Supplementary Information

Excitation-wavelength-dependent Emission of a Luminescent Host-guest Zn(II) Metal-organic Framework for High-performance White LEDs

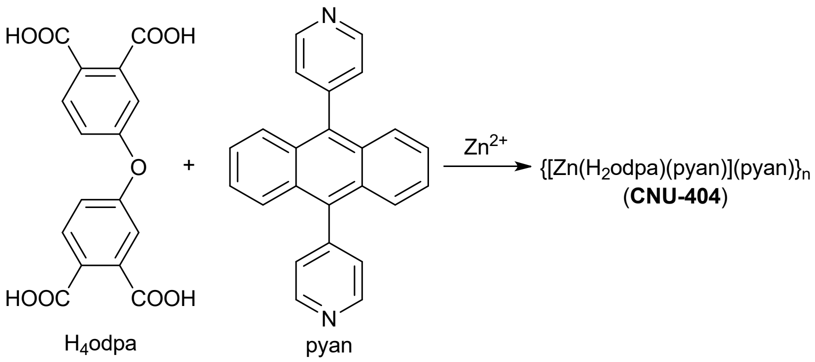
Xiaoqi Feng, Xin Chen, Xinyan Li, Kunlin Huang* and Xi Liu*

College of Chemistry and Materials Science, Chongqing Normal University, Chongqing 401331, P. R. China. E-mail: kunlin@cqnu.edu.cn(K. Huang), xliu@cqnu.edu.cn(X. Liu).

1. Materials and characterizations

All reagents used were purchased from Alfa Aesar, or other commercial vendors and used without further purification. Powder X-ray diffraction (PXRD) patterns were performed on a Lab XRD-6100 diffractometer. Data were collected between 4° and 40° of 2θ with a scan speed of 10.0 deg/min. Elemental analyses for C, H, and N were carried out on a Perkin-Elmer 2400 elemental analyzer. Thermogravimetric analysis (TGA) data were recorded on a HENVEN-HJ HCT-3 Analyzer with a temperature ramping rate of 10 ° C/min from RT to 800 ° C under nitrogen atmosphere. The IR spectrum was recorded in the range of 4000-400 cm^{-1} on a PerkinElmer FT-IR Spectrometer with KBr pellets. UV-Vis measurement was performed on an Agilent Cary 5000 UV-Vis-NIR spectrophotometer. Photoluminescence measurement was conducted with an Edinburgh FLS1000 unit and internal quantum yield was evaluated by a Hamamatsu Photonics K.K. analyzer. Single-crystal X-ray diffraction data were collected at 296 K on a Bruker APEX-II CCD diffractometer using mirror optics monochromated Mo *K*α radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined by full matrix least-squares on F^2 using the Bruker SHELXTL package.

2. Synthesis of {[Zn(H_2odpa)(pyan)](pyan)}$_n$(**CNU-404**)



Scheme S1 The synthesis route of Zn(II)-MOF(**CNU-404**)

A mixed solution of CH_3CN (1 mL) and H_2O (9 mL) containing $Zn(NO_3)_2·6H_2O$ (0.1 mmol), 3,3’,4,4’-oxydiphthalic acid (H_4odpa, 0.1 mmol) and 9,10-bis(4-pyridyl)anthracene (pyan, 0.1 mmol) was sealed in a reactor of 25 mL and heated at 120ºC for 72 h, then cooled at to room temperature. The crystals were washed with distilled water to give compound **CNU-404** with 70% yield based on the usage of pyan. Element analysis for $C_{64}H_{40}N_4O_9Zn$ (%), Calcd: C 71.55, H 3.75, N 5.21; found: C 71.58, H 3.72, N 5.20. FT-IR(KBr,cm^{-1}):3062(w),2892(w),1698(m), 1598(s),1367(vs),1250(vs),1065(s),1002 (m), 811(vs),769(vs),669(s),644(vs).

3.Fabrication of WLED prototypes

Tri-color phosphor **CNU-404** and commercial red phosphor N630 [(Ca,Sr)$AlSiN_3$:Eu^{2+}] were separately mixed with a stoichiometric amount of the encapsulant (LD-800) and stirred for approximately 5 minutes. The resulting uniform phosphor paste was then carefully dispensed onto InGaN blue chips (chip-1: $\lambda_{em,max}$ = 433 nm; chip-2: $\lambda_{em,max}$ = 444 nm). The mass ratios of phosphor **CNU-404** to red phosphor N630 were approximately 6:1 for prototype WLED-1 (fabricated with chip-1), and 8:1 for WLED-2 (chip-1) and WLED-3 (chip-2), respectively. The assembled devices were subsequently cured at 100 °C for 1 hour to form the final WLED prototypes. All devices were operated under a forward bias current ranging from 10 to 300 mA.

