Electronic Supplementary Information for

RGB tri-luminescence in organic-inorganic zirconium halide perovskites

Chuying Wang[a], Wen Meng[a], Guigen Luo[a], Guangyong Xu[a], Min Peng[a], Bin Xu[a], Shuming Nie[b] and Zhengtao Deng[a]*

a. College of Engineering and Applied Sciences, State Key Laboratory of Analytical Chemistry for Life Science, National Laboratory of Micro-structures, Nanjing University, Nanjing, Jiangsu, 210023, P. R. China.

b. Departments of Bioengineering, Chemistry, Electrical and Computer Engineering, and Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, 61801, USA

*E-mail: dengz@nju.edu.cn

Table S1 The fitting results of the PL decay curves of red, green and blue, $((C_2H_5)_4N)_2ZrCl_6$ powders under different irradiation.

Sample	Blue powder			Red powder									Green powder		
Excitation (nm)	254			254		310		320		340		350	254		310
Emission (nm)	500 (77 K)	500 (273 K)	500 (300 K)	500	620	500	620	500	620	500	620	620	500	527	527
A_1	47.1	102.9	106.8	92.6	107.3	117.3	106.4	129.8	100.2	120.0	422.9	108.5	97.8	98.4	110.0
A_1%	19.0	95.9	100	96.2	100.0	68.9	100.0	68.3	100.0	52.6	100.0	100.0	93.3	92.2	71.2
τ_1 (μs)	38.6	4.1	3.9	4.6	4.9	1.5	7.7	1.6	7.9	1.4	8.6	8.7	4.0	4.1	1.6
A_2	45.2	0.7	/	0.6	/	5.9	/	7.3	/	15.1	/	/	2.1	2.8	3.7
A_2%	81.0	4.1	/	3.8	/	31.1	/	31.7	/	47.4	/	/	6.7	7.8	28.8
τ_2 (μs)	171.9	25.3	/	28.1	/	13.5	/	13.0	/	10.2	/	/	13.5	12.4	19.7
τ_{ave} (μs)	146.7	4.9	3.9	5.5	4.9	5.3	7.7	5.2	7.9	5.6	8.6	8.7	4.7	4.8	6.8

Time-resolved PL decay curves of the perovskite are fitted by single or bi-exponential functions (see Eqs. 1 and 2):

$$A(t)=A_1\exp(-t/\tau_1) \quad \text{(Eqs.1)}$$

$$A(t)=A_1\exp(-t/\tau_1)+A_2\exp(-t/\tau_2) \quad \text{(Eqs.2)}$$

The ratio of lifetimes is calculated using

$$A_i\%=(A_i\tau_i)/(A_1\tau_1+A_2\tau_2) \quad \text{(Eqs.3)}$$

The average lifetimes are calculated using

$$\tau_{ave}=(A_1\tau_1^2+A_2\tau_2^2)/(A_1\tau_1+A_2\tau_2) \quad \text{(Eqs.4)}$$

Table S2 Summary of crystal data and reflection collection parameters.

Empirical formula	$C_{16}H_{40}Cl_6N_2Zr$
Formula weight	564.1134
Crystal system	Monoclinic
Space group	C2/c
a, Å	14.0708(17)
b, Å	14.4783(19)
c, Å	13.253(2)
α, degree	90
β, degree	90.530(5)
γ, degree	90
V, $Å^3$	2699.8(6)
Z	4
ρcalc., g cm^{-3}	1.389
μmm-1	1.006
F000	1159.947
2θ max, deg(Completeness)	50.5(100%)
Total reflections	21777
Unique reflections	3102
Highest peak	0.6652
Deepest hole	-0.4520
R_{int}	0.0535
R_1 [obs I>4σ (I)]	0.0429
R_1 (all data)	0.0527
wR_2	0.1249
Goodness-of-fit on F^2	1.0477

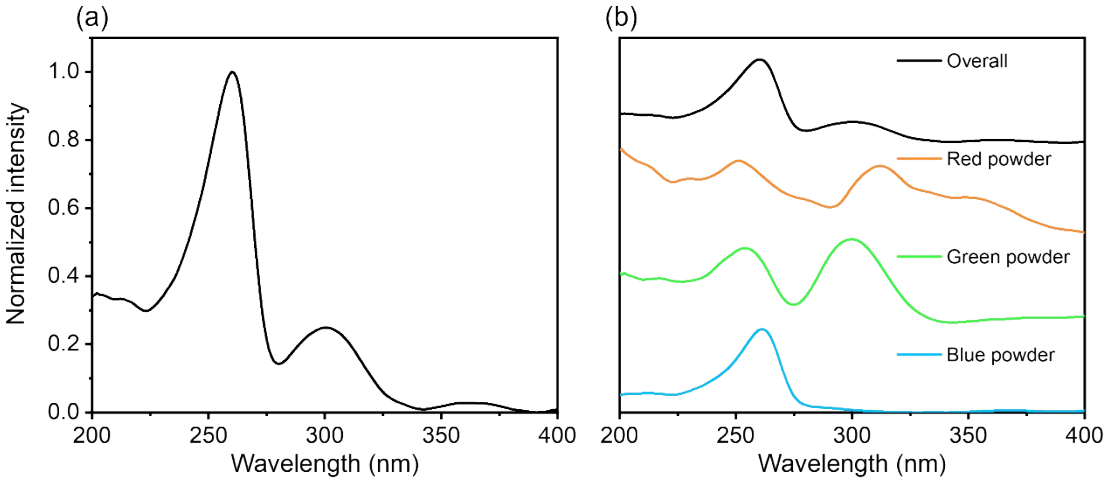

Fig.S1 (a) Overall excitation spectrum of all samples and (b) of blue, green and ren powder samples. The overall excitation is by adding the original excitation in Fig.1b.

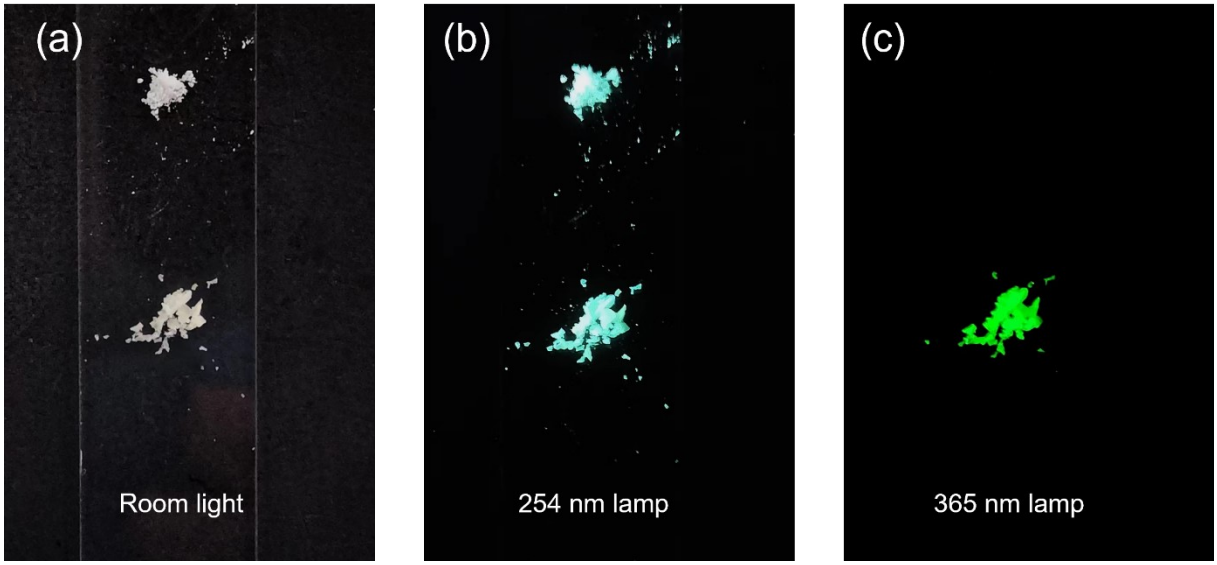

Fig.S2 Photo images under (a) room light, (b) 254 nm lamp and (c) 365 nm lamp of blue and green powder samples.

