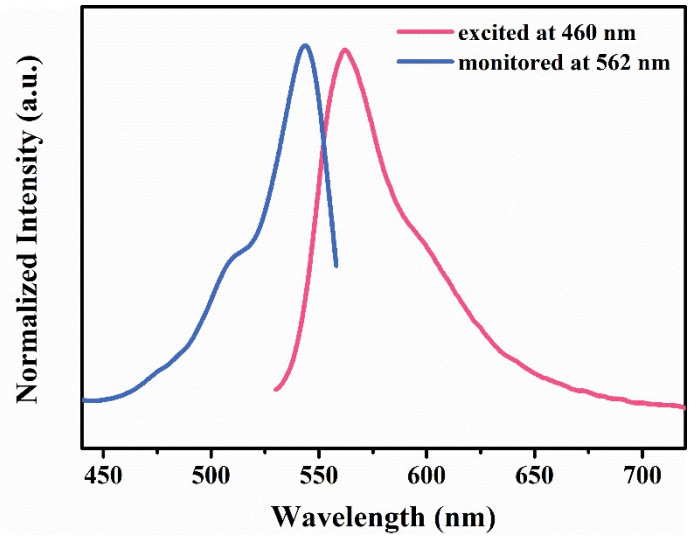

Fig. S2. The emission and excited spectrum of pm605 dilute solution.

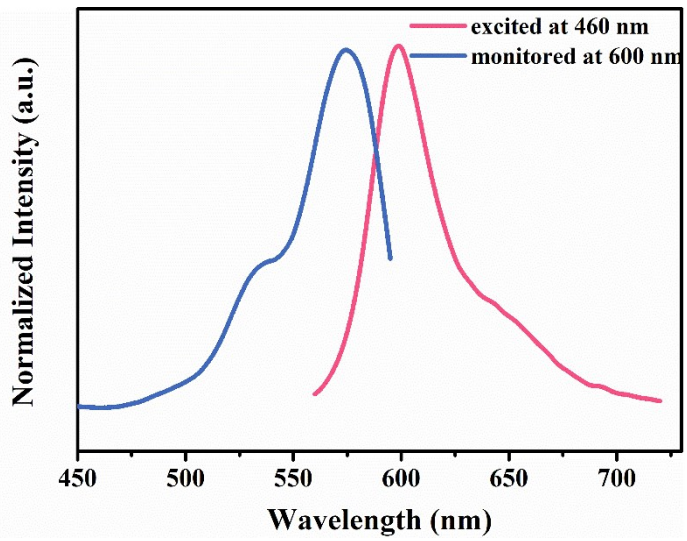

Fig. S3. The emission and excited spectrum of SRh101 dilute solution.

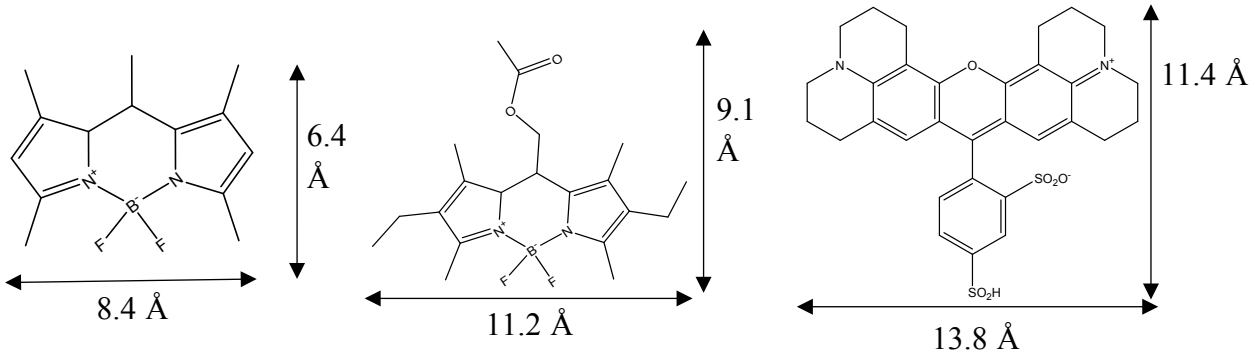

Fig. S4. Chemical structures of pm546, pm605, SRh101 with the corresponding molecular dimensions.