4. Supplementary Figures

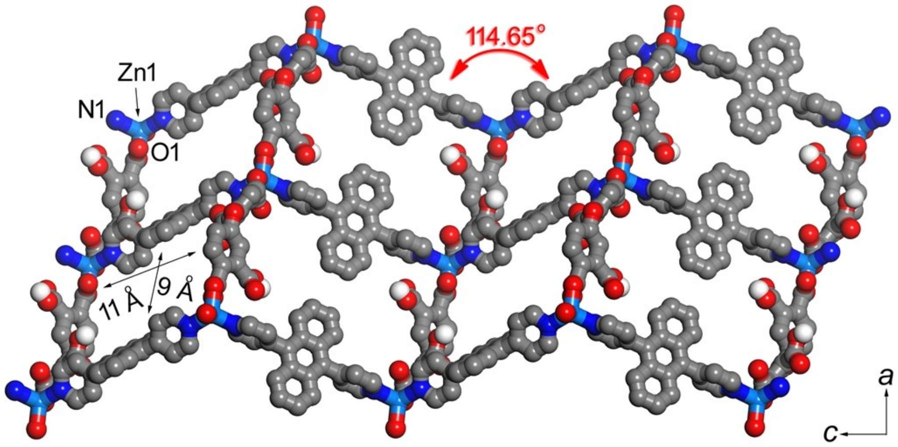


Fig.S1 View of the wave-type 4-connected 2D coordination polymeric layer composed of $[Zn(H_2odpa)(pyan)]_n$.

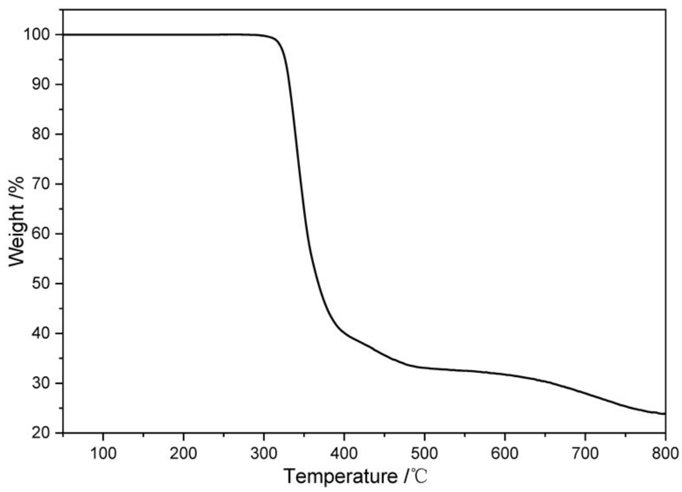


Fig.S2 TGA profile of compound **CNU-404** under N_2 atmosphere.

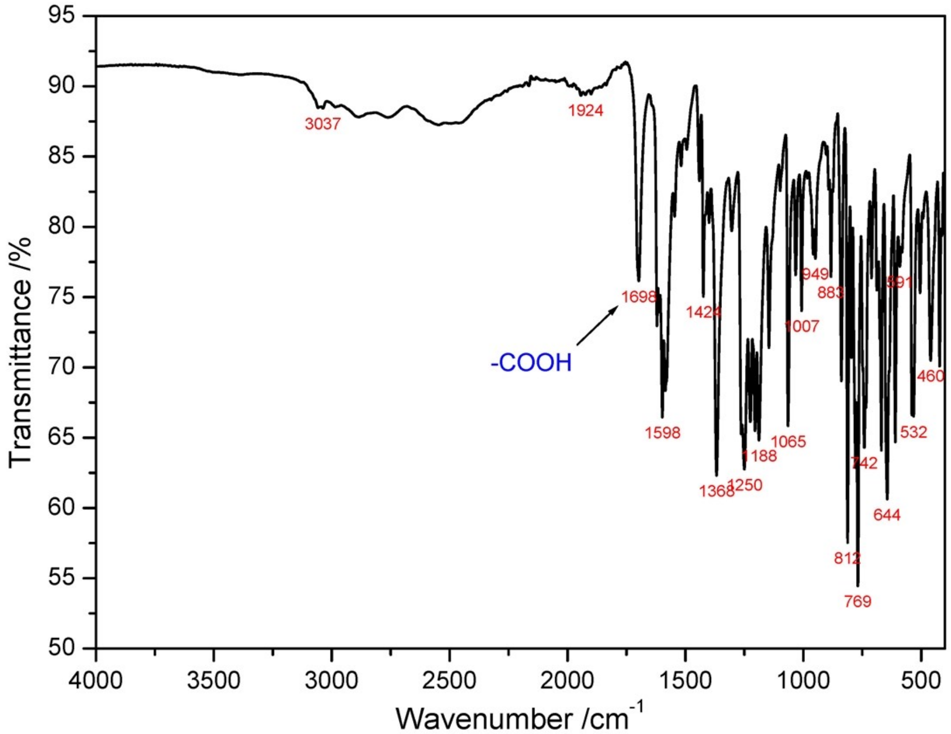


Fig.S3 Fourier-transform infrared spectrum of **CNU-404**.