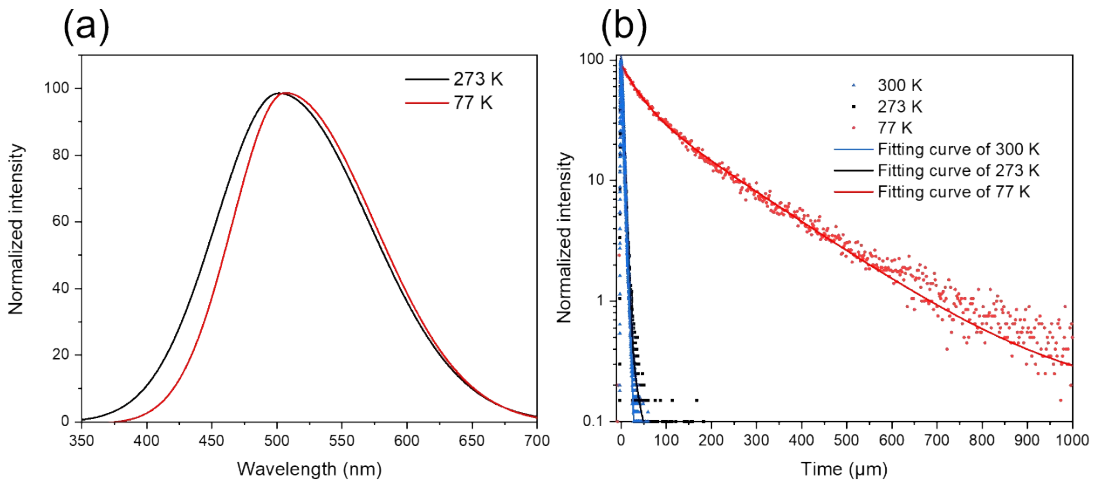

Fig.S3 (a) PL emission spectra and (b) time-resolved photoluminescence spectra of $((C_2H_5)_4N)_2ZrCl_6$ blue samples under different temperature.

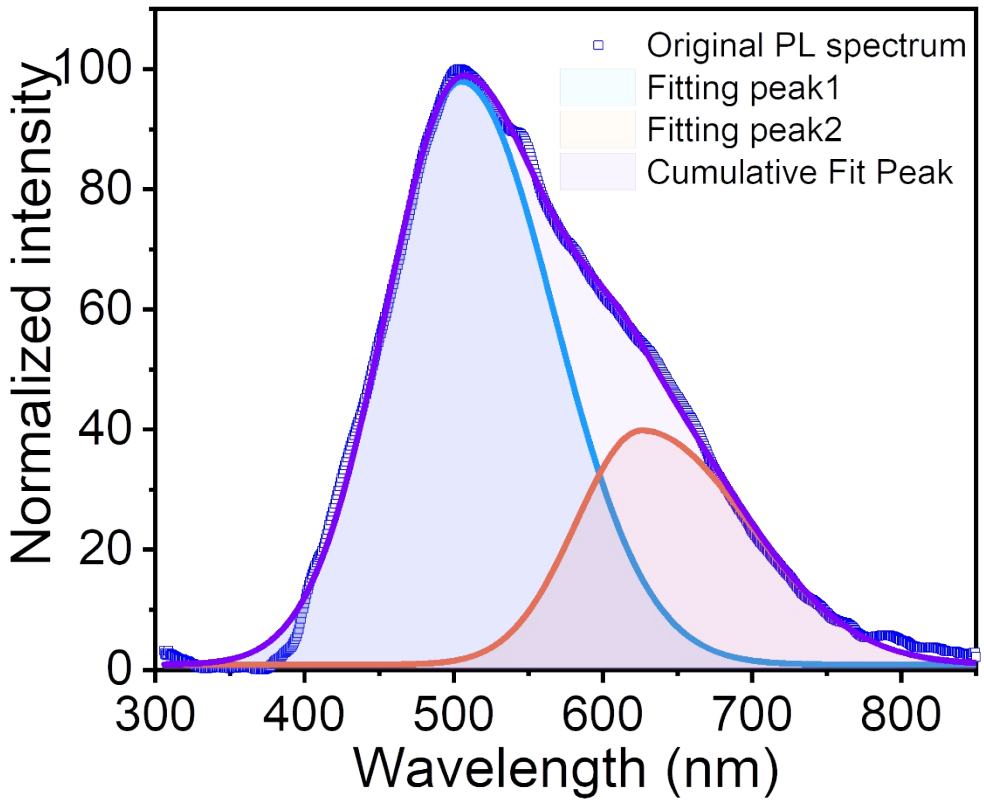

Fig.S4 PL emission spectrum and fitting curves of red $((C_2H_5)_4N)_2ZrCl_6$ powder under excitation at 265 nm.

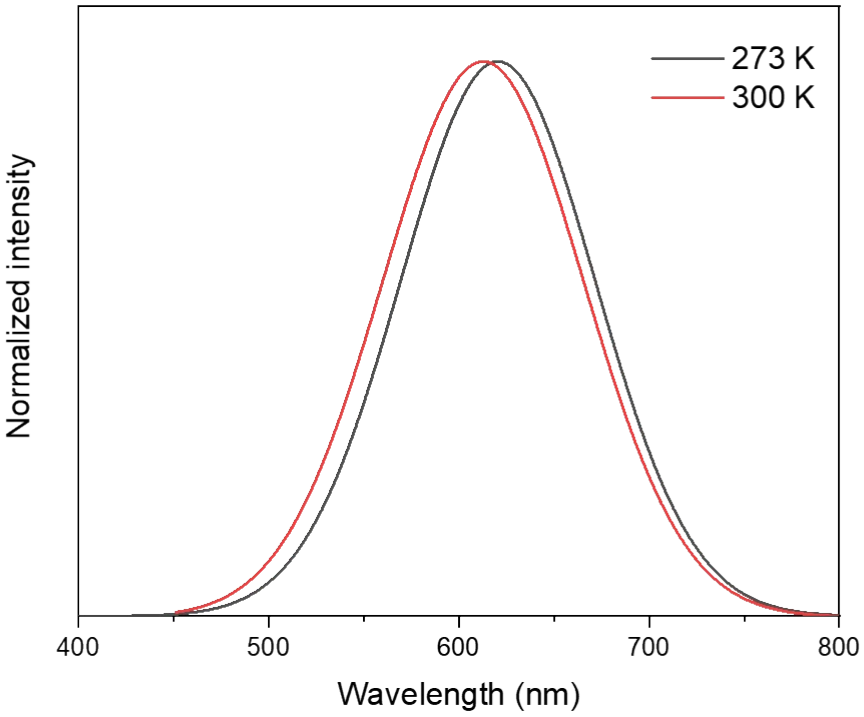

Fig.S5 PL emission spectra of $((C_2H_5)_4N)_2ZrCl_6$ red samples under different temperature at 365 nm lamp.

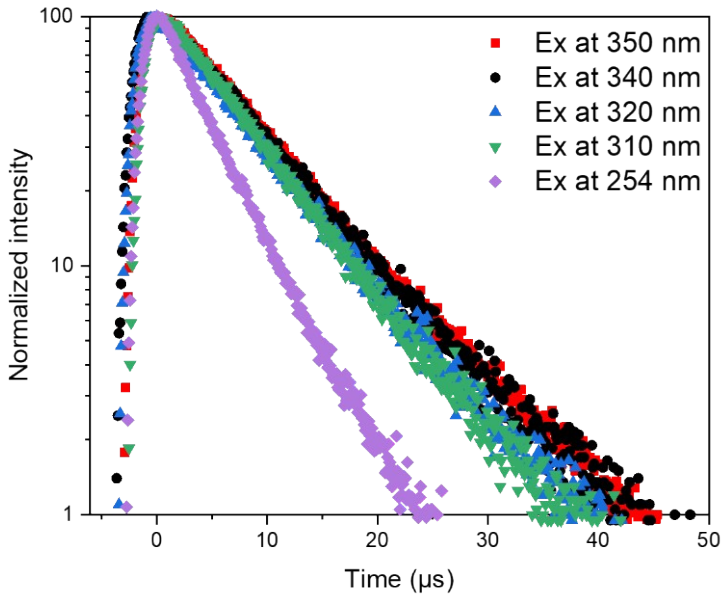

Fig.S6 Time-resolved photoluminescence spectra of $((C_2H_5)_4N)_2ZrCl_6$ red powder samples with different excitation.

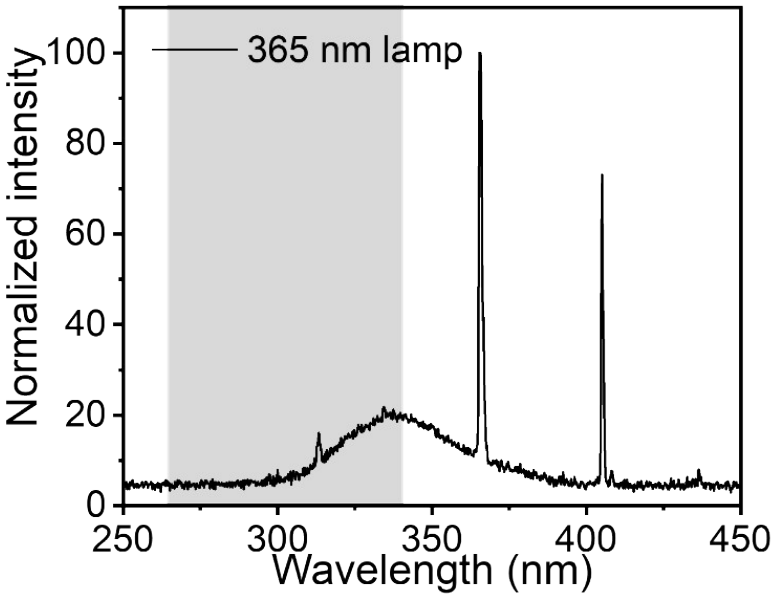

Fig.S7 Spectrum 365 nm lamp.