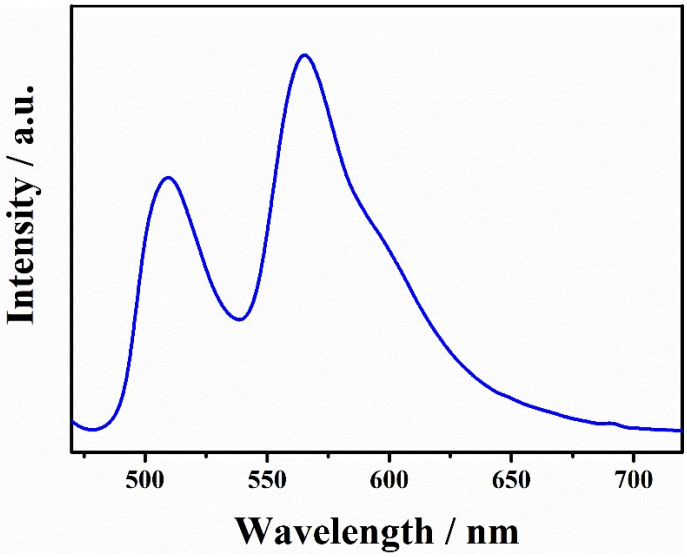

Fig. S5. The emission spectrum of ZIF-8⊃pm546/pm605 excited at 460 nm.

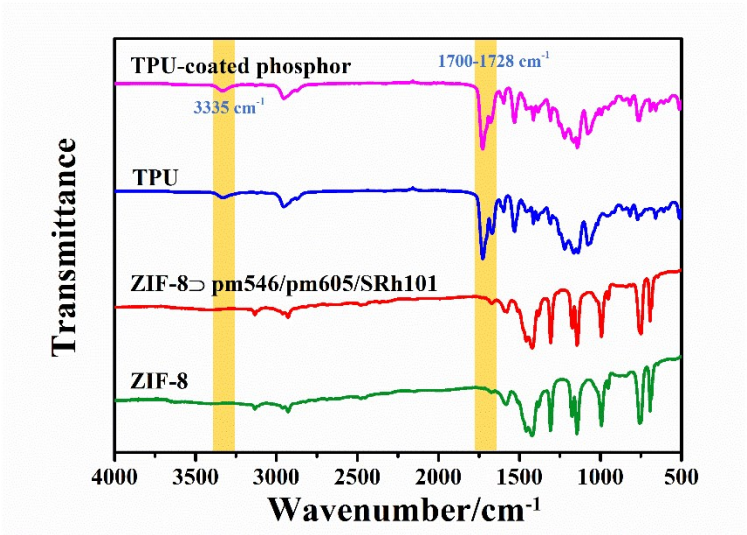

Fig. S6. FTIR spectrum of ZIF-8, ZIF-8⊃pm546/pm605/SRh101 (0.013 wt% pm546, 0.084 wt% pm605, 0.011 wt% SRh101), TPU and TPU-coated ZIF-8⊃pm546/pm605/SRh101 (phosphor).

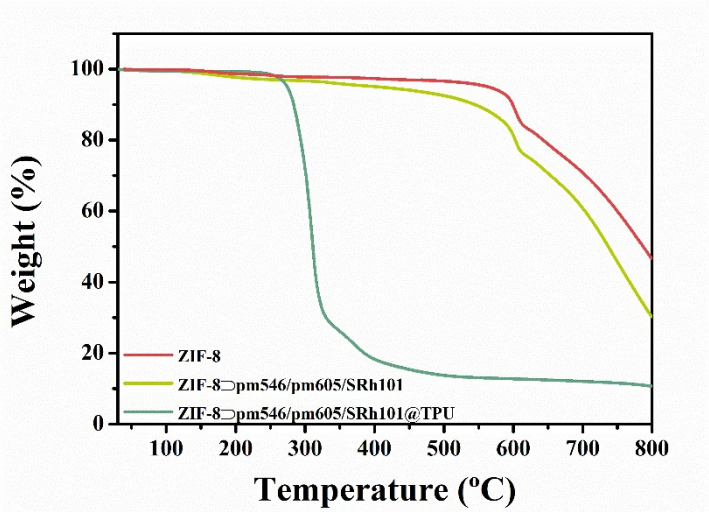

Fig. S7. Thermogravimetric curve of ZIF-8, ZIF-8⊃pm546/pm605/SRh101, TPU and TPU-coated ZIF-8⊃pm546/pm605/SRh101.