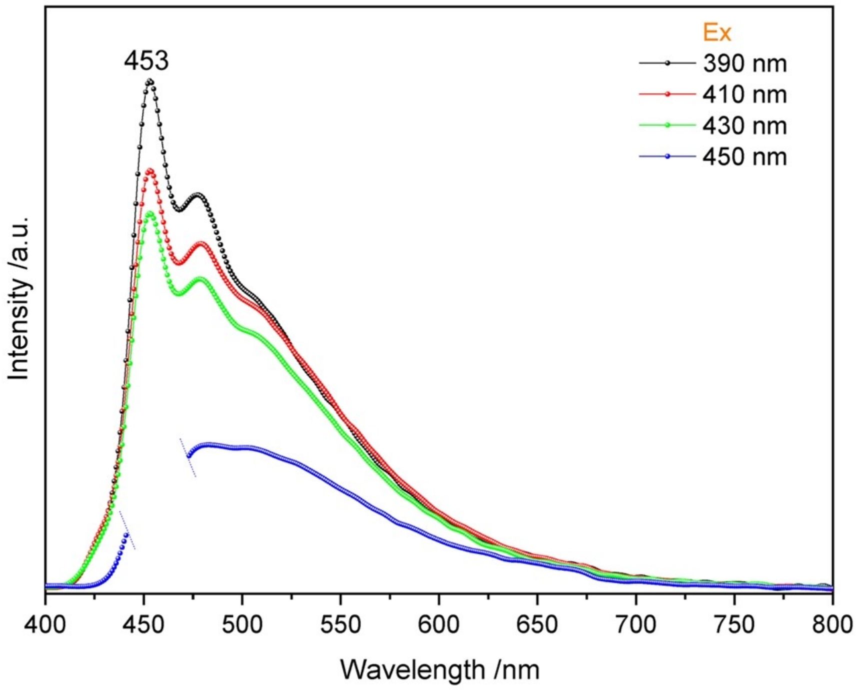


Fig.S4 Emission spectra of free pyan upon excitation in the range of 390-450 nm in solid state measured at room temperature.

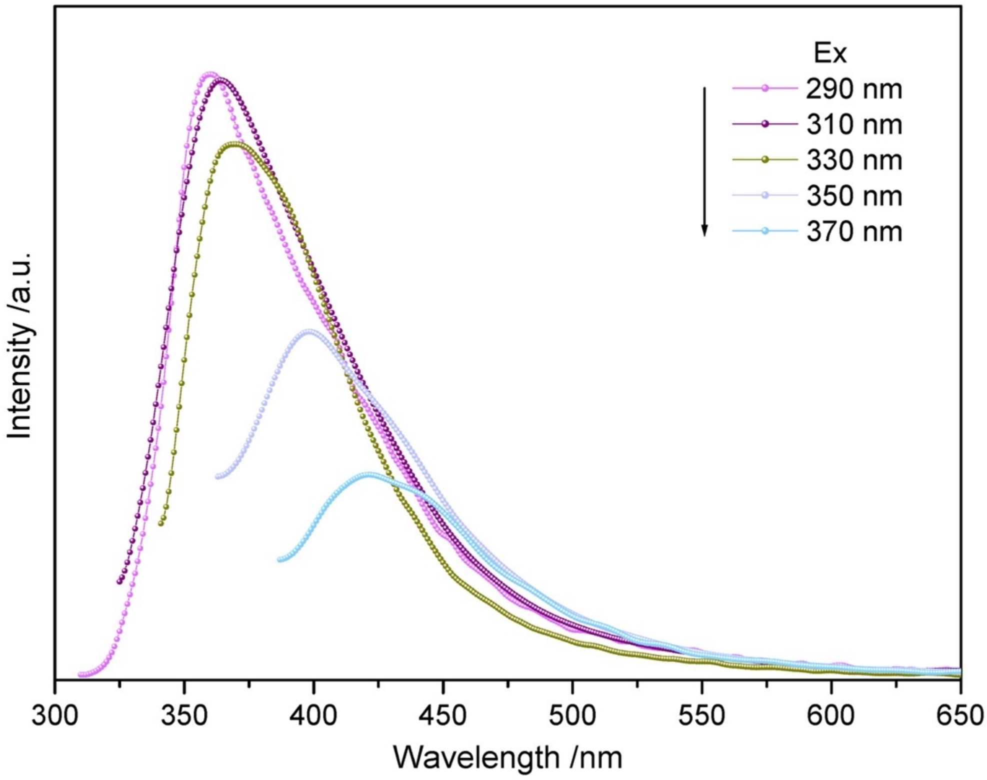


Fig.S5 Emission spectra of free H_4odpa upon excitation in the range of 290-370 nm in solid state measured at room temperature.