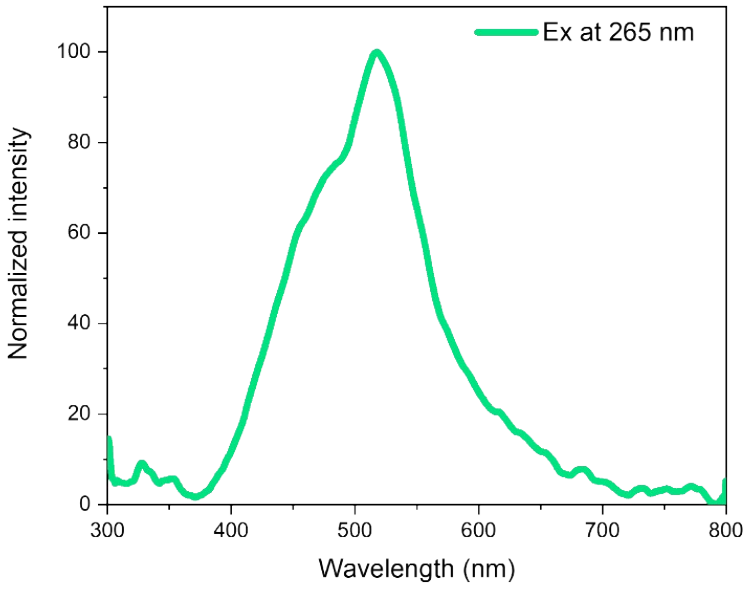

Fig.S8 PL emission spectrum of green $((C_2H_5)_4N)_2ZrCl_6$ powder under excitation at 265 nm.

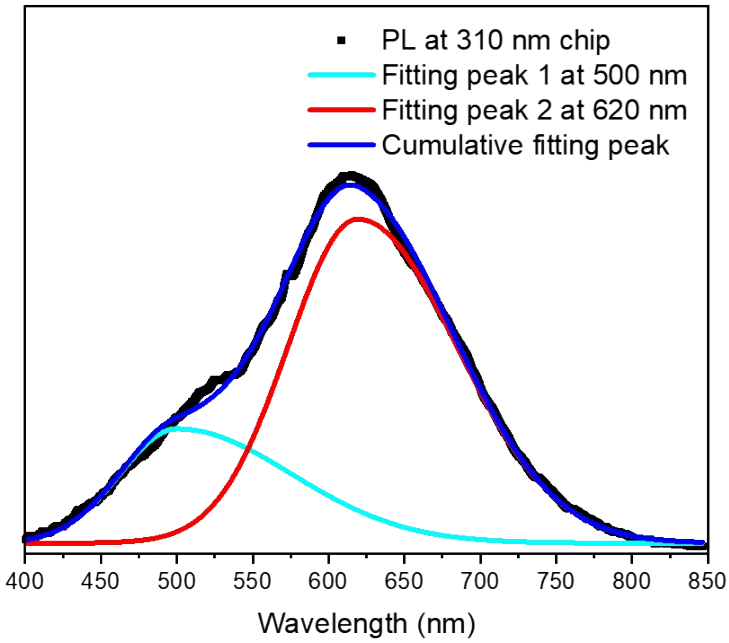

Fig.S9 PL spectrum and fitting curves of red $((C_2H_5)_4N)_2ZrCl_6$ powder on 310 nm chip.

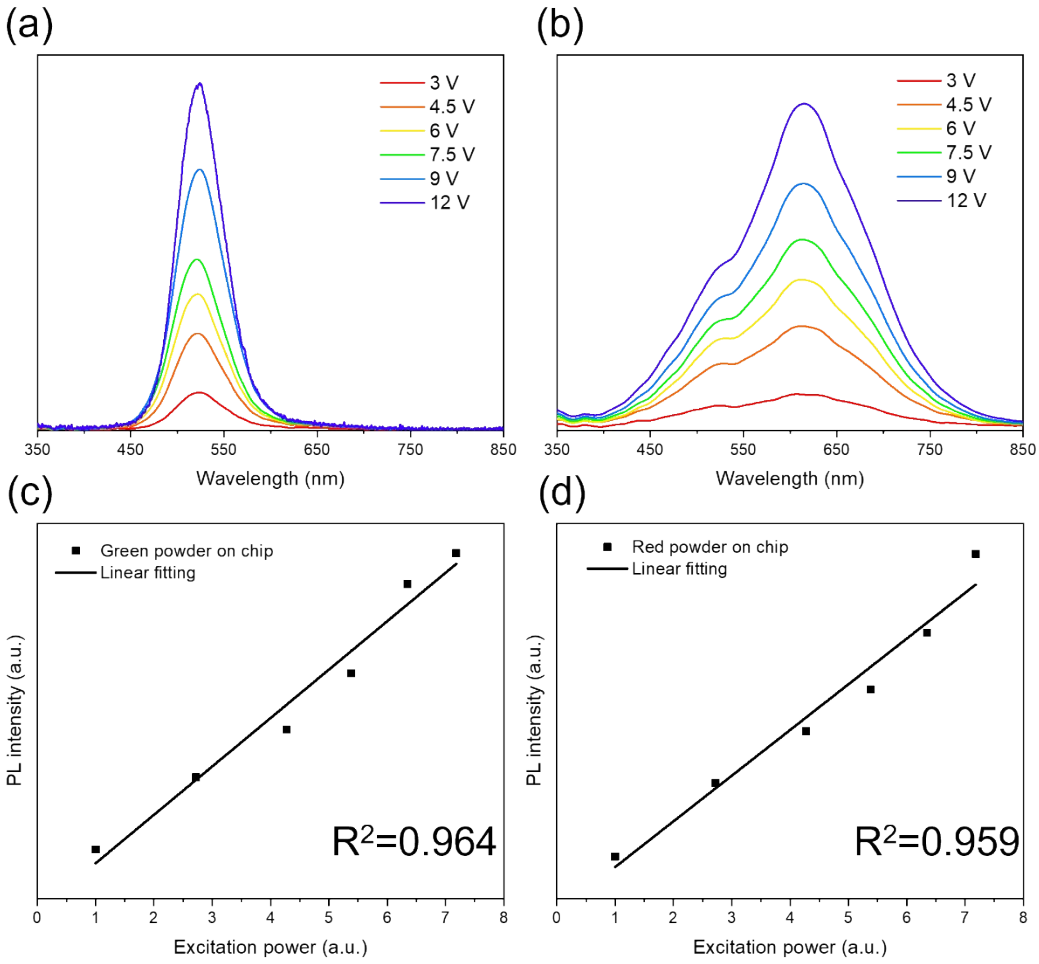

Fig.S10 Relatively power-dependent (driven voltage from 3 V to 12 V) PL spectra of (a) green and (b) red powder samples. Fitting curves of (c) green and (d) red powder samples. The X-axis in (c) and (d) is calculated based on the integrated PL intensity of 310 nm chip under different driving voltage, and divided by integrated PL result at 3 V.

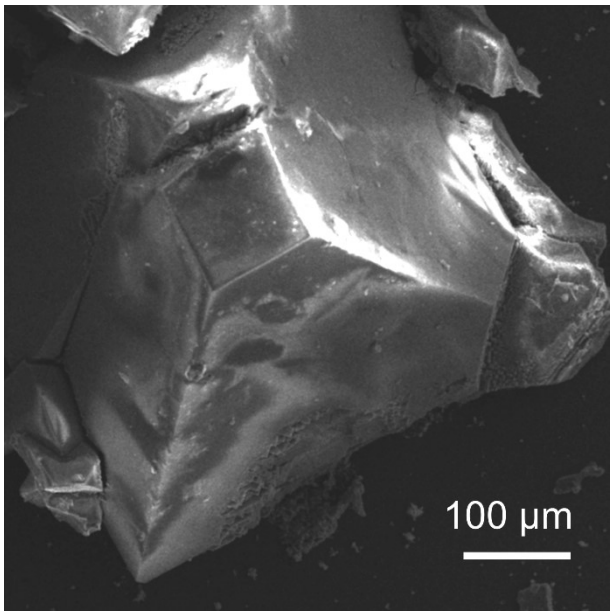

Fig.S11 SEM image of $((C_2H_5)_4N)_2ZrCl_6$ single crystals.