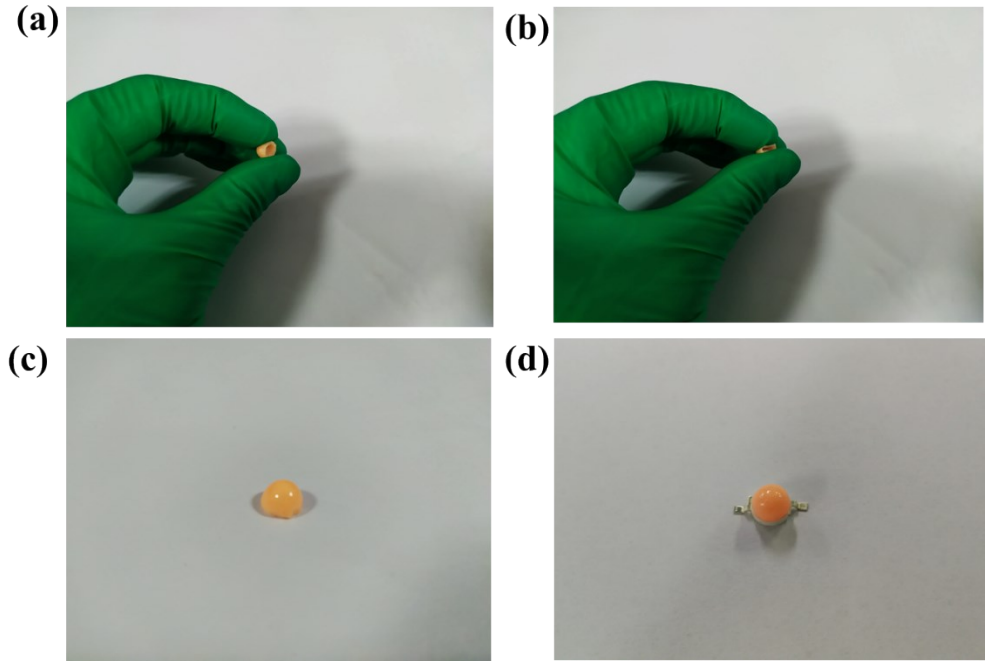

Fig. S8. The photographs of the hemispherical phosphor layer made of TPU-coated ZIF-8⊃pm546/pm605/SRh101 composites.

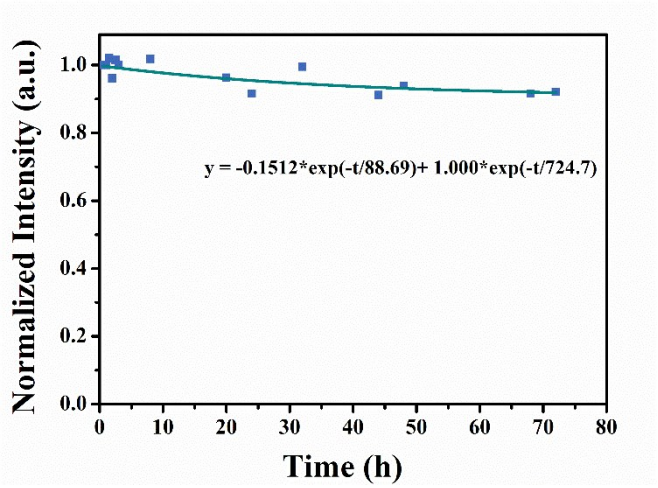

Fig. S9. The decay curve of as-fabricated white LED device when being lighted continuously.

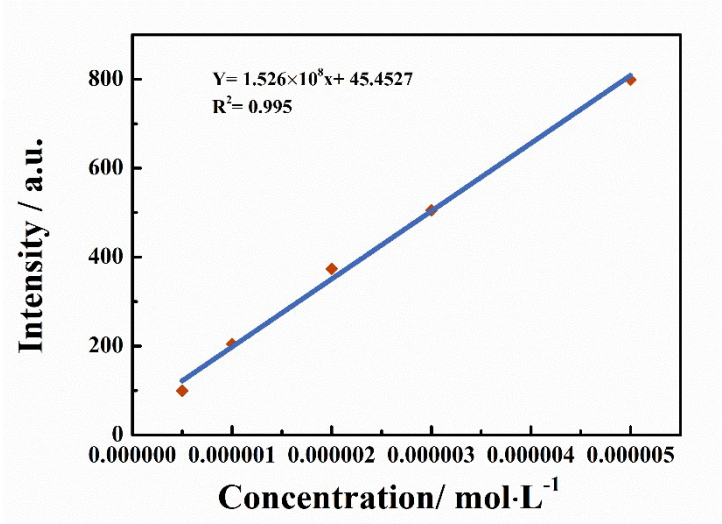

Fig. S10. The intensity-concentration relationship of pm546 in dilute solution.