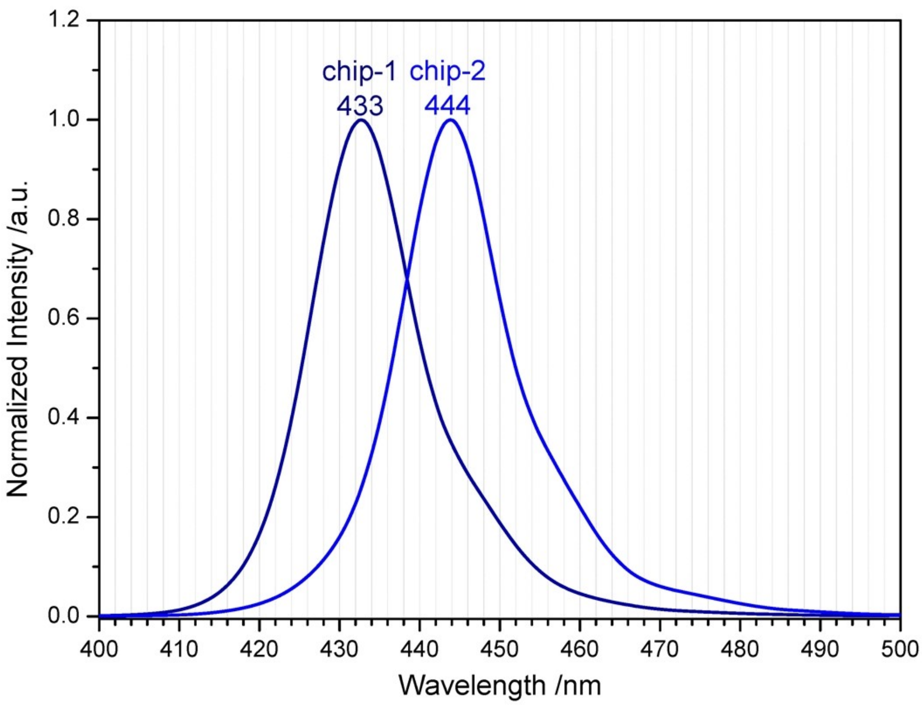


Fig. S6 Emission spectra of free InGaN blue LED chip-1 and chip-2.

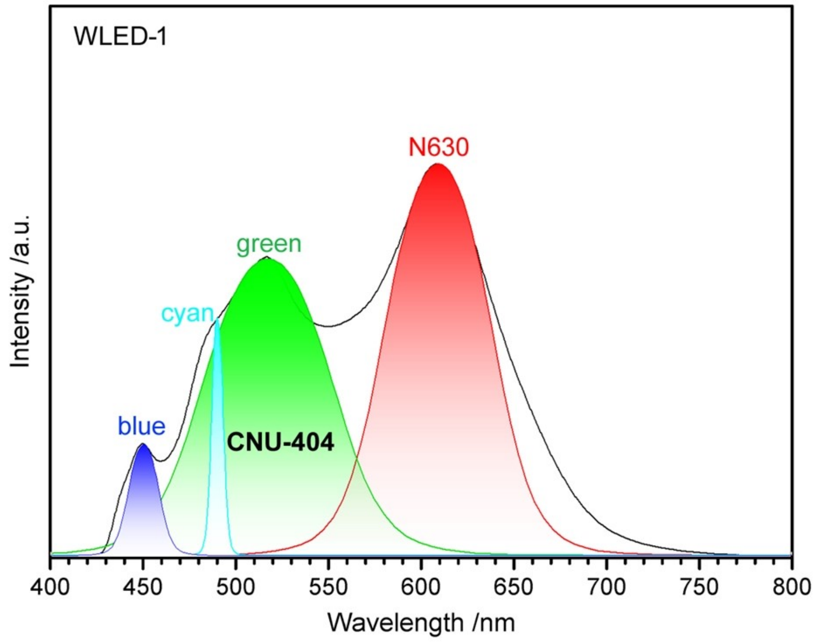


Fig. S7 Deduction of the potential blue-cyan-green tri-color emission of phosphor **CNU-404** from the emission spectrum of WLED-1 *via* Gaussian fitting.