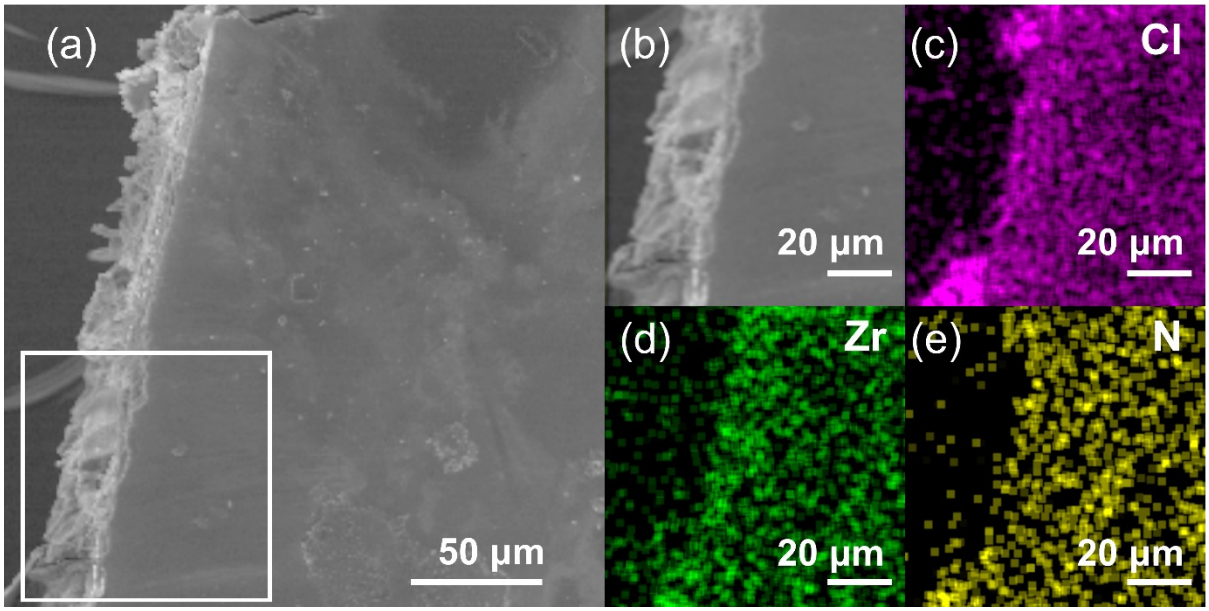

Fig.S12 SEM image and EDS mappings of $((C_2H_5)_4N)_2ZrCl_6$ single crystals.

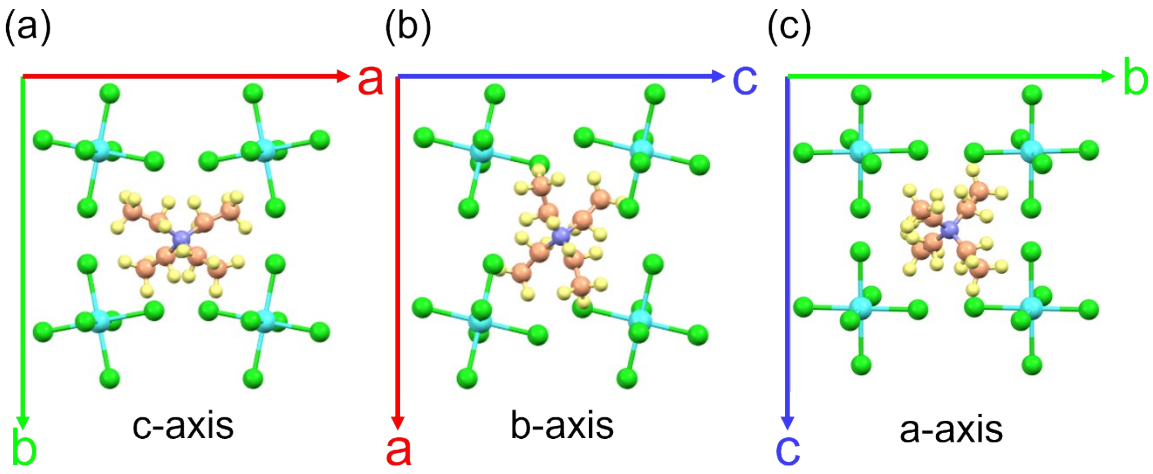

Fig.S13 The crystal structures of $((C_2H_5)_4N)_2ZrCl_6$ viewed along a axis, b axis, and c axis.

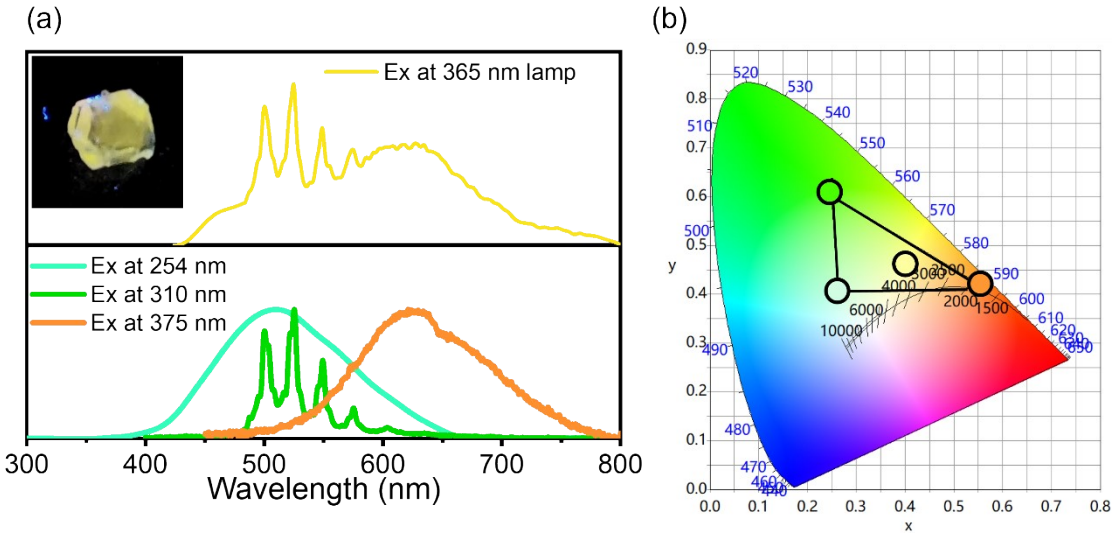

Fig.S14 (a) PL emission spectra and (b) CIE chromaticity diagram of $((C_2H_5)_4N)_2ZrCl_6$ single crystals.

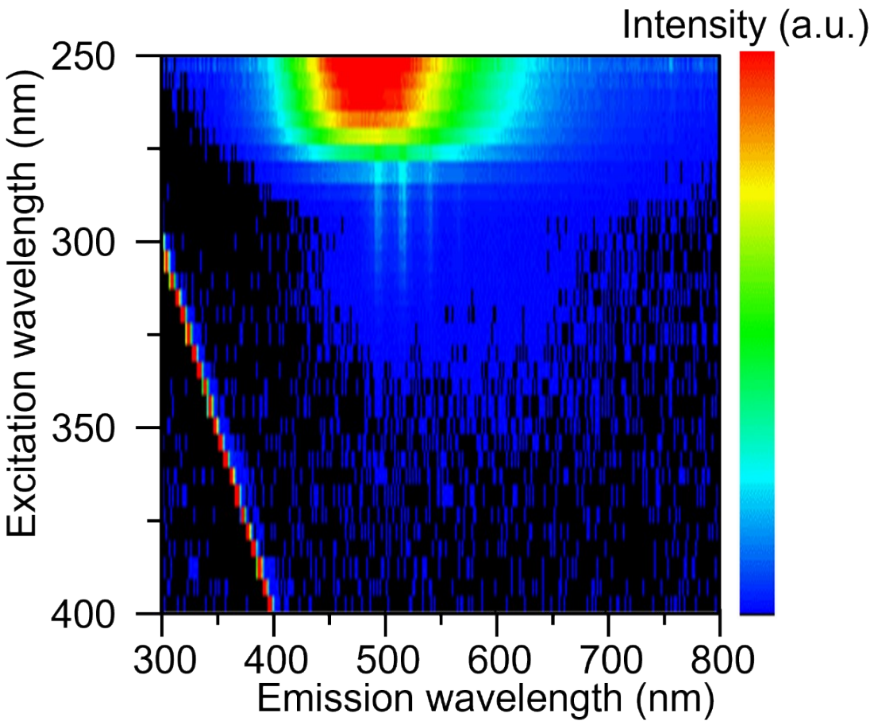

Fig.S15 Three-dimensional excitation-emission matrix (EEM) fluorescence spectra of $((C_2H_5)_4N)_2ZrCl_6$ single crystals.

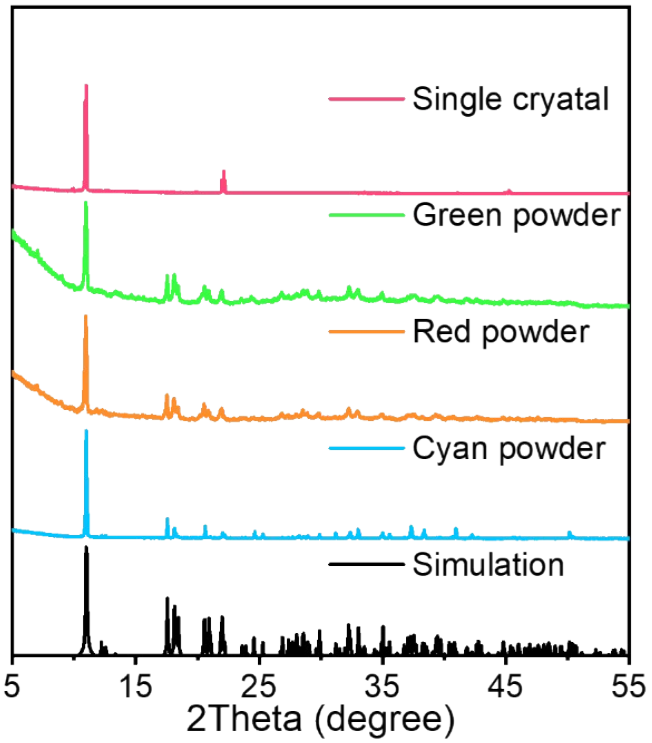

Fig.S16 XRD patterns of $((C_2H_5)_4N)_2ZrCl_6$ samples.