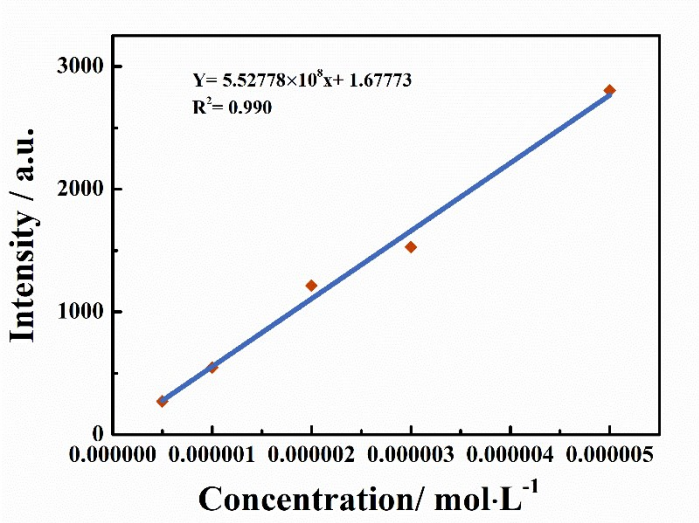

Fig. S11. The intensity-concentration relationship of pm605 in dilute solution.

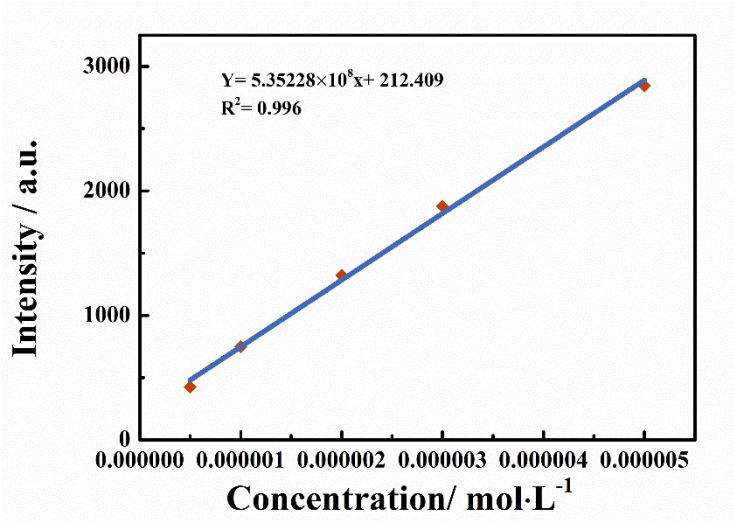

Fig. S12. The intensity-concentration relationship of SRh101 in dilute solution.

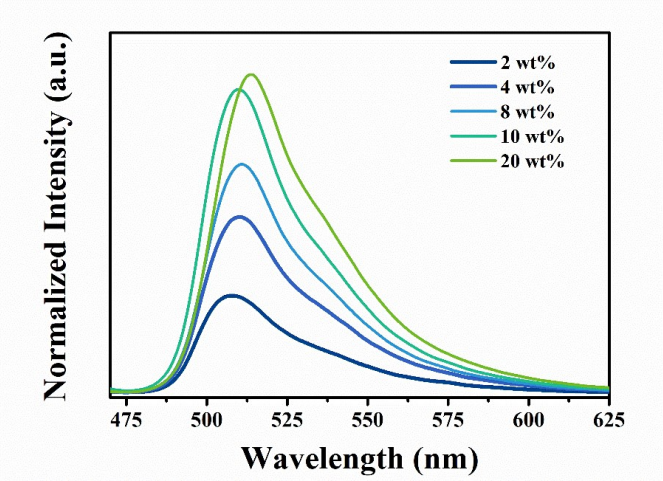

Fig. S13. The emission spectra of ZIF-8⊃pm546 with different concentrations doped in TPU.

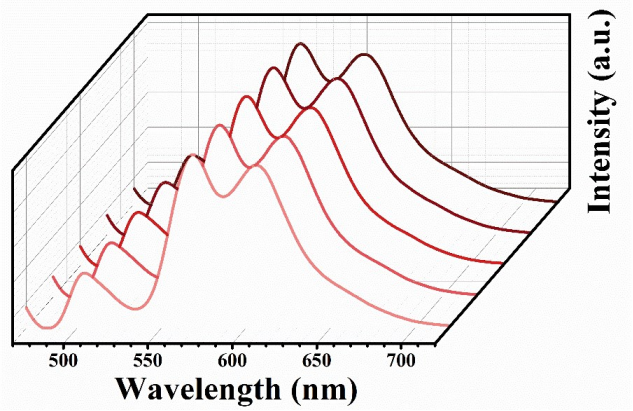

Fig. S14. The emission spectra of ZIF-8⊃pm546/pm605/SRh101 synthesized with same dye concentration but in different batches.