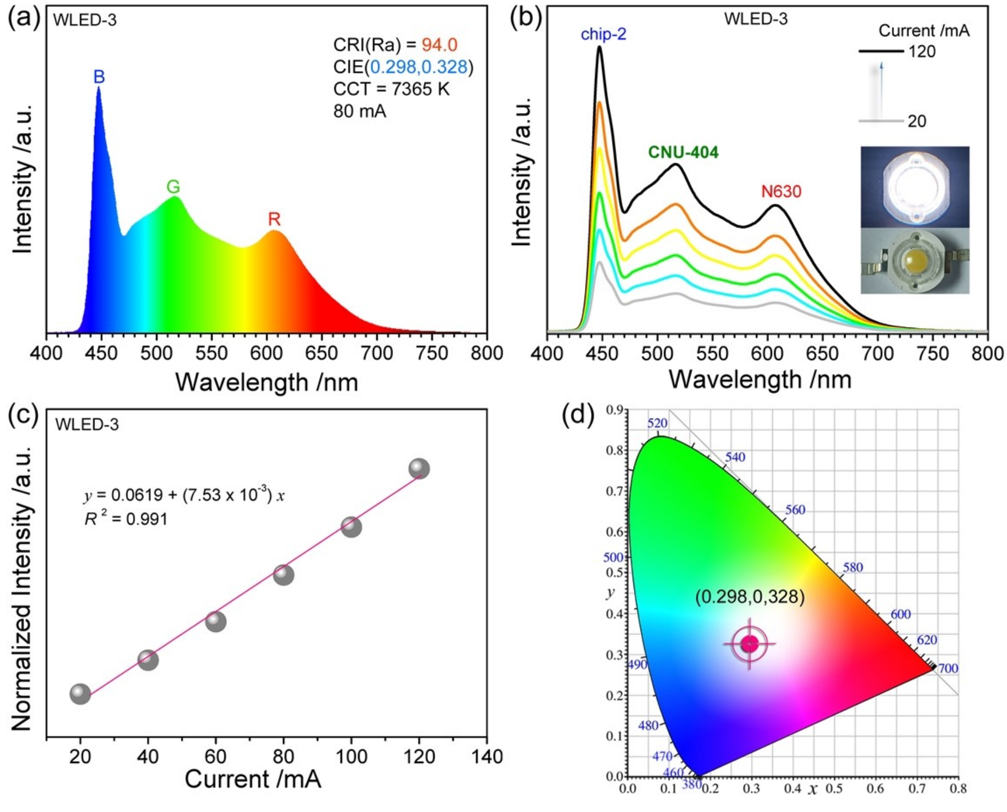


Fig. S8 (a) Emission spectrum of prototype WLED-3 with the InGaN blue chip-2 at a driving current of 80 mA. (b) Emission spectra of prototype WLED-3 under different driving currents; inset: operating photograph of WLED-3 at a driving current of 20 mA. (c) Emission intensity as a function of driving current for prototype WLED-3. (d) 1931 CIE chromaticity diagram showing the corresponding chromaticity coordinates of (0.298, 0.327).

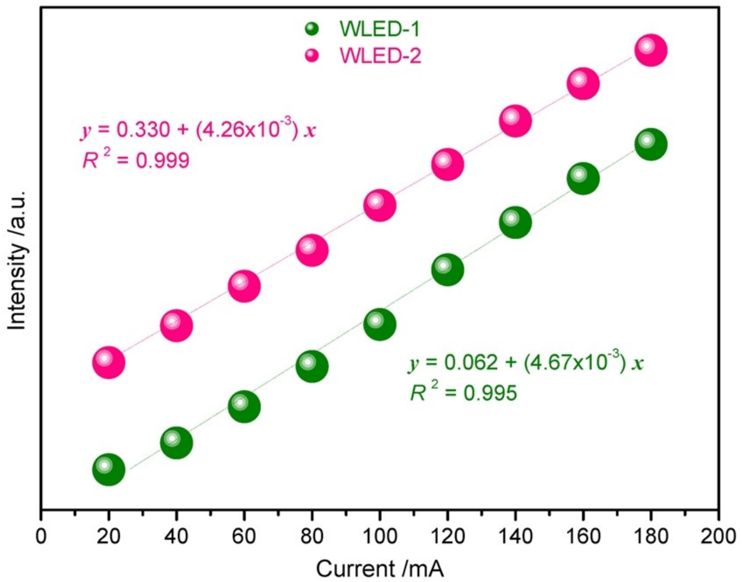


Fig. S9 The emission intensity of prototype WLED-1 and WLED-2 as a function of applied driving current, demonstrating the linear response of the devices to current variation.