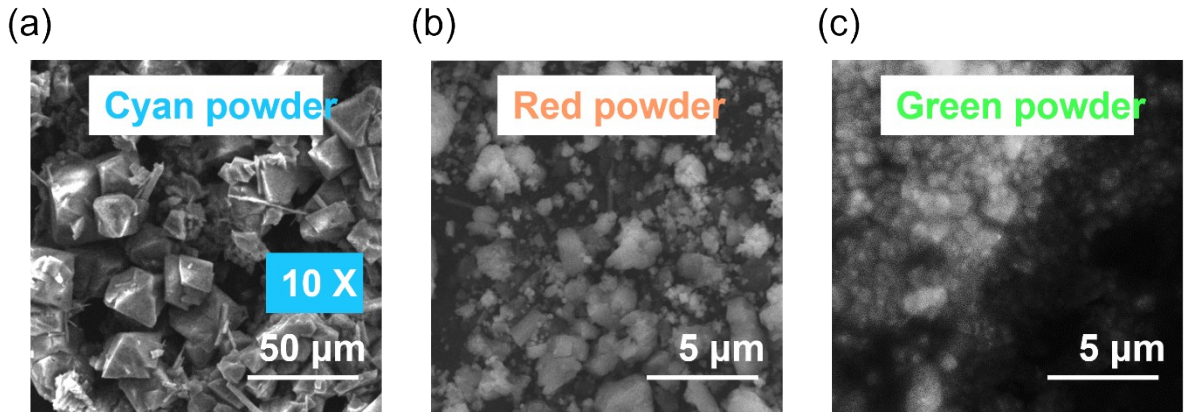

Fig.S17 SEM images of cyan, red and green $((C_2H_5)_4N)_2ZrCl_6$ powder samples.

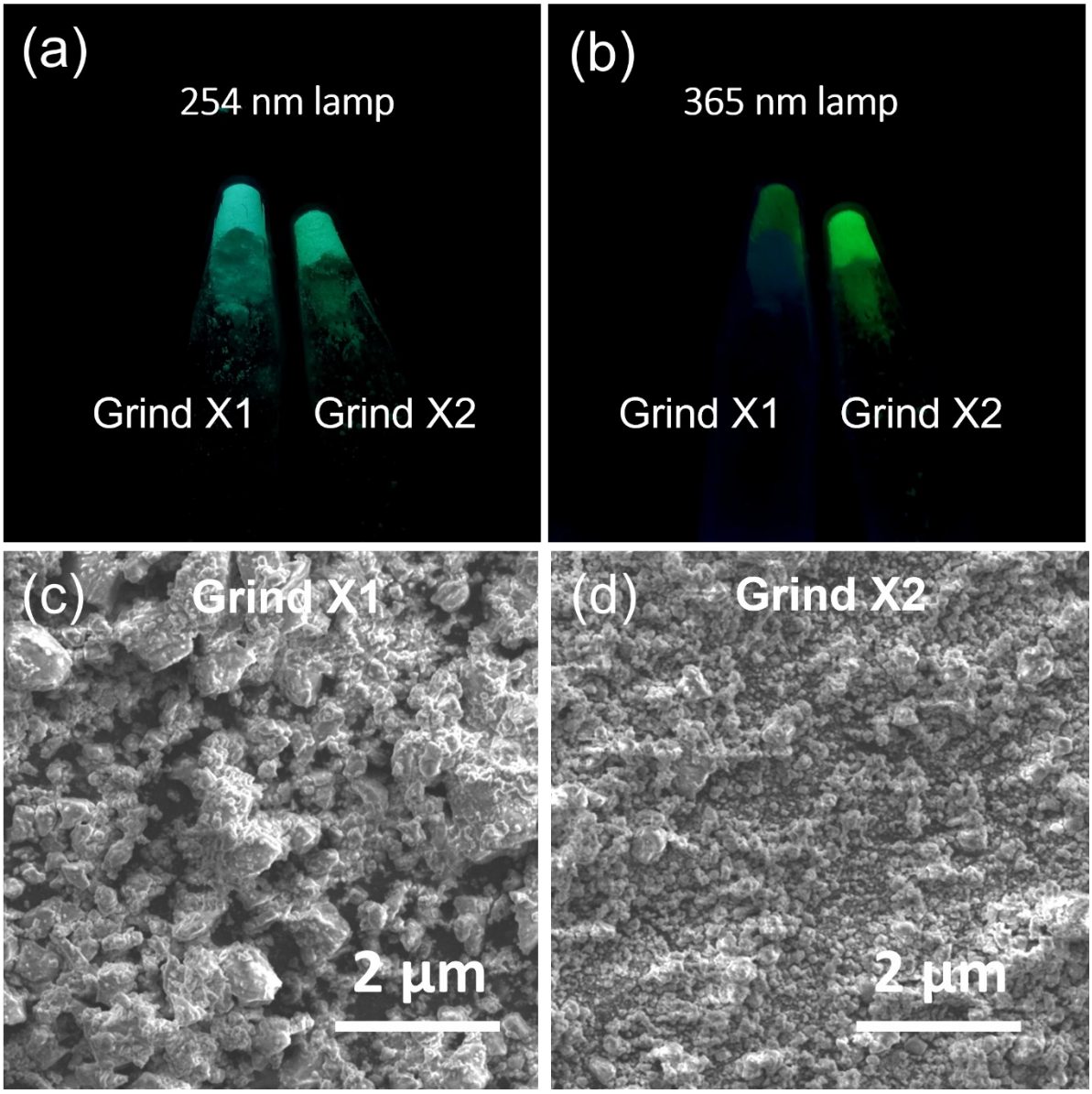

Fig.S18 Photographs of $((C_2H_5)_4N)_2ZrCl_6$ powder grinded by different times under (a) 254 nm lamp and (b) 365 nm lamp. SEM images of $((C_2H_5)_4N)_2ZrCl_6$ powder grinded by (c) once and (b) twice.

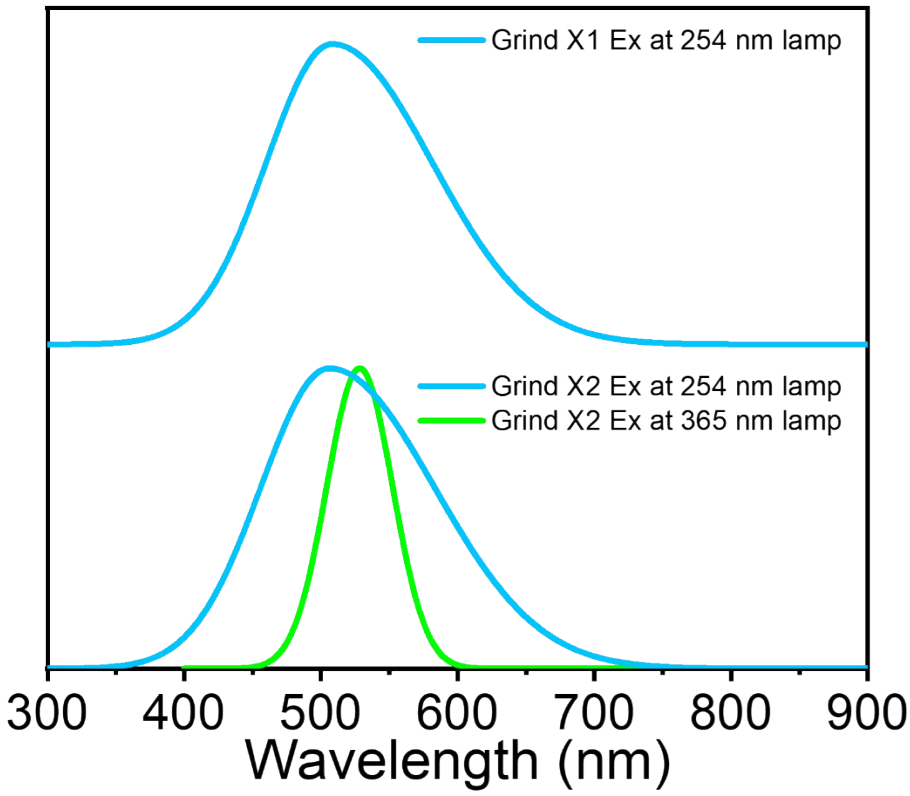

Fig.S19 PL emission spectra of $(C_{13}H_{30}N)_2ZrCl_6$ powders grinded by different times .