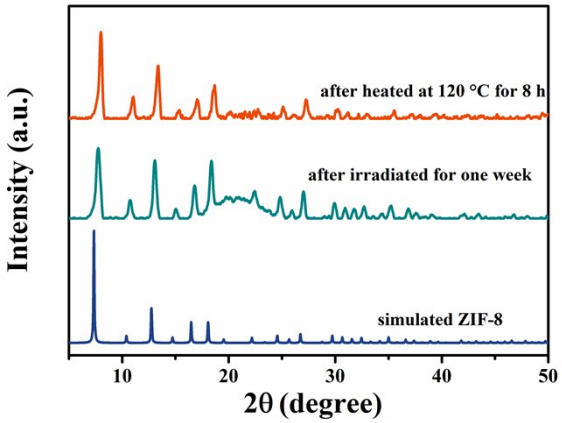

Fig. S15. The PXRD patterns of simulated ZIF-8 and ZIF-8⊃pm546/pm605/SRh101 coated with TPU after irradiated under 460-nm for one week and heated at 120 ℃ for 8 h, respectively.

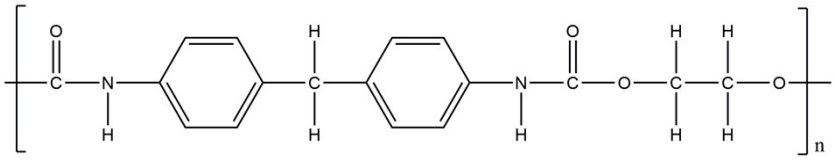

Fig. S16. The molecular structure diagram of TPU polymer.

Table S1 Data of quantum yields of ZIF-8⊃pm546 with different contents of pm546, excited at 460 nm.

Sample	Quantum Yield (%)
ZIF-8⊃pm546 (0.00264 wt% pm546)	74.0 %
ZIF-8⊃pm546 (0.00528 wt% pm546)	81.5 %
ZIF-8⊃pm546 (0.00792 wt% pm546)	80.5 %
ZIF-8⊃pm546 (0.01057 wt% pm546)	79.8 %
ZIF-8⊃pm546 (0.01585 wt% pm546)	74.0 %

Table S2. Data of quantum yields of ZIF-8⊃pm605 with different contents of pm605, excited at 540 nm.

Sample	Quantum Yield (%)
ZIF-8⊃pm605 (0.0094 wt% pm605)	43.0 %
ZIF-8⊃pm605 (0.0187 wt% pm605)	55.0 %
ZIF-8⊃pm605 (0.0468 wt% pm605)	75.4 %
ZIF-8⊃pm605 (0.0702 wt% pm605)	99.1 %
ZIF-8⊃pm605 (0.094 wt% pm605)	85.1 %

Table S3. Data of quantum yields of ZIF-8⊃SRh101 with different contents of pm605, excited at 587 nm.

Sample	Quantum Yield (%)
ZIF-8⊃SRh101 (0.00217 wt% SRh101)	11.2 %
ZIF-8⊃SRh101 (0.00303 wt% SRh101)	17.8 %
ZIF-8⊃SRh101 (0.00477 wt% SRh101)	31.8 %
ZIF-8⊃SRh101 (0.00650 wt% SRh101)	44.2 %
ZIF-8⊃SRh101 (0.0130 wt% SRh101)	38.8 %

Table S4. White-light performance of as-fabricated WLEDs with a series of phosphor

with different dye loadings.

Relative Sample-fabricated WLED	CCT (K)	CRI	CIE coordinates
A (0.013 wt% pm546, 0.084 wt% pm605, 0.003 wt% SRh101)	3577	73	(0.410, 0.412)
B (0.013 wt% pm546, 0.084 wt% pm605, 0.006 wt% SRh101)	2564	75	(0.478, 0.424)
C (0.013 wt% pm546, 0.084 wt% pm605, 0.011 wt% SRh101)	2642	85	(0.465, 0.413)
D (0.013 wt% pm546, 0.084 wt% pm605, 0.014 wt% SRh101)	3182	84	(0.428, 0.407)