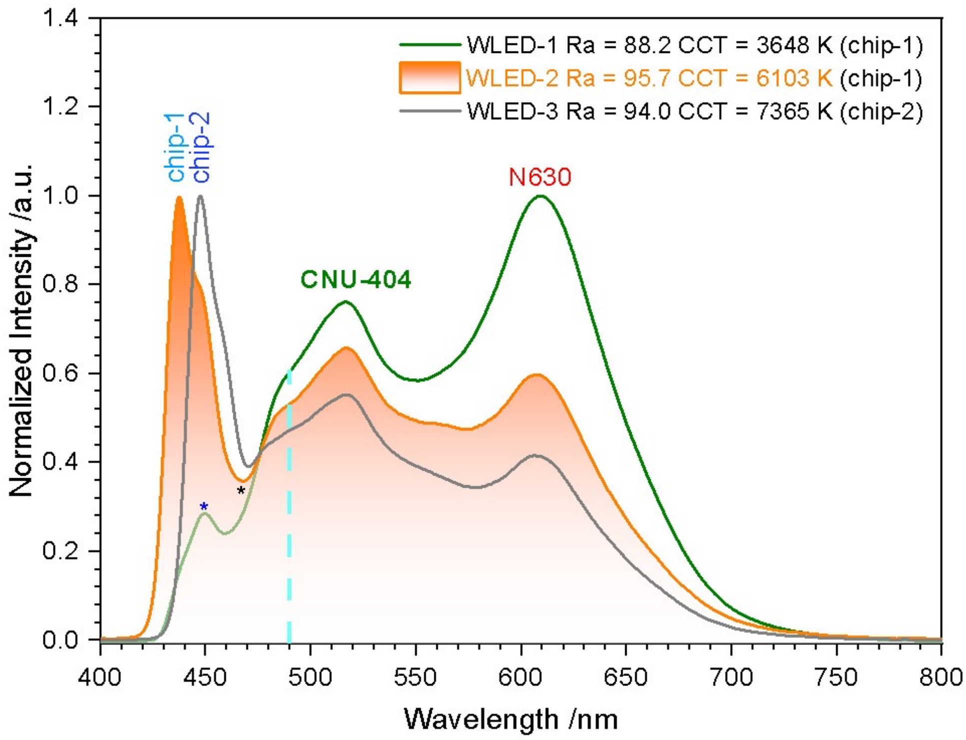


Fig. S10 Emission spectra summary for the three WLED prototype devices.