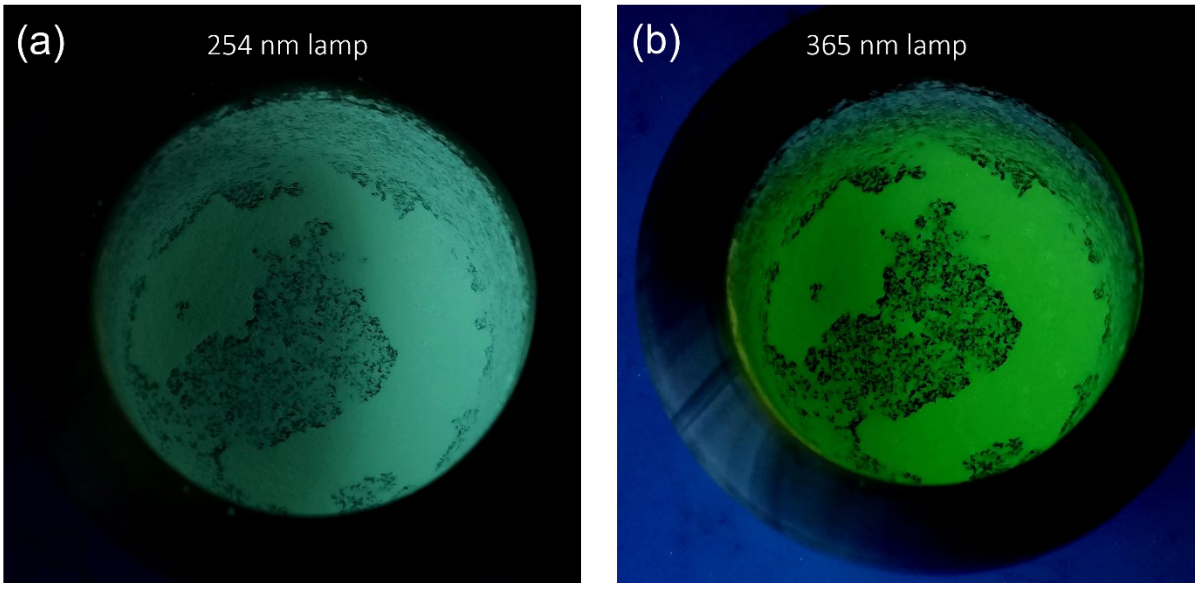

Fig.S20 Photographs of $((C_2H_5)_4N)_2ZrCl_6$ powder through ball milling under (a) 254 nm and (b) 365 nm lamp.

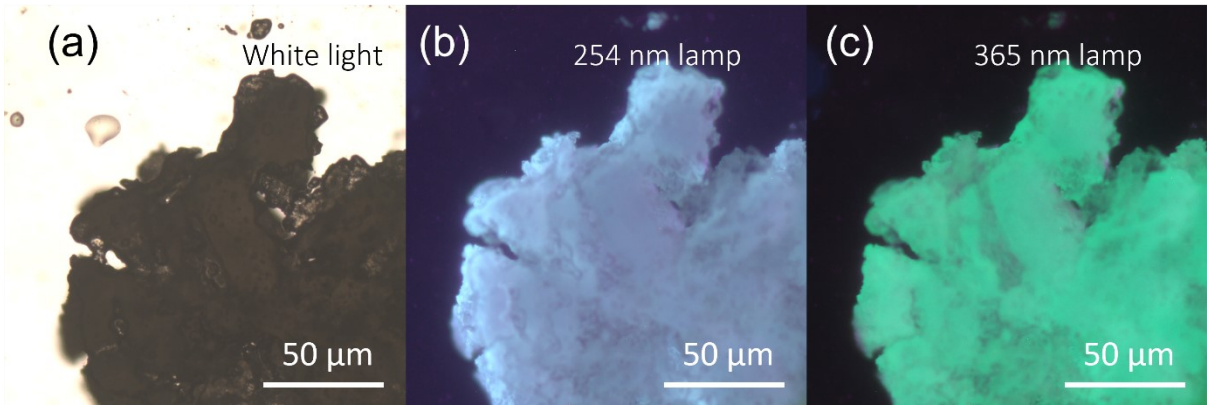

Fig.S21 Microscope images of $((C_2H_5)_4N)_2ZrCl_6$ powder under (a) white light, (b) 254 nm and (c) 365 nm lamp.

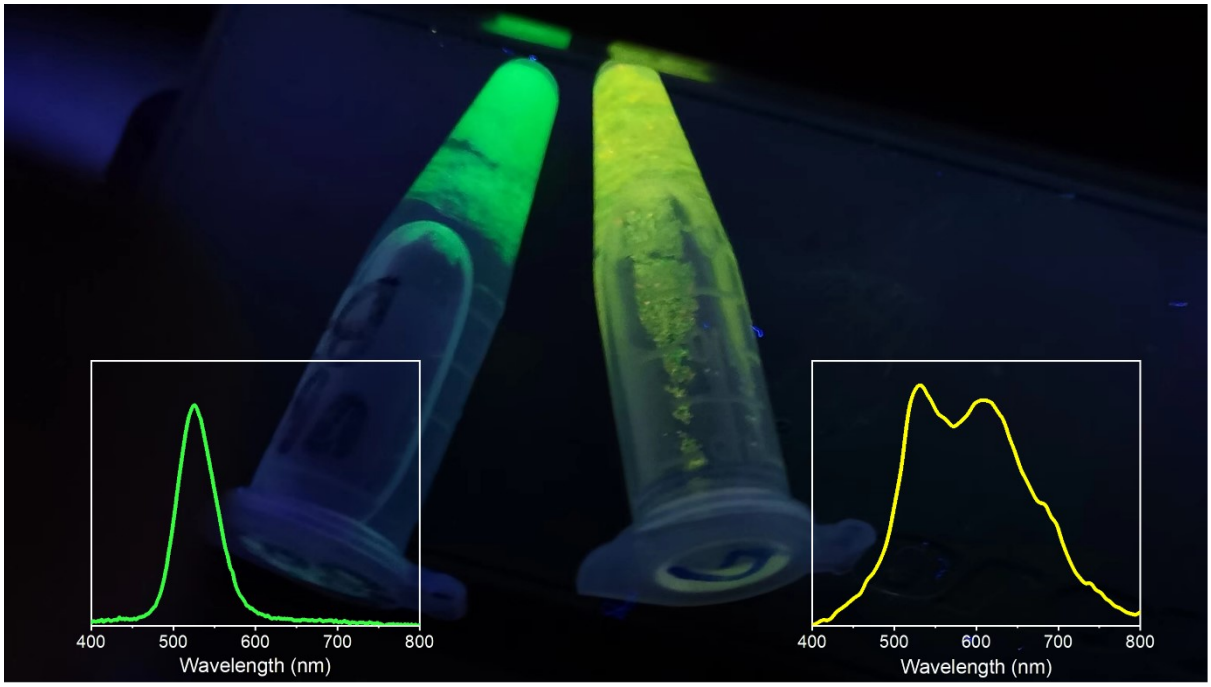

Fig.S22 Photographs of green powder stored before (left) and after (right) a day at RF of 100% under 365 nm lamp. The insets are the corresponding PL emission spectra of the samples.

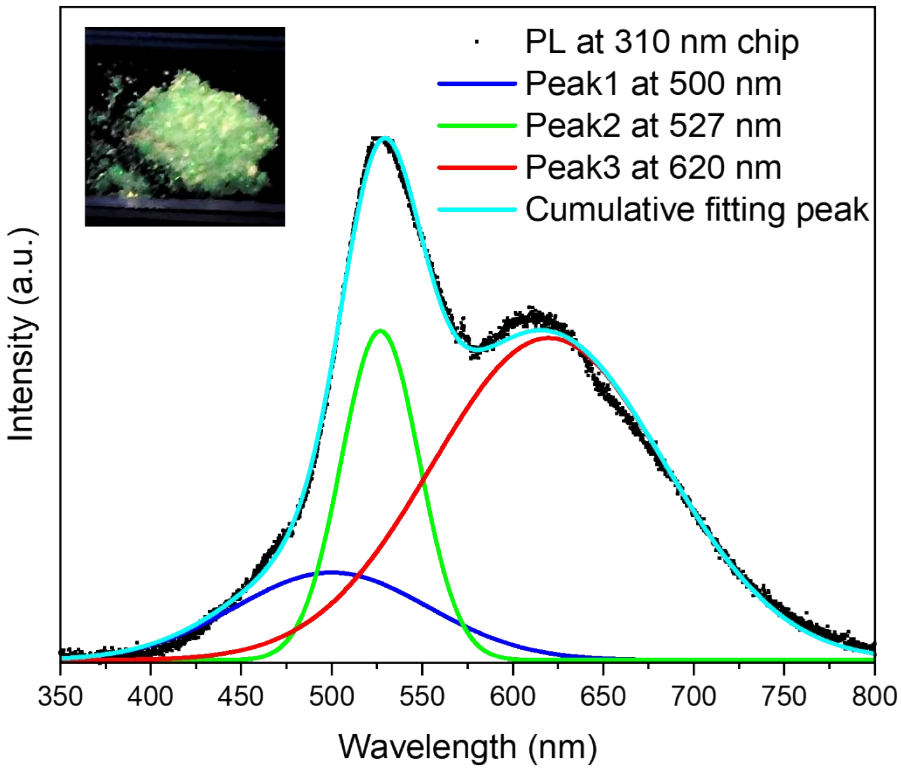

Fig.S23 PL spectrum and fitting curves of $((C_2H_5)_4N)_2ZrCl_6$ powders on 310 nm chip.

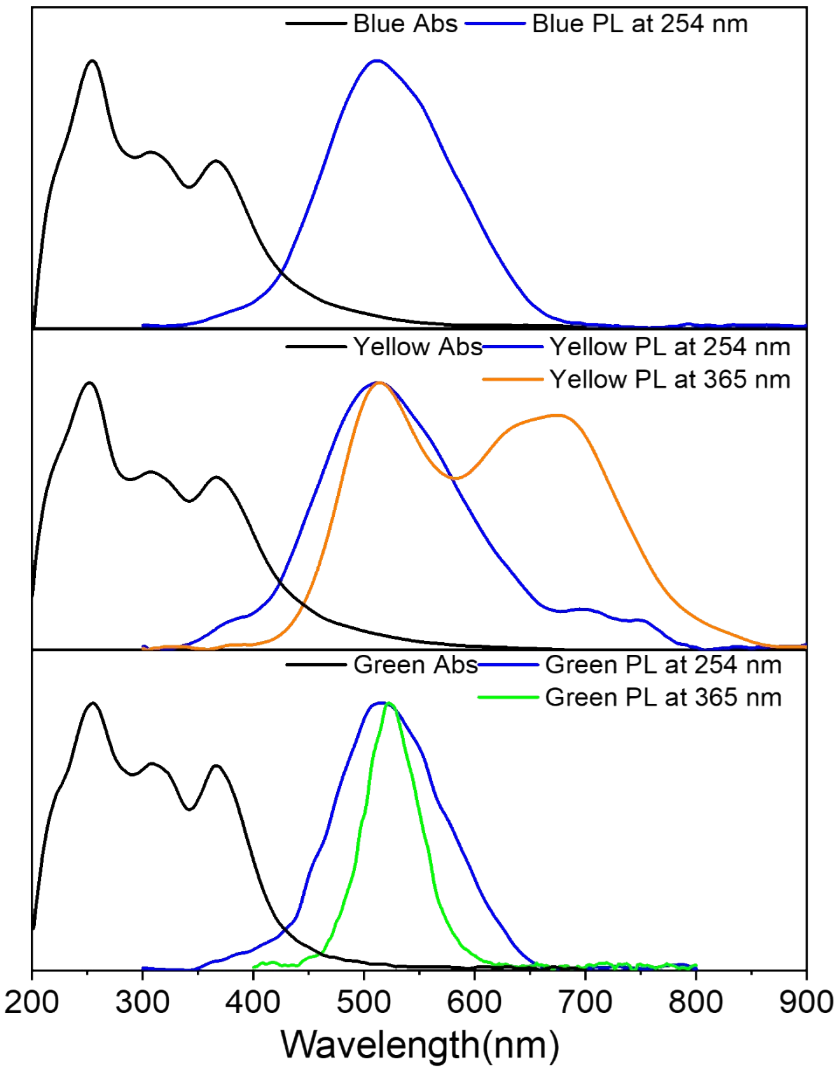

Fig.S24 Absorption and PL emission spectra of $(C_{13}H_{30}N)_2ZrCl_6$ powders under different excitation.

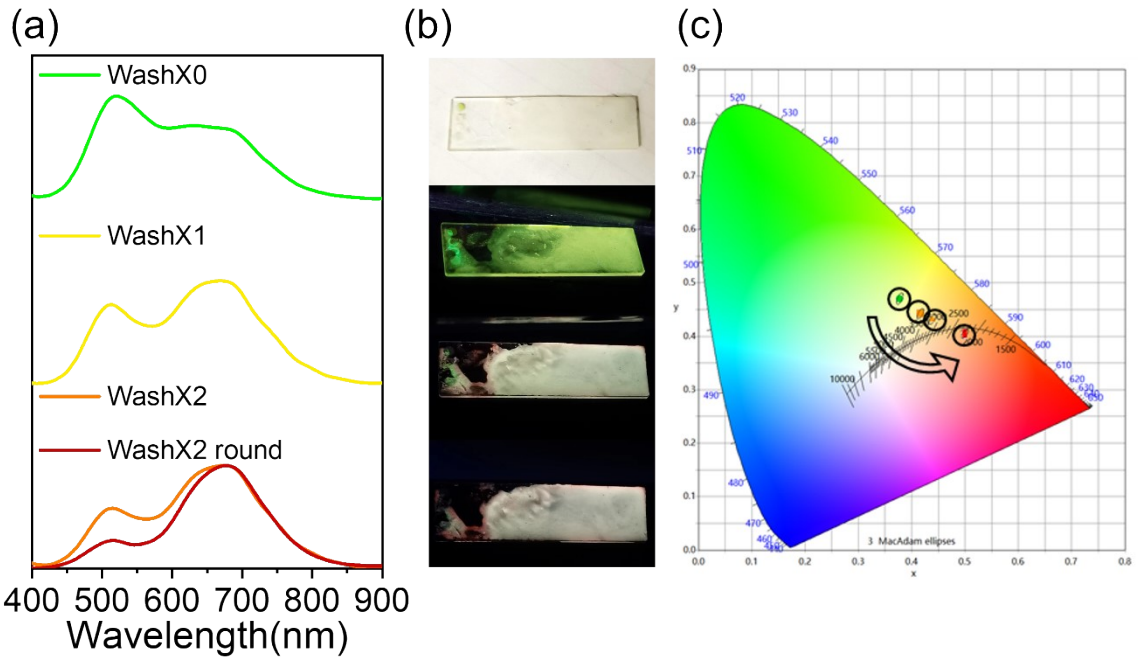

Fig.S25 (a) PL emission spectra, (b) photographs and (c) CIE chromaticity diagram of of $(C_{13}H_{30}N)_2ZrCl_6$ powders with different wash times.

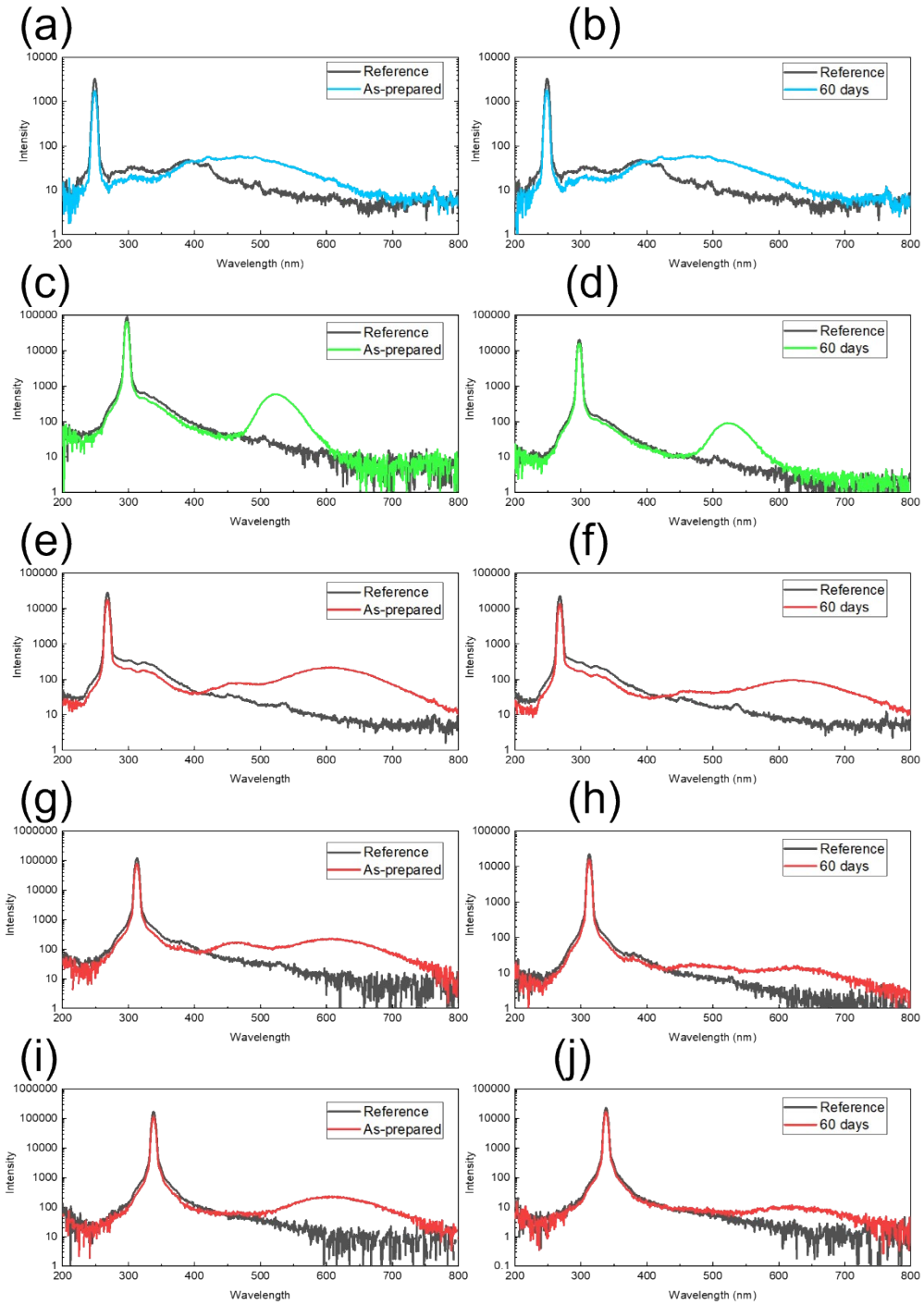

Fig.S26 PLQY of $((C_2H_5)_4N)_2ZrCl_6$ powder samples. PL spectra excited at 250 nm of (a) as-prepared blue powder and (b) samples stored for 60 days. PL spectra excited at 300 nm of (c) as-prepared green powder and (d) samples stored for 60 days. PL spectra excited at 270 nm of (e) as-prepared red powder and (f) samples stored for 60 days. PL spectra excited at 315 nm of (g) as-prepared red powder and (h) samples stored for 60 days. PL spectra excited at 340 nm of (i) as-prepared red powder and (j) samples stored for 60 days.