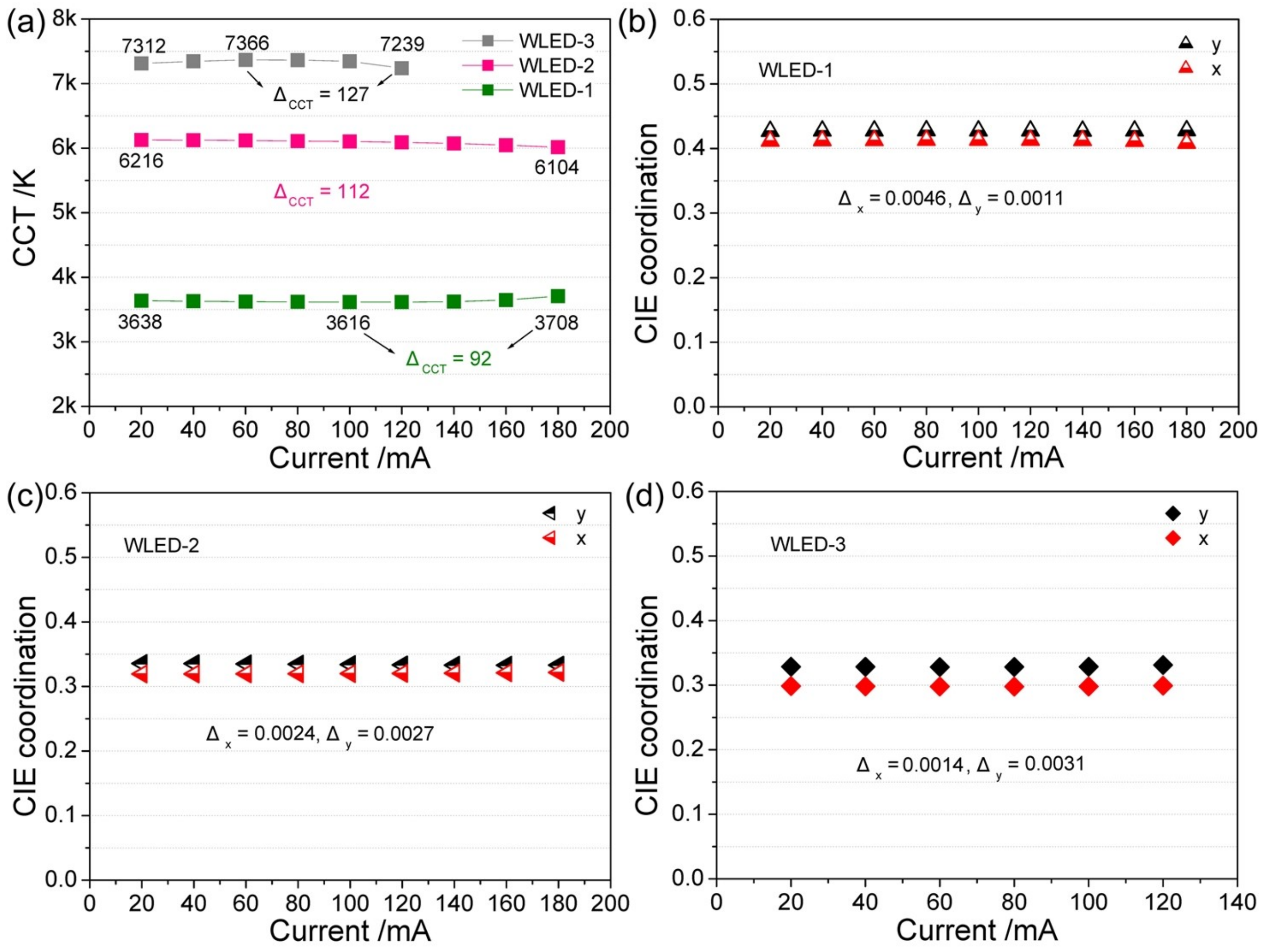


Fig. S11 (a) CCT values for three prototype WLED devices under varying driving currents ranging from 20-180 mA and 20-120 mA, demonstrating excellent color stability. (b)-(d) Corresponding CIE coordinate variations of these WLEDs under different operating currents.

5. Supplementary Tables

Table S1 Crystallographic data for **CNU-404**.

Crystallographic data	**CNU-404** (CCDC No. 2519391)
Formula	$C_{64}H_{40}N_4O_9Zn$
Formula weight	1074.39
Temperature /K	296
Wavelength /Å	0.71073
Crystal system	Monoclinic
Space group	*P*2/*c*
a /Å	15.1823 (7)
b /Å	6.5451(3)
c /Å	25.8783(13)
α /°	90
β /°	99.655(2)
γ /°	90
V / Å^3	2535.1(2)
ρ_{calc} g/cm^3	1.408

$F(000)$	1108.0
Z	2
μ /mm^{-1}	0.552
GOOF	1.004
Final R indices [$I>2\sigma(I)$]*	$R_1 = 0.0281$, $wR_2 = 0.0823$
Final R indices (all data)	$R_1 = 0.0327$, $wR_2 = 0.1025$
Largest diff. peak and hole/e.Å^{-3}	0.277 , -0.516

* $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma_w(F_o^2-F_c^2)^2/\Sigma_w(F_o^2)^2]^{1/2}$

Table S2 Selected bond lengths (Å) and angles (deg) for **CNU-404**.

Bond lengths (Å)		Bond angles (deg)	
Zn1-O1	1.9632(15)	O1-Zn1-O1$^{\#1}$	101.26(9)
Zn1-N1	2.0239(16)	O1-Zn1-N1	105.54(7)
Hydrogen bond		O1$^{\#1}$-Zn1-N1	117.34(7)
O4····N2	2.709	N1-Zn1-N1$^{\#1}$	110.06(10)

Symmetry transformations used to generate equivalent atoms in **CNU-404**:
#1 -x+1,y,-z+3/2,z

Table S3 CIE coordinates corresponding to emission spectra of **CNU-404** upon excitation at different wavelengths

Ex /nm	410	420	430	440	450	460
CIE(x,y)	(0.185,0.200)	(0.188,0.217)	(0.224,0.329)	(0.290,0.502)	(0.329.0.551)	(0.350,0.564)
$\lambda_{em,max}$	447	447	450	519	525	529

Table S4 Representative of MOF-based phosphors for high-performance pc-WLEDs.