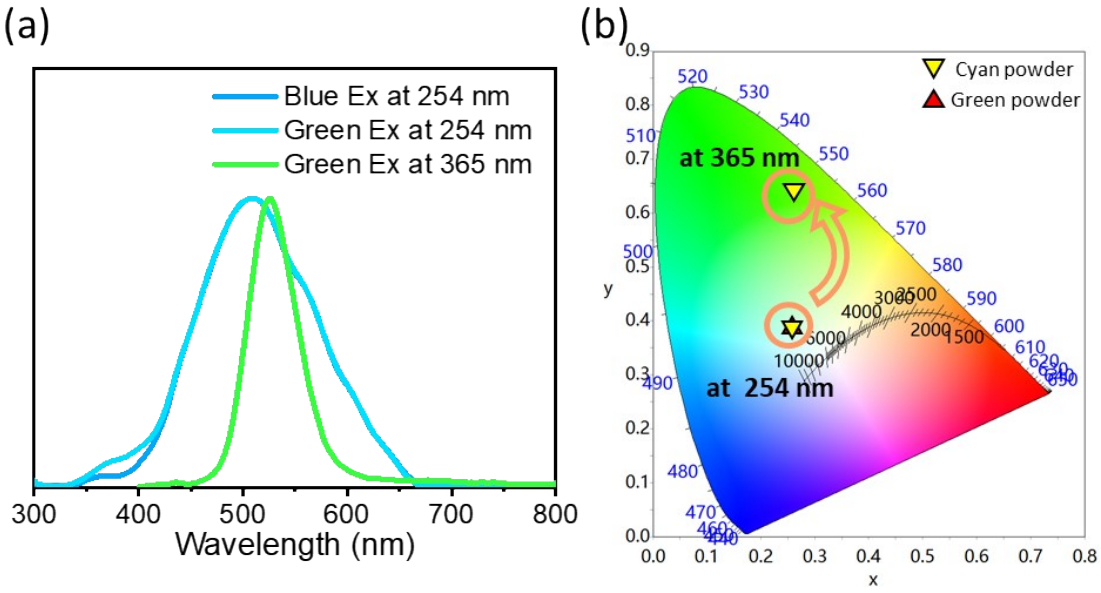

Fig.S27 (a) PL emission spectra and (b) CIE chromaticity diagram of cyan and green powders under different irradiation.

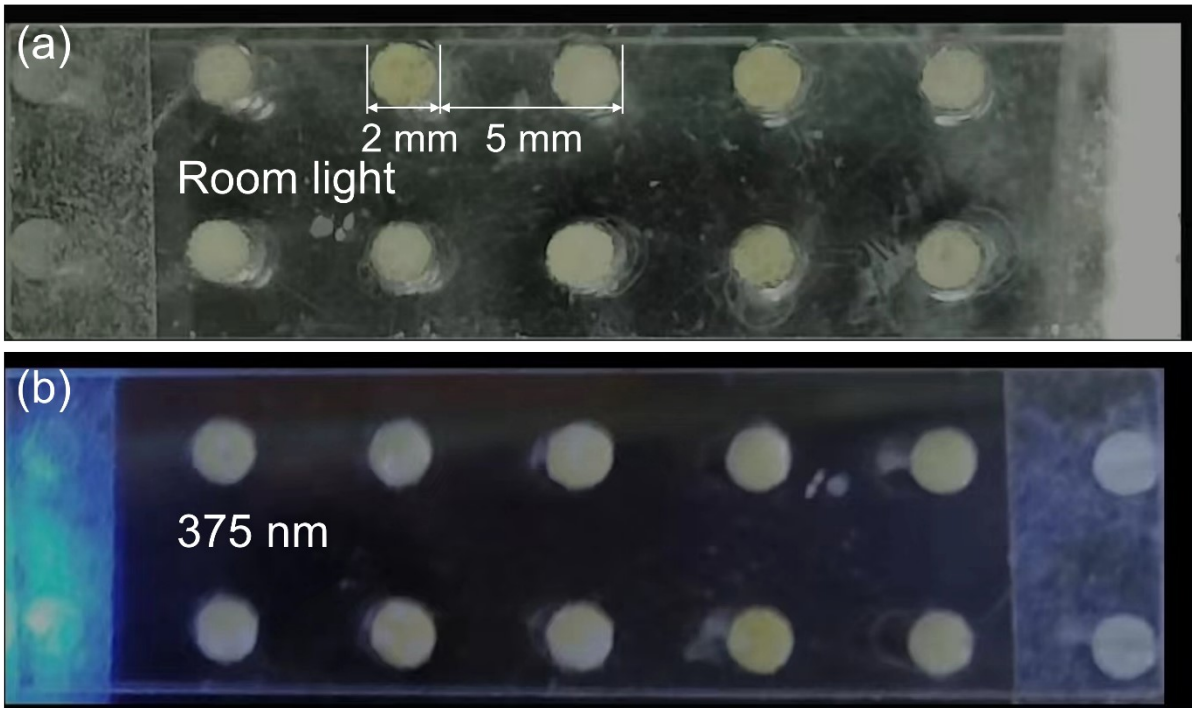

Fig.S28 Photographs of pixelated patterns of the green and cyan powders under (a) room light and (b) 375 nm irradiation.

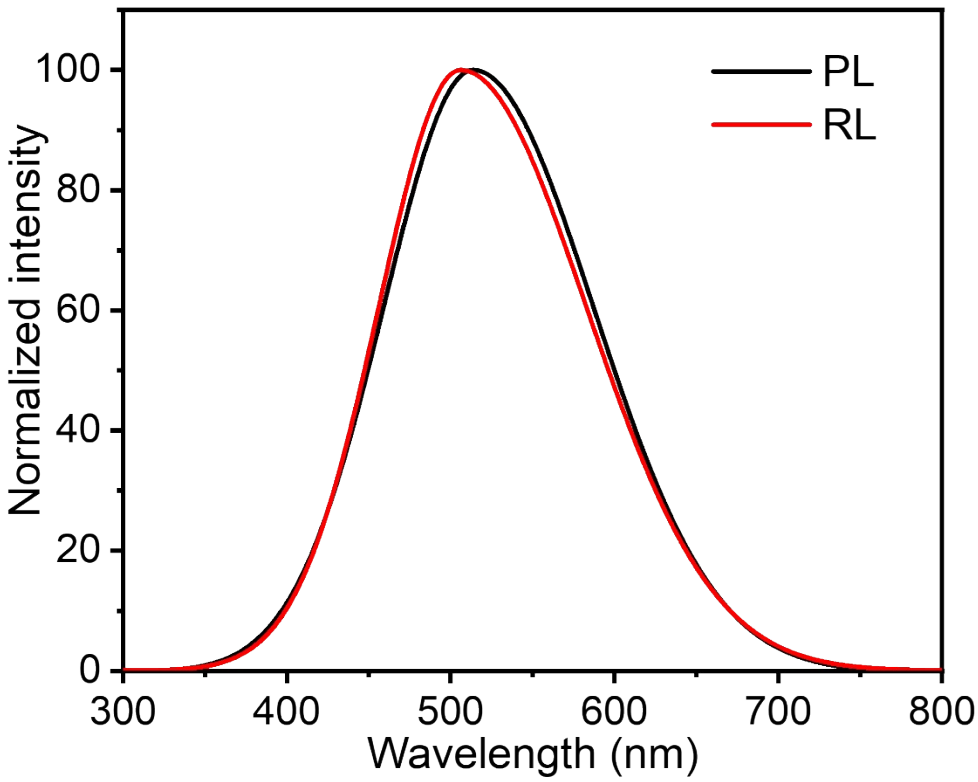

Fig.S29 RL and PL spectra excited under 254 nm lamp of blue $((C_2H_5)_4N)_2ZrCl_6$ powder.