MOF-based phosphors	QY	Chip/nm	CRI(Ra)	CCT/K	Reference
{[Zn(H_2odpa)(pyan)](pyan)}$_n$	31.18%	433/444	95.7 94 88.2	6103 7365 3648	This work
[$CdCl_2$(AD)]$_n$	65%	460	81.1	6821	*Chem. Sci.*, 2024, **15**, 14202-14208 https://doi.org/10.1039/d4sc04228j
pm567A/SRh101/$CsPbClBr_2$-SiO_2@ZIF-8	70%	460	88 87	4350 6148	*J. Mater. Chem. C* ., 2024,**12**, 1047-1054 https://doi.org/10.1039/d3tc03610c
Zn-TPPA	92.7%	460	66	-	*Adv. Optical Mater.* 2022,**10**, 2101461 https://doi.org/10.1002/adom.202101461
R6G/R101@ ZJU-28	82.9%	460	88	4446	*Adv. Optical Mater.*, 2018, **6**, 1800968. https://doi.org/10.1002/adom.201800968
Eu-MOF	10.46%	365	86.9	5620	*Inorg. Chem.*, 2025, **64**,17313-17321 https://doi.org/10.1021/acs.inorgchem.5c02457
[Cd(5-BIPA)(phen)]$_n$	28%	365	77	7813	*Inorg. Chem.* , 2023,**62**,19389-19394 https://doi.org/10.1021/acs.inorgchem.3c03348
$CsGeBr_3$@Eu-MOF	-	290-330	92	3020	*Chem. Eng. J.*, 2023, **470**, 144160 https://doi.org/10.1016/j.cej.2023.144160
AIEgens@MOF	64.9%	395	86	4076	*Adv. Optical Mater.*, 2022,2200174 https://doi.org/10.1002/adom.202200174
AF/BR@BUT-119	22%	360	94	5284	*ACS Materials Lett.*, 2022, **4**, 2345-2351 https://doi.org/10.1021/acsmaterialslett.2c00558
TMOF-5(Br)	1.5%	380	89	4258	*Angew. Chem.Int. Ed.*, 2019,**131**, 7818-7822 https://doi.org/10.1002/anie.201903665

CDs-3@Ln-MOF	12%	370	93	5443	*ACS Appl. Mater. Interfaces*, 2019, **11**, 44421. https://doi.org/10.1021/acsami.9b13814
Dye@MOF	39.4%	365	91	6186	*Inorg. Chem. Front.*, 2018,**5**, 2868-2874 https://doi.org/10.1039/C8QI00747K
DCM/C6a/CBS-127@ HSB-W1	26%	365	90	6638	*Adv. Mater.*, 2017, **29**, 1700778 https://doi.org/10.1002/adma.201700778
$CdSe_xS_{1-x}$/ZnS @ZIF-8	86%	405	90	5600	*ChemSusChem*, 2017, **10**, 1346-1350. https://doi.org/10.1002/cssc.201700223
DSM/AF@ZJU-28	31-59%	365	91	5327	*Adv.Funct. Mater.*, 2015, **25**, 4796-4802. https://doi.org/10.1002/adfm.201501756

Table S5 CCT and CIE coordinates of the three WLED devices at various driving currents in this work.

Current/mA	WLED-1		WLED-2		WLED-3	
	CCT/K	CIE(x,y)	CCT/K	CIE(x,y)	CCT/K	CIE(x,y)
20	3638	(0.4116,0.4267)	6126	(0.3193,0.3356)	7312	(0.2986,0.3286)
40	3629	(0.4123,0.4273)	6124	(0.3193,0.3354)	7345	(0.2981,0.3284)
60	3624	(0.4125,0.4275)	6120	(0.3195,0.3349)	7366	(0.2979,0.3280)
80	3619	(0.4129,0.4277)	6110	(0.3197,0.3345)	7365	(0.2978,0.3283)
100	3616	(0.4130,0.4274)	6103	(0.3199,0.3340)	7345	(0.2980,0.3286)
120	3617	(0.4129,0.4274)	6091	(0.3202,0.3334)	7239	(0.2992,0.3311)
140	3622	(0.4125,0.4271)	6072	(0.3206,0.3330)		
160	3648	(0.4112,0.4273)	6047	(0.3211,0.3329)		
180	3708	(0.4084,0.4278)	6014	(0.3217,0.3331)		
Maximum shift	Δ_{CCT} = 92	Δ_x = 0.0046 Δ_y = 0.0011	Δ_{CCT} = 112	Δ_x = 0.0024 Δ_y = 0.0027	Δ_{CCT} = 127	Δ_x = 0.0014 Δ_y = 0.0031

Table S6 Maximum shifts in CCT and CIE coordinates of representative WLEDs at various driving currents reported in the literature.

Current/mA	Δ_{CCT}/K	Δ_x	Δ_y	Reference
20-200	232	0.0088	0.0081	*Inorg. Chem.,* 2023, **62**, 19573-19581 https://doi.org/10.1021/acs.inorgchem.3c02888
20-100	1023	0.0207	0.0157	*J. Mater. Chem. C*, 2022, **10**, 5905-5913 https://doi.org/10.1039/D2TC00355D
20-100	1566	0.0308	0.0247	*J. Phys. Chem. Lett.*, 2022, **13**, 198-207 https://doi.org/10.1021/acs.jpclett.1c